

Background contaminants values in groundwater: methodological analysis in the case study of Turin plain (NW Italy)



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Short note

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ABSTRACT

Background Values (BVs) of diffuse pollutants in groundwater represent a very important information for the correct comprehension of contaminant phenomena and constitute an operative tool for local authorities.

The aim of the study is to highlight the Background Values (BVs) differences between the use of local or regional data in the same sector in the Piedmont plain shallow aquifer considering different chemical parameters. More specifically, chlorinated solvents and nickel were considered at a local and provincial scale in the Metropolitan City of Turin. The concentrations data of the chemicals derived from the Regional Monitoring network (RMRAS) for the Metropolitan City of Turin and from local analyzes of Regional Agency for Environmental Protection (ARPA Piemonte) in the local site.

The use of the RMRAS monitoring points was resulted inappropriate to define BVs in groundwater due to the low density of monitoring wells. On the contrary, the analyzes in the local study area made it possible to understand and characterize correctly numerous specific aspects, recognizing the diffuse pollution and identifying new potential punctual contamination.

In conclusion, the study made it possible to define the BVs in groundwater at a local scale and to propose possible improvements of analysis methodology.

KEY-WORDS: background values, diffuse pollution, chlorinated solvents, nickel.

INTRODUCTION

Background Values (BVs) of diffuse pollutants in groundwater are important for understanding contamination phenomena, and are indicated by the normatives as remediation objectives.

According to National Guideline 174/18 for BVs definition (SNPA, 2018), the “Natural” BVs (NBVs) indicate the distribution

in groundwater derived from natural processes with possible anthropic components that are not detectable. The “Anthropic” BVs (ABVs) correspond to the distribution of pollutants derived from anthropic sources in groundwater. *Diffuse contamination* is considered contamination determined by diffuse sources and not attributable to a single origin, while *diffuse anthropic sources* correspond to anthropic sources for which it is not possible to discriminate the contribution of individual sources, e.g., vehicular traffic, agriculture, urban centres, and industrial emissions.

The problems connected to the evaluation of the BVs of diffuse contamination in groundwater were evidenced in the 1980s, when the EPA (U.S. Environmental Protection Agency) (U.S. EPA 1989) set up the first methodologies to solve these problems. Subsequent studies conducted by various entities (U.S. EPA, 2000, 2013; Battelle Memorial Institute, 2004) integrated and updated these methodologies, enhancing the knowledge of the problem.

In the European context, the BRIDGE methodology (Muller et al., 2006) established a basic community guideline applicable in different European countries according to the level of knowledge. A valid reference is represented by the “Derivation of natural background levels and threshold values for groundwater bodies in the Upper Rhone Valley (France, Switzerland and Germany)” (Wendland et al., 2008), which faces the problem of investigating large and heterogeneous sectors of a specific territory. The Irish experience (Tedd et al., 2017) was interesting and highly detailed on numerous chemical parameters.

At the Italian national level, an important study is represented by the *Plumes Project* (2016), relating to the diffuse contamination of chlorinated solvents in groundwater; furthermore, several works investigated metals and NBVs in the Emilia Romagna Region

(Rotiroti et al., 2014; ARPAE Emilia Romagna, 2016) and the diffuse contamination of organo-halogenates in the Tuscany Region (Menichetti & Doni, 2017).

In the Piedmont context, a smaller number of studies investigated this issue, obtaining partial and not exhaustive results. In particular, the “Project on pollution from diffuse sources: study of some sample areas aiming to prepare regional intervention plans” (ARPA Piemonte, 2005) involved the Turin and Vercelli plains sectors, investigating the diffusion of various parameters through the use of the Regional Monitoring System.

In 2012, two attempts were carried out by ARPA Piemonte (2012) and Destefanis (2012) on heavy metal content, while the BVs of chlorinated solvents in the Turin and Biella areas were defined by the regional agency. Sacchi et al. (2021) dealt with the determination of NBVs of heavy metals in areas with low concentrations.

However, local-scale studies performed in the Piedmont Region did not consider groundwater, investigating only the soil matrix.

