ARTICLE

https://doi.org/10.1590/2317-4889202220220018

BJGEO
Brazilian Journal of Geology

Methodological approach and general guidelines to geochemical mapping and background-baseline analysis for environmental assessment: a case study in the Carajás Mineral Province, Brazil

Pedro Walfir Martins Souza-Filho[1,2]*, Prafulla Kumar Sahoo[1,3], Marcio Sousa da Silva[1,2], Roberto Dall'Agnol[1,2], Carlos Augusto Medeiros Filho[4], Alessandro Sabá Leite[1,2], Jair da Silva Ferreira Júnior[1], Wilson da Rocha Nascimento Junior[1], Géssica da Silva e Silva[1], Gabriel Negreiros Salomão[2], Fabiana Sarracini[5], Renato Oliveira Silva Junior[1], Marlene Furtado da Costa[6]

Abstract

We present this manuscript as a methodological approach and general guidelines for geochemical mapping and background/baseline projects for environmental assessment in tropical areas. A case study was carried out in the Itacaiúnas River watershed (IRW), Eastern Amazon, to fill in a gap in knowledge on the distribution of chemical elements, particularly those potentially toxic, in the near-surface environment of the area. The high-impact results of this research project revealed the need for similar scientific investigation across the globe with the implementation of a systematic methodology. The study shows, for example, the importance of well-planned field activities, multi-medium sampling, analytical methods, laboratory procedures, database construction, and general aspects of data processing and statistical treatment. The importance of this contribution is that it can be used as a reference in support of geospatial analysis in research within the scope of geochemical mapping and background-baseline projects. The database is accessible through a web-based geographic information system front-end; a Geochemical Atlas of the IRW will be available as soon as possible.

KEYWORDS: sampling methodology; geochemical mapping; soil; stream sediment; stream water; GIS.

INTRODUCTION

Regional geochemical surveys have been used in mineral exploration since the mid-20th century for the location of mineral deposits. In the 1990s, an international project was created to stimulate geochemical surveys on all continents, following a standardized methodology to ensure comparability of the data from different areas and countries (Darnley 1997). With the advancement of environmental awareness and the strengthening of sustainability principles, geochemical mapping has been used to identify anthropogenic effects on the natural environment and the possibility of better quantification of environmental impacts (Reimann *et al.* 2005). The regional studies available in the literature reveal that geological setting, geomorphology, pedology, regional climate, and soil cover and use are among the main determinants of the geochemical distribution of elements in the landscape (Birke *et al.* 2015a, Zuo *et al.* 2016, Sahoo *et al.* 2020a). These factors are largely responsible for the geogenic, or "natural" geochemical signature of a given region. Anthropogenic actions can modify the original geochemical signature and generate disturbances in the environment, but the geogenic signature is usually dominant (Wang and CGB Sampling Team 2015, Gloaguen and Passe 2017, Reimann *et al.* 2017).

In addition to the experience established by geological surveys in regional geochemical studies around the world, several studies have been carried out on geochemical mapping at continental and regional scales (Birke *et al.* 2015b, Liu *et al.* 2015, Woodruff *et al.* 2015). Continental mapping scales range from 1:10,000,000 (1 sample/10,000 km^2) to 1:5,000,000 (1 sample/1,600 km^2), while regional mapping scales range

---

Supplementary data

Supplementary data associated with this article can be found in the online version: Supplementary Table A.

---

[1] Instituto Tecnológico Vale – Belém (PA), Brazil. E-mails: pedro.martins.souza@itv.org, walfir@ufpa.br, prafulla.iitkgp@gmail.com, marcio.sousa.silva@itv.org, roberto.dallagnol@itv.org, alessandro.leite@pq.itv.org, jair.junior@itv.org, wilson.nascimento@itv.org, gessicaesilva@gmail.com, renato.silva.junior@itv.org

[2] Geosciences Institute, Universidade Federal do Pará – Belém (PA), Brazil. E-mail: salomao.gn@gmail.com

[3] Department of Environmental Science and Technology, School of Environmental and Earth Sciences, Central University of Punjab – Punjab, India.

[4] Mineral Exploitation, Vale S.A. – Parauapebas (PA), Brazil. E-mail: carlosaugusto.caca@gmail.com

[5] Zoobotanical Park, Environmental Studies Management, Vale S.A. – Parauapebas (PA), Brazil. E-mail: fabiana.sarracine@vale.com

[6] Environmental Management of Port and Railway, Vale S.A. – São Luís (MA), MA, Brazil. E-mail: marlene.costa@vale.com

*Corresponding author.

from 1:1,000,000 (1 sample/100 km^2) to 1:10,000 (1 sample/10,000 m^2) (Demetriades *et al.* 2015, 2018). Geochemical mapping data are typical geospatial data, where X and Y represent geographic coordinates and Z represents geochemical attributes, and the development of computational geographic information system (GIS) platforms has facilitated the manipulation of geochemical data and geospatial statistical analysis (Smith *et al.* 2018).

A search carried out in the Scopus database using three keywords ("geochemical mapping," "geochemical background," and "geochemical baseline") shows that research on this topic is especially concentrated in China, North America, Australia, and several countries in Europe. In developing countries with historical mineral extraction industries, such as Brazil, India, and South Africa, these studies are still in the initial phase (Fig. 1). In Brazil, we highlight the studies carried out in the Carajás Mineral Province in the State of Pará (Sahoo *et al.* 2019a, 2019b, Salomão *et al.* 2018, 2019) and in the Iron Quadrangle region in the state of Minas Gerais (Costa *et al.* 2015a, Costa *et al.* 2018, Larizzatti *et al.* 2018), where the largest and oldest mineral provinces in Brazil are located.

Systematic studies of geochemical mapping in Brazil date from the 1970s to 1980s, when the first regional geochemical surveys were carried out in the Precambrian terranes of Paraná state. They were followed by the geochemical mapping of stream sediments and soils in the entire Paraná state, covering 199.315 km^2 (Licht 2018). In the past decade, low-density sampling studies were carried out in northeastern Brazil to determine the geochemical baseline of some elements in soil samples (Matschullat *et al.* 2012, Schucknecht *et al.* 2012, Gloaguen and Passe 2017). Geochemical mapping results have been published more frequently in the past decade. Notably, the first high-density surveys in the Iron Quadrangle have allowed us to recognize the role of lithology in the elemental composition of stream sediments and to establish reference values for the main river basins (Costa *et al.* 2015b, Costa *et al.* 2018). The second high-density survey have been performed in the Itacaiúnas River watershed (IRW), the objective of this study case (Fig. 2), where high-resolution hydrogeochemical surveys were carried out to estimate baseline concentrations of trace elements in surface water (Sahoo *et al.* 2019b), to elaborate geochemical mapping and determination of the background concentrations of iron and potentially toxic elements in active stream sediments in Carajás (Salomão *et al.* 2019), and to determine the source and background threshold values of potentially toxic elements in soils from multivariate statistics and GIS-based mapping (Sahoo *et al.* 2020a).

Advances in geochemical mapping in the IRW have occurred following the development of the Itacaiúnas Geochemical Mapping and Background Project (ItacGMBP). The aim of this study is to present the methodological approach and general guidelines to support geochemical mapping and background projects for environmental assessment, particularly in tropical rainforest areas like the

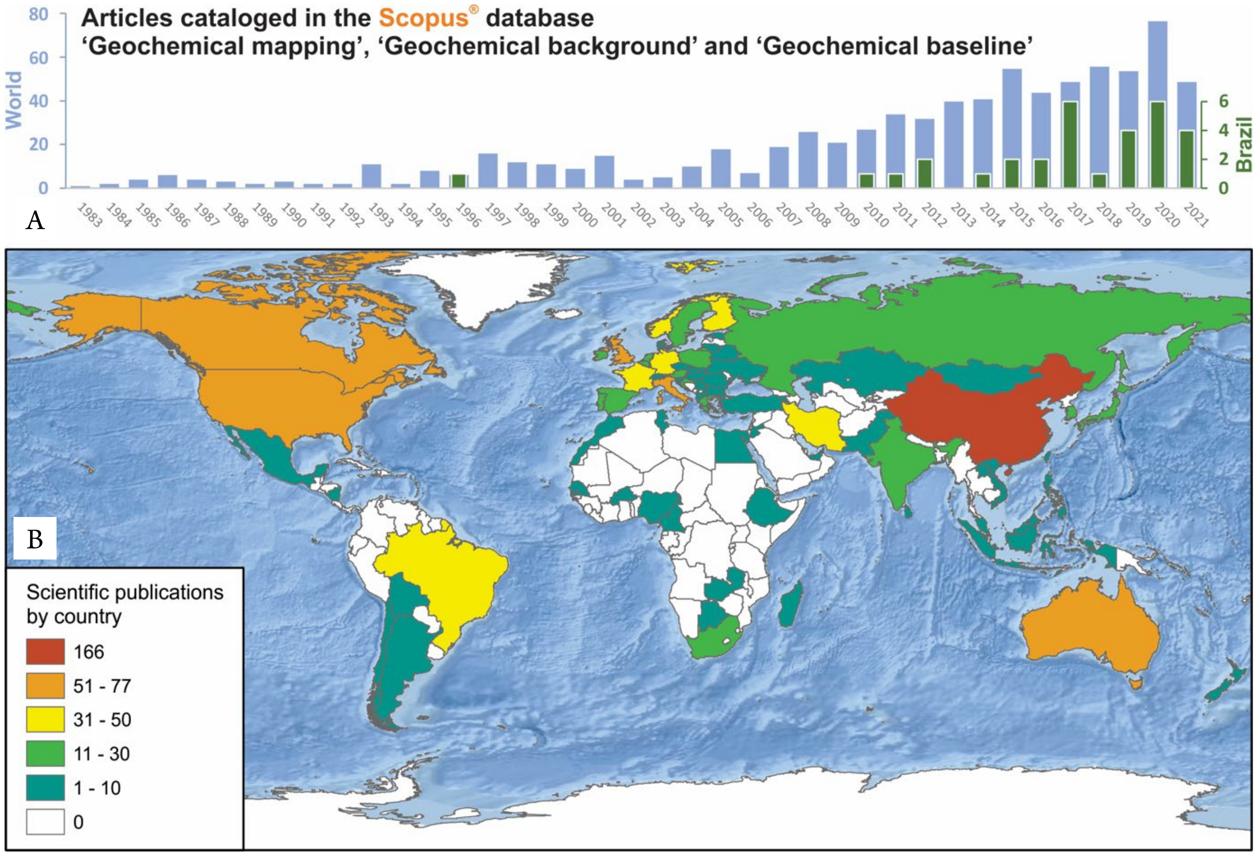
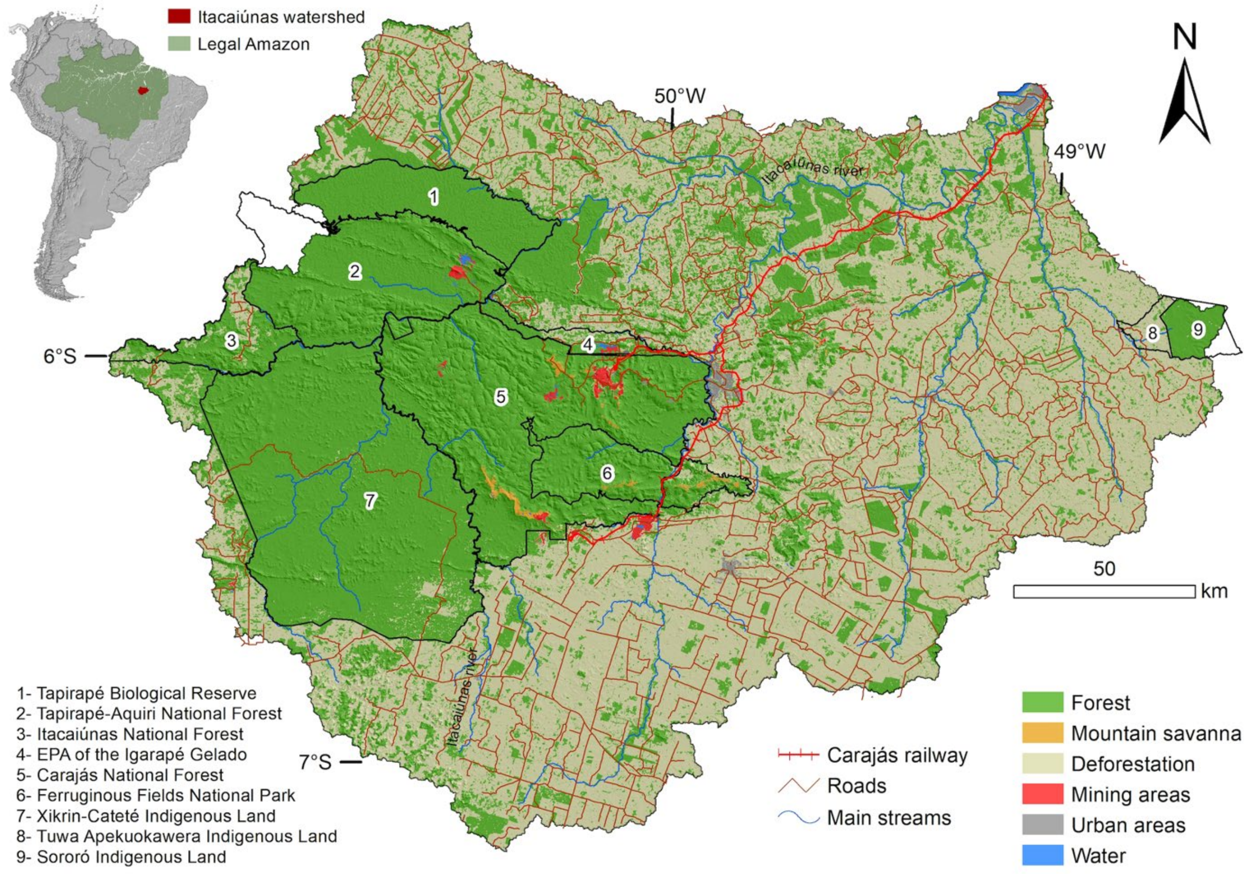


Figure 1. Search results in the Scopus database using the following keywords: "Geochemical mapping," "geochemical background," and "geochemical baseline." (A) Time series plot of the number of articles published annually in the world (Kuenzer *et al.* 2011) and in Brazil (green) from 1983 to 2021. (B) Spatial distribution of the cumulative number of articles published by country.



