Geochemical Specifics and Patterns of the Distribution of Heavy Metals in the Opuksky Sanctuary, Republic of Crimea

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Abstract. This paper evaluates the ecological and geochemical status of soils in the Opuksky Sanctuary, Republic of Crimea, Russia. The Sanctuary has been a nature reserve since the mid-20th century. It is located on the Black Sea coast of the Kerch Peninsula, the Republic of Crimea. This is an integrated sanctuary established to preserve the unique steppe ecosystems associated with the limestone massif of Mount Opuk and Lake Koyashskoye, a salt lake which has a number of one-of-a-kind nature sites within a small area and features several rare species. The water area of the Sanctuary is a wetland protected international under the Ramsar Convention. The increasing anthropogenic pressure arising from agricultural and industrial development of the Crimean Peninsula, as well as the increasing tourist flow that must be controlled is what makes monitoring the area critical. Soil is the most sensitive natural environmental component to anthropogenic effects; as such, it was monitored over three years from 2017 through 2019 as part of St. Petersburg State University, Department of Environmental Geology’s student internship co-organized with the administration of the Sanctuary. This effort produced a map of heavy metals in the local soils. The authors described the patterns in pollutant migration; they also prove why the soil was vulnerable to contamination. The research effort was the first to collect data on the background presence of trace elements in the soils of potentially uncontaminated areas; this data could be of use for engineering and environmental surveying across the region. Such data is becoming relevant and essential as the Republic of Crimea’s heavy industry and agriculture are rising.

1. Introduction

According to Russia’s Specially Protected Natural Areas Act, there are several categories of nature reserves. A sanctuary constitutes the most important component of Russia’s network of protected sites. Sanctuaries have the strictest internationally recognized protections: strict nature reserve (IUCN category Ia) or wilderness area (IUCN category Ib). It is mainly intended to preserve biodiversity and assist in research. Its secondary but no less important objectives include environmental education and ecotourism. Besides, since nature reserves are least affected by man, it is there that the quality of natural environmental components and the background indicators are monitored. This data is used for
environmental research for scientific and economic purposes. Besides, since a nature reserve must help further ecotourism and education, it is subject to continuous monitoring and adjustment.

The Opuksky Sanctuary is a state-funded nature reserve in Crimea, located in the south of the Kerch Peninsula. It covers an area of 1592.3 hectares. The Sanctuary was established to preserve and reproduce the natural steppes of the Crimean plains as well as the aquatic areas of the Black Sea. The location is on the IBA list of areas critical for the conservation of bird populations in Europe. The Aquatic Coastal Complex of Cape Omuk has been an internationally protected wetland under the Ramsar Convention since 2004.

It contains Mount Omuk, a carbonate massif bordered by steep cliffs and dissected by wide, deep (down to 20 m) tectonic fractures into separate units; the Complex also contains Lake Koyashskoye that is chemically similar to the Field of Saki. In additional to natural sites, the Sanctuary has preserved the ruins of the Ancient Greek city of Kimmerikón (6th century BC to 4th century AD), the ruins of a citadel, and dozens of ancient wells and captations. The relief of Mount Opuk’s slopes is of tectonic and landsliding nature. The seaside slope shows a massive and complex earthflow that is incompletely developed.

The soil cover features a considerable variety; it combines southern chernozems, alkali chestnut soils, black alkali soils, and salt marshes. The soil phase distribution, the degree of salinity, the depth of soil horizons mainly depend on the altitude above seal level and the nature of the rocks constituting the local soil. The richest chernozem and dark chestnut soils emerged on loess clays in synclinal basins as well as on the limestone diluvial deposits in anticlinal structures. Cliffs, screees, gravels, shell deposits, as well as steep slopes and precipices of Mount Opuk have no solid soil cover. Mount Opuk is extremely diverse in its soil composition due to a complex geological structure. Soils are more homogeneous in the plains. This complexity of soil cover arises from the salinity of soils in their geological past and present [1, 2].

The east of the Opuksky Sanctuary is partly within the region of southern carbonate chernozems on an eluvium of dense carbonate rocks. Deep southern carbonate chernozems on rubble and clay deposits are suitable for fruit orchards and vineyards. The slopes have eroded soils that need anti-erosion measures in place for optimal use [3].

The Sanctuary has several core biotopes that ecological fauna complexes (steppe, shrubland, near-water, and rock complexes) emerge within. Rock complexes in turn fall into rock-steppe and rock-sea complexes plus marine and accumulative complexes. The area has at least 90 species of terrestrial vertebrates. These include 55 common species, 28 rare and protected species; the coastal area is also quite diverse. Besides, the reserve has a diverse bird population thanks to its variety of avian habitats including maritime coastal, wetland, and rock-steppe complexes. As of now, at least 60 bird species nest in the area [4].

