Human health risk areas in the State of Paraná, Brazil: results from low density geochemical mapping

Otavio Augusto Boni Licht
Minerais do Paraná – MINEROPAR
Curitiba – State of Paraná – Brazil
otavio@pr.gov.br

ABSTRACT *Geochemical maps show the distribution of elements and chemical compounds in natural materials, such as stream water and the sediment of hydrographic basins, which reflect natural and man-made sources. For this reason, they have been considered as basic tools in multipurpose environmental investigations, including medical geology and ecotoxicology. Compiling geochemical data produced by mineral exploration projects and drawing integrated geochemical maps could be the first approach to indicate health risk areas. However, the proper application of geochemical maps when investigating the relationship between environmental geochemistry and endemic diseases can only be achieved if the analytical data are produced and interpreted according to the (bio-) availability of chemical elements and compounds. Weak extractions in stream sediment samples and chemical analysis of filtered water samples are adequate, since they are able to quantify the amount that can be absorbed by the food chain. The association of fluorine and the occurrence of dental fluorosis, as well as chlorine and bromine as geochemical indicators of liver cancer risk areas are relationships between geochemical abundance and geographically well delimited endemic diseases found in the State of Paraná, Brazil. Further investigations are required to establish the real meaning, from the public health point of view, of some risk areas indicated by barium, potassium, calcium and aluminum in stream water and mercury in stream sediments.*

KEYWORDS: *Medical geology, fluorine, fluorosis, bromine, chlorine, liver cancer*

Introduction

The environment is an intrinsically complex system made up of countless variables. The co-variations between its components and geographic position produce an enormous diversity of effects, reflecting the complexity and the interactions of the processes taking place in nature and those caused by the lives and activities of men. Environmental studies must be performed with the collection and analysis of the widest number and kinds of variables, in order to describe this complex system in the most accurate and complete way possible. Applying this statement to geochemical studies, one could observe that until recently, these investigations were performed almost exclusively directed to geological investigations such as mineral exploration. From the reliable results achieved in 1932 in the former Soviet Union by a "*metalometric survey*" devised to find tin ore deposits, the technique of exploration geochemistry spread out across the planet with countless cases of success. In the period between 1930 to 1960, Vinogradov, Vernadsky, Fersman, Ginzburg and Sokolov in the former USSR; Govett and Warren in Canada; Hawkes, Lovering and Bloom in the USA; Webb in England; Bianchini and Salvadori in Italy; Cotelo and Neiva in Portugal and Granier in France pioneered research to identify the behavior of chemical elements in geologic materials and the pathways of its dispersion (Fortescue, 1992). In the last twenty years, some researchers and institutions have conducted investigations using exploration geochemistry techniques to cover huge areas, in a regional or national scale, identifying a wide spectrum of chemical elements, aiming to develop complete geochemical databases and also to create maps of the geographical distribution of chemical elements and compounds from both natural and man-made sources. However, it is important to consider that geochemical studies are unable to completely describe the environment, since analytical techniques are able to identify just a small part of the total amount of chemical species that the samples are made up of. It is important to consider that the elements could be in many forms or chemical species: linked to Fe and Mn hydrous-oxides, loosely bonded to organic matter, sorbed to clay minerals or composing the structure of highly resistant minerals. For these reasons, some processes cannot be clearly detected or identified because of the inadequacy of the sampling plan, the improper preparation of samples, the analytic techniques or the determined group of elements or compounds. Since geochemical techniques are been applied to get a wider and deeper insight of the natural environment as well as the anthropogenic impacts imposed on it, which is very important because life began and evolved on Earth in the presence of all chemical elements even in extremely low concentrations, multipurpose geochemical investigations are demanding more sensitive analytical techniques to reveal subtle but significant regional geochemical structures and anomalies. The improvement of laboratory techniques and the lowering of detection limits have made it possible to add more and more elements each decade to the list of the bioactive elements (Darnley *et al.,* 1995).

Multipurpose applications for geochemical data

Holistic environmental investigations and even multipurpose applications for the geochemical data can include the compilation of data produced by previous surveys designed and performed for specific purposes: geochemical exploration, soil fertility and environmental surveillance. The recovery of former databases is an intelligent method to make data available for purposes completely different from the original, even taking into account that the geochemical maps produced with these geochemical data should be considered as a rough sketch of the actual situation. Several geochemical atlases and articles have been published with geochemical maps based on this kind of data. In addition, the production of new data obtained from especially designed surveys is the most modern and widely accepted source of geochemical data that can correctly contribute to the diagnosis of the processes occurring in the environment. Many geochemical atlases and articles have been published based on geochemical data produced by multi-elemental geochemical surveys at a regional or on a national scale, e.g. Northern Scandinavia, Finland, Great Britain, Costa Rica, Barents quadrangle, Alaska and the Peoples' Republic of China. All of them have contributed to establish the methodology of the UNESCO and IUGS Projects IGCP-259 and IGCP-360 (*International Geological Correlation Program*). The first step is to establish the methods required for planning and performing multi-elemental geochemical surveys. The second step is the design of protocols for sampling natural materials in a regular grid showing the distribution of these elements on a global scale.

The interpretation of geochemical data should be based on multi-source databases, each one produced and managed by the governmental institutions in charge of geology, agriculture, public health, environmental monitoring, social and economic planning. Considering this, the ideal conception of a geochemical database designed to cover all aspects, purposes and application of geochemical data, should be multi-media (samples of many types of materials) and multi-elemental (wide spectrum of elements and compounds). Geochemical data could be used in medical and epidemiological research in the determination of health risk areas, since the occurrence of many kinds of endemic diseases are being explained using this approach. The potential of geochemical surveys to point out the primary evidences of diseases related to the excess and lack of chemical elements in the food chain where clinical signs are non specific has been emphasized by the World Health Organization (Mills, 1993). Conditions of intense oxidation weathering, lack of organic detritus and formation of secondary stable and insoluble minerals e.g. clays, could lead to severe deficiencies in trace elements. Regions covered with lateritic crusts are especially susceptible to this problem, producing severe lack of Se, Mo, Zn and I which are essential to health.

