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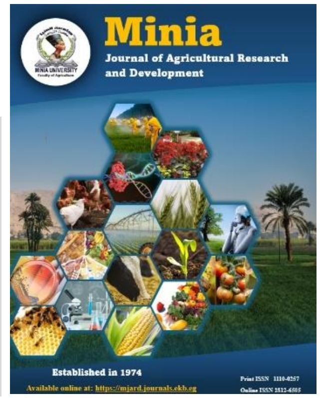

Review of phosphogypsum as a soil conditioner and/or fertilizer under arid conditions

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ABSTRACT

Phosphogypsum is an environmental concern and an opportunity to encounter soil abiotic stresses under arid conditions. The objective of this review is to present an overview of the literature on phosphogypsum (PG) with an emphasis on its agricultural use in Egypt and worldwide, the chemistry of the substance and environmental potential issues that might arise if its leachates encounter soil environment. Phosphogypsum is produced in large quantities by the phosphate industries and is frequently dumped in open areas or released into aquatic habitats. It has detrimental effects on both the environment and human health. However, phosphogypsum is used in a variety of industries, including agriculture for fertilization and soil amendment, the manufacture of cement and bricks, and road construction. Due to the different quantities of heavy metals and radionuclides present in PG, all these uses raise environmental concerns. The advantages to the phosphate industry and costs to the environment and pollution harm must be considered by policymakers. There are a number of variables that affect the usage of PG in agriculture, including PG composition, soil type, area, crop and environmental restrictions. Therefore, each country should carry out independent study specific to its agroecosystems and agricultural regions.
Keywords: Phosphogypsum, Heavy metals, Radionuclides.

INTRODUCTION

This review will go through the chemistry of phosphogypsum as well as the environmental issues connected to its storage in waste facilities or usage as a soil amendment for agriculture. An overview of the physicochemical characteristics of phosphogypsum is also included in this literature review, along with some new conclusions about the consideration of sedimentary and magmatic phosphate rocks and how the processing parameters of these **PGs** outline the **PG** composition. Additionally, this critical review emphasizes offering insightful observations to categorize **PG** impacts by their properties affecting

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various soil-plant and aquatic ecosystems. This is especially important if **PG** is being researched for future usage as a fertilizer and/or soil conditioner without posing any environmental problems. Therefore, this literature review is grouped under the following headings:

1. **Phosphogypsum production and characteristics.**
    - 1.1. Sedimentary phosphate rock(**s-PG**) and magmatic phosphate rock (**m-PG**).
    - 1.2. Phosphogypsum chemical and mineralogical properties.
    - 1.3. Phosphogypsum physical characteristics.
2. **Phosphogypsum radioactivity and storage environmental risks.**
    - 2.1. Impacts of heavy metals in phosphogypsum (**PG**) on agroecosystem.
    - 2.2. Impacts of radioactive impurities in phosphogypsum (**PG**) on agroecosystem.
3. **Phosphogypsum usage in agriculture.**
    - 3.1 Phosphogypsum usage as a soil conditioner.
    - 3.2 Phosphogypsum usage as a fertilizer.
    - 3.3 Phosphogypsum impacts on soil physical properties.
    - 3.4 Phosphogypsum impacts on soil chemical properties.
    - 3.5 Phosphogypsum impacts on soil biological properties.

1. Phosphogypsum production and characteristics.

There are to main ways to make phosphoric acid from phosphate ore: the wet process, which uses potent mineral acids to break down the phosphate, and the dry process, which involves heating the ore in an electric furnace to create elemental phosphorus as a bridge chemical (Abouzeid, 2008). The most common method of producing phosphoric acid nowadays is the wet process, which typically involves treating phosphate rock with sulfuric acid (Bilal *et al*., 2023). Significant amounts of hydrated calcium sulfate, often known as **PG**, are produced because of this process. Calcium sulfate is converted to dihydrate, hemihydrate or anhydrite depending on the temperature, phosphate content, and sulfate content of the Solution. Due to its popularity and adaptability in treating various types of phosphate rock, the dehydrate (DH) process is regarded as a reliable method for producing phosphoric acid on an industrial scale (Abdelouahhab *et al*., 2022).

Gypsum (dihydrate: $CaSO_4$.$2H_2$ O), which is calcium sulfate, is produced in this method at a temperature of between 70 and 80 ^{0}C with a moderate acid content. Wet phosphoric acid (WPA) is the common name for phosphoric acid produced by the dihydrate method. The Hemihydrate method (HH) uses somewhat higher temperatures (90-110 ^{0}C) to treat phosphate rocks (Jansen *et al*., 1984; Bilal *et al*., 2023). By using this process, **PG** is Produced, however it contains radioactive and heavy metal contaminants. Although the HH method uses less grinding, the recovery rate of P_2O_5 is a little bit lower (Abu-Eishah and Abu-Jabal, 2001; Bilal *et al*., 2023).

Phosphogypsum (**PG**) is the main by-product created when calcium phosphate (apatite) ore is converted into phosphoric acid, a step in the production of phosphate fertilizer (Bilal *et al*., 2023; Mahmoud et al., 2023; Qin *et al*., 2023). In the production of wet phosphoric acid (WPA) phosphate rock (pre-concentrated phosphate ore) is digested with sulfuric acid at a temperature of around 80 ^{0}C. Worldwide, the manufacture of phosphate fertilizer results in the creation of almost 300 million tons of phosphogypsum (**PG**) each year (Bilal *et al*., 2023; Qin *et al*., 2023). Only 14% of this **PG** is subjected to additional processing, while approximately 58 % is stacked and 28 % is released into coastal seas (Bilal *et al*., 2023; Qin *et al*., 2023).

