

# Provenance, Guideline Values and Trace and Minor Elements in Bottom Sediments of Tebicuary River and Tapiracuai Stream from Eastern Paraguay by X-Ray Fluorescence

Juan F. Facetti Masulli<sup>1,2</sup>, Peter Kump<sup>3</sup> and Mirna Delgado<sup>2</sup>

1. Universidad Nacional de Asunción, San Lorenzo, Paraguay

2. Hydroconsult SRL, Asunción, Paraguay

3. Jožef Stefan Institute, Ljubljana, Slovenia

**Abstract:** Selected major, minor and trace elements in bottom sediments from the Tebicuary River, a tributary of the Paraguay River, as well as from Tapiracuai Stream on the left side of the large basin of the latter river have been investigated by EDXRF (Energy Dispersive X-Ray Fluorescence) techniques to determine their correlation as well as sediments provenance. The analysis of complex spectra was performed by the AXIL software and the quantitative analysis by the QAES software. Analyzed trace and minor elements were the refractory Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Nd as well Ti, Cr, V, Mn, Fe, Cu and Zn from the 3d series and Cd and Pb of known toxicity. The spidergrams of refractory elements normalized to PM (Primordial Mantle) and UC (Upper Crust) values suggest the recycling of materials of the sediments i.e., they have been subjected to weathering cycles. Spidergrams of the 3d elements normalized to UC and comparing with current sediment quality guidelines indicate that the normalized values are low and no harmful effect should be expected from them. In addition it can infer that normalization of the concentration of elements to UC values is a good approximation to estimate if the levels could be considered risky.

**Key words:** Bottom sediments, sediment quality guidelines, 3d series, refractory elements, PM, UC, provenance.

## 1. Introduction

Sediments, both bottom and suspended, have a prominent role in the distribution and interaction of metallic elements at major, minor and trace levels, which also have their role in the evolution in/of a water body, its eventual history, its “provenance” etc.; but just as sediments act as reservoirs and sinks for metals, they are also a fundamental component of aquatic habitat [1].

Provenance studies seek to elucidate the origin of sediments, sedimentary rocks, eventually the tectonic setting; for this they are based *inter alia* on their mineralogical, geochemical composition. In addition,

they are the key factor in determining and reconstructing the paleogeography of a sedimentary basin [2, 3].

On the other hand, taking into account that a variety of these metals are toxic and some of them, from certain concentrations can trigger potentially harmful effects for biota, international and national health agencies are trying to establish criteria for maximum recommended tenors in sediments, that is, SQG (sediment quality guidelines) [4-6].

The crust and the mantle of the solid earth are reservoirs that sediments are related to.

### 1.1 Water Bodies

Bottom sediments investigated were from Tebicuary River and Tapiracuai Stream. The latter

---

**Corresponding author:** Juan F. Facetti-Masulli, Dr., emeritus professor, research fields: radio & environment chemistry.

was also studied by spectrophotometry in a previous work [7]. The present is an extension of that effort.

Tebicuary River (Tbk) is one of the main tributaries of the Paraguay River, where it discharges approximately at coordinates 26°36'10" S and 58°11'35" W. It has a length of 360 km and its average flow is ~506 m<sup>3</sup>/s [8]. It is an important component of the profuse water resources of the Department of Itapúa [8-13]. It originates in the fan shaped streams of its headwaters. To the south of the town of Tavaí (~26°13' S, 55°33' W and ~143 masl) it forms a more or less defined channel that is fed by several bodies of water which springs varying heights (~395 to 405 masl). It runs through the departments of Caazapá, Itapúa, Misiones, Paraguari, Ñeembucú, enriched in its flow by the discharges of numerous streams that thus present a wide range of flows. At the point of coordinates ~26°32'30" S and 56°50'54" W, it receives the waters of the Tebicuary-mi River, which is considered its northern arm and whose hydrological and water quality regimes were published [14, 15].

Tapiracuai Stream (Tpk) is an extensive water course whose main channel is ~82 km length in a basin of 19,068 ha with 3.48% general slope. Its headwaters in Santa Rosa del Mbutuy are at a height of 334 masl and discharge at a height of 99 m above sea level in the marshlands of Tapiracuai [16].

