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Metal deposition in deep sediments from the Central and South Adriatic Sea

Nikolina Ilijanić[1], Slobodan Miko[1], Branko Petrinec[2] and Zdenko Franić[2]

[1] Croatian Geological Survey, Sachsova 2, HR-10000 Zagreb, Croatia;
(corresponding author: nilijanic@hgi-cgs.hr)

[2] Institute for Medical Research and Occupational Health, Radiation Protection Unit, Ksaverska cesta 2,
HR-10001 Zagreb, Croatia

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ABSTRACT

Geochemical analysis and trace element distribution were performed on the marine sediments from short cores (30 to 50 cm) from the Middle (Jabuka and Palagruža pits, depth 230 m and 170 m, respectively) and South Adriatic Sea (depth 1030 m) and the Albanian offshore (50 m depth). The distribution of trace elements (As, Co, Cd, Cu Cr, Ni, Zn, Hg, and Pb) and major elements (Al, Ca and Mn) and mineralogy in the sediments is presented. Sediments are highly heterogeneous and consist of carbonate and detrital aluminosilicate minerals. The main mineral phase is calcite, followed by quartz, feldspars, micas and clay minerals (smectite, chlorite, illite and kaolinite). The cores were dated using ^{137}Cs. The cores from the South Adriatic Pit and Palagruža Sill gave estimated sedimentation rates of 1.8 mm y^{-1} and 3.1 mm y^{-1} in Jabuka Pit. Distributions of Ni and Cr showed that they can be used as tracers of sediment provenance along the southern part of the Eastern Adriatic Current. Calculated enrichment factors for Pb, Cd and Hg are highest in the top 2 cm of the cores. Mercury shows the highest degree of enrichment in 0–2 cm sediment intervals (the highest in the Albania core). Generally the estimated surface enrichment follows the order: Hg>Pb>Cd. No enrichment was found for Zn, Ni and Cr.

Keywords: trace metals, accumulation rate, marine sediment record, enrichment factors, Adriatic Sea, Eastern Adriatic Current

1. INTRODUCTION

Down-core and surface geochemical and mineralogical analysis have been successfully used as tools in reconstructing past variations in sedimentation, provenance and pollution studies of the Adriatic Sea. The trace element geochemistry studies of the Adriatic basin can be divided into several groups, the pollution and provenance studies related to the Western Adriatic Current (WAC) along the eastern coast of Italy (DINELLI & LUCCHINI, 1999; AMOROSI et al., 2002; DINELLI et al., 2007; SPAGNOLI et al., 2008; ANNIBALDI et al., 2009; AMOROSI, 2012; GOUDEAU et al., 2013; ROMANO et al., 2013), the pollution related to the studies of the Gulf of Trieste (COVELLI et al., 2001, 2006, 2007; FAGANELI et al., 2003; COVELLI et al., 2006, 2007; ACQUAVITA et al., 2012; EMILI et al., 2012), the coastal marine and estuarine environments along the eastern Adriatic coast (PROHIĆ & KNIEWALD, 1987; BOGNER et al., 1998; MIKO et al., 2007; SONDI et al., 2008; CUCULIĆ et al., 2009; CUKROV et al., 2011, OBHODAŠ et al., 2012; LOVRENČIĆ MIKELIĆ et al., 2013). Trace metal data are also available from relatively few long cores spanning through the Holocene and into the Pleistocene (CALANCHI et al., 1996; LUCCHINI et al., 2003) in Mid Adriatic Depression (MAD), and basin-wide low sampling density geochemical studies of surface sediments (DOLENEC et al., 1998; DE LAZZARI et al., 2004). SPAGNOLI et al. (2010) gave a detailed overview of the studies of trace elements in sediments of the central-southern Adriatic Sea, concluding that data indicating contamination are only limited to specific areas. Based on the analysis of a core from the MAD, CALANCHI et al. (1996) concluded that it is consistent with the average composition of fine-grained Middle Adriatic sediments, and that major variations in trace element concentrations depend on changes in the silicate/carbonate ratios, and the type and abundance of silicate supply. The study by TANKÈRÉ et al. (2000) used a simple box mass balance model for Mn, Fe, Pb, Zn, Cu, Ni on an annual scale for the different compartments of the Adriatic Sea. The model was based on fluxes along the WAC. They concluded that the contribution of the Northern Adriatic to the rest of the Adriatic Sea was relatively small because of the restricted water exchange and the loss due to burial in the sediment. On an annual scale, the Adriatic Sea appeared to be a source of dissolved Cu, Mn and Fe for the Mediterranean Sea through the Strait of Otranto whereas for dissolved Zn and Pb the Adriatic Sea appeared to be a net sink. For dissolved Ni, inputs and outputs through the Strait of Otranto balanced each other.

TOMADIN (2000) used clay mineral composition and distribution in the central and southern Adriatic Sea, as tracers of sediment provenance, indicating longitudinal dispersion connected with the general Adriatic cyclonic circulation. He recognized fluxes directed south-westward along the Italian offshore – the Apennine flux (Western Adriatic Current-WAC) near the coast and Padane flux in the open sea. The NW flux flows along the eastern coast (Eastern Adriatic Current–EAC, GIANI et al., 2012), of the central and southern Adriatic basin, which he termed as the "Albanian flux".

Studies on the geochemistry of the core samples have been undertaken for the western part of the Adriatic Sea, using the geochemistry as a tracer for both provenance and pollution studies along the WAC (AMOROSI et al., 2002; DINELLI et al.; 2007; WELTJE & BROMMER, 2011; GOUDEAU et al., 2013; ROMANO et al., 2013). Only the studies of DOLENEC et al. (1998) and DE LAZZARI et al. (2004) provided geochemical data for surface sediments along the southern part of the Eastern Adriatic Current (EAC). DOLENEC et al. (1998) indicated that the main sources of trace element accumulation in the central Adriatic were both the WAC and EAC. The EAC was responsible for the accumulation of As, Co, Cr, Cu and Ni, V, and Zn with a contribution of WAC to Cu, V and Zn. The sources of Hg were considered to be the northern Adriatic and the Apennine mainland (DOLENEC et al., 1998). The geochemistry and mineralogy of Mn from the central Adriatic in surface sediments was also given by DOLENEC et al. (1998). The Albanian River inputs are considered to be major sources of Co, Cr, Ni, V and Zn in the eastern part of the southern Adriatic (DOLENEC et al., 1998) as a consequence of weathering and erosion of catchments containing ophiolitic mélanges associated with ophiolitic sequences in the Mirdita–Subpelagonian zone. The high concentrations of transition metals (such as Ni, Co, Cr and V) are one of their primary geochemical features (SACCANI & PHOTIADES, 2005).

This study reports the depth profiles of the eight trace elements usually identified as priority contaminants in aquatic systems As, Cd, Cr, Cu, Hg, Ni, Pb and Zn as well as Mo, Mn, Al and Ca as geogenic elements in 5 short marine sediment cores, collected at locations on a transect along the western rim of the EAC. Sediment cores provided evidence for the accumulation of metals in the deep sea environments of the Adriatic. This study provides an insight to the possible anthropogenic influences in the area. To assess the distribution and the degree of sediment contamination and to distinguish natural and anthropogenic inputs, metal-enrichment factors (EF) were calculated (FÖRSTNER & WITTMANN, 1981; LI, 1981). Mineralogical analysis was performed in order to determine the nature and their mutual comparability as well as down-core variations of the analyzed cores. Based on the metal concentrations measured in both surface and deeper sediments, trace element enrichment factors were also calculated. The depth profiles represent the signature of historical contamination. Radioactive isotopes (^{137}Cs) coupled with variations in elemental concentrations allowed reconstruction of the history of trace element accumulations in Adriatic sediments through time.

2. STUDY AREA

The Adriatic Sea is a narrow and shallow epicontinental basin (approximately 200×800 km), forming a distinct sub-region within the Mediterranean Sea (Figure 1). The surface area of the whole Adriatic Sea is 138,595 km^2 (BULJAN & ZORE-ARMANDA, 1976).

The Adriatic Sea may be divided into three parts (Figure 1): (1) the Northern Adriatic Sea from the Trieste gulf to the Ancona promontory and the island of Pag; (2) the Central Adriatic Sea from the Ancona promontory and the island of Pag up to the transect Gargano-Split; and (3) the Southern Adriatic Sea from the Gargano-Split to Otranto. The central Adriatic Sea again lies on the continental shelf, but is characterized by raised areas, which sometimes emerge to produce isles, and by a large depression up to 272 m deep. The Southern Adriatic Sea is very different and can be divided into three units: the continental shelf, the continental slope and a bathyal plain at 1233 m. The seabed is covered with sand and in some places with a mixture of sand, mud and silt. The northern part is sandy, while the middle and southern parts are dominantly covered in silt (PIGORINI, 1968; LEDER, 2004; SPAGNOLI et al., 2008, SPAGNOLI et al., 2010).

The Adriatic Sea is located between two major climatic regimes. The northern part is highly influenced by the temperate and humid climate of southeast Europe, while the southern part is governed by the arid conditions of the Mediterranean and northern Africa. The Adriatic Sea has a microtidal regime and is dominated by a cyclonic circulation driven by thermohaline currents (ORLIĆ et al., 1992). The surface water of the Adriatic Sea circulates in an anticlockwise direction. It flows parallel to the eastern coast to the north (NW direction, EAC; GIANI et al., 2012), then turns towards the western part on the Italian coastline to the south (Western Adriatic Current – WAC). Global cyclonic circulation is divided into three re-circulation cells (Figure 1) in the northern, central and southern sub-basins, induced by the strong Bora wind and being controlled by the bathymetry of the Jabuka and South Adriatic Pits (ZORE ARMANDA & GAČIĆ, 1987; ORLIĆ et al., 1992).

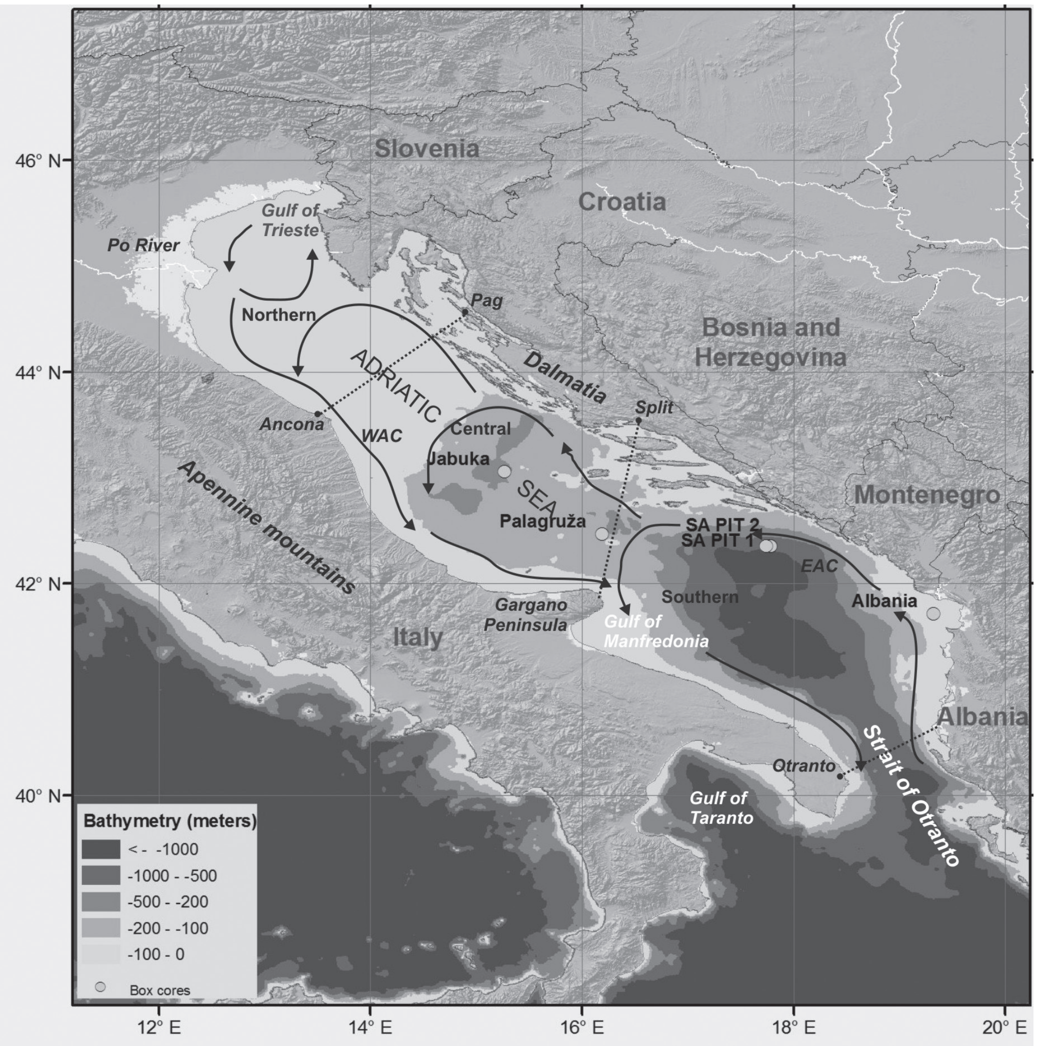

Figure 1: Map showing the Adriatic Sea and locations from which sediment cores were taken. Global cyclonic circulation (arrows) of the marine currents in the Adriatic Sea is broken into three re-circulation cells in the northern, central and southern sub-basins, being controlled by the bathymetry of the Mid Adriatic Depression and South Adriatic Pits. WAC=Western Adriatic Current; EAC=Eastern Adriatic Current.

