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Contamination of seabed sediments around a shipyard in the Adriatic Sea (Ugljan island)

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ABSTRACT

Geochemical, mineralogical and grain size data from sediment cores in the Lamjana Bay shipyard were obtained to determine the extent of contamination due to ship refits. The concentration and distribution of Ni, Pb, Cr, Zn, Cu, Mn, Cd, As and Fe in 9 sediment samples were measured. No increase of the analysed elements above natural background levels was detected, but contamination was not excluded due to possible dilution of seabed sediment by quartz sand used in process of abrasive blasting.

Keywords: marine sediment, geochemistry, contamination, shipyard, adriatic Sea

1. INTRODUCTION

Lamjana Vela Bay is located in the southwestern part of Ugljan Island, one of the islands of the North Dalmatia region. Ugljan Island is the most inhabited island of the Zadar archipelago in Croatia (MAGAŠ & FARIČIĆ, 2000). The investigated area has been used as a shipyard for ship remounts (repairs) since 1978. The shipyard is located in a natural bay, 300 m wide and up to 30 m deep. The area of interest is shown in Figure 1. The surrounding terrain is composed of Cretaceous and Eocene limestone (MAJCEN et al., 1970). This shipyard has been studied as a source of possible contamination of the seabed sediments as connections between harbour activities and contamination of seabed sediment have been demonstrated in many publications (GIBBS & GUERRA, 1997; CEULEMANS et al., 1998; TURNER, 2010; FATOKI & MATHABATHA, 2001; CHAMP, 2003). As a result of similar activity, the most common alterations in seabed sediments are an increase in toxic metals, harmful organotin compounds from antifouling paints, and quartz sand used in the process of abrasive blasting. The Raša River estuary was used not only as a natural model control system to study the accumulation pattern in a similar environment (SONDI et al., 1994; 2008), but also for observing the fate of the heavy metal contaminants, studied in this investigation.

2. MATERIALS AND METHODS

2.1. Sampling

Four sediment samples were collected with a corer by SCUBA diving. These were frozen and divided into smaller sub-samples, each 2 cm thick. Full depth of each core sample was approximately 30 cm. Each core was not analysed in total i.e. not all sub-samples from one core were analysed, but rather only the upper-most part (0–2 cm depth); middle part (6–8 cm depth), and deepest part of the core (13–15 cm depth). All together, nine sub-samples were analysed. Water depths where the samples were taken ranged from 8 to 30 m, and all samples were taken along a single line transect

