Environmental aspects of the evaluation of the total pollution of soils with heavy metals in the coastal zone of the Caspian Sea at cape peschany

S Syrlybekkyzy¹, S E Koibakova¹*, G Zh Kenzhetaev¹, L S Taizhanova¹, Zh K Altybayeva¹ and V N Permyakov²

¹Yessenov University, Aktau, Kazakhstan
²Tyumensk Industrial University, Tyumen, Russia

* E-mail: symbat.koibakova@yu.edu.kz

Abstract. This study is aimed to analyze the total contamination of the soil of the CAPE with heavy metals and metalloids in the area, the ferry complex and farms on the Sandy Cape. During the survey of the coastal zone of Cape Peschanyi, the route method with the laying of 7 trial plots (TP) with background TP-7 was used. Total content of the heavy metals (HM) was determined by a laboratory spectrophotometer of HACH DR-2400 (USA). Studies of the ecological state of the coastal zone of Cape Sandy, after the introduction of an international multimodal transport hub that provides access to Europe, are the first and allowed us to identify the degree of anthropogenic transformation. The availability of farms testifies to the suitability of the Cape's soils for cultivation and crops. The assessment of the ecological state of the soils of the ferry complex, "melon" farms, and the territory of the national reserve with a conservation status is relevant and timely. The results of the analysis of the content of heavy metals and metalloid allowed us to identify pollutants that affect melons. According to the results of calculations, on P-2, ST=16.5 the level of pollution is moderately dangerous, on the other PP, within the acceptable level. The range of a variation less than 1, only for hexavalent chrome Cr⁶⁺, is bound to the fact that chrome is easily mobilized in alkaline soils. Statistical processing of the results by Statistica 10 had shown that the Kruskal-Wallis criterion is statistically significant for the elements Cr, Cd, Cu and Co.

1. Introduction

On August 12, 2018, in the Mangistau region, a multimodal transport hub was opened - a ferry complex in the port of Kuryk, located on Cape Peschanyi. The Kuryk port is included in the network of international transport corridors. The Trans-Caspian route through the Kuryk port opens access to Europe, through Turkey and the Mediterranean Sea. The port already has railway and automobile tracks. The capacity of the Kuryk port is 7 million tons per year. According to the soil-geographical characteristics, the described territory is located in a desert zone and is divided into two subzones, namely, deserts with a predominance of brown soils and southern deserts (gray-brown soils) [1]. The presence of groundwater in the area provides opportunities for the cultivation of various vegetables, melons and fruit trees. However, along with this, it is necessary to assess the anthropogenic impact on natural landscapes in the area of Cape Peschanyi, where a ferry complex had been built, infrastructure has been developing, and land development works for crops are intensively carried out.
Comprehensive studies to assess the state of the degree of soil pollution by heavy metals on the territories of Cape Peschanany have not been previously conducted, especially the nature and degree of influence of the ferry complex on the coastal zones of the Caspian Sea remain unexplored. The problem of studying the state of existing technogenic objects of the coastal zone is very acute, and therefore, the studies carried out seem especially relevant. The results will allow to take the appropriate measures to achieve sustainable development of this region, based on the results of the study of soil quality [2].

The aim of the work is to assess the soil condition of various objects at Cape Peschanyi, as well as to analyze the total soil pollution with heavy metals (HM). To achieve this goal, field studies of soils were carried out to determine the HM content in the soils of the coastal zone of Cape Peschaniy in the area of the ferry complex and a complex indicator of total soil pollution was calculated.

2. Methods and Materials
The studied coastal zone of Cape Peschanyi developed due to abrasion during the whole Quaternary period. In this regard, the regressive coastlines, which are now under the sea, are represented by abrasive forms. Physical weathering processes prevail here. They contribute to the entry of coarse gravel material into the coastal zone. Alluvial inflow is completely absent. The deposits generally consist only of biogenic and chemogenic components (rakusha and dolita). There is a wide development of abrasive forms (carbonate-clay composition of the rock). This territory adjoins to two-tiered South Mangyshlak plateau, the surface of which is broken by deep closed drainage depressions - Karagye (- 132 m) and Ashysor (- 33.5 m) [3].

2.1. The Ferry complex of Kuryk
The trial plot TP-1 (research ground RG-1) is located in the Northern part, at a distance of 150 meters from the fencing of the ferry complex and 500 meters far from the sea. TR-1 is situated at an altitude of 33 m above sea level. The ecosystem is a plateau with a predominance of gray-wormwood communities and crushed-sand soils. The soil cover is saline coastal sands with low reserves of organic matter. The mechanical composition of the sands is layered. The structure of the soil profile is represented by numerous inclusions of shell rocks (up to 85 %). Project coverage is 25 %. The soil condition is moderately disturbed.

