

Using local mineral materials for the rehabilitation of the Ustya River – a case study

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ABSTRACT

The process of eutrophication has a negative impact on the water body (flora and fauna) and decreases its aesthetic and recreational values. In this work, we propose to combine chemical and physical methods for the restoration of rivers and lakes in Ukraine with the help of regionally occurring carbonates and quartz-glauconite sand. Experimental studies have shown that their use should have a high environmental effect on the improvement of the river water quality, that is, after the use of the Fe-coagulant. The addition of this coagulant can removal prostates and organic matter but may reduce the water pH. Therefore, to prevent stress recurrence in the aquatic ecosystem after adding natural calcium carbonate to water, its optimal doses were determined experimentally. It was found that the optimal application dose depended on the initial pH value of water and its mineralization. Experimental studies of the physical and chemical properties of quartz-glauconite sands have shown high values of the filtration coefficient, the capability of increasing the water pH value and improving the water reducing properties. These properties of natural reactive materials (limestones and quartz-glauconite sand) were used to design and construct earth structures for river rehabilitation. Reactive materials can be placed on the river banks, parallel to the direction of the water flow, or as permeable reaction barriers constructed perpendicular to the river flow direction. After the rehabilitation works are completed, the area on the river banks may be adapted as a public space for the local residents.

Keywords: Lake; River; Liming; Quartz-glauconite; Reaction barriers

1. Introduction

The contamination of freshwater bodies is one of the most important environmental impacts being threats to sustainable development. According to Beretta-Blanco and Carrasco-Letelier [1] the protection of freshwater bodies and water quality, mainly against anthropic eutrophication processes, is one of the Sustainable Development Goals. Eutrophication is the enrichment of minerals and nutrients that increase the natural primary production (i.e., algae and

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macrophytes) of water bodies [2]. One of the major stressors on the aquatic biota in European streams and rivers is enrichment in nutrients [3,4]. The eutrophication of large and small rivers is a current problem in Ukraine [5–7]. This is especially true for rivers that flow through cities, especially in densely populated areas [8]. Flora and fauna suffer from eutrophication, such rivers silt their banks and may have an unsatisfactory aesthetic appearance. This also applies to the Ustya River (Rivne town, Ukraine) [9]. Eutrophication of the Ustya River is shown in Fig. 1.

It is commonly known that the process of eutrophication is associated with high concentrations of PO_4^{3-} and NO₃ and low values of water pH. Sukhodolska and Gryuk [10] informed about different water pH values in the Ustya River depending on seasonal changes. Their analysis showed that high concentrations of nitrate (NO_2) and phosphate (PO₄³⁻) occurred in May-June (0.047, 0.025 mg/ dm³ and 4.255, 6.124 mg/dm³, respectively) and in October-November (0.017, 0.072 mg/dm3 and 5.726, 2.370 mg/dm3, respectively). Thus, the lowest pH values were observed in June and September (5.9, 5.04, 4.14 and 4.89, respectively). Low water pH impairs the natural process of denitrification and mineralization of contaminants on the river bottom. The above analysis shows that the natural process of self-purification is impossible in the Ustya River. This problem is closely related with recreational issues. Residents of the nearby settlements in Rivne, Zdolbuniv, Kvasyliv and their surroundings are short of sandy beaches. The existing muddy banks and pollution make the water unsuitable for fishing. In order to restore the natural self-purification ability of the river, it is necessary to eliminate or minimize the impact of NO_3^- and PO_4^{3-} sources and induce direct self-purification of the river water.

Methods of reducing PO₄³⁻ from river sediments include: physical (i.e., hypolimnetic aeration, artificial destratification, controlled lake desludging and dredging) and geochemical technologies (i.e., implementation of alum and iron as coagulants) [11–13]. The capping materials may be either passive physical barriers (e.g., sand, gravel, clay) or active barriers. Active barrier systems are composed of generally permeable chemical or geochemical materials capable of binding contaminants by adsorption or precipitation processes [14,15]. The removal of NO₃⁻ may occur due to increased pH and activation of denitrification. This process may follow after the removal of PO_4^{3-} from a river or lake [13].

A new method that may solve the problem of the presence of high PO_4^{3-} concentrations is the addition of modifying bentonite lanthanum (Phoslock) to water [16–18]. Phoslock is a modified clay product, consisting of lanthanum (5%) and bentonite (95%), developed in the 1990s by the Australian Government Commonwealth Scientific and Industrial Research Organization to combat eutrophication in waterways. Lanthanum is a rare earth element which strongly binds to phosphate, making it a valuable tool in the control of phosphorus pollution in water bodies. Benefits of this method include the removal of PO_4^{3-} and lack of impact on the decrease of water pH [19,20]. As a result, phosphate lanthanum is insoluble at low pH, which allows for efficient mineralization of phosphates in river or lake sediments.