With the WPA approach and sulfuric acid, **PG** can be produced as a dihydrate ($CaSO_4$. $2H_2O$), as opposed to other processes that produce hemihydrates ($CaSO_4$.O.5H_2O) or anhydrite ($CaSO_4$). Typically, 0.6 ton of concentrated sulfuric acid is used to attack one ton of phosphate rock, producing 0.4 tons of phosphoric acid and 1.2 tons of **PG** (Van Selst *et al*., 1997; Bilal *et al*., 2023). Consideration of **PG** as a by-product of WPA production that could be used in agriculture and construction to replace natural gypsum has grown in interest due to the importance of calcium sulfate dihydrate ($CaSO_4.2H_2O$) in industrial and agricultural fields as well as potential environmental risks associated with **PG** stacking and disposal in coastal waters (Haneklaus *et al*., 2022; Jia *et al*., 2022; Bilal *et al*., 2023).

Additionally, phosphate ore can have high quantities of rare earths and uranium, two valuable trace elements (Haneklaus, 2021; Ramirez *et al*., 2022; Akfas *et al*., 2023). Uranium transfers primarily (> 80 %) to the phosphoric acid product during wet-phosphoric acid (WPA) production using sulfuric acid, whereas rare earths primarily (> 80 %) transfer to the **PG** matrix (Rutherford *et al*., 1994; Bilal *et al*., 2023). Research into the potential recovery of rare earths from **PG** and the techno-economic viability of uranium recovery from WPA has been sparked by considerations of the circular economy in the processing of phosphate rock, increased demand for uranium and rare earths, as well as geopolitical supply risks (Ye *et al*., 2019; Liu and Chen, 2021; Bilal *et al*., 2023).

The creation of sustainable techniques for the entire (zero-waste) usage of **PG** is the only rational way to handle this material in the context of current rules and circular economy concerns (Bilal *et al*., 2023). It is not surprising that many researchers have already investigated and reviewed potential zero-waste strategies for **PG** utilization, given the significant amounts of PG tailings produced each year (El-Didamony *et al*., 2013; Rashad, 2017 ; Mohammed *et al*., 2018; Cao *et al*., 2021 ; Bouargane *et al*., 2023; Qin *et al*., 2023).

The trace heavy metals (especially the radioactive ones) linked with **PG** are typically the limiting factor to zero-waste **PG** consumption, although being present in relatively small quantities by weight and volume. According to Macias *et al*. (2017) the amounts of these trace elements in the **PG** are mostly dependent on the processing of phosphate ores and the chemical processes (typically, the WPA process with sulfuric acid) used to produce phosphoric acid. Thus, a thorough understanding of the trace elements present in various **PG** stacks is of utmost importance when creating zero-waste **PG** utilization techniques that should be relevant to a variety of locations throughout the world.

Despite the emphasis in recovering rare earth elements (REE), gypsum still makes up the majority of **PG** (approximately 96 % Wt.).The most prevalent and important trace elements in **PG** , depending on the kind of phosphate ore, are traces of Cd, Zn, Pb, Hg, Zr, Cu, Ba, REEs,Y,Th, U and ^{226}Ra (which emits ^{222}Ra). According To Several Studies El-Bahi *et al*. (2017); Hakkar *et al*. (2021); Arhouni *et al*. (2022) The radioactivity of the **PG** is typically 3- 4 times greater than that of the phosphate ore. When producing WPA, **PG** often forms slurry; the ensuing acidic process fluids are recycled. The trace elements in the PG are further concentrated by the recycling of the process fluids, and the substance is acidic due to the acids used in the synthesis of WPA. Additionally, there is fluorine from the phosphate ore (Bilal *et al*., 2023).

1.1. Sedimentary phosphate rock (s-PG) and magmatic phosphate rock (m-PG).

All phosphogypsum (**PG**) samples have a high concentration of Na_2O (rock phosphate initials formed nepheline ($Na_3KAL_4Si_4O_{16}$), while **PG** samples made from sedimentary phosphate rock (s-**PG**) typically have higher SiO_2 contents than **PG** samples made from magmatic phosphate rock (m-**PG**) (Abbes *et al*., 2020). In comparison to sedimentary ores treated with sulfuric acid, volcanic apatite-derived m-**PG** has substantially greater Y, Zr, Cu and Ba concentrations. For instance Cd, Hg and Zn concentrations in Tunisian **PG** (an s-**PG**) are comparatively high (Abbes *et al*., 2020). According to Rutherford *et al*. (1994) about 80 % of the Cd content goes preferred to phosphoric acid. When using clean sulfuric acid, the trace elements primarily depend on the place of origin of the ore whereas the primary components of the **PG** composition change depending on how the phosphate rock is treated (Bilal *et al*., 2023).

