

LANDSCAPE GEOCHEMICAL TRACERS OF CONTAMINATION IN DELTAS OF RIVERS DISCHARGING INTO THE ARCTIC BASIN

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Terrestrial ecosystems located in the Yenisei and Pechora delta and estuary zones have been studied for radionuclide and heavy metal contamination from remote global and regional sources. Radionuclides and heavy metals in soil, water, and plants were determined at different distances from the sea on landscape-geochemical transects across riverbanks and delta islands. In the Yenisei delta and estuary zone, local ¹³⁷Cs accumulation was found being associated with operation of the Krasnoyarsk Chemical Combine. The highest ¹³⁷Cs were measured at test sites located on islands within the Yenisei delta front, which thus appears to be a natural barrier for river-borne contaminant fluxes into the Arctic basin. Heavy metals (Cu and Ni) in mosses and willow (leaves) species collected on terraces and watersheds in the lower Yenisey showed a slowly increasing trend toward the Norilsk Combine. The measured ¹³⁷Cs contamination of the Pechora test sites was within the global background. Relatively high Cu and Zn were revealed in Pechora water sampled 3 km downstream of Naryan-Mar city. These patterns may be used for purposive contamination tracing.

INTRODUCTION

The deltas of the Yenisei and the Pechora, two large rivers in northern Russia, are of interest for their terrigenous input into the Arctic basin. The reported study focuses on radionuclide and heavy metal contamination of terrestrial ecosystems in the lower reaches of the Yenisei and Pechora rivers at different distances from global- and regional-scale polluters, and on redistribution of this contamination in the conjugated landscapes.

Pollution in the region comes mostly from the Norilsk Nickel Combine (NNC) with its influence zone exceeding 150 km [Ermakov and Ukraintseva, 2005] and from the Krasnoyarsk Chemical Combine (KCC) which has contaminated the Yenisei floodplain downstream of the Combine [Vakulovsky et al., 1995; Kuznetsov et al., 2000; Sukhorukov et al., 2004]. The Pechora catchment belongs to few areas with almost undisturbed ecosystems and thus may serve for a reference standard against which to study natural processes in deltas and estuaries of large northern rivers [Resolution..., 2000]. Nevertheless, its territory has suffered from atmospheric radionuclide fallout during nuclear tests and from the consequences of the Chernobyl accident. According to Nifontova [2000] and the *Radioactive Contamination Atlas* [1998], ^{137}Cs contamination has duplicated after the Chernobyl accident (as measured in 1995).

METHODS

Landscape geochemical transects across different floodplain levels, ancient terraces of the Yenisei and Pechora, and the watershed periphery were located at different distances from the sea. The sampling sites were chosen at places of geochemical contrasts with presumably maximum accumulation of river- and airborne radioactive elements. The soil profiles were sampled in increments of 2, 5 and 10 cm down to the table of permafrost or groundwater (30 to 120 cm).

The sampled plants were dominant species of high food and tracer importance (mosses, lichens, grasses, sedges, horsetail, willow and alder). The concentration of radionuclides was measured in air-dried samples (as air-dry weight) using a *Canberra* gamma-ray spectrometer (USA), analysts Borisov A.P. (Vernadsky Institute of Geochemistry, Moscow) and Kirov S.S. (*Radon R&D Company*), to an accuracy no worse than 5–10 % (^{137}Cs in soil) and 3 to 35 % (^{137}Cs in plants). The content of heavy metals in soil and plant samples was measured by XFA with the help of *ORTEC-TEFA* and *SPARK-1* mass spectrometers, analysts Sorokin S.E. (Dokuchaev Institute of Soil, Moscow) and Sizov E.M. (Vernadsky Institute of Geochemistry, Moscow). Samples of water and aqueous extracts were analyzed at the Dokuchaev Institute of Soil, Moscow (analyst Grishina R.V.) and at the Esenin Ryazan' State University, by Atomic Adsorption Spectroscopy, AAS (analyst Tobratov S.A.). Micrometer- and nanometer-size particles from groundwater were extracted on membrane filters following the procedure developed at the Vernadsky Institute of Geochemistry (Moscow) [Shkinev, 2009]. Trace elements in these size fractions were determined by V.K. Karandashev.

CONCENTRATIONS AND DISTRIBUTION OF ^{137}Cs

The average concentration of ^{137}Cs in soils and plants is on the average within the global background. However, it may vary markedly (Table 1) depending on the polluting source, the geomorphology of the test sites, the type of soil and fluvial deposits, and the plant species.