Successful implementation of management actions aimed at reducing algal blooms in rivers requires an integrated approach [12,21–23]. In many countries such technical solution is very expensive, because the manufacture of such material requires substantial capital investments and power inputs for the modification of bentonite lanthanum. Most of these problems may be resolved in a cheaper way by using natural regional materials. This also applies to solving the pollution issue in the Ustya River (Rivne, Ukraine).

The choice of PO_4^{3-} remediation methods to achieve the objectives of river management is influenced by the suitability of the remediation method (regional availability of necessary natural resources) and by the nature of the river environment. As practiced in many countries [22,24,25], high PO₄³⁻ concentrations are reduced by adding environmentally safe coagulants, that is, ferric chloride (FeCl₂), to water. Its addition, at a predetermined optimal dose, reduces not only the phosphate content but also the concentration of organic suspended solids. In this case, the coagulated organic suspended solids together with hydrolyzed iron will settle on the reservoir bottom, where their mineralization will take place. FeCl, application takes place usually in late spring, with the coagulant introduced by direct injection into the water. The main disadvantage of natural water purification with the FeCl₂ coagulant is that its



Fig. 1. Ustya River in Rivne, Ukraine.

addition significantly reduces water pH. As recommended by the National Swedish Environmental Protection Agency [26] and Håkanson [27], safe reduction of water pH for living aquatic organisms is a change not exceeding 1.5, whereas with the addition of the iron-containing coagulant, the reduction in water pH may exceed 2.5. Researchers note that addition of iron to lakes/rivers is inappropriate, due to the fact that it reduces the water pH. As a result, the pH value may be less than 4 [28]. If this method is used alone, not combined with other methods, this may lead to undesirable impact on the environment and aquatic biota. In that case, denitrification cannot be accomplished.

The purpose of this work is to propose an approach using the FeCl₂ coagulant to reduce phosphates, integrated with other approaches for water purification, which will provide a high degree of water purification and ensure safe conditions for living aquatic organisms. The water pH value in the lake and in the river may be increased by using calcium carbonate (CaCO₂) and quarts-glauconite sand from the local Zdolbunivsky Quarry. The problem may be solved by installing filtration reaction barrier-dams and beaches comprising local quartz-glauconite sands which have unique properties and distribution in the Ustya River basin. Therefore, the aim of this work is to study how selected chemical properties of different types of water change after contact with local natural materials, which are waste of mining. This work is a continuation of previously conducted experimental studies focused on determining the mineralogy and grain-size composition of quartz-glauconite sands, which are widespread in the Ustya River basin [29].

2. Material and methods

2.1. Geographic characteristics of the Ustya River basin

Ustya is a small river in Ukraine, in the Rivne region $(50^{\circ}36'52.4''N \ 26^{\circ}14'26.2''E)$ (Fig. 2). The river is a 68 km long left tributary of the Goryn River (Pripyat basin). Its catchment area covers 762 km². The river slope is 1.6 m/km. The valley is trough-shaped, with clear outlines, up to 4 km wide and up to 60 m deep. The floodplain is up to 1–1.2 km

wide, with wetlands. The river is winding, 25 m wide, 8 m wide in the middle course, 1.6 m deep, straight in some places. Artificial reservoirs and drainage systems were created in the Ustya River basin. The river water is used for domestic and industrial water supply, and for fish farming.

2.2. Geological characteristics of deposits of natural $CaCO_3$ (chalk) and quartz-glauconite sands of the Ustya River basin

Chalk deposits attain a thickness of up to 50 m and are abundant in the Ustya River basin (Fig. 3).

The Zdolbunivsky Quarry is intensively mined by "Dickerhoff Cement Ukraine" for cement production, as well as for local household needs. In terms of mineral composition, natural CaCO₂ (chalk) contains at least 95% of calcite (up to 55.6% CaO and up to 43.6% CO₃). The material has the following properties: natural humidity 8.63%-36.20%; average bulk density 1.87 g/cm3; compressive strength 14.40-26.30 kg/cm², loosening coefficient 1.32-1.75 [30]. In a dry state, chalk is easily ground into powder and can be used as a natural material to increase the pH of soils. All quartz-glauconite sand samples were found to contain two types of aluminosilicate glauconite: one with concentrated Fe, and the other with less iron, which was replaced by Al and Mg. However, neither the filtration coefficients of these sand samples nor their impact on water pH have been studied. Glauconite and quartz-glauconite sands are interesting due to the high content of K₂O < 12% [29]. There are many studies about the potential leaching of K into quartz-glauconite sands and their use to decrease soil acidity by water treatment. This valuable alkali metal K is as ion change cations because easy can go in water. Therefore, it can be predicted that when glauconite is introduced into water, the water pH increases. Quartz-glauconite sands, together with Sarmatian sands and limestones from the lower part of the Neogene form a large erosional remnant east of Rivne and Zdolbuniv in the form of hills with absolute heights up to 250 m. In the Zdolbuniv deposit, the balance reserves of sand represent 6,998 thousand tons, but are stored in dumps as waste of mining [31]. According to



Fig. 2. Geographic location of the Ustya River basin within the Rivne district and region.



