Long term geochemical variation of brines derived from a major phosphogypsum pond of SW Europe

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Abstract

The chemical evolution of brines resulting from an inactive phosphogypsum pond derived of fertilizer industry located in Huelva (Spain, SW Europe) has been studied based on a weekly sampling from 2014-2017. Long-range time variation of metals and ions concentrations in brines are expected to depend on environmental parameters such as rainfall and evaporation. The results show that brines are enriched in F^- (1.7 - 2.0 g/l), Cl^- (13 – 24 g/l), SO_4^{2-} (7.2 – 9.3 g/l), V (70 - 128 mg/l) and U (55 – 98 mg/l). A great variation of chemical concentrations has been found, due to dilution, recharge and evaporation processes. Most of the elements show peak concentrations in summer, coinciding with the lowest pH values (< 1), high conductivity (> 133 mS/cm), and high evaporation rates as expected. Nonetheless, F^- shows an opposite behaviour, varying its concentrations between 0.9 g/l in summer and 3.7 g/l in the rainy season. According to the results, a future restoration plan for PG ponds should include the removal of brines and layered salts during summer in order to avoid the annual generation of brines and their impact on the environment.

Keywords: phosphogypsum, brines, process water, layered salts, fluoride

1. Introduction

The phosphate fertilizer industry provides the phosphorous needed for farming production worldwide (Smil, 2000). The process is based on the treatment of phosphate rock with H_2SO_4, generating phosphogypsum (PG) as a waste. Worldwide PG generation is estimated to be 180 million tonnes per year (Parreira et al., 2003) with 85% disposed in open-air piles covering vast areas of land normally near waterbodies (Tayibi et al., 2009).

The production of phosphate fertilizer involves the generation of an acidic residual aqueous phase. This process water is transported by a pipeline system to a PG pond for evaporation, originating the precipitation of layered salts. Moreover, the interaction between layered salts and rain can generates brines (Lieberman et al., 2019). The chemical composition of process water is related to the raw material and the fertilizer manufacture process (Battistoni et al., 2006a). Despite of this, the process water worldwide is characterised by pH values lesser than 2, high conductivity values (9.5 - 24 mS/cm), and high concentrations of species such as F^-, PO_4^{3-}, SO_4^{2-} and metals (Battistoni et al., 2006a; Lysandrou et al., 2008).

Similar chemical characteristics are also found in brines (Pérez-López et al., 2015; Lieberman et al., 2018; Cánovas et al., 2018a). During heavy rains events, due to the accumulation of brines, the pond can collapse and produce leakage to the surroundings, posing a risk to the environment (Perpich et al., 2005). In addition, there are scarce toxicological studies about the harmful effects of process water and brines, which can produce oxidative damage to DNA, being dangerous for nearby aquatic organisms (Durgo et al., 2018). Furthermore, they can also affect vegetation through foliar damage, chromosomal aberration and inhibition of root growing (Pavlica et al., 2000; Lewandowska et al., 2013).

Despite the environmental pollution potentially derived from brines, information in the scientific literature about their chemical composition and long-term geochemical variation is scarce. Only a few studies have referenced the sampling of brines directly from PG ponds. However, they are unable to provide information about temporal evolution due to the sporadic sampling methodology (Battistoni et al., 2006b; Lysandrou et al., 2008; Gázquez et al., 2014). Recently, a study has highlighted a large variation in concentrations of brines over a one-year period (Lieberman et al., 2019b). Taking into account that PG ponds maintain their locations over decades, it is crucial to study the long-term geochemical evolution to properly characterized the residue. An accurate characterization of the waste is important for its management and the choice of potential restoration strategies.

Several PG deposits are located throughout Europe, for example France (Bisone et al., 2017), Poland (Lewandowska et al., 2013), and Croatia (Pavlica et al., 2000). One of the largest PG deposit is located in Huelva, in the southwest (SW) of Spain, which is of especial interest due to the proximity (ca. 500 m) to population (ca. 140 000 inhabitants) (e.g. Bolívar et al., 2002; Pérez-López et al., 2007). This PG deposit has been accumulated for 40 years over a marshland zone. It covers 1200 ha of which 400 ha are unrestored (PG pyramidal stack and PG evaporation pond). In 2010, the obligation of the PG restoration was established as well as the PG and process water dumping was forbidden. Since then, the unrestored PG deposit has remained exposed to weathering agents, with scarce environmental control measurements to prevent leakages (e.g. perimeter channel). Due to the interaction of rainfall with PG and layered salts, a high volume of brines (more than 1 Mm^3) has been annually generated since 2010. The interannual geochemical evolution is an issue of special importance regarding its future restoration strategy.

The scope of this work is to characterize the long-term geochemical variation of brines in an inactive PG evaporation pond. The geochemical evolution has been related to pluviometry, evaporation and recharge. Chemical composition of PG and layered salts resulting from evaporation of brines has been also characterized.

2. Methodology

2.1. The study area

The city of Huelva (ca. 140 000 inhabitants) is located at the estuary formed by the Odiel and Tinto Rivers (**Fig. 1a**). The study area comprises several zones with high ecological value such as Marismas del Odiel, a biodiversity hotspot (Myers et al., 2000). Nonetheless, the high industrialization from the 1960s generated two industrial estates (Querol et al., 2002) and great PG deposit (Bolívar et al., 2002; Pérez-López et al., 2007) derived from imported phosphate rock from Western Sahara and Togo.

