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Using the mineralogy of river sediments as pollution indicator of clay mining activity

Utilização da mineralogia dos sedimentos fluviais como indicador de poluição da atividade de mineração de argila

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ABSTRACT

View of the difficulty to elect standards for water pollution control in clay mining activity, this study aimed to verify the possibility of using the mineralogy of river sediments as a pollution indicator of clay mining activity. The study was carried out in the Assistência Stream basin, located in the largest ceramic pole of the Americas. Surface water samples of Assistência Stream were collected in 67 field campaigns in 2014. This stream showed an average annual discharge of 0.8 m³.s⁻¹ with an annual flux of suspended solids of 3,680 t.year⁻¹ and an annual flux of dissolved solids of 4,234 t.year⁻¹. The mineralogical analysis of fluvial sediments indicated the presence of quartz, montmorillonite, illite and kaolinite in the fraction <53 micrometers. The kaolinite is from the surface soil erosion. However, the illite, predominant clay mineral in the rocks explored by mining, is practically absent in the surface horizon of the Assistência Stream basin. Thus, its presence in the suspended solids transported by Assistência Stream is associated with atmospheric deposition of dust produced during clay mining activities present in this watershed.

Keywords: Water resources; Clay minerals; Hydro-sedimentology; Pollution control.

RESUMO

Frente à dificuldade de eleger padrões para o controle da poluição hídrica em atividade de mineração de argila, este trabalho tem como objetivo verificar a possibilidade de uso da mineralogia dos sedimentos fluviais como indicador de poluição da atividade de mineração de argila. O estudo foi desenvolvido na bacia do Córrego Assistência, situada no maior pólo cerâmico das Américas. Ao todo foram realizadas 67 campanhas de campo no ano de 2014 para coleta de água superficial do Córrego Assistência. Este córrego apresentou uma vazão média anual de 0,8 m³.s⁻¹, com descargas anuais sólidas de 3.680 t.ano⁻¹ e, dissolvidas de 4.234 t.ano⁻¹. A análise mineralógica dos sedimentos fluviais indicou a presença de quartzo, montmorillonita, illita e caulinita na fração <53 µm. A caulinita é proveniente da erosão superficial do solo. Contudo, a illita, argilomineral predominante nas rochas exploradas pela mineração, é praticamente ausente no horizonte superficial do solo da bacia do Córrego Assistência. Assim, sua presença entre os sólidos em suspensão transportados pelo Córrego Assistência está associada pela deposição atmosférica da poeira produzida durante as atividades de mineração de argila presentes nesta bacia hidrográfica.

Palavras-chave: Recursos hídricos; Argilominerais; Hidrossedimentologia; Controle da poluição.



INTRODUCTION

Mining is an activity with high potential for environmental degradation, because its implementation implies the removal of vegetation, fauna and soil of the required area, with significant changes in terrain and topography that cause consequences in the hydrological regime and in the dynamics sediments of watershed. The potential pollution of these activities may be enhanced depending on the composition and chemical stability of the mining overburden and the waste produced, and how they are disposed on the environment (CARVALHO et al., 2000; BONUMÁ; GASTALDINI; PAIVA, 2008; MECCHI; SANCHES, 2010; CRISTOFOLETTI; MORENO, 2011). The densification of clay mining ventures have caused negative impacts, mainly due to the emission of particulate matter into the atmosphere and the fine sediment entrainment to water bodies (CRISTOFOLETTI; MORENO, 2011). In areas of influence of mining activities is common the increased turbidity in rivers and reservoirs, causing negative impacts in the multiple uses of water resources, mainly to public supply.

In Brazil, the ecological importance of the river sediment is still neglected by legal guidelines to control water pollution established by the CONAMA Resolutions 357/05 (BRASIL, 2005) and 430/11 (BRASIL, 2011). The parameter “sedimentary materials” is the main analysis of solid release conditions in receivers water bodies. This parameter is successfully applied in punctual pollution sources, where the volume and the concentration of effluent are known and easily controlled. However that does not occur to diffuse effluent sources, such as those from the clay mining. The difficulty of establishing legal standards for diffuse and intermittent loads inhibits pollution control action and effective conservation practices in the sector (NOVOTNY, 2003).

According to Minella and Merten (2011), hydro- sedimentometric monitoring programs associated with the techniques of sources identification have been successfully used in the design of effective strategies for the control of the erosion and the diffuse pollution in watersheds.

The fluvial sediments have the capacity to retain some physical and chemical characteristics of their origin place that can be used to elucidate its provenance within the watershed (WALLING, 2005). Among the parameters that can be used for this purpose, highlights the mineralogical, magnetic, geochemical, organic, radiometers and isotopic (MINELLA; MERTEN, 2011). However, the selection of natural markers (tracers) should consider the characteristics of the studied site, since they can vary from place to place, depending of the land use, geological context and geomorphological history (DAVIS; FOX, 2009).

The clay minerals are presented as potential tracers due to their sensitivity to chemical weathering since the mineral composition of clays indicates weather conditions (precipitation and temperature) and the geological context (lithology and morphology) of its origin, thus allowing the determination of the provenance of sediments in water bodies (WANG et al., 2011; LI et al., 2012; GARZANTI et al., 2014; HU et al., 2014.).

Clays may occur as primary components of sedimentary rocks, for example, illite ($KAl_2Si_4O_{10}(OH)_2$) and chlorite ($(Mg,Al,Fe)_{12}(Si,Al)_8O_{20}(OH)_{16}$), indicating slightly chemically altered environments. Already in environments where chemical weathering is intense, the rock alteration process results in clays

of the kaolinite ($Al_2Si_2O_5(OH)_4$) and montmorillonite ($(Mg,Ca)O.Al_2O_3.Si_5O_{10}.nH_2O$) groups, both formed by partial hydrolysis processes (ZANARDO, 2003; CONCEIÇÃO; BONOTTO, 2006; ZANARDO et al., 2009; ROVERI, 2010; HE et al., 2013).

A number of intrinsic difficulties present in the hydro-sedimentometric monitoring operation has prevented its integration with the other water management and pollution control fronts. Among them, we highlight the sampling difficulty of fluvial sediments in the peak discharge events, the absence of consensus about the fluvial sediment flux considered “acceptable” in the water resource, the occurrence of multiple sources of sediment and contaminants performing in different times and places that make unfeasible the applicability of the “polluter pays” principle (WHITE; APITZ, 2008).

A research in Lageado Grande, São Martinho da Serra – RS, found a possible diffuse impact in the charge of suspended sediments related to agricultural activities and extraction of precious stones (BONUMÁ; GASTALDINI; PAIVA, 2008). Unfortunately, there are no scientific studies to report the use of mineralogy for evaluation of diffuse impacts from clay mining. Thus, the aim of this paper was to investigate the possible use of a mineralogical indicator to identify the clay mining activity pollution in a watershed located in the influence area of the largest pole of clay mining and ceramic industries of the Americas, from the qualitative analysis of clay minerals.

STUDY AREA CHARACTERIZATION

The Assistência Stream basin has 38 km² and is located between the municipalities of Iracemópolis, Rio Claro and Santa Gertrudes, São Paulo State (Figure 1). This is a second order basin that integrates the middle course of the Corumbataí River. The landscape is characterized by Peripheral Depression of the eastern border of the Paraná Basin typical relief, with a predominance of medium-sized hills and top interfluvies planed, crossed out by valleys whose slopes rarely reach 200 m (CUNHA, 2007).

The lithology of the study area is inserted in the Paraná Sedimentary Basin context (Figure 2). In the valleys and lower topographical areas are the Itararé Subgroup and Tatuí Formation, the center of the basin is occupied by the Irati and Corumbataí Formations, while the higher regions are supported by intrusive bodies of tholeiitic basic magma (diabase) in threshold form and associated dykes, which represent the Serra Geral Formation (ZAINÉ, 2000). Due to topographical and geographical positioning of lithologies, the Corumbataí, Irati and Serra Geral Formations were considered the main sources of sediments, originated by the surface soil erosion process and the availability of material from clay mining and dolomitic limestone.

