2005 WORKSHOP
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OF MEDICAL GEOLOGY

RIO DE JANEIRO , BRAZIL

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**ENVIROMENTAL AND HEALTH
EFFECTS OF TOXIC
ON MATERIALS
GEOLOGICAL FACTORS**

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SUMMARY

PRESENTATION

T his book aims to share the concepts, methodologies and results of recent studies developed under the multidisciplinary context of Medical Geology. It presents the work of Brazilian authors in the International Medical Geology Workshop that was held in Rio de Janeiro in June 2005 at the Brazilian Geological Survey-CPRM head office. This initiative does not intend to encompass the whole universe of researchers working at the interface between Health and Geology, but to present a scenario that significantly reflects the state of the art of this important issue amidst existing health problems. The basic notions of this new field of science and its historical evolution in a global context are presented by the paper written by Dr. Olle Selinus (IMGA).This introduction is followed by a description of the actual Brazilian Medical Geology scenario, with emphasis on the importance of Epidemiology, as a basis to assess public health issues. In this context, the National Health Vigilance Program related to chemical substances is also exposed. The following articles present the research results of Medical Geology issues developed by a large number of institutions, from geographical regions all over the country. According to these studies, geological data has been correlated with the health data of a given population in order to search and define the casual nexus or even to launch a new work hypothesis. Finally, we would like to thank all the authors for their valorous contribution. Our thanks and appreciation are extended especially to the Rio de Janeiro State Research Foundation-FAPERJ, for its financial support and to the Brazilian Geological Survey-CPRM, the Brazilian Geochemistry Society-SBGq, and to the International Medical Geology Association-IMGA for their incentives and logistical support. We are confident our contribution to foster and develop Medical Geology in Brazil will subsequently raise the quality of life of our population.

The Editors.

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MEDICAL GEOLOGY

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SUMMARY

Medical geology is defined as the science dealing with the influence of ordinary environmental factors on the geographical distribution of health in humans and animals. Accordingly this is a complicated subject and interdisciplinary contributions from essentially different scientific fields are required when these problems are to be solved. This paper discusses the background of medical geology with examples from all over the world. Emphasis is placed on the serious effects of acidification of soil and water that pose a potential threat against the health of humans and animals. All living organisms are composed of major, minor and trace elements, given by nature and supplied by geology.

Why is geology important for our health?

Our environment is the entire web of geological and biological interactions that characterize the relationship between life and the planet earth. Essential and toxic elements in bedrock or soils may become a direct risk for human and animal health; and may be the underlying cause of both deficiency and toxicity. Some naturally occurring elements are necessary for our wellbeing while others are detrimental to our health.

Before resources are committed to clean up or protect the environment from man-made contamination, it would seem prudent to determine how much of the "contamination" merely reflects the preexisting natural background levels. Naturally occurring elements can have detrimental effects on health when ingested in increasing quantities. Metals have always existed and will forever exist, but we cannot avoid the fact that the health of human beings and animals are influenced by metals in the environment. Geological processes along with human activities of all kinds have redistributed metals from sites where they are fairly harmless to places where they affect humans and animals negatively.

Earth is the ultimate source of all elements. Metals are ubiquitous in the lithosphere, where they are inhomogenuously distributed and occur in different chemical forms. Ore deposits represent natural concentrations that are commercially exploitable. While such anomalous accumulations are the focus of economic geology, the background concentrations of metals that occur in common rocks, sediments, and soils are of greater significance to the total metal loading in the environment. All known elements are present at some level of concentration throughout the natural environment in humans, animals, vegetables and minerals, and their beneficial and harmful effects have been present since evolution began.

Geology may appear far removed from human health. However, rocks are the source of all the naturally occurring chemical elements found on the earth. Many elements in the right quantities are essential for plant, animal and human health. Most of these elements enter the human body via food and water in the diet and through the air that we breathe. Through the weathering processes, rocks break down to form soils on which crops and animals that constitute the food supply are raised. Drinking water moves through rocks and soils as part of the hydrological cycle. Much of the dust and some of the gases present in the atmosphere are the result of geological processes. Hence, a direct link exists between geochemistry and health due to ingestion and inhalation of chemical elements by eating and drinking food and water and breathing air.

We need to understand the nature and magnitude of these geological sources to develop approaches to assess the risk posed by metals in the environment. It is very important to distinguish between natural and anthropogenic contributions to metal loadings. Concentrations of metals can range over orders of magnitude among different rocks. For example, the concentrations of metals such as nickel and chromium are much higher in basalts than in granites, whereas the reverse is true for lead. Weathering of these types of bedrocks results in the mobilization of elements in the environment. In sediments, the heavy metals tend to be concentrated in fractions with the finest grain size and the highest content of organic matter. Black shales, a fine grained rock, for example, tend to be enriched in these elements.

In addition, knowledge of geological processes is fundamental to understand the fate of those metals, which are released as a result of human activity.

Volcanism and related igneous activities are the principal processes that bring elements to the surface from deep inside the earth. For example, the volcano Pinatubo ejected in just over two days in June 1991, about 10 billion

tonnes of magma and 20 million tonnes of SO_2 and the resulting aerosols influenced the global climate for three years. This event alone introduced 800,000 tonnes of zinc, 600,000 tonnes of copper and 1,000 tonnes of cadmium to the surface environment. In addition to this, 30,000 tons of nickel, 550,000 tonnes of chromium and 800 tonnes of mercury were also added to the earth's surface environment. Volcanic eruptions redistribute some of the harmful elements, such as arsenic, beryllium, cadmium, mercury, lead, radon and uranium, plus most of the remaining elements, many of which have still undetermined biological effects. It is also important to realize that there are on an average 60 subaerial volcanoes erupting on the earth's surface at any given time, releasing various elements into the environment. Submarine volcanism is even more significant than those at continental margins and it has been conservatively estimated that there are at least 3,000 vent fields on the mid ocean ridges. One interesting fact is that about 50% of SO_2 is of natural origin, mainly from volcanoes, and only 50% is from human sources.

The naturally occurring elements are not evenly distributed across the surface of the earth and problems can arise when element abundances are too low (deficiency) or too high (toxicity). The environment's inability to provide the correct chemical balance can lead to serious health problems. The links between environment and health are particularly important for subsistence populations that are heavily dependent on the local environment for their food supply. Approximately 25 of the naturally occurring elements are known to be essential to plant and animal life in trace amounts, including Ca, Mg, Fe, Co, Cu, Zn, P, N, S, Se, I and Mo. On the other hand, an excess of these elements can cause toxicity problems. Some elements such as As, Cd, Pb, Hg and Al have no or limited biological function and are generally toxic to humans

Many of these elements are known as trace elements because they generally occur in minute (mg/kg or ppm) concentrations in most soils. Trace element deficiencies in crops and animals are therefore commonplace over large areas of the world and mineral supplementation programs are widely practiced in agriculture. Trace element deficiencies generally lead to poor crop and animal growth and to reproductive disorders in animals. These problems often have the greatest impact on poor populations who can least afford nutritional interventions for their animals.

Interactions, speciation and bioavailability

In addition to understanding both natural and anthropogenic sources of harmful substances in the environment, it is also important to consider exposure and bioavailability. Exposure is the qualitative and/or quantitative description of total intake/assimilation of a given chemical substance via a range of pathways. Bioavailability is the proportion of a chemical available for uptake into the systemic circulation of a organism, following a given mode of exposure.

Bioavailability directly influences exposure and therefore the effect and risk of health detriments. Large quantities of a potentially harmful substance may be present in the environment, but if it is in a non-bioavailable form, the risk to health may be minimal. Bioavailability depends not only on the physical and chemical forms in which the element is present, but also on other factors in the environment, such as pH, temperature and moisture conditions. The bioavailability and mobility of metals like zinc, lead and cadmium is greatest under acidic conditions, while increased pH reduces bioavailability. Also, soil type such as clay and sand content and its physical properties affect the migration of metals through soils. The organisms present in soils also affect metal solubility, transport and bioavailability

Furthermore, as will be demonstrated with the arsenic case study from Bangladesh, a potential hazard only becomes a problem if there is an exposure route. The potential hazard of high arsenic groundwater has existed for thousands of years but it is only in recent years with the sinking of water wells to access this water that an exposure route has been established and a health effect manifested. In the absence of exposure, there is no adverse effect.

Exposure pathways include ingestion (food, water and deliberate/inadvertent soil ingestion), dermal absorption and inhalation. In terms of ingestion, much emphasis has been placed on water, simply because it is an easy sample type to analyze. However, soils and food are likely to be far more important dietary contributors because the concentrations of potentially harmful substances in soils are much greater (parts per million) than in water (parts per billion). Whether soil ingestion is inadvertent or via the deliberate eating of soil known as geophagia, this exposure route should not be underestimated. For example, studies in Kenya have shown that 60 – 90% of children between 5 – 14 years of age practice geophagia and each child consumes an average of 28g of soil per day.

In discussing medical geology it is also necessary to know which elements are essential for humans and animals. The main essential elements are: calcium, chlorine, magnesium, phosphorus, potassium, sodium and sulphur. Essential trace elements are: chromium, cobalt, copper, fluorine, iron, manganese, molybdenum, zinc, and selenium. Elements with probably no recognized biological role are called non-essential elements, often with harmful properties, e.g. cadmium, arsenic, mercury and lead. Exposure to heavy metals could result in negative effects

Most of the heavy metals are essential in different amounts for biological functions of organisms (e.g. cobalt, copper, manganese, molybdenum, zinc, nickel, and vanadium). They are called micronutrients. In high concentrations, however, all metals produce adverse effects on organisms. The large scale introduction of heavy metals in society - the technosphere - and eventually into the biosphere has given rise to toxic effects in animals and plants and non-

sustainable loading. Cadmium, mercury, lead, copper, and other metals have all been linked to various toxic effects in living organisms. Of these, mercury and lead do not seem to serve any biological functions in living organisms.

Examples of medical geology.

Inorganic **arsenic** is one of the oldest known poisons. Chronic arsenic exposure particularly affects the skin, mucous membranes, nervous system, bone marrow, liver and heart. Arsenic toxicity is strongly dependent on its chemical form. Essentiality of arsenic has been shown in studies with animals but not in humans. Worldwide natural emissions of arsenic into the atmosphere in the 1980s were 1.1 to 23.5 tonnes per year, derived mostly from volcanoes, wind-borne soil particles, sea spray and biogenic processes. Coal combustion alone accounts for 20 percent of the atmospheric emission, and arsenic from coal ash may leach into soils and water.

There is growing concern over the toxicity of arsenic caused by exposure to elevated concentrations in the geochemical environment. The danger to human health due to arsenic poisoning has now been recognized by the World Health Organization (WHO), which has lowered the safe level for arsenic in drinking water from 50 μg/1 to 10 μg/l. Among the countries that have well documented case studies of arsenic poisoning are Bangladesh, India (West Bengal), Taiwan, China, Mexico, Chile and Argentina. The common symptom of chronic arsenic poisoning is conjunctivitis, melanosis, depigmentation, keratosis and hyperkeratosis. As in the case of India and Bangladesh, the relationship between excess arsenic exposure and skin and internal cancers is established in Taiwan. The source of arsenic is geochemical, the element being present in many rock-forming minerals, including iron-oxides and clays but mostly in sulphide minerals, especially in pyrite and arsenopyrite.

Radon is a naturally occurring radioactive gas that is colorless, odorless, and tasteless and can only be detected with special equipment. It is produced by the radioactive decay of radium, which, in turn, is derived from the radioactive decay of uranium. Uranium is found in small quantities in all soils and rocks, although the amount varies from place to place. Radon decays to form radioactive particles that can enter the body through inhalation. Inhalation of the short-lived decay products of radon has been linked to an increase in the risk of cancers of the respiratory tract, especially the lungs. Breathing radon in the indoor air of homes contributes to about 20,000 lung cancer deaths each year in the United States and 2,000-3,000 in the U.K. Only smoking causes more lung cancer deaths.

Geology is the most important factor controlling the source and distribution of radon. Relatively high levels of radon emissions are associated with particular types of bedrock and unconsolidated deposits, for example some, but not all, granites, phosphatic rocks, and shales rich in

organic materials. The release of radon from rocks and soils is controlled largely by the types of minerals in which the uranium and radium occur. Once radon gas is released from minerals, its migration to the surface is controlled by the permeability of the bedrock and soil; the nature of the carrier fluids, including carbon dioxide gas and groundwater; and meteorological factors such as barometric pressure and rainfall.

Radon dissolved in groundwater may migrate over long distances along fractures and caverns depending on the velocity of fluid flow. Radon is soluble in water and may thus be transported for distances of up to 5 km in streams flowing underground in limestone. Radon remains in solution in water until a gas phase is introduced. If emitted directly into the gas phase, as may happen above the water table, the presence of a carrier gas, such as carbon dioxide, would tend to induce migration of the radon. This appears to be the case in certain limestone formations, where underground caves and fissures enable the rapid transfer of the gas phase. Radon in water supplies can result in radiation exposure of people in two ways: by ingestion of the water or by release of the radon into the air during shower or bathing, allowing radon and its decay products to be inhaled. Radon in soil under homes is the biggest source of radon in indoor air, and presents a greater risk of lung cancer than radon in drinking water. However radon in drinking water could be a problem for small children.

The connection between goitre and **iodine** deficiency is a classic example of medical geology even though the relationships are somewhat more complicated than formerly believed. The connection between geology-water-food chain-diseases can clearly be shown for iodine. Goiter was common in ancient China, Greece, Egypt and amongst the Inca, where the soil and/or water is usually deficient in iodine, but was successfully treated by seaweed which contains high levels of iodine. Iodine, being a component of the thyroid hormone thyroxine, has long been known as an essential element for humans and mammals. Deficiency of iodine results in a series of Iodine Deficiency Disorders (IDD) the most common of which is endemic goiter. The areas where IDD are concentrated tend to be geographically defined. Thus the most severe occurrences of endemic goiter and cretinism have been found to occur in high mountain ranges, rain shadow areas, and central continental regions.

Goitre occurs due to enlargement of the thyroid gland as it attempts to compensate for insufficient iodine. It has been estimated for example that out of a population of 17 million in Sri Lanka, nearly 10 million people are at risk of goitre. Iodine deficiency in pregnant mothers can also lead to cretinism and impaired brain function in children. The World Health Organization estimates that currently over 1.6 billion people are at risk from iodine deficiency and that it is the single largest cause of mental retardation in

the world today. China alone has 425 million people who are at a risk in regard to IDD.

Another important element is **fluorine**. The geochemistry of fluorides in groundwater and the dental health of communities, particularly those depending on groundwater for their drinking water supplies, is one of the best known examples of the relationships between geochemistry and health. Many water supply schemes, particularly in developing countries where dug wells and deep bore holes form the major water sources, contain excess fluoride and as such are harmful to dental health.

Fluorine is an essential element with a recommended daily intake of 1.5 – 4.0 mg/day. Health problems such as caries or dental mottling and skeletal fluorosis may arise from deficiency or excess. Unlike other essential elements for which food is the principal source, the main source of fluoride is water. Fluorine in surface and groundwater is derived from the following natural sources: (a) leaching of the rocks rich in fluorine; (b) dissolution of fluorides from volcanic gases by percolating groundwater along faults and joints at great depth and discharging in springs; (c) rainwater; which may acquire a small amount of fluoride from marine aerosols and continental dust; (d) industrial emissions and effluents:(f) run-off from farms, ostensibly using phosphatic fertilizers.

For example, after the eruptions of the volcano Hekla in Iceland in 1693, 1766, and 1845, severe incidents of fluorosis were recovered. Acute poisoning was described. Since World War II, Hekla has erupted in 1947, 1970, and 1980, and a number of analyses for fluorine have been performed. The volcano delivered huge amounts of fluorine and concentrations of 4,300 ppm in grass has been found.

In the beginning of the 20th century it was known that high contents of fluorine could cause fluorosis. The natural concentration of fluorine in drinking water is normally 0.1-1 ppm. In many countries, however, the concentration could be as high as 40 ppm that could lead to serious fluorosis. Yes the picture is rather complicated because there are also antagonistic effects. Molybdenum and selenium can reduce the effects of high concentrations of fluorine. One of the major benefits of fluorine seems to stem from its antagonism with aluminum. In Ontario, Canada, there is less Alzheimer disease where the drinking water contains more fluorine.

One quite different aspect of medical geology is **geophagia**, which is the deliberate eating of soil. In many ancient and rural societies, and amongst a wide variety of animals, exposure to chemical elements occurs principally through the deliberate ingestion of soil, or soil-derived `medical' preparations (often associated with immigrant communities). Such behavior is medically known as either pica or more specifically as geophagia. Geophagia is common among traditional societies and has been recognized since the time of Aristotle as a cure-all for health problems. Soil from the ground may be eaten in the form of paste but in many situations there is a cultural preference for soil from special sources, such as termitaria.

Even today the theory of geophagia as a subconscious response to dietary toxins or stress must be balanced against the habitual eating of soil that has been reported to develop into extreme, often obsessive, cravings. These cravings are often reported to occur immediately after rain. Typical quantities of soil eaten by geophagists in Kenya have been reported to be 20 grams per day. This is almost 400 times more than typical quantities of soil thought to be ingested as a result of inadvertent ingestion through hand-to-mouth contact (e.g. 50 milligrams per day). Whilst eating such large quantities of soil increases exposure to essential trace nutrients, it also significantly increases exposure to biological pathogens and to potentially toxic trace elements, especially in areas associated with mineral extraction, or in polluted urban environments.

Geophagia is also increasing in developing countries. Because of immigration the tradition of geophagia is brought into western societies and imported soils can often be found in local ethnic food stores for sale to immigrants.

Naturally Occurring Dusts. Exposure to mineral dusts can cause a wide range of respiratory problems. The health effects of exposure to mineral dusts have been recognized for decades, with asbestos being the classical example. Dust exposure can also affect broad regions such as the dust stirred up by earthquakes in the arid regions of the southwestern U.S. and northern Mexico. Dust exposure can even take on global dimensions. Ash ejected form volcanic eruptions can travel many times around the world and recent satellite images have shown wind blown dust picked up from the Sahara and Gobi deserts blown more than halfway around the world. Of greatest concern for effects upon human health are the finer particles of the respirable (inhalable) dusts. In this regard, considerable work is being conducted in identifying dust particles derived from soils, sediments and weathered rock surfaces.

3.0 The future of Medical Geology

Naturally occurring materials such as rocks, minerals, dust and water can have profound effects on the health of humans, plants and animals. Understanding the complex relationship between the natural environment and the health of animals and humans requires close collaboration between medics, veterinarians, geoscientists, and toxicologists for mitigation. The emerging field of medical geology plays a key role in these fields of interdisciplinary collaboration. It also requires close coordination between developed and developing countries.

Medical geology is an interdisciplinary science that is growing rapidly. Because of the importance of geological factors on health the IUGS commission COGEOENVIRONMENT (Commission on Geological Sciences for Environmental Planning) established in 1996 an International Working Group on Medical Geology led by the Geological Survey of Sweden, SGU, with the primary aim of increasing awareness of this issue among scientists, medical specialists, and the general public. In 2000 a new IGCP project was also established by UNESCO; "IGCP#454 Medical Geology". The International Council of Scientific Unions (ICSU) also sponsored 2002-2003 international short courses in this subject, a cooperation involving SGU, United States Geological Survey and the US Armed Forces of Pathology in Washington DC. These courses have then continued all over the world and the most recent one was in Brazil, June 2005. As a result of the significant achievements to date the Commission's Working Group was given a Special Project status by the IUGS. In March 2002 the IUGS announced that the International Working Group on Medical Geology would be assigned Special Project status operating directly under the IUGS. Olle Selinus is Director of this activity. Jose Centeno and Bob Finkelman are Co-Directors. A new international association, International Medical Geology Association (IMGA) is now also being established with one councilor from Brazil. Further on the United Nations is planned to decide on the Year of Planet Earth. One main topic of this initiative will be medical geology.

Geological surveys, universities, and geological societies should take a continuing active role in providing useful geologic information related to medical geology and encourage the development of local working groups of multi-disciplinary medical geology experts. It would also be useful to encourage research in the area to produce more effective methodologies for the study of geological factors in environmental medicine and formulate recommendations to mitigate the effects of natural and man-induced hazardous geochemical conditions.

MEDICAL GEOLOGY IN BRAZIL

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HISTORY

In Brazil, the integration of the specific knowledge of Earth Sciences and Health Sciences has had a long and relatively profitable history in the diagnosis and proposals to control some endemic diseases. Studies that were more concerned with descriptions of the climate, hydrography and biogeographical conditions, at that time known as botanical landscape and zoogeography, were the basic components of Medical Geography. This was defined as the study of the geography of diseases or pathology in the light of geographical knowledge. Geographical Pathology, Geopathology or Medical Geography were synonyms with Geographical Medicine (Lacaz, 1972). Geographical Medicine was considered to be a branch of Geography, as were Biogeography, Human Geography and Physical Geography.

Geomedicine, defined by Zeiss (apud Lacaz, 1972) as the branch of medicine that studies the influence of climatic and environmental conditions on health, was included in Medical Geography, widening its horizons. However, most studies in Medical Geography were related to infectious-parasitic diseases, within a theoretical framework given by Tropical Medicine. This has always valued climatic, physical and geographical aspects in its epidemiological studies, investigating factors connected to the ecology of transmitter insects and carriers of bacteria, virus and protozoa, for example. In these situations, geological and geochemical aspects of the studied regions were not taken into account, as the explicative model of the diseases origins did not process this kind of data. An atypical reference in the context of Medical Geography, that usually privileged infectious-contagious diseases, was the study carried out by the Manguinhos Institute (Instituto de Manguinhos), today FIOCRUZ, and the National Health Department (Departamento Nacional de Saúde) on the prevalence of endemic goiter in various Brazilian regions in the 1950s. A lower prevalence of the disease in the coastal areas compared to the west-center regions, where the diseased rate reached up to 54% of the population, drew the attention to a causal geographical/geological factor (Sampaio, 1972).

Since the 1980, researchers of the Federal University of Bahia (Universidade Federal da Bahia) established a field base to evaluate studies of children and adults contaminated by lead and cadmium in Santo Amaro da Purificação (BA). Here the waste of lead ore metallurgy had contaminated the soil and the shallow city aquifer. They became the pioneers of this approach to this kind of problem in Brazil (Carvalho et al. 1984; Carvalho *et al.* 1985).

More recently, Licht (2001), initiating a low density geochemical survey, sampling sediment, water and soil across the whole State of Paraná, identified dental fluorosis in children from the Itambaracá (PR) region associated with the groundwater. Furthermore, bromide and chloride in the soil was possibly related to the cancerogenic diseases occurring in the State's northern area.

Researchers from the Campinas State University (UNICAMP) the Minas Gerais State Environmental Agency (Fundação Estadual de Meio Ambiente– FEAM) and other institutions, in collaboration with the Freiberg University in Germany (Matschullat, *et al.* 2000), identified high concentrations of As in the urine of children living near old Au mines in ferriferous districts in Minas Gerais State (Quadrilátero Ferrífero). In Amapá state, Santos et al. (2003), of the Evandro Chagas Institute (Instituto Evandro Chagas), researched exposure to As in a population living near a manganese refinery waste site (Mineração ICOMI). They analyzed samples of hair and blood, without, however, identifying any significant risk to the people.

Between 1998 and 2003, UNICAMP researchers, in partnership with public health institutions, identified lead contamination in the blood of children and adults living near the Plumbum S.A. Plant in Adrianópolis, PR (Paoliello, 2002; Cunha, 2003; Figueiredo, 2005). In the same region, in Iporanga, São Paulo State, although

anomalous concentrations of arsenic were found in the soil and sediments, the levels of human exposure were low, representing no risk to the population's health (Sakuma, 2004).

Many studies on the human risk evaluation of mercury assimilation from artisanal gold extraction sites (garimpo), especially in the Amazon region, have been carried out by researchers of CETEM, FIOCRUZ, Evandro Chagas Institute (Instituto Evandro Chagas), UFPA, INPA, UFAM and UFRO. In their websites several studies on this subject can be found.

In 2002, after the Brazilian Congress of Geology in João Pessoa (PB), a research group formed from more than ten universities and institutions, created a discussion group called Environmental Geochemistry and Medical Geology Research Network - REGAGEM (Rede de Pesquisa em Geoquímica Ambiental e Geologia Médica) – regagem@ige.unicamp.br, currently with 345 members. The group's aim was to conceive and propose the National Program for Environmental Geochemistry and Medical Geology Research – PGAGEM (Programa Nacional de Pesquisa em Geoquímica Ambiental e Geologia Médica) and make available this program's information, links and other data related to medical geology on the website www.cprm.gov.br/pgagem.

The first Brazilian medical geology event, the International Workshop on Medical Geology, was held in October 2003 at UNICAMP. A mini-course was given by Olle Selinus, Robert Finkelman and José Centeno from the IGCP 454 of IUGS-UNESCO, to 110 Brazilian participants, mostly from the fields of geosciences, health and chemistry. An interesting outcome of that occasion in the scientific community happened as early as September 2004, at the Medical Geology Symposium of the 32nd International Congress of Geology, held in Florence – Italy, when 4 of the 33 presentations were given by Brazilian researchers.

The second workshop took place in June 2005 in Rio de Janeiro, hosted by the Brazilian Geologic Survey, offering an updated version of the previous mini-course conducted by the same international researchers mentioned above. In that event Brazilian research was represented by a surprising number of 56 studies (12 oral presentations and 44 posters). 210 professionals from different disciplines (geosciences-48%, health-16%, chemistry-4%, other professions-11%, including undergraduate and graduate geology students-21%) participated in the event coming from many Brazilian states (Rio Grande do Sul, Santa Catarina, Paraná, São Paulo, Rio de Janeiro, Minas Gerais, Goiás, Distrito Federal, Bahia, Pernambuco, Ceará, Rio Grande do Norte, Pará, Amazonas and Rondônia).

The quality and quantity of the studies presented by Brazilian researchers at the International Workshop on Medical Geology in Rio de Janeiro, which covered issues related to As, Hg, F, Pb, asbestos, organic substances and the quality of public water supplies, made it possible to publish this book.

MEDICAL GEOLOGY

In Brazil, Medical Geology researchers are referred to the books and articles by Selinus et al., (2005), Skinner & Berger (2003), Cortecci (2002), Singh (2002), Licht (2001) and Figueiredo (2005b).

Therefore, based on these authors, Medical Geology may be defined as "the study of the relationship between natural geological factors and health, aiming at the well-being of people and other living organisms". Another more concise understanding is that it is "the study of the impact of geological materials and processes on public health". According to this vision medical geology includes "the identification and characterization of natural and anthropogenic sources of noxious material in the environment, trying to foresee the movement and alteration of chemical and infectious agents as well as other disease causing agents over time and space, besides understanding how people are exposed to such material and what can be done to minimize or avoid such exposure".

The link between geologists and other scientists from the medical, odontological, biological and veterinary fields was allowed by the medical geology research area, in an effort to locally and globally solve health issues. It aims to strengthen and integrate technical cooperation to reduce environmental threats to health and improve the well-being of humans and animals.

Issues associated with health usually refer to human beings and other living creatures, whereas the focus of geology is on the inanimate and the distant past. Thus, although they may be part of distinct knowledge domains or require different investigation approaches, the direct relationship cannot be ignored. "Life develops in a matrix of materials from the earth – rocks, minerals, soil, water, air – whose availability exerts a deep control over what all living creatures ingest and how they develop biologically and culturally", so "we are what we eat and drink".

The air we breathe, the water we drink and the nutrients we consume depend on the geological environment, which we can only partially control. As we struggle to adapt to a world where 10 billion people live, a better understanding of the processes through which the natural environment influences our health would allow more appropriate decisions in the future. It is a general consensus that global changes are related to the powerful impacts produced by humans on their surroundings. It is precisely the noxious or beneficial effects sometimes caused by geological material and processes on human beings that constitute the main concern of Medical Geology.

The combination of knowledge of the earth sciences with that of medicine and life sciences offers an opportunity of several applications and possibilities to solve questions concerning health. This integration of efforts may improve the problem definition, help in approach strategies, define and locate sources of drinking water and develop economic solutions based on geological principles that can help minimize and, most of all, hinder suffering and disease.

There is an expectation that geoscientists, together with health professionals, will significantly contribute to the improvement of public health quality. According to European geoscientists, the studies carried out in the last 15 years are only the tip of an iceberg, a little sample of the research spectrum that is now initiating and that will transit in the wide space between geology and medicine.

Medical Geology is a team "science", requiring teamwork and agreement with other sciences. In detail, it studies regional or local variations in the distribution of elements, especially the metallic and metalloids, their geological-geochemical behavior, natural and artificial contamination and the damages to human, animal and vegetable health because of abundances or deficiencies.

Life on earth developed in the presence of all 97 elements that occur naturally, including the ones we call essential, non-essential, toxic and possibly toxic (Garret, 2005). The human body needs 25 elements, recognized until this moment, as essential for it to function properly. Among these elements the most important one is carbon (C), without which there would be no life as it is known today. Carbon molecular chains are the structural basis for thousands of different compounds constituting cells such as proteins and the DNA. Since more than 60% of the corporal mass is composed of water (H_2O), oxygen and hydrogen have a significant participation as essential elements. Oxygen surmounts in quantity any other element in the human body (61% of the corporal mass) because it is also present in the bone structure as calcium phosphate. Nitrogen (N) is also part of this selected group of the four most important essential elements (together with O, H and C), since it participates in practically all proteins and the DNA. The other 21 essential elements are usually divided into macronutrients (which need to be absorbed through diet in large quantities) participating in the corporal mass in concentrations higher than 0,1% (Ca, Cl, P, K, Na, S) and micronutrients, in corporal concentrations below 0,1% (Mg, Si, Fe, F, Zn, Cu, Mn, Sn, I, Se, Ni, Mo, V, Cr, Co). Table 1.

Though not essential, many elements are regularly absorbed through diet (food and water) and inhaled with the breathed air. Therefore, there can be variable quantities of these elements that get deposited in the human body according to their chemical affinity with certain tissues, like, for example: aluminum (Al), barium (Ba), cadmium (Cd), lead (Pb), arsenic (As), mercury (Hg), strontium (Sr), uranium (U), silver (Ag) and gold (Au) (Emsley, 2001).

The element constituents of rocks, when they become available due to weathering, may be absorbed in soil, get dissolved by runoff drainage and percolating groundwater or be carried with soil into superficial water bodies. In the soil they may be assimilated by plants, becoming part of the food chain. They also become part of the food chain when they are carried in solution through drainage and assimilated by aquatic species. However, besides through diet, the chemical substances can also be assimilated by living beings through inhalation or through the skin.

Generally speaking, the soil, running water and plants reflect the composition of the underlying rocks, their relationship being an important method to discover new ore deposits. When feeding on vegetation, wild animals also reflect the chemical fingerprint of the region where they live. This relationship is observed in humans as well, there being classical cases of diseases occurring along geological zones with lithological or geochemical anomalies (Figures 1 and 2). Anomalies are also related to pollution effects. However, natural contaminations such as the ones provoked by the deposition of ashes ejected in volcanic eruptions and by dust clouds generated in desert areas cannot be ignored.
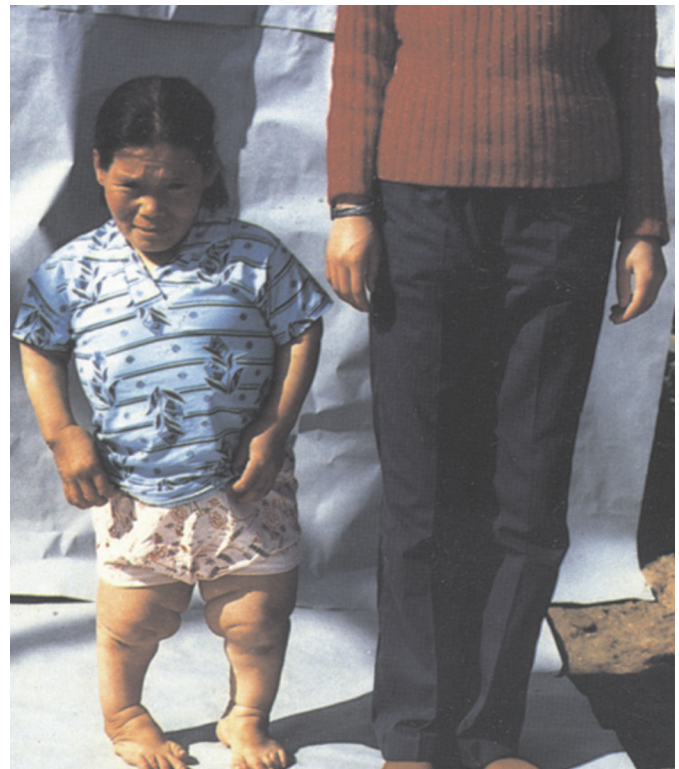

Figure 1 – Kaschin-Beck Disease, China. Bone formation disorder affecting growth and producing deformities, caused by deficiency of selenium in the water and soil.

Table 1 – Function of the chemical elements in the human bodies (Scarpelli, 2003)

	FUNCTION OF THE ELEMENTS CONSIDERED ESSENTIAL TO HUMAN BEINGS
O, H, N and C	See discussion about these elements in the text above.
Ca	It is the most abundant metal in the human body in the form of calcium phosphate in bones and teeth. It is essential to the regulation of cellular membranes activity, especially in muscular contraction and conduction of nervous impulses. It participates in blood coagulation, cellular division and hormones liberation (total quantity in the body = 1200g).
Cl	Maintenance of the **hydroelectrolytic balance** balance and body secretions; digestion of food as hydrochloric acid in the stomach (total quantity in the body = 95g).
K	Maintenance of the fluids balance on intracellular level (it is concentrated inside the cells), participating in muscular contraction and nervous conduction (total quantity in the body = 110-140g)
Mg	It operates in the maintenance of the bones structure; it regulates the passage of substances through the cellular membranes; it participates as a co-factor in more than 100 enzymes and in the production of proteins, being extremely important to the normal growth and development process (total quantity in the body = 25g).
Na	Maintenance of the **hydroelectrwolytic balance,** always remaining outside the cells, participating in muscular contraction and nervous conduction (total quantity in the body = 100g).
P	Constituent of bones and teeth in the form of calcium phosphate. It is essential to the process of chemical energy production through organic molecules of the ATP type (adenosine triphosphate), as well as being part of the DNA molecule (total quantity in the body = 780g).
S	It is part of the structure of keratin, the main constituent of hair, nails and external layer of skin. It is part of several enzymes that are essential to the normal metabolism and also of vitamin B1 (total quantity in the body = 140g).
Co	Constituent of vitamin B12 involved in the maintenance of the nervous system's integrity and in the production of red blood cells.
Cr	Essential to the metabolism of glucose. Despite its probable relationship with the developing of diabetes mellitus in adults, clinical cases of this element's deficiency in humans have not yet been described.
Cu	Constituent of about ten enzymes important to the human metabolism such as the superoxide dismutase, involved in the control of free radicals.
F	Essential to the maintenance of a healthy structure of teeth (enamel) and bones in minimal doses.
Fe	Component of hemoglobin, it is responsible for the transport of oxygen in the blood and for the reserve of this element in the muscles.
I	Essential to the normal functioning of the thyroid, since it is a constituent of the thyroid hormones, thyroxine and triiodothyronine. The nutritional deficiency of hormones is well known for producing a deficit in normal growth and serious mental and cognitive disorders.
Ni	Considered essential and linked to the control of growth, but not well known as to its action mechanisms in the normal metabolism.
Mn	Though considered to be essential, its specific functions are little known; it participates in enzymatic reactions and in the activity of vitamin B1 in minimal quantities.
Mo	Constituent of several important enzymes, among them the xanthine-oxidase, involved in the metabolism of proteins, and the aldehyde-oxidase, involved in the biotransformation of ethyl alcohol.
Se	The definition of selenium's essentiality is recent (1975), when it was found that it is a constituent of the molecule of glutathione-peroxidase enzyme, extremely important in the control of free radicals formation in the human metabolism. In 1991 it was found that it is also part of the deiodinase molecule, which participates in the production of the thyroid hormones.
Si	In 1972 it was defined that silicon is essential and linked to the process of bones growth.
Sn	It is still controversial as to its actual essentiality in humans. Effects of its deficiency are not known. It was previously considered essential for its supposed participation in the gastrin hormone.
V	It is related to the regulation of the enzymes involved in the sodium-potassium balance in the nervous system. Less than 0.5% of the ingested vanadium is absorbed in diet.
Zn	It exists in all tissues, especially in bones, muscles and skin; it acts in the immune system; it regulates corporal growth, protection of the liver. Its deficiency reduces corporal growth.

Figure 2 – More than a 100 million people in the world suffer from fluorosis. In Brazil it occurs, mainly in children, in the regions of São Francisco (MG) and Itambaracá (PR).

NATIONAL PROGRAM FOR ENVIRONMENTAL GEOCHEMISTRY AND MEDICAL GEOLOGY

The National Program for Environmental Geochemistry and Medical Geology Research – PGAGEM, coordinated by the Brazilian Geological Service – CPRM, is characterized by its multi-institutional and interdisciplinary concept giving multi-usage results. It was elaborated by researchers from: the Brazilian Geological Service – (CPRM), Campinas State University (UNICAMP), Paraná State Geological Survey (Minerais do Paraná – MINEROPAR), São Paulo University (Universidade de São Paulo – USP), Pará Federal University (Universidade Federal do Estado do Pará – UFPA), Londrina State University (Universidade Estadual de Londrina – UEL), the Evandro Chagas Institute (Instituto Evandro Chagas), the Adolfo Lutz Institute (Instituto Adolfo Lutz), the National School of Public Health (Escola Nacional de Saúde Pública – ENSP/FIOCRUZ and the Brazilian Agricultural Research Corporation (Empresa Brasileira de Agropecuária – EMBRAPA).

Today it enjoys international partnerships with the U.S. Geological Survey (USGS), U.S. Armed Forces Institute of Pathology (AFIP), Geological Survey of Sweden (SGU), International Union of Geological Sciences (IUGS), International Medical Geology Association (IMGA) and the University of Freiberg – Germany.

This program was conceived in 2003 with the following specific objectives:

- to carry out geochemical studies, preferably through partnerships, to identify and evaluate possible sources of natural and anthropogenic contaminations, integrate the data with information on public health, seeking to point out which areas and communities are exposed to the adverse effects related to the toxic elements and substances;
- to make available the analytic results for mineral prospecting purposes;
- to subsidize studies of geo-environmental information, in partnership with governmental bodies, universities and research institutes in the fields of toxicology and epidemiology;
- to indicate strategies and technologies in the field of environmental geochemistry for studies on environmental remediation;

- to contribute to the diagnosis of soils with deficiency in micro and macronutrients for agriculture;
- to develop an environmental education program for the affected populations in collaboration with public health agencies

In addition, PGAGEM contemplates other developments, such as:

- establishing sampling methods and standards, as well as standards and chemical laboratorial certification to develop analytical methodologies for geological materials in environmental studies;
- contribute to the development of the Environmental Geochemistry and Medical Geology Research Network – REGAGEM, to establish partnerships with city, state and federal institutions of public health and environmental sectors, using possible correlations between the geochemical data and the data on mortality and diseases incidence in humans and animals, and in due course, make it available in Brazil;
- encourage and subsidize data integration studies on environmental geochemistry, epidemiology and ecotoxicology generated in the research network using multidisciplinary teams;
- qualify human resources at graduate and undergraduate level for field and laboratory work and for treatment and interpretation of geological and geochemical data with multidisciplinary purposes related to the environment and public health, in addition to mineral research;
- support the strengthening of analytical laboratories infrastructure in the fields of geochemistry and toxicology in Brazil, encourage network collaboration in specific projects, proficiency tests and interlaboratory certification;
- create a referential data bank for the whole national territory, with the field and laboratory information generated by CPRM and participating actors; and establish a collection of geological material (sediment, soil and rock) related to environmental studies.

Through these proposals, it is expected the program will be useful to all participant institutions and for their correlated multidisciplinary programs, such as:

- plan local public health policies in areas with identified contamination risks by chemical elements to the population;
- plan environmental activities for the Ministries of Health and Environment and other municipal and state environmental institutions, the National Water Agency (Agência Nacional de Águas – ANA) and the hydrographic basins committees;

- identify surface sources of natural or anthropogenic contamination in urban or rural areas;
- the geochemical and environmental characterization of aquifer recharge areas;
- determine the magnitude of the contamination plume in surface and groundwater, especially those near irregular waste disposal sites and landfills;
- elaborate soil and groundwater vulnerability maps as well as risk maps;

generate information on soil geochemistry for pedological studies on fertility and for agricultural and cattle breeding use.

The methodological procedures used by PGAGEM were adjusted, as far as possible, to the geochemical standards set by the UNESCO–IUGS, IGCP-259 project and by the Working Group on Global Geochemical Baselines of IUGS – IAGC, to facilitate comparisons with similar studies in other countries. The following projects are examples of successful low density geochemical mapping to develop multiuse maps: the "Environmental Geochemical Atlas of the Central Barents Region" – Kola Project (600 sample locations in 188,000 km²), the Barents Ecogeochemistry (1,373 sample locations in 1,500,000 km²), the Geochemical Chart of the Paraná State -Atlas Geoquímico do Estado do Paraná (697 sample locations in 166,000 km²) and those made by the CPRM in Rio de Janeiro State (200 sample locations in 44,000 km²), in the Mogi Guaçu and Pardo river basins (99 sample locations in 21,000 km²) and the Ribeira river valley (187 sample locations in 28,000 km²).

PGAGEM encompasses the whole Brazilian territory, focusing initially on regions and hydrographic basins where health problems exist that may be related to the environment. Areas with some alteration features in the quality of water bodies and soil that may cause adverse effects on the health of living beings will also be studied as a priority.

The geochemical sampling includes surface water sample collection (where they occur), with varying sampling densities, and active streamed sediments along the region's hydrographic basins. In the Amazon region, due to the access problem, sampling will take place in basins with catchment areas of about 2,000 km² (1,000 – 3,000 km²). In other regions the selected basins have between 100 and 200 km².

Sampling campaigns of water for domestic use is also foreseen in cities without efficient water treatment plants or where there is none at all, and also of agricultural soils (0-25 cm), at the rate of 3 samples from each region.

Figure 3 shows the sampling programs per region, with around 29,700 sampling stations of sediment and water that generate around 59,400 samples in total. A further 5,000 samples of supply water and 10,000 soil samples is estimated to be collected, totalizing 74,000 samples for the entire program.

North
3,800,000 km²
8,250 sampling locations

Northeast
1,600,000 km²
7,750 sampling locations

Center-west
1,614,000 km²
6,200 sampling locations

South
580,000 km²
2,900 sampling locations

Total
8,514,000 km²
29,700 sampling locations

Southeast
920,000 km²
4,600 sampling locations
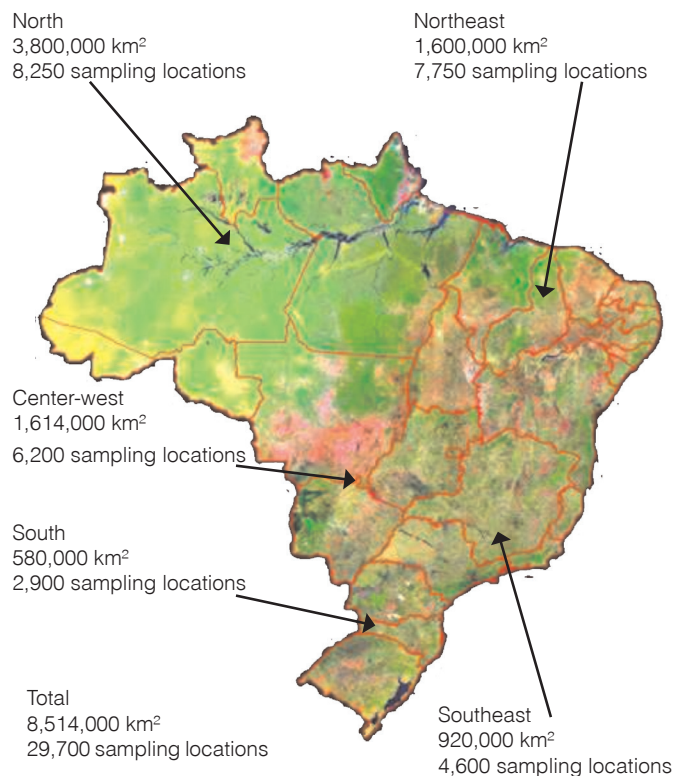
Figure 3 – Regional distribution of the sampling stations for streambed sediment (streambed and flowing water).

More details about the methodological procedures adopted by PGAGEM can be obtained at www.cprm.gov.br/pgagem, Lins (2002).

Partial Results

In just two years, 2003 to 2005, several studies were achieved within the scope of PGAGEM.

Under the responsibility of CPRM and partner institutions, about 4,041 samples of water, streamed sediments and soils were collected. Of these, about 2,960 samples were analyzed and the results of certain areas such as: Parintins in the Amazon; the NE region of Pará State; Lagoa Real in Bahia State; Vale do Ribeira, between the States of São Paulo and Paraná; in Ceará State, and Lavras in Rio Grande do Sul State, are to be found in this book. Results of other regions (Rondônia State, Goiás State, Teresina – capital of Piauí State - and Itinga –Minas Gerais State) should be published in 2006.

Parintins island situated on the right bank of the Amazon River about 350 km downstream of Manaus, is nowadays an important tourist region because of the traditional Boi-Bumbá festivity. The population had been experiencing health problems, probably associated with the bad quality of the public water supply, due to the important population influxes, especially during festivity time. The research activities developed on the island by Marmos & Aguiar (2006) included the analysis of 6

samples of stream water and 33 from tubular wells. The former group showed normal results, whereas among the groundwater samples about 63% revealed high contents of NO_3 (11-49 mg/L), Al (0.3-2.0 mg/L) and ammonia (2.9 mg/L) that were attributed to anthropogenic contamination, as only the wells less than 65 meters deep presented such high values.

In the Northeast of Pará State, according to Macambira & Viglio (2006), the results of the analysis of 77 samples from the public water supply, covering 80% of the studied area, showed excessive values of Al and Pb, respectively 18 and 145 times the maximum permissible concentration according to the National Environmental Council - CONAMA and WHO, followed by B, Cd, Fe, Cu, K, Mn, Zn and P. This water quality data is being correlated with the high incidence of endemic diseases like verminous diseases, digestive system diseases (cancer), dental caries, anemia and hepatitis.

Frizzo (2006) presents analytical results obtained from 234 samples of the public water supply from tubular wells and hand dug wells, ponds and lakes, springs and streams in Ceará State, in an area of 146,000 km². Concentrations beyond those permitted by CONAMA were detected in 43% of the samples for the elements considered toxic: Al (0.11 – 0.80 mg/L), As (0.02 mg/L) B (0.63 mg//L), Cd (0.001 – 0.02 mg/L) and Pb (0.01 – 0.46 mg/L) and for those considered toxic and essential: Ba (0.71 – 5.59 mg/L), Fe (0.31 – 12.1 mg/L), Mn (0.11 – 1.21 mg/L), Ni (0.26 mg/L) and Zn (0.18 – 0.76 mg/L). This information was given to the state sanitation department, which is conducting a re-sampling of the water to get a better definition of the mitigating measures to be taken.

In Lagoa Real, Bahia State, Oliveira (2006) carried out a sampling in groundwater (n=32), soil (n=32) and streambed sediment (n=42), in a 1,126 km² area. He recommends special attention to water consumption in that region, considering the analytical results that showed uranium concentrations in a range between 0.041 and 0.566 mg/L in 8 tubular wells, exceeding the maximum admitted value of 0.02 mg/L of U. He also foresees, in the near future, a shortage of the actual groundwater and a lack of this mineral's benefits due to excessive extraction.

The Project Geochemical and Environmental Landscapes of the Ribeira Valley – Evaluation and Prevention of Risks to the Physical Environment and Human Health Related to the Exposure to Arsenic and Heavy Metals, carried out by geologists, chemists, doctors and toxicologists of UNICAMP, Londrina State University (Universidade Estadual de Londrina), the Adolfo Lutz Institute (Instituto Adolfo Lutz) and the Brazilian Geological Survey – CPRM, according to Figueiredo (2005b), created the Geoenvironmental Atlas (Upper and Middle Ribeira Valley), the Geochemical Atlas of Sediment of the Ribeira Valley and the generation of totally new data about the exposure to Pb and As in ecosystems and human settlements in the Upper and Middle Ribeira Valley. Many of the results obtained from this project are presented as papers in this book and in the website www.ige.unicamp.br/geomed.

In southern Brazil, Grazia & Pestana (2006) studied the auriferous district of Lavras do Sul – RS, in view of the residues left by mining and artisanal ore extraction since the end of the 19th century; 43 samples of streambed sediments and 11 samples of soil were analyzed. The soil samples indicated contamination, especially in the areas close to the mining companies' processing plants, at levels higher than the intervention level of CETESB (2005) of 5 ppm for Hg. The highest concentrations found for Hg were (10.3 – 18.5 ppm), for As (24.5 – 163 ppm), Cu (124 – 1,469 ppm) and Pb (719 – 1.465 ppm). The authors recommend the remediation of the soil around the processing plants of CRM, Chiapetta and Cerro Rico, which may represent a risk factor to human health.

The examples above reveal that the activities under development in the PGAGEM framework have reached a significant level, though there is still much to be done. Usually, after the identification and observation of anomalous values of toxic elements that may cause adverse effects on public health, the health professionals/institutions are expected to be able to take over the issue to apply techniques of risk analysis to which the public is subjected. The results related to geochemistry as well as those concerning the medical aspects must be communicated to the public health departments to instigate coordinated actions yet avoid unnecessary alarmist disturbances.

It is also advisable that, according to the analyzed area and the type of contamination, communication programs of the risks and environmental education of the affected population should be developed in partnership with health departments.

PGAGEM may also serve as an incentive to the researchers connected to REGAGEM to establish partnerships, through their institutions, with SGB-CPRM and others, to obtain resources from financing agencies (CNPq, FINEP, Research Funds and Project Funds) for the execution of new projects. There are many other specific projects that may be proposed for metropolitan regions, hydrographic basins, mining districts and agriculture zones with active participation of federal, state and municipal research bodies as well as universities.

In this geochemical program we must emphasize the importance of homogenization of sampling analysis procedures by the institutions and researchers, therefore ensuring consistency of the data bank for all Brazil, which is available and accessible on the internet for all the scientific community and the public in general.

FINAL CONSIDERATIONS

In parallel to the PGAGEM implementation and considering that Medical Geology is still an unknown and innovative activity in Brazil, the REGAGEM participants have carried out countless dissemination activities, including the distribution of folders, in Portuguese and English, seminars and courses. They have also participated in workshops at congresses and symposiums related to geology, water resources, environment and to the medical field, as well as in seminars promoted by undergraduate geology students in several universities around the country.

The Campinas State University – UNICAMP and the Goiás Catholic University – PUC/GO, have already included in their post graduate programs some Medical Geology content. There is a growing tendency to include this new subject at graduate and post graduate geology and medicine courses, based on the diffusion of the recently published text book "Essentials of Medical Geology". Copies of this book were recently acquired and distributed among Brazilian Geological Survey – CPRM professionals and researchers from several institutions and regions across the country.

The facts and data related above show that Medical Geology in Brazil has had a significant growth since 2003 mainly due to the creation of the REGAGEM network, the implementation of the national research program PGA-GEM and the maintenance of its own website. With less than 10 researchers in 2000, it is estimated that today about 80 researchers work in the Brazilian Medical Geology field. To reinforce this progress, it is important that periodic scientific meetings and mini-courses continue to be held, henceforth counting on the support of the International Medical Geology Association – IMGA.

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EPIDEMIOLOGY AND MEDICAL GEOLOGY

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INTRODUCTION

Medical geology is defined by Selinus (2005) as "the science that deals with the relationships between natural geological factors and human and animal health." According to this author, it is also "… the science that seeks to understand the influence of ordinary environmental factors on the geographical distribution of such health problems". The term "factor" and the expression "health problems" in this definition lead to the concept of "cause and effect" that, in turn, leads to the concept of "epidemiology" in the realm of health.

Epidemiology is the discipline that "studies the way diseases or events related to the binomial health-disease are distributed among populations and what are the factors that determine such distribution" (Gordis, 1996). Thus, it is at the base of epidemiology to study all the possible factors involved in the health-disease complexity, such as genetic and infectious factors, those related to habits (including the type of diet, tobaccoism, alcohol consumption, the pattern of physical exercises practice, etc.), occupational factors as well as those related to the environment (including natural geological, scope of medical geology and anthropogenic factors).

There are just a few diseases of environmental origin that are pathognomonic in the sense that only that specific exposure is related to that group of signs and symptoms. Usually, several substances or chemical elements can produce the same type of symptomatology or disease. Likewise, there are several possibilities of habit, genetic and occupational factors causing the same problems (Nielsen & Jensen, 2005).

Therefore, in any study related to medical geology, where it is necessary to define whether a certain natural geological factor is associated or not with the cause of the observed health problems, the cooperation with epidemiology is essential.

Epidemiology is based on the postulate that a disease does not occur randomly; on the contrary, its occurrence is linked to the specific characteristics of the given population. The definition of a cause related to a natural geological factor or an ordinary environmental one, as stated by Selinus (2005), necessarily goes through an epidemiologic study of that specific situation, where the geologic hypotheses will be one among other possibilities, at first.

EPIDEMIOLOGY GOALS

Epidemiology studies have the following goals (Gordis, 1996):

a) Identify the etiology (or cause) and the so-called risk factors to the investigated disease occurrence, to define the way it is transmitted or the mode of exposure, for example;

b) Determine the extent of the disease within the community;

c) Study the natural history of the disease (e.g., whether the appearance of the event is acute, sub-acute or chronic; the duration of the problem; what is the prognosis concerning cure; chronicity; sequela and death);

d) Study the change in the disease distribution over time as, for example, changes in the mortality pattern and in the disease incidence according to gender, age group, life expectancy, etc.;

e) Assess therapeutic and preventive measures;

f) Based on the results of the studies, create a framework for public policies and decision making about regulations related to problems of environmental contaminations, for example.

EPIDEMIOLOGIC APPROACH

Epidemiology studies are usually initiated by describing the situations based on the incidence and prevalence data available or collected for that purpose.

The incidence of a disease or health event is defined as the number of new cases over the number of people exposed to the risk in that particular community (neighborhood, town, state, country, continent, etc.) per time period (usually a year or during epidemics, a month or a week).

Prevalence relates to the number of cases accumulated during a certain time period, including the incidents and those that became chronic or were not yet cured. This is the data concerning morbidity.

Morbidity is a "generic term used to designate the set of cases of a given infection or the total health incidents that attain a group of individuals" (Pereira, 2000). The estimations of morbidity for a given population are based on different register sources such as health services dossiers; compulsory notification of certain diseases (usually infecto-contagious); special registers for diseases like cancer, tuberculosis, AIDS, leprosy; archives from pathologic anatomy laboratories; data on hospitalizations in the Public Health System – (Sistema Único de Saúde – SUS), and other sources. The quality of this data is always linked to the extent of the register's coverage and to the quality of the medical assistance that is offered.

Data about mortality is also extremely important and, depending on the situation, may carry more epidemiological relevance than the morbidity data.

The mortality data is founded on registers of internationally standardized death certificates or declarations which must report information about: a) the basic cause of death (that is, the disease or lesion that brought about the series of pathologic events and resulted directly in death); b) possible incurred complications; and c) other significant pathologic states that did not have a direct relation with the death.

The standardization of death certificate completion has brought great benefits such as the possibility to compare data at an international level. However, the quality of the procedure is still a big problem around the world since it depends on: the local medical assistance level; the specific training received by doctors; the personal interest of the doctor; the standardization of medical terms; etc.

Thus, faced with morbidity or mortality data, it is necessary to ask, first of all, whether the data is authentic. In other words, does it describes a given population health situation and if it is comparable with other regions (sampling quality, degree of that population health cover, etc.). Any inference made at the epidemiological study close dealing with a causal relationship among determined factors (environmental, occupational, genetic, related to food habits, etc.) has to refer to the quality of the morbidity and mortality data.

Regarding the etiology definition of a given health incident, the investigator must follow two essential steps in the epidemiological reasoning: 1º) to determine whether there is an ASSOCIATION between a factor (e.g., a given environmental exposure) and the health incident and, 2º) in case the association exists, to derive appropriate inferences about the existence of a causal relationship in that association following well defined judgment criteria (see below).

TYPES (DIAGRAMS) OF EPIDEMIOLOGICAL STUDIES

Epidemiological studies may be didactically divided into observational and experimental (Table 1). The observational studies are divided into descriptive, on the one hand, and analytical, on the other.

Experimental studies in epidemiology are basically limited to the so-called controlled therapeutic clinical tests, used to evaluate the effectiveness of new medicines or treatments. In such tests one tries to control all the variables that interfere in the treatment process, selecting the patients appropriately, defining criteria for the diagnosis of the disease, determining exposure doses and establishing the type of result expected from a new medicine or treatment compared to the traditional ones or even to a placebo treatment (medicine without active ingredients, for example).

Table 1 - Types of epidemiological studies

OBSERVATIONAL
1. Descriptive (describe the situation and generate causal relationship hypotheses) • Prevalence / incidence • Cross sectional studies • Ecology studies
2. Analytical (investigate the cause) • Case control studies (retrospective) • Cohort studies (prospective sequence)
EXPERIMENTAL
1. Controlled therapeutic clinical tests 2. Intervention in the community

WWithin environmental epidemiology, experimental studies are represented only by the study of the intervention in the community. It is useful when proposing, for instance, to add a given vitamin supplement or chemical

element to the diet or drinking water of certain populations, based on preliminary studies that show a beneficial effect of that addition (e.g., iodine in the salt, fluorine in the drinking water, etc.). The experimental studies, whether clinical with new medicines or of intervention in the community, must consider and respect several ethic aspects that are involved in their planning and execution.

Within observational studies, i.e., without experimental intervention, we have two basic types: the descriptive and the analytical. The descriptive studies, as the name says, describe the situations and generate hypotheses about possible statistical or epidemiological associations between certain factors and the health incidents being studied. They investigate the incidence and the prevalence of the problems being examined and have, in general, a character of cross section in time, that is, they study the situation within a narrow time limit, producing a static portrait of the situation at that moment. Investigating the factors that may be related to the health incidents, these studies generate causal relationship hypotheses from existing associations between the variables. However, they don't have the power to establish causal correlations in most of epidemiological situations.

Inferences of the causal type are easier to make using an analytical approach. In a study of this kind the hypothesis in tested about the causal association generated by the descriptive study. To achieve this, three basic sub-types of studies are available and they are employed depending on the health incident characteristics being analyzed and on the specific exposure type and characteristics.

In an analytical observational study such as the case control type, the researcher starts with the diagnosed health problem (a specific disease, a symptom, the result of a complementary examination, etc.) and tries to define which type of factor is causally associated with it in a retrospective way. The basic scheme of this kind of study involves the grouping of several individuals with the same problem ("cases") that will be compared with another grouping of individuals with a different kind of problem ("controls"). In both groups the same factors will be investigated (variables related to diet, past occupations, hobbies, use of medicines, habits, geographical origin, ethnic group, etc.). The factor or variable that predominates significantly in the study group ("cases") may be imputed as the probable causal factor, in case it fulfills most of the epidemiological criteria of causation established by Hill (1965) that are discussed later.

An analytical study of the cohort type, starts with the common exposure of a given population group and looks for the occurrence of the health incident over time, comparing the incidence of the problem in that group with a non-exposed population group. This is called a prospective scheme over time. These studies demand

a lot of work and are very expensive as they imply all kinds of operational problems related to the necessity of keeping track of a large number of people during long periods of time (the time period depends on the type of health problem, whether it is acute, sub-acute or chronic). For instance, a given type of cancer study and the environmental exposure to a particular chemical element. As cancer is a disease of late occurrence, with long latency periods – 20 to 30 years – gives an idea of the difficulty in maintaining entire populations under surveillance for 30 or 40 years. This study type is quite powerful in the sense of establishing the relation of the causal nexus between exposure and the health incident.

Still, within the observational studies there are ecological studies that compare data, such as weight, height, weight at birth, nutritional data, prevalent diseases, specific laboratorial parameters on populations in different geographical areas, or even comparing this data in the same population in different moments. This type of study is very descriptive, generating causal relation hypotheses that have to be tested using other more appropriate schemes. The difference from the basic descriptive studies is that it doesn't collect individual data. They are very useful in evaluations of the impact of intervention measures in populations, such as health programs (Kleinbaum et al., 1982).

CAUSAL ASSOCIATION CRITERIA

Faced with a statistically significant association between a variable (investigated factor) and the disease or health incident (issue), the decision whether it is causal or not goes through a series of logical considerations that must be carefully examined. To make it easier and, in addition, to standardize this reasoning, Hill has established a list of causation criteria (slightly changed over the years) that must be fulfilled for an association between the variables to be considered as of the causal nexus (Hill, 1965; Gordis, 1996). Table 2 exposes these criteria and their meanings in a didactical way. For specific details and examples, the reader should consult the references cited at the end of this text. These criteria remain basically the same until today, though modified by other authors so as to make them clearer. The non-fulfillment of all criteria does not necessarily exclude the possibility of the causal nexus, but it weakens, more or less, the possible causal inference in that situation.

This study does not intend to substitute the search for more profound information in the many existing textbooks on epidemiology. It only intends to raise the discussion about the complexity of epidemiology involved in medical geology studies that may be developed in our midst. In addition to the methodological and logistical aspects involved in the planning and execution of epidemiological studies, it must always take into account the ethical prob-

Table 2 - Judgment criteria of the causal association in epidemiological studies

Time relationship	Specificity
▪ the cause must always precede the effect	▪ the observed effect must not occur without the exposure to the presumed cause (if this criterion is not fulfilled, this does not deny the cause and effect relationship defined by other criteria)
Strength of the Association	Coherence with today's knowledge
▪ the greater the relative risk (RR) or the chance rate (OR) the greater the causal association strength	▪ the causal association must not conflict with already established facts
Relationship of response-dose	Considerations of Alternative Explanations
▪ the risk of becoming ill must increase with the increase of the exposure dose (in the same population the group of people who are most exposed must have the greatest incidence of health incidents)	▪ interpretation of a causal association must go through a discussion of all possible factors involved
Consistency (replication of the findings)	Ceasing of the Exposition
▪ the causal relationship observed in this study must be replicated in other studies	▪ if a factor causes a disease, it is expected that the removal of this factor will reduce or eliminate the disease occurrence
Biological Plausibility	Analogy
▪ the causal relationship must be based on recognized biological mechanisms	▪ similarity to other causal association accepted beforehand

lems that any type of study can impose on the involved populations. Its purpose was not to raise this particular discussion, but to state that it must be present every time this kind of study is planned and that it must go through the evaluation of an ethics committee of the research institutions involved.

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HEALTH SURVEILLANCE RELATED TO CHEMICALS IN THE AMBIT OF THE BRAZILIAN UNIFIED HEALTH SYSTEM (SISTEMA ÚNICO DE SAÚDE-SUS)

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The Brazilian Federal Constitution promulgated in 1988, The Brazilian Federal Constitution promulgated in 1988, establishes a set of obligations and rights that are fundamental to improve the Brazilian population's life quality.

The Chapter on Health, established and expanded in law nº8080, known as the Unified Health System Law (Sistema Único de Saúde – SUS), determines that health is a citizen's right and a duty of the State, based on principles that ensure the population's universal access to health promotion, prevention, treatment and rehabilitation services.

The complexity of today's life, in which development and the application of science and technology on a large scale coexist with deep social and economical inequity, reveals multiple new health risks whether in formal or informal work settings, domestic environments or public and communitarian surroundings.

In this context, there is a constantly growing human exposure to chemical substances derived from different sources and activities: products and services that contain them; laboratories that produce and manipulate them (mineral extraction, industrial processing and transformation); inappropriate waste disposal; environmental contamination of water bodies, the atmosphere and soil, among others.

International initiatives by the United Nations are demonstrating it is important to treat the chemical security issue appropriately. Thus, protocols and commitments such as the International Forum for Chemical Security, the Ban on Persistent Organic Products, the Preliminary Report on the Commercialization of Chemical Products, the International Regulation of Dangerous Waste Transport and, more recently, the Global Strategy on Chemical Security endeavor to reduce health and environmental risks by applying control mechanisms to chemical substances throughout their life cycles.

In Brazil, the National Commission on Chemical Security (Comissão Nacional de Segurança Química – CONASQ) presided by the Ministry of the Environment and where the Ministry of Health is a member, expresses the concerns and initiatives of the Brazilian government and society about this issue.

The Ministry of Health is structuring itself and organizing services that will collaborate with the chemical security strategy. Among these should be highlighted the National Program for Health Surveillance related to Chemical Substances (Programa Nacional de Vigilância em Saúde Relacionada a Substâncias Químicas – VIGIQUIM), which is already in a pilot stage.

VIGIQUIM seeks to detect, acquire knowledge, map and monitor populations exposed to chemical substances that are known for their harmful effects to health. At this stage, five contaminants have been elected as priorities: asbestos; agrochemicals; benzene; lead and mercury.

Another initiative is the National Program for Health Surveillance in Communities Exposed to Contaminated Soil (Programa Nacional de Vigilância em Saúde de Populações Expostas a Áreas com Solos Contaminados – VIGISOLO), which seeks to detect, assess, map and monitor populations exposed to areas with contaminated soil. Analyzed data obtained by the Ministry of Health informs there are at least 689 sites where health risk evaluation methodologies should be applied.

The health risk control standards for water contamination by chemicals have been adjusted by Regulation nº518 from the Ministry of Health. Its implementation and monitoring is carried out by the National Program for Health Surveillance related to Water Quality for Human Consumption (Programa Nacional de Vigilância em Saúde Relacionada à Qualidade da Água para Consumo Humano – VIGIÁGUA).

With these and other initiatives, the Ministry of Health, in cooperation with other Ministries, is effectively contributing to the construction of a strong chemical security agenda in Brazil, directed to ensure that public health and environmental protection are taken into account in the economic development.

SURFACE MULTI-ELEMENT GEOCHEMISTRY FOR RISK AND ENVIRONMENTAL IMPACT ASSESSMENTS, PARANÁ STATE BRAZIL

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INTRODUCTION

A proper environmental diagnosis necessarily deals with an adequate knowledge of the chemical characteristics of the physical environment. These characteristics are identified through surveys based on collecting samples from different environments, such as water, soils and bottom sediments within hydrographic basins. Geochemical maps present the distribution of the elements and chemical compounds in natural material samples representing the sum effects of natural and anthropogenic sources. Therefore, they are considered as basic instruments for multipurpose environmental assessments, including geo-medicine, medical geology and ecotoxicology. The compilation of geochemical data produced by mineral exploration projects and the elaboration of integrated geochemical maps may be a first approach to reveal health risk regions. However, the correct use of geochemical maps, when researching correlations between environmental geochemistry and endemic diseases, will only be successful if the data produced is interpreted considering the bioavailability of the elements and chemical compounds. Weak extraction methods in active stream sediment samples and ions determination in a filtered water sample are adequate for this purpose, as they only identify a fraction of the total element content liable to be absorbed by the food chain. The comparison between geochemical maps of some elements such as samples from water with bottom sediment samples perfectly demonstrates this concept as well as the considerable differences between total chemical species in both environments (Figures 7, 8, 9 and 10). It is necessary to determine the largest possible number of analytical variables (physical-chemical parameters, ions, elements and oxides) with the lowest possible detection limits, to constitute a powerful data base to make maps. Thus, many diverse interpretations are possible and cause-effect correlations obtained when the geochemical data is compared with the parameters of: spatial distribution of human and animal mortality; agricultural fertility; diffused and point sources of pollution among others. In this way multi and trans-disciplinary interpretations may determine potential areas for prospecting ore and identifying health risk regions. The association of fluorine with dental fluorosis occurrence as well as chlorides and bromides as risk indicators for liver cancer areas are connections already defined in the Paraná state. More research is necessary to establish the real threats of some risk areas indicated by barium, potassium, calcium, aluminum in water and lead, lanthanum, cadmium and mercury in active stream sediments and soil.

Geo-Graphical Location

Paraná State is located in South Brazil and occupies an area of 199,575 km² (ITCF, 1987 apud Licht, 2001a). To the north it is bordered by São Paulo State, to the east by the Atlantic Ocean, to the south by Santa Catarina State, to the southwest by the Republic of Argentina, to the west by the Republic of Paraguay and to the northwest by Mato Grosso do Sul State (Figure 1). The Curitiba base map (SG-22-X-D-I, 1:100,000) is situated in the Curitiba City metropolitan region and includes the northern part of its urban area in addition to the cities of Rio Branco do Sul, Almirante Tamandaré, Colombo, Piraquara, Pinhais and São José dos Pinhais (Figure 2).

THE GEOCHEMICAL DATA BASES

Geochemical surveys have been extensively applied everywhere in the world since the 1930s. They have been directed to mineral prospection and there have
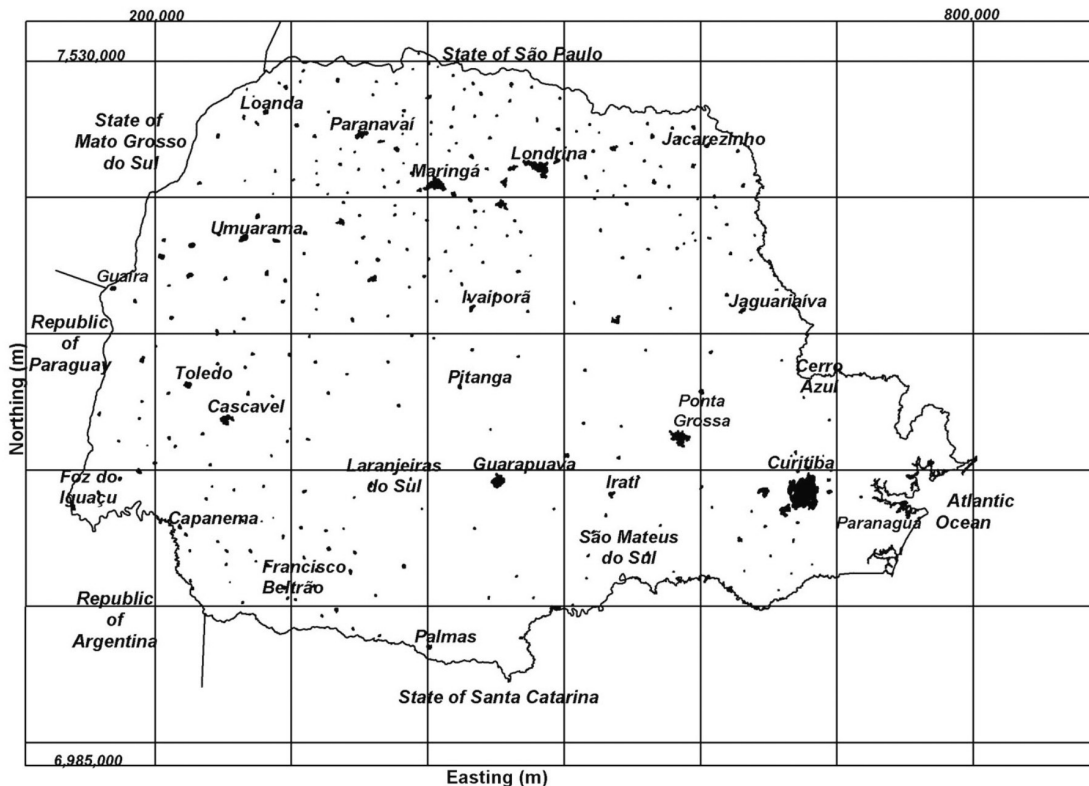

Figure 1 – Geographical location of Paraná State.

Figure 2 – Borders and main urban agglomerations of Paraná State.

been countless successful cases in all regions and environments. In Paraná State, geochemical surveys have been employed since the 1970s by several private and state organizations. They have resulted in the discovery of several occurrences and processes of mineralization such as the fluorite deposit in Volta Grande and the W-Sn mineralized greisens of Cantagalo. In 1995, on an initiative of Minerais do Paraná S.A. – MINEROPAR, the Low Density Multi-elemental Geochemical Survey of Paraná State was begun, based on the collection of 696 samples of water and active stream sediments within hydrographic basins across the whole 200,000 km^2 state area. In 2002, the second stage of the survey was carried out with a collection of 307 samples of B horizons from soils in a regular grid. The project followed the World Geochemical Map criteria and standards established by the IGCP-259 and IGCP-360 projects (Darnley, 1995). According to those recommendations, 43 composite samples were produced from the original ones, each one representing a unit cell of 80 x 80 km of the grid denominated GGRN (Global Geochemical Reference Network) (Figures 3 and 4).

The geochemical sampling campaign of the Curitiba Base Map, in its turn, was planned and executed in 1995 together with the Brazilian Geological Survey (Compan-

hia de Pesquisa de Recursos Minerais – CPRM), when 392 samples of active stream sediments were collected, including the densely urbanized area of Curitiba city and adjacent towns (Figures 5 and 6).

THE GEOCHEMICAL DATA BANK

Water from watersheds within Paraná State – The 696 original samples were analyzed in the Mineral Analyses Laboratory (LAMIN/CPRM) to determine Al^{3+}, Ba^{2+}, Br, Ca^{2+}, Cl^-, F^-, Fe^{3+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, NO^{2-}, NO^{3-}, PO_4^{2-}, SO_4^{3-}, Sr^{2+}, pH and conductivity (Licht, 2001b).

Bottom sediments from watersheds within Paraná State – The 696 original samples were analyzed in the LAMIN/CPRM to determine Co, Cu, Cr, Fe, Li, Mn, Mo, Ni, Pb, V, Zn (Licht, 2001b). The 43 GGRN samples were analyzed in the Institute of Geophysical and Geochemical Exploration – IGGE laboratory, situated in Lanfang, China, to determine Ag, Al_2O_3, As, Au, B, Ba, Be, Bi, Br, CaO, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Fe_2O_3, Ga, Gd, Ge, Hg, Ho, I, K_2O, La, Li, Lu, MgO, Mn, Mo, Na_2O, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, S, Sb, Sc, Se, SiO_2, Sm, Sn, Sr, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, with analytical detection limits lower than the respective Clarke (Licht, 2001a).
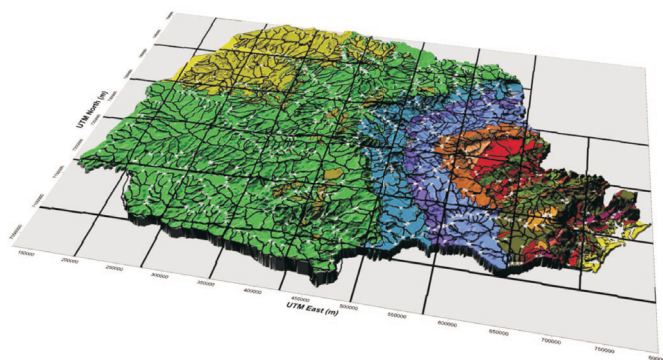

Figure 3 – The GGRN unit cells in the Paraná State, the watershed and the stream sediment collection sites (Licht, 2001).

Figure 4 – The GGRN unit cells in the Paraná State and the soil – horizon B collection sites (Licht and Plawiak, 2005).
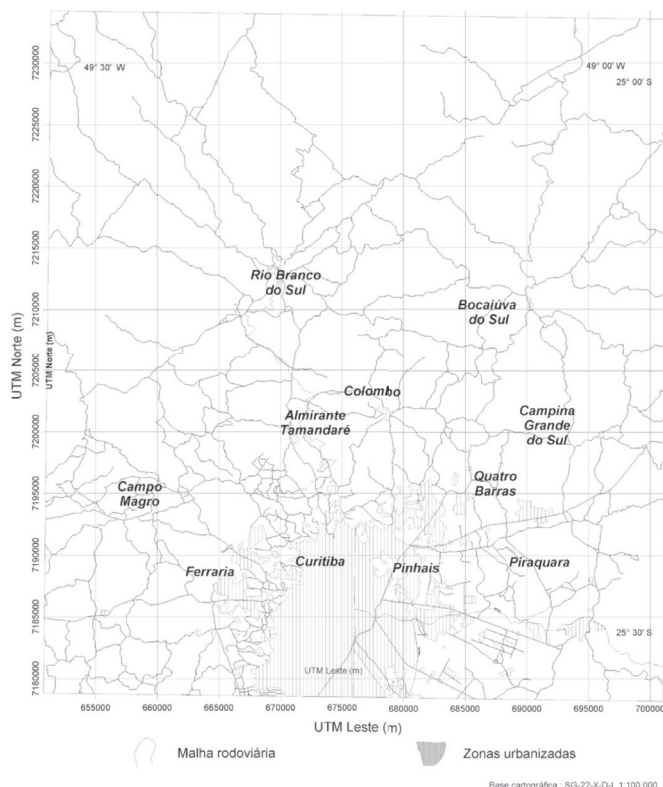

Figure 5 – Main urban concentrations and road network of the Curitiba base map (SG-22-X-D-I).
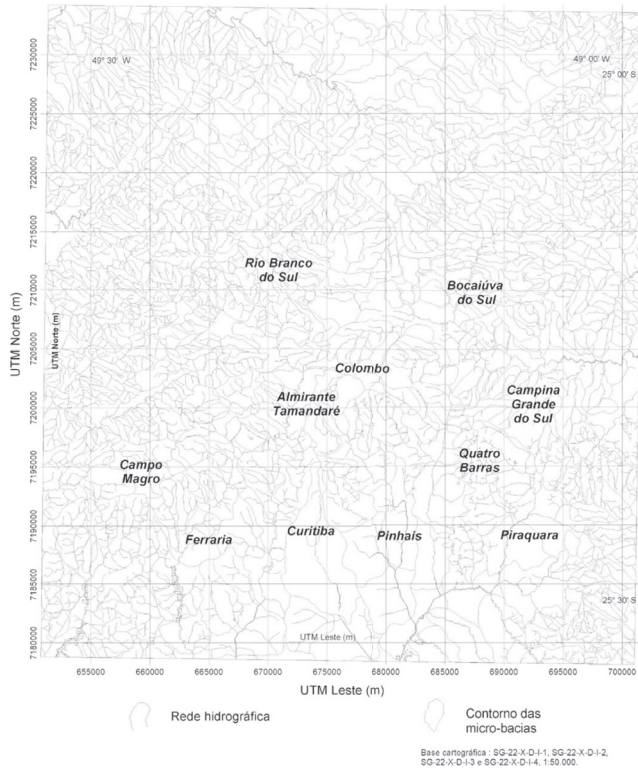
Figure 6 – Hydrographic network (blue) and the 392 watersheds (red) of the Curitiba base map (SG-22-X-D-I).

Figure 7 – Geochemical surface of F- in 696 water samples from watersheds .
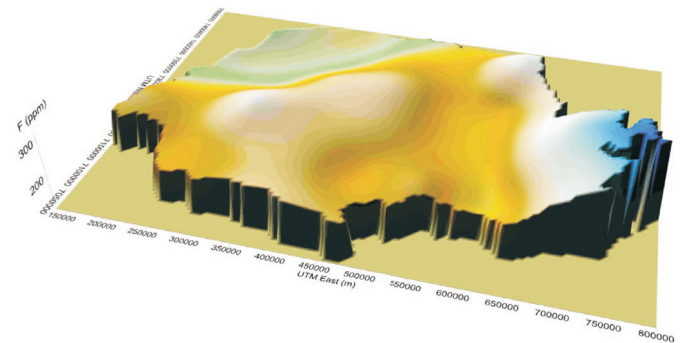
Figure 8 – Geochemical surface of F in 39 GGRN samples (composed of 698 samples of active stream sediments).
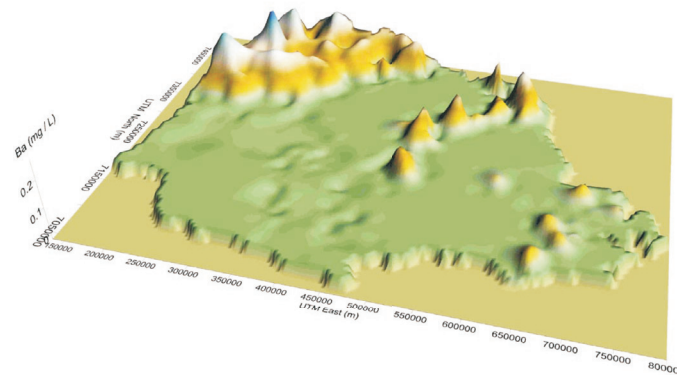
Figure 9 – Geochemical surface of Ba^{2+} in 696 water samples of watersheds.

B-horizon from soils of the Paraná State – The GGRN samples were analyzed in the IGGE to determine Ag, Al_2O_3, As, Au, B, Ba, Be, Bi, Br, CaO, Cd, Ce, Cl, Co, $C_{organic}$, Cr, Cs, C_{total}, Cu, Dy, Er, Eu, F, Fe_2O_3, Ga, Gd, Ge, Hf, Hg, Ho, I, In, K_2O, La, Li, Lu, MgO, Mn, Mo, N, Na_2O, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, S, Sb, Sc, Se, SiO_2, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, with analytical detection limits lower than the respective Clarke. In addition, to determine U, K, Th and total counting through gamaespectrometry and magnetic susceptibility was carried out by the Applied Geophysics (LPGA) Laboratory of the Paraná Federal University (Universidade Federal do Paraná – UFPR). Finally, the agricultural chemistry parameters were determined in the Laboratory for Soil and Vegetal Tissues of the State Agronomic Institute (Instituto Agronômico do Paraná – IAPAR). These parameters were: pH, $Al_{changeable}$, $Ca_{assimilable}$, $Mg_{assimilable}$, $P_{assimilable}$, $K_{assimilable}$, C, $H^+ + Al^{3+}$, $Cu_{extractible}$, $Zn_{extractible}$, $Fe_{extractible}$, $Mn_{extractible}$, $S_{extractible}$, $B_{extractible}$, Al%, V% (bases saturation), T (sum of the positive changeable charges) and S (sum of the changeable bases) (Licht & Plawiak, 2005).

Bottom sediments from watersheds of the Curitiba base map – The 392 samples were analyzed in the LAMIN/CPRM and in a commercial laboratory, with determination of Hg, Nb, F, Zr with strong extractions and P, Cr, Li, W, As, V, Sc, Ni, K, Sr, La, Mg, Mn, Na, Y, Co, Pb, Cu, Ca, Zn, Al, Ba and Fe with weak extractions (Licht, 2001c).

RESULTS OBTAINED

Evaluations made so far with the geochemical data base produced by the previously described survey associated with sanitary and epidemiological data, revealed a clear scenario of the cause-effect relationships in some regions bearing health risk potential. A special reference should be made of fluorides in the water and the prevalence of dental fluorosis, as well as chlorides and bromides as risk area indicators considering the prevalence and increased mortality rate by hepatic neoplasias. To better spatially define the risk area to start epidemiological studies as in the case of mercury in stream sediments and soils, other results are being analyzed. There is other data still awaiting more detailed analysis, for example, lanthanum, mercury and lead in the Curitiba region.

Figure 10 – Geochemical surface of Ba 39 samples GGRN (composed of 698 samples of active stream sediments).

Table 1 - Prevalence and severity of dental fluorosis in school children in the São Joaquim do Pontal borough of Itambaracá, Paraná.

N = 135 patients (Morita et al, 1998)					N = 1129 patients (Cardoso et al, 2001)					
Normal	Uncertain	Very mild	Mild	Moderate	Normal	Uncertain	Very mild	Mild	Moderate	Severe
52	5	31	38	9	410	30	478	165	41	5
38.52%	3.7%	22.96%	28.15%	6.67%	36.3%	2.7%	42.3%	14.6%	3.6%	0.4%
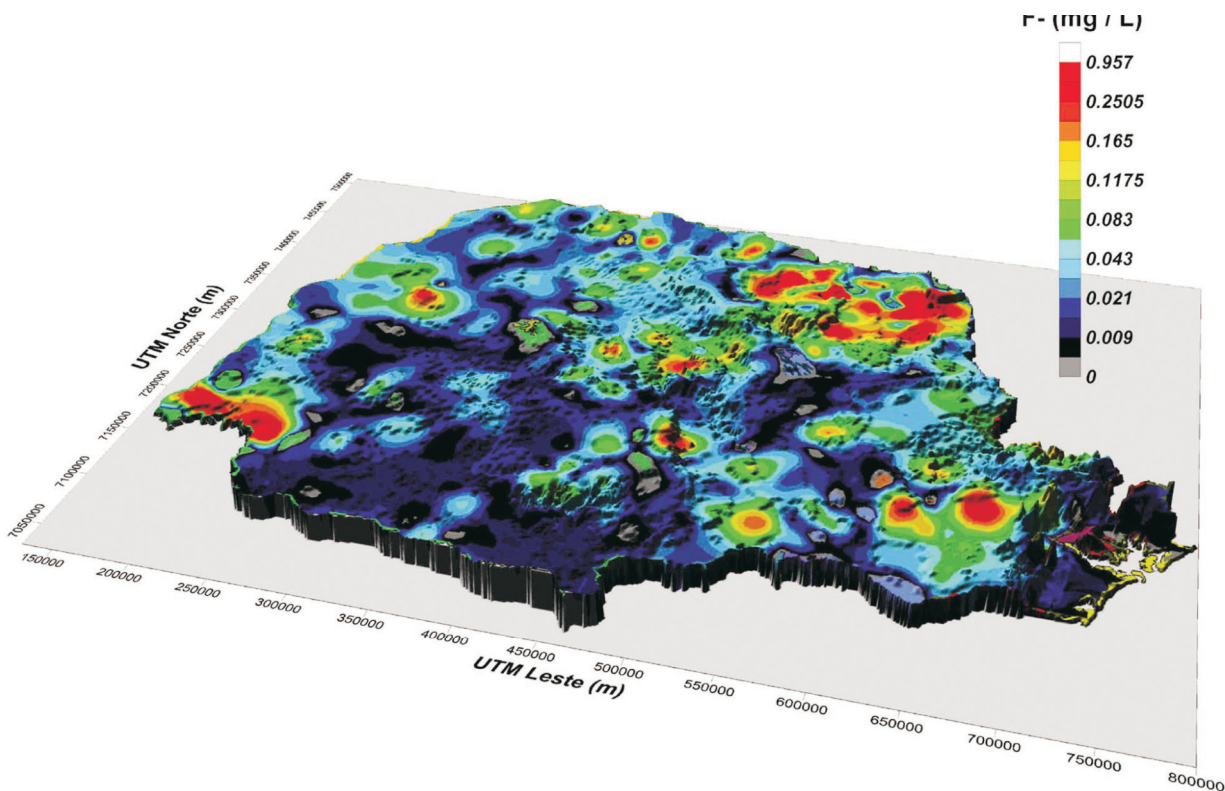
Figure 11 – Geochemical map of F^- (mg/L) in water samples from watersheds. The fluorine-anomalous area situated in the north of the state is the cause of the high incidence of dental fluorosis in children.

Fluorides and dental fluorosis – this is a concrete example of the cause-effect relationships between geology and human health. Its confirmation was based on two epidemiological investigations carried out in the fluorine-anomalous region, previously delimited by the geochemical survey (Table 1).

The anomaly of about 10,000 km², situated in the north of Paraná State (Figure 11) includes 47 cities and a population of about 700,000 inhabitants. It is a region where the water for human consumption is taken from deep tubular wells which has high fluoride content, reaching 2.2 mg/L F⁻ and causing serious sanitary problems with endemic characteristics (Figure 12). Surface water from local drainages also present high fluoride content, identified by the Geochemical Survey, reaching 0.9 mg/L F⁻.

Bromides, chlorides and hepatic neoplasias – The Paraná State northern region is a traditional coffee beans and cotton growing area (Figures 13 and 14). For a long time, until its ban, chlorinated and bromated pesticides were freely used in the control of crop pests building an environmental passive of unknown dimensions. Marzochi et al. (1976) had already identified not only the prevalence but also the high mortality rate due to hepatic neoplasias (liver cancer) in that region. They related this health problem to the use of agrochemicals, especially those with chlorine and bromide.

The Geochemical Survey identified the existence of an increase in background concentrations of bromides and chlorides in river basin surface waters (Figures 15 and 16).

