

Drain flow and related salt losses as affected by phosphogypsum amendment in reclaimed marsh soils from SW Spain

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A B S T R A C T

Phosphogypsum (PG), a by-product of the P industries, has been widely applied as an amendment to reduce Na saturation in soils. However, some concern arises due to its content of some metals and radionuclides. Thus, it is necessary to optimize the PG rates to avoid excessive accumulation of such pollutants in soil. To evaluate the effects of PG on drain flow and on the displacement of Na by Ca in soils, a three-year field experiment was conducted in a commercial farm located in a reclaimed marsh area from SW Spain. It involved two treatments (control – without PG – and 25 Mg ha⁻¹ of PG, applied in April 2003 and again in September 2004), done in triplicate in 250 × 20 m plots, following a randomized block design. Drainage flows were monitored, and drain-water samples were analyzed for Na and Ca concentrations. The recorded hydrographs revealed unexpected high lateral flows of water within these soils. No statistically significant differences were found in drained volumes, nor in Na and Ca losses through drainage, between both treatments in each of the three growing seasons (*Gossypium hirsutum* L. in 2003 and 2005; *Beta vulgaris* L. in 2003–2004). Losses of Na and Ca in each irrigation event were linearly related to the drainage to irrigation volume ratio ($p < 0.001$); Ca, however, showed significantly different slopes for both treatments. Cation concentration, Na adsorption ratio (SAR), and electrical conductivity (EC) in the saturation extract of soil at different depths were significantly affected by PG and by the oscillation of saline water table during the experiment. The efficiency of PG in displacing Na by Ca was estimated to be about 30%, with the PG-attributable changes in Ca and SAR also appearing in deeper soil layers and in adjacent control plots.

Keywords:

Phosphogypsum
Salinity
Sodicity
Soil amendment
Irrigation
Tile drain

1. Introduction

Soil reclamation and the agricultural use of marsh soils have accounted for an important technical problem in many regions of Europe (Hodkinson and Thorburn, 1996; Moreno et al., 2004; Tanton et al., 1995). A sizeable portion of the Guadalquivir river marshes has been reclaimed for agricultural use (around 40,000 ha), accounting for one of the largest reclaimed marsh areas in southern Europe and featuring an important irrigated-agricultural production (Delgado et al., 2006; Domínguez et al., 2001; Moreno et al., 2001). Before reclamation, these soils were highly saline and sodic, resulting from the presence of a shallow and extremely saline water table (Andreu et al., 1994; Moreno et al., 1981).

Conversion of marshes to arable land usually requires an artificial drainage system (Peck and Hatton, 2003), not only to avoid flooding, but

also to ensure that the saline water table does not encroach into the root zone and to reduce salt content in soils by leaching (Ben-Hur et al., 2001; Moreno et al., 1995, 2001). In cracking clay soils, such as those in the Guadalquivir marshes, leaching efficiency of irrigation water decreases when rapid non-equilibrium water movement through cracks predominates (Andreu et al., 1994, 1996; Moreno et al., 1995). This so called “bypass flow” preferentially occurs when high-intensity irrigation systems are used (Crescimanno and De Santis, 2004; Huang et al., 2000). The efficiency of leaching in sloping soils increases when water retention is enhanced by tillage (Ben-Hur and Assouline, 2002; Huang et al., 2000). Under conditions of restricted water supply, the removal of salt through aerial parts of plants can contribute to the remediation of saline soils (Qadir and Oster, 2004; Qadir et al., 2000).

Reclamation of sodic soils is driven by providing a source of Ca to replace excess Na from the cation exchange sites (Qadir and Oster, 2004). Soils in Guadalquivir river marshes are calcareous and the endogenous gypsum content of surface horizons is usually negligible (Moreno et al., 1981). Calcite is not sufficiently soluble to promote soil reclamation at partial pressures of CO₂ present in the atmosphere, thus justifying the application of more soluble chemical amendments (Qadir and Oster, 2004). Only when the dissolution of carbonates is enhanced by plant roots through respiration and acidification it can be

Abbreviations: PG, phosphogypsum; SAR, sodium adsorption ratio; ESP, exchangeable sodium percentage.

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¹ María Dolores Hurtado died in February 2010. The present work was a part of her unfinished Ph. D. Thesis. Her colleagues and friends wish to dedicate this article to her memory.

expected some contribution to sodic soil reclamation (Qadir and Oster, 2004; Qadir et al., 2001, 2003).

Gypsum and gypsum-rich industrial by-products have been traditionally described as efficient amendments to decrease sodicity in soils and improve their physical properties, such as aggregate stability (Lebron et al., 2002), water infiltration, and hydraulic conductivity (Agassi et al., 1986; Ben-Hur et al., 1992; Lee et al., 2010; Sahin et al., 2003; Tang et al., 2006; Yu et al., 2003). Mamedov and Levy (2001) proved that, in effluent-irrigated soils with clay content lower than 40%, phosphogypsum (PG), a by-product of the P fertilizer industry, prevented the physical-chemical dispersion of clays and improved infiltration.

