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Influence of Fly Ash of KarGRES-1 on decrease of risk posed by mercury pollution of the Nura River

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The Nura River is an internal river of Central Kazakhstan with a length of 978 km. Its source lies at a height of 1060 m on north-west spurs of Karkaralinsk Mountains. The river average annual flow is 0.6 km^3 80% of which falls at spring flood. The Nura River terminates in the wetlands of Tengiz-Kurgaldzhino depression at a height of about 300 m. The river passes on its course three major cities of Central Kazakhstan region such as industrial centers of Karaganda (population 420 thousand) and Temirtau (populations 170 thousand) as well as Astana (population 520 thousand) a new capital of the country. The average of many years discharge of the Nura River in the cross-section of Temirtau is 7.3 m^3/s and in the cross-section of Astana – 19.4 m^3/s. Salinity of the river water in the cross-section of city of Temirtau is 0.6-0.9 mg/l and its pH is 7.2-8.6. Until the 1940s the river was the only source of water supply for scarce population of the region mainly occupied in agricultural sector. In order to provide water supply for developing industry in cities of Karaganda coal-field region started from the 1930s two reservoirs: Samarkandskoe (254 million m^3) and Sherubainurinskoe (274 million m^3) were constructed in the basin of the Nura River. Alluvial groundwater underflow was also widely used. Vyacheslavskoe reservoir with capacity of 410 million m^3 was constructed on the Ishim River for water supply of Astana. However these water sources were not sufficient and in 1962 construction of Canal Irtysh-Karaganda was started to overcome this constraint. The canal has a length of 458 km and designed capacity up to 2 km^3 per year lifting up water from the Irtysh River by 416.6 m and delivering it to Karaganda, Temirtau and Astana cities since 1975. The cost of water at the end of the canal reaches 0.5 USD per m^3 [1]. In Soviet time this water was delivered to consumers almost free of charge.

Operation of the canal led to excessive amount of water in the region and as a result irrigation was flourishing both along the canal and in the Nura River valley. However due to the lack of consumption the actual water delivery of the canal reached only 1 km^3 per annum. After the USSR collapse the government of independent Kazakhstan had to impose a part of the canal's operational costs on the consumers and annual rate of water delivery decreased to 0.3-0.5 km^3. At present World Bank of Reconstruction and Development regards the Nura River as a water-supply alternative to the Canal Irtysh-Karaganda. The rate of regional water consumption is expected to rise which is associated with fast development of new capital of

Kazakhstan – Astana City. However the potential of water supply of Astana using water from the Nura River is limited due to contamination of the river with industrial effluents from upstream cities of Karaganda and Temirtau.

In 2004 the designing phase of the Nura River Clean-up Project was started. It was focused on clean-up from mercury which polluted the river for 47 years as a result of wastewater discharge from the acetaldehyde production of the chemical plant "Karbid" located in Temirtau and launched in 1950. For the period of operation the plant consumed 2351.6 tons of mercury [2]. Until 1975 this plant did not have special facilities for wastewater treatment from mercury. The general biological wastewater treatment facilities were only designed for treating various types of water-soluble organic matter. According to some data [3] in the mid 1960s concentration of mercury in treated wastewater reached 1.0-50.0 mg/l. At that time "Karbide" plant often discharged wastewater into the Nura River just after settling in stabilization ponds by-passing the wastewater treatment facilities [4]. The field investigations carried out in 1997-1998 [5-7] allowed estimating the amount of Hg deposited along 70-km river section downstream the city of Temirtau in soils within the river floodplain, bank deposition of technogenic silts, bottom sediments of riverbed, backwaters and oxbow lakes. The total amount of mercury was estimated as 135 tons.

In 1942 the first turbo-unit of power station KarGRES-1 was launched in Temirtau. By 1950 the capacity of this power station had reached 271 000 kW (the capacity had been doubled by the later 1950s and tripled in the 1960s). Local and Ekibastuz power-generating coals and flotation wastes of Karaganda coal-cleaning factories were combusted at the power station. These materials had the ash content of 20-50% (Table 1). Until 1968 the power station discharged the fly ash to the Nura River at 1 km upstream wastewater outlet of Karbide plant. Concentration of suspended solids in wastewater of KarGRES-1 reached 2.5 g/L according to [8], and 8.5 g/L – according to [3]. After 1967 ash from power plant was being disposed to "old" and "new" ash lagoons located in the vicinity of the river. During emergency situation occurring in winter time ash was still released to the Nura River and the last event took place in 1997/98 (40300 tons was released). Total amount of ash released to the Nura River can be estimated as 6 million tons.

