



Assessment of natural background levels in potentially contaminated coastal aquifers



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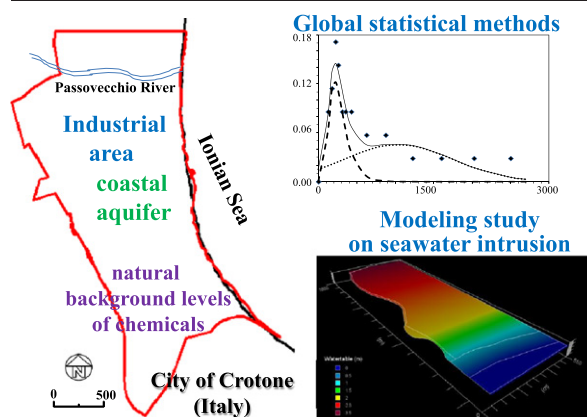
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HIGHLIGHTS

- Component Separation (CS) is applied to study natural background levels (NBL).
- Seawater intrusion could originate dispersive processes acting as external forcing.
- Mn status classified by CS is consistent with natural composition of the soil matrix.
- Sulfate status classified by CS is not consistent with seawater intrusion processes.
- CS interprets natural seawater intrusion as an anthropogenic source.

GRAPHICAL ABSTRACT



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ABSTRACT

The estimation of natural background levels (NBLs) of dissolved concentrations of target chemical species in subsurface reservoirs relies on a proper assessment of the effects of forcing terms driving flow and transport processes taking place within the system and whose dynamics drive background concentration values. We propose coupling methodologies based on (a) global statistical analyses and (b) numerical modeling of system dynamics to distinguish between the impacts of different types of external forcing components influencing background concentration values. We focus on the joint application of a statistical methodology based on Component Separation and experimental/numerical modeling studies of groundwater flow and transport for the NBL estimation of selected chemical species in potentially contaminated coastal aquifers. We consider a site which is located in Calabria, Italy, and constitutes a typical example of a Mediterranean coastal aquifer which has been subject to intense industrial development. Our study is keyed to the characterization of NBLs of manganese and sulfate and is geared to the proper identification of the importance of a natural external forcing (i.e., seawater intrusion) on NBL assessment. Results from the Component Separation statistical approach are complemented by numerical simulations of the advective–dispersive processes that could influence the distribution of chemical species (i.e., sulfate) within the system. Estimated NBLs for manganese are consistent with the geochemical composition of soil samples. While Component Separation ascribes the largest detected sulfate concentrations to anthropogenic sources, our numerical modeling analysis suggests that they are mainly related to the natural process of seawater intrusion. Our results indicate that the use of statistical methodologies in complex groundwater systems should be

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assisted by a detailed characterization of the dynamics of natural (and/or induced) processes to distinguish effective anthropogenic contamination from natural conditions and to define realistic environmental clean-up goals.

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1. Introduction

During the last decades, pressure loads acting on the soil–water environment have caused a remarkable increase in the number of locations where concentrations of one or multiple chemical species exceeding threshold values imposed by regulations are detected. Chemical compounds might also occur at naturally large concentrations for reasons which are unrelated to the effect of anthropogenic activities. The abundance of some species in groundwater might be linked, for example, to the petrographical composition of the aquifer (Hinsby and Condeso de Melo, 2006) or to the site-specific occurrence of organic matter (e.g., vegetal matter) which can enhance the release of chemical species to groundwater (Redman et al., 2002; Molinari et al., 2013). Because of factors such as (a) the strength of water–rock interactions, (b) solute residence times, (c) chemical and biological processes taking place in variably saturated host porous media, (d) interactions with other water bodies, (e) climate impacts on the subsurface environment, and (f) temporal fluctuations of flow field patterns, a given groundwater body is characterized by its own natural chemical signature. The latter may display significant space–time heterogeneity (Edmunds et al., 2003; Wendland et al., 2005; Panno et al., 2006; Edmunds and Shand, 2008; European Commission, 2009). In some cases, the application of technologies aimed at bringing the chemical status of an aquifer to a level of compliance with current regulations might not be feasible and all remediation strategies would prove to be ineffective and economically unaffordable because of unrealistic clean-up goals that might correspond to concentration levels which should be considered as the system natural background level (NBL). Procedures and criteria for a proper interpretation of the actual status of a groundwater body are outlined in the EU Water Framework Directive, WFD (2000/60/EC) and the GroundWater Daughter Directive, GWDD (2006/118/EC). These define the NBL as “the concentration of a substance or the value of an indicator, in a groundwater body, corresponding to no, or only very minor, anthropogenic alterations to undisturbed conditions”. A reliable estimation of the NBL of a target compound is required to (a) define threshold values which are consistent with specific natural features of water bodies; (b) discriminate between effective anthropogenic contamination and natural conditions; and (c) properly identify the chemical status of a groundwater body. Achieving these objectives is a critical aspect especially within regions where detected concentrations attain large values which can in turn lead to the classification of a site as potentially highly contaminated.

The most reliable approach for the estimation of the NBL of given inorganic compounds within a groundwater body is based on the analysis of samples collected at locations where water quality has not been altered by anthropogenic activities (Banks et al., 1995; Lahermo et al., 1995). The difficulty of identifying pristine portions of aquifers in populated areas has contributed to the development of other approaches. Estimating NBLs by means of global statistics of monitored data represents a relatively recent and useful tool for applications involving large scale groundwater bodies (Edmunds et al., 2003; Wendland et al., 2005; Panno et al., 2006; Edmunds and Shand, 2008; Walter, 2008). Klusman (1996) suggested grouping samples collected within target aquifer bodies into uncontaminated and contaminated sets through statistically based arguments. The idea that the empirical frequency distributions of available monitored concentration can be decomposed into a mixture composed by the contributions of natural and/or anthropogenic origin underpins the Component Separation (CS) method (Wendland et al., 2005). Application of this procedure is recommended by the EU research project BRIDGE (2007), Background cRiteria for the

Identification of Groundwater thresholds, in cases where the quality and quantity of data is sufficient for the consistent application of statistical analysis tools. Molinari et al. (2012) applied CS to assess (a) NBLs of chemical compounds in a series of large scale groundwater bodies in the Emilia Romagna Region, Italy and (b) the temporal dynamics of NBL variations. A key conclusion of this study is that, when possible, methodologies based on global statistics should be coupled with improved process understanding through robust experimental campaigns and/or detailed mathematical modeling studies aimed at characterizing the actual chemical–physical processes contributing to background concentration values within the investigated groundwater body. Following these conclusions, here we propose coupling methodologies based on global statistical analyses and conceptual/mathematical modeling of system dynamics to distinguish between the impact of different types of external forcing components influencing background concentration values.