The PG deposits were settled between 1997 and 2010. Two major structures were generated: a PG pyramidal stack (190 ha) and a PG evaporation pond (62 ha) (**Fig. 1a**). In order to reduce the weight in the PG pyramidal stack containing brines and to avoid the leakage, these are transported using a pipeline system to the PG evaporation pond. From a geochemical point of view, the PG localized in Huelva are enriched in metals (As, Fe, Pb, Sb, Mn, V, Cu, Co, Ni and Cr) compared to others PG worldwide (Macías et al., 2017). Furthermore, high concentrations of radioactive elements (^{226}Ra, ^{238}U and ^{210}Po) have been measured in PG (Dueñas et al., 2007; Abril et al., 2009). The influence of PG resuspension on bulk atmospheric deposition in the city has been recently characterised by the authors (Torres-Sánchez et al., 2019).

Due to the location over a marshland, several studies about estuarine pollution derived from the PG deposit in Huelva have been performed (Gázquez et al., 2014; Pérez-López et al., 2015; Macías et al., 2017). The leaching of PG produced by the groundwater flow from the tide, could incorporate thousands tons of Sr, Ti, and Cr (70 000, 1 100 and 1 200 t, respectively), hundreds tons of V (300 t) and almost one hundred ton of U (80 t) to the estuary (Pérez-López et al., 2010; Pérez-López et al., 2015). Regarding sediment pollution, the salt-marshes act as a natural barrier for pollutants due to their small particle size, which prevent the infiltration of leachates in depth. Nevertheless, the horizontal migration of the leachates can cause the pollution of the first 0.5 m of soil beneath the deposit, especially for P, that has proved to be a good tracer for PG derived pollution (Guerrero et al., 2019).

Fig. 1. a) Location of the city of Huelva and PG deposit: restored areas (1) and unrestored areas (PG pyramidal stack (2) and PG evaporation pond (3). Star: Meteorological monitoring station. Sampling point of brines in PG evaporation pond (A, B and C). Sampling points of layered salts and phosphogypsum: AS0 (1); AS1 (2); AS2 (3); AS3 (4); AS4 (5); AS5 (6); AS6 (7); AS7 (8); PG+AS1 (9); PG+AS2 (10). **b)** Detailed photographs of sampling points A, B and C.

2.2. Sampling

2.2.1. Brines

Samples of brines were collected every week between March 2014 - June 2017 (343 samples). Each sample corresponded to a volume of 0.5 L of brines, which were stored in PET containers. Three sampling points were selected at the PG evaporation pond (**Fig. 1b**):

1. Sampling point A: Located in the South of the PG evaporation pond. Occasionally, this point can reach dryness. In absence of recharge pumping with brines from the PG pyramidal stack, only a few small pools remain by the end of summer, being isolated from the main volume of brines (sampling point B). A total of 153 samples were collected between March 2014 - May 2017.
2. Sampling point B: Located at Southwest of the PG evaporation pond. In this point, brines are present during the whole year. A total of 140 samples were collected between May 2014 - May 2017.
3. Sampling point C: This sampling point represents the pipeline discharge of brines from the PG pyramidal stack into the PG evaporation pond. The sampling in this point was episodic. A total of 50 samples were collected between October 2014 - May 2017.

2.2.2. PG and layered salts

In order to study the chemical composition of PG and layered salts, a total of 10 samples were collected in the PG evaporation pond. The sampling took place between September and October 2016, coinciding with the period of maximum evaporation (**Fig. 1b**). Eight samples corresponded to layered salts (AS0-AS7) while 2 samples corresponded to a mixture of PG and layered salts (PG+AS1 and PG+AS2). Besides, three PG samples from the pyramidal stack (PG1, PG2 and PG3) derived from Western Sahara and Togo phosphate rocks were analysed.

2.3. Sample preparation

2.3.1 Brines

The physicochemical properties (pH, conductivity and redox potential) of brines were measured immediately after sampling in the laboratory using CRISON PH25+ and CRISON Conductivity Meter 524 equipment. Afterwards a diluted aliquot (1:100) was used for its chemical characterization.

2.3.2. PG and layered salts

The PG and layered salts samples, once air-dried were milled with agate mortar. A portion of 0.1 g of sample were treated with a HF:HNO_3 mixture (8:3 mL) in PTFE containers (Savillex®), heated to 90 °C overnight, and dried at 180 °C in a hotplate (de la Rosa et al., 1996). Afterwards, 3 ml HNO_3 were added, heated at 90 °C overnight and dried again at 180 °C. Finally, 3 mL HCl were added, heated at 90 °C overnight and dried again at 180 °C. The solid residue was diluted in 2% HNO_3 at 100 mL. All acids were Suprapur® grade.

2.4 Chemical analysis

Principal ions (SO_4^{2-}, Cl^-, NO_3^- and F^-) and NH_4^+ were determined by Ion Cromatography (Methrom 883 Basic IC Plus), calibrated with standard solutions for anions and cations (0.05-200 ppm). Trace elements (Li, Be, Cu, Ni, Cr, REE, Pb, Th and U among others) were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, AGILENT 7700), calibrated by cocktail solutions (Agilent Technologies) with concentrations ranging between 1 - 250 ppb. As internal standard ^{103}Rh was used. Major elements concentration (e.g. Al, Fe, Mg, Ca, Na, K) was measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Jobin Yvon Ultima 2). Multielemental solutions (AGILENT) (0.05-100 ppm) were employed for external calibration. Detection limit were 0.01-1 ppb for most analysed elements.

