ISSN 1067-4136, Russian Journal of Ecology, 2013, Vol. 44, No. 5, pp. 371–374. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © I.V. Molchanova, L.N. Mikhailovskaya, V.N. Pozolotina, Yu.N. Zhuravlev, Ya.O. Timofeeva, M.L. Burdukovskii, 2013, published in Ekologiya, 2013, No. 5, pp. 334–338.

Technogenic Pollution of Soil and Plant Cover in Southern Primorye

I. V. Molchanova[a], L. N. Mikhailovskaya[a], V. N. Pozolotina[a], Yu. N. Zhuravlev[b], Ya. O. Timofeeva[b], and M. L. Burdukovskii[b]

[a] *Institute of Plant and Animal Ecology, Ural Branch, Russian Academy of Sciences, ul. Vos'mogo Marta 202, Yekaterinburg, 620144 Russia*
e-mail: molchanova_i_v@mail.ru

[b] *Institute of Biology and Soil Science, Far East Branch, Russian Academy of Sciences, pr. 100-letiya Vladivostoka 159, Vladivostok, 690022 Russia*
e-mail: timofeeva@biosoil.ru

Received December 3, 2012

Abstract—Evaluation of technogenic load on ecosystems of southern Primorye has shown that the soil contents of ^{90}Sr and ^{137}Cs vary within the ranges of 0.3–1.3 and 0.4–3.0 kBq/m^2, respectively; i.e., they do not exceed the level of background radioactivity that is considered normal at latitudes between 50° and 60° N. The presence of ^{134}Cs in the samples indicates a contribution from radionuclides discharged by the Fukushima nuclear accident. According to calculations, the additional ^{137}Cs input into the soils of the study area varies between 0.03 and 0.30 kBq/m^2. Soil analysis for heavy metals and trace elements has revealed an approximately twofold excess over safety norms (MACs) in the concentrations of technogenic Cu and Pb. For other elements, the excess is within the range of 8–32%.

Keywords: monitoring, radionuclides, the Fukushima accident, heavy metals, Primorye

