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POTENTIALLY TOXIC ELEMENT CYCLES AND CHARACTERIZATION OF MULTIPLE SOURCES IN THE IRRIGATION DITCHES FROM THE RAVENNA COASTAL PLAIN THROUGH TRACE ELEMENTS AND ISOTOPE GEOCHEMISTRY

CYCLE DES ÉLÉMENTS POTENTIELLEMENT TOXIQUES ET CARACTÉRISATION DES DIFFÉRENTES SOURCES DANS LES EAUX DES CANAUX D'IRRIGATION DE LA PLAINE CÔTIÈRE DE RAVENNE PAR LES ÉLÉMENTS EN TRACE ET LA GÉOCHIMIE DES ISOTOPES

CICLO DEGLI ELEMENTI POTENZIALMENTE TOSSICI E CARATTERIZZAZIONE DELLE SORGENTI MULTIPLE NELLE ACQUE DEI CANALI D' IRRIGAZIONE DELLA PIANURA COSTIERA DI RAVENNA ATTRAVERSO ELEMENTI IN TRACCE E GEOCHIMICA ISOTOPICA

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Abstract

While monitoring the physico-chemical characteristics, trace elements and O-H-Sr-B isotopic data were obtained in superficial waters from a number of irrigations canals and ditches in the Ravenna coastal plain, in order to highlight the cycling of potentially toxic elements and the different sources of the solutes. Surveys were conducted during March and July 2008, and considered as representative of the waters in winter and summer, respectively. In summer, the water mass balance in the network is mostly controlled by the ingression of freshwaters from the Canale Emiliano Romagnolo (CER). The O-H isotopic data indicated that, in winter, waters are primarily recharged from Apennine catchments and undergo evaporation to different extents.

The boron isotopic signature indicates the important role played by the marine component. A major seawater contribution was evidenced in canals close to the coastline; however, the process controlling the origin of dissolved boron is not solely related to direct mixing with sea water but comprises an additional source probably related to water-soil exchanges and boron of marine origin leaching, owing to the prolonged exposure of alluvial sediments to sea water. An additional boron contribution from the agricultural practice was is also evidenced. Calculation

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based on the conservative behaviour of chloride ions indicated that in canals and ditches not directly connected with the sea up to the 80% of the Sr budget did not originate from seawater, indicating a source from Al-silicate minerals and supporting the hypothesis of significant soil-water interactions and chemical exchanges.

The positive correlation between pH and dissolved oxygen in winter waters is likely to reflect CO_2 consumption during algal photosynthesis, favouring the in-situ generation of colloidal particles due to the oxidative precipitation of ferric iron oxy-hydroxides and probably small carbonate particles able to adsorb trace metals on their surface and contribute to the ecosystem dynamics facilitating the transport of metals and affecting their bio-availability and cycling. During summer, the input of freshwater from CER lowered the concentration of most ions and became superimposed to the evaporation-precipitation-exchange cycle, possibly dispersing the colloidal particles which could act as pollutant carriers and enhancing flocculation and precipitation, scavenging trace metals into the sediments.

Key words: *surface waters; coastal plain; geochemistry; metals; isotopes; water/rock interaction*

Résumé

Outre le suivi des paramètres pysico-chimiques, la concentration des éléments - trace et la composition isotopique de O-H-Sr-B ont été obtenus dans les eaux superficielles d'un certain nombre de canaux et de fossés d'irrigation dans la plaine côtière de Ravenne, pour mettre en évidence le cycle des éléments potentiellement toxiques et le rôle des différentes sources du solutés. Deux échantillonnages différents ont été menés au cours de Mars et Juillet 2008 et considérés comme représentatifs des périodes d'hiver et d'été. En été l'équilibre des masses d'eau dans le réseau est principalement contrôlé par l'ingression des eaux douces du Canal Emilien-Romagnien (CER). Les données isotopiques sur O-H indiquent que pendant l'hiver, les eaux sont principalement rechargée à partir des bassins des Apennins et sont ensuite l'objet d'évaporation à des degrés divers.