Phosphogypsum has been effective in reducing sodium saturation in marsh soils from SW Spain, where PG, at rates of 25 Mg ha⁻¹ (wet weight, after being sun-dried, and with typical remaining water content of 20%), were applied every 2–4 years (Abril et al., 2008; Delgado et al., 2006; Domínguez et al., 2001). With this amendment management, an ESP decrease in soils of the area from ESP > 15% to less than 5% has been achieved (Domínguez et al., 2001). At this ESP levels, the efficiency of PG for decreasing Na saturation is expected to be low (Levy, 2000). There is, however, a lack of information about the effect of this amendment on water and salt balance in soil when it is applied at soils with this degree of reclamation. Even more, most of the information available about the effect of water management on the leaching of salts was obtained in the nineties, and it is necessary to study how the same management of water and soils can affect the leaching of salts with lower ESP levels promoted by the usual PG amendments.

Restrictions in the agricultural use of PG arise from its content in some metals and natural radionuclides (particularly ²²⁶Ra and its decay products, Abril et al., 2009a,b; Alcorido et al., 1999; El-Mrabet et al., 2003; Papastefanou et al., 2006; Rutherford et al., 1994). However, with some considerations regarding this potential pollution, its use is allowed in the Spanish, European, and American directives.

The main objectives proposed in this work were to study in the reclaimed marshes from SW Spain the differential effect (with respect to control plots) of PG amendment: (i) on Na saturation in soil and the efficiency of water and amendment management in avoiding resalinization of soil; and (ii) on water and salt balance under the usual management of water and crops. This information could be interesting for updating the PG application rates, avoiding unnecessary high inputs, and minimising some potential environmental and health impacts. Additionally, this work can provide reliable data of broad interest in a scenario with a worldwide increase in the agricultural use of PG as an efficient way of elimination of this byproduct (stockpiling PG has shown to be expensive and unsafe, after the 1997 accident in Piney Point, Tampa Bay, Florida).

2. Materials and methods

2.1. Experimental site and experimental design

The experiment was conducted on a commercial farm, located in the “Marismas de Lebrija,” in the reclaimed marsh soils of the estuarine region of the Guadalquivir river, SW Spain (37° 01' N, 6° 7' W). Before reclamation, soils were completely waterlogged with a very shallow watertable during winter. After reclamation, waterlogging was reduced and cracking became apparent (Domínguez et al., 2001; Moreno et al., 1981). These soils can be classified as *Aeric Endoaquepts* (Soil Survey Staff, 2003). Abril et al. (2008) studied the PG-associated ²²⁶Ra enrichment in soils from this farm relative to non-reclaimed soils in the area (without any PG amendment). They found that these soils had received six typical PG doses of 25 Mg ha⁻¹ before the beginning of the present field experiment. An intensive agriculture production under irrigation is developed in the area, with sugar beet, cotton, tomato, and corn as main crops. More detailed information about the area, soils, reclamation practices, and agricultural use can be found elsewhere (Delgado et al.,

2006; Domínguez et al., 2001; Moreno et al., 1981, 1995). The mean temperature ranged from 10.0 °C in January to 25.5 °C in August. The annual total rainfall was 694, 407 and 241 mm for the years 2003 to 2005, with corresponding mean potential evapotranspiration of 1423, 1444 and 1544 mm (data registered in the closest agro-meteorological station from the Andalusia government; 36° 58.7' N, 6° 7.5' W).

A randomised complete block design with three replications (250 × 20 m plots) was performed (see Fig. 1), involving two treatments: (i) control (no new amendments applied) and (ii) two additional PG amendments, applied at a rate of 25 Mg ha⁻¹ (after being sun dried) in April 2003 and in September 2004 following current practices in this area: PG was spread over a previously tilled soil, then a deep tillage (up to 40 cm depth) was immediately applied. Applied PG is the available product resulting from the phosphoric acid industry; thus grain sizes of PG ranged from sub-millimetre up to several cm. Each plot was longitudinally crossed by ceramic drainage pipe-lines spaced 5 m apart that were placed at a depth of ca. 1 m (see Fig. 1). Two of these pipe-lines were coincident with the plot boundaries (250 m length), and they were not included in this study to prevent cross-contamination among treated and untreated plots. The drainage flow was monitored in 2 (connected between them by a pipe) of the 3 central tile-drains of each plot. This drainage system controls the water table level, which remains at a depth of approximately 0.9 m. The electrical conductivity of the water table is > 80 dS m⁻¹ (Moreno et al., 1995).

The Southern side (20 m wide) of all plots was adjacent to a small channel that removed the drainage water to the Guadalquivir River. Drain lines had a 0.15% slope towards the channel (the long axis of the plot ran slopewise). Also, the surface of the plots had a 0.1% slope towards the channel in order to facilitate furrow irrigation and avoid flooding in rainy years without allowing surface runoff in normal years. The North side of the plots corresponded to the boundary with another commercial farm. In order to minimize the potential influence of such a farm on the experimental plot, a 5 m non-cropped border was inserted. On the other farm, the surface and tile-drain slope were towards another drainage channel running in the opposite direction.