IL: indigenous lands; EPA: environmental protected areas.

Source: Modified from Souza-Filho *et al.* (2018).

Figure 2. Land cover and land use map of the Itacaiúnas River watershed, generated from 2017 Landsat-8 OLI mosaic images.

Eastern Amazon. Important characteristics are discussed, which include the project setup, field activities, multimedium sampling, analytical methods, laboratory procedures, database construction, general aspects on data processing, and statistical treatment.

A GENERAL OVERVIEW OF THE ITACAIÚNAS GEOCHEMICAL MAPPING AND BACKGROUND PROJECT

Timeline

The ItacGMBP project planning started in the first half of 2016. Following the sampling plan, fieldwork was initiated in February 2017, including the initial training of sampling teams, and was concluded in February 2018. Stream water sampling in the rainy season was carried out from February to June 2017 and in the dry season from July to October 2017. Stream sediment sampling was carried out from February 2017 to January 2018 due to different water discharge conditions. The soil sampling campaign started in April 2017 and finished in February 2018. Sample preparation and chemical analysis were started in mid-2017 and finished in mid-2019. Mineralogical analysis of surface soil and stream sediment samples were started in mid-2018 and finished in mid-2019. Data analysis, reporting, and the first scientific publications took place in early 2018. The official and integrated dataset of the project, which includes data from all three-sampling mediums, was concluded in mid-2019.

SAMPLING METHODOLOGICAL APPROACH

Construction of the GIS database

The collection of georeferenced socioenvironmental data was the first step in the development of the project. Information related to geographic space was collected and stored in a GIS database. All vector and raster data were properly classified or converted into the geographic reference system (datum) WGS 84 (World Geodetic System) in order to standardize the systems of reference of the different sources used. Supplementary A summarizes the main information acquired, which includes: the land cover and land use layers from the sampling period, highlighting potential areas of anthropogenic impacts (e.g., urban areas, mining, and pasturelands); the simplified geological map, considering the four main geological domains of the IRW, determined accordingly to their surface geochemical response (Rio Maria — Sapucaia — Canaã dos Carajás domains: RM-S-CC; Carajás Basin: CB; Bacajá Domain: BD; Araguaia belt: AB); geomorphological units of the area, derived from digital elevation model; and climatological and hydrological information of the study area. For the management of the GIS environment, data treatment, and creation of thematic maps, the ArcGIS 10.4 (https://doc.arcgis.com/pt-br) and QGIS (https://docs.qgis.org) software were used.

Data collection and GIS computer-based framework for sampling and data validation

A computer-based framework was developed for sample collection and data storage, screening, validation, and visualization (Fig. 3). The framework is composed of three main components: an iPad application mobile front-end; a server back-end; and a GIS web application front-end.

The iPad application helps field teams locate planned collection points, ensures samples are collected in the correct location, validates sample data input, and prevents field teams from collecting multiple samples in the same microbasin, except for duplicates. Additionally, the iPad application uses the Internet to connect to a server back-end to send new sampling information stored in the current iPad and to receive samples stored on other teams' iPads. The combination of these capabilities minimizes field registration errors, improves information accuracy, and enhances field team communication.

The server back-end receives sample data from iPads in the field and, later, chemical analysis data from laboratories. In particularly, it enables sample data sharing and synchronization between different field teams and matches chemical analysis data from laboratories with their corresponding samples in the database, working as a central sampling and analysis repository. It also performs several additional validations, such as ensuring the uniqueness of collected samples and detecting anomalous analysis results needing clarification.

Finally, the GIS web application provides online geochemical maps and statistical plots that make project data available to stakeholders and project team members. In short, the computer-based framework provides fast data processing, early error detection, and data visualization tools that enable the high-density sampling presented in this work.

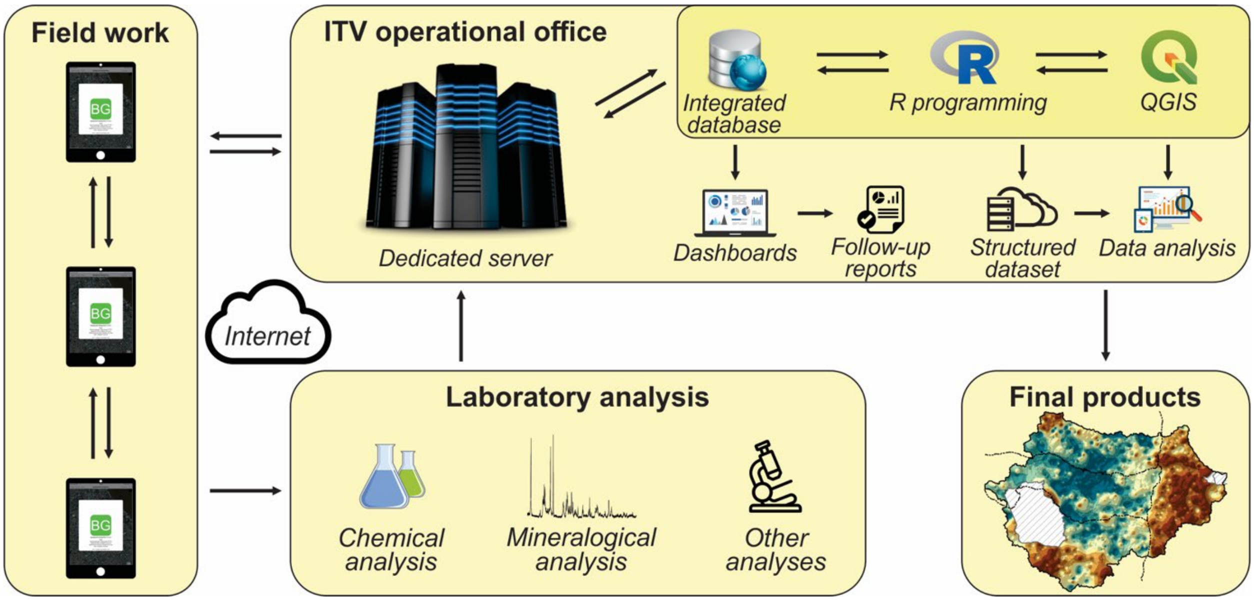
General strategies for site selection based on GIS tools

The general approach used for the planning field survey based on GIS and the entire sampling campaign in the ItacGMBP was defined to perform systematic geochemical mapping, considering the best available method to determine the level of chemical elements in soil, stream sediment, and stream water samples.

The choice of mapping scale, sampling density, and computational site selection

The ItacGMBP geochemical mapping was carried out at different sampling densities during the regional-scale survey.

- Figure 4 shows the sample points plotted over maps of elevation, geomorphological landscape, geology (lithology), and land cover and land use. This sampling strategy guided the location of all sample points (soil, stream water, and sediments) in the IRW.
- The sampling density of the soil geochemical mapping included grid and graticule layers that were generalized data displayed on the map. The grid and graticule tools were used to produce grids that contain geographic location indicators based on user-specified shapes, scales, coordinate systems, and units. In this study, one sample was taken in a grid of 5 km × 5 km (i.e., 1 sample/25 km^2), with a map scale equal to 1:250,000, totaling 1,790 sample points in the 41,342 km^2 area of the IRW (Fig. 5A). For quality control, for every 20 samples of water, stream sediment, and soil samples, a duplicate sample was collected, representing in the case of soils a total of 89 samples, and for stream sediments and water a total of 46 samples each;



Source: Salomão *et al.* (2020).

Figure 3. Schematic representation of the ItacGMBP's framework.

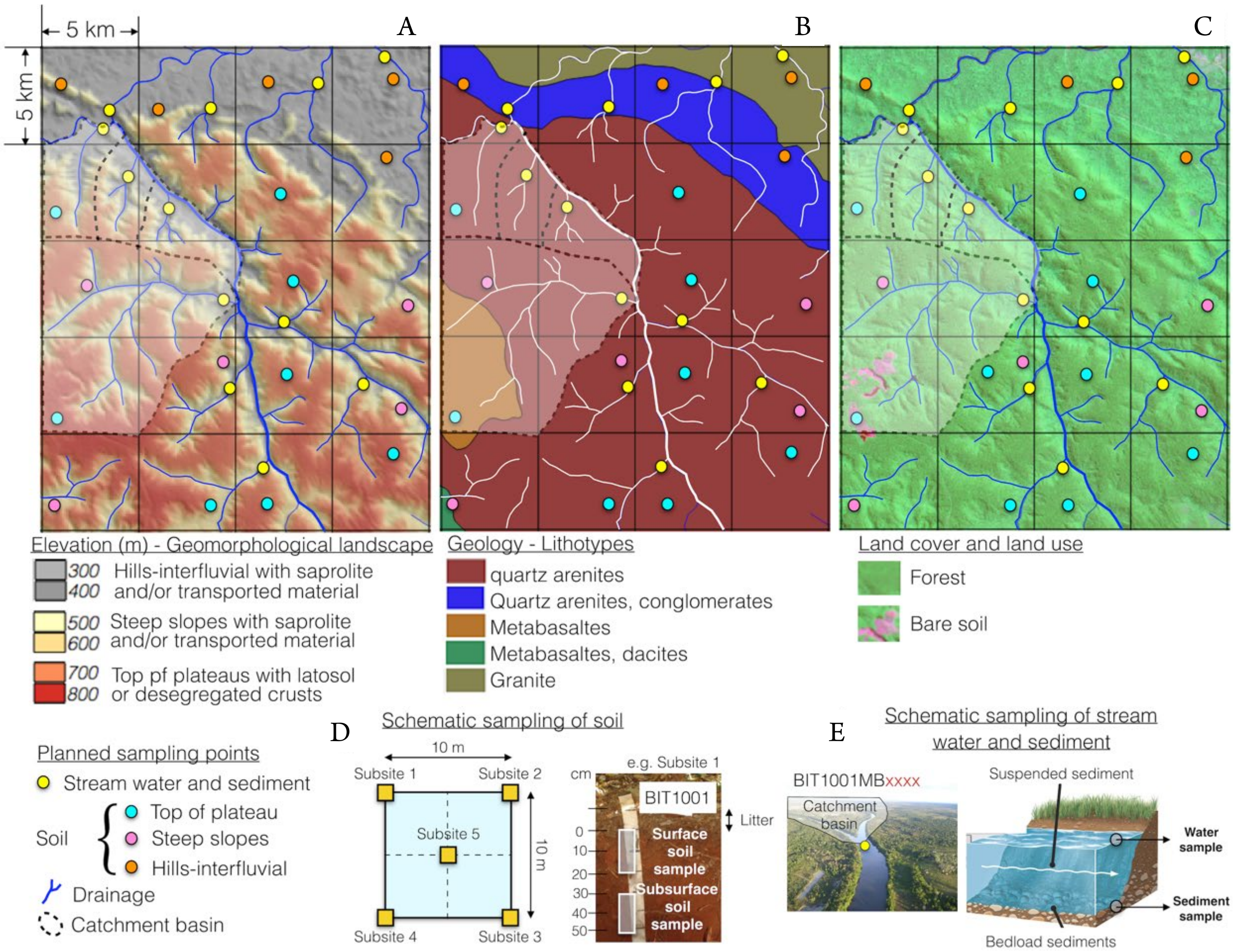


Figure 4. Sampling layout of soil samples superimposed on (A) elevation and geomorphological landscape, (B) geology (lithology), and (C) land cover and land use maps. Observe the schematic sampling layout of (D) soil samples and (E) stream water and sediment samples.

