# Evaluation of the influence of the granulometric composition of soils and marine sediments of the South of Kamchatka on the content of acid-soluble forms of lead

Olga Nesterova<sup>1</sup>, Viktoriia Semal<sup>1,2\*</sup>, Anastasia Brikmans<sup>1</sup>, Andrey Gilev<sup>1</sup>, and Andrey Egorin<sup>3</sup>

<sup>1</sup>FEFU, Far Eastern Climate Smart Lab, 10 Ajax Bay, Russky Island, 690922 Vladivostok, Russia <sup>2</sup>Federal Scientific Center of the East Asia Terrestrial Biodiversity, Far Eastern Branch of the Russian Academy of Sciences, Prospekt Stoletiya Vladivostoka Ave. 159, 690022 Vladivostok, Russia <sup>3</sup>Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences, Prospekt Stoletiya Vladivostoka Ave. 159, 690022 Vladivostok, Russia

**Abstract.** The influence of anthropogenic and natural factors on the content of lead in the surface horizons of coastal soils and bottom sediments in the south of the Kamchatka Territory was studded. It was revealed that no significant excesses of acid-soluble forms of lead were found, however, a gradual increase in the content of this element in urban soils is observed. The most likely reason for the content of lead in the soils of this area can be considered pyroclastic material, which prevails in the composition of fine earth.

# 1 Introduction

The assessment of the influence of soils forming in the south of the Kamchatka Peninsula as a source of terrigenous runoff has become especially relevant in connection with the search for the causes of the mass death of animals that occurred in 2020 [1,2]. The composition and properties of terrigenous runoff may be one of the reasons for the environmental problems of coastal areas and bays of the peninsula.

One of the most common pollutants of anthropogenically modified territories are heavy metals, and in particular, lead (the impact of vehicles, thermal power plants, etc.).

The soils of the south of Kamchatka are unique in terms of soil genesis, as they are formed under the influence of volcanism and are enriched with various chemical elements, including heavy metals [3], also the south of Kamchatka is the most developed and is under the influence of active anthropogenic activity (agriculture, urban infrastructure, etc.).

The purpose of this study is to evaluate the surface horizons of soils as a possible source of pollution of the coastal zone south of the Kamchatka Peninsula for lead.

The soil cover is an important part of the ecosystem and an indicator of the ecological state of landscapes. The composition and properties of individual soil components can

<sup>\*</sup>Corresponding author: semal.va@dvfu.ru

contribute to the accumulation of pollutants in soils or their free movement and entry into groundwater and further into the marine coastal ecosystem.

The soils of Kamchatka have their own soil-forming characteristics, which is due to a combination of a number of soil-forming factors: features of woody vegetation interspersed with fragments of mountain-tundra and mountain-meadow associations, the specific nature of soil-forming rocks (layered pyroclastic deposits of different ages, mechanical and chemical composition), periodic burial earlier existing genetic horizons and "rejuvenation" of surface organogenic soil horizons during volcanic eruptions, climatic features of the region. The soil cover from the south of the peninsula up to its central part is formed on mainly acidic ashes [3].

The soils of Kamchatka are characterized by a stratified profile, light mechanical composition, friability of structure, poverty of nutrients, weakness of microbiological processes, and poverty of invertebrates [4]. The humid and cold humid climate of Kamchatka determines the leaching water regime of soils, illuvial soil processes, and weak transformation of volcanic ash, which forms the mineral basis of soils. The presence of predominantly volcanic glass and an insignificant amount of silicate minerals in the ashes determines their low geochemical potential as a source of chemical elements for soils. The general level of availability of mobile forms of Mn, Co, Mo, and Zn for plants in volcanic soils of Kamchatka is low [3].

Common to all soils of Kamchatka is the presence of a leaching process, which causes an acidic reaction and unsaturation of soils with bases, the presence of illuvial-humus horizons during soil formation under conditions of good drainage and the presence of gley horizons under conditions of difficult drainage, vertical zonality of soils corresponding to a change in plant formations.