Certified reference materials for brines (NIST-1640a, trace elements in natural water acidified ca. 2% HNO_3) and layered salts and PG (SARM-4 norite, Geological Survey of South Africa, and

AGW-1 andesite, US Geological Survey) were used as control quality of the analysis. Accuracy ranged between 5-10% for every element.

The chemical results have been used for the statistical analysis by the Open-air package for Rstudio (Carslaw, 2012). To study the time series variation, the smoothtrend function has been performed.

2.5. Meteorology

Meteorological data (precipitation and temperature) were provided by The State Meteorological Agency of the Spanish Government (Ronda Este meteorological station). This station is located 1.5 km northward from the PG evaporation pond (**Fig. 1a**).

3. Results and discussion

3.1. Physical parameters and chemical composition of brines

Table 1 shows average values for physical parameters and chemical composition (ions, major and trace elements) in brines. The high standard deviation of concentrations for all elements explain the high variability in concentrations depending on the season. For this reason, percentile 10-90 (p10-90) are also considered in this study.

They are characterized by a high acidity with average pH values of 1.1 ± 0.4, 1.2 ± 0.3 and 1.2 ± 0.3 in A, B and C sampling points, respectively (**Table 1**). Conductivity in A is usually lower than 250 mS/cm, and lower than 150 mS/cm in B and C sampling points. Redox potential (Eh) values range between 350 and 500 mV for most of the brines, reaching values of 728 mV, 579 mV and 513 mV in A, B and C, respectively.

Table 1.

Average pH, conductivity (mS/cm), Eh (mV), ions and major elements on brines samples (mg/l). SD: standard deviation Average concentrations of trace elements in brines samples from PG evaporation pond in mg/l. SD: standard deviation. p 10: percentile 10. p 90: percentile 90. N: number of samples.

Sample	A				B				C			
	Average	SD	p 10	p 90	Average	SD	p 10	p 90	Average	SD	p 10	p 90
N	153				140				50			
pH	1.1	0.4	0.6	1.6	1.2	0.3	0.9	1.7	1.2	0.3	0.9	1.6
C (mS/cm)	126	81.7	38	193	102	43.1	37	162	98.5	40.9	39	133
Eh	458	65	374	538	452	53.7	374	508	424	52.6	343	476
g/l												
NH_4^+	2.14	2.22	5.88	0.67	1.55	0.90	0.72	2.74	1.32	0.54	0.88	1.74
F^-	1.68	1.12	0.75	3.86	1.99	1.64	0.95	3.72	1.92	0.96	1.20	3.87
Cl^-	24.7	28.8	9.4	66.6	15.0	8.47	8.38	26.6	13.7	5.07	9.82	19.7
SO_4^{2-}	9.35	5.28	5.29	15.1	8.39	3.59	5.64	12.30	7.20	1.98	4.75	9.12
PO_4^{3-}	122	129	36.1	321	83.2	46.5	37.2	152	74.8	26.5	42.4	111
Ca	2.27	0.57	1.65	3.02	2.32	0.63	1.76	3.13	2.10	0.55	1.79	2.69
K	1.25	1.38	0.44	3.39	0.85	0.41	0.47	1.53	0.71	0.21	0.47	0.95
Mg	3.93	4.43	1.28	9.51	2.59	1.38	1.35	4.94	2.15	0.73	1.46	3.27
Na	14.7	13.8	5.94	38.0	9.96	5.19	5.89	18.8	8.31	2.49	6.06	11.7
S	2.55	1.02	1.60	4.11	2.38	0.78	1.62	3.56	2.06	0.59	1.67	2.60
Br	0.37	0.62	<0.1	0.88	0.33	0.43	<0.1	0.83	0.27	0.35	<0.1	0.76
NO_3^-	0.23	0.22	<0.1	0.53	0.23	0.57	<0.1	0.44	0.18	0.18	<0.1	0.51
Al	0.33	0.32	0.11	0.80	0.24	0.13	0.11	0.42	0.24	<0.1	0.13	0.33
Fe	0.37	0.36	0.11	0.94	0.27	0.15	0.12	0.48	0.21	<0.1	0.13	0.29
mg/l												
Mn	70.2	88.1	18.0	189	92.0	479	19.0	82.7	43.2	63.1	21.8	49.0
Ti	5.51	5.02	0.35	12.8	3.39	4.34	<0.1	7.45	3.04	1.95	<0.1	5.17
Li	2.06	2.59	0.07	6.84	1.23	0.84	0.16	2.46	1.00	0.79	<0.1	2.04
Be	1.05	1.23	0.27	2.84	0.67	0.38	0.26	1.25	0.59	0.36	0.05	1.06
B	36.2	54.0	2.77	110	27.3	53.0	3.27	65.5	32.1	64.8	0.63	103
Sc	1.70	1.48	0.34	3.92	1.14	0.74	0.33	2.08	0.99	0.82	<0.1	2.66
V	128	154	32.7	399	80.1	46.7	32.0	153	69.8	35.8	6.32	107
Cr	113	132	26.5	343	69.2	41.9	24.9	116	61.4	31.6	5.42	95.9
Co	2.67	3.06	0.80	7.73	1.62	0.94	0.66	2.94	1.47	0.78	0.13	2.30
Ni	25.0	29.8	6.96	76.8	15.9	9.2	6.6	29.9	14.4	7.54	1.35	22.1
Cu	40.2	47.6	10.3	126	24.9	14.3	9.4	46.9	22.1	11.2	1.98	33.6
Zn	250	314	<0.1	718	161	109	<0.1	334	137	102	<0.1	265
Ga	0.35	0.34	0.93	0.12	0.24	0.13	0.1	0.46	0.23	0.13	<0.1	0.38
Ge	4.76	16.7	<0.1	0.68	4.29	14.0	<0.1	0.56	3.59	13.9	<0.1	0.25
As	118	144	32.8	363	72.0	40.7	32.1	141	66.4	35.3	106	6.84
Se	0.70	0.72	0.15	1.79	0.44	0.28	0.14	0.89	0.49	0.32	0.95	0.05
Rb	1.12	1.49	0.29	3.05	0.62	0.35	0.26	1.15	0.53	0.26	<0.1	0.83
Sr	73.6	51.1	31.7	155	60.7	31.3	27.8	111	53.6	26.5	79.6	5.21
Y	7.98	7.93	2.82	20.2	5.55	3.08	2.61	10.1	7.57	3.97	11.9	0.54
Zr	1.37	1.52	<0.1	3.68	0.78	0.68	<0.1	1.68	0.64	0.54	<0.1	1.36
Nb	1.16	4.51	<0.1	0.14	0.88	2.87	<0.1	<0.1	0.57	2.26	<0.1	<0.1
Mo	0.88	0.99	0.24	2.39	0.49	0.29	0.18	0.92	0.44	0.29	<0.1	0.81
Cd	36.4	34.1	13.0	90.6	27.3	14.2	12.0	50.6	23.8	12.7	2.40	39.0
Sn	0.7	2.6	<0.1	0.29	0.56	1.82	<0.1	<0.1	0.45	1.79	<0.1	<0.1
Sb	1.6	1.8	0.3	4.10	1.00	0.58	1.81	0.28	0.85	0.51	0.05	1.31
Cs	2.8	10.3	<0.1	5.08	1.67	5.33	<0.1	0.12	1.16	4.47	<0.1	0.10
Ba	3.5	13.5	<0.1	0.90	6.62	22.0	<0.1	1.59	6.05	24.1	<0.1	0.53
REE	22.7	54.8	4.27	32.6	17.4	34.1	3.45	19.4	21.2	44.6	0.74	20.2
Hf	0.60	2.38	<0.1	0.07	0.43	1.38	<0.1	<0.1	0.34	1.31	<0.1	<0.1
Ta	0.28	0.83	<0.1	0.44	0.26	0.70	<0.1	0.43	0.18	0.52	<0.1	0.21
W	1.99	6.96	<0.1	0.30	1.86	6.17	<0.1	0.17	1.08	4.30	<0.1	0.18
Tl	0.25	0.29	<0.1	0.63	0.16	0.10	<0.1	0.31	0.12	0.08	<0.1	0.22
Pb	1.26	1.66	<0.1	3.48	1.02	2.11	<0.1	1.78	0.88	0.66	<0.1	1.59
Bi	1.02	3.88	<0.1	0.13	0.60	1.95	<0.1	<0.1	0.56	2.22	<0.1	<0.1
Th	2.48	10.1	<0.1	0.28	1.94	6.23	<0.1	0.14	2.37	9.27	<0.1	0.14

