LITHOLOGICAL FEATURES AND TITANIUM-CONTAINING MINERALS IN BOTTOM SEDIMENTS OF SMALL RIVERS OF SOUTHERN UKRAINE

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Abstract. This paper provides a lithological description for the bottom sediments of small rivers from southern Ukraine. This research is focused on the first-order small rivers of the Azov Sea region: Obytichna, Solona, Mokra Bilosaraika, and Komyshuvatka rivers. Grain size compound, bulk density, and specific salt content were measured. According to the Folk diagram, the bottom fluvial sediments vary from sandy-gravel to gravelly-sand. All the mentioned parameters are described through comparative analysis of samples from different rivers. The results of mineralogical analysis showed the presence of different pollutants in the sediments. Pollutants are represented by metal spheres (magnetic and non-magnetic), metal flakes of various degrees of oxidation, wires, plastic particles, and technogenic glass. The titanium-containing minerals found in riverine samples from the northern Azov region include ilmenite, rutile, titanite and leucoxene. All these minerals are present only in the Obytichna River, yet ilmenite is present in the sediments of all studied rivers. The highest amount of ilmenite is in the sediments of the Obytichna River – up to 3042 grams/ton, though this amount is too low for economically purposes.

Key words: bottom sediments, Southern Ukraine, Sea of Azov, minerals, grain size distribution

1. INTRODUCTION

Modern riverine sediments are an extremely informative component of the geological framework. Comprehensive studies of this component give opportunities to describe the process of sedimentogenesis, changes in the hydrodynamic characteristics of reservoirs and watercourses, and the pollution grade defined by the presence of fine-grained anthropogenic particles.

In terms of structural, chemical and mineral composition, modern sediments differ noticeably from sedimentary rocks. They are characterized by a significant content of components, usually absent in old sedimentary rocks: unaltered remains of plants, insects, technogenic particles, etc. Most of them cannot overcome the barrier of diagenesis and, usually are not included into the composition of sedimentary rocks. At the same time, the abovementioned formations reveal information that is important for describing the conditions of modern sedimentogenesis (climate change, geomorphology, anthropogenic load). Furthermore, using the same knowledge the ecological state of the environment can be determined (Cutroneo *et al.*, 2020).

Fluvial bottom sediments are a product of the deposition environment and their chemical composition reflects several patterns of long periods of continued sedimentation. Modern rivers discharge a great amount of pollution into the Ocean. Detailed lithological description of river sediments can be applied in different fields. For example, mineral compound offers information of potential economic value and grain size distribution is important for choosing the way of mineral extraction. The presence of anthropogenic particles can be used in ecological studies regarding the ecosystem characterization, searching pollution sources or studying the impact of these particles on the environment. Comparative analysis of all lithological features is a subject of theoretical geology and sedimentology.

The global titanium market size was estimated at USD 2.44 billion in 2023 and is projected to grow at a Compound Annual Growth Rate (CAGR) of 6.2% from 2024 to 2030. The increasing demand for titanium is primarily driven by its exceptional properties including high strength-to-weight ratio, corrosion resistance, and biocompatibility, which make it indispensable in aerospace, automotive, medical, and industrial applications. The global growth of the aerospace and defense expenditures, coupled with the rising demand for lightweight and durable materials in automotive manufacturing, are considered the key drivers propelling the market forward. Additionally, advancements in titanium production technologies and expanding applications in emerging industries such as renewable energy and consumer electronics further bolster its demand (Grand View Research, 2023). Therefore, the search for additional sources of raw titanium materials is highly relevant.

According to geological and mineralogical zoning of Ukraine, the studied area represents a part of the placer zone located in the Ukrainian subprovince of the East European Placer Province (Atlas, 2001, Komiliev *et al.*, 2020). Since the late 1950s, the Ukrainian titanium ore province has been known, which is spatially contained within the contours of the development of Precambrian rocks of the southwest shield of the East European Craton (also known as the Ukrainian Shield or the Ukrainian Crystalline Massif) and its weathering crust. Placer deposits contain tens of kilograms of ilmenite per cubic meter (Mykhailov *et al.*, 2007).

2. MATERIAL AND METODOLOGY

2.1. Study area and sampling

In this article, we described the bottom sediments of several small rivers from the south-eastern Ukraine. The category „small river" includes rivers with a catchment area of up to 2,000 square kilometres according to the Ukraine Water Code (Database «Legislation of Ukraine», 1995).

The Obytichna, Solona, Mokra Bilosaraika, and Komyshuvatka rivers are considered the first-order type due to their discharge directly into the sea (Fig. 1, Table 1). These rivers were sampled at the river mouth in August 2021 (Mokra Bilosaraika and Komyshuvatka rivers) and in august 2018 (Obytichna River). The samples from the Solona River were collected from the river mouth and from the middle stream in august 2018.

Fifteen samples were studied as follows: five samples each from the Solona and Obytichna rivers, three samples from the Mokra Bilosaraika River and two samples from the Komyshuvatka River.

