# **Transport of mercury by the Katun river, West Siberia**

Sergey A. Sukhenko ', Tatjana S. Papina' & Shamil R. Pozdnjakov <sup>2</sup>

<sup>1</sup> Institute for Water and Environmental Problems, Papaninzev Str., 105, 656099, Barnaul, USSR; <sup>2</sup> State *Hydrological Institute, V.O., 2-nd line, 23, 199053, St. Petersburg, USSR*

*Key words:* mercury, river transport, suspended sediments, river pollution

#### **Abstract**

Some results of a 2-year study of mercury pollution of the Katun river (Siberia) are summarised. Measurements of water flow, sediment transport and mercury concentrations were made and used to calculate the amount of mercury transported by the river. The distribution of transport between water phase and suspended material is calculated. It is concluded that suspended sediments play the main role in this process. The significance of different fractions of suspended sediment is also discussed.

## **Introduction**

Mercury is one of the substances well recognised as extremely toxic (W.H.O., 1989; Hutchinson & Meema, 1987). Another very essential property of Hg is its ubiquity. This is the reason why the measurement and evaluation of the occurrence of Hg in the environment has received much attention.

Such studies were carried out in the Altai mountains (West Siberia) in connection with the possible construction of a hydro-electric complex on the Katun river. In this investigation we measured the amount of Hg transported by the Katun river in order to evaluate the Hg mass balance in the projected reservoir. This mass balance may be used as a base for estimating the changes in the Hg loading on the lower Katun and Upper Ob and the possible ecological consequences of these changes in case this project is realised.

Hg in rivers can be transported downstream in three different ways:

- (1) dissolved in the water phase;
- (2) by the suspended sediments;

(3) by the bed sediments which move along the river bottom, commonly referred to as the bed load (Lau *et al.,* 1989).

In order to study the fate of the contaminants it is necessary to know how the loading is distributed among these three phases. Although most of the Hg in water bodies is attached to the consolidated sediments, this does not mean as a rule that river bed sediment transport is the most important mechanism for geographical movement of Hg (Ottawa River Project Group, 1979). As shown in many case studies the contribution by the suspended material and water carries most of the Hg and inclusion of bed sediments to the Hg transport may be omitted (Ottawa River Project Group, 1979; Nelson *et al.,* 1977; Potter *et al.,* 1975; Mudroch & Clair, 1986; Voznesensky *et al.,* 1983; Sahu, 1988). No doubt the Katun river is no exception to this rule, although direct quantitative measurement of bed transport is not possible now because of its hydrological features. These bed sediments are made up of stones, gravel and rough sand fractions, and the character of their movement is very complicated.

This paper describes the results of a study to determine the Hg quantity transported by the Katun river and the relative importance of the water and the suspended sediments in this process. In order to carry it out, measurements of water flow, sediment transport and Hg concentration in the water and on the suspended particles were used. These data were collected during a two year study of Hg in the Katun river basin (Siberian Division of the USSR Academy of Sciences, 1990).

# **Study area**

The region under study is situated in the southern part of West Siberia (see Fig. 1). The Katun river watershed consists mainly of mountainous terrain. The river is approximately 690 km long and drains an area of 60 900 km2. The mean annual water discharge in the mouth constitutes  $630 \text{ m}^3 \text{ s}^{-1}$ . It joins the Bija river forming the Ob river, one of the largest rivers of Siberia as well as the world. In its upper and middle parts (the site of this investigation) it is a typical mountain river, descending 1729 m from its origin to its mouth. It receives the largest amount of water during snow and glacier melt. This period (spring and early summer) spans 80-100 days. During this time water flow can increase by a factor 10 or 20 and transport of suspended material is very significant too.

The area of the Katun river drainage basin has not undergone extensive industrial development. This is reflected by the water quality: high  $O<sub>2</sub>$ content  $(10-12 \text{ mg l}^{-1})$ , low content of dissolved organic matter (COD ranged from 0.4 to  $4.5 \text{ mg l}^{-1}$ ) and low contents of dissolved nutrients (inorg- $P < 0.01$  mg  $1^{-1}$ , inorg- $N = 0.01 0.1$  mg  $1^{-1}$ ). The pH ranges between 6.5 and 8.

As a remote region isolated from populated centers and industrial development the Katun river drainage has no anthropogenic Hg source. But it is the area of geologic formations containing Hg carrying minerals such as cinnabar. More exactly it is a part of the large Kuznetz-Altai Hg belt stretching along the USSR territory up to

1000 km and reaching Mongolian territory. It is the deep seated fractures which serve as oresupplying structures. Within the Hg mineralised zones ore is located extremely irregularly - oreless zones alternate with intensive concentrations. Three Hg deposits are of industrial interest: Aktash, Chagan-Uzun and Sarasa (see Fig. 1). All of them are situated in the Katun river watershed. By eroding, naturally, or more rapidly as a result of mining, they provide a large supply of Hg to the watersheds of the region.