3. MATERIALS AND METHODS

In this study 5 box-cores were analysed, from the central and southern part of the Adriatic sea (Figure 1, Table 1). One core was from the Mid Adriatic Depression ("Jabuka pit", the core was termed as Jabuka), while a second came from the Palagruža Sill ("Palagruža" core). Two cores are from the South Adriatic Pit (cores SA PIT-1 and 2) and an offshore core came from the Albanian coast ("Albania core"). The sediment cores were collected by means of a box-corer, which provided virtually undisturbed samples up to 50 cm long. The cores were cut into 2 cm intervals, freeze-dried after coring on the boat and transported to the laboratory. Samples were powdered manually in an agate mortar and

Table 1: List of the samples, coordinates and depths of the locations.

Location	Geographic coordinates		Depth (m)	Core length
Jabuka	N 43°03'10.25"	E 15°16'30.94"	230.8	50 cm
Palagruža	N 42°28'34.86"	E 16°11'27.09"	169.8	40 cm
SA PIT 1	N 42°20'20.77"	E 17°47'18.21"	1041.4	42 cm
SA PIT 2	N 42°20'44.70"	E 17°44'49.09"	1030.0	42 cm
Albania	N 41°43'24.33"	E 19°19'54.29"	59.0	38 cm

analysed for bulk mineral and geochemical composition and total mercury concentrations.

The mineral composition of all samples was determined by a PANalytical X'Pert Powder X-ray diffractometer, equipped with Ni-filter Cu*Kα* radiation, vertical goniometer with θ/θ geometry and a PIXcel detector. Scan conditions were: 45kV and 40 mA, ¼ divergence slit and antiscatter slits, step size 0.02° 2θ, time per step 2s, in the range of 5–65° 2θ. After grinding, samples were sieved through a 0.4 mm sieve and ground in McCrone micronizing mill to reduce material to <5 μm powder samples and ensure random mineral orientation. This preparation method facilitated semi-quantitative analysis, according to EBERL (2003). In addition, oriented samples were prepared for clay mineral analysis. Calcite was removed by treating the sample with buffered sodium acetate (NaOAc) solution at pH 5.0 in a 1:10 sediment/buffer ratio. The pH of the slurry was lowered to 5.0 using HCl. The <2μm fraction was separated from selected samples by centrifugation (1 minute, 2000 rpm) to obtain mineralogical details about the clay-size fraction and clay minerals. Oriented mounts were prepared on glass slides with an eye-dropper. These samples were analyzed in air-dried, ethylene glycol-solvated, and heated (400°C and 550°C) states and scanned in the range of 2–30° 2θ. The XRD patterns were interpreted following MOORE & REYNOLDS (1997). Quantitative mineral analysis was undertaken using the RockJock, computer program for QXRD (RkJock.xls; EBERL, 2003). The wt% of minerals in a sample was calculated from integrated X-ray intensities. The RockJock technique has been checked for accuracy using artificial mixtures and generally produced answers that are within ± 2 to 5 % of actual values (EBERL, 2003).

Chemical analysis was conducted on all 41 samples. The dissolution of 0.25 g of sediment was performed with a mixture of $HCl–HF–HClO_4–HNO_3$ acids on a hot plate until dry. The residue was then treated with diluted $HCl–HNO_3–H_2O$ (15% aqua regia) in a hot bath (> 95 °C) for 30 min. The resulting solutions were analyzed by mass spectroscopy using a Perkin Elmer Elan 6000 or 9000 ICP-MS for a set of 41 elements: Ag, Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hf, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, S, Sb, Sc, Sn, Sr, Ta, Th, Ti, U, V, W, Y, Zn, and Zr. Total mercury concentration was determined after $HCl:HNO_3$ (3:1, aqua regia) extraction of subsamples by cold vapour AAS. From this set of elements potential contaminants including As, Cd, Cr, Cu, Ni, Hg, Pb and Zn were selected to evaluate metal/contamination in the cores, as well as Mo, Mn, Al and Ca as the presumed natural variables. The chemical analysis was performed at the ACME Analytical Laboratories in Vancouver, Canada. The accuracy was checked with certified reference materials (GXR-2, GXR 5, and SJS-1; USGS). The accuracy for most elements analysed in reference materials was <10 % of the certified values. Precision was determined by repeated analyses of both certified reference samples and randomly selected sediment samples (every 5th sample in the batch) with the resulting average coefficient of variation of approximately 5%.

The five sediment cores were measured for ^{137}Cs activities in order to derive sediment accumulation rates. Details of the performed analysis and calculations of accumulation rates are given in PETRINEC et al. (2012).

Descriptive data analyses (mean, standard deviation, maximum and minimum concentrations) and calculation of enrichment factors (FERGUSON, 1990; RIDGWAY & SHIMMIELD, 2002) were carried out. In addition, correlation factors were calculated to determine and the island of Pag up to the transect Gargano-Split; asses the processes involved. The data sets for the analyzed cores (this study) and the data from DOLENEC et al. (1998) were analyzed using the STATISTICA 7 (StatSoft, 2006) statistical program. The comparison of geochemical data available for Adriatic marine sediments given by DOLENEC et al. (1998) and GOUDEAU et al. (2013) was possible since the same methods based on dissolution with the mixture of $HCl–HF–HClO_4–HNO_3$ for determination of element contents were used in their studies.

4. RESULTS

4.1. Sediment characteristics

Mineral composition of analysed sediment samples is shown in Figure 2, and Table 2. The predominant mineral phase in all samples was calcite (14–34%), the highest values were in Palagruža (28–34%) and the lowest in the Albania samples (10–15%). Mg-calcite was present in all samples in concen-

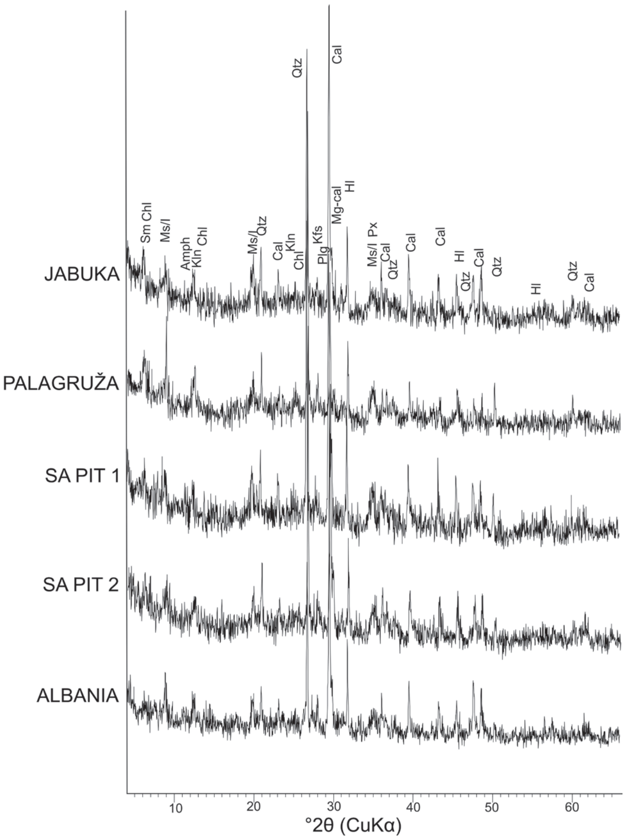

Figure 2: Mineral composition of the representative samples from the five locations. Symbols: Qtz-quartz, Cal-calcite, Kfs-potassium feldspar, Plg-plagioclase, Ms/I-muscovite/illite, Sm-smectite, Chl-chlorite, Kln-kaolinite, Px-pyroxene, Amph-amphibole, Mg-cal-Mg calcite, Hl-halite.

Table 2: Quantitative mineral analysis of the samples (SA PIT 1, SA PIT 2, Jabuka, Palagruža, Albania) (RockJock; EBERL, 2003). Results are in wt% and represent average data of the samples in the 10 centimetre interval.

	JABUKA			PALAGRUŽA			SA PIT 1			SA PIT 2			ALBANIA		
Minerals	0–10	10–20	20–30	0–10	10–20	20–30	0–10	10–20	20–30	0–10	10–20	20–30	0–10	10–20	20–30
Quartz	8	7	6	9	12	8	9	7	8	13	13	6	9	9	7
Calcite	23	29	30	22	12	27	23	24	24	13	13	20	21	23	20
Mg-calcite	4	4	5	5	2	2	4	4	4	–	1	3	4	2	2
K-feldspar	6	8	9	5	8	7	7	7	6	7	7	7	7	6	6
Plagioclase	5	6	7	5	8	6	7	4	5	9	8	5	5	6	6
Illite	5	5	6	10	11	7	10	9	10	14	15	6	11	8	6
Smectite	33	23	23	26	24	24	37	26	25	21	21	32	24	29	34
Chlorite	9	7	7	8	14	9	12	8	9	13	12	10	9	9	11
Kaolinite	4	6	5	6	6	5	5	6	6	7	7	5	6	5	4
Pyroxene	1	1	1	1	–	1	–	1	1	–	–	3	–	–	2
Amphibole	1	3	2	2	2	3	3	1	2	2	2	2	2	3	2
Halite	1	2	2	2	2	2	2	2	1	1	1	1	2	2	2

trations from 1–7%, and seems to be higher in Palagruža (up to 10%). Quartz occurs in amounts from 3–15% and it was higher in samples from Albania (10–15%) and lower in Palagruža (2–10%), (Figure 3). Feldspars are also abundant, and potassium feldspars dominate over plagioclase. Trace amounts of pyroxene and amphibole appeared in some samples. Clay minerals are represented by smectite, illite, chlorite and kaolinite (Figure 4). Smectite is the dominant clay mineral in all the analysed sediment cores (15–43%), but with a slightly lower presence in the Albania cores (18–27%). Illite and chlorite have the highest contents in sediments from the Albania core (7–18%, 11–16%, respectively), while illite was depleted in the Palagruža core (3–9%). Kaolinite is present in all samples, and the content ranging from 1–9%.

4.2. Accumulation rates

The highest sedimentation rates have been found in the cores from Albania (~4 mm/y) and Jabuka (3.1 mm/y), and 1.8 mm/y in Palagruža. In the south Adriatic, where two peaks are more easily identified, sedimentation rate could be estimated to be approximately 1.8 ± 0.5 mm/y which is quite similar to the value estimated for Palagruža. Results indicate that for the Palagruža Sill and the South Adriatic Pit, an annual average sedimentation rate of 1.8 ± 0.5 mm is likely and that the top 10 cm interval of the sediment core represents approximately 50 years of history and a 40 cm core could be an equivalent to 200 years. The Jabuka and Albania cores therefore span much shorter histories (approximately 130 and 100 years, respectively). However, it should be noted that these results are only approximate due to the method limitations and large uncertainties in the estimation of the exact location of ^{137}Cs activity concentration peaks in the sediment profiles.

