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Unsupervised classification and multi-criteria decision analysis as chemometric tools for the assessment of sediment quality: A case study of the Danube and Sava River

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ABSTRACT

The aim of this study was to evaluate the quality of freshwater sediments by means of three chemometric techniques for multi-criteria analysis and decision: self-organizing network (SON), self-organizing map (SOM) and PROMETHEE&GAIA (Preference Ranking Organization Method for Enrichment Evaluation with Geometrical Analysis for Interactive Aid). Selected chemometric techniques were applied to the results of Pb, Cd, Zn, Cu, Ni, Cr, Hg and As content in thirty Danube and fourteen Sava river sediment samples from Serbia. The potential toxicity of sediments was estimated using Probable Effect Concentrations quotients (mean PEC-Q).

According to the SON analysis the Danube sediment samples were divided into three classes, Class I (mean PEC-Q range 0.27–0.51), Class II (mean PEC-Q range 0.50–0.70), and Class III (mean PEC-Q range 0.77–0.97), while the Sava samples were divided into two classes, Class II (two samples, mean PEC-Q values 0.65 and 0.69) and Class III (mean PEC-Q range 0.69–1.00). Using the SOM cluster analysis, both Danube and Sava sediment samples were classified into five subclusters, on the basis of the metal concentration level and further ranked into three levels (for remediation, moderately polluted and not polluted) by the use of multi-criteria ranking PROMETHEE method. Graphical presentation of the results obtained by PROMETHEE method using GAIA descriptive tool has provided an insight into the distribution of examined elements in sediments and has shown a significant correlation between some elements.

On the basis of the results obtained, it has been concluded that the proposed chemometric approach could provide useful information in the sediment quality assessment.

1. Introduction

Almost twenty years ago Kokot et al. (1998) emphasized that univariate data analysis is no longer sufficient for exploring fully the complexity of the vast amounts of available information. Since then, multivariate analysis methods have been used as efficient tools for the extraction of meaningful information from environmental monitoring datasets (Y.-B. Wang et al., 2015), but their application in such studies has been fairly limited up to now. Classical univariate statistics are preferred for processing data and mostly used chemometric techniques are Principal Components Analysis (PCA) and Cluster Analysis (CA).

Sediments serve as both sinks and potential secondary sources of heavy metals, and researches on heavy metals in surface sediments provide significant insights into their role in metal pollution of aquatic systems (Y. Wang et al., 2015). Consequently, the preservation of this compartment is an important step to maintain the full quality of the water body (Palma et al., 2015).

For the evaluation of the sediment toxicity the mean PEC-Q value (mean PEC quotient) is often used, meaning that measured concentrations are compared to the values of MacDonald's Probable Effect Concentrations (PEC). Even they were developed from sediment dataset from North America, they were applied also for the evaluation of the effects of heavy metals to European aquatic ecosystems (Gati et al., 2016; Hamzeh et al., 2013; Louriño-Cabana et al., 2010; Veses et al., 2014, 2013), as well as worldwide (Hanif et al., 2016; Mataba et al., 2016; Niu et al., 2009; Tejeda-Benitez et al., 2016; J. Wang et al., 2015). These consensus-based sediment quality guidelines (SQGs) provide a reliable basis for classifying sediments as not toxic or toxic (MacDonald et al., 2000).

The application of Multi-criteria Decision Analysis (MCDA) to rank different areas, according to their need for sediment management, provides a great opportunity for prioritization, a first step in an integrated methodology that finally aims to assess and select suitable

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Fig. 1. Sediment sampling sites along the Serbian part of Danube and Sava River.

alternatives for managing the identified priority sites (Alvarez-Guerra et al., 2009). Measures to limit or to eliminate pollutant sources may be suggested through the use of ranking and multi-criteria decision analysis, by employing the Preference Ranking Organization Method for Enrichment Evaluation (PROMETHEE) and its associated graphic output, Geometrical Analysis for Interactive Aid (GAIA). PROMETHEE is considered as one of the most efficient and suitable ranking methods (Bilsel et al., 2006). Flexibility and simplicity of this outranking method makes it more desirable for its users (Geldermann et al., 2000). PROMETHEE and GAIA are the preferred multivariate methods, which have been commonly used in chemometric studies (Herngren et al., 2006).