The fact that some trace elements were added to the **PG** by the sulfuric acid, which did not come from the phosphate rock itself, demonstrates that the acid employed for digestion can itself be a source of impurities (Bilal *et al*., 2023). For s-**PG** and the mixed **PG** (m-**PG** and s-**PG**), radioactive elements, most notably ^{226}Ra, ^{232}Th and ^{40}K, provide the normal radioactivity indexes (I = (Ra /300) + (Th /200) + (K/3000)) of 1.33-2.59. As a result, m-**PG** and mixed **PG** frequently exhibit radioactivity indices (I< 1), especially for m-**PG** from Russia and some **PG** from China, which typically exhibit relatively low radioactivity indices of 0.24-0.45 (Bilal *et al*., 2023). The quantities of radiation and contaminants have been reduced nonetheless merits to advancements in **PG** treatment. To eliminate contaminants and further lower the radiation levels, various treatment techniques may be used, including washing, filtering, calcination, neutralization, leaching and purification. The specific procedure employed is determined by the **PG**`s composition and the intended end use (Bilal *et al*., 2023).

1.2 Phosphogypsum chemical and mineralogical properties.

The chemical and mineralogical properties of phosphogypsum are influenced by the type of wet process employed, the efficiency of plant operation, the age of the stockpile and any pollutants that may be introduced into the phosphogypsum at the manufacturing plant (Arman and Seals, 1990). Because phosphogypsum contains a little over 90% gypsum, calcium and SO_4^{-2} predominate in its composition (Berish, 1990). Due to residual phosphoric acid, sulfuric acid and fluoride acids present in the porosity, phosphogypsum is acidic.

PG is primarily made up of $CaSO_4$ and $2H_2O$, along with impurities such free phosphoric acid, phosphates, fluorides and organic compounds (IAEA, 2013). Three chemical compound classes are typical of organic materials: linear hydrocarbons, isoprenoids and hopanes (Mechi *et al*., 2016). Statistics from the International Atomic Energy Agency (IAEA) show that **PG** contains significant amounts of SO_4, CaO, SiO_2 and P_2O_5. Depending on the type of wet phosphoric acid treatment used, the primary elemental composition of phosphogypsum varies. Minor element composition in phosphate rock might differ greatly depending on where it was mined. Ag, Au, Cd, Se, S, certain light rare earth elements and Y are all present in phosphogypsum at higher overall amounts than in shale (IAEA, 2013). Phosphogypsum from central Florida included more As, Sb, and Mo than phosphogypsum from Alberta, but less Ag, Ba, Cd and Sr. According to Bilal *et al*. (2023) phosphogypsum could not be classified as a toxic waste in terms of total concentrations because it was neither corrosive (pH was>2 and 12.5) nor did it exceed the allowable toxic elemental criteria for toxic hazardous waste set by the E.P.A. (As, Ba, Cd, Cr, pb, Hg, Se and Ag).

The raw material for making phosphoric acid, a vital component of fertilizer, is phosphate rock, a geological deposit that includes phosphorus. It is mainly discovered in igneous rocks, guano, and marine sedimentary deposits. According to Pufahl and Groat (2017); Bilal *et al*. (2023) igneous deposits account for between 20 and 25 percent of the world`s phosphate resources, whereas roughly 75 percent come from sedimentary phosphate rocks. Despite having a high phosphate concentration, guano cannot be used globally because there are not enough supplies (Pufahl and Groat, 2017; Bilal *et al*., 2023).

1.3. Phosphogypsum physical characteristics.

Physically, phosphogypsum is comparable to natural gypsum. A grey, moist, fine-grained powder, silt or Silty-Sand material known as phosphogypsum has a maximum size range between 0.5 and 1.0 mm and contains 50–75 % of particles that are smaller than 0.075 mm (IAEA, 2013). Phosphogypsum has a specific gravity that ranges from 2.3 to 2.6. Typically, the moisture content is between 8% and 30%. According to SENES (1987) particle density ranges between 2.27 and 2.40 g cm^3. Between 0.9 and 1.7 g cm^3 of bulk density have been reported to exist within phosphogypsum stacks (Vick, 1977). Most of the particles in phosphogypsum are typically of medium to fine grained size. According to Bilal *et al*. (2023) medium-sized particles (0.250- 0.045 mm in diameter) made up 36–60 % of the mass of seven samples of phosphogypsum, while 0.045 mm or less in diameter made up between 24% and 49% of the bulk material.

In comparison to mined natural gypsum, phosphogypsum dissolves at a faster rate due to its fine particle size (Keren and Shainberg, 1981). Gypsum`s solubility product was calculated by Harvie *et al*. (1984) to be 2.63×10^{-5} at 25 ^{0}C. According to SENES (1987) the vertical hydraulic conductivity of phosphogypsum ranges between 1×10^{-3} and 2×10^{-5} cm s^{-1}. The amount of free water in phosphogypsum may vary greatly depending on how long it has been allowed to drain after being sluiced to the stack and on the local weather conditions. By drying at 65 ^{0}C for 5 hours, the free water content of phosphogypsum is frequently ascertained. When drying takes place above 60 ^{0}C, this approach may cause some water to be lost from hydration. Because drying at a lower temperature can take a long time (Averitt and Gliksman, 1990) Advise drying at 50 ^{0}C for 5 hours while under vacuum.