4.3. Variations of elemental concentrations with space and depth

The tables containing geochemical data are given as online supplementary tables. The concentrations of analyzed major and trace elements are summarized in Supplementary Table 1. The down-core contents of major elements Ca and Al dis-

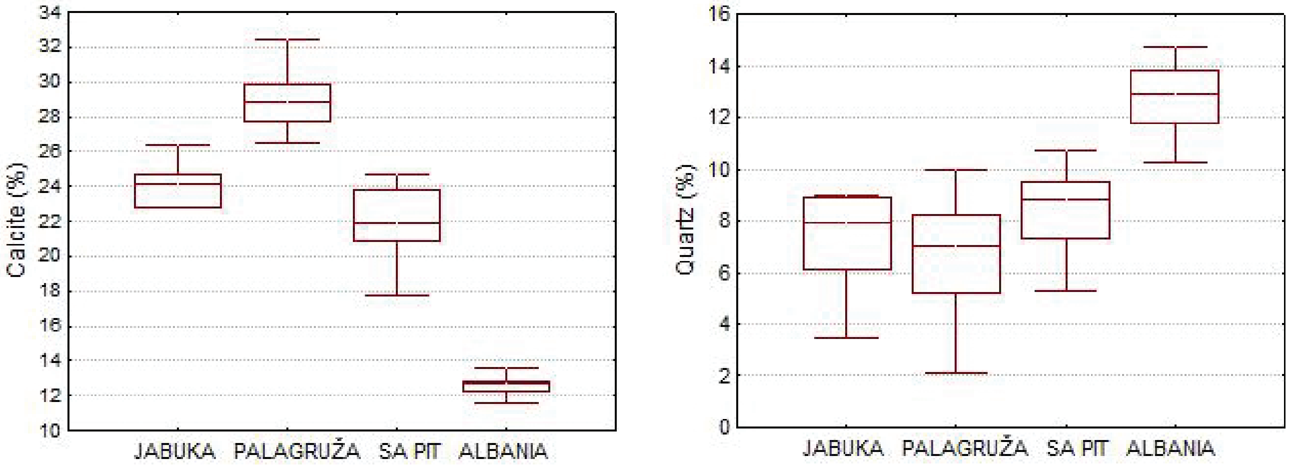

Figure 3: Distribution and abundance of calcite and quartz in the studied cores (SA PIT 1 and 2 are merged into SA PIT).

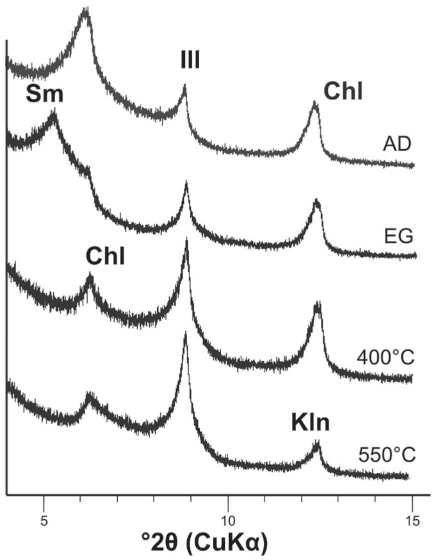

Figure 4: A representative (SA PIT 1 6-8 cm) oriented sample of the clay mineral fraction, with basal reflections of clay minerals after treatments (AD-air dried, EG-ethylene glycolated, heated to 400°C and heated to 550°C). Symbols: Sm-smectite, Chl-chlorite, Ill-illite, Kln-kaolinite.

play narrow ranges in the individual cores. The Ca concentrations are highest in the Palagruža core (13.68–16.81%) and the lowest in the Albania core (4.83–5.19%). Several samples that have higher Ca contents and fall outside the Ca-calcite line indicate Ca to be linked with some aluminosilicate phases (smectite, chlorite). Relationships between major elements Ca, Al, Ti and calcite and muscovite/illite in Figure 5 clearly display these relationships. Most samples in the cores contain on average < 30% smectite and < 10% chlorite with the exception of the Albania core where the contents of chlorite range from 12–14% (Table 2). Such a deviation in Ca content that is not related to carbonate content could be attributed to the presence of Ca-rich plagioclase, as a signature of a high detrital siliciclastic input. The cores from the Mid Adriatic Depression (Jabuka) and South Adriatic Pit (SA PIT 1&2) have similar Ca content (11.1% and 10.7%, respectively) as well as calcite (20–24%).

Al and Ti contents are indicative of detrital delivery and the highest contents are in the Albania offshore cores. Average Al content ranged from 6.6% in the Albania core to 4.9% in the Palagruža core. The cores from the depressions had average Al contents from 5.7 % (Jabuka) to 6.1% (SA PIT). Ti contents were similar in the Jabuka, SA PIT and Palagruža cores (Supplementary Table 1), while it was higher in the Albanian core (0.34 to 0.37%). These elements and their relationship to trace elements are important in evaluating possible pollution.

The trace element composition of the analyzed cores shows higher spatial and down-core variability (Supplementary Table 1). The down-core concentration profiles of Pb, Hg, Zn, Cd, Cr, Ni, Cu, As, Mo Mn and Zn are presented in Figure 6.

The mean concentrations of Cd in the cores range from 0.06 mg/kg (SA PIT1) to 0.14 mg/kg (Albania). These concentrations correspond to the median of 0.11 mg/kg given by DE LAZZARI et al. (2004), although their data shows large variability across the northern and central Adriatic with a concentration range from 0.04 to 0.97 mg/kg. The highest concentration of Cd determined in the Albania core was in the deeper part of the core (22–24 cm).

Total mercury concentrations in the sediment cores range from 13 to 106 µg/kg, with the mean concentration between 26 and 34 µg/kg. The Hg depth profiles show a clear upward increase in the analyzed cores (Figure 6), with the exception of the Palagruža core where Hg slightly decreases in the top section. The lower sections of the cores (SA PIT, Palagruža, Jabuka) have low Hg concentrations in a narrow range between 13 and 23 µg/kg. The Albania core has higher contents of Hg in the lower sections of the core ranging from 33–50 µg/kg. The Jabuka and Palagruža cores have generally slightly higher contents of Hg in comparison to the South Adriatic Pit cores (Figure 6).

Pb concentrations show a general increase in the upper core samples (Figure 6), there is a wide peak in the SA core between 30–32 cm depth. This interval also contains elevated concentrations of other trace elements (Ba, Rb) and magnetic

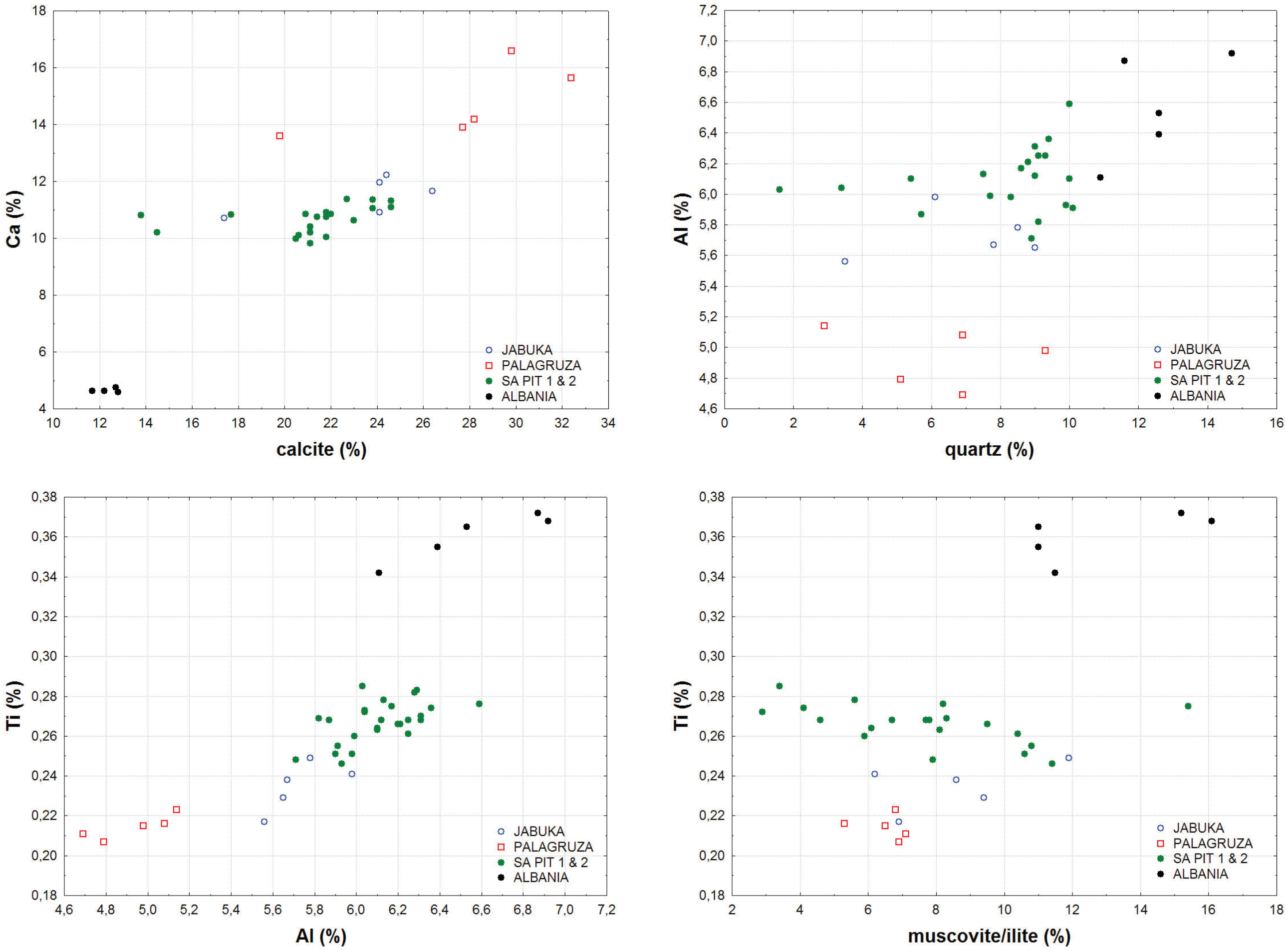

Figure 5: Relationships between the major elements (Ca, Al, Ti) and selected mineral phases (calcite and muscovite/illite).

susceptibility that could possibly be related to tephra. There is a slight decrease of Pb in the tops of the Palagruža and Albania cores. In all the cores the Pb concentrations exhibit slight variation from 14.9 to 24.5 mg/kg, with mean values ranging from 18.1 to 20.2 mg/kg (Supplementary Table 1).

Down-core variations in Cr and Ni are not pronounced and the difference between the cores (Supplementary Table 1, Figure 6) lies in the total contents along the EAC transect from the Albania core with the high concentrations of Cr (mean 263 mg/kg), and the lowest in the Palagruža core (120 mg/kg). The mean concentrations of Cr in the SA PIT cores (152 and 146 mg/kg) and the Jabuka core (131 mg/kg) falls between these two. The concentrations of Ni show exactly the same behaviour (r=0.99, Supplementary Table 2, Figure 6). The lower Ni and Cr contents in the Palagruža core are a consequence of carbonate dilution, since the Palagruža cores contain more calcite than the other cores (Table 2., Figure 5).

The down core distributions of Mn, As, Mo and Cu are quite complex in the analyzed cores especially in the South Adriatic Pit. The concentrations of Mn in the analyzed cores range from 700 mg/kg (Palagruža) to 5201 mg/kg (SA PIT). The down-core distribution of Mn in the South Adriatic pit substantially differs from that of the other core exhibiting the highest concentration (5201 mg/kg) in the 18–20 cm interval and a peak (3942 mg/kg) in the 32–34 cm interval (Figure 6).

