POLLUTION OF THE PUNAT BAY BY Zn, Cu AND Pb

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ABSTRACT

Distribution of heavy metals Zn, Cu and Pb in the water column and sediments of the Punat Bay is presented. Measurements of sea currents and concentrations of metals in the water column and sediments are used to estimate the total inflow rate in the bay by an inverse modeling method. Reliability of estimated input is assessed by comparison to an independed set of data.

1. Introduction

Pollution of coastal waters by heavy metals comes as a waste from sites of human activities. Among them are shipyards, harbours, chemical industry and households waste[1]. Since the precise locations of sources of heavy metals are often unknown or the input is discontinuous, an average inflow rate can not be determined in a direct way, instead an inverse modelling method should be used[2,3,4,5].

The objectives in this paper are to:

a) report on concentrations of Zn, Cu and Pb in water and recent sediment of the Punat Bay,

b) to estimate the total inflow rate of the above metals that comes from the coast into the bay.

2. Theory

We consider the transport of metal in a basin with a flat bottom. The transport is caused by two mechanisms: current field, and turbulent diffusion. The name current field is reserved here for the average current field, i.e. the one obtained after the statistical averaging. In addition, it is supposed that the conventional steady state transport equation for concentration C of nutrient in two dimensions can be used as the basic model:

$$-\alpha\Delta C + v\nabla C + E(c) = q \quad (1)$$

The parameter α is the turbulent diffusion coefficient, v is the current field in considered two-dimensional basin, E is the extinction function and q is the input. The parameters v, E and q are functions, while α is supposed to be a constant. The model (1) is valid at all interior points of the basin. In order to obtain the unique solution C from given parameters, boundary conditions must be supplied to equation (1).

Because of a small concentrations of metals in water, the extinction function E(C) is linearized:

$E(C) = k(C-C_n)$,

where C_n is the background concentration. Therefore, we can use the reduced concentration $c = C-C_n$ in (1) and obtain the following linear law of transport:

$$-\Delta c + v\nabla c + kc = q \quad (2)$$

The bacground concentration is assumed to be a constant while k is a function.

The main task in our study is to connect the concentrations in water and sediment by a relation. In the case of dominant lateral transport of particles and consequently an uniform sedimentation over the considered basin, even one-dimensional models[6] can be efficiently used. Data on concentrations in sediments of the Punat Bay show that the sedimentation of metals as well as other nutrients is not uniform, implying that the vertical transport, i.e. sedimentation, is dominant. Hence, the reduced trace element concentration in sediment s(r) at a location r is proportional to the corresponding concentration c(r) in water at the same location, so that

$$\frac{s(r)}{c(r)} = \lambda k(r)/w(r), \qquad (3)$$

where w(r) is the annual width of sediment at the location r, and λ is the scaling factor.

Now we define our problem.

Find c(r), k(r), q(r) and the natural concentration S_n in sediment so that

(i) the transport in water is defined by (2)

(ii) the mean calculated concentration in water is equal to the mean measured concentration:

$$\sum_{j=1} c(r_j) = \sum_{j=1} c_{ms,j} ;$$

(iii) the least squares error between calculated and measured concentrations in sediment:

$$\mathcal{E}(c,k,q,S) = \sum_{j=1} (s(r_j) - S_{ms,j})^2$$

accepts the minimum value.

3. Experimental methods

Trace element analysis of water and sediment samples was performed using X-ray emission specroscopy as an analytical tool. In our measurements sample irradiation was accomplished with photons obtained from an X-ray tube with a Mo-anode and scattered at a Mo and Eu target. A Phillips X-ray apparatus model PW 1010/30 was used with working parameters of 34 kV and 16 mA. Irradiation time was 1000s. A Si(Li) detector was used for X-ray detection. This enabled the simultaneous detection of characteristic K-lines of elements with $Z \leq 70$, with very low background intensity.

Prior to analysis, sediment samples were dried for two days at 150° C, and then sieved and grounded to dust.