2. Phosphogypsum radioactivity and storage environmental risks.

Phosphogypsum is radioactively enriched compared to most geological and soil components because it is produced from phosphate rock, which has relatively high amounts of naturally occurring radionuclides. The radioactivity is produced by two decay series that are produced by the parent radionuclides U -238 and Th-232. In addition, phosphogypsum (**PG**) often contains trace levels of U. During the acidulation process, most of the U from phosphate rock is partitioned into the phosphoric acid (Hurst and Arnold, 1980); however, the partitioning is influenced by redox conditions and the presence of other ions. According to Gorecka and Gorecki (1984) organic chemicals in processed phosphate rock tend to raise the phosphogypsum U concentration. It is easier for uranium to dissolve from phosphate rock when acidulation is done under oxidizing circumstances. Under oxidizing circumstances and when HNO_3 is present, 90 – 95 % of U stays in the liquid phase. Small amounts of Urany1 ion (UO_2^{2+}), which is present in the remaining phosphoric acid after filtration and sluicing to the stack, may be found in phosphogypsum.

In phosphogypsum stacks, Ra^{-226} and its daughter radionuclides constitute a direct source of gamma radiation. According to Horton *et al*. (1988) gamma radiation was discovered 1 m above the surface of five phosphogypsum stacks. According to Berish (1990) only people who spend a large amount of time working on the stack or living close would be at risk for health issues because irradiation decreases exponentially with distance. According to Roessler (1986) this level of gamma radiation did not pose harm to environmental health.

The majority of the produced phosphogypsum worldwide is kept in stacks. All phosphogypsum must be stored in stacks or mines, According to a recent U.S E.P.A. final ruling (Federal Regulation, 1990). Potential sources of environmental contamination resulting from the storage of phosphogypsum include radon gas, inhalation of radioactive dust, mobile anions, acidity, trace elements, or radionuclides, and direct exposure to gamma radiation. Other storage-related problems include the stack`s stability, erosion and surface runoff (Rydzynski, 1990). Several authors have documented methods for decreasing fluoride, radionuclides, and heavy metals in phosphogypsum by using treatments before, during, or after the wet phosphoric acid process (Becker, 1989; Habashi, 1989; Berish, 1990; Moisset, 1990).

Studies have investigated groundwater contamination and the potential leach ability of phosphogypsum components. Groundwater contamination can result from process water seepage when a stack is in use or from the long-term downward leaching that takes place when rainwater infiltrates through a stack that is not in use (Wrench and Smith, 1986). Although it is obvious that there is a chance of groundwater pollution beneath a phosphogypsum stack in some circumstances, the results are not consistent. Site-specific conditions such as (i) adequate subsurface geology that can neutralize acidic seepage, (ii) building the stack on an impermeable layer, and (iii) building interceptor wells or ditches may lessen the impact of potential contaminants on groundwater. Other sources (Wrench and Smith, 1986; Rouis and Ben-Salah, 1990) have described techniques for decreasing the seepage of contaminants from both active and dormant stacks.

2.1 Impacts of heavy metals in phosphogypsum (PG) on agroecosystem.

The composition of the phosphate rock determines the concentration of heavy metals, and the phosphate rock appears to have a far higher contaminating potential than the waste **PG**. Due to the association of most trace elements with mobile fraction, the latter has a larger contamination potential (Zmemla *et al*., 2016; Saadaoui *et al*., 2017). Except for Sr, Ce, Y and Pb, which are known for substantial transfer (66, 56, 41 and 27 %, respectively), between 2 and 12% of each trace element in phosphate rock is transferred to **PG** during the synthesis of phosphoric acid (Saadaoui *et al*., 2017).

Heavy metal degrees of mobility in **PG** were divided into three categories: high mobility elements included Sr and Zn, moderately mobile elements included As, Ba, Cd, Cr and low mobility elements included Cu, Ni, Pb, Se, V, Y and Zr. In acidic conditions (pH 2- 4) **PG** is also prone to leaching off metals (Saadaoui et al., 2017). Heavy metals were examined for various crops in the vicinity of a phosphogypsum waste heap in Wilinka (northern Poland), and elevated quantities were noted when compared to a control region (Borylo *et al*., 2013). **PG** is now utilized in Northern Kazakhstan to fertilize spring wheat, and it has no adverse effects on the environment. The maximum permitted quantities of heavy metals and radionuclides are not exceeded in the soil or grain (Muhanbet *et al*., 2016). A rise in P content is seen in Tunisia, but there is no increase in soil Cd rate when mildly acid forest polluted soil is treated with 8 tons per hectare on the surface (Bejaoui, 2016).

The elements in **PG** that appear to be the most harmful to human health in agriculture are heavy metals. Consuming vegetables and fruits cultivated on **PG**- amended soils was not generally related with any health problems, According to Al-Hwaiti and Al-Khashman (2015); Mahmoud and Abd El-Kader (2015). Also employed **PG** alone or mixed with compost (mix ratio of 1:1) at 10 or 20 g/ kg dry soil to mobilize heavy metals in contaminated soil, and they demonstrated that this method promotes canola growth and mostly immobilizes heavy metals for **PG** alone.

