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Influence of Phosphogypsum Dump on the Soil Ecosystem in the Sumy region (Ukraine)

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Abstract: This paper investigates the influence of a phosphogypsum dump on the surrounding environment (soil ecosystem) in the Sumy region (Ukraine). Analysis of the surrounding soils was performed to study the possible presence of compounds leaching from the dump. For physical chemical analysis of samples, X-ray fluorescence (XRF) analysis, X-ray diffraction (XRD) analysis, and Fourier transform infrared spectrophotometry (FTIR) were used. XRF analysis did not confirm the contamination of soils around the phosphogypsum dump, and the soil fluoride levels measured in this study were comparable to the average soil fluoride concentration of soils globally. The colonization of the surface of the phosphogypsum dump by living organisms after the reclamation process was also analyzed. Field research was carried out on the routes, which specify the boundaries of the contours of plant communities, for description of phytocenoses in the territory of the dump, where the pH value ranged from 2.5 to 5.3, depending on the age of phosphogypsum terraces. Annual and perennial herbaceous plants are dominant on the reclaimed dump slopes. On the third and fourth phosphogypsum terraces (20 and 25 years old, respectively), tree forms have begun to settle, represented mainly by *Populus tgemula*, *Populus alba*, *Betula pendula*, and *Robinia pseudoacacia*. The studied patterns of ecological groups of plants growing under natural change of species can be used for the complete reclamation of the dump.

Keywords: phosphogypsum dump; soil ecosystem; plant communities; reclamation

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1. Introduction

Phosphogypsum is a by-product of the chemical reaction called the “wet process”, whereby sulfuric acid is reacted with phosphate rock to produce the phosphoric acid needed for fertilizer production [1]. The quality and quantity of phosphogypsum generation depends upon the quality of the phosphate rock, the process used to produce phosphoric acid, and the calcium sulphate generated either in di-hydrate ($CaSO_4{\cdot}2H_2O$) or hemi-hydrate ($CaSO_4{\cdot}1/2H_2O$) form. Production of 1 ton of phosphoric acid generates 5 ton of phosphogypsum [2]. The presence of harmful impurities and their concentration depends on the composition of the phosphate rock. The reaction of the interaction of fluorapatite and acid mixture is:

$$Ca_5(PO_4)_3F + 5H_2SO_4 + nH_3PO_4 + mH_2O \rightarrow (n+3)H_3PO_4 + 5CaSO_4{\cdot}mH_2O + HF$$

Fluorine compounds and sulfur are primary pollutants in industrial emissions generated by the production of wet-process phosphoric acid and phosphate fertilizers. Possible heavy metal pollution in areas of phosphorus-containing fertilizer production is caused by the presence of metals in phosphorite raw materials in the form of ballast elements, as described in a number of works [2–9].

Phosphogypsum is stocked in large open areas or accumulated in lakes, resulting in a major environmental problem due to the presence of toxic elements dispersed by wind (dust) and water. Metal contamination may affect the functionality, sustainability, and biodiversity of ecosystems [10]. At the same time, estimates on the severity and frequency of acute exposures deriving from old generation facilities are important, so as to estimate the extent of local health impacts. Similarly, much better and more complete data are needed on informal waste management activities and illegal operations, given the likely substantial magnitude of the health burden suffered by the people involved [11].

The main challenges regarding phosphogypsum management are:

- high fluoride concentration (in the range of 0.5%–1.5%), which can be leached and contaminate groundwater;
- presence of radionuclides;
- occurrence of heavy metals (Cd, Cr, Pb, etc.) that may enter into the food chain through potable water and agriculture products [2].

According to Perez-Lopez et al. [12], the amounts of mobile contaminants that could be released for every ton of phosphogypsum are approximately 7×10^2 g Sr, 1.1×10^2 g Fe, 55g Y, 30 g Ce, 12 g Cr, 11g Ti, 5 g Zn, 4 g each of Cu and Pb, 3 g each of V and Cd, 2 g each of As and Ni, and 1 g U. Multiplying these amounts by 100 Mt and 20–25 t/ha, it is possible to calculate risk assessments for phosphogypsum for both estuarine zones (e.g., in a hypothetical stack collapse resulting in spilling of waste and in agricultural soils). Tóth et al. [13] proposed that in some cases (e.g., Hg and Cd), the high concentrations of soil heavy metals attributed to human activity can be detected at a regional level. While the immense majority of European agricultural land can be considered adequately safe for food production, an estimated 6.24%, or 137,000 km^2, needs local assessment and eventual remediation action.

The fluorine compounds emitted by this production can reach the soil by dry deposition, rainfall, or decomposition of plant residues contaminated by fluorine [14]. The fluoride distribution in the environment is controlled by physical–chemical parameters of emission, rain intensity, and soil properties [15]. Fluoride accumulates in the top soil layer because it is retained by the iron, aluminum hydroxide, oxide, and silicate compounds in the soil [16]. The mobility of some elements [17] (such as divalent iron) is reduced by specific and concurrent conditions of pH from near-neutrality to moderately high values and positive potential; opposite conditions favor mobility of potentially toxic metals, such as Cr, As Cd, and Pb.

According to the investigation by Samira et al. [18], groundwater below phosphogypsum dumps and downstream of aquifers showed the highest concentrations of orthophosphates, fluorides, sulphates, acidity, and total dissolved solids, which significantly exceed those of the upstream water.