In the lower reaches of the Yenisei, the ^{137}Cs density is the highest (up to 88 kBq/m²) in the delta front near settlement Ust'-Port within the low floodplain of the Pashkov Island. The contamination is regional-scale and comes from the Krasnoyarsk Chemical

Table 1. ^{137}Cs in landscape components, air-dry weight (at time of measurements)

Location of landscape transects	Number of test sites	^{137}Cs , Bq/kg			
		Soil	Plants		
			<i>Mosses</i>	<i>Willow leaves</i>	<i>Horsetail</i>
Yenisei delta, settlement Ust'-Port					
High terraces	6	1.3–282	10–137	26–108	12–53
Right-bank floodplain	5	0.2–117	30; 49	21–81	9–15
Island floodplain	7	0.8–325	10	17–61	19–44
Pechora Gulf, Bolvansky Cape	3	16–156	62; 118	67; 142	54–119
High terraces					
Pechora delta (settlements Yushino, Bol. Sopka, Iskateli)	5	30–215	31–125	n/d	–
High terraces					
Riverbank floodplain	1	10	–	56	–
Island floodplain	5	2.5–20	–	24–51	7–109

Note. Dash is not sampled, n/d is not determined.

Combine. The ^{137}Cs concentrations are notably lower in the Yenisei intradelta (floodplain of the Tysyara Island) (20 and 25 kBq/m²) but are likewise above the global background (2.0–2.9 kBq/m²). According to our estimates, the Tysyara site receives up to 30 % of total river discharge. The high floodplains and terraces are contaminated to a lesser degree, about the global fallout (0.4–2.8 kBq/m²). Relatively enhanced contamination (twice the background) observed in transaccumulative (interhill) depressions may be produced by ^{137}Cs transport with surface run-off.

In the lower reaches of the Pechora, the ^{137}Cs activity and density (Table 1) are the highest (150 to 215 Bq/kg) in tundra soils on watersheds and on terraces of different heights (from 7.6 to 30 m above the low-water river level). The southern terraces are less contaminated (settlement Bol. Sopka) than the northern ones (Bolvansky Cape, settlement Yushino). The greater contamination in the latter may be due to their proximity to nuclear test sites. Unlike the Yenisei lower reaches, the activity of radiocesium in floodplain soils (2.5–25 Bq/kg) is an order of magnitude lower than on terraces. This is consistent with the absence of considerable regional radioactive pollutants in the Pechora drainage area. Yet, the total contamination in floodplain soils (especially on islands: 2–6 kBq/m²) is commensurate with or locally higher than that on terraces (1.0–2.4 kBq/m²), i.e., contaminants accumulate in floodplain areas.

The ^{137}Cs patterns in soil profiles are of three main types: (1) maximum element concentration near the soil surface; (2) contaminated top organic soil layer buried as a result of solifluction or slumping; (3) contaminated horizons repeatedly buried during seasonal cycles of flooding and alluvial deposition. The three patterns are characteristic of soils from, respectively, watershed and terrace (1), hillslope (2), and floodplain (3) landscapes. Peat-gley and especially

peat soils in terraces show relatively enhanced ^{137}Cs concentrations at the active layer base where soil solutions accumulate at the boundary with permafrost and are subject to periodic freezing.

The general trend of ^{137}Cs biosorption by dominant plant species is an increase in the series grasses < alder, willow (leaves) < lichens < horsetail < mosses (green part) < mosses (lower brown part). The tundra plants show the highest soil-plant transfer factors (TF), as high as transfer from hydromorphic soil in the zone of Chernobyl pollution. The species that are more active potassium accumulators commonly have lower TF for ^{137}Cs [Korobova, 2009].

CONCENTRATIONS AND DISTRIBUTION OF HEAVY METALS (Cu, Ni, Zn)

Test sites in the lower reaches of the Yenisei show insignificant contamination with heavy metals. Their concentrations and distribution depend on the distance from the regional source. For instance, Ni concentrations increase toward the Norilsk Combine in mosses (3–5 times) and willow leaves (2–3 times) that grow on terraces and in watersheds (Fig. 1). The distribution of copper has the same patterns. The reason is obviously the air transport and the subsequent fallout of metals, as well as their secondary redistribution with river and surface runoff. The redistribution is evident in relatively higher concentrations of elements in fine alluvium and, as well as in the presence of buried contaminated floodplain soils. Enhanced Cu, Ni, and Zn in top and supra-permafrost soil horizons of high terraces in the Yenisei delta front (Fig. 2) result either from local surface contamination or from natural biological and cryogenic accumulation. Heavy metals, especially Ni and Zn, have relatively high concentrations in fine suspended sediment load in floodplain soil groundwater. The highest