- The sampling density of the stream sediment and water geochemical mapping was generated from the watershed task in a GIS to delineate watersheds, for which one sample per each confluence point in the main 3rd- or 4th-order catchment microbasins was chosen, covering an approximate area of 10 km × 10 km (i.e., 1 sample/100 km^2), with a map scale equal to 1:1,000,000 (Fig. 5B), totaling 900 sample points in 41,342 km^2 of the IRW.

Prenumbered sample coding

Samples were always collected as close as possible to the location defined in the original planning. However, the collection teams had the autonomy to decide upon the final location of the sampling points, mainly due to access conditions. Each sample was identified with an alphanumerical code (ID) as follows:

- A three-digit code to identify the IRW (BIT in Portuguese);
- A four-digit sample number (e.g., 0246), and a code identifying the soil sample type: SS for superficial sample (0–20 cm) and SP for sub-superficial sample (30–50 cm); the sample codes are given as BIT0934SS and BIT0246SP;
- For stream water and sediment samples, a code identifying the microcatchment basin (MB) was inserted, followed by a four-digit microcatchment basin number (e.g., 0934), and a letter code identifying the nature of the sample, "A_ES" for stream water samples collected during the dry season (e.g., BIT0246MB0934A_ES), "A_EC" for stream water samples collected during the rainy season (e.g., BIT0246MB0934A_EC) and "C" for stream sediment samples (e.g., BIT0246MB0934C);
- In case of duplicate samples, the letter "_D" was added at the end of the code ID (e.g., BIT0934SS_D and BIT0246MB0934C_D).

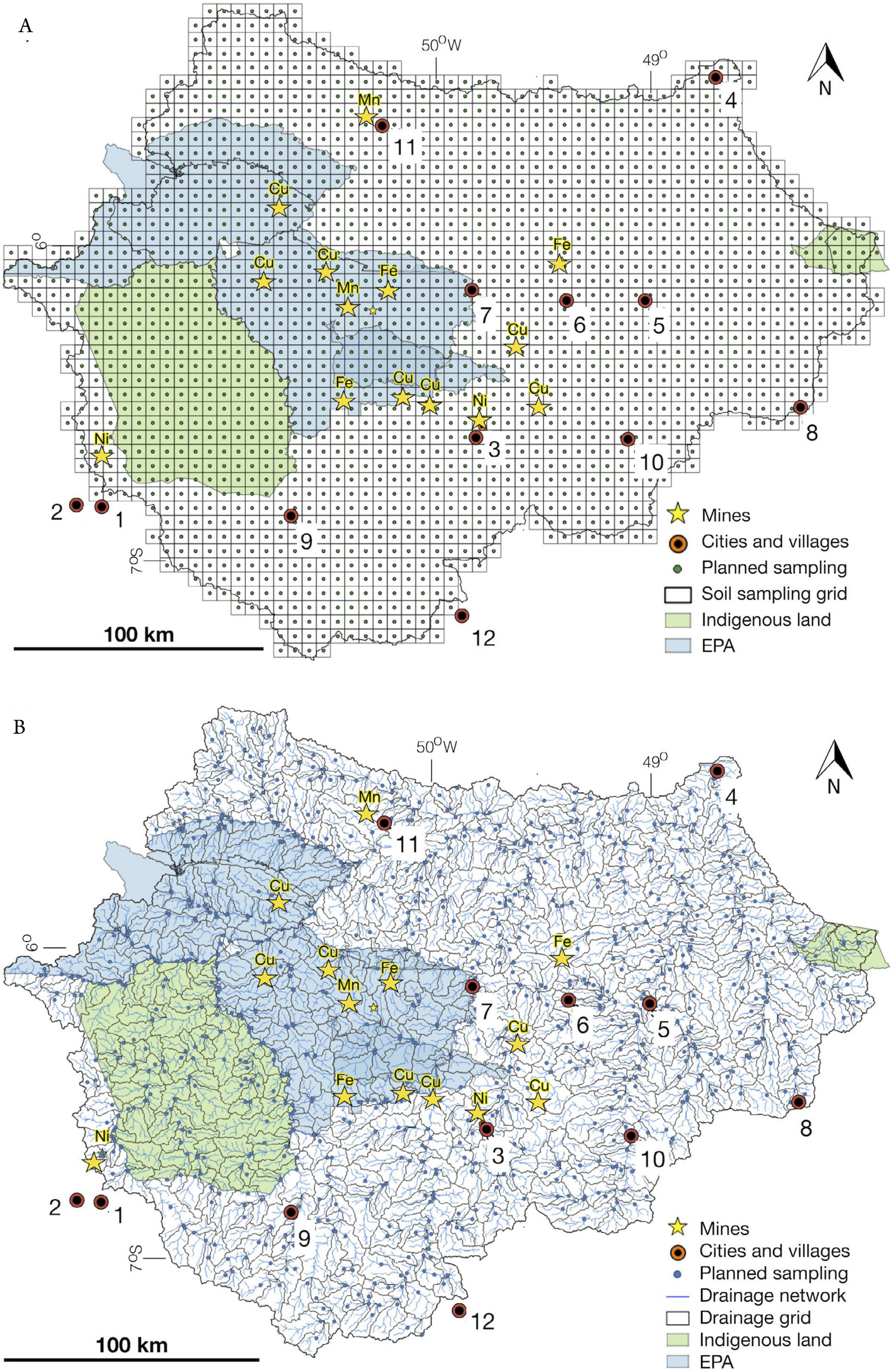
In-field site selection and final sampling network

The final distribution of the samples collected in the ItacGMBP is shown in Figure 6. Unfortunately, the ItacGMBP project did not obtain permission to collect samples in the areas of indigenous lands (cf. Fig. 1). Nevertheless, 83.2, 80.9, 73.7, and 70.9% of total planned samples of soils, stream sediments, stream water in the wet period, and stream water in the dry period, respectively, were collected. The grid and soil sampling points are shown in Figure 5A, and the microcatchments with the locations of sampling points for stream sediment and water in the rainy and dry periods are given in Figures 5B, 5C, and 5D, respectively.

Sample collection and documentation

Soil sampling guidelines

Soil sampling followed international procedures (Reimann 2014). The samples were collected at each sampling point on



1: Ourilândia do Norte; 2: Tucumã; 3: Canaã dos Carajás; 4: Marabá; 5: Eldorado dos Carajás; 6: Curionópolis; 7: Parauapebas; 8: Piçarra; 9: Água Azul do Norte; 10: Gogó da Onça; 11: Vila União; 12: Xinguara.

Figure 5. (A) Distribution of grid cells with soil sample locations and (B) distribution of water and sediment stream samples in 5th-order catchment basins in the ItacGMBP.

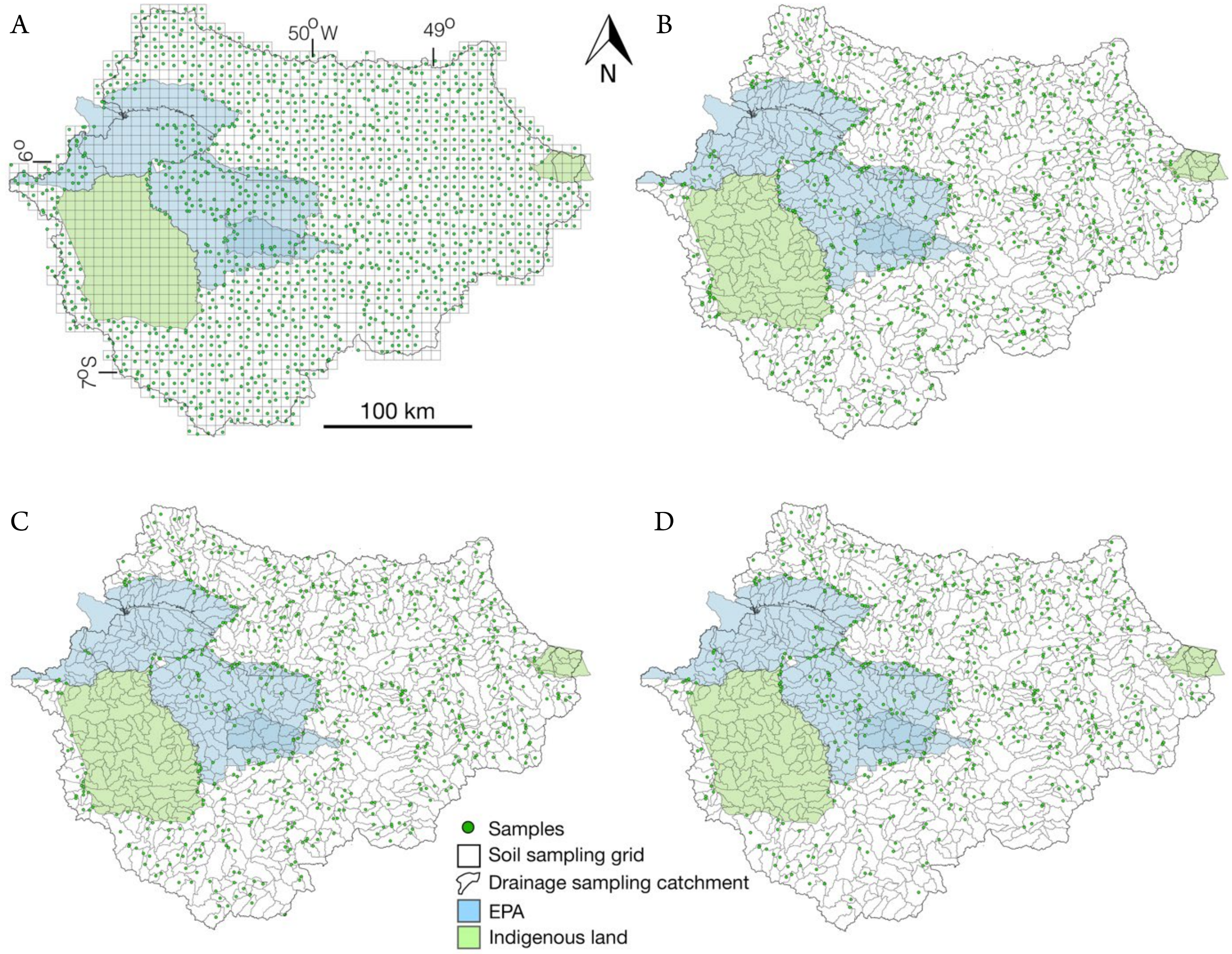


Figure 6. Distribution in the IRW of (A) the grid with soil sampling points; microcatchments showing (B) stream sediment; stream water sampling points during (C) the wet season and (D) the dry season based on ItacGMBP data.

the 5×5 km grid. All samples weighed approximately 4–5 kg, and they were composite samples collected from five pits at each corner and the center of a 10×10 m square (Fig. 4D) and homogenized to provide a representative field sample from the site. In all geomorphological landscapes, holes were dug with a fence posthole soil digger/grabber. After removal of the litter, samples were collected at different depth intervals of 0–20 cm (surface soil sample for the environmental background) and 30–50 cm (subsurface soil sample for the geogenic background) (Fig. 4D). Each composite sample (surface and subsurface soil) was placed directly into polyamide plastic sample bags with low migration, good oxygen, and moisture barrier properties. Figure 7 illustrates the procedures of soil collection from the site location to packing the sample in bags. All soil and stream sediment samples were weighed under natural conditions to obtain their wet weight.

Stream sediment and water sampling guidelines

The collection of stream sediments was carried out in an active depositional area, preferably in the middle of the channel to minimize contamination occurring at the margins. The sample was ideally taken from a small, 2nd- or 3rd-order drainage basin (~100 km^2) at the confluence with the main 3rd- or 4th-order basin to avoid any contamination that may lie upstream and to be representative of the microbasin. Before sampling, the oxidized layer from the stream bedload sediments was removed. A total of approximately 3 kg of superficial sediments was collected, and the material was packed in a polyamide plastic sample bag. The stream sediment sampling equipment, such as buckets, funnels, rubber gloves, spades, van Veen grabbers, and stainless steel trays and cups, was washed with stream water before and after sampling. Figure 8 shows the different steps of stream sediment sample collection. At each sample site, the sample ID, geographic coordinates, and other information mentioned in the soil sampling section were also recorded in the iPad. Preparation of the stream sediment samples followed the same procedure described for soil preparation.

