

# Distribution, Partition and Fluxes of Trace Heavy Metals in the Lower Danube River

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*Hazardous substances are distributed in aquatic environments between water body and sediments, in particular cases, sediments being re-suspended in large amounts into the water body (high water flow). These substances can be of synthetic or non-synthetic nature, being characterized by relatively low water solubility and high capacity of chemisorption at the surface of solid suspended particles. This study presents an integrated approach of both transport and transfer processes of heavy metals (lead and nickel) in the lower Danube River between km 375 to km 175. This is a location of interest, considering that in this part of the river there is possible an increased accumulation level of heavy metals related to the recent construction works in the area for the improvement of navigation conditions. Based on the partition coefficient ( $K_p$ ), the transfer of the heavy metal ions from the soluble phase to the suspended matter bound phase has been determined. In order to assess the transport phenomena in aquatic environment, the associated mass flow rate related to the water body also was calculated.*

**Keywords:** *aquatic environment, lead, nickel, dissolved and particle concentration*

The heavy metals aquatic environment pollution represents an important global issue ever since the early 1970s [1] because of their extremely toxic effect even at low concentrations [2]. After their penetration into the aquatic environment, these metals accumulate in the suspending matter and in sediments, becoming long term pollution sources [3] due to their suspension-sedimentation-resuspension processes. Metal pollution of aquatic environments can reduce biodiversity, their bioaccumulation into mollusks and fish species can be a thousand times greater than for the environment.

Lead and nickel are some of the heavy metals pollutants originating from various sources [4]. Nickel is commonly used in the production of modern technology, from performance analysis equipment of various pollutants to nickel-cadmium batteries [5]. Due to the larger scale use of products containing nickel, this is released into the environment in various stages of use and production. Many of its effects on health such as allergies, lung fibrosis, cardiovascular system damage and stimulation of neoplastic transformation are documented [6, 7]. Some of the effects of chronic exposure to lead on human health are: behavioral deficiencies, anemia, hypertension and renal failure [8]. Lead and nickel are hydrophobic elements, being transported as associated pollutants to suspended matter [9]. Danube river has an approximate length of 2,800 kilometers [10] and almost 38 % of it lies on Romania's territory [11], representing the general collector of wastewater discharges and soil leachate from the 10 crossed countries on its course. Therefore, all the pollutants accumulated by Danube River pose a serious risk on Black Sea's ecosystem. Numerous studies have been conducted regarding the distribution of metal concentrations between the dissolved and particulate phase [12, 13].

## Experimental part

For monthly monitoring of the concentration of lead from water, 10 sampling points were established (table 1 and

**Table 1**  
THE MONITORING CONTROL SAMPLING POINT

Crt. No.	Control Sampling point name	Km
1	SP1	347
2	SP2	345
3	SP3	344
4	SP4	343
5	SP5	340
6	SP6	341
7	SP7	334
8	SP8	197
9	SP9	196
10	SP10	195

fig. 1) to the lower Danube section for a period of 12 months (September 2011 - August 2012).

## Sampling and analysis

The water samples were collected according to SR ISO 5667-6/1998: Sampling Part 6: Guidance on sampling of water from rivers and streams. Polyethylene bottles were used for collection of the water samples. They have been previously washed with nitric acid solution and then rinsed with water. For each established sampling point, water samples were collected at three depths (0.5, 1.5 and 3 m) from 3 zones (left bank, right bank and river course). A volume of 500 mL from the water samples taken from each point was filtered on a filtering membrane (0.45  $\mu$ m pore size) and pre-cleaned with ultrapure  $\text{HNO}_3$  (1.5 mol/L) to determine the dissolved form of the metal as soon as the samples were delivered to the laboratory. For the determination of the total concentration, a volume of 1 L taken from the test water was acidified to prevent hydrolysis of the metals [14], by adding 2 mL of  $\text{HNO}_3$  (65 %) in it [15].

