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The mobilization of hazardous elements after a tropical storm event in a polluted estuary

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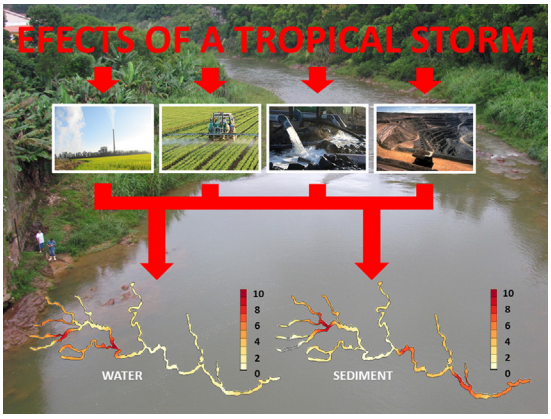
HIGHLIGHTS

- The highest water HEs concentrations were identified in the sampling sites closest to the coal mines.
- The presence of gypsum downstream is due to the remobilisation of upstream sediments by storm flow.
- The HEs composition of the Tubarao River sediments changes due to strong rainfall events.

GRAPHICAL ABSTRACT



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ABSTRACT

The Tubarão River (Santa Catarina, Brazil) is affected by hazardous elements (HEs) pollution from abandoned coal mines, agricultural activities, urban discharges, industrial and leisure zones, etc. In order to study the distribution and sources of HEs contamination in a polluted estuary after a tropical storm, waters and surface sediments were collected from 15 sampling sites along the Tubarão River. The concentration of 24 elements (Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, W, and Zn) were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and the mineralogical composition of the sediments by Raman spectroscopy and X-ray diffraction (XRD). The metal concentrations in water and sediment showed wide spatial variation due to the variability in water discharges and anthropogenic inputs after a storm. In general, higher metal concentration in water and lower in sediments were found upstream (closer to coal mining). Downstream sampling sites and the Oratorio River sampling site (one of the eight tributaries of the estuary) showed the highest values in sediment samples. Normalized and Weighed Average Concentrations (NWAC) were calculated, which allow us to identify, in a very simple way, the sampling sites of higher concern (hotspots of contamination) in the studied area. NWAC suggested that the strong rainfall events could affect to the metal distribution in sediments. The results of this study were compared with a previous study in the same area during dry season by

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Principal Component Analysis (PCA), showing changes in environmental pollution of the sediment after a strong storm event.

1. INTRODUCTION

Estuarine waters receive contaminants such as hazardous elements (HEs) via anthropogenic activities and/or through riverine inputs. The distribution of soluble and particulate trace HEs are controlled by physical-chemical processes (Windom et al., 1988), daily tidal currents, and regimes of alluvial loading. This last factor can be environmentally relevant in the case of tropical estuaries (Balachandran et al., 2005). Strong tropical storm events can resuspend superficial sediments with different particle size, dispersed and accumulated across different sedimentary environments (Guillén et al., 2006). Furthermore, the amount of water coming from the leachate of the surrounding soils increases during storm events (Zimmer and Lautz, 2014). Fine-grained sediments tend to accumulate HEs due to their sorptive nature, and thus can act as an important reservoir of contaminants with risk of mobilization (Eggleton and Thomas, 2004; Towler and Smith, 2000). The increase on the solubility of the mentioned HEs from sediment could result in an increase of the total concentration of HEs in the estuarine water and can affect the bioavailability and toxicity of HEs ions in the aquatic ecosystem (Sparks, 2005).

The Tubarão River (Santa Catarina, Brazil) has been affected by coal mining activities for over 50 years (Kagey and Wixson, 1983; Sekine et al., 2008; SIECESC, 2008; Zheng et al., 2007). Nowadays, most of the mines in the Santa Catarina region are abandoned, but as this region is highly drained by streams, trenches, and water channels, among others, the effect of mineral wastes and abandoned mines is important regarding the characteristics of the water and sediments of the river (Prefeitura de Lauro Muller, 2014). The estuary has other sources of contamination such as coal-combustion power plant, traffic road, agricultural and industrial zones, and industry and wastewater effluents (Prefeitura de Lauro Muller, 2014). In addition, the rapid population growth of the area, together with the lack of efficient urban planning and economic development, has brought about serious problems of environmental degradation (Henrique et al., 2013).

The Tubarão estuary is affected regularly by strong storms, which could change or affect the biogeochemistry of the area. The environmental effect of these strong rainfall events on a polluted aquatic system is not usually studied (Birch and Taylor, 1999). Therefore, the aims of the present work were: *i*) determine the spatial variability and the tendencies of metal pollution along the estuary, *ii*) identify the potential contamination sources, and *iii*) estimate the significance of storm events for mobility of HEs from polluted sediment in a tropical estuary.