Concentration of trace elements in the sea water are often on the ppb level, therefore a suitable preconcentration procedure must be applied. In our measurements water samples were collected using teflon sampler[7]. Samples were transported to the laboratory in clean polyethylene one liter containers, and 10ml of 10% HNO_3 were added to prevent losses of heavy metals. All the samples were prepared for X-ray analysis by complexation with chelating agent ammonium- pyrroldine-dithiocarbamate (APDC)[8,9].

After complexation the suspension was filtered through membrane filter and irradiated.

4. Numerical methods

The tidal current in the bay is calculated by using standard models of tidal currents with included Coriolis force[10], where the bottom friction and tidal level in the gate are determined by fitting theoretical solutions to data. Similarly, the residual current, caused by underwater springs of fresh water is calculated from the data on salinity[4]. The sum of two reconstructed current fields is assumed to be the mean current field in the bay. Fluctuations of this current field are obtained by Monte Carlo methods.

The diffusion constant is determined using the Okubo formula[11]. The extinction parameter k in (1) is estimated by solving the main problem of Section 2. In this way the neccessary parameters and input of the model (1) have been determined.

The linearity of the model (2) enables us to decompose the reduced concentration field into components, each being caused by one of studied inputs

$$c = c_0 + c_1 + c_2 + c_3 + c_4, \qquad (4)$$

where the indices, 0,1,2,3,4, refer to the yacht harbour, collector, shipyard, marina working area and beach, respectively. Let B_i, $1 \le i \le 4$, be portions of the boundary at the four boundary points r_i, $1 \le r \le 4$ through which inputs enter the bay and let D_o be a region covering yacht harbour as illustrated in the Fig.1. The remaining part of the boundary, together with the open boundary, is denoted by B_r. Five concentration fields(4) satisfy the following transport equations:

$$
\begin{aligned}
-\alpha\Delta c_o + v\nabla c_o + kc_o &= q, \\
-\alpha\Delta c_i + v\nabla c_i + kc_i &= 0, \quad 1 \le i \le 4,
\end{aligned}
\qquad (5)
$$

and fulfill the following boundary conditions

$$
\begin{aligned}
c_o|B_i = 0, \quad c_i|B_j &= \delta_{ij} c_{ms,j}, \quad 0 \le i,j \le 4, \\
\frac{\partial c_i}{\partial n}|B_r &= 0, \qquad\qquad 0 \le i \le 4,
\end{aligned}
\qquad (6)
$$

where $\delta_{ii} = 1$, $\delta_{ij} = 0$ for $i \neq j$, and $c_{ms,j}$ are measured reduced concentrations at B_j.

The decomposition (4) enables us to determine inputs Q_i from each of the five recognized sources of pollution by heavy metals. Using the expression

$$Q_i = H \int k(\vec{r})c_i(r)dr \qquad (7)$$

where H is the depth of the basin the input rates are readily obtained.

5. Case Study: Punat Bay

5.1 Description of the area

Punat Bay on the island Krk in the Northern Adriatic has the area of 2.4 km^2, the average depth equal to 3.2 m, and the volume of 7.7.x 10^6 m^3 (Fig.1). The bay is conected to the rest of the sea through a narrow 200m wide gate. Among potential sources of heavy metals in the bay are: a yacht harbour, sewage collector of the small town Punat, the shipyard and the working area of the marina. Additional sources are run-off waters from a large surrounding area.

Natural concentrations for nearby open waters of the Rijeka Bay are 6.0μg Zn/l, 0.5μg Cu/l, 0.2μg Pb/l, [11].