The stream water sampling was performed in the same area as the stream sediment sampling during the dry and rainy seasons. Water samples were collected in the middle of the fluvial channel at a location upstream from the collection point of the stream sediments before the bottom was stirred to avoid contamination from resuspended sediments and other chemical and organic compounds.

At each location, two water samples were collected and stored in a high-density polyethylene bottles, one of approximately 30 mL for larger anion determination and the second

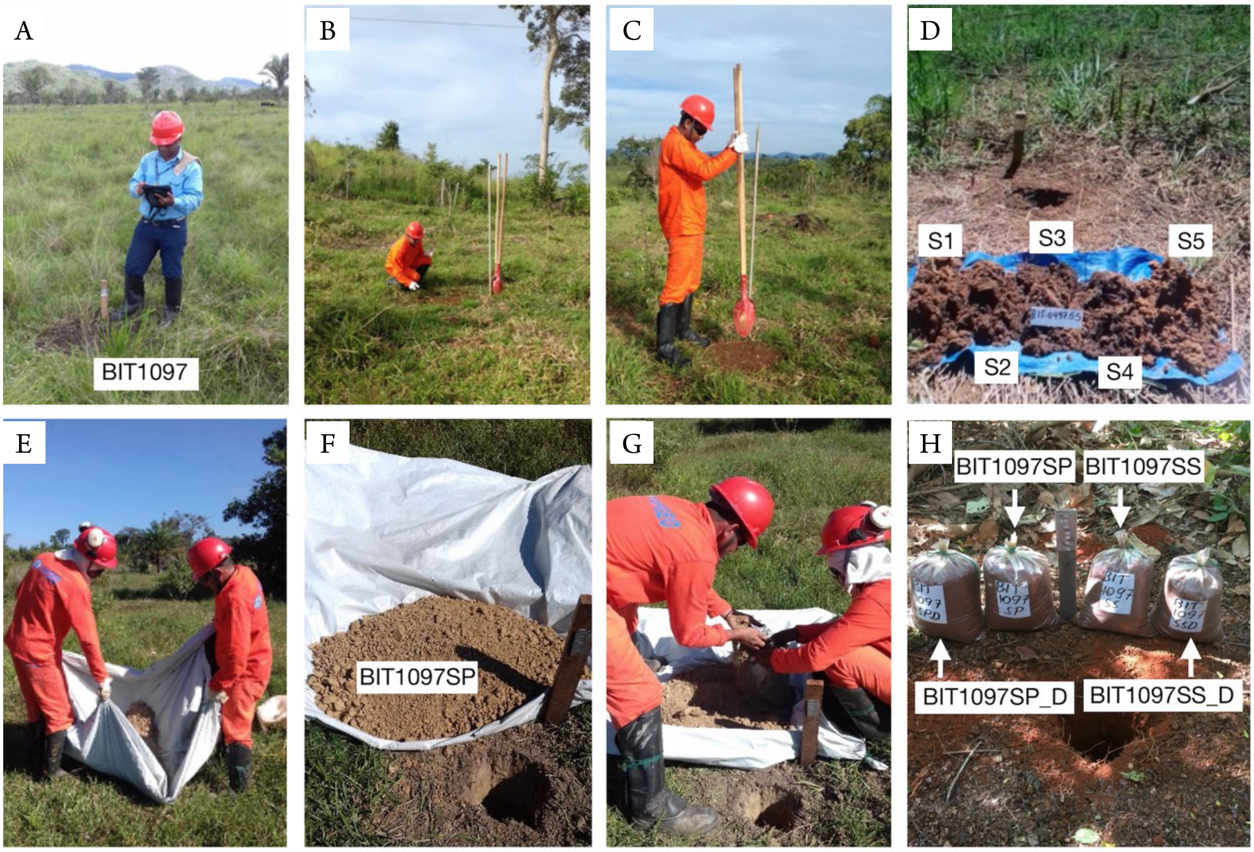


Figure 7. Example of soil sampling in a pastureland area. (A) Location of sample center subsite and collection of sample ID (BIT1097), geographic coordinates, and other information; (B) grass removal; (C) digging hole in the ground; (D) composite soil sample representative of five different subsites (S1, S2, S3, S4, and S5; cf. Fig. 8D); (E) homogenization of composite soil sample; (F) composite soil sample ready to be packed; (G) composite soil sample being placed in the bag; and (H) surface (BIT1097SS) and subsurface (BIT1097SP) composite soil samples and duplicates (BIT1097SS_D) (BIT1097SS_D) packed into bags.

one of approximately 60 mL for metals and metalloids quantification. The unfiltered water samples used to determine metals were acidified with 1 M ultrapure nitric acid ($pH < 2$) at the time of collection (Sahoo *et al.* 2019b). All stream water samples were refrigerated after collection until analysis. The analytical methods used for the determination of the variables followed the procedures and methodologies recommended in the Standard Methods for the Examination of Water and Wastewater (SMWW) methods 1060 and POP LB 010 (APHA, 2012).

Figures 8D–8H shows the different steps of stream water sample collection. Stainless steel trays, bottles, decanters, funnels, buckets, rubber gloves, syringes, and other equipment were washed twice with stream water before and after the sampling. Sample identifiers were marked on the bottle with a permanent label.

Field measurements and in-field documentation

At each location, five in situ physicochemical parameters (pH, electrical conductivity, dissolved oxygen, temperature, and redox potential) were measured with a multiparameter probe (HI 98194 from Hanna Instruments®).

At each sample site, sample ID, geographic coordinates, site location, high-resolution digital photographs of the general landscape and composite samples, and field observations, such as geomorphological landscape, soil texture, predominant land cover or land use, and presence of rock outcrops, were recorded on a high-spatial-resolution satellite image and stored in the iPad. Field observations, such as sample ID, geographic coordinates, and other information, were also recorded in the GIS web application.

LABORATORY PROTOCOLS, ANALYTICAL METHODS, AND QUALITY CONTROL

The analytical methods adopted for water samples were previously determined for the entire set of samples of the BGI project. Protocols for sample preparation and analytical methods are similar to those adopted in geochemical mapping projects by the Geological Survey of Brazil (CPRM, Companhia de Pesquisa de Recursos Minerais) and worldwide, for instance, in Europe (Salminen 2005), Australia (Caritat *et al.* 2009, Caritat 2018), and China (Wang and CGB Sampling Team 2015).

Chemical and mineralogical analyses of soil and sediment samples

Soil and stream sediment samples were prepared before sending to the laboratory for analysis. The samples were oven-dried at 45°C, disaggregated manually using a porcelain mortar and pestle, and homogenized. Then, each sample was split into two subsamples, one of 1,000 g for storage and future investigation,

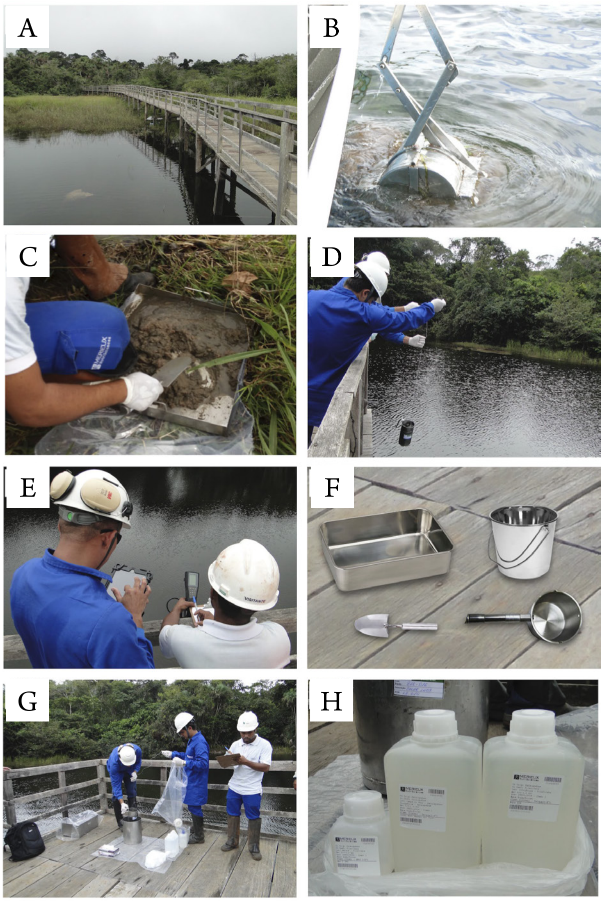


Figure 8. (A) General view of the landscape; (B) stream sediment sampling in a deep stream with a van Veen grabber; (C) homogenization of the sediment sample; (D) water sampling with buckets; (E) location of sample and collection of sample ID, geographic coordinates with iPad and other physicochemical parameters of water with a multiparameter probe; (F) stainless steel trays, buckets, spade, and cup with a long handle used during water sampling; (G) subsamples of stream water in different bottles; and (H) water bottles with permanent labels ready to be refrigerated.

and the remainder material was sieved to < 0.177 mm (80 mesh; ASTM standard) fraction using a nylon screen for laboratory analysis. Five splits of each sample with different weights were prepared for specific laboratory procedures:

- 300 g on average as a replicate;
- 50 g for chemical analysis;
- 20 g for spectroradiometer analysis;
- 20 g for x-ray diffraction (XRD) analysis;
- 200 g for grain size analysis.

The sampling materials selected for chemical analysis were sent to ALS Brasil Ltda, a certified/accredited laboratory. In the laboratory, the samples were grounded, sieved through a < 0.075 mm (200 mesh; ASTM standard), and digested in a microwave-assisted system using aqua regia (1HNO_3:3HCl; ISO 11466.3 — https://www.iso.org/standard/19418.html). The concentrations of 51 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, and Zr) were determined by a combination of Inductively Coupled Plasma — Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma — Mass Spectrometry (ICP-MS; ME-MS41). In addition, the total concentrations of major and minor oxides (Al_2O_3, BaO, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SO_3, SiO_2, SrO, and TiO_2) were obtained via x-ray fluorescence (XRF) on fusion beads (ME-XRF26) combined with the quantification of Loss on Ignition (LOI) at 1,000°C (OA-GRA05). See for more information.

The surface soil and stream sediment samples selected for mineralogical analysis were sent to the Mineral Characterization Laboratory (Institute of Geosciences), Universidade Federal do Pará-Brazil. The samples were manually pulverized in a mortar and manually mounted in a sample holder using the back-loading method. The measurements were performed using a divergent beam diffractometer (Empyrean, PANalytical), with a θ-θ goniometer, a sealed ceramic Co x-ray tube ($K\alpha 1 = 1.78901$ Å), with a fine long focus of 1,800 W, a Fe kβ filter, and a PIXel3D 2×2 area detector, operating in a linear scanning mode, with an active length of 3.3473° 2θ (255 active channels). Data acquisition was performed with the PANalytical X'Pert Data Collector software version 5.1, and mineralogical identification was performed with the PANalytical X'Pert HighScore Plus software version 4.0, using the Powder Diffraction File of the International Center for Diffraction Data (PDF-ICDD) database.

Analyses of physicochemical parameters in stream water samples

The chemical analyses of the water samples were carried out in the certified laboratory of Merieux NutriSciences Brazil. The total contents of 35 elements (Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Hf, Hg, K, La, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, Tl, V, W, and Zn) were analyzed by ICP-MS (). Anions (F^-, Cl^-, NO_3^-, and SO_4^{2-}) were analyzed by ion chromatography and total phosphorus by colorimetry () after sample digestion using sulfuric acid at pH < 2. Total dissolved solids and turbidity were also measured in the laboratory ().

Quality assurance and quality control (QA/QC) of the geochemical data

The reliability of the geochemical data of soils, stream sediments, and water was evaluated by determining the precision and accuracy of the analytical results. Precision was determined by calculating the Relative Standard Deviation (RSD, Eq. 1) for each geochemical parameter:

$$RSD = \frac{\sqrt{\frac{\sum_{i=1}^{n}(S_R - S_D)^2}{n-1}}}{\frac{\sum_{i=1}^{n}(S_R + S_D)}{n}} \times 100\% \qquad (1)$$

n: The number of pairs of duplicates.
S_R: The concentration of the routine sample.
S_D: The concentration of the duplicate sample.

