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Pollution of the coastal bottom sediments at the Middle Primorie (Russia) due to mining activity

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Abstract

The contents and geochemical forms of Mn, Zn, Cu, Pb and Cd were studied in the coastal sediments at the Sea of Japan, an area adjacent to the watershed with a developed mining industry (Rudnaya River basin, middle Sikhote-Aline). Solid discharge into the Rudnaya River has abnormally high metal contents that are in leachable forms, including sulfides. Metal levels in the coastal sediments were elevated as a result of this polluted matter dissipation. Sediment pollution by Pb, Cd, Cu and Zn (normalized Clark Concentration measure) exceeds 20–50 within Rudnaya Bight and varies from 5 to 10 within a 25-km plume southward of the bight due to current action. An alteration of the metal forms also occurred, due to mechanic decomposition of the sulfide minerals and dissipation of all river-derived forms.

Keywords: Trace metals; Bottom sediments; Pollution; Mining activity; Sea of Japan

1. Introduction

On the east side of the middle Sikhote-Aline ridge is a region of high mining activity that includes crop, ore-dressing, and melting of polymetalic Pb–Zn ores. Accordingly, drainage waters, wastes and tailings contaminate the nearby environments (Arzhanova et al., 1995; Yelpatyevsky, 1995). The most polluted area is localized in the Rudnaya River basin. As a result, the Rudnaya River carries considerable amounts of pollutants, such as Pb, Zn, Cu, Mn and Cd (Arzhanova et al., 1995) to the Rudnaya Bight and farther out to sea. Our objective was to assess the influence of Rudnaya River discharges on the metal contents of nearby coastal bottom sediments in the Sea of Japan. Contaminated sediments can be toxic for organisms, but determination of adverse effects is complicated by complex composition of sewage. The Rudnaya River contaminates the adjacent coastal sediments by metals only and, therefore, can serve as a convenient model.

2. Materials and methods

The sampling was carried out in June 1987, after a winter period of active hydrodynamic conditions. The sediments were taken by Van-Veen grab and the surface layer (about 2 cm) was sampled for chemical analysis. The sampled sediments (Fig. 1(a)) varied from sands at the bight, to silts and muddy gravels at the offshore stations. The fraction, less than 0.1-mm, was used for analysis to avoid a grain size influence. The samples were dried at 105°C and ground to a fine powder. After acid digestion ($HF–HNO_3–HClO_4$) metals were determined by flame atomic absorption spectrophotometry (AAS); accuracy and precision were estimated by analysis of the standard reference materials (NBS/646). The differences with NBS/646 data were within 3–5%. Moreover, a part of the samples (on the line I–II, Fig. 1) was treated with a sequential extraction procedure that involved: (1) $NH_2OH.HCl + HOAc$ at pH = 2.8; (2) $H_2O_2 + HNO_3$ at pH = 2; and (3) $HF + HNO_3 + HClO_4$. Despite concerns regarding a change of metal forms during pretreatment and extraction (Martin et al., 1987), sequential extraction is still a much accepted method to determine metal speciation in the sediments. We interpret the extraction data as follows: (1) leachable forms, including Fe–Mn hydroxides; (2) oxidizable forms, connected with sulfidic and/or organic matter; and (3) residual forms, associated with silicate crystalline structures. The differences did not exceed 15% between the sum of steps (1)–(3) and data for the initial samples treated by strong acids (step (3)) at once.