In the first and third seasons (2003 and 2005), cotton (*Gossypium hirsutum* L.) was grown under sprinkler the two first irrigations at 10 mm h⁻¹, and after, under furrow irrigation (furrows parallel to the

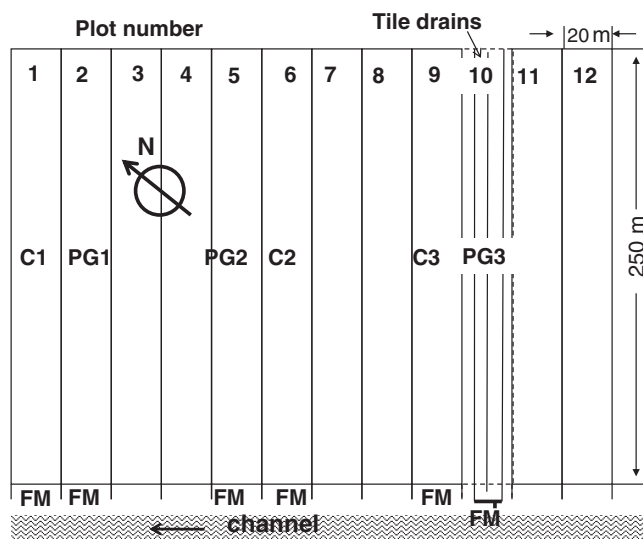


Fig. 1. The experimental setup included two treatments (control and PG) and a randomised complete block design with three replications (each one corresponding to 250 × 20 m plots). For plot PG-3, details for the tile-drain lines (spaced 5 m apart) have been plotted, two of them are coincident with the plot boundaries. Only two of the central drain lines were used for monitoring drainage waters (connected between them by a pipe). The six additional plots were not used for our experiment. Crop and irrigation covered the whole farm's surface. The position of the flow meters (FMs) is also indicated.

longest side of each plot) at a rate of 7.5 mm h^{-1} . Cotton was sown in March and harvested in October – a typical cycle in Mediterranean region. Electrical Conductivity and concentrations of Ca, Mg, and Na were determined in irrigation water during both seasons. Calcium and Mg were determined by atomic absorption spectrometry and Na by flame photometry, allowing calculating the Na adsorption ratio (SAR). Electrical conductivity in irrigation water ranged from 0.97 to 1.23 dS m^{-1} and SAR from 1.35 to $1.47 \text{ mmol}_c^{1/2} \text{ L}^{-1/2}$.

Due to limitations in the availability of irrigation water under the furrow system, only one third of the farm was irrigated at the same time (thus, irrigation was organized in three shifts). In most of the cases, but not always, fixed pairs of control and PG-plots (the adjacent ones) were simultaneously irrigated, altogether with other two non-experimental plots (see Fig. 1). The first furrow irrigation in 2005 started on May 17th, and the time required to irrigate the first shift was 23–26 h (furrows were 250 m long), which progressively fell to 10–12 h in subsequent irrigation episodes, due to the closing of soil cracks.

In the second season, sugar beet (*Beta vulgaris* L.) was grown under sprinkler irrigation at 5 mm h^{-1} , from October 2003 to July 2004, which is the typical cycle in South Spain. We note that crop rotation, tillage and irrigation systems were decided by the farmer, since the farm maintained its commercial use during the experiment.

2.2. Soil and water analysis

Soil in the experimental site was sampled taking 18 soil cores at three different depths (from 0 to 30, 30 to 60 and 60 to 90 cm), regularly distributed within each elemental plot ($250 \times 20 \text{ m}$), with four sampling campaigns: January 2003, November 2003, September 2004, and January 2006. Non-reclaimed marsh soil (not in agriculture use and not PG applied) was sampled (January 2006, three cores with the same depth intervals) in an area close to the experimental farm ($37^\circ 1.5' \text{ N}$; $6^\circ 7.9' \text{ W}$). Soil samples were air dried and ground to pass a 2 mm screen. A complete soil characterisation was done with samples taken in January 2003, involving: particle size analysis using the hydrometer method following treatment with a HOAc–NaOAc buffer (pH 4.75) to remove carbonates (Gee and Bauder, 1986), organic carbon by dichromate oxidation (Walkley and Black, 1934), pH measured in the 1:5 soil to water extract, the cation exchange capacity (CEC) by using 1 M NH_4OAc buffered at pH 7 (Sumner and Miller, 1996), the total CaCO_3 equivalent (CCE) determined from the weight loss upon treatment with 6 M HCl. Main soil properties are shown in Table 1. With soil samples taken in all the campaigns, the electrical conductivity, and K, Na, Ca and Mg concentrations were determined in the saturation extract, obtained using the method described by Rhoades (1996). In the extracts, Na and K were determined by flame photometry and Ca and Mg by atomic absorption spectroscopy after filtering through a $0.22 \mu\text{m}$ membrane filter.

Rain, irrigation, and drainage were registered, and a regular sampling of irrigation and drainage water was done in each rain or irrigation event during the growing seasons of 2003 and 2004 (at least

four samples per event). In the first two growing seasons, drain flows were measured through the time required to fill up a known volume. In 2005, six recording drainage meters of original design based on the ultrasonic measurement of water levels in a grooved U-pipe were installed to measure drain flow. The design, with three grooves of different width in a U-pipe, allowed precise flow measurements in the range $0\text{--}4 \text{ L s}^{-1}$, and the ultrasonic probe produced high temporal resolution records (Enamorado et al., 2007). The records of discharges enabled the construction of the drainage hydrograph for each drainage event and for the whole season. The total drainage volume during a drainage event or during the season was estimated by integrating the drainage hydrographs. After sampling, Na and Ca concentrations in drainage waters were determined using the methods described above for soil saturation extracts. The drainage-associated losses of Na and Ca from each plot were determined by multiplying their respective concentrations in water samples by the corresponding flow rate, and integrating over each drainage episode.

2.3. Statistical analysis

The analysis was intended to expose the effects of the PG treatment on drainage, salt losses, exchangeable cations and composition and properties of the saturation extract of the soil. To this end, the General Linear Model procedure in Statgraphics Plus 5.1 (StatPoint, 2000) was used and means were compared via LSD test. This software was also used for regressions analyses.