La signature isotopique du bore indique le rôle important joué par la composante marine. Une contribution importante d'eau de mer est attestée dans les canaux échantillonnés près de la cote. Néanmoins, l'origine du bore dissous n'est pas uniquement due au mélange direct avec l'eau de mer. Une source supplémentaire existe, probablement liée à des échanges eau-sol et au lessivage de bore d'origine marine par suite de l'exposition prolongée des sédiments alluviaux à l'eau de mer. Une contribution supplémentaire de bore venant de la pratique agricole est également mise en évidence. Le calcul basé sur le comportement conservateur des ions chlorure indique que dans les canaux et les fossés qui ne sont pas directement connectés à la mer, jusqu'à 80% du budget du Sr ne proviennent pas de l'eau de mer, ce qui indique une source de Sr par des Al-silicates, et suggère des interactions importantes d'échanges ioniques entre le sol et l'eau. La corrélation positive entre le pH et l'oxygène dissous dans les eaux d'hiver est susceptible de refléter la consommation de CO_2 lors de la photosynthèse des algues, favorisant la production in situ de particules colloïdales en raison de la précipitation des oxy-hydroxydes de fer ferrique et probablement de petites particules de carbonate, qui sont capables d'adsorber les métaux-traces sur leur surface et de contribuer à la dynamique des écosystèmes en favorisant le transport de métaux et leur biodisponibilité. Pendant l'été, l'entrée d'eau douce du CER abaisse la concentration de la plupart des ions et se superpose au cycle évaporation-précipitation-échange, favorisant probablement la dispersion des particules colloïdales qui pourraient agir en tant que fixatrices de polluants, avec floculation subséquence et précipitation des métaux-traces dans les sédiments.

Mots-clés: *eaux de surface; plaine côtière; géochimie; métaux; isotopes; interaction eaux/roche*

Riassunto

Questo lavoro illustra i dati raccolti durante il monitoraggio di diversi corpi idrici naturali ed artificiali presenti nella pianura costiera di Ravenna. I canali presenti in questa zona garantiscono l'apporto idrico alle attività agricole. Oltre al monitoraggio dei parametri chimico fisici delle acque sono stati analizzati i contenuti di elementi in tracce e i rapporti isotopici di O-H-Sr-B al fine di evidenziare il ciclo di elementi potenzialmente tossici e il ruolo delle diverse fonti di soluto.

I dati ottenuti dalle analisi dei campioni prelevati nel mese di marzo, rappresentativo delle acque invernali, sono stati messi a confronto con quelli ottenuti dai campioni di luglio, quando il bilancio di massa nella rete idrica è in gran parte controllata dalla ingressione di acque dolci dal Canale Emiliano Romagnolo (CER). I dati isotopici di O-H indicano che, durante l'inverno, le acque dei corpi idrici della zona sono principalmente ricaricate da bacini appenninici e sottoposti in diversa misura ad evaporazione. La firma isotopica del boro indica l'importante ruolo svolto dalla componente marina. Un contributo importante di acqua di mare è evidenziato nei canali campionati vicino alla linea di costa. Tuttavia, il processo che controlla l'origine del boro disciolto non è esclusivamente legato al diretto mescolamento con l'acqua di mare, ma è probabilmente determinato da una fonte supplementare come l'acqua proveniente dal suolo. I sedimenti alluvionali lungamente esposti all'acqua di mare rilasciano boro di origine marina attraverso i processi di lisciviazione.

È anche evidenziato un contributo aggiuntivo di boro proveniente dalle pratiche agricole. Sulla base del comportamento conservativo dello ione cloruro ed applicando bilanci di massa si è evidenziato che nei canali che non sono direttamente collegati al mare circa l'80% dello Sr ha origine da minerali Al-silicatici, suggerendo una significativa interazione tra suolo e acqua e la presenza di fenomeni di scambio ionico.

È probabile che la correlazione positiva tra il pH e l'ossigeno disciolto nelle acque prelevate in inverno riflettano il consumo di CO_2 durante la fotosintesi delle alghe.