Thus, it is expedient to establish a general practice aimed at the restoration of degraded areas [19]. It should be noted that for the safety and cost-effectiveness of storage of chemical waste dumps, prediction of deformations, and timely prevention of dangerous geodynamic processes are needed [20].

A large number of studies have been aimed at assessing of the impact of dumps on surface and groundwater resources [21–23]. Nevertheless, bio-monitoring is an important element in the analysis of the dump impact on the ecosystem [21,24].

The aim of this research was to assess the potential influence of a phosphogypsum dump on the environment (soil ecosystem and vegetation) in the Sumy region, Ukraine. To achieve this aim, the following tasks were set:

- study of the soil from different horizons in the area of the phosphogypsum dump;
- study of the terraces of the dump and their biochemical transformations under the plant succession process.

2. Materials and Methods

2.1. Study Area

The phosphogypsum dump is located behind the town of Tokari in the Sumy region (Ukraine), at a distance of 800 (direct measurement)–1300 m (measured via road) from a residential area, and continues to receive new deposits of dihydrate phosphogypsum formed at the Public Joint-Stock Company (PJSC) "Sumykhimprom" location (Figure 1). Within the city of Sumy, dumps of phosphogypsum began in 1972, and today amount to about 15 million tons.

Figure 1. Phosphogypsum terraces from the southeast side of the dump, Sumy region (Ukraine).

Initially, the dump was organized on the site of the natural ravine "Glubokij Yar", at about 40 m deep. The presence of the ravine led to the formation of a dump with displacement of the terraces. As can be seen in Figure 1 terraces form a single frontal surface from the southeast side. The area of the dump is 492 m^2, with a sanitary protection zone of 637 m^2, and the perimeter of the active dump is about 1900 m. The phosphogypsum dump is conserved by loamy soil, and on the west side forms four terraces 12–15 m high, which can easily be seen. A new line of waste forms the upper phosphogypsum area. In order to protect this from drainage, a protective reservoir was built near the dump to its northwest.

As a result of reclamation of the surface of the embankments of the dump, a layer of 20 to 40 cm of loamy soil is, to a certain extent, mixed with mineral particles of phosphogypsum.

The body of the phosphogypsum dump also contains a waste repository of iron sulphate (copperas), which is waste from the production of titanium whitewash at Public Joint-Stock Company (PJSC) "Sumykhimprom" location. This waste repository promotes the sealing of iron sulphate in the body of phosphogypsum waste. However, it does not solve the problem of the accumulation of chemical waste in a given territory, which requires a solution to anthropogenic strain on the environment. The model of the geological structure of the dump is shown in Figure 2.

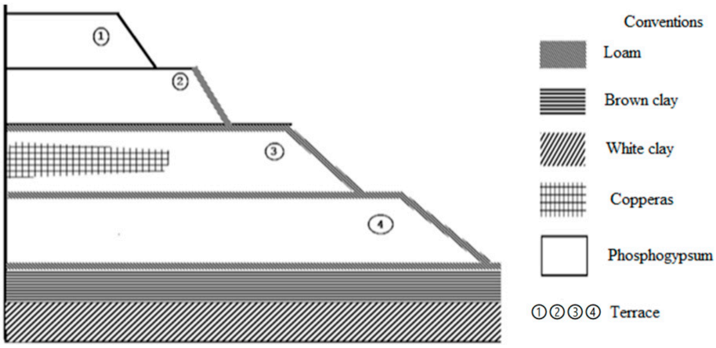

Figure 2. Model of the phosphogypsum dump of PJSC "Sumykhimprom".

The phosphogypsum waste in the dump contains a certain amount of bound and free water. Part of the free water in the process of hydration of stored phosphogypsum causes the chemical–mineralogical transformation of hemihydrates into dihydrates. Part of the moisture, in conjunction with atmospheric precipitation, forms an anthropogenic aquifer, which is infiltrated into the lower layers of the body of phosphogypsum. The bottom of the dump was constructed from natural clay soil, and then built up by dried phosphogypsum, forming original terraces. An anti-filter screen with a clay base filled and compacted with sand protects the ground under the dump.

There is no vegetation on the fresh slopes of the dump, but on the slopes that are freshly covered with loamy substrate, the mosaic of the vegetation cover is observed, from single specimens over a larger area to the overgrowth of one-third of the projected covering of the area.

The dump is blocked by loam and soil, and its vegetation has spontaneously grown. We investigated the patterns of succession of the spontaneous population of the dump with plants and their change over time. In areas (terraces) that were built up more than 10 years ago, the vegetation cover is dense and there are tree species. Vegetation has not yet developed on fresh phosphogypsum, which has been laid more recently.

On the old reclaimed slopes of the canopy, the covering of the grassy perennial vegetation is complete. On the lowest terrace, in addition to the herbaceous annual and perennial vegetation, young trees are found, which indicates ongoing successional changes in plant communities. On the three lower slopes of the dump, the projective covering of the vegetation is maximally complete. On the upper part of the terraces, especially the recent subjects of reclamation, the quantity and species diversity of plants decrease.

2.2. Sampling Stations

The sampling sites located on the dump and at different distances from the dump, are noted as the points in the Figure 3. Their GPS coordinates are listed in Table 1.

Figure 3. Location of sampling sites in the vicinity and terraces of the dump in the Sumy region (Ukraine).

Table 1. GPS coordinates of sampling points.