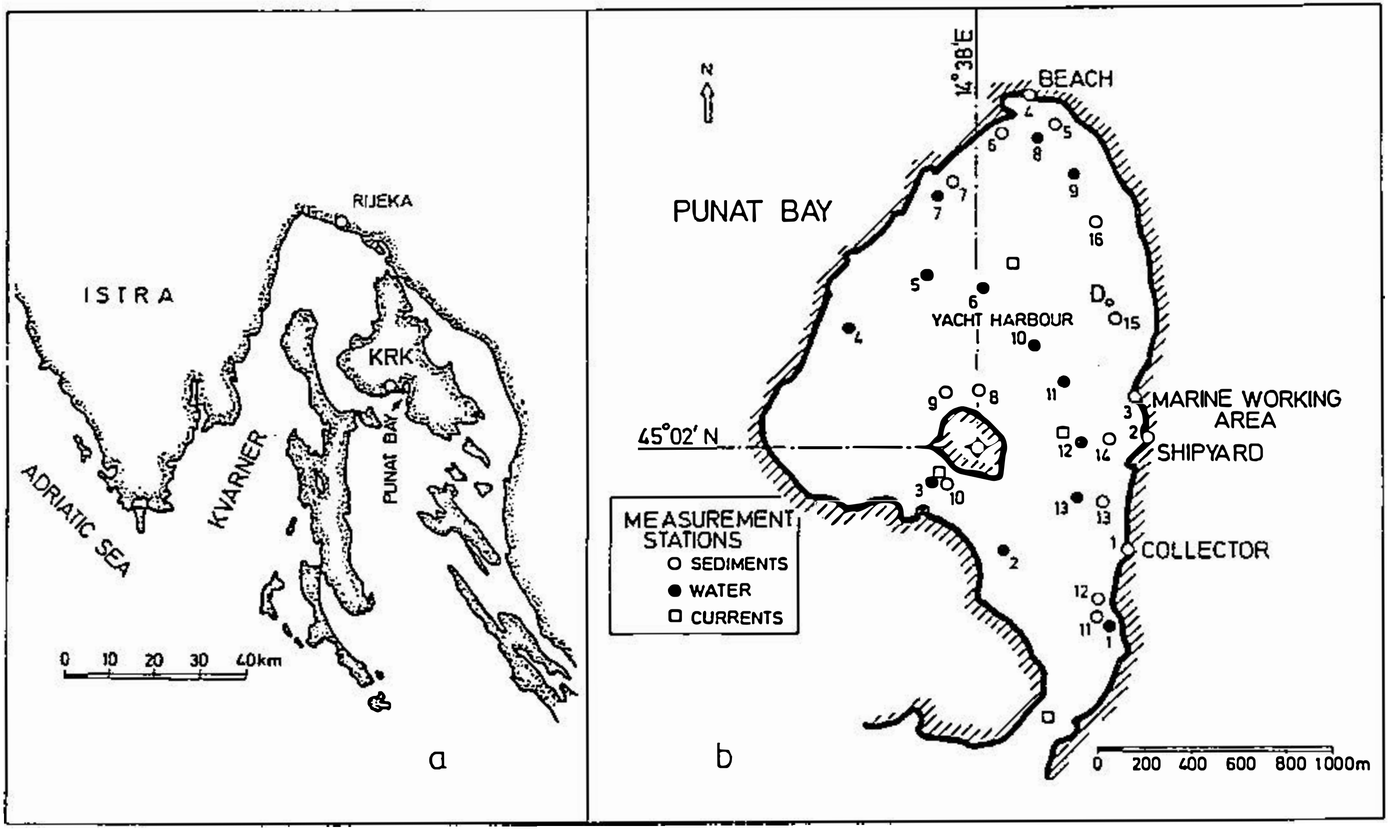

Figure 1. a) Location of the Punat Bay in the Adriatic Sea.

b) Location of measurement stations and inputs into the Punat Bay. Shaded area represents the position of the yacht harbour. The other inputs are : collector shipyard, marine working area and an unknown source at thebeach area.

5.2 Sampling

Water samples were collected on 9 June 1987. at the stations shown in Fig.1. Sediment samples were collected during 29. and 30 July 1987 by an alluminum corer at another set of stations which are also shown in Fig.1. Currents were measured during 15 days in June at four stations (Fig.1.). Since no significant stratification of the water column was present the current meters were placed in the midle of the water column.
The dominant component of currents in the gate is due to tides. The component has the amplitude of 15 cm/s. Currents at measuring stations in the bay have the amplitude of only 1-2 cm/s and only the tidal component has been extracted.

Salinity was measured at the stations were samples for heavy metals in water were taken. Salinity has smaller value in the middle part of the bay for 1% - 3% due to the springs of fresh water at the bottom of the bay.

6. Results

The results of seawater analysis are presented in Table 1 while the results of sediment samples are given in Table 2.