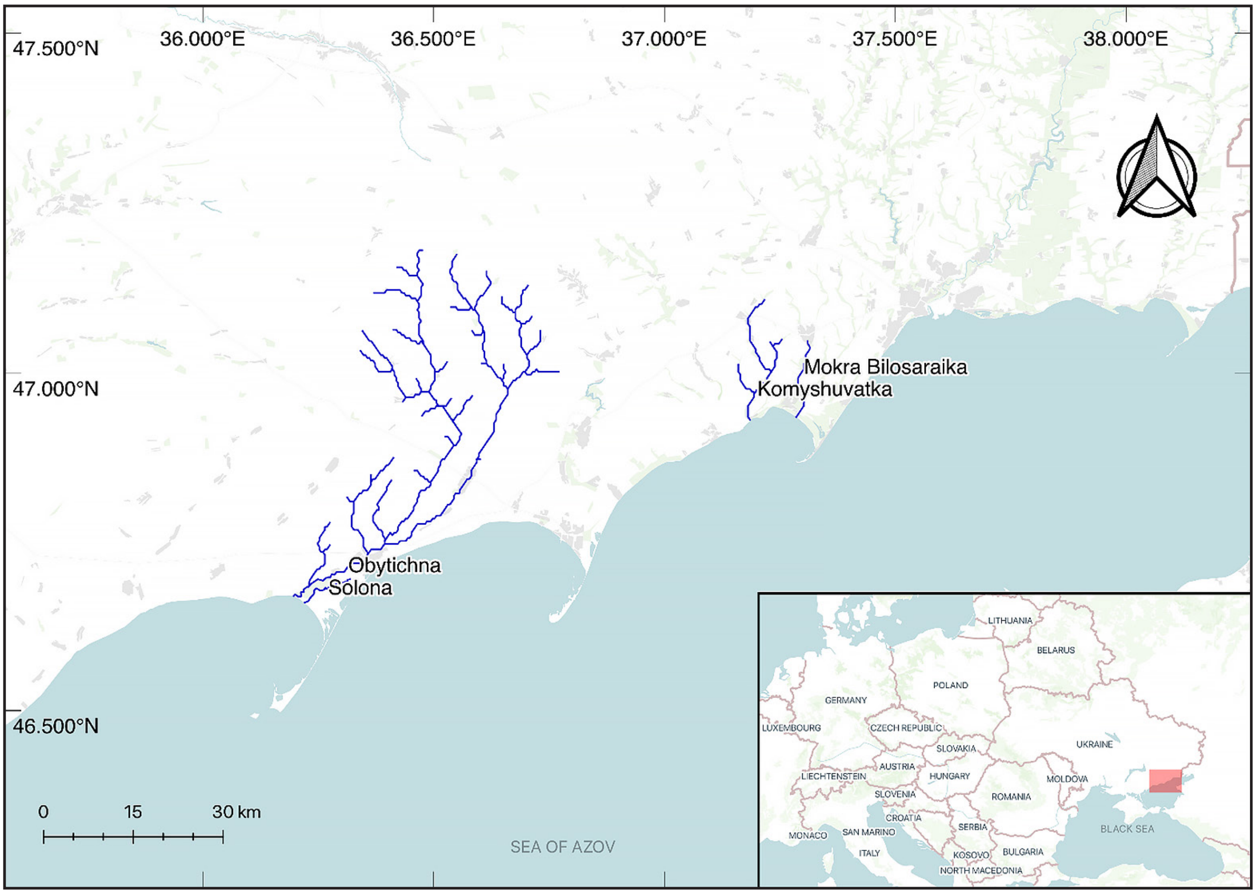

Fig. 1. Geographical location of the studied rivers, south-eastern Ukraine.

Table 1. Parameters of the studied rivers

River name	Length, km	Drain basin area, km^2
Obytichna	96	1437
Solona	18	22.6
Mokra Bilosaraika	14	49.8
Komyshuvatka	30	187

The bottom sediments of the Obytichna are represented by gray mud with a high amount of broken shells, detritus – a mixture of crushed remains of decomposing animals and plants, and fragments of sedimentary rocks consisting of skeletons of invertebrate animals and bones of vertebrates (Lanovenko, 2013) – and a combination of blue and brown clay. Samples of the Solona are represented by dark gray mud with high amount of algae. The Komyshuvatka sediments are represented by gray sand with detritus. The material from the Mokra Bilosaraika River is represented by gray mud with broken shells and algae.

2.2. Grain size compound

The grain size distribution was calculated by the sieve method (DSTU B V.2.1-19:2009). Twelve classes were isolated after sieving: +10 mm; -10+5 mm; -5+3 mm; -3+2 mm; -2+1 mm; -1+0.45 mm; -0.45+0.315 mm; -0.315+0.25 mm; -0.25+0.1 mm; -0.1+0.063 mm; -0.063+0.04 and -0.04 mm. The results obtained from the sieving were grouped according to the grain size scale (MAREANO, 2023). The Folk classification scheme (Folk, 1954) was chosen for further granulometric analysis. It groups grains into mud, sand and gravel, on the basis of their diameter with the boundary between mud and sand at 0.063 mm and the boundary between sand and gravel at 2 mm. The relative proportion of the grains in the three categories is further used to describe the sediment and is displayed in a diagram commonly referred as the "Folk triangle" (Long, 2006).

2.3. Bulk density

Determination of the bottom sediments bulk density was carried out by the quantitative hydrostatic method (Bahrii, 2000). To obtain statistically significant results, five parallel experiments were conducted. If the standard deviation was greater than 0.2 g/cm^3, a repeated series of five samples was carried out (up to a confidence level of 95%, $\sigma = \pm 0.05$).

2.4. Specific salt content

The content of water-soluble salts in bottom sediments simultaneously reflects several characteristics:

- sorption capacity, which depends on the granulometric composition;
- correlation with the salt content of the water body from which the sediment was taken;
- the nature of the pollution of the watercourse and the catchment area.

The high amount of water-soluble salts present in riverine sediments has a significant impact on their physicochemical properties. This impact can be reflected in changes in plasticity, moisture capacity, compactness ability, etc. The degree of sediment salinity is determined by the total content of water-soluble salts in a given sample, or in a given layer, and it is expressed as a percentage of the mass of a dry sample. The total specific salt content in the studied material was determined by the adapted method (Byriukov, 1975). This method consists in determining the dry sediment in an aqueous extract, which is a solution of salts contained in the samples. This indicator is measured in percentage per 100 grams of dry material.

2.5. Mineralogical analysis

The steps for the mineralogical analysis used in this research are:

- Mechanical separation of the samples into fractions according to the differences of the physical properties of the minerals. The preparation of samples for mineralogical analysis was carried out in accordance with the method of slag analysis with custom additions and improvements (Ivanchenko *et al.*, 2021).
- Stereomicroscope was used for mineral characterisation by external features. For a more detailed definition several unusual mineral grains were studied at the electron microscope and microprobe analysis. At this stage, photographs of the material under study were taken using an optical microscope.
- Determination of the quantitative amount of minerals in fractions and in the bulk sample. Results are presented in volume percentages, mass percentages and grams per ton (g/T).
- Processing the acquired data and analysing it by using MS Excel and Matplotlib (Hunter, 2007) along Python programming.

