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A 600 years sediment record of heavy metal pollution history in the Danube Delta

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Abstract

Heavy metal pollution in the Danube Delta (in sediments, water and living organisms) has recently received increasing attention due to its impact on ecosystems health and water quality. However, long term records of heavy metal contamination are not available to date. In this study radiometric dating and geochemical analyses for major elements (Al, Fe, Ca and S) and metals (Cu, Zn, Pb, Ni, Cr and Cd) were performed on the top 4 m of a 9-m sediment core retrieved from the alluvial plain of Sulina distributary channel aiming to reconstruct the

heavy metal geological background and contamination history and discuss the possible origins (natural vs. anthropogenic) of metals and the main factors driving their temporal variation. Chronological analysis revealed that the top 4 m of the core span the last ~600 years. Three distinct sediment units (U1: 400-200, U2: 200-140, U3: 140-15) were identified based on the downcore element concentration variation. The lower unit (400-200 cm, ~1450-1700 CE) shows an upward increase of Cu, Zn, Pb, Ni, Cr and Cd metal contents, which are strongly correlated with Al. Enrichment factor (EF) analysis indicates that metals detected in this unit are derived primarily from natural sources. In contrast, metals show elevated EF values within the middle (200-140 cm, ~1700-1770 CE), and upper unit (140-15 cm, ~1770 CE to present). The highest degrees of enrichment of Cu, Zn and Cd occur in the peat layer of the middle unit (U2) which displays higher organic carbon and sulfur contents, indicating that diagenetic enrichment of detected metals occurs under reducing condition. Overall, sediment contamination is moderate while the level increases with time. This study provides new insights into the metal contamination history of deltaic environments and yields baseline values for heavy metal contents in pristine sediments deposited prior to the onset of anthropogenic impact.

Keywords: heavy metals; pollution history; particle size effect; diagenesis; Danube Delta

1 Introduction

Deltas are located at the sea-land interface and constitute environments of crucial importance both from a natural and a societal standpoint. Deltas typically sustain high population

densities (i.e., they host close to half billion people, Syvitsky and Saito, 2007) living in large agricultural and urban centres (Woodroffe et al., 2006). Furthermore, they are also important for commercial navigation and water supply and provide a variety of ecosystem services such as biodiversity hosting, carbon sequestration and nitrate removal (Rovai et al., 2018; Twilley et al., 2018). The latter functions are critical and have led to increased protection of deltaic environments (Harris et al., 2016).

However, an important number of human activities occurring both in river basins and locally within the deltas generate and discharge pollutants into deltaic environments through fluvial and aeolian pathways. Among these contaminants some of the most prominent in terms of their prevalence and effects are the elements commonly known and referred to in the literature as heavy metals (Gustin et al., 2021), which have long been studied due to their potential toxicity, non-degradability and bio-magnification. Globally, deltaic sediments show heavy metal pollution of varying degrees (e.g., Presley et al., 1980; Santschi et al., 2001; Zhang et al., 2009; Chen et al., 2010; Nguyen et al., 2016; Begy et al., 2018), depending on the extent of specific human pressure in the drainage basin and the characteristics of sedimentary environments. Metals in sediments may be remobilized due to changing environmental conditions or by human intervention (e.g., dredging, water course channeling, channel island and bank management), thus generating secondary pollution which affects water quality and aquatic organisms (Burdige, 1993; Williams et al., 1994). To date, numerous studies have been carried out to assess the heavy metal contamination of sediments, their sources, speciation and potential health risks (Chen et al., 2010; Nguyen et al., 2016; Zhang et al., 2009).

The Danube Delta ranks among the largest deltas in the world and second largest in Europe. It stands out as the widest remaining natural wetland in Europe and home to the world's most sizeable reed bed expanse. Overall, Danube Delta has the third largest biodiversity in the world (over 5500 flora and fauna species), surpassed only by the Great Barrier Reef in Australia and the Galapagos archipelago in Ecuador (Claudino-Sales, 2019). The deltaic area of the Danube is regarded as one of the best-preserved natural areas and has been designated in 1998 as Biosphere Reserve under UNESCO's MAB program (Danube Delta Biosphere Reserve – DDBR) and Wetland of International Importance under the RAMSAR Convention in 1991. DDBR covers a total 732,220 hectares of which the core area with integral reserve status amounts to nearly 68,600 hectares.

Despite the environmental significance and current conservation status of Danube Delta, deltaic ecosystems are affected by upstream conditions, as the Romanian Danube is the end carrier of all wastewater discharges from upstream countries to the Black Sea. Significant inputs of pollutants reaching the delta originate in diffuse agricultural sources (due to chemical fertilizers and pesticide usage), metal mining activities and the improper or absent wastewater treatment in the drainage basin of the Danube which overlies a large part of Central and Eastern Europe (Despina et al., 2020).

The occurrence of heavy metals in lacustrine and river channel sediments of Danube Delta has been well documented in the literature (e.g., Dinescu et al., 2004; Gati et al., 2016; Begy et al., 2018; Irina et al., 2018; Tiron Dutu et al., 2019), albeit the majority of these studies have focused exclusively on surface sediments (e.g., Vignati et al., 2013; Irina et al., 2018). A small number of studies have reported on heavy metal pollution history based on short core

(<80 cm) analyses which cover the last ~120 years (Dinescu et al., 2004; Begy et al., 2018).

However, considering the lengthy history of agricultural and metal mining activities in the drainage basin of the Danube (Bird et al., 2010; Giosan et al., 2012), a long-term view on metal contamination beyond recent decades is required. To date, lacustrine sediment records from the Danube Delta have not produced long sequences that allow for the study of heavy metal contamination history over a multi-centennial time scale. Therefore, we have opted to test the potential of a wetland located in an alluvial plain as a metal contamination record. In this study we report the first multi-centennial sediment record of heavy metal pollution (i.e., the last ~600 years) from the Danube Delta and discuss the natural and anthropogenic origins of these elements of environmental concern and the driving mechanisms behind their temporal variations.