Regarding pedology, the basin areas with condition to provide sediment to drainage are covered by developed soils, where Ustisol predominate, followed by Oxisol and Neossolos (VALENTE, 2005). The land use in the basin is a predominantly rural, with emphasis on agriculture, mining and pasture, which occupy approximately 60%, 10% and 5% of the total area, respectively. The climate of the region studied is classified as tropical humid, i.e. with wet summer and dry winter, the average annual temperature above 18°C and average annual rainfall of about 1500 mm/year (CONCEIÇÃO; BONOTTO, 2006).

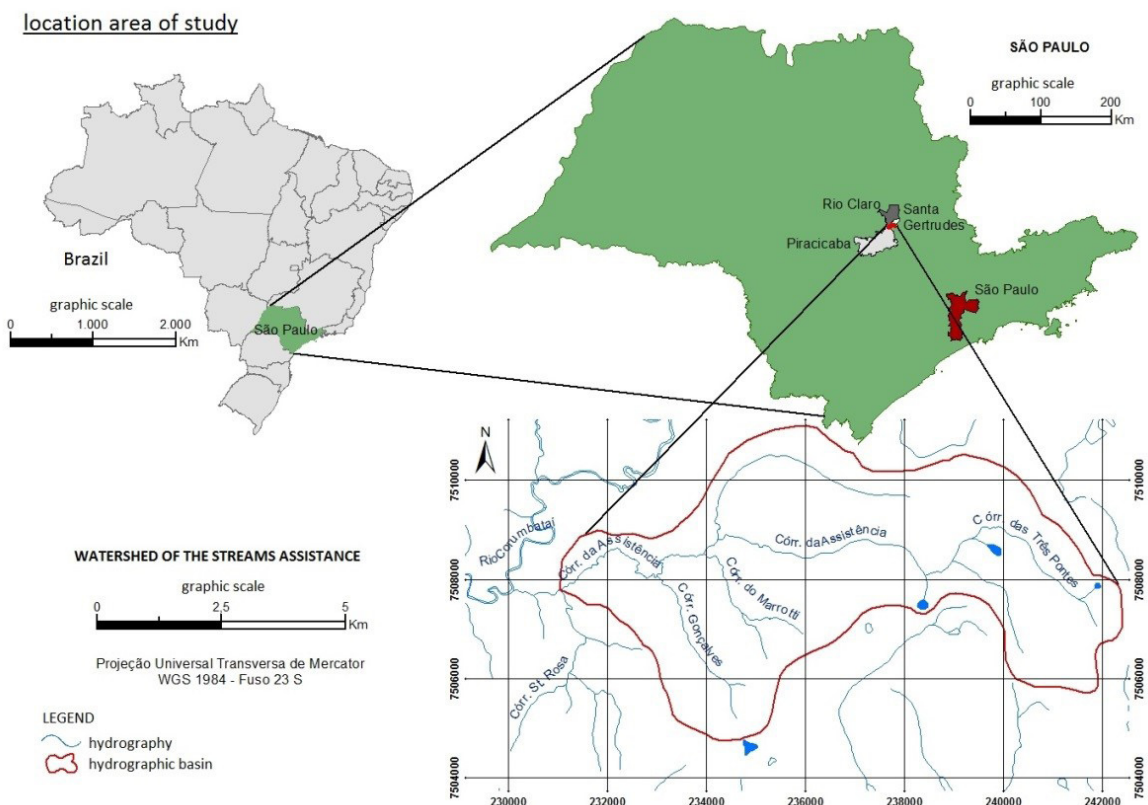


Figure 1. Geographical map of the Assistência Stream basin.

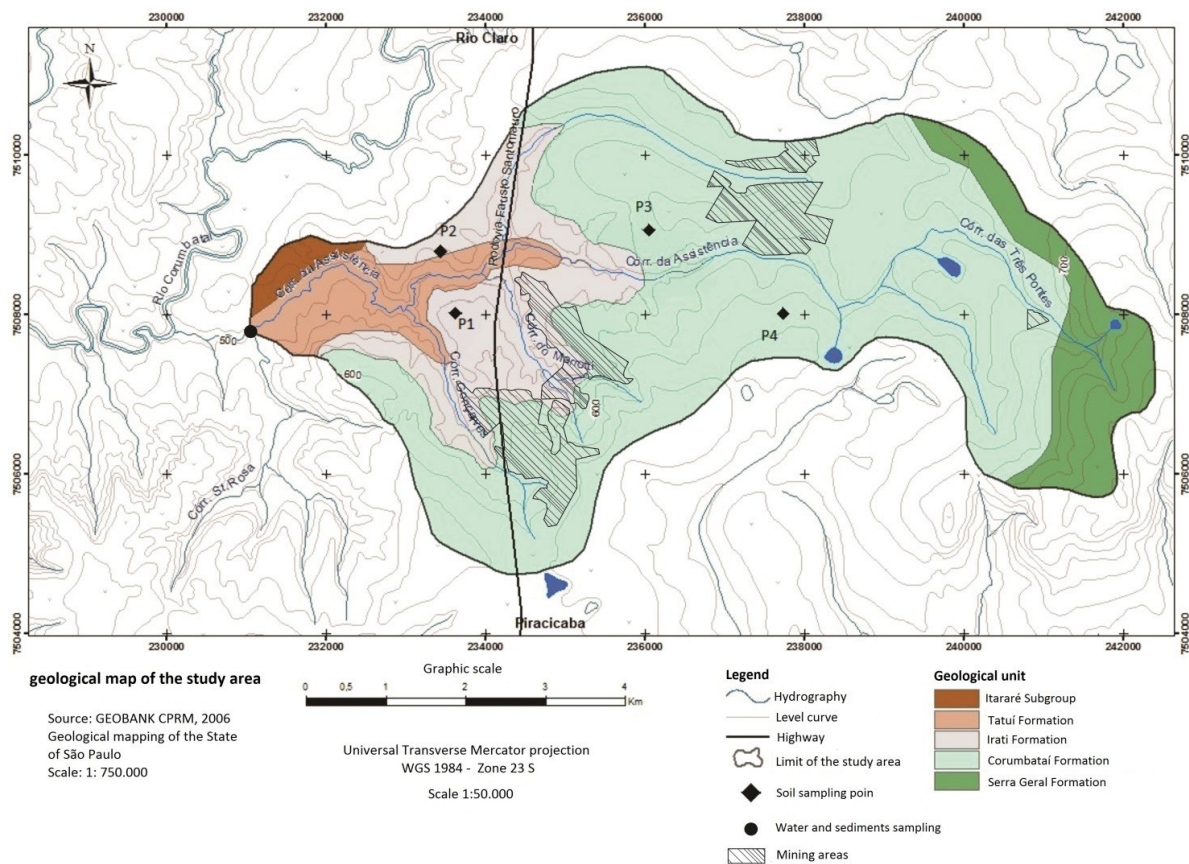


Figure 2. Geological map of the Assistência Stream basin, indicating the mining areas and the surface waters and the soils sampling points.

MATERIALS AND METHODS

The hydrosedimentometric monitoring was conducted in the Assistência Stream basin exutory during 2014, we performed weekly fieldworks and eventually extra campaigns in the rain events. The campaigns data were segregated as to the occurrence of significant rainfall events, with capacity to generate runoff and to carry large amounts of sediment into the stream. In order to identify these events was adopted turbidity > 100 NTU as standard condition, which were classified as flood event.