Based on these results and on the Ministry of Health Mortality Data Bank – DATASUS, Licht (2001a) the spatial

Figure 12 – The teeth of the superior dental arcade are corroded by the continual intake of water with high doses of fluorides.
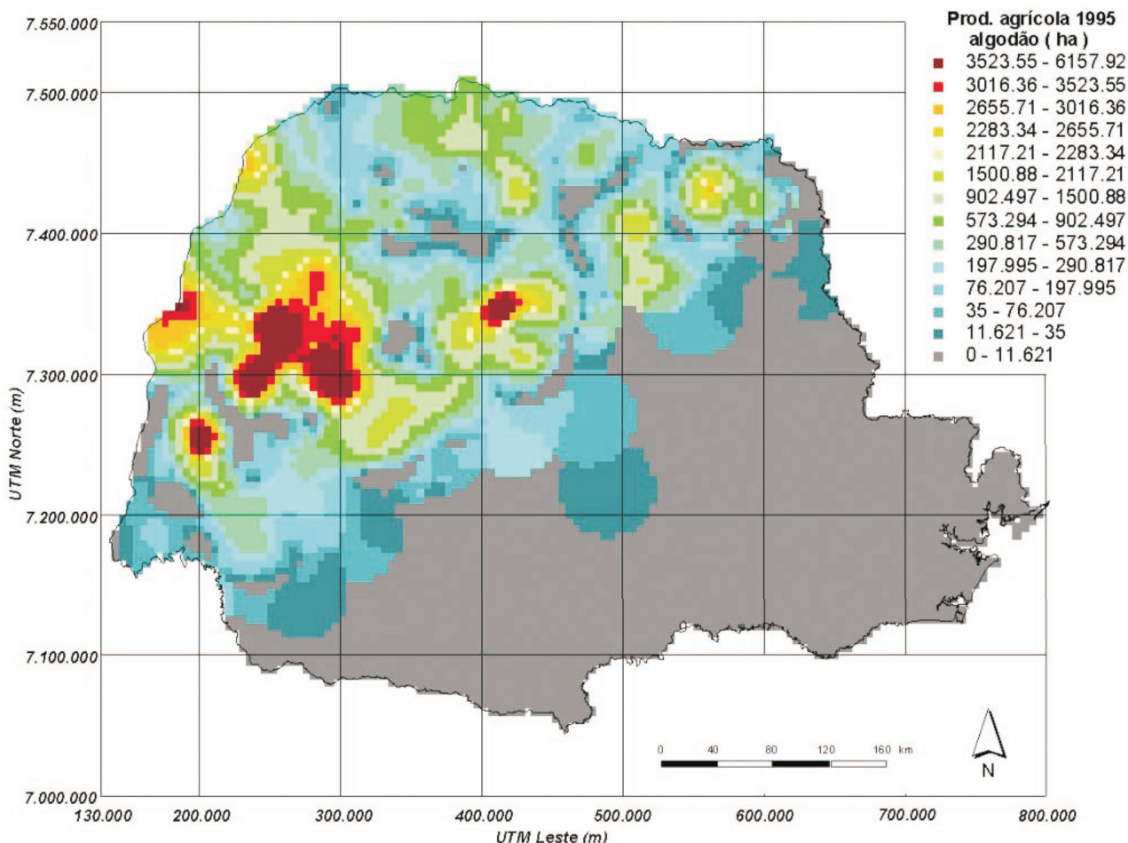
Figure 13 – Area (in hectares) planted with cotton in the 1995 harvest.
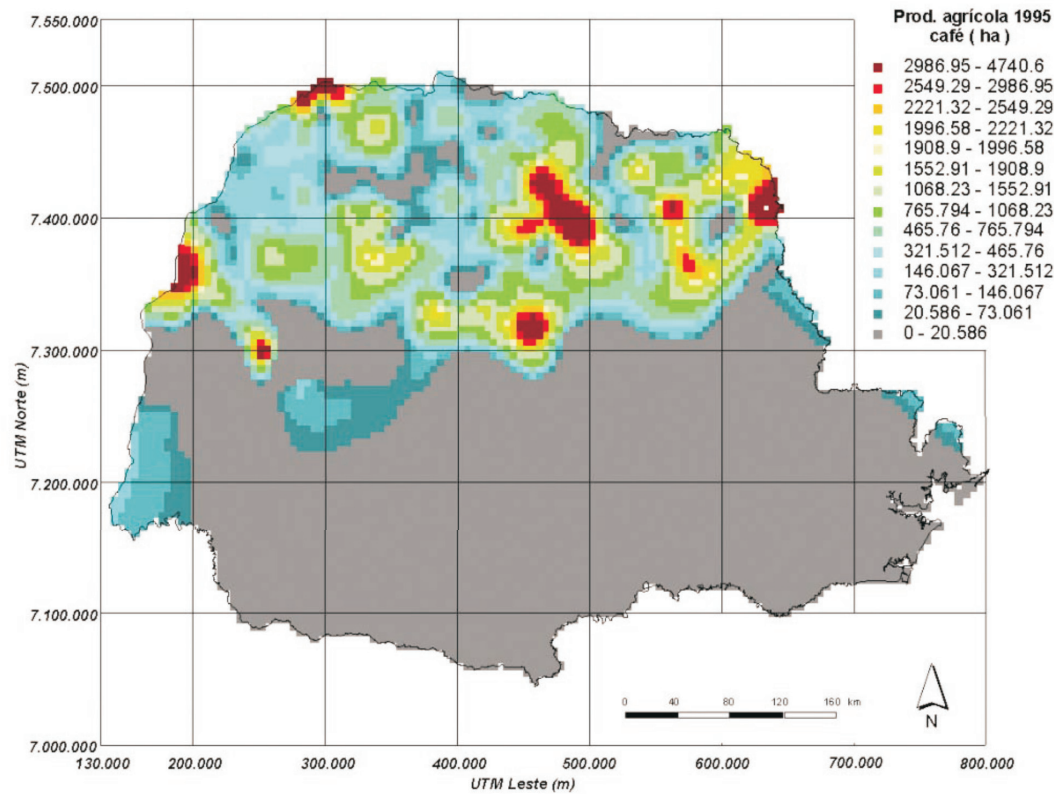
Figure 14 - Area (in hectares) planted with coffee beans in the 1995 harvest.
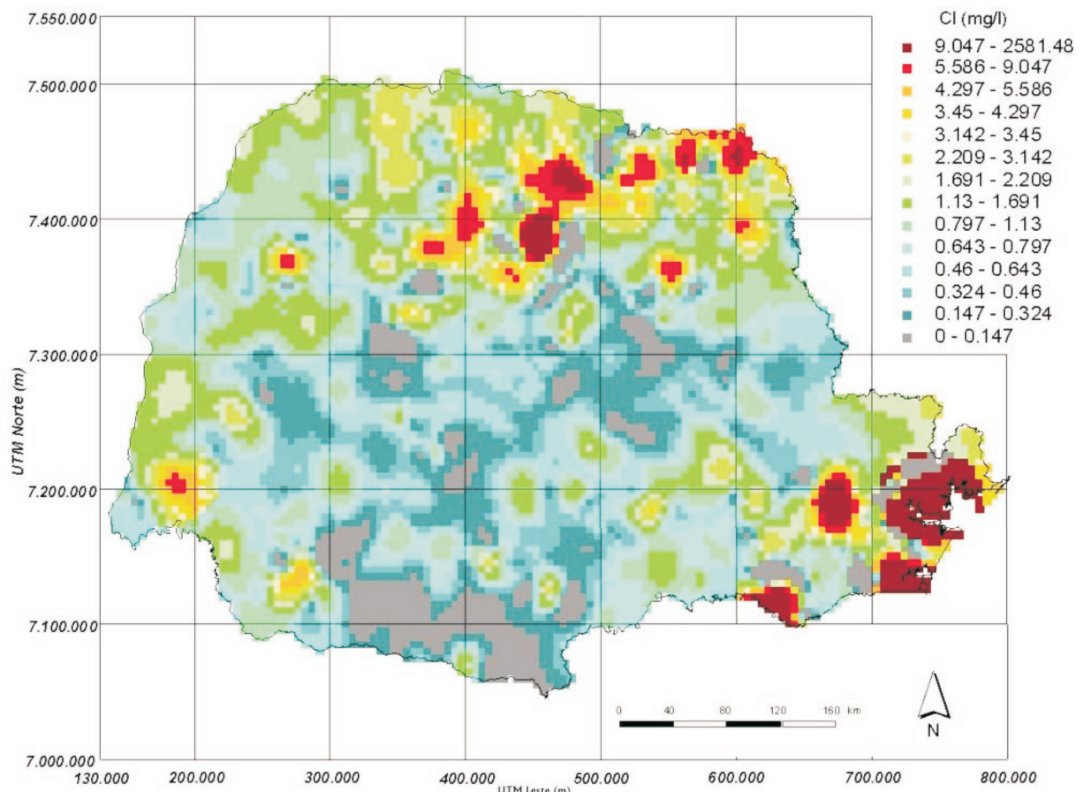
Figure 15 – Map of the distribution of Cl⁻ (mg/L) in the waters of 696 watersheeds.
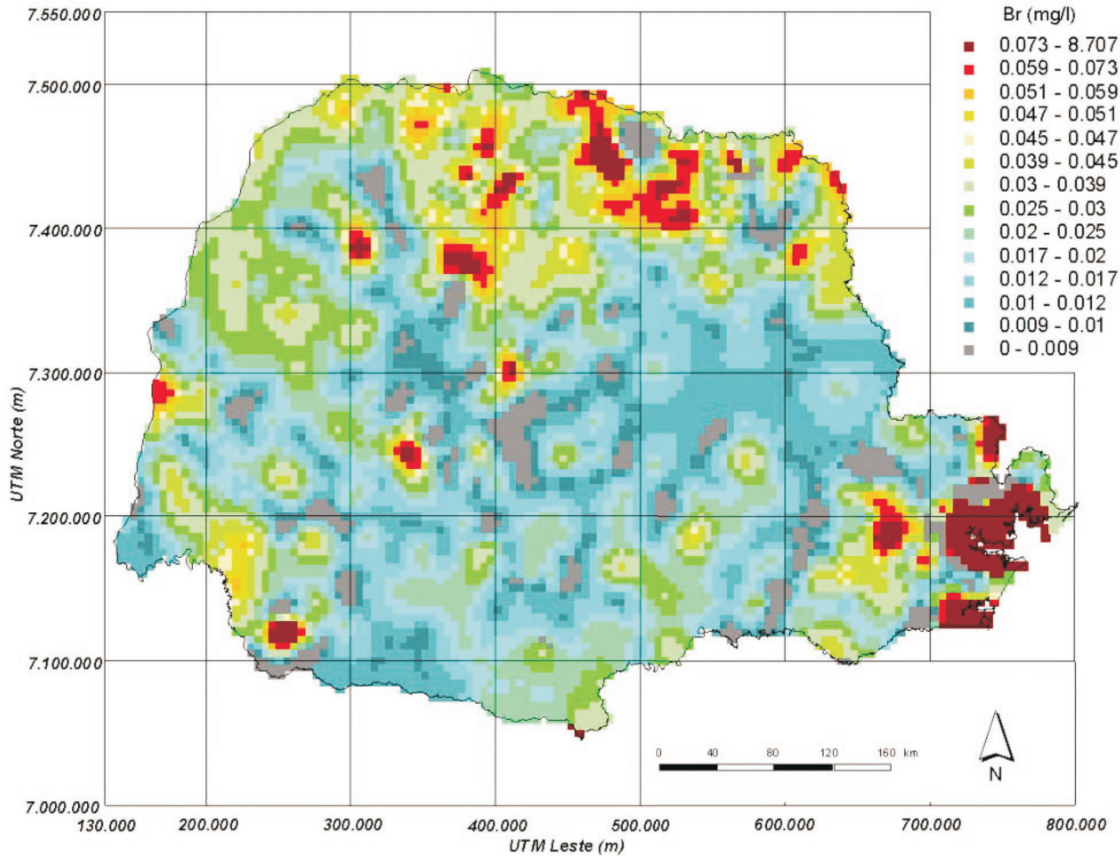
Figure 16 – Map of the distribution of Br (mg/L) in the water of 696 watersheds.

relationship was established between the mortality rates, crop types and geochemical anomalies, considering chlorides and bromides in the surface water as a geochemical indicator for that sanitary problem.

The prevalence of hepatic neoplasias as well as the increase in mortality rates is indeed associated with the use of chlorinated and bromated agrochemicals accumulated for decades in the areas of coffee and cotton plantations building geochemical anomalies of Cl⁻ and Br (Figures 17, 18 and 19).

The mortality rates due to hepatic neoplasias in Brazil increase from the northern region (2.14/100,000) towards the south (3.64/100,000) (Figure 20), following the tradition and intensity of the agricultural activity. Mortality rates in the ten cities of Paraná with the highest values (from 7.47/100,000 to 9.29/100,000) (Figure 21) can be twice to three times higher than those of the southern region of Brazil as a whole (Figure 20).

The ten cities with the highest mortality rates are included in the large chlorides and bromides anomalous spot.

Barium – Barium does not have a known biological function (Winter, 1998 apud Licht & Plawiak, 2005). The insoluble compounds are not dangerous to health and that

is why they are used in medicine as a contrast medium for X-Rays. Barium compounds that are very soluble in water, however, may aggravate human health, since this element is highly toxic in its ionic form (Koljonen et al., 1992 apud Licht & Plawiak, 2005). High levels of Ba intake can cause problems like high blood pressure, breathing difficulties, changes in the cardiac rhythm, stomach soreness, muscular flaccidity and damage to the heart, liver, kidney and other organs (ATSDR, 1999 apud Licht & Plawiak, 2005).
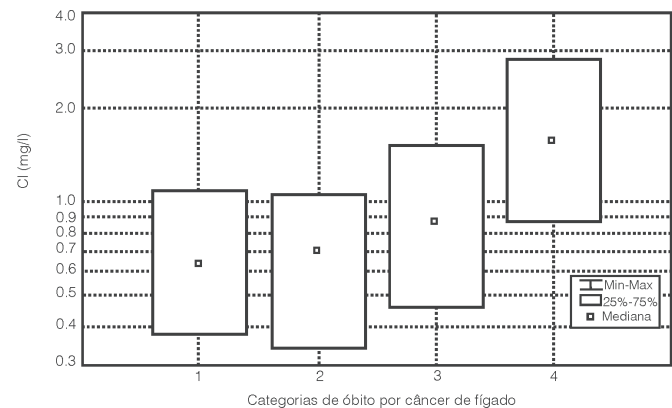
Figure 17 – Mortality rates due to hepatic neoplasias (1980-1997 period) related to Cl⁻ (mg/L) in the water of 696 watersheds.
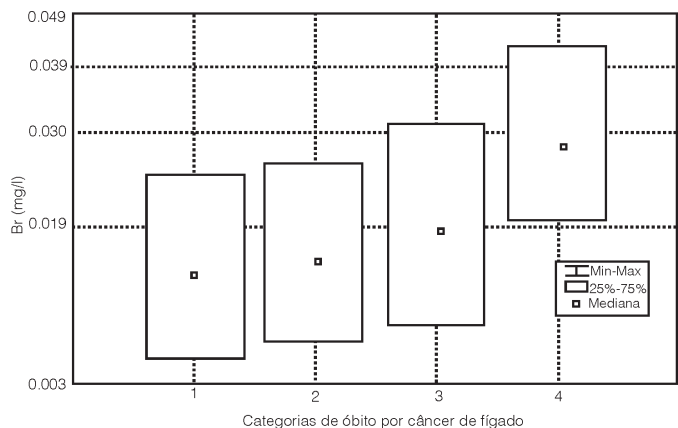
Figure 18 – Mortality rates due to hepatic neoplasias (1980-1997 period) related to Br (mg/L) in the water of 696 watersheds.
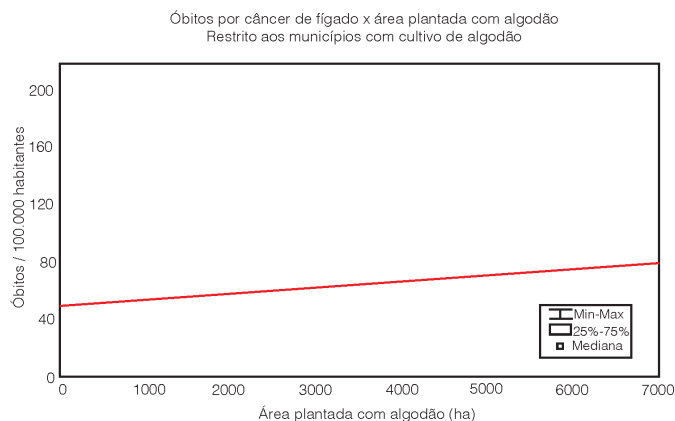
Figure 19 – Mortality rates due to hepatic neoplasias (1980-1997 period) related to the area planted with cotton in the 1995 harvest.

Figure 20 – The five regions of Brazil with their respective mortality rates due to hepatic neoplasias. Deaths average/100,000 between 1980-1997.

Data obtained by the Low Density Regional Survey with water samples from 696 watersheds (Figure 22), showed a large positive anomaly, in the northwest of Paraná State, coincident with areas of cretaceous sedimentary rock outcrops of the Bauru and Caiuá groups. These siltites, sandstones and conglomeratic sandstones were deposited in a desert environment, in close association with chemical sediments justifying the existence of the hydrogeochemical anomaly with contents up to 0.3 mg/L Ba^{2+}. The public water supply, in this region, is mainly provided by tubular wells with water entrance levels situated at this sedimentary sequence. The Maximum Permitted Value (VMP) established in the Ministry of Health Regulation nº 518 is 0.7 mg/L Ba^{2+}, but in some of these wells the Ba^{2+} concentration of the 30 m deep groundwater fluxes reached 1.3 mg/L. The Paraná State Sanitation Company (SANEPAR) solved the problem by sealing undesired groundwater entrances at specific depths and admitting groundwater influxes from shallow aquifers (SANEPAR, personal communication, 2005).

Arsenic - Concentrations higher than 10 µg/L As in drinking water are considered to be a human and animal health risk factor. Several endemic affections have been reported in regions with high arsenic contents, especially skin and mucous membrane lesions, hyperpigmentation, keratosis, skin and lung cancer, peripheral vascular disorders and damage to the respiratory, circulatory and central nervous systems (Varsányi et al., 1991 apud Licht & Plawiak, 2005). Contrary to mercury, the inorganic compounds of As are more toxic that the organic. Many studies have shown that As in its inorganic form can increase the risks of skin, lung, bladder, liver, kidney and prostate cancer (ATSDR, 1999 apud Licht & Plawiak, 2005).

The geochemical map of As around Curitiba (Figure 23) identifies a regional anomaly of SW-NE orientation coincident with the transcurrent fault system of the Lancinha Fault, as well as the flanks of the Setuva antiform. The groundwater tapped from tubular wells by the Paraná State Sanitation Company from karst aquifer have As concentrations below the VMP of 0.01 mg/L As (SANEPAR, personal communication, 2005).

The geochemical map of As around Curitiba (Figure 23) identifies a regional anomaly of SW-NE orientation coincident with the transcurrent fault system of the Lancinha Fault, as well as the flanks of the Setuva antiform. The groundwater tapped from tubular wells by the Sanitation Company of the Paraná state from karst aquifer have As concentrations below the VMP of 0.01 mg/L As (SANEPAR, personal communication, 2005).

Mercury The toxicity of mercury is especially known in the vapor form and for its organic compounds. The methyl-mercury is produced by bacterial activity on metallic mercury mainly in reducing conditions.
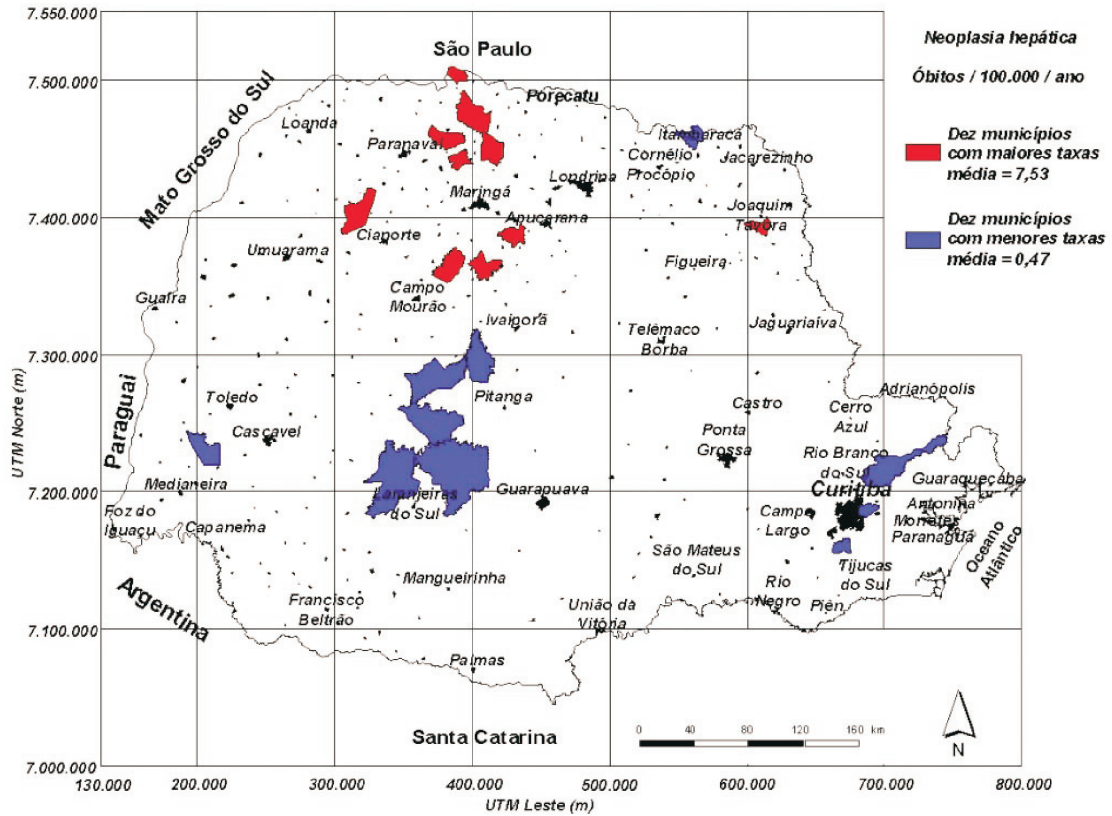
Figure 21 – The ten cities in Paraná with the highest (in red) and lowest (in blue) mortality rates due to cancer. Average deaths/100,000 between 1980-1997.
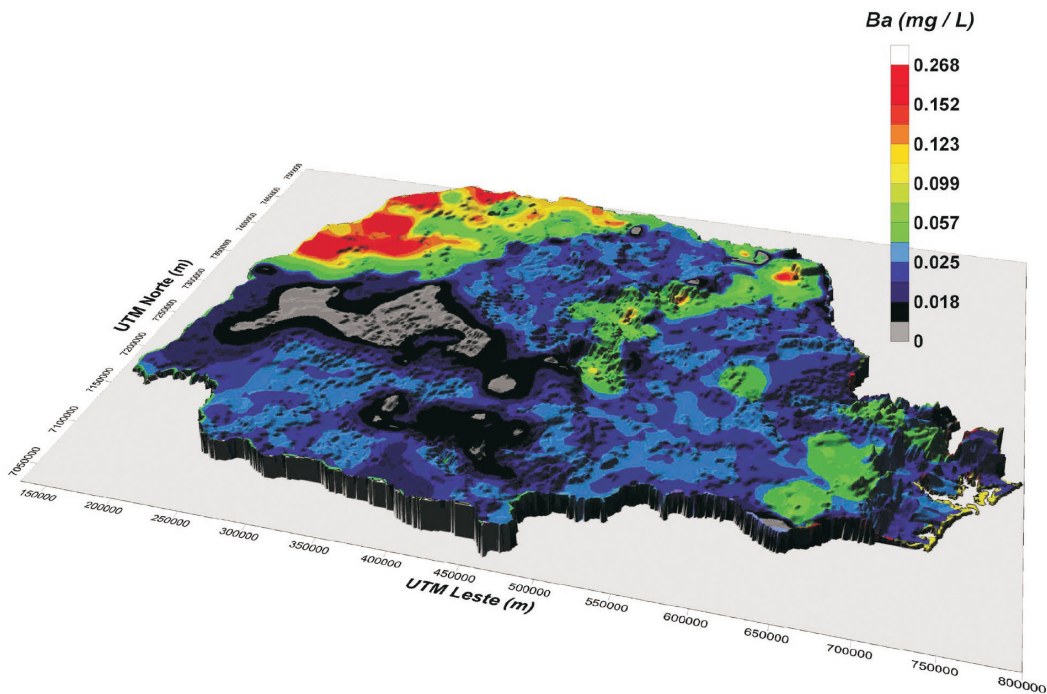
Figure 22 – Geochemical map of Ba (mg/L) in the water from 696 watersheds in Paraná. The great positive anomaly in the northwest coincides with the sandstones of the Bauru and Caiuá Groups.
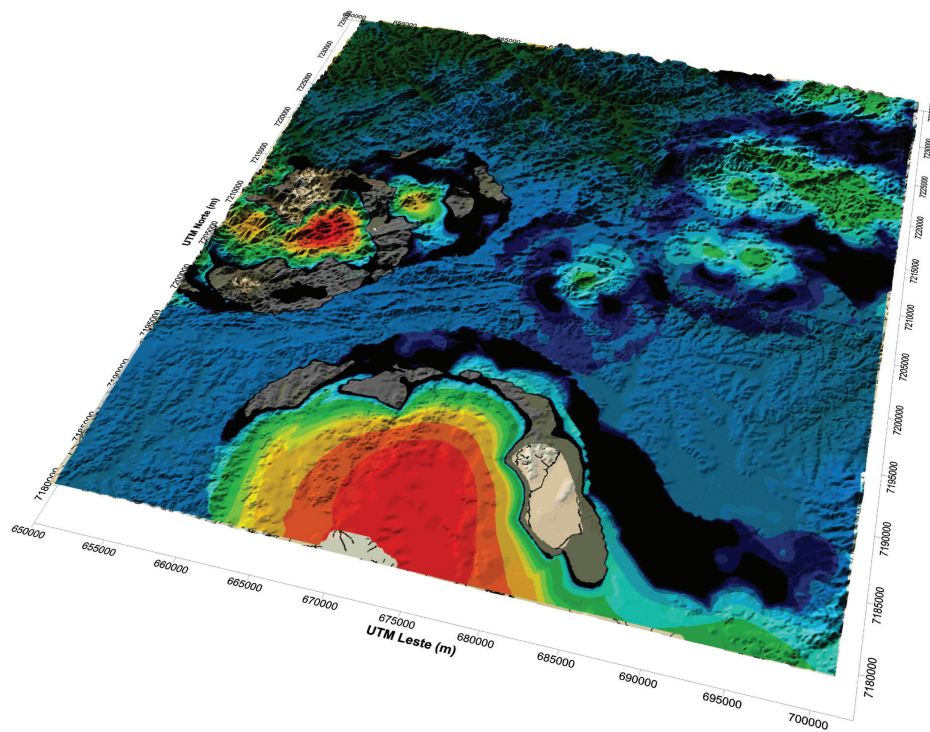
Figure 23 – Geochemical map of As (ppm) in the Curitiba base map. The large positive anomaly with SW-NE orientation is related to the Zone of the Lancinha Fault and Setuva Antiform.
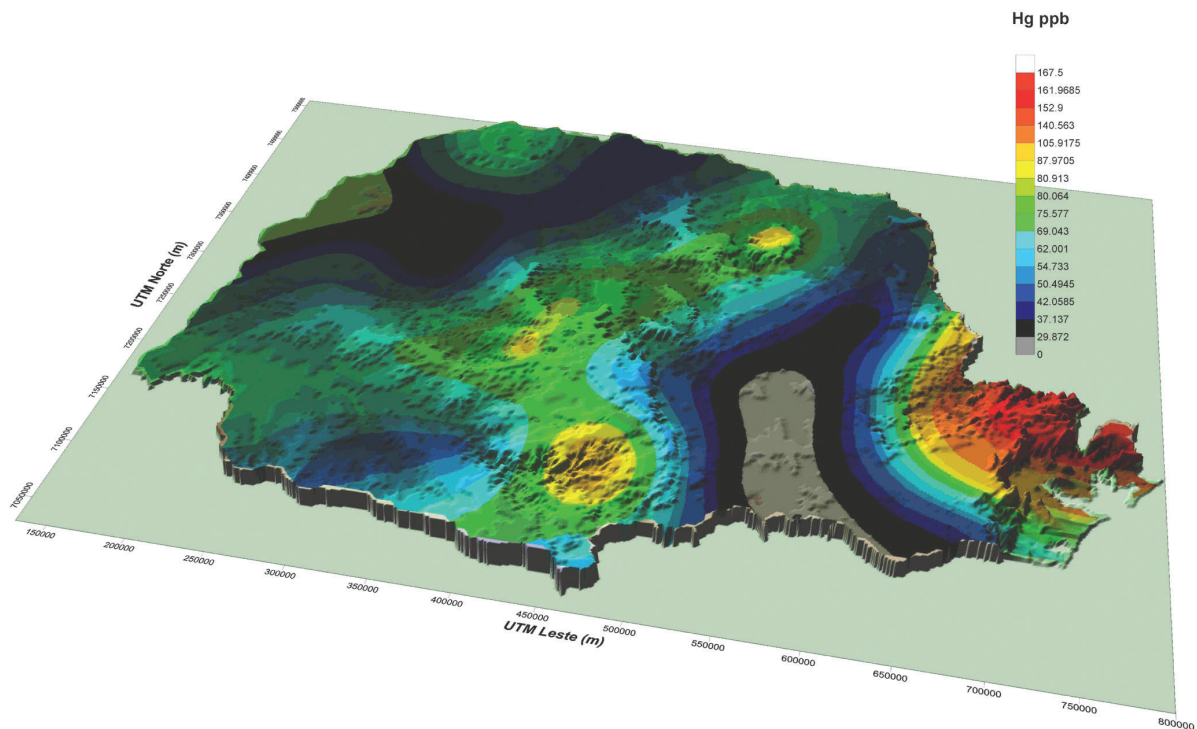
Figure 24 – Geochemical map of Hg (mg/Kg) in the GGRN unit cells (composed of 696 samples of active stream sediments).
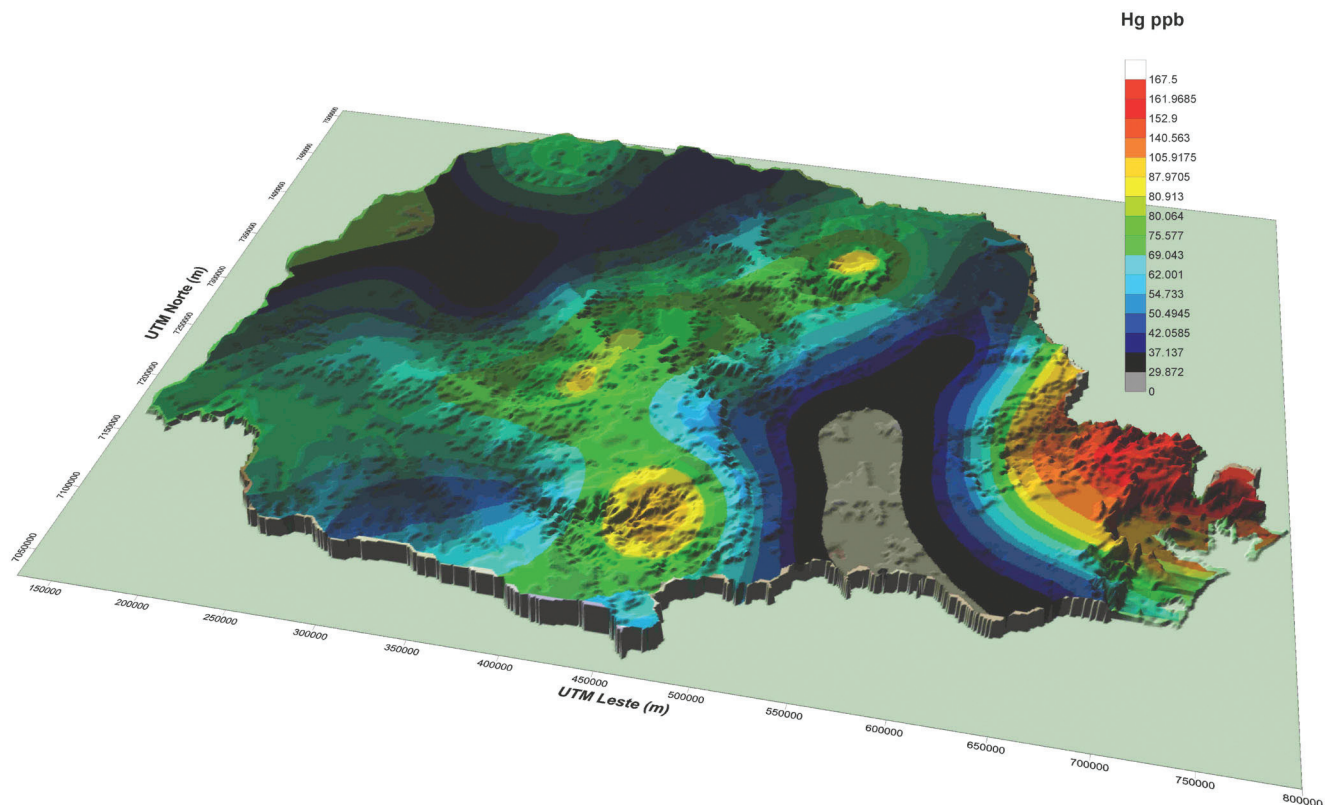
Figure 25 – Geochemical map of Hg (mg/Kg) in the GGRN unit cells (composed of 307 samples of soil – horizon B).

The maps of mercury distribution in active stream sediments (Figure 24) as well as in soils (Figure 25) in the northeast of the Paraná State show great regional anomalies. The anomaly situated in the Ribeira valley (Figure 25) in the northeast region of the state is related to the mineralization of Pb-Zn-Ba with contents reaching 14,000 ppb Hg (Daitx, E.C. personal communication, 2005). The anomalies situated in the central portion of the state might be related to Hg concentrations in sedimentary rocks rich in organic matter and coal which might have been mobilized by thermal waters. Its migration would occur along deep fractures up to the surface where it would be deposited due to the abrupt temperature drop (Plawiak et al., 2005). Even if this Hg low content migration occurs, expressed in the range between 40 and 80 ppb, there will be transport of the metal through the surface water and deposition in water bodies such as dam lakes. Thus, these anomalies configure health risk areas, being evident targets for epidemiological and toxicological investigations.

The eastern Paraná coastal region deserves investigations of this nature too because of its history. Paraná was occupied by European colonizers as early as the 16th century, when from the village of Cananéia in the São Paulo State, an expedition was sent by Martim Afonso de Souza searching for alluvial gold (Carneiro, 1962; Martins, 1969

apud Licht & Plawiak, 2005). The first gold mines were in this environmentally fragile region where frequently mercury was used for gold retrieval with a consequent built up of an environmental passive in soil and bottom sediments of the Antonina and Paranaguá bays. The anomaly coincident with the Curitiba urban region, for instance, may result from the impacts of several activities, from dentists' clinics to mercury vapor lamps for public lighting (Figure 26).

Lead - The industrial sources of lead are mainly related to batteries and energy accumulators (50–70% of the total consumption), electrical cables coating (3–4%), pipes and bars, alloys, paint pigment (red and white) and anti-radiation shields. Its use as an anti-detonation additive (5%) in gasoline is quickly declining due to its environmental impact (Koljonen et al., 1992 apud Licht & Plawiak, 2005). In spite of its virtual elimination as an anti-detonation agent in fuel (gasoline and diesel oil) the impacts of the use of this form of lead are evident in the map constructed with the data of Pbchangeable in the bottom sediments of some watersheds of the Curitiba base map (Figure 27). A general increase of the bottom contents with strong positive anomalies, coincides with the urban concentrations as well as with the outline of the main roads which support a large volume of vehicles.
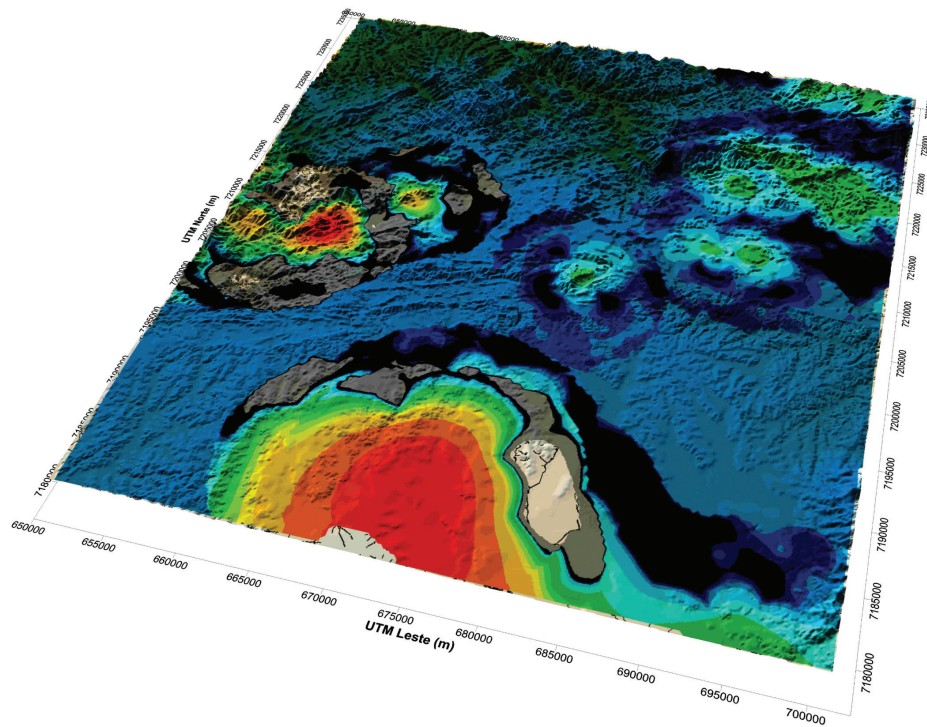
Figure 26 – Geochemical map of Hg (ppb) in the Curitiba base map. The anomaly situated in the center-south portion coincides with the densely urbanized area.
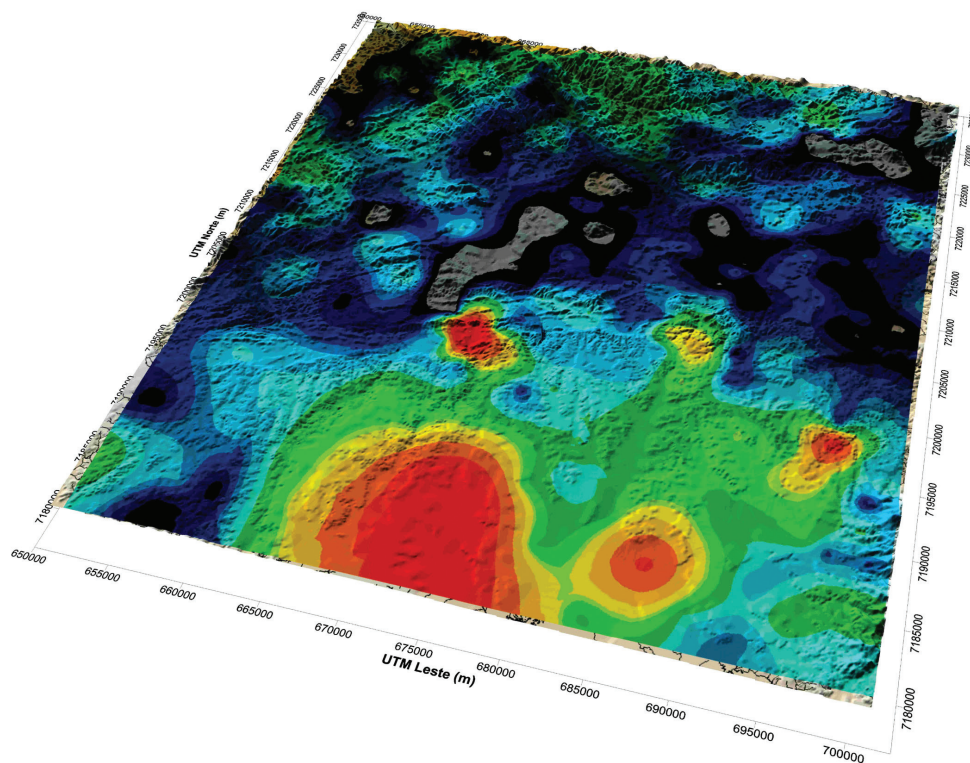
Figure 27 – Geochemical map of Pbchangeable (ppm) in the Curitiba base map. The anomaly situated in the center-south portion coincides with the densely urbanized area.

Calcium – The region situated to the northwest of Curitiba, encompassing the cities of Almirante Tamandaré, Rio Branco do Sul and Colombo. It is an area of traditional calcitic and dolomitic limestone exploration used in the making of cement, quicklime and lime for agriculture. The activity of a large number of mining and transformation companies of these raw materials generate an environmental impact in the form of suspension dust that, through the prevailing winds, is disseminated and deposited throughout a large area. The geochemical map of Cachangeable in the Curitiba Basic Map (Figure 28) delimits with great accuracy the outline of road PR-092, known as the Road of Ores (Rodovia dos minérios), where calcareous rock mining and processing activities are concentrated. The risks for human health, however, are more linked to the inhaling of solid particulates in suspension, especially near the triturating and grinding stations, than through geochemical impacts.

Lanthanum – Lanthanum doesn't have a known function in the animal aLanthanum doesn't have a known function in animal and vegetal physiology. However, all La compounds must be treated as highly toxic since lanthanum salts can be aggressive and damage the liver funtion (Winter, 1998 apud Licht & Plawiak, 2005). In the tertiary sediments of the Guabi-rotuba Formation, in the Curitiba Basin, there are occurrences of the double carbonate of La and Nd (Nd-lanthanite) that were deposited under supergenic conditions in the form of cement and veins in arkosic sandstone horizons and lenses (Licht, 2001a). Up to this moment epidemiological investigations related to La are not known, although the anomalous area (Figure 29) is situated near the Curitiba urban area with a dense human occupation.

CONCLUSIONS

Geochemical cartography has proved its usefulness as a territorial diagnosis and characterization instrument. Geochemical surveys with low density sampling are useful to support larger structures that, at another opportunity, could be a more detailed investigation seeking to obtain more knowledge about its characteristics as well as its origin and possible reflections on the trophic chain. Traditional techniques of geochemical exploration, followed by multi-elemental analyses with low limits of analytical detection are imperative for the success of this kind of research. The results obtained with surface geochemical surveys are essential tools to determine the health risk areas, needing multidisciplinary teams for trustworthy interpretations.
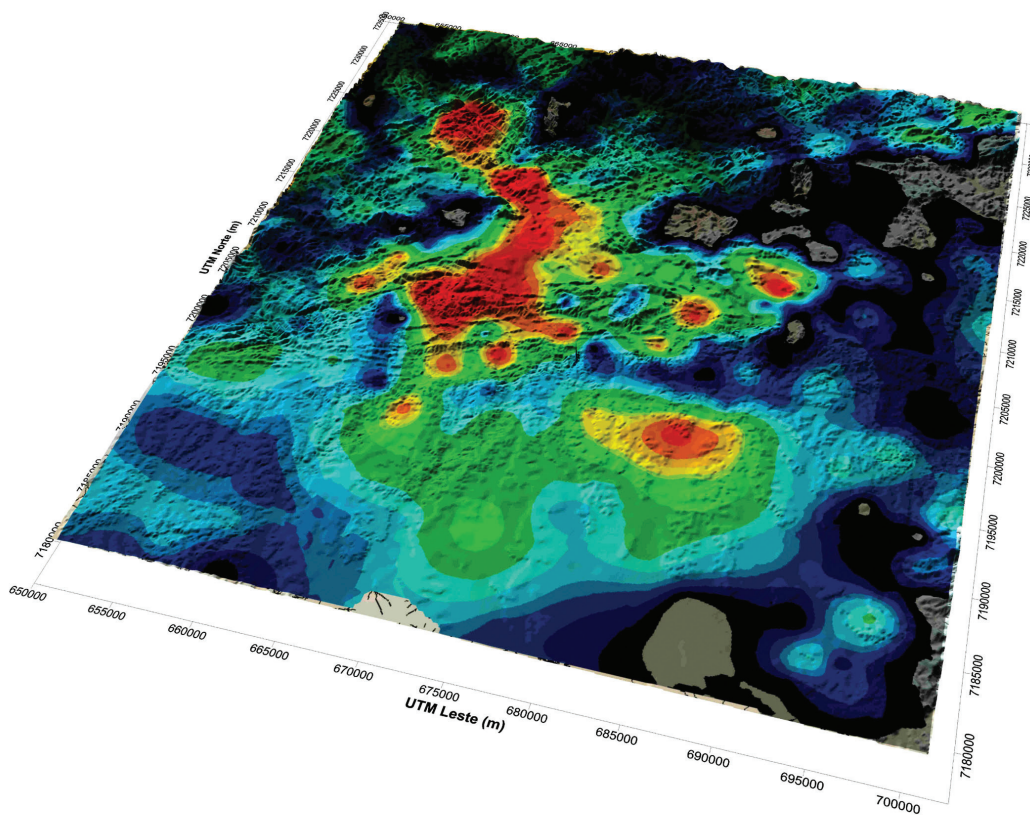
Figure 28 – Geochemical map of Cachangeable in the Curitiba base map. The large anomaly in the northwest portion coincides with the limestone exploration and lime and cement production areas.
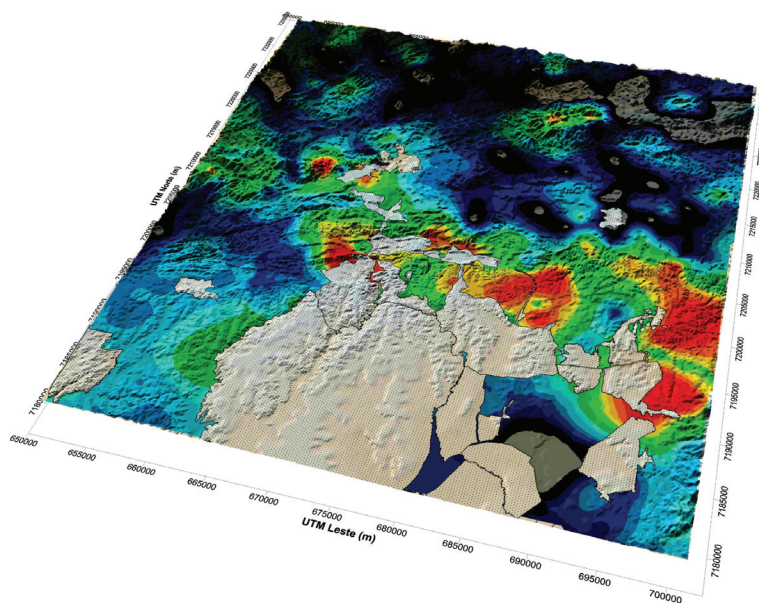
Figure 29 – Geochemical map of La in the Curitiba Basic Map. The grayish spot in the center-south portion represents the densely urbanized region.

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GEOCHEMISTRY OF BRAZILIAN SOILS: PRESENT SITUATION

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ABSTRACT

Geochemical soil analysis is largely used to identify areas with high and low concentrations of trace-elements. It is also an excellent criterion to assess a given metal's accumulation in the soil, to guide studies on potential occurrences of nutritional (in plants and animals), human health and environmental problems.

The chemical composition data of Brazilian soils is scarce and concentrated in a few regions of the country, particularly São Paulo, and only for a couple of elements, usually micro-nutrients.

This study presents an up-to-date panorama of soil geochemistry research in Brazil and suggests improvement initiatives to establish reference trace-metal values important to human health.

INTRODUCTION

Pedology (the study of soil) evolved to the state of science in 1883 when the Russian scientist Dokuchaev realized the soil is, in fact, a natural and dynamic body, result of differentiated and organized entities and not merely a heap of mineral particles with organic matter on its surface (Moniz, et al.,1972). Hans Jenny in his book "Factors of Soil Formation" (1941), based on the ideas of soil genesis, until then diffusely presented, offered for the first time an equation to mathematically express the relationship between the properties and variables of soil:

$$S = f (Cl, O, R, M.O., T)$$

Thus, it is understood that any property of the soil (S) is a function of the climate (Cl), living organisms (O), relief (R), source material (M.O.) and time (T). It must be pointed out that McBratney et al. (2003) also included the question of spatialization as a key factor in digital mapping issues, as examined later.

In this sense, geology, through source material studies by petrology and geochemistry, had a strong influence on the research at that time, since the development of genesis studies and soil classification was largely dependent on the stage of the basic correlated sciences (Moniz, et al., 1972). Considering that the American School is one of the world's most influential in geology and soil studies, its development will receive a greater emphasis.

Shacklette & Boerngen (1984) reported the United States have used soil analysis in mineral prospection since the 1940s. However, there were serious hindrances to trace-element analyses due to the lack of equipment with better detection limits. This situation changed in the 1960s with the introduction of the first commercial atomic spectroscopy equipment. Nevertheless, only in the 1970s a substantial improvement occurred in trace-element detection limits following a series of new instrumentation developments of atomic absorption/emission spectrophotometers (Cienfuegos & Vaitsman, 2000). Then also the first studies were produced to establish a relationship between human health problems and the geographical distribution of metals in the soil (Shacklette

& Boerngen, 1984). The development of new research confirmed that source material was the primary origin of trace-elements in the soil (Alloway, 1995; Kabata-Pendias & Pendias, 2001). In that view, one would expect basic rock originated soils to have higher contents of Zn, Cu, Ni, Mn and others, than those originated from granites, gneisses, limestones and sandstones. However, several works, especially Chen et al. (1993), have indicated that besides the source material, other pedogenetic factors exert a fundamental role in trace-element distribution in soil. In the last 20 years, the focus of geochemical soil analysis has been to establish reference values for toxic metals to introduce legislation that regulates the use of soil in relation to domestic/industrial waste and agriculture (USEPA 40 CFR Part 503 and Council Directive 86/278/ EEC). It should be noted most European countries have established maximum permissible main toxic element (Cd, Zn, Cu, Cr, Hg, Ni and Pb) limits in soils (Table 1). Countries such as Spain, Portugal and the United Kingdom have even established variable values according to the soil pH. However, only a few countries followed the USA example to maintain a long established routine of soil analyses to form a data bank. This is able to indicate, more precisely, the mean trace-metal values in "natural" soils and man- changed soils (Shacklette & Boerngen, 1984; Holmgren et al., 1993; Burt et al., 2000; Burt et al., 2003). The limit values established, though, are still arbitrary, usually based on 95%.

In Brazil, like the United States, most geochemical soil studies initially followed the international tendency to give mineral prospection support and to understand soil genesis (Melfi & Pedro, 1977; Melfi & Pedro, 1978). With improved analytical techniques, new studies were directed towards correlating trace-element amounts with soil formation and classification (Araujo, 1994; Horbe, 1995; Ker, 1995; Oliveira, 1996; Castro, 1998; Lacerda, 1999). Following these initiatives, Ker (1995) and Lacerda (1998), for example, cite several authors who indicate certain iron oxides in the soil are important trace-element sources, particularly, Zn, Cu, Co and Ni. Specific Brazilian soil characterization studies of various metal concentrations (micronutrients, toxic or trace) have not been well

developed and most, initially, were concentrated in São Paulo State (Valadares, 1975; Valadares & Catani, 1975; Furlani et al., 1977; Valadares & Camargo, 1983). Based on that same international concern, some Brazilian groups began searching for background values of several elements in national soils. Pérez et al. (1997) analyzed 30 samples (A horizon and B diagnostic) of 15 Brazilian soil profiles for several elements (Co, Cr, Cu, Mo, Pb, Zn, Mn, Fe, Cd, Sr, Zr, Ba, Rb, U, Th, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). Besides developing a pedogenetic field thesis Marques (2000) also produced new data on a series of trace-elements in soils in Minas Gerais State. However, Cetesb (2001) defined soil quality reference values on the base of specific sampling, following Dutch methodology. From 13 different representative soil profiles of São Paulo, 84 composite samples were collected, representing the 0-20 and 80-100cm depth levels. The following elements were analyzed: aluminum, antimony, arsenic, barium, cadmium, lead, cobalt, copper, chromium, iron, manganese, mercury, molybdenum, nickel, silver, selenium, vanadium, zinc. Finally, Fadigas et al. (2002), analyzing a set of 256 Brazilian soil samples, separated in seven groups based on their soil properties similarities, determined reference values for Cd, Co, Cr, Cu, Ni, Pb and Zn.

OBTAINING REFERENCE OR BACKGROUND VALUES

If tlf there is no knowledge of what can be considered the "natural" level of a given element in the soil, how can it be determined if it was anthropogenically contaminated, for instance, or if it had a considerable chemical deficiency that may affect the nutrition of living beings?

The national data base, as mentioned above, is concentrated on certain elements and limited to São Paulo State. Moreover, the soil sampling, preparation and extraction methodologies are usually different and not correlatable. However there are ways of planning the sampling to obtain mathematical functions that, through correlation with other soil properties (Pedotransfer), facilitate data prediction in unsampled regions. Fadigas *et al.* (2002), for example, suggested a model to estimate the

Table 1 – European limits of heavy metal concentration (mg/kg) in soils.

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
EU Directive 86/2781	1-3	----	50-140	1-1.5	30-75	50-300	150-300
France[2]	2	150	100	1	50	100	300
Germany[2]	1.5	100	60	1	50	100	200
Italy[2]	1.5	----	100	1	75	100	300
Netherlands[2]	0.8	100	36	0.3	35	85	140
Sweden[2]	0.4	60	40	0.3	30	40	100-150

1.Long (2001); 2. Europe (2005)

"natural" contents of Cd, Co, Cr, Cu, Ni, Pb and Zn based on silt, clay, Mn, Fe contents and CEC. Data spatialization, as part of digital mapping procedures, contributes considerably to the pedotransfer validating process and reorientation of new sampling campaigns. According to (McBratney et al., 2003) few of the mentioned studies are considering these methodologies.

With respect to the analytical methods, extraction and analysis provided "Totals" produce little useful information since the chemical element's ecotoxicological effects and environmental behavior (transport, reactivity, mobility, etc.) totally depend on its chemical form (Allen, 1993; Tack & Verloo, 1995; Hani, 1996; Quevauviller, 1998; Kot & Namiesnik, 2000; Abreu et al., 2001). Methods considered "Pseudo-Total" allow the anthropogenic influence to be determined and therefore can be used for environmental monitoring (Alloway, 1995; Walter & Cuevas, 1999; Scancar et al., 2000). However, if no standard analytical methodology is chosen, the data bank consolidation question returns, since most methodologies do not have the same extraction capability (Mattiazo et al., 2001). Likewise, there are methods that assess a given element's transference potential to a plant ("available"). In that case, however, care must be taken not to use internationally recognized methods that have not been developed for our conditions and therefore do not allow proper interpretations. An example is shown in Figure 1, taken from Wasserman (1977), which presents Cs transfer factors from the soil to the plant (absorption similar to K) in some Brazilian soils and based on international data. The important difference found is a result of physical-chemical processes that typi-

cally occur in tropical soils and that have little influence in Northern Hemisphere soils. In Brazil, the most usual extraction methods for "available" micronutrients as well as "available" toxic metals, are DTPA and Mehlich 1 solutions (Cantarella et al., 2001; Mattiazo et al., 2001). Some research aimed at using this type of result to determine reference values for certain toxic elements in soils is being developed. Finally, there are other studies based on the complexity of possible soil reactions that use sequential extractions to identify where a given element is located (Ure, 1991; Das et al., 1995; Hayes & Traina, 1998). Most environmental studies that involve this technique generally consider the following stages (McLean & Bledsoe, 1992; Das et al., 1995; Morrow et al., 1996):

- soluble in water
- changeable
- linked to carbonates
- linked to Fe/Mn oxi-hydroxide
- linked to organic matter
- residual

There are several extraction technique problems (Ross, 1994; Hayes & Traina, 1998; Kot & Namiesnik, 2000): i) the lack of extractor selectivity; ii) element readsorption and redistribution during the extraction process; iii) the soil-extraction solution relationship influence on the analyzed element distribution; iv) the mineral and organic compounds solubility change during the extraction progress. Even though, as it allows the comparison of chemically similar fractions, sequential extraction is pre-
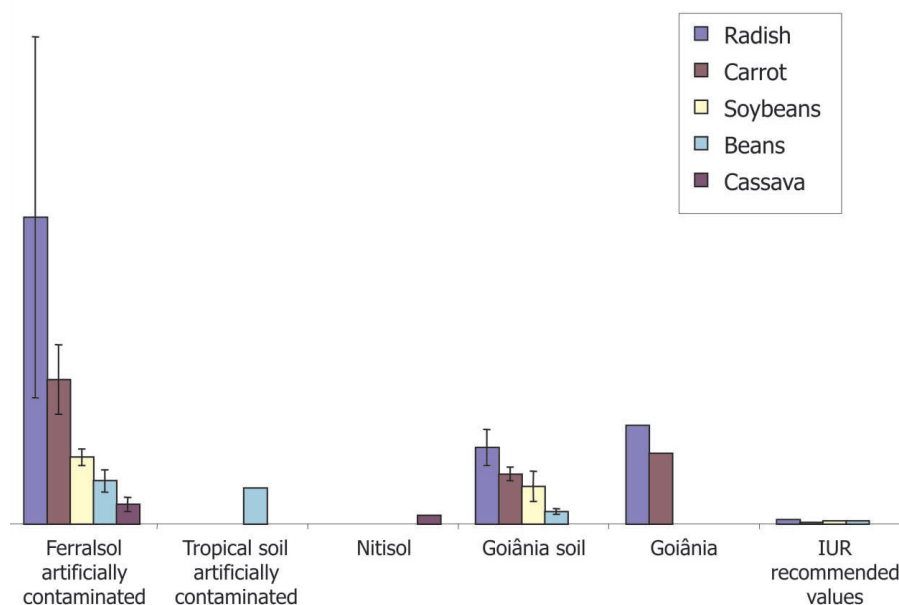
Figure 1 – Transference factors of Cs137 to radish, carrot, soybean, black bean and cassava crops in some Brazilian soils compared to international data generated in temperate climate (IUR).

ferred in soil solid phase speciation studies to determine the mobility potential and environmental bioavailability of several metals and radionuclides (Candelaria & Chang, 1997; Dean et al., 1998, Quevauviller, 1998; Wasserman et al., 2002). Figure 2, extracted from Mavropoulos et al. (2005), illustrates this case. Note, although the Pb total content remains unchanged in both soils (7.0g/kg), there was an element differential migration to distinct phases, representing a different mobility risk potential and bio-availability.
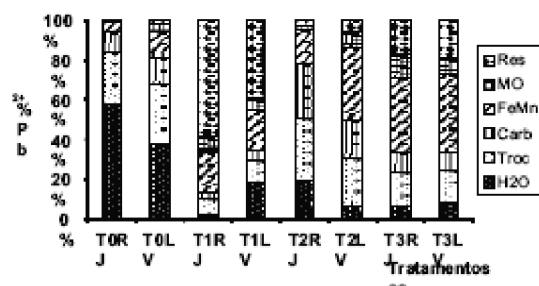
Figure 2 – Participation percentage of Pb obtained from two soils (RJ in an yellow-red Argisoil, LV is a red Latosoil) contaminated with 7.0g/kg and submitted to three remediation treatments (T1, T2, T3) in the six extractible phases in water (H_2O), changeable (Chang.), in carbonates (Carb), in Fe and Mn oxides (FeMn), in organic matter (MO) and residual (Res). TO is the control sample.

EXCESS X DEFICIENCY

The main purpose to establish soil reference values has always been linked to concerns regarding its contamination. However, due to the development of high-tech agriculture there is a strong tendency of certain micronutrients deficiencies because of the soil's low restoration ability, the low use of agrochemicals based on these elements and the low effectiveness of micronutrients in fertilizers (Yamada & Lopes, 1998; White & Zasoski, 1999; Welch & Graham, 2005). In Brazil, for instance, there is ample literature indicating the natural deficiency of Zn and Cu in our soils (Abreu *et al.*, 2001). Furthermore, the misuse of certain agricultural practices, especially soil liming (soil pH correction with limestone), can lead to the unavailability of otherwise naturally available micronutrients in soils, such as Fe and Mn (Figure 3). So, confirming previous observations, it is more important to know the conditions of the soil in which an element occurs than knowing its total content as a way of predicting its availability.

It is important to note, in cases of metal pollution of soil, plants have "defense" mechanisms that guarantee the low transference of these elements to the various vegetal organs, in particular those situated in the aerial parts (Shaw, 1989). However, if there is a given micronutrient deficit in the soil, the plant will hardly absorb it in
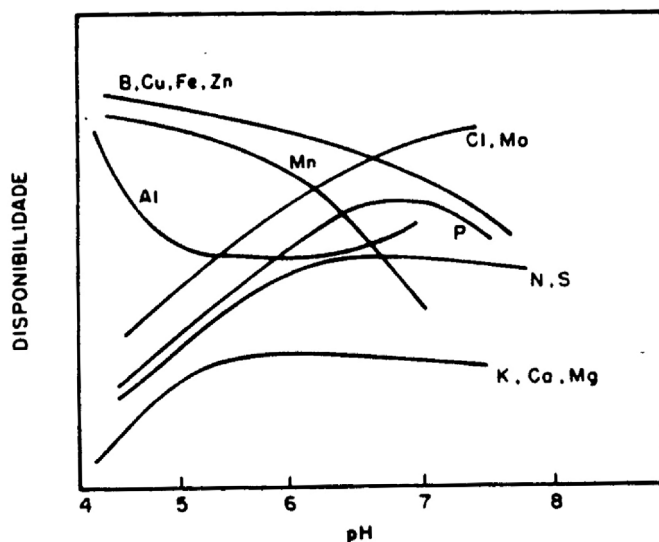
Figure 3 – Availability of several elements related to the soil pH (Nascimento, 1995).

sufficient amounts for its nutrition, although often no visual deficiency symptom is perceived ("hidden hunger"). However, this nutritional shortage may affect the animals and humans that depend on the plant for their nourishment (Welch & Graham, 2005)..

FINAL CONSIDERATIONS

Having recognized the need to establish trace-metal reference values, be they micronutrients or potentially toxic, it is fundamental to standardize the sampling, sample preparation and soil analysis methodologies based on a national work commission. However, because of the large area to be covered, it is evident that studies have to be carried out at a regional level, with a view to build a national geo-spatialized data bank. Efforts are being made in some states to research regional reference values but most of them collide with the lack of funds. Thus, it is extremely important to raise awareness among decision makers (the competent authorities), to enable state and federal Science & Technology development agencies to create specific research funds to subsidize this kind of study.

Finally, for those who intend to make a profound study of the implications of soil in human health, there are some international references that merit examination, namely: Oliver (1997); Dissanayake & Chandrajith (1999); Abrahams (2002); Deckers & Steinnes (2004).

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BIOFORTIFICATION AS A COMBAT TOOL FOR MICRONUTRIENT DEFICIENCIES

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INTRODUCTION

Diets with a lack of iron and zinc can provoke anemia, a work capability reduction, immune system problems, development retardation and even death. Iron-deficiency anemia is probably the most important nutritional problem in Brazil, with a prevalence ranging from 30 to 80% in groups of children under five. It is remarkable that this deficiency occurs independently of social class or geographical distribution. Black beans (32%) and meat (20%) are the most important iron sources for the Brazilian population are the absorption potential of this mineral ranges between 1 and 7%.

Although zinc deficiency is not studied with the same intensity as iron deficiency, considering the same source foods provide these nutrients, a high incidence of the former can be expected. Biochemical data obtained from population groups with this nutrient lack in their diets, sustain this tendency and therefore, it should be considered as important. Zinc participates in more than 300 enzymes active in the immune system, in the genetic expression, among other functions. Little is known about zinc deficiencies in developing countries, however, in general, sources rich in bioavailable iron are also rich in bioavailable zinc.

The micronutrient content variations in food can be attributed to: 1) the plant characteristics, such as its age, maturation, species, variety, cultivation, diet; 2) the environmental variables, such as climate, soil, rainfall, season, and; 3) processing factors such as storage duration, temperature, preservation methods, food preparation.

The importance of calcium should also be observed. Its nutritional ingestion in Brazil varies between 300mg and 500mg per day, whereas the DRI (Dietary Reference Intake) recommended value for the USA and Canadian populations, is between 1000mg and 1200mg for adults. Brazil is a tropical country offering the population sufficient vitamin D giving a greater efficiency in calcium absorption and utilization. However, because of skin cancer risks, the population is increasingly concerned about protection from UV rays using solar filters that will certainly diminish this vitamin's synthesis by the organism. The long term effects of this attitude could result in an increased incidence of rickets, osteomalacia and osteoporosis.

Selenium is another important nutritional element, not only because of its role in the antioxidant defense system but also because of its likely action in cancer risk reduction, which is still under evaluation. In Brazil the selenium content in food varies according to the soil, as demonstrated by food obtained in São Paulo and Mato Grosso States has an inferior content of this element,

whereas food from Ceará or Amazonas States has higher values. Furthermore, selenium deficiency is correlated to the individual's nutritional state regarding iodine, as to transform T4 into T3 (the thyroid hormone active form), a selenium dependent deiodinase is needed.

Vitamin A is an essential micronutrient for good vision and a healthy immune system. It is estimated that a vitamin A deficiency has a significant effect on school children's health in about 80 countries all around the world. Vitamin A deficiency is a serious problem in developing countries, causing blindness in thousands of children. Increased pro-vitamin A or carotenoids intake is a preconized means to fight this deficiency.

NUTRIENT INGESTION IN BRAZIL

Literature data indicates the Brazilian ingestion of some elements (iron, calcium, zinc and selenium) is below recommended levels or they have low dietary bioavailability. This indicates the biochemical parameters are below the reference values in the population's risk groups, thus confirming the need for intervention. A joint action by the scientific and industrial communities together with the government, to seek and implement dietary alternatives, may be a possible solution to minimize this problem.

More than 840 million people do not have sufficient food to meet their basic daily energy needs. A much larger number of people – about three billion – suffer from micronutrients deficiency effects due to being too poor to buy adequate quantities of red meat, chicken, fish, fruit and vegetables. Women and children from the Sub-Saharan Africa, South and Southeast Asia, Latin America and the Caribbean are those who present the greatest risk of contracting illnesses, premature death and cognitive ability deterioration because of their essential micronutrient limited diets – particularly iron, vitamin A, iodine and zinc.

World Health Organization data on micronutrients deficiency have shown this is not only a developing countries problem but also of developed countries as well. The deficiency in minerals and vitamins can affect the people's full development, with both physical and socio-economical consequences interfering in the country's development. Among the most studied micronutrients, iron, vitamin A and iodine continue to be indicated as those representing the greatest public health problem in Brazil, as well as on a world scale. Calcium, zinc, selenium and copper, among other essential elements are also of extreme importance to a proper nutrition and proper human development.

FOOD FORTIFICATION AS A PUBLIC POLICY IN BRAZIL

Countries that have adopted public policies to solve micronutrients deficiency problems, have obtained successful results with food fortification programs and/or medicated supplements. In Brazil, measures have been introduced to fortify salt with iodine, the fluoridation of water supplies in some regions and, more recently, with the compulsory fortification of wheat and corn flour with iron and folic acid, aimed at reducing high levels of anemia and neural tube defects, respectively.

Vitamin A and iron fortified food, as well as the distribution of micronutrient supplements to target populations have been the most frequent strategies used in most developing countries to fight hypovitaminosis A and iron-deficiency anemia. Recent research has demonstrated that the development of plants with higher vitamin A contents and other minerals can help improve the human diet and this is the research project goal being developed by EMBRAPA.

The approach to fight malnutrition in developing countries is with vitamin supply and mineral supplements to pregnant women and young children, in addition to the food fortification with these nutrients through post harvest processes. Many results have already been achieved with this strategy. In regions with appropriate infra-structure and facilitated with well established distribution markets for processed food such as salt, sugar and cereal flour, the food fortification can greatly improve the intake of micronutrients by the vulnerable populations.

BIOFORTIFICATION – A TOOL FOR THE IMPROVEMENT OF HUMAN HEALTH

However, there are limits for food fortification and the supply of commercial supplements. It is possible that fortified food may not reach a large part of the needy population due to a poor distribution infra-structure. Likewise, supplements depend on a health system with a highly functional infra-structure which is rarely found in developing countries. So, considering that new approaches are necessary to complement interventions already in process, the Biofortification proposal emerges, as a new paradigm for agriculture and a tool to improve human health.

The introduction of biofortified agricultural products – improved varieties bearing a higher content of minerals and vitamins – will complement the existing nutritional interventions and will provide a sustainable and low cost way of reaching populations with limited access to formal market and health systems. Once the investment in the development of nutritionally improved varieties in centralized research facilities is made, the obtained seeds can be adapted to growth conditions in many different countries. Biofortified varieties present the potential to provide continuous benefits in devel-

oping countries, at lower recurrent costs than those of supplementation and post harvest fortification.

The final solution for the eradication of malnutrition in developing countries is to substantially increase the consumption of red meat, chicken, fish, fruit and vegetables by the destitute population, which can take many decades and cost billions of dollars. Biofortification, however, may reduce malnutrition by approaching the food system in an integrated way. It attacks the root of the malnutrition problem, has as its target the most deprived population, uses incorporated distribution mechanisms, is scientifically viable and effective in terms of cost, in addition to complement other interventions to control micronutrients deficiencies. It is, in short, an essential step that will allow families in need to improve their nutrition and health in a sustainable way.

The Biofortification HarvestPlus Challenge Program

The Biofortification HarvestPlus Challenge Program was elaborated to improve the nutritional qualities of the main food crops that are adapted to the world's marginal zones. It was idealized to guarantee the advances in science and technology be used to enrich the nutritional diet of poor populations who practice subsistence agriculture in tropical regions.

The focus of biofortification is based on solid scientific principles. Preliminary research analyzed the viability of the employment of plant improvement, to increase the micronutrient content of staple food products by identifying the following premises: there is a considerable and useful genetic variation in basic agricultural products; the plant breeding programs can easily manipulate nutritional quality characteristics, since they are inherited in high proportions in some agricultural products and are easy to be selected; desirable characteristics are stable enough in a great variety of agricultural environments; and characteristics of high nutrient content can be combined with agronomical characteristics of superior quality and high yield characteristics.

The International Center for Tropical Agriculture - CIAT and the International Food Policy Research Institute - IFPRI coordinate the phyto-improvement activities, human nutrition, diffusion, policies analysis and impact assessment to be carried out in international research and agricultural extension centers and in vegetal production and human nutrition departments in universities of developed and developing countries. Non-governmental Organizations (NGOs) of developed and developing countries, farmer organizations and partnerships between the public and private sectors will consolidate this alliance and promote the connection with consumers. The first initiatives on biofortification will concentrate on six staple food crops, for which pre-viability improvement studies have already been concluded: black beans, cassava, maize, rice, sweet-potato and wheat.

The program will also study the nutrients content improvement potential in ten other products that are important diet components of populations showing micronutrients deficiency: banana, barley, cowpea-beans, peanuts, lentils, millet, guandu beans, potato, sorghum and yam.

HarvestPlus is a Global Challenge Program of the Consultative Group on International Agricultural Research (CGIAR), which involves not only several associated research centers such as the International Center for Tropical Agriculture (CIAT), the International Maize and Wheat Improvement Center (CIMMYT), the International Potato Center (CIP), the International Center for Agricultural Research in Dry Areas (ICARDA), the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT), the International Food Policy Research Institute (IFPRI), International Institute of Tropical Agriculture (IITA), the International Rice Research Institute (IRRI), but also several collaborative partner institutions such as the National System for Agricultural Research (SNPA) in developing countries; human nutrition departments of universities in developed and developing countries; NGOs; Adelaide University; Freiburg University; Michigan State University; US Plant, Soil and Nutrition Laboratory, the US Department of Agriculture; the Agricultural Research Service (USDA-ARS); the Children's Nutrition Research Center and the Baylor College of Medicine.

The Biofortification HarvestPlus Challenge Program has been conceived for a 10-year period and counts on the Bill and Melinda Gates Foundation for financial support, the Danish Agency for International Development (DANIDA), the Swiss Agency for International Development (SIDA), the American Agency for International Development (USAID) and the World Bank.

The goals of HarvestPlus are:
From the 1st to the 4th year:
    determine nutritionally optimal breeding objectives;
- select germoplasm from CGIAR bearing high levels of iron, zinc and beta-carotene and initiate cross-breeding of the highly adaptive and high yielding selected germoplasm;
- make a survey on farming practices and food processing to determine their effect on the micronutrient content and bioavailability;
- study the genetics related to high levels of micronutrients and identify the available markers to facilitate the transference of characteristics through conventional breeding and new breeding techniques;
- perform studies in vitro and with animals in order to determine the bioavailability of high contents of micronutrients in promising varieties;

- initiate studies on bio-effectiveness in humans in order to determine the biological effect of the biofortified products in the micronutrient levels in nutrition;
- initiate tendencies identification studies and sensitivity factor analysis considering the quality of malnourished populations' diet;
- make a cost-benefit analysis of plant breeding strategies and other interventions related to food to control micronutrients deficiency..

From the 5th to the 7th year:
- continue bioeffectiveness studies;
- initiate breeding with the farmers' participation;
- adapt the high yield varieties, with high micronutrients contents and conventionally improved, to the selected regions;
- make new conventionally improved biofortified varieties available to farmers;
- identify genes with a potential to increase the nutritional value beyond that obtained with conventional improvement methods;
- produce transgenic varieties in an experimental level and select them for their micronutrients content before testing them according to the biosecurity norms;
- develop and implement a marketing strategy to promote the improved varieties;
- start production and distribution.

From the 8th to the 10th year:
- increase the production and distribution scale of the improved varieties;
- determine the nutritional effectiveness of the program and identify factors that affect the adoption of the biofortified food, the impact on the destitute families' resources and the effects on the individuals' health.

HarvestPlus in Brazil

In Brazil, currently the main component of HarvestPlus, is the Research Program on Biofortified Crops for Better Human Nutrition. This project aims to define the population segregation of/for manioc, black beans and maize with agronomical potential and higher nutritional value (higher contents of iron, zinc and pro-vitamin A), which can improve the population's health and promote sustainable development, more social equality and larger use of these products in the international market.

The research network participants at the moment are: Embrapa-Food Technology , Embrapa-Rice & Beans, , Embrapa-Cassava & Tropical Fruits, Embrapa-Maize & Sorghum, Embrapa-Genetic Resources & Biotechnology, Embrapa-Mid-North and Campinas State University

(Unicamp). The inclusion of Embrapa-Soils, which can supply data referring to the composition of micronutrients in Brazilian soils, has been suggested.

The vegetables included in the HarvestPlus program are already largely produced and consumed in this country, which means that farmers and consumers do not have to change their nutrition habits to benefit from biofortification. Besides, the improvement to upgrade the mineral content does not necessarily have to change the aspect, flavor, texture, or the culinary quality of the food.

In those cases where a high micronutrient content can be combined with a high yield, the adoption of the improved products by farmers and markets is almost ensured. In fact, research demonstrates that high levels of minerals in seeds also contribute to the plant's nutrition thereby increasing expectations of productivity gains of biofortified varieties.

One way to ensure the farmers interest in the new varieties is to let them give their opinion on which characteristics should be improved in the plants. During the plant improvement process, the scientists consider the farmers' perspectives and preferences, which is more cost-effective than to confine the improvement to research stations.

A common developing country problem is the lack of a delivery and distribution system for certain products – for example, health supplies or agricultural products – to the poorest populations. HarvestPlus is overcoming this limitation through the use of technologies that are based on the seed, according to the biofortification approach mentioned above. When micronutrient rich food is cultivated in family farming, the micronutrients distribution system is incorporated in the existing production and market process. Once the farmers have adopted the new seed, little intervention or investment is necessary. In addition, micronutrient rich seeds can be easily stored or shared even by the poorest families.

The EMBRAPA centers have a valuable experience in creating and promoting local seeds distribution systems, thanks to the work they have developed with seed production systems and their contribution to programs that offer assistance during natural disasters. These established systems, facilitate the dissemination of biofortified seeds. In particular, local agricultural committees and small-scale seed processing factories will play a crucial role in getting the micronutrient rich varieties to the farmers.

RESULTS ALREADY OBTAINED AND FINAL CONSIDERATIONS

In the project's first year about 3,000 varieties of manioc, black beans and maize were selected and

multiplied, and 1,000 samples of each crop will be evaluated as to their contents of iron, zinc, total carotenoids and beta-carotene. The promising varieties will be further improved to develop the biofortified varieties. By 2005 the studies on retention of beta-carotene in manioc and iron and zinc in black beans, will have been made in conventional varieties, to estimate the nutrients' losses during processing and stocking the goods.

An interesting integration between Latin American, Caribbean, African and Southeast Asian countries is also foreseen in this project, where Brazil is expected to develop and transfer not only the biofortified crops but also post harvest technology.

RISK EVALUATION A SOCIAL AND ENVIRONMENTAL MANAGEMENT TOOL: THE CASE STUDY OF THE NORTHERN REGION OF THE STATE OF MATO GROSSO

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INTRODUCTION

Gold was discovered in the Northern region of Mato Grosso State in 1978 followed by two decades of intense mining activity. This region became the second most important mining center of the Amazon Basin; an area 1,878Km^2 was mined for gold during the whole of the 80's until the middle 90's. During this period, this region's gold production reached between 200 and 300 tons (Hacon et al. 2003). The extracted gold became the major income source for the entire region whereas mercury, used as amalgam, became in the 90's, the most serious risk factor for the environment and human health. As a direct consequence, the region experienced changes in its socio-economic profile as well as in the relationships between health and

the environment among the urban and rural population (Hacon 1996). According to Farias et al (2001), while gold commercialization estimates for the Alta Floresta region reach 800 kg/year, a large amount of this gold originated in the neighboring Pará State. Despite the accentuated decline in the actual mining activity, the region's fish stocks continue to show high mercury concentrations, reflecting a process of large scale biomagnification in the Northern region of Mato Grosso. In 1994, aquaculture projects were launched in the region as new socioeconomic opportunities for ex-gold miners.. Former mining areas are considered to be large environmental and social liabilities for landowners and local authorities. However, the first aquaculture projects were implemented without any risk evaluation of the mercury contamination in relation to fish

consumption from fish farming sites. From 1999 to 2001, fish production from aquaculture projects in the region was estimated at 100 tons/year, with less than 30% supplying the local markets and the rest being exported to other markets around the country (Hacon et al. 2003). The main fish species currently farmed in the aquaculture projects are: Tambaqui (*Colossoma macropomum*); an hybrid from the Tambacú (*Colossoma macropomum*) with Pacú (*Piaractus mesopotamicus*), all being non-piscivorous, Pintado (Pseudoplastystoma corrruscans) and the Jundiá (*Leiarius marmoratus*), both piscivorous.

2. CASE STUDY AND METHODOLOGY

The studied region is situated between latitudes 7º 37' to 11º 00' South and longitudes 52º 31' to 58º 13' West;

see Figure 1. There are 5 sites , which were selected considering factors such as, the existence of former mining degraded areas, the production and commercialization of gold, the location of aquaculture projects and the fish species that are farmed and consumed in the region. The Alta Floresta urban area, with 46,982 inhabitants (IBGE 2000), was the main gold commercialization center. Paranaíta and Matupá were important mining areas, with extractions located mainly in the Teles Pires River basin. This area consequently became extensively and intensively contaminated with mercury in the 80's. This transformed it into a potential pathway for methylmercury exposure to humans due to interactions with the mercury loadings in the MeHg production. However, the magnitude and timing of this outcome vary with the type of Hg contamination and the ecosystem characteristics (Hacon *et al* 1995).
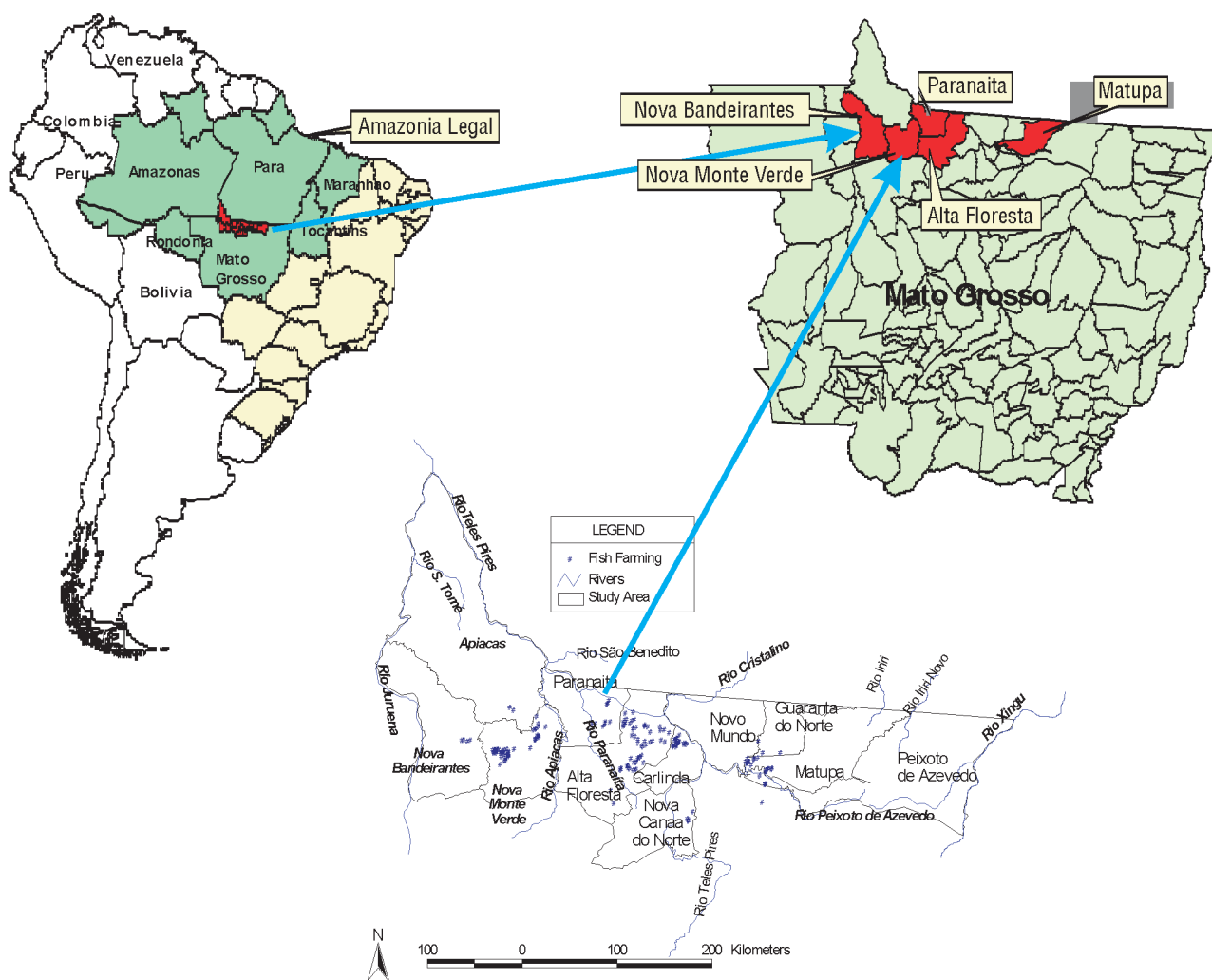
Figure1 – *Localización de la región Norte del Mato Grosso.*
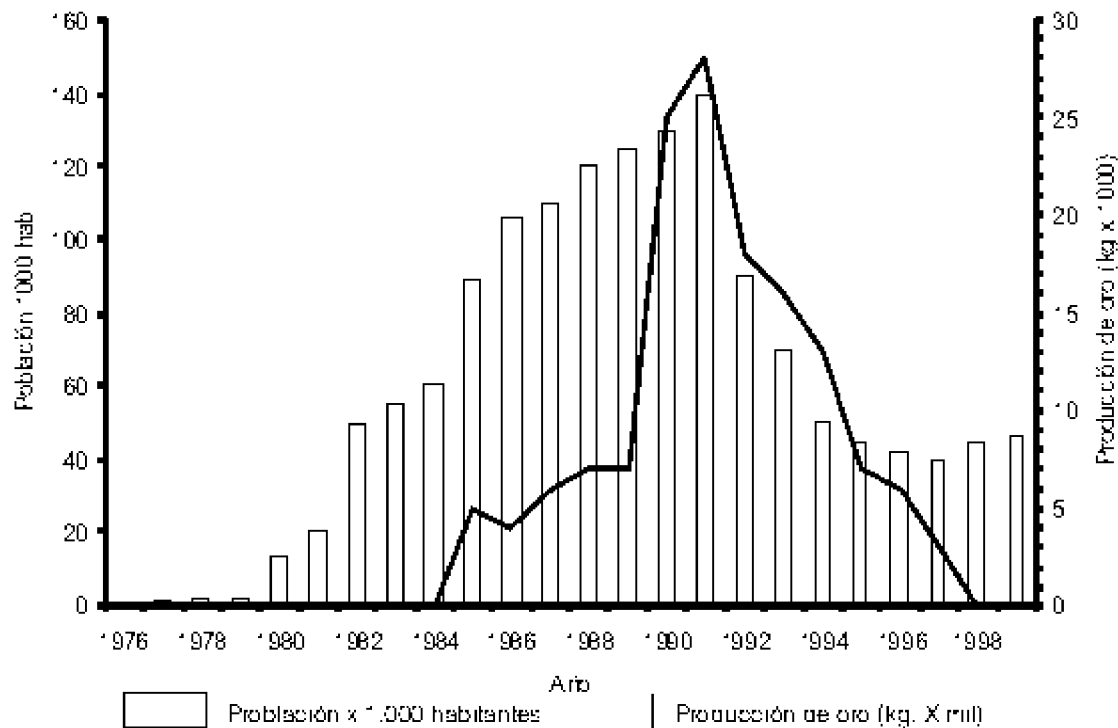
Figure 2 – Relación entre la producción de oro y el contingente demográfico durante el período de la "fiebre del oro" en la región norte del Mato Grosso (Farias 2002).

Paranaíta has a population of 10,250, Matupá 11,300, Nova Monte Verde 6,500 and Nova Bandeirante 9,535 inhabitants (IBGE 2000). During the "gold rush" period, from the end of the 70's until the early 90's, demographic growth reached annually rates of 12%. The relationship between gold production and the demographic influxes during the gold rush period in the Northern region of Mato Grosso is illustrated in Figure 2 (Farias 2002). For this study, two reference areas around Nova Monte Verde and Nova Bandeirantes were selected as sites for mercury contamination comparison, since they have never had mining activity.

Since its earlier stages, the study was developed in an inSince the outset, the study was developed with the integrated social participation from cooperative representatives, aquaculture associations, public sector and the local university. Approximately 180 aquaculture project initiatives from five regions were visited from which, 36 were then selected according to a defined criteria, such as i) fish production for subsistence as a first priority and ii) for regional and national commercialization as a second priority; iii) how long a time this activity is operating and; iv) the fish farming system. In order to evaluate the emerging aquaculture activity in the region interviews based on qualitative and quantitative questions were applied to workers directly and indirectly engaged in the industry. The questionnaire dealt with variables related to the social and nutrition behavior with emphasis on the consumption and origin of the fish, water quality in the dams, aquaculture project location in relation to old degraded mining areas. In total 254 fish from the main rivers and regional fish farms were sampled and analyzed between September 2000 and April 2002. Researchers from Mato Grosso State University (Universidade Estadual do Mato Grosso - UNEMAT) identified the species, measured and weighed the fish. Total mercury content was carried out by Rio de Janeiro Catholic University (Pontificia Universidade Católica do Rio de Janeiro - PUC) based on cold vapor spectrophotometry as described by Campos & Curtis (1990). The analytical quality control included blank analysis and duplicate samples for further comparisons with reference results. A data bank was built of all the information collected in the interviews, whereas all field data was geo-referenced. All the data was analyzed using the statistical software SPSS version 8.0 and Epinfo version 6.0. Descriptive statistics were used for the mercury concentrations analyses in the fish and their relationship with the other variables in the

exposure model. Comparisons of the mean values through parametric and non-parametric trials complemented the final analysis. Evaluation of different exposure scenarios and uncertainties were classified using the software Cristal Ball version 2000. Exposure estimates were obtained by considering daily fish ingestion by part of the adult population in every region through the general equation to assess chronic exposure.

GENERAL EQUATION TO EVALUATE EXPOSURE SCENARIOS:

Daily ingestion of Hg (mg/kg/d) = Concentration of Hg in fish (mg/kg) x daily rate of fish ingestion (kg/d) / body weight of the exposed individual.

RESULTS AND DISCUSSION

In the Northern region of Mato Grosso, the aquaculture activity started as a joint initiative between the Alta Floresta Municipality and the Mato Grosso State University (UNEMAT). In order to strengthen the region's economic activity, a project called "Peixe" (fish) was created in 1994. The aquaculture projects evaluation study revealed that the majority of the fish farms were based on extensive systems, meaning little control over farming environmental conditions and physical-chemical water parameters resulting in low fish production rates as seen in Table 1.

Today, there are many discussions and uncertainties regarding the sources and mercury types in the Amazon (Wasserman et al 2003). Nevertheless informal gold mining and the use of large quantities of metallic mercury as amalgam is still a reality in the Amazon region. However, comparing today's extraction levels with those reached 20 years ago, the informal gold mining represents very low activity scales, only 3-5% of the overall gold production in the Amazon region. Despite this, informal gold mining is still the main anthropogenic mercury source, causing high concentrations of methylmercury in piscivorous

fish caught in the Amazon Basin. These high levels of mercury pose a serious risk for the sustainability of the aquaculture activity in some areas of Mato Grosso. This study measured mercury levels in 19 fish species, those most consumed by local communities in the five studied areas. The results of mercury levels, shown in Table 3, are from river fish as well as from fish farms around those communities.

As indicated in Table 2, the Paranaíta and Alta Floresta regions present higher mercury concentrations in fish samples from the Brachyplatystoma spp (Piraíba) species, caught in the Apiacás River, with a mean concentration of 2.02 mg/kg (SD±1.04) ranging from 1.2 to 3.5 mg/kg, and samples from the Paulicea lutkeni (Jaú) species, caught in the Paranaíta River with a mean concentration of 1.03 mg/kg (SD±0.4) ranging from 0.5 to 1.7 mg/kg. Both rivers were intensively affected by mining activity in the last decades. The statistical analysis based on the Kruskal-Wallis test made evident a significant difference (p< 0.001) between piscivorous and non-piscivorous species from both rivers and fish farms. The mercury levels found in piscivorous river fish are two times higher than the concentrations measured in the same species taken from fish farms.

