

A TIERED APPROACH TO NATURAL BACKGROUND LEVEL (NBL) ASSESSMENT IN GROUNDWATER UNDER A NON HAZARDOUS WASTE LAND FILL IN LATIUM REGION (ITALY)

Giuseppe Sappa, Stefania Vitale
Department of Civil, Building and Environmental Engineering
Sapienza, University of Rome
via Eudossiana, 18 - 00184 Rome (Italy)
ITALY
giuseppe.sappa@uniroma1.it
<http://w3.uniroma1.it/giuseppe.sappa>

Abstract: - This paper deals with the results of investigation and monitoring activity on groundwater flowing under an area of a non hazardous waste landfill, placed in the Agro Romano, in the South Rome town area, near to Colli Albani Volcanic region. The geological framework is mainly dominated by pyroclastic deposits of Colli Albani Volcanic Complex named *pozzolanelle* and *tufo lionato*. The purpose of the study has been the investigation of the origin of concentration values referred to Arsenic, Manganese, and Fluoride, exceeding the European law limit values. In order to identify whether the observed concentrations represent a naturally-occurring condition or they are due to an anthropogenic source, it was applied a tiered up approach. As a matter of fact in the aim of following a tiered approach, they were analyzed, different aspects like: the impacts coming from anthropogenic activities, regional and site specific geology knowledge, the mineralogic properties of the geological outcrops, site specific geochemistry, statistical approach. Carrying on a background analysis early may become an important guideline for statutory requirements in the site assessment based on legal fixed concentrations.

Key-Words: - arsenic, site specific bedrock geology, natural background level, statistical approach, background concentration

1 Introduction

Arsenic, Manganese, Fluorine had been detected at concentration values, exceeding the European law limits, in the area of concern. As a consequence of this condition they have been required further evaluations.

The nowadays anthropogenic activity, in the area under study, is a non hazardous waste landfill (Fig.1), actually a solid inert waste one. There is no evidence of a chemical release that could affect groundwater quality at the site. As a matter of fact inert solid wastes have negligible activity or effect on the environment. Anthropogenic processes cannot locally affect these elements concentration in groundwater.

The purpose of this study has been to identify the origin of these anomalies, considering its geological features, that might have caused the enrichment of this element in groundwater, together with other factors, which could affect mobility and dispersion of these elements, and are useful to define a natural background range. The aim of a tiered approach is

to apply multiple steps to support the position that high concentrations of some elements are naturally occurring, because they are due to the specific geochemical and hydrogeological site conditions.

The mineralogical and chemical properties knowledge of these geological outcropping rocks has been the first step to set up the background for this set of chemical elements. Most of the solutes, present in natural groundwater, especially metals, come from the dissolution of rocks, soils, and sediments minerals forming

The chemical composition of natural groundwater, therefore, is closely related to the properties of the minerals, groundwater has been in touch, along its flowpath.

In such natural scenario, the occurrence of these elements is mainly associated to the weathering and dissolution of volcanic rocks.

Arsenic occurrence in groundwater has been identified in many parts of the world. Much of this presence is shown to arise from natural sources. It seems to be mainly influenced by water rock

interaction processing involving volcanic and sedimentary formations. Arsenic bearing minerals are commonly found in rocks. Therefore natural geologic sources of As dominate the environmental conditions for As inputs in groundwater: such as most primary As minerals, among which Arsenopyrite is the most common. Arsenic in crustal rocks is also associated with pyrite or Fe hydroxides and oxides, and is strongly adsorbed by clay minerals and hydroxide of Iron, and Manganese.

The As content in groundwater of the volcanic areas of central and southern Italy covers a wide range of values and very often it exceeds the limit of 10 µg/L [1].

Regarding the area of concern and the geochemical characteristics of aquifers in central Italy, recent studies show that As concentrations data recently detected have a good correlation with ones collected about twenty years ago in the same aquifers.

This evaluation supports the natural As source hypothesis. The main target of this study have been to investigate the original source of As, and the main factors controlling their chemical behaviour in this natural environment, on the basis, also, of setting up the spatial distribution of their concentrations.

Manganese occurrence and its concentration, in groundwater flowing in volcanic rock is related to the sediments lithology. This metallic element has more than one oxidation state. These different oxidation states can determine different geochemical conditions, which mobilize Manganese. Clay minerals, like illite+, muscovite and chlorite could be potential sources of exchangeable Manganese.

