

Mobilisation processes responsible for iron and manganese contamination of groundwater in Central Adriatic Italy

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Abstract Iron and manganese are two of the most common contaminants that exceed the threshold imposed by international and national legislation. When these contamination occurs in groundwater, the use of the water resource is forbidden for any purposes. Several studies investigated these two metals in groundwater, but research focused in the Central Adriatic area are still lacking. Thus, the objective of this study is to identify the origin of Fe and Mn contamination in groundwater and the hydrogeochemical processes that can enrich aquifers with these metals. This work is based on hydrogeochemical and multivariate statistical analysis of analytical results undertaken on soils and groundwater. Fe and Mn contamination are widespread in the alluvial aquifers, and their distribution is regulated by local conditions (i.e. long residence time, presence of peat or organic-rich fine sediments or anthropic pollution) that control redox processes in the aquifers and favour the mobilisation of these two metals in groundwater. The concentration of iron and manganese identified within soil indicates that the latter are a concrete source of the two metals. Anthropogenic impact on Fe and Mn contamination of groundwater is not related to agricultural activities, but on the contrary, the contribution of hydrocarbons (e.g. spills) is evident.

Keywords Anthropogenic impact · Central Italy · Metal mobilisation · Natural groundwater contamination · Redox processes · Statistical analysis

Introduction

Deterioration of groundwater quality, connected to both anthropogenic influences and natural processes, is becoming a source of major concern for the wider communities. Greater demands for clean water and the need to protect the environment make good water resource management an important theme for the protection of both groundwater and surface waters.

Iron and manganese are two of the most common elements in the environment, and thus, humans are exposed to significant quantities of these metals that are present in food and water. Some studies show negative health effects, at least on the neonatal population (Ritter et al. 2002; Grazuleviciene et al. 2009).

Iron is considered as non-desirable in water when it reaches concentrations of as little as 0.3 mg/l, due to its tendency to alter the water turbidity, the colour (yellow-reddish) and the taste (WHO 2003, 2006, 2011b). The health-based threshold for manganese is set to 0.4 mg/l, which is significantly higher than the concentration normally found in potable water supply (WHO 2011a). For this reason, a formal maximum concentration has never been set. Manganese alters the taste of water with concentrations as low as 0.1 mg/l. Such small concentrations also stain toilet and sink units and clothes. Therefore, the maximum acceptable concentration for manganese in water is below the health-based threshold of 0.4 mg/l (WHO 2011b).

Iron and manganese are considered contaminant in the international and national legislation (EU 1998, 2000, 2006; IR 2006, 2009; WHO 2011a), and for this reason, Concentration

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Limits of Contamination (CLCs) are defined for groundwater (Table 1). In particular, for the Italian legislation, when groundwater concentrations for specific parameters exceed the CLC, the site is considered potentially contaminated and the use of the water resource is forbidden for any purposes. In these cases, the site is considered potentially contaminated and additional site investigation is required to identify the origin of the contaminant. Containment and remediation are necessary if the source of contamination is anthropogenic, while they are not required when high contaminant concentrations are naturally occurring. In such cases, the natural background levels should be increased, taking into account the naturally occurring high concentrations at the site

The objective of this study is to identify the origin and the hydrogeochemical processes that are responsible for the elevated concentrations of Fe and Mn detected in groundwater, in order to correctly address the use of water resources and the management of the polluted sites.

The study focused on a Central Adriatic area of about 5400 km² in which a large amount of groundwater and soils chemical analysis were observed (Fig. 1). The geological and hydrogeological framework of the study area is similar to several Mediterranean areas; thus, principles and methodology used in this research should be of benefit for them.

Although several studies have investigated the presence of these two metals in groundwater within different geographical and geological contexts (O’Day et al. 2004; Wang et al. 2006; Root et al. 2009; Homoncik et al. 2010; Rotiroti et al. 2014; Upadhyaya et al 2014; Huang et al. 2015), studies focused on this topic, even at regional scale, are still lacking in the study area.

The presence of iron and manganese in the environment has been widely investigated in the literature. These two metals share many chemical properties and in many aspects have similar behaviour in aquatic environments (Giblin 2009). Both of them are redox-sensitive metals that are highly common in nature. Their oxidised forms are not soluble, while the reduced forms have a greater solubility (Schwab and Lindsay 1983; WHO 2003, 2011b). For this reason, iron and manganese in natural waters can be found dissolved, as colloids or as ionic or organic-metal complexes (Waber et al. 1990; Postma

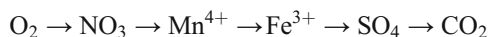
and Appelo 2000; Cornell and Schwertmann 2006; Appelo and Postma 2005).

Almost all rocks have some percentage of iron and manganese. Weathering processes mobilise these metals from the primary minerals (Langmuir et al. 1997; Cornell and Schwertmann 2006; Bradl 2005; Gilmour and Riedel 2009) to enrich soils and subsoil as residual phase (Shacklette and Boerngen 1984; Botes 2004; Botes and Van Staden 2007; Alloway 2013; Palmucci and Rusi 2013).

In general, metals are present in soils as free ionic forms, as organic and inorganic soluble complexes, related with organic and inorganic mobile colloidal forms, or as mineral phases. The total content in each metal is the sum of the different form present; thus, iron and manganese mobilisation is related to the correspondent form in pedogenic layer (Bowen 1979; Howe et al. 2004; Vance 1994). When soil leaching occurs, for rainfall seepage or for piezometric level raising in shallow aquifers, the most mobilisable iron and manganese forms move to groundwater (McLean and Bledsoe 1992; Ford et al. 2007).

In the saturated zone, redox processes influence the quality of groundwater through the mobilisation of the metal elements that are present in the subsurface (McMahon and Chapelle 2008; Jurgens et al. 2009). Iron and manganese are two of the metals that are commonly involved in the redox reactions, which in turn determines the distribution and concentration of the metals. Reducing conditions are generally favoured by the presence of micro-organisms that facilitate the transfer of electrons between the different ions. The redox processes are heavily influenced by the organic matter oxidation (Lindsay 1991; Chen et al. 2003; Pezzetta et al. 2011; Molinari et al 2014; Rotiroti et al. 2014) and by the complexity of the hydrogeological context, with particular reference to the groundwater residence times within the aquifer (McMahon and Chapelle 2008).

The compounds that produce the largest amount of available energy are reduced first. The least favourable are subsequently reduced based on the following order:



This process continues until the electron donor and acceptor have been completely used (Berner 1981; McMahon and Chapelle 2008; Jurgens et al. 2009).

Human activities can also contribute to the release of iron and manganese into the environment as these metals are commonly used in industry, agriculture or landfilling activities (Ferraz et al. 1988; Ruijten et al. 1994; Mikac et al. 1998; WHO 2003). Further, hydrocarbon spills also contribute to the mobilisation of iron and manganese in waters as the degradation of the organic compounds favours the redox reactions that cause their mobilisation (Tucillo et al. 1999; Berbenni et al. 2000; Atekwana et al. 2005).

Table 1 National and international limits for iron and manganese concentration in groundwater and public water supply

	Drinking water ^a			Groundwater	
	WHO	EU	IR	EU	IR
Fe	0.3 ^a	0.2 ^a	0.2 ^a	0.2	0.2
Mn	0.1 ^a	0.05 ^a	0.05 ^a	0.05	0.05

Concentrations are expressed as milligrams per litre

^a These are qualitative guideline values and not standards as there is no health based threshold

