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DANUBE SEDIMENT CONTAMINATION WITH POLYCHLORINATED BIPHENYLS: NEW INTERPRETATION OF SEDIMENT QUALITY ASSESSMENT

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Among the contaminants of greatest concern, it is still possible to detect in aquatic systems "old" classics such as polychlorinated biphenyls (PCBs). Since PCBs are detected in all environmental matrices and have been identified as harmful substances due to their toxicity, persistence, and bioaccumulation in humans and wildlife, they are still one of the important groups of POPs. For this reason, this original approach studies the toxicological influence of PCBs, quantified in sediment samples collected at ten sites along the river Danube, by an application of advanced classification and clustering methods such as hierarchical cluster analysis (HCA) and Kohonen's self-organising maps (SOMs). Selected multivariate techniques were applied to the monitoring dataset in order to obtain visual images of the components distributed at each sampling site when all components are included in the classification and data projection procedure. After analyzing the data set using both techniques were isolated groups that exhibit similar behavior. In the hexagon and dendogram of variables three main clusters were distinguished. Towards the identification of pollutant spatial patterns, the SOM did not isolate a clear phenomenon probably due to the absence of local pollution sources contributing to the elevated concentrations of these compounds. The presented assumptions indicated that the supplemental application of SOM and HCA offers advantageous features over the usually rough interpretation of PCBs pattern and over the single use of the methods.

Keywords: PCBs, SOM, HCA, sediment, Danube

INTRODUCTION

Polychlorinated biphenyls are purely man-made products, either synthesized as industrial chemicals for commercial purposes or generated unintentionally by combustion processes, especially during incineration of waste. PCBs were first manufactured commercially in 1929, and serious concerns about the distribution of PCBs in the global environment were raised in the 1960s when PCBs were found in soil, water, and animals (1). The production/usage of PCBs has been banned/restricted worldwide since the early 1970s, but a large amount of PCBs was already produced. They are among the so-called dirty-dozen, i.e. the first group of chemicals listed for elimination by the Stockholm Convention. PCBs are classified as persistent organic pollutants (POPs) with high toxicity and have undesirable effects on the environment and on humans. Once released into the environment PCBs could bioaccumulate within the food chain, due to their high affinity for organic materials. They have been found in human tissues, blood, and breast milk and are introduced via the consumption of meat, fish, and dairy products (2). Consequentially, they have been linked to chronic effects in humans including immune system damage,

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decreased pulmonary function, bronchitis, and interferences with hormones leading to cancer (3). PCBs are chemically inert and thermally very stable. Hence, they became very useful as insulating material in electric equipment such as transformers and capacitors and also in heat transfer fluids and in lubricants. They have also been used in wide range of products such as plasticizers, surface coatings, ink, adhesives, flame retardants, paints, and carbonless duplicating paper.

PCBs primarily accumulate in soils and sediment as a result of spills, leaking toxic landfills, or contamination from products containing the chemicals. While PCBs do pollute the air via volatization and dispersion, the contaminants are most problematic in soils and sediments where they adhere to organics and are very slow to degrade. The primary route of exposure for humans and wildlife is through the ingestion of contaminated dietary items. A number of studies from both the developed and developing countries of the Asian region showed environmentally concerned levels of PCBs in various matrices of the ecosystem, particularly in surface water, sediment and biota (4, 5, 6).

This study was initiated and intended to provide baseline information of the local level along with spatial trends of certain PCBs in the aquatic sediment of Danube River. Grouping of sampling localities with different properties of sediment that are responsible for the distribution of pollutants in the aquatic environment will also be evaluated by an application of advanced multivariate techniques. Danube pollution by PCBs might be a potential threat to aquatic organisms including fish and other benthic organisms. Sediments are good indicators to elucidate the contamination status and distribution of PCBs in the aquatic ecosystems. Unfortunately, the accumulation of PCBs in Serbian stretch of Danube has been paid less attention and no complete study has been carried out so far. Thus, it is vital to identify the contemporary issues impacting PCB concentrations and their distribution in the aquatic ecosystem. Therefore, the aim of this research work is to determine the concentrations of certain PCBs in sediment, giving emphasis on most contaminated localities assessment in the Danube area of Serbia.