The obtaied concentration fields in water for Zn, Pb and Cu are shown in Figures 2-4. Note that the highest concentrations of Zn and Cu are found near the collector while the highest concentrations of Pb are located near the shipyard and marina working area. Elevated concentration of Zn is also visible in the beach area. A careful examination of the area showed no visible source, however uphill the beach area a village is located that has no sewage system. Furthermore the beach is the lowest part of the drainage area that includes a depositof crude waste on the land.

The estimated values of extinction parameter k are used to determine the half-life of metals in the water column.The obtained half-lives are 12, 12.5, and 10.5 days for Zn, Cu and Pb, respectively for the largest part of the bay.

Around the collector, shipyard and marina working area in the neighbourhood of 150m, the extinction parameter for Zn and Cu turned to the higher by 70% and 30% respectively.

The estimared natural concentrations in the sediments are practically zero in all three cases.

Station No.	concentrations in water (µg/l)		
	Zn	Cu	Pb
1	17	17	3.1
2	5	2	1.8
3	6	12	3.2
4	9	5	2.5
5	32	15	4.4
6	37	12	2.7
7	33	9	2.7
8	18	7	2.2
9	10	17	2.5
10	20	20	5
11	4	17	1.3
12	5	3.5	2
13	6.3	3.3	2.3

Table 1. Concentrations of Cu, Zn and Pb (ug/l) in water of Punat Bay during summer. The values are the averages over the water column. Positions of stations are shown in Figure 1.

Station No.	concentrations in sediments (ppm)		
	Zn	Cu	Pb
1.	185.7	69.4	105.4
2.	88.1	76.4	97.4
3	162.8	92.8	129.0
4	104.0	42.9	69.3
5	27.0	40.0	82.0
6	89.0	38.6	87.0
7	80.0	33.3	27.0
8	44.3	26.1	48.8
9	27.8	27.7	40.8
10	24.9	31.3	16.4
11	84.5	56.4	93.0
12	96.7	41.0	-
13	55.6	49.0	101.2
14	59.3	41.3	55.2
15	96.7	46.9	51.5
16	84.5	46.1	109.0

Table 2. Concentrations of Cu, Zn and Pb (ppm) in upermost 2 cm of sediment in the Punat Bay. Positions of stations are shown in Figure 1.

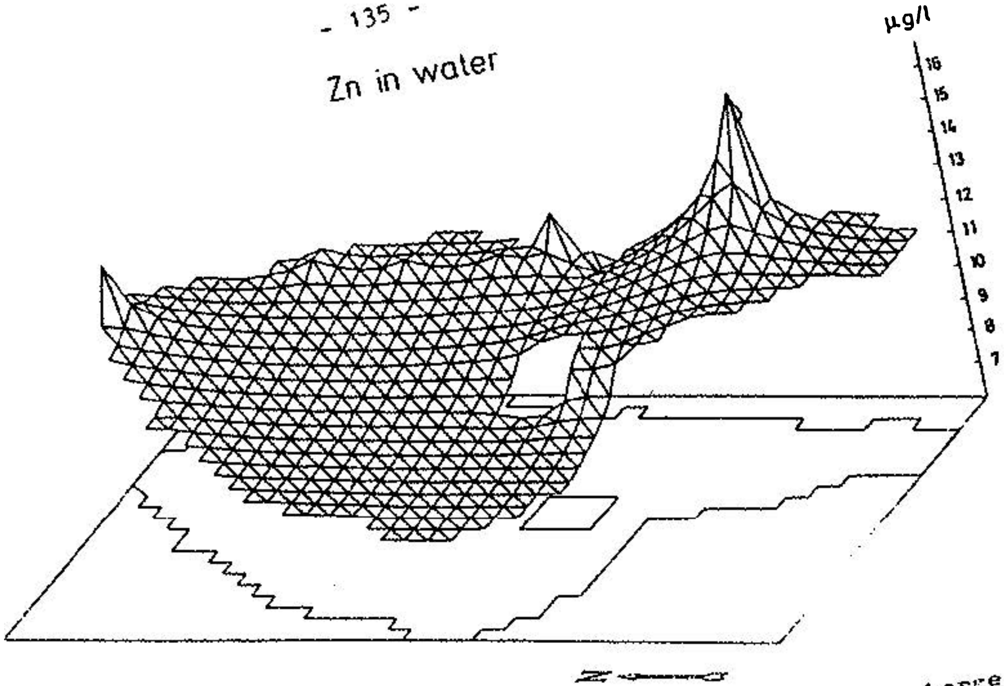

Figure 2. Estimated concentration field for Zn in water. Large values are located in front of the collector and the beach