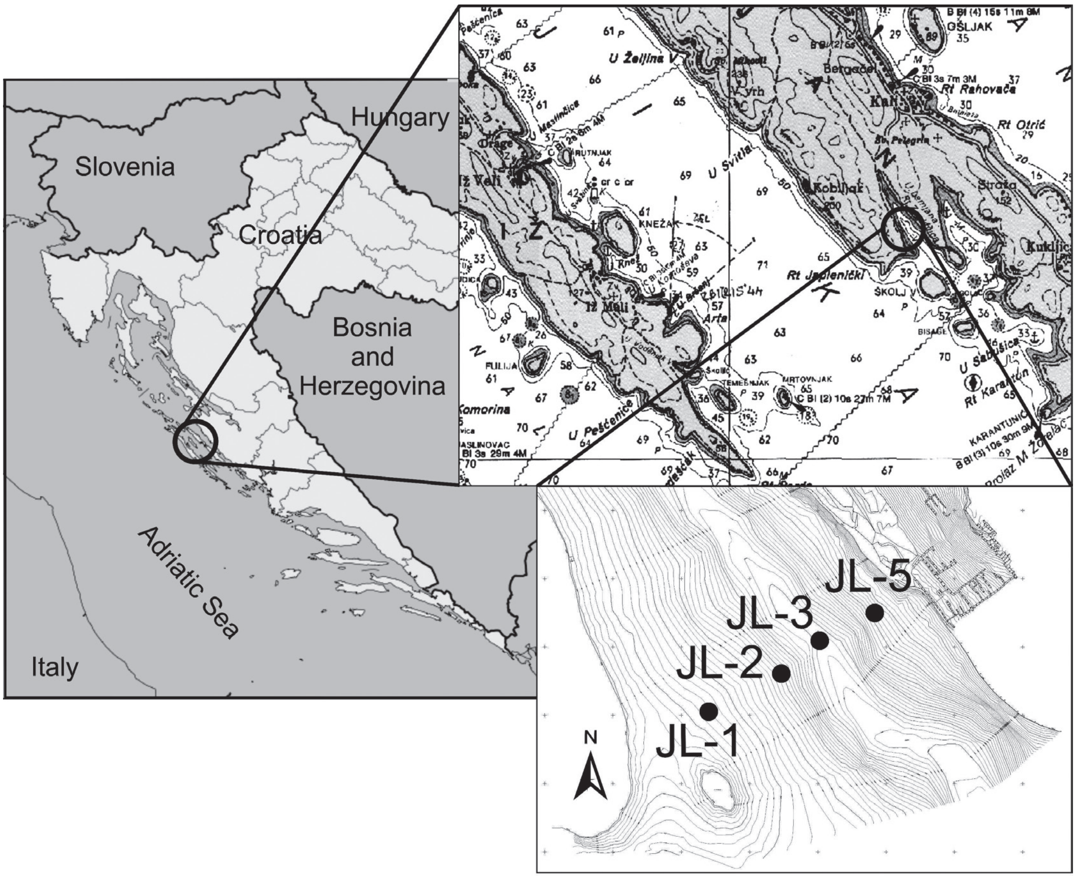

Figure 1: Geographic location of the study area with the sampling sites.

(Fig. 1.). Before further analyses, sub-samples were dried at 50°C and homogenized.

2.2. Grain-size analysis

Grain-size analyses were accomplished on all nine dry samples. Sediment grain-size distribution was performed by wet sieving using ASTM standard stainless steel sieves. The Internationally accepted classification of sediments (FOLK, 1954) was used to classify samples.

2.3. Mineralogical analysis

The mineralogical composition was determined by X-ray powder diffraction (XRD) on a Philips X-pert diffractometer using CuKα radiation. It was applied to three sub-samples from the core taken in the deepest part of the bay, in 30 m of water. Analyses were done on the upper-most part of the core (0–2 cm), middle part of the core (6–8 cm), and deepest part (13–15 cm). The main objective was to identify the mineral composition of the sediment and to see if there were changes connected with the depth of the seabed.

2.4. Chemical analysis

The size fraction below 63 μm was used for the chemical analyses. Nickel, Pb, Cr, Zn, Cu, Mn, Cd, As and Fe were determined by AAS with a PerkinElmer AAnalyst700. Estimates of total concentrations, or “pseudo-totals”, were determined by digesting with aqua regia, for which a widely used procedure was used, one standardized by ISO international standards (ISO 11466 1995).

RESULTS

3.1. Grain-size analysis

The results of the grain size analysis are shown in a Table 1. According to FOLK’S (1954) sediment classification, five samples were sand; three were muddy sand and only one was slightly gravelly sand (Fig. 2.). In all samples, sand was a dominant fraction. The results show an absence of vertical

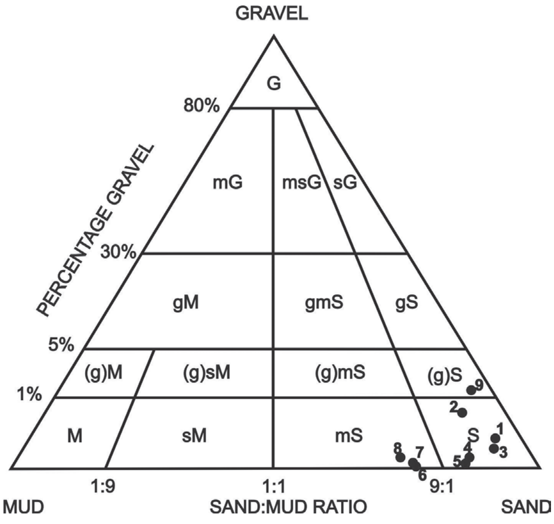

Figure 2: FOLK classification diagram (1954) with the samples according to their analyses.

Table 1: Results of the grain size analysis.