In this work elemental content and provenance of refractory IE (incompatible elements) in bottom sediments of the above cited water bodies are investigated as well as the toxic metals Cd and Pb and those that from certain concentrations can trigger effects that are potentially harmful to the biota due to the presence/action of unpaired electrons with the formation of free radicals, such as elements of the 3d series of the periodic system [17].

## 2. Experiment

### 2.1 Sampling

The samples were collected in triplicate in two sampling stations in each stream; they were dried at

air then in an oven at 110 °C, ground and sieved; each sample was a compositum of the materials taken from the two stations, prepared by quartering. The finely pulverized materials were pressed into pellets for the XRF measurements.

### 2.2 XRF Measurements and Analysis

For the excitation of the fluorescence radiation the X-ray tube (at 40 kV and 20 mA) with the Mo anode and a Mo filter was used. The energy dispersive X-ray spectrometer attached to the tube excitation system was based on a Si (Li) semiconductor detector.

The analyses of complex spectra were performed by the AXIL software [18] which is based on iterative nonlinear least square fit of the spectra by the Gaussian shaped spectral lines. The resulting intensities of pure K<sub>α</sub> and L<sub>α</sub> lines of measured elements were then utilized in quantitative analysis, employing the quantification software of QAES (quantitative analysis of environmental samples) designed by Kump [19, 20].

This software utilizes i.e. the transmission-emission (TE) method for determination of the absorption in the sample and then iteratively finds the solution of the system of basic XRF equations (for each measured element there is one equation). The basic XRF equation namely relates the measured intensity to the respective concentration of the element in the sample.

As standards, the IAEA reference materials SL-1 and SL-3 sediments were used.

## 3. Results

Results are broken down in Table 1.

### 3.1 The Earth

For the earth structure, three approaches are used: (1) seismic profiles of the nucleus and mantle, (2) comparison of the systematic of the composition of primitive meteorites and the solar photosphere, (3) use of chemical and petrologic models of the peridotite-basalt melting relationship [21].

**Table 1 Results of analyzed major, minor and trace elements by XRF.**

Element (%)	F1 Tap	F4 Teb	Element (%)	F1 Tap	F4 Teb
Al	0.93	1.21	Si	45.10	42.9
Element (µg/g)	F1 Tap	F4 Teb	Element (µg/g)	F1 Tap	F4 Teb
S	223	ND	Rb	6.2*	5.8*
K	1,780	1,140	Sr	8.3*	5.9*
Ca	346	285	Y	7.3*	2.5*
Ti	1,360	787	Zr	715	37
V	35	28	Nb	3.1*	2.2*
Mn	88.3	94.6	Ba	52.3	41.8
Fe	2,010	2,600	La	4.4*	3.1*
Cu	18.4*	14.4*	Ce	10*	6.6*
Zn	25.2	22	Nd	2.4*	3.2*
Cd	ND	ND			

Relative SD: 10%-15%; \* Relative SD 20%-25%: they are used just as pattern indicators; ND: not detected.

In the differentiation of the elements in the melt, Fe, according to its high density moved towards the center of the earth reducing compounds of and forming alloys with less reactive metals such as Ni, Au, Pt etc. On the other hand, silicates, oxides, sulfides, materials of lower density, did so towards the surface. In this way the core (metallic) and the Primordial/Primitive Mantle (PM) differentiated i.e., the most prominent portions of the earth: metallic and silicate. The PM is the total structure of silicates that also is differentiated, being subdivided into the crust, and the mantle [22].

Seeking to establish the abundance of the elements on the earth, samples in large scale were collected and analyzed, in particular from the continental crust.

Modern analytical methods developed in the last century, such as spectrographic analysis, neutron activation, atomic absorption, X-ray fluorescence, ICP-MS, electron probe etc., contributed to this aim, allowing knowing the concentration of elements down to the trace level with relative reliability in geological materials.

In this way, pioneering works performed in sedimentary materials of different ages, such as sandstones, shales, limestones etc. [23-25], showed a very similar distribution/pattern of rare earth elements in these varied samples although different in basalts, chondrites etc.; the analysis and conclusions of these and other works allowed the development and

publication of a “new” table [26], improved and expanded subsequently [27-29].