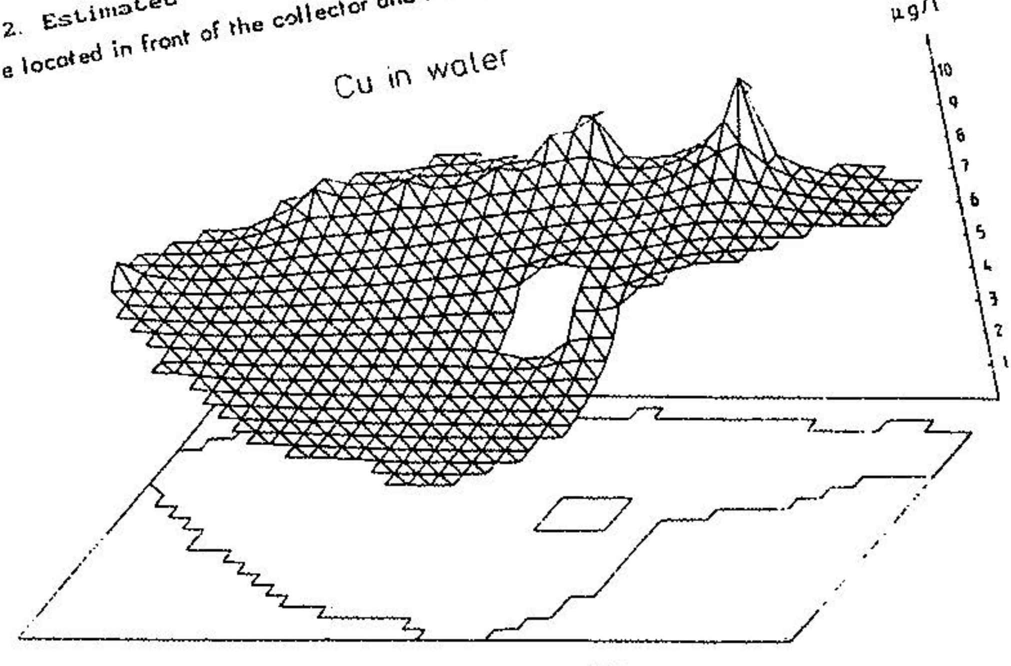

Figure 3. Estimated concentration field of Cu in water.