3. Results and discussion

3.1. Water balance (irrigation and drainage)

Drain discharge started 1–2 h after the beginning of the irrigation (Fig. 2a shows an example for 2005), which is supposed to be the time required by infiltration water to reach the drain line (1 m depth). This time lag progressively increased in subsequent irrigation events. Drainage increased as water advanced in the furrow, and the maximum flow was reached approximately when irrigation finished. At the end of the irrigation, drainage decreased slowly during 24–30 h. These observations are in agreement with previous findings in similar soils by Moreno et al. (1995). When the drainage water front reaches the depth of tile drains, there is a local rise of the water table (Martinez Beltran, 1988), and thus, an increase of the lateral flow. The observation of secondary peaks in the drain flow with time, coincident with the irrigation of the neighbouring plots (Fig. 2c), can be considered as an evidence of this lateral flow, previously described by Moreno et al. (1995) in similar soils.

Non-significant differences between treatments were observed in the drained volumes within each cropping season (Table 2). The drainage to irrigation volume ratio was significantly higher in 2005 than in 2003 (cotton and furrow irrigation in both seasons), for both control and PG treatments (at 95% CL).

Under furrow irrigation, water losses by drainage decreased with time (Fig. 3) as a result of the progressive closing of cracks during the season (Bouma et al., 1978).

3.2. Salt balance (irrigation and drainage)

A PG rate of 25 Mg ha^{-1} (wet weight) incorporates about 4600 kg ha^{-1} of Ca. Mean Na and Ca concentrations in irrigation water were 66.8 ± 1.6 and $62 \pm 4 \text{ mg L}^{-1}$, respectively, during the three growing seasons. This accounts for mean inputs through irrigation (for all the plots) of 750, 266 and 478 kg ha^{-1} of Na and 696, 247 and 444 kg ha^{-1} of Ca, respectively, in each growing season (Table 2). No significant differences in Na and Ca losses in drainage water between treatments were observed (Table 2). Taking into account inputs through irrigation and losses through drainage water,

Table 1
General soil properties.^a

Depth cm	Texture			Organic Carbon	CCE	pH ^b	CEC cmol _c kg ⁻¹
	Sand	Silt	Clay				
0–30	85	372	543	6.4	235	8.5	32
30–60	94	332	574	3	360	8.3	21.5
60–90	78	341	581	3	351	8.2	26.5
NR ^c	170	410	420	25.8	N.M.	8.4	25.8

^a CCE, calcium carbonate equivalent; CEC, cation exchange capacity, EC (electrical conductivity) and exchangeable cations for the farm soils are reported in Table 3 (January 2003 correspond to the initial state).

^b Determined in the 1:5 soil extract.

^c NR, non reclaimed soils (0–30 cm); N.M., not measured.