MATERIAL AND METHODS

Sediment samples collection

The sampling was performed in October 2012. For this investigation, 10 samples of bottom sediment from different sites of Danube River through Serbia (Apatin - D1 (1401 km), Labudnjača - D2 (1367 km), Neštin - D3 (1264 km), Begeč - D4 (1275 km), Ratno Ostrvo - D5 (1257 km), Šangaj - D6 (1250 km), Knićanin - D7 (1214 km), Belegiš - D8 (1199 km), Ritopek - D9 (1141 km), Dubravica - D10 (1103 km)) were collected using a grab sampler (Fig. 1). Samples were taken to the laboratory in an ice cooler, where they were weighed and sealed to avoid contamination. All sediment samples were analyzed in the laboratory of Research Centre for Toxic Compounds in the Environment - RECETOX (Brno, Czech Republic) after two days. Before analysis, wet sediment samples were sieved through 2 mm sieve to remove leaves, stoned and roots. The sediments were well homogenized and subsamples were taken in 150 ml glass jar for freeze-drying.

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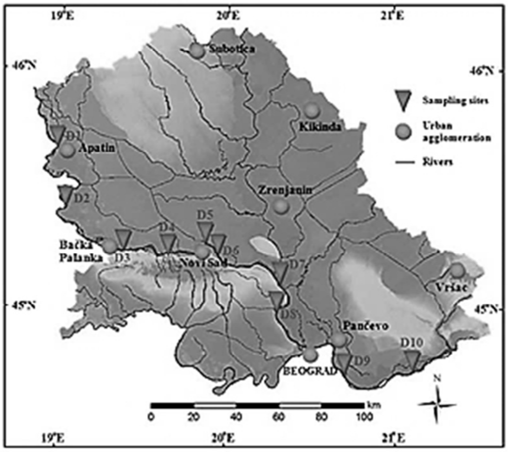

Figure 1. Danube River sampling sites

Sample analysis

Freeze-dried sediment samples were extracted with dichloromethane in a Büchi System B-811 automatic extractor. One laboratory blank and one reference material were analyzed with each set of ten samples. Surrogate recovery standards (PCB 30, PCB 185 in the amount of 10 ng for PCBs analysis) were spiked in each sediment prior to extraction. After extraction the sample volume was reduced and transferred to hexane using azeotrope principle on Kuderna-Danish evaporation unit having finally 1 ml of extract in hexane. For PCBs clean up and analysis, the extract went through activated silica gel modified with sulphuric acid column and eluted with hexane: dichloromethane. The volume of the extracts was again reduced and transferred to hexane using Kuderna-Danish evaporation. The extracts were further reduced under soft nitrogen flow. The extract was quantitatively transferred to GC-MS vial and the final volume was brought to 1ml. For quantification of PCBs 10 ng of PCB 121 was added as syringe internal standard. The extract was quantitatively transferred to GC-MS vial and the volume was reduced to about 0.1 ml. Samples were analyzed using a GC-MS/MS (GC 7890/MS-MS Triple Quadrupole 7000B; Agilent) supplied with a SGE-HT8 (60m x 0,25 mm x 0,25 um) column for PCBs PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180.

Data analysis

In order to increase the performance of the modelling procedure, applying the hierarchical cluster analysis approach to recognize and group the subsets of the large amount sediment samples data with a similar pattern can be helpful [7]. HCA allowed grouping the sampling localities depending on the concentration levels of PCBs in the Danube sediment. Also, the unsupervised artificial neural network (ANN) used in this study was the Kohonen Self-Organizing Map (SOM) which has been successfully applied in the classification of aquatic pollution [8,9]. The classification of data by Kohonen's SOM allowed understanding and visualizing the spatial distribution of samples. This approach allowed a precise point of pollution to be identified, as well as the possible transport routes of contamination to be defined. The findings yielded can assist in future remediation initiatives aimed at eradicating PCBs from the Danube river sediment. Statistical analysis was

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implemented applying the IBM SPSS Statistics 22 software (IBM Corporation, Armonk, New York, U.S.) and MATLAB 2.0 software (Mathworks Inc., USA). The proposed methodologies and results obtained in this paper provided valuable assessment using the HCA and SOM visualization capabilities and highlighted zones of priority that might require additional investigations and also provide productive pathway for effective decision making and remedial actions.

RESULTS AND DISCUSSION

PCB contamination

The spatial trend of polychlorinated biphenyls in the collected samples of sediment within the research at 10 sampling sites is presented in Figure 2. The highest concentration levels of PCBs were detected in the areas of the most developed industrial centers in AP Vojvodina near Bačka Palanka city (Neštin: 3.54 µg/kg) and Pančevo (Ritopek: 3.27 µg/kg), which is the consequence of today's active industrial activities amplified by the historical pollution of industrial waste released into the environment of such past, but also possible accumulation of these toxic pollutants in the Danube sediment after NATO aggression in 1999 years.