Table 1.
Processing characteristics of power station KarGRES-1, Temirtau city, 1950-1997

Year	Electricity generated, million kwh	Amount of fuel burnt, thousand tonnes	Ash content in coal or sludge of concentrating mills, %	Amount of ash transported to ash lagoon, thousand tonnes (calculation data)
1950	482.3	506.4	25	126.6
1951	547.1	576.1	25	144.0
1952	631.3	682.8	25	170.7
1953	722.9	695.3	25	173.8
1954	862.7	897.5	25	224.4
1955	1018.9	1030.9	25	257.7
1956	1459.9	1445.8	25	361.5
1957	1634.4	1755.5	25	438.9
1958	1792.2	1946.8	25	486.7
1959	1925	1889.5	25	472.4
1960	1751,9	1625,8	25	406,5
1961	1783.5	1655.2	25	413.8
1962	1637.3	1644.6	25	411.2

1963	1258.4	1406.8	25	351.7
1964	1203.9	1328.2	25	332.1
1965	1321.8	1339.9	25	335.0
1966	1264.5	1315.2	25	328.8
1967	1177.9	1146.4	45	515.9
1968	1303.9	1275.8	45	574.1
1969	1396.2	1318.5	45	593.3
1970	1391.7	1356.1	45	610.2
1971	1423.8	1283.1	45	577.4
1972	1459.9	1518.3	45	683.2
1973	1550.3	1489.3	45	670.2
1974	1490	1528.7	45	687.9
1975	1389.9	1462.2	45	658.0
1976	1300.9	1399.8	45	629.9
1977	1343.7	1395.3	45	627.9
1978	1300.5	1416.6	45	637.5
1979	1376.8	1449.5	45	652.3
1980	1300.6	1406.9	45	633.1
1981	792.5	958.1	45	431.1
1982	630.8	914.6	45	409.3
1983	751.3	1026.6	45	462.8
1984	723.9	1042.9	45	469.7
1985	433.9	785.2	48	378.1
1986	537.2	835.1	42	354.2
1987	469.4	817.8	42	342.5
1988	548.3	837.4	42	351.0
1989	613.6	845.9	42	356.9
1990	594.4	800.9	43	341.8
1991	459.6	677.5	43	293.9
1992	234.4	494.9	45	223.2
1993	374.5	652.3	46	299.2
1994	413.6	640.1	45	291.3
1995	414.2	595.7	45	269.3
1996	218.4	389.2	48	186.5
1997	134.6	212.3	46	98.3
			Total:	**19745.6**

Comments:

- *since 1950 till 1966 KarGRES-1 power station burnt generally Karaganda coal and sludge of concentrating mills with ash content of 26-27%; since 1966 it burnt Ekibastuz coal with ash content of 47-50%; since 1997 KarGRES-1 power station works on Shubarkol' coal;*
- *in the table when calculating amount of ash transported to ash lagoon ash content was considered to be 25% since 1950 till 1966; 45% since1967 till 1981; since 1982 KarGRES-1 data were used calculated on the basis of average annual ash content in coal;*
- *until 1968 fly ash was released directly to the Nura River (in total 6.0 million tonnes have been released);*
- *the old ash lagoon was in operation since 1968 till 1991(in total 12.4 million tonnes have been released);*
- *the new ash lagoon was set in operation on the 24.10.1991 (in total 1.4 million tonnes have been released since 1992 till 1997);*
- *the data given in the table were kindly provided by N.S. Korotkova an engineer on technical operation of KarGRES-1.*

The typical isotherm curve of mercuric chloride adsorption with ash of Karaganda coal at different levels of pH obtained during laboratory study [9] is given on Fig. 1. It shows that adsorption rate decreases at the increase of acidity. Laboratory studies have shown that ash particulates with concentration 10 g/L can fully adsorb mercury from $HgCl_2$ solution with concentration 1 mg/L and natural pH. In case of more concentrated solutions of mercuric chloride ash is capable of the mercury binding up to saturation at 0.7 g Hg/kg.

