TOPOLOGICAL MAPS OF KOHONEN SELF-ORGANIZATION (SOM) APPLIED TO THE STUDY OF SEDIMENTS CONTAMINATED WITH PBDEs: SUPPORT FOR CLIMATE EXTREMES RISK ASSESSMENT

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Abstract

Riverine sediments, collected during 2012 from ten sites in a mixed land use region of the Serbian were analysed for seven emergent PBDE congeners. All PBDEs were detected in sediments with the total concentrations range from 0.52 μg/kg (Ratno Ostrvo) to 31.19 μg/kg (Neštin) with mean levels of 8.08 μg/kg and median of 3.14 μg/kg. The classification of data by Kohonen's self-organizing maps (SOM) allowed understanding and visualizing the spatial distribution of samples. Principal component analysis (PCA) was used for validating the obtained results. Correlations and relationships between the samples and the variables can be easily visualized using the viewing of SOM planes of components. The results have highlighted the dependencies between the different PBDEs and the classification of studied sediments into three classes into function of ten stations coring and their pollution levels.

Keywords: polybrominated diphenyl ethers, emergent substances, sediment, self-organizing maps Kohonen, Danube River

Introduction

Emerging contaminants (ECs) are chemicals that have been detected in aquatic ecosystems at trace levels and for which the risk to human health is not yet known. Due to the relatively new introduction or detection of these pollutants, there exists a gap in the knowledge on their fate, behaviors and effects, as well as on treatment technologies for their efficient removal [1, 2, 3]. Furthermore, despite the advances in treatment technologies, the design of existing treatment plants is not suited to remove these ECs, in addition to there being a lack of published health standards that provide guideline in treating these pollutants. Many new ECs are being introduced into the environment without detection. In that context, this paper reviews existing research that provide reliable and quantitative information on PBDEs in aquatic sediment of Danube River.

Also, in this paper will be considered the application of self-organizing maps of Kohonen using an artificial neural network based on unsupervised learning algorithms for data classification and visualization of the spatial distribution of the content into PBDEs of sediments from 10 sampling sites along the river Danube in Serbia. The expected results should lead to a definition of existing relations between the PBDE congeners content of the sediments studied as a function of the situation of stations and sources of contributions. To confirm the results obtained by SOM, these analyzes are completed by a principal component analysis (PCA).

In adition, floodwaters are usually contaminated with infectious microorganisms, agricultural or industrial chemicals and hazardous agents present. Water and sediment contaminated with organic/inorganic chemicals and trace pollutants can heavily affect wastewater treatment plants, residential septic systems and municipal sanitary sewer systems during and after the flood event. For this reason, ensuring their climate resilience (that their capacity and technology is adapted to possible extreme events and specific pollution under current and climate change conditions) is essential.

Experimental

Sediment sampling and preservation

The sampling was performed during October, 2012. For this investigation, ten samples of bottom sediment from different sites of Danube River (Apatin (D1), Labudnjača (D2), Neštin (D3), Begeč (D4), Ratno Ostrvo (D5), Šangaj (D6), Knićanin (D7), Belegiš (D8), Ritopek (D9), Dubravica (D10)) (Fig. 1)) were collected using a grab sampler in order to obtain representative composite samples. All sediment samples were analyzed in the laboratory of Research Centre for Toxic Compounds in the Environment - *RECETOX* (Brno, Czech Republic) after two days. Prior to analysis wet sediment samples were sieved though 2 mm sieve to remove leaves, stoned and roots and the lower particle size fraction (<63 µm) was retained and analyzed. Sediment samples were extracted with toluene in a Soxhlet extractor with toluene in a B-811 extraction unit (Büchi, Switzerland). Prior to extraction, the samples were spiked with 13C BDEs (47, 99, 100, 153, 154, 183, 209). PBDEs were analysed using 7890A gas chromatography–mass spectrometry (Agilent, USA).