Estuary zones and coastal zones, most actively developed by man, include soils that form under conditions of low temperatures and sufficient moisture - fluvisols. Most fluvisols are of volcanic origin due to the fact that alluvial sediments, especially fine fractions, are formed from volcanic deposits washed off the slopes [5]. Soils of Kamchatka formed on volcanic ashes are characterized by low diversity and total content of elements. Restrictions on elemental diversity and content, the specific genesis of soil formation, specific natural and climatic conditions are the reason for the poor geochemical composition of the volcanic soils of the peninsula.

Of greatest interest are areas experiencing the greatest anthropogenic load, namely, those close to large settlements, such as Petropavlovsk-Kamchatsky, Yelizovo, etc.

According to the annual report of the government of the Kamchatka Territory on the ecological state in the region for 2021, there are significant problems in the south of Kamchatka in the field of land use [5]. The report refers to the development of negative processes associated with technogenic or anthropogenic impact in the form of contaminated atmospheric precipitation, aerosol fallout, household and industrial waste from settlements, littering, misuse, unauthorized occupation of land plots, unauthorized changes in land use boundaries, etc. According to the report of the federal service for surveillance on consumer rights protection and human wellbeing (Rospotrebnadzor) for the Kamchatka territory in 2021, the one soil sample (0.4%) did not meet the sanitary and chemical parameters (exceeding the MPC for heavy metals), the sample was taken in a residential area. In 2021, compared to 2020, the soil condition improved in all studied indicators: in terms of sanitary and chemical (from 0.7% to 0.4%), microbiological (from 0.9% to 0%) and parasitological (from 0.4% to 0.2%) [5].

According to some researchers, the Avachinsko-Koryakskaya group of volcanoes, namely the active volcanoes Avachinskaya Sopka and Koryakskaya Sopka, are a natural source of heavy metals entering the soil of the city [3, 6]. The Avachinsky-Koryakskaya group of volcanoes is located at a distance of 25 - 30 km from the city of Petropavlovsk-

Kamchatsky. With ash emissions, heavy metals can enter the atmospheric air in small quantities, be transported over long distances by air currents and, as a result, accumulate in the soil. Thus, the main sources of heavy metals in the atmospheric air, and, consequently, in the soil of the city of Petropavlovsk–Kamchatsky, are thermal power plants, boiler houses, vehicles, and volcanic activity [6]. In the work of Avdoshchekno and Klimov, it was noted that the content of Zn and Cu in the soils of Petropavlovsk–Kamchatsky is due to the natural features of the city, their concentration varied in a small range in different areas, in contrast to lead, the presence of which is determined by the influence of the anthropogenic factor. The authors note that the content of lead in urban soils corresponded to a very strong or severe degree of pollution [6]. Therefore, our studies were focused on determining the content of lead in the soils of the coast of southern Kamchatka.

### 2 Materials and Methods

To assess the ecological state of soils in freshwater and semi-aquatic ecosystems, areas with an expected anthropogenic impact were selected: r. Avacha (settlement of Severnye Koryaki, area of the Ketkinsky bridge, Cordon No. 13), Lake Khalaktyrskoye and the Khalaktyrka River (mouth zone), the Kirpichnaya River in the territory of the city of Petropavlovsk-Kamchatsky, the Kozelsky stream, the channel and estuarine part of the Paratunka River. A total of 11 soil sections were laid, morphological descriptions were made, soil samples were taken from surface horizons, and basic indicators were determined to identify possible soil contamination. In addition to terrigenous soils, marine sediments were taken from Avacha Bay from depths of 1 to 20 m; samples were taken from surface horizons using a bottom grab (Fig. 1).

