

**AVERAGE REFERENCE VALUES OF GEOCHEMICAL AND
GEOPHYSICAL VARIABLES IN STREAM SEDIMENTS AND SOILS,
STATE OF PARANÁ, BRAZIL**

*VALORES MÉDIOS DE REFERÊNCIA DE VARIÁVEIS GEOQUÍMICAS E
GEOFÍSICAS EM SEDIMENTOS DE DRENAGEM E SOLOS, ESTADO DO
PARANÁ, BRASIL*

Otávio Augusto Boni LICHT¹
Xie XUEJING²
Zhang QIN²
Mario MIYAZAWA³
Francisco José Fonseca FERREIRA⁴
Rafael André Belotto PLAWIAK⁵

RESUMO

A coleta de 696 amostras de sedimentos de drenagem e 307 de solo – horizonte B, segundo os padrões estabelecidos pelos Projetos IGCP-259 e IGCP-360 (UNESCO e IUGS), e a determinação de variáveis geoquímicas, geofísicas e de fertilidade de solos nas amostras compostas representando as células Global Geochemical Reference Network (GGRN) permitiram a constituição de uma robusta base de dados cobrindo os 200.000 km² do Estado do Paraná, na região Sul do Brasil. As 39 amostras representativas de células GGRN de sedimentos ativos de drenagem foram analisadas para Ag, Al₂O₃, As, Au, B, Ba, Be, Bi, Br, CaO, Cd, Ce, Cl, Co, C_{orgânico}, Cr, Cs, C_{total}, Cu, Dy, Er, Eu, F, Fe₂O₃, Ga, Gd, Ge, Hg, Ho, I, K₂O, La, Li, Lu, MgO, Mn, Mo, N, Na₂O, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, S, Sb, Sc, Se, SiO₂, Sm, Sn, Sr, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn. As 43 amostras representativas de células GGRN de solos – horizonte B foram analisadas para Ag, Al₂O₃,

1 Minerais do Paraná S.A. (Mineropar) State of Paraná Geological Survey. P.O. Box 15.026. CEP 80531-970 Curitiba, State of Paraná, Brazil. Email: otavio@pr.gov.br

2 Institute of Geophysical and Geochemical Exploration - IGGE Langfang, Province of Hebei, P. R. China.

3 Soils and Vegetal Tissues Laboratory Agronomic Institute of Paraná (Iapar). Londrina, State of Paraná, Brazil.

4 Applied Geophysical Researches Laboratory (LPGA) Federal University of Paraná (UFPR). Curitiba, State of Paraná, Brazil.

5 Geosciences Post Graduation Course University of Campinas (Unicamp). Campinas, State of São Paulo, Brazil.

As, Au, B, Ba, Be, Bi, Br, CaO, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Fe₂O₃, Ga, Gd, Ge, Hf, Hg, Ho, I, In, K₂O, La, Li, Lu, MgO, Mn, Mo, N, Na₂O, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, S, Sb, Sc, Se, SiO₂, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr. Nas 307 amostras originais de solo – horizonte B foram determinados parâmetros de fertilidade de solos Al, Al_{trocável}, Ca_{disponível}, Mg_{disponível}, B_{trocável}, C, Cu_{trocável}, Zn_{trocável}, Fe_{trocável}, H⁺ + Al³⁺, Mn_{trocável}, P_{disponível}, K_{disponível}, pH, S_{trocável}, Zn_{trocável}, V, S, T, bem como a suscetibilidade magnética e contagem total, eU, eTh e K por gamaespectrometria. Os valores médios dessas variáveis no território paranaense, assim como sua comparação com as médias globais para a superfície terrestre, permitiram estabelecer valores de referência que poderão ser utilizados em pesquisas multipropósito de geologia, exploração mineral, delimitação de áreas de risco à saúde humana, fauna e flora, planejamento agrícola e monitoramento ambiental. O conteúdo dessa base de dados, que descreve algumas características ambientais do território paranaense, representa uma primeira abordagem em escala regional que servirá como referência tanto para estudos localizados e de maior detalhe no estado do Paraná quanto para a investigação do território de outros estados brasileiros ou mesmo dos países limítrofes.

Palavras-chave: valores de referência; amostragem regional de sedimentos de drenagem; amostragem regional de solos; análise multielementar; estado do Paraná; Brasil.

ABSTRACT

The collection of 696 samples of stream sediments and 307 of soil - horizon B, according to the standards and recommendations of the Project IGCP-259 and IGCP-360 (UNESCO and IUGS) and the determination of geochemical, geophysical and soils fertility parameters, allowed the constitution of a robust data base covering the 200,000 km² of the State of Paraná, southern Brazil. The 39 composite samples representing the GGRN (*Global Geochemical Reference Network*) from original stream sediments samples were analysed for Ag, Al₂O₃, As, Au, B, Ba, Be, Bi, Br, CaO, Cd, Ce, Cl, Co, C_{organic}, Cr, Cs, C_{total}, Cu, Dy, Er, Eu, F, Fe₂O₃, Ga, Gd, Ge, Hg, Ho, I, K₂O, La, Li, Lu., MgO, Mn, Mo, N, Na₂O, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, S, Sb, Sc, Se, SiO₂, Sm, Sn, Sr, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn. The 43 composite samples representing the GGRN (*Global Geochemical Reference Network*) from original soil - B horizon samples were analysed for Ag, Al₂O₃, As, Au, B, Ba, Be, Bi, Br, CaO, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Fe₂O₃, Ga, Gd, Ge, Hf, Hg, Ho, I, In, K₂O, La, Li, Lu, MgO, Mn, Mo, N, Na₂O, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, S, Sb, Sc, Se, SiO₂, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr. In the 307 original soil samples – B horizon, were determined the soil fertility variables Al, Al_{exchangeable}, Ca_{available}, Mg_{available}, B_{extractable}, C, Cu_{extractable}, Zn_{extractable}, Fe_{extractable}, H⁺ + Al³⁺, Mn_{extractable}, P_{available}, K_{available}, pH, S_{extractable}, Zn_{extractable}, V, S, T, as well as the magnetic susceptibility and total counts, eU, eTh and K by gamma-spectrometry. The average values for these variables in the State of Paraná's territory, as well as its comparison with the global averages - for the Earth's rocks and soils, allowed to establish reference values that can be used in multipurpose researches like geology, mineral exploration, delimitation of health risk areas to humans, fauna and flora, agricultural planning, environmental monitoring. The content of this data base, that describes some environmental characteristics of the Paraná's territory, represents a first approach in a regional basis that will serve so much as reference for more detailed studies focusing limited areas in the state, as for the investigation of the territory of other Brazilian states or even bordering countries.

Key-words: Reference values; stream sediment regional sampling; soil regional sampling; multielemental analysis; State of Paraná; Brazil.

INTRODUCTION

When exploring the superficial environment, geochemical techniques are useful and applicable to many purposes since are based on multielemental analysis of samples of stream water and sediments, soils, rocks, plant tissues as well as gaseous leaks either from natural or anthropic sources. One of the most useful applications for the multielemental databases that cover wide areas is the establishment of reference levels which

means the average contents of each variable in the sampled media, determined by the application of a specific analytical technique, in the studied region or environment. These surveys can be planned to cover areas ranging from a local to a global scale.

The content of the chemical elements in every material is controlled by a number of factors like its mineralogical and chemical composition, climate, vegetation, hydrography and topography. These factors acting together will modify the mobilization, migration,

dispersion and concentration of the chemical elements that constitute any material either from natural or man made source. The establishment of reference levels for the elements or any other physical and chemical variable is useful for studies dealing with geology, mineral prospecting, agronomy, environmental monitoring and the delimitation of risk areas for human health.

The Low Density Geochemical Survey of the State of Paraná was planned to cover its 200,000 km² territory, collecting widely spaced stream sediments and soils followed by the determination of a wide spectrum of physical and chemical variables. The project followed the sampling and analytical protocols for the *Global Geochemical Mapping*, established by the Projects IGCP 259 and 360, sponsored by Unesco (*United Nations Educational, Scientific and Cultural Organization*), IUGS (*International Union of Geological Sciences*), IAGC (*International Association of Geochemistry and Cosmochemistry*), AEG (*Association of Exploration Geochemists*), IAEA (*International Atomic Energy Agency*) and *The Royal Society* (Darnley et al. 1995).

Many countries all over the world are accomplishing geochemical mapping projects following the above mentioned protocols, e.g., Finland (Koljonen et al. 1992), Greenland (Steenfelt 1985), Croatia (Miko et al. 2001), Portugal (Ferreira 2000), P.R. of China (Xie & Tiangxiang 1993) and Germany (Birke et al. 1997, Birke 2003).

The Forum of European Geological Surveys – FOREGS is in charge to integrate and standardize the geochemical mapping projects covering European countries and/or regions. To this date in Brazil, the efforts to cover the country with a geochemical mapping project are sparse and weak, despite the interest of earth, environmental and health scientists in the results of such a project (Plant et al. 2004; Salminen et al. 2004; Tarvainen et al. 2004).

The State of Paraná Geological Survey (Mineropar) is in charge of the project planning and its general coordination, as well as the preparation and storage of the samples; the sampling was performed by Mineropar and Emater-PR (State of Paraná Company for Rural Assessment and Development) field teams. The determination of the chemical and physical variables was performed by researchers of Mineropar, Institute of Geophysical and Geochemical Exploration (IGGE) China, Soils and Vegetal Tissues Laboratory of the Agronomical Institute of the State of Paraná (Iapar) and Applied Geophysical Researches Laboratory of the Federal University of Paraná (UFPR).

In the present paper, data and results are presented without any interpretation of causal relationships between the contents and abundance of the variables and natural

or anthropic factors, whereas the authors believe that the wealth of information contained in this robust database, demands that the interpretations on the abundance and geographic distribution of the variables must be done by multi- and interdisciplinary teams. The results of this crossed interpretation will contribute to the knowledge of the natural environment and its anthropic alterations and impacts, as well as the influences of the environmental chemistry on the human, crops and cattle health in the State of Paraná.

THE STATE OF PARANÁ

The State of Paraná, with a surface area of 199,575 km² (ITCF 1987), is located in Southern Brazil (figure 1). It is bordered by the State of São Paulo to the north; the Atlantic Ocean to the east; the State of Santa Catarina to the south; the Republic of Argentina to the southwest; the Republic of Paraguay to the west and the State of Mato Grosso do Sul to the northwest (figure 2).

The predominant climate is sub-tropical with temperatures ranging from 0 °C to 36 °C; the rainiest area, with an average of 4,000 mm/year, is located in the eastern slope of Serra do Mar with precipitation decreasing to the north with averages between 1,200 and 1,300 mm/year. These characteristics allowed the identification of the following Köppen climatic types: Cfa, Cfb, Af (ITCF 1987, Corrêa et al. 1994).

The State of Paraná contains a dense and perennial hydrographic network, and the Serra do Mar is the main divide, separating the basins of the Coastal Plain from those of the other geographic divisions. The geomorphic structure with westward dipping forces the rivers to flow toward the Paraná River valley, except for the Ribeira and Coastal Plain basins that flow to the Guaratuba and Paranaguá bays or directly to the Atlantic Ocean (figure 3 and figure 4).

From east to west, the State of Paraná is characterized by four successive plateaus, namely: Coastal Plain, First, Second and Third Plateaus (Maack 1968) (figure 4).

The Coastal Plain is mainly composed by holocenic mangroves, terraces and sand strings along coast lines and beaches and the soils are mainly podzolic and hydromorphic. The transition from the Coastal Plain to the First Plateau is made by Serra do Mar, an abrupt scarp with altitudes reaching 1,922 meters above sea level, composed of Archean (Serra Negra Complex) and Proterozoic rocks (Pré-Setuva Complex), mainly granulites, norites, migmatites, gneiss, magnetite quartzites, dolomitic marbles, magnesian schists, amphibolites, metabasites, metapyroxenites, granites and



Figure 1 - Location map of the State of Paraná.

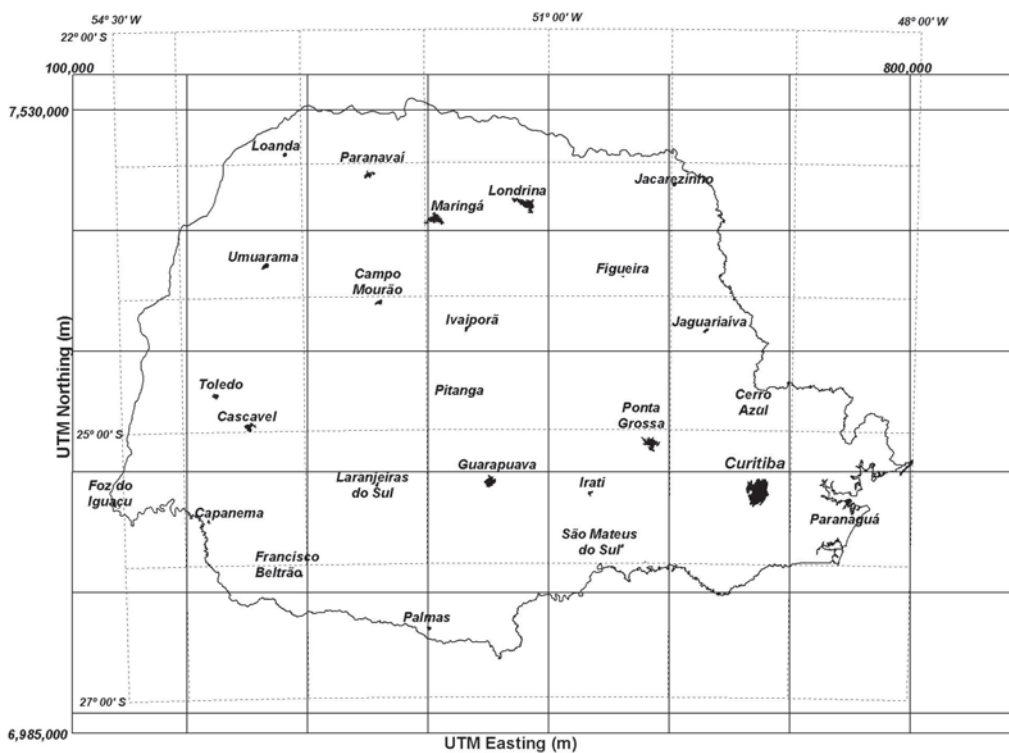


Figure 2 - Limits of the State of Paraná, geographic grid (dotted lines), UTM grid (SAD69, zone 22), and some selected cities (Licht 2001).