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La presenza di CO_2 verosimilmente favorisce la generazione in situ di particelle colloidali a causa della precipitazione ossidativa di ossi-idrossidi di ferro e piccole particelle di carbonato, tali particelle sono in grado di adsorbire sulla loro superficie i metalli in tracce e contribuiscono alla dinamica dei metalli nell'ecosistema agevolandone il trasporto e interessando il loro ciclo e quindi la loro biodisponibilità. Durante l'estate, l'ingresso di acqua dolce dal CER abbassa la concentrazione della maggior parte degli ioni e si sovrappone al ciclo di evaporazione – precipitazione - scambio, probabilmente favorendo la dispersione delle particelle colloidali che possono fungere da vettori di sostanze inquinanti.
Parole chiave: *acque superficiali; pianura costiera; geochimica; isotopi; interazione acqua/roccia*

Introduction

The inventory of the sources and sinks of potentially toxic elements is of the uppermost importance in the overall control of water quality, in particular in agricultural lands were the application of manure and fertilizers and the artificially-controlled irrigation water recharge strongly control the release and deposition of trace metals in the water-sediment-soil system (Adriano, 2001).

The complex dynamics which characterize these ecosystems influences the biological and geochemical cycling of trace metals, including their availability from dissolving minerals, the scavenging by secondary phases precipitation in soils or aquifers and the role of particle surfaces in absorption processes, in particular if iron and Al-silicates are present in the parent rocks. Furthermore, the mixing of waters differing in quality, as in coastal zones between freshwater and seawater or in irrigated crops, represents an additional mechanism for dispersion and transport of pollutant, also driving dissolution-precipitation reactions for a number of minerals.

The contribution of rainwater inputs, aerosol deposition, evapo-transpiration, respiration-photosynthesis processes and more in general the role of biomass also contribute to the elemental mass-balance timing, influencing the geochemical equilibria which establish in areas exploited for agricultural uses. In this context, in addition to major ions and trace element analysis, isotopic investigations provide valuable indications on the ecosystem dynamics.

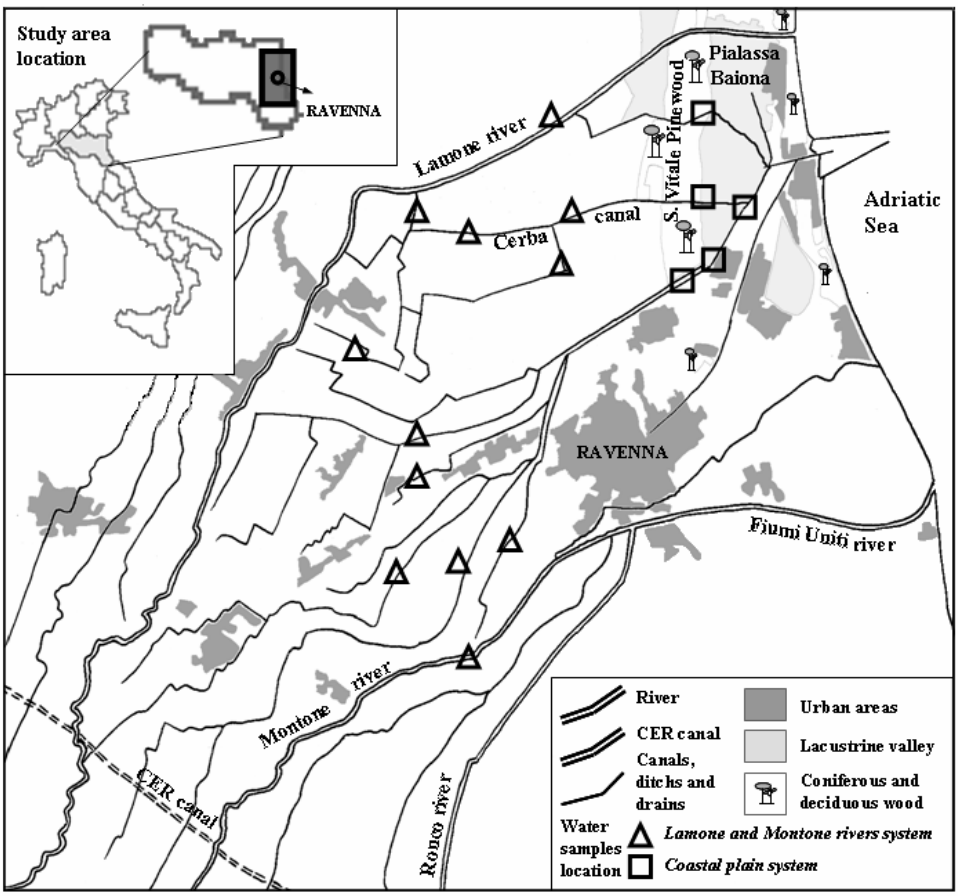
The present study is focused on the seasonal distribution of some potentially toxic trace metals (Fe, Mn, Cu, Ni, Zn, and As) in the network of canals and small ditches which serves the water demand for irrigation in the Ravenna coastal plain, an area limited by the Lamone and Montone rivers to the North-West and to the South, respectively, and by the Adriatic Sea coast to the East. During summer, the water mass balance in the canal network is mostly controlled by the deliberate ingression of freshwaters from the Canale Emiliano Romagnolo (CER), where a pumping station takes water directly from the Po River.