There are many ways to explain the different mercury concentration levels in fish from the Teles Pires River basin and the aquaculture activity. Emphasis was put on the size, weight and age of the piscivorous fish, together with their trophic level, food availability, exposure period and ecosystem characteristics. The mean mercury concentration in piscivorous fish (n=125 samples) is about 0.6 mg/kg (SD±-0.54) and in non-piscivorous fish (n=129 samples) is about 0.03 mg/kg (SD±0.03). The mercury levels measured in piscivorous fish were statically significant (p< 0.001). The Matupá region had the highest mercury levels in farmed fish; in Tambacús and Tambaquis, both non-piscivorous fish mercury levels reached values higher than 0.1 mg/kg. This was an un-

Table 1 - Aquaculture characteristics in the northern region of Mato Grosso

Variables Localities/	Alta Floresta	Matupá	Nova Monte Verde	Nova Bandeirante	Paranaíta
Total Area IBGE 1998 (km²)	9310	7213	4898,2	9172	4857,3
Nº of evaluated aquaculture sites	71	16	55	16	22
Nº of selected aquaculture sites	15	3	4	4	10
Mean Fish Production (t/2001)	30	5	2	1,5	32
Area degradated by mining (km²)	19	50	0	0	60
Cultivation Period (year)	7	4,2	3,1	4	2,6
Nº of evaluated aquaculture sites	3	14	0	0	9
Nº of aquaculture with water quality control	5	7	1	0	5

Table 2 - Mercury levels in fish from the northern region of Mato Grosso

Sites	Trophic level (n)	Mean mg/kg (w.w)	± SD Hg	Range concentration Hg
Alta Floresta	P* (27) NP** (56)	0.541 0.002	0.658 0.001	0.020 – 2.700 0.015 – 0.110
Paranaíta	P (53) NP (30)	0.674 0.003	0.627 0.002	0.086 – 3.500 0.010 – 0.100
Matupá	P (13) NP (5)	0.359 0.156	0.123 0.005	0.230 – 0.640 0.090 – 0.210
Nova Monte Verde	P (7) NP (24)	0.564 0.003	0.412 0.002	0.073 – 1.100 0.015 – 0.097
Nova Bandeirante	P (25) NP (14)	0.457 0.005	0.346 0.003	0.140 - 1.800 0.15 – 0.110

* P = Piscivorous   ** NP = Non Piscivorous

expected result considering both species. In the Matupá aquaculture projects these species indicated a smooth tendency for mercury bioaccumulation. In two reference areas of Nova Monte Verde and Nova Bandeirante (n=70), mercury levels in non-piscivorous fish (n=38) presented mean values of 0.04 mg/kg (SD±0.02) and a range from 0.01 to 0.11 mg/kg. For piscivorous fish (n=32), the mean value was 0.5 mg/kg (SD±0.36) with a range from 0.73 to 1.10 mg/kg. These results appear statistically significant when related to the trophic levels ($p = < 0.001$). The medians shown in Figure 3, 5%, 25%, 75% and 95% are the mercury levels in piscivorous and non-piscivorous species from rivers and aquacultures consumed by the population in the different studied areas. Extreme values were removed from the descriptive analyses for a better representation of the actual exposure magnitude. The results emphasize the differences in mercury concentrations in piscivorous and non-piscivorous species from rivers and aquaculture projects. The migratory specie Tucunaré, known to be an invader specie, showed mean values of 0.33 mg/kg (SD±0.16) and a range from 0.06 to 0.66 mg/kg in Alta Floresta and Paranaíta region farmed fish. That particular specie, depending upon the food availability, can reach 5 kg and may become a threat to the aquaculture activity due to its fast growth and mercury biomagnification capacity. A large number of studies show a strong correlation between mercury levels, weight and growth among piscivorous fishes (Farias 2002, Wasserman *et al* 2003).

For the statistical analyses, Pearson's correlation between mercury levels and fish specie standard length or weight was used. Some Tucunaré specie samples taken both from the Teles Pires River and some fish farms in the region exhibited significant results ($p < 0.01$) with correlation coefficients about 0.95 and 0.51 respectively.

Despite non-piscivorous species from aquaculture projects presented higher mercury levels than those from rivers, these results were not statistically significant.

Some values related to mercury levels in farmed fish consumed by local communities in this region of Mato Grosso are presented in Table 3. Comparing the results according to the fish source, 37% of the fish caught in rivers bear mercury levels higher than the maximum values recommended by the WHO, against only 6% for farmed fish. These results indicate a potential risk in river fish consumption in the region, mainly from the Teles Pires, Apiacás and Paranaíta Rivers.

The exposure variation rates in the five sites visited are presented in Table 4. The Nova Bandeirante site revealed the lowest Hg doses, 0,09 mg/kg/d, indicating that the fish can be consumed with no risk to the com-
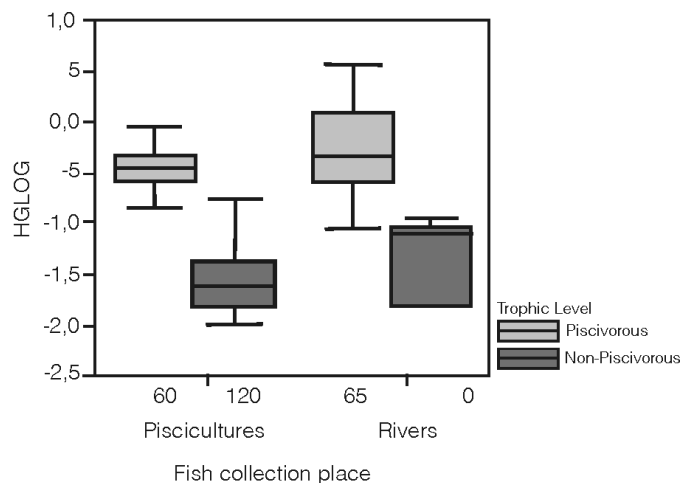
Figure 3 – Distribution of mercury levels in different municipalities in the northern of Mato Grosso.

Table 3 - Comparison of mercury levels in aquaculture and river fish from the Northern region of Mato Grosso

Fish source	<0,3mg/kg	0,3-0,5 mg/kg	>0,5mg/kg
Piscicultures n=219	67,5% (NP) 14,5% (P)	12% (P)	6% (P)
Rivers n=106	27% (NP) 13% (P)	22,5% (P)	37% (P)

P=Piscivorous; NP=Non Piscivorous

munity. The remaining sites showed small mean value variations in the exposure dose values. Matupá has the highest exposure dose (0.,5 mg/kg/d) and Paranaíta the largest dose variability (0.03 – 3.9 mg/kg/d). The most important justification factors for this variability are: fish consumption rates; the fish consumption preference by part of the rural and urban community and; the mercury level of consumed fish in the different evaluated communities. Fish is the principal protein source in the diet for 70% of the rural population.

These results highlight that fish consumption in the region is deep rooted in local diet habits and, consequently, increasing the potential risk of mercury contamination. In a majority of the areas, the non-piscivorous Tambaqui and Tambacú may be consumed without posing risk to human health, with the exception of the Matupá site. Here, with mercury levels in contaminated fish higher than 0.5 mg/kg, exposure management should be a priority policy in the region. This study has sought to emphasize the importance of risk evaluation processes as planning and management tools to develop sustainable projects. These results are intended to support local decision makers and their communities to face the risks associated with mercury contamination and take remedial action.

CONCLUSIONS

The results of this study indicate the environmental liability of mercury contamination is a reality in the Northern region of Mato Grosso. This occurs in many areas such as rivers and sites with or without a mining background, and presents strong evidence of extensive mercury transport mechanisms. The consumption of large quantities of piscivorous fishes, such as 700g/week may represent an exposure risk to the communities. The Jaú fish specie presents a higher risk for human contamination due to its lower cost and therefore, higher accessibility to poorer communities. The daily mercury dose for an adult population should not exceed 0,3 µg/kg/d, considered as an acceptable exposure limit.

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Table 4 - Potential dosis (mg/kg/d) of mercury exposition in the northern region of Mato Grosso

Localities	Mean Dosis	± SD	Dosis Variation (min –max)	Confiability limits (95%)
Paranaíta	0,36	0,31	0,03-3,9	1,2
Matupá	0,5	0,24	0,13-1,3	0,9
Alta Floresta	0,4	0,07	0,19-0,7	0,5
Nova Bandeirante	0,09	0,11	0,01-0,9	0,3
Nova Monte Verde	0,4	0,28	0,09-1,8	1,0

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RISKS TO HEALTH FROM ORGANIC SUBSTANCES

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INTRODUCTION

The last century saw important changes for humanity, with the great international conflicts in 1914-18 and 1939-45, followed by the enormous population and industrial growth which brought great hopes and life improvement, on the one hand, yet caused serious environmental degradation, on the other. The first books that approached these ominous facts, such as "Silent Spring" by Carson (1962) began to appear in the second half of the 20th century. They gave rise to the need to control the environmental impacts, showing the close link between the binomial cause-effect, health and environment. Also worth mentioning is the classic book "The Tragedy of the Commons" in which Hardin (1968) warned of the dangers and consequences of a future nuclear war to humanity and the environment.

In spite of this gradual awakening to environmental issues, the perplexed world watched monumental incidents, such as the accident of Minamata, Japan (Allchin, 2002), related to the noxious effects of mercury, or the chemical leak of methyl-isocyanate and other lethal gases that killed thousands of people in Bhopal, India (Greenpeace, 2002). Other important environmental accidents happened elsewhere in the world, such as the dioxin release in Saveso (Italy), the Chernobyl nuclear disaster in the Soviet Union, the 50 million liters of petroleum spill in Alaska by the ship Exxon Valdez, the deliberate burning of oil wells during the Gulf War. These tragedies make it clear to all mankind urgent actions ought to be taken to respect the environment. Consequently, from the 1970's, a series of events occurred, including reports, protocols, conventions, resolutions, conferences, assemblies, treaties, summit meetings and agreements resulting in statements to be assumed in international agency forums and even UNESCO. Among the vital issues considered, the following are highlighted: the environment, growth limits, wild species extinction danger, ozone layer destruction, sustainable development, climate change, chemical weapons convention, the struggle against desertification, nuclear tests ban and the implementation of Agenda 21 (UNEP, 2002).

During this paradigm breaking period and great environmental impact caused by industrial activity, it was thought that contaminant agents were essentially of anthropogenic origin.

Nevertheless, with the evolution of studies, it was also established that substances of natural origin such as asbestos, radon, mercury, arsenic and crystalline silica were noxious to human beings when used without security criteria (Geotimes Staff, 2001). Furthermore, population statistics indicated a high correlation between endemic areas and specific geologic structures such as mining zones and certain litho-structural features. The results indicated, for instance, skin cancer incidences related both to arsenic of the carboniferous

zones in China, and to the pyritic zones in Bangladesh (Fazal & Kuwushi, 2001). In Brazil there is an incidence of fluorosis in zones in Paraná State (Licht, 2001), where the water supply is based on fluoride rich groundwater extraction. At the end of the 20th century, many nations, especially those most developed, such as England, Finland and France, started to map their territories to know the real potential of natural elements and obtain basic data to assess their risks to living organisms.

The evaluation of substances and elements affecting public health and their behavioral and distribution processes, including environmental management, is today the assignment of Medical Geology, which was created in the last century and is undergoing strong development in this 21st century. Medical Geology concentrates mainly on the knowledge of natural risk sources to health and human well-being, thus contributing to prevent diseases caused by excesses or shortages of given substances and elements in the geological substrate (Moeller, 1997, Cunha et al., 1997). In short, Medical Geology seeks to understand of the correlation and interactions between geological, physical and biological processes of the Earth system (Sigh, 2000).

THE ORGANIC SUBSTANCES APPROACH IN MEDICAL GEOLOGY

Although the classical Medical Geology approach takes into account the inorganic elements and substances because of their noxious effects provoked in living beings, as is the case of mercury, arsenic, lead, fluorine, selenium, zinc, aluminum, cadmium, asbestos, silica and others (Oliveira et al., 2002, Pinese et al., 2002), the natural organic substances have been presented as responsible for many troubles that affect living beings as well (ATSDR, 2001, WHO, 2000). Many of these substances, such as benzene, benzopyrene, polycyclic aromatic hydrocarbons in general (PCAs), including benzofluoranten, together with some of the inorganic substances mentioned above, appear in the list of the 20 most toxic substances according to the Agency for Toxic Substances and Disease Registry – ATSDR. Natural organic contamination such as the groundwater rich in BTEX (benzene, toluene, ethyl-benzene and xylene) found in aquifers next to oil fields, oil and gases exudations existing abundantly in the region of the Mexican Gulf among others, phenol rich waters found in coal mines, hydrocarbons released by mud volcanoes, organic contaminations carried by intercontinental sand storms, are all significant examples for study in the field of Medical Geology (Bandeira *et al.*, 2004, Bandeira & Françolin, 2003). Finally, one should remember that many organic substances are responsible for asphyxia processes, toxicity, respiratory system attacks, cancer and even death.

UNDERSTANDING THE INTERRELATIONSHIP BETWEEN THE DIFFERENT SPHERES ON EARTH

The Earth can be divided in four main domain spheres: geosphere, hydrosphere, atmosphere, biosphere (Larocque & Rasmussen, 1998). These domains are interconnected through physical, chemical and biological processes (Figure 1). The geosphere is the original source of the entire planet matter except for the mass originated in space as meteors or cosmic dust. Exchanges occur between the geosphere and the hydrosphere, biosphere and atmosphere domains, as well as the relationships interconnecting the geosphere and the atmosphere. The organic compounds contribution has its main origin in aerosol emanations, volcanic gases - including those originated in mud volcanoes, gaseous hydrocarbons and vapors originated in sedimentary basins through natural seeps, and intercontinental sand storms. From the geosphere to the hydrosphere there are the organic products from the chemical weathering of mineral substances such as coal phenols and solid, liquid and gaseous hydrocarbons.

The relationship between the hydrosphere and biosphere occurs through the consumption and excretion of organic products by animals and vegetables that live in an aqueous environment. These products include the chemosynthetic communities found in the bathyal seep zones rich in gaseous hydrocarbons, from oil producing basins of the geosphere (Mbari, 2005, Dunaway, 2005).

The biosphere and the atmosphere relate to each other through the burning of biomass and the biogenic aerosols with biogenic hydrocarbons. The hydrosphere and the atmosphere are connected through marine aerosols, the rain and also through gaseous hydrocarbons and vapors that are released from hydrocarbon enriched zones. In fact, the atmosphere is the pathway of many nutrients such as nitrates, ammonium, nitrogen organic compounds and other bioactive elements (Solas, 2004).

EFFECTS OF ORGANIC PRODUCTS AND THEIR ORIGINS

The list of anthropogenic organic products that are harmful to living beings is immense and every day new ones are produced. However, this study focuses on the principal organic substances from geological sources. These substances can either have a gradual continuous action, like gas hydrates, aerosols and hydrocarbon seeps, or, a catastrophic and often lethal impact as in the case of sand storms, volcanoes and mud volcanoes. The main natural organic products and their respective effects of organic substances on living beings is shown in Table 1.
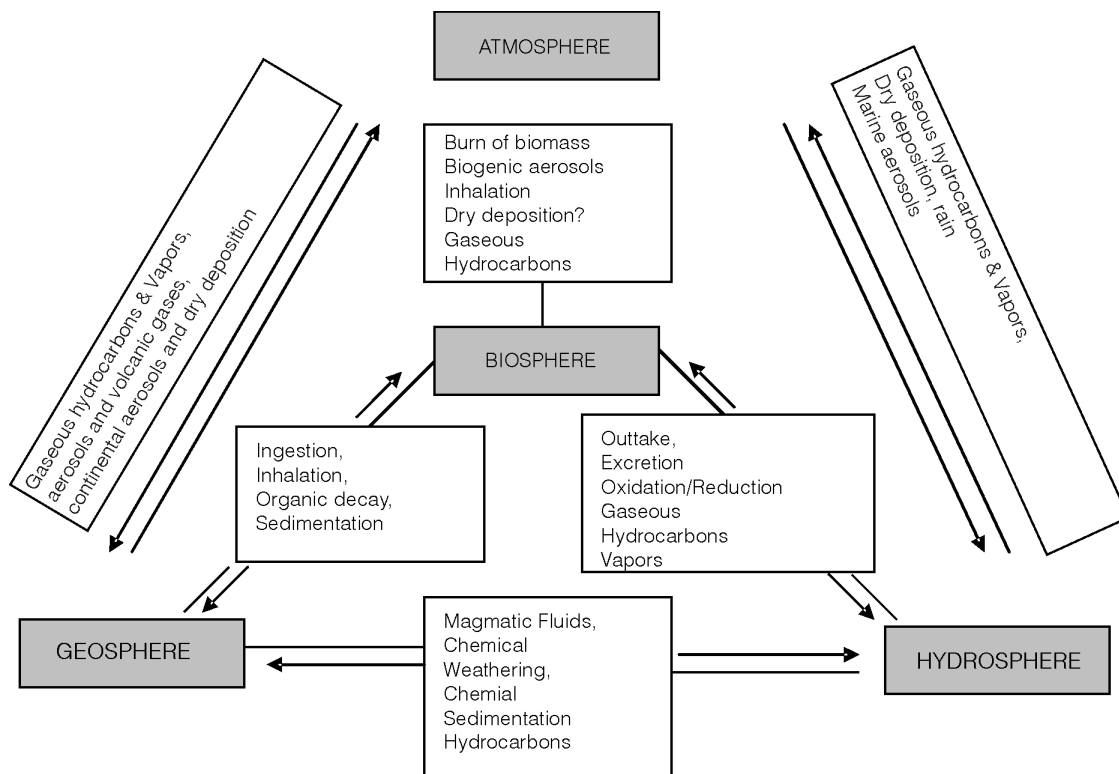
Figure 1 – Relationships between the earth's domain spheres

Table 1 - Effects caused by organic substances and their natural sources

Product	Effects	Natural Sources	References
BENZENE	Dizziness, drowsiness, loss of consciousness. Long exposures cause effects on bone marrow and anemia and leukemia. Death.	Petroleum systems in general. (Uinta Basin - USA).	ASTDR (2001) http://www.atsdr.cdc.gov/tfacts3.html
BTEX (benzene, toluene, ethyl-benzene, xylenes)	Effects on liver, kidneys, heart and lungs. Acute toxicity for aquatic life. Skin irritation and nervous system depression.		
CARBON DIOXIDE	Asphyxia. Greenhouse effect.	Volcanoes and mud volcanoes.	ASTDR (2001) http://www.atsdr.cdc.gov/tfacts67.html
PHENOLS	Liver damage, diarrhea, hemolytic anemia.	Coal Mines	
METHANE (C1)	Asphyxia. Greenhouse effect. Ability to accumulate 21 times more heat p/molecule than CO_2.	Fossil fuels in general (oil, gas and coal). Seeps, volcanoes, mud volcanoes.	NIOSH – National Institute for Occupational Safety and Health http://www.skcinc.com/nioshdbs/rtecs/pa16bc50.htm#W
NAPHTHALENE	Destruction or damage to red blood cells.	Fossil fuels (Oil, gas and coal).	ASTDR (2001) http://www.atsdr.cdc.gov/tfacts115.html
POLYCYCLIC AROMATICS (PAHS)	Some are carcinogenic if inhaled.	Volcanoes, dust particles petroleum systems, sandstorms	ASTDR (2001) http://www.atsdr.cdc.gov/tfacts69.html

Aerosols

Global aerosols are composed of multiple components such as dusts from windstorms (crustal elements); biomass smoke (organic); marine salts (NaCl); biogenic (sulfate and organic); volcanic (sulphuric acid and diverse gases) and industrial urban fogs (Husar et al., 2001). Each aerosol component has specific sources and peculiarities, occurring in a particular region and at preferential strata. Some aerosols occur naturally following sandstorms, volcanoes, fires and oceanic sprays (NASA, 2001).

Sands Storms

Most sediments carried by "sand" storms are, in fact, less than silt-size granulometry. They affect crops, people, villages, climates and can have an intercontinental character. In 1971 the planet Mars was entirely covered by a sandstorm. This phenomenon, repeated in 2001, was observed and photographed with the Hubble telescope (NASA, 2001). Atmospheric temperatures were affected during such storms both through absorption and reflection of solar radiation by the particles. Marine primary products influence the climate with consequences on the engendered cloud convection activities. When a sandstorm originates in a region of dry lakes it produces a high salinity environment. The resulting particles are harmful to the lungs. The high incidence of respiratory diseases in the recently exposed Aral Sea area may be linked to these kinds of sandstorms.

To Meskhidze (2005) sandstorms are not always a source of pollutants. They may also contribute to the formation of nutrients in oceanic zones. The process occurs when a sandstorm containing dusts rich in iron oxides passes over an industrialized area. Under special circumstances sulfur dioxide and several types of acid may be captured. Continuing over an oceanic area, the iron may suffer reduction through chemical reactions and transform into soluble iron, which will help form micronutrients for the marine phytoplankton.

Nowadays, scientists study the types of reactions that may occur during sandstorms which, in many cases, can travel thousands of kilometers. In April 1988, a sandstorm removed fine sediments from the Gobi desert in Mongolia and the polluted industrial area in China. Having crossed the Pacific Ocean, it covered 25% of North America – Canada and United States (Guo et al., 2004). The phenomenon occurred again in 2001 when NASA satellites detected a dust cloud larger than 2,000 km. Originating in China, covering Japan and North Korea, crossing the Pacific Ocean and reaching North America, from Alaska to Florida, it spread dust and contaminants from one continent to another. Tracking the dust cloud revealed, though it passed over China and Mongolia, it had, in fact, originated in Siberia. Satellites also observed that between April 6-9, millions of tons of dust from the Takla Makan deserts in China and the Gobi in Mongolia were transported away. On April 7 the Baicheng streets, in Jilin Province, Northern China, were covered by a thick dust cloud (NASA, 2001).

In 2004, scientists from Hong Kong and Chinese universities studied 18 samples from three different sandstorms in 2002 in Qingdao village – China. The chemical analyses revealed that besides elements from the Earth's crust, organic compounds such as phenanthrene, fluoranthene, pyrene, benzopyrene, benzofluoranthene, perylene, anthracene and coronene were also detected. Through the carbon preference index (CPI) and other analyses, Guo et al., (2004) concluded that they were petroleum residuals originated from anthropogenic contributions that included aromatic polycyclic, fatty acids, as well as hydrocarbons from vehicles. They also detected organic products related to waxy plants probably originated from the abrasion of the storm particulates in contact with the leaf cover.

In the Middle East deserts, sandstorms happen most frequently between April and May. On April 26, 2005 the air force base of Al Asad, in Iraq, was struck by a heavy sandstorm. The dust cloud front progressed at a speed estimated at 60 miles/hour. In May 2005, the dust clouds from the Sahara reached the Canary Islands and more distant areas situated in Europe and the Amazon Region. In the latter, it was estimated that the total dust originated in the Sahara every year lay between 20-50 kg per hectare (Artaxo et al., 2004).

Besides the possible consequences to eyes and lungs caused by the particulates, sandstorms help disseminate microorganisms. In Sub-Saharan Africa, it was observed that the bacteria causing cerebrospinal meningitis (inflammation of the spinal marrow or of the brain) develop more during certain year periods when sandstorms occur coinciding with the low rain and humidity season (FAPESP, 2005). Facing this reality, doctors have been researching the large dust clouds that were triggered in the Sahara desert and reached many African countries, using the European Space Agency (ESA) satellites. This weekly monitoring task seeks to discover possible connections between the dust and epidemics.

Until recently UV rays were supposed as lethal to the microorganisms found in sandstorms. However, observations do not support this hypothesis in reality. In England a direct relation has been established between sandstorms and the viral foot-and-mouth disease, which affects domestic livestock, and which has sometimes been mistaken for mad cow disease (Mckie, 2001). Also the disease occurring in Caribbean sea corals has been identified as caused by a fungi commonly found in soils, namely the Aspergillus sydo-wii. Since this fungus does not multiply in sea water, its origin depends on a fresh source of continuous soil spreading, which occurs through

sandstorms that have happened in the region (Pohl, 2003 and Goudie et al., 2004).

In dry regions of the USA and Mexico a disease caused by the Coccidioides immitis fungus, the coccidioidomycosis or valley fever, often endangers the respiratory system of people, cattle, dogs, horses, llamas and, sometimes, cats through infections (Finkelman, 2001, Deaner & Einswtein, 1999). The disease presents a granulomatous form in the respiratory system and, secondarily, disseminates in the entire organism, affecting especially skin, bones, articulations and the meninges (Costa, 2003). The fungi vegetative life stage presents two types of mycelia that, reaching the lungs transform in spongean or coccidian spheres (Kuhl, et al.,1995). Many endospores develop and the spheres are capable of producing new spherules that constitute the saprophytic stage of the disease. The dissemination and the most severe cases of the disease usually occur in the aftermath of earthquakes, when the removed soils are taken by the wind as dust, reaching great distances, as occurred in Northridge in 1994. In some situations the disease can be lethal (Williams et al., 1979).

As a consequence, sandstorms have the capability to transport both the organic versus inorganic contaminations naturally found in nature, and those of anthropogenic origin as well. The storm field has been the target of many studies which are being carried out by concerned governmental agencies of several nations.

Volcanoes

Volcanoes generally occur explosively and spread chemical products and substances from the planet's interior over the Earth's surface. In June 1991 the Pinatubo volcano in the Philippines, ejected 42 million tons of carbonic gas, great amounts of rocks, water and sulphates as well as smaller, though significant, quantities of chlorides and heavy metals such as zinc, copper, chrome, lead, nickel, cadmium and mercury (Terrence et al., 1996). The aerosols originated from that explosion affected the global climate for 3 years (Gerlach, 1996; Selinus, 2004).

Volcanic explosions can project large quantities of fragments, dusts and gases to great altitudes. On October 1, 1994 NASA satellites detected an eruption of the Klyuchevskaya volcano, situated 4,750 meters above sea level, in Russia. The contamination plume reached an altitude between 10 and 14km (NASA, 2005). The Tambora volcano eruption in 1815 on the island of Sumbawa, Indonesia, ejected about 100km³ rocks into the atmosphere and the average temperature in central England decreased by about 4.5° F. The main emission of the Etna volcano, in Italy, is carbonic gas, but important methane emissions are also present (Veschetti *et al.*, 1999 and Pecoraino & Giammanco, 1998). There are volcanoes that emit sulphidric gas, which can provoke

serious effects on human health. Also, there are reports of health risks caused by volcanic pollution in Hawaii, where there is a relationship between mortality rates and the distance from eruptions and gases (Grattan et al., 2002, 2003).

Mud Volcanoes

Mud volcanoes originate in petroleum and gas rich zones forming structures of tens of meters in height and diameter, with the expulsion of solid and gaseous material provoking the deposition of breccia and gas ignition. During each eruption hundreds of tons of mud and millions of cubic meters of gases are expelled, usually in the form of huge flaming mushrooms (Table 2). Such explosions have been registered since 1882. The last big explosion was in 2001. After the explosive event the volcano usually becomes dormant, a stage that can last for decades. During this stage it continues to pour mud, gases and petroleum in structures called gryphons that are situated inside or near the main crater. In some volcanoes there are also circular structures that expel salty water and gas, called salsas. There are more than 700 mud volcanoes in the world distributed in 25 countries. Most of them are situated in Azerbaijan ("fire country" in the Azeri language) and nearby regions that include the Caspian Sea region (Françolin, 2002). The hydrocarbons can burn for several days and involve colossal gas volumes, generating flames hundreds of meters high. In 1947, some 500 million cubic meters of gas were ejected into the atmosphere during the Tourogay mud volcano eruption. During their dormant period the total of gas emitted by the Charagan and Dashgil mud volcanoes was, respectively, to 44,000 m³/year and 165,000 m³/years (Akper, 2003) The most serious accidents with people and animals are due to the colorless methane flame and its sudden spontaneous ignition.

The Caspian Sea, around Baku, capital of Azerbaijan, usually has a hydrocarbon film on its surface due to the mud volcanoes and also to faulty piping formerly used in oil and gas exploration (Françolin, 2002).

Table 2 - Mean gas content of various volcanoes in Azerbaijan (Akper, F., 2003).

Gases	(Methane) C_1	(Nitrogen) N_2	(Carbonic gas) CO_2	(Ethane) C_2
Percentage	84.0	9.0	5.0	2.0

Gas Hydrates

Also known as clathrates (from Latin – cage), they resemble compact snow or ice and are, in reality, a crystalline structure composed of 46 water molecules and 8 gas molecules, with a predominance of methane (REDQ, 2002), or other gases with low molecular weight such as ethane, propane and also carbon dioxide (Sloan, 1998 and Clennell, 2000). Methane can have a thermogenetic as well as biogenic formation. In the biogenic case, it comes mainly from the initial diagenesis stages of organic matter and may be part of the hydrates found in continental shelf sediments. There are also biogenic gases that proceed from the bacterial decay originated in petroleum reserves. In the thermogenetic case, methane relates to gas fields situated in sedimentary basins. Geologically, hydrate gases may occur in two distinct situations, namely in marine shelf sediments of worldwide distribution or in onshore polar regions situated beneath the polar ice layer (permafrost). Under appropriate pressure, the hydrates may exist in temperatures significantly above the water freezing point. On the other hand, the maximum temperature for the gas hydrate existence depends on the gas composition and its resident pressure. Methane, for example, in the presence of water with 600 psia forms hydrates at $5^{o}C$. At this same pressure, if the composition has 1% propane, it can form gas hydrates at $10^{o}C$. Other factors such as salinity can also influence the hydrates (Edmonds *et al*., 1996). According to Kvenvolden (1993), the amount of gas contained in a cubic meter of hydrate, when dissociated in the atmosphere under normal temperature and pressure conditions, may form 164 m³ of natural gas and 0.8 m³ of water.

Methane is listed in the Kyoto protocol as one of the 6 gases that cause the greenhouse effect. The potential of a gas to build the greenhouse effect depends on its nature and respective life time in the atmosphere. Thus, the methane global warming potential for 20 years (GWP20) is 62 times higher than CO_2, whereas its potential for 100 years (GWP100) is only 23 times higher (UKERC, 2004). In fact, methane has the capacity to accumulate 21 times more heat per molecule than CO_2, though proportionally it occurs in smaller amounts. In England, in 2002, methane with a much lower percentage than carbonic gas was responsible for 7% of the greenhouse effect, compared to 84% of CO_2 (UKERC, 2004).

The amount of potential energy generated by the methane in hydrates worldwide, far from being negligible, is equivalent to twice the energy of the fossil fuels found up to the present (Clennell, 2000). In the United States alone, the United States Geologic Survey – USGS - has estimated the existence of 600 trillion m³ of methane, which would be enough to supply the nation for 2000 years - (REDQ, 2002). The detection of hydrates is usually made through seismic profiling, geochemical and drilling surveys. The largest hydrates deposits are situated in Alaska, in the Mackenzie delta, on the Canadian archipelago, in the Siberian Basin and the Vilyuy Basin in Russia. In Brazil hydrates are reported in the Pelotas and Amazon Basins (Clenell, 2000).

Hydrocarbon seeps

Seeps are natural hydrocarbons leakages evident on the surface originated from gas and oil fields in sedimentary basins. They can occur both on the seabed and on the continent. On the coast of California alone, there are more than 2,000 natural seeps. The largest seep is situated in the town of Santa Barbara where 100 oil barrels and 2 million m³ gas are collected daily (WSPA, 2001). In the seep called Coal Oil Point, near Santa Barbara (Table 3) 16,400 m³ of hydrocarbons, predominantly methane, are produced daily (Washburn, 1998). The methane collection zone is situated in a 70-meter deep water table and is the main source of atmospheric pollution in that town. The hydrocarbons found there contain reactive organic gases (ROGs) that are the precursors of ozone. The oil seeps bring to the surface benzene, toluene, ethyl-benzene and xylene (BTEX) contaminations endangering the marine biota. In addition, the gaseous seeps emit gases that contribute to the greenhouse effect.

Table 3 - Composition of the gases of the Coal Oil Point Seep (Washburn, 1998).

Gaseous components	Percentage
(methane) C_1	87.5
(ethane) C_2	5.1
(propane) C_3	3.1
(butane) C_4	1.3
(carbonic gas) CO_2	1.3
(nitrogen) N_2	0.8
(pentane) C_5	0.5
(hexane) C_6^+	0.3
(oxygen) O_2	0.1

CONCLUSIONS

The organic products of non-anthropogenic origin can also affect the health of living organisms, influence the climate, contribute to the greenhouse effect and affect the ozone concentrations on the planet.

The amount of natural organic products generated in geological activities in the environment through aerosols, sandstorms, volcanoes, mud volcanoes, hydrates and seeps must be taken into account by the scientific community and be carefully studied, especially through Medical Geology.

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HUMAN EXPOSURE TO ARSENIC IN BRAZIL

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INTRODUCTION

There has been a growing concern of scientists and public opinion regarding arsenic contamination of humans since the disclosure of the tragedies in West Bengal, Bangladesh, Mexico and other countries. There is very little reference in the literature to Brazil in respect of human and environmental exposure to arsenic due to the lack of research on this subject in the country. Arsenic is a metalloid of low mean concentration on the Earth's crust (1.8 ppm) and it occurs in different types of mineral deposits, mainly as arsenopyrite (FeAsS) and arseniferous pyrite. These mineral phases can be altered to arsenates and sulfo-arsenates on the surface, the arsenic can be partially released to water and also immobilized via adsorption in iron oxides-hydroxides, aluminum and manganese or in clay minerals.

In water, the most common forms are As(V) oxyanions in high to moderate Eh conditions, and As(III) in more reducing conditions. The As concentration in drinking water, according to the World Health Organization, should not exceed 10 mg/L. This value was also adopted by the Brazilian Ministry of the Environment for surface water suitable for treatment for human consumption, according to Resolution 357 of CONAMA March 17 2005 (http://www.mma.gov.br/port/conama/res/res05/res35705.pdf).

Arsenic is a carcinogenic substance and its inorganic form is the most harmful to humans. The As(III) species toxicity is considered to be several times higher than the As(V) species. The most common human exposure path is through contaminated water consumption but gas inhalation and dust ingestion may also be important. Chronic As exposure can cause serious metabolic problems in people, including hyperkeratosis, skin cancer, lung cancer, nervous system disorders, increased frequency of spontaneous abortions and other serious body disorders (Abernathy et al., 1997).

The most serious cases of arsenic intoxication occurred in West Bengal, Bangladesh and, in Latin America, in Mexico, Chile and Argentina. Those cases were principally caused by contaminated groundwater consumption, pumped from regional aquifers formed by arseniferous geological formations (Smedley & Kinniburgh, 2002).

To date, integrated studies on environment and human exposure to arsenic have only been carried out in three areas in Brazil. These areas are indicated in Figure 1: (i) the Quadrilátero Ferrífero, in Minas Gerais, where a large quantity of arsenic has been released to drainages, soils and the atmosphere as a result of centuries long gold mining; (ii) the Ribeira Valley, in Paraná and São Paulo, where arsenic was released to the environment from mining activities and metal refining in the Upper Valley and also, naturally, through rock weathering and the formation of arsenic rich soils in the Middle Valley; (iii) Santana, in Amapá, where the arsenic was associated with the manganese ore mined from the Serra do Navio over the last 50 years.

The human exposure evaluation studies carried out in these 3 areas included As concentrations analyses in children and adult urine in 5 towns of the Ribeira Valley and 2 towns in the Quadrilátero Ferrífero area, as well as
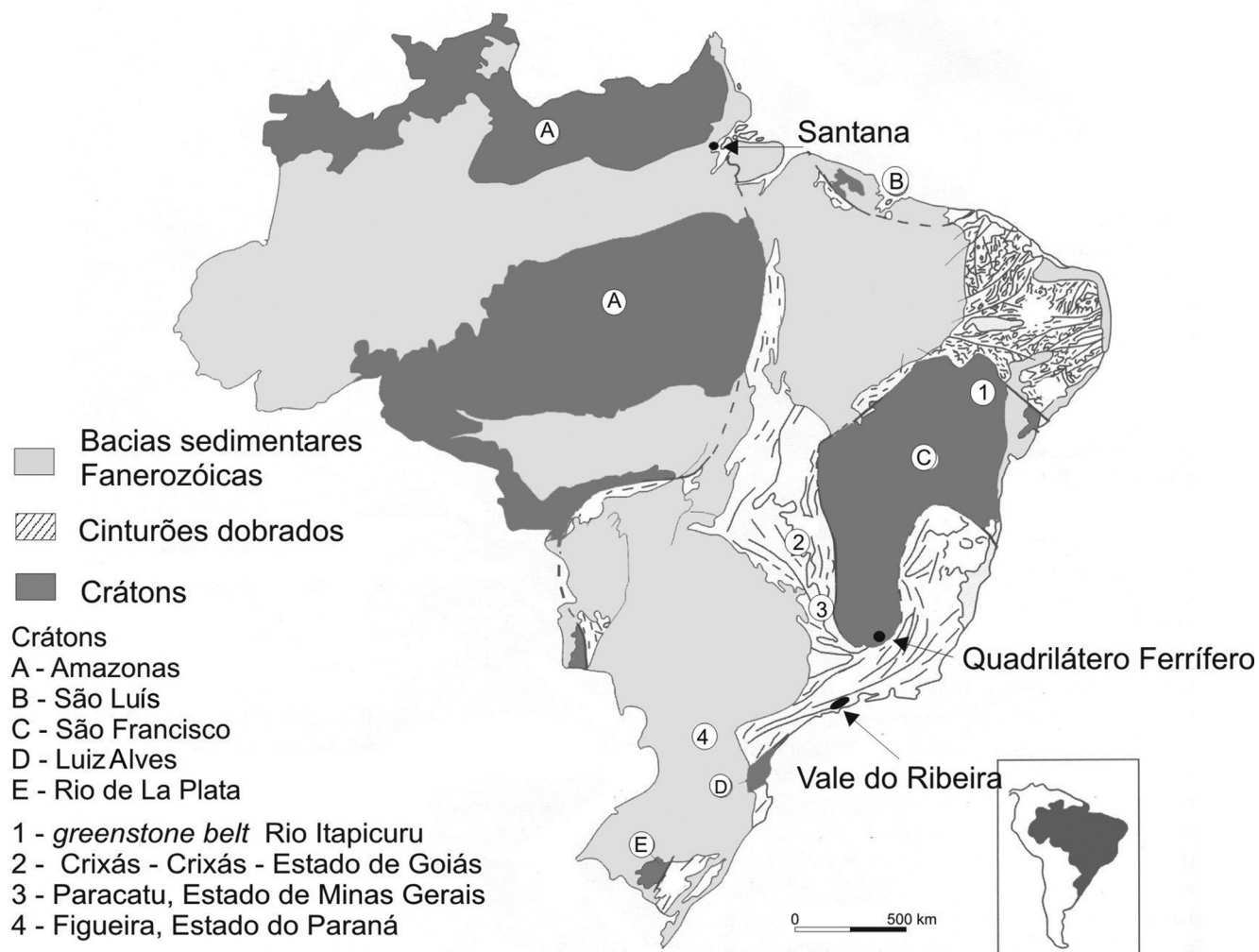
Figure 1 – Situation map of the study areas and geologic-tectonic unities of Brazil.

As detection in hair and blood samples from Santana inhabitants.

On the other hand, integrated studies of nonpoint sources of arsenic, such as geologic formations or large shallow aquifers, described in other parts of the world (Smedley & Kinniburgh, 2002), have never been carried out in Brazil.

This study seeks to gather the available information on these 3 contaminated areas and other As occurrences taken from literature. Furthermore, it contributes to the discussion of surface geochemical processes that favor the mitigation and reduction of exposure risks of arsenic to populations in tropical and subtropical regions.

METHODS AND MATERIALS

In the 3 targeted areas, the composition of surface water and stream sediments were sampled and studied from 1998 to 2003. The filtered water samples (millipore 0.45mm) were collected at least twice a year and the physical-chemical parameters of water quality were measured in situ. The As concentrations were determined through HG-AAS and the total compositions (cations and anions) by ICP-OES and ionic chromatography. Similar procedures were followed for water samples from natural springs, mine drainages and tap water from residences.

The sediment and soil samples were naturally dried, homogenized and sieved using a nylon mesh. Both sediments (according to the granulometric fraction <63μm) and the soils (in the fraction <177μm) were analyzed by FRX and, in the case of As contents in sediments from Santana, HG-AAS analysis were also carried out. The analytical accuracy was controlled by means of simultaneous analysis of certified reference material.

First morning urine samples, collected from residents in Ribeira Valley, were analyzed (Sakuma, 2004) for As

(As^{3+} + As^{5+} + MMA + DMAA) by hydride generation atomic absorption using a flow injection system, at the Adolfo Lutz Institute (São Paulo), according to a procedure recommended by Guo et al. (1997) and using certified reference material NIST 2670 (0.06μm/mL As).

Arsenic concentrations in urine samples collected in the Quadrilátero Ferrífero area, refer to total inorganic As, determined using HG-AAS (Matschullat et al., 2000). At the Evandro Chagas Institute, blood and hair samples, from the town of Santana, were analyzed in a graphite furnace using Zeemann background correction (Santos et al., 2003).

RESULTS

In the three denominated study areas arsenic exposure can be identified with processes induced by mining and metallurgy activities. However, in the Ribeira Valley, besides the contamination caused by the industrial activities in the Upper Valley, the occurrence of the geochemical anomaly of As associated with the rocks and soils of the Piririca Unit (Açungui Group) characterized in previous CPRM (1982) and Perrota (1996) studies is also considered.

Arsenic in the Quadrilátero Ferrífero (MG)

The Quadrilátero Ferrífero area is the most important auriferous province in Brazil. It is produced about 600t of gold in the last 300 years. The gold ore contains arsenic in minerals such as arsenopyrite and lollingite or as an impurity in pyrite. The lithologies are composed of: metabasalts, metamorphic banded iron formations, schists and granitoids that present important carbonatic alteration in the vicinity of the deposits. These sites of Archean and Paleoproterozoic age represent an important As geochemical anomaly in the Southern portion of the São Francisco Craton. The contribution of mining and metallurgy activities to the processes of As release to the environment has been studied by several authors like Oliveira et al. (1979), Borba et al. (2000), Deschamps et al. (2002), Borba et al. (2003) and Borba & Figueiredo (2004).

In the entire region the As concentrations in the stream sediments (<63μm) were elevated, and reached 4,000mg/kg As in the mine surroundings. However, the surface water rarely presented concentrations higher than 50μm/L As, which was, at the time, the legislation established limit for non-treated water. A few water samples from natural springs also presented low arsenic concentrations, while the samples collected from mine surroundings and tailings presented 350 μg/L As and samples from mine drainages, up to 3,000 μg/L As.

In 1998 a human monitoring campaign was carried out among populations of school age children (7-12 years) in the towns of Santa Bárbara and Nova Lima,

using arsenic in urine as a bioindicator (Matschullat et al., 2000). The average As concentration in the 126 urine samples was 25.7 μg/L As and 20% of the examined children presented more than 40μg total inorganic As per urine liter, a threshold above which long term adverse effects on health may occur. The most likely means of arsenic exposure would have been with soil and dust contact, since the As concentrations in drinking water were well below 10μg/L (limits established by the Ministry of Health and World Health Organization for drinking water).

Monitoring campaigns carried out at the same schools in subsequent years revealed average values inferior to those of 1998 and the percentage of children with concentrations above 40μg/L As in urine did not exceed 5% of the population sampled in 2002 (Matschullat, 2004, oral communication).

Arsenic in Ribeira Valley (PR-SP)

The Ribeira Valley extends from the Northeast of Paraná to the South coast of São Paulo State and supports a great part of the remaining Atlantic Tropical Forest - Mata Atlântica - and has an important fresh water reserve of the country's Southeast region.

During the 20th century, the Upper Valley region hosted several Pb-Zn-Ag mining operations, as well as a lead refining plant (Plumbum), in Adrianópolis town (PR), operating from 1945 to 1995. The region's main mineralization contained significant amounts of arsenic (arsenopyrite and tennantite), especially in the filonean deposits of Panelas and Furnas, hosted in Mesoproterozoic dolomitic limestones.

In the Middle Valley, the Mesoproterozoic Piririca Unit, made up of schists and metabasic rocks, with quartz, gold and sulfide veins (including arsenopyrite), extends between the towns of Iporanga and Itapeúna. High As concentrations in stream sediments and soils define a NE direction zone (CPRM, 1982; Perrota, 1996), that represents a natural As anomaly, because modern mining was never established in that area.

Human monitoring campaigns for arsenic were carried out in five towns throughout the Upper Valley regions (1999-2001) and Middle Valley (2001-2003). The As concentrations in early morning urine collected among children and adults were determined (Sakuma, 2004). The population of Cerro Azul town (PR), situated outside the area under mining influence and distant from the natural arsenic anomaly, was chosen as a reference group. Among the mining area communities of the Upper Valley, the highest As medians in urine (8.94 μg/L in children, n=89, and 8.54 μg/L in adults, n=86) was from the Bairro da Serra neighborhood in Iporanga. This is situated near the Furnas and Ribeirão Betari mines, which was known for its high arsenic and lead concentrations in sediments at the time of the mining activities.

In the Middle Valley 6 communities were monitored and the average As concentrations in urine of children and adults varied between 2.24 and 11.35 µg/L As. These results are indicated in Table 1, where the medians of Cerro Azul and the Bairro da Serra neighborhood are shown for comparison purposes (Sakuma, 2004 and De Capitani et al., 2005).

Though the arsenic concentrations in urine cannot be considered elevated, some average contents keep a statistically significant difference compared with the results obtained for the Cerro Azul reference group (3.60 µg/L As in children, n=73 and 3.87 µg/L As in adults, n=83). In Cerro Azul the highest medians were the populations of Galvão, São Pedro, Ivaporunduva and Castelhanos, coincidently those closest to the Piririca arsenic anomaly. Whereas the lowest medians were the communities that are the farthest away from the anomaly.

The surface water quality of the Ribeira River and tributaries in the Middle Valley region was monitored from 2001-2003 in 5 sampling campaigns. The As concentrations varied between 1 and 9 µg/L and the highest concentrations were found in the Piririca creek which drains rocks presenting auriferous veins and arsenic rich soils (Takamori & Figueiredo, 2002). In that same creek, previous studies had indicated contents of up to 345 mg/kg As in stream sediments (Toujague, 1999). Soils rich in arsenic and heavy metals occur in the Piririca zone too, resulting from the intense chemical weathering that affected rocks and arsenic mineralization. Abreu & Figueiredo (2004) found concentrations from 25 to 754 mg/kg in surface soil (0-30 cm depth) in that area.

Arsenic in Santana (AP)

In Amapá State, arsenic occurs in arsenopyrite associated with Precambrian magnesiferous formations, mined for over 50 years in the famous Serra do Navio mine. The arsenic source is not situated in the mine but in Santana, 350 km away, on the Amazon River margins, where the manganese ore was processed and loaded. In the town, ore and wastes exposed in an open pit contained up to 0.17% As and groundwater sampled in monitoring wells close to those deposits had high arsenic concentrations of up to 2,000 µg/L.

Geochemical studies carried out in the area (Lima, 2003), revealed As concentrations in surface water between 5 and 231 µg/L As (2001-2002) but most values were below 50 and 10 µg/L As. Samples of fluvial sediments and suspension material presented contents varying from 1,600 to 696 mg/kg As. On the other hand, concentrations in tap water from residences did not exceed 0.5 µg/L As.

The local population (about 2,000 inhabitants) was assessed for arsenic exposure using blood and hair analyses (Santos et al., 2003). Inorganic arsenic has a special affinity with hair and other keratin rich tissues, so the As content in these tissues is a good exposure bioindicator. Concentrations of up to 1 ppm of arsenic in hair and fingernails can be considered normal, according to Choucair & Ajax (1988) and Franzblau & Lilis (1989), threshold also used by ASTDR (2000).

A population of 512 people analyzed in Santana, produced a median of 0.20 g/g As in hair (Table 2). According to other countries' results (Granero et al., 1998; Pazirandeh et al., 1998; Saad & Hassanien, 2001, among others), the arsenic exposure levels in the Santana community cannot be considered elevated, although complementary data of urinary arsenic are still necessary in the area.

Table 2 - Arsenic Concentrations in hair – Santana, Amapá State (2001-2002)

Population	n	Median µg/L As	Min µg/L As	Max µg/L As
Men	182	0.200	0.074	1.936
Women	330	0.200	0.063	1.855
Total	512	0.200	0.063	1.936

Source: Santos et al.(2003)

Other arsenic occurrences in Brazil

The above three cases represent the only examples of integrated studies on environmental geochemistry and human exposure assessment being performed. They are related to environmental impacts induced by mineral refining and ore processing activities, in the form of exposed mining tailings and soil contamination and surface drainage. Their pollution sources may be considered punctual even though along the Piririca Belt in the Middle Ribeira Valley, arsenic rich soils cover a large area.

Table 1 - Arsenic concentration in children and adults urine in the Ribeira Middle Valley (2002-2003), Cerro Azul and Bairro da Serra (Iporanga)

Locality	n	Median µg/L As	Min µg/L As	Max µg/L As
Cerro Azul	156	3.86	1	34.12
Bairro da Serra - Iporanga	175	8.90	1	62.54
Iporanga	112	8.14	1	33.49
Pilões	73	3.97	1	68.92
Castelhanos	58	9.48	1	60.32
Galvão	35	15.02	2.36	55.69
São Pedro	51	11.35	1	76.19
Ivaporunduva	30	10.02	1.77	34.57
Nhungara	22	5.84	1	25.95

Source: Sakuma(2004) and De Capitani et al. (2005)

Other arsenic point sources can be identified in the auriferous districts of the Itapicuru River greenstone belt (Bahia State), Crixás (Goiás State) and Paracatu (Minas Gerais State). In these sites, auriferous ore, rich in arsenopyrite, as described in the Quadrilátero Ferrífero area, is or was mined, except these mining activities are more recent compared to those in the Quadrilátero area in Minas Gerais.

In the South Region of Brazil, arsenic associated with coal deposits has also been confirmed. Coal mining in Santa Catarina and Rio Grande do Sul States has produced significant environmental impacts, caused by huge mining waste deposits and sulfurous lagoons.

A wider assessment of the literature and geological documentation in Brazil is still to be made, to identify diffuse sources of arsenic. In the geochemical data bank of the Brazilian Geological Service (Lins, 2004, oral communication) up to 18,670 analyses of stream sediment and soil samples for arsenic can be found. About 20% of the samples presented arsenic contents higher than 100 ppm. The highest sediment and soil concentrations were found in the Ribeira Valley (Piririca zone), the gold prospection areas in the greenstone belts of Amapá State, in the Quadrilátero Ferrífero area and in certain places in the Northeast region of Rondônia State.

Inferences of probable non-point As sources can be drawn from the low density geochemical mapping of Paraná State. Licht (2001) has described a positive As anomaly associated with the occurrence of bituminous shales and Paleozoic carboniferous formations of the Paraná Basin, as well as an occurrence of arsenic associated with the carboniferous and uraniferous formation in the Figueira region, in Paraná State.

With regard to surface water in humid tropical regions, the As concentration data in this study is coherent with those obtained at other sites in the country. It is difficult to find more systematic information about arsenic occurrence in groundwater, especially in those regions where the population and economic activity depend on shallow aquifers. Similarly, no information can be found concerning the release of arsenic to the environment due to agricultural activities (intensive use of pesticides).

CONCLUSIONS

In Brazil, as in other developing countries, exposure to toxic substances affects mainly the lower income population being also subject to food deficiency. In the North and Southeast regions, referred to in this study, the population has access to abundant water resources, being areas with high rainfall, as compared to the different situation experienced in regions of serious As intoxication levels, where populations depend on groundwater for their consumption.

The tropical climate favors the predominance of chemical rock weathering processes resulting in deeper soil profiles, enriched in iron and aluminum, as well as fine sediments, that function as geochemical barriers preventing the release of As to the water. These processes could explain the reason for the low As concentrations in surface water and, in some cases, in samples from springs found in the studied areas, contrasting with the elevated As concentrations in soils and sediments.

In the three described areas regardless of their industrial activity, they present natural arsenic anomalies. To the natural availability processes of Arsenic, significant As amounts are also released into the environment from ore mineral processing and refining activities. Fortunately, however, the current low levels of human exposure to the toxic element represent a controllable and reversible risk situation. In addition, for a proper risk evaluation, complementary studies are necessary on As speciation in water and As availability in soils and sediments, as total As concentrations in the different geochemical compartments alone are not sufficient.

At yet, Arsenic rich geological formations and contaminated aquifers, such as those indicated in other World regions by Smedley & Kinniburgh (2002), have not been described in Brazil. A more complete inventory of Arsenic occurrences in Brazil is still a challenge for the Geosciences to face in the future.

ACKNOWLEDGMENTS

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ARSENIC IN GROUNDWATER IN OURO PRETO (MG)

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INTRODUCTION

Water used for human consumption with As (arsenic) concentrations above the limits established by the environmental control agencies are considered dangerous for human health (Hopemhayn-Rich et al., 1996; National Research Council, 1999).

Arsenic is found in a long list of minerals such as sulfides, arsenides and sulfo-arsenides, the later being the most common. In natural water As occurs in organic and inorganic compounds. In solution, the inorganic compounds encountered in water with high to moderate Eh conditions are H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-} whereas H_3AsO_3 predominates in reducing conditions with As in the oxidized states 3+ and 5+ (Thornton & Farago, 1997).

As is a toxic and carcinogenic element. The main pathologies caused by acute and chronic As intoxication are: metabolism problems, skin tumors, ulcers, gastritis, diarrheas, cardiac arrhythmia, pancreas and lung cancer, spontaneous abortions, low weight fetus, headaches, mental confusion and anemia (Hutton, 1987; Morton & Dunnette, 1994; Chen & Lin, 1994; USEPA, 2000; WHO, 2001).

In Ouro Preto city, the public water supply relies on surface sources, spring catchments and groundwater drawn from tubular wells and also old goldmines. Considering its geological environment, there is a possibility the water has a high As concentration, turning the water inappropriate for human consumption.

Geographically As is distributed in the Quadrilátero Ferrífero area rocks, in close association with sulfide-rich, gold bearing rocks.

The origin of As in the water, soil and sediments, is due to a natural anomaly of this element in the region. This anomaly is related to the genesis of the auriferous deposits. Weathering of rocks with anomalous As contents promotes the metal liberation to the environment.

This is a hydrogeochemical study of the Ouro Preto water supplied to its population, by means of periodic monitoring of the As temporal behavior, from January 2003 to January 2004.

GENERAL CHARACTERISTICS OF THE STUDIED AREA

The studied area is located in the Southeastern portion of the Quadrilátero Ferrífero area of 7,200 km², situated in the Southern center portion of Minas Gerais State. The geological constitution of Ouro Preto (Figure 1) is a set of metasedimentary and metavolcanic rocks belonging to the Minas and Rio das Velhas Supergroup.

The Ouro Preto climate is a Cwb type, according to Rodrigues (1966), who adopted the KOPPEN international classification that is, humid mesothermic, with a dry winter and mild summer.

A large part of the Ouro Preto urban area is settled in a valley formed between the Itacolomi and Ouro Preto ridges, with elevations varying from 1,060 to 1420m.
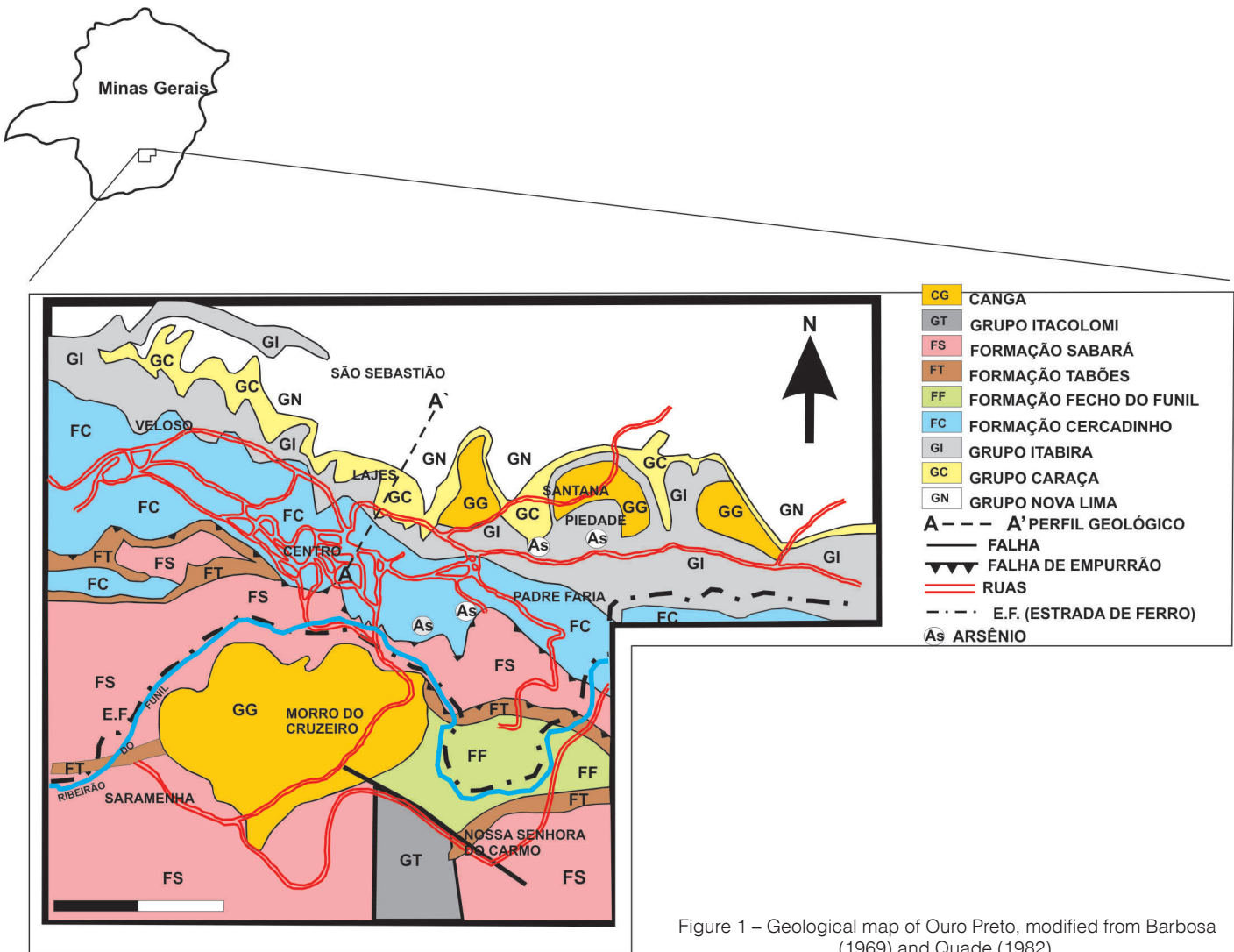
Figure 1 – Geological map of Ouro Preto, modified from Barbosa (1969) and Quade (1982).

HYDROGEOLOGY – THE AQUIFER SYSTEMS: DESCRIPTION AND CHARACTERIZATION

Three categories of aquifer systems were identified: a granular aquifer characterized by weathering mantles and undivided detrital covers; a granular-fractured aquifer, constituted by itabiritic rocks; and a fractured aquifer, represented by chists and quartzite rocks, (Chart 1).

MATERIAL AND METHODS

Among the several groundwater and superficial water extraction sources used by the population of Ouro Preto, 17 sampling sites (SS) were chosen for study. The water samples (Table 1) were collected along the year 2003, during six sampling campaigns (SC) in January, March, Mai, July, September and November. In each sampling site in situ measurements of pH, Eh, temperature, total dissolved solids and electric conductivity were taken.

The analysis method for As speciation was by square wave voltammetry (Gonçalves et al., 2004). The experiments were carried out using a Metrohm polarograph, model 757 VA Computrace, equipped with a working dropping mercury electrode, a reference electrode Ag/AgCl/KCl 3mol.L^{-1} and an auxiliary platinum electrode.

RESULTS AND DISCUSSION

Of the 17 studied sites (Table 1), 13 didn't show the presence of As. However, in four sites, the As (V) was detected in concentrations that varied between 9 and 224 µg.L^{-1}. Of the total water samples that were analyzed, 75% had presented As concentrations above the values

compatible for human consumption, which is 10 µg.L^{-1} of As (FUNASA, 2001). The most toxic As form, the As(III), was not detected in any of the water samples analysed. The water samples that presented As concentrations inadequate to human consumption were found in the sampling sites SS14 (Mina do Chiquinho), SS15 (Chafariz/fountain – Barão Street), SS16 (Piedade-Tassara) and SS17 (Biquinha of Santa Rita Street – Mina Velha).

The direct and narrow relationship between the climate seasonality and the As concentrations, found in some of the water sites studied (SS14, 15, 16 and 17) is clearly shown in Figure 2.

In all of these sites the curves representing the rain rates and the As concentration values, show the same tendency, that is, the periods of greater rain incidence are also the ones that present the highest values for As contents (period between December and March).

On the other hand, in the driest season, between June and September, the As concentration in water presented the lowest values whereas in the sites SS14 and 16 As was not detected at all. For all the sites with As presence, the maximum and minimum As content values coincide with the maximum and minimum pluviometric rate values.

Two hydrogeochemical conditions can lead to variations in water quality (Rose et al., 1991):

the decline in the water levels after the rainy season promotes the beginning of the oxidation processes in the aquifer systems;

during rainy periods the salts formed in the oxidation zones during the dry period are dissolved and transported;

In addition to the climatic conditions and operating concomitantly, the trajectory of the rainfall, both by superficial runoff and infiltrated waters, finds, in the geomorphology and in the abrupt relief of the area the proper conditions for rapid flows, enabling interactions between water and rock, causing dissolution and transport of higher quantities of substances and elements.

The existing aquifer systems also contribute significantly to the dissolution and liberation of As to the environment. Phyllites and ferruginous quatzites, Cercadinho Formation rocks (fractured aquifer), and mainly the Caue Formation itabirites and dolomitic itabirites, Gandarela Formation dolomitic phyllites and dolomitic iron formations, schistose rocks (granular-fractured aquifer) present good porosity and permeability conditions, a dense network of fractures, micro-fractures and foliation planes. In these formations, which correspond to the points where As was detected in groundwater, oxidized sulfide minerals and secondary minerals are exposed in the surface.

The oxidation of sulfide mineral bodies starts with the reduction of water inflow at the end of the rainy period, extending throughout the dry period, producing a considerable amount of soluble salts. These first reactions occur mainly in the recharge areas of the groundwater and slopes, where the weathering processes in the non-saturated zone, rich in free O_2, cause the oxidation of sulfide minerals, in special arsenopyrite. The arsenopyrite oxidation reaction, according to Plumlee (1999) is: $FeAsS + 3.25O_2 + 1.5H_2O = Fe^{2+} + 2H^+ + HAsO_4^{2-} + SO_4^{2-}$.

Under these acid conditions, As is highly mobile (Mok et al. 1988), being released from the mineralized rocks by means of inorganic or biotic processes (Nordstron and Southam 1997).

Chart 1 - The aquifer systems, predominant lithologies and associated geological units (modified from IGA, 1995)

Aquifer Systems	Predominant Litology and Geological Units
Granular media	
Aquifers in weathering mantle and detrital covers	This system constitutes the superficial aquifers associated with the weathering mantle (saprolites, colluvia, lateritic covers, and canga) and detrital deposits of the Tertiary-Quaternary cover.
Granular – Fractured media	
Aquifers in Itabiritic rocks	Finely-laminated itabirite and dolomitic itabirite from the Cauê Formation / dolomitic phyllite and dolomitic iron formations from the Gandarela Formation
Fractured media	
Aquifers in schistose rocks	Schists, chloriteschists, quartzchlorite, quartz-chlorite-sericite schist from the Nova Lima Formation / dolomitic phyllite, phyllite and iltite from the Fecho do Funil Formation / mica, chloriteschists and quartzites from the Sabará Formation
Aquifers in quartzitic rocks	Quartzite, ferruginous quartzite, and phyllite from the Cercadinho Formation / conglomeratic quartzite from the Itacolomi Group

Table 1 - Situation of the sampling sites (SS) and chemical composition of the groundwater

SS01	Rua Tomé Vasconcelos – 438 / Bairro São Cristóvão————— Water Catchment: Old gold mine————— As not detected over the year
SS02	Travessa Sargento Francisco Lopes-1————— Water Catchment: Spring————— As not detected over the year
SS03	Travessa Sargento Francisco Lopes-2————— Water Catchment: Old gold mine ————— As not detected over the year
SS04	Jardim Botânico————— Water Catchment: Superficial stream————— As not detected over the year
SS05	Água Limpa – Caixa 4 (Quadra de Futebol)————— Water Catchment: Spring ————— As not detected over the year
SS06	Água Limpa – Caixa 5 (Banheira)————— Water Catchment: Spring ————— As not detected over the year
SS07	Nossa Senhora do Carmo————— Water Catchment: Superficial stream ————— As not detected over the year
SS08	Saramenha de Cima————— Water Catchment: Superficial stream ————— As not detected over the year
SS09	Morro São Sebastião————— Water Catchment: Tubular well————— As not detected over the year
SS10	Estação de Tratamento do Itacolomi————— Water Catchment: Superficial stream ————— As not detected over the year
SS11	Biquinha – Rua 13 de Maio (Frente ao número 160)————— Water Catchment: Old gold mine ————— As not detected over the year
SS12	Mina do Bem Querer————— Water Catchment: Old gold mine ————— As not detected over the year
SS13	Morro São João————— Water Catchment: Tubular well————— As not detected over the year

SS14	Mina do Chiquinho							Water Catchment: Old gold mine						
	pH	Temp	TDS	CE	Eh	As III	As V	Na	Mg	Al	K	Ca	Mn	Fe	Ba
SC1	7.43	19.7	14.12	21.38	0.397	< 5	27	1.06	0.26	< LQ	0.94	1.35	58.8	< LQ	7.87
SC 2	6.62	19	16.38	25.15	0.433	< 5	14.8	1.8	0.4	< LQ	1.03	1.35	127.9	< LQ	6.27
SC 3	6.57	17.5	17.39	25.99	0.488	< 5	< 5	1.78	0.5	< LQ	1.03	1.23	124.4	< LQ	5.96
SC 4	6.37	18.3	16.63	25.9	0.398	< 5	< 5	1.58	0.49	< LQ	1	1.2	53.1	< LQ	26.87
SC 5	6.3	20	16.5	25.35	0.383	< 5	< 5	1.61	0.48	< LQ	1.04	1.22	7.58	< LQ	14.13
SC 6	6.59	20.6	15.13	22.63	0.387	< 5	< 5	1.68	0.44	< LQ	0.88	1.23	18.05	< LQ	4.75

SS 15	Chafariz – Rua do Barão-30 (Vicentão)							Water Catchment: Spring						
	pH	Temp	TDS	CE	Eh	As III	As V	Na	Mg	Al	K	Ca	Mn	Fe	Ba
SC 1	7.16	19.6	54.21	80.85	0.399	< 5	71	7.15	1.12	< LQ	2.8	4.28	10.34	< LQ	9.03
SC 2	6.24	19.4	48.24	73.33	0.497	< 5	62.9	7.32	1.02	< LQ	2.62	2.97	15.51	< L.Q.	7.42
SC 3	6.28	18.6	48.23	71.49	0.469	< 5	48	7	1.1	1.76	2.53	2.45	14.95	4.33	7.59
SC 4	6.67	18.2	49.03	75.45	0.335	< 5	25	6.9	1.08	< LQ	2.6	2.43	15.04	< L.Q.	39.61
SC 5	7.82	19.5	49.25	74.65	0.412	< 5	25	7.14	1.02	3.13	2.64	2.46	15.38	5.05	28.5
SC 6	7.31	20.7	49.95	73.9	0.365	< 5	26.5	1.26	0.44	38.2	0.35	1.22	9.49	12.3	4.72

SS16	Piedade							Water Catchment: Old gold mine						
	pH	Temp	TDS	CE	Eh	As III	As V	Na	Mg	Al	K	Ca	Mn	Fe	Ba
SC	1 7.21	18.7	46.7	69.5	0.42	< 5	29	5.65	0.93	3.35	2.3	3.63	29.6	< L.Q.	13.61
SC	2 6.65	18.6	48.43	73.55	0.488	< 5	22.8	6.7	1	7.97	3.17	3.38	31.54	< L.Q.	12.95
SC	3 6.61	18.4	47.15	69.83	0.517	< 5	< 5	6.23	1.07	5.83	2.92	2.75	32.38	< L.Q.	12.13
SC	4 6.55	18.1	49.22	75.75	0.414	< 5	< 5	5.65	1.04	< LQ	2.78	2.73	27.19	< L.Q.	25.25
SC	5 6.53	19	42.87	64.88	0.4	< 5	15.2	5.46	0.99	3.83	2.72	2.73	31.63	< L.Q.	22.16
SC	6 6.73	20.4	41.47	61.13	0.408	< 5	9	6.6	1.12	4.49	2.93	3.58	30.26	< L.Q.	13.2

SS17	Biquinha da rua Santa Rita (Mina Velha)							Water Catchment: Old gold mine						
	pH	Temp	TDS	CE	Eh	As III	As V	Na	Mg	Al	K	Ca	Mn	Fe	Ba
SC 1	7	19.2	90.74	135.7	0.42	< 5	224	8.36	2.02	30.4	3.86	11.96	20.53	< L.Q.	12.73
SC 2	6.92	19.2	82.05	125	0.495	< 5	125.9	8.97	1.74	27.76	3.6	9.53	38.6	< L.Q.	11.51
SC 3	6.42	18.6	82.88	123.01	0.532	< 5	68	9.39	1.84	7.41	3.75	6.79	57.3	< L.Q.	14.61
SC 4	5.93	18.4	82	126.5	0.408	< 5	17	9.47	1.85	< LQ	3.9	6.3	68	< L.Q.	33.64
SC 5	6.56	18.6	80.9	122.7	0.388	< 5	< 5	9.93	1.74	11.53	3.97	6.09	71.1	< L.Q.	25.86
SC 6	6.87	19.1	85.94	127.1	0.397	< 5	27	9.44	2.03	25.33	3.37	10.73	30.18	< L.Q.	11.3

| Limits for the Quadrilátero (LQ) | | | | | | (5μgL⁻¹) | (5μgL⁻¹) | (0.15mgL⁻¹) | (0.01mgL⁻¹) | (4μgL⁻¹) | (0.05mgL⁻¹) | (0.01mgL⁻¹) | (4μgL⁻¹) | (9μgL⁻¹) | (0.2μgL⁻¹) |
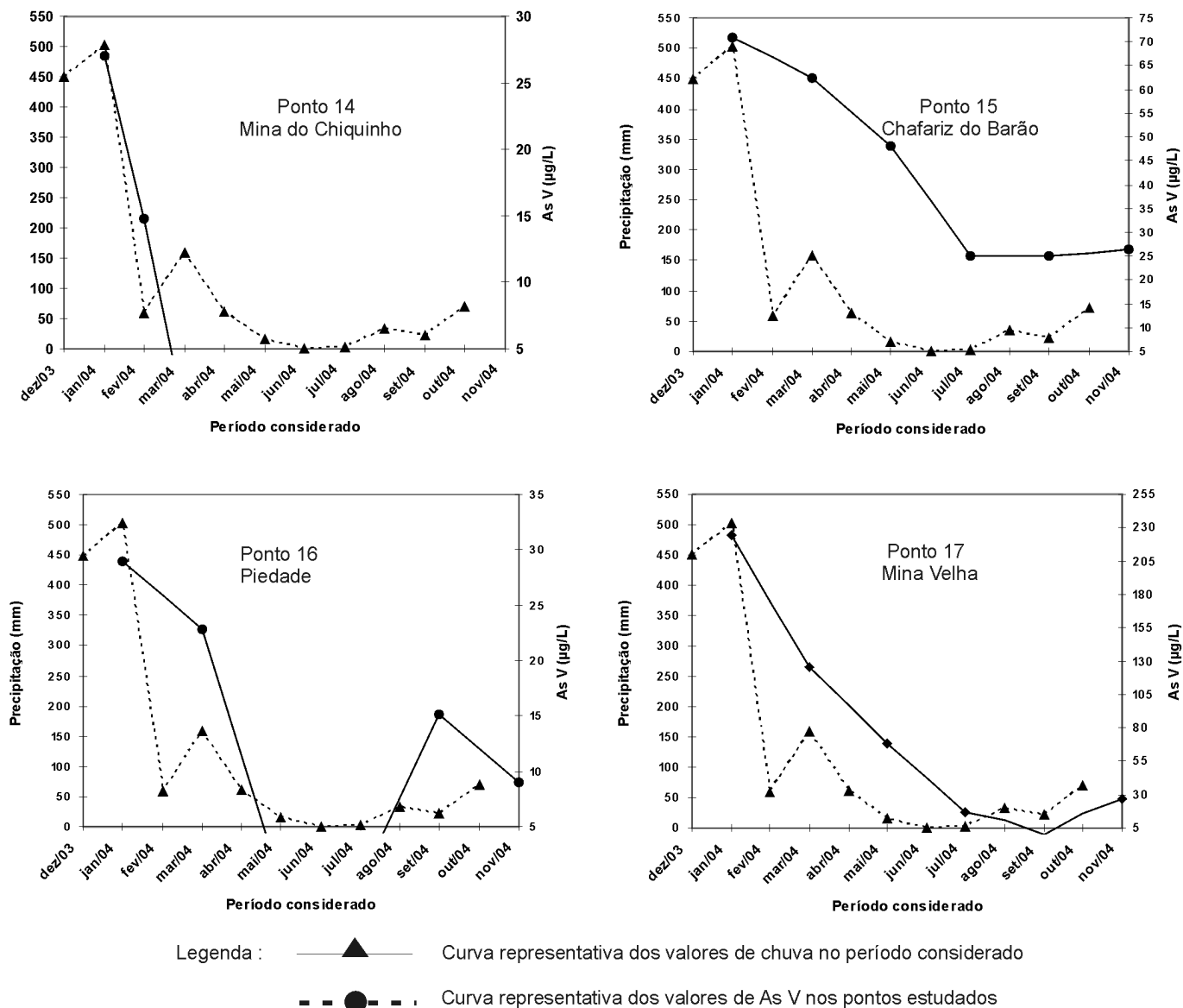
Figure 2 – Graphic representation of the relationship between rainfall rates and As(V) concentrations from December 2004 until November 2004

Borba (2002) attributes the presence of As in the groundwater, some Ouro Preto mines and in the Passagem de Mariana mine, to this mineral and to its incongruent dissolution, due to the pH increase. In the Zimapa´m Valley in Mexico, Armienta et al. (2001) report groundwater contamination by As resulting from the oxidation of arsenopyrite and dissolution of the scorodite present in sulfide mineralizations hosted by carbonaceous rocks.

STUDY OF AS PRESENCE IN RESIDENCES OF THE PADRE FARIA NEIGHBORHOOD

The Padre Faria neighborhood is supplied with water from several sources. Water samples were collected in 42 residences of that neighborhood (Table 2), chosen in order to guarantee the randomness of the sampling sites. The residences were selected by systematic sampling, where one in every ten residences existing in the street was selected.

CONCLUSIONS

The method used allows a quick quantification of the inorganic species As(III) and As(V) in natural waters at a relatively low cost and with high sensitivity. Contents above 5 lg L^{-1} can be easily determined, covering an ample range of concentrations. The answers for real sample analyses are perfectly similar to those of the standards, with no detrimental interference from the matrices.

Table 2 - Total As concentrations in some residences of the Padre Faria neighborhood

Sample	As µg/L	Sample	As µg/L
PF 01	< D.L.	PF 22	189
PF 02	< D.L.	PF 23	9.88
PF 03	8.66	PF 24	10.76
PF 04	8.57	PF 25	7.47
PF 05	8.82	PF 26	55.52
PF 06	8.54	PF 27	16.11
PF 07	< D.L.	PF 28	9.74
PF 08	9.23	PF 29	10.91
PF 09	9.62	PF 30	< D.L.
PF10	11.51	PF 31	< D.L.
PF 11	9.9	PF 32	< D.L.
PF 12	10.14	PF 33	< D.L.
PF 13	< D.L.	PF 34	< D.L.
PF 14	< D.L.	PF 35	7.47
PF 15	8.9	PF 36	< D.L.
PF 16	8.42	PF 37	< D.L.
PF 17	8.04	PF 38	< D.L.
PF 18	8.17	PF 39	< D.L.
PF 19	< D.L..	PF 40	< D.L.
PF 20	127	PF 41	< D.L.
PF 21	13.46	PF 42	< D.L.
PF – Padre Faria		D.L. – Detection Limit	

According to Smedley et al., 2002, the great spatial variability of the As concentrations is a remarkable characteristic of areas presenting high As contents. Thus, it can be difficult or impossible to predict the As concentration of a single sampling site considering the results of neighboring springs or wells. Aquifers contaminated by As may be restricted to certain environments, show an erratic spatial behavior and seem to be the exception rather than the rule.

The variation of As concentrations in the groundwater of the studied area, along a period of one year, is related to the climatic seasonality. During seasons of pluviometric deficit, the reduction of water levels in the aquifers favors the oxidation of sulfide minerals. During the rainy seasons, the dissolution of those minerals will occur, mobilizing and lixiviating the As to the environment (Banks et al., 1997; Freeze & Cherry, 1994), increasing the concentrations of this element in the groundwater, at the same time that the original concentrations are diluted. The As concentration values found in the water samples are representative of the time of sampling and the season, varying to higher or lower values along time.

Due to the presence of As in groundwater used by the population of some neighborhoods of Ouro Preto city,

measures must be taken by the municipal agencies responsible for the water supply. An effective and efficient water supply system must contemplate the identification and characterization of contaminated areas, an inventory of all water catchments, and the preparation of a control system that includes a systematic water monitoring plan.

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ARSENIC IN ESTUARIAL SEDIMENTS OF THE ANTONINA BAY ACCESS CHANNEL, PARANÁ STATE BRAZIL

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INTRODUCTION

The estuarial complex of the Paranaguá Bay, situated on the south coast of Brazil, between 25°16' and 25°34' S and 48°17' and 48°42' W, is formed by the Paranaguá Bay itself including the region of Antonina and Laranjeiras (Figure 1).

This system is of extreme importance to the coastal ecosystem and in the social and economic development of the State of Paraná, once it constitutes a favorable geographical area for industrial and harbor facilities, fishing activities (reproduction and growing site of commercially interesting species) and tourism. The region of Antonina Bay, situated in the most internal portion of the estuarial complex of Paranaguá Bay, has undergone a reactivation of the harbor facilities due to the growth of these activities in the region. As a consequence, the remodeling of the Paranaguá and Antonina harbors access channels has become necessary demanding periodical dredging for the improvement of drought.

In the region of the estuarial complex of the Paranaguá Bay urban, harbor and industrial (fertilizer, storage of chemical products and bulk grain) activities coexist along with fishing activities, dredging and many others (Figure 2).
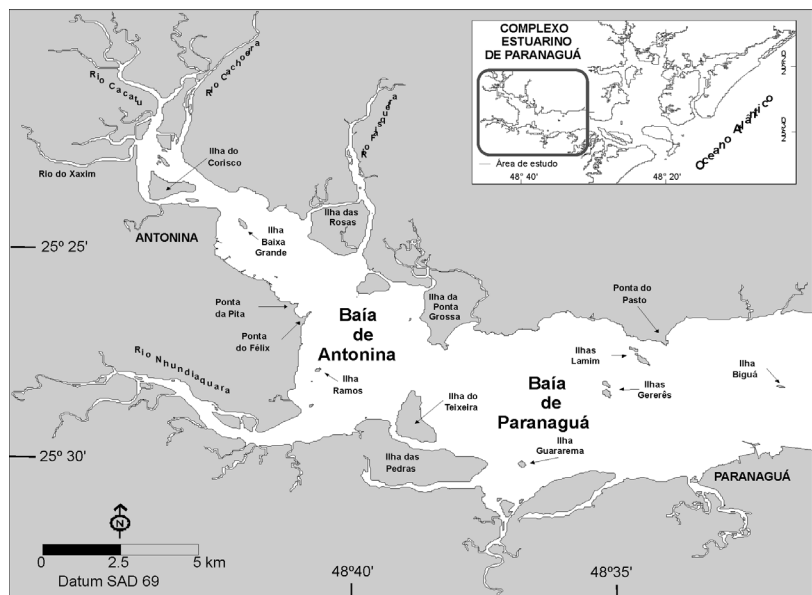
Figure 1 – Map of the E-W axis of the Paranaguá Bay estuarial complex.

METHODS

The surface sediment sampling in May 2001, (Figure 3) was carried out at nine sites distributed in three sections along the 12 km channel between the Ponta do Félix and Petrobras terminals.

Figure 2 – Industrial/urban and harbor activities that occur concomitantly in the region: a) un-planned waste dumping; b) dredging activities; c) domestic/industrial sewage emissary.
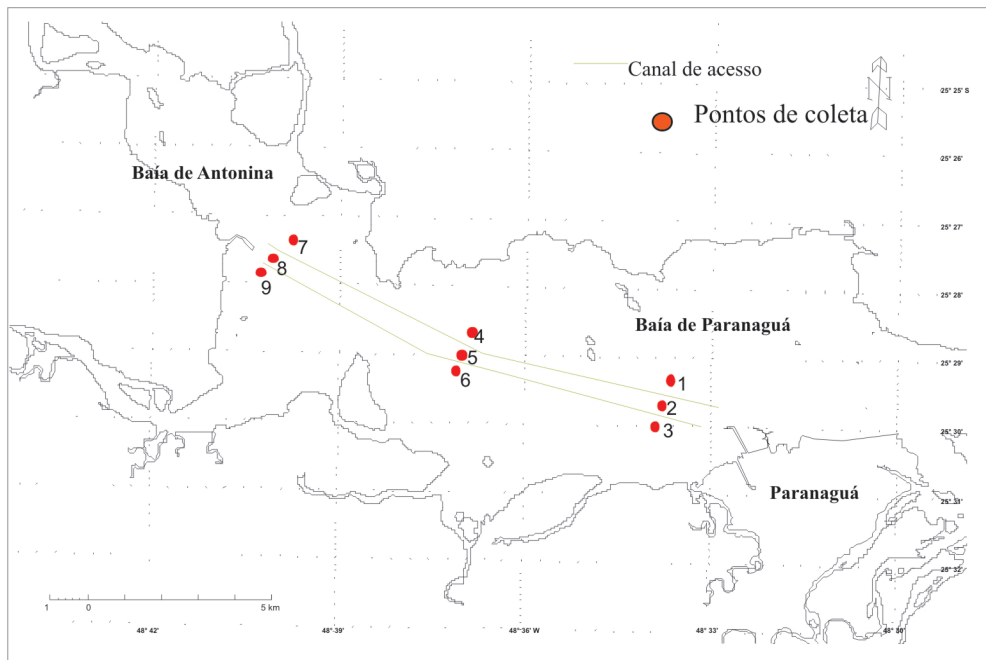
Figure 3 – Sampling point locations and identification of the access channel to the Harbor Terminals Ponta do Félix and Barão de Teffé, Antonina.

A strong extraction using HF and HNO$_3$ with heating was made to completely dissolve the whole grain crystalline structures present in the sediment, releasing both the natural metallic elements and those resulting from anthropogenic activities. The element arsenic was identified through the atomic absorption spectrophotometry method (AAS) in the Geological Oceanography Laboratory (Laboratório de Oceanografia Geológica) of the Rio Grande Federal University Foundation (Fundação Universidade Federal de Rio Grande -FURG).

PHYSICAL FACTORS

Marone & Jamiyanaa (1997) classified the Paranguá Bay Estuarial Complex tide as micro-tide, predominantly semi-diurnal with diurnal differences, the mean amplitude being 1.4m neap tide and 1.7 spring tide. Knoppers et al., (1987) interpreted the E – W sector of the Paranaguá Bay Estuarial Complex as a partially mixed type 2 estuary, in the Stratification – Circulation diagram of Hansen & Rattray (1965).

According to Noernberg (2001) this sector suffers a greater fresh water inflow influence in its drainage basin compared to the N – S axis. The former presenting a quicker and more intense response to the water column stratification processes of the, saline intrusion, fluvial sediments supply and formation of a maximum turbidity zone (MTZ). This author mapped the maximum turbidity zone in this sector between the Gererês Islands and Paranaguá Harbor and he added; this zone is directly related to the estuarial body's geometry, the tide current flow intensity and the stratification of the water column.

RESULTS AND DISCUSSION

The As concentrations detected in the surface sediment samples varied between 7.9 and 30.9 ppm (Figure 4). Analyzing the As concentration distribution in the surface sediments from the estuarial complex E – W axis, a significant increase towards the town of Paranaguá was observed (Figure 5), demonstrating the maximum turbidity zone influence on this element's removal from the water column. A study conducted by Sá (2003) also found high concentrations at this same site for several other metallic elements (Table 1). This author also warned a potential source could exist in Paranaguá town as the arsenic concentrations are even higher around the city.

Another important aspect of this kind of system is the abundant fish diversity, which widens the metallic elements access routes from its water and sediments to the local urban population centers where the diet is based on seafood. These populations generally access a variety of food sources such as fish and some invertebrates: shellfish, mollusks - sururu (Mytella guyanensis), oysters in general, crabs and siris (Callinectes danae). Kolm *et*

Table 1

Station	Cd (ppm)	Pb (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Hg (ppm)
1	2.075	24.750	57.250	15.250	30.922	0.400
2	1.394	21.663	48.805	13.197	21.499	0.930
3	2.225	23.250	52.000	9.250	20.982	0.247
4	2.488	19.652	28.358	5.224	14.112	0.262
5	1.990	18.657	27.363	4.478	18780	0.094
6	2.498	25.475	48.202	15.734	19.986	0.091
7	2.714	19.173	34.114	5.976	7.900	0.076
8	2.545	19.212	44.162	10.978	19.795	0.299
9	2.679	21.825	29.018	5.456	9.006	0.047
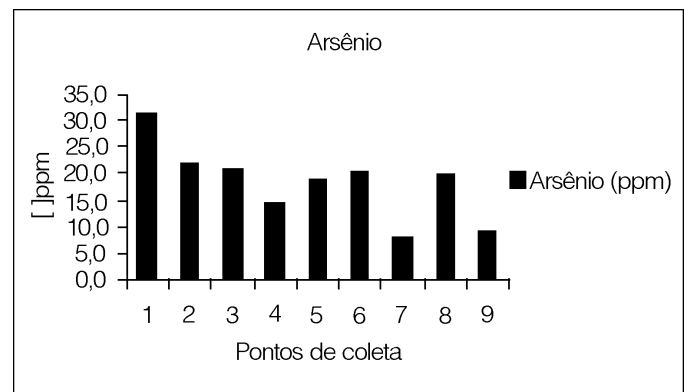
Figure 4 – AS Concentration in the field samples.

al. (2002) conducted analyses of metallic elements in the liver of Cathorops spixii (Ariidae), from Antonina Bay. The results showed Arsenic concentrations of up to 518.69 µg/kg, demonstrating bioaccumulation and biomagnification processes in this environment, suggesting a still unknown amount of this element exists in a bioavailable form.

Due to the incomplete range of geochemical information from the Paranaguá Bay estuarial complex region, studies continue to gather knowledge about the speciation of the different elements in the surface sediments, establishing reference levels (background) and actual concentrations in the water column. These studies will serve: i) future scientific research; ii) the management of dredging activities; iii) support decision making regarding issues such as the destination of dredged material and the main sources of these elements into the system.

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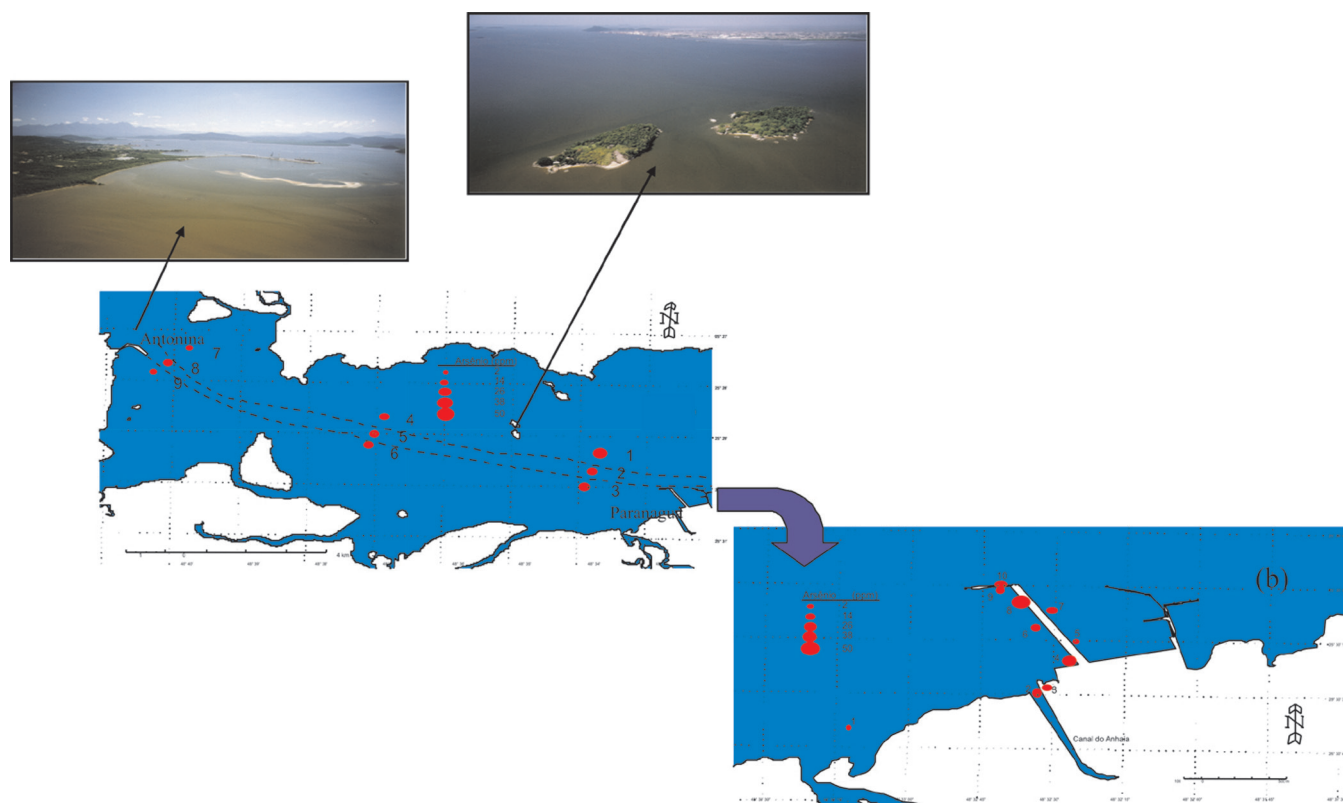
Figure 5 – Map of Arsenic concentrations in surface sediments with emphasis on the Harbor Terminal Ponta do
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HUMAN EXPOSITION TO ARSENIC IN THE MIDDLE RIBEIRA VALLEY, SÃO PAULO STATE BRAZIL

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INTRODUCTION

The hydrographic basin of the Ribeira do Iguape River extends from the Southeastern regions of São Paulo State (SP) to the East of Paraná State (PR). The region's mining and metallurgy activities had highly polluting processes and they contributed to the contamination of streams and soils surrounding a refinery situated in Adrianópolis town (PR).

