

NATURAL MERCURY LEVELS IN GEOLOGICAL ENRICHED AND GEOLOGICAL ACTIVE AREAS: CASE STUDY OF KATUN RIVER AND LAKE TELETSKOYE, ALTAI (SIBERIA)

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Abstract. Natural geological Hg deposits control the Hg levels in the upper Katun river. Very high levels of total Hg are observed in the watercolumn (up to 20 ng L⁻¹) and the sediments (up to 244 µg g⁻¹) close to the deposit area, but almost normal levels (1.8 ng L⁻¹ in the water column and 0.14 µg g⁻¹ in the sediments) are reached 60 km downstream of that zone. In general, low dissolved methylmercury (MMHg) concentrations were found (0.04–0.05 ng L⁻¹) due to unfavourable methylation conditions. The MMHg concentrations in the sediments vary from 23.3 ng g⁻¹, in the vicinity of the geological Hg deposits, to 0.17 ng g⁻¹ 60 km downstream. Total Hg levels in Lake Teletskoye (a geological active area) are slightly increased (1.1–1.8 ng L⁻¹) compared to Lake Baikal and fairly constant allover the Lake, suggesting multiple sources. High mercury concentrations in springs and soils coincide with high radon concentrations in the same compartments as well as high soil exhalation fluxes. These results in combination with the fact that Lake Teletskoye is located in an active fault zone suggest that the Rn and Hg sources may be fault aligned spring waters and deep seated gases escaping through open cracks. Methylmercury concentrations in the Lake (0.03–0.1 ng L⁻¹) were comparable to the concentrations found in Katun river but relative to the total Hg burden this means a higher percentage.

Keywords: air, exhalation, geological deposits, Katun river, mercury, natural sources, radon, sediments, Teletskoye, water

1. Introduction

In recent years new analytical techniques have become available leading to a more correct understanding of the mercury behaviour in natural systems. Consequently new attempts have been made to establish global and regional Hg cycles and mass balances (Mason *et al.*, 1994; Fitzgerald and Mason, 1996; Iverfeldt *et al.*, 1996; Sukhenko and Vasiliev, 1996). However, these budgets still suffer from relative large uncertainties regarding the contribution from various natural Hg sources such



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as earth crust degassing or volcano emissions. A major reason is that in many regions anthropogenic activities jeopardize the quantification of those natural processes. It is therefore interesting to study natural Hg sources in areas remote from anthropogenic activities.

Mercury is relatively homogeneously spread over the lithosphere, forming a natural geochemical background (see for example Adriano (2001), or Kabata-Pendias and Pendias (2000)), but local anomalies caused by Hg concentrated deposits and ores are interposed. These natural enriched deposits are located within 3 planetary belts (Pacific, Mediterranean and Central Asian), confined to global structures of the earth. A peculiar feature of these belts is that they are specifically situated in actively developing parts of the lithosphere such as the Mesozoic and present day subduction zones, island formations, hot spots and rifting structures of continental margins and their inner parts (Obolensky *et al.*, 1995). The localization of Hg deposits within these planetary belts is related to deep lithospheric faults of mantle origin. The transcontinental central Asian Hg belt, a 1000 km stretch along the southern border of Siberia, includes three ore zones: Altai-Sayan, Transbaikalia and the upper Yana-Kolyma regions. The Altai-Sayan region contains the largest number of geological Hg deposits with abundant explored Hg resources, but is remote from large settlements and from anthropogenic activities others than mining

In the Altai Mountains, a region of the size of France, Lake Teletskoye and the Katun river, a major tributary of the Ob River, are of particular interest (Figure 1): both are situated in the Altai-Sayan Hg belt but Hg exposure seems to follow quite different pathways. Lake Teletskoye's drainage Basin includes no major geological Hg deposits but it is located in a geological active zone while in the Katun river Basin several large geological Hg deposits are present. The Aktash geological deposits (upper Katun river, Gorny Altai) are the most important from a point of view of mining: between 1941 and 1991 about 5000 tons of metal mercury were produced (Obolensky *et al.*, 1995). During that production process river water was abundantly used for rinsing purposes. Our first goal was therefore to assess the influence of the Aktash geological Hg deposits and the related mining activities on the Katun river ecosystem. Lake Teletskoye, whose morphology is controlled by fault zones, is one of the major neotectonic structures in Altai. These fault zones form an open crack system allowing gases of deep origin to migrate towards the surface by advection. By assessing vertical fluid transport through radon emanation and exhalation as well as Hg and Rn levels in soils and spring waters we tried to better understand the observed Hg distribution in and around the Lake.

2. Sampling Area

During two summer expeditions (1995 and 1997) the Altai Region (Figure 1) was studied.