These studies have practical importance for professionals and local authorities in the contamination context. For these reasons, it

is essential to understand whether monitoring groundwater network data, which constitute the largest chemical analysis database, can be used to define reliable BVs in groundwater.

The aim of the study is to highlight the BVs differences between applications in which local data is used versus applications in which regional data is used in the same sector. This comparison of the two results will define whether the regional data can be exhaustive and sufficient for a correct BV definition.

The study is focused on the assessment of diffuse contamination BVs in the shallow groundwater of chlorinated solvents and nickel at the local site (Turin City along the Sangone River) and provincial site (plain sector of the Metropolitan City of Turin) (Fig. 1).

STUDY AREAS

The study areas, presented in the following, are located in the Piedmont Region in the Western sector of the Po Plain (Northern Italy).

The plain, which is part of the Turin Metropolitan City District and extends 1550 km², is located between the Alpine relief and the

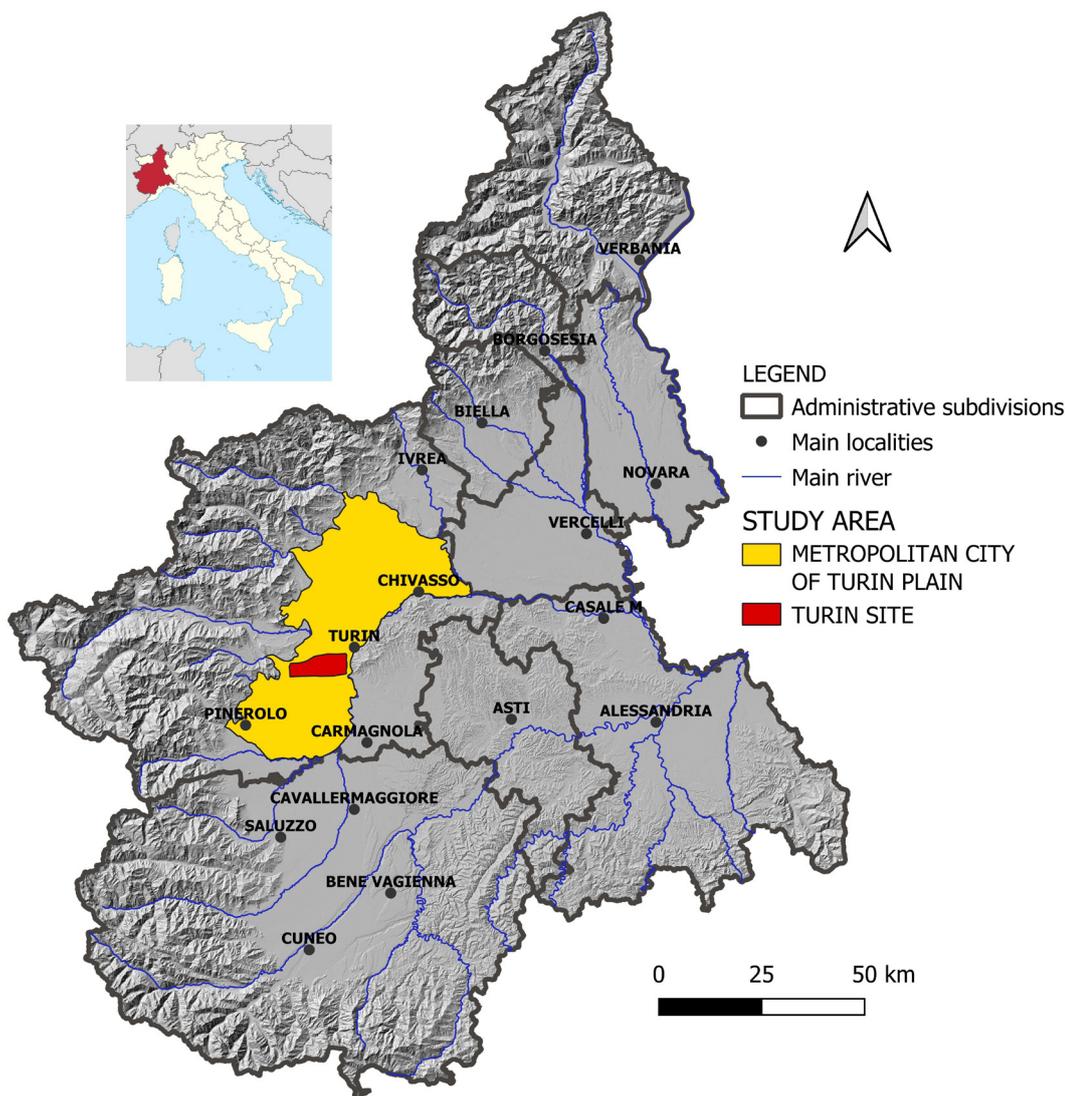


Fig. 1 - Investigated study areas.

Turin hills and is characterized by Pleistocene fluvial-fluvioglacial deposits consisting of sandy gravel levels that are 30-50 meters thick (Balestro et al., 2009, Carraro et al., 1969).

The shallow aquifer flows in the W–E direction, is governed by the Po River, and is characterized by an average water table level that swings from 5 to 50 meters from the surface (De Luca et al., 2020).

The local-scale site of Turin occupies an area of 62 km², including the municipalities present along the Sangone River, and shows the same characteristics as the provincial site (Benenati, 2014) (Fig. 2).

