

INVESTIGATION OF THE RADIOACTIVE AND HEAVY METAL POLLUTION OF THE DANUBE DELTA LACUSTRINE SEDIMENTS AND SOIL

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ABSTRACT

Results obtained for five lacustrine sediment cores and three soil samples, collected in 1996 from Danube Delta, by using INAA, ICP-MS, and TTPIXE analytical methods, are presented. The measured vertical profiles identified as possible pollutants the following elements: Al, Cu, Zn, As, Ag, Cd, In, Sn, Sb, Hg, Tl, Pb, and Bi. In the sediment cores, the determined elements, except V and Ni, show near-surface enrichment relative to the lower part (1.3–3 enrichment factor, except 5 - 7 for Cd and Hg). In some few cases, As, Cd, Cu, Cr, Mn, and Pb exceeded the minimum threshold of safety defined by the Romanian legislation. For soil samples, increased (1.5–3 times) values at surface in comparison with the 30 cm depth was also found, but values much lower compared to lacustrine sediments, indicating the riverine transport as the main source of heavy-metal near-surface contamination of the lacustrine sediments.

Keywords: "Danube Delta", "Sediment and soil", "Heavy metal pollution", "INAA", "TTPIXE", "ICP-MS"

INTRODUCTION

During recent decades, the rapid industrial development in European countries has had a side effect by the introduction of toxic metals, fertilizers, or pesticides in many ecosystems [1,2,3,4]. Released into environment, these pollutants enter the atmospheric and hydrological circulation and are finally deposited on riverbeds, in reservoirs or river deltas. In this way, the lacustrine sediments, continuously enriched by all kinds of pollutants, become a long term record for the past history of the contamination processes [5,6]. For that reason, investigation of the vertical distribution of various pollutants in sedimentary cores can furnish useful information concerning these processes. At the same time, the radioactive caesium released between 1948 and 1964 by atmospheric nuclear tests and in 1986 by Chernobyl accident can be successfully used as time marker [5,7,8].

Danube Delta represents a flat region with a surface of 5,640 km² (Fig. 1), its history beginning by the end of the last glaciation [9]. Both morphologically and historically, the Danube Delta can be divided in two regions [10]: fluvial (western part) and fluvial-marine (eastern part including the Razelm-Sinoe lacustrine complex). More than 150 lakes and swamps are spread



over the entire delta. The bottom sediments are intensively bioturbated by various invertebrates which spend their life cycle buried in the mud [11,12]. This fact contributes to the dissemination of pollutants within the sediments.

In the absence of any noticeable mixing or other processes, the presumed pollutants usually exhibit increased concentrations in the upper layers of the sediments [3,4,5,13]. Each country has issued its own regulations stating the limits of concentrations of heavy metals or other pollutants that can be considered acceptable or dangerous. In Romania, these limits have been established by the Minister of the Environmental Protection and published in the Official Monitor of Romania [14]. Since the Danube Delta sediments are derived from a large part of the European continent a comparison of the obtained data with the mean concentrations of the same elements in Upper Continental Crust [15] could be very useful in interpreting experimental data with respect to a possible pollution origin.

High precision nuclear and atomic techniques, such as Instrumental Neutron Activation Analysis (INAA), Thick Target Proton Induced X-ray Emission (TTPIXE) and Induced Coupled Plasma–Mass Spectrometry (ICP-MS), are currently used in the investigation of environmental samples, such as sediments or soils [16,17]. In the present work, these three analytical techniques were used to study the vertical distribution of major and trace elements in three sediment cores (Lake Mesteru, Lake Furtuna -eastern part and channel Sontea), as well as some soil samples collected in the south-eastern part of Danube Delta (Caraorman bar). Other two sediment cores, collected from the lakes Lung and Matita, were analysed by INAA. ^{137}Cs vertical distribution and the total ^{137}Cs inventory have been determined in the analysed cores by using γ -ray spectrometry. The recent sediment accumulation rate and age have been estimated.

The main purpose of this work was to uncover the existence of any pollution of the Danube Delta sediments and soil with the elements in question.