The Self-Organizing Map (SOM) and Self-Organizing Network (SON) (Kohonen, 1982a, 1982b) are types of artificial neural networks (ANNs) with unsupervised learning for multi-dimensional data reduction and display (Kohonen, 2001). The SOM has been recently applied as an alternative to classical multivariate statistical techniques in environmental studies, mainly in water sediments and air pollution and indoor air quality (Kwon et al., 2015; Pearce et al., 2014; Veses et al., 2014), to cluster the data by recognizing different patterns.

Veses et al. (2014) utilized PCA and SOM as multivariate techniques to determine the pollution distribution pattern of eight trace elements (Cd, Cu, Ni, Pb, Zn, Hg, Ad and Cr) and eight PAHs in river sediments. They emphasized that sediment sample classification provided by PCA was not as useful as the one provided by SOM, which revealed itself as a powerful tool to be incorporated in the first steps of sediment quality assessments. Also, some authors have pointed out that SOM can be used to determine the similarity between the monitored datasets and to identify contaminated hotspots as a prerequisite for control measures (Alvarez-Guerra et al., 2008; Tsakovski et al., 2011; Veses et al., 2014, 2013).

A lot of studies reported on the pollution of heavy metals in the Danube and Sava River Basin. In Serbia, the concentration of heavy metals in Danube and Sava sediments has been analyzed using the control network as well as through scientific researches. The quality of sediment was determined mostly by comparison of the obtained results with diversified sediment quality criteria (Antonijević et al., 2014; Crnković et al., 2008; Milenkovic et al., 2005; Pavlović et al., 2016).

The present study aimed to evaluate the sediment quality on the basis of multi-element concentration level and to determine the distribution patterns of the examined heavy metals in the surface sediments of Danube and Sava River in Serbia. The SON was used for the classification of sediments, while the SOM was applied for sediment cluster analysis. This is the first time that a comprehensive sediment quality evaluation and ranking approach has been developed using PROMETHEE and GAIA method.

Table 1
Serbian sediment quality criteria (Sl. glasnik RS No 50/2012), PEC values and PROMETHEE weights.

Heavy metal	Target value (TV) (mg/kg)	MPC (mg/kg)	Remediation value (RV) (mg/kg)	PEC[a] (mg/kg)	Weights
Arsenic (As)	29	42	55	33	2.83
Cadmium (Cd)	0.8	6.4	12	4.98	18.46
Chromium (Cr)	100	240	380	111	0.49
Copper (Cu)	36	110	190	149	1.07
Mercury (Hg)	0.3	1.6	10	1.06[b]	73.82
Lead (Pb)	85	310	530	128	0.38
Nickel (Ni)	35	44	210	48.6	2.68
Zinc (Zn)	140	430	720	459	0.27
			Sum of weights		100

[a] MacDonald et al. (2000).
[b] not included in mean PEC-Q calculation.

2. Materials and methods

2.1. Study area

The Danube, the second largest river in Europe, has a total length of 2875 km between the source and mouth, and a catchment area of 817,000 km^2, with the Serbian sector being 588 km long (from 1433 to 845 km) (Vukovic et al., 2014). The Sava River, the biggest tributary to the Danube River, is 945 km long and it flows through Slovenia, Croatia, Bosnia and Herzegovina and Serbia. It enters Serbia at 210.8 km and confluences Danube at its right bank, at 1169.9 km.

Thirty sampling sites were chosen along a 573 km stretch of the Danube river in Serbia, from Bezdan (River-km 1425) to Radujevac (River-km 852). Also, fourteen sampling locations were selected along