Geochemical Monitoring of Groundwaters, Rivers and Swamps in the Lomonosov Diamond Mine Surrounding, Arkhangelsk Region, Northern Russia

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At the Lomonosov diamond deposit, the Arkhangelskaya pipe has been under development since 1995 through open-pit mining, and the Karpinsky pipe is supposed to be mined in the near future. Among the main problems is how to utilize mine waters, which discharge into the quarry from Paleozoic and Vendian water-bearing beds, and which are mineralized in comparison to surface waters. In the first stage of mine development these waters were pumped out of the pit to adjacent swamps which had been isolated by special barriers to prevent direct flow into the rivers. To monitor and control this process, we have carried out geochemical monitoring of both ground and surface waters, and of peats in the swamps.

The diamond-bearing kimberlite pipe Arkhangelskaya, about 0.4 km in diameter at the surface level, breaks through Paleozoic and Vendian sedimentary rocks. The surrounding area is a swampy plain. The brook Svetly crossing the marginal part of the pipe falls into the small river Svetlaya, which flows into the Zolotitsa river with the mouth approximately 1 km north of the pipe. Both surface run-off and groundwater discharge are responsible for the chemical composition of stream waters.

The first stage of the environmental geochemical investigation was conducted in 1994–1995 just before the beginning of the preparatory phase of mine development. The survey included the geochemical sampling of stream and swamp waters, stream sediments, and peats in the swamps in the vicinity of the Arkhangelskaya pipe. The peat samples were taken at depths of 0.1 through 0.7 m, and swamp waters were sampled near the surface at the same locations. Stream waters were sampled at several stations located on the Svetly brook and Zolotitsa river and used by hydrologists to monitor the rate of stream flow and the contents of dissolved components in water.

The concentrations of chemical elements in the peat ash and stream sediments were determined by different methods which included atomic emission spectrography (Si, Al, Mg, Ca, Fe, Mn, Ni, Co, Ti, V, Cr, Mo, Zr, Nb, Cu, Pb, Ag, As, Zn, Cd, Sn, Ge, Ga, Y, Ba, Sr), flame photometry (K, Na, Li, Rb, Cs), atomic absorption analysis (Ag, Sb, Cd, Tl), and X–ray fluorescence spectrometry (Mo, Zr, Nb, Pb, As, Y, Sr, U, Th, Se). The contents in dry peats were calculated from the contents in ash using the loss on ignition (LOI) values. The principal ions in waters (Ca^{++}, Mg^{++}, K^+, Na^+, $HCO3^-$, $SO4^{--}$, Cl^-) were analysed by chemical methods. The total water mineralization (TM) was calculated as a sum of contents of dissolved components. Trace elements in waters were preconcentrated in dry residues, co-sedimentated from water samples with special reagents, and their contents were determined by the same methods as used for the stream sediment and ash analyses. Data obtained in our study were supplemented with data from the hydrological and hydrochemical monitoring carried out by other organizations in 1991–1994. Groundwater information, obtained during exploration of the diamond deposit, was also involved for a comparative data analysis.

These geochemical investigations, conducted before mining began, established the initial contents of both macro- and micro-components in the waters and the peat (Table 1). The swamp waters, due to the organic acids, have pH in the range from 4.2 up to 6.2 with a median value of 4.8, whereas the stream waters are usually neutral with pH in the range from 6.8 to 7.8. The composition of studied media did not show any significant deviations from the background levels of TM, pH and contents which are, according to published data (Spravotchnik, 1990; Fortescue, 1980; Kabata-Pendias and Pendias, 1984), typical for natural environments. Hence, there were no obvious indications of environmental pollution at that time. This data set can be used as a starting point when studying further impact of mining on the environment. Some important features of geochemical migration in such an environment can be described by means of two coefficients Ax and Bx. The former is a biogenic enrichment coefficient, calculated as a content of an element in the mineral residue of peat, e.g., the content in the peat ash (Ca), divided by the content of the same element in adjacent stream sediments (Css):

$$Ax = Ca / Css \qquad [1]$$

The latter is a coefficient of peat-water distribution, computed as the content in the peat ash divided by the content of an element in the mineral residue of swamp water (Csw/TM):