Legend: a - Novomilsky pond, b - Staromilsky pond, c - Irpin ponds, d - Bridge of the Rivne-Kvasyliv highway on the Ustya riverbed, e - Gorges in the relief on the floodplain and the Ustya riverbed, f - At the confluence of Ustya River with the Basivkutsk reservoir; g - Basivkutsk reservoir.



3 - Upper Paleogene, Eocene and Oligocene tiers (quartz-glauconite sands); 4 - Lower Sarmatian (clay sands);
5 - Upper Sarmatian (limestones); 6 - Neopleistocene Eluvial-deluvial deposits; 7 - Neopleistocene Lakealluvial deposits; 8 - Neopleistocene Deluvial-aeolian deposits; 9 - Location of the designed beaches (quartz-glauconite sands) 10 - Location of the designed filtration barrier-dams (quartz-glauconite sands).

Fig. 3. Scheme of the geographic distribution of chalk deposits and quartz-glauconite sands in the Ustya River basin and the location of the designed filtration barrier-dams and beaches.

the mineralogical analysis of Natkaniec-Nowak et al. [29], sand samples occurring in the upper part of the succession in the Zdolbuniv Quarry are coarser than the sand samples occurring in the lower part of this succession. They comprise psammitic fraction with grain sizes at 0.3–0.12 and 0.6–0.3 mm, composed of approximately 86%–91% of rubbles - mainly quartz with a subordinate amount of glauconite (up to 20%). They comprise psammitic fraction with grain sizes at 0.3–0.12 and 0.6–0.3 mm, composed of approximately 80%–85% quartz and glauconite (up to 15%–20%).

The analysed sands, according to standard methods [32,33], were classified according to their physical properties as: "heavy" (particle density); "crumbly" (dry skeleton density), "low degree of water saturation" (coefficient of water saturation), and "natural" (origin). According to the grain-size composition, grain-size modulus, and fraction content below 0.16 mm [34], the sands belong to the "fine" group, and according to the content of dust and clay particles to the group "with low and very low content"; however, they do not contain significant amounts of silt, clay and organic inclusions, the content of which does not exceed 1%.

2.3. Determination of the filtration coefficient of quartz-glauconite sands

Determination of the filtration coefficient of quartzglauconite sands was performed according to [35]. The calculation of the filtration coefficient (K_{f} m/d) was conducted using the formula:

$$K_f = \frac{Q}{F \cdot I \left(0.7 + 0.03 \cdot t \right)} \tag{1}$$

where Q – constant water consumption, m³/d; F – area of the transverse diameter of driving cylinder, m²; I – hydraulic gradient, t – water temperature, °C.

2.4. Studies of changes in the water parameters at contact with natural CaCO₃ and quartz-glauconite sand

Experimental studies of changes in the water parameters at contact with natural CaCO₃ and quartz-glauconite sand were performed in static conditions. Natural CaCO₃ and quartz-glauconite sand samples were collected in the Zdolbuniv Quarry (Fig. 4). The samples were dried at 105° C to a constant weight, the CaCO₃ was ground to a grain size less than 0.01 mm. Three types of water were used for the studies, with mineralization equal to 0 mg/dm³, 0.23 g/dm³ and 0.53 g/dm³, respectively. For each type of the prepared water solutions (by mineralization), the pH value was 4.5. The water pH was adjusted using 0.1 N HCl.

Natural CaCO₃ was added at a rate of 0.05 and 0.1 g/ dm³ to 500 mL of water and then the solution was mixed. Selected doses are typical for the introduction into acidic natural waters [36]. After adding CaCO₃ to the water, the following parameters were determined simultaneously with the water pH value measured every 10 min: redox potential (Eh), electrical conductivity (EC) and total dissolved solids (TDS). These values were measured using a multimeter. Measurements were taken three times. Water samples and CaCO₂ were mixed using a magnetic stirrer. Increase of water alkalinity (AL) was determined before and after the addition of CaCO₂ and reaching equilibrium constants of the water pH. AL was determined using the titrimetric method with 0.1 N HCl and methyl orange. Experimental studies of changes in the values of pH and Eh in water at contact with quartz-glauconite sand from Zdolbuniv Quarry were performed at a rate of 2 g of sand per 200 mL of water. All experimental studies were conducted at a temperature of 17°C.

3. Results and discussion

3.1. Results of determining the change in water quality indicators at contact of water with natural CaCO, (chalk)

The determined filtration coefficients of the quartzglauconite sand from the river bank varied in the range of 9.8–16.4 m/d (Table 1), which significantly were higher than the limit required for the balanced absorption of surface runoff. The studied permeable sands are suitable as filtration barriers for the construction of beaches along the Ustya River and associated artificial reservoirs.



Fig. 4. Samples of natural (a) $CaCO_3$ (chalk) and (b) quartz-glauconite sand taken from Zdolbuniv Quarry.