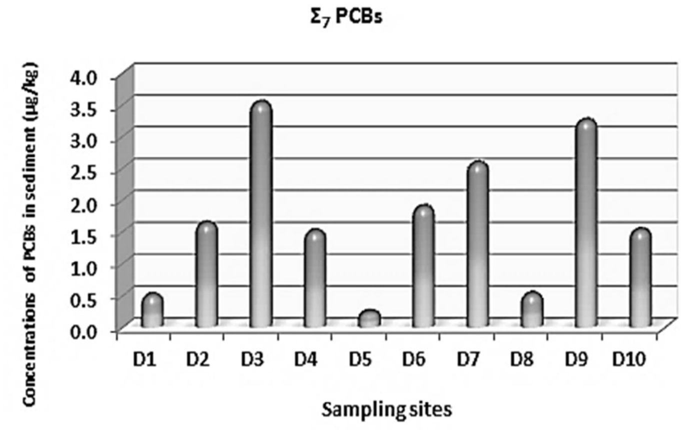

Figure 2. Spatial distribution of PCBs in sediment samples Figure 3. Composition of PCBs in sediment samples

Figure 3 shows the values of PCB congeners grouped by the number of substituted Cl atoms at the benzene ring. The most commonly used PCB congeners in sediment samples were with six and seven chlorine atoms in samples collected at three sites around Novi Sad (77.2%, 81.9% and 84.3% for Begeč, Ratno Ostrvo and Šangaj, respectively of the total value of analyzed PCBs) and at the site near Pančevo (73.1% for Ritopek). The presence of PCB congeners chlorinated with a large number of Cl atoms (5-7 Cl) indicates their long presence, and therefore their significant negative impact on the environment.

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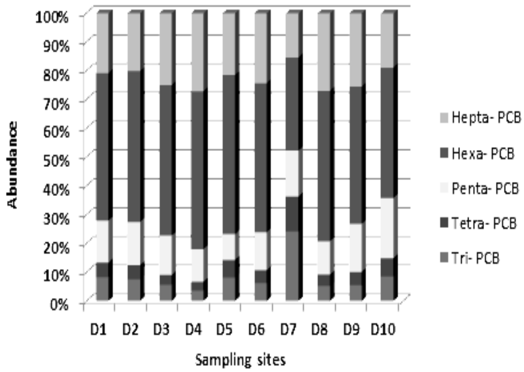

Figure 3. Composition of PCBs in sediment samples

Hierarchical cluster analysis

Data integration included firstly a cluster analysis to investigate for similarities between the objects (sampling stations or variables), using Euclidean distance as distance measure and Ward's method as a linkage method. The result of cluster analysis performed on sampling stations (Fig. 4) showed the formation of 3 major clusters. The first included stations D1, D8, and D5, with lower levels of PCBs. A second cluster joined stations D2, D4, D6, D10 and D7 with moderate levels of PCBs; this cluster was formed by 2 subgroups, as D7 presented the influence of the Tisa River on Danube. The third cluster comprised the stations D3 and D9, with the highest concentration levels of PCBs. The elevated values at sites D9 and D3 are probably conditioned by the proximity of the Belgrade municipal waste landfill in Vinča, i.e. the municipal waste landfill in Bačka Palanka (distance less than 10 km from the sampling site). Also, the proximity of the industrial centers of Belgrade-Pančevo and Bačka Palanka, as well as developed arable production and thus uncontrolled disposal of waste, are certainly one of the important implications that these two sites are separated with the highest concentration levels of the given chemical spices.

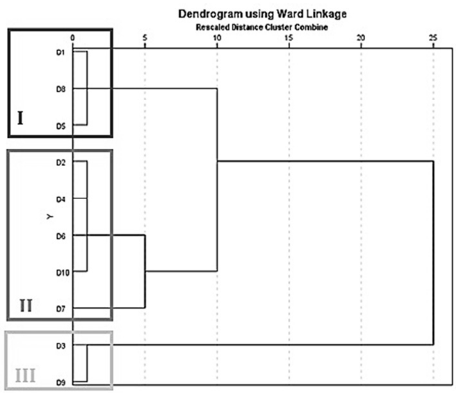

Figure 4. Hierarchical dendogram for sediment data clustering of sampling sites from the Danube

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Kohonen Self-Organizing Map

The plans SOM components of the dataset are shown in Figure 5. The vertical bars in the component plane presented the gradients of PCB congeners concentrations. The identical color patterns between the variables correspond to a positive correlation; this can be considered among the variables: (a) PCB 28, PCB 52, PCB 101 and PCB 118 and (b) PCB 138, PCB 153 and PCB 180. There were no negative correlations between the variables. These results further confirmed that low halogenated PCBs often existed together, which may originate from the degradation of high halogenated compounds. Each map corresponding to one variable was compared to the distribution of the sediment samples.