### 3.2 The Crust [7]

The earth’s crust is bimodal. On the one hand the oceanic, of thickness of ~7 km, the age of which is less than 200 Ma, composed mainly by basalts. On the other hand, the continental crust, thick ~40 km, which contains practically all the rocks and minerals observed so far on earth and is between 4.0-4.4 Ga old. Thus, the continents indicate/testify the geological history of the evolution of our planet. The continental crust constitutes approx. 0.6% by weight of the planet’s silicates, contains a high proportion of IE and extends vertically from the surface to the Mohorovic (Moho) discontinuity, which is interpreted as the crust-mantle border (~40 km) [30]. Discontinuity stands for a layer at which seismic waves change speed and direction; waves *s* and *p* refract or reflect where layer components change their physical properties and reduce velocity when moving through hotter material.

From recent approaches based on seismic research and on the composition of rocks from the crystalline basement and its sedimentary cover, three layers are identified. The UC (upper crust) thickness is estimated at ~12-15 km [29]; the middle crust of about 12 km from the surface to the Conrad discontinuity and

finally the lower crust from this discontinuity to the Moho that extends for about 23 km. Likewise, the cortex becomes more mafic [31].

Due to its accessibility, the UC has undergone a large number of studies; there are two basic methods used: the weighted average of the composition of outcropping rocks and the mean of the composition of insoluble/poorly soluble elements (especially CFSE (elements of high-field stabilization energy)), rare earths etc.), in fine-grained sedimentary clastic rocks or glacial deposits. Thus the composition of the UC is inferred [7].

### 3.3 *The Mantle [21, 22]*

The mantle, under the Moho, extends ~2,890 km deep to the Gutenberg discontinuity (D<sup>''</sup>) and is subdivided into the UM (upper mantle), transition zone and LM (lower mantle). Their physical properties are different which could be attributed to compositional or/and phase changes. UM beneath the Moho, with olivine, pyroxene and garnet as essential minerals, down to the 416 km seismic discontinuity corresponds to a change in olivine structure. Transition Zone from 416 km with ringwoodite and garnet as essential minerals to 616 km discontinuity corresponding to the change of all minerals into perovskite and in lesser extend to Fe-Mg oxides. LM from the 616 km discontinuity until the Gutenberg discontinuity marks the boundary with the core with perovskite and Mg-wüstite as essential minerals [22]. For the purpose of this work, we are using the tables from Refs. [27-29].

To analyze and compare the concentration/occurrence of the elements in rocks, sediments etc., it is customary to refer/normalize said concentration to the recommended values of the UC or of the primordial mantle (PM) and by building the arachnograms or geochemical discriminating multi-element diagrams. The unit value obviously corresponds to those of the analyzed component layer [7]. When referring to the UC, higher values indicate that the element is concentrated at the point of sampling; in certain cases

this is used for prospection.

Usually in geochemical studies, the analysis is made in the context of the occurrence of other elements (arachnograms). If the interest refers to magmatic composition/changes, normalization is made basically on PM recommended values.

### 3.4 *SQG (Sediments Quality Guidelines)*

In our previous work there is a discussion about to the stipulation of standard (limit) values of elements concentration in bottom sediments and the following points are remarked: (i) traditionally sediment contamination has been determined by evaluating the concentration of individual components; (ii) the subject is by now also focused in the light of possible biological effects; (iii) sediments are a long-term source of contamination of the food chain; (iv) may occur sediment contaminants transfer to the liquid medium that interferes the trophic network in aquatic biota; (v) the reference standard values were developed seeking to coordinate/match the chemistry of sediments with biological information; (vi) regarding inorganic metal pollutants, efforts have so far focused on a few elements of more or less known biological effects that cover just a good part of the 3d series and others such as As, Cd, Pb etc.; (vii) because “standard” has imperative, mandatory meaning not always accepted by regulatory agencies, seeking consensus on the term and its meaning, the terminology has been changed to SQG line, which had good acceptance; (viii) several guide values have been proposed according to their level of effects, inter alia, TEL (threshold effects level), PEL (probable effects level), LEL (lower effects level), SEL (severe effects level), LRE (low range effects) etc.; (ix) these have resulted in the stipulation of the SQG by several agencies [7]; (x) the normalization of a few SQGs [4-6] to UC recommended values results in Fig. 1.

