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PRELIMINARY RESULTS ON THE OCCURRENCE OF RARE EARTH ELEMENTS IN THE AQUATIC SYSTEM OF THE PIALASSA BAIONA, RAVENNA (ITALY)

RÉSULTATS PRÉLIMINAIRES SUR LA PRÉSENCE DES ÉLÉMENTS DE TERRES RARES DANS LE SYSTÈME AQUATIQUE DE LA PIALASSA BAIONA, RAVENNE (ITALIE)

RISULTATI PRELIMINARI SULLA PRESENZA DI TERRE RARE NEL SISTEMA DELLE ACQUE DELLA PIALASSA BAIONA, RAVENNA (ITALIA)

Rosa Cidu*, Stefania Da Pelo, Raffaele Caboi

Dipartimento di Scienze della Terra, Università di Cagliari
***** Corresponding author: e-mail: cidur@unica.it

Abstract

The Site of Community Importance of the Pineta S. Vitale, bordered by the Pialassa Baiona lagoon system, is submitted to increasing deterioration due to a subsiding phenomenon, groundwater salinization and contamination from the industrial sites of Ravenna. Within a multidisciplinary research project, evaluation of the background level of Rare Earth Elements (REE, not regulated at present, but potentially harmful to human health) and the characterization of processes which control their migration and retention were performed to contribute to the knowledge on the present environmental quality of the Ravenna area. Concentrations of total and dissolved elements were determined in 40 water samples comprising surface waters, soil waters, shallow and deep groundwater. Dissolved major and minor components generally showed increasing concentrations from West to East (i.e. towards the sea) and appeared mostly derived from a marine source. Marked correlations between dissolved ΣREE and Al and Fe concentrations in the filtered fraction <0.4 μm were observed, especially in the soil waters. Shale-normalized patterns of the dissolved REE in the soil waters showed an enrichment in the Middle REE (MREE); such patterns being attributed to preferential adsorption of the MREE onto colloidal particles (<0.4 μm).

Keywords: *Pineta di S. Vitale; rare earth elements; soil waters; surface waters; groundwaters.*

Résumé

La Pineta de S. Vitale, site d'intérêt de la Communauté Européenne, située au bord du système lagunaire de la Pialassa Baiona, se détériore de plus en plus à cause des phénomènes de subsidence, de salinisation des aquifères, ainsi que des processus résultant de la contamination par la zone industrielle de Ravenne. Dans le but de

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contribuer à la connaissance des conditions de l'environnement actuelles, à l'intérieur d'un programme de recherche multidisciplinaire, on a évalué le teneur de fond des éléments de Terres Rares (qui sont potentiellement pathogènes mais pas encore régulés par la normative). On a aussi essayé d'évaluer les processus géochimiques qui contrôlent la migration et la rétention de ces éléments.

Les concentrations totales et en solution d'éléments majeurs et mineurs ont été analysées dans 40 échantillons sélectionnés parmi les eaux superficielles, les eaux de la zone saturée des sols, les eaux des nappes superficielles et profondes. La plupart des composants montrent une augmentation de la salinité en s'approchant à la mer. Une corrélation linéaire entre les concentrations de ΣREE et celles de Al et Fe dans la fraction filtrée <0.4 µm a été vérifiée, surtout dans les eaux des sols. En outre, les patrons des Terres Rares, normalisés par les *shale*, montrent dans les eaux des sols un enrichissement en Terre Rares Moyennes (MREE). Cette distribution pourrait être attribuée à une absorption préférentielle des MREE dans la fraction colloïdale (<0.4 µm).