Table 1: *Background contents of chemical elements in swamps, surrounding the Lomonosov diamond pipe, and adjacent Zolotitsa river.*

Chemical elements	Swamps			Rivers		
	Peats[1]		Waters[2]	Stream Sediments [1]	Waters[2]	
	Ash	Dry peat			Low water level	High water level
Si	7	0.2	NA	35	3.1	1.1
Al	1	0.03	NA	1.5	5.9	68
Mg	2	0.06	1.2	0.3	10.9	3.7
Ca	4	0.1	2.6	0.7	24	4.9
K	3.5	0.1	NA	0.95	1.3	1
Na	2.4	0.07	NA	1	8.4	3.4
Fe	0.7	0.02	1	2	0.28	0.5
Mn	700	20	14.5	300	6.2	13
Ni	40	1.1	0.075	20	2	1.6
Co	10	0.3	ND	7	ND	ND
Ti	300	8.4	22.5	2000	<1	1.8
V	20	0.6	0.6	20	<0.5	<0.5
Cr	70	2	1	30	<1	2.7
Mo	9	0.25	<1	2	1.1	1.4
Zr	146	4.1	NA	150	NA	NA
Cu	70	2	0.65	<20	2.2	1.1
Pb	209	5.9	0.55	6	<1	<1
Ag	0.8	0.02	0.1	0.04	<0.1	<0.1
Sb	0.5	0.01	NA	0.1	NA	NA
As	7	0.2	<1	<4	<1	<1
Zn	1000	30	3.5	40	6.3	5.1
Cd	8	0.2	NA	<10	<1	<1
Sn	10	0.3	<3	<1	3.6	3.3
Ge	3	0.08	NA	<1	NA	NA
Ga	10	0.3	NA	15	NA	NA
Y	20	0.56	NA	7	NA	NA
Li	13	0.36	NA	6.1	NA	NA
Rb	74	2.1	NA	34	NA	NA
Cs	2.2	0.06	NA	1.5	NA	NA
Sr	470	13	NA	130	NA	NA
Ba	200	6	NA	<200	NA	NA
Tl	0.1	0.003	NA	0.2	NA	NA
Th	4	0.1	NA	<3	NA	NA
Se	4	0.1	NA	<2	NA	NA
TM[3]	—	—	13	—	123	31

1. Contents of Si through Fe in % , Mn through Se in ppm.
2. Contents of Si through Fe in ppm, Mn through Se in ppb.
3. TM = total mineralization in ppm

NA = not analyzed;
ND = not detected.

$$Bx = Ca / (Csw/TM) \qquad [2]$$

Both Ax and Bx characterize an ability of chemical elements to be absorbed or sedimentated by the organic matter in the swamps. Most of the elements studied, excluding Ti, Si, Fe, Tl, Al, Zr, and Ga, have rather high levels of biogenic absorption (Figures 1 and 2). Some other elements (As, Sn, Cd, Ge, Ba, Th, Se), not shown on graphs because the analytical detection limit was not sufficient for calculations according to the data of Table 1, are able to be concentrated in peats as well. This supports the idea that swamps may serve as a natural geochemical barrier to filter the contaminated mine waters.

To appreciate any possible water contamination in the case of mine development, a brief characterization of groundwaters is necessary. The main sources of possible hydrochemical impact during the first step of mining are Paleozoic and upper Vendian aquifers. The Paleozoic aquifers are close to the surface and are slightly alkaline (pH=7.9–8.2) and lowly mineralized (TM=130–330 ppm), but nevertheless contrast with the surface waters. The Vendian water-bearing beds, laying beneath the Paleozoic, have the average pH=8.3 with extreme values up to 10.0, and the groundwater contains more dissolved components: TM=140–420 ppm, the sum of Ca^{++} and Mg^{++} is 2.2 mg-eq./l. The deep aquifers, lying below 100–150 m depth, are much more mineralized (TM up to 1–10 g/l), but their influence on the composition of mine waters will become significant only in future steps of mine operation.