2 Study area and methodology

2.1 Study area

The Danube is the second longest river in Europe, stretching over 2860 km in length, and crossing or bordering the territories of ten Central and Eastern European countries (Germany, Austria, Slovakia, Hungary, Croatia, Serbia, Romania, Bulgaria, Republic of Moldova and Ukraine) before reaching the Black Sea. Its drainage basin covers a total area of 817,000 km² and extends into the territories of 19 countries, hosting a population of more than 80 mil. inhabitants. Throughout the 20th century more than 80% of the length of the Danube has been regulated with over 700 dams and weirs built along its main tributaries, the largest and most impactful of which is the Iron Gate Dam system consisting of two sizeable dams jointly

operated by Romania and Serbia since the early 1970s (ICPDR, 2005).

As it discharges into the Black Sea the Danube builds a prominent eastward prograding delta of ca. 4800 km² which is regarded as an archetypal lobated fluvial dominated delta (Galloway, 1975). According to earlier studies, the Holocene Danube Delta started to build out of a Black Sea embayment 5200 yr ago (Giosan et al., 2006). However, more recent research on the deltaic evolution timeline suggests that its inception dates back to more than 1000 years before the relative stabilization of sea level and of the initial spit/barrier formation, which are estimated at 6.7/6.5 - 5.8 ka BP (Vespreanu-Stroe et al., 2017).

Classically, the Danube Delta was divided into two major units separated by the Letea-Caraorman sand spit (Fig. 1):

1) East of the sand spit, the downstream part consists of a prograding fluvio-marine delta with a typical multi-lobate architecture built by the three major distributary channels: Chilia, Sulina and Sf. Gheorghe (also known as St. George in the literature) from north to south, respectively. This unit of the Delta was investigated to a larger extent during the past half century and recent studies have shown the role of human-induced increasing sediment transport rates in the acceleration of lobe progradation during the last centuries (Giosan et al., 2012).

2) West of the sand spit the fluvio-lacustrine part of the delta or the blocked delta (Panin, 2003) has evolved as a large floodplain occupied by shallow lakes and swamps separated by second-order distributary channels and associated natural levees. This unit remains less documented. Therefore, its evolution is understood to a lesser extent and its chronology is poorly constrained. While some studies focusing on the fluvio-lacustrine part of the delta

have attempted to showcase its recent evolution (Panin and Overmars, 2012; Carozza et al., 2013; Vespremeanu-Stroe et al., 2017), the heavy metal contents and potential contamination of deltaic sediments have not been investigated to date.

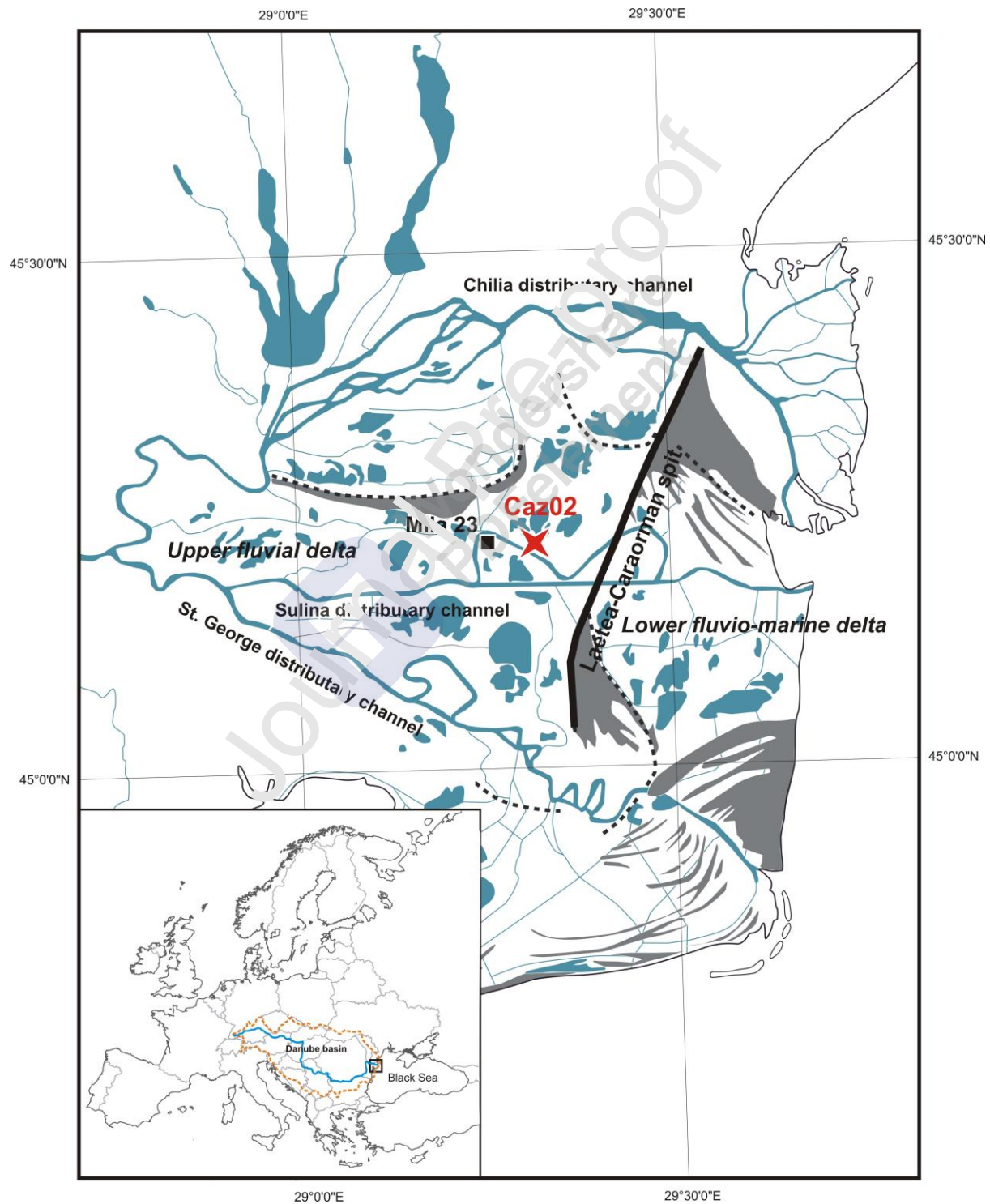


Figure 1 Major geomorphological units of Danube Delta and location of coring site Caz02.