Environmental isotopes (H, O, B, and Sr) were included in the geochemical investigation in order to shed light on the provenance of waters, as well as on water/rock interaction, the origin of salinity and the occurrence of anthropogenic contamination.

Materials and methods

Twelve superficial water samples were collected during two different surveys on March and July 2009, and are intended as representative of the quality of waters during winter and summer, respectively.
The site of sampling are illustrated in Fig. 1.

Figure 1 - *Sketch map of the canals and ditches in the investigated area; open triangles locate sampling sites.*



Water temperature, bulk Eh, pH, and electrical conductivity (EC) were measured in the field. The redox potential (Volts) was reported to SHE by contemporary measuring a ZoBell's solution. Alkalinity was also measured in the field by acidimetric titration with 0.1N HCl. Total amount of alkalinity was attributed to HCO_3^-. The dissolved oxygen was also measured on site using an Aqualitic Ox 24 portable instrument.

Samples for chemical and isotopic analysis were stored in polyethylene bottles, after cleaning. For major cations and trace element analyses water samples were filtered using a 0.45 μm nylon filter, and stabilized by ultrapure HNO_3. Major and trace constituents were determined by Spectros (Circular Optical System CIROS) Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES).

H and O isotopic determinations on water samples were performed by the technique of CO_2/H_2 water equilibration by means of an automatic equilibration device on line with a Finnigan Delta Plus mass spectrometer. The O and H isotopic data are expressed as per mil deviation from the V-SMOW standard (Vienna Standard Mean Oceanic Water) using the conventional $\delta^{18}O$ and δD notation ($\delta=[(R_{sample}/R_{standard})-1]*1000$ (‰) where R represents the $^{18}O/^{16}O$ or D/H isotopic ratio). Analytical precision is better than 0.2‰ for $\delta\,^{18}O$ and 0.5‰ for δ D.

The $^{87}Sr/^{86}Sr$ isotope-ratio (referred to as Sr isotopic composition) on water samples was obtained after Sr separation from the chemical matrix by conventional ion-exchange chromatography. The Sr isotopic composition was measured using a VG-Micromass 54E mass-spectrometer. The isotopic data are fractionation-corrected to $^{86}Sr/^{88}Sr = 0.1194$. The experimental uncertainties represent in-run statistics at 95% confidence level. Repeated analyses on the NBS 987 Sr isotopic standard gave an average value of $^{87}Sr/^{86}Sr=0.71025\pm0.00002$ (n=15), and no correction for instrumental bias was applied to the measured ratios.