Sampling Point Number	GPS Coordinates
S1	50°55′03.3″ N 34°57′33.2″ E
S2	50°55′01.1″ N 34°58′05.0″ E
S3	50°55′14.3″ N 34°58′07.1″ E
1	50°55′07.3″ N 34°57′46.3″ E
2	50°55′06.6″ N 34°57′44.1″ E
3	50°55′06.1″ N 34°57′42.3″ E
4	50°55′05.6″ N 34°57′39.8″ E
5	50°55′08.6″ N 34°57′51.0″ E
6	50°55′05.5″ N 34°58′03.0″ E

Figure 4 shows the profile of gray forest soil near the phosphogypsum dump from which the soil samples of different horizons were collected. In the profile of Haplic Luvisols soils near the phosphogypsum dump, the following horizons were distinguished (Figure 4):

- S1 is the litter layer (capacity up to 2 cm). This horizon is also called a surface organogenic horizon, consisting of the remains of plants from recent years. It contains at least 70% by volume of organic matter of varying degrees of decomposition;
- H is humus cumulative with dark gray turf with silicates (7–11 cm);
- E1 is eluvial grayish-white color, with a structural composition of powdered-lime with carbonate inclusions, and contains many plants roots (18–20 cm);
- E2 is transient, eluvial/illuvial-plated nougat with carbonate inclusions, with a compacted, gradual transition (6–10 cm);
- I is illuvial brown color, lobed prismatic (32–35 cm);
- P is soil-forming rock, with a depth of 60–80 cm.

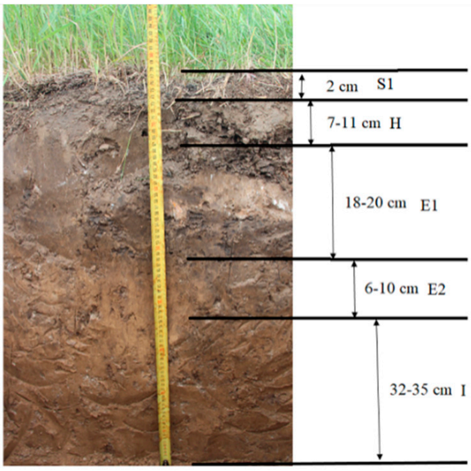

Figure 4. Profile of Haplic Luvisols soil near the phosphogypsum dump (sampling point S1).

Point samples were taken at a test site from several layers or horizons using the envelope method, so that each sample represented a part of the soil typical of genetic horizons or layers of a given soil type. The combined sample was made by quartering (i.e., mixing point samples taken at one test site). For chemical analysis, the pooled sample was composed of five spot samples taken from one sample site. The mass of the combined sample was at least 1 kg. To control pollution with heavy metals, point samples of soil were taken in layers from a depth of 0–5 cm and 5–20 cm, each weighing no more than 200 g. Also, to control soil contamination of territories adjacent to the dump, point samples were taken at genetic horizons along the depth of the soil profile. Spot soil samples designed to determine heavy metals were taken with a plastic spatula. All combined and spot samples were recorded in the journal and numbered [25].

Soil samples for chemical analysis were dried to an air-dried state. Air-dried samples were stored in glass containers. The soil was ground in a mortar with a pestle and sieved through a sieve with a hole diameter of 1 mm. The selected neoplasms were analyzed separately and prepared for analysis in the same way as for soil samples. To determine the gross content of mineral components from a sifted sample, a representative sample of no more than 20 g was taken and ground in a mortar to a powder state [26].

2.3. Methods of Investigation

Fourier Transform infrared spectrophotometry (FTIR) measurements of phosphogypsum and soil samples were carried out on a Bruker Alpha Platinum-Attenuated Total Reflection (ATR) spectrometer (Bruker Optics, Ettingen, Germany). A total of 24 scans were performed on each sample in the range of 4000–400 cm^{-1}.

The basic chemical composition of phosphogypsum and soil samples was determined by X-ray fluorescence analysis (XRF). A SPECTRO iQ II (Ametek, Berlin, Germany) operating with a silicon drift detector (SDD; resolution of 145 eV at 10,000 pulses) was used.

Mineralogical analyses of the samples were carried out by X-ray diffraction (XRD) using a diffractometer Bruker D2 Phaser (Bruker AXS, GmbH, Germany) in Bragg–Brentano geometry (configuration Theta-2Theta), using 1.54060 Å CuKα radiation, Ni Kβ filters, and a scintillation detector at a voltage of 30 kV and 10 mA current. Scan conditions: recording time of about 2.5 h, a step size of 0.04° (2Θ), and step time of 5 s. The XRD patterns were processed using the software Diffrac.EVA v. 2.1. The International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF) database (ICDD PDF—2 Release 2009) was utilized for the phase identification. The pH was analyzed by pX-150 pX-meter (ionometer).

Field research was carried out on the previously planned routes, which specify the boundaries of the contours of plant communities for description of phytocenoses in the territory of the phosphogypsum dump. The cenopopulation (CP) of any plant is a historical and dynamic phenomenon that constantly changes and develops. The CP is a set of individuals of the species within the same phytocenosis, occupying a specific habitat.

The study of CPs occurred in accordance with the standard method described in [27]. All dimensional and quantitative characteristics of plants in a CP vary over a wide range. Indices of a CP, such as total number and density, phytomass, area occupied by the population, projective cover, and age spectrum, are subject to change. The number of a CP is determined by the number of generative individuals and their shoots, potential and real seeds, vegetative productivity, diaspora stock in the soil, seed germination, and survival rate of undergrowth. Seed productivity, real and potential, can vary markedly in different age conditions and over time, depending on weather conditions, the impact of phytophages, etc. In most meadow plants, seed regeneration is limited by the survival rate of seedlings.