3. RESULTS AND DISCUSSIONS

3.1. Grain size description

The results of sieving procedure were grouped into three components (Fig. 2). The granulometric compound of these bottom sediments is characterized by a low content of the mud component. The percentage of mud does not exceed 2%. Only in the samples collected from the Solona River, the content of mud varies between 4 and 10%.

Sand is the dominant fraction, as shown by the grain size distribution of all bottom sediments. The content of sand fraction found in all samples range from 50% to 90%. The highest percentage of gravel has been identified in sediments from the Mokra Bilosaraika River. The proportion of this fraction and sand is approximately equal.

According to the Folk classification scheme (Fig. 3), all samples of the Mokra Bilosaraika River are sandy-gravel. The Komyshuvatka sediments are gravelly-sand. The Obytichna samples vary from sandy-gravel to gravelly-sand. The Solona material are mainly gravelly-sand, yet there are differences that range from sand and gravelly-muddy-sand.

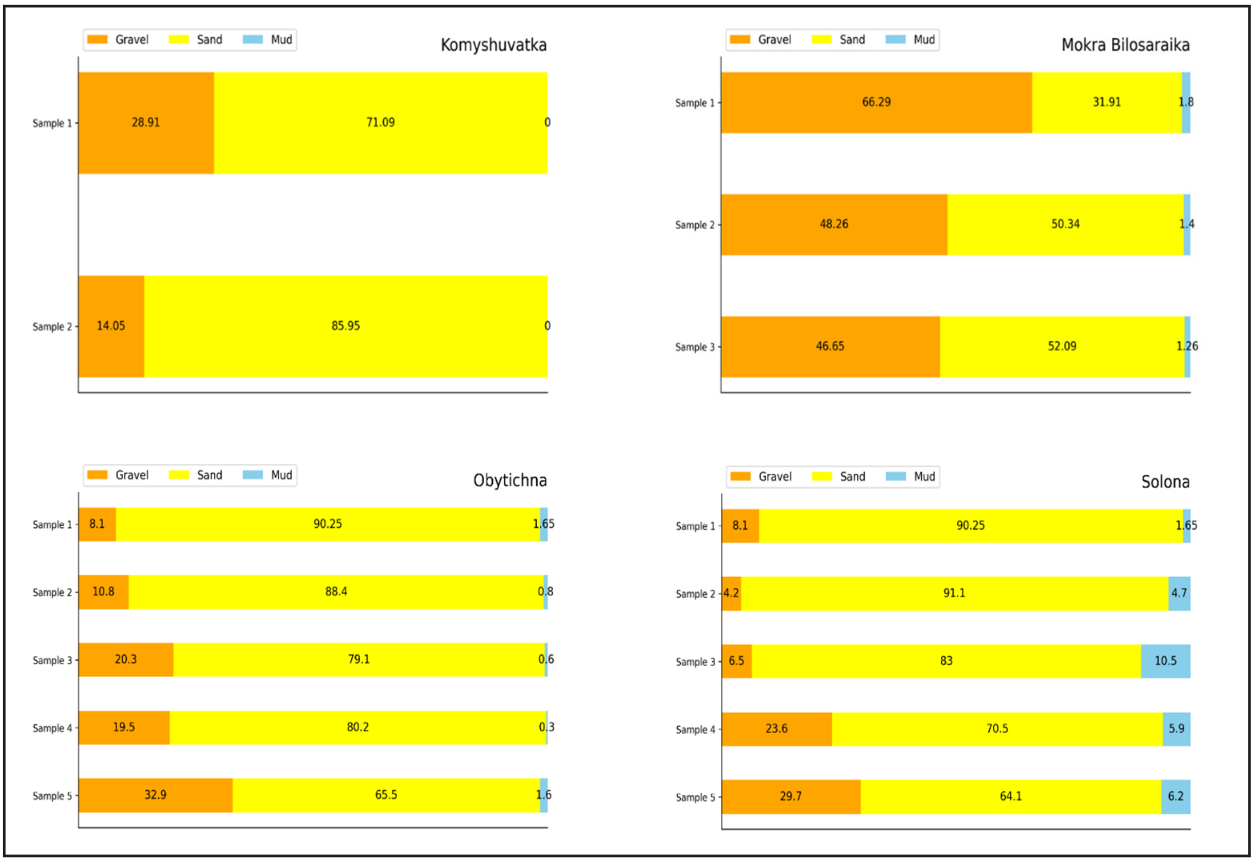

Fig. 2. Granulometric compound for each river.

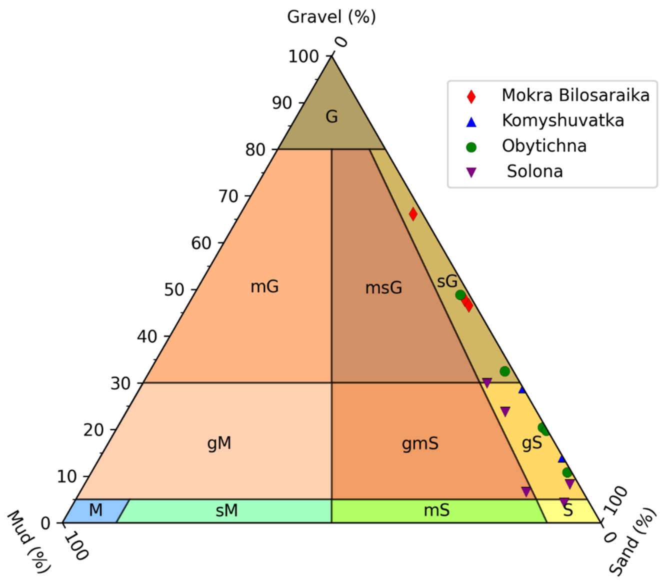

Fig. 3. Sample characterization using Folk's triagram after Folk, 1954 and Long, 2006.

3.2. Bulk density

The bulk density indicator is relatively constant in the samples from all rivers and is typical for such sediments.