The values corresponding to low and threshold effects are close to the line of unit. On the other hand, severe effects are present in an upper line; low range

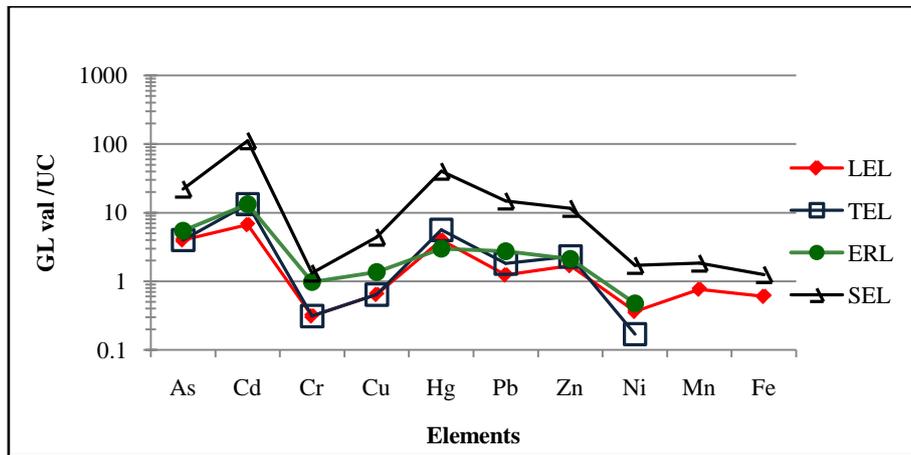


Fig. 1 Arachnograms of some of the proposed series, normalized according to the UC values (from Ref. [7]).

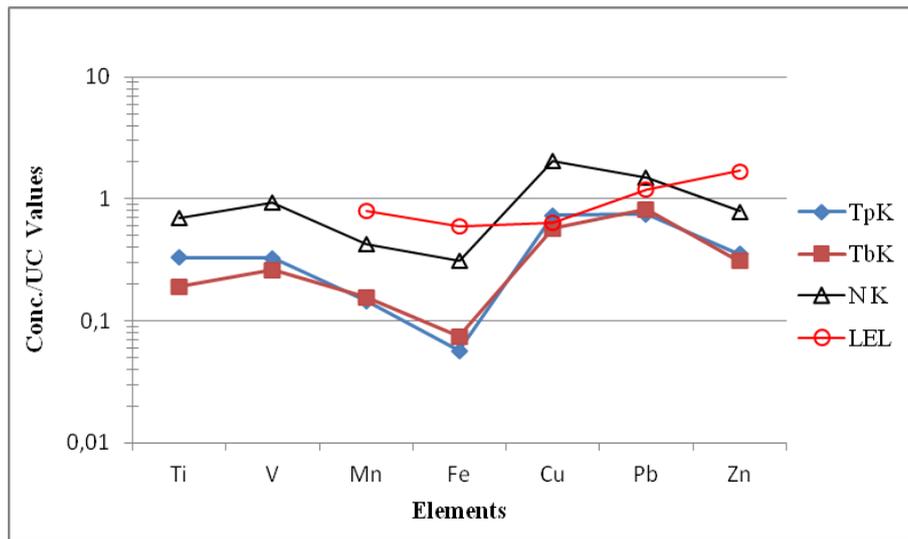


Fig. 2 Arachnogram of normalized values to UC obtained by XRF from BS of TbK & Nk rivers and Tpk stream; LEL is included for comparison.

effects line is a little bit over unit line.

It follows that the construction of the diagrams of analyzed elements, normalized to those of the UC, allows expeditious estimate levels of undesirable effects. It is in that sense, a very useful tool.

The arachnograms of values obtained by XRF of 3d and Pb elements from BS of Tebicuary River and Tapiracuai Stream normalized to UC, are presented in Fig. 2; in it normalized values of Negro River from Western Paraguay were included [32] as well as normalized LEL values. The occurrence values of measured elements are below the unit line as well as those of Negro River (Nk), close to that line. LEL values are included for comparison.

Note that these normalized records are lower than the UC unit line and that in general, the recorded levels of these elements in the sediments of such streams would be below the levels that could be considered risky.