The As concentrations in the analyzed cores were generally higher than those reported by DOLENEC et al. (1998) for the southern Adriatic. The Palagruža core samples (mean 7.4 mg/kg) and the Jabuka core samples (mean 13.2 mg/kg) were within the range of the As proportions in sediments in the Gulf of Manfredonia (SPAGNOLI et al., 2008). If we exclude the anomalous concentrations (64 mg/kg) measured in the bottom part of the SA PIT core (Figure 6), the highest mean concentrations were in the Albania core (22 mg/kg). High As concentrations occur in the samples from 30–38 cm depth (Figure 6).

Cu concentrations in the cores show similar ranges in the SAP PIT and Albania cores with a narrow average 38.9 mg/kg and 41.1 mg/kg (Supplementary Table 1). The mean Cu contents of both the Palagruža and Jabuka are lower (21.6 and 29.4 mg/kg, respectively). The positive correlation with Al (r=0.83) is indicative, (as in case of the analyzed transition metals) that concentration is related to detrital aluminosilicates. Similar values for the Adriatic surface sediments were discovered by DOLENEC et al. (1998).

The concentration of Zn in the analyzed cores ranges on average from 68 mg/kg in the Palagruža core to 105 mg/kg

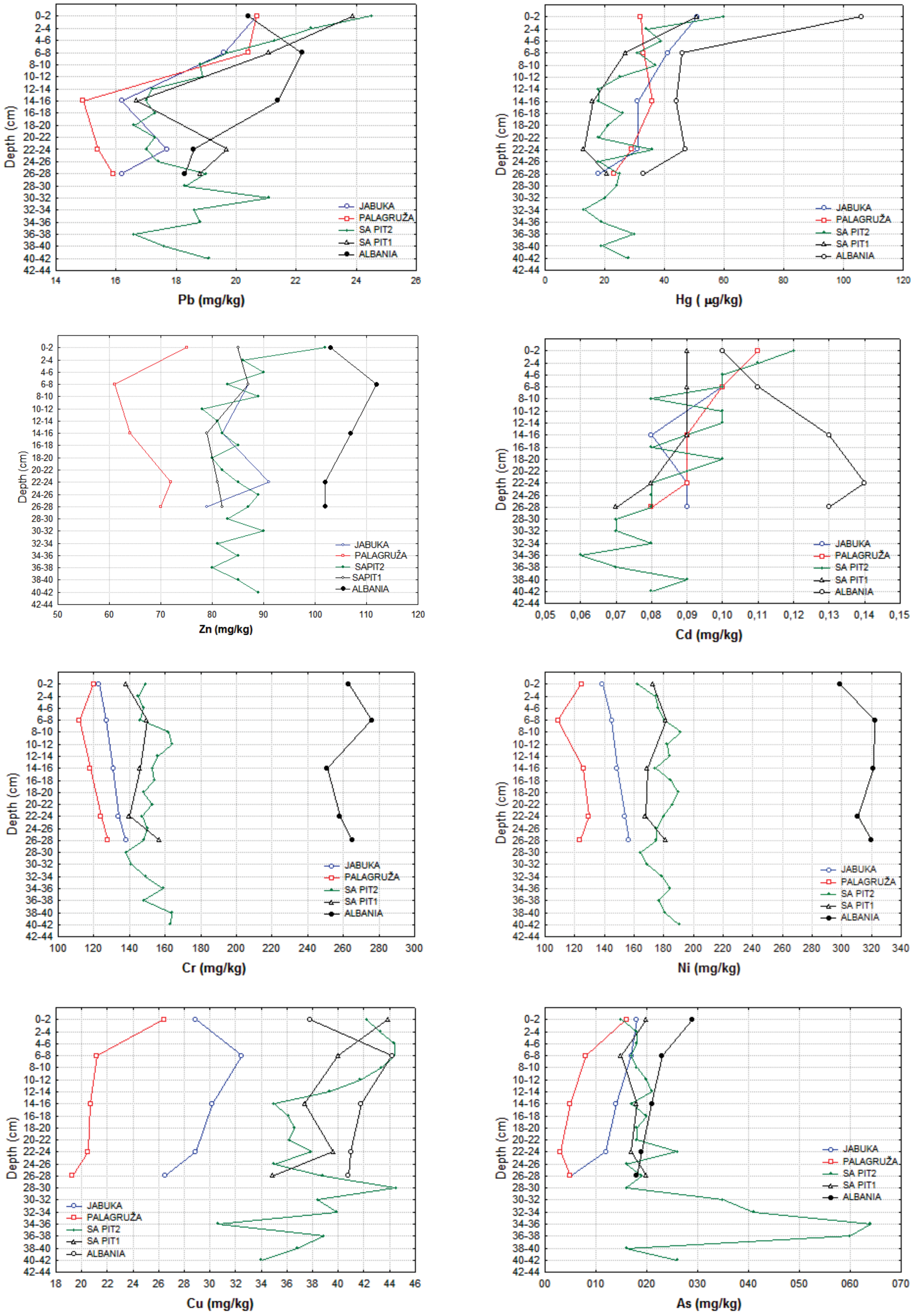

Figure 6: Down-core variability of Pb, Hg, Zn, Cd, Cr, Ni, Cu, Mn, and Mo in the studied sediment cores.

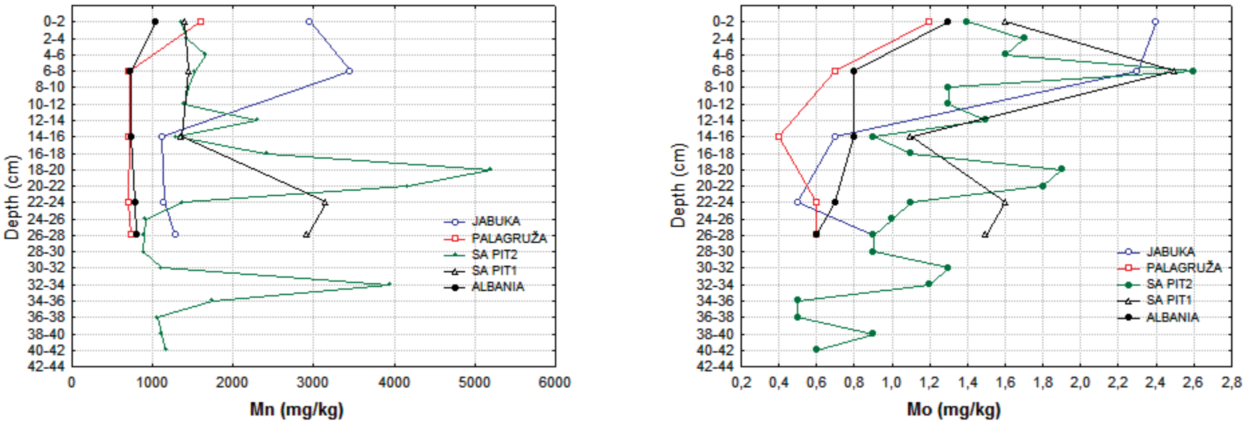

Figure 6: Continued.

Supplementary Table 1: Metal concentrations ranges, mean, and standard deviation (std) in the analyzed cores.

	Core	JABUKA	PALAGRUŽA	SA PIT 1	SA PIT 2	ALBANIA
Cd (mg/kg)	mean	0.094	0.094	0.087	0.084	0.122
	std	0.011	0.011	0.015	0.009	0.016
	min.	0.080	0.080	0.060	0.070	0.100
	max.	0.110	0.110	0.120	0.090	0.140
Hg (ug/kg)	mean	34	31	27	26	55
	std	12	5	11	15	29
	min.	18	23	13	13	33
	max.	51	36	60	51	106
Mo (mg/kg)	mean	1.36	0.70	1.24	1.66	0.84
	std	0.92	0.30	0.51	0.51	0.27
	min.	0.50	0.40	0.50	1.10	0.60
	max.	2.40	1.20	2.60	2.50	1.30
Cu (mg/kg)	mean	29.4	21.6	38.9	39.2	41.1
	std	2.2	2.8	3.9	3.3	2.3
	min.	26.5	19.3	30.6	34.9	37.8
	max.	32.5	26.4	44.5	43.9	44.2
Pb (mg/kg)	mean	18.1	17.5	18.8	20.0	20.2
	std	2.0	2.8	2.1	2.7	1.7
	min.	16.2	14.9	16.6	16.7	18.3
	max.	20.7	20.7	24.5	23.9	22.2
Zn (mg/kg)	mean	85	68	85	83	105
	std	5	6	5	3	4
	min.	79	61	78	79	102
	max.	91	75	102	87	112
Cr (mg/kg)	mean	131	120	152	146	263
	std	6	6	7	8	9
	min.	123	112	138	138	251
	max.	138	128	164	157	276

Supplementary Table 1: Continued.

	Core	JABUKA	PALAGRUŽA	SA PIT 1	SA PIT 2	ALBANIA
Ni (mg/kg)	mean	149	122	179	175	315
	std	7	8	8	7	10
	min.	139	109	162	168	299
	max.	156	130	192	182	323
As (mg/kg)	mean	13.2	7.4	24.7	18.0	22.0
	std	5.2	5.1	14.0	2.1	4.4
	min.	5.0	3.0	15.0	15.0	18.0
	max.	18.0	16.0	64.0	20.0	29.0
Mn (mg/kg)	mean	1990	892	1826	2059	820
	std	1125	397	1181	900	131
	min.	1120	700	882	1362	732
	max.	3457	1602	5201	3156	1047
Ca (%)	mean	11.06	15.02	10.77	10.66	5.02
	std	0.95	1.36	0.61	0.48	0.14
	min.	9.95	13.69	9.27	10.05	4.83
	max.	12.29	16.81	11.63	11.11	5.19
Ti (%)	mean	0.23	21	0.27	0.27	0.36
	std	0.01	0.01	0.01	0.01	0.01
	min.	0.22	0.21	0.25	0.26	0.34
	max.	0.25	0.22	0.29	0.27	0.37
Al (%)	mean	5.73	4.94	6.12	6.06	6.56
	std	0.16	0.19	0.20	0.20	0.34
	min.	5.56	4.69	5.71	5.87	6.11
	max.	5.98	5.14	6.59	6.36	6.92

in the Albania core. The high positive correlation with Cr (r=0.83, Supplamentary Table 2) is indicative of a similar source related to detrital aluminosilicates.

5. DISCUSSION

5.1. Sedimentation rates

The natural and artificial radionuclide activity concentrations in the sediments from the central and south Adriatic Sea are comparable with other reported values from the Mediterranean (OTHMAN et al. 2000) and Adriatic Sea (FRIGNANI et al., 2004, 2005; ŠTROK et al., 2010). In addition, their values in seawater and sediments throughout the Eastern Adriatic coast indicate that the determined values do not pose a significant risk for most marine biota (PETRINEC et al., 2013). The Adriatic Sea sedimentation rates have been mainly studied in the North Adriatic in which sedimentation is highly influenced by the Po River (PALINKAS & NITTROUER, 2007). Therefore, sedimentation in that area is quite high, and the sedimentation rate was estimated to be between 5–18 mm/y (FRIGNANI et al, 2004.).

Sedimentation rates estimated for the Mid and South Adriatic using ^{137}Cs as a radiotracer are consistent with sedimentation rates estimated for the rest of the Mediterranean sea, i.e., 1.1–8.7 mm/y (OTHMAN et al., 2000) using other radiotracer methods. PALINKAS & NITTROUER (2007) showed that sediment accumulation on the Po shelf is largely controlled by the flood sedimentation near the mouth of the main tributaries, with the highest sedimentation rates of 10-40 mm/y, while in the southern area of the dispersal system, accumulation is lower (< 10 mm/y), reflecting sedimentation during non-flood periods. The available data for the Adriatic Sea (FRIGNANI et al., 2005) shows that about 45% of values of the accumulation rates are lower than 2 mm/y.