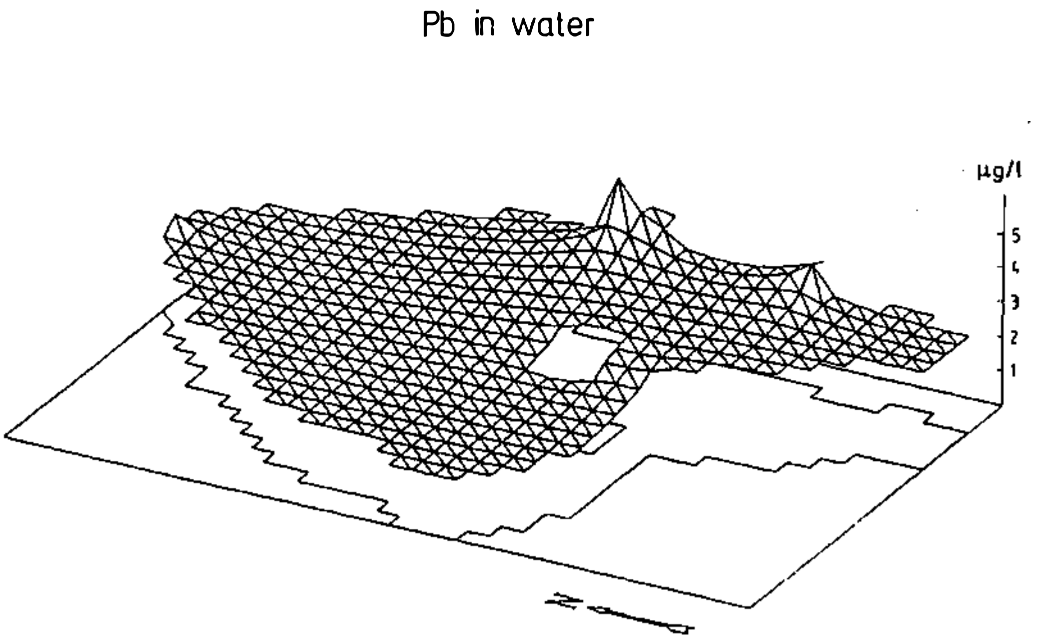

Figure 4. Estimated concentration field of Pb in water. Large values exist at the marina working area and shipyard.

Relatively short half-lives of metals in the water column mean that metals are rapidly lost from water. There are three relevant clearance processes. One is the wash-out of metals from the bay. It has been shown that the wash out is too small to account for the above loss rate[5]. The other two processes are uptake and apsorption to partic les. The content of metals in water column is then lost by sedimentation. Hence, sedimentation is the dominant clearance mechanism. This implies the following simple rule for the inputs of considered three metals:

Input into the bay = Input into sediments of the bay

The total input rate is obtained by the integration of input over the area of the bay.

The results are presented in Table 3.

Total input rate can also be obtained from reconstructed concentration field of metals in sediments and an estimate of annual growth of sediment. In the first two centimeters at the yacht harbour, the metal concentrations are elevated. Since the age of the harbour is 25 y, the annual growth of the sediment is $w \approx 0.8$ mm/y. The specific weight of wet samples is 1.45 kg/dm^3. Hence, an upper value for the estimate of the total input rate of metals into the bay is readily obtained. The results are presented in Table 3.

A test of the reliability of input estimates follows from comparison of model results with either data which are not used in the process of modelling or results of some other verified models. This universal principle can be applied in our case by comparing inputs of heavy metals from hull paints of yachts and boats in the yacht harbour, that are computed by our models, to data on the annual consumption of paints in marina. The results are presented in Table 4. Inspecting Tables 3 and 4, we see that our results about lead are more reliable than the ones about zinc and copper. This can be easily explained in the following way. The estimated inputs by the model are sensitive to the ratio of the background and actual concentrations in the basin. The relative error of estimated inputs is proportional to this ratio. In the case of lead, the ratio is small (0.01-0.1), and in the case of zinc and copper, it is large ($\approx$ 1). Thus the estimate of the input of zinc increases (decreases) for about 14% when its background concentration is decreased (increased)

Estimated total inflow rates		
kg/month	by model in water	by model in sediment
Zn	107,0	98.2
Cu	139.0	49.3
Pb	43.3	72.5

Table 3. Comparison of calculated inflow rates for the whole bay from the basic model for the water column and from reconstructed concentration in the sediment.

kg/month	by model in water	from data on consumed paints
Zn	21.6	45.9
Cu	21.4	10.9
Pb	7.4	8.2

Table 4. Comparison of estimated inputs of Zn, Cu and Pb. in kg/month for the yacht harbour and data on consumption of hull paints.

for one ppb.

6. Conclusions

Distributions of Zn, Cu and Pb indicate that the west part of the bay is more polluted then the east side. This conclusion is not at all surprising when we know that all of the expected polluters are on that side of the bay.

A source of Zn found in the beach area was unexpected but it seems real in the view of the arguments put forth and the existence of small peaks in both Cu and Pb.

Regarding the location of the beach, we may conclude the following. First, according to Figures 2-4 and the maximum allowable concentrations set up by the lawmaker (50μg Zn/l, 5μg Cu/l, 12μg Pb/l)[12], the only strech barely suitable for a beach location is the coast west of the island Košljun. Second, during a typical summer day, Maestral wind blows from NW, W, SN direction and due to the geometry of the bay and proximity of the beach from main pollutant sources, any surface resident pollutant reaches and accumulates very near the present beach area.

The first and the second point combined, suggest that the beach should be relocated to the stretch of the coast that lies the most west in the bay.

Acknowledgments

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