Other elements that in different tenors occur in sediments are IE and refractory (RE), such as Rb, Sr, Ba, Nb, La Ce Nd, Zr, Ti, Y, of interest in this effort. They have not yet well established level effects for the current SQG, despite recent biologic/toxicology studies, inter alia those of Refs. [33-37].

However, if their concentration values are normalized to UC values, from the resulting arachnogram (Fig. 3), it can be concluded that no

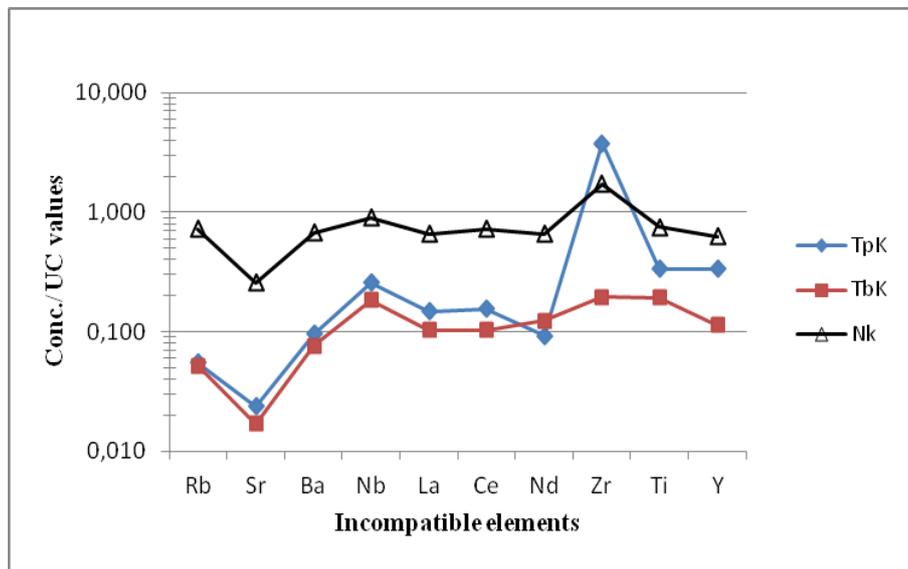


Fig. 3 Arachnograms of IE from BS normalized to UC of Tbk & Nk rivers and Tpk stream.

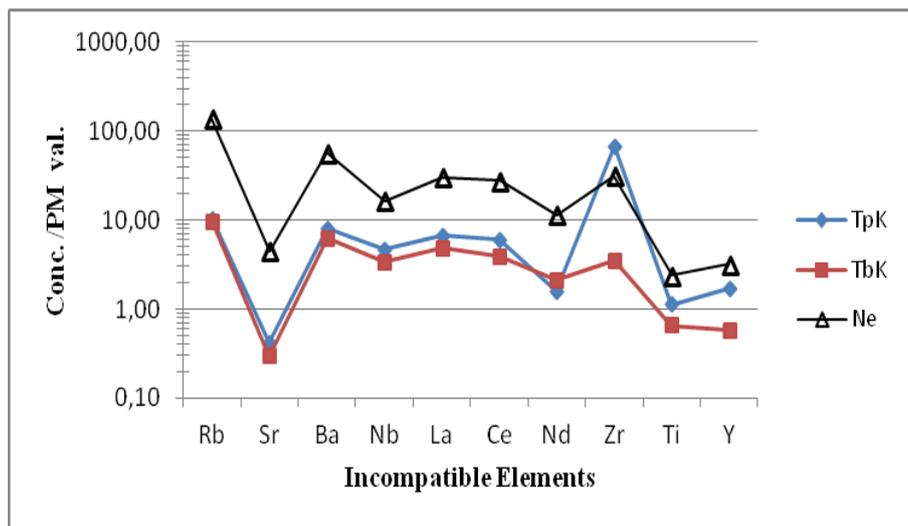


Fig. 4 Arachnograms of IE from BS of Tpk, Tbk, Nk, normalized to PM values.

undesirable effects should be expected.

In addition, registered values of Tbk and Tpk are well below the unit, indicative of strong weathering/denudation effects on sedimentary material [32, 38-40] taking into account the high Si (~43%, 45%) and Al (1%, 2% & 0.9%) tenors found. Note that they follow the same pattern as Nk River. Zr values above unit could be expected because according to their strong refractory properties, the major part of zirconium compounds remains unattacked [3, 32].