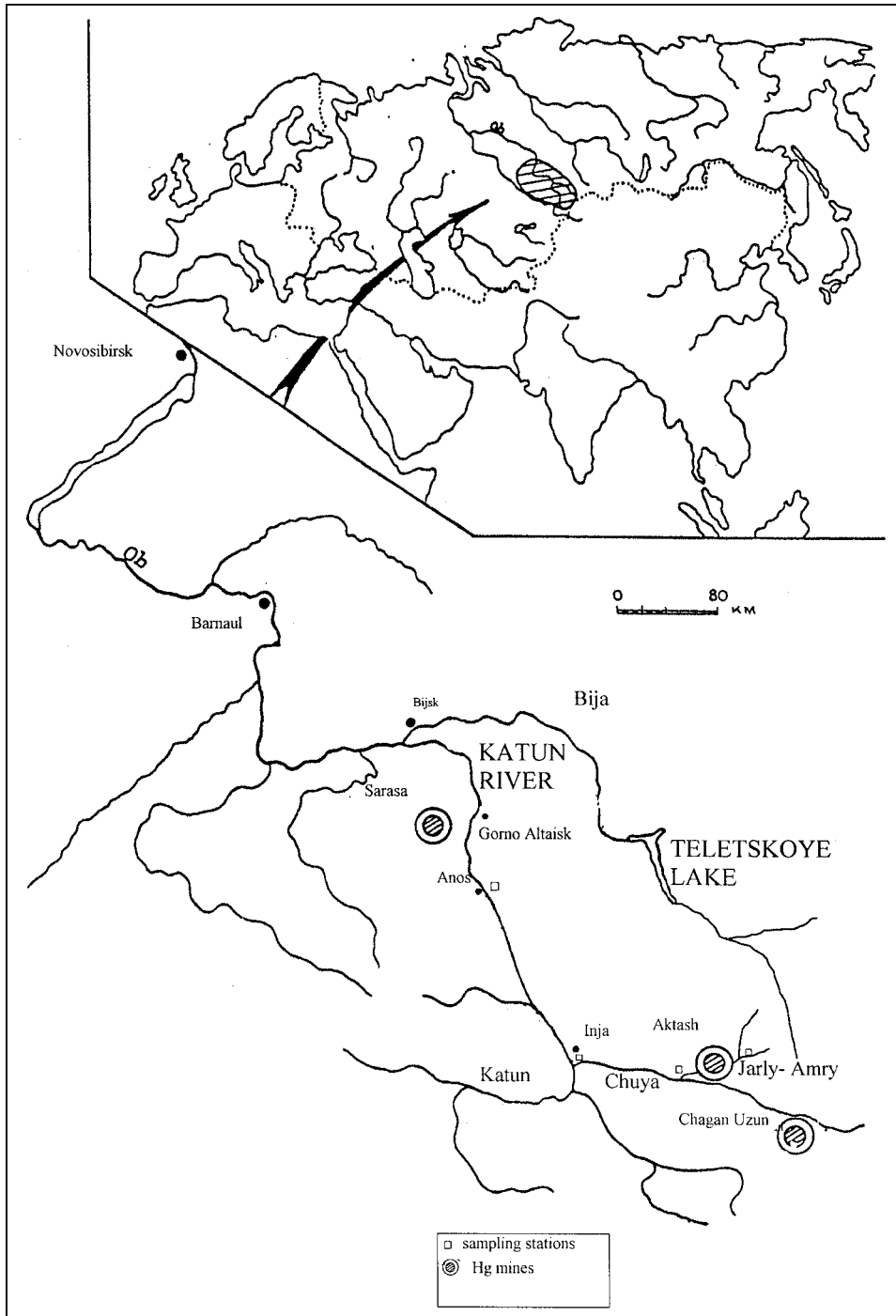


Figure 1. Map of the study area.

The Katun River is the main Altai River. It is approximately 690 km long, draining an area of 60 900 km², mainly mountainous terrain. It joins the Biya River to form the Ob River. The mean flow rate (freshwater discharge) is 2–3 m³ s⁻¹, however, in the period of snow and glacier melt, the water flow can increase by a factor of 10–20.

Lake Teletskoye is the largest body of fresh water in south-western Siberia and Siberia's second largest after Lake Baikal and has remained virtually free of development. Lake Teletskoye is composed of two basins perpendicular to each other: one is 30 km long and oriented from west to east, the other is 50 km long and oriented from North to South. In the west-east basin the depth increases from 5 to 300 m, while the North-South basin has a more uniform depth between 200 and 300 m, except at the southern border. The lake is fed in the south by two rivers, Chulyshman (west side), which is responsible for 70% of the total water inflow and Kyga (east side), while river Biya forms the outflow.

3. Methods and materials

3.1. MERCURY

3.1.1. *Air*

The sampling set-up consists of three gold traps placed in line. The first two gold traps are sampling columns while the third column (back diffusion column), serves to eliminate possible contamination from the pump. A quartz wool plug is placed in front of the first column to retain particulate phase Hg. Sampling is performed at a flow rate of 250 mL min⁻¹ and sample volumes vary from 100 to 400 L (measured with a calibrated gas meter).

Under these conditions concentrations down to 0.001 ng m⁻³ can be measured. After sampling the collection and control columns were closed with Teflon plugs and stored in P.E.-tubes until analysis by a two-stage gold amalgamation procedure (Baeyens and Leermakers, 1989).

3.1.2. *Water*

In Katun river and its tributaries, surface water samples were collected by hand by submerging rigorously cleaned Teflon (FEP) and borosilicate glass bottles approximately 20 cm beneath the water surface. The bottles were filled with a 1% HCl solution (Merck, suprapur) and stored double bagged until use. The sampling bottles were rinsed twice with the sample water before being filled. Sampling on Lake Teletskoye was performed from the scientific vessel 'Biosphera' from the Institute for Water and Environmental Pollution (IWEP), Novosibirsk. Samples from surface to bottom were collected from the vessel using NOEX (Technicap, France) (Go-Flo type) sampling bottles, Kevlar cable and plastic coated messengers.

3.1.3. Sample Handling

Filtration is performed directly after collection with a filtration unit that avoids any contact between the sample and the ambient air. The filtration unit consists of a FEP separating funnel onto which a Teflon filter holder is connected. Filtration is performed by pressure filtration using N₂ gas. Hg is removed from the gas stream by a gold column. Each batch of filters (Nuclepore polycarbonate) was analysed before use to check the blank. These filters had low blanks.

The filtered samples are collected in acid cleaned borosilicate or FEP-bottles. The acid in the bottle is discarded and the bottle placed under the filter holder. The first 20 mL are discarded. After filtration, samples are acidified with 0.5% HCl (Merck, suprapur) whereas samples for dissolved methylmercury (MMHgD) are stored deep-frozen and unacidified. The sampling bottles are tightly capped and double bagged in zip-loc bags. The filters are stored in Millipore filter holders, sealed in PE bags and stored deep-frozen. Analysis is performed on the wet filters. Parallel filters are taken for turbidity measurements.

Analytical methods used for Hg speciation (see also Leermakers *et al.*, 2001): Total dissolved Hg (HgTD), was determined by cold vapour atomic fluorescence spectrometry using a BrCl oxidation step and reduction with NH₂OH.HCl prior to reduction with SnCl₂ and Au-amalgamation preconcentration step (Gill and Fitzgerald, 1987). The detection limit was 0.25 pmol L⁻¹ for HgTD. Total dissolved MMHg (MMHgD) was analysed by aqueous phase ethylation - gas chromatography - AFS detection (Liang *et al.*, 1994). Hg species are transformed to their volatile ethylderivates (methylmercury and diethylmercury) using sodium tetraethylborate, purged out of solution and collected on Carbotrap or Tenax columns. GC separation is performed isothermally (Liang *et al.*, 1994). In this procedure the GC column was held at a constant temperature of 75 °C and the Tenax column is heated for 20 s at 350 °C. The resolution between Hg⁰ and methylmercury is 2 and between methylmercury and diethylmercury is 1.8. Extraction blanks are typically 5 ± 1 pg. This results in a detection limit of 0.3 pmol L⁻¹ (60 pg L⁻¹) for a 50 mL sample and 0.075 pmol L⁻¹ (15 pg L⁻¹) for a 200 mL sample.