Fluoride concentration values exceeding the European law limit are a feature of a large number of aquifer. Fluoride is found in association with crystalline rocks containing fluorine-rich minerals, especially volcanic rocks: this association occurs because of the high fluoride mineral presence such as biotite, apatite and fluorite.

2 Problem Formulation

Waste solid landfill, even when they store inert waste solid, are usually considered a hazard for soil and groundwater. As a consequence of it, they are subjected to strict monitoring programs, aimed to control if they could impact on groundwater quality. According to the specific European Directive, the 2001/42/CE, in any waste solid landfill, groundwater have to be monitored, as during its activity, as for twenty years, after the end of its activity. The groundwater monitoring activity is

generally driven by a network of boreholes where, periodically, they are taken groundwater samples. These samples have to be analysed in certified laboratories in the aim to detect that concentration values of elements, included in a special table of the above mentioned European Directive, are not higher than limit level values, present in the same table. These limit level values have been set up referring to potential toxicity of the elements dissolved in groundwater, in the aim of preserving groundwater quality, as condition to preserve human healthness. Sometimes when the concentration values of these elements overpass the limit level, this is due to anthropogenic impact, and they are markers of groundwater contamination. On the other hand, sometimes, depending on the specific geological, hydrogeological and geochemical framework, these values, exceeding the european level limits, have a natural origin, and they can't be referred to anthropogenic activities. Very often, when groundwater analysis results, referred to waste solid landfill, but also to any industrial plant, which can have a potential environmental impact on groundwater, show concentration values, for some elements, exceeding the european law limit, it is necessary to assess if these exceeding values are natural or they are due to anthropogenic activities impact. This is the case under study, presented in tis paper, where some concentration values of Mn, As and F, detected in groundwater, exceeded the limit level. To this data set, coming from groundwater, it was applied a tiered approach, which couple geochemical and statistical techniques, to assess the actual source of these overpassing values.

2.1 Study Area



Fig.1 Study area.

The study site is located in the south part of the Agro Romano, at South of Rome, where the North-Western part of the Colli Albani District outcrops, which large part of its weathering products.

The explosive activity of the Colli Albani Volcano have been made of several evolution stages, which caused the emplacement of many pyroclastic deposits, covering large part of Rome Municipality territory. The main pyroclastic deposits of Volcano Laziale are: Ancient Tuffs, Pozzolane Inferiori Complex, Tufo lionato, Pozzolane Superiori and Tuff Villa Senni [2].

The Colli Albani Volcanic District is a complex made of different lithological formations, the hydraulic conductivity of which varies in a large range. Each geological set (Ancient Tuffs, Pozzolane Inferiori Complex, Tufo lionato, Pozzolane Superiori and Tuff Villa Senni) affect the direction of groundwater flow, depending on these heterogeneous properties.

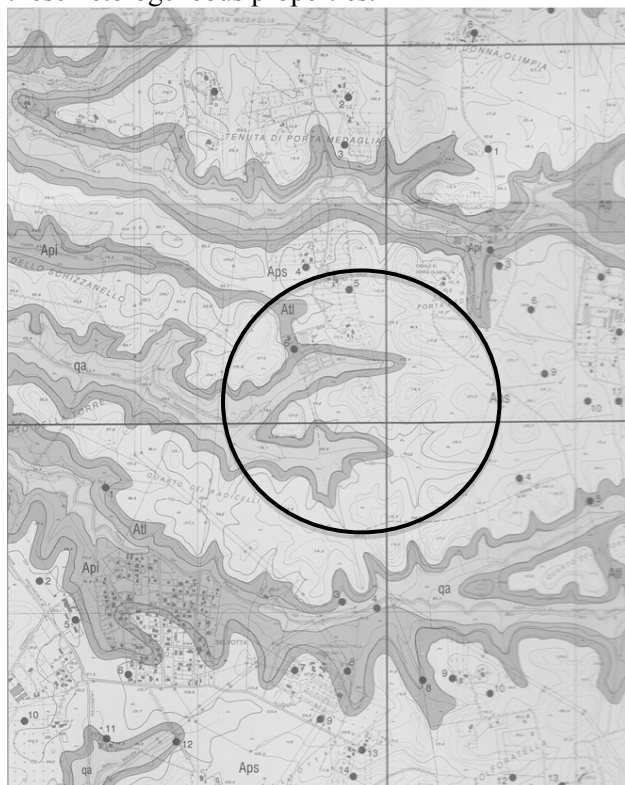


Fig.2 Study area geological map

The bottom boundary of the hydrogeological unit is a Pliopleistocene clay complex, which is covered by sedimentary deposits, outcropped before the volcanic activity.