The chlorinated solvents present in the areas represent numerous compounds derived from aliphatic or cyclic hydrocarbons (Bortolami et al., 1988). The most widespread ones are tetrachloroethylene (perchloroethylene - PCE), chloroform (trichloromethane), trichloroethylene (TCE), trichloroethane, and carbon tetrachloride. They behave like DNAPL, forming a nonaqueous liquid phase denser than water and tending to migrate downwards, showing high mobility and low degradability (Feenstra et al., 1996).

The natural metal anomalies in groundwater are linked to the aquifer deposit composition and to water–rock interaction

processes. In the Turin Metropolitan City plain, there exists an area characterized by high concentrations of nickel. The natural source is to be found in deposits derived from the ophiolites of the Lanzo Massif characterized by an abundance of ferromagnesian minerals (Carraro et al., 1969). In this sector, the concentrations exceed the CSC (20 µg/L) at several points only for nickel (Destefanis, 2012).

Furthermore, anthropic pressure characterized the area due to the manufacturing activities of metalworking, mainly related to the automotive industry (ARPA Piemonte, 2013).

Materials and methods

The analysis of BVs determination methodology issued by SNPA (“Linea Guida per la determinazione dei valori di fondo per i suoli e per le acque sotterranee, 174/18”) was applied at the Turin site, analysing chlorinated solvents and nickel as contaminants in groundwater. Different conditions were imposed, such as dataset and area subdivisions. Unconfined shallow aquifers were preferred to deep aquifers due to the higher amount of available data and environmental issues.

The investigated parameters (chlorinated solvents and nickel) were chosen with the aim of analysing the BV determination