Vinogradov (1959) has already identified the importance of rare elements in biology, emphasizing inter-connections between the health of crops, humans and household animals with the abundance of many elements in soil, as well as the inter-dependence between geochemical provinces and endemic diseases. He called this branch of science *chemical ecology* because the public health expression *epidemiology* had for quite some time been applied exclusively to infections and transmissible diseases. The inclusion of diseases whose etiology is related to interactions between physiology and environmental factors was accepted later (Låg, 1990). It is widely accepted that some chemical substances could cause toxic effects in specific nodes of the ecosystems and food chain; this lead to the emergence of a new branch of toxicology, *eco-toxicology* (OPS, 1980), which could be confused with *geomedicine*, the branch of medicine that investigate the influence of environmental components on the geographic distribution of health problems (Låg, 1990). The cartographic display of the occurrence of human and animal diseases has been used from long time. Zeiss (1931, *apud* Låg, 1990) presented the expression *geomedicine* as a synonym of *geographic medicine*, meaning the branch of medicine that handles geographic and cartographic techniques to display the results of medical investigations, emphasizing the need for interaction between healthcare workers, veterinarians, biologists, geographers, meteorologists and geologists. More recently, the expression *medical geology* has been applied to the interdisciplinary scientific research carried out by physicians and geoscientists to identify the health effects caused by exposure to natural geological factors and geological events (Selinus, 2003). The scope of medical geology includes the identification and characterization of natural (and anthropogenic) sources of harmful materials in the environment, learning how to predict the movement and alteration of chemical, infectious and other disease-causing agents, and understanding how people may be exposed to such materials (Centeno, 2003).

Toxicity is the property inherent to the chemical structure of a substance or property of an element that defines its capacity to cause injury to a living organism (NAS/NRC, 1970, *apud* OPS, 1980; Sanockij, 1970, *apud* OPS, 1980). The toxic action of a chemical substance and/or an element generally affects all parts of the organism, even the primary injury could be located in one specific addressee organ, in which the injury appear as an organic malfunction or disease (NIEHS, 1977 *apud* OPS, 1980). Long term exposure or the absorption of recurrent low doses of a toxic substance can lead to chronic effects (OPS, 1980).

The occurrence of *kwashiorkor* in Jamaica, a tropical disease, was related to the lack of Se. This relationship emerged from the interpretation of data produced by the multi-elemental geochemical mapping of Jamaica along with epidemiologic data (Garret and Geddes, 1991). In addition, the lack in Se (food-shortage) is related to the endemic Kaschin-Beck (osteo-arthropathy) and Keshan (cardio-miopathy) diseases in China (Tan *et al*., 1988 *apud* Darnley *et al*., 1995). Many other examples are known which clearly connect environmental geochemical excesses or deficiencies to health: lack of fluorine and dental caries, excess of fluorine and dental or skeletal fluorosis, iodine and goiter, arsenic and skin cancer and the Jashi disease (human sterility) with high contents of Mg, SO_4, Na, K and Sr, and low contents of Zn and Mn in drinking water in China. There are also a number

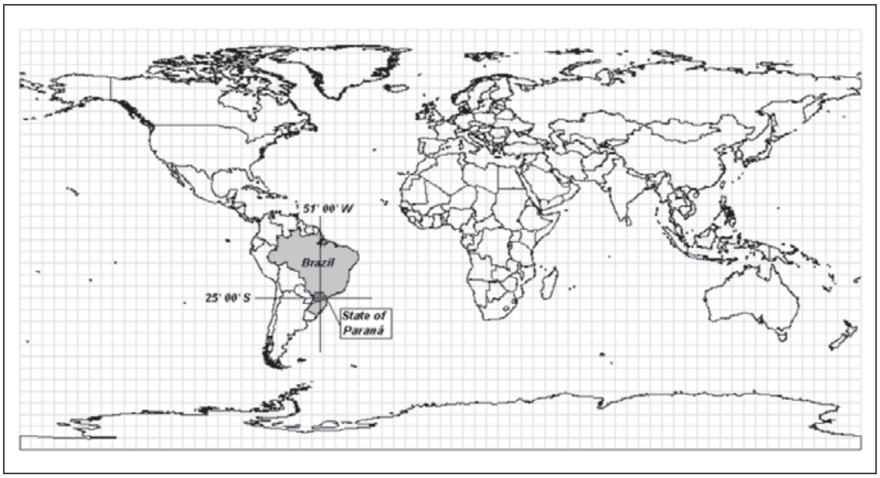

Figure 1 – Location of the State of Paraná

of cases without a clear and proven cause-effect relationship even though there is statistical correlation, e.g. water hardness and cardiovascular diseases, lead and multiple sclerosis, cadmium and hypertension and arteriosclerosis, aluminum and Alzheimer's disease. These relationships remain controversial and much more research is needed to prove its significance.