Referring to the local site stratigraphy, the Pozzolane Superiori represents the last explosion, which ended the Volcano Laziale and they overlay the ancient units (Fig. 2).

The specific geological properties of this site, make it rich of glassy volcanic grains, which are the last product coming from the dismantling of pyroclastic deposits in the Colli Albani Volcano, and represent the chemical less stable ones, among the natural components, because they have not reached yet an equilibrium within the atmospheric surface conditions.

As a matter of fact, they are more sensitive to the chemical and physical reaction with other substances and in with groundwater flowing in rocks they are forming.

To understand these complex phenomena, it's important to assess mineralogy and chemical composition of the main lithological outcropping rocks.

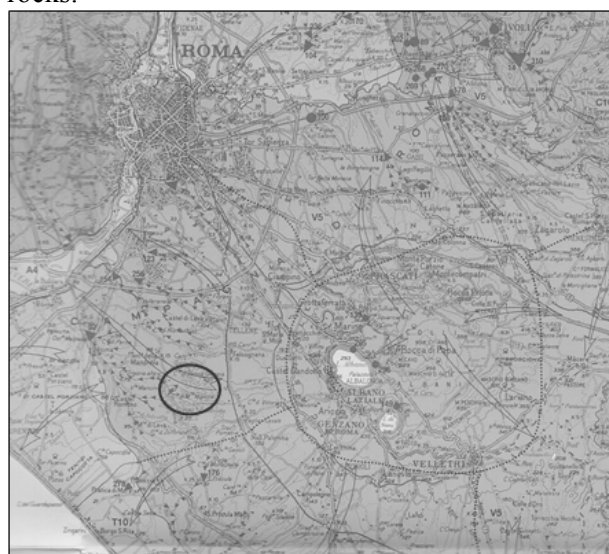


Fig.3 Hydrogeological units map of South part of Rome

In fact they drive the interaction water-rock and, as a consequence of it, the mobilization of elements present like oxides (Tab.1), which are the most present minerals in crustal rocks and groundwater dissolving them [3].

In the area under study, the Malafede Fosso Basin, drained by the Fosso Malafede, left tributary of Tiber River is included.

The multiple depositional units, with their different permeability, which extend over all the area under study, separate the groundwater flows in more paths, not hydraulically isolated. To set up a right and updated piezometric scenario, the piezometric levels detected in the wells around the landfill from 2001 to 2013, were represented. The hydrogeological map (Fig.2) shows local groundwater flow going from South to North and, consequently, the monitored boreholes, Pz3 and Pz4 are upward in respect of the landfill.

Oxide	Tufo lionato	Pozzolanella
SiO ₂	43.21	46.09
TiO ₂	0.80	0.67
ZrO ₂	0.03	0.04
Al ₂ O ₃	19.02	19.56
Fe ₂ O ₃	8.30	6.50
FeO	0.10	1.55
MnO	0.17	0.13
MgO	1.85	2.90
CaO	5.38	7.23
BaO	0.65	0.27
K ₂ O	2.06	4.51
Na ₂ O	1.39	2.92
Cl	0.02	0.01
SO ₃	0.05	0.03
P ₂ O ₅	0.03	0.10
H ₂ O-	7.48	1.82
H ₂ O+	11.13	5.52

Table 1. Chemical Analyses of Tufo lionato and Pozzolanella [3]