The tested sands are highly permeable, considering the norms subdividing soils according to the degree of water permeability [32]. Traditionally, the Fe-coagulant (FeCl₃) was added to reduce the intensity of eutrophication, that is, to reduce the concentration of phosphates in natural water bodies. It is proposed to add such coagulant to the river source and to the Basiv Kut lake. With addition of the FeCl₃ to water, the water pH is reduced. In some cases, it decreases to pH = 4. A quarry was established for the production of CaCO₃ in the area of the studied lakes (Fig. 2). It was suggested to add samples of this natural material after the addition of FeCl₃ in order to increase the pH of lake water. Changes of pH, Eh, EC and TDS kinetics in time are presented in Fig. 5.

Changes in the water pH at contact with natural $CaCO_{3'}$ the kinetics of these changes, values of Eh, EC and TDS, and the increase of AL were determined simultaneously. Results of the experimental studies are presented in Table 2.

As shown in Table 2, the increase in ΔpH , ΔEh , ΔEC , Δ TDS and Δ AL values depended on the initial water pH value, TDS value, and the dose of CaCO₂. The lower the initial water pH value, the higher the value of all these parameters. Thus, addition of 0.1 g/dm³ of CaCO₂ at initial values of pH = 4 and TDS = 0.01 g/dm³ resulted in increase of $\Delta pH = 3.78$, $\Delta Eh = -120$ mV, $\Delta EC = 0.13$ mSm/cm, and $\Delta TDS = 0.09 \text{ g/dm}^3$. At a similar initial water pH and CaCO₂ dose but increased salinity, the trend growth of ΔpH , ΔEh , ΔEC and ΔTDS shows a reduction of these characteristics in the three analysed water types. Therefore, after analysis of the experimental results (Table 2), it can be stated that the values of pH, Eh, EC and TDS were reduced with increase of initial pH and TDS values. When analysing the kinetics of the pH value changes and the dependence of these changes on the dose of the added $CaCO_{u}$ at moderate water mineralization (TDS = 0.23 g/dm^3) and initial value of pH = 5, it can be observed that the value of water ΔpH increases. When CaCO₃ was added to water at a dose of 0.1 g/dm³, the ΔpH increase was 1.87, at the dose of $0.05 \text{ g/dm}^3 - \Delta pH$ was 1.51, whereas at the dose of 0.025 g/ dm^3 – the ΔpH was 1.04. Addition of CaCO₂ to water at a dose of 0.025 g/dm³ did not increase the water pH to a neutral value and the increase was clearly below 1.5. Based on the recommendations of the Swedish National Environmental Protection Agency [26], a safe change of water pH value for living aquatic organisms should

Table 1

Filtration coefficients of quartz-glauconite sands in Zdolbuniv Quarry

Coil complex	Filtration coefficients					
No well/depth m						
	CIII/S	III/d				
Well 1/0.0–2.0	0.019	16.41				
Well 1/2.0-5.0	0.011	9.84				
Well 2/2.0-3.5	0.02	17.28				
Well 2/4.0-4.5	0.015	13.42				
Well 2/5.0-6.0	0.012	11.06				
Well 2/6.0-8.0	0.012	10.42				



Fig. 5. Changes of pH, Eh, EC, and TDS kinetics in time (initial values of pH = 4; TDS = 0.01 and 0.1 g/dm³ dose of CaCO₃).

Types of water	CaCO ₃ , g/dm ³	рН	ΔрН	Eh, mV	ΔEh	EC, mS/cm	ΔEC	TDS, mg/dm ³	ΔTDS	П, mg/ dm³	ΔΠ	<i>t,</i> equilibrium time, min
Distilled water Moderately mineralized water Mineralized water	0.1	4.05	3.73	380	-120	0.02	0.14	10	100	12.2	48.8	90
	0.05	4.05	3.55	396	-108	0.02	0.13	10	90	12.2	24.2	90
	0.025	4.05	2.15	386	-80	0.02	0.08	10	20	12.2	11.6	60
	0.1	5	3.56	320	-145	0.02	0.05	10	40	12.2	48.8	80
	0.05	5.1	3.31	320	-109	0.02	0.04	10	30	12.2	14.4	80
	0.025	5.1	2.02	320	-70	0.01	0.02	10	10	12.2	10.5	50
	0.1	4.02	2.98	402	-103	0.55	0.14	230	70	12.2	42.6	120
	0.05	4.02	2.81	405	-104	0.55	0.11	230	40	12.2	23.18	120
	0.025	4.02	1.9	400	-80	0.55	0.05	230	20	12.2	15.3	80
	0.01	5.03	1.87	314	-79	0.55	0.07	230	40	24.4	54.9	100
	0.05	5.05	1.51	315	-50	0.55	0.05	230	40	24.4	24.4	100
	0.025	5.5	1.04	320	-20	0.55	0.02	230	20	24.4	12.6	70
	0.1	4.05	2.72	415	-79	0.79	0.04	550	50	6.1	61	140
	0.05	4.08	2.89	389	-59	0.79	0.07	520	40	6.1	41.48	140
	0.025	4.05	1.85	410	-30	0.79	0.03	520	20	6.1	11.2	100
	0.1	5.07	1.65	310	-116	0.79	0.08	520	60	36.6	42.6	120
	0.05	5.02	1.76	298	-50	0.79	0.04	520	30	30.6	26.1	120
	0.025	5.07	0.85	300	-25	0.79	0.02	520	20	30.3	9.5	100