U	98.5	111	29.3	240	63.8	37.9	25.8	124	55.3	29.1	4.91	83.6

High concentrations for F^-, Cl^-, SO_4^{2-} and PO_4^{3-} have been found in brines (**Table 1**). F^- is of especial interest, showing high and similar average values (1.7-1.9 g/l) in the three sampling points. The average concentration of Cl^- is 24 g/l in A sampling point, ca. twice than in B and C sampling point (13-15 g/l). A similar tendency as Cl^- has been found in PO_4^{3-}, K, Mg, and Na concentrations, with higher concentrations in A than B-C sampling points. Nonetheless, concentration of NO_3^-, SO_4^{2-} and Ca are similar in all sampling points (**Table 1**).

Trace elements more concentrated in brines compared to Upper Continental Crust (UCC, Rudnick and Gao, 2003) are As, U and Cd which are enriched in A sampling point (118, 98, 36 µg/l, respectively) compare to B (72, 63, 27 µg/l, respectively) and C (66, 55, 24 µg/l, respectively) (**Fig. A1** in appendix A). Other elements of interest are V (128, 80 and 70 mg/l for A, B and C, respectively), Cr (113, 69 and 61 mg/l for A, B and C, respectively), and REE (22, 17 and 21 mg/l for A, B and C, respectively). Regarding trace elements, high average concentrations of Zn (250, 161 and 137 mg/l for A, B and C sampling points, respectively), V (128, 80 and 70 mg/l for A, B and C, respectively) (**Table 1**) are displayed.

The p10 values are associated to the dilution effect derived from the interaction between pluviometry and brines, mostly during the rainy season. At this time, all volume of brines present in the PG evaporation pond are connected (sampling points A and B), explaining the similar concentrations. On contrast, p90 values are associated to summertime when the brines from A and B sampling point are separated, when evaporation produced by high temperature is the main weathering agent. Therefore, p90 concentrations are higher in A due to the scarce volume of brines.

3.2. Seasonal variability of brines

Seasonal variation in the period March 2014 - May 2017 of pH, conductivity, Eh, ions, major and trace element concentrations in brines from PG evaporation pond is shown in **Fig. 2** and **3,** and **Fig. A2** and **Fig. A3**. Maximum pluviometry occurs during October-November and March-April. Lowest values of pH took place during summertime in the A sampling point. However, in B and C sampling points, pH values are nearly constant during all the period (**Fig. 2**). Conductivity and redox potential have an opposite annual evolution to pH values.