The average values of bulk density [g/cubic centimetre (cc)] for the rivers are: Mokra Bilosaraika - 2.46 g/cc, Komyshuvatka - 2.45 g/cc, Obytichna - 2.43 g/cc, and Solona – 2.21 g/cc. The largest range of values is from 1.85 g/cc to 2.47 g/cc in the samples from the Solona River. In other samples, this indicator fluctuates within 2.28-2.6 g/cc.

3.3. Specific salt content

The value of the specific salt content varies considerably. These differences are explained by the fact that the bottom sediments are sampled in the estuaries (transitional zones). The content of water-soluble salts reflects the sorption capacity of the sediments, which in turn correlates with the granulometric composition that is dominated by sand. This type of sediment is relatively well washed by sea waves and contains lower amounts of salts. The average percentages (%/100g of sediment) of the specific salts content by rivers are: Mokra Bilosaraika - 0.34%/100g, Komyshuvatka - 0.046%/100g, Obytychna - 1.99%/100g, Solona – 3.53%/100g.

The bottom sediments of the Komyshuvatka River are the least saturated in salts (the indicator does not exceed 0.07%/100g). The highest average value of the specific salt content of the Obytychna River is explained by the typical marine sediments saturated in salts. The higher values of the Solona River are caused by the fact that samples were collected from the middle stream, which contain gypsum and potassium salts in the mineral composition. In addition, the samples from this river have a higher percentage of mud compared to bottom sediments from other rivers.

3.4. Mineralogical analysis

The mineralogical composition of the bottom sediments is similar for all studied rivers. The mineral composition of the light fraction is mainly represented by quartz and organogenic calcite, both in various ratios. The only exception is the samples of the Solona River, collected from the middle stream, where the light fractions contain high amounts of gypsum, halite and other salts.

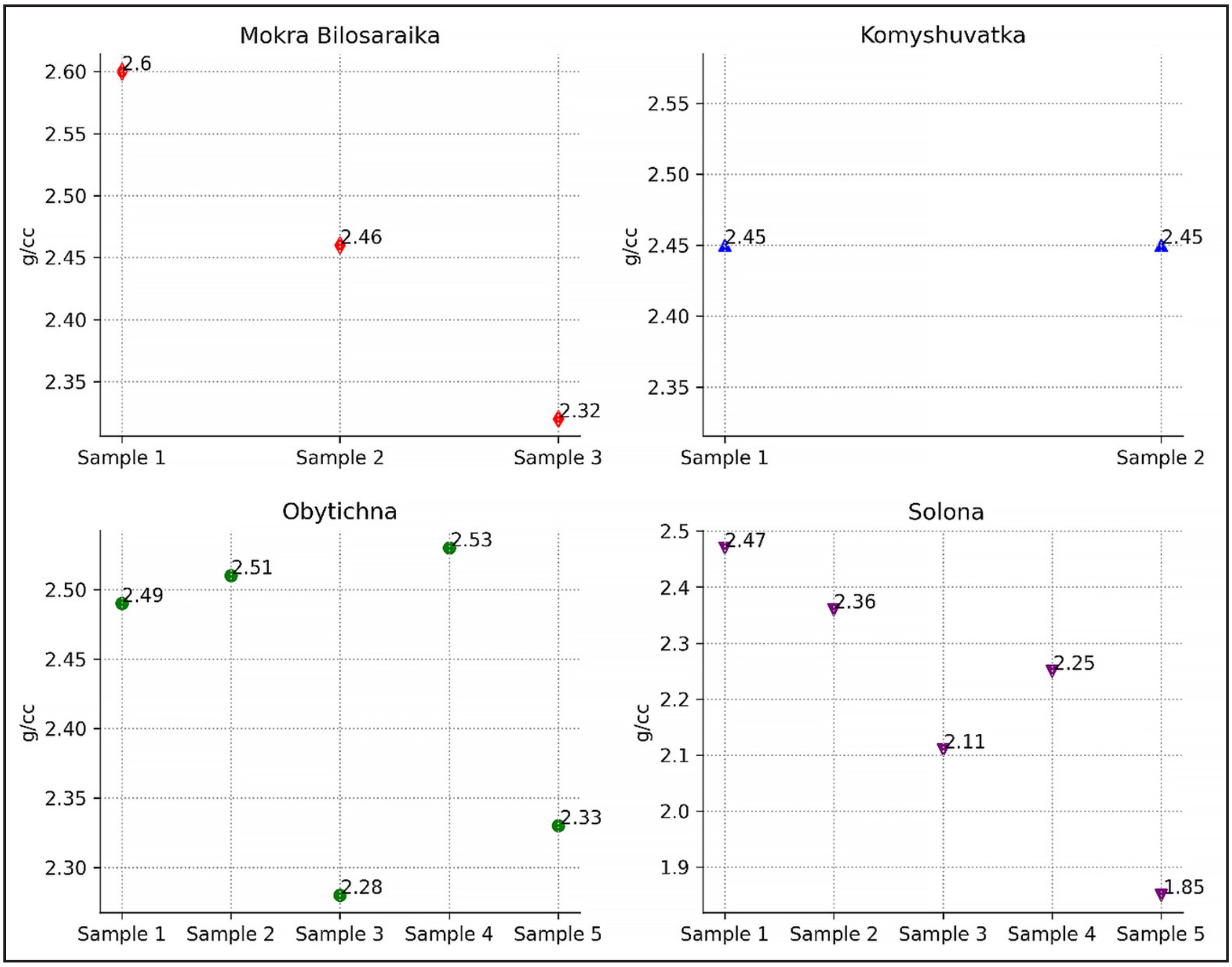

Fig. 4. Bulk density in the samples collected from studied rivers.