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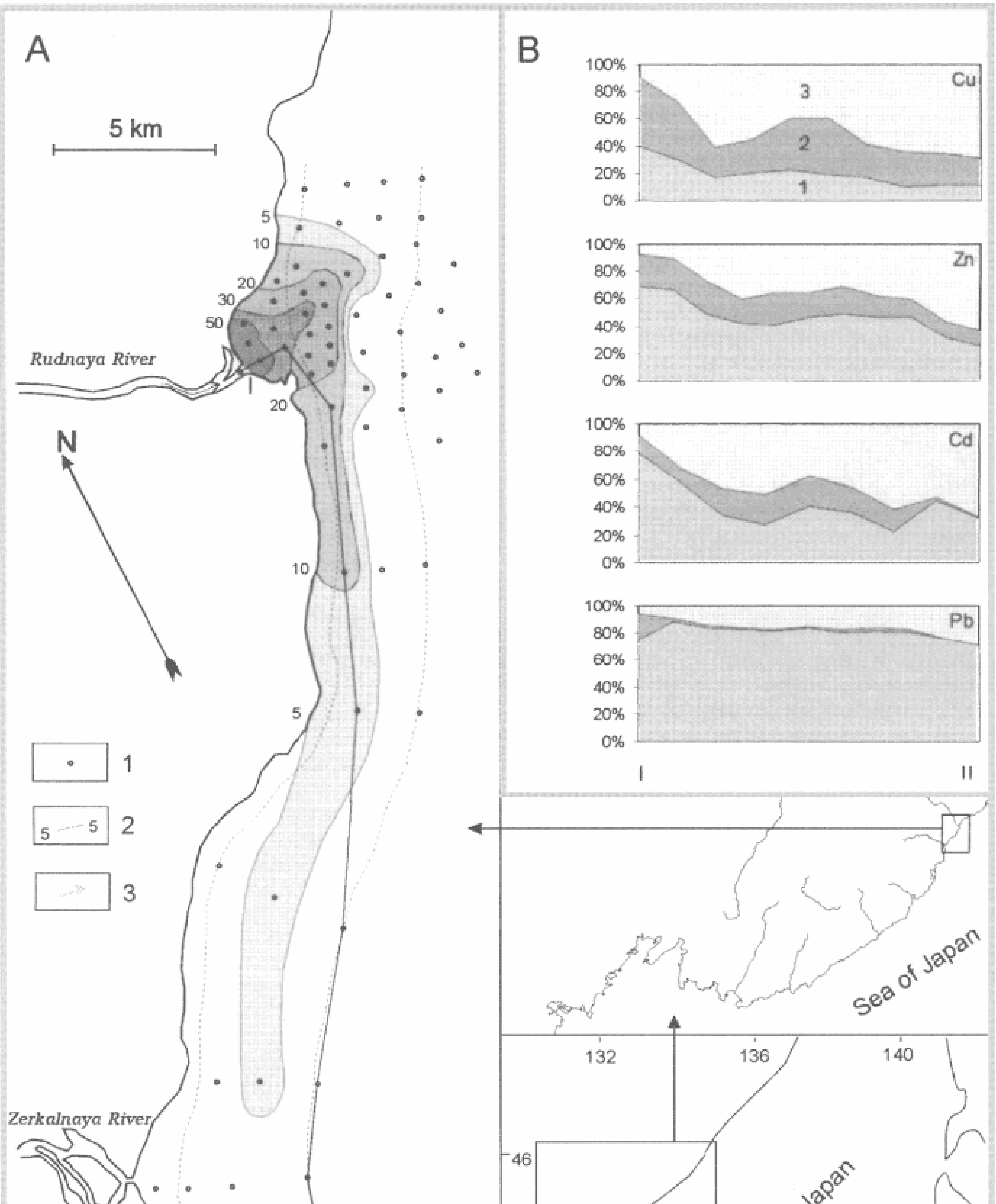

Fig. 1. (A) The study area and structure of the metals anomaly: (1) sampling locations; (2) lines of equal pollution in normalized Clark Concentration units; (3) pollution input. (B) The alteration of the metal forms fractions (%) with distance from pollution input (on line I–II (A)): (1) fraction of the leachable forms; (2) fraction of the oxidizable (sulfide and organic) forms; (3) fraction of the residual forms.

3. Results and discussion

The metal levels in the sediments from the different areas of the Rudnaya Bight neighborhood are presented in Table 1. Levels of Pb, Zn, Cu, Cd and Mn were highly elevated in the initial river-derived matter as well as in the Rudnaya Bight sediments. Within Rudnaya Bight, metal levels in the sediments exceeded those at heavily polluted coastal localities (Table 1). Levels of metals were also elevated in nearby coastal bottom sediments. One-way analyses of variance (groups presented in Table 1 as main effect) showed that variance of all metals, excluding Ni, between groups were significantly higher than within. Moreover, variances of the Pb, Zn, Cu and Cd contents were strongly correlated (Table 2). Thus, we suggest that concentrations of Pb, Zn, Cu and Cd were determined by dissipation of the river-derived matter. The enrichment (pollution degree) of the sediments by these metals was estimated in each sample by the Clark Concentration (CC) measure (Perel'man, 1967). This normalized measure allowed us to assess the overall pollution degree by metals with different absolute abundances:

$$CC_{\mathrm{M}} = C_{\mathrm{iM}}/C_{\mathrm{bM}} \text{ and } CC_{\Sigma} = \Sigma CC_{\mathrm{M}}/n,$$

where: CC_{M} = Clark Concentration for metal M; C_{iM} = content of the metal M in the sample i; C_{bM} = content of the metal M in the background sediments; and CC_{Σ} = summary Clark Concentration for n metals.