EXPERIMENTAL

Lake hydrology

The two lakes, *Lung and Mesteru*, are located in the western part of the fluvial delta (see Figure 1) and communicate between themselves through a small natural channel and two small lakes. Both lakes have a relatively small surface (3.6 km² and 2.9 km²) and are permanently fed by the channel Mila 35. They are characterized by soft, lacustrine sediments having a thickness up to 50 cm and a low sedimentation rate (0.18 - 0.20 g cm⁻²y⁻¹).

The lake *Furtuna*, located in western part of fluvial delta, is a relatively large lake (surface: 11.6 km²), and communicates with Sulina Branch through at least five channels (the most important being Sontea channel), which determine a higher sedimentation rate (0.6 - 0.8 g cm⁻²y⁻¹), especially in the south-western part of the lake, where the sediments are of fluvial type. The eastern part of the lake is characterized by soft, lacustrine sediments and low sedimentation rate (0.18 g cm⁻²y⁻¹).

The lake *Matita* (6.44 km²), located in the north-eastern part of the Delta (Fluvial delta), is connected to Sulina branch by the channel Lopatna and to the lake Merhei by the channel Rosca. Both, Lopatna and Rosca channels present a very meandered pattern and thus, a considerable amount of sediments do not reach the lake. This fact determines a very low sedimentation rate (0.04 g cm⁻²y⁻¹). There is also a permanent communication with the lake Merhei. According to the radiocarbon data [18] the thickness of lacustrine sediments is in the range of 35 - 50 cm.

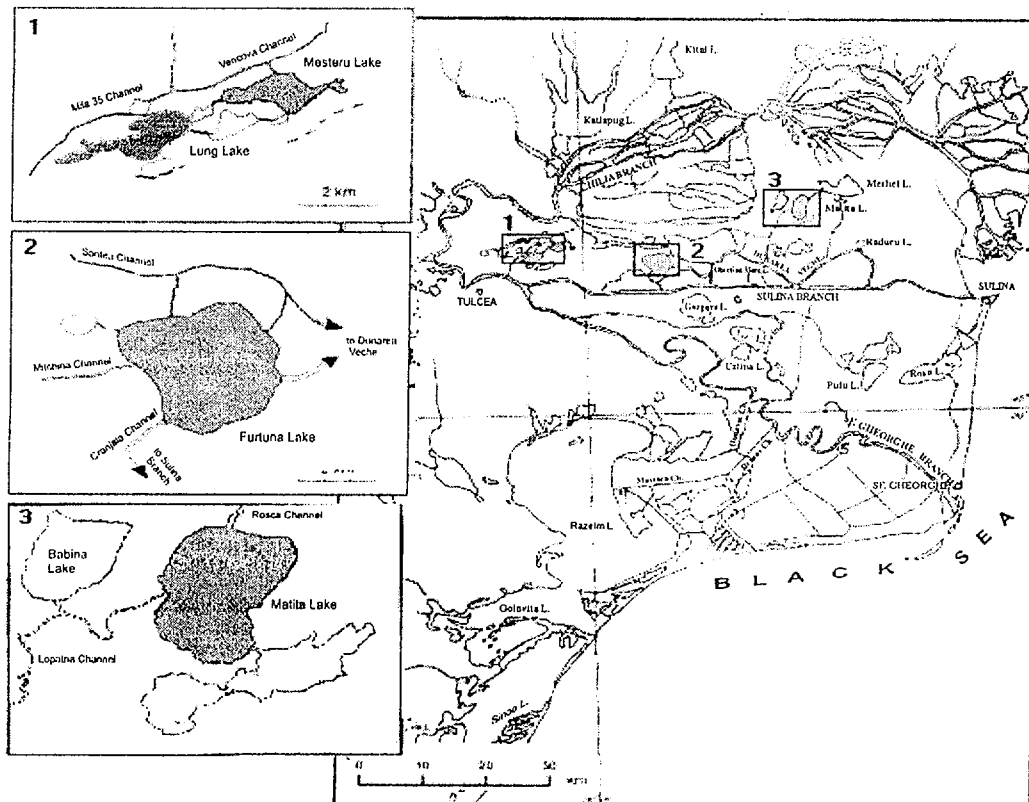


Fig. 1. Danube Delta schematic map showing the location of the investigated lakes.

