METHODICAL ASPECTS OF GEOCHEMICAL MONITORING OF RIVER DEPOSITS

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Abstract
The distribution of 15 metals in Svisloch river deposits on all its watercourse length (in Minsk and approximately 200 km down-stream) has been investigated. The six mechanisms of metal fixation in deposits have been examined. These included: 1) gravitational settling; 2) sorption; 3) alkaline settling; 4) oxidizing/reduction settling; 5) complexion formation with fulvic acids; 6) colloid flocculation with humic acids. The geochemical behavior of Cr in recent Svisloch river deposits and possibilities of using the ratio Cr/Fe in conditions of industrial contamination of river systems described in detail.

Introduction
The distribution of 15 metals (Sc, Cr, Mn, Fe, Co, Ni, Zn, Zr, Ag, Cd, Sb, Cs, Ba, La, W) in Svisloch river deposits on all its watercourse length (in Minsk and approximately 200 km down-stream) has been investigated. Sampling has been carried out during August 26—28, 1987 by Oleg V. Lukashev and Vladimir V. Savchenko (ex-laboratory of hypergenesis geochemistry of Institute of geological sciences (National Academy of Sciences of Belarus)). The results of studies conducted in 1987 — a kind of out of date «momentary photography», which probably does not reflect any more the real geochemical situation, but these results are very interesting from point of view of «heavy environmental pollution situation», which existed before the economic crisis, affected Belarus as one of the former Soviet Union republics at the beginning of the 1990s.

Methods
Sampling and preparation of samples to an analysis have been carried out in correspondence with (1). The standard emission spectrum analysis method has been used to determine a content of chemical elements in samples of river deposits.

Results
Studying of the follow sections of Svisloch river watercourse has been carried out: I. Minsk, the «clean» part of the city; II. Minsk, the «industrial» part; III. From the Chizhovka reservoir to the spot of pour in of great bulk of city sewage; IV. 5 km down the watercourse; V. From the Mihanovichi village to the Volma river mouth; VI. From the Puhovichi settlement to the Osipovichi reservoir; VII. From the Osipovichi reservoir to Berezina river (Fig. 1). The received data (7—12 samples per section) roused the main interest for geochemical behavior of the some of Fe-group elements [1] (Tab. 1).

Discussion
Geochemical behavior of Mn, Fe and Co in our case is determined by natural factors (river erosion of deposits, organic matter content etc. (Fig. 2)), whereas Cr and Ni behavior — by pollution processes mainly (factor of the sewage). Problem is: why the highest values of Cr and Ni were not marked only at the spot of pour in of the great bulk of the city sewage (section IV), but at a long distance from it down the Svisloch river watercourse? For example, concentrations of Cr 2 740 ppm and Ni 430 ppm were marked at the distance of 25 km, concentrations of Cr 1 800 ppm and Ni 370 ppm — at the distance 50 km (section V). What is that? Is that display of the elements accumulation peculiarities or unknown local sources of industrial pollution?

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[1] The geochemical group of elements, include Ti, V, Cr, Mn, Fe, Co, Ni (2).