To date, the Sanctuary’s infrastructure for tourism and recreation is underwhelming. Tourism and recreation is present here in organized and unorganized forms. Ecotours are available as one-day hiking routes varying in length: 3 ecological routes and 1 maritime route under development. The tourist flow has been rising in recent years, which might degrade the soil cover and the plant communities in the area while also altering the soil geochemistry. This is why monitoring the condition and the quality of soils is important. It is also crucial to analyze the patterns of the distribution of chemical elements in the uncontaminated soils. Detailed background concentrations of heavy metals serve as the informational foundation for environmental research, engineering and ecological surveying, etc. on a region-wide basis [5, 6]. There is no such data for the Republic of Crimea [3, 7, 8].

2. Materials and methods
In 2017-2019, St. Petersburg State University and the Sanctuary’s administration held joint monitoring of the local soils and plant communities. Over the course of three years, 105 surface soil samples were collected in the Opuksky Sanctuary, four test pits were made and described. Samples were taken by the ‘routing’ method per GOST 17.4.4.02-83. At each sampling site, ~1 kg of soil was sampled form
the upper horizon (10-15 cm off the surface) using the technique referred to as “the envelope method” in GOST (five sampling points: one in the center and four placed equidistantly around it forming a square—translator’s note).

Soil profiles were located as follows: one on the top of Mount Opuk, two on adjacent slopes, and one in the plains near Lake Koyashkoye; thus, the research team was able to assess the key sites and to determine the soil types. The team identified textured carbonate chernozem on the southern slope and in the plains near the salt lake, and dark humus residual-carbonate soils on the mountain top and on the western slope. The soil profiles were embedded down to the bedrock (up to 85 cm) and described by the accepted methodology. The team assessed such parameters as the genetic horizons and their depth, as well as how layers transitioned into each other. For each horizon, we also described the color, the particle size distribution, the structure, the humidity, the consistency, the density, the presence of novel formations and inclusions on an individual basis. Soil was sampled from the pits for each of the identified horizons to evaluate the vertical migration of elements, see Figure 1.

Once sampling was done, soil was preliminarily prepared for further analysis. This procedure included drying in a chamber to reach an airdry state, sieving through a large sieve to remove organics and stones. Then soil was ground to fine particles in a ceramic mortar or using a ball mill in portions of 50 grams to make powder suitable for further analysis.

The samples were analyzed by atomic emission spectroscopy of inductively coupled plasma (AES ICP) in the chemistry laboratories of St. Petersburg State University as well as by X-ray fluorescence using the equipment of the Environmental Geology Department, Institute of Earth Sciences, SPSU. The goal was to evaluate the presence of heavy metals: Pb, Zn, Ni, Cu, Co, Cd, Cr, Fe, As, Mn.

Figure 1. Soil profile examples: (a) Dark humus residual-carbonate soil on carbonates; (b) Textured carbonate chernozem on carbonates.

3. Results and discussion
Testing the soil samples for heavy metals revealed no excess of MAC values. Cadmium, arsenic, and cobalt were not detected by the methods in use in any sample (the detection threshold was 1 ppm for cadmium, 10 ppm for arsenic and cobalt). However, all other metals were detected with confidence. To assess the geochemical background, the researchers used the median as a robust indicator [7, 9, 10, 11, 12].
Table 1. Concentration of the tested elements, mg/kg (A is for the mean concentration in the soils of the Republic’s residential areas, mg/kg).

| Element | A    | Median | Max  | Min |
|---------|------|--------|------|-----|
| Pb      | 27.6 | 40     | 80   | 16  |
| Cu      | 58.2 | 25     | 57   | 10  |
| Cr      | 77.5 | 67     | 140  | 22  |
| Ni      | 46.2 | 33     | 72   | 10  |
| Zn      | 135.0| 71     | 175  | 27  |
| Fe      | -    | 43,872 | 70,962 | 14,894 |
| Mn      | -    | 1063   | 1759 | 846 |

The results of the analysis were then compared against those shown in a similar paper on this region [3] that analyzed soils sampled in settlements. The Sanctuary’s soils were less contaminated with heavy metals compared to their counterparts in residential areas, meaning they were relatively clean. Notably, chromium and nickel were slightly less concentrated in the Sanctuary’s soil compared to the Crimean average, while zinc and medium concentrations were half the average. On the other hand, the median concentration of lead was 40 mg/kg against 27 mg/kg in the residential areas of the Republic of Crimea.

