

UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II
CENTRO INTERDIPARTIMENTALE DI RICERCA “AMBIENTE” (C.I.R.A.M.)



PhD in

ANALISI DEI SISTEMI AMBIENTALI

XXVIII CICLO

ASSESSMENT AND SPATIAL DISTRIBUTION OF NATURAL
BACKGROUND LEVELS (NBLs) IN GROUNDWATER
AFFECTED BY NATURAL AND ANTHROPOGENIC
CONTAMINATION: A CASE STUDY IN SOUTHERN ITALY

MARIANGELA SELLERINO

Coordinatore

Prof. Maurizio Fedi

Tutor

Prof.ssa Daniela Ducci

Co-Tutor

Prof. Alfonso Corniello

a.y. 2013-2017

Acknowledgements

Firstly, I would like to express my sincere gratitude to my advisor Prof. Daniela Ducci and co-advisor Prof. Alfonso Corniello for the continuous support of my Ph.D study and related research, for their patience, motivation, and immense knowledge. Your advice on both research as well as on my career have been priceless. Thanks for all the opportunities that you gave to me and that allowed me to grow as a research scientist.

I would also like to thank my thesis reviewers: Prof. Lucila Candela and Prof. Paolo Fabbri, for their insightful comments and suggestions, that contributed to improve my thesis.

My sincere thanks also goes to Dr. Elisabetta Preziosi at CNR-IRSA in Rome and Dr. M. Teresa Condesso de Melo and Prof. Luis Ribeiro at “Instituto Superior Técnico” of the University of Lisbon, who provided me an opportunity to collaborate with them. Without their precious support it would not be possible to conduct this research.

Thanks to Dr. Serena Tessitore and Dr. Elena del Gaudio for the funny and sunny road trips across the Piana Campana, searching for wells and piezometers to collect groundwater samples and to measure the piezometric head. It was a pleasure to work with you and I hope to continue the collaboration.

I would also like to thank all of my friends who supported me spiritually in writing this thesis, and incited me to strive towards my goal. Your thoughts for me was what sustained me, even from a distance.

A special thanks to my family. Words cannot express how grateful I am to my mother, father, my sister, and brother for all of the sacrifices that you've made on my behalf. I deeply love you

Thanks to my husband Luigi, because being married with a Ph.D candidate it's more difficult than earning doctoral degree itself. Thanks for the love, the support, the music, the life...

And thanks to my daughter Chiara, for bearing my absences, for having always greeted with a hug in the morning and always smile on my return at home, not making me weigh the late hour... for giving me a new life as mother.

This thesis is dedicated to my grandparents, always on my mind and forever in my heart.

1. Introduction	5
1.1. Research objectives	7
2. Research in the framework of scientific projects	9
2.1. The Life+ ECOREMED project	9
2.2. Regional projects	12
2.3. Scientific collaborations	13
3. The study area	14
3.1. Geological and hydrogeological setting	16
3.2. Piezometric pattern	18
3.3. Hydrochemical setting	19
4. Methods	23
4.1. The natural background levels	23
4.1.1 Definitions	23
4.1.2 State of the art	24
4.2. The NBLs assessment	26
4.2.1 Conceptual model	26
4.2.2. Data base organization and analysis	28
4.2.3. The adopted methodologies	31
4.3. Probability Plot	32
4.4. Component separation method	33
4.5. Pre-selection criteria	36
4.6. Probability map	39
4.6.1. Indicator kriging	39
4.6.2. Cross validation	41
4.7. Software used	36
5. Hydrochemical data	43
5.1. The historical data set	46
5.2. The new data set	46
6. Results	48
6.1. Data analysis	48
6.1.1. Piper diagram and Schoeller diagram	48

6.1.2. Box plot	49
6.1.3. Arsenic and fluoride	50
6.1.4. Iron and manganese	51
6.2. The natural background assessment	55
6.2.1. Arsenic	57
6.2.2. Fluoride	61
6.2.3. Iron and manganese	65
6.3. Definition of the threshold value	74
6.4. Probability maps	75
6.4.1. Arsenic	76
6.4.2. Fluoride	77
6.4.3. Iron	79
a) Oxidizing conditions	79
b) Reducing conditions	80
6.4.4. Manganese	81
a) Oxidizing conditions	80
b) Reducing conditions	83
6.4.5. Iron and manganese	84
7. Discussion	85
7.1. The comparison between the results obtained with the three different methods for the NBLs assessment.	85
7.2. The natural and anthropogenic contamination	87
7.3. The potentiality of the probability maps	88
8. Conclusions	91
9. References	94
Appendix A: Acronyms and Abbreviations	104
Appendix B: Variograms	107
Appendix C: Data set	109

1. INTRODUCTION

The identification of natural geochemical processes and the assessment of the impact of anthropogenic actions on groundwater quality are important challenges to water sustainable management worldwide. Representative surveillance monitoring is required to assess groundwater body status and track the evolution of the water quality, especially in those areas where anthropogenic stresses are more intensive and widespread. There is also an increasing need, for water authorities and managers, to have sound indications on the location of good quality groundwater reserves, in order to develop long-term protective management strategies that guarantee an adequate supply and quality of water, in light of both increasing human needs and climate variability (Ducci et al., 2016).

The Water Framework Directive 2000/60/CE (WFD; European Commission, 2000), transposed into Italian law as D.lgs 152/2006, requires member states to protect, enhance and restore waters with the goal of achieving “good status” for both surface and groundwater bodies. For groundwater, good status covers both quantitative and chemical status (Fig. 1.1).

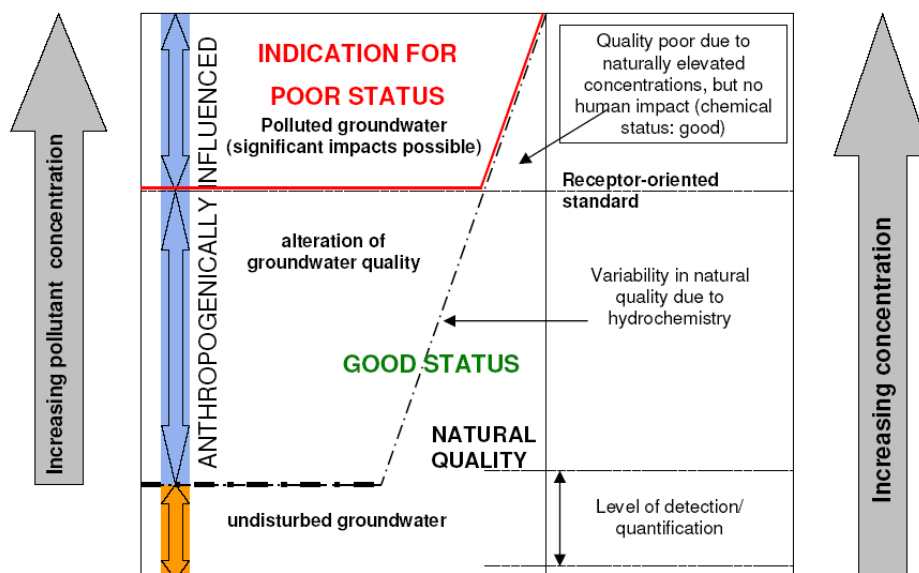


Fig. 1.1. General relationship of groundwater quality and status under the EU Water Framework Directive (Muller et al., 2006)

As the “good chemical status” is not clearly defined in the WFD, the Groundwater Daughter Directive 2006/118/EC (GWDD; European Commission, 2006) was published to set criteria for evaluating groundwater chemical status (Ducci & Sellerino, 2012). The GWDD was transposed into Italian law as D.lgs 30/2009. Nowadays the assessment of the groundwater body (GWB) quality is inherently related to the definition of the natural background level (NBL) and threshold values (TV). According to the GWDD, the TV is defined as a quality standard for pollutants in groundwater, i.e., a concentration of pollutant which should not be exceeded in order to protect human health and the environment. The TV is determined on the basis of the NBL, as request by the D.lgs 30/2009. In the Art. 2.5 of the GWDD the ‘background level’ is defined as *“the concentration of a substance or the value of an indicator in a body of groundwater corresponding to no, or only very minor, anthropogenic alterations to undisturbed conditions”*.

Under peculiar hydrogeological conditions (e.g. presence of tectonic structures, upwelling of hydrothermal fluids, and interactions with other groundwater bodies) the concentrations of certain elements can widely vary, and therefore the differences in groundwater chemistry inside a groundwater body can be remarkable.

In the highly impacted zones some important aspects should be evaluated, such as whether an element was already present prior to human impacts, and which was its content or, in case of remediation of a site, which is the area to be eventually restored and to which extent (e.g. the natural background level) should the concentration be lowered through the remediation measures.

For these reasons, TV and NBL are crucial in environmental management, but they are theoretic values whose geochemical significance cannot reliably be derived by applying methodologies, as much as sophisticated, purely based upon samples data. Moreover, although the European legislation requires the assessment of NBL in order to evaluate the groundwater chemical status, there is no indications about which method should be used.

The NBL evaluation provides one value (or sometimes a range of values) for an area, while groundwater quality changes continuously in space. In according to the European Directive 2014/80/UE (European Commission, 2014) the determination of the background levels it should be based on the characterization of groundwater bodies in accordance with Annex II of European Directive 2000/60/EC (European Commission,

2000). Indeed the extension of a groundwater body is often very large and it is very important that management groundwater quality tools take into account the scale and heterogeneity of groundwater bodies.

Contaminant distribution mapping is an important component of the risk assessment, and it demands for a spatial analysis involving probability assessment. The object should be to delineate between “contaminated” and “clean” groundwater for management purposes (e.g. for drinking water abstraction, delimitation of polluted sites to be restored, etc.).

If the groundwater quality is poor and unsuitable e.g. for human consumption, does it depend only on its natural origin? Or on the contrary, is it human induced and therefore the restoration of the aquifer is needed and reasonable at the same time?

These considerations and questions, raised by the outlined state of the art, led to this thesis topic. The objectives of the thesis will be discussed in the next section.

1.1. Research objectives

Indicator Kriging (IK) allows estimating the probability of exceeding a critical threshold concentration. This technique has been largely used for the evaluation of the quality of soils (Cattle et al. 2002; Smith et al. 1993) and groundwater (Liu et al., 2004; Stigter et al., 2005; Lee et al., 2007; Delbari et al., 2016).

In this thesis the NBL concept has been revisited in the light of the spatial analysis using IK, in order to link the conditional probability estimation of the IK to the local NBL, to be able to individualize:

- the anthropogenic polluted areas;
- when to consider NBL instead of the law reference value and the extend of the area of the validity of the NBL within a large area;
- the areas not usable for human consumption, regardless the origin of contamination.

The methodology was applied in an area located in Campania Region, southern Italy. The study area is a portion of the very large Volturno Plain-Regi Lagni GWB, as defined in Water Management Plan “2015-2021” (European Directive 2000/60/CE, D.lgs 152/06, L. 13/09), that extends between the provinces of Naples and Caserta. It is a

densely populated area, with a poor reputation for contamination, caused by illegal dumping of industrial and municipal waste (US Navy, 2013). Indeed, it is located in the Regional Interest Priority Site “*Litorale Domizio-Agro Aversano*” (LDDA), owing to the large number of potentially polluted sites. In the last five years, the LDDA has been object of several studies by the University of Naples “Federico II” (*Life+ECOREMED project*) and Campania region (*Strumenti operativi di valutazione e controllo delle qualità dei sistemi agricoli della Piana Campana*).

Over the PhD years, I had the opportunity to take part in both projects as a fellow. Moreover, I collaborated with the *Instituto Superior Técnico* of the University of Lisbon and the *National Research Council - Water Research Institute IRSA-CNR*. Through all these experiences and projects, I was able to study in depth the area and carry out the methodology reported in this research project with the aim to support the reclamation practices that are testing and promoting on the area and the management of the aquifers of the study area.

2. RESEARCH IN THE FRAMEWORK OF SCIENTIFIC PROJECTS

2.1. The Life+ ECOREMED project

Life+ ECOREMED "IMPLEMENTATION OF ECO-COMPATIBLE PROTOCOLS FOR AGRICULTURAL SOIL REMEDIATION IN COAST DOMIZIO-AGRO AVERSANO NIPS", aims to develop and demonstrate the **bio-remediation protocol effects of agricultural polluted soils** which include growing biomass crops with dual objective of clean-up and produce useful materials for agro-energy and green chemistry with the perspective to propose it in other polluted area too. In Campania region, Southern Italy, (Napoli Orientale, Litorale Domitio-Agro Aversano L. 426/98, Napoli Bagnoli Coroglio L. 388/2000, Litorale Vesuviano L. 179/2002, Bacino idrografico del Sarno L. 266/05; Aree di Pianura DM 445/2008) there were identified four National Interest Priority Sites (NIPSS), for a total surface of about 200,000 ha, with different levels and sources of pollution. *Litorale Domitio-Agro Aversano* (LDAA) NIPS (nowadays downgraded from "national" to "regional", not for a decrease of the contamination status but to transfer the competence of reclamation works to the Campanian regional authorities) includes a large part of the polluted agricultural lands, belonging to more than 61 municipalities in the Naples and Caserta provinces. In this area a high level spotted soil contamination is moreover due to the legal and outlaw industrial and municipal wastes dumping, with hazardous consequences also on the quality of the water table (www.ecoremed.it). The LDAA area encompasses the whole Garigliano plain GWB, and parts of the GWBs of the Volturno river plain – Regi Lagni, the eastern Plain of Naples, and the Phleagrean Fields.

The project has many objectives, divided into different actions. During my PhD studies, I had the opportunity to take part in the LIFE11/ENV/IT/275 - ECOREMED project. The participation is started because I was not holding a doctoral fellowship and I availed of the fellowships of the Life+ project since January 2013 until December 2016. In this project, I participate to action B1 "Environmental characterization of the area" (Action leader: D. Ducci) and action C3 "Groundwater monitoring" (Action leader: A. Corniello).

The action B1 aims to provide the environmental characterization of the LDDA site considering the contribution of environmental matrices (air, soil, soil hydraulic and groundwater) and the effect of their contamination on human health. The use of Geographic Information System (GIS) has made possible a georeferenced inventory and, by overlaying environmental information, operational synthesis of comprehensive environmental conditions. The cumulative effects on environmental features are evaluated, taking into account superposition effects, by means of the spatial multi-criteria decision analysis, to draw up the suitability map for the application of the ECOREMED protocol. In particular, I was involved in the sub-action B1c1 "Hydrogeological characterization". The objectives were:

- To define the stratigraphy of the area through boreholes, hydrogeological maps and sections, gathered by government agencies, private companies and survey campaigns.
- To determine the piezometric pattern through the interpolation of piezometric data, collected or obtained with new measures conducted in the available wells.
- To evaluate the quality status of groundwater (sensu Directive 2000/60/EC) and the natural background values for certain ions (Directive 2006/118/EC), on the basis of chemical analysis already available or obtained with new samples.
- To assess the vulnerability to contamination of the aquifers.

The effects of the protocol were tested in specific polluted areas that have been selected at the beginning of the project in the Municipalities of Trentola-Ducenta (an area bordering the landfill "Taverna del Re" with organic and metal pollution), Castel Volturno (a public retro-dunal of 5000 m² area called "Soglitelle" near "Laghetti di Castel Volturno" polluted used as shooting range and contaminated by metals of the bullets) and Teverola (a public area of 3000 m² used for temporary storage of urban wastes). In particular, the action C3 aims to define a set of indicators for monitoring environmental quality that could be used in environmental regulatory framework. The monitoring was performed in Teverola and Soglitelle sites, where the shallow aquifer is present. The monitoring was performed installing two multi-parametric data loggers, one for each piezometer of each site (Fig. 2.1), and a periodical sampling in all control piezometers

built in the two sites.

Some of the piezometric measures and the chemical analyses of the water samples collected in this project (those that fall in the area and appropriate to the proposed methodology), have been joined to the data set used in this study (§ 5); moreover some of the results obtained are presented in this study (study area § 3; geochemical maps § 6.1).

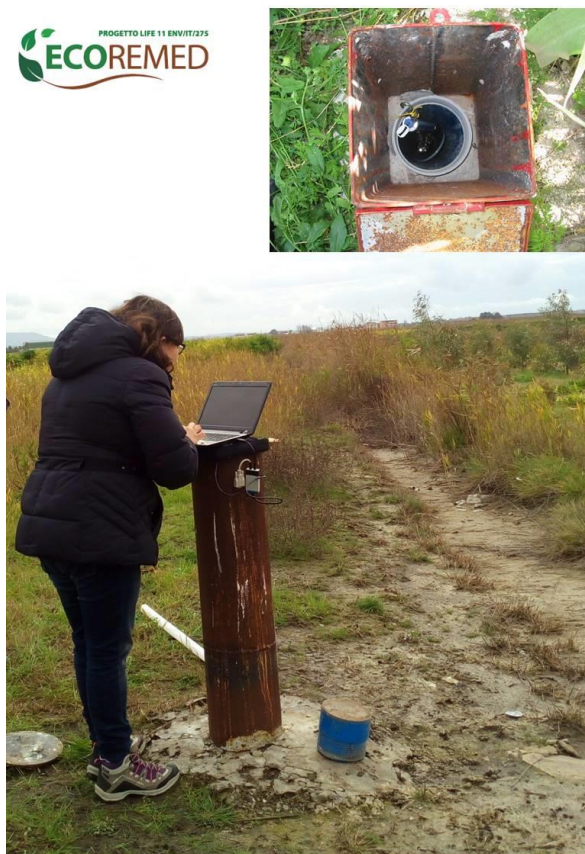


Fig. 2.1. Soglitelle - Laghetti di Castel Volturno (CE): the downloading of the data by the multi-parametric data-logger. In the right corner, a view above the piezometer and the multi-parametric data-logger installed.

The results of this project were presented in several congresses and workshops; the following are workshops and congresses which I attended and in which I presented the preliminary results of the thesis:

- Workshop “The definition of natural background levels (NBLs) in groundwater and soils – Case studies in Italy and Portugal”, CIRAM - University Federico II of Naples, 26/02/2014.

- FLOWPATH 2014 – Viterbo, 18-20 Giugno 2014: Ducci, D., Sellerino, M., Preziosi, E., Parrone, D., de Melo, M. T. C., & Ribeiro, L. (2014) - The importance of distinguishing between anthropogenic pollution and natural origin in groundwater of highly deteriorated areas.
- 42nd IAH International Congress “Hydrogeology: Back to the future!”, University “La Sapienza” Rome, 13-18/09/2015: Corniello A., Ducci D., Sellerino M.- Investigating Groundwater Systems from regional scale to site-scale. Abstract published on Rend. Online Soc. Geol. It., Suppl. n. 1 al Vol. 39 – 2016, pag. 825.
- 10th Congress of “Giovani Ricercatori di Geologia Applicata” AIGA, Alma Mater Studiorum University of Bologna, 18-19/02/2016: Corniello A., Ducci D., Sellerino M.- Investigation of Groundwater Systems at different scale: the case study of the Volturno River Plain (Campania, Italy)”. Abstract published on Rend. Online Soc. Geol. It., Vol. 41 -2016- pagg. 76-79.
- 88th Congress of Italian Geological Society (SGI), University Federico II of Naples, 7-9 / 09/ 2016: Corniello A., Ducci D., Sellerino M., Stellato L., Del Gaudio E., Di Rienzo B. & Tessitore S. - New considerations about nitrate content in groundwater of the alluvial-pyroclastic aquifer of the Campanian Plain (southern Italy). Abstract published on Rend. Online Soc. Geol. It., Suppl. n. 1 al Vol. 40 (2016) pag. 787.

2.2. Regional projects

The government of the Campania Region carried out different projects for the environmental study and monitoring. In particular the project "Strumenti operativi di valutazione e controllo delle qualità dei sistemi agricoli della Piana Campana" (CUP E69E12000590006) allowed us the in-depth analysis of the groundwater bodies of the Campanian Plain (Phleagrean Fields, Eastern plain of Naples and Volturno plain-Regi Lagni) and provided the tools to new campaign of piezometric measurements and the collection of groundwater samples (§ 5). The aim was the chemical characterization of the groundwater of the Campanian plain for identifying threshold values of some ions that are indicators of the anthropogenic contamination and the subsequent local

calibration of the reference value for the irrigational use.

2.3. Scientific collaborations

Life+ ECOREMED and the regional project were useful to the study of the area and the collection of new data, but the bases of this research were born during the scientific cooperation between the Portuguese Foundation for Science and Technology (FCT), the National Research Council of Italy Water Research Institute IRSA-CNR and the University of Naples “Federico II”. The methodology proposed in this thesis has been preliminarily applied with a different data set (smaller) and on a slightly different distribution area (the extension of the GWB has been slightly modified by the Water Management Plan “2015-2021”) and the main results were published on a scientific journal: Ducci, D., de Melo, M. T. C., Preziosi, E., Sellerino, M., Parrone, D., & Ribeiro, L. (2016) - Combining natural background levels (NBLs) assessment with indicator kriging analysis to improve groundwater quality data interpretation and management. *Science of The Total Environment*, 569, 569-584. <http://dx.doi.org/10.1016/j.scitotenv.2016.06.184>

3. THE STUDY AREA

The Campania (southern Italy – Fig. 3.1) is the second most populated region in Italy. It is spread over an area of 13,671 km² with a population of about 6 million of inhabitants, which makes it very densely populated. The economy of the region is based mainly on agriculture and food industry, but it can also count on a large number of industrial plants.

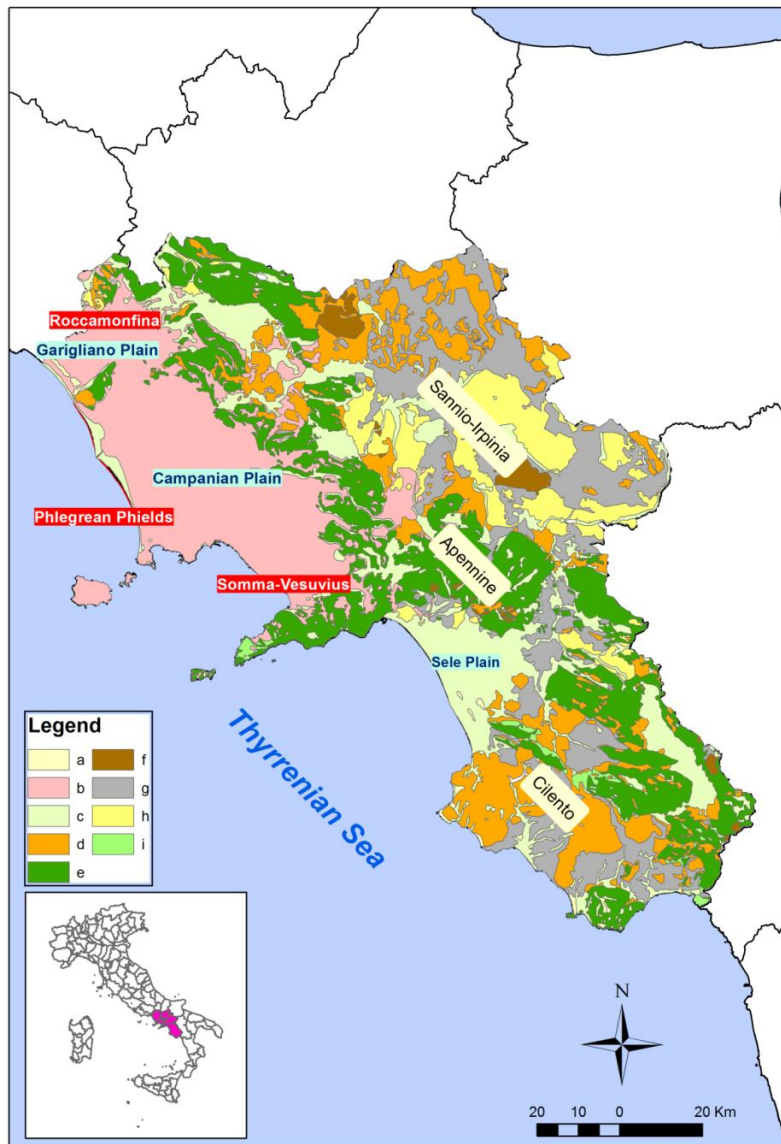


Fig. 3.1. Hydrogeologic scheme of the Campania region (Italy: a) Quaternary marine deposits; b) Quaternary volcanic deposits; c) Quaternary slope-fan deposits; d) Flysch; e) Mesozoic limestones; f) Marlstone and Limestone; g) Limestone and clay; h) Molasse deposits; i) Limestones. (mod. from Allocca et al., 2005)

The Campania is characterized (Fig. 3.1) by three coastal alluvial plains overlooking the Tyrrhenian Sea on the west, which cover about 30% of the territory (Garigliano Plain p.p., Campanian Plain and Sele Plain), by the inland Apennine mountains which constitute the main orographic barriers and cover 25% of the area, by the hilly areas of Sannio-Irpinia and Cilento (over 40% of the territory) and, by the Vesuvius and the Roccamonfina volcanoes and Phleagrean pyroclastic hills (about 5% of the surface).

The study area is located in the central part of the Campanian Plain, corresponding to the southern part of the *Volturno Plain-Regi Lagni* (P-VLTR) groundwater body (GWB), as defined in the Water Management Plan or “Piano di Gestione delle Acque 2015-2021” (2000/60/EC, D.lgs 152/06, L. 13/09), at the left side of the Volturno river (Fig. 3.2) and here and after called P-VLTR_{sx}. The P-VLTR_{sx} is hydrogeologically homogeneous and it presents strong differences from the northern part of the GWB (Capri et al., 2009; Corniello & Ducci, 2014).

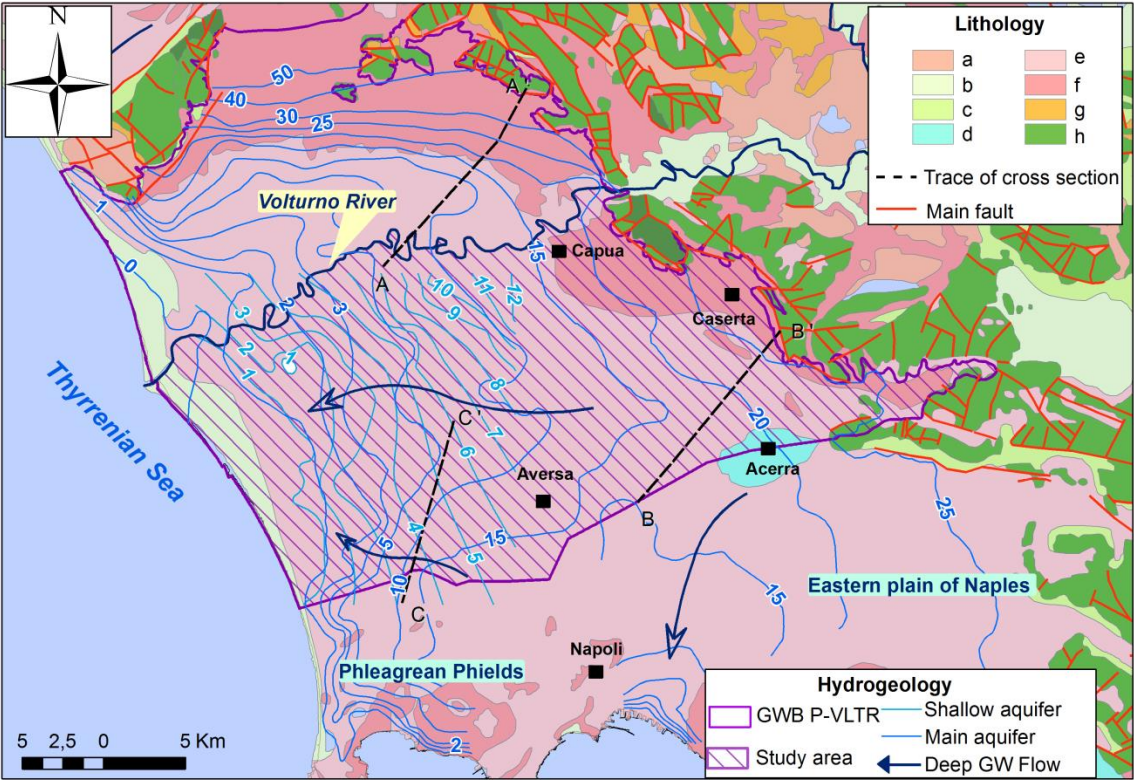


Fig. 3.2. The study area (P-VLTR_{sx}): the southern part of the Volturno Plain-Regi Lagni (P-VLTR) groundwater body.: a) Arenaceous – conglomeratic deposits; b) Alluvial –coastal deposits; c) Slope-fan deposits; d) Travertine; e) Pyroclastic deposits; f) Campanian Ignimbrite tuff (CI); g) Arenaceous-clayey flysch; h) Limestone. Piezometric levels in m a.s.l. (mod. Allocca et al. 2005). Trace of the cross sections of Fig. 3.3

The P-VLTR_{sx} is bounded by the Tyrrhenian sea (W), by the Volturno River (N), by the Mesozoic limestone mountains (E), by the eastern plain of Naples (SE) and by the pyroclastic hills of the Phleagrean Fields (SW) (Fig. 3.2).

The area is prevalently agricultural, but it is characterized, especially in the northern part, by widespread settlements, with population densities exceeding 1,000 inhabitants/km² in municipalities near Naples (located at the SE of the area) (Ducci et al., 2016). Since the 90's the area is affected by severe nitrate contamination, mainly due to diffuse sources (agriculture and breeding). The industrial and civil contribution to groundwater contamination is less marked and mainly local. In the last years, the local presence of dumping sites and illegal wastes has been also recorded (Albanese et al., 2015).

3.1. Geological and hydrogeological setting

The study area is located in the Volturno river plain (Fig. 3.2), in the northern sector of the Campanian Plain, that is, from a geological point of view, a deep subsiding *graben* (rate 1.5–2 mm/y, Brancaccio et al., 1995). The origin of the *graben* is the result of an extensional phase began in the Early Pleistocene (Brancaccio et al., 1991; Cinque et al., 1993; Santangelo et al., 2017), that generated a fault systems (Fig. 3.2), trending NW - SE (parallel to the Apennine), or NE - SW (normal to the Apennine) and, to a lesser extent, in the longitudinal direction (SO). Along the faults, the Meso-Cenozoic carbonate units lowered at depths between 5,000 and 3,000 meters (Ippolito et al., 1973; AGIP, 1977; Ortolani & Aprile, 1985; Romano et al., 1994; Milia & Torrente, 1999; Cinque et al., 2000; Aprile et al., 2004). During the late Quaternary, a strong volcanic activity was registered in the Campanian coastal graben along the main tectonic faults, with the growth of the Roccamonfina, the Somma-Vesuvius and the Phleagrean Fields volcanoes (Oliveri, 1966; Ippolito et al., 1973; Rolandi et al., 2003).

Therefore, the current stratigraphy of the Campanian Plain is the result of marine, fluvial, and volcanic processes. Marine-transitional deposits are the deepest ones, overlying directly the Mesozoic carbonate deposits (Ippolito et al., 1973; AGIP, 1977; Ortolani & Aprile 1985; Romano et al., 1994; Brancaccio et al., 1995; Bellucci, 1998; Aprile et al., 2004; Putignano et al., 2007, Santangelo et al., 2010). The products of the

intense volcanic activity of Phleagrean Fields and Vesuvius filled the plain. Some volcanic products, put in place over the last 39,000 years, are important stratigraphic markers. They are useful in achieving stratigraphic correlations between the units in the Plain.

Campanian Ignimbrite (CI; also known as Grey Campanian Tuff) is the most widespread volcanic product across the Plain and it is located above transitional-marine deposits (Fig. 3.3). The CI extends over an area of about 30,000 km², including the Volturno river plain (De Vivo et al., 2001; Corniello & Ducci, 2014) with thickness between 30 and 60 m (Budetta et al., 1993). The CI is absent close to the Volturno river, due to river erosion, and near the coast line (Corniello et al., 2010).