Monitoring wells	Date	As	F	Mn
PZ1	31/03/2014	15,2	2360	5,1
PZ2	31/03/2014	11,9	1705	4,4
PZ3	31/03/2014	6,5	1370	105
PZ4	31/03/2014	2,6	350	48,2
PZ5	31/03/2014	1,7	185	3,3
PZ6	31/03/2014	0,19	1705	97,9
PZ1	14/05/2014	15,4	2095	2,3
PZ2	14/05/2014	12,3	1640	5,5
PZ3	14/05/2014	5,4	905	131
PZ4	14/05/2014	2	165	0,66
PZ5	14/05/2014	2	165	0,18
PZ6	14/05/2014	0,33	1765	75,2
PZ1	25/06/2014	13,8	2045	6,8
PZ2	25/06/2014	12,5	1630	2,4
PZ3	25/06/2014	7,1	885	78,2
PZ4	25/06/2014	3,5	170	8,8
PZ5	25/06/2014	3,5	150	2,6
PZ6	25/06/2014	1,8	1305	67,8
PZ1	23/07/2014	14,9	1600	2,4
PZ2	23/07/2014	11,9	1230	1,3
PZ3	23/07/2014	8,3	840	40
PZ4	23/07/2014	2,1	105	4,6
PZ5	23/07/2014	2,3	95	2
PZ6	23/07/2014	5,2	1025	47,2
PZ1	08/10/2014	14,9	2375	1,8
PZ2	08/10/2014	13,8	2000	3,2
PZ3	08/10/2014	4,2	795	80,4
PZ4	08/10/2014	2	255	18
PZ5	08/10/2014	3,3	325	12,7
PZ6	08/10/2014	0,74	1600	70,6

Table 2. Analytical data from monitoring wells

2.2 Materials and methods

After evaluating the local and regional geology and hydrogeology features, a spatial and temporal data analysis for the selected trace elements has been carried out, from several location points Pz1, Pz2, Pz3, Pz4, Pz5, Pz6 of the monitoring network (Table 2), as trace elements distribution could support the identification of some elements concentration origin [4].

The results show that there isn't an increasing concentrations of As, F, Mn along the groundwater flow direction, supporting the hypothesis that the present anthropogenic activity cannot affect the high concentration of these elements.

The spatial and temporal plots show Arsenic concentrations range is approximately between 0.19 µg/l and 15.4 µg/l, with the highest value in the well Pz1. Fluorine concentrations range is between 95 µg/l and 2375 µg/l, with the highest observed concentration in Pz1.

Manganese concentrations range is approximately between 0.18 µg/l and 131 µg/l. Manganese highest concentration occurs in Pz3.

The application of multiple box plots seems to be the most effective tool for representing by graphics, all the data set, referred to each element analyzed As, F, Mn in order to show the potential spatial trend among these data, as it is represented in the following Fig. 3,4,5.

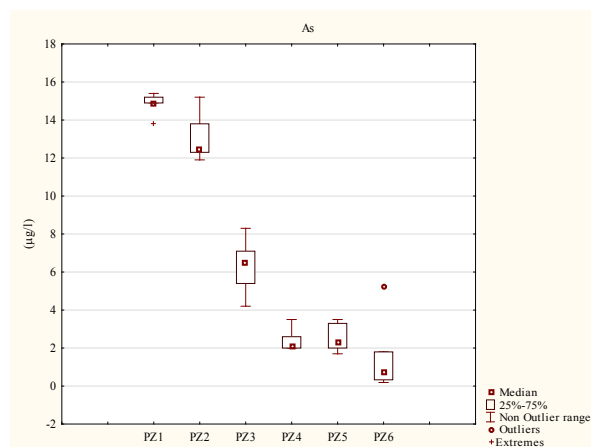


Figure 4. Boxplot of the whole dataset for As

The highest concentrations of As and Mn are found in the deepest monitoring boreholes.

As regard to geochemical conditions measured in these boreholes, pH ranged between 5.7 and 6.9 and dissolved oxygen, DO, between 0.24 mg/l and 5.2 mg/l.

The As and F concentrations are strongly influenced by environmental conditions. High concentrations of Arsenic and Fluorine are often related to low DO and high depth.

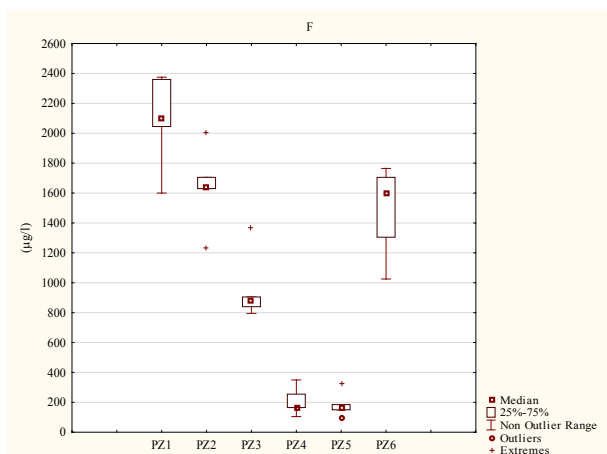


Figure 5. Boxplot of the whole dataset for Fluoride

The dissolution of arsenic from soil and/or bedrock into groundwater is highly dependent on geochemical conditions in the aquifer.