## **Methods**

During two years (1988 and 1989) samples of water and suspended sediment were collected from many stations in the area understudy. The most regular and careful measurements were made on two transects across the Katun river during the spring-summer flood when most of the water and sediments were transported. Their locations are shown on Fig. 1. For hydrological transects the sites were chosen taking into account their maximum vicinity to the projected reservoir region and their availability for special hydrological equipment. The upstream transect is situated near the village of Inya approximately 355 km from the river mouth and 140 km from the projected dam. The downstream transect is situated near Anos village approximately 185 km from the river mouth and 30 km down along the river from the projected dam.

At each transect measurements of depth, velocity and suspended sediment concentration were made at seven locations across the river at five different depths. Raw watersamples were also collected from each point for chemical analysis. Only preliminarily acid-washed polyethylene bottles were used for this purpose.

Hg content in samples were determined by using the cold vapor technique of atomic absorption spectrometry (Oda & Ingle, 1982). Immediately after collection the raw water samples were passed through a set of clean plastic filters with 5.0, 1.0, 0.45 and 0.1  $\mu$ m pore size. The fractions



Fig. 1. Geographical setting and map of study area.

 $> 5 \mu$ m were the object of further separation after washing off into the following size classes: 5-10, 10-50, 50-100, 100-200, 200-500, 500-1000  $\mu$ m by means of a fractiometer and pipette set. Then particles of these classes were collected on the 5 *m* filters.

The filters with suspended sediment were freeze-dried and weighed. The sediments were washed off with a small volume of  $HNO<sub>3</sub> (1 M)$ and digested in  $2 \text{ ml}$  of  $H_2SO_4$  plus  $2 \text{ ml}$  of  $KMnO<sub>4</sub> (2% w/v)$ . The solution was then diluted to 200 ml with deionized water and allowed to stand for 10 hr on a water bath at  $45^{\circ}$ C. Hg ions were converted to elemental Hg by the addition of  $SnCl<sub>2</sub>$  in the presence of HCl.

The filtered water (500 ml) was acidified with  $5 \text{ ml } H_2SO_4$  (conc.) in the presence of  $5 \text{ ml}$  $KMnO<sub>4</sub> (2<sup>o</sup>/<sub>0</sub> w/v)$  and allowed to stand for 12 h. Hg from this solution was transferred by the air flow into 3 ml of KI  $(1\%)$  in I<sub>2</sub> (0.1 M) solution. The subsequent reduction to elemental form was brought about by ascorbic acid in the presence of NaOH.

Preparation of samples and analysis were carried out in the field immediately after collection. The portable Hg field analyser 'Julia-2' was used for the final determination.

## **Results and discussion**

The complex hydrological regime of the Katun river, stream level fluctuations, high flow rates (up to 5 m s<sup> $-1$ </sup>) make water discharge and flow turbidity evaluations rather problematic. These technical difficulties were successfully overcome and the data, especially concerning the year 1989, seem to be reliable. The most careful daily measurements at transects were made in the period of highest river discharge. The information received in the first research year (1988) is not so detailed and reliable as that received in 1989. The annual Hg transport in the transect region of projected dam can be evaluated at  $6 \cdot 10^3$  kg y<sup>-1</sup>. Approximately  $1.7 \cdot 10^3$  kg y<sup>-1</sup> of this quantity is transported in dissolved form  $(0.45 \mu m)$  filter, which corresponds to the standard 'operational' definition of the dissolved pollutant), and  $4.3 \cdot 10^{3}$  kg y<sup>-1</sup> is transported on the fractions of all sizes of the suspended material. The simultaneous measurement of water discharge and suspended sediments enabled us to evaluate their annual value as  $18.6 \text{ km}^3$  and  $3.4 \cdot 10^9 \text{ kg y}^{-1}$ , respectively. On the basis of these data annual weighted averages of Hg concentration in water and suspended sediments were found to be

