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Potentially Toxic Elements (PTEs) distribution and main geochemical processes in Sabato river catchment basin (Southern Italy): a focus on cadmium

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Abstract

The Sabato river (~50 km) is located in a large industrial and urbanized area of the Campania region (Southern Italy), between the cities of Avellino and Benevento. Thus, a study on the distribution of Potentially Toxic Elements (PTEs) and their potential sources was done. Here, we focused on the particular behavior of Cadmium. Firstly, we compared the raw geochemical dataset and the log-ratio (clr) transformed one, found that the latter can improve the readability of the Cd data distribution. Applying a linear regression between the clr-values and the log-transformed cumulative area (estimated by the sample catchment basin approach), we emphasized a possible contaminant source at the headwaters followed by a decreasing trend, potentially explained by a downstream dilution effect. Since there is no evidence of any Cd-related industrial activity at the headwaters, and anomalies seem to be highly localized in the southern part of the basin, we supposed that its main source could be found in the use of some phosphate fertilizers for local agricultural practice.

Keywords: Potentially toxic elements; compositional data analysis; environmental characterization

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1. Introduction

In the last few years, the potentially toxic elements (PTEs) are increasingly focusing the attention from geochemists and environmental scientists worldwide, due to their well-known negative effects on human health. In Campania (Southern Italy) the area between the two main cities of Avellino and Benevento, which belongs to the Sabato river catchment, has been historically characterized by the presence of urban and industrial settlements. Hence, a study on the distribution of PTEs and their potential sources in the river basin was needed. Specifically, we choose to focus our attention on cadmium (Cd) due to its toxic effects on the kidneys as well as the skeletal and respiratory systems. Cd is naturally released into the environment mainly through chemical weathering of geological materials, but also forest fires and volcanic events. It is also introduced in the environment as a by-product of zinc, lead and copper extraction and by industries which use the metal as a major component of batteries (Ni-Cd); further, Cd is used for pigments, coatings, as stabilizers for plastic, and it takes part in the production process of artificial phosphate fertilizers.

Human exposure to Cd occurs mainly from the consumption of contaminated food, active and passive inhalation of tobacco smoke, and inhalation of dust generated by industrial processes (www.who.int).

2. Material and methods

A total of 35 stream sediment samples was collected in 2019 from the main course of the river right after any tributaries inlet and upstream and downstream of the main industrial and urbanized areas within the basin. Thus, a sample catchment basin (SCB) approach (Carranza & Hale, 1997) was applied. An SCB is a portion of the area of the whole catchment mainly defined by geomorphological and hydrological features (as slope, flow direction, etc.). It outlines the region which directly affects, in terms of geochemical concentrations, the downstream sample, located at its outlet (Fig. 1).

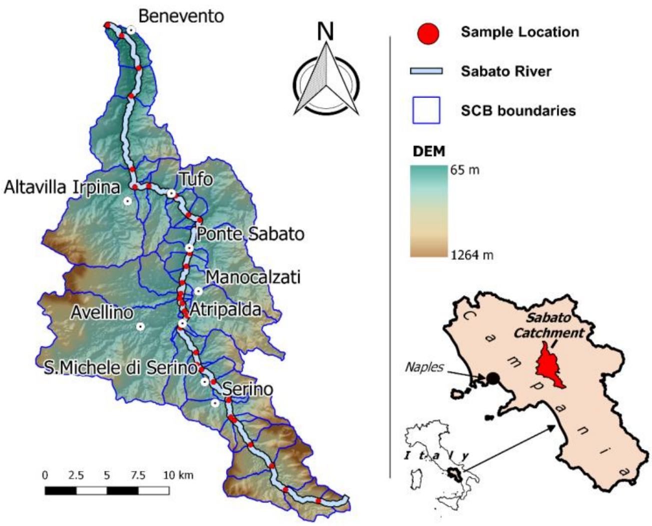

Fig. 1. Framing of the study area. The Digital Elevation Model (DEM) of the catchment area was used to outline the Sample Catchment Basins (SCBs)

After their collection, samples were oven-dried (temperature was kept below 37°C to preserve Hg content) and sieved (<200 mesh) at the Environmental Geochemistry Laboratory (EGL) of University of Napoli Federico II; an aliquot of each sample was sent to Bureau Veritas Laboratories (Vancouver, Canada) for chemical analysis. The concentrations of 53 elements were determined through a combination of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) following a modified *Aqua Regia* digestion. Grain size analysis was also performed at Nanjing University (China). For the purpose of this study, geochemical data have been processed according to Compositional Data Analysis fundamentals (Aitchison, 1984) and the dataset has undergone a centred log-ratio (clr) transformation due to its capability of preserving both geometric properties and one-to-one relationship within the variables. Then, both Cd raw geochemical data and clr values have been plotted, from source to sink (S2S). Data variations along the river course were also compared with the clay/silt ratio (C/S ratio) and sedimentation transport index (STI) (Mehnatkesh et al., 2013) to recognize any hydrogeological effect on concentration distribution (Fig. 2). The STI is based on a proportion between the sample site's upstream area and the line of maximum slope along the river path. The upstream area of each sample location has been estimated by using its SCB area in a GIS environment. Raw concentrations have been compared with the Upper Baseline Limit (UBL) (0.69 mg/kg for Cd) estimated by Albanese et al. (2007) for stream sediments of Campania region to determine any potential anomaly. The anomaly threshold (AT) for clr-transformed data have been also established following a robust estimator suggested by Reimann et al. (2005):

$$AT = \tilde{X} + 2[\text{median}\ (|\ X_i - \tilde{X}\ |)]$$

Where:

- $[\text{median}\ (|\ X_i - \tilde{X}\ |)]$ is defined as median absolute deviation (MAD);
- X_i is the clr value for Cd of the *i-esim* sample and $\tilde{X}$ is the median clr value for Cd based on all the samples in the dataset.

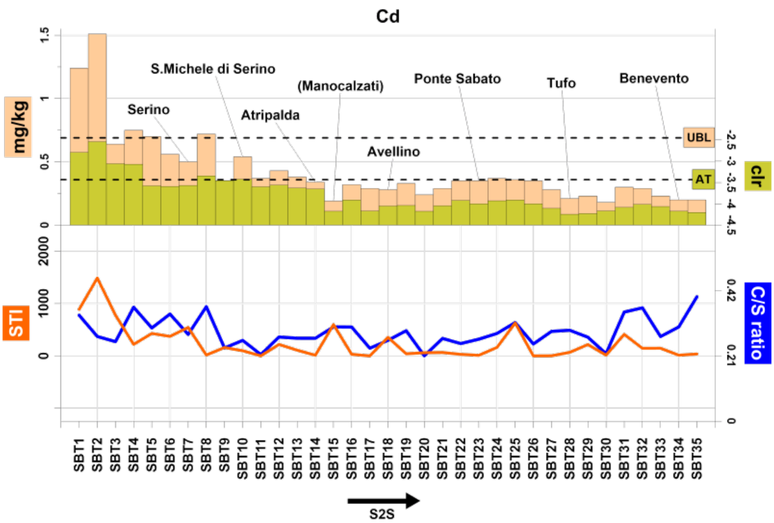

Fig. 2. Source to sink geochemical distribution: raw concentrations (in pink/salmon) and clr values (in green). For definition of UBL, AT, STI and C/S ratio see the text

3. Results and discussions

By observing geochemical (compositional) data reported in Fig. 2, Cd shows some samples overcoming UBL in correspondence with the headwater of the Sabato river course. Specifically, samples SBT1 and SBT2 (the first two starting from the top) reach values that even doubled the reference threshold (1.24 and 1.51 mg/kg, respectively). On the other hand, the clr transformation seems to emphasize the behavior of the following two samples (SBT3 and SBT4) which clearly stand over the AT line. However, both distribution (raw and transformed) show a general decreasing trend from source to sink (S2S), except for the samples (SBT8 and SBT10) located just after Serino and S. Michele di Serino urban settlements. Cd concentrations and clr-values seem to be not very influenced by grain size variations, since the highest clay/silt ratios are spatially related to both relatively high and low concentrations. Conversely, despite a few local discrepancies (i.e. SBT15 in Manocalzati), STI variations seem to grossly follow the decreasing trend of Cd values.

Once revealed the greater stability of transformed data against the raw ones, we decided to investigate further any potential relationship between clr-values and other available variables.

A potentially meaningful relationship was observed between clr-values and the cumulative area of the sequential sample catchment basins moving source to sink (Fig. 3). In fact, in this plot, the samples are distanced by a factor that is proportional to the area of the comprised SCB. This allows us to make some considerations on the potential amount of sediments introduced in each sample site and, then, on a potential dilution effect.

Since the trend of the data was following an exponential curve, we log-transformed the cumulative area values to linearize the trend. We then generated a model through regression analysis and we quantified the goodness of this fit through its statistics. Looking at the model parameters, it seems to fit well the trend. Further, the statistics confirm that the model is statistically consistent and a correlation between the two variables exists (R^2 = 0.823, *p*-value: 5.886e-14).