Therefore, the analyses of the structure of the CP are a complex formation consisting of several categories [27]:

- composition;
- quantitative participation and the ratio of elements with different properties;
- spatial structure;
- mutual arrangement of plants in space;
- functional structure;
- a set of links between the elements, as well as between the system and the environment.

Fluctuations in the number of seedlings in a CP are significant both during the season and over a span of years, and numbers range from 1–2 to 100–1000 per m^2. An indicator of dynamic processes can be a change in the age spectrum of a CP. The populations of different species have different degrees of dynamism: (1) Population waves move gradually, while the type of age spectrum does not change and remains full-term. This occurs with regular, but relatively small, replenishment of young individuals. (2) Population waves move quickly, and the age spectrum can be broken and incomplete. The great lability of all population indicators is characteristic of pioneering plants, capable of very quickly capturing vacant areas, but also freeing them when crowded out by competitive species. Various transitions are distinguished between these two types of dynamics.

3. Results and Discussion

3.1. Phosphogypsum Characterization

Powder X-ray diffraction was used to characterize the phosphogypsum samples. The diffraction pattern of the representative sample is shown in Figure 5. All samples from different horizons (terraces I–IV) exhibited an almost identical composition, excluding the quartz (SiO_2) presence in the sample from the second terrace. The results confirmed the major presence of calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$) together with brushite ($CaPO_3(OH) \cdot 2H_2O$). As mentioned above, silicon oxide (SiO_2) was also present. The dehydrate or hemihydrate phase of sulphate is missing, so it can be stated that the samples from all horizons were completely hydrated.

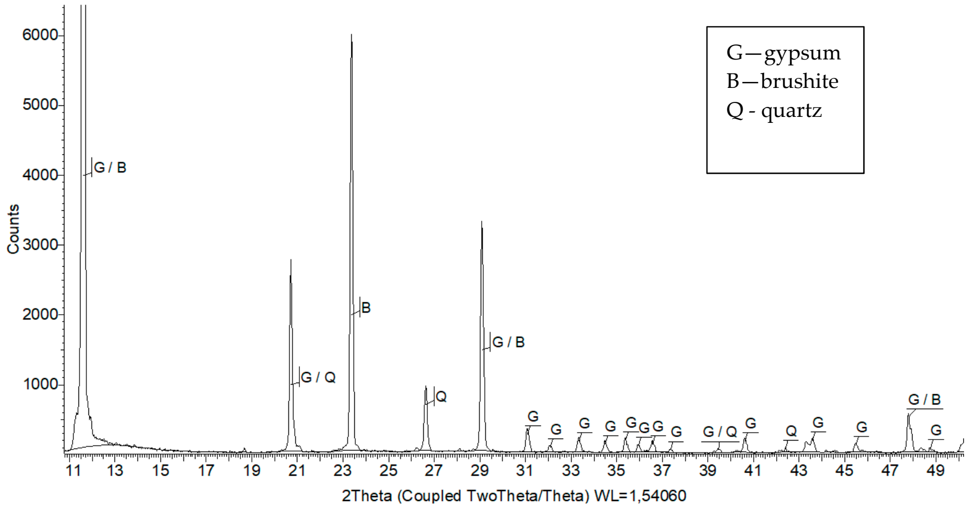

Figure 5. The X-ray diffraction pattern of phosphogypsum (sampling point 1, terrace I).

X-ray fluorescence analysis of the samples from all horizons of the phosphogypsum dump was also performed. The overall results are listed in the Table 2. The results of the analyses support the statements based on X-ray diffraction, thus the samples exhibit relatively identical composition and the presence of silicon oxide in the second horizon is several times higher than in the other three horizons, which is probably caused by inflation of soil particles.

Table 2. Composition of phosphogypsum in terms of oxides (%).

Sample	Al_2O_3	SiO_2	P_2O_5	SO_3	CaO	Fe_2O_3	SrO	F
1. Terrace	<0.004	1.54	0.78	60.9	34.37	0.257	1.782	0.56
2. Terrace	0.167	19.87	0.31	51.8	27.63	0.078	0.059	0.21
3. Terrace	<0.004	2.68	1.19	60.5	35.46	<0.0009	0.112	0.9
4. Terrace	<0.004	1.23	0.72	61.7	35.99	0.183	0.123	1.33
5. Fresh	<0.004	2.59	1.28	60.2	35.75	<0.0009	0.112	0.66
6. Internal	<0.004	1.22	0.7	61.5	36.39	0.023	0.093	2.27

The largest amount of strontium was found in raw phosphogypsum from terrace 1, which had just entered production. Its presence is associated with the process of production of phosphoric acid, and more precisely, with raw materials (phosphorites). Changes in the quality of raw materials affect the change in the content of impurities in phosphogypsum, particularly strontium.

3.2. The Study of the Soil from Different Horizons in the Territory Near the Phosphogypsum Dump

A subtype of grey forest soils, characterized by a large, deep, fairly loose, granular, and densely permeated humus-accumulative plant root horizon (humic content from 3%–4% to 6%–8%), formed over a larger area around the dump, which is explained by the predominance of the salinization process. Salinization of the soil with neutral salts (for example, chlorides and sulphates) leads to the formation of a neutral and slightly alkaline reaction of the medium (pH = 7.2), but when exposed to phosphogypsum, which has an acid reaction, the soil pH becomes acidic. Soils are characterized by a lower acidic pH value (on average, from 5.8 to 6.5) and the absence or masking of transitional horizons along the soil profile, weakly expressed by the brown-colored eluvial and well-defined illuvial horizon.