TP-2 (RG-2) was laid at a distance of 50 m, near the apple orchard of the Zhanbyrshi farm, at a distance of 8,118 m far from TP-1, to the west of the ferry complex of Kuryk. TP-2 is located at an altitude of 32 m above sea level. For irrigation, mineralized groundwater (GW) is used from wells with a depth of about 50 m and a salt content of 3-4 g/dm³. The content of nitrates and nitrites in GW is in the range of up to 144 g/dm³. Groundwater after desalination and purification may be suitable for drinking purposes. The TP-2 ecosystem is a plateau with a prevalence of ephemeroïd-cereal-sagebrush communities on brown desert normal saline soils. Projective covering is 76 %. The soil condition is moderately disturbed, and there is a mechanical disturbance of the soil cover. The vegetation is important and it includes complexes with a predominance of white-earth wormwood, which is used by residents as the most valuable forage plant for desert regions.

TP-3 (RG-3) was laid at a distance of 3870 m from TP-2 and at a distance of 2000 m from the sea and directly opposite Cape Peschanyi, within the limits of distribution of seaside residual saline soils. The site is located at an altitude of 36 m above sea level. There are ecosystems of marine sand and shell beaches. The soil is represented by a coastal salt marsh with an abundance of shells on the surface, layers of shells in the profile, rusty spots and compaction in the middle part of the profile. Projective cover is 60-65 %. Disturbance of the soil cover is medium, mainly mechanical. The vegetation of TP-3 is of high importance. This category includes all the communities with the participation in their composition of saxaul, which are confined to the Peschanyi massifs. Peschanyi massifs play a very important role in stabilizing the landscape, which is manifested in the fixing the substrate, the prevention of wind erosion, and the deflation of sand. These psammophytic plants grow only in this area, and therefore the problem of preserving this original floral diversity has arisen. The
condition of the soil and soil cover is disturbed as a result of overgrazing of livestock and due to the passage of motor transport.

TP-4 (RG-4) was laid at a distance of 50 m from the fencing of the pharos in the southern part and 2870 m from TP-3 in the area of the lighthouse of Cape Peschanyi. It is located at an altitude of 39 m above sea level. The soil cover is saline coastal sands. The sands are of stratified structure, with numerous inclusions of shell rock - up to 95-100 %, this is due to the fact that at a distance of about 1000 meters there is a quarry for sawing limestone shell rock. Projective cover is 25 %. The condition of the soil is disturbed in an average degree, mainly by road transport. The vegetation is of moderate importance.

TP-5 (RG-5) is laid at a distance of 70 meters from the fencing of the crops of the farm “Venera”, which grows vegetables (cucumbers, tomatoes and eggplants) both in open ground and in greenhouses. It is located at an altitude of 35 m above sea level, to the northward from TP-2 and removed 4700 m from TP-4. The groundwater (GW) is mineralized with a salt content of 3-4 g/dm³, which is diluted with potable water produced by MAEK Kazatomprom LLP. The location of TP-5 refers to a plateau with a predominance of ephemeroïd-cereal-wormwood communities on brown desert normal saline soils. Projective cover is 70 %. The vegetation is important. White-land wormwood communities predominate.

TP-6 (RG-6) is located in the area of the Ashysor depression at 33.5 m below sea level (-33.5 m). Ashysor is a salt lake surrounded by a sor strip of 3-5 km wide. TP-6 was laid in the eastern part on the sor strip of the Ashysor basin, northerly of TP-1 and removed 7886 m far from TP-5. Soils are represented by salt marshes on the subordinate plains and poorly affected by the process of soil formation. The high value of evaporation in the summer period with a small amount of atmospheric sites determines the crystallization of salts in the upper horizons. A solid salt crust up to several centimeters thick is formed on the soil surface. The degree of land use is negligible. The border of the Karakiya-Karakol reserve is located along the eastern and northern parts of the depression. Soil cover disturbance is medium. By the type of salinization chemistry almost all studied soils are chloride-sulfate soils by anions, calcium-sodium soils by cations. There are also soils with sulfate-chloride, chloride and sodium-carbonate chemical salinization types.

2.2. Physical and chemical characteristic of soils

For the study of soil samples, the following methods were used: color was determined on the A. Mansell scale, granulometric composition – by N.A. Kaczynski, humus (soil oxidation with potassium dichromate) – according to I.V. Tyurin, nitrogen total – by J. Kjeldahl, phosphorus total – for carbonate soils – by B.G. Machigin and the sodium exchange – by Gedroyts. Magnesium exchangeable and calcium exchangeable were determined by Druino-Gale. Conventional methods were used to determine the volume mass, the density of the solid phase, hydrolytic acidity, the amount of absorbed bases. The determination of the amount of humus in the soil was performed by I.V. Tyurin in modification of B.A. Nikitin [4-10].

pH - measurement. Water extraction of soil samples was carried out by standard potentiometric method using a pH meter MP 220 (Mettler Toledo, Switzerland). Standard error is ±0.1. Physical and chemical properties of the studied soils are given in Table 1.

| Physical and chemical properties of soils on trial plots (TP) | Trial plots |
|-------------------------------------------------------------|------------|
|                                                           | TP-1      | TP-2     | TP-3     | TP-4     | TP-5     | TP-6     |
| Humus, (%)                                                  | 0.29-0.51 | 0.43-1.07| 0.21-0.49| 0.31-0.53| 0.31-0.57| 0.23-0.47|
| Nitrogen total, (%)                                         | 0.08-0.13 | 0.09-0.16| 0.03-0.15| 0.05-0.14| 0.07-0.12| 0.02-0.12|
| Phosphorus (gross), mg/kg                                    | 697-871   | 958-1059 | 589-937  | 611-871  | 601-793  | 458-744  |