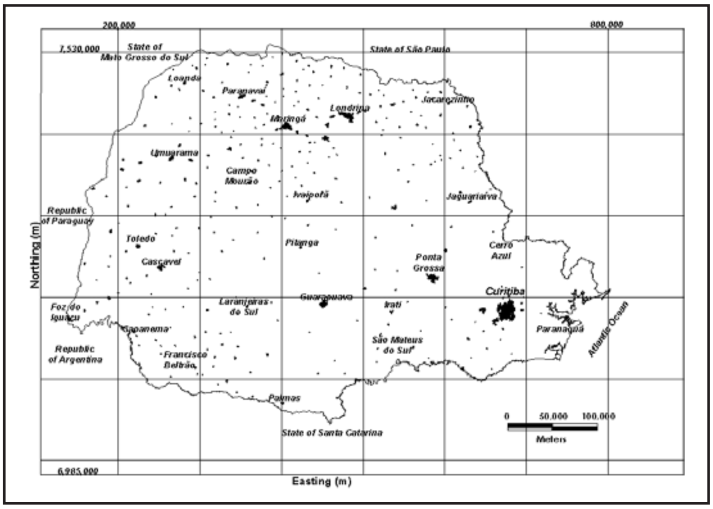

Figure 2 – The borders and main urban centers

The State of Paraná

The State of Paraná is located in Southern Brazil (Fig. 1; Fig. 2), has a surface area of 199,727 km^2 and can be divided into the following four main physiographic divisions: Coastal Plain, First, Second and Third Plateaus (Maack, 1968) (Fig. 3). The Coastal Plain is located between the coast line and the Serra do Mar buttresses (Sea Mountain Range), and is composed of Archean and Proterozoic metamorphic and igneous rocks. The First Plateau has a complex geology represented by Proterozoic and Paleozoic metamorphic, igneous and sedimentary rocks. The Second Plateau is made up by a 600-meter thick sequence of the Paraná Basin Paleozoic sedimentary rocks dipping gently to the west. The Third Plateau, includes the Paleozoic igneous system of the Paraná Basin, composed of thick flows, dikes and sills of basic, intermediate, and acidic composition, partially covered by Cretaceous sandstones, siltstones and shales. The very fertile soils of the region are derived from basic volcanic rocks. This region is made up of deep-red lateritic soils, structured terra-rossa and red/yellow podzols. The predominant climate is sub-tropical with temperatures ranging from 0 °C to 36 °C. The State of Paraná contains a dense and perennial hydrographic network. Serra do Mar is the main division, separating the basins of the Coastal Plain from those of the other geographic divisions. The geomorphic structure dipping westward forces the rivers to flow toward the Paraná River valley, except for the Ribeira and Coast Plain basins that flow to the Guaratuba and Paranaguá bays or directly to the Atlantic Ocean.

Due to the natural fertility of its soils, almost all the territory is farmable, except for the mountainous areas. The occupation of the State of Paraná territory by the Europeans began in the end of the16th century. Now its economy is strongly concentrated on agro-industry (grains, milk, chicken meat, pork and eggs) but the machinery, vehicle, wood, paper and textile industries are also important.

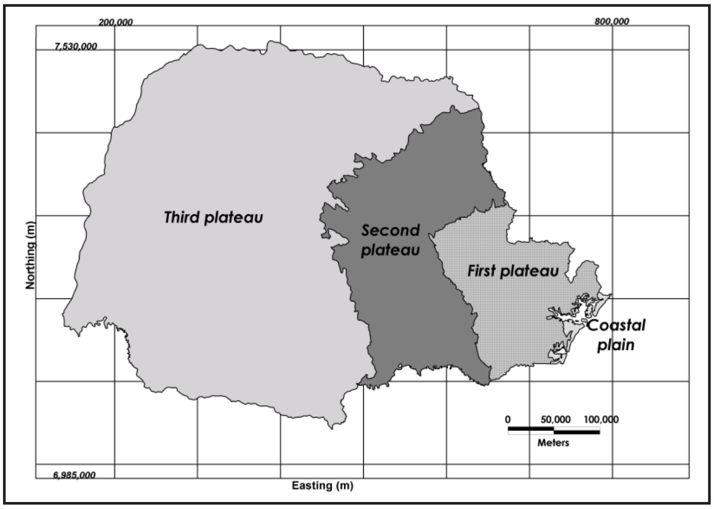

Figure 3 – The main physiographic divisions of Paraná

The multielemental geochemical surveys of the State of Paraná

The project known as the Paraná State Geochemical Information System - (SIGEP) has been active since June 1994, aiming not only to recover old geochemical data but more importantly to produce new geochemical databases with multipurpose applications. The leading institution is Minerais do Paraná – MINEROPAR (the Paraná Geological Survey).

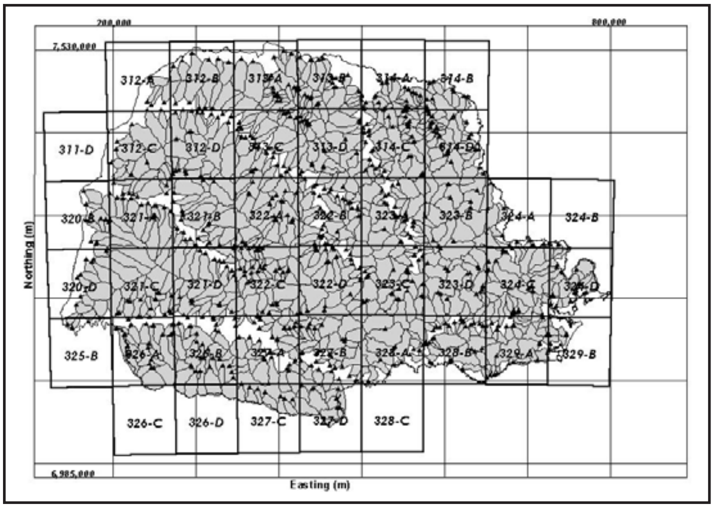

Figure 4 – The catchment basins, the water and sediment samples collection points and the GGRN sub-cells

Historical data sets

Some articles have been published dealing with multipurpose geochemical mapping using previous geochemical data sets. Licht and Tarvainen (1996a) presented maps showing Cu, Pb, Zn, Ni, Co, Fe, Mn, As and F distribution in the Paraná Shield and the base of the Paleozoic sedimentary sequence of the Paraná Basin. Those maps were based on the compilation of 24 old geochemical exploration surveys. The authors tried to correlate the excess (positive anomalies) and lack (negative anomalies) of the elements with several rock types and to circumscribe mineral exploration targets. Otherwise, a holistic approach was made, emphasizing the applications to environmental and human health and soil fertility. Licht *et al.* (1996b) used the fluorine data on stream sediments, pan concentrates and soil samples produced by historical geochemical exploration surveys performed in the Ribeira river valley. The fluorine contents that reach 1,200 ppm F in stream sediment and 8,700 ppm F in soil samples were used to outline some positive anomalies as risk areas for the occurrence of fluorosis in children, suggesting further detailed studies.

