Cadmium Distribution Between Aqueous Phase and Sediments in the Danube Delta Biosphere Reserve

The Equilibrium Partitioning Method

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In this study, we applied the equilibrium partinioning method to the Danube Delta lakes sediments, to derive an applicable set of quality criteria for aquatic ecosystems. The partition coefficients, K_{sp} were calculated for the Danube Delta three lakes type, using the medium cadmium concentrations (between 1997-2007) and the suspended matter concentrations. According to the value established by Romanian Normative 161/ 2006, for the 1st quality class, for the standard concentration of dissolved form, the cadmium standard concentrations in suspended matter, sediments and total (dissolved and particulate) forms were calculated, and then, compared with the determinated heavy cadmium concentrations. The partition coefficients, the cadmium sediment standard concentrations, the cadmium concentrations in suspended matter decrease from the first type to third lake type.

Keywords: equilibrium partitioning method, cadmium

The sediments serve as the ultimate sink for most persistent pollutants introduced into aquatic ecosystems.

In cases of legacy pollution, sediments are often the source of ongoing contamination.

A generally applicable aproach to derive a sediment quality criteria is the equilibrium partitioning method [9,10].

In this method, the co-occurrence of chemicals in water and sediment are modeled as a state of thermodynamic equilibrium, as a sorption equilibrium [10].

Provided that such a direct relationship can be quantitatively formulated from the quality criteria for water, and in turn are derived from the results of standard set of aquatic toxicity sets.

The applicability of sediment quality criteria result for: assessment of sediment quality, deriding on remedial actions to ealleviate environmental degradation related to sediment contamination, assessing the quality of sediments in discharges impact areas, designing and evaluating monitoring programs, assessing potential impact on benthos, establishing waste load allocations [3, 10].

The name of the Danube Delta refers to the downstream of the first bifurcation of the Danube river at Cheatal Chilia bordered by the Black Sea to the east, the floodplain of the Danube river Chilia branch to the north and the Razim lagoon to the south [7].

In the Danube Delta, Type 1 lakes are located in the deeper parts of the original marine lagune on which the Delta is formed. These lakes are relatively deep (2-4m) and large (>200ha), with sand-silt susbtrate and intermediate inflow of river water. The lakes are turbid, have a high abundance of cyanobacteria and cladocera, a low abundance of aquatic vegetation and a predominantly eurytopic and limnophilic fish comunity in which „black fish'' are scarce.

Type 2 lakes are in the zone with a high river water input. These lakes are intermediate in size and water depth and have a strong dynamics in water level. The lakes are clear, zooplankton in scarce, but aquatic vegetations is abundant, mainly *Potamogeton trichoides* community. Filamentous algae are abundent and the fish community is predominantly eurytopic.

Type 3 lakes are in the shallower parts furthest removed from the river where reeed colonization and peat accumulation is dominant. These lakes are relatively small and shallow; the lakes are clear, with low abundance of aquatic vegetation, mainly *Nitellopsis obtusa* and a fish community in which „black fish" are abundant and eurytopic fish are scarce [7].

The limnosoils (underwater soils) are the lacustrine/ lagoonal deposists from the lake bottoms. These sediments are mostly composed of mineral suspensions carried down by the riverine down by the riverine waters and those produced by chemical and biological processes which take place in eutrophic water bodies and sediments. [6].

In "Lacul Fortuna" the predominant limnosols are coprogenic limnosols.

In " Lacu Roşu" the predominant limnosols are hyper calcareous limnosols.

In "Lacul Cuibul cu Lebede" the predominant soils are histic limnosols, partly acid sulphate.

One of the ecological properties of the dominant soils is the vulnerability to chemical contamination with heavy cadmium. From this point of view, Lacu Fortuna sediment has medium vulnerability, Roşu low and Cuibul cu Lebede low. [6]

Delta ares are thought to be the most polluted parts of a river system because of the decreasing flow velocity.