Table 2 Results of changes of water quality indicators at contact of water with natural $CaCO_3$

not exceed 1.5. Comparing the change in ΔpH values at CaCO₂ doses of 0.05 and 0.1 g/dm³, this value is approximately the same. Thus, it is advisable to add CaCO₂ to moderately mineralized water at a dose of 0.05 g/dm3 and at initial water pH values of 4.5. Such dose should increase the water pH to a safe value and thus eliminate its overconsumption. As shown above in Table 2, the added CaCO₂ is not completely soluble in water. Hence, it can be argued that the sedimentation of CaCO₃ on the reservoir bottom may maintain a prolonging action to protect/maintain the neutral pH value of water over a long time. Undissolved CaCO₃ may for some time prevent the dissolution of previously sedimentary phosphates such as ferric phosphate (FePO₄). Moreover, data analysis (Table 2) shows that after addition of natural CaCO₂ to water with pH 4 and 5 a decrease in the water Eh value can be observed. This fact results in a positive effect, because it proves that water has reducing properties. In addition, the positive effect of adding CaCO₃ to acidic and moderately acidic water is that it always increases carbonate alkalinity. Lower initial water pH and higher doses of CaCO₂ result in a higher alkalinity increase. Alkalinity of natural water is very important to maintain the buffering of natural water and controlling the water acidity.

3.2. Physical and chemical characteristics of water

Results of changes in the physical and chemical characteristics of the three types of water at contact with quartzglauconite sands point to higher pH and Eh values. The results of experimental studies are presented in Fig. 6 and Table 3. At initial values of water pH = 4, the equilibrium time when the water pH did not change was 20, 25 and 30 min for distilled, moderately mineralized and mineralized



Fig. 6. Values of pH and Eh in the analysed water types.

water, respectively. The value of water pH increased to 8.2, but the time equilibrium was different. At pH = 5, the equilibrium time was 25, 30, and 35 min, respectively. Besides, studies of the changes of water Eh after addition of

quartz-glauconite sand were performed. Change of Eh values depended on the initial mineralization of water and pH. Thus, as a result, the reducing properties of water improved.

Changes in the pH and EC values of water are explained by the properties of the mineral glauconite which is a component of the studied sands. This mineral belongs to silicates of the hydromica group and contains more than 10% of potassium. Apparently, this alkaline metal interacts with water and, as a result, the water pH value increases and the water Eh value decreases. The impact of natural minerals on the physical and chemical composition of water was also studied by Trach et al. [37] and Reczek et al. [38].

3.3. Location and features of the designed sandy beaches and filtration barrier-dams

Beaches composed of quartz-glauconite sands in the Ustya River basin (Fig. 7) are planned to be constructed in the Basivkutsk Reservoir. Such placement of the beach will contribute to the rehabilitation of the Ustya River basin after its cleaning with the coagulant and to further use by the residents for recreational purposes. The beaches composed of quartz-glauconite sands designed to be coastal strips. In cross-section they will be triangle-shaped, about 10 m wide at the base, up to 1 m high, and with underwater inclined and surface subhorizontal surfaces (Fig. 7). Abrasion of the sandy beach by waves will help spreading the quartz-glauconite sand to the bottom of the reservoir and burial of the contaminated silt.

Construction of filtration barrier-dams from quartzglauconite sands in the Ustya River basin is designed in the following sections: (1) in front of the bridge of the Rivne-Kvasyliv highway across the Ustya River, (2) at the junction of the Ustya River with the Basivkutsk Lake (Fig. 7). Structurally, the filtration barrier-dam in cross-section will represent a prism with a width of 5-6 m at the base and a height of 1-1.5 m (Fig. 8). To improve the stability of bulk barrier-dams against possible suffusion processes, boulders and rubble of porous Upper Sarmatian shelly limestones, occurring in the Zdolbunivsky, Zdovbytsky and other local quarries, will be added to the sand at a ratio of 1:5. This technological solution has proven successful in the construction of the retaining shaft around the Novomysl hydraulic dump and may be considered as a sufficiently reliable hydraulic structure with satisfactory filtration properties.

In each filtration barrier-dam, in the part that will block the Ustya River bed, a sluice built of concrete and metal structural elements is planned to regulate the flow and control the flood water level. The optimal design of the sluice will be the subject of a separate study by hydraulic engineers [39,40]. An advantage of this approach is that the new capping sediment may provide an improved habitat for sediment-dwelling organisms. However, the potential for extensive smothering of benthos with addition of a thick capping layer poses a disadvantage. Targeting of capping to areas where hypolimnetic anoxia occurs will reduce the possible adverse effects on the benthos.