Within the framework of brownfield remediation strategies, such as in the case of the site we consider in our demonstration study, the evaluation of the actual levels of anthropogenic contamination is key to define reliable clean up goals and avoid unnecessary and unrealistic actions under scenarios where a specific natural condition is demonstrated to take place. This issue could be addressed through the application of CS procedures. These are typically associated with an intrinsic inability to ground NBL estimates on the analysis of the key chemical–physical processes taking place in the system. In this context, a critical point is the validation of the estimated quantities through appropriate hydrogeochemical and hydrogeological studies. Coupling CS with process modeling is relevant in all coastal aquifers where the identification of the effects of tides and seawater intrusion can play a significant role for the definition of NBL (Benedini et al., 1983; Troisi et al., 1994; Bear et al., 1999; Werner and Simmons, 2009).

Coastal regions are among the most productive areas in the world. Their beauty and richness have made them popular settlement areas and tourist destinations, important business and industrial zones and transit points. The high density of population and excessive exploitation of natural resources within these areas puts enormous pressure on coastal ecosystems leading to biodiversity loss, habitats destruction, pollution, as well as conflicts between potential uses. Since the well-being of populations and the economic sustainability of a variety of businesses in coastal zones depend on the environmental status of these areas, it is essential to make use of appropriate management tools to enhance the protection of coastal resources and increase the efficiency of their uses (Al-Otaibi et al., 2006; European Commission, 2013).

As mentioned above, this paper illustrates issues related to the reliability of the results stemming from the application of the Component Separation method for NBL estimation in potentially contaminated coastal aquifers. We consider a site which is located in Calabria, Italy, and constitutes a typical example of a Mediterranean coastal aquifer which has been subject to intense industrial development. The site under consideration is part of an industrial area close to the city of Crotone and is described in details in Section 2.1. We focus our study on the characterization of NBLs of manganese (Mn) and sulfate, which are found to be associated with dissolved concentration levels which are significantly larger than threshold values defined by Italian regulations. We examine the way a natural external forcing term, as represented by the seawater intrusion process, acts on groundwater NBLs by complementing the NBL assessment procedure, based on CS, with experimental and modeling studies. To the best of our knowledge, no other studies documented the effect of such a natural external

forcing on NBLs through a joint analysis performed through CS and hydrogeological flow and transport modeling.

2. Materials and methods

2.1. History and hydrogeological settings of the study area

Fig. 1 illustrates the location of the area under study. It is located north of the city of Crotona in the Calabria Region, Italy. It is delimited to the west by the sea (Ionian Sea), and is crossed by the Passovecchio river. The development of the area was based mainly on agriculture until the late 1960. It was then devoted to intense industrial activities until 1990. Because of very large concentrations of several chemical species detected within the area (Frega et al., 2000), the industrial site was included in the wider Site of National Interest of “Crotona-Cassano-Cerchiara” whose perimeter (Fig. 1) had been established by the Italian Ministry of Environment with the DM 468/2001. The site is currently managed by private companies which are primarily involved in the (a) collection, transport, storage and shipping to disposal of hazardous wastes, (b) selection and sorting of wastes from separate collection, and (c) treatment of special wastes through advanced technology systems.

The site is part of the sedimentary basin of Crotona. The main lithological feature is constituted by the deposits of the Passovecchio river, which flows on a substrate of Pliocene clays. This alluvial debris-based lithology and the proximity to the sea give rise to a strong natural interaction between fresh groundwater and seawater (Straface, 2009).

The subsoil in the area is characterized, from bottom to top, by the lithotypes described in the following. Fig. 2 depicts a vertical section reconstructed from the core samples collected during the drilling operations for the implementation of the wells.

(a) *Silty clay with a color from gray-light to gray-blue (upper-middle Pliocene)*. This represents the base which underlies the recent

alluvial sedimentary deposits; direct investigations show that the clay formation has a thickness of over 400 m and a granulometry close to the one of silty clay.

(b) *Sands, conglomerates and biological calcarenites*. These occur upstream of the hydrogeological basin and form the coverage terracing on the Plio-Pleistocene blue clays; they extend up to a height of about 160 m above sea level and give rise to a ground surface which is almost flat and slightly sloping to the east. The biological calcarenite is strongly cemented and passes into sand in the upper layers. These sediments show some variability with depth, the fine sands near the surface giving place to thick sand and gravel layers showing increasing hydraulic conductivity (with values ranging between 10^{-5} and 10^{-3} m/s) with depth. Several surveys performed in the area showed the aquifer to be approximately 30 m deep, with the water table located at approximately 3 to 4 m below ground level.

(c) *Recent alluvial terraces*. These are emplaced on the riversides and are produced by the erosion of the blue clays and of the Pleistocene geological formation and were created by the detritic contribution due to the erosion of the hills in the area. The alluvial deposit has a variable granulometric composition, which ranges from clays to silts and sands. The thickness of these deposits varies with distance from the close clay reliefs. Outcrop analyses show that the thickness of the deposits ranges between 1 and 6 m. Well sorted deposits are alternating in space with some locations where a single granulometric fraction is dominant. The average hydraulic conductivity is within the range of 10^{-5} – 10^{-4} m/s.

The northern limit of the hydrogeological basin is characterized by a set of chalk quarries and sulfur springs marking the natural occurrence of sulfate in the basin.