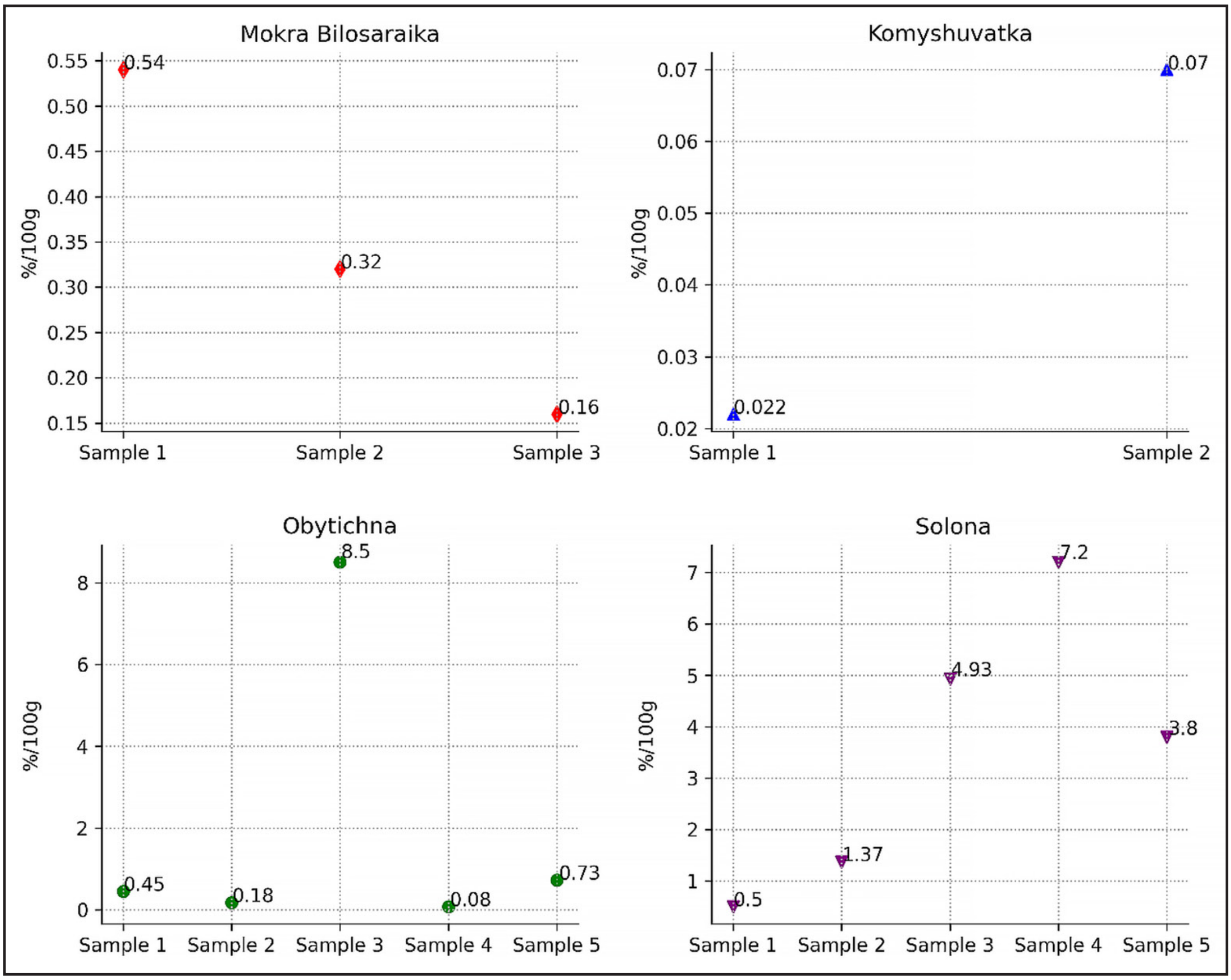

Fig. 5. Specific salt content in the analysed samples, grouped by rivers.

In the samples from the Obytichna and the Mokra Bilosaraika rivers, organogenic calcite prevails with mass percentage of 58 - 70%, while the mass percentage of quartz range between 23 and 37%. In the samples of the Komyshuvatka and the Solona rivers, quartz granules are dominant. The mass percentage of quartz for the Komyshuvatka River is 75-80%, while the organogenic calcite percentage range between 15 and 18%. In the bottom sediments of the Solona River, the mass percentage of quartz varies within 52 and 77%, organogenic calcite range between 5 and 36%, and gypsum varies between 18 and 43%.

Light mineral fractions are represented by quartz, organogenic calcite with minor admixtures of plant and insect remains, sometimes these being carbonized.

The main amount of quartz is angular and slightly rolled grains, it is mostly transparent, yet both milky white or cloudy grains are also found, last type having suffered minor damage on their surface. The grain size of quartz grains varies considerably (Fig. 6a). Organogenic calcite is represented by fragments of mollusc shells, mostly with a rolled to a spherical morphology, ranging between 0.1 and 0.4 mm in size and are light brown or purple coloured.

The heavy fraction is represented by granules of magnetite (usually in small quantities), arfedsonite (amphibole), ilmenite, almandine (garnet) and biotite, all present in all samples. Sillimanite, rutile, leucoxene, goethite, tourmaline, epidote, and titanite are present just in several samples.

Arfvedsonite is represented by crystal fragments dark green coloured, observed in thin sections, having an aquamarine tint. The grains habitus varies from triangular with sharp boundaries to flatten rectangular, with signs of a prismatic habitus, and less often with elongated shapes. The grain sizes range from 0.06 mm to 0.2 mm (Fig. 6b).

It is worth noting that all samples contain technogenic particles. Usually, these are represented by metal spherules (magnetic and non-magnetic), metal flakes of various degrees of oxidation, elongated shaped particles (metal and nonmetal fibres), plastic particles and technogenic glass (Fig. 7).

The titanium-containing minerals were found in all samples from small rivers of the northern Azov region. They are represented by ilmenite, rutile, titanite, and leucoxene (Fig. 8). All these minerals are present only in the bottom sediments of the Obytichna River (table 2).