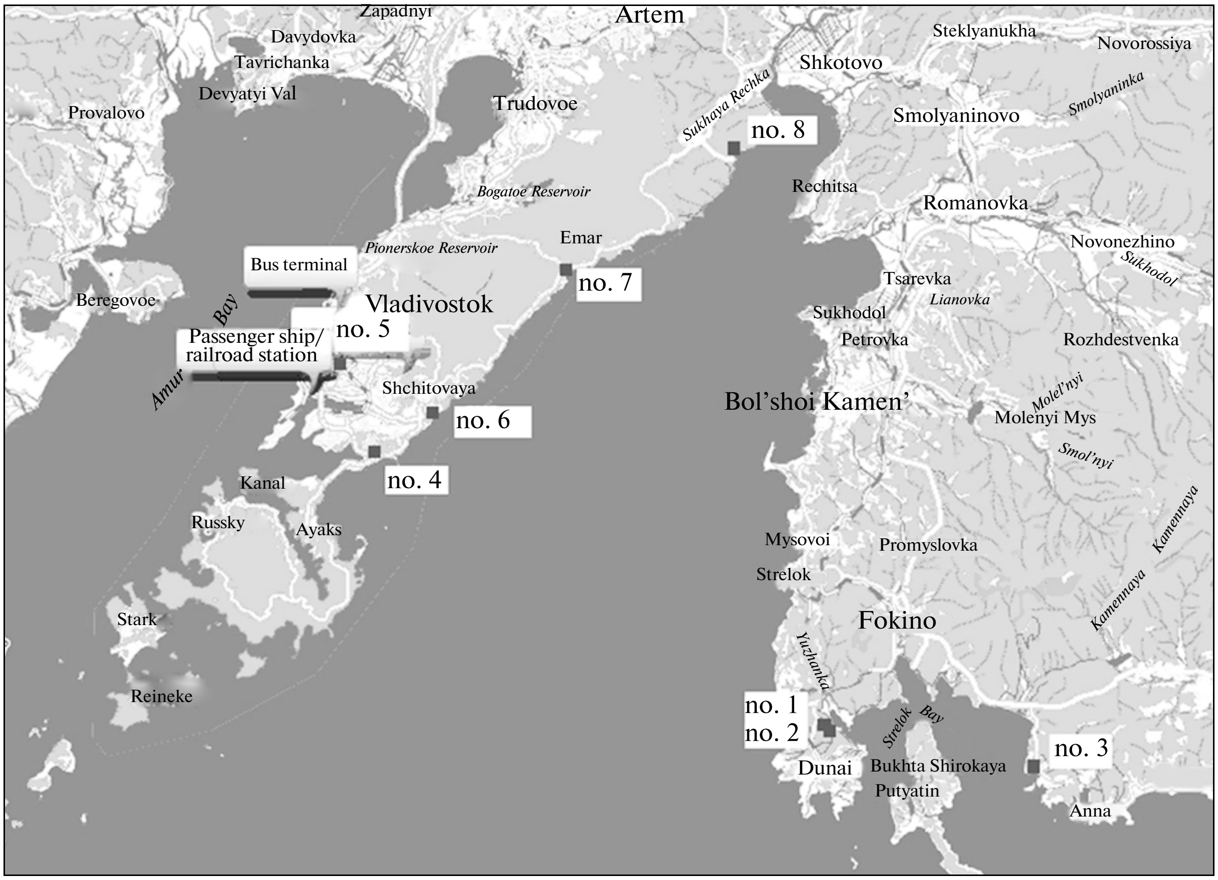
DOI: 10.1134/S1067413613050111

Environmental monitoring aimed at assessing the impact of industries, including nuclear power production, and the consequences of nuclear accidents is a major tasks for ecologists. The Russian Far East, with its specific climate and topography, is of special interest in this context, the more so that the recent Fukushima nuclear accident occurred in close vicinity of this region. Publications provide little data on technogenic and, in particular, radiation load on natural ecosystems of the region, although the need for such data is considerable. Thus, the coastal zone of the Muravyov-Amursky Peninsula accommodates major metal industries and until recently, has provided port facilities for the naval nuclear fleet. Today, decommissioned nuclear submarines are stored at the Pavlovskoe naval base. Weakly radioactive wastes from nuclear-powered vessels have been dumped into the Sea of Okhotsk and Sea of Japan. Moreover, there are 13 nuclear power plants (NPPs) near the Russian Far East coasts, including 9 NPPs on the western coasts of Japan and 4 NPPs on the eastern coast of the Korean Peninsula. All these factors present a potential hazard for the territory of Primorye. This hazard strongly manifested itself after the Fukushima accident. According to expert evaluation, the resulting radioactive discharge into the atmosphere amounted to about 150×10^{15} Bq of ^{131}I and $6–15 \times 10^{15}$ Bq of ^{137}Cs (Masson et al., 2011). Fallout from the accident has been recorded throughout the Northern Hemisphere, including the territory of Russia (Bolsunovsky and Dementyev, 2011; *Statement...*, 2011; Kirchner, Bossew, and De Cort, 2012).

The purpose of this study was to evaluate the load of technogenic radionuclides and heavy metals on ecosystems of densely populated areas in the south of Primorye.

MATERIAL AND METHODS

Studies were performed in the coastal zone of the Muravyov-Amursky Peninsula (figure). Most of this area has a hillocky topography with residual outliers, which usually have deluvial trains formed at their bases. The vegetation is represented by broadleaf and conifer–broadleaf forests dominated by the Japanese emperor oak (*Quercus dentata*), Mongolian oak (*Q. mongolica*), Manchurian walnut (*Juglans mandshurica*); birches *Betula pubescens*, *B. platyphylla*, *B. lantana*, and *B. davurica*; lindens *Tilia amurensis* and *T. mandshurica*; maples *Acer ginnala*, *A. mandschuricum*, *A. mono*, and *A. tegmentosum*; pilose filbert *Corylus mandshurica*; and numerous willow (*Salix*) species. Among conifers, the most widespread are the Korean pine (*Pinus koraiensis*), Korean spruce (*Picea*



Schematic map of the study region.

koraiensis), Manchurian fir (*Abies holophylla*), East Siberian fir (*A. nephrolepis*), and Dahurian larch (*Larix gmelinii*) (Seledets, 2011). Primorye has a temperate monsoon climate with little snow in winter and moist tropical weather in summer, which contributed to rapid decomposition of plant debris. The prevailing soils are burozems (brown soils) formed on the weathering crust of acid rocks and deluvial deposits (Ivanov, 1976).

Test plots (100 × 100 m) were established at a distance of 500–800 m from the shoreline in the following localities: Chazhma Bay (plots 1 and 2), Pavlovsky Bay (plot 3), Patroclus Bay (plot 4), Gornostai Bay (plot 6), Lazurnaya Bay (plot 7), Muravyinaya Bay (plot 8), and also in the Pokrovsky Park (plot 5). Samples of plant debris, forest litters, and soils were collected according to standard schemes used in landscape–geochemical research. In particular, individual samples taken at the corners of an equilateral triangle with 10-m sides were pooled to improve the representativeness of the material.