Among the several other statistical strategies (Piercey 2014), the RSD is a reasonable estimator of precision, widely used in large geochemical surveys (Reimann *et al.* 2012, Wang and CGB Sampling Team 2015). A low RSD value indicates high precision. Quality control of the chemical analysis results shows a high quality for most elements. Elements with a large number (> 70%) of concentrations below the LLD of samples were not considered for this statistical procedure. The most problematic elements are Au, B, Re, Ta, and W (Table 1). The remaining elements show acceptable and usable results for this quality control assessment. The overall RSD of the parameters analyzed in soils, stream sediments, and water is mostly ± 15% (Table 1), which implies a good level of analytic data. Poor precision values (> 30%) were observed for Te in soils and sediments and Zn in water during the dry season. It is important to highlight

Table 1. Geochemical parameters analyzed in the ItacGMBP. For each parameter, it is presented the measurement unit, the lower limit of detection (LLD), the analytical methods, and precision control results using relative standard deviation (RSD, %) values for each group of samples: surface soil (SS; number of pairs of duplicates, n = 73), bottom soil (SP; n = 73), stream sediment (SC; n = 33), and stream water in the dry (ES; n = 28) and rainy (EC; n = 29) seasons.

Soils and stream sediments							**Stream water**					
Parameter	**Unit**	**LLD**	**Method (ALS code)**	**%RSD**			**Parameter**	**Unit**	**LLD**	**Method**	**%RSD**	
				SS	**SP**	**SC**					**ES**	**EC**
Ag	mg/kg	0.01	ME-MS41	18.0	13.6	16.8	Ag_{Total}	µg/L	1	ICP-MS	*	*
Al	%	0.01	ME-MS41	5.8	6.9	25.0	Al_{Total}	µg/L	5	ICP-MS	5.2	18.1
As	mg/kg	0.1	ME-MS41	6.4	9.7	14.3	As_{Total}	µg/L	1	ICP-MS	*	*
Au	mg/kg	0.02	ME-MS41	*	*	*	–	–	–	–	–	–
B	mg/kg	10	ME-MS41	*	*	*	B_{Total}	µg/L	1	ICP-MS	*	10.7
Ba	mg/kg	10	ME-MS41	5.1	8.3	7.4	Ba_{Total}	µg/L	1	ICP-MS	6.2	4.6
Be	mg/kg	0.05	ME-MS41	8.7	12.4	11.3	Be_{Total}	µg/L	1	ICP-MS	*	*
Bi	mg/kg	0.01	ME-MS41	7.5	7.6	10.6	–	–	–	–	–	–
Ca	%	0.01	ME-MS41	14.0	8.2	11.4	Ca_{Total}	µg/L	20	ICP-MS	3.6	15.1
Cd	mg/kg	0.01	ME-MS41	20.1	19.7	13.2	Cd_{Total}	µg/L	1	ICP-MS	*	*
Ce	mg/kg	0.02	ME-MS41	5.5	4.4	15.4	Ce_{Total}	µg/L	5	ICP-MS	*	*
Cl	–	–	–	–	–	–	Chloride (Cl^-)	mg/L	0.5	IC	9.0	18.8
Co	mg/kg	0.1	ME-MS41	9.6	18.0	8.9	Co_{Total}	µg/L	1	ICP-MS	*	*
Cr	mg/kg	1	ME-MS41	3.2	5.4	6.5	Cr_{Total}	µg/L	1	ICP-MS	*	*
Cs	mg/kg	0.05	ME-MS41	5.1	5.6	7.8	Cs_{Total}	µg/L	5	ICP-MS	*	*
Cu	mg/kg	0.2	ME-MS41	5.0	4.6	9.7	Cu_{Total}	µg/L	1	ICP-MS	8.8	28.1
F	–	–	–	–	–	–	Fluoride (Hauck *et al.* 2012)	mg/L	0.05	IC	*	*
Fe	%	0.01	ME-MS41	3.7	4.6	6.3	Fe_{Total}	µg/L	20	ICP-MS	3.2	6.4
Ga	mg/kg	0.05	ME-MS41	4.2	4.1	5.9	Ga_{Total}	µg/L	5	ICP-MS	*	*
Ge	mg/kg	0.05	ME-MS41	14.4	17.1	10.4	Ag_{Total}	µg/L	1	ICP-MS	*	*
Hf	mg/kg	0.02	ME-MS41	19.1	12.7	38.9	Hf_{Total}	µg/L	10	ICP-MS	*	*
Hg	mg/kg	0.01	ME-MS41	15.7	15.3	23.6	Hg_{Total}	µg/L	0.1	ICP-MS	*	*
In	mg/kg	0.005	ME-MS41	7.2	4.9	7.0	–	–	–	–	–	–
K	%	0.01	ME-MS41	15.4	19.2	25.3	K_{Total}	µg/L	5	ICP-MS	4.7	6.8
La	mg/kg	0.2	ME-MS41	5.6	11.0	16.8	La_{Total}	µg/L	5	ICP-MS	*	*
Li	mg/kg	0.1	ME-MS41	15.6	10.5	12.2	–	–	–	–	–	–
Mg	%	0.0	ME-MS41	8.0	8.5	13.1	Mg_{Total}	µg/L	5	ICP-MS	2.7	23.0
Mn	mg/kg	5	ME-MS41	3.6	6.8	9.7	Mn_{Total}	µg/L	1	ICP-MS	6.1	7.9
Mo	mg/kg	0.05	ME-MS41	15.5	12.7	11.5	Mo_{Total}	µg/L	5	ICP-MS	*	*
N	–	–	–	–	–	–	Nitrate (NO_3^-)	mg/L	2.2	IC	*	*
Na	%	0.01	ME-MS41	0	10.9	31.4	Na_{Total}	µg/L	10	ICP-MS	3.6	16.1
Nb	mg/kg	0.05	ME-MS41	6.2	5.9	15.4	–	–	–	–	–	–
Ni	mg/kg	0.2	ME-MS41	5.0	10.1	12.4	Ni_{Total}	µg/L	1	ICP-MS	*	6.8
P	mg/kg	10	ME-MS41	3.2	4.8	6.7	P_{Total}	µg/L	10	CI	17.7	15.9

Continue...

Table 1. Continuation.

Soils and stream sediments							**Stream water**					
Parameter	**Unit**	**LLD**	**Method (ALS code)**	**%RSD**			**Parameter**	**Unit**	**LLD**	**Method**	**%RSD**	
				SS	**SP**	**SC**					**ES**	**EC**
Pb	mg/kg	0.2	ME-MS41	4.2	5.8	8.8	Pb_{Total}	µg/L	1	ICP-MS	*	*
Rb	mg/kg	0.1	ME-MS41	7.5	7.5	10.4	Rb_{Total}	µg/L	5	ICP-MS	10.9	8.5
Re	mg/kg	0.001	ME-MS41	*	*	*	–	–	–	–	–	–
S	%	0.01	ME-MS41	18.4	16.0	26.7	Sulfate (SO_4^{2-})	mg/L	0.5	IC	*	*
Sb	mg/kg	0.05	ME-MS41	8.4	8.3	15.6	Sb_{Total}	µg/L	1	ICP-MS	*	*
Sc	mg/kg	0.1	ME-MS41	11.2	9.8	5.4	–	–	–	–	–	–
Se	mg/kg	0.2	ME-MS41	16.5	15.5	29.2	Se_{Total}	µg/L	1	ICP-MS	*	*
Sn	mg/kg	0.2	ME-MS41	10.2	15.5	14.0	Sn_{Total}	µg/L	1	ICP-MS	17.8	*
Sr	mg/kg	0.2	ME-MS41	8.8	9.1	8.9	Sr_{Total}	µg/L	1	ICP-MS	6.6	6.2
Ta	mg/kg	0.01	ME-MS41	*	*	*	–	–	–	–	–	–
Te	mg/kg	0.01	ME-MS41	62.4	72.0	39.4	–	–	–	–	–	–
Th	mg/kg	0.2	ME-MS41	5.4	4.3	12.3	–	–	–	–	–	–
Ti	%	0.005	ME-MS41	8.1	7.8	31.5	Ti_{Total}	µg/L	1	ICP-MS	10.9	14.2
Tl	mg/kg	0.02	ME-MS41	6.1	8.2	13.0	Tl_{Total}	µg/L	1	ICP-MS	*	*
U	mg/kg	0.05	ME-MS41	5.5	5.3	6.0	–	–	–	–	–	–
V	mg/kg	1	ME-MS41	3.0	4.1	7.9	V_{Total}	µg/L	1	ICP-MS	*	*
W	mg/kg	0.05	ME-MS41	*	*	*	W_{Total}	µg/L	5	ICP-MS	*	*
Y	mg/kg	0.05	ME-MS41	5.1	5.9	8.8	–	–	–	–	–	–
Zn	mg/kg	2	ME-MS41	10.6	13.3	12.8	Zn_{Total}	µg/L	1	ICP-MS	38.6	24.0
Zr	mg/kg	0.5	ME-MS41	10.6	9.9	39.8	–	–	–	–	–	–

ME-MS41: aqua regia soluble concentrations + Inductively Coupled Plasma Optical Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS); IC: ion chromatography; *values not calculated (large proportion of samples below LLD); –: not analyzed.

that RSD is dependent on the material in question and on the limit of detection.

For soils and sediments, the accuracy of the analytical methods was monitored using repeated analyses of certified reference materials (CRMs: GBM303-4, MRGeo08, GBM908-10, SRM88B, AMIS0096, BCS-348, BXMG-5, GBM303-4, GBM908-10, and MRGeo08). The results show good agreement between the CRMs and the data obtained in the present work.

GENERAL ASPECTS ON DATA PROCESSING AND STATISTICAL TREATMENT OF GEOCHEMICAL DATA

The present topic summarizes the main data processing and statistical treatment of surface water (Salomão *et al.* 2018, Sahoo *et al.* 2019b), soil (Sahoo *et al.* 2020a, 2020b), and stream sediments (Salomão *et al.* 2019, 2020) geochemical data used in the ItacGMBP. It is important to highlight that these methods are standard procedures widely used by various researchers (Reimann *et al.* 2005, Reimann and Caritat 2017).

Data preparation and statistical treatment

The first step is to verify any anomalous results due to laboratory error or contamination, which includes the QA/QC results presented herein. Then, the proportion of censored data (censored values are values that have concentrations below the DL of the analytical technique [BDL]) of each element in the whole geochemical dataset was estimated. The elements with a high proportion of censored data (> 90% BDL values) were removed, and for those with only sporadic BDL values, the BDL values were replaced with a value equivalent to 1/2 of the DL. Data preparation also included normalizing the distribution because normality is essential for the calculation of background values and various univariate and multivariate statistical analyses (e.g., correlation matrix, cluster analysis, principal component analysis, and factor analysis). Exploratory data analysis, including histograms, box plots, density plots, Q–Q plots, and edaplots (Fig. 9), was also employed. This analysis was performed using the raw data, $\log_{10}$-transformed data, and transformations under the Composition Data Analysis (CoDA) concept (e.g., centered log ratio [CLR] and isometric log ratio [ILR]). It is important to highlight that after the data transformation, using both $\log_{10}$ and clr, the overall concentration data of Al, Fe, and Mn tend to approximate a normal distribution, which is highly indicative for further statistical investigations (Fig. 9). All statistical treatments and graph generations were performed using the R Studio software (The-R-Development-Core-Team 2013).