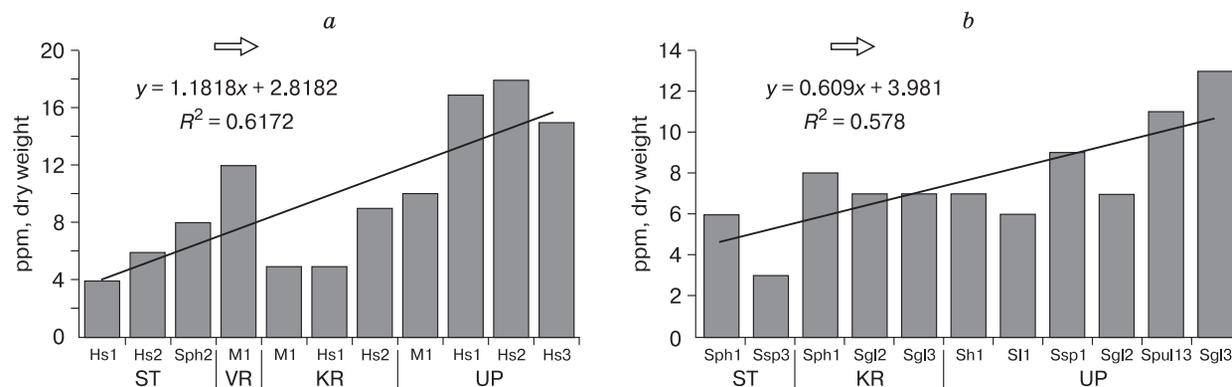


Fig. 1. Ni in mosses (a) and willow leaves (b) samples from terrace ecosystems in the Yenisei delta.

Arrow points to the Norilsk Nickel Combine. Capitalized abbreviations stand for names of test sites: ST – Cape Shaitansky; VR – settlement Vorontsovo; KR – settlement Karaul; UP – settlement Ust'-Port. 1, 2, 3 are elementary landscape systems: 1 – eluvial (high terraces), 2 – transitory (slopes), and accumulative (depressions) (3). Other abbreviations are plant species: Hs – *Hylocomium splendens*; Sph – *Sphagnum* sp.; M – mean *Sphagnum* sp. sample; Sgl – *Salix glauca* L.; Sh – *Salix hastata* L.; Sl – *Salix lanata* L.; Spul – *Salix pulchra* Cham.; Sph – *Salix phylicifolia* L.; Ssp – *Salix* sp.

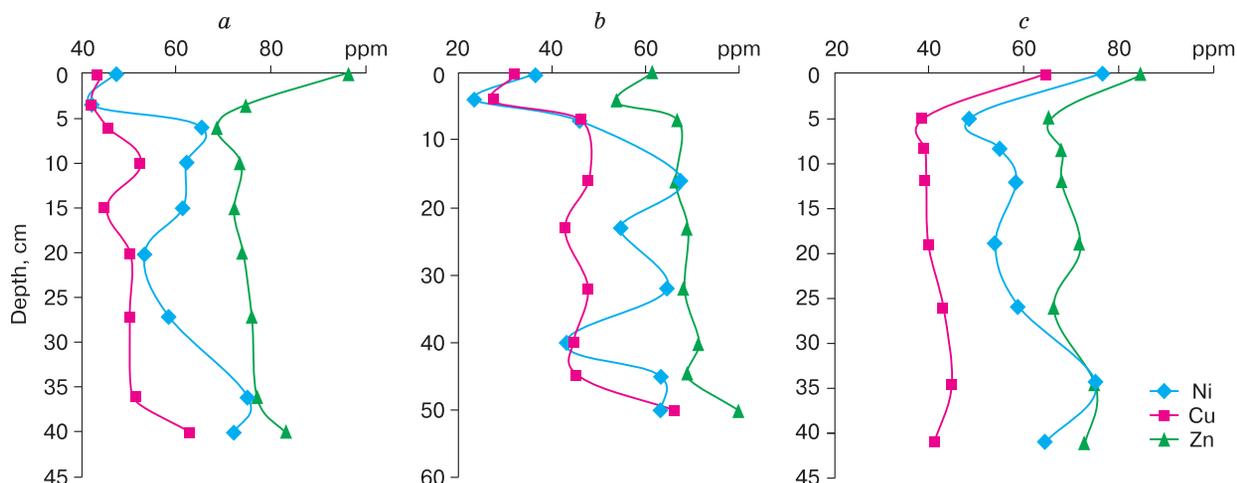


Fig. 2. Vertical profiles of Cu, Ni, Zn in soils of chemically conjugate tundra systems (settlement Ust'-Port):

a – eluvial system, *b* – transitory system, *c* – eluvial-accumulative system.

Ni percentages (30–80 %) occur in suspended particles larger than 0.45 μm (Fig. 3)¹.

Floodplain soil groundwater bears higher Ni concentrations in islands within the delta front (Pashkov Island). Therefore, the delta front landscape systems serve as barriers to riverine transport of contaminants.