To determine the concentration of heavy metals from water samples, an atomic absorption spectrometry

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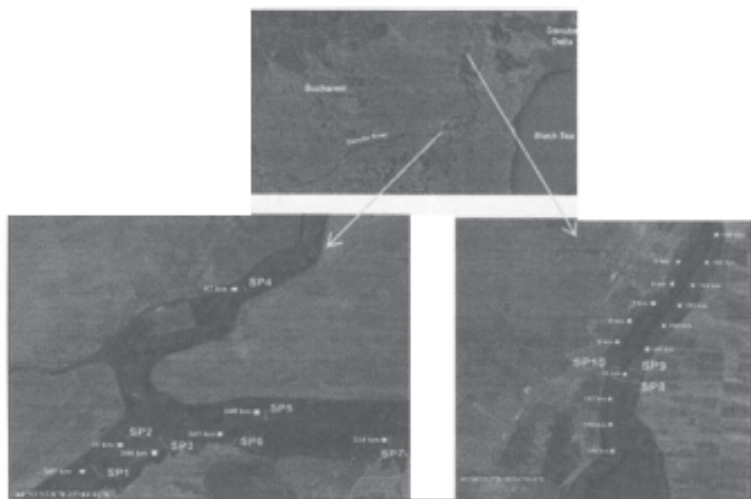


Fig.1. Map of monitoring sampling points

(Thermo M5) with flame and graphite furnace was used [16].

### Reagents and quality assurance

All solutions for calibration, samples, and rinsing were prepared using ultrapure water and Suprapur® nitric acid (65 %, v/v) purchased from Merck, Germany. The stock solutions were prepared using ultrapure water, which was obtained through a Micropure Ultrapure water system (TKA, Germany). The quality of the results was ensured by testing a reference material (T.M-28.3) provided by the National Water Research Institute, from Canada. The obtained analytical results for references materials recorded a variation of less than 10 % compared to the certified values.

## Results and discussions

### Complying with quality standards

For the analysis regarding compliance with the quality standards, annual averages data of total lead and nickel concentrations were used for each established sampling point. From the string of monthly values of concentrations on transversal section, the highest value representing the maximum annual concentration (AMC) was extracted.

The annual average concentration (AAC) for lead (fig. 2) and nickel (fig.3) during the 12 months of monitoring was plotted, according to the specific values of first quality class from Order No 161/2006 [17] and AMC according to Government Decision 1038/2010 [18]. The recorded concentrations for nickel and lead were below the values of quality standards according to the national law.

### Basic equations regarding lead and nickel transport through the water column

Travel speeds of metals can be differentiated both for the water column through the dissolved and particle fractions, and for the sediment, depending on hydrological conditions which can influence the displacement of sediments from upstream to downstream, being slower comparative to the water column speed. In figure 4 the variations of lead and nickel concentrations (fig.4.a) and suspended solids (fig.4.b) are represented depending on the water flow rate. It is noted that the variation of the metals concentration decreases with increasing flow rate and the concentration of suspended solids increases with flow rate.

An important objective of monitoring activity is the characterization of the spatio-temporal evolution of mass flow associated to pollutant. To calculate the mass flow associated,  $Li$  (kt/year) is used the following formula (1) [9, 19].