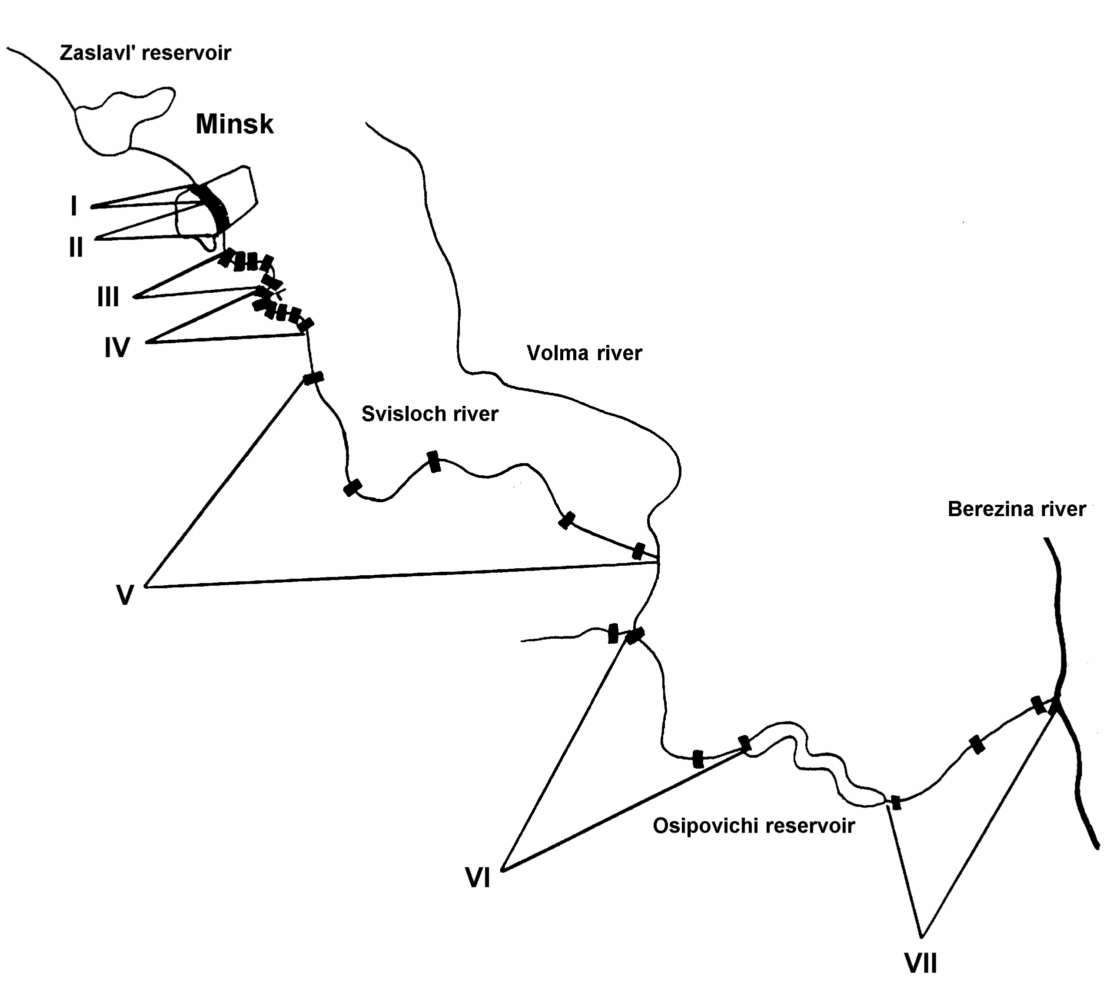

Fig. 1. Sampling of the Svisloch river deposits. Sections I—VII.

Table 1. The Fe-group chemical elements concentrations in Svisloch river deposits, ppm d. w.

Section (n)	Cr	Mn	Fe*	Co	Ni
I (10)	15 (10—33)**	280 (140—560)	0.86 (0.49—1.7)	1.9 (1.0—4.1)	3.2 (1.4—8.4)
II (12)	24 (13—83)	170 (110—360)	0.70 (0.44—1.6)	1.8 (1.1—4.0)	5.1 (2.7—14)
III (10)	120 (25—320)	650 (180—1 050)	1.6 (0.77—3.4)	5.2 (1.1—10)	21 (4.6—83)
IV (12)	360 (100—2 060)	370 (250—660)	1.5 (0.94—2.4)	4.9 (2.5—9.1)	83 (30—360)
V (10)	340 (38—2 740)	420 (140—960)	1.6 (0.66—3.5)	4.9 (1.5—14)	89 (12—430)
VI (8)	110 (12—510)	320 (90—630)	1.2 (0.27—2.2)	2.6 (1.0—6.7)	22 (3.2—140)
VII (7)	21 (12—39)	160 (110—450)	0.50 (0.38—0.90)	1.4 (1.0—3.3)	6.8 (3.7—10)

* — %.
** — mean (limits).

This question in relation to Cr was studied by Oleg V. Lukashev (3, 4). The six mechanisms of Cr fixation in river deposits have been examined. These included: [1] gravitational settling; [2] sorption (on $Fe(OH)_3$, organic matter, silicates); [3] alkaline settling ($Cr(OH)_3\downarrow$, co-settling $Cr(OH)_3 + Fe(OH)_3\downarrow$); [4] reduction settling ($Cr^{6+} \rightarrow Cr^{3+}\downarrow$, see [3]); [5] complexion formation with fulvic acids; [6] colloid flocculation with humic acids. The study has been carried out in correspondence with the «stage by stage» extraction method (5) shows that in natural geochemical conditions the mechanisms [1], [3], [5] are most important, than in conditions of industrial pollution — the mechanisms [3]—[5].