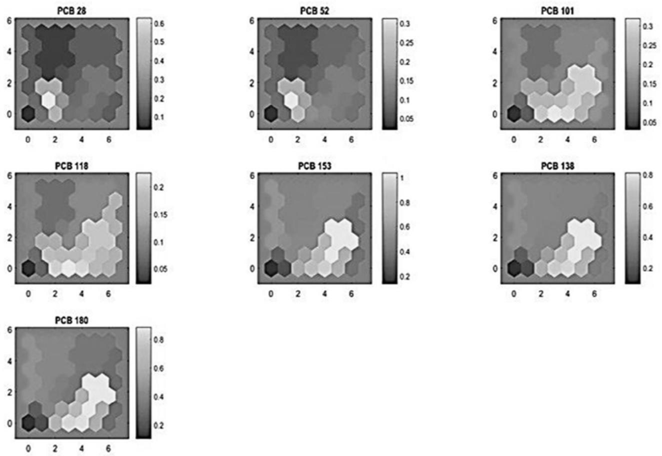

Figure 5. SOM component planes for the seven input variables

Figure 6 showed the three clusters of samples, were obtained after classification by k-means algorithm to weight vectors of ten variables of SOM. All the 10 sediment sources were classified into three clusters, as well as applying HCA.

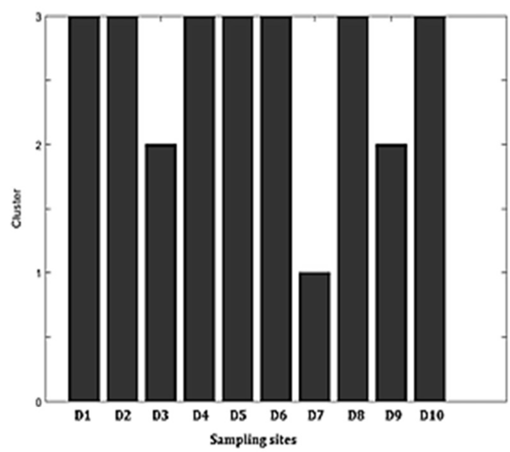

Figure 6. The distribution of ten sediment sources on the SOM

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Cluster 1 with seven nodes, grouped from D1, D2, D4, D5, D6, D8 and D10. The concentrations of halogenated compounds in this cluster were lower than the other clusters, indicating that the pollution of mentioned sampling sites was at low level. Cluster 2, including D3 and D9, was activated with high intensity in total PCBs concentration levels. Using the k-means algorithm, the localities grouped into this cluster are completely matched to the third cluster obtained by the application of HCA. Cluster 3, including only site D7.

CONCLUSIONS

The research under this study was based on the monitoring carried out in 2012 to determine the concentration levels and spatial distribution of polychlorinated biphenyls, specific lipophilic persistent organic pollutants in complex aquatic sedimentation systems of the river Danube on sites with significant anthropogenic influence in the Republic of Serbia. Ten sediment sample models were compiled, containing PCB congeners from the group so-called EPA PCBs (representing environmental pollution indicators). At all analyzed samples, concentration levels of total PCB congener values were below the remediation values prescribed by the Regulation of the Republic of Serbia (10). The lowest concentration at most samples was PCB 28 concentration and the minimum total concentration of all congeners was recorded at site D5 (0.25 μg/kg), while the highest concentrations were recorded at D3 (3.54 μg/kg) and D9 (3.27 μg/kg). Considering the inclusion of PCB congeners classified on the basis of the number of Cl atoms contained in their structure, it was concluded that all sites have the highest presence of hexa- and hepta-PCBs, except for D7 sites, where hexa and hepta- PCBs dominate PCBs with three Cl atoms. The self-organizing map SOM was used in this study for distribution of seven EPA PCBs in sediment samples collected from Serbia's stretch of the Danube River. The comparison with the HCA, showed, therefore that the results obtained with the SOM were generally similar to findings of HCA statistical method. But, the SOM method has also provided more detailed classification of PCBs congener from sediments of the Danube River.

Based on the overall analysis of the obtained results, it can be established that the Danube riverbank flow at the territory of Serbia still has significant potential pollution sources of aquatic systems with PCBs, which is important information to conduct more extensive monitoring and prevent further disposal of equipment that containing these pollutants by adequate controls, thus diminishing the extremely negative ecotoxicological effects currently present in the aquatic system. Within the framework of such a systematized research process, it would be necessary to include more media (biotic and abiotic) in the analysis as well as more specific points.

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