The hydrometric data of water velocity and average depth river channel were obtained using a hydrometric flow probe and bathymetry in nine vertical sections distributed along the channel width, respectively. With this data were calculated the wet area section and the average instantaneous discharge. The suspended solids discharge was obtained using Equation 1.

$$Q_{SS} = 0,0864 \cdot Q \cdot CSS \quad (1)$$

At where:

Q_{SS} = solid discharge measured ($t \cdot y^{-1}$);

Q = average instantaneous discharge ($m^3 \cdot s^{-1}$);

CSS = measured concentration of total suspended solids ($mg \cdot L^{-1}$)

In each field campaign were read in situ the pH, water temperature ($^{\circ}C$), dissolved oxygen ($mg \cdot L^{-1}$) and the total dissolved solids concentration ($mg \cdot L^{-1}$), using a multiparametric probe YSI-556. At the time, were also collected two water river aliquots, one with 500 ml and another with 20 L, which were stored in polyethylene containers and sent for laboratory analysis. The 500 ml aliquots were used to determine the total suspended solids concentration ($mg \cdot L^{-1}$) and turbidity (NTU). These two measurements were performed in triplicate, immediately after collection. The total suspended solids concentration was quantified by the gravimetric method, according the Standard Methods procedures (APHA; AWWA; WEF, 1998). Turbidity was measured using a Hach portable turbidimeter, 2100P model, that utilizes the relationship between the scattered light nephelometric signal (90°) and the transmitted light, with the concentration range from 0 to 1000 NTU and accuracy of 2%. The 20 L aliquots were passed by successive decanting and siphoning processes to obtain the suspended sediments mass. These sediments mass were sieved in mesh 53 μm , by wet process, and sent to mineralogical analysis by X-ray diffraction (XRD).

In order to evaluate the source-areas of the suspended sediment transported by the Assistência Stream, the characterization of mined materials and the minerals contained in the basin soil was required. The rock mineralogy of clay extraction areas was described using literature data, specifically the studies of Zanardo et al. (2004) and Roveri (2010). To identify the dominant clay minerals in the soil were collected four surface soil samples in the study area (Figure 2), two samples on the Irati Formation and other two samples on Corumbataí Formation. At each sampling point were opened three trenches and the bottom material was collected, and after were composed in a single sample per point.

The composite soil sample pretreatment before to subjected to XRD mineralogical analysis consisted of quartering each sample and drying the selected portion in a stove at $60^{\circ}C$. After drying, the removal of possible interferences was performed, for example the grass roots, and the sample was sent to the PFAFF vibrating

mill for 20 seconds. The fine fraction of the soil sample was obtained using the deflocculation process in aqueous medium with sodium hexametaphosphate solution (10%). After eight hours of reaction, the fine particles still suspended in the water column were transferred to another bottle and submitted to XRD analysis.

To perform the XRD analysis, two laminae were prepared for each sample. The first laminae was read by diffractometry after drying at room temperature and thereafter it was placed in ethylene glycol atmosphere for 24h before to be analyzed again. The second laminae was heated at $500^{\circ}C$ for 2 hours before each new reading. This procedure is performed to assist the clay minerals identification. The ethylene glycol treatment is used to identify expansible minerals, allowing distinguish the smectite group minerals, while the heat treatment promotes the disappearance of the kaolinite, smectite and gibbsite peaks due to loss of the mineral crystalline structure that becomes amorphous to X-rays (SCAPIN, 2003).

The difratograms of fluvial sediments and soils were interpreted by software X'pertHighscore Plus[®], with ICDD PDF2 database that has more than 70,000 crystalline compounds.

RESULTS AND DISCUSSIONS

Analysis of the quality water and of the solid and dissolved discharges

Were performed sixty-seven field campaigns, being fourteen classified as flood events, i.e. showed turbidity greater than 100 NTU, and the other fifty-three were considered to belong to the dry weather. It should be emphasized that the data obtained in 2014 expressed an extreme drought atypical scenario, which was recorded as the worst drought since the beginning of meteorological measurements in the Southeastern Brazil, over more than eighty years (ORSI, 2015). This condition was certainly decisive in sediment transport processes, with significantly reducing of the quantity removed out of the study basin.

The pH values of the Assistência Stream waters have varied from 6.1 to 7.4, being close to neutral and within the classification range for Rivers Class II, according to CONAMA Resolution No. 357/05 (BRASIL, 2005) (pH values between 6 and 9). The surface water average temperature in the study period was $20.2^{\circ}C$, being that the lowest water temperature was $11.8^{\circ}C$, measured in 07.21.2014, and the highest was $24,0^{\circ}C$, in 12.22.2014. The dissolved oxygen (DO) average concentration was $5.0 mg \cdot L^{-1}$, in accordance with Class 2 classification rivers, established in CONAMA Resolution No. 357/05 (BRASIL, 2005). However, during the dry season, some days of Assistência Stream water sampling had values of dissolved oxygen concentration lower than $5.0 mg \cdot L^{-1}$, which may be associated with the *Pistia stratiotes* L. macrophyte proliferation. According to Esteves (1998), the reduction of the water turbulence and increase of the nutrients concentration favor the proliferation of this species, that is also associated with high pH.

Among the human activities developed upstream of the monitoring point, highlights the sugarcane fertirrigation as the main nutrient source in the dry season. It also should be considered the intensive livestock activity, with cattle freely moves in the permanent preservation areas (APP) and in the stream channel.

The wastewater from the urban area has been treated since 1987, by septic tank filter system, and from 2005 by the biofilter process (RIO CLARO, 2012).

The average discharge of Assistência Stream was $0.8 \text{ m}^3 \cdot \text{s}^{-1}$, with maximum and minimum values of 8.4 and $0.1 \text{ m}^3 \cdot \text{s}^{-1}$, quantified in the 12.23.2014 and 10.20.2014, respectively. The average discharge in the rainy season was $1.2 \text{ m}^3 \cdot \text{s}^{-1}$, and this value was three times higher than the average of the dry period ($0.4 \text{ m}^3 \cdot \text{s}^{-1}$).

Figure 3 shows the water column depth (H) vs discharge (Q) relationship observed in the field. In this figure also was plotted the QxH adjustment curve function (Equation 2), obtained from a nonlinear optimization model that considers the adjustment parameters a , b and H_0 in addition to Q and H parameters, where a and b are dimensionless parameters and H_0 is the water level when the discharge is equal to zero. The adjustment parameters were obtained by trial and error using the Solver interactive tool (Excel Microsoft®), according Porto et al. (2001).

$$Q = a (H - H_0)^b \tag{2}$$

The observed discharge (Qobs) vs calculated discharge (Qcal) relationship is illustrated in Figure 4. The distance between the lines of the perfect adjust model and the data linear regression represents the embedded errors in the model used.