| Size of fraction,<br>$\mu$ m     | Annual flow                                       | Average                                    |                                   |  |  |
|----------------------------------|---|--|-----------------------------------|--|--|
|                                  | Suspended sediment,<br>$10^9$ kg yr <sup>-1</sup> | Mercury on solids,<br>$10^3$ kg yr $^{-1}$ | concentration,<br>$kg^{-1}$<br>mg |  |  |
| $0.1 - 1.0$                      | 0.14<br>$8\%$                                     | 0.67<br>22%                                | 4.79                              |  |  |
| $1.0 - 10$                       | 0.46<br>25%                                       | 1.60<br>$53\%$                             | 3.48                              |  |  |
| $10 - 10^2$                      | 0.81  | 0.60                                       | 0.74                              |  |  |
|                                  | 45%   | 20%  |                                   |  |  |
| $10^2 - 10^3$                    | 0.39<br>22%                                       | 0.16<br>$5\%$                              | 0.41                              |  |  |
| All fractions<br>1.80<br>$100\%$ |   | 3.03<br>$100\%$                            | 1.68                              |  |  |

*Table 1.* Mercury transport by different fractions of suspended sediment (Anos village transect, 1989)

*Table 2.* Season variation in mercury transport (Anos village transect, 1989)

| Period                               | Suspended<br>sediment<br>transport,<br>$10^9$ kg | Mercury<br>transport,<br>$10^3$ kg |  |  |
|--------------------------------------|--|------------------------------------|--|--|
| Spring-summer flood<br>$(Apr.-Aug.)$ | 1.73 $(96\%)$                                    | 2.69(89%)                          |  |  |
| Low water<br>$(Sept.-Mar)$           | $0.07$ $(4\%)$                                   | 0.34 $(11\%)$                      |  |  |
| Total                                | $1.80(100\%)$                                    | 3.03 $(100\%)$                     |  |  |

0.1  $\mu$ g l<sup>-1</sup>, and 1.2 mg kg<sup>-1</sup>, respectively. These values do not exceed the limits typical for other rivers unpolluted by anthropogenic Hg (Moore & Ramamoorthy, 1984).

In 1989 the study on the Anos river transect was more detailed. The Hg transport by different fractions of suspended material was evaluated (see Table 1). As expected, the main part of the Hg was transported by the fine fraction of the suspended material. Thus, particles of  $0.1-10 \ \mu m$ which constituted one-third of the suspended material transported  $75\%$  of the Hg.

According to size class the Hg 'weighted' concentration can differ substantially (from 0.41 to 4.79 mg kg<sup>-1</sup>) at such a size class selection. Maximum Hg concentration on particle samples amounted to  $109$  mg kg<sup>-1</sup> and was found in the  $0.1 - 0.5 \mu m$  fraction.

Hg transport is distributed irregularly in time (see Table 2). The largest part of Hg is transported during the spring and summer flood. It is provided by the passing of the peak water volume (about  $70\%$ ) and most of the suspended material (approximately  $96\%$ ).  $90\%$  of the annual Hg flow in particulate form and  $70\%$  of the annual dissolved Hg flow fell in the period from April to August. During this period the river transports on the whole approximately  $85\%$  of the annual Hg discharge.

In 1989 the Katun river transported  $3.6 \cdot 10^3$  kg of Hg in the region of the proposed dam. So the transport of the dissolved form  $(0.45 \mu m)$ amounted to  $0.9 \cdot 10^3$  kg which, with an annual water discharge of  $16.4 \text{ km}^3$  allowed us to esti-

mate the 'annual mean' value of the Hg concentration in the water at  $0.06 \mu g l^{-1}$ . Hg transport on suspended material constituted  $2.7 \cdot 10^3$  kg which with an annual discharge of suspended sediments of  $1.8 \cdot 10^9$  kg gives a 'weighted' concentration of 1.5 mg kg<sup>-1</sup>.

Data of the two years are compared in Table 3. The annual mean Hg concentrations for these two years appear to be rather close, both for the soluble and the suspended form; the difference between these two years was mainly caused by the difference in the quantity of suspended material. The fraction of Hg transported on the suspended material during these two years remained the same (1988:  $72\%$ , 1989:  $75\%$ ). The suspended material plays the main role in Hg transport by the Katun river, in contrast with some other rivers. In the Hg transport e.g. by the Kuskokwim river (Alyaska) and the Ottawa river (Canada), suspended material constituted 20% (see Table 3). The Katun river carries a rather high quantity of suspended material: its mean yearly concentration was  $0.1-0.2$  g  $1^{-1}$ .

These results are of interest for the evaluation of possible changes in the Hg loading of the Ob river and the densely populated territories of West Siberia in case of a hydroelectric dam on the Katun river is built. The reservoir with a total volume of  $5.8 \text{ km}^3$  will create conditions for retention of the main part of the suspended material, mainly the large fractions. Information on Hg distribution in different sediment fractions makes it possible to complete a quantitative evaluation of Hg flux after the project will have been realised.