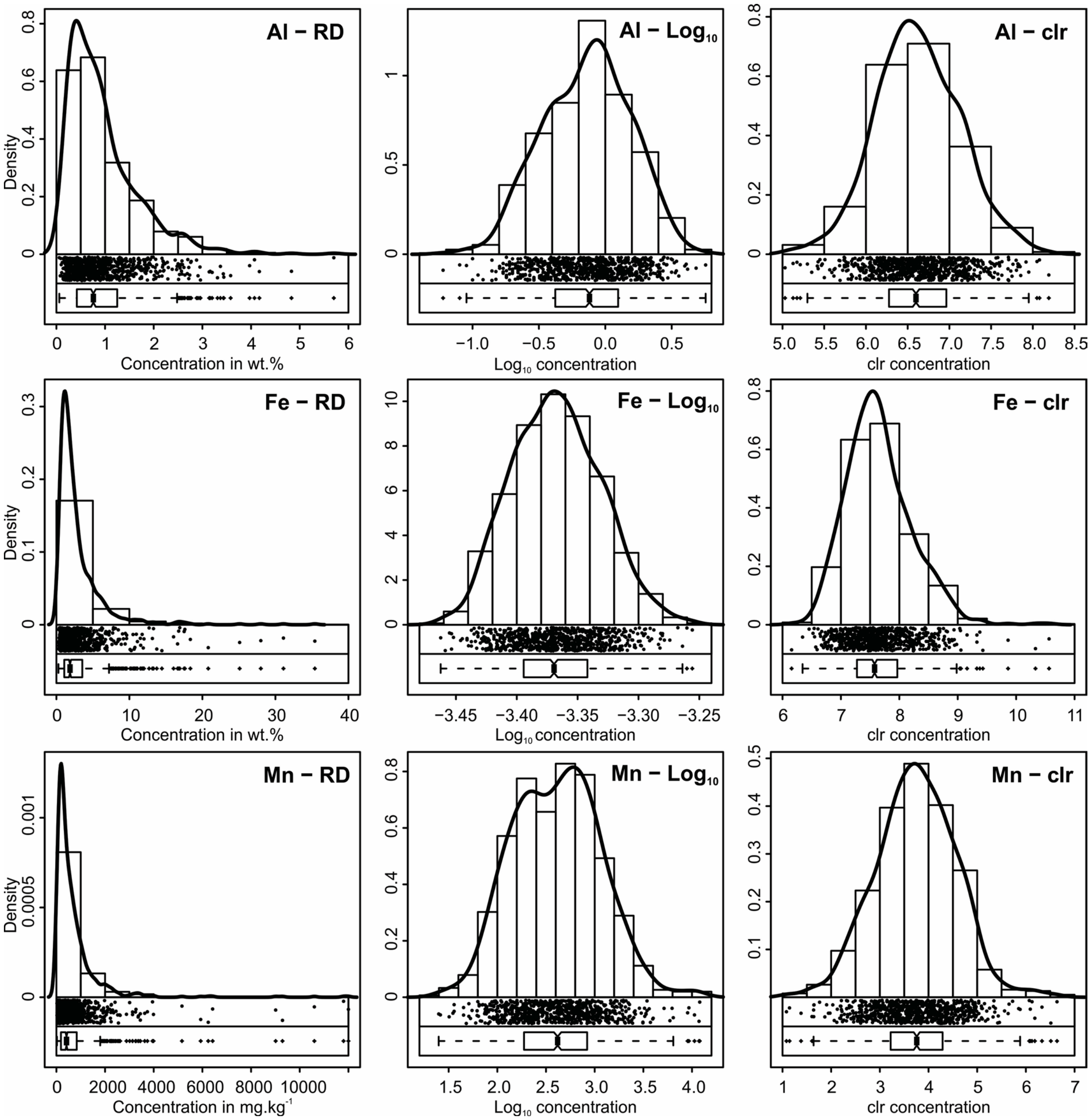


Figure 9. Exploratory data analysis (EDA) diagrams (histogram, density plot, and boxplot) of the composition of selected chemical elements (Al, Fe, and Mn) in stream sediments in the IRW showing the distinction between raw data (RD) and the transformation of the data by common logarithm (Log10) and centered log-ratio (clr). The raw concentrations are extremely skewed, but when transformed to a log10 or clr scale, they are more symmetrically distributed. Refer to Figures 10, A4, and A5 for the geochemical distribution maps of the selected elements.

Geochemical mapping

Color surface distribution maps were produced to show the spatial variation in different elements in surface and subsurface soils, stream sediment, and rainy and dry season water in the context of IRW. The color soil maps of ItacGMBP were prepared in the QGIS Web front-end and are based on a grid calculation using ordinary kriging for interpolation and carried out cross-validation procedures, following the mapping approach of other continental- and regional-scale baseline geochemical studies (Filzmozer *et al.* 2014). Geochemical maps were constructed based on several techniques (Carranza 2011, Cheng *et al.* 2014, Salomão *et al.* 2021): point representation, the graduated symbols were based on the percentile-based approach of data distribution, defining five classes that were distinguished with different shapes; using inverse distance weighting (Midwood and Chow-Fraser 2010) interpolation; and catchment-based representation of uni-element concentrations for transported materials data (surface water and stream sediments). For instance, Figure 10 shows the geochemical distribution map of Fe in the IRW following the different methods described previously. The geochemical distribution maps were fundamental to the evaluation of regional geochemical patterns and the identification of concentrations above the regional background. For more information about the regional interpretation of the elements in the IRW, refer to Sahoo et al. (2019b, 2020b) and Salomão *et al.* (2020, 2021).

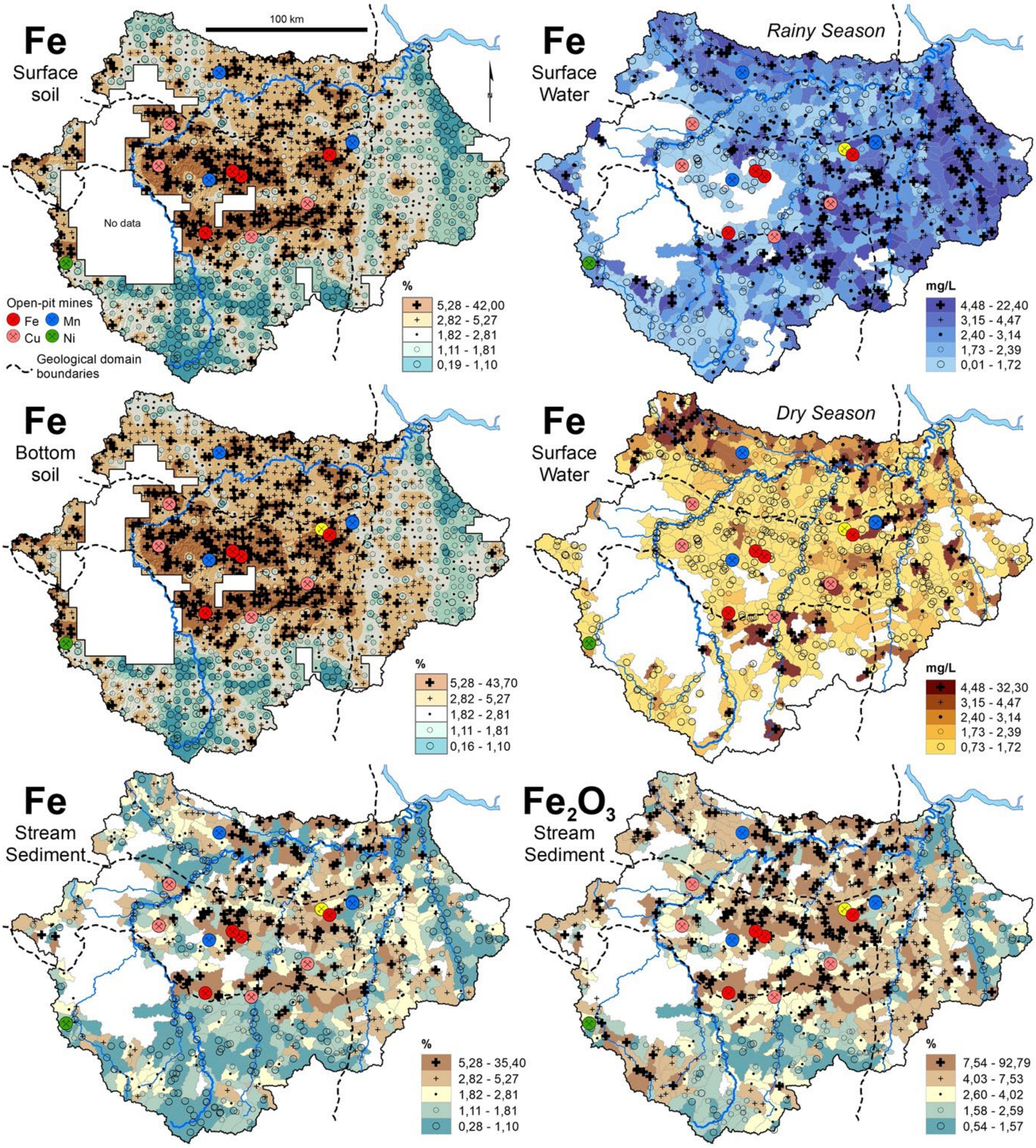


Figure 10. Geochemical distribution maps for Fe (aqua regia digestion; ICP-AES) in surface soils, bottom soils, and stream sediments; Fe_2O_3 (fused beds; XRF) in stream sediments; and Fe_{Total} in surface water collected in the rainy and dry seasons. Additionally, geochemical maps of Al and Mn are given in Figures A4 and A5, respectively.

Statistical methods used for the calculation of geochemical background values

Several methods have been proposed for the estimation of the GB (Matschullat *et al.* 2000), although each method has its limitations, and the lack of uniform criteria for the determination of the GB has also been discussed. In the ItacGMBP, background values were calculated by using multiple statistical methods (Table 2) widely applied (Reimann *et al.* 2005, Ander *et al.* 2013, Reimann and Caritat 2017): Tukey's inner fences (TIF), median+2*median absolute deviation (mMAD), and percentile-based approaches (95th and 98th). The descriptions and math equations for each method can be found in Matschullat *et al.* (2000), Reimann and Caritat (2005), Ander *et al.* (2013), and references therein.

Implication of geochemical mapping and background/baseline values for environmental assessment

High-density geochemical mapping associated with background values assists the identification of potential anomalies and provides more detailed information on potential sources, either anthropogenic or geogenic (Reimann *et al.* 2018, Sahoo *et al.* 2020, in soils; Salomão *et al.* 2020). In this regard, the ItacGMBP revealed a remarkable study case for the IRW.

Table 2. Geochemical threshold values for nine selected elements in soils, stream sediments, and surface water of the Itacaiúnas River watershed estimated by a variety of methods: Tukey inner fence (TIF), median ± 2*median absolute deviation (mMAD), and percentile-based approaches (P98 and P95).

Sample Type	Method	Al	Fe	Mn	As	Cr	Cu	Ni	Pb	Zn
Surface Soil[a]	**TIF**	9.44	25.7	6,166.0	30.2	595.66	334.97	63.1	31.62	94.41
	mMAD	6.03	13.8	2,691.5	10.47	229.09	112.2	26.92	19.95	51.29
	P98	8.51	19.5	2,691.5	11.48	371.54	213.8	81.28	20.89	93.33
	P95	4.90	11.75	1,778.3	6.46	154.88	120.23	38.90	15.85	56.23
Bottom Soil[a]	**TIF**	9.89	29.17	4,677.4	28.18	638.26	402.72	67.61	35.48	84.14
	mMAD	6.31	16.22	1,905.5	9.77	257.04	141.25	27.54	23.44	51.29
	P98	8.91	20.42	2,454.7	14.13	407.38	229.09	83.18	23.99	83.18
	P95	5.37	12.88	1,584.9	8.13	165.96	128.82	41.69	20.42	52.48
Stream Sediments[b]	**TIF**	6.42	21.16	7,862.8	30.81	323.09	320.30	60.93	58.79	91.12
	mMAD	3.84	10.65	3,759.7	7.57	154.78	138.15	33.90	35.55	59.90
	P98	2.90	13.06	3,368.0	11.38	224.40	178.70	59.04	29.08	99.77
	P95	2.47	8.48	2,100.0	7.40	140.00	118.50	36.00	25.40	59.00
Surface Water – Rainy season[c]	**TIF**	2.99	11.61	1.91	–	7.08	35.48	12.59	–	316.23
	mMAD	1.48	7.76	0.91	–	–	21.38	–	–	128.82
	P98	1.41	11.82	1.83	1.77	8.88	28.63	10.46	2.80	88.12
	P95	1.05	7.08	0.89	–	3.98	8.51	6.03	1.82	50.12
Surface Water – Dry season[c]	**TIF**	0.97	13.96	4.95	–	–	19.95	4.73	–	121.62
	mMAD	0.49	7.59	1.55	–	–	19.95	–	–	51.29
	P98	1.00	11.22	3.80	1.93	4.50	8.82	8.10	1.81	118.44
	P95	0.48	6.46	1.78	–	2.69	4.57	5.25	1.10	47.86

In soils and sediments, the concentrations of Al and Fe are expressed in % and the remaining elements in mg/kg. In surface water, only the total concentration was determined; the concentrations of Al, Fe, and Mn are expressed in mg/L and the remaining elements in µg/L; [a]values presented in Sahoo *et al.* (2020b); [b]values presented in Salomão *et al.* (2020, 2021); [c]values presented in Sahoo *et al.* (2019b).