The degree of arsenic exposure in children and adult residents in the Upper Ribeira Valley was evaluated by Sakuma (2004) in a previous epidemiological study. In that study, the investigated population included residents of the urban areas of Ribeira (SP), Adrianópolis (PR), and small rural villages, such as Vila Mota and Capelinha. These two villages are situated 500 and 1,000 meters from the former lead refinery (Adrianópolis), deactivated in 1995, and another, Bairro da Serra situated in the rural area of Iporanga (SP), was near the old Furnas mine. In both studies the population used as the non-exposed control reference group were from Cerro Azul (PR), a town situated upstream of the contaminated areas, away from the mining and refining areas.

In the Middle Valley, As rich rock and soils are found especially throughout the Piririca zone, situated between Iporanga and Eldorado towns. This zone has soil with up to 2,000 mg/kg As resulting from the weathering of rocks with auriferous veins containing sulfides and arsenopyrite (Toujague, 1999; Braga & Figueiredo, 2002). The level of habitation in those areas justified the work of the exposure assessments. The population of the Middle Ribeira Valley is mainly composed of slave descendents who worked in the mines until the end of the 19th century. They still maintain their ancient traditions based on the use of local natural resources, and subsistence farming practices.

Environmental exposure to high arsenic levels (trivalent and pentavalent inorganic forms) can cause vascular and skin diseases as well as lung, liver, bladder and skin cancer. The absorption of arsenic depends on several factors such as the nutritional state of the individual, the ingested dose and the exposure period time (Sakuma et al., 2003; ATSDR, 2000). The methylated arsenic compounds (organic forms) react less with the tissues and are excreted faster than the inorganic forms, therefore presenting a lower toxicity.

This study sought to evaluate the As degree of exposure of the Middle Ribeira Valley population, especially in the region influenced by the natural As anomaly (Piririca zone), by analyzing their urinary arsenic levels. The study also endeavored to identify the socio-demographic factors that influence the degree of exposure.

STUDY POPULATION

The Middle Valley studied population was made up of 378 children and adults from eight different places, grouped according to their respective geologic characteristics (inside or outside the Piririca zone – Figure 1).

Group 1 had 112 participants, resident from the urban area of Iporanga (SP), outside the Piririca zone, but likely to be influenced by the Furnas mining activities. Group 2 had 192 residents from the neighborhoods of Nhunguara and Castelhanos and the settlements of São Pedro, Galvão and Ivaporunduva, rural regions located within the extension of the Piririca zone. The residents from the Pilões and Maria Rosa settlements, situated in a more distant region, outside the Piririca zone, formed group 3 with 74 participants.

The control group (Cerro Azul) referred to in the results were obtained from the 156 inhabitants previously studied by Sakuma (2004).

Terms of consent, properly approved by the Ethics Committee of the Medical Sciences Faculty of UNICAMP, were read and individually signed by each participant or the participant's legal representative. Then a questionnaire was given to the participants to gather information about their socioeconomic conditions, food habits, occupational activities and hobbies.

MATERIAL AND METHODS

Between April 2003 and March 2004 first morning urine samples were collected in polyethylene flasks, previously decontaminated with nitric acid. They were maintained refrigerated and with no conserving additives until delivered to the laboratory.

The arsenic compounds were identified through HG-AAS. An atomic absorption spectrometer, Perkin-Elmer, Analyst 100 model, with hydride generator and flow injection system Perkin-Elmer, FIAS 400 model, was used. The analytical method describe by Guo et al. (1997) was applied. It is based on the complexity of the toxicologically important arsenic compounds: As(III) + As(V) + monomethylarsenic acid (MMA) + Dimethylarsenic Acid (DMA) with cysteine. The analytical method was previously validated, using certified reference material (NIST 2670), with a certified value of 60 µg L^{-1}. The method quantification limit was 0.4 µgL^{-1} in the five times diluted samples, corresponding to 2.0 µg L^{-1} As in the sample.

The statistical analyses were made with the SPSS 10.0 program for windows (Statistical Package for Social Science). For the arsenic in urine results (As-u) below the detection limit (LD), the value of 1.0 µg L^{-1} was attributed, which corresponds to half the analytical method's detection limit. No adjustment was made regarding urinary creatinine.

RESULTS

The Box plot of the results of As-u median concentration (µg L^{-1}) in the control population (Cerro Azul) compared to the groups 1, 2 and 3 are shown in Figure 2.

The descriptive analysis of As-u concentration for each of the studied groups are presented in Table 1.

The urinary arsenic median concentrations for groups 1 (8.07 µg L^{-1}) and 2 (11.04 µg L^{-1}) were statistically different when compared to the control group (3.86 µg L^{-1}) (r < 0.0001). On the other hand the median

Figure 1 – Location of the Ribeira Valley and Piririca zone.

concentration of group 3 (3.62 µg L^{-1}), outside the Piririca zone, was not statistically different from the control group median (r=0.92). It is clear the As exposure is greater in the population resident in the Piririca zone area, where there is a natural presence of As.

Comparing the As-u medians between children and adults, in the three groups there is an absence of significant differences, showing the following results: r=0.707; r=0.544 and r=0.811, for groups 1, 2 and 3, respectively.

Of the total analyzed samples, 11.6%, 10.4% and 39.2% of the individuals, respectively in groups 1, 2 and 3, presented As concentrations lower than the detection limit of the study (2.00 µg L^{-1}). Whereas, the control
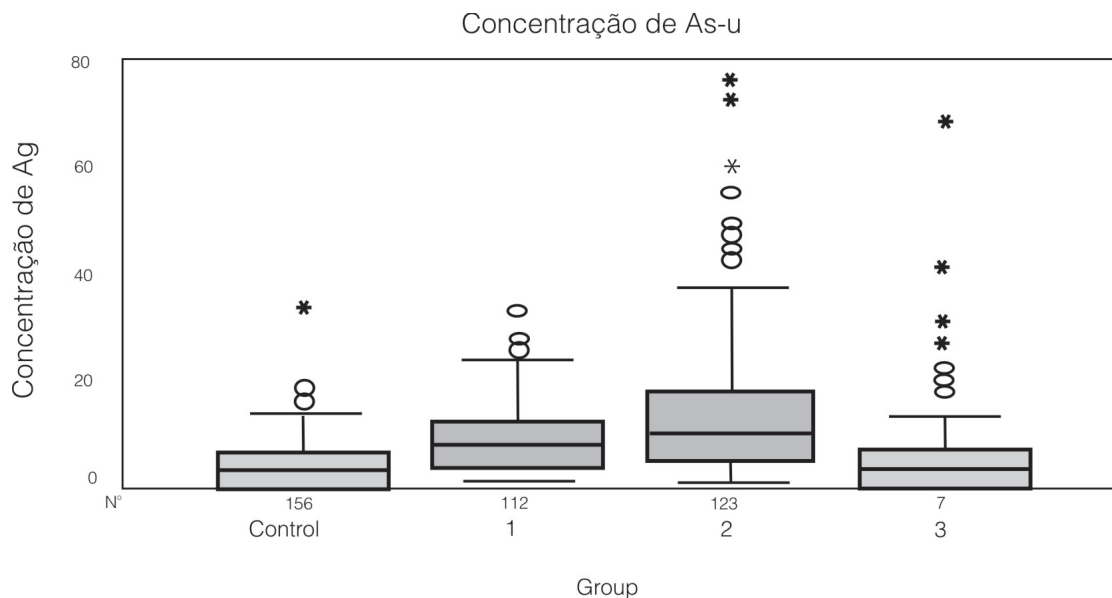
Figure 2 – Box Plots of As-u(µg.L^{-1}) from the population of Cerro Azul and group 1, 2 and 3 population.

Table 1 - Urinary As concentrations in the target population

Group	Location	Age	N	As-Urine (µg.L-1)			N(%) > 40 µg.L	N(%) < LD
				median	minimum	maximum		
Controle	Ribeira de Iguape River spring	children*	73	3.60	1.00	34.12	0 (0%)	
	Cerro Azul – PR (pop. control)	adults	83	3.87	1.00	16.00	0 (0%)	
		total	156	3.86	1.00	34.12	0 (0%)	51 (32.9%)
1	Iporanga (urban area)	children	82	8.35	1.00	33.49	0 (0%)	
	outside Piririca zone	adults	29	7.42	1.00	27.55	0 (0%)	
		total	111	8.07	1.00	33.49	0 (0%)	13 (11.6%)
2	Piririca zone	children	67	9.85	1.00	55.69	3 (4.5%)	
	Nhunguara, Castelhanos, Galvão,	adults	123	11.68	1.00	76.19	7 (5.7%)	
	São Pedro, Ivaporunduva	total	190	11.04	1.00	76.19	10 (5.3%)	20 (10.4%)
3	outside Piririca zone	children	28	3.64	1.00	31.28	0 (0%)	
	Pilões, Maria Rosa	adults	46	3.11	1.00	68.92	2 (4.3%)	
		total	74	3.62	1.00	68.92	2 (2.7%)	29 (39.2%)
Total	Middle Valley	children	177	7.99	1.00	55.69	3 (0.8%)	
		adults	198	9.09	1.00	76.19	9 (2.4%)	
		total	375 *	8.21	1.00	76.19	11 (2.9%)	62 (16.4%)

* 7 to 14 years   ** Detection limits (2,00 µg.L-1)

group (Cerro Azul) presented 32.9% cases below the detection limit.

There was no statistically significant difference between the medians related to gender among both children and adults.

In this study, other variables that could influence the levels of urinary arsenic were evaluated, such as: the consumption of milk, meat, chicken, fish, vegetables and fruit locally produced, besides the water consumption (White & Sabbioni, 1998), since the nutritional state influences directly the absorption of arsenic (Mandal et al., 1998). Residents were asked about their weekly intake of meat, chicken, fish, milk, fruit and vegetables cultivated in their own backyards. For statistical evaluation of the consumption of meat and chicken, the population was divided into: "consumes once a week or less" and "more than once a week". With respect to the other types of food, a qualitative evaluation was made with the options "consumes" or "does not consume".

Considering only the child population, those with the habit of playing in contact with the soil did not present an As-u median statistically different from those who do not.

Table 2 shows that there is no significant difference between the As-u medians of those who consume fish, meat or chicken at least once a week and those who don't. However, people from groups 1 and 3 who do not consume milk and dairy products have higher As-u median concentrations.

Using the multiple logistic regression model, the variables which together best explain the As-u concentrations were: living location (variable "population group"), number of times meat is consumed per week, and number of times fruit and vegetables are consumed per week (r < 0.10) (Table 3).

DISCUSSION

The value of 40 µg L^{-1} for As-u is considered critical for long term exposure, since adverse effects to health may occur above this limit (Trepka, 1996). The mean As-u value obtained by Matschullat et al. (2000) was of 27.7 ± 19.2 µg L^{-1} in the Nova Lima and Santa Bárbara mining region, Southeast Minas Gerais State. They noted 19.2% of the children presented levels above 40 µg L^{-1}. The per-

Table 2 - Median As-u Concentrations according to food consumption among children and adults within three Middle Valley groups

Group	P Values								
	Meat Consumption (more than once a week)			Chicken consumption (more than once a week)			Milk and dairy products consumption		
	Adults	Children	Total	Adults	Children	Total	Adults	Children	Total
1	1.000	0.117	0.141	–	0.964	1.000	0.054	0.223	0.027
2	0.914	1.000	0.953	1.000	0.24	0.612	0.838	0.723	0.856
3	0.549	0.678	1.000	0.749	0.678	0.445	0.412	0.041	0.027

Table 3 - Multiple logistic regression analysis with the influence variables regarding selected population from the Middle Valley (Final Model As > 3,86 µg.L^{-1} [median de As-u from the control group])

Multiple logistic regression (As > 3,86 µg.L-1 / control Group)		β	ρ	Chance Rate (CR)		
Variable				Estimative	ICI (95%)	ICS (95%)
Constant		0.728	0.040	2.071		
Meat	Weekly meat consumption	-0.181	0.024	0.835	0.714	0.976
Vegetable and Fruits	Weekly consumption of vegetables and fruits home cultivated	-0.130	0.042	0.878	0.774	0.995
Place of living	Group 3 (Pilões; Maria Rosa)		0.000			
	Group 1 (Iporanga , área urbana)	1.417	0.000	4.126	1.903	8.945
	Group 2 (Nhunguara; Castelhanos; São Pedro; Galvão; Ivaporunduva)	1.596	0.000	4.934	2.680	9.082

centage in this study was equal to 0%, 5.2% and 2.7%, respectively, in groups 1, 2 and 3. The control group did not present results above this limit.

In Sakuma's research (2004), children living near the Furnas mine (neighborhood of Iporanga Ridge), presented the As-u median of 8.94 µg L^{-1} (interval of 1.00 – 63.0), whereas children living near the lead refinery that processed arsenic containing ore, presented a median of 6.40 µg L^{-1} (interval of 1.00 – 50.0).

The studied populations of group 1 (Iporanga, urban zone, outside the Piririca zone, but likely to be environmentally influenced by the Furnas mine proximity) and group 2 (inhabiting the Piririca zone), presented 4.126 and 4.934 times more chance (CR) of presenting arsenic concentrations superior to 3.86 µg L^{-1} (control population As-u median), respectively, compared to group 3 (living outside the Piririca zone).

The main non-occupational arsenic exposure path is through ingesting water or food. The total daily As intake depends on dietary habits. Takamori & Figueiredo (2002), evaluated the Piririca zone surface water, analyzed in five campaigns between 2001 - 2003. No sample presented As concentrations exceeding 10 mg L^{-1}. Groundwater consumption by local populations from tubular wells indicated similar low concentrations.

This study investigated the probable As food sources, and found the increase of a single unit in the weekly intake of meat, fruit and vegetables avoids As concentrations in urine higher than 3.86 µg L^{-1}.

In the Middle Ribeira Valley, the natural presence of arsenic in the Piririca zone rocks and soils, is the probable source of the As-u concentrations found in the local inhabitants. However, the magnitude of the urinary concentrations found (medians of 8.07 µg L^{-1} in Iporanga – urban zone, and 11.04 µg L^{-1} in the Piririca zone inhabitants) do not indicate an elevated risk to human health. The results, however, warn the need to seek solutions for the region's economic development, preserving the natural land cover to avoid deforestation and erosion, risking exposure of the naturally rich arsenic soil.

ACKNOWLEDGMENTS

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LEAD AND ARSENIC IN SEDIMENTS OF THE RIBEIRA DE IGUAPE RIVER, SP/PR

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INTRODUCTION

The Ribeira do Iguape River hydrographic basin has an area of about 28,000 km^2 and is situated in the Northeast of Paraná State and Southeast of São Paulo State (Figure 1). It has more than two million hectares of forest, roughly 21% of the Atlantic Forest (Mata Atlântica) remnants in the country. The Ribeira River is 470 km long, of which 120 km is in Paraná and 350 km in São Paulo.

The Upper Ribeira Valley saw intense mining activity during decades, directed at lead, zinc and silver production. In 1996 the last mines were closed down, leaving damage to the vegetation and the landscape, especially from the open pit mines. With the ore processing (Rocha and Panelas Mines) and metal refining, tailings of waste were produced that are still exposed and subject to periodic flooding. On the Ribeira River right margin, in Adrianópolis, residents continue to be exposed to lead intoxication, even after the lead plant's shutdown. In the Furnas Mine region, studies carried out in 2003, with fish from the Furnas stream, showed that two species of sheatfish and catfish were contaminated with lead. These bottom fish species search for food in the clayish sediments where the lead fraction is more concentrated

and therefore suffer a serious impact. In the Furnas Mine, the lead is associated with arsenic. In fact, the arsenic begins to present anomalous concentrations from the Betari River onwards, a tributary on the Ribeira River left margin, where the former Furnas mining fronts are situated. A little further downstream, in the Castelhanos and Nhunguara neighborhoods and especially in the São Pedro and Ivaporunduva rural settlement areas, on the floodplains of their designated rivers (Ribeira River left margin), there were ancient gold mineralization sites (known since the Portuguese colonization) associated with arsenopyrite. This region, where the predominant lithology is metapelites intercalated with metabasic/ultrabasic rocks, is geologically known as the Piririca zone. All these facts motivated the UNICAMP Geosciences Institute together with the Brazilian Geological Survey (Serviço Geológico do Brasil – CPRM/SP), the Adolfo Lutz Institute, the UNICAMP Medical Science Faculty and the Londrina State University to elaborate and execute this study, financially sponsored by the São Paulo State Research Foundation - FAPESP. The study seeks to assess the impact of arsenic and lead on the health of local inhabitants and the environment. The Low Density Multi-elemental Geochemical Mapping was accomplished
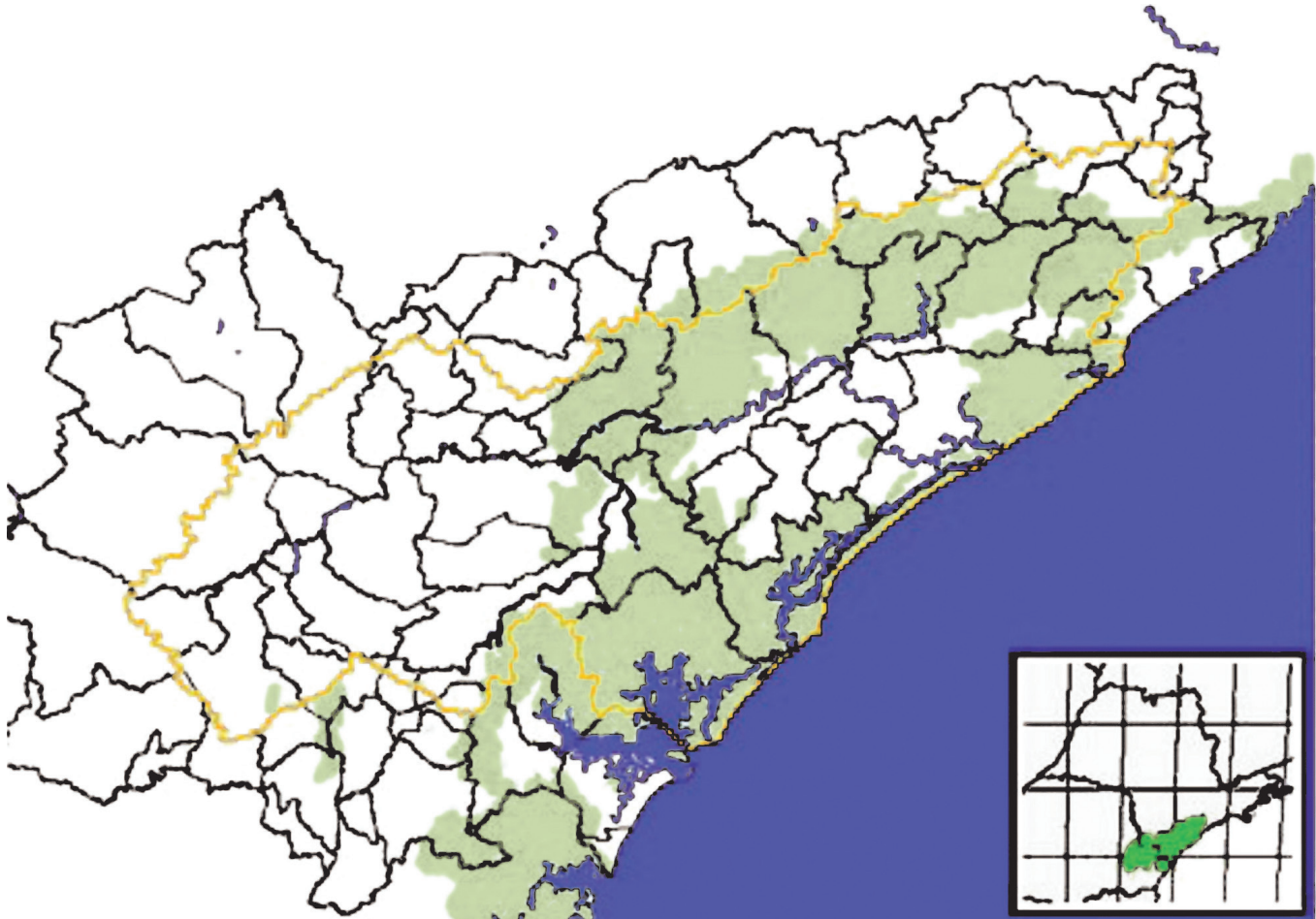
Figure 1 – Location of the Ribeira do Iguape River Basin showing administrative limits, the Basin contour and Atlantic Forest remnants.

using stream bottom sediment samples of the Ribeira Basin to observe how these elements are distributed or, in other words, to discover its geochemical landscapes.

MATERIALS AND METHODS

The geochemical mapping was based on 187 stream sediment samples from all over the Ribeira do Iguape River Basin. An additional 25 "overbank" samples were collected to observe the paleo-landscapes and compare them with those of today. The samples were gathered during the dry season to obtain the most representative material of the basin upstream, avoiding lateral contributions that always occur during torrential rain periods. Before each sample was extracted, fluvial water physical-chemical parameters were measured with appropriate equipment: pH, Eh, DO (dissolved oxygen), conductivity, turbidity and temperature. The "overbank" samples were taken from the first 30 cm of top soil of paleo alluvial cover.

In the IG-UNICAMP laboratories these sediment samples were dried, sieved and analyzed through fluo-rescence X-ray, in the fractions smaller than 180μm (80#) and 63μm (230#), for 10 oxides (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, P_2O_5) and 21 trace-elements (As, Ba, Co, Cr, Cu, Ga, Mo, Nb, Ni, Pb, S, Sb, Sn, Sr, Th, U, V, Y, Zn, Zr). Stream sediment geochemical mappings for As in Brazil, like other countries, usually the fractions smaller than 180mm are analyzed. However, considering that in many Medical Geology/Environmental Geochemistry studies it is very common to analyze fractions smaller than 63mm, in this study both granulometric fractions were analyzed. In due course it was confirmed that the responses of both fractions, with regards to geochemical anomalies identification, are very similar. All the results are gathered in the Geochemical Atlas of the Ribeira Valley (2005).

ARSENIC

Arsenic (As) can occur in four oxidation states: arsenate (+5), arsenite (+3), arsine (-3) and the metal (0). The soluble species are, generally, in the oxidation states +3 and +5. It rarely occurs in the free form and it is usu-

ally bound to sulfur, oxygen and iron (sulfides). The As compounds present different toxicities depending on the chemical form. Thus, the As(III) species are ten times more toxic than As(V). In environmental and biological monitoring it is important to know which chemical species are present, and therefore, the geochemical speciation tests with arsenic are fundamental.

Arsenic has an average mobility, a little higher than lead, both in acid and alkaline environments, which explains its proximity to its source, as observed in the geochemical maps (Figures 2 and 3). The main host of gold is arsenopyrite, but as the gold exploration here was not intense, on the contrary to lead, there was no As pollution due to this activity along the Ribeira River.

On the maps, the sub-basin sediments enriched and very enriched with As (Figures 2 and 3) accurately reflect the influence areas of the ancient lead mines strongly associated with arsenic (Rocha, Panelas, Laranjal and Furnas Mines). They also reveal the zones with gold mineralization associated with arsenic, zinc and copper sulfides (Piririca zone-São Pedro, focused on the Ivaporunduva River, represented by the sub-basin sampling point 132 and the headwaters of the Pedro Cubas River, upstream of the sampling site 140). The sub-basins, which contain the Ribeira River whose sediments are enriched with As in the Piririca zone, reflect a geochemical dispersion effect of those mineralized zones, as well as the presence of mineralized veins that intersect the Ribeira River in the Castelhanos neighborhood. The values found in stream sediments are always lower that those found in the soils that originated the geochemical anomalies. According to the D.D. nº 195-2005 of 11.23.2005 from CETESB, the As intervention value (above which there are direct or indirect potential risks to human health, considering a generic exposure setting) for agricultural soils is 35 ppm and 55 ppm for residential soils.

During the multidisciplinary project, the populations exposed to those arsenic geochemical anomalies were studied through urinary arsenic analysis of adults and children. Although surface water monitoring has shown an As enrichment in the rivers that drain the mineralized zones, its concentrations are inferior to the limit of 10 g/L established by the National Environmental Council (Conselho Nacional de Meio Ambiente- CONAMA) and by the WHO (World Health Organization).

LEAD

Lead is a naturally occurring element, relatively abundant on the Earth's crust, almost always as lead sulfide (galena), generally associated with other elements such as zinc, copper, cadmium, silver and gold. In contaminated aquatic systems, most of the metal is strongly fixed to bottom sediments. In aquatic organisms, the lead accumulation in sediments is influenced by sev-

eral environmental factors such as temperature, pH, Eh, salinity, in addition to the humic acids content. As a salt, lead presents high toxicity for aquatic invertebrates, in concentrations above 0.1 mg/L for fresh water organisms and 2.5 mg/L for sea organisms. High metal levels in soil can lead to its capture by plants and lixiviation to surface and groundwater. In São Paulo State, the CETESB established reference values for soil and groundwater (D.D. nº 195-2005-E of 11.23.2005). For lead in agricultural soil, the intervention value is 180 ppm and for residential soils 300 ppm. Considering the high geochemical anomalies in the Ribeira Valley stream sediments, and that these concentrations are considerable diluted compared to the corresponding soil anomalies, therefore, there is a constant exposure risk to lead toxicity by the various valley settlements.

Lead exploration in the Ribeira Valley, until the mid-nineties, is well portrayed on the geochemical lead maps (Figures 4 and 5). The ore wastes thrown into the drainages and stocked on their margins, associated with steep topography and frequent torrential rains, were responsible for the enrichment of the Ribeira River sediments from the Rocha Mine in Paraná State until its mouth in the Iguape-Cananéia estuarial complex on the South coast of São Paulo.

The Panelas Mine, which belonged to the Plumbum Company, in Adrianópolis –Paraná State, may be considered principally responsible for the lead concentrations on the Ribeira River bed. That company, situated on the river's right margin, processed the ore (predominantly galena) and, in addition to dumping residues and effluents directly into the river, piled up waste and refining residues on it's margins, as observed until recently. Part of the contaminated material has also reached the streets and yards of the workers settlements (Mota and Capelinha Neighborhoods) adjacent to the mine. Previous studies developed in that region, with 7 to 14 year-old children, showed mean concentrations of 11.89 g/dL Pb in their blood (health control agencies stipulate a maximum value is 10 g/dL), reaching 37.8 g/dL in some of them.

Lead is an element that has low mobility in any environment (oxidant, reducing, acid and alkaline) and co-precipitates easily with Fe-Mn oxides; therefore the stream sediments quickly lose Pb content from an occurrence or a mineral deposit. The SGB/CPRM developed gold research during many years in the Piririca zone-São Pedro and finally discovered a gold deposit associated with arsenic, lead, zinc and copper sulfides. This deposit is situated at the watershed of the São Pedro River (Figures 4 and 5 - a drainage on the Pilões River left margin, a little upstream from sampling point 133, close to the Pilões River mouth with the Ribeira River) and the Ivaporunduva River (sub-basin of the point 132). Here

Figure 2 – *Arsenic geochemical pattern in fractions < 180µm. The blue sub-basin area presented samples with values < 2,3ppm; green between 2,3 and 11,9ppm and the regional background samples presented values; orange, between 12 and 34ppm and red values > 34ppm.*

Arsênio - As
Fração < 63 micras (230 #)

Bacias Empobrecidas (< 3 ppm)
Bacias com Valóres de Background (3 a 12,3 ppm)
Bacias Enriquecidas (12,4 a 29,6 ppm)
Bacias Muito Enriquecidas (> 29,7 ppm)

Valor Médio = 6,8 ppm

Figure 3 – Arsenic geochemical pattern in fractions < 63µm. The blue sub-basin area presented samples with values < 3ppm; green between 3 and 12,3ppm and the regional background samples presented values; orange between 12,4 and 29,6ppm and red values > 29,7ppm.

Figure 4 – Lead geochemical pattern in fractions < 180µm. The blue sub-basin area resented samples with values < 14ppm; green between 14 and 36,9ppm, and the regional back-ground samples presented values; orange between 37 and 124ppm and red values > 124ppm.

Chumbo - Pb
ção < 63 micras (230 #)

Bacias Empobrecidas (<18 ppm)
Bacias com Valôres de Background (18 a 49,9 ppm)
Bacias Enriquecidas (50 a 123 ppm)
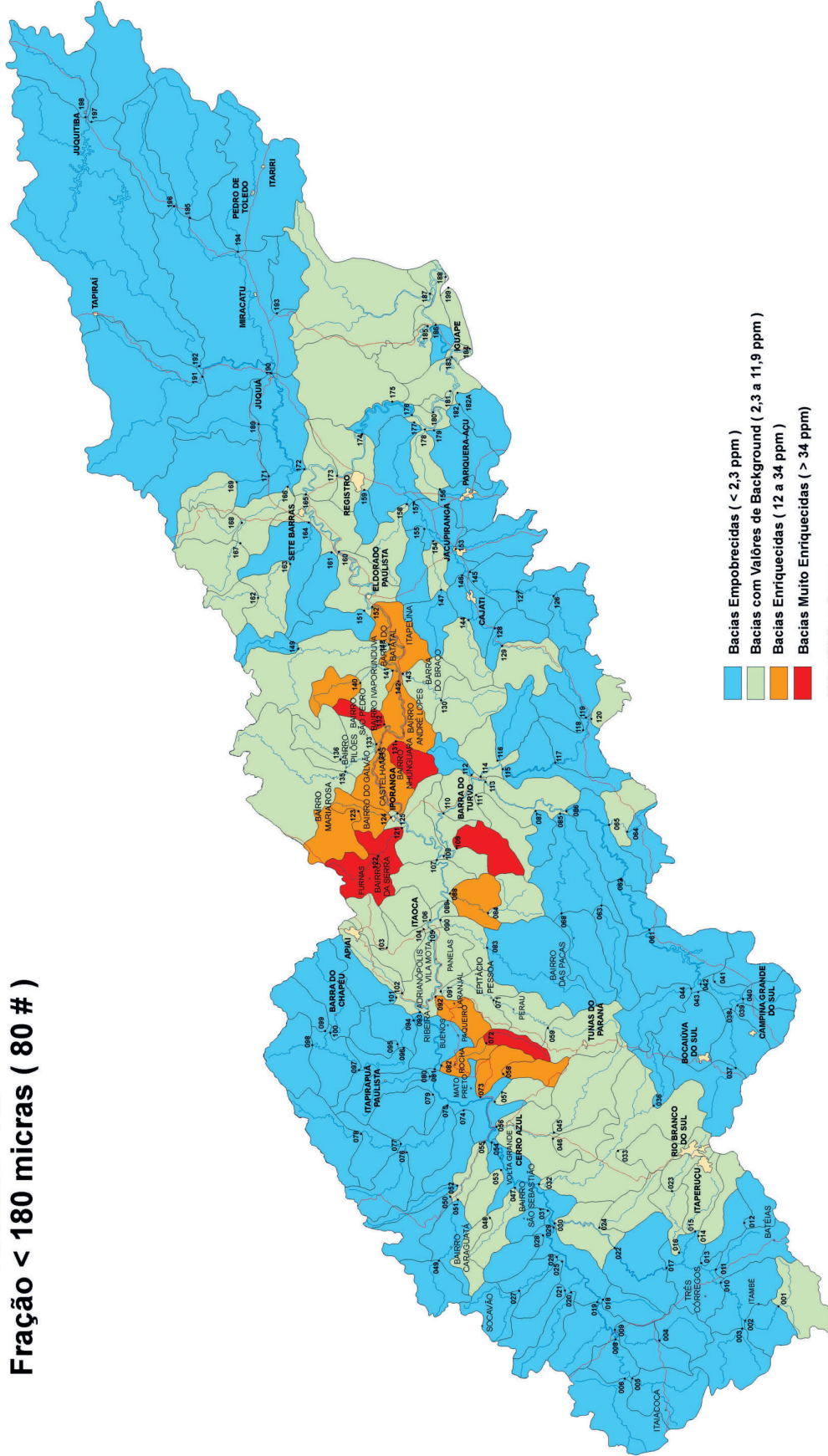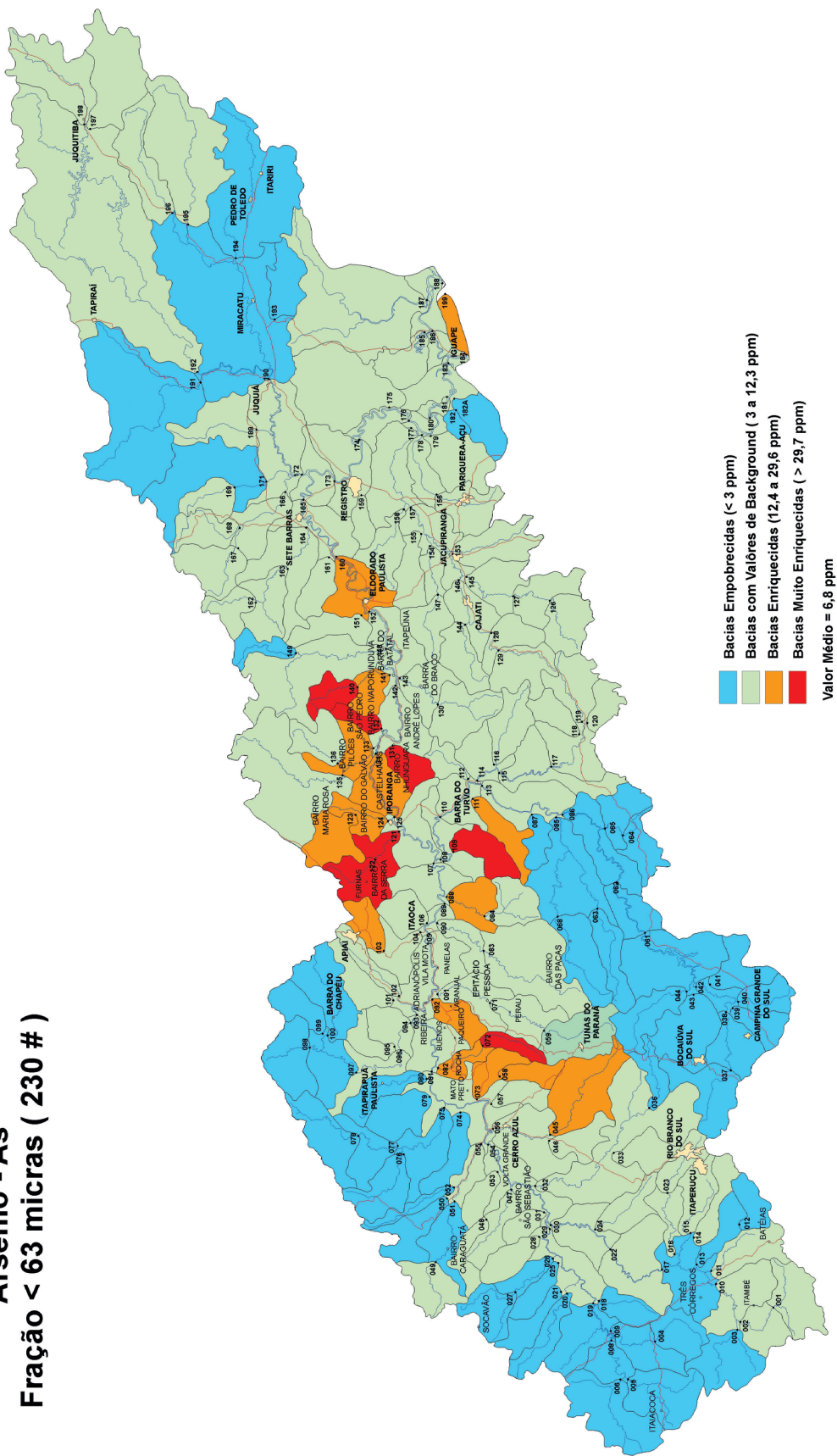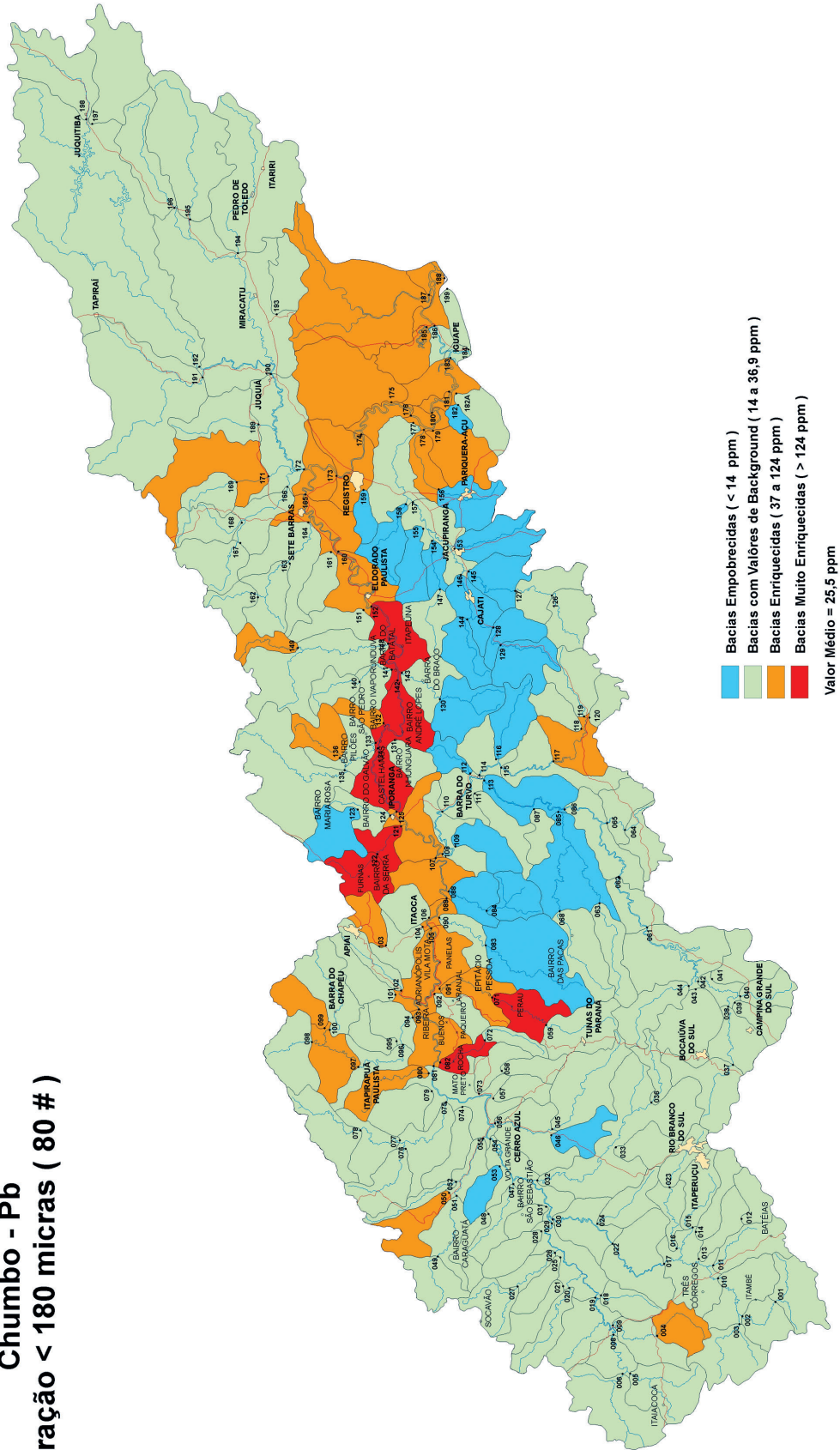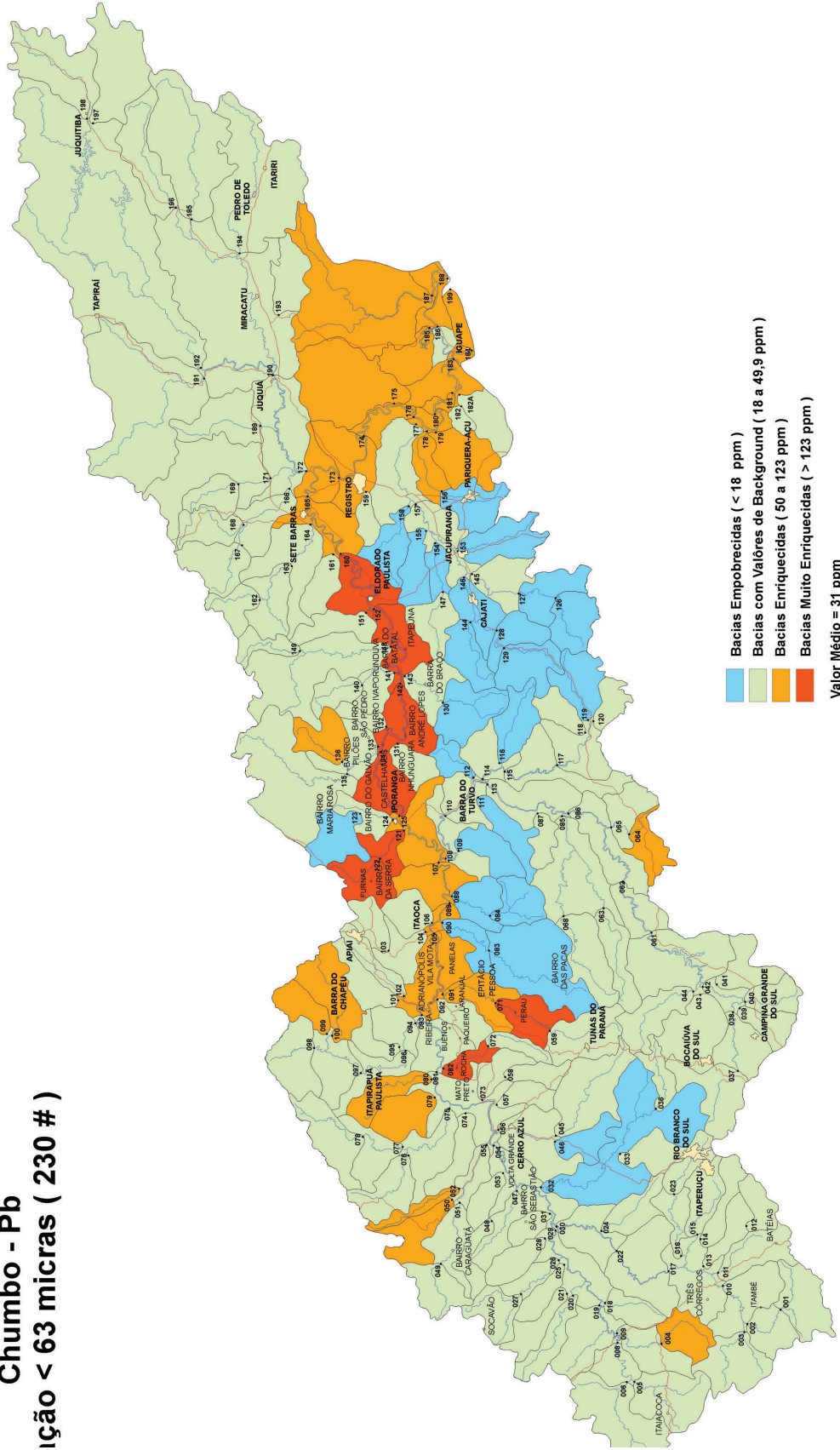Bacias Muito Enriquecidas (>123 ppm)

Valor Médio = 31 ppm

Figure 5 – Lead geochemical pattern in fractions < 63μm. The blue sub-basin area presented sample with values < 18ppm; green between 18 and 49,9ppm and the regional back-ground samples presented values; orange between 50 and 123ppm and red values > 123ppm.

the lead anomalies in the soil exceeded values of 500 ppm, whereas in the stream sediments sampling points, close-by, they were not anomalous (point 133) or did not exceed 124 ppm (point 132).

Thus, the difference between the lead ionic dispersion in the Piririca zone-São Pedro and the predominantly clastic dispersion (ore and slag particulate) in the Ribeira River bed stands out as being the only source of the sediments anomalous values hundreds of kilometers downstream from the last lead source. This is even with the daily removal of tens of tons of civil construction sand from the Ribeira River channel near the town of Registro.

Lead was not found in the Ribeira River water or its main tributaries between Iporanga and Eldorado cities, confirmed by the monitoring during the project, and thus presenting no risks to health and the environment. However, the same does not apply to the Ribeira River bed sediments and all its tributaries that have lead mines in their catchments. In a study of fish from Furnas Creek, sampled between 1998 and 2000 by a team from Chalmers Technology University of Göteborg, Sweden, two species of catfish and sheatfish were found, that presented 50% less enzyme ALAD activity, compared to those of the same species from non-contaminated rivers. (This enzyme is related to red blood cells synthesis and normally used as an environmental lead presence indicator.) These bottom fish species are affected by pollution because they take their food from the clayish sediments where lead is highly concentrated. High concentrations of Pb were observed in these fish tissues, as well as a lower relation length/weight, low reproductive capacity and consequently a smaller number of fish (75% less) per area compared to other non-contaminated creeks of similar size in the region.

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ENVIRONMENTAL AND HUMAN HEALTH DIAGNOSIS: LEAD CONTAMINATION IN ADRIANÓPOLIS, PARANÁ STATE BRAZIL

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INTRODUCTION

During many decades the Upper Ribeira Valley had been under the influence of lead mining activities and a refining and processing plant for the ore produced in the region's Plumbum Company mines. All operations ceased in 1996, leaving the Ribeira River margins heaped with waste and slag residues from the refinery's activities. During the 50 years of Plumbum operations, a great amount of lead enriched particulate material was released into the atmosphere which became deposited on the surrounding soil surface. The local population also used these residue materials for street paving in Mota and Capelinha neighborhoods, rural areas of Adrianópolis, near Plumbum, in Paraná State.

Between 1999 and 2001 an environmental assessment associated with a human monitoring program was developed in the Upper Ribeira Valley region with residents in areas close to the mines and to the Plumbum plant: Ribeira and Iporanga (Serra neighborhood) in São Paulo State and Adrianópolis (Mota, Capelinha and Porto Novo neighborhoods), in Paraná State. The assessment also included the Cerro Azul population situated upstream of the mining area, in Paraná. It sought to investigate if environmental contamination caused by the lead mining activities was impacting the populations living in the Upper Ribeira Valley.

PHYSIOGRAPHIC ASPECTS

The studied area is situated in the Ribeira Valley, in the South of São Paulo State and the East of Paraná State, delimited by the coordinates latitudes

25º00' - 25º30' South and longitudes 48º30' - 49º30' West (Figure 1).

The Ribeira do Iguape River hydrographic basin consists of the areas (about 25,000 km²), drained by the Ribeira River and its main tributaries, 61% in São Paulo State. On its initial course the Ribeira river stretches 120km across Paraná State, acting as a border between the two states for about 90km. After being joined by the Pardo River, it extends for a further 260km in São Paulo State until reaching its mouth in the important Iguape-Cananéia estuarine-lagoon complex on the South coast of São Paulo.

The region's climate is humid subtropical. The mean annual temperatures oscillate around 20ºC. On the coastal area, December, January and February are the hottest months with average temperatures of 25ºC, and May through August the coldest with average temperatures of 18ºC. In June and July minimum daily temperatures of 0ºC are common, frost occurring quite frequently. The average annual rainfall is around 1,500 and 2,500 mm. The coastal and mountain areas receive more of the rain. The heaviest daily rainfalls occur between October and March. According to the National Meteorological Institute-Instituto Nacional de Meteorologia, the predominant winds in the Upper Valley area are West-Southwest (WSW).

The high regional rainfall contributes to the exuberance of the Sub-deciduous Tropical Forest that still covers vast extents of the region and that are preserved as primitive forests. These areas constitute reserves and state parks. The secondary forests already occupy a much larger area than the primary ones and they are spreading even further due to the parks' insufficient delimitation and control. Completing the vegetation cover pattern, about 30% of the region is occupied by banana and tea plantations, shrubs and pastures.

SOCIO-ECONOMIC ASPECTS

In the past the Ribeira do Iguape Valley was one of the largest lead metallogenetic provinces in Brazil and had the Plumbum refining plant, as a parallel activity to mining. It was installed at the entrance to the Panelas de Brejaúva Mine, in Vila Mota neighborhood, in Adrianópolis and used to process the ore produced in the whole region. Mineral production in the Ribeira Valley today is reduced to non-metal exploration such as limestone, clay, ornamental rocks and fluorite.

The mining activities represented a temporary prosperity period for the Upper Ribeira Valley region and its decline lead to a significant fall of income and employ-
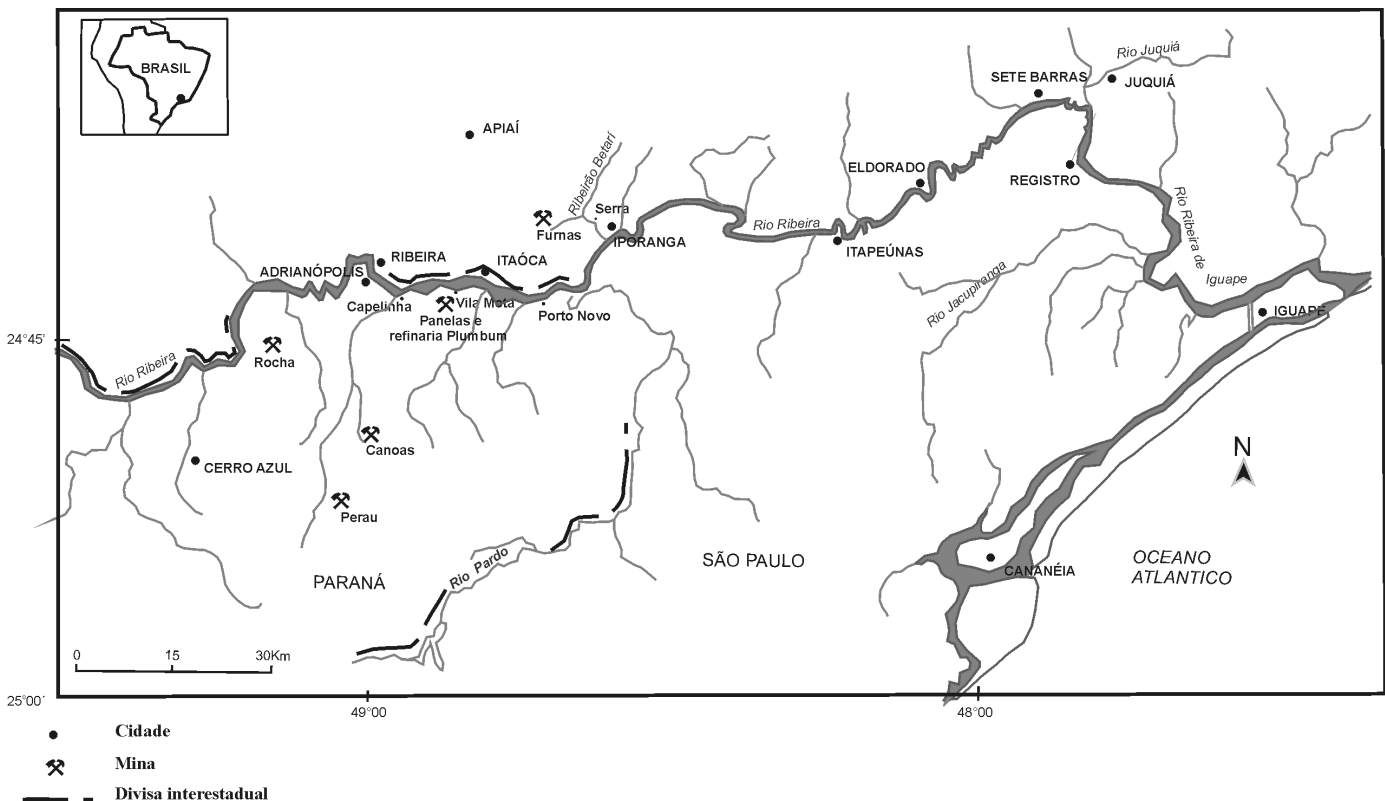

Figure 1 – Location of the Ribeira Valley.

ment levels for the local population. The human development indexes (IDH-M) of these cities, according to PNUD, are the lowest in the Ribeira Valley and far inferior to the São Paulo and Paraná States' means. The different social indicators, such as income level, employment, industrial investments, education, infant mortality and public health converge characterize the Ribeira Valley as relatively poor, though some areas, more oriented to the banana culture, trade and tourism, present a greater economic dynamism.

GEOLOGY

The Ribeira Valley region, from the geotectonic point of view, is inserted in the Ribeira Fold Belt Zone, characterized by a large number of longitudinal sub-vertical faults representing shear zones. These shear zones affect both the basement rocks and the metasedimentary sequences that define a corridor about 100km wide and 1,000km long, denominated Apiaí-São Roque Fold Belt Zone. It is NE-SW oriented, characterized by intercalation of low to medium degree metamorphic sets, granite complexes and gneiss-granite and/or gneiss-migmatitic/granulitic complexes (Daitx, 1996; Dardenne & Schobbenhaus, 2001).

The Archean gneisses and migmatites, which were described as the basement (crystalline complex) for the supracrustal sequences belonging to the Açungui Group (deposited in the medium-superior Proterozoic), predominate regionally. The Açungui Group is subdivided in the Setuva (basal), Capiru, Itaiacoca, Votuverava and Água Clara Formations, Lageado Subgroup, Perau Complex and the Turvo-Cajati Sequence. The lithostratigraphic units (carbonates) showing (Pb-Zn) mineralization are in the Perau Complex and in the Lageado Subgroup.

LEAD: HUMAN CONTAMINATION

Both children and adults are susceptible to ill-health effects due to lead exposure. However, the exposure path and the effects can be very different. Children are more exposed in regions presenting environmental contamination due to their behavior and physiology, whereas adults are more exposed in their working activities, as in industries and refineries.

The lead absorbed through the gastrointestinal tract in older children and adults comes mainly from the ingestion of food and water, whereas in younger children it comes from the inhalation of dust and ingestion of small soil particles (WHO, 1995).

Children are considered a high risk group since they absorb and retain a greater quantity of the ingested lead than adults.

The CDC (1991) recommended, as a maximum limit, 10mg Lead/dL blood in children to define a high lead dose exposure risk and consequent long term adverse effects.

Chronic exposure to levels above this value can lead to damaging effects to health irreversibly compromising the central nervous system and also causing anemia, renal and vitamin D metabolism alterations.

Adults with contents between 40 and 60 g/dL Lead in the blood may present neurobehavioral symptoms such as humor disorders and peripheral neuropathies as well as general symptoms such as fatigue, somnolence, irritability, dizziness, muscular pains and gastrointestinal problems. Levels above 60 g/dL can produce significant symptoms of mental and neurological alterations in addition to typical abdominal cramps.

POPULATION AND METHODS

To put into practice the human monitoring program, the project had to be submitted to the Ethics Committee of the UNICAMP Medical Sciences Faculty, followed by meetings with city representatives and health secretaries involved in the study. Subsequently, school headmasters, teachers, parents and those responsible for public school children received explanations about the goals of the assessment and request their authorization for the voluntary participation.

Blood samples of 335 children between 7 and 14 years old and 350 adults between 15 and 70 years old were collected in Ribeira and Iporanga cities in São Paulo State and Adrianópolis (Capelinha, Vila Mota and Porto Novo) and Cerro Azul in Paraná State.

At the time of the blood sampling, questionnaires were applied for information about food habits, health, parents' occupation, time of residence, among other questions, necessary for the final data interpretation.

The lead in the blood samples was analyzed through atomic absorption spectrophotometry coupled to a graphite oven, in the Adolfo Lutz Institute, in São Paulo.

To address the environmental contamination, 13 samples of domestic tap water used for consumption were collected from some residences situated within the studied area. In addition to those, 21 surface soil samples (0-20cm depth) at a distance of up to 9.5km from Plumbum, including 4 samples of domestic vegetable garden soil, were collected as well as samples of the waste piles and slag.

The water consumed by the population living in the urban area of Adrianópolis and Cerro Azul is supplied by the Paraná State Water Services Company-Companhia de Saneamento do Paraná (SANEPAR), and in the urban area of Ribeira and Iporanga by the Water Company of São Paulo-Companhia de Saneamento Básico do Estado de São Paulo (SABESP). The residences of the rural area of Vila Mota, Capelinha and Porto Novo do not belong to the treated water network instead they take water from springs and directly from the Ribeira River.

The selection of the residences was based on random assignments, but at least one sample was collected in each studied area and from different sources used by the population.

The water samples were filtered in 0.45m cellulose acetate membranes and stored in sterilized 50ml centrifuge type polyethylene tubes and soon after acidified with 1ml nitric acid 1:1, maintaining the pH 2, to preserve the sample until analyzed.

For the analysis of lead concentrations in soils, the granulometric fraction smaller than 177μm (fine sand to very fine clay) was used, considering that the soil contamination by this metal through atmospheric sources (refinery emissions) tends to disperse as fine particles. It is in this finer fraction that lead tends to accumulate.

Lead contents in water, soils and waste samples were analyzed through atomic absorption spectrometry with plasma source (ICP/AES), in the Mineral Analysis Laboratory-Laboratório de Análises Minerais (LAMIN), of SGB, in Rio de Janeiro.

RESULTS

Human contamination

Children

The lead content arithmetic mean in the blood samThe lead content arithmetic mean in the children's blood samples (PbS) was 7.40 g/dL, varying between concentrations lower than 1.8 g/dL and 37.8 g/dL. Figure 2 shows the lead content arithmetic means of the children according to the sampled sites.

The highest arithmetic mean occurred among children living closer to the Plumbum refinery and to the Panelas Lead Mine in a 2km perimeter in Vila Mota and Capelinha, rural area of Adrianópolis. Vila Mota showed the highest values for PbS, a value corresponding to nearly four times the value suggested by CDC (1991) and WHO (1995) as a limit to maintain children's health (10 g/dL). On the other hand, the arithmetic mean found in the children population living in Cerro
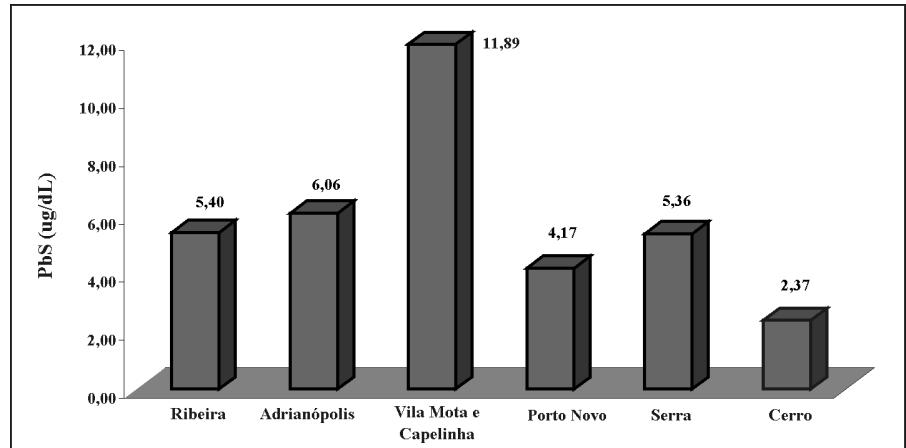
Figure 2 – Lead content arithmetic mean in the blood samples of children.

Azul (2.37 g/dL) is twice to three times less than those of the other studied populations. Cerro Azul is situated upstream of the Upper Valley lead mines and did not suffer the influence of the mining activities. Therefore the value 2.37 g/dL can be considered as a reference value or background for lead in the blood of children living in the Upper Ribeira Valley region.

The differences of lead concentration means between boys and girls were significant in all of the studied populations. Boys presented higher values than girls (Figure 3).

The questionnaire data assessment confirmed that the children who ate home grown vegetables showed higher Pb S contents than those who ate food from other sources. This may indicate that food is one of the lead entrance paths to a child's organism (Figure 4).

The assessment results showed that all participant children, except those from Cerro Azul, had Pb S above 10 g/dL, characterizing a long term health risk,

Figure 3 – Lead content arithmetic mean in the blood samples of children according to their sex.

according to CDC (1991). Furthermore, it was evident that 59.6% of the children living in Vila Mota and Capelinha, in the Plumbum refinery proximity, presented even higher lead contents, needing periodical medical examinations, and 12 children showed lead contents in blood above 20 g/dL, already requiring medical intervention.

Adults

The results showed that the adults living in the Plumbum refinery proximity, in Vila Mota and Capelinha, presented blood lead contents higher than those of the other populations (Paoliello et al. 2003), similar to the analytical data found for children (Figure 5).

According to the questionnaire data, the adults who presented the highest lead content in blood were male who had worked in the lead refining plant. This means part of the lead found in the blood samples can be residual. Recent studies showed that the adult male, even when exposed to low concentrations, can present health problems as, for example, a diminishing of the cognitive functions.

Environmental Contaminatio

Drinking water

Lead concentrations in residential tap waters were veryLead concentrations in residential tap water were very low (<0.005 to 0.008mg/L) compared to the allowed value for lead in drinking water according to the Brazilian Ministry of Health (Brasil, 2005). This showed that domestic water was not contaminated with lead, independent of its origin.

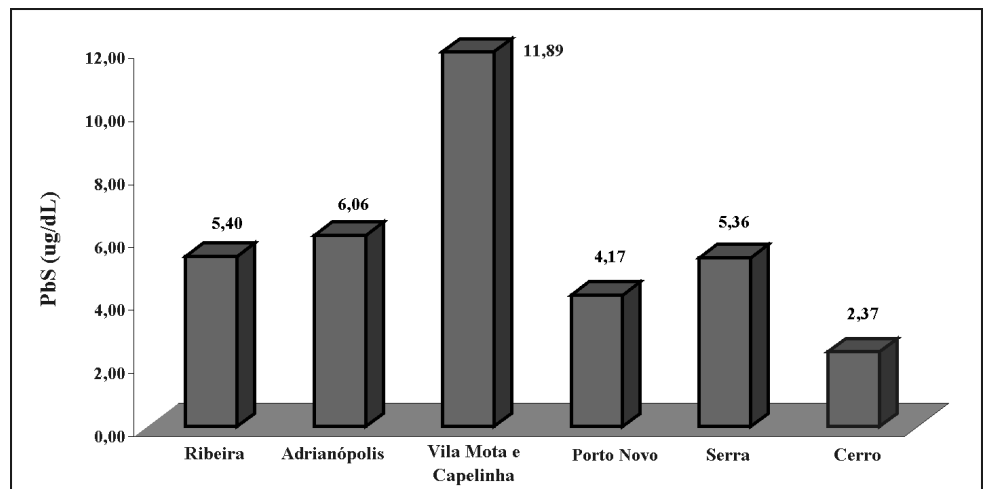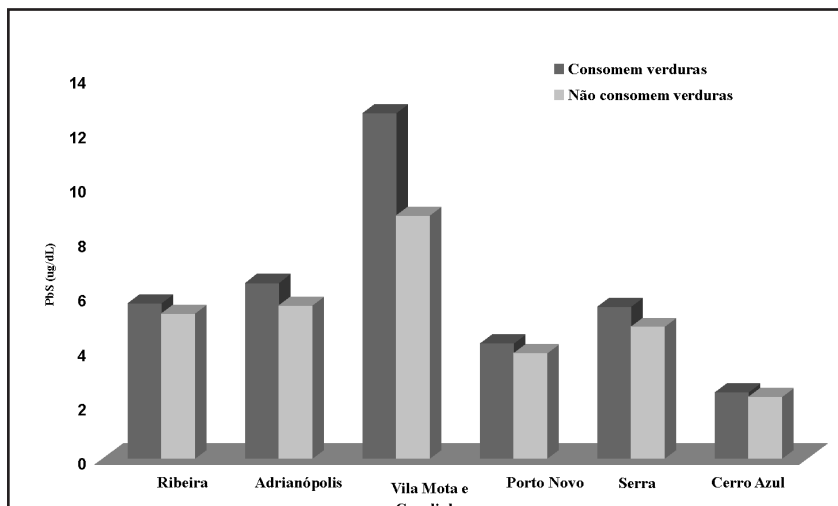*Figure 4 – Lead content arithmetic mean in the blood samples of children according to their food ingestion behavior.*

Surface soils, material from the piles of waste and slag

The lead concentrations in the soil samples varied between 21 and 916 µg/g, the highest contents occurring in the sites closer to the Plumbum refining plant (Table 1). In the slag residues and waste, concentrations were respectively 2.5% and 0.7% of lead. These are extremely high values, especially considering these are places where children play everyday.

According to the CETESB (2001), soils with lead contents above 100µg/g can indicate a quality alteration presenting a potential risk to human health, and values exceeding 350µg/g remediation environmental studies become necessary. Based on this evidence the soil in the Plumbum proximity can be considered lead contaminated presenting a health risk to the populations living there. These results include the residential garden soil that demand further investigation regarding the lead contents in the food cultivated there.

FINAL CONSIDERATIONS

The results for lead in the blood of the Upper Ribeira Valley inhabitants and in the soil samples indicate that the activities resulting from the lead ore refining processes by Plumbum affected all the assessed population, except for the reference population (Cerro Azul).

However, the Vila Mota and Capelinha child populations had the highest number of blood samples with lead values above 10µg/dL (about 60%) compared to the other populations (about 8%). Several factors may have contributed to these results, such as the direct involvement of a family member at the refinery (work position); nevertheless

Figure 5 – Lead content arithmetic mean in the blood samples of adults.

Table 1 - Lead Concentration in topsoil samples

Sample Number	Lead content (ug g-1)	pH	Distance from Lead Plant
1	175	6.6	5km
2	432	6.6	2.5km
3	343	7.9	1.2km
4	63	6.2	1km
5	672	6.7	1km
6*	904	6.5	300m
7	397	6.5	500m
8	916	6.3	900m
9*	802	5.5	900m
10	76	5	1km
11	117	6.7	1.4km
12	245	5.9	1.5km
13*	217	7.2	1.7km
14*	293	6.3	1.8km
15	37	5.9	2km
16	52	5.6	3.5km
17	76	5.9	3.6km
18	58	5.8	4.5km
19	21	5.6	6.5km
20	37	5.8	6.0km
21	26	5.5	9.5km

* soil from residential gardens

the proximity to the refinery, where the soils presented high lead concentrations, was the most important one. The children's habits of putting dirty hands and toys in their mouth make the ingestion of soil particles possible, characterizing an entrance path of the metal into the child's organism.

The results of the adult population blood samples analyses showed that those living near the Plumbum refinery presented higher lead levels, similar to the analytical data found for children. The adults who presented the highest blood lead contents (48μg/dL) were males who had worked in the lead refining plant. According to WHO (1995) these lead contents in adults do not present

health risks, though more recent studies point to health risks in even lower concentrations.

The lead in the particulate material dispersed through the refinery's chimney and deposited on the adjacent soil surface (residual contamination) suggest that currently the children of Vila Mota and Capelinha are exposed to lead intoxication and, consequently, present the most elevated lead blood contents.

These results show the necessity of environmental studies to rehabilitate the area and provide medical assistance and monitoring programs, especially designed for the children living close to the Plumbum refinery.

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STUDY OF AEROSOLS ISOTOPIC (Pb) COMPOSITION AND SOURCES IN BRASÍLIA (DF) – CENTRAL BRAZIL

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ABSTRACT

This study reported the first Brazilian aerosols composition data using both TIMS, to determine Pb concentrations and isotopic compositions, and PIXE, to obtain multi-elemental chemical concentrations. The particulate material was collected at the University of Brasília (UnB), in Brasília and in a remote area, to characterize the background composition. The atmospheric particulate was separated in two fractions of mean aerodynamic diameter of (Φ)– 2.5µm< Φ <10µm (coarse or $PM_{10\text{-}2.5}$) and Φ < 2.5µm (fine or $PM_{2.5}$), with a 12-hour sampling (day and night). Two sampling periods, one in winter and the other in summer allowed specific seasonal characterization. The project's goal was to investigate the impact of increased anthropogenic activities in the region and identify the main local sources of air pollution.

There was a contribution of the larger elements in both fractions, showing the geogenic input was quite significant during winter. The anthropogenic elements in the fraction $PM_{2.5}$ (as Pb and S) represented, mainly, the combustion of fossil fuels, though it may be also attributed to increased human activity and spot fires in the savannah (cerrado). The isotopic Pb compositions defined a diagram with ternary mixtures, indicating the contribution of: (i) anthropogenic sources, such as vehicle exhaust (combustion), (ii) industrial emissions and (iii) rocks and soils, which represent the natural sources.

INTRODUCTION

The chemical and isotopic composition of atmospheric particulate material and aerosols has been extensively used as a reliable tool to track pollution sources all over the world (Chow *et al.*, 1975; Rosman et al., 2000). In Brazil more detailed studies of this kind are rare (e.g., Aily, 2001), therefore, this study, made a comprehensive investigation of the chemical and isotopic composition of aerosols in Brasília.

The construction of Brasília, the Federal Capital of Brazil, started in 1956, in the Brazilian Central Highlands. The climate is very dry and mild in winter and hot and humid in summer. In 2000, the population of the Pilot Plan (Plano Piloto) and some adjacent areas reached 272,000 inhabitants. The city's progressive increase in the surrounding area infrastructure introduced many expressive environmental changes to the region such as, the transit of 733,000 vehicles (IBGE, 2005; http://www.ibge.gov.br). The air quality had been considered excellent; however, such an intense urban growth suggests that a routine air quality control should be established.

The atmospheric particles were collected at two sites (one urban the other remote), in two fractions with a mean aerodynamic diameter of $PM_{10-2.5}$ and $PM_{2.5}$, during 12-hour periods (day and might), in summer and winter. Pb concentration and isotopic composition, chemical elements and total mass were investigated in the aerosols, associating these with the seasonal variability and the sources' location. Two methods were used to analyze the aerosols: 1) Particle Induced X-ray Emission (PIXE), to determine the chemical elements with atomic number higher than 12; 2) Isotopic Dilution-Thermal Ionization Mass Spectrometry (ID-TIMS) to determine the concentration and the Pb isotopic compositions (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb).

EXPERIMENTAL

Local Geology

The local geology (Figure 1) is characterized by the low degree metamorphic rocks of the Meso- to the Neoproterozoic, represented by pelitic, psamitic and carbonatic metasediments, belonging to the Canastra, Paranoá, Araxá and Bambuí Groups.

Sampling Procedures

Sample data of the urban and the remote sites in Brasília (Figure 1) is shown in Table 1. The remote area lies approximately 40km to the Southwest of the UnB (University of Brasília) sampling site. Fuel samples and particulate material from industrial emissions and landfill soils (considered here to be the main anthropogenic pollution sources) were analyzed. The rock and soil samples were analyzed to characterize the isotopic composition of geogenic Pb in the region.

TIMS Analytical Procedure

The soil, rock and particulate samples were treated with a mixture of HF, HNO_3 and HCl acids for total decomposition. The whole procedure for the particulate material, fuel, rock and soil analyses is detailed in Gioia (2004). The Pb isotopic ratios were measured by thermionic mass spectrometry, using a Finnigan MAT 262 multi-collector, at the Geochronology laboratory of the University of Brasília. The Pb analytical white for the total procedure was=120 pg.

PIXE Analytical Procedure

The analyses were made according to the procedure set by the LAMFI Ion Beam Materials Laboratory of the Physics Institute of the University of São Paulo. The data reduction was made using the software Axil (Espen *et al.*, 1991), the spectrum adjustment having presented x 2 smaller than 2.0.

RESULTS AND DISCUSSION

Pb isotopes

The urban aerosols (at the UnB site) showed ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios varying from 1.1219 to 1.2062 and 2.0094 to 2.1337, respectively, forming a linear trend (Figure 2).

Most samples include ^{206}Pb/^{207}Pb ratios in the interval between 1.150 and 1.200, approximately, and concentrations between 10.7 and 0.07ng/m^3, during summer, and 25.4 and 0.04ng/m^3, during winter (Figure 3a). At the remote area (CIAB site) the interval of the ^{206}Pb/^{207}Pb ratios was very similar to those found at the UnB site, although with low Pb concentrations (Figure 3b). Usually, the particulate compositions were very homogeneous. They were, however, more radiogenic and tend to present low concentrations during the winter and in summer during the night; elevated Pb concentrations occur by day

Table 1 - Sampling sites (Brasília, summer and winter 2003)

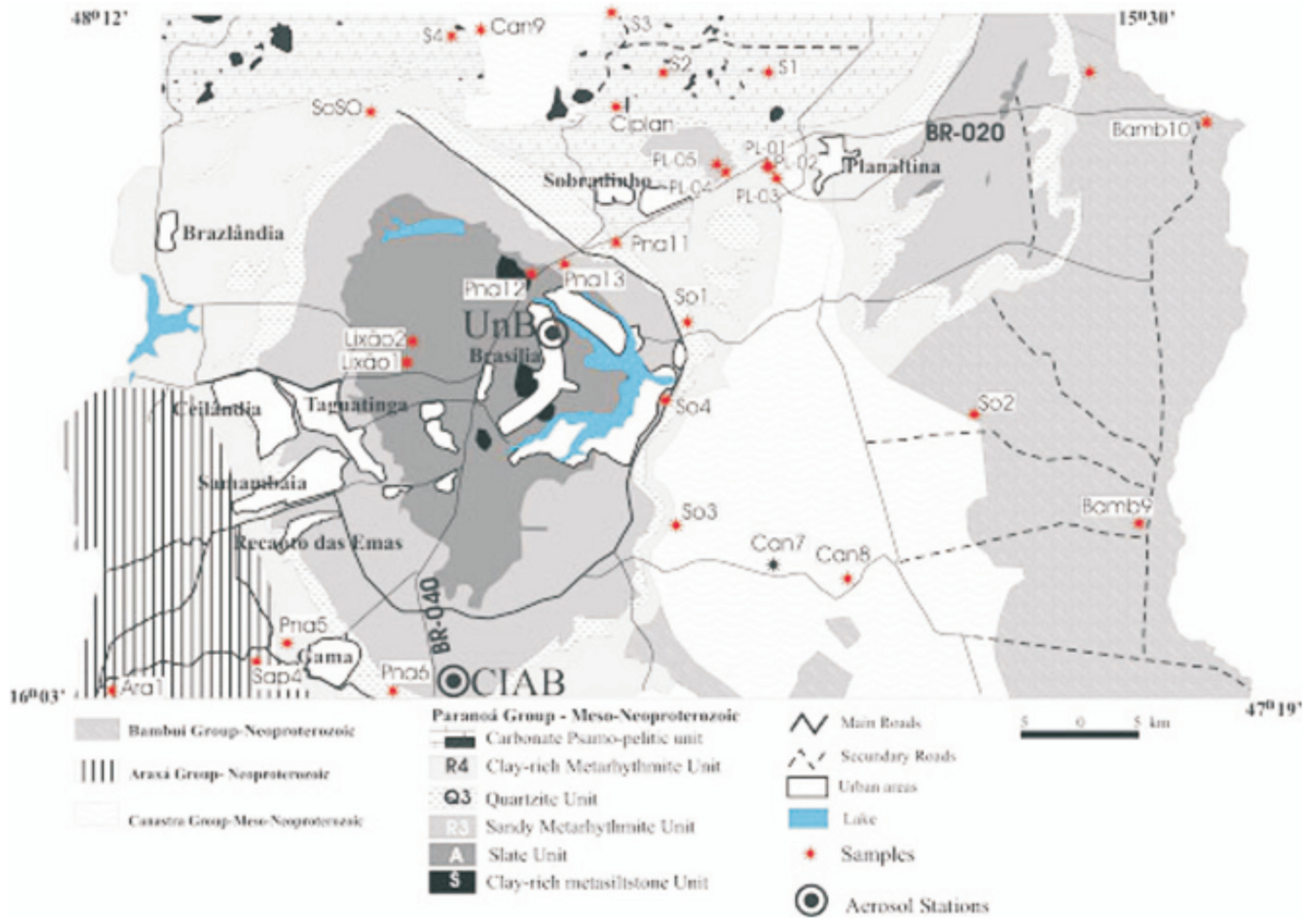| Sampling Sites		Samples (1W2h, day and night)			
Ident.	Location	Summer		Winter	
		Period	Samples	Period	Samples
UNB	Urban – University Campus (UNB)	01/16-23 01/28-02/21	47	07/14-20 07/28-08/23	56
CIAB	Remote – Preserved Area (CIAB)	01/29-02/08	10	08/12-08/23	12

Figure 1 – Schematic geological map of the Federal District (modified by Freitas-Silva & Campos 1998) and sampling site locations.
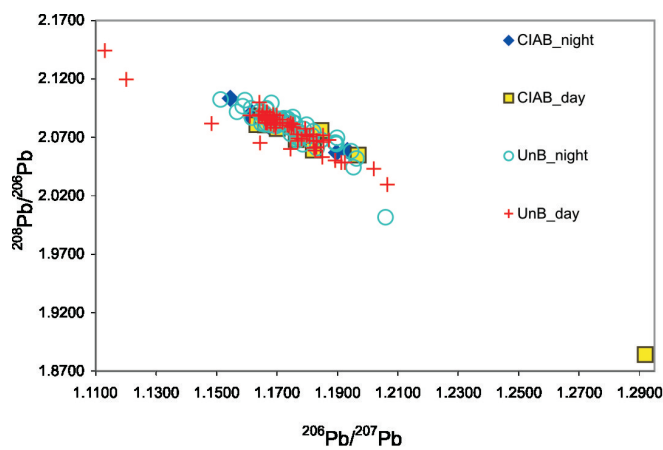

Figure 2 – Comparison between the 208Pb/206Pb and 206Pb/207Pb rates obtained in this study.
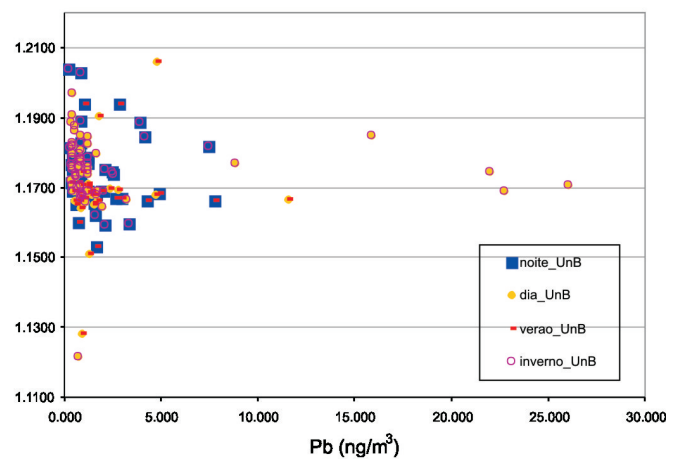
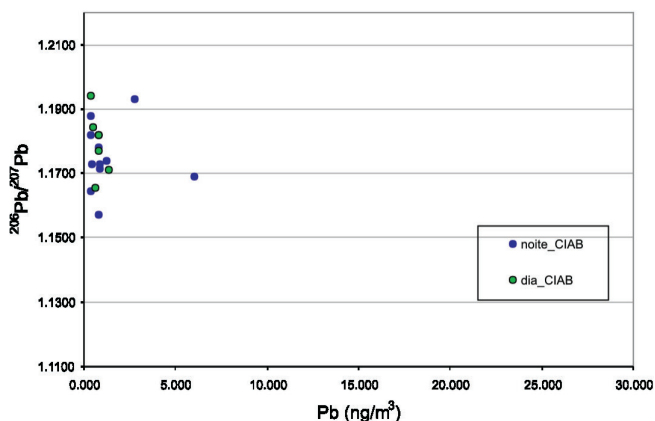Figure 3a – Comparison between the 206Pb/207Pb rates and the Pb concentration for summer and winter at the UNP sampling point.

Figure 3b – Comparison between the $^{206}Pb/^{207}Pb$ rates and the Pb concentration for summer and winter at the CIAB sampling point.

during winter. That indicates an important anthropogenic contribution by day, when human activity is elevated and the traffic is more intense. Less radiogenic compositions were observed mainly in the fraction PM$_{2.5}$ by day.

Comparing the Brasília aerosol data with the Pb isotopic compositions in fuel ($^{206}Pb/^{207}Pb$ = 1.1298-1.192), industrial filters collected at the central bus station in Brasília ($^{206}Pb/^{207}Pb$ = 1.1682) and in industries ($^{206}Pb/^{207}Pb$ = 1.2240-1.2569 to the North and 1.1740 to the South), it became clear that vehicle exhaust represents the main contributor to air pollution both in the remote (CIAB) and UnB areas, whose Pb isotopic compositions were found in the interval of the atmospheric particulate samples (Figure 04).

However, the study shows geogenic sources also contribute with Pb in aerosols. This is demonstrated by the isotopic compositions of the region's rocks and soils (Figure 4). The rocks presented $^{206}Pb/^{207}Pb$ rates/ratios varying between 1.1643 and 1.5993 and the most radiogenic came from the PPC unit samples of the Paranoá Group carbonates, situated to the North of Brasília. The soil samples presented an interval of 1.1762-1.2569 for the $^{206}Pb/^{207}Pb$ rate/ratio; however soils that were lixiviated with weak acid attack, presented less radiogenic isotopic compositions than those obtained with total attack: for lixiviated ($^{206}Pb/^{207}Pb$ = 1.1762-1.2228) and total ($^{206}Pb/^{207}Pb$ = 1.1976-1.2569).

Multielemental Analyses with PIXE

Significant contributions of the elements Al, K, Si, Ti and Fe (Figure 4) were observed during winter and summer in the coarse fraction that is typical of the geogenic contribution. In urban environments the elements Pb and S (Figure 5) are normally associated with the anthropogenic sources. They are found in the fine and coarse particles but S is abundant in the PM$_{2.5}$ fraction that represents the burning of fossil fuels. This identifies

with the increase of human activity and natural fires, very common in winter. The isotopic results showed that the anthropogenic sources are common to the vehicle exhaust (fossil fuels combustion) and cement industrial emissions, whereas the natural sources are rocks and soils.

Although Brasília has a good air quality, the inhalable particulate concentrations are smaller than 24.1 ± 7.2 µg/m³ (winter) and 11.0 ± 4.3 µg/m³ (summer), showing an evident influence of urbanization. Within the urban fringe, concentrations are higher than in the remote area – 19.7 ± 5.3 µg/m³ (winter) and 10.1 ± 3.9 µg/m³ (summer) – when compared to the same sampling period.

CONCLUSION

The contribution of larger elements in the fraction PM$_{2.5-10}$ is very significant during winter showing an elevated geogenic contribution. Pb and S were present in the fine and coarse fractions indicating both anthropogenic and geogenic action. Pb was more abundant during winter in the coarse fraction, according to the isotopic data.

The Pb isotopic compositions define a ternary diagram, indicating the contribution from: (i) anthropogenic sources, such as vehicle exhaust (combustion), (ii) industrial emission and (iii) rocks and soils of the Paranoá, Bambuí and Canastra Group, representing the natural sources. There was a minority sample group with less radiogenic and torogenic isotopic composition similar to alcohol and galena deposits of the Brasília Belt (Morro do Ouro, Morro Agudo, Paracatu and Vazante). Probably the residence time of this material was elevated in the atmosphere to transport the Pb long distances depositing it mainly in the fine filters.

The seasonal difference between the PM$_{10-2.5}$ and PM$_{2.5}$ concentrations has an important correlation with the winter season in Brasília, characterized as an extremely dry period. The presence of anthropogenic elements (Pb and S) in the PM$_{2.5}$ fraction represents particularly the burning of fossil fuels, though it may be also attributed to increased human activity and wild fires of the savannah. Low Ca concentrations can be attributed to the cement industries to the North of the city. The aerosols isotopic pattern differs totally from other industrialized cities, showing an elevated contribution of geogenic material and low anthropogenic action.

Additional research will be necessary to evaluate the influence of traffic, as well as other anthropogenic sources, which will probably increase with a population growth.

ACKNOWLEDGEMENTS
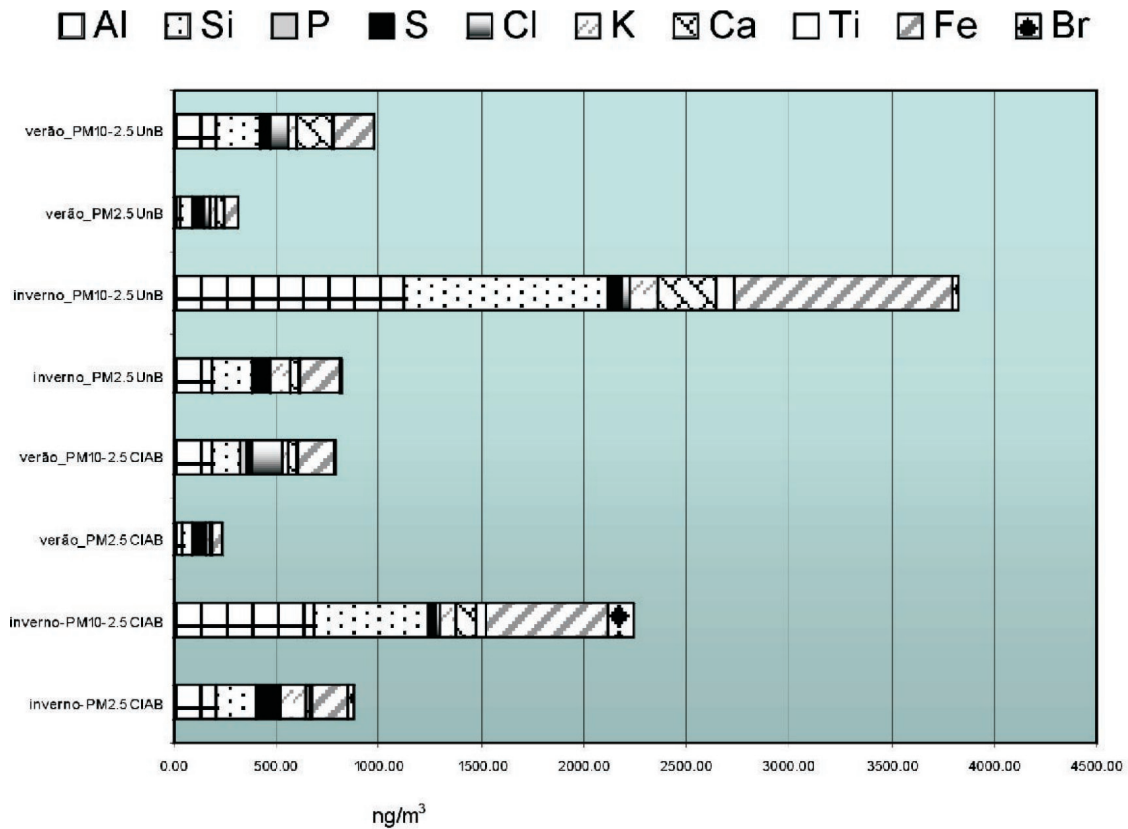
Figure 4 – Results from the PIXE analysis of major elements during summer and winter at both sampling sites (UnB and CIAB).
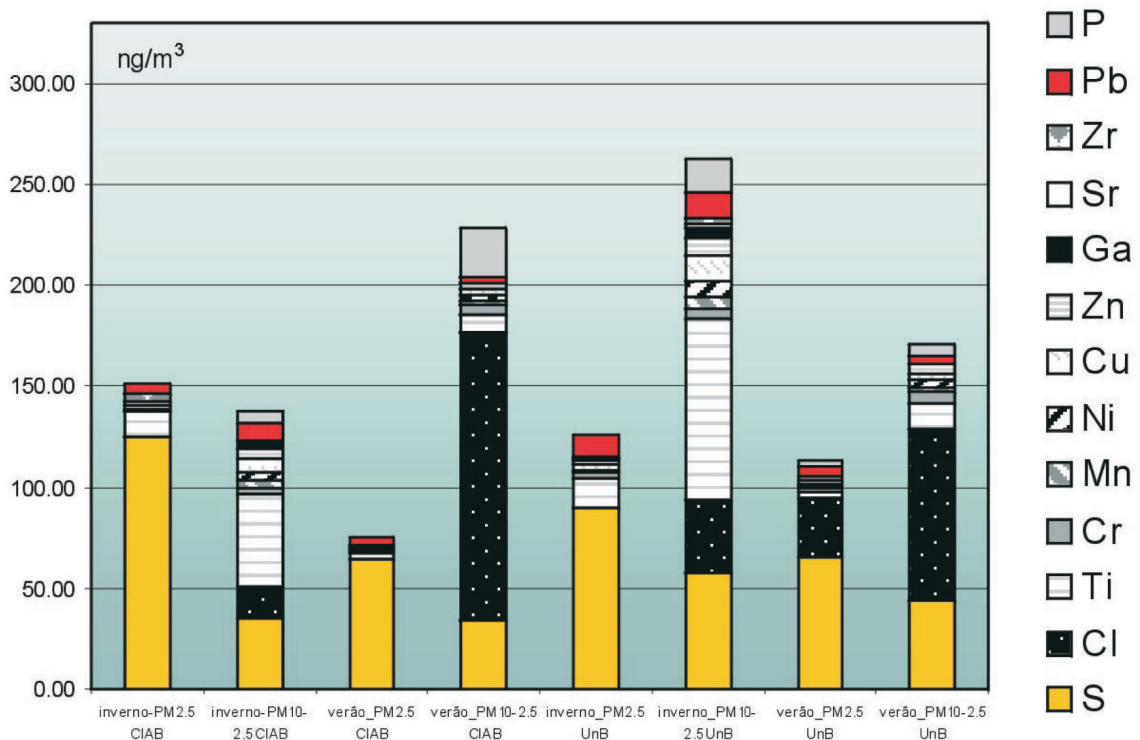
Figure 5 – Results from the PIXE analysis of trace elements during summer and winter at both sampling sites (UnB and CIAB).

