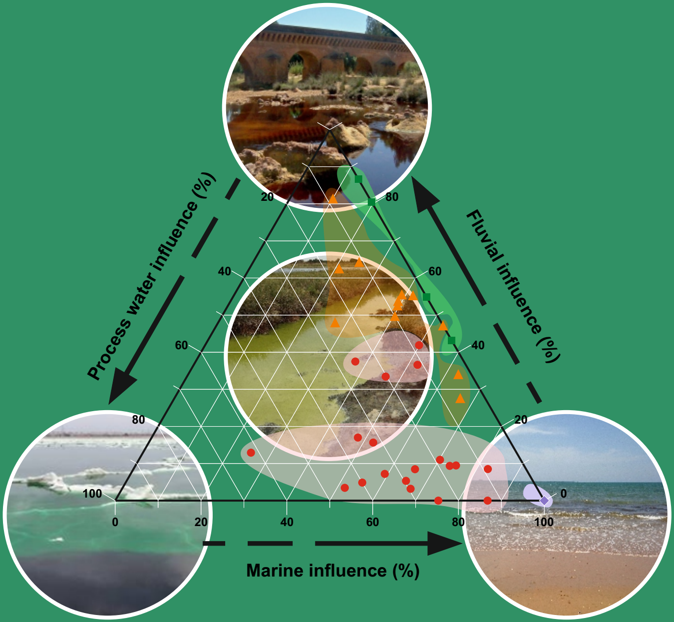
Environmental implications of a phosphogypsum disposal area (Huelva, SW Spain): Weathering processes and mobility of contaminants



Evgenia-Maria Papaslioti

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PhD Program in Earth Sciences

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Environmental Implications of a Phosphogypsum Disposal Area (Huelva, SW Spain): Weathering Processes and Mobility of Contaminants

Memorandum presented by EVGENIA-MARIA PAPASLIOTI, under the supervision of Dr. RAFAEL PÉREZ LÓPEZ and Dr. ANNIKA PARVIAINEN, to obtain the International PhD Degree.

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PhD Program
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PhD candidate

Evgenia-Maria Papaslioti

Thesis Directors:

Dr. RAFAEL PÉREZ LÓPEZ
Departamento de Ciencias de la Tierra
Universidad de Huelva

Dr. ANNIKA PARVIAINEN
Instituto Andaluz de Ciencias de la Tierra (IACT)
Universidad de Granada

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Rafael Pérez-López

Fdo./*Signed*:

Annika Parviainen

Fdo./*Signed*:

SR. COORDINADOR DEL PROGRAMA DE DOCTORADO EN CIENCIAS DE LA TIERRA
COORDINATOR OF THE EARTH SCIENCES DOCTORAL PROGRAMME

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∞ In memory of my beloved father T.T., who guided me through life and taught me the value of education.

∞ To my mother and to my husband, with love and eternal appreciation.

The mind is not a container that has to be filled, but a fire that has to light up.

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ABSTRACT

Phosphogypsum (mainly gypsum) is a highly acidic waste by-product produced by the phosphate fertiliser industry through the wet chemical digestion of phosphate ore (mainly apatite). It is usually stack-piled near coastal areas worldwide or even thrown directly to the sea, threatening the adjacent environment, as it is considered a major potential hazard with high concentrations of contaminants and radionuclides containing many dangerous chemical reagents. A huge waste facility of phosphogypsum (100 Mt; 1200 ha), stacked from 1968 until 2010, is located near the Atlantic coast of SW Spain, in an estuary formed by the confluence of the Odiel and Tinto Rivers (Huelva province). Phosphogypsum is stored in piles on the salt marshes of the Tinto River without any type of isolation, very close to the city of Huelva. The piles contain highly-contaminated groundwater that flow laterally and reach the edge of the stack forming the "edge outflows", which are acidic leakages that continuously pollute the estuary until nowadays. Another source of contamination is the water stored on the surface of the piles, known as process water, which was used to slurry the phosphogypsum and to transport it from the industry to the stack.

Preliminary restorations have taken place in some parts of the phosphogypsum disposal area and similar ones are planned for the future in the unrestored areas. Those restorations are based on a technical report that recognises process water as the main washing agent of phosphogypsum. According to this previous weathering model, the process water ponded on the surface of the stack was thought to be the main leaching agent through its infiltration and subsequently the main component of the leakages emerging as the edge outflows. However, this weathering model is questionable considering that some supposedly restored zones, i.e. without ponded process water, still discharge highly-polluted edge outflows to the estuary. In this context, the present Ph.D. Thesis focused on three lines of investigation including (i) the weathering processes occurring in the phosphogypsum stack, and on the metal mobilisation (ii) under seawater mixing with the phosphogypsum leachates and (iii) under redox oscillations in the phosphogypsum and the salt marshes.

The Ph.D. Thesis examines the possible pollution pathways originating the phosphogypsum leachates using stable isotopes ($\delta^{18}O$, $\delta^{2}H$, and $\delta^{34}S$) as geochemical tracers in order to evaluate the relationship between leachates and weathering agents of the stack. Quantification of the contribution of all possible end-members to the phosphogypsum leachates was also conducted using ternary mixing of the isotopic tracers. Accordingly, most of the outflows proved to be connected with the Tinto River and seawater end-members rather than the process water, denoting an estuarine influence and as such, presenting a different weathering model of the phosphogypsum stack, which is subjected to an open system. Hence, the access of intertidal water inside the phosphogypsum stack, for instance through secondary tidal channels, is the main responsible for the weathering of the waste. Therefore, these findings point out the ineffectiveness of the current restorations of the waste in depth and the need for a different remediation approach, because otherwise phosphogypsum leachates will continue to discharge and contaminate the estuarine environment.

Phosphogypsum stacks lie within the tidal prism of the estuary resulting to the interaction of acid wastewaters and seawater. Therefore, the effects of pH increase on contaminant mobility in phosphogypsum leachates by seawater mixing were also elucidated in the current thesis. Different types of acid leachates from the phosphogypsum stack were mixed with seawater to gradually achieve pH 7. Concentrations of Al, Fe, Cr, Pb and U in mixed solutions significantly decreased with increasing pH by sorption and/or precipitation processes. Nevertheless, new insights were provided on the high contribution of the phosphogypsum stack to the release of other toxic elements (Co, Ni, Cu, Zn, As, Cd and Sb) to the coastal areas, as 80-100% of their initial concentrations behaved conservatively in mixing solutions with no participation in sorption processes. These toxic elements remain mobile even after mixing with the alkaline seawater and finally end up to the Atlantic Ocean contributing significantly to the total metal loads and threatening the environmental conditions of the littoral. So, these findings highlighted the urgent need to adopt new effective restoration measures to minimize the impact of the phosphogypsum leachates on the estuarine environment and subsequently on the Atlantic Ocean.

The studied phosphogypsum stack, along with its basement formed by marsh soil, is a redox sensitive system and thus, the mobility of the contaminants and the related geochemical processes were studied under experimentally-controlled redox

oscillations; phosphogypsum and marsh soil suspensions were subjected to six 7-day cycles of reduction and oxidation alternately, using a bioreactor system. According to the main outcomes of the last investigation line of the thesis, Eh-pH conditions and Fe (and less S) precipitation or release during redox conditions control the geochemical processes and the mobility of the contaminants; although important metal immobilisation was not observed under the studied conditions. The formation of Fe^{3+} oxyhydroxides was favoured during oxic conditions following Fe oxidation, mostly at the phosphogypsum and less at the marsh soil due to the lower pH. The expected subsequent precipitation process of metal sulphides during anoxic conditions -after the release of Fe and other metals by reductive dissolution processes- was masked by the dominant precipitation of Fe phosphates that mainly controlled the behaviour of the metals. Nevertheless, the microbial activity of sulphate-reducing bacteria at the end of the experiment appeared to enhance and be consistent with the rare cases of sulphide precipitation under anoxic conditions, and it should be considered for similar future studies and potential treatment plans for the contaminants related to the phosphogypsum waste.

RESUMEN

Los fosfoyesos (principalmente formados por yeso) son residuos altamente ácidos producidos por la industria de fertilizantes fosfatados a través de la digestión química húmeda de roca fosfatada (principalmente formada por apatito). Normalmente, se apilan cerca de zonas costeras en todo el mundo o incluso se vierten directamente al mar, amenazando el entorno adyacente, ya que se consideran un riesgo potencial importante para el medioambiente debido a las altas concentraciones de contaminantes y radionucleidos, así como otros muchos reactivos químicos peligrosos. Una gran balsa de fosfoyesos (100 Mt; 1200 ha), apilados desde 1968 hasta 2010, está situada cerca de la costa Atlántica, en un estuario formado por la confluencia de los Ríos Odiel y Tinto (provincia de Huelva). Los fosfoyesos se han almacenado en pilas sobre las marismas del Río Tinto sin ningún tipo de aislamiento, muy cerca de la ciudad de Huelva. La balsa de fosfoyesos contiene aguas subterráneas altamente contaminadas que fluyen lateralmente alcanzando el borde de la balsa y formando flujos llamados "salidas de bordes", que son fugas ácidas que contaminan continuamente el estuario hasta hoy en día. Otra fuente de contaminación es el agua almacenada en la superficie de la balsa, conocida como agua de proceso, que se usó para mezclar el fosfoyeso y transportarlo desde la industria hasta la balsa.

Algunas restauraciones preliminares se han llevado a cabo en algunos módulos de la balsa de fosfoyesos y se planean acciones similares para el futuro en las zonas sin restaurar. Esas restauraciones se basan en un informe técnico del gobierno regional que indica que el agua de proceso embalsada en superficie es el principal agente de lavado de los fosfoyesos. Según ese modelo previo de meteorización, se pensaba que el agua de proceso apilada en la superficie de la balsa era el principal agente de lixiviación a través de su infiltración y, posteriormente, el componente principal de las fugas que emergen en el borde de la balsa. Sin embargo, este modelo de meteorización es cuestionable teniendo en cuenta que algunas zonas supuestamente restauradas, es decir, sin agua de proceso embalsada, todavía descargan salidas de borde altamente contaminantes al estuario. En este contexto, la presente Tesis Doctoral se centró en tres líneas de

investigación que incluyen (i) los procesos de meteorización que ocurren en la balsa de fosfoyeso, y la movilización de metales (ii) cuando el agua de mar se mezcla con los lixiviados de fosfoyeso y (iii) durante oscilaciones redox en el fosfoyeso y en las marismas que sustenta a la balsa.

La Tesis Doctoral examina las posibles rutas de contaminación que originan los lixiviados de fosfoyeso usando isótopos estables ($\delta^{18}O$, $\delta^{2}H$, y $\delta^{34}S$) como trazadores geoquímicos para evaluar la relación entre los lixiviados y los agentes de meteorización de la balsa. La cuantificación de la contribución de todos los miembros extremos posibles a los lixiviados de fosfoyeso también se realizó utilizando mezcla ternaria a través de los trazadores isotópicos. En consecuencia, se demostró que la mayoría de los lixiviados estaban conectados con los miembros extremos de Río Tinto y agua de mar en lugar que con el agua de proceso, lo que denota una influencia estuarina, revelando un modelo de meteorización de la balsa de fosfoyeso diferente, el cual está sujeto a un sistema abierto. Por lo tanto, el acceso del agua intermareal al interior de la balsa de fosfoyeso, por ejemplo a través de canales de marea secundarios, es el principal responsable de la meteorización del residuo. Por consiguiente, estos hallazgos señalan la ineficacia de las restauraciones actuales y la necesidad de un enfoque de remediación diferente, ya que de lo contrario los lixiviados de fosfoyeso continuarán descargando contaminantes al medioambiente estuarino.

La balsa de fosfoyeso se encuentra dentro del prisma de marea del estuario, lo que resulta en la interacción de las aguas residuales ácidas y el agua de mar. Por tanto, los efectos del aumento de pH sobre la movilidad de contaminantes en los lixiviados de fosfoyeso por la mezcla con agua de mar también se estudiaron en la presente tesis. Diferentes tipos de lixiviados ácidos de fosfoyeso se mezclaron con agua de mar para lograr gradualmente un pH de 7. Las concentraciones de Al, Fe, Cr, Pb y U en las soluciones resultantes de la mezcla disminuyeron significativamente al aumentar el pH por procesos de sorción y/o precipitación. Sin embargo, se obtuvieron nuevos conocimientos sobre la alta contribución de la balsa de fosfoyeso a la liberación de otros elementos tóxicos (Co, Ni, Cu, Zn, As, Cd y Sb) a las zonas costeras, ya que un 80-100% de sus concentraciones iniciales se comportaron conservativamente en las soluciones de mezcla sin participación en procesos de sorción. Estos elementos tóxicos permanecen móviles incluso después de mezclarse con el agua de mar alcalina y finalmente terminan en el Océano

Atlántico, contribuyendo significativamente a las descargas de metales totales y amenazando las condiciones ambientales del litoral. Por lo tanto, estos hallazgos destacaron la necesidad urgente de adoptar nuevas medidas efectivas de restauración para minimizar el impacto de los lixiviados de fosfoyeso en el ambiente estuarino y, posteriormente, en el Océano Atlántico.

La balsa de fosfoyeso estudiada, junto con su basamento de marismas, es un sistema sensible a los cambios redox y, por lo tanto, la movilidad de los contaminantes y los procesos geoquímicos relacionados se estudiaron bajo oscilaciones redox controladas experimentalmente; suspensiones de fosfoyeso y de suelos de marisma se sometieron a seis ciclos de 7 días de reducción y oxidación alternativamente, usando un sistema de biorreactor. De acuerdo con los principales resultados de la última línea de investigación de la tesis, las condiciones de Eh-pH y la precipitación o liberación de Fe (y en menor medida S) durante las condiciones redox controlan los procesos geoquímicos y la movilidad de los contaminantes; aúnque no se observó inmovilización importante de los metales bajo las condiciones estudiadas. La formación de oxihidróxidos de Fe^{3+} estuvo favorecida durante condiciones óxicas después de la oxidación de Fe, principalmente en el fosfoyeso y, en menor medida en las marismas debido al pH más bajo. El proceso de precipitación posterior esperado de sulfuros metálicos durante condiciones anóxicas -después de la liberación de Fe y otros metales debido a procesos de disolución reductiva- quedó enmascarado por la precipitación dominante de fosfatos de Fe, los cuales controlaron principalmente el comportamiento de los metales. Sin embargo, la actividad microbiana de bacterias sulfato-reductoras pareció mejorar al final del experimento y ser consistente con algunos eventos de precipitación de sulfuros en condiciones anóxicas, y debería considerarse para futuros estudios similares y planes potenciales de tratamiento de los contaminantes relacionados con los residuos de fosfoyeso.

ΠΕΡΙΛΗΨΗ

Η φωσφογυψος (κυρίως γύψος) είναι ένα πολύ όξινο απόβλητο παραπροϊόν που παράγεται από τη βιομηχανία φωσφορικών λιπασμάτων μέσω της χημικής αντίδρασης ενός φωσφορικού ορυκτού (κυρίως απατίτη) με θειικό οξύ. Συνήθως αποτίθεται κοντά σε παράκτιες περιοχές σε όλο τον κόσμο ή αποβάλλεται απευθείας στη θάλασσα, απειλώντας το παρακείμενο περιβάλλον, καθώς θεωρείται σημαντικός δυνητικός κίνδυνος με υψηλές συγκεντρώσεις μολυντών και ραδιονουκλεϊδίων που περιέχουν μεγάλη ποικιλία επικίνδυνων χημικων. Μια τεράστια εγκατάσταση αποβλήτων φωσφογύψου (100 Mt, 1200 εκτάρια), τοποθετημένη από το 1968 έως το 2010, βρίσκεται κοντά στην ακτή του Ατλαντικού ωκεανού της νοτιοδυτικής Ισπανίας, σε μια ευρύτερη περιοχή εκβολής που σχηματίζεται από τη συμβολή των ποταμών Odiel και Tinto (Huelva). Η φωσφογυψος αποθηκεύεται σε σωρούς στα αλμυρά έλη του ποταμού Tinto χωρίς κανένα τύπο απομόνωσης, πολύ κοντά στην πόλη της Huelva. Οι σωροί περιέχουν πολύ μολυσμένα υπόγεια ύδατα που ρέουν πλευρικά και φτάνουν στην άκρη της σωρού σχηματίζοντας τις επονομαζόμενες «πλευρικές εκροές», οι οποίες είναι όξινες διαρροές που μολύνουν συνεχώς την περιοχή της εκβολής μέχρι και σήμερα. Μια άλλη πηγή μόλυνσης είναι το νερό που αποθηκεύεται στην επιφάνεια της στοίβας, γνωστό ως νερό επεξεργασίας ή βιομηχανικό νερό, το οποίο είχε χρησιμοποιηθεί για την μετατροπή της φωσφογύψου σε μορφή λασπης και τη μεταφορά της από τη βιομηχανία στη σωρό.

Προκαταρκτικές αποκαταστάσεις έχουν πραγματοποιηθεί σε ορισμένα τμήματα της περιοχής απόθεσης της φωσφογύψου και παρόμοιες προγραμματίζονται για το μέλλον στις μη αποκατεστημένες περιοχές. Αυτές οι αποκαταστάσεις βασίζονται σε μια τεχνική έκθεση που αναγνωρίζει το νερό επεξεργασίας ως τον κύριο παράγοντα εκπλύσης της φωσφογύψου. Σύμφωνα με το προηγούμενο μοντέλο διάβρωσης, το νερό επεξεργασίας που περισσεύει στην επιφάνεια της σωρού είναι ο κύριος παράγοντας έκπλυσης μέσω της διείσδυσής του και συνεπώς το κύριο συστατικό των διαρροών που εμφανίζονται ως πλευρικές εκροές. Ωστόσο, αυτό το μοντέλο διάβρωσης είναι αμφισβητήσιμο δεδομένου ότι ορισμένες δήθεν αποκατασταθείσες ζώνες, δηλαδή χωρίς νερό επεξεργασίας, εξακολουθούν να εκκενώνουν ιδιάιτερα μολυσμένες πλευρικές εκροές στην περιοχή

της εκβολής. Σε αυτό το πλαίσιο, η παρούσα διδακτορική διατριβή επικεντρώθηκε σε τρεις γραμμές έρευνας που περιλαμβάνουν: (i) τις διεργασίες διάβρωσης που επικρατούν στη σωρο της φωσφογύψου, και την κινητικότητα των μετάλλων (ii) υπό ανάμιξη θαλάσσιων υδάτων με τις εκροές της φωσφογύψου και (iii) υπό οξειδοαναγωγικές εναλλαγές στη φωσφογύψο και στα αλμυρά έλη.

Η διδακτορική διατριβή εξετάζει τις πιθανές οδούς ρύπανσης των εκροών της φωσφογύψου χρησιμοποιώντας σταθερά ισότοπα ($\delta^{18}O$, $\delta^{2}H$ και $\delta^{34}S$) ως γεωχημικούς ιχνηθέτες προκειμένου να αξιολογηθεί η σχέση μεταξύ των εκροών και των παραγόντων διάβρωσης της σωρού. Επίσης, διεξήχθη η ποσοτικοποίηση της συμβολής όλων των πιθανών τελικών μελών στις εκροές της φωσφογύψου χρησιμοποιώντας τριμερή ανάμιξη των ισοτοπικών ιχνηθετών. Σύμφωνα με τα αποτελέσματα, οι περισσότερες εκροές αποδείχθηκαν συνδεδεμένες με τον ποταμό Tinto και το θαλάσσιο νερό παρά με το νερό επεξεργασίας, γεγονός που υποδηλώνει μια επιρροή από τις εκβολές των ποταμών και ως εκ τούτου παρουσιάζει ένα διαφορετικό μοντέλο διάβρωσης της στοίβας της φωσφογύψου που υπόκειται σε ένα ανοικτό σύστημα. Ως εκ τούτου, η πρόσβαση των παλοιρροϊκών νερών στο εσωτερικό της στοίβας της φωσφογύψου, για παράδειγμα μέσω των δευτερογενών παλιρροιακών διαύλων, είναι ο κύριος υπεύθυνος για τη διάβρωση των αποβλήτων. Συνεπώς, τα ευρήματα αυτά υπογραμμίζουν την αναποτελεσματικότητα των σημερινών αποκαταστάσεων των αποβλήτων σε βάθος και την ανάγκη για διαφορετική προσέγγιση αποκατάστασης, διότι διαφορετικά οι εκροές απο τη φωσφογύψο θα συνεχίσουν να εκκενώνονται και να μολύνουν το περιβάλλον των εκβολών των ποταμών.

Οι στοίβες φωσφογύψου βρίσκονται μέσα στο παλιρροιακό πρίσμα των εκβολών, με αποτέλεσμα την αλληλεπίδραση των λυμάτων με το θαλασσινό νερό. Ως εκ τούτου, οι επιδράσεις της αύξησης του pH στην κινητικότητα των μολυσματικών ουσιών στις εκροές της φωσφογύψου λόγω ανάμιξης με θαλασσινό νερό επίσης, επεξηγήθηκαν στην τρέχουσα εργασία. Διαφορετικοί τύποι όξινων εκροών από τη στοίβα φωσφογύψου αναμίχθηκαν με θαλασσινό νερό ώστε να επιτευχθεί σταδιακά pH 7. Οι συγκεντρώσεις των Al, Fe, Cr, Pb και U στα μικτά διαλύματα μειώθηκαν σημαντικά με την αύξηση του pH μέσω διεργασιών προσρόφησης και / ή απόθεσης. Παρ 'όλα αυτά, δόθηκαν νέες πληροφορίες σχετικά με τη μεγάλη συμβολή της στοίβας φωσφογύψου στην απελευθέρωση άλλων τοξικών στοιχείων (Co, Ni, Cu, Zn, As, Cd και Sb) στις παράκτιες περιοχές, καθώς το

80-100% των αρχικών συγκεντρώσεων τους συμπεριφέρθηκε συντηρητικά στα διαλύματα ανάμιξης χωρίς συμμετοχή σε διεργασίες προσρόφησης. Αυτά τα τοξικά στοιχεία παραμένουν κινητικά ακόμη και μετά από την ανάμειξη με το αλκαλικό θαλασσινό νερό και τελικά καταλήγουν στον Ατλαντικό Ωκεανό συμβάλλοντας σημαντικά στα συνολικά φορτία μετάλλων και απειλώντας τις περιβαλλοντικές συνθήκες της παραλιακής περιοχής. Συνεπώς, τα ευρήματα αυτά υπογράμμισαν την επείγουσα ανάγκη να υιοθετηθούν νέα αποτελεσματικά μέτρα αποκατάστασης για την ελαχιστοποίηση των επιπτώσεων των λυμάτων της φωσφογύψου στο περιβάλλον των εκβολών των ποταμών και, στη επομένως, στον Ατλαντικό Ωκεανό.

Η σωρός φωσφογύψου που μελετάται, μαζί με το υπέδαφός της που σχηματίζεται από έλη, είναι ένα σύστημα που υπόκειται σε οξειδοαναγωγή και έτσι μελετήθηκε η κινητικότητα των μολυσματικών ουσιών και οι σχετικές γεωχημικές διεργασίες υπό πειραματικά ελεγχόμενες οξειδοαναγωγικές εναλλαγές˙ η φωσφογύψος και το ελώδες υπέδαφος υποβλήθηκαν σε έξι εναλλάξ κύκλους αναγωγής και οξείδωσης των 7 ημερών, χρησιμοποιώντας ένα σύστημα βιοαντιδραστήρα. Σύμφωνα με τα κυριότερα αποτελέσματα της τελευταίας γραμμής έρευνας της διατριβής, οι συνθήκες Eh-pH και η καθίζηση ή απελευθέρωσης του σιδήρου (και λιγότερο του θείου) κατά τη διάρκεια των οξειδοαναγωγικών συνθηκών ελέγχουν τις γεωχημικές διεργασίες και την κινητικότητα των μολυντών. Παρ'όλα αυτά. δεν παρατηρήθηκε σημαντική ακινητοποίηση των μετάλλων υπό τις υπό μελέτη συνθήκες. Ο σχηματισμός Fe^{3+} οξυυδροξειδίων ευνοήθηκε κατά τις οξικές συνθήκες μετά την οξείδωση του Fe, κυρίως στη φωσφογύψο και λιγότερο στα έλη λόγω του χαμηλότερου pH. Η αναμενόμενη επακόλουθη διαδικασία απόθεσης σουλφιδίων κατά τη διάρκεια των ανοξικών συνθηκών - μετά την απελευθέρωση του Fe και άλλων μετάλλων με διαδικασίες αναγωγικής διάλυσης - καλύφθηκε από την κυρίαρχη διαδικασία απόθεσης των φωσφορικών αλάτων του Fe, τα οποία κυρίως ελέγχουν τη συμπεριφορά των μετάλλων. Ωστόσο, η μικροβιακή δραστηριότητα των βακτηρίων που ανάγουν τα θειικά άλατα φάνηκε να ενισχύεται στο τέλος του πειράματος και να είναι συμφωνεί με τις σπάνιες περιπτώσεις απόθεσης σουλφιδίων κάτω από ανοξικές συνθήκες και θα πρέπει να ληφθεί υπόψη για παρόμοιες μελλοντικές μελέτες για πιθανά σχέδια αποκατάστασης των σχετικών μολυντών στα απόβλητα της φωσφογύψου.

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Part I

INTRODUCTION, AIMS AND RESEARCH IMPACT

CHAPTER 1

INTRODUCTION

1. Introduction

Peri-urban areas are transition zones between urban and rural activities that are often affected by elevated contamination levels. They are highly influenced by anthropogenic activities due to rapid industrialisation and urbanisation that damage the soil quality and natural landscape. Most industrial complexes pose in severe environmental hazards as the waste management is not sufficient and tends to be unregulated (Fernández-Caliani, 2012). A prime example of such an area is the city of Huelva, in western Andalusia (Spain), which is one of the first industrial cities in Europe. This zone has become heavily contaminated in an extent that might pose significant risk to human health and ecosystems. This doctoral thesis focuses on the mobilisation of metals from a waste disposal area from the fertiliser industry, located in the vicinity of Huelva. In the following, a description of the study site and the problem setting is given.

1.1 Estuary of Huelva: General setting

Huelva is situated in an estuarine system known as "Ria de Huelva", which is composed by the confluence of the Odiel and Tinto Rivers, on the Atlantic coast of South Spain **(Fig. 1.1; Fig. 1.2A)**. It belongs to the northwest coasts of the Gulf of Cadiz at the confluence of the Atlantic Ocean and the Mediterranean Sea (Grande et al., 2003). This estuary system includes one of the most important marsh ecosystems in Europe (Borrego et al., 2013), declared as UNESCO Biosphere Reserve and RAMSAR-NATURA wetland with high-priority protection status. It may seem paradoxical, however, that the Estuary of Huelva can also be considered as one of the most polluted aquatic systems in the world. The main pollution sources are the abandoned mining activity from the Iberian Pyrite Belt (IPB) and, secondarily, the current industrial activity from the Huelva Industrial Estate.

The estuary in the study area is an aquatic system that is subjected to fluvio-marine interactions. As a result, hydrochemistry and the properties of the sediments and the suspended matter are controlled by the fluvial input, the marine contribution and by the mixture processes in the estuarine system. All these processes, in combination with the anthropogenic activities in the area, cause modifications on the biogeochemical conditions inside the estuary and on the nature of the fluvial inputs (Borrego et al., 2013). In addition, degradation of the ecosystem may occur due to the alterations and anomalies in the chemistry of the waters and sediments caused by the anthropogenic activities, leading to subsequent contamination.

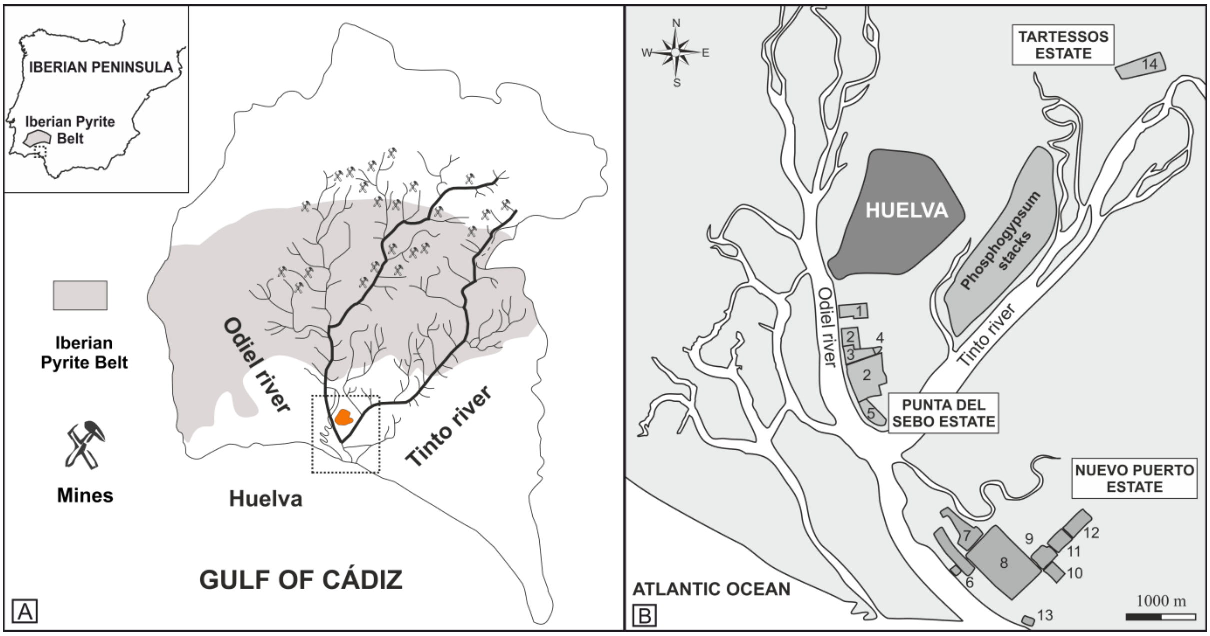


Figure 1.1: (A) Sketch showing the Huelva province with the Iberian Pyrite Belt (IPB) and the main mines. **(B)** Sketch showing the Huelva city including the Industrial State and the phosphogypsum stack; Punta del Sebo industrial estate: (1) fertilizer plants, (2) fertilizer plants, (3) metallurgical plants, (4) air gases plants and (5) power generation plants; Nuevo Puerto industrial estate: (6) chemical plants, (7) hydrocarbons storage, (8) petrochemical plants, (9) petrochemical plants, (10) fertilizer plants, (11) chemical plants, (12) pigment plants and (13) hydrocarbons storage; Tartessos industrial estate: (14) cellulose paste plants.

1.1.1 Environmental implications from the mining activity

The main pollution source of the studied estuarine system is the abandoned mining activity from the IPB that is located in the central part of Huelva Province **(Fig. 1.1A)**. It is one of the largest massive sulphide deposits worldwide with original reserves in the order of 1700 Mt (Sáez et al., 1999). The mining and metallurgical wealth of the IPB was the economic support for numerous civilizations that settled there from prehistoric times (Nocete et al., 2005). The mining activity has almost totally ceased now and the legacy of this historic tradition left over a hundred abandoned mines with open pits and about 200 million m^3 of sulphide-rich mining wastes. The oxidation of sulphide wastes in atmospheric conditions produces an extremely acidic drainage with high content of sulphate and potentially toxic elements in solution know as acid mine drainage (AMD). Large quantities of these acidic leachates are drained by the Tinto and Odiel Rivers, causing their total degradation, while both rivers act as a vehicle for the pollutant load to the estuarine-coastal system of Huelva (Olías et al., 2006; Nieto et al., 2007; Sarmiento et al., 2009). Consequently, fluvial waters and sediments are characterised by extremely low pH values and high concentrations of metal(loid)s (i.e. As, Cu, Cd, Pb, Sb, Zn; Nieto et al., 2013). In such aquatic environment affected by high salinity waters and AMD, adsorption or desorption processes occur due to strong pH variations when river water mixes with seawater in the estuary. Therefore, these modifications can influence the transference of contaminants from dissolved phases to suspended particulate matter and subsequently to sediments (López-González et al., 2006).

1.1.2 Industrial activity in the Estuary of Huelva

Intensive industrial activity in the Huelva Industrial Estate began in the 1960's due to the aforementioned sulphide mining activity and thus, a huge complex of chemical and petrochemical industries was installed in the Estuary of Huelva **(Fig. 1.1B)**. Besides the production of both copper and sulphuric acid from local and imported sulphides, the industrial activity included pulp for paper manufacture, titanium dioxide pigment and fertilisers from phosphate rock ore, among others. Therefore, the industrial discharges from the current industrial activity at the Huelva Industrial Estate represent a secondary pollution source for the estuarine system (Pérez-López et al., 2011a). Dissolved Pb is recognized as causing significant contamination, and its isotopes (^{210}Pb) have been traced in the industrial wastes (Braungardt et al., 2003). Furthermore, the estuarine system is greatly affected by the phosphate industry, which accounts for a huge plant producing large volumes of phosphogypsum waste. These wastes are deposited adjacent to the estuary and discharge leachates into it (Davis et al., 2000). This latter source of contamination is examined in this doctoral thesis, as the influence of phosphogypsum has been proved to be important to the area of interest with many aspects worth being investigated.

1.2 Phosphogypsum waste

The phosphate fertiliser industry is responsible for the generation of a waste by-product, known as phosphogypsum (mainly gypsum, $CaSO_4 \cdot 2H_2O$), during the production of phosphoric acid (H_3PO_4) via the wet chemical digestion of phosphate ore (fluorapatite, $Ca_5(PO_4)_3F$) with sulphuric acid (H_2SO_4), and for stacking of this waste on disposal areas. The overall chemical reaction can be written ideally as (Eq. 1):

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4{\cdot}2H_2O + HF \quad (1)$$

Phosphogypsum is dominated by calcium and SO_4^{2-}, as it is >90% of gypsum, having similar physical properties to natural gypsum, and it is formed mainly of medium to fine-grained particles. The phosphate rock that is mainly used is fluorapatite ($Ca_5(PO_4)_3F$) and is pre-concentrated by flotation, a process enhanced by reagents such as ammonium hydroxide or amine (Rutherford et al., 1994). The raw phosphate ore has elevated contents of potentially toxic metal(loid)s (e.g. Zn, As, Cd, Cu, Fe, Ni and Pb), organic compounds and radioactive elements (e.g. radionuclides from the ^{238}U series, such as U, Ra and Rn), which are transferred to the phosphogypsum waste during the industrial process, according to their solubility (Rutherford et al., 1994; Bolívar et al., 2009; Pérez-López et al., 2010). Except for some elements with chemical affinity to Ca (e.g., Ra, Sr, Y), most of the contaminant impurities are partitioned into the commercial phosphoric acid during the manufacturing process, resulting in both a decrease in the quality of the final acid product and the need for various purification processes to remove these impurities (Bolívar et al., 1996a; 2009; Pérez-López et al., 2010). Phosphogypsum contains residual reagents and products from the industrial process trapped in its interstices, mainly phosphoric acid, which is not fully separated in the factory, but also an excess of sulphuric and hydrofluosilicic acids (Lottermoser, 2010). These reagents and their reaction products make phosphogypsum extremely acid, while the majority of the metals in phosphogypsum are contained in the residual phosphoric acid. Most of the potentially toxic contaminants contained in the phosphogypsum are associated with the mobile fraction, which poses a threat to the environment under extremely acidic conditions (Pérez-López et al., 2010). Special attention has been drawn on the high content of radionuclides in the phosphate ore and thus, in the radioactivity of the waste and as such, the radioactive impacts of phosphogypsum have been well-studied (e.g. Bolívar et al., 1996a, 1996b, 2002). In particular, U, Th and ^{210}Pb are concentrated and remain in the phosphoric acid, while ^{226}Ra and ^{210}Po are finally transferred to phosphogypsum (Lottermoser, 2010). Therefore, phosphogypsum is considered as a significant source of environmental contamination (Pérez-López et al., 2016). The free water content of phosphogypsum varies and depends on the duration of its drainage after sluicing to the stack and on the meteorological conditions. According to Rutherford et al. (1994), the chemical and mineralogical characteristics of phosphogypsum are influenced by the wet process and depend on the type and the particle size of the phosphate rock, the concentration of the phosphoric acid, the solid content and the excess sulphuric acid in the slurry, the impurities in the phosphate rock, the temperature and the reaction system.