The contents of ^{90}Sr in the samples were determined radiochemically, by daughter ^{90}Y. Measurements were made using an UMF-2000 radiometer (Russia) with a detection limit of 0.2 Bq. The contents of ^{137}Cs and ^{134}Cs were measured in an ORTEC (United States) multichannel γ-analyzer with a germanium semiconductor detector (detection limit 0.1 Bq). Error of the methods was below 20%. Quantitative analysis for soil heavy metals was performed in vacuum using an EDX-800 X-ray fluorescence spectrometer (Shimadzu, Japan) and state standard reference samples. Samples of leaf debris and litter were incinerated at 450°C and analyzed in air using a qualitative–quantitative approach. The results were processed statistically by conventional methods.

RESULTS AND DISCUSSION

Analysis of the samples has shown that contributions of individual radionuclides to the specific radioactivity of leaf debris (Bq/kg dry matter) decrease in the series ^{90}Sr > ^{137}Cs > ^{134}Cs, with the specific radioactivities of these radionuclides varying within the ranges of 10–40, 2–10, and 0.2–1 Bq/kg, respectively. The same series generally holds for the forest litter, but the content of ^{137}Cs in it is slightly higher (15–20 Bq/kg). Samples of plant debris from plot 8 (Muravyinaya Bay) are an exception, because the contents of ^{137}Cs and ^{134}Cs in them reach 150 and 12 Bq/kg, respectively.

Table 1. Radionuclide contents in organogenic layers (forest litters and leaf debris) and soils in southern Primorye, Bq/m^2

Plot no.	Organogenic layers			Soils			$^{137}Cs/^{90}Sr$
	^{90}Sr	^{137}Cs	^{134}Cs	^{90}Sr	^{137}Cs	^{134}Cs	
1, 2	23 ± 6	10 ± 1.0	0.4 ± 0.2	1330 ± 380	2190 ± 200	184 ± 45.0	1.6
3	3 ± 1	2 ± 0.2	0.2 ± 0.05	520 ± 150	1530 ± 75	11 ± 2.6	3.0
4	10 ± 3	6 ± 0.6	0.05 ± 0.02	610 ± 200	800 ± 80	28 ± 7.5	1.3
5	2 ± 0.5	3 ± 1	0.4 ± 0.2	270 ± 54	430 ± 40	10 ± 5.0	1.6
6	17 ± 3.4	11 ± 0.6	1 ± 0.5	610 ± 60	1200 ± 150	15 ± 8.0	1.9
7	18 ± 3	1 ± 0.3	0.1 ± 0	940 ± 180	3040 ± 30	30 ± 12.0	3.2
8	24 ± 4	140 ± 15	6 ± 2.0	600 ± 200	1140 ± 140	33 ± 3.0	2.1

Table 2. Heavy metal contents in soil and plant cover of the coastal zone of southern Primorye, mg/kg

Component	Co	Cu	Zn	Pb	Mn
Lithosphere (Kovalevskii and Kovalevskaya, 2010)	18	47	83	32	1000
Soil, C_{max}	25	38	90	27	1930
Plant debris	0.1 (0.1–0.3)	1.4 (1.0–2.0)	9.0 (3.0–27.0)	7 (1.0–46)	76 (57–106)
Forest litter	1.0 (0.3–2.0)	20.0 (6–39)	13 (7.0–33.0)	7 (4.0–10)	220 (150–312)
Soil (0–20 cm)	27 (20.0–61)	75 (24–188)	119 (12–496)	64 (2.0–683)	2210 (1718–2954)

In organogenic horizons (leaf debris + forest litter), the content of ^{90}Sr does not exceed 24 Bq/m^2; of ^{137}Cs, 140 Bq/m^2; and of ^{134}Cs, 6 Bq/m^2; these values are equal to 4, 11, and 15% of their total contents in the upper 20-cm soil layer, respectively (Table 1). Similar levels of contamination with ^{134}Cs and ^{137}Cs in organogenic soil horizons after the Fukushima accident have been recorded in the Urals and Siberia (Bolsunovsky and Dementyev, 2011; Molchanova et al., 2012).

The contents of ^{90}Sr in the soils of test plots vary from 270 to 1330 Bq/m^2; of ^{137}Cs, from 430 to 3040 Bq/m^2. The lowest values were recorded in the Pokrovsky park (plot 5), a recreational area; the highest values, in Chazhma Bay (plots 1 and 2), where a nuclear reactor accident aboard a submarine took place in 1986, and in Lazurnaya Bay (plot 7).