The aim of this study is to apply the equilibrium partinioning method to the Danube Delta lakes sediments, to derive an applicable set of quality criteria for aquatic ecosystems. For this, we calculated and compared the partition coefficients, K_{sl}, the standard concentrations for cadmium in suspended matter, standard concentrations for sediment cadmium, the total (dissolved and particulate) standard concentrations of cadmium, the experimental and standard concentrations.

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Table 1
SAMPLING POINTS SPATIAL DISTRIBUTION

Nr.crt	Lake	Aquatic complex	Coordinates
1	Roşu	Roşu-Puiu	X: 45^{0}03'59" Y: 29^{0}34'32"
2	Fortuna	Şontea-Fortuna	X: 45^{0}13'18" Y: 29^0 8'16"
3	Cuibul cu Lebede	Gorgova-Uzlina	X: 45^{0}08'59" Y: 29^{0}19'59"

Experimental part

Sampling area

Taking into account the lake categories for the achivement of the goals stated in this document, the following areas were considered: Roşu-Puiu, Şontea-Fortuna and Gorgova-Uzlina [1].

Roşu-Puiu area is located between the Sulina branch, Caraorman sandy-land and the Black Sea and it stretches over a depression with an area over 35.000 ha, from which 11700 ha are below the sea level. In this area are located about 60 large lakes, they cover about 20% of the depression surface (6220 ha). Lacu Roşu is also included in this area (type I lake), with 1365 ha of water surface, and 2243 ha of reed bed.

Şontea-Fortuna area is located between the Stipoc sandy-land in north and Sulina branch in south. The Sontea channel splits from Chilia branch and is the main lane of this large lacustrine area. The most important lake is Fortuna (type II lake), and the total area of 4908 ha is divided in 779 ha of water surface, without reed bed, and 4129 of reed bed.

The Gorgova-Uzlina boundaries are as follows: Sulina sandy-lands in north, Sf. Gheorghe in south, Rusca in west and maritime sandy-land in east. The main lane of this area is Litcov channel, which splits from Sf. Gheorghe branch and ends in the Roşu-Puiu area. Cuibul cu lebede is included in this area (type III lake), its surface is 1246 ha, divided in 196 ha of water surface, 427 ha of reed bed, and 623 ha of reed bed.

Samples of water and sediments were taken from these three lakes in each quarter, between 1997 and 2007.

For the method of equilibrium partition, Roşu, Fortuna and Cuibul cu Lebede lakes were selected.

The coordinates were established by GPS and are listed in table 1.

Sampling Methods

Water Sampling

Samples of the water lakes were collected in accordance with SR ISO 5667/1998. Sampling according to the standard above, which action is taking a part of water considered representative for the purpose of examining the characteristics defined. Sampling area is a mass of surface water sample that are collected (SR ISO 6107-2) and the sampling position is precisely determined by its geographic coordinates. Each sample is considered representative for water quality in time and point of sampling. In most cases occurring in sampling for chemical analysis, is sufficient to immerse the container with a wide mouth below water surface (a bucket), known as the sampled surface. For determination of the cadmium are taken 500 mL of water, which is fixed with 2.5mL concentrated nitric acid. Determination of metal content is on the unfiltered water sample.

Sediment sampling

The sediment samples are sampling according with SR ISO 5667 -12: September 2001- Water quality – Sampling, Part 12: Guidance on sampling of bottom sediments with dredge. The sediment samples were dried at room temperature, for avoid losing organic micro pollutant.

To obtain sub samples approaching 20g, it is made a pretreatment to a portion from the sample air - dried, ground fine and sprinkled through a sieve with meshes of 150 μm.

Reagents

All reagents used, have high chemical purity, and are Merck. For the heavy cadmium extraction we use concentrated nitric acid and hydrogen peroxide, mainly used to increase the oxidizing effect of HNO_3 to destroy matrix residues.

Calibration solutions

For all the heavy cadmium are made the flow charts and the calibration curves.