The phosphate fertiliser industry is witnessing growth in order to comply with the farming production worldwide. Approximately 5 tons of phosphogypsum are generated for every ton of phosphoric acid manufactured (Pérez-López et al., 2011b) and the production of the waste is estimated to be about 100-280 Mtons/year worldwide (Yang et al., 2009). While huge amounts of phosphogypsum are produced, the potential applications of reuse do not often meet the condition of high-consumption (Cánovas et al., 2018). Phosphogypsum is a low-cost waste, which is often used as an additive in agricultural soils or for the formation of ettringite-based binders, as a raw material in plastic bricks, masonry walls, sodium sulphate, soil limestone and ammonium sulphate, as a building material and as a soil amendment for stabilisation (Pérez-López et al., 2010). However, these applications are limited due to the high content of potentially toxic impurities that could harm human health; in fact, only 15% of its worldwide production is recycled. In general, the sources of environmental contamination due to phosphogypsum storage include: (1) atmospheric pollution with fluoride, or other toxic elements; (2) groundwater pollution including acidity, mobile anions, trace elements and radionuclides; (3) radon gas; (4) radioactive dust; (5) gamma radiation; (6) surface runoff and (7) erosion and stability of the piles (Rutherford et al., 1994).

Phosphoric acid plants and, hence, phosphogypsum stacks are often located in coastal areas, due to their relatively flat surface for the industrial activity, the nearby water availability and the proximity of the sea as a means of communication (Lysandrou and Pashalidis, 2008; Sanders et al., 2013; El Samad et al., 2014; El Zrelli et al., 2015). Phosphogypsum stacks in such areas are affected by weathering processes and could cause severe environmental damages.

The wet chemical process that produces phosphoric acid requires large volumes of water, commonly known as process water, for a multitude of uses in the industrial complex. Process water is used, for instance, to slurry the phosphogypsum and to transport it to storage in large stacks close to the fertiliser plants that are exposed to weathering conditions. Additionally, process water is often stored in ponds on top of the stacks, forming a waste facility that can pose serious threat to the adjacent environment due to their potential leaching (Tayibi et al., 2009). Nevertheless, there are no formal regulations for the management of such hazardous material (Macías et al., 2017), despite its worldwide impact in many phosphogypsum disposal areas (see review in Tayibi et al., 2009).

1.3 Study area: Environmental setting

A paradigmatic example of phosphogypsum disposal area is located in the Huelva Estuary (SW Spain), in the confluence of the Tinto and Odiel Rivers **(Fig. 1.2A)**. The industrial production of phosphoric acid in Huelva mainly used sedimentary phosphorite imported from Morocco. Between 1968 and 2010, this activity led to the disposal of approx. 100 Mt of phosphogypsum wastes in stacks covering an area of 12 km^2 directly on the salt marshes on the right margin of the Tinto River. The phosphogypsum stacks are exposed to weathering conditions. On the one hand, the disposal area is in the tidal prism of the estuary, which ranges between 37 and 82 hm^3 during a half cycle (6 hours) (Grande et al., 2000). On the other hand, the region is characterised by Mediterranean climate with rainy winters and warm and dry summers: annual average precipitation of 490 mm and temperature of 19.2 °C (1990–2010; National Meteorology Institute) (Pérez-López et al., 2015). Consequently, the stack could be weathered by several agents: (i) seawater intrusion during the tidal cycles, and (ii) rainwater during rainy seasons, which are rare but intense due to the climate (Cánovas et al., 2017).

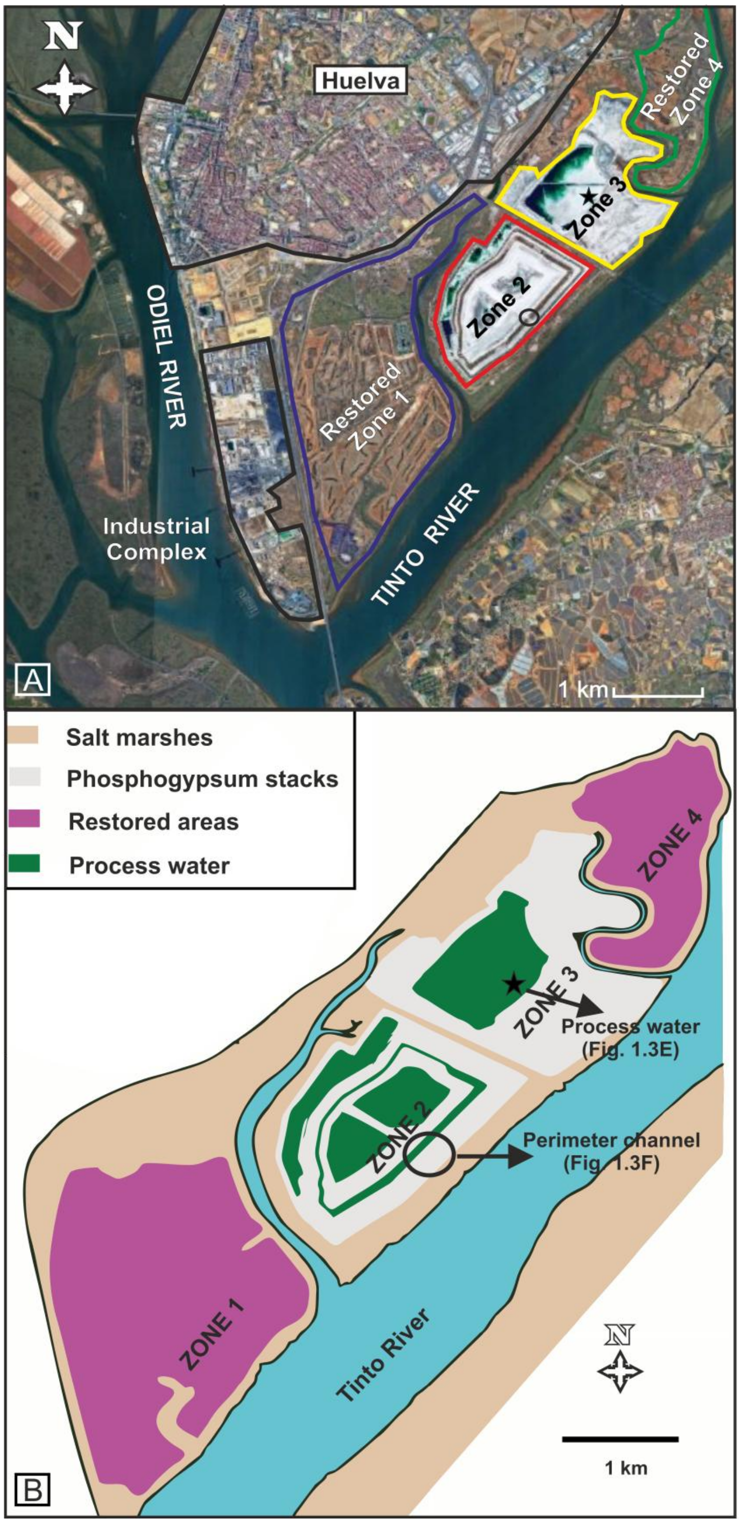


Figure 1.2: (A) Aerial photo of the Tinto-Odiel estuarine system of Huelva and the study area of the phosphogypsum stack. Process water on surface ponds and in perimeter channels of zones 3 and 2, respectively, is also highlighted. (**B)** Arrangement of the four zones in which the phosphogypsum stack is divided.

The phosphogypsum stacks are directly settled on bare marshland soils without isolation to prevent leaching. The presence of the residual acids trapped in the interstices of the gypsum particles makes the piles behave as an unconfined aquifer, clearly distinguishing an unsaturated zone and a saturated zone with contaminated groundwater flow. The marsh soils act as an impermeable barrier that withholds groundwater in depth and forces the water to flow laterally. When the groundwater reaches the edge of the stack, acidic polluted effluents emerge forming superficial drainages, known as edge outflows, which release high load of contaminants into the estuary **(Fig. 1.3A-D)**. The edge outflows contribute significantly to the contamination of the estuary by increasing the concentration of contaminants related to the AMD and by entering new contaminants such as ammonia, Ce, Cr, Ti, V, Y, Sr, U and Ba (Pérez-López et al., 2007; 2010). These effluents might even affect some remote zones of the estuaries due to the tidal action (Bolívar et al., 2002). Another factor that influences the weathering of the waste is the absence of any impermeable barrier between the stack and the organic matter-rich marshland, resulting in their interaction. Thus, the weathering of phosphogypsum is favored under oxidizing conditions in the shallowest part and under reducing conditions in its contact with the marsh sediment (Pérez-López et al., 2015).

A brief historical review is necessary to understand the current configuration of the phosphogypsum stack. From 1968 to 1997, 80% of the produced phosphogypsum was transported as aqueous slurry to four decantation zones, in an open-circuit system, using seawater, while the rest 20% was disposed directly to the Odiel River estuary (Martínez-Aguirre et al., 1996). However, due to the enforcement of more strict environmental regulations according to the OSPAR convention (OSPAR, 2002; 2007), the factory was forced to avoid any direct discharge to the estuary. As such, from 1997 to 2010 -when phosphogypsum disposal was ceased- the new waste management plan included the deposition of 100% of the phosphogypsum waste in a large pyramidal pile over a single zone using a closed-circuit system with freshwater as process water instead of seawater. In this latter system, large superficial ponds were created on the stacks in order to contain the process water **(Fig. 1.2A; Fig. 1.3E)** and lose it by evaporation, along with perimeter channels to collect all leachates from the piles **(Fig. 1.2A; Fig. 1.3F)** (Pérez-López et al., 2015). Process water ponds are an additional source of contamination as they reach the estuarine environment through some point discharges (Pérez-López et al., 2016).

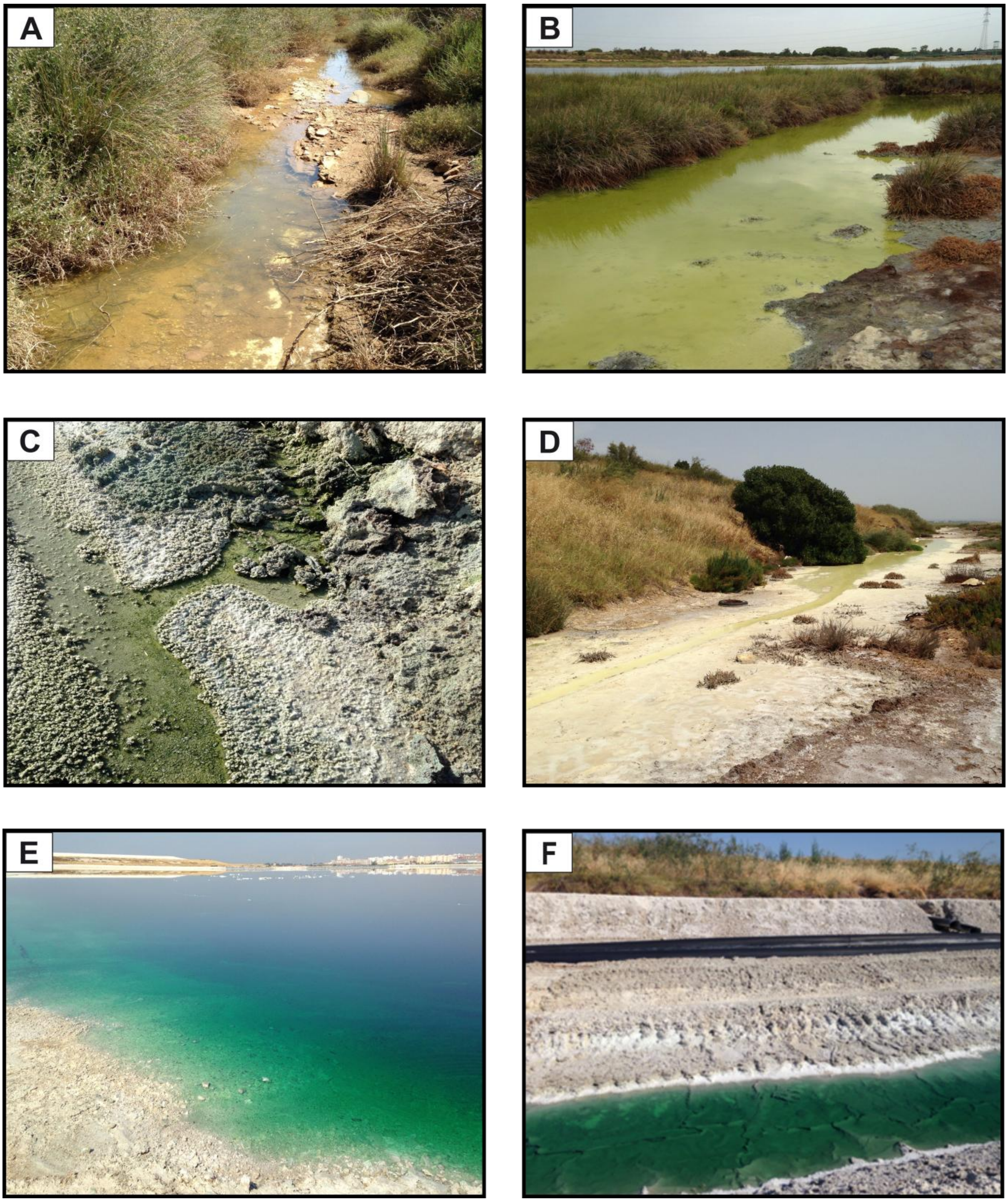


Figure 1.3: Edge outflows from **(A)** Zone 1, **(B)** Zone 2, **(C)** Zone 3, and **(D)** Zone 4. **(E)** Process water ponded on the surface of zone 3. **(F)** Perimeter channel built to collect the phosphogypsum lixiviates from zone 2.

1.4 Arrangement, weathering model and restoration actions of the phosphogypsum stack

At present, the disposal area is clearly divided into four zones **(Fig. 1.2B)**; the zones 1 (35 Mt; 400 ha; 2–3 m in height) and 4 (30 Mt; 280 ha; 8–10 m) are currently considered as restored areas, i.e. without process water pond and with a top cover. In particular, zone 1 is covered by 25 cm natural soil and vegetation, while zone 4 has a more complex cover including 1 m of building wastes, 2 m of inert industrial wastes and 30-50 cm of topsoil. On the other hand, the zones 2 (25 Mt; 240 ha; up to 30 m) and 3 (15 Mt; 200 ha; 8–12 m) are directly exposed to weathering without restoration actions, i.e. uncovered and with surface ponds of process water. The phosphogypsum of zones 1, 3 and 4 was deposited using the open-circuit system with seawater; whereas, the dumping sequence in the pyramidal zone 2 comprises a first filling stage with seawater before 1997 and a second stage with process water after 1997. Despite their different arrangement, all disposal modules are source of numerous edge outflows discharging into the estuarine environment (Pérez-López et al., 2016).

Similar restorations that have been already applied in zones 1 and 4 are planned for the other zones in the future, relying on some guidelines taken by the regional government based on a preliminary report (Junta de Andalucía, 2009). Roughly, these actions include: (i) the removal of the process water from surface ponds, (ii) the pumping and removal of the pore water inside the stack to prevent its lixiviation, (iii) the *ex-situ* treatment of those wastewaters, and (iv) the covering of the piles surface with artificial soil including a drainage system that will remove rainwater (Pérez-López et al., 2015). Those restoration plans are based on the assumption that the process water ponded on surface is the main route of dispersion of pollutants to the environment; the leaching of the edge outflows towards the estuary originates mainly from the downward infiltration of the process water from the surface to the piles and the groundwater that eventually reaches the edge of the stack **(Fig. 1.4A)**.

However, these guidelines were issued without proving clearly the connection between the process and the edge outflow waters. Hence, there is lack of information on the weathering process regarding leaching and transport of the contaminants to the estuary. In fact, Pérez-López et al. (2015) suggested that the two types of phosphogypsum leachates are poorly connected based on Cl/Br ratios and rare earth elements (REE) as geochemical tracers. According to that study, process water has typical geochemical characteristics of phosphate fertiliser, while deep pore-waters and edge outflows are more connected to the AMD-impacted Tinto River. Thus, Pérez-López et al. (2015) proposed a possible pollutant dispersion pathway associated with the weathering of the phosphogypsum in depth through the upward input of estuarine waters, resulting in the seawater source to be the main washing agent **(Fig. 1.4B)**. Taking into account these latter suggestions, the proposed restorations would not be effective and the lixiviation of phosphogypsum will not cease **(Fig. 1.4C)**. Indeed, the absence of process water ponded on the surface of a 'supposedly' restored zone has not prevented the presence of numerous discharge points reaching the estuary until nowadays, which demonstrate the real inefficiency of the already-implemented restorations (Pérez-López et al., 2016).

While pollution from abandoned mining activities and wastewater effluents discharged directly from industries to estuary, is well characterized (e.g. Pérez-López et al., 2011b), there is an obvious lack of information on the pollution related to the phosphogypsum stack. The contamination related to the edge outflows deriving from the stack is well known, but some related aspects are not adequately characterised until now: (1) the weathering model of the phosphogypsum stack; i.e., the agents that intervene in the leaching of pollutants; (2) the behaviour of the pollutants when the acidic leachates mix with the estuarine waters and (3) the behaviour of the contaminants in the anoxic interface between the stack and the marsh basement. Therefore, the current doctoral thesis aimed at bridging these knowledge gaps. The combination of marsh ecosystem and contamination from mining and industrial activities establish the study site as a unique and paradigmatic area worth being thoroughly investigated. Another singularity of the Huelva phosphogypsum is its anomalously high metal(loid) concentrations (mainly As) and their higher mobility compared to other stacks worldwide (Macías et al., 2017).

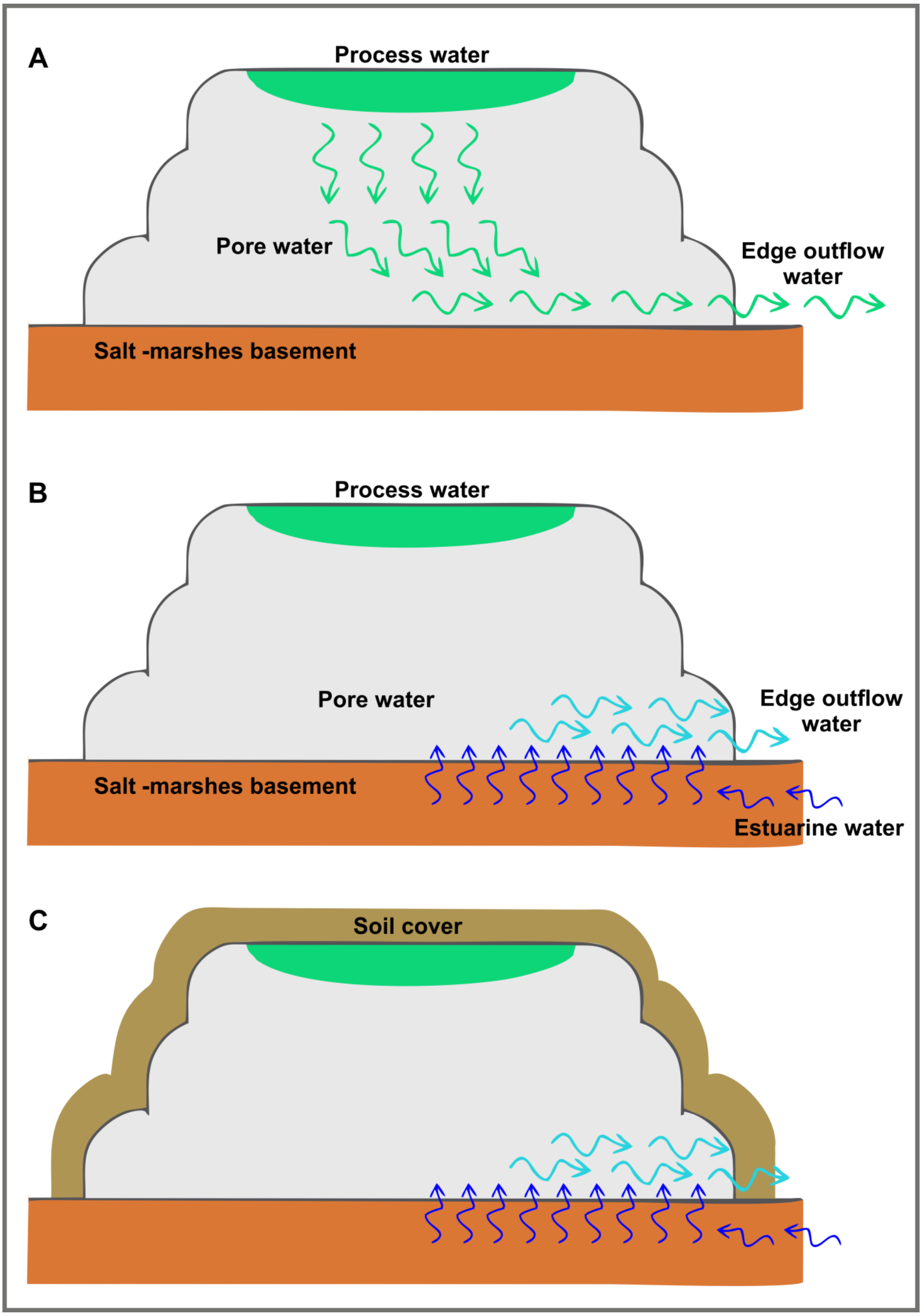


Figure 1.4: (A) Weathering model of the Huelva phosphogypsum stack according to the report of Junta de Andalucía (2009), **(B)** Suggested weathering model of the stack according to Pérez-López et al. (2015), and **(C)** Restoration plan based on weathering model (A) and the potential effect of leaching of phosphogypsum suggested by the weathering model (B).

1.5 Thesis structure

The thesis is composed of this introduction, aims and research impact, three main chapters and the final chapter of general and combined conclusions. In turn, each main chapter comprises of an introduction, a methodology, results and discussion, and conclusions, so that they can be read individually. This structuring has the disadvantage that certain information may be redundant; nevertheless due to the variety of the topics and approaches used in the three main chapters, it was preferable to construct each chapter independently for its optimal understanding.

CHAPTER 2

AIMS AND RESEARCH IMPACT

2. Aims and research impact

2.1 Thesis aims

The general goal of the thesis was to contribute to the investigation of the phosphogypsum waste, which is an environmental hazard in many areas worldwide, aiming at the paradigmatic study site of the stacks located in the Estuary of Huelva. This thesis focused on three interconnected lines of investigation including (i) the weathering processes occurring in the phosphogypsum stack, (ii) the metal behaviour under seawater mixing with the phosphogypsum leachates, and (iii) the metal mobilisation under redox-sensitive conditions in the contact between phosphogypsum and salt marsh basement. General characterisation, hydrochemistry, evaluation of the environmental impact and valorisation of the waste were studied in detail to fulfil the aims of the three main lines of the thesis.

2.1.1 Weathering model of phosphogypsum

The first aim was to establish a weathering model of the phosphogypsum. Phosphogypsum stacks are presently subjected to continuous weathering. There are previous guidelines set by the regional government (Junta de Andalucía, 2009) for the implementation of actions aimed at restoring the phosphogypsum disposal area. Some of the zones have been partially restored and future actions are planned for the remaining zones. However, these preliminary guidelines were issued with an obvious lack of information on the weathering process; i.e., on those agents involved in leaching, release and transport of contaminants from the stack to the estuarine environment. In fact, recent studies (Pérez-López et al., 2015; 2016) indicated the poor geochemical connection between the process water -that is supposed to be the main pollution agent according to the already-implemented restoration actions- and the edge outflow waters.

Therefore, the first line of investigation of this thesis aimed to corroborate the findings by Pérez-López et al. (2015; 2016) and bridge the gap on the existing pollution pathway by providing a full insight into the weathering processes occurring in the disposal area using stable isotopes as one of the most powerful proxies for tracing contamination in environmental systems. For that purpose, stable hydrogen, oxygen and sulphur isotopes were used for the first time regarding the phosphogypsum, in order to identify and quantify -using ternary mixing- the exact contribution of the possible weathering agents (process water, seawater and river water) that lead to the formation of edge outflows. These findings will allow the validation of the pollution pathway, which will be invaluable for the design and optimization of effective remedial actions, as the appliance of the current measures does not prevent the contaminated leachates from reaching the estuarine and the coastal environment.

2.1.2 Mobility of metals in phosphogypsum related leachates

Another main aim of this thesis was to evaluate the mobility of the metals from the phosphogypsum considering the surrounding environmental conditions. A comprehensive understanding of the contaminant concentrations, their mobility and their potential to precipitate or to remain in solution is crucial for the geochemical evaluation of contaminated sites. Thus, a crucial objective of the doctoral thesis was to provide information on the mobility of the most important inorganic contaminants in the phosphogypsum-related leachates and consequently, to enhance the research on a feasible future long-term treatment. Hence, the second and the third lines of investigation aimed to study the mobility of the contaminants during seawater mixing with acidic phosphogypsum leachates and during redox cycles in salt marshes, respectively, with the aim to monitor the influence of these processes on the contaminant concentrations.

2.1.2.1 Effects of seawater mixing

Estuarine systems are responsible for the mass flux of elements entering the coastal areas, as they serve as transition zones between freshwater and seawater (Lian and Wong, 2003). Mixing affects the geochemical processes and the mobility of contaminants altering the elemental concentrations, while pH is one of the principal controlling parameters. Therefore, the aim of the second thesis line was to provide a clear insight into the geochemical processes taking place when acid phosphogypsum leachates reach the estuarine environment and mix with seawater. To achieve this aim, two sub-aims were set: i) simulation of behaviour of contaminants (Al, As, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sb, U and Zn) in the different types of leachates undergoing seawater mixing and pH rise, and ii) evaluation of driving geochemical processes that take place in these mixing solutions. As such, *in-situ* mixing experiments were conducted to assess the effect of pH increase on the mobility of contaminants of highly polluted acid leachates arising from the phosphogypsum stacks. The main motivation of this study resides in the importance to understand the impact of seawater mixing on metal behaviour in phosphogypsum leachates reaching the Estuary of Huelva and in the awareness of the metal loads that are subsequently transported to the Atlantic Ocean.

2.1.2.2 Redox oscillations in the phosphogypsum and the salt marsh sediment

It is largely known that near-surface natural biogeochemical systems have the ability to alternate between oxic and anoxic conditions (references). The changes are periodic and the inorganic contaminants that are easily influenced by redox variations are subjected to speciation, mobility and toxicity changes (Couture et al., 2015). The phosphogypsum stack of Huelva is a redox active system, influenced strongly by its basement, the salt marsh soil, which has a high content of organic matter and serves as natural inoculum of sulphate-reducing bacteria (Castillo et al., 2012a). In deep saturated zones around the water table, the level of water varies depending on the tidal action, and the phosphogypsum can undergo alternating oxidation-reduction cycles. Thus, the objective of the third line of investigation was to assess the behaviour of some important contaminants related to the phosphogypsum waste and the marsh sediment when undergoing cyclic redox alternations. For this purpose, redox changes were induced experimentally in phosphogypsum and marsh sediments by alternating between cycles of oxic and anoxic conditions using a bioreactor system. Contaminant concentrations were subjected to continuous monitoring in order to compare their mobility between oxic and anoxic conditions related to tidal cycles. The comprehensive awareness of the redox processes occurring in a redox-dynamic phosphogypsum stack will provide important insights into using bioremediation strategies to mitigate the release of contaminants into the environment.

2.2 Importance of the research

Huge amounts of phosphogypsum wastes are produced annually from fertiliser industries around the world, while they are usually dumped directly in marine or estuarine environments with no formal regulations for their management. Given the frequent dumping of such a hazardous material on coastal systems worldwide, phosphogypsum is considered one of the major sources of seawater contamination until nowadays. Due to these facts and also because of the growing public concern about soil and water contamination, the scientific impact of the current research is considerably high in a global scale.

Taking into account the large amount of the waste in the study area and the fact that the leachates reach the estuarine environment and subsequently, add to the total contamination of the Atlantic Ocean, the full awareness of the geochemical processes and the behaviour of the contaminants are of high importance. So far, the leachates from the Huelva phosphogypsum reaching the estuarine environment are not adequately characterised. As the guidelines already proposed for remediation are based on this insufficient knowledge and assume the process water as major leaching agent, they are not suitable for a permanent and efficient restoration of the phosphogypsum disposal area. This fact leads to the necessity of detailed characterisation of phosphogypsum leachates and, subsequently, seeking new remediation techniques for the lixiviation of the phosphogypsum stack, including the zones already considered restored. The proposed methodology in the doctoral thesis concerning the identification and quantification of the possible washing agents of the waste may be useful for further knowledge of the pollution pathway in phosphogypsum stacks located in other coastal areas worldwide.

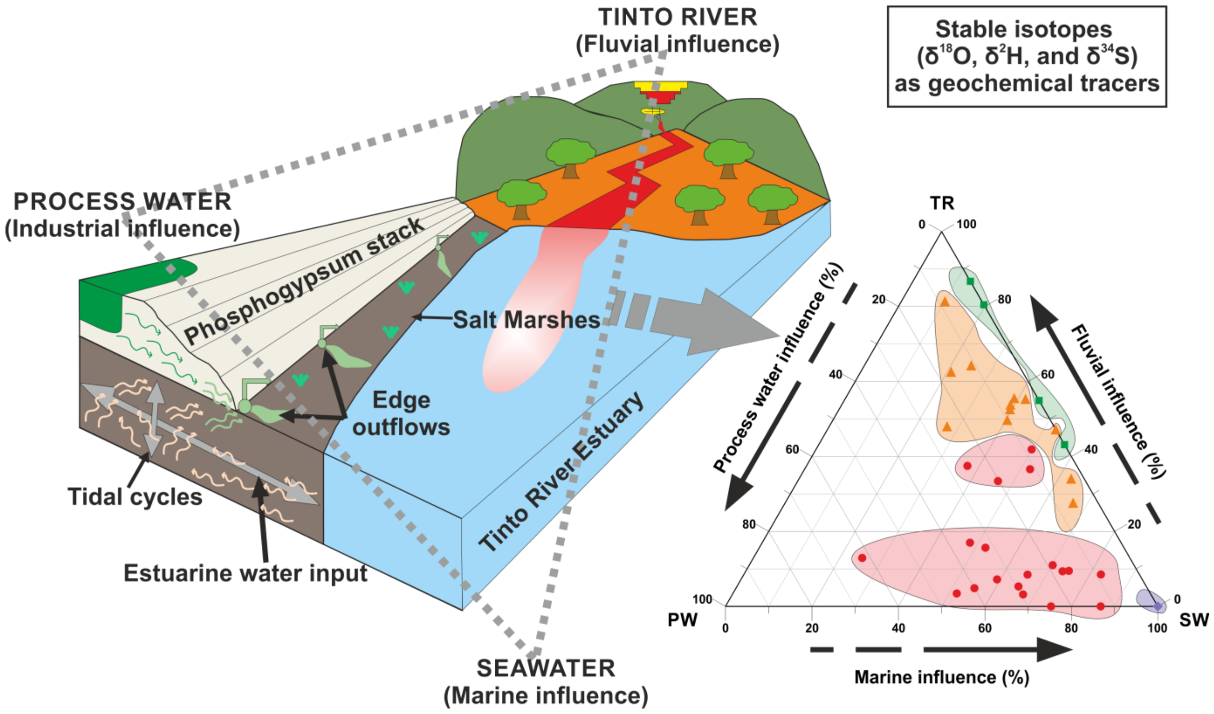
In addition, the importance of the thesis project lies in the exclusive and remarkable study area, which combines AMD-affected fluvial systems due to one of the largest massive sulphide deposits worldwide, estuarine waters and industrial wastes including the phosphogypsum, while it is one of the most important marsh ecosystems in Europe. Thus, it is a unique site for the observation and investigation of different chemical processes and characteristics.

Part II

RESULTS

CHAPTER 3

Stable isotope insights into the weathering processes of a phosphogypsum disposal area



BASED ON:

Papaslioti, E. M., Pérez-López, R., Parviainen, A., Macías, F., Delgado-Huertas, A., Garrido, C. J., Claudio, M., & Nieto, J. M., 2018. Stable isotope insights into the weathering processes of a phosphogypsum disposal area. *Water Research*, 140, 344-353.

3. Stable isotope insights into the weathering processes of a phosphogypsum disposal area

3.1 Introduction

Some preliminary restorations have been already applied in some of the Huelva phosphogypsum modules and similar ones are planned for the future, as already described in more detail in Chapter 1. These actions are based on the assumption that edge outflows originate mainly from the process water ponded on surface that infiltrates the piles and reaches the edge of the stack and, hence, they focus on eliminating only that agent. However, Pérez-López et al. (2015) suggested that both types of phosphogypsum leachates are poorly connected using Cl/Br ratios and rare earth elements (REE) as geochemical tracers. Indeed, the absence of process water ponded on the surface of a 'supposedly' restored zone has not prevented the presence of numerous discharge points reaching the estuary until nowadays, which demonstrate the inefficiency of the restorations (Pérez-López et al., 2016). These authors proposed a possible pollutant dispersion pathway associated with the leaching of the phosphogypsum in depth through the input of estuarine waters.

Therefore, the current research aims to corroborate these previous studies by providing a full insight into the weathering processes occurring in the disposal area, to validate the main pollution pathway on which restorations should be based and more importantly, quantify the exact contribution of all the possible end-members as washing agents. Stable isotopes are widely used in numerous environmental studies as one of the most powerful tool for determining water sources and fluxes in a wide variety of systems (Peterson and Fry, 1987). One of their main applications is the determination of the proportional contribution of more than one end-member to a final solution for the identification of pollution sources (Phillips, 2001; Zencich et al., 2002; Phillips and Gregg, 2003). Hence, in the present study stable isotopes served as undeniable tracers for determining the main weathering agent promoting pollution from the phosphogypsum waste. Stable hydrogen, oxygen and sulphur isotopes were used for the first time as geochemical tracers regarding the phosphogypsum, in order to identify and quantify -using ternary mixing- the contribution of the possible weathering agents (process water, seawater and river water) that lead to the formation of edge outflows. The validation of the pollution pathway would be of paramount importance for future effective restoration plans, as the appliance of the current measures does not prevent the contaminated leachates from reaching the estuarine and the coastal environment. The proposed methodology and the results obtained could be useful for further knowledge of the pollution pathway in phosphogypsum stacks located in coastal areas worldwide.

3.2 Additional considerations about the study area

The particular localisation of the studied phosphogypsum stack can offer some helpful insights into the weathering model that allow the development of the proposed methodology. The stacks are located within the tidal prism of the Huelva Estuary, which is between 37 and 82 hm^3 during a half cycle (6 hours) (Grande et al., 2003). Its localisation and the lack of composite liners at the bottom of the pile, could have a great influence on the possible weathering model of the phosphogypsum wastes by means of estuarine water, as can be elucidated simply by looking at the marshlands prior to the dumping. In 1956, numerous secondary tidal channels were present in the area, which were regularly flooded by the tides **(Fig. 3.1A)**. Currently, those channels are covered by phosphogypsum, although they are probably preferential flow zones that allow the intertidal water to access the interior of the stack **(Fig. 3.1B)**. In fact, some of the secondary tidal channels are sensed below the phosphogypsum stack and act as preferential via for the discharge of ponded process water in the zone 3 **(Fig. 3.1C)**.