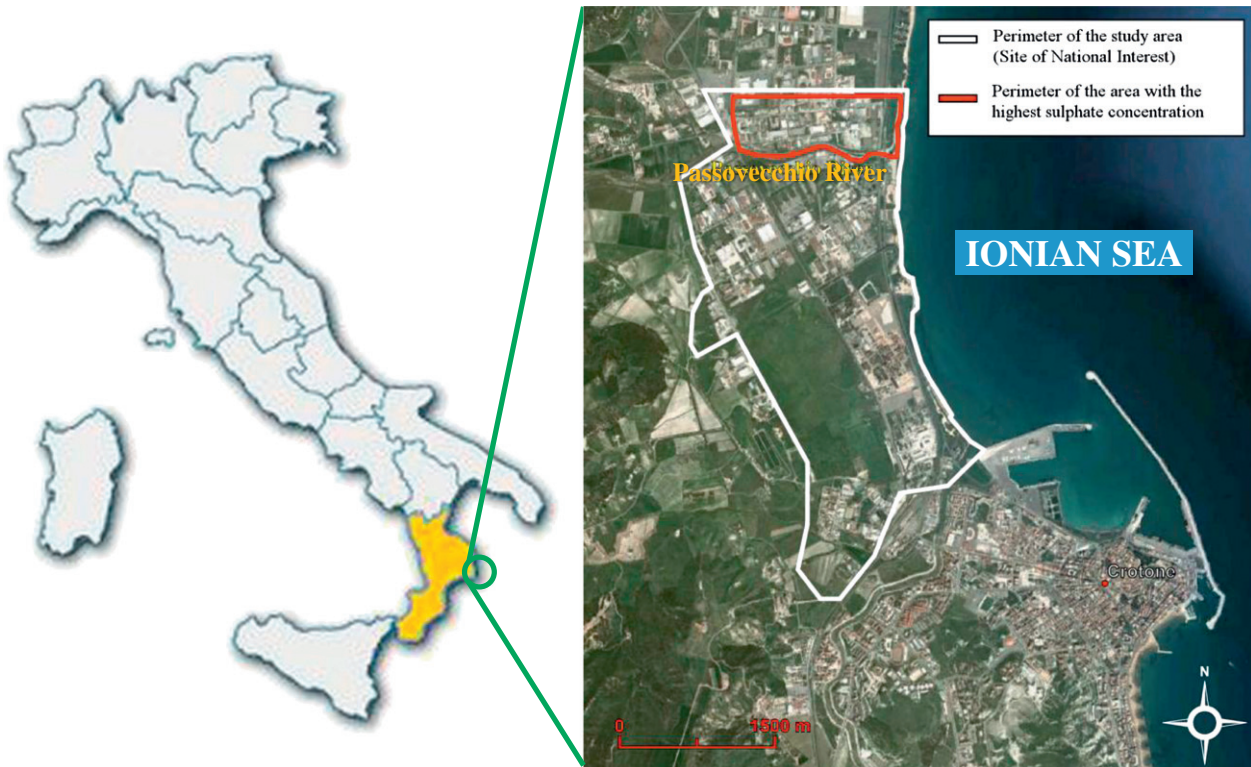


Fig. 1. Aerial photogrammetry of the region around the city of Crotona (Italy) and limits of the Site of National Interest. (Image taken from Google)

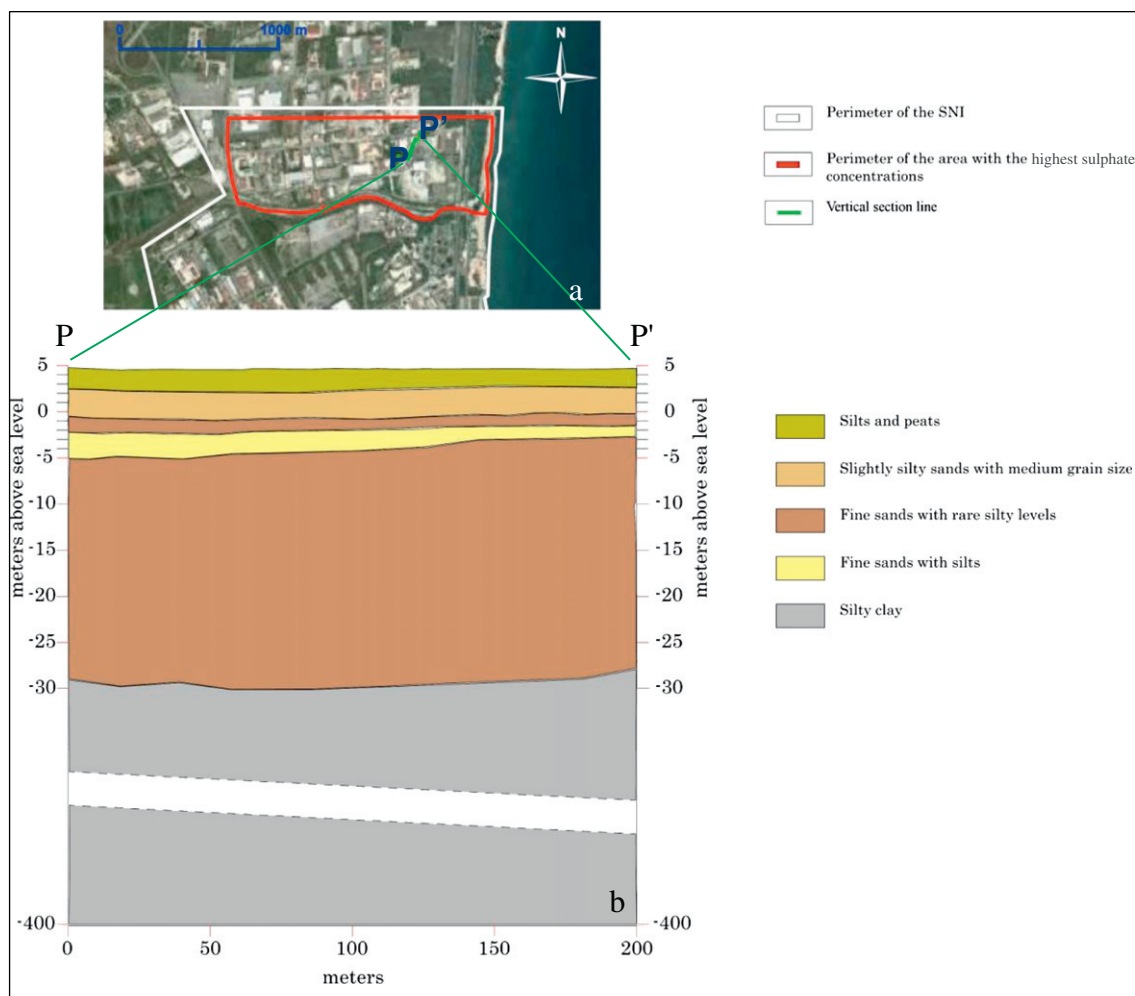


Fig. 2. (a) Trace of the cross-Section P–P' within the study area and (b) stratigraphic sequence along the trace.

2.2. Sources and mobility control factors of the selected chemical species

2.2.1. Manganese

Manganese (Mn) is one of the most abundant metals in the Earth's crust, usually occurring with iron (Graedel, 1978; Klein and Hurlbut, 1985). It can exist in 11 oxidation states ranging from -3 to $+7$. The most common oxidation states in aquatic environments are Mn(II) and Mn(IV). Transition between these two forms is largely governed by pH and redox conditions. Oxidation rates of Mn tend to increase with increasing pH or with the presence of catalytic surfaces such as manganese dioxide (Huntsman and Sunda, 1980). At lower pH and redox potential the dominant form is Mn(II) (LaZerte and Burling, 1990). In groundwater with low oxygen levels, Mn(IV) can be reduced both chemically and bacterially to the Mn(II) oxidation state (Jaudon et al., 1989). The Mn(II) ion is more soluble than Mn(IV); therefore, the bio-availability of Mn tends to increase with decreasing pH and redox potential (Heal, 2001).

Typically acceptable concentration levels of Mn in drinkable water are below 0.1 mg/L while larger values produce an undesirable taste (WHO, 1993a). Important natural sources of Mn include soils, sediments, and metamorphic and sedimentary rocks (Reimer, 1999). Manganese is found in more than 100 minerals, including various sulfate, oxides, carbonates, silicates, phosphates, and borates (Gerber et al., 2002; Howe et al., 2004). Manganese is also found as pavement-like encrustations of ferromanganese oxides on exposed abyssal hard substrates related to all types of submarine elevations (Ahnert and Borowski, 2000).

Natural levels of total Mn in soil typically range from <1 to 4000 mg/kg dry weight, with average values around 300–600 mg/kg dry weight (Cooper, 1984; Adriano, 1986; Rope et al., 1988). As an example, the Arabian Gulf contained Mn concentrations ranging from 29 to 170 mg/kg dry weight, with the highest concentrations associated with local geology (Shriadah, 1999). Similar total Mn values were found in the northern Adriatic Sea (Italy), where Mn ranges between 200 and 800 mg/kg dry weight, with an average of 370 mg/kg dry weight (Fabbri et al., 2001). Consistent with these large values in soils, dissolved Mn concentrations detected in natural waters which are not subject to anthropogenic sources can range between 10 and $>10,000$ $\mu\text{g/L}$ (Reimer, 1999).