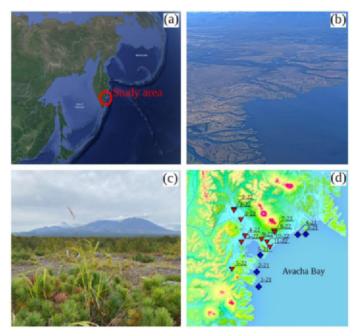


Fig. 1. Research area; a — geographic location of the research area, b, c — general view of the study area, c — sampling points, ( $\nabla$ ) - soil sampling points, ( $\Phi$ ) - marine sediment sampling points.

According to the morphological properties, determined directly during sampling, the soils are anthropogenically undisturbed, no visual disturbances (turbations) have been

identified and correspond to the descriptions presented in publications [3]. According to the World Reference Base of Soil Resources, the soil in the studied areas is represented by Fluvisols. Marine sediments are predominantly homogeneous sandy material.

The soil samples were placed indoors for air drying. After removing gravel and plant residues, they were ground and screened with 1 mm. The percentage of clay, silt and sand in the soil was determined by standard method [7]. Soil water content (SWC) was determined using a drying method 118 [8]. The pH value of aqueous soil extract was deter- 120 mined with a pH meter [9]. Soil organic matter (SOM) was determined 121 using the Walkley–Black method [10]. AA 6800 was used to determine the contents of acid-soluble forms Pb, extraction was carried out with a solution of five molar nitric acid [11].

### 3 Results and Discussion

The soil is the initial and final link of trophic relationships in ecosystems and, in the case of anthropogenic impact, it actively accumulates various pollutants. Such soil, under certain conditions (changes in temperature, pH, erosion, etc.), can itself become a source of secondary pollution of atmospheric air, water bodies, groundwater, food of plant origin, animal feed, which is certainly negative affect the quality of life of the population and its health.

The hydrogen index of the water extract of fluvisols fluctuates within a fairly narrow range (pH 5.6–6.9), namely, from weakly acidic to neutral, which is typical for surface horizons formed on river banks [3]. Such pH values make a number of elements sufficiently mobile, including heavy metals, which, when the soil solution is acidified, can turn into a water-soluble form. The transition of metals into a water-soluble form leads to pollution of water bodies and can distort the results of assessing the intake of pollutants due to anthropogenic impact. The acidity value for all marine sediments corresponds to a slightly alkaline reaction (pH 7.4-7.9). The values of marine precipitation are closest to neutral values at the mouth of the Nalycheva River due to the influence of fresh waters.

The content of organic carbon in the soils of the study area ranges from 0.3% to 9.2%. According to the degree of humus content, almost all the studied soils can be classified as low-humus, which is obvious, given the predominance of sandy and sandy loam composition [12]. The only exceptions are sections 4 - 22 and 10 -22, which have horizons in which slightly decomposed plant remains are determined (Fig. 1). The average content of organic carbon in marine sediments is in the range of -0.3%.

The granulometric composition is inherited from soil-forming rocks and determines the properties of soils and soils: physical, physico-chemical and chemical). The percentage content of fractions of physical sand and physical clay explains the mechanisms of fixation of organic matter and pollutants in the surface layer of soils. Most researchers note the predominance of a light granulometric composition for soils formed in the estuarine zone of southern Kamchatka [3, 13].

As shown by our previous and present study the soils of estuarine zones, due to their light granulometric composition, are a source of terrigenous runoff of material from the mainland into the water area in the form of alluvial fans due to marine abrasion or deltaic sediments due to river accumulations of watercourses from the territory [14].

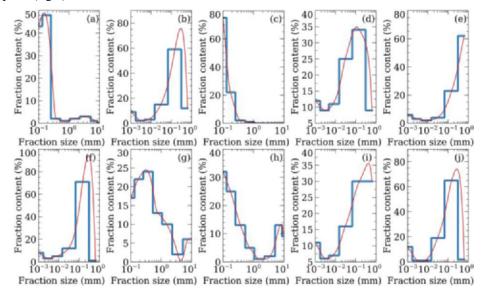
The results of granulometric analysis of fluvisols show that the type of the predominant particle size fraction depends, first of all, on the position of soils in the relief; soils formed on high floodplain terraces have a loamy granulometric composition; sandy granulometric composition.