Accordingly, the weathering processes related to the leaching of the phosphogypsum stack could be influenced by the different morphodynamic domains in which the Estuary of Huelva is divided. The fluvial domain comprises the upper part of the estuary with a greater influence of the Tinto River and its pollution by AMD, the inner domain is characterised by mixing of fluvial and tidal waters, while the central and the marine domains are dominated by tidal-related processes (Morales et al., 2008). In this respect, zone 1 is close to the marine domain, zones 2 and 3 are in the central domain, and zone 4 is within the inner domain near the fluvial domain **(Fig. 3.2A)**.

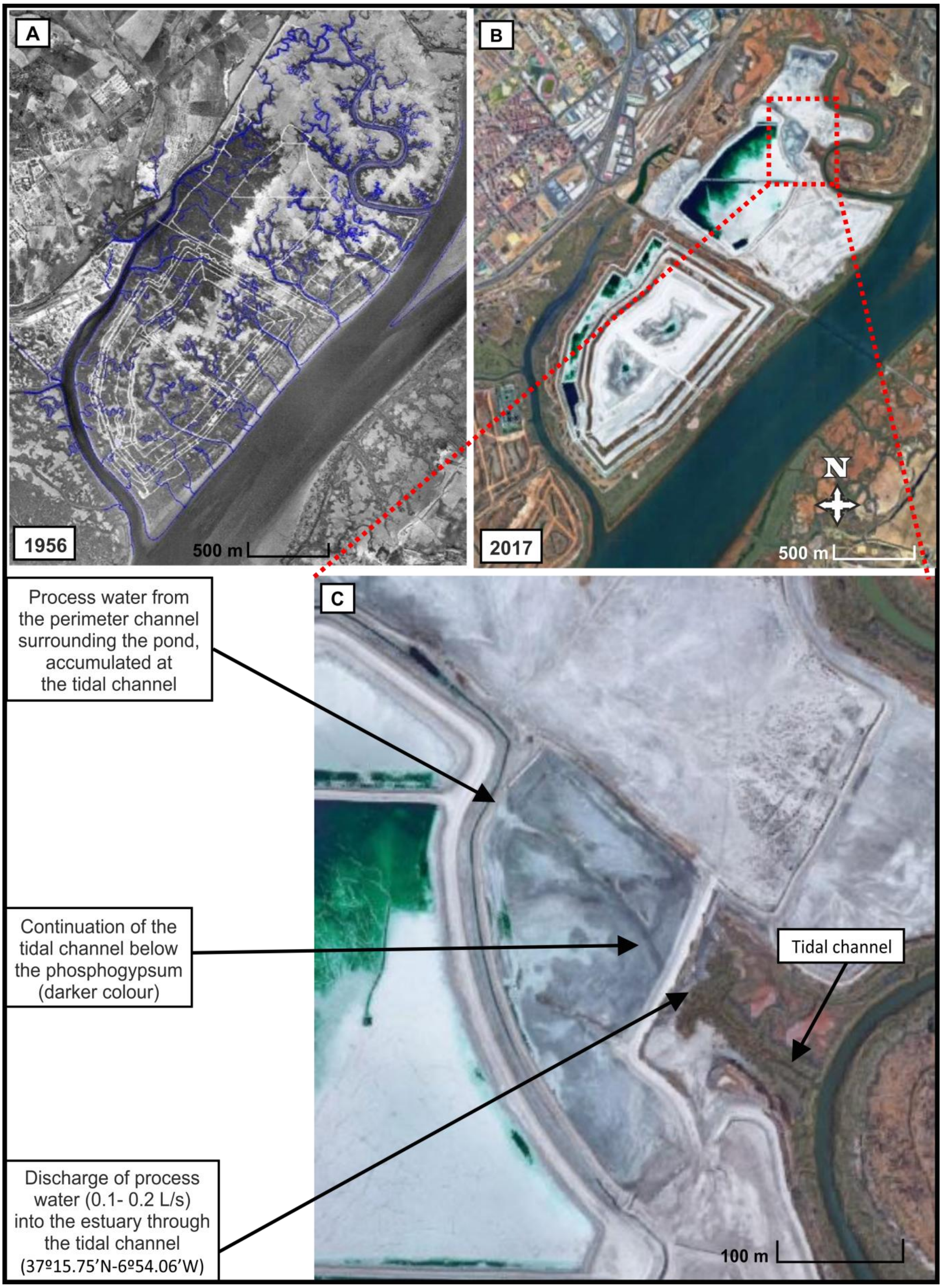


Figure 3.1: The figure shows -using Google Earth© images- the site before the deposition of the waste, where the secondary tidal channels can be clearly defined **(A)**, and the site nowadays covered with phospogypsum **(B)**, where some tidal channels can be distinguished below the waste **(C)**.

3.3 Materials and methods

3.3.1 Sampling and preparation

In June 2016, a total of 40 edge outflow samples were collected at different locations in the perimeter of the phosphogypsum stack **(Fig. 3.2B)**; at zone 1 only one possible point was identified and sampled, whereas the most outflow points were sampled at zones 2 (n = 19), 3 (n = 12) and 4 (n = 8). Process water of the surface pond from the zone 3 (PW), river water from the upstream Tinto River (TR) and seawater (SW) closer to the oceanic coast were also sampled for comparison purposes as the possible end-members associated with the weathering of the phosphogypsum stack; SW was also used for the seawater mixing experiments described in chapter 4.

Physicochemical parameters (pH, electrical conductivity (EC) and redox potential) of the solutions were measured *in-situ*, using a portable multi-parameter electrode (Hach, sensION^{TM}+ MM150) previously calibrated. Measured redox potential was referenced to standard hydrogen electrode (Eh), as proposed by Nordstrom and Wilde (1998). All samples were collected in polyethylene bottles and were transported directly to the laboratory for treatment. At the laboratory, the samples were immediately filtered (0.45 µm pore size), and subsequently two aliquots were stored in polyethylene vials, one for cation analysis after being acidified with 1% supra-pure nitric acid and another without acidification for anion analysis. Aliquots were also collected in polyethylene vials for analysis of the isotopic composition; one for ^{2}H and ^{18}O of H_2O and another for ^{34}S of sulphates.

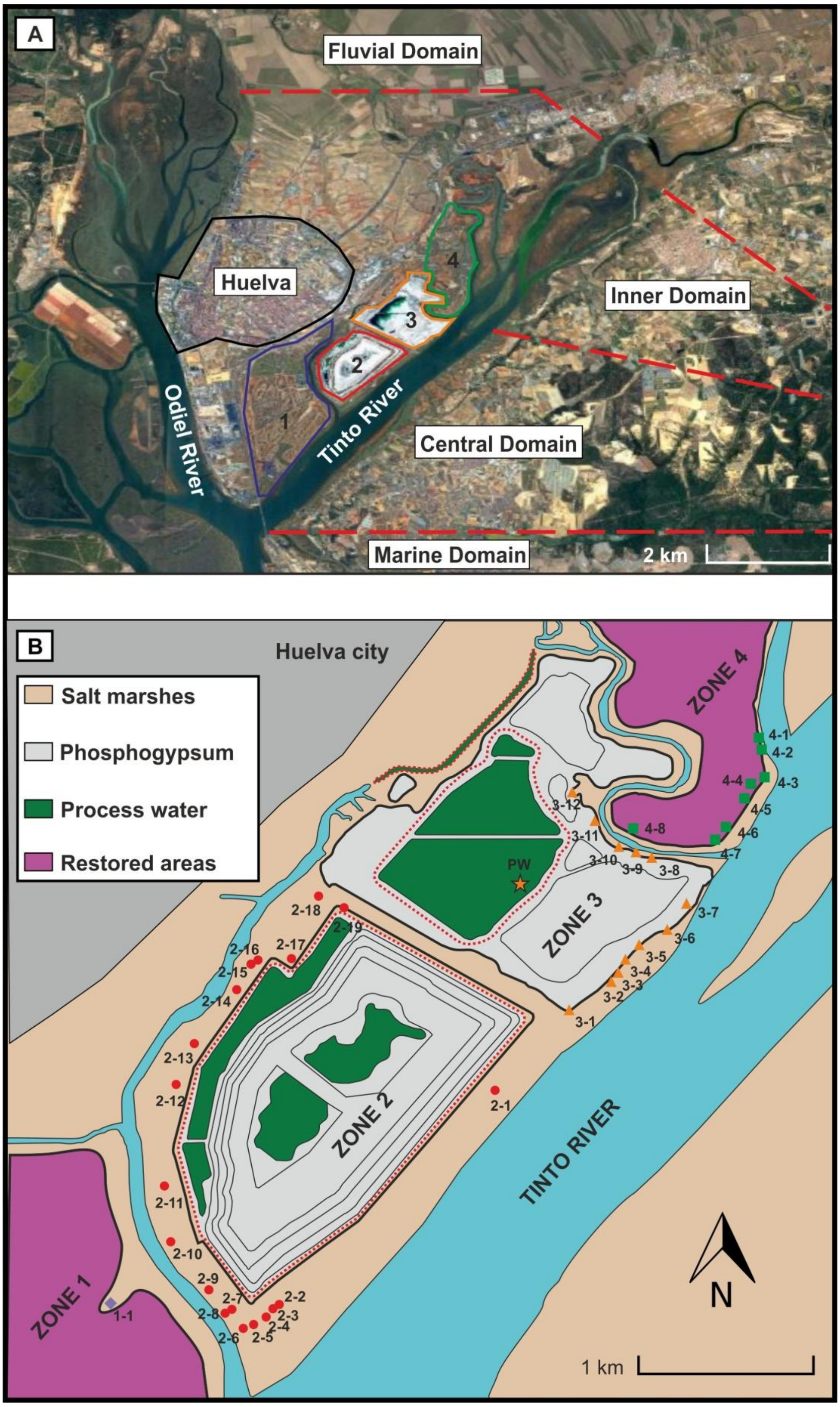


Figure 3.2: Location map of the different zones of the phosphogypsum stack within the Estuary of Huelva: **(A)** Google Earth© image with the morphodynamic domains of the estuary according to Morales et al. (2008), and **(B)** Schematic image with the sampling points of all the edge outflows and the process water at zone 3 (PW).

3.3.2 Analytical methods

3.3.2.1 Aqueous elemental analysis

Major element (Ca, K, Mg and Na) concentrations were obtained via Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) by a Jobin Yvon Ultima 2 instrument at the University of Huelva (Spain). Concentrations of anions (F^-, Cl^-, Br^-, SO_4^{2-}, PO_4^{3-}) and ammonia in all the unacidified samples were also analysed at the University of Huelva by a high performance liquid chromatography system (HPLC) using a Metrohm 883 basic ion chromatograph (IC) equipped with Metrosep columns. Aluminum, Fe, Mn and trace elements (Cr, Co, Ni, Cu, Zn, As, Cd, Sb, Pb, and U) were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) by an Agilent 8800 Triple quadrupole device at the Andalusian Institute of Earth Sciences (IACT) in Granada (Spain). Detection limits were: 0.2 mg/L for S, 0.1 mg/L for Na, 0.05 mg/L for K and Mg, 0.02 mg/L for Ca and P, 2 µg/L for Al, 0.5 µg/L for Fe, 0.04 µg/L for Mn and 0.02 µg/L for trace elements. Certified Reference Materials SLRS-5 (river water) and CASS5 (seawater) supplied by the National Research Council of Canada (CNRC), as well as 1640A (natural water) by the National Institute of Standards and Technology (NIST), were analysed by ICP-MS as external standards every four samples. Dilutions were performed to ensure that the concentrations of the samples were within the concentration range of instrument calibration. Blank solutions with the same acid matrix as the samples were also analysed. The average measurement error was below 5% for all the analyses. Determination of Fe(II) and total Fe (following reduction with hydroxylamine hydrochloride) in the phosphogypsum leachates was undertaken in the geochemical laboratory of the University of Huelva on the same day of the sampling by colorimetry at 510 nm using a SHIMADZU UVmini-1240 spectrophotometer. The detection limit was 0.3 mg/L and the measurement error was less than 5%; Fe(III) was calculated as the difference between total Fe and Fe(II).

3.3.2.2 Isotopic measurements

All stable isotope analyses, including oxygen and hydrogen (from H_2O) and sulphur (from SO_4^{2-}), were carried out by Isotope-Ratio Mass Spectrometry (IRMS) at the Stable Isotope Laboratory of IACT. The stable isotope compositions are reported as δ values per mil (Eq. (3.1)):

$$\delta = (R_{sample}/R_{standard} - 1) * 1000 \qquad (3.1)$$

where R= $^{18}O/^{16}O$ for $\delta^{18}O$, R= $^{2}H/^{1}H$ for $\delta^{2}H$ (or δD) and R= $^{34}S/^{32}S$ for $\delta^{34}S$.

Oxygen isotope measurements were performed using a GasBench II peripheral system coupled with Delta Plus XP mass spectrometer (ThermoFinnigan, Bremen, Germany), using the CO_2 - H_2O equilibration system (Epstein and Mayeda, 1953). H_2 and CO were produced by injecting the water sample onto a ceramic column containing a glassy carbon tube at 1400 ºC, following the protocol described by Sharp et al. (2001). These gases were separated for H_2 isotopic measurement by chromatography using a helium carrier gas stream, connected online with a TC/EA interfaced with a Delta Plus XP mass spectrometer. The analytical error was ± 1‰ for $\delta^{18}O$ and better than ± 0.1‰ for $\delta^{2}H$. The standard for reporting oxygen and hydrogen is the V-SMOW (Vienna Standard Mean Ocean Water).

Samples were analysed for the isotopic composition of sulphur by means of combusting with V_2O_5 and O_2 at 1030 ºC in a Carlo Elba NC1500 (Milan, Italy) elemental analyser online with a Delta Plus XL (ThermoQuest, Bremen, Germany) mass spectrometer (EA-IRMS), after the precipitation of SO_4^{2-} as $BaSO_4$ by adding a $BaCl_2$ solution. Commercial SO_2 was used for the preparation of three internal standards of +23.25 ‰, +6.03 and -6.38 ‰ compositions of $\delta^{34}S$. The precision calculated -after correction of the mass spectrometer daily drift- from standards systematically interspersed in analytical batches was better than ± 0.2‰. The standard for reporting sulphur is the V-CDT (Vienna Canyon Diablo Troilite).

Ternary mixing was applied for quantification purposes of the contribution of all possible end-members (Tinto River, seawater and process water) to the formation of the edge outflows. Mixing ratios of the three end-members were calculated based on the $\delta^{18}O$ and $\delta^{2}H$ compositions using the equations (Eq. (3.2) to (3.4)) provided at Clark (2015):

$$f_{TR} = (\delta^2H_S - \delta^2H_{SW} - f_{PW}(\delta^2H_{PW} - \delta^2H_{SW})) / (\delta^2H_{TR} - \delta^2H_{SW}) \qquad (3.2)$$

$$f_{SW} = (\delta^{18}O_S - \delta^{18}O_{TR} - f_{PW}(\delta^{18}O_{PW} - \delta^{18}O_{TR})) / (\delta^{18}O_{SW} - \delta^{18}O_{TR}) \qquad (3.3)$$

$$f_{PW} = 1 - f_{TR} - f_{SW} \qquad (3.4)$$

where f is the factor for each end-member (TR, SW and PW) and s (subscript) represents each measured edge outflow.

3.4 Results and Discussion

3.4.1 Chemical characterisation

The high levels of acidity and EC characterise the edge outflow waters from both the restored (zones 1 and 4) and unrestored modules (zones 2 and 3) with mean pH values of 4.75, 2.27, 2.04 and 2.18 **(Fig. 3.3)**, and mean EC values of 56.0, 54.4, 48.4 and 18.7 mS/cm, respectively. These characteristics are in accordance with the elevated concentrations of all the dissolved contaminants investigated here (SO_4^{2-}, PO_4^{3-}, Al, Cr, Fe, Co, Ni, Cu, Zn, As, Cd, Sb, Pb and U), with some variations depending on the zone of the stack. All the physicochemical parameters along with the total concentrations of the samples can be found in the **Table 3.1**.

The zones 1 and 4 are ‘supposedly’ restored, with no process water ponded on the surface of the stack and with a top cover. Regarding zone 1, only one edge outflow sample was obtained at a secondary tidal channel where interaction of estuarine water and outcropping phosphogypsum occurs during the rising tide (Pérez-López et al., 2016). This sample has lower acidity and metal concentrations than the leachates originated from the other zones **(Fig. 3.3)**. All the obtained samples from zone 4 were acidic edge outflow waters with elevated elemental concentrations, though both acidity and concentrations were slightly lower than in the unrestored zones **(Fig. 3.3)**. This can be owed to the complex soil cover that was applied to this zone as restoration measure, which includes a vegetation layer rich in organic matter that has the potential to act as carbon source for enhancing the activity of naturally-occurring sulphate reducing bacteria in the phosphogypsum (Castillo et al., 2012b). Organic carbon-rich amendments over phosphogypsum stacks can lead to immobilisation of part of the metal loading of leachates resulting from weathering by sulphide precipitation (Pérez-López et al., 2018). In phosphogypsum-related leachates, the sulphur is in excess in comparison to metals, which implies that sulphide precipitation can contribute to the low availability of metals in solution without significant changes in the aqueous sulphate concentration **(Fig. 3.3)**. Nevertheless, numerous edge outflow points still discharge to the estuary, with leachates significantly concentrated in many potentially toxic elements - e.g. Cu up to 4.16 mg/L, Zn up to 24.0 mg/L and As up to 13.4 mg/L. This is proof of the ineffectiveness of the current restoration measures and that the process water is not the only route of contamination, as there are no surface ponds in the zone 4.

The acidic edge outflows from the zones 2 and 3 presented even higher concentrations than those from the restored zones **(Fig. 3.3).** In turn, the zone 2 exhibited the highest contamination level; e.g. Cu, Zn and As reached values up to 14.8, 99.7 and 44.9 mg/L, respectively, whereas the corresponding values at zone 3 were up to 5.74, 24.4 and 22.1 mg/L. The process water from zone 3 (PW) exhibited conditions of extreme acidity (pH=0.80) and contaminants concentration (EC=108 mS/cm) far more elevated than in the edge outflows, as it is subjected to re-concentration by the closed-circuit and to a high level of evaporation; i.e. 50.2 mg/L for Cu, 285 mg/L for Zn and 146 mg/L for As, among others **(Fig. 3.3)**.

Table 3.1. Physicochemical parameters and total concentrations of all the edge outflows and end-members collected. Total concentrations are given in mg/L for all elements except for where indicated.

Sample	pH	EC (mS/cm)	Eh (mV)	F^-	Cl^-	Br^-	SO_4^{2-}	PO_4^{3-}	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Sb	Pb	U
1-1 J	4.75	56.0	480	63.7	19587	52.8	4085	282	0.69	0.01	0.83	0.03	0.01	0.02	0.17	0.31	0.05	0.02	3.60*	0.01	0.01
2-1 J	2.73	59.6	503	51.2	24472	63.0	4805	1200	1.74	0.14	1.06	1.97	0.08	0.21	0.34	2.87	1.87	0.30	0.03	0.22	0.46
2-2 J	1.95	41.4	474	1039	9998	25.0	5062	21987	9.28	9.07	17.9	197	0.58	3.59	6.12	39.7	24.6	5.42	0.23	0.34	12.7
2-3 J	1.92	40.4	486	1161	9039	20.6	5058	21005	9.65	9.27	17.7	198	0.59	3.67	6.21	40.0	24.5	5.36	0.23	0.34	12.5
2-4 J	1.90	38.2	495	1390	8850	18.6	5598	37155	10.5	10.4	15.2	171	0.66	3.88	7.24	44.6	27.4	5.58	0.24	0.31	14.3
2-5 J	1.97	36.8	468	2541	7731	15.9	5076	19480	7.68	6.23	13.4	204	0.62	3.79	4.38	41.7	24.0	5.21	0.19	0.25	6.64
2-6 J	2.03	35.2	479	725	7036	14.6	4818	20850	17.4	4.56	13.4	122	0.67	3.97	3.87	42.5	23.6	5.18	0.13	0.35	10.8
2-7 J	1.78	53.5	573	2054	11415	21.8	7849	63605	508	21.3	30.7	294	1.35	9.54	14.8	99.7	44.9	14.0	0.50	1.01	39.5
2-8 J	2.03	56.9	519	635	18103	45.7	5589	14851	175	2.17	12.4	63.5	0.52	3.19	2.10	31.5	15.6	4.08	0.05	0.11	9.55
2-9 J	1.99	61.1	508	740	22237	59.1	5466	13901	33.0	1.77	23.8	54.5	0.38	2.20	2.83	21.0	12.2	2.63	0.10	0.18	5.26
2-10 J	2.67	63.3	492	339	22362	60.5	5094	9479	20.1	0.08	14.8	2.99	0.27	1.37	1.15	12.7	8.52	1.55	0.01	3.29*	0.47
2-11 J	2.07	63.6	527	422	20598	58.4	4703	9402	108	1.43	8.27	29.1	0.28	1.94	3.15	18.9	8.43	2.76	0.03	0.02	5.51
2-12 J	2.00	46.1	515	673	12630	33.8	4781	19509	184	5.48	10.5	91.2	0.45	3.10	5.31	29.1	12.5	4.41	0.12	0.27	10.3
2-13 J	2.03	54.1	535	437	17036	47.9	4741	9740	99.3	2.52	6.80	37.8	0.29	1.91	4.21	18.3	8.58	2.70	0.06	0.10	6.13
2-14 J	1.84	41.6	523	1445	8537	21.0	6313	39156	105	1.47	8.17	29.2	0.28	1.91	3.17	19.1	8.30	2.75	0.03	0.02	5.42
2-15 J	1.87	45.1	510	848	10794	28.6	6109	34805	179	10.1	17.6	190	0.68	5.08	6.56	48.6	22.8	7.75	0.26	1.30	18.5
2-16 J	1.92	38.0	492	1091	7502	18.5	5877	31172	178	9.54	13.7	208	0.70	5.16	4.83	48.6	22.4	7.67	0.23	0.88	16.7
2-17 J	2.18	49.0	505	448	15119	42.0	4111	9553	136	1.03	8.79	23.7	0.37	2.40	3.84	21.0	8.64	3.32	0.04	0.11	5.38
2-18 J	2.11	59.6	541	416	22435	55.1	4477	5639	3.61	0.67	3.26	10.4	0.15	0.91	0.95	10.0	5.20	1.32	0.07	0.81	2.52
2-19 J	1.86	36.0	452	1519	6086	<ld	5547	34778	11.4	11.4	14.0	207	0.73	5.33	4.07	58.0	26.5	8.56	0.34	1.51	17.5
3-1 J	2.19	17.1	481	962	10373	23.6	4075	4877	2.51	1.34	3.03	88.5	0.11	0.90	1.51	7.42	12.4	1.13	0.14	0.23	2.24
3-2 J	2.37	17.0	499	589	15738	46.0	4773	1827	0.67	0.76	2.17	23.5	0.07	0.49	0.91	4.49	5.77	0.55	0.11	0.18	1.10
3-3 J	2.21	17.2	496	784	10834	30.4	4371	2620	6.89	1.23	3.18	57.7	0.11	0.74	1.62	6.78	8.79	0.83	0.17	0.09	2.34
3-4 J	2.09	17.9	477	927	12296	32.9	4371	9014	8.85	2.61	5.55	85.0	0.22	1.56	3.22	15.9	17.2	1.92	0.21	0.34	4.01

Table 3.1. Continued.

Sample	pH	EC (mS/cm)	Eh (mV)	F^-	Cl^-	Br^-	SO_4^{2-}	PO_4^{3-}	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Sb	Pb	U
3-5 J	2.01	18.5	485	867	12770	35.3	4576	7931	1.87	1.27	2.31	46.6	0.14	0.85	2.58	10.0	9.23	1.13	0.16	0.21	2.01
3-6 J	2.03	17.1	483	1324	8688	18.3	4442	7294	2.09	1.95	3.59	76.0	0.27	1.76	4.83	21.3	18.5	2.17	0.41	0.36	4.03
3-7 J	2.06	18.3	471	1064	11757	28.4	5891	5539	2.15	2.54	8.89	225	0.29	1.97	3.63	24.4	10.7	1.83	0.61	0.21	3.28
3-8 J	2.51	18.8	453	294	12189	29.4	4735	6051	51.0	0.48	7.42	47.8	0.27	1.80	3.47	17.7	13.9	1.77	0.03	0.01	1.73
3-9 J	2.04	27.1	482	874	13827	36.7	4717	8911	9.89	3.82	6.49	83.8	0.26	2.06	4.77	18.7	18.9	2.38	0.29	0.33	5.51
3-10 J	2.09	20.0	480	762	17636	48.0	5406	9800	8.42	2.42	14.8	75.2	0.32	2.10	4.43	21.7	22.1	2.22	0.24	0.19	3.48
3-11 J	2.09	17.4	474	1051	11109	26.7	4811	8487	2.73	5.43	8.14	114	0.31	3.22	5.74	23.0	18.8	2.03	0.37	0.16	5.83
3-12 J	2.43	17.8	528	130	18260	52.0	3524	1520	10.3	0.48	1.48	4.42	0.06	0.27	0.57	3.21	1.22	0.38	0.01	0.07	0.80
4-1 J	2.26	48.1	456	737	14007	35.0	5959	4669	0.99	1.12	11.3	165	0.24	0.94	0.77	10.9	7.68	1.14	0.27	0.30	0.84
4-2J	2.29	52.1	460	552	16259	44.9	6285	3319	3.30	1.08	14.6	202	0.17	0.59	0.59	6.82	3.68	0.68	0.12	0.18	0.55
4-3 J	2.17	52.8	480	836	15817	38.6	6367	5343	4.53	0.94	12.1	117	0.24	0.92	2.90	10.1	7.43	1.07	0.27	0.19	1.60
4-4 J	2.26	47.5	453	846	14206	40.2	5670	4517	1.40	1.56	14.2	247	0.32	0.80	1.17	15.4	5.73	1.13	0.35	0.25	0.96
4-5 J	2.33	46.5	448	897	13365	32.5	6025	4579	1.07	0.97	10.8	192	0.18	0.73	0.50	10.0	6.18	1.05	0.48	0.39	0.98
4-6 J	2.27	75.5	473	446	29690	85.2	7191	3991	1.56	0.61	22.5	91.3	0.40	0.93	0.76	14.2	9.61	0.94	0.37	0.28	0.79
4-7 J	2.39	72.1	481	389	25373	73.7	8398	2995	3.53	0.49	24.8	51.2	0.58	1.24	0.83	24.0	13.4	1.18	0.57	0.15	0.52
4-8 J	2.19	40.5	481	900	8143	16.7	4563	3751	2.66	3.01	12.9	155	0.28	1.02	4.16	14.6	3.22	0.85	0.28	0.11	2.47
TR	2.30	n.a	n.a	n.a	n.a	n.a	n.a	n.a	80.1	0.02	7.98	109	0.64	0.11	18.3	25.7	0.01	0.11	0.05*	0.07	0.01
SW	7.94	55.2	n.a	n.a	n.a	n.a	n.a	n.a	0.13	1.02*	0.01	0.01	0.11*	0.70*	4.26*	0.05	3.35*	0.23*	0.31*	2.99*	2.21*
PW	0.80	108	668	1378	12417	16.7	6668	195853	439	143	78.4	473	3.32	32.4	50.2	285	146	50.6	1.98	3.54	127

***concentration in µg/L**

n.a. not analysed

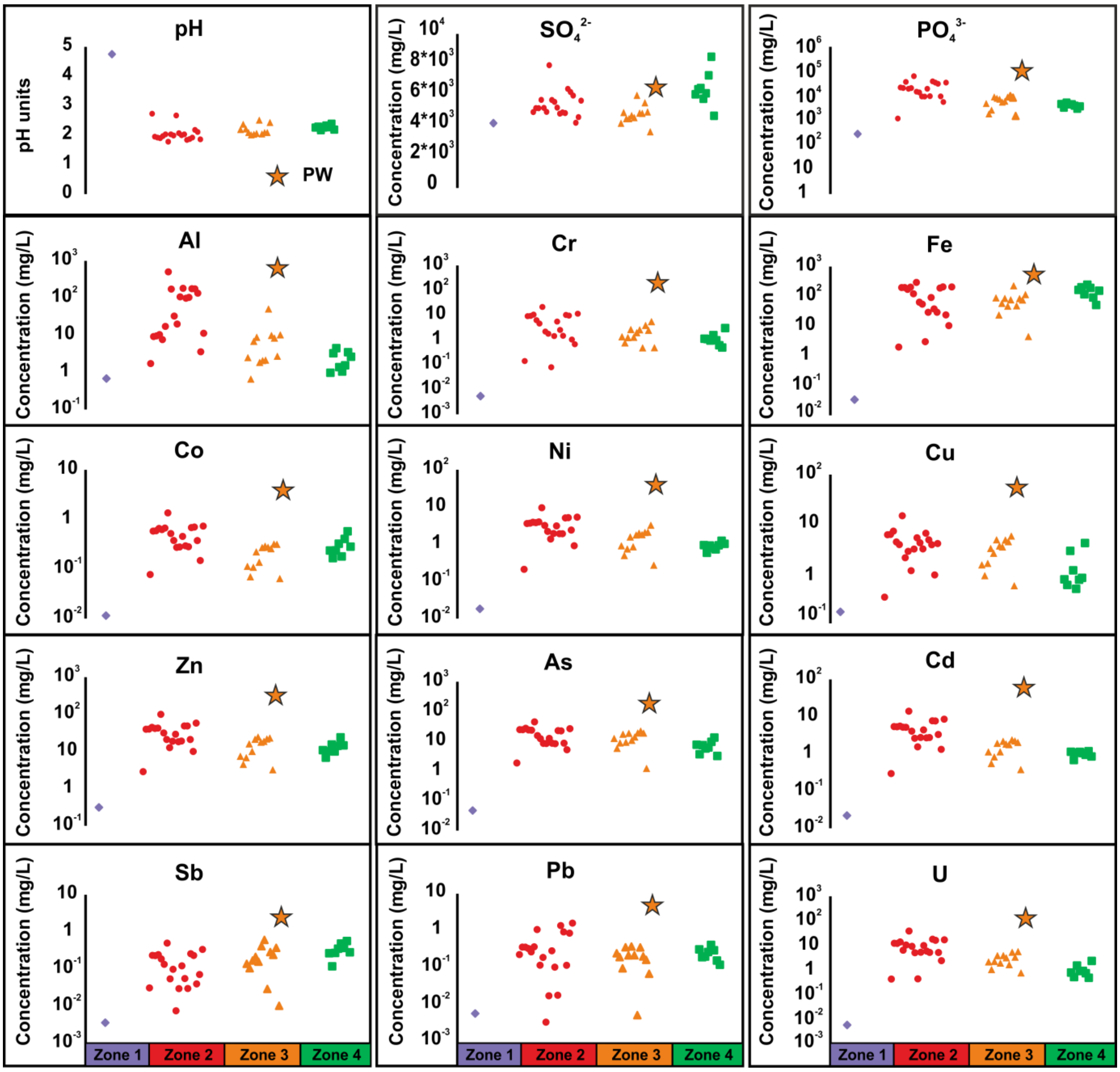


Figure 3.3: Values of pH and total concentration of the phosphogypsum-related contaminants for the edge outflows and the process water (illustrated with a star) divided by zones of the stack (1-4).

3.4.2 Isotopic signatures

The measured values for the stable isotopes analysed, including $\delta^{18}O$, $\delta^{2}H$, and $\delta^{34}S$, for all the edge outflows are plotted in **Figure 3.4** and presented in **Table 3.2**. The results for the three end-members representing the possible inputs of weathering agents, i.e. TR for the fluvial area, SW for the coastal area and PW for industrial water ponded on the stack surface, are also compiled in **Figure 3.4** and **Table 3.2**.

Table 3.2. Isotopic compositions of all the edge outflows and end-members collected.

Sample	$\delta^{18}O$ (VSMOW)	δD (δ^2H) (VSMOW)	$\delta^{34}S$ (CDT)
1-1	1.33	6.45	14.8
2-1	1.71	7.88	14.4
2-2	0.95	3.85	2.05
2-3	-0.62	-6.34	2.30
2-4	-0.12	-4.35	2.39
2-5	0.79	-2.26	3.80
2-6	1.04	-2.77	3.77
2-7	5.28	9.23	4.29
2-8	4.25	9.93	9.84
2-9	2.96	8.08	5.12
2-10	1.64	4.67	9.89
2-11	2.69	10.7	13.3
2-12	1.69	4.35	9.79
2-13	2.87	7.44	11.6
2-14	2.80	4.59	4.04
2-15	2.61	4.62	3.98
2-16	3.12	7.38	3.25
2-17	1.50	4.44	11.4
2-18	3.79	8.95	14.2
2-19	2.41	6.01	3.28
3-1	-1.78	-9.28	2.92
3-2	-0.72	-4.64	8.69
3-3	-0.86	-11.6	4.89
3-4	-1.14	-9.64	1.37
3-5	0.50	-6.13	1.47
3-6	-1.49	-10.9	2.09
3-7	-1.69	-11.1	3.66
3-8	-1.41	-12.8	4.08
3-9	-1.26	-10.1	2.11
3-10	-0.84	-8.52	2.43
3-11	-2.40	-18.3	3.06
3-12	-0.19	-2.34	17.9
4-1	-3.56	-13.8	2.95
4-2	1.84	2.70	3.60
4-3	-1.80	-0.74	5.08
4-4	-3.67	-11.4	5.84
4-5	-3.09	-24.2	6.05
4-6	1.15	-5.61	6.89
4-7	1.95	-0.18	7.08
4-8	-3.57	-21.3	5.24
TR	-3.98	-25.0	1.80
SW	0.58	5.30	20.3
PW	9.13	18.0	3.63

3.4.2.1 $\delta^{18}O$ and $\delta^{2}H$ compositions

The $\delta^{18}O$ and $\delta^{2}H$ compositions for the three end-members were -3.98‰ and -25.0‰ for TR, 0.58‰ and 5.30‰ for SW, and 9.13 and 18.0‰ for PW, respectively. With respect to the edge outflows, the samples from the zones 3 and 4, as well as some samples from the zone 2, fall mainly along the mixing line between two end-members, TR and SW, while the point from zone 1 is significantly closer to the SW (red line in **Fig. 3.4A**). The different isotopic signatures observed reveal different ratios of influence from the two end-members depending on the location of each zone of the stack in the different morphodynamic domains within the estuary, from marine (closer to SW) to fluvial (closer to TR) influence. Thus, the leachate from zone 1 had the same isotopic signature as SW because zone 1 is under higher influence of tidal seawater in the marine domain. Zone 2 is located in the central domain, although also close to the marine and as such, those outflows falling between the TR and SW end-members had signatures closer to those of SW. On the other hand, zone 3 is located in the central domain, having all its leachates with negative values for both stable isotopes falling midway between the TR and the SW compositions and with nearly no influence of the PW end-member. Zone 4 is located in the inner domain, close to the fluvial influence and thus, some of the edge outflows had an isotopic signature closer to that of TR end-member. Nevertheless, other edge outflows from zone 4 presented heavier values, but these leakages were sampled in puddles of stagnant water, which can be subjected to evaporation, as indicated by their displacement along the evaporation tendency line **(Fig. 3.4A)**.

However, many leachates originated from zone 2 exhibit a distinct pattern. As stated before, the dumping in zone 2 comprises two stages, with seawater before 1997 and with freshwater after 1997, following the change in phosphogypsum management policy. In this second stage, the continuous reuse of freshwater in a closed-loop system yielded highly acidic and pollutant-rich process water. Thus, edge outflows of zone 2 mainly show a seawater origin due to its location close to the marine domain, but with a notable contribution of the PW from the second filling stage in some edge outflows, as suggested by their distribution along the mixing line constructed in the $\delta^{18}O$ and $\delta^{2}H$ plot between the SW and PW end-members (black line in **Fig. 3.4A**). Moreover, the infiltration of process water stored on surface of the zone 2 could also contribute to these findings, mainly considering the proximity between some ponds and most of the samples found in this zone **(Fig. 3.2B)**. The contribution of process water in the edge outflows from the zone 2 could be also the explanation for the highest contaminant concentrations observed in relation to edge outflows of the remaining zones.