The calibration curves were made using the Perkin Elmer Pure Plus Atomic Spectroscopy Standard, certified reference material 10 μg/mL, Multi-element ICP-MS calibration STD.3, matrix 5% HNO_3. The calibration curves are linear and they are made in five points. Using the Excel interface, for each calibration curves, were calculated, the equations and the R^2 coefficients.

The coefficient R^2, for the calibration curves has the values between 0.9994 - 0.9997, that represents a very good correlation between the intensity and the standard concentrations.

Instruments

Microwave digestion, necessary for heavy cadmium determination was made using the microwave oven Anton Paar, Multiwave 3000.

The cadmium contents were analyzed using the ICP MS Elan DRC-e. Inductively coupled plasma – mass spectrometry (ICP-MS) is applicable to the determination of small concentrations of a large number of elements. When dissolved constituents are required, samples must be filtrated and acid-preserved before the analysis.

The optimization solution used, was ELAN 6100Setup / Stab./Masscal. Solution. The optimization solution contains the elements: Mg, Cu, Rh, Cd, In, Ba, Ce, Pb, U. The labeled concentrations are 10 ppb for each element.

Sample preparation

The mineralization stage is made differently depending on the type of sample respecting standards and recommendations suggested by the manufacturer Anton Paar oven.

For the water, in vessels of quartz oven Anton Paar we introduce 25 mL of sample and add 6 mL HCl and 2 mL HNO_3. After a short pre-reaction time (10 min), the vessels are hermetically sealed using special device then are inserted into the protective sheath and protective cover is set and then is fixed properly in the rotor. The fixing screws are progresively turned, then the rotor head is fixed into the indicated position and the rotor is introduced in the oven. Then the working instructions from the oven memory are followed. The power is raised to 1200 W in 5.5 min and this value is maintained for 4.5 min. After completing the program and the cooling time, the rotor is moved out, the vessels are open and the content is moved in 50 mL flasks and brought to the sign with bidistilled water.

For heavy cadmium determination from the sediments these are introduced in quartz vessels, weighed, then 5 mL nitric acids and 2 mL hydrogen peroxide are added. After 15 min of pre-reaction time, the vessels are hermetically closed with protective cap, and protective casings and then the rotor is put into microwave oven. When the program and the cooling time end, the rotor is taken out, the digestion vessel are open and the content is removed in the graduated flask and diluted to 100 mL.

Analysis

The ICP MS method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosols are transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier.

Results and discussions

In this method, we take into account the heavy metal concentrations in different forms: in aqueous phase (dissolved), in the suspended matter, total (dissolved and particulate) and sediments.

$$K_{sl} = C_s / C_l \quad (1)$$

where:

K_{sl} =the partition coefficient, $L \cdot g^{-1}$

C_s = heavy metal concentration in the solid phase, $mg \cdot kg^{-1}$

C_l = heavy metal concentration in the water phase, $\mu g \cdot L^{-1}$

The partition coefficients can be derived from the field measurements of concentrations in water before and after filtration.

$$K_{sl} = C_{susp}/C_l = (C_{tot} - C_l) / C_{SM} * C_l \quad (2)$$

where:

C_{susp} =heavy metal concentration in the suspended matted. $mg \cdot kg^{-1}$

C_{tot} =total (dissolved and particulate) heavy metal concentration before the filtration, $\mu g \cdot L^{1}$

C_l=heavy metal concetration in the water phase, $\mu g \cdot L^{-1}$

C_{SM}= concentration of suspended matter, $g \cdot L^{-1}$

According with the literature, for the heavy cadmium, the ratio between the heavy metal concentrations in the suspended matter and the concentrations of the heavy metal in sediment is 1.5. So, if the ratio in the concentrations in the suspended matter and water is a measure of K_{sl} the heavy metal cocentration in sediment can be calculated as folows:

$$C_{sed} = C_{susp} / r = K_{sl} * C_l / r \quad (3)$$

where:

C_{sed}= heavy metal concentration in sediment, $mg. kg^{-1}$

C_{susp}= heavy metal concentration in the suspended matter, $mg \cdot kg^{-1}$

r =empirical ratio between heavy metal concentration in the suspended matter and heavy metal concentration in sediment and is 1.5