In the dry period, the average depth ranged from 0.3 to 0.5 m and the discharge below $0.5 \text{ m}^3 \cdot \text{s}^{-1}$, which may be related to decreased water velocity due to the increase of macrophyte proliferation. During the rainy period, the average depth variation was from 0.35 to 0.75 m and, as expected, the highest discharge values were related to greater depths. However, to depths between 0.35 and 0.5 m were observed higher discharges during the rainy period when compared to the recorded in the dry period. This may be associated with increased water velocity, caused by the removal of macrophyte vegetation to outside the drainage basin in the

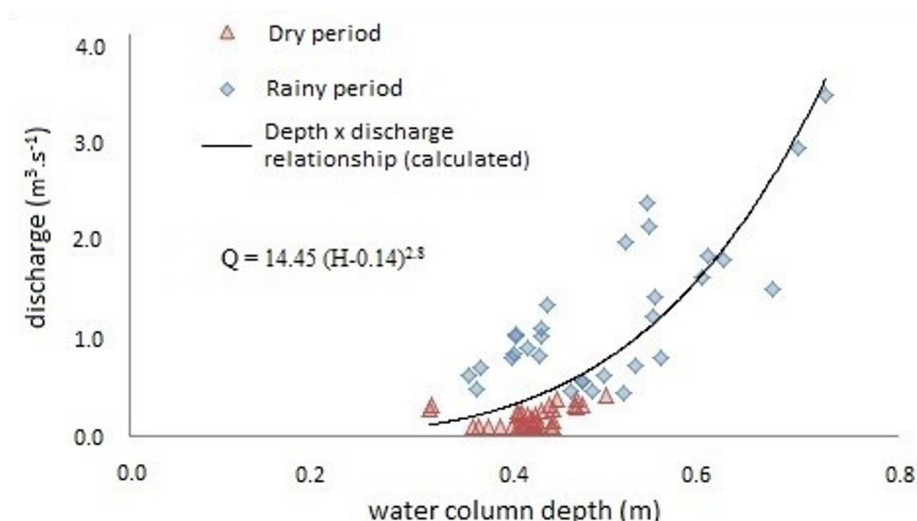


Figure 3. Average depth vs discharge relationship for the Assistência Stream in the study period and the QxH adjustment curve function.

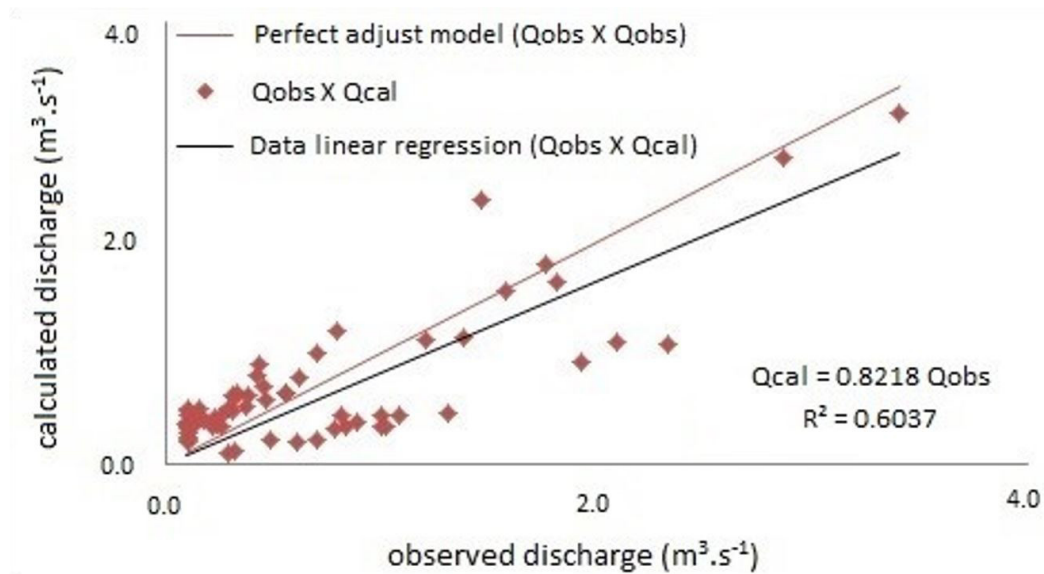


Figure 4. Observed discharge vs calculated discharge (Qobs x Qcal) relationship.

first rainfall events and the consequent discharge increase and its drag force.

The total suspended solids concentrations transported in the stream ranged from 1 to 576 mg.L⁻¹, being the simple arithmetic average of the observed values along the study period equal to 46 mg.L⁻¹. The solid discharge in the study period was 3,680 t.y⁻¹, corresponding to an average daily of 10.1 t. The average discharge of the suspended solids in flood events was 50.2 t.day⁻¹, whereas the average for the dry period was 0.4 t.day⁻¹, showing the rain events influence in the sediments transport of Assistência Stream basin. Regarding the specific solid discharge, it was observed an average of 98.2 t.km².y⁻¹.

The discharge rate vs solid discharge relationship (Figure 5) was obtained from the campaign data set and has shown that

the solid discharge started being expressive in full events, where the discharge rate was higher than 1.5 m³.s⁻¹. In the 12.23.2014 sampling day was recorded an extreme precipitation event which resulted in higher values of discharge and suspended sediment flux observed during the study period, i.e. 8.38 m³.s⁻¹ and 298.3 t.day⁻¹, respectively.

The positive and significant correlation between turbidity and total suspended solids concentration ($r = 0.994$ and $P < 0.01$) indicates the possibility to indirectly determine the suspended solids concentration from the turbidity data measured in situ and in real time using the equation $[TSS] = 0.3068 \cdot \text{turbidity} + 2.6961$ (Figure 6). When converting the turbidity in the suspended solids concentration it is possible to determine the solid discharge, considering that the discharge at the time of monitoring is known.

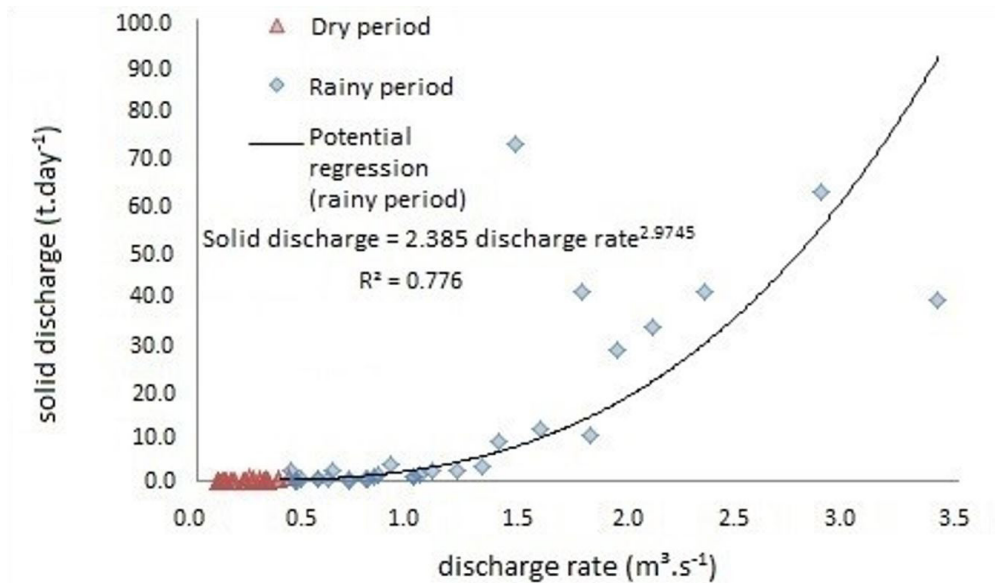


Figure 5. Discharge rate vs solid discharge relationship for Assistência Stream in the study period.

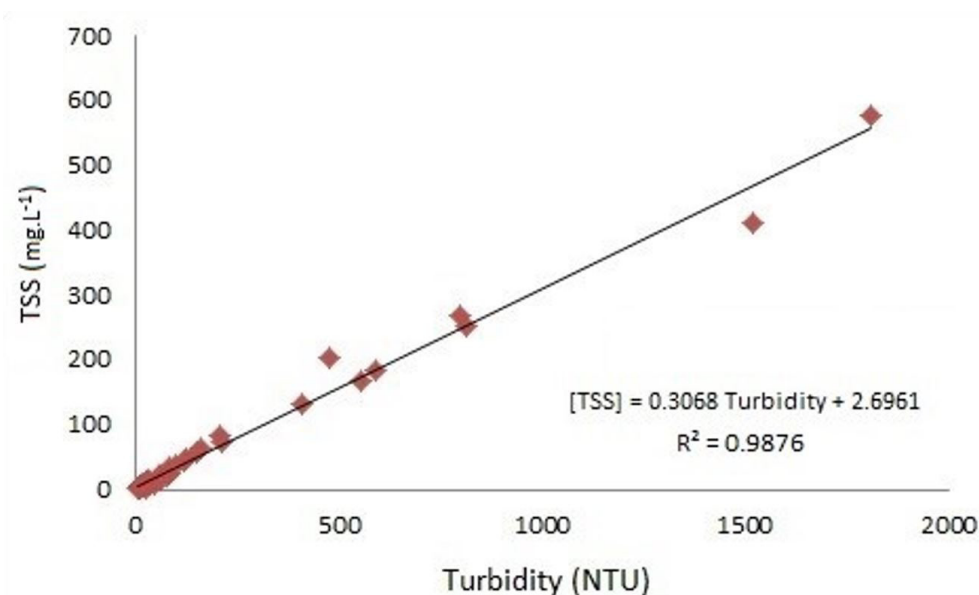


Figure 6. Turbidity vs TSS concentration relationship for the Assistência Stream in the study period.