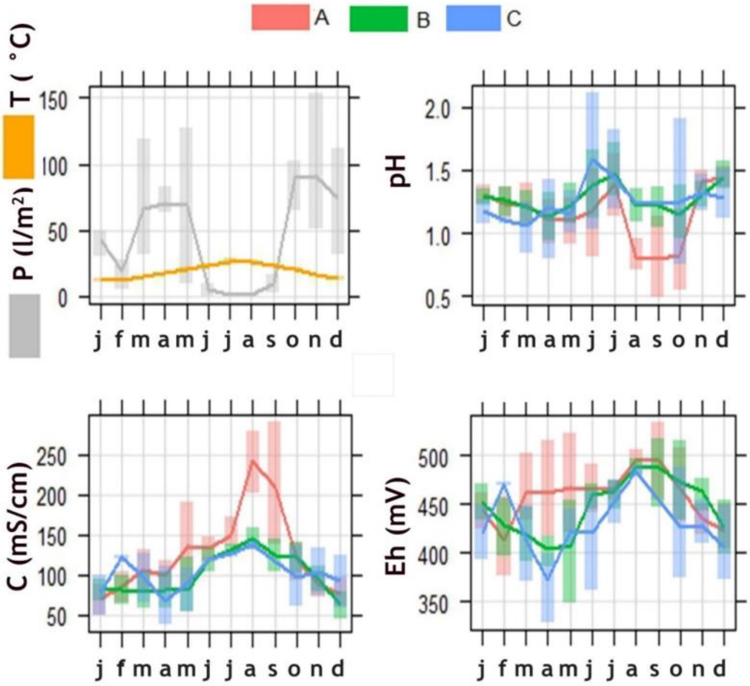

Fig. 2. Monthly evolution of pluviometry (l/m^2) and temperature (°C) in the city of Huelva. And, monthly evolution of pH, conductivity (mS/cm) and Eh (mV) on brines collected in PG evaporation pond over a three years sampling period. Shading shows the 95% confidence intervals of the average. A, B and C stand for the three sampling points.

Most of analysed elements display high concentrations in summertime (**Fig. 3**) coinciding with the lowest pH and associated to evaporation (see **Fig. 2**). However, F$^-$ shows highest concentration during rainy season opposite to the rest of elements. Due to the fact that A sampling point contains less volume of brines and they are localized in small pools, highest concentrations of most elements are obtained in this sampling point compared to B and C.

In October-November, rain water produces a dilution of brines, decreasing the element concentrations. It is noteworthy that seasonality on concentrations have been found, reaching similar concentrations of elements associated to evaporation and pluviometry in every year of sampling (**Fig. A3**). The results suggest a cyclic pattern occurring since the dumping was forbidden in 2010.