5.2. Mineral composition

The mineral composition of the analysed cores shows good agreement with CALANCHI et al. (1996) who described the main mineral phases in the Adriatic sea sediments as quartz, calcite, dolomite, feldspars, micas, clay minerals (muscovite-illite, smectite and chlorite) with occasional occurrences of amphiboles and serpentine. Furthermore, several authors (PIGORINI, 1968; NELSON, 1972; TOMADIN, 2000) an-

Supplementary Table 2: Spearman correlation matrix (qtz-quartz, cal-calcite, k-fs-potassium feldspar, ms/i-muscovite/illite, sm-smectite, chl-chlorite).

	Cd	Hg	Mo	Cu	Pb	Zn	Ni	Mn	As	Ca	Cr	Ti	Al	qtz	cal	k-fs	ms/i	sm	chl
Cd	1.00																		
Hg	0.42	1.00																	
Mo	0.02	0.06	1.00																
Cu	0.21	0.15	0.37	1.00															
Pb	0.43	**0.51**	0.41	0.53	1.00														
Zn	0.51	**0.51**	0.03	**0.65**	0.49	1.00													
Ni	0.56	0.41	–0.13	**0.56**	0.25	**0.83**	1.00												
Mn	–0.12	–0.23	**0.63**	0.08	–0.06	–0.13	–0.17	1.00											
As	0.17	0.38	0.33	**0.74**	0.40	**0.62**	**0.59**	0.22	1.00										
Ca	–0.56	–0.50	–0.08	**–0.67**	–0.42	**–0.93**	**–0.91**	0.06	**–0.67**	1.00									
Cr	**0.58**	0.47	–0.21	0.48	0.23	**0.81**	**0.99**	–0.24	**0.54**	–0.88	1.00								
Ti	0.48	0.32	–0.10	**0.62**	0.22	**0.81**	**0.98**	–0.10	**0.61**	–0.89	0.95	1.00							
Al	0.24	0.11	0.19	**0.83**	0.27	**0.76**	**0.74**	0.06	**0.70**	–0.79	0.67	0.81	1.00						
qtz	0.46	0.38	–0.23	0.43	0.24	**0.66**	**0.69**	–0.41	0.34	–0.61	0.68	0.62	0.54	1.00					
cal	–0.41	–0.35	–0.13	**–0.59**	–0.36	**–0.75**	**–0.78**	–0.07	**–0.56**	0.84	–0.76	–0.81	–0.69	–0.22	1.00				
k-fs	0.43	0.13	–0.14	0.07	0.07	0.16	0.36	–0.24	0.00	–0.24	0.38	0.34	0.00	0.10	–0.27	1.00			
ms/i	**0.65**	0.44	–0.17	0.35	0.33	**0.57**	**0.56**	–0.42	0.10	–0.56	0.58	0.51	0.40	0.69	–0.35	0.19	1.00		
sm	–0.51	–0.32	0.34	–0.01	–0.17	–0.22	–0.33	**0.61**	0.11	0.21	–0.39	–0.24	0.01	–0.65	–0.11	–0.27	–0.63	1.00	
chl	0.14	0.20	0.02	0.19	0.08	0.38	**0.48**	0.07	0.29	–0.48	0.50	0.51	0.30	–0.18	–0.80	0.29	–0.04	0.25	1.00

alyzed the clay mineral distribution in superficial sediments of the central and southern Adriatic Sea. They reported that in the Mid Adriatic Depression, clay minerals of Apenninic origin dominate, whereas in the southern Adriatic Sea clay minerals show a depth-controlled distribution, suggesting strong hydrodynamic selection which is indicated by relative quartz dilution in offshore cores in comparison with the near shore Albania core (Figure 3). The distributions of illite, chlorite, and quartz seem not to be depth related but are a consequence of the carbonate content of the sediments. Apennine sediments (pelitic sediments rich in smectite) are dispersed transversally to the central basin and overlie the Padane, longitudinal, southward dispersion of fine-grained sediments (illite- and chlorite-rich sediments). Smectite (which is the dominant clay mineral in all the analysed sediment cores), shows the afore mentioned non depth-controlled distribution with higher mean contents in the Jabuka and South Adriatic Pit (25%) and lower (20%) mean contents in the shallower Palagruža and Albania cores. This could be in accordance with the findings of TOMADIN (2000) and due to the southern Adriatic basin turbidity currents which flow transversely to the basin carrying clay sediments from the Apulian shelf and the Albanian–Montenegrin shelf into the bathyal basin. TOMADIN (2000) used the clay mineral composition and distribution in the central and southern Adriatic Sea as tracers of sediment provenance, indicating longitudinal dispersion connected with the general Adriatic cyclonic circulation. He recognized fluxes directed south-westward along the Italian offshore – the Apennine flux near the coast (along the WAC) and the Padane flux in the open sea; and a northenward flux, along the eastern coasts of the central and southern Adriatic basin, the Albanian flux (along the EAC). Based on the contents of illite, chlorite, quartz and calcite along the EAC (Table 2, Fig. 3) a trend is observed indicating an enrichment of calcite and depletion of the other three minerals along the EAC.

5.3. Geochemical considerations

5.3.1. Major elements

The down-core contents of the major elements Ca, Al and Ti display narrow ranges in the individual cores. These elements and their relationship to trace elements are important in evaluating possible pollution. Al, Ti as well as Zr, Sr Li, Rb are considered as conservative during chemical weathering (SHOTYK et al., 2001; VAN DER WEIJDEN, 2002). Most methods used assume aluminum as present only in clays and detrital aluminosilicates (VAN DER WEIJDEN, 2002) and the metals are attributed to the clay fraction. Titanium is commonly hosted in high specific gravity minerals that are not easily transported aerially (Reimann & DE Caritat, 2005) and indicates detrital, coarser fractions, deposited in higher energy environments (SPAGNOLI et al., 2008). In the analyzed cores, Ti has very high correlation coefficients with Ni (r=0.98) and Cr (r=0.95) and correlates well with muscovite/illite (r=0.65) and quartz (r=0.62), indicating a presence in the silty fractions (Supplementary Table 2) (SPAGNOLI et al., 2008). The relationships between Ti, Al, quartz and muscovite/illite are illustrated in Figure 5. Ca is mainly derived from marine biogenic carbonate and Al from detrital aluminosilicates (DOLENEC et al., 1998 and GOUDEAU et al., 2013). This is confirmed by a high correlation (r=0.8) between Ca and calcite content indicating that most of Ca is derived from calcite (Supplementary Table 2.).

5.3.2. Trace elements

The analyzed trace elements based on their distributions can be divided into 4 groups; a) the "pollution"-related elements Pb, Hg, and Cd (REIMANN & DE CARITAT, 2005) showing a distinct concentration increase in the 0–2 cm core intervals (Figure 6); b) Cr and Ni which are the most commonly used trace elements for sediment provenance studies in the Adriatic basin (AMOROSI et al., 2002; DINELLI et al., 2007; LUCCHINI et al., 2003; SPAGNOLI et al., 2010; AMOROSI, 2012; GOUDEAU et al., 2013); c) Zn, Cu, As that display a complex distribution probably related to the clay and detrital aluminosilicate fractions with relatively high correlation (r>0.7) with Al (Supplementary Table 2). The distribution of As and Cu could also partially be controlled by redox processes (NAMEROFF et al., 2002), but due to the lack of correlation with Mn and Mo they are treated as a separate group: d) redox-sensitive trace metals Mn and Mo which were found to be significant features of the bottom sediments of MAD (DOLENEC, 2003) but also in numerous shallow marine sediments (ANSCHUTZ et al., 2005; BECK et al., 2008).

Lead and mercury – DOLENEC et al. (1998) suggested Pb concentration ranges for the central Adriatic sediments from 5–18 mg/kg and 7–14 mg/kg. SPAGNOLI et al. (2010) in their overview of trace element data cited 34 mg/kg as a background value for the Mid Adriatic Depression and 9.76 mg/kg for the Albanian coast. ROMANO et al., 2013 determined that sediments along the WAC had mean Pb concentrations ranging from 26–48 mg/kg. It is considered that Pb emissions are a result of many human activities including coal combustion, use of leaded gasoline, metal smelting, and mining. EICHLER et al. (2012) gave historical Pb emission estimates for the former U.S.S.R. Countries which considerably increased after 1935 with maximum values between 1970 and 1975. After this peak period Pb concentrations subsequently decreased and returned in the 1990s to the level of 1940−1950 (EICHLER et al., 2012). In the analyzed cores from the Adriatic the slight decrease of lead in the surface (0–2 cm) intervals in the Albania core could be interpreted as a consequence of this Pb emission decrease. ANNIBALDI et al. (2009) determined that Pb concentrations in Adriatic Sea water have shown a substantial decrease since 2001, as a consequence of decreased Pb emissions to the atmosphere in Italy. The absence of this diminution in the Mid Adriatic Depression (Jabuka) and the Southern Adriatic Pit (SA PIT1) surface sediments could be explained by substantially lower sedimentation rates in the depressions, and that analysis of 2 cm intervals did not give adequate temporal resolution.

The Hg depth profiles show a clear upward increase in the analyzed cores and that the background Hg concentration values for deep Adriatic sediments are less than 25 μg/kg. MASON et al. (2012) stressed that anthropogenic activities have enriched Hg in the biosphere by at least a factor of three, and that it is supplied to the offshore regions in the form of wet and dry atmospheric deposition. The background values for the northern Adriatic (Gulf of Trieste and Po delta) given by COVELLI et al. (2006) and RAJAR et al. (2006) are approximately 130 μg/kg. DOLENEC et al. (1998) concluded that most of the Hg supplied to the central Adriatic was derived from the northern Adriatic with minor influences from the Croatian coast, where Kaštela bay sediments near Split could be a possible localized source (LOVRENČIĆ MIKELIĆ et al., 2013). SPAGNOLI et al. (2010) cite a range of 67–224 μg/kg, for the Mid Adriatic Depression and 17 μg/kg, as the background for the coastal sediments of Albania.

Chromium and nickel – Most authors for provenance studies in the Adriatic basin use Cr and Ni to define sources of sediment to the Adriatic along the Western Adriatic Current and its mud belt (AMOROSI et al., 2002; LUCCHINI et al., 2003; DINELLI et al., 2007; WELTJE & BROMMER, 2011; AMOROSI, 2012; GOUDEAU et al., 2013) influenced by sediment discharge from the Po river and the Apennine rivers. The Ofanto River contributes most to the coastal sediments south of the Gargano promontory along the south eastern coast of Italy (GOUDEAU et al., 2013). GOUDEAU et al. (2013) concluded that a negligible contribution of mineral matter from the eastern Adriatic coast is possible. Using a chemostratigraphical approach in determining the spatial and temporal supply in long Adriatic cores from the Adriatic Shelf, the MAD and the South Adriatic Pit, LUCCHINI et al. (2003) showed that Cr and Ni were supplied by the Po River. The Holocene sediments of MAD have mean concentrations of 191 mg/kg Cr and 195 mg/kg Ni while the Last Glacial Maximum (LGM) sediments have lower mean concentrations 117 mg/kg Cr and 79 mg/kg Ni (LUCCHINI et al., 2003). The analyzed cores mainly lie along the western side of the Adriatic and the influence by the EAC is probably insignificant (GOUDEAU et al., 2013). The mean concentrations of Cr and Ni for the southern and central Adriatic given by DOLENEC et al. (1998) are lower than those in the analyzed cores but plot within the concentration ranges. The concentrations are dependent on the carbonate dilution i.e. the content of calcite in the sediment. They have high negative correlation coefficients with calcite content (Supplementary table 2) and are positively correlated with the muscovite/illite phase.

High Cr and Ni proportions in the Albania core are most probably a consequence of weathering and erosion of catchments containing ophiolitic mélanges associated with ophiolitic sequences which are part of the Mirdita–Subpelagonian zone. High concentrations of transition metals (such as Ni, Co, Cr and V) are one of their primary geochemical features

(SACCANI & PHOTIADES, 2005). The link with detrital aluminosilicates is displayed by correlation with both muscovite/illite, chlorite mineral phases (Supplementary Table 2).

A contribution of Ni and Cr is also possible from the Dalmatian region in the form of soil dust transported by the strong Bora wind especially to the eastern side of the MAD, or colloid suspensions from the eastern Adriatic rivers. Based on the geochemical soil data (MIKO et al., 2001; HALAMIĆ et al., 2012), soils developed on karst in Dalmatia contain high concentrations of Cr (mean 119 mg/kg) and Ni (mean 79 mg/kg) and due to the lack of vegetation cover are susceptible to wind and water erosion.