Thus, using only data of water column depth and turbidity, can be obtained quickly and less costly information about the solid discharge in the Assistência Stream basin.

Figure 7 shows the hydrogram and the variation of turbidity parameter during the study period (2014) in the Assistência Stream basin. The turbidity showed a similar behavior to that observed for the discharge, indicating the dependence of this parameter with the hydrological events. Generally, the diffuse pollution in rural basins is associated with the input of sediment, nutrients, pesticides and animal waste husbandry, and the surface runoff is the main mechanism pollution load input. Also to be considered the other system input components, such as atmospheric deposition and the carry of air pollutants by rainwater (REIS; BRANDÃO, 2013).

The total dissolved solids average concentration in the study period was 180 mg.L^{-1} . From the total dissolved solids concentration

can be expressed the salinity in parts per thousand (‰), which along the studied year varied between 0.09 and 0.36 ‰. According to CONAMA Resolution No. 357/05 (BRASIL, 2005), the waters of Assistência Stream are classified as freshwater, because it presented salinity below of the limit for this classification, which is 0.5 ‰ (Figure 8). The average salinity of the Assistência Stream was 0.18 ‰ in the study period, with values of 0.15 ‰ in flood events and 0.18 ‰ in dry weather conditions.

The total dissolved solids discharge in the study period was $4,234 \text{ t.ano}^{-1}$, which corresponded to a daily average of 11.6 t and a specific average production of dissolved solids $112.9 \text{ t.km}^{-2}.\text{y}^{-1}$. The specific transport of the total load (dissolved and suspended) was $211.1 \text{ t.km}^{-2}.\text{y}^{-1}$, with the dissolved discharge accounted for 54% this total load.

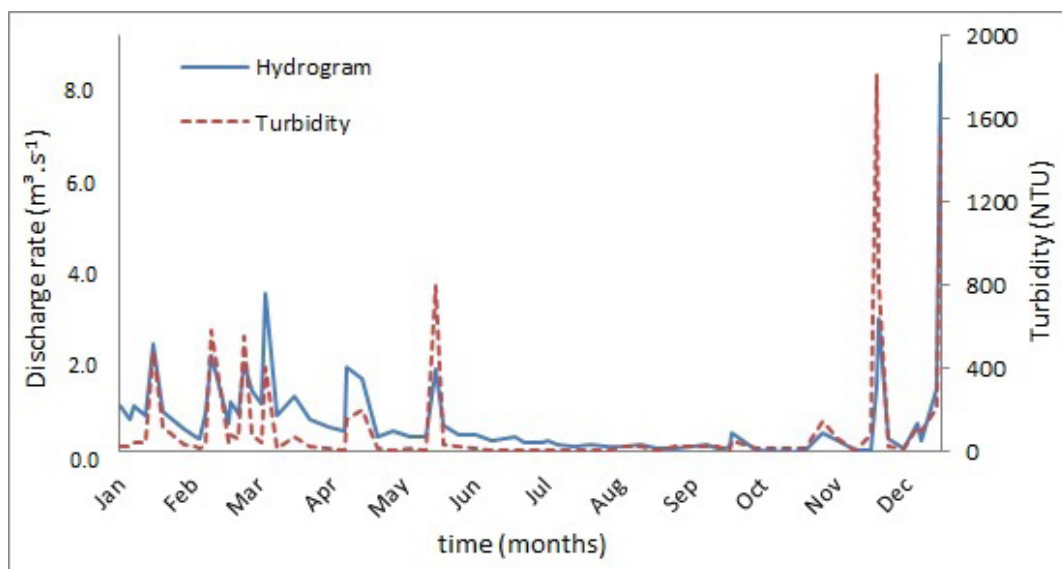


Figure 7. Variation of discharge rate and turbidity parameter during the study period in the Assistência Stream basin.

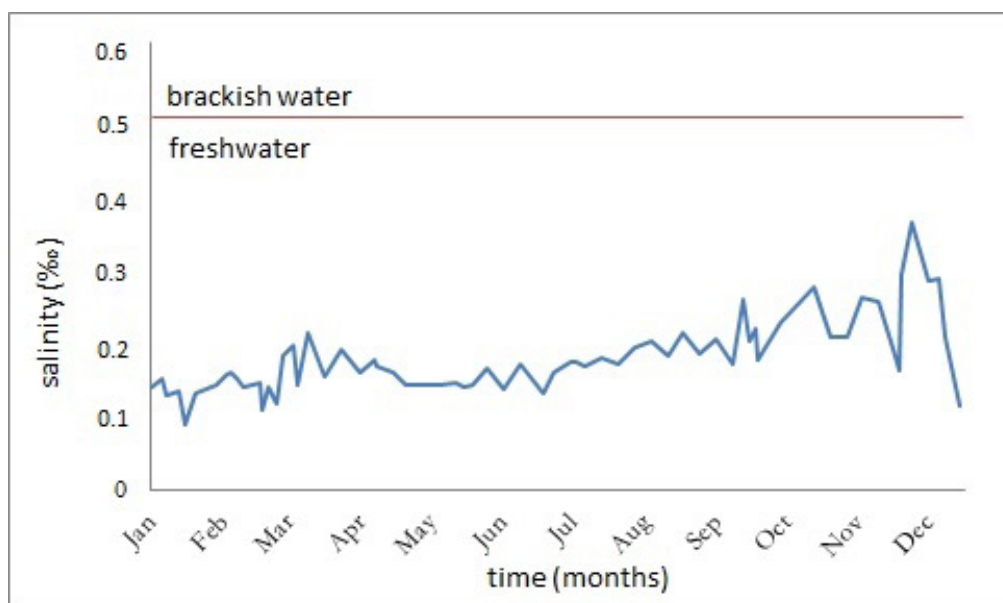


Figure 8. Salinity variation in the Assistência Stream basin during study period.

At the occurrence of rainfall events, the salinity tended to decrease, because the dilution process of salts occurs with increasing discharge rate. It is believed that the salinity of the Assistência Stream is associated, in part, to the presence of elements/chemical compounds derived from the partial hydrolysis process of silicate minerals and dissolution of carbonates (calcite - CaCO_3 and dolomite - $\text{Ca, Mg (CO}_3)_2$) that compose the study area rocks. Sulphates (SO_4^{2-}) in surface waters are coming from the organic matter decomposition and from the chemical weathering of rocks and soils, with the dissolution of gypsum (CaSO_4) and magnesium sulfate (MgSO_4) and pyrite oxidation (FeS_2). Pyrite is common in shales of the Irati Formation and its oxidation originates gypsum, epsomite and others minerals.