New data sets

The low density and multi-elemental geochemical surveys were designed to be multi-media, multi-elemental and based on low-density sampling. An area of 165,646 km^2 was sampled, corresponding to 83% of the Paraná State territory, with an average area of sampled basis of 222.87 km^2 (Licht, 2001a).

Materials and methods

Stream Water Geochemistry – 697 samples were obtained in a single collection in the middle of the river channel where water flows regularly and homogeneously (Fig. 4). The one-liter samples, without acidification, were packed in polyethylene flasks. In the laboratory, they were filtered through Millipore filters (90 μm opening) and analyzed by inductively coupled plasma emission spectrometry (ICP-ES) for selected cations and by ion chromatography for selected anions. The analysis was performed in the Mineral Analysis Laboratory (LAMIN) of the Brazil Geological Survey – CPRM (Licht, 2001a).

Stream Sediment Geochemistry – The 697 stream sediment samples were collected in river channels where sediments are submitted to a constant homogenization (Fig. 4). To produce a more representative sample, at least five sub-samples a few meters apart were collected at each site and combined into one ten-liter sample for chemical analysis. The samples were dried at room temperature, disaggregated in a porcelain mortar with a rubber pestle and sieved to minus- 80 mesh (177 μm) through a nylon screen (Licht, 2001a).

The Global Geochemical Reference Network (GGRN) is a cell grid with 1° 30' to a side, conceived as a global scale by International Geological Correlation Program Project 259 (International Geochemical Mapping) (Darnley *et al.*, 1995). However, these cells were considered too large for an adequate representation of Paraná's geochemical patterns. To improve the spatial resolution, each GGRN cell was subdivided into four 45' sub-cells (approximately 80 x 80 km) (Licht, 2001b). The 100 g samples, representative of the GGRN sub-cells, were obtained with equal portions of the samples from the basins contained in the sub-cell. The geochemical analysis for 71 elements on the 39 GGRN sub-cells was performed in the Institute for Geophysical and Geochemical Exploration (IGGE) located in the city of Langfang, Hebei, in the Peoples' Republic of China. The analytical standards used by the laboratory included GSD 9-12 sample series.

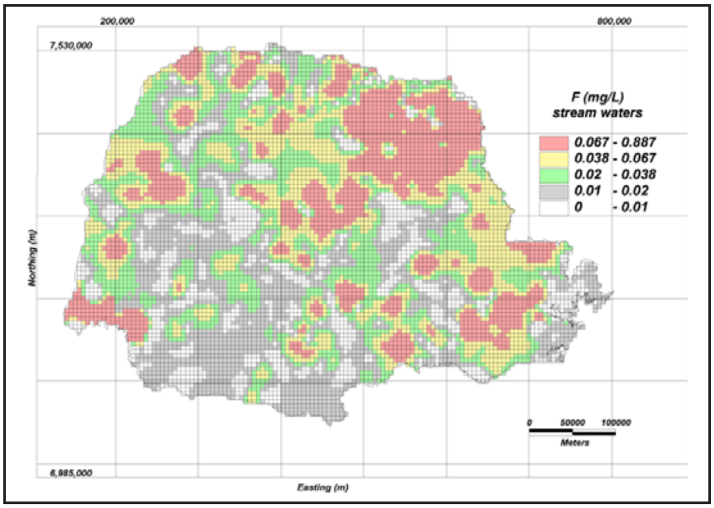

Figure 5 – Geochemical surface of F^- in stream water. Case I - dental fluorosis occurs mainly in the northern region (highest peaks)

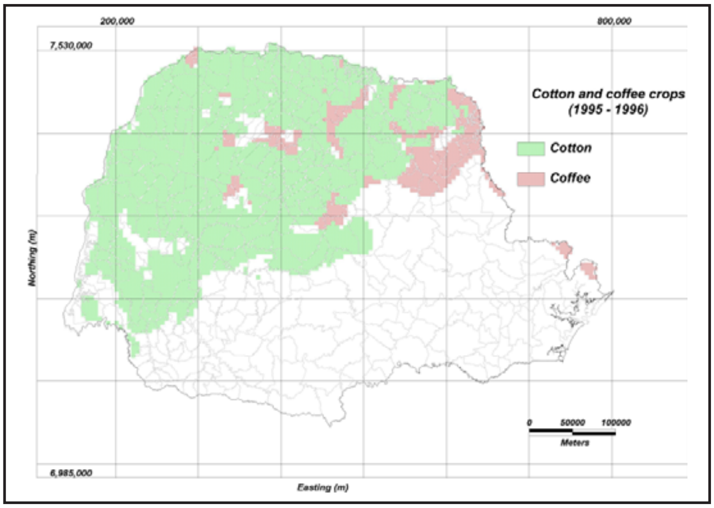

Figure 6 – Distribution of the cotton and coffee crops (harvest 1995-1996)