The successive steps to determine total particulate Hg were:

- (1) digesting the filters in 5 mL HNO₃/HCl (4:1) at 60 °C for 12 hr in Teflon digestion vessels;
- (2) diluting the sample to 50 mL;
- (3) analysis of a fraction of the sample by CVAFS as described above.

Particulate MMHg was extracted by distillation (Horvat *et al.*, 1993). After extraction the Hg compounds are analysed in the same way as MMHgD.

3.1.4. *Sediment and Soil*

Sediment samples were collected by Van Veen grab. All samples were deepfrozen, lyophilized (Leybold Heraeus Lyophilizer), grinded in a mechanical agate mortar (Fritsch Pulverisette) and stored in clean PE containers. Total Hg and MMHg in sediments were determined in the same way as in suspended matter.

QC procedures and participation in intercomparison exercises: Blanks, spiked samples and certified reference materials (CRM's) are added to each batch of samples. As no CRM's exist for MMHg in water, CRM's of biological material are used (NRC DORM-2, NRC DOLT-2, NRC TORT-2) and sediments (IAEA 405, BCR 580).

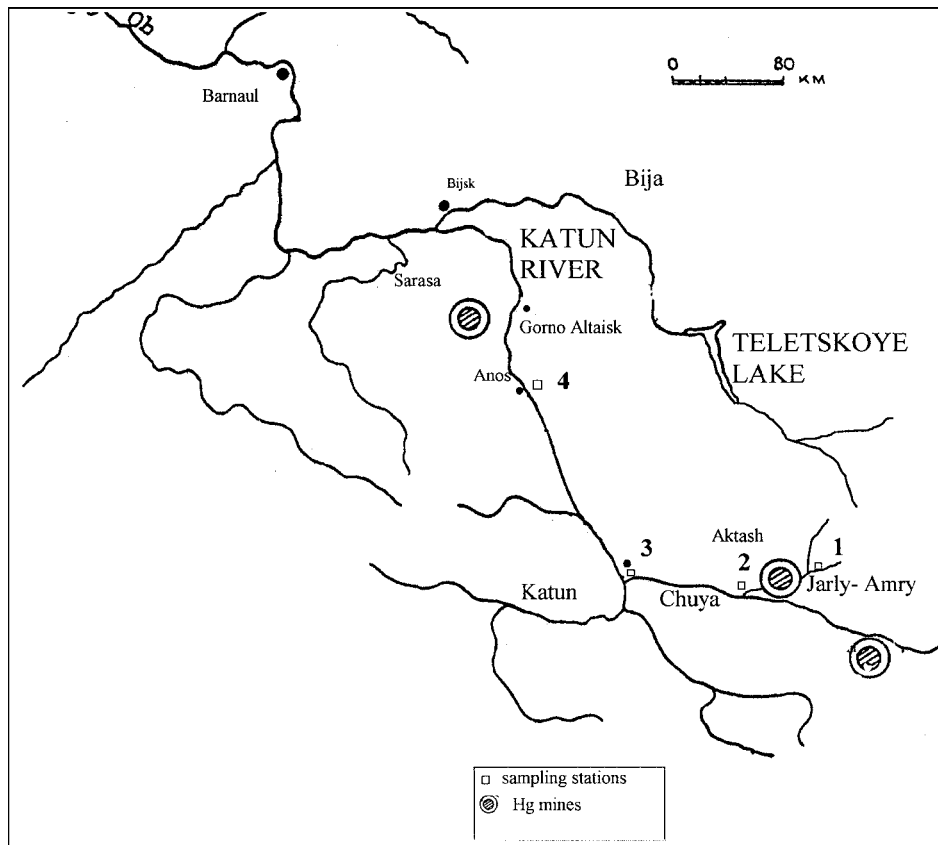
From 1993–1996 we participated in Aquacheck intercomparison exercises for total mercury in water and from 1996 onwards we participated in the Quasime intercomparison exercises for total Hg in water. We also participated in an intercomparison exercise for the analysis of total Hg and MMHg in fresh water in November 1993 (Bloom *et al.*, 1995) as well as in the certification of the BCR 580 sediment sample for MMHg.

3.2. RADON

Rn concentrations in soil gas (emanation) were determined with two different methods along traverses running perpendicular to the West-Sayan fault zones, in the northern part of Lake Teletskoye (Dehandschutter *et al.*, 1997).

The radon activity (emanation) was measured in soil-gas extracted by a syringe through a hollow tube that was inserted about 80 cm into the ground to avoid the influence of meteorological fluctuations on the radon soil gas concentration. In the first method radon concentrations were determined by injecting the soil-gas in an electret-ionization chamber (E-PERM) where the ^{222}Rn activity is deduced from the reduction of surface potential of a charged synthetic layer (electret) inside the ionization chamber (Kotrappa *et al.*, 1988). Ten min of sample equilibration before injection into the electret cell brought the thoron concentration to a negligible level ($T_{1/2} = 56$ s). In the second method, the soil gas was directly pumped from the hollow tube into a scintillation chamber, using a hand-pump. Because both radon (^{222}Rn) and thoron (^{220}Rn) decay by means of alfa-emission, counting was performed during 4 intervals of 100 sec each. The concentration of both isotopes could be determined by solving a set of equations. Additionally to the soil gas concentration measurements, radon concentrations in spring-waters were determined by an E-PERM electret device for water sample measurements, and by a SARAD scintillation counter for water samples.

To determine the radon flux (exhalation) radon was trapped on active charcoal by Van der Waals forces (Gustafsson and Hildingson, 1984). The charcoal was buried in the ground at 15 cm depth for 12–24 hr. Sample distance was 20 m. Radon concentrations were determined according to Cohen and Cohen (1984).



Hg concentrations in sediments			Hg concentrations in water		
station	Hgtot ng/g	MMHg ng/g	station	Hgtot ng/L	MMHg ng/L
1	8700	8.6	1	9.8	0.04
2	244000	23.3	2	20.14	0.051
3	720	0.6	3	12	0.047
4	140	0.17	4	1.8	0.055

Figure 2. Katun river and tributaries: Total Hg and methylmercury concentrations in sediments (ng-Hg g^{-1} – dry weight) and in river water (ng-Hg L^{-1}).