According to the heavy metal measurements of 2010 in the Pechora water, contamination is low (0.5 $\mu\text{g}/\text{l}^3$ Cu and 2.8 $\mu\text{g}/\text{l}^3$ Zn on average) in the large river arms but increases three- to five-fold in small tortuous channels and near delta islands where water is slow (up to 1.5–2.0 $\mu\text{g}/\text{l}^3$ Cu and 7–15 $\mu\text{g}/\text{l}^3$ Zn). Significant pollution in the river is due to the

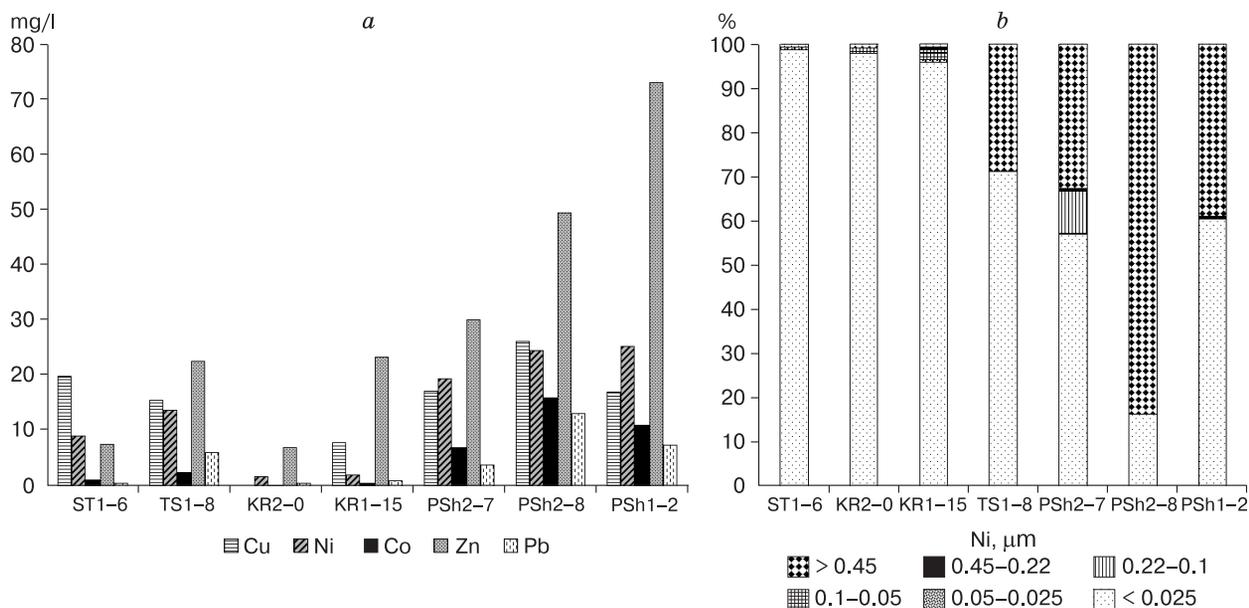


Fig. 3. Heavy metals in soil groundwater (*a*) and Ni partitioning among fractions of micrometer- and nanometer-size particles (μm) extracted by membrane filtration from soil groundwater samples (*b*).

Capitalized abbreviations stand for names of test sites: ST – Cape Shaitansky; KR – settlement Karaul; TS – Tysyara Island; PSh – Pashkov Island. 1–6, 2–7, etc. are indices of transects (left) and sampling sites (right).

¹ The fraction $<0.45 \mu\text{m}$ is commonly classified as a natural soil solution. Actually, these are solutions of dispersed soil particles, which is confirmed by membrane filtration.

Naryan-Mar city: Zn is as high as $28 \mu\text{g}/\text{l}^3$ in the river water 3 km downstream of Iskateli neighborhood (northern outskirts of the city), which is almost three times the maximum permissible concentration (MPC) for fisheries waters ($10 \mu\text{g}/\text{l}^3$).

CONCLUSIONS

Landscape-geochemical studies in the lower reaches of the Yenisei and Pechora rivers discharging into the Arctic basin have confirmed the possibility of tracing radionuclide and heavy metal contamination of landscape systems due to global- and regional-scale sources. Delta front island systems can act as barriers to riverine transport of contaminants. The observed accumulation patterns of elements in different components of chemically conjugated landscape systems can be used for reference in pollution tracing and monitoring.

The cooperation of the crew of R/V *Akademik Boris Petrov* and the researchers from SevPINRO in the organization of cruises is greatly appreciated. The work was carried out as part of the INCO-COPERNICUS Project *Establish* and was supported by the Earth Science Department of the Russian Academy of Sciences, as well as by grants 08-05-00872 and 10-05-10027k from the Russian Foundation for Basic Research.

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Received
14 February 2011