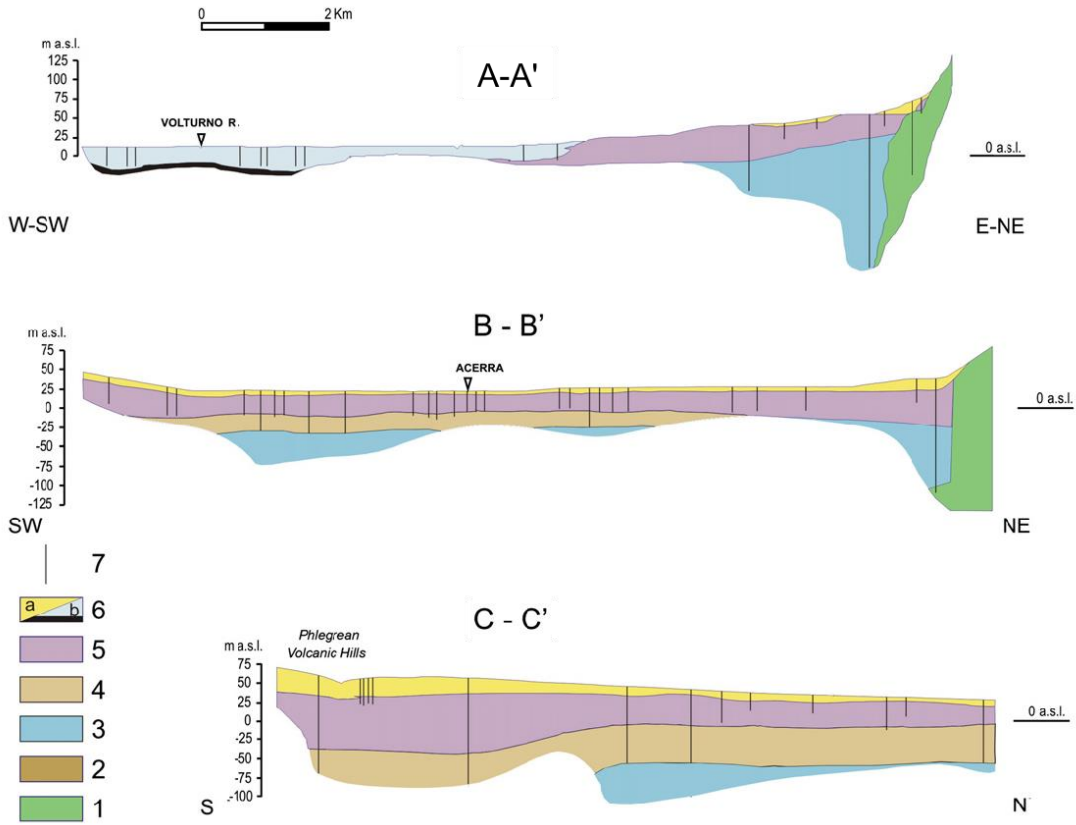


Fig.3.3. Hydrogeological cross sections (mod. from Corniello & Ducci, 2014). Traces in Fig. 3.2. 1) limestone, 2) arenaceous-clayey flysch, 3) old alluvial deposits, 4) old pyroclastics, 5) Campanian Ignimbrite (CI), 6) pyroclastic deposits a) and alluvial deposits b) with peat level (in black), 7) boreholes

Almost everywhere the CI underlies younger alluvial and pyroclastic sediments and overlies Plio-Pleistocene pyroclastic, lacustrine, palustrine, and marine deposits

(numbers 3 and 4 in Fig. 3.3). The stratigraphic sequence rests on the depressed part of the carbonate platform which however has never been identified from the investigation carried out in a central part of the area (Budetta et al., 1993). In the Volturno River Plain the main aquifer is located in the alluvial, pyroclastic and marine porous sediments underlying the CI (Fig. 3.3).

This aquifer is strongly related to the thickness and the physical characteristics (lithification, granulometry, amount of scoria, etc.) of CI, which plays, where present, the role of a semi-confining or confining bed. The groundwater is semi-confined almost everywhere in the southern sector and phreatic only near the coast. Along the Volturno river the CI is absent or very thin due to river erosion and there is a widespread presence of peat lenses that determines redox conditions (section A-A' Fig. 3.3).

The average *transmissivity* of the main aquifer is about $10^{-2} - 10^{-3}$ m²/s, and the minimum values are identified along the Volturno river and in the coastal sector (10^{-4} up to 2×10^{-5} m²/s) and the *storage coefficient* is about $S = 10^{-2} - 10^{-4}$ (Nicotera & Tonnetti, 1972), these values confirm that the aquifer is confined or semi-confined.

3.2. Piezometric pattern

The piezometric surface indicates a general groundwater flow from the mountains (at east) towards the sea (west and south-west) (Fig. 3.2).

Rainwater infiltration and groundwater outflows from Mesozoic limestone mountains and from volcanic adjacent aquifers contribute to the recharge of the aquifers of the plain. The conspicuous groundwater flow from adjacent aquifers is confirmed by (Corniello et al., 1990; Corniello & Ducci, 2014):

1. the higher piezometric levels (around 24-26 m a.s.l., Fig. 3.2) at the piedmont area;
2. the decrease of the $r(\text{Ca}^{2+} + \text{Mg}^{2+})/r(\text{Na}^{+} + \text{K}^{+})$ ratio (see § 3.3) moving away from the carbonate mountains.

In the period 1990-2005 in Campanian plain, a negative fluctuation of the water table was recorded, due to a decrease in rainfall. The coastal plains, bounded by massive carbonate and hydraulically connected to them, have been, in some cases, generalized lowering of the piezometric surface up to 6 m (Corniello & Ducci, 2004).

In relation to the local stratigraphy, there are local shallow aquifers of small thickness (Fig. 3.2). In the P-VLTR_{sx}, the interaction between the main aquifer and the shallow one is very low, due the presence of impervious thick layers, and it occur in zones of normal faulting or where there are discontinuities in the CI (Corniello et al., 1990; Corniello & Ducci, 2009).

3.3. Hydrochemical setting

The hydrochemical pattern is linked with the groundwater flow pattern in the plain. Near the limestone mountains, where there is a conspicuous groundwater outflow (§ 3.2), the $r(\text{Ca}^{2+} + \text{Mg}^{2+})/r(\text{Na}^+ + \text{K}^+)$ ratio, and the HCO_3^- content are high, while along the coastal areas more alkaline conditions occur (Ducci et al., 2016).

Hot springs and thermal areas testify the occurrence of a hydrothermal system, which strongly influence the groundwater features (Ducci & Sellerino, 2012). The Acerra mineralized area, with higher EC values, coincides with two mineralized spring discharge areas. Elsewhere, close to the limestone mountains, the EC values are about 500–600 $\mu\text{S}/\text{cm}$ increasing north of Capua, due to local inflows of highly mineralized waters (Corniello & Ducci, 2014). The origin of the mineralization (Maisonneuve & Risler, 1979; Schoeller & Schoeller, 1979; Corniello, 1996; Goldshschider et al., 2010) is due to the presence of important faults; along these tectonic lineaments, deep natural gases (chiefly CO_2) rise and they increase the solubility of the carbonate rock. High EC values are also observed in the Phleagrean Fields aquifer, due to the interaction between deep volcanic fluids, fresh groundwater and sea water, and near the Volturno river mouth, due to saltwater intrusion (Corniello & Ducci, 2014).

In the P-VLTR_{sx} there are different types of “natural contamination” linked to volcanic formations such as high fluoride content (almost everywhere $> 1.5 \text{ mg}/\text{l}$) and high arsenic content (close to the Phleagrean Fields). The high As values derive mainly from water–rock interaction, but they are favored, also in terms of mobility, by the presence of steam-heated groundwater (Aiuppa et al., 2003).

Moreover, there is a widespread nitrate contamination, prevalently caused by intensive agricultural and livestock activities (Corniello et al., 2007). Nitrate leaching is particularly important in areas of intensive agriculture, where intensive irrigation and

fertilization are predominant (Candela et al., 2008). The prevalent land use in the study area, provided by the CORINE Land Cover inventory in Europe (CLC, 2012), is:

- the level 2.1.1 i.e. “Not irrigated arable land” (in particular corresponding to the 4th level 2.1.1.1 i.e. “Arable land without dispersed vegetation”) that covers the 26% of the total area;
- the level 2.1.2 i.e. ‘Permanently irrigated land’ (18% of the total area);
- the level 2.4.2 i.e. ‘Complex cultivation patterns’ (18% of the total area).

Last two classes of land use, that cover more than one third of the study area, require the use of fertilizers, chemical and natural ones (i.e. manure). Moreover, the use of manure is common due to the presence of buffalo farming in the study area, used in the production of “Mozzarella di Bufala”.

Nitrate can also derive from feedlots, dairy and poultry farming, sewerage systems and septic tank drainages (Madison & Burnett, 1985), all present in the study area, having characteristics of mainly agricultural, but also urban and peri-urban environment. Studies using nitrogen and oxygen isotopes ($\delta^{15}\text{N-NO}_3$, $\delta^{18}\text{O-NO}_3$) have been conducted to better assess the types of sources and contributions of nitrate to the groundwater as well as the presence of denitrification processes (Clark & Fritz, 1997). In a part of the study area, located near the Acerra area (province of Napoli, Fig. 6.3) the $\delta^{15}\text{N-NO}_3$, $\delta^{18}\text{O-NO}_3$ were used to define the source of nitrates (Corniello & Ducci, 2009). The results of the isotopic analysis highlight the prevalence of nitrates of agricultural origin.

During the PhD studies, on a limited number of groundwater points in the area, were also carried out sampling to perform isotopic analysis (Research project “*Strumenti operativi di valutazione e controllo delle qualità dei sistemi agricoli della Piana Campana*” By Campania Regional Authorities) to verify both the source of the high content of nitrates and the belonging of groundwater to the same groundwater basin. These samples, analyzed by the CIRCE laboratory (Department of Mathematics and Physics of the Second University of Naples), clearly indicate that the origin of the contamination by nitrates is linked prevalently to agricultural sources, and secondarily to septic waste (the sewerage system is absent in some cases).

The lower nitrate content, close to the Volturno river, with low content in sulphates, respect to the typical hydrochemical facies, and high Fe and Mn concentrations are related to reducing conditions (Corniello et al., 2010; Ducci et al., 2016).

The intensive agricultural and livestock activities are also the cause of the high level of the nitrate risk contamination, while the vulnerability to contamination of the aquifers (Fig. 3.4) varies from low to moderate (Corniello et al., 2007).

In the study area, some contaminated sites, called “Aree vaste”, are individuated during the drafting of the regional remediation plan “*Piano regionale di bonifica dei siti inquinati della regione Campania*”. The contaminated sites, defined by ARPAC, are waste landfills and storage sites. The contaminated sites that fall in the study area are: Maruzzella, Lo Uttaro and Masseria del Pozzo-Schiavi (Fig. 3.5).

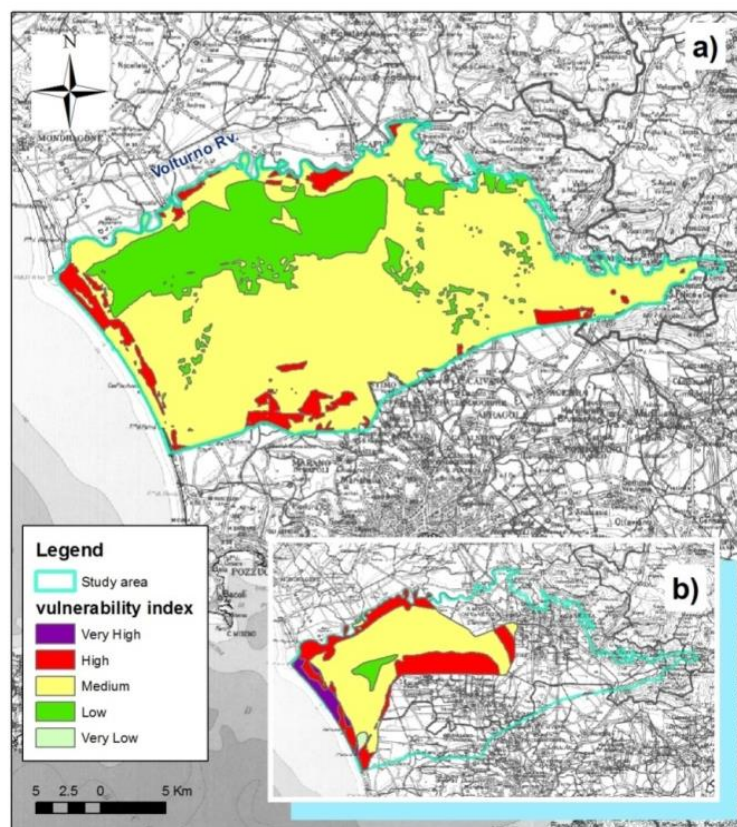


Fig. 3.4. Vulnerability map drawn up by SINTACS method (Civita & De Maio, 2000) of: a) main aquifer; b) shallow aquifer. (mod. from Corniello & Ducci, 2005)

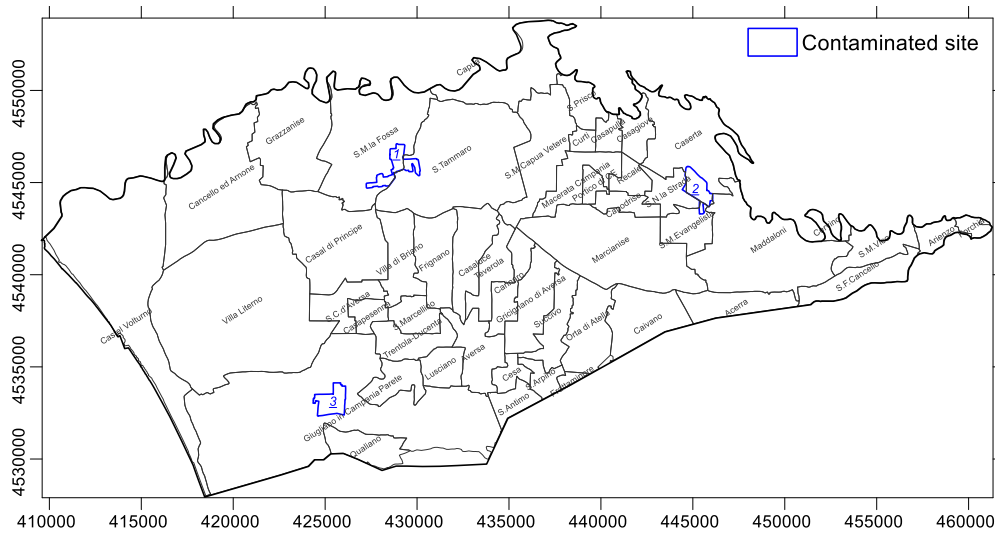


Fig. 3.5. Location of contaminated sites, also called “Aree vaste”: 1) Maruzzella; 2) Lo Uttaro; 3) “Masseria del Pozzo-Schiavi

4. METHODS

4.1. The natural background levels

4.1.1 Definitions

The natural background level (NBL) of a substance or element in groundwater may be defined as “the concentration of a substance or the value of an indicator in a body of groundwater corresponding to no, or only very minor, anthropogenic alterations to undisturbed conditions” (Art. 2.5 of the GWDD). The NBL is the results of the interaction of different natural atmospheric, geological, chemical and biological processes during groundwater infiltration and circulation, and uninfluenced by human activities (Reimann & Garrett, 2005; Edmunds & Shand, 2008; Hinsby et al., 2008). Rainfall composition, water-gas-rock interactions in both vadose and saturated zone, exchanges with other water bodies and residence time also contribute to determine the groundwater natural composition (Fig. 4.1).

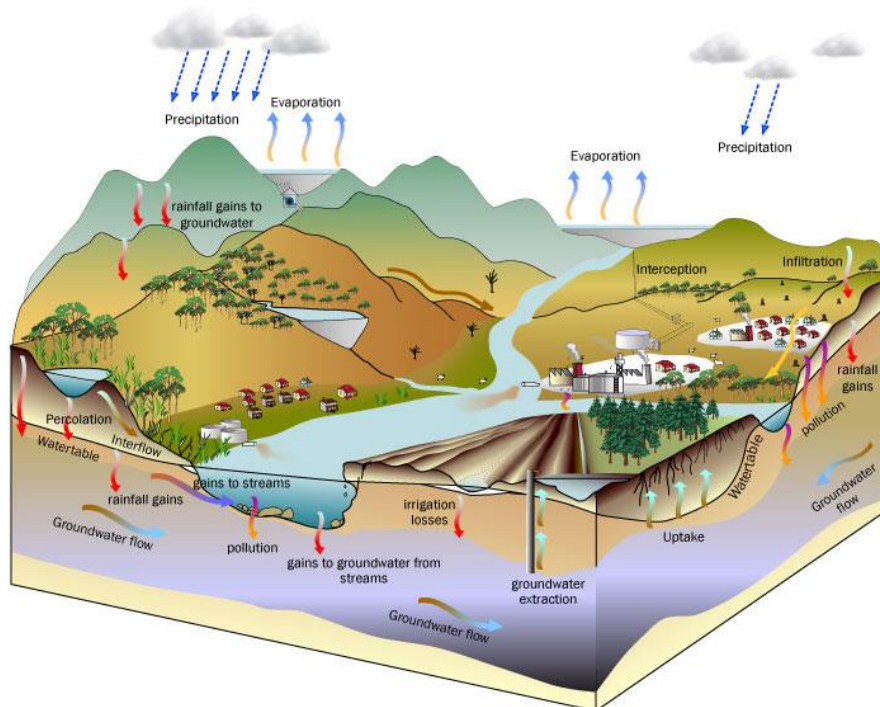


Fig. 4.1. Atmospheric, geological, chemical and biological interaction processes during groundwater infiltration and circulation that contribute to determine the groundwater natural composition (WRON Alliance, 2006)

The concept of NBL is generally used to indicate a range of geochemical values that reflects the impact of natural biogeochemical processes on groundwater quality and comes originally from exploration geochemistry, where it was used to distinguish between natural concentrations and anomalies that could be indicative of either an ore occurrence or an anthropogenic impact (Hawkes & Webb, 1962). In order to differentiate between background and anomaly, the term 'threshold' was introduced corresponding to the upper limit of background variation (Reimann & Garrett, 2005) or, as for the European Commission, to refer to a groundwater quality standard for groups of pollutants and indicators of pollution, which have been identified as contributing to the characterization of groundwater bodies as being at risk (European Commission, 2006).

The term 'ambient background' has also been used to describe both the immeasurably perturbed and no longer pristine natural background or for a modified background in an area close to human activities (Reimann & Garrett, 2005), while the 'baseline' concept is often used as an equivalent term to 'natural background' and it corresponds to a reference or starting level in order to quantify future changes. In Edmunds et al. (2003) the baseline concentration of a substance in groundwater is defined as "the concentration of a given element, species or chemical substance present in solution, which is derived from natural geological biological or atmospheric sources".

4.1.2 State of the art

In the last two decades, several methods and approaches have been proposed.

Geochemical methods are based on the analysis of groundwater samples collected in undisturbed conditions, i.e. samples from deeper aquifers (Muller et al., 2006), samples of ancient groundwaters or historical data collected in periods in which anthropogenic activities had a low impact (Griffioen et al., 2008). Typically the NBL is calculated as a fixed value (mean, median or 90th percentile) of the "undisturbed" population. The French Geological Survey (BRGM) proposed a method to determine the geochemical background of an aquifer, according to the level of knowledge about the physical system. The natural geochemical background is reconstructed by the correlation between geology and geochemical background, by defining the magnitude of the concentration of a particular substance on the basis of the lithology of the aquifer, or by analyzing

existing data and excluding indicators of anthropogenic contamination (Chery, 2006).

Statistical methods aim to identify the natural background population from the sample data available. The identification of the natural background population can be made:

- assuming a normal distribution (Matschullat et al., 2000; Gałuszka, 2007; Nakić et al. 2007, 2010; Urresti-Estala et al., 2013);
- assuming log-normal distribution of the samples, e.g. in the component separation approach (Wendland et al., 2005; Molinari et al., 2012, 2014; Rotiroti, 2015);
- with techniques that are not based on a priori hypothesis of normal or log-normal distribution, e.g. probability plot (Sinclair, 1974; Tobías et al., 1997; Edmunds et al., 2003; Wendland et al., 2005; Panno et al., 2006; Walter, 2008; Morgenstern & Daughney, 2012; Potot et al., 2012; Preziosi et al., 2014; Zabala et al., 2016) or the pre-selection approach (Muller et al., 2006; Hinsby et al., 2008; Wendland et al., 2008; Coetsiers et al., 2009; Ducci & Sellerino, 2012; Molinari et al., 2012; Rotiroti & Fumagalli, 2013; Preziosi et al., 2010, 2014).

In Europe, the Background cRiteria for the IDentification of Groundwater thrEshold (BRIDGE) protocol (Muller et al. 2006) gives clear guidelines on criteria for establishing groundwater natural background level. The national approaches of France and Germany, and other local case study have been studied in order to develop a tiered approach for the derivation of pollutant threshold values for groundwater bodies in support of the Water Framework Directive (WFD) and the Groundwater Daughter Directive (GWDD).

The BRIDGE project proposed, mainly, two methodologies for the assessment of the NBL in groundwater: the Component separation method (§ 4.4) and the Pre-selection criteria method (PS) (§ 4.5).

The Bridge protocol was transposed in Italy by ISPRA (Bellucci et al., 2009). In the Italian protocol the probability plot method (§ 4.3), also was taken into account.

4.2. The NBLs assessment

The workflow in Fig. 4.2 summarizes the procedure required in the NBL assessment, proposed by the ISPRA protocol (Bellucci et al., 2009) and inspired by the BRIDGE guidelines.

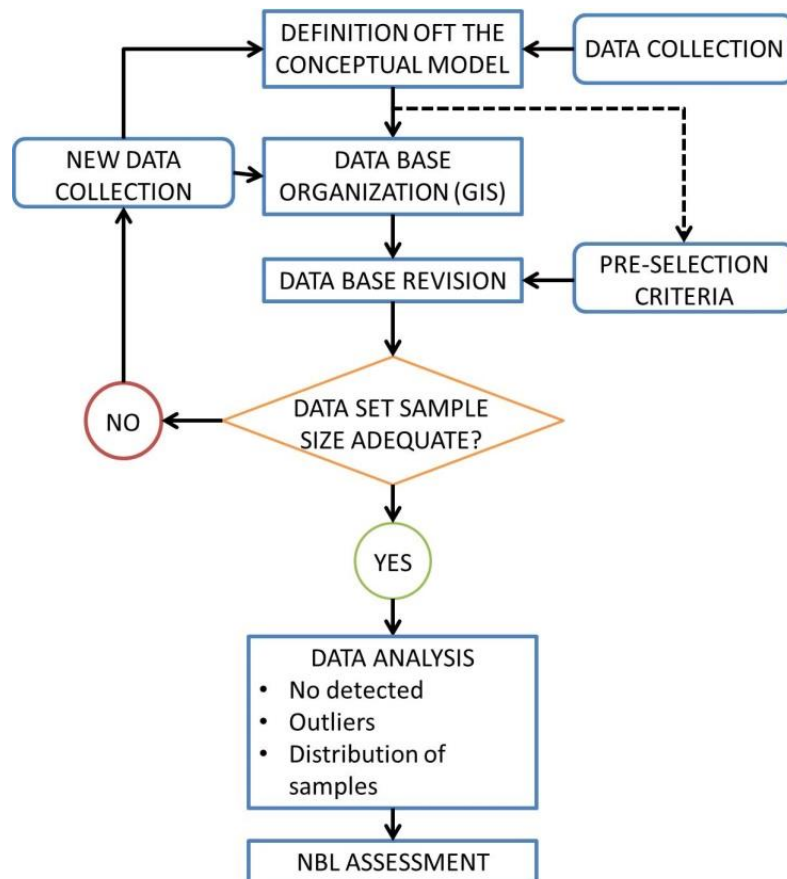


Fig. 4.2. Workflow of the methodology to assess the NBL (Bellucci et al., 2009)

4.2.1 Conceptual model

Generally, the definition of the NBL requires a preliminary hydrogeological study of the area in order to **identify the conceptual model** on the basis of which to conduct critical application of the methods described below. The geological and the hydrogeological background are important to identify the GWB boundaries and the presence of one or more aquifers in the GWB (in case of multilayered aquifer), as well as the interconnections between them. The NBL of an element must be assessed for the

whole GWB and for each aquifer, or for the aquifer of interest. The hydrochemical study of the area (§ 3.3) allows the identification the potential natural contamination, and to project the architecture of the database.

Some graphical representation of the chemistry of the water samples can help the definition of the conceptual model.

The **Piper diagram** (Piper, 1944) provides a quick graphical method of groundwater characterization in groups with homogeneous chemical and physical characteristics. It consists of two equilateral triangles: the left triangle represents the cations (Ca^{2+} , $\text{Na}^+ + \text{K}^+$, Mg^{2+}), the right one the anions ($\text{HCO}_3^- + \text{CO}_3^{2-}$, Cl^- , SO_4^{2-}). Each vertex represents the 100 percent of a selected ion or group of ions (respect to the total concentration of the cationic or anionic group, expressed in meq/L). The triangles are surmounted by a diamond-shaped field. The points plotted in the central diamond-shaped field are originated by the projection of the points plotted in the anion and cation triangles (Fig. 4.3).

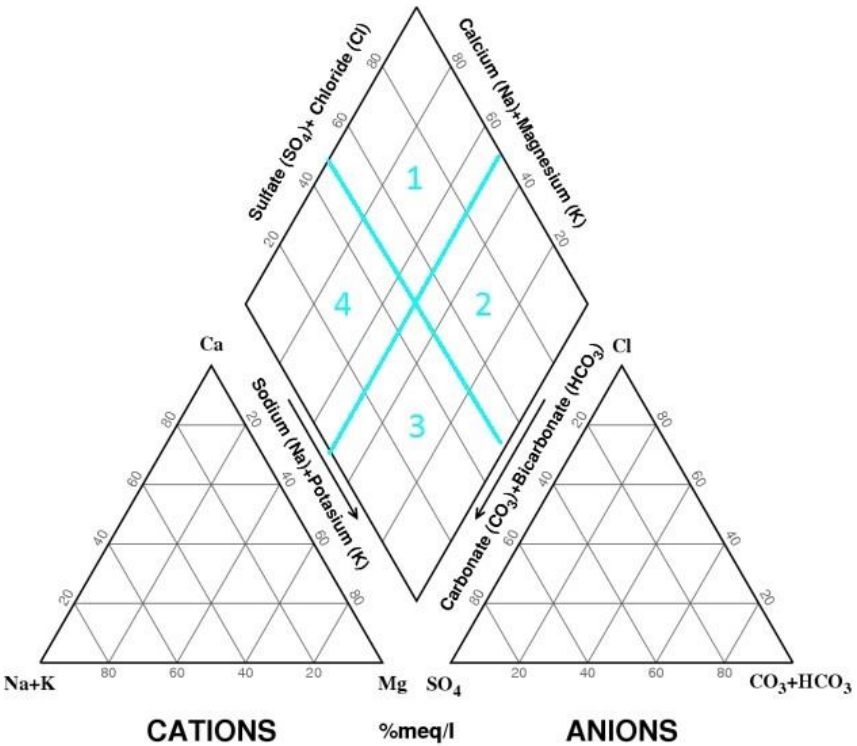


Fig. 4.3. Piper diagram (Piper, 1944). 1) chloride - calcium sulfate - magnesium water, 2) sodic and potassic chloride or sodium sulfate water, 3) bicarbonate alkaline water, 4) bicarbonate calcium and magnesium water

It is important to consider that one point in the diamond can represent different waters (Celico, 1988): i) in terms of different content of $\text{SO}_4^{2-} + \text{Cl}^-$ and $\text{Ca}^{2+} + \text{Mg}^{2+}$ along the projection line (the check of the position of the points in the two triangles can solve this problem) or ii) in terms of more mineralized waters with the same proportional content (being a percentage). The advantage of this diagram is to offer a possibility to draw together a lot of analysis and to have a first, but rough, characterization and differentiation of the different waters. Within the diamond, waters can be divided into four groundwater types by splitting the main diagram in four smaller diamond shapes (Fig. 4.3): 1) the uppermost diamond : chloride - calcium sulfate - magnesium waters, 2) the right diamond: sodic and potassic chloride or sodium sulfate waters, 3) the bottom diamond: bicarbonate alkaline waters, 4) the left diamond: bicarbonate calcium and magnesium waters.

The **Schoeller diagram** is a semi-logarithmic diagram. The main ionic concentrations (Ca, Mg, Na+K, Cl, SO_4 , HCO_3) expressed as meq/l, are plotted on six equally spaced logarithmic scales and the points so plotted are then joined by straight lines (Bowen, 1986). This diagram gives the absolute concentration of each ion and the straight lines also gives the ratio between two ions in the same sample. In addition the diagram gives the concentration differences among various analyses of groundwater or it highlights the similarity among various analyses.

4.2.2. Data base organization and analysis

The large amount of stratigraphic, piezometric and chemical data must be organized in such a way to be used for the subsequent analysis of the data. The **Geographic Information Systems (GIS)** are very powerful tools for storage, manipulation, analysis and visualization of environmental spatial data.

The methodologies for assessing the NBLs are mainly based on a statistical approach. The **statistical analysis** requires a minimum of samples, in according to the boundary conditions, e.g. the extension of the GWB, the spatial distribution of the values; typically the sample size must be greater than 10 (Bartolucci et al., 2009). The number of samples can change from the initial database because of some **necessary revisions** to the

application of the methods. First of all, samples with incorrect ionic balance (error exceeding 10%) and unknown depth (or information about the aquifer of interest) should be removed. Some pre-selection criteria can be applied in order to identify the natural population (§ 4.5).

If the **samples size is adequate** to the application of the methodology, the **data set** is subjected to **analysis**.

The constituents with values lower than the **detection limits** (DL) have been treated considering a value lower than the DL, equal to $DL - x$, where x is proportional to DL, as suggested by Bartolucci et al. (2009). In § 6.2 (Tab. 6.1) will be reported the correction for each case. Since the chemical data collection comprises analyses from different analytical laboratories, with different detection limits, the adopted method can generate different values. This simple substitution can produce biased estimates of summary and descriptive statistics (Lopaka & Helsel, 2007).

The identification of **outliers** is an important step in the assessment of the NBLs. The outliers are those values of a data set that are not representative of the data set as a whole. However, in general, these extreme values can be "real outlier" or "false outlier". As for outliers, Bartolucci et al. (2009) say: *"Outliers [...] are not representative because, in general, they are quantitatively a very small number and qualitatively they assume of very large or very small values compared to the rest of the data set. In the environmental field [...], generally very high concentration values correspond to the peaks (hot spots) local concentration. However, in general, these extreme values can be "real outlier" or "false outlier". The former can result from transcription errors, data encryption or any inefficiency of the tools of the data collection system. The second are those real extreme values, often present in this type of investigation especially, as already said, in the environmental field. The removal of the second ones and / or the non-removal of the first ones can lead to a mistaken view of the data set (U.S. EPA, 2000). It is crucial to take into account and therefore not remove "false outlier" from the data set (U.S. EPA, 2002). If the data set available it has already been validated automatically excludes the presence of real outlier "*. About the decision of excluding the outliers from the data set, Bartolucci et al. (2009) say: *"This decision can take place only if it is possible to accompany the results of*

statistical tests [...] with a valid scientific justification".

A good way of identifying outliers, and in general graphically representing the data set of concentration of a specific ion, is **the box and whisker plot** (here and after "box plot"). The box plot is used to visually summarize and compare groups of data. The box plot (Fig. 4.4) uses the median, the first and the third quartiles, and the lowest and highest data points to convey the level, spread, and symmetry of a distribution of data values. It can also be easily refined to identify outlier data values. The minimum is the smallest value in the data set, and the maximum is the largest value in the data set. The quartiles of a ranked set of data values are the three points that divide the data set into four equal groups: each group comprises a quarter of the data. A quartile is a type of quantile. The first quartile (Q1) is defined as the middle number between the smallest number and the median of the data set. The second quartile (Q2) is the median of the data. The third quartile (Q3) is the middle value between the median and the highest value of the data set.

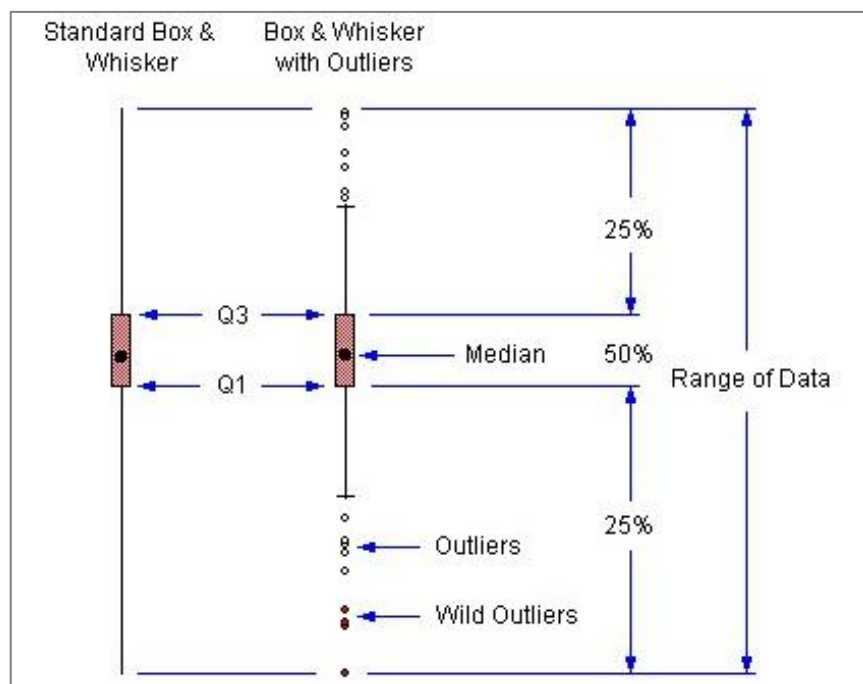


Fig. 4.4. Box and Whisker Plot. Q1: first quartile; Q3: third quartile

The body of the boxplot consists of a "box" (hence, the name), which goes from the first quartile (Q1) to the third quartile (Q3). Within the box, a horizontal line is drawn at the Q2, the median of the data set. Two vertical lines, called whiskers, extend from the

front and back of the box. The front whisker goes from Q1 to the minimum, and the back whisker goes from Q3 to the maximum. To determine whether or not outliers are present, the Interquartile Range (IQR) is calculated; IQR is found by subtracting Q3 – Q1; then multiply IQR by 1.5. Add this amount to the value of Q3 and subtract this amount from Q1. This gives you a wider boundary around the median than the box does. Any data points that fall outside this boundary are determined to be outliers (Fig. 4.4).