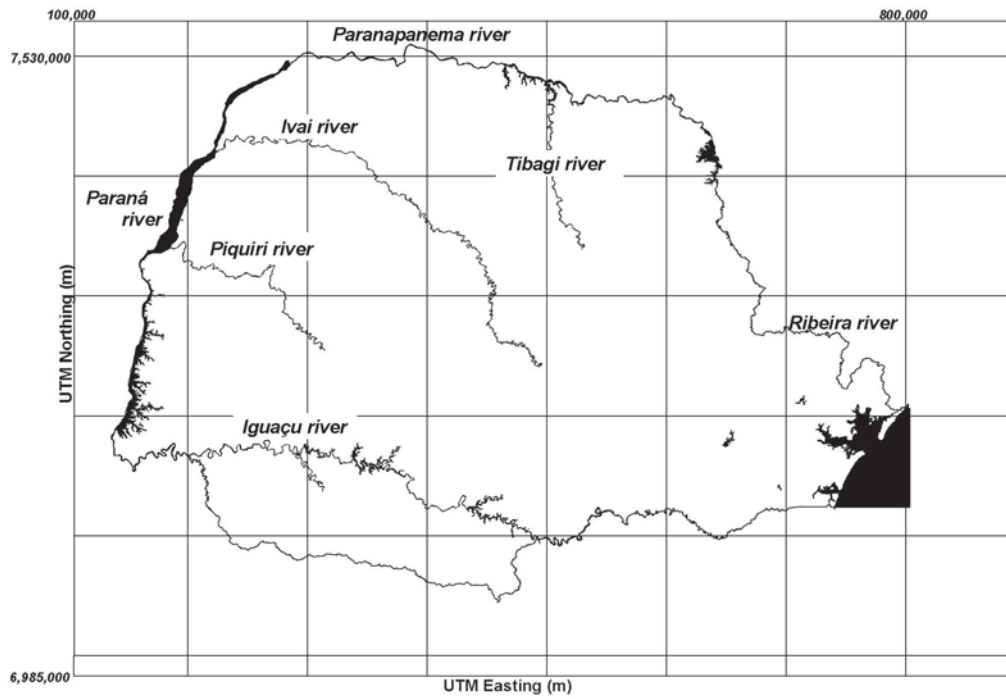


Figure 3 - The main rivers of the state of Paraná.

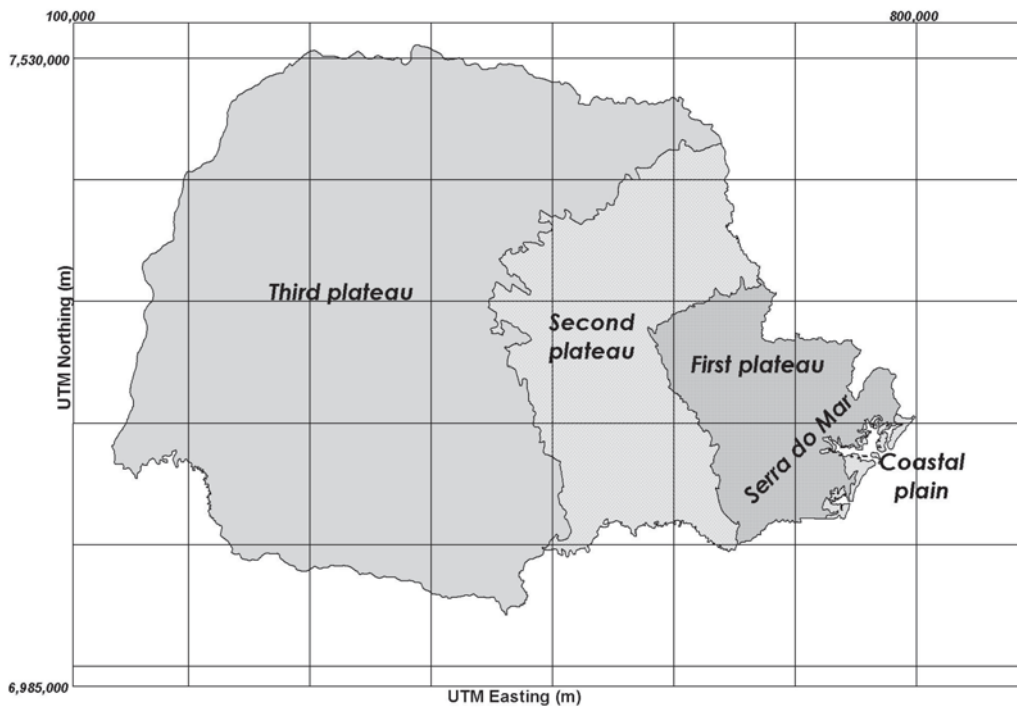


Figure 4 - The four geologic-geomorphological compartments of the state of Paraná and the Serra do Mar (after Maack 1968).

anatectic granodiorites, and the soils of this transition zone are dominantly cambic, litholic and stony. The First Plateau is represented by: (1) Lower Proterozoic (Setuva Group) - migmatites and gneiss, pelitic schists, calc-schists and marbles, quartzites and metabasites; (2) Upper Proterozoic (Açungui Group) - metaconglomerates, metasandstones, quartzites, phyllites, metamorphosed limestones and dolomites, metabasites and amphibolites and metamorphosed basic lavas and tuffs; (3) Brazilian cycle – huge granitic, alkali-granitoid, granodioritic, monzonitic and alaskitic anatectic bodies; (4) Palaeozoic (Camarinha Formation) - siltstones, sandstones and conglomerates; (5) Palaeozoic (Guaratubinha Formation and Castro Group) - siltstones, sandstones and conglomerates, andesites, rhyolite domes and flows, ignimbrites, pyroclastites and cineritic tuffs, breccias and volcanic agglomerates. The Curitiba Basin is filled with Tertiary sediments associated with the Guabirota Formation and consisting of gravels, arkoses, silts and clays (Licht 2001). The Second Plateau is underlain by a 600 meter thick sequence of Paraná Basin Palaeozoic sediments dipping gently to the west. The basal section of the Paraná Group (Devonian) is composed of conglomerates, sandstones, siltstones and shales. The Paraná Group is overlain by the Itararé Group, which is composed of thick horizons of sandstones, siltites, shales, rythmites and diamictites, with rare coal seams. It is overlain by the Guatá Group composed of sandstones, siltstones, shales, with carbonate zones, organic-rich shales and coal seams. It also is overlain by the Passa Dois Group, composed of sandstones, siltstones, shales, claystones, limestones, calcareous sandstones and oil bearing shales. The soils feature a thin profile and have low fertility with prevalence of litholic, cambic, podzols and lateritic soils developed to the expenses of sedimentary rocks (Licht 2001). The Third Plateau geology include the São Bento Group of the Paraná Basin. This unit contains conglomeratic sandstones, sandstones and siltstones interbedded (Botucatu Fm) with thick flows, sills and dykes of basic (gabbro-norite, gabbro, dolerite and basalt), intermediate (andesitic basalt and andesite) and acidic (dacite, rhyodacite and rhyolite) composition (Serra Geral Fm). In the northwest, the Caiuá Formation (Bauru Group), consisting of Cretaceous sandstones, siltstones and shales is found. The very fertile soils of the region are derived from basic igneous rocks, and comprise deep-red lateritic soils, structured terra-rossa and red/yellow podzols (Licht 2001).

By the end of the XIXth century, the State of Paraná had lush vegetation consisting of pines, Brazilian nuts, perobas (*Aspidosperma macrocarpon*), cedars, cinnamons and ipês (*Tabebuia chrysantha*) hosting a rich

fauna, composed of apes, tapirs, caitetus, capybaras, deer, onças (*Panthera uncia*), pacas (*Agouti paca*), parrots and macaws (ITCF 1987). Today, only 5% of the original forest covering remains.

The State of Paraná economy is based on agriculture due to the natural fertility of its soils. Almost all the territory is farmable, except for the mountainous areas. The State of Paraná is the largest grain producer in Brazil. It is responsible for 10% of the national milk production, and it is also the third largest producer of chicken meat, swine and eggs in Brazil. The Paraná economy is strongly concentrated on agro-industry (soy bran and oil, alcohol and fertilizers) with food, machinery, wood, paper and textile industries also being important. The mineral industry stands out for the production of talc (first national producer), dimension marble (third national producer) crushed rocks (fourth national producer), dimension granite (fifth Brazilian producer), red ceramic, limestone, bituminous shale, dolomite, mineral water and sand and gravel for building and construction.

MATERIALS AND METHODS

Sampling

The first phase of the Multielementar Geochemical Survey of the State of Paraná, known as Low Density Geochemical Survey was based on stream sediments samples collected from 696 catchment basins with an average area of 222.87 km² (figure 5). To produce a more representative sample of the active stream sediments, at least five sub-samples, few meters apart, were hand collected in each site and composited into one ten-liter sample for chemical analysis.

The second phase, B horizon - Soils Geochemical Survey, was based on the collection of samples from the B horizon of the soil by excavating a channel on road cuts or by digging a pit. The sampling sites were distributed in a similar way to the soil geochemical survey of the USA (Shacklette & Boerngen 1984 apud Gustavsson et al. 2001), since the 307 sampling stations were located in the center of each 1:50,000 maps, following a regular and wide spaced grid of 15' x 15' (approximately 25 km x 25 km in the latitudinal position of the State of Paraná). The sampling stations were planned to be (a) as closest as possible to the centre of the 1:50,000 maps, (b) in the vicinity of a road to increase the speed of sampling, and (c) on top of a hill to avoid sampling of transported soils (figure 6).

The project adopted the Global Geochemical Reference Network (GGRN) established by the International Geological Correlation Program Project IGCP

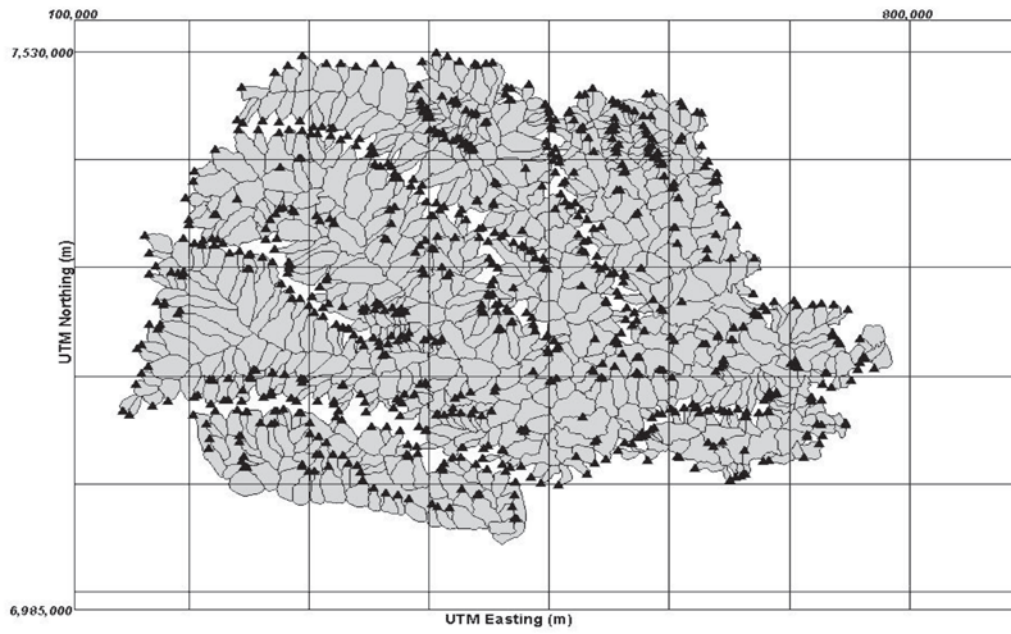


Figure 5 - The catchment basins and the respective stream sediments sampling sites (Licht et al. 1997 apud Licht 2001).

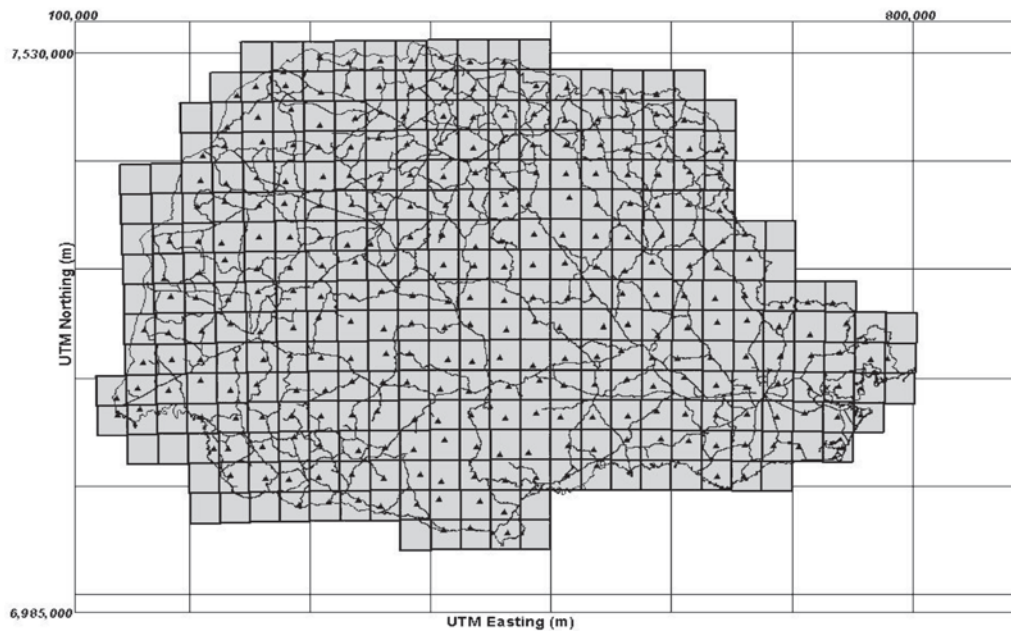


Figure 6 - Soil – B horizon sampling sites, limits of the 1:50,000 maps and the road network (Licht & Plawiak 2005).

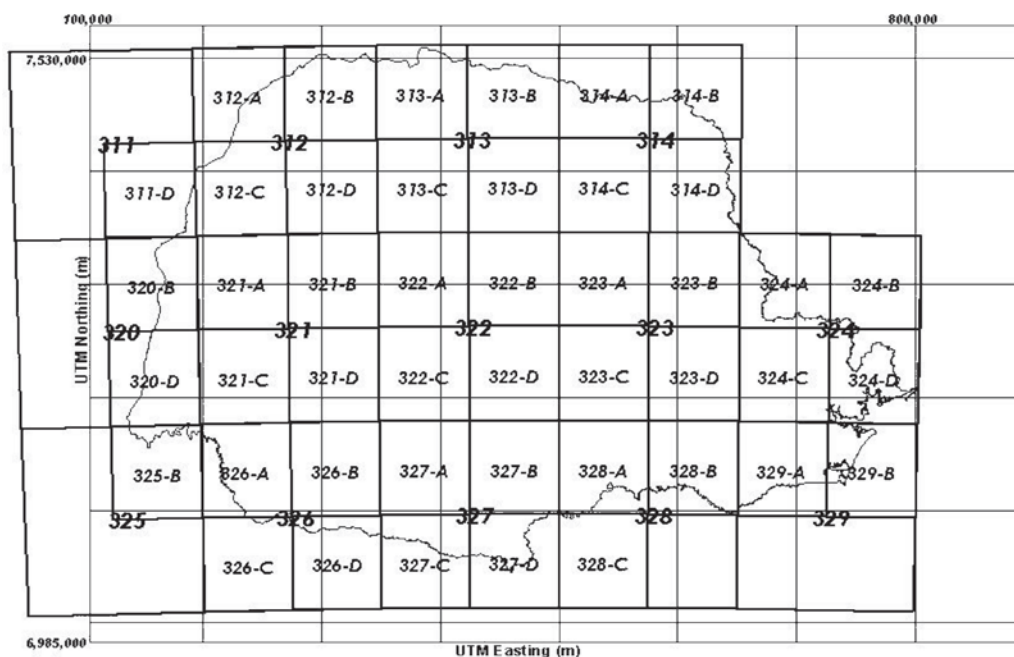


Figure 7 - The Global Reference Network - GGRN (e.g. 322) and the sub-cells for the State of Paraná (e.g. 322-A, 322-B, 322-C and 322-C) (Licht et al. 1996 apud Licht 2001).