The isotopic analyses of boron were performed on about 2 μg of boron purified by a two-step ion exchange through columns of Amberlite IRA 743 (boron specific) and cation resin AG 50W-X8 (200-400 mesh). Boron isotopic ratios were measured by PTIMS (positive thermal ionization mass spectrometry) on $Cs_2B_4O_7$ deposited on the ion source filament with graphite and mannitol, which produces $Cs_2BO_2^+$ ions. The analyses were performed on a VG 54-E mass spectrometer. The boron isotope ratio variations are expressed as $\delta^{11}B$ ‰, i.e. in terms of the difference in parts per mil by comparison to the reference material NIST SRM-951:

$\delta^{11}B$ ‰ $= [(^{11}B/^{10}B)_{SAMPLE}/(^{11}B/^{10}B)_{NIST\text{-}SRM\text{-}951} - 1]*10^3$

The reproducibility of measurements is about 0.5 ‰, or slightly worse for water samples with boron concentrations below 0.5 mg L^{-1}.

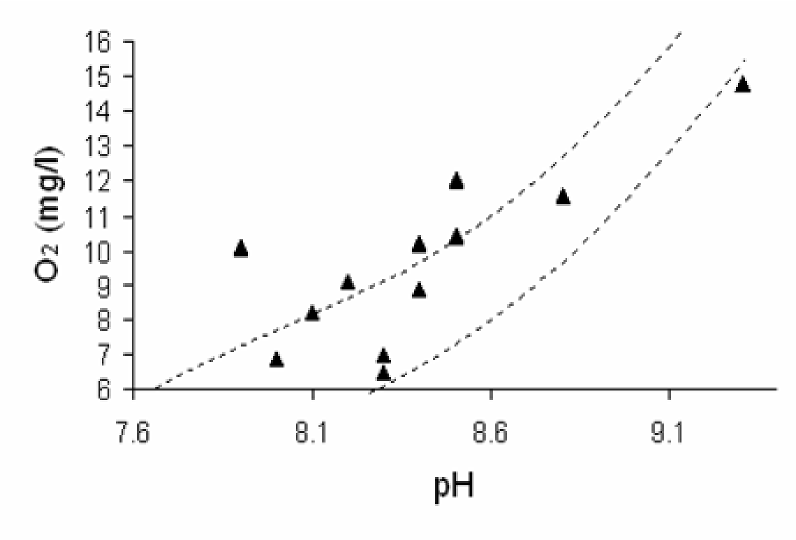
Results and discussion

Significant seasonal variations are recorded on the physico-chemical parameters measured in waters from the irrigation network of the Ravenna coastal area, that are strictly related to land exploitation by the local agricultural activity. Winter waters are characterized by EC values up to 3800 μS/cm, high chloride contents (up to 1000 mg/L), and are classified as Na(K)-chloride and Ca-bicarbonate waters. A dominant marine origin of solutes through intrusion of sea water into the canal network, or by aerosol sea salts deposition in soils, is hence likely. A chloride input from the use of mineral fertilizers in agriculture seems to be ruled out by the lack of correlation with nitrate.

During summer (July sampling), canals and ditches are characterized by a significantly decrease in EC and chloride content and by an increase in pH values, the water chemistry becoming of the Ca-bicarbonate-chloride type. The observed variations are explained by the admixing of the low-salinity, Ca-rich, water from the "Canale Emiliano Romagnolo" (CER), that since June yearly feed the local irrigation network.

During summer, trace metals (Ni, Mn and Fe) show decreasing abundance and a lower spread in concentration, compared with the winter samples. Cu differs, and shows similar concentrations in the two periods; this behavior remains unclear, considering the amount of Cu that are carried along with the CER freshwater. It is hence clear that the input of CER modifies the geochemical patterns reached during winter in the surface hydrologic system. Prior to the input of waters from CER, the pH of waters positively correlates with the amount of dissolved oxygen (Fig. 2), suggesting different extent of algal photosynthesis, with the conversion of CO_2 to organic matter plus oxygen.