The group composition of humus in grey forest soils is characterized by an insignificant predominance of humic acids in the composition of soil humus, and the saturation of the bases with 18–30 mg equivalent per 100 g of soil. In the illuvial horizon, the absorption capacity is markedly increased. The eluvial horizon is fairly dense, mostly of a nut-prismatic structure.

Behind the sanitary protection zone of the dump are agricultural lands, where the upper horizons of the soils, primarily the humus-accumulative horizon and part of the eluvial horizon, are impacted by plowing. Although grey forest soils differ from light grey soils, with slightly better agronomic indices, they are united by acid reaction in the upper horizons, unsaturation of bases, and low content of nutrients.

Soil humus possesses high sorption properties, forming complex compounds in soils with a high content of heavy metals. An essential factor determining the behavior of chemical elements in soils is the presence of acidic, water-soluble, and therefore mobile fulvic acids, which cause the process of intensive leaching out of the soil profile of many trace elements (Fe, Mn, Zn, Cd, Pb, and Sr), including heavy metals. This process is also characteristic of grey forest soils.

The diffractometric analysis of these soils did not reveal the presence of compounds coming from the phosphogypsum dump. The samples from different horizons (H, E_1, E_2, and I) exhibited comparable results, except for the missing phase of calcium carbonate in horizon I. A representative pattern is shown in Figure 6. The patterns confirmed a major presence of silicon oxide (SiO_2), together with alumino-silicate compounds (illite and nontronite). As mentioned above, calcium carbonate was also present in horizons H, E_1, and E_2. None of the dominant compounds listed in the diffraction pattern of phosphogypsum (calcium sulphate dihydrate and brushite) were found.

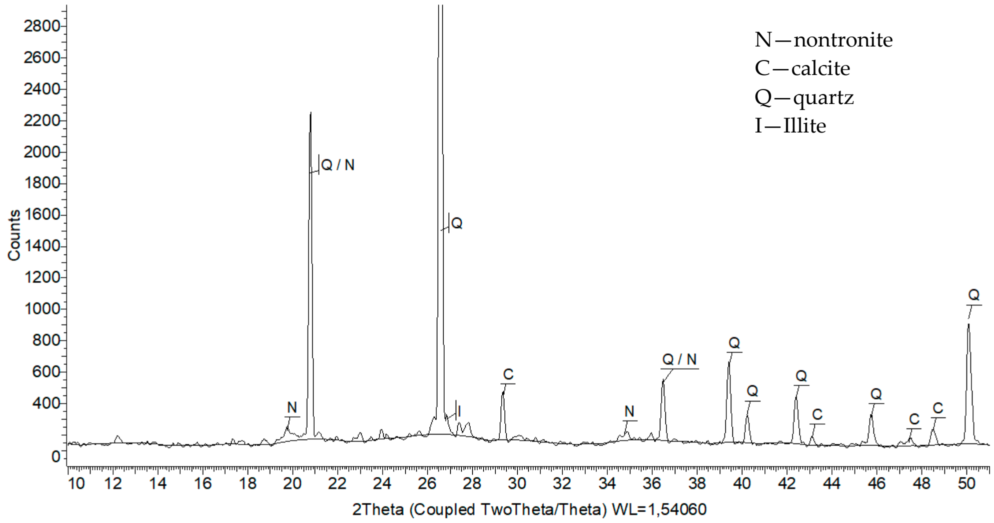

Figure 6. The X-ray diffraction pattern of a soil sample (sampling point S1) (horizon H).

Based on the results from the XRF analysis (Table 3), it can be stated that the samples of soils coming from the profile of Haplic Luvisols soil were mostly not significantly affected by the phosphogypsum dump. From Table 3, a higher concentration of phosphorus and sulfur in the upper horizons can be observed. Moreover, the same results were also achieved in the soil samples located around the phosphogypsum dump (samples S1, S2, and S3). The analysis of soil samples from sampling points S2 and S3 was taken from horizon H, which was generally most susceptible to the anthropogenic influence and the accumulation of pollutants.

Strontium is ubiquitous in nature and one of the most abundant of the trace elements in surficial deposits and rocks, acting as a proxy for Ca because both are alkaline earth elements with a similar ionic radius and the same valence [28]. Strontium is easily mobilized during weathering, especially in oxidizing acid environments, and is incorporated in clay minerals and strongly fixed by organic matter. The Sr content in soil is highly controlled by parent rocks and climate, and therefore, its concentrations ranges from 50 to 1000 mg.kg^{-1} [29]. Nevertheless, content of strontium can be associated with the influence of the phosphogypsum dump in the Sumy region, which requires further monitoring. The soil fluoride levels measured in this study were comparable to the average soil fluoride of soils globally [24].

Table 3. Chemical composition of soil horizons from Haplic Luvisols soil (sampling point S1) and soils around the phosphogypsum dump (in %).