2. Materials and methods

2.1. Study area and sampling procedures

The Tubarão estuary (Santa Catarina, Brazil) is 120 km long, with a water flow that increases toward the estuary and a drainage area of 4728 km^2, it receives contributions from seven principal freshwater inputs: the Bonito, Rocinha, Orotoria, Capivaras, Braco do Norte, Palmeiras, and Capivari rivers (Silva et al., 2012; Prefeitura de Lauro Muller, 2014).

Waters and sediments samples were collected at 15 sampling sites (BO, RO, TBLM, OR, ORTB, LA, TBLA, PL, PLTB, BN, PD, NCTB, CA, FITB, and ES) along Tubarão estuary in January of 2013 (Fig. 1). The sampling was carried out after four days of rainy season with strong storms; the storms caused the increases of the water fluxes in the estuary and floods in many places. The precipitation accumulated in the four days previous to the sampling was 114 in., comparing with the 68 in. of annual rainfalls in the area (National Institute of Meteorology, 2015).

Superficial sediments (0–2 cm) were collected at each sampling sites in the centre of the riverbed by hand using latex gloves or by means of Ponar dredge depending on the depth and the flow). Superficial water (top 10 cm) was also collected with a 50 mL HNO_3 precleaned polypropylene bottle. The first water sample was used to homogenise the bottle and then to fill it to the top. At the same time pH, electrical conductivity and redox potential were measured in situ in the water samples. The sediment samples stored in 500 mL polyethylene bottles and water bottles protected against light using aluminium foil were transported to the laboratory at 4 °C in a cool box. Blank samples (pre-cleaned bottles filled with Milli-Q quality water at the beginning of the sampling day) were handled in a similar way.

Once in the laboratory, sediment samples were air dried. The dry samples were sieved to assure a maximum particle size of 65 μm and kept in the refrigerator at 4 °C until analysis.

2.2. Analytical procedure

All plastic and glass material was firstly washed with soap and water, rinsed with Ellix quality water ($\kappa < 0.2$ μS cm^{-1}, Millipore), and left in a 10% nitric acid (Panreac) bath for 24 h. Afterwards, it was thoroughly rinsed with Ellix and MilliQ water ($\kappa < 0.05$ μS cm^{-1}, Millipore) before use.

The extraction of the sediments was carried out with HNO_3/HCl (45/55) using focused ultrasound assisted energy by means of HD 2070 Sonoplus Ultrasonic Homogenizer (Bandelin) equipped with a 6 mm glass probe. More details about the analytical procedure can be found elsewhere (Fdez-Ortiz de Vallejuelo et al., 2009). The acid extracts were filtered through a 0.45 μm filter and diluted in MilliQ water. The HNO_3 concentration in the diluted acid extracts was adjusted to 1% before the analysis.

Water samples were filtered through 0.45 μm PVDF filters (Milles-HV, Millipore) and acidified to 1% HNO_3. All acidified samples were stored in 10 mL polyethylene vials at 4 °C and protected against light until analysis.

The concentrations of a wide range of elements (Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, W and Zn) were simultaneously determined by ICP/MS (NexION 300, Perkin Elmer, Ontario, Canada) with Sc, Y, In, Bi, and Ge internal standards supplied by Alfa Aesar (SpecpureR, Plasma standard solution, Karlsruhe, Germany) in a Class 100 clean room.

The accuracy and reproducibility of the method was checked by repetitive analysis ($n = 5$) of the NIST 1646a certified reference material (estuary sediment, National Institute of Standards and Technology). In the case of the water, the freshwater NIST SRM 1640 containing metal and metalloids (Natural Water, National Institute of Standards and Technology, Gaithersburg, USA) was used. Finally, eight blanks were prepared for sediments and waters and analysed as well for the procedural detection limit calculations following the IUPAC rules, defined as blank signal + 3 SD, where SD is the standard deviation of eight measurements of a blank ($n = 8$) (Table 1).

All the sediments samples were mineralogical characterized as well by powder X-ray diffraction (XRD) of dust and Raman Spectroscopy (RS).

In the case of XRD characterization, a portion of sediment sample was analysed by a powder diffractometer PANalytical Xpert PRO that incorporates a copper tube ($\lambda Cu_{K\alpha media} = 1.5418$ Å, $\lambda Cu_{K\alpha 1} = 1.54060$ Å,