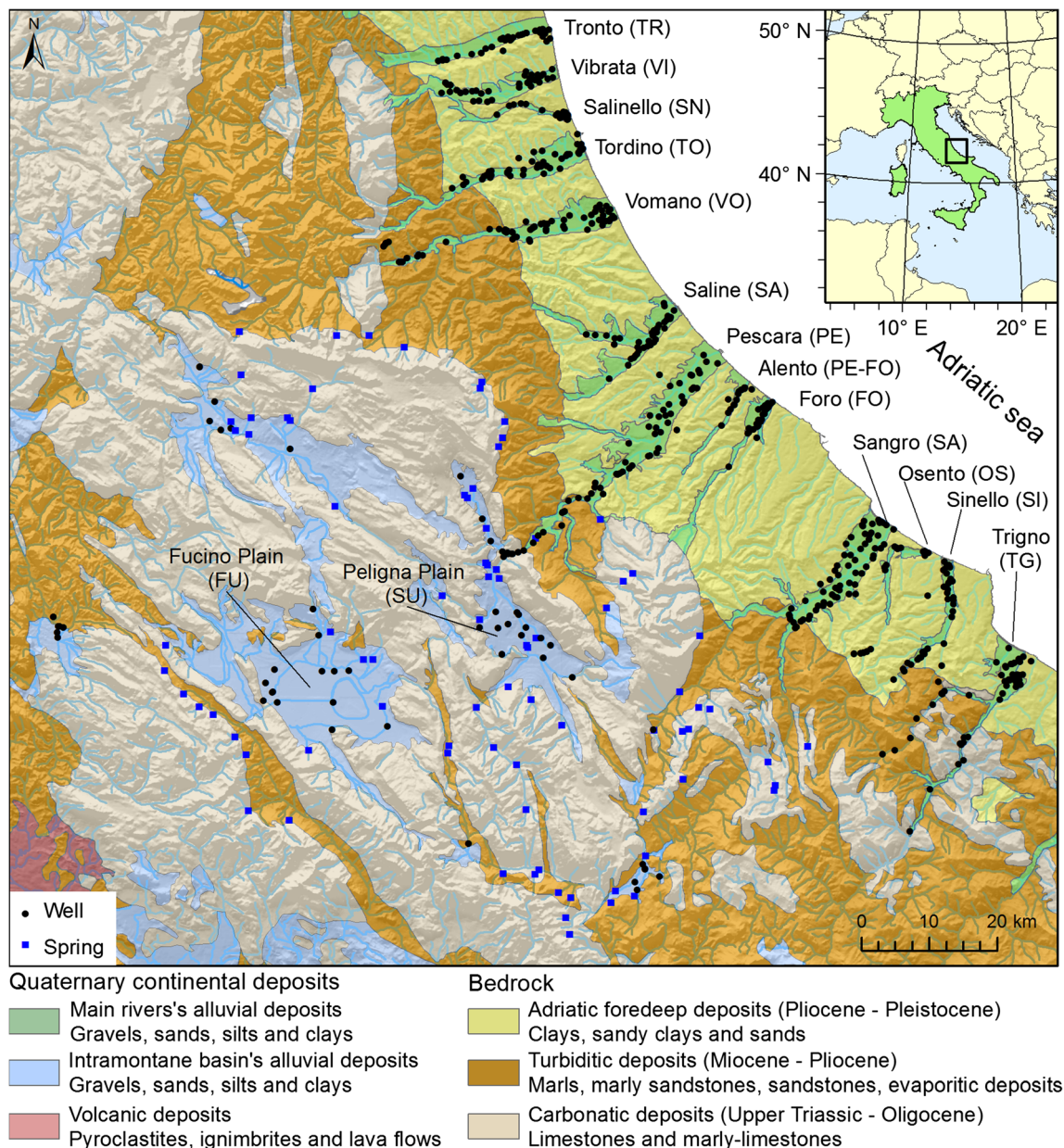


Fig. 1 Main lithotypes present in the study area and locations of the monitoring points

Geological and hydrogeological framework

The litho-structural characteristics of the study area support the identification of three distinct types of aquifers (Fig. 1).

The Apennine Chain carbonatic aquifers lie to the west. Moving to the east, these are followed by the alluvial aquifers of the intramontane basins and, finally, the alluvial aquifers of the fluvial plains that extend towards the Adriatic Sea (Desiderio and Rusi 2004; Desiderio et al. 2010; Desiderio et al. 2012; Fiorillo et al. 2015) (Fig. 1).

The limestone aquifers are constituted by limestone-dolomitic and limestone-marly successions belonging to various paleogeographic domains. These aquifers, which

are dominated by secondary permeability connected to fracturing and karst, supply high-yield springs or spring lines. These springs generally show little seasonal variability and thus prove that they are fed by extensive recharge areas. The main springs are located at the margins of the aquifers where these come into contact with the aquicludes, represented by the silico-clastic deposits of the Adriatic foredeep, or with the aquitards, represented by quaternary continental deposits (Celico 1983; Boni et al. 1986; Nanni and Rusi 2003; Fiorillo et al. 2015). The main springs are generally either contact springs or depression springs, and many are captured for public water supply or hydroelectric power generation.

The intramontane alluvial aquifers are located within tectonic depressions and surrounded by limestone structures. The aquifers are constituted by terrigenous, detritic, lacustrine and alluvial deposits that originated from the weathering of the surrounding mountains and which filled the tectonic depressions since the Pliocene (Burri and Petitta 2004; Desiderio et al. 2010, 2012) (Fig. 1).

The deposits that fill the depressions are lithologically and granulometrically heterogeneous. This gives rise to multi-layered aquifers which are delimited by low permeability sediments and can locally determine semi-confined conditions (Desiderio et al. 2012). Recharge to the intramontane aquifers is from discharge from the surrounding mountains and from overlying surface water bodies. These aquifers are exploited through boreholes for civil, industrial and agricultural use.

The alluvial valley aquifers are made up of alluvial bodies constituted by levels and lenses of gravels and sands that are immersed in a silty-clayey or silty-sandy matrix. The plio-pleistocene bedrock deposits underlie and border the alluvial valley aquifers (Fig. 1). In general, these aquifers can be considered shallow phreatic aquifers; however in some areas and particularly in the coastal areas, the aquifers can become multi-layered. These aquifers can locally be semi-confined due to thick and laterally extensive low permeability deposits (Desiderio et al. 1999, 2003, 2010). The alluvial bodies are permeable due to primary porosity, which varies based on the granulometric properties of the deposits. The hydraulic conductivity of the more permeable deposits varies between 10^{-3} and 10^{-4} m/s, while hydraulic conductivities in the silty and silty-clayey deposits vary between 10^{-5} and 10^{-6} m/s (Celico 1983; Desiderio et al. 2007). Therefore, aquifer yields vary as a function of the permeability and of the thickness of the deposits, which increases moving downstream to thicknesses of up to 50 m (Desiderio et al. 1999). The alluvial valley aquifers are frequently used for civil, industrial and agricultural purposes.

The hydrochemical classification (Fig. 2) shows that samples from the Apennine limestone aquifers have a Ca-HCO₃ facies with frequent enrichments of Mg and SO₄. The main facies of the intramontane aquifers is Ca-HCO₃ with enrichments of Na, Mg and Cl. The groundwater hydrochemistry of the alluvial valley aquifers is more variable and complex. The main hydrochemical facies is Ca-HCO₃, but Ca-SO₄ and Na-Cl facies are frequent.

Iron and manganese are among the most common contaminants in this hydrogeological framework. Approximately 14 % of the samples show iron contamination (i.e. concentration above the CLC), with maximum concentrations reaching 45.8 mg/l. Manganese is even more widespread with 30 % of the samples showing exceedance of the CLC and maximum concentrations of 13.6 mg/l.

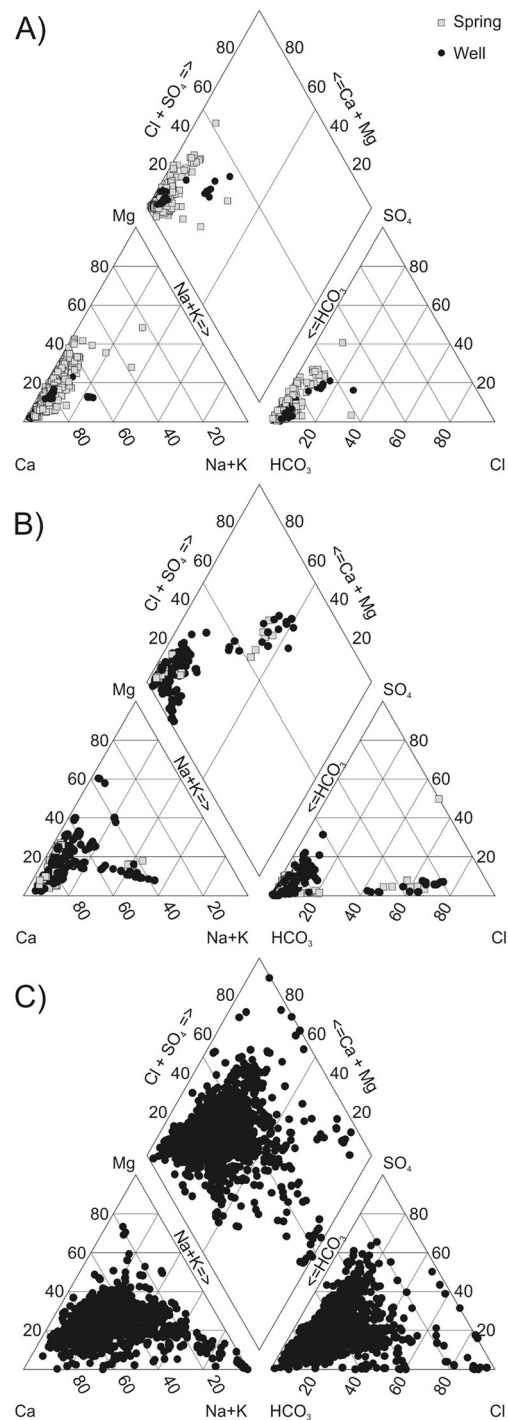


Fig. 2 Piper diagram for the three main types of aquifers. **a** Apennine limestone aquifers. **b** Intramontane alluvial aquifers. **c** Adriatic alluvial valley aquifers