SAMPLES

Sediment

The sediment cores, containing mainly recent deposits, were collected in November 1996 from the following lakes: Furtuna (western and eastern part), Mesteru, Lung and Matita, and from the channel Sontea. The cores were stored in vertical position. Prior to analysis, the cores were sectioned into pieces of 1-2 cm thick. These samples were dried at 105°C, homogenized by grinding, sieved (1.6 mm) and measured by γ -ray spectrometry. After that, for element content analysis by INAA and TTPIXE in IFIN-HH, aliquots were taken from each sample. For TTPIXE analysis, about 1 g of sample was pressed (60 ton) into pellets of 8-12 mm diameter and 1-3 mm thickness; samples of the reference sediment IAEA SL1 were prepared in the same way. For ICP-MS analysis, realized at NTNU-Trondheim, about 2 g of some selected samples were used. Dry bulk density and cumulative dry mass have been calculated for each sediment core.

Soil

In September 2001, soil samples were collected at three sites within the region of Caraorman bar. Samples were taken at the surface (5 cm thick) and at approximately 30 cm depth. The samples were dried at 105°C, ground and homogenized. The same procedure as above was used for sample preparation.

MEASUREMENTS

Radiometric

The sediment samples were measured by γ -ray spectrometry in efficiency calibrated geometry. The measurements have been performed by using a HPGe detector, having a FWHM of 1.9 keV at 1332 keV (^{60}Co) and a relative efficiency of 30%. The detector was connected to a CANBERRA S400 system through an AccuSpec A board. OS2/Genie-PC software was used for gamma spectra processing. The ^{137}Cs concentration has been calculated for each analysed sample.

INAA

The samples and standards (0.25 - 0.3 g each) were wrapped in plastic bags and irradiated for 4 hours in a wet vertical channel of the VVR-S Reactor of the Institute of Physics and Nuclear Engineering, at a thermal neutron flux of $1.2 \cdot 10^{13} \text{ n cm}^{-2}\text{s}^{-1}$. The irradiated samples were measured after a cooling time of 6 to 8 days (counting time: 1000 s) and 20 to 25 days (counting time: 5000 s), by using the same system as above [13]. The accuracy of the analyses was controlled by means of the IAEA reference materials SL1 and SL3.

TTPIXE

Pressed pellets were analyzed by TTPIXE using 3 MeV protons delivered by the 9 MV Van de Graaff tandem accelerator of NIPNE. The analyses were carried out in vacuum. A collimated beam (3 mm diameter) bombarded the target oriented at an angle of 45° with respect to the beam direction. The beam current entering the scattering chamber was maintained at 1-10 nA, and the samples were typically irradiated for a collected charge of 10 μC . The emitted X-rays were measured by a Canberra Ge(HP) detector, having an energy resolution of 180 eV/5.9 keV, and placed at an angle of 90° to the incident beam direction. For the present measurements, the X-rays passed through the Be windows of the scattering chamber (0.25 mm thick), detector (76 μm thick), and a 3 cm air gap. The signals from the detector preamplifier were processed with a Tennelec spectroscopic amplifier model TC244, enabling pile-up rejection, and then fed into a model 1520 Canberra ADC and mixer-router. Data processing and storage were performed with a Canberra S100 system, based on an IBM personal computer. The X-ray spectra [19,20] were analyzed using the code LEONE, which models the X-ray peaks with Gaussian functions and subtracts a polynomial background (1 to 3 degree). The peak areas derived from the fitting routine, corrected for X-ray attenuation and detector efficiency, were then used to determine the elemental concentrations. Quantitative analysis was based on normalization to the beam charge and measuring a sample of the standard reference material IAEA SL-1 in identical conditions.

ICP-MS

Samples of about 0.4 g were weighed into Teflon bombs and decomposed with 4 ml 14 M HNO_3 in a microwave oven. After dilution to 0.5 M HNO_3 , the samples were subjected to analysis by sector field ICP-MS using a Thermo (Finnigan) Element instrument (Bremen, Germany). The RF power was 1150 W. The sample was introduced using a CETAC ASX 500 auto sampler (Omaha, USA) with a peristaltic pump (pump speed 1 ml per min). The instrument was equipped with a concentric Meinhard nebulizer connected to a Scott spray chamber, and a quartz burner with a guard electrode. The nebulizer argon gas flow rate was adjusted daily to give a stable signal with maximum intensity for the nuclide ^{115}In .