4.2.3. The adopted methodologies

The final purpose is to identify the **probability distribution** which best approximates the available data set.

The identification of the type of distribution that best approximates the data sample is used to define the most appropriate statistical descriptors and to estimate the NBL.

In this study three statistical methods for assessing the NBLs were considered:

- a. the “Probability plot” method (PP);
- b. the “Component separation” by concentration distribution analysis (CS).
- c. the “Pre-selection criteria” method (PS).

Statistical methods are chosen because they are more suitable for aquifer subject to sever anthropogenic impacts, or highly contaminated, or under peculiar hydrogeological conditions.

4.3. Probability Plot

The probability plot method (PP) is grounded on the hypothesis that diverse phenomena generate statistically distinguished populations (Edmunds et al., 2003; Wendland et al., 2005; Walter, 2008; Panno et al., 2006). To derive the limits between populations, data are plotted on a probability scale (Fig. 4.5). Generally are used both normal and lognormal plots.

The hypothesis that background population of the geochemical data has a lognormal distribution is prevalent in many scientific papers (Sinclair, 1974; Wendland et al., 2005, Masetti et al., 2009; Molinari et al., 2012 and others), although other distributions are often claimed. Normal distribution is proposed by e.g. Wendland et al. (2005) and Molinari et al. (2012) for the “influenced population” possibly related to anthropogenic contamination, even if it is not always true (Reimann & Filzmoser, 2000) as reported in § 4.4.

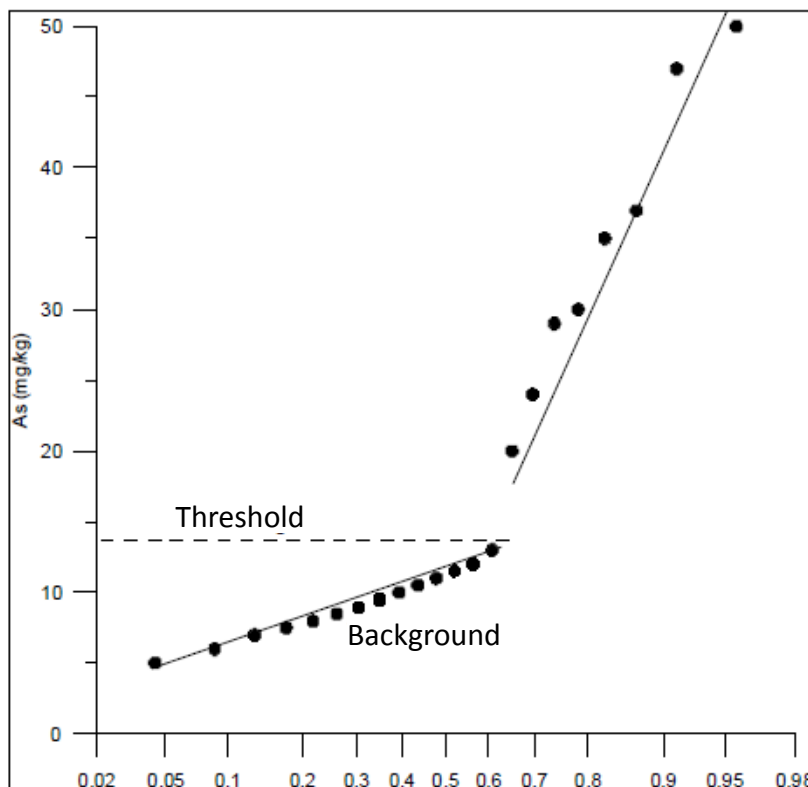


Fig. 4.5. Probability plot (mod. from Bartolucci et al., 2009)

Probability plots allow displaying the data and graphically observing the main trends, discontinuities, and outliers. In a probability plot (also called a "Q-Q plot"), the sorted data are plotted vs. values selected to make the resulting image look close to a straight line if the data are approximately normally (or lognormally) distributed.

Deviations from a straight line suggest departures from normality (or lognormality) and a possible limit between natural and influenced concentrations (NBL_{PP}), but they could also mark natural variation of geochemical facies as well or a local geochemical anomaly (Preziosi et al., 2014). Several types of geochemical reaction can alter distributions by removing or limiting concentrations in solution including redox processes, adsorption onto solid mineral phases and saturation with respect to minerals which will limit the solubility of one or more elements (Edmunds et al., 2003).

4.4. Component separation method

The component separation (CS) method assumed that the observed frequency distribution (PDF_{obs}) of the concentration (X) of a given environmental parameter may be expressed by the superposition of two distribution functions (Fig. 4.6): the natural component and the influenced component (Molinari et al., 2012; 2014; Wendland et al., 2005; Muller et al., 2006).

The PDF_{obs} (in green in Fig. 4.6) is not known a priori but it is possible to assume that: the natural process are well described by the lognormal frequency distribution (PDF_{logn} in blue in Fig. 4.6), whereas the anthropogenic component should usually follow a normal frequency distribution (PDF_{norm} in red in Fig. 4.6) because the concentration patterns originating from direct inputs from the soil are more or less proportional to the inputs into the soil.

The assumption that the natural component is represented by a log-normal distribution is not always true (Reimann & Filzmoser, 2000), as reported, for example, by Molinari et al. (2014) who identified a normal distribution of SO_4 concentration frequency attributable to the natural process of seawater intrusion.

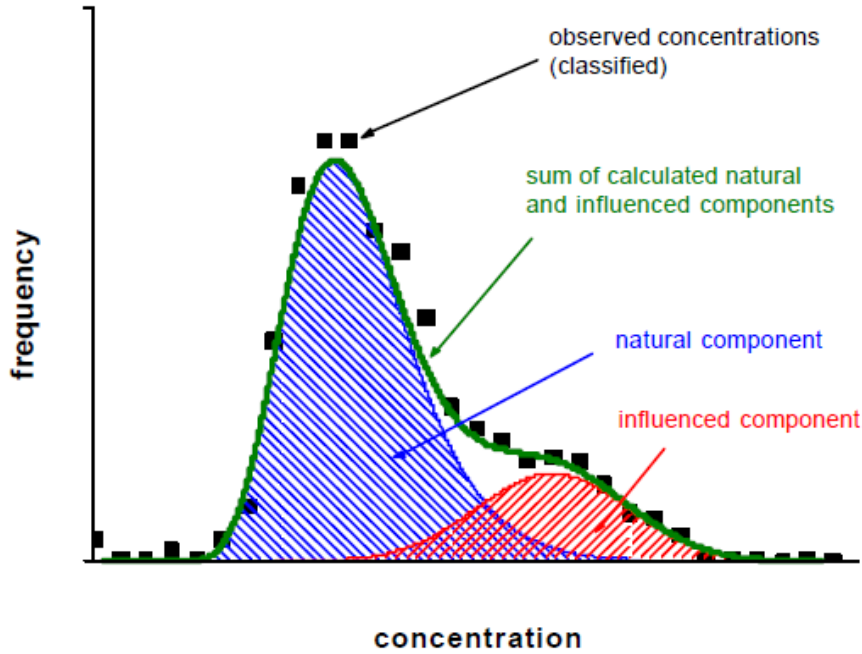


Fig. 4.6. Basic approach of separating the natural and influenced component from an observed groundwater concentration pattern (Muller et al., 2006)

The PDF_{obs} is given by the sum of these two known distribution mixed by a parameter of partition p [0,1]:

$$PDF_{obs}(X) = p \cdot PDF_{logn}(X) + (1 - p) \cdot PDF_{norm}(X) \quad [1]$$

The CS allows to use the whole data set for NBL assessment (as in PP) because no criteria for identifying the anthropogenic component are needed (as required by PS), but it means that a large data set is required for the application of this methodology. Moreover proper tools of statistical analysis are required by the operator (instead of PS method).

A MATLAB® algorithm (§4.7) called COMPSEC was developed to estimate the NBLs using the CS approach (Rotiroti et al., 2015). The algorithm calculates the PDF_{mod} (equal to PDF_{obs} as defined in Eq. [1]) by estimating the following parameters through maximum likelihood estimation (MLE):

- the mixing factor p ;
- the mean and the standard deviation of PDF_{logn} (μ_{log} , σ_{log});
- the mean the standard deviation of PDF_{norm} (μ_{norm} , σ_{norm}).

The MLE is performed by varying the initial value of p from 0 to 1 with an iterative procedure. For each solution, the NBL_{CS} is valued as the cumulative density function (CDF) at 90% of the log-normal component (a conversion of PDF into CDF is applied) and the goodness of fit (R^2 and RMSE) is calculated by applying an ordinary least square (OLS) (Fig. 4.7).

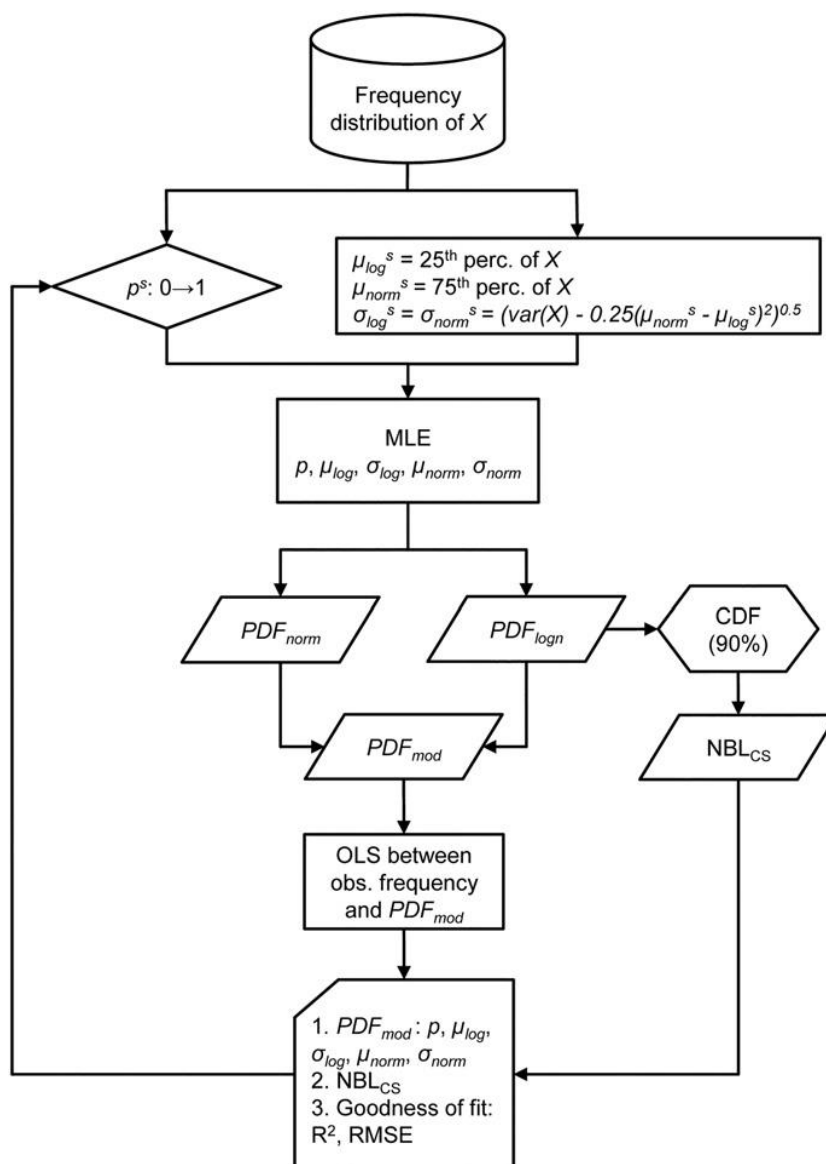


Fig. 4.7. Workflow of the COMPSEC (Rotiroti et al., 2015). The frequency distribution of chemical concentrations of each species (X) is modeled as a mixture of normal and log-normal distributions by maximum likelihood estimation (MLE)

4.5. Pre-selection criteria

As a general rule, frequency distributions of groundwater samples result from the superposition of background populations, reflecting long term natural conditions and not influenced by human activities, and one or more anomalies, caused by impacts of natural (e.g. reducing conditions, soil mineralization) or anthropogenic. Thus, a reasonable procedure of determining natural background values consists in filtering out the anomalous fraction and consists in determining the distribution parameters for the remaining background population.

The pre-selection method (PS) proposes to remove from the initial data set those samples which are characterized by markers of human activities (e.g. organic compounds, nitrate, and nitrite). The samples which do not show evidence of anthropogenic inputs may be considered as original groundwater and used to assess the NBL for the GWB (Hinsby et al., 2008).

The preselection methods are appropriate to derive NBLs, especially for large-scale considerations. They require “no deeper knowledge” about statistical analysis, and they can be applied by non-experts and to groundwater bodies, for which only few samples are available (Wendland et al. 2005).

The PS method adopted in this study follows the BRIDGE guidelines (Muller et. al., 2006) and the Italian protocol developed by the ISPRA Institute - Italian Institute for Environmental Protection and Research - (Bartolucci et al., 2009) with some modifications due to the GWB peculiarities (explained in the chapter 3). The data set was selected applying the following criteria:

1. Data from hydrothermal aquifers should be removed.
2. Data from salty aquifers (coastal or influenced by evaporites), i.e. with $[NA^+] + [Cl^-] > 1000$ mg/l, were removed. Salty aquifers must be considered as a separate.
3. Samples with $NO_3 > 50$ mg/l (or NO_3 content unknown/not available) are removed. The threshold value of the nitrate, proposed by the BRIDGE guidelines and set as 10 mg/l, could not be used because it would have led to the exclusion of almost all the sampling points, due to the intensive farming of the study area and to the consequent diffuse groundwater contamination by nitrates (see chapters 2 and 3). It was considered appropriate to raise the threshold value of nitrate to the EU Drinking Water Standard (98/83/EC7; DWD, 1998), equal to 50

mg/l (Preziosi et al., 2010; 2014; Ducci and Sellerino, 2012).

4. Data with presence of other anthropogenic contaminants (e.g. benzene or pesticides) were removed.
5. Data of aquifers under both, oxidizing and reducing conditions, were separated. This can be done using the oxygen content: ≥ 1 mg/l O_2 for aerobic and < 1 mg/l O_2 for anaerobic groundwater. If no reliable O_2 data are available, Fe(II) and Mn (II) concentrations may be used for separating aerobic groundwater instead. The separation of oxidizing (ox) versus reducing (red) samples was performed using the following criteria:
 - if $Mn \geq 50$ $\mu\text{g/l}$ and $Fe \geq 200$ $\mu\text{g/l}$, the sample is classified as “red”
 - if $Mn < 50$ $\mu\text{g/l}$ and $Fe < 200$ $\mu\text{g/l}$, the sample is classified as “ox”
 - otherwise, the sample was classified “ox” or “red” on the basis of some chemical or geological features, as a low content of NO_3 (and/or a content of NO_2) or as the presence of peat levels, that can indicate reducing conditions.

In this case additional PS should be used: samples with $NH_4 > 0.5$ mg/l in reducing conditions were discarded (Wendland et al., 2008).

6. All the data available can be used (no restriction on the time series to consider) but time series should be eliminated by median averaging (in order to guarantee that all sampling sites contribute equally to the NBL derivation). After this data processing only one representative groundwater analysis remains for all the remaining monitoring stations.
7. Limits quantification cannot be too high for traces elements. In particular, limits quantification equal to drinking water standards DWS should be removed.

Normality, or log-normality, of the selected data set was verified first of all observing the linear pattern displayed by a plot of the quantiles (Q-Q plot) suggests approximate goodness-of-fit for the selected distribution. Significant and obvious jumps and breaks in a Q-Q plot (for any distribution) are indications of the presence of more than one population. In addition to informal graphical normal and lognormal Q-Q plots, formal Goodness-of-Fit test are also needed to test the normality or lognormality of the data set. Shapiro & Wilk (S-W) Test (1965) is a test used for samples of size smaller than or equal to 50 (≤ 50). The Lilliefors Test (1967) has no applicable upper limit for the sample.

Once it was verified that the pre-selected data set represents a single population, through the analysis of the QQ-plots and the Shapiro & Wilk (S-W) Test (1965) or the Lilliefors Test (1967), then the calculation of the percentiles was performed in order to evaluate the NBL.

The NBL_{PS} is assumed to be represented by the 90th percentile of the remaining data (Hinsby et al., 2008; Muller et al., 2006; Griffioen et al., 2008; Wendland et al. 2008; Rotiroti, 2015; Ducci et al., 2016). For iron and manganese, the NBL_{PS} were calculated for reducing and oxidizing conditions because these are redox-sensitive elements in groundwater, being soluble in their reduced form but forming insoluble oxy-hydroxides under oxidizing conditions (Shand & Edmunds, 2008; Ducci et al., 2016). In the case of arsenic, the NBL was calculated for the whole data set due to the observation that redox conditions in these case studies were not affecting the concentration distribution of this metalloid (Ducci et al., 2016). Similarly, redox controls can be important in influencing As mobilization, through reductive dissolution and sorption to Fe oxyhydroxides (Carraro et al., 2013; 2015). The control of arsenic occurrence in volcanic environment is discussed very deeply in Preziosi et al. (2014) and in Smedley et al. (2002).

Preziosi et al. (2014), assert that sometimes arsenic does not show any correlation with iron, manganese nor with the observed redox potentials, because it is not coming from the desorption from Fe-Mn-oxy-hydroxides but rather from the water – volcanic rock interaction in oxidizing conditions. Smedley et al. (2002), studying high arsenic in a South-American aquifer in oxidizing conditions, have found that As correlates positively with pH, alkalinity, F and V in ascribed arsenic release to desorption from metal oxides including Mn and Fe oxides, but also to weathering of primary silicate minerals and accessory minerals such as apatite coming from volcanic ash, which could be also the case of the study area.

Therefore, “red” and “ox” NBL values were calculated for Fe and Mn, but not for As, where NBL was calculated for the whole data set.

4.6. Probability map

4.6.1. Indicator kriging

Kriging geostatistical algorithms allow the construction of models of random distribution variables, which are used to assume the attribute's values and to estimate the uncertainties associated to such values (Goovaerts, 1997; Deutsch & Journel, 1998). Kriging takes into account the stochastic dependence among the data, that is a result of a geological process, which could have possibly acted over a large area over geological time scales (e.g. sedimentation in large basins) or in fairly small domains for only a short time (e.g. peat sedimentation). Geological characteristics that were formed in a slow and steady geological environment are better correlated to each other than if they were results of an often abruptly changing geological process (Marinoni, 2003). Groundwater quality data (physic-chemical parameters, major constituents or contaminant concentrations) often show high variability in small distances. Otherwise, data can rarely be considered as uncorrelated in space and/or time. The detection of the patterns of spatial correlation is fundamental to better characterize the physical phenomena and it allows an adequate spatial interpolation (Ducci et al., 2016).

The most common geostatistical tool to model the spatial correlation is the variogram (Journel, 1987). It allows the quantitative representation of variation of a parameter in space. The variogram function $\gamma(h)$ is determined from the sample set, by:

$$\gamma(h) = \frac{1}{2n(h)} \cdot \sum_{i=1}^{n(h)} [Z(x_{i+h}) - Z(x_i)]^2 \quad i = 1, \dots, n \quad [2]$$

where $Z(x_i)$ and $Z(x_{i+h})$ are the values of the variable Z measured in the points x_i and x_{i+h} , respectively, and $n(h)$ denotes the number of pairs of points separated by a lag h .

The experimental variogram functions must be fitted by theoretical models and cross validated with experimental data. The most widely used is the spherical model expressed by the following equations:

$$\gamma(h) = C \left[\frac{3h}{2a} - \frac{1}{2} \left(\frac{h}{a} \right)^3 \right] \quad \text{if } h < a$$

$$\gamma(h) = C \quad \text{if } h \geq a$$
[3]

where C is the sill (in most of the cases is equal to the sample variance) and a is the range, a distance beyond which the variable is uncorrelated.

In some cases we need to add a 2nd structure, the nugget effect C_0 , to take into account the sampling errors and the short scale variability i.e. spatial variation within distances smaller than the sample spacing, C_0 is estimated by the discontinuity in the origin of the experimental variogram.

Indicator kriging (Journel,1983) is a kriging analysis based on data transformed from continuous values to binary values, giving 0 to all values below or equal to the threshold value and 1 to the remaining values (higher than). Threshold levels can be associated either to characteristic values (DWD, 1998) and referred hereby as 'REF' (or the NBL values for each ion) or to certain statistical percentiles of the original data.

The new variable I_{Z_c} (where Z_c is the user-defined threshold value) is build according to the expression:

$$I_{Z_c}(x) = \begin{cases} 1 & \text{if } Z(x) \geq Z_c \\ 0 & \text{if } Z(x) < Z_c \end{cases}$$
[4]

The Indicator Kriging results are then values between 0 and 1, representing the probability that the estimated value in an unknown location exceeds the user-defined threshold value Z_c .

All experimental variograms and maps were done in **Surfer 11** (Golden Software, LLC §4.7), belonging to Department of Department of Civil, Constructional and Environmental Engineering (DICEA) of University of Naples Federico "II".

4.6.2. Cross validation

Given the known values at N observation locations in the original data set, cross validation, also called “leave-one-out method” allows you to assess the relative quality of the grid by computing and investigating the gridding errors (Isaaks & Srivastava, 1989; Kitanidis, 1997; Olea, 1999; Chiles & Delfiner, 2009).

The cross validation process was done using the software **Surfer**.

The error is calculated by removing the first observation from the data set, and using the remaining data and the specified algorithm (Kriging) to interpolate a value at the first observation location. Using the known observation value at this location, the interpolation error is computed as:

$$\text{error} = \text{predicted value} - \text{observed value}$$

Then, the first observation is inserted into the data set and the second observation is removed from the data set. The interpolation error is computed as before.

The second observation is put back into the data set and the process is continued in this way for the third, fourth, fifth observations, etc., all the way through up to and including observation N, the last observation in the data file. This process generates N interpolation errors. Various statistics computed for the errors can be used as a quantitative, objective measure of quality for the gridding method.

4.7 Software used

All statistical and graphical processing, as well as the Normality or Lognormality Tests (Shapiro–Wilk test and Lilliefors Test), will be done with the help of software ProUCL, a free software package developed by the Environmental Protection Agency (EPA). It is a comprehensive statistical software package with statistical methods and graphical tools to address many environmental sampling and statistical issues (Singh et al., 2010).

Variograms and probability maps were done in Surfer 11 (Golden Software, LLC). Surfer is a contouring and 3D surface mapping software program. Surfer software's provides sophisticated interpolation (e.g. kriging) and gridding methods and control over gridding parameters, including customized variograms. Moreover, the software allows producing publication quality maps.

For the CS approach, a MATLAB function called COMPSEC was used. MATLAB is a high-performance language for technical computing. It integrates computation, visualization, and programming in an single environment. It allows matrix manipulations (basic data element is an array), plotting of functions and data, implementation of algorithms, creation of user interfaces, and interfacing with programs written in other languages, including C, C++, C#, Java, Fortran and Python. In fact, MATLAB features a family of application-specific solutions called toolboxes that are comprehensive collections of MATLAB functions (M-files) that extend the MATLAB environment to solve particular classes of problems.

5. HYDROCHEMICAL DATA

Hydrochemical data, collected for the study area refer to the main aquifer because those of shallow groundwater would be elaborated separately and they are insufficient to enable any statistical approach. The data has been organized in a database GIS, in which were stored information about location of the samples (coordinate were homogenized in the UTM-33N coordinate system), depth of the well (or aquifer of interest), and physical and chemical information.

The monitoring network is constituted by private wells mainly for agricultural use and secondarily for industrial supply and urban needs. The presence of more aquifers overlapped can be a problem when there is a lack of information about the construction scheme, and especially about the position of the well screen. In order to solve this problem and to select only the sample points from the main aquifer (located below the CI), GIS tools were used to select wells on the basis of their location and their depth. The depth of the well, or piezometer, was compared to the depth of the top of the confining layer (i.e. CI, Fig. 5.1). The top of the CI was reconstructed interpolating 216 boreholes, belonging to the database of the DICEA.

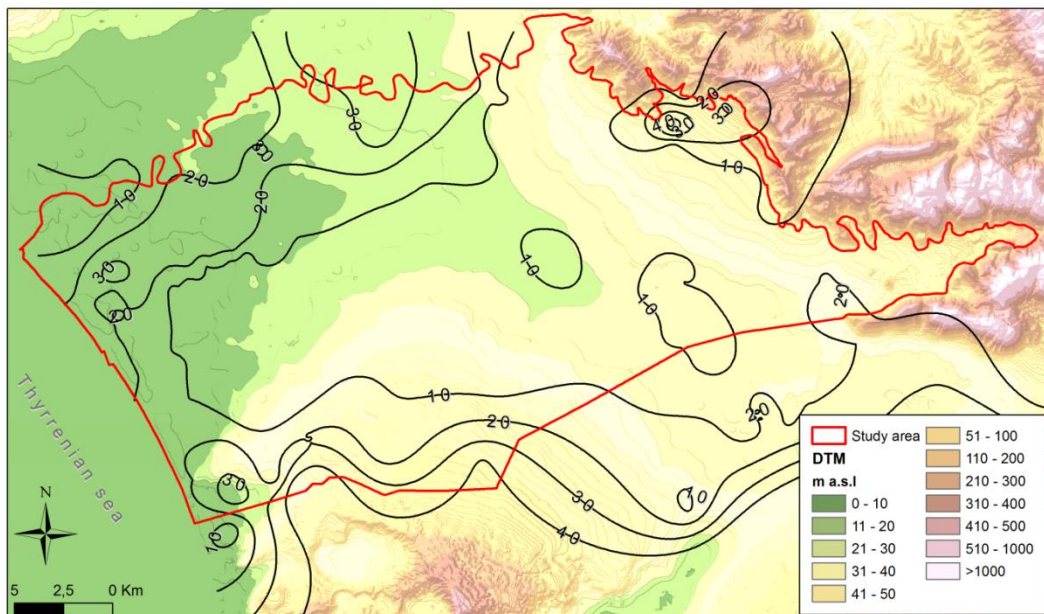


Fig. 5.1. Depth of the top of the Campanian Ignimbrite (m) and digital terrain model with a cell size 20 m (source: Campania Region) of the study area

This method allowed the elimination of the wells drawing water only from the upper shallow aquifer, but it does not exclude the possibility of considering water of both, the shallow aquifer and the deep one, if the well screen is extended to the whole length.

The data set is composed by 129 water samples (Fig. 5.2), collected in two different temporal range (2003-2006 and 2014-2016) with different purposes, prevalently for research and water resources management.

The chemical elements chosen for the application of the methodologies are arsenic, fluoride, iron and manganese, because of their diffuse presence in the study area, linked to the geological nature of the soils and/or to natural processes. The nitrate content is crucial in the application of the pre-selection criteria method.

The goodness of the data set was verified by checking that for each chemical analysis the ionic balance had an error less than 10%, as required by the methodologies (§ 4.2.2).

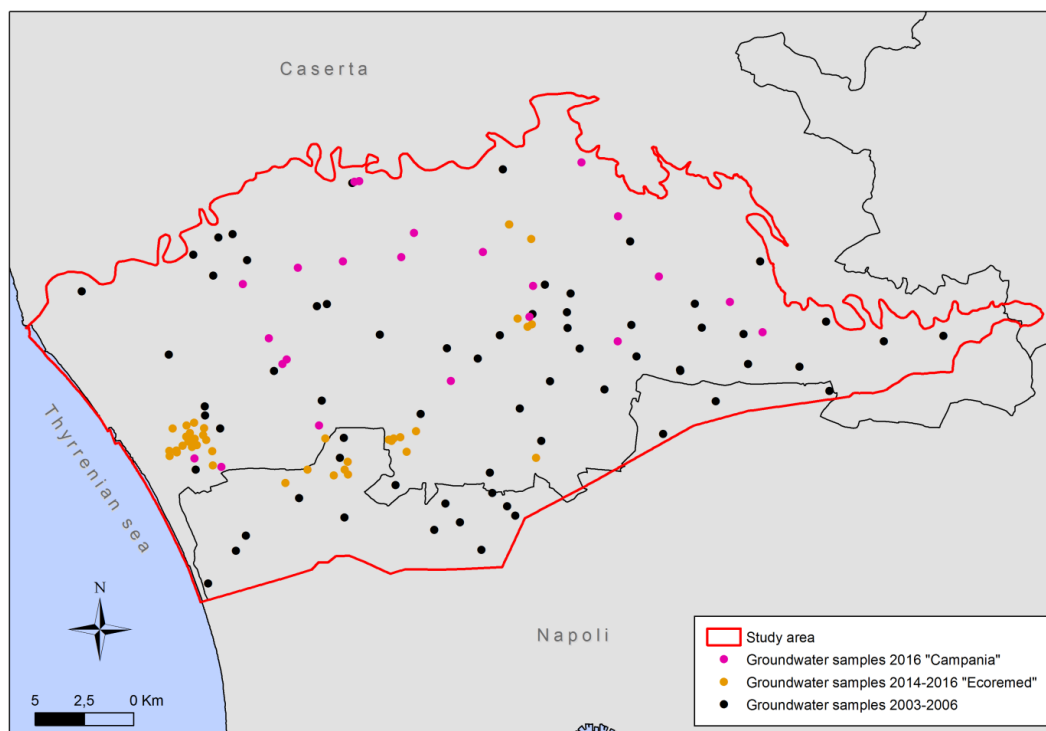


Fig. 5.2. Groundwater samples data set (see § 5.1 and § 5.2)

Tab. 5.1. Main statistical measure of the whole data set for the ions of interest

Variable	u.m.	Num. Obs.	Minimum	Maximum	Mean	25%ile(Q1)	Median (Q2)	75%ile(Q3)	Variance	SD	Skewness	Kurtosis	CV
NO₃	mg/l	128	0.01	148.1	41.91	11.5	42	61.9	1078	32.83	0.82	0.714	0.783
As	µg/l	107	0.34	112	6.127	1	3.6	97.78	162.9	12.76	6.3	46.94	2.083
F	µg/l	127	300	3800	1610	9	1500	74.83	380738	617	1.093	2.012	0.383
Mn	µg/l	128	0.05	6412	479.1	40.9	6	93.6	1446687	1203	2.939	8.408	2.511
Fe	µg/l	122	0.06	7428	412.2	1.9	20	5.5	1441620	1201	4.133	18.88	2.913

5.1. The historical data set

The hydrogeochemical setting was defined on the basis of 66 samples (black points in Fig. 5.2) collected between 2003 and 2006 (Autorità di Bacino della Campania Nord-occidentale, 2004; Adamo et al., 2007). The water samples were collected with several methods/instruments at different times and analyzed in two laboratories (Department of Chemical Sciences of University of Naples “Federico II” –DCS- and ARPAC - Regional Agency for Environmental Protection of Campania).

All the samples had been analyzed on site for temperature, pH, and electrical conductivity. Afterwards, the water samples were pre-washed and stored in PE bottles. For trace element analysis and Fe and Mn content analysis in 2006 the polyethylene bottles were previously washed several times with 2% nitric acid to avoid the successive release of trace components from the PE bottles. Then, they were acidified respectively with ultrapure HNO₃ (0.5 ml) and pure HNO₃ (2 ml). Once in the laboratory, the samples were analyzed for free CO₂ and major ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, F⁻, Cl⁻, SO₄²⁻, HCO₃⁻, NO₃⁻). Moreover, a great number of samples were tested more extensively, analyzing more ions (Al, As, Ba, Cd, Co, Cr, Cu, F, Fe, Mn, NH₄, NO₂, Ni, Pb, Sb, Sn, Sr, U, V, Zn). In the laboratory, major and minor elements were analyzed by ion chromatography and mass spectrometry on samples unfiltered and stored at 4 °C (Corniello and Ducci, 2014).

5.2. The new data set

In the last two year (2014-2016) 63 water samples were collected in the framework of two project: 40 samples for the LIFE+ ECOREMED project (orange points in Fig. 5.2), 23 for the research project “*Strumenti operativi di valutazione e controllo delle qualità dei sistemi agricoli della Piana Campana*” by *Regione Campania* (magenta points in Fig. 5.2). In the last project, I personally followed the collection of the water samples, as well as to *in situ* measurement of certain physical parameters (temperature, pH, conductivity) and piezometric level (with a phreatimeter), and their consignment in the laboratory (DCS) for the chemical analysis.

Samples were analyzed for basic physic-chemical parameters (T, pH, conductivity), major ions (Mg, Ca, K, Na, Cl, NO_x, HCO₃, SO₄, NH₄, NO₃) and additional parameters (Al,

Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, F, Fe, Li, Mn, NH₄, NO₂, Ni, Pb, Sb, Sn, Se, Te, V, Zn).