2.2. Impacts of radioactive impurities in phosphogypsum (PG) on agroecosystem.

Phosphogypsum is radioactively enriched; the main sources of radioactivity are ^{238}U and ^{232}Th (Bituh *et al*., 2015). The primary environmental radiotoxic element linked to the formation of phosphoric acid is Uranium, which is transported from the phosphate rock non-mobile fraction to the bioavailable fraction in phosphogypsum (Saaddaoui *et al*., 2017). In phosphogypsum-tilled agricultural soil in northern Greece, ^{226}Ra ranges in **PG** from 261 to 688 Bq kg^{-1}and from 50 to 479 Bq kg^{-1}. Higher levels of radium (^{226}Ra) were found in rice harvested from **PG** – tilled fields. Before phosphogypsum is used for agricultural purposes, ^{226}Ra must be controlled (Saadaoui *et al*., 2017). However, no increase in **^{226}Ra** and ^{228}Ra activities was seen in a field experiment carried out in Brazil with increasing phosphogypsum rates (4, 8 and 12 ton per hectare for soybean culture).

According to Dias *et al*. (2010) using **PG** for soybean production is a practice without radiation risks. Despite the known radioactivity in **PG**, the radiation dose experienced by workers as a result of using phosphogypsum piles is insignificant when compared to the annual effective dose from natural sources on average (Ali and Awad, 2015). Additionally, the radiation dose that results from using phosphogypsum as a building or plaster material can be regarded as insignificant.in Tunisia, (Gabsi *et al*., 2023), carried out a study on degraded Oasis soil to determine the effect of phosphogypsum on agronomic and radioactive parameters as well as the improvement of soil fertility . Increased soil characteristics brought forth by the agronomic usage of **PG** as an amendment and increased germination rate and productivity. However, there was no heavy metals toxicity or an excess of radioactivity because of phosphogypsum application to degraded soils.

3. Phosphogypsum usage in agriculture.

Phosphogypsum (**PG**) has been used and acknowledged in agriculture for a long time. Positive effects of **PG** are demonstrated in soil, water, and plants (Mesic̀ *et al*., 2016). Waste **PG** is primarily utilized in agriculture and is recycled in a variety of ways to improve soil fertility. Four prominent agricultural applications include land reclamation, saline and Sodic soil remediation, soil amendment to prevent crusting and improve water retention, and fertilization of soil for grazing and crop growth. Its inclusion during manure composting is its fifth known use. In fact, **PG** is a productive substitute for amending, desalinizing, and desodifying saline sodic soils (Mesic̀ *et al*., 2016). Phosphogypsum has been widely used as a soil amendment and fertilizer in various countries despite the abovementioned environmental issues (Bereteka, 1990; Novikov *et al*., 1990; Mahmoud *et al*., 2021; Hasana *et al*., 2022; Ibrahim *et al*., 2023; Jamal *et al*., 2023). However, use as a soil amendment and fertilizer has been documented most frequently (Mahmoud *et al*., 2023; Ibrahim *et al*., 2023). Phosphogypsum has also been used in agriculture as a feed supplement for cattle (Golushko, 1984) and as a fertilizer amendment to minimize ammonia volatilization from urea fertilizer (Boyrakli, 1990).

The effects of phosphogypsum treatments on soil physical, chemical and biological properties and their fertility and nutrient levels availability have been the subject of several studies (Mahmoud *et al*., 2021; Hasana *et al*., 2022; Ibrahim *et al*., 2023; Jamal *et al*., 2023). According to Mahmoud *et al*. (2023) for the following types of soil, phosphogypsum has been demonstrated to be useful as an amendment: (i) highly weathered soils with relatively low exchange capacities and / or low levels of extractable nutrients ;(ii) soils with high sodicity resulting in dense subsoil horizons; (iii) soils with variable sodicity at the surface; and (iv) sandy or sandy calcareous soils. Crop yields and quality of numerous fruits, vegetables, grains, pasture and oilseeds have been proven to be higher on soils treated with phosphogypsum.

Phosphogypsum has been employed as a source of Ca, S and P in plant nutrition experiments on a variety of soil types with varying pH levels and fertility levels. The effectiveness of phosphogypsum as a nutrient source has been linked to its capacity to give comparatively significant amounts of soluble nutrients during crucial stages of crop growth and its relatively quick rate of dissolution (Bianco *et al*., 1990; Hasana *et al*., 2022; Mahmoud *et al*., 2023; Ibrahim *et al*., 2023). Although $P_2 O_5$ only makes up about 1 % of the phosphogypsum material, large application rates can greatly enhance the amount of soils P that is available (Khalil *et al*., 1990; Mahmoud *et al*., 2023; Gabsi *et al*., 2023; Ibrahim *et al*., 2023).

3.1. Phosphogypsum usage as a soil conditioner.

The primary reason **PG** is used as a soil conditioner is because $CaSO_4$ has certain properties that make it better for roots to penetrate the soil. It increases the amount of calcium in the soil, lowers aluminum saturation, aids in the development of the plant root system and facilitates the uptake of water and nutrients (Nisti *et al*., 2015). In comparison to calcareous rock, **PG** is 150 times more soluble in water. The use of **PG** as an amendment in agriculture has drawn a lot of attention due to worries about how it should be handled, stored, and recycled. For instance, **PG** has been used extensively to improve the physical and chemical characteristics of degraded soils, such as sodic and acid soils (Outbakat *et al*., 2022).