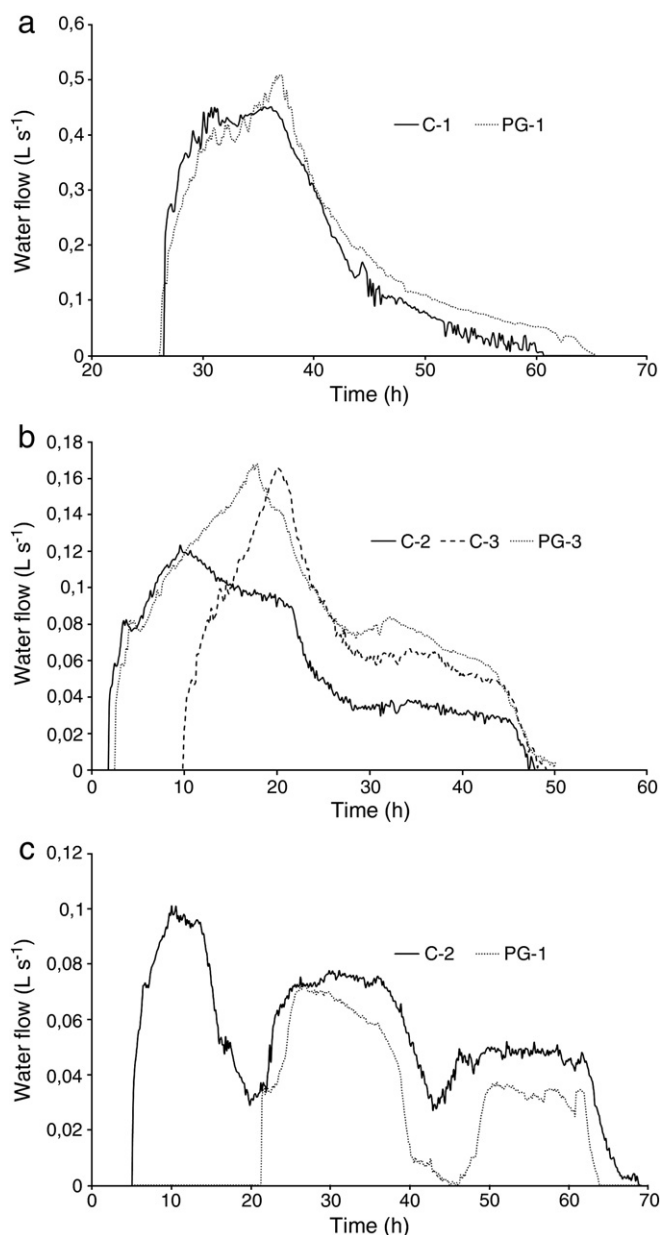


Fig. 2. Hydrographs (the origin of time corresponds to the beginning of the first turn within each irrigation episode) for cotton crop under furrow irrigation (2005): a) Plots control-1 and PG-1, corresponding to the irrigation episode of July 10th (irrigation started at time $t = 25$ h and lasted 12.5 h). b) The irrigation episode of July 25th started with plots control-2 and PG-3 (applying water during 9 h) and continued with plots control-3 (and PG-2). c) control-2 and PG-1, corresponding to the irrigation episode of August 19th (the second irrigation turn, which included plots 1, 2 – PG1-, 4, 5, 8 and 9, started 18.1 h later; and thus, it influenced the drainage hydrograph from plots irrigated in the first turn: 3, 6-C2-, 10, 11 and 12). The last relative maximum in drainage is due to the irrigation of the neighboring farm (the separation between the furrow's heads from both farms was about 10 m).

there were net Na losses of 700, 240 and 520 kg ha⁻¹ in each of the three growing seasons, respectively, and net gains of Ca of 390 and 176 kg ha⁻¹ in 2003 and 2004, respectively. Only in PG during the third growing season (after two PG applications) there was a net Ca loss of 300 kg ha⁻¹, attributable to the applied amendment.

Sodium loss by drainage was significantly related to the drainage to irrigation ratio (D/I) (Fig. 4a, $R^2 = 0.9$, $p < 0.001$). Although Ca loss was also linearly related to D/I, the slope was higher in PG than in control (Fig. 4b), likely due to the addition of Ca through the amendment. Sodium and Ca concentrations in drainage waters decreased logarithmically at increasing drain flow for both treatments

(Fig. 5a). However, Ca concentration was less dependent on the drain flow rates, and their decrease at increasing drain flow rates was lower in PG than in control (Fig. 5b). Since Ca concentrations in drainage waters were less dependent on instantaneous flow rates than Na concentrations, the associated Ca losses were mainly governed by the drained volume (and being greater for PG than for control plots, as can be deduced from Fig. 5b). For Na, the higher concentrations occurring at low flow rates had only a small contribution to the total Na losses.

First estimates of the Na losses associated to drainage after rain events produced before cotton sown (not monitored) can be done assuming the same mean percentage of drainage (3.5%) and Na concentrations in drainage water (3.2 g L⁻¹) measured under sprinkler irrigation. Thus, Na washout with rain could be around 780, and 270 kg ha⁻¹ in 2003 and 2005, respectively (no additional losses were considered for the 2004 growing season, because all the rain events were monitored, as rain season was coincident with the growing season). Similarly, for Ca (mean concentration in drainage water was 0.5 g L⁻¹) the estimated losses were 15.6% of those found for Na.

3.3. Effect of phosphogypsum on the soil salinity

At the beginning of the experiment (January 2003), there were significant differences in sodium adsorption ratio (SAR) and electrical conductivity in the saturation extract (EC_{SE}) between the three soil horizons studied: SAR was $2.18 \pm 0.12 \text{ cmol}_c^{1/2} \text{ L}^{-1/2}$ and EC_{SE} $1.64 \pm 0.09 \text{ dS m}^{-1}$ at 0–30 cm, meanwhile at 30–60 cm, the soil was saline ($EC_{SE} = 5.8 \pm 0.5 \text{ dS m}^{-1}$) but not sodic, and at 60–90 cm it was saline ($EC_{SE} = 12.5 \pm 0.8 \text{ dS m}^{-1}$) and sodic (SAR = 13.8 ± 0.4) (Table 3). After the first growing season (cotton), in November 2003, SAR significantly increased in control plots (from 0 to 60 cm depth), meanwhile it did not increase in PG plots. Calcium and EC_{SE} significantly increased at 0–30 cm for both treatments (Table 3). In September 2004, after the second growing season and prior to the second PG application, SAR and EC_{SE} increased significantly in PG at 0–30 cm depth relative to November 2003. At this depth Ca concentration in the saturation extract was higher in PG than in control. At 30–90 cm, a significant increase was observed in Ca in the saturation extract, in both treatments. The observed behaviour of Ca suggests, by one hand, a slow dissolution of PG and, by other hand, its ability for both vertical and horizontal mobility within these soils under the current agriculture practices in the area.

In January 2006, SAR, Na and Ca concentrations decreased in control and PG plots at 0–30 cm, when compared with September 2004 (end of the second growing season, Table 3), the decrease in SAR being greater in PG than in control. When compared with the initial values (January 2003), SAR did not change in control nor in PG amended plots after three growing seasons, except in the deeper horizon of control plots, where it increased as the probably result of the influence of the saline watertable (Table 3). The increment in SAR after the second growing season (Table 3) was the result of an increased Na concentration in the saturation extract as the likely consequence of the lower Na losses through drainage in comparison to the other two growing seasons (Table 2).