6. RESULTS

6.1. Data analysis

6.1.1. Piper diagram and Schoeller diagram

Groundwater type is dependent on many factors, like lithological characteristics of the aquifers, retention time and flow pattern. In order to recognize the dominant water type through the aquifer and to better identify the distribution of the water facies on the area, the Piper diagram and the Schoeller diagrams were used (§4.2.1).

The Piper diagram (Fig. 6.1a) shows that groundwater of the study area are mainly bicarbonate calcium waters. A smaller group of samples falls in the sub-diamond, where there are bicarbonate-alkaline waters. However, in the first triangle on the left, the half part of the samples fall in the mixed waters portion. The position of the samples in the Piper diagram agrees with the origin of these waters, coming by underflow from the carbonate aquifers, but also leaching pyroclastic sediments (§ 3.3).

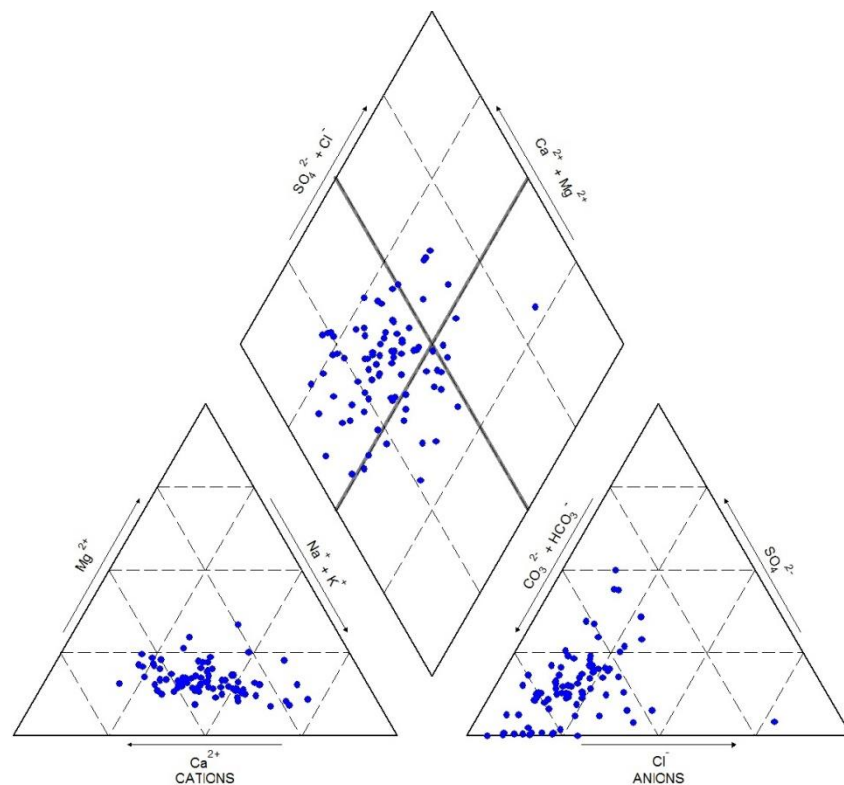


Fig. 6.1a. Representation of the sample data set in the Piper diagram

The Schoeller diagram was drawn up for each sample and subsequently grouped by equivalent facies. In Fig. 6.1b the facies identified thanks to Schoeller diagrams are represented. Moreover, an illustrative delimitation of the areas, with the corresponding diagram, has been represented.

The predominant facies is the type "a", corresponding to calcium bicarbonate waters (coming from the carbonate reliefs) enriched in alkaline ions to the effect of leaching of volcanic rocks (alluvial pyroclastics deposits). This facies was also detected by the Piper diagram.

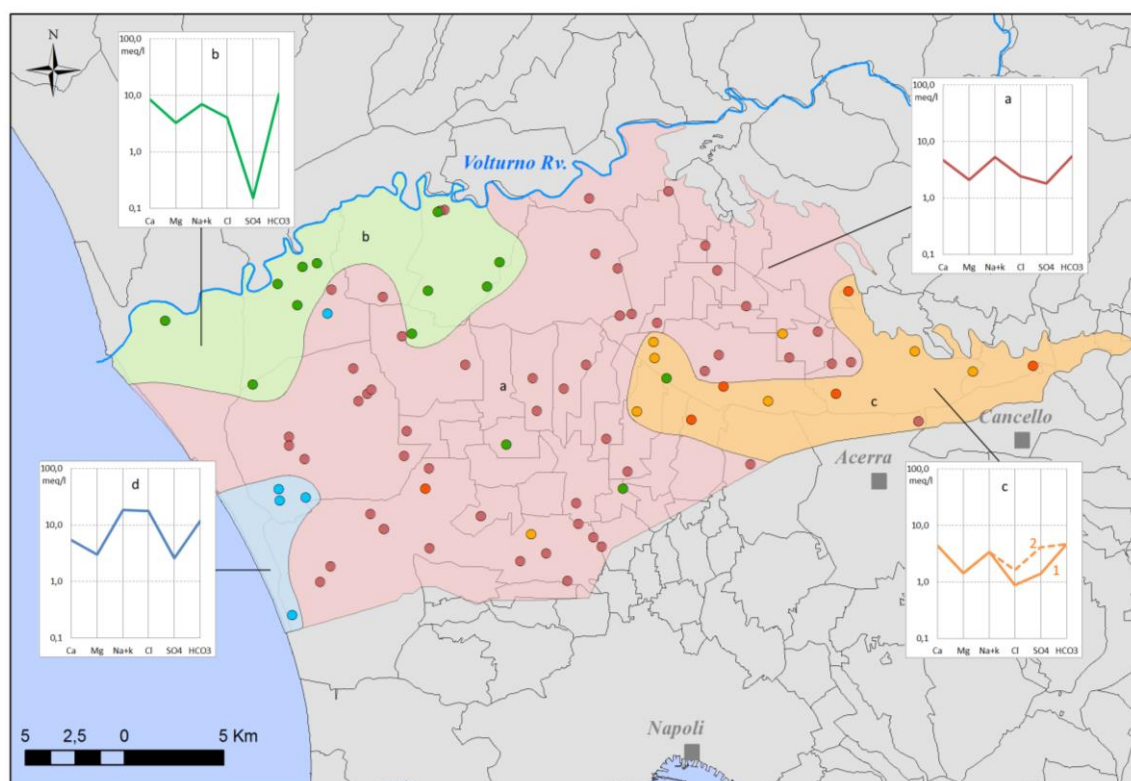


Fig. 6.1b. Map of the groundwater facies according to Schoeller diagrams

Behind the Voltorno River the predominant facies is present but with a strong reduction in sulphate content coupled with high HCO_3 (facies type "b"). This modification is due to the predominantly presence of reducing sectors in the aquifer. Because of the closeness of the Voltorno River to the sectors, the reducing conditions are mainly due to the widespread and detected occurrence of peaty lenses straddles the river (Fig. 3.3, section A-A ').

In the southeast part of the study area, the groundwaters (facies type "c") have been

probably influenced by the presence of a mineralized area, with presence of springs, in the municipalities of Acerra and Cancellò (Corniello & Ducci, 2014 – Fig. 6.1b). The origin of the mineralization (as well explained in §3.3) is due to the proximity of important faults and upwelling, along these tectonic lineaments, of deep natural gases (mainly CO₂). Because of the mineralization, this facies can be more or less rich in sulfates (type c1 and c2).

Along the coastal area, the facies “d” is clearly influenced by a saltwater intrusion; that phenomenon spreads until the Volturno river mouth (Fig. 6.1b), where the saltwater, lying in the deepest part of the riverbed, can propagate inland, through the alluvial deposits, due to the effects of the groundwater withdrawals.

6.1.2. Box plot

Box plots are useful for identifying outliers and for comparing distributions. In Tab. 5.1 the statistical measures useful for the construction of the box plot are reported (first and third quartiles, median, minimum and maximum values). For the construction of the box plot refer to § 4.2.2.

In Fig. 6.2 the box plots are shown for the ions of interest: fluoride, arsenic, iron and manganese.

The distributions are compared with the law reference value (REF) as indicated in D.lgs. 31/2001, transposition of the Council Directive 98/83/EC (European Commission, 1998). The discussion of the box plots will be carried out, ion by ion, in the following paragraphs.

6.1.3. Arsenic and fluoride

The hydrogeochemical map in Fig. 6.3 shows the *arsenic* concentrations in the study area. The contours are drawn up by interpolating the “historical data set” (§ 5.1) with Inverse Distance Weighting (IDW) method. The contamination is low: the values are below the reference value (10 µg/l in D.lgs. 31/2001), except for some extreme value (outliers), whose origin should be verified (see the box plot in Fig. 6.2). The arsenic contamination generally is associated with industrial activities or the use of pesticides, but it can be correlated also to the closeness with the Phlegrean Field area (Fig. 3.2),

where the amount of As in groundwater is very high and of natural origin (Ducci & Sellerino, 2012). The comparison (Fig. 6.3a) between the interpolated historical values (§ 5.1), and the new collected data (§ 5.2) show that in the last 10 years significant change has not occurred, except for some spots in which probably the contamination occurs.

The **fluoride** contamination is widespread in the study area, as shown by hydrogeochemical map in Fig. 6.3b. The range of values is huge, with concentrations far above the reference value (1500 µg/l in D.lgs. 31/2001), as evidenced by the presence of outliers in the box plot in Fig. 6.2. The contamination has a natural origin (Ducci et al., 2016), closely related to the pyroclastic deposits constituting the main aquifer (§ 3.1). The comparison (Fig. 6.3b) between the historical values (§ 5.1), interpolated in order to draw up concentration contours with the IDW method, and the new collected data (§ 5.2) shows that in the last 10 years significant change has not occurred.

6.1.4. Iron and manganese

The situation for **iron** and **manganese** is more complex. The presence of iron and manganese in concentrations over the reference values (for Fe 200 µg/l and for Mn 50 µg/l), as shown in the hydrogeological maps in Fig. 6.4, and a large number of outliers in box-plots in Fig. 6.2, is due to natural causes (Kehew, 2001; Matthes, 1982). Reducing conditions and/or the hydro-mineral areas are present in the sector near the Volturno River and in some sectors near Acerra (NA) (Corniello et al. 2010; Corniello & Ducci, 2014; § 3.3). Nevertheless, it is not possible to exclude an anthropogenic input.

The historical data set (§ 5.1), interpolated with IDW method in order to draw up concentration contours, and the new collected data (§ 5.2) have been compared in Fig. 6.4. The figure show that in the last 10 years significant change has not occurred, except for some spots in which probably the contamination occurs.

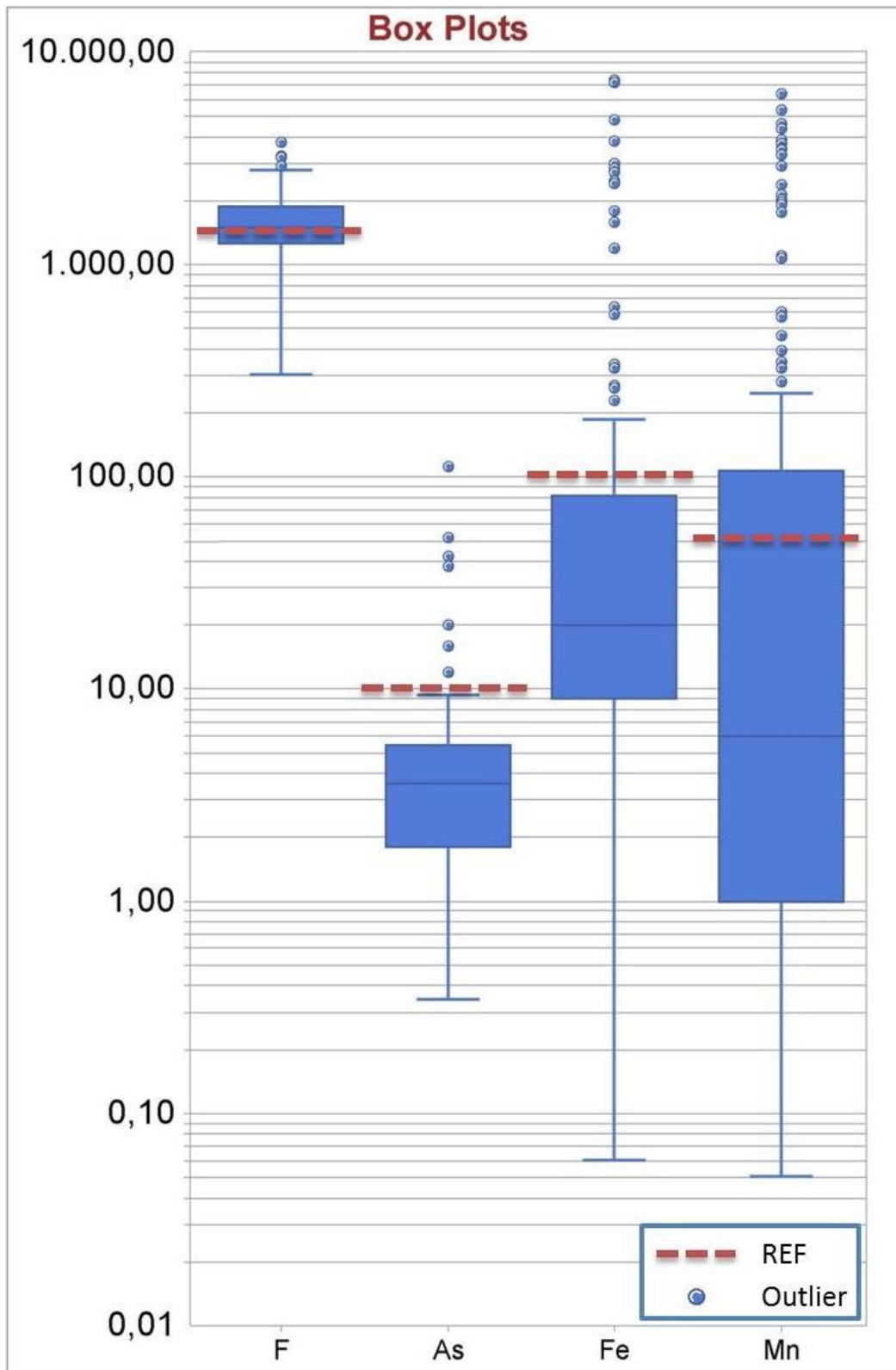


Fig. 6.2. Box plot of fluoride, arsenic, iron and manganese data set (concentrations in $\mu\text{g/l}$). REF = reference value. Statistical measures (quartiles, minimum and maximum values) and sample size in Tab. 5.1

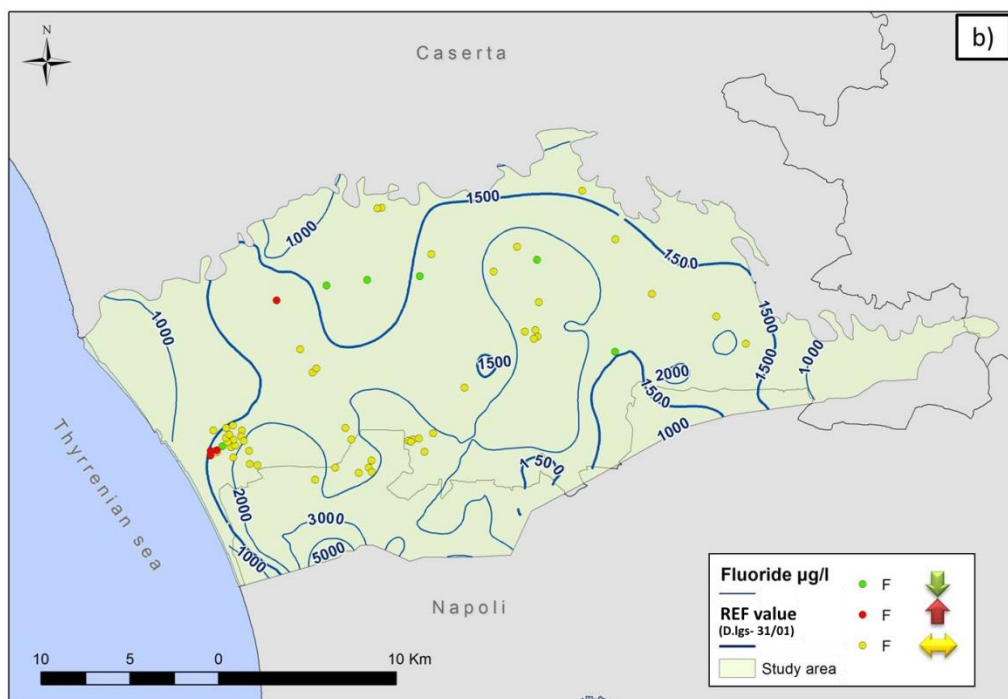
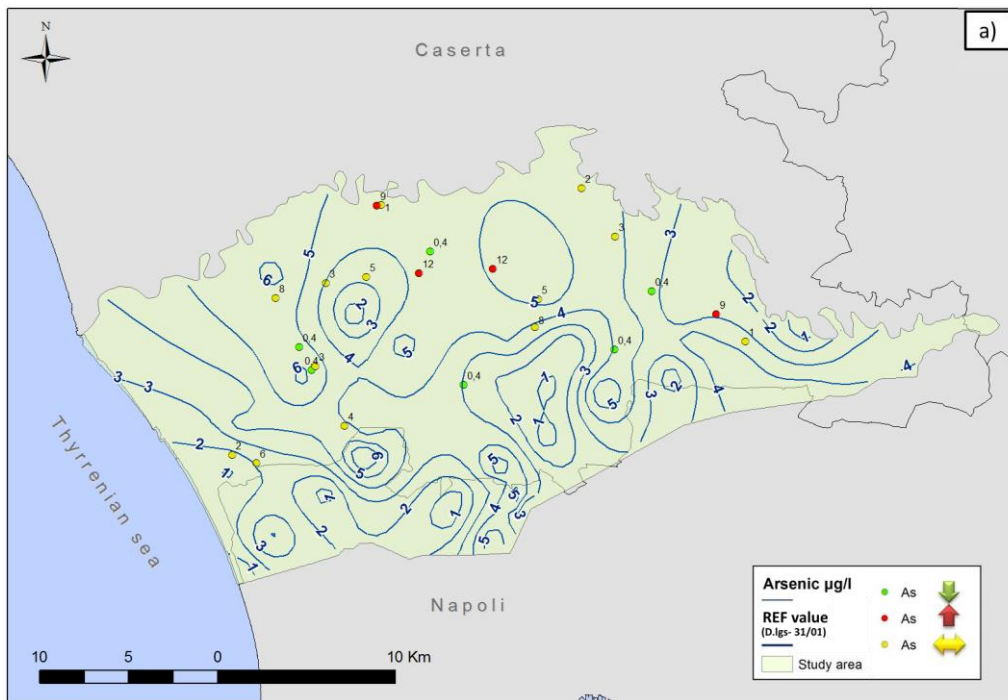


Fig. 6.3. Geochemical map of the a) arsenic and b) fluoride. Comparison between the contours of historical concentration values (Autorità di Bacino della Campania Nord-occidentale, 2004; Adamo et al., 2007) and new groundwater data points acquired (2014-2016). In red groundwater points with an increase in the ionic content, in green the groundwater points with a decrease, in yellow groundwater points without significant changes.

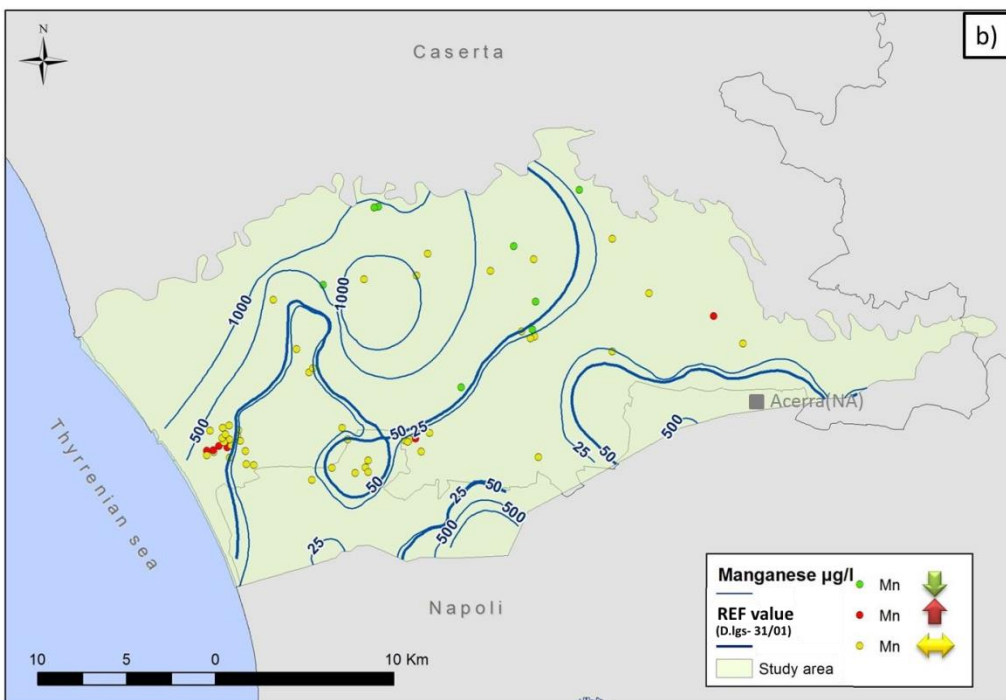
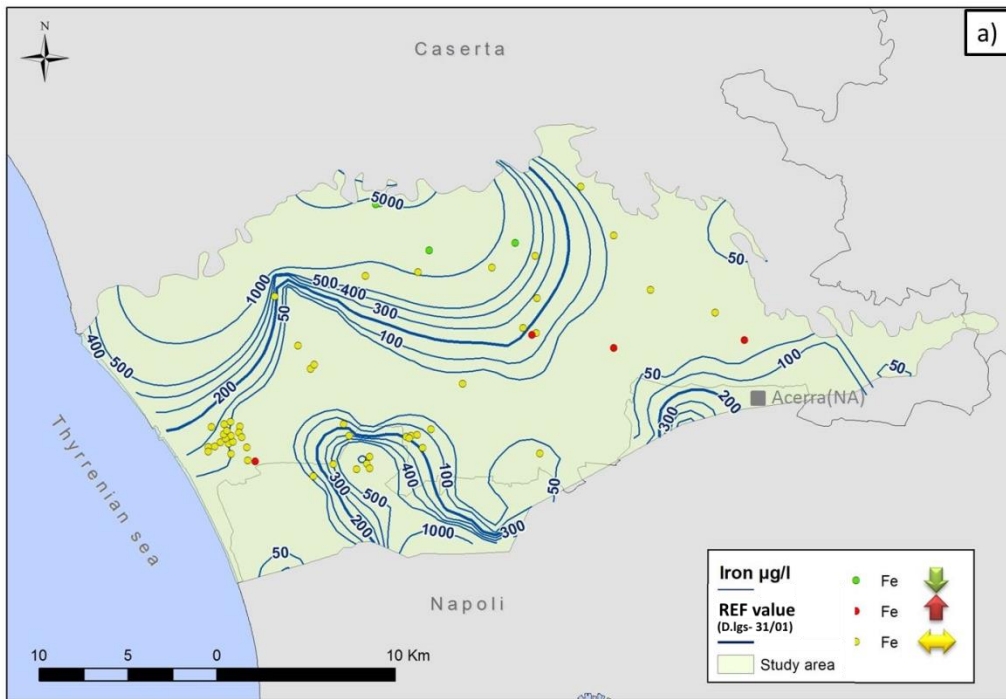


Fig. 6.4. Geochemical map of the a) iron and b) manganese. Comparison between the contours of historical concentration values (Autorità di Bacino della Campania Nord-occidentale, 2004; Adamo et al., 2007) and new groundwater data points acquired (2014-2016). In red groundwater points with an increase in the ionic content, in green the groundwater points with a decrease, in yellow groundwater points without significant changes.

6.2. The natural background assessment

The natural background levels were assessed for arsenic, fluoride, iron and manganese by using three different methods: probability plot (PP) method, pre-selection criteria method (PS) and, component separation (CS) method, deeply described at chapter 4.

The data set, composed by 129 water samples, was preliminarily treated to make data uniform and consistent, as reported in § 4.2.2. In particular, the concentrations below the detection limit (DL) were treated considering a value lower than the DL, equal to $DL - x$, where x is proportional to DL (Tab. 6.1).

Tab. 6.1. Replacement of detection limit (DL) with a lower value for each ion.

<i>Ion</i>	<i>DL ($\mu\text{g/l}$)</i>	<i>DL-x ($\mu\text{g/l}$)</i>
<i>Arsenic</i>	<i>0.5</i>	<i>0.4</i>
<i>Iron</i>	<i>10</i>	<i>9</i>
<i>Manganese</i>	<i>5</i>	<i>4</i>
	<i>1</i>	<i>0.8</i>

The whole data set was used in the application of probability plot (PP) method and of the component separation (CS) method. For the CS the NBL is assumed to be represented by the 90th percentile of the probability density function of the natural component, supposed as log-normal distributed, according to Molinari et al. (2014). For PS method (§ 4.5), the NBL is assumed to be represented by the 90th percentile of the remaining data after the application of pre-selection criteria (Tab. 6.2 and Fig. 6.5).

In this chapter, the results will be presented and analyzed ion by ion. The NBLs were compared with the REF provided in D.lgs. 31/2001.

Tab. 6.2. Sample size before (N) and after (N_{PS}) the application of the pre-selection criteria for each ion; red = number of samples in reducing conditions; ox = number of samples in oxidizing conditions.

Ion	N	N_{PS}
Arsenic	107	49
Fluoride	127	61
Iron	122 26 (red)+ 96 (ox)	61 15 (red) + 46 (ox)
Manganese	128 26 (red) + 102 (ox)	63 15 (red) + 48 (ox)

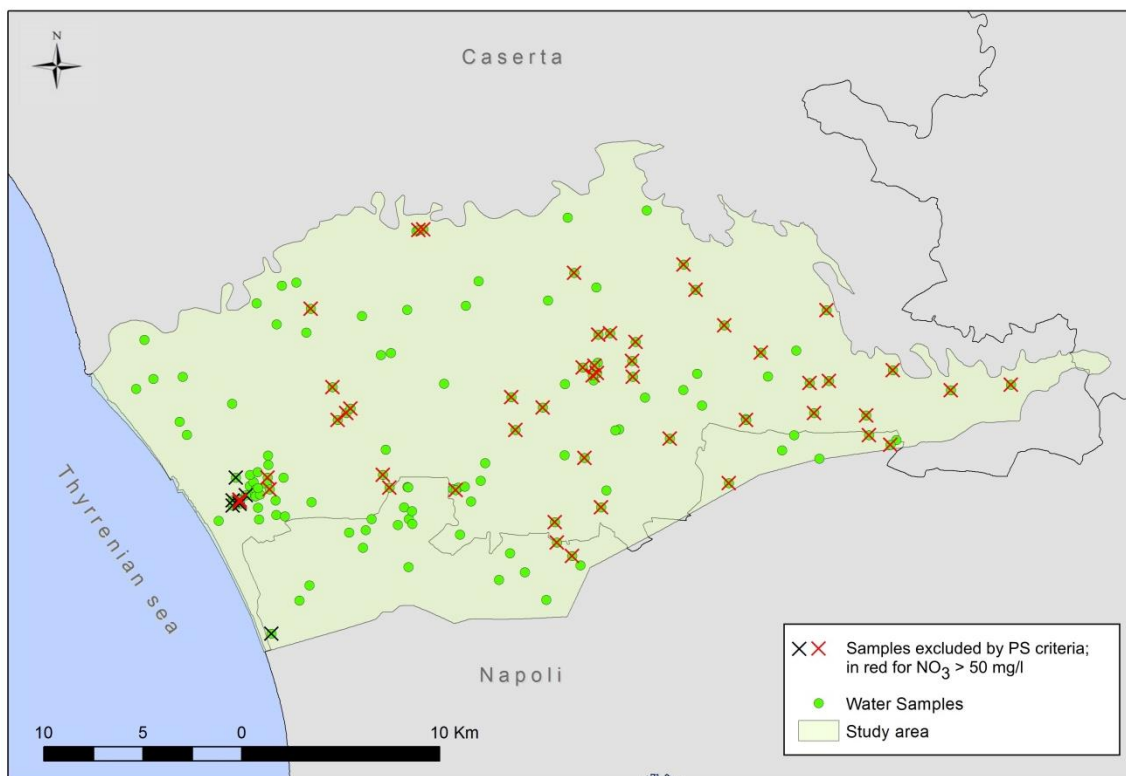


Fig. 6.5. Samples before and after pre selection criteria application

6.2.1. Arsenic

PP method

The **PP method** was applied to the whole data set (107 samples, see Tab. 6.2). First of all, the probability plot allows the identification of two groups of points (group 1 and 2 in Fig. 6.6), with a value almost constant of 0.4 $\mu\text{g/l}$ for the group 1 (points in which the concentration of arsenic was below the DL of 0.5 $\mu\text{g/l}$ replaced with the value 0.4 $\mu\text{g/l}$) and of 2 $\mu\text{g/l}$ for the group 2. The points of group 2 are prevalently (60%) located in the municipality of Trentola Ducenta (for the location see Fig. 6.20) with the same content of arsenic due to the proximity.

Excluding the flat trend of the points of the group 1 and 2, the probability plot shows a significant slope change in correspondence of the point 3 (Fig. 6.6), associated with the **NBL_{PP}**, equal to **9 $\mu\text{g/l}$** .

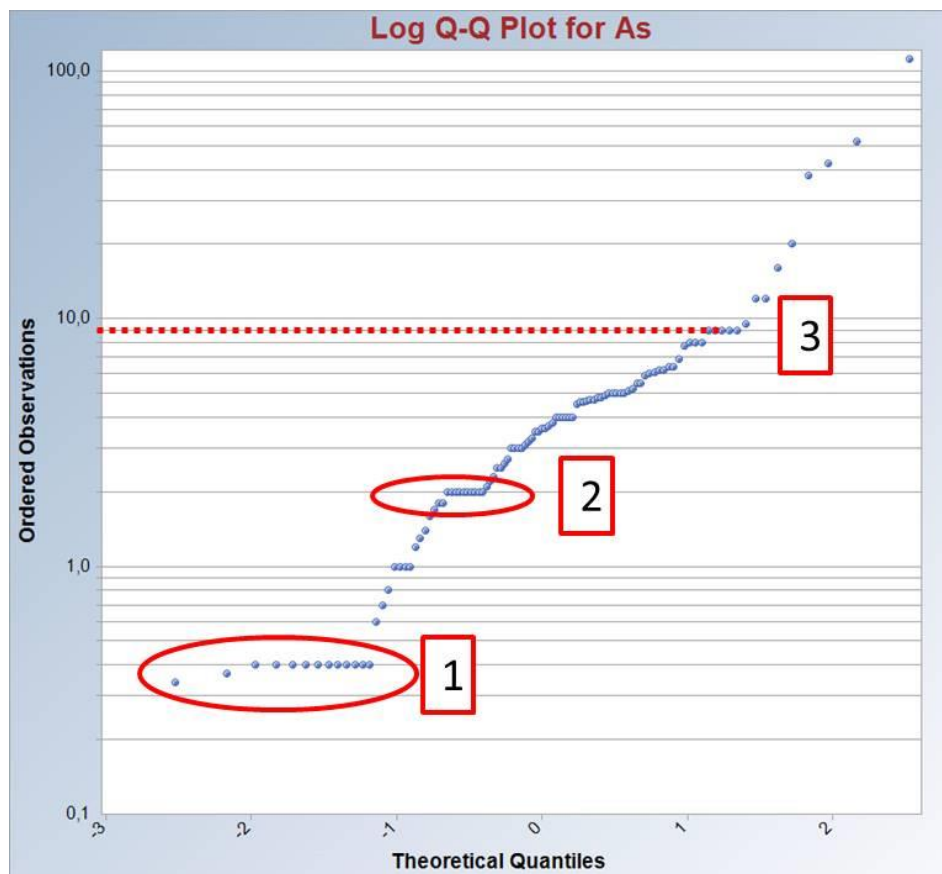


Fig. 6.6. Probability plot of arsenic. The groups of points 1 and 2 and the change of slope indicated by 3 are explained in the text

The background value is placed below all the outliers (identified by the box plot in Fig. 6.2). A probability plot that excludes the outliers was made. The exclusion of these points does not involve changes in the determination of the slope change, and therefore of the background level.