Materials and methods

The groundwater chemistry was assessed through the data made available by the Regional Environment Protection Agency (Agenzia Regionale per la Tutela dell’Ambiente, ARTA, Progetto regionale “Inquinamento Diffuso”,

ARTA - Abruzzo, unpublished data, 2011–2012) and by the Abruzzo Region (Piano di Tutela delle Acque, Regione Abruzzo, unpublished data, 2010–2011). Groundwater samples were collected in a monitoring network of 653 points distributed within the principal aquifer of the study area.

Approximately 2000 samples, collected between 2010 and 2012 and analysed at the ARTA laboratories, were assessed as part of this work. The electrical conductivity (EC), pH and ORP (using Ag/AgCl reference) were measured in the field with a portable multi-parameter unit. Water samples were filtered in field at 0.45 µm in nitrogen flux, collected in polyethylene bottles and stored in refrigerated containers. One fraction was acidified with HNO₃ in the field after filtration for major cations and trace elements determination. Subsequently, the samples were analysed to the standard methods set out in the Italian legislation (APAT 2003). In particular, the major anions (Cl, SO₄) were analysed by ion chromatography, the major cations (Ca, Mg, Na, K) by optical emission spectroscopy (ICP-OES), the bicarbonates in laboratory by HCl titration, the dissolved oxygen by iodometric titration and the trace elements, including Fe and Mn, by inductively coupled plasma mass spectrometry (ICP-MS). Finally, total hydrocarbons were analysed by IR spectroscopy, while pesticides by Gaschromatografy.

A representative set of results was selected and used for charts in this study for those locations that had more than one set of results. The representative set of results was selected on the basis of the completeness of the analytical set, the ionic balance (<10 %), the timing of the sampling and the level of contamination.

A set of 360 analytical results from soils taken at 302 locations (whose distribution is shown in part 4.4) were also assessed. The soil sampling sites and the groundwater monitoring points do not overlap; however, they were executed in the same areas.

The analytical results were made available by the regional agency of agriculture (Agenzia Regionale per l' Agricoltura). The soil samples were collected as part of an assessment

programme on soil fertility (Studio regionale della fertilità dei suoli, ARSSA - Agenzia Regionale per l' Agricoltura, unpublished data, 1999).

The soil samples were collected at depths between 40 and approximately 150 cm. The study assessed various properties of the soil and also several minor inorganic elements like iron and manganese, in terms of total and solubilisable concentration. Total concentrations were assessed through solubilisation in a heated nitric-hydrochloride solution and determination with a plasma emission spectrometer (ICP-AES). Solubilisable concentrations were also assessed with a ICP-AES following the extraction process with diethylene triamine pentacetic acid (DTPA). The iron and manganese concentrations from soils were correlated to the concentrations of the two metals within groundwater.

The large quantity of available data suggested an explorative statistical approach to address the analysis. This was undertaken by means of a principal component analysis (PCA) that was chosen, as it is one of the most powerful and used techniques to analyse the interrelationship among different sets of groundwater (Briz-Kishore and Murali 1989; Voudouris et al. 1997; Dragon 2006; Furi et al. 2012; Belkhiri and Narany 2015).

PCA was undertaken using the Varimax criteria (Kaiser 1958), and components were extracted in agreement with both the Kaiser criteria (eigenvalue >1) and with the Scree plot criteria (Cattel 1966). The parameters introduced in the factorial analysis were selected after assessing the availability, spatial frequency and role within the hydrogeochemical processes that occur in the aquifer. Temperature was not considered as its variability is related to the seasons rather than the hydrochemical processes that occur in the aquifer. The pH was excluded because this parameter, in this particular hydrogeological context, is strongly dependent on hydrochemical facies. Therefore, the statistical method used would not have allowed to individuate significant correlation with iron and manganese contamination, which is less common than water-rock interaction and salinisation processes. Furthermore, in these hydrogeological context, the pH values

Table 2 Principal categories and dominating redox processes within groundwater

Redox category	Redox process	Description
Anoxic	Fe ³⁺ /SO ₄ ^a	Fe ³⁺ reduction or SO ₄ reduction
	Mn ⁴⁺	Mn ⁴⁺ reduction
	NO ₃	NO ₃ reduction
Mixed (anoxic)	Fe ³⁺ /SO ₄ ^a -NO ₃	Co-existence of reduction processes of Fe ³⁺ /SO ₄ and NO ₃
	NO ₃ -Mn ⁴⁺	Co-existence of reduction processes of NO ₃ -Mn ⁴⁺
Mixed (oxic-anoxic)	O ₂ -Fe ³⁺ /SO ₄ [*]	Co-existence of two separate redox processes
	O ₂ -Mn ⁴⁺	Co-existence of two separate redox processes
Oxic	O ₂	Aerobic respiration/oxygen reduction

^a The method does not permit distinguishing between reduction of iron and reduction of sulphates as the presence of sulphurs was not undertaken

show a small variability (mean 7.1–7.7; standard deviation 0.3–0.4).

Subsequently, the spatial distribution of iron and manganese in groundwater was assessed to identify the most contaminated aquifers and the possible local conditions influencing Fe and Mn presence in groundwater. Groundwaters were classified, according to the criteria set out by Berner (1981), McMahon and Chapelle (2008) and Jurgens et al. (2009), in order to verify the role of redox processes in Fe and Mn contamination.

The classification permitted organising the samples on the basis of the dominating redox process (Table 2).

Given that soils are generally considered an important source of iron and manganese, a comparison between the presence of these two metals in soils and in groundwater was performed. Further, seasonal effects due to the rising of groundwater levels were analysed, in order to assess the influence of soil leaching on iron and manganese concentrations. This analysis was performed on 33 monitoring points selected for redox classification of groundwater (mixed or anoxic), water table shallower than 3 m (comparable with soil thickness) and sampling results available over different periods of the year (wet and dry season).

The possible effects of human activities on the contamination were assessed by identifying possible correlations with other contaminants that may originate from human activities. In particular, correlation with the presence of total hydrocarbons (THC) and total pesticides (TPs) in groundwater was considered.

Hydrocarbons do not include iron or manganese in their molecule. However, hydrocarbons were selected for their

mostly organic nature that favour reducing conditions able to mobilise iron and manganese (Holliger and Zehnder 1996; Tucillo et al. 1999; Berbenni et al. 2000; Roychoudhury and Merrett 2006).

Pesticides were analysed due to the fact that the presence of iron and manganese can be correlated to the use of plant protection products and fertilisers.

A total of 54 different pesticides are analysed in the monitoring network, but none of them include iron and/or manganese in its molecules. However, the analysed pesticides are the most commonly used within the study area; therefore, it is believed that total pesticides can be representative of agricultural impact.

Being unable to exclude the use of agricultural products containing iron and manganese in the agricultural land use area, it was decided to carry out a qualitative comparison between the sum of the analysed pesticides (TPs) that are considered to be representative of the agricultural impact, and the content of iron and manganese.

To confirm the connection between hydrocarbons, pesticides and human activities, their presence was compared with the land use using data from Corine Land Cover project (EEA 2006).