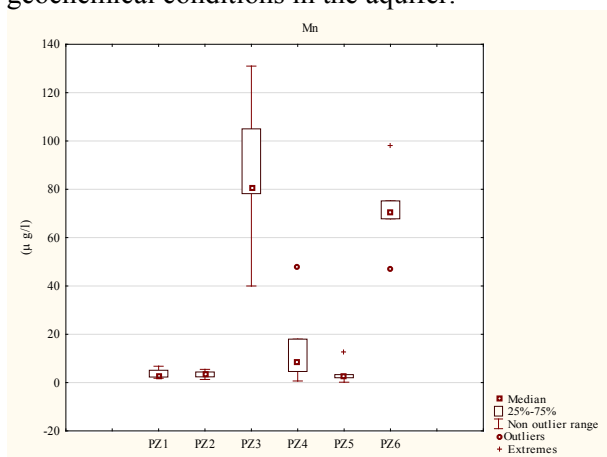


Figure 6. Boxplot of the whole dataset for Mn

Most arsenic in groundwater occurs in one of two oxidation states, arsenate [As(V)] or arsenite [As(III)]. Arsenite is more mobile and is the predominant species under reducing conditions: low dissolved oxygen values and near neutral pH. Scatterplots have been set up for analyzing possible relationships.

Arsenic is strongly adsorbed to clay minerals and hydroxides of iron, aluminum and calcium, which coat clay particles. The geochemical environment found in the silt/clay unit is more favorable for the dissolution of arsenic from mineral grains into the groundwater. The cap rock made of clay and mild clay prevented atmospheric O₂ intrusion and thus produced a reducing environment.

High As and F concentrations are related to volcanism [6].

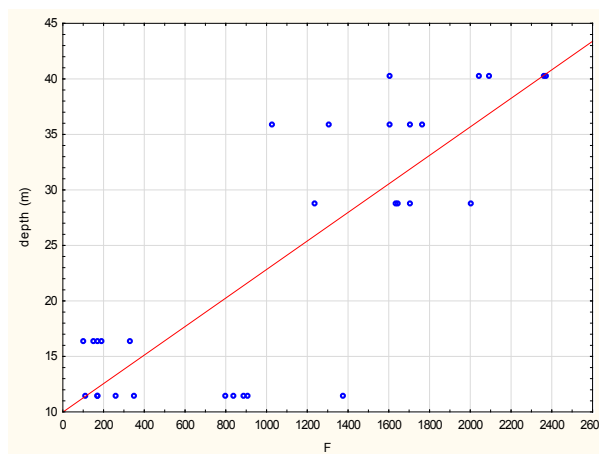


Figure 7. Relationship between well depth and Fluorine (µg/l) concentration in groundwater

High values for Manganese have been detected in the focus area, related to the redox conditions encountered, probably due to low content of nitrates (between 1 mg/l and 5 mg/l).

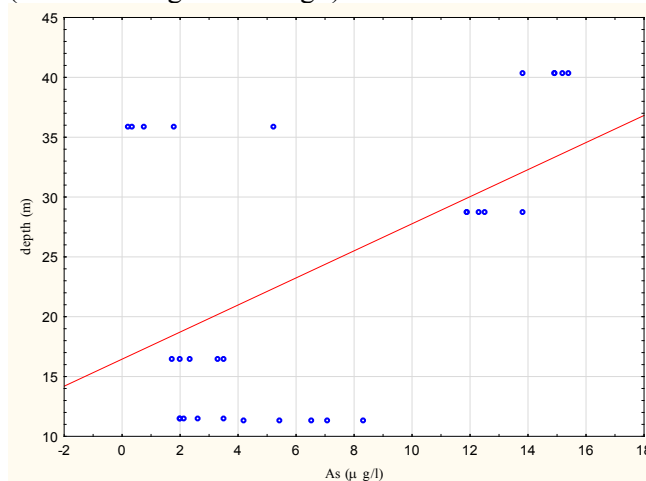
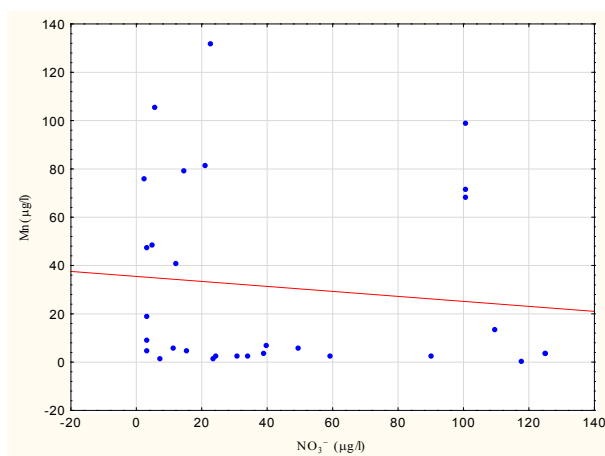