4. Results and Discussion

4.1. KATUN RIVER

The highest levels of Hg in sediments ($244 \mu\text{g g}^{-1}$, see Figure 2) and in water (20 ng L^{-1} , see Figure 2) were found downstream of the Aktash mining area located on Chuya river a tributary of Katun river. Large amounts of mercury were discharged into Katun River Drainage Basin (KRDB) during processing of mercury-rich ores. In the period 1941 to 1991 about 5000 tons of metal mercury were

produced at Aktash. In addition, weathering of the mine tailings also contributed to the strong pollution of Chuya river. At the confluence of Chuya and Katun river (30 km from Aktash), Hg concentrations have dropped to $0.72 \mu\text{g g}^{-1}$ in sediments and 12 ng L^{-1} in water. Further downstream, at the town of Anos (30 km from the Chuya mouth) concentrations amounted to $0.14 \mu\text{g g}^{-1}$ in sediments and 1.8 ng L^{-1} in water, which are 1000 (sediments) and 15 times (dissolved water column) lower than at Aktash.

MMHg concentrations in sediments vary from a maximum of 23.3 ng g^{-1} downstream of the Aktash mining area to 0.17 ng g^{-1} in the lower Katun river (at Anos) and account for 0.01 to 0.1% of the total Hg burden in the sediments. In water, MMHg shows very little variation in concentration ($0.04\text{--}0.05 \text{ ng L}^{-1}$) accounting from 0.25–2.7% of the total Hg. The low methylmercury fraction confirms previous findings of low bioaccumulation of Hg in this area (Sukhenko and Vasiliev, 1995). The low water temperature, low contents of dissolved organic matter and nutrients, high pH and high Ca concentrations are factors which hinder the methylation of Hg in agreement with literature data (Watras *et al.*, 1995).

In Table I a comparison is made with the Ob estuary (Coquery *et al.*, 1995), about 3500 km downstream Katun river, and with the Scheldt estuary (Leermakers *et al.*, 2001), an anthropogenic polluted estuary. It appears that the dissolved Hg levels in Katun river at Anos (60 km downstream the Hg deposits) are about 1.5 times higher than the actual levels in the upper part of the Scheldt estuary, an anthropogenic polluted estuary. A few years ago (1991–1996) the dissolved Hg levels in the upper Scheldt estuary (Baeyens, 1998) were similar to those at Anos. The Hg concentrations in the suspended matter and in the sediments at Anos and in the upper part of the Scheldt estuary are also comparable. Much lower values are observed in suspended matter of the Ob estuary (Coquery *et al.*, 1995) and in sediments of the downstream part of the Scheldt estuary (Leermakers *et al.*, 2001). The dissolved MMHg levels at Aktash and Anos, in Katun river, are only slightly higher than in the Scheldt estuary, but this is due to the low methylation rate in Katun river as mentioned before. In the sediments at Aktash, very high MMHg levels were observed although they only account for 0.01% of the total Hg amount in the sediments. At Anos MMHg levels in the sediments are comparable to those in the upper part of the Scheldt estuary.

The impact of the Hg deposits on the water quality and the sediments of Katun river is visible up to Anos, somewhat 60 km downstream. However, according to Mal'gin and Puzanov (1995) the atmospheric levels are enhanced over a much larger area. Highest values were observed at Aktash – between 12 and 200 ng m^{-3} with an average of 62 ng m^{-3} – but at Anos the average concentration of 7 ng m^{-3} is still exceeding typical background atmospheric values as measured at Mace Head (Ireland) which range between $1\text{--}3.5 \text{ ng m}^{-3}$ (Ebinghaus and Krüger, 1996).

TABLE I
Hg distribution in Katun river, Ob and Scheldt estuaries

	Katun river		Ob estuary ^a	Scheldt estuary ^b	
	Aktash	Anos		Upstream	Downstream
Watercolumn					
Hg-total					
(ng L ⁻¹)	20 (14–25)	1.8 (1.3–2.3)	0.56 (0.48–0.64)	1.1 (0.55–1.6)	0.61 (0.32–0.73)
Particulate					
(ng L ⁻¹)	8400 (60–58000)	40 (4–400)		35 (24–47)	12.7 (3.8–33)
(ng g ⁻¹)	153000 (53000–375000)	700 (70–1400)	50 (44–56)	960 (730–1140)	370 (200–440)
Total					
(ng L ⁻¹)	8400	42		36	13
MMHg					
Dissolved					
(ng L ⁻¹)	0.051 (0.046–0.057)	0.055 (0.049–0.060)		0.037 (0.015–0.058)	0.028 (0.012–0.043)
Particulate					
(ng L ⁻¹)				0.050 (0.030–0.071)	0.031 (0.029–0.032)
(ng g ⁻¹)				2.19 (2.03–2.34)	1.72 (1.22–2.23)
Total					
(ng L ⁻¹)				0.087	0.059
Sediments					
Hg-total					
(ng g ⁻¹)	244000 (90000–410000)	140 (30–330)		530 (420–730)	89 (4–264)
MMHg					
(ng g ⁻¹)	23.3 (15–34)	0.17 (0.03–0.44)		0.26 (0.14–0.47)	0.058 (0.007–0.16)

^a Coquery *et al.* (1995).

^b Leermakers *et al.* (2001); concentration ranges are based on cruise averages.