3.4. Revitalization of the Ustya River

Projects of development and revitalization of rivers and lakes are presently some of the most interesting examples of contemporary public spaces. Green areas are becoming increasingly important for residents of urban space during the COVID-19 pandemic [41]. The projects assume the restoration of natural and functional values of areas often destroyed by human activities, due to which the offer of recreational space for residents may be extended and at the same time the landscape values of a local natural environment may be emphasized. The proposed revitalization project of the Ustya River in Rivne will include the improvement of the water quality and an architectural design of public space for the residents (Figs. 9 and 10).

The main assumption of this architectural project is to create an open public space that will allow residents to use the natural values of the river. Due to the length of the river, the project assumes the introduction of various characteristic functional zones: (i) Urban zone. The first functional zone will comprise recreational areas with an urban character, designed in the city along the river. This space is designed to be the most representative and eye-catching, with various types of urban attractions for the residents. The urban zone should include sports, and recreational and cultural activities, due to which residents will gain new space for meetings, interactions and leisure; (ii) Sport and recreational zone. The second zone will include sport and recreational areas, where the residents will experience various types of sport activities, such as: pitches, courts, and playgrounds. The revitalization project assumes that bicycle, skateboard and roller paths will be created along the river. The nearby wasteland will be transformed into a sport space; (iii) Natural and recreational zone. The farthest zone will be a natural and recreational area, where the residents will have the largest contact with natural and exceptional environmental

Table 3 Dependence of water pH and Eh change on the mineralization

Types of water	TDS, mg/dm ³	pН	ΔpH	Eh, mV	ΔEh , mV	<i>t</i> , equilibrium time, min
Distilled	10	4	4.2	310	-50	20
		5	3.2	300	-35	30
Moderately mineralized	230	4	4.2	280	-40	30
		5	3.2	290	-35	35
Mineralized	520	4	4.2	310	35	35
		5	3.2	300	-20	40



Fig. 7. Cross-section through the designed quartz-glauconite sand beach.



Fig. 8. Cross-section across the designed filtration barrier built of quartz-glauconite sands with blocks of shelly limestones.



Fig. 9. The concept of the development of public space in an urban zone.

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Fig. 10. Visualisation of the river valley after rehabilitation.

values. The space is also needed for the separation of the flood zones, therefore it should be least urbanized.

The conducted research and a proposal of measures aiming at improvement of the river water quality, together with the architectural revitalizing project, allows to present a comprehensive concept for the development of the Ustya River. The design assumptions attempt to revitalize natural and functional river and lake banks into a green, friendly space for the residents. The project should consider local nature protection, which should be the primary and most important task.

4. Conclusions

The combination of chemical and physical river remediation methods may result in a high ecological effect for improving the river water quality, that is, the use of Fe-coagulants, and regional limestone and quartz-glauconite sand deposits. Due to the nearby location of limestone quarries and the high amount of glauconite (over 20%) in the quartz-glauconite sands, the materials may be used to improve the physical and chemical parameters of water quality after the addition of the Fe-coagulant. It was proved that in contact with water, addition of natural calcium carbonate and quartz-glauconite sands increases the water pH and decreases its redox potential. In addition, the dissolution of natural calcium carbonate increases the hydrocarbonate alkalinity in three types of water and thus increases the water buffering capacity. Partial dissolution of calcium carbonate and its accumulation on the lake bottom will allow to keep the deposited phosphates in the form of ferric phosphate for a long time. To increase the pH of water that moves from the lake to the river mouth, it is proposed that water would pass through a bulk reaction barrier composed of quartz-glauconite sands. As a result, increased pH and decreased redox potential may optimize denitrification and decrease the value of nitrate. Sandy beaches should be covered with quartz-glauconite sands, the volume of which should be supplemented annually in the wave area. The filtration barrier should be constructed in areas of floodplain water outflow, it will not decrease the water level in the river and will not cause significant coastal flooding of residential areas. The revitalization project of the Ustya River in Rivne will include the improvement of water quality and create an open public space along the river banks, which will allow local residents to use the natural values of the river.