The instrument was calibrated using 0.5 M HNO₃ solutions of multielement standards at appropriate concentrations. Internal standards were not used. After each sample, 0.1 M HNO₃ (Suprapur) was flushed through the sample introduction system to reduce memory effects. To check for possible drift in the instrument, a standard solution with known elemental concentrations was analysed for every 10 samples. In addition, blank samples (0.5 M HNO₃, Suprapur) were analysed for approximately every 10 samples. The samples were analysed in random order.

RESULTS AND DISCUSSION

¹³⁷Cs vertical distribution

The vertical distribution of ¹³⁷Cs was obtained (see Figure 2). ¹³⁷Cs profiles, excepting Furtuna-eastern part, are characterized by a single maximum and a long tail, due to bioturbation phenomena occurring in lacustrine sediments by the action of living organisms.

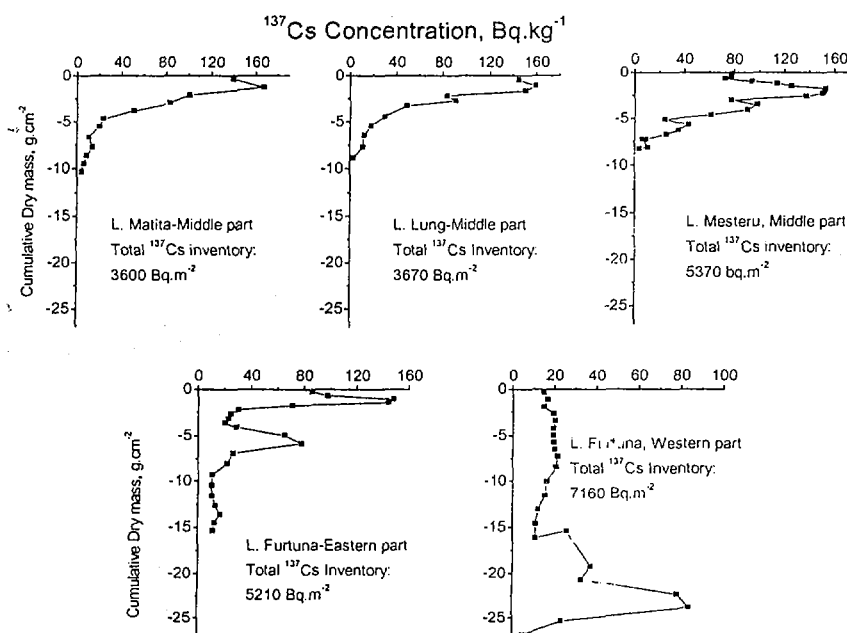


Fig. 2. ¹³⁷Cs vertical distribution in four lakes of the Danube Delta.

The sediment accumulation rates have been estimated, using the position of 1963 peak and assuming a constant rate of deposition at sampling points. Total ¹³⁷Cs inventory (Bq m⁻²) was calculated for each of the investigated sediment cores. The obtained results are presented in Table 1.

The values of the total ¹³⁷Cs inventory obtained for Matita and Lung lakes, closer to the local atmospheric fallout (≈ 3000 Bq.m⁻²), correlated with a low sedimentation rate show that the atmospheric fallout has the main contribution to these values. In the case of Mesteru and Furtuna lakes, the values of total ¹³⁷Cs inventory were 1.7 - 2.4 times higher, indicating an important contribution of the catchment-derived radiocaesium input [7,8].