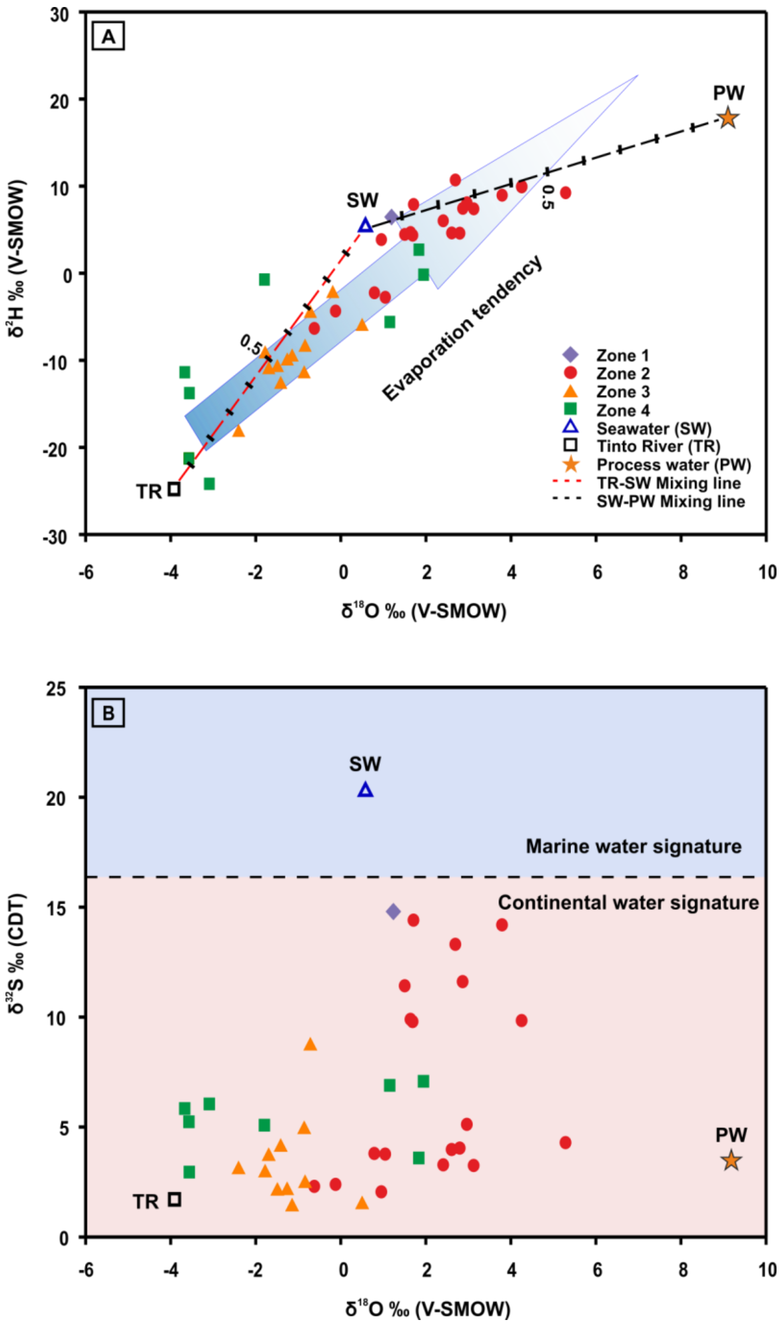


Figure 3.4: Stable isotope signatures of edge outflows and end-members related with the phosphogypsum stack are plotted as **(A)** $\delta^{18}O$ vs. δ^2H and **(B)** $\delta^{18}O$ vs. $\delta^{34}S$. The two mixing lines connecting the Tinto River with the seawater (red line) on the one hand and the seawater with the process water (black line) on the other hand, are also provided.

3.4.2.2 δ^{34}S compositions

The δ^{34}S composition was 1.80‰ for the TR and 3.63‰ for the PW, both very close to most of the edge outflows at zones 2, 3 and 4 **(Fig. 3.4B)**, and close to the composition range of the sulphides from the IPB (Velasco et al., 1998). The δ^{34}S signatures of TR and PW end-members, along with the majority of the outflows, indicated a typical continental origin with values that are consistent with sulphate from sulphide oxidation. In the case of TR, it is a reasonable outcome, as this water is severely affected by AMD that leads to high concentrations of sulphates and metal(loid)s due to the oxidation of the sulphide-rich mining wastes from the IPB. With respect to the PW, the sulphur composition was inherited from the sulphuric acid, which was produced by pyrite roasting and SO_2 recovery, used for the phosphoric acid manufacturing in Huelva during the wet chemical digestion. The pyrite used was obtained from the Tharsis Mine (IPB), which contained up to 0.4% of As – thus explaining the high level of As found in this waste (Macías et al., 2017).

On the contrary, the leachate from the zone 1 and a few samples belonging to zone 2 approached the SW signature, which gave a typical marine water signature at 20.3‰, corresponding to the amount of dissolved SO_4^{2-} contained in seawater **(Fig. 3.4B)**. As such, they exhibited a signature between the typical marine and the continental one, implying a slightly higher influence from the seawater and the estuarine environments compared to the remaining outflows.

In general terms, the δ^{34}S signatures of the edge outflows also suggested a mixing behaviour between river water and seawater, where the plotting of the sample points would also seem to depend on the estuarine morphodynamic domain in which each zone is located. Thus, most of the edge outflows of zone 4 are closer to TR end-member, while the fluvial influence is progressively lost (increasing the marine influence) towards the zones 3, 2 and 1 **(Fig. 3.4B)**. Numerous edge outflow points of zone 2 are distributed close to the PW end-member **(Fig. 3.4B)** confirming again the influence of the process water. However, the mixing behaviours are better defined from the δ^{18}O and δ^{2}H compositions, since the ^{34}S data for most of the edge outflows has less deviation probably due to that the origin of S in two of the three end-members (i.e. TR and PW) is the same (sulphides from IPB).

3.4.3 End-members contribution to edge outflows

The spatial distribution of the influence of the end-members to the edge outflows can be described based on their $\delta^{18}O$ and $\delta^{2}H$ compositions, as calculating the mixing fraction of three components requires two conservative parameters. The mixing ratio of the three end-members was calculated for each edge outflow **(Fig. 3.5)** following the ternary mixing described by Clark (2015). It is noteworthy that the isotopic signature of the only leachate collected in the zone 1 was identical to seawater (100% SW composition). Samples 4-2, 4-3, 4-6 and 4-7 were excluded from the graphs, as they cannot be considered as representative samples for zone 4, due to the evaporation of the stagnant puddles from where they were collected.

At zone 2, edge outflows from 2-1 to 2-6 were collected towards the Tinto River estuary main channel compared to the remaining samples, and most of them at the southwest part of the zone **(Fig. 3.2B)**. Thus, up to 87% of the composition of these samples was that of seawater **(Fig. 3.5)**, as they are close to the marine domain. In addition, four samples out of these six (2-3, 2-4, 2-5 and 2-6) show a notable influence from the TR end-member (up to 42%), which is consistent taking into account their proximity to the main fluvial channel **(Fig. 3.5)**. The contribution of process water increased moving to the western part (samples from 2-7 to 2-13) and the northern part of the zone (samples from 2-14 to 2-19) with a mixing ratio of up to 62%, but still the average proportion of seawater was higher in most of the samples, while the impact of river water was low **(Fig. 3.5)**. On the other hand, the influence of Tinto River is evident in all edge outflows at zone 3, with seawater following, while a slight influence of process water, with an average of 9%, cannot be excluded. So the mixing ratio is mainly transitional between TR and SW end-members with an average of 52% and 38%, respectively, as shown in **Figure 3.5**. Zone 4 belongs to the inner domain, close to the fluvial one and at the same time farther from the marine domain, so mainly TR (up to 87%) affects the composition of the respective edge outflows compared to SW (up to 20%), while there is no apparent influence from PW **(Fig. 3.5)**.

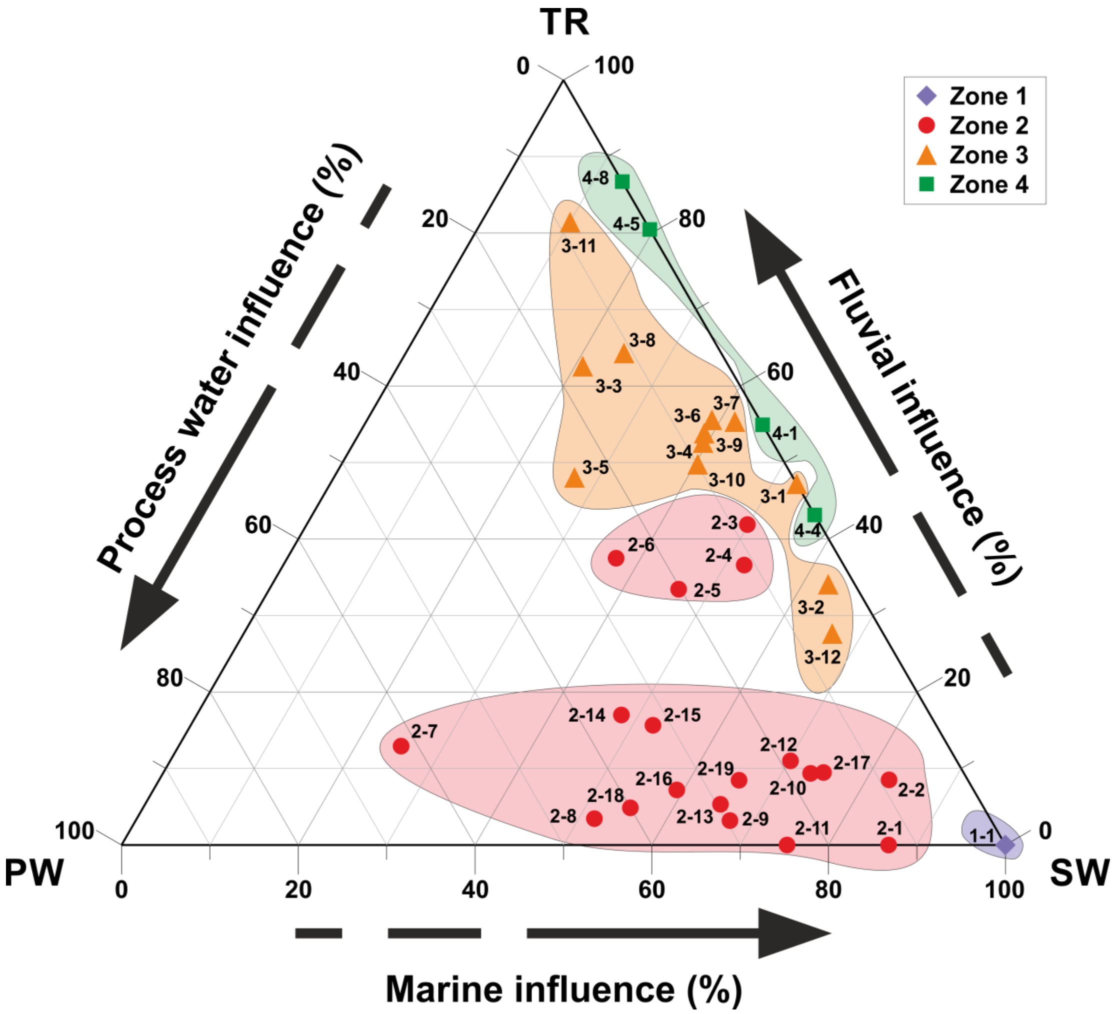


Figure 3.5. Ternary diagram describing the contribution of end-members to the edge outflows based on their mixing ratios calculated by their $\delta^{18}O$ and $\delta^{2}H$ compositions.

3.4.4 Weathering model

The most significant outcome based on the $\delta^{18}O/\delta^{2}H/\delta^{34}S$ composition is that the edge outflows for all the zones are dominantly connected with the SW and/or the TR end-members, as they presented isotopic signatures denoting a clear estuarine influence. The contribution of the PW end-member to the isotopic signature of the edge outflows is nil for zones 1 and 4, low for zone 3, and more significant but not dominant for zone 2. In the restored zones, these findings are expected since there are no process water ponds. In zone 3, the process water stored on surface seems to be, geochemically, poorly connected to the edge outflows. Infiltration could occur but not reach the front or side edge of the stack where samples were taken due to the distance with respect to ponded process water. On the other hand, in zone 2 the influence of the process water seems to occur due to the second filling stage and/or from the infiltration from nearby surface ponds **(Fig. 3.2B)**.

These findings on the source of the edge outflows and their geochemical difference with respect to the PW are consistent with the suggestions published by Pérez-López et al. (2015) which were based on REE and Cl/Br ratios as geochemical tracers. According to that study, process water had geochemical characteristics typical of phosphate fertilisers. On the contrary, the respective tracers of the edge outflows were identical to those of Tinto River estuary waters, indicating an estuarine origin. Therefore, the disconnection between the edge outflows and the PW, also suggested by the previous work, was a reasonable outcome. However, previous studies did not clarify whether the estuarine origin of edge outflows was related to the seawater used to transport phosphogypsum as a slurry.

In the current study, the $\delta^{18}O/\delta^{2}H/\delta^{32}S$ signatures validate that the phosphogypsum stack appertains to an open circulation system, where the continuously incoming estuarine water at the stack bottom appears to be the main mechanism of weathering of the waste in depth, ruling out the infiltration of the process water as the main source of contamination to the Estuary of Huelva (on which assumption the current restoration plan is based). The excess of (already acidic and contaminated) water discharges into the estuary in the form of the edge outflows. In fact, zone 4 does not have ponds of process water and continues to leach edge outflow waters after restoration. Moreover, the type of estuarine water entering and washing the waste will depend on the location of each zone of the stack within the estuary, which clarifies the uncertainties of previous works. The isotopic signatures of the seawater used for phosphogypsum disposal seem to be 'erased' by the continuous deep washing through the edge outflows. However, process water used since 1997 for filling the upper part of zone 2 could contribute to their edge outflows. This is likely due to the fact that this higher pyramidal part is less washed by the deep input of estuarine water.

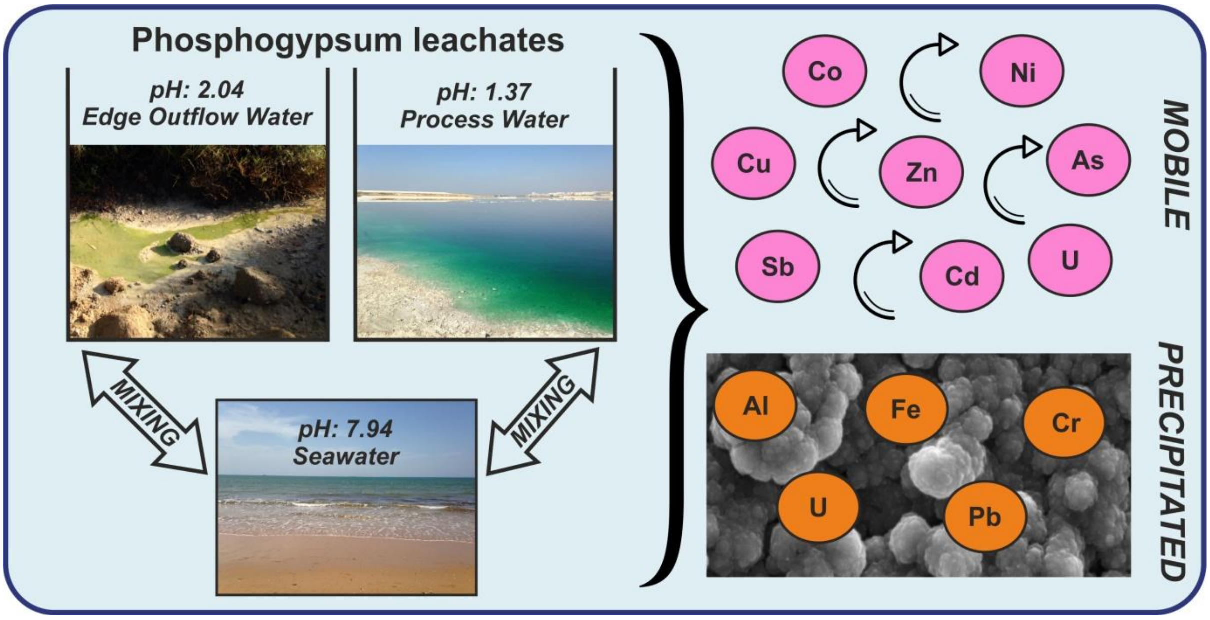
3.5 Conclusions

Phosphogypsum is a highly contaminated waste that threatens the environmental welfare through pollutant leaching in many coastal areas worldwide, where is usually disposed. This paper focuses on the weathering processes of a phosphogypsum stack in the Estuary of Huelva, which discharges highly acidic and contaminated edge outflows to the estuarine environment. The process water that was used to transfer the waste as slurry is ponded on the surface of the piles. It was believed until now that this extremely acidic and contaminated water was the main route of pollutant diffusion from phosphogypsum to the environment through its downward infiltration inside the stack and all restorations are based on that assumption. In the present study, we hypothesised that this is not the case and stable isotopes were used as geochemical tracers to describe the relation among the edge outflows and the phosphogypsum related end-members (process water, seawater and river water) with the aim to validate the pollution washing agent of the waste and quantify for the first time the contribution of each end-member to the leachates reaching the Estuary. Indeed, the isotopic signatures highlighted the poor geochemical connection between ponded process water and edge outflows ruling out the previous weathering model. Moreover, most of the outflows proved to be connected with the Tinto River and seawater end-members denoting an estuarine influence, depending on the morphodynamic domains to which the disposal zones belong. Before the deposition of the waste, secondary tidal channels flooded temporarily the salt marshes of the study area during the tidal cycles and are currently covered by the waste. As such, we suggest that the intertidal water access to the phosphogypsum stack through the secondary channels could act as one of the preferential paths that lead to the leaching mechanism.

Considering the high toxicity and acidity of the waste and that the current and the future restoration plans are based on the previous weathering mechanism (discarded by the present work), there is an urgent need for new effective measures to prevent phosphogypsum leachates from reaching the estuarine and subsequently, the coastal environment.

CHAPTER 4

Effects of seawater mixing on the mobility of trace elements in acid phosphogypsum leachates



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Papaslioti, E. M., Pérez-López, R., Parviainen, A., Sarmiento, A. M., Nieto, J. M., Marchesi, C., Delgado Huertas, A., & Garrido, C. J., 2018. Effects of seawater mixing on the mobility of trace elements in acid phosphogypsum leachates. *Marine Pollution Bulletin*, *127*, 695-703.

4. Effects of seawater mixing on the mobility of trace elements in acid phosphogypsum leachates

4.1 Introduction

Coastal systems are responsible for the mass flux of elements entering the deep ocean, because they serve as transition zones between freshwater and seawater environments. At coasts, significant modifications of seawater chemistry occur concerning salinity, ionic composition and redox conditions depending on the tidal cycles and the temporal variations in freshwater inputs (Hierro et al., 2014; Liang and Wong, 2003). During mixing of wastewaters and seawaters, a variety of geochemical processes take place, such as precipitation and adsorption onto newly-formed solid phases or dissolution, desorption and migration, resulting in the change of elemental concentrations in solution (Asta et al., 2015; Hierro et al., 2014; Zhou et al., 2003). Given the frequent dumping of phosphogypsum on coastal systems worldwide, their leachates are often subjected to changes of pH induced by mixing with seawater, and subsequently to geochemical processes that regulate the behaviour of trace elements and control their partitioning into dissolved concentrations and solid phases. Thus, a clear insight into the geochemical processes occurring during the mixing of phosphogypsum leachates with seawater in coastal environments is vital for the assessment of the total metal loads transported to the oceans.

One of the principal parameters during the seawater mixing is the pH, which controls the resulting chemical composition of waters and the mineralogy and the precipitated solid phases. Therefore, this chapter focuses on the effect of pH increase on the mobility of contaminants in phosphogypsum leachates during seawater mixing. The aim was to simulate and evaluate: i) the behaviour of contaminants including Al, As, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sb, U and Zn when the leachates are released to the coast undergoing seawater mixing and pH rise, and ii) the driving geochemical processes that take place in these solutions.

4.2 Materials and methods

4.2.1 Seawater mixing experiments

Seawater mixing experiments were performed in controlled-conditions to study the geochemical processes occurring when phosphogypsum leachates reach the estuary. Three leachate samples -collected during sampling described in section 3.2.1- were used to conduct such experiments; two edge outflow samples at discharge points of an unrestored disposal area (sample 3-9; zone 3) and a ‘supposedly’ restored area (sample 4-8; zone 4). This allowed the comparison between restored and non-restored phosphogypsum areas in terms of mobilisation of metals during seawater mixing. Process water was also the objective of the mobility experiments, as this industrial water is released to the estuary in some point discharges (Pérez-López et al., 2016), hence the sample collected at the surface pond of the unrestored zone 3 (PW), was also subjected to seawater mixing experiments. To avoid additional contamination, seawater samples for the experimental mixtures were collected at Playa de Espigón closer to the ocean coast in a contamination-free underway without AMD interference since the marine currents are towards the Mediterranean Sea (Van Geen et al., 1991).

Fifteen experiments were carried out in total for the three different types of samples (edge outflow waters from zones 3 and 4, and process water from zone 3) by mixing the acidic phosphogypsum leachates and seawater to different ratios with the aim of obtaining pH values of approx. 3, 4, 5, 6, and 7. The adequate amounts of wastewaters, that would provide sufficient newly-formed precipitates for their characterisation, required huge volumes of seawater in order to obtain the target pH values. Therefore, mixtures were prepared directly on the coast site using plastic containers of 15 L. Nevertheless, the pH values that could be reached on site were < 7, so additional experiments were performed in the laboratory to form circumneutral mixtures using smaller amounts of leachate samples and thus obtaining small amounts of precipitates. Titration curves were previously carried out in the laboratory for all the studied phosphogypsum leachates in order to estimate the amount of seawater required for each target pH value.

The resulting solutions and precipitates from each mixing experiment were collected for further analyses. Measurements of the pH, the electrical conductivity and the redox potential of the mixing solutions were conducted in situ, while treatment and preparation of the samples for cation, anion and stable isotopes analyses were conducted in the laboratory, directly after sampling. Seawater and original phosphogypsum wastewaters were prepared in a similar manner as their mixtures. More details on the measurements and treatment of the samples can be found in Chapter 3 (section 3.3.1). The solid precipitate samples for the different pH values were collected on filter paper (0.45 μm of pore size) by filtration of the total amount of the solutions using a vacuum pump. These solid samples were examined for mineralogical characterisation of newly-formed solid phases.

4.2.2 Aqueous analysis

Major element (Ca, K, Mg and Na) concentrations were obtained via Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) by a Jobin Yvon Ultima 2 instrument at the University of Huelva (Spain). Concentrations of anions (F^-, Cl^-, Br^-, SO_4^{2-}, PO_4^{3-}) and ammonia were also analysed at the University of Huelva by a high performance liquid chromatography system (HPLC) using a Metrohm 883 basic ion chromatograph (IC) equipped with Metrosep columns. Aluminum, Fe, Mn and trace elements (Cr, Co, Ni, Cu, Zn, As, Cd, Sb, Pb, and U) were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) by an Agilent 8800 Triple quadrupole device at the Andalusian Institute of Earth Sciences (IACT) in Granada (Spain). Determination of Fe(II) and total Fe (following reduction with hydroxylamine hydrochloride) in the phosphogypsum leachates was undertaken in the geochemical laboratory of the University of Huelva on the same day of the sampling by colorimetry at 510 nm using a SHIMADZU UVmini-1240 spectrophotometer. For a detailed description of all the aforementioned analyses, please go to Chapter 3 (section 3.3.2.1).

4.2.3 Isotopic measurements

Stable isotopes including oxygen and hydrogen (from H_2O) and sulphur (from sulphates) isotopes were measured by Isotope-Ratio Mass Spectrometry (IRMS) at the Stable Isotope Laboratory of the IACT. The purpose of these analyses was to evaluate the source of the acidic leachates and their connection with the different end-members used for the experiments. The stable isotope compositions are reported as $\delta^{18}O$ and $\delta^{2}H$ (or δD) referred to the standard V-SMOW (Vienna Standard Mean Ocean Water) and $\delta^{34}S$ referred to the standard V-CDT (Vienna

Canyon Diablo Troilite). Detailed description of the analyses of stable isotopes can be found in Chapter 3 (section 3.3.2.2).

4.2.4 Geochemical modelling

Geochemical calculations were performed for all the solutions, which were collected after seawater mixing, by the PHREEQC-2 code (Parkhurst and Appelo, 2005) using the Minteq.v4 database (Allison et al., 1991), allowing evaluation of the conservative or non-conservative behaviour of the dissolved compounds, along with the geochemical processes occurring during seawater mixing. More importantly, the model was used to determine saturation indices (SI) with respect to relevant mineral phases that may play a key role in the mobility of the dissolved species at the seawater mixing. Negative SI indicates that the solutions are undersaturated with respect to the target minerals and, therefore, their dissolution is thermodynamically favored over precipitation. On the contrary, positive SI indicates that mineral precipitation is favored. Finally, SI close to zero indicates that solutions are close to equilibrium with respect to a given mineral phase and neither dissolution nor precipitation is thermodynamically predicted. Note that samples with high seawater ratios exhibited high values of ionic strength (up to 0.7), thus speciation analysis and saturation indices calculated for these samples could present some uncertainty.

4.2.5 Solid phase analysis

Solid phase analysis was performed on the precipitates collected after seawater mixing. The solid phases were analysed by a Field-Emission Scanning Electron Microscope with an AURIGA system (FESEM; ZEIS SMT), an Environmental SEM (ESEM; FEI, QEMSCAN 650F) and Scanning Electron Microscope of Variable Pressure (VPSEM; ZEIS SUPRA^{TM} 40VP), all equipped with backscattered and secondary electron detectors coupled with Energy Dispersive x-ray Spectrometer (EDS), at the Instrumentation Centre (CIC) of the University of Granada, Spain.

4.3 Results and Discussion

4.3.1 Mixing ratios of seawater to phosphogypsum leachates

The respective amounts of seawater and acidic leachates used for each target pH, along with all the physicochemical parameters for all samples are compiled in **Table 4.1**. The phosphogypsum leachates displayed conditions of high acidity and extreme contamination, with pH values of 2.04 (edge outflow from zone 3), 2.19 (edge outflow from zone 4) and 1.37 (process water from zone 3), and electrical conductivities of 27.1, 40.5 and 55.6 mS/cm, respectively. On the other hand, seawater exhibited typical alkaline pH values of 7.94 and electrical conductivity of 55.2 mS/cm.

The extreme acidity of the leachates required large amounts of seawater to reach circumneutral pH values **(Fig. 4.1)**; to produce pH around 7, 227 mL, 160 mL and 1.6 L of seawater were needed per each mL of edge outflows from zones 3 and 4 and process water, respectively **(Table 4.1)**. Even for achieving pH 4, around 22 mL, 21 mL and 190 mL of seawater were required for every mL of each leachate, respectively. Large seawater quantities explain the constant electrical conductivity of the mixing solutions at around 55 mS/cm, while the pH increased **(Table 4.1)**.

For all types of acidic leachates used in mixing experiments, the seawater amount necessary to reach pH up to 6 - 6.5 increased gradually, while the following rise to pH 7 required much more amount of seawater **(Fig. 4.1)**. The ratio of seawater to phosphogypsum leachates corresponding to pH 7 was two to four times higher compared to that of pH 6, indicating a buffer zone for pH > 6 likely due to changes in the aqueous speciation or mineral solubility, that hinder further rise of the pH.

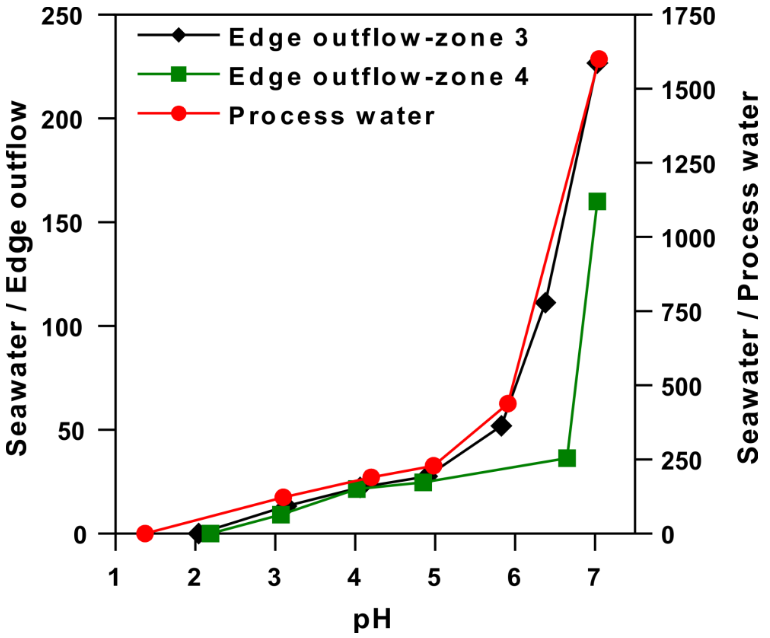


Figure 4.1: Mixing ratios of seawater to phosphogypsum leachates used for the experiments for each target pH.

Table 4.1. Physicochemical parameters, quantities of seawater and acidic leachates used for the experiments, major anion and cation concentrations (mg/L) in the starting and mixing solutions for each target pH.

Sample	pH	EC (mS/cm)	Eh (mV)	PG leachate (mL)	Seawater (mL)	Seawater-PG water ratio	Ammonium	Fluoride	Chloride	Bromide	Sulphate	Phosphate	Ca	K	Mg	Mn	Na
Seawater	7.94	55.2	n.a	-	-	-	2.40	111	21666	69.0	3288	791	418	445	1301	0.01	10985
Edge Ouflow-zone 3	2.04	27.1	482	-	-	-	58.0	874	13827	36.7	4717	8911	1260	353	1039	6.49	8484
	3.14	55.4	500	700	9300	13.3	3.71	66.0	20195	68.7	2829	1015	488	427	1340	0.45	11065
	4.06	55.4	469	430	9570	22.3	1.38	37.0	20442	66.2	2809	534	470	420	1224	0.33	11346
	4.90	55.3	464	350	9650	27.6	28.4	30.3	20331	65.9	2752	353	448	428	1346	0.34	11230
	5.83	55.5	424	208	10792	51.9	2.46	18.9	20657	68.3	2735	346	445	421	1366	0.19	11159
	6.38	55.6	396	90.0	10010	111	2.23	7.34	20844	73.2	2719	124	407	434	1351	0.10	11128
	7.03	55.0	n.a	1.50	340	227	1.55	5.80	20661	72.2	2681	127	428	431	1366	0.04	11286
Edge Ouflow-zone 4	2.19	40.5	481	-	-	-	50.1	900	8143	16.7	4563	3751	931	282	871	12.9	6871
	3.07	54.1	496	990	9010	9.10	22.4	94.9	19848	71.0	3011	416	451	415	1308	1.40	10798
	4.02	54.4	445	445	9555	21.5	10.5	50.0	20225	74.8	2810	221	434	426	1291	0.66	10925
	4.85	54.4	462	390	9610	24.6	16.5	43.1	21583	74.9	3159	252	454	434	1301	0.59	10854
	6.65	54.4	443	295	10705	36.3	3.65	28.4	20758	79.2	2790	138	413	439	1317	0.41	11099
	7.03	55.0	n.a	3.00	480	160	<3	10.1	21029	58.1	2711	58	416	440	1348	0.10	10812
Process water-zone 3	1.37	55.6	638	-	-	-	997	1378	12417	16.7	7556	95671	2127	597	1757	24.6	8107
	3.10	55.9	522	82.0	10018	122	9.88	32.6	20892	63.0	2994	795	416	408	1264	0.35	11155
	4.20	55.6	483	53.0	10047	190	4.96	25.1	20750	59.2	2950	529	409	410	1378	0.20	11205
	4.98	55.4	462	44.0	10066	229	2.65	20.5	20575	62.3	2807	640	407	414	1259	0.19	10922
	5.91	55.6	439	23.0	10077	438	22.7	6.96	20524	72.6	2654	277	403	425	1387	0.11	11392
	7.05	55.0	n.a	0.15	240	1600	1.90	4.04	20689	74.5	2677	100	399	419	1358	0.03	10999

n.a not analysed

4.3.2 Chemistry of starting solutions

The geochemical characteristics of starting and mixing solutions are summarised in **Table 4.1** for major compounds and **Table 4.2** for trace elements. As expected from extreme acidity and high conductivity, initial phosphogypsum-related wastewaters contain high concentrations of anions and cations, some of them being potentially toxic pollutants. The edge outflow from the non-restored zone 3 had concentrations of around 10 g/L for Cl and PO_4, 8 g/L of Na, 5 g/L for SO_4, and lower, but significant, contents of Ca, Mg, F, K, Br and NH_4^+ **(Table 4.1)**. Concerning the main contaminants of this sample, concentrations were around 80 mg/L of Fe (mainly as Fe(II)), 20 mg/L of As and Zn, 10 mg/L of Al, 5 mg/L of U, Cu and Cr, 2 mg/L of Cd and Ni, and 0.5 mg/L of Sb, Pb and Co **(Table 4.2)**.

Concentrations in the process water from the same non-restored zone were much higher than those found in the edge outflow, even between 3 and 10 times higher for PO_4 and metals **(Tables 4.1 and 4.2)**. This owes to the fact that process water comes directly from the industrial process and is concentrated in a closed-circuit system, as stated before. In addition, the geochemical characteristics of this type of water are related to the elevated evaporation rate taking place in the central ponds where it is stored, resulting in the accumulation of contaminants and increasing acidity (Pérez-López et al., 2015). On the other hand, concentrations of the edge outflow leachate from zone 4, in which some restoration actions have been undertaken, were within the same order of magnitude as those found in the edge outflow of zone 3, but with significantly lower values **(Tables 4.1 and 4.2)**. Although contamination still persists in the restored zone 4 through edge outflows, relatively lower concentrations were observed likely due to the organic matter-rich layers of the complex artificial-soil cover, which seems to act as a carbon source that enhances the activity of naturally-occurring sulphate reducing bacteria in the phosphogypsum (Castillo et al., 2012b), resulting in removal of part of the contamination.

In contrast, oceanic water sample showed typically high concentrations of Na, which is the dominant cation with around 10 g/L concentration, and to a lesser extent Mg, Ca and K. Anionic contents of seawater were also high, with chloride and sulphate as main anions with concentrations of 20 and 3 g/L, respectively **(Table 4.1)**. All the contaminants detected in the phosphogypsum leachates were in negligible abundances in seawater, and thus the latter does not contribute to the resulting concentrations after mixing experiments **(Table 4.2)**.

Table 4.2. Trace elements concentrations (mg/L) in the starting and mixing solutions for each target pH. Isotopic signatures of $\delta^{2}H$ (δD), $\delta^{18}O$ and $\delta^{34}S$ are also shown.