Results and discussion

Explorative statistical approach

Given the significant amount of data involved, statistical approach was undertaken to assess the main chemistry

Table 3 Descriptive statistics for the physico-chemical parameters and the parameters involved in the statistical analysis

	T	EC	pH	ORP	HCO ₃	Cl	SO ₄	Ca	Mg	Na	K	NO ₃	Fe	Mn
Carbonatic aquifers														
Min	3.0	105	7.0	-255	103	1	1	28	1	1	ND	0.4	<MDL	<MDL
Max	24.9	790	8.4	487	421	29	105	112	32	37	6	72.3	168	250
Med	10.2	327.0	7.7	123.2	222.9	5.6	9.5	62.9	8.9	4.0	1.1	4.2	<20	12.1
St. dev.	4.7	110.7	0.4	91.9	62.1	4.6	14.6	18.4	6.5	4.6	1.1	10.7	0.05	0.03
Intramontane alluvial aquifers														
Min	5.0	259	7.1	-154	174	3	1	48	2	2	1	0.4	<MDL	<MDL
Max	24.0	3070	8.2	191	2000	859	94	291	150	359	60	96.3	45800	1400
Med	12.9	666.4	7.5	68.1	367.8	52.6	20.2	104.6	17.5	27.6	3.7	12.1	334	80
St. dev.	4.6	513.7	0.3	72.4	238.4	141.1	18.9	44.1	20.0	58.9	8.3	18.1	2.88	0.93
Adriatic alluvial valley aquifers														
Min	5.7	100	6.5	-277	10	3	1	13	1	3	1	0.1	<MDL	<MDL
Max	31.1	8440	9.2	369	1280	2598	808	245	482	1671	184	316.3	19500	13600
Med	16.5	996.5	7.1	115.3	472.8	117.4	142.1	121.3	41.1	104.1	10	31.9	272	120
St. dev.	4.0	628	0.4	100.4	143.9	212.7	120.1	43.5	29.7	153.1	12.4	39.6	1.16	0.44

Fe and Mn concentrations are expressed as micrograms per litre, while the concentrations of other elements are expressed as milligrams per litre. EC is shown as microsiemens per centimetre and ORP is expressed in millivolt

and its relationship with iron and manganese. The physico-chemical parameters of the groundwater and the concentration of major ions are characterised by significant variability that is related to the hydrogeological context (Table 3).

The lower values of electrical conductivity (EC) are found in the limestone aquifers (327 $\mu\text{S}/\text{cm}$ on average), while the highest concentrations are recorded in the alluvial valley aquifers (996 $\mu\text{S}/\text{cm}$ on average) with a maximum of 8440 $\mu\text{S}/\text{cm}$. The variability of the electrical conductivity is justified by the concentration of the major ions that tend to increase from the Apennine carbonatic aquifers towards the Adriatic alluvial aquifers.

The redox potential (ORP) varies between -277 and $+487$ mV with negative values being present in all three types of aquifers. However, negative values are mostly found in the alluvial aquifers. The pH values are relatively constant in the limestone and intramontane aquifers, while they tend to be more variable in the alluvial valley aquifers. Temperature is an extremely variable parameter and varies as a function of water table depth and period of the year in which the sampling is undertaken.

The correlation matrix (Table 4), calculated on the basis of the chemical data described in Table 3, shows a significant positive ratio ($0.80 < r < 0.82$) between EC, Cl and Na. Additionally, the strong correlation between Na and Cl ($r = 0.86$) indicates the chemical relationship of these two analytes. Another significant correlation is that between HCO_3 , Mg, Ca, and SO_4 , with r values between 0.4 and 0.63. The correlation matrix does not show a clear relationship between iron and manganese with the other parameters because the samples affected by Fe and Mn contamination are the minority with respect to the whole dataset. Therefore, the Pearson coefficient values are low.

The PCA allows to identify three principal components (PCn) (Fig. 3) that explain almost 59 % of the total variance (Table 5). The *PC1* component explains 34 % of the original variance of the dataset. It is characterised by extreme positive loadings for HCO_3 , Mg, Ca and SO_4 , and thus, it is representative of the bicarbonate-calcium groundwater which is the most common hydrochemical facies in the study area. This component can be interpreted as being representative of the groundwater-aquifer matrix interaction. The *PC2* component explains 13.3 % of the variance and shows extremely high positive loadings for Na, Cl and EC. It can be interpreted as the mineralisation of the groundwater with chloride and sodium enrichment due to salinisation process that is common in the Adriatic alluvial aquifers (Nanni and Vivalda 1999; Desiderio and Rusi 2004; Desiderio et al. 2010; Palmucci and Rusi 2013, 2014; Palmucci et al. 2016).

The *PC3* component explains 11.4 % of the variance, and it is characterised by moderately high positive loadings for Fe and Mn and significant negative loadings for NO_3 and ORP. This component highlights the inverse correlation between these parameters that was not highlighted by mean of the correlation matrix.

The correlations highlighted by the PCA indicate that Fe and Mn mobility is independent from other elements, but rather, it is regulated by redox processes that occur within the aquifers.

Spatial distribution and redox zonation

The distribution of iron (Fig. 4) indicates that this element is present in all the hydrogeological domains of the study area. Concentrations in the limestone aquifers are modest (max 0.17 mg/l), and there are never exceedances of the CLC. On

Table 4 Correlation matrix for the selected physico-chemical parameters

	EC	ORP	HCO_3	SO_4	Cl	Mg	Na	K	Ca	NO_3	Fe	Mn
EC	1.00											
ORP	<u>-.15</u>	1.00										
HCO_3	.50	<u>-.18</u>	1.00									
SO_4	.40	.02	<u>.40</u>	1.00								
Cl	<u>.80</u>	<u>-.07</u>	.19	.21	1.00							
Mg	.37	<u>-.14</u>	<u>.63</u>	<u>.56</u>	<u>.26</u>	1.00						
Na	<u>.82</u>	<u>-.12</u>	<u>.44</u>	.31	<u>.86</u>	.24	1.00					
K	.34	<u>-.02</u>	.37	.29	.24	.24	.31	1.00				
Ca	.44	.02	<u>.45</u>	<u>.58</u>	<u>.28</u>	<u>.48</u>	.15	.20	1.00			
NO_3	.14	.12	.08	.08	.07	.14	.04	.11	.28	1.00		
Fe	.24	<u>-.16</u>	.27	.08	.16	.20	.16	.15	.15	<u>-.08</u>	1.00	
Mn	.12	<u>-.13</u>	.14	.18	.06	.17	.07	.06	.12	<u>-.12</u>	.09	1.00

The numbers represent the Pearson correlation index. Underlined bold text indicates very significant correlation, while bold only text indicates significant correlation

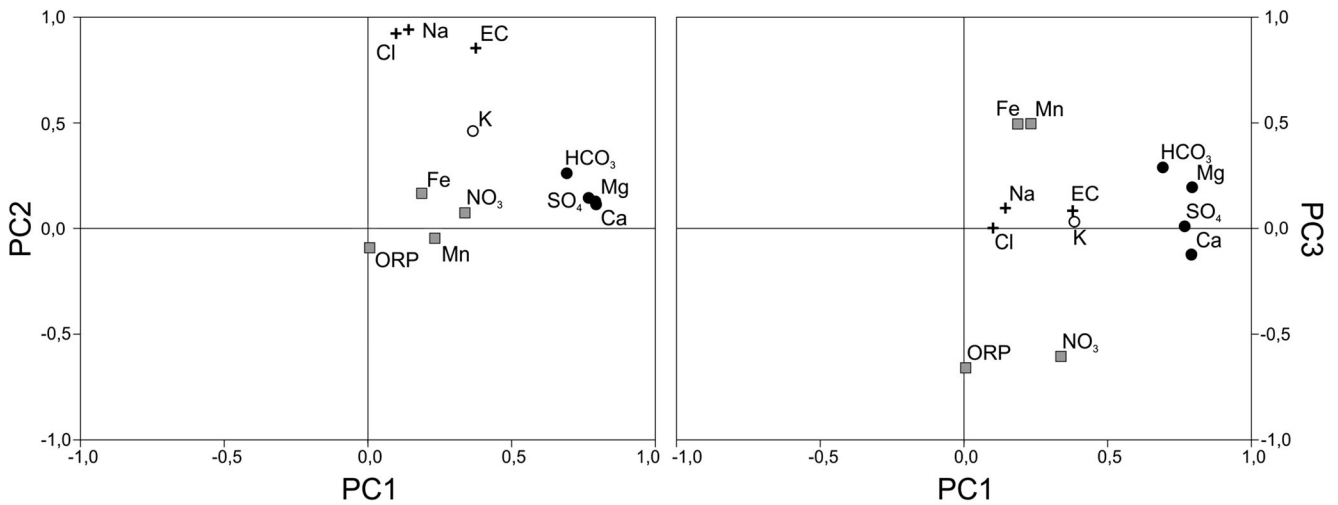


Fig. 3 Projection of the factor loading for the different components. PC1 vs PC2 to the left PC1 vs PC3 to the right. The black circles indicate the PC1, the black crosses indicate the PC2 and the grey squares indicate the