Table 1. The estimated values of the total ^{137}Cs inventory (I), sedimentation rate (R, v), and sediment dry bulk density (DBD)

Lake	I Bq m ⁻²	R g cm ⁻² y ⁻¹	v cm y ⁻¹	DBD g cm ⁻³
Lung - Middle Part	3670 ± 550	0.18 ± 0.06	0.60 ± 0.20	0.30
Mesteru - Middle Part	5370 ± 800	0.20 ± 0.07	0.50 ± 0.17	0.25
Matita - Middle Part	3600 ± 540	0.04 ± 0.02	0.09 ± 0.05	0.43
Furtuna - Western Part	7160 ± 1070	0.65 ± 0.20	0.81 ± 0.24	0.80
Furtuna - Eastern Part	5210 ± 780	0.18 ± 0.06	0.42 ± 0.14	0.43

Data from different analytical techniques

The data obtained by the three analytical techniques mentioned before include totally 42 elements. The results of different analytical techniques however are not directly comparable in all cases. The concentration values from INAA and TTPIXE represent the total contents of the elements in samples and are therefore directly comparable. The elements determined by INAA were: K, Na, Sc, Cr, Fe, Co, Zn, As, Br, Rb, Sb, Cs, Ba, Ta, Hf, Th, and U. INAA is also favourable for the determination of several lanthanoides. The REE geochemistry of these elements in Danube Delta sediments had been discussed in detail in a previous paper [13]. The elements determined by TTPIXE were: K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Br, Rb, Sr, Zr, and Pb. The results obtained by the two techniques for the same element are in good agreement. Since these two techniques are based on different physical principles, the agreement between them indicates that the accuracy of the data is generally good. Also, an intercomparison between IFIN-HH (INAA) and JINR Dubna – Russia (by Epithermal Neutron Activation Analysis - ENAA) has been performed. A good correlation has been obtained between the concentration values for almost all elements determined by both techniques [21].

The ICP-MS data are based on the fraction of each element in the sample dissolved by the treatment with concentrated nitric acid. Any form of the elements bound to the surface of the soil or sediment particle, including additions by water or air pollution, will be soluble in the acid. When it comes to the fraction of an element bound in the lattice of mineral particles, however, it depends on the character of the mineral whether that fraction is soluble or not. In the case of typical lithophilic elements, contained in silicate minerals, a considerable fraction is generally insoluble in nitric acid. This means that the ICP-MS data in many cases do not represent the total content in the sample and thus, they are not directly comparable with the INAA and TTPIXE data. On the other hand, the ICP-MS data are likely to be better suited for disclosing any contribution from pollution or other processes concentrated in the surface sediment or soil, since they are less likely to reflect the part of the element contained in the natural mineral material.

The elements determined by ICP-MS were Be, Na, Mg, Al, P, S, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Ag, Cd, In, Sn, Sb, Cs, Ba, Ce, Pr, Sm, Hg, Tl, Pb, Bi, and U, 36 in all. A comparison of ICP-MS values with either INAA or PIXE, for sediment samples below 20 cm depth, indicate that the following percentages are dissolved by nitric acid: Ni, As, Br, Pb: >95%; Ca, Fe, Zn: 80-90%; Co, Cu, Mn: 70-80%; Sc, Cr, Rb: 50-60%.

Vertical distribution of metals in sediments

By using the concentration values, the vertical distribution of each element in the investigated cores was obtained and the presumed pollutants were identified. The vertical distribution of some elements concentration in the lake Mesteru is presented in Figure 3.