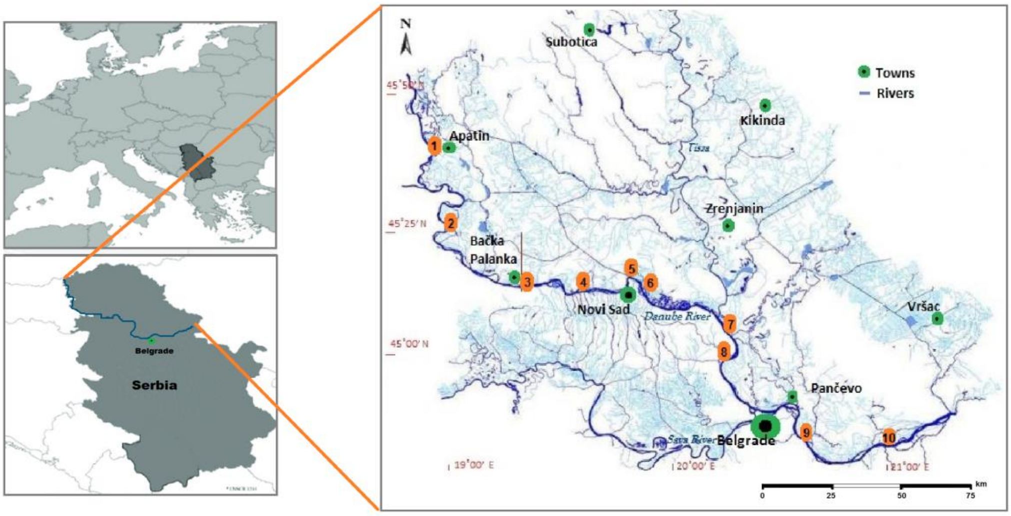

Figure 1. Map of the sampling sites

Data analysis

The artificial neural network (ANN) used in this study was the Kohonen Self-Organizing Map (SOM) [4]. SOM is an unsupervised artificial neural networks technique, which has been successfully applied in the classification of aquatic pollution [5,6,7]. These networks are composed of a grid of neurons (also called nodes); each unit of the grid is connected to the input vector through the N synapse weight W_{ij}. In fact, at each unit is associated with a vector of dimension N that contains the weight W_{ij} (Fig. 2). Therefore, sedimet samples within the same node have more similarity in terms of sediment variable patterns, while more distinct patterns will be positioned at larger distances in the map [5, 6].

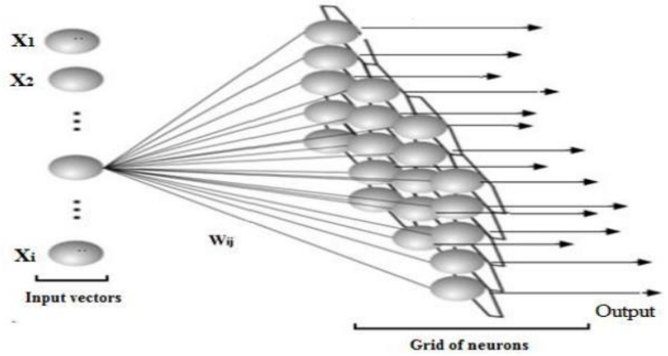

Figure 2. Scheme of a map Kohonen

In this study, the input layer (input vector) is composed of 8 neurons representing an 7 polybrominated diphenyl ethers that are BDE 47, 99, 100, 153, 154, 183, 209. These neurons are associated with every 10 neurons that represent 10 samples studying sediments. All values in the database are normalized in the range [0,1] in order to adapt to the transmission requirements function used by neural networks.

Results and discussion

Spatial distribution of PBDEs

The concentrations and distribution of PBDE congeners (BDE 47, 99, 100, 154, 153, 183, 209) were investigated in ten bottom sediment samples. The results showed that all these pollutants were detected in sediments and the mean levels of Σ_7PBDE compounds were ranged from 0,52 µg/kg (site D5) to 31.19 µg/kg (site D3) (Fig. 3.). Among the PBDE congeners, BDE 209 was predominant, with contributions to the total PBDEs ranging from 22.9% (site D3) to 99.3% (site D10) in sediment samples. For the lowly brominated congeners (tri- to penta-BDEs), BDE 100 were the most abundant at the sampling site Neštin.

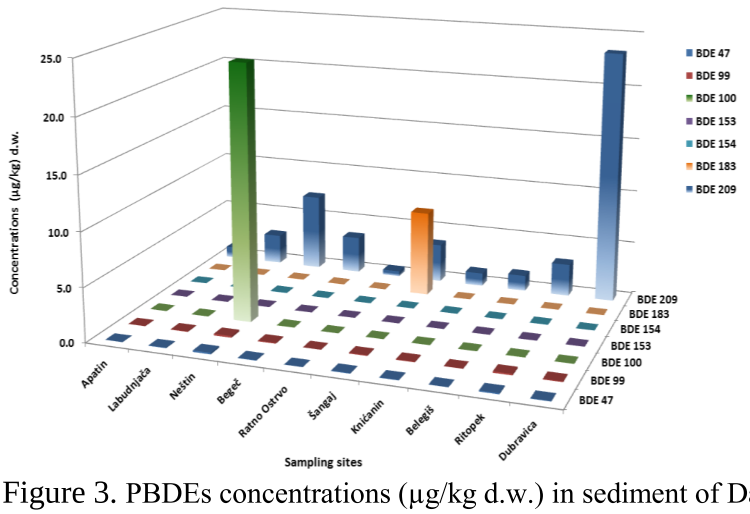

Figure 3. PBDEs concentrations (µg/kg d.w.) in sediment of Danube River, Serbia.

Self-organizing maps of PBDEs in the sediment profiles

The plans SOM components of the dataset are shown in Figure 4. The identical colour patterns between the variables correspond to a positive correlation; this can be considered among the variables BDE 47, BDE 99, BDE 100, BDE 153 and BDE 154. There were no negative correlations between the variables. The other variables are neither positive nor negative correlations in particular those relating to the BDE 100, BDE 183 and BDE 209 that vary independently of the others (Fig. 4).