Mots-clés: *Pineta di S. Vitale*; *terre rares; eaux des sols; eaux superficielles; eaux des nappes.*

Riassunto

Il Sito di Interesse Comunitario della Pineta di S. Vitale, al bordo del sistema lagunare della Pialassa Baiona, è soggetto ad un crescente deterioramento dovuto a fenomeni di subsidenza, salinizzazione degli acquiferi e a processi di contaminazione derivanti dalla prospiciente area industriale di Ravenna. Al fine di contribuire alla conoscenza dello stato ambientale attuale dell'area, nell'ambito di un programma di ricerca multidisciplinare, è stato valutato il tenore di fondo delle *terre rare* (attualmente non regolamentate dalla normativa, ma considerate potenzialmente patogene) e sono stati condotti studi per la valutazione dei processi che controllano la migrazione e la ritenzione di questi elementi. Sono state pertanto determinate le concentrazioni totali e disciolte di un *set* di elementi in 40 campioni selezionati fra acque superficiali, acque della zona satura dei suoli, acque delle falde superficiali e profonde. I componenti maggiori e minori mostrano un generale andamento crescente spostandosi dall'entroterra verso il mare. E' stata riscontrata una correlazione lineare fra la concentrazione della ΣREE e le concentrazioni di Al e Fe nelle frazioni filtrate a <0.4 µm, specialmente nelle acque dei suoli. Inoltre, l'andamento dei *pattern* delle terre rare normalizzati agli *shale* mostra nelle acque dei suoli un arricchimento delle terre rare intermedie (MREE). Tali andamenti possono essere attribuiti ad un preferenziale adsorbimento delle MREE nella frazione colloidale (<0.4 µm).

Parole chiave: *Pineta di S. Vitale*; *terre rare; acque dei suoli; acque superficiali; acque di falda.*

Introduction

Elements usually present at trace level in natural waters might be potentially harmful to human health, and more generally to the biosphere. Among such elements, the rare earth elements (REE), although not regulated at present, are potentially pathogens on the basis of recent epidemiological investigations. The geochemical behavior of REE in water may give a valuable contribution in distinguishing the natural sources of aqueous components from the anthropogenic ones. This study is part of an interdisciplinary project being carried out in the Pialassa Baiona (Ravenna), a complex lagoon system close to the Adriatic Sea. The study area comprises the Pineta San Vitale, which is part of the Natural Regional Park of the Po River.

Materials and methods

Water samples have been collected at 40 sites in the Pineta San Vitale. They consist of surface water (5 sites including the Lamone River), soil water (18 sites), shallow groundwater (12 sites) and deep groundwater (5 sites) (Fig.1).

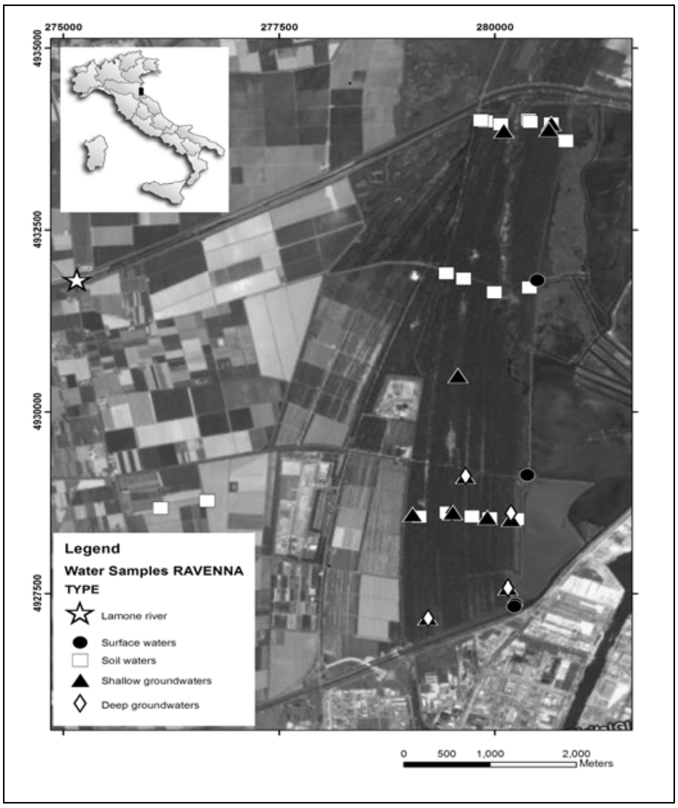

Figure 1

Samples location.

At selected sites, sampling was carried out under different seasonal conditions in October 2008 and March 2009. Physical-chemical parameters, dissolved oxygen

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and alkalinity were measured at the sampling site. For the determination of aqueous REE concentrations, different aliquots have been collected: one non-filtered (total amount), one filtered through 0.4 µm and the other filtered through 0.01 µm pore-size filters. Each aliquot has been stabilized using HNO_3 ultrapure grade.