Sample		Seabed depth (cm)	Gravel %	Sand %	Mud %	Sediment type
JL 1a	1	0-2	6	89	5	Sand
JL 1d	2	6-8	12	80	9	Sand
JL 2a	3	0-2	4	90	6	Sand
JL 2d	4	6-8	2	86	12	Sand
JL 2g	5	12-14	1	86	13	Sand
JL 3a	6	0-2	/	77	23	Muddy sand
JL 3d	7	6-8	1	76	23	Muddy sand
JL 3h	8	12-14	2	73	25	Muddy sand
JL 5	9	0-2	17	79	4	Slightly gravelly sand

change in grain size, but some distinctions between samples were observed. Samples with the highest proportion of mud were from the deepest point in the bay. Sample JL 5, the one taken closest to the shipyard, cannot be seen as being representative, since the area of sampling was in a zone of shipyard reconstruction where the seabed was covered with concrete blocks. Data from a previous investigation of seabed and surface sediments can be found for the Kvarner region (JURAČIĆ et al., 1999), located north of the study area, and so can be used for comparison, with expectancy in similar sediment grain size distribution for both areas. In Kvarner region, the prevalent type of sediment is sandy mud, while in Lamjana Bay it is sand (i.e. muddy sand) in deeper areas of the bay. The differences between these results could be

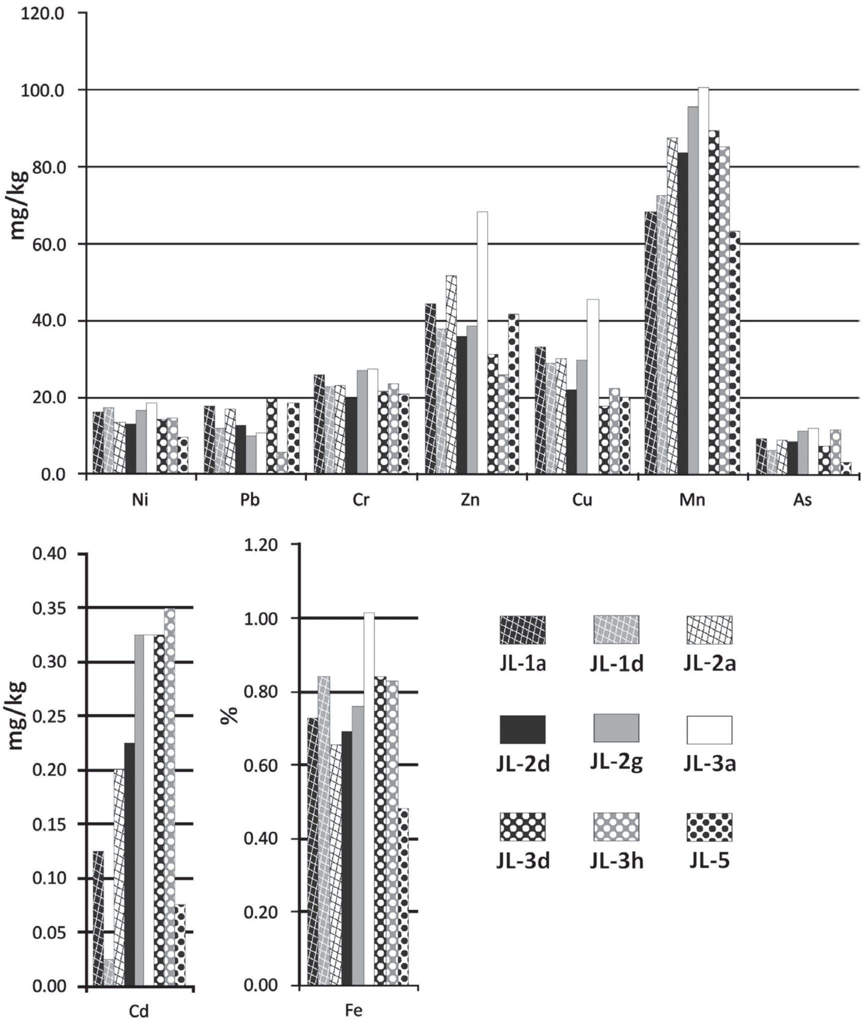

Figure 3: Distribution of elements in accordance with depth and sample locations.

Table 2: Basic statistical parameters of Ni, Pb, Cr, Zn, Cu, Mn, As and Cu expressed in mg/kg; Fe expressed in %. N – number of results, $\bar{x}$ – mean value, SD – standard deviation.