- 259 (*International Geochemical Mapping*) (Darnley et al. 1995), however, the GGRN cells of 1° 30' side (approximately 160 km in the State of Paraná latitude) conceived for a global scale, were *a priori* considered too large to represent adequately the geochemical patterns of the State of Paraná. To improve the spatial resolution, each GGRN cell was subdivided into four 45' sided sub-cells (approximately 80 km), totaling 39 sub-cells in the case of stream sediments and 43 sub-cells for soil sampling (Licht 2001) (figure 7).

PREPARATION

The samples were dried at room temperature, disaggregated in a porcelain mortar with rubber pestle and sieved to minus 80 mesh (0.162 mm) through a nylon screen, whereas the 100 g samples, representative of the GGRN sub-cells, were obtained with equal portions of the samples from the catchment basins (figure 8) or soil sampling stations (figure 9) contained in each sub-cell.

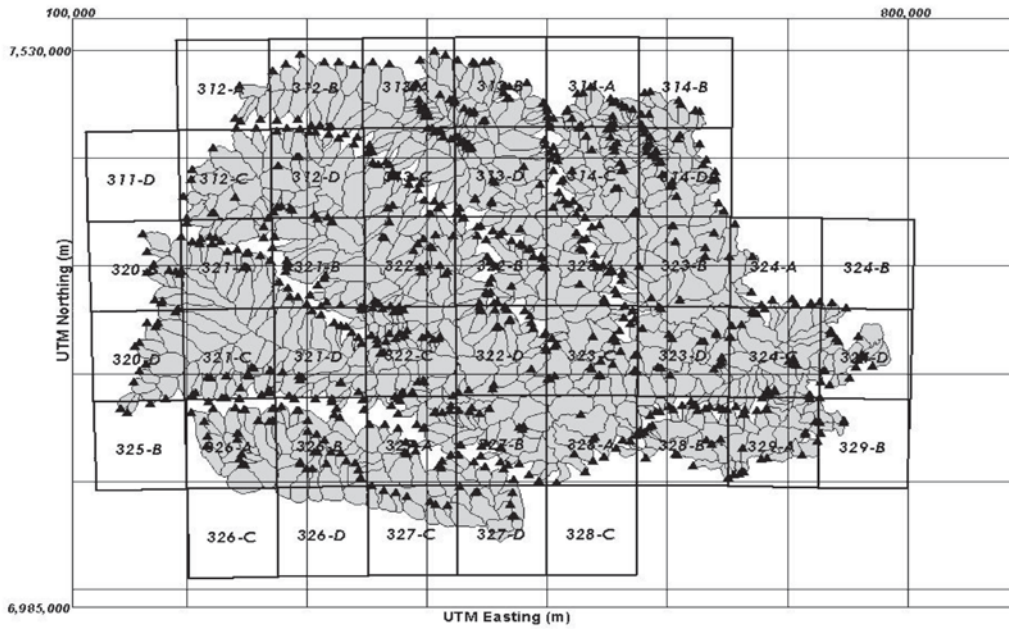


Figure 8 - The 39 GGRN sub-cells and the respective 696 catchment basins (Licht et al. 1996 apud Licht 2001).

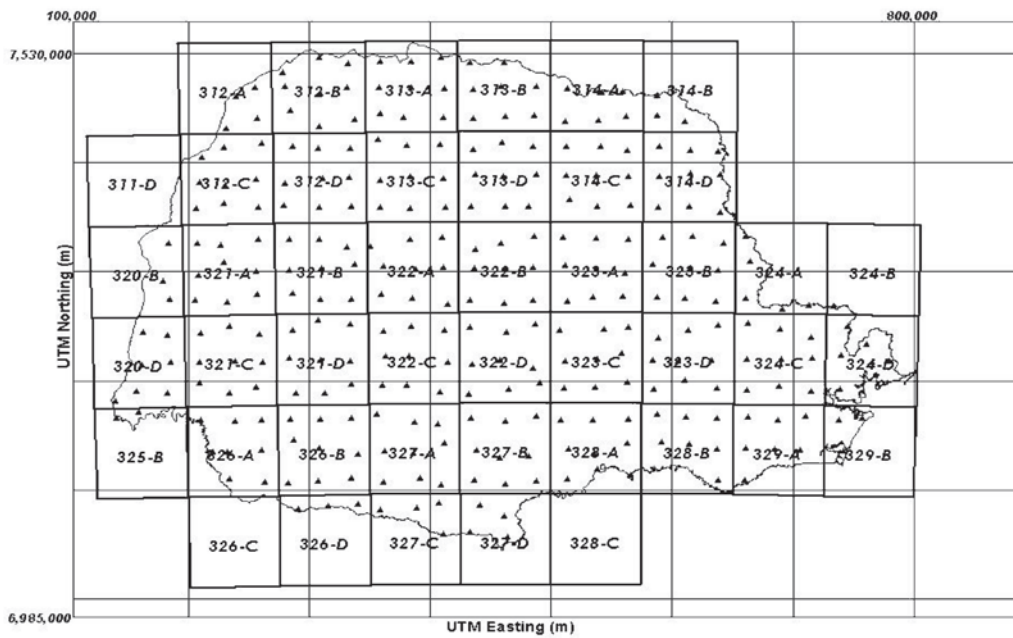


Figure 9 - The 43 GGRN sub-cells and the respective 307 soil - B horizon sampling sites (Licht & Plawiak 2005)

ANALYTICAL PROCEDURES

The multielementar geochemical analysis of the GGRN sub-cells composite samples, were performed at the laboratories of the Institute of Geophysical and Geochemical Exploration (IGGE) and are presented in the tables 1 and 2. The determination of the soil fertility parameters on the 307 original soil samples were

performed at the Soil and Vegetal Tissues Laboratory, Agronomic Institute of the State of Paraná (Iapar) and are shown in table 3. The determination of magnetic susceptibility and gamma-spectrometry on the 307 original soil samples were performed at the Laboratory of Applied Geophysical Researches (LPGA), Federal University of Paraná (UFPR) and are presented in table 4.

Table 1 - Analytical techniques applied to the 39 GGRN sub-cells (composited from 696 stream sediment samples).

Determination	Digestion	Elements / oxides (Detection limit: $\mu\text{g/g}$)
X-ray fluorescence spectrometry (XRF)	Pressed powder pellet	Ba (50); Co (1); Cr (15); Mn (30); Nb (5); Ni (2); P (100); Pb (2); Sc (2); Sr (5); Th (4); Ti (100); V (20); Zn (10); SiO ₂ (1000); Al ₂ O ₃ (1000); Fe ₂ O ₃ (1000); MgO (1000); CaO (1000); Na ₂ O (1000); K ₂ O (1000); Rb (3); Br (1.5); Ga (5); Cl (20); La (15); Ce (20); Y (5)
Graphite furnace, Atomic Absorption Spectrometry (GF-AAS)	HF + HNO ₃ + HClO ₄	Ag (0.02); Cd (0.01); Tl (0.1)
Flame Atomic Absorption Spectrometry (FAAS)	HF + HNO ₃ + H ₂ SO ₄	Cs (1)
Flame Atomic Absorption Spectrometry (FAAS)	HF + HNO ₃ + HClO ₄	Cu (1); Li (5)
Colorimetry (COL)	HF + HNO ₃ + HClO ₄	U (0.5)
Colorimetry (COL)	Fusion (ZnO + Na ₂ CO ₃)	I (1.0)
Hydride generation, Atomic Fluorescence Spectrometry (HG-AFS)	Aqua-Regia	As (1.0); Sb (0.1); Bi (0.1)
Cold Vapor Atomic Fluorescence Spectrometry (CV-AFS)	Aqua-Regia	Hg (0.010)
Hydride generation, Atomic Fluorescence Spectrometry (HG-AFS)	Melt (C + MgO + NaCO ₃)	Se (0.01)
Hydride generation, Atomic Fluorescence Spectrometry (HG-AFS)	HF + HNO ₃ + HClO ₄	Te (0.005)
Hydride generation, Atomic Fluorescence Spectrometry (HG-AFS)	HF + HNO ₃ + H ₂ SO ₄ + H ₃ PO ₄	Ge (0.1)
Cathalitic Wave Polarography (CWPOL)	Fusion (Na ₂ O ₂)	W (0.5); Mo (0.5)
Specific Ion Eletrode (SIE)	Fusion (Na ₂ O ₂)	F (100)
Powder Quantitative Atomic Emission Spectrometry (QA-AES)		B (5); Be (0.5); Sn (1)
Volumetry with Acid Digestion (VOL)		N (50)
Fire Volumetry (VOL)		S (50)
Fired-Potentiometry		C _{total} (1000); C _{organic} (1000)
Quantitative Atomic Emission Spectrometry (QA-AES)	Aqua-Regia	Au (0.0003); Pt (0.0002); Pd (0.0002)
Induced Coupled Plasma Spectrometry (ICP-ES)	Fusion (Na ₂ O ₂)	Pr (0.1); Nd (0.1); Sm (0.1); Eu (0.1); Gd (0.1); Tb (0.1); Dy (0.1); Ho (0.1); Er (0.1); Tm (0.1); Yb (0.1); Lu. (0.1)

NOTE: Analysis performed in 1997, by the Institute of Geophysical and Geochemical Exploration (IGGE).

Table 2 - Analytical techniques applied to the 43 GGRN sub-cells (composited from 307 soil – B horizon samples).

Determination	Digestion	Elements / oxides (detection limit; 6s; µg/g)
Induced Coupled Plasma Mass Spectrometry (ICP-MS)	HF + HNO ₃ + HClO ₄ + aqua regia	Bi (0.010); Cd (0.019); Cs (0.003); Hf (0.030); In (0.002); Mo (0.014); Sc (1.3); Ta (0.003); Th (0.006); Tl (0.004); U (0.014); W (0.015)
Induced Coupled Plasma Mass Spectrometry (ICP-MS)	HF + HNO ₃ + H ₂ SO ₄ + aqua regia	Ce (0.27); Dy (0.030); Er (0.033); Eu (0.007); Gd (0.023); Ho (0.008); La (0.25); Lu (0.007); Nd (0.089); Pr (0.016); Sm (0.029); Tb (0.015); Tm (0.006); Yb (0.033)
Induced Coupled Plasma Optical Emission Spectrometry (ICP-OES)	HF + HNO ₃ + HClO ₄ + aqua regia	Be (0.044); Co (0.55); Cu (1.5); Li (1.1); MgO (29); Na ₂ O (450); Ni (0.76); Zn (1.4)
X-ray Fluorescence (XRF)	Powder Pressed Pellet	Al ₂ O ₃ (80.0); Ba (9.0); Br (0.6); CaO (60.0); Cl (8.0); Cr (3.3); Fe ₂ O ₃ (80.0); Ga (0.8); K ₂ O (60.0); Mn (6.1); Nb (1.0); P (4.6); Pb (1.8); Rb (1.4); S (7.8); SiO ₂ (130); Sr (1.2); Ti (12.0); V (4.8); Y (0.9); Zr (3.8)
Graphite furnace, Atomic Absorption Spectrometry (GF-AAS)	Aqua regia	Au (0.04 ng/g)
Quantitative Atomic Emission Spectrometry (QA-AES)	Aqua-Regia	Pt (0.0002); Pd (0.0002)
Emission Spectrometry (ES)		Ag (0.013); B (0.83); Sn (0.23)
Hydride generation, Atomic Fluorescence Spectrometry (HG-AFS)	Aqua regia	As (0.069); Sb (0.028)
Hydride generation, Atomic Fluorescence Spectrometry (HG-AFS)	HF + HNO ₃ + HClO ₄	Se (0.0057)
Hydride generation, Atomic Fluorescence Spectrometry (HG-AFS)	HF + HNO ₃ + H ₂ SO ₄	Ge (0.02)
Cold Vapor – Atomic Fluorescence Spectrometry (CV-AFS)	Aqua regia	Hg (0.53 ng/g)
ion selective electrode (ISE)	Fusion (NaOH)	F (52)
Colorimetry (COL)	Echika flux	I (0.15)
K-method (VOL)		N (20)
Fired-Potentiometry (POT)		C _{total} (0.1%); C _{organic} (0.1%)

NOTE: Analysis performed in 2003, by the Institute of Geophysical and Geochemical Exploration (IGGE).

Table 3 - Analytical techniques for soils fertility, applied to the 307 soil – B horizon samples.

Extractor	Relation soil:solution	Element / variable
		Al
Potassium chloride 1.0 mol/L	1:10	Al _{exchangeable}
		Ca _{available}
HCl 0.05 N	1:2	Mg _{available}
Walkley – Black (K ₂ Cr ₂ O ₇ + H ₂ SO _{4 conc.})		B _{extractable}
		C
Hydrochloridric acid 0,1 M	1:10	Cu _{extractable}
		Zn _{extractable}
		Fe _{extractable}
Buffer solution SMP		H ⁺ + Al ³⁺
Amonium acetate 1.0 M, pH 7.0	1:10	Mn _{extractable}
Mehlich I (HCl 0,05 N + H ₂ SO ₄ 0,025 N)	1:10	P _{available}
		K _{available}
Calcium chloride, 0.01 mol/L	1:2.5	pH
Mono calcic phosphate + Acetic acid 2M	1:2.5	S _{extractable}
		V ⁽¹⁾
		S ⁽²⁾
		T ⁽³⁾

NOTE: (1) Cations Exchange Capacity; (2) Sum of the Excheangeable Basis; (3) Sum of the Excheangeable Cations. Analysis performed in 2003 by the Soils and Vegetal Tissues Laboratory, Iapar-Ld., following Embrapa (1999).

Table 4 - Determination techniques for gamma-spectrometry and magnetic susceptibility, applied to the 307 soil – B horizon samples.

Variable	Equipment specification	Determinations
Total count		
eU	Gamma-spectrometer GS-512, Geofyzika, Q.S. Brno / Scintrex 512 channels, NaI(Tl) cintilation detector, 76 x 76 mm.	Arithmetic mean of 3 determinations, 3 minutes each
eTh		
K		
Magnetic susceptibility	Kappameter KT-5, Mikrokappa Geofyzika, Q.S. Brno Sensitivity: 1×10^{-5} units SI; range: $9.99 \text{ a } 999 \times 10^{-3}$ units SI; Operation frequency: 10 kHz	Arithmetic mean of 3 determinations, 5 seconds each

NOTE: Analysis performed in 2003 by the Applied Geophysical Researches Laboratory (LPGA / UFPR).

QUALITY CONTROL

The chemical analysis of the 307 original soil samples or the GGRN sub-cells were monitored by control samples inserted on each 25 samples batch sent to the laboratories, whereas the analysis of the GGRN subcell samples were monitored following internal protocols of the IGGE laboratory, by using the certificated standard samples: GPt 1-8 for Pt and Pd analysis, GAu 8-11 for Au analysis, GSS1, GSS3, GSD9, GSD10 for other elements, as well as duplicate analysis of randomly selected samples in each analytical batch.

DATA ANALYSIS

In the analysis of the results, were adopted the statistical estimates mean, variance and standard deviation, but due to the presence of extreme values, were also used median and quartiles, less biased by the outliers influence, then, the reference values are presented in the form of tables containing the minimum and maximum values, arithmetic mean, median, standard deviation, variance and 1st and 3rd quartile (Licht 2001, Licht & Plawiak 2005) (tables 5, 6, 7 and 8).

Table 5 - Statistical estimates for the geochemical variables determined in the 39 GGRN sub-cells (composited from 696 stream sediment samples) (Licht 2001).