The geochemical observations carried out during the preparatory stage of mining demonstrated a pH increase from 4.8 to 7.4, and rising levels of HCO3- (177 ppm), Ca^{++} (16 ppm), Mg^{++} (14 ppm), Ti (100 ppb), V (2 ppb), and Ag (2 ppb) in the swamp waters close to the source of mine waters. At the same point, the ash of the swamp peat was slightly enriched with Al (5%), Be (3 ppm whereas background is <1 ppm), Y (43 ppm), Sc (10 ppm, the value at the detection limit), U (10 ppm whereas background is <2 ppm), Th (10 ppm). Most of the elements mentioned, according to Perelman (1989), have a limited ability for aquatic migration that results in their fixation in organic or inorganic sediments. The high levels of biogenic absorption, determined for Pb, Zn, Ag, Mg, Ca, Sb, Mo, K, Sr, Y and some other elements in the environment studied, enable us to predict a trend of their chemical deposition in peats, if they flow into the swamps with the mine waters. Furthermore, the pH increase would lead to sedimentation of dissolved Fe^{++} and Mn^{++} in the hydroxide forms and sequential adsorption of trace elements by authigenic Fe and Mn hydroxides. These phenomena make it possible to forecast the natural cleansing of surface swamp waters during the mine development.

Monitoring the nearby Svetly brook and the rivers Svetlaya and Zolotitsa revealed a correlation between the contents of most dissolved components and the time-related rate of stream flow Q(t). There is a strong negative correlation between Q(t) and the total water mineralization, as well as contents of Si, Mg, Ca, Na, Cu and some other elements (see Table 1). On the other hand, some of the elements such as Al, Fe and Mn, show the inverse trend. The following simple mathematical model, which takes into account the changeable surface/underground run-off ratio, is proposed to explain these phenomena:

$$Q(t)\, C(t) = Qs(t)\, Cs\ ^+ Qg\, Cg\, ;$$
$$Q(t) = Qs(t)\ ^+ Qg\, ; \qquad [3]$$

where C(t) is the time-dependent concentration of a component in a stream, Cg and Cs are those in contributing ground and surface waters,
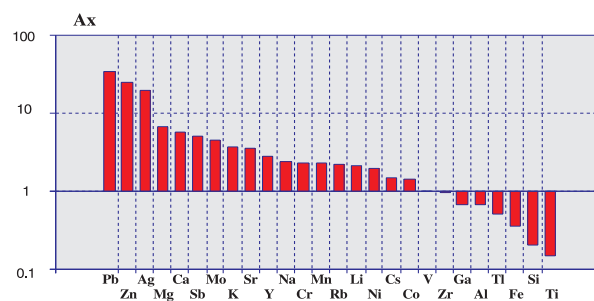

Figure 1: *Biogenic enrichment coeficients for swamp peats in relation to the adjacent stream sediments.*
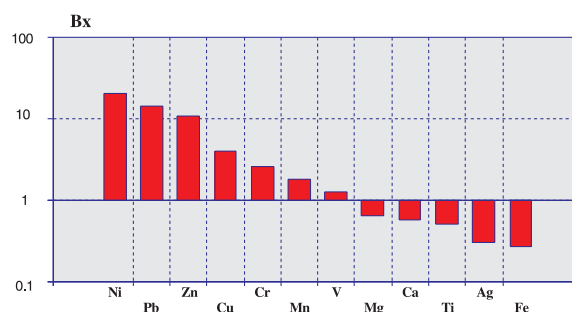

Figure 2: *Coefficients of the peat – water distribution in swamps.*

Qs(t) is the time-dependent surface run-off, and Qg is the rate of groundwater discharge. Solving these equations for C(t), we get:

$$C(t) = Qg\, (Cg - Cs)\, /\, Q(t)\ ^+ Cs \qquad [4]$$

If variations of Cs, Cg, and Qg are not very large, we have a simple inverse proportion between C(t) and Q(t), and the linear correlation between C(t) and 1/Q(t) is positive when Cg>Cs and negative when Cg<Cs. On the basis of this model it is possible, using data from stream monitoring, to estimate separately the contents of chemical components in the surface run-off and subsurface drainage.