Mineralogy of suspended solids and its relationship with the rocks and soils in the Assistência Stream basin

The qualitative mineralogical analysis of the suspended solid load revealed the presence of quartz, montmorillonite, illite and kaolinite in the fraction <53 micrometres, both in the dry period (Figure 9) as in flood events (Figure 10). The presence of illite in suspended sediments drew attention, which should not be happening, because this mineral is susceptible to partial hydrolysis and is transformed into kaolinite during the interaction water-rock/soil process.

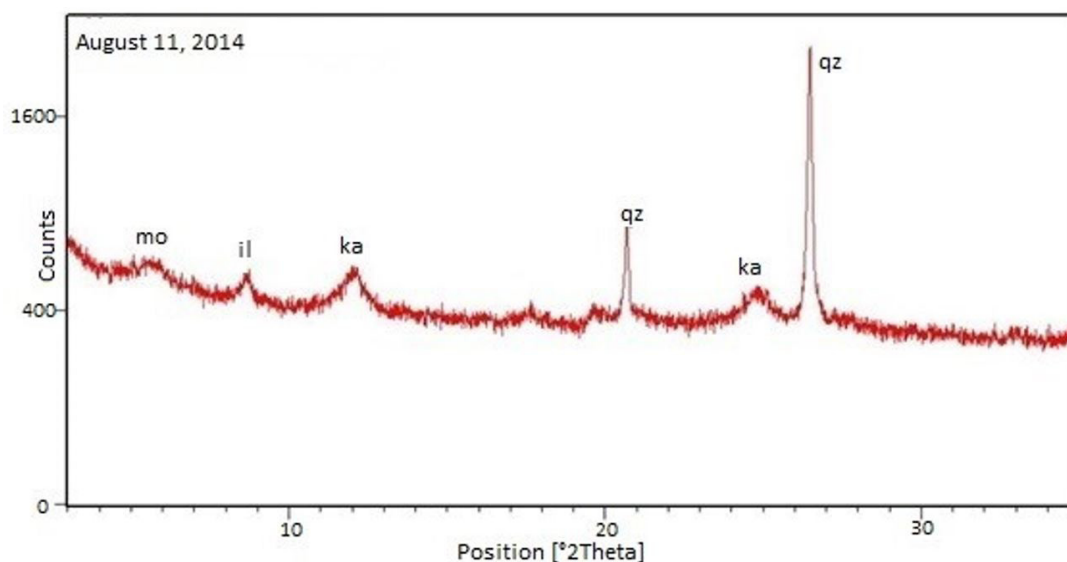


Figure 9. Typical diffractogram of the dry period, where *il* is Illite, *ka* is Kaolinite, *mo* is Montmorillonite and *qz* is Quartz.

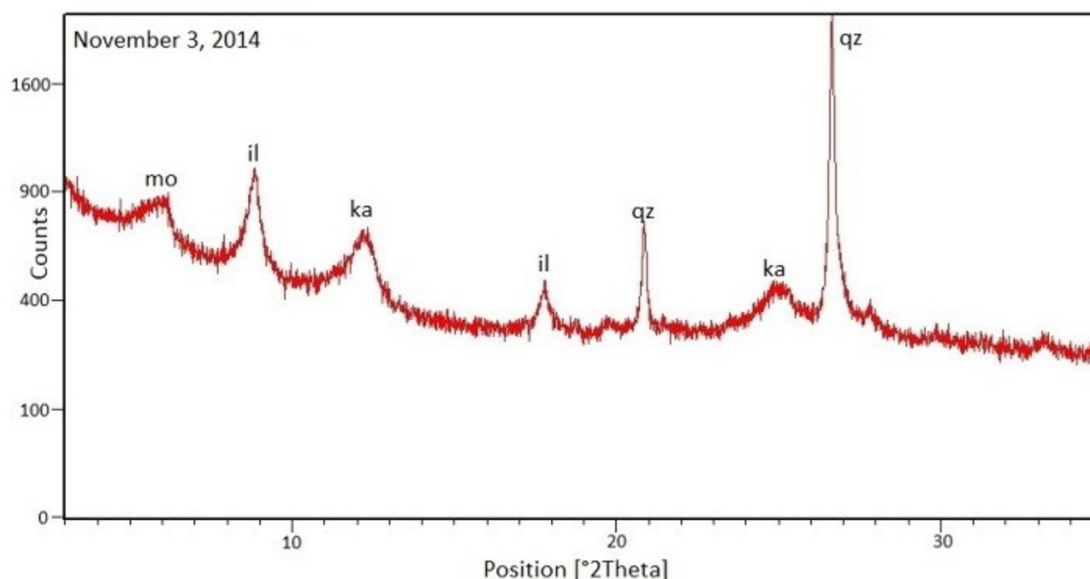


Figure 10. Typical diffractogram of flood events, where *il* is Illite, *ka* is Kaolinite, *mo* is Montmorillonite, *qz* is Quartz and *hm* is Hematite.

In dry period, when the suspended sediment flux was not significant, the kaolinite peak in the diffractogram indicated the predominance of this clay mineral over all other minerals. This fact was associated with its occurrence in greater quantities in the soil where drainage occur and also because it has a lower density than the illite, which allows to the kaolinite stay longer time suspended in the air, cross a greater distance and arrives in greater quantities in watercourses, using the wind like transport medium. The illite presence in dry period, even in small amounts, is associated with atmospheric deposition of particles from mining enterprises in operation. Already in flood events, time of higher flow of suspended sediment, the peaks of illite and kaolinite has showed to be equivalent. However, the expressive charge of illite leads us to believe that the mining sector contributed significantly to the suspended solid load.

To assess the origin of suspended material carried by the Assistência Stream, was used the mineralogy of the rocks and soils of the watershed. The mineralogy of the mined material is composed of illite, montmorillonite and chlorite (ZANARDO et al 2004; ROVERI, 2010). The mineralogical characterization of the soil surface horizons of studied watershed is presented in Table 1.

The P1 and P4 soil samples showed mainly secondary minerals, characteristic in soil with advanced pedogenetic processes

whose illite is no longer present. The P4 sample showed typical mineralogical characteristics of a Oxisol, where also was verified the absence of montmorillonite (Figure 11). The P2 and P3 soil samples showed traces of illite, revealing it is little evolved soils, considering that this mineral is more abundant in rocks. In the P2 soil sample prevails the montmorillonite, that characterizes the horizon of rock alteration, and in the P3 was the kaolinite that predominated, indicating the occurrence of monosalitization process in pedogenetic evolution soil (Figure 12).

In order to confirm this hypothesis was selected data from a single flood event (12.03.2014) among the 14 flood events analyzed in the study period. This event corresponded to the first significant rainfall after a severe drought period. When analyzing the hydrometric data, this flood event was what had the lowest recorded values, i.e. turbidity of 147.5 NTU, discharge of $0.43 \text{ m}^3 \cdot \text{s}^{-1}$, average water velocity of 0.21 ms^{-1} and the solid discharge of $2.16 \text{ t} \cdot \text{day}^{-1}$.

In this selected event, it was possible to observe an high amount of illite in relation to other events, as illustrated in Figure 10. After to analyze these datas it was possible to reject the illite origin related with old deposits in the fluvial channel, because the property of remobilising the river bottom is determined by river flow velocity, which in this selected event was relatively low. Also been possible to eliminate the possibility of leakage of mine ponds tailing and drying areas, which would require extreme precipitation events.

Thus, the presence of illite in suspended solids transported by the Assistência Stream is justified by the atmospheric deposition of dust produced in the operation of these enterprises. The suspension of dust clouds configures the major particulate removal mechanism of mining areas (mines and drying patios) and much of this dust is deposited on vegetation and terrain surface,

Table 1. Soil mineralogy of the Assistência Stream basin.