Element / oxide	Unit	Minimum value	1 st Quartile	Median	Arithmetic mean	3 rd Quartile	Maximum value	Variance	Standard deviation
Ag	ppb	31.00	53.00	62.00	62.487	70.00	94.00	219.362	14.811
Al ₂ O ₃	%	0.94	6.98	12.29	10.893	14.43	20.35	26.577	5.155
As	ppm	1.00	1.13	1.91	2.019	2.60	4.65	0.842	0.9173
Au	ppb	0.00	1.44	2.26	2.992	3.90	14.56	8.027	2.833
B	ppm	3.30	8.70	23.40	31.733	43.20	206.60	1358.016	36.851
Ba	ppm	94.00	169.00	264.00	311.153	320.00	1064.00	50744.555	225.265
Be	ppm	0.98	1.27	1.69	1.812	2.25	3.40	0.369	0.607
Bi	ppm	0.05	0.10	0.14	0.137	0.16	0.31	0.003	0.058
Br	ppm	1.00	2.90	6.10	6.287	9.40	16.50	16.748	4.092
C _{org}	ppm	0.05	0.49	0.73	0.78	1.03	1.94	0.173	0.416
CaO	%	0.14	0.34	0.68	0.689	0.96	1.47	0.160	0.400
Cd	ppb	10.00	41.00	69.00	74.846	104.00	300.00	2600.870	50.998
Ce	ppm	6.70	29.30	48.80	67.136	82.40	373.70	4256.929	65.245
Cl	ppm	5.00	21.00	42.00	44.538	49.00	391.00	3550.887	59.589
Co	ppm	1.70	11.60	43.00	63.754	118.70	172.20	3403.751	58.341
Cr	ppm	14.00	39.00	78.00	92.641	134.00	213.00	3946.447	62.820
Cs	ppm	1.00	2.50	4.10	4.767	7.30	10.40	7.691	2.773
Cu	ppm	5.30	18.30	110.70	163.785	303.40	491.40	26050.273	161.401
Dy	ppm	0.67	3.82	5.15	5.167	5.82	19.70	9.508	3.083
Er	ppm	0.62	2.40	3.07	3.176	3.48	12.90	3.602	1.897
Eu	ppm	0.10	0.92	1.33	1.311	1.79	3.10	0.441	0.664
F	ppm	100.00	134.00	174.00	185.128	220.00	322.00	3392.536	58.245
Fe ₂ O ₃	%	0.83	5.14	11.54	12.047	19.76	24.61	63.925	7.995
Ga	ppm	3.50	10.20	18.60	19.338	29.20	38.40	112.303	10.597
Gd	ppm	0.45	4.08	5.55	5.595	6.66	19.00	10.386	3.223
Ge	ppm	0.70	0.83	0.87	0.923	0.96	1.46	0.028	0.168
Hg	ppb	4.10	23.90	35.60	33.338	40.80	56.50	186.485	13.656
Ho	ppm	0.18	0.83	1.09	1.109	1.23	4.38	0.435	0.659
I	ppm	0.40	1.60	3.00	3.385	5.30	8.40	4.699	2.167

K ₂ O	%	0.12	0.28	0.40	0.695	0.90	3.98	0.539	0.734
La	ppm	1.90	23.70	29.30	35.577	37.70	139.00	728.372	26.988
Li	ppm	3.60	12.70	14.90	18.269	21.70	53.00	114.345	10.693
Lu	ppm	0.16	0.42	0.47	0.531	0.55	2.09	0.092	0.304
MgO	%	0.04	0.35	0.56	0.522	0.66	1.22	0.069	0.263
Mn	ppm	161.00	578.00	1883.00	1761.846	2665.00	4755.00	1323584.976	1150.471
Mo	ppm	0.30	0.60	0.86	0.890	1.14	1.61	0.120	0.346
N	%	0.01	0.05	0.08	0.09	0.13	0.17	0.002	0.047
Na ₂ O	%	0.04	0.10	0.15	0.201	0.24	0.70	0.026	0.161
Nb	ppm	4.70	18.40	42.50	39.620	53.50	82.20	462.147	21.497
Nd	ppm	2.20	21.80	27.90	30.731	34.30	110.00	382.772	19.564
Ni	ppm	4.40	13.30	31.20	39.931	59.40	108.10	942.597	30.702
P	ppm	57.00	367.00	807.00	799.154	1210.00	1664.00	230284.081	479.879
Pb	ppm	4.60	14.30	20.80	20.682	28.20	52.00	104.860	10.240
Pd	ppb	0.00	0.23	1.12	2.593	5.19	11.73	8.523	2.919
Pr	ppm	0.74	5.72	7.14	8.026	8.66	28.90	26.106	5.109
Pt	ppb	0.00	0.62	1.12	3.297	5.38	14.01	15.706	3.963
Rb	ppm	4.10	14.10	24.10	29.695	41.10	148.40	625.157	25.003
S	ppm	0.01	0.01	0.02	0.023	0.03	0.05	0.0001	0.011
Sb	ppm	0.12	0.23	0.35	0.329	0.41	0.60	0.013	0.116
Sc	ppm	1.10	8.30	20.50	22.915	37.80	48.30	251.340	15.854
Se	ppm	0.04	0.13	0.28	0.260	0.37	0.49	0.020	0.143
SiO ₂	%	30.89	41.19	57.36	59.945	79.63	90.86	431.891	20.782
Sm	ppm	0.39	4.22	5.62	5.927	6.76	20.40	12.694	3.563
Sn	ppm	0.59	2.06	2.56	2.820	3.16	7.63	2.244	1.498
Sr	ppm	11.00	31.00	45.00	54.589	64.00	200.00	1679.248	40.978
Tb	ppm	0.14	0.73	0.92	0.946	1.07	3.35	0.280	0.529
Te	ppm	10.00	16.00	24.00	27.077	35.00	69.00	181.862	13.485
Th	ppm	0.00	7.70	10.20	13.231	12.50	74.40	169.664	13.025
Ti	ppm	0.22	1.31	2.74	2.827	4.26	6.17	2.814	1.677
Tl	ppm	0.04	0.13	0.22	0.288	0.37	1.12	0.049	0.221
Tm	ppm	0.13	0.39	0.47	0.514	0.53	2.09	0.093	0.305
U	ppm	0.50	0.80	1.30	1.797	2.00	10.00	2.956	1.719
V	ppm	33.00	120.00	491.00	576.538	1004.00	1509.00	233063.045	482.766
W	ppm	0.32	0.42	0.70	0.807	0.98	2.60	0.242	0.492
Y	ppm	4.60	20.80	25.70	26.513	29.10	116.00	293.282	17.125
Yb	ppm	0.88	2.59	3.08	3.297	3.45	13.40	3.715	1.927
Zn	ppm	4.10	38.20	121.80	128.151	192.20	280.70	8316.486	91.195
Zr	ppm	280.00	444.00	662.00	948.667	1002.00	4175.00	777354.281	881.677

NOTE: Analysis performed in 1997, by the Institute of Geophysical and Geochemical Exploration (IGGE).

Table 6 - Statistical estimates for the geochemical variables determined in the 43 GGRN sub-cells (composited from 307 soil – b horizon samples) (Licht & Plawick 2005).

Element / oxide	Unit	Minimum value	1 st Quartile	Median	Arithmetic mean	3 rd Quartile	Maximum value	Variance	Standard deviation
Ag	ppb	38.00	47.00	54.00	54.93	61.00	78.00	93.590	9.674
Al ₂ O ₃	%	17.64	21.75	23.03	23.28	24.94	29.48	6.250	2.500
As	ppm	2.40	4.40	5.50	7.25	9.80	29.40	22.361	4.729
Au	ppb	0.52	1.27	2.08	2.71	3.99	6.64	2.887	1.699
B	ppm	6.00	11.00	24.00	27.37	36.00	99.00	409.144	20.227
Ba	ppm	43.00	107.00	147.00	171.07	193.00	502.00	10556.828	102.746
Be	ppm	0.39	1.25	1.61	1.51	1.82	2.74	0.243	0.493
Bi	ppm	0.13	0.20	0.28	0.30	0.34	0.57	0.014	0.120
Br	ppm	1.00	7.30	10.70	11.32	13.90	25.60	32.188	5.673
C	%	0.29	0.75	0.97	0.96	1.20	1.60	0.088	0.297
C _{org}	%	0.14	0.53	0.77	0.76	1.00	1.43	0.074	0.272
CaO	%	0.05	0.07	0.12	0.13	0.18	0.35	0.006	0.074
Cd	ppb	48.00	124.00	181.00	181.79	221.00	457.00	7258.646	85.198
Ce	ppm	41.00	74.00	89.00	96.40	113.00	220.00	1431.102	37.830
Cl	ppm	22.00	36.00	41.00	41.74	45.00	60.00	83.052	9.113

Co	ppm	3.90	6.70	18.90	23.84	41.80	61.90	344.789	18.568
Cr	ppm	43.00	69.00	87.00	105.42	139.00	230.00	2451.821	49.516
Cs	ppm	2.10	3.10	4.80	5.19	6.20	19.40	8.521	2.919
Cu	ppm	20.40	40.20	117.20	141.72	267.90	318.80	12109.980	110.045
Dy	ppm	2.21	3.91	5.86	5.80	6.73	12.76	5.397	2.323
Er	ppm	1.18	2.19	3.13	3.18	3.78	6.27	1.239	1.113
Eu	ppm	0.53	1.10	1.54	1.63	1.98	3.60	0.523	0.724
F	ppm	99.00	202.00	269.00	272.33	325.00	631.00	12127.415	110.125
Fe ₂ O ₃	%	4.96	8.75	16.87	15.05	21.22	26.34	47.344	6.881
Ga	ppm	11.80	26.20	31.40	30.74	36.50	46.50	76.587	8.751
Gd	ppm	2.21	3.89	5.49	5.69	6.59	12.31	5.125	2.264
Ge	ppm	0.97	1.56	2.02	2.02	2.47	3.14	0.285	0.534
Hf	ppm	8.90	11.20	12.90	14.13	15.90	27.30	17.798	4.219
Hg	ppb	13.40	40.20	52.50	60.90	71.40	160.70	1051.154	32.422
Ho	ppm	0.43	0.77	1.06	1.08	1.28	2.18	0.149	0.387
I	ppm	3.33	8.22	12.84	12.83	16.14	27.84	32.523	5.703
In	ppm	0.04	0.09	0.12	0.11	0.13	0.19	0.001	0.032
K ₂ O	%	0.07	0.12	0.22	0.44	0.72	1.91	0.209	0.457
La	ppm	16.00	28.00	35.00	37.95	44.00	72.00	193.664	13.916
Li	ppm	9.60	17.00	24.70	25.67	33.30	54.20	118.003	10.863
Lu	ppm	0.23	0.39	0.53	0.54	0.68	1.01	0.030	0.174
MgO	%	0.15	0.28	0.39	0.39	0.49	0.80	0.020	0.141
Mn	ppm	135.00	315.00	538.00	736.84	1094.00	1980.00	226981.997	476.426
Mo	ppm	0.73	1.34	1.64	1.68	1.90	3.17	0.260	0.510
N	ppm	204.00	518.00	686.00	702.1628	882.00	1106.00	54211.14	232.833
Na ₂ O	%	0.02	0.03	0.04	0.06	0.06	0.31	0.003	0.052
Nb	ppm	14.00	22.00	27.00	28.16	33.00	63.00	109.235	10.452
Nd	ppm	14.00	23.00	34.00	33.86	39.00	73.00	176.028	13.268
Ni	ppm	8.00	17.00	26.00	34.16	53.00	87.00	422.092	20.545
P	ppm	266.00	452.00	593.00	627.53	850.00	1179.00	53384.207	231.050
Pb	ppm	15.00	19.00	22.00	23.21	26.00	45.00	36.979	6.081
Pd	ppb	0.54	1.25	3.23	5.55	9.97	15.91	24.546	4.954
Pr	ppm	4.20	6.50	8.40	9.09	10.70	19.30	11.962	3.459
Pt	ppb	0.32	0.70	2.37	4.80	7.92	19.92	25.036	5.004
Rb	ppm	7.00	12.00	19.00	28.16	36.00	124.00	574.711	23.973
S	ppm	111.00	151.00	207.00	222.30	274.00	451.00	7076.835	84.124
Sb	ppm	0.26	0.48	0.60	0.74	0.98	1.81	0.133	0.365
Sc	ppm	7.30	16.70	33.90	31.04	46.50	57.10	246.125	15.688
Se	ppm	0.16	0.30	0.47	0.53	0.56	2.84	0.185	0.430
SiO ₂	%	30.41	36.75	41.29	43.88	51.28	62.59	88.208	9.392
Sm	ppm	2.73	4.70	6.79	6.94	8.05	15.34	7.685	2.772
Sn	ppm	1.50	2.50	3.20	3.38	3.92	8.99	2.093	1.447
Sr	ppm	12.00	19.00	25.00	36.95	48.00	126.00	777.474	27.883
Ta	ppm	0.88	1.80	2.30	2.46	2.86	6.00	1.054	1.027
Tb	ppm	0.37	0.68	0.97	0.99	1.16	2.05	0.146	0.383
Th	ppm	4.10	8.60	11.20	13.30	18.50	28.30	31.677	5.628
Ti	ppm	6156.00	8929.00	16602.00	15726.47	21407.00	32176.00	52039234.4	7213.822
Tl	ppm	0.15	0.27	0.36	0.40	0.51	1.42	0.045	0.213
Tm	ppm	0.21	0.37	0.53	0.53	0.65	1.08	0.032	0.179
U	ppm	1.00	2.00	2.90	3.02	4.00	7.60	1.669	1.292
V	ppm	81.00	129.00	360.00	370.37	570.00	856.00	60563.668	246.097
W	ppm	0.62	1.02	1.44	1.57	2.01	3.40	0.408	0.639
Y	ppm	9.60	22.80	27.50	27.64	33.70	50.30	67.572	8.220
Yb	ppm	1.35	2.34	3.27	3.35	4.09	6.45	1.199	1.095
Zn	ppm	24.00	47.00	77.00	75.26	103.00	124.00	1003.719	31.682
Zr	ppm	299.00	376.00	431.00	455.67	519.00	776.00	10926.987	104.532

NOTE: Analysis performed in 2003, by the Institute of Geophysical and Geochemical Exploration (IGGE).

Table 7 - Statistical estimates for the soil fertility parameters determined in the 307 soil samples (B horizon) (Licht & Plawiak 2005)

Variable	Unit	Minimum value	1 st Quartile	Median	Arithmetic mean	3 rd Quartile	Maximum value	Variance	Standard deviation
Al _{exchangeable}	cmol _c /dm ³ (1)	0.00	0.10	0.55	1.34	1.69	10.98	3.864	1.966
B _{extractable}	mg/dm ³	0.20	0.60	0.09	0.11	0.12	0.61	0.006	0.797
C	g/dm ³	3.70	4.10	4.30	4.55	5.00	6.70	0.372	0.610
Ca _{available}	cmol _c /dm ³	0.07	0.25	0.76	1.87	2.53	17.63	6.428	2.535
K _{available}	cmol _c /dm ³	0.03	0.05	0.07	0.13	0.14	2.35	0.039	0.197
Mg _{available}	cmol _c /dm ³	0.02	0.11	0.29	0.74	0.98	8.56	1.155	1.075
P _{available}	mg/dm ³	0.10	0.40	0.90	1.72	1.70	40.30	11.328	3.366
pH	-	3.70	4.10	4.30	4.55	5.00	6.70	0.372	0.610
V (2)	%	0.85	5.64	15.91	26.71	44.41	83.16	598.015	24.454
Zn _{extractable}	mg/dm ³	0.01	0.19	0.42	0.77	0.74	17.05	2.10	1.44
Al	%	0.00	0.21	33.32	39.12	75.00	97.78	1260.611	35.505
Cu _{extractable}	mg/dm ³	0.20	0.95	2.63	6.01	9.42	46.64	48.238	6.945
Fe _{extractable}	mg/dm ³	3.98	13.42	20.88	22.86	28.64	100.10	180.077	13.419
H ⁺ +Al ³⁺	cmol _c /dm ³	1.62	3.68	5.55	7.08	9.00	21.99	22.387	4.732
Mn _{extractable}	mg/dm ³	0.04	0.06	1.18	2.61	2.74	67.58	35.365	5.947
S _{extractable}	mg/dm ³	0.06	181.20	6.51	11.13	12.86	181.20	231.033	15.199
S (3)	cmol _c /dm ³	0.12	0.46	1.19	2.74	3.64	22.73	12.647	3.556
T (4)	cmol _c /dm ³	2.62	5.65	9.12	9.82	12.55	27.33	25.686	5.068

NOTE: Analysis performed in 2003 by the Soils and Vegetal Tissues Laboratory, Iapar-Ld., following Embrapa (1999).