Table 1. Physical and chemical properties of soils of trial plots
| Carbonates, (%) | 1.6-9.17 | 2.31-7.38 | 2.9-9.25 | 2.3-9.31 | 1.4-8.18 | 1.2-7.79 |
|----------------|----------|-----------|----------|----------|----------|----------|
| Exchange capacity, mg-Eq/100 g of soil | 7.33-21.6 | 8.15-22.5 | 6.59-20.7 | 5.93-21.3 | 7.21-21.5 | 7.3-18.3 |
| Exchange calcium, mg-Eq/100 g of soil | 13.4-35.7 | 12.7-29.5 | 12.8-33.6 | 13.6-31.9 | 13.1-33.2 | 14.1-29.8 |
| Exchange magnesium, mg-Eq/100 g of soil | 65.7-85.3 | 66.3-87.2 | 59.2-84.9 | 61.4-83.3 | 66.1-82.5 | 63.8-86.9 |
| Exchange sodium, mg-Eq/100 g of soil | 1.85-6.37 | 2.09-5.71 | 2.01-5.97 | 1.81-6.14 | 1.79-6.03 | 2.03-6.41 |
| The amount of salts | 0.08-6.23 | 0.06-5.71 | 0.09-6.11 | 0.07-5.79 | 0.07-6.41 | 0.09-6.81 |
| pH | 6.9-7.35 | 6.85-7.13 | 7.1-7.36 | 7.0-7.33 | 6.6-7.29 | 7.2-7.41 |

2.3. Sample selection

Soil samples were taken by the sampler, by the envelope method, from depths of 0-5 and 5-20 cm. More than 30 samples were studied, which were collected on the trial plots, indicated above, in different parts of Cape Peschanyi. A mixed sampling was performed as well. A mixed sample consisted of 5 soil samples, that were taken from 5 point locations by an envelope. Then an average sample weighing 300-400 g was chosen.

2.4. Preparation and analysis of soil samples

In the laboratory of the "Department of Ecology in Mangistau", samples were prepared for analysis with a laboratory spectrophotometer HACH DR-2400 (USA), according to the method [11] certified by the Kazakhstan Institute of Metrology. The gross content of heavy metals such as Cu, Pb, Cd, Zn, Ni, Cr⁶⁺, Co and arsenic (As) in soil samples from trial plots TP was determined.

2.5. Statistical processing of research results

Statistical processing was performed in the analytical software interface Statistica 10. The choice of the analysis method using the statistics of the Kruskal-Wallis criterion (Kruskal-Wallis ANOVA) was determined by a small number of research samples with different distribution laws. The Kruskal-Wallis criterion is used in studies to compare three or more samples and is based on ranks and not on averages.

2.6. Methods of geographic information systems (GIS)

GIS family programs (Google Maps, SAS Planet) were used to create a map-scheme of the study area. Editing the map-scheme was performed using Corel Draw and Paint graphics programs. In order to assess the degree of soil pollution, based on the results of analyzes, the concentration coefficient of the identified elements was calculated. The concentration coefficient $K_C$ of the chemical substance is calculated by the following formula 1.

$$K_C = \frac{C_i}{C_{back}}$$

Where $C_i$ – the actual content of the substance in the soil, mg/kg; $C_{back}$ – zonal background indicator of the substance, mg/kg.

When calculating the coefficient of concentration of chemical substances, their zonal background values are used. We used background values, which are soil indicators in the area of the natural reserve.

In order to obtain an objective assessment of the soil condition, the total pollution indicator was calculated using several formulas. The well-known indicator, which uses background concentrations of substances, and has the hygienically reasonable scale of soil pollution, is an indicator of the total soil pollution (TSP) or $Z_C$. Indicator of Y.E. Saet (TSP) or $Z_C$, in which the values less than 1 are not taken into account, is calculated by the formula 2 [12]:

$$Z_C = \frac{C}{C_{back}}$$
Where $K_C$ is the concentration coefficient of $i$ – chemical substance; $n$ – the number of substances to be determined with concentration $K_C$ more than one.

According to the results of calculations, the level of soil pollution is low with $Z_C$ less than 16, medium (moderately hazardous) with (16-32), high (dangerous) with (32-128) and extremely dangerous – If $Z_C$ is more than 128.

It should be noted that this indicator does not take into account the varying degree of toxicity of substances, which leads to incorrect results.

The indicator of TSP, taking into account the different toxicity of heavy metals [11-16] is calculated by the formula 3.

$$Z_{C_H} = \sum (K_{C1} \times K_{T1}) - (n - 1)$$

Where $K_{T1}$ is the coefficient of toxicity of $i$ – element.