To calculate the total (dissolved and particulate) heavy metal concentration in water if the dissolved heavy metal concentration in water is given, the ecuation becomes:

$$C_{tot} = C_l * (1 + K_{sl} * C_{SM}) \quad (4)$$

In this study, it was applied the equilibrium partitioning method to cadmium, because of its toxic effect. The toxicity of cadmium in sediment, the free and dissolved, uncomplexed cadmium was found to be the toxic form of metal. The authors concluded that cadmium adsorbed to the sediment had negligible toxicity and the toxic effects of cadmium associated with sediments could be predicted from the concentration of unbound cadmium in the pore water [2, 8].

Analysis of cadmium content

In order to find a quality criteria for water and sediments, there were used the yearly average values for metal concentrations recorded between 1997 – 2007.

Knowing the total (dissolved and particulate) cadmium concentration, cadmium concentration in dissolved phase, and the concentration of suspended matter, there were calculated the distribution constants according to formula (2), for these three types of lakes: type I lake – Roşu , type II lake – Fortuna and type III lake – „Cuibul cu Lebede".

Comparing the partition coefficients, K_{sl}

The partition coefficients were calculated according with formula 2.

We can notice a decrease of these partition coefficients for cadmium, from type I lake to type III lake (fig.1).

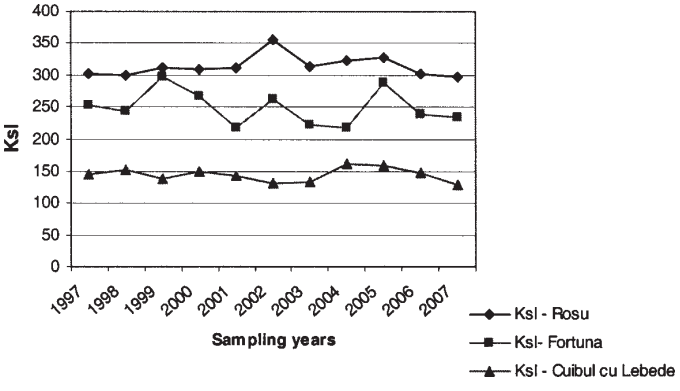

Fig. 1. Dynamics of cadmium partition coefficients for the three lakes

Kooij was computed, for the Dutch surface water, (1983-1986), the cadmium partition coefficients, and the values are between 50-493 L/g^{-1}[10].

Comparing the standard concentrations for cadmium in suspended matter

In order to define the quality criteria, we used the prior calculated partition coefficients, the suspended matter concentration and the concentration of dissolved metal as standard values. The standard concentration of the metal in disolved phase is in compliance with Normative 161/2006 regarding the classification of surface water quality with the purpose of ecological status assessment of water bodies, issued in Monitorul Oficial part 1 nr.511Bis, 16.06.2006. Thus, the values for high quality ecological class can be found in table C – „Elements and standards of chemical and physico-chemical quality in water". These values were established as standard concentrations for dissolved metals and for cadmium is 0.5 ppb.

In relation with this standard value, we can calculate for the three categories of lakes the following: the standard concentrations for the cadmium in suspended matters, standard concentrations for sediment cadmium and also total (dissolved and particulate) standard concentration for cadmium.

The standard concentrations of cadmium in suspended matter proved the same decreasing dynamics from lake type I to lake type III.

Lacu Roşu , which is a type one lake, is turbide due to the phytoplankton and solid matters included in suspended.