Figure 2 - *pH vs. dissolved oxygen (mg/L) correlation diagram for the winter waters; possible trends for photosynthesis reactions calculated using PHREEQC (Parkhurst and Appelo, 1999) are also superimposed (dashed lines).*



This process, probably controlled by a diurnal cycle, concurs to Fe(II) oxidation through bacterial catalysis (Brons et al., 1991) and precipitation of iron oxyhydroxide particles, that act as a strong trace metals adsorber (Sparks, 2005). The ingression of the CER waters hence has the effected to dilute the concentration

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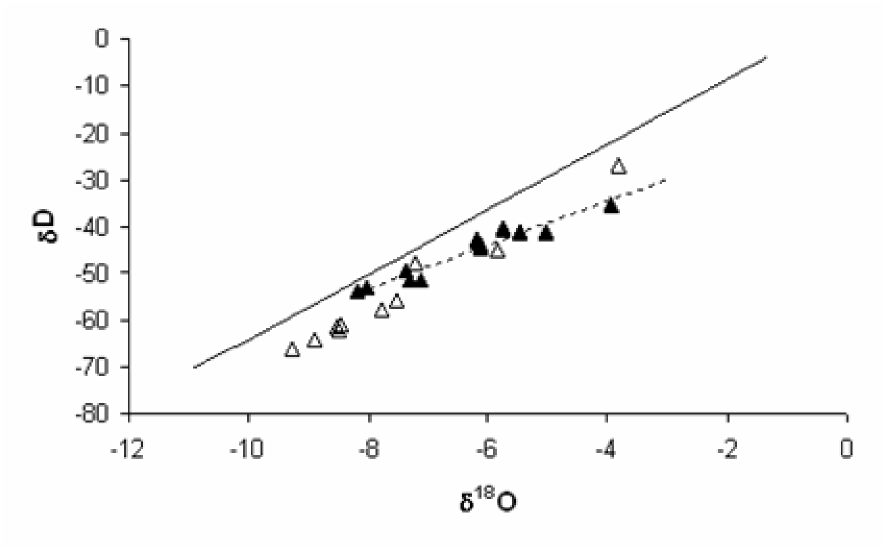
of such trace metals and to interrupt the flocculation process that concur to reduce trace metals content in the superficial waters.

The stable isotopes of the water molecule (expressed δas^{18}O and δD) provide characteristic fingerprint to investigate the provenance and the physical processes affecting the investigated shallow δwaters. During the two sampling periods the^{18}O and δD values show significant variations (Fig. 3).

In winter, waters follow a linear distribution which deviates from the local precipitations water line, indicating that evaporation is the main process controlling - at different degrees - the δ^{18}O δand δD isotopic signatures of waters. The^{18}O and δD values also suggest that the common source that feed the canals and ditches network during winter originated from the Apennine catchments, as indicated by the interception between the evaporated and meteoric lines. During summer the isotopic composition of water changes, and records the input of CER that originated in a different catchments area, i.e. the Po river one, superimposing to the evaporated waters.

Figure 3 - *δ^{18}O vs. δD diagram for the winter (solid triangle) and summer (open triangle) waters. The lines for local precipitations (solid line) and evaporation (dashed) are also shown.*