CC_{Σ} shows the pollution degree of the sediments by potentially toxic metals (Zn, Pb, Cu, Cd). Within the Rudnaya Bight CC_{Σ} exceeds 20–50 (Fig. 1(a)), i.e. sediments are polluted 20–50 times above background levels. Ten times enrichment was observed 5 km from the Rudnaya Bight. A plume with five times enrichment extended 25 km south of the pollution source. The direction of the contaminated plume in the bottom sediments is explained by the Primorskoe Current action, which transports matter from north to south.

The main feature of the metals' speciation in the initial polluted solids, incoming to the coastal area, was the prevalence of the leachable, geochemically labile forms (Fig. 1(b)). Forms leached by reducing agents (hydroxilamine, step 1) were dominant for Pb, Cd and Zn, but for Cu the oxidizable (sulfide) forms prevailed. The diminishing of the sulfide fractions in the order Cu > Zn > Cd > Pb corresponded with mechanic stability of the associated minerals: chalcopyrite ($CuFeS_2$)–sphalerite (ZnS)–galenite (PbS). With removal from the

Table 2
Correlation between metal contents in the bottom sediments at the Rudnaya neighborhood

	Mn	Zn	Cu	Pb	Cd
Mn	1.00	0.64	0.46	0.58	0.60
Zn		1.00	0.83	0.94	0.98
Cu			1.00	0.83	0.81
Pb				1.00	0.90
Cd					1.00

Number of samples = 48, $r_{0.05}$ = 0.29.

Table 1
Metal contents in the Rudnaya River's solid matter and in the bottom sediments at the adjacent coastal area and at some other polluted localities

		n	Mn	Zn	Cu	Pb	Cd	Ni
Initial Rudnaya River's matter								
Suspended matter	*x*	7	3534	4227	364	1061	47.2	36
	s		924	871	86	151	12.1	6
Alluvial deposits	*x*	5	6064	3390	255	906	20	34
	s		1022	623	54	121	4.2	5
Rudnaya Bight's sediments	*x*	15	1066	2085	280	1345	9.5	30
	s		359	1167	141	725	6.6	12
Sediments eastwards off the bight	*x*	29	816	225	41	136	1.13	27
	s		837	354	29	107	1.30	3
Sediments southwards off the bight	*x*	17	1467	339	61	151	1.12	24
	s		922	197	46	69	0.86	4
Unpolluted coastal sediments (silts)	*x*	20	321	95	22	25	0.25	24
of the northwestern Sea of Japan	*s*		46	18	6	8	0.11	3
Golden Horn Bay (Tkalin et al., 1996)			226	362	181	214	3.2	26
Masan Bay (Lee and Min, 1990)			561	690	140	54	3	53
Manila Bay (Prudente et al., 1988)			656	136	55	35	2.2	15

x, average; *s*, standard deviation; *n*, number of samples.

pollution source (river mouth), the part of the leachable forms was decreased in the metal pools and residual unlabile forms began to dominate for Zn, Cu and Cd. The portion of residual Pb forms also increased, but a prevalence of the leachable forms was maintained (Fig. 1(b)). Moreover, fast diminishing occurred for sulfide Pb forms (Fig. 1(b)), indicating a low stability of the galenite. The fraction of Cu, Zn and Cd oxidizable forms decreased more gradually but Cu and Cd fractions increased at the outer part of the anomaly (Fig. 1(b)). It is possible that labile Cu and Cd, bound with organic matter, leached together with sulfides.

4. Conclusions

Vast and distinct geochemical anomalies have been formed in the coastal sediments adjacent to the Rudnaya River mouth due to mining activity at the watershed and discharge of the polluted solids to the sea. As a result, Zn, Cu, Pb and Cd contents are elevated 20–50 times in the Rudnaya Bight sediments and 5–20 times in the sediments southward of the Bight in comparison with unpolluted sites. Levels of metals in sediments were equal to the heavily polluted coastal localities even when the sediments were situated 5–10 km from the Rudnaya River mouth. The action of the southward Primorskoe Current determined the shape and direction of the contaminated plume. The increased metal levels were stipulated by the leachable forms. Therefore, an increase of the residual metal fractions was observed with polluted matter dissipation. The portions of sulfide forms were diminished in the order Cu > Zn > Cd > Pb in accordance with mechanic stability of the main sulfide minerals (chalcopyrite, sphalerite, galenite).

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