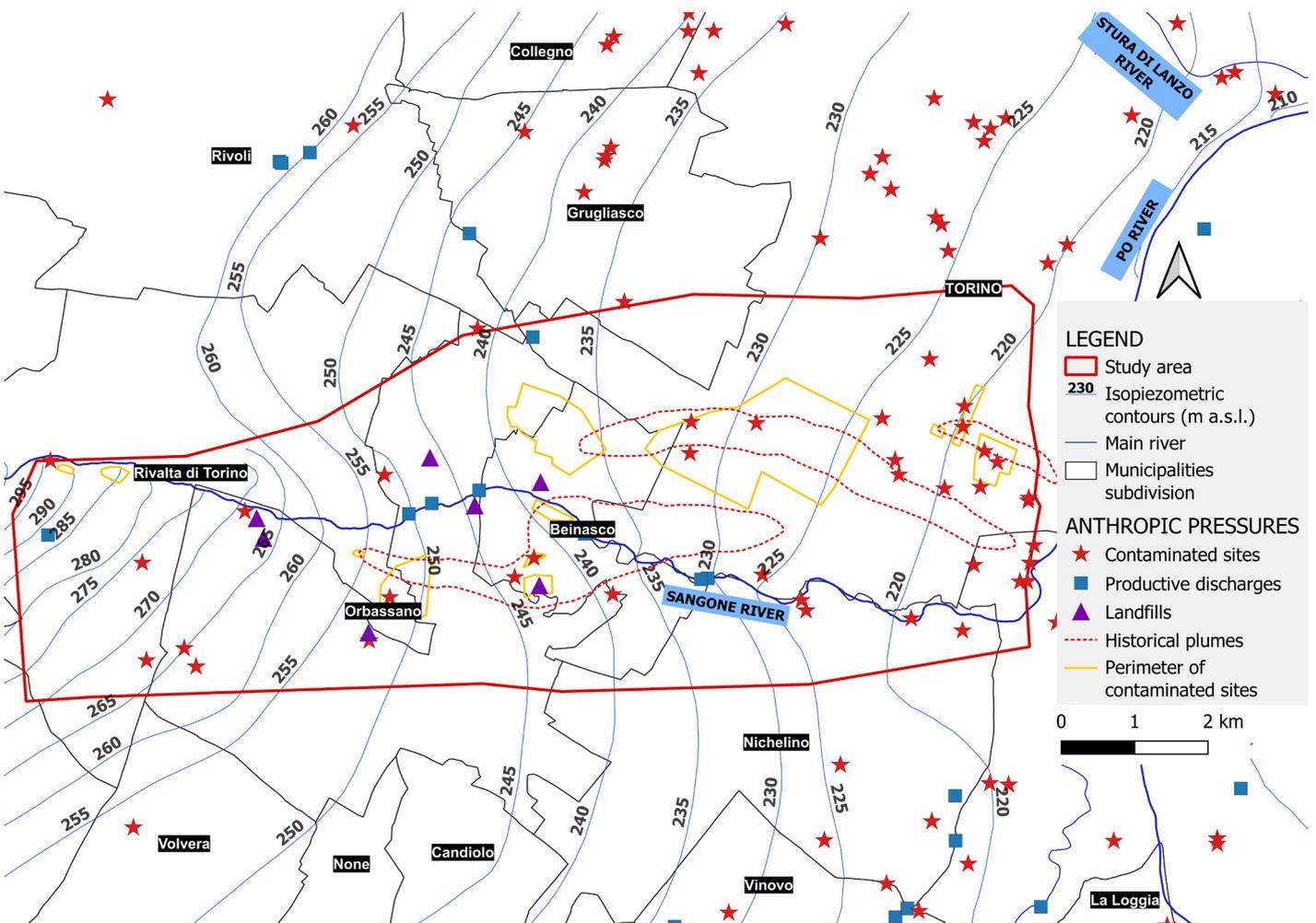


Fig. 2 - Isopiezometric contours and anthropic pressures existing in the Turin site, respectively from De Luca et. (2020) and Regione Piemonte. (https://www.geoportale.piemonte.it/geonetwork/srv/ita/catalog.search#/metadata/r_piemon:1fa04620-c1d6-4512-8434-5cf7dd5b301b).

methodology for substances of exclusively anthropic origin (chlorinated solvents ABVs) and for substances of dual origin, that is, natural and anthropic (nickel NBVs). The chlorinated solvent data of the ARPA Piemonte sampling carried out in 2019 (ARPA Piemonte, 2020) for the Turin site (71 monitoring points) were processed.

In the provincial case study, the PCE and Nickel Regional Groundwater Monitoring Network data (RMRAS) were processed using 45 monitoring points and collecting the data observed in the last 5 and 10 years (2009-2018) (Fig. 3). These points have two annual observations in the greater completeness conditions. For the nickel parameter, the points with zinc and lead concentrations, which can be associated with anthropic pressures, were excluded. The annual averages of each year for every monitoring point were first calculated, and then the average of the annual averages was used directly in the BV procedure.