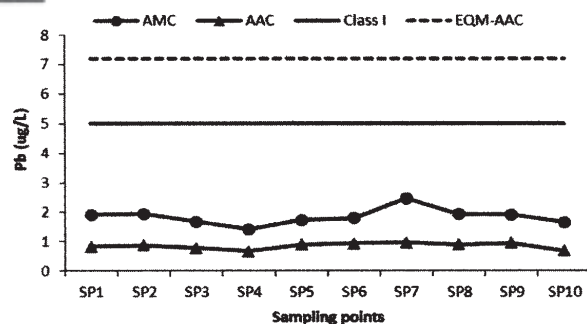


Fig. 2. Compliance with the quality standards of lead concentration

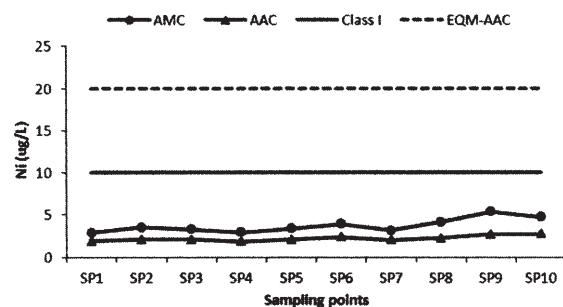


Fig. 3. Compliance with the quality standards of nickel concentration

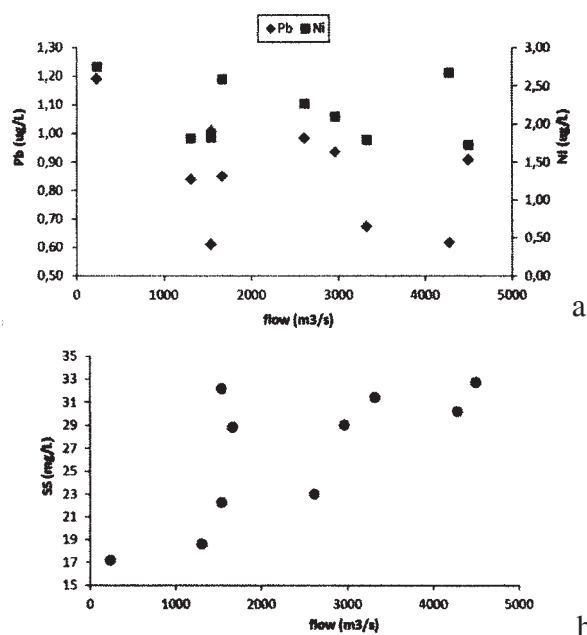


Fig. 4. Variation of the concentration of metals and of suspended solids according to the flow

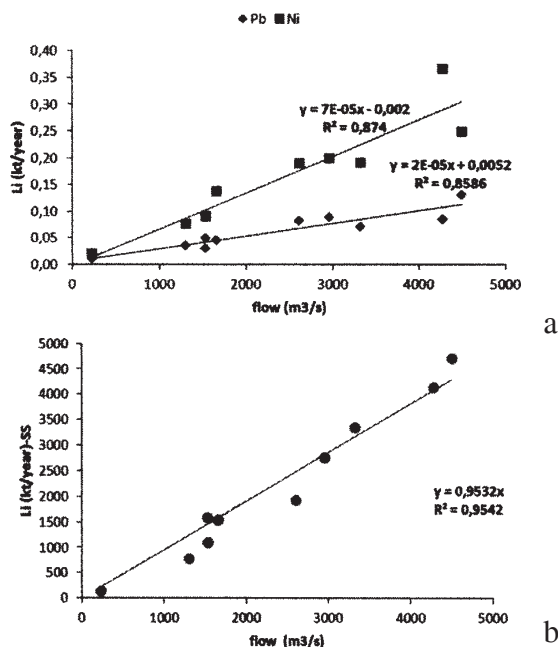


Fig. 5. Variation of associated loadings of heavy metal concentrations and suspended solids according to flowL

$$Li = 0.032 \cdot Ci \cdot Qi \quad (1)$$

where:

Li = mass flow associated (kt/year)

0.032= constant of calculation

Ci = metal concentrations (mg/L)

Qi = Danube flow (m³/s)

For a good characterization of heavy metals transport in the aquatic ecosystem, the first useful tool is the evaluation of the mass flow through the water column. The conducted research showed that this phenomenon is dependent on both metals concentration and water flow.

In figure 5 graphical variations of associated loading with metal concentrations (fig.5.a) and suspended solids (fig.5.b) are represented according to the flow variation. From these graphs it can be seen that the analytic function,  $Li = f(Qi)$ , is linear with a correlation coefficient of 0.8586 for associated loading of lead concentration, of 0.874 for nickel and of 0.9542 for associated loading of suspended solids.