In general, in terms of granulometric composition, the surface horizons are characterized by the predominance of the sandy fraction, which makes soils with such a horizon quite vulnerable to active anthropogenic impact (erosion processes may develop in the absence or damage of the vegetation cover) and water-permeable, which means that in the event of pollutants entering that they can easily enter groundwater and rivers flowing into the sea.

The chemical-ecological assessment of the content of acid-soluble forms of heavy metals in soils showed that almost all heavy metals in acid-soluble form are within the official norms adopted in Russia, such as maximum allowable concentrations and amount to 32 mg/kg [15].

In the study area, the content of acid-soluble forms of lead does not exceed the maximum allowable concentrations. The lowest values are noted in the soils formed in the area of Petropavlovsk-Kamchatsky (p. 9-22 and 10-22) and at the foot of the Vilyuchinsky volcano (p. 5-22) and is about 20 - 22 mg/kg. For other soils, lead content fluctuates from 0.1 to 7.0 mg/kg.

As a factor influencing the content of lead in soil samples, the average size of the diameter in mm of the predominant fraction was chosen. The calculations were carried out by interpolating the histograms of the percentage distribution of soil fractions using Akima's spline (fig.2).



**Fig. 2.** Granulometric composition of soils; **a** - 22-1, **b** - 22-2, **c** - 22-3, **d** - 22-4, **e** - 22-5, **f** - 22-6, **g** - 22-7, **h** - 22-8, **i** - 22-9, **j** - 22-11, the red line is the result of smoothing histograms with Akima's spline.

On Fig.2. the percentage distribution of soil fractions for the selected samples is given. The granulometric composition of samples 1-22, 3-22, 7-22, 8-22 was evaluated using a sieve method, samples 2-22, 4-22, 5-22, 6-22, 9-22, 11-22 - with using the pipet method. The particle size distribution of the surface horizon from section 10-22 was not assessed, since it was a peat mass.

When using linear regression for the dependence of the content of lead in the upper horizon of the soil cover on the average size of the predominant fraction, the values of R and  $R^2$  were 0.781 and 0.610.

This fact may indicate that there is a significant relationship between the presence of a coarse soil fraction and the content of the acid-soluble fraction of lead. Such a large fraction can be pyroclastic material containing significant amounts of lead and entering the environment as a result of volcanic activity.

Figure 3 shows histograms of the distribution of the percentage of soil fractions in the selected marine sediments. In contrast to soils, no reliable statistical significance was found for marine sediments between the average size of the predominant soil fraction and lead

content (R = 0.420, R2 = 0.176). However, a significant relationship was found between the average size of the predominant soil fraction and the carbon content (R = 0.976, R2 = 0.952), which probably comes with runoff from the mainland and is involved in the formation of the structure of marine sediments. In general, in comparison with the samples of selected soils, bottom sediments are characterized by a low content of lead, which, unlike carbon, is in the composition of poorly soluble pyroclastic deposits and does not enter the coastal zone.

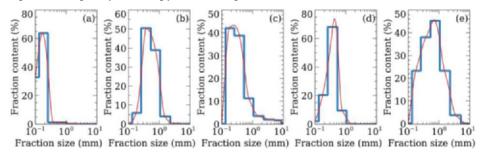


Fig. 3. Dependence of lead content in samples on the average size of the predominant marine sediment fraction; a - 1-21, b - 2-21, c - 3-21, d - 4-21, e - 5-21.