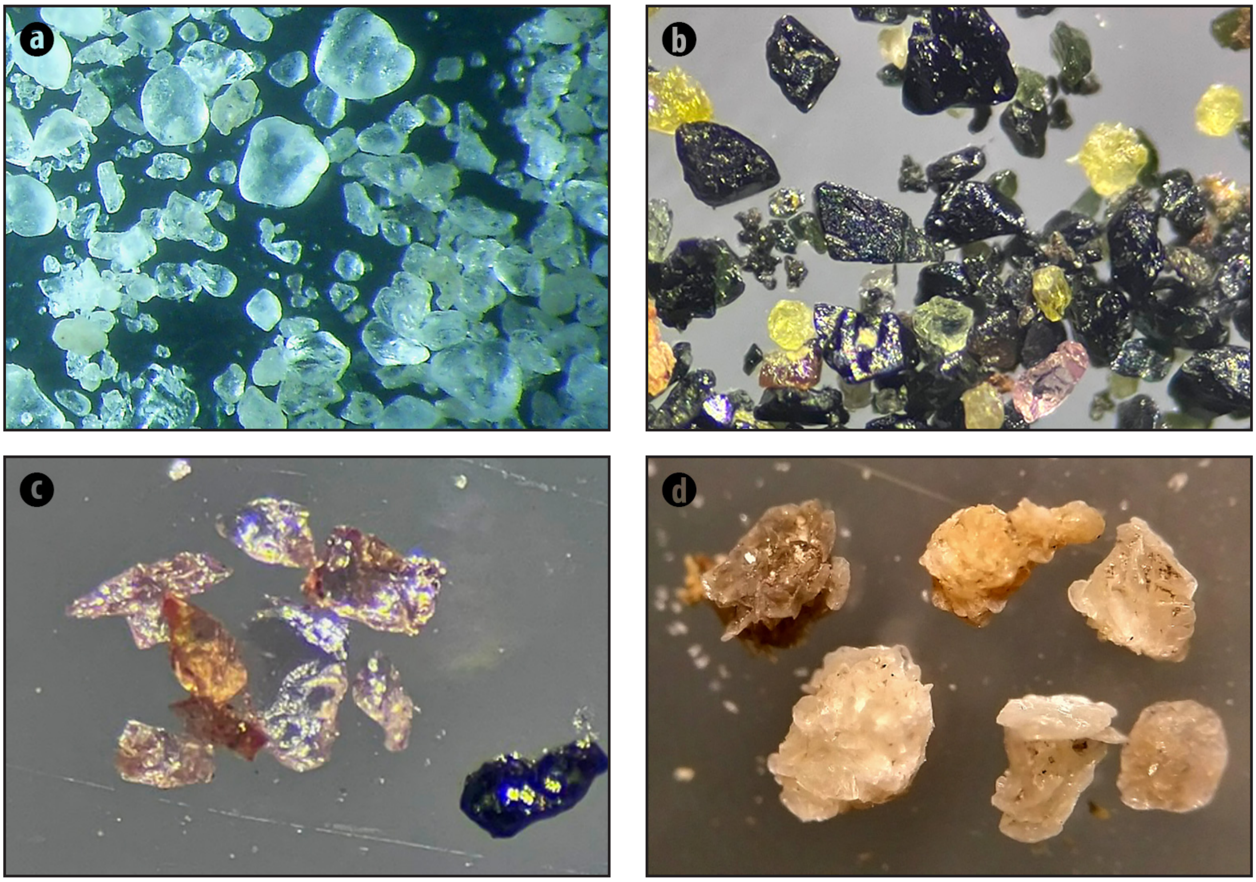

Fig. 6. The most identified mineral grains in samples: (**a**) quartz, grain sizes of 0.08 to 0.8 mm; (**b**) arfvedsonite (amphibole), grain sizes of 0.06 to 0.2 mm; (**c**) almandine (garnet), grain sizes of 0.32 to 0.44 mm; (**d**) aggregates of gypsum, sizes of 0.6 to 1.4 mm.

Table 2. Amount of titanium-containing minerals in bottom sediments compound, gram per ton

River	Sample	Ilmenite	Rutile	Titanite	Leucoxene
Mokra Bilosaraika	1	43.3	0	0	0
	2	134.7	0	0	0
	3	51.4	0	0	0
Komyshuvatka	1	75.6	0	0	0
	2	329.9	0	67.5	<0.1
Obytichna	1	252.3	3.1	7.9	63.1
	2	2084.6	<0.1	99.4	231.8
	3	3042.1	15.9	1.9	455.5
	4	<0.1	0.1	<0.1	0.1
	5	15.9	1.9	<0.1	5.5
Solona	1	852.7	1.5	0	44.6
	2	<0.1	0	0	0
	3	0.1	0	0	0
	4	0.1	0	0	0
	5	0	0	0	0