Sample	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	Fe_2O_3	SrO	F
S1 (S1)	1.231	9.19	49.98	0.17	0.31	1.71	0.50	4.07	0.019	<0.05
H1 (S1)	1.048	7.65	56.09	0.42	0.53	1.34	3.19	2.33	0.018	0.06
E1 (S1)	1.104	8.25	57.4	0.46	0.55	1.47	4.13	2.61	0.022	0.05
E2 (S1)	1.094	8.159	55.22	0.44	0.35	1.52	3.77	2.66	0.021	0.05
I1 (S1)	1.715	10.79	61.63	0.16	0.10	1.90	0.96	3.61	0.012	0.05
H2 (S2)	1.067	8.54	58.85	0.16	0.17	1.64	0.74	2.66	0.016	<0.05
H3 (S3)	1.073	8.83	64.66	0.28	0.20	1.81	1.13	2.77	0.018	<0.05

Based on the results from XRF analysis (Table 3), as well as the diffraction pattern, the chemical compositions of soil horizons indicate the presence of alumino-silicates in the studied samples. Figure 7 shows the infrared spectra of soil horizons. The absorption peaks at wavenumbers 3620, 3363, and 1633 cm^{-1} are assigned to H–O–H stretching vibrations of water molecules that are weakly hydrogen-bonded to the Si–O surface [30]. The spectra of the soil horizons show an intensive band at 1003 cm^{-1} attributed to the Si–O stretching vibrations, and at 693 and 453 cm^{-1}, which could be assigned to Si–O–Al (octahedral Al) and Si–O–Si bending vibrations, respectively. Another characteristic band of amorphous silica was observed at 776 cm^{-1} [31]. In addition, three horizons revealed the presence of an absorption band at 1434 and 875 cm^{-1}, referring to the stretching vibrations of CO_3 groups [32].

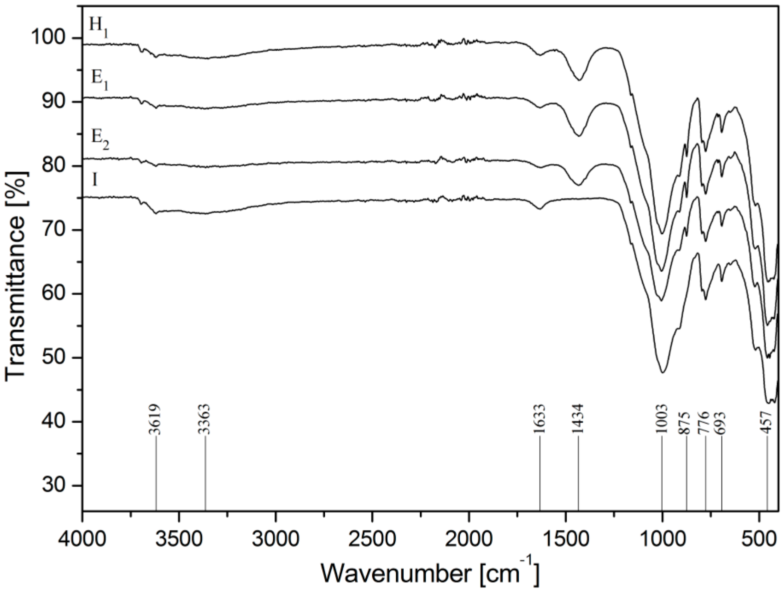

Figure 7. Infrared spectra of soil horizons (sampling point S1).

3.3. The Study of Biochemical Transformations of the Technogenic Array of Phosphogypsum

It has been established that for all phosphogypsum samples, irrespective of the residence time in the dump, an increased acidity is characteristic [33]. Thus, the aqueous extract of hydrolyzed phosphogypsum at a temperature of 24 °C had a pH of 2.3–2.8 for fresh phosphogypsum from a new dump taken from above the platform. For phosphogypsum stored in the dump, depending on the storage terrace, the pH value ranged from 3.8 to 5.8, depending on the age of the terrace [34]. The changes in the pH of the aqueous extract of phosphogypsum, depending on the terrace, and hence the residence time in the heap, are shown in Figure 8.

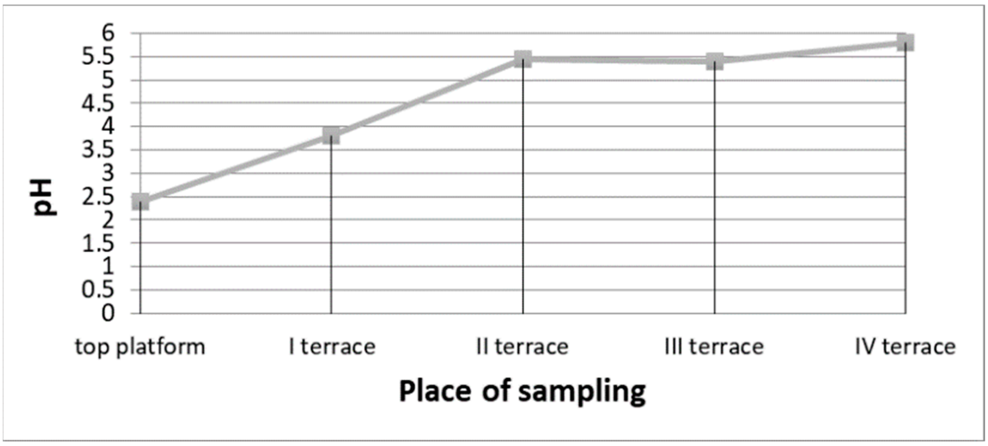

Figure 8. The pH values of an aqueous extract of phosphogypsum samples depending on the place and time of stay in the dump.

The low pH level of fresh phosphogypsum samples can be due to the presence of water-soluble fluorine compounds (possibly H_2SiF_6, Na_2SiF_6, K_2SiF_6, and HF), traces of non-void phosphoric acid and its salts, and sulfuric acid. The decrease in acidity in older terraces is explained by the gradual elution or evaporation of acidic compounds from the phosphogypsum stored earlier in the terrace under the influence of various natural factors.