References

- A. Beretta-Blanco, L. Carrasco-Letelier, Relevant factors in the eutrophication of the Uruguay River and the Río Negro, Sci. Total Environ., 761 (2021) 143299, doi: 10.1016/j. scitotenv.2020.143299.
- [2] M. Gerke, D. Hübner, J. Schneider, C. Winkelmann, Can top-down effects of cypriniform fish be used to mitigate eutrophication effects in medium-sized European rivers?, Sci. Total Environ., 755 (2021) 142547, doi: 10.1016/j. scitotenv.2020.142547.
- [3] V. Dahm, D. Hering, D. Nemitz, W. Graf, A. Schmidt-Kloiber, P. Leitner, A. Melcher, C.K. Feld, Effects of physico-chemistry, land use and hydromorphology on three riverine organism groups: a comparative analysis with monitoring data from Germany and Austria, Hydrobiologia, 704 (2013) 389–415.
- [4] D. Hering, R.K. Johnson, S. Kramm, S. Schmutz, K. Szoszkiewicz, P.F.M. Verdonschot, Assessment of European streams with diatoms, macrophytes, macroinvertebrates and fish: a comparative metric-based analysis of organism response to stress, Freshwater Biol., 51 (2006) 1757–1785.
- [5] O. Bilous, S. Barinova, P. Klochenko, Phytoplankton communities in ecological assessment of the Southern Bug River upper reaches (Ukraine), Ecohydrol. Hydrobiol., 12 (2012) 211–230.
- [6] N. Hagemann, F. Blumensaat, F. Tavares Wahren, J. Trümper, C. Burmeister, R. Moynihan, N. Scheifhacken, The long road to improving the water quality of the Western Bug River (Ukraine) – a multi-scale analysis, J. Hydrol., 519 (2014) 2436–2447.
- [7] V. Yakovlev, Y. Vystavna, D. Diadin, Y. Vergeles, Nitrates in springs and rivers of East Ukraine: distribution, contamination and fluxes, Appl. Geochem., 53 (2015) 71–78.

- [8] J. Rozemeijer, R. Noordhuis, K. Ouwerkerk, M. Dionisio Pires, A. Blauw, A. Hooijboer, G.J. van Oldenborgh, Climate variability effects on eutrophication of groundwater, lakes, rivers, and coastal waters in the Netherlands, Sci. Total Environ., 771 (2021) 145366, doi: 10.1016/j.scitotenv.2021.145366.
- [9] Y.R. Grokhovska, I.O. Parfeniuk, S.V. Konontsev, T.V. Poltavchenko, Analysis of surface water quality and crustacean diseases in fish (the Ustya River basin, Ukraine), Ukr. J. Ecol., 11 (2021) 94–102.
- [10] I.L. Sukhodolska, I.B. Gryuk, Seasonal Variability of the Chemical Composition of Surface Waters of the Ustya River, BIOLOGICAL RESEARCH: Collection of Scientific Works of the V All-Ukrainian Scientific-Practical Conference of Young Scientists and Students, ZhSU Publishing House, I. Franko, Zhytomyr, 2014, pp. 437–440.
- [11] S.L. Yun, S.J. Kim, Y.L. Park, S.W. Kang, P.J. Kwak, J.J. Ko, J.H. Ahn, Evaluation of capping materials for the stabilization of contaminated sediments, Mater. Sci. Forum, 544–545 (2007) 565–568.
- [12] H.B. Yin, J.C. Zhu, W.Y. Tang, Management of nitrogen and phosphorus internal loading from polluted river sediment using Phoslock[®] and modified zeolite with intensive *tubificid oligochaetes* bioturbation, Chem. Eng. J., 353 (2018) 46–55.
- [13] A. Siciliano, G.M. Curcio, C. Limonti, Experimental analysis and modeling of nitrate removal through zero-valent magnesium particles, Water, 11 (2019) 1276, doi: 10.3390/w11061276.
- [14] D. Burska, D. Pryputniewicz-Flis, A. Bankowska-Sobczak, G. Brenk, T. Woszczyk, The efficiency of P-removal from natural waters with sorbents placed in water permeable nonwovens, *IOP Conf. Ser.: Earth Environ. Sci.*, 362 (2019) 012099.
- [15] A. Sieczka, E. Koda, A. Miszkowska, P. Osiński, Identification of Processes and Migration Parameters for Conservative and Reactive Contaminants in the Soil-Water Environment, L. Zhan, Y. Chen, A. Bouazza, Eds., Proceedings of the 8th International Congress on Environmental Geotechnics, Volume 1, The International Congress on Environmental Geotechnics, Environmental Science and Engineering, Springer, Singapore, 2019, pp. 551–559.
- [16] F. Haghseresht, S. Wang, D. Do, A novel lanthanum-modified bentonite, Phoslock, for phosphate removal from wastewaters, Appl. Clay Sci., 46 (2009) 369–375.
- [17] M. Kasprzyk, M. Gajewska, Preliminary results from application Phoslock[®] to remove phosphorus compounds from wastewater, J. Ecol. Eng., 18 (2017) 82–89.
- [18] A. Grela, M. Łach, J. Mikuła, An efficacy assessment of phosphate removal from drainage waters by modified reactive material, Materials, 13 (2020) 1190, doi: 10.3390/ma13051190.
- [19] K. Finsterle, Overview of Phoslock[®] Properties and its Use in the Aquatic Environment, Phoslock Europe GmbH, 2014.
- [20] M.A. Zeller, M.J. Alperin, The efficacy of Phoslock[®] in reducing internal phosphate loading varies with bottom water oxygenation, Water Res., 11 (2021) 100095, doi: 10.1016/j. wroa.2021.100095.
- [21] L. Zhang, X. Gu, C. Fan, J. Shang, Q. Shen, Z. Wang, J. Shen, Impact of different benthic animals on phosphorus dynamics across the sediment-water interface, J. Environ. Sci., 22 (2010) 1674–1682.
- [22] Y. Zhang, L. Cheng, K.E. Tolonen, H. Yin, J. Gao, Z. Zhang, K. Li, Y. Cai, Substrate degradation and nutrient enrichment structuring macroinvertebrate assemblages in agriculturally dominated Lake Chaohu Basins, China, Sci. Total Environ., 627 (2018) 57–66.
- [23] B. Gao, Q. Yue, J. Miao, J. Evaluation of polyaluminium ferric chloride (PAFC) as a composite coagulant for water and wastewater treatment, Water Sci Technol., 47 (2003) 127–132.

