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Research article

Phosphogypsum effect on soil, rainwater incubated and soil respiration

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Abstract
Phosphogypsum (PG) is a byproduct issued by fertilizer industry, which has been used as soil fertilizer in many countries in the world for long time. The most positive effect of phosphogypsum is ameliorating soil properties and increasing crop yields. Recently, disquiets are growing related to the increase of the acidity and metal ions concentration in soils. This work is a study on the short term impact of using phosphogypsum, as an amendment in El Fja region (Mednine, Tunisia). Physico-chemical characterizations (pH, electrical conductivity, P_2O_5 concentration, chloride concentration, calcium and magnesium conentration) of rain water, incubated at room temperature with soil and also with a (soil, phosphogypsum) mixture during 37 days, were investigated. The dissolution of this product and its impurities in the first period of incubation releases the ions usuful for agricultural use like calcium, magnesium, sulphate and phosphate ions. In addition, the effect of amending phosphogypsum on the increase of organic carbon mineralisation, which is an indicator for soil respiration, was revealed.
Key words: Arid zone, phosphogypsum, organic carbon mineralisation, water and soil incubation.

1. Introduction

Tunisian South Est is an arid zone which is characterized as an area of low precipitation, high temperature, and high rate of evaporation(You, 2016). The soil in this zone is characterized by neutral, high salt content, and low organic matter (Kayouli, 2006; Jeddi, 2010).

Hence, its agronomic potential can be easily weakened by erosion overgrazing or agriculture activity. Subsequently amendments are added to enhance physico-chemical properties of soil (Cherifa, 2009). Several trials have been performed using soil conditioners such as farmyard manure, compost, biochar (Cherifa, 2009; Uchimiya, 2010).

These amendments have beneficial outcome on agricultural productivity, but their effect on soil (microbiological and physico-chemical aspects), water table and global environment are to be investigated seriously. Mineral amendments are known to ameliorate the quality of soil, but their effect is not simultaneous, several weeks are required and even months to notice this effect as reporeted by the FAO.

This work deals with the use of phosphogypsum PG as an amendment in the arid zone soil by studying its effect on soil-rain water incubated mixtures and soil respiration. In Tunisia, huge amounts of phosphogypsum, estimated to be 10.5 million tons annually (Ben Amor, 2012), are induced by phosphate fertilizer industry. Hence, numerous trials were performed, with the target of reducing the volumes of PG to be disposed in landfill, and to provide new soil conditioners to balance the use of industrial fertilizers in agriculture especially in poor soil like those in arid zone.

Phosphogypsum dumps constitutes a real environmental struggle as only a small quantity of this production is recycled, athough only 15% of world PG production is rehabilitaed as building materials (Degirmenci, 2008), as additive in road constraction (Sizyakov et al. 2012), as agricultural fertilizers or soil stabilization amendments such as reported by Tayibi (2009). In addition, phosphogypsum can be processed to extract rare-earth metal compounds, because it contains a mass fraction in rare earth oxyde Ln_2O_3 varing from 0.1 to 0.8 %, similar to the fraction found in some ores (Akhmetov et al. 1992). Moreover, PG might be treated to produce marketable products like; ammonium sulfate and technical calcium carbonate, calcium sulfide, hydrogen sulfide, sulfuric acid and cement (Genkin et al. 2013).

When it comes to the valorisation of PG in the agriculture, various researches focused their interest on the effect of adding PG into soil. Carvalho, (1997) found that PG can be used as a good amendment for acidic subsoils that present toxic levels of aluminium and/or calcium deficiency. Garrido, (2006) found that gypsum-rich industrial by-products could regulate the mobility of toxic metals like Cd, Cu and Pb in acid soils. Kumpiene (2008) reported findings about a success in immobilizing toxic poluant metals for example As, Cr, Cu, Pb and Zn in soil by phosphorus amendments and clays. In a recent study Hentati, (2015) studied the eco-toxicity of amended soil with PG and its impact on bacteria, invertebrates, algae and plants, highlighting the necessity of setting limits for PG application in soils. In a detailed review on the use of Gypsum on Soils, Shainberg (1989) reported the favorable effect of PG on both soil physical properties (especially on dispersive soils), by fighting restricted rooting, and on chemical properties (on acid soils). The PG is also said to be a nutrient source for Ca or S, retainter for water in semiarid or marginal rainfall areas, and a booster to agricltural production.