In order for the scale of critical general indicators of Y.E. Saet to remain relevant for TSP using formula 3, for elements of the second hazard class $K_T = 1.0$ is used, of the third hazard class $K_T = 0.5$, of the first hazard class $K_T = 1.5$. The heavy metals Pb, Cd, Zn and Cr studied in the work belong to the first (highly dangerous) hazard class, Cu and Ni belong to the second moderately dangerous class [12].

Currently, to assess the soil condition [17,18], the indicator of total pollution is widely used, taking into account the average geometric coefficient of the concentration of heavy elements $Z_{C(r)}$, which is calculated by the formula 4.

$$Z_{C(r)} = n \times (K_{C1} \times K_{C2} \times K_{Cn})^{1 \over n} - (n - 1)$$

The formula of the complex indicator of total soil pollution, which takes into account the geometric mean value of the coefficient $K_C$, as well as the toxicity of heavy metals, $Z_{C(r)}$ [17], can be written as follows:

$$Z_{C_H(r)} = n \times [(K_{C1} \times K_{T1}) \times (K_{C2} \times K_{T2}) \times (K_{Cn} \times K_{Tn})]^{1 \over n} - (n - 1)$$

3. Results and Discussion
Field studies were performed on seven TPs, namely, on the six TPs described above and the seventh background TP-7, which is the RG-7 (background plot – BP). Background RG-7 values, according to soil indicators in Cape Peschanyi, on the border of the Karakiy-Karakol State Nature Reserve (Table 1), were used for calculation of the index of $Z_C$. The area is 137.5 thousand hectares; a nature reserve is located in the territory of the Karakiyansky region. TP-background with coordinates: N43°21'09,06'', E51°37'12,42 '', was laid at a distance of 23 km far from the contour of all studied TP. A total of 7 TPs were investigated, in different parts of Cape Peschanyi. The content of heavy metals and metalloid, as well as their background values of TP-7 (background) are presented in Table 1. The results of the calculated coefficients of concentration of HM and M are given in Table 2.

| Sampling depth, cm | Cu  | Pb  | Cd  | Zn  | Ni  | As  | Cr$^{6+}$ | Co  |
|-------------------|-----|-----|-----|-----|-----|-----|-----------|-----|
| TP-1. Region of the ferry complex Kuryk. Coordinates: N43°10'01,90'', E51°26'11,17'' |
| (0-5)             | 8.94| 9.3 | 0.975 | 13.06 | 3.013 | 21.35 | 0.117     | 3.15 |
| (5-20)            | 7.85| 10.4| 0.825 | 13.02 | 4.01 | 20.25 | 0.115     | 3.01 |
| TP-2. Orchard. Farm “Zhanbyschi”. Coordinates: N43°10'17,38'', E51°20'11,81'' |
| (0-5)             | 18.36| 10.05 | 0.14 | 12.14 | 9.065 | 12.2 | 0.429     | 8.2  |
| (5-20)            | 17.20| 10.01 | 0.17 | 11.9 | 9.063 | 12.3 | 0.408     | 7.8  |
| TP-3. The coastal area of Cape Peschanyi. Coordinates: N43°09'50,25'', E51°17'24,30'' |

Table 2. Content of heavy metals and metalloid, (mg/kg) in TP soils.
For the region, excess for arsenic is natural. For chromium, a high excess is fixed at observed within (3) and TP (2.4) on TP-6 (hollow). For cadmium, an excess was observed within (3.0) on TP-6, (1.2) on TP-1 and (1.53) on TP-3. There is no excess in samples for zinc and nickel. Excess for arsenic was detected in all TP samples, from (3.4) on TP-1, to (1.4) on TP-6. Its sources are herbicides and insecticides (chemicals against weeds and harmful insects, respectively) [6]. For the region, excess for arsenic is natural. For chromium, a high excess is fixed at TP-1 (2.4), TP-2 (8.5) and TP-5 (7.3). The main source of soil pollution with chromium is motor transport exhaust and tractor equipment. In these areas there is a large amount of land disturbed by the indiscriminate passage of transport. Identified Cr\textsuperscript{6+} is easily mobilized in alkaline soils. Presence of