The difference between the concentration measured in the 0.4 µm filtered aliquot and the 0.01 µm filtered aliquot will be attributed to the colloidal and very fine fraction. In each aliquot, Y, REE e Th have been determined by ICP-MS. On the 0.4 µm filtered aliquot concentrations of major components by ionic chromatography and ICP-OES, and the trace elements Li, Be, Al, B, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Sb, Ag, Ba, Tl, U by ICP-MS were also determined (Gherardi et al., 2009; Vittori Antisari et al., 2009)

Results and discussion

The studied waters show near-neutral or slightly alkaline pH values and redox potential varying from oxidizing to reducing conditions. Apart a few waters showing a prevalent bicarbonate component and relatively low total dissolved solids (TDS <2 g/L), most waters have a dominant Na-Cl composition with TDS in the range of 2 to 24 g/L. Dissolved Na, Cl, Mg, SO_4 concentrations increase with increasing TDS (Fig.2a, b).

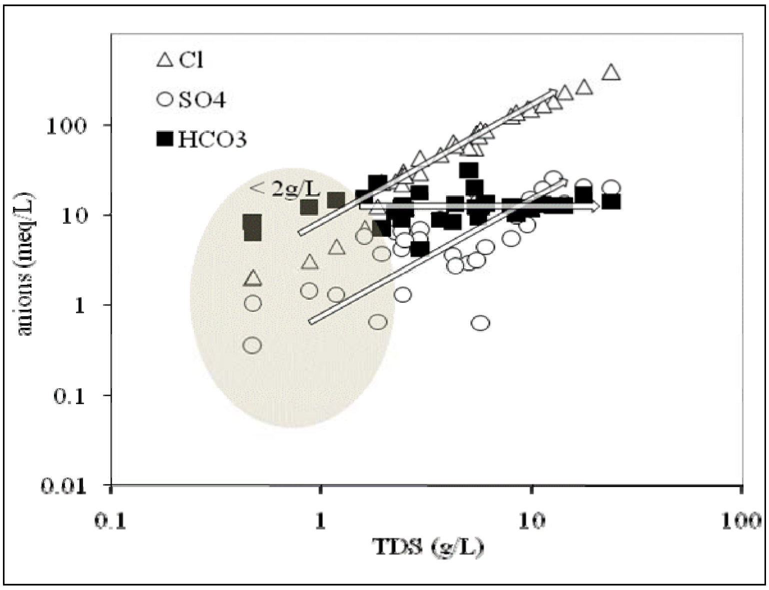

Figure 2a

Variation of major anion concentrations with TDS.

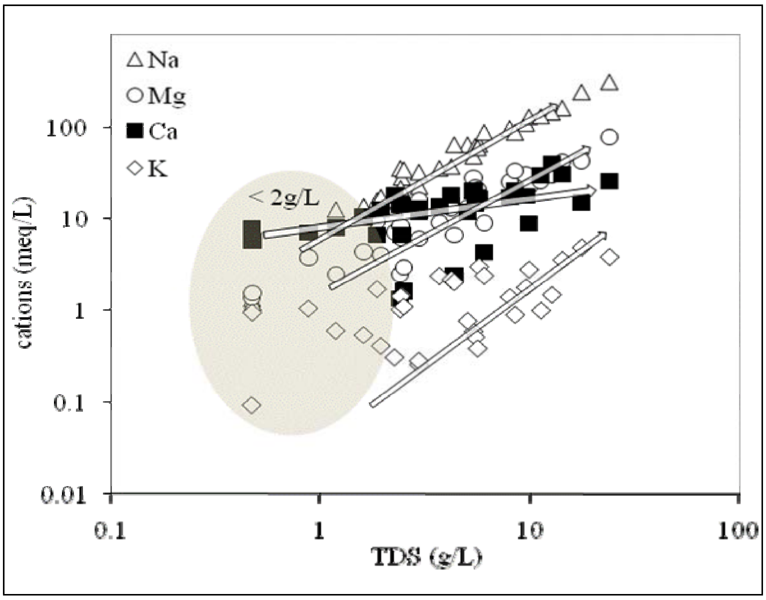

Figure 2b

Variation of major cation concentrations with TDS.