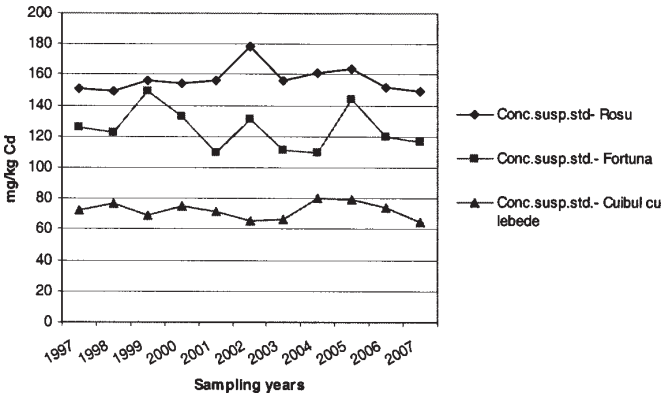

Fig. 2. Dynamics of cadmium standard concentrations in suspended matter

Thus, high concentrations of solid matter in suspended entail high concentrations of cadmium both in matters in suspended and sediments (cadmium) (fig. 2).

Comparing the standard cadmium concentrations in sediment

The standard cadmium concentrations in sediments were calculated according with equation 3, as shown in figure 3. The standard concentrations of cadmium contained in sediments proved the same decreasing variation from lake type I to lake type III.

Comparing the total (dissolved and particulate) standard concentrations of cadmium

Total (dissolved and particulate) standard concentrations were calculated according to formula 4 for all three types of lakes.

Total (dissolved and particulate) standard concentrations of cadmium proved the same general

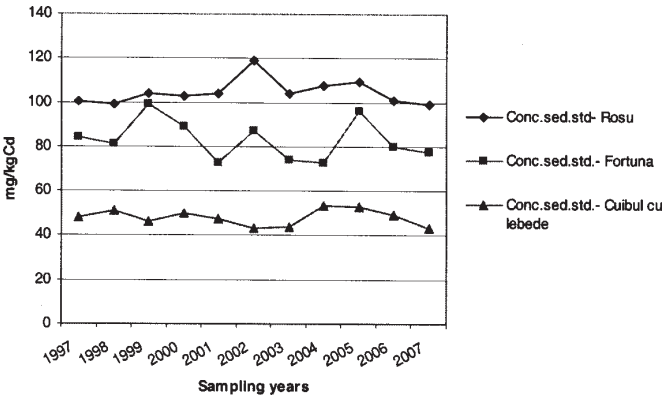

Fig. 3. Dynamics of standard concentrations in sediments

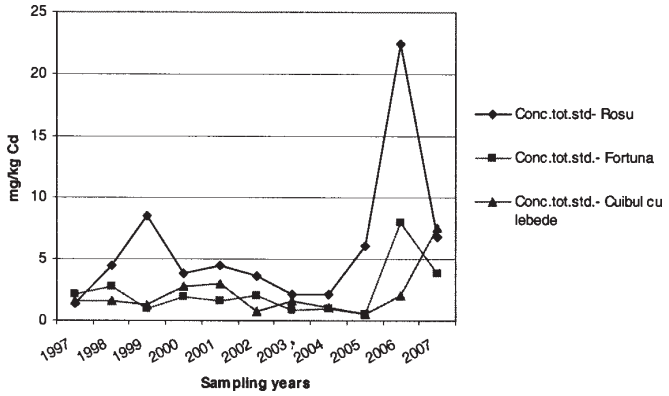

Fig. 4. Dynamics of cadmium total (dissolved and particulate) standard concentrations

dynamics regarding maximum values for lake type I and minimal values for lake type III (fig. 4).

Comparing the experimental and standard concentrations

The calculated standard concentrations for cadmium in suspended matter, sediments and total (dissolved and particulate) heavy metal concentration were subsequently used as an input, with the purpose of comparing with the experimental values.

The calculated values for cadmium are lower than the concentrations which were found by experiment and this is confirmed by the fact that cadmium concentrations recorded in surface water exceed the limits for the 1st quality class, in compliance with the normative N 161/2006. (fig. 5).