Otherwise, the richness of soils with organic matter (OM) is one of the main indicators of soil fertility. Soil is an overwhelming living site, so the OM can be involved in the formation or the decomposition processes (Rastetter et al, 1991; Raich et al, 1991). It is also an increasingly feature in a global climate change context where carbon storage in soils is a serious alternative that is predicted to limit CO_2 concentrations in the atmosphere (Wu et al., 2003).

The second part of this research is related to study the kinetic of mineralization, which is an indicator of soil respiration, of the organic matter in an arid zone soil and the impact of adding PG as an amendment on this kinetic. In fact, several researches have been conducted on soil respiration and the effect of adding fertilizers or amendments on this soil activity. Annabi, (2009) showed in a study on the status and dynamics of OM in cultivated and forest soil in the north of Tunisia, that the resistant organic carbon rate to mineralization is bigger in forest soils then in cultivated soils. In another study, Zoghlami, (2016) found that the amendment of soil with 120 t ha-1 as optimal amount has the best potential for mineralization, which is related to the existing microbial biomass.

Hence, the second part of this work was dedicated to study adding PG and its effects on soil respiration, during 34 days. The kinetic of mineralization of the organic matter is known to be an indicator of the microorganism activity in soil.

2. Materials and methods

El Fje soil has a sandy texture with small amounts of silt (4.92%) and clay (2.17%) which were determined by Robinson pipette (Robinson 1922).

During this study, physico-chemical characterizations (electrical conductivity CE, pH, (Ca^{2+} Mg^{2+}) chloride concentrations, and soluble orthophosphate amount) in rainwater were measured. This later was incubated at room temperature with soil and with a (soil, PG: 10% by weight) mixture during 37 days according to the proportions (900 ml rain water, 500g soil with volume ratio 2/1). This amendment amount 10% of PG in soil was found to be the most suitable for plant development (Ardhaoui, 2017) and closed soil incubation experiments are performed during periods of about one month as stated in literature (Mackay, 1986). The concentration of (Ca^{2+} and Mg^{2+}) was determined by Dugain methods (Dugain, 1961).

Organic matter was measured by rapid oxidation and subsequent titration with ferrous ammonium sulphate (Walkley, 1934). Total nitrogen was determined using the Kjeldahl's method (Bremner 1982) by attacking at high temperatures the matter using concentrated sulfuric acid in the presence of a catalyser ($MgSO_4$, $CuSO_4$, Se).

The mineralogical components of the PG were identified by X-ray Diffraction (XRD) using a Bruker (D8 advance) powder diffractometer with a tube Cu anode (40 kV, 40 mA).

In an other set of experiments, the amount of carbon dioxide released by soil respiration during 34 days was captured by a (NaOH (1M, 20ml); $BaCl_2$ (1M, 5ml)) mixture solution maintained during incubation with slightly moisturized soil in a 1 liter glass bottel at 28 °C. The remaining soda concentration, after neuralization with the released CO_2, was obtained by titration with HCl (0.1 M) using phenolphtalein indicator.

3. Results and discussion

Data displayed in a previous research (Ardhaoui et al., 2017) describes the physico-chemical properties of the studied soil, pH is near neutral about 7.5 and the electrical conductivity is (2.33 mS/cm) showing a moderately saline soil (Wong 2009) with a limited cation exchange capacity (4.3 meq/100g), low organic carbon (0.58%) and active carbonate (1.2%) percentages respectively. The total nitrogen amount is 0.18% and that of phosphates (P_2O_5) is 901 ppm.

The Tunisian Chemical Groupe in Gabès furnished Posphogypsum samples. The composition of PG varies depending upon the source of rock phosphate and the process for manufacturing phosphoric acid (Wright 1998). The common composition (Zairi 1999) of PG is: calcium sulfate dihydrate, orthophosphoric acid various salts and trace metals.

It is noteworthy to mention that powdered samples of PG were analyzed by X-ray diffraction, PG is mostly formed by calcium sulfate dihydrate polymorphs and some slight impurities like $Mg(OH)_2$, SiO_2, $MgSiO_3$ and Na_2SiF_6 (Figure 1).

Supplementary analysis showed that PG has low pH (2.3) due to the acid remaining (Phosphates P2O5 1209 ppm) from fertilizer manufacture. Additionally, it has an important cation exchange capacity (7.1 meq/100g) and gypsum percentage (97.5%). The organic carbon (1%) and total nitrogen (0.3%) percentages were also obtained.