PS method

By the **Pre Selection criteria**, 58 points have been eliminated, the majority (42) due to the content of $\text{NO}_3 > 50$ mg/l. The remaining points (Tab. 6.2 and Fig. 6.5) were represented in the box plot of Fig. 6.7. The box plot shows the presence of 3 outliers. The treatment of the outliers was explained in § 4.2. The data set available is validated, therefore it can be excluded that these values are "true outliers". Moreover Bartolucci et al. (2009) say (as already stated in § 4.2): "*This decision (Excluding the inclusion of outliers from the data set) can take place only if it is possible to accompany the results of statistical tests [...] with a valid scientific justification*". *The outliers were included in the background value determination because there aren't scientific justifications to exclude them.*"

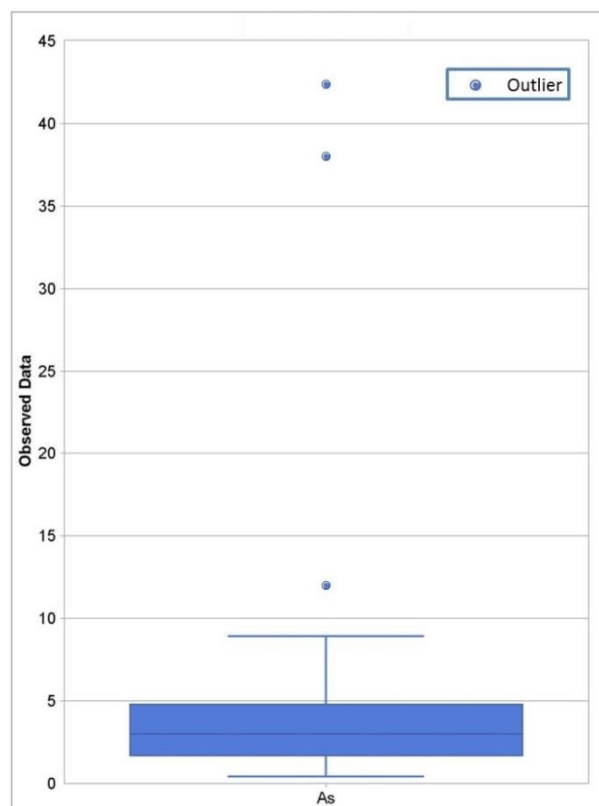
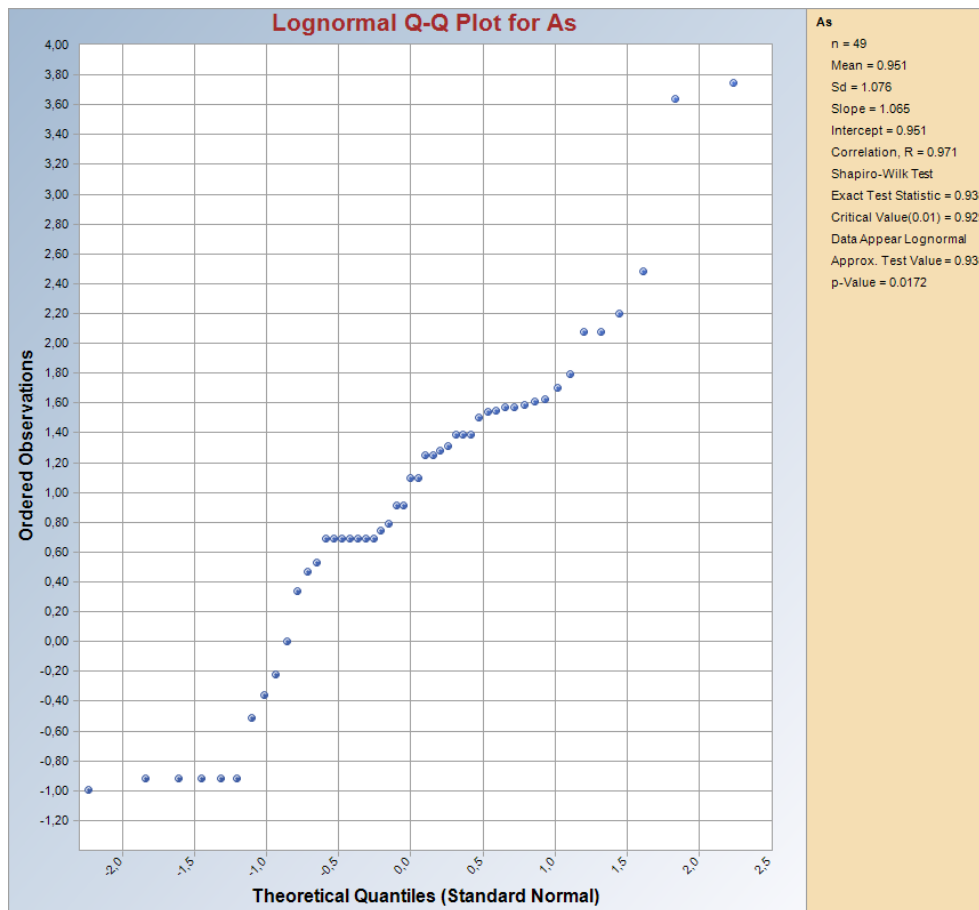


Fig. 6.7. Box plot of arsenic pre-selected data set

For this data set the log-normal distribution hypothesis was confirmed with the Shapiro–Wilk test. Therefore, the calculation of the percentiles was performed and the **NBL_{ps}**, equal to the 90th percentile, is **8 µg/l** (Fig. 6.8).



5%ile	10%ile	20%ile	25%ile (Q1)	50%ile (Q2)	75%ile (Q3)	90%ile	95%ile	99%ile
0.4	0.4	1.24	1.7	3	4.8	8	10.8	40.29

Fig. 6.8. Distribution of arsenic and table of the quantiles of the distribution (concentration in µg/l)

CS method

The **CS approach** was applied using the COMPSEC code in order to calculate the NBL_{CS} with this method (§ 4.4). In Tab. 6.3 and Fig. 6.9 the solutions from COMPSEC for arsenic are shown. The algorithm identifies clearly one solution (As1), and estimate the NBL_{CS} equal to **13.5 $\mu\text{g/l}$** . The value is according to conceptual model and the previous value of NBL estimated, even if this NBL_{CS} is greater than the REF (10 $\mu\text{g/l}$).

Tab. 6.3. Solutions from COMPSEC for the arsenic ion (in bold the selected solution).

<i>As</i>	<i>f(%)</i>	<i>p</i>	<i>μ_{logn}</i>	<i>μ_{norm}</i>	<i>σ_{logn}</i>	<i>σ_{norm}</i>	<i>R²</i>	<i>RMSE</i>	<i>NBL ($\mu\text{g/l}$)</i>
As1	99	0.77	0.99	4.53	1.26	1.07	0.90	0.009	13.5
<i>Other sol.</i>	1	1	1.85	5.5	12.6	12.6	0.20	0.03	-

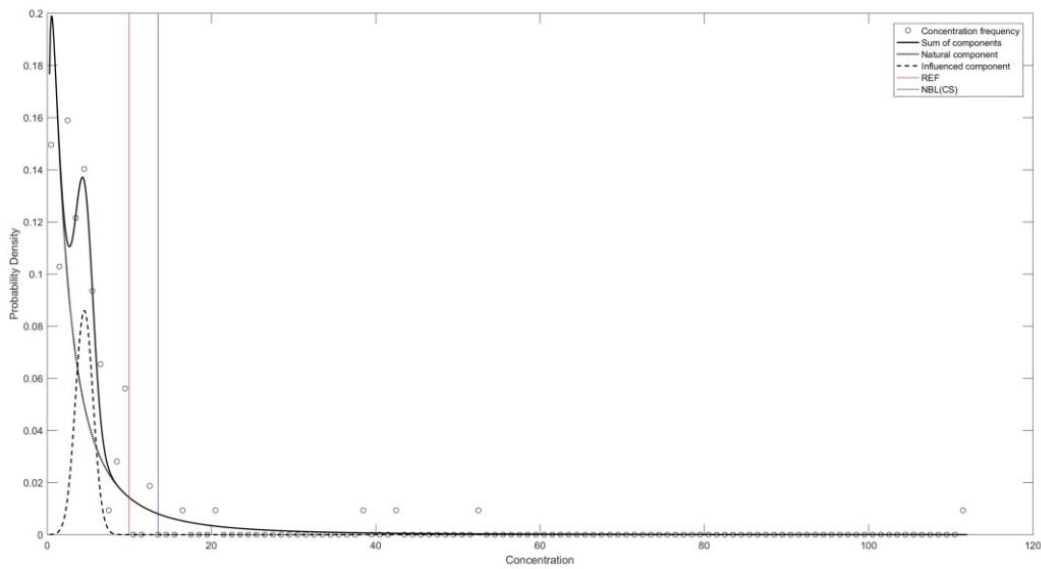


Fig. 6.9. Plot of the selected COMPSEC solution for As

6.2.2. Fluoride

PP method

The **PP method** has been applied to the whole data set (127 samples, see. Tab. 6.2). In the probability plot (Fig. 6.10) there are two significant slope changes (point 1 and 2), which are associated with a value of 1100 $\mu\text{g/l}$ and of 2750 $\mu\text{g/l}$.

The high fluoride content is a constant phenomenon over time as already shown in Fig. 6.3b. It depends on the presence of volcanic deposits which are found widely on the area, except in some coastal area (§ 3). Therefore, the hypothesis is to exclude a widespread anthropic contamination and to consider the 15 points below 1100 $\mu\text{g/L}$ not very representative of the hydrogeological background of the area. Hence, for this ion, it proposed a **NBL_{PP}** equal to **2750 $\mu\text{g/l}$** .

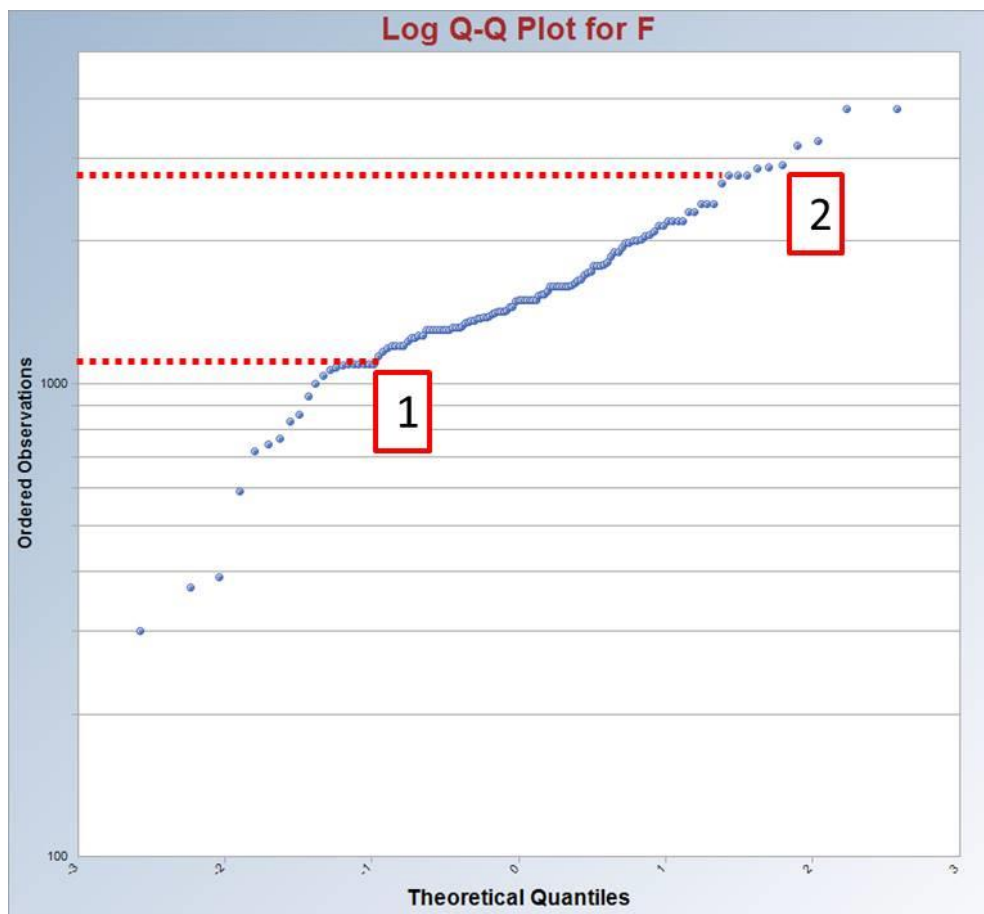


Fig. 6.10. Probability plot of fluoride. The changes of slope indicated by 1 and 2 are explained in the text.

PS method

Using the **Pre Selection criteria**, 66 points have been eliminated, the majority (48) due to a content of $\text{NO}_3 > 50 \text{ mg/l}$. The remaining points (Tab. 6.2 and Fig. 6.5) were represented in the box plot in Fig. 6.11, which shows the presence of 7 outliers.

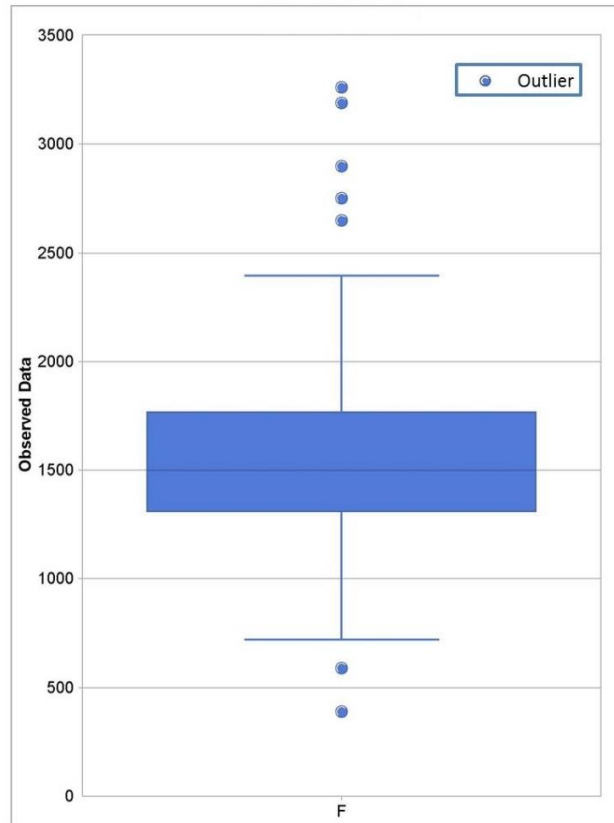
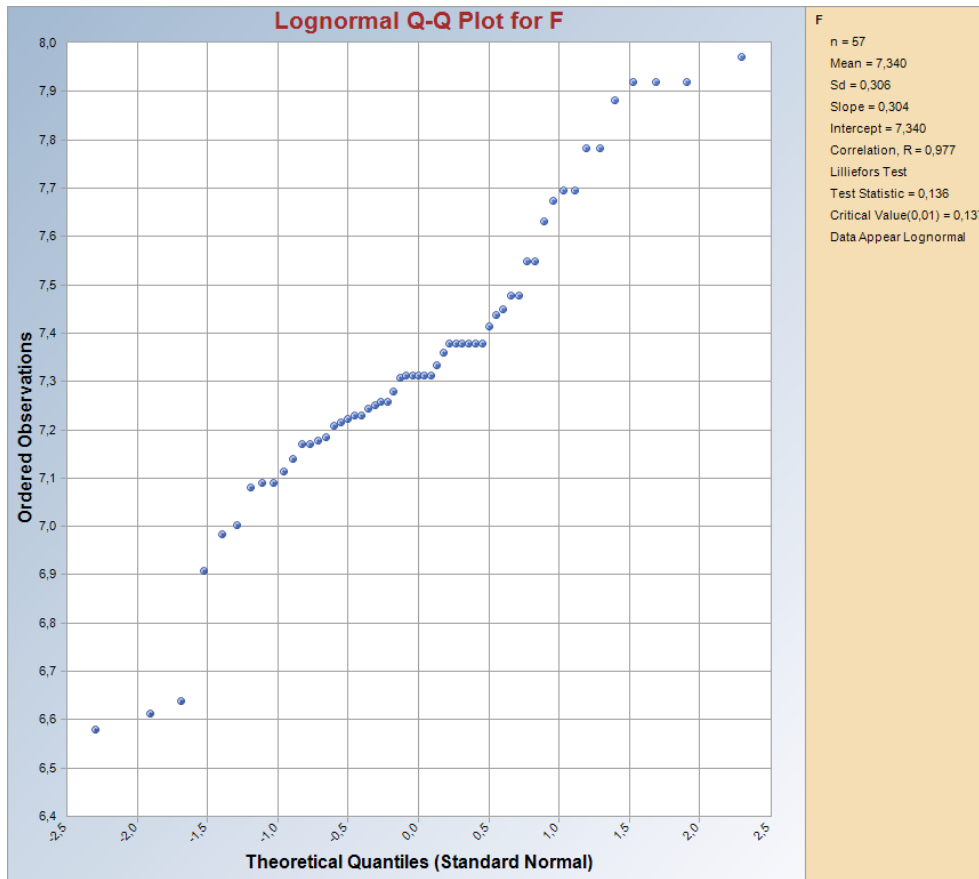


Fig. 6.11. Box plot of fluoride pre-selected data set

The data set available is validated, therefore it can be excluded that these values are "true outliers". Nevertheless, the normal and the log-normal distribution hypothesis were not verified by the statistical tests.

The distribution does not represent a unique population, due the presence of several outliers. For this reason, it was tried to delete one by one the outliers, beginning from the minimum outlier, and then eliminating the maximum one and so on. Finally, eliminating 3 outliers the distribution appeared log-normal (tested by Shapiro-Wilk test).

Therefore the calculation of the percentiles was performed and the **NBL_{PS}**, equal to the 90th percentile, is **2400 $\mu\text{g/l}$** (Fig. 6.12).



5%ile	10%ile	20%ile	25%ile (Q1)	50%ile (Q2)	75%ile (Q3)	90%ile	95%ile	99%ile
953	1154	1300	1320	1500	1770	2400	2750	2816

Fig. 6.12. Distribution of fluoride and table of the quantiles of the distribution (concentration in $\mu\text{g/l}$)

CS method

The **CS approach** was applied using the COMPSEC code in order to calculate the NBL_{CS} with this method. In Tab. 6.4 the solutions from COMPSEC for the fluoride are shown. The algorithm identify clearly only one stable solution; this solution has $p= 0$, implying the exclusive presence of a normal component (Tab. 6.3). In this case the influenced and natural components cannot be separated on the basis of the Eq. (1) in §4.4, therefore NBL cannot be estimated by the CS method. This will be addressed in detail in the § 7.

Tab. 6.4. Solutions from COMPSEC for the fluoride.

<i>F</i>	<i>f(%)</i>	<i>p</i>	μ_{logn}	μ_{norm}	σ_{logn}	σ_{norm}	R^2	<i>RMSE</i>	<i>NBL (μg/l)</i>
<i>F1</i>	99	0	1184.5	1610	478.6	614.6	0.11	0.00	-
<i>Other sol.</i>	1	1	1260	1900	527.6	527.6	0	0.00	-

6.2.3. Iron and manganese

PP method

For the **iron and manganese**, the **PP method** has been applied to the whole data set (122 samples for Fe and 128 samples for Mn, see Tab. 6.2). The application of this method doesn't require the separation of the data-set on the basis on the redox conditions, in contrast to the PS and CS methods as mentioned in the next sections.

The probability plot of iron allows the identification of two groups of points (group 1 and 2 in Fig. 6.13), with a value constant of 9 µg/l for the group 1 (points in which the concentration of iron was below the DL of 10 µg/l, replaced by the value 9 µg/l) and of 19 µg/l for the group 2 (points in which the concentration of iron was below the DL of 20 µg/l, replaced by the value 19 µg/l). The presence of a large number of points with a concentration below the DL creates problems in the interpretation of the probability plot. Excluding the flat trend of the points of the groups 1 and 2, the probability plot shows 3 different slope changes in correspondence of the points 3, 4 and 5 (Fig. 6.13); the slope changes are not very evident at points 3 and 4, but they were validated using the linear regression for small groups of points between the inflection points. The slope changes (3, 4 and 5), are associated with the values of 60, 200 and 1500 µg/l.

The probability plot of manganese allows the identification of one group of points (group 1 in Fig. 6.14), with a value constant of 4.9 µg/l (points in which the concentration of iron was below the DL of 5 µg/l replaced with the value 4.9 µg/l). The probability plot shows 3 different slope changes in correspondence of the points 2, 3 and 4 (Fig. 6.14); the slopes changes, as well as in the case of the iron, are not very evident.

The slope changes (3, 4 and 5), are associated with the values of 30, 50 and 1900 µg/l.

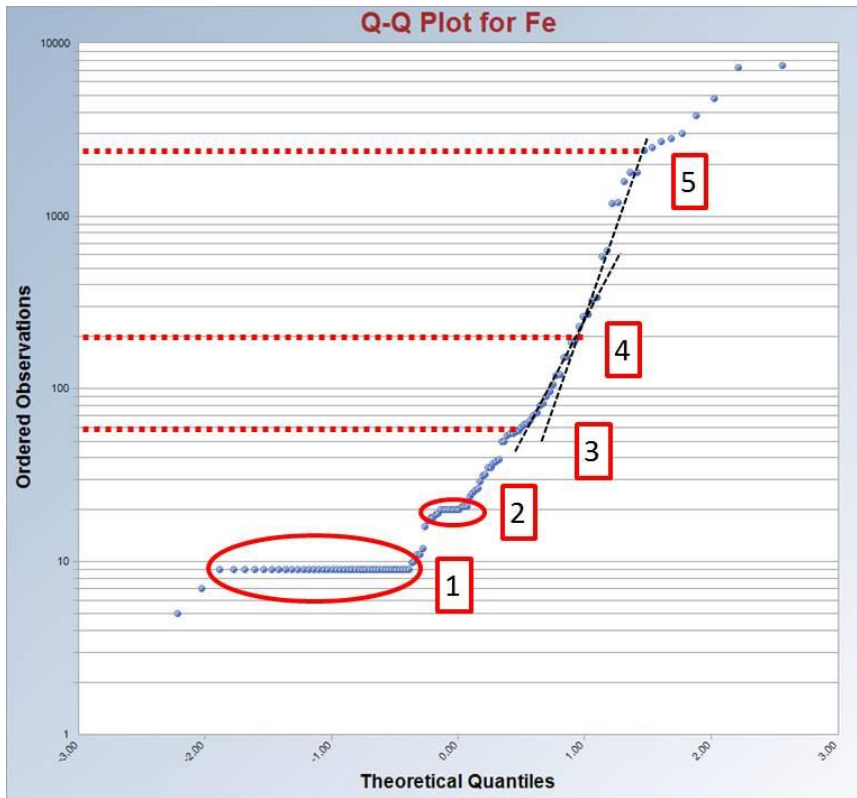


Fig. 6.13. Probability plot of iron. The groups of points 1 and 2 and the changes of slope indicated by 3, 4 and 5 are explained in the text.

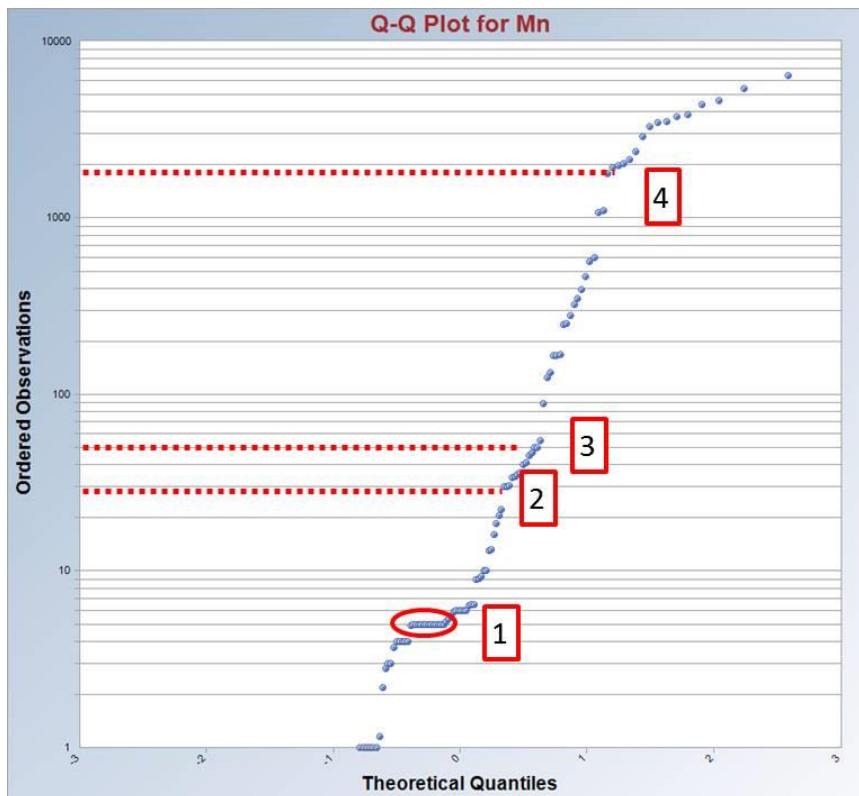


Fig. 6.14. Probability plot of manganese. The group of points 1 and the changes of slope indicated by 2, 3 and 4 are explained in the text.

For **both ions**, the **PP method** gave a poor representative NBL, because there are different stages of “transition” between the reducing and the oxidant phase, therefore it is difficult to locate univocal slope changes on the probability plot and to identify a NBL. For this reason, the NBLs in this case are supposed on the basis of the conceptual model, that considers the presence of two different sector in the study (one sector in which there are oxidizing conditions and the Fe and Mn, and one sector in which reducing conditions are present and influence the content of these metals) and the information that can be deduced by the interpretation of the probability plot.

For iron in oxidizing conditions (Fe_{ox}) the **NBL_{PP}** is supposed equal to **200 $\mu\text{g/l}$** , because this value is placed before the stages of “transition” and can represent the oxidized population, instead for Fe in reducing conditions (Fe_{red}) the **NBL_{PP}** is supposed equal to 1500 $\mu\text{g/l}$, the point is at the end of the “transition” phase.

For manganese in oxidizing conditions (Mn_{ox}) the **NBL_{PP}** was considered in the middle between 30 e 50 $\mu\text{g/l}$, i.e. **40 $\mu\text{g/l}$** , and for Mn in reducing conditions (Mn_{red}) the **NBL_{PP}** was considered equal to **1900 $\mu\text{g/l}$** .

PS method

In order to apply the **PS method**, and afterwards the CS method, the iron and manganese samples were divided in two different population, “ox” or “red”, referring to oxidizing o reducing conditions. The criteria used to divide the data sample were (§ 4.5 and Wendland et al., 2008):

- a. if $\text{Mn} \geq 50 \mu\text{g/l}$ and $\text{Fe} \geq 200 \mu\text{g/l}$, the sample is classified as “red”
- b. if $\text{Mn} < 50 \mu\text{g/l}$ and $\text{Fe} < 200 \mu\text{g/l}$, the sample is classified as “ox”
- c. Otherwise, the sample was analyzed and classified “ox” or “red” on the basis of different considerations, as a low content of NO_3 or the location.

This is the case of only 10 samples.

The data set was classified following these criteria. Measures of iron were not available for all samples, but only for 122: for Fe 96 samples were classified as “ox” and 26 as “red”, for Mn 102 samples were classified as “ox” and 26 as “red” (see Appendix C).

By the **Pre Selection method**, 61 points have been eliminated from iron data set, the majority (43) due to the content of $\text{NO}_3 > 50 \text{ mg/l}$ and 6 points because of the $\text{NH}_4 > 0.5 \text{ mg/l}$ in reducing conditions.

For the **iron**, the remaining samples (Tab. 6.2 and Fig. 6.5) were represented in the box plot of Fig. 6.15, showing the presence of 6 outliers for the “ox” data set. The presence of the outliers will be discussed in the probability map section.

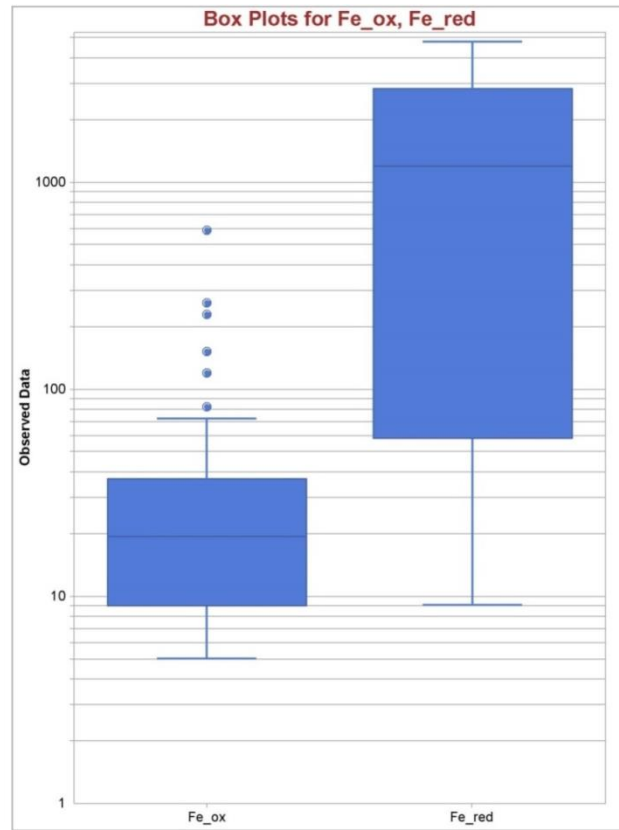
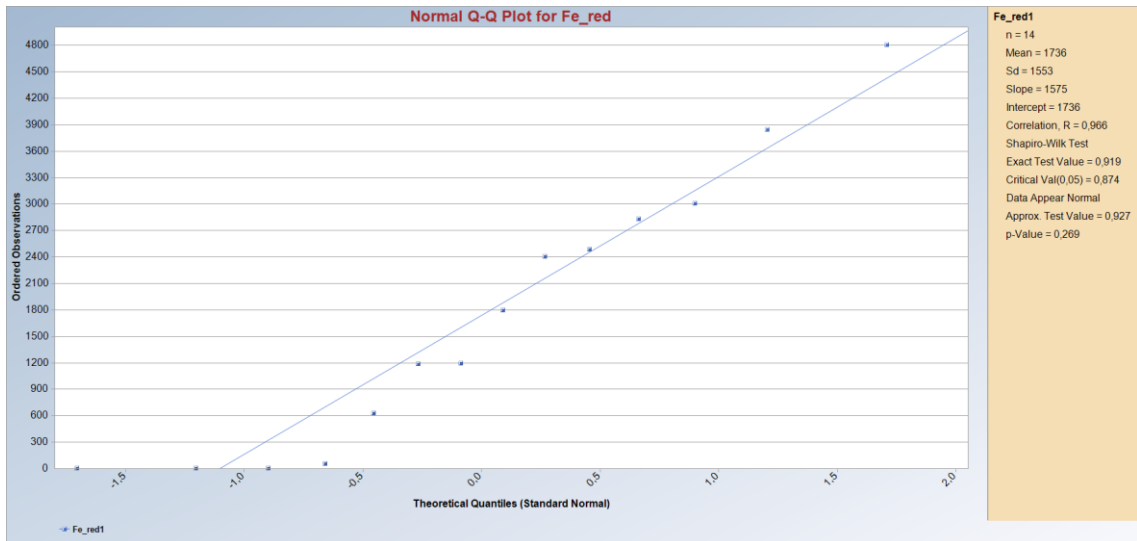
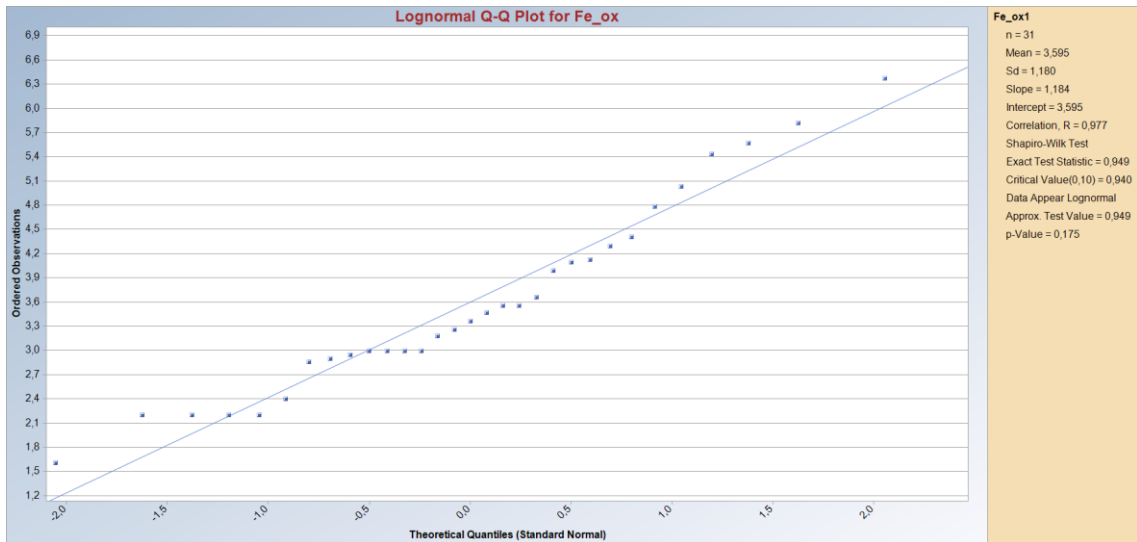


Fig. 6.15. Box plot of iron pre-selected data set

The presence of a large number of points with a concentration equal to DL makes difficult the interpretation of the distribution, and also the application of the normality/log-normality test. For this reason, the duplicate values are reduced to a maximum of 4 points with equal value (that means that if there are 5 or more samples with the same value, a reduction to 4 samples is applied).