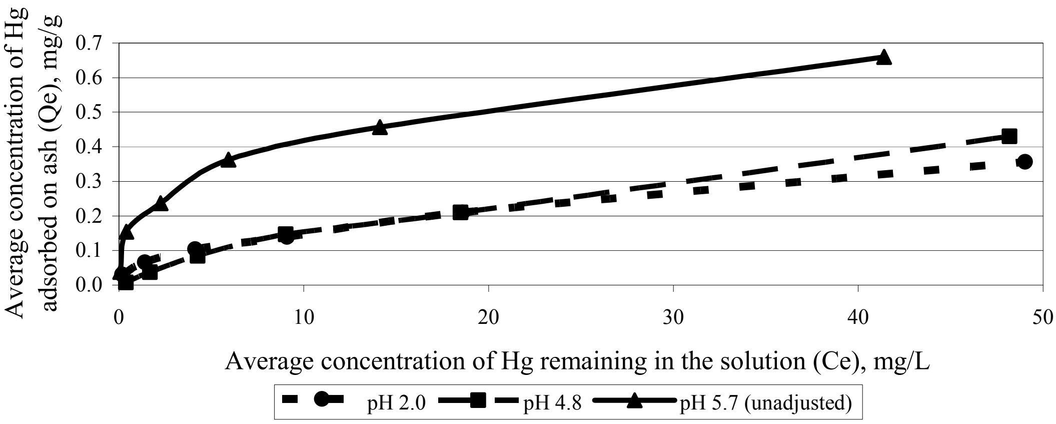

Figure 1. Isotherms of mercury adsorption onto power station ash of Karaganda coal at different levels of pH (initial [$HgCl_2$] varied from 0.5 to 50 mg Hg*L^{-1}, C_{ash}=10 g/L, T=25^{0}C, 4-hour experiment)

Ash materials have formed a new type of alluvial depositions within the Nura River known as "technogenic silts" [10]. Their properties significantly differ from natural the riverbed alluvium*. The study of 1997-1998 [5-7] showed that within the first 30 km downstream Temirtau the riverbed is almost everywhere covered with these silts having the typical depth of 1-2 m and reaching 3.5 m at some sites. Along this section of the river the technogenic silts carried away from the riverbed have formed large depositions on the banks (area of about 130 Ha) also reaching a depth more than 3 m. These depositions often contain interlayers of typical river alluvium. Sometimes they are covered with the 0.5-1.0 m layer of fertile soil overgrown with shrubs. Technogenic silts deposited near Temirtau have a typical appearance of local coal-fired ash (including bluish color). As going downstream these silts are mixed with big volumes of fertile soil carried away from irrigated fields located within the floodplain. The appearance and color of silts are gradually changing with the distance from the town. The areas and layers contaminated with mercury are clearly associated with presence of ash materials. As a rule the highest content of Hg could be found in silts which look similar to ash. At present about 1 million tonnes of technogenic silts containing more than 10 mg Hg/kg ("intervention" level adopted in West Europe) are deposited in the riverbed and river banks within first 35-km section downstream Temirtau. Maximum concentration of mercury in ash materials reaching 420 mg/kg (d.w.) was found in the riverbed. Area within the floodplain of the Nura River having topsoil layer (0-15 cm) containing more than 2.1 mg Hg/kg (MPC_s **for soil) occupies 2400 Ha including 600 Ha containing more than 10 mg Hg/kg.

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* The assumption was made in [11] that composition of the Nura River technogenic silts is also determined to some extent by carbide sludge (calcium hydroxide) as well as sludge of metallurgical works "IspatKarmet". Comparison of amounts of suspended materials released to the river shows that influence of solid industrial wastes other than ash on the technogenic silts composition is negligible.

** Maximum Permissible Concentration - sanitary standard adopted in Kazakhstan.

The data gathered during various laboratory experiments [9] and related to desorption of mercury from different ash materials are given at Figures 2 and 3, and Table 2. The curve on Figure 2 shows the effect of leaching solutions of different pHs on mercury (II) freshly loaded onto ash of Karaganda coal from mercuric chloride solution (HgCl2). Even at moderate deviation of pH from neutral level 20% of freshly adsorbed mercury (II) can be leached both at acidic and at alkaline conditions. Same effect is observed at increase of ionic force of neutral solution higher than 0.1 M. Up to 85% of freshly adsorbed mercury (II) is leached from ash of Karaganda coal when washed by 1M solution of either hydrochloric acid or ammonium acetate. Aging of ash with adsorbed mercury, e.g. when drying (see Table 2), leads to significant decrease of capability of Hg (II) to be mobilized by chemical way. Figure 3 shows the curves of mercury desorption from two ash-containing samples of natural sediments from the Nura River originally containing 20 and 117 mg Hg/kg respectively. These curves demonstrate transformation of adsorbed mercury into less mobile forms when ash is being aged. This process protects mercury from noticeable mobilizing in the range of pH 4.5-9.0. These samples also become more resistant to leaching by buffer solutions and mineral acids: less than 2% could be leached by either sodium acetate, or sodium tetraborate, or ammonium acetate; strong mineral acids could leach not more than 45% of mercury. Results given in Table 2 also demonstrate stronger biding of aged ash with mercury (II) in comparison with elemental mercury. Conducted experiments may suggest the chemical nature of mercury immobilization by ash particles. More specifically this process may occur due to the formation of oxide forms of mercury for which there are known several modifications with different chemical stability turning into each other.