#### 4. Provenance

When studying sediments provenance, refractory (RE) and IE are very important. REs are those which maintain their primary relationships and are transferred almost directly into sediments, being fractionated very little, by diagenetic and metamorphic processes. IEs are those that during the crystallization processes of the magma, although the solid fraction shows enough sites to locate them, remain in the magma due to their high charge, large radius, etc.; most of them are refractory. Typical IEs are REE (Rare Earth Elements) as well as Zr, Nb, Ba, etc. They are useful tracers of geochemical changes

(geoindicators).

At this point, eventual changes in the magma could be of interest, therefore normalization is made on PM recommended values.

According to spidergrams normalized to PM, IE concentrations (Fig. 4), both, Tpk and Tbk, the last to a lesser degree, present an enrichment of the incompatible elements due to the magma differentiation processes. They also show troughs at Nb and Ti, a positive anomaly at Zr and a close resemblance to the spidergrams of sandstones from the Carboniferous/Permian ages [41] of Eastern Paraguay as well as to a passive continental margin setting [42, 43]; this is also confirmed from Nk River pattern of such a provenance [32]. From Ref. [44], “*continental margin* is the immersed region of the edge of a continent making the connection with the oceanic bottom. It is distinguished the *continental passive margins*, where the passage of the continental crust to the oceanic crust is done within the same lithospheric plate, and the *active continental margins* where the oceanic crust sinks by subduction under the continental crust”.

## 5. Conclusion

Arachnograms of 3d elements and Pb and that of IE normalized to UC, show values that are lower than those of the UC and the registered values of these metals in the sediments of such water bodies would be below the levels that could be considered risky. In general, such diagrams, normalized to those of the UC, allow expeditious estimate levels of undesirable effects. It is in that sense, a very useful tool.

Likewise, the spidergram of IE normalized to PM values indicates a passive continental margin setting provenance, as well as an enrichment of these elements due to magma differentiation processes, while the arachnograms of IE normalized to UC registered values are below the unit, indicative of strong weathering/denudation effects on sedimentary material.

## References

- [1] Facetti, M. J. F., Kump, P., and de Diaz Zulma, V. 2003. “Selected Trace and Minor Elements in Sediments of Itaipu Dam Reservoir.” *Czechoslovak J Physics* 53: 209-15.
- [2] Pe-Piper, G., Triantafyllidis, S., and Piper, D. J. 2008. “Geochemical Identification of Clastic Sediment Provenance from Known Sources of Similar Geology: The Cretaceous Scotian Basin, Canada.” *J. Sedimentary Research* 78 (9): 595-607. doi: 10.2110/jsr.2008.067.
- [3] Haughton, P. D. W., Todd, S. P., and Morton, A. C. 1991. “Sedimentary Provenance Studies.” In *Developments in Sedimentary Provenance Studies*, edited by Morton, A. C., Todd, S. P., and Haughton, P. D. W. London: Geological Society Special Publication, No. 57, pp. 1-11. Researchgate.net/publication/249549126\_Sedimentary\_provenance\_studies.
- [4] Burton, G. A. 2002. “Sediment Quality Criteria in Use around the World.” *Limnology* 3: 65-75.
- [5] Deckere, E. D., Cooman, W. D., Leloup, V., Meire, P., et al. 2011. “Development of Sediment Quality Guidelines for Freshwater Ecosystems.” *J Soils and Sedim.* 11: 504-17.
- [6] Canadian Council of Ministers of the Environment (CCME). 1995. “Protocol for the Derivation of Canadian Sediment Quality Guidelines for the Protection of Aquatic Life.” In *Technical Secretariat of the CCME Task Group on Water Quality Guidelines*, Ottawa.
- [7] Flores, F., Delgado, M., and Facetti, M. J. F. 2018. “Bottom Sediments from Tapiracuai and Cuarepotí Brooks.” *Rev Soc Cient Paraguay* 23 (2): 251-62. (in Spanish)
- [8] Surface Water Balance of Paraguay. 1992. Directorate of Meteorology and Hydrology of Paraguay and UNESCO Regional Office for Latin America and the Caribbean. (in Spanish)
- [9] UNESCO-International Hydrologic Program. 1996. *Hydrologic Map of South America & Explanatory Text*.
- [10] Secretary of the Environment, Paraguay and Federal Ministry of Economic Cooperation and Development (BGR) Germany. 2005. *Hydrogeological Map-Eastern Paraguay*.
- [11] National Cards. 1993. SG 21-2; SG21-4, Escale 1:250.000, 5472, 5572, 5571, 5671 Escale 1:100.000. Military Directorate of Geographic Service. (in Spanish)
- [12] Cáceres, D. F., Parra, V., Alonso, P., and Facetti, M. J. F. 2017. “Hydrological Studies in the Syryryka, Yukyray and Bobi Streams, Eastern Paraguay.” *Rev Soc Cient Paraguay* 22 (2): 47-60. (in Spanish)
- [13] Cáceres-Dueñas, F., Parra, V., Alonso, P., Facetti, M. J. F. 2017. “Hydrometric Studies at the Upper Basin of Tebicuary River—Eastern Paraguay.” *Rev Soc Cient Paraguay* 22 (2): 173-82. (in Spanish)