A plausible explanation could be a significant source of Cd at the headwaters, which should explain the very high values of the firsts samples, followed by a massive chemical dilution-effect which should explain the negative exponential curve. Further, the values of

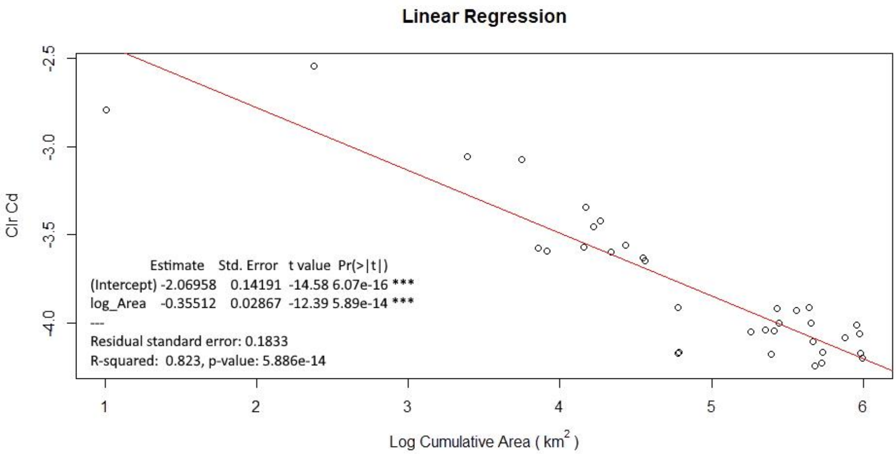

Fig. 3. Linear Regression. Cd clr-values (as dependent) vs Log-transformed sequential cumulative area (km^2) of the SCBs. (***) indicates the significance level (0.001)

the residuals generated by regression analysis were assigned to their relative SCBs and mapped accordingly (Fig. 4). As expected, the highest positive residuals (in red and orange) are concentrated in the southern side of the catchment (SBT2, SBT3 and SBT4), suggesting the presence of a Cd source far from the main urbanized areas. The lowest residuals (in blue and light blue) are located close to Manocalzati and right after the Avellino outlet (SBT15, SBT17 and SBT20) while the rest of basins displayed an oscillating trend but still within the range -1 to +1 standard deviation.

A previous study on a wider scale, carried out by Zuzolo et al. (2017), observed a spatial relationship between Cd enrichments and the occurrence of carbonates. In fact, in oxidizing conditions, Cd has a tendency to be quite mobile (in solution) at pH from acid to neutral but tends to precipitate at higher pH (e.g. alkaline environments). However, according to the pattern of residuals, anomalies seem to be highly localized in the southern part of the basin, showing a very poor spatial relationship with any lithology or soil system. Conversely, according to satellite images, the three SCBs that revealed the highest residual values place in the widest agricultural area of the catchment and, probably, they can be related to the use of some phosphate fertilizers.

4. Conclusions

This study tried to highlight the behavior of Cd within the Sabato river catchment area. Comparing the raw and the clr-transformed data, we found that the latter can improve the readability of the Cd data distribution. Both datasets showed no correlation with the clay/silt ratio, excluding any grain size effect. Conversely, a slight relationship between clr

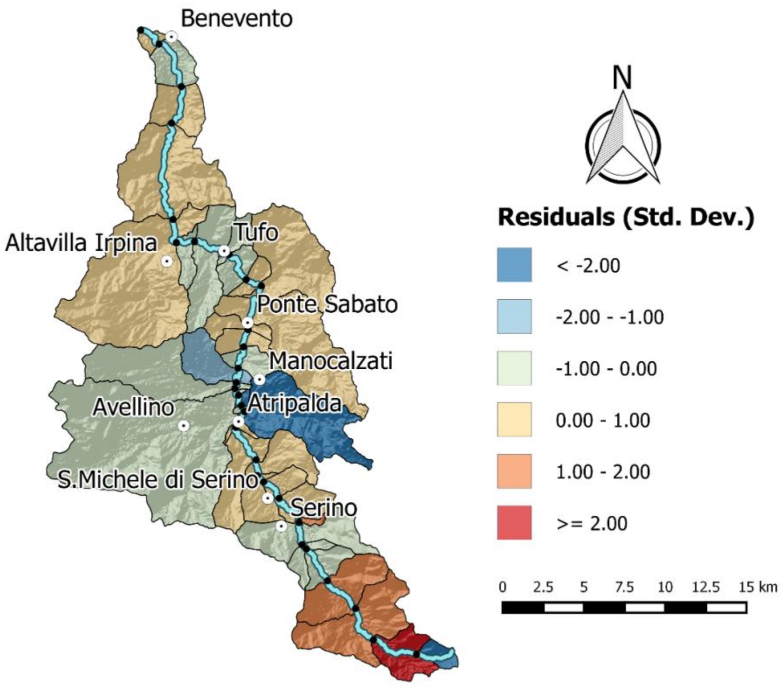

Fig.4. Map of the residuals came out from the linear regression. Class breaks were estimated according the standard deviation classification

values and STI was observed. To investigate further into the data, we also applied a linear regression between the sequential cumulative area (as independent, on a log scale) and clr values (as dependent). The main outcomes highlighted a possible contaminant source at the headwaters, where the highest values are located, followed by a decreasing trend potentially explained by a downstream dilution effect. Since in the southern area there is no evidence of any industrial activity potentially related to Cd release, and anomalies seem to be highly localized in the southern part of the basin, we supposed that the use of some phosphate fertilizers for local agricultural practice could be considered as a potential source of contamination.

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