PC3. Potassium (empty circle) is a parameter that is characterised by low loadings for all three components

the contrary, iron is widespread with high concentrations (up to 45.8 mg/l) in the intramontane and alluvial valley aquifers. However, some of the Adriatic alluvial aquifers (e.g. Vibrata, Salinello, Tordino and Vomano) show iron concentration that are generally low, and only rarely, there are exceedances of the CLC. The distribution of manganese (Fig. 4) is similar to that of iron, although it is more widespread, with exceedances of legislative limits occurring even in the limestone aquifers (Table 1). Manganese reaches significant concentrations (up to 13.6 mg/l) in all alluvial bodies of the intramontane and

alluvial valley aquifers. Generally, the alluvial aquifers of the Adriatic area are the ones that are mostly contaminated, and the contamination tends to be more severe towards the coastal areas of the aquifer.

A deeper analysis of iron and manganese spatial distribution (Fig. 4) shows a high incidence of samples that exceed the CLC as well as a high percentage of sample with very low concentration (i.e. non-detects). Therefore, the percentage with intermediate concentrations, between the CLC and the limit of detection, is small. The great variability of Fe and Mn in groundwater suggests that there are local conditions controlling redox processes and the mobilisation of the two metals within the aquifers.

Iron and manganese distribution indicates that the alluvial aquifers are the most sensitive to contamination. This hypothesis is supported by the peculiar characteristics of the alluvial aquifers in terms of low permeability and long residence time, for the presence of organic matter (e.g. peats, fine sediments rich in organic matter) and because these areas are the most exposed to possible anthropogenic pressure (Desiderio et al. 2000, 2002; Caschetto et al. 2014; Rotiroti et al. 2014; Kim et al. 2014; Yadav et al. 2015).

The classification of the redox processes agrees with the spatial distribution of iron and manganese. In fact, the results shown in Table 6 indicate that the majority of the samples are in a condition of oxidation, with maximums recorded in the Apennine limestone aquifers. On the other hand, the less common conditions are the anoxic conditions recorded in less than 8 % of the samples. The samples that are in a “mixed” condition are relatively common. Amongst these, two distinct anoxic forms coexist in approximately 12 % of the samples, while in the remaining samples, there is coexistence of both oxidised and anoxic forms.

Table 5 Rotated matrix of the components

Matrix of the rotated components	Principle components		
	PC1	PC2	PC3
HCO ₃	.69	.26	.29
Mg	.79	.11	.19
Ca	.79	.13	-.12
SO ₄	.77	.14	.01
K	.38	.32	.03
EC	.37	.85	.09
Cl	.10	.93	.01
Na	.14	.94	.10
ORP	.01	-.09	-.66
NO ₃	.34	.07	-.61
Fe	.19	.17	.50
Mn	.23	-.05	.50
Total eigenvalues	4.08	1.60	1.36
% variance	33.99	13.35	11.36
% cumulative variance	33.99	47.34	58.69

The loadings for each different factor, the percentage variance and the cumulative variance are shown in the table

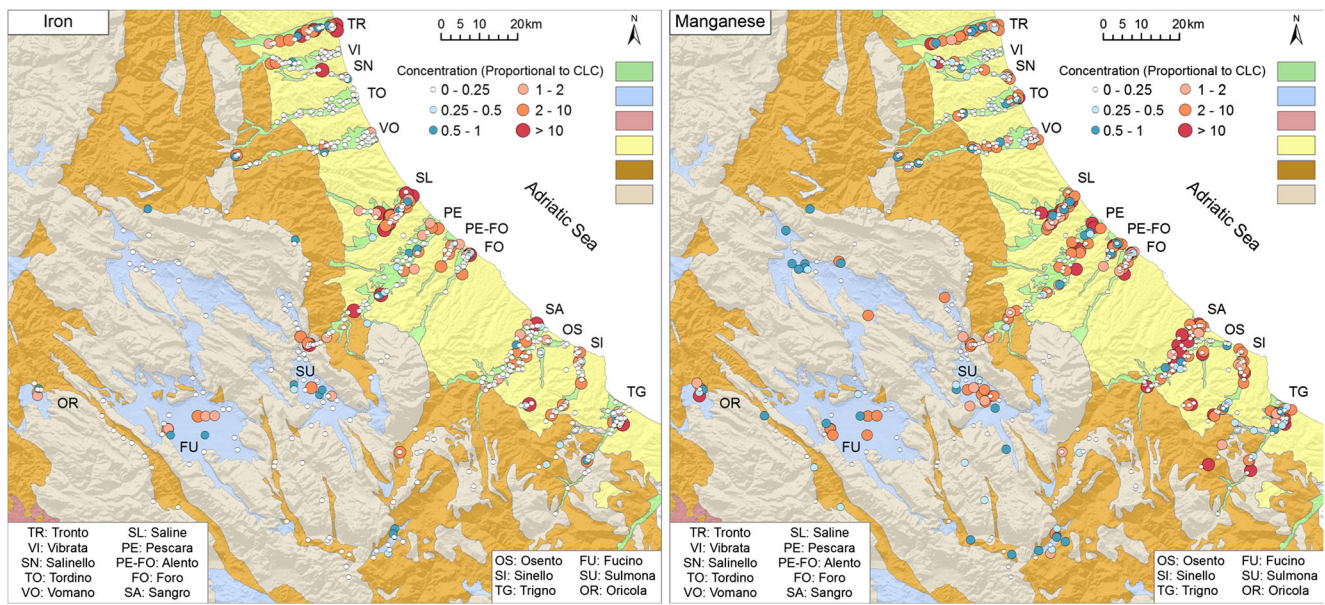


Fig. 4 Distribution of iron and manganese concentration in groundwater within the study area. Colour scheme of lithology is referred to Fig. 1

The classification of the main redox processes (Table 6) indicates that the Apennine aquifers are the least heterogeneous with a net dominance of oxygen reduction processes. On the contrary, oxygen reduction processes within the alluvial aquifers are equally spread with reduction processes of other redox species (NO_3 , Mn^{4+} , Fe^{3+}). Redox processes distribution confirms that the local hydrogeological setting influences the mobilisation of iron and manganese, and as a consequence, the groundwater contamination.

There is a net dominance of the reducing processes of NO_3 and Mn^{4+} compared to the reducing processes of Fe^{3+} in both the intramontane and in the Adriatic alluvial aquifers. The dominance is due to the hydrogeologic characteristics of the

assessed aquifers. These are generally water bodies of modest size, with a shallow (<25 m) water table, and it is quite uncommon that iron reduction can be established in such conditions.

Iron and manganese in soils

The analytical results indicate that all samples have total iron and manganese concentrations above 8000 and 800 mg/kg, respectively, and this confirms that these two metals are always present in the soils of the study area. However, these concentrations are not representative of the true iron and manganese quantities that can be leached to groundwater under neutral conditions.

Table 6 Classification of the main redox processes within the different aquifers present in the study area

Redox category	Redox process	Apennine aquifers	Intramontane alluvial aquifers	Adriatic alluvial aquifers	Total
Anoxic	$\text{Fe}^{3+}/\text{SO}_4$	0	2	10	12
	Mn^{4+}	0	1	18	19
	NO_3	5	0	108	113
	Total anoxic	5	3	136	144
Mixed (anoxic)	$\text{Fe}^{3+}/\text{SO}_4\text{-NO}_3$	0	4	91	95
	$\text{NO}_3\text{-Mn}^{4+}$	0	0	128	128
	Total mixed (anoxic)		4	219	223
Mixed (oxic-anoxic)	$\text{O}_2\text{-Fe}^{3+}/\text{SO}_4$	18	72	153	243
	$\text{O}_2\text{-Mn}^{4+}$	1	44	105	150
	Total mixed (oxic-anoxic)	19	116	258	393
Oxic	O_2	273	152	690	1115
	Total oxic	273	152	690	1115

Sample total 1875

The solubilisable concentrations are more significant. In fact, after the metal has been released into solution, it can freely move and be considered available for dissolution (Lindsay and Norvell 1978). The solubilisable fraction was determined using an extraction solution that dissolves both the exchangeable fraction (the fraction that is not soluble in water but easily absorbed by plants) and the more soluble fraction associated with organic matter present in the soil.