The estimate of the differences in exchangeable Na percentage (ESP), based on changes in SAR in the saturation extract (Levy, 2000), and considering a bulk density of 1.3 Mg m⁻³ (Moreno et al., 1995) and CEC from Table 1, show that exchangeable Na had increased in 580 kg ha⁻¹ in control plots and decreased in 175 kg ha⁻¹ in PG plots at 0–30 cm after the first growing season. In the 30–60 cm interval, Na increased in 500 kg ha⁻¹ in control plots, and only in 60 kg ha⁻¹ in PG plots. At 60–90 cm depth, it decreased in 430 and 1000 kg ha⁻¹ for control and PG plots, respectively. The global balance of exchangeable Na for the 0–90 cm soil column, accounting for changes in ESP, leads to net losses of 900 and 2600 kg ha⁻¹ for control and PG, respectively. Assuming that the net Na losses, in excess with respect to control (0–90 cm depth), were attributable to the PG application, then, the efficiency for Na/Ca displacement was roughly of 34% for the first growing season.

Table 2Water balance and Na and Ca losses by drainage for the different treatments during the three crop seasons.^a

	Control					PG			
	Rain ^b	Irrigation	Drainage	Na	Ca	Irrigation	Drainage	Na	Ca
	mm			kg ha ⁻¹		mm		kg ha ⁻¹	
Season 2003	79	1096 ± 9	80 ± 10	1500 ± 200	275 ± 26	1148 ± 24	93 ± 12	1400 ± 400	340 ± 40
Season 2003/04	491	399 ± 1	13 ± 2	511 ± 160	65 ± 12	399 ± 1	15 ± 2	500 ± 140	76 ± 20
Season 2005	33.6	704 ± 10	125 ± 3	970 ± 90	324 ± 19	728 ± 19	118 ± 10	1030 ± 90	740 ± 160

Non-significant differences were found between treatments (control and PG) for inputs of irrigation water, drainage, and Na and Ca associated losses within each cropping season. Statistically significant differences between 2003 and 2005 seasons were found only for drainage to irrigation ratios for control and PG plots, and for Ca losses within PG plots (at 95% CL).

^a Mean and standard deviation of mean for plots with the same treatment (n = 3); PG, phosphogypsum. Na and Ca losses only include drainage after irrigation episodes for cotton (seasons 2003 and 2005) and irrigation and rain for sugar beet (season 2003/04). Averaged Na and Ca concentration in irrigation water were 66.8 ± 1.6 and 62 ± 4 mg L⁻¹, respectively.

^b Rain registered within the cropping season (from March to October for cotton in 2003 and 2005, and from October to July for sugar beet in 2003–2004).

After the second growing season (September 2004), in the 0–30 cm soil layer, Na increased by 230 kg ha⁻¹ in control, and by 610 kg ha⁻¹ in PG; at 30–60 cm, Na decreased in control plots but increased in PG plots, when compared with values found at the end of the first growing season (November 2003, Table 3). In terms of Na balance in the entire soil column, PG plots showed an increase of 1440 kg ha⁻¹ during the second growing season, while it increased only in 250 kg ha⁻¹ in control plots. Thus, spatial gradients produced by the PG amendment during the first growing season seem to be now compensated by Na dynamics within the soil matrix, which may involve some additional Na supply due to the influence of the saline watertable.

After the third growing season (January 2006), Na decreased in the 0–30 cm soil horizon, by 690 and 770 kg ha⁻¹ in control and PG, respectively. At 30–60 cm, there was a slight gain of 60 kg ha⁻¹ in control, and a loss of 190 kg ha⁻¹ in PG. In the deeper horizon, there was an important increase of 740 and 860 kg ha⁻¹ in control and PG, respectively, probably ascribed to salt intrusion from the saline water table. This intrusion, which was not observed in 2003, can be explained because rain and irrigation rates in 2005 were lower than those in 2003. This salt intrusion makes difficult to estimate from the previously stated method the efficiency of this second application of PG in displacing Na.

The composition of drainage waters only showed a partial view of the PG effect on salt movement and on salt content of the soil. Within the entire soil column studied (at 0–90 cm depth), PG had worked maintaining spatial gradients in SAR in both vertical and horizontal directions (this last related at least in part to the particular experimental setup in which PG and control plots were adjacent). The horizontal mobility of Ca could be related with the observed lateral flow of

irrigation water in soil (Fig. 2c). This horizontal mobility of Ca contributes to explain the lack of significant effects of PG on drainage volumes and on the Na and Ca losses, when compared with control plots within a growing season (Table 2). The vertical mobility of PG-associated Ca seems to be relatively large, thus affecting the properties of the saturation extract not only at 0–30 cm, but also at 30–60 cm depth in PG amended plots. This vertical mobility of such a reactive cation can be explained, at least in part, in terms of the relevance of the preferential flow through cracks during drainage, which shortcuts the sorption capacity of the soil matrix (Delgado et al., 2006).

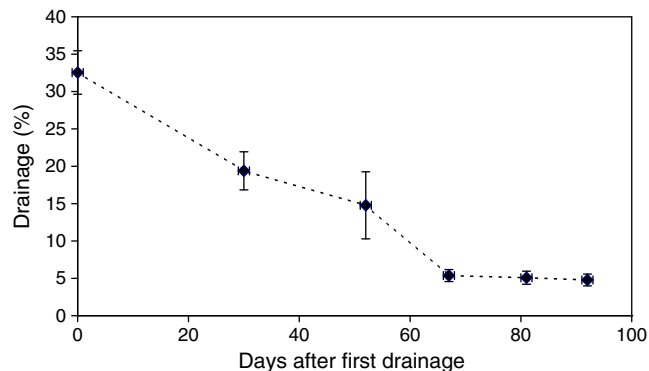


Fig. 3. Percentage of drained water with respect to applied water (by irrigation) for all the plots (mean and standard deviation of mean, n = 6) as a function of time after the first drainage (May 17th, 2005).