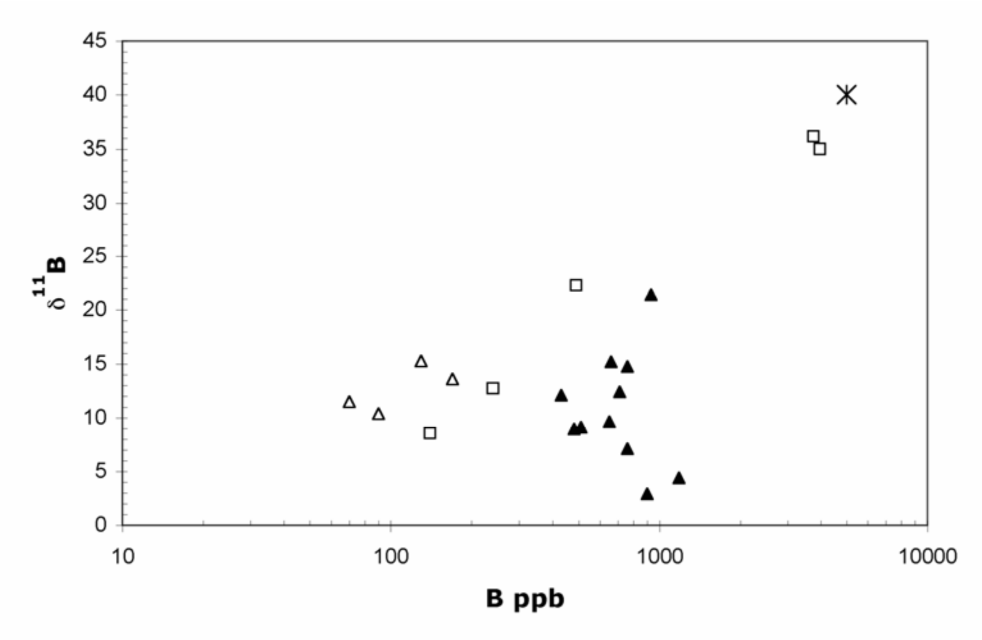
Some constrains on the origin of salinity and occurrence of anthropogenic contamination are inferred by the application of the B and Sr isotopic systematics. The boron isotopic signature of shallow waters sampled in the Ravenna costal area is generally greater than +10‰, and indicates the important role played by the marine component. A major seawater contribution is evidenced in canals sampled nearshore, as supported by the B/Cl wt ratio of 0.00026 and by δ^{11}B values of +36‰ (sea water = +40‰).

However, the process controlling the origin of dissolved boron in ditches and canals waters is not simply related to direct mixing with sea water. In fact, the B/Cl ratios higher than the marine one measured in surface waters when the irrigation network is not diluted by CER water (winter samples) indicate the existence of an additional source for boron.

This source could be related to water-soil exchanges during runoff, releasing boron adsorbed on the surfaces of Al-silicate minerals (Spivack et al., 1986). The $\delta^{11}B$ of waters is consistent with leaching of boron of marine origin, and represents a fingerprint of the prolonged exposure to sea water of the reactive fraction of alluvial sediments, as determined by the hydro-geological setting of the area (Antonellini et al., 2007).

An additional boron contribution from agricultural return flow is also evidences in some of the investigated ditches through boron isotopes (Widory et al., 2005). The B vs. $\delta^{11}B$ plot (Fig. 4) evidences that the most boron-rich samples shift their isotopic composition towards lower values (down to +3‰). This variation could be explained by an anthropogenic contribution from agricultural practice.

Figure 4 - *B vs. $\delta^{11}B$ plot. Symbols as in Fig.3, and: sea water (star), nearshore water samples (open square).*



Mass-balance calculations assuming a conservative behaviour for Cl^- ions in winter waters indicate that in canals and ditches not directly connected with the sea up to the 80% of the Sr budget did not originated from seawater.