Major anthropogenic sources of Mn in the environment include municipal wastewater discharges, sewage sludge, mining and mineral processing, emissions from alloy, steel, and iron production, combustion of fossil fuels (Schiele, 1991; WHO, 1993a). Manganese is also used in some glazes, varnishes, ceramics, and fungicides (Windholz, 1983) and can be released in the aqueous environment by industrial discharges and/or as a leachate from landfills and soil (Francis and White, 1987).

The key parameters controlling Mn concentrations in groundwater are pH and redox conditions (LaZerte and Burling, 1990). Manganese is mobilized under acidic conditions. High Mn concentrations are often found in acidic waters jointly with large concentrations of other metals such as iron, copper, zinc and arsenic, as well as sulfate, all of which are a result of oxidation of the sulfide minerals (Hem, 1992).

2.2.2. Sulfate

Sulfate occur naturally in numerous minerals, including barite (BaSO_4), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which represents the main natural sources of these compounds (Greenwood and Earnshaw, 1984). In igneous rocks sulfur occurs mostly as metallic sulfate and is rather evenly distributed in the various rock types. In shales sulfur occurs mainly as pyrite or similar iron sulfate. Coal is also an important bearer of sulfur, both as pyrite and organic matter (e.g., peat). In reduced unconsolidated sediments, in both fresh and salt-water, sulfur is also commonly found as sulfate (Cox, 1995; Hitchon et al., 1999). High sulfate concentrations in groundwater can also be attributed to thermal groundwater circulation within the host porous matrix, as suggested by Grassi and Cortecchi (2005) who detected high sulfate concentrations (up to 1680 mg/L) in the Pisa alluvial plain (Tuscany, Italy).

Regarding anthropogenic sources, sulfate are mainly employed in the chemical industry for the production of, e.g., fertilizers, dyes, glass, paper, soaps, textiles, fungicides, insecticides, astringents and emetics. They are also used in the mining, wood pulp, metal and plating industries, in sewage treatment and leather processing (Greenwood and Earnshaw, 1984). Aluminum sulfate (alum) is used as a sedimentation agent in drinking-water treatment technologies. Copper sulfate has been used for the control of algae in raw and public water supplies (McGuire et al., 1984). Atmospheric sulfur formed by the combustion of fossil fuels and metallurgical processes combined with water vapors is one of the main causes of acids rains, which are also an important anthropogenic source contributing to observed rise of sulfate concentrations in groundwater (Delisle and Schmidt, 1977).

Sulfate in drinking-water carry a distinctive taste and may contribute to the corrosion of the distribution system infrastructure. Very high sulfate levels might cause a laxative effect. It is generally considered that taste impairment is minimal at concentration levels below 250 mg/L (WHO, 1993b).

The mobility of sulfate in aquifers is mainly controlled by precipitation/dissolution of sulfate minerals (e.g., gypsum) and redox transformations between sulfate and sulfite coupled with the precipitation/dissolution of metal sulfate (Singh, 1984; Reuss and Johnson, 1986).

2.2.3. Available data

The SNI (site of national interest) area we consider in this work is heavily monitored, with a total of 66 monitoring boreholes which have been drilled at different distances from the sea and are managed by the “Agenzia Regionale per la Prevenzione e l’Ambiente della Calabria” (ARPACal – Regional Agency for Environmental Protection of Calabria). A preliminary exploratory statistical analysis of available data has been performed to identify species which can be considered as critical to the chemical status of the investigated area. Here, we base our analysis on manganese and sulfate, which are characterized by strong concentration peaks.

Manganese concentrations in the study area are found to exceed by a factor of about 80 the limit set by Italian Regulations (D.Lgs. 152/06; D.Lgs. 30/09). Manganese occurrence within the brown-field analyzed can be related to the presence of metamorphic and sedimentary rocks which is also linked to submarine elevations characterizing Calabria’s underground systems. On the other hand, because of industrial activities taking place in the study area, Mn occurrence can also be linked to emissions from alloy, steel and iron production.

Sulfate concentrations are found to exceed by a factor of about 7 the limit set by Italian Regulations (D.Lgs. 152/06; D.Lgs. 30/09). Their occurrence in the study area can be related to (a) the presence of gypsum in the soil composition, (b) the intense industrial activities (metal industries and leather processing) which took place until 1990 within the area and (c) sulfur springs located in the area.

2.3. Statistical analysis

We consider the Component Separation (CS) method (Wendland et al., 2005; Molinari et al., 2012 and references therein) which has been shown by, e.g., Molinari et al. (2012) to be compatible with the quantity and quality of the available data in a large scale aquifer of the type we investigate here. It leads to estimates of the Natural Background Level (NBL) and of the associated threshold values (TV) of the two chemical species (i.e., manganese and sulfate) which are identified as critical for the system.

2.3.1. Component Separation method

Component Separation is intended to provide a separation between natural and anthropogenically influenced contributions through a global statistical analysis of concentration series. The procedure is based upon the idea that the concentration distribution of a dissolved chemical species detected in a groundwater system is due to the combination of two components. These are respectively linked to (a) natural processes which usually result in concentrations which are distributed within the whole aquifer system and (b) the occurrence of external forces producing diffusive effects which typically result in large and isolated concentration areas. The natural component is essentially associated with the chemical-hydrogeological characteristics of the aquifer and to solid–water interaction processes. The effect of external forces is implicitly correlated to the occurrence of anthropogenic activities. In environmental settings it is particularly critical to clearly distinguish between the two types of pressure to avoid misleading representation of a system contamination source.

As detailed in previous works (see e.g., Molinari et al., 2012 and references therein), the empirical distribution of concentration values is interpreted as a mixture of distributions, i.e.,

$$f_{obs}(c) = A f_{nat}(c) + (1-A)f_{inf}(c) \quad (1)$$

where c is concentration of a given species, f_{obs} are the observed frequencies and f_{nat} and f_{inf} are the frequency distributions respectively associated with the natural and influenced components, and A is the mixture weight. Wendland et al. (2005) suggest that f_{nat} and f_{inf} are respectively described by a Log-Normal and a Normal distribution. The parameters of these two probability density functions (pdfs) are typically estimated by a calibration procedure relying on a suitable optimization criterion. Here, we have adopted the Maximum Likelihood (ML) criterion, which provides reliable estimates of distribution parameters and their associated uncertainty (see e.g., Molinari et al., 2012 and references therein).

Following the procedure suggested by Wendland et al. (2005), we constructed the empirical frequency distribution (Eq. (1)) on the basis of the set of median values which have been calculated from each available concentration time series. Parameter calibration is then followed by the computation of the range of concentrations comprised between the 10th (NBL_{10}) and the 90th (NBL_{90}) percentile of the identified Log-Normal pdf. We finally set $\text{NBL} \equiv \text{NBL}_{90}$.