Statistical parameter	Ni	Pb	Cr	Zn	Cu	Mn	As	Cd	Fe *
N	9	9	9	9	9	9	9	9	9
$\bar{x}$ (mg/kg)	14.87	13.91	23.51	41.68	27.77	82.89	8.63	0.22	0.76
SD (mg/kg)	2.68	4.64	2.70	12.43	8.49	12.52	2.92	0.12	0.15
Min. (mg/kg)	9.68	5.98	19.65	25.70	17.73	63.30	2.90	0.03	0.48
Max. (mg/kg)	18.63	19.80	27.30	68.28	45.60	100.70	12.08	0.35	1.01
Median (mg/kg)	14.50	12.93	23.15	38.53	29.13	85.15	8.83	0.23	0.76
O. & V. (a)	15.50	9.80	43.90	33.60	16.20	75.60	6.60	/	/
O. & V. (b)	/	249.00	/	2777.40	3467.90	/	95.70	/	/
D. et al.	34.00	27.00	73.00	64.00	15.00	242.00	9.00	/	1.79

* Statistical parameters for Fe are expressed in %
O. & V. (a) – Natural background values from OBHOĐAŠ and VALKOVIĆ (2010)
O. & V. (b) – Values from marine service areas from OBHOĐAŠ and VALKOVIĆ (2010)
D. et al. – Natural background values. location "v70" from DOLENC et al. (1998)

connected with the process of abrasive blasting during shipyard activities, in which tonnes of quartz sand were used, which ended up in the bay.

3.2. Results of mineralogical analysis

The results of the three analysed samples were uniform. Subsamples were taken from one core, and vertical variation was not observed. In all samples quartz, calcite and aragonite were determined. After analysis of the bulk mineralogical composition, the samples were treated with HCl (1:5) to dissolve the carbonate components, after which they were again analysed. When carbonate components were removed, quartz, mica and plagioclase minerals were detected.

3.3. Results of Chemical analysis

The chemical analysis for "pseudo-total" concentrations of the observed elements (Ni, Pb, Cr, Zn, Cu, Mn, Cd, As and Fe) and their distribution are presented in Fig. 3. The results can be divided into two groups. The first group consists of elements Ni, Cr and As. These elements show uniformity (horizontal and vertical); the concentration of certain elements does not change considerably with the depth, with a mean value for Ni, Cr and As as follows: 14.9 ± 2.68, 23.5 ± 2.70 and 8.6 ± 2.92 mg/kg. In the second group, the elements include Pb, Zn, Cu, Mn, Cd and Fe with a mean value: 13.9 ± 4.64, 41.7 ± 12.43, 27.8 ± 8.49, 82.9 ± 12.52, 0.2 ± 0.12 mg/kg; 0.8 ± 0.15 %, respectively. These show differences in concentration according to the depth of the sub-sample, as well as a lateral difference i.e. differences between samples.

4. DISCUSSION

Geochemical results are often hard to interpret, due to the complexity of seabed genesis, anthropogenic impact and frequent absence of background information. There is no previous analysis of the study area, though two studies (OBHOĐAŠ & VALKOVIĆ, 2010; DOLENC et al., 1998) provide a frame of reference from which to work. OBHOĐAŠ & VALKOVIĆ (2010) published natural background values for concentrations of chemical elements in coastal sediments of the Eastern Adriatic Sea, calculated from 101 samples in the region. DOLENC et al. (1998) reported measurements of major, minor and trace elements for 35 locations in the Adriatic. Their "Sample 70" best compares with the location of Lamjana Bay. Results from these two publications were used to indicate possible natural background values for Lamjana Bay as they are the most suitable according to location and proximity. SONDI et al. (1994, 2008) indicated the possibility of contaminants bound to particles, mostly heavy metals, such as strong adsorption to clay minerals, and their organic coating. The basic statistical parameters of measured elements (Ni, Pb, Cr, Zn, Cu, Mn, As, Fe and Cu) from all samples are presented in Table 2.