2.2 Sediment core sampling

A 9 m-long core (Caz02) was extracted in 2017 using a Cobra TT vibrate corer from the central part of the fluvio-lacustrine (western) part of Danube Delta. The coring site is located 11 km upstream of the main coastal spit separating the fluvial unit from the marine unit of the delta, close to Mila 23 village (Fig. 1). In this area the central branch of the Danube (i.e., Sulina branch) formed a set of meanders that were cut-off mainly for navigation purposes, known as the “big M” or Mila 23 double meander structure. The core was retrieved from a backswamp in the floodplain of Sulina distributary channel.

The first meter of the core was affected by compaction due to the sampling process using a vibrate corer. Decompression was operated to obtain an accurate age-depth model and the sedimentation rate for the top section.

2.3 Dating and age-depth modelling

Radiocarbon ^{14}C dating was performed on 6 samples from the Caz02 sediment core at Poznan Radiocarbon Lab. (Table 1). Radiocarbon dates were modelled using R package CLAM (Blaauw, 2010) and InterCal13 curve.

Table 1 Summary of ^{14}C dating on core Caz02

Sample code	Depth (cm)	Dating material	Measured age (aBP)	Calibrated age (2 σ range, cal. aBP)	Lab code
Caz-02 150-151	150	Organic sediment	210 \pm 30	150-309	Poz-73386
Caz-02 450-452	450	Organic	570 \pm 35	525-648	Poz-73387

Caz-02 552	552	sediment Organic sediment	800 ± 30	676-765	Poz-73388
Caz-02 691	691	Plant remains	2305 ± 30	2185-2357	Poz-76454
Caz-02 784	784	Charcoal	4080 ± 35	4441-4808	Poz-76455
Caz-02 863-864	863	Organic sediment	6010 ± 35	6751-6944	Poz-73389

In order to constrain the recent sediment chronology (i.e., the last ~100 years), we determined ^{210}Pb and ^{137}Cs activity (Appleby and Oldfield, 1978; Appleby, 2001). Sediment samples were sealed in holders for 3 weeks and then counted using an HPGe γ spectrometer (GWL-120-15-XLB-AWT) (Appleby et al., 1988). Total ^{210}Pb and ^{214}Pb were quantified from the gamma emissions at 46.5 keV and 351.9 keV, respectively. ^{214}Pb is used as supported ^{210}Pb . The difference between total ^{210}Pb and supported ^{210}Pb is designated as excess ^{210}Pb . ^{137}Cs was determined from the gamma emissions at 661 keV (Appleby et al., 1988).

2.4 Geochemical analysis, loss on ignition and particle size

Sample aliquots allotted for geochemical analysis were dried at a low temperature of 40°C and ground into powder. Total digestion of samples was carried out for the analysis of major elements Al, Fe and Ca, metals Cu, Zn, Pb, Ni, Cr and Cd, and sulfur (S) concentrations using a mixture of concentrated HF-HNO₃-HClO₄ acids following a Chinese standard for sediment analysis (MLRC, 2016). A similar procedure of sediment digestion has been described in Zhang et al. (2009). Concentrations of Al, Fe, Ca and S were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Perkin Elmer OPTIMA 8300), while metals concentrations were measured using an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Fisher X Series II). A sample of China National Reference

Material GSD-9 was analysed along with the samples for quality control, with reported values within 10% for S and 5% for the remainder of the reference value.

Organic matter (OM) and carbonate (C) contents were estimated using loss on ignition (LOI) according to the standard protocol using a Nabertherm L15/11 furnace (Heiri et al., 2001).

Particle size distribution (PSD) was determined using laser diffraction particle size analyser Horiba LA950-V2 following the treatment protocol suggested by Fisher et al. (2017).

3 Results

3.1 Core description

The Caz02 core comprises a bottom coarser-grained section (900-380 cm) and a top finer-grained unit (380-0 cm) which reflect the traits of the channel and floodplain facies, respectively (Fig. 2). For the purpose of this study, we analysed the top 4 m of core Caz02.

The lithological composition of the top section of the core is dominated by silts (mean grain size $\sim 10 \mu\text{m}$) with interbedded fine sands. Silty sedimentation is interrupted between 1.70 to 1.44 m by peat accumulation, with organic matter via loss on ignition (LOI) values as high as $\sim 8\%$. Conversely, the carbonate content is minimal in the peat layer (Fig. 2).