The spatial distribution of Fe is strongly correlated between surface soil and bottom soil, as well as with stream sediments (Fig. 10). Clearly, high concentrations of Fe in soils and sediments are observed in the Carajás Basin geological domain (Fig. A2 in Suppl. A), which is a clear indication of geogenic sources, mainly controlled by local lithologies, such as continental meta-tholeiitic basalts and rhyolites of the Parauapebas Formation, associated with banded-iron formation and volcanogenic sediments of the Carajás Formation (Sahoo *et al.* 2020, Salomão *et al.* 2020).

In contrast, the spatial distribution of Fe in surface water in both rainy and dry seasons is clearly different from soils and sediments (Fig. 10). Higher concentrations of Fe were observed in areas of predominance of pastureland (Fig. A1 in Suppl. A), particularly in the eastern part of the IRW region, comprising the Vermelho and Sororó sub-basins (Salomão *et al.* 2018). For this reason, the distribution of Fe in SW could not be solely explained by the geology, which was previously expected to have major influence by the Archean to Paleoproterozoic terrains of the Amazonian Craton. It was concluded that the enrichment of Fe in SW was due to a sum of environmental conditions prevalent in the Amazonian region, particularly the conversion of forest to pastureland, which favored the runoff and increase of metal concentrations in water (Salomão *et al.* 2018, Sahoo *et al.* 2019b).

In the case of Cu spatial distribution, a similar pattern was also observed among the different sampling mediums (see the geochemical maps in Sahoo *et al.* 2019b, 2020, Salomão *et al.* 2020). The highest concentrations and anomalies of Cu observed in the Carajás Basin domain were interpreted as a regional influence of two E-W hydrothermal corridors called, Northern — Cinzento strike-slip fault, 2.57 Ga (Pinheiro and Holdsworth 1997) – and Southern copper belts – Canaã strike-slip fault, 2.71–2.68 Ga (Moreto *et al.* 2015, Salomão *et al.* 2020). Similar behavior was observed for stream water in which maximum levels and anomalies of Cu in both climatic seasons are basically concentrated along these two hydrothermal belts (Sahoo *et al.* 2019b). This further supports a strong geogenic control of Cu in the soils, sediments, and water of the IRW.

In terms of geochemical background and baseline concentrations, Table 2 summarizes the threshold concentration values of surface and bottom soils, stream sediments, and stream water (rainy and dry seasons) for the entire IRW, which were available from previous studies of the ItacGMBP Project (Sahoo *et al.* 2019a, 2019b, in SW; Sahoo *et al.* 2020, in SS and BS; Salomão *et al.* 2020, in SD). Although, the GB values vary among the methods with the order TIF > 98th > mMAD or TIF > mMAD > 98th, with a few exceptions, for soils and sediments, mMAD (which mostly estimated values between the 95th and 98th percentiles) was considered as more robust and provided more realistic threshold values as it was inherently stable against outliers (Reimann *et al.* 2018). Thus, potential anomalies were distinguished based on mMAD, and then possible sources were discussed using geochemical distribution maps, such as the one present for Fe herein (Fig. 10).

The results obtained by the ItacGMBP indicate that regional geochemical background values along with high-density spatial mapping should always be considered as a tool for identifying pollution hotspots and the accurate assessment of metal contamination. It was concluded that the maximum values proposed as a reference of quality in the Brazilian environmental regulations, proposed by the Conselho Nacional do Meio Ambiente (CONAMA), are not realistic for the Amazonian region (Sahoo *et al.* 2019a, Sahoo *et al.* 2020, Salomão *et al.* 2020). Other studies also criticize the use of a single national/global reference value (Gough and Erdman 1983, Reimann *et al.* 2005, Licht *et al.* 2006, Rodrigues *et al.* 2013), as the latter does not consider the effect of specific environmental characteristics of a given area, particularly the heterogeneity of the geological setting.

CONCLUSION

This manuscript briefly presents the refined guidelines for sampling methodology centered on the GIS platform-based framework for baseline mapping and definition of the GB in the ItacGMBP. The methods employed for soil, stream sediment and water sampling, sample preparation and analysis, as well as for geochemical mapping and delineation of geochemical anomalies caused by geogenic or anthropogenic drivers are emphasized. A large number of collected, stored, and analyzed data, including color surface distribution maps, required the development of software tools for their management and sharing with the operational sectors of the mining company. The ItacGMBP results have shown that our methodological approach promoted advances in field data collections from a mobile App development for the acquisition of geographical information, pictures and chemical parameters, and a GIS platform implementation to manage the geochemical database and maps. Furthermore, the results have shown that there is a strong relationship between chemical element concentrations and geogenic rather than anthropogenic contamination in soils, stream sediments, and stream water. Papers have been published in scientific journals as referenced in this manuscript; the database is accessible for Vale S.A. teams through a web-based GIS front-end and the Geochemical Atlas of the IRW will be available as soon as possible. Future studies should focus on the development of statistical functions, such as background calculation in a web-based GIS platform.

ACKNOWLEDGMENTS

This work is part of the Itacaiúnas Geochemical Mapping and Background Project — ItacGMBP, currently being undertaken at Instituto Tecnológico Vale (ITV), Belém, Brazil. This was supported by Vale (Gerência de Meio Ambiente do Corredor Norte); Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) (DTI scholarship to GNS Proc. 380.418/2018-5 and 380998/2019-0; grants to RD Proc. 306108/2014-3 and Proc. 443247/2015-3, and PWMSF Proc. 306450/2013-5 and 310283/2019-1). The authors acknowledge the anonymous reviewers for their constructive reviews and Francisco Bêrredo, José Francisco Ramos, Luiz Roberto G. Guilherme, Marcondes L. Costa, Rômulo S. Angélica, and Otavio A. Boni Licht for their scientific collaboration with the ItacGMBP.

ARTICLE INFORMATION

Manuscript ID: 20220018. Received on: 8 APR 2021. Approved on: 4 SEPT 2022.

How to cite this article: Souza-Filho P.W.M., Sahoo P.K., Silva M.S., Dall'Agnol R., Medeiros Filho C.A., Leite A.S., Ferreira Júnior J.S., Nascimento Junior W.R., Silva G.S., Salomão G.N., Sarracini F., Silva Junior R.O., Costa M.F. 2022. Methodological approach and general guidelines to geochemical mapping and background-baseline analysis for environmental assessment: a study case in the Carajás Mineral Province. *Brazilian Journal of Geology*, **52**(4):e20220018. https://doi.org/10.1590/2317-4889202220220018

P.S.-F. concepted this study, wrote the first draft of the manuscript, and prepared Figures 1, 2, 4, 5, 6, 7, and 8. P.S. carried out geochemical analysis and interpretation and prepared Table 1. M.S. and A.L. collected, processed, and provided geochemistry and environmental data of the study site. R.D. and C.M.-F. provided advisorship regarding the Amazonian craton geology and improved the manuscript through discussion. J.F.-J. developed the computer system to collect, storage, and analysis geochemical and environmental data. W.N.-J., G.S., and G.N.S. organized and manipulated geodatabase to generate geochemical maps, Figures 3 and 9, and improved the manuscript through corrections and suggestions. R.S.-J., F.S., and M.C. contribute to the conception of this study and provided advisorship regarding the logistic and strategic plain of sample collection along the study site.

Competing interests: the authors declare no competing interests.

REFERENCES

American Public Health Association (APHA). 2012. *Standard methods for the examination of water and wastewater*. 22nd ed. Washington, D.C.: American Public Health Association.

Ander E.L., Johnson C.C., Cave M.R., Palumbo-Roe B., Nathanail C.P., Lark R.M. 2013. Methodology for the determination of normal background concentrations of contaminants in English soil. *Science of The Total Environment*, **454-455**:604-618, https://doi.org/10.1016/j.scitotenv.2013.03.005

Birke M., Rauch U., Reimann C. 2015a. Supporting information for interpretation of geochemical maps. In: Reimann C., Birke M., Demetriades A., Filzmoser P., O'Connor B. (Eds.), *Chemestry of Europe's Agricultural Soils.* Part A: Methodology and interpretation of the GEMAS data set. Hannover: Geologisches Jahrbuch B102, p. 93-102.

Birke M., Rauch U., Stummeyer J. 2015b. How robust are geochemical patterns? A comparison of low and high sample density geochemical mapping in Germany. *Journal of Geochemical Exploration*, **154**:105-128. https://doi.org/10.1016/j.gexplo.2014.12.005

Caritat P. 2018. Continental-scale geochemical surveys and mineral prospectivity: Comparison of a trivariate and a multivariate approach. *Journal of Geochemical Exploration*, **188**:87-94. https://doi.org/10.1016/j.gexplo.2018.01.014

Caritat P., Cooper M., Lech M., McPherson A., Thun C. 2009. National Geochemical Survey of Australia: Sample Preparation Manual. In: 2009/08, R. (Ed.), *Geoscience Australia, Record 2009/08*. Geoscience Australia, p. 28.

Carranza E.J.M. 2011. Analysis and mapping of geochemical anomalies using logratio-transformed stream sediment data with censored values. *Journal of Geochemical Exploration*, **110**(2):167-185. https://doi.org/10.1016/j.gexplo.2011.05.007

Cheng Z., Xie X., Yao W., Feng J., Zhang Q., Fang J. 2014. Multi-element geochemical mapping in Southern China. *Journal of Geochemical Exploration*, **139**:183-192, https://doi.org/10.1016/j.gexplo.2013.06.003

Costa R.V.F., Leite M.G.P., Mendonça F.P.C., Nalini Jr. H.A. 2015a. Geochemical mapping of arsenic in surface waters and stream sediments of the Quadrilátero Ferrífero, Brazil. *Revista Escola de Minas*, **68**(1):43-51. https://doi.org/10.1590/0370-44672015680077

Costa R.V.F., Matschullat J., Leite M.G.P., Nalini Jr. H.A., Leão L.P. 2018. Geochemical mapping of potentially hazardous elements in surface waters and stream sediments of the Quadrilátero Ferrífero, Brazil. *Geochimica Brasiliensis*, **32**(2):243-267. https://doi.org/10.21715/GB2358-2812.2018322243

Costa R.V.F., Matschullat J., Leite M.G.P., Nalini Jr. H.A., Mendonça F.P.C. 2015b. Iron Quadrangle stream sediments, Brazil: geochemical maps and reference values. *Environmental Earth Sciences*, **74**:4407-4417. https://doi.org/10.1007/s12665-015-4508-2

Darnley A.G. 1997. A global geochemical reference network: the foundation for geochemical baselines. *Journal of Geochemical Exploration*, **60**(1):1-5. https://doi.org/10.1016/S0375-6742(97)00020-4

Demetriades A., Birke M., Albanese S., Schoeters I., De Vivo B. 2015. Continental, regional and local scale geochemical mapping. *Journal of Geochemical Exploration*, **154**:1-5. https://doi.org/10.1016/j.gexplo.2015.02.011

Demetriades A., Smith D.B., Wang X. 2018. General concepts of geochemical mapping at global, regional, and local scales for mineral exploration and environmental purposes. *Geochimica Brasiliensis*, **32**(2):136-179. https://doi.org/10.21715/GB2358-2812.2018322136

Filzmozer P., Reimann C., Birke M. 2014. Univariate data analysis and mapping. In: Reimann C., Birke M., Demetriades A., Filzmoser P., O'Connor B. (Eds.), *Chemestry of Europe's Agricultural Soils*. Part A: Methodology and interpretation of the GEMAS data set. Hannover: Geologisches Jahrbuch B102, p. 67-81.

Gloaguen T.V., Passe J.J. 2017. Importance of lithology in defining natural background concentrations of Cr, Cu, Ni, Pb and Zn in sedimentary soils, northeastern Brazil. *Chemosphere*, **186**:31-42. https://doi.org/10.1016/j.chemosphere.2017.07.134

Gough L.P., Erdman J.A. 1983. Baseline Elemental Concentrations for Big Sagebrush from Western U.S.A. *Journal of Range Management*, **36**(6):718-722. https://doi.org/10.2307/3898194

Hauck J., Gerdes D., Hillenbrand C.-D., Hoppema M., Kuhn G., Nehrke G., Völker C., Wolf-Gladrow D.A. 2012. Distribution and mineralogy of carbonate sediments on Antarctic shelves. *Journal of Marine Systems*, **90**(1):77-87. https://doi.org/10.1016/j.jmarsys.2011.09.005

Kuenzer C., Bluemel A., Gebhardt S., Quoc T.V., Dech S. 2011. Remote sensing of mangrove ecosystems: a review. *Remote Sensing*, **3**(5):878-928. https://doi.org/10.3390/rs3050878

Larizzatti J.H., Marques E.D., Silveira F.V. 2018. Geochemical Mapping of Iron Quadrangle region by active stream sediments, State of Minas Gerais, Brazil. *Geochimica Brasiliensis*, **32**(2):268-292. https://doi.org/10.21715/GB2358-2812.2018322268

Licht O.A.B. 2018. Multiscale, multimedia and multi-element geochemical mapping of the State of Paraná, Brazil. *Geochimica Brasiliensis*, **32**(2):209-242.