2.3.2. Threshold value evaluation

European Regulations require the quantification of the threshold values (TVs) of the chemical species considered of particular interest for the good chemical status of the investigated water body. The TV represents the pollutant concentration which must not be exceeded to protect human health and environment.

TVs can be estimated on the basis of the methodology proposed by Muller et al. (2006). These authors suggest to compare the estimated NBL with the reference standard (REF) of the receiving groundwater body. Possible cases include: (a) if $\text{NBL} < \text{REF}$, then $\text{TV} = (\text{REF} + \text{NBL}) / 2$; (b) if $\text{NBL} \geq \text{REF}$, then $\text{TV} = \text{NBL}$. Appropriate reference values (REF) which are typically selected include the drinking water standards (DWS) or the environmental quality standards (EQS). In

this work we consider the threshold concentrations imposed by Italian regulations (D.Lgs. 152/06 and D.Lgs. 30/09).

3. Results and discussion

The target chemical species analyzed have not been selected on the basis of the potential toxicity related to their intrinsic chemical features but rather considering the relatively large documented number of point values exceeding the current Regulation Limits, which can be linked to a potential natural occurrence of the selected species in the groundwater system analyzed. The results of this application are supported by combining CS with (a) direct experimental observations for manganese and (b) a detailed modeling study of the groundwater system for sulfate.

3.1. Manganese

Fig. 3 shows the results of the application of CS for manganese (Mn) by depicting the empirical relative frequencies and the ML estimated components, f_{nat} and f_{inf} , contributing to the distribution (1). The reference threshold value for Mn (D.Lgs. 152/06) is $REF_{Mn} = 50 \mu\text{g/L}$, and all observed concentrations are above this limit (Section 2.2.3), suggesting the potential for a natural occurrence of this species within the investigated site.

Fig. 3 highlights that the lowest monitored concentrations (which are always larger than the regulation limit) are always associated by high relative frequencies. Low and seemingly uniform frequency values are linked to concentrations larger than about $1200 \mu\text{g/L}$. The distribution which is used to interpret the experimental data is characterized by a natural component, f_{nat} , which displays a sharp and narrow peak at about $220 \mu\text{g/L}$. On the other hand, one can note that f_{inf} is characterized by a significant spread.

Table 1 lists estimated parameters for the distributions associated with f_{nat} and f_{inf} where μ and σ respectively represent the mean and the standard deviation, and A is the mixture weight.

The estimated natural background concentrations (NBLs) obtained from the 10th and 90th percentiles of the cumulative distribution associated with f_{nat} are $NBL_{10} = 146.0 \mu\text{g/L}$ and $NBL_{90} = 463.5 \mu\text{g/L}$, respectively. Following Muller et al. (2006), then $TV_{Mn} = NBL_{Mn} = NBL_{90} = 463.5 \mu\text{g/L}$, since $NBL_{Mn} > REF_{Mn}$. The estimated threshold value is almost one order of magnitude larger than the value which is currently set through the Italian regulation.

The results stemming from the application of CS are consistent with direct experimental observations suggesting that the solid matrix of the host porous medium in the region has a rich Mn content. Analyses

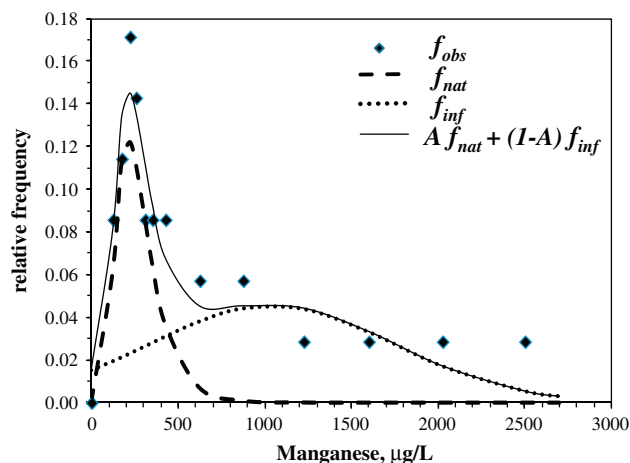


Fig. 3. Empirical frequencies, f_{obs} , of Mn together with the estimated natural (f_{nat}) and anthropogenic (f_{inf}) components, and their weighted sum ($A f_{nat} + (1 - A) f_{inf}$).

Table 1

Estimated parameters for f_{nat} and f_{inf} distributions and mixture weight of Mn concentrations.

	f_{nat}	f_{inf}
Mean μ ($\mu\text{g/L}$)	259.75	1042.03
Standard deviation σ ($\mu\text{g/L}$)	0.45	700.90
Mixture weight A	0.17	

of the total chemical element concentrations carried out by means of the UNIEN, 12457-2:2004 + UNIEN, 12506:2004 + APAT-IRSACNR 3190/B ETA-AAS methodology and performed on two soil cores collected at a depth of about 15 m in two different locations within the study area evidence Mn concentrations of 130 mg/kg and 132 mg/kg, respectively. As the possibility of an anthropogenic contribution of Mn at such depths is unlikely in the area, these large values can be solely attributed to the natural composition of the soil. This conclusion is also supported by the analysis of water samples collected from the observation wells within the study area (see Fig. 3). A clearly visible sediment layer was deposited within the sample vials after one day and independent analysis of Mn in aqueous solution and in sediments was carried out by means of the UNIEN, 12457-2:2004 + UNIEN, 12506:2004 + APAT-IRSACNR 3190/B ETA-AAS protocols. These analyses showed that: (a) dissolved Mn concentration was always below the regulation limit, while (b) a considerable amount of Mn was detected in the deposited sediments. This high concentration level of Mn associated with the sediment is similar to what observed in the soil samples mentioned above. The large Mn concentration observed in the groundwater samples can be mainly attributed to the effect of acid rainfall whose pH can reach values as low as, e.g., 4.5. Most of the manganese salts have a considerable solubility at such pH levels. These conditions are therefore consistent with (a) concentrations of Mn in soils in the order of hundreds of mg per kg and (b) the occurrence of dissolved Mn concentrations of the order of hundreds of micrograms per liter in the aquifer. On these bases, the origin of large Mn concentration detected within the investigated groundwater body appears to be associated with the specific composition of the host porous matrix constituting the examined costal system.