Observations : (1) cmol_c/dm³ = meq/100 g or meq/100 cm³; (2) Cations Exchange Capacity; (3) Sum of the Exchangeable Basis; (4) Sum of the Exchangeable Cations.

Table 8 - Statistical estimates for the variables determined by gamma-spectrometry and magnetic susceptibility in the 307 soil samples (B horizon) (Licht & Plawiak 2005)

Variable	Equipment specification	Determinations
Total count		
eU	Gamma-spectrometer GS-512, Geofyzika, Q.S. Brno / Scintrex 512 channels, NaI(Tl) cintilation detector, 76 x 76 mm.	Arithmetic mean of 3 determinations, 3 minutes each
eTh		
K		
Magnetic susceptibility	Kappamer KT-5, Microkappa Geofyzika, Q.S. Brno Sensitivity: 1x10 ⁻⁵ units SI; range: 9.99 a 999 x 10 ⁻³ units SI; Operation frequency:10 kHz	Arithmetic mean of 3 determinations, 5 seconds each

NOTE: Analysis performed in 2003 by the Applied Geophysical Researches Laboratory (LPGA / UFPR).

RESULTS

The data processing allowed to establish reference values for a wide spectrum of analytical variables, determined in two sampling media (stream sediments and soils – B horizon).

Furthermore, it was also possible to group the elements determined in the GGRN sub-cells into some categories, delimited by its average absolute values in the Paraná's territory, as well as standardized by the global average values.

Unfortunately were not found in the literature, global average values neither for the soil fertility parameters nor for the gama-spectrometric or magnetic susceptibility values. Then the grouping was made only for the total contents of the elements in the GGRN sub-cells.

CATEGORIES BASED ON ABSOLUTE AVERAGE VALUES

The first grouping of the elements determined on the GGRN sub-cells, was based on its abundance in each sampling media. The elements were arranged accordingly to its abundance and classified into the four following categories as presented in tables 9 and 10:

- **Ultra-trace elements** – contents in ppb or lower than 1 ppm;
- **Trace elements** – contents between 1 and 100 ppm;
- **Minor elements** – contents between 100 and 1000 ppm;
- **Major elements** – contents higher than 1000 ppm or reaching %.

Table 9 - Grouping of the variables analysed in the 39 GGRN sub-cells composited from 696 stream, sediment samples, accordingly to its average (arithmetic mean) (Licht & Plawiak 2005).

Ultra-trace elements contents in ppb or lower than 1 ppm			Trace elements contents between 1 and 100 ppm			Minor elements contents between 100 and 1000 ppm			Major elements contents higher than 1000 ppm		
variable	average	unit	variable	average	unit	variable	average	unit	variable	average	unit
Pd	2.593	ppb	Ho	1.109	ppm	Zn	128.151	ppm	Mn	1761.846	ppm
Au	2.992	ppb	Eu	1.311	ppm	Cu	163.785	ppm	N	0.09	%
Pt	3.297	ppb	U	1.797	ppm	F	185.128	ppm	Na ₂ O	0.201	%
Hg	33.338	ppb	Be	1.812	ppm	Ba	311.153	ppm	MgO	0.522	%
Ag	62.487	ppb	As	2.019	ppm	V	576.538	ppm	CaO	0.689	%
Cd	74.846	ppb	Sn	2.820	ppm	P	799.154	ppm	K ₂ O	0.695	%
S	0.023	ppm	Ti	2.827	ppm	Zr	948.667	ppm	Al ₂ O ₃	10.893	%
C _{org}	0.78	ppm	Er	3.176	ppm				Fe ₂ O ₃	12.047	%
Bi	0.137	ppm	Yb	3.297	ppm				SiO ₂	59.945	%
Se	0.260	ppm	I	3.385	ppm						
Tl	0.288	ppm	Cs	4.767	ppm						
Sb	0.329	ppm	Dy	5.167	ppm						
Tm	0.514	ppm	Gd	5.595	ppm						
Lu	0.531	ppm	Sm	5.927	ppm						
C _{org}	0.78	Ppm	Br	6.287	ppm						
W	0.807	ppm	Pr	8.026	ppm						
Mo	0.890	ppm	Th	13.231	ppm						
Ge	0.923	ppm	Li	18.269	ppm						
Tb	0.946	ppm	Ga	19.338	ppm						
			Pb	20.682	ppm						
			Sc	22.915	ppm						
			Y	26.513	ppm						
			Te	27.077	ppm						
			Rb	29.695	ppm						
			Nd	30.731	ppm						
			B	31.733	ppm						
			La	35.577	ppm						
			Nb	39.620	ppm						
			Ni	39.931	ppm						
			Cl	44.538	ppm						
			Sr	54.589	ppm						
			Co	63.754	ppm						
			Ce	67.136	ppm						
			Cr	92.641	ppm						

Table 10 - Grouping of the variables analysed in the 43 GGRN sub-cells composited from 307 soil – b horizon samples, accordingly to its average (arithmetic mean) (Licht & Plawiak 2005).

Ultra-trace elements contents in ppb or lower than 1 ppm			Trace elements contents between 1 and 100 ppm			Minor elements contents between 100 and 1000 ppm			Major elements contents higher than 1000 ppm		
variable	average	unit	variable	average	unit	variable	average	unit	variable	unit	average
Pd	5.55	ppb	Ho	1.08	ppm	Cr	105.42	ppm	Ti	15726.47	ppm
Au	2.71	ppb	Be	1.51	ppm	Ba	171.07	ppm	Na ₂ O	0.06	%
Pt	4.80	ppb	W	1.57	ppm	Cu	141.72	ppm	CaO	0.13	%
Ag	54.93	ppb	Eu	1.63	ppm	S	222.30	ppm	MgO	0.39	%
Hg	60.90	ppb	Mo	1.68	ppm	F	272.33	ppm	K ₂ O	0.44	%
Cd	181.79	ppb	Ge	2.02	ppm	V	370.37	ppm	C _{org}	0.76	%
In	0.11	ppm	Ta	2.46	ppm	Zr	455.67	ppm	C	0.96	%
Bi	0.30	ppm	U	3.02	ppm	P	627.53	ppm	Fe ₂ O ₃	15.05	%
Tl	0.40	ppm	Er	3.18	ppm	Mn	736.84	ppm	Al ₂ O ₃	23.28	%
Se	0.53	ppm	Yb	3.35	ppm	N	702.162	ppm	SiO ₂	43.88	%
Tm	0.53	ppm	Sn	3.38	ppm						
Lu	0.54	ppm	Cs	5.19	ppm						
Sb	0.74	ppm	Gd	5.69	ppm						

Tb	0.99	ppm	Dy	5.80	ppm
			Sm	6.94	ppm
			As	7.25	ppm
			Pr	9.09	ppm
			Br	11.32	ppm
			I	12.83	ppm
			Th	13.30	ppm
			Hf	14.13	ppm
			Pb	23.21	ppm
			Co	23.84	ppm
			Li	25.67	ppm
			B	27.37	ppm
			Y	27.64	ppm
			Nb	28.16	ppm
			Rb	28.16	ppm
			Ga	30.74	ppm
			Sc	31.04	ppm
			Nd	33.86	ppm
			Ni	34.16	ppm
			Sr	36.95	ppm
			La	37.95	ppm
			Cl	41.74	ppm
			Zn	75.26	ppm
			Ce	96.40	ppm

GROUPING BASED ON RELATIVE AVERAGE VALUES

Besides the establishment of the absolute reference values, the arithmetic means of the elements, calculated for both sampling media, were compared to the global average values for soils (tables 11 and 12).

Table 11 - Average values - local Clarke - for the Variables determined in the 39 GGRN sub-cells composited from 696 stream sediment samples and its comparison to the soils global average values (exception made to C and N) (Licht & Plawiak 2005).

Reported analytical variable	Arithmetic mean	Values recalculated to (1)	Local Clarke for stream sediments (ppm)	Soils global average value (ppm) (2)	\bar{K} (relative to soils) (3)
Ag (ppb)	62.487	Ag (ppm)	0.06249	0.28 ^(a)	0.22
Al ₂ O ₃ (%)	10.893	Al (ppm)	57622.7	80000 ^(b)	0.72
As (ppm)	2.019		2.02	7.83 ^(a)	0.26
Au (ppb)	2.992	Au (ppm)	0.00345	0.0013 ^(b)	2.65
B (ppm)	31.733		31.73	48 ^(a)	0.66
Ba (ppm)	311.153		311.15	682 ^(a)	0.46
Be (ppm)	1.812		1.81	1.69 ^(a)	1.07
Bi (ppm)	0.137		0.14	0.33 ^(a)	0.42
Br (ppm)	6.287		6.29	27 ^(a)	0.23
C _{org} (ppm)	0.78		0.78	N.A.	N.C.
CaO (%)	0.689	Ca (ppm)	4917.09	14000 ^(b)	0.35
Cd (ppb)	74.846	Cd (ppm)	0.07485	0.62 ^(a)	0.12
Ce (ppm)	67.136		67.14	64 ^(a)	1.05
Cl (ppm)	44.538		44.54	300 ^(b)	0.15
Co (ppm)	63.754		63.75	8.15 ^(a)	7.82
Cr (ppm)	92.641		92.64	71 ^(a)	1.30
Cs (ppm)	4.767		4.77	2.54 ^(a)	1.88
Cu (ppm)	163.785		163.78	32 ^(a)	5.12
Dy (ppm)	5.167		5.17	5.82 ^(a)	0.89
Er (ppm)	3.176		3.18	3.28 ^(a)	0.97
Eu (ppm)	1.311		1.31	0.85 ^(a)	1.54

F (ppm)	185.128		185.13	476 ^(a)	0.39
Fe ₂ O ₃ (%)	12.047	Fe (ppm)	84282.2	36000 ^(b)	2.34
Ga (ppm)	19.338		19.34	28 ^(a)	0.69
Gd (ppm)	5.595		5.60	5.29 ^(a)	1.06
Ge (ppm)	0.923		0.92	0.42 ^(a)	2.19
Hg (ppb)	33.338	Hg (ppm)	0.03334	0.04 ^(a)	0.83
Ho (ppm)	1.109		1.11	0.73 ^(a)	1.52
I (ppm)	3.385		3.38	6.56 ^(a)	0.52
K ₂ O (%)	0.695	K (ppm)	5810.9	17000 ^(b)	0.34
La (ppm)	35.577		35.58	43 ^(a)	0.83
Li (ppm)	18.269		18.27	46 ^(a)	0.40
Lu (ppm)	0.531		0.53	0.53 ^(a)	1.00
MgO (%)	0.522	Mg (ppm)	3136.5	9000 ^(b)	0.35
Mn (ppm)	1761.846		1761.85	600 ^(a)	2.94
Mo (ppm)	0.890		0.89	2.12 ^(a)	0.42
N (%)	0.09		0.09	N.A.	N.C.
Na ₂ O (%)	0.201	Na (ppm)	1483.8	10000 ^(b)	0.15
Nb (ppm)	39.620		39.62	17 ^(a)	2.33
Nd (ppm)	30.731		30.73	35 ^(a)	0.88
Ni (ppm)	39.931		39.93	28 ^(a)	1.43
P (ppm)	799.154		799.15	750 ^(b)	1.07
Pb (ppm)	20.682		20.68	43 ^(a)	0.48
Pd (ppb)	2.593	Pd (ppm)	0.00299	0.0004 ^(b)	7.48
Pr (ppm)	8.026		8.03	7.83 ^(a)	1.03
Pt (ppb)	3.297	Pt (ppm)	0.00380	0.0005	7.60
Rb (ppm)	29.695		26.69	77 ^(a)	0.35
S (%)	0.023	S (ppm)	200	800 ^(b)	0.25
Sb (ppm)	0.329		0.33	0.81 ^(a)	0.41
Sc (ppm)	22.915		22.92	8.26 ^(a)	2.77
Se (ppm)	0.260		0.26	0.55 ^(a)	0.47
SiO ₂ (%)	59.945	Si (ppm)	280086.5	280000 ^(b)	1.00
Sm (ppm)	5.927		5.93	6.67 ^(a)	0.89
Sn (ppm)	2.820		2.82	3.6 ^(a)	0.78
Sr (ppm)	54.589		54.59	434 ^(a)	0.13
Tb (ppm)	0.946		0.95	0.79 ^(a)	1.20
Te (ppb)	27.077	Te (ppm)	0.027	0.0040	6.75
Th (ppm)	13.231		13.23	7.94 ^(a)	1.67
Ti (%)	2.827	Ti (ppm)	28300	5069 ^(a)	5.58
Tl (ppm)	0.288		0.29	0.35 ^(a)	0.83
Tm (ppm)	0.514		0.51	0.53 ^(a)	0.96
U (ppm)	1.797		1.80	4.97 ^(a)	0.36
V (ppm)	576.538		576.54	87 ^(a)	6.63
W (ppm)	0.807436		0.81	1.06 ^(a)	0.76
Y (ppm)	26.513		26.51	27 ^(a)	0.98
Yb (ppm)	3.297		3.30	3.6 ^(a)	0.92
Zn (ppm)	128.151		128.16	70 ^(a)	1.83
Zr (ppm)	948.667		948.67	290 ^(a)	3.27

Observations: (1) the contents reported as oxides were recalculated for the element with the gravimetric conversion factors (Rankama & Sahama 1954); (2) soil global average values: (a) Kabata-Pendias & Pendias (1992); (b) Koljonen et al. (1992); since there are no Te and Pt soil global average values in the literature, it were considered identical as the Clarke (global average value for the crustal rocks); (3) Concentration Clarke (*K*) calculated by dividing the Local Clarke by the soil global average values. N.A. = non available; N.C. = non calculated.

Table 12 - Average values - local Clarke - for the Variables determined (excpeition made to C and N) in the 43 GGRN sub-cells composited from 307 soils – b horizon samples and its comparison to Clarke (average values for the crustal rocks) and to the soils global average values (Licht & Plawiak 2005).

