

Metal contamination of surface waters of Primorye

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Introduction

Surface water can carry many types of pollutants existing in catchments. This investigation is connected with Primorye region (Area = 165000 sq. km) bordering the Sea of Japan. The territory is characterised by a humid climate with annual meteoric precipitation about 1000 mm as rain and snow. This is a mountain region composed of volcanic and plutonic rocks, but sedimentary deposits of different ages also contribute. Some mining activity of non-ferrous metal ore deposits has taken place.

Primorye is a lesser contaminated region compared with central Russia, but in the southern part of the territory the pollution problems are quite serious. Efforts for the clean-up of water are unsatisfactory and contamination by municipal wastes, fertilizers and pesticides in agricultural regions, heavy metals from the mining industry and other sources take place. The main focus of this study is on the concentration of heavy metals, their distribution in the solid phase and the extent of pollution of surface waters of Primorye.

Methods

The samples of water were collected with every precaution to avoid contamination and divided into dissolved and suspended forms by membrane filtration. In addition accumulation of suspended material by ultracentrifugation from large (100-1000 l) volumes of river water was used for chemical and mineralogical analysis. Determination of heavy metals included dissolved and suspended contents. The distribution of chemical elements was studied in the different size fractions and extraction carried out with successively stronger reagents. We obtained: (1) easily mobile phase, extracted with 5% CH_3COOH ; (2) organic phase after treatment with H_2O_2 ; (3) moderately reducible inorganic mobile phase, combined with Fe and Mn oxides, extracted with 35% CH_3COOH + 25% hydroxylamine; (4) phase from extraction with hydrochloric acid/alcohol. This phase identified crystalline oxides of Fe and Mn. (5) the residual phase was obtained after decomposition with HClO_4 + HF. All analyses were carried out by atomic absorption spectrometry.

Results and discussion

The average concentrations of some metals in dissolved and suspended material is given in Table 1 in relation to four main parts of Primorye having different geological features. Sulphide minerals are more common in the Eastern Sikhote-Alin; the extent of weathering is greater to the south and west (catchments of Amur and Ussury Bays and Khanka lake catchment); kaolinite and smectite were only found in these areas. These differences are clearly shown in the suspended solids. From Eastern Sikhote-Alin to the catchments of Amur and Ussury Bays an increase in suspended concentrations of Fe, Mn, Cr takes place with a corresponding decrease of the Zn, Cu, Ni, Pb which are specific metals for ore minerals of Eastern Sikhote-Alin. For the central part of Primorye suspended metal concentrations connected with sulfide mineral sources is less than in the Eastern Sikhote-Alin. Using the data obtained in the field trips (Chudaeva, 1988, 1990; Chudaeva and Chudaev 1992) and some published data of Hydrological Survey of Russia

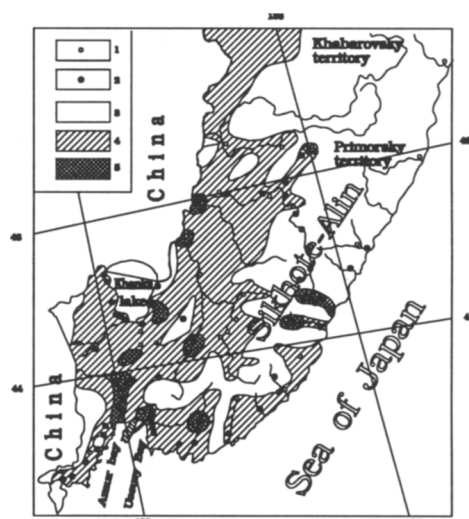


FIG. 1. Contamination of surface water by heavy metals. 1 - points sampled by Russian hydrological survey; 2 - points sampled by author in field trips; 3 - natural concentration areas; 4 - moderate contaminated areas; 5 - the most contaminated areas.