Zinc, Copper and Arsenic – Although Zn, Cu and As are often considered as indicators of possible anthropogenic influences, the high positive correlation with Cr (Supplementary Table 2) is indicative of a similar source related to detrital aluminosilicates. The concentrations fall within the ranges given by DOLENEC et al. (1998) and DE LAZZARI et al. (2004) for the central and southern Adriatic and SPAGNOLI et al. (2008) for the Gulf of Manfredonia. Also the concentrations are dependent on the carbonate dilution i.e. the content of calcite in the sediment as in the cases of Ni and Cr in the Palagruža core. Concentrations of As in the analyzed cores are generally higher than those reported by DOLENEC et al. (1998) for the southern Adriatic, and slightly lower than those for the sediments in the Gulf of Manfredonia given by SPAGNOLI et al. (2008).

Manganese and molybdenum – The concentrations of Mn are comparable with those of DOLENEC et al. (1998) from the Jabuka pit and the southern Adriatic. The measured concentration of 3457 mg/kg is similar to the 3760 mg/kg of DOLENEC et al. (1998). Mn in the southern Adriatic according to DOLENEC et al. (1998) could have been derived from the detrital material from the Albanian hinterland. DE LAZZARI et al. (2004) also determined that the Mn proportion was much higher in the MAD than other areas of the central and northern Adriatic. The Albanian core has the lowest concentration of Mn (732–1047 mg/kg). With the exception of the SA PIT cores the other three cores show relative surface increases in Mn concentrations (Figure 6). DOLENEC (2003) described the manganate crusts at the sediment-water interface in the Jabuka pit and their genesis as a result of processes linked with oxic diagenesis and the observation that sediments below 5 cm contain considerably less Mn. ANSCHUTZ et al. (2005) and CHAILLOU et al. (2008), showed that in the first few centimetres of the sediment, Mn undergoes several redox cycles with numerous possible reactions generally resulting in an aerobic surface layer enriched in Mn (III, IV) phases, as in the case of the Albania, Palgruža and Jabuka cores. At deeper levels, these oxides are reduced to soluble Mn (II) (CHAILLOU et al., 2008). The vertical distributions of Mo follow a similar pattern with Mn in the Albania, Palagruža and Jabuka cores which are a consequence of the high affinity of the molybdate (MoO_4^{2-}) ion, (the soluble form of Mo in oxic water), with Mn-oxides in marine sediments (CHAILLOU et al., 2008). These features are also revealed from the association of Mo and Mn in other sediments and ferromanganese nodules.

The sediment geochemistry of Mo may indicate short-term variations in pore water chemistry, or the influence of Mn diagenesis (MORFORD & EMERSON, 1999). The decoupled distributions of Mn and Mo (Figure 6) indicate that in the SA PIT an anoxic horizon is present in the 2–10 cm interval. This could have led to a partial decrease in Mn concentrations and authigenic enrichment of Mo as a consequence of the reduction of Mo (VI) to Mo (IV) due to sulfate reduction (CHAILLOU et al., 2008). In marine sediments Mo authigenesis is controlled by authigenic sulphide phases (CHAILLOU et al., 2008). The formation of Mn (oxyhydroxides-oxides?) enriched layers in the analyzed cores is to a degree favoured by the presence of smectite (r =0.61) where their formation is probably as coatings on the clay minerals which are considered to be uniformly negatively charged over their (001) crystal faces (FÖRSTNER & WITTMAN, 1983).

5.4. Normalization and enrichment factors

Trace metals may be introduced in the surface layers of marine sediments as a result of both natural processes (e.g. chemical weathering and erosion) and human activities within the catchment. The trace metals are mainly contained within the inorganic material which consists of silicate minerals such as quartz, feldspar, but more relevant micas and clay minerals and smaller amounts of metal oxides and sulfide phases. Differing contents of trace element and heavy metals in sediments do not necessarily indicate varying degrees of pollution, but could reflect dissimilarities in grain size and mineralogical composition or post depositional remobilization.

Normalization with respect to characteristic elements used as proxies for grain size or differing sediment sources is often used to distinguish anthropogenic pollution effects from natural variability. A variety of approaches for reducing natural variability have been used to improve the statistical power in data inter-comparison (WINDOM et al., 1989; VAN DER WEIJDEN, 2002; REIMANN & DE CARITAT, 2005). There is no consensus on the appropriate sediment component to be used for normalization i.e. to factor out the variability in natural trace element concentrations. In most cases, the source of the natural material making up the sediment has been assumed to be constant so the emphasis has been placed on accounting for the "grain size effect" (WINDOM et al., 1989). Metals are not homogeneously distributed over the various grain size fractions, and large differences in total concentrations are observed in sediment samples from a single locality. Within the grain size spectrum, the finer-grained fraction consisting mainly of clay minerals, show relatively high metal contents. In the silt and fine sand fractions the metal concentrations generally decrease as those fractions are dominated by quartz and feldspars with low metal contents, although the occurrence of heavy minerals may cause an increase in selected elements (VITAL & STATTEGGER, 2000; GARCIA et al., 2004; DINELLI et al., 2007).

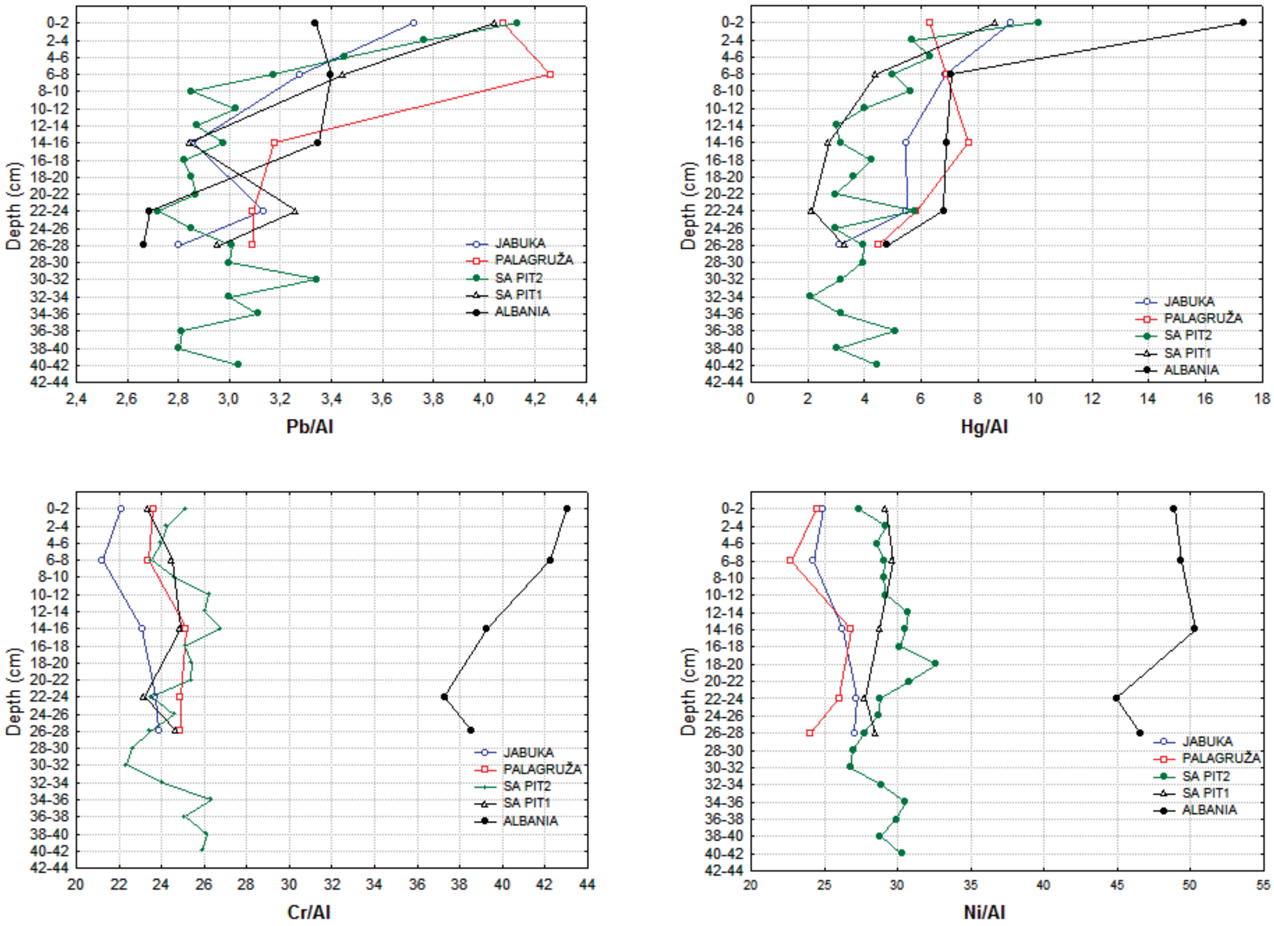

Figure 7: Down-core variability of Metal/Al-normalized values in the studied sediment cores.

The basic geochemical approach is to normalize geochemical data by means of a conservative component the levels of which are unaffected by contaminant inputs, for example, grain size, Al, Fe, Sc, Ni, TOC and Li. Consequently, changes/dilutions by the $CaCO_3$, silica, or organic matter content, especially in the upper layers, can be corrected (FÖRSTNER & WITTMANN, 1981) and be used for comparison with standard reference materials such average shale, upper crust (SHOTYK et al., 2001; VAN DER WEIJDEN, 2002). This approach has several limitations, and was not used in this study. In particular, concentrations for crustal abundances are not appropriate because they do not represent regional background levels because element ratios differ substantially from rock type to rock type and the ratios in actual rocks do not reflect calculated or modeled crustal ratios (REIMANN & DE CARITAT, 2005).

Typical normalization approaches identify one or several reference elements as a most frequently used conservative element. Aluminum is the most commonly used conservative normalization for trace element sediment data (VAN DER WEIJDEN, 2002, DI LEONARDO et al., 2006, SPAGNOLI et al., 2008), alternatively this element is replaced by Sc (SHOTYK et al., 2001). The concentration of normalizing metal is used to establish the relationship between natural trace metal concentrations in sediments from different areas. The normalization procedure with Al as a conservative element involving transitional elements was also widely used for provenance studies in the Adriatic basin. Here, Cr/Al and Ni/Al were useful geochemical tracers used to define sources of sediment to the Adriatic along the Western Adriatic Current and its mud belt (AMOROSI et al., 2002; LUCCHINI, et al.; 2003, DINELLI et al.; 2007; SPAGNOLI et al., 2008; AMOROSI, 2012; GOUDEAU et al., 2013). The normalization of element contents to a reference element was applied to compensate for grain size and mineralogical effects. Al and Ti are generally used to estimate the percentage of terrestrial materials in marine sediments, and to subtract the contribution of detrital materials when calculating the authigenic components of marine sediments. For both pelagic and terrigenous materials-dominated sediments, the Ti/Al ratio has also been found to reflect the average grain size of silicate minerals in marine sediments (SHOTYK et al., 2001).

Elevated heavy metal concentrations in the surface layers of marine sediments are also sometimes attributed to anthropogenic heavy metal input to the environment (VAN DER WEIJDEN, 2002). In order to verify possible anthropogenic input regarding heavy metals, enrichment factors of selected elements were calculated. Also the EFs were calculated for Ni and Cr to in order to identify possible temporal changes in the supply of these elements.

Table 3: Concentration values and enrichment factors (EF) for Pb, Hg, Cd, Zn, Cr and Ni in the top sections (0-2 cm) of the cores.