Physics Institute of the São Paulo University; Dr. Maria de Fátima Andrade, of the Institute for Astronomy and Geophysics of the São Paulo University and meteorologist Maria Cristina G. Costa, of INMET.

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DENTAL FLUOROSIS AND FLUORINE ANOMALIES IN GROUNDWATER OF SÃO FRANCISCO TOWN, MINAS GERAIS STATE BRAZIL

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ABSTRACT

The main water source for the rural population's consumption in São Francisco, North Minas Gerais, is the karstic aquifer in the carbonate rocks of the Bambuí Group. Epidemiologic and geologic-hydrogeologic studies found fluoride anomalies in those water sources and established a relationship between the anomalies and dental fluorosis incidence in that area. Minerals with fluorine occur disseminated in the Bambuí Group rocks and, especially, fluorite disseminated in fractures and calcite veins throughout the limestone. There is a remarkable correlation between the stratigraphy, the rock fractures system, the wells' discharge and the fluorine concentrations in the groundwater. A hydrogeochemical survey of 78 tubular wells revealed a fluoride variation from 0 to 3.9mg/L and background of 0.45mg/L. In 16.7% of the wells, the fluoride concentrations exceeded the local potability limit (0.8mg/L). The epidemiologic and clinical survey of the population between 6 and 22 years old indicated a dental fluorosis prevalence rate of 81.5% to 97.7% in four districts, with 30% of the teeth in a severe

damage stage. In these four districts, the water consumed by the population is taken from karst aquifers that have fluorine concentrations higher than 1.18mg/L.

INTRODUCTION

Integrated water resources management practices imply quality assessments of surface water and groundwater especially that destined for human consumption. In the karstic terrains of carbonate provinces, that assessment is also necessary to prevent and control of hydric diffused diseases. The karstic areas situated in the Middle São Francisco River hydrographic basins, in the North of Minas Gerais State, were chosen as a case study. These areas are characterized by a rainfall concentration in just a few months, higher rates of seepage through the carbonate substrate and across sub-surface karstic structures and a consequently larger groundwater availability compared to the surface bodies. Thus, the aquifers in the carbonate rock domains constitute the main water sources for human and animal consumption and for agricultural and industrial activities.

In these domains, several inorganic chemical substances, present as mineral phases in limestone and associated rocks, are naturally incorporated to the groundwater by dissolution processes. Many of these mineral substances are central to human health, but their effects in the organism depend, among other factors, on the quantities taken by each individual. A paradigmatic example of this relationship concerns fluorine and fluorosis.

Fluorine assimilation in appropriate doses is beneficial to health, since it promotes increased mineral matrix resistance of the teeth and bones. However, the continuous assimilation of quantities exceeding the maximum recommended can induce deformities of the dental enamel (dental fluorosis) and even of the bones (skeletal fluorosis or osteofluorosis).

Dental fluorosis is an anomaly of the teeth's development linked to enamel deformation following a prolonged fluorine intake in excessive amounts in children up to 5 years old, when the enamel is being formed. The disease is characterized by increased enamel porosity, which becomes opaque and stained with white or even brown or black spots. The maximum fluoride content in water for human consumption depends on the local climatic conditions, as established by the World Health Organization-WHO (1999). This limit varies according to the maximum mean air temperature values, which are related to the volume of water consumed by a given population. In São Francisco, the mean maximum air temperature is 32.3°C, indicating a recommended maximum limit for fluoride concentration in potable water of 0.8mg/L, according to Resolution 1469/00 from the Ministry of Health (Brazil, 2000).

In São Francisco, dental fluorosis affects mainly children and young adults living in the rural area. The disease, of permanent character, requires corrective treatment and dental restoration, usually inaccessible to the affected populations. This treatment consists of polishing the porous external enamel until the stain caused by the food pigments impregnation is removed. In severe cases it is necessary to implant crowns or dental facets.

São Francisco is situated in the North macro-region of Minas Gerais State, in the Middle São Francisco River hydrographic basin, about 578km from Belo Horizonte (Minas Gerais State capital). It has a population of 52,639 inhabitants (IBGE, 2003), 46% of which live in the rural area. The population faces many difficulties caused by the lack of an integrated water resources planning, which, combined with the socio-economical background of significant poverty rates, contributes to the occurrence of water transmitted diseases.

The limited availability of surface water results from the combination of two main factors: 1,132.9mm/year rainfall concentrated in four months followed by a long drought period and high water infiltration rates through the karstic domain of fractured Bambuí Group limestones. On the other hand, there are important groundwater springs which represent the only water resources available during the whole year in the rural area.

The water supply for the urban area population situated on the São Francisco River margins is provided by the Minas Gerais State Water Works Company - Companhia de Saneamento de Minas Gerais (COPASA MG), mainly through the catchment and treatment of the river's water. The rural area's water supply is the responsibility of the city administration and is provided mainly through tubular wells drawing groundwater. These wells are the main water source for the geographically dispersed rural communities, which are often situated in areas where the perennial surface water bodies do not exist. In the late 1970´s several tubular wells were drilled in the rural zone to minimize the serious water supply problem and the first wells started functioning in the 1980´s.

The Mocambo public supply well, situated 14km South of São Francisco, was opened in 1979. Fifteen years later, the region's community and dental surgeons diagnosed the nature of the stains in their children's permanent teeth. In 1995, following a request of the São Francisco administration the National Health Foundation - FUNASA analyzed the Mocambo tubular well water, where it found 3.2mg/L of fluoride, four times the region's recommended maximum limit Between 1995 and 1997, two other wells were built in Mocambo without being pumped due to the elevated fluorine contents in the water.

In 2002 and 2003, five of this survey's authors sought to characterize the endemic in some communities by assessing the local aquifer systems (geometry, dynamics

and hydrogeochemical characteristics) to determine the elevated fluorine content origin in the groundwater. The taskforce was based on interdisciplinary methodologies and on the search for interrelations of the epidemiological data with the geologic-hydrogeologic investigation. (http://www.odonto.ufmg.br/odonto/geologia_saude. html).

The study recognized the intake of naturally enriched fluorine groundwater as the cause of dental fluorosis and confirmed the fluoride concentrations correlation with the tectonic structures, stratigraphy and aquifer hydraulic parameters. The results indicate the areas of greater vulnerability to fluorine rich groundwater and also technical criteria for well locations were established. At present the study is expanding methodologically and geographically towards North São Francisco, where 24 other cities present similar geological contexts together with isolated cases of dental fluorosis.

THE INTERDISCIPLINAR RESEARCH OF DENTAL FLUOROSIS IN SÃO FRANCISCO

Methods in the Field of Geosciences

This study included the geological mapping, stratigraphic sequence definition, the macro- and microscopic petrographic and deformational structures characterization and the associated karstic dissolution features.

The regional geological mapping was made in the scale 1:250,000. However, more detailed mapping was done to better characterize the fluorite occurrences and elevated prevalence of dental fluorosis in the Mocambo district. This included a (1:60,000) map of the Mocambo creek sub-basin and of two key-areas (1:25,000) with an emphasis on the facies associations and the stratigraphic control of the fluorite occurrences.

The hydrogeologic assessment included the physical and hydrochemical characterization of the aquifers and the elaboration of a conceptual model explaining its dynamics and flow system. Beginning with a well inventory, the groundwater sampling and hydrochemical analyses were carried out pursuing the following goals: a general hydrogeochemical characterization of the groundwater, quantify the fluorine contents, confirm the associations between fluorine and other hydrochemical parameters and the fluorinate background definition. The sample was considered to be contaminated when the concentration was above 0.8mg/L, maximum value recommended for the region.

The sampling procedures, preservation and water analyses were carried out according to the 20th Standard Methods for the Examination of water and wastewater (1998). The most important analyzed parameters were: pH, CE, T, DTS, alkalinity (total, bicarbonate, carbonates and hydroxides), total hardness, major ions and F⁻. The statistical analyzes were made with the software SSPS – Statistical Package for the Social Science – SSPS and contour maps were elaborated using the software Surfer32.

Methods in the Field of Health Sciences

For the clinical and epidemiological studies, four districts of the São Francisco rural area with cases of the disease were selected (Mocambo, Vaqueta, Alto São João, Novo Horizonte) and a district as a control area (Retiro), where the water supply is under the responsibility of COPASA-MG.

For the epidemiological inquiry, 288 individuals, between 6 and 22 years old were examined, regarding the presence of permanent teeth and length of time the water had been consumed. The clinical examinations were conducted by a single examiner, under natural light, after teeth brushing and using sterilized gauze to dry the teeth. An inquiry on teeth brushing with dentifrice and other methods of fluorine application, information about the duration of residence in the area and the consumed water origin was included. In the assessment, the CPO-d indexes (decayed, lost and filled teeth) according to WHO (1997) and TF-Thylstrup and Fejerskov criteria (Fejerskov et al., 1994) were employed. The data base was developed in the software EPI INFO of WHO. The data collection was carried out with the authorization of the City Council, after written information was sent to the parents or guardians of the children to be examined.

To evaluate the local resident's perception of fluorosis, interviews were made with affected individuals and teachers in the four communities that presented excessive fluorine intake. The methodology used in the qualitative assessment was based on open and semi-structured interviews with result analysis according to Bardin (1977). In the case of adolescents, the interviews were divided into the following contexts: dental health, perception of fluorosis and expectations. The sample comprised of 17 young people between 12 and 22 years old who presented staining due to fluorosis in degrees between 1 and 9 in the TF index.

GEOLOGICAL CONTEXT

São Francisco is located in the central compartment of the São Francisco Basin, in a less deformed neoproterozoic cover area in the central South of the São Francisco craton. There is a predominance of rocks with horizontal to sub-horizontal structures, represented, from bottom to top, by a carbonatic-pelitic Neoproterozoic sequence of the Bambuí Group, Cretaceous sandstones, shales and siltites of the Areado Group; Cenozoic colluvial-alluvial sediments, probably Tercio-Quaternary and, finally, Quaternary alluvial sediments (Figure 1).

The limestone lithotypes of the Bambuí Group consist mainly of allochemical rocks, with a predominance of calcareous sandstones and calcareous lutites. Among

the allochemical components, the most common are peloids, intraclasts, ooids and microphytoliths. They consist of grains dispersed in a matrix of thin carbonate mud or the framework of calcareous sandstones and calcareous rudites with micritic matrix and spatic cement. Locally, dolomite terms may occur. The terrigenous lithotypes are predominantly pelites, metaclaystones and metasandstones. The faciological observations suggest paleoenvironmental conditions of tide plains, intern platform and platform bars with sedimentation cycles marked by recurrences of storm events.

Purple to pink fluorite crystals with 0.3mm-2cm edges occur in a small proportion, disseminated preferably in re-crystallized white calcite veins, associated with fractures sub-parallel to calcareous sandstones bedding. The fluorite occurrences partly respond for the anomalous fluorine concentrations in the groundwater, but other fluorine carrying minerals, neither identifiable macroscopically nor through conventional optical microscopy, may be present.

The Areado Group is represented by pelite basal facies and psamitic facies thicker than the former and covering a larger area. The pelite facies are formed by claystones and finely laminated shales and the psamitic facies, with a thickness up to 40m, consists of quartz sandstones with mature texture.

The Cenozoic sediments usually present less thickness and reduced area extension. The alluvial deposits of greater extension correspond to the sandy covers developed from the cretaceous sandstones that are distributed on the tabular elevations above 700m. They are generally associated with colluvial sediments and clastic material built after a relief regression process.

The fracture pattern defined by photoanalysis and field work consists of a distensive system N70°-90°W, a decompressive system N0°-30°E, a dextral shear system N50°-70°E and a sinistral shear system N30°-50° W.

In São Francisco, the altitudes vary from 455m to 815m, with a predominance of flat and dissecated areas, developed mostly on the metasediments of the Bambuí Group. Extensive and tabular platforms, situated in the most elevated areas, especially in the South portion of the city, correspond to cretaceous sandstones deposited on top of the Bambuí Group metasediments.

HYDROGEOLOGY

The stratification of carbonate and Bambuí Group pelitic rocks and the Cenozoic cover sandy sediments and the Areado Group sediments define two aquifer systems hydraulically connected: one a karstic-fractured system and the other a sedimentary granular system.

The karstic-fractured system is made up of the BamThe karstic-fractured system is made up of the Bambuí Group carbonate politic rock sequences (75% of the area), sub horizontally accommodated with an

outcrop thickness around 170m. The carbonate units have undergone an intense karstification and fracturing process. The areas with greater storage capabilities are the zones more intensively fractured in the carbonate and politic sequences or in the zones with pronounced karstic dissolution evidence in the carbonate sequences. Generally, the karstic-fractured system is considered to be unconfined, with a water table around 14m, even though locally the pelitic sequences may confine the carbonate sequences, acting as aquicludes, giving rise to artesianism. With regard to anisotropic media, such as karstic-fractured aquifers, the flow directions and gradients are extremely complex and depend mostly on the rock discontinuity patterns. Therefore, in the politic aquifers the vertical components of the hydraulic gradients are larger whereas in the karstic-fractured aquifers the horizontal components predominate. The recharge in the karstic aquifers occurs in three different ways: i) through the Areado Group sandstones (East and Southeastern side of the city) and the Tercio-quaternary detrital cover; ii) by leakage through the pelitic units; iii) directly due to the pluviometric infiltration in limestone outcrop areas through open fractures and karstic features. The discontinuity directions representative of the main water flow are N70°-90°W, N0°-30°E, N50°-70°E and N30°-50°W. The extremely variable well discharge rates vary from a few m^3/h to 260m^3/h reflecting the high aquifer anisotropy and the need for precise geological knowledge to enhance drilling success. This aquifer system is the most important water source for the rural population.

The granular aquifer system is made up of the following units: Areado Group sedimentary sequences, Tercio-quaternary detrital cover and recent alluvionar-colluvionar deposits. Recharge of the granular system is through direct precipitation. Despite being exploited by deep wells (Areado Group) and by hand dug wells (detrital cover), this aquifer system receives the discharge of some surface streams which drain the area.

The regional groundwater flow is towards the São Francisco River main channel, which is also the regional base flow level. However, many other local flow directions can be expected when dealing with karstic domains.

RESULTS

Epidemiology
The epidemiological survey of dental fluorosis showed a prevalence rate of 81.5% to 97.7%, with 30% of the teeth in a severe stage of damage (Figure 2).

The fluorosis prevalence exceeded 80% in all the affected districts (Table 1). Considering the TF equal or superior to 4 (most severe aesthetic and/or functional tooth failure), the fluorosis prevalence affected 45.6%
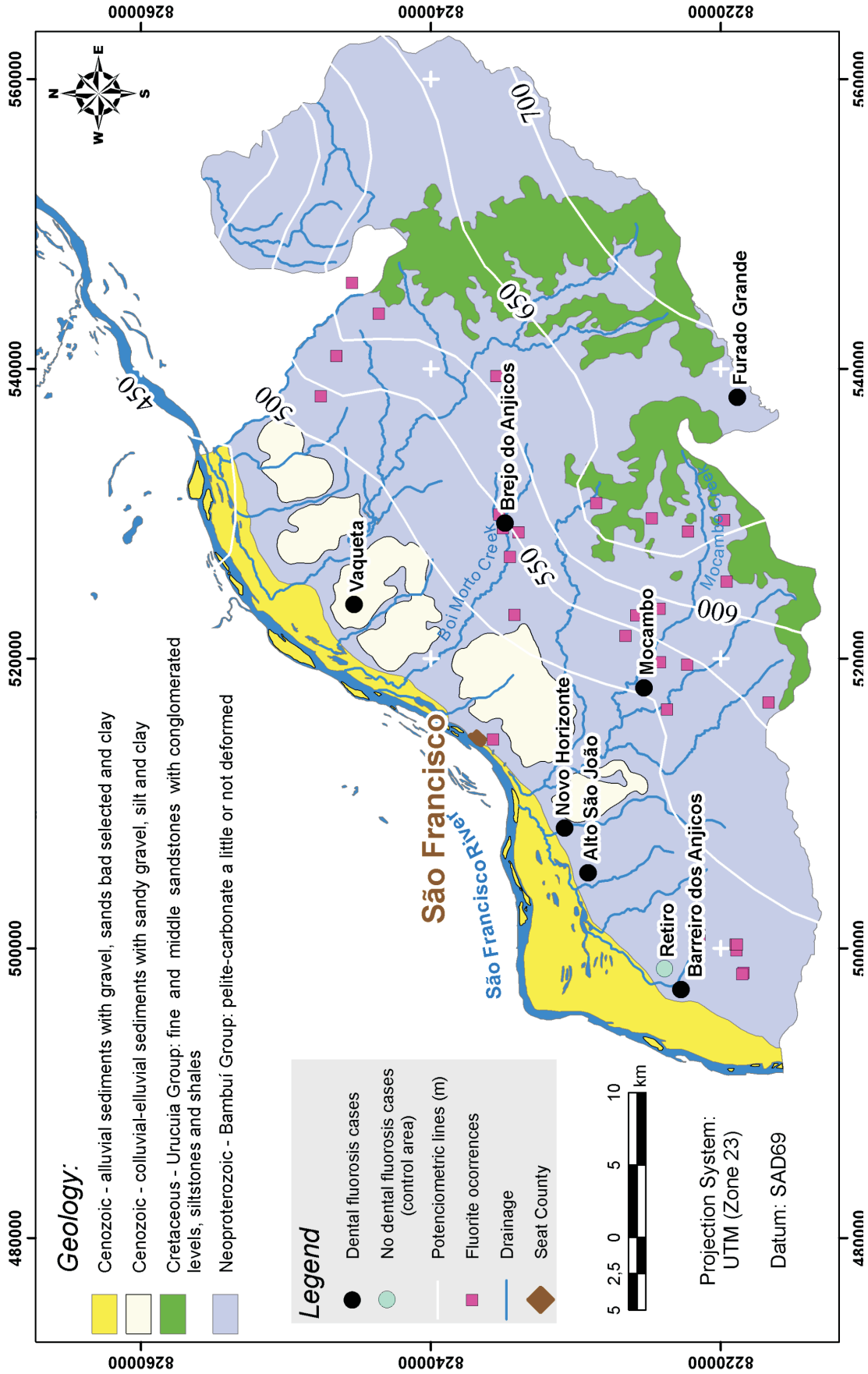
Figure 1 – Dental fluorosis in Mocambo – (Photo: E.F.Ferreira, 2008).

of the examined people in Alto São João, 61.5% in Mocambo, 72.3% in Vaqueta and 82.2% in Novo Horizonte (Table 2). Such numbers are most alarming and show a typical public health problem related to the environment. In the four communities where dental fluorosis occurs, the consumed water comes from the carbonate aquifer, with fluorine concentrations higher than 1.18mg/L. In the district of Retiro, the control area, fluorosis does not occur, due to the low fluorine concentration at that site (0.2 mg/L).

Figure 2 – Dental fluorosis in Mocambo – (Photo: E.F.Ferreira, 2008).

Table 1 - Prevalence of people with fluorosis (TF), per district, 2002 (percentage)

Age	Mocambo	Vaqueta	Novo Horizonte	Alto São João	Retiro
7 a 9	57.8	95.5	100	88.0	0
10 a 12	87.0	100	100	75.0	0
13 a 15	92.8	100	100	91.6	7.7
16 a 22	100	60	83.3	100	0
Total	81.5	93.6	97.7	87.7	0.3

Table 2 - Prevalence of people with fluorosis in a degree equal or superior to 4 (TF), per district, 2002 (percentage)

Age	Mocambo	Vaqueta	Novo Horizonte	Alto São João	Retiro
7 a 9	21.0	63.6	86.6	28.0	0
10 a 12	65.2	81.2	76.9	33.3	0
13 a 15	92.8	100	81.8	83.3	0
16 a 22	88.8	60.0	83.3	62.5	0
Total	61.5	72.3	82.2	45.6	0

The interviews showed that young people exhibit socialization problems, difficulties to participate in collective school activities as well as feelings of embarrassment and shame due to the teeth lesions. The youths affected by fluorosis relate it mainly to the ingestion of calcareous water and are worried that the fluorine stains may be mistaken as a "lack of hygiene". Individuals who present fluorosis in the anterior labial region tend to systematically hide their smile (putting their hand in front of their mouth, smiling with lips shut), avoid taking pictures, believe that the fluorosis stains may upset their professional future and, finally, they believe that fluorosis stains may upset affective relationships with the opposite sex.

The characteristics (explicitly named in the interviews) related to the present state of the teeth and smile of the studied population: ugly, dirty, yellow and rusty. Adolescents report that they feel ashamed, sad and without freedom which is confirmed by the teachers.

Fluorine hydrochemistry in the groundwater

The epidemiological survey in the endemic communities identified the fluoride anomalies in groundwater as the main fluorine intake source and the cause of the dental fluorosis.

The hydrogeochemical evaluation of 78 tubular wells indicated a fluoride variation between 0 and 3.9mg/L and background of 0.45mg/L. In 16.7% of the wells the concentrations exceeded the local potability limit (0.8mg/L). These samples correspond to the most recent wells.

The pH showed a variation between 7.0 and 8.8 with a 7.5 median. The Total Dissolved Solids (TDS) varied between 43.3mg/L and 517mg/L with a 407.5 median and 370.2mg/L mean. The alkalinity of bicarbonate varied between 94mg/L $CaCO_3$ and 481.3mg/L $CaCO_3$ with a median of 39.3mg/L $CaCO_3$.

The hydrochemical facies verified in the Piper diagram (Figure 3) revealed three main hydrochemical types: calcium bicarbonate (32.3%); sodium bicarbonate, sodic-calcic a calcic-sodic (21.5%) and bicarbonate calcic-magnesian (15.4%). The direct association of
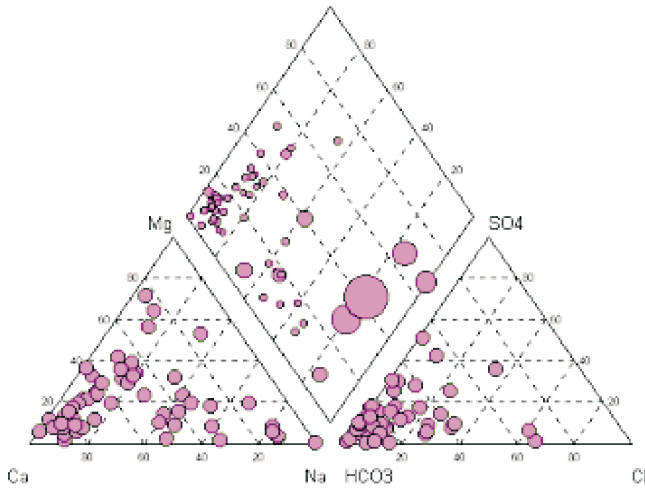
Figure 3 – Piper diagram (points' dimension is proportional to the fluorine concentration).

fluorine with sodium is clear, given the high solubility of the latter.

The areas of higher natural vulnerability to contamination risk (>0.8mg/L) are distributed according to the alignment N40 E, parallel to the São Francisco River main direction, in the central and Southeastern portions of the studied area. In the latter, fluoride is found in the limestones under the Areado Group sediments.

Relationships of fluoride with geological factors

The wells have a great production variation, which reflects the aquifers' great heterogeneity and anisotropy. There are dry wells and wells with discharges of 264m³/h; most of them however (56%) have discharges of up to 20m³/h.

Based on the field observations, two more developed karstification directions were confirmed: N70-90 W (distensive system) and N0-30 E (decompression system). Two other systems identified are a shear zone oriented N50-70E (dextral) and N30-50 W (sinistral). The higher well discharges (around 100m³/h reaching exceptionally 260m³/h) indicate a high degree of karstification as well as artesianism conditions. Once the relationship between well discharge and fracturing system is established it can be confirmed that karstification occurs in all fracturing directions and that the higher yields are associated with the distensive system N70-90 W.

The F⁻ concentrations are higher in those systems showing smaller productivity, that is, according to the decompressive and sinistral shear directions. The average concentration of fluoride in wells located distant from shear zones is close to the background values, 0,49mg/l, whereas, along the distensive system, mean concentration reaches 0,54mg/l, along the sinistral

shear system 0,73mg/l and in the decompressive system, 0,8 mg/l. Among the five (5) wells located in the distensive system coinciding with the higher productivity zone, bearing fluoride concentrations higher than 0,8mg/l, four (4) of them show lower yields, between 2,5 and 10,56m³/h. The relationship between the fluoride concentration and altimetry of the water entries inside the wells substantiate that it is closely associated with carbonate sandstones of the Bambuí Group inferior and middle parts in the area (45,8% of the wells with fluoride above 0,8mg/l are lying on altitudes between 480 and 600m).

Nine (9) other communities were identified, whose water supplies are taken from new wells are contaminated with fluoride, however no measure have been adopted to warn the exposed population.

CONCLUSIONS

The interdisciplinary methodology applied to this study was fundamental to understand the geoenvironmental processes and the characteristics of the dental fluorosis endemic in São Francisco.

The epidemiological study of dental fluorosis confirmed that there is a worrying endemic situation, requiring immediate action to provide corrective treatment for the already developed lesions and prevention of new cases. The fluorosis lesions cause great embarrassment in affected youths, and can even make social contact difficult in some cases. Measures to correct the fluoride content of the wells and odontological facilities for oral health, including the broadcast of information as to the lesions' origin, need to be undertaken to achieve a comprehensive health improvement for the affected population.

Fluoride anomalies in the studied communities' water indicate that the groundwater is the main fluorine intake source and the main cause of fluorosis. The disseminated fluorite crystals in calcite veins across the Bambuí Group calcarenites are the groundwater natural contamination source-mineral, but other minerals with fluorine may be present in the Bambuí Group carbonate and pelite facies, also contributing to the fluoride anomalies in the groundwater.

The fluoride concentrations in the groundwater reach a maximum of 3.9mg/L. The association of F-concentrations with the brittle structures, the stratigraphy and the wells' hydraulic parameters provide the technical criteria to locate new tubular wells in regions with lower vulnerability to fluorine contamination. The most important being: to avoid the directions N0-30 E and N30-50 W; to prioritize the direction N70-90 W, which is also the most promising in terms of production and finally to prioritize water entries with altitudes above 600m.

Nine other communities were found in the same town, whose water supply came from newer wells contaminated with fluoride. This is a worrying fact, since no measure has been adopted to warn the exposed population.

ACKNOWLEDGMENTS

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FLUORINE GEOCHEMISTRY IN FLUVIAL WATERS AND SEDIMENTS OF THE CERRO AZUL REGION, PARANÁ STATE: DEFINITION OF RISK AREAS FOR HUMAN CONSUMPTION

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INTRODUCTION

Fluorine is ingested mainly through water intake, and is considered an essential element for human health, though excess ingestion may cause problems with teeth and bones, a disease known as fluorosis.

In the Ribeira Valley region, near the towns of Cerro Azul and Adrianópolis, Paraná State, there are large fluorite deposits (CaF_2), and the operational Mato Preto mine (Figure 1). These deposits coincide with fluorine anomalous areas, identified from previous studies of fluvial sediments and soils (Biondi et al., 1985, Martini, 1985, Mattos, 1989, Licht et al., 1996a, Licht et al., 1996b, Licht et al., 1997, Licht 2001). Weathering mechanisms on these soils and rocks can lead to a fluorine enrichment of surface and groundwater.

This study seeks to determine the surface water quality in the fluorite deposit regions of Volta Grande (VG) and Mato Preto (MP) and define exposure risk zones. Additionally, it analyzes the region's population water consumption to define the mineral phases that bring fluorine to the water and sediments.

FLUORINE GEOCHEMISTRY

Fluorine is commonly related to the igneous processes (Bell, 1998). During the magmatic evolution, fluorine usually occurs as a volatile phase component, becoming concentrated in the final stages of the evolution in alkaline rocks, carbonatites, hydrothermal deposits, alteration zones and pegmatites (Dardenne et al.,1997), generally as fluorite and fluorapatite.

Released by mineral weathering, fluorine is transferred to the supergenic aqueous solutions in the form of the dissolved free fluoride ion (F^-), with high mobility. In low pH, the HF species may be stable (Bell, 1998). The fluorine mean concentration in sea water is 1-1.3mg/L F^-. In groundwater it can vary from less than 1 to more than 35mg/L F^-, whereas in river and lake waters the concentrations are usually low (0.01-0.3mg/L) (UNICEF, 2003).

Among the factors that control the fluoride concentration in natural water are: temperature, pH, presence of ions and complexation inducer colloids, solubility of fluorine containing minerals, ion exchange capacity of the aquifer's material (OH⁻ for F⁻), size and type of geologic formations percolated by the water and the length of time the water is in contact with a particular formation (Apambire et al., 1997).

Fluorine is found in silicate rock constituents, where apatite, $Ca_{10}(PO_4)_6F_2$, is one of the minerals richest in fluorine. Only in fluorite (CaF_2) and topaz ($Al_2SiO_4(OH,F)_2$) is fluorine an essential component. It can also be fixed in hydroxy-silicates and complex hydroxy-aluminum-silicates, in which the hydroxyl ions (OH)⁻ can be extensively substituted by F⁻, as is the case of the amphiboles and minerals of the mica group (biotite and muscovite) (Goldschmidt, 1970). Allmann & Koritning (1972) comment on studies made on the change-adsorption of F⁻/OH⁻ in clay minerals, where the concentrations and pH of the percolating solutions had a great influence on the F lixiviation and adsorption.

In most environments, fluorite is the main mineral that controls the fluoride geochemistry in natural water. The F⁻ concentration in water is limited by the fluorite solubility. Its low solubility product (at 20°C it is 3.9×10^{-11}) implies that water with low calcium content could have high fluorine concentrations (Bell, 1998). The amount of F released by the fluorite dissolution in water with low ionic potential is around 8-10ppm, but the concentration of Ca^{2+}, Na^+, OH⁻ and certain complexing ions, such as Fe, Al, B, Si, Mg and H can modify this F⁻ concentration interval (Apambire *et al.*, 1997).

The ionic exchange (OH⁻ for F⁻) involving several types of clay is a process that can explain very high F⁻ concentrations in water (values above 30mg/L). This ionic

exchange process also includes the bases exchange (Ca^{2+} and Mg^{2+} for Na^+), promoting the progressive pH elevation to alkaline values (pH 9-10.5) (Apambire et al.,1997). Thus, the Ca^{2+} reduction in water favors higher fluoride concentrations.

FLUORINE AND HUMAN HEALTH

People can be exposed to fluoride through the air, food, contaminated soils and water intake, the latter being the main intoxication path. The F⁻ maximum content in drinking water, recommended by the World Health Organization (WHO, 1996) is 1.5mg/L, with variations admitted mainly due to the region's mean annual temperature (18°C = 1.2mg/L; 19-26°C = 0.9mg/L; 27°C or more = 0.7mg/L F⁻). In Brazil, the National Environmental Council -CONAMA Resolution 020/86 establishes an acceptable maximum content of 1.4mg/L F⁻, and the Administrative Act N 518 of the National Agency for Sanitary Vigilance - Agência Nacional de Vigilância Sanitária - ANVISA of 1.5mg/L F⁻ For São Paulo State, Resolution SS-293/96 establishes classification criteria for the water distributed by public supply systems and considers adequate F⁻ contents of between 0.6 and 0.8mg/L.

The affinity of calcified tissues for fluorine determines its persistent and cumulative retention in bones, being greater in growing organisms (Ortiz Ruiz, 1997). Drinking water containing about 1mg/L F⁻ promotes a significant caries reduction in children (ATSDR 2001). Fluorine plays a re-mineralizing role, through the chemical reactions in the surface enamel. If a reasonable level of F⁻ is present in the diet during the teeth growth stage, a significant amount of fluorapatite ($Ca_{10}(PO_4)_6F_2$) is incorporated in the enamel in place of hydroxy-apatite ($Ca_{10}(PO_4)_6(OH)_2$). Fluorapatite is less soluble in the buccal environment acids, making the teeth less susceptible to caries. Fluorine also performs a bacteriostatic function, since its presence in the buccal environment inhibits the bacteria enzymatic system, blocking the sugar unfolding and the consequent formation of acids that act on the enamel.

However, if fluorine is ingested in excess, during the teeth growth period, a chronic intoxication may occur and originate dental fluorosis, a pathology that is manifested through whitish to brownish stains on the teeth surface enamel or even through losses in its structure (Cardoso *et al.*, 2001, UNICEF, 2003). Skeletal fluorosis also develops a hardening or abnormal increase of the bones density in people who continually ingest quantities higher than 3 or 4mg/L F⁻. The maximum adverse effects are detected in the neck, back, knee, pelvis and shoulder articulations as well as hands and feet articulations (Gupta & Deshpande, 1998).

Fluorosis is endemic in at least 25 countries including China (where more than 100 million people suffer from fluorosis), Mexico (with 5 million people affected

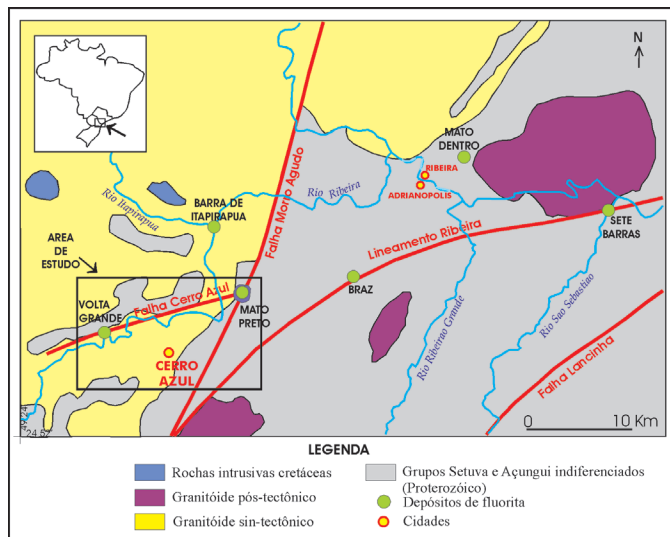Figure 1 – Location of the studied area and regional geological context (Ronchi et al. 1995).

LEGENDA

Rochas intrusivas cretáceas
Granitóide pós-tectônico
Granitóide sin-tectônico
Grupos Setuva e Açungui indiferenciados (Proterozóico)
Depósitos de fluorita
Cidades

by fluorine in groundwater), India (UNICEF, 2003) and Argentina (Bonorino et al., 2002, Warren et al., 2002, Blarasín et al., 2003).

Cangussu et al. (2002) observed a great variability of fluorosis prevalence in Brazil, according to the region, but confirmed that even with high prevalence, the proportion of people who present moderate or severe forms is still small. This incidence, increases only in sites where fluorosis is endemic due to the high content of fluoride in natural water.

In the Mocambo and Boca do Mato communities, in São Francisco, North Minas Gerais State, the groundwater fluoride content in some areas varies between 1,17 and 5,2mg/L F⁻ (Meneasse et al., 2002). In this town, prospective surveys for fluorite and galena have been carried out in areas of the Bambuí Group carbonate rocks.

Several articles (Licht et al., 1996b, Licht et al., 1997; Licht 2001), based on the Low Density Multielemental Geochemical Survey of Paraná, have delimited a large anomalous area in the North of the State, where contents up to 1.9mg/L F⁻ were found in water samples. In the São Joaquim do Pontal community, in Itambaracá, the prevalence of dental fluorosis found among the school children population was 72%; 61% of which had severity levels 4 and 5 (Cardoso et al., 2001).

Another fluorine exposure path is through inhalation. Finkelman *et al.*, (1999) describe health problems caused by fluorine excess, emitted from stoves that use coal and clay with high fluorine contents, for food drying and house warming.

GEOLOGICAL CONTEXT OF THE STUDIED AREAS

The Ribeira Valley lithological units belong to a NE Proterozoic mobile belt made up of an East domain (coastal complex) formed by Archean gneisses, migmatites and granulites reworked in the superior Proterozoic, and a West domain (Apiaí folding belt) which includes Proterozoic low to medium metamorphic grade volcano-sedimentary sequences and a small domain of Archean rocks. The metamorphic event happened between 600 and 700 Ma and both domains were intruded by granitoids ((Três Córregos and Itaóca) during the Brasiliano orogenic cycle (450-700 Ma) (Ronchi *et al*. 1995). During the Mesozoic, intense fissural basic volcanism correlated with the Paraná Basin igneous spills, took the form of Jurassic diabase dykes in a N45E direction. In the Cretaceous the emplacement of alkaline- carbonatite intrusions (sometimes bearing F, F, P and REE mineralization) occurred. The Phanerozoic sedimentary sequences from the Paraná Basin protected the Proterozoic mobile belt until its Tertiary uplift, when weathering processes ended up exposing basement rocks (Ronchi et al. 1995). In the VG deposit, fluorite is embedded in enclaves of carbonate rocks within the Três Córregos granites. The carbonate rocks were affected by a substitution processes involving

fluorite and silica (Ronchi et al. 1987). The deposit is built of three main bodies 460m in length, varying between 5 and 20m thick and as deep as 120m (Ronchi et al. 1995). Reserve estimations equals 1.1 Mt of ore bearing 35-40% of CaF_2, with the ore mainly composed of fluorite, quartz and secondarily by calcite, dolomite, pyrite and mica (muscovite and biotite), and very often the presence of barite and adularia (Dardenne et al. 1997).

The MP alkaline-carbonatite complex is situated on the margins of the Pinheirinho and Mato Preto Rivers, both tributaries of the Ribeira River. It shows a reserve of 2.16 Mt of ore with an average 60% CaF_2 content (Jenkins 1987).The complex builds a small stock located along the Morro Agudo fault zone, which represents the contact between metasedimentary rocks from the Açungui Group and the Três Córregos granites.

Many alkaline metamorphic stages had alternated in the complex formation and late-magmatic phenomena were responsible for silicification and fluorite enrichment processes. The alkaline rocks are Cretaceous and they are represented mainly by carbonatites, nepheline syenites and phonolites (Mattos 1989).

In the central Northwest part of the complex lays the largest volume of fluorite and sulfide rich carbonatites (Loureiro & Tavares 1983). The fluorite occurs in four N50-60E subparallel lenticular bodies measuring 250m long, 80m thick and up to 120m deep, according to soundings (Jenkins 1987). The carbonatite building activity has promoted, besides the fluorites, a concentration and enrichment process in magnetite, apatite, pyrite, bornite and in elements such as REE, niobium, thorium, zirconium, titanium and uranium (Loureiro & Tavares 1983).

MATERIALS AND METHODS

Surface water samples were collected from 18 sites during two sampling campaigns (July 2003 and March 2004), as well as two groundwater samples near the town of Cerro Azul. Water supplied by SANEPAR for consumption in Cerro Azul, as well as water from a spring that supplies the Mato Preto community were also collected. The physical-chemical parameters (pH, Eh, conductivity, dissolved oxygen, temperature, turbidity, SDT) were measured in situ. On the same day as sampling, the alkalinity analyses in non-filtered samples were made, through the titration method, using four drops of bromocresol and H_2SO_4 0.16 N. The samples for cation analyses were acidified with 4 drops of concentrated HNO_3 in a 50ml sample. The filtered water samples (Millipore <0.45µm) were analyzed by the Laboratory for Mineral Analysis - Laboratório de Análises Minerais (LAMIN), the anions Cl⁻, NO_2^-, Br⁻, NO_3^-, PO_4^{-3} and SO_4^{-2} by ionic chromatography and the cations Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sc, Se, Si, Sn, Sr, Ti, V, W and Zn, by ICP-OES. Na and K were analyzed by atomic absorption spectrophotometry.

The F⁻ contents were determined at the Geosciences Institute (IG) of UNICAMP with an ion selective electrode (EIS), Orion, model 96-09. The calibration curve was build from three reference solutions, each of them prepared with a 5ml solution of TISAB III, 50ml of standard solution 0.1, 1 and 10 mg/l of F⁻, respectively. To determine F⁻, 50ml of the filtered sample water and 5ml of the TISAB III solution were used, always in plastic beakers. In the same field campaign, another 14 flow sediment samples were collected (July 12 and march 2), which were analyzed for 30 elements in the granulometric fractions < 177mm and < 63mm, by an FRX at the IG of UNICAMP, using pressed powder samples. The F⁻ content was determined following procedures proposed by Hopkins (1977), consisting of the sample's fusion with a Na_2 and K_2CO_3 solution, followed by nitric acid addition and a buffer solution of sodium citrate before the EIS analysis. Two different reference materials were used for the F- analysis, giving acceptable results. The mineralogical composition of the sediments was determined by DRX at the X-Ray Laboratory of the Center for Geosciences of the Federal Pará University (UFPa). In some samples, the separation of dense minerals using bromoform and its difratometric analysis was carried out whereas in others, the clay fraction was analyzed (oriented, glycolated and heated sample). Complementary observations were made with a scanning electronic microscope (MEV).

RESULTS AND DISCUSSION

Water quality

In the Piper diagram the water shows a calcic bicarbonate type composition. Only sample 24 (groundwater) was within the limit between the fields of calcic bicarbonate and sodic bicarbonate water (Figure 2).

The physical-chemical parameters and the different ions analyzed for the water – including elements that represent a health risk - were compared with the maximum values allowed by the ANVISA Administrative Act Nº 518. Most of the analyzed water was found to be within the potability standards after conventional treatment.

The pH values were between 7.3 and 8 in the July/03 sampling and between 7.7 and 8.3 in March/04. The other water quality parameters presented these variations, respectively in the two sampling periods: Eh in the intervals 452-532 mV and 444-502 mV; electric conductivity/conductance 0.06-0.21 mS/m and 0.10-0.34 mS/m; OD 8.1-10.3 mg/L and 7.8-10.1 mg/L.; temperature 14.7-18.5 °C and 21.1-27.8 °C. During the March sampling the total dissolved
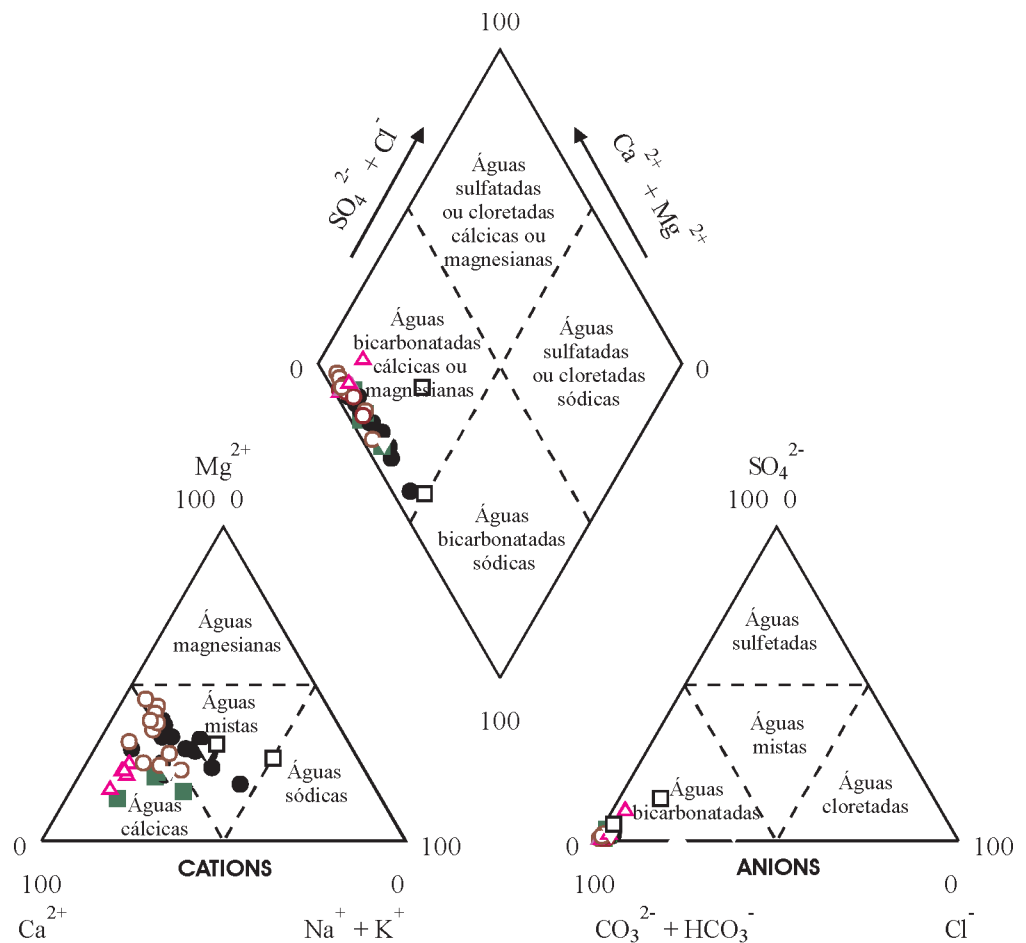
LEGENDA

● Águas superficiais de cursos não influenciados pelas mineralizações. Coleta julho/03

○ Águas superficiais de cursos não influenciados pelas mineralizações. Coleta março/04

■ Águas superficiais de cursos próximos aos depósitos de fluorita. Coleta julho/03

△ Águas superficiais de cursos próximos aos depósitos de fluorita. Coleta março/04

□ Águas subterrânea

Figure 2 – Piper Diagram for water classification.

solids concentrations (TSD) varied between 0.06 and 0.22 g/L, and the turbidity values between 2 and 45 UTN.

The concentration of Be, Cd, Co, Cr, Cu, Ni, Pb, Sc, Se, Sn, Ti, W and V were below their respective detection limits in all samples.

Fluorine contents exceeding the permitted limits were detected in the streams near the MP mine. The F⁻ concentrations in surface water varied between 0.07 and 2.54mg/L F⁻, the highest values corresponding to the samples situated in streams influenced by both mineralizations (Figure 3). It must be noted the July/03 sampling was planned to represent the dry period; however, there were strong rains the day before sampling, which provoked the dilution of the water samples. Thus, it was not possible to determine the maximum F⁻ contents in the region's water. Therefore it is possible there are other streams exceeding the permitted limit, for example the Pinheirinho River, where the F⁻ concentration was close to this limit.

For both campaigns, the samples with highest F⁻ contents also presented higher concentrations of Ca²⁺, Sr²⁺ and Ba²⁺, elements with geochemical affinity, whereas the highest values of F⁻ did not always coincide with the highest values of Si⁴⁺. In the groundwater samples (both situated within the granitic environment) contents of 1.13 and 0.33 mg/L F⁻ were detected.

The water catchment area for treatment and distribution to the Cerro Azul population by SANEPAR is situated in the Três Barras creek, where sample 12 was collected. This presented 0.12 and 0.14 mg/L F⁻ in the July and March campaigns, respectively. The F⁻ contents in the samples of consumption treated water were 0.84 and 1.02 mg/L F⁻ for Cerro Azul, in July and March, respectively and 0.23mg/L F⁻ for the Mato Preto community in March.

Analysis of the Stream Sediments

The sediment samples had F contents between 330 and 1,300 mg/g. In general, the F concentrations in the fraction <63mm were higher than those in the fraction <177mm, except for those samples close to the Mato

Preto mine (15a and 15b), due to its proximity to the spring and the shorter transport distance (Figures 4 and 5). It should be noted for some samples the difference between the contents determined for both fractions is within the analytic error of the method.

Of these mineral phases, those that possibly bring fluorine to the sediments are hornblende, illite and smectite. In the diffractograms of samples originating from sites near the mineralized areas, fluorite peaks were not identified, possible due to the experimental conditions of the diffraction analysis, where phases with a concentration lower than 1-2% in weight are not detected. For this reason these samples were also observed by the MEV, in which fluorite was confirmed through the elements mapping by dispersed electrons images. Other identified mineral phases were apatite (probably fluorapatite), baryta, biotite, zircon, rutile, ilmenite, quartz, feldspar and iron oxides.

CONCLUSIONS

With regards to surface water quality in the Cerro Azul region, this study revealed a risk area, situated near the Mato Preto deposits, where the water was not fit for human consumption because of the high fluoride concentrations. On the other hand, it was confirmed the F⁻ contents in the distributed water for consumption in
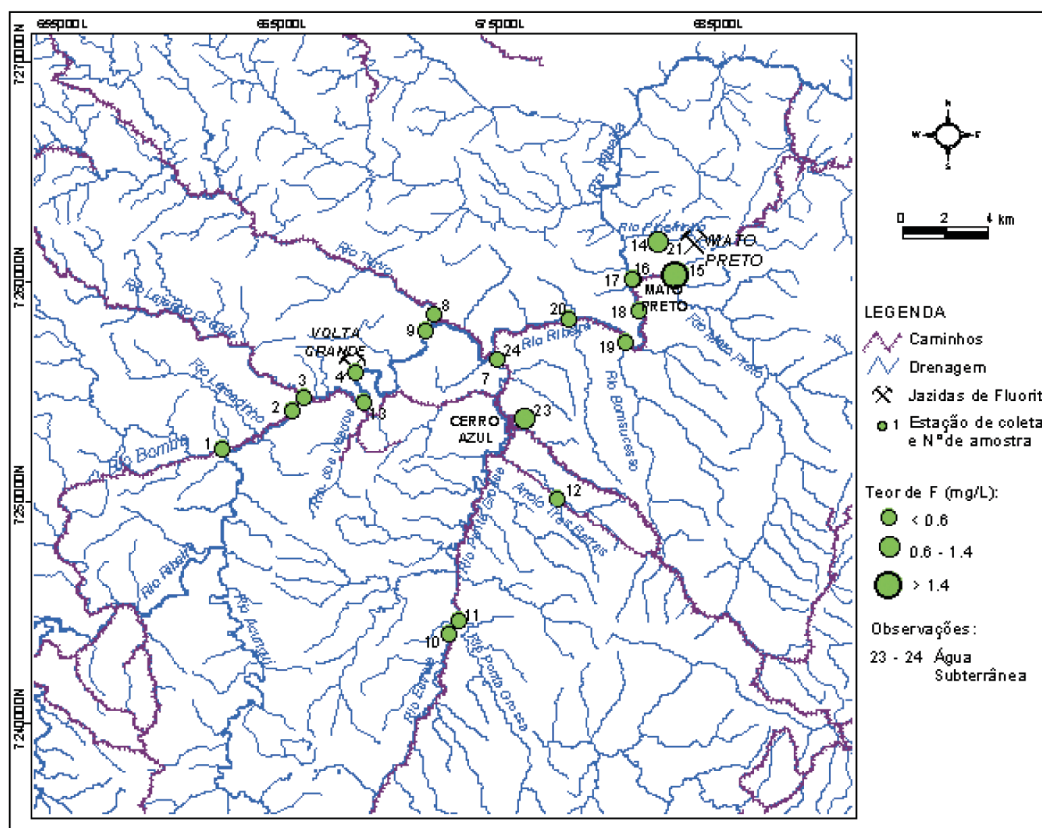
Figure 3 – Areal distribution of the fluoride contents in the surface water.
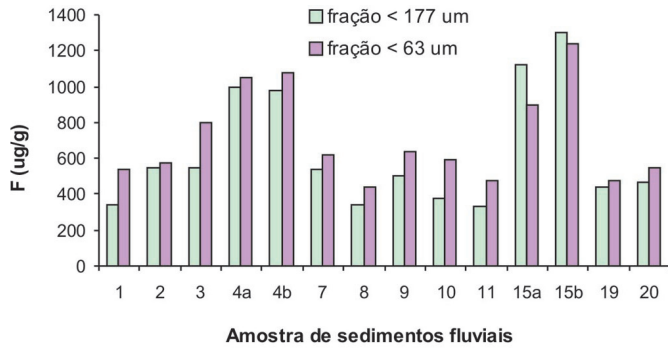
Figure 4 – Fluorine contents in both granulometric fractions from fluvial sediments.

Cerro Azul and the Mato Preto community were inferior to those established by law.

In the case of the stream sediments, the <63 mm fraction presented, in general, higher F contents than the <177 mm. This is due to the fluorine retention in clay minerals (especially illite and smectite) also present in this granulometric fraction, as well as fluorite, which due to its fragility, is more concentrated in the smaller fraction. Based on the region's mineralogical composition of the fluvial sediments and rocks, the possible F sources in the sediments may be: i) fluorite and apatite (probably fluorapatite) from the mineralized areas; ii) hornblende and biotite (and accessory minerals such as apatite and titanite) from granitic rocks, and iii) illite and smectite resulting from the alteration of the different minerals and from the siltic clayed metasediments of the Açungui Group.

Although the results show that the population's exposure risk to fluoride from surface water is low, it is estimated that the fluoride contents in groundwater are higher, given the longer interaction period of this water with the surrounding rocks. The well water sample (23), situated on a granitic area, presented contents close to
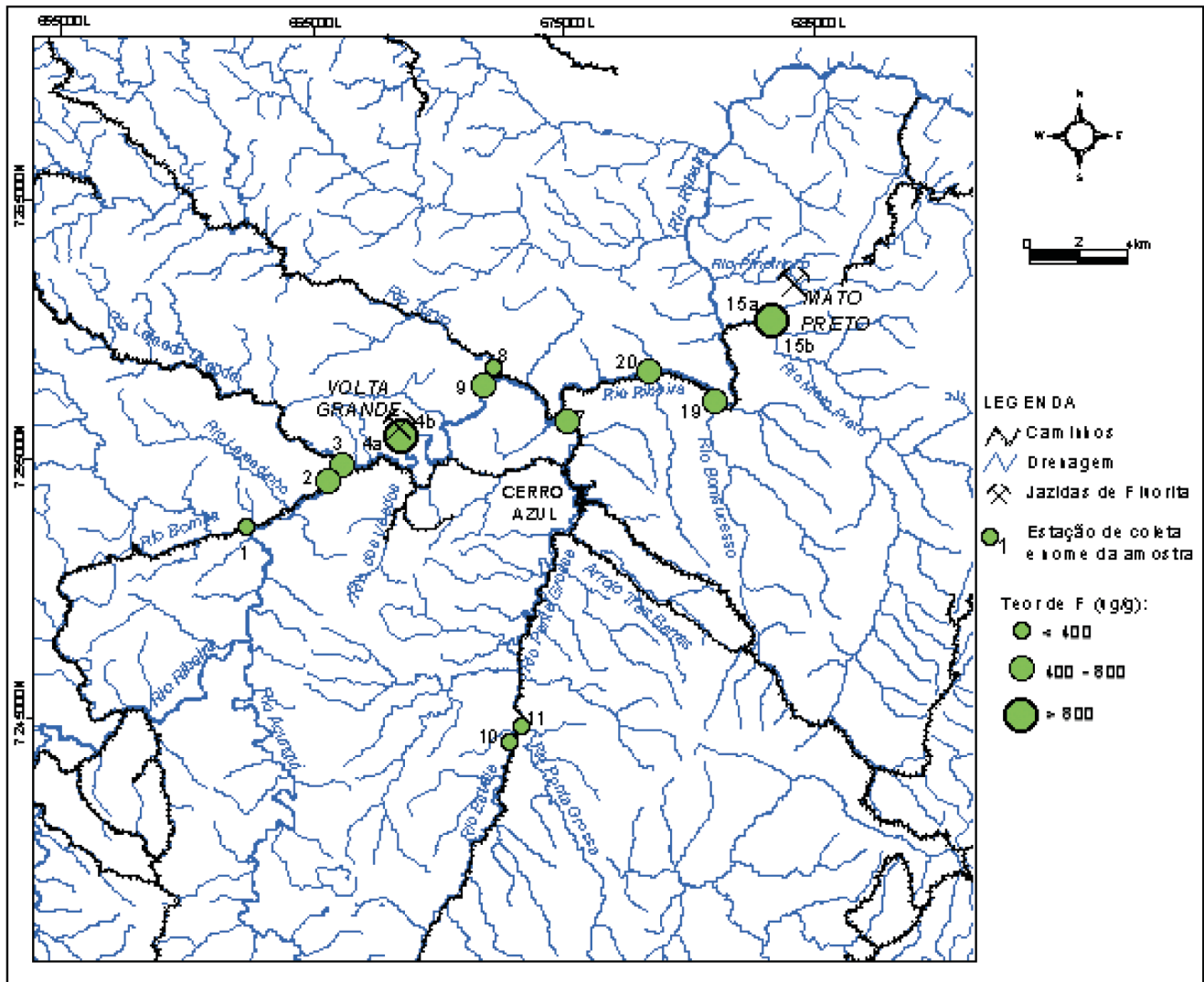
Figure 5 – Areal distribution map of the fluorine contents in stream sediments (fraction <177mm)

1 mg/L F⁻. Water from those aquifers situated in carbonate and alkaline-carbonatite conditions deserve special attention as the highest F⁻ contents were registered here. Therefore it is recommended, groundwater intended for consumption from private wells, is previously analyzed for F⁻ in addition to an exposure risk evaluation. It would also be interesting to determine the fluorine content in the region's soil and crops, which may pose as another fluorine source (via food) increasing the risk of fluorosis among these populations.

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HYDROGEOCHEMICAL STUDY OF FLUORINE IN GROUNDWATER OF THE CASSERIBÚ, MACACÚ AND SÃO JOÃO RIVER BASINS, RIO DE JANEIRO STATE BRAZIL

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INTRODUCTION

The studied region (Figure 1) is experiencing rapid demographic growth, which generates an increasing demand for water resources. Because of the lack and/or costs of a public supply (a water distribution network has been recently initiated by CEDAE), groundwater is being increasingly explored through wells, both shallow and deep, to meet the local commercial activities and population's demands.

This area has fluorite vein occurrences (a mineral composed of calcium and fluorine), of hydrothermal origin and embedded in normal and directional faults, 1 to 2 meters thick and tens of meters long. As a result, the groundwater in this region may present concentrations anomalies for certain chemical elements, fluorine among them.

Fluorine is a chemical element principally ingested by humans in drinking water (more than 70%) (Bowell et al., 1997 and Plant et al., 2001). In low concentrations (1mg/L), fluorite prevents the occurrences of dental caries, but excessive intake of the element (>4mg/L) can
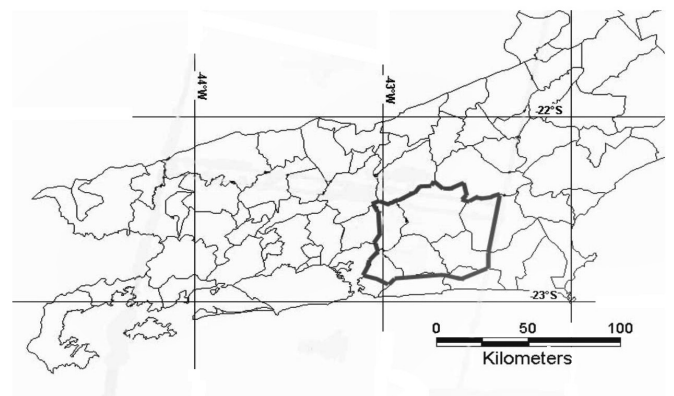

Figure 1 – Map of the State of Rio de Janeiro and location of the studied area

result in public health problems (ranging from dental fluorosis to skeleton deformation) (Moller, 1982), as well as problems when the water is used for other purposes (such as irrigation and animal demands). The relationship between fluorine and public health problems is well registered in areas of alkaline volcanic lithologies, as in parts of India, Sri Lanka, China and Eastern Africa (Dissanayake, 1996), but little is known of areas where fluorine originates from hydrothermal occurrences (Ferrari et al., 1982; Maddock and Dias, 1989).

Therefore, this region, due to its geological characteristics, its pattern of soil occupation and the incidence of human and animal fluorosis, merits a study on the occurrence, spatial distribution and geochemical behavior of this element to better manage the use of groundwater.

THEORETICAL FRAMEWORK

Groundwater is water that infiltrates rocks and soil, percolating until the hydrostatic level. Given that surface catchments (with an acceptable quality level) are becoming increasingly more distant (e.g. the Imunana CEDAE center, in Magé, to supply the populations of São Gonçalo and Niterói) and the treatment of excessively degraded water, or its reuse is restricted by technical and economical limitations, the use of groundwater is the most promising technical-economical alternative (Da Silva, 1984).

Groundwater is a natural renewable resource, therefore its long term exploration must be balanced and based on the available natural recharge.

Groundwater is considered polluted when the concentration of total dissolved ions or suspended solids, caused directly or indirectly by man, is higher than the maximum national (such as the CONAMA Resolutions) and international (WHO) permitted standard concentrations for potable water or for use in certain commercial activities.

In the case of groundwater unaffected by man with elements in concentrations exceeding such limits, the contamination can be defined by values in excess of global natural mean values for the contents in a given water source (Matthes, 1982).

Therefore it is essential to know the quality of a region's aquifers to define the naturally enriched element's variation, the geochemical mobilization mechanisms of these elements in the water, the cost/benefit for consumption and its viability for use in specific commercial activities.

There are countless factors considered responsible for groundwater contamination (Geraghty & Miller, 1972). In the studied region, possible contamination sources could be: i) fluorine rich mineral vein occurrences (Fluorite); ii) atmospheric emission from brick factories and mining companies and; iii) domestic and/or industrial sewage.

In recent studies (Maddock & Dias, 1988 and Maddock & Dias, 1989) of this region, anomalies in surface water fluoride concentrations of 12.5 mg/L were detected.

If ingested in low concentrations (1 to 3 mg/day), fluorine is recommended as a dental prophylactic and the appropriate development of bones. To be effective, almost all fluorine (>90%) must be dissolved in water in its most abundant form: fluoride. The intake of elevated doses (>40 mg/day) can cause the loss of the teeth glossiness and, in some cases, it can reach the stage of skeletal deficiency, causing rheumatic pains and/or arthritis (OMS/WHO, 1970).

Natural fluorine concentrations can vary from trace-concentrations to 2.800 mg/L, as in East Africa (Gaciri & Davies, 1993). Fluorine concentrations in natural water depend on several factors such as: temperature, pH, the presence or not of mineral complexes, precipitated ions and colloids, a mineral's solubility, its ionic exchange capacity, granulometry and the type of lithology and the waters' time of residence (Apambire et al., 1997).

Minerals that influence the fluoride hydrogeochemical concentration variation are: fluorite, apatite, mica, amphibole, certain types of clay and vermiculite. Fluorite is the main mineral controlling the fluoride concentration in water. The total fluoride released in water with weak ionic potential for fluorite dissolution is about 8 to 10 mg/L (Boyle, 1976). However, the concentrations of Ca, Na, hydroxyls and certain ionic complexes can change this dissolution rate. Studies have indicated a high negative correlation between Ca and F concentrations in water with Ca concentrations above that for the F solubility (Boyle 1976, 1992). Voroshelov (1966) demonstrated that water with high Ca contents influence the fluorine dissolution.

Sodium usually presents a positive correlation with fluoride in different types of groundwater, especially those with low Ca concentrations. High Na concentrations increase the fluoride solubility in water (Apambire, 1997). This process results in high fluoride concentrations in water (>30 mg/L), but in the presence of clay this is not the case as the process involves base exchanges (Ca and Mg for Na) that progressively shift the pH to more alkaline water, typical of sedimentary basins (Boyle, 1992).

Recent studies have demonstrated that fluorine forms mono and difluor complexes with REE and that this mechanism of fluorine mobility into water is not fully understood (Sallet *et al.*, 2000 and Schijf & Birne, 1999). Fluorite is a mineral that commonly presents REE and Y concentrations. Certain occurrences with elevated concentrations (above 13% of the total Y weight and 14.1% of the total Ce weight) have already been mentioned in specialized literature. The REE tend to replace the Ca in the mineral structure, indicating that an enrichment of the concentrations of both heavy and light REE can occur. Rocks in hydrothermal deposits exhibit concentrations of the whole REE series and studies have demonstrated that

REE rates, such as Tb/Ca X Tb/La, can indicate whether the fluorite deposit is from hydrothermal origins or from sedimentation processes, due to the REE fractionation in fluorite (Henderson, 1984). In the case of apatites, secondary minerals in the region's lithologies, some group members have relative ERR concentration, but the fluorapatites, generally have low, but significant, concentrations, which vary between 0.01% and 12% (alkaline rocks). The REE replace the Ca in the apatites structure, forming Ce and Y complexes (Henderson, 1984). In addition, the ERR behavior and complexation in water, related to the water's acidity or alkalinity, mainly for minerals like apatite (Johannesson et al., 1996 and Fleet & Pan, 1997) and/or phosphate minerals with fluorine content, is not well explained.

As a consequence, it is important to carry out ERR hydrogeochemical analyses in the region to define the hydrogeochemical mechanisms that make fluorine available in the environment.

PARTIAL RESULTS AND DISCUSSION

The results were plotted on a map showing the F- concentration contour curves (Figure 2). The map indicates the highest concentrations (>6 mg.L^{-1}) were obtained between the towns of Tanguá and Rio Bonito, a region with fluorite vein occurrences, especially affecting deep wells. Shallow wells presented low concentrations of the element, suggesting that the water is diluted by rain and/or that these wells receive infiltration from surface water. The highest concentrations obtained are within the maximum potability standards established by the WHO and the Ministry of Health. Analyzing the correlations between elements, a close to negative correlation is confirmed between the Ca and F concentrations in water with Ca concentrations above that for F solubility (Boyle,

1976, 1992). Voroshelov (1966) demonstrated that water with high Ca contents condition the fluorine dissolution. Analyzing the correlations between F and Na, an element that normally has a positive correlation with fluoride in several kinds of groundwater, especially those with low Ca concentrations; the Na concentrations increase fluoride solubility in water (Ampabire, 1997). This process is not well understood when it involves several lithologies, since the process involves base exchanges (Ca and Mg for Na) that progressively shift the pH to the field of alkaline water. Based on the results of the concentrations' spatial distribution, it is confirmed that the region's groundwater is inadequate for consumption due to the high fluorine concentrations.

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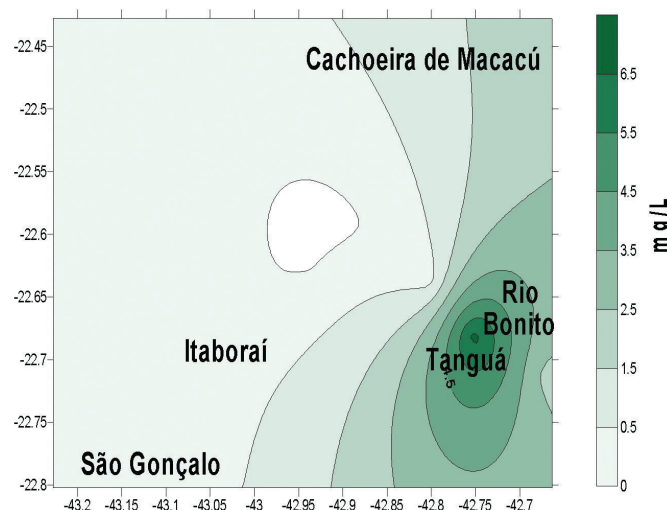
Figure 2 – Distribution of Fluorine in the studied area groundwater.

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MERCURY NATURAL OCCURRENCES IN PARANÁ STATE BRAZIL

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INTRODUCTION

The regional geochemical surveys carried out in Paraná State, North Brazil, indicated extensive positive mercury anomalies. One, identified in a geochemical survey of active stream sediments (ASS), showed a geographical correlation with some deep tectonic structures that cut across the Paraná Basin igneous rocks (São Bento Group – Mesozoic) that has many thermal artesian water springs. Whereas, the geochemical survey on the B soil-horizon (SOLO) showed a regional anomaly coinciding with the carbon rich sedimentary sequences of the Paraná Basin (Paraná, Itararé and Passa Dois Groups – Paleozoic). In another geological context related to the Proterozoic, both surveys, but especially the SOLO, showed that the known Ribeira Valley Pb-Zn deposits and mineralizations may be responsible for this geochemical anomaly.

These geologic-geochemical correlations enabled the authors to build the following study hypotheses: a) existing metal mobilization within some of the sedimentary sequences of the Paraná Basin through thermal water percolation along deep faults, followed by the metal deposition on the surface and b) association with the Ribeira Valley Pb-Zn-Ba ore processes.

OBJECTIVES

This study sought at this stage to compile the available data on the presence of mercury in Paraná State (Figure 1), related to different geological settings. These support the genetic hypotheses for the geochemical anomalies on the surface and on the regional scale (geochemical survey of active stream sediments, and geochemical survey of soils-horizon B – SOLO) as well as on a detail scale (Salto do Itararé region – SOLO and Palmeira region – SAD), Figure 2 and Figure 3 respectively.
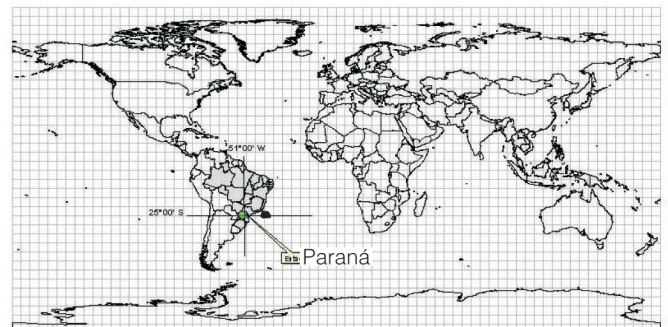
Figure 1 – Geographical location of Paraná State.
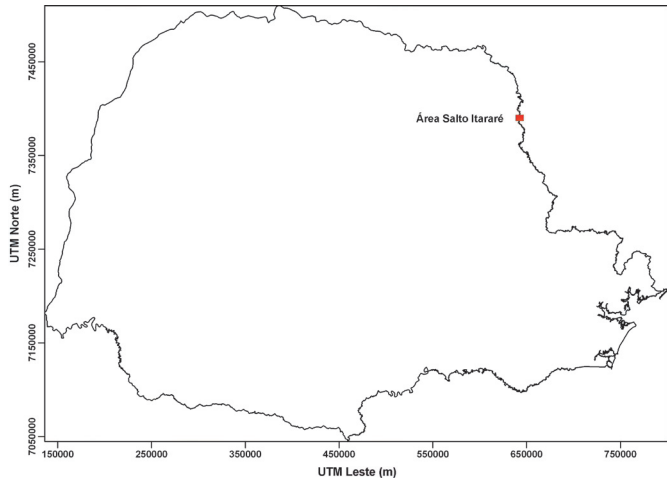
Figures 2 – Geographical location of the Salto do Itararé area in Paraná State.
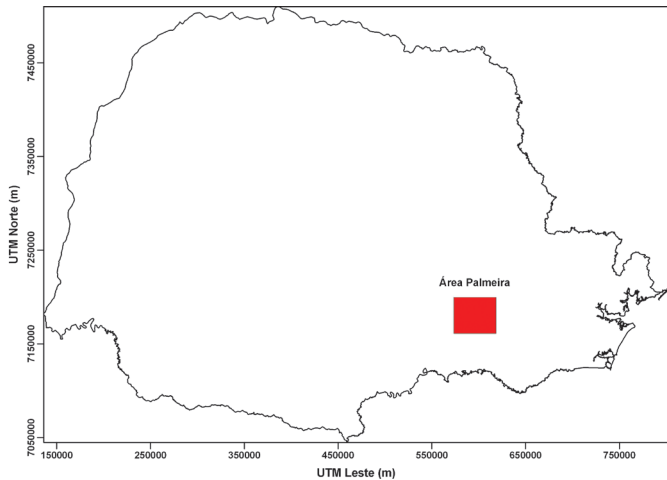
Figure 3 – Geographical location of the Palmeira area in Paraná State.

HISTORY

The study revealed that since the early 19th century, there have been many references to mercury in several Paraná State communities.

Ferreira (1885) refers to a "mercury mine" discovered in 1842 in the Palmeira region, near the Castelhanos River, an Iguaçu River tributary (Figure 4). Located 13 kilometers from the "Palmeira community", Ponta Grossa municipality, there is a quicksilver /mercury mine which was later examined by the Kellers - father and son engineers, who found it to be important. Furthermore, Dr. Paulo José d'Oliveira informs in his memories (sic) published elsewhere: - "The creek on whose bed the quicksilver/mercury was found, originates in a swamp formed by a water spring. Further below there are some loose stones to be found among which, in drought times, the aforesaid

mineral can be collected with ease. The Baron of Tibagy asserts that a naturalist, who visited the place, had told him that the mine was very rich and on another occasion he had already obtained, with ease, half a pound of quicksilver/mercury on his request." The same author later refers: "It is impossible that the least doubt still remains today about the existence of quicksilver /mercury mines in the Province. Samples of the famous liquid metal had already been sent to various expositions. The Kellers, German father and son engineers, had examined the mine situated 13 kilometers from Palmeira." Finally, the author makes the following reference "Manoel de Assis Drumond and Bernardo Pinto de Oliveira – Decree n° 6246 of July 12th 1876 – They are granted permission to explore quicksilver/mercury in Villa da Palmeira. This grant was extended (sic) by Decree nº 6876 of July 20th 1878, and later by Decree nº 7392 of July 31st 1879."

The Collection of Laws of the Brazilian Empire – 1876, Acts of the Executive Power confirms - Decree nº6246 of July 12th 1876 where the Regent Imperial Princess grants Manoel de Assis Drumond and Bernardo Pinto de Oliveira the authorization to explore quicksilver/mercury mines in the Province of Paraná. Decree nº 6976 of July 20th 1878, extends the concession for another year (Figure 5).

HgS) grains were found in the marmites excavated by the water on the river bed made of sandstones of the Itararé Group (Paleozoic). The transcription states: "The presence of mercury was signaled in the Castelhanos
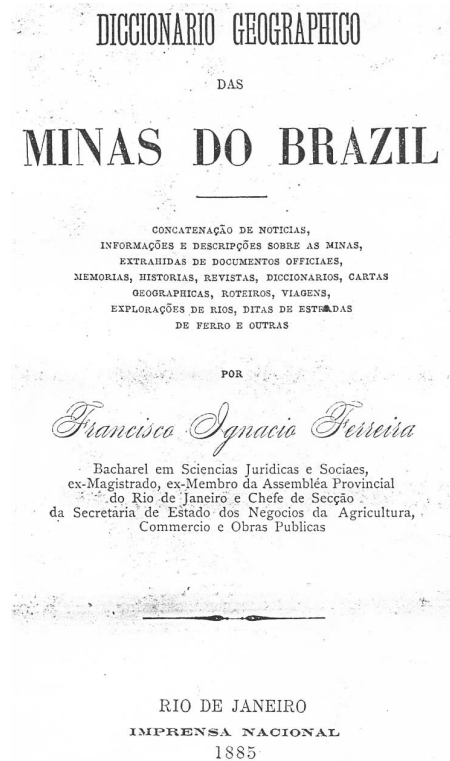
Figure 4 – Front page of the Geographical Lexicon of Mines in Brazil - "Diccionario Geographico das Minas do Brazil" (Ferreira, 1885).
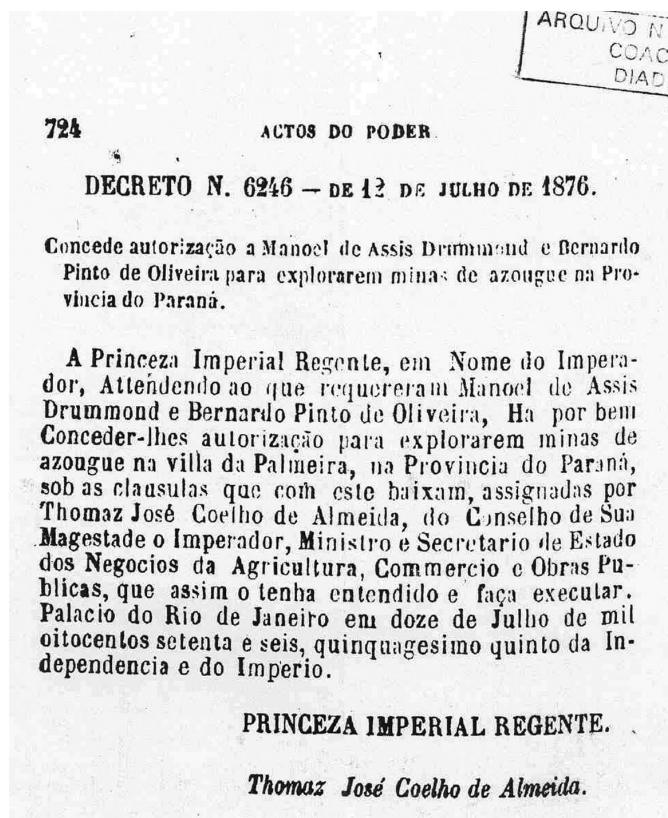
Figure 5 – The Imperial Decree nº 6246 of July 12th 1876, for the exploration of the mercury mine in Villa de Palmeira (National archives).

creek, a tributary of the the Iguassú River, in the town of Palmeira. The first notice appeared in the report of the engineers Keller on the exploration of Ivahy River. Lead by wrong observations, they made the description of the deposit. Drops of the metal were found in potholes open in sandstone of the Itararé Series. In 1902, Drs. F. de Paula Oliveira and Eugenio Elmo made the very detailed examination of this region, having studied almost all the creeks, from Restinga Secca to Porto Amazonas on the Iguassu. The investigations were negative, but Dr. Elmo assured me that he had found some grains of a mineral that, after having been analyzed, revealed sulphide of cinnabar mercury. As for native mercury nothing was found."

The National Department of Mineral Production (Departamento Nacional de Produção Mineral – DNPM) granted, in 1935, the mining license nº 3127 for mercury in the region of Salto do Itararé. The original document has not been found in the DNPM archives.

MATERIAL AND METHODS

Seeking to confirm these historical references to the occurrence of mercury in Paraná State, some periodic geochemical surveys were carried out by MINEROPAR.

In 1984, on the Paranapanema River right margin, near Salto do Itararé, in a regular grid with a base line orientation N75E, 110m wide transects with sampling sites every 45m, 75 soil (horizon B) samples were collected (MINEROPAR, unpublished, apud Plawiak et al., 2004). The fraction <0.177mm (<80#) of the soil samples was analyzed in a commercial laboratory through Atomic Absorption Spectrophotometry with cold steam.

In 2003, in Palmeira, 70km west of Curitiba, 17 samples of active stream sediments were collected in the Tibagi and Iguaçu River basin head areas (MINEROPAR and Evandro Chagas Institute – ECI, unpublished, apud Plawiak *et al.*, 2004). The basin areas varied between 10 and 60km². The samples were analyzed by the Toxicology Laboratory, Environment Section of the ECI, in two granulometric fractions: <0.104mm (<150#) and <0.062mm (<230#), through Atomic Absorption Spectrophotometry with cold steam.

The mercury distribution on a regional scale was identified by two ultra low density surveys that followed the standards established by the Global Geochemical Reference Network – GGRN. The first Low Density Multi-elemental Geochemical Survey (Licht, 2001), was based on 696 samples of active stream sediments representing practically all hydrographic basins in Paraná State, from which 39 composite samples were produced, representing the GGRN cells (Figure 6). The second Low Density Multielemental Geochemical Survey was based on 307 samples of the soils' horizon B (Licht & Plawiak, 2005) representative for the whole Paraná State territory, from which 43 samples were built representing the 43 GGRN cells, (Figure 7).

The Hg geochemical data of both regional surveys were obtained through Atomic Fluorescence Spectrophotometry with cold steam in the Institute of Geophysical and Geochemical Exploration – IGGE Laboratory, Langfang, Hebei, China.

The geochemical maps were combined with the digital terrain model (DTM) for the entire Paraná State, built with 900,000 altitude points extracted from topographic maps on the scale of 1:250.000 published by the Brazilian Institute for Geography and Statistics – IBGE. The DTM was projected with an azimuth of 345°, inclination of 45°, light source of a horizontal angle of 135° and a vertical angle of 45°. The coordinate system used was the UTM with SAD 69 horizontal datum and central meridian of 51°.

To explain the mercury distribution on the surface allowing correlations with geological settings (having the Figure 8 geological map as a layer – MINEROPAR, 1986), the main tectonic features(Figure 9) (such as that identified by Zalán et al., 1987) and the data obtained by the regional and detailed surveys, a Geographical Information System - GIS was developed. The geological cross-section NW-SE of the Paraná Basin was used as a secondary background information, (Figure 10) (Bizzi *et al.*, 2001).
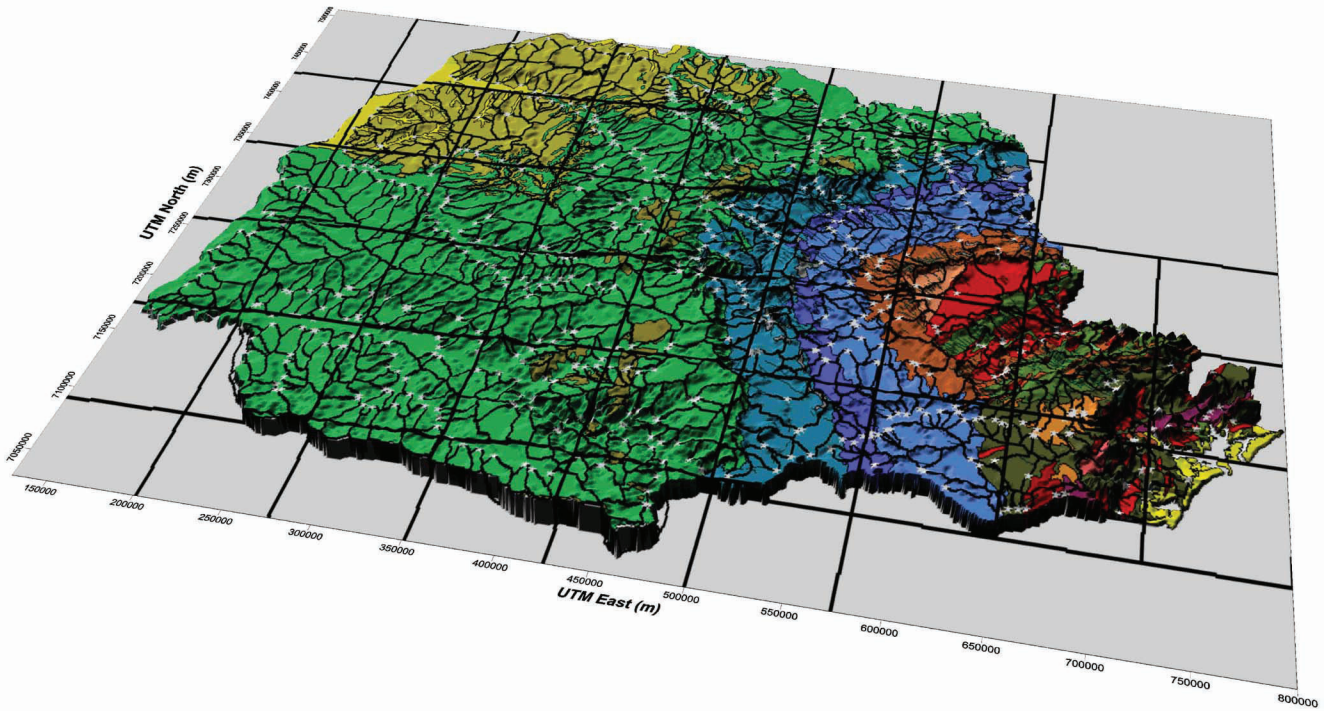
Figure 6 – The GGRN cells, the 696 sediment samples and their watersheds (modif. Licht,2001).
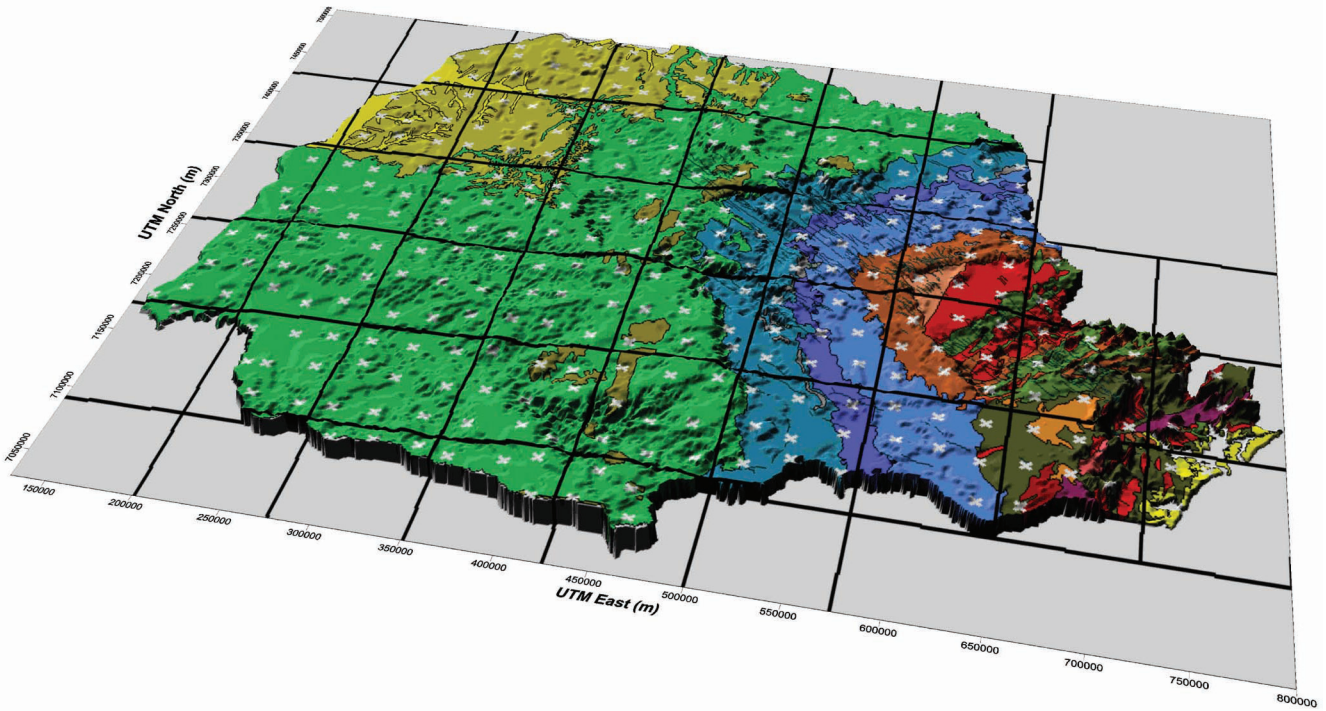
Figure 7 – The GGRN cells and the 307 soil samples – B horizon (Licht and Plawiak, 2005).
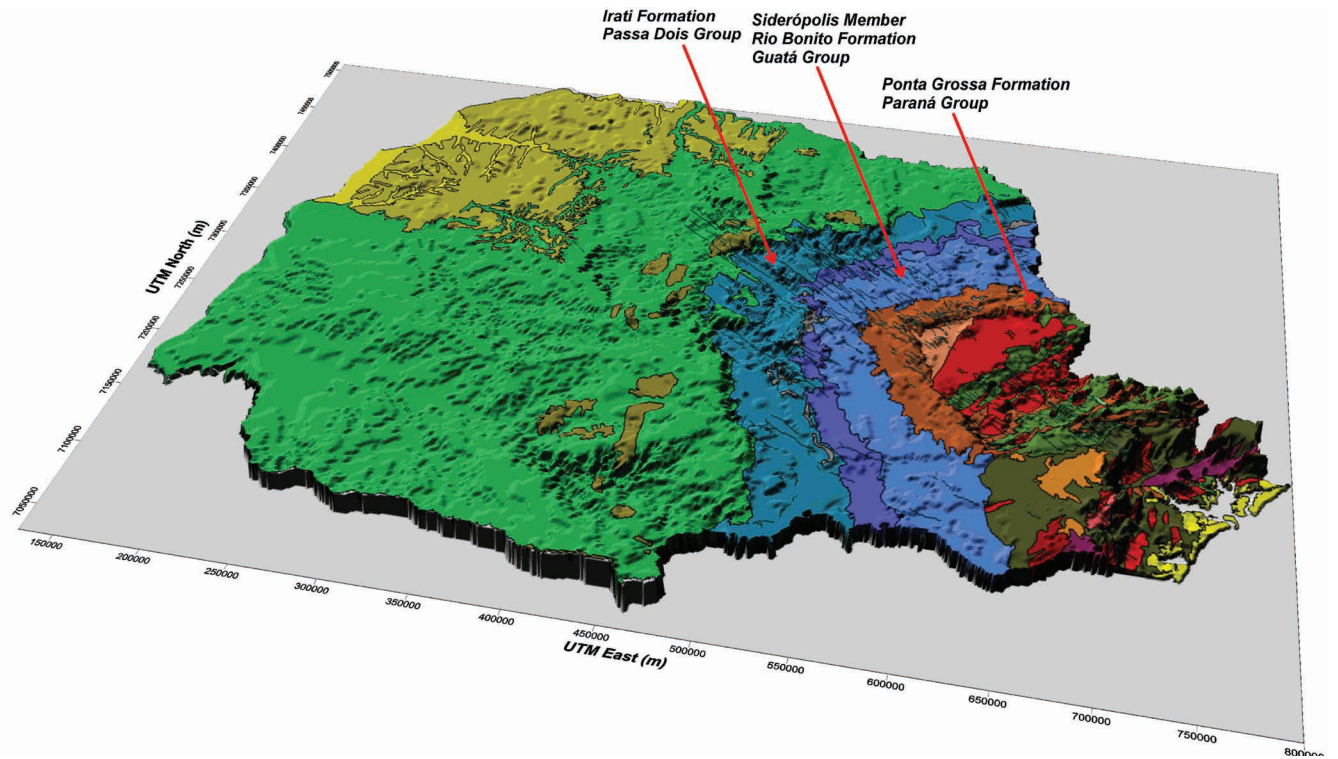
Figure 8 – Simplified Geological Map of Paraná State (modif. MINEROPAR, 1986).
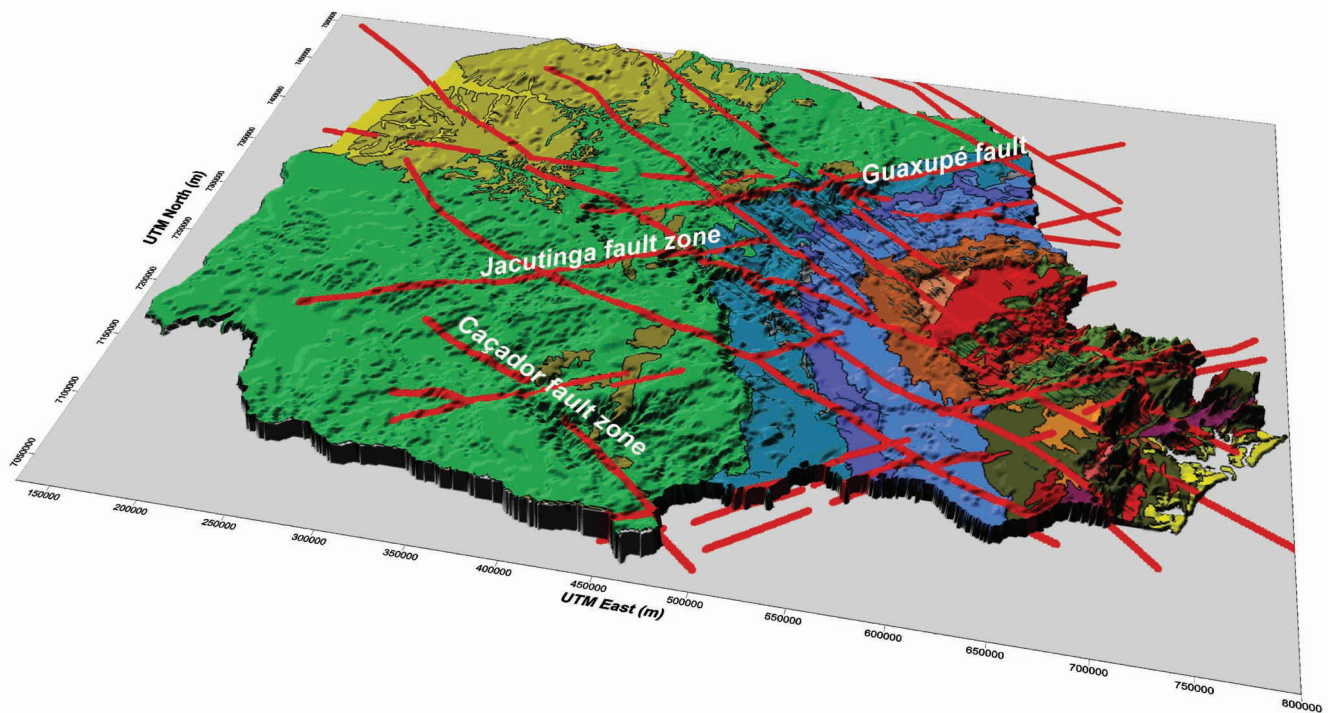
Figure 9 – The main fault zones of Paraná State (modif. Zalán et al., 1987).
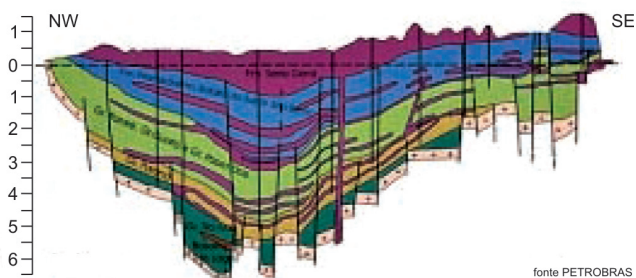
Figure 10 – Schematic cross section NW-SE of the Paraná Sedimentary Basin (Bizzi et al., 2001).