12 **Provenance, Guideline Values and Trace and Minor Elements in Bottom Sediments of Tebicuary River and Tapiracuai Stream from Eastern Paraguay by X-Ray Fluorescence**

- [14] Cáceres, D. F., Parra, V., and Facetti, M. J. F. 2005. "Hydrometric Study in the Tebicuary-mi River." *Rev Soc Cient Paraguay* 10 (17): 9-19. (in Spanish)
- [15] Facetti, M. J. F., Lozano, A. F., Urbieta, A., Delgado, M., and Dávalos, A. 2006. "Water Quality in the Tebicuary-mi River." *Rev Soc Cient Paraguay* 11 (20): 12-39. (in Spanish)
- [16] Cáceres, F., Parra, V., and Alonso, P. 2016. "Hydrological Studies in the Tapiracuai and Cuarepoti Streams." *Rev Soc Cient Paraguay* 21 (2): 169-80. (in Spanish)
- [17] Romero de Gonzalez, V., De Lorenzi, A., Kump, P., and Facetti, M. J. F. 2012. "Selected Mineral Content in Wheat from Paraguay by X-Ray Fluorescence." *J. Chem & Chem Eng.* 6: 1114-20.
- [18] Van Espen, P., Nullens, H., and Adams, F. 1977. "A Computer Analysis of X-Ray Fluorescence Spectra." *Nucl. Instrum. Meth.* 142: 243.
- [19] Kump, P. 1988. "QAES Instruction Manual." *J Stefan Institute*, Ljubljana.
- [20] Kump, P., Necemer, M., and Kupnic, P. 2005. "Development of the Quantification Procedures for *in Situ* XRF Analysis." In *In Situ Applications of X-Ray Fluorescence Techniques*. IA E A-TECDOC-1456: 217-29.
- [21] McDonough, W. F., and Sun, S. 1995. "The Composition of the Earth." *Chemical Geology* 129: 223-53.
- [22] Albaréde, F. 2004. *Geochemistry*. Cambridge: Cambridge University Press.
- [23] Haskin, L., and Gehl, M. 1962. "The Rare Earth Distribution in Sediments." *J. Geophys. Res.* 67: 2537-41.
- [24] Haskin, L. A., Wildeman, T. R., Frey, F. A., Collins, K. A., et al. 1966. "Rare Earths in Sediments." *J. Geophys. Res. B: Solid Earth* 71 (24): 6091-105.
- [25] Schmitt, R., Smith, R., Lasch, J., Mosen, A., et al. 1963. "Abundances of the Fourteen Rare-Earth Elements, Scandium and Yttrium in Meteoritic and Terrestrial Matter." *Geochim. Cosmochim. Acta* 27: 577-622.
- [26] Taylor, S. R. 1964. "Abundance of Chemical Elements in the Continental Crust: A New Table." *Geochim. Cosmochim. Acta* 28: 1273-85.
- [27] Taylor, S. R., and Mc Lennan, S. M. 1985. *The Continental Crust: Its Composition and Evolution*. Carlton: Blackwell Scientific Publication.
- [28] Rudnick, R., and Gao, S. 2003. "Composition of the Continental Crust." In *Treatise Geochem*, edited by Turekian, K., and Holland, D. Vol. 3. New York: Elsevier, 1-64.
- [29] McLennan, S. M. 2001. "Relationships between the Trace Element Composition of Sedimentary Rocks and Upper Continental Crust." *Geochemistry, Geophysics, Geosystems* 2: 154-5.
- [30] Rudnick, R., Gao, S., and Rudnick, R. 2014. "The Crust." In *Treatise of Geochem*, Vol. 4, 2nd ed. New York: Elsevier Science.