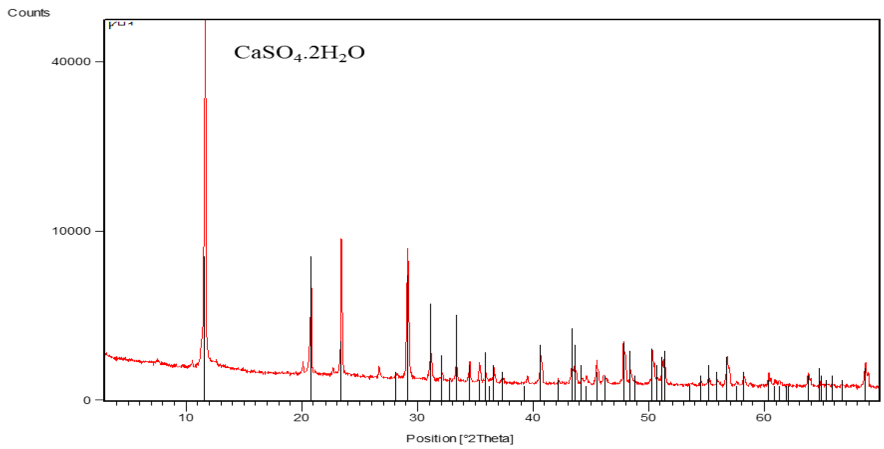

Fig. 1: X-Ray pattern of powdered PG (α Cu=1.54 Å)

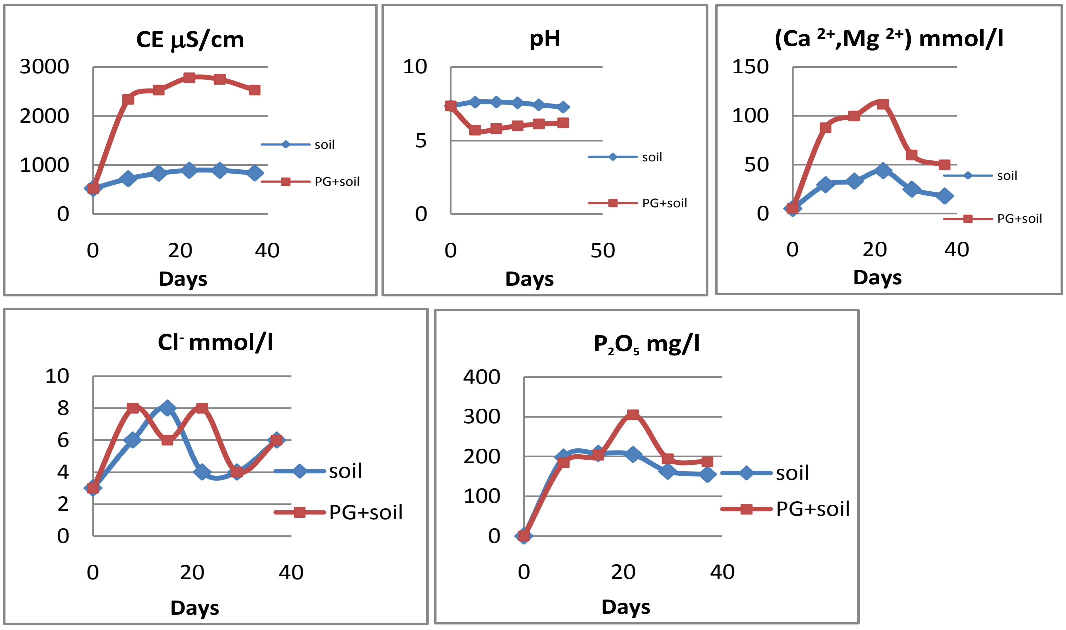

Fig. 2: Kinetic evolution of physico-chemical properties of incubated rain water with soil and (soil+PG) mixture

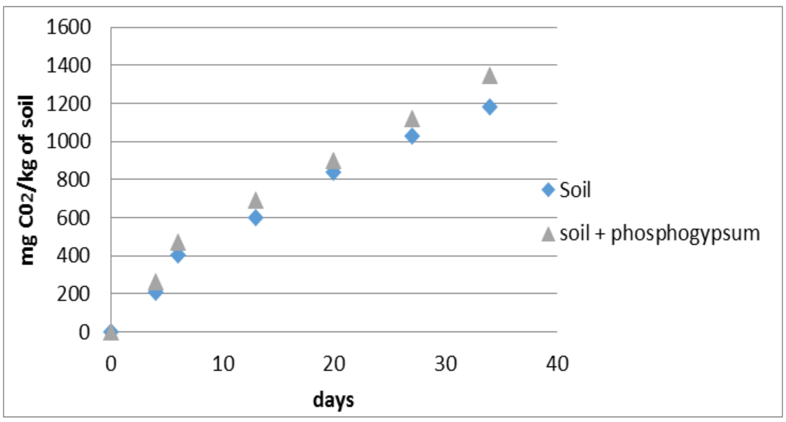

Fig. 3: Total amount of carbon dioxide released by soil and (soil+PG) mixture

Furthermore, PG has high ion concentrations due to its mineral composition previously described and to potential crystalline and non-crystalline impurities like chlorate, silicate, phosphate and carbonate known to be present in the phosphate rock generating PG (Drouet 2015; Zairi 1999). All these evidences go with the important EC measured (18 mS/cm).