#### The distribution of trace metals at the water column level

The following basic relationships were considered to characterize the distribution equilibrium processes. At the column level of water, the total concentration of metal is given by the relation (2). The particulate metal phase is calculated by subtracting the dissolved metal concentration from the total metal concentrations. Partitioning is critical for understanding bioavailability thus toxicity of heavy metals and for its treatment selection. The partition coefficient,  $K_p$  is calculated from measured values of adsorbed metal per unit adsorbent, divided by the concentration of dissolved metal [12, 20-22]. It is given by the relation (3):

$$C_T = C_d + C_p(SS) \quad (2)$$

$$K_p = \frac{C_p}{C_d} \quad (3)$$

$$C_T = C_d(1 + K_p \cdot SS) \quad (4)$$

where:

$C_T$  = total heavy metal concentration ( $\mu\text{g/L}$ )

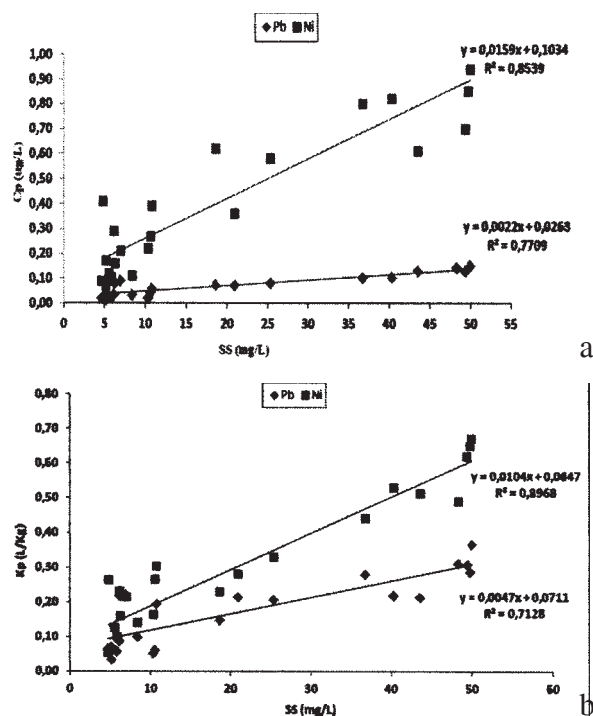


Fig. 6. Variation of particulate matter concentration and the partition coefficient depending on the variation of the suspension concentration

$C_d$  = concentration of the metal in water (dissolved form of the metal) ( $\mu\text{g/L}$ )

$C_p$  = concentration of metal in the suspended particulate matter (particulate form of the concentration) ( $\mu\text{g/L}$ )

SS = concentration of suspended matter (mg/L)

$K_p$  = the partition coefficient (L/kg)

In figure 6 the variation of the particulate concentration (fig.6.a) and the partition coefficient (fig.6.b) is represented according to the variation of the concentration of solid suspensions for samples taken from the river course (center). The affinity of metals to accumulate in suspended solids in the water depends on both the properties of heavy metals and on solid particle size and organic matter content of the water [21].

The analytic function  $C_p = f[SS]$  (fig. 6.a) is linear, with a coefficient of linearity of 0.8539 for nickel and respectively 0.7709 for lead and they have a positive slope. For the analytical function  $K_p = f[SS]$  (fig. 6.b), a correlation coefficient higher in nickel (0.8968) compared to that of lead (0.7128) is reported. Higher  $K_p$  values indicates that the metal has affinity for the solid phase, while lower values indicate that the metal tends to be found in dissolved form or ions.

#### Conclusions

In order to characterize the transport of heavy metals in aquatic ecosystems, the decisive role is played by the evaluation of the associated mass flow related to the water column. From this study and based on the literature, these loads are dependent on both the metal concentration and the water flow. Based on that, the type of correlations  $Li = f(Qi)$  are linear.

The equilibrium partitioning method of the heavy metals concentrations represents a water quality assessment in terms of their content in dissolved phase, in the particle phase and in sediments.

Since most heavy metals are characterized by low solubility in water and by their retention on solid matters, through chemisorption processes, the second tool which should be applied is the evaluation of metals transfer from

the soluble phase to suspended solids phase. Depending on the partition coefficient and on the content of suspension materials, the percentage of the material in suspension and lately in sediments varies between 50-85 %.

Good exponential correlation was observed between the metal partition coefficient and the content of water suspended solids.

The study showed that heavy metals (Pb, Ni) concentrations in aqueous phase decreased while they increased in the solid phase (as material in suspension and/or sediment) and in biota, conclusion which is useful in performing as assessment of water quality and heavy metals pollution impact on coastal and marine ecosystems.

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