Table 3. Concentration coefficient \(K_C\) of heavy metals and metalloid

| Sampling depth, cm | Cu (0-5) | Pb (0-5) | Cd (0-5) | Zn (0-5) | Ni (0-5) | As (0-5) | Cr\textsuperscript{6+} (0-5) | Co (0-5) |
|-------------------|----------|----------|----------|----------|----------|----------|-----------------|----------|
| TP-1. Region of the ferry complex Kuryk. Coordinates: N43°10'01,90", E51°26'11,17" |
| \(K_C\) (0-5)     | 0.87     | 0.79     | 1.3      | 0.66     | 0.18     | 3.48     | 2.48             | 0.76     |
| \(K_C\) (5-20)    | 0.76     | 0.8      | 1.1      | 0.71     | 0.24     | 3.31     | 2.44             | 0.73     |
| TP-2. Orchard. Farm Zhanbyrschi. Coordinates: N43°10'17,38", E51°20'11,81" |
| \(K_C\) (0-5)     | 1.8      | 0.85     | 0.18     | 0.62     | 0.55     | 2        | 9.12             | 2        |
| \(K_C\) (5-20)    | 1.6      | 0.8      | 0.22     | 0.61     | 0.55     | 2.01     | 8.68             | 1.9      |
| TP-3. The coastal area of Cape Peschanyi. Coordinates: N43°10'09,50", E51°17'24,30" |
| \(K_C\) (0-5)     | 0.79     | 0.7      | 1.6      | 0.74     | 0.25     | 0.8      | 0.65             | 0.98     |
| \(K_C\) (5-20)    | 0.91     | 0.7      | 1.46     | 0.71     | 0.31     | 0.94     | 0.57             | 0.96     |
| TP-4. Lighthouse on the Cape Peschanyi. Coordinates: N43°11'21,91", E51°17'06,66" |
| \(K_C\) (0-5)     | 2.1      | 0.81     | 0.9      | 0.65     | 0.37     | 2.5      | 0.87             | 0.97     |
| \(K_C\) (5-20)    | 2.09     | 0.79     | 0.93     | 0.66     | 0.37     | 2.5      | 0.59             | 0.85     |
| TP-5. Peasant economy Venera. Coordinates: N43°12'26,81", E51°20'15,57" |
| \(K_C\) (0-5)     | 0.89     | 0.85     | 0.57     | 0.68     | 0.31     | 1.8      | 9                | 2.4      |
| \(K_C\) (5-20)    | 0.98     | 0.81     | 0.34     | 0.72     | 0.55     | 1.77     | 6.95             | 2.19     |
| TP-6. Ashysor trench. Coordinates: N43°12'18,34", E51°26'05,27" |
| \(K_C\) (0-5)     | 0.9      | 1.3      | 3        | 0.75     | 0.5      | 1.5      | 0.25             | 0.63     |
| \(K_C\) (5-20)    | 0.96     | 1.25     | 2.97     | 0.77     | 0.49     | 1.46     | 0.29             | 0.75     |
| TP-7 (background). Background concentration of HM and M |
| \(K_C\) (0-5)     | 10.2     | 11.7     | 0.75     | 19.5     | 16.4     | 6.1      | 0.047            | 4.1      |

Analysis of the content of HM and arsenic in soils and their comparison with background values were performed for samples of all TP (Table 2). For copper, excess of the background value was observed in the TP-2 (1.7) and TP-4 (2.07) samples. Copper is transported over long distances with air and water, and can accumulate in plants.

For lead, a slight excess (1.2) was detected on TP-6 (hollow). For cadmium, an excess was observed within (3.0) on TP-6, (1.2) on TP-1 and (1.53) on TP-3. There is no excess in samples for zinc and nickel. Excess for arsenic was detected in all TP samples, from (3.4) on TP-1, to (1.4) on TP-6. Its sources are herbicides and insecticides (chemicals against weeds and harmful insects, respectively) [6]. For the region, excess for arsenic is natural. For chromium, a high excess is fixed at TP-1 (2.4), TP-2 (8.5) and TP-5 (7.3). The main source of soil pollution with chromium is motor transport exhaust and tractor equipment. In these areas there is a large amount of land disturbed by the indiscriminate passage of transport. Identified Cr\textsuperscript{6+} is easily mobilized in alkaline soils. Presence of
As a part of chlorophyll, gives leaves of plants green color. The excess of cobalt over the background value was found on TP-2 and TP-5 plots of the orchard and melon crops by 2.3 times, respectively. Sources of income are transport, fertilizers and pesticides. The total indicator of soil pollution was calculated using the formulas 2, 3, 4 and 5. Results of values of total pollution of soils (TSP) by the heavy metals HM and arsenic are shown in Figure 1.

Calculation using formula 2. When calculating $Z_{C}$, the values of $K_{C} > 1$ (Table 2) were taken into account (the values of the actual concentration of HM, exceeded the value of the background concentration by TP-Background). Results on the accumulation of HM in the soil are obtained.

Calculation using formula 3. It was made according to the indicator $Z_{CH}$, taking into account the degree of toxicity (danger) of the studied HM and As. At the same time, the value of the indicator $Z_{CH}$ with respect to $Z_{C}$ (at $K_{C} > 1$) increased for all TPs (Fig. 1). So, for TP-1 (ferry complex) increase by 66.5%, for TP-2 (orchard) by 43.4%, TP-3 (coastal area of Peschanyi Cape) by 50.9%, TP-4 (pharos) by 40.7%, TP-5 (Venera peasant farm) by 38.2%, TP-6 (Ashysor depression) by 53.5%. The range is from 38.2% (TP-5) to 66.5% (TP-1). The $Z_{CH}$ calculation gives the highest values as compared to others. This is due to the fact that an elevated content in soils was recorded for HM (lead, cadmium, chromium) and metalloid (arsenic), belonging to the first class of danger ($K_{T} = 1.5$).

Calculation using formula 4. The $Z_{C(r)}$ indicator is widely used to estimate multi-element pollution, as well as when calculating the average HM content in soils in non-CIS countries, for example, in the USA [18-20]. From Figure 1, it can be seen that the results of $Z_{C(r)}$ compared to $Z_{C}$ (with $K > 1$) decreased from 1.07% on TP-6 to 32% on TP-1 (excluding the negative value on TP-3). This result is obtained at dispersion between the values of the $K_{C}$ (Table 2) [17].