Also Br, B, Sr, Li and Rb show higher concentrations in the more saline waters. These major and minor components generally show increasing concentrations from West to East (i.e. towards the sea) and appear mostly derived from a marine source, in agreement with previous records indicating an intrusion of seawater in the Pineta San Vitale. Particularly, increasing salinity in groundwater occurs from West to East at the same depth, but at the same location salinity increases with depth (Fig.3).

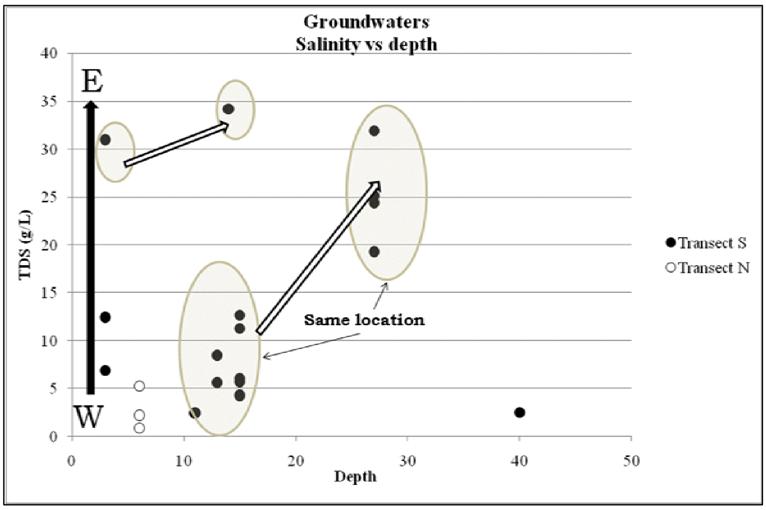

Figure 3

Variation of salinity with locations and depth in groundwaters s

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Moreover, this process is clearly recognized by isotopic data acquired on the same water samples considered in this study (see Petrini et al., 2009, these Proceedings). Notwithstanding the prominent role of saline intrusion, other processes need to be considered to explain the observed water chemistry. In particular, the dissolution of minerals, exchange between dissolved cations and solid phases and sorption processes may play a significant role in the geochemical behavior of some elements in the studied waters. Concentrations of Y and REE show a range of four orders of magnitude, with the highest values being observed in the soil waters (Fig. 4).

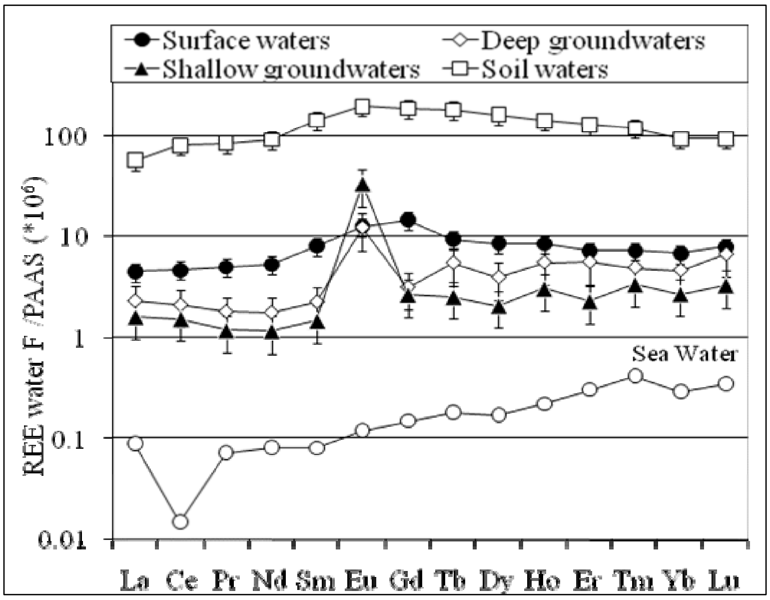

Figure 4

Mean and standard deviations of REE patterns in 0.4 µm pore size filtered waters. Concentration normalized to the Post-Archean average Australian Shale (PAAS)

A comparison between concentrations measured in non-filtered and filtered water samples indicate that about 50% of REE occur in the <0.4 µm aqueous fraction (Y+REE: 0.1 - 220 µg/L). Considering that water filtration through 0.01 µm pore-size filters removes >90% of the REE hosted in the <0.4 µm aqueous fraction, it can be argued that only a small amount of REE occurs in true solution while a large REE amount is hosted in very fine and/or colloidal particles. Indeed, marked correlations between dissolved ΣREE and dissolved Al and Fe concentrations have been observed, especially in the soil waters.