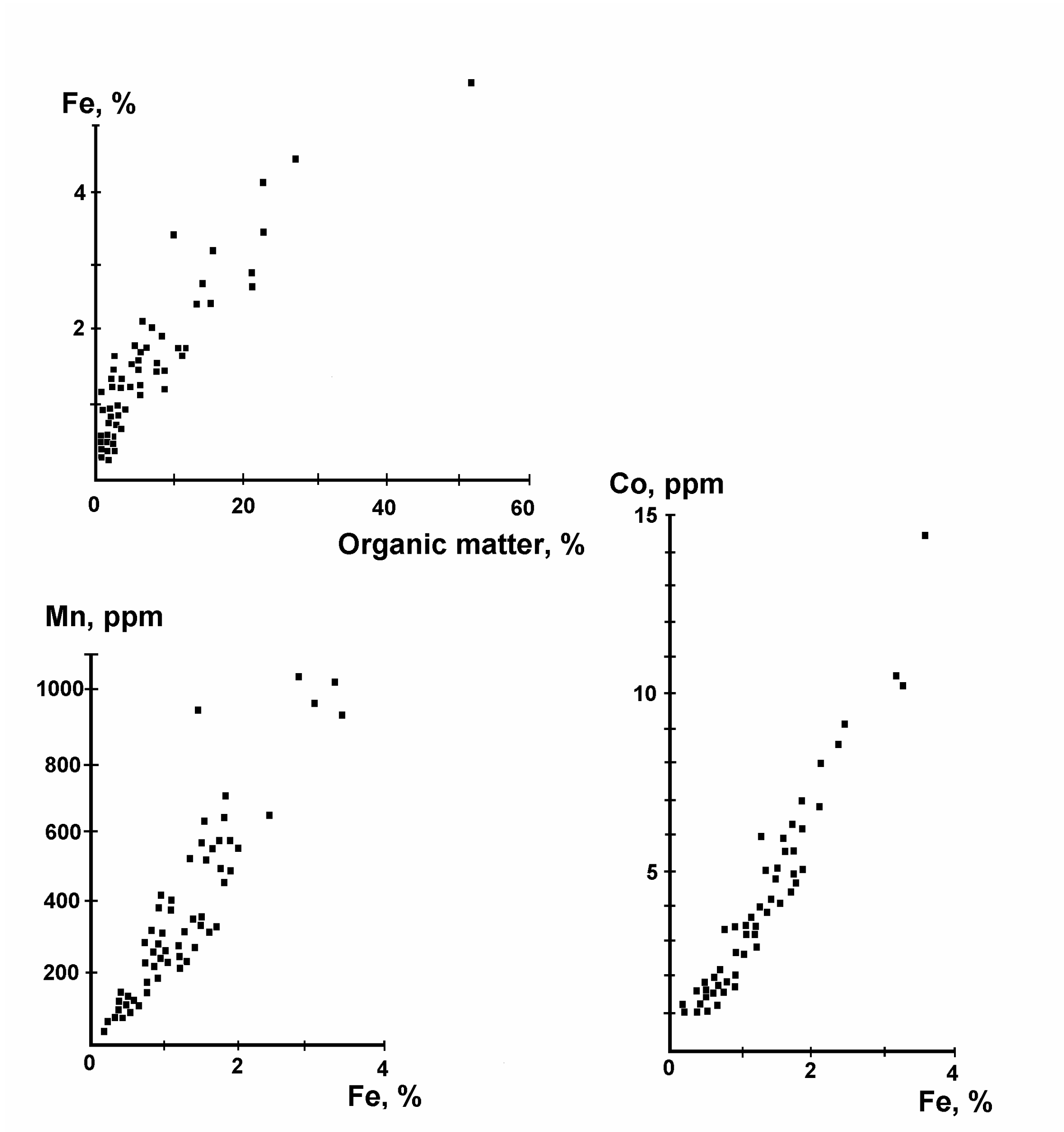

Fig. 2. Some dependences between Fe, Mn, Co and organic matter content in the Svisloch river deposits.