It is vital to find practical ways to reduce subsoil acidity because many acid soils in tropical and subtropical climates are used for food production. Phytotoxic Al levels, which are occasionally accompanied by low Ca levels and / or clay hardpans, may make it difficult for roots to access subsoil layers (Rutherford *et al*., 1994). Such soils inhibit crops from utilizing moisture and nutrients under the enhanced surface layers. Field and laboratory research on the impact of adding phosphogypsum to acid soils have revealed the following results: (i) lower levels of exchangeable and solution Al; (ii) higher levels of exchangeable and solution Ca; (iii) minor and / or variable effects on **PG**; and (iv) accelerated root growth (Alva *et al*., 1991; Rutherford *et al*.,1994; Bouray *et al*., 2023).

Phosphorus (P) is a necessary component of all living things. It is the second- most important macronutrient after nitrogen that regularly limits plant productivity in agricultural and natural environments around the world (Hou *et al*., 2020; Bouray *et al*., 2022). One of the main problems with acid soils, which make up more than 50% of the World`s potentially arable lands, is low P availability, notably in ultisols and Oxisols (Bouray *et al*., 2023). Due to low pH, large concentration of iron (Fe) and aluminum (Al) oxides and hydroxides, and high concentrations of adsorption and sorption processes to organic matter and clay particles, P availability in acidic soils is primarily constrained (Bouray *et al*., 2023). Phosphorus use efficiency (PUE) in acidic soils ranges from 10% to 15% , but only because the soluble forms of P fertilizer are frequently and excessively applied to the soil due to easy precipitation of the insoluble forms of P fertilizer with poor recovery (Cordell *et al*., 2011).

On the other hand, sodic clay usually has poor soil structure because of the dispersion of clay particles brought on by excessive salt levels on the exchange complex of the soils. In contrast to the larger, highly hydrated Na cation, smaller, divalent Ca cations are better at filling negative charges on clay surfaces, which reduces dispersion and promotes flocculation of soil particles (Rutherford *et al*., 1994). Because it provides enough Ca to remove Na from soil exchange complex, phosphogypsum is a successful ameliorator for sodic soils. Additionally, it dissolves rather quickly and has a high solubility (Okorkov, 1988; Orlov *et al*., 1989; Bouray *et al*., 2023).

3.2. Phosphogypsum usage as a fertilizer.

A reduction in fertilizer use would undoubtedly assist to prevent the accumulation of **PG** stocks, but it would also necessitate drastic adjustments in agricultural practices in developed nations, particularly in developing nations that fight for the right to the same standard of living as developed nations. Due to the high levels of calcium, phosphorus and sulfur contents, phosphogypsum is employed as a fertilizer in agriculture (Gennari *et al*., 2011; Ibrahim *et al*., 2023).for several species, **PG** treatment enhances seed development and production. (Liu *et al*., 2010). Put three different quantities (15, 30 and 45 tons per hectare) to rice fields in saline- sodic soils in North- East China and obtained large increases mostly for 30 tons per hectare. Individual grain mass, spikelet count, panicle count, filled spikelet percentage and 1000 – grain weight are all improved. (Li *et al*., 2015), reported that the use of **PG** (2100 kg / hectare) increased seed yield in wheat culture by 37.7%. In Brazil, the addition of 12 tons per hectare of **PG** on a loamy Oxisols improves yields of wheat (*Triticum aestivum* L) and maize (Zea mays). The provision of Ca^{2+} and $S\text{-}SO_4^{-2}$ to plants has been used to explain this enhancement (Blum *et al*., 2013). With an increase in calcium and sulfate content in the soil (0 – 40 cm), but no change in potassium content, an increase in **PG** rate for alfalfa (Medicago sativa) stimulated increases in shoot dry weight (SDW) (Al- Hwaiti and Al-Khashman, 2015).

Numerous studies have demonstrated that phosphogypsum, whether surface applied (Caldwell *et al*., 1990), or sub-soiled (McCray *et al*., 1991), can reduce some of the negative effects of subsoil acidity on plant growth. According to Sumner (1990) there is essentially no difference between phosphogypsum and mined gypsum when it comes to fixing issues with subsoil acidity. On apple trees growing in Brazilian soils (Pavan *et al*., 1987) evaluated the effects of applications of phosphogypsum, lime, calcium chloride, or magnesium (a magnesium- lime substance). According to Sumner (1990) lime and phosphogypsum both considerably boosted rooting density in a high- aluminum soil top layer, but the phosphogypsum application also caused this impact to reach a depth of 60 cm. In comparison to other treatments, phosphogypsum or lime application considerably boosted fruit size and yield due to plant improved roots and water availability. In a coarse sandy loam soil with an argillic layer in the subsoil (Sumner, 1990) contrasted the effects of applying phosphogypsum to soil surface with those of mechanically mixing the soil or adding lime to the soil mechanically. When phosphogypsum was surface applied, peaches, barely responded, but they significantly responded to both mechanical treatments. The lack of response to gypsum was attributed to peach roots increased sensitivity to physical barriers in the subsoil as opposed to chemical ones.

In Egypt, (Ibrahim *et al*., 2023) concluded that all research parameters, including cotton leaf chemical contents, growth, yield components, and fiber qualities, were considerably improved by the interaction between **PG** application at a rate of 2.5 tons per fed and FYM treatment (5 tons per fed). The bioavailability and absorption of P by cotton plants were both improved by the combined use of **PG** and natural stimulants (FYM and PSB). In addition, applying **PG** alone or in combination with FTM and PSB decreased soil pH while increasing the amount of macro- and micronutrients in the soil as compared to calcium superphosphate treatment. The growth and production of cotton plants were typically improved. So, using **PG** instead of or along with chemical fertilizer can be advised.