To analyze the samples element-by-element and to see the distribution and the outliers, the research team plotted box-and-whisker diagrams, see Figure 2.

Figure 2. Scales of Pb, Zn, Cu, and Ni concentrations.
Each element had a normal distribution. Only the distribution of zinc and lead had outliers. These matched the sampling sites on the ecological routes: the springs and the abandoned quarry. Most of the ecological routes pass through the springs; the quarry is also an interesting site popular with tourists, as it has a population of bats and offers a scenic view of the Sanctuary. Lead concentration was abnormally high only at a single site: the top of Mount Opuk; this needs to be verified.

The distribution of the gross content of all elements was normal with the Lilliefors test returning > 20 for all elements. Normal distribution is not typical of natural ecosystems, which leads to a suggestion is or was affected somehow.

Since the concentrations of heavy metals in the area were found to be quite low, the research team mapped the coefficients of the tested concentrations in the area to confirm this suggestion, see Figure 3. The interpolation field was made by the method of inverse distance weighting. The total concentration factor calculated by the formula (1) was used as the baseline:

\[ K_c^* = \sum \left( \frac{C_i}{C_b} \right) \]

where \( C_i \) is the site-specific concentration of an element, \( C_b \) is the back concentration for the same element.

This coefficient was calculated specifically to improve the data contrast. Geochemical conditions of the territory were quite homogeneous. As shown in the map in Figure 3, the relief had no significant effect on the migration and accumulation of elements. The underlying bedrock was the same for the entirety of Mount Opuk and its surroundings: limestone. The vegetation and the soils were not very diverse, mainly grass steppes on chernozem. This is why the authors hereof believe the results were mainly affected by anthropogenic impact. As can be seen in the map, relatively high \( K_c^* \) values were observed where the settlements of Novy Koyash and Chekur-Koyash had used to be as well as where the road network was dense.

Importantly, all the business facilities shown in the map (which is dated 1953) except the springs haven’t functioned for over fifty years. The landscapes bear no traces of anthropogenic influence. However, human activity is still traceable.
If anthropogenic effects remain traceable for that long, it can only mean the element migration is weak. This is actually typical of these soils. The Sanctuary is dominated by textured carbonate chernozems on limestone. The top of Mount Opuk mainly has dark humus residual-carbonate soils on limestone. All of these are pH-neutral (closer to alkaline) [8]. The tested elements migrate only slightly in such soils; they tend to remain where they first entered the soil [7]. Notably, the Sanctuary has a dry climate; precipitation is rare and not abundant, which contributes to the preservation of the elements [14].

To confirm the assumption that the geochemical anomalies were of anthropogenic origin, the research team ran factor analysis on the elements that were sampled in the largest quantity. This analysis highlighted two factors, see Figure 4. For a better contrast of the distribution of factor loads, the factor axes were rotated by varimax raw. Factor 1 was found to explain the greater variance of Fe, Ni, and Cr concentrations, while Factor 2 controlled Pb, Zn, and Cu. The variables split into three associations: Cu, Pb, and Zn associated with Factor 2; Cr associated with Factor 1; and Fe and Ni controlled mainly by Factor 1 but also affected by Factor 2. Apparently, Factor 2 was an anthropogenic factor, likely related to transport, as both lead and zinc had a normal distribution with a few outliers. Besides, the concentration of lead correlated with its presence in settlement soils. Whilst other elements were undoubtedly affected by human activity, the effect was insignificant.

![Figure 4](image.png)

**Figure 4.** Factor number to value correlation (a), distribution of factor loads after rotating the axes (b).

4. Conclusions
The research team quantified the presence of heavy metals and metalloids (As, Co, Cr, Cu, Ni, Pb, Zn, Fe, Mn) in the soils of the Opuksky Sanctuary, and calculated the background concentrations adjusted for the history of the area. No metal was present in quantities exceeding MAC values or the concentrations of the same metal in the residential areas of the region. Comparing the collected data against the gross concentrations of these elements in the residential-area soil of the Republic of Crimea showed that the Sanctuary’s concentrations were below those in the settlements by a factor of 1.5 to 2 for all elements except lead. Lead had a median concentration of 40 ppm, which on the contrary was above the residential average of 28 ppm, likely due to residual contamination.

The distribution of heavy metals within the Sanctuary was non-homogeneous. There were still residual higher concentrations at former residential sites that had used to be there in the first half of the 20th century, i.e. before the area became protected.
To calculate the background presence of heavy metals, one should bear in mind the anthropogenic activity in the surroundings for at least the last 50 years; affected sites must be excluded from the calculations. This is due to trace elements being quite stagnant in soils lying on carbonate bedrock.

5. References

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