Case I - Fluorine anomalies and the occurrence of dental fluorosis

Fluorine is an essential element to mammals, since it promotes the hardening of the mineral matrix of bone and teeth, by displacing hydroxyl from the original hydroxyaphatite which is changed to fluoraphatite. This mineral transformation increases the resistance of enamel, cement and dentin, which becomes less soluble and less susceptible to bacteria. Fluorine ingested while teeth are forming produces a 40 to 60% reduction in the prevalence of dental caries (Licht *et al.,* 1996). In addition, fluorine plays an important bactericidal and bacteriostatic role, since it hinders the action of bacterial enzymes on sugars which leads to the production of acids which act on the enamel making it less soluble and disintegrable (Fejerskov *et al.,* 1994, *apud* Licht *et al*., 1996b). The upper limit of fluorine in drinking water is 1.2 mg/L F^- (this limit is also related to temperature: higher temperature means higher water ingestion, meaning higher daily doses of fluorine) (OMS, 1986, *apud* Licht *et al.,* 1996b). High doses of fluorine can cause fluorosis, a disease of bones and teeth which mainly occurs in children. Since fluorosis is non reversible, its effects will impact the health of the patients during their lifetime. The diagnosis of dental fluorosis is based on macroscopic alterations of tooth enamel, which ranges from thin white lines (very mild) to deep and brownish cavities (severe fluorosis).

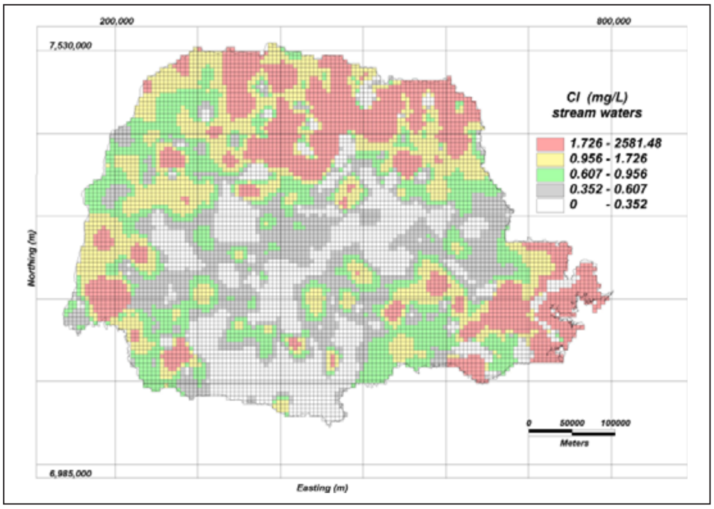

Figure 7 – Geochemical map of Cl^- in stream water. The chlorine anomalies covering the northern and western borders of Paraná are related to pesticide residues

Weathering acting on mineral deposits contributes to promote a local rise of the contents of major, minor and trace elements. These anomalies can be identified in soil, stream water and sediment samples. In the case of fluorspar (CaF_2) deposits, despite the relatively low solubility of this mineral, significant amounts of fluorine will be released to the environment. In Paraná, two important fluorine anomalies are known: one has been described in the area near the Volta Grande fluorspar mine, where soil samples showed up to 8,700 ppm F, 1,200 ppm F in stream sediment samples (Licht *et al.,* 1996b) and 0,15 ppm F^- in stream water (MINEROPAR, unpublished). A second type of F^- anomaly is a large hydrogeochemical positive anomaly of fluorine covering approximately 20,000 km^2 identified by the Regional Geochemical Survey in the region known as Norte Pioneiro (Fig. 5). In this region, the contents reach 0.98 mg/L F^- in stream water samples collected in catchment basins averaging 220 km^2. These contents are near the upper limit of 1.2 mg/L F^- at 18º C, (OPS, 1980), and 1.4 mg/L F^- (Brasil/CONAMA, 1986) established for drinking water. Anomaly boundaries and higher fluorine contents are perfectly aligned with ring shaped magnetic anomalies caused by deep geological sources (Ferreira *et al.*, 1996). Two epidemiologic studies with children, living in the village of São Joaquim do Pontal, Itambaracá, located in the northern border of the fluorine anomaly of the Norte Pioneiro region of Paraná, showed the existence of dental fluorosis in 61.48 % (Morita *et al.*, 1998) or 63.3% (Cardoso *et al.*, 2001) of the examined population (Table 1).

Until endemic fluorosis was identified, the main source of drinking water in São Joaquim do Pontal was a tube well containing up to 1.8 mg/L F^-. Following these public health findings, two new tube wells were dug and the water from these three sources was blended, reducing the fluorine content in the drinking water.

The geochemical map, produced by demonstrating the geographical distribution of fluorine

Table 1 – Prevalence and severity of dental fluorosis in children living in the village of São Joaquim do Pontal, Itambaracá, State of Paraná, Brazil

Severity											
Morita *et al.* (1997)						Cardoso *et al.* (2001)					
Normal	Doubtful	Very mild	Mild	Moderate		Normal	Doubtful	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%

contents in stream waters, proved to be useful in indicating health risk areas also related to ground water. Many other risk areas are known, with the occurrence of dental fluorosis recognized but not yet measured in the municipalities of Curitiba, Castro, Marechal Cândido Rondon, Foz do Iguaçu, Nova Tebas, Bandeirantes, Figueira and Curiúva (Morita, M.C., personal. com. 1999). All of the occurrences of endemic fluorosis are associated with positive anomalies in the fluorine geochemical map.

Measurements of fluorine content in stream water samples and the preparation of hydro-geochemical maps are important tools to support modern epidemiological investigations, since regions with high contents, or positive anomalies, are easily identifiable, capable of causing endemic dental fluorosis, osteoporosis and/or skeletal malformations. On the other hand, regions with lower fluorine contents, or negative anomalies, could suggest risk areas for a high incidence of dental cavities and/or bone fractures.