Sample	pH	Al	Cr	Fe	Co	Ni	Cu	Zn	As	Cd	Sb	Pb	U	$\delta^{18}O$ (VSMOW)	δD (VSMOW)	$\delta^{34}S$ (CDT)
Seawater	7.94	0.13	1.02*	8.09*	0.11*	0.70*	4.26*	0.05	3.35*	0.23*	0.31*	2.99*	2.21*	0.58	5.33	20.3
Edge Ouflow-zone 3	2.04	9.89	3.82	83.8	0.26	2.06	4.77	18.7	18.9	2.38	0.29	0.33	5.51	-1.26	-10.1	2.11
	3.14	1.00	0.16	3.43	0.02	0.12	0.29	1.20	1.34	0.16	0.02	0.02	0.34	-2.07	-6.81	17.7
	4.06	0.62	0.05	0.11	0.01	0.08	0.19	0.80	0.89	0.10	0.01	0.01	0.06	-1.91	-5.38	18.98
	4.90	0.64	0.02	0.04	0.01	0.08	0.16	0.77	0.81	0.09	0.01	2.02*	0.01	-1.02	-1.73	19.00
	5.83	0.13	0.68*	4.35*	0.01	0.04	0.07	0.33	0.41	0.04	0.01	0.68*	0.87*	-1.27	2.10	19.4
	6.38	0.01	0.57*	0.01	2.54*	0.02	0.03	0.15	0.21	0.02	2.73*	0.18*	0.01	0.52	-3.10	19.9
	7.03	0.01	0.89*	4.26*	0.96*	0.01	0.01	0.08	0.10	0.01	1.42*	0.03*	0.01	2.09	2.35	20.00
Edge Ouflow-zone 4	2.19	2.66	3.01	155	0.28	1.02	4.16	14.6	3.22	0.85	0.28	0.11	2.47	-3.57	-21.3	5.24
	3.07	0.61	0.26	13.2	0.03	0.09	0.37	1.36	0.38	0.08	0.03	0.01	0.23	1.26	4.98	16.3
	4.02	0.28	0.08	1.33	0.01	0.04	0.18	0.65	0.17	0.04	0.01	2.96*	0.06	0.94	4.64	18.5
	4.85	0.25	0.03	0.01	0.01	0.04	0.14	0.55	0.14	0.03	0.01	0.61*	1.36*	1.03	4.65	18.7
	6.65	0.20	2.55*	0.01	0.01	0.03	0.10	0.41	0.11	0.02	0.01	0.17*	0.34*	0.86	6.39	19.1
	7.03	0.02	0.55*	4.11*	2.90*	0.01	0.02	0.10	0.03	0.01	2.06*	0.01*	0.01	2.06	4.58	19.7
Process water-zone 3	1.37	102	50.6	162	1.25	11.5	19.2	112	49.3	19.3	0.74	1.00	52.0	4.54	19.5	3.14
	3.10	1.75	0.21	0.45	0.01	0.11	0.19	1.13	0.61	0.19	0.01	0.02	0.47	-0.96	-15.9	19.5
	4.20	0.89	0.02	0.03	0.01	0.06	0.10	0.60	0.32	0.10	4.44*	0.01	0.09	-0.73	-12.7	19.8
	4.98	0.65	3.28*	0.01	0.01	0.05	0.08	0.53	0.29	0.09	4.01*	2.19*	0.03	2.20	-7.45	19.7
	5.91	0.06	0.84*	0.01	3.09*	0.03	0.04	0.31	0.14	0.04	2.01*	0.47*	2.28*	0.66	-16.4	19.7
	7.05	0.02	0.99*	4.22*	0.93*	0.01	0.01	0.08	0.04	0.01	0.75*	0.02*	0.01	1.51	8.11	20.2

*** Values are in µg/L**

4.3.3 Trends in solution chemistry during mixing experiments

Given the high amounts of seawater used in the mixing experiments, the resulting solutions, reasonably, exhibited concentrations approaching those typical of seawater, especially at high pH values **(Tables 4.1 and 4.2)**. In fact, concentrations of major anions and cations in mixtures with pH 3 to 7 of the three leachate samples were almost duplicates of seawater, and as such, they exhibited a conservative trend during the experimental mixings. Exceptions to this case were phosphates, fluorides and, to a lesser extent, sulphates, as their concentrations decreased significantly, while the pH increased **(Table 4.1)**. Thus, mainly fluoride and phosphate presented a non-conservative behaviour indicating precipitation processes at pH values higher than 3.

Concerning the contaminants, their concentrations decreased significantly from initial values in the pure phosphogypsum leachates as a result of dilution, although the concentrations observed in the mixing solutions at pH 7 were slightly higher than those found in seawater **(Table 4.2)**. In order to evaluate the behaviour of the pollutants during the experimental runs, relative concentrations were calculated from the analysed concentrations by multiplying them by the dilution factor; i.e. the total amount of solution (leachate plus seawater) divided by the initial amount of leachate. Results are plotted in **Figure 4.2** and are described in the next two subsections according to the observed behaviour; similarly are described the precipitated phases calculated by PHREEQC.

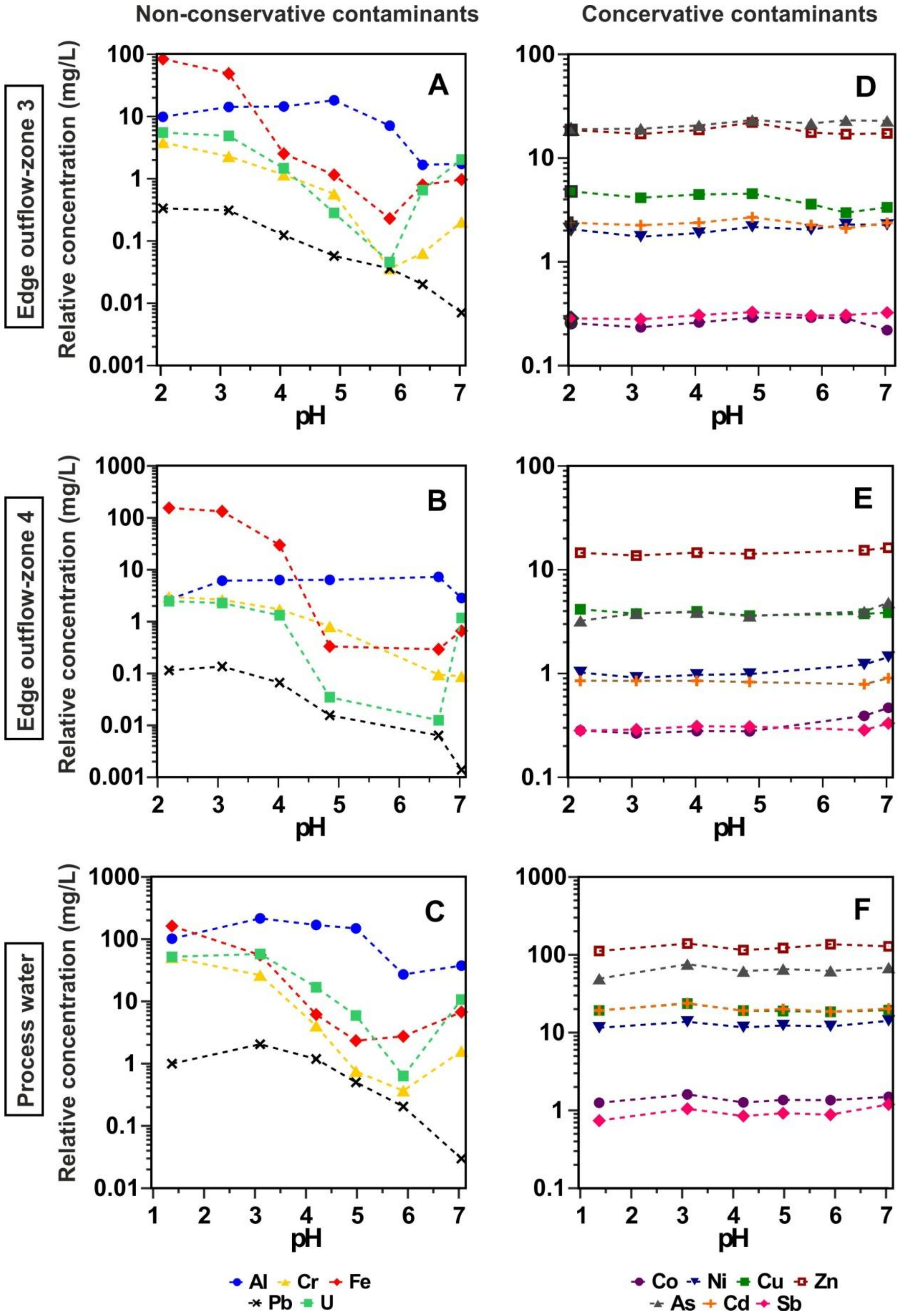


Figure 4.2: Behaviour of non-conservative **(A, B** and **C)** and conservative **(D, E** and **F)** phosphogypsum-related contaminants with pH increase. The graphs are based on the relative concentrations in solution, calculated from the analysed concentrations multiplied by the dilution factor, which is the ratio of the total volume (leachate + seawater) to the volume of the leachate, for each experiment.

4.3.3.1 Non-conservative contaminants

Some metals such as Al, Fe, Cr, Pb and U exhibited a non-conservative behaviour throughout the seawater mixing experiments **(Fig. 4.2A-C)**. Iron concentrations decreased with increasing mixing ratio and pH; only around 0.4 - 4.2% of Fe in relation to the initial concentration remained in solution at neutral pH, while most Fe was depleted from the solution at pH around 4. The solid phases that precipitated according to PHREEQC calculations are in accordance with the depletion of Fe from the solution **(Table 4.3; Fig. 4.2A-C)**. Supersaturation in Fe(II) phosphates was noted in the form of strengite at pH > 3. Moreover, Fe(III) produced by Fe(II) oxidation, an increasingly rapid process as pH increases (Singer and Stumm, 1970), is predicted to precipitate as oxyhydroxide phases; i.e. goethite at pH>4, lepidocrocite nearly at pH>5 and ferrihydrite at pH>6. According to the geochemical modelling, $Fe(OH)_{2.7}Cl_{0.3}$ is another supersaturated Fe phase at pH>3 , although minor compared to the other iron phases, as Cl behaved conservatively.

On the other hand, Al concentration also decreased but only at pH>5, with 18-37% of the initial amount remaining in solution at neutral pH, except for the experiments regarding zone 4, where Al behaved conservatively. The aluminium phases that supersaturated in solution, according to the geochemical modelling, included phosphate, sulphate and oxyhydroxide minerals, i.e. plumbogummite, alunite, boehmite and gibbsite at pH>6 **(Table 4.3)**. Supersaturation in Al phases was reached at higher pH values and involved fewer phases in mixtures of zone 4 leachate compared to the other leachates, which could justify the conservative behaviour of Al in this case.

The non-conservative behaviour of phosphate concentration is consistent with geochemical modelling that indicated supersaturation in phosphate phases, not only strengite and plumbogummite, as indicated previously, but also $MnHPO_4$ at pH>3, hydroxylapatite at pH>5.5-7 and pyromorphite at pH 5.5-6.5. Major precipitation of hydroxylapatite at pH higher than 5.5-7 is expected due to the relative abundance of Ca in the starting solutions with respect to other cations **(Table 4.1)**. The precipitation of most of the newly-formed phases releases protons **(Table 4.3)**, but probably hydroxyapatite precipitation reaction at pH 5.5-7 strongly contributes to the existence of the previously mentioned buffering zone for these pH values. The decrease in fluoride concentrations in solution as the pH increases is also consistent with the PHREEQC simulations that indicated supersaturation with respect to fluorite at all pH range (from 3 to 7) for the three acidic leachates **(Table 4.3)**.

The amounts of minor Pb and Cr also decreased with increasing pH and the resulting neutral mixing solutions of the outflows and the process water contained only around 1-5% of the initial dissolved amounts of these metals **(Fig. 4.2A-C)**. Both metals behaved similarly to iron and phosphates, implying that they were likely retained by sorption processes in Fe phosphate or oxyhydroxide precipitates, which can act as important sinks for trace elements. In addition, Pb probably precipitated as phosphate phases, a hypothesis consistent with the PHREEQC modelling, which showed supersaturation with respect to pyromorphite at pH around 5.5-6.5 and plumbogummite for the outflow of the zone 3 and the process water at pH 7, this last case in accordance with the behaviour of Al in solution **(Table 4.3)**.

A different -although still non-conservative- pattern was observed for uranium in all three types of wastewaters, due to variations of U solubility during pH-induced seawater mixing. The amount of U in solution strongly decreased from pH 4 to pH 6 (0.5-1.2% of the initial value). No supersaturation in U phases was predicted by the geochemical modelling, probably indicating sorption processes onto other newly-formed phases. Indeed, some studies of this and other coastal systems observed U adsorption onto Fe oxyhydroxide and aluminium particles (Hierro et al., 2013a; Hierro et al., 2014; McKee et al., 1987). However, increase of U in solution was again favoured at pH > 6 **(Fig. 4.2A-C)**, which could be due to a decrease of surface adsorption processes from the particulate phases and formation of soluble carbonate complexes (Hierro et al., 2013b), resulting in a positive U flux. The dissolved amount of U in the mixtures increased and 20-48% of the initial amount remained at neutral pH values. The same release behaviour was observed, although in a much lesser extent, for Fe and Cr at pH 7 **(Table 4.2, Fig. 4.2A-C)** probably due to a decrease in the supersaturation state of neutral solutions in relation to strengite according to the geochemical modelling performed **(Table 4.3)**.

Table 4.3. Ideal reactions, equilibrium constants and saturation indices (SI) for supersaturated minerals according to PHREEQC simulations from the database of model MINTEQ, at all the studied mixing solutions. Negative and positive SI indicate undersaturation and supersaturation, respectively.

Mineral	**Reaction**	**LogKeq**	**Saturation index**															
			Edge outflow-zone 3						**Edge ouflow-zone 4**					**Process water**				
			3.14	4.06	4.90	5.83	6.38	7.03	3.07	4.02	4.85	6.65	7.03	3.10	4.20	4.98	5.91	7.05
Alunite	$KAl_3(SO_4)2(OH)_6 + 6H^+ \Leftrightarrow K^+ + 3Al^{+3} + 2SO_4^{-2} + 6H_2O$	-1.35	-24.8	-18.8	-12.8	-7.63	-3.81	-1.49	-26.4	-21.3	-16.0	-7.63	-1.32	-21.4	-15.6	-10.8	-4.56	0.04
Boehmite	$AlOOH + 3H^+ \Leftrightarrow Al^{+3} + 2H_2O$	8.58	-11.2	-8.31	-5.47	-2.84	-1.01	0.34	-11.9	-9.17	-6.63	-2.84	0.45	-10.1	-7.10	-4.74	-1.72	0.88
Diaspore	$AlOOH + 3H^+ \Leftrightarrow Al^{+3} + 2H_2O$	6.87	-9.54	-6.62	-3.78	-1.15	0.68	2.04	-10.2	-7.48	-4.94	-1.15	2.14	-8.42	-5.41	-3.05	-0.04	2.58
$Fe(OH)_{2.7}Cl_{0.3}$	$Fe(OH)_{2.7}Cl_{0.3} + 2.7H^+ \Leftrightarrow Fe^{+3} + 2.7H_2O + 0.3Cl^-$	-3.04	1.66	2.28	4.05	4.00	5.78	5.24	1.15	2.93	2.49	5.30	6.15	1.13	2.35	3.64	4.46	5.30
Ferrihydrite	$Fe(OH)_3 + 3H^+ \Leftrightarrow Fe^{+3} + 3H_2O$	4.89	-5.20	-4.30	-2.27	-1.16	-0.11	0.44	-4.83	-3.65	-2.97	-1.16	0.46	-5.74	-4.18	-2.67	-0.67	0.51
Fluorite	$CaF_2 \Leftrightarrow Ca^{+2} + 2F^-$	-11.0	1.79	1.55	1.33	1.01	0.10	-0.02	1.93	1.77	1.75	1.01	0.38	1.09	1.08	0.97	0.08	-0.36
Gibbsite	$Al(OH)_3 + 3H^+ \Leftrightarrow Al^{+3} + 3H_2O$	8.29	-11.5	-8.53	-5.69	-3.06	-1.23	0.13	-12.1	-9.39	-6.85	-3.06	0.23	10.3	-7.32	-4.96	-1.95	0.67
Goethite	$FeOOH + 3H^+ \Leftrightarrow Fe^{+3} + 2H_2O$	0.50	-0.74	0.16	2.19	3.30	4.33	4.89	-0.38	0.81	1.50	3.30	4.92	-1.27	0.27	1.79	3.79	4.95
Hematite	$Fe_2O_3 + 6H^+ \Leftrightarrow 2Fe^{+3} + 3H_2O$	-4.01	3.55	5.34	9.40	11.6	13.7	14.8	4.27	6.65	8.01	11.6	14.9	2.48	5.56	8.60	12.6	14.9
Hydroxylapatite	$Ca_5(PO_4)_3OH + H^+ \Leftrightarrow 5Ca^{+2} + 3PO_4^{-3} + H_2O$	-44.3	-12.8	-6.98	-1.55	3.98	5.80	8.56	-14.0	-8.60	-2.81	3.98	7.94	-13.5	-6.40	-1.22	4.22	8.89
Lepidocrocite	$FeOOH + 3H^+ \Leftrightarrow Fe^{+3} + 2H_2O$	1.37	-1.67	-0.77	1.26	2.36	3.42	3.97	-1.30	-0.13	0.56	2.36	3.99	-2.21	-0.66	0.86	2.85	4.03
MnHPO4	$MnHPO_4 \Leftrightarrow Mn^{+2} + PO_4^{-3} + H^+$	-25.4	0.44	1.02	1.75	2.31	1.77	1.59	0.86	0.89	1.84	2.31	1.59	0.24	0.90	1.58	2.12	1.53
Plumbogummite	$PbAl_3(PO_4)_2(OH)_5{:}H_2O + 5H^+ \Leftrightarrow Pb^{+2} + 3Al^{+3} + 2PO_4^{-3} + 6H_2O$	-32.8	-28.4	-20.7	-12.8	-5.17	-2.20	0.11	-30.3	-24.3	-16.4	-5.17	-0.97	-25.2	-16.8	-10.6	-2.08	1.77
Pyromorphite	$Pb_5(PO_4)_3Cl \Leftrightarrow 5Pb^{+2} + 3PO_4^{-3} + Cl^-$	-84.4	-6.23	-4.55	-1.83	1.94	-0.90	-3.73	-7.50	-7.07	-3.05	1.77	-6.33	-6.87	-2.33	-1.41	1.57	-4.22
Strengite	$FePO_4{:}2H_2O \Leftrightarrow Fe^{+3} + PO_4^{-3} + 2H_2O$	-26.4	0.78	0.56	1.63	1.45	1.37	0.61	0.98	0.85	0.63	1.45	0.48	0.24	0.50	1.15	1.82	0.76

4.3.3.2 Conservative contaminants

On the contrary, increasing mixing ratio and pH rise had no significant impact on the concentrations of the majority of potentially toxic elements in the phosphogypsum leachates. Around 80-100% of Co, Ni, Cu, Zn, As, Cd and Sb were kept into solution until neutral pH with no fluctuations over the gradual pH increase **(Fig. 4.2D-F)**. These trace elements thus exhibited a conservative behaviour during seawater mixing and did not participate in sorption processes. This conservative trend is explained by the formation of ion complexes in the studied pH range, hindering the partitioning of these trace elements in precipitated solid phases. Indeed, this behaviour was supported by PHREEQC simulations, as no supersaturated phases containing these trace elements were predicted. In addition, these results show that sorption to other solid phases must not occur through the mixing experiments.

4.3.4 Solid phase characterisation

The chemical analyses of the mixing solutions showed that major elements, such as P, F, and Fe, were largely removed from solutions with increasing pH, implying that their concentrations decreased due to precipitation processes. Thus, the characterisation of these solid phases was required in order to provide a full insight into the geochemical processes controlling metal mobility during mixing of phosphogypsum leachates with seawater. According to previous studies in similar acidic systems (Carrero et al., 2015; Yu et al., 1999), newly-formed Fe-bearing precipitates, formed as a consequence of the progressive increase of pH, are amorphous or poorly-crystalline, which limits the use of conventional X-ray techniques for a full characterisation. Hence, high resolution SEM-EDS was used to perform a more detailed study.

SEM-EDS images revealed that the newly-formed precipitates are submicrometer agglomerates of globular phases chemically composed mainly of iron **(Fig. 4.3)**. Identification of individual phases was not possible due to the cryptocrystalline size of the solids. Semiquantitative microanalyses accomplished by SEM-EDS allowed to identify in the matrix the presence of aggregates constituted by P and Fe at pH>4 **(Fig. 4.3A)**, indicating phases similar to strengite, which is consistent with the geochemical modelling. More importantly, according to the EDS analysis, Fe oxyhydroxides precipitated at pH 3 from all types of wastewater mixtures, but the formation of Fe-rich phases was more abundant at pH values >4 **(Fig. 4.3B-E)**, being consistent with the decreasing amount of dissolved Fe in the solutions and the nature of solid phases calculated by PHREEQC (i.e. goethite, lepidocrocite and ferrihydrite). Other metals, such as Cr, were detected together with Fe in the aggregates of newly-formed phases at pH 5 and 6 **(Fig. 4.3D)**, in agreement with the composition of solutions **(Fig. 4.3A-C)**.

Despite chemical analyses showed the depletion of fluoride with increasing pH and PHREEQC calculations predicted the supersaturation of fluorite, fluoride phases were not detected by EDS analyses. This is probably due to the very small amount of fluoride precipitates, associated with phosphate or oxyhydroxide phases, which hinder their identification under the SEM.

EDS analyses detected significant concentrations of Ca and P in precipitates corresponding to pH 5.5-7, which can be attributed to the presence of hydroxyapatite **(Fig. 4.3F)**. Other minor phases that were identified by SEM-EDS analyses included gypsum, Ca-Mg-aluminosilicates and quartz, in the form of particulate matter suspended in the acidic leachates and seawater used for the experiments.

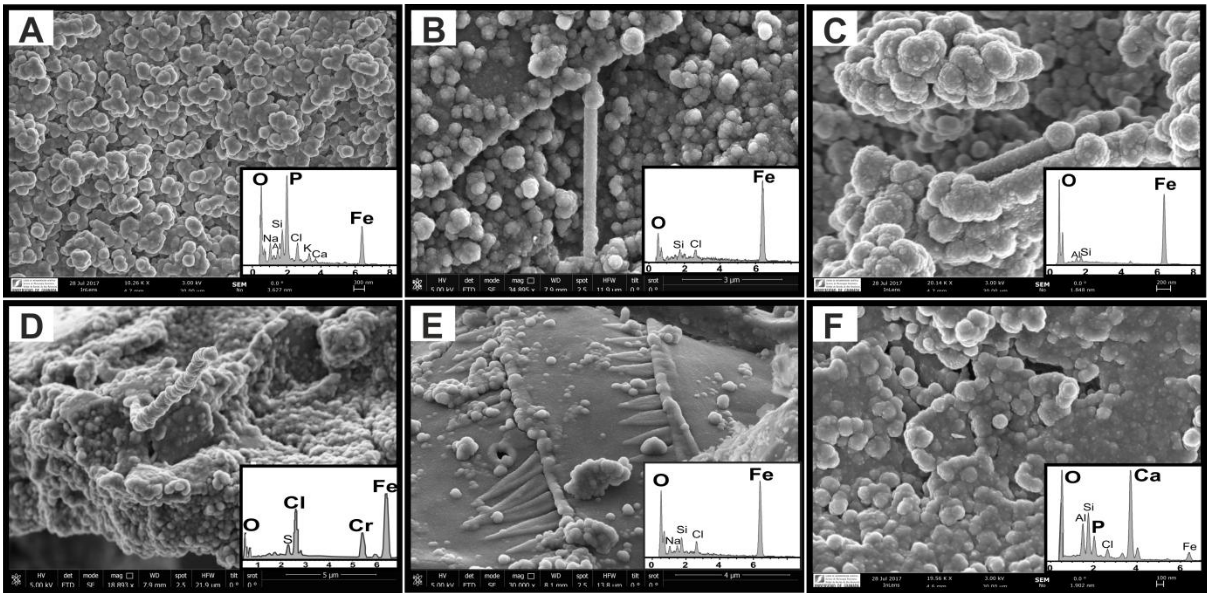


Figure 4.3: SEM images and EDS spectra of the newly-formed precipitates collected from the mixing solutions at different target pH values: **(A)** aggregates of Fe-phosphates at pH 4, **(B)** and **(C)** Fe-oxyhydroxide phases in the shape of aggregated globules at pH 4 and 7 respectively, **(D)** plates and fibbers forming Fe-oxyhydroxide aggregates at pH 5, **(E)** horizontally aligned triangle-like structures of Fe-oxyhydroxide precipitates at pH 6 and **(F)** Ca-phosphate (i.e. hydroxyapatite) as phase identified among the major Fe phases at pH 6.

4.3.5 Isotopic signature

The acidic leachates presented a different isotopic signature, at least in terms of $\delta^{18}O$ and $\delta^{2}H$, depending on the type of source water **(Table 4.2)**. The process water revealed a higher level of evaporation compared to the outflow waters **(Fig. 4.4A)**, in agreement with the elevated evaporation taking place in the surface ponds. Differences in the $\delta^{18}O$ and $\delta^{2}H$ compositions and, subsequently, in the degree of evaporation were also observed between the two studied edge outflows, with higher values in the outflow from zone 3. The minimal imprint of process water on the isotopic chemistry of leachates of zone 3 suggests poor connection between process water ponded on its surface and edge outflows. In addition, the edge outflows from zone 4, which still leak from the phosphogypsum stack despite the absence of ponded process water and the presence of a complex artificial soil cover, exhibited an isotopic signature very different from that of the process water.

The $\delta^{34}S$ compositions of pure edge outflows and process water were similar ($2‰<\delta^{34}S<5‰$) and indicated a continental signature implying that sulphates in the solutions derive from oxidation of sulphide ores **(Fig. 4.4B)**. This outcome is unexpected considering that phosphogypsums in zones 3 and 4 were transported from the industry to the stack before 1997 using exclusively seawater, which exhibited a different $\delta^{34}S$ value (around 20‰). Thus, the $\delta^{34}S$ signature of the phosphogypsum leachates is more similar to the composition of sulphides from the IPB (median $\delta^{34}S$ = 0.8 and SD = 7.1; Velasco et al., 1998). Accordingly, two possible origins could explain these similar values: (1) the existence of weathering inputs of the Tinto River estuarine water, which is affected by acid mine drainage from aqueous sulphide oxidation in IPB mining districts, to the interior of the stack, and/or (2) an inheritance of the sulphuric acid used during the wet chemical digestion for the phosphoric acid manufacturing in Huelva (reaction (1)), which is obtained by roasting of pyrite from the Tharsis Mine (IPB) and later recovering of the SO_2 from the gas with water.

With respect to the mixing solutions, their $\delta^{18}O$ and $\delta^{2}H$ compositions ranged from -2.07 to 2.2 ‰ and from -16.4 to 8.11 ‰, respectively **(Fig. 4.4A)**. The isotopic signatures of the mixtures corresponding to the edge outflow from zone 3 are broadly between their two end-members (seawater and corresponding acidic leachate), whereas those of zone 4 plot close to the seawater composition. On the contrary, the mixtures with pH between 3 and 6 corresponding to the process water surprisingly presented lighter values of δ^2H and, in some mixing solutions of $\delta^{18}O$, than both end-members. The absence of other end-members could explain these discrepancies observed for $\delta^{18}O$ and δ^2H in the mixing solutions of the three types of leachates. On the other hand, the sulphur isotopic tracers presented, mainly, a marine influence for all the experimental mixtures, with $\delta^{34}S$ varying from 16.3 to 20.2 ‰ **(Fig. 4.4B)**. The $\delta^{34}S$ values of mixtures with the three wastewater types are consistently closer to the seawater value ($\delta^{34}S$ ‰ around 20) with increasing amount of seawater used for each mixing solution.

Restoration actions in zones 1 and 4 and those planned for zones 2 and 3 are based on the assumption that infiltration of ponded process water through the porous media and its subsequent emergence as edge outflows is the main vector of contamination to the estuary. However, according to these isotopic findings, the apparent poor connection between the ponded process water and the edge outflows, the different isotopic fractionation observed in the interactions between phosphogypsum-related wastewaters and seawater, and the possible input of water from the Tinto River estuarine to the phosphogypsum stack, reveal a new focus on the weathering processes of the phosphogypsum related to its location in the tidal prism of the estuary, which confirms some suggestions previously reported by Pérez-López et al. (2015). Full details can be found in Chapter 3.

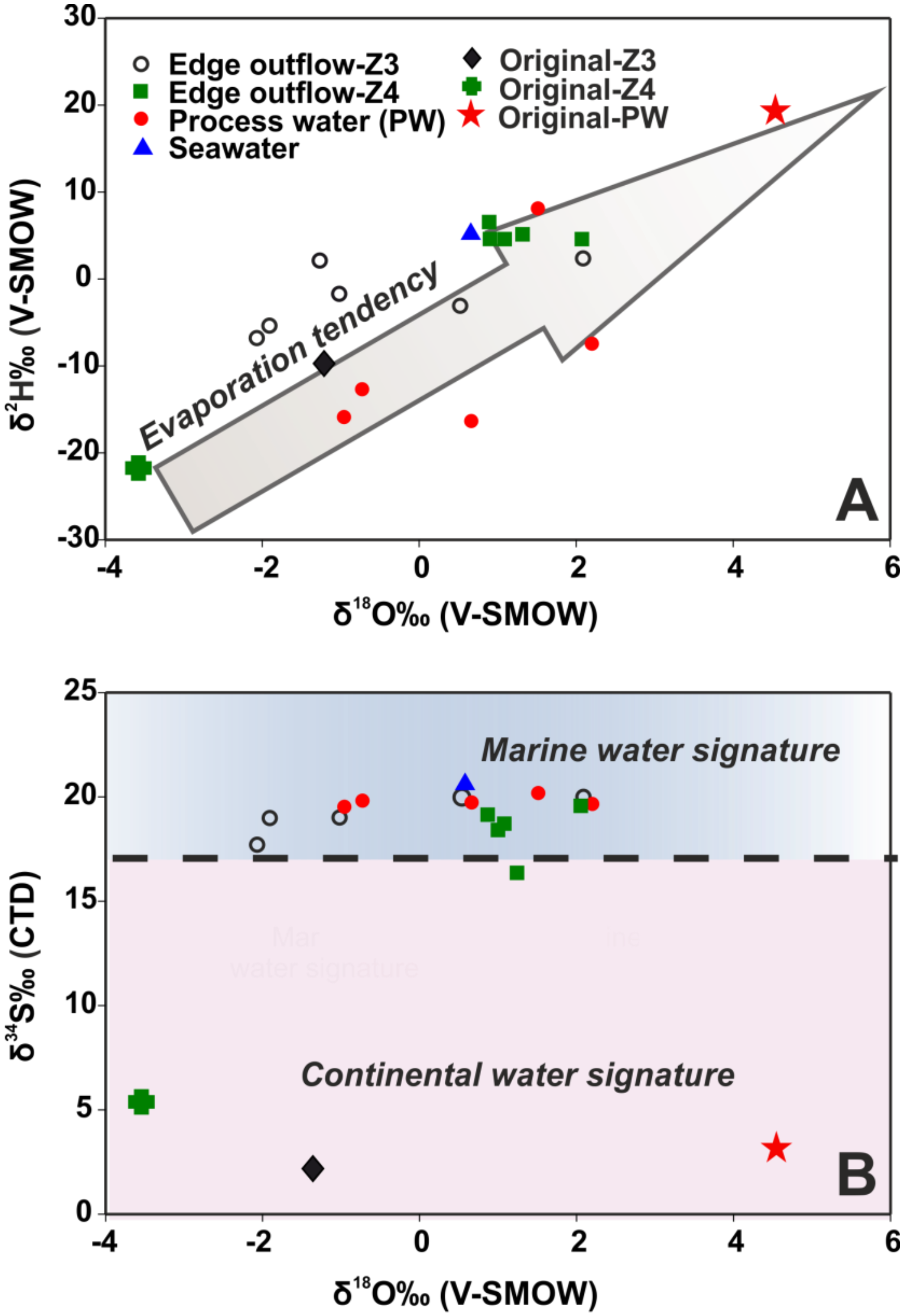


Figure 4.4: Stable isotope signatures of the mixing solutions, the wastewater end-members (illustrated with diamond, cross and star for the edge outflow of zone 3, zone 4 and process water, respectively) and the seawater end-member; **(A)** δ^{18}O vs. δ^{2}H (δD) composition, and **(B)** δ^{18}O vs. δ^{34}S composition.

4.3.6 Environmental implications

The results of this study indicated that leaching of the phosphogypsum stack causes a continuous discharge of some of the most toxic contaminants, which threaten the environmental welfare, into the Estuary of Huelva. In addition to the other pollution sources of the study area, the highly acidic nature of these wastewaters, combined with their elevated dissolved concentrations of trace elements, contribute significantly to the total contamination of the Estuary of Huelva and subsequently of the Atlantic Ocean. The phosphogypsum stack is responsible for important amounts of contaminants reaching the Huelva Estuary, i.e. 42 ton/y of Fe, 12 ton/y of Zn, 6.9 ton/y of As, 1.6 ton/y of Cd, among others (Pérez-López et al., 2016), while the respective concentrations discharging to the estuary from IPB mining districts through Tinto and Odiel River basins were estimated to be 7922 ton/y of Fe, 3475 ton/y of Zn, 36 ton/y of As, and 11 ton/y of Cu (Olías et al., 2006). Accordingly, the phosphogypsum stack releases up to 16% of As and 13% of Cd of the total content reaching the estuary. The extent of phosphogypsum-related contamination is especially significant taking into account the small area covered by the stack (12 km^2) in comparison to both fluvial basins (3979 km^2). Moreover, the stack releases additional contaminants, e.g. phosphate, fluoride and uranium (Pérez-López et al., 2016), whose concentration ranges and geochemical behaviours have been highlighted in the current study. As such, this study reports that most of the released contaminants (i.e. Co, Ni, Cu, Zn, As, Cd and Sb) do not undergo a significant depletion in phosphogypsum leachates in spite of their mixing with more alkaline waters. These findings emphasise the necessity of adopting efficient restoration plans in order to manage successfully the phosphogypsum contamination at the Estuary of Huelva, and, more importantly, prevent these wastewaters from reaching the estuary.