Figure 8. Relationship between well depth and Arsenic (µg/l) concentration in groundwater

In this redox environment, Mn is reduced to more soluble species. Mn-oxides, present in the sediments, are the first to be reduced, hence it appears in groundwater.

Low levels in nitrates probably indicate denitrification processes, due to oxidation of organic matter such as decayed vegetable matters (Fig.8).

Due to the local groundwater flow, the dataset, considered for determining the background value is made of concentrations values detected in samples coming from Pz3 e Pz4 boreholes, which are placed upward in respect to waste solid landfill location, from hydrogeological point of view.

Figure 9. Scatterplot Mn-NO₃⁻

As a matter of fact the monitoring boreholes Pz3 e Pz4 are the only ones, which are representative in order to set up a background range, because they are placed upward the groundwater flow, in respect of the landfill location, so they can't be influenced by potential incoming water flow, due to the waste solid landfill activity. So the data referred to groundwater samples coming from them have been considered for the following application.

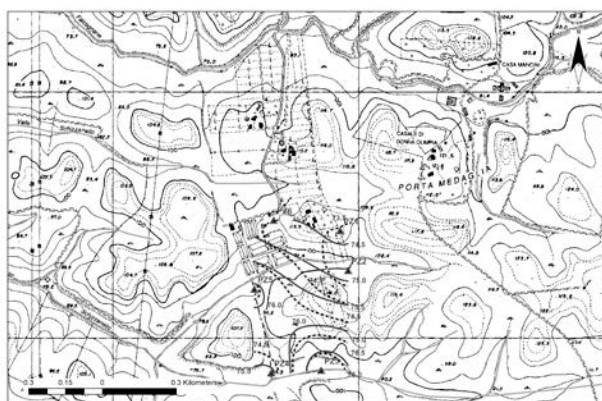


Figure 10. Monitoring network location

The Italian document, *Guidelines for the evaluation of Background values in groundwater* [7], provides step-by-step instructions for characterizing background conditions at groundwater site based on a statistical and geostatistical assessment [8]. The number of data selected should have a statistical significance, because they have to be enough for the scale of the interested area. Anyway they have to be more than 10.

The techniques presented in these guidelines focus primarily on the identification of the extreme values that may be potential outliers, in the aim to identify, on the first, data affected by analysis or writing mistakes.

For each analyte in the selected dataset, statistical analysis computes the main statistical parameters, useful for studying the appropriate data distribution. The statistical evaluation of each selected parameter for each monitoring borehole was performed to determine if the data are best represented by a normal or lognormal distribution, to choose the appropriate statistical test for data, that follows a particular distribution, in the aim of identifying potential outliers. Graphical representations of the data may also indicate unexpected events, that may influence the analysis of the data. They play an important role to select the range values that fit more observations and to check homogeneity.

Analytes	Min	Max	Median	Interquartile R
As	2	8.3	3.85	4.40
F	105	1370	572.5	715
Mn	0.66	131	44.10	71.6

Table 3. Main statistical parameter for selected analyte

For this subdataset, Arsenic concentrations ranged from 2 µg/l to 8.3 µg/l with a median value of 3.85 µg/l, and an interquartile range of 4.40 µg/l. Fluorine concentrations range is from 105 to 1370 µg/l, with a median value of 572.5 and an interquartile range of 715 µg/l. Manganese concentrations varied from 0.66 µg/l to 131 µg/l with a median value of 44.10 µg/l and an interquartile range of 71.6 µg/l, where the European Law limit are for Mn 50 µg/l, As 10 µg/l and for F 1500 µg/l. The subdatasets of As, Fluorine and Manganese data don't show outliers values that are potential values, extremely larger or smaller than the rest of data and therefore can be suspected of misrepresenting the population from which they were collected, because they are probably due to analytical determination mistakes, or to simple writing mistakes.