Calculation using formula 5. The results that were obtained in terms of the indicator Vodyanitsky [14], $Z_{CH(r)}$, have deviations from the indicator of Y.E. Sayet, $Z_{C}$ (with $K > 1$) from 42% on TP-4 to 60% on TP-2. The advantage of $Z_{CH(r)}$ is that HM toxicity is taken into account in the calculations, and errors are eliminated at high KC values due to consideration of the geometric average. So, according to the results of the TSP calculation, only in terms of $Z_{CH} = 16.5$, on TP-2 in the orchard area, the level of pollution is average (moderately dangerous).

As for the complex indicator, the lower value of $Z_{CH(r)}$ on TP-3 ($Z_{CH(r)} = 0.67$) and the highest on TP-2 ($Z_{CH(r)} = 6.95$) and TP-5 ($Z_{CH(r)} = 4.91$).

The calculation results show that the complex indicator of the total pollution of Yu.N. Vodyanitsky provides an opportunity to account for all parameters and obtain specific results. Exceeding the allowable value of the TSP, on a scale of Yu.E. Saet, according to calculations, is observed only at TP-2, $Z_{CH} = 16.5$, the category of pollution is moderately dangerous (Fig. 1).
Figure 1. Map of the study area (SAS Planet).

Statistical processing of research results. The results of the Table 2 show that the Kruskal-Wallis test is statistically significant for As metalloid, heavy metals Cr and Cd (first hazard class) and Cu, Co (second hazard class) (p < 0.05). Samples made by TP-1 (ferry complex) (61.0 and 57.0, respectively) and TP-2 (orchard) (56.0 and 87.0), as well as to the content of Co on TP-2 and TP-5 (51.0 and 57.0) and Cu on TP-4 (lighthouse) (51.0 and 53.0), Cd on TP-6 (hollow) (60.0 and 59.0) are characterized by the largest rank sums in relation to the content of As, Cr.

Figure 2. Indicators of TSP ($Z_C$) of soils by heavy metals and arsenic
Table 4. The average content of heavy metals (HM) and arsenic for layers 0-20 in trial plots of Cape Peschanyi

| Heavy metals | Mean ±SD | Kruskal-Wallis ANOVA |
|--------------|----------|----------------------|
|              | TP-1 (n = 2) | TP-2 (n = 2) | TP-3 (n = 2) | TP-4 (n = 2) | TP-5 (n = 2) | TP-6 (n = 2) | Average (n = 6) | p  |
| Cu           | 8.4±0.77  | 17.8±0.82 | 8.7±0.84 | 21.4±0.01 | 9.6±0.64 | 9.68±0.6 | 13.2±6.0 | 0.04 |
| Pb           | 9.85±0.77 | 10.0±0.03 | 8.07±0.2 | 9.42±0.13 | 9.8±0.3 | 14.5±0.4 | 9.4±0.84 | 0.57 |
| Cd           | 0.9±0.1  | 0.16±0.02 | 1.15±0.07 | 0.69±0.01 | 0.3±0.12 | 2.2±0.01 | 0.6±0.52 | 0.03 |
| Zn           | 13.04±0.0 | 12.02±0.1 | 14.2±0.4 | 12.8±0.09 | 14±0.8 | 15±0.3 | 13.2±0.9 | 0.83 |
| Ni           | 3.51±0.7 | 9.06±0.00 | 4.61±0.7 | 7.12±1.3 | 7.11±2.8 | 8.2±0.002 | 6.3±2.34 | 0.91 |
| As           | 20.8±0.7 | 12.2±0.07 | 5.32±0.6 | 15.3±0.03 | 10.9±0.1 | 9.04±0.16 | 13±5.7 | 0.02 |
| Cr<sup>6+</sup> | 0.12±0.00 | 0.42±0.01 | 0.03±0.00 | 0.03±0.00 | 0.4±0.06 | 0.01±0.00 | 0.2±0.19 | 0.01 |
| Co           | 3.08±0.09 | 8±0.2 | 4.01±0.05 | 3.75±0.3 | 9.42±0.6 | 2.85±0.3 | 5.65±2.8 | 0.04 |

Table 4 shows the results of calculating the statistical parameters of the span diagram for the concentrations of HM and M for the 0-20 cm layer, obtained when using the STATISTICA 10 package.