Licht O.A.B., Xuejing X., Qin Z., Miyazawa M., Ferreira F.J.F., Plawiak R.A.B. 2006. Average reference values of geochemical and geophysical variables in stream sediments and soils, state of Paraná, Brazil. Boletim Paranaense de Geociências, (58):59-87.

Liu X., Wang X., Caritat P., Salminen R. 2015. Comparison of datasets obtained by global-scale geochemical sampling in Australia, China and Europe. *Journal of Geochemical Exploration*, **148**:1-11. https://doi.org/10.1016/j.gexplo.2013.11.005

Matschullat J., Höfle S., Silva J., Mello J., Melo Jr. G., Pleßow A., Reimann C. 2012. A soil geochemical background for northeastern Brazil. *Geochemistry: Exploration, Environment, Analysis*, **12**(3):197-209. https://doi.org/10.1144/1467-7873/10-RA-046

Matschullat J., Ottenstein R., Reimann C. 2000. Geochemical background – can we calculate it? *Environmental Geology*, **39**:990-1000. https://doi.org/10.1007/s002549900084

Midwood J., Chow-Fraser P. 2010. Mapping Floating and Emergent Aquatic Vegetation in Coastal Wetlands of Eastern Georgian Bay, Lake Huron, Canada. *Wetlands*, **30**:1141-1152. https://doi.org/10.1007/s13157-010-0105-z

Moreto C.P.N., Monteiro L.V.S., Xavier R.P., Creaser R.A., DuFrane S.A., Melo G.H.C., Delinardo da Silva M.A., Tassinari C.C.G., Sato K. 2015. Timing of multiple hydrothermal events in the iron oxide–copper–gold deposits of the Southern Copper Belt, Carajás Province, Brazil. *Mineralium Deposita*, **50**:517-546. https://doi.org/10.1007/s00126-014-0549-9

Piercey S.J. 2014. Modern Analytical Facilities 2. A Review of Quality Assurance and Quality Control (QA/QC) Procedures for Lithogeochemical Data. *Geoscience Canada*, **41**:75-88. https://10.12789/geocanj.2014.41.035

Pinheiro R.V.L., Holdsworth R.E. 1997. Reactivation of Archean strike-slip fault systems, Amazon region, Brazil. *Journal of the Geological Society of London*, **154**(1):99-103. https://doi.org/10.1144/gsjgs.154.1.0099

Reimann C. 2014. Sample material, site selection and sampling. In: Reimann C., Birke M., Demetriades A., Filzmoser P., O'Conner P. (Eds.), *Chemestry of Europe's Agricultural Soils*. Part A: Methodology and interpretation of the GEMAS data set. Hannover: Geologisches Jahrbuch B102, p. 31-36.

Reimann C., Caritat P. 2017. Establishing geochemical background variation and threshold values for 59 elements in Australian surface soil. *Science of the Total Environment*, **578**:633-648. https://doi.org/10.1016/j.scitotenv.2016.11.010

Reimann C., Demetriades A., Birke M., Eggen O.A., Filzmoser P., Kriete C. 2012. *The Eurogeosurveys Geochemical Mapping of Agricultural and Grazing Land Soils Project (Gemas)*: Evaluation of Quality Control Results of Particle Size Estimation by Mir Prediction, Pb-Isotope and Mmi®-Extraction Analysis and Results of the GEMAS Ring Test for the Standards Ap and Gr. Trondheim: Geological Survey of Norway.

Reimann C., Fabian K., Birke M., Filzmoser P., Demetriades A., Négrel P., Oorts K., Matschullat J., Caritat P. 2017. GEMAS: Establishing geochemical background and threshold for 53 chemical elements in European agricultural soil. *Applied Geochemistry*, **88**(PartB):302-318. https://doi.org/10.1016/j.apgeochem.2017.01.021

Reimann C., Fabian K., Birke M., Filzmoser P., Demetriades A., Négrel P., Oorts K., Matschullat J., Caritat P., Albanese S., Anderson M., Baritz R., Batista M.J., Bel-Ian A., Cicchella D., De Vivo B., De Vos W., Dinelli E., Ďuriš M., Dusza-Dobek A., Eggen O.A., Eklund M., Ernsten V., Flight D.M.A., Forrester S., Fügedi U., Gilucis A., Gosar M., Gregorauskiene V., De Groot W., Gulan A., Halamić J., Haslinger E., Hayoz P., Hoogewerff J., Hrvatovic H., Husnjak S., Jähne-Klingberg F., Janik L., Jordan G., Kaminari M., Kirby J., Klos V., Kwećko P., Kuti L., Ladenberger A., Lima A., Locutura J., Lucivjansky P., Mann A., Mackovych D., McLaughlin M., Malyuk B.I., Maquil R., Meuli R.G., Mol G., O'Connor P., Ottesen R.T., Pasnieczna A., Petersell V., Pfleiderer S., Poňavič M., Prazeres C., Radusinović S., Rauch U., Salpeteur I., Scanlon R., Schedl A., Scheib A., Schoeters I., Šefčik P., Sellersjö E., Slaninka I., Soriano-Disla J.M., Šorša A., Svrkota R., Stafilov T., Tarvainen T., Tendavilov V., Valera P., Verougstraete V., Vidojević D., Zissimos A., Zomeni Z., Sadeghi M. 2018. GEMAS: Establishing geochemical background and threshold for 53 chemical elements in European agri- cultural soil. *Applied Geochemistry*, **88**(Part B):302-318. https://doi.org/10.1016/j.apgeochem.2017.01.021

Reimann C., Filzmoser P., Garrett R.G. 2005. Background and threshold: critical comparison of methods of determination. *Science of the Total Environment*, **346**(1-3):1-16. https://doi.org/10.1016/j.scitotenv.2004.11.023

Rodrigues A.S.L., Malafaia G., Costa A.T., Nalini Júnior H.A. 2013. Background values for chemical elements in sediments of the Gualaxo do Norte River Basin, MG, Brazil. *Revista de Ciências Ambientais*, **7**(2):15-32. https://doi.org/10.18316/1142

Sahoo P.K., Dall'Agnol R., Salomão G.N., Silva Ferreira Junior J., Silva M.S., Martins G.C., Souza Filho P.W.M., Powell M.A., Maurity C.W., Angélica R.S., Costa M.F., Siqueira J.O. 2019a. Source and background threshold values of potentially toxic elements in soils by multivariate statistics and GIS-based mapping: a high-density sampling survey in the Parauapebas basin from Brazilian Amazonia. *Environmental Geochemistry and Health*, **42**(1):255-282. https://doi.org/10.1007/s10653-019-00345-z

Sahoo P.K., Dall'Agnol R., Salomão G.N., Silva Ferreira Junior J., Silva M.S., Souza Filho P.W.M., Powell M.A., Angélica R.S., Pontes P.R., Costa M.F., Siqueira J.O. 2019b. High resolution hydrogeochemical survey and estimation of baseline concentrations of trace elements in surface water of the Itacaiúnas River Basin, southeastern Amazonia: Implication for environmental studies. *Journal of Geochemical Exploration*, **205**:106321. https://doi.org/10.1016/j.gexplo.2019.06.003

Sahoo P.K., Dall'Agnol R., Salomão G.N., Silva Ferreira Junior J., Silva M.S., Martins G.C., Souza Filho P.W.M., Powell M.A., Maurity C.W., Angelica R.S., Costa M.F., Siqueira J.O. 2020a. Source and background threshold values of potentially toxic elements in soils by multivariate statistics and GIS-based mapping: a high density sampling survey in the Parauapebas basin, Brazilian Amazon. *Environmental Geochemistry and Health*, **42**:255-282. https://doi.org/10.1007/s10653-019-00345-z

Sahoo P.K., Dall'Agnol R., Salomão G.N., Silva Ferreira Junior J., Silva M.S., Souza Filho P.W.M., Costa M.L., Angélica R.S., Filho C.A.M., Costa M.F., Guilherme L.R.G., Siqueira J.O. 2020b. Regional-scale mapping for determining geochemical background values in soils of the Itacaiúnas River Basin, Brazil: The use of compositional data analysis (CoDA). *Geoderma*, **376**:114504. https://doi.org/10.1016/j.geoderma.2020.114504

Salminen R., Batista M.J., Bidovec M., Demetriades A., De Vivo B., De Vos W., Duris M., Gilucis A., Gregorauskiene V., Halamic J., Heitzmann P., Lima A., Jordan G., Klaver G., Klein P., Lis J., Locutura J., Marsina K., Mazreku A., O'Connor P.J., Olsson S.Á., Ottesen R.T., Petersell V., Plant J.A., Reeder S., Salpeteur I., Sandström H., Siewers U., Steenfelt A., Tarvainen T. 2005. *Geochemical Atlas of Europe*. Part 1 — Background Information, Methodology and Maps. Espoo: Geological Survey of Finland.

Salomão G.N., Dall'Agnol R., Sahoo P.K., Angélica R.S., Medeiros Filho C.A., Ferreira Júnior J.S., Sousa da Silva M., Souza Filho P.W.M., Nascimento Junior W.R., Costa M.F., Guilherme L.R.G., Siqueira J.O. 2020. Geochemical mapping in stream sediments of the Carajás Mineral Province: Background values for the Itacaiúnas River watershed, Brazil. *Applied Geochemistry*, **118**:104608. https://doi.org/10.1016/j.apgeochem.2020.104608

Salomão G.N., Dall'Agnol R., Sahoo P.K., Ferreira Júnior J.S., Silva M.S., Souza-Filho P.W.M., Berrêdo J.F., Nascimento Jr. W.R., Costa M.F. 2018. Geochemical distribution and thresholds values determination of heavy metals in stream water in the sub-basins of Vermelho and Sororó rivers, Itacaiúnas River watershed, Eastern Amazon, Brazil. Geochimica Brasiliensis, **32**(2):180. https://orcid.org/0000-0003-3729-7840

Salomão G.N., Farias D.D., Sahoo P.K., Dall'Agnol R., Sarkar D. 2021. Integrated Geochemical Assessment of Soils and Stream Sediments to Evaluate Source-Sink Relationships and Background Variations in the Parauapebas River Basin, Eastern Amazon. *Soil Systems*, 5. https://10.3390/soilsystems5010021

Salomão G.N., Figueiredo M.A., Dall'Agnol R., Sahoo P.K., Medeiros Filho C.A., Costa M.F., Angélica R.S. 2019. Geochemical mapping and background concentrations of iron and potentially toxic elements in active stream sediments from Carajás, Brazil – implication for risk assessment. *Journal of South American Earth Sciences*, **92**:151-166. https://doi.org/10.1016/j.jsames.2019.03.014

Schucknecht A., Matschullat J., Caritat P., Silva J., Melo G., Pleßow A., Mello J.W.V. 2012. Pedogeochemistry in NE-Brazil — Compared to Australia and Europe. *Science of the Total Environment*, **438**:342-356. https://doi.org/10.1016/j.scitotenv.2012.08.059

Smith D.B., Demetriades A., Caritat P., Wang X. 2018. The history, progress, and future of global-scale geochemical mapping. *Geochimica Brasiliensis*, **32**(2):115. https://doi.org/10.21715/GB2358-2812.2018322115

Souza-Filho P., Nascimento W., Santos D., Weber E., Silva R., Siqueira J. 2018. A GEOBIA Approach for Multitemporal Land-Cover and Land-Use Change Analysis in a Tropical Watershed in the Southeastern Amazon. *Remote Sensing*, **10**(11):1683. https://doi.org/10.3390/rs10111683

The-R-Development-Core-Team. 2013. *R:* A Language and Environment for Statistical Computing. Vienna: R Foundation for Statistical Computing.

Wang X., CGB Sampling Team. 2015. Reprint of "China geochemical baselines: Sampling methodology". *Journal of Geochemical Exploration*, **154**:17-31. https://doi.org/10.1016/j.gexplo.2015.04.005

Woodruff L., Cannon W.F., Smith D.B., Solano F. 2015. The distribution of selected elements and minerals in soil of the conterminous United States. *Journal of Geochemical Exploration*, **154**:49-60. https://doi.org/10.1016/j.gexplo.2015.01.006

Zuo R., Carranza E.J.M., Wang J. 2016. Spatial analysis and visualization of exploration geochemical data. Earth-Science Reviews, **158**:9-18. https://doi.org/10.1016/j.earscirev.2016.04.006