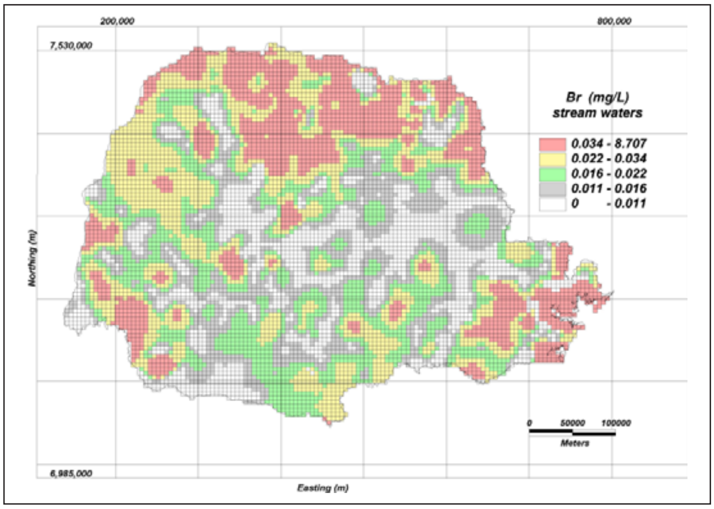

Figure 8 – Geochemical map of Br^- in stream water. The bromine anomalies covering the northern and western borders of the State of Paraná are related to pesticide residues

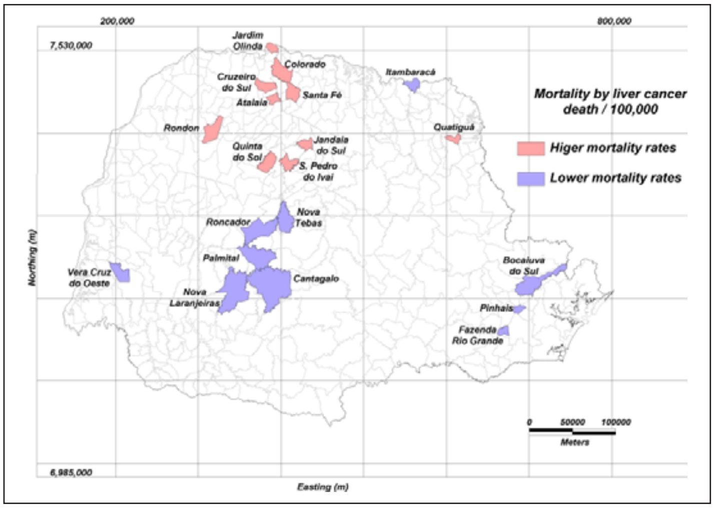

Figure 9 – Municipalities with higher and lower liver cancer mortality rates (average in the period between 1980 and 1997)

Case II – Chloride and bromide in water as identifiers of liver cancer risk areas

The liver plays an important role in the neutralization and elimination of toxic substances entering the organism in the form of food and medicines. Depending on the type, source, dose and time of exposure, the liver may be permanently affected by a wide range of environmental, natural, agricultural or medical toxins. One of the most studied exposures are those liver diseases developed from exposure to environmental organic contaminants such as the widespread use of pesticides.

On this regard, the carcinogenic role of pesticides, mainly of the organ-chlorinated group, has been pointed out by Marzochi *et al. (*1976). Of all kinds of internal cancer, Primary Liver Carcinoma is the most related to environmental causes (Davies, 1973, *apud* Marzochi *et al.,* 1976). Focusing the northern region of Paraná, Marzochi *et al. (*1976), emphasized that the active compounds, pesticides, used in agriculture, mostly organ-chlorinated, display an important role in triggering liver carcinogenesis. Chlorinated and brominated compounds are highly resistant to the micro-flora metabolism and are therefore more highly environmentally persistent, and acquiring priority in medical investigations. In 1996 in Paraná, approximately 400 active principles of pesticides were identified in up to 700 trademarks, of which only 20 were legally monitored. Taking into

Table 2 –Twenty municipalities of the State of Paraná, divided in two categories, based on the liver cancer death rate/100,000 inhabitants, in the period between 1980 and 1997

Municipalities with lower rates	Death/ 100,000		Municipalities with higher rates	Death/ 100,000
Roncador	0.6277		São Pedro do Ivaí	9.2924
Pinhais	0.5922		Quatiguá	8.9031
Itambaracá	0.5915		Quinta do Sol	8.2345
Bocaiúva do Sul	0.5492		Jandaia do Sul	8.2052
Vera Cruz do Oeste	0.4756		Jardim Olinda	7.9856
Nova Laranjeiras	0.4715		Atalaia	7.8335
Palmital	0.4637		Cruzeiro do Sul	7.5300
Cantagalo	0.4420		Santa Fé	7.5028
Nova Tebas	0.3261		Colorado	7.5020
Fazenda Rio Grande	0.1521		Rondon	7.4733
Average rate	**0.4715**		**Average rate**	**7.53**

Source of data: Paraná Department of Health

consideration only six regions of Paraná, the use of pesticides in 1996 reached 9,500 tons (Andreoli and Ferreira, 1998). Surface and ground water sources within these agriculturally active regions, received pesticide residue loads applied not only to the present crop but also in the past. In 1984, ten pesticides (BHC, DDT, Lindane, Chlordane, Aldrin, DDE, Endrin, Dieldrin, TDE and Heptachlor) were identified in water, suspended material and bottom sediments in the water treatment facilities of 16 municipalities, distributed across Paraná. The results showed that pesticide residues accumulated in the sludge (Medeiros *et al.* 1984). The population of urban areas had low exposure to these agents because of the significant reduction of pesticide contents obtained by the water treatment facilities, but the benefits of water purification are not available to the rural population.