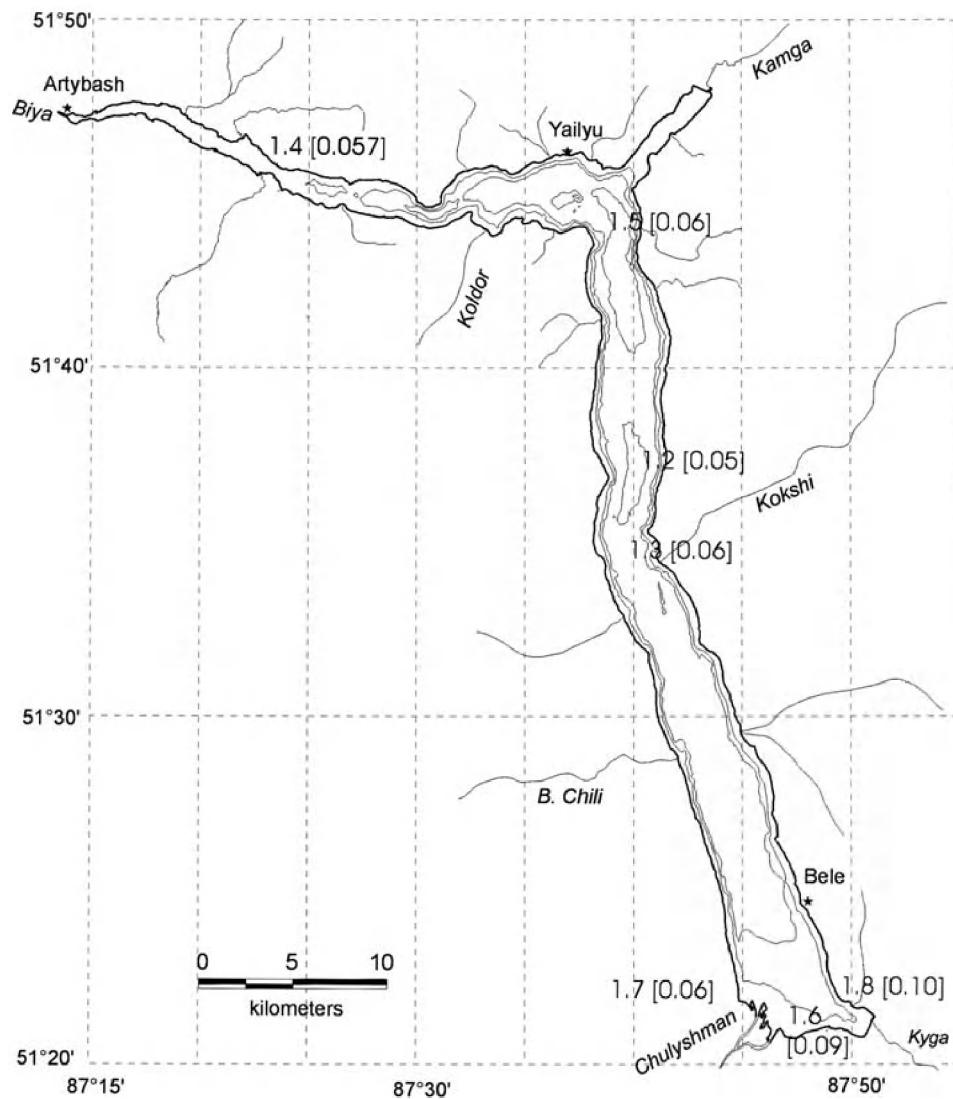


Figure 3. Total Hg and methylmercury [between brackets] concentrations (ng-Hg L⁻¹) in water of Lake Teletskoye.

4.2. LAKE TELETSKOYE

4.2.1. Mercury

Spatial distributions of Hg and MMHg in the water column, the sediments and the atmosphere are shown in Figures 3 to 5. Total Hg concentrations in surface waters of the Lake are fairly constant (1.1–1.8 ng L⁻¹) with slightly higher concentrations in the southern end of the Lake at the entrance of the rivers Chulyshman and Kiga. MMHg concentrations range from 0.03–0.1 ng L⁻¹, accounting for 3–5% of the

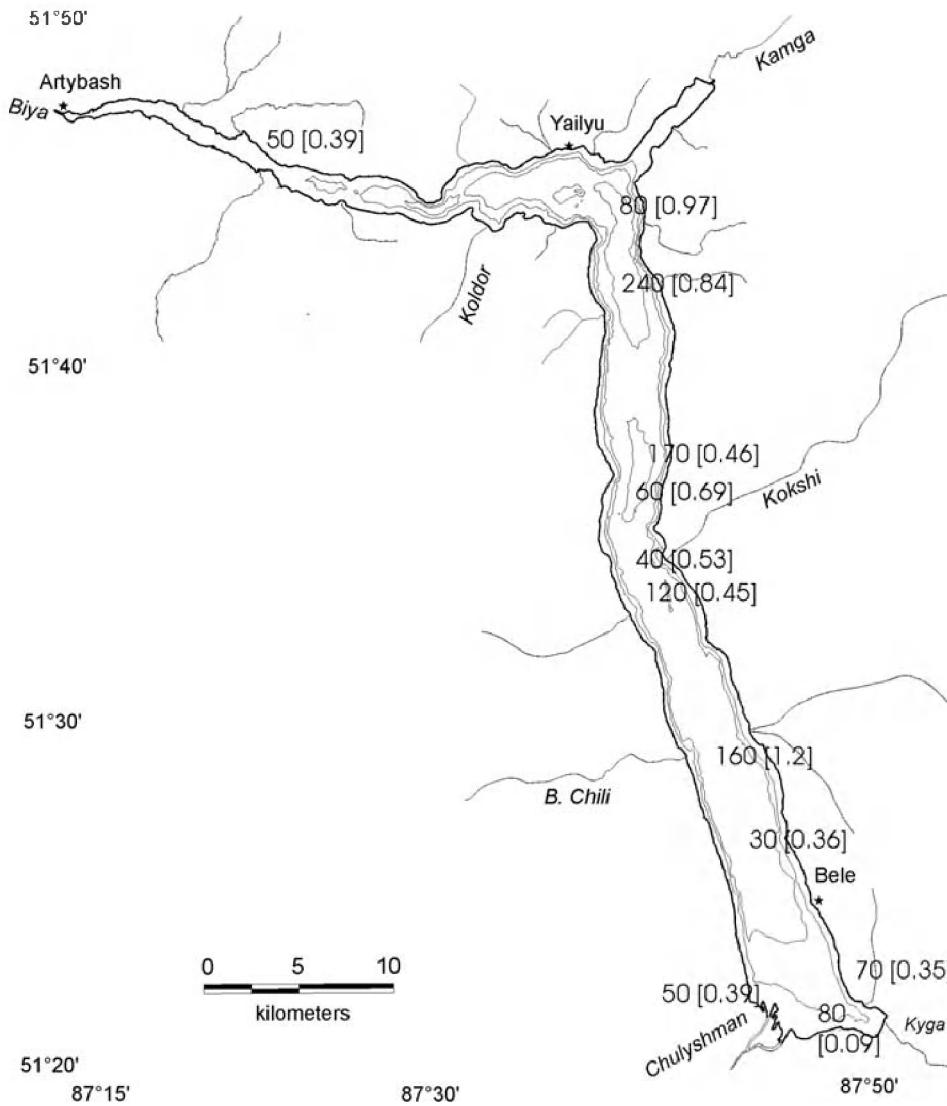


Figure 4. Total Hg and methylmercury [between brackets] concentrations (ng-Hg g⁻¹ – dry weight) in sediments of Lake Teletskoye.

total Hg concentrations and are comparable to the concentrations found in Katun river. Vertical profiles of MMHg in the water column show either a maximum in the surface waters or no vertical gradient. The concentrations of total Hg are higher than those observed in Lake Baikal in June 1992 (0.14–0.77 ng L⁻¹) (Meuleman *et al.*, 1995).