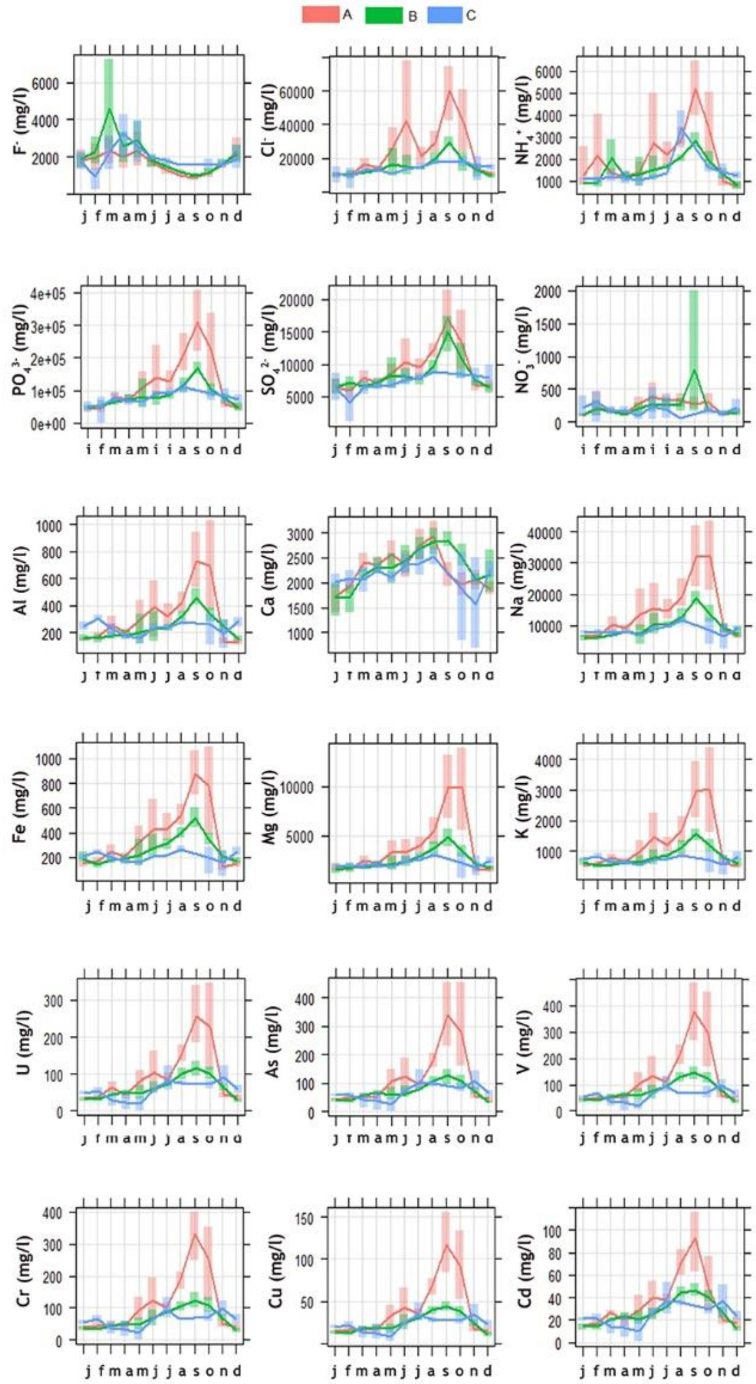

Fig. 3. Seasonal evolution of ions, major and trace elements in brines from PG evaporation pond in mg/l. Shading shows the 95% confidence intervals of the average. A, B and C stand for the three sampling points.

As it has been described above, F$^-$ shows a different behaviour compared with other elements, with higher concentrations associated to the rainy period and lower concentrations in summertime (**Fig. 4**). Geochemical evolution of F$^-$ in brines is related with the existence of F$^-$ mineral (malladrite, Na_2SiF_6) in the layered salts (Lieberman et al. 2019), which are dissolved by rainfall and incorporating F^- into brines. The positive trend observed for F^- (**Fig. A3**) is explained by the high pluviometry events during the last year of the studied period (see **Fig. A2**). The availability of F^- in brines is of especial interest regarding atmospheric pollution, due to the fact that HF can evaporate at 20 ° C, a temperature reached in Huelva at least 6 months per year (**Fig. A2)**. Due to the behaviour of F^- and its high concentrations, it can be considered as a good tracer of environmental pollution derived from the brines. Furthermore, it has been proved to be a good tracer regarding fugitive particles (Torres-Sánchez et al., 2019) and soils (Dartan et al., 2017).

Brines in PG evaporation pond of Huelva are enriched in most of the elements and compounds (e.g. F^-, Ca, Na, PO_4^{3-}, NH_4^+ and SO_4^{2-}) compared to process water and brines in literature (Table 2). This is reflected in acidic conditions (lower pH) and high conductivity. In addition, the sampling strategy followed in this study, using a sampling frequency of one sample per week during three years, allows the assessment of chemical evolution and seasonality.

Table 2.

Average composition of wastewaters and acid leachates from PG ponds in literature.

Samples and references	PROCESS WATER (Perpich et al., 2005)	PROCESS WATER (Durgo et al., 2008)	PROCESS WATER (Pavlica et al., 2000)	BRINES (Battistoni et al., 2006a)	BRINES (Lysandrou et al., 2007)	BRINES (This study B point)
n	3	1	Not indicated	Not indicated	3	140
Location	Florida, USA	Kutina, Croatia	Croatia	Not indicated	Vasiliko, Greece	Huelva, Spain
pH	2.85	1.79	-	2.33	3.1	1.28
Conductivity µS/cm	10500	-	-	24070	3199.8	102290
mg/l						
F^-	170	1540	2500-3500	767	76	1987
Ca	591	503	960	1268	858	2317
PO_4^{3-}	1600	-	3200-3800	15712	1005	83239
NH_4^+	700	-	23	1145	-	1554
SO_4^{2-}	210	-	3599	4088	4403	8394
Pb	-	0.72	-	-	-	1.02
V	-	1.72	-	-	-	80.06
Mn	-	2.74	-	-	-	91.97
Fe	-	25.8	55	50	-	269.91
Ni	-	1.1	-	-	-	15.94
Cu	-	0.58	-	-	-	24.91
Zn	-	5.75	-	-	-	161.43
K	-	71	53	381	612	849.43
Na	-	1012	1313	2712	76	9958

The chemical composition variability of brines is due to several processes: 1) dilution by pluviometry, 2) evaporation and concentration of brines, and precipitation of layered salts, principally in summer, and 3) dilution in summer and concentration in winter by pumping recharge of brines from pyramidal stack (**Fig. 4**). Taking into account the complexity of the processes affecting the brines concentrations, it has been proved that an extensive sampling strategy is necessary in order to properly evaluate the potential pollution derived from brines. In the case of Huelva, high concentrations of most toxic elements are expected in summer, when volume of brines is minimum. Taking into account that a restoration plan must be developed for the PG pond near the city of Huelva, the results of this work suggest that the brines should be removed in summertime and later treated in storage plant,