The concentration of phosphorus compounds decreases with the storage time of phosphogypsum, which is mainly due to the gradual transition of its compounds into water-soluble forms and washing out into the dump or the soil of the adjacent territories under the influence of hydraulic forces or atmospheric precipitation.

It should be noted that the inclusion of silicon in the phosphogypsum structure occurs during deformation and fracture of mineral components, as the sealing load on the phosphogypsum layers increases in the dump. The change in the Sr content in the phosphogypsum samples (Table 2) can depend both on the composition of raw materials used for the production of fertilizers, and possibly the tendency to migrate its compounds.

The conducted observations in the territory of the phosphogypsum dump showed that over time (more than 10 years), as a result of natural processes of soil formation and passages of succession, a vegetative crust occurred with a thickness of no more than 3–4 mm on the surface of non-cultivated phosphogypsum embankments [35]. Open areas of the phosphogypsum dump act as a substratum for settling on their surface, primarily by algae and moss, and in the future, gradually, higher herbaceous vegetation (Figures 9 and 10).


(**a**) (**b**)

Figure 9. Surface layer of non-cultivated areas of the phosphogypsum dump with settlements of algae (**a**) and moss (**b**).

Figure 10. *Calamagrostis epigejos*, which dominates in restorative plant groups on the surface of the phosphogypsum dump.

The walls of the heap, after lying dormant with a mixture for reclamation, unlike open areas, are easily and quickly covered with light-responsive grassy vegetation. The surface roughness of phosphogypsum in the form of depressions and cracks, and also its significant moisture capacity, contributes to the settlement of the heap by plants, so phosphogypsum also contains a sufficient amount of residual phosphorus, sulfur, calcium, and other substances that act as macro- and micro-elements, becoming a good substratum, especially for ruderal and meadow vegetation. Pietrzykowski et al. [36]

revealed that wood small-reed had been proven to be extremely resistant to sulfur contamination and the relatively high salinity of soils, and occurred even on extremely sulphated soils.

On the freshly formed open slopes of the phosphogypsum dump, vegetation is absent; on the slopes of the fresh loamy substratum, mosaic vegetation is observed, from single specimens to overgrowth of one-third of the projected covering of the area. On old, reclaimed loams and slopes of the canopy, the projective covering of the herbaceous perennial vegetation is complete; on the lowest terrace, apart from the grassy annual and perennial vegetation, young trees have started to settle, which indicates the slow progressive succession changes in plant groups. Hou et al. [37] reported that changes in plant communities are based on their visibility, and plants are usually used to predict the success of the restoration of degraded environments. On the three lower slopes of the heap, the projective covering of the vegetation is as complete as possible; in the upper part of the terraces, especially of those recently subjected to reclamation, the quantity and species diversity of plants decreases. The annual and perennial herbaceous plants are dominant on the reclaimed slopes of the phosphogypsum dump of the PJSC "Sumykhimprom" (Table 4).

Table 4. Herbaceous plants that dominate the reclaimed slopes of the phosphogypsum dump of PJSC "Sumykhimprom".

Named Family of Plants	Representatives
Gramíneae	*Calamagróstis epigéios* *Elytrigia repens* *Echinochloa crusgalli* *Setaria viridis* *Poa annua*
Fabaceae	*Lotus corniculatus* *Trifolium pratense* *Trifolium repens* *Trifolium ochroleucum* *Melilotus officinalis*
Compósitae	*Tussilago farfara* *Erigeron canadensis* *Achillea millefolium* *Erigeron annuus* *Tanacétum vulgare* *Artemisia vulgaris* *Sónchus arvénsis* *Cirsium arvense*
Polygonaceae	*Polygonum aviculare*
Onagraceae	*Onagra biennis*
Plantaginaceae	*Linaria vulgaris*
Salicaceae	*Populus tremula*
Betulaceae	*Betula pendula*
Leguminosae	*Robinia pseudoacacia*

On the lower terraces (third and fourth), tree forms have begun to settle, represented mainly by *Populus tremula*, *Populus alba*, *Betula pendula*, and *Robinia pseudoacacia*.

The stage of the formation of a permanent herbaceous cover with a full projection of the substrate coating lasts at least a decade for extreme substrates, including phosphogypsum.

The acidity of the environment affects the plant growth and species dominance, and this effect is limited by a number of factors:

- the features of the technogenic relief of the dump;
- the high concentration of certain chemical elements (calcium);
- the inconstant availability of water;
- a small length along the depth of the recultivating substrate.

The formation of tree stands was observed mainly 20 years after dumping. This process of self-growth is affected by the high acidity of the substrate and the high concentration of chemical elements, which is mainly determined by the intake of chemical elements and their compounds from the dump [34]. Figure 11 shows a general diagram of the process of self-growth vegetation in the dump.