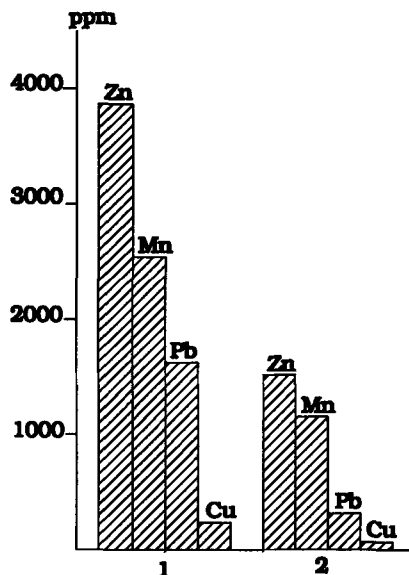


FIG. 2. Diagrams of some metal concentrations in suspended sediments of Rudnaya river (1) and rivers of Eastern Sikhote-Alin (2).

(Redkovskay,1988) as well as extrapolation to similar territory, the extent of contamination of Primorye surface waters was defined (Fig. 1).

The degree of pollution was considered for each area based upon the background values for surrounding fresh waters as well as the legally permitted concentrations for certain elements. The northern part together with all upland areas and thinly populated places of the south do not contain such serious pollution (first degree). The greater part of the territory of southern Primorye is moderately contaminated: an increase in concentration of one or more components above the background of surrounding fresh waters was found (second degree). In some places municipal or factory wastes input a lot of contaminating components to the surface water (third degree). These areas are mainly connected with the towns (Vladivostok, Ussuriysk, Partizansk, Dal-nerechensk, Lesozavodsk, Spassk, Dalnegorsk), as well as mining activity elsewhere. The type of chemical impact on the waters was studied for Rudnaya river the most contaminated stream in the Eastern Sikhote-Alin. Here the mines and factories contribute some wastes to the Rudnaya river that make significant changes in concentrations of the main chemical components. The ratios and amounts of the major ions also differ considerably to the natural background (Elpatievsky *et al.*,1976). The changes in the levels and forms of heavy metals

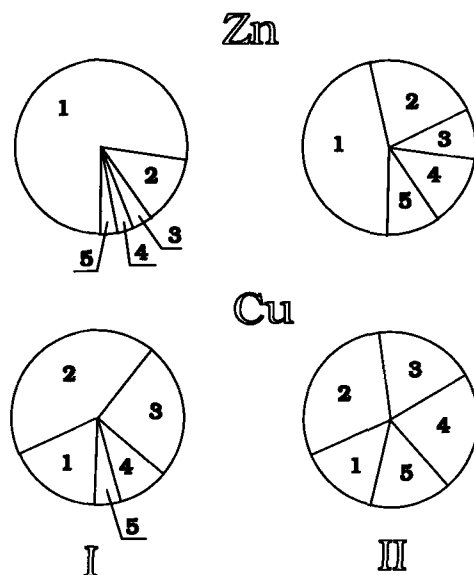


FIG. 3. Suspended transported forms of Zn and Cu in Rudnaya river (1) and rivers of Eastern Sikhote-Alin (2). Numbers of forms related to the part 'Methods'.

in the Rudnaya river were also observed. The main control on the decrease in concentration of heavy metals is dilution with water from clean tributaries. There are rather high concentrations of heavy metals both in solution and suspensions. The most abundant metals in suspended solids are shown in Fig. 2. The role of mobile forms of metals in the Rudnaya river is greater than in others of the Eastern Sikhote-Alin (Fig. 3). Metals in mining suspensions also entered the river sediments as detrital minerals (Voroshilova and Elpatievsky,1976) and possibly also as dissolved and particulate mobile forms of metals which are transported to the sea. Towards the mouth of the river the mobileforms correlation becomes similar to the other rivers but the concentrations are higher and a large amount of these metals reach the Sea of Japan as dissolved and suspended (mainly 0.01–0.1 size fraction) forms. Fortunately this is not a large river (catchment = 1140 sq.km) and it contributes to the Sea of Japan not more than 1% of total water discharge from the Eastern Sikhote-Alin.

Conclusion

There are several natural and anthropogenic sources from which the chemical elements may be transported in the surface waters of Primorye. The mining and industry is a serious factor contaminating of surface water by heavy metals.