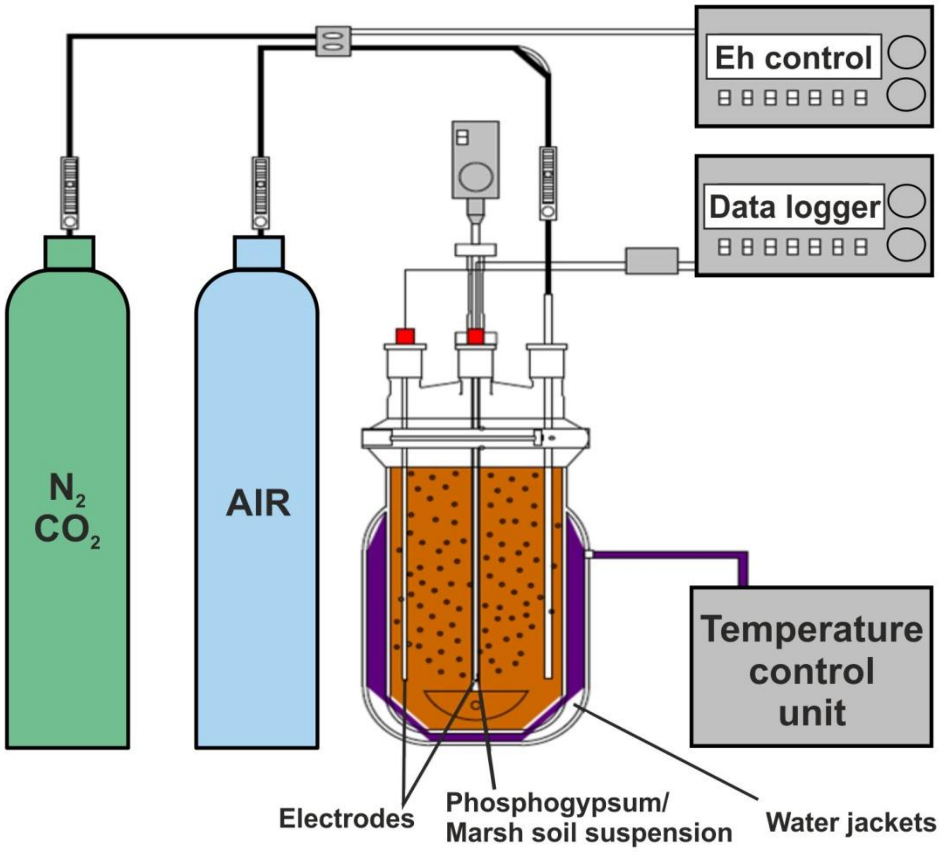
4.4. Conclusions

The acidic and contaminant-rich leachates from a phosphogypsum stack discharge, up to day, directly into the Estuary of Huelva (SW Spain) and undergo seawater mixing. Seawater mixing experiments were carried out in this study using three types of phosphogypsum leachates. Owing to mixing with the alkaline oceanic waters, different geochemical processes alter the concentrations and influence the mobility of the meta(loid)s contained in the leachates. The current research reports on two main conclusions through experimental and theoretical simulations of mixing of phosphogypsum wastewaters with seawater: a) the high acidity of the leachates hinders the rise of the pH requiring enormous amounts of seawater compared to the wastewaters in order to achieve circumneutral pH values, and b) most of the toxic contaminants including Co, Ni, Cu, Zn, As, Cd and Sb behave conservatively, whereas Fe, Al, Cr, Pb and U decrease significantly with increasing pH and participate in precipitation/sorption processes. According to the results of this study, the behavior of the contaminants during the mixing experiments was similar among the different types of phosphogypsum leachates, suggesting that the origin of wastewater (edge outflows vs. process water) or the restoration actions (unrestored zone 3 vs. supposedly-restored zone 4) did not control their mobility.

Our findings have provided important insight into the problematic of the phosphogypsum waste worldwide and, more importantly, into the pollution of the Estuary of Huelva by phosphogypsum contaminants. The toxic elements that remain mobile after reaching the estuary, finally end up to the Atlantic Ocean contributing significantly to the total metal loads and threatening the environmental conditions of the littoral. It is, therefore, urgent to adopt effective restoration measures to minimise the impact of the studied phosphogypsum leachates on the estuarine environment and subsequently on the Atlantic Ocean, as well as of other phosphogypsum areas worldwide especially in coastal regions.

CHAPTER 5

Effects of redox oscillations on the phosphogypsum waste and the salt marsh soil



5. Effects of redox oscillations on the phosphogypsum waste and the salt marsh soil

5.1 Introduction

Significant pollution sources including metal mining, industrial activity and waste disposal have lead to extensive contamination of environmental systems, such as marsh soils (e.g. Vega et al., 2008; 2009). Such systems can act as important sinks for great loads of contaminants, both organic and inorganic, that are transferred through the estuarine water and the suspended sediments affected by tidal variations (Andrade et al., 2002; 2004; Vega et al., 2008).

The biogeochemical cycling and the behaviour of elements on such ecosystems worldwide depend, among others, on redox reactions. Redox processes play a key role in many environmental systems as they control the mobility, the chemical speciation and the toxicity of major and trace elements (e.g. Fe, Mn, C, P, N, S, Cr, Cu, Co, As and U), as well as the formation and/or dissolution of the solid phases (Borch et al., 2010; Frohne et al., 2011). Redox oscillations in the oxic-anoxic interface are frequent in estuarine salt-marsh systems due to changes at the water table levels (Ann et al., 2000; Du Laing et al., 2009). Oxidation produces protons and thus, pH is decreased, while the opposite happens during reduction (Yu et al., 2007), which means that pH and Eh have reversed behaviour during redox processes. Hence, the frequent Eh changes that occur in salt marsh soils due to oscillation of the water table, lead to subsequent pH alterations (Frohne et al., 2011), which also is a defining factor for elemental behaviour.

Contaminants could also be released from the redox-dynamic marsh soil systems depending on the hydraulic regime (Ann et al., 2000). During dry periods, the top soil of near-surface systems is subjected to oxic conditions, but under water saturation anaerobic conditions prevail as the oxygen diffusion from the atmosphere is decreased and the remaining is consumed by aerobic bacteria that develop due to the mineralisation of organic material (Couture et al., 2015). Hence, microbial processes affect the mobility and speciation of redox-sensitive elements and the solubility/dissolution of mineral phases (Watts et al., 2013). Some non-redox active elements could also participate indirectly in redox processes related to transformations of natural organic matter and mineral phases such as Fe and Mn (hydr)oxides (Borch et al., 2010). The importance of understanding redox processes, especially in environmental systems with potential contamination, lies in the opportunities for remediation strategies -e.g. based on microbial degradation or reductive sequestrations- and thus, in the promotion of the environmental welfare (Polizzotto et al., 2008; Wu et al., 2006).

Phosphogypsum wastes deposited on coastal areas represent, usually, a case of the aforementioned redox-dynamic estuarine salt-marsh systems. Redox potential affects the stability or leaching of phosphogypsum-related contaminants by controlling the oxidation states of many compounds associated with the waste and thus, affecting their mobility (Papanicolaou et al., 2010). Large disposal phosphogypsum stacks could exhibit different redox gradients with depth as the upper unsaturated zones are likely to be subjected to oxidizing conditions, whereas saturated deeper zones are expected to show anaerobic conditions (Lottermoser, 2007).

5.2 Additional considerations about the study area

One interesting case of redox-dynamic system is the phosphogypsum disposal area located in Huelva (Spain) that is directly stack-piled over the salt marsh soil of Tinto River estuary without any impermeable barrier. The stacks are located within the tidal prism of the Huelva Estuary, which has a great influence on the weathering model of the phosphogypsum wastes by means of estuarine water (see Chapter 3). The direct contact of the phosphogypsum stack with the basement of organic matter-rich marsh sediments implies weathering under reducing conditions. In deep zones with stagnant and non-renewable waters, anaerobic conditions are imposed by organic matter decomposition associated with microbial activity of sulphate-reducing bacteria (SRB), resulting in aqueous reduction of sulphate from phosphogypsum to sulphide. This process leads to the restriction of metal mobility due to their precipitation as metal sulphides (Pérez-López et al., 2011; 2018). However, partial oxidation of these sulphides in the marsh contact also occurs due to the hydrological connection between the stack and the estuary by saline intrusion (Pérez-López et al., 2018). Therefore, phosphogypsum can be subjected to weathering under reduction-oxidation cycles likely controlled by tidal variations.

Additionally, the Huelva phosphogypsum is also affected by redox processes because of a complex soil cover applied in two disposal modules -out of the four in which the stack is divided. This cover, which was implemented as restoration measure, includes a vegetation layer rich in organic matter that also has the potential to act as carbon source for enhancing the activity of naturally-occurring SRB in the phosphogypsum (Castillo et al., 2012). Even low levels of organic material could be sufficient for aqueous oxygen depletion and thus, establishment of anaerobic conditions, as oxygen solubility in water is low (Pérez-López et al., 2011).

The full awareness of the redox processes occurring in a redox-dynamic phosphogypsum stack, which is the aim of the current study, will provide important insights into an effective remediation in order to promote the attenuation of the contaminants to the environment. As such, this study evaluates the mobility of some contaminants related to the phosphogypsum waste and its marsh basement separately, under controlled conditions during experimentally induced redox oscillations.

5.3 Materials and methods

5.3.1 Preparation of suspensions

Solid samples were collected for the redox oscillations experiment including: (i) phosphogypsum at 5 m depth (zone 3), where the availability of metals in the pore water is higher (Pérez-López et al., 2018), and (ii) salt marsh soil at 8 m depth (zone 3), which could serve as source of organic C due to the high organic matter content and as inoculum of SRB.

Two kinds of soil suspensions were used for the purpose of the experiments, one with phosphogypsum and another with salt marsh soil with a 1:10 soil:water ratio. The suspensions were prepared by equilibrating in anoxic conditions 100 g of the respective sample with 1 L of synthetic degassed pore water for 1 week prior to the experiments. Each synthetic water was prepared by mimicking the solution composition of the phosphogypsum in depth for the one bioreactor and the salt marsh soil for the other. They were enriched with an aliquot of some metal salts (iron chloride, sodium arsenate, cadmium chloride, zinc sulphate, disodium hydrogen phosphate, calcium chloride, sodium chloride, sodium sulphate) and Inductively Coupled Plasma-Mass Spectrometry solution of U in order to simulate the natural waters (pore water) occurring with the soil samples (phosphogypsum and marsh soil) (**Table 5.1**).

Table 5.1. Compounds (salts and ICP-MS solution) added in the phosphogypsum and marsh sediment suspensions prior to the experiments.

Compound added in the suspensions	**Amount**
Salt	**g/L**
$FeCl_2*4H_2O$	0.38
$ZnSO_4*7H_2O$	0.07
$Na_2HAsO_4*7H_2O$	0.008
$CdCl_2$	0.003
$CaCl_2*2H_2O$	4.21
NaCl	23.6
HNa_2O_4P	7.21
Na_2SO_4	5.82
Solution	**mL**
ICP solution (100 mL) of 1000 ppm U	0.381

5.3.2 Experimental set-up and sample treatment

The experiment was performed using a custom two part Pyrex® glass redox stat bioreactor system designed by Thompson et al. (2006) and modified later by Parsons et al. (2013) **(Fig. 5.1)**. The lower part of the reactor (Ace-Glass Inc, NJ, USA) contained a working volume of 1 L including the use of a water jacket to allow precise temperature control. Ethylene glycol was added to the temperature regulating circuit to avoid fungal and bacterial growth. The upper part of the reactor contained a headspace volume of approximately 300 mL and used ace-glass threaded connections for sampling, electrodes and mechanical agitation (seals secure up to 2.4 bar of internal/external pressure difference). Two water baths were connected to the system; one to maintain the temperature at 25±1 °C inside the reactors and another at 5 °C to keep cool the distillations columns. The agitation shaft and blades were Teflon coated in order to avoid any metal contamination and prior to the introduction of soil suspensions, the reactor and all glass and plastic parts were washed with 5% HNO_3.

The suspensions were pre-equilibrated inside a glove box prior to their introduction in the reactors and then, they were subjected to six 7-day cycles of reduction and oxidation alternately. To achieve redox potential (Eh) variation, the sparging gas was modulated between N_2:CO_2 (392 ppmv) for 7 days and compressed air O_2:N_2:CO_2 for another 7 days under constant pCO_2 ($10^{-3.5}$ atm) and temperature (25 ±1 °C), via the Agilent switching unit, a relay board and a system of solenoid valves. Gas flow was adjusted at 30 mL/min using the flow meter connected to the bioreactors. Samples were then centrifuged at 4000 rpm, filtered using a 0.45 μm nylon membrane and stored until analysis. Those taken during anoxic cycles were introduced to a N_2-filled anaerobic chamber ($O_{2(g)}$ < 1 μL/L) for the treatment to avoid oxidation. Reactors were covered with foil during the experiments to prevent the formation of hydrogen peroxide and photo-degradation of the contaminants.

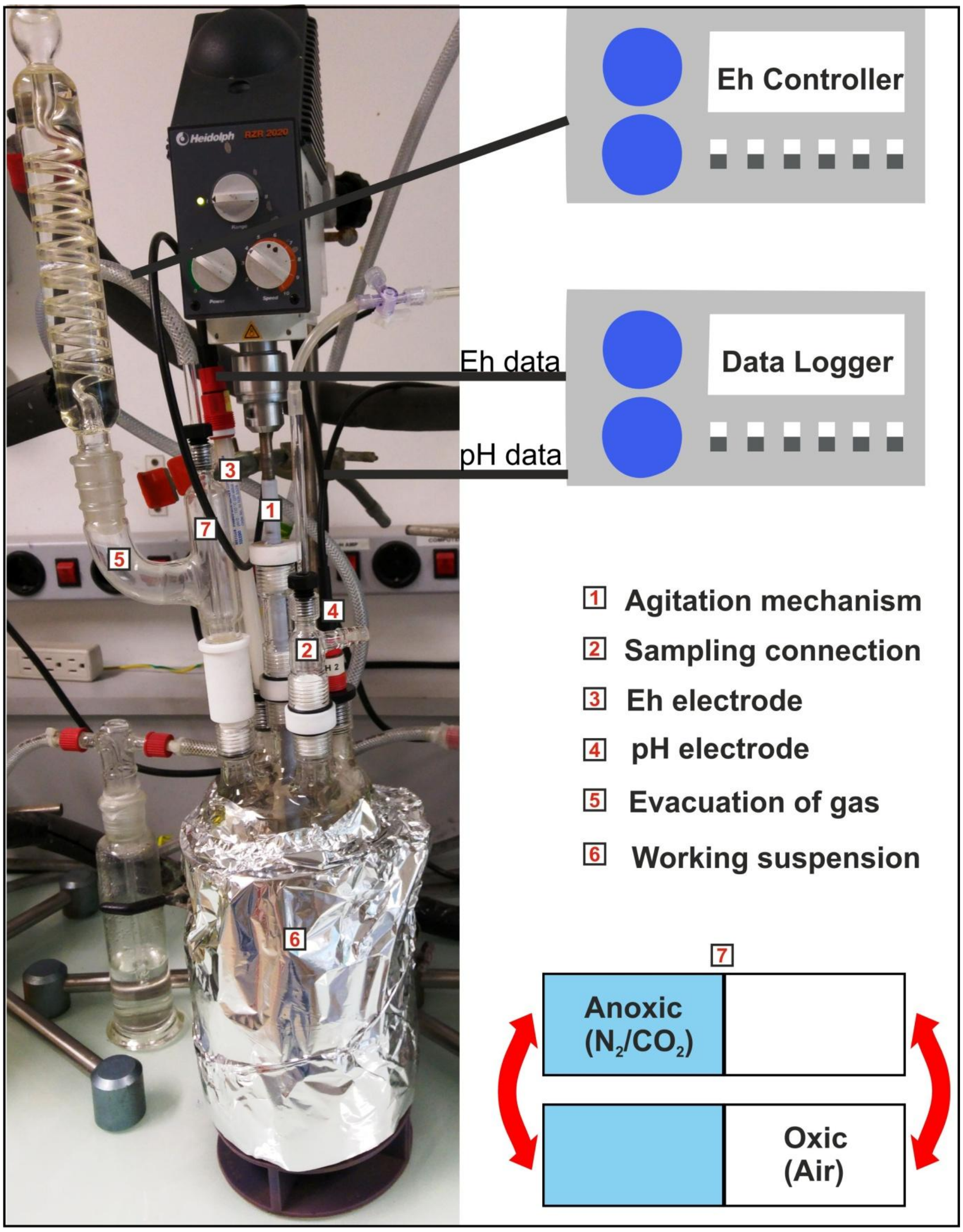


Figure 5.1: Arrangement of the bioreactor used for the redox experiments.

During the experiment the bacteria present in the suspension consume the existing organic matter and produce carbon dioxide during both oxic and anoxic cycles (via aerobic respiration during the oxidising cycles and by using alternative electron acceptors such as nitrate and ferric iron during reducing cycles). During subsequent oxidising half cycles, Dissolved Organic Carbon (DOC) is consumed by bacteria faster than it is replenished by hydrolysis, so its concentration decreases constantly (Parsons et al., 2013). Thus, cellobiose ($C_{12}H_{22}O_{11}$ – Sigma-Aldrich) with 8.33 mmol/L final concentration of total DOC was added in the suspensions at the start of every reducing cycle in order to replace the labile organic matter that is needed to stimulate the bacteria and therefore avoid the depletion of the electron donor.

5.3.3 Eh-pH measurements

Continuous monitoring (every 30 min) of the Eh and pH was conducted during the 6-weeks experiments using electrodes inserted in the suspensions **(Fig. 5.1)**. Solid polymer open junction pH and Eh electrodes (Mettler-Toledo Xerolyt, France), which were selected for their long-term stability and low electrolyte leak rates, were placed inside the reactors through the corresponding connections. The electrode signals were connected to field-effect transistor (FET) instrumentation amplifiers with high input impedance. The signal was then passed to an Agilent acquisition/switching unit (34970a) connected to a PC running Agilent BenchLink Data Logger 3 software. The calculations of the real values of Eh were performed according to the user manual of the gel filled Redox probes used (Hach company). In detail, Eh readings are reported relative to the standard hydrogen electrode (SHE), also called normal hydrogen electrode (NHE), and measured data were corrected using the calculation:

Eh = E + Eref, where:

Eh = oxidation reduction potential of the sample relative to the SHE

E = potential developed by the ORP/Redox electrode

Eref = potential developed by the reference electrode portion relative to the SHE according to the temperature of the solution (+207mV at 25°C).

A three-point calibration (pH 4, 7 and 10) was performed for the pH electrodes at the start and end of the experiments showing that electrode response had not shifted importantly. Real values were calculated based on the calibration of the electrodes performed prior to the experiments.

5.3.4 Analytical methods

5.3.4.1 Aqueous elemental analysis

Major element (Ca, K, Mg and Na) concentrations were obtained via Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) by a Jobin Yvon Ultima 2 instrument at the University of Huelva (Spain). Concentrations of anions (F^-, Cl^-, Br^-, SO_4^{2-}, PO_4^{3-}) and ammonia were also analysed at the University of Huelva by a high performance liquid chromatography system (HPLC) using a Metrohm 883 basic ion chromatograph (IC) equipped with Metrosep columns. Aluminum, Fe, Mn and trace elements (Cr, Co, Ni, Cu, Zn, As, Cd, Sb, Pb, and U) were determined by ICP-MS by an Agilent 8800 Triple quadrupole device at the Andalusian Institute of Earth Sciences (IACT) in Granada (Spain). A detailed description of all the aforementioned analytical techniques can be found at Chapter 3 (section 3.3.2.1). For arsenic speciation, 2 mL samples of filtered aqueous phase were diluted with 7.8 mL of 18.2MQ water and were added to a mixture of acetic acid and EDTA (Leblanc et al., 2004). Determination of inorganic arsenite (As^{3+}) and arsenate (As^{5+}) was conducted at the University of Montpellier (France) (AETE-ISO platform, OSU-OREME/Université de Montpellier) using coupling LC (Thermo Scientific, SpectraSystem P4000) with ICP-MS with the internal standard Ge (Thermo Scientific, XSeries 2) according to the method described by Bohari et al. (2001). The LC system consisted of Varian ProStar gradient solvent delivery system equipped with a 100 µL injection loop (Interchim). An anion-exchange column (Hamilton, PRP-X100) and an 80 eluent 30 mM $(NH_4)_2HPO_4/NH_4H_2PO_4$ (pH = 8.1) was conducted at a flow rate of 1 mL/min. The detection limit was 0.09 µg/L for As^{3+} and 0.41 µg/L for As^{5+}, with a precision better than 5%.

Both sulphide and ferrous iron analyses in solution were conducted at the Institute of Earth Sciences (ISTerre) in Grenoble (France). The "methylene blue method" previously described by Cline (1969) and also, published by Parsons et al. (1984) was applied for sulphide determination. An amount of 2 mL of filtered supernatant of every sample was collected for S^{2-} analysis in which 0.25 mL of zinc acetate (5%) was added. Standard stock Na_2S was used for the preparation of the standard solutions in order to build the calibration curve and to treat the results. Prior to analysis 80 μL of the reagent "Cline" were added to the solution formed by the sample and the zinc acetate, already transferred in cells of 1 cm wide, so that the reagent reacts with the sulphide and forms a blue complex. To measure the reduction of ferric to ferrous iron over time during the redox oscillations performed, a modification of the ferrozine assay was used according to Viollier et al. (2000). The ferrozine compound (monosodium salt hydrate of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p'-disulfonic acid) is used as a reagent, because when it complexes with ferrous iron its visible absorption spectrum displays a strong peak at 562 nm. To obtain mobilised Fe^{2+} concentration in solution we added 50 μL of sample to 2.45 mL ferrozine solution in a cuvette. Standard stock solution was prepared using $FeCl_2*4H_2O$ and standards of different concentrations were prepared via serial dilutions using HCl in order to mobilise Fe^{2+}. Samples and standards were measured immediately after preparation via UV-Vis spectroscopy (Lamda 35, Perkin Elmer) at 664 nm and 562 nm absorbance for sulphide and iron, respectively.

5.3.4.2 Adenosine tri-phosphate

The adenosine tri-phosphate (ATP) test is a process of rapidly measuring actively growing microorganisms through detection of ATP. The ATP is a molecule found in and around living cells, and as such it gives a direct measure of biological concentration (Karl, 1980). It is quantified by measuring the light produced through its reaction with the naturally occurring firefly enzyme luciferase using a luminometer. The amount of light produced is directly proportional to the amount of ATP present in the sample. An ATP reagent is necessary for the measurement in order to destroy the microbial cell, to release intracellular ATP into the sample and to bind ATP to make it detectable by luminescence. A luminometer measures the luminescence intensity, which can be correlated to ATP concentration by doing calibration with standards of known composition.

For the purposes of the present study, the ATP concentrations were determined by measuring luminescence levels in relative light units (RLU) using the BacTiter-Glo Microbial Cell Viability Assay Kit (G8233; Promega Corporation, Dübendorf), following an optimized protocol based on the method of Hammes at al. (2010). Measurements were performed via Lumar LB 9507 luminometer (Berthold Technologies, Bad Wildbad, Germany) at the Institute of Geosciences of the Environment (LTHE), Grenoble (France). The detection limit of the luminescence-based ATP protocol that was used is 0.0001 nM with a standard deviation of <5%. The ATP reagent was prepared by mixing the BacTiter-Glo™ Buffer with the BacTiter-Glo™ Substrate and was equilibrated at room temperature for at least 15 minutes before use. 100 µL of the reagent were added to 100 µL of slurry sample placed in glass tubes (ratio 1:1). Each sample was prepared and measured in triplicates after 5 minutes sharply. The intensity measured was correlated to ATP concentration using an ATP standard (BioThema Luminescent Assays, 45-051 ATP Standard 10 µM 5 mL, Sweden) for calibration.

5.3.4.3 Dissolved Organic Carbon

Filtered supernatants of 1 mL were placed into glass tubes while being diluted with 15 mL of 18.2 MQ water and preserved by adding 32 µL HCl (32%). All glassware was previously heated at 400 °C for 3 hours avoiding DOC contamination. DOC measurement was conducted by Shimadzu VCSN analyser (TOC-5000A, Shimadzu, France) at the Institute of Earth Sciences (ISTerre) in Grenoble (France), via the direct NPOC (Non-purgeable Organic Carbon) method by pre-acidifying and pre-purging the sample to remove the Total Inorganic Carbon (TIC) and Purgeable Organic Carbon (POC), respectively. POC was partly removed from the sample by gas stripping, while the sample was acidified within pH 2 and 3 by adding a small portion of acid (HCl) and then TIC was removed from the acidified sample by purging with a purified gas. Thus, DOC was determined directly by means of Total Carbon (TC) measuring method as TC equal Total Organic Carbon. The detection limit was 0.3 mg/L and the precision was better than 2.5%.

5.3.5 Geochemical modelling

Geochemical calculations were performed for all the solutions, which were collected during the redox oscillations experiments, by the PHREEQC-2 code (Parkhurst and Appelo, 2005) using the Minteq.v4 database (Allison et al., 1991), allowing evaluation of the contaminants behaviour, along with the geochemical processes occurring during redox oscillations. More details are given in Chapter 4 in section 4.2.4.

5.3.6 Solid phase analysis

Solid phase analysis was performed on the dried slurry collected during the redox experiments. The solid phases were analysed by a Field-Emission Scanning

Electron Microscope with an AURIGA system (FESEM; ZEIS SMT), an Environmental SEM (ESEM; FEI, QEMSCAN 650F) and Scanning Electron Microscope of Variable Pressure (VPSEM; ZEIS SUPRA^{TM} 40VP), all equipped with backscattered and secondary electron detectors coupled with Energy Dispersive x-ray Spectrometer (EDS), at the Instrumentation Centre (CIC) of the University of Granada, Spain.

5.4 Results

5.4.1 Eh and pH

The redox potential of the suspensions subjected to redox oscillations was relatively high, with Eh values ranging between 170 and 560 mV at the phosphogypsum and between 265 and 772 mV at the marsh soil **(Table 5.2)**. Both suspensions followed similar trend and as expected, Eh decreased during the anoxic cycles and increased after the provision of oxygen. However, the Eh cycle was non-repeatable, but increased with time, which means that every full cycle (2 weeks) presented higher Eh values than the previous one **(Fig. 5.2A)**. As such, oxic regeneration rose after the completion of a full cycle.

Generally, oxidation processes produce protons and consequently decrease pH, while the opposite processes prevail during reduction (Yu et al., 2007). Thus, a negative correlation would be expected between pH and Eh in our case as well. Nevertheless, this trend was followed only in the first full cycle (first two weeks), while a slight positive correlation was observed throughout the following weeks in both reactor systems with insignificant oscillations. In detail, pH range was very small, from 4.59 to 4.69 and from 3.16 to 3.51 in the phosphogypsum and the marsh soil suspensions, respectively **(Table 5.2)**. The only important changes in pH included an abrupt decrease at the marsh soil at the beginning of the experiment (less obvious in phosphogypsum), a rise in both systems at the first day of the second oxic cycle, and an increase in phosphogypsum whereas a decrease in the marsh soil at the beginning of the last oxic cycle **(Fig. 5.2B)**. Apart from those fluctuations, the two systems managed to keep the pH conditions constant until the completion of the experiment and were not greatly affected by the redox oscillations, while the higher pH in the phosphogypsum experiment (>4.5) compared to the marsh soil (<3.5) should be highlighted.

The weak positive correlation between Eh and pH in our experiment was also described in similar studies on other redox sensitive systems (Antić-Mladenović et al., 2010; Frohne et al., 2014).. The dynamics of pH might be affected by other factors during redox oscillations, e.g. the presence of microorganisms and organic matter (Husson, 2013; Wang et al., 2013). The pH in the present experiment could have been affected by those factors and as such, display distinct behaviour than the expected.

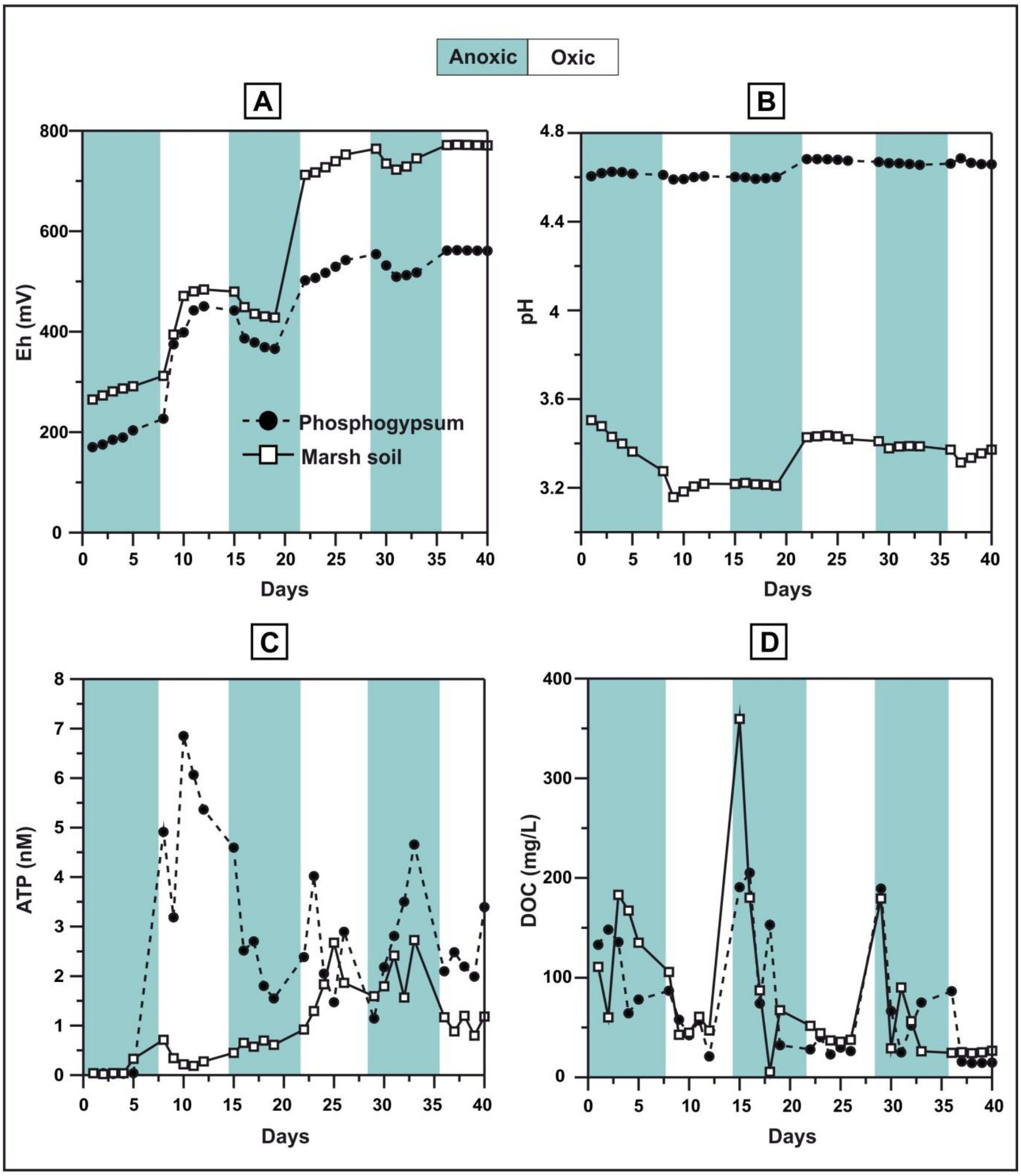


Figure 5.2: Physicochemical parameters (**A**-Eh, **B**-pH), microbial activity (**C**-ATP) and organic matter (**D**-DOC) of the two experiments during redox oscillations.

5.4.2 ATP levels as tracers of the microbial activity

At the first two full cycles of the phosphogypsum experiment, ATP concentration was lower during the anoxic conditions and higher during the oxic cycles due to the presence of aerobic bacteria **(Fig. 5.2C)**. On the other hand, the microbial inactiveness in the marsh soil suspension was highlighted during that period (both oxic and anoxic cycles) **(Fig. 5.2C)**, especially when compared to the phosphogypsum matrix. This behaviour was expected due to the strong anoxic environment that exists naturally in the marsh soil because of the high content in decomposing organic matter, which probably does not favour the aerobic bacteria growth. Nevertheless, ATP concentration slightly increased during the second oxic cycle in the marsh soil, but decreased at the end of it indicating a short growth of aerobic organisms. The pattern of the microbial activity changed at the last full cycle in both experiments displaying lower activity during oxic conditions and higher during anoxic, indicating that the bacterial community was appreciably active at the depletion of oxygen possibly due to the development of anaerobic bacteria, i.e. SRB. This is very common in the marsh soils, where SRB occur naturally resulting in sulphate reduction processes, but the results highlighted that phosphogypsum could also be an inoculum of SRB, as already described by Castillo et al. (2012).

5.4.3 DOC consumption

Both suspensions subjected to redox oscillations followed similar trend with respect to DOC; phosphogypsum samples presented slightly lower values (from 14.4 mg/L to 205 mg/L) than those corresponding to the marsh soil (from 5.60 to 360 mg/L) **(Table 5.2)**. After the addition of the cellobiose at the onset of every anoxic cycle, the DOC amount decreased until reaching the lowest levels at the following oxic cycle, while at the phosphogypsum experiment it was preserved for more days compared to the marsh soil **(Fig. 5.2D)**. The DOC was generally at higher levels during reduction and decreased during the oxic cycles due to respiration and oxidation of Fe^{2+}, S and As (Van Phan et al., 2018) **(Fig. 5.2D)**. The correlations between DOC with Eh and pH were not significant, a case also described by Frohne et al. (2011).

5.4.4 Sulphur release and iron cycling

The total amount of S in solution presented weak correlation with the Eh in both suspensions, as significant and consistent differences between oxic and anoxic conditions were not found in our study. Despite following similar pattern, S concentrations presented higher values in the phosphogypsum compared to the marsh soil **(Table 5.2; Fig. 5.3A and B)**. On the other hand, abrupt decreases of aqueous S^{2-} concentration in the phosphogypsum experiment occurred at the beginning of the anoxic half cycles, but the amount was recovered the following day (**Figure 5.3A)**. With respect to the marsh soil experiment, the variations of sulphide were less evident **(Fig. 5.3B)**.

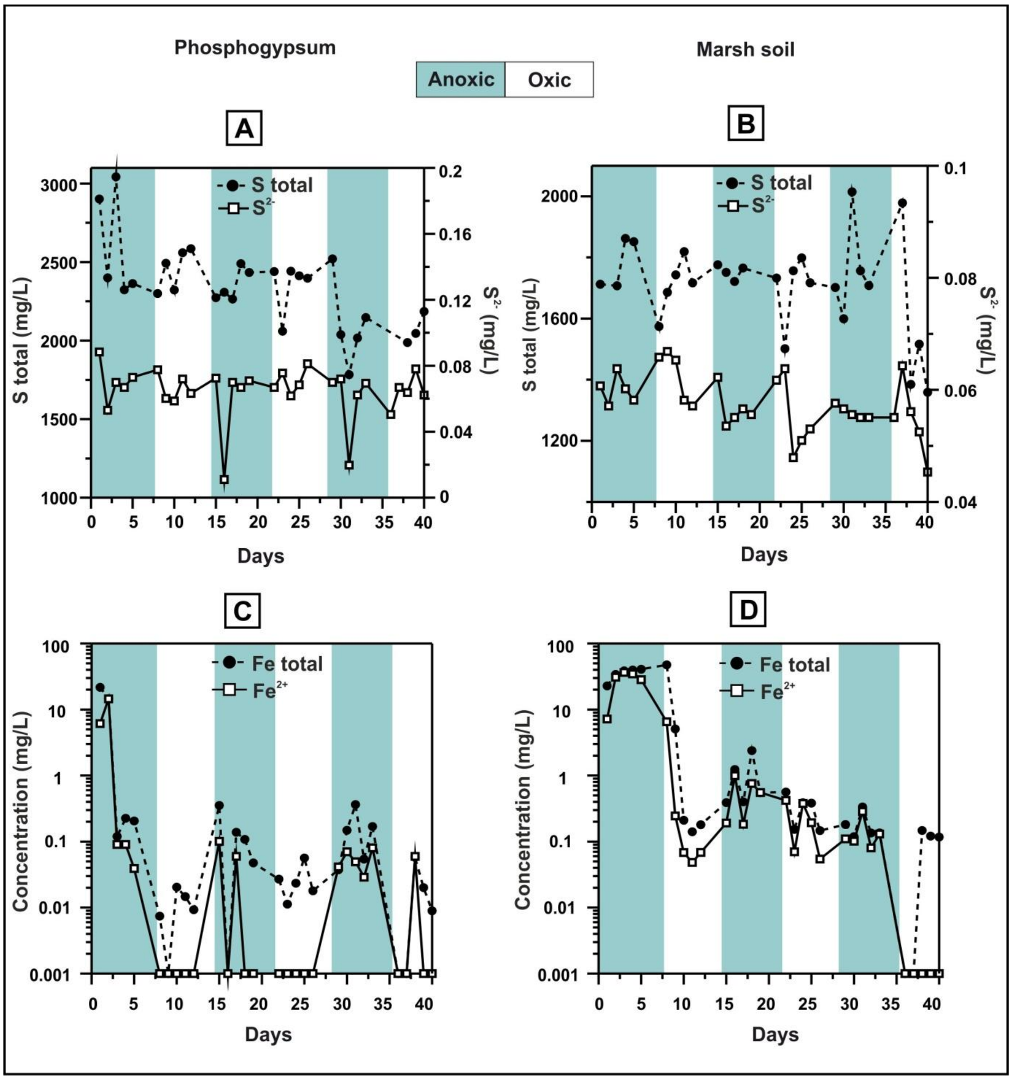


Figure 5.3: Concentrations of sulphur (total and S^{2-}) and iron (total and Fe^{2+} in log scale) during redox oscillations; **(A)** S in phosphogypsum, **(B)** S in marsh soil, **(C)** Fe in phosphogypsum, and **(D)** Fe in marsh soil.