Thus we must stop to consider the deposits even of one small river as a matter with the «standard properties of elements accumulation». Simpler speaking, it is necessary to work out some easy method (or way), which allow to take into account (and to smooth over) the influence of «Fe-factor» and «organic matter-factor». In relation to Cr we propose: 1) to exclude from the examination (calculation of the statistic data etc.) samples [2] with content of organic matter >10 %; 2) to calculate ratio Cr/Fe (g/10 000 g) for every sample in rest of the samples group and to use ratio Cr/Fe in the statistic data calculation.

It's important to note that comparatively simple diagram (Fig. 3) allow to differentiate the fields of the mechanisms [3, 4] and [5] action. Really, in the field with values of organic matter content ≤10 % and Cr/Fe ≤ 350 [3] Cr accumulation in accordance with Fe accumulation and organic matter content in the river deposits independent (the mechanisms [3, 4], «Fe-factor» action only), than in the field with

[2] 10 % of samples in our case.
[3] Correspond with Cr concentration 700 ppm and Fe concentration 2 %.

values >10 % and >350, correspondingly, ratio Cr/Fe and organic matter content are bound up with linear dependence (the mechanisms [3, 4] + [5], «Fe-factor» and «organic matter-factor» common action).

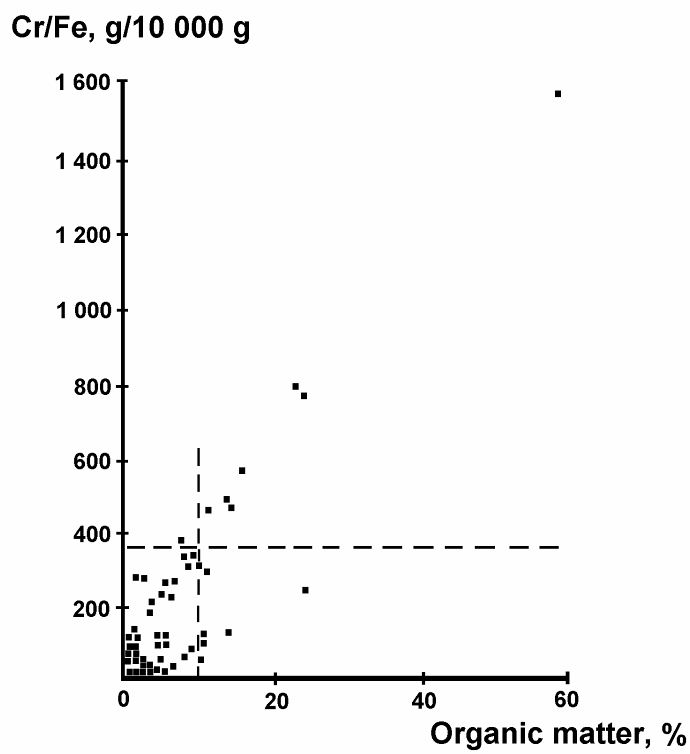

Fig. 3. Dependences between values of Cr/Fe ratio and organic matter content in the Svisloch river deposits.

The analogous operations with Mn/Fe, Ni/Fe and Co/Fe ratios in our case for some reason or other got unsatisfactory results (this problem is at the stage of studying).

Using the proposing method we can replace the range of Cr mean concentrations (Tab. 1) by the ranges of Cr/Fe and coefficient of concentration mean values (Tab. 2). Thus the real mean values of Cr pollution of river deposits at the sections III—V are 1.7—2.6 times lower than usual calculations show (see Cr_x/Cr_1 and $(Cr/Fe)_x/(Cr/Fe)_1$ values), and section VI may be unite with sections IV, V into one zone of maximum Cr pollution (zone of the Minsk sewage influence).

Table 2. Cr concentration, Cr/Fe and coefficient of concentration mean values in the Svisloch river deposits

Value	Saction						
	I	II	III	IV	V	VI	VII
Cr	15	24	120	360	340	110	21
Cr_x/Cr_1	1	1.6	8	24	23	7.3	1.4
Cr/Fe	18	34	83	170	178	173	42
$(Cr/Fe)_x/(Cr/Fe)_1$	1	1.9	4.6	9.4	9.9	9.6	2.3

Conclusion

Proposing method allow to eliminate effect of «imaginary» Cr pollution of river deposits when high concentrations of this element in reality are bound up with heightened content of Fe (able to reaction) in deposits.

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