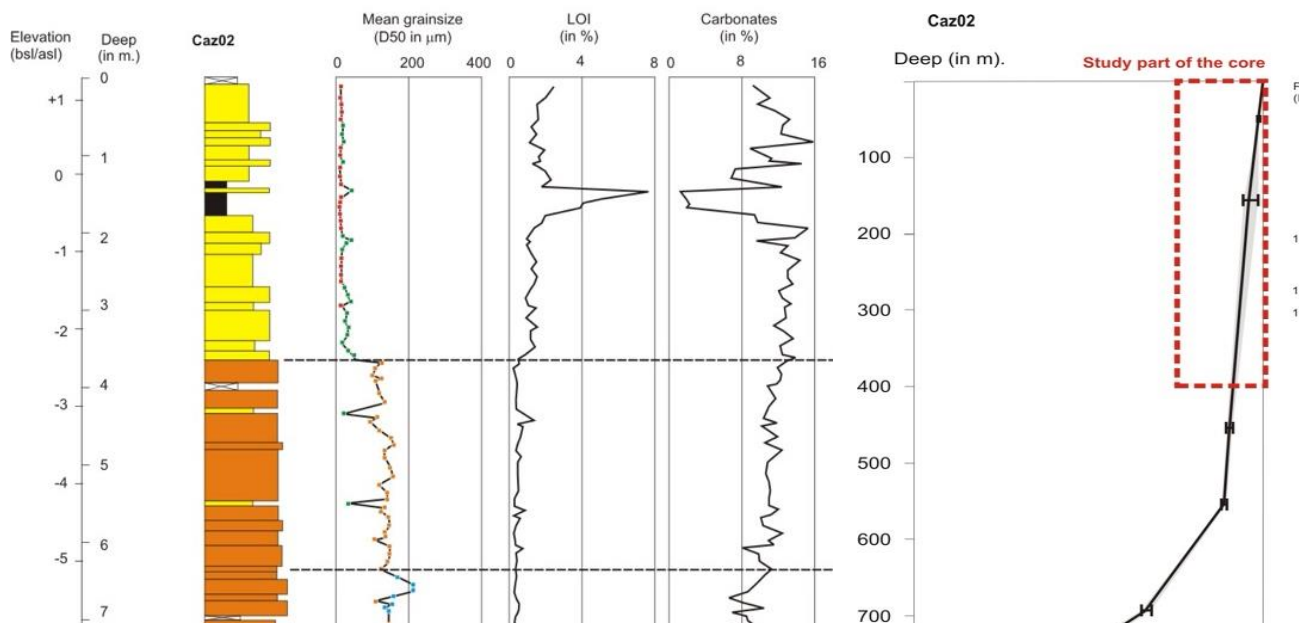


Figure 2 Lithology of core Caz02 (left) and downcore variations of mean grain size, organic matter and carbonate content via loss on ignition (LOI). Also shown is the core chronology (right) with the red square illustrating the 4 m-long core section analysed in this paper.

3.2 Chronology

The first meter of the core showed compaction due to the extraction process which was performed using a vibrato corer. Decompression was applied to reconstitute the original length of the sedimentary record, assuming linear stretching according to the homogeneity of core granulometry and water content. The ^{137}Cs signal was determined from the top of the core to a depth of 100 cm. Only sediments above 40 cm (i.e., unadjusted depth, corresponding to 34 cm after compaction correction applied to the Caz02 core) show detected ^{137}Cs activity, while the level of ^{137}Cs activity in sediments below 40 cm is under the lower limit of detection (LLD, 1.8 Bq/kg). In the measured time frame the ^{137}Cs activity showed a single peak (Fig. 3). The ^{137}Cs signal of the Chernobyl nuclear event in 1986 is typically recorded in the Danube Delta by much higher values compared to the maximum value determined in our core (e.g., Cremer et al., 2004; Begy, 2018). Therefore, we assume that the ^{137}Cs peak detected in the Caz02 core corresponds to the deposited 1960s nuclear bomb-derived ^{137}Cs fallout, which amounts to ca. 5-7 kBq/m² for sites at medium latitudes with continental climate (Ritchie and McHenry, 1990). Consequently, we suggest that the 0-34 cm section (i.e., depth range

corrected for compaction) has deposited since the early 1950s. Based on this assumption we infer a mean sedimentation rate of 0.48 cm/yr for the top 34 cm, which is similar to values reported for lakes in the Danube Delta (Cremer et al., 2004), as well as for lacustrine sediment depositions from other areas of Romania (e.g., 0.25 cm/yr for the top 11.5 cm at Bolătău lake; Mîndrescu et al., 2016).

The ^{210}Pb profile is irregular, which prevents the use of this radionuclide for deriving the sediment chronology. However, the undetectable excess ^{210}Pb below 40 cm could suggest that the layer below 40 cm may be older than ~100 years (Appelby, 2001).

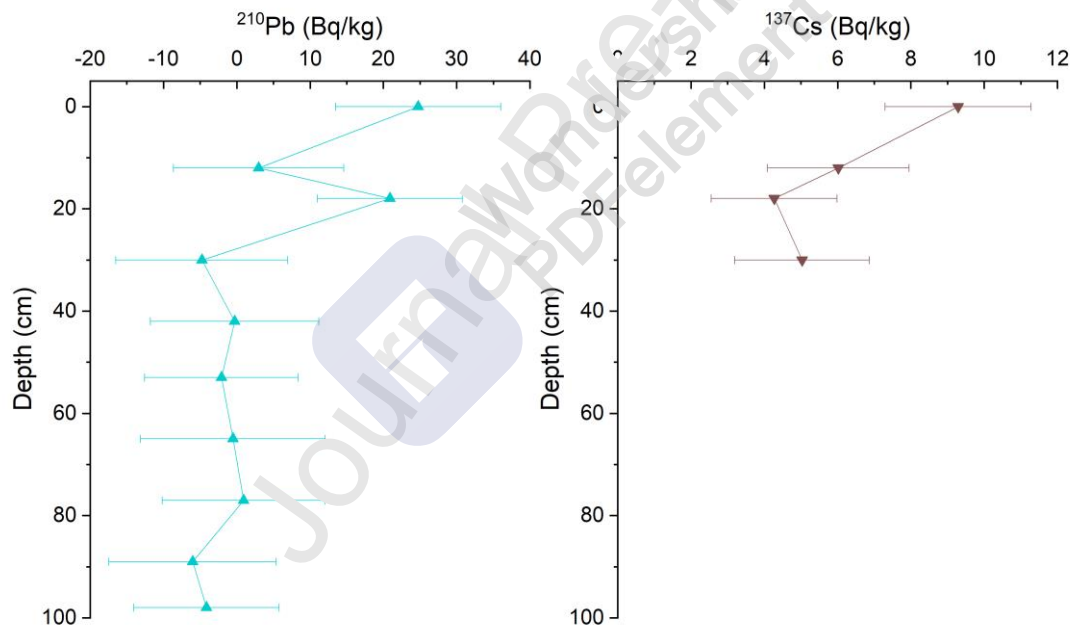


Figure 3 Distributions of ^{210}Pb and ^{137}Cs in Caz02 sediment record.