Reported analytical variable	Arithmetic mean	Values recalculated to	Local Clarke for soils (ppm) (1)	Clarke Global mean for crustal rocks (ppm) (2)	K (relative to crustal rocks) (3)	Global mean for soils (ppm) (4)	K (relative to soils) (5)
Ag	54.93 ppb	Ag ppm	0.0549	0.08	0.687	0.28 ^(a)	0.196
Al ₂ O ₃	23.28 %	Al ppm	123181.46	83600	1.473	80000 ^(b)	1.539
As	7.25 ppm		7.25	1.8	4.028	7.83 ^(a)	0.926
Au	2.71 ppb	Au ppm	0.0027	0.004	0.675	0.0013 ^(b)	2.077
B	27.37 ppm		27.37	9.0	3.041	48 ^(a)	0.570
Ba	170.84 ppm		170.84	390.0	0.438	682 ^(a)	0.251
Be	1.51 ppm		1.51	2.0	0.755	1.69 ^(a)	0.716
Bi	0.3 ppm		0.3	0.0082	36.585	0.33 ^(a)	0.909
Br	11.32 ppm		11.32	2.5	4.528	27 ^(a)	0.419
C	0.96 %	C ppm	9600.00	N.A.	N.C.	N.A.	N.C.
C _{org}	0.76 %	C _{org} ppm	7600.00	N.A.	N.C.	N.A.	N.C.
CaO	0.13 %	Ca ppm	929.097	46600	0.0199	14000 ^(b)	0.066
Cd	181.74 ppb	Cd ppm	0.1817	0.16	1.136	0.62 ^(a)	0.293
Ce	96.4 ppm		96.4	66.4	1.461	64 ^(a)	1.506
Cl	41.74 ppm		41.74	126.00	0.331	300 ^(b)	0.139
Co	23.84 ppm		23.84	29.0	0.822	8.15 ^(a)	2.925
Cr	105.42 ppm		105.42	122.0	0.864	71 ^(a)	1.485
Cs	5.19 ppm		5.19	2.6	1.996	2.54 ^(a)	2.043
Cu	141.72 ppm		141.72	68.0	2.084	32 ^(a)	4.429
Dy	5.8 ppm		5.8	5.0	1.160	5.82 ^(a)	0.998
Er	3.18 ppm		3.18	3.46	0.909	3.28 ^(a)	0.969
Eu	1.63 ppm		1.63	2.14	0.776	0.85 ^(a)	1.917
F	272.33 ppm		272.33	544.0	0.501	476 ^(a)	0.572
Fe ₂ O ₃	15.05 %	Fe ppm	105265.72	62200.0	1.607	36000 ^(b)	2.924
Ga	30.74 ppm		30.74	19.0	1.618	28 ^(a)	1.098
Gd	5.69 ppm		5.69	6.14	0.933	5.29 ^(a)	1.076
Ge	2.02 ppm		2.02	1.5	1.347	0.42 ^(a)	4.809
Hf	14.13 ppm		14.13	2.8	5.046	6.46 ^(a)	2.187
Hg	60.9 ppb	Hg ppm	0.0609	0.086	0.708	0.04 ^(a)	1.523
Ho	1.08 ppm		1.08	1.26	0.857	0.73 ^(a)	1.479
I	12.83 ppm		12.83	0.46	27.891	6.56 ^(a)	1.956
In	0.11 ppm		0.11	0.24	0.458	0.07 ^(a)	1.571
K ₂ O	0.44 %	K ppm	3652.57	18400.0	0.198	17000 ^(b)	0.213
La	37.95 ppm		37.95	34.6	1.097	43 ^(a)	0.883
Li	25.67 ppm		25.67	18.0	1.426	46 ^(a)	0.558
Lu	0.54 ppm		0.54	0.54	1.000	0.53 ^(a)	1.019
MgO	0.39 %	Mg ppm	2352.36	27640.0	0.085	9000 ^(b)	0.261
Mn	736.84 ppm		736.84	1060.0	0.695	600 ^(a)	1.228
Mo	1.68 ppm		1.68	1.2	1.400	2.12 ^(a)	0.793
N	702.16 ppm		702.16	19.0	36.955	N.A.	N.C
Na ₂ O	0.06 %	Na ppm	445.15	22700.0	0.0196	10000 ^(b)	0.045
Nb	28.16 ppm		28.16	20.0	1.408	17 ^(a)	1.656
Nd	33.86 ppm		33.86	39.6	0.847	35 ^(a)	0.967
Ni	34.16 ppm		34.16	99.0	0.345	28 ^(a)	1.22
P	627.53 ppm		627.53	1120.0	0.560	750 ^(b)	0.837
Pb	23.21 ppm		23.21	13.0	1.785	43 ^(a)	0.539
Pd	5.55 ppb	Pd ppm	0.0056	0.015	0.37	0.0004 ^(b)	14.0
Pr	9.09 ppm		9.09	9.1	0.998	7.83 ^(a)	1.16
Pt	4.8 ppb	Pt ppm	0.0048	0.0005	9.6	0.0005	9.6
Rb	28.16 ppm		28.16	78.0	0.361	77 ^(a)	0.366
S	222.3 ppm		222.3	340.0	0.654	800 ^(b)	0.278
Sb	0.74 ppm		0.74	0.2	3.7	0.81 ^(a)	0.914
Sc	31.04 ppm		31.04	25.0	1.242	8.26 ^(a)	3.758
Se	0.53 ppm		0.53	0.05	10.6	0.55 ^(a)	0.963

SiO ₂	43.88 %	Si ppm	205007.36	27300	7.509	280000 ^(b)	0.732
Sm	6.94 ppm		6.94	7.02	0.988	6.67 ^(a)	1.040
Sn	3.38 ppm		3.38	2.1	1.609	3.6 ^(a)	0.939
Sr	36.95 ppm		36.95	384.0	0.096	434 ^(a)	0.085
Ta	2.46 ppm		2.46	1.7	1.447	1.59 ^(a)	1.547
Tb	0.99 ppm		0.99	1.18	0.838	0.79 ^(a)	1.253
Th	13.30 ppm		13.30	8.1	1.642	7.94 ^(a)	1.675
Ti	15726.47 ppm		15726.47	6320.0	2.488	5069 ^(a)	3.102
Tl	0.4 ppm		0.4	0.72	0.556	0.35 ^(a)	1.143
Tm	0.53 ppm		0.53	0.5	1.060	0.53 ^(a)	1
U	3.02 ppm		3.02	2.3	1.313	4.97 ^(a)	0.608
V	370.37 ppm		370.37	136.0	2.723	87 ^(a)	4.257
W	1.57 ppm		1.57	1.2	1.308	1.06 ^(a)	1.481
Y	27.64 ppm		27.64	31.0	0.892	27 ^(a)	0.913
Yb	3.35 ppm		3.35	3.1	1.081	3.6 ^(a)	0.931
Zn	75.26 ppm		75.26	76.0	0.990	70 ^(a)	1.075
Zr	455.67 ppm		455.67	162.0	2.813	290 ^(a)	1.571

NOTE: Observations: (1) the contents reported as oxides were recalculated for the element with the gravimetric conversion factors (Rankama & Sahama 1954); (2) Clarke (global average value for the crustal rocks) from Fortescue (1985); (3) soil global average values: (a) Kabata-Pendias & Pendias (1992); (b) Koljonen et al. (1992); since there are no Te and Pt soil global average values in the literature, it were considered identical as the Clarke (global average value for the crustal rocks); (4) Concentration Clarke (K) calculated by dividing the Local Clarke by the Clarke (global average value for the crustal rocks); (5) Concentration Clarke (K) calculated by dividing the Local Clarke by the soils global average value. N.A. = non available; N.C. = non calculated.

The *Clarke* concept was proposed by A. E. Fersman (1883-1945), a Russian geochemist, as a tribute to F. W. Clarke (1847-1934), an American geochemist, to establish a reference baseline for the abundance of the elements in the Earth's crust. On the other hand, the *concentration Clarke* (K) is an index obtained by dividing the arithmetic value of the element in the interest area (*local Clarke*) by the Clarke value (Fortescue 1985). This procedure means a standardization of the elemental abundance, respective to the global average levels considered as a reference, so this index, allows the identification of enrichments or depletions (positive or negative anomalies, respectively) in relation to the global patterns.

The global average values for the elements in soil samples were obtained from Kabata-Pendias & Pendias (1992) and Koljonen et al. (1992), and these reference values were used to standardize both soils and stream sediments average values, since to this date there are no global average values for stream sediments available in the literature. Therefore, it must be considered that the

adoption of global values for soils as a reference, could carry some bias to the final values because the elements in each sampling media suffer the influence as well as answer in different ways to the geochemical processes acting in the surface environment. Then, the values of the Concentration Clarke (K) for the elements determined in stream sediment GGRN cells must be considered as indicative. The *Concentration Clarke* – K , was used to establish a second kind of grouping for the elements analysed in the GGRN cells in both sampling media (tables 13 and 14), into the four following categories:

- A first group of elements considered as **depleted** in stream sediments or soils of the State of Paraná (K lower than 1);
- A second group of elements with abundance considered as **normal** (K between 1 and 2);
- A third group of elements considered as **abundant** (K between 2 and 5);
- A fourth group of elements considered as **anomalous** (K higher than 5).

Table 13 - Grouping of the analytical variables (exception made to C and N) analysed in 39 GGRN sub-cells (composited from 696 stream sediment samples), by its *Concentration Clarke* (\underline{K}) in relation to soils global average content (Licht & Plawiak 2005).

Depleted $\underline{K} < 1$		Normal $1 < \underline{K} < 2$		Abundant $2 < \underline{K} < 5$		Anomalous $\underline{K} > 5$	
Element	\underline{K}	Element	\underline{K}	Element	\underline{K}	Element	\underline{K}
Ag	0.22	Lu	1.00	Ge	2.19	Cu	5.12
Cd	0.12	Si	1.00	Nb	2.33	Ti	5.58
Sr	0.13	Pr	1.03	Fe	2.34	V	6.63
Cl	0.15	Ce	1.05	Au	2.65	Te	6.75
Na	0.15	Gd	1.06	Sc	2.77	Pd	7.48
Br	0.23	Be	1.07	Mn	2.94	Pt	7.60
S	0.25	P	1.07	Zr	3.27	Co	7.82
As	0.26	Tb	1.20				
K	0.34	Cr	1.30				
C	0.35	Ni	1.43				
Mg	0.35	Ho	1.52				
Rb	0.35	Eu	1.54				
U	0.36	Th	1.67				
F	0.39	Zn	1.83				
Li	0.40	Cs	1.88				
Sb	0.41						
Bi	0.42						
Mo	0.42						
Ba	0.46						
Se	0.47						
Pb	0.48						
I	0.52						
B	0.66						
Ga	0.69						
Al	0.72						
W	0.76						
Sn	0.78						
Hg	0.83						
La	0.83						
Tl	0.83						
Nd	0.88						
Dy	0.89						
Sm	0.89						
Yb	0.92						
Tm	0.96						
Er	0.97						
Y	0.98						

Table 14 - Grouping of the analytical variables (exception made to C and N) analysed in 43 GGRN sub-cells (composited from 307 soils - B horizon samples), by its *Concentration Clarke* (\underline{K}) in relation to soils global average content (Licht & Plawiak 2005).

Depleted $\underline{K} < 1$		Normal $1 < \underline{K} < 2$		Abundant $2 < \underline{K} < 5$		Anomalous $\underline{K} > 5$	
Element	\underline{K}	Element	\underline{K}	Element	\underline{K}	Element	\underline{K}
Na	0.05	Tm	1	Cs	2.04	Pt	9.6
Ca	0.07	Lu	1.02	Au	2.08	Pd	14
Sr	0.09	Sm	1.04	Hf	2.19		
Cl	0.14	Zn	1.08	Fe	2.92		
Ag	0.19	Gd	1.08	Co	2.93		
K	0.21	Ga	1.10	Ti	3.10		
Ba	0.25	Tl	1.14	Sc	3.76		
Mg	0.26	Pr	1.16	V	4.26		
S	0.28	Ni	1.22	Cu	4.43		
Cd	0.29	Mn	1.23	Ge	4.81		
Rb	0.37	Tb	1.25				
Br	0.42	Ho	1.48				
Pb	0.54	W	1.48				
Li	0.56	Cr	1.49				
B	0.57	Ce	1.51				
F	0.57	Hg	1.52				
U	0.61	Al	1.54				
Be	0.72	Ta	1.55				
Si	0.73	In	1.57				
Mo	0.79	Zr	1.57				
P	0.84	Nb	1.66				
La	0.88	Th	1.68				
Bi	0.91	Eu	1.92				
Y	0.91	I	1.96				
Sb	0.91						
As	0.93						
Yb	0.93						
Sn	0.94						
Se	0.96						
Nd	0.97						
Er	0.97						
Dy	0.99						

GEOGRAPHIC DISTRIBUTION OF THE ELEMENTS

The geographic distribution of the elements and other physical and chemical parameters determined in both sampling media, shows an enormous heterogeneity, depending on several factors and origins. From one side, there is a strong influence coming from the natural inheritance, e.g., the geological background or the presence of mineral deposits; otherwise must be considered the influences coming from the land use like the urban nuclei, the agriculture, the road network and

the industrial centres. From this point of view, the grand sum of these factors compose the *geochemical signal* achieved in the samples, strongly contributing for the heterogeneity in its geographical distribution. These concepts became clearly exemplified and defined by the comparison of some geochemical maps, e.g., Al_2O_3 (figures 10 and 11) and $Al_{exchangeable}$ (figure 12), pH (figure 13), Ba (figures 14 and 15), Cu (figures 16 and 17), Gd (figures 18 and 19) and magnetic susceptibility (figure 20), to the geology and the land use and occupation.

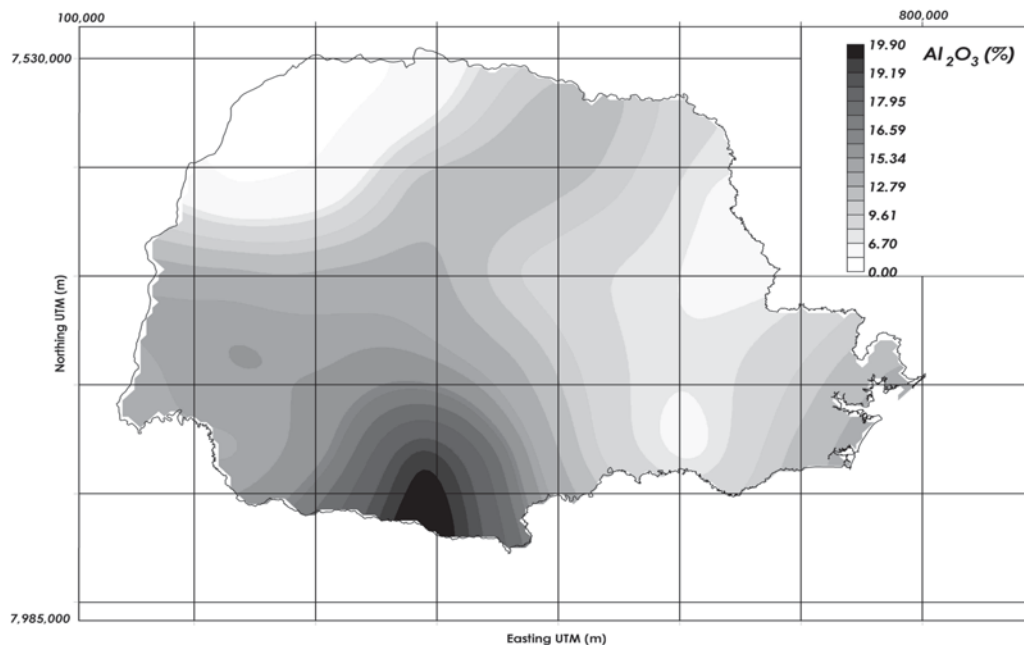


Figure 10 - Geochemical map for Al_2O_3 (%) for 39 GGRN sub-cells composited from 696 stream sediment samples (Licht 2001).