In 1997, the Brazilian liver carcinoma death rate (IDC-9, C-22.0) showed a regular increase from the *North* (2.137 deaths/100,000 inhabitants), *Northeast* (2.486), *Middle-west* (3.225), *Southeast* (3.642) reaching its highest value in the *South* (3.642) (Inca, 2000). This rise shows a direct relationship with more intense and widely developed agriculture from north to south, even taking into consideration the difficulties of disease notification in the North and Northeast regions. In Paraná, the death rate in ten municipalities with the highest ratios, ranging from 7.47/100,000 in Rondon to 9.29/100,000 in São Pedro do Ivaí. The average death rate for these ten municipalities, 7.53, is 2.5 times higher than the death rate for the *South* region, in which Paraná is included. Some crops such as cotton and coffee which use pesticides composed of chlorine and bromine have been planted in northern Paraná since 1930 (Table 2).

The degradation of this environment by agrochemicals is the chief cause for the release of chlorine and bromine into the water of the catchment basins of this region. In Paraná, the ten municipalities with the highest liver cancer death rates are located in the main region of cotton and coffee production (Fig. 6), which shows a geographic correlation with relatively high Cl^- (Fig. 7) and Br^- (Fig. 8) values in stream waters. On the other hand, the ten municipalities with the lowest liver cancer death rates (average = 0.4715/100,000) are located outside this area (Fig. 9). It is worth mentioning that the study also considered the regions with potato and tobacco crops in the southern portion of Paraná, but no relationship was shown. The geochemical maps showing the geographic distribution of Cl^- and Br^- proved useful as geochemical indexes not only to define liver cancer risk areas but also serving as a reference to more detailed environmental and public health investigations demonstrating the characterization of environmental exposures to pesticide residues.

Other cases to be investigated

Many other geochemical anomalies, with high contents of ions or elements, were identified by the data obtained from the geochemical surveys of Paraná. Further investigations are required to establish the significance, of some areas with high contents of Ba^+ (Fig. 10), K^+, Ca^{2+}, Al^{3+} in stream water and Hg in stream sediments (Fig. 11). These areas must be investigated by toxicologists, epidemiologists, and geoscientists in order to reveal how these tools may assist in the development of preventive public health measures and the identification of disease risk areas.

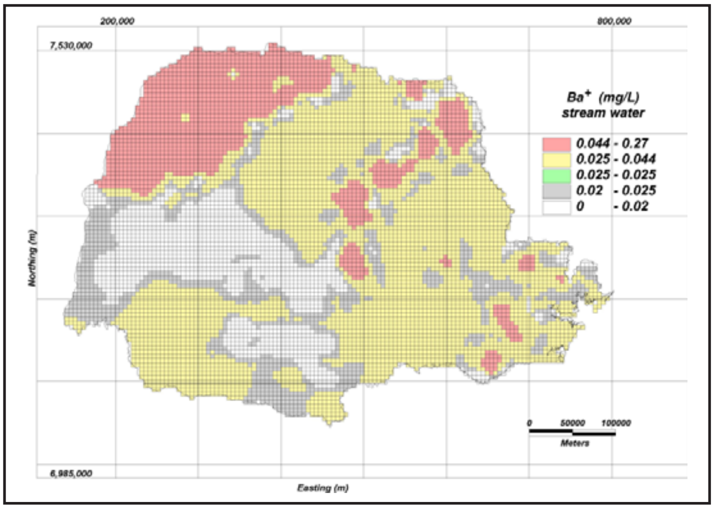

Figure 10 – Geochemical map of Ba^+ in stream water. The northwestern anomalous region is related to Cretaceous sandstones deposited under arid conditions

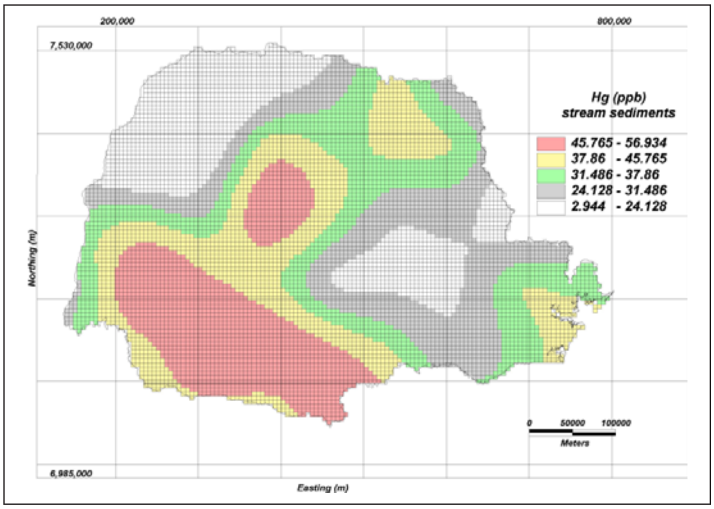

Figure 11 – Geochemical map of Hg in stream sediments. The southern SE-NW anomalous region has been interpreted as the effect of fault zones carrying Hg to the surface from deep carbon rich sedimentary rocks

Acknowledgements

Many researchers must be acknowledged for their helpful discussions, comments and criticisms: Maria Celeste Morita (Dept. Odontology, University of Londrina - UEL), Luciana Cardoso (Dept. Odontology, UEL), José Paulo P. Pinese (Dept. Earth Sciences, UEL), João Carlos Alves (Dept. Chemistry,UEL), João Bosco Strozzi (Dept. Medicine, Catholic University of Paraná - PUC-PR), Luiz Antônio Negrão (Cancer Hospital, Federal University of Paraná - UFPR), Reinaldo Skalisz (Paraná Department of Agriculture - SEAB). Edir E. Arioli (MINEROPAR), Luiz Sobral (Mineral Technology Center - CETEM) and Jose A. Centeno (Armed Forces Institute opf Pathology - AFIP) are also acknowledged for reviewing the manuscript.