The concentrations of all elements of interest in Lamjana Bay, except Cu, are within the background range and no amplification from natural background values was detected. The higher value of Cu in the sediments can be due to the use of anti-fouling paints in the shipyard, which up until the late 1960s were almost invariably copper based (WALKER et al., 2005). From these results, it can be concluded that the shipyard only has a negative influence on sediment with respect to an increase in the Cu value. Still, it should be kept in mind that the large quantity of quartz sand used in the process of abrasive blasting may have diluted sediment pollution, as has already been noticed (KENNICUTT et al. 1996). Further, while analysing the results of chemical analysis, it should be considered that the quartz dilution depends on its content in the <63 µm fraction, in which it has been detected.

OBHOĐAŠ & VALKOVIĆ (2010) investigated both natural background values and concentrations of chemical elements in sediments around a marina service area. As presumed, the concentration of analysed elements in the marina service area was several orders of magnitude greater than the background values.

The element showing the least increase was arsenic. Its concentration in the sediment of the marina service area is

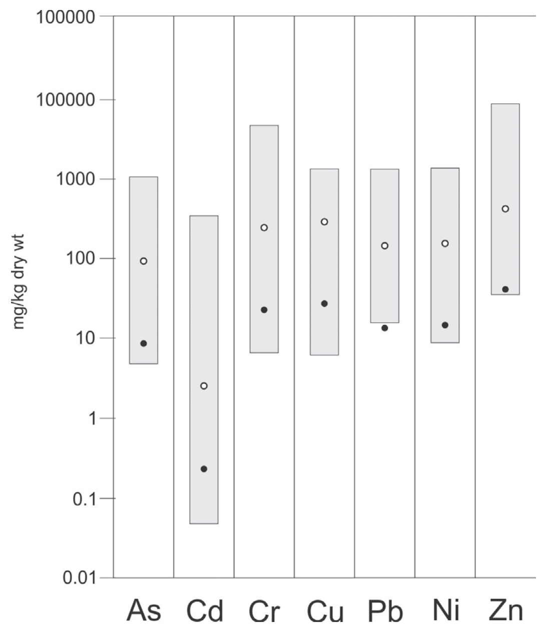

Figure 4: The range of world-wide sediment quality values (moderately contaminated sediments) for selected metals and a metalloid (grey zone) (CHAPMAN & MANN, 1999), with the mean value of observed elements (black dot), and one order of magnitude amplified values (white dot).

14.5 times the natural background values. With an assumption that pollution levels will be similar in similar conditions (a marina service area), it is possible to estimate the amount that the quartz debris diluted the pollution levels. From the value of As (95.7 mg/kg) in the marine pier service area (OBHOĐAŠ & VALKOVIĆ, 2010) and that recorded in Lamjana Bay (8,63 mg/kg), the dilution of seabed sediment by quartz could be determined. The estimated values and that recorded in Lamjana Bay differ by one order of magnitude. It follows from these results that the values of the other observed elements are also one order of magnitude greater in terms of their input into the environment, but due to the high amount of quartz, the recorded values are lower.

Results of the sampled sediment from Lamjana Bay do not vary significantly from the natural background values; hence the sediment could be considered as unpolluted. But if the measured values are enlarged by one order of magnitude (the assumed dilution factor), then the situation is rather different. In that scenario, the value of lead, iron, copper, and zinc would be greater than the natural background value, which can be connected to the shipyard and quantity of abrasives used in the refurbishing process (ALEBIC-JURETIC & MATKOVIC, 2000; SINGH & TURNER, 2009). Figure 4 shows a comparison of the measured values (mean) with the different international values for sediment quality criteria, which show the range in which sediments in seawater are considered uncontaminated, moderately contaminated and highly contaminated (CHAPMAN et al., 1999).

Concentrations below the grey field are unlikely to have adverse biological effects, and concentrations above the grey field are very likely to have severe adverse biological effects. The grey zone can be observed as suitable for open water marine disposal (CHAPMAN et al., 1999). The range is large since it is a comparison of different international values. All values of the analysed elements from Lamjana Bay sediments, except Pb, are in the lower part of the “moderately contaminated” range, and for one shipyard environment, these results are satisfactory.

5. CONCLUSONS

Geochemical analyses of sediments from the studied shipyard are showing values commensurate with a range of a background values. Nevertheless, a conclusion of no pollution from the shipyard activities should be made with caution due to the high amount of quartz used with the ship refitting and its subsequent dilution effect on the seabed sediment.

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