In-situ concentration of total mercury in the Nura River water downstream Temirtau is relatively low. For example, it did not exceed 126 ng/L even at the most contaminated river cross-section (8.2 km downstream the wastewater outlet) in autumn 2001 when the water flow was 16 m^3/s. Only during moderate flood period when the water flow is about 100 m^3/s (Table 3) concentration of total mercury in water exceeds MPC_w for water (500 ng/L) along 15-km river section. In spring 2004 during the high flood event when water flow was125 m^3/s total Hg concentration reached 4200 ng/L. However at further increase of water flow up to 650 m^3/s Hg concentration became decreasing to the level of 1200 ng/L due to dilution. In spring 2004 contamination of water exceeded MPC_w along 50-km river section. However when samples were filtered through 0.45-µm membranes total Hg concentration fell to 5-20 ng/L. It is evidence that transport of mercury downstream currently takes place predominantly by means of silt movement and not as dissolved species.

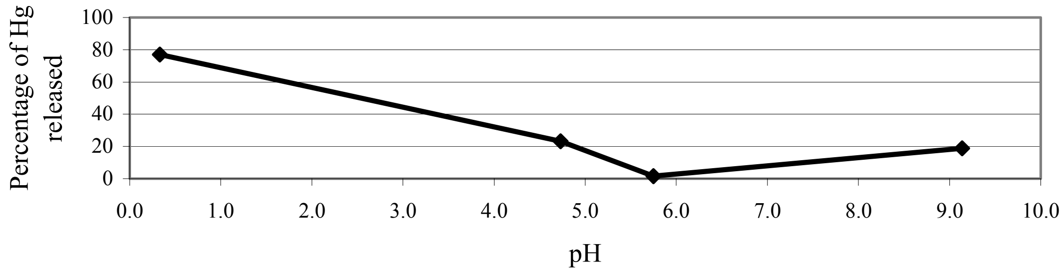

Figure 2. Release of mercury from the wet Hg-loaded ash of Karaganda coal at various pHs (C_{ash} = 10 g/L, $C_{Hg\ on\ ash}$ = 82 - 87 mg/kg on dry weight basis, T=25^{0}C, 24-hour experiment)

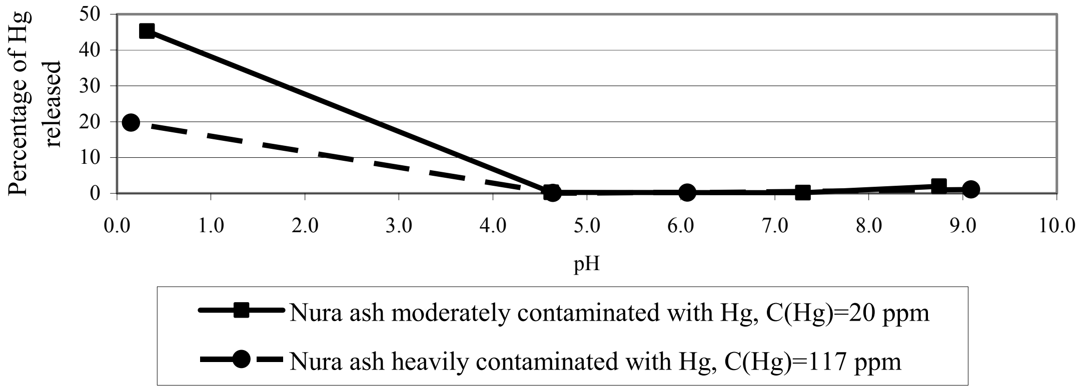

Figure 3. Percentage of Hg released at various levels of pH from dry contaminated ashes taken from the Nura River bank deposits (C_{ash} = 10 g/L, T=25^{0}C, 24-hour experiment)

Table 2.
Release of mercury from wet and dried Hg-loaded ashes into 1 M ammonium acetate (C_{ash} = 10 g*L^{-1}, T=25^{0}C, 1-hour experiment)

Type of ash	pH at the end of experiment	Content of Hg in ash, ppm (dry weight basis)	Percentage of mercury leached by 1M ammonium acetate
Wet power station ash of Karaganda coal loaded with $HgCl_2$	6.81	81.5	**85.2**
Dried power station ash of Karaganda coal loaded with $HgCl_2$	6.60	21.0	**15.3**
Dry power station ash of Karaganda coal loaded with elemental Hg vapor	6.52	283.9	**47.3**
Power station ash from bank deposits at the Nura River floodplain (moderate Hg content)	6.60	20.2	**0.2**
Power station ash from bank deposits at the Nura River floodplain (high Hg content)	6.70	117.1	**0.1**

Table 3.