By using combined ^{137}Cs and ^{14}C dating we derived the age-depth model shown in Fig. 4. The ^{14}C dating yielded the ages 178 cal. BP at 150 cm and 575 cal. BP at 450 cm. Based on these ^{14}C dates we calculated the sedimentation rate for the entire sediment record which

showed a significant decline throughout the last ~600 years from 0.73 cm/yr, to 0.48 cm/yr. The diminishing sedimentation rates documented during the past half century could account for the absence of the 1986 ^{137}Cs peak in the sediment record, and are likely related to i) the low flood regime during the last 40 years (Tiron Jugaru, 2009), (ii) the construction of the Iron Gate Dams which retain a significant share of the sediment load, thus leading to a critical decrease in the amount of sediment delivered to the Danube Delta by approx. 50% (i.e., ~67 mil. t/yr to 30–40 mil. t/yr) (Teodoru and Wehrli, 2005, Panin et al., 2016; Tiron Jugaru, 2009), and (iii) the improvement of the embankment at the site close to Mila 23.

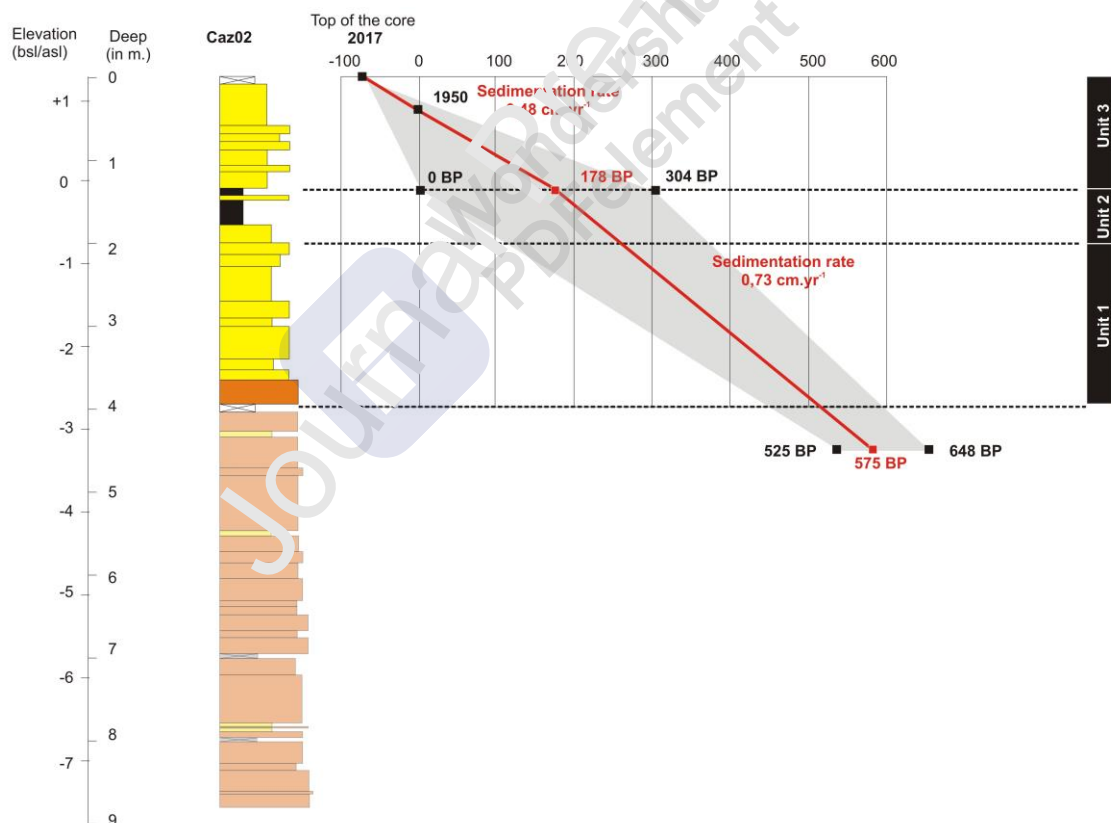


Figure 4 Age-depth curve derived based on combined ^{137}Cs and ^{14}C dating.

3.3 Geochemical analysis, loss on ignition and particle size

Based on the variations of Al, Fe and S, the core was divided into three distinct sections: the lower unit (U1, 400-200 cm), the middle unit (U2, 200-140 cm) and the upper unit (U3, 140-0 cm). In U1, Al and Fe show an upward trend ensued by a decline near the boundary between U1 and U2. In U2 and U3, Al and Fe exhibit a slight increasing trend with minor fluctuations. S shows two elevated values in the 375-300 cm (U1) and 220-140 cm (U2) intervals which are much higher compared to those of U3. Whereas the Mn/Fe ratio is relatively stable in U1, it exhibits a significant drop in the upper part of U2 followed by an increase toward the top of the core. Heavy metals generally follow the trends of Al and Fe; however, Cu, Zn and Cd show considerably higher values around 150 cm depth in U2, coinciding with S peaks and with the lowest Mn/Fe ratios (Fig. 5).

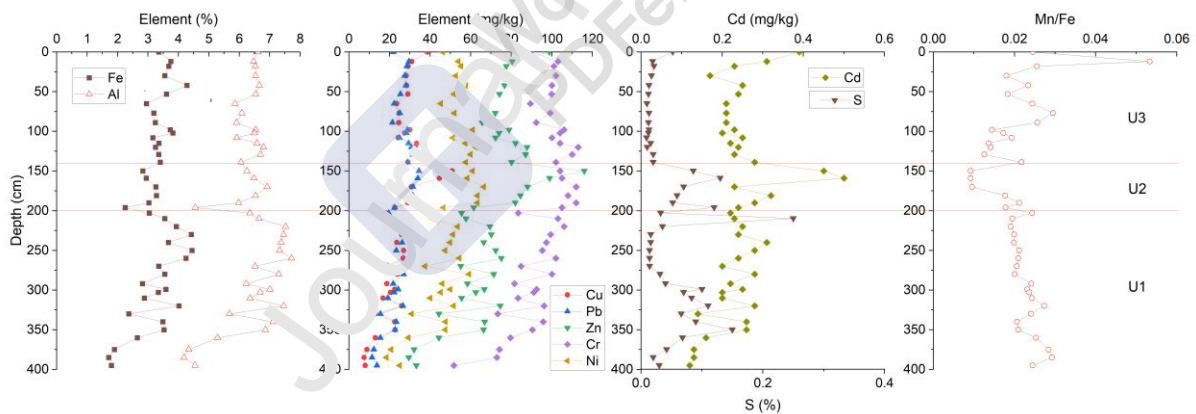


Figure 5 Distributions of Al, Fe, S, Mn/Fe ratios and heavy metals.