- [31] Gao, S., Luo, T.-C., Zhang, B.-R., Zhang, H.-F., and Hu, Y. K. 1998. "Chemical Composition of the Continental Crust as Revealed by Studies in East China." *Geochim. Cosmochim. Acta.* 62: 1959-75.
- [32] Facetti Masulli, J. F., and Kump, P. 2010. "Selected Minor and Trace Elements from Water Bodies of Western Paraguay." *J. Radioanalytical Nucl. Chem.* 286: 441-8.
- [33] Kabata Pendias, A., and Pendias, H. 2001. *Trace Elements in Soils and Plants*. 3rd ed. Boca Ratón: CRC Press.
- [34] Pagano, G., Guida, M., Tommasi, F., and Oral, R. 2015. "Health Effects and Toxicity Mechanisms of Rare Earth Elements—Knowledge Gaps and Research." *Ecotoxicology and Environmental Safety* 115: 40-8. <http://dx.doi.org/10.1016/j.ecoenv.2015.01.030>.
- [35] Nordberg, G. 2001. "Metals: Chemical Properties and Toxicity Chapter 63." In *Encyclopaedia of Occupational Health and Safety*, 3rd ed. International Labor Organization ILO, Ministry of Labor and Social Affairs. NIPO: 201-01-080-7-Spain. (in Spanish)
- [36] Hua, D., Wang, J., Yu, D., and Liu, J. 2017. "Lanthanum Exerts Acute Toxicity and Histopathological Changes in Gill and Liver Tissue of Rare Minnow (*Gobiocypris rarus*)." *Ecotoxicology* 26: 1207-15. doi: 10.1007/s10646-017-1846-8.
- [37] Mesa-Pérez, M., Díaz-Rizo, O., Tavella, M. J., Bagué, D., and Sánchez-Pérez, J. 2018. "Soil-to-Plant Transfer Factors of Rare Earth Elements in Rice (*Oryza sativa* L.)." *J Agricultural Technical Sciences* 27 (2): 1-9.
- [38] Gaillardet, J., Dupre, B., Louvat, P., and Allegre, C. J. 1999. "Global Silicate Weathering and CO<sub>2</sub> Consumption Rates Deduced from the Chemistry of Large Rivers." *Chem. Geol.* 159 (1-4): 3-30. doi: 10.1016/S0009-2541(99)00031-5.
- [39] Gaillardet, J., Dupre, B., and Allegre, C. J. 1998. "Geochemistry of Large River Suspended Sediments: What Can We Learn about Present Day Weathering of Silicates?" *Mineralogical Magazine* 62: 489-90. doi: 10.1180/minmag.1998.62A.1.259.
- [40] Yang, S., Jung, H. S., and Li, C. 2004. "Two Unique Weathering Regimes in the Changjiang and Huanghe Drainage Basins: Geochemical Evidence from River Sediments." *Sedimentary Geology* 164 (1-2): 19-34. doi: 10.1016/j.sedgeo.2003.08.001.
- [41] Facetti Masulli, J. F., Kump, P., and Gonzalez Erico, E. 2010. "Selected Trace and Minor Elements in Sandstones from Paraguay." *Radiochim. Acta* 98: 441-6.
- [42] Roser, B. P., and Korsch, R. J. 1998. "Provenance Signatures of Sandstone-Mud Stone Suites Determined

Using Discriminant Function Analysis of Major Element Data." *Chemical Geology* 67: 119-39.

- [43] Burnett, D. J., and Quirk, D. G. 2001. "Turbidite Provenance in the Lower Palaeozoic Manx Group, Isle of

Man: Implications for the Tectonic Setting of Eastern Avalonia." *J. of Geolog Soc.* 158: 913-24.

- [44] Foucault, A., and Raoult, J. F. 2000. *Dictionary of Geology*. Paris: Dunod. (in French)