Soil analysis, with regard to the solubilisable concentrations, highlights that iron and manganese are commonly present in soils with maximum concentrations exceeding 20 mg/kg. In some areas, like the Fucino Plain and the Pescara Valley, the frequency of samples with high concentrations of iron and manganese is certainly higher (Fig. 5).

The statistical comparison between the presence of iron and manganese in soils and in groundwater indicates that the degree of contamination of the groundwater is not dependant exclusively on the absolute concentration of the two metals within the soil (Fig. 6).

Closer examination of the iron concentration in soils within the Vomano and Vibrata valleys indicates that these tend to be above the average, while the concentrations of the metal in the groundwater of the respective aquifers are amongst the lowest. The reasons behind these trends are to be found in the redox conditions of the aquifers and the consequent redox processes that arise from these conditions. The Vomano and Vibrata aquifers are in fact the ones with the highest number of locations with oxic conditions (68 and 91 %, respectively). Therefore, the reducing conditions needed to mobilise the iron present in the soils does not arise and, consequently, the

groundwater cannot be enriched with this metal from soil leaching.

The opposite is true for the Saline River where the prevailing of reducing conditions (81 % of the monitoring locations) occurs, which can then mobilise the iron in the soils, allowing the iron migration towards the groundwater. The relationships described for iron are also applicable to manganese (Fig. 6).

The selected locations selected for assessing the seasonal variability of iron and manganese concentrations show differences between the minimum and maximum groundwater levels of 0.2 to 2.1 m. Comparison of the concentrations relative to minimum groundwater levels and the concentrations relative to maximum groundwater levels indicates that there is a significant seasonal variability at 14 of the 33 selected monitoring locations, while the remaining monitoring points do not show a significant variability of concentration because of their limited piezometric fluctuation.

The seasonal variability of concentration is connected to the rise of groundwater levels (Fig. 7) and is observed for both iron and manganese. There is no monitoring point where the increase in concentrations is observed for only one of the metals. Multi-seasonal analytical results over the period 2010 and 2011 are available for monitoring locations SL3, SL34 and TG16. The difference in concentrations between minimum and maximum groundwater levels is confirmed for both years at these monitoring locations.

In summary, rising groundwater levels during the wet season are responsible for increases in iron and manganese concentrations at many of the assessed monitoring locations. This

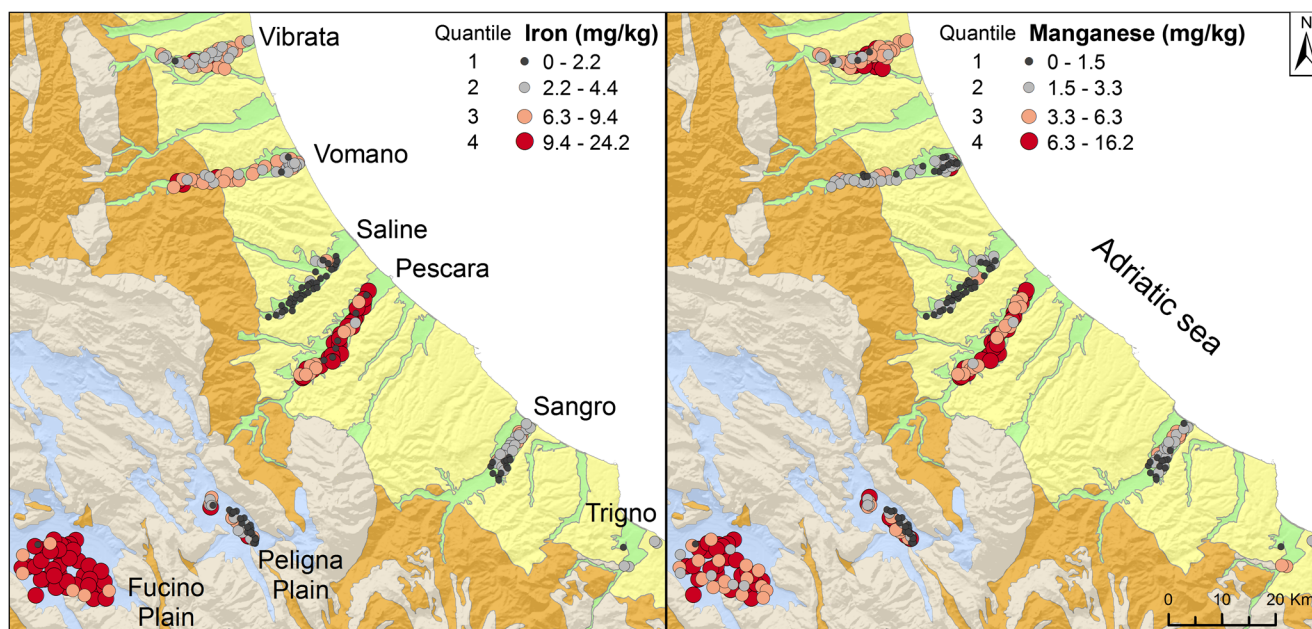


Fig. 5 Distribution of iron and manganese within the soils of the study area

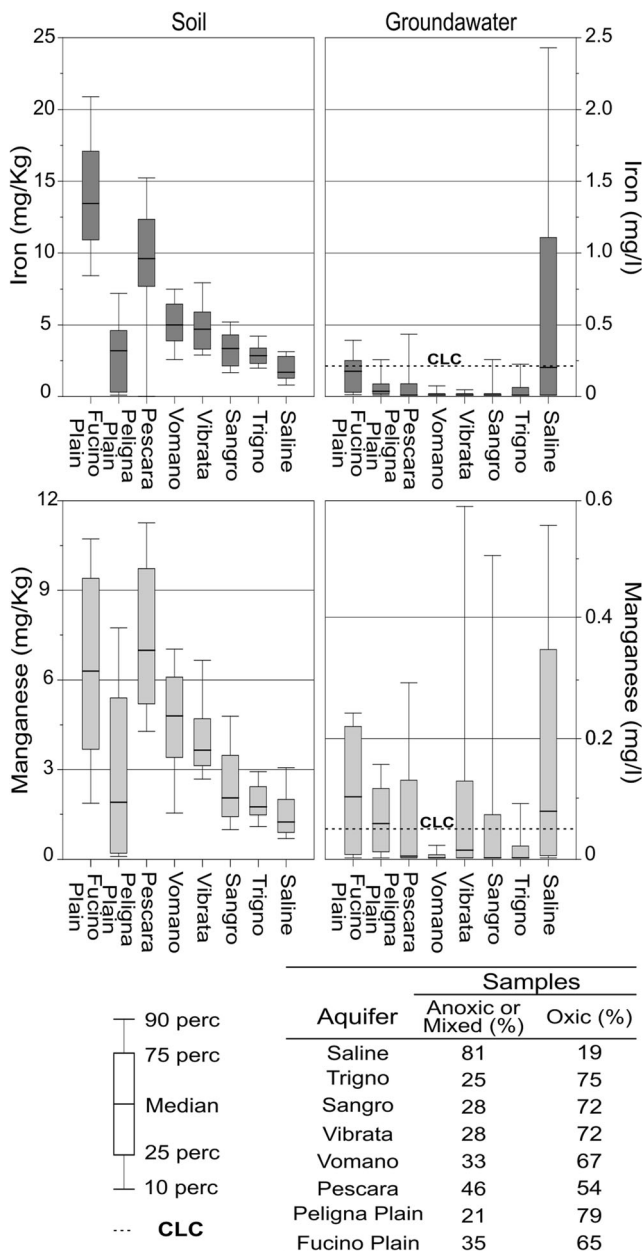


Fig. 6 Box plot showing the presence of iron and manganese in soils and groundwater within the study area (see Fig. 1 for the location of the aquifers)

is probably due to a higher degree of leaching from soils and the consequent mobilisation of oxides and hydroxides of iron and manganese that are present in the soil. Once mobilised, the solid phases of the two metals can be solubilised due to the reducing conditions of the groundwater which cause the concentrations of iron and manganese to increase.