The abundance of heavy metals in the three sediment units is summarized in Table 2 which shows that the highest values for Cu, Zn, Pb, Cr, Ni and Cd are reached in Unit 2 while Fe shows the highest values in Unit 3 and Ca in Unit 1. The metal contents yielded by this study are comparable to the values reported by previous studies in this area for lakes, soils and

channel bedload (Secieru and Secieru, 2002; Dinescu et al., 2004; Tiron Dutu, 2019).

Table 2 Summary of heavy metal contents in core Caz02 and comparison with results reported by other studies in the Danube Delta and other deltas (unit in mg/kg, with the exception of Fe and Ca which are shown as g/kg)

	Cu	Zn	Pb	Cr	Ni	Cd	Fe	Ca	Reference
Unit 3 (140-0 cm)	28.7±3.5	76.8±6.4	27.4±2.9	101.7±5.9	54.6±5.2	0.23±0.03	35±3	49±11	This study
Unit 2 (200-140 cm)	34.8±10.7	88.5±18.2	31.0±4.3	107.7±3.6	59.8±7.0	0.34±0.11	29±4	30±17	
Unit 1 (400-200 cm)	19.4±6.2	58.5±14.2	21.3±5.2	88.3±13.1	42.2±11.4	0.22±0.06	33±8	66±6	
Lake Mesteru	49-74	109-134	26-40	94-124	59-76		40-46	14-36	Dinescu et al., 2004
Lake Furtuna	69	107-118	21	81-90	50		34-40	98	
Sontea Channel	31-46	85-125	19.0	86-142	27-35		34-41	82-88	
St. George Branch	21.8±20.7	58±39.3	10.9±9.6	56.2±27.2	31±16.9	0.28±0.22	29±10	46±19	Tiron Dutu et al., 2019
Northwest Black									
Sea shelf	32.2	64.6	15.0	61.7	66.4	0.75	26	124	Secieru and Secieru, 2004
Yangtze River delta	30.7±9.7	94.3±23.9	27.3±5.6	71.9±19.7	31.8±7.2	0.261±0.125	33.4±6.3		Zhang et al., 2009

4 Discussion

4.1 Influence of particle size, organic carbon and iron oxide on distribution of metal elements

Heavy metals in sediments can be influenced by particle size, iron oxides, organic carbon and sulfides (Williams et al., 1994). In general, fine-grained sediments have higher contents of clay minerals and iron oxides, which are good carriers for heavy metals (Rae, 1997). Al can be used as a proxy for clay minerals and Fe for iron oxides (Zhang et al., 2009), which is supported in this case by the overall positive correlations between heavy metals and Al and Fe (Table 3). The heavy metals vs. Al scatter plot reveals that samples in U1 show significantly stronger correlations with Al, thus suggesting a stronger particle size effect on

heavy metals in U1 (Fig. 5; Table 4). In contrast, while heavy metals in U2 and U3 are less influenced by particle size (i.e., lower correlations), they can also depend on the organic carbon and sulfide contents. Organic carbon can bind metals in surface geochemical processes (Rae, 1997), whereas sulfur can accumulate in sediments under reducing conditions (Bernier, 1982). U2 is a peat-containing unit with reducing conditions, as supported by the increased S content and lower Mn/Fe ratios (Fig. 4). Manganese is more easily reduced under reducing conditions compared to iron, therefore a depletion of Mn relative to Fe occurs under anoxic conditions (Burdige, 1993). The Cu, Zn and Cd peaks in this layer may reflect the binding of heavy metals with organic carbon and sulfide (Calvert and Pedersen, 1993; Nijenhuis et al., 1999). Therefore, the enrichment of metals in the deltaic sediment in the U2 unit (ca. 1700-1770 CE) is not ascribed solely to the increased anthropogenic input, but also to the influence of early diagenesis. As such, understanding the processes of sediment delivery and deposition, as well as sediment sources and the human activities which can generate an influx of metals-rich sediment could provide a robust interpretation of heavy metal contamination history in Danube Delta based on sediment records.

Table 3 Pearson correlation coefficients between heavy metals and Al, Fe, S and Ca for the entire core

	Al	Fe	S	Ca
Cu	0.47	0.45	-0.02	-0.69
Pb	0.60	0.57	-0.08	-0.58
Zn	0.55	0.51	-0.03	-0.63

Cr	0.56	0.59	0.02	-0.43
Ni	0.64	0.62	-0.09	-0.48
Cd	0.43	0.33	0.25	-0.47

The bold type indicates values that are statistically significant at $p < 0.01$.

Table 4 Pearson correlation coefficients between heavy metals and Al, Fe, S and Ca for the lower part of the core (400-200 cm)

	Al	Fe	S	Ca
Cu	0.98	0.98	0.06	0.58
Pb	0.96	0.91	0.01	0.55
Zn	0.99	0.95	0.09	0.57
Cr	0.88	0.78	0.22	0.64
Ni	0.96	0.69	0.06	0.53
Cd	0.91	0.87	0.12	0.57

The bold type indicates values that are statistically significant at $p < 0.01$.