Consequently they are, actually, representative of their relative population.

Scatterplots have been set up for analyzing any possible relationships such as the one related to deepness of boreholes (Fig. 6 and 7). To determine the NBL, Natural Background Level for As, Mn, F in the area of concern the 95th percentile has been chosen, as it is suggested by the Italian document, *Guidelines for the evaluation of Background values in groundwater* [7], which provides, step-by-step, instructions for characterizing background conditions at groundwater site based on a statistical and geostatistical assessment [8].

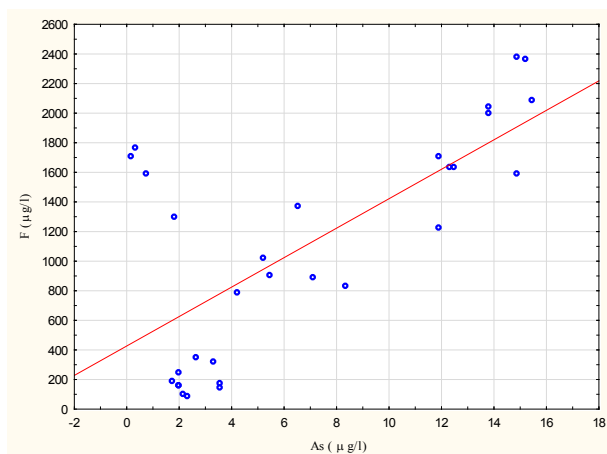


Figure 11. Relationship between As and Fluorine concentration in groundwater

The 95th percentile, calculated for each selected element, becomes the threshold. Each concentration value exceeding it, indicates that the chemical characteristics of groundwater may represent anomalous values, due maybe, to anthropogenic impact. Each concentration value, which is lower than threshold belongs to background concentration range for the focused site groundwater.

In geochemical data interpretation, the threshold value represent the number, below which the variations of element concentration are related to natural chemical interaction between groundwater and rocks, the flow in, and so they represent only natural effects. On the contrary when concentration values for some elements come out bigger than threshold value, than they can point out a significant enrichment and source of arsenic, manganese and fluorine dissolved, coming from anthropogenic activities impact.

In the area under study, following the statistical approach, mentioned above, it has been assessed the NBL for As, F and Mn, and they have been obtained the following values: As, 8.3 µg/l, F, 1370 µg/l, and Mn, 131 µg/l.

3 Conclusions

Groundwater flowing under industrial plants, or waste solid landfills, even inert waste solid ones, can present concentration values in some elements, which can be contamination markers or simple natural enrichment tracers, due to geological, hydrogeological settings of the area. The distinction between these two different sources of high values of concentration in groundwater of some elements, like, as in this case, As, Mn and F, is very important. In fact if it is a groundwater contamination case,

European law drives to a rehabilitation activity of the area. If it is a natural geochemical enrichment case the only thing to do is to forbid some groundwater uses, without any charge for the management of the activity, driven in that area. This has been the case presented in this paper, where, on the first, geological settings and geochemical conditions have been analyzed in the area, under study, placed in the south part of Rome, where the northern part of Albano Volcan outcrops with part of its weathering products. This peculiar geological framework makes it easy to expect trace elements mobilization in groundwater, and their natural geochemical enrichment in some of them.

Volcanic origin of rock masses, and the glassy state of many minerals forming them, make it easier coming out some chemical elements in their interaction with groundwater, and their concentration values in them become, sometimes, higher than European laws admitt.

This study shows how these exceeding values are related to geochemical environment groundwater flow through, highlighting how it is important in this kind of elaboration to make in account the natural geochemical framework, also when they are applied statistical approaches, like the one it has been followed in this study, according to what is suggested by the Italian document, Guidelines for the evaluation of Natural Background values in groundwater [7], between statistical elaborations outputs and geochemical properties of aquifers.

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