Sample	Minerology of Soil
P1	kaolinite, montmorillonite and hematite
P2	montmorillonite, quartz, kaolinite and illite.
P3	kaolinite, illite and montmorillonite
P4	kaolinite, gibbsite and hematite

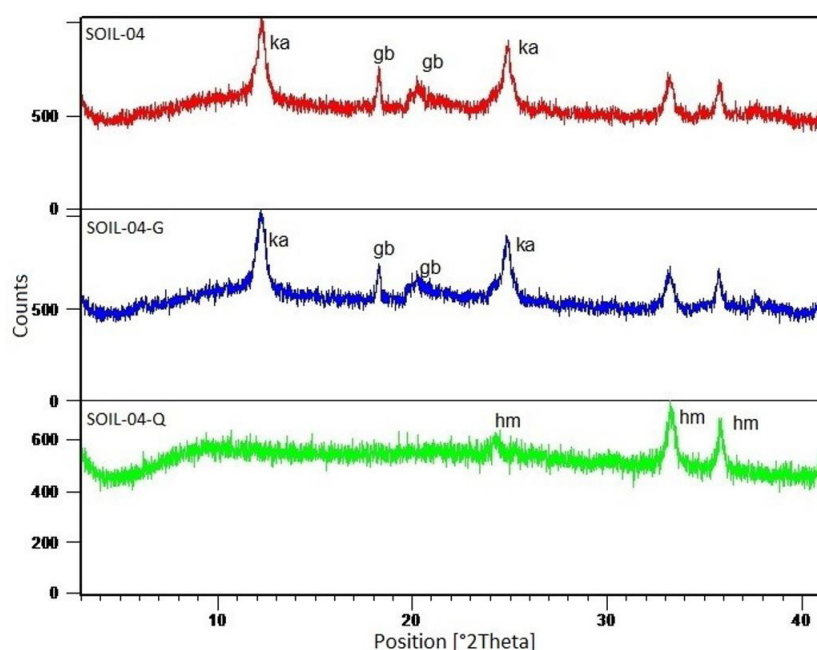


Figure 11. Diffractogram of P4 soil sample, where *gb* is Gypsum, *hm* is Hematite and *ka* is Kaolinite, and *Solo-04* is natural fine fraction, *Solo-04-G* is glycol and *Solo-04-Q* is burning.

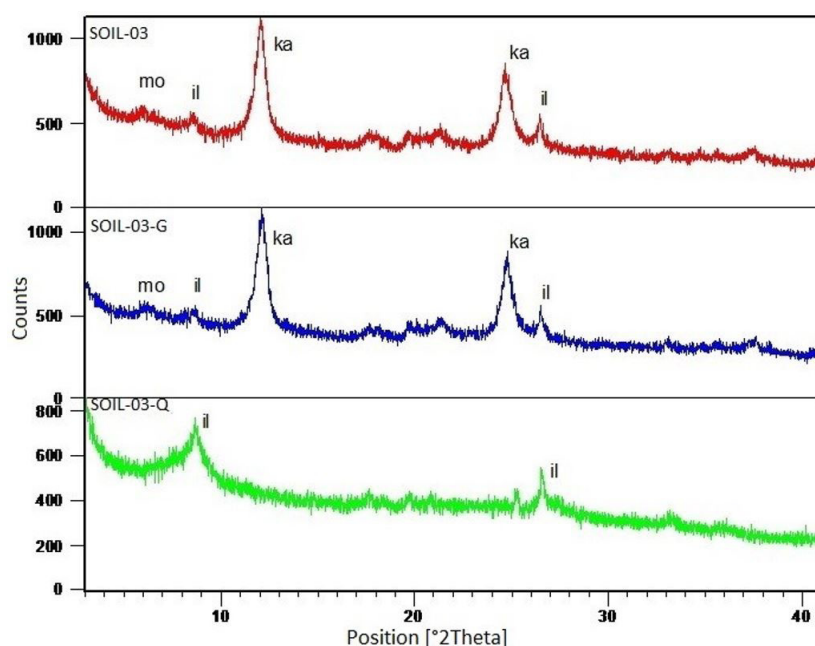


Figura 12. Diffractogram of P3 soil sample, where *il* is Illite, *ka* is Kaolinite and *mo* is Montmorillonite, and *Solo-03* is natural fine fraction, *Solo-03-G* is glycol and *Solo-03-Q* is burning.

and then transported by rainwater to the drainage system, with small amounts deposited directly on the river channel. A similar process of suspension, deposition and transport can be considered for dust of roads, where the capstone material is composed by the sterile clay mining and ceramic bits.

CONCLUSION

The Assistência Stream basin presents a clayed lithology and its annual production of sediment was characterized by the suspended load (3,680 t), whose mineralogical composition indicated the constant presence of quartz, montmorillonite, illite and kaolinite. Despite the pressure of the clay mining enterprises in the Assistência Stream basin, the results showed that the dissolved load (4234 t.ano⁻¹) was slightly higher than the solid discharge. This fact combined with the macrophyte proliferation episode observed in the dry period suggest that the organic and nutrients loads also needs a better control. For flood events with discharge higher than 1.5 m³.s⁻¹, the loads of illite and kaolinite were considered as equivalent. The origin of kaolinite was related with the surface soil erosion of areas where not occur mining activities. The illite, practically absent in the soil, was a good indicator of the contribution of materials derived from clay mining activities, i.e., the material from mining areas (mining and drying patios), paved roads with sterile materials from mines and the dust produced in the operation of these enterprises. It is recommended a long-term monitoring of the quantity and quality of sediments transported by the Assistência Stream. This practice can generate essential information for the management of the water bodies integrity, especially regarding the sediment dynamics in the basins that compose the ceramic pole and the efficiency of pollution control programs to diffuse sources.

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REFERENCES

- APHA – AMERICAN PUBLIC HEALTH ASSOCIATION; AWWA – AMERICAN WATER WORKS ASSOCIATION; WEF – WORLD ECONOMIC FORUM. *Standard methods for the examination of water and wastewater*. 20th ed. Washington: APHA, 1998.
- BONUMÁ, N. B.; GASTALDINI, M. C. C.; PAIVA, J. B. D. Análise da carga difusa de poluição gerada por atividades de mineração. *RBRH - Revista Brasileira de Recursos Hídricos*, v. 13, n. 3, p. 105-115, July/sept. 2008.
- BRASIL. Ministério do Meio Ambiente. Conselho Nacional do Meio Ambiente. *Resolução nº 357, de 17 de março de 2005. Dispõe sobre a classificação dos corpos de água e diretrizes ambientais para o seu enquadramento, bem como estabelece as condições e padrões de lançamento de efluentes, e dá outras providências*. Diário Oficial da União, Brasília, 18 de março de 2005.
- BRASIL. Ministério do Meio Ambiente. Conselho Nacional do Meio Ambiente. *Resolução nº 430, de 13 de maio de 2011. Dispõe sobre as condições e padrões de lançamento de efluentes, complementa e altera*