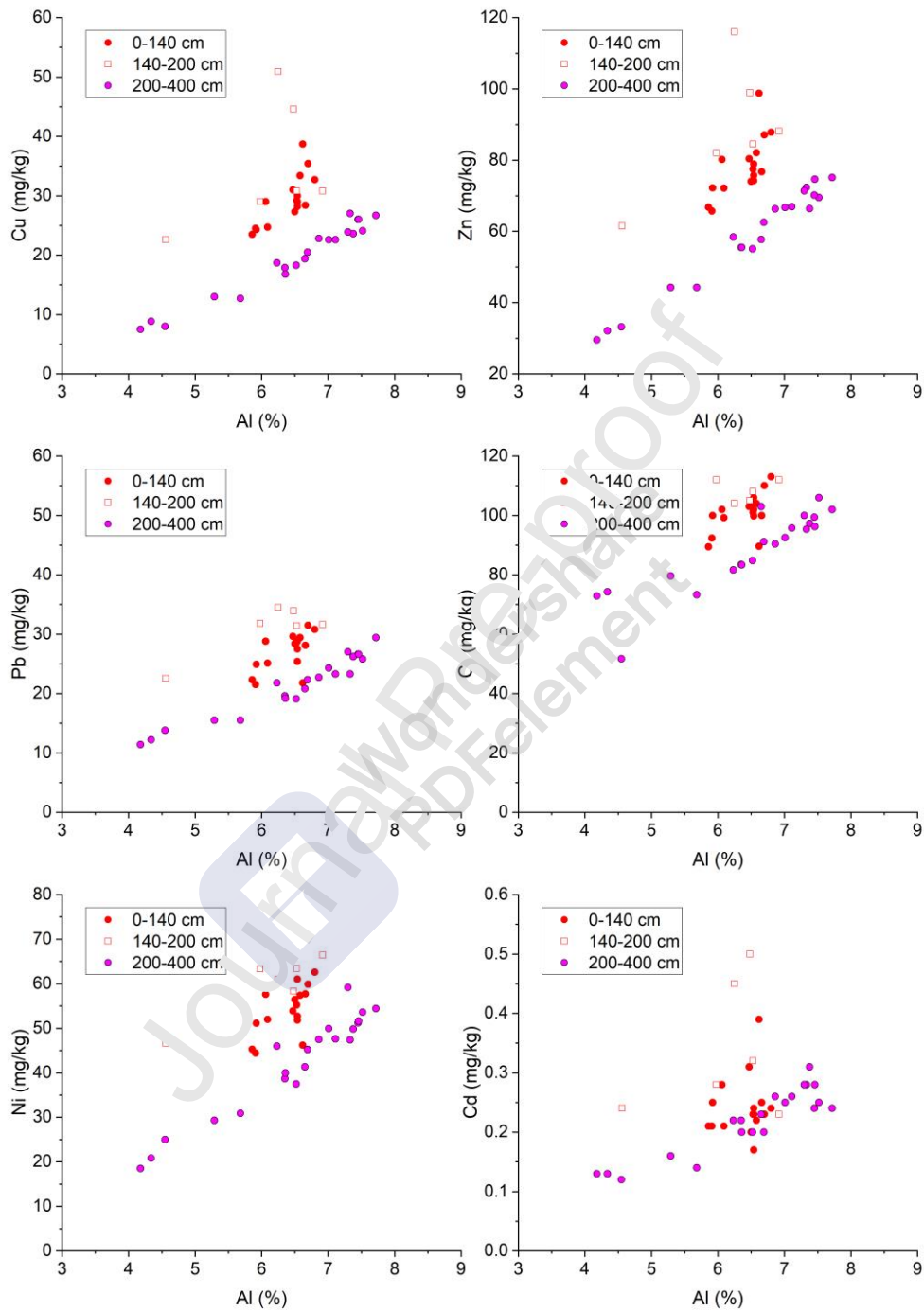


Figure 6 Scatter plot of heavy metals (Cu, Zn, Pb, Cr, Ni and Cd) vs. Al.

4.2 Enrichment factor and temporal/downcore variation

The enrichment factor (EF) is typically used to differentiate between the natural and anthropogenic origins of heavy metals in sediments, with a value >1.5 indicating anthropogenic inputs (Zhang et al., 2009). EF is commonly defined as the observed metal to aluminum (Al) ratio in the sample divided by the background metal/Al ratio. We use upper crust abundance as background values, i.e., 8.04% for Al, 0.05 mg/kg for Cd, 25.0 mg/kg for Cu, 20.0 mg/kg for Ni, 20.0 mg/kg for Pb, and 71.0 mg/kg for Zn, respectively (Taylor and McLennan, 1995) while for Cr we use the revised value of 73 mg/kg (Hu and Gao, 2008).

According to EF results shown in Fig. 7, we determined that, with the exception of Cd, heavy metals in U1 typically have values below 1.5, thus pointing to their natural origins. However, EF values are elevated in U2 and U3, especially for Cr, Ni and Cd, which are higher than the 1.5 threshold value. Moreover, EF values for Cu, Zn and Pb range above 1.5 at depths where S contents are higher.

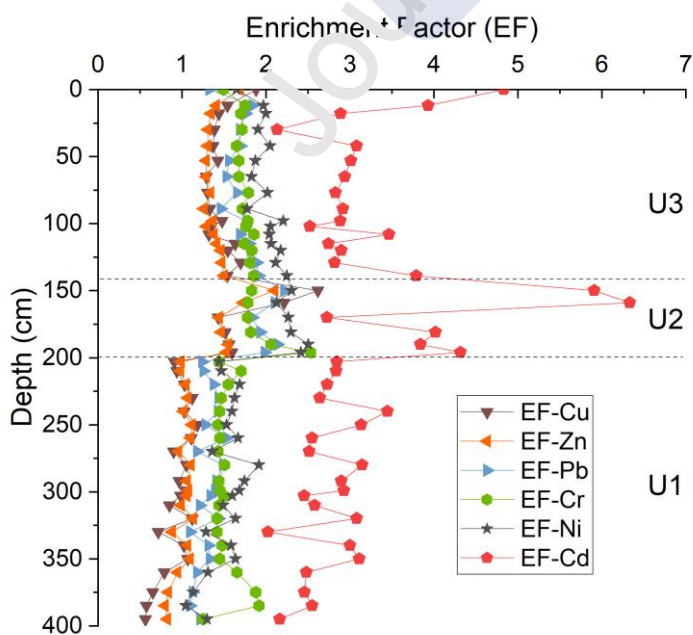


Figure 7 Downcore variation of enrichment factor (EF) of heavy metals.