Also, shale-normalized patterns of the dissolved REE in the soil waters show an enrichment in the middle REE (MREE) (Fig. 5); such patterns being attributed to preferential adsorption of the MREE onto colloidal particles. Similar pattern have been previously reported by Elderfield *et al.* (1990) in water filtered through 0.4 µm, but known to support relatively high concentrations of colloids and dissolved organic matter. Moreover Steinmann and Still (1997), applying a sequential extraction procedure to a heavy metals contaminated soil, show that MREE are preferentially extracted from the Fe-Mn-Al oxide-hydroxide fraction.

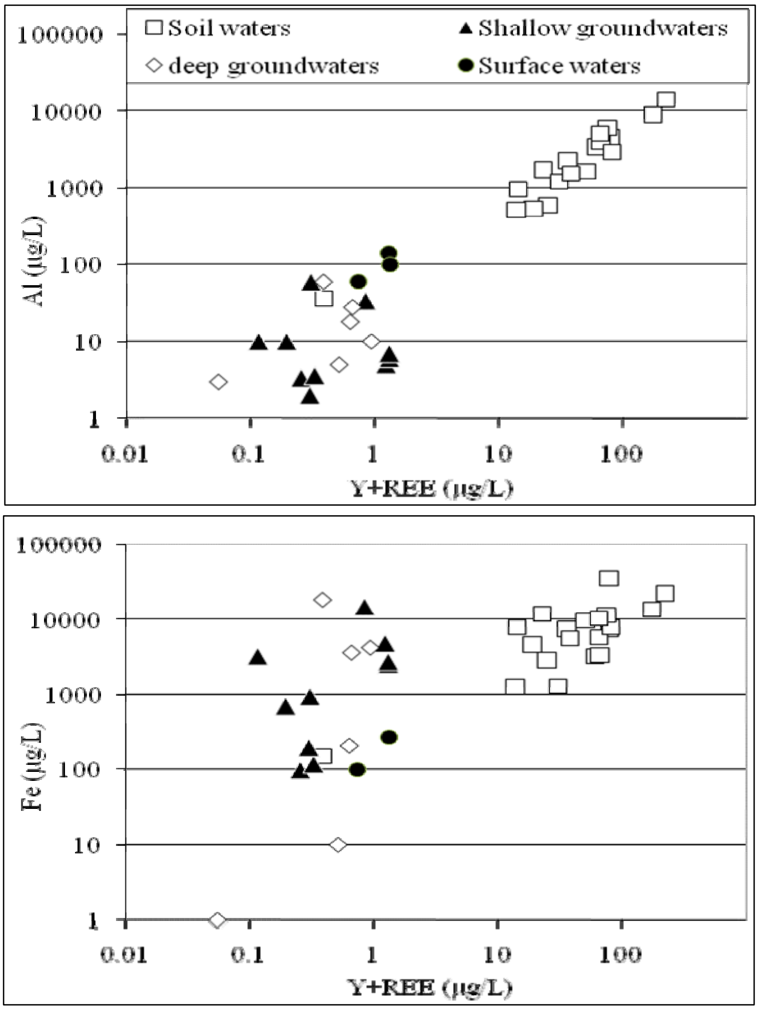

Figure 5

Plots showing the ΣREE versus Al and Fe concentrations in 0.4 µm pore-size filtered waters.

Conclusion

Although the role of anthropogenic processes on the occurrence of aqueous REE still needs to be assessed, the acquired data indicate that chemical and biological processes occurring in the soil are able to enhance the mobility of REE in the Pineta San Vitale aquatic system.

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