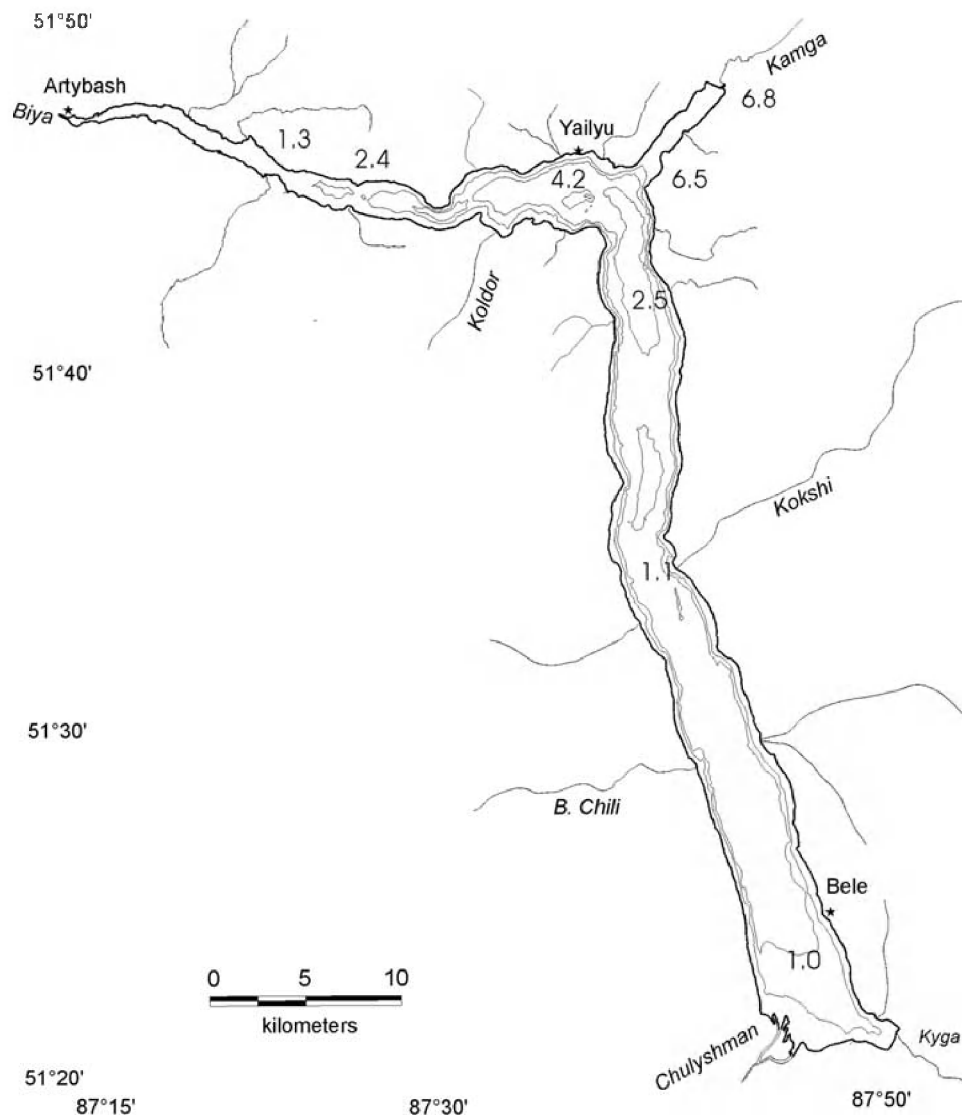


Figure 5. Atmospheric gaseous Hg concentrations (ng-Hg/m³) on Lake Teletskoye.

Total Hg in the sediments of the Lake range from 0.03 to 0.24 $\mu\text{g g}^{-1}$ with MMHg concentrations ranging from 0.36–1.21 ng g^{-1} , accounting for 0.3–1.2% of the total Hg.

Atmospheric Hg concentrations are highest (up to 7 ng m^{-3}) at the Northeastern end of the Lake. A clear North-South and East-West concentration gradient was observed with lowest values (1 ng m^{-3}) at the southern end of the Lake. A comparison (Table II) with Lake Baikal (Meuleman *et al.*, 1995) reveals that total Hg levels in

TABLE II
Hg distribution in lakes Baikal and Teletskoye

	Baikal ^a	Teletskoye
Watercolumn		
Hg-total (ng L ⁻¹)		
Open water	0.14–0.77	1.1–1.8
Shallow bays	0.15–2.0	
MMHg (ng L ⁻¹)		
Open water	0.002–0.038	0.03–0.10
Shallow bays	0.024–0.16	
% MMHg		
Open water	1–15	3–5
Shallow bays	8–35	
Sediments		
Hg-total (ng g ⁻¹)	6.0–72	400–2400
MMHg (ng g ⁻¹)		0.36–1.4
% MMHg		0.06–0.09
Atmosphere		
Hg-gaseous (ng m ⁻³)		
Summer	0.73–2.3	1.0–7.0
Winter	1.2–6.2	

^a Meuleman *et al.* (1995).

Lake Teletskoye are much more constant, clearly higher than in open water in Lake Baikal but lower than the shallow bay levels there. Most of the shallow bay levels in Lake Baikal are directly controlled by riverine input (Selenga, upper Angara, Barguzin) while in Lake Teletskoye river impact is more limited, resulting in a more uniform distribution.