In general, the contents of these radionuclides in the soils of Primorye do not exceed the normal level of background radioactivity at latitudes between 50° and 60° N, which is 1.3 kBq/m^2 for ^{90}Sr and 2.2 kBq/m^2 for ^{137}Cs, with the $^{137}Cs/^{90}Sr$ being 1.7 (*Atlas*..., 2007). In the study area, the $^{137}Cs/^{90}Sr$ averaged 2.1, with the relative increase in ^{137}Cs being attributable to the radioactive discharge from Fukushima. This is confirmed by the presence of ^{134}Cs in the samples. One year after the Fukushima accident, the contents of this isotope in the upper soil layer ranged from 10 to 184 Bq/m^2, being 10 to 100 times lower than the ^{137}Cs contents. Taking into account that the $^{134}Cs/^{137}Cs$ ratio in the gas–aerosol discharge at the time of the accident was almost equal (Onishchenko et al., 2011; Kirchner, Bossew, and De Cort, 2012), we calculated the amounts of ^{137}Cs that have contaminated soils in different areas of Primorye over the period after the accident. The results are in the range of 30–300 Bq/m^2, which is higher than in the Urals and Siberia (0.9–42 Bq/m^2) but incomparably lower than in the zone of the accident (600–3000 kBq/m^2) (Yoshida and Kanda, 2012).

Along with radioecological analysis of soils, we have evaluated the contents and distribution of heavy metals and trace elements, which are essential components of all natural objects. Many of them (mineral nutrients) are indispensable for any form of life. The background content of an element in the soil depend on its natural abundance ratio (soil clarke) and global technogenic input (Kovalevskii and Kovalevskaya, 2010). Analysis of our own and published data (Ivanov, 1976; Timofeeva and Golov, 2007; Semal', 2010) has allowed us to estimate the maximum background level (C_{max}) of different elements in soils of Primorye, with the excess over this level being indicative of local technogenic impact. As follows from Table 2, the maximum contents of Co, Zn, and Mn in soil samples slightly exceed their clarkes. The contents of test elements are minimal in plant debris (as a rule, 10 to 100 times lower than their clarkes), increase in litter, and reach a maximum in the upper 20-cm soil layer, indicating that soils are the main depot retaining chemical elements. Comparisons of clarke values with the actual contents of test elements (averaged over all plots) have revealed a twofold excess for Cu and Pb and a smaller excess (8–32%) for other test elements. The highest heavy metal contents are characteristic of stratified urban burozem from the Pokrovsky Park: the maximum allowable concentrations (MACs) of chemical elements in soils (*GOST*..., 1990) are exceeded by factors of 12.4 for Pb, 3.2 for Cu and Zn, and 1.6 for Mn.

In addition to "traditional" toxic heavy metals, soil samples proved to contain rare elements such as Sc, Ga, V, Rb, Sr, Y, Zr, and Nb. With respect to average concentration, they can be arranged in the following descending series: Sr (202.7 mg/kg) > Rb (87.5 mg/kg) > Y (31.3 mg/kg) > Nb (20.3 mg/kg) > Sc (11.2 mg/kg) > Ga (10.9 mg/kg), which generally coincides with the series of their clarke values in sedimentary rocks (Chertko and Chertko, 2008). The exceptions are Zr (289.2 mg/kg) and V (114.2 mg/kg), as their concentrations exceed the clarke values by factors of 2.9 and 9, respectively.

The absence of specified MACs for rare dispersed elements makes it impossible to assess the level of soil contamination from the sanitary–hygienic aspect. It can only be noted that soil concentrations of V, Rb, Sr, Y, and Zr vary depending on the type of land use. The concentrations of Rb and Zr reach a peak in typical burozems of plot 4 on the coast of Patroclus Bay (a residential area with a highway). The highest Sr concentrations are characteristic of plots 1–3 in coastal zones of Chazhma and Pavlovsky bays (formerly occupied by nuclear fleet facilities). The concentrations of V are increased in the former territory of a maintenance and repair facility for nuclear submarines and in stratified burozems of areas exposed to strong recreational load (Pokrovsky Park and Muravyinaya Bay coast).