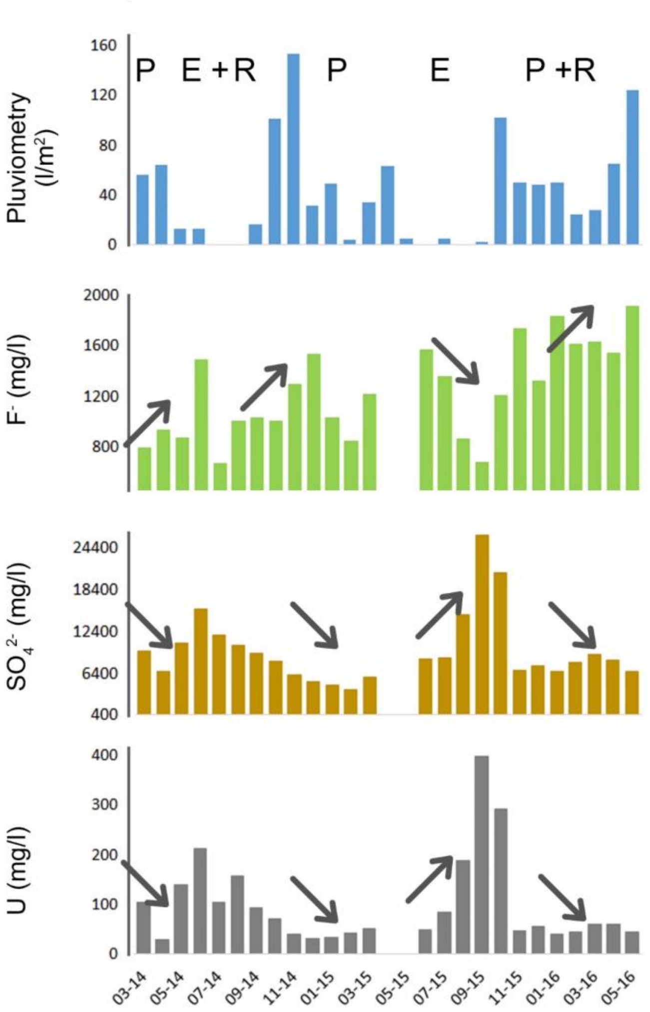

Fig. 4. Representation of the three scenarios controlling the chemical composition of brines. Dilution due to pluviometry (P), evaporation (E) and recharge (R). Arrows indicate the tendency of geochemical evolution.

3.3 Chemical composition of PG and layered salts

Major and trace elements in PG and layered salts samples are shown in **Table 3**. Detailed mineralogical and geochemical composition of the layers is described by Lieberman et al. (2019), which consist of a rhythmic layering of gypsum, phosphate and malladrite. Geochemical anomalies have been found compared to UCC (Rudnick and Gao, 2003) (Fig. A4). PG are enriched in Ca (34.3 g/kg) and S (24.5 g/kg) due to the gypsum content, which is the main component of PG (Rutherford et al., 1995). In the layered salts, high concentrations of Ca and S (14.1 g/kg and 11 mg/kg) have been found, as well as high concentrations of Na (13.4 g/kg) and P (1.47 mg/kg), derived from the malladrite and phosphates (Lieberman et al., 2019; Bisone et al., 2017).

Table 3.

Major (g/kg) and trace elements (mg/kg) chemical composition in PG (samples PG1, PG2, and PG3), layered salts (samples AS0, AS1, AS2, AS3, AS4, AS5, AS6, and AS7), and mixed PG and acid salt samples (PG+AS1 and PG+AS2) collected in PG evaporation pond.

	PHOSPOGYPSUM			LAYERED SALTS								PG + SALTS	
Sample	PG1	PG2	PG3	AS0	AS1	AS2	AS3	AS4	AS5	AS6	AS7	PG+AS1	PG+AS 2
g/kg													
Ca	34.8	39.4	28.5	13.0	14.4	29.4	14.0	12.0	9.42	10.4	10.2	7.26	6.14
Fe	<0.1	<0.1	<0.1	0.3	0.37	0.18	0.37	0.36	0.2	0.7	0.2	0.40	0.18
Mg	<0.1			<0.1	<0.1	0.12	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Na	<0.1	<0.1	<0.1	13.1	14.8	0.65	13.3	14.9	17.8	16.8	16.2	19.9	21.0
P	0.3	0.40	0.26	1.36	1.71	1.99	1.33	1.67	1.14	1.39	1.13	1.26	0.93
S	26.6	26.3	20.7	10.2	11.4	23.1	10.9	9.34	7.28	8.03	7.90	5.57	4.85
B	2.59	0.80	1.36	1.58	1.21	1.17	0.87	1.33	1.01	1.91	0.25	2.23	2.09
V	0.72	0.38	0.31	4.36	5.28	6.02	4.49	5.86	3.72	5.11	3.55	4.31	3.10
Cr	1.52	0.74	0.94	8.67	11.36	8.31	10.47	11.98	6.78	18.26	6.10	11.35	6.11
Cu	2.22	0.58	0.56	1.58	1.69	1.65	1.51	1.80	1.22	1.12	1.60	0.99	0.74
Zn	0.74	1.55	1.10	5.66	5.64	10.14	4.63	6.22	5.65	2.11	6.76	4.90	4.14
As	0.49	0.20	0.22	4.49	5.75	6.24	5.06	6.33	4.01	7.50	3.57	5.51	3.39
Se	1.21	0.87	0.86	0.28	0.32	0.79	0.32	0.29	0.22	0.31	0.24	0.17	0.14
Rb	0.10	<0.1	<0.1	0.16	0.22	0.14	0.22	0.22	0.13	0.42	0.12	0.22	0.12
Sr	65.9	51.9	54.0	39.1	42.5	61.4	39.6	55.4	47.3	25.7	46.1	22.5	22.2
Y	17.1	12.7	12.6	2.65	3.18	11.28	4.01	2.57	1.64	3.23	1.72	1.50	1.05
Zr	0.48	0.99	0.55	1.71	2.11	0.98	1.93	1.89	0.99	4.19	0.95	2.24	1.05
Mo	0.19	<0.1	<0.1	0.19	0.16	0.11	0.15	0.15	0.11	0.24	0.16	0.13	0.07
Cd	0.13	0.15	0.16	0.78	0.88	1.54	0.56	1.09	1.02	0.30	0.88	0.66	0.59
Sb	<0.1	<0.1	<0.1	0.14	0.14	0.13	0.13	0.15	0.12	0.17	0.11	0.12	0.08
Ba	10.8	5.39	5.45	3.04	3.25	4.99	4.95	4.38	1.91	4.50	2.31	4.31	3.68
REE	8.59	6.08	6.02	1.13	1.29	5.53	1.84	1.28	0.96	1.78	0.99	0.66	0.49
Hf	3.62	2.78	2.87	0.87	0.89	2.30	1.14	1.02	0.84	2.01	0.93	0.62	0.38
Ta	1.31	0.96	0.95	0.24	0.27	0.90	0.34	0.27	0.21	0.37	0.23	0.15	0.11
W	5.80	4.24	4.21	1.12	1.23	4.00	1.52	1.23	0.97	1.62	1.03	0.68	0.51