Looking into detail, slightly higher Hg concentrations in the southern part of the Lake are observed (1.6–1.8 ng L⁻¹), compared to its average value (1.48 ± 0.21 ng L⁻¹). This is an indication that river runoff, although to a more limited extend than for Lake Baikal, also contributes to the Hg burden in the Lake. The drainage basin of Chulyshman, the main river, is situated north of major geological Hg deposits and not directly influenced by them. However, small, not spotted deposits or spring

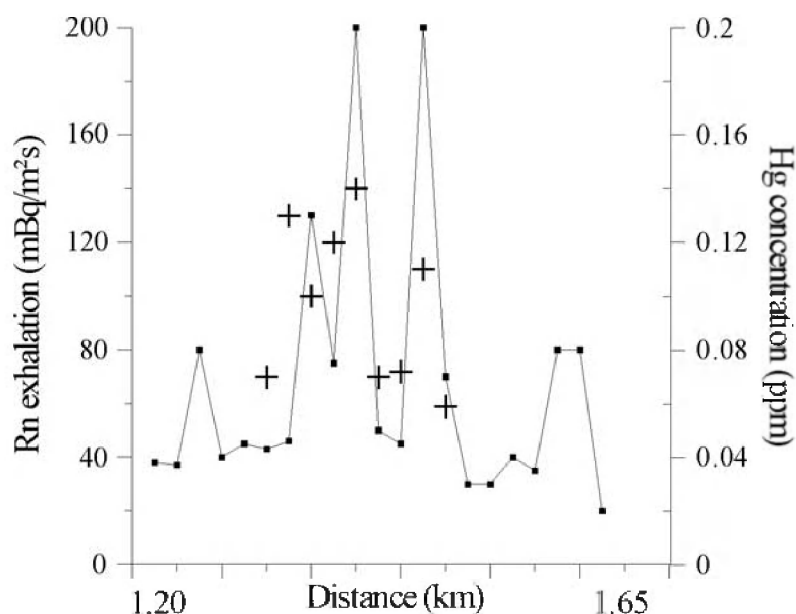


Figure 6. Radon exhalation fluxes ($\text{mBq/m}^2\text{s}$) and Hg concentrations ($\mu\text{g g}^{-1}$) in soils around Lake Teletskoye. Rn (dots) and Hg (crosses).

waters may enhance the Hg levels in that river. The highest MMHg percentages (about 5%) are found in the mixing zone of Chulyshman and Kyga in the southern part of the Lake, coinciding with higher levels of organic and suspended matter. The methylation rate (3–5%) is comparable to that in Lake Baikal (1–15%) but higher than in Katun river (0.25–2.7%).

4.2.2. Radon and Mercury

The West-Sayan fault zone is a reactivated Paleozoic shear zone that controls the morphology of Lake Teletskoye. Its movement is responsible for the opening of the northern basin, the deepest and youngest sub-basin of lake Teletskoye (Dehandschutter *et al.*, 1997). Local zones of anomalous high radon activity are observed. They indicate that the West-Sayan fault zone is characterized by highly permeable deep fracture zones with gas-carrying fluid circulation.

Mercury concentrations in soils along the zone with radon anomalies are significantly higher (around $0.12 \mu\text{g g}^{-1}$) than outside the anomaly zone (around 0.06 – $0.07 \mu\text{g g}^{-1}$ which falls in the background range of 0.014 to $0.073 \mu\text{g g}^{-1}$ of Hg soil values in West Siberia; see Anoshin *et al.*, 1996). High mercury concentrations coincide with high radon exhalation as well as high emanation values (Figure 6). Therefore, according to Dehandschutter *et al.* (1997), the common source of the gases should be rather deep seated than superficial. Comparing mercury and radon concentrations in spring waters (Figure 7), it turns out that higher mercury concentrations generally correspond to higher radon values. These 'geochemical active

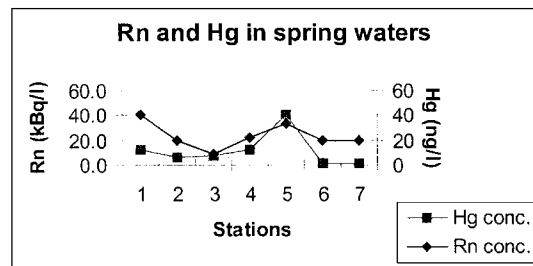
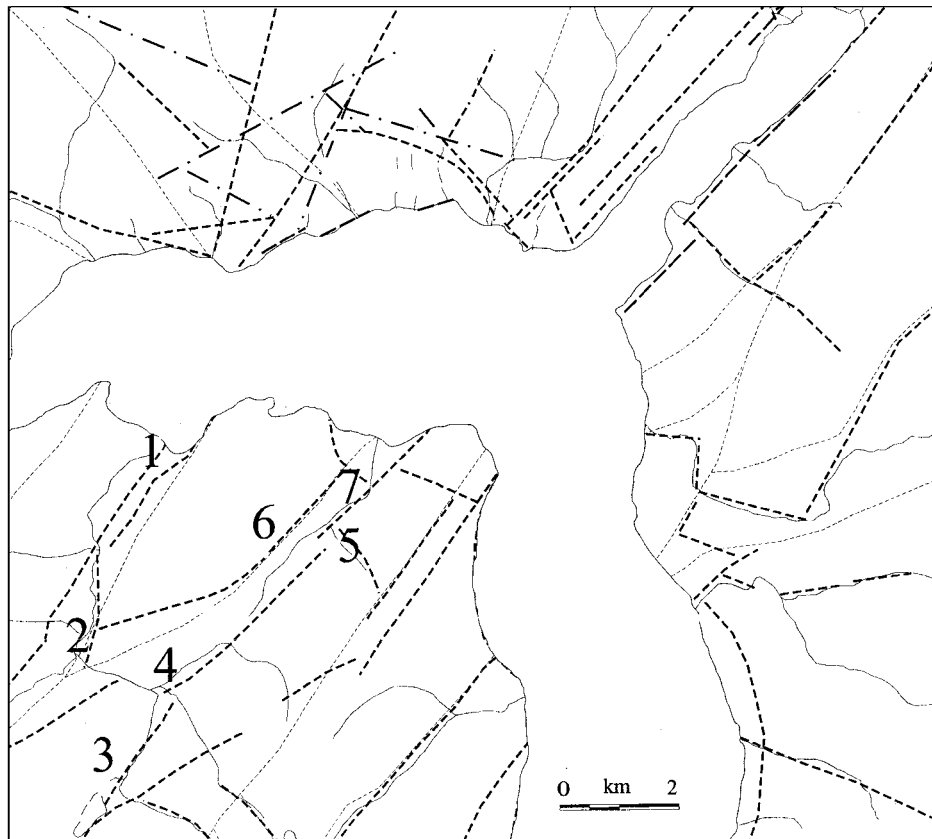


Figure 7. Spring water sampling locations around Lake Teletskoye. Radon (kBq L^{-1}) and Hg (ng L^{-1}) concentrations in these spring waters.

springs' occur along the West-Sayan fault zone. They can be correlated to the high radon fluxes and most of the anomalies in emanation pattern.

The enhanced Hg levels in Lake Teletskoye (water and sediments) and in the atmosphere (especially the northern part) must result from natural sources since there exist no anthropogenic activities. These sources most probably include advection of fluids and gases through open cracks, but further research should confirm this.