#### **Acknowledgements**

This paper presents some results of work started in the spring of 1988 by the provisional interinstitutional scientific group of the Siberian Division of the USSR Academy of Sciences with participation of other scientists. The financial support was given by the Siberian Division of the USSR Academy of Sciences and the USSR Ministry of Energy. The work is being supervised by Professor Oleg F. Vasiliev. The hydrological measure-

| Object                                   | Waterflow<br>rate<br>$\rm km^3\,yr^{-1}$  | Suspended<br>sediment flow<br>$10^9$ kg yr <sup>-1</sup> | Mercury flow, $10^3$ kg                |           | Mercury concentration |                                       |   |   |                                  |
|--|---|--|--|-----------|-----------------------|---------------------------------------|---|---|----------------------------------|
|  |   |  | Dissolved<br>$(0.45 \mu m)$<br>filter) | Suspended | Total                 | Dissolved.<br>$\mu$ g l <sup>-1</sup> | Suspended particles                             |   | Total<br>$\mu$ g l <sup>-1</sup> |
|  |   |  |  |           |                       |                                       | per unit<br>solids mass.<br>mg kg <sup>-1</sup> | per unit<br>volume<br>$\mu$ g l <sup>-1</sup> |                                  |
| Katun, 1988                              | 18.6                                      | 3.4  | 1.7                                    | 4.3       | 6.0                   | 0.1                                   | 1.2   | 0.2   | 0.3                              |
| Katun, 1989                              | 16.4                                      | 1.8  | 0.9                                    | 2.7       | 3.6                   | 0.06                                  | 1.5   | 0.16  | 0.2                              |
| Kuskokwim<br>(Nelson <i>et al.</i> 1977) | 44.3                                      | 0.9  | 13.4                                   | 3,3       | 16.7                  | 0.3                                   | 3.9   | 0.08  | 0.38                             |
| Ottawa                                   | 66.0<br>(Ottawa River Project Group 1979) | 0.6  | 1.3                                    | 0.3       | 1.6                   | 0.02                                  | 0.44  | 0.01  | 0.03                             |

*Table 3.* Comparison of mercury transport by different rivers

ments were conducted by the State Hydrological Institute, Leningrad. The authors wish to express appreciation to them and to chemists of the Institute for Water and Environmental Problems (especially S. Artemjeva & L. Dolmatova) for their cooperation in analysing samples. Mrs J.C. Golterman-Hardenberg helped with editing the manuscript.

## **References**

- Hutchinson, T. C. & K. M. Meema (eds.), 1987. Lead, mercury, cadmium and arsenic in the environment. Wiley & Sons, Chichester *et al.,* 360 pp.
- Lau, Y. L., B. G. Oliver & B. G. Krishnappan, 1989. Transport of some chlorinated contaminants by the water, suspended sediments and bed sediments in the St. Clair and Detroit Rivers. Envir. Toxicol. Chem. 8: 291-301.
- Moore, J. W. & S. Ramamoorthy, 1984. Heavy metals in natural waters. Applied monitoring and impact assessment. Springer-Verlag, New-York *et al.*
- Mudroch, A. & T. A. Clair, 1986. Transport of arsenic and mercury from gold mining activities through an aquatic system. Sci. Tot. Envir. 57: 205-216.
- Nelson, H., B. R. Larsen, E. V. Jenne & D. H. Sorg, 1977. Mercury dispersal from lode sources in the Kuskokwim River drainage, Alaska. Science 198: 820-824.
- Oda, C. E. & J. D. Ingle, 1982. Continuous flow gold vapour atomic absorption determination of mercury. Analyt. Chem. 53: 2030-2033.
- Ottawa River Project Group, 1979. Mercury in the Ottawa River. Envir. Res. 19: 231-243.
- Potter, L., D. Kidd & D. Standiford, 1975. Mercury levels in lake Powell. Bioamplification of mercury in man-made desert reservoir. Envir. Sci. Technol. 9: 41-46.
- Sahu, K. C., 1988. Mercury and lead contamination along Ib River, a tributary of Mahanandi. Poll. Res. 7: 171-176.
- Siberian Division of the USSR Academy of Sciences, 1990. Ecologicheskie aspekty realisazii proekta Katunskoi GES. Novosibirsk, 59 pp.
- Voznesensky, G. F., V. V. Ispravnikova, I. A. Koloskov & Z. L. Sinitsyna, 1983. Isledovanie ruslovoi migrazii rtuti. Meteorologia i gidrologia, 1: 71-78.
- World Health Organization, 1989. Mercury environmental aspects. Environmental health criteria 86. Geneva, 115 pp.