The potential anomalous “intra-point” data processing (data series of a single monitoring point) was carried out, evaluating the presence of data that strongly differs one point from other points by calculating the “RSD%”, which corresponds to the percentage ratio between the standard deviation and the mean.

An initial collection of the hydrogeological-geological available information deemed useful as well as the current and previous data concerning the characterization of the contamination level was carried out, followed by the methodological path for BV determination.

The Guideline proposes a methodological path for BV determination, describing the organization and processing of data, BV determination and results management, briefly reported below.

A first aspect to take into consideration is the minimum number of observations necessary to ensure the statistical significance of the determined value, between 10 and 30.

For the *treatment of Non Detected* (ND), which can affect the statistical proceedings, “simple substitution” has been applied.

During *outlier identification and treatment* (values that are configured as anomalies), it is essential to identify a physical meaning to the data. Outlier identification was performed graphically (box plot, Normal QQ-plot) and through statistical tests (Rosner, Dixon, Huber).

The *identification of multiple populations* and their physical connotation are the key elements to decide which observations must be excluded and which observations describe the population of interest. Among the graphical methods, the “probability plot”, where the deviations from linearity or continuity identify anomalous observations or observations afferent to multiple populations, was used.

For the processing and analysis of environmental data, it is necessary to verify the assimilability of a data distribution to a distribution model. The recommended and used statistical tests have been the Shapiro-Wilk test and Lilliefors test.

With *time data processing*, it is necessary to verify the time stationarity of the observed concentrations. The Mann-Kendall test and Theil-Sen estimator were used for the time series analysis. Multivariate analysis was not carried out because chemical-physical analyses were not obtained.

In this study, the BVs were identified through statistical parameters (percentiles, maximum value, Upper Tolerance Limit (UTL), Upper Prediction Limit (UPL), and Upper Confidence Limit (UCL)). Once defined, it is necessary to compare them with the punctual observations; if the latter are higher than the BVs, they may correspond to potential punctual contamination. The statistical analysis, described above, was carried out using