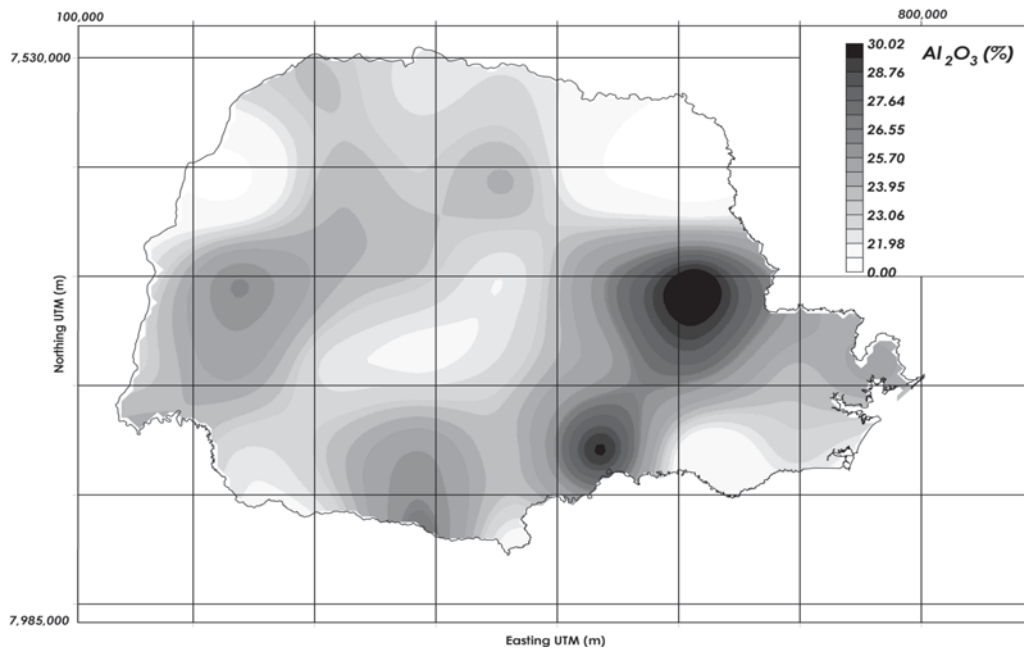


Figure 11 - Geochemical map showing the geographic distribution of Al_2O_3 (%) for 43 GGRN sub-cells composited from 307 soil – B horizon samples (Licht & Plawiak 2005).

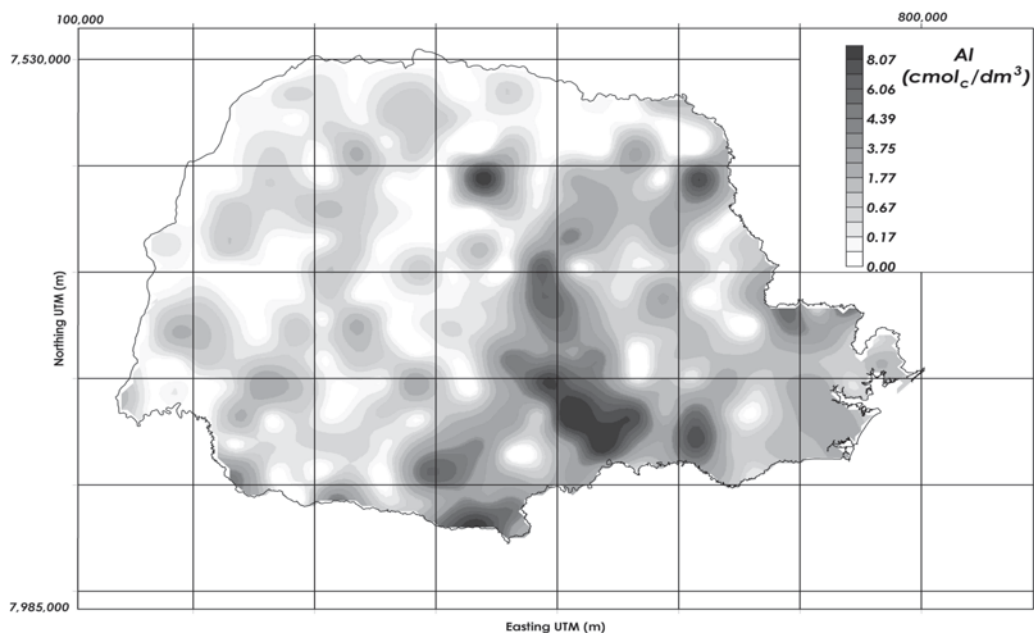


Figure 12 - Geochemical map showing the geographic distribution of Al_{exchangeable} (cmol_c/dm³) for 307 soil - B horizon samples (Licht & Plawiak 2005).

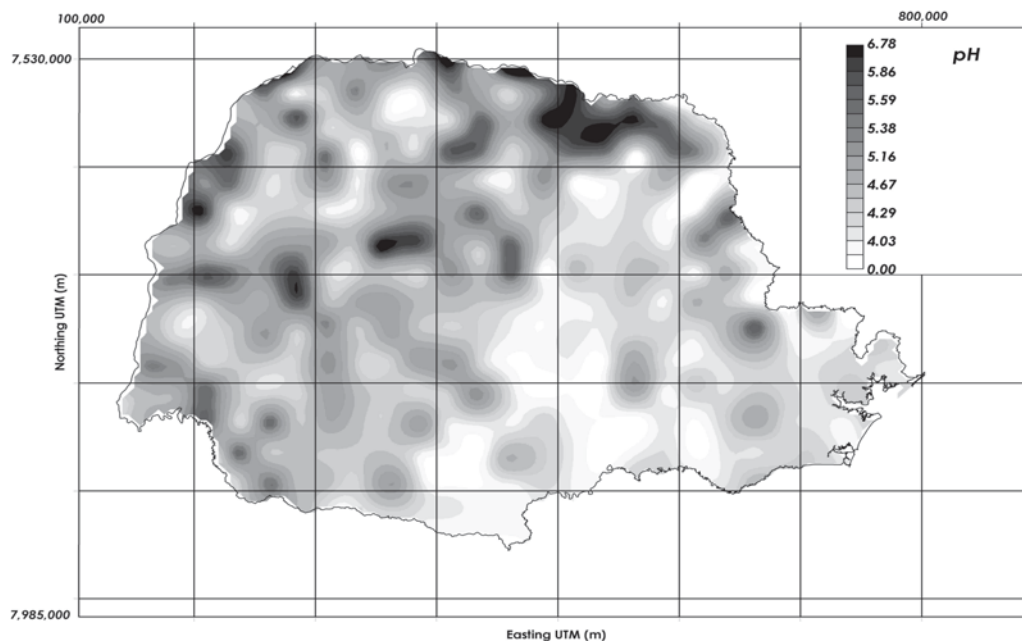


Figura 13 - Geochemical map showing the geographic distribution of pH for 307 soil - B horizon samples (Licht & Plawiak 2005).

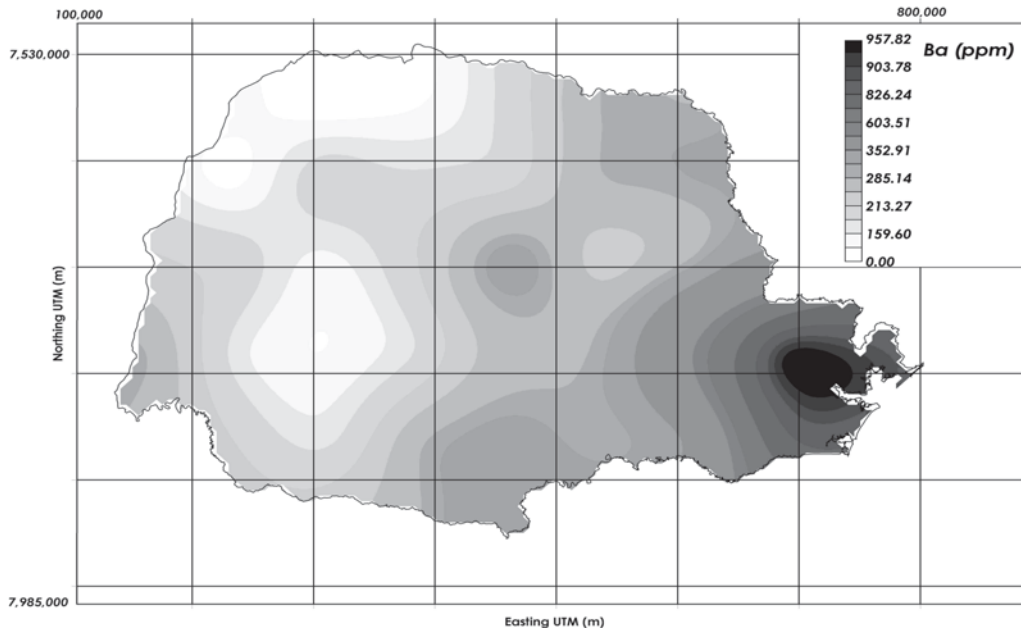


Figure 14 - Geochemical map showing the geographic distribution of Ba (ppm) for 39 GGRN sub-cells composited from 696 stream sediment samples (Licht 2001).

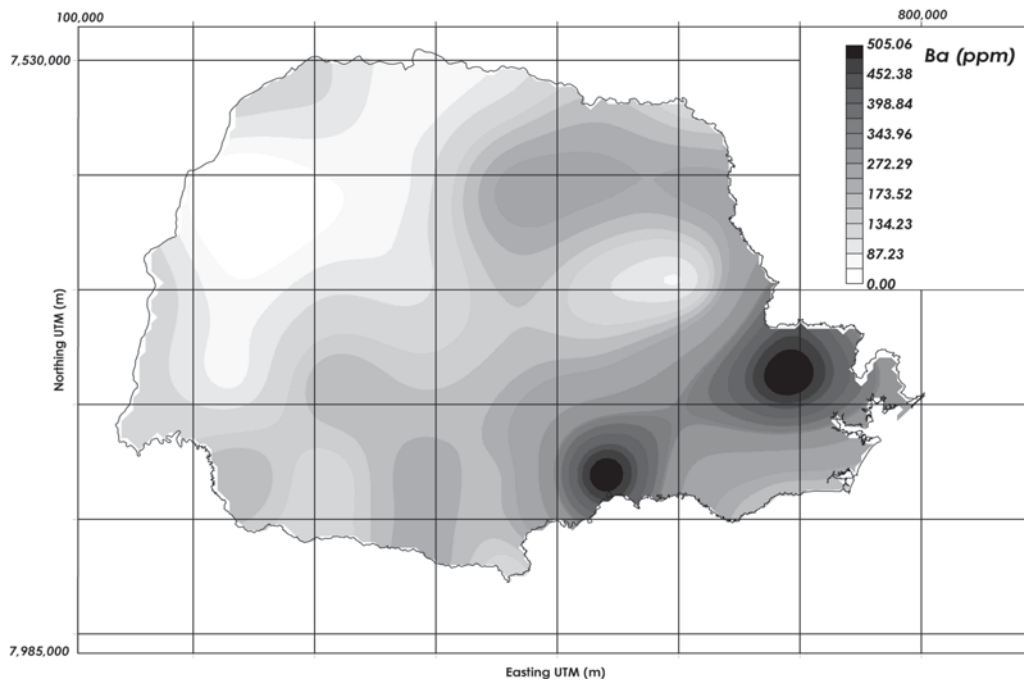


Figure 15 - Geochemical map showing the geographic distribution of Ba (ppm) for 43 GGRN sub-cells composited from 307 soil - B horizon samples (Licht & Plawiak 2005).

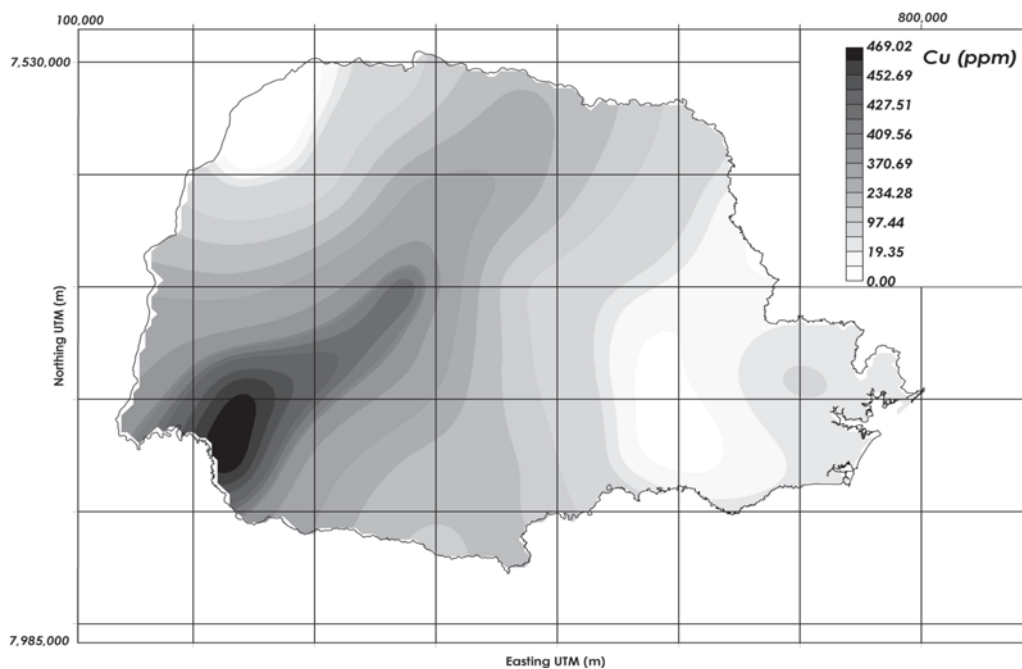


Figure 16 - Geochemical map showing the geographic distribution of Cu (ppm) for 39 GGRN sub-cells composited from 696 stream sediment samples (Licht 2001).

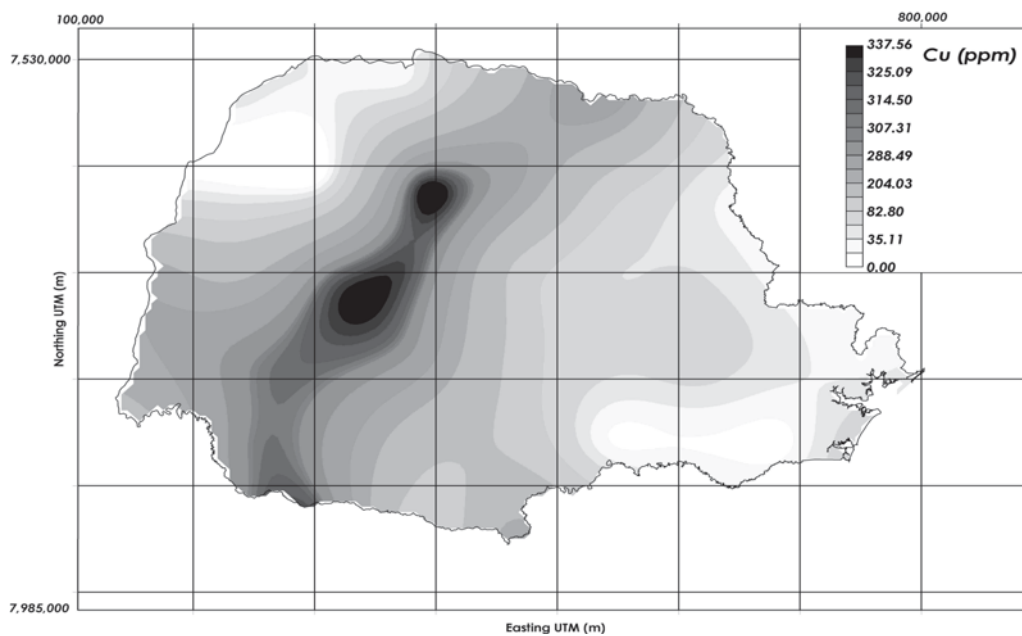


Figure 17 - Geochemical map showing the geographic distribution of Cu (ppm) for 43 GGRN sub-cells composited from 307 soil - B horizon samples (Licht & Plawiak 2005).