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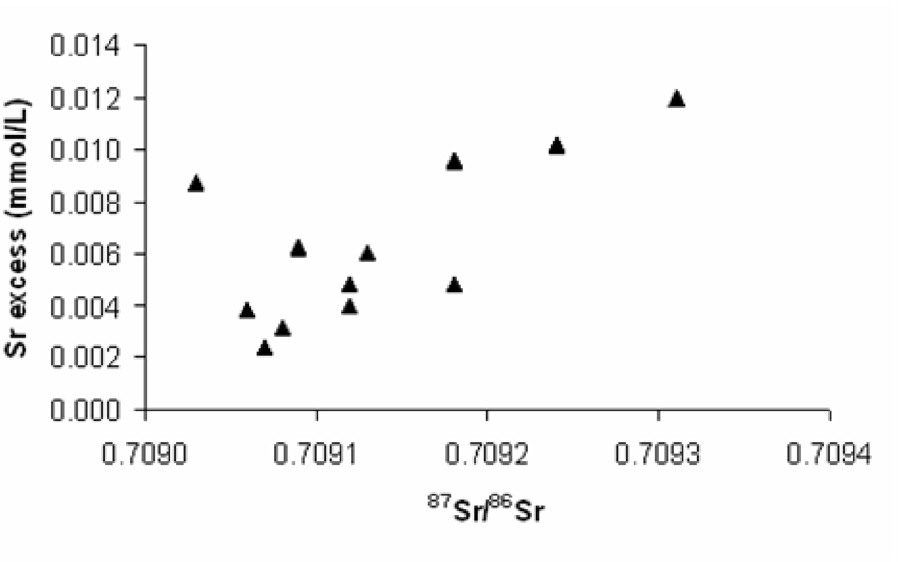
This “excess” of Sr with respect to a seawater source positively correlates with the $^{87}Sr/^{86}Sr$ ratio (Fig. 5), suggesting a source from Al-silicates mineral leaching and supporting the hypothesis of significant soil-water interactions and chemical exchanges.

Figure 5 - *“excess” Sr (mmol/L) vs.* $^{87}Sr/^{86}Sr$ *ratio diagram for winter waters (see text for explanations).*



Further constrain to this process derive from the observation that the Cl^- and Na^+ ion content in some of the waters deviates from the Na/Cl molar ratio of 0.86 expected for a seawater source towards an exceedingly high Na content, supporting Na addition to waters by weathering of the detrital silicate minerals which characterize soils.

The chemical and isotopic data indicate that the artificial recharge of waters of different quality have significant effects in diluting pernicious environmental contaminant, but at the same time deeply perturbs the natural cycling of the canal and ditch ecosystems. Related effects are likely to include mobilization and release of the small iron (and aluminum and manganese) particle precipitates, facilitating the transport of adsorbed trace metals which diffuse in the environment.

The sorption of As, Zn, Cu and Ni on $(Fe(OH)_3$-like particles has been addressed starting from their abundance in waters and surface complexation model (data-base from Dzombak and Morel, 1990), and the obtained results have been compared with the actual amount of the same trace elements measured in sediments at the water-sediment interface. It is observed that the expected concentration in sediments largely exceed what measured for As, Cu and Zn.

A great number of parameters influence sorption; however, the departure from experimental data could reflect the interruption of the oxidative precipitation cycle of iron oxyhydroxides due to the ingression of the CER waters, allowing the mobilization of colloids prior to flocculation.

The sediments in the canal network have hence the properties to retain and accumulate large amounts of potentially toxic elements, representing geochemical barriers.

Differently from As, Cu and Zn, the amount of Ni measured in sediments is higher compared with what calculated from adsorption on Fe(III)-oxyhydroxides.

A possible explanation involves the role of Mn oxides, since Ni which preferentially adsorbs on $MnO_{1.9}$-like structures.

Conclusions

The present study highlights the delicate balance of evaporation, photosynthesis-respiration, generation of colloidal particles, adsorption of trace metals, soil-water chemical exchanges and weathering reactions which establishes in canals and ditches during winter. These processes control the fate of trace metals in the crop.

The waters here investigated all have Zn, Cu, and Ni concentration lower than the limit value of the 152/2006 Normative. It is worth to note that manganese , (and seldom Fe), exceeds the Normative limit in some waters.

The addition of low ionic strength waters from CER dilutes the concentration of pernicious contaminants, but also suppresses the reactivity of the ecosystem, allowing the transport and dispersion of suspended Fe-oxide particles with sorbed potentially toxic elements such as As, Zn, Cu towards the Piallassa lagoons, where these elements are probably accumulated in the sediments, according to the process described above.

Vice-versa, Ni seems to be efficiently scavenged into the sediments of the ditches, probably through precipitation of Mn oxides. If the Mn oxides become reduced (e.g. by reaction with Fe^{2+}), large amount of Ni^{2+} might mobilize representing a potential environmental hazard.

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