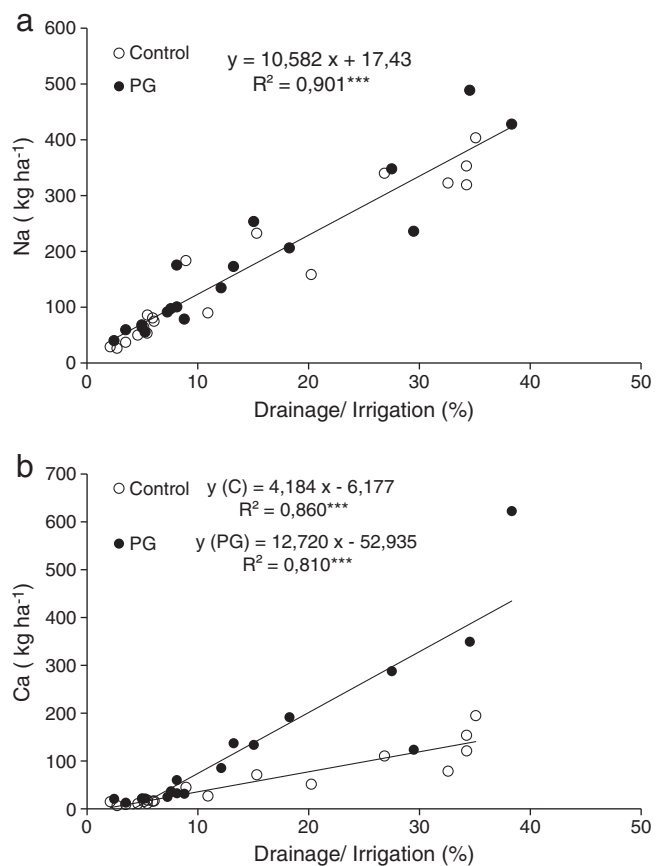


Fig. 4. a) Na losses through drainage waters (kg ha⁻¹) as a function of the D/I ratio for all the plots and irrigation episodes (cropping season 2005, cotton crop under furrow irrigation). b) As a, but Ca losses through drainage waters (kg ha⁻¹) for control and PG-amended plots. *** significant at a probability level $p < 0.001$.

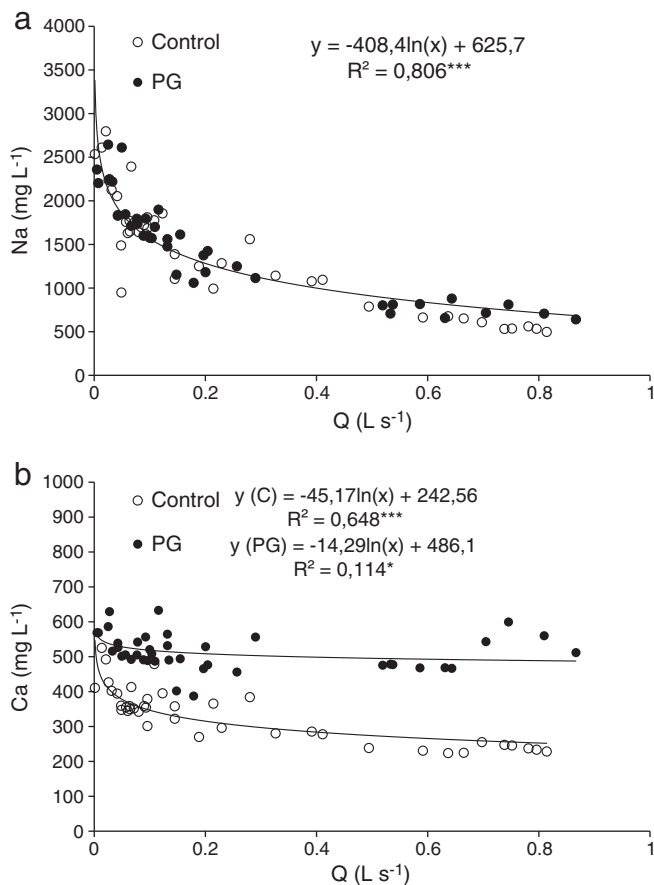


Fig. 5. a) Na concentration in drainage water versus instantaneous water flow in tail drain, for plots control-2 and PG-2. b) As a, but for Ca concentration for PG-2 and control-2 plots. Samples cover all the irrigation campaign (cotton crop under furrow irrigation, 2005). * significant at a probability level $p < 0.05$ and *** at $p < 0.001$.

The present results help to better understand the effect of PG amendments in these soils, but development of strategies to improve its efficiency should require further work. At the present stage it can be suggested that strategies to optimize PG applications should

involve: (i) application of PG amendment only when ESP in soil reached critical values (our results revealed a very low efficiency in decreasing soil sodicity at the present SAR values in soil); (ii) a better control of granulometry, which should improve, through a better dissolution, the short term efficiency of PG, and (iii) mixing PG within a thinner soil layer so as to concentrate its effects in the arable layer (due to the observed mobility of Ca).

4. Conclusions

Phosphogypsum amendment did not significantly affect drainage volumes, and associated Na and Ca losses, in comparison with non-amended plots in each of the three studied growing seasons (under our experimental conditions). The ratio of drainage to irrigation volumes (D/I) under furrow irrigation decreased in successive irrigation episodes. The total Na and Ca losses through drainage were linearly related to D/I ratio. Sodium and Ca concentrations in drainage waters decreased at increasing drain flow rates, the changes in Na concentrations with flow rates being greater in comparison to Ca.