3.2. Sulfate

Fig. 4 depicts the results of the application of CS to the available sulfate data. It can be noted that the empirical frequency distribution peaks around the reference threshold value which is $REF_{sulf} = 250 \text{ mg/L}$ (D.Lgs. 30/09). Close inspection of Fig. 4 reveals that the natural component f_{nat} is dominant for concentrations lower than (approximately)

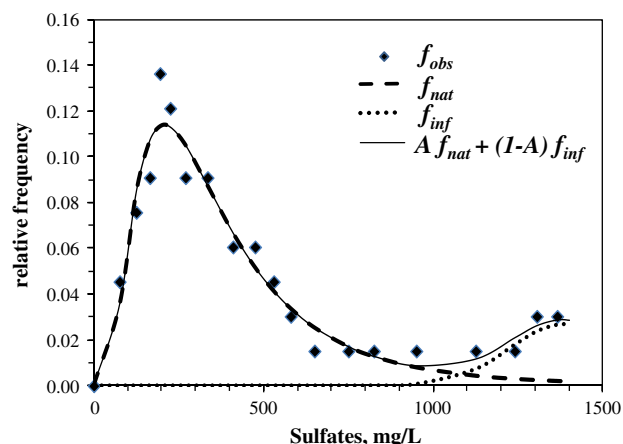


Fig. 4. Empirical frequencies, f_{obs} , of sulfate together with the estimated natural (f_{nat}) and anthropogenic (f_{inf}) components, and their weighted sum ($A f_{nat} + (1 - A) f_{inf}$).

1000 mg/L. The influenced component f_{inf} , is negligible for concentration values up to about 900 mg/L and appears to be significant at the largest concentration levels, i.e., above 1000 mg/L. These results suggest that sulfate concentrations exceeding 1000 mg/L could be mainly related to anthropogenic sources. Table 2 lists estimated parameters for f_{nat} and f_{inf} .

The estimated natural background concentrations (NBLs) obtained from the 10th and 90th percentiles of the cumulative distribution associated with f_{nat} are $NBL_{10} = 138.0$ mg/L and $NBL_{90} = 743$ mg/L, respectively. Following Muller et al. (2006), then $TV_{sulf} = NBL_{sulf} = NBL_{90} = 743$ mg/L, since $NBL_{sulf} > REF_{sulf}$. The latter value is more than twice the current regulation limit and suggests the occurrence of a high natural concentration of sulfate within the study area.

The statistically based estimation derived on the basis of the results reported above should be complemented with a proper understanding of the flow and reactive transport processes and/or geochemical dynamics taking place in the investigated area. With reference to this aspect, it is important to observe that the study area is part of a coastal system. Considering that seawater typically contains sulfate concentrations in the range of about 2700 mg/L (Hitchcock, 1975), it is clear that the examined water body is potentially exposed to seawater intrusion which is characterized by large dissolved sulfate concentrations. According to previous studies, seawater intrusion represents one of the main natural factors for increased sulfate concentrations detected in several coastal aquifers in southern Spain (up to 2070 mg/L) (Sánchez-Martos et al., 2002), Italy (2305 mg/L) (Grassi and Netti, 2000), and Cyprus (Milnes and Renard, 2004). On the other hand, saline intrusion can also be promoted by anthropogenic activities such as excessive aquifer exploitation by means of abstraction wells. This is not the case for our brownfield where anthropogenic activities have not taken place since several years. This enables us to exclude the possibility of any anthropogenic influence on saline intrusion which is considered as a natural forcing for the purpose of our study.

The investigated groundwater body is subject to seawater intrusion and related to variations of salinity content which can also promote dissolution of the host porous formation. The latter is mainly constituted by chalk ($CaSO_4$) whose dissolution can increase dissolved sulfate concentration in groundwater. From a physical standpoint, seawater intrusion can be considered as an external pressure acting on the groundwater system and originating advective–diffusive–dispersive processes which could influence dissolved concentrations and ultimately NBLs of target chemical species.

Close inspection of the spatial distribution of the monitoring wells (Fig. 5) employed for CS analysis highlights that the empirical frequencies associated in Fig. 4 with concentrations larger than 1300 mg/L are related to observation wells characterized by the shortest distance from shoreline. These wells appear to be more exposed to the effect of seawater intrusion than the other boreholes.

This observation supports the idea that seawater intrusion effects govern sulfate dynamics at these locations rather than anthropogenic actions. This observation further suggests that CS (Fig. 4) might provide misleading results by identifying the effect of an external natural pressure as an anthropogenic influence. The effect of seawater intrusion on the local groundwater system is analyzed in details in Section 3.3 through the application of a groundwater circulation model.

Table 2
Estimated parameters for f_{nat} and f_{inf} distributions and mixture weight of Sulfates concentrations.

	f_{nat}	f_{inf}
Mean μ (mg/L)	320.04	1383.77
standard deviation σ (mg/L)	0.65	160.42
mixture weight A	0.69	

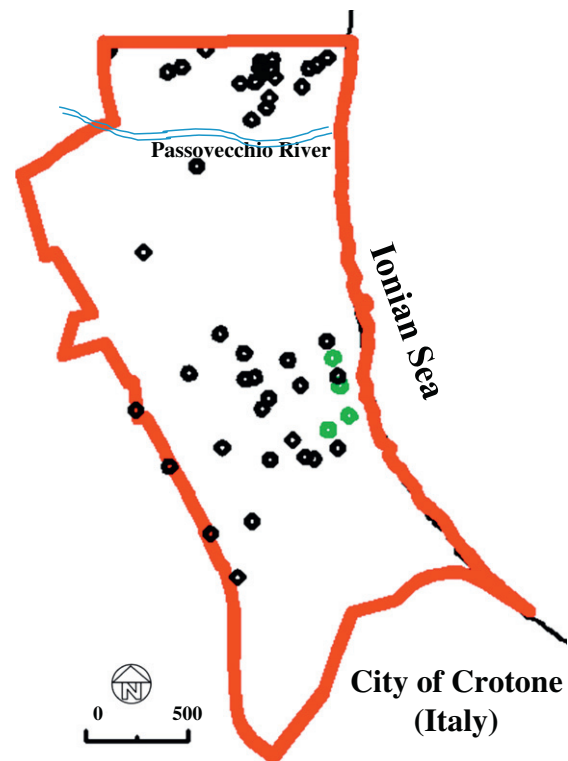


Fig. 5. Sketch of the spatial distribution of the monitoring wells within the study area. Boreholes where monitored concentrations of sulfate are larger than 1300 mg/L are highlighted in green.

3.3. Numerical modeling study on sulfate

Section 3.2 shows that the application of the Component Separation method ascribes large sulfate concentrations to the effect of anthropogenic activities. As noted by Molinari et al. (2012), this methodology is based on a global statistical analysis of data collected at a site and the results are not framed in the context of the (typically complex) hydrogeochemical processes developing in the groundwater system. To analyze these aspects, we consider the area characterized by the highest sulfate pollution (marked in red in Fig. 1) and perform numerical simulations of the advective–dispersive processes that could influence sulfate distribution in the investigated system. This area is placed on the seashore (eastern boundary) and sulfate concentration in this area tends to consistently increase with proximity to the sea. Fig. 6 depicts a sketch of the area reporting the location of the sampling boreholes. The figure also illustrates the way the average values of monitored sulfate concentration vary with distance from the sea showing that concentrations increase from a value of about 100 mg/L at a distance of 1.5 km from the sea to about 1000 mg/L in the sea.