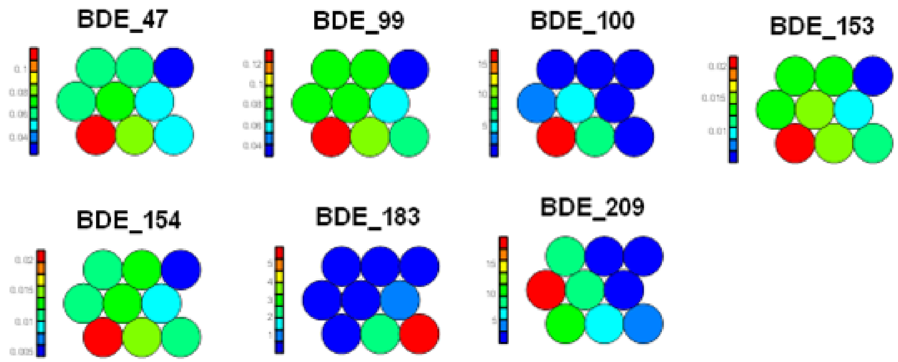

Figure 4. SOM component planes for the seven input variables

Principal component analysis (PCA)

The result of PCA with varimax rotation shows the route of score formed by the two components PC1 and PC2, which are considered the most informative since they account for the largest proportion of the variance. In our case, three principal components (PC1, PC2 and PC3) were extracted, accounting for 93.85% of the total variances, with 64.24%, 14.85% and 14.76% for PC1, PC2 and PC3, respectively. Figure 5 shows the component plot of correlations between variables on the factorial design.

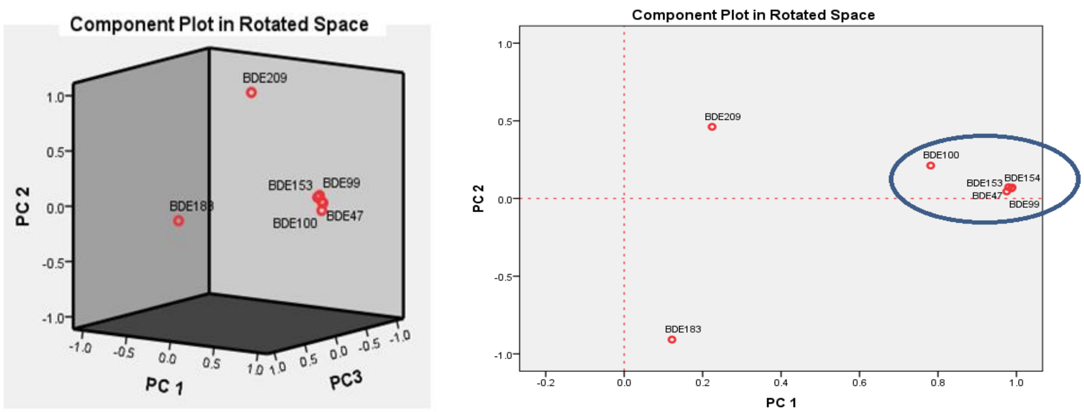

Figure 5. Component plots for PBDE congeners

The component plot of correlations between variables on the factorial design (PC1 X PC2) shows that the BDE 47, BDE 99, BDE 100, BDE 153 and BDE 154 correlate positively with the PC1 axis with respective coefficients of 0.99, 0.98, 0.78, 0.96 and 0.99. However the BDE 183 and BDE 209 correlate positively and are very poorly correlated with PC1, with respective coefficients of 0.13 and 0.22.

Conclusion

In conducted study we are presented the concentration levels of ten PBDE congeners in the Danube sediment at 10 locations. The highest level of PBDEs was recorded at the locality D5, while the lowest at the locality D3. The results obtained within our study suggest the dominance of the deca-BDE congener.

The self-organizing map SOM was used in this study for distribution of seven emerging PBDEs in sediments samples collected from Serbia's stretch of the Danube River. The comparison with the Principal component analysis (PCA), showed, therefore that the results obtained with the self-organizing map SOM were generally similar to those of these statistical method. But, the SOM method has also provided more detailed classification of PBDE congener from sediments of the Danube River.

Despite the extensive investigations that have been done globally on persistent organic pollutants, there is a lack of information about BFRs in the Serbian environment. This study addresses a knowledge gap by providing the data on contamination status of aquatic body by PBDEs, which is an important contribution regarding environmental matters on new emerging contaminants. A more comprehensive understanding would be achieved by further studies on the dynamic pollution mechanism and the status of aquatic biota in this region. Systematic ecological and ecotoxicological effects of BFRs and associated contaminants on aquatic biota would provide a significant indication of the bioavailability of these new emerging contaminants.

At the end, obtain results will be very useful for the risk assessment, vulnerability functions and exposure database of the Danube regional multi-hazard and multi-risk model.

Acknowledgements

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