Table 5. The main descriptive indicators of the heavy metals span chart

| HM and M | M | Median | Min | Max | R | σ | D | ±SD |
|----------|---|--------|-----|-----|---|---|---|-----|
| Cu       | 13.10 | 9.655  | 7.85 | 21.42 | 13.57 | 0.774 | 0.074 | ± 0.730 |
| Pb       | 9.36  | 9.775  | 8.23 | 10.23 | 1.99  | 0.751 | 0.557 | ± 0.871 |
| Cd       | 0.91  | 0.762  | 0.14 | 2.25  | 2.11  | 0.789 | 0.623 | ± 0.174 |
| Zn       | 13.22 | 13.250 | 11.91 | 15.11 | 3.21  | 0.784 | 0.614 | ± 0.031 |
| Ni       | 6.41  | 7.124  | 3.01 | 9.12  | 6.11  | 2.294 | 5.263 | ± 0.618 |
| As       | 19.51 | 11.950 | 4.89 | 21.35 | 16.46 | 6.610 | 23.73 | ± 0.714 |
| Cr<sup>6+</sup> | 0.19 | 0.078  | 0.01 | 0.43  | 0.42  | 0.187 | 0.034 | ± 0.001 |
| Co       | 5.52  | 3.975  | 2.60 | 9.84  | 7.24  | 2.683 | 7.117 | ± 0.09 |

Explanation: HM and M – heavy metals and metalloid, M – expectation, Median – median, Min, Max – maximum, minimum of span values, R – span of variation, σ – standard deviation, D – sample variance, ± SD – standard medium error.
According to Table 4 and Figure 2, the span of variation of less than 1 is observed only for hexavalent chromium Cr\textsuperscript{6+}, which is explained by the fact that chromium is easily mobilized in the soils of the study area, which are alkaline. The maximum of span for copper Cu is justified by its transfer over long distances due to the transfer by wind and also with air and water.

The obtained samples of metalloid and heavy metals (As, Cr, Cd, Cu, Co) make the maximum contribution according to their content in the soils of the studied TP.

The TP-6 near the Ashysor Basin is characterized by the lowest rank sums for As and Cr (28.3; 21.7). The soils of the trial plots differ significantly from each other in the content of As, Cr, Cd, Cu, and Co.

For the first time, an assessment of soil contamination with heavy metals, subject to anthropogenic influence, was performed in the area of the Kuryk ferry complex on the Sandy Cape. The area is distinguished not only by the greatest depth of the sea, the suitability of the soils of the coastal zone for the development of agriculture, as well as its proximity to the territory of the national reserve, which in General gives it a reference value.

It is established that recently, the attention of researchers has been directed to the assessment of marine water pollution by oil-containing films accumulating in the coastal and coastal strip [21-28]. Methods and technologies developed by scientists began to be applied in practice [29-33]. For example, in the Baltic sea, HELCOM (Helsinki Commission) monitors and annually publishes summary maps of the distribution of oil spills, but only those that were detected by aerial photography, which is only a few dozen per year [30]. Significantly more oil spills are detected using remote sensing data, such as the Clean Sea Net project, implemented by the European Maritime Safety Agency (EMSA), which publishes summary maps of ship spills. These maps are not drawn for the Eastern parts of the Black and Baltic seas, nor are they drawn for the Caspian sea as a whole. None of the Caspian countries (with the exception of Russia) conducts comprehensive satellite monitoring of the Caspian sea. In this regard, it should be noted that complex mapping of pollution, distribution of suspended matter and water blooming, as well as pollution of coastal zones of the Caspian sea in the event of run-up phenomena is carried out only by the authors of the article.

The analysis of actual problems of the Caspian sea, and the analysis of previously implemented scientific and applied research makes it possible to justify that the study of the Caspian coastal zone of the Kazakh sector is a necessary condition for further rational use of natural resources of coastal zones while maintaining a safe level of vital environmental parameters.
4. Conclusion

Studies have established the content of heavy metals in the soils of the coastal zone of Cape Peschanoy in the area of the ferry complex "Kuryk". The presence of arsenic in all samples of the studied trial plots, with insignificant exceedances of the background value, is of a natural origin. Significant excess of chromium and arsenic was recorded in soil samples TP-1 (ferry complex), TP-2 (vegetable garden) and TP-3 (Venera farm) over background indicators (relative to TP background).

TP-6 (hollow) soils are polluted with cadmium. Basically, significant exceedances of the background value are single, and depend on the local pollution characteristics at the sampling sites.

Based on the results of analyzes of samples on the content of the HM and arsenic in soils, the calculation of the total pollution index was carried out, which allowed to reveal the assessment of the degree of pollution of the studied TP.

Only the value of $K_C > 1$ was taken into account. Thus, when calculating $Z_C$ at $K_C > 1$, on TP-1 $K_C$ was not taken into account for Cu, Pb, Zn, Ni, and Co. On TP-2 $K_C$ for Pb, Cd, Zn, Ni was not taken into account. On TP-4 $K_C$ was considered for copper and arsenic. On TP-5 $K_C$ was taken into account only for As, $Cr^{6+}$ and Co. On TP-6 $K_C$ was considered for Pb, Cd and As.

At the trial plot TP-3 (orchard), the coefficients of the $K_C$ are not taken into account for Cu, Pb, Zn, Ni, As, $Cr^{6+}$ and Co. As a result, for TP-3, in the area of apple orchard and melon crops, the smallest total indicator of soil pollution was obtained, including those with negative values of $Z_C(r)$.

Thus, on other TPs, soil pollution with HM was not detected, their content is characterized by background values, that is, data on the soils of the Karakia-Karakol state nature reserve.