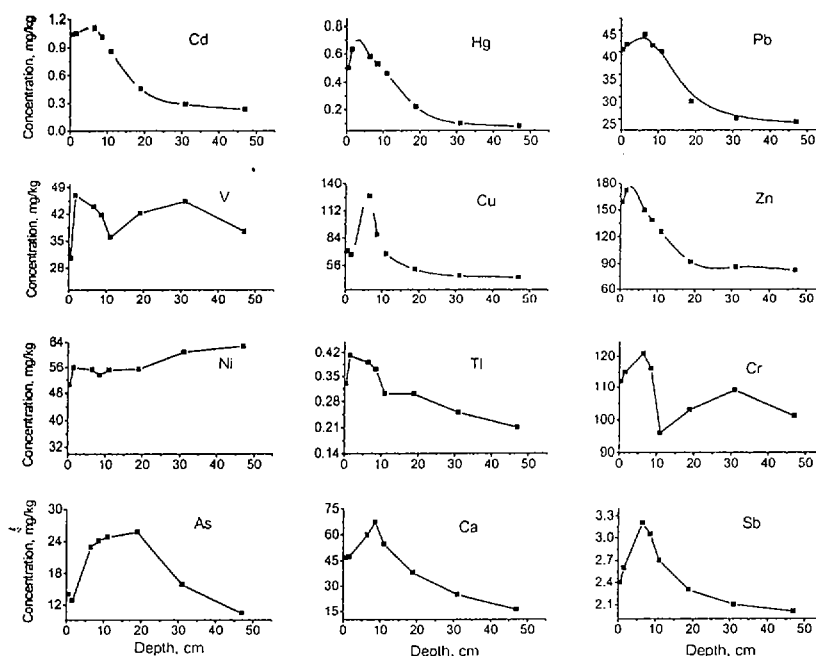


Fig. 3. Vertical profiles in lacustrine sediments from the lake Mesteru for Cd, Hg, Pb, V, Cu, Zn, Ni, Tl, and Ca, determined by ICP-MS, and for Cr, As, and Sb, determined by INAA; Ca concentration is given in g/kg

As indicated above, the ICP-MS results are probably most suitable to indicate any surface enrichment of elements caused by pollution or other factors. Results from the upper 50 cm of a sediment core from lake Mesteru evidenced the elements that have increased concentration near the sediment surface due to pollution of the Danube water. As seen in Fig. 3, some of these elements, *i.e.* As, Cu, Zn, Cd, Sb, Hg, Tl, and Pb, are enriched in the upper sediment layer. However, the maximum concentrations are evident a few cm below the sediment surface, probably indicating a significant reduction of industrial activity during the last decade in the former communist countries within the Danube river drainage area [5,6]. On the other hand, elements also generally known to be associated with pollution, such as Al, V, and Ni, show no such surface enrichment. A closer look at the data reveals that also Bi, Ag, In, and Sn are enriched near the sediment surface. The near-surface enrichment is most prominent for Cd and Hg, by about a factor of 5. All the above elements are known as air pollutants [22].

Most of the other elements show no appreciable variation in their HNO₃-soluble concentrations within the upper 50 cm of the sediment, which is to be expected for typically lithophilic elements during a time period with small variations in sedimentation rate. In addition to Al, V, and Ni, this type of distribution is evident for Na, Mg, Sc, Cr, Fe, Co, Rb, Cs, Ba, Hf, REE (La, Ce, Pr, Eu, Sm, Lu, Tb, Yb, Y), and Th.

Some elements show a variation with depth in the sediment that may be due to natural factors rather than pollution. In the case of P, S, Mn, and U, there is a maximum at about 20 cm depth which is probably related to variations in the red-ox level with depth in the sediment. The concentrations of Ca and Sr are markedly higher in the uppermost 15 cm of the sediment than at greater depth. This difference is also evident in the INAA and TTPIXE data

for the total concentrations of the same elements. The concentrations of potential pollutant elements are presented in Table 2.

Table 2. Average concentrations of potential pollutant elements, determined by INAA, TPIXE, and ICP-MS; all values are given in mg/kg, except Mn given in g/kg

Element	Mesteru L.			Sontea Ch.			Caraorman Bar		
	INAA	PIXE	ICP-MS	INAA	PIXE	ICP-MS	INAA	PIXE	ICP-MS
Be	-	-	0.91	-	-	0.74	-	-	0.11
V	-	-	41.8	-	-	25.4	-	-	6.20
Cr	108	111	61.0	101	115	44.2	61.6	43.0	8.67
Co	16.8	-	14.2	15.5	-	11.4	4.80	-	2.78
Ni	-	59.1	56.7	-	36.0	52.7	-	-	9.87
Mn	-	1.58	0.69	-	0.82	0.56	-	0.49	0.27
Cu	-	126	69.1	-	45.9	23.9	-	8.67	5.20
Zn	187	182	153	114	105	80.4	41.8	42.7	33.4
As	18.9	-	15.2	11.8	-	10.1	2.60	-	2.17
Se	-	-	1.35	-	-	0.74	-	-	0.23
Br	11.6	13.8	11.3	9.90	10.5	9.40	23.6	29.6	27.2
Ag	-	-	0.23	-	-	0.11	-	-	0.03
Cd	-	-	1.01	-	-	0.22	-	-	0.11
Sb	3.45	-	-	2.2	-	-	0.52	-	-
Tl	-	-	0.32	-	-	0.17	-	-	0.04
Hg	-	-	0.54	-	-	0.11	-	-	0.04
Pb	-	39.4	35.6	-	23.3	22.3	-	-	6.57