3.1 Soil incubation in rain water

The Kinetic study (Figure 2) of the physico-chemical properties of rainwater incubated with soil and (soil+ PG) mixture at room temperature showed a significant repercussion of the introduction of PG on these properties. During the period of study, PG amendment enhances EC, (Ca^{2+}, Mg^{2+}) and P_2O_5 concentrations. Chloride ion concentration remained relatively low and the pH decreases while PG is present. This general trend is seen during the first twenty days of incubation. These facts were due, in a first level, to the gradual dissolution of PG producing calcium and sulfate ions and in a second level to the impurities dissolution, that accompany this industrial byproduct. The noteworthy exemples of impurities are, iron, aluminum and magnesium sulfates and sulfuric, phosphoric and fluorhydric acids (Zairi, 1999).

During the final period of incubation, the physico-chemical parameters have a tendency to stabilisation and/or the values for the (soil + PG) mixture are getting close to those of soil. At this period, the interaction with soil components begins and then enhances the reactions of precipitation leading to an equilibium state (Endovitsky, 2016).

These results approve the use of PG as an agriculture fertilizer in different parts of the world for years (Hentati 2015, Mullins 1990). In fact, It has been spread in agricultural soils as a calcium, phosphorus and sulfate supplement to boost crop production and reducing Al-toxicity (Toma 1997) and sodic soils (Enamorado 2014).

It was also used raw or combined with other synthetic organic polymers (polyacrylamide) for preventing seal formation, runoffs and erosion in agricultural soils exposed to heavy deluges (Tang 2006).

3.2. Carbon mineralization

In addition, the initial (C/N) ratios are 3.22 for soil and 3.25 for the (soil + PG) mixture which are favorable to the mineralisation of the organic matter in soil. The investigation of the rate of release of carbon oxide(fig. n°3) from the soil and from a (soil + PG) mixture, revealed the mineralization process of the carbon in soil. The mineralization rates are maximum at the beginning of the incubations. They are more important with (soil + PG) mixture than with soil. The rates of mineralization decrease rapidly during the incubations.

This reaction followed the first kinetic order, as described in literature (FAO). Furthermore, PG facilitated organic matter decomposition and especially after one month of incubation at 28°C.

The fitting of this mineralization kinetic according to an exponential low ($C_t = C_0\ (1- e^{-kt})$) (Annabi 2009) led to the determination of the amount of labile compartment in soil C_0 (Saidi 2015).

C_t (mg C kg^{-1}) is the total amount of mineralized carbon at the duration of incubation t (day) per one kilogramme of soil, and k is the mineralization reaction rate constant (day^{-1}). The results are gathered in the following table 1.

Table 1: Kinetic parameters of the mineralization reaction

	Soil	PG + Soil
C (mg C kg^{-1})	378.2	399.3
k (day^{-1})	0.048	0.055

At the end of this incubation period 85% of COT in soil and 91% of COT in (soil + PG) mixture were minirealised, which is similar to the results found in cultivated soil in north Tunisia (Annabi 2009).

This result reveals that besides the utility of adding the PG to ameliorate some physicochemical properties of soil, it may alter the reserve of carbon in soil by accelerating the mineralization process. Amending PG in soils has an inhibitory effects on the reproduction of terrestrial invertabrates like earthworm known to be resourses and factors for the stabilisation of oraganic carbon in soil (hentati earth worm). In addition, acid traces in PG contribute to the decomposition and dissolution of the oraganic carbon in soil, similarly to the effect of acidic rain on soil (Francis1982).

4. Conclusion

This research was performed in order to investigate the effect of PG on rain water incubated and on soil respiration. The results found can help with better understanding of PG behavior in the environment. Amended in agricultural soil, PG is an efficient fertilizer enhancing crop productivity, as it is solved by rain or irrigation water and then delivring some nutrients. Nevertheless, trace impurities in PG like acids may increase the kinetic of the mineralization of the organic carbon which has an impoverishment effect on soil. Combined amendments PG with manure or compost are planned to be studied to reveal their global effect on the soil.

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