In order to increase agricultural productivity and increase land productivity, it is necessary to have an information base on soil resources. The expected socio-economic effect of applying the scientific results obtained for the study of the Caspian coastal zone in the area of the multi-modal port of Kuryk will provide an information base on the components of the environment in the research area. The results of the monitoring of the fertile soil layer allowed us to solve the problem of the “Zhanbyrshy” farm by identifying the causes of changes in the breed and variety composition of perennial plantations of apple, grapes, apricots, etc.

This leads to the conclusion that the obtained scientific data on the study of the ecological sensitivity of coastal zone ecosystems can be used for decision-making in the field of environmental quality management and ensuring environmental safety of the Caspian sea coastal zone in the areas where a man-made object is located.

References

[1] Syrlybekkyzy S, Kenzhetaev G Zh, Suleimenova N Sh, Permyakov V N and Nurbayeva F K 2014 *Or j of chem* **30** 1631
[2] Alekseenko V A, Buzmakov S A and Panin M S 2013 *Per St Un*
[3] Koibakova S, Kenzhetaev G, Syrlybekkyzy S, Janaliyeva N, Tazhanova L and Altybayeva Zh 2018 *Ec. Env and Cons* **24** 1451
[4] Semendyayev N V, Marmulev A N and Dobrotvorskaya N I 2015 *Meth of stud soil and soil cov: stud guid* (Novosibirsk)
[5] Mandzhieva S, Mashtykova L, Minkina T, Motuzova G and Chaplygin V 2016 *Intern Multid Sc GeoConfer Surv Geol and Min Ec Man, SGEM* **2** 477
[6] Vodyanitskii Yu N, Plekhanova I O, Prokopenovich E V and Savichev A T 2011 *Eur S Sci.* **44** (2) 217-226
[7] Kashulina G M 2018 *Eur Soil Sci* **51** (4) 467-478
[8] Karpova E A and Mineev V G 2015 *Heav Met in Agroec* (Moscow)
[9] Xiao R, Guo D, Ali A, Li R and Zhang Z 2019 *Chin Envir Poll* **248** 349-357
[10] Yudina E V 2017 *Samara Sci. Bull* **6** (3) 56-63
[11] The method of measurement of the Kazakhstan Institute of Metrology No. MVI 20658-1917-NPO LLP 001-2018. Water quality and soil extracts
[12] Okolelova A A, Kozhevnikova V P, Kunitsyna I A and Tarasov A P 2014 Fund Res 3 296.
[13] Andreev D N, Gatina E L and Dzyuba E A 2016 New of the Sam Sc Cen of the Rus Acad of Sc 18 283
[14] Vodyanitsky Y N 2013 Soil Sc 7 872
[15] Saet Y E and Revich B A 1990 Nedra
[16] Vodyanitsky Y N 2010 Soil Sc 10 1276
[17] Alekseev I I, Abakumov E V, Shamilishvili G A and Lodygin E D 2016 Hyg and san 95 818
[18] Cambier P, Michaud A, Paradelo R, Germain M, Mercier V, Guerin-Lebourg A, Revallier A and Houot S 2019 Sc of the Tot Env 651 2961
[19] Zglobicki W, Telecka M, Skupinski S, Pasierbinska A and Koziel M 2018 Envir Ear Sc 77 774
[20] Cipullo S, Snapir B, Tardif S, Campo P, Prpich G and Coulon F 2018 Sc of the Tot Envir 645 662
[21] Pocora A, Purcarea A A, Nicolae F and Cotorcea A 2018 IOP Conf Ser: Earth and Envir Sc 172(1) 012012
[22] Carpenter A 2019 Hydrobiologia 845 109–127
[23] Prasad Dr R G and Anuprakash Mr M V V S 2016 IOSR J of Env Sc, Toxic and F Tech 2319-2402 01-08
[24] Crocker R I, Matthews D K, Emery W J and Baldwin D G 2007 Geosc and Rem Sens 45(2) 435–447
[25] Lu J 2003 Int J Rem Sens 24(15) 3013–3032
[26] Topouzelis K, Bernardini A, Ferraro G, Meier-Roux S and Tarchi D 2006 Fres Envr Bull 15(9A) 1009–1014
[27] Redondo J M, Platonov A and Tarquis A 2008 Det and pred from SAR mult anal
[28] Shi L, Ivanov A Yu, He M-X and Zhao C 2008 Int J Rem Sens 29(21) 6315–6329
[29] Lavrova O Yu, Mityagina M I and Sabinin K.D 2011 Rep of the Acad of Sc 436(3) 407–411
[30] Kostianoy A G and Lavrova O Yu 2014 Oil pollution in the Baltic Sea 27 268
[31] Jorgensen K S, Kreutzer A, Lehtonen K K, Phuong-Dang N and Wang F 2019 Environ Sc Eur 31(1) 44
[32] Gaulier C, Zhou C, Guo W, Baeyens W and Gao Y 2019 Sc of the Tot Env 692 701-712
[33] Baniamam M, Moradi A M, Bakhtiar A R, Fatemi M R and Khanghah K E 2019 Ind J of Geo-Mar Sc 48(5) 765-771