For both data set the normal or log-normal distribution was tested (Shapiro–Wilk test).

The **NBL_{PS}** considered equal to the 90th percentile is **230 µg/l for Fe_{ox}** and **3597 µg/l for Fe_{red}** (Fig. 6.16).



Variable	5%ile	10%ile	20%ile	25%ile (Q1)	50%ile (Q2)	75%ile (Q3)	90%ile	95%ile	99%ile
Fe _{ox}	9	9	17.4	18.55	29	67.5	230	300	511.6
Fe _{red}	9	9	38.34	201.4	1500	2749	3597	4186	4687

Fig. 6.16. Distribution of iron, separated for oxidizing (ox) -reducing (red) conditions. Quantiles of the distribution in table (concentration in µg/l)

For **manganese**, 65 points have been eliminated from manganese data set, the majority (47) due to the content of $\text{NO}_3 > 50 \text{ mg/l}$, 6 points because of the $\text{NH}_4 > 0.5 \text{ mg/l}$ in reducing conditions.

The remaining points (Tab. 6.2 and Fig. 6.5) were represented by a box plot (Fig. 6.17) which shows the presence of 5 outliers for the Mn_{ox} data set.

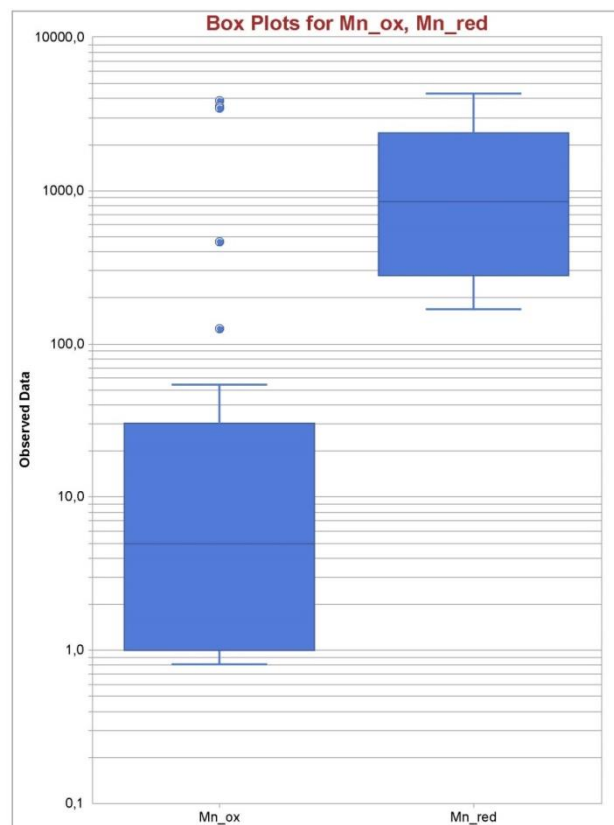
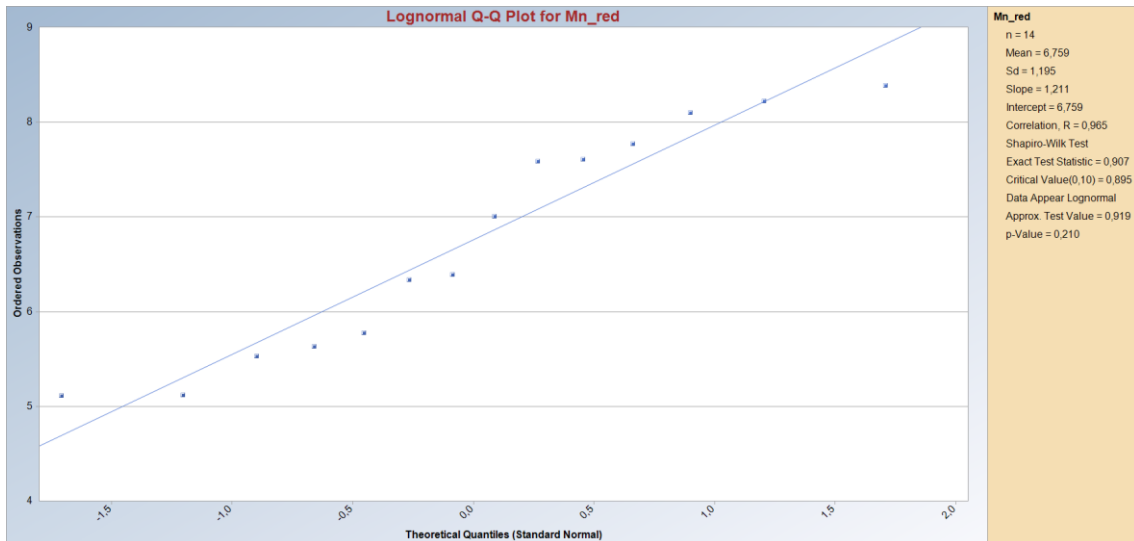
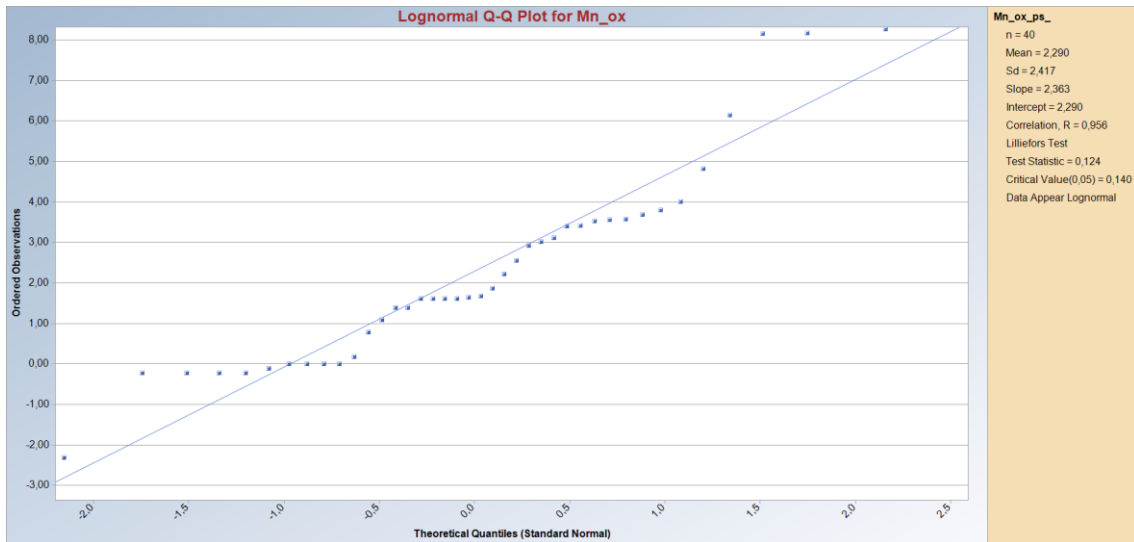


Fig. 6.17. Box plot of manganese pre-selected data set

The data set available is validated, therefore it can be excluded that these values are "true outliers".

The Mn_{ox} data set was modified in order to avoid the above mentioned problem, of the presence of a large number of points with a concentration equal to DL. The Shapiro–Wilk test failed for the “ox” data, unlike the Lilliefors Test. The **NBL_{PS}** was considered equal to the 90th percentile and it is **159 $\mu\text{g/l}$ for Mn_{ox}** and **3492 $\mu\text{g/l}$ for Mn_{red}** (Fig. 6.18).



Variable	5%ile	10%ile	20%ile	25%ile (Q1)	50%ile (Q2)	75%ile (Q3)	90%ile	95%ile	99%ile
Mn _{ox}	0.8	0.8	1.0	1.15	5.3	34.33	159.1	3473	3747
Mn _{red}	167	193	269	291	852	2299	3611	3974	4315

Fig. 6.18. Distribution of manganese, separated for oxidizing (ox) -reducing (red) conditions. Quantiles of the distribution in table (concentration in $\mu\text{g/l}$)

CS method

The **CS method** was applied to the iron and manganese, considering the dataset divided in reducing and oxidizing condition. The method doesn't give clear results in relation to the "red" data set. In fact, for both ions, the algorithm identifies only a stable solution; this solution has $p = 0$, which implies the exclusive presence of a normal component.

For the "ox" data-set (Tab. 6.5), instead, the algorithm identifies only one stable solution for the Fe, corresponding to a $p=0.99999$, that implying the almost totally presence of a log-normal component and a $NBL_{CS} = 137.2 \mu\text{g/l}$ (Fig. 6.19a); for manganese the most frequent solution (indicated as Mn_ox1 in Tab. 6.5), identifies a solution corresponding to a $p=0.99999$, that implying the almost totally presence of a log-normal component and a $NBL_{CS} = 73.2 \mu\text{g/l}$ (Fig. 6.19b)

The fact that the CS method, applied to Fe and Mn, identifies solutions that implying the almost totally presence of a log-normal component, confirms that the criteria used for the separation of the whole data set in two different population, "ox" and "red", are adequate. The use of certain criteria to separate the data set, if reducing conditions occur, is necessary before the application of the CS method, because the method cannot recognize the difference between the two populations, even if a separation could reduce drastically the size of the dataset and compromise the success of the method.

Tab. 6.5 Solutions from COMPSEC for the Fe and Mn (in bold the selected solution).

	<i>f (%)</i>	<i>p</i>	<i>μlogn</i>	<i>μnorm</i>	<i>σlogn</i>	<i>σnorm</i>	<i>R²</i>	<i>RMSE</i>	<i>NBL (μg/l)</i>
Fe_ox1	24	0.99	3.2	38.8	1.4	76.3	0.823	0.001	137.2
Fe_ox2	76	var	var	var	var	var	var	var	var
Mn_ox1	34	0.99	1.65	15.04	2.06	20.34	0.30	0.002	73.2
Mn_ox2	66	var	var	var	var	var	var	var	var

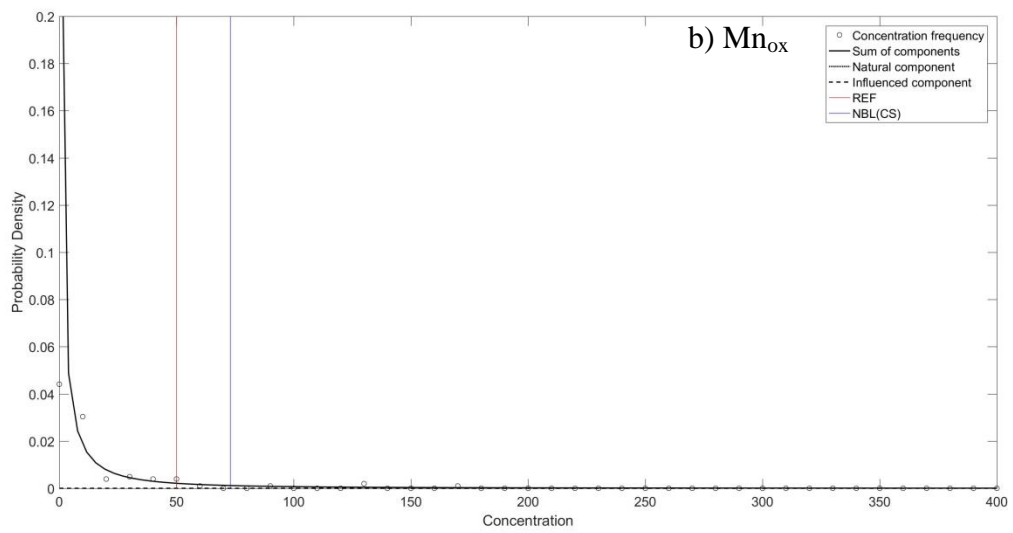
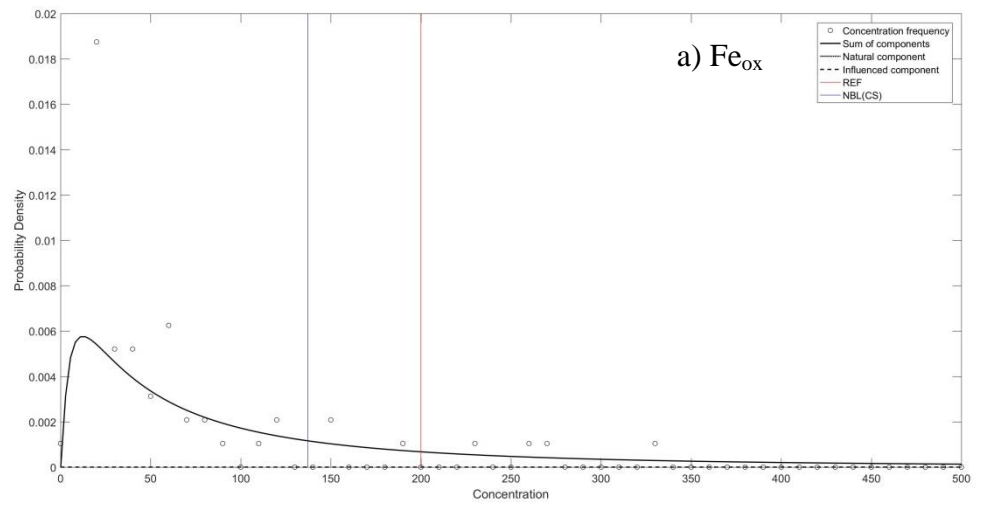


Fig. 6.19. Plot of the selected COMPSEC solution for a) Fe_{Ox} e b) Mn_{Ox}

6.3. Definition of the threshold value

The BRIDGE guidelines propose to two different cases in the definition of threshold values (TV):

1. if $NBL < REF$ (case1) $TV = (REF + NBL) / 2$
2. if $NBL \geq REF$ (case 2) $TV = NBL$

Tab. 6.6 resumes the results of the elaborations described in the previous chapter for assessing the NBL.

Tab. 6.6. Summary of Natural Background Levels (NBL) calculated using three different methods: probability plot (PP); Pre-selection criteria (PS); component separation (CS). red:reducing conditions; ox: oxidizing conditions.

<i>ION</i>	<i>u.m.</i>	<i>NBL_{PP}</i>	<i>NBL_{PS}</i> <i>(90° percentile)</i>		<i>NBL_{CS}</i> <i>(90° percentile)</i>	
<i>Arsenic</i>	<i>µg/l</i>	9	8		13.5	
<i>Fluoride</i>	<i>µg/l</i>	2750	2400		-	
<i>Iron</i>	<i>µg/l</i>	200-1500	3597	230	-	137
<i>Manganese</i>	<i>µg/l</i>	40-1900	3611	159	-	73
			<i>red</i>	<i>ox</i>	<i>red</i>	<i>ox</i>

Since NBLs were estimated with PP (NBL_{PP}), PS (NBL_{PS}) and CS (NBL_{CS}) methods, it is proposed to use the arithmetic average of the three values in the TV evaluation.

Tab. 6.7. Summary of TV calculated for arsenic, fluoride, iron and manganese. red: reducing conditions; ox: oxidizing conditions. REF: Reference value.

	<i>u.m.</i>	<i>REF</i>	<i>TV</i>	
<i>Arsenic</i>	<i>µg/l</i>	10	10	
<i>Fluoride</i>	<i>µg/l</i>	1500	2575	
<i>Iron</i>	<i>µg/l</i>	200	2549	195
<i>Manganese</i>	<i>µg/l</i>	50	2756	91
			<i>red</i>	<i>ox</i>

For As and Fe_{ox} the NBL is less or almost the same of the REF (Tab. 6.7) and therefore

for these ions: REF=TV=10 µg/l for As, and REF=TV=200 µg/l for Fe_{ox}.

In this study the probability maps will be drawn up with the Indicator kriging method, considering two different user-defined threshold values (§ 4.6.1): REF and TV.

6.4. Probability maps

The Indicator kriging (IK) method was used to estimate the probability of exceeding the REF or the TV (Tab. 6.7) for each ion. In the case of arsenic and iron (in oxidizing conditions) the REF=TV.

All experimental variograms and maps were done in Surfer 11 (Golden Software, LLC). The best-fitted variograms model frequently used are the spherical model (F TV, Mn_{ox} REF) and the exponential model (As, F REF, Fe_{ox} REF=TV, Fe_{red} REF, Mn_{red} TV). It was considered the Gaussian model only for Mn_{ox} TV and the linear model for Fe_{red} TV. In some cases it was necessary to consider a nugget effect (Fe_{ox} REF=TV). When necessary, a cross validation was performed in order to choose the best-fitted variograms model. The variograms are attached in appendix B.

6.4.1. Arsenic

For arsenic, TV=REF (10 µg/l). The results of the cross validation are in Tab. 6.8. Two models were compared: spherical (sph) and exponential (exp). The best-fitted variogram model is the exponential one (lower RMSE).

Tab. 6.8 Results of the cross validation: Root Mean Square Error (RMSE) and Mean Error (M.Er.)

model	RMSE	M. Er.
exp	0.2566	-0.00172
sph	0.2680	-0.00334

The probability of exceeding the TV is almost everywhere zero, except for some “hot spots”, in which the arsenic content is very high (Fig 6.20). The “hot spots” are wells for irrigation use and in Fig. 6.3a and some of these “hot spots” were indicated as potentially contaminated and identified as “contaminated” by the PS criteria. The arsenic contamination can be associated with the organ-arsenical pesticides use. Moreover one of the “hot spot”, the one in S.M. la Fossa, falls into the contaminated site “Maruzzella” (Fig. 3.5). Hence, the probability map shows that the TV=REF value is a threshold suitable for the study area and the exceeding of the TV is due to an anthropogenic contamination.

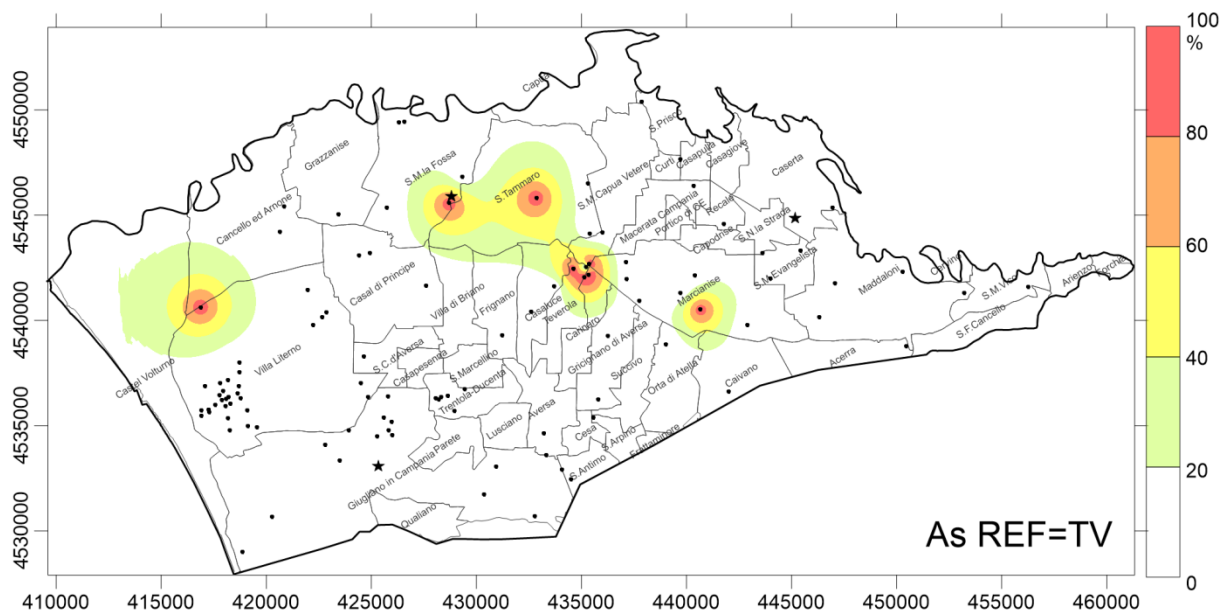


Fig. 6.20. Probability of arsenic being over TV=REF 10 µg/l. Black dots are water samples. Black stars are “contaminated sites”. Percentage scale on the right.

6.4.2. Fluoride

For fluoride, the probability of exceeding the REF (1500 µg/l) is almost everywhere > 20%, with higher values in the southern part, in proximity of the Phleagrean Fields (Fig. 6.21). The REF value is not representative of the nature of the groundwater of the area that is naturally rich in this ion. Hence, the REF value is not a threshold suitable for the study area. Moreover, the groundwater is not good for drinking use, because the probability of the exceeding the REF value is almost everywhere > 20%.

The probability of exceeding the TV=NBL (2550 µg/l) is shown in Fig. 6.22. The results of the cross validation are in Tab. 6.9. Two models were compared: spherical (sph) and exponential (exp). The best-fitted variograms model is the spherical one (lower RMSE).

Tab. 6.9 Results of the cross validation: Root Mean Square Error (RMSE) and Mean Error (M.Er.)

model	RMSE	M. Er.
exp	0.2631	-0.00110
sph	0.2625	-0.00334

The probability of exceeding the TV = NBL is almost everywhere zero (Fig. 6.22). The presence of "hot spots" in the southern part, where the fluoride content is very high (Fig. 6.3b) because of the proximity to Phleagrean Fields, can be related to a natural contamination, even if an anthropogenic contamination cannot be excluded. In fact one of the "hot spots" falls in the area of the contaminated site of "Lo Uttaro" in Giugliano in Campania (Fig. 3.5).

Hence, the probability map shows that the TV=NBL, is a threshold suitable for the study area, nevertheless the influence of the Phleagrean Fields in the southern part that should be considerate separately.

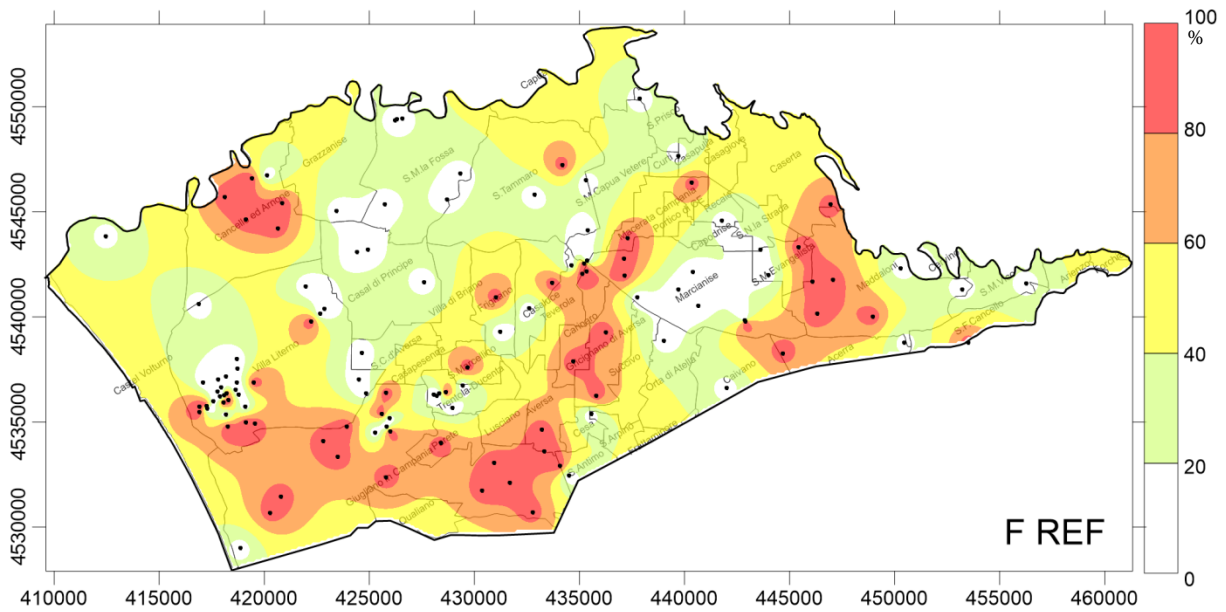


Fig. 6.21. Probability of fluoride being over REF= 1500 µg/l. Black dots are water samples. Percentage scale on the right.

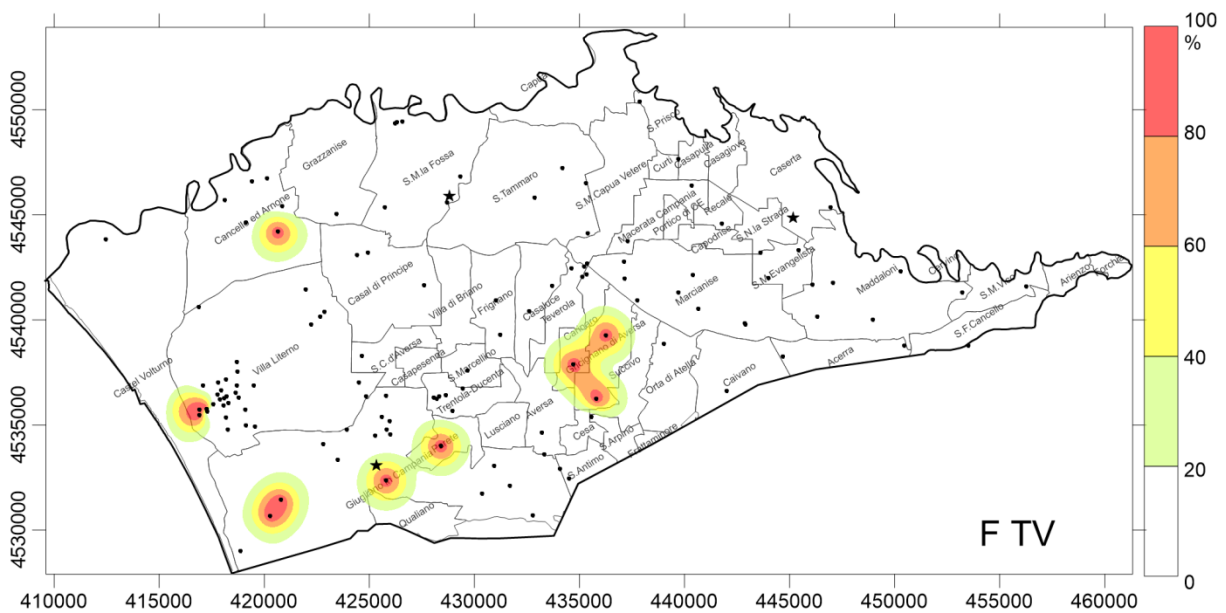


Fig. 6.22. Probability of fluoride being over TV= 2575 µg/l. Black dots are water samples. Black stars are "contaminated sites". Percentage scale on the right.

6.4.3. Iron

a) Oxidizing conditions

For Fe_{ox} , $TV=REF$ (200 $\mu g/l$). The results of the cross validation are in Tab. 6.10. Two models were compared: exponential (exp) and exponential with nugget effect (exp nug). The best-fitted variograms model is the exponential with nugget effect (lower RMSE).

Tab. 6.10 Results of the cross validation: Root Mean Square Error (RMSE) and Mean Error (M.Er.)

model	RMSE	M. Er.
exp	0.2986	0.00015
exp nug	0.2728	0.00026

The probability of exceeding the REF value is almost zero in the study area (Fig. 6.23). The presence of some “hot spot” is probably associated with sources of pollution (see Fig. 6.4b). In fact, there are some points in which a possible contamination of arsenic was already supposed in the § 6.4.1. (blue circle in Fig. 6.23). Hence, the probability map shows that the REF value is a threshold suitable for the study area, where it is in oxidizing conditions and a probably contaminated area has been individuate.

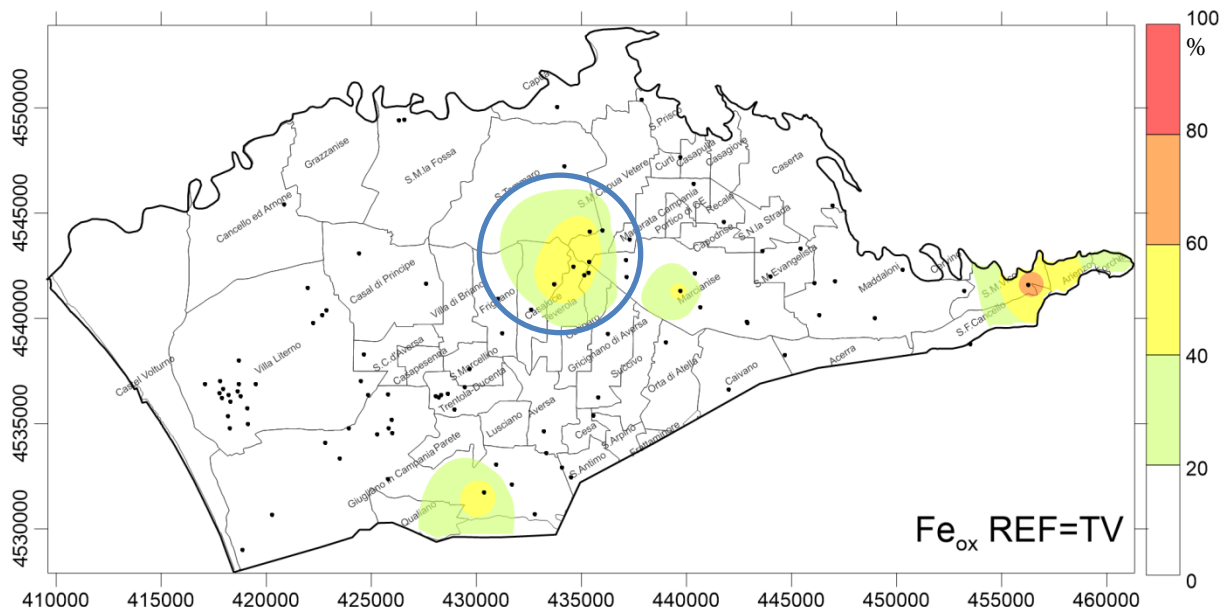


Fig. 6.23. Probability of iron in oxidizing conditions being over $TV=REF=200 \mu g/l$. Black dots are water samples. Percentage scale on the right. Blue circle indicates a probably contaminated area, in which iron and arsenic exceeding the natural background level.

b) Reducing conditions

For Fe_{red} , the probability of exceeding the REF (200 $\mu\text{g/l}$) is very high (>60%) almost everywhere (Fig. 6.24). The reliability of the map is greater in the area covered by water samples (black dots in Fig. 6.24).

Nevertheless there are small areas where the probability of exceeding the REF value is very low. The map in Fig. 6.24 shows that the REF value is not a threshold suitable for the study area, where reducing conditions occur. Moreover, the groundwater is probably unsuitable for human consumption where the probability of the exceeding the REF value is > 20%.

The probability of exceeding the TV=NBL (2549 $\mu\text{g/l}$) is shown in Fig. 6.25. The probability map shows clearly that the reducing conditions have to be considered in the northern part of the area, and even here in some sectors the NBL value is exceeded. The “hot spots” in Villa Literno and S.M. la Fossa are the same in which an arsenic contamination has been supposed, in § 6.4.1.; the “hot spot” in S.M. la Fossa fall in the contaminated site “Maruzzella”.

The probability map does not change even considering, as a threshold value, the higher between the proposed NBL (the NBL_{PS}). The reliability of the map is greater in the area covered by reduced water samples (black dots in Fig. 6.25).

6.4.4. Manganese

a) Oxidizing conditions

For Mn_{ox} , the probability of exceeding the REF (50 $\mu\text{g/l}$) and TV (91 $\mu\text{g/l}$) is substantially equivalent. In fact, the percentage of the total area, in which the probability of exceeding the threshold value, is almost the same in the two scenarios (Figs. 6.26 and 6.27). The presence of “hot spots” in both scenarios is probably due to anthropic contamination. In fact, one of the hot spots falls into the contaminated site “Lo Uttaro” in S.M. Evangelista. In this case it is possible to consider the REF value a threshold suitable for the study area, where oxidizing conditions are present.