Core	Sediment interval (cm)	Depth (m)	Pb		Hg		Cd		Cu	
			(mg/kg)	EF	(mg/kg)	EF	(mg/kg)	EF	(mg/kg)	EF
JABUKA	0-2	230.8	20.7	1.3	51	2.9	0.11	1.3	31.78	1.1
PALAGRUŽA	0-2	169.8	20.7	1.3	32	1.4	0.11	1.4	25.48	1.4
SA PIT 1	0-2	1041.4	24.5	1.4	60	2.3	0.12	1.6	44.59	1.3
SA PIT 2	0-2	1030	23.9	1.4	51	2.6	0.09	1.4	42.51	1.4
ALBANIA	0-2	59	20.4	1.3	106	3.6	0.1	0.9	31.82	1.0

Core	Sediment interval (cm)	Depth (m)	Ni		Cr		Zn			
			(mg/kg)	EF	(mg/kg)	EF	(mg/kg)	EF		
JABUKA	0-2	230.8	141.3	0.9	77	0.9	85	1.1		
PALAGRUŽA	0-2	169.8	114.5	1.0	67	0.9	75	1.1		
SA PIT 1	0-2	1041.4	167.2	0.9	91	1.0	102	1.2		
SA PIT 2	0-2	1030	164.2	1.0	94	0.9	85	1.1		
ALBANIA	0-2	59	268.2	1.1	152	1.1	103	1.1		

Supplementary Table 3: Mean values of metal/Al ratios in surface sediments and cores along the Eastern Adriatic Current (EAC) transect going from ALBANIA to the Gulf of Trieste (**NAS Tri**), and along the Western Adriatic Current (WAC) transect along the coast of Italy to the southern Adriatic. Expl. **ALBANIA, SAPIT1, SAPIT2, PALAGRUŽA, JABUKA** cores from this study. Data from DOLENEC et al., (1998) was classified as follows **SAS ALB** south Adriatic sediments along the Albanian coast, **SAS Cro** south Adriatic sediments along the Croatian coast, **CASJABUKA** sediments from the Meso-Adriatic Depression, **CASCro** central Adriatic sediments along the Croatian coast, **NASCroa** northern Adriatic sediments along the Croatian coast, NASTri sediments from the Gulf of Trieste, **NASPo** northern Adriatic sediments under the influence of the Po River, **NASap** northern Adriatic sediments along the eastern coast of Italy, **SASap** southern Adriatic sediments along the coast of Italy. The data shown for **Gargano** peninsula and the Gulf of **Manfredonia** is from GOUDEAU et al. (2013).

		Ca/Al	Al/Ti	Cr/Al	Ni/Al	Hg/Al	Pb/Al	Zn/Al	Cu/Al	As/Al
ALBANIA*	EAC	0.77	18.2	40.1	48.0	155	3.09	16.1	6.27	3.38
SAS ALB^a		1.69	20.9	20.6	1.0	337	1.88	14.5	7.51	1.58
SA PIT2*		1.76	23.0	24.8	29.3	100	3.07	13.9	6.36	4.05
SA PIT1*		1.76	22.7	24.1	28.8	97	3.31	13.7	6.48	2.97
SAS Cro^a		2.17	21.5	33.9	36.1	448	2.74	16.0	5.95	3.62
PALAGRUŽA*		3.05	23.0	24.4	24.8	143	3.54	13.8	4.38	1.49
JABUKA*		1.93	24.4	22.8	25.9	149	3.16	14.8	5.13	2.31
CAS JABUKA^a		2.43	22.8	26.0	26.3	677	2.21	16.3	5.52	0.51
CAS Cro^a		4.57	20.8	35.6	33.4	525	3.49	17.3	5.69	4.72
NAS Cro^a		4.42	13.6	19.2	9.1	1737	4.26	14.0	3.02	1.03
NAS Tri^a	WAC	2.51	19.3	18.1	13.1	1729	5.03	20.8	5.59	0.99
NAS Po^a		2.90	20.7	17.6	9.7	1451	5.15	19.1	3.51	0.61
NAS Ap^a		2.26	23.0	13.8	8.0	2959	2.30	15.5	4.71	0.52
CAS Ap^a		2.83	22.5	19.9	18.7	775	2.49	16.0	5.61	3.28
Gargano^b		1.65	nd	19.1	13.9	nd	nd	9.7	4.20	nd
Manfredonia^b		1.87	nd	18.9	12.4	nd	nd	10.8	4.30	nd
SAS Ap^a		2.49	21.2	12.4	10.9	612	2.25	13.8	6.60	0.60

*This study, ^{a} DOLENEC et al., 1998; ^{b} GOUDEAU et al., (2013); nd-no data.

The estimation of heavy metal enrichment (VAN DER WEIJDEN, 2002) was made by a calculation procedure which uses concentrations of heavy metals and conservative elements from deeper layers (RIDGWAY & SHIMMIELD, 2002) as background reference for the uppermost sediments. The EF is a concentration ratio of a given element ($C_{nsample}$) to the conservative element (Al in this study) in the sample ($C_{cons.sample}$) with respect to the same ratio in the reference

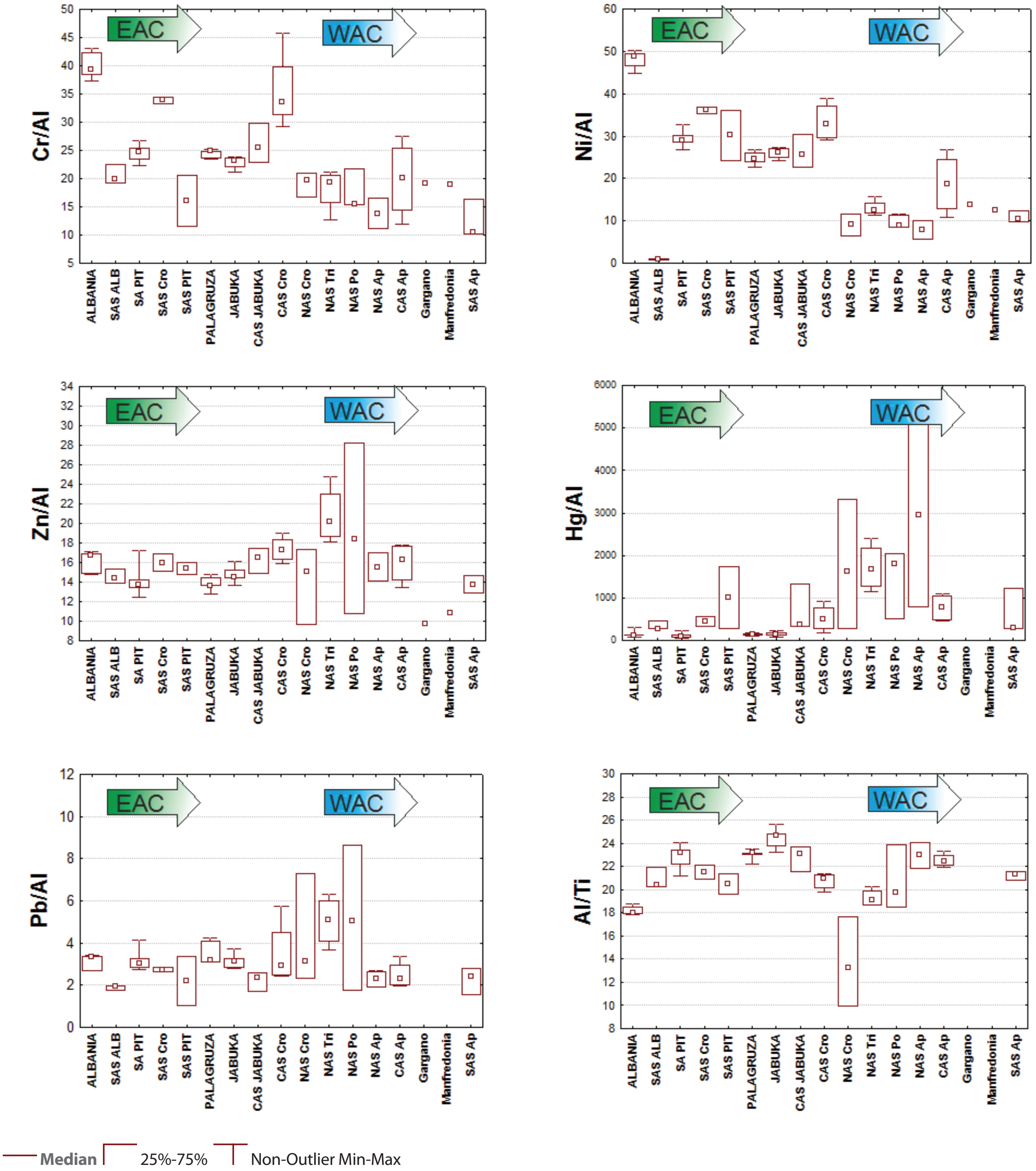

Figure 8: Box plots of metal/Al ratios in surface sediments and cores along the Eastern Adriatic Current (EAC) transect going from ALBANIA to the Gulf of Trieste (NAS Tri), and along the Western Adriatic Current (WAC) transect along the coast of Italy to the southern Adriatic. Expl. **ALBANIA, SAPIT (1&2), PALAGRUŽA, JABUKA** cores from this study. Data from DOLENEC et al., (1998) was classified as follows **SAS ALB** south Adriatic sediments along the Albanian coast, **SAS Cro** south Adriatic sediments along the Croatian coast, **CASJABUKA** sediments from the Meso-Adriatic Depression, **CASCro** central Adriatic sediments along the Croatian coast, **NAS Cro** northern Adriatic sediments along the Croatian coast, **NAS Tri** sediments from the Gulf of Trieste, **NAS Po** northern Adriatic sediments under the influence of the Po River, **NASap** northern Adriatic sediments along the eastern coast of Italy, **SAS Ap** southern Adriatic sediments along the coast of Italy. The data shown for **Gargano** peninsula and the Gulf of **Manfredonia** are from GOUDEAU et al., (2013).

material $C_{n\ ref.}/C_{cons.\ ref.}$ (FÖRSTNER & WITTMANN, 1981; LI, 1981):

$$EF = (C_{nsample}/C_{cons.sample}) / (C_{n\ ref.}/C_{cons.\ ref.}).$$

Five degrees of contamination are commonly defined (SUTHERLAND, 2000): EF < 2: deficiency to low enrichment; EF 2–5: moderate enrichment; EF 5–20: significant enrichment; EF 20–40: very high enrichment; EF > 40: extremely high enrichment. The down-core variations of Pb/Al, Hg/Al, Zn/Al, Cr/Al and Ni/Al (Figure 7) in general show some smoothing of the profiles, in comparison with elemental distributions. Hg, and Pb show distinct higher values in the top sediment intervals. Generally the Cr/Al and Ni/Al ratios decrease from the Albania core (40.1 and 48.0 respectively) along the EAC transect to the Jabuka core (22.8 and 25.9 respectively; Supplementary Table 3, Figures 7 and 8). Since the metal/Al ratios can be applied to determine metal excesses or to account for natural changes, they were used to give an insight to the changes in trace metal proportions along the transect of the Eastern Adriatic Current (EAC) from Albania, along the Croatian coastal islands, through the Northern Adriatic and then along the Western Adriatic Current (WAC) to the south. An overview of the provenance of surface sediments along the WAC on the southeastern coast of Italy was given by GOUDEAU et al. (2013). They used a multi-proxy approach which included Cr/Al and Ni/Al ratios. These data were used together with the ratios calculated from the data of DOLENEC et al. (1998).