References

Andreoli C.V., Ferreira A.C. 1998. Levantamento quantitativo de agrotóxicos como base para a definição de indicadores de monitoramento de impacto ambiental na água. Curitiba, *Sanare*, **10**(10):30-38.

Cardoso L.deM., Morita M.C., Alves J.C., Licht O.A.B. 2001. Anomalia hidrogeoquímica e ocorrência de fluorose dentária em Itambaracá, PR. *In:* SBGq, VIII Congresso Brasileiro de Geoquímica e I Simpósio Geoquímica dos Países do Mercosul. Curitiba. *Anais...*, CD-ROM.

Centeno J.A. 2003. Medical geology: an interdisciplinary and emerging discipline in support of public health. Lecture. In: *2003 International Workshop : Medical Geology* : Metals, Health and The Environment. University of Campinas (UNICAMP). Campinas, October.

Brasil, Ministério do Meio Ambiente e da Amazônia Legal, CONAMA - Conselho Nacional do Meio Ambiente. 1986. Resolução n° 20 de 18 de junho de 1986. s.e. *Diário Oficial da República Federativa do Brasil.* Brasília, 30/07/1986.

Darnley A.G., Björklund A., Bølviken B., Gustavsson N., Koval P.V., Plant J.A., Steenfelt A., Tauchid M., Xuejing X. 1995. *A Global Geochemical Database for Environmental and Resource Management* : Recommendations for International Geochemical Mapping : Final Report of the IGCP Project 259. Paris: Unesco Publ.

Ferreira F.J.F., Forlin M., Donatti L.M., Rostirolla S.P., Soares P.C. 1996. Assinatura magnética de estruturas dômicas da região de fartura. *In:* SBG, Congresso Brasileiro de Geologia, 39. *Anais...* Salvador : SBG. v.2:341-343.

Fortescue J.A.C. 1992. Landscape geochemistry: retrospect and prospect. *Appl. Geochem.,* **1**(7):1-53.

Garret R.G., Geddes A.J.S. 1991. Studies of regional drainage geochemistry in Jamaica. *Trans. Inst. Min. Metall.* (Appl. Earth Sci., Sec. B : 100).

Hawkes H.E. 1985. *Exploration geochemistry bibliography to January 1981*. Rexdale : Association of Exploration Geochemists.

ITCF - Instituto de Terras, Cartografia e Florestas. 1987. *Atlas do Estado do Paraná*. Curitiba: ITCF.

Inca - Instituto Nacional do Câncer. 2000. Available: *http://www.inca.org.br*. Accessed: 20/Oct/2000.

Låg, J. 1990. General survey of geomedicine. *In:* J. Låg. *Geomedicine*. Boca Raton : CRC Press, p. 1-23.

Licht O.A.B., Tarvainen T. 1996a. Multipurpose geochemical maps produced by integration of geochemical exploration data sets in the Paraná Shield, Brazil. *J. Geochem. Explor.*, **56**(3):167-182.

Licht O.A.B., Morita M.C., Tarvainen T. 1996b. A utilização de dados de prospecção geoquímica de fluorita no primeiro planalto paranense, na identificação de áreas de interesse para a saúde pública. Uma abordagem preliminar. *Geochimica Brasiliensis*, **10**(1):57-69.

Licht O.A.B. 2001a. *Atlas geoquímico do Estado do Paraná*. Curitiba: MINEROPAR.

Licht, O.A.B., 2001b. *A geoquímica multi-elementar na gestão ambiental. Identificação e caracterização de províncias geoquímicas naturais, alterações antrópicas da paisagem, áreas favoráveis à prospecção mineral e regiões de risco para a saúde no Estado do Paraná, Brasil*. PhD thesis. Curitiba: Departamento de Geologia, Universidade Federal do Paraná (UFPR).

Maack R. 1968. *Geografia física do Estado do Paraná*. Curitiba: BADEP/IBPT.

Marzochi M.C.A., Coelho R.B., Soares D.A., Zeitune J.M.R., Muarrek F.J., Cecchini R., Passos E.M. 1976. Carcinogênese hepática no norte do Paraná e uso indiscriminado de defensivos agrícolas. São Paulo, *Ciência e Cultura*, **28**(8):893-901.

Medeiros M.L.M.B., Vianna P.C.G., Fowler R.B., Zappia V.R.S. 1984. *Poluição das águas internas do Paraná por agrotóxicos*. Internal report. Curitiba: SUREHMA.

Mills C.F. 1993. Geochemical aspects of the aethiology of trace element – related diseases. A review of pathways of trace elements into the food chain. *In:* Environmental Geochemistry and Health in Developing Countries, AGID/SEGH British Geological Survey Meeting. London, October. *Abstracts...* London: Geological Society. p. 30-31.

Morita M.C., Carrilho Neto A., Licht O.A.B. 1998. Use of geochemistry data in the identification of endemic fluorosis areas. *In :* 1st World Congress of Health in Urban Environment. Madrid, July. *Abstracts...* Madrid : IOA.

OPS – Organización Panamericana de Salud. 1980. *Criterios de salud ambiental 6* : Principios y métodos para evaluar la toxicidad de las sustancias químicas. Washington : OPS/OMS. (Publicación Científica, n. 402, Parte 1).

Selinus O. 2003. Medical geology: an emerging discipline in environmental and human health. Lecture #1. In: *2003 International Workshop : Medical Geology :* Metals, Health and The Environment. University of Campinas (UNICAMP). Campinas, October.

Vinogradov A.P. 1959. *The geochemistry of rare and dispersed chemical elements in soils*. New York : Consultants Bureau, 2nd ed.

Submitted in July, 2005
Accepted in October, 2005