- [24] L. Chekli, C. Eripret, S.H. Park, S.A.A. Tabatabai, O. Vronska, B. Tamburic, J.H. Kim, Shon, Coagulation performance and floc characteristics of polytitanium tetrachloride (PTC) compared with titanium tetrachloride (TiCl₄) and ferric chloride (FeCl₃) in algal turbid water, Sep. Purif. Methods, 175 (2017) 99–106.
- [25] S. Ding, Y. Deng, H. Li, C. Fang, N. Gao, W. Chu, Coagulation of iodide-containing resorcinol solution or natural waters with ferric chloride can produce iodinated coagulation by-products, Environ. Sci. Technol., 53 (2019) 12407–12415.
- [26] EPA, Acidification and Liming of Swedish Freshwaters, National Swedish Environmental Protection Agency, Solna, 1991.
- [27] L. Håkanson, A general management model to optimize lake liming operations, Lakes Reservoirs Res. Manage., 8 (2003) 105–140.
- [28] M.J. Brandt, K.M. Johnson, A.J. Elphinston, D.D. Ratnayaka, Chapter 8 – Storage, Clarification and Chemical Treatment, M.J. Brandt, K.M. Johnson, A.J. Elphinston, D.D. Ratnayaka, Eds., Twort's Water Supply, 7th ed., Butterworth-Heinemann, Boston, 2017, pp. 323–366.
- [29] L. Natkaniec-Nowak, M. Dumańska-Słowik, B. Naglik, V. Melnychuk, M. Krynickaya, W. Smoliński, M. Sikorska-Jaworowska, P. Stach, D. Kubica, K. Ładoń, Depositional environment of paleogen amber-bearing qurtz-glauconite sands from Zdolbuniv (Rivne region, NW Ukraine): mineralogical and petrographical evidences, Miner. Resour. Manage., 33 (2017) 45–62.
- [30] http://minerals-ua.info/zviti-map.php?rep=mpasp_30&pas port=541
- [31] http://minerals-ua.info/zviti-map.php?rep=mpasp_30&pas port=1565
- [32] DSTU B.V. 2.1-2-96 State Standard. Bases and Foundations of Buildings and Structures, Soils. Classification. Kyiv, The State Committee of Ukraine, 1997, 47 p.
- [33] DSTU B V. 2.7-232:2010 Construction Materials. Dense Natural Sand for Construction Materials, Products, Structures and Operations, Technical Specifications, UKRA34425, 2011, 31 p.
- [34] DSTU B.V. 2.7-29-95 Building Materials. Natural Fine Aggregate from Waste Industry for Artificial Building Materials, Products, and Construction Works, Classification. Kyiv. Ministry of Regional Development of Ukraine, 1996, 35 p.
- [35] GOST 25584-90 Soils. Methods of Laboratory Determination of Filtration Coefficient.
- [36] W. Dickson, Y-W. Brodin, Strategies and Methods for Freshwater Liming, L. Henrikson, Y.W. Brodin, Eds., Liming of Acidified Surface Waters: A Swedish Synthesis, Springer, Berlin, 1995, pp. 81–124.
- [37] Y. Trach, V. Kosinov, G. Melnichuk, M. Michel, L. Reczek, The use of saponite tuffs in technologies to improve groundwater quality for drinking, Bulletin of NUWM 2, (2018) 210–221.
- [38] L. Reczek, M.M. Michel, Y. Trach, T. Siwiec, M. Tytkowska-Owerko, The kinetics of manganese sorption on Ukrainian tuff and basalt—order and diffusion models analysis, Minerals, 10 (2020) 1065, doi: 10.3390/min10121065.
- [39] A. Miszkowska, S. Lenart, E. Koda, Changes of permeability of nonwoven geotextiles due to clogging and cyclic water flow in laboratory conditions, Water, 9 (2017) 660, doi: 10.3390/ w9090660.
- [40] S. Bajkowski, The inflow length of the stream on the crest of the permeable sill with sharp-crested weir on the upstream slope, Acta Sci. Pol. Architectura, 19 (2020) 73–84.
- [41] E. Maciejewska, Redefining cities in view of climatic changes "Sponge City" – examples of solutions in Chinese cities at risk of flooding – Wuhan, Changde and Jinhua, Acta Sci. Pol. Architectura, 19 (2020) 11–19.

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