TABLE III
Hg distribution in two geological enriched areas: Katun and Carson River Drainage Basins

	Katun river		Carson river ^a	
	Aktash	Anos	Bessel Mill/ Six Mile Canyon	Lousetown Creek
Water total (ng L ⁻¹)	60–58000	4–400	3880–35400	8–10
Water MMHg (ng L ⁻¹)	0.046–0.057	0.049–0.060	7.2–9.4	0.4
Sediments (μg g ⁻¹)	90–410	0.03–0.33	66–610	0.1–1.6
Atmosphere (ng m ⁻³)	12–200 ^b	<7> ^b	51.9–294	<3>
Plants (μg g ⁻¹ d.w.)	16–86 ^c	0.06–0.27 ^c	0.43–2.40 (overall area)	
Fish (μg g ⁻¹ w.w.)		0.04–0.23 ^c	up to 5.5 (overall area)	

^a Gustin *et al.* (1994).

^b Mal'gin and Puzanov (1995).

^c Sukhenko and Vasiliev (1995).

4.3. THE ALTAI REGION, AND ESPECIALLY KATUN RIVER DRAINAGE BASIN, IN TERMS OF Hg HAZARD

Geological enriched areas and in particular those where mining takes place show enhanced Hg concentrations in various environmental media. On the scale of the Katun River Drainage Basin, which covers almost 61 000 km², the mercury mines (Aktash, which is the major one, Chagan-Uzun and Sarasa, see Figure 1) are all situated along a limited stretch of about 100 km along the river. It is in this zone that atmosphere, water column and sediments are contaminated with Hg. The interpretation of these data in terms of Hg hazard needs an understanding of the pathways of mercury exposure to the different trophic levels of the ecosystem and to humans. Considering that a somehow similar situation is encountered in the Carson River Drainage Basin (CRDB) of Nevada (Gustin *et al.*, 1994), a comparison between both sites offers a number of advantages. Both sites are situated in a natural mercuriferous belt resulting in regional higher background concentrations. In addition, large amounts of mercury were discharged into the CRDB during processing of gold- and silver-rich ores, while Hg pollution of Chuya and Katun river in the KRDB was caused by the processing of mercury-rich ores. In Table III mercury

concentrations in various media of CRDB and KRDB are compared. Values for the CRDB were reported by Gustin *et al.* (1994) while for KRDB, in addition to our data, atmospheric values were reported by Mal'gin and Puzanov, plant and fish concentrations by Sukhenko and Vasiliev (1995). In each of the Drainage Basins we choose a contaminated site (Bessel Mill or Six Mile Canyon for CRDB and Aktash for KRDB) and a regional background site (Lousetown Creek for CRDB and Anos for KRDB). Very high total mercury concentrations in the atmosphere, water and sediments were found at both contaminated sites, while levels in the same compartments at Lousetown Creek and Anos were much lower. The most striking difference between both Drainage Basins is the much lower methylmercury levels in KRDB: 100 times lower at the contaminated and 10 times lower at the background site. As discussed yet before, methylation conditions in Katun river system (low water temperature, low contents of dissolved organic matter and nutrients, high pH and high Ca concentrations) are rather unfavourable.

Low MMHg concentrations in the water column will normally result in low MMHg levels in fish, but it is difficult to verify it in the Katun river system since, unfortunately, no fish data for the contaminated site are available. At Anos fish levels vary from 0.04 to 0.23 $\mu\text{g g}^{-1}$ w.w. which agrees well with natural background levels in fish that lay in the range 0.02 to 0.2 $\mu\text{g g}^{-1}$ w.w. according to Huckabee *et al.* (1974). Gustin *et al.* (1994) reported that fish species from several sites in the CRDB exceeded the federal action level of 1.0 $\mu\text{g g}^{-1}$ w.w. and that even mercury concentrations in fish from an area outside the CRDB were somewhat higher than the natural background level, although lower than 0.5 $\mu\text{g g}^{-1}$ w.w. While it is widely assumed that the principal pathway for mercury exposure in humans is food consumption, in particular fish, this might not be the case for the KRDB. On the other hand, the mercury concentrations observed in plants (Sukhenko and Vasiliev, 1995) are very high at the contaminated site and are 30 km downstream at Chuya mouth still around 0.24–4.3 $\mu\text{g g}^{-1}$ d.w. comparable to values reported for CRDB (Gustin *et al.*, 1994). Animals feeding on these plants may exhibit adverse health effects. As in the case of CRDB, the pathways by which humans are exposed to mercury in KRDB are likely complex, including inhalation, dermal contact and ingestion of contaminated water. Fish consumption, however, might not be a major health risk.

The atmospheric concentrations measured in the KRDB and also at Lake Teletskoye (see Table II) can give us information about natural emissions in geological Hg enriched areas. Natural global emissions are estimated at 3000 tons yr^{-1} or 6 $\text{g km}^{-2} \text{yr}^{-1}$ by Nriagu and Pacyna (1988), but according to Mason *et al.* (1996), these 3000 tons yr^{-1} can be subdivided in an ocean flux of 2000 tons yr^{-1} and an earth crust flux of 1000 tons yr^{-1} . The ocean respectively earth crust flux results in an average Hg emission rate of 5 respectively 10 $\text{g km}^{-2} \text{yr}^{-1}$. Using an earth crust emission rate of 10 $\text{g km}^{-2} \text{yr}^{-1}$ for a background atmospheric concentration of 1–3.5 ng m^{-3} , emission fluxes at Anos (average atmospheric concentration of 7 ng m^{-3} for KRDB), Lousetown (average atmospheric concentration of 3 ng m^{-3}

for CRDB) and Lake Teletskoye (average atmospheric concentration of 3.2 ng m^{-3}) can be estimated. They amount to $20\text{--}70 \text{ g km}^{-2} \text{ yr}^{-1}$ at Anos, $10\text{--}30 \text{ g km}^{-2} \text{ yr}^{-1}$ at Lousetown and $10\text{--}30 \text{ g km}^{-2} \text{ yr}^{-1}$ at Lake Teletskoye. Despite the relative large uncertainty on the estimated emission fluxes, the calculated values suggest that earth crust emissions inside mercuriferous belt zones are larger than outside them, enhancing the atmospheric Hg concentrations there. Hence, the effect would be noticeable on a much larger scale than that of a river drainage basin, but more studies about natural Hg degassing and atmospheric Hg concentrations in mercuriferous belt zones are needed to reduce the uncertainty range on fluxes and concentrations.

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