Possible anthropogenic influences

Hydrocarbons and pesticides were selected to assess the anthropogenic contribution to iron and manganese

contamination of groundwater, since they can be representative of human activities such as agriculture and fuel storage or distribution. The comparison between the presence of hydrocarbons and pesticides with land use (EEA 2006) confirms that the polluted monitoring points are located in agricultural or anthropic areas (Fig. 8). The intramontane and the Adriatic alluvial aquifers, mainly affected by agricultural and anthropic activities, are the most polluted areas.

The presence of hydrocarbons within groundwater is relatively limited in the study area. In fact, their presence is detected in only 7 % of the samples, and in less than 1 % of the samples, the concentrations exceed the legislative limits. The possible correlation with iron and manganese contamination was investigated by considering all the samples in which concentration of THC exceeded the limit of detection (Fig. 9). The reducing conditions chart indicates that higher concentrations of iron and manganese often coincide with higher concentrations of hydrocarbons. In the observed samples, iron concentrations remain below the CLC when total hydrocarbon concentrations are below 200 $\mu\text{g/l}$, while manganese concentrations quite often exceed the CLC. This behaviour probably depends on the reducing condition that moderate hydrocarbon concentrations could determinate. It is reasonable to assume that the degradation of moderate quantities of hydrocarbon cannot provide the amount of electrons necessary to reduce iron. Thus, in these cases, iron is not mobilised and its concentration in groundwater remains low.

High concentrations of iron and manganese occur at lower concentrations of hydrocarbons (THC < 100 $\mu\text{g/l}$ in the analysed samples), and this is probably connected to the rise of anoxic conditions that are independent from the presence of hydrocarbons (e.g. presence of peat or long residence time).

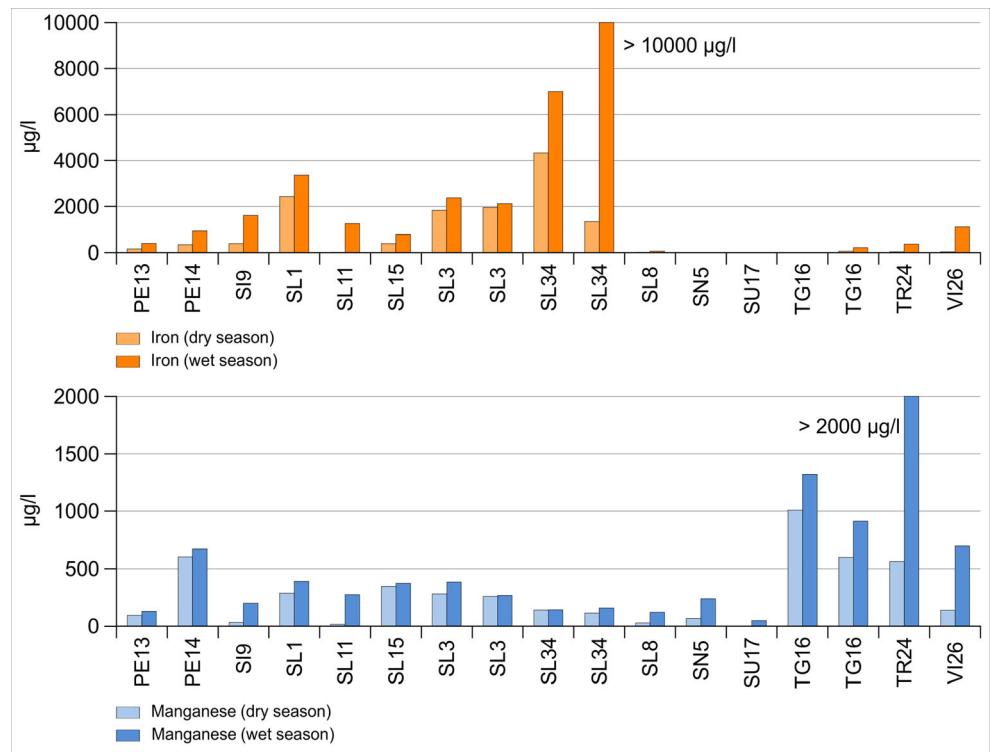
With oxidising conditions, the concentration of THC is always observed to be low except for one sample (TR16).

Ultimately, although hydrocarbons are not a direct source of Fe and Mn, their presence is indicative of anthropogenic influences that favour the reducing conditions for the release of these two metals, providing electron donors from the oxidation of the organic matter. Therefore, it can be inferred that Fe and Mn contamination is related to anthropogenic influence for those samples that show high concentrations of THC.

Similar observations can be made with the presence of pesticides. In fact, pesticides are observed at only 4 % of the monitoring locations. Total pesticides (TPs) within samples are above the legislative limits at only 2 % of the monitoring locations.

The charts (Fig. 10) show that Fe and Mn concentrations exceed their respective CLC at some of the locations where pesticides were detected. However, the Fe content is not related to the concentration of pesticides. In fact, iron is constantly below the detection limit for those

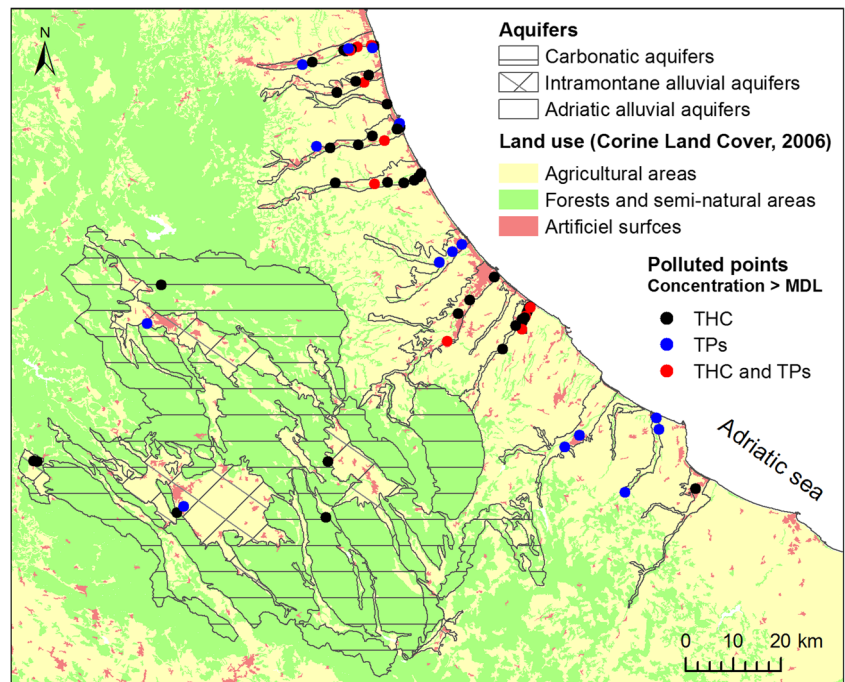
Fig. 7 Iron and manganese concentrations during dry and wet seasons at selected monitoring points



points on the left of the chart corresponding to the highest concentrations of pesticides. Even for manganese (Fig. 10), clear correlation with pesticides cannot be identified; in fact, manganese exceeds CLCs at both low and high concentrations of pesticides. Although iron and manganese are not present in the molecules of the analysis

pesticides, these are believed to be representative of the agricultural impact. For this reason, since there is no correlation between iron and manganese and the presence of pesticides, it can be assumed that agricultural activities do not significantly affect the content of the two metals in groundwater.