3.3. Phosphogypsum impacts on soil physical properties.

Although soil is private property, it is at the same time a public asset, and therefor soil is considered one of the most important natural resources that may be subject to various forms of degradations. In arid and semi-arid regions, such as a significant portion of Egyptian desert, salinity is one of the most important obstacles to crop production and soil and water management. These desert areas are characterized by irregularly distributed low rainfall, protracted droughts, and high evaporation, which leads to salt buildup in the soil top layer and degradation of the soil and water resources. Phosphogypsum (**PG**) may therefore be a potential amendment to lessen the effects of salinity and enhance soil quality in salt-affected soils.

Outbakat *et al*. (2022) concluded that to restore soil structure, alleviate water stress, and lessen the processes and effects of soil degradation, phosphogypsum may be used as an amendment during the reclamation of problematic soils due to its general efficacy in many soil types. Application of phosphogypsum generally enhanced soil physical qualities, especially for soils in the regions of Ras El Ain and Chichaoua. The byproduct of phosphate rock processing, phosphogypsum holds promise as a means of enhancing soil quality. The physical characteristics of the soil can be improved, which will benefit plant development at the root, vegetative and fructification stages. This will increase agricultural yields, particularly in arid and semiarid regions. The overall effectiveness was due to the fact that the calcium provided by the **PG** amendment was sufficient to replace sodium in the clay fragment. Soil physical properties (aggregation, water retention, porosity and bulk density) are improved, and the clay sodium – induced dispersive impact is diminished.

3.4. Phosphogypsum impacts on soil chemical properties.

The addition of **PG** improves soil chemical properties since it has higher amounts of calcium (Ca^{2+}), phosphorus (P) and sulphur (S), as well as lower pH values (Ibrahim, Mahmoud and Ibrahim ., 2015; Munir, Ghoneim, Al- Oud, Alotaibi , and

Nadeem., 2019). (Crusciol *et al*., 2016) revealed that addition of phosphogypsum to lime and /or silicate improved the chemical properties of soil surface and subsurface twelve months after application. The combinations increased the concentrations of K, Ca, Mg, N-NO_3 and S-SO_4^{-2} in the underlying layers. The surface application of phosphogypsum mixtures and soil acidity amendments significantly increased the grain production and panicles per square meter of upland rice.

Mahmoud *et al*. (2021) Revealed that available P decreased as water treatment residuals (WTR) increased, however available Ca and Mg all experienced significant increases with the application of **PG** and WTR. Grain yield and main stem diameter of maize plants improved with the application of **PG** at a rate of 10 t ha^{-1} and N fertilizers at a rate of 285 kg N ha^{-1}. The combination of **PG** and WTR boosted soil fertility provided essential nutrients to plants and encouraged the growth and production of maize. The **PG** and WTR improved the enzyme activities and microbial respiration by boosting the microbial activity, which boosted the nutrients available to agricultural crops. In order to prevent adverse effects on the soil environment, it is required to calculate the appropriate application rates of **PG**. According to their findings, applying 10 t ha^{-1} of **PG** was the most effective way to increase yields and the chemical and microbial properties of the investigated clay soils.

According to Lee *et al*. (2009) the **PG** amendment had a favorable effect on the soil biological and chemical characteristics as well as the production of cabbage in China. Due to its high P, Ca and S content, **PG** addition had a positive effect on maize production. According to earlier research Blum *et al*.(2013); Nayak *et al*.(2011); Mahmoud *et al*.(2021) the addition of **PG** increased the amount of nutrients that were readily available, which in turn increased the yield of rice grain and bean. With **PG** additives, maize responded quadratically while barley increased linearly, according to Michalovicz *et al*. (2014).

Mahmoud *et al*. (2021) revealed that with an increase in **PG** application rates, soil pH dropped. (Al- Enazy *et al*., 2018; Lee *et al*., 2009) both came to Similar conclusions. According to research by Chung *et al*. (2001) **PG** treatment of 2.5 and 5.0 g / kg^{-1} soil decreased pH by 0.7- 0.8 units. According to Mahmoud *et al*. (2021) increasing **PG** levels led to a significant decrease in soil pH from 8.09 to 7.64, which is consistent with earlier findings. (El-Gundy, 2005) demonstrated that the addition of gypsum resulted in a drop in soil pH, EC and exchange sodium percentage (ESP) but an increase in CEC.

3.5. Phosphogypsum impacts on soil biological properties.

Soil microbial population plays a vital role in the decomposition of organic matter and the preservation of soil nutrients. However, soil microbial biomass and microbial activity have been suggested as indicators of soil quality (Machulla *et al*., 2005). Soil enzymes catalyze biochemical processes in the soil. Measuring soil enzyme activity is a part of general biological research on soil and provides a comparative evaluation of several biochemical processes (Behera and Mishra, 1989). The enzyme dehydrogenase, which is present in all healthy microbial cells, can be used to assess the metabolic fitness of soil microorganisms (Watts *et al*., 2010). Due to its high sensitivity, dehydrogenase activity (DHA) is one of the best bio indicators of soil quality (Wolinska and Stepniewska, 2012).