4.3 Link to human activity in the catchment

The EF change can be explained by two possibilities. One relies on the changes in terms of the sediment source around 200 cm depth, whereas the other takes into account the increasingly intensive human activities of the recent period. The 200 cm depth corresponds to an age of ~250 cal. BP according to ^{14}C dating, indicating that prior to ~1700 CE sediments are relatively pristine without noticeable anthropogenic inputs. Therefore, these can be regarded as baseline values and could be used for pollution assessment in the study area.

With the exception of the peat layer at 170-144 cm depth, Units 2 and 1 have similar EF values which are overall higher compared to those of Unit 3, suggesting increased anthropogenic activities in recent time (~1700 CE to present). However, since the EF values are generally below 2, the pollution degree appears moderate (Zhang et al., 2009). The Danube and its tributaries receive contaminant inputs from municipal, industrial and agricultural sources which can generate toxic elements through untreated water discharge and use of agrochemical substances (Simionov et al., 2021). These results are consistent with previous studies which show that sediment quality on the Danube is relatively good, despite the fact that significant heavy metal contamination occurs on its tributaries (Bird et al., 2010). Similar moderate contamination has been observed for the intertidal sediments of the Yangtze river delta (Table 2; Zhang et al., 2009). In both cases, the moderate levels of contamination can be explained by the diluting effect of the huge amount of 'clean' sediment relative to pollutant inputs (Zhang et al., 2009). In Danube, this dilution effect is achieved despite the

numerous sources discharging metal contaminants on major tributaries of the Danube which are well documented in the literature, thus acting as a large-scale natural filtering system. This hypothesis is in agreement with the findings of a recent study (Simionov et al., 2021) which measured potentially toxic as well as essential elements (Pb, Cd, As, Cu, Fe, Zn, Mg, Ca, Na, K) in water, sediment and fish samples collected at 7 sites along the lower Danube, the delta and the Black Sea shore, and concluded that the Danube Delta system plays an important role in filtering pollutants.

5 Conclusions

The top 400 cm part of the 900 cm-long core Caz02 retrieved from the floodplain of Sulina distributary provides a record of heavy metal content history over the last 600 years. Metals Cu, Zn, Pb, Cr and Ni appear mainly natural in origin in the lower part of the core (Unit 1, 400-200 cm, 600 to ~250 cal. BP), with their variability largely influenced by particle size. Above 200 cm depth (~1700 CE to present), these metals as well as Cd show elevated concentrations reflected by enrichment factors of Cr, Ni and Cd greater than 1.5. These values, which are consistently higher compared to the previous time frame (i.e., prior to ~1700 CE), could be ascribed to anthropogenic inputs originating in the extensive drainage basin of the Danube. In addition, diagenesis in the peat layer (170-140 cm) of U2 likely results in enhanced organic carbon and sulfide levels, which can lead to the accumulation of metals Cu, Zn, Pb and Cd to a higher extent in the deltaic sediment.

The moderate degree of heavy metal contamination documented in the past ~250 years in the Danube Delta seemingly attests to the fact that a sizeable river basin comprising a large delta

such as the Danubian basin has the ability to dilute and diminish contaminant contents (including metal elements of environmental concern) in water and sediment.

As the first study to address heavy metal contamination throughout the past ~600 years in the largest remaining natural wetland in Europe, host to unparalleled biodiversity at continental scale, this research provides baseline values for minor element contents in pristine deltaic sediments which have deposited prior to the manifestation of impactful anthropogenic activities in the drainage basin of the Danube and could be used for more in-depth pollution assessments. This investigation further provides a record of recent human-induced contamination with heavy metals in the Danube Delta which can inform decision-making regarding biodiversity conservation and protection, and the sustainable development of local communities in the Danube Delta biosphere reserve.

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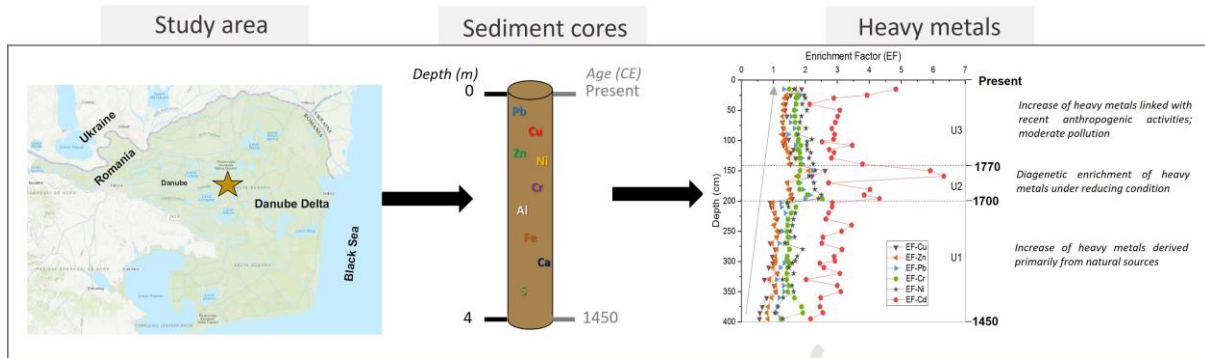
Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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**Highlights:**

- i) the first heavy metal pollution history study in Romania spanning the last 600 years;
- ii) three periods were defined downcore based on major elements and metals variation;
- iii) an interplay between natural vs anthropogenic metal origins of Danube Delta sediments;
- iv) human-induced heavy metals pollution is discernable in the recent period;
- v) such findings can support policies and decision-making for Danube Delta biosphere reserve.