Tl	1.16	0.84	0.84	0.25	0.28	0.81	0.32	0.28	0.22	0.33	0.23	0.16	0.12
Bi	1.49	1.09	1.09	0.31	0.35	1.03	0.40	0.33	0.25	0.35	0.26	0.18	0.14
Th	0.22	0.16	0.16	<0.1	<0.1	0.16	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
U	1.49	1.10	1.10	0.36	0.39	1.07	0.42	0.38	0.29	0.34	0.30	0.20	0.17
mg/kg													
Pb	294	212	215	66.2	73.6	210	83.8	71.9	55.6	80.0	59.2	39.4	31.6
Li	9.74	26.7	8.74	105	34.4	102	25.4	95.7	34.3	0.3	65.8	44.4	52.9
Be	30.7	23.0	28.5	25.7	27.4	56.5	37.3	46.3	11.3	67.7	5.7	35.3	23.8
Sc	62.1	57.7	69.3	604	851	353	799	807	391	1763	380	981	459
Co	16.4	6.18	4.38	56.3	59.4	94.4	42.7	69.6	51.3	18.9	50.2	41.3	38.6
Ni	157	141	97.8	521	545	986	433	646	485	169	513	375	361
Ga	416	309	307	157	183	304	206	183	121	320	129	148	84.6
Ge	349	258	260	102	77.9	241	106	83.8	67.9	112	81.2	46.7	45.0
Nb	47.6	53.4	42.7	24.8	27.9	37.0	32.9	28.9	14.4	44.5	16.5	26.1	15.6
Sn	20.8	14.8	6.89	54.1	44.2	27.8	42.5	54.0	49.8	91.1	50.5	49.9	41.7
Cs	4.49	0.27	0.65	8.30	10.7	7.23	11.0	10.9	6.37	20.0	5.66	10.4	5.67

Regarding trace elements, high concentrations of Sr and Cu have been determined in both, PG (57.2 and 11.1 g/kg, respectively) and layered salts (44.6 and 15.2 g/kg, respectively). Elements such as Y and REE, are enriched in PG (14.1 and 6.90, g/kg, respectively) compared to layered salts (3.78 and 1.85 g/kg, respectively) (**Fig. A5**). The samples composed by a mixture of PG and layered salts present a profile similar to the layered salts with high concentrations of Cr (8.73 g/kg), Zn (4.52 g/kg), As (4.45 g/kg), V (3.70 g/kg), Zr (1.64 g/kg), Sc (0.72 g/kg) and Cd (0.62 g/kg) (**Fig. A5**).

In the case of Huelva, similar to other worldwide PG ponds, the variability of the chemical composition of PG samples is strongly dependent on the phosphate rock used in the production process, the composition of the H_2SO_4, and the efficiency of the process (Santos et al., 2006; Silva et al., 2010). Therefore, it is possible that layered salts derived from the process water produced in the same fertilizer factory and dumped in the same PG pond show different concentrations (Santos et al., 2006), highlighting the complexity in the characterization of the residue (Lieberman et al., 2019)

In this study, the samples derived from phosphate rock from Western Sahara (PG3 and PG1) show higher concentrations of metals (e.g. Fe, Na, Cu, Rb, Sr, Mo and REE) than the PG derived from phosphate rock from Togo (PG2). On the contrary, PG produced by phosphate rock from Togo shows higher concentrations of P, S, Zn and Zr.

The generation of process waters and precipitation of layered salt is an important issue, due to the fact that most of the toxic elements are transferred from phosphate rock to the process waters during the fertilizer production (Bolívar et al., 2009). Similar to brines, layered salts represent geochemical anomaly. Therefore, they must be removed in summertime in order to avoid the interaction with rainfall and subsequent brines generation.

5. Conclusions

In this work, we have documented the geochemical evolution of brines during three years (March 2014 - May 2017) in a major inactive PG evaporation pond near the city of Huelva (SW of Spain).

The geochemical variation for most of the compounds of brines is mainly based on dilution produced by rainfall in winter and concentration produced by evaporation in summer. The recharge with brines from other part of the PG deposits produces opposite effects depending on the season in which is performed. The recharge in summer produces dilution while in winter produces an increase in concentrations. F- presents an opposite behaviour with higher concentrations in winter due to the re-dissolution of layered salts, while in summer F- precipitates into malladrite. F- is considered a good tracer of brines in PG studies. Finally, interannual variations are cyclic and similar, depending mostly on pluviometry, evaporation and recharge by pumping.

In conclusion, this study suggests that the removal of brines and layered salts in PG ponds should be a priority in order to avoid the generation of new brines and their negative impact on the environment.

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