Thus, the results of this study show that the contents of long-lived radionuclides ^{90}Sr and ^{137}Cs in soils of the Primorye coastal zone are at the level of background radioactivity values characteristic of temperate latitudes (0.3–1.3 and 0.4–3.0 kBq/m^2, respectively). Additional 0.03–0.30 kBq/m^2 of ^{137}Cs (1–10%) was contributed by the Fukushima fallout. Organogenic soil horizons contain the minimal amounts of heavy metals and trace elements. The contents of Cu and Pb in the upper 20-cm soil layer are, on average, twice higher than the corresponding clarke values.

ACKNOWLEDGMENTS

This study was supported by the Integration Research Program for Institutes of the Ural and Far East Branches of the Russian Academy of Sciences, project no. 12-S-4-1001.

REFERENCES

Atlas geoekologicheskikh kart na territorii zony nablyudeniya FGUP PO "Mayak" (Geoecological Maps of the Control Area around the Mayak Federal Production Association: An Atlas), Moscow–Ozersk: ZAO Geospetsekologiya, 2007.

Bolsunovsky, A. and Dementyev, D., Evidence of the radioactive fallout in the center of Asia (Russia) following the Fukushima accident, *J. Environ. Radioact.*, 2011, vol. 102, no. 11, pp. 1062–1064. doi 10.1016/j.jenvrad.2011.06.007

Chertko, N.K. and Chertko, E.N., *Geokhimiya i ekologiya khimicheskikh elementov: Spravochnoe posobie* (Geochemistry and Ecology of Chemical Elements: A Reference Book), Minsk: Belarus. Gos. Univ., 2008.

GOST (*State Standard*) *17.4.1.02-83*, 1990.

Ivanov, G.I., *Pochvoobrazovanie na yuge Dal'nego Vostoka* (Soil Formation in the Southern Far East), Moscow: Nauka, 1976.

Kirchner, G., Bossew, P., and De Cort, M., Radioactivity from Fukushima Daiichi in air over Europe: 2. What can it tell us about the accident?, *J. Environ. Radioact.*, 2012, vol. 114, pp. 35–40. doi 10.1016/j.jenvrad.2011.12.016

Kovalevskii, A.L. and Kovalevskaya, O.M., *Biogeokhimiya uranovykh mestorozhdenii i metodicheskie osnovy ikh poiskov* (Biogeochemistry of Uranium Deposits and Methodological Foundations of Prospecting for Them), Novosibirsk: Geo, 2010.

Masson, O., Baeza, A., Bieringer, J., et al., Tracking of airborne radionuclides from the damaged Fukushima Daiichi nuclear reactors by European networks, *Environ. Sci. Technol.*, 2011, vol. 45, no. 18, pp. 7670–7677. doi 10.1021/es2017158

Molchanova, I.V., Mikhailovskaya, L.N., Pozolotina, V.N., et al., Cesium isotopes from Fukushima-1 nuclear accident in components of terrestrial ecosystems in the Urals, *Semipalatinskii Ispytatel'nyi poligon. Radiatsionnoe nasledie i perspektivy razvitiya: Tez. dokl. V mezhdun. nauchno-praktich. konf.* (The Semipalatinsk Nuclear Weapons Test Range: Radioactive Heritage and Prospects for Development, Abstr. V Int. Sci.–Pract. Conf.), Kurchatov, 2012, pp. 89–90.

Onishchenko, G.G., Romanovich, I.K., Barkovskii, A.N., et al., First results of emergency response to the Fukushima-1 nuclear accident: 2. Measures taken by Rospotrebnadzor at early stages of the accident to protect from radiation the population of the Russian Federation, *Radiats. Gigiena*, 2011, vol. 4, no. 2, pp. 13–22.

Seledets, V.P., *Ekologicheskaya otsenka territorii Dal'nego Vostoka Rossii po rastitel'nomu pokrovu* (Ecological Assessment of the Far East Territory Based on the State of Vegetation), Vladivostok: Dal'nauka, 2011.

Semal', V.A., Properties of soils in southern Sikhote-Alin using the example of the Ussuri Reserve, *Euras. Soil Sci.*, 2010, no. 3, pp. 278–286.

Statement on Recent Finding in West Coast States and Hawaii, EPA: March 22, 2011. http://www.epa.gov/japan2011/

Timofeeva, Ya.O. and Golov, V.I., Sorption of heavy metals by iron–manganic nodules in soils of Primorskii region, *Euras. Soil Sci.*, 2007, no. 12, pp. 1308–1315.

Yoshida, N. and Kanda, J., Tracking the Fukushima radionuclides, *Science*, 2012, vol. 336, pp. 1115–1116. doi 10.1126/science.1219493

Translated by N. Gorgolyuk