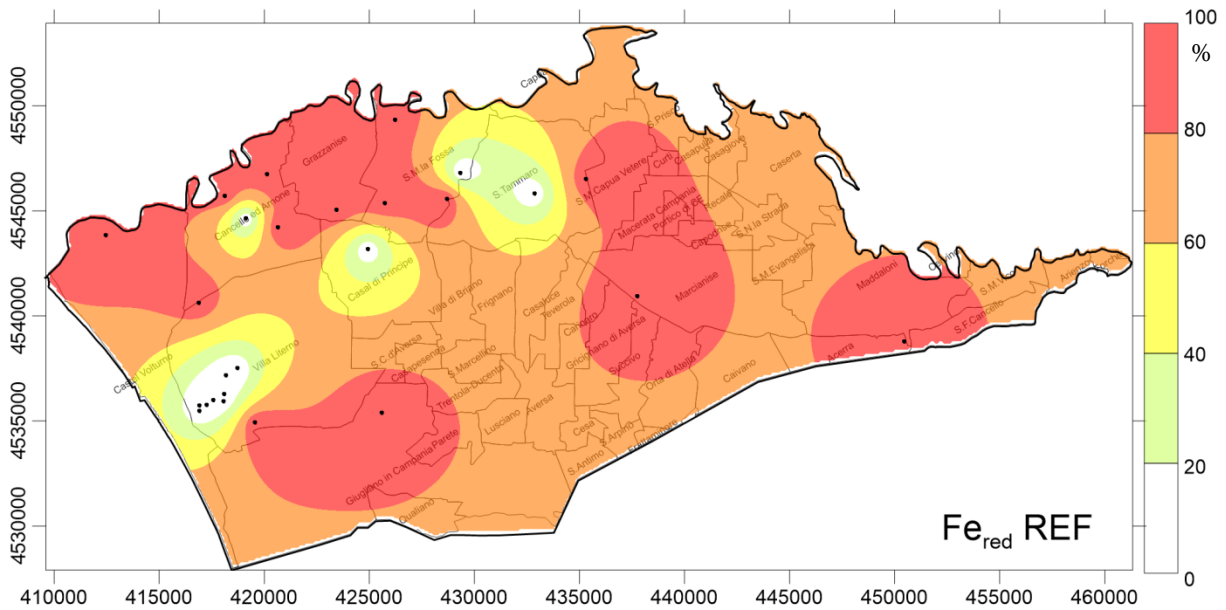


Fig. 6.24. Probability of iron in reducing conditions being over REF= 200 µg/l. Black dots are water samples. Percentage scale on the right.

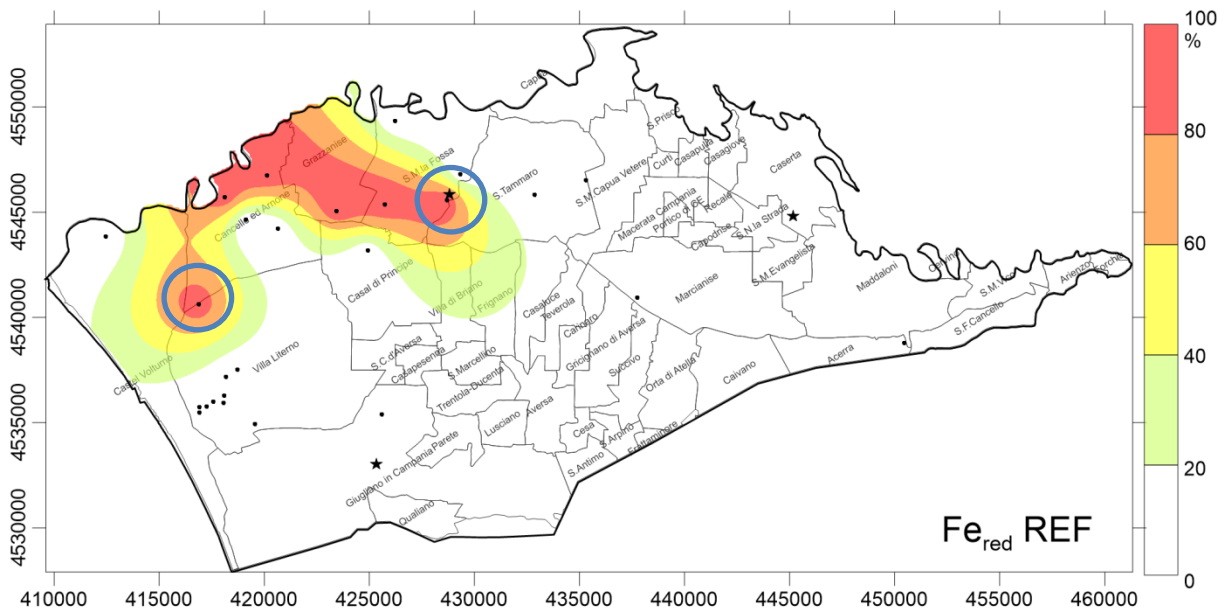


Fig. 6.25. Probability of iron in reducing conditions being over TV= 2549 µg/l. Black dots are water samples. Black stars are "contaminated sites".. Blue circles indicate two probably contaminated areas in S.M. la Fossa and Villa Literno, in which iron and arsenic exceeding the natural background level. Percentage scale on the right

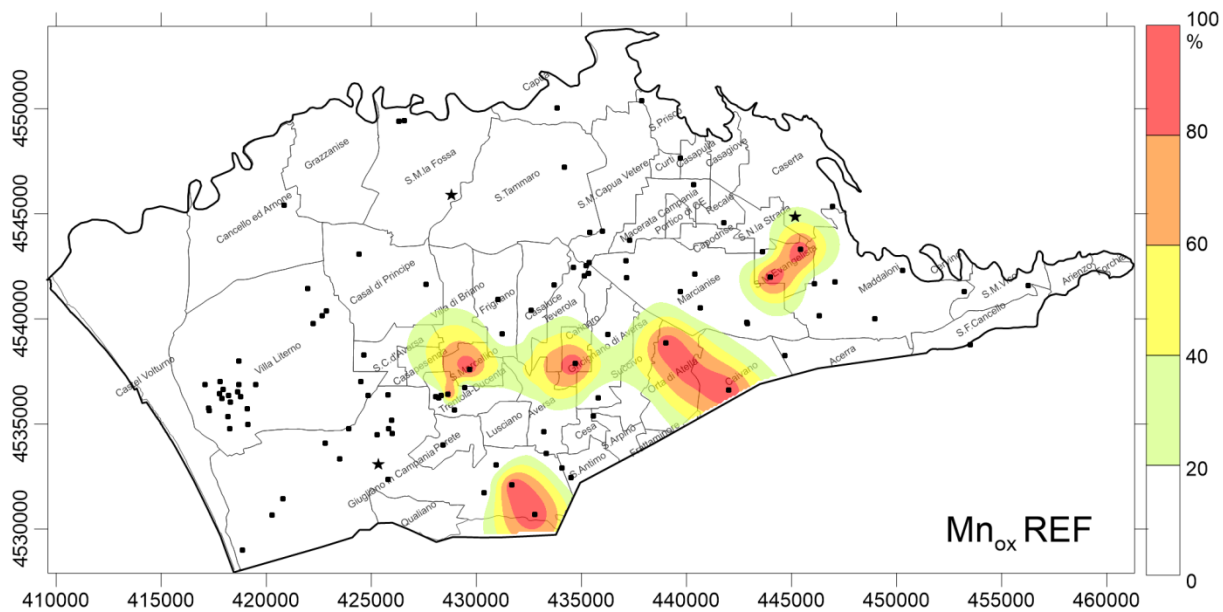


Fig. 6.26. Probability of manganese in oxidizing conditions being over REF= 50 µg/l. Black dots are water samples. Percentage scale on the right.

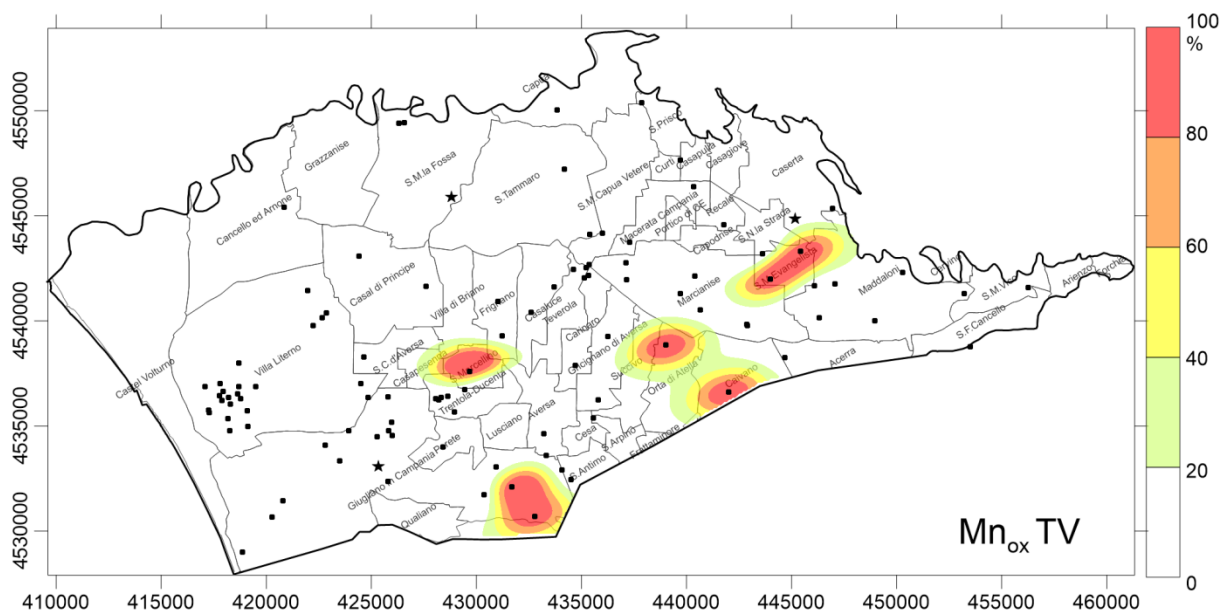


Fig. 6.27. Probability of manganese in oxidizing conditions being over TV= 91 µg/l. Black dots are water samples. Percentage scale on the right.

7. DISCUSSION

7.1. The comparison between the results obtained with the three different methods for the NBLs assessment.

The results of the comparison between the NBLs obtained with the three different methods are shown in Fig. 7.1.

The three methods gave always comparable results of the same order of magnitude and they corroborate in some cases the need of a different, higher, reference value. That is especially significant in the study area where a mixing of waters contaminated from anthropogenic and natural sources exists in some sector (Ducci et al., 2016) and the use of different approach to assess the NBLs facilitates the determination of a valid threshold value. In most of the cases, the NBL calculated with the probability plot (PP) method is lower than the one calculated value with the pre-selection criteria (PS) method (Mn and Fe in both conditions), or almost the same (As and F). The PP method considers the background value in correspondence of the slope change of the distribution data, which arises generally below the highest percentile of the data set. The PS method instead, although considering a data distribution different from that considered in the PP, evaluate the NBL as the highest percentile (in the study the 90th percentile).

Each method has shown strengths and weaknesses that will be discussed in this chapter.

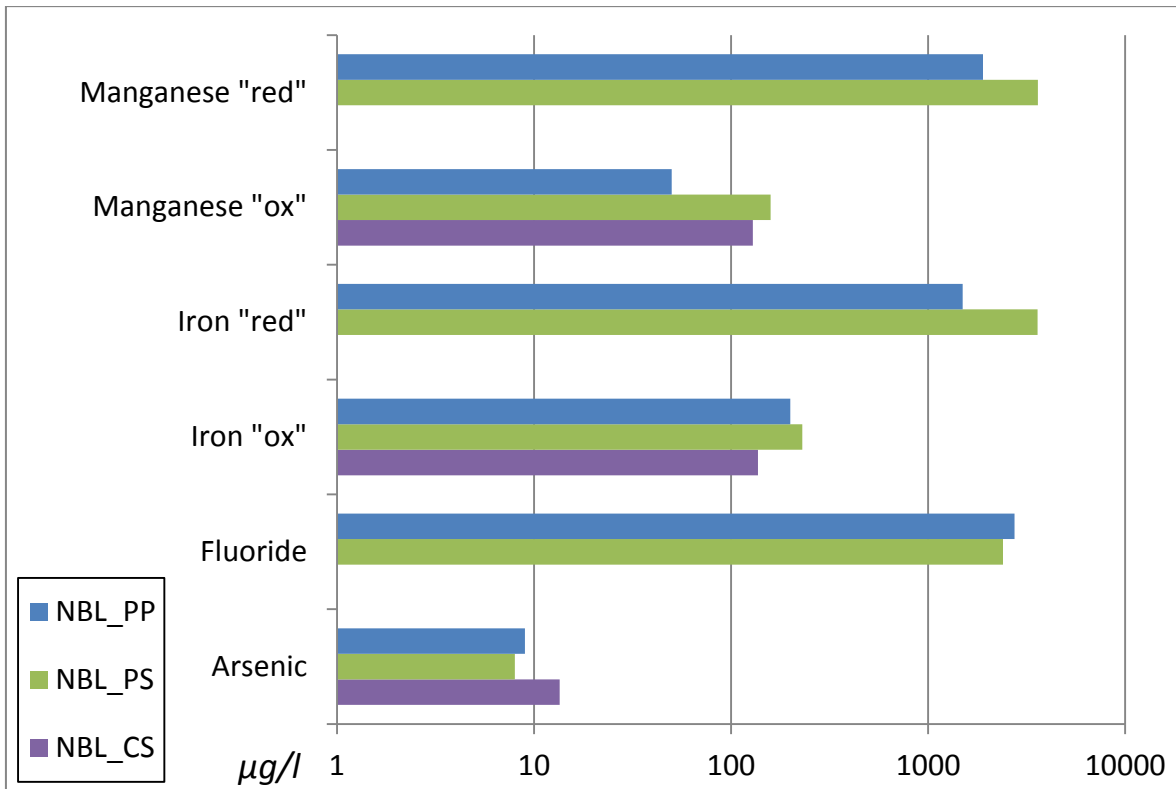


Fig. 7.1. Comparison between results obtained with probability plot method (PP), pre-selection criteria method (PS) and component separation approach (CS).

The component separation approach (CS) was the method that produced the poorest results. The application of the method gave good results only for arsenic and manganese and iron in oxidizing condition. The limit of the CS approach is that the superimposition of a log-normal distribution for the natural component cannot be appropriate in some cases (Reimann & Filzmoser, 2000; Rotiroti, 2015). Moreover, in case of oxidizing/reducing conditions, it is required a separation of the sample before the application of the method. Nevertheless, the separation of the sample can reduce the size of the data set and compromise the successful application of any statistical approach. This is probably the reason why the CS method has not gave results for Fe_{red} and Mn_{red}.

For iron and manganese, the probability plot (PP) method provided a poorly representative NBL, because there are different stages of transition between the reducing and the oxidant phase, therefore it is difficult to locate univocal slope changes on the probability plot. On the contrary, for As ad F the method gave good results, in according with the conceptual model and the results deriving from others methods.

The large number of values below the detection limit has been a problem for PP and PS method. For PS method it was necessary to consider a maximum of four points with the same value to avoid the problem.

The PS method should be taking into account the peculiarities of the study area, in order to give reliable results. In this study, the pre-selection criteria were chosen on the basis of the land use of the area; e.g. the limit of the nitrate of 10 mg/l proposed by the BRIDGE guidelines was raised to 50 mg/l (EU Drinking Water Standard), due to the intensive farming of the study area. Otherwise it would be necessary to exclude almost all of the samples. The separation of the data set into oxidizing versus reducing waters makes it possible to highlight the presence of negative redox conditions and to calculate two values of NBL for Mn and Fe. However, the number of available samples after the division of the data set could be too small and may lose its statistical significance. For this reason it is necessary have a large number of samples.

7.2. The natural and anthropogenic contamination

The NBLs help to identify whether a natural contamination is present or not. The natural contamination occur if the NBL is greater that the REF. In this case, the groundwater quality is poor, due the naturally elevated concentrations and the groundwater cannot be used for the human consumption, but the phenomenon is not caused by anthropogenic impacts, which can be mitigated or removed, and the chemical status can be considered good.

The Tab. 7.1 shows that the NBLs are always greater than the REF, in some cases by several orders of magnitude, for fluoride, iron and manganese. Therefore a natural contamination by fluoride, iron and manganese occurs.

Tab. 7.1. Difference (in percentage) between NBL (obtained with probability plot method (PP), pre-selection criteria method (PS) and component separation approach (CS) and law reference value (REF).

ION	NBL_{PP} VS REF	NBL_{PS} VS REF	NBL_{CS} VS REF
Arsenic	-10%	-20%	+35%
Fluoride	+83%	+60%	-
Iron_{ox}	0%	+15%	-32%
Iron_{red}	+650%	+1699%	-
Manganese_{ox}	-20%	+218%	+46%
Manganese_{red}	+3700%	+7122%	-

The fluoride contamination is the result of the natural leaching of volcanic rock aquifer.

The high iron and manganese content are due to the reducing conditions, for the presence of thick peaty levels, especially in the "non-saturated" and/or hydromineral areas (with significant contribution of CO₂ and H₂S).

For arsenic, instead, a natural contamination has not found. Only the CS method provides a NBL greater than the REF.

To estimate the extent of the contamination and the applicability of the NBL in the study area, the use of the probability maps was helpful (§7.3).

The NBL is calculated as a percentile of a distribution in the CS and PS method. The choice of any percentile of the data set as a threshold between "natural" and "anthropic" values should always be considered carefully and the exceedances must be considered as an indication of attention needed for that area and not as "pollution" tout-court. In this study, the 90th percentile provides a cautionary threshold, which is useful for the identification of those areas where a more in-depth analysis could be carried out.

7.3. The potentiality of the probability maps

The main outcomes of this study are the probability maps. The application of NBL concept revisited in the light of the spatial analysis using Indicator Kriging (IK) brings to many relevant issues.

The probability maps have proved to be a useful tool for the following purposes:

1. To identify points that probably are not naturally contaminated: for this purpose the maps drawn up considering the TV value (As REF=TV; F TV; Fe_{ox} REF=TV; Mn_{ox} TV; Figs: 6.20-22-23-27) have been useful. In fact in the maps, the probability of exceeding the TV=NBL is very low (<20%) except in some "hot spot" in which an exceeding of the threshold occurs, probably associated with a source of anthropogenic pollution. These points are wells or limited areas to be kept under observation or study. The use of these maps indicates localized contaminated sectors. In some case it has been possible to verify that the "hot spot" correspond to a contaminated area (for example the "Area vasta" defined by ARPA). However, in the study area the presence of numerous dumping sites (both legal and illegal) has been widely documented (Corniello and Ducci, 2014).
2. To evaluate when to consider TV instead of REF: for this purpose the maps of As REF = TV, Fe_{ox} REF = TV, Mn_{ox} REF and Mn_{ox} TV (Figs. 6.20-23-26-27) have been helpful. For As and Fe_{ox} the REF=TV is a good threshold value for the area. This is confirmed by the probability maps. For Mn_{ox}, the probability maps show that the probability of exceeding the REF is equal to the probability of exceeding the TV. Therefore, it could be useless to propose a new legislative threshold value (TV) and it could be better consider valid the REF.
3. To identify the area of validity of the TV, in particular for the Fe_{red} and Mn_{red}: for this purpose the maps of the Fe_{red} TV and Mn_{red} TV were helpful (Figs. 6.25-28). In this case there are large sectors, where the REF is exceeded. In this case it was crucial to consider two different values of NBL, one for the reduced conditions and one for the oxidizing conditions, in order to distinguish the natural contamination component from the anthropogenic one. The IK method, by definition, estimates the probability of exceeding an user-defined threshold, independently from the local concentration. For this reason, in order to be sure to identify the most significant area, the areas where the probability of exceeding the proposed TV is greater than 20% have been considered (Fig. 6.29).
4. To identify areas probably not usable for human consumption: the adopted methodology allows for a distinction between areas "probably exceeding the

NBL”, hence probably polluted, or areas “probably exceeding the drinking water standards”, hence not usable for human consumption regardless the origin of contamination.

8. CONCLUSIONS

This thesis deals with the request of the Groundwater Daughter Directive 2006/118/EC to EU Member States to derive appropriate threshold values (TV) for several potentially harmful substances, taking into account the natural background levels (NBL, in order to assess the chemical status of groundwater bodies).

The study area has been selected for its peculiar hydrogeological settings i.e. volcanic-pyroclastic aquifer with some sectors where reducing conditions occur, the widespread nitrate contamination of the aquifers and spotted sectors with high levels of contamination, prevalently due to legal and outlaw industrial and municipal wastes dumping, with hazardous consequences on the groundwater quality. Indeed the area is under interest of regional authorities and under continuous environmental studies.

The hydrogeochemical study was focused on arsenic, fluoride, iron and manganese, because of their diffuse presence in the study area, linked to the geological nature of the soils and/or to natural processes.

The NBLs were calculated with three different statistical methods: the probability plot method, the component separation method and the pre-selection criteria method. Statistical methods are chosen because they are more appropriate for aquifer subject to sever anthropogenic impacts, or highly contaminated, or under peculiar hydrogeological conditions.

The application of the three method highlights that the methods didn't give the same results and the most suitable method for the study area was the PS criteria, because the PS method is better able to distinguish the mixing of waters contaminated from anthropogenic and natural sources that occur in some sector of the study area. The choice of the percentile in the PS and CS method, as a threshold between “natural” and “anthropic” values, should always be considered wisely. As a matter of fact, the exceedances must be considered as a suggestion of attention for the study area and not as “contamination” in any absolute sense. In the study, the 90th percentile provides a rather cautionary threshold, which is useful for the identification of those areas where a more in-depth analysis could be carried out.

The first result of the this study is the assessment of the natural background levels for the arsenic, fluoride, iron and manganese, both in oxidizing and reducing conditions. The

NBL assessment provides a first step in the definition of the natural contamination in the groundwater body.

A natural contamination by fluoride, iron and manganese have been confirmed, in fact the NBLs for these ions, are always greater than the REF, in some cases by several orders of magnitude.

The fluoride contamination is the result of the natural leaching of volcanic rock constituting the aquifer.

The high iron and manganese content are due to the reducing conditions, for the presence of thick peaty levels.

For arsenic, the NBLs provide by PP method and PS method are lower than the REF value, only the CS method provides a NBL greater than the REF. Therefore a contamination by arsenic is not verified in the study area.

To estimate the extent of the contamination and the applicability of the NBL in the study area, the use of the probability maps was helpful.

The novelty of the study is the revisiting of the NBL concept in the light of the spatial analysis using Indicator Kriging (IK), in order to link the conditional probability estimation using IK to the local NBL. The combined use of IK and NBL produces maps that have useful potentiality.

The analysis of the probability maps, considering the NBL as threshold value, shows that the maps facility the identification of the points where a *not natural* contamination probably occurs i.e. area where concentrations exceed the established threshold values, from those where the high concentrations can be justified by the combination of different natural processes (rainfall composition, water-rock interactions, and exchanges with other water bodies, redox conditions and residence time). As stated before, the anthropogenic contamination should be verified with in-depth investigations at local scale because the exceedances must be considered as an indication of attention needed for that area and not as “pollution” tout-court. In some case it has been possible verify that the exceeding of the NBL corresponds to a point in a contaminated area. The probability maps proposed are meant to give a preliminary overview and an order of magnitude of the potentially contaminated areas from human impacts.

The probability maps are also a useful tool to endorse the application of the NBL value within a large study area. In this study the NBLs of arsenic and fluoride are suitable threshold value for the study area, the probability of exceeding these value is

very low in the GWB. For iron and manganese the probability maps have identified large sectors, where it would be desirable consider the NBL of Fe_{red} and Mn_{red} . In order to distinguish the natural and the anthropogenic contamination, it was decisive to assess two different values of NBL, one for the reduced conditions and one for the oxidizing conditions. These sectors were identified by considering the areas where the probability of exceeding the proposed TV is greater than 20%.

Moreover, this methodology may sustain the application of European Water Framework Directive and other legislation on groundwater quality or provide a support for groundwater management during the planning process, or in the remediation strategies. The success of the maps at distinguishing natural versus anthropogenic contamination, on high levels of contaminant elements, is subject to in-depth studies based on accurate analysis.

This method could be applied to any other element or compound and to any geological setting, as long as a valid hydrogeological conceptual model has been defined. The methodology can be tested to support the protection of associated aquatic and dependent terrestrial ecosystems and the uses and functions of groundwater (mainly drinking water use).

9. REFERENCES

Adamo, N., Imperatrice, M.L., Mainolfi, P., Onorati, G., Scala, F. (2007). *Acqua. Il Monitoraggio in Campania 2002–2006*. ARPAC, Napoli, 95–160.

AGIP Azienda generale italiana petroli (1977). *Temperature sotterranee: inventario dei dati raccolti dall'Agip durante la ricerca e la produzione di idrocarburi in Italia*. Agip, 1977.

Aiuppa, A., Bellomo, S., Brusca, L., d'Alessandro, W., Federico, C., (2003). Natural and anthropogenic factors affecting groundwater quality of an active volcano (Mt. Etna, Italy). *Appl. Geochem.* 18 (6), 863–882.

Albanese, S., Fontaine, B., Chen, W., Lima, A., Cannatelli, C., Piccolo, A., Qi, S., Wang, M., De Vivo, B. (2015). Polycyclic aromatic hydrocarbons in the soils of a densely populated region and associated human health risks: the Campania Plain (Southern Italy) case study. *Environmental geochemistry and health*, 37(1), 1-20.

Allocca, V., Celico, F., Celico, P., De Vita, P., Fabbrocino, S., Mattia, C., Musilli, I., Piscopo, V., Summa, G., (2005). *Hydrogeological Map of Southern Italy*. Istituto Poligrafico e Zecca dello Stato, Roma.

Aprile, F., Sbrana, A., Toccaceli, R. M. (2004). Il ruolo dei depositi piroclastici nell'analisi cronostratigrafica dei terreni quaternari del sottosuolo della Piana Campana (Italia meridionale). *Il Quaternario*, 17, 547-554.

Autorità di Bacino della Campania Nord-occidentale (2004). *Piano Stralcio di Tutela delle Acque (D. Lgs. 152/99 e s.i.m.)* 3 Vols.

Bartolucci E., Bussetini M., Calace N., D'Aprile L., Fratini M., Guerra M., Marangio L., Pirani G., Vecchio A. (2009). Protocollo per la definizione dei valori di fondo per le sostanze inorganiche nelle acque sotterranee "Protocol for defining background levels for inorganic species in groundwater". ISPRA - Servizio Interdipartimentale per le Emergenze Ambientali, Settore Siti Contaminati.

Bellucci, F. (1998). Nuove conoscenze stratigrafiche sui depositi effusivi ed esplosivi nel sottosuolo dell'area del Somma-Vesuvio. *Bollettino della Società geologica italiana*, 117(2), 385-405.

Bowen, R. (1986). *Groundwater*. Springer Science & Business Media

Brancaccio, L., Cinque, A., Romano, P., Roskopf, C., Russo, F., Santangelo, N. & Santo, A. (1991). Geomorphology and neotectonic evolution of a sector of the Tyrrhenian flank of the southern Apennines (region of Naples, Italy). *Z. Geomorphol., Suppl.* 82, 47–58.

Brancaccio, L., Cinque, A., Romano, P., Roskopf, C., Russo, F., & Santangelo, N. (1995). L'evoluzione delle pianure costiere della Campania: geomorfologia e neotettonica. *Memorie della Società Geografica Italiana*, 53, 313-336.

Budetta, P., Calcaterra, D., Corniello, A., De Riso, R., Ducci, D., Santo, A. (1993). *Appunti di Geologia dell'Appennino meridionale*. *Ist. Geol. Appl.* 332, 1-39.

Candela, L., Wallis, K. J., Mateos, R. M. (2008). Non-point pollution of groundwater from agricultural activities in Mediterranean Spain: the Balearic Islands case study. *Environmental Geology*, 54(3), 587-595.

Carraro A., Fabbri P., Giaretta A., Peruzzo L., Tateo F. & Tellini F. (2015). Effects of redox conditions on the control of arsenic mobility in shallow alluvial aquifers on the Venetian Plain (Italy). *Sci. Total Environ.*, 532, 581-594.

Carraro A., Fabbri P., Giaretta A., Peruzzo L., Tateo F., & Tellini F. (2013). Arsenic anomalies in shallow Venetian Plain (Northeast Italy) groundwater. *Environ. Earth Sci.*, 70, 3067-3084.

Capri, E., Civita, M., Corniello, A., Cusimano, G., De Maio, M., Ducci, D., ... & Vassallo, M. (2009). Assessment of nitrate contamination risk: the Italian experience. *Journal of Geochemical Exploration*, 102(2), 71-86.

Cattle, J. A., McBratney, A., & Minasny, B. (2002). Kriging method evaluation for assessing the spatial distribution of urban soil lead contamination. *Journal of Environmental Quality*, 31(5), 1576-1588.

Celico, P. (1988). *Prospezioni idrogeologiche (Vol. 1)*. Liguori Editore Srl.

Chery, L. (2006). *Qualité naturelle des eaux souterraines–Méthode de caractérisation des états référence des aquifères français*. Rapport BRGM-editions, Orleans, 238.

Chiles, J. P., Delfiner, P. (2009). *Geostatistics: modeling spatial uncertainty (Vol. 497)*. John Wiley & Sons.

Cinque, A., Patacca, E., Scandone, P. & Tozzi, M. (1993). *Quaternary kinematic*

evolution of the Southern Apennines. Relationships between surface geological features and deep lithospheric structures. *Ann. Geofis.* 36, 2, 249–259.

Cinque, A., Ascione, A., Caiazza, C. (2000). Distribuzione spazio-temporale e caratterizzazione della fagliazione quaternaria in Appennino meridionale. In: F. Galadini, C. Meletti, A. Melez (a cura di): *Le Ricerche del GNDT nel Campo della Pericolosità Sismica*: Rome, Consiglio Nazionale delle Ricerche, Gruppo Nazionale per la Difesa dai Terremoti, 203-218.

Civita, M., & De Maio, M. (2000). Valutazione e cartografia automatica della vulnerabilità degli acquiferi all'inquinamento con il sistema parametrico-SINTACS R5-A new parametric system for the assessment and automatic mapping of ground water vulnerability to contamination (Vol. 72, pp. 226-226). Pitagora.

Clark, I. D., Fritz, P. (1997). *Environmental isotopes in hydrogeology*. CRC press.

CLC 2012. Copernicus Service - Pan-European Component: CORINE Land Cover. <http://land.copernicus.eu/pan-european/corine-land-cover/clc-2012>.

Coetsiers, M., Blaser, P., Martens, K., Walraevens, K. (2009). Natural background levels and threshold values for groundwater in fluvial Pleistocene and Tertiary marine aquifers in Flanders, Belgium. *Environ. Geol.* 57 (5), 1155–1168

Corniello, A., De Riso, R., Ducci, D. (1990). Idrologia ed idrogeochimica della Piana Campana. *Memorie della Società Geologica Italiana*, 45(1), 351–360.

Corniello A., Ducci, D. (2004). Stato ambientale dei corpi idrici sotterranei. In AA.VV.: *Lo stato delle conoscenze acquisite sulle acque sotterranee del Bacino Nord - Occidentale propedeutico alla redazione del Piano di tutela delle Acque*. Volume II, pp 93-94. TPS - Selca

Corniello, A., Ducci, D. (2005). Carta della Vulnerabilità all'inquinamento del settore meridionale della Piana del F. Volturno. *Aquifer Vulnerability and Risk*. In 2nd International Workshop Aquifer vulnerability assessment and mapping. 4th Congress on the Protection and Management of Groundwater, Colorno (pp. 21-23).

Corniello, A., Ducci, D. (2009). Origine dell'inquinamento da nitrati nelle falde dell'area di Acerra (Piana Campana). *Engineering Hydro Environmental Geology*, 12, 157-166.

Corniello, A., Ducci, D. (2014). Hydrogeochemical characterization of the main aquifer of the “Litorale Domizio-Agro Aversano NIPS” (Campania—southern Italy). *Journal of Geochemical Exploration*, 137, 1-10.

Corniello, A., Ducci, D., Ruggieri, G., (2007). A real identification of groundwater nitrate contamination sources in periurban areas. *J. Soils Sediments* 7 (4), 159–166.

Corniello, A., Ducci, D., Trifuoggi, M., Rotella, M., Ruggieri, G. (2010). Hydrogeology and hydrogeochemistry of the plain between Mt. Massico and the river Volturno (Campania region, Italy). *Italian Journal of Engineering Geology and Environment*, 10(1), 51-64.

De Vivo, B., Rolandi, G., Gans, P. B., Calvert, A., Bohron, W. A., Spera, F. J., Belkin, H. E. (2001). New constraints on the pyroclastic eruptive history of the Campanian volcanic Plain (Italy). *Mineralogy and Petrology*, 73(1-3), 47-65.

Delbari, M., Amiri, M., & Motlagh, M. B. (2016). Assessing groundwater quality for irrigation using indicator kriging method. *Applied Water Science*, 6(4), 371-381.

Deutsch, C. V., Journel, A. G. (1998). *Geostatistical software library and user's guide*. Oxford University Press, New York.

Ducci, D., Condesso de Melo, M. T., Preziosi, E., Sellerino, M., Parrone, D., Ribeiro, L., (2016). Combining natural background levels (NBLs) assessment with indicator kriging analysis to improve groundwater quality data interpretation and management. *Science of The Total Environment*, 569, 569-584.

Ducci, D., Sellerino, M. (2012). Natural background levels for some ions in groundwater of the Campania region (southern Italy). *Environmental Earth Sciences*, 67(3), 683-693.

DWD (1998) Drinking Water Directive, 1998/83/CE. Council Directive of 3 November 1998 on the quality of water intended for human consumption

Edmunds, W. M., Shand, P., Hart, P., Ward, R. S. (2003). The natural (baseline) quality of groundwater: a UK pilot study. *Science of the Total Environment*, 310(1), 25-35.

Edmunds, W.M., Shand, P. (2008). *Natural Groundwater Quality*. Wiley-Blackwell (488 pp. ISBN 978-14051- 5675-2).