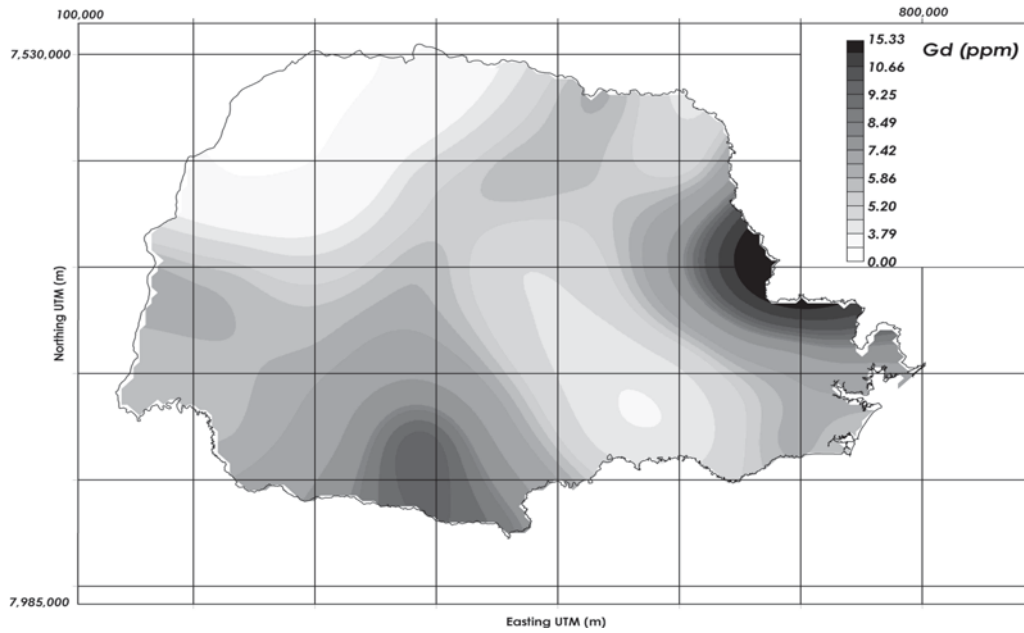


Figure 18 - Geochemical map showing the geographic distribution of Gd (ppm) for 39 GGRN sub-cells composited from 696 stream sediment samples (Licht 2001).

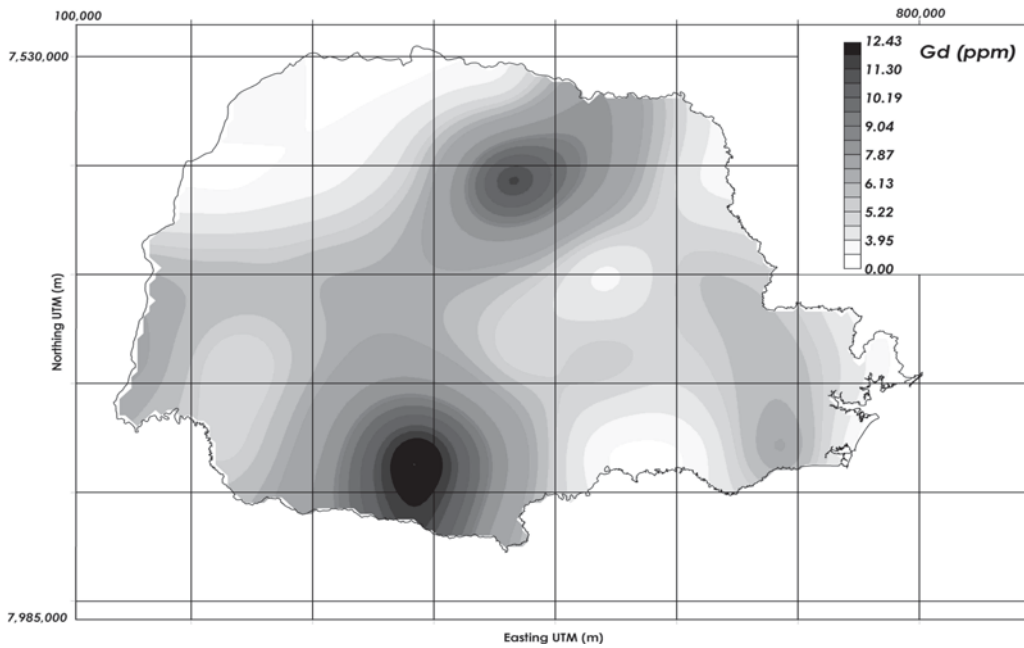
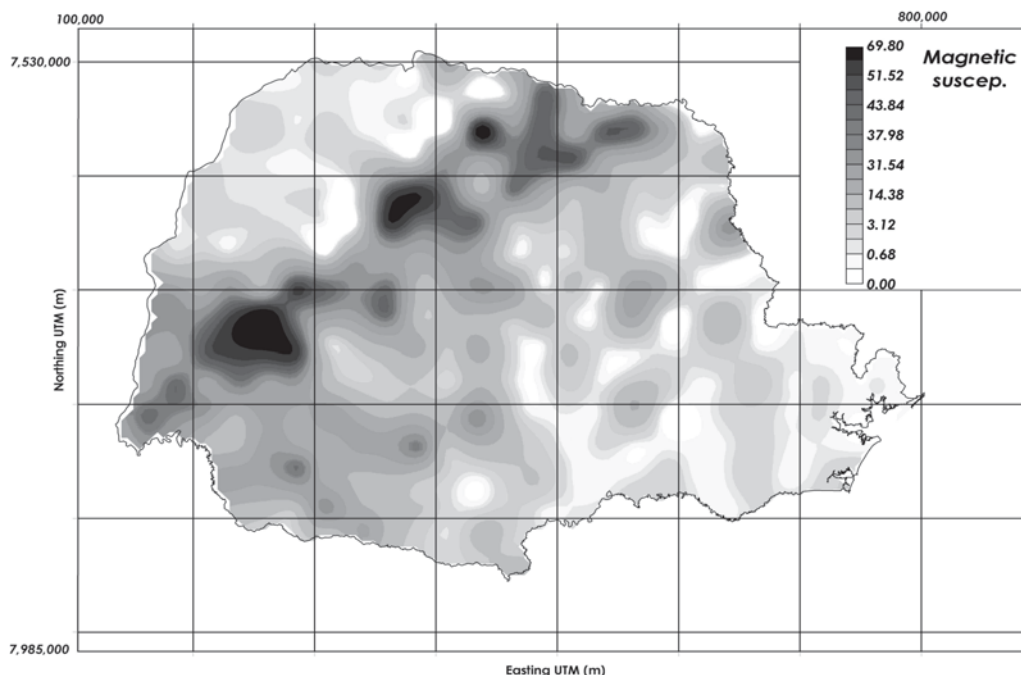


Figure 19 - Geochemical map showing the geographic distribution of Gd (ppm) for 43 GGRN sub-cells composited from 307 soil – B horizon samples (Licht & Plawiak 2005).

Figure 20 - The geographic distribution of the magnetic susceptibility for 307 soil – B horizon samples (Licht & Plawiak 2005).



CONCLUSIONS

The constitution of this robust database, based on stream sediment and soil samples, allowed to establish reference levels for a number of variables, acting as a milestone to other researches dealing with the distribution of the analysed elements and other physical and chemical parameters in the State of Paraná's territory.

Comparing the tables, it is possible to identify great consistency and coherence in the elemental distribution in both sampling media, reflecting the representativeness of the sampling procedures, the adequacy of sampling spacing to the regional scale of the surveys and the high quality of the laboratory techniques reaching ultra-low detection limits, specially for the trace and ultra-trace elements.

It is necessary to take into consideration that the elements contents are not homogeneously distributed over the whole territory, but showing regionalized variations due to several factors coming from diverse origins. To be appropriately used, and to establish causal relationships, maps

showing the geographic distribution of the variables must be considered along other types of maps like

geological, pedological, the land use and occupation and even maps showing the distribution of endemic diseases in humans, flora and fauna.

Conclusively, the authors suggest that the investigation must continue, by (a) collection of stream and ground water, other soil horizons and rocks following methodologies strictly compatible to the applied to stream sediments and soils - B horizon; (b) determination of chemical speciation mainly the bio-availability, to amplify the application and use of the results in environmental, biological, sanitation and epidemiological researches.

ACKNOWLEDGEMENTS

The authors thank to all people direct or indirectly involved in the project, mainly the field and laboratory teams from Mineropar, Emater-PR, IGGE, Iapar/Ld and LPGA/UFPR. Dr. Eduardo Salamuni (Mineropar and UFPR), Dr. Edir Edemir Arioli (Mineropar) and Prof. Dr. Reijo Salminen (Geological Survey of Finland - GSF) and an anonymous referee of the Boletim Paranaense de Geociências are acknowledged for their criticisms and suggestions that played an important role to improve the manuscript.

REFERENCES

- BIRKE M. 2004. *Geochemical Atlas of Germany*. In the Internet: http://www.bgr.bund.de/cln_030/nn_454944/EN/Themen/Geoumweltschutz/Projekte/Geochemical__Atlas__of__Germany/Geochemischer__Atlas__Deutschl.html. Access: June, 12th. 2005
- BIRKE M. U. & RAUCH. 1997. Geochemical mapping in the new Federal States of Germany. *Abstracts of the 4th Internat. Sympos. on Environm. Geochemistry*, Open File Report 97-496, U.S. Geological Survey, 11-12.
- 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*. Paris, Unesco. Final Report of IGCP Project 259.
- EMBRAPA - Empresa Brasileira de Pesquisa Agropecuárias. 1999. *Manual de análises químicas de solos*. In: DA SILVA F. C. (Org.) Brasília, EMBRAPA Informática Agropecuária. In Portuguese.
- FERREIRA A. M. P. J. 2000. *Dados geoquímicos de base de sedimentos fluviais de amostragem de baixa densidade de Portugal Continental: estudo de factores de variação regional*. Dept. of Geosciences, Univ. Aveiro, Aveiro. (Doctor These). In Portuguese.
- FORTESCUE J. A. 1985. *A standardized approach to the study of the geochemistry of humus*. Williams property, Hemlo. Tunder Bay District. Ontario, Ontario Geol. Survey. (Map 80 754, Geochemical series).
- GUSTAVSSON N., BØLVIKEN B., SMITH D. B., SEVERSON R. C. 2001. *Geochemical landscapes of the conterminous United States – new map presentations for 22 elements*. U.S. Geological Survey Prof. Paper 1648.
- IAPAR. 1994. *Cartas climáticas do Estado do Paraná*. In: CORREA A. R. (Org.) Londrina, Iapar. (Documento 18). In Portuguese.
- INSTITUTO DE TERRAS, CARTOGRAFIA E FLORESTAS – ITCF. 1987. *Atlas do Estado do Paraná*. Curitiba, ITCF / DIOE. In Portuguese.
- KABATA-PENDIAS A. & PENDIAS H. 1992. *Trace elements in soils and plants*. 2 ed. London, CRC Press.
- KOLJONEN T. (Ed.), ELO S., GUSTAVSSON N., HUUMA L. K., KAURANNE K., KOLJONEN T., NORAS P., PESONEN L. J., RUOTOISTENMÄKI T., SALTIKOFF B., SILLANPÄÄ M., TANSKANEN H., VAASJOKI M., VUORELA P. 1992. *The geochemical atlas of Finland*. Helsinki, Geol. Survey of Finland.
- LICHT O. A. B. 2001. *A geoquímica multielementar 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. Dept. of Geology, Univ. Federal Paraná, Curitiba (Doctor These). In Portuguese.
- LICHT O. A. B. & PLAWIAK R. A. B. 2005. *Geoquímica de Solo do Paraná - horizonte B*. Curitiba, Mineropar. 2 v. 740 p. In Portuguese.
- MAACK R. 1968. *Geografia física do Estado do Paraná*. Curitiba, Badep / UFPR / IBPT. In Portuguese.
- MIKO S., HALAMIÆ J., PEH, Z., GALOVIÆ, L. 2001. Geochemical baseline mapping of soils developed on diverse bedrock from two regions in Croatia. *Geologia Croatica*, 54(1):53-118.
- MINEROPAR – MINERAIS DO PARANÁ S.A. 1986. *Mapa geológico do Estado do Paraná*. Curitiba, Mineropar 1:1,400,000. in Portuguese.
- PLANT J. A., SALMINEN R., BIDOVEC M., DE ALMEIDA FARINHA M., DE VIVO B., DEMETRIADES A., DE VOS W., HAUGLAND T., KORRE A., LIMA A., O'CONNOR P. J., OTTESEN R. T., PIRC S., REEDER S., SALPETEUR I., SIEWERS U., SMITH B., SVECOVA J., TARVAINEN T. 2004. The surface geochemistry of Europe: preliminary findings of the Foregs geochemical baseline study. In: International Geological Congress, 32, IUGS, Florence. *Abstracts...* part 2, 1530.
- RANKAMA K. & SAHAMA Th. 1954. *Geoquímica*. Madrid, Aguilar.
- SALMINEN R., AHLSSVED C., BATISTA M. J., BIDOVEC M., DEMETRIADES A., DE VIVO B., DE VOS W., DURIS M., FRIZZO P., GILUCIS A., GREGORAUSKIENE V., HALAMIC J., HAUGLAND T., HEITZMANN P., JORDAN G., KIVISILLA J., KLAVER G., KLEIN P., LIMA A., LIS J., LOCUTURA J., MARSINA K., MAZREKU A., MRNKOVA J., O'CONNOR P. J., OLSSON A. A., OTTESEN R. T., PASIECZNA A., PETERSELL V., PIRC S., PLANT J. A., REEDER S., SABATINI G., SALPETEUR I., SANDSTRÖM H., SCHERMANN O., SIEWERS U., STEENFELT A., TARVAINEN T., VAN DER SLUYS J. 2004. FOREGS Geochemical baseline mapping programme – a new European wide database and geochemical atlas. In: International Geological Congress, 32, IUGS, Florence. *Abstracts...* part 2, 1531-1532.
- STEENFELT A. 1985. Geochemical mapping and prospecting in Greenland – A review of results and experience. In: GARRET R. G. (Ed.) *Geochemical Exploration 1985. J. Geochem. Explor.* 29():183-205.
- TARVAINEN T., AHLSSVED C., ALBANESE S., REEDER S., SALMINEN R., SANDSTRÖM H. 2004. FOREGS geochemical mapping programme: assessment of analytical and data quality. In: International Geological Congress, 32, IUGS, Florence. *Abstracts...* part 2, 1530.
- XUEJING X. & TIANGXIANG R. 1993. Geochemical mapping and environmental geochemistry: progress in China. *Jour. of Geoch. Explor.*, Vancouver, 49():15-43.