### 4 Conclusions

- 1. According to the morphological properties of the soil, they are anthropogenically undisturbed; no visual disturbances (turbations) have been identified.
- 2. According to the granulometric composition, most of the studied soils have a sandy and sandy loamy granulometric composition, and the soil-forming layers are layers of sandy and pebble deposits typical of alluvial soils, which makes them the most vulnerable in case of contamination on the surface due to the high filtration rate.
- 3. In terms of physicochemical properties, the studied soils are classified as slightly acidic and neutral.
- 4. The degree of humus content in most of the studied soils is low, which is within the normal range for soils with leaching water regime.
- 5. Exceeding the maximum permissible concentrations of lead was not detected in the study area.
- 6. The relationship between the lead content and the fraction inherited from pyroclastic sand deposits was revealed.

The work was supported by the Ministry of Science and Higher Education of the Russian Federation, project No. FZNS-2022-0001 "Study of natural and anthropogenic impacts on freshwater and estuary ecosystems of the Kamchatka Peninsula using bioindication and biotesting methods."

## Reference

- T.Y. Orlova, A.I. Aleksanin, E.V. Lepskaya, K.V. Efimova, M.S. Selina, T.V. Morozova, I.V. Stonik, V.A. Kachur, A.A. Karpenko, K.A. Vinnikov, A.V. Adrianov, M.A. Iwataki, Harmful Algae 120, 102337 (2022)
- 2. A.M. Tokranov, D.D. Danilin, G.G. Zhigadlova, K.E. Sanamyan, N.P. Sanamyan, I.A. Usatov, *Marine Research and Education (MARESEDU-2021), Proceedings of the X International Scientific and Practical Conference. Volume II (III)* (Limited Liability Company "PolyPRESS", Tver, 2021)
- 3. L.V. Zakharikhina, Y.S. Litvinenko, Eurasian Soil Science 49.3, 305-314 (2016)

- 4. N.A. Sokolov, N.I. Belousova, Eurasian Soil Sci. 5, 67-78 (1996)
- Report on the state of the environment in the Kamchatka Territory in 2020 (Ministry of Natural Resources and Ecology of the Kamchatka Territory, Petropavlovsk-Kamchatsky, 2022)
- 6. V.G. Avdoshchenko, A.V. Klimova, *Heavy metals in the soil and plants of the city of Petropavlovsk-Kamchatsky (Kamchatsky Krai): monograph* (Kamchat GTU, Petropavlovsk-Kamchatsky, 2021)
- 7. GOST 12536-2014. Interstate soil standard. Methods for laboratory determination of granulometric (grain) and microaggregate composition. soils. Methods of laboratory granulometric (grain-size) and microaggregate distribution (Standartinform, M., 2019)
- 8. L. Gong, Q. Ran, G. He et al., Soil and Tillage Research **146**, 223-9 (2015)
- 9. G. Rayment, F.R. Higginson, *Australian laboratory handbook of soil and water chemical methods* (Inkata Press Pty 586 Ltd, 1992)
- 10. A. Walkley, I.A. Black, Soil science **37(1)**, 29-38 (1934)
- 11. Guidance document. Methodical instructions. Methodology for measuring the mass fraction of acid-soluble forms of metals (copper, lead, zinc, nickel, cadmium, cobalt, chromium, manganese) in soil samples by atomic absorption analysis in the laboratories of the National Service for Observation and Control of Environmental Pollution. RD 52.18.191-89 (M., 1990)
- 12. D.S. Orlov, *Soil Chemistry* (M., 1985)
- 13. A.A. Zenkevich, Biology of the seas of the USSR (1963)
- 14. A.I. Ivankova, A.S. Frolova, I.V. Golyukov, V.A. Semal, O.V. Nesterova, Agrarian Bulletin of Primorye **4(24)**, 7-10 (2021)
- 15. SanPiN 2.1.7.1287-03. Sanitary and epidemiological requirements for soil quality: Sanitary and epidemiological rules and regulations (Federal Center for State Sanitary and Epidemiological Surveillance of the Ministry of Health of Russia, M., 2004)