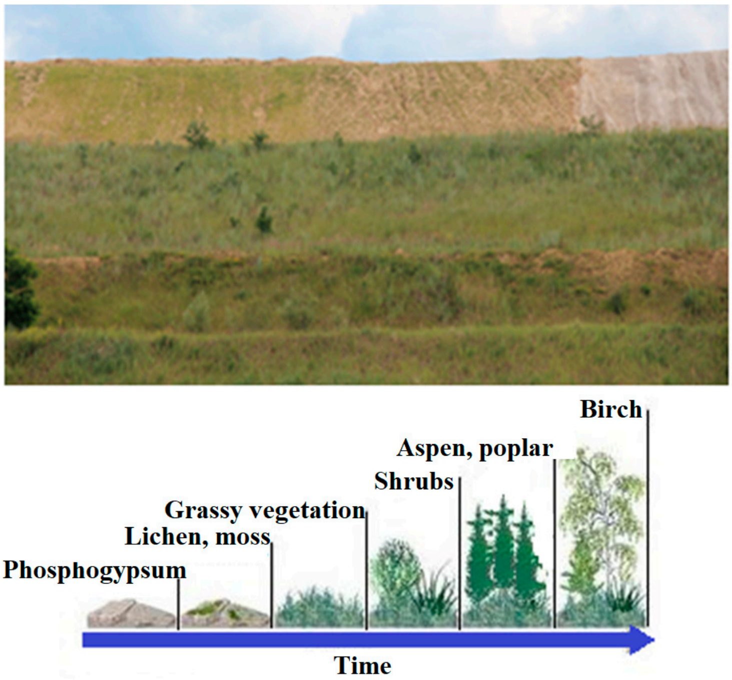

Figure 11. Plant formation occurring naturally in the process of succession.

The degree of projective coverage on the terrace 4 is almost 95%, then it decreases on terrace 3 (75%), terrace 2 (45%), and terrace 1 (5%). The upper deck is fully open, without vegetation. This trend in the blade covering depends on the arrival of new lots of fresh phosphogypsum, which contributes to the uneven distribution of vegetation. Thus, terrace 4 is the most reclaimed.

A substrate is formed, which is to be populated with living organisms, primarily microorganisms and plants [35,38]. According to Yakhnenko [39] and Shulipa et al. [40], microorganisms carry out the transformation (oxidation, reduction) of a number of inorganic compounds of the substrate, including mineral particles of phosphogypsum, transferring their components more or less conversely, depending on the conditions (pH, Eh).

The roots of plants gradually settle on the surface of the substrate of the dump and absorb substances directly from the soil solution and in contact with the particles of the soil-absorbing complex. Cations and anions that are in the absorbed state on colloidal particles of the soil are exchanged for ions adsorbed on other colloidal particles or on the surface of the root cells [41]. Thus, the intake of cations K^+, Ca^{2+}, and Na^+ are exchanged by micelles for proton H^+, and anions of NO^{3-}, $SO_4{}^{2-}$, $PO_4{}^{3-}$, and others are exchanged for anions of organic acids (malic, citric, and oxalic) directly by the cells of the root. Particularly effective is absorption by contact exchange, in which there is an exchange of ions between colloidal soil particles and plant roots without entering them into the soil solution. Ions are adsorbed on the surface of the cell membranes of the root rhizoderm and are absorbed by the plant [42].

The removal of a certain element from the minerals of the substrate is carried out in the process of biological and physical–chemical (exchange) absorbency. As a result, either the complete dissolution of the mineral or the replacement of the mineral ions by hydrogen ions occurs, releasing the roots in the composition of organic acids without destroying the crystal lattice of the mineral.

Thus, organic compounds directly or indirectly interact with mineral particles of phosphogypsum, destroying the crystal lattices, transferring elements from one form to another with a change in valence and mobility. The chemical elements that are part of the phosphogypsum, or associated with it, are not necessarily withdrawn in proportion to their content and the relationship in the material. Biological weathering can lead to the transformation of this mineral into another due to a change in chemical composition with selective absorption of elements [39,43,44].

The reactions of the soil solution, its concentration, and its ratio of salts have a particularly strong influence on the supply of nutrients [39]. For most plants, a weak acid (pH 5–6) or neutral conditions are most favorable. In slightly acidic soils, which include the substrate of the reclaimed terraces of this dump, nutrients such as phosphorus, iron, zinc, manganese, boron, and others are more easily assimilated by plants, due to the lower pH values of phosphogypsum.

We suggest that the large concentration of calcium, due to its presence in phosphogypsum, allows plants to adapt to the conditions and continue to populate the surface of the dump. It should also be taken into account that Ca^{2+} in high concentrations can inhibit excess intake of K^+, Na^+, or Mg^{2+} by the plant, and vice versa.

4. Conclusions

Physical–chemical analyses were performed to estimate the impact on the surrounding soil of a phosphogypsum dump. The content of strontium can be associated with the influence of the phosphogypsum dump in the Sumy region, which requires further monitoring. The change in the Sr content in the phosphogypsum samples can depend both on the composition of raw materials used for the production of fertilizers, and possibly, the tendency to migrate its compounds. It is necessary to take into account the change in the acidic–alkaline balance, which can affect the future migration processes of various elements in the soil.

The possibility of colonization by living organisms of the substrate was analyzed after the reclamation process of phosphogypsum in the dump (Table 4). It can be concluded that despite the high acidity of phosphogypsum itself (from 2.5 to 5.3, depending on the age of storage in the dumps) and the acidity of the substrate (from 6 to 6.5), a high calcium content in a part of the dump substrate can neutralize the effect of low acidity. It is necessary to continue comprehensive monitoring of the impact of the phosphogypsum dump on the environment. Therefore, carrying out a complete recultivation of the dump is an important task, taking into consideration the studied patterns of the development of ecological groups of plants under the succession process.

Further research will be focused on the estimation of new opportunities for phosphogypsum recycling, since all new batches of phosphogypsum are transported to a landfill, which requires an expansion of the dumping zone.

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