- a Resolução no 357, de 17 de março de 2005, do Conselho Nacional do Meio Ambiente-CONAMA. Diário Oficial da União, Brasília, 16 de maio de 2011.
- CARVALHO, N. O.; FILIZOLA JÚNIOR, N. P.; SANTOS, P. M. C.; LIMA, J. E. F. W. *Guia de práticas sedimentométricas*. Brasília: ANEEL, 2000.
- CHRISTOFOLETTI, S. R.; MORENO, M. M. T. Sustentabilidade na mineração do Polo de Santa Gertrudes, São Paulo – Brasil. *Cerâmica Industrial*, v. 16, n. 3, p. 3, may/june 2011.
- CONCEIÇÃO, F. T.; BONOTTO, D. M. Dose de exposição radiométrica e composição das rochas sedimentares e ígneas na Bacia do Rio Corumbataí. *Revista Brasileira de Geofísica*, v. 24, n. 1, p. 37-48, 2006. <http://dx.doi.org/10.1590/S0102-261X2006000100003>.
- CUNHA, C. M. L. A. Geomorfologia da Bacia do Rio Corumbataí. In: LOMBARDO, M. A. *Cenário em ação: paisagem do Rio Corumbataí*. Rio Claro: Universidade Estadual Paulista, 2007.
- DAVIS, C. M.; FOX, J. F. Sediment fingerprinting: review of the method and future improvements for allocating nonpoint source pollution. *Journal of Environmental Engineering*, v. 135, n. 7, p. 490-504, July 2009. [http://dx.doi.org/10.1061/\(ASCE\)0733-9372\(2009\)135:7\(490\)](http://dx.doi.org/10.1061/(ASCE)0733-9372(2009)135:7(490)).
- ESTEVEZ, F. A. *Fundamentos de limnologia*. 2nd ed. Rio de Janeiro: Editora Interciência, 1998. p. 107.
- GARZANTI, E.; PADOAN, M.; SETTI, M.; LÓPEZ-GALINDO, A.; VILLA, I. M. Provenance versus weathering control on the composition of tropical river mud (Southern Africa). *Chemical Geology*, v. 366, p. 61-74, Feb. 2014. <http://dx.doi.org/10.1016/j.chemgeo.2013.12.016>.
- HE, M.; ZHENG, H.; HUANG, X.; JIA, J.; LI, L. Yangtze River sediments from source to sink traced with clay mineralogy. *Journal of Asian Earth Sciences*, v. 69, p. 60-69, June 2013. <http://dx.doi.org/10.1016/j.jseas.2012.10.001>.
- HU, B.; LI, J.; CUI, R.; WEI, H.; ZHAO, J.; LI, G.; FANG, X.; DING, X.; ZOU, L.; BAI, F. Clay mineralogy of the river in sediments of Hainan Island, South China Sea: Implications for weathering and provenance. *Journal of Asian Earth Sciences*, v. 96, p. 84-92, Dec. 2014. <http://dx.doi.org/10.1016/j.jseas.2014.08.036>.
- LI, C.; SHI, X.; KAO, S.; CHEN, M.; LIU, Y.; FANG, X.; LÜ, H.; ZOU, J.; LIU, S.; QIAO, S. Clay mineral composition and their sources for the fluvial sediments of Taiwanese rivers. *Chinese Science Bulletin*, v. 57, n. 6, p. 673-681, Feb. 2012. <http://dx.doi.org/10.1007/s11434-011-4824-1>.
- MECHI, A.; SANCHES, D. L. Impactos ambientais da mineração no Estado de São Paulo. *Estudos Avançados*, v. 24, n. 68, p. 209-220, 2010. <http://dx.doi.org/10.1590/S0103-40142010000100016>.
- MINELLA, J. P. G.; MERTEN, G. H. Monitoramento de bacias hidrográficas para identificar fontes de sedimentos em suspensão. *Ciência Rural*, v. 41, n. 3, p. 424-432, Mar. 2011. <http://dx.doi.org/10.1590/S0103-84782011000300010>.
- NOVOTNY, V. The next step: incorporating diffuse pollution abatement into watershed management. In: DIFFUSE POLLUTION CONFERENCE, 7., 2003, Dublin. *Proceedings...* Dublin: IWA, 2003. p. 1-8. Available from: <http://www.ucd.ie/dipcon/docs/keynote_paper.pdf>. Access on: 20 Feb. 2015.
- ORSI, C. A era dos extremos. *Jornal da Unicamp*, n. 623, p. 12, Apr./May 2015.
- PORTO, R. L.; ZAHED FILHO, K.; SILVA, R. M. *Hidrologia aplicada*. São Paulo: Universidade de São Paulo, 2001.
- REIS, L. F. R.; BRANDÃO, J. L. B. Impactos ambientais sobre rios e reservatórios. In: CALIJURI, M. D.; CUNHA, D. G. F. *Engenharia ambiental: conceitos, tecnologia e gestão*. Rio de Janeiro: Elsevier, 2013.
- RIO CLARO. Prefeitura. Departamento Autônomo de Água e Esgoto de Rio Claro. *ETE - Estação de Tratamento de Esgoto - Distrito de Batovi, Assistência e Ferraz*. Rio Claro, 2012. Available from: <<http://www.daaeriolclaro.sp.gov.br/pagina.geral.php?pagina=ego-batovi>>. Access on: 8 Jan. 2016.
- ROVERI, C. D. *Petrologia aplicada da Formação Corumbataí (região de Rio Claro - SP) e produtos cerâmicos*. 2010. 200 f. Tese (Doutorado) - Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista, Rio Claro, 2010.
- SCAPIN, M. A. *Aplicação da difração e fluorescência de raios X (WDXRF): ensaios em argilominerais*. 2003. 80 f. Dissertação (Mestrado) - Instituto de Pesquisas Energética e Nucleares, Universidade de São Paulo, São Paulo, 2003.
- VALENTE, R. O. A. *Definição de áreas prioritárias para conservação e preservação florestal por meio da abordagem multicriterial em ambiente SIG*. 2005. 121 f. Tese (Doutorado) - Escola Superior de Agricultura Luiz de Queiroz, Universidade de São Paulo, Piracicaba, 2005.
- WALLING, D. E. Tracing suspended sediment sources in catchments and river systems. *The Science of the Total Environment*, v. 344, n. 1-3, p. 159-184, 2005. <http://dx.doi.org/10.1016/j.scitotenv.2005.02.011>. PMID:15907516.
- WANG, H.; LIU, Z.; SATHIAMURTHY, E.; COLIN, C.; LI, J. R.; ZHAO, Y. L. Chemical weathering in Malay Peninsula and North Borneo: clay mineralogy and element geochemistry of river surface sediments. *Science China Earth Sciences*, v. 54, n. 2, p. 272-282, 2011. <http://dx.doi.org/10.1007/s11430-010-4158-x>.
- WHITE, S. M.; APITZ, S. E. Conceptual and strategic frameworks for sediment management at the River Basin Scale. In: OWENS, P. N. *Sustainable management of sediment resources: sediment management at the River Basin Scale*. Oxford: Elsevier, 2008. chap. 2, p. 31-51.

ZAINE, J. E. *Mapeamento geológico-geotécnico por meio do método do detalhamento progressivo: ensaio de aplicação na área urbana do município de Rio Claro (SP)*. 2000. 149 f. Tese (Doutorado) - Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista, Rio Claro, 2000.

ZANARDO, A. *Pesquisa geológica e de matérias primas cerâmicas do centro Nordeste do Estado de São Paulo e vizinhanças - sistematização crítica da produção técnico-científica*. 2003. 283 f. Tese (Livre Docência) - Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista, Rio Claro, 2003.

ZANARDO, A.; MORENO, M. M. T.; ROVERI, C. D.; MASSON, M. R.; BERNARDES, E. S. Petrografia na formação Corumbataí na Região de Rio Claro, SP. In: CONGRESSO BRASILEIRO DE GEOLOGIA, 42., 2004, Araxá, MG. *Anais...* Araxá: Sociedade Brasileira de Geologia, 2004. v. 1. Versão digital.

ZANARDO, A.; MORENO, M. M. T.; ROVERI, C. D.; ROCHA, R. R. Critérios de avaliação de intemperismo e sua relação com

as propriedades tecnológicas das matérias-primas cerâmicas da formação Corumbataí (Região de Rio Claro - SP). In: CONGRESSO BRASILEIRO DE CERÂMICA, 53., 2009, Guarujá, SP. *Anais...* São Paulo: Associação Brasileira de Cerâmica, 2009. v. 1, p. 1-12. CD-ROM.

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Antenor Zanardo: Conduction and support in the execution of work, analysis and interpretation of results.

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Alexandre Martins Fernandes: Support in the preparation of the manuscript, with periodic evaluations for text closure.