The conclusion, after the review of metal concentrations analysed from the sediments and the ones that were calculated according with the partition equilibrium model, was that all experimental values are in general lower than

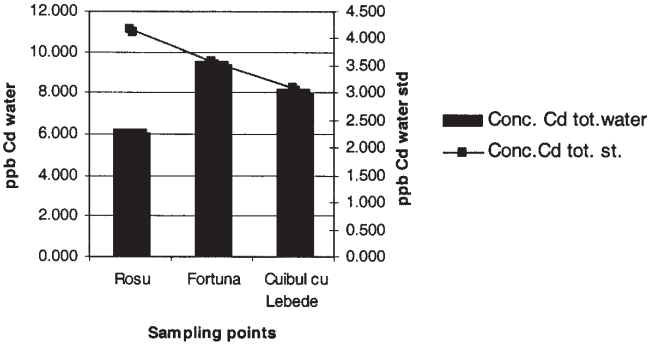

Fig. 5. Comparing the cadmium total (dissolved and particulate) concentrations (analysed and calculated) for the three types of lakes

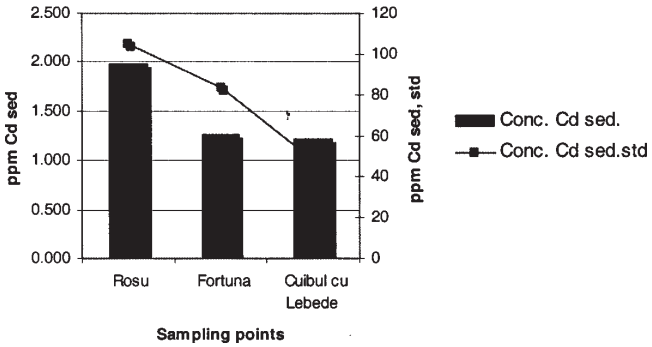

Fig. 6. Comparing the cadmium concentrations in sediments (recorded and calculated) for the three types of lakes

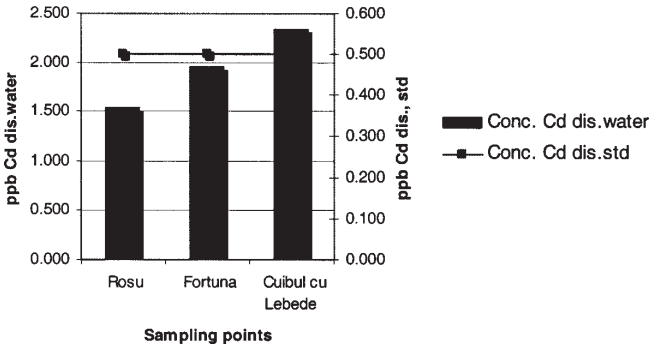

Fig. 7. Comparing the concentrations for the dissolved cadmium (recorded and standard) for the three types of lakes

the ones that were calculated according to the standard criteria (fig. 6).

Long and Morgan computed a standard concentration for cadmium in sediment and are obtained the value of 6 ppm [5].

In figure 7 are shown the average values of the mean concentrations for the cadmium in liquid phase (dissolved), dependent on standard values, values according to the 1st quality class (Normative 161/2006).

Thus, the experimental values for cadmium are in general higher than the standard ones.

Decreasing water levels can lead to a significant increase in dissolved cadmium. The dissolved cadmium concentration decreases from " Lacul Cuibul cu Lebede" to "Lacu Roşu" (more deep) [4].

Conclusions

The equilibrium partitioning method offers a coherent set of quality criteria for Danube Delta lakes, criteria for the water phase (dissolved), for the suspended particles, for the total (dissolved and particulate) and for the concentrations in sediments.

The cadmium partition coefficients, the standard concentrations of cadmium contained in sediments, the total (dissolved and particulate) standard concentrations of cadmium proved the same decreasing variation, from "Lacu Roşu", which is a type I lake, turbide due to the phytoplankton and solid matters included in suspended, to "Lacul Cuibul cu Lebede ", which is a type III lake.

Using the equilibrium partitioning method, we can compare the experimental and standard concentrations. So, the dissolved cadmium concentrations and the total (dissolved and particulate) exceed the standard computed values and the sediment cadmium concentrations are lower than the standard values.

The problem of water pollution in Romania had been studied also by other researchers [11-14].

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