Iron amount in solution decreased dramatically soon after the first days of the experiment -already on the 3rd day in the phosphogypsum (from 14.6 to 0.12 mg/L) and at the beginning of the first oxic half cycle in the marsh soil (9th day from 47.5 to 5.07 mg/L) **(Table 5.2)**. These low values were preserved until the completion of the experiment for both suspensions, with slightly higher concentrations in the marsh soil **(Table 5.2; Fig. 5.3C and D)**. Cycling of redox conditions led to higher amounts of total Fe in solution during the anoxic cycles and lower during the oxic ones, especially in the phosphogypsum experiment **(Fig. 5.3C)**. A clear variation between oxic and anoxic conditions was observed in the phosphogypsum with respect to iron speciation as well. Ferrous iron increased during the anoxic half cycles, while it was almost depleted from solution at the oxic ones, as it was likely oxidised to Fe^{3+} and precipitated as new-formed phase explicating the decrease in total Fe, with only some exceptions (e.g. 38th day) **(Fig. 5.3C)**. On the other hand, total Fe and Fe^{2+} followed similar pattern in the marsh soil experiment under both oxic and anoxic conditions, a behaviour consistent with the fact that most of the Fe was present as Fe^{2+} rather than Fe^{3+} **(Table 5.2; Fig. 5.3D)**.

Table 5.2. Physicochemical parameters, biological activity (as ATP) and organic matter amount (DOC) of the phosphogypsum and marsh soil suspensions during redox oscillations. Greyish cells correspond to the anoxic and white to the oxic conditions. Elemental concentrations are given in mg/L.

Sample	Day	Eh (mV)	pH	ATP (nM)	DOC	S	S2-	Fe2+	Fe3+	F-	Cl-	P	Ca	K	Mg	Na
Phosphogypsum																
PG-01	1	170	4.60	0.04	133	2902	0.09	6.13	15.5	39.9	16745	719	1281	n.a.	39.6	15968
PG-02	2	175	4.62	0.04	148	2400	0.05	14.5	0.1	35.6	16737	461	867	32.2	23.9	9994
PG-03	3	185	4.62	0.02	136	3043	0.07	0.09	0.03	22.8	12731	572	1004	55.0	28.6	13064
PG-04	4	189	4.62	0.03	64.3	2324	0.07	0.09	0.13	20.6	11288	592	1043	61.0	30.6	13014
PG-05	5	203	4.62	0.04	78.1	2363	0.07	0.04	0.17	17.9	6065	590	975	67.5	28.6	12480
PG-06	8	227	4.61	4.91	86.8	2300	0.08	<LD	0.01	38.5	17032	622	1054	86.8	30.9	12888
PG-07	9	375	4.59	3.19	57.9	2492	0.06	<LD	<LD	11.0	13528	681	1479	96.8	31.2	12924
PG-08	10	399	4.59	6.85	42.2	2322	0.06	<LD	0.02	10.9	16417	632	1046	101	31.0	12844
PG-09	11	442	4.60	6.07	56.9	2560	0.07	<LD	0.01	11.0	15855	617	1017	100	29.8	12377
PG-10	12	450	4.60	5.36	21.0	2586	0.06	<LD	0.01	13.3	11157	652	1065	111	31.3	13108
PG-11	15	442	4.60	4.59	191	2273	0.07	0.10	0.25	8.66	16520	632	991	132	30.2	13276
PG-12	16	387	4.60	2.52	205	2308	0.01	<LD	<LD	10.0	16677	662	1094	4.91	31.9	12484
PG-13	17	379	4.59	2.70	74.2	2265	0.07	0.06	0.08	10.1	16916	661	1014	133	31.9	12822
PG-14	18	369	4.60	1.80	153	2490	0.07	<LD	0.11	10.5	16949	737	1168	166	34.4	13940
PG-15	19	366	4.60	1.55	32.3	2434	0.07	<LD	0.05	11.0	17030	676	1094	147	32.2	13277
PG-16	22	502	4.68	2.38	28.0	2440	0.07	<LD	0.03	16.3	17220	686	1096	168	30.6	13267
PG-17	23	507	4.68	4.02	40.3	2060	0.08	<LD	0.01	15.4	17052	602	978	142	28.0	11555
PG-18	24	517	4.68	2.05	23.0	2442	0.06	<LD	0.02	15.9	17226	719	1097	183	32.2	14239
PG-19	25	529	4.68	1.47	29.9	2413	0.07	<LD	0.06	15.8	17066	747	1099	190	33.7	13777
PG-20	26	542	4.68	2.90	26.4	2397	0.08	<LD	0.02	11.6	17070	699	1104	192	31.5	13294
PG-21	29	554	4.67	1.14	189	2521	0.07	0.04	<LD	17.4	16797	730	1164	196	33.6	13923
PG-22	30	532	4.66	2.18	66.5	2038	0.07	0.07	0.08	11.5	17652	612	950	178	27.9	11610

Table 5.2. Continued

Sample	Day	Eh (mV)	pH	ATP (nM)	DOC	S	S2-	Fe2+	Fe3+	F-	Cl-	P	Ca	K	Mg	Na
PG-23	31	509	4.66	2.81	25.1	1784	0.02	0.05	0.31	8.64	16914	646	979	266	60.5	11832
PG-24	32	512	4.66	3.50	51.9	2017	0.06	0.03	0.03	11.3	17088	580	913	210	31.5	11906
PG-25	33	518	4.66	4.66	75.0	2147	0.07	0.08	0.09	14.9	17081	619	960	229	33.4	12794
PG-26	36	562	4.66	2.10	86.4	n.a.	0.05	<LD	<LD	12.7	17558	n.a.	n.a.	n.a.	n.a.	n.a.
PG-27	37	562	4.69	2.48	15.8	n.a.	0.07	<LD	<LD	14.0	17318	n.a.	n.a.	n.a.	n.a.	n.a.
PG-28	38	562	4.67	2.19	14.4	1988	0.06	0.06	<LD	13.9	17239	574	906	226	32.4	11499
PG-29	39	561	4.66	1.99	14.6	2046	0.08	<LD	0.02	13.3	17354	617	927	202	27.7	11275
PG-30	40	561	4.66	3.39	14.9	2186	0.06	<LD	0.01	13.8	17392	660	985	223	31.1	11707
Marsh soil																
MS-01	1	265	3.51	0.04	111	1712	0.06	7.19	15.6	42.3	16672	833	1237	180	79.1	12533
MS-02	2	273	3.48	0.02	60.2	n.a.	0.06	30.8	3.20	39.1	9581	n.a.	n.a.	n.a.	n.a.	n.a.
MS-03	3	281	3.43	0.04	183	1707	0.06	36.4	2.13	51.1	17376	898	1324	222	85.6	12538
MS-04	4	287	3.40	0.04	167	1862	0.06	34.6	5.04	54.1	17546	1039	1444	239	95.7	13311
MS-05	5	291	3.36	0.33	135	1851	0.06	28.3	12.4	54.5	18149	1015	1443	246	88.5	12934
MS-06	8	312	3.28	0.71	106	1574	0.07	6.53	40.9	54.8	15749	695	1207	241	80.4	11593
MS-07	9	394	3.16	0.34	42.7	1686	0.07	0.24	4.83	55.3	15472	739	1092	221	69.5	11056
MS-08	10	471	3.18	0.22	44.8	1743	0.07	0.07	0.14	63.1	17836	905	1292	288	89.4	11921
MS-09	11	480	3.21	0.19	60.9	1819	0.06	0.05	0.09	63.1	17886	951	1367	288	87.7	13450
MS-10	12	484	3.22	0.28	47.0	1717	0.06	0.07	0.11	49.8	17718	846	1244	264	77.5	11640
MS-11	15	480	3.22	0.45	360	1776	0.06	0.19	0.20	54.0	17602	934	1363	301	86.3	12747
MS-12	16	449	3.22	0.65	180	1751	0.05	0.99	0.24	52.9	17837	911	1365	289	82.2	12113
MS-13	17	436	3.22	0.57	87.3	1721	0.06	0.18	0.22	55.2	17989	933	1327	297	85.6	12301
MS-14	18	430	3.21	0.70	5.60	1765	0.06	0.76	1.63	55.3	17887	922	1392	305	83.8	12462
MS-15	19	428	3.21	0.61	67.4	n.a.	0.06	0.55	<LD	51.3	18235	n.a.	n.a.	n.a.	n.a.	n.a.
MS-16	22	712	3.43	0.92	51.8	1732	0.06	0.42	0.14	60.9	18027	918	1325	317	84.6	12636
MS-17	23	717	3.43	1.29	44.2	1501	0.06	0.07	0.08	59.4	18053	798	1142	284	76.2	10967

Table 5.2. Continued

Sample	Day	Eh (mV)	pH	ATP (nM)	DOC	S	S2-	Fe2+	Fe3+	F-	Cl-	P	Ca	K	Mg	Na
MS-18	24	727	3.44	1.84	37.0	1756	0.05	0.38	0.01	59.8	18046	932	1369	317	84.9	12540
MS-19	25	739	3.43	2.68	35.7	1799	0.05	0.19	0.19	61.1	18073	956	1335	351	87.2	12598
MS-20	26	752	3.42	1.86	37.6	1717	0.05	0.05	0.09	57.4	18386	883	1287	332	84.0	12381
MS-21	29	764	3.41	1.59	179	1702	0.06	0.11	0.07	57.7	18065	920	1295	320	84.8	12475
MS-22	30	735	3.38	1.79	29.2	1599	0.06	0.10	0.02	60.8	18024	852	1236	296	76.5	11442
MS-23	31	723	3.39	2.41	90.1	2015	0.06	0.29	0.05	60.2	19884	790	1157	262	56.1	12664
MS-24	32	729	3.39	1.57	56.4	1756	0.06	0.08	0.05	56.3	18202	877	1314	320	84.4	12177
MS-25	33	745	3.39	2.73	26.2	1708	0.06	0.13	<LD	59.2	18413	906	1336	350	87.9	12501
MS-26	36	772	3.37	1.17	24.6	n.a.	0.06	<LD	<LD	60.1	18394	n.a.	n.a.	n.a.	n.a.	n.a.
MS-27	37	772	3.31	0.88	25.3	1978	0.06	<LD	<LD	61.3	18474	902	1599	356	87.8	12054
MS-28	38	772	3.34	1.20	24.3	1385	0.06	<LD	0.15	59.8	18461	697	1058	324	83.9	10594
MS-29	39	771	3.36	0.80	25.2	1516	0.05	<LD	0.12	39.4	18951	761	1128	358	87.9	10919
MS-30	40	771	3.37	1.18	26.6	1359	0.05	<LD	0.12	60.9	18498	707	1068	333	81.7	11321

n.a. = not analysed; LD = limit of detection

5.4.5 Mobility of trace elements

The mobility of the trace elements during redox oscillations was slightly different between the phosphogypsum and the marsh soil experiments. Zinc and As displayed similar behaviour during the redox oscillations in each suspension separately, although Zn was present at higher levels, especially in the marsh soil. The range of elemental concentrations was small indicating a slight conservative behaviour during the cycles with no consistent alternations between oxic and anoxic conditions; e.g. As fluctuated between approx. 2 - 3.5 and 6 - 8.5 mg/L, in phosphogypsum and salt marshes, respectively **(Table 5.3)**. Exception to that range in phosphogypsum was the concentrations at the onset of the experiment and an occasional abrupt rise at the last anoxic half-cycle (at the 31st day) that did not last for more than 24 h **(Fig. 5.4A)**; this increase matches the decrease of total S and S^{2-} in solution and the increase of the ATP, probably related to the activity of the SRBs (see Discussion section). On the other hand, Zn and As concentrations decreased approx. 30% in the marsh soil on the 31st day, a behaviour coinciding with the increase of total S **(Fig. 5.4B)**. Concerning As speciation, the results indicated that most of the total amount was present as As^{5+}, while As^{3+} was present at minimal concentrations.

The behaviour of Cd and U was similar to that of Zn and As in both the phosphogypsum and the marsh soil, separately. On the one hand, their behaviour was more conservative in phosphogypsum remaining at quite low concentrations (up to 0.015 mg/L) with only one increasing shift on the 31st day **(Table 5.3; Fig. 5.4C)**. On the other hand, Cd and U concentrations in the marsh soil changed frequently during the experiment, and especially, the mobility of U presented numerous fluctuations (approx. 0.01 to 0.2 mg/L), although with no consistent changes between anoxic and oxic conditions **(Table 5.3; Fig. 5.4D)**. Nevertheless, Cd and U amounts in solution decreased on day 31 (anoxic conditions), a behaviour in correlation with that of other trace elements.

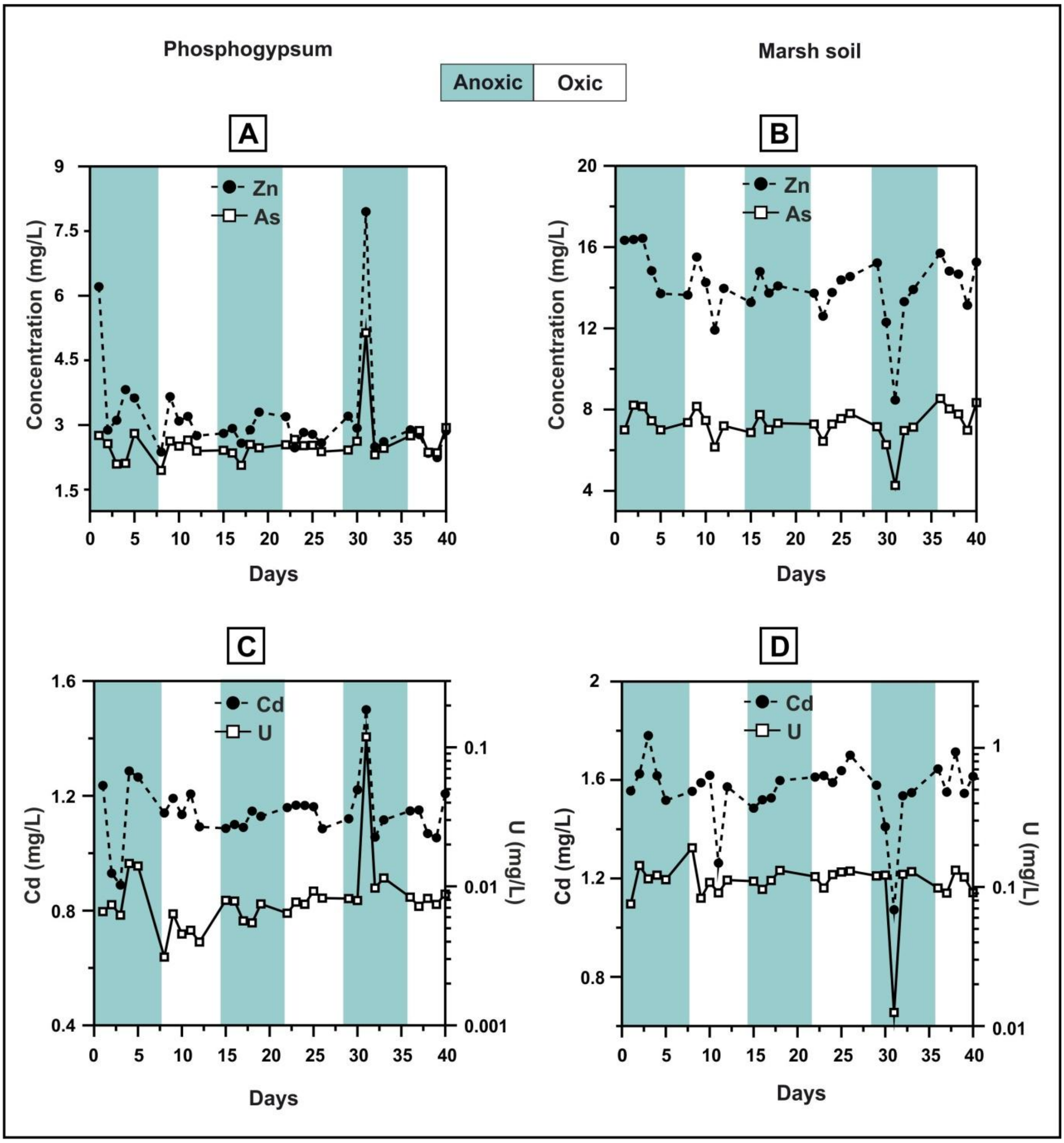


Figure 5.4: Concentrations of trace elements during redox oscillations in the phosphogypsum **(A** and **C)**, and in the marsh soil **(B** and **D)**. Uranium is presented in log scale to show more clearly its trend, due to the quite low values.

Table 5.3. Total elemental concentrations (in mg/L) in the phosphogypsum and the marsh soil suspensions during redox oscillations. Greyish cells correspond to the anoxic and white to the oxic conditions.

Sample	Day	Al	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Sb	Pb	U
Phosphogypsum													
PG-01	1	1.38	0.04	0.26	0.03	0.16	2.10	6.21	2.76	1.24	0.04	0.002	0.007
PG-02	2	0.17	<LQ	0.20	0.02	0.16	0.42	2.88	2.57	0.93	0.04	<LD	0.007
PG-03	3	0.31	0.01	0.16	0.02	0.12	0.26	3.11	2.09	0.89	0.02	0.001	0.006
PG-04	4	0.22	0.01	0.25	0.03	0.18	0.43	3.82	2.11	1.29	0.03	0.003	0.015
PG-05	5	0.01	<LD	<LD	<LD	<LD	<LD	3.63	2.80	1.27	<LD	<LD	0.014
PG-06	8	0.05	0.00	0.15	0.02	0.11	0.26	2.37	1.95	1.14	0.03	0.000	0.003
PG-07	9	0.27	<LQ	0.19	0.02	0.16	0.45	3.66	2.63	1.19	0.04	0.009	0.006
PG-08	10	0.09	0.00	0.20	0.02	0.14	0.35	3.09	2.51	1.13	0.03	0.001	0.005
PG-09	11	0.11	<LD	0.20	0.02	0.15	0.34	3.20	2.65	1.21	0.04	0.001	0.005
PG-10	12	0.06	<LD	0.18	0.02	0.13	0.27	2.75	2.40	1.09	0.03	0.000	0.004
PG-11	15	0.11	<LD	0.19	0.02	0.14	0.27	2.80	2.41	1.09	0.03	0.001	0.008
PG-12	16	<LQ	<LD	0.24	0.03	0.20	0.39	2.92	2.35	1.10	0.05	<LD	0.008
PG-13	17	0.08	<LD	0.15	0.02	0.11	0.24	2.58	2.06	1.09	0.02	0.001	0.006
PG-14	18	0.09	<LD	0.19	0.02	0.15	0.30	2.89	2.55	1.15	0.03	0.001	0.005
PG-15	19	0.11	<LD	0.18	0.02	0.14	0.29	3.30	2.47	1.13	0.03	0.001	0.007
PG-16	22	0.13	<LD	0.18	0.02	0.15	0.27	3.19	2.54	1.16	0.03	0.001	0.006
PG-17	23	<LQ	<LD	0.18	0.02	0.16	0.26	2.47	2.66	1.17	0.03	<LD	0.008
PG-18	24	0.13	<LD	0.19	0.02	0.15	0.25	2.83	2.52	1.17	0.03	0.001	0.007
PG-19	25	0.18	<LD	0.18	0.02	0.14	0.25	2.78	2.53	1.16	0.03	0.001	0.009
PG-20	26	0.08	<LD	0.18	0.02	0.14	0.22	2.59	2.38	1.09	0.03	0.001	0.008
PG-21	29	0.10	<LD	0.18	0.02	0.14	0.22	3.20	2.42	1.12	0.03	0.001	0.008
PG-22	30	<LQ	<LD	0.18	0.02	0.15	0.24	2.93	2.62	1.22	0.03	<LD	0.008

Table 5.3. Continued.

Sample	Day	Al	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Sb	Pb	U
PG-23	31	4.90	0.01	0.60	0.03	0.16	6.72	7.95	5.14	1.50	0.01	0.004	0.119
PG-24	32	0.14	<LD	0.17	0.02	0.13	0.22	2.49	2.31	1.06	0.03	0.001	0.010
PG-25	33	0.20	<LD	0.17	0.02	0.14	0.23	2.61	2.46	1.12	0.03	0.001	0.011
PG-26	36	<LQ	<LD	0.18	0.02	0.17	0.24	2.89	2.75	1.15	0.03	<LD	0.008
PG-27	37	0.27	<LD	0.19	0.02	0.17	0.21	2.77	2.87	1.15	0.03	<LD	0.007
PG-28	38	0.16	<LD	0.17	0.02	0.14	0.19	2.34	2.37	1.07	0.03	0.001	0.008
PG-29	39	0.14	<LD	0.16	0.02	0.13	0.16	2.24	2.36	1.05	0.02	0.000	0.007
PG-30	40	0.16	<LD	0.19	0.02	0.17	0.20	2.86	2.94	1.21	0.03	<LD	0.009
Marsh soil													
MS-01	1	4.97	0.05	0.58	0.03	0.15	3.27	16.3	7.00	1.56	0.02	0.001	0.076
MS-02	2	9.78	0.04	0.64	0.03	0.18	1.36	16.4	8.22	1.62	0.01	<LD	0.143
MS-03	3	7.36	0.04	0.66	0.03	0.18	1.29	16.4	8.15	1.78	0.01	0.002	0.114
MS-04	4	7.48	0.03	0.63	0.03	0.16	1.16	14.8	7.45	1.62	0.01	0.002	0.122
MS-05	5	6.16	0.03	0.56	0.02	0.15	1.13	13.7	7.00	1.52	0.01	0.002	0.113
MS-06	8	7.58	0.02	0.58	0.03	0.16	0.93	13.6	7.36	1.55	0.01	0.001	0.191
MS-07	9	11.2	0.02	0.64	0.03	0.18	2.59	15.5	8.16	1.59	0.01	<LD	0.083
MS-08	10	8.07	0.02	0.62	0.03	0.16	8.81	14.3	7.47	1.62	0.01	0.003	0.108
MS-09	11	6.71	0.02	0.51	0.02	0.14	7.99	11.9	6.16	1.26	0.01	0.003	0.091
MS-10	12	8.18	0.02	0.60	0.03	0.17	10.2	14.0	7.20	1.57	0.01	0.003	0.112
MS-11	15	7.59	0.02	0.58	0.03	0.15	11.5	13.3	6.87	1.49	0.01	0.004	0.110
MS-12	16	11.0	0.02	0.62	0.03	0.18	11.6	14.8	7.76	1.52	0.01	<LD	0.096
MS-13	17	7.47	0.02	0.57	0.03	0.15	10.9	13.7	7.02	1.53	0.01	0.003	0.111
MS-14	18	8.23	0.02	0.61	0.03	0.16	11.3	14.1	7.33	1.60	0.01	0.005	0.132
MS-15	19	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
MS-16	22	8.23	0.01	0.61	0.03	0.17	10.4	13.7	7.28	1.61	0.01	0.005	0.119
MS-17	23	8.12	0.01	0.66	0.03	0.19	13.8	12.6	6.44	1.62	0.01	0.004	0.098

Table 5.3. Continued.

Sample	Day	Al	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Sb	Pb	U
MS-18	24	8.31	0.01	0.61	0.03	0.16	14.5	13.8	7.29	1.59	0.01	0.004	0.123
MS-19	25	8.57	0.01	0.62	0.03	0.17	14.57	14.4	7.56	1.64	0.01	0.011	0.128
MS-20	26	9.27	0.01	0.65	0.03	0.18	17.2	14.5	7.81	1.70	0.02	0.004	0.130
MS-21	29	8.43	0.01	0.59	0.03	0.17	15.9	15.2	7.16	1.58	0.01	0.005	0.120
MS-22	30	7.93	0.01	0.60	0.03	0.16	15.3	12.3	6.27	1.41	0.02	0.004	0.121
MS-23	31	7.53	0.00	0.16	0.02	0.13	6.22	8.47	4.27	1.07	0.03	0.001	0.013
MS-24	32	8.04	0.01	0.60	0.03	0.16	15.5	13.3	6.97	1.54	0.01	0.004	0.123
MS-25	33	9.13	0.01	0.59	0.03	0.17	16.1	13.9	7.13	1.55	0.01	0.004	0.129
MS-26	36	10.8	0.01	0.67	0.03	0.20	17.3	15.7	8.55	1.64	0.02	<LD	0.098
MS-27	37	10.2	0.01	0.63	0.03	0.19	16.3	14.8	8.03	1.55	0.02	<LD	0.090
MS-28	38	9.51	0.01	0.66	0.03	0.17	16.9	14.7	7.78	1.71	0.02	0.005	0.132
MS-29	39	8.24	0.01	0.58	0.03	0.15	15.1	13.1	6.98	1.55	0.01	0.004	0.118
MS-30	40	8.35	0.01	0.66	0.03	0.19	16.5	15.3	8.34	1.61	0.02	0.004	0.091

n.a. = not analysed; LD = limit of detection

5.5 Discussion

5.5.1 Fe and S redox processes

Iron and sulphur are the predominant redox-sensitive elements in the phosphogypsum and therefore, the occurring geochemical processes during redox oscillations would affect the concentration of their species (Pérez-López et al., 2011). The Eh, and consequently the redox conditions, is one of the parameters controlling the behaviour of Fe and its species, as can be observed from their consistent redox cycling **(Fig. 5.3C and D)**. Another driving parameter of Fe behaviour could be the pH, controlling the geochemical processes of dissolution/precipitation during the experiments, as the difference in the pH values between the two experiments was quite significant with the phosphogypsum having higher pH (>4.5) than the marsh soil (<3.5). In detail, in the phosphogypsum experiment, the concentrations of total Fe and Fe^{2+} were higher in anoxic than in oxic conditions, because Fe^{2+} was oxidised to Fe^{3+} in the oxic half cycles and part of it precipitated as Fe^{3+} oxyhydroxides and Fe^{3+} phosphates. In turn, these precipitated Fe phases re-dissolved in the subsequent anoxic cycle releasing Fe, which was again reduced to Fe^{2+}. These processes are especially evident in the second oxic and the third anoxic cycles **(Fig. 5.3C)**, and this behaviour has already been reported by similar studies (Antić-Mladenović et al., 2011; Frohne et al., 2011; 2014). On the other hand, in the marsh soil experiment most of the total Fe was in the form of Fe^{2+} at both oxic and anoxic cycles **(Fig. 5.3D)**, possibly because of the lower pH conditions that do not favour oxidation of Fe^{2+} to Fe^{3+}. Thus, Fe^{2+} concentration was always above the limit of detection **(Table 5.2)** and potential Fe precipitation should have been also lower compared to phosphogypsum. Nevertheless, the differences between Fe^{2+} and Fe-total are slightly higher in oxic cycles than in anoxic cycles, when Fe^{2+} is almost equal to Fe-total. Therefore, there should be some oxidation and precipitation although not as evident as in the phosphogypsum experiment. This is especially clear at the last oxic cycle, when Fe-total is mostly in the form of Fe^{3+}, implying oxidation of iron and subsequent precipitation; this could be explained by the slight increase of the pH during the last half cycle **(Fig. 5.2B)**.

The depletion of Fe from the solution was consistent with the solid phases that precipitated according to PHREEQC calculations; Fe^{3+} produced by Fe^{2+} oxidation was predicted to precipitate as oxyhydroxide phases; i.e. goethite and lepidocrocite **(Table 5.4)**. This was mainly evident in the phosphogypsum and less in the marsh soil, where the calculated SI corresponded either to undersaturation or close to saturation with respect to the Fe phases, a case consistent with the arguments raised about the poor oxidation of Fe during the oxic cycles. Moreover, supersaturation in Fe^{3+} phosphates was noted in the form of strengite at both experiments **(Table 5.4)**. The Fe phosphate precipitation would explain the decrease of the iron amount in solution in the marsh soil experiment during the oxic cycles, despite there is no strong oxidation of Fe.

In general, the behaviour of Fe, which decreased dramatically from the solution soon after the first days of the experiment, was also observed in other studies (e.g. Parsons et al., 2013). The low amount of Fe in solution might be attributed to the slow potential dissolution of iron oxyhydroxides and/or to the immediate sorption or precipitation of Fe as secondary minerals (Kocar et al., 2009; Weigand et al., 2010). The reduction of Fe oxyhydroxides is catalyzed by microorganisms and in every anoxic cycle a certain time is needed for the development of anaerobic microbial activity (Rinklebe and Langer, 2008; Langer and Rinklebe, 2009). Hence, the fact that the time needed for the microbial incubation might be short during the anoxic cycles of the current experiments, especially compared to nature, could also explain the low concentrations of soluble Fe (Frohn et al., 2014).

One of the most important processes during anaerobic conditions is the reduction of sulphate to sulphide, which may limit the release of pollutants from phosphogypsum leaching. This process is usually associated with negative Eh and circumneutral pH values. Nevertheless, the positive Eh and lower pH conditions noticed during the current experiments were also described by other studies (Church et al., 2007); anaerobic conditions, high amount of organic carbon and the presence of SRBs would be necessary, as already observed in the Tinto River sediments (Florentino et al., 2015). Another explanation for sulphate reduction activity in acidic environments would be the existence of more alkaline and reducing pore-water microenvironments that enhance the bacterial activity. In anoxic and acidic environments (around pH 4), the sulphur produced during the oxidation of organic matter can react with the dissolved Fe^{2+}, which is produced from the bacteria-catalyzed reduction of Fe^{3+} oxyhydroxides, to form monosulphides of insoluble Fe (Berner, 1970). The overall reaction would be (Eq. 5.1):

$$4FeOOH_{(s)} + 4SO_4^{2-} + 9CH_2O + 8H^+ \rightarrow 4FeS_{(s)} + 9CO_2 + 15H_2O \quad (5.1)$$

Therefore, during the experiments the available Fe and the rest of the metals that were released during the anoxic half cycles would precipitate as metal sulphides. This process was more apparent during the phosphogypsum experiment - although not often- where some occasional abrupt decreases of sulphide concentration (e.g. 31st day) coincided with the anoxic cycles **(Fig. 5.3A)**, a behaviour probably controlled by the activity of the SRBs and the consequent precipitation of sulphur, consistent with the higher microbial activity observed. This was not obvious in the marsh soil experiment, probably due to the lower pH conditions that do not favour the sulphate reduction, in addition to the lower microbial activity compared to phosphogypsum. Nevertheless, the abnormal behaviour of sulphide with respect to the marsh soil -low peaks (although not significant) during the last two oxic half cycles **(Fig. 5.3B)**- could be explained by the decomposition of the present organic matter that favoured the development of anoxic microenvironments.

Table 5.4. Saturation indices (SI) for supersaturated minerals according to PHREEQC simulations from the database of model MINTEQ, at all the precipitates collected from the two experiments (phosphogypsum and marsh soil). Negative and positive SI values indicate undersaturation and supersaturation, respectively.