Concentration of total mercury in surface water of the Nura River during spring flood of 2002, sampling period – April 8-13 (water flow in the cross-section of Temirtau was 70 m^3/s).

Conventional distance downstream wastewater outlet in Temirtau, km	Average concentration of dissolved mercury, ng/L	Average concentration of total mercury, ng/L	Average concentration of mercury in suspended solids, ng/L	Average content of suspended solids in water, mg/L	Calculated concentration of mercury in suspended solids, mg/kg	pH
0		128.47				
1.8	10.50	304.39	203.5	14.8	13.8	7.24
4.6		894.46				
8.4		1043.56				
14.4		824.17				
18.3	5.02	451.25	383.5	34.7	11.1	7.46
29.7		377.67				
53	4.40	161.96	116.5	34.6	3.4	7.56
71		38.20				
84	2.33	7.93	11.5	28.8	0.4	7.46
109		12.79				
167		8.70				
200		5.45				7.63
252		6.29				
281		4.08		36.4		
236		6.98				
342		4.74				
381		7.38				
467		3.86				

Monitoring of the Nura River conducted by Karaganda Center of Hydro-Meteorology in 2004 [12] proves generally the data mentioned above. In the most contaminated section of the river (5.7 km downstream the wastewater outlet of the town of Temirtau) average concentrations of total mercury were as follows: 3970 ng/L - at flood rise, 1355 ng/L - at flood peak, 592 ng/L - at flood recession, 580 ng/L - at summer low water; 380 ng/L – at fall low water. At that already in Intumak reservoir head water (60 km downstream the wastewater outlet) maximal concentration of total mercury at flood peak was only 210 ng/L. Unfortunately findings of the monitoring of 2004 do not allow estimating proportion of suspended solids, dissolved and organic forms of mercury in the Nura River water.

High mercury immobilization with technogenic silts formed on the basis of power station ash made difficult to justify the necessity of treatment of mercury-containing bottom sediments of the Nura River on the World Bank project. In its current status the mercury does not pose evident human health risk for the cities of Temirtau and Astana when using the river for water supply as well as cultural and economic purposes even during high flood events when considerable rearrangement of mercury-containing technogenic silts takes place. There is an exception for the 50-60 km river section downstream the wastewater outlet of Temirtau city where inhabitants of villages of Chkalovo, Gagarinskoe, Samarkand, Tengiz-Zhol, Molodetskoe, Volkovskoe and Aktobe have no possibility of safe water consumption from the

Nura River during two months of spring flood (at present the river water is used mainly for irrigation and livestock watering). However the risk goes down considerably during the other ten months of a year as well as after precipitation of the surface water used.

Meanwhile the Nura River pollution poses a substantial risk to local population due to their consumption of mercury-containing fish. Sport fishing is ubiquitous at the Nura River including estuary of wastewater Main Drain of the town of Temirtau and commercial fishing occurs in Samarkandskoe, Intumakskoe and Samarskoe reservoirs near village Sabyndy as well as in upper Kurgaldzhinskie lakes. From standpoint of fish industry standards for surface water where $MPC_{f.i.}$ for total mercury is 10 ng/L, the river poses a threat to population along its whole length downstream Temirtau city. A matter of justification and rigidity of fish industry sanitary standards has been discussed repeatedly (e.g. [13]). According to our data obtained based on quite little material (66 non predatory fishes were caught) maximal concentrations of mercury in fish samples reach 1.5 mg/kg (that five times as much as $MPC_{n.p.f.}$ for non predatory fish) near the wastewater outlet in Temirtau and in Samarkand reservoir. According to the data [12] (27 fish samples were analyzed) maximal concentrations of mercury in non predatory fish reach 0.8 mg/kg (that two and half times as much as $MPC_{n.p.f.}$) near the wastewater outlet in Temirtau and in perch and pike – 0.6 mg/kg (on the level of $MPC_{p.f.}$ for predatory fish) near Kievka village.

It is necessary to conduct more detail study of conditions of bioavailability and methylation of mercury in technogenic silts of the Nura River, its reservoirs, oxbow lakes as well as mercury accumulation over food chains and in fish of different species (especially predatory ones). Only such a study can become justification of a necessity to clean the river from mercury-containing technogenic silts and allow developing reasonable temporary MPC for mercury in bottom sediments and bank depositions of technogenic silts.

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