The relatively high values of sulfate concentration detected far from the sea are consistent with the presence of chalk quarries and sulfur springs in the northern limit of the hydrogeological basin. Additional water samples were collected at points located at a distance of a few meters from the sea and arranged along different arrays normal to the coastline. The trend illustrated in Fig. 6 suggests that sulfate detected in the boreholes within the area could be consistent with the effect of seawater intrusion which tends to locally raise concentration values promoting the dissolution of the host porous matrix. A three-dimensional numerical model of density dependent groundwater flow in the area has been developed to study the impact of these processes on the groundwater system. Modeling was performed through the module SEAWAT, which is part of the widely tested numerical code MODFLOW (Hill et al., 2000). Further details on the modeling assumptions and

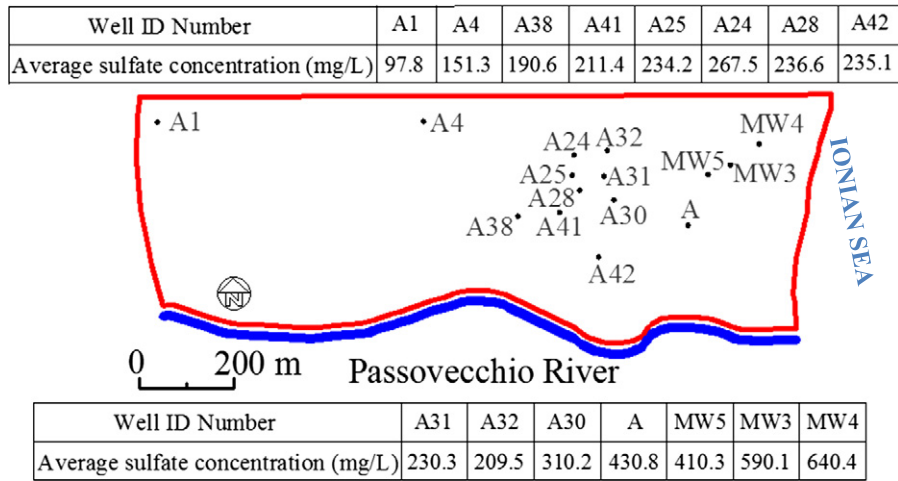


Fig. 6. Location of monitoring wells in the area where the highest sulfate concentrations are detected (see Fig. 1). Average values of monitored sulfate concentrations are reported for each borehole.

techniques adopted to simulate seawater intrusion are reported in Appendix A.

The coastal aquifer has been modeled as a homogeneous and isotropic medium with a uniform saturated thickness of 30 m. This conceptual scheme is consistent with the lithological features of the area which were evidenced from the analysis of stratigraphic columns drilled during the characterization plan of the investigated area (Straface, 2009). The coupled (transient) groundwater flow and transport problems have been solved over a simulation time of 50 years. The following boundary conditions were adopted: (1) Dirichlet boundary conditions were set on the west, south and east sides of the domain, while (2) no-flow conditions have been imposed on the north boundary of the model domain. Hydraulic head values set along the west boundary are consistent with the presence of the Passovecchio river in the south-west corner of the domain and the well A1 close to the north-west corner (see Fig. 5). Hydraulic heads determined by the Passovecchio river are imposed along the south side.

Hydraulic parameters (hydraulic conductivity and porosity) have been estimated through a calibration procedure, based on measured hydraulic head values at the site. The reference hydraulic head distribution employed for the definition of the boundary conditions and the experimental head observations within the site considered for hydraulic parameter calibration have been measured in October 2007. This scenario corresponds to the lowest seasonal fluctuation of the water table level, which occurs after the summer period (i.e., it is the condition of minimum natural recharge for the aquifer), and represents the natural condition of highest vulnerability to the seawater intrusion phenomenon. Estimation of hydraulic parameters has been performed through minimization of the residual between observed and simulated hydraulic heads by an inverse modeling procedure which relies on coupling a steady state groundwater flow model with the optimization code PEST (Parameter ESTimation model by Doherty, 2006). This resulted in a hydraulic conductivity value of 3.9×10^{-5} m/s, and a porosity of 0.25, which are consistent with information taken from the geological maps of the area and characterization studies carried out in the SNI (Straface, 2009). Fig. 7 shows a scatterplot of hydraulic head values calculated through the calibration procedure against the corresponding observed values.

Quantification of sulfate intrusion in the aquifer has been performed by adopting the following input data in the numerical transport model. A constant sulfate concentration of 1026.1 mg/L is set on the eastern boundary, as obtained from the analysis of samples collected in the sea. A constant sulfate concentration of 97.8 mg/L is imposed along the western boundary, consistent with concentrations detected in the monitoring well A1, located at a distance of about 1.5 km from the sea

(Fig. 6). This value is not associated with the effect of seawater intrusion, given the distance from the sea as is consistent, as stated above, with the presence of chalk quarries and sulfur springs at the northern limit of the hydrogeological basin. A longitudinal dispersivity coefficient of 200 m is employed, while the transverse dispersivity coefficient was set to be one-tenth of the longitudinal one. This value is consistent with previous studies (e.g., Troisi et al., 1992) for sandy aquifers with an extension of a few kilometers.

Fig. 8 juxtaposes the modeled and observed sulfate concentrations. The model-calculated curve represents concentration values which are reached in the system when steady flow conditions are attained and detected along a line perpendicular to the coast that passes through the center of the model domain depicted in Fig. 6. Fig. 8 highlights that at distances which are less than about 450 m from the sea, the seawater intrusion leads to sulfate concentrations exceeding $REF_{sulf} = 250$ mg/L, which represents the threshold concentration imposed by the Italian legislation. Oscillations observed in the experimental data can be attributed to local aquifer heterogeneities which are not explicitly included in the numerical model.

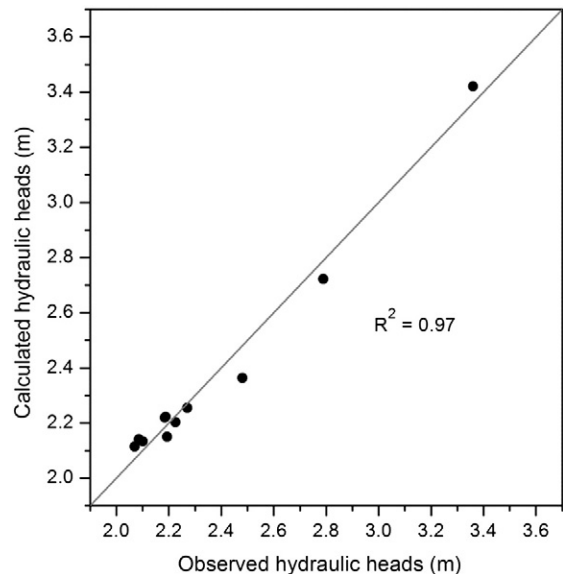


Fig. 7. Scatterplot between observed and calibrated hydraulic head values. Observed heads were measured in the monitoring wells reported in Fig. 5.