Data from monitoring carried out at the 152 km station on the Zolotitsa river, downstream of the Lomonosov diamond deposit, show the practical applications of this model which, in part, gives a good approximation for the total mineralization values C(TM) depending on the rate of stream flow (Figure 3). The correlation coefficient between C(TM) and 1/Q(t) is very high (r=$^+$ 0.95). To estimate the mineralization of corresponding surface and underground water sources, we replot the diagram using C(TM) and 1/Q(t) axes (Figure 4). It has been known that Qg value is close to Q(t) in low-water winter period. Using the value on the regression line that corresponds to the observed maximum 1/Q, we get an estimate for the contributing groundwater's average mineralization Cg(TM)=150 ppm. On the other hand, the intersect of the regression line with the C(TM) axis yields an estimate for the average
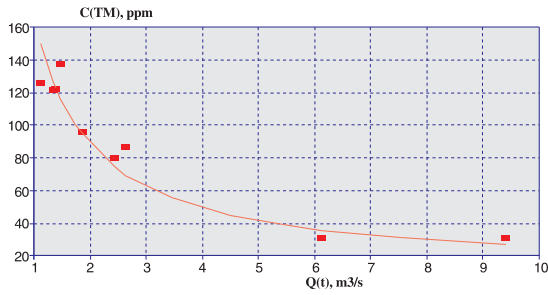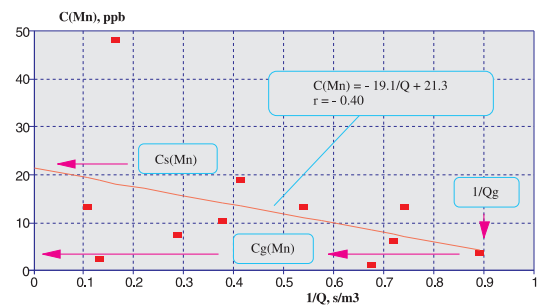
Figure 3: *The total water mineralization Cs(TM) in the Zolotitsa River depending on the rate stream flow Q(t).*
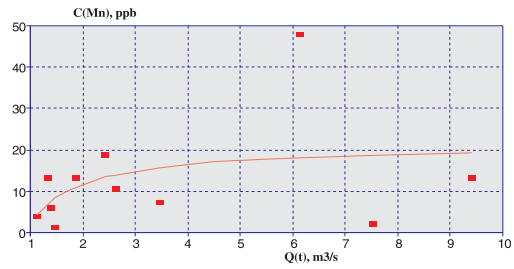
Figure 5: *The naganese content C(Mn) in the water of the the Zolotitsa River depending on the rate of stream flow Q(t).*
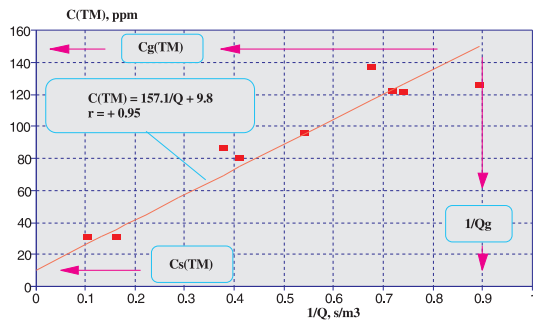
Figure 4: *Diagram to interpret the total water mineralization in the Zolotitsa River.*

Figure 6: *Diagram to interpret the manganese content in the Zolotitsa River water.*

surface swamp waters mineralization Cs(TM)=10 ppm. These estimates are in a good accordance with the independent determinations of Cg(TM) for the Paleozoic and upper Vendian aquifers, and of Cs(TM) for the swamp waters, discussed above.

The statistical link between the contents of manganese and Q(t) in the river waters is very weak and of a direct character (Figure 5). Nevertheless, despite of the low absolute score of a correlation coefficient between C(Mn) and 1/Q(t), the estimates for average manganese contents in the sources of river waters Cg(Mn)=4 ppb, Cs(Mn)=21 ppb, obtained by means of the similar diagram (Figure 6), proved to be close to the independent hydrochemical determinations.

The results described in this paper are of a preliminary character. To increase our understanding of the impact of mining on this environment, it is essential that this geochemical monitoring be continued.

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