Sample	**Mineral phase**												
	Anilite	**Chalcocite**	**Chalcopyrite**	**Covellite**	**CoFe2O4**	**Cuprousferrite**	**Galena**	**Goethite**	**Greenockite**	**Lepidocrocite**	**Pyrite**	**Sphalerite**	**Strengite**
Phosphogypsum													
PG-01	17.8	19.4	15.6	12.5	14.1	12.5	0.32	4.06	3.81	3.18	9.91	1.97	4.92
PG-02	16.6	18.0	15.7	12.0	10.2	9.77		2.07	3.93	1.19	11.0	1.86	2.74
PG-03	16.1	17.3	13.4	11.9	8.84	8.75	0.23	1.46	3.89	0.58	9.21	1.90	2.22
PG-04	16.4	17.7	13.6	12.1	10.3	9.60	0.78	2.09	4.13	1.21	9.20	2.04	2.87
PG-05*													
PG-06	15.2	16.1	11.6	11.9	7.82	7.60	-0.21	0.94	4.06	0.06	8.67	1.93	1.75
PG-07	11.7	11.5	11.5	12.1	5.64	4.30	1.17	-0.12	4.00	-1.00	13.3	1.93	0.73
PG-08	11.0	10.5	11.5	12.0	8.30	5.09	0.26	1.20	4.03	0.32	14.2	1.91	2.03
PG-09	9.82	8.94	11.5	12.0	7.77	4.05	0.26	0.92	4.06	0.04	15.8	1.93	1.74
PG-10	9.46	8.49	11.4	11.9	7.70	3.80	-0.04	0.90	4.01	0.02	16.1	1.86	1.74
PG-11	9.71	8.82	13.5	11.9	10.5	5.36	0.35	2.31	4.10	1.43	17.8	1.95	3.14
PG-12	11.0	10.6	10.7	11.7	5.91	4.09		-0.10	3.62	-0.98	13.0	1.47	0.74
PG-13	11.5	11.2	11.6	12.0	9.64	6.08	0.83	1.80	4.49	0.92	13.6	2.22	2.64
PG-14	11.9	11.7	11.6	12.1	9.85	6.47	0.80	1.92	4.49	1.04	13.2	2.24	2.79
PG-15	11.7	11.4	11.5	12.0	9.08	5.95	0.31	1.59	4.08	0.71	13.2	1.99	2.44
PG-16	8.25	6.84	11.6	12.0	9.09	3.61	0.40	1.51	4.18	0.63	18.0	2.07	2.29
PG-17	8.14	6.69	11.8	12.0	8.30	3.09		1.08	4.30	0.20	18.3	2.06	1.81
PG-18	7.81	6.28	11.5	12.0	8.67	3.15	0.38	1.32	4.16	0.44	18.5	1.99	2.11
PG-19	7.51	5.87	11.6	12.0	9.61	3.39	0.42	1.78	4.20	0.90	19.0	2.02	2.59
PG-20	7.09	5.32	11.6	12.0	8.72	2.64	0.47	1.33	4.22	0.45	19.5	2.04	2.11
PG-21	6.77	4.90	13.1	11.9	6.01	1.10	0.41	-0.01	4.17	-0.89	21.4	2.07	0.80
PG-22	7.43	5.76	13.5	12.0	9.98	3.49		1.94	4.28	1.06	20.9	2.09	2.70

Table 5.4. Continued

Sample	Mineral phase												
	Anilite	**Chalcocite**	**Chalcopyrite**	**Covellite**	**CoFe2O4**	**Cuprousferrite**	**Galena**	**Goethite**	**Greenockite**	**Lepidocrocite**	**Pyrite**	**Sphalerite**	**Strengite**
PG-23	9.99	8.90	13.5	12.8	11.3	5.97	0.46	2.52	3.77	1.64	18.7	1.90	3.29
PG-24	7.85	6.35	13.1	11.9	9.16	3.38	1.06	1.53	4.21	0.65	19.9	2.01	2.27
PG-25	7.75	6.20	13.5	12.0	10.0	3.75	1.06	1.99	4.23	1.11	20.5	2.03	2.74
PG-26	6.45	4.50	12.0	11.9	8.14	1.79		0.89	4.04	0.01	20.5	1.89	
PG-27	6.40	4.42	12.1	11.9	8.26	1.75		0.92	4.16	0.04	20.8	1.99	
PG-28	6.50	4.55	13.4	11.9	6.27	1.02	0.47	0.08	4.22	-0.80	21.9	1.99	0.80
PG-29	6.38	4.41	11.6	11.8	8.78	2.15	0.04	1.34	4.30	0.46	20.3	2.07	2.10
PG-30	6.53	4.60	11.5	11.9	8.10	1.98		1.01	4.24	0.13	20.0	2.05	1.80
Marsh soil													
MS-01	14.6	13.2	-0.84	11.4	7.70	8.01	-1.19	1.88	2.74	1.00	10.3	1.16	3.88
MS-02	13.5	14.2	13.9	10.9	9.91	8.26		2.83	2.58	1.95	11.9	1.01	
MS-03	13.4	14.0	13.3	10.9	5.43	6.2	-0.97	0.82	2.71	-0.06	11.4	1.07	2.94
MS-04	13.1	13.7	13.0	10.8	5.84	6.27	-1.05	1.08	2.59	0.20	11.4	0.95	3.28
MS-05	12.9	13.5	12.8	10.8	6.24	6.47	-1.12	1.4	2.49	0.52	11.4	0.85	3.63
MS-06	12.2	12.5	12.0	10.6	7.38	6.50	-1.44	1.92	2.48	1.04	11.4	0.81	4.07
MS-07	10.6	10.4	10.6	10.8	4.72	4.21		0.71	2.23	-0.17	12.2	0.61	3.01
MS-08	9.59	8.85	10.5	11.3	1.56	1.88	-1.23	-0.87	2.23	-1.75	14.2	0.57	1.49
MS-09	9.28	8.45	10.3	11.3	1.09	1.56	-1.24	-1.02	2.11	-1.9	14.4	0.49	1.33
MS-10	9.38	8.55	10.6	11.4	1.66	1.77	-1.22	-0.87	2.23	-1.75	14.7	0.58	1.43
MS-11	9.57	8.79	11.1	11.5	2.06	2.11	-1.11	-0.65	2.19	-1.53	15.0	0.54	1.69
MS-12	10.3	9.77	11.7	11.4	2.26	2.73		-0.56	2.14	-1.44	14.5	0.53	1.77
MS-13	10.7	10.3	11.0	11.4	2.16	2.88	-1.22	-0.61	2.22	-1.49	13.4	0.57	1.73
MS-14	10.8	10.4	11.6	11.4	3.84	3.83	-0.73	0.25	2.21	-0.63	13.9	0.55	2.59
MS-15*													
MS-16	3.99	1.25	12.0	11.7	3.03	-1.34	-0.68	-0.38	2.56	-1.26	23.7	0.89	1.75

Table 5.4. Continued

Sample	Mineral phase												
	Anilite	**Chalcocite**	**Chalcopyrite**	**Covellite**	**CoFe2O4**	**Cuprousferrite**	**Galena**	**Goethite**	**Greenockite**	**Lepidocrocite**	**Pyrite**	**Sphalerite**	**Strengite**
MS-17	4.05	1.30	11.4	11.9	2.73	-1.49	-0.76	-0.56	2.59	-1.44	23.2	0.87	1.52
MS-18	3.73	0.88	12.0	11.8	0.79	-2.61	-0.84	-1.51	2.49	-2.39	24.2	0.82	0.62
MS-19	3.41	0.46	11.6	11.8	3.25	-1.58	-0.47	-0.26	2.47	-1.14	24.2	0.82	1.89
MS-20	3.22	0.19	11.1	11.9	2.63	-2.02	-0.88	-0.57	2.48	-1.45	24.0	0.81	1.55
MS-21	2.90	-0.24	11.5	11.9	2.31	-2.41	-0.44	-0.72	2.49	-1.60	24.8	0.88	1.43
MS-22	3.59	0.70	11.4	11.8	1.15	-2.53	-0.85	-1.29	2.43	-2.17	23.8	0.76	0.86
MS-23	3.24	0.34	11.6	11.5	1.82	-2.3	-1.47	-0.85	2.29	-1.73	24.0	0.6	1.27
MS-24	3.75	0.91	11.3	11.8	1.95	-2.01	-0.87	-0.88	2.45	-1.76	23.5	0.78	1.27
MS-25	3.33	0.35	11.5	11.8	-1.49	-4.00	-0.86	-2.59	2.46	-3.47	24.3	0.81	-0.43
MS-26	2.56	-0.66	9.88	11.8	2.18	-2.87		-0.93	2.30	-1.81	23.5	0.7	
MS-27	2.45	-0.79	9.16	11.7	-1.96	-4.75		-2.75	2.29	-3.63	22.9	0.68	-0.52
MS-28	2.72	-0.45	9.38	11.8	2.88	-2.23	-0.78	-0.41	2.49	-1.29	22.9	0.81	1.70
MS-29	2.61	-0.58	9.27	11.7	2.71	-2.36	-0.92	-0.5	2.41	-1.38	22.8	0.72	1.62
MS-30	2.71	-0.47	9.34	11.8	2.83	-2.25	-0.87	-0.45	2.47	-1.33	22.9	0.82	1.63

***Available data were not sufficient for PHREEQC calculations.**

5.5.2 Fate of trace elements

The precipitated Fe minerals mostly during the oxic half cycles at the phosphogypsum suspension could be important sinks for many elements (Cd, Cu, Ni and Zn). However, in our experiment co-precipitation or adsorption of metals to Fe minerals did not appear to be important, as their concentrations did not decrease along with Fe; a behaviour in agreement with other studies (Frohne et al., 2011; 2014) that reported possible explanations. Low pH conditions could have prevented those processes, as the adsorption capacity of metals to Fe minerals is low at acidic environments (Schulz-Zunkel and Krüger, 2009). Thus, the results revealed higher soluble concentrations than expected and a general conservative behaviour, especially at Zn, As and Cd concentrations in solution. High mobilization of metals during acidic conditions (pH 3 - 5) was also detected in other studies on redox dynamics (e.g. Chuan et al., 1996; Wiegand et al., 2009; Miller et al., 2010). Organic matter is another important parameter that controls the fate of metals in redox dynamics, as reported by Grybos et al. (2007), due to its high affinity to complex and adsorb metal cations (Cd, Cu, Ni and Zn) because of the negatively charged groups it contains (Laveuf and Cormu, 2009; Frohne et al., 2011). The relative conservative behaviour of the metals could also be attributed to the synergic effect of the presence of various contaminants included in the same suspension at the beginning of the experiment, which could affect each other's behaviour and compete for ion complexation (Couture et al., 2015).

Nevertheless, the scenario of the participation of the contaminants in solution to the precipitation processes of Fe (and less of S) phases during the oxic and the anoxic cycles, respectively, should not be overruled; the non-reduction of their concentration -or even increase in some cases- could be explained by the dissolution of some solid phases on which they were adsorbed and their subsequent release. More specifically, during the anoxic cycles and especially on day 31 at the phosphogypsum experiment, sulphide concentration decreased **(Fig. 5.3A)**, while the amount of metals in solution increased **(Fig. 5.4A and C)** possibly due to the dissolution of Fe oxyhydroxides that were formed in the previous oxic cycles. This would imply the coupled reaction 5.1 of reductive dissolution of Fe oxyhydroxides and sulphate reduction with precipitation of metal sulphides. However, since there is no evident decrease of trace metals during oxic cycles despite Fe oscillation, the Fe oxyhydroxides that dissolved could be also contained in the initial phosphogypsum and not only in the newly formed phases during the oxic half cycles. Nevertheless, the available metals were in higher concentrations than the aqueous sulphide and therefore the former increased, while the latter decreased. In addition, the solubility difference between $CaSO_4$ and CaS solid phases and the possible degeneration of gypsum might increase the weathering of phosphogypsum and the subsequent release of contaminants (Papanicolaou et al., 2010). These processes might have been enhanced by the reduction of sulphate to sulphide during the current experiment affecting the stability of phosphogypsum.

On the other hand, in the marsh soil experiment the precipitation of Fe^{3+} oxyhydroxides, which work as sinks of metals, during the oxic cycles was less evident than in the phosphogypsum experiment, and subsequently metal release from Fe phases during anoxic cycles was minimal. This explains why during anoxic conditions -where possible precipitation of metal sulphides occurred- the decrease of the available metals was greater than the decrease of sulphide concentrations; i.e. at the 31st day at the last anoxic cycle **(Fig. 5.4B and D)**. This decrease of trace elements in solution could be due to precipitation processes of sulphide minerals, in agreement with the increasing presence of SRBs, which is connected to sulphate reduction processes and precipitation of metals, and with the predictions of PHREEQC modelling in the form of sulphide minerals (e.g. chalcocite, pyrite, sphalerite) **(Table 5.4)**.

Given that As was detected mostly as As^{5+} under both oxic and anoxic conditions, no correlation was identified between As species and redox conditions. Arsenate, on the contrary to As^{3+}, is chemically similar to phosphate, so they compete for the same binding sites in soils (Manning and Goldberg, 1996; Signes-Pastor et al., 2007). Huge phosphate concentrations at both the phosphogypsum and the marsh soil could be responsible for As conservative high mobility, as As^{5+} was the predominant species during the experiment. Phosphate is competing effectively As in terms of sorption processes on iron minerals and has a strong affinity to sorb onto iron oxide minerals (Manning and Goldberg, 1996; Gao and Mucci, 2001; Dixit and Hering, 2003), hence preventing the decrease of As mobility during the presented experiments, among other reasons. The fact that As^{5+} did not reduce to As^{3+} during the anoxic conditions did not favour the formation of arsenic sulphide minerals, as mainly arsenite has a strong affinity for S (Signes-Pastor et al., 2007). For this reason As mainly remained in solution during the redox experiments, apart from some exceptions, e.g. day 31 at the marsh soil.

With respect to U, it presented a less conservative behaviour during redox cycling than the rest of the contaminants, as it displayed often fluctuations even during the same half cycle. Uranium is most likely present as U^{6+} in oxic conditions, while it could be reduced to the less soluble form of U^{4+} in anoxic conditions and thus, be immobilised by precipitation of UO_2. This process could occur through several reduction pathways in organic-rich zones -including the materials of the presented experiments that are organic matter rich-, such as abiotic reduction by iron sulphides that produces uraninite or as biological mediation via enzymatic activity (Hyun et al., 2012). This was more evident in the marsh soil experiment and especially, at the last two anoxic half cycles, being in agreement with the elevated values of organic matter **(Figs. 5.2D and 5.4D)**.

5.5.3 Solid phase characterisation

The chemical analyses of the aqueous phases of both phosphogypsum and marsh soil suspensions after being subjected to redox oscillations showed that Fe was largely removed from the solutions, implying that Fe participated in the precipitation processes. Indeed, SEM-EDS analyses revealed the presence of Fe solid phases at the precipitates, being in agreement with the Fe phases predicted to precipitate according to PHREEQC modelling **(Table 5.4)**. In the phosphogypsum samples, iron phosphate phases were commonly detected independently of the redox conditions and Cr was found to be adsorbed to them in some cases (e.g. at the first oxic and at the last full cycle) **(Fig. 5.5A)**. On the other hand, Fe oxyhydroxides were not detected until the second full cycle with Cr, Cu and Zn sorbed onto them at oxic and less in anoxic conditions **(Fig. 5.5B)**. It should be also noted that Fe was also detected in the spectra corresponding to major phases already present in the original suspensions, such as gypsum, barite or fluoride, indicating that some amount of the Fe depleted from the solution was accumulated on those phases. This is concomitant with the hypothesis raised that the high amounts of contaminants in solution, despite precipitation processes, could be explained by their release from phases existing in the original samples. With respect to the marsh soil samples, Fe was also accumulated on the already existing major solid phases, while Fe phosphate was the most commonly identified Fe phase in the precipitates **(Fig. 5.5C)**. Iron oxyhydroxide phases were also identified, while Cr, Cu and Zn were found to be sorbed onto them in many cases **(Fig. 5.5D)**.

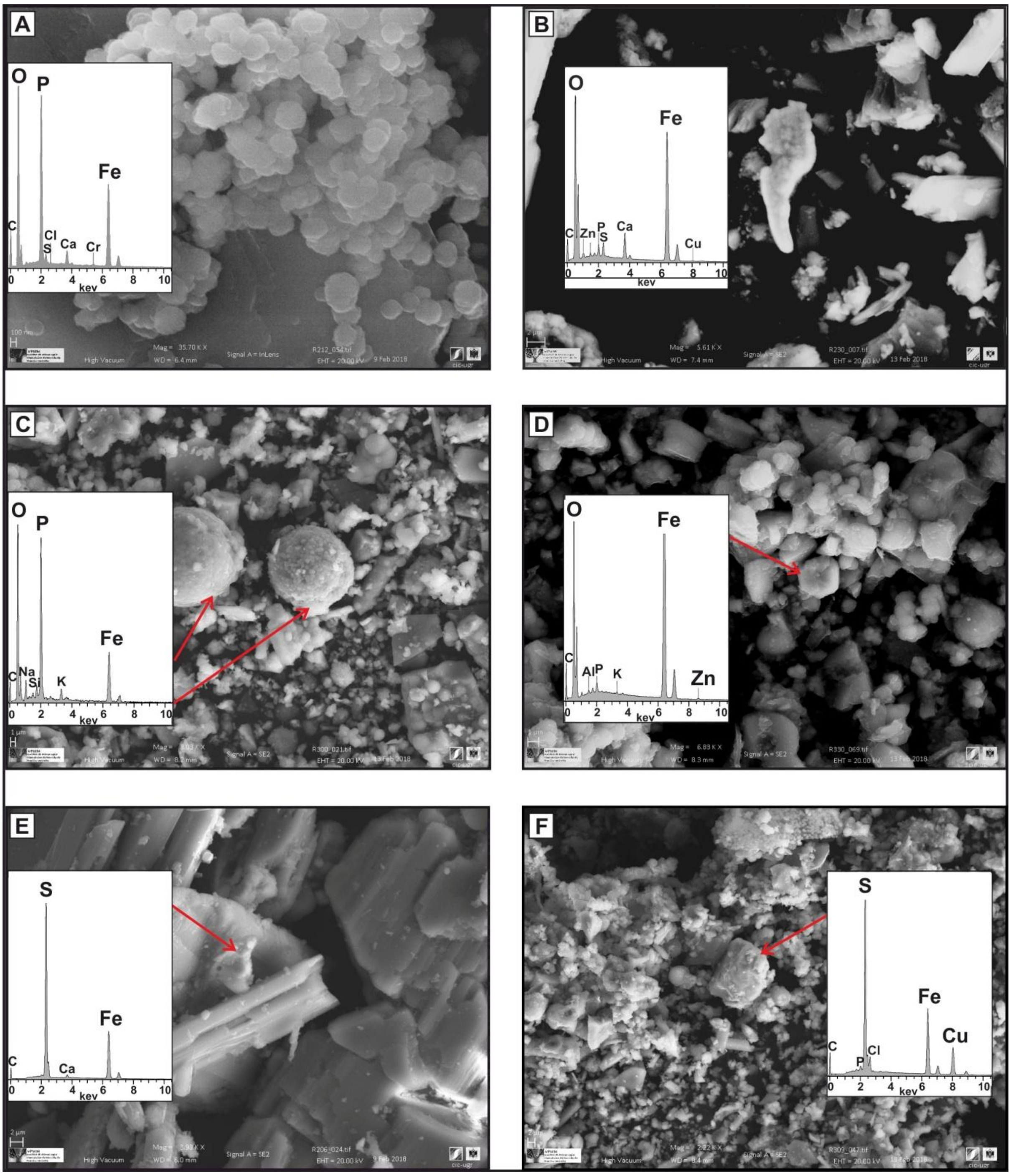


Figure 5.5: Solid phases identified by SEM-EDS analysis in the precipitates collected during the experiments. **(A)** Fe phosphate in the phosphogypsum; **(B)** Fe-Cu oxyhydroxide at the phosphogypsum; **(C)** Fe phosphates at the marsh soil; **(D)** Iron oxyhydroxide as a sink for Zn at the marsh soil; **(E)** Fe sulphide at the phosphogypsum; and **(F)** Fe-Cu sulphide at the marsh soil.

The identification of metal sulphides was challenging in both matrices, probably, due to their low quantities that were difficult to be identified by SEM-EDS analysis. The abundant Fe phosphates that were detected at the samples of both experiments indicate that their formation was the main precipitation process that controlled the mobility of the metals, while it was most probable that masked the respective formation of sulphides. Other explanations could be the low pH that might have prevented the preservation of these precipitates, as they are reported to be rather soluble under acidic conditions (Liu et al., 2009; Frohne et al., 2011). Nevertheless, some metal sulphide phases were detected in the solid samples of both experiments (**Fig. 5.5E and F)**.

5.6 Conclusions

Phosphogypsum stacks, such as the case of the Huelva phosphogypsum that is disposed directly on the salt marshes of Tinto River, are redox sensitive systems. Thus, Eh conditions were expected to control the cycling of Fe and S that are the dominant redox sensitive species in phosphogypsum, in addition to many contaminants that discharge from the waste and reach the environment. Redox oscillation experiments were performed in phosphogypsum and marsh soil matrices under laboratory-controlled conditions in order to evaluate the mobility of the contaminants and the role of microbial activity on the geochemical processes that take place. The results of the current study revealed a consistent cycling behaviour of Fe (and less of S), which controlled the potential precipitation processes of the metals. Iron oxyhydroxide formation was favoured under oxic conditions due to the oxidation of Fe^{2+}, providing available sinks for metals; while metal sulphide precipitation was more probable to occur under anoxic conditions, after the reaction of S with the released Fe and other metals. Nevertheless, the formation of metal sulphides appeared to be a secondary process in relation to the precipitation of Fe phosphates, which seemed to control the mobility of the metals independently of the redox conditions and the matrix. The activity of the SRBs, on the other hand, during the anoxic cycles could probably enhance the precipitation of sulphides -as observed at the end of the phosphogypsum experiment-, which could be used to promote a potential bioremediation for the contamination problem of the phosphogypsum stacks around the world.

Important immobilisation of the contaminants of interest was not favoured during the current experiments, possibly due to the elevated release of metals during anoxic conditions and subsequently, during reduction processes, in addition to the insufficient amount of sulphide available in relation to the metals. The constant acidic conditions that dominated during the experiments could be another explanation, among other reasons. Another driving parameter of the geochemical processes during the redox cycling was the pH, as in more acidic environments, i.e. the marsh soil, oxidation of Fe was not favoured and thus, total Fe was mostly in the form of Fe^{2+} continuously during the experiment, hindering the formation of Fe^{3+} oxyhydroxides during oxic conditions. In addition, the relatively short period of each half-cycle should be taken under consideration for the presented mobility of contaminants that possibly did not provide the ideal conditions for the development of microbial activity and thus, affecting the precipitation processes.

PART III

CONCLUSIONS

CHAPTER 6

CONCLUSIONS

6. Conclusions

The current Ph.D. Thesis focused on the geochemistry of the phosphogypsum waste that derives from the phosphate fertiliser industry; an environmental issue with a worldwide impact, mainly on coastal areas where the waste is usually disposed or directly poured into the sea. This research was achieved through the study of the paradigmatic site of the Estuary of Huelva (Spain), which contains on the one hand, a huge area covered with phosphogypsum and on the other hand, one of the most important marsh ecosystems in Europe. This thesis examined in detail the two sources of contamination from the phosphogypsum, including the process water ponded on the surface of the stack -initially used to slurry the waste- and the outflows that reach the edge of the stack and flow freely into the estuarine environment. The findings of this thesis have provided important insights into two main subjects: (I) the weathering processes that originate the discharges of the waste to the adjacent environment, and (II) the mobility of the phosphogypsum-related contaminants under seawater mixing and redox oscillations.

This thesis reports that the preliminary restorations that have taken place in some parts of the Huelva phosphogypsum disposal area are based on an unsuitable weathering model of the waste, which considers the ponded process water as the main washing agent of the stack. In the first line of investigation of this thesis, further investigation was conducted on the pollution pathway of the leachates using stable isotopes ($\delta^{18}O$, $\delta^{2}H$, and $\delta^{34}S$) as geochemical tracers for recognizing the influence of the three possible phosphogypsum-related end-members (process water, seawater and river water) and, so providing new significant knowledge to the weathering model of the stack and the origin of the edge outflows.

The results unveiled a strong geochemical connection of the outflows with the Tinto River and seawater end-members implying an estuarine influence, while ruling out process water as the main washing agent of the waste. The exact contribution of each end-member to the studied leachates that reach the estuary was, also, quantified via ternary mixing. The results indicated a progressive contribution downstream from fluvial to marine signatures, depending on the location of each disposal zone within the different estuarine morphodynamic domains. Therefore, the waste is subjected to an open system with a continuous infiltration of estuarine waters likely through the secondary channels that could act as one of the preferential paths that lead to the leaching mechanism. The revelation of the different pollution pathways and the newly introduced weathering processes that control the leaching of the waste pointed out that the parts considered to be restored continue to contaminate the environment until nowadays.

Phosphogypsum stacks lie within the tidal prism of the estuary, resulting in the continuous interaction of the discharges of acid wastewaters with seawater in the estuarine environment, as discussed previously. Therefore, as a continuation of the research, the second line of investigation elucidated the fate of contaminants after interaction through experimental and theoretical simulations of mixing of the phosphogypsum leachates with seawater. The pH is, as expected, one of the principal parameters controlling the geochemical processes during the mixing and the high acidity of the leachates results in the need to use large quantities of seawater in order to reach circumneutral pH values. Most of the toxic contaminants including Cu, Zn, As, Cd and Sb behave conservatively remaining mobile even after mixing with the alkaline seawater and do not participate in sorption processes. Those toxic elements finally end up into the Atlantic Ocean contributing significantly to the total metal loads and threatening the environmental conditions of the littoral. On the other hand, Fe, Al, Cr, Pb and U are immobilised when mixing with seawater and they participate in precipitation/sorption processes.

The current research was completed with the study of the redox processes, as Eh is another important factor that controls the geochemistry of phosphogypsum-related contaminants, given that the stack is subjected to a redox dynamic estuarine salt-marsh system. The last line of the thesis focused on the behaviour of the contaminants during redox cycles, in addition to the role of the microbial activity, with respect to the phosphogypsum and its basement, the marsh soil. The results revealed that the redox and the pH conditions play an important role to the cycling of Fe, S and other redox sensitive elements, controlling the precipitation/dissolution processes, although immobilisation of contaminants is not significant, at least during the current experiments. In the phosphogypsum, Fe^{2+} is oxidised to Fe^{3+} during oxic conditions and is subsequently precipitated in the form of oxyhydroxides, a case not so evident at the marsh soils due to the lower pH conditions. In the anoxic cycles, Fe and other metals are released from the subsequent dissolution of the precipitated (or existing) phases and thus, favouring metal sulphide precipitation due to their reaction with sulphur. However, Fe phosphates were identified as the most abundant precipitated phase at both matrices during oxic and anoxic conditions, which eventually appeared to dominate over the formation of metal sulphides and thus, controlling the mobility of the metals. Nevertheless, the activity of the sulphate-reducing bacteria seems to favour the formation of metal sulphides -even if their formation was a secondary process during the current study- and should be taken into account for future remediation actions.

In overall, the results of the thesis highlighted the inefficiency of the current restoration actions and of those planned for the future. Moreover, Fe mobility is controlled mostly by phosphate precipitation, while most of the potentially toxic elements in the edge outflows behave conservatively, both under seawater mixing and under redox oscillations. This translates into the immediate need for new, more effective treatment plans in order to prevent phosphogypsum leachates from reaching the coastal environment. Useful techniques were presented regarding the weathering processes dominating at the waste stack and the sources of the contaminated leachates, which could be applied to other phosphogypsum-contaminated areas around the world and broaden the respective knowledge. In addition, the outcomes with respect to the mobility of the contaminants should apply to other phosphogypsum areas worldwide in coastal regions, highlighting the harmful effects of the waste in a global scale.

PART IV

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PART V

PUBLICATIONS

Publication I

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Stable isotope insights into the weathering processes of a phosphogypsum disposal area

Evgenia-Maria Papaslioti [a, b, *], Rafael Pérez-López [b], Annika Parviainen [a], Francisco Macías [b], Antonio Delgado-Huertas [a], Carlos J. Garrido [a], Claudio Marchesi [c], José M. Nieto [b]

[a] *Instituto Andaluz de Ciencias de la Tierra, CSIC & UGR, Avenida de las Palmeras 4, 18100 Armilla Granada, Spain*
[b] *Department of Earth Sciences & Research Center on Natural Resources, Health and the Environment, University of Huelva, Campus 'El Carmen', E-21071 Huelva, Spain*
[c] *Department of Mineralogy and Petrology, UGR, Avda. Fuentenueva s/n, E-18002 Granada, Spain*

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ABSTRACT

Highly acidic phosphogypsum wastes with elevated potential for contaminant leaching are stack-piled near coastal areas worldwide, threatening the adjacent environment. Huge phosphogypsum stacks were disposed directly on the marshes of the Estuary of Huelva (SW Spain) without any impermeable barrier to prevent leaching and thus, contributing to the total contamination of the estuarine environment. According to the previous weathering model, the process water ponded on the surface of the stack, initially used to carry the waste, was thought to be the main washing agent through its infiltration and subsequently the main component of the leachates emerging as the edge outflows. Preliminary restorations have been applied to the site and similar ones are planned for the future considering process water as the only pollution agent. Further investigation to validate the pollution pathway was necessary, thus an evaluation of the relationship between leachates and weathering agents of the stack was carried out using stable isotopes ($\delta^{18}O$, $\delta^{2}H$, and $\delta^{34}S$) as geochemical tracers. Quantification of the contribution of all possible end-members to the phosphogypsum leachates was also conducted using ternary mixing via the stable isotopic tracers. The results ruled out ponded process water as main vector of edge outflow pollution and unveiled a continuous infiltration of estuarine waters to the stack implying that is subjected to an open weathering system. The isotopic tracers revealed a progressive contribution downstream from fluvial to marine signatures in the composition of the edge outflows, depending on the location of each disposal zone within the different estuarine morphodynamic domains. Thus, the current study suggests that the access of intertidal water inside the phosphogypsum stack, for instance through secondary tidal channels, is the main responsible for the weathering of the waste in depth, underlying the necessity for new, more effective restorations plans.

1. Introduction

The phosphate fertilizer industry is responsible for the generation of a waste by-product, known as phosphogypsum (mainly gypsum, $CaSO_4 \cdot 2H_2O$), during the production of phosphoric acid (H_3PO_4) via the wet chemical digestion of phosphate ore (fluorapatite, $Ca_5(PO_4)_3F$) with sulphuric acid (H_2SO_4). The overall chemical reaction can be written ideally as (Eq. (1)):

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF \quad (1)$$

The phosphate rock containing potentially toxic metal (loid)s and radionuclides as impurities is pre-concentrated by flotation, a process enhanced by reagents such as ammonium hydroxide or amine (Rutherford et al., 1994). Elevated concentrations of contaminants from the raw phosphate ore are then transferred into the

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* Corresponding author. Instituto Andaluz de Ciencias de la Tierra, CSIC & UGR, Avenida de las Palmeras 4, 18100 Armilla Granada, Spain.

E-mail addresses: empapaslioti@correo.ugr.es (E.-M. Papaslioti), rafael.perez@dgeo.uhu.es (R. Pérez-López), aparviainen@iact.ugr-csic.es (A. Parviainen), francisco.macias@dgeo.uhu.es (F. Macías), antonio.delgado@csic.es (A. Delgado-Huertas), claudio@ugr.es (C.J. Garrido), carlos.garrido@csic.es (C. Marchesi), jmnieto@uhu.es (J.M. Nieto).

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Publication II

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Effects of seawater mixing on the mobility of trace elements in acid phosphogypsum leachates

Evgenia-Maria Papaslioti[a,b,*], Rafael Pérez-López[b], Annika Parviainen[a], Aguasanta M. Sarmiento[c], José M. Nieto[b], Claudio Marchesi[a,d], Antonio Delgado-Huertas[a], Carlos J. Garrido[a]

[a] *Instituto Andaluz de Ciencias de la Tierra, CSIC & UGR, Avenida de las Palmeras 4, 18100 Armilla, Granada, Spain*
[b] *Department of Earth Sciences & Research Center on Natural Resources, Health and the Environment, University of Huelva, Campus 'El Carmen', E-21071 Huelva, Spain*
[c] *Department of Mining Engineering, Mechanics, Energy and Construction, University of Huelva, 21819 Palos de la Frontera, Huelva, Spain*
[d] *Department of Mineralogy and Petrology, UGR, Avda. Fuentenueva s/n, E-18002 Granada, Spain*

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ABSTRACT

This research reports the effects of pH increase on contaminant mobility in phosphogypsum leachates by seawater mixing, as occurs with dumpings on marine environments. Acid leachates from a phosphogypsum stack located in the Estuary of Huelva (Spain) were mixed with seawater to achieve gradually pH 7. Concentrations of Al, Fe, Cr, Pb and U in mixed solutions significantly decreased with increasing pH by sorption and/or precipitation processes. Nevertheless, this study provides insight into the high contribution of the phosphogypsum stack to the release of other toxic elements (Co, Ni, Cu, Zn, As, Cd and Sb) to the coastal areas, as 80–100% of their initial concentrations behaved conservatively in mixing solutions with no participation in sorption processes. Stable isotopes ruled out connexion between different phosphogypsum-related wastewaters and unveiled possible weathering inputs of estuarine waters to the stack. The urgency of adopting effective restoration measures in the study area is also stressed.

1. Introduction

The phosphate fertilizer industry produces huge amounts of a waste by-product, known as phosphogypsum (mainly gypsum, $CaSO_4 \cdot 2H_2O$) through the wet chemical digestion of phosphate ore (fluorapatite, $Ca_5(PO_4)_3F$) with sulphuric acid (H_2SO_4) to generate phosphoric acid (H_3PO_4). The theoretical overall chemical reaction is (Eq. (1)):

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF \quad (1)$$

Most of the contaminants in the raw phosphate ore are transferred to the phosphoric acid during the wet chemical process (Bolivar et al., 2009; Pérez-López et al., 2010). Phosphogypsum has high acidity and concentration of contaminants due to the occurrence of residual phosphoric acid that has not been fully separated during the industrial process and that remains trapped in the interstices of gypsum grains. The waste also contains other chemical reagents and products from reaction (1), such as sulphuric and hydrofluoric acids, ammonium hydroxide or amine (Lottermoser, 2010). These impurities strongly limit the potential of phosphogypsum for recycling, e.g. as agricultural additives or for building materials (see review in Cánovas et al. (2018)).

Phosphogypsum wastes are often dumped directly in the marine environment and considered one of the major sources of seawater contamination, as occurs in the Gulf of Gabes (SE Tunisa) (El Zrelli et al., 2015). They are transported as an aqueous slurry and without any prior treatment are usually stockpiled in coastal areas close to phosphate fertilizer plants, where they are exposed to weathering conditions (Tayibi et al., 2009) and physical and geochemical processes associated with coastal systems (Sanders et al., 2013). These stacks are considered as a significant source of environmental contamination under leaching conditions (Lottermoser, 2010; Pérez-López et al., 2016).

Coastal systems are responsible for the mass flux of elements entering the deep ocean, because they serve as transition zones between freshwater and seawater environments. At coasts, significant modifications of seawater chemistry occur concerning salinity, ionic composition and redox conditions depending on the tidal cycles and the temporal variations in freshwater inputs (Hierro et al., 2014; Liang and

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* Corresponding author at: Instituto Andaluz de Ciencias de la Tierra, CSIC & UGR, Avenida de las Palmeras 4, 18100 Armilla, Granada, Spain.
E-mail addresses: empapaslioti@correo.ugr.es (E.-M. Papaslioti), rafael.perez@dgeo.uhu.es (R. Pérez-López), aparviainen@iact.ugr-csic.es (A. Parviainen), aguasanta.miguel@dgeo.uhu.es (A.M. Sarmiento), jmnieto@dgeo.uhu.es (J.M. Nieto), claudio@ugr.es (C. Marchesi), antonio.delgado@csic.es (A. Delgado-Huertas), carlos.garrido@csic.es (C.J. Garrido).

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were carried out in this study using three types of phosphogypsum leachates. Owing to mixing with the alkaline oceanic waters, different geochemical processes alter the concentrations and influence the mobility of the meta(loid)s contained in the leachates. The current research reports on two main conclusions through experimental and theoretical simulations of mixing of phosphogypsum wastewaters with seawater: a) the high acidity of the leachates hinders the rise of the pH requiring enormous amounts of seawater compared to the wastewaters in order to achieve circumneutral pH values, and b) most of the toxic contaminants including Co, Ni, Cu, Zn, As, Cd and Sb behave conservatively, whereas Fe, Al, Cr, Pb and U decrease significantly with increasing pH and participate in precipitation/sorption processes. According to the results of this study, the behaviour of the contaminants during the mixing experiments was similar among the different types of phosphogypsum leachates, suggesting that the origin of wastewater (edge outflows vs. process water) or the restoration actions (unrestored zone 3 vs. supposedly-restored zone 4) did not control their mobility.

Our findings have provided important insight into the problematic of the phosphogypsum waste worldwide and, more importantly, into the pollution of the Estuary of Huelva by phosphogypsum contaminants. The toxic elements that remain mobile after reaching the estuary, finally end up to the Atlantic Ocean contributing significantly to the total metal loads and threatening the environmental conditions of the littoral. It is, therefore, urgent to adopt effective restoration measures to minimize the impact of the studied phosphogypsum leachates on the estuarine environment and subsequently on the Atlantic Ocean, as well as of other phosphogypsum areas worldwide especially in coastal regions.

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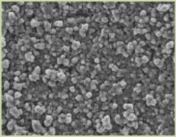

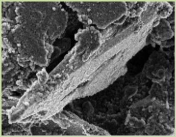

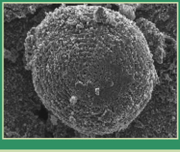

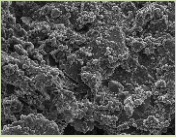

Phosphogypsum, produced by the phosphate fertiliser industry, is highly concentrated in heavy metals and is considered one of the most harmful wastes near coastal areas worldwide. The present Ph.D thesis aims to shed light on the environmental implications and the pollution pathways of the waste, focusing on the huge phosphogypsum facility of the *Estuary of Huelva*, which is disposed directly on the salt marshes of the *Tinto River*. In this context, this study focuses on three lines of investigation including (i) the weathering processes occurring at the phosphogypsum stack, and the metal mobilisation (ii) under seawater mixing with the phosphogypsum leachates and (iii) under redox oscillations in the phosphogypsum and the *salt marshes*. The stack produces two sources of contamination to the estuarine environment; the groundwater that flows laterally and reaches the edge of the stack forming the *edge outflows* and the *process water* stored on the surface of the waste, initially used to slurry and transport the phosphogypsum. Until nowadays, process water was recognised as the main washing agent of the waste and all the restorations were based on that assumption. However, further investigation conducted in the framework of the current thesis on the pollution pathway of the phosphogypsum leachates used stable isotopes ($\delta^{18}O$, $\delta^{2}H$, and $\delta^{34}S$) as geochemical tracers and ruled out process water as the main vector of edge outflow pollution. The results suggested that the access of intertidal water inside the stack, for instance through secondary tidal channels, is the main responsible for the weathering of the waste in depth. Thus, the ineffectiveness of the current restorations and the necessity for new, more effective ones was highlighted. In addition, this research revealed a high mobilisation of most metals contained in the phosphogypsum leachates both under seawater mixing and redox oscillations. Most contaminants (i.e. Co, Ni, Cu, Zn, As, Cd and Sb) behaved conservatively, while their behaviour was mostly controlled by precipitation/dissolution processes of Fe phosphates and less by the formation of Fe oxyhydroxides or metal sulphides. Therefore, the high contribution of the waste to the total contamination of the estuarine environment and subsequently of the Atlantic Ocean was stressed out, along with the urgency of adopting effective restoration measures in the study area and similar ones around the world.

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