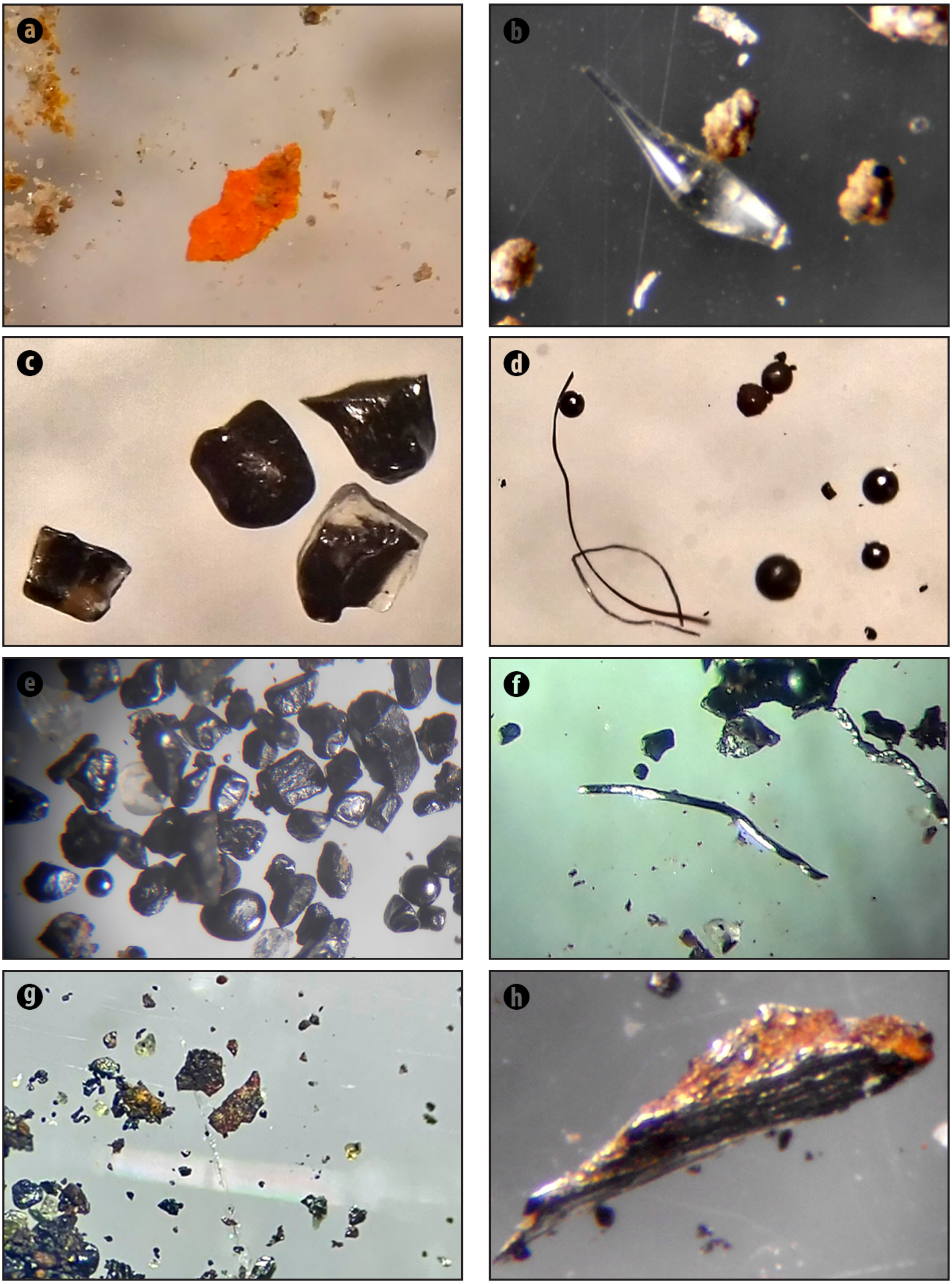

Fig. 7. Technogenic components in samples: (**a**) plastic particle, size 0.76 mm; (**b**) gran slag, 0.68 mm; (**c**) bitumen, 0.8 mm; (**d**) magnetic metal spherules and wires; (**e**) magnetic metal spherules among minerals of electromagnetic fraction; (**f**) metal wire, 0.7 mm; (**g**) metal flakes, 0.38 – 0.44 mm; (**h**) oxidised metal piece, 1.4 mm.

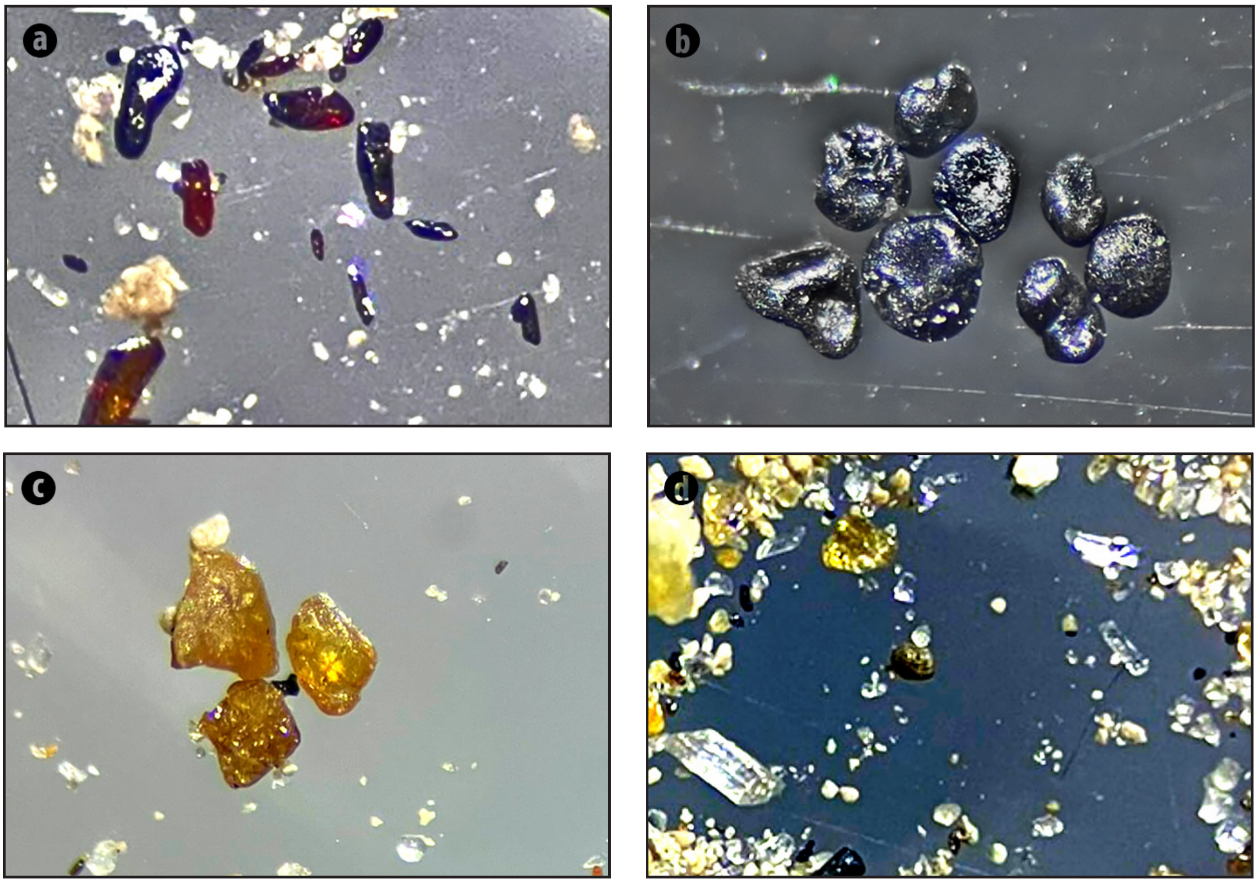

Fig. 8. Titanium-containing minerals: (**a**) rutile, grain sizes of 0.08-0.28 mm; (**b**) ilmenite, grain sizes of 0.1-0.5 mm; (**c**) titanite, grain sizes of 0.28-0.36 mm; (**d**) leucoxene, grain size of 0.16 mm.