Vertical distribution of metals in soils

In a similar way as for the sediments, the ICP-MS results for soils from the surface layer and at 30 cm depth may indicate contribution from pollution due to atmospheric deposition or occasional flooding. However, the action of plants to transport elements from deeper layers to the soil surface by root uptake and transfer to the green parts works in the same direction. After the death of the green parts of the plant, the elements are enriched in decaying organic material at the soil surface.

Surface enrichment of some elements in the soil relative to the level at 30 cm depth was observed as follows (mean value for 3 sites):

S	8.3
Cu, Zn, Br, Ag, Cd, Sb, Ba, Hg, Pb	2.5 – 3.1
Be, P, Rb, In, Tl	2.0 – 2.5
V, Mn, As, Sn, Cs	1.5 – 2.0
Mg, Al, Ca, Cr, Fe, Co, Ni, Sr, Y, Ce	< 1.5

Among the elements most enriched in the surface layer are Zn, Ag, Cd, Sb, Hg, and Pb, which are all typical components in long-range transported pollution aerosols in the atmosphere [22]. On the other hand, Cu, Zn, Cd, and Ba are known to be appreciably enriched in top soils due to the upward transport by plants [23]. It seems still reasonable to assume that the relative surface enrichment with Ag, Sb, Hg, and Pb is due to air pollution.

However, the observed surface soil levels are low compared to areas where air pollution is a major source of these metals to the topsoil [24] and indicate that atmospheric deposition is of much less importance than riverine transport in contributing to the surface contamination of sediments in the Danube Delta.

Time evolution of the pollution of Danube Delta sediments

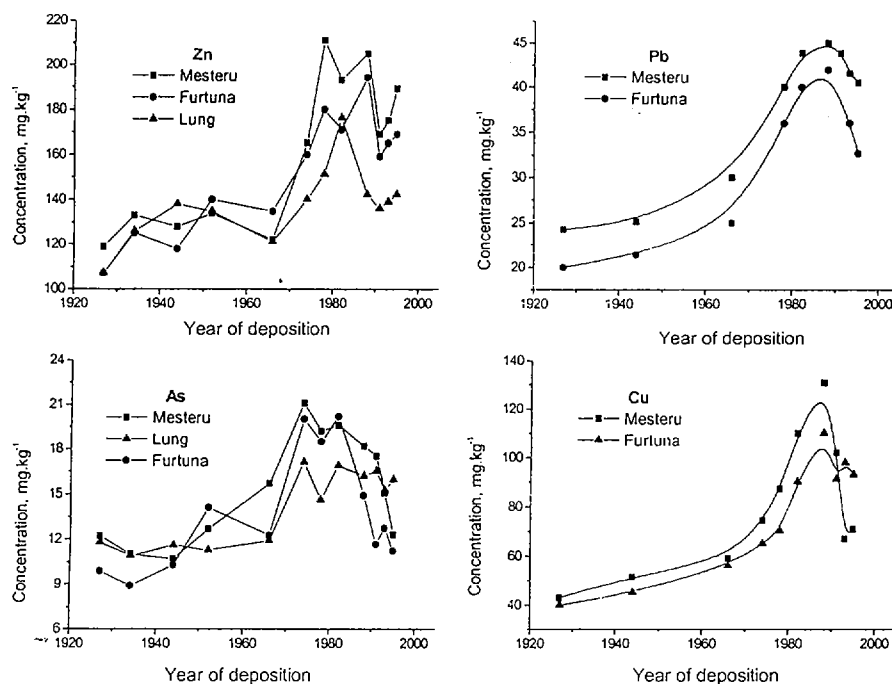


Fig. 4. Estimated evolution of the Danube Delta sediment pollution with Zn, As, Cu, and Pb in the last 70 years.