Ratios of Cr and Ni (the trace metals used in provenance studies), (AMOROSI et al., 2002; LUCCHINI, et al., 2003; DINELLI et al., 2007; SPAGNOLI et al., 2008; AMOROSI, 2012; GOUDEAU et al., 2013), are significantly different (higher) in the southern and central Adriatic along the EAC (Figures 8 and 9), compared to those of the surface sediments of the Northern Adriatic and along the WAC (lower). GAUDEAU et al. (2013) give a Cr/Al ratio of 27.3 for the Po River and an approximate value of 15.5 for sediments influenced by the Apennine rivers. The Gargano peninsula sediments and the Gulf of Manfredonia have mean higher Cr/Al ratios of 19.1 and 18.1, respectively. The values of these ratios are similar to those given by LUCCHINI et al. (2003) for the Adriatic shelf cores of both Holocene and Pliocene age. The Cr/Al ratios for Holocene sediments from the MAD and SA cores given by LUCCHINI et al. (2003) have mean values higher than 23 that correspond to the Cr/Al ratios in the SA PIT cores (24.8), Palagruža core (24.4) and the Jabuka core (26.0). The Pleistocene sediments from the cores in the Mid Adriatic Depression have Cr/Al ratios lower than 20 and are comparable to the Adriatic shelf Cr/Al ratios (LUCCHINI et al., 2003). The high Cr/Al (40.1) ratio from Albania, which is a signature of weathering and erosion of catchments Mirdita ophiolitic sequences, is carried as the "Albanian flux" (TOMADIN, 2000) along the EAC. The plotted Cr/Al vs Ni/Al ratios (Figure 9) for the analysed cores and the data from DOLENEC et al. (1998) and GOUDEAU et al. (2013) showed that a linear dilution path between Albania and the Apennine (WAC) signature is distorted. This indicates the possible influence of another source that is decreasing the ratios, possibly from the Dinaric/Dalmatian source of minerals. The distortion could also be attributed due to preferential changes in grain size towards finer fractions which were not compensated by the normalization procedure. Both of these issues need to be addressed in the future through more detailed studies on a larger sample and methods with more discriminating power (not just bulk geochemical data), as well as more data from the eastern Adriatic coastal sediments.

The ratios from the Palagruža core show a tendency towards the Apennine ratios indicating a possible influence from the WAC (Figure 9). The mean Ca/Al ratios (Supplementary Table 3) along the AEC indicates an increase of calcite/carbonate from Albania (0.77) along the eastern side of the Northern Adriatic (4.42) and then a decrease along the WAC (2.26) and the Gargano peninsula and Gulf of Manfre-

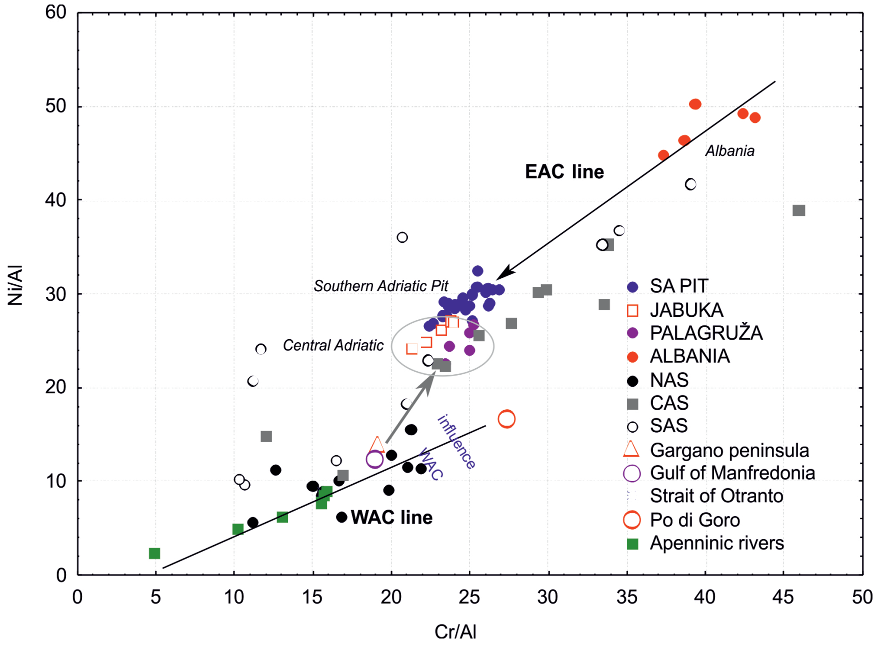

Figure 9: The relationship between Ni/Al and Cr/Al ratios. The ALBANIA, SA PIT, PALAGRUŽA, JABUKA cores are from this study. Data from DOLENEC et al. (1998) includes the SAS-South Adriatic sediments, CAS-Central Adiatic sediments; NAS-North Adriatic sediments. The data shown for the Gargano peninsula, Gulf of Manfredonia, Strait of Otranto, Po di Goro and the Apenninic Rivers are from GOUDEAU et al. (2013).

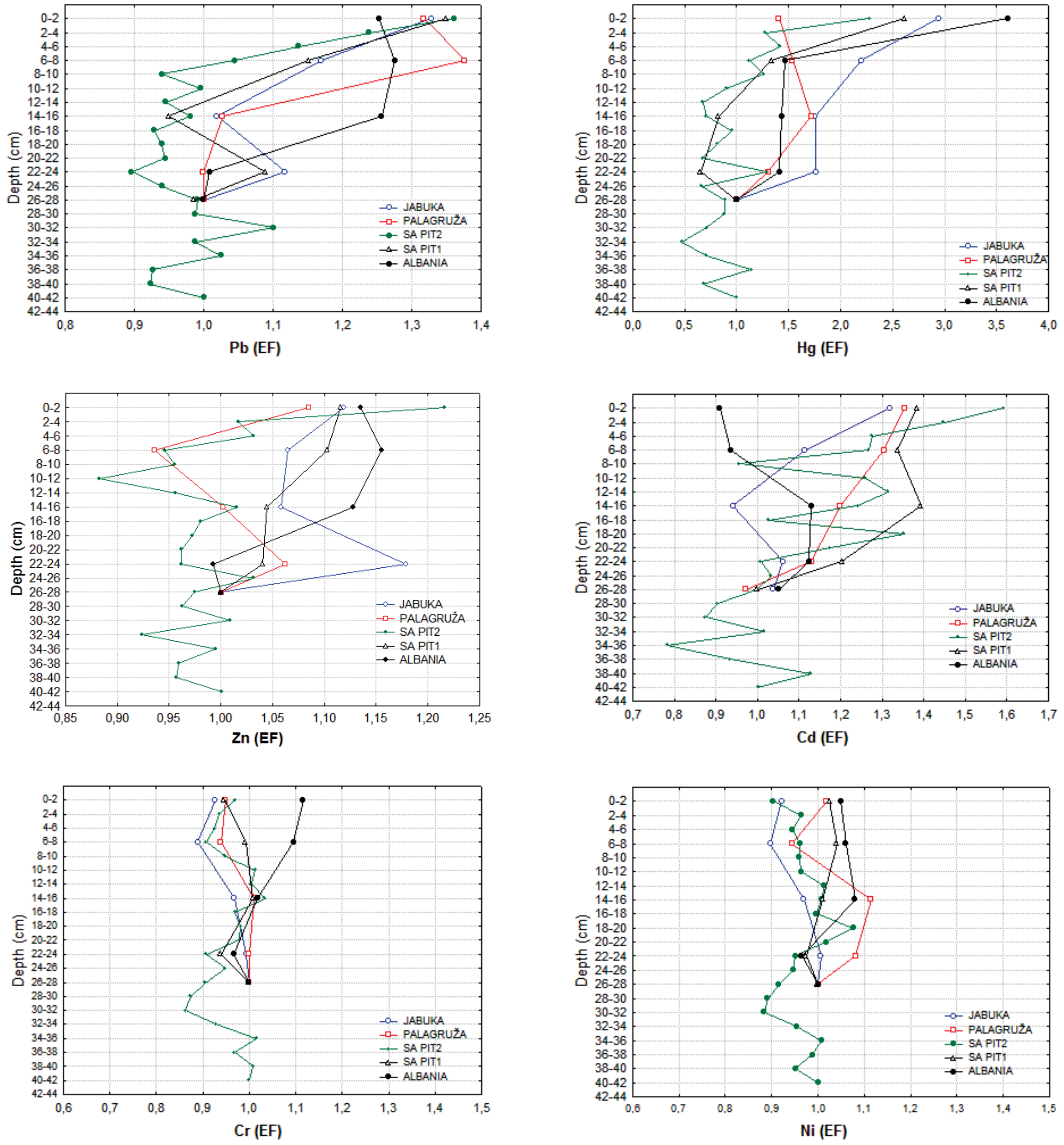

Figure 10: Enrichment factors (EF) estimated for Pb, Hg, Zn, Cd, Ni and Cr.

donia have Ca/Al ratios (average 1.65 and 1.87) similar to the SA PIT (1.76) cores.

The ratios for "pollution elements", Pb/Al, Hg/Al and Zn/Al (Supplementary Table 3, Figure 8) were only available for the data from DOLENEC et al., (1998) and show that the lowest values are in the southern and central part of the eastern Adriatic and that high values characterise the northern Adriatic sediments.

The down-core distribution of estimated EFs for Hg, Cd, Zn, Cu, Pb, Ni and Cr are given in Figure 10. The calculated EFs for the top interval (0–2 cm) of each core are given in Table 3. The estimated EFs in the sediments show that only Hg can be considered as a moderate contaminant in the analyzed cores. Other elements have EF>2 but based on the classification by SUTHERLAND (2000) contaminating enrichment of trace metals has not occurred. Generally the estimated surface enrichment follows the order: Hg>Pb>Cd, the estimated EFs for Zn, Ni and Cr do not indicate any degree of enrichment. Mercury has the highest calculated EF of 3.6 in the Albania core while the Palagruža core has the lowest one (1.4). DOLENEC et al. (1998) concluded that most of the Hg has a source in the northern Adriatic with minor influences from the eastern coast of the Adriatic. The possible contribution from the eastern coast was detected by CUCULIĆ et al. (2009) who measured 10 times higher than average Hg concentrations in Malo Jezero on Mljet Island (located along the rim of South Adriatic Pit) during a heavy rainfall event with strong easterly winds.

6. CONCLUSIONS

This study reports the concentrations of the eight trace elements usually identified as priority contaminants in aquatic systems As, Cd, Cr, Cu, Hg, Ni, Pb and Zn as well as Mo, Mn, Al, Ti and Ca as lithogenic elements, in 5 short marine sediment cores, collected at locations on a transect along the western rim of the southern part of the Eastern Adriatic Current (EAC).

The sediment accumulation rate for the Palagruža Sill and the South Adriatic Pit is ~0.18 cmy^{-1} and the top 10 cm interval of the sediment core represents approximately 50 years and a 40 cm core could have an equivalent to 200 years of deposition. The Jabuka and Albania cores presumably span shorter times (approximately 130 and 100 years, respectively). The sediments are highly heterogeneous and consist of carbonate and detrital aluminosilicates. The main mineral phase is calcite, followed by quartz, feldspars, micas and clay minerals (smectite, chlorite, illite and kaolinite).

The trace metal down-core distributions and relations with mineral and clay composition allowed the distinction of several groups of trace metals. The "pollution elements" Pb, and Hg showed increased concentrations in the top sections of the cores.

Concentrations of redox-sensitive metals, Mn and Mo have vertical distributions that followed similar patterns and were used to identify the redox state of sediments. The down-core distribution of redox-sensitive trace metals are complex in the South Adriatic Pit core.

The metal/Al ratios were applied to determine metal excesses or to account for natural changes. They were used to give an insight to the changes in trace metals along transect of the Eastern Adriatic Current (EAC) from Albania, along the Croatian coastal islands through the Northern Adriatic, and then along the Western Adriatic Current (WAC) to the south. The Cr/Al and Ni/Al ratios used for provenance discrimination have ratios that are significantly different (higher) in the southern and central Adriatic along the EAC compared to those of the surface sediments of the Northern Adriatic and along the WAC (lower).

The plotted Cr/Al vs Ni/Al ratios for the analysed cores, along with the available literature data (DOLENEC at al., 1998; GOUDEAU et al., 2013) show that a linear dilution path between Albania (along the AEC) and the Apennine (WAC) signature is distorted. This could indicate the potential influence of another source that is decreasing the ratios, possibly from the Dinaric/Dalmatian source of minerals. The distortion could also be attributed to preferential changes in grain size towards the finer fractions which were not compensated by the normalization procedure. Both of these issues need to be addressed in the future through more detailed studies on a larger sample and methods with more discriminating power (not just bulk geochemical data), as well as more data from the eastern Adriatic coastal sediments.

Generally, the surface estimated enrichment follows the order: Hg>Pb>Cd, the estimated EFs for Zn, Ni and Cr do not indicate any enrichment. The estimated EFs in the sediments show that only Hg can be considered as a contaminant in the analyzed sediments.

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