Rutile, titanite and leucoxene appear episodically in the studied samples. Ilmenite is present in all samples collected from the river mouths. Ilmenite grains have a rolled morphology and smooth surfaces, ranging 0.1 to 0.5 mm in size. Ilmenite amounts vary depending on the sample location (river). The highest amount of ilmenite is found in the bottom sediments of the Obytichna River, summing up to 3,042 grams/ton. The Obytichna River bed is located on the Azov megablock of the Ukrainian Shield. The basement structure is dominated by anticlinorium structures composed of plagiogranitoids (Sherbakov, 2005). The quaternary layer of this area is aeolian-diluvial deposits with thickness less than 10 m. The lower course of this river is part of the Azov Sea iron ore basin. According to metallogenic zoning of Ukraine, this territory is part of the Archean and Proterozoic formations area. Present metals identified in rocks from this area are: Al, Ti, Cr, Fe, Co, Ni, Cu, Zn (Grachev, 2023). Thus, Obytichna Rivers erodes rocks with titanium-containing minerals. In addition, this river has the highest velocity, so it is able to transport more dense materials.

5. CONCLUSIONS

The northern coast of the Sea of Azov is represented by the following depositional factors: coastal embankments, bars and spits. Geomorphologically, this area is the most favourable for the formation of placers. The number of coastal embankments increases near the river mouths; therefore they play an important role in the formation of depositional underwater slope structures. The development of sedimentological formations is one of the key factors in the accumulation of placers. In the coastal zone, heavy minerals accumulate in high quantities in sand strips. The most noticeable concentrations of this heavy fraction are observed at the influence area defined by the separating action of the waves.

The sand fraction is dominant in the granulometric composition of the bottom sediments of all the studied rivers. The results of mineralogical analysis show that titanium-containing minerals (ilmenite, rutile, titanite, and leucoxene) are present in the bottom sediments in various concentrations. Yet, these amounts are too low for economic importance. The highest ilmenite content in the sediments of the Obytichna River is up to 3,042 grams/ton. This can be explained by the fact that the Obytichna River originates at the outcrops of the Ukrainian Shield. Additionally, there are many various technogenic particles in the bottom sediments of the studied rivers.

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REFERENCES

Bahrii, I.D., Bilous, A.M., Vilkul, Yu.H. (2000). Experience in comprehensive assessment and mapping of man-made impacts on the natural environment of the cities of Kryvyi Rih and Dnipropetrovsk. Feniks. (in Ukrainian)

Byriukov, N.S., Kazarnovskyi, V.D., Motylev Yu.L. (1975). Methodological manual for determining the physical and mechanical properties of soils Nedra. (in Russian)

Cutroneo, L., Carbone, C., Consani, S., Capello, M. (2020). Sediment distribution on the continental shelf in relation to stream inputs and contamination: Hydrodynamic, chemical, mineralogical, and sedimentological characteristics (Ligurian Sea, Italy). *Environmental Science and Pollution Research*, **27**(*35*): 43755-43768. https://doi.org/10.1007/S11356-020-10259-4/FIGURES/8

Database «Legislation of Ukraine» (1995). The Water Code of Ukraine Law, Code on June 6, 1995 № 213/95-BP. https://zakon.rada.gov.ua/go/213/95-%D0%B2%D1%80

DSTU B V.2.1-19:2009 (2009). Bases and foundations of buildings and structures. Soils. Methods of laboratory granulometric (grain-size) and microaggregate distribution. (in Ukrainian)

Folk, R.L. (1954). The Distinction between Grain Size and Mineral Composition in Sedimentary-Rock Nomenclature. *The Journal of Geology*, **62**(*4*): 344-359. https://doi.org/10.1086/626171

Grachev, A. (2023). Maps of Ukraine. https://geomap.land.kiev.ua/index.html (in Ukrainian)

Atlas (2001). Geology and Minerals of Ukraine. Kyiv. (in Ukrainian).

Grand View Research (2023). Titanium Market Size, Share & Growth Analysis Report, 2030 (Report ID: GVR-4-68040-331-4; 100 p.). https://www.grandviewresearch.com/industry-analysis/titanium-market-report

Hunter, J.D. (2007). Matplotlib: A 2D Graphics Environment. *Computing in Science & Engineering*, **9**(*3*): 90-95.

Ivanchenko, V., Berozkina, L., Stetsenko, V., Kovalchuk, L. (2021). Schlich mineralogical analysis for research of modern bottom sediments. *Visnyk of Taras Shevchenko National University of Kyiv. Geology*, **2**(*93*): 24-31. https://doi.org/10.17721/1728-2713.93.03 (in Ukrainian)

Komliev, O.O., Zhylkin, S.V., Vasylenko, S., Remezova, O.O, Iaremenko O.V., Okholina, T. (2020). The role of neotectonic activations in the formation of the Ukrainian sub-province of titanium and titanium-zirconium placer deposits (scientific and applied aspects). *XIV International Scientific Conference "Monitoring of Geological Processesand Ecological Condition of the Environment"* 10-13 November, Kyiv, Ukraine: 1-5. https://doi.org/10.3997/2214-4609.202056071

Lanovenko, O.H., Ostapishyna, O.O. (2013) Dictionary ecology reference book, PP Vyshemyrskyi V.S. (in Ukrainian)

Long, D. (2006). BGS detailed explanation of seabed sediment modified folk classification. British Geological Survey.

Mareano (2023). Graine size scale. https://www.ngu.no/Mareano/Grainsize.html

Mykhailov, V.A., Shevchenko, V.I., Ohar, V.V., Kurylo, M.V., Shunko, V.V., Hrinchenko, O.V., Omelchuk, O.V., Mykhailova, L.S. (2007). Metallic mineral resources of Ukraine. VPTs "Kyivskyi universytet". http://www.geol.univ.kiev.ua/lib/RKK_metalichni_kk.pdf (in Ukrainian)

Sherbakov, I.B. (2005). Petrology of Ukrainian Shield. (in Ukrainian)