RESULTS

Several mercury anomalies are shown in the geochemical maps (regional or detail) within the Paraná State territory.

Relatively elevated mercury contents occur in both granulometric fractions of the samples collected in the Palmeira region (N=17) of the Tibagi River head. The mean content in the fraction <150# is 30 mg/kg Hg with the highest values between 41 and 62 mg/kg Hg (Figure 11). In the fraction <230#, the mean content is 27 mg/kg Hg, with the highest values between 29 and 67 mg/kg Hg (Figure 12).

The mean of the significant values (higher than the detection limit) (N=10) of the soil samples from Salto Itararé is 56 mg/kg Hg with the highest value of 80 mg/kg Hg in the center-West portion of the sampling grid (Figure 13). The other samples (N=65) showed Hg contents lower than the detection limit of 5 mg/kg Hg.

The mean content of the GGRN-ASS samples is 33.34 mg/kg Hg. The highest contents, between 49.47 and 53.08 mg/kg Hg, are situated in the South-East region of Paraná State in the direction N53W, practically restricted to the Iguaçu River valley coinciding with the Caçador fault zone (Figure 14).

The mean mercury content in the GGRN-SOIL samples is 60.90 mg/kg Hg. The large geochemical anomaly along the Caçador Fault zone, identified on the map after the active stream sediments, is no longer evident due to the overall higher background values (between 80.91 and 167.5 mg/kg Hg) (Figure 15). This regional mean increase of Hg content is largely caused by the effect of the mineralizing processes (Pb-Zn-Ba) that occurred in Ribeira River valley, as identified by Daitx (pers. com. Elias C. Daitx, 2004). High mercury values were found in the ore of Pb-Zn (14,000 mg/kg Hg) and in the barite gangue.

In the regional geochemical surveys, the mean mercury content of the Paraná Basin igneous rocks (Serra Geral Formation) are between 42.73 and 49.47 mg/kg Hg in the GGRN-ASS samples and between 69.04 and 80.91 mg/kg Hg in the GGRN-SOIL. A tectonic control

seems to play an important role since they coincide with the Guaxupê and Jacutinga Fault directions (N60E).

CONCLUSIONS

The great regional geochemical structures may be understood as the surface expression, of the interaction of several geological and geochemical factors. Some hypotheses must be investigated to establish the veracity of cause-effect relationships between the geology and the tectonic structures.

An important research field deals with the mobilization of Hg within the carbon rich horizons of the Paraná Basin sedimentary sequence. The lithostratigraphic units containing rocks favorable to Hg accumulation are: a) Ponta Grossa Formation, Paraná Group; b) Siderópolis Member, Rio Bonito Formation, Guatá Group; c) Irati Formation, Passa Dois Group. The mercury mobilization at relatively low temperatures (about 40°C) may occur through remaining and residual hydrothermal activity, along the fault zones of Caçador (NW), Guaxupé (NE) and Jacutinga (NE), which cut deeply across these sedimentary units.

Many thermal water springs and artesian springs are known in the South-West of Paraná, which reinforces the possibility of fluids migration from the Paraná Basin deep regions, with temperatures capable of mobilizing and transporting Hg to the surface, where the metal would be precipitated by the sudden fall in temperature. Bingqiu & Hui (1995) came to similar conclusions about the presence of Hg in thermal water springs.

In the Salto do Itararé region, the Guaxupé and Jacutinga faults may be the structures responsible for the Hg mobilization. In the Palmeira region, the geochemical anomaly on the surface must be related to the Cândido de Abreu/Campo Mourão fault zones intersection with the Lancinha/Cubatão fault zones.

In the case this hypothesis is confirmed, remobilization of Hg by thermal waters from the Paraná Basin Paleozoic sedimentary sequences along the Fault zones are likely to occur, particularly in carbon rich horizons, black shale deposits and coal deposits.

Finally, the cause-effect relationships between the large anomalous areas of the Ribeira River valley and the mineralizing processes of Pb-Zn-Ba deserves special attention, particularly considering the risk to the population's health in the area adjacent to the former ore processing plant and concentrate melting process site in Adrianópolis.
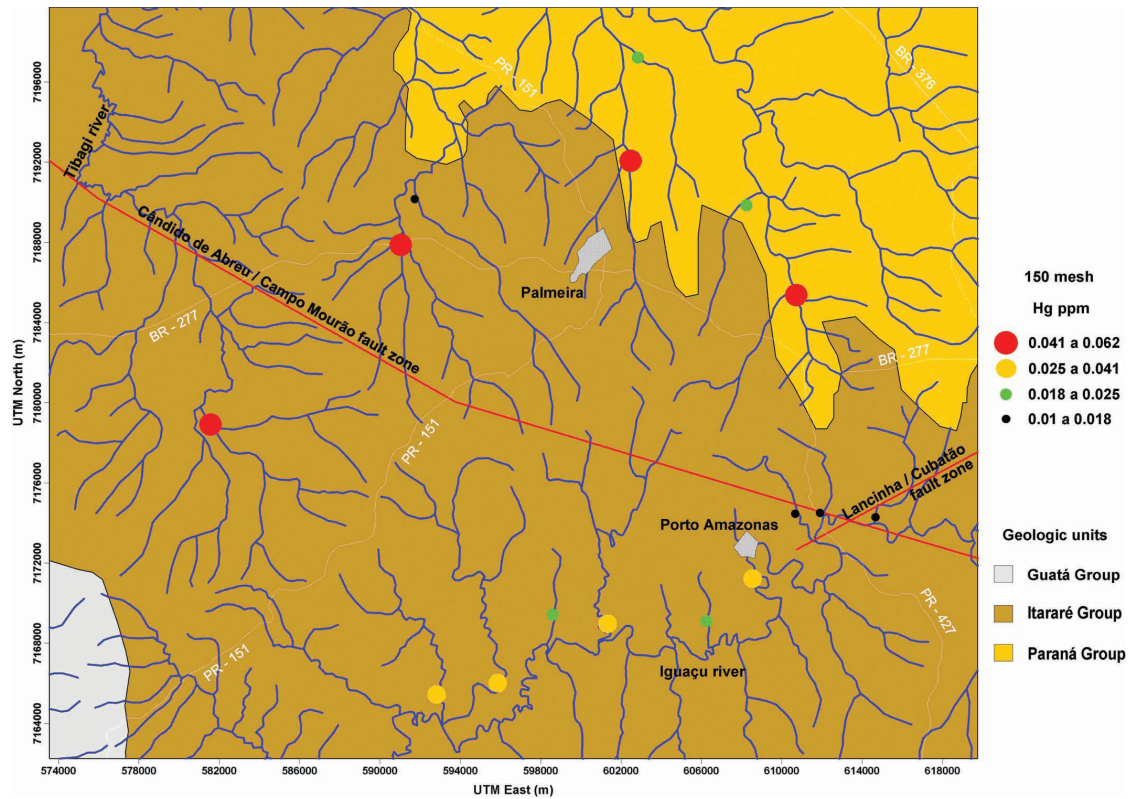
Figure 11 – Geochemistry Map of the Hg in the fraction < 150# from active stream sediments of the Palmeira region
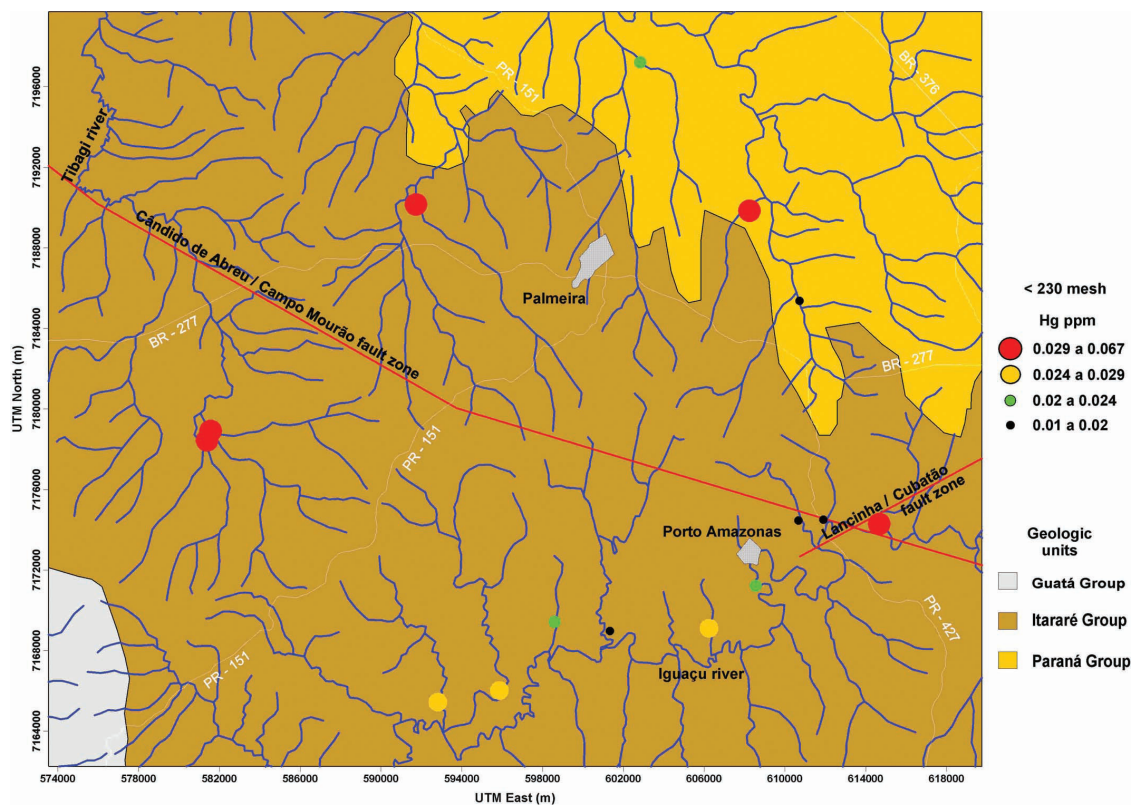
Figure 12 – Geochemistry Map of Hg in the fraction < 230 # from active stream sediments in the Palmeira region.
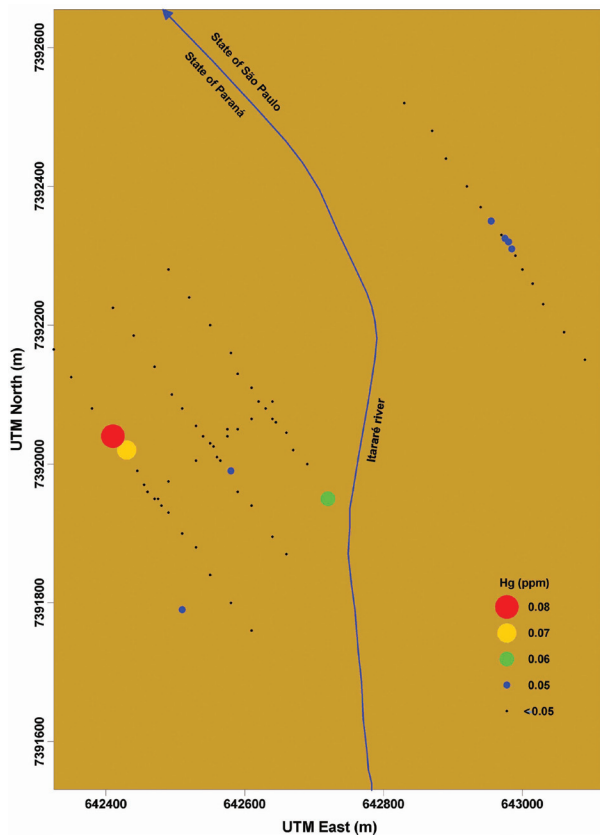
Figure 13 – Geochemistry Map of Hg in the fraction < 150 # from soils in the Salto do Itararé region.
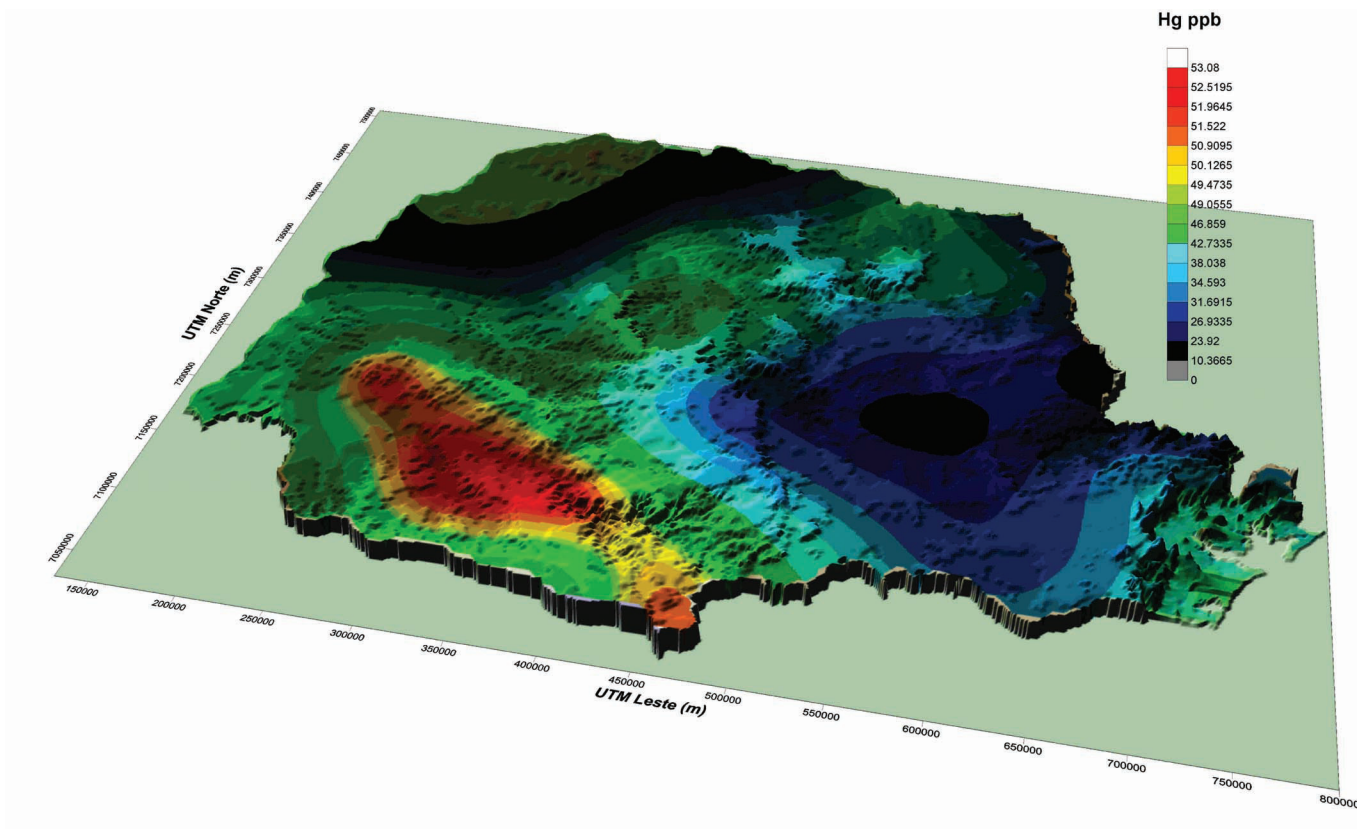
Figure 14 – Geochemistry map of Hg (mg/kg) in GGRN – ASS cells.
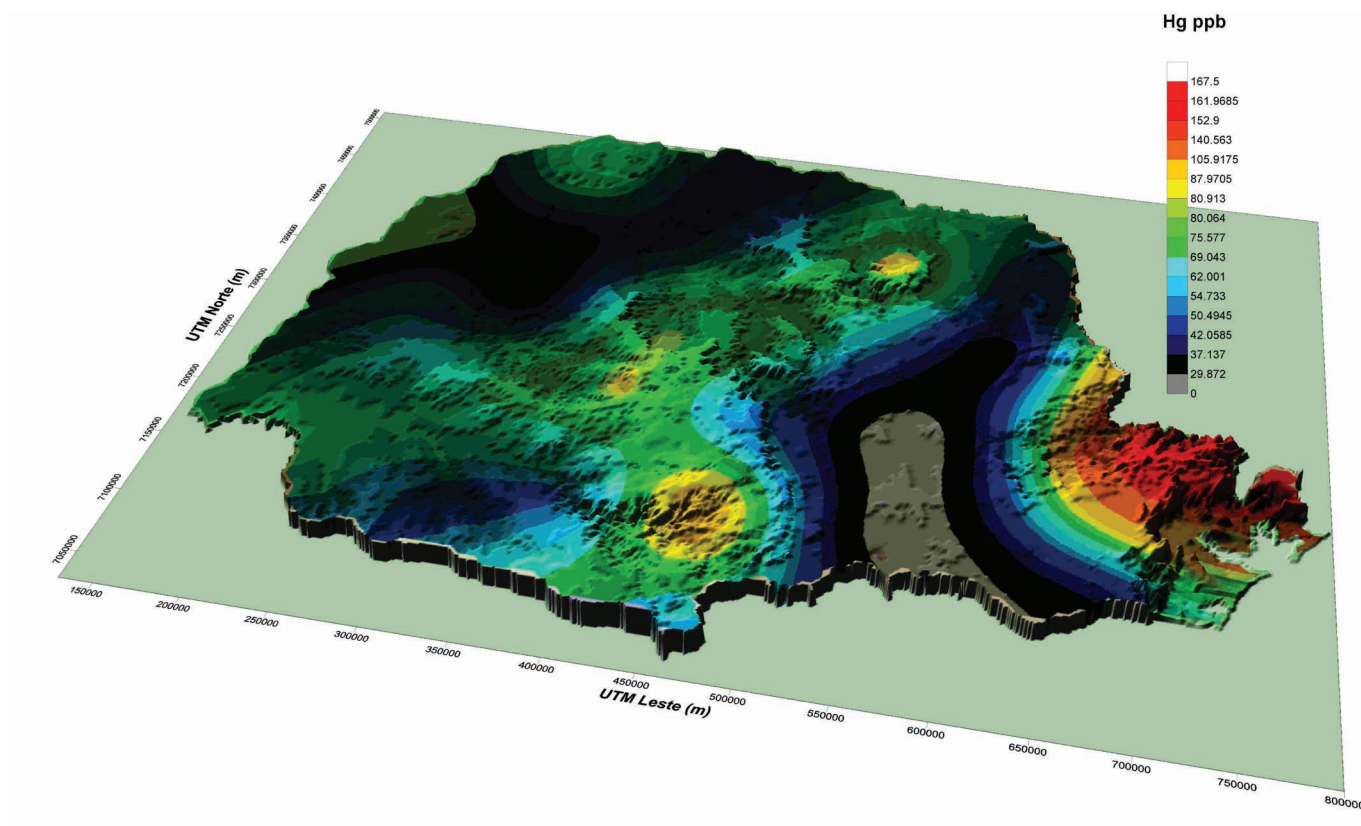
Figure 15 – Geochemistry map of Hg (mg/kg) in GGRN – SOIL (B horizon).

To Dr. Edilson da Silva Brabo, from the Evandro Chagas Institute, for the mercury contents made on the active stream sediment samples from the Palmeira region.

To Mrs. Kátia Borges and M. Antonio Carlos G. Valério from the National Archives for the research and identification of the 19th century documents.

To Dr. Paulo Roberto Amorim dos Santos Lima for his kindness of sending me a copy of the Diccionario Geographico das Minas do Brazil (Ferreira, 1885) from his private library.

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CONTAMINATION BY ANTHROPOGENIC MERCURY IN SOIL AND STREAM SEDIMENTS IN LAVRAS DO SUL MUNICIPALITY – RS BRAZIL

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INTRODUCTION

This study is part of the Project "Anthropogenic Mercury in Streams Associated with the Auriferous Mining in Lavras do Sul", which is being made in partnership with the Brazilian Geological Service – CPRM (Serviço Geológico do Brazil) and the State Foundation for Environmental Protection – FEPAM, Rio Grande do Sul State. This Project integrates the National Research Program in Environmental Geochemistry and Medical Geology (Programa Nacional de Pesquisa em Geoquímica Ambiental e Geologia Médica – PGAGEM), coordinated by the CPRM.

Gold mining in the Lavras do Sul – RS auriferous region (Figure 1) officially dates from the late 19th century. The mineralization originated through hydrothermal processes occurs as E-W auriferous quartz veins with Fe, Cu and/or Pb sulphides. They are surrounded by andesites and associated volcaniclastic rocks from the Hilário Formation and by some granite from the Lavras do Sul intrusive complex, as described by Gastal, 1997.

The gold content in the mineralization was low, on average 5g/t (Calógeras, 1938). Most of the ore extracted from several region mines was processed by one of three grinder plants in Chiapetta, Paredão and Cerro Rico, that functioned in different periods until the early 20th
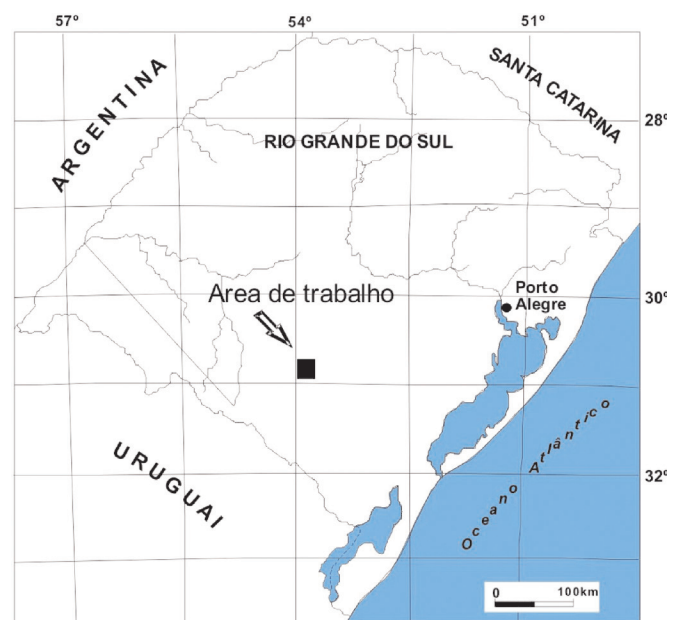
Figure 1 – Location of the research area.

century. Mercury was used as amalgam in the grinders, and also by the gold diggers and, in the late 1980s, by the Mining Company of Rio Grande do Sul (Companhia Riograndense de Mineração -CRM). The resulting residual Hg contamination in the neighborhood of some of these processing units was confirmed by Pestana & Formoso (2003) in soil samples from the CRM and Chiapetta Grinder areas and by Pestana et al. (2000) in sediment samples from the Cerro Rico Grinder treatment pool.

OBJECTIVES

To confirm the presence of Hg contamination in soil near the processing units in comparison to soil from more distant sites;

To check the dispersion degree of Hg contaminated soil through the analyses of stream sediments;

To establish the thresholds and background mean values for Au, Fe, Mn and other elements of environmental interest, such as As, Cd, Cu, Hg, Pb and Zn in soils and stream sediments over the granites and andesites;

To compare the obtained thresholds with current Brazilian guidelines (CONAMA and CETESB).

METHODOLOGY

Eight soil samples over andesitic rocks were collected: one adjacent to the CRM processing area, another near the Cerro Rico processing unit and six samples from sites far from the processing plants. In the granite areas, three samples were collected from: i) inside the Chiapetta Grinder processing area; ii) outside the same location and iii) a reference non-contaminated soil, far from the processing area. 24 stream sediments were collected

in streams draining granite rocks and 19 over andesitic drainage areas.

The soil samples belong to the A horizon. They were sieved with PVC sieves and nylon grid by wet process for the fraction <230 mesh, and subsequently dried at ambient temperature. The stream sediments were also dried at ambient temperature before being disaggregated by a quartz mortar and separated in the fractions <120 mesh with PVC sieves and nylon grid. The granulometric fractions <230 mesh and <120 mesh of the soil and stream sediment samples, respectively, were treated with an aqueous solution (6ml / 1g of sample), at 95°C during one hour to test for 51 elements by ICP-MS at the ACME Laboratories (Canada). The As, Au, Cd, Cu, Fe, Hg, Mn, Pb and Zn concentrations were evaluated in this study. Within the sample collection, a blank sample previously certified for Hg (NIST-8407) was included, the result of which showed an analytical error < 7%.

RESULTS AND DISCUSSION

Soils

The element concentration values in analyzed soil samples from sites distant from the gold processing areas were extracted from Grazia & Pestana (2005a) as shown in Table 1. The 5 soil samples' mean concentration values (VM) in andesitic terrains and the values referring to a sample taken over granite rocks were used as a reference to calculate the sample contamination rates from the processing areas.

The comparison of the andesitic terrains soil VM (mean values) with the reference soil values, according to CETESB (2001), described below Table 1, showed naturally elevated backgrounds for As, Cu and Pb in

Table 1 - Element concentration in non-contaminated soil from andesitic and granite areas (fraction < 230 mesh)

Sample	Rocha	As (µg/g)	Au (ng/g)	Cd (µg/g)	Cu (µg/g)	Fe (%)	Hg (ng/g)	Mn (µg/g)	Pb (µg/g)	Zn (µg/g)
2	Andesito	23.10	35.7	0.03	57	1.91	39	384	29.40	44.6
3	Andesito	13.70	40.9	0.03	108.2	4.16	44	901	26.30	74.7
4	Vulcanoclástica	10.20	11.3	0.04	11	2.62	57	334	24.10	60.5
5	Andesito	6.10	6.1	0.06	62.70	3.23	25	369	13.20	46
6	Andesito	8.50	3.9	0.04	33.90	2.09	16	410	12.10	48.9
11	Andesito	8.70	26.5	0.09	60.90	2.71	58	350	32.70	57.2
8	Granito	8.20	6	0.03	10.30	1.84	54	131	18.90	38.7
VM	Andesito	12.30	19.6	0.04	54.60	2.8	36.2	480	21,00	54.9
Reference Value		3.50	nr	<0.5	35	nr	50	nr	17	60
Alert Value		15	nr	3	60	nr	500	nr	100	300

> or = the reference value ⌐ - - - - - - - - - - - ⌐   > or = the alert value ⌐ - - - - - - - - - - - - ⌐

The VM was calculated with samples 2 and 6. Sample 11 was excluded from the calculation, since it was taken from a sulfide quartz vein.
nr= element without reference according to CETESB (2001).   [1] Reference soil values in total samples from CETESB (2001)

Table 2 - Element concentration in soil located next to the gold processing plant and their respective contamination rates (fraction < 230 mesh)

Sample	Geologic background	As (µg/g)	Au (ng/g)	Cd (µg/g)	Cu (µg/g)	Fe (%)	Hg (ng/g)	Mn (µg/g)	Pb (µg/g)	Zn (µg/g)
7	Andesite CRM	24.5 (2)	688 (35)	0.20 (6.8)	270 (4.9)	3.03 (1.1)	18508 (511)	626 (1.3)	79 (3.8)	113 (2.0)
9	Granite within Chiapetta	127 (15)	13173 (2195)	1.34 (44)	270 (26)	4.86 (2.7)	43497 (805)	418 (3.2)	1465 (77)	661 (17)
10	Granite outside Chiapetta	59.3 (7.23)	2870 (478)	1.63 (54)	124 (12)	2.84 (1.5)	11021 (219)	566 (4.3)	1100 (58)	500 (13)
12	Andesite Cerro Rico	163 (13.2)	1533 (78)	0.29 (7.2)	1469 (27)	5.68 (2)	10379 (287)	1029 (2.1)	719 (13)	250 (4.5)
	[1]Reference Value	3.5	nr	<0.5	35	nr	50	nr	17	60
	[1]Alert Value	15	nr	3	60	nr	500	nr	100	300
	[1]Agricultural Intervention Value	25	nr	10	100	nr	2500	nr	200	500
	[1]Residential Intervention Value	50	nr	15	500	nr	5000	nr	350	1000
or = the reference value .... > or = the alert value .... > or = the agricultural intervention value										

[1] Reference soil values in total samples from CETESB (2001 – contamination rates ( ); nr= element without reference according to CETESB (2001)

this volcanic areas. The reference values also exceeded those for As, Hg and Pb in the sample 08 (taken over granite areas).

The soil sample element concentrations obtained in the ore processing areas, as well as their respective contamination rates are found in Table 2. These rates were calculated as the quotient between the sample concentration and the respective mean value (VM) from Table 1, which, for granites, refer to the sample 08 value. In Table 2 the reference values were also included, according to CETESB (2001), except for those of industrial intervention.

Considering the soil's multi-functionality in environmental management, the use of intervention values as an agricultural use reference in this evaluation is more suitable, as these are more restrictive than those for residential use. Furthermore, the sampled sites are situated in a predominantly rural area.

Hg showed the highest contamination rates, followed by Pb, Cu and As. The most Hg and Au contaminated soils were sampled inside the Chiapetta ore processing plant and in the CRM area, showing a clear association with losses in the amalgam processes. The most As, Cd, Pb and Zn contaminated samples were those from the Chiapetta ore processing plant (inside and outside) and the most Cu contaminated samples, from the Cerro Rico ore processing plant. The elements Fe and Mn, with weak or no association with the sulfide mineralization presented the lowest contamination rates.

The comparison of contaminated soil data with the reference values adopted by CETESB (2001) showed the Hg and Cu concentrations exceeded the respective intervention values for agricultural use soil in 100% of the samples and 75% of the As and Pb indicating a potential risk to human health. Zn exceeded the agricultural intervention value in 50% of the samples from the ore processing areas, more specifically in both samples collected in the Chiapetta ore processing plant. However, it must be noted the element concentrations analyzed for the Lavras do Sul soil were determined in the silt-clay fraction, whereas the CETESB (2001) report does not specify the granulometric fraction, which suggests these were total samples.

Recently CETESB published on November 23rd 2005 in the internet, new guidelines Nº 195-2005, which reviews the reference values of 2001. According to the new values, the Chiapetta ore processing plant contaminated soil would be also exceeding the prevention value for Cd (1.3 g/g), which is more restrictive than the previous alert value (3.0 g/g). However, regarding Hg, the new decision is much more permissive, as the residential intervention values passed from 5,000 g/g in 2001 to 36,000 g/g in 2005, and the agricultural intervention values, from 2,500 g/g to 12,000 g/g respectively. Therefore, only the samples collected inside the Chiapetta and CRM ore processing plant areas would remain in the same category. The others, in respect of Hg concentrations, would be classified as above the prevention value, which in this case, coincides with the former alert value. For the other analyzed elements there would be no alterations to the evaluation in Tables 1 and 2. In this study we will continue to adopt the orienting values of 2001 since we have no knowledge of the technical basis that lead to the 2005 alterations.

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STREAM SEDMENTS

The analytical data interpretation of the stream sediments consisted of basic statistical treatment (software NCSS Statistical System for Windows) that established statistical parameters for each element, such as the mean background values, its standard deviations and the thresholds values (upper limit of the background boundary).

Considering the limitations of the methodology used to prepare and extract the samples, the environmental evaluation was made based on the recently implemented CONAMA Resolution Nº 344/2004 (abbreviate to RC) that establishes two quality levels for material dredged in Brazilian territorial water. These are: level 1, below which a low probability of adverse effects to the biota is expected; level 2, above which a probable adverse effect to the biota

is expected. However, the subaqueous sediments with As, Cd, Hg or Pb concentrations above level 1, must be submitted to ecotoxicological tests (Art. 7 of the same RC).

The analyzed element concentrations, the background zone mean values and its thresholds were calculated for the stream sediment samples from the granite and andesitic areas. They are shown in Tables 3 and 4, respectively, together with the RC level 1 and 2 values. Thresholds above level 1 were found for As in the granite area sediments, and for As, Cu and Pb, in the andesitic area. These observations are in agreement with the naturally elevated background values, confirmed for the three elements, in the volcanic lithology soil. In the latter, the threshold of 31 g/g As for stream sediments exceeded even the RC level 2.

In isolated samples, the RC level 2 is exceeded for Cu in the andesitic area sample 27 and for As and Cu in

Table 3 - Element concentration in stream sediments over granite areas Fraction < 120 mesh

Sample	UTM N	UTM L	As (µg/g)	Au (ng/g)	Cd (µg/g)	Cu (µg/g)	Fe (%)	Hg (ng/g)	Mn (µg/g)	Pb (µg/g)	Zn (µg/g)
OC-01	6594158	225352	7.8	7	0.04	25.11	1.84	20	404	20.47	32
OC-02	6592775	225263	7.2	8.8	0.03	23.06	1.67	19	321	12.53	35.4
OC-03	6594516	224244	16.2	40.7	0.04	56.18	2.09	195	331	68.59	39.2
OC-04	6585911	225975	4.9	85.3	0.04	7.67	1.39	38	270	21.07	30
OC-05	6585591	226953	5.4	4.7	0.05	5.59	1.11	40	151	22.44	32.2
OC-06	6585477	227337	3.7	36.2	0.03	5.16	0.78	39	169	14.06	22.2
OC-07	6596230	221950	3.7	7.2	0.04	11.85	1.94	13	563	17.57	39.3
OC-10	6584020	228044	48.1	5518.2	0.16	306.27	2.33	112	455	57.39	62
OC-15	6585317	224966	5.8	6	0.02	8.47	1.44	25	229	15.3	32.2
OC-18	6585720	224663	2.2	17.4	0.01	3.16	0.65	13	105	7.94	12.9
OC-19	6584948	219677	3.3	107.8	0.02	5.99	1.5	21	191	16.18	38.4
OC-20	6586709	224088	9.9	47.9	0.12	16.71	1.89	145	807	32.69	65.7
OC-21	6584989	222577	3.1	13.8	0.02	2.85	0.85	17	189	9.67	18.4
OC-32	6592436	228758	12.7	77.3	0.05	27.34	1.94	31	415	21.55	36.5
OC-34	6590920	228193	13.7	18.8	0.06	37.03	2.27	31	483	28.7	47
OC-35	6587961	223424	9.4	92.3	0.03	3.56	1.03	72	318	19.27	20.9
OC-36	6587482	220938	4.3	140.8	0.03	6.64	0.92	42	202	30.78	32
OC-37	6586794	220119	4	63.4	0.03	3.51	1.03	24	235	17.28	25.6
OC-38	6586622	220269	3.2	51.7	0.04	9.84	1.45	19	737	13.23	33.1
OC-39	6588862	218307	3	34.7	0.03	4.26	0.89	20	250	15.13	20.9
OC-40	6589096	218428	2.7	14	0.04	4.89	0.85	22	103	15.7	42
OC-41	6588172	222058	3.5	6.5	0.02	2.12	0.66	19	124	8.26	11.6
OC-42	6587523	224320	6.1	15.3	0.02	4.89	1.11	48	222	12.79	23.5
OC-43	6584672	217343	5.3	6	0.03	3.77	1.2	27	581	14.1	18.3
Mean background value1			6.13	28.1	0.03	10	1.3	28	286	17.5	30.6
Threshold1			12	35	0.05	24	2	56	572	31	56
CONAMA2 Level 1			5.9	nr	0.6	35.7	nr	170	nr	35	123
CONAMA2 Level 2			17	nr	3.5	197	nr	486	nr	91.3	315

[1]This Study - Resolution Nº 344/04 – The resolution CONAMA Nº 344/04 refers only to the elements As, Cd, Cu, Hg, Ni (not assessed in this study) Pb and Zn   nr = not referenced by CONAMA

Table 4 - Element Concentration in stream sediments over andesitic areas. Fraction < 120 mesh

Sample	UTM N	UTM L	As (µg/g)	Au (ng/g)	Cd (µg/g)	Cu (µg/g)	Fe (%)	Hg (ng/g)	Mn (µg/g)	Pb (µg/g)	Zn (µg/g)
OC-08	6584931	229021	5	28.5	0.03	8.75	1.04	63	322	16.13	27
OC-09	6584504	228739	19.8	6.4	0.06	40.24	2.59	18	444	25.13	64.8
OC-11	6585068	232706	8.1	30.3	0.07	17.08	1.85	62	614	22.89	49.5
OC-12	6584941	232789	14.8	11	0.08	26.84	3.83	24	1119	16.6	64.6
OC-13	6585932	234374	21.1	13.5	0.1	19.46	3.25	27	731	20.73	70.3
OC-14	6586710	236173	24.6	7.5	0.13	20.5	2.84	92	951	27.62	79
OC-16	6586455	232551	24	22.9	0.22	28.09	2.55	64	845	134.14	104.8
OC-17	6589066	234283	22.4	1.4	0.07	18.66	3.16	89	929	36.92	80.9
OC-22	6585425	231162	17.4	37.5	0.07	65.53	3.32	46	1039	28.58	71.7
OC-23	6585169	231050	7	12.5	0.04	19.05	1.64	55	465	18.45	42.2
OC-24	6586142	230366	16.9	5.9	0.07	59.72	3.72	50	1012	29.94	80.3
OC-25	6585819	230231	23.3	11	0.05	119.11	4.6	41	1152	29.86	73.6
OC-26	6589451	231218	73.9	1.6	0.08	41.53	3.24	82	914	44.54	66.5
OC-27	6589303	230534	50.6	2760.9	0.09	238.23	3.96	958	1165	94.52	76.3
OC-28	6589482	230360	29.4	9	0.06	49.76	2.72	61	723	30.62	54.6
OC-29	6593372	231887	21.8	10.6	0.08	33.08	2.52	77	1393	22.56	47.7
OC-30	6592326	231879	12.5	1.4	0.04	32.23	2.59	37	634	18.59	51.7
OC-31	6593355	230599	12.4	320.6	0.05	35.63	2.29	34	695	25.02	55.1
OC-33	6592090	228972	17.9	4.5	0.09	37.28	3.13	38	876	27.71	55.5
Mean background value1			6.13	28.1	0.03	10	1.3	28	286	17.5	30.6
Threshold1			12	35	0.05	24	2	56	572	31	56
CONAMA2 Level 1			5.9	nr	0.6	35.7	nr	170	nr	35	123
CONAMA2 Level 2			17	nr	3.5	197	nr	486	nr	91.3	315

[1]This Study - Resolution Nº 344/04 – The resolution CONAMA Nº 344/04 refers only to the elements As, Cd, Cu, Hg, Ni (not assessed in this study) Pb and Zn   nr = not referenced by CONAMA.

the granite area sample 10. In the former, the As, Hg and Pb concentrations also exceeded the respective level 2 values. In this sample, the Hg concentration (958 g/g) is of anthropogenic origin, due to the Cerro Rico ore processing plant proximity, situated upstream. This explains its elevated value, the only one higher than the RC level 2 for Hg. However, a natural Hg contribution is also possible, as the sediment sample speciation analysis from the water reservoir used by the Cerro Rico ore processing plant (Pestana et al., 2000) showed a higher percentage Hg sulfide than metallic Hg. In addition, Toniolo et al. (2005) mention the occurrence of cinnabar (Figure 2) sampled East of sample 27, in the same geological context.

In sample 10, the elevated As, Au, Cu and Pb concentrations, the latter superior to the RC level 1 are explained by the Valdo Teixeira mine proximity. Also the concentrations higher than the thresholds for Cd, Fe, Hg and Zn suggest stream sediment contamination by wastes from the same mine.

The 195 g/g Hg concentration of sample 03 (granite area), superior to the threshold and to the RC level 1 for this element, is probably related to the area mineralizations, since not only Hg but also the Au, Fe, As, Cu and Pb concentrations in that sample exceeded the respective thresholds. The concentrations of the last three elements also being higher than the RC level 1. This sample, however, seems not to have contributions from mining wastes because it is far from the mined areas to the South and because the Au content is not as high as areas with known mining wastes.

Finally, granitic area sample 20 with 145 g/g Hg and values superior to the thresholds for Cd, Pb and Zn, represents a mixture of anthropogenic contaminations, both by mining processing and urban wastes, due to its situation downstream from the Chiapetta ore processing plant and the Lavras do Sul urban area.

The Hg concentrations in soil and stream sediments found in Lavras do Sul are summarized on the Mercury Distribution Map (Figure 3). Mercury was chosen because this is a high potential toxicity element for human health and its concentrations showed major anthropogenic enrichment in soil samples.
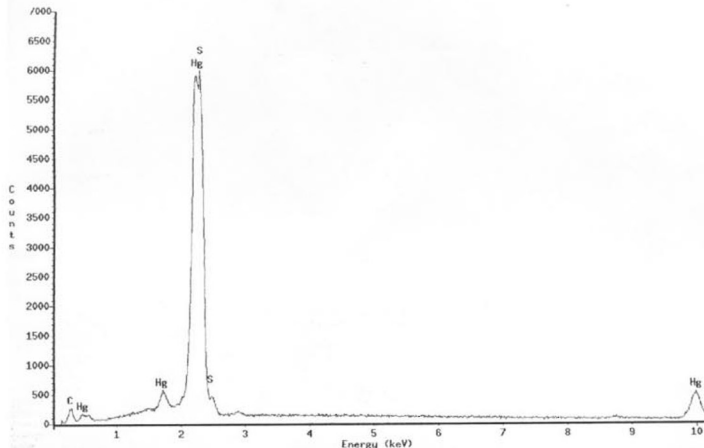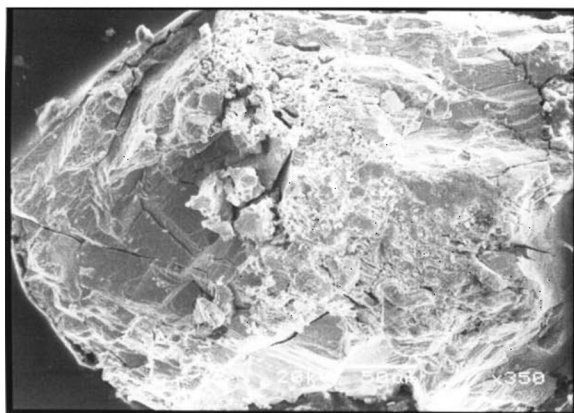
Figure 2 – Electronic Microscope detail of a Cinnabar grain.

Figure 3 exhibits the connection between granites and andesites (Porcher & Lopes, 2000) and the obtained results correlation when the old gold mines and processing plant locations are added. Furthermore Figure 3 highlights the Hg concentration values, according to this study's criteria and these infer high concentration dispersion levels in contaminated soil relative to the nearby stream sediments. These results, the data evaluation compared to the orienting values (alert and agricultural intervention) for soil (CETESB, 2001) as well as the nearby stream dispersion degrees are summarized in Table 5.

Table 5 - Classification of soil contamination according to CETESB 2001 reference values and Hg dispersion degree in nearby drainages.

Location	Alert	Intervention	Hg Diapersion in drainages
CRM	As	Hg	No dispersion
Chiapetta	Cu e Zn	As, Hg e Pb	Discret dispersion
Chiapetta	Cu e Zn	As, Hg e Pb	Discret dispersion
Cerro Rico	none	As, Cu, Hg e Pb	Notable dispersion

CONCLUSION

Soils

Background values naturally elevated for As (12.3 µg/g), Cu (54.6 µg/g) and Pb (21.0 µg/g) were found in soil samples over andesitic terrains

The highest enrichment factors relate to Hg in the Chiapetta ore processing plant internal area and the CRM area.

Soil close to the three processing sites CRM, Chiapetta and Cerro Rico, are anthropogenically contaminated by As, Cu, Hg, Pb and Zn.

According to CETESB (2001) the contamination impacted: i) Cu and Hg agricultural intervention values in the three processing sites, As and Pb in the Chiapetta and Cerro Rico ore processing plants and Zn in the Chiapetta area; ii) Residential intervention values for Hg in the three processing sites, As and Pb in the Chiapetta and Cerro Rico ore processing plant and Cu only inside the Chiapetta area; iii) Alert value for As in the CRM area.

Stream sediments

The andesitic stream sediments presented elevated thresholds for As (31 µg/g), Cu (66 µg/g) and Pb (40 µg/g) and compared to the RC, exceeded level 1 for Cu and Pb, and even level 2 for As;

The Hg thresholds inferior to the RC level 1 in granite (50 g/g) and andesitic (88 g/g) stream sediments, highlight the Hg concentration of 958 g/g, superior to the RC level 2 found in stream sediment downstream from the Cerro Rico ore processing plant;

Three types of anthropogenic contamination were indicated: a) ore processing, downstream from the Cerro Rico ore processing plant; b) ore front, downstream from the Valdo Teixeira mine; and c) a mixture of mine processing and urban effluents, downstream from Chiapetta plant and the Lavras do Sul urban area;

Natural contamination associated with probable mineralization was identified with 195 g/g Hg, in the North-Eastern part of the granite area;

High dispersion of Hg contamination from the soil to stream sediments became evident for the Cerro Rico ore processing plant only

RECOMMENDATIONS

1) Soil remediation for areas close to the processing sites, due to contamination levels exceeding those of intervention for Hg and/or As, Pb and Cu, representing a potential risk to human health;

2) Detailed evaluation of the confirmed contamination levels, including risk analyses and surveys within those

MATERIAL ANALISADO
Abertura: Água Régia
Leitura: ICP-MS

● Argila de veio aurífero (< 230 mesh)
■ Solos (< 230 mesh)
Valores orientadores para Hg (ppb) em solos [1]

< Referência	Referência	Alerta	Intervenção uso residencial
< 50	50	500	5000

● Sedimentos de corrente graníticos (< 120 mesh) Hg (ppb)

Limiar [2]	Conama [3]
Valor > limiar [2]	
Valor > limiar e > Conama [3]	Hg = 56 ppb	Hg = 170* ppb

● Sedimentos de corrente andesíticos (< 120 mesh) Hg (ppb)

Limiar [2]	Conama [3]
Valor > limiar [2]	
Valor > limiar e > Conama [3]	Hg = 88 ppb	Hg = 170* ppb

1 Cetesb (2001) 2 Este trabalho 3 Conama - Resolução 344 / 2004
* Valor acima do qual há necessidade de ensaios ecotoxicológicos

LEGENDA

Contato geológico
Área de andesitos
Área de granitóides
Vias
Estrada Pavimentada
Drenagem simples
Drenagem de margem dupla
Lavras do Sul
⊗ Mina ou Garimpo Desativado
🏭 Instalação de Beneficiamento

0   2   4   6 Km

Figure 3 – Hg Content Distribution Map.

populations potentially more exposed to contamination by these elements.

ACKNOWLEDGMENTS

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RADIOELEMENTS IMPACT ON THE ENVIRONMENT, AGRICULTURE AND PUBLIC HEALTH IN LAGOA REAL, BAHIA STATE BRAZIL

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IINTRODUCTION

This study integrates the National Research Program of Environmental Geochemistry and Medical Geology (Programa Nacional de Pesquisa em Geoquímica Ambiental e Geologia Médica – PGAGEM), developed by CPRM in partnership with universities and other governmental institutions. The studied area is situated in the center-South region of Bahia State, between latitudes 13°45'30" and 14°07'30"S and longitudes 42°07'30" and 42°22'30"W. Gr, in Lagoa Real and covers 1,126km² (Figure 1).

The region is known as the Lagoa Real Uraniferous Province. Mining exploration carried out by the Brazilian Nuclear Industry - INB (Indústrias Nucleares do Brasil S.A.) started in 2000 as a mining-industrial business, initiated to promote the exploration and production of U_3O_8 in reserves estimated as 100 thousand tons.

The extracted uranium ore is first crushed and then subjected to a lixiviation process in piles (static), where the material is irrigated with a sulfuric acid solution
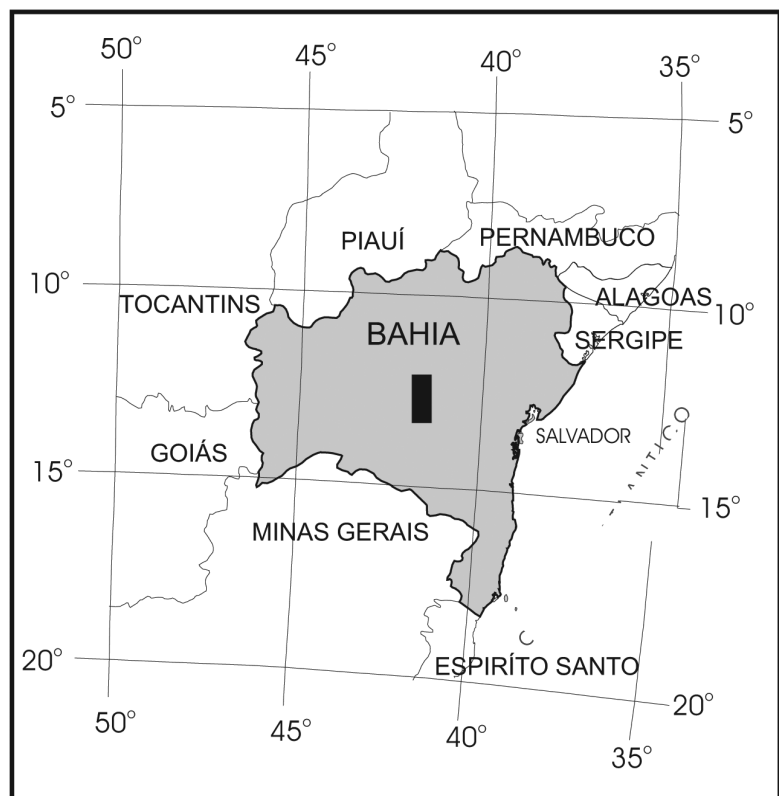
Figure 1 – Location of the Lagoa Real Project area.

to remove the uranium. The uranium concentration is made by an organic solvents extraction process, followed by separation through precipitation, drying and conditioning to produce the concentrate (yellow cake). This is stored in special drums made to the specifications established by the National Commission for Nuclear Energy (Comissão Nacional de Energia Nuclear – CNEN – www.inb.gov.br). The yellow cake (ammonium diuranate) is transported to Salvador (Bahia State – BA) by road. This material needs to be transformed into uranium hexafluoride gas and enriched in Germany, Netherlands or England, to be used in Brazil as a nuclear fuel in the Angra I and II Power Plants.

INB seeks to guarantee the implementation of control operations and remediation of eventual environmental impacts. In the case of the workers, each one receives a badge with a dosimeter that measures the radiation dose he is receiving. With regard to the environment, air, soil, rain and ground water, animals and plants are monitored. INB maintains frequent contact with CNEN, IBAMA and the Environmental Resources Center (CRA) of the Bahia State Government.

This study aims to identify environmental problems that may be correlated with public health, especially those related to uranium exposure, as well as to small watersheds management and, with geochemical data and parameters, to monitor Lagoa Real Uraniferous Province programs.

GEOLOGY AND ENVIRONMENT

The Lagoa Real Uraniferous Province is situated in the center-South portion of the São Francisco Craton in the orthogneisses belonging to an intrusive suite along the Paramirim shear belt. These Mesoproterozoic gneisses present cataclastic zones which were metasomatized to albite-oligoclase and sometimes to uranium. The mineralization control is mainly due to tectonics with a preferential distribution along the lineation. Uranite is the principal ore, followed by pitchblende dispersed in the mafic layers.

The mineralized extensions vary between a couple to hundreds of meters long, whereas the thickness varies between a few centimeters and tens of meters; a depth continuity reaching almost 700m was confirmed with soundings

The secondary uranium minerals (Uranophane and autunite) are restricted to the weathered zones, conditioned mainly by the fracture system. In the region there is a predominance of morphogenetic processes associated with chemical weathering and fluvial erosion.

The widespread uranium abundance in mineralized zones and this element's increased dispersion in the environment activities like mining can lead to toxicity problems. In these cases, knowledge of geochemical

processes is important to understand the migration paths and uranium exposure routes regarding plants, animals and human populations.

Even outside the mining area, natural uranium contents in water and soil can be toxic and cause adverse effects to human health. Over the last five years, INB has built wells to meet the demands of the mining activities and the local population and to avoid the consumption of surface water. Unfortunately the geochemical characteristics of these aquifers have not been considered and, though the soil and aquifer sediments are not mineralized, the concentrations of this element are elevated enough to cause serious health problems, as is the case at the Fazenda Juazeiro.

Radon 222 is a natural gas formed during the radioactive transformation of uranium in lead. Although it has a very short mean life, of only 3.8 days, being a gas it is very mobile and thus, easily inhaled in closed environments and likely to provoke lung cancer. 222Ra limits are part of the INB environmental impact control and remediation operations.

AGRICULTURE AND GEOCHEMISTRY

The region's water use is mainly for domestic animal consumption and irrigation. The United States Salinity Laboratory – U.S.S.L. (1954) established 16 classifications of water for agriculture uses based on the RAS index and electrical conductivity. 5 classes were identified for this region (Figure 2 and Table 1).

The area's agricultural production is restricted to pineapple, sugar-cane, beans, castor bean and sorghum crops. Banana, persimmon, orange and mango are cultivated as permanent crops.

In the region's podzolic soil, plant roots usually have a certain difficulty to breach the horizon A. This phenomenon naturally makes the cultures very sensitive to droughts and the phreatic water becomes useless. This could partly explain the relative enrichment of some ions in the A horizon (Figure 2). Regarding uranium there is the possibility of toxicity but the effects related to phytotoxicity have not been studied yet.

The lack of water in the region restrains the systematic application of surface water geochemistry.

GEOCHEMISTRY AND PUBLIC HEALTH

Geochemistry in its strict sense is the study of the chemical composition of the Earth and, on a first approach, there seems to be little connection between the material composition and human health. However, there are 92 of the different types of geological chemical elements naturally found on the earth's surface. About 25 of these elements are either essential or toxic to animal and vegetable life. For human beings Ca, Cl, Mg, P, K,
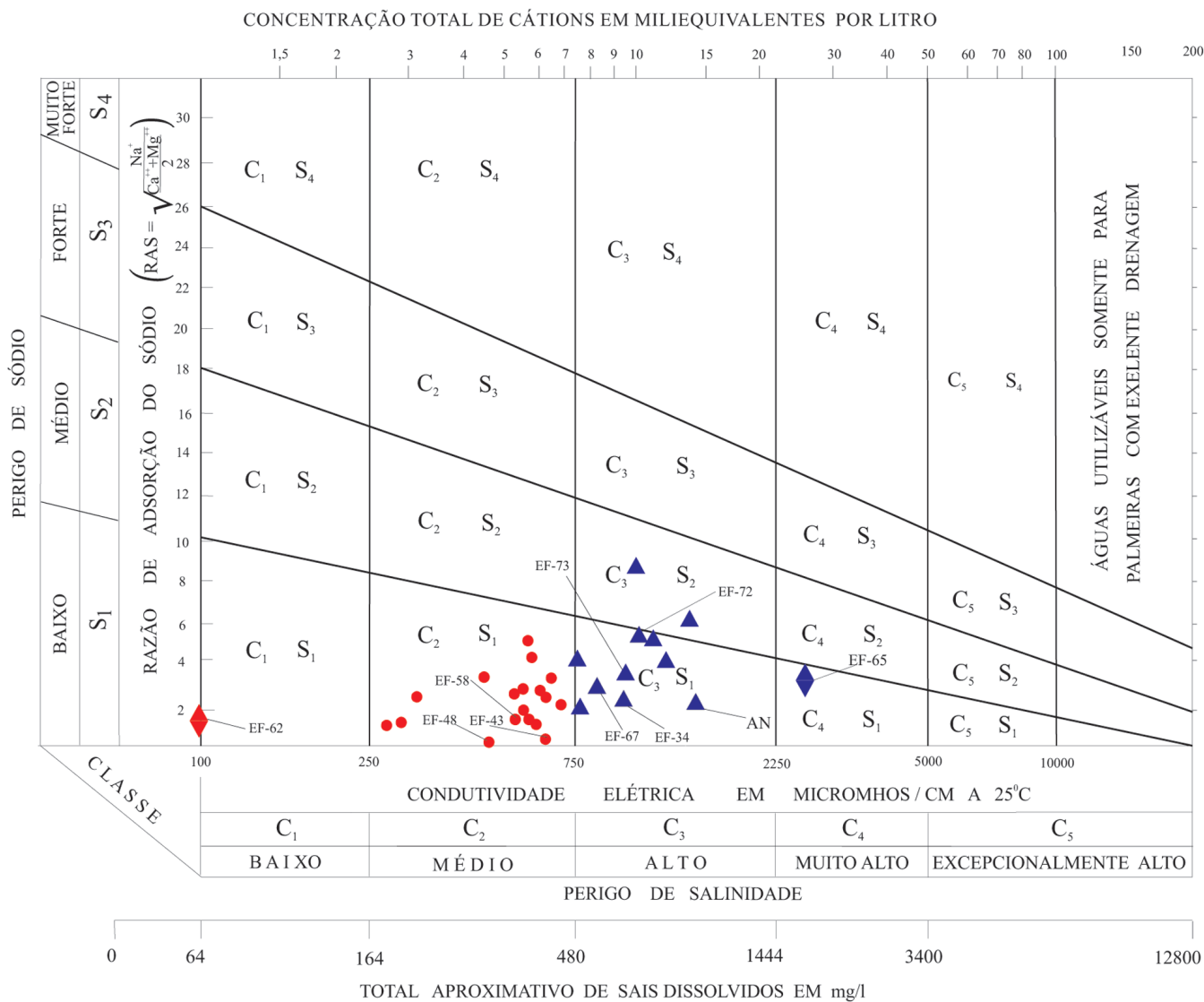
Source: Figure adapted from the United States Department for Agriculture, manual 60 1954.

Figure 2 – Classification scheme for irrigation waters.

Table 1 - Classification for irrigation water in the area of the PGAGEM Lagoa Real

Class	Frequency	Salinity	Na content	Irrigation	Potability
C_1-S_1	1	low	low	Suitable for most of the soul types and crops	Within potabilty limits
C_2-S_1	17	medium	low	Suitable only at well drainned soils and salt tolerant crops	Some contents above potability standards (chloride, total dissolved soil, etc)
C_3-S_1	8	high	low		
C_3-S_2	4	high	medium	Not suitable	

Na, S and H are essential as macro-nutrients and Co, Cr, Cu, F, I, Fe, Mn, Mo, Se, V and Zn as micro-nutrients. Some elements have no or limited biological function and are generally toxic: As, Cd, Pb, Hg and Al. These include also the radioactive element uranium.

Uranium is carcinogenic and lethal. Water contamination can be considered the most serious impact associated with the mineral extraction and uranium ore processing. The effluent quality parameters can be altered in many ways, especially by chemical substances added during the ore processing.

In Lagoa Real, between April 20th and 23rd 2000, there was a 5,000m³ leak of an uraniferous effluent into the treatment basin from the acid lixiviation of the ore pile by sulfuric acid. The leak neither reached the aquifer, nor the rivers and no company employee was contaminated. However it is difficult to estimate the extent of the leakage and how much soil was contaminated.

Drinking water contamination by uranium mining sites has occurred at other sites around the world. The most recent occurred in March 2001 when the Ranger uranium mine (Australia) was closed down due to water contamination. Ranger workers drank and bathed in water contaminated with uranium ore, with levels exceeding 400 times the country's maximum security standard. As a result 28 workers became sick. The Australian Energy Resources Company (ERA) temporarily suspended its operations to make improvements to the mine's security. The mine has had a troubled history with 120 leakages, spillages and operational errors since opening in 1981. The workers suffered from headaches, nauseas, sickness and skin irritations as a result of the incident. Those affected by the contamination needed to submit to blood checks to control the exposure.

In Lagoa Real the studies do not show a clear relationship between uranium radiation and cancer. Between 1999 (uranium mineralization pre-operational stage) and 2002 (Cachoeira uranium mine operating), the DATASUS Information System for mortality through neoplasias (tumors) registers only eight cases (www.datasus.gov.br).

MATERIALS AND METHODS

This study carried out a low density multi-elemental geochemical survey, allowing the results to be used for several purposes. This model is based on the standardizations of the International Geochemical Mapping – IGCP (Danrley et al., 1995) and Foregs Geochemical Mapping (Salminen et al., 1998).

To establish the geochemical model base, different migration paths were assumed together with the chemical element concentrations at the soil-water-rock-stream sediment interface (Figure 3). A total of 32 groundwa-ter samples were collected from tubular wells, 32 soil samples, 30 rock outcrop samples from the tubular wells proximity and 42 stream sediment samples in the granulometric fractions < 230 mesh (silt and clay), seeking to quantify the geochemical baselines, focused on environmental monitoring.

The soil samples, important for monitoring radioactive elements, were stored in 50ml graduated polyethylene tubes, after being filtered in 0.45mm microporous filter, for the cations analysis. To preserve the soluble cations in the samples, 1ml of HNO_3 1:1 was added, maintaining the pH<2. For the physical-chemical parameters analyses, two liters of the water sample remained refrigerated until analyzed.

The stream sediment, soil and rock samples chemical analyses by ICP-MS were made at the Acme Analytical Laboratories, in Canada, for a protocol of 51 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn and Zr).

To determine the 72 elements in the tubular well water samples, 21 elements were added to the above mentioned package (Br, Cl, Dy, Er, Eu, Gd, Ho, Ir, Lu, Nd, Os, Pd, Pr, Pt, Rb, Ru, Si, Sm, Tb, Tm and Yb). These chemical analyses were also made at the Acme laboratory by ICP-MS. The physical-chemical parameters were defined by the National Department for Drought Relief Work (Departamento Nacional de Obras Contra as Secas – DNOCS).

The individual and mean analytical data on the soil, rock and sediment samples were standardized according to Clarke's values, an important parameter to define the geochemical and environment signatures.

For the water chemical analyses, values published by Levinson (1980) for natural water (ppb) were used. The levels considered dangerous for living beings, the class II river limits were used, from Resolution nº 357/2005 of the National Environmental Council (Conselho Nacional do Meio Ambiente) – CONAMA,.

RESULTS

Based on the concentrations and dispersions in the studied area of the 51 chemical elements analyzed at the rock-soil-water and stream sediment interface, it was hypothetically estimated that about 10% of the elements, on average, remain in the primary environment (rock). Of the 90% of the elements from the primary to secondary environments, approximately 54% remain in the soil matrix and 36% are dispersed in the drainage network (stream sediment). Less than 0.1% of the chemical elements are solubilized. This panorama will probably be modified after the inclusion of the vegetable-animal-man cycle in the system.
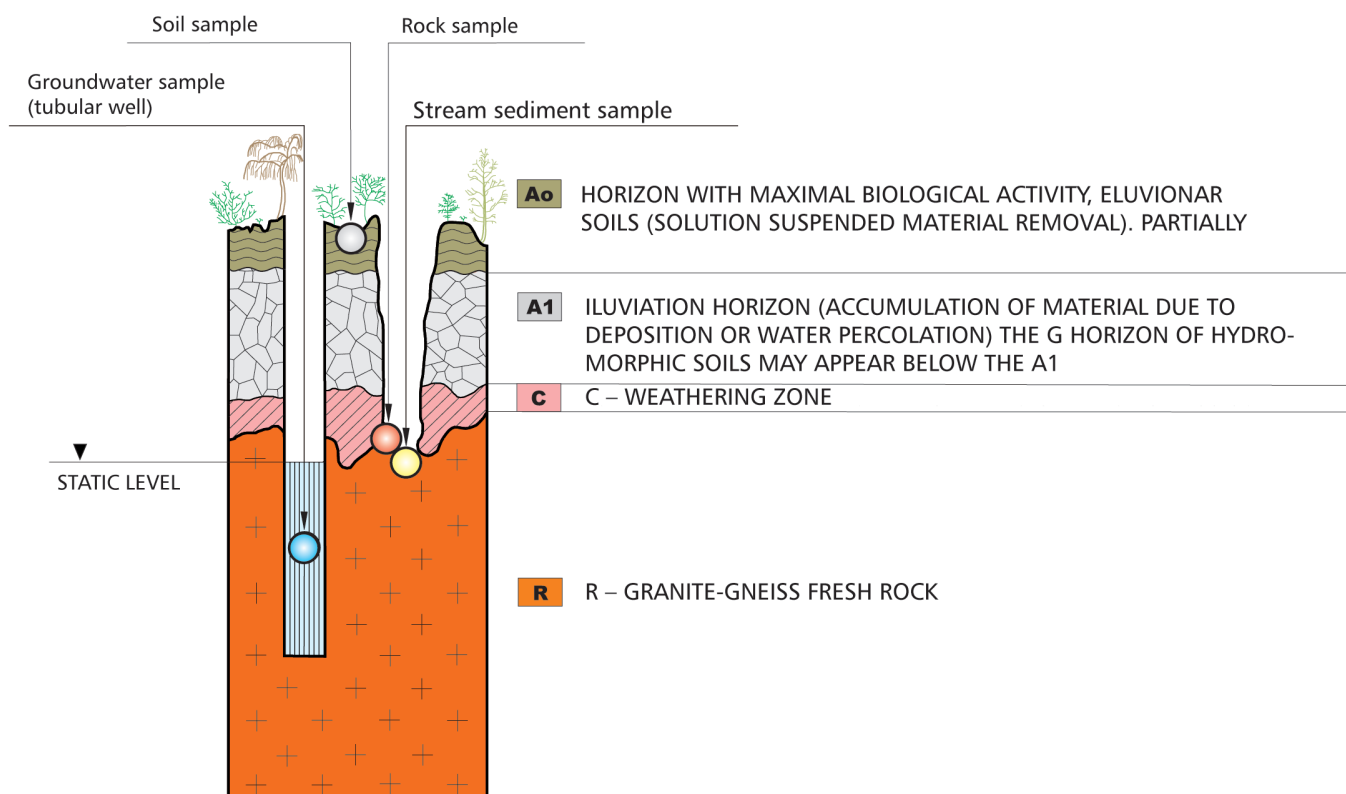
Figure 3 – Schematical representation of a podzolic soil profile, showing the main horizons and the sampling points.

Uranium arose as one of the ten enriched elements when comparing the mean content on the earth's crust (xi/c>1) with the stream sediments, soil and rock. In this aspect 10 elements stand out: Se (13.78x), Bi (5.50x), Ce (4.61x), La (4.48x), Th (2.84x), Y (2.42x), Mo (1.82x), U (1.43x), Pb (1.28x) and Sn (1.14x). The remaining 41 analyzed elements were considered impoverished (xi/c<1) or depleted (Figure 4).

In the rock samples the outliers to the mineralized zone were avoided. The lithotype enrichment is geographically restricted, with a mean equal to 1.920ppm U, slightly depleted (0.83x).

The predominance of morphogenetic processes in the region associated with the chemical weathering and with the fluvial erosion, favors the high mean contents of 4.480ppm U and 3.480ppm U, equivalent to an enrichment of 1.94x and 1.51x in soil and stream sediment, respectively.

For uranium, a distribution pattern associated with the Th and ETRL (La and Ce) was registered, with a geochemical behavior characterized by the abundance of the HFS (High Field Strength), according to Oliveira (2004).

Eight groundwater wells stand out due to radioactive element pollution (uranium). All the other 71 analyzed elements do not present, a priori, significant importance to the radioactive pollution of the aquifers. The water contamination risk by radiation was defined by the probability of the well's contamination level exceeding the CONAMA (2005) quality standards for human consumption water supplies after conventional treatment (0.02 mg/L U).

The conversion from risk into threat of soil and rock contamination (dust) was 3.0 ppmU. Based on the obtained results, target-areas were selected for later studies, in a detail scale.

Selected target-areas

Three target-areas were selected for detailed study projects with human and environmental monitoring, in partnership with health professionals (Figure 5).

The first, the INB mining-industrial complex of Lagoa Real situated in area nº1 (12 km²). The Cachoeira mining company, operating since 2000, has reserves superior to 20,400 t U_3O_8 and an annual production estimated in 300t of yellow cake. The permanent control/monitoring of the environment and employees are recommended.

For the two other selected study areas, environmental monitoring and programs related to public health, if
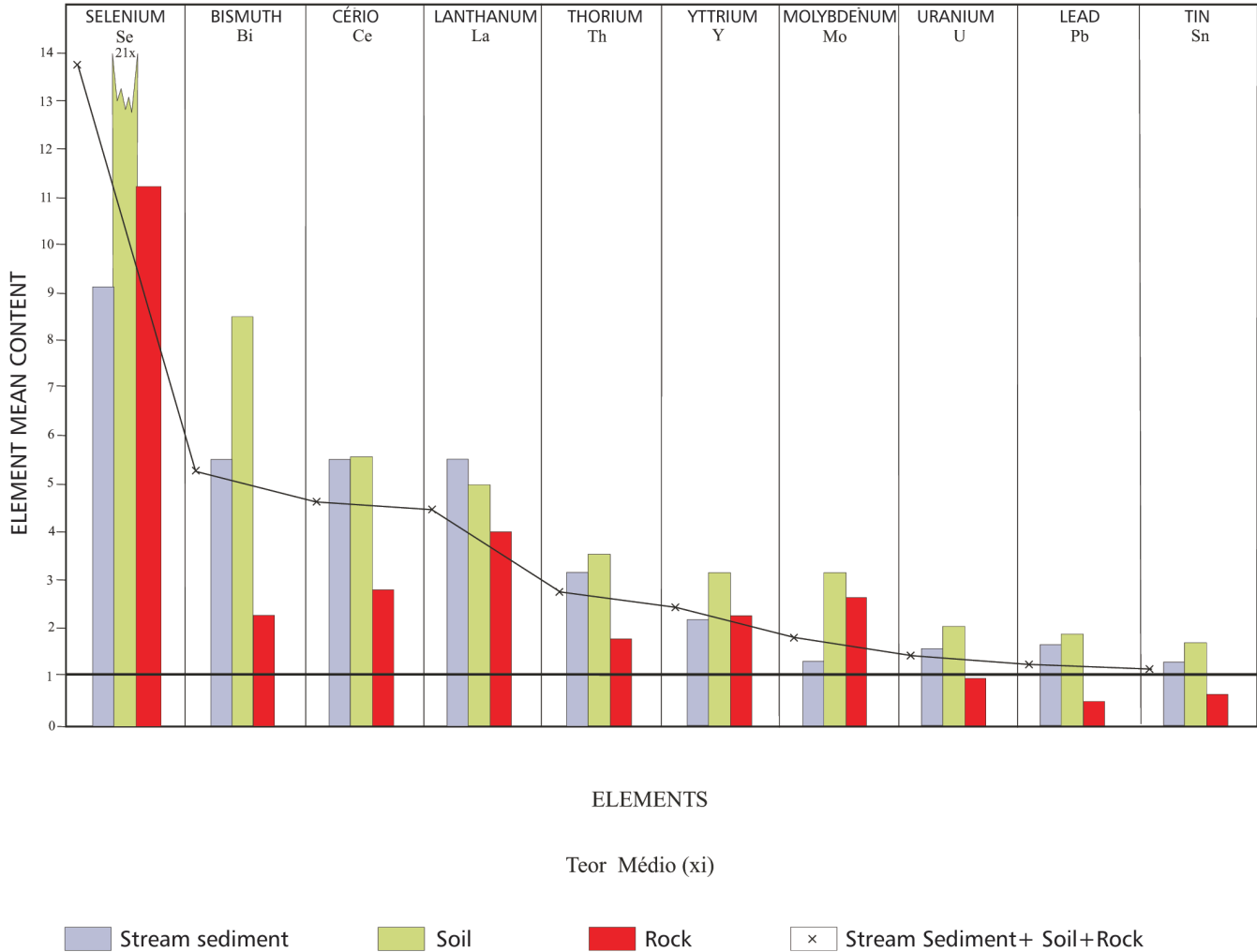
Figure 4 – Geochemical signatures in stream sediments, soil and rock.

necessary are recommended. Area nº2 was delimited within the region of Fazenda Juazeiro, which has elevated uranium contents in the groundwater (85ppb U and 93ppb U) and includes the Engenho deposit, sampling site of the soil sample with 8.3ppm U and with a total reserve estimated in 27,600 t of U_3O_8. Area nº3 was delimited from geochemical baselines (≥5.0ppm U), reached in stream sediment samples in the region of the Monsenhor Bastos deposit with a total reserve estimated in 2,200t U_3O_8.

The groundwater wells situated in São Timóteo, Fazenda Muquila and Lagoa Grande are also recommended for complementary studies in environmental geochemistry and medical geology (Figure 5 and Table 2).

CONCLUSIONS

Over the last 50 years, scientists worldwide have been investigating the correlations between geochemistry and

health. But, in Brazil this theme has only acquired more importance in the last 5 years. Work groups of geoscientists, doctors, biologists, geographers, chemists and experts from other scientific areas, several governmental institutions and universities, have been developing this new science of medical geology in Brazil. The National Program for Environmental Geochemistry and Medical Geology Research (Programa Nacional de Pesquisa em Geoquímica Ambiental e Geologia Médica) – PGAGEM unites these researchers through an internet network (regagem@ige.unicamp.br).

From the methodological application, evaluation, interpretation and integration of data from the Lagoa Real region study, the following conclusions were made:

The method used identified the geochemical and hydro-geochemical signatures compatible with the standards obtained through the analyses of rocks and soils sampled from the same sites and indicated eight groundwater wells as polluted or, particularly contaminated by radioactive pollutant (uranium).
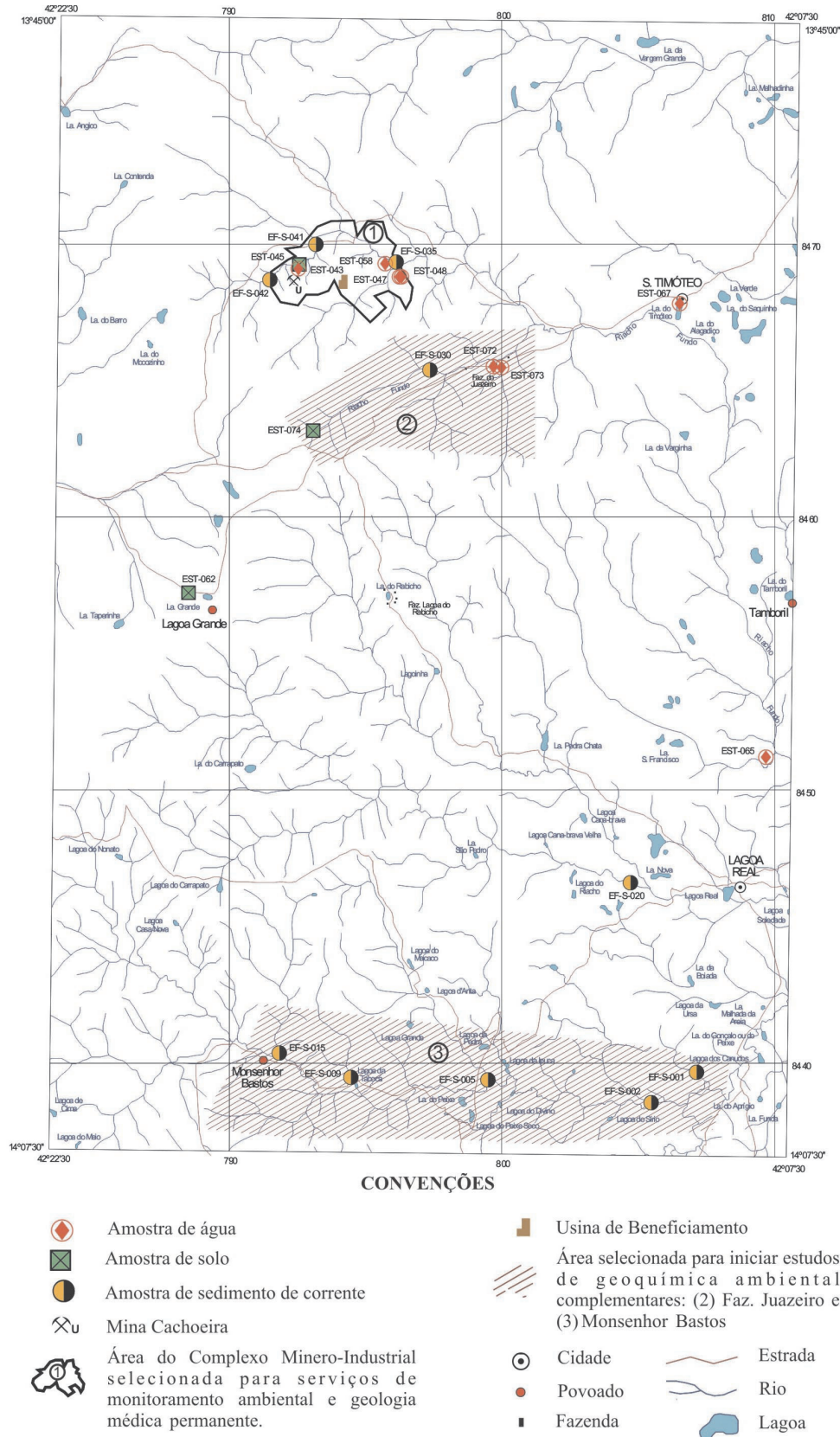
Figure 5 – Sampling sites and area selected for complementary research within PGAGEM Lagoa Real.

Table 2 -Target areas and selected samples for complementary research within Lagoa Real

Sampling sites	Target area (Nº) Individual sample (*)	Analized material (Uranium content)	LONGITUDE UTMmE	LATITUDE UTMmE
EF-S-035	(1)	S (5.2ppm)	796,109	8,469,380
EF-S-041	(1)	S (14.9ppm)	793,170	8,470,054
EF-S-042	(1)	S (6.3ppm)	791,503	8,468,748
EST-043	(1)	A (29.89ppb) R (9.9ppm). S (8.7ppm) R (9.9ppm). S (8.7ppm)	92,554	8,469,283
EST-045	(1)	L (13.1ppm)	792,554	8,469,283
EST-047	(1)	A (158.79ppb)	796,258	8,468,982
EST-048	(1)	A (41.39ppb)	796,349	8,468,982
EST-058	(1)	A (42.11ppb)	795,749	8,469,438
EF-S-030	(2)	S (5.0ppm)	797,341	8,465,425
EST-072	(2)	A (566.85ppb)	799,705	8,465,694
EST-073	(2)	A (105.93ppb)	799,993	8,465,635
EST-074	(2)	L (8.2ppm)	793,075	8,463,199
EF-S-001	(3)	S (5.2ppm)	807,105	8,439,738
EF-S-002	(3)	S (5.2ppm)	805,444	8,438,631
EF-S-005	(3)	S (5.8ppm)	799,481	8,439,462
EF-S-009	(3)	S (5.0ppm)	794,461	8,439,563
EF-S-015	(3)	S (6.3ppm)	791,835	8,440,462
EST-062	(*)	L (10.7ppm)	788,513	8,457,279
EST-065	(*)	A (21.03ppb)	809,690	8,451,388
EST-067	(*)	A (98.48ppb)	806,517	8,467,984

Sampled material: A (water), L (soil) R (roch) and S (stream sediment), (1) target area at the INB mineral-industrial complex, (2) target area at Fazenda Juazeiro, (3) Target area Monsenhor Bastos, (*) Tubular wells selected for monitoring campaigns

In Lagoa Real, more recently greater importance has been given to human health risk related to groundwater contamination than to the intrinsic problems related to the Cachoeira uranium mine exploration. This is due to the aquifer's slow, predominantly fractured, water renovation, making it difficult to measure its qualitative characteristics.

Most uranium polluted wells are aquifers with average to high salinity and also with expressive selenium contents, which means the water is neither suitable for human consumption nor other activities such as irrigation and cattle.

Since this is a rural zone, agricultural soil samples must be studied considering that some of them are likely to be irrigated with polluted or contaminated water.

The exclusive dependence of both the local population and the INB mining company on a groundwater supply leads to possible use conflicts. This may also make it impossible to sustain the hydric resource, mainly in the case of the aquifer/groundwater contamination.

Although the mining company's present water production/demand situation can be considered satisfactory, this condition may be short lived as several regional wells are drying up.

With respect to uranium, in spite of technological progress, it is nevertheless a radioactive and lethal substance with high contamination risks. Therefore, constant human and environmental monitoring is vital. The Lagoa Real yellow cake industry is the first processing stage of the nuclear fuel cycle, and the technique of lixiviation in

piles eliminates many process stages, which means lower risk to the environment, agriculture and public health.

Though the number of deaths caused by cancer in recent years in Lagoa Real is statistically very small, the results of this study emphasize the need for complementary research on the correlation between uranium and cancer in the Lagoa Real Uraniferous Province area.

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ASBESTOS: WHAT IS IMPORTANT TO CONSIDER

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INTRODUCTION

To the layman, asbestos is a mineral to be avoided at all costs, because of its carcinogenic properties. As there are many cancer cases due to asbestos it warrants a closer study to propose possible measures to ban or control its use when noxious. However, it should bourn in mind there are a great number of minerals that present the same physical characteristics as asbestos which could be used as a substitute. As these minerals have both different chemical compositions as well as physical behavior from each other, they have different potential levels of being carcinogenic.

DEFINITION OF ASBESTOS

The American Geological Institute (1980), Glossary of Geology presents a clear definition of asbestos: "Asbestos – a commercial term used for a group of silicates minerals which breakdown into fine strong fibers, flexible, heat and chemical attack resistant, used mainly for paper, paints, brake systems, ceramics, cement, fillings and filters where it is necessary to use non combustible material, of low electric conductibility. These exceptional physical and chemical characteristics make it an advantageous material for industrial use."

MINERALS USED AS ASBESTOS

Asbestine minerals, of acicular habit and usable as asbestos, are found in two mineral groups, serpentines and amphiboles. Among serpentines there is only one mineral, chrysotile a hydrated silicate of magnesium. Among amphiboles there are five minerals, all containing iron: actinolite, anthophyllite, crocidolite, cummingtonite and tremolite. In addition to containing iron, an element that does not occur in chrysotile, the fibers of the amphiboles are less flexible and more rigid than the chrysotile fibers. Figure 1 presents details of these minerals usable as asbestos.

ASBESTOS AND HEALTH

The human body has, in the nostrils, ways of detaining and removing small fragments inhaled when breathing preventing them from reaching the lungs. However, many fragments, usually smaller than 10 microns, can enter the lungs. There, these fragments are enveloped by macrophagic cells, forming little masses that are expelled through short coughs.

Asbestosis

Asbestosis and other forms of lung cancer occur when of these mineral fibers, breathed in together with other everyday dust particles, do not get expired and remain in the lungs, eventually causing inflammations and abnormal cell growths. This process is not efficient with long, rigid prismatic particles that are more difficult to be enveloped especially if containing iron. Details and photos are presented in Figure 2.

Influence of smoking on the incidence of asbestosis

A very important factor to be considered is the incidence of asbestosis is expressively greater in smokers than non-smokers. The vast majority of people suffering from asbestosis are smokers. Although tobacco has its own numerous carcinogenic components, considering the heated air breathed into the lungs by smokers can be a chemical reaction accelerating agent this leads to the

oxidization of the fibers with iron. In this case there are similarities with what occurs with rock weathering, where heat is an important factor in the intensity of the chemical reactions that alter them.

Asbestosis in soapstone workers

Cancer due to amphiboles present in soapstone have been described in the literature, occurring mainly in regions where the soapstone is cut and polished for the production of ornamental pieces, construction and architecture. Bezerra et al. (2003), researching the situation of soapstone workers in Ouro Preto, Minas Gerais, conclude that "the study of the dust's composition revealed the presence of breathable asbestos fibers of the amphibole group (tremolite-actinolite). These results suggest the occurrence of talc-asbestosis among soapstone handicraftsmen." To call such cancer forms "talcosis" does not seem to be correct, since the causing minerals are asbestine amphiboles.

Asbestosis in other deposits with asbestine amphiboles

One of the most representative cases of asbestosis due to amphiboles resulted from the mineral extraction front of a vermiculite deposit in Libby, Montana, United States. The ore contains small amounts of asbestine tremolite and its mineral extraction and grinding led to a large number of cancer cases due to asbestos, not only in Libby but also in other communities where the tremolite containing vermiculite was sent for use in constructions and additions to soil.

GEOLOGICAL CONSIDERATIONS ON THE CAUSE OF ASBESTOSIS

When they involve the iron containing fibers, the macrophagic cells may react with them oxidizing the bivalent iron to trivalent, causing iron hydroxide to be formed, such as goethite or limonite. These can adhere to the lung walls and prevent the removal of the mineral. This alteration does not occur with chrysotile, a mineral that does not contain iron. In the case macrophagic cells should chemically react with chrysotile, the fibers will be destroyed because there is no formation of a magnesium secondary mineral.

This alteration process is very similar to what occurs during rock weathering with these minerals. There are few rock outcrops with amphiboles that present these minerals without alteration on the surface. In comparison, the chrysotile serpentine is very resistant to weathering, normally outcropping without weathering in serpentinite ultramafic rocks.
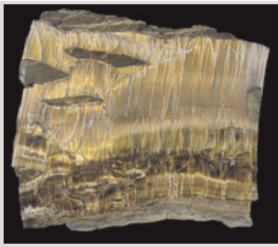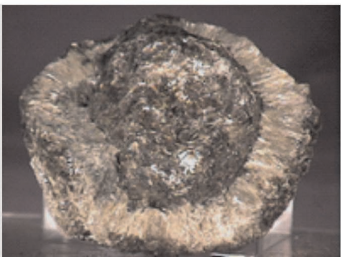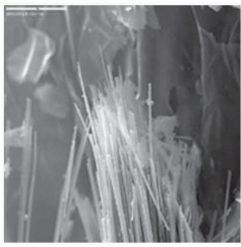
Serpentinite Mineral Group	Anphibolite Mineral Group	
Micaceous and fibrous minerals, weathering products from olivines and pyroxenes.	Fibrous minerals, primary constituents of metamorphic and igneous rocks.	
In serpentinites and serpentinized ultramafic rocks.	In acid, intermediary , basic and alkaline igneous rocks and in metamorphic rocks (gneiss, amphibolite and schist)	
Crysotile - $Mg_3Si_2O_5(OH)_4$	Anthophyllite	- $(Mg,Fe)_7Si_8O_{22}(OH)_2$
	Actinolite	- $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
	Crocidolite (reibeckite)	- $Na_2(Fe_{23},Fe_{32})Si_8O_{22}(OH)$
	Cummingtonite (amosite)	- $(Fe,Mg)_7Si_8O_{22}(OH)_2$
	Tremolite	- $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
Asbestiform Chrysotile	Asbestiform Anthophyllite	Asbestiform Tremolite

Figure 1 – Relation and chemical composition of the minerals used as asbest

"Asbestos fibers in the lungs. Most of the fibers are expelled, but some may cause inflammation. Infection by asbestos occurs when there is a long lasting and strong exposure. Long durable fibers, such as in amphibole are the worst. Smoking habits increase the lung cancer risks." ASTDR (2005)

"Asbestos fibers in alveolar bronchiolitis fluids, retrieved from the lungs of a man with strong exposure to asbestos. Macrophagic cells stick to a larger fiber. Below, on the right, a small fiber is enveloped by a group of macrophagic cells." (Agius, 2005)

"Asbestos fibers, in larger scale, enveloped by macrophagic cells. The fibers are covered with iron hydroxide and proteins. There are small dark inclusions in many cells, probably as result of smoking." (Agius, 2005)

Figure 2 – Asbestos fibers in the lungs.