Phosphogypsum amendment had a short term effect (during the growing season after application) on Na saturation in soil, decreasing values of SAR and CE_{SE} in the 0–30 cm soil horizon. PG-attributable changes in Ca and SAR also were observed in deeper soil layers and in adjacent control plots, suggesting an important mobility of Ca cations, as a result of water dynamics in soil.

These results can be helpful to revisit current management of PG applications as soil amendment. Particularly, in SW Spain one should consider its application only when ESP is above a certain threshold level, and to mix PG within a thinner soil layer so as to concentrate its effects in the arable layer.

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Table 3
Exchangeable cations ($mmol_c L^{-1}$), EC_{SE} ($dS m^{-1}$) and SAR ($cmol_c^{1/2} L^{-1/2}$) in the saturation extract of soils from control and PG-amended plots after two PG applications (April 2003 and September 2004).^a

Depth (cm)		All plots (Jan. 2003)	Control (Nov. 2003)	PG (Nov. 2003)	Control (Sep. 2004)	PG (Sep. 2004)	Control (Jan. 2006)	PG (Jan. 2006)
0–30	K^+	0.79 ± 0.04	1.24 ± 0.12	1.15 ± 0.07	0.94 ± 0.06	1.08 ± 0.11	0.69 ± 0.05	0.81 ± 0.07
	Na^+	5.1 ± 0.5 A	10 ± 2 B	6.8 ± 0.4 AB	14.3 ± 1.5 C	14.6 ± 1.8 C	7.1 ± 1.8 AB	4.0 ± 0.8 A
	Ca^{2+}	8.0 ± 0.8 A	25 ± 3 BC	28.4 ± 1.1 C	19.7 ± 1.1 B	43 ± 8 D	11.0 ± 2.1 A	24.6 ± 0.23 BC
	Mg^{2+}	3.1 ± 0.4	12 ± 3	9.90 ± 0.06	12.4 ± 1.3	19.6 ± 2.2	4.0 ± 1.4	6.20 ± 0.12
	SAR	2.18 ± 0.12 A	4.2 ± 1.7 BC	1.57 ± 0.10 A	5.0 ± 0.4 C	3.70 ± 0.26 BC	2.6 ± 0.3 AB	1.01 ± 0.21 A
	EC_{SE}	1.64 ± 0.09 A	4.7 ± 1.2 CD	3.57 ± 0.04 BC	4.8 ± 1.7 CD	6.1 ± 1.1 D	2.2 ± 0.5 AB	2.46 ± 0.04 AB
	30–60	K^+	1.11 ± 0.03	1.35 ± 0.05	1.22 ± 0.02	1.10 ± 0.16	0.7 ± 0.3	1.12 ± 0.21
Na^+		26.0 ± 1.2 A	41 ± 12 AB	29 ± 7 AB	34 ± 5 AB	31 ± 4 AB	41 ± 15 B	30 ± 8 AB
Ca^{2+}		18.3 ± 1.1 A	21 ± 7 AB	21 ± 8 AB	38.3 ± 1.1 D	34 ± 5 CD	28 ± 3 BCD	24 ± 3 ABC
Mg^{2+}		12.4 ± 0.7	18 ± 6	15 ± 5	38 ± 6	34 ± 5	21 ± 6	15.6 ± 1.9
SAR		6.68 ± 0.23 A	9.3 ± 0.6 B	7.00 ± 0.08 AB	7.7 ± 0.7 AB	7.6 ± 0.4 AB	8.0 ± 2.2 AB	6.6 ± 1.4 AB
EC_{SE}		5.8 ± 0.5 A	7.4 ± 1.5 AB	5.8 ± 0.8 AB	7.0 ± 0.8 AB	7.1 ± 0.5 AB	8.7 ± 1.7 B	5.7 ± 1.1 AB
60–90		K^+	1.65 ± 0.06	1.3	1.0	1.33 ± 0.06	1.26 ± 0.21	1.7 ± 0.3
	Na^+	66.6 ± 2.8 A	57	42	71 ± 7 AB	61 ± 14 AB	97 ± 24 B	92 ± 25 AB
	Ca^{2+}	22.4 ± 0.5 A	26	22	32.5 ± 1.5 B	31 ± 10 B	27 ± 3 A	28 ± 3 A
	Mg^{2+}	24.1 ± 1.2	20	18	57 ± 6	52 ± 14	33 ± 9	30 ± 5
	SAR	13.8 ± 0.4 A	12	9.4	14.4 ± 1.0 AB	13.4 ± 1.0 AB	17.5 ± 2.7 B	17 ± 3 AB
	EC_{SE}	12.5 ± 0.8 B	9.3 ± 1.7 AB	7.4 ± 1.2 A	9.5 ± 1.4 AB	10.4 ± 1.4 AB	13 ± 3 B	12 ± 3 AB

Means followed by the same letter in each row were not significantly different (from the LSD test at a probability level of 0.05). Attending to depth distributions, there were statistically significant differences in SAR among the three intervals in Jan. 2003 and Sep. 2004; and 60–90 cm interval showing statistically significant differences with upper layers in Jan. 2006.

^a Mean and standard deviation of mean (n = 6 for January 2003 and n = 3 for the rest, except for Nov.2003 at depth 60–90 cm, with a single measurement).

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