Fig. 8 Comparison between land use and the locations of the monitoring points affected by total hydrocarbon (THC) and/or total pesticides (TPs) pollution. The image shows all the monitoring point with concentrations of THC or TPs above the method detection limits



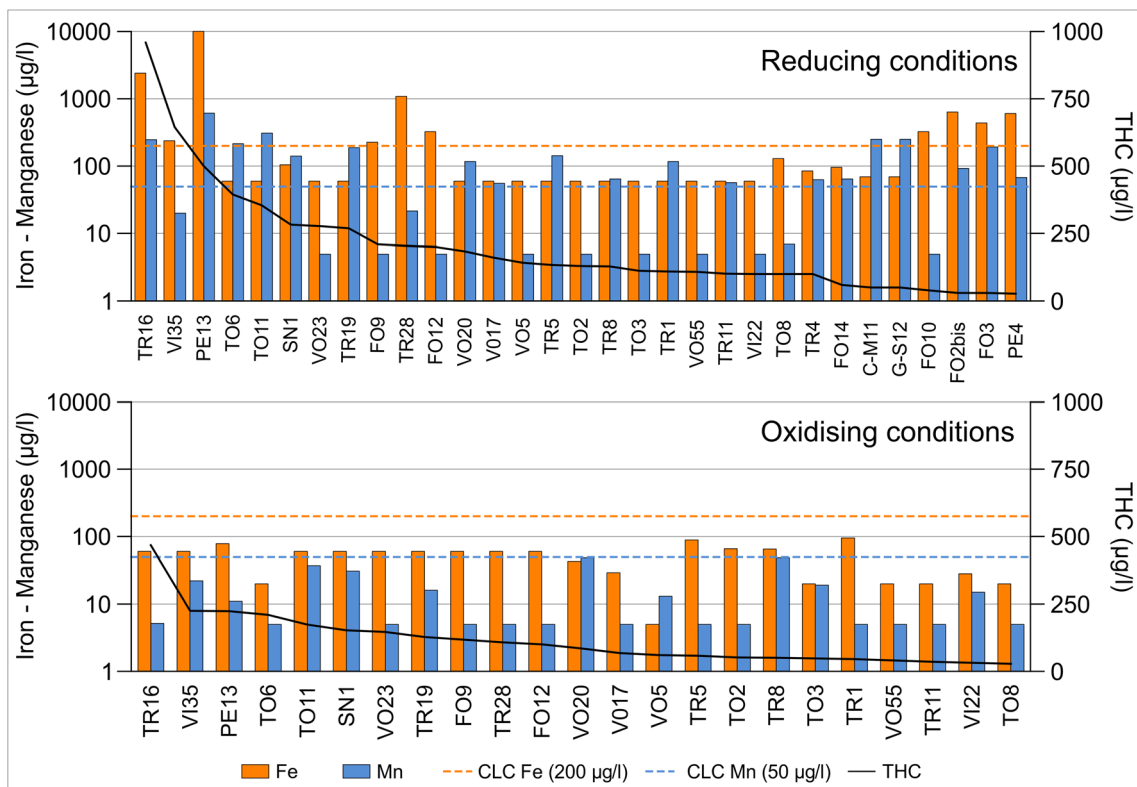


Fig. 9 Iron and manganese concentrations at the monitoring locations where hydrocarbons were detected

Summarising, the assessment of anthropic impact on iron and manganese contamination of groundwater

suggests that there is no connection with the use of pesticides and fertilisers and, more generally, with

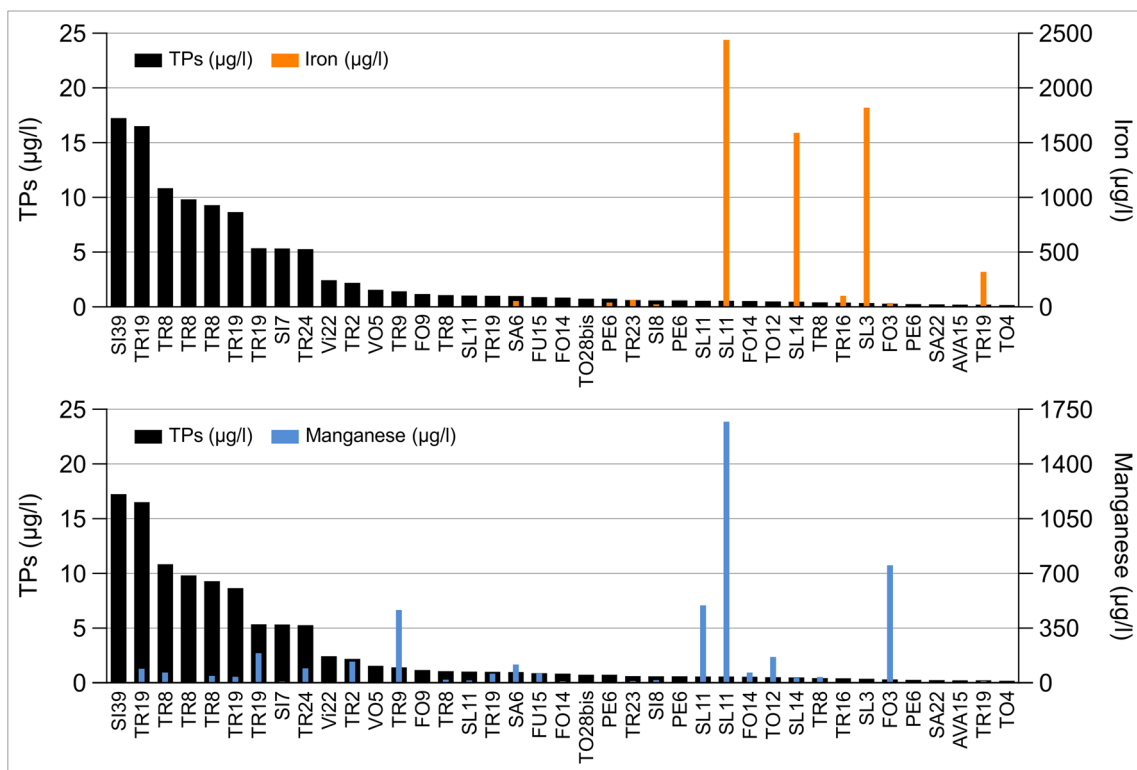


Fig. 10 Comparison of total pesticides and iron and manganese concentrations. Samples with total pesticides above the detection limit are only shown

agriculture. On the contrary, anthropic influence related with hydrocarbons pollution is evident. This is due to the redox conditions that arise following the presence of hydrocarbons, although they are not a direct source of Fe and Mn.

Conclusions

A conceptual model that explains the hydrogeochemical processes that govern iron and manganese concentrations in groundwater was derived from the processing and assessment of the data used for this work.

Both the hydrogeochemical and the statistical analyses highlight a general independence of iron and manganese contaminations from the principal ions and, more generally, from the groundwater chemistry. On the contrary, a clear inverse correlation with nitrate and ORP suggests the main role of redox processes.

The spatial distribution of the two metals indicates that the alluvial aquifers, both intramontane and Adriatic, are the most sensitive to Fe and Mn contamination, although their distribution is irregular (patchy).

Also, the redox zonation confirms that reduction of iron and manganese takes place almost only in the alluvial aquifers. These processes are regulated by local conditions that are long residence time, presence of peat or organic-rich fine sediments and anthropic pollution, which are able to mobilise these two.

The concentration of iron and manganese identified within soil indicates that the latter is a concrete source of the two metals. However, also in this case, the local conditions regulate Fe and Mn mobility in groundwater after soil leaching.

The presence of point contamination connected to direct anthropogenic sources of Fe and Mn contamination (industrial discharges, leachate from landfills, etc.) will clearly require site-specific investigations that will need to assess the redox conditions within the aquifer. The evolution over time of a contamination, and therefore its persistence, will depend on the redox conditions within the aquifer or induced by the contamination itself.

Summing up, research results suggest that the elevated iron and manganese concentration not necessarily depend on anthropic pollution, but rather on the local conditions that favour redox processes. When Fe and/or Mn CLC exceedances are detected, it will be necessary to investigate aquifer's hydrodynamic (i.e. residence time) and the presence of natural (e.g. peat) and/or anthropic (e.g. oil spills) organic matter that, all together, determinate the reducing condition needed to mobilise iron and manganese.

Thus, two cases can occur: the first one, in which high concentrations of Fe and Mn in groundwater, with CLC exceedances, are not related to anthropic pollution but rather

to natural occurring iron and manganese (i.e. in soils) mobilised due to redox processes occurrence; and the second one, related to Fe and Mn releases caused by anthropic pollution. In this case, the presence of iron and manganese, clearly originated from anthropic pollution, can give CLC exceedances, if the redox condition, needed for these two metals mobilisation, will occur in groundwater. However, if the redox processes do not arise, there would not be necessarily CLC exceedances of Fe and Mn in groundwater, even though the anthropic pollution.

The dealt issues allow to assess the contribution of anthropic impact, in order to properly address water management policies and, in particular, whether to consider a site polluted or to derivate Fe and Mn natural background levels suitable for the different aquifers.

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