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THE CRENOTHERAPY OF RIO DE JANEIRO STATE BRAZIL MINERAL WATER

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INTRODUCTION

Drinking mineral water is one of the most ancient means of health treatment used by man. Through millenary clinical proof it has been shown by its widespread and efficient use to heal a wide range of illnesses in different periods around the world.

In ancient times the virtues of hydromineral springs were considered supernatural manifestations and religious phenomena. Gods, nymphs and other symbols were the first protectors of springs and the first hydrotherapists were priests and healers. In Ancient Greece, Aristotle proclaimed the virtue of the vapors emanated from thermal springs, whereas Plato discussed the origin of mineral water. Herodotus, one of the greatest Roman thinkers, outlined the principles of crenotherapy (from the Greek Crenos=spring).

Facts related to mineral water use are frequent found in historical documents. The Bible mentions crowds of sick people gathered around the spring of Bethsaida, in Jerusalem, seeking a cure. In Europe, before the Roman occupation, the Gauls already used some of its numerous thermal springs. However organized resorts were started by Julius Caesar. During the Middle Ages the pagan divinities were replaced by the Catholic Church saints in the springs under their responsibility.

Scientific documentation on the subject only appeared in 1604, when the first mineral water legislation was passed in France, by Henry IV. In the 18th century, Hydrology was consolidated with the results of a study with more than 2,000 observations made in Barèges, by Theophile de Bordeu and several publications of the French Royal Society of Medicine (Duhot & Fontain, 1963). The period between the two world wars saw the rise of the modern industry of bottled water.

In Brazil, Emperor D. Pedro II created in 1848 the hydromineral station of Caldas da Imperatriz, in Santa Catarina State, which initiated the country´s use of mineral water in health resorts. The first studies of Brazilian mineral water appeared in the early 20th century, especially after 1930 with the creation of the National Department for Mineral Production (Departamento Nacional da Produção Mineral) – DNPM. Since then the mineral water industries of health resorts and bottled water became established. This was largely due to the discovery of springs in the South of the country and Minas Gerais (São Lourenço, Caxambu, Lambari, Araxá, Poços de Caldas, Cambuquira, etc.) and São Paulo (Lindóia, etc.). In 1945, the Mineral Water Code (Decree- nº7841, Official Diary August 20th 1945) that defined and classified mineral water came into effect, regulating its research, exploration, industrialization and commercialization.

Rio de Janeiro State had its first hydromineral spring discovered in 1887, in Paraíba do Sul. This spring's water, today inactive, was classified as alkaline-sodic bicarbonated, and was known as salutary, which origi-

nated the trademark "Salutaris". The water has been bottled since 1898 under this name. In 1941 a hotel and leisure area were built – the buildings still remain – and the area was called " Salutáris Water Park - Parque de Águas Salutáris", being the first Hydromineral Resort of Rio de Janeiro State.

One year later, the Santa Cruz Mineral Water was discovered by the former slave Domingo Camões, known as "Beiçola". In 1909, he established a home-bottling plant called Saint Water (Água Santa), producing 5 liter wine bottles delivered from door to door on donkey back. The company Águas Santa Cruz Ltda was founded in 1914, which still exists in the Água Santa district, perpetuating the spring's name.

Currently there are 34 mineral water bottling companies in Rio de Janeiro State.

CONCEPTUALIZATION

Mineral water is the name given to "water from natural springs or artificially extracted, that have a chemical composition or physical or physical-chemical proprieties distinct from common water, with characteristics that confer on them a medicinal action" (DNPM, 1966). This concept, from the National Mineral Water Code, is the most accepted, though there are other definitions based on types of mineral water that do not completely fit the above criterion.

For the French, for instance, mineral water is any natural spring water endowed with therapeutic proprieties, even if it does not have the mentioned physical, chemical or physical-chemical content distinct from other water, a phenomenon often observed and confirmed with clinical proof. This characteristic is attributed to infinitesimal concentrations (ppb) of elements or chemical substances, generically denominated as oligoelements, responsible

for its medicinal properties. This water is denominated oligomineral or oligometallic. In Brazil, these waters are classified as oligomineral.

In 1972, in Vienna, FAO – Food and Agriculture Organization and WHO – World Health Organization, both United Nations entities, organized a meeting of several countries seeking a World Mineral Water Code. The most controversial topic was precisely the concept of "health enhancement properties" for which no agreement was reached.

Based on the Brazilian Code, water can be considered mineral (Caetano & Yoshinaga, 2003; Caetano 2005) according to:

a) Its chemical composition (Table 1) – when the presence of a given element or substance is predominant;

b) When it has proved medicinal action confirmed and approved by the Permanent Commission for Crenotherapy (Comissão Permanente de Crenologia), linked to DNPM (oligominerals); and;

c) Its physical-chemical characteristics at the spring:

• when there is a gaseous radon yield between 5 and 50 Mache units (radioactive);

• when there is a gaseous thorium yield equal to 2 Mache units (thorium-actives);

• when it has a clear release of sulfuric gas (sulfurous) and;

• cold, hypothermal, mesothermal, isothermal and hyperthermal: when the temperature is, respectively, inferior to 25°C, between 25 and 33°C, between 33 and 36°C, between 36 and 38°C and above 38°C.

Today, the WHO, through the Codex Alimentarius defines natural mineral water as only that which is characterized by the concentration of certain mineral salts, by the presence of oligoelements or other constituents. In the United States, the agency responsible for this sec-

Table 1 - Mineral water characteristics (modified by Caetano & Yoshinaga, 2003; Caetano, 2005)

Classification	Characteristics
Radiferous	Permanent radioactivity potential
Alkaline Bicarbonate	Sodium bicarbonate = or > 200mg/L
Alkaline Terrous	Calcium Carbonate = or > 120mg/L
Alkaline Calcic Terrous	Calcium = or > 48mg/L as calcium bicarbonate
Alkaline Magnesian Terrous	Mg = or > 30mg/L as magnesium bicarbonate
Sulfated	Na, K and/or Mg Sulfate = or > 100 mg/L
Nitrated	Nitrates of mineral origin = or > 100 mg/L
Chlorinated	Sodium Chloride = or > 500mg/L
Ferruginous	Iron = or > 5mg/L (Ex.: Salutaris - RJ)
Carbo-Gaseous	Dissolved carbonic gas = or > 200 mg/L
Predominant Element0.01mg/l)	Iodinated; Lithinated; Fluorinated; Brominated; Vanadic, etc.

tor, the Food and Drug Administration (FDA), requires a minimum of 250mg/L of dissolved total solids to classify the water as mineral.

According to the Economic European Community – EEC (Directive 80/777/CEE/1980), mineral water is distinguished from other water for its nature and is characterized by the concentration of minerals, oligoelements or other constituents and, if not, by certain effects and by its original purity, with one or the other characteristic kept intact, due to its underground origin, protected from any risk of pollution.

Before the EEC legislation, the presentation of a minimum dissolved total solids equal or superior to 1,000mg/L or 250mg/L free CO_2 was required for its classification as natural mineral water. The present classification of natural mineral water in the European Community follows the standards reported in Table 2.

In France, the establishment of a mineral water bottling industry depends on the Service of Mines (Ministry of Industry, General Directions of the Industry, of Research and of the Environment) and on the Ministry of Health, after obtaining a certification from the Medicine Academy regarding the therapeutic properties of the water.

There us a growing concern surrounding the criteria for mineral water classification and also a tendency to adopt minimum limits for mineral salt content. The National Mineral Water Code reform is a requirement of the professional and scientific community.

Two attempts to alter the Code were made respectively by the Republic Presidency, in 2002 and by the DNPM, in 2003, which issued a text for public consultation. The text had proposed that any groundwater, since potable and tapped in a way avoiding contamination, could be considered as mineral water bearing low, medium and high mineralization. Based on those generic criteria, the Brazilian law would contrast with the European and American mineral water framework. After receiving many contributions however, the initiative did not succeed and the reform did not take place.

Besides mineral water, the Brazilian Code defines table potable water as water bearing normal composition from natural springs or artificially extracted which fulfills the potability requirements for a given region. This water is called natural water by the National Sanitary Vigilance – ANVISA, linked to the Health Ministry. ANVISA also gives permission to produce bottled purified water, with the addition of salt, as water with diverse origin, artificially mineralized or ozonized.

MINERAL WATERS CONSUMPTION IN PRESENT DAYS

There are justifications which explain the growing consumption of mineral water. The human rift with nature produced by technological progress, has generated a resistance by humanity's collective unconscious. The search for an alternative between artificially treated, public supply water and the contaminated water from increasingly polluted sources, found an outlet in mineral water which, in addition, is good to health. Thus, a continuously expanding mineral water market arose used as a drink or food complementation.

In addition to the dissemination of bottled water consumption, hydromineral resorts are enjoyable. In some European countries, France for example, the tradition of famous resorts such as Vichy and Aix-les-Bains are maintained and their tourist potential generates substantial revenues.

In Brazil famous resorts such as Caxambu, São Lourenço and Poços de Caldas in Minas Gerais and Lindóia and Serra Negra in São Paulo attract large numbers of national and international tourists. Nowadays, after a decline in the crenological medicine, there is a renewed interest in mineral water, supported by the development of new medicine specialization fields, such as orthomolecular. This new tendency fulfills the search for a new way of life, away from the artificiality predominating industrialized food, pollution and sedentary stagnation. According to orthomolecular medicine, a large number of toxins and products dangerous to our health are ingested. These include: synthetic food additives, agrochemicals, heavy metals and transgenic foods (the effects of which are not yet clarified) that have a negative impact in our metabolism, giving rise to biological and energetic weaknesses leading to diseases. Within this context, mineral water appears as a means not only to the combat these symptoms, but also to act in a more integrated way. Therefore, mineral water is seen as a source to replenish the body's depleted mineral salts and micronutrients (Bontempo, 2002).

Table 2 - Mineral water classification by CEE (modified by Caetano & Yoshinaga, 2003; Caetano, 2005)

Classification	Requirement
Very low mineralization	<ou = 50mg/L of TDS
Low mineralization (oligominerals)	between 50mg/L and 500mg/L of TDS
High mineralization	> 1,500mg/L of TDS

GEOLOGICAL ASPECTS

Based on today's knowledge of the Earth's water cycle and distribution, mineral water has its origin, like groundwater, in pluviometric precipitation flowed by percolation towards underground reservoirs. So, mineral water is a special type of groundwater with springs that depend on the vertical movement across faults and fractures under very low velocities. Being affected by the weight of the water column above, and sometimes by gas and vapor, this water tends to rise to the surface (Figure 1). The mineral water formation begins in the atmosphere, where, as rain drops, it absorbs elements from the air. As it percolates through the soil, it becomes affected by the non-saturated zone until it reaches the water table and rock media, its last mineralization stage. The time gap between the infiltration and discharge depends on the geographical extension, varying from tens to thousands of years. The chemical composition reflects this percolation process through the geological media, where, moving downwards under rising temperature and pressure, it dissolves rocks and minerals (Martins et al. 2002). This theory is based on the geothermal gradient, which foresees an increase of 1°C for every 30 meters of depth.

The magmatic theory argument is supported by the thermal and gaseous sources and the spring's richness in elements, which rarely occur in the upper layers of the earth's crust. Although, this theory is considered old-fashioned, it is still possible to conceive a double source, initially the meteoric water becoming saturated with the salt content while percolating in the geological media and the other related to volcanism and plutonic events (Figure 2).

Andrade Júnior (1937), a pioneer researcher of mineral water origins in Brazil, based on the geographical distribution of the main springs, has confirmed they are situated in NE-SW shear belts from North to South coinciding with the nation's mountain ranges. This geological interpretation led to the conclusion these hydromineral springs are related to alkaline magmatism and to a deep fracture system. This opinion is also shared by Frangipani (1995), who correlates those springs with shear and folding belts near Cratonic areas and sedimentary basins, and also, near areas where the basement was affected by tectonics. Those regions have structures that allow deep water circulation until it reaches the surface as a spring.

The Rio de Janeiro State mineral water occurs, in general, in natural springs, which were discovered by local inhabitants and used empirically for medical purposes before they had been formally analyzed. This was the case of the Iodine rich water from Pádua and Raposo Mineral Water. The simplified State geological map in Figure 3, shows the known mineral water distribution according to their predominant composition.
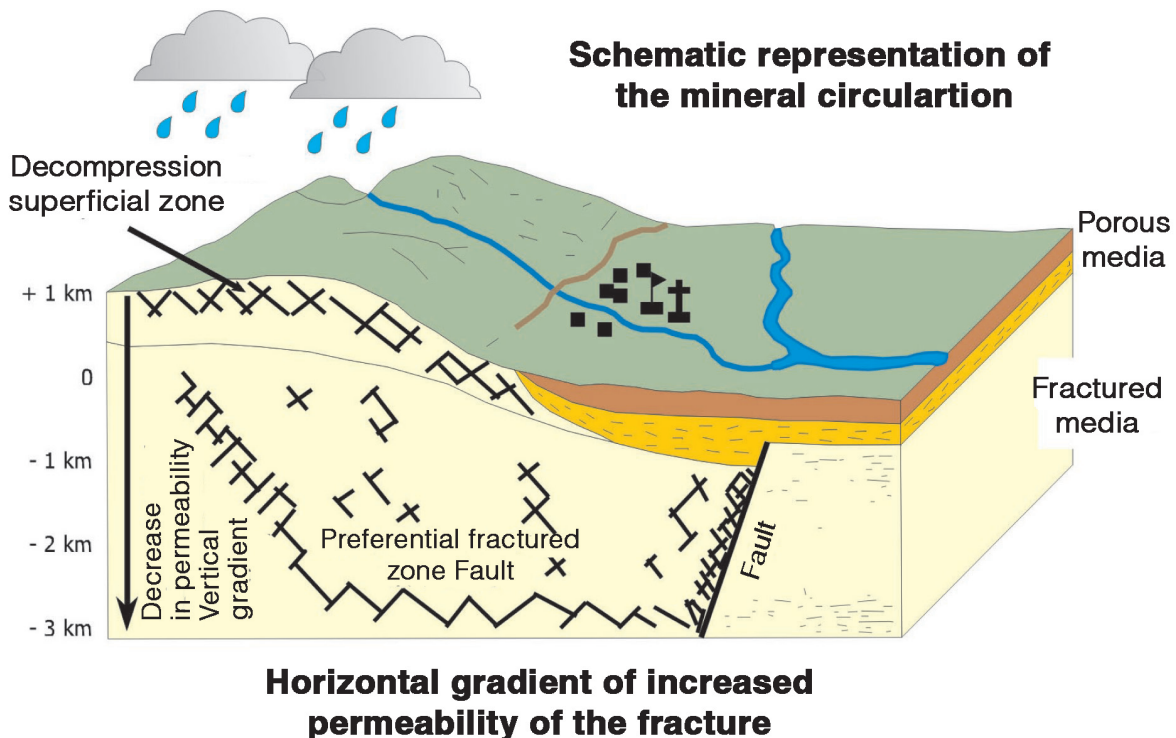
Figure 1 – Origin of the Mineral Waters

Thermal Circuit
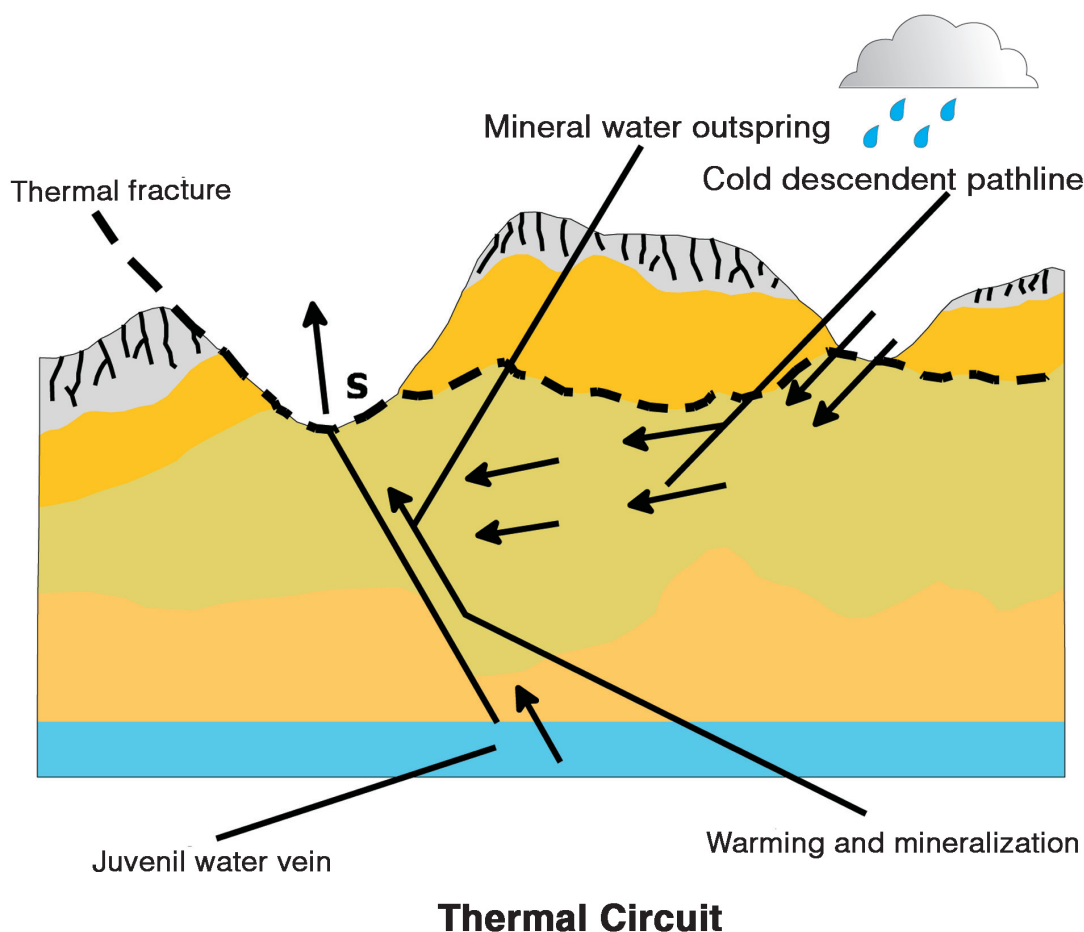
Figure 2 – Composed origin for the mineral waters.

RIO DE JANEIRO STATE MINERAL WATER THERAPEUTIC INDICATIONS

Crenotherapy treatment must be conducted by a professional who will be responsible for the important periodic examinations. Furthermore it must be done on-site, as the water only has its full potential within the spring areas. There are two types of treatment: internal (water ingested as medication) and external. The internal treatment, besides simple oral ingestion, there are subcutaneous, intramuscular and intravenous injections, which may be done with isotonic water. The external techniques are based on showers and pools, saunas, aerosols, even through local application with a compress etc. Despite the innumerous proprieties shown in Table 3 (only by ingestion), the mineral water consumption must be oriented by a professional. There are contra-indications according to the water type and each person's metabolism. This is

the case for water with high salt contents that can not be ingested by people with hypertension. In the same way, water with a high calcium concentration is not suitable for people with a potential high tendency of renal and vesicular problems.

Regarding radioactive water, there are divergences as to their health benefits. The allopathic medicine praxis manifests some concern about the radiation effects. According to Mourão (1992), a famous crenologist doctor, in his book "Hydrological Medicine", Rio de Janeiro State presents three main categories of hydromineral springs:

Radioactive;

Alkaline-terrous bicarbonate;

Carbo-gaseous.

A special mention is made of the Pádua iodine-rich water, considered rare due to its iodine concentration, used therapeutically in circulation diseases, such as arteriosclerosis and hypothyroidism.

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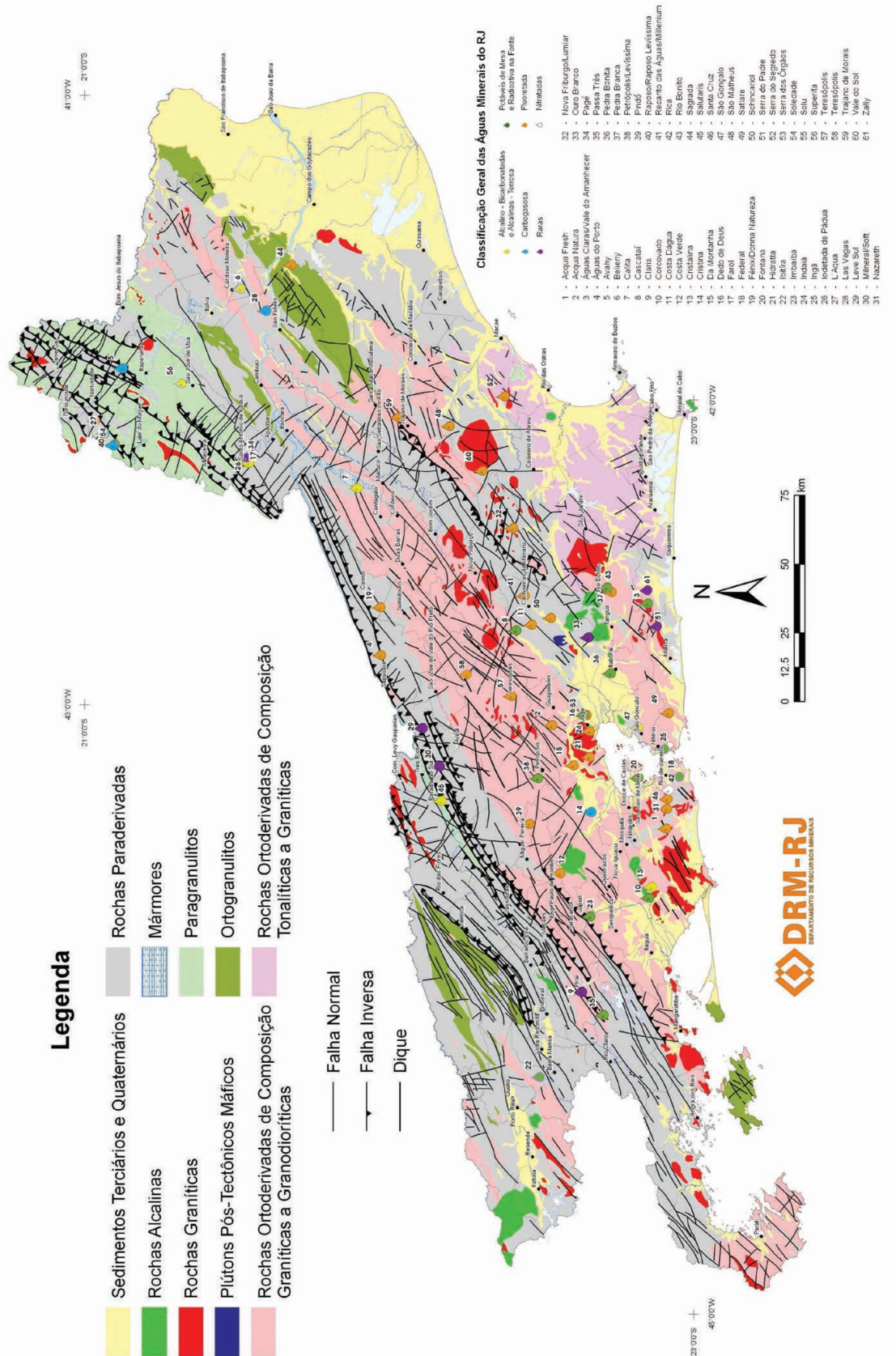
Figure 3 – Simplified geological map for the State of Rio de Janeiro and the location of the most important mineral springs.

Table 3 – Therapeutically properties of some mineral water (Lopes, 1956; Untura Filho, 1995; ABINAM, 1996).

Mineral Waters Branch	Therapeutical functions								
	Classification	Gastric	Hepatic	Dermatologic	Metabolic	Intestinal	Nervous	Teeth's and Bones	Renal
Aqua Fresh	Fluorinated							X	
Acqua Natura	Fluorinated and low radioactivity at spring							X	X
Águas Claras/Vale do Amanhecer	Very low radioactivity at spring								X
Águas do Porto	Fluorinated and low radioactivity at spring							X	X
Avahy	Carbo-gaseous		X						
Belieny	Alkaline Bicarbonate	X	X	X		X		X	
Calita	Alkaline-calcic fluorinated terrous	X		X				X	
Cascataí	Very low radioactivity at spring								X
Claris	Litinated and Fluorinated						X	X	
Corcovado	Very low radioactivity at spring								X
Costa Dágua	Fluorinated							X	
Costa Verde	Fluorinated and Very low radioactivity at spring							X	X
Cristalina	Alkaline-fluorinated terrous		X	X				X	
Cristina	Fluorinated							X	
Da Montanha	Fluorinated and Very low radioactivity at spring							X	X
Dedo de Deus	Fluorinated and Very low radioactivity at spring							X	X
Farol	Hypothermal at spring								
Federal	Oligomineral								
Fênix/Donna Natureza	Fluorinated and Very low radioactivity at spring							X	X
Fontana	Radioactivity at spring							X	X
Hidratta	Fluorinated and radioactivity at spring								X
Ibitira	Potable bottled water								
Imbaíba	Very low radioactivity at spring								X
Indaiá	Fluorinated and radioactivity at spring								X
Ingá	Potable bottled water								
Iodetada de Pádua	Lodinated, Litinated, Brominated, Alkaline, Bicarbonate and Fluorinated	X	X	X	X	X	X	X	
L'Aqua	Fluorinated							X	
Las Vegas	Carbo-gasous	X	X					X	X
Leve Sul	Fluorinated and radioactivity at spring							X	X
Milneral/Soft	Fluorinated and lithinated						X	X	
Nazareth	Fluorinated and hypothermal							X	
Nova Friburgo/Lumiar	Fluorinated and low radioactivity at spring							X	X
Ouro Branco	Alkaline – Fluorinated Lithinated terrous	X	X	X			X	X	
Pagé	Lithinated						X		
Passa Três	Radioactive at spring								X
Pedra Bonita	Very low radioactivity at spring								X
Pedra Branca	Fluorinated and radioactivy at spring							X	X
Petrópolis/Levíssima	Radioactivity at spring								X
Pindó	Fluorinated and radioactivity at spring							X	X
Raposo/Raposo Levíssima	Carbo-gasous Fluorinated	X	X					X	
Recanto das Águas/ Millenium	Fluorinated and radioactivity at spring							X	
Rica	Nitrated							X	
Rio Bonito	Radioactivity at spring								X
Sagrada	Fluorinated and hypothermal at spring							X	
Salutaris	Alkaline-ferruginous terrous	X		X				X	
Santa Cruz	Fluorinated and hypothermal at spring							X	
São Gonçalo	Alkaline-carbonate terrous	X		X				X	X

ASSESSMENT OF GROUNDWATER CONTAMINATION LEVELS IN PARINTINS CITY, AMAZONAS STATE BRAZIL

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INTRODUCTION

Parintins municipality, with an area of 6,100 km², is situated in the East of Amazonas State, on the border with Pará State. Parintins Island, is located on the right bank of the River Amazon, has about 70,000 inhabitants, an area of 45 km² and is the seat of the municipality. It is about 350 km from Manaus and stands out as the State's main tourist center due to the traditional Boi-Bumbá festival.

The island has a rather flat relief, with the lowest altitudes, around 15 m near Lake Francesa and the Paraiba Pumping Station (extreme NE), and the highest, about 30 m, in the central area, neighboring the Bosque da Seringueira. The internal drainage is reduced to Lake Francesa and several small tributaries that flow into Lake Macurany.

Geologically, it is seated on Cretaceous sandy sedimentary rocks of the Alter do Chão Formation, which do not outcrop in the studied zone due to the intense degree of weathering. The local decomposition of these sediments gave origin to the predominantly thick yellow clayish-sandy latosoils, and secondarily sand rich soils probable fluvial neosoils. The native vegetal covering has been almost entirely removed to give place to dwellings and farms. Only some patches of campinarana (shrubby vegetation) can still be observed on the sandy soils and restricted riparian that grow along branches/inlets of Lake Macurany (Figure 1).

All the public water supply for human consumption comes from underground catchments, through tubular wells, distributed by three supply stations (Paraíba, SHAM and Itaúna), under the responsibility of SAAE, Autonomous Municipal Water and Sewerage System (Sistema Autônomo de Água e Esgoto Municipal).

Residents' reports and local chemical analyses, promoted by the SAAE laboratory, indicate that this water's quality is jeopardized, with chemical contamination probably linked to the precarious basic sanitation. Chemical analyses of water collected in public supply wells, in the ambit of PGAGEM – National Program for Environmental Geochemistry and Medical Geology (Programa Nacional de Geoquímica Ambiental e Geologia Médica), coordinated by CPRM – Brazilian Geological Service, confirmed the problem, registering nitrate and aluminum contents well above the maximum values allowed by law (BRASIL, 2004).

Recent studies suggest that high aluminum concentrations in water may unleash, after longer consumption periods, renal and motorial coordination troubles, as well as deficiencies in the immune system (Centeno, personal communication). The nitrate ion, though not very toxic, can be reduced to nitrite ions in the human organism. These
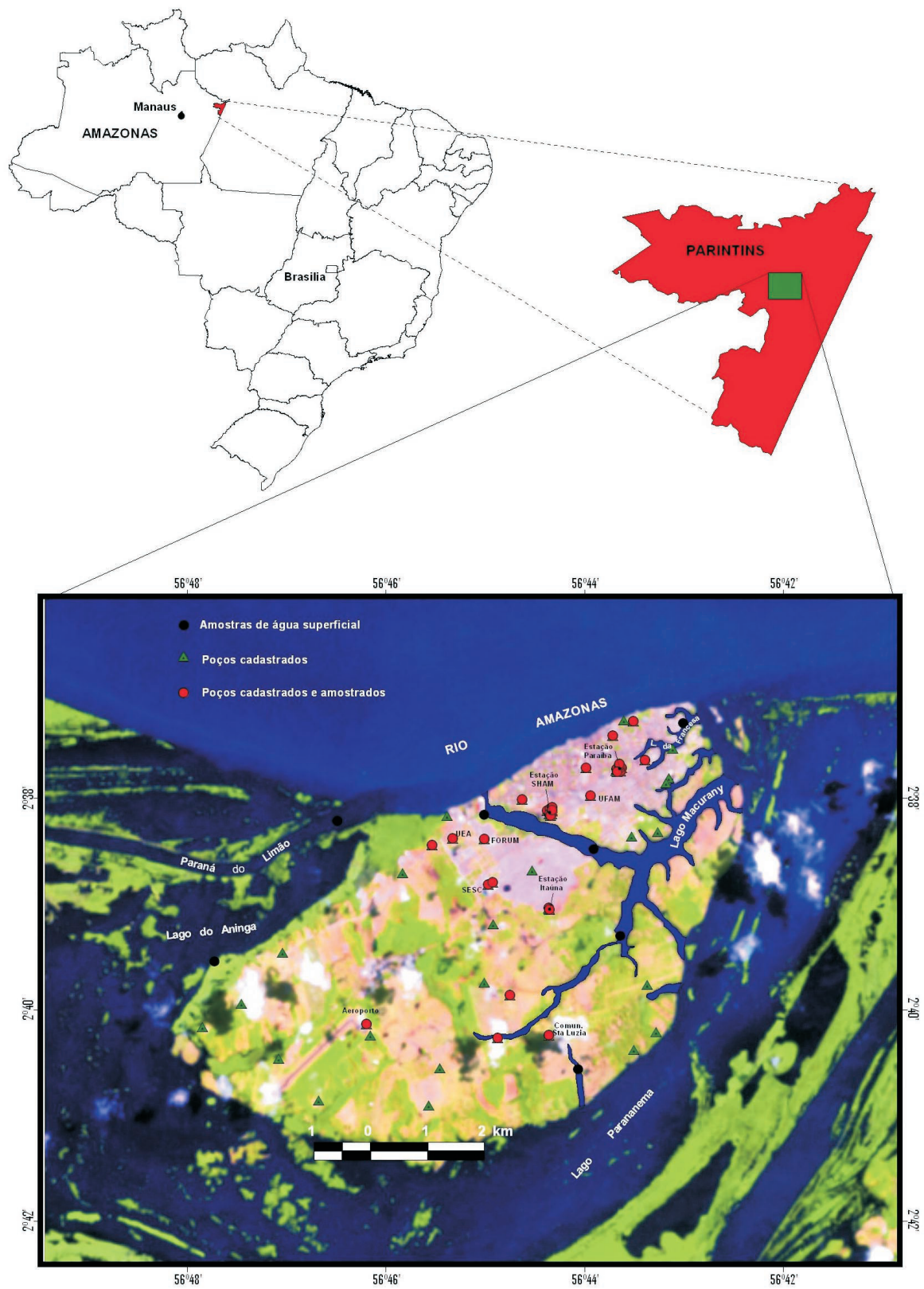
Figure 1 – Satellite Images showing Paritins island location, the registered wells and the water sampled.

are noxious to health because they induce methemoglobinemia, a disease that leads to the hypoxygenation of the blood in children and can be fatal. Moreover, nitrites can react, in the human body, with amines, producing nitrosamines in the stomach, substances recognized as potential carcinogenic agents by laboratory studies (Cortecci, 2003; Freitas et al., 2001).

Through the study of the physical characteristics of several public and private wells, associated with chemical analyses and instantaneous measurements of physical-chemical parameters (pH and electric conductance/conductivity) of surface and groundwater samples, the intensity of the contamination was evaluated and solutions for the problem's mitigation proposed.

MATERIALS AND METHODS

- The field and laboratory work, developed between April and May 2005, involved the following activities:
- fluvial recognition around the whole island perimeter, assessing the natural and anthropogenic features of the entire island, such as: geology, declivity, soil type, vegetation, urban occupation, etc.
- Tubular well and hand dug well inventory covering urban and rural areas, registering data such as: well head altitude, depth, static level, dynamic level, yield, filter position, lithological profile, etc.
- Groundwater and surface water sampling for laboratorial analysis at the Laboratories of the Catholic University of Brasilia for the following ions:
  - As, Al, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Se, Sn, V and Zn.
  - Chloride, ammonium, nitrate, nitrite, sulfate and silica were analyzed at the Laboratory of the National Institute for Amazonian Research-INPA.
- On-site analysis through digital sensors to measure pH, electrical conductivity and temperature.
- Mechanical soundings in public land, next to water wells to determine the water static level.

DISCUSSION AND RESULTS

Distributed in the interior part f the island, six samples from streaSix stream water samples were collected from around and in the central part of the island. The results indicated a good homogeneity in the physical chemical characteristics of these water samples: pH around 6,1 and 6,5; electrical conductivity between 41 and 50 µS/cm; nitrate content and Al below the 0,1mg/L: ammonium around 0,3mg/L and chloride 1,2 mg/L. This homogeneity was due to the season in which the sampling was conducted. This was the River Amazon flood period, when the river invades the whole low lands and get mixed with other water bodies, such as lakes, boreholes and the island's backwaters and surroundings, diluting eventual surface

and localized contamination. Regarding the groundwater, 33 tubular wells, 28 in urban areas and 5 rural zones were sampled (Figure 1). The results reveals that among the 18 wells from the public supply system, only two presented contents of Al (<0,2mg/L), nitrate (<10mg/L) and ammonium (1,5mg/L) obeying the levels established by the national legislation (Brasil, 2004). The others showed nitrate concentrations varying from 11 to 49mg/L, Al from 0,3 to 2,0 mg/L and ammonium up to 2,9 mg/L. They also show high levels of nitrate and Al in three public and two private supply wells. The urban area wells can be separated in two categories, according to their depths: deeper and shallower than 65 meters; the former showing nitrate levels and/or Al according to the legislation, whereas in the others the situation was reversed. This contamination is strongly associated with the well depths. Also the water from the shallow wells is always more acidic than from the deep wells (Figure 2), suggesting an inverse correlation between the pH values and the nitrate contents, especially when considering only the contaminated wells (Figure 3). The correlation between the water acidity with the nitrate is explained by the ion's origin, representing the final stage of organic matter oxidation. Effluents are rich in nitrogen and degrade into nitrates in the presence of oxygen, according to the organic nitrogen cycle >ammonium>nitrite>nitrate:

$NH_4^+ + 3/2 O_2 ? + NO_2^- + H_2O + 2H^+$ and
$NO_2^- + 1/2 O_2 ? NO_3^-$; or, simply:
$NH_4^+ + 3/2 O_2 ? NO_3^- + 4H^+$ (the production of nitrate increases the acidity)

The origin of the high nitrate levels in the shallow wells in the Parintins urban fringe is related to the lack of an adequate catchment system and sewage treatment in the city. This leads to liquid sewage wastes, dumped into septic tanks or open cesspits, infiltrating until contaminating the upper levels of the aquifer. An example is the Paraiba pumping station in whose terrain all the wells are situated besides being in a very low area flanked by urban occupation. This is a system of homes on stilts, where the residents dump all their waste directly into a surface channel that connects with Lake Francesa (Figure 4). The general lack of sanitation within the city is the main nitrate contamination source. The Parintins nitrate distribution map developed from the results, shows a clear tendency of higher concentrations along the island's main urban occupation. The Al distribution is similar, suggesting a strong correlation between these two elements (Figure 5). The high acidity in the nitrate contaminated water is also responsible for the process that triggers the Al contamination. This metal is an element known to have very low mobility within a pH in the range 4,0 to 8,0, typical for natural environments. Therefore, it is not easily liberated, as a ionic specie in the aqueous media, being fixed in the solid phase, as a clay mineral. However, under low pH, below 4,0, as found in many wells, together with the
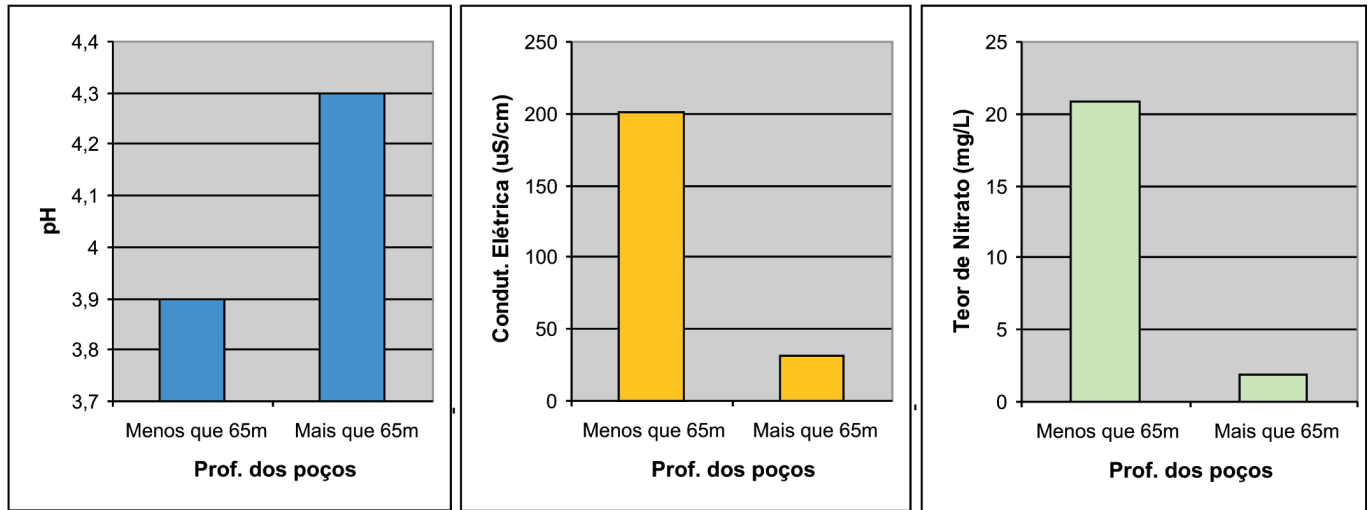
Figure 2 – Comparison between the mean pH values, conductivity and nitrate content for two different depth levels defined for urban wells.
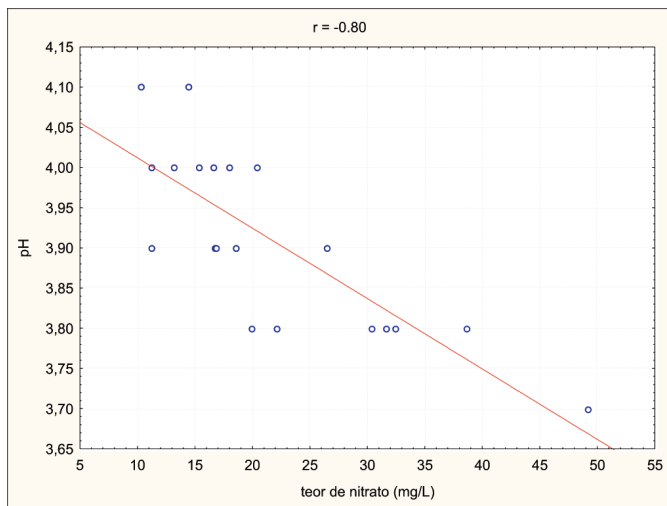
Figure 3. Strong inverse correlation between pH values and the nitrate concentration in Parintins well water.

high organic acids concentration, the Al may be soluble in the aqueous media, due to complexation, followed by a migration to solid phase building complex ions (Carvalho, 1995). The strong correlation between the nitrate contents with Al contents corroborates the suggested hypothesis (Figure 5). Among the metals analyzed in the groundwater samples, none registered a concentration above the permitted maximum values. In the rural areas, despite the shallow well depths, there is no evidence of organic contamination.

CONCLUSIONS AND RECOMENDATIONS

The majority of Parintins public water wells produce water with a chemical composition that does not obey the pertinent legislation, with emphasis on nitrate, ammonium and aluminum. The high nitrate concentrations are due to deficiencies in the urban waste system. The Parintins island aquifer has water, which is naturally acidic (pH 4,0 to 4,5), representing a natural constraint to the public health. This acidity increases in the wells with high nitrate contents providing conditions for the aluminum in soil particles to mobilize into the aqueous media, generating a composite of natural and anthropogenic contamination. As an immediate action, it is recommended pumping in six public wells with the highest contamination levels should be ceased (PT-6, PT-17, PT-22, PT-11, PT-20 and PT-19). Initiate the operation of two 80 m deep wells with good yields, in the Itaúna Station, which will replace the well closures. The actual Parintins demand considering the system losses (30%), is about 17.000 m³/day. The 12 remaining public system wells according to actual daily discharge data can produce more than 18.000 m³. In the short term, it is suggested a gradually deactivation

Figure 4 – Open sewage channel near the public water wells at the Paraiba pumping station.
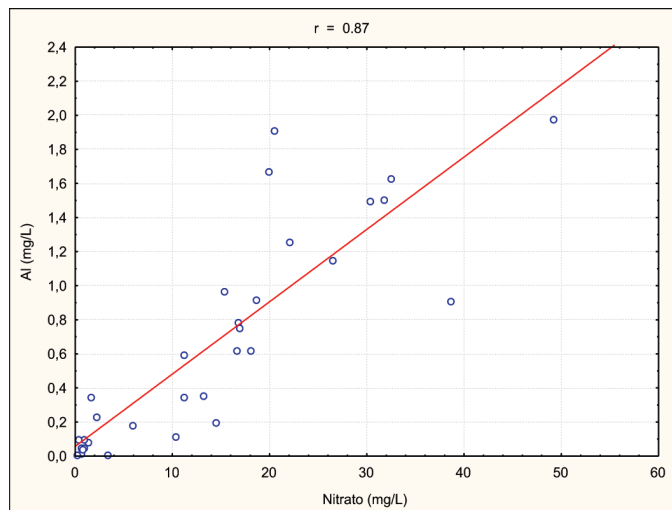
Figure 5 – Strong correlation between the nitrate and aluminum content in Parintins groundwater.

of the Paraiba Station wells, due to its precarious location (lowlands submitted to flooding and surrounded by open sewage channels) and the shallow wells (PT-10, PT-14 e PT-16) in the SHAM Station. At the same time, foreseeing 100.000 inhabitants in the city (daily water demand of 26.000 m^3), 5 new wells should be drilled (2 at the SHAN station and 3 at Itaúna), each more than 100 meters deep with an initial 50 meter cement liner. The 10 wells could produce about 14.000 m^3/day of water. In order to supply 100.000 inhabitants, it's crucial to lower the groundwater natural acidity. The alternative would be to install a catchment and treatment plant, with intake from the River Amazon, with a capacity of at least 15.000 m^3/day of treated water, with a pH around 6,0 to 6,5 to be mixed with the acidic groundwater. Above all, resources must be allocated to build a waste water system connected to a treatment plant covering the whole Parintins urban zone.

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GEOCHEMICAL CHARACTERIZATION OF THE EASTERN AMAZONAS PUBLIC WATER SUPPLY SYSTEM

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ABSTRACT

This study is part of the National Program for Environmental Geochemistry and Medical Geology Research (Programa Nacional de Pesquisa em Geoquímica Ambiental e Geológica Médica) – PGAGEM and it was made by the Brazilian Geological Survey through their Belém Office, in the States of Pará and Amapá, and part of Maranhão, Piauí, Tocantins, Mato Grosso and Amazonas. During the field work, 77 public water supply samples were collected in some cities covered by the study. The samples were analyzed for 6 anions (F, Cl, NO_2, Br, SO_4 and PO_4) through ion chromatography and for 25 cations (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, Ti, V and Zn) through ICP-AES. The result interpretations were based on statistical calculations and the maximum values permitted for human consumption, according to the CONAMA 357/2005 Standards and Resolution MS 518/2004. The elements Be, Ca, Co, Cr, Li, Mg, Mo, Na, Ni, Sr, Cl and F presented concentrations below the limits established by the legislations in all samples. However, the elements Pb, Al, Cu, Fe, B, Ba, As, Se, Br, Cd, K, Mn, Zn and PO_4 showed values improper for human consumption in the water samples of some communities. Although there are no studies showing a direct relationship between the elevated concentrations of these elements and diseases among the population, the confirmed Al and Pb contents (18 and 145 times higher than the maximum permitted values) are particularly worrying because they are elements considered toxic, which may cause adverse effects to human health.

INTRODUCTION

The studied area covers about 2,000,000 km^2 comprised of the whole States of Pará and Amapá and part of the States of Maranhão, Piauí, Tocantins, Mato Grosso and Amazonas. To optimize the operational activities and follow its physiographic and logistic characteristics, the area was divided in 10 work blocks: I – Northeastern Pará, II – Pará-Maranhão, III Tocantins-Piauí, IV – Southern Pará, V – Altamira, VI – Marajó, VII – Macapá, VIII – Trombetas, IX – Santarém and X – Tapajós (Figure 1).

77 public water supply samples were collected during four field work stages. The largest work volume was carried out in Block I (47 samples in Pará and 14 in Maranhão). Another stage was carried out in Blocks II
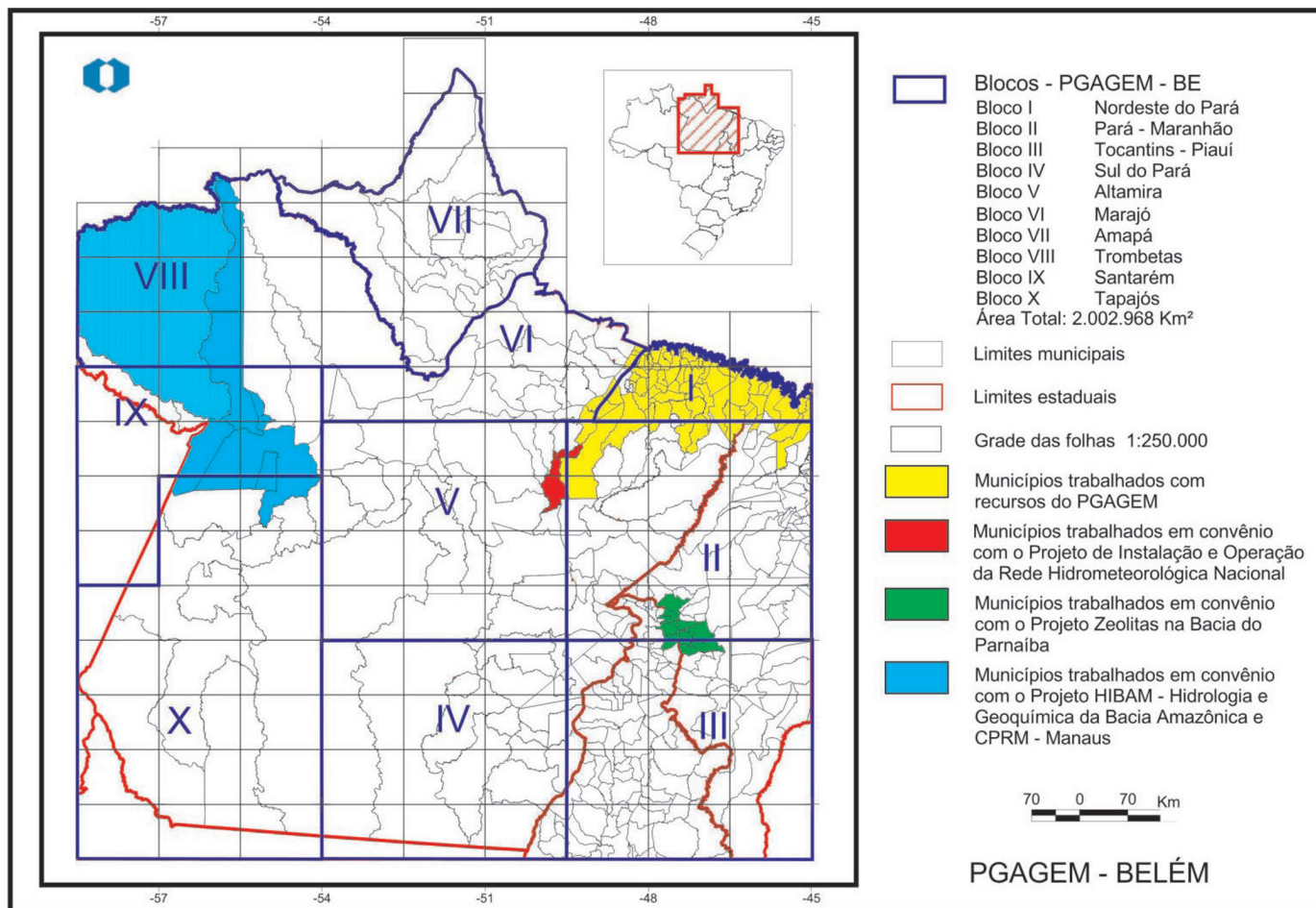
Figure 1 – Location map of the PEGAGEM-Belém executed studies.

and III in partnership with the Zeolitas Project in the Paranaíba Basin (10 samples). The third stage was carried out in Block IX in partnership with the Amazonian Basin Hydrology and Geochemistry Project (Projeto Hidrologia e Geoquímica da Bacia Amazônica) – HIBAM, product of a partnership between the National Water Agency (Agência Nacional de Águas) – ANA, the National Research Council (Conselho Nacional de Pesquisa) – CNPq and the Institut de Recherche pour le Développement – IRD, of France (4 samples). The last field work stage was carried out in Block V together with the Hydrometeorological National Network Program (Projeto Instalação e Operação da Rede Hidrometeorológica Nacional) (2 samples).

In each municipality one water supply sample was collected, the chosen site being always the station or well with the largest distribution system. During sampling, forms were filled out with the descriptive parameters of the sampling site and the pH measurement. The samples were collected directly from the well, spring or drainage, before any treatment was made. They were kept in polyethylene graduated tubes, with a 50ml capacity,

after being filtered in a micropore 0.45 m for cations and anions analysis. To preserve the soluble cations in the samples, 1ml HNO_3 1:1 was added to keep the pH < 2. The samples were kept refrigerated until analysis. 24 cations were analyzed (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, Ti, V and Zn) through ICP-AES and 6 anions (F, Cl, NO_2, Br, SO_4 and PO_4) through ion chromatography, in the Laboratory for Mineral Analysis (Laboratório de Análises Minerais) – LAMIM, of CPRM, in Rio de Janeiro.

SOCIO-ECONOMIC, PHYSIOGRAPHIC AND GEOLOGICAL ASPECT

The Amazon Craton is main geotectonic unit in the area, a complex tectonic-stratigraphic array of Archean-Proterozoic age, made up of a diversity of geological environments, such as greenstone belts (Rio Maria, Tacumã, Vila Nova, etc) shear belts (Itacaíunas, Jarí, Araguaia, etc) orogenic provinces (Tapajós), transcurrent basins (Carajás, Aquiri, São Félix, etc), old terrains (Cupixi) and high metamorphic degree terrains (Bacajá)

among others. In the extreme Eastern part of the region, the São Luis Craton and the Gurupi belt deserve special attention. Surrounding the Cratonic areas, are Paleozoic sedimentary basins, such as the Amazon and Parnaíba Basins. A large area is covered by Quaternary sedimentary layers related to the main water bodies and the coastal zone (Faraco et al. 2004).

The River Amazon and its largest tributaries constitute the studied region's main hydrographic system. In Amapá State, the Oiapoque and Araguari rivers are the most important, as in the States of Maranhão-Piauí, the Gurupi/Parnaíba system.

The highest population density levels are situated in the Eastern portion of the studied region with an emphasis on the Southern border too, and along certain stretches of the main waterways and highways. In the remaining regions a great demographic emptiness predominates, particularly on the left margin of the River Amazon. As a consequence, in those regions where the human concentrations are higher, the main economic activities are also established: mining, metallurgy, timber industry, farming and cattle breeding, fishing and trade.

The studied area has a precarious basic sanitation system, even in the large cities. Malaria, leprosy and leish-maniasis are endemic to the region and several water born diseases and/or alimentary propagation (vermin, hepatitis, diarrhea, etc.) reach high incidence rates (DATASUS).

OBTAINED RESULTS

The program Statistic was used for the statistical calculations and the software ArcView 3.2 for the maps. For result interpretations the standards used (chemical elements maximum concentrations in water for human consumption) were those established by the National Environmental Council (CONAMA Resolution 357, March 17, 2005) and the Ministry of Health (Resolution 518, March 29, 2004) and the values recommended by the WHO (World Health Organization – WHO, 2004).

Block I – Northeast of the state of Pará

This block covers approximately 50,000 km², about 80% forming the Northeastern region of Pará and the remainder the Northwestern portion of Maranhão State (Figure 2). This is the most densely inhabited Pará State region, served by a good logistic infra-structure and with an economy based on farming and fishing activities.
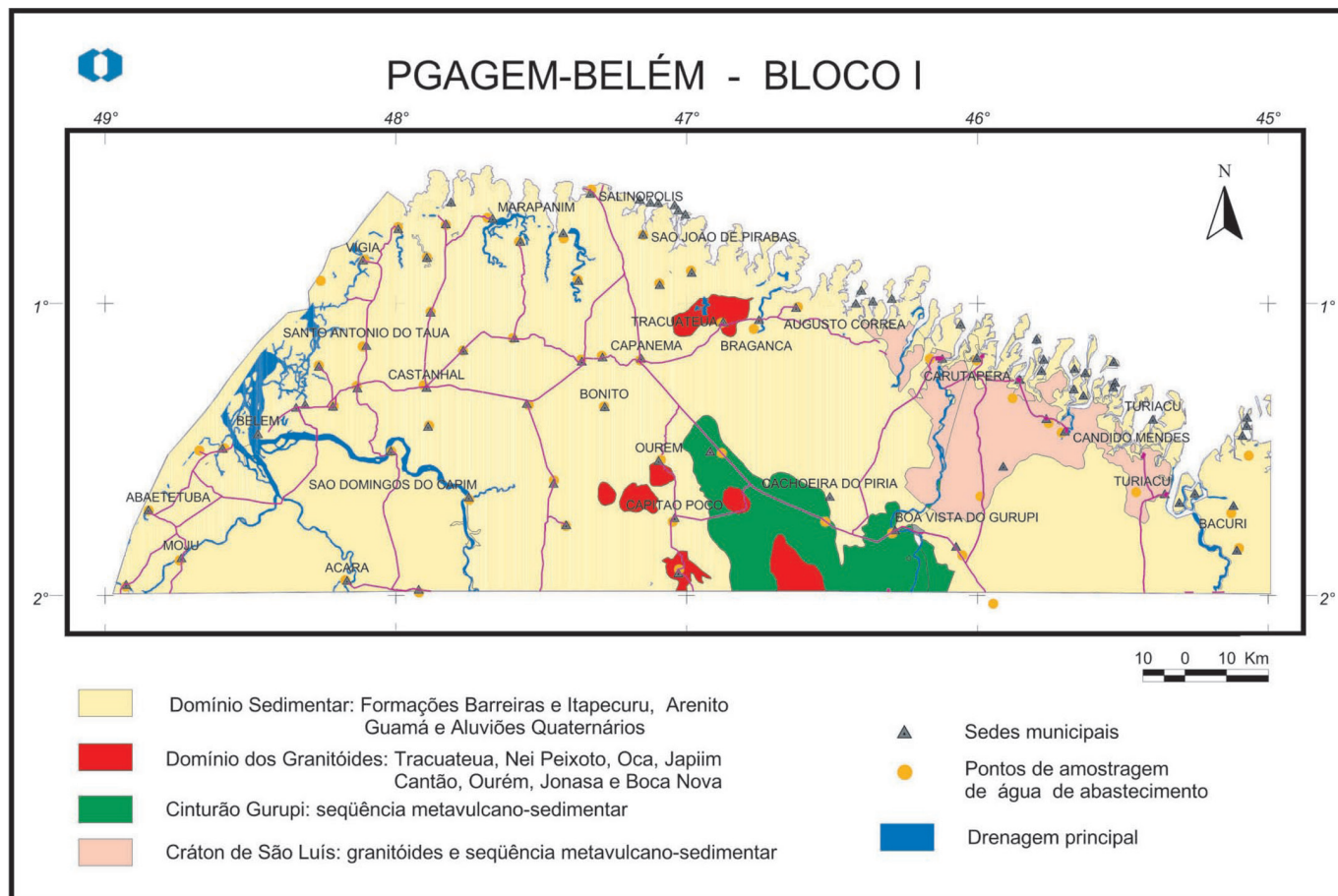

Figure 2 – Simplified geological map of Block I Northeast Pará State (CPRM/Projeto GIS do Brasil, Faraco et al. 2004).

From a geological point of view, the greatest portion of Block I is occupied by the Barreiras Group (sandstone, siltites and claystones). The São Luis Craton is found in the Gurupi region (granites and a metavolcanic sedimentary sequence)., There are sedimentary units distributed in the region, such as the Guamá Sandstone, Itapeçuru Formation and intrusive granites (Tracuateua, Nei-Peixoto, Cantão, Japiim, Oca, etc). Along the main water courses and in the coastal zone, there is the Quaternary sedimentary cover (Figure 2).

The sampling sites are shown in Figure 2. Of the 31 analyzed elements and chemical compounds, As (<0.01 mg/L), Mo (<0.005 mg/L), Se (<0.02 mg/L), V (<0.02 mg/L), Be (<0.001 mg/L) and NO_2 (=0.1 mg/L) had results below the analytical method's detection limit and therefore were not submitted to statistical calculations. The elements Cd (<0.001 mg/L), Co (<0.002 mg/L), Cr (0.02 mg/L), Ni (0.004 mg/L), Ti (0.05 mg/L) and PO_4 (0.2 mg/L) also had more than 90% of their results below the analytical method's detection limit, being interpreted only visually. The other elements were submitted to statistical calculations and the main parameters are shown in Table 1.

Table 1 - Statistical parameters – Block I – Northeast Pará / Northwest Maranhão

Element	Population	Minimum Value	Maximum Value	Mean	Standard deviation	Max. Value permitted for Class I fresh water - Resolution CONAMA 357
Al	59	0.005	1.8	0.2043	0.3033	0.1 mg/L
As	59	0.005	0.005	0.005	0	0.01 mg/L
B 5	9	0.001	2	0.1331	0.3118	0.5 mg/L
Ba	59	0.001	0.163	0.0228	0.0372	0.7 mg/L
Be	59	0.0005	0.0005	0.0005	0	0.04 mg/L
Ca	59	0.1	60.05	77.517	125.985	10 a 100 mg/L **
Cd	59	0.0005	0.002	0.0006	0.0004	0.001 mg/L
Co	59	0.001	0.004	0.0011	0.0004	0.05 mg/L
Cr	59	0.01	0.03	0.0108	0.0034	0.05 mg/L
Cu	59	0.001	0.05	0.009	0.0088	0.009 mg/L
Fe	59	0.002	6.66	0.3614	10.445	0.3 mg/L
K	59	0.1	101	41.441	134.763	12 mg/L **
Li	59	0.001	0.02	0.0027	0.0036	2.5 mg/L
Mg	59	0.09	15.27	22.615	29.889	1 a 40 mg/L **
Mn	59	0.001	0.223	0.038	0.0608	0.1 mg/L
Mo	59	0.0025	0.0025	0.0025	0	0.07 mg/L **
Na	57	0.1	42	9.456	10.512	200 mg/L *
Ni	59	0.002	0.015	0.003	0.0026	0.025 mg/L
Pb	59	0.0025	1.45	0.17	0.3146	0.01 mg/L
Se	59	0.01	0.01	0.01	0	0.01 mg/L
Sr	59	0.001	0.652	0.0545	0.1105	1 mg/L **
Ti	59	0.025	0.06	0.0256	0.0046	***
V	59	0.01	0.01	0.01	0	0.1 mg/L
Zn	59	0.001	0.274	0.044	0.0681	0.18 mg/L
Br*	58	0.025	0.81	0.0626	0.1059	0.025 mg/L *
Cl	57	1.58	61.63	11.41	12.296	250 mg/L
F	58	0.005	0.75	0.0594	0.1035	1.4 mg/L
NO_2^-	58	0.05	0.05	0.05	0	1.0 mg/L
$PO4^{-3}$	58	0.1	1.4	0.1466	0.2121	0.1 mg/L
SO_4^-	58	0.4	38.4	47.638	67.064	250 mg/L
PH	59	4	7.5	52.136	0.8653	de 6 a 9

* set by the Ministry of Health, Resolution nº 518, de 25/03/04 ; ** World Health Organization (WHO, 2004). Values in mg/L or ppm; *** The max. Values for Ti were not obtained.

The following considerations are presented based on the above information:

- The sedimentary units represented by the Barreiras Group, Itapecuru Formation, Guamá sandstone and Quaternary alluvial deposits form the largest aquifers in the region, due to the great territorial extension, thickness and permo-porosity index. In the other units (granite zone, Gurupi belt and São Luís Craton) the possibility of aquifers is limited, being restricted to fracture zones (Figure 2).
- Among the analyzed elements, the As, Ba, Be, Ca, Co, Cr, Li, Mg, Mo, Na, Ni, Se, Sr, Ti, V, Cl and F and the compounds NO_2 and SO_4 had results in the range considered fit for human consumption according to the CONAMA, MS and OMS standards mentioned earlier.
- The Al, B, Cd, Cu, Fe, K, Mn, Pb, Zn and PO_4 presented results higher than the above referred standards indicating them as unsuitable for human consumption.
- In about 80% of the study area, the Al and the Pb presented inadequate values for human consumption (Al=0.1 mg/L; Pb=0.01 mg/L). The highest Al content was of 1.8 mg/L, equal to 18 times the maximum permitted limit, and for Pb, the highest value was of 1.45 which is 145 times the tolerated limit. There is no perfect correlation with the geographical distribution of the two elements (Figure 3).
- The Cu values inadequate for human consumption (>0.009 mg/L) occupy about 60% of the studied area, particularly the Eastern portion (Figure 3).
- The water for the Western portion public supply (Figure 3) is characterized by Fe values exceeding the permitted limit for human consumption (0.3 mg/L).
- Zn, B, Mn and K presented small areas with inadequate contents for human consumption. These areas are spread throughout the study area and apparently there is no correlation with the mentioned elements.
- Cd and PO_4 presented point values distributed over the whole studied region in this Block. For Cd, 3 samples were detected that presented values of 0.002 mg/L, which is higher than those permitted for human consumption (0.001 mg/L). Contents of 0.7 mg/L and 0.9 mg/L PO_4 were also observed. These values are higher than those permitted for human consumption (0.1 mg/L).
- With regards to the pH, 90% of the values lay between 4 and 6, characterizing acidic to slightly acidic water. In only 8 samples the confirmed values lay between 6 and 7.5, which is within the acceptable pH range according to CONAMA (6 to 9).
- Fitting the anomalous values in the geological context the geochemical anomalies are found in the 4 mapped domains. The Sedimentary Domain encompasses the largest number of anomalous samples, possibly as a consequence of its larger geographical occurrence. In regional terms the background trends for Al and

Pb coincide with the NNW orientation, parallel to the Gurupi belt.

Block II – Pará-Maranhão / Block III – Tocantins-Piauí

The research area occupies approximately 9,300 km², about 2/3 of which is in Maranhão State and the rest in Tocantins (Figure 1). It is a relatively inhabited area (25 to 100 inhabitants/km²), served by a good logistical infrastructure and with an economy based on agricultural and cattle breeding activities.

It is situated in the North-West portion of the Parnaíba Basin (Figure 4). The oldest stratigraphic unit is the Mosquito Formation (Jurassic), made up of basalt sheets, covered by the Corda Formation, considered to have the greatest territorial extension and represented by sandstones, and red shales. Above them are the Grajaú and Codó Formations, both Cretaceous and interbedded. The Grajaú Formation is composed of sandstones while the Codó by shales, limestones and sandstones. The Itapecuru follows, also of Cretaceous age, made up mainly by sandstones and claystones. In the Northeastern portion of the studied area, the detritic and/or lateritic cover predominate whereas alluvial deposits are found along the river bodies.

10 public water supply samples were collected (Figure 4).

The field work and the analytical results lead to the following considerations:

- About 80% of the studied region is made up of sedimentary units, the formations Corda, Itapecuru and Grajaú highlighted as excellent aquifers.
- The elements B, Be, Ca, Co, Cr, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, SO, Zn, F and Cl presented results below the maximum permitted value for human consumption according to current Brazilian environmental laws.
- Ba presented the most samples with inadequate contents for human consumption.
- Al presented all results equal to the lowest limit of the analytical method (0.1 mg/L), which coincides with the maximum permitted content for human consumption, except for one sample collected in Imperatriz that had 0.2 mg/L. A similar coincidence was confirmed for As, Cd, Cu, Se, V, Br and PO.
- Of the samples collected in the municipal seats, only those from Ribamar Freire were found concentrations low enough for human consumption.
- Plotting the sampled sites on a geological basis, with their respective results – those with values inadequate for human consumption – there is no correlation between the elements with the various stratigraphic units.
- Although below the maximum permitted values by environmental laws, the Itaguatins water supply precipitates a white powder on the bottom of the aluminum pan when it is boiled. This material was analyzed at UFPA with the following results: Aragonite (69%), Magnesian Calcite (9%) and Cesarolite (8%).
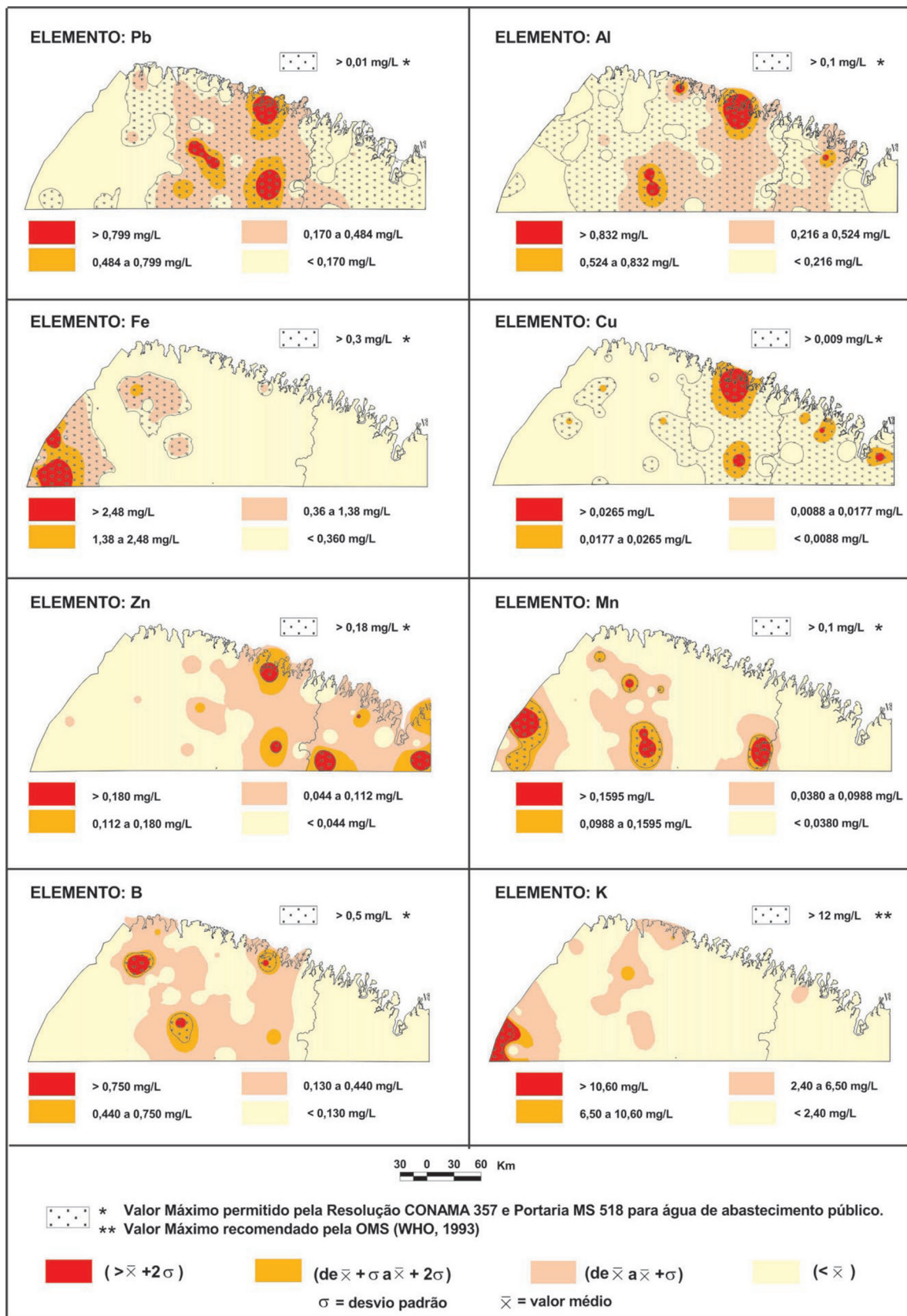
Figure 3 – Variation on the content of Pb, Al, Fe, Cu, Zn, Mn, B and K in in the water supply system in the Block I – Northeast of the Pará State.
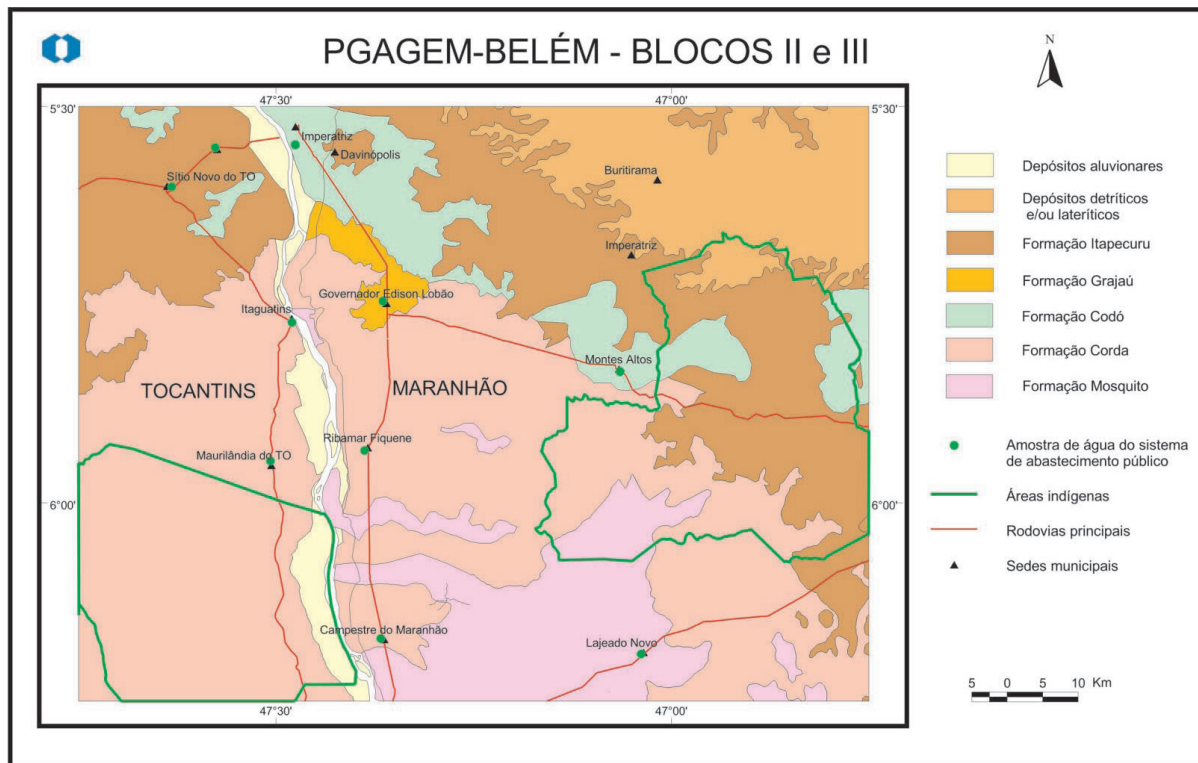
Figure 4 – Geological Map of the Southern region of Tocantins State and the Western part of Maranhão State (CPRM/Projeto GIS do Brasil, Faraco et al . 2004).

Block V – Altamira

In this block only two water supply samples were collected. The studied area is situated in the Lower Amazonas Basin, mainly in the Altér do Chão Formation region (Cretaceous-Tertiary). Lithologically it is similar to the Barreiras Group and is represented by layers of sandstones, siltites and claystones. It presents a high permo-porosity which is why it constitutes an excellent aquifer. The studied region is situated on the River Tocantins right bank presenting good logistic facilities with its economy based on agricultural and cattle breeding activities. It has a low population density (2 to 5 inhabitants/km^2).

Based on the studies, the following considerations were established:

- The contents of the elements B, Ba, Ca, Co, Cr, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, V, Zn, Be, F, Cl and SO$_4$ presented results below the limits established for human consumption.
- In all samples, the results of Al, As and Cd presented contents that coincide with the analytical inferior limit and with the maximum content permitted by CONAMA Resolution 357/2005 and the Ministry of Health Ordinance 518/2004.
- The contents of Cu, Se, Br and PO$_4$ exceeded those permitted for human consumption.
- Generally speaking, the water sample contents in both municipalities are similar, principally for the elements whose values are above the allowed standards.

Block IX – Santarém

The sampling studies (4 samples) were made in partnership with the HIBAM Project. The studied region is situated in the States of Pará and Amazonas border zone. The sample collection sites are situated in the Middle Amazonas Basin, predominantly in the Quaternary alluvial deposit regions related to the Amazon and Tapajós Rivers. These are sandy and clayish sediments, with high permo-porosity and constitute excellent aquifers. Among the sampled towns, Santarém stands out for its greater population and economic development. However, all towns present good logistic facilities, the economy based on agricultural and cattle breeding activities and they all have a low population density.

Based on the results the following considerations are made:

- The contents of elements B, Ba, Ca, Co, Cr, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Sr, V, Zn, Be, F, Cl and SO$_4$ were below the limits established for human consumption.
- For As and Cd, the contents found are coincident with the limits established by the environmental legislation for human consumption and the analytical inferior limit.
- In most samples, the elements Al, Cu, Pb, Se, Br and PO$_4$ presented contents that exceeded those permitted for human consumption.
- It was confirmed that all samples presented excessive contents for human consumption for the elements Se,

PO_4 and Br. However the sample collected in Santarém presented the greatest number of elements harmful to health, because in addition to those already mentioned, Al and Pb were also confirmed. In Curuá the Cu content was higher than the maximum permitted value for human consumption.

CONSIDERATIONS AND CONCLUSIONS

The 4 studied areas are good representations of the Amazon region environmental and hydrogeologic systems as its 4 main aquifers were targeted: Corda, Grajaú, Codó and Itapecuru Formations, in the Parnaíba Basin; Altér do Chão Formation in the Amazon Basin; and Barreiras Group, Itapecuru Formation, Guamá Sandstone and Quaternary fluvial and marine deposits.

The economy of these regions is mainly based on agricultural activities, cattle breeding, fishing and the forest products extraction. The population density is less than 100 inhabitants/km². In this region, endemic diseases transmitted through water and food, such as vermin, digestive system diseases and dental caries predominate. Frequent cases of anemia, hepatitis, malaria and malnutrition are also observed.

The supply systems are usually shallow tubular wells (<100m). In some cases the water consumded by the population is canalized directly from rivers. In most towns the supplied water receives no kind of treatment and chlorination is made in just a few towns.

These conclusions are based on the results obtained:

1. Block I
The results showed that the elements As, Ba, Be, Ca, Co, Cr, Li, Mg, Mo, Na, Ni, Se, Sr, Ti, V, Cl and F, and the NO_2 and SO_4 compounds had concentrations below the maximum values for human consumption (CONAMA Resolution 357/2005, Ordinance MS 518/2004 and/or WHO/1993). The elements Al, B, Cd, Cu, Fe, K, Mn, Pb, Zn and PO_4 had contents exceeding the standards mentioned above, indicating it unfit for human consumption.

Regarding the toxicity, the elements Al and Pb presented respectively, contents of up to 18 times and 145 times the maximum permitted value by environmental laws. In the literature no quotations with such high values of Pb in a potable water supply were found. These elements occur in about 80% of the studied region, however there is not a good geochemical correlation among them/ with each other. The elements Fe and Cu also showed concentrations exceeding that permitted for human consumption.

The region's enormous area, allied to the magnitude of the results for Al, Pb, Fe and Cu, substantiate the supposition that there is a natural origin for these contents. The other elements (Zn, B, Mn, K, Cd and PO_4) are distributed in small areas or present point val-

ues, which may also suggest possible anthropogenic contamination.

The pH presented values from 4 to 6 indicating an acidic nature in 90% of the studied area. These values are considered inappropriate for human consumption and may be related to the intense decomposition of organic substances and high regional rainfall, evapotranspiration and lixiviation.

Augusto Correa town presented the largest number of elements noxious to health (Al, Pb, Cu, Fe, Zn, B and Cd). In second place are the towns of Cachoeira do Piriá (Pb, Cu, Zn) and Boa Vista do Gurupi (PO_4 and Mn).

2. Block II and III
The results of Block II and III confirmed the contents of B, Be, Ca, Co, Cr, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, SO_4, Zn, F and Cl were adequate for consumption. The elements Al, As, Ba, Cd, Cu, Se, V, Br and PO_4 had concentrations unfit for human consumption, The element Ba was present in the largest number of samples with contents exceeding the permitted level by environmental legislation. Among the town water supplies sampled, only Ribamar Freire had no contents inadequate for human consumption.

3. Block V
The samples from Block V presented contents of B, Ba, Ca, Co, Cr, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, V, Zn, Be, F, Cl and SO_4 below the maximum permitted limits for human consumption. The elements Al, As and Cd had levels equal to the maximum values determined by CONAMA and MS. The concentrations of Cu, Se, Br and PO_4 exceeded the maximum permitted value for human consumption.

4. Block IX
In Block IX, the elements B, Ba, Ca, Co, Cr, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Sr, V, Zn, Be, F, Cl and SO_4 presented values appropriate for consumption. For As and Cd, the contents were coincident with the limits established by legislation and with the analytical inferior limit. For Al, Cu, Pb, Se, Br and PO_4, however, the concentrations exceeded the standards established for consumption. The town of Santarém presented the largest number of elements with inappropriate concentrations for human consumption: Al, Pb, Se, PO_4 and Br.

At this stage of the study it is difficult to determine the source of cations, particularly those which presented contents above the maximum permitted value by CONAMA and the Ministry of Health. Due to the erratic nature of the results of the elements and anomalous values, the possibility of a systematic sampling error can be eliminated. One of the Pb anomalies of Block I was analyzed by another method (Atomic Absorption) confirming the value obtained with ICP/AES; as a consequence, the possibility

of analytical errors are rejected. In the sampled sites there were no landfills, industries, sewage or other contamination sources, which reduces the possibility of a localized environmental contamination. In the face of the results the elevated contents of several elements found in the public supply systems are related to natural aspects, especially to hydrogeologic factors.

In Block I, where the greatest volume of work was done, the main aquifer is the Barreiras Group, lithologically made up of sandstones, siltites and claystones with inter-bedded lenses rich in organic matter. According to recent studies by Miranda (2004) the source areas of these sediments would be located in the Tocantins-Araguaia zone, the Borborema province with its gneissic and migmatitic complexes, the Gurupi Group (neoproterozoic granites and greenstone terrains) and the Carajás province, mainly composed of granitoids.

All the elements (Al, B, Cd, Cu, Fe, K, Mn, Pb, Zn and P) that presented content levels above those permitted by legislation may well proceed from the source areas mentioned. Therefore these elements, according to their geochemical properties, could be associated with the different geochemical-stratigraphic conditions present in the Barreiras Aquifer, for example: the rich levels of organic matter, adsorbed in the clay, forming compounds with the oxides and hydroxides, making a coating on the different minerals. The acidic pH would facilitate the solubilization of compounds with the metals. In this way the elements would be easily incorporated in the groundwater caught by the public supply systems and may be causing several health problems, such as the large number of digestive system cancer cases that occur in Pará State (the largest in Brazil) made public by the Public Health Secretary of Pará State - Secretaria de Saúde Pública do Pará.

One of the contributions of this study is to warn governmental authorities about the occurrence of elements harmful to human health, in potable water supplied to the populations of various cities. These contents exceed those levels permitted by CONAMA (2005) and the Ministry of Health (2004). Complementary and multidisciplinary studies in partnership with specialists from the medical field are necessary, to confirm any influence of these anomalous contents on public health, to adopt preventive measures to avoid future endemic diseases.

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CHEMICAL ELEMENTS IN THE PUBLIC WATER SUPPLY IN CEARÁ STATE BRAZIL

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INTRODUCTION

Regarding human and animal health, water carries many Regarding human and animal health, water carries many chemical components that are easily absorbed by their body cells. Many are beneficial and essential to life (Ca, K, Mg, Fe, etc.). Others (F, Se, Mo, Cr, etc.) can bring benefit or toxicity depending on their respective concentrations in drinking water. As, Pb, Hg and Cd, however, do not play any known physiological roles, being toxic especially for the renal and nervous systems.

The intoxication usually happens through a prolonged intake of toxic substances (chronic exposure), or indirectly, through the consumption of organisms that absorbed such substances from water and concentrated them. For instance, there are cases of intoxication with arsenic in the water consumed by populations in China, India, Mexico, Chile and Argentina, affecting thousands of people (Scarpelli, 2003); the poisoning of a population through the consumption of fish contaminated with mercury from industrial effluents dumped into Minamata Bay, in Japan (Kudo et al., 1998) and the frequent intoxi-cation cases among the inhabitants of Fungang, Japan, due to rice consumption from paddy fields irrigated with cadmium rich waters from the River Shentong, that passes through zinc mining areas (Yama, 1987, apud Nian-Feng et al., 2004).

The real dimension of the salubrity of consumption water, that tends to worsen on a global level, is best assessed following the almost daily information about the subject in the press.

In Ceará, only 470 of the territory's 760 districts (forming 184 municipalities) have a water supply system and in 154 of them there is no treatment at all. The remaining 290 districts have alternative supplies, such as tubular wells, hand-dug wells, fountains, water bowsers , etc (IBGE, 2005). The state public agencies and distribution companies are only concerned about the quality of consumption water regarding the presence of pathogenic microorganisms and salinity. The concentration of known toxic chemical elements, that may be imperceptibly corroding the population's health, is neither identified in a systematic nor even on a sporadic basis.

This article presents a summary of the study developed by Frizzo (2006). There are also some observations

on the results of chemical element analyses in water samples from dams, springs, rivers and wells that are the main public sources of cities in Ceará State. This study seeks to confirm the water quality on-site before treatment and distribution. It is part of the National Program for Environmental Geochemistry and Medical Geology Research (PGAGEM) being developed by the Brazilian Geological Survey - Serviço Geológico do Brasil – CPRM. This program had the support of the National Water Agency (ANA), through the partnership between ANA/CPRM. PGAGEM aims to study the relationships between the chemistry of geological occurrences and their influence on the environment and public health.

THE WATER IN CEARÁ

According to IBGE and SUDENE (1966), Ceará State has a great abundance and wide distribution of surface water. It is a mixed type of Bicarbonate and Sodium Bicarbonate, occurring respectively in the North and South of the State and in the region close to Fortaleza (capital of Ceará); mixed chlorinated which occurs in the State territory center, in a zone extending to the North coast and another almost until the Northeast coast; Sodium chlorinated and mixed sodium in the West-centre of the State. The potability (based on the main cations concentrations and hardness) is good, except for a small basin in the Alto River Banabuiú and with restrictions in the area close the mouth of the River Jaguaribe of higher salinity. For irrigation, the water is inadequate in the State central region, in the Quixeramobim and Alto Banabuiú Rivers and near the mouth of the River Jaguaribe, due to the high content of dissolved salts (Figure 1a).

As for the groundwater, there is primary classification between fresh, brackish and salt, based on the concentration of total dissolved solids (TDS). This is calculated from the electric conductivity measured in 7,092 wells, among the more than 13,000 wells registered by the Ceará State Well Inventory Program carried out by CPRM in 1999 (CPRM, 1999). These results delineate the known hydrogeologic provinces of the State: Cenozoic, Mesozoic and Paleozoic sedimentary coverings to the North (coast), to the South (Araripe Plateau) and to the East (Ibiapaba Plateau – on the border with Piauí State), respectively, where there is predominance of fresh water wells, and the crystalline basement, in the wide central region covering almost the whole State, where brackish and salt groundwater predominate (Figure 1b).

In spite of the great geologic diversity in the State and the irregular territorial catchment sites distribution, conditioned by economic, social or politic conveniences, there is a logical relationship between the lithologies and the water catchment types adopted as public supply sources for the municipality seats.

The tubular and Amazon type wells are dominant in land covered with unconsolidated sediments, sands, clays and gravel from the Quaternary. Several tubular type wells that supply the municipalities are also registered in the sandstones and siltites of the Neogenic Barreiras Group; in sandstones, siltites and shales from the many Mesozoic geological formations and also in sandstones and conglomerates of Silurian age.

A minority of wells, less than 60 m deep, occur in the Proterozoic and Archean crystalline rock domain; these domains have a varied mineral composition and, generally do not favor groundwater circulation that happens through fracture systems, with a high content of dissolved salts.

In surface water streams the water composition has the contribution of solubilized material from the whole hydrographic basin upstream from the sampling site, and has a more important seasonal variation (due to differences of flow, variable rain fall in the area of influence, etc.) than that found in the groundwater. Regarding the river catchment samples, the highest number occur in belts of sand, gravel and the Quaternary unconsolidated clay, perennial river alluvial deposits.

Dams and lakes are the State's main public water sources; the waster should also reflect the river basin's composition that originates them, with intermediary variations due to seasonality. They are established preferably on crystalline terrains made up of ancient igneous and sedimentary rocks affected by metamorphic processes: granites, granodiorites, ortho and paragneisses, metabasic rocks, quartzites, micaschists, limestones, Phyllites etc that compose several stratigraphic units positioned in the Proterozoic and Archean.

WORK METHODOLOGY

Most of the 184 municipalities and 46 districts that were visited (area exceeding 1,000 km^2) have their water supply from dams (130) and tubular wells of different depths and yields (51), wells of the amazon type (28) and direct intake from rivers (20) and springs (4) have also been registered (Figure 2). In some towns, the catchment system is mixed, composed of tubular + amazon wells or amazon wells + direct stream intake. At the time the sampling was made, Ibaretama was being supplied by water bowser and in Sucatinga, a Beberibe district, the wells are individual domestic. When the catchment unit installation was common for several towns and districts, the corresponding number of samples were taken from that common site.