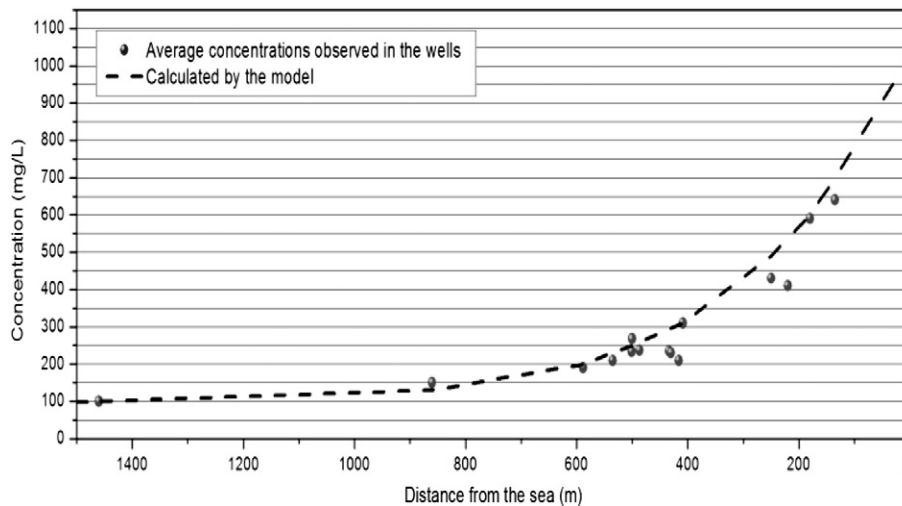


Fig. 8. Comparison between average experimental measurements and model-calculated sulfate concentrations.

Comparison between the results stemming from the modeling study on sulfate in the context we analyzed and the global statistical method based on Component Separation suggests that the latter identifies the existence of an apparent anthropogenic contamination component while the detected large concentration levels can be related to the influence of a specific natural condition. This observation strengthens the idea that the application of the Component Separation method, especially on localized scenarios of the kind we analyze in the target system, should always be accompanied by a careful examination of the site-specific situation and should be assisted by modeling studies which enable one to (a) describe the actual effect of processes occurring in the environment under investigation and (b) avoid providing estimates of NBL which are not consistent with the actual dynamics taking place in the investigated system.

4. Conclusions

We discussed the joint application of the Component Separation method, experimental site characterization studies and conceptual/mathematical modeling of flow and transport processes taking place in the system for NBL estimation in a coastal area which can be considered as a typical example of a Mediterranean coastal aquifer where heavy industrial development has taken place. The site we consider is located in Calabria, Italy, and is characterized by potentially high contamination levels. We focused on two chemical species, manganese and sulfate, which are found in the system with concentrations significantly larger than threshold values provided by Italian regulations. Our work leads to the following major conclusions.

1. Component Separation provided an NBL value of 463.5 $\mu\text{g/L}$ for manganese. The latter is more than nine times larger than the current limit set by Italian regulations. We show that this result, which associates the detected large dissolved Mn concentration with natural forcings, is supported by manganese concentration levels measured in undisturbed soil cores collected in the study area. These experimental evidences support the conclusion that the manganese detected with large concentrations in groundwater, is due to (a) its high occurrence in the soil and (b) the effect of acid rainfalls which infiltrate into the subsoil.
2. The application of the Component Separation method for sulfate revealed that concentrations larger than 1000 mg/L could be mainly related to anthropogenic sources. The spatial trend observed for sulfate concentration (with values increasing with

proximity to the sea) suggested that sulfate levels detected in monitoring boreholes can also be consistent with seawater intrusion processes. This hypothesis has been assessed through a detailed modeling study focused on seawater intrusion in the coastal aquifer. Results from the modeling study suggested that seawater intrusion can be the main reason for increased sulfate concentrations in the tested coastal aquifer.

3. Seawater intrusion in a coastal aquifer could be considered as an external forcing acting on the investigated groundwater system and able to originate diffusive processes directly linked to natural phenomena. These can be interpreted by the Component Separation method as the occurrence of an anthropogenic source within a given area while they can be unrelated to human activities, as in the case we have examined. For these reasons, global statistical methods such as Component Separation could lead to severe underestimation of NBLs in presence of a natural external forcing component. This is related to the observation that the methodology does not take into account the effect of the diverse types of physical-chemical-biological processes which take place within a reservoir and may occur through interface/boundary regions of the delineated groundwater system.
4. As a major consequence, our study highlights the need to validate current statistically based NBL assessment procedures with accurate hydrogeochemical/hydrogeological modeling results to minimize the possibility of interpreting naturally induced concentrations as anthropogenic effects. Complex groundwater systems of the kind we analyze here require a detailed characterization of the dynamics of natural (and induced) processes to distinguish effective anthropogenic contamination from natural conditions and to define clean-up goals consistent with the specific natural features of the analyzed water body. This is dramatically important, especially in light of the costs of aquifer management practices and remediation actions.
5. The methodological nature of our study renders it transferable to diverse situations, which are not necessarily restricted to coastal aquifers. As such, while the specific application might be of local nature, the framework is of broad transferability.

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Appendix A

The density dependent groundwater flow equation employed in the numerical model is:

$$\nabla \cdot \left[\rho \frac{\mu_0}{\mu} K_0 \left(\nabla h_0 + \frac{\rho - \rho_0}{\rho_0} \nabla z \right) \right] = \rho S_{s,0} \frac{\partial h_0}{\partial t} + \theta \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t} - \rho_s q_s \quad (\text{A.1})$$

where ρ is the fluid density [ML^{-3}] at the reference concentration and reference temperature, μ is dynamic viscosity [$\text{ML}^{-1} \text{T}^{-1}$], K_0 is the hydraulic conductivity tensor of the porous medium saturated with freshwater [LT^{-1}], h_0 is the hydraulic head [L] measured in terms of freshwater, $S_{s,0}$ is specific storage [L^{-1}], θ is porosity [–], C is salt concentration [ML^{-3}] and q_s is a source/sink [T^{-1}] of fluid with density ρ_s .

Solute transport is modeled through:

$$\nabla \cdot [\theta D \cdot \nabla C - \nabla \cdot (qC)] = \left(1 + \frac{\rho_b k_d}{\theta} \right) \frac{\partial (\theta C)}{\partial t} + q_s C \quad (\text{A.2})$$

where D is the hydrodynamic dispersion tensor [$\text{L}^2 \text{T}^{-1}$], q is specific discharge [LT^{-1}], ρ_b is the bulk density [ML^{-3}], k_d is the distribution coefficient of solute [$\text{L}^3 \text{M}^{-1}$] and C_s is the source/sink concentration [ML^{-3}]. The equation of state, which relates fluid density to solute concentration, temperature, and pressure, is obtained using the first term of a series expansion of the volumetric expansion coefficients for solute concentration, temperature and pressure (Bear, 1979):

$$\rho = \rho_0 + \frac{\partial \rho}{\partial C} (C - C_0) + \frac{\partial \rho}{\partial T} (T - T_0) + \frac{\partial \rho}{\partial p} (p - p_0) \quad (\text{A.3})$$

where T is temperature [K] and p is pressure [$\text{ML}^{-1} \text{T}^{-2}$].

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