On the basis of the concentration values of some pollutant elements, correlated with the sedimentation rates, determined from ¹³⁷Cs vertical profiles, it was possible to reconstruct the time evolution of these concentrations in the last seventy years. The obtained results are presented in Figure 4 for Zn, As, Cu, and Pb.

From Figure 4, a steady increase of the element concentration can be observed, starting with the beginning of 60's until the end of 80's, followed by a slow decrease after 1990. These variations generally reflect the history of the recent sediment pollution and can be correlated with the evolution of the industrial activity in Central and Eastern European Countries.

The mean concentration values determined in the four lakes by INAA for the potential pollutant elements and their natural content (below 20 cm) are presented in Table 3.

By analysing the data given in Table 3, it can be observed that, the difference between the concentration values of the same element in the four lake sediments is not significant.

CONCLUDING REMARKS

¹³⁷Cs vertical distribution and the total ¹³⁷Cs inventory have been determined in sediment cores collected from four Danube Delta lakes - Matita, Lung, Mesteru, and Furtuna, by using gamma-ray spectrometry. The values obtained for the total ¹³⁷Cs inventory in the investigated sediment cores were 1.3 – 2.4 times larger than the local fallout, indicating an important contribution of the catchment-derived radiocaesium input.

Table 3. Mean concentration values determined by INAA of Cr, Co, Zn, As, Sb, and Br in the sediments from the lakes Mesteru, Lung, Matita, and Furtuna-eastern part.

Lake	Period	Cr mg kg ⁻¹	Co mg kg ⁻¹	Zn mg kg ⁻¹	As mg kg ⁻¹	Sb mg kg ⁻¹	Br mg kg ⁻¹
Mesteru	1966-1996	108±16.2	16.8±1.6	187±18.5	18.9±2.8	3.45±0.73	11.6±2.41
	Before 1950	94.0±14.1	17.1±1.8	126.4±9.8	10.5±2.1	2.02±0.40	8.74±1.22
Lung	1966-1990	99.0±8.6	15.7±1.7	149±16.4	15.5±2.3	2.69±0.54	9.70±2.78
	Before 1950	91.3±7.4	15.6±1.8	108±11.5	11.4±1.68	2.29±0.45	7.49±0.52
Furtuna	1966-1996	103±7.3	14.9±1.5	156±11.5	15.7±1.8	2.74±0.8	12.9±3.01
	Before 1950	85.5±6.0	13.6±1.5	112±8.9	12.2±2.0	1.90±0.38	8.97±2.10
Matita	1966-1990	89.4±8.93	14.5±1.7	93.0±11.2	18.8±2.07	3.65±0.8	13.8±2.2
	Before 1950	45.0±4.64	10.3±1.2	49.1±3.24	8.75±1.49	1.93±0.31	9.49±1.52

The concentrations of 42 elements in all were determined by using three analytical methods: INAA, TPIXE, and ICP-MS. By taking into account their vertical distribution, the following conclusion can be drawn:

- The elements identified as potential pollutants are: Cu, Zn, As, Ag, Cd, In, Sn, Sb, Hg, Tl, Pb, and Bi. The concentrations of these elements show a near-surface enrichment relative to the lower part of the sediment core.

- The enrichment factor was generally 1.3 – 3 for most of them, and 5 – 7 in the case of Cd and Hg. V and Ni do not show a surface enrichment.

- In some cases, the concentrations of As, Cd, Cu, Cr, Mn, and Pb exceeded “minimum thresholds of safety”, as defined by the Romanian legislation.

- The vertical distribution of these elements in the investigated cores, correlated with ¹³⁷Cs vertical distribution, generally reflected the pollution history of recent sediments in Danube Delta, showing a steady increase until the end of the 1980s, followed by a slow decrease after 1990.

- The vertical profiles of the remaining elements were characterized by a relatively uniform distribution along the cores.

- The concentrations of As, Sb, Hg, and Pb in three soil samples, collected from the eastern part of the Danube Delta, showed increased values (1.5 – 3 times higher) at surface as compared to 30 cm depth, but much lower than those obtained in the lacustrine sediments, indicating that the heavy metal, near-surface contamination of the lacustrine sediments was mainly by riverine transport.

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