The samples were collected in plastic containers, at the sites (wells and springs) or near the suction pumps (in dams and rivers), always situated before the treatment stations, pre-distribution. From that container 50ml volumes were separated in two appropriate containers, using a disposable syringe connected to a 0.45mm "Mil-
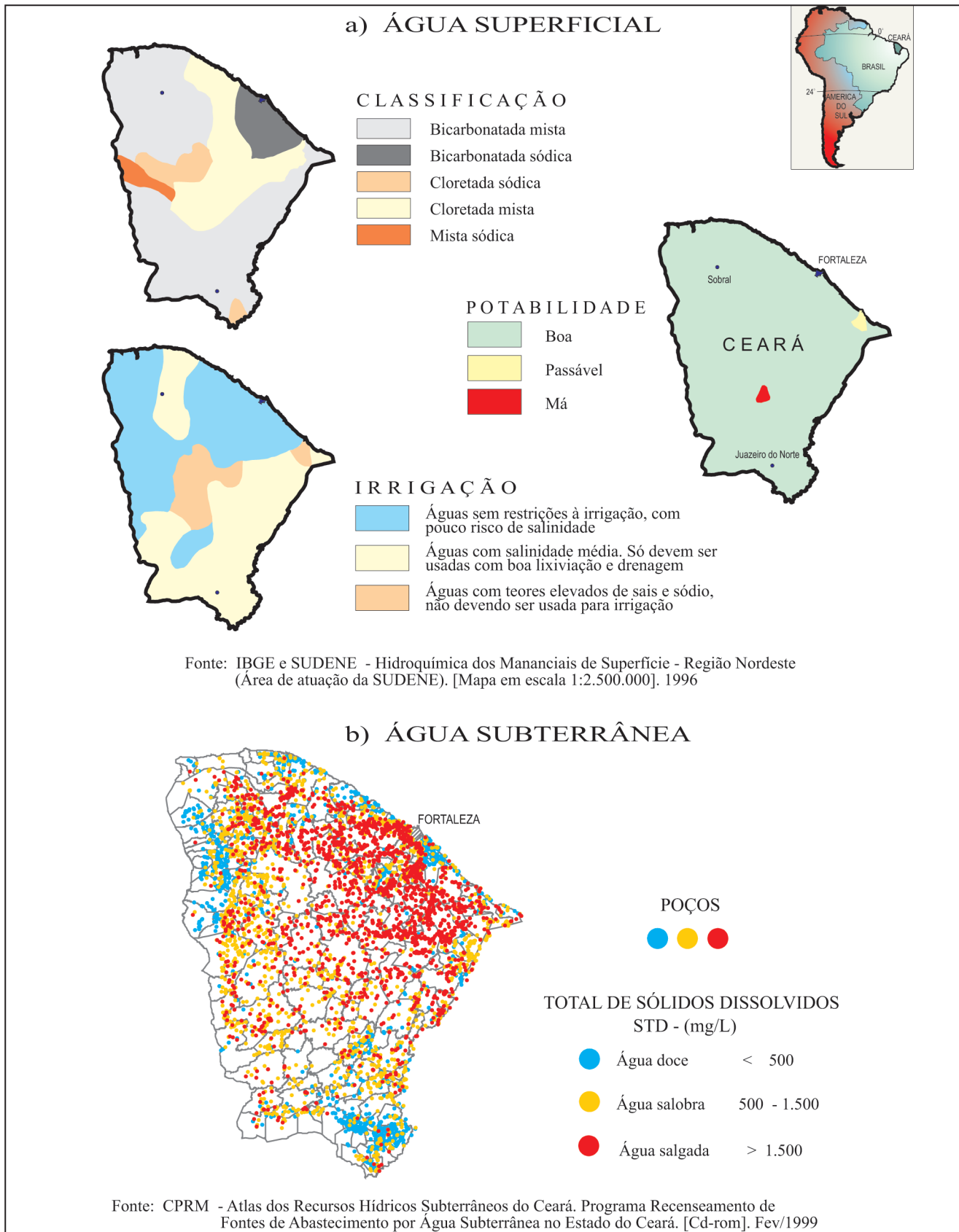
Figure 1 – Characteristics of water in Ceará.

lipore" membrane filter. One volume was acidulated with 10 drops of superpure HNO_3 for the cations analyses. During the field stage the samples were kept refrigerated.

The cations analyses were made through Atomic Emission Spectrometry with plasma source (ICP-AES) in the CPRM and EMBRAPA laboratories and the anions analyses, through Ionic Chromatograph in the Chemistry Institute of UFRJ (Federal University of Rio de Janeiro) and in the Water Laboratory of PUC-RJ (Catholic University of Rio de Janeiro). The concentrations of cations Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, Ti, V and Z and anions Br, Cl, F, NO_2, NO_3, PO_4 and SO_4 were evaluated.

Maps of the geographical distribution of those elements' concentration that presented sufficient results amplitude were generated. In Figures 3 and 4 are the results for some selected elements, whose higher values are likely to be originated from pollution or contamination and from the substrate's lithology, respectively.

RESULTS

Tdoes not reach the reference values of CONAMA (2005). The elements V, Cr, Ti, Mo and Be were not studied because they had less than 3% of defined results and all were inferior to the respective CONAMA (2005) references.
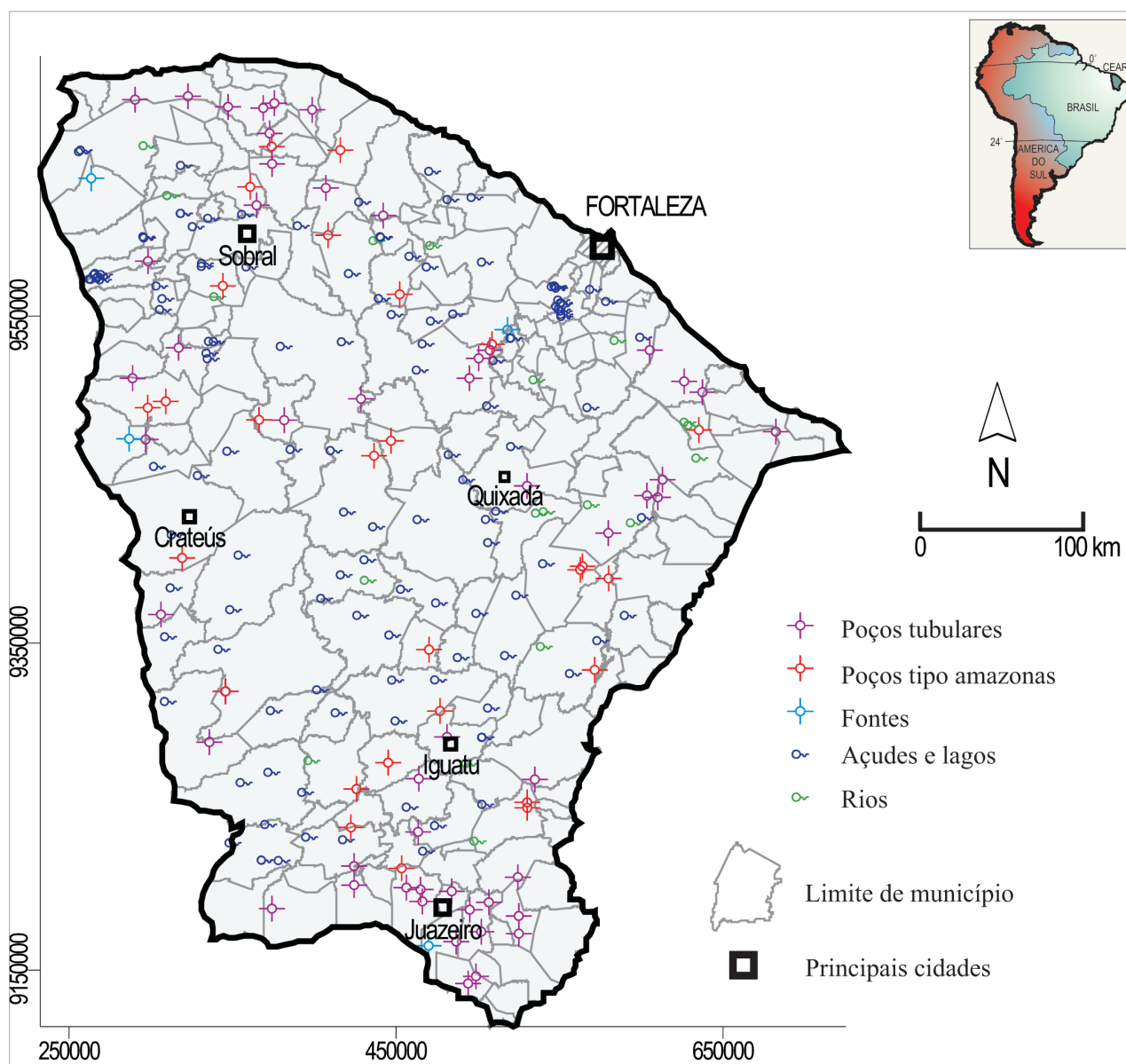
Figure 2 – Water sampling sites in Ceará.
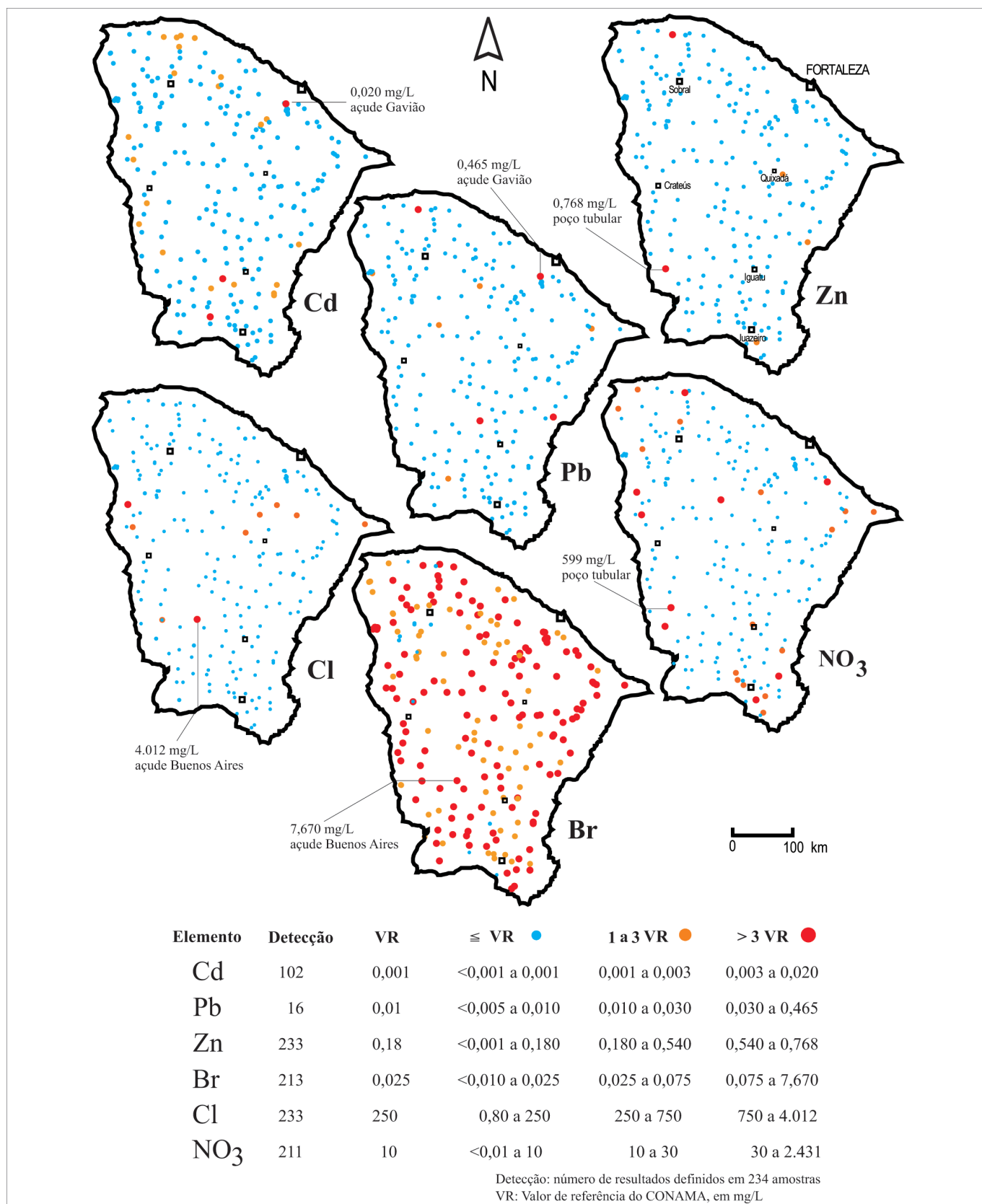
Figure 3 – Results of the element distribution in Ceará public water supply.

The following data appears within the figure:

0,020 mg/L
açude Gavião

0,465 mg/L
açude Gavião

0,768 mg/L
poço tubular

FORTALEZA

Sobral

Crateús

Quixadá

Iguatu

Juazeiro

Cd

Pb

Zn

599 mg/L
poço tubular

NO₃

Cl

4.012 mg/L
açude Buenos Aires

7,670 mg/L
açude Buenos Aires

Br

0   100 km

Elemento	Detecção	VR	≤ VR ●	1 a 3 VR ●	> 3 VR ●
Cd	102	0,001	<0,001 a 0,001	0,001 a 0,003	0,003 a 0,020
Pb	16	0,01	<0,005 a 0,010	0,010 a 0,030	0,030 a 0,465
Zn	233	0,18	<0,001 a 0,180	0,180 a 0,540	0,540 a 0,768
Br	213	0,025	<0,010 a 0,025	0,025 a 0,075	0,075 a 7,670
Cl	233	250	0,80 a 250	250 a 750	750 a 4.012
NO₃	211	10	<0,01 a 10	10 a 30	30 a 2.431

Detecção: número de resultados definidos em 234 amostras
VR: Valor de referência do CONAMA, em mg/L

5,59 mg/L
poço tubular

N

FORTALEZA

Sobral

12,19 mg/L
poço amazonas

Crateús

Quixadá

0,80 mg/L
rio Patu

Iguatu

Juazeiro

Ba

Al

Fe

1,204 mg/L
poço tubular

6,29 mg/L
poço tubular

Mn

F

65,5 mg/L
poço tubular

Mg

0   100 km

Elemento	Detecção	VR	≤ VR ●	1 a 3 VR ●	> 3 VR ●
Al	20	0,10	<0,10 a 0,10	0,10 a 0,30	0,30 a 0,80
Ba	234	0,70	0,004 a 0,70	0,70 a 2,20	2,20 a 5,59
Fe	233	0,30	<0,001 a 0,30	0,30 a 0,90	0,90 a 12,19
Mn	234	0,10	<0,001 a 0,10	0,10 a 0,30	0,30 a 1,21
F	227	1,4	0,4 a 1,4 [1]	1,4 a 4,2	4,2 a 6,3
Mg	234	sem	0,08 a 6,96 [2]	6,96 a 30,0	30,0 a 65,5

1 - valores inferiores a 0,4 (× no mapa) indicam deficiência em flúor
2 - as classes correspondem a 0-50%, 50-95% e >95% da frequência
Detecção: número de resultados definidos em 234 amostras
VR: valor de referência do CONAMA, em mg/L
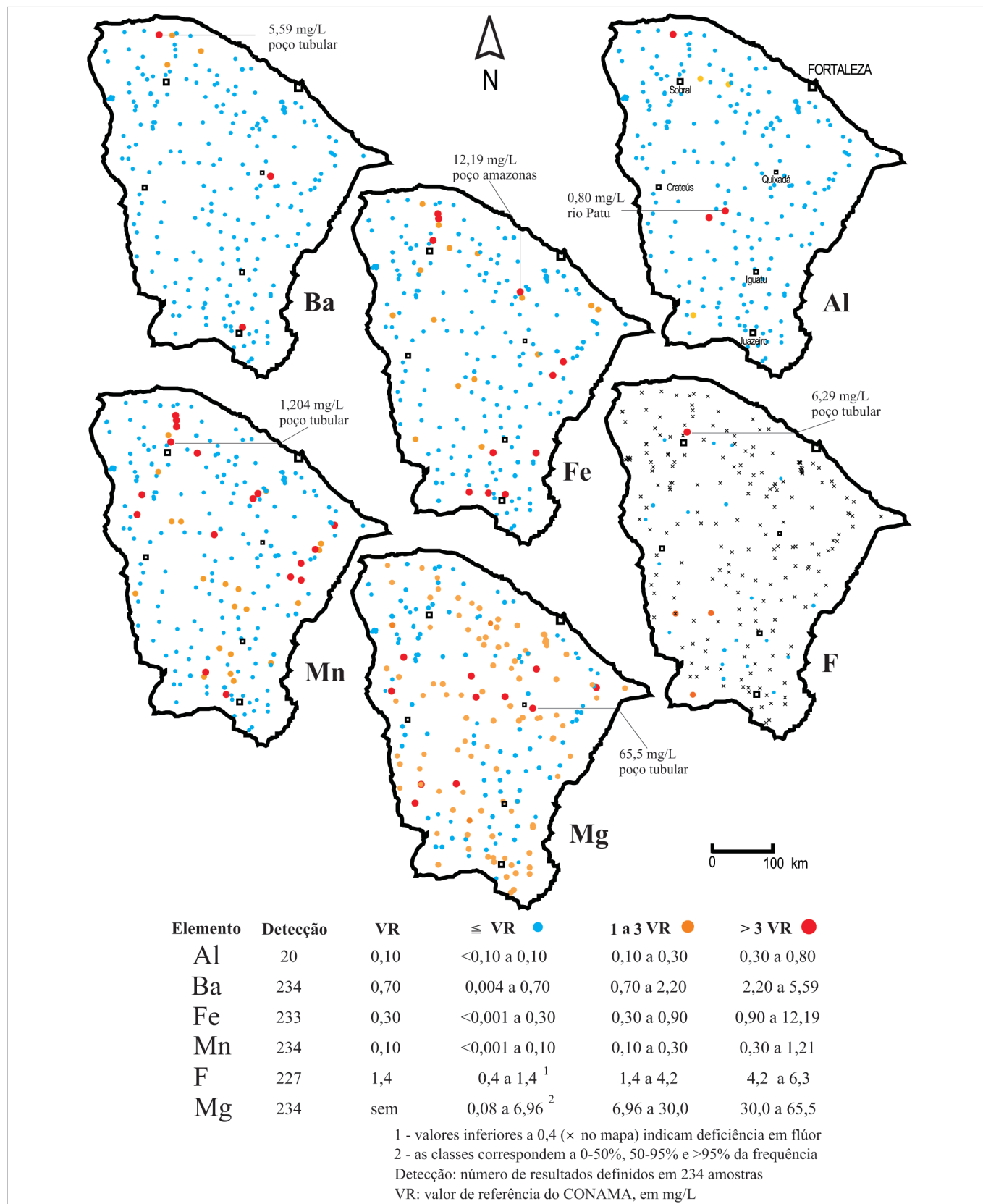
Figure 4 – Result of the element distribution in Ceará public water supply.

A small set of samples were collected at the same sites before and after the annual rain period. This permitted the assessment that the temporal variation has little effect and reflects the processes of rain water flowing into the streams. This results in the dilution of components in the dams and rivers and increases the contents in groundwater due to the dissolution of salts during infiltration and percolation to the aquifers.

The downstream-upstream and lateral compositional differences and similarities that express the represented environment homogeneity were estimated with samples from the same water bodies, sampled at short distances from each other. It was confirmed the content variation is almost inexistent for the elements that are solubilized and somewhat divergent for those transported preferably as colloids. In the rivers the variations are greater than in dams. These small variations seem to be episodic and from sources of little expression as to their origin or they are situated far away, which may weaken an expressive geological origin. Such variations are, nonetheless, the essence for local environmental studies.

Among the elements most noxious to human health that may not be retained during the conventional treatment (Angino, apud Thornton, 1983, p.171), highlighted are the high values for Cd and Pb (0.02 and 0.465 mg/L, respectively) found in the Gavião dam water that supplies several towns of the Metropolitan Region of Fortaleza (capital of Ceará State) (Figure 3). In the 4 samples from this dam, one contained a Pb content above the CONAMA (2005) reference value and in the other 3, Cd occurred within the limit determined by the legislation. These concentrations probably proceed from atmospheric pollution, as the Gavião dam is close to several towns with important and diversified industrial areas (Fortaleza, Eusébio, Itaitinga, Maracanaú and Horizonte).

The higher results for Br and Cl (7.67 and 4,012 mg/L, respectively) were found in the Buenos Aires dam sample, the water catchment for Catarina the State center-South region and the anions F and PO_4 values both exceed the CONAMA maximum levels. Anthropogenic pollution is the most likely source for this contamination. Brome merits being highlighted because almost 88% of the Ceará State public water supply samples had elevated concentrations, considered a risk to human health, with values between 0.03 and the maximum of 7.67 mg/L, already mentioned.

The water from the Salitre deep tubular well (far South-West of the State) contains 2.56 mg/L Brome from a natural lithological source, influenced by the Santana Formation evaporite saline deposits. On the other hand, in the other samples this anion must come from secondary pollution sources (anthropogenic), due to the brome derivatives found in fuel, herbicides, insecticides, paints and pharmaceutical preparations. The purification treatment itself for potable water can introduce or increase this element in the consumption chain, since there is evidence that commercial products such as sodium hypochlorite solutions contain brome as a contaminant (Thompson & Megonnell, 2003).

For nitrates (NO_3), the highest result was 599 mg/L, recorded for the tubular well water sample that supplies the Marrecas community, Tauá district, South-West of the State. There is another record of 59 mg/L NO_3 for the amazon type water well also used by the population. Both have high associated Br, Cd and PO_4 values. Of course, there is no relationship with the region's lithologies, paragneisses with Proterozoic granitoids. Nitrogen compounds are commonly used in fertilizers, which are the main regional sources of surface and groundwater pollution. In the mentioned places, however, the likely contamination of the aquifer comes from inadequate sewage systems.

In Cococi, Parambu, in the far South=West of Ceará, a tubular well sample had the highest result for zinc – 0.768 mg/L. There are occurrences of shales, claystones and calciferous siltites of the Cococi Formation, Rio Jucá Group, attributed to the Cambro-Ordovician period. With a somewhat lower content, the sample collected from the Lagoa dos Monteiros well, that supplies Jijoca de Jericoacoara on the North coast region, registered 0.736 mg/L for the metal, together with several other elements with values above the respective reference levels; the local ground is composed of clay sandstones with conglomeratic lenses and lateritic nodules of the Neogen Barreiras Group. Though this is a common element in rock accessories, in these cases, the high Zn concentrations are probably due to contamination through the very material used for building the wells, as this metal is used in the galvanization of steel pipes and ducts.

Of the elements related mainly to the lithological composition (Figure 4), aluminum presented the smallest detection, having an irregular distribution in the State territory; the results that stand out occur mainly in dams and rivers. The highest content (0.8 mg/L) was found in the River Patu, that supplies Mineirolândia, district of Pedra Branca, associated with a high iron content. This stream cuts across Archean rocks of the Cruzeta Complex, gneisses and migmatites, quartzites, limestones, ferriferous formations and calcissilicates. The weathering of these rocks may result in these high detected values, with the release of clays and fluvial colloids.

Water containing barium in concentrations of 5.588 (highest value) and 1.727 mg/L come from tubular wells that supply the towns of Jijoca de Jericoacoara and Cruz, about 20 km to the East, respectively. The local land is composed of clay sandstones of the Barreiras Group, which suggests a possible relationship with local facies of this lithological unit.

The most elevated result for iron (12.19 mg/L) was found in the amazon well sample that supplies Pacoti,

about 100 km South-West of the capital. The highest value for manganese (1.204 mg/L) was obtained in a tubular well sample in Santana do Acaraú, North of the State. The association Fe-Mn confirmed in the elements distribution maps, is typical of colloidal oxides-hydroxides that may contain other adsorbed ions, from oxidization in the aquifer fluctuation level zone.

Magnesium, as well as K and Ca, with which it is strongly related, is essential to life and has no content restriction in water. The highest result (65.5 mg/L) was found in the a tubular well sample in Cipó dos Anjos, Quixadá district; it indicates the Eastern limit of a magnesium enriched stripe that extends 100 km towards the North-West. Here 42.14 mg/L was measured in Choró (Choró Limão dam), 45.16 mg/L in Madalena (amazon well) and 51.76 mg/L in a tubular well sample in Itatira. Although the rocks that occur in these sites are varied, it suggests a lithogenic origin, as this element is a product of the weathering of a wide range of rock forming minerals (amphiboles, piroxenes, biotites, clorites, dolomites, etc).

For fluorine, the highest registered content was 6.29 mg/L in a tubular well sample part of the Santana do Acaraú supply system, North Ceará. The likelihood is a lithogenic origin, either through enrichment in alkaline facies of the Parapuí volcanic rocks or through circulating hydrothermal fluids in faults and fractures. This is due to a confirmed fluorite occurrence 120km to the SW, following the wide fault system that cuts across the area. Fluorine being an essential element, the World Health Organization recommends it be added during the potability treatment, when the contents are inferior to 0.4 mg/L in the water supplies. The fluorine distribution map shows this is the case for almost all (about 90%) of the supply sources of the Ceará State municipalities.

In short and considering all the evaluated elements, the public water supply of 211 communities out of the 230 visited, (91%) contained at least 1 element in a level exceeding that recommended, and in 49 (21%), there are 3 or more elements in the same situation.

CONCLUSIONS AND RECOMMENDATIONS

This study sought to determine the existence or not of heavy metals in the Ceará State public water supply. The results convincingly portray a serious situation, not only because of the elevated levels of known toxic elements but also due to the quantity and amplitude of the samples' distribution that contains them throughout the State territory.

However it is too soon at present to claim these water supply sources inadequate for human consumption. In addition to factors such as concentration, local variations in the same water body and the persistence of the high values over prolonged periods, the individual chemical

speciation also has to be taken into account (state of oxidization /valence). This affects the respective mobility and bioavailability and impacts their risk evaluation (Centeno, oral communication, International Medical Geology Workshop, 2005).

These results, though consistent, must be considered as clues. They indicate the water is inadequate for human consumption but more studies are necessary to confirm this data and characterize the Ceará State water supply throughout the whole territory. It is important to carry out detailed work and systematic monitoring at those sites with result tendencies that negatively influence the inhabitants' health. The aim would be to identify the original contamination source (natural or anthropogenic) and confirm if these factors persist in the local environment so as to remediate it. If the evidence is confirmed, the public health authorities must be immediately warned to carry out epidemiological studies as well as appropriate toxicological examinations of the population in risk situations.

The governmental agencies should also control mineral water quality. This is mostly from groundwater prone to enrichment by toxic elements and sold in 20-liter bottles that usually have no treatment or purification prior to distribution. Official data (DNPM, 2005) indicates a production of 115,609,000 liters of mineral water in Ceará in 2004. This represents about 5.7 million 20-liter water bottles; in current compulsory characterization analyses, the identification of heavy metals is not required.

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CONTAMINATION ASSESSMENT OF POTABLE WATER IN THE UFRN (FEDERAL UNIVERSITY OF RIO GRANDE DO NORTE) CAMPUS REGARDING NITRATES FROM SEPTIC TANKS

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ABSTRACT

This study seeks to analyze the potable water quality in the UFRN (Federal University of Rio Grande do Norte) campus in Natal (capital of Rio Grande do Norte State). 60 water sampling sites were selected: the supply source outlet of the Campus internal network and various drinking fountains around the sector classrooms. The sampling was made in May and June 2003, within the school term. The water samples were chemically analyzed and a databank built with information of the sampled sites, to allow future monitoring and water quality management.

A Geographic Information System (GIS) was used to visualize and integrate the results of nitrate concentrations in the drinking water fountains. The contaminants were identified and quantified together with their influence on the water quality and visualize their spatial distribution. This system is based on CAD cartographical plans of the whole campus and a databank of existing contamination contents. The study aims to provide a bases to discuss the issues related to water quality vigilance and control.

The approach of this study is based on diverse variables to characterize the critical points for possible decision making. In the GIS, the inter-related information plans included spatial data inherent to the water quality on a map of permanent control sites. The monitoring program standard values used were taken from environmental control agencies based on the standards established by

the World Health Organization (WHO) and the National Environmental Council - Conselho Nacional do Meio Ambiente (CONAMA).

To assess the water quality, the samples were submitted to nitrates and nitrites analyses, as well as total fecal coliforms with the membrane filter technique; general counting of heterotrophic mesophyll bacteria through the Pour Plate technique, according to the Standards Methods. In some locations, rests of organic matter in suspension were visually identified, and based on the evaluation of the 60 analyses, it was confirmed that the nitrate contents of some sections are altered, for example, in the Geology Laboratory, where contents above the maximum permitted limit were found. The project also implemented a digital cartographic map of the Campus showing the permanent control sites, by academic block and geo-referenced by GPS. This database contained comprehensive information to allow a continuous and systematic monitoring to take remedial precautions and establish policies to control water potability and quality standards in the UFRN Campus.

INTRODUCTION AND CONTEXT

Water pollution may be generated by (i) domestic effluents (biodegradable organic pollutants, nutrients and bacteria), (ii) industrial effluents (organic and inorganic pollutants, depending on the industrial activity) and (iii) urban and rural diffuse discharges (pollutants drained from fertilizers, pesticides and animal excrements). There are contaminants that only affect the water's appearance, whereas others are not that obvious but may cause serious health problems, for example, toxic pesticides and coliform bacteria, in addition to nitrate and nitrite ions.

In the spatial analysis of water contamination related problems, the modern geo-processing technologies, Global Positioning System (GPS) and Geographical Information Systems came to the fore in recent years as being very effective in potential risk identification of hydric resources. They also facilitate long term monitoring of pollution problems and the relationship between life and health quality and the consumed water quality. GIS has often been used to consolidate and analyze large health and environmental data bases to bring new planning subsidies and help administrative activities based on the analysis and spatial distribution of the events, accurately locating the environmental risks.

Geo-processing is, thus, a very useful organizational tool for health and environmental strategic planning, where continuous decision taking must prioritize actions according to a given reality (Barcellos, 1998). Together, the GIS and the created models, managed by a graphic and friendly interface, form the most modern decision support systems, which are being used evermore fre-

quently to plan and manage hydric and environmental resources.

This study considered the GIS a suitable project platform due to its interrelated information plans. These included: a) an integrated spatial information database; b) the university campus private water supply network; c) its main springs and dams; d) the data of the Water and Sewage Company - Companhia de Águas e Esgotos do Rio Grande do Norte – CAERN; e) the water quality standards; (provided by the state environmental control agencies' monitoring program, namely: 1) Institute for Economical Development and the Environment (Instituto de Desenvolvimento Econômico e Meio Ambiente do Rio Grande do Norte) – IDEMA/RN, 2) the State Secretary for Water Resources (Secretaria de Recursos Hídricos do Rio Grande do Norte) – SERHID) and 3) the Municipal Secretary for Urbanism and Environment (Secretaria Especial do Meio Ambiente e Urbanismo) – SEMURB). These were all represented in thematic maps through permanent geo-referenced control sites/points.

The studied area geological context (the Federal University of Rio Grande do Norte Campus) consists of Quaternary sediments, typical of dunes, and sediments from the Barreiras Group that, in turn, are covered by Cretaceous sediments (Superior Mesozoic) detected in some profiles. These are highly porous sediments, composed of well selected grains giving the region high permeability. The sand dunes/Barreiras aquifer structure (which supplies the town of Natal) is varied, with high permeability of the soil made up of eolic sands that present high infiltration rates.

Contamination due to inadequate, unplanned urban occupation regarding soil, rivers and lacustrine ecosystems in the area surrounding the capital city of Natal, has become a serious environmental problem. There is a distinct lack of a sewage system in much of Natal town, which allows domestic effluents (disposed in septic tanks and unprotected drains) to reach aquifer levels. This increases the chances of groundwater contamination and the affected area has substantially increased in recent years, impacting important supply sources for the population.

Currently, the Central Campus academic community consists of 15,338 students, 3,605 employees and 1,523 professors concentrated in a 123 ha area, surrounded by vast walls of coastal dunes on one side, and by the access roads to downtown Natal, on the other (Figure 1).

The university campus is somewhat far from downtown, where the water should, theoretically, be less polluted. However, this study will show all five supply stations are already contaminated – inappropriate for human consumption. The water from these wells is confirmed as inadequate for human consumption and shall be used, from now on, only for washing laboratory glass ware, cleaning physical space, irrigating gardens and similar activities.
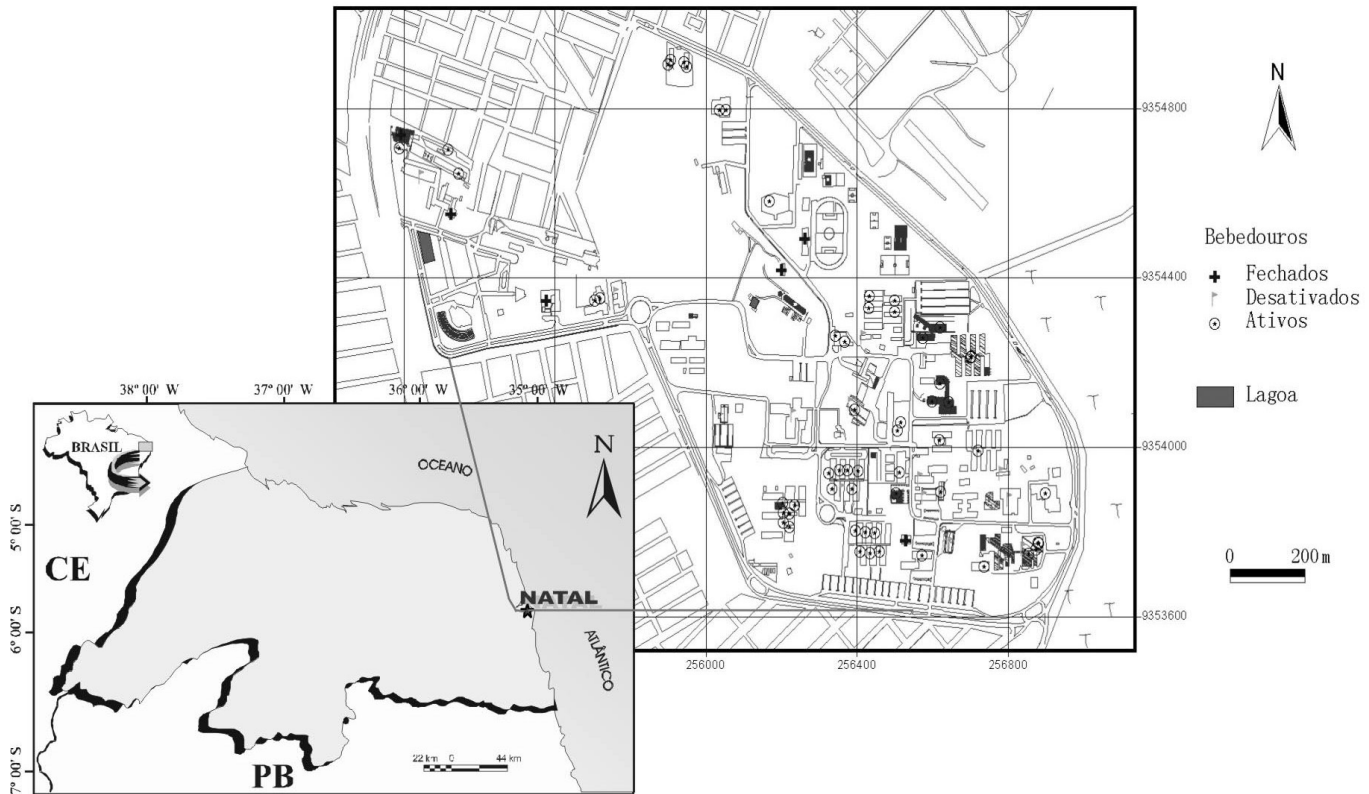
Figure 1 – Location of the studied area.

MATERIALS AND METHODS

The water samples from the selected sites were chemically analyzed and a data bank established with the relevant information of the sites to allow future monitoring and water quality management (Figure 2). This study was based on different variables using the systemic, exact or heuristic approach, among others, to characterize the points considered critical for decision making.

The study followed these stages: (i) Cartographic Survey and Field work: in this stage wells, ponds and drinking fountains were localized by means of GPS. Simultaneously, water samples were taken and all the relevant site information registered. The software Excel was used for that purpose. (ii) Chemical Analysis of the samples: the samples were analyzed in the CEFET/RN laboratory, with geochemical kits. These analyses identified those sites with nitrate contamination (Table 1). (iii) Elaboration of the GIS: with this data and the geo-referenced maps, the GIS was calibrated, seeking to understand the quantity and quality spatial distribution of the UFRN campus water.. (iv) GIS Visualization and analysis of the UFRN Campus using the different information plans, identifying the main drinking fountains and the water quality (Figure 3). Some of the information sets were structured as Themes, which

are information levels structured in the ArcView itself and may be summarized as follows:

- Census and cartographic sectors: the census sector boundaries – SC of Natal town. These were digitally transcribed, from the cartographic base of IBGE to plans in the scale 1:2,000 obtained from IDEMA/RN, CAERN together with the Campus from the University Campus city hall - UFRN. These sectors were divided in two information plans, one of Natal – a larger area – the other the Campus-UFRN.
- Private water supply system: this information plan includes the identification and localization of private wells, treatment and pumping stations and their respective information, located with GPS;
- Drinking fountains: this information plan covers the active, deactivated and closed drinking fountains. The sites were obtained in the field with GPS, together with the material sampling and the respective data;
- Water quality: identification of the sites and their affected degree by the ion nitrate.

ASSESSMENT OF THE SYSTEM: SIG-CAMPUS

This system is composed of information plans on the CAD cartographic base of the whole campus and a

Table1 - NO$_3$ (mg/L) content in drinking water sources at the University Campus

Water source	NO$_3$ mg/L		Water source	NO$_3$ mg/L
Sector II - Classroom	18		Sector IV – Classroom	68
CCHLA – Sector Library	22.05		Chemistry Lab.	68.4
Sector I - Classroom	24.75		Sector III - Classroom	70.65
Sector V - Classroom	32.4		Garage	71.95
CT	32.8		School of Music	72.39
CCHLA – Geography Secretary	32.85		University Lodgings	73.23
			University Restaurant	73.71
Sector I - Classroom	35.1		Sector IV – Classroom	73.8
CCSA – Social Services	38.25		University Restaurant	74.08
TVU	40.5		University Lodgings	74.08
Sector I - Classroom	40.5		University Lodgings	74.08
BCZM	41		University Lodgings	74.08
DIMAP Lab.	41.4		Sector IV – Classroom	75.6
Geology Lab.	42.4		Sector III - Classroom	76.05
CCHLA – Lunch room	43.2		Sector III - Classroom	76.63
CCSA – Law	43.65		IT Lab.	77.85
Chemistry Lab.	46.35		Sector III - Classroom	77.85
BCZM	46.8		Sector IV – Classroom	78.3
TVU	51.3		Convenience Center	81.45
Sector I - Classroom	51.3		Garage	84.74
Sector III - Classroom	55.8		Multisports Court	87.3
Sector III - Classroom	56.25		Sector IV – Classroom	88.65
Amphitheater	56.7		Biosciences Center	114.5
Sector IV - Classroom	63		Biosciences Center	116.46
School of Music	63.42		Biosciences Center	116.46
Chemical Engineering Lab.	65.25		Biosciences Center	116.73
Human Resources Dept.	65.55		Biosciences Center	116.73
Chemical Engineering Lab.	67.5		Biosciences Center	122.05

data bank of the existing contamination contents. This data was the basis for the discussion on water vigilance and quality control related issues. The "SIG" elaboration enabled the identification and quantification of the nitrate contaminant (NO$_3$) in the potable water from the Campus drinking fountains and the visualization of the spatial distribution (Figures 2 and 3).

From the evaluation of a duplicated set of the 60 water sample analyses from drinking fountains distributed in the UFRN Campus, it was confirmed that the nitrate concentrations, mostly from the water fountains, were above the maximum limit of 45 mg l-1 NO$_3$ - established by the World Health Organization (WHO) and CONAMA. As examples of sites where the NO$_3$ concentration was well above the mean value (Table 1), these are highlighted: Classroom Sector III (56 to 78 mg/L) and IV (63 to 78 mg/L), Chemical Engineering Laboratories (65 to 78 mg/L), Amphitheatre – CCET (57 mg/L), Soil Laboratories (76 mg/L), Music School and University Restaurant (63 to 72 mg/L), Arts – former Engineering School (83 mg/L), Recreational Center (81 mg/L), restaurant and university dorms (74 mg/L) and other sectors where contents very much above the maximum permitted limit were found, such as the Biosciences Center (114 to 122 mg/L), garage (72 to 85 mg/L) and the gym (87 mg/L).

Other analyzed sectors show the presence of NO3 in concentrations below or very close to the permitted limit as, for example: CCSA – Social Service (44 mg/L), ADURN (42 mg/L), Central Library (47 mg/L), Geology Laboratory (42 mg/L), Classroom sector I – Block F (51 mg/L) and CCHLA (43 mg/L). On the other hand, some sectors, such as Sectors I and II presented values compatible with the
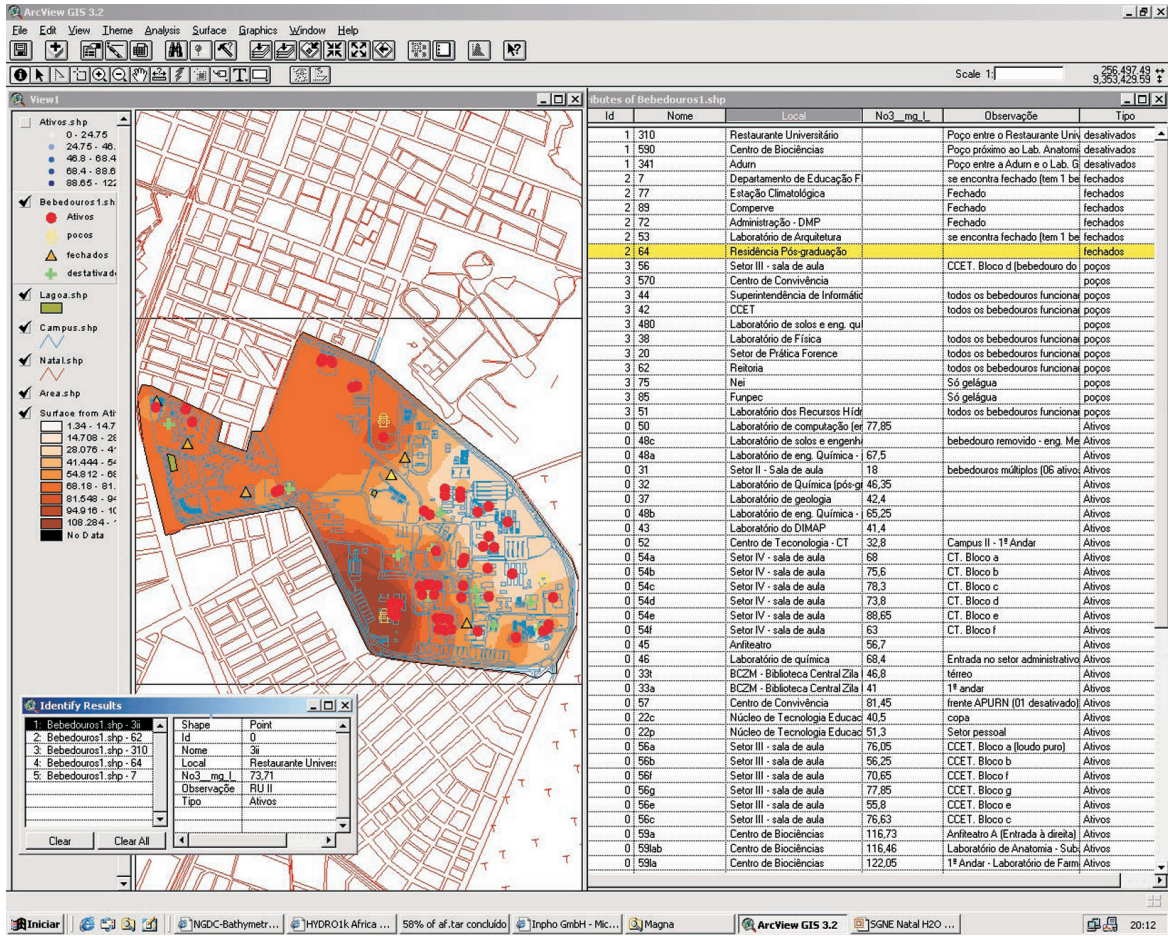
Figure 2 – Visualization and integration of all data types.

Figure 3 – Spatial distribution of the results for nitrate content in the UFRN Campus water supply.

OMS standard, registering even lower values (18 mg/L). It is also confirmed this is neither a punctual problem nor is it restricted to the Campus.

The NO_3 concentrations exceeding 45 mg/L are mainly a result of the lack of basic sanitation in Natal, especially in the dense habitation complexes around the campus. The NO_3 - concentration contents found in areas adjacent to the campus, such as "Mirassol" and "Conjunto dos Professores", had lower values because the potable water there is from a mixture of water from public system wells (CAERN) and water from the Jiqui Lake. However, if only the well water is analyzed in this area, similar values to those detected in the Campus will be found.

Figure 4 illustrates the characteristics of the NO_3 concentrations in the campus water fountains. The highest values occur in the SW portion of the area and the lowest values are distributed in the NE. The intermediary NO_3 concentrations should be given attention because of their rates exceed the WHO recommended value. Thus, the spatial patterns of the concentrations of these contents facilitate positive actions to be adopted.

CONSIDERATIONS

The values detected in the Campus are well above or close to the permitted limit. They are worrying and show that the UFRN potable water monitoring initiative must be continued. The high nitrate values in the UFRN Campus is mainly due to the water being extracted directly from the ground and so it has the contents identified in the aquifer itself. These are regional distribution values and, as mentioned before, are linked to the lack of sanitation in the city. The nitrate concentration values are higher in the campus because the well water does not undergo any dilution, as in the case of the water obtained from wells neighboring the campus.

The contamination mainly reaches the most inhabited areas due to the edification process (sinkholes) and pavement (waterproofing) and areas, such as the university campus that concentrate areas favorable to infiltration, are affected by the groundwater flux dynamics.

The Bioscience Center was confirmed as having the samples with the highest concentrations and, in view of this measures were taken to find the problem source. It was proved that the supply origin, a well situated in that Center was inadequate for human consumption. The well was closed down and the network connected to another well with lower values. The supply to these drinking fountains continues with water from another better quality source. As for the remaining fountains, measures were taken to reduce the contamination rates.

The university campus data base with the hydrochemical control sites map of the nitrate parameters, through the systematic monitoring implemented by this study, will make it possible to have a continuous and systematic monitoring. This will enable precautions to be
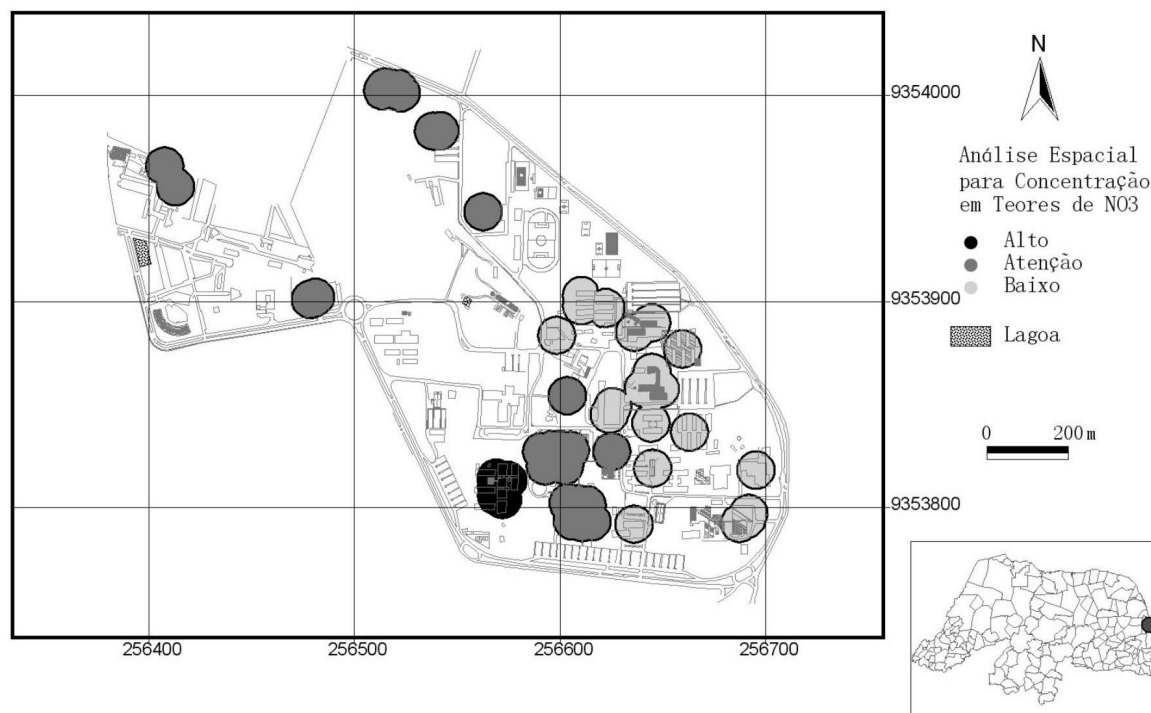

Figure 4 – Spatial distribution of the results for nitrate content in the UFRN Campus water supply showing the contamination hot spots.

taken and policies made to control the water potability and quality standards in the area of the campus.

The campus is indeed facing a dilemma that requires a reorientation of practices and emergency measures must be taken, with the participation of the whole community, to find solutions to improve the quality of these hydric resources. This will, in turn, benefit the campus and the life standard of the population using it. Otherwise, the degradation of the sand dunes and barriers type aquifer through the observed propagation of contamination is eminent. The preservation of this reservoir is important and measures must be taken to maintain the physical-chemical and bacteriologic integrity of its water.

CONCLUSIONS

Considering these results it can be concluded that:
1 – The study's aims were attained: i) to generate and use the System SIG - Campus - UFRN; ii) to identify and characterize the nitrate concentrations; iii) to control the potability standard of the campus water supply. These were achieved through a different approach, which enabled a topic analysis and the future water quality management and monitoring in the university campus.
2 – The data capture steps, treatment and conversion of maps and alphanumeric data from an analogical to a digital format, when associated with the system, supplied satisfactory results.
3 – It is necessary to evaluated the contamination impacts on the current potable water sources and their relationship with the health of the consumers. Left unchecked, the ingestion of chemical contents can occur, such as nitrogenous compounds that in high concentrations provoke hypertension, methemoglobin, certain types of cancer and lymphoma. Therefore the condition of the water consumed must be addressed in appropriate future planning.
4 – The methodologies used in the arrangement of the geographical entities permitted the digital environment representation of the phenomena present in the real world, and met expectations.
5 – The software used demonstrated a good capacity in the sampling and treatment, conversion and integration of data. This generated diversified information levels in the form of maps and attributes giving a wide view of the studied geographic space.
6 – The elaborated SIG creates scenarios that allow a better focalization of the most diverse groups of thematic maps and the planning of actions in sanitation and health vigilance in the area. The developed SIG can also be used as a didactic and debate instrument with students, teachers and the neighboring population about the conditions and occupation of the urban space.

7 – The aggregated value resulting from this study, will allow public and private municipal institutions, especially administrative authorities related to hydric resources and public health, a wide vision of the problems related to the subject, within their geographical limit. The interactivity of the different subjects that integrate the administrative unit will allow public policies in the area to be guided in the best practices concerning the different thematic compositions.
8 – It must be emphasized that some information concerning the urban zone collected for the whole town of Natal, were not specifically processed in this study as they did not have a direct relationship with this process. However the criteria used in this study are the same applied to the town as a whole and may be applied in the future to better identify other areas and other risk groups.
9 – This being a pioneering study at a local, municipal and state level, the impact of the GIS technology will bring a new conscience: that it is necessary to any decision maker to master the geographical knowledge and its components.

RECOMMENDATIONS

After the first results of this study were published, some emergency measures were taken, including the hiring of a firm specialized in deep wells, that could drill beyond the limestone level, just below the sand dunes-Barriers Aquifer System, reaching deeper water from, as yet uncontaminated levels. Originally that water is more acidic and a much lower discharge rate, but, being uncontaminated, it was the best solution found.

The other recommendations in this case address, first of all, the need to adopt simple, reasonable measures and procedures to minimize nitrate originated contamination problems. These could include: the cleaning of water tanks; the changing of drinking fountains; the installation of filters and, especially, the catchment of uncontaminated surface water (distributed by CAERN) to be mixed with the campus well water and lower their contamination levels. However, emergency governmental measures on a regional level should be adopted as soon as possible, with the participation of the whole community to seek solutions to improve the quality of these hydric resources and consequently the living standard of the population. Otherwise the degradation of the Dunas/Barreiras Aquifer through the spreading of the still punctual contamination is imminent.

The reservoirs preservation in the Greater Natal area is important and measures have to be taken to maintain the physical-chemical and bacteriological integrity of its water, thus minimizing the cost of public health. It is also necessary to urgently implement policies to protect the public with an efficient sewage system, as problems

occur due to illegal connections that contaminate the environment.

Finally, it is convenient to mention that the tool used to generate the SIG-Campus/UFRN is not, the only one available for this kind of work. There are several market options, with different ways of processing the subjects inherent to the inventory, some of them with more resources than others.

This system was used due to its ease of operation, the ability to integrate the various information plans (chemical and cartographical data, databank) and its wide use by the technical-academic community. However, the technological evolution allows the migration to open data that can be read in different software, permitting wider access to the information.

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DISSOLVED ALUMINUM IN THE WATER OF SAND EXTRACTION PITS – A STUDY OF POSSIBLE TOXICITY IMPLICATIONS – SEROPÉDICA MUNICIPALITY – RJ

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INTRODUCTION

Sepetiba Basin occupies an area of about 4.4% of Rio de Janeiro State. It is bounded by the Serra do Mar mountain crest line, where the rivers that flow into the Sepetiba Basin initiate, forming the hydrographic basin of Guandu river (SEMA, 1996 apud Berbert, 2003). This hydrographic basin occupies an area of about 2,000 km², 90% being an alluvial plain, where the studied area is situated (Figure 1), inserted between the horizontal (7,470,000 and 7,478,000 North) and vertical (630,000 and 638,000 East) UTM coordinates.

Unconsolidated Quaternary deposits form the local geology, made up of alluvial environment sediments (fluvial, fluviomarine and fluvio-lacustrine), superimposed on a Precambrian basement. The sediments integrate the Piranema Formation (aquifer) (Góes, 1994 apud Barbosa et al., 2002) represented by two units. The lower unit has Pleistocene sandy facies, with medium to coarse size sands of quartz and feldspar with gravel, normally at the basal strata. The upper unity, an alluvial cover, is formed by silt-clay Holocene facies. Area drillings indicate thicknesses vary between 10 and 25 meters. Geophysical soundings register basement depths of about 35 to 40 meters in the Piranema area. However, there are literature registrations indicating a thickness of 75 meters (CEDAE, 1986 apud Barbosa et al., 2002).

Regarding the local hydrogeology, preliminary observations suggest multiple or superimposed aquifers, usually of free occurrence, locally confined, made of a coarse arkosic matrix, possibly separated by clays of variable occurrence and thickness. The level of ground
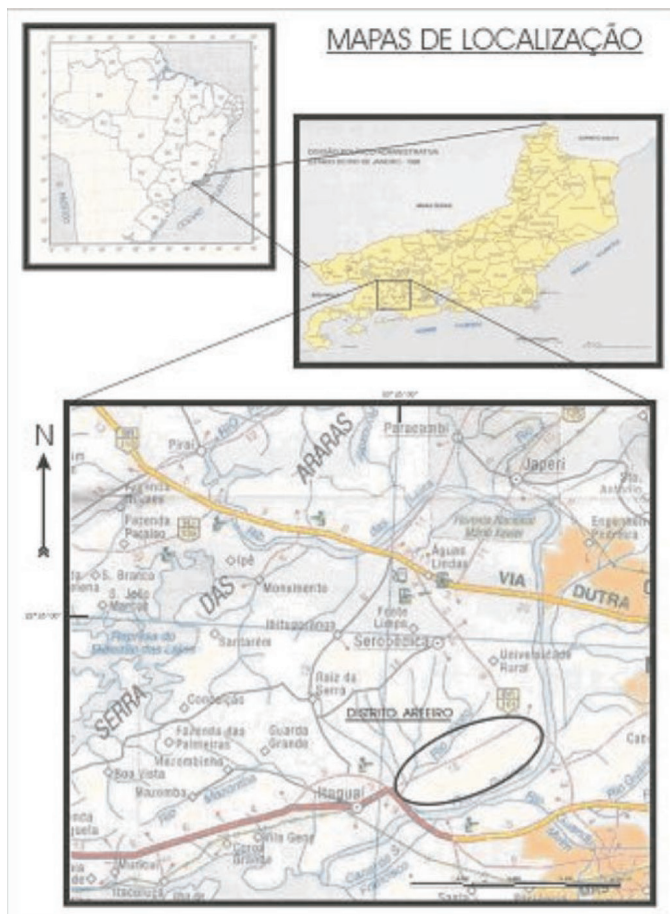
Figure 1 – Location map of the studied area (Berbert, 2003).

Figure 2 – Aerial Image showing the extraction sites.

Figure 3 – Distribution of the studied sand pits (blue dots)
(BERBERT, 2003).

water varies between 3 and 7.5 meters, according to season. The ground water is little mineralized, presenting low values of electrical conductivity and pH (Tubbs, 1999).

The region's main socioeconomic activity, considering the local geology, is sand mining. The Sand District of Itaguaí – Seropédica is the main sand supplier for the Rio de Janeiro State building industry (90% for Rio de Janeiro city), with about 80 mining businesses, 71 of which are legally entitled to explore mineral sand (Figures 2 and 3). However, the mining activity causes environmental conflicts not only by exposing the phreatic aquifer but also lowering it. Furthermore, the aquifers are subject to fuel oil spills from the suction pumps installed on floating drags as well as waste dumping from the processing activities (Berbert, 2003) (Figures 4 and 5).

Governmental authorities, pushed by society, have been urging the sand firms to find solutions to lessen the several environmental impacts caused by this activity. This study seeks to characterize the water hydro-geochemistry in the sand extraction pits and considers the recuperation proposals for the area of providing subsidies to introduce

pisciculture in the extraction pits as an alternative business.
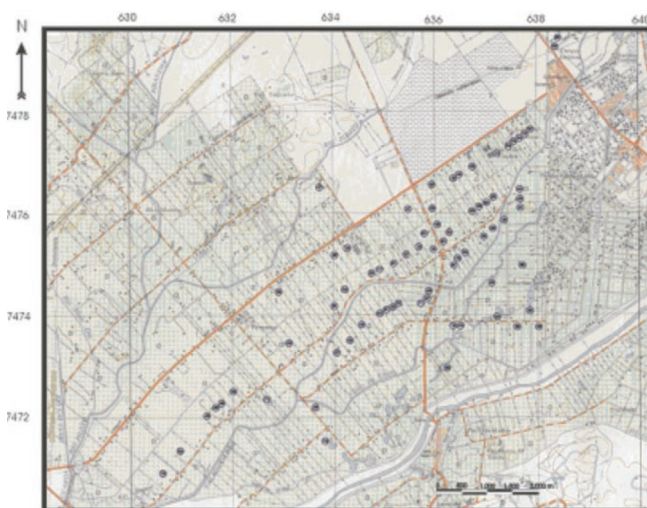
MATERIALS AND METHODS

In four active sand pits 10 samplings were carried out between January 2004 and February 2005, to determine the behavior of some physical-chemical parameters. Electrical conductivity, pH, temperature and total dissolved solids were measured in the field with portable WTW-LF 330 equipment. Samples were filtered with 22µm pellicles and separated in sub-samples to determine metal contents, acidified to pH2 with concentrated nitric acid, and to identify anions, frozen until analyzed.

Figure 4 – Sand extraction operations.

Figure 5 – Sand pit irmãos Unidos.

The anions identifications (F⁻, SO_4^{2-}) were made through ionic chromatography, SHIMADZU CDD-6A equipment; to determine the cations (Ca^{2+}, Mg^{2+}), atomic absorption spectrometry was used with VARIAN equipment; to detect aluminum, the optical emission spectrometry in inductively coupled plasma (ICP-OES), JOBIN YVON – HORIBA (model ULTIMA 2) equipment with an aluminum detection limit of 0.015 mg/L ; the silica presence was made by the colorimetric method through the formation of silicomolybdic acid, spectrophotometer HITASHI (model U-1100).

RESULTS AND DISCUSSIONS

The water monitoring preliminary results of four selected sand pits between January 2004 and April 2005

showed low pH (3.11 – 4.95) (Figure 6), variable sulfate (2 – 65 mgL-1) and aluminum (0.015 – 14 mgL⁻¹) concentrations (Table 1). The anomalous aluminum values occur between May and August. This may probably be associated with the low regional rain fall in this period (annual mean for this period is 50 mm). This would impact the water's pH zones making the aluminum to be presented as Al^{3+} and as the pH increases, $Al(OH)^{2+}$ and $Al(OH)_2^+$. Such substances are considered toxic because of their greater reactivity with the cell membrane's surface of aquatic organisms. They can, for example, react with fish gills, which have higher pH values than the water, causing aluminum hydroxide to precipitate in the form of gel. This gel prevents the water oxygen assimilation by the gills, suffocating the fish, causing ionoregulatory and respiratory effects (Baird, 2002). Because of the high sulfate and aluminum values, there will probably be the formation of $AlSO_4^+$ and $Al(SO_4)_2^-$ (Yariv & Cross, 1979). Thus, according to the pH zones, there is a predominance of these sulfates. However, with the pH elevation, aluminum hydrolysis occurs, turning the hydroxides into the predominant element species. The hydroxides are responsible for the adsorption of suspension particles in the water, making them coagulate and then decant. This process gives the water a clean aspect.

Aluminum organic species are not expected in large amounts in this water, since these are artificial pits and so there is vegetation removal due to the mining activity. Thus, the addition of organic matter, highly reactive with aluminum, into the pits should be minimal. However, the Rio de Janeiro State Departamento de Recursos Minerais (DRM-RJ) points out occurrences of peat deposits in the sand mining region, which could support the hypotheses origin of the pit water low pH values and would confirm the presence of aluminum organic species.

Aluminum toxicity can be reduced by the presence of silica in the water, an experimentally proved fact, though it does not occur in practice, since aluminum tends to be more reactive with the organic matter or with other complexing agents present in higher amounts in the water (Camilleri et al., 2003). In the case of sand pits, the concentration of silica in the water is relatively high (Table 1) and it probably occurs, according to the found pH zones, in the colloidal fraction in the form of silicon acid (H_4SiO_4). On the other hand, because of the greater

Table 1 - Mean cations and anions concentration in the water

Sand pit	SO_4	Al	Ca	Mg	F	SiO_2
1	61.54	2.54	6.93	2.68	0.196	26.3
2	29.78	2.84	2.86	1.54	0.193	27
3	3.31	1.53	1.92	0.54	0.198	21.07
4	60.9	2.95	5.71	3.63	0.212	25.5

Lagoa 1

Lagoa 2

Lagoa 3

Lagoa 4
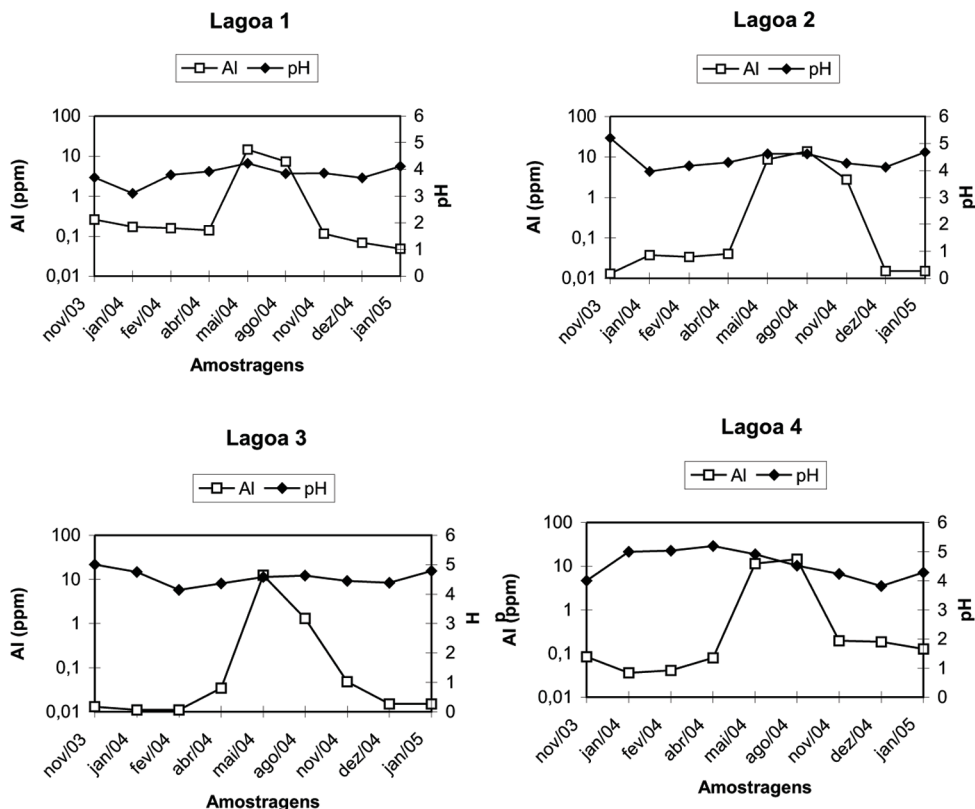
Figure 6 – Aluminum concentration variations versus pH in four pits.

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affinity and high sulfate concentrations in the pits, it is more probable that the aluminum will form complexes with this anion rather than silica. Small concentrations of fluorine and low water hardness favor the bioavailability of aluminum (Table 1).

CONCLUSION

The preliminary results presented indicate that the alternative of introducing pisciculture to the sand extraction pits of the Itaguaí-Seropédica mining district must consider the bioavailability and toxicity of aluminum on aquatic organisms.

THE INFLUENCE OF THE SPECIFIC SURFACE AREA OF PARTICLES ON TRACE-ELEMENTS ADSORPTION BY BOTTOM SEDIMENTS: A CASE STUDY IN THE SURROUNDINGS OF MACAÍBA CITY, RIO GRANDE DO NORTE STATE BRAZIL

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ABSTRACT

This study evaluates the influence of the particles' specific surface area characteristics on the retention of trace-elements by bottom sediments. The fine fraction (<0.063 mm) of the River Jundiaí bottom sediments, sampled upstream and downstream of the Macaíba city urban center Rio Grande do Norte State, was analyzed for trace elements through inductively coupled plasma – atomic emission spectrometry (ICP-AES) for Pb and Zn, and atomic absorption spectrometry – cold vapor generation (AAS-CV) for Hg, after strong acid digestion with aqua regia. The chemical element contents varied within the following ranges (unit mg/kg): Pb (12-91), Zn (24-141) and Hg (0.005-0.355). The enrichment degree was obtained by comparing these sampled contents with

the average concentration found in samples from sites in the same catchment basin, deemed free of anthropogenic influence. The results show higher values for the elements analyzed in the urban center. X-ray diffraction data and stereomicroscope observations indicate that quartz and feldspar are the samples' main constituents. The identified clay mineral is kaolinite. The specific surface area (unit m^2/g) was used to calculate each element's adsorption density (unit μm/m^2) on the particles surface. This includes all the inaccessible internal surface portions (especially the pore wall surfaces). Considering both internal and external surfaces are accessible to strong acid lixiviation, the relationship between trace-element concentration, organic matter total content and specific surface area, is discussed. It is suggested that, in the case of partial digestion of the bottom sediment fine fractions used for environmental studies, with either simple or sequential extraction, occasional anomalies may be adjusted to the correct results through the adsorption density calculation (the ratio between a given lixiviated element concentration and the sample specific surface area). The use of the adsorption density to measure bottom sediment trace-elements retention may present important implications in environmental risk analysis.

INTRODUCTION

The cumulative and rearrangement properties of a species in sediments qualify them as being extremely important in environmental impact studies, registering more permanently the contamination effects (Förstner & Wittmann, 1981; Bevilacqua, 1996).

To correctly assess the amount of chemical species in sediments, it is necessary to distinguish natural origin processes from anthropogenic action origins. A sediment is usually formed of solid phases, composed of different chemical elements, which may originally be in high concentrations or have been added to the environment from anthropogenic sources. In natural water, the sediments consist predominantly of organic waste, colloidal matter, living cells (bacteria and algae) and inorganic solids, such as Fe and Mn oxides and hydroxides, carbonates, sulfides and clay minerals. Many factors influence the adsorption and retention of contaminants on the particles surface. Size is one of the main factors. The observed tendency is the smaller the particles, the higher the concentrations of adsorbed nutrients and chemical contaminants. This primary tendency is due to the small particles having elevated specific surface areas, that favor the adsorption and occasional fixation of what is available in the aqueous environment. The drainage channel bottom sediments of rivers play an important role in the evaluation of their pollution, since they reflect part of the phenomena occurring in the water and particulate matter compartments.

Several researchers prefer the fine fractions of silt-clayish particles (<0.063 mm) for sampling and analyses, using these fractions to determine the presence of contaminants in surface water (Lacerda et al., 1990; Davidson et al., 1994; Droppo & Jaskot, 1995; Truckenbrodt & Einax, 1995; Gatti, 1997; Liu et al., 1999; Soares, 1999). As for the chemical treatment used to quantify the chemical element's availability in the aqueous environment, there are authors who choose the so-called simple extraction, with a strong or weak acid (Novozamsky et al., 1993; Bevilacqua, 1996; Gatti, 1997); or the sequential extraction with different acids of varied concentrations (Davidson et al., 1994; Daus et al., 1995; Gonzales et al., 1994; Krause et al., 1995; Urasa & Macha, 1996).

The studied area is in the town of Macaíba, 22 km from Natal city, Rio Grande do Norte State. The River Jundiaí crosses Macaíba, which is in the upper fluvial portion of the River Potengi estuary. This area is characterized by both the addition of fresh water and the direct daily tide action. Considerably high levels of Pb, Zn and Hg in the water and bottom sediments of the River Jundiaí have been reported before (Guedes, 2003; Guedes et al., 2003a; Guedes et al., 2003b). The River Jundiaí course, from the upper to the middle part, is characterized as an intermittent river. The environmental problems in these sections are typically of natural origin, even when crossing urbanized areas. However, as it approaches Macaíba, a medium sized town, the problems get worse due to the occupational and horizontal growth. The basic sanitation issue is one of the greatest problems this town faces, since only 3% of the town has a sewage system. It has a surface aquifer, the domestic septic tanks are very shallow and the town council undertakes removal for the poorer population. However, most of the waste goes clandestinely to the pluvial drains, which consequently ends up becoming perpetual, taking the "in natura" sewage into the River Jundiaí. Solid waste disposal is another environmental problem with which the Macaíba population cohabits, as the town does not have a specific landfill area. As a result, part of the domestic waste is dumped directly into the river or near it. Moreover, in the three downstream sampling sites from the studied area, where the river depth and width are greater, the influence of the saline environment is clearly suggested by the high values found for the electrical conductivity, salinity, calcium, potassium, magnesium, sodium, sulfate, chloride, total solids and dissolved solids parameters (Guedes, 2003).

The previous studies carried out on the River Jundiaí bottom sediments were based on the chemical analyses results of the bottom sediment's fine fraction (<0.063 mm), without considering the specific surface area parameter. This is defined as the ratio A/m (unit m^2/g) between the absolute surface area of a solid and its mass. The specific surface area includes the external surfaces of the solid particles and all the inaccessible internal surface portions

(mainly the internal pore wall surfaces). The ratio between the specific surface area (unit m^2/g) and the adsorbed chemical element concentration on the samples (unit mg/kg) was used to calculate the adsorption density (unit $\mu g/m^2$) of that element on the particles surface. This study evaluates the influence of the particles' specific surface area on the retention of trace-elements by bottom sediments.

METHODOLOGY

The samplings were made in January and February 2001, during the dry period, when the fresh water contribution to the River Jundiaí is basically represented by the "in natura" sewage. This enters the stream through the pluvial drains that clandestinely receive the discharged urban waste. Samples were collected in 10 sites (Figure 1). The sites P3 to P9 are distributed 01 km apart; of these, the sites P4 to P9 are in an urban area which is also influenced by the tide. The samples P13 and P14 were collected in the same catchment, in places deemed free from anthropogenic influence, 50 and 27 km from Macaíba, respectively. Upstream from the town, the sampling sites are distributed in a tide and possibly urban influence free area of the River Jundiaí. The bottom sediment samples were collected to accurately obtain the material from the superior interval (0 to 5 cm) of the active stream channel.

In the laboratory, the samples were dried at 60°C for 24 hours, disaggregated and sieved. The sediments' fine fraction (<0.063 mm) sampled upstream and downstream from the Macaíba urban center was analyzed for Pb and Zn through inductively coupled plasma – atomic emission spectrometry (ICP-AES), and for Hg by atomic absorption spectrometry – cold vapor generation (AAS-CV), after strong acid digestion with aqua regia.

The total organic matter content analysis was carried out in two stages. In the first, humidity was removed from the sediment for 12 hours in a tray dryer at 105°C. In the second stage, about 2 grams of this material was maintained at 600°C for 4 hours in a muffle furnace. The organic matter content calculation was based on the mass difference between the humidity free sample and the mass after heating at 600°C.

The specific surface area was determined using the Brunauer, Emmett and Teller method (BET). The analyzed samples went through a degassing step at 110°C for 4 hours in a nitrogen atmosphere. The precise specific surface area measurement of solids through gas adsorption, according to Brunauer, Emmett and Teller, is to determine the adsorbate amount (or gas that adsorbs) necessary to cover the external and internal surfaces of the pores of a solid, with a monolayer of adsorbate. That monolayer capacity can be calculated from the adsorption isotherm by using the BET equation.

Mineralogical data was obtained by observing the samples in the stereomicroscope and X-ray diffraction. For the clay fraction X-ray diffraction analyses, oriented sections were prepared, mounted from a clay-water suspension with a concentration of 60 mg clay for 1 ml distilled water, carefully placed on a glass plate, and then dried on a hot plate at 60°C. The scanning was conducted from 2 to 32º (scale 2), with a velocity of 1º/minute.

Fonte: Ministério do Exército: Diretoria de Serviço Geográfico, Folha SB.25- V-C-V, 1983.
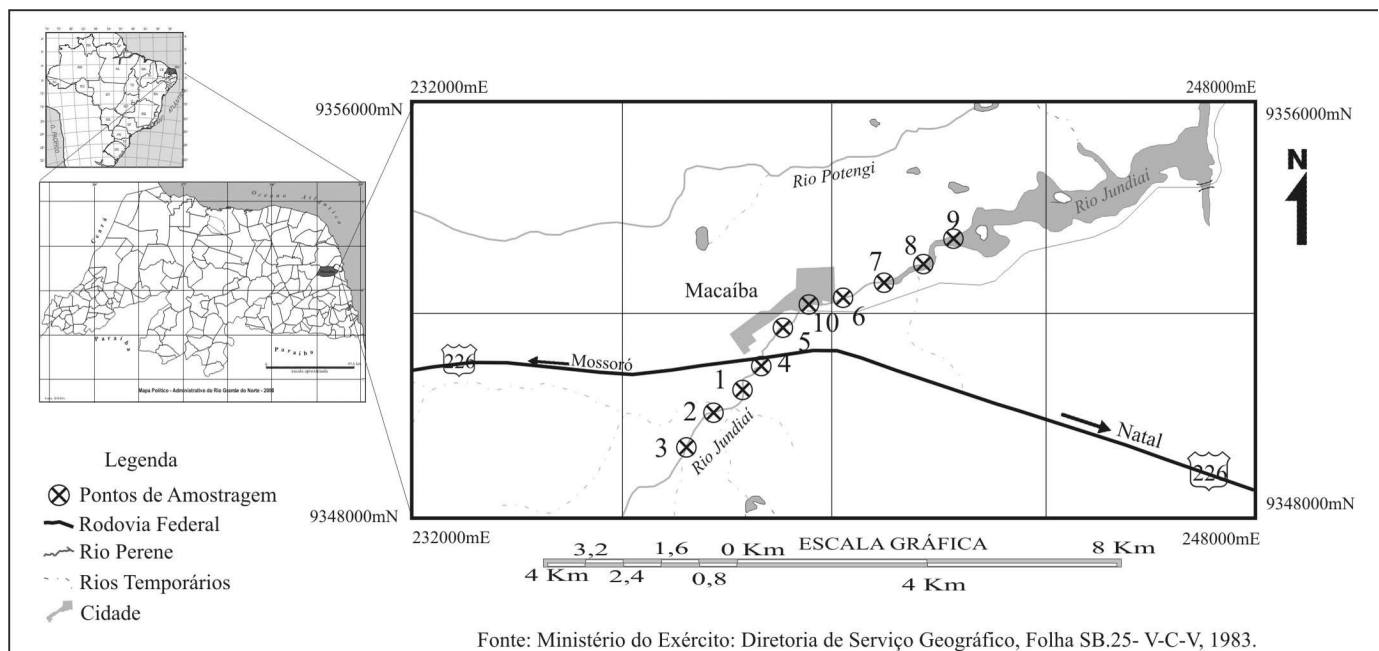
Figure 1 – Location map of the studied area and sampling sites.

RESULTS

The chemical element content varied within the following ranges (unit mg/Kg): Pb (12-91), Zn (24-141) and Hg (0.005-0.355). The results show elevated values for the analyzed elements in the urban center, as shown in Figure 2. The 3 graphs present, on the horizontal axis, the sampling sites distribution and, on the vertical axis, the chemical elements concentrations of Pb, Zn and Hg, in mg/kg (represented by diamonds), and the adsorption density in g/m² (represented by squares). The vertical axis scale is logarithmic to facilitate the visualization and comparison, on the same graph, between the two different approaches used (concentration and adsorption density). Upstream and downstream directions, as well as the sampling sites in urban area are indicated. The urban area and Macaíba town sites are placed about 1 km apart. The two left-hand sites on the graphs (P13 and P14) are located upstream in the same catchment area, in a position considered free of anthropogenic contribution, 50 and 27 km from Macaíba respectively. The horizontal lines on each graph represent the arithmetic mean of the P13 and P14 site results. These values, in this study, are called threshold. The ellipses highlight zones of remarkable contrast between the chemical elements concentrations and the adsorption density of the chemical elements adsorbed in the bottom sediment fine fractions collected in the River Jundiaí.

In the urban area and downstream from Macaíba, the values for Pb, Zn and Hg concentrations are all above the threshold, with the maximum contents always in the urban area (Pb: maximum in P4, Zn and Hg: maximum in P10). In this same zone, the adsorption density follows the same variation tendencies observed for the three chemical elements concentrations with the maximum adsorption density of Pb in site P4 and Zn and Hg in site 10.

The three sampling sites upstream and near Macaíba (P3, P2 and P1) highlighted with ellipses in the three graphs, represent the zone where the chemical elements concentrations and adsorption densities present considerable differences from each other. It is important to emphasize this is the studied section of the river where lower concentrations in relationship to the urban area were expected. The Pb concentration values are above the threshold with the maximum in P3 and the minimum in P2; the Pb adsorption density values are below the threshold adsorption density with a maximum in P3 and a minimum in P1. In the case of Zn, 2 of the 3 concentration values are above the threshold (P3 and P1), with the maximum in P3 and minimum in P2; the Zn adsorption density values are all below the threshold, with a maximum in P2 and minimum in P3. The chemical element Hg has one of the 3 concentration values above the threshold (P1), with a maximum in P1 and minimum in P2; the adsorption density values for Hg are all below the threshold, with a maximum in P1 and minimum in P3.

X-ray diffraction data and stereomicroscope observations indicate that quartz and feldspar are the samples' main constituents. The clay mineral identified is kaolinite.

The horizontal axis in Figure 3 shows the bottom sediments sampling sites distribution on the River Jundiaí, in the urban area and around Macaíba. On the vertical axis are shown data on specific surface area in m²/g (diamonds) and organic matter content in % (squares). The specific surface area (diamonds) varies between 4.5 and 42.2 m²/g, with the highest values found in the 3 sites sampled upstream of Macaíba. The organic matter content varies from about 10% in the upstream sites, taken as the threshold, to about 20% in the sites further downstream, with a growing content in the sediments from within and after the urban zone (squares). Apparently there is no significant correlation between the organic matter content and the specific surface area.

DISCUSSION

Guedes (2003) reports results of analyses carried out in water samples collected in the same period and in the same bottom sediments sampling sites in the River Jundiaí, near Macaíba. These results show elevated Pb, Zn and Hg concentrations in the River Jundiaí urban zone. The Pb, Zn and Hg contents in water varied between 0.04 and 0.19 ppm, 0.02 and 0.05 ppm and 0.0002 and 0.0003 ppm, respectively. According to this data, the elements Pb, Zn and Hg added to this environment have an anthropogenic origin.

Among the factors that influence the contaminants adsorption and its retention on the surface of particles in natural water, highlighted is the particle's size. Usually, the smaller the particles are the higher the concentrations of adsorbed nutrients and chemical contaminants. This primary tendency is due to the small particles having elevated specific surface areas, which favor the adsorption and occasional fixation of what is available in the aqueous environment.

This study used the fine fractions of silt-clayish particles (<0.063 mm) for the analyses, being the usual practice in many studies (Lacerda et al., 1990; Davidson et al., 1994; Droppo & Jaskot, 1995; Truckenbrodt & Einax, 1995; Gatti, 1997; Liu et al., 1999; Soares, 1999). These study results serve as support for environmental risk diagnosis, monitoring and analysis.

As shown in Figure 2, in the urban area and downstream from Macaíba (sites P4, P5, P10, P6, P7, P8 and P9), the Pb, Zn and Hg concentration values in the bottom sediments fine fractions and the adsorption densities, follow the same variation tendencies, with even the same sites with the maximum concentration and adsorption density: Pb in site P4, and Zn and Hg in site P10. However, in the 3 sampling sites situated upstream but near Macaíba town (P3, P2 and P1), emphasized by ellipses in the 3 graphs
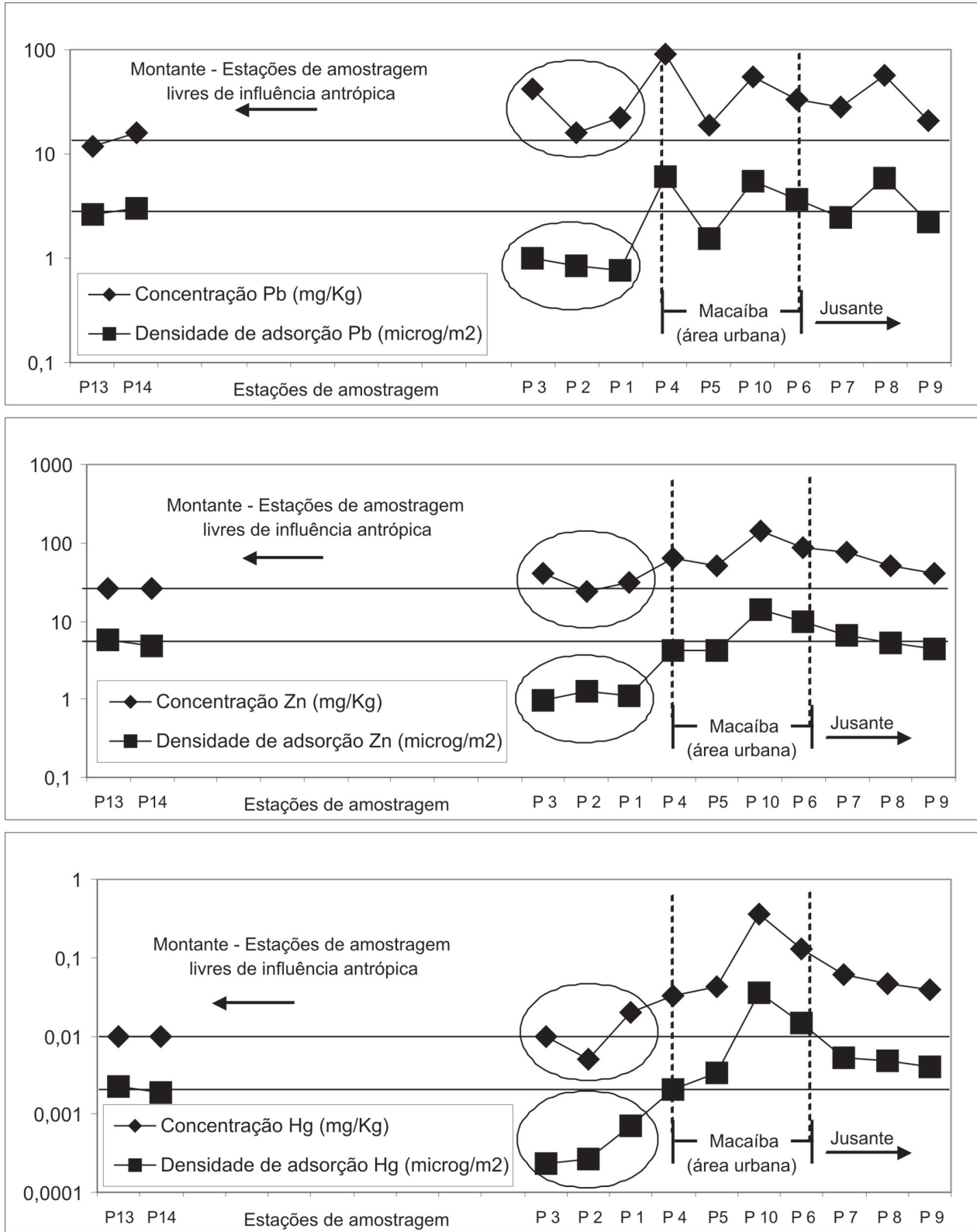
Figure 2 – Horizontal axis: sampling points distribution of the River Jundiaí bottom sediments, in urban areas and the vicinity of Macaíba City. Vertical Axis: concentration in mg/kg (diamonds) and adsorption density in mg/m² (squares) of the chemical elements Pb, Zn and Hg. Sampling sites to the left in the graph (P13 and P14): threshold values. Ellipses: sections where concentration and adsorption density in the bottom sediments fine fractions present controversial tendencies and smaller values related to the threshold values.
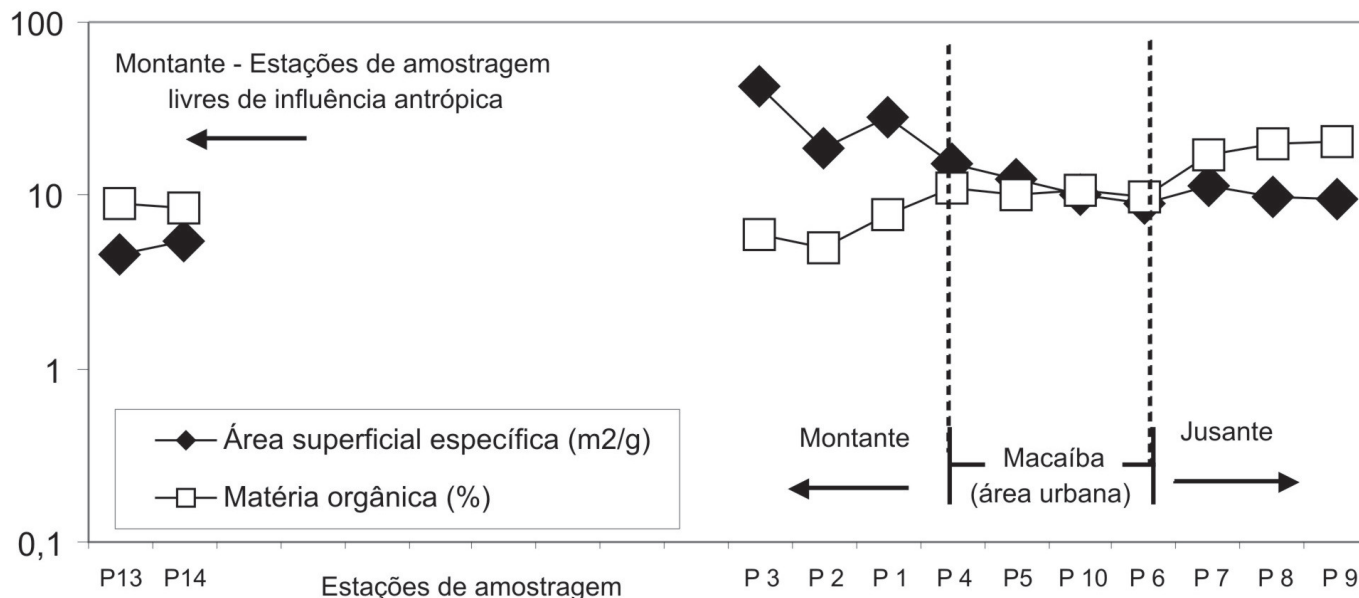
Figure 3 – Horizontal axis: of the sampling points distribution of the River Jundiaí bottom sediments, in urban areas and the vicinity of Macaíba City. Vertical Axis: specific surface area in m²/g (diamonds) and organic matter content in % (squares). Sampling sites to the left in the graph (P13 and P14): threshold values.

of Figure 2, the concentrations and adsorption densities present remarkable differences compared to the threshold values, and display even opposed tendencies, as is the case of Zn. It is important to emphasize this is the studied section where the results of the investigated element concentrations were expected to be lower, compared to the urban area.

The high Pb, Zn and Hg concentrations in water in the River Jundiaí urban zone reported by Guedes (2003), confirm the hypothesis of anthropogenic contribution for the Pb, Zn and Hg in the bottom sediments. Among the possible alternatives to justify these chemical elements in the bottom sediments upstream of Macaíba, the first is that in the absence of an anthropogenic source, Pb, Zn and Hg are present in high concentrations in the rock substratum of that area. This alternative does not seem acceptable, since the average contents registered in the sediments fine fractions sampled 27 and 50 km from Macaíba do not present high values. A second alternative, which a more quantitative approach, suggests that the use of the chemical element adsorption density, rather than the element's net concentration value leached from the surface of the particles, should be used in environmental risk analyses.

CONCLUSIONS

The data from this study, mainly that obtained in the sites upstream from the Macaíba urban area (ellipses), suggest that, in the case of the partial digestion of the bottom sediment fine fractions used for environmental studies, be it simple or sequential extraction, occasional

anomalies can be adjusted to the correct result through the adsorption density calculation (the ratio between the concentration of a given leached element and the sample's specific surface area). The use of adsorption density as a measure of trace-elements retention by bottom sediments may represent important implications in environmental risk analyses.

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