European Commission (1998). Council Directive 98/83/EC of 3 November 1998 on

the quality of water intended for human consumption. Official Journal of the European Communities L330: 32 - 54

European Commission (2000). Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy. Official Journal of the European Communities L327: 1–73.

European Commission (2006). Groundwater Directive 2006/118/CE, Directive of the European Parliament and of the Council on the Protection of Groundwater Against Pollution and Deterioration, Official Journal of the European Communities L372: 19–31.

European Commission (2014). Directive 2014/80/EU amending Annex II to Directive 2006/118/EC of the European Parliament and of the Council on the Protection of Groundwater Against Pollution and Deterioration, OJ L182, 21/6/2014. pp. 52–55.

Gałoszka, A., (2007). A review of geochemical background concepts and an example using data from Poland. *Environ. Geol.* 52 (5), 861–870.

Goovaerts, P. (1997). *Geostatistics for natural resources evaluation*. Oxford University Press on Demand.

Griffioen, J., Passier, H.F., Klein, J. (2008). Comparison of selection methods to deduce natural background levels for groundwater units. *Environmental science & technology*, 42(13), 4863-4869.

Hawkes, H.E., Webb, J.S. (1962). *Geochemistry in Mineral Exploration*. Harper, New York.

Hinsby, K., Condesso de Melo, M.T., Dahl, M. (2008). European case studies supporting the derivation of natural background levels and groundwater threshold values for the protection of dependent ecosystems and human health. *Science of the Total Environment*, 401(1), 1-20.

Ippolito, F., Ortolani, F., Russo, M. (1973). Struttura marginale tirrenica dell'Appennino campano: reinterpretazione di dati di antiche ricerche di idrocarburi. *Mem. Soc. Geol. Ital*, 12, 227-250.

Isaaks, E. H. and R. M. Srivastava. (1989). *Applied Geostatistics*. Oxford University Press, Inc., New York, 561 pp.

Journel, A. (1987). *Geostatistics for the Environmental Sciences*, EPA Project n° CR

811893. Technical Report. US EPA, EMS Lab, Las Vegas, NV (135 pp).

Journel, A. G. (1983). Nonparametric estimation of spatial distributions. *Journal of the International Association for Mathematical Geology*, 15(3), 445-468.

Kehew, A.E., 2001. *Applied Chemical Hydrogeology*. Prentice Hall (363 pp.).

Kitanidis, P. K. (1997). *Introduction to Geostatistics: Applications in Hydrogeology*. Cambridge University Press, Cambridge, 249 pp.
<https://www.cambridge.org/core/books/introduction-to-geostatistics/0B048A09F7FF60C2CCC852E418AF778D>

Lee, J. J., Jang, C. S., Wang, S. W., & Liu, C. W. (2007). Evaluation of potential health risk of arsenic-affected groundwater using indicator kriging and dose response model. *Science of the Total Environment*, 384(1), 151-162.

Liu, C. W., Jang, C. S., & Liao, C. M. (2004). Evaluation of arsenic contamination potential using indicator kriging in the Yun-Lin aquifer (Taiwan). *Science of the Total Environment*, 321(1), 173-188.

Lee, L., Helsel, D. (2007). Statistical analysis of water-quality data containing multiple detection limits II: S-language software for nonparametric distribution modeling and hypothesis testing. *Computers & Geosciences*, 33(5), 696-704.

Madison, R.J., Burnett, J.O. (1985). Overview of the occurrence of nitrate in ground water of the United States. *National Water Summary 1984 - Hydrologic Events*, 93-105.

Marinoni, O. (2003). Improving geological models using a combined ordinary-indicator kriging approach. *Engineering Geology*, 69(1), 37-45.

Masetti, M., Sterlacchini, S., Ballabio, C., Sorichetta, A., Poli, S. (2009). Influence of threshold value in the use of statistical methods for groundwater vulnerability assessment. *Science of the total environment*, 407(12), 3836-3846.

Matschullat, J., Ottenstein, R., Reimann, C. (2000). Geochemical background — can we calculate it? *Environ. Geol.* 39 (9), 990–1000.

Matthess, G., 1982. *The Properties of Groundwater*. John Wiley & Son (406 pp.).

Milia, A., Torrente, M. M. (1999). Tectonics and stratigraphic architecture of a peri-Tyrrhenian half-graben (Bay of Naples, Italy). *Tectonophysics*, 315(1), 301-318.

Molinari, A., Chidichimo, F., Straface, S., Guadagnini, A., (2014). Assessment of natural background levels in potentially contaminated coastal aquifers. *Sci. Total Environ.* 476–477, 38–48.

Molinari, A., Guadagnini, L., Marcaccio, M., Guadagnini, A. (2012). Natural background levels and threshold values of chemical species in three large-scale groundwater bodies in Northern Italy. *Sci. Total Environ.* 425, 9–19.

Morgenstern, U., Daughney, C.J., (2012). Groundwater age for identification of baseline groundwater quality and impacts of land-use intensification. The National Groundwater Monitoring Programme of New Zealand. *J. Hydrol.* 456/457, 79–93

Muller, D., Blum, A., Hart, A., Hookey, J., Kunkel, R., Scheidleder, A., Tomlin, C., Wendland, F. (2006). Final proposal for a methodology to set up groundwater threshold values in Europe. Report to EU project BRIDGE, Deliverable D18.

Nakić, Z., Posavec, K., Bačani, A. (2007). A visual basic spreadsheet macro for geochemical background analysis. *Ground Water* 45 (5), 642–647

Nakić, Z., Posavec, K., Parlov, J. (2010). Model-based objective methods for the estimation of groundwater geochemical background. *Aqua Mundi*, 1(1), 65-72.

Nicotera, P., Tonnetti, G. (1972). Su una ricerca idrica per l'agglomerato di Giugliano-Qualiano. *Memorie e Note dell'Istituto di Geologia Applicata della Facoltà di Ingegneria di Napoli*, 12.

Olea, R. (1999) *Geostatistics for Engineers and Earth Scientists*. Kluwer Academic Publishers, Boston, 303 pp.

Oliveri Del Castillo, A. (1966). Considerazioni gravimetriche sul bacino eruttivo e sedimentario campano (anomalie residue di ordine nI). *Annali dell'Osservatorio Vesuviano*, series, 6.

Ortolani, F., Aprile, F. (1985). Principali caratteristiche stratigrafiche e strutturali dei depositi superficiali della Piana Campana. *Bollettino della Societa Geologica Italiana*, 104(2), 195-206

Panno, S. V., Kelly, W. R., Martinsek, A. T., Hackley, K. C. (2006). Estimating background and threshold nitrate concentrations using probability graphs. *Ground Water*, 44(5), 697-709.

Piper, A.M. (1944). A graphic procedure in the geochemical interpretation of water analyses. *Transactions of American Geophysical Unions*, 25: 914–923

Potot, C., Féraud, G., Schärer, U., Barats, A., Durrieu, G., Le Poupon, C., Travi, Y., Simler, R. (2012). Groundwater and river baseline quality using major, trace elements, organic carbon and Sr–Pb–O isotopes in a Mediterranean catchment: the case of the lower Var Valley (south-eastern France). *J. Hydrol.* 472–473, 126–147.

Preziosi, E., Giuliano, G., Vivona, R. (2010). Natural background levels and threshold values derivation for naturally As, V and F rich groundwater bodies: a methodological case study in Central Italy. *Environmental Earth Sciences*, 61(5), 885-897.

Preziosi, E., Parrone, D., Del Bon, A., Ghergo, S. (2014). Natural background level assessment in groundwaters: probability plot versus pre-selection method. *J. Geochem. Explor.* 143, 43–53.

Putignano, M. L., Ruberti, D., Tescione, M., & Vigliotti, M. (2007). Evoluzione tardo quaternaria del margine casertano della Piana Campana (Italia Meridionale). *Italian Journal of Geosciences*, 126(1), 11–24.

Reimann, C., Filzmoser, P., (2000). Normal and lognormal data distribution in geochemistry: death of a myth. Consequences for the statistical treatment of geochemical and environmental data. *Environ. Geol.* 39 (9), 1001–1014.

Reimann, C., Garrett, R.G. (2005). Geochemical background—concept and reality. *Sci. Total Environ.* 350 (1), 12–27.

Rolandi, G., Bellucci, F., Heizler, M. T., Belkin, H. E., De Vivo, B. (2003). Tectonic controls on the genesis of ignimbrites from the Campanian Volcanic Zone, southern Italy. *Mineralogy and Petrology*, 79(1-2), 3-31.

Romano, P., Santo, A., Voltaggio M. (1994). L'evoluzione geomorfologica della pianura del Fiume Volturno (Campania) durante il tardo Quaternario (Pleistocene medio-superiore-Olocene). *Il Quaternario*, 7, 41-56.

Rotiroti, M., Di Mauro, B., Fumagalli, L., Bonomi, T. (2015). COMPSEC, a new tool to derive natural background levels by the component separation approach: application in two different hydrogeological contexts in northern Italy. *Journal of Geochemical Exploration*, 158, 44-54.

Rotiroti, M., Fumagalli, L. (2013). Derivation of preliminary natural background levels

for naturally Mn, Fe, As and NH₄⁺ rich groundwater: the case study of Cremona area (Northern Italy). *Rend. Online Soc. Geol. Ital.* 24, 284–286.

Santangelo, N., Ciampo, G., Di Donato, V., Esposito, P., Petrosino, P., Romano, P., Russo Ermolli, E., Santo, A., Toscano, F., Villa, I. (2010). Late Quaternary buried lagoons in the northern Campania plain (southern Italy): evolution of a coastal system under the influence of volcano-tectonics and eustatism. *Italian journal of geosciences*, 129(1), 156-175.

Santangelo, N., Romano, P., Ascione, A., & Russo Ermolli, E. (2017). Quaternary evolution of the Southern Apennines coastal plains: a review. *Geologica Carpathica*, 68(1), 43-56.

Shand, P., Edmunds, W. M. (2008). The baseline inorganic chemistry of European groundwaters. *Natural groundwater quality*, 22-58.

Shapiro, S. S., Wilk, M. B. (1965). An analysis of variance test for normality (complete samples). *Biometrika*, 52(3/4), 591-611.

Sinclair, A. J. (1974). Selection of threshold values in geochemical data using probability graphs. *Journal of Geochemical Exploration*, 3(2), 129-149.

Singh, A., Maichle, R., Armbya, N. (2010). ProUCL Version 4.1. 00 User Guide (Draft). EPA/600/R-07/041, May 2010. Office of Research and Development, US Environmental Protection Agency, Washington, DC.

Smedley, P.L., Nicolli, H.B., Macdonald, D.M.J., Barros, A.J., Tullio, J.O., (2002). Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. *Appl. Geochem.* 17, 259–284.

Smith, J. L., Halvorson, J. J., & Papendick, R. I. (1993). Using multiple-variable indicator kriging for evaluating soil quality. *Soil Science Society of America Journal*, 57(3), 743-749.

Stigter, T., Almeida, P., Carvalho Dill, A. M. M., & Ribeiro, L. (2005). Influence of irrigation on groundwater nitrate concentrations in areas considered to have low vulnerability to contamination. *Groundwater and Human Development. Selected Papers on Hydrogeology*, 6, 69-85.

Tobías, F.J., Bech, J., Algarra, P.S., (1997). Establishment of the background levels of

some trace elements in soils of NE Spain with probability plots. *Sci. Total Environ.* 206 (2-3), 255-265

U.S. EPA (2000). 'EPA QA/G-9, QA00 Update, Guidance for Data Quality Assessment, Practical Methods for Data Analysis.' Rep. No. EPA/600/R-96/084, Office of Environmental Information, Washington, D.C

U.S. EPA (2002). Calculating Upper Confidence Limits for Exposure Point Concentrations at Hazardous Waste Sites. Publication OSWER 9285.6-10, Office of Emergency and Remedial Response, Washington D.C.

Urresti-Estala, B., Carrasco-Cantos, F., Vadillo-Pérez, I., Jiménez-Gavilán, P., (2013). Determination of background levels on water quality of groundwater bodies: a methodological proposal applied to a Mediterranean River basin (Guadalhorce River, Málaga, southern Spain). *J. Environ. Manag.* 117, 121-130

US Navy (2013). Naples Public Health Evaluation - A Risk Communication Case Study, 53 pp. Short URL: <http://2cg.it/33>

Walter, T. (2008). Determining natural background values with probability plots. EU Groundwater Policy Development, 80.

Wendland, F., Berthold, G., Blum, A., Elsass, P., Fritsche, J.G., Kunkel, R., Wolter, R. (2008). Derivation of natural background levels and threshold values for groundwater bodies in the Upper Rhine Valley (France, Switzerland and Germany). *Desalination*, 226, 160-168.

Wendland, F., Hannappel, S., Kunkel, R., Schenk, R., Voigt, H. J., Wolter, R. (2005). A procedure to define natural groundwater conditions of groundwater bodies in Germany. *Water Science and Technology*, 51(3-4), 249-257.

WRON Alliance (2006). Groundwater theme report. National Water Commission, Canberra.

Zabala, M.E., Martínez, S., Manzano, M., Vives, L. (2016). Groundwater chemical baseline values to assess the recovery plan in the Matanza-Riachuelo River basin, Argentina. *Sci. Total Environ.* 541, 1516-1530

APPENDIX A: ACRONYMS AND ABBREVIATIONS

ARPAC: Regional Agency for Environmental Protection of Campania

As REF=V: Probability map of As considering as threshold value REF=TV

CDF: cumulative density function

CI: Campanian Ignimbrite

CIRAM: Centro Interdipartimentale di Ricerca «Ambiente»

CS: Component separation

DCS: Department of Chemical Sciences of University of Naples “Federico II”

DICEA: Department of Department of Civil, Constructional and Environmental Engineering

EC: Electrical conductivity

F REF: Probability map of F considering as threshold value REF

F TV: Probability map of F considering as threshold value TV

Fe_{ox}: Iron in oxidizing conditions

Fe_{ox} REF=TV: Probability map of Fe_{ox} considering as threshold value REF=TV

Fe_{red}: Iron in reducing conditions

Fe_{red} REF: Probability map of Fe_{red} considering as threshold value REF

Fe_{red} TV: Probability map of Fe_{red} considering as threshold value TV

GWB: Groundwater Body

GWDD: Groundwater Daughter Directive 2006/118/EC

IK: Indicator Kriging

LDDA: Litorale Domizio-Agro Aversano

MLE: maximum likelihood estimation

Mn_{ox}: Manganese in oxidizing conditions

Mn_{ox} TV: Probability map of Mn_{ox} considering as threshold value TV

Mn_{ox} REF: Probability map of Mn_{ox} considering as threshold value REF

Mn_{red}: Manganese in reducing conditions

Mn_{red} TV: Probability map of Mn_{red} considering as threshold value TV

NBL: Natural Background Level

NBL_{CS}: Natural Background Level assessed by Component separation method

NBL_{PP}: Natural Background Level assessed by Probability plot method

NBL_{PS}: Natural Background Level assessed by Pre-selection criteria method

NIPS: National Interest Priority Site

OLS: ordinary least square

ox: Oxidizing conditions

PDF_{logn}: lognormal frequencydistribution

PDF_{norm}: normal frequencydistribution

PDF_{obs}: the observed frequency distribution

PP: "Probability plot" method

PS: "Pre-selection criteria" method

P-VLTR: Volturno Plain-Regi Lagni groundwater body

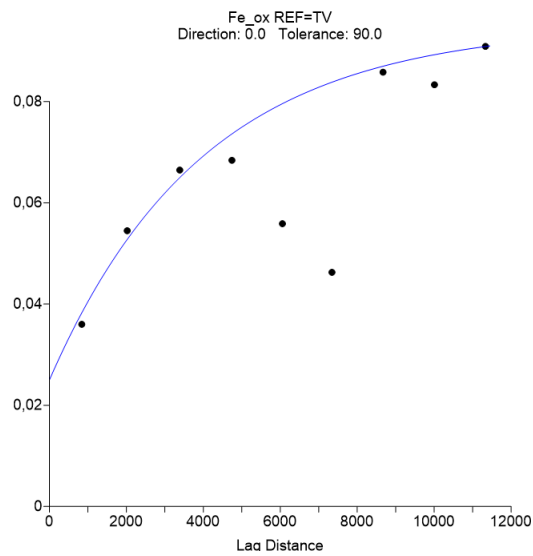
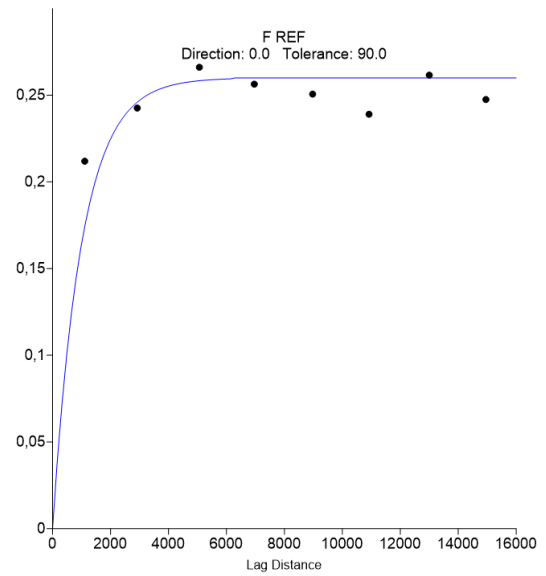
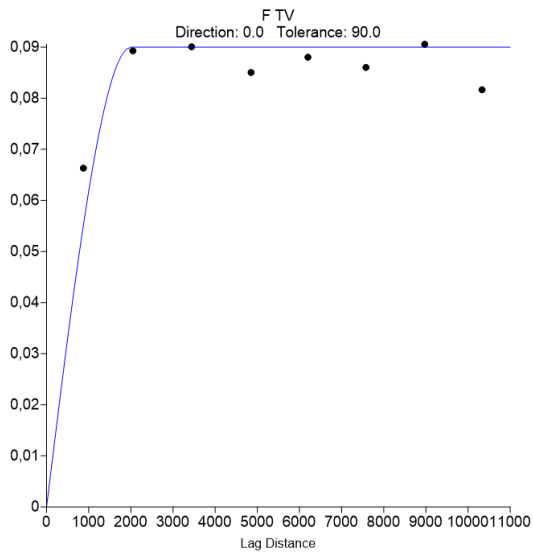
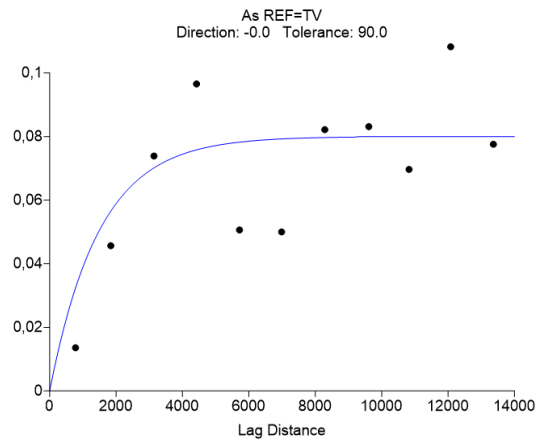
red: Reducing conditions

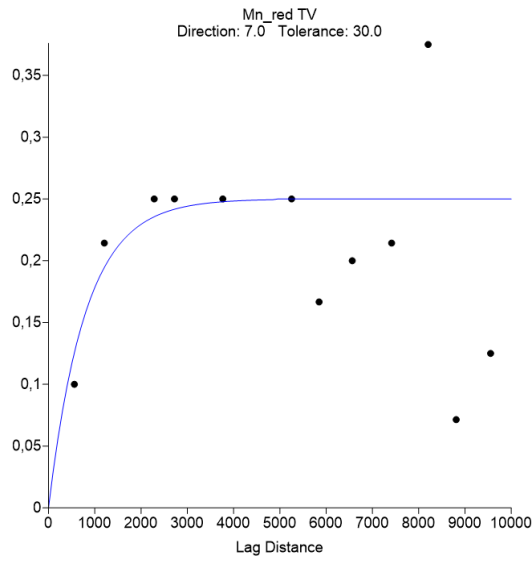
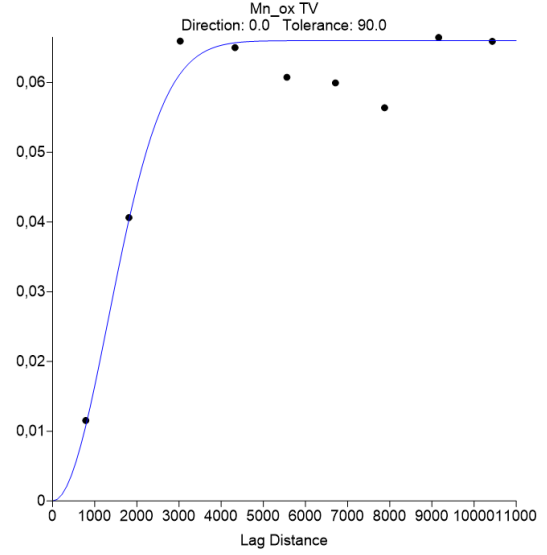
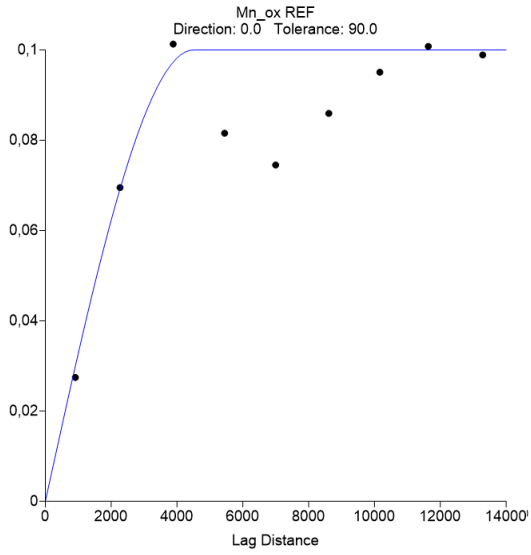
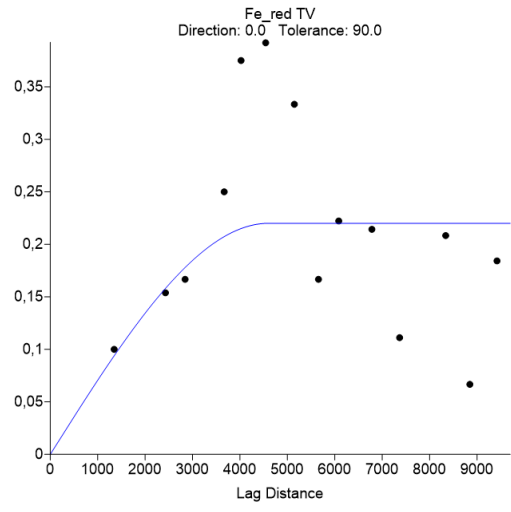
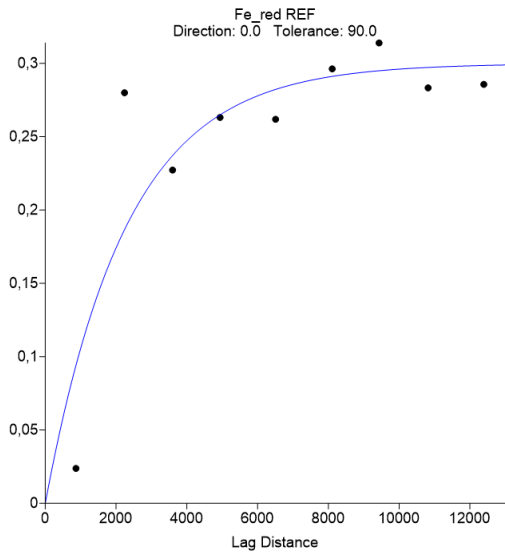
RMSE: root-mean-square error

TV: Threshold Values

WFD: Water Framework Directive 2000/60/CE

APPENDIX B: VARIOGRAMS





APPENDIX C: DATA SET

ID	X	Y	NO ₃	Mn	Fe	As	F	Mean value
1	422811	4534094	19.4	1.0	19.0	9.0	1900	
2	435557	4535370	75.2	0.8	11.0	5.2	1300	
3	442870	4539842		0.1	55.6		1500	
4	448952	4540009	84.7	0.05	153.6		2200	
5	453515	4538761	52.5	0.05	122.1		1600	
6	434493	4532437	39.9	2.2	82.3	1.7	1410	*
7	432774	4530698	1.74	3470	73.1	5.9	1980	*
8	430377	4531711	14	5	262	0.4	1600	*
9	450469	4538772	42.0	324.0	632.0	4.9	1100	*
10	416882	4540615	2.0	4400.0	3010.0	42.4	1000	*
11	427612	4541628	42.5	5.0	20.0	5.5	1190	*
12	437762	4540928	1.2	394.0	1800.0	1.6	1080	*
13	440401	4542129	48.8	5.0	20.0	4.7	1350	*
14	443978	4541985	21.3	125.0	24.0	4.8	1200	*
15	418720	4537526	36.6	167.9	57.9	5.1	1420	*
16	436005	4544173	85.0	0.9	25.0	5.5		*
17	433858	4550023	44.0	0.1	0.1			*
18	422230	4539785	79.0	0.5	9.0	6.4	1540	
19	433205	4534625	53.0	0.8	9.0	6.1	2000	*
20	434077	4532913	85.0	2.8	21.0	6.9	1650	*
21	434186	4547225	68.2	0.95	21.00		2300	
22	434719	4537875	88.0	88.70			2850	
23	437300	4543729	79.9	0.95	38.00		2300	
24	446101	4541665	73.0	5.63	37.10		2150	
25	419138	4544627	0.8	1923.00	26.60		2050	
26	419403	4546574	0.3				2200	
27	419495	4536868	28.0	34.10	17.40		2150	
28	420799	4531427	26.8	30.40			2750	
29	425803	4532345	29.4	5.40	18.10		2650	
30	428406	4533990	12.4	0.90			2750	
31	429684	4537598	0.5	3539.90	35.00		1900	
32	431018	4540934	65.4	22.40	18.70		1850	
33	431688	4532096	10.8	466.20	61.90		2400	
34	418130	4545690	5.1	1981.0	2835.0		1718	
35	420127	4546737	2.0	2025.0	3849.0		745	
36	412459	4543834	10.7	3300.0	1192.0		765	
37	426215	4549340	3.9	599.0	2405.0		1228	
38	420860	4545410	51.3	13.2	18.0	6.2	1720	*

ID	X	Y	NO ₃	Mn	Fe	As	F	Mean value
39	435309	4546496	12.3	166.0	1800.0	0.4	390	
40	435409	4544104	96.9	10.0	325.0	5.0	1310	
41	432857	4545822	5.3	2390.0	9.0	12.0	1490	
42	447072	4541758	55.3	6.0	185.0	1.0	2020	
43	445415	4543295	3.3	3879.0	32.0	9.0	1540	
44	439709	4541301	1.7	45.0	586.0	0.4	590	
45	441790	4544576	55.7	0.8	9.0	0.4	1340	
46	437857	4550379	17.1	5.0	9.0	2.0	1380	
47	439717	4547643	62.8	0.8	9.0	3.0	1100	
48	431215	4539284	138.0	5.0	63.0	0.4	1310	
49	420639	4544204	5.9	1106.0	2491.0	8.0	3260	
50	423448	4545036	10.7	253.0	4812.0	3.0	720	
51	440333	4546374	58.0	5.0	16.0	4.0	1770	*
52	443632	4543194	73.0	1.0	20.0	2.0	1450	*
53	424921	4543183	5.9	2140.0	190.0	1.0	1170	*
54	424408	4543071	43.0	20.6	5.0	2.5	1360	*
55	437119	4542769	89.0	6.0	55.0	3.3	1780	*
56	450300	4542300	60.0	9.1	9.9	0.3	1390	*
57	437150	4541963	110.0	6.0	10.0	1.3	2400	*
58	433709	4541607	46.0	9.3	230.0	4.0	1770	*
59	456266	4541575	120.0	6.4	270.0	3.8	1090	*
60	453227	4541288	68.0	5.0	20.0	3.1	1070	*
61	440653	4540523	49.0	35.0	60.0	38.0	1320	*
62	432595	4540413	64.0	5.0	57.0	2.0	1260	*
63	446328	4540142	52.0	5.9	50.0	5.0	1630	*
64	442887	4539783	57.7	3.0	31.5	1.2	2200	*
65	436265	4539268	27.6	1.0	35.0	0.7	2750	*
66	439029	4538842	148.1	133.0	7.0	6.4	1040	*
67	424654	4538279	44.6	5.0	20.0	3.6	1370	*
68	442016	4536598	72.9	166.0	80.0	2.7	1140	*
69	425783	4536384	18.5	1.0	26.0	3.7	2200	*
70	435813	4536231	2.3	5.0	9.0	0.4	2900	*
71	425585	4535377	48.9	280.0	1200.0	8.0	1530	*
72	418252	4534769	30.0	5.0	54.0	0.8	2060	*
73	423509	4533326	34.8	1.0	20.0	0.4	1770	*
74	420287	4530650	22.5	1.0	20.0	4.5	3190	*
75	418877	4528989	5.5	30.0	20.0	0.4	300	*
76	433320	4533593	83.2	3.7	106.7	2.6	1980	*
77	418709	4537992	9.8	18.6	11.0	3.0	1310	*
78	446951	4545345	73.0	5.0	12.0	1.8	1940	*
79	430945	4533057	33.3	5.2	29.0	0.6	1660	*
80	428698	4545570	1.7	1780.0	7232.0	12.0	940	

ID	X	Y	NO ₃	Mn	Fe	As	F	Mean value
81	429344	4546804	5.2	1075.0	70.0	0.4	1100	
82	425739	4545357	1.4	2911.0	7428.0	5.0	830	
83	426562	4549432	50.6	47.0	50.0	1.0	1300	
84	426318	4549398	63.5	5.0	21.0	9.0	1370	
85	417879	4536204	21.3	6.5	9.0	3.2	1500	
86	417776	4536448	38.0	4.0	9.0	5.0	1250	
87	417961	4536641	44.2	3.0	9.0	3.5	1260	
88	417793	4537013	46.8	6.5	9.0	4.8	1300	
89	418683	4536882	52.5	41.0	9.0	4.6	1250	
90	418630	4536536	38.5	13.0	9.0	2.5	1420	
91	418781	4536283	76.5	4.0	9.0	4.6	1420	
92	419089	4535720	49.5	4.0	9.0	3.5	1380	
93	419121	4534985	44.8	4.0	9.0	2.2	1570	
94	417082	4536869	6.1	4.0	9.0	2.3	1430	
95	417583	4535989	14.7	5396.0	9.0	1.8	370	
96	418173	4537155	37.4	248.0	9.0	4.7	1360	
97	418082	4536275	42.7	3744.0	9.0	1.4	1450	
98	416914	4535728	11.5	4618.0	9.0	9.5	3800	
99	416920	4535467	18.6	348.0	9.0	6.2	3800	
100	418064	4535925	1.3	565.0	9.0	4.7	2400	
101	418304	4536022	22.2	34.0	9.0	3.6	2000	
102	418196	4536351	32.8	36.0	9.0	2.1	1600	
103	417270	4535749	0.0	6412.0	97.0	7.8	2860	
104	417271	4535743	61.6	10.0		9.0	1300	
105	417295	4535646	61.3	16.0		9.0	1100	
106	435367	4542680	0.6	50.0	2710.0	16.0	860	
107	434618	4542440	101.0	9.0	66.0	20.0	1200	
108	435339	4542156	69.2	6.0	90.0	112.0	2100	
109	435128	4542035	148.0	50.0	1590.0	52.0	1800	
110	435211	4542535	65.3	4.9		8.0	1610	
111	425830	4534783	30.5	40.0	120.0	0.4	1200	
112	428971	4535677	44.1	0.8	9.0	2.0	1300	
113	429448	4536721	10.7	0.8	9.0	5.0	1500	
114	424840	4536366	54.9	0.8	9.0	4.0	1300	
115	425265	4534481	31.1	0.8	9.0	2.0	1500	
116	425991	4534535	34.8	0.8	9.0	2.0	1600	
117	428065	4536303	11.5	30.0	9.0	2.0	1500	
118	425974	4535183	31.7	0.8	9.0	2.0	1500	
119	428323	4536362	2.0	0.8	9.0	1.0	1400	
120	428651	4536421	10.4	55.0	39.0	4.0	1600	
121	423936	4534772	26.3	0.8	9.0	4.0	1600	
122	428205	4536240	59.8	0.8	9.0	2.0	1100	

ID	X	Y	NO ₃	Mn	Fe	As	F	Mean value
123	418187	4535352	42.0	0.8	9.0	2.0	1500	
124	419557	4534915	45.6	6.0	338.0	6.0	1600	
125	424512	4537013	59.5	0.8	9.0	4.0	1100	
126	422659	4540142	80.9	0.8	9.0	0.4	1300	
127	422872	4540365	77.3	0.8	9.0	3.0	1200	
128	421963	4541444	77.0	0.8	9.0	0.4	1300	
129	444691	4538253	4.9	1.2	153.0		1700	