Mahmoud *et al*. (2021) showed that the injection of phosphogypsum (**PG**) or water treatment residuals (WTR) considerably increased soil microbial biomass carbon (MBC), CO_2 evolution and dehydrogenase activity (DHA). In comparison to the other treatments, the application of **PG** with nitrogen fertilizer (NF) at a rate of 10 t ha^{-1} resulted in the highest levels of microbial activity, nutrients accessible in the soil, grain production and yield component of maize plants. In comparison to the NF treatment, the additions of NF + **PG** at rates of 10 and 5 t ha^{-1} and NF+ WTR at rates of 10 and 5 t ha^{-1} raised DHA by 1.70 , 1.60, 1.40 and 1.20 times, respectively. It could be concluded the qualities of heavy clay soils could be improved by applying **PG** and WTR at the approved application rates. The results demonstrated that the addition of WTR and **PG** enhanced soil properties and increased maize production. Dehydrogenase activity, CO_2 evolution and microbial biomass carbon all significantly enhanced with the addition of WTR and **PG**. Grain yield rose by 10 t ha^{-1} when **PG** was used in place of WTR.

Soil microbial biomass contributes to the preservation of organic matter and the fertility of soils. For agricultural functions, microbial biomass and enzymatic activity are crucial soil indicators. Because it conducts key ecosystem tasks like the breakdown of organic matter and nutrient cycling, soil fauna is a crucial part of soil health. Organic matter and the availability of soil nutrients are necessary for the soil fauna. The activity of the soil fauna enhances soil structure, breaks down organic matter, and boosts soil fertility (Di *et al*., 2021; Mahmoud *et al*., 2023). Mahmoud *et al*. (2021) stated that high dehydrogenase activity (DHA) found in **PG-** amended soil correlated with high SOM content and soil pH Gypsum addition has been shown to increase DHA and SMB in soil used to grow maize plants (Chandrakar and Jena, 2016). The **PG** –amended soils high P and S content as well as their low pH values may have improved soil characteristics and increased DHA and microbial biomass. With the addition of gypsum, enhanced soil microbial biomass and cumulative CO_2 throughout the incubation period have also been documented (Amini, 2015).

Mahmoud *et al*. (2023) revealed that in a comparison to the control treatment, the addition of **PG** and /or PM greatly boosted the barely yield and its constituent parts. Similar findings were made by Ali *et al*. (2021) they noted that the use of organic amendments considerably improved the plant height of newly planted seeds when compared to the control. This could be because of the addition of **PG** and/or PM enhancing nutrient release either directly through amendment application or indirectly through increased microbial activity that decomposes OM and increases soil fertility.

CONCLUSIONS

In conclusion, phosphogypsum (**PG**) is a waste material produced by the phosphate industry (**PG**: $CaSO_4\ 2H_2O$). More than 300 million tons of this trash is produced worldwide each year. There is a worry over the environmental effects of **PG** because it contains toxic substances that are harmful to ecosystems and human health, such as heavy metals and radionuclides, when it is released into the ocean, waterways, or in wilderness stocks. Each of these elements requires a unique and specific follow-up following the release of **PG** and throughout its use because the concentrations change depending on the regions and techniques used. In addition to being utilized in the brick and cement industries, as well as in the construction of roads, phosphogypsum is also employed in agriculture as a safe fertilizer and/or soil amendment.

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الملخص العربي

تقييم الفوسفوجيبسوم كمحسن للتربة و/أو سماد في ظل الظروف القاحلة

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يعد الفوسفوجيبسم مصدر قلق بيئي وفرصة لمواجهة الضغوط غير الحيوية للتربة في ظل الظروف القاحلة. يهدف هذا البحث إلى تقديم نظرة عامة على الدراسات المتعلقة بالفوسفوجيبسوم (PG) مع التركيز على استخدامه الزراعي في مصر وفي جميع أنحاء العالم، والكيمياء الخاصة بهذه المادة والقضايا البيئية المحتملة التي قد تنشأ إذا تعرضت سوائله لبيئة التربة. يتم إنتاج الفوسفوجيبسم بكميات كبيرة بواسطة صناعات الفوسفات ويتم إلقاؤه في كثير من الأحيان في المناطق المفتوحة أو إطلاقه في الخزانات المائية وبهذا فأن له آثار ضارة على البيئة وعلى صحة الإنسان. ومع ذلك، يتم استخدام الفوسفوجيبسم في مجموعة متنوعة من الصناعات مثل تصنيع الأسمنت والطوب، وبناء الطرق وفي الزراعة للتسميد وتحسين التربة. ونظراً للكميات المختلفة من المعادن الثقيلة والعناصر المشعة الموجودة في الفوسفوجيبسم، فإن كل هذه الاستخدامات تثير مخاوف بيئية. ويجب على صناع القرار أن يأخذوا في الاعتبار المزايا التي تعود من صناعة الفوسفات والتكاليف التي تتكبدها البيئة والأضرار الناجمة عن التلوث. هناك عدد من المتغيرات التي تؤثر على استخدام الغاز الفوسفوجيبسم في الزراعة، بما في ذلك تركيبه، ونوع التربة، والمساحة، والقيود المفروضة على المحاصيل والبيئة. لذلك، ينبغي على كل دولة إجراء دراسات مستقلة خاصة بنظمها البيئية الزراعية ومناطقها الزراعية.

الكلمات المفتاحية : الفوسفوجيبسم – العناصر الثقيلة – العناصر المشعة