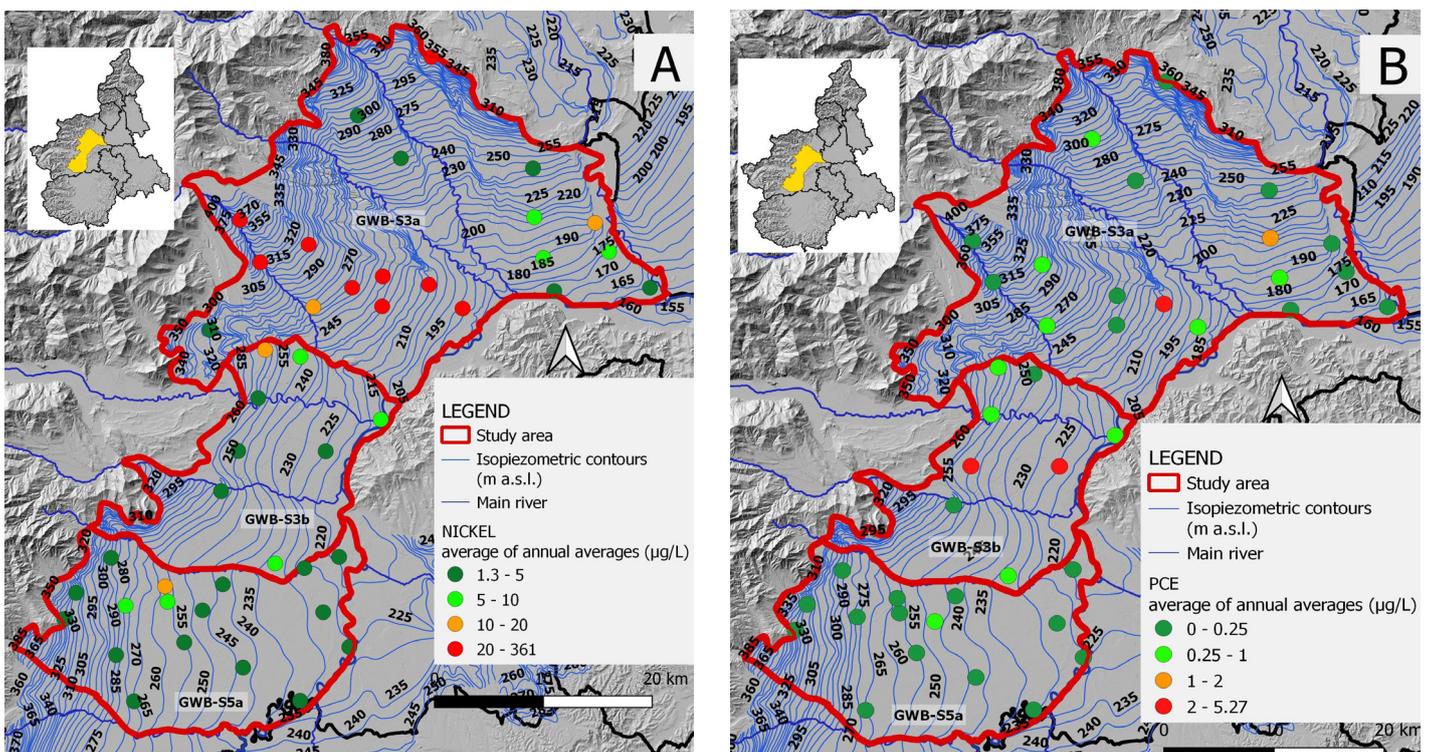


Fig. 3 - Distribution of nickel (A) and PCE (B) in the Turin Metropolitan City plain.

ProUCL 5.1 software (U.S. EPA 2013) and the electronic sheet present in the Guideline.

RESULTS AND DISCUSSION

Different results, particularities connected to the applied procedure and the areas emerged.

Metropolitan City of Turin site

The synthesis of the numerical results defined in the different provincial case studies is summarized in Fig. 4.

The results arising from the investigated case studies highlighted some procedural criticalities about the BV definition using the Regional Groundwater Network (RMRAS). These critical issues are as follows:

- use of a monitoring network with few points, widely spaced (several km) and therefore not sufficient as a control network of diffuse pollution, mainly for a nonhomogeneous areal distribution;
- the presence of portions of territory without contamination that can influence, in the processing data, adjacent sectors that are truly contaminated;
- large study areas, heterogeneous from the hydrogeological and chemical points of view.

The areal characterization was not carried out considering the BVs but rather by the reference values imposed, this is due to the fact that each delimited sub-area shows a few points.

The processing of time data did not involve specific issues; it only regards the identification of few non stationarity points as well as the control and confirmation of the substantial equivalence between time series of 5 or 10 years' analysis.

Turin Local site

PCE was found at 69/71 monitoring points, while for the other chlorinated solvents, none were "totally absent" (Fig. 5).

The chlorinated solvents show a different spatial distribution with the highest contamination level within the historical plumes, connected to the PCE degradation; this suggests the existence of PCE sources and not of individual compounds.

The comparison between concentrations and CSCs shows PCE with the highest number of exceedances (52), followed by Dichloroethylene (43) and Trichloromethane (28) (Table 1).

Difficulties emerged in the application of the statistical analysis for chlorinated solvents different from PCE due to the low concentrations ($<0.5 \mu\text{g/L}$). For the solvent summation, an ABV (95% UTL with 95% coverage) equal to $2.4 \mu\text{g/L}$ was obtained, proving to be conceptually invalid, being numerically lower than the ABV referred to as PCE ($9.1 \mu\text{g/L}$). This situation highlights a weak point in the identification of multiple population phases.

The study of the local sector showed some problems:

- BV definition exclusively using the sampling data carried out in 2019 constitutes an indication of diffuse contamination for this specific time moment and is potentially unreliable for different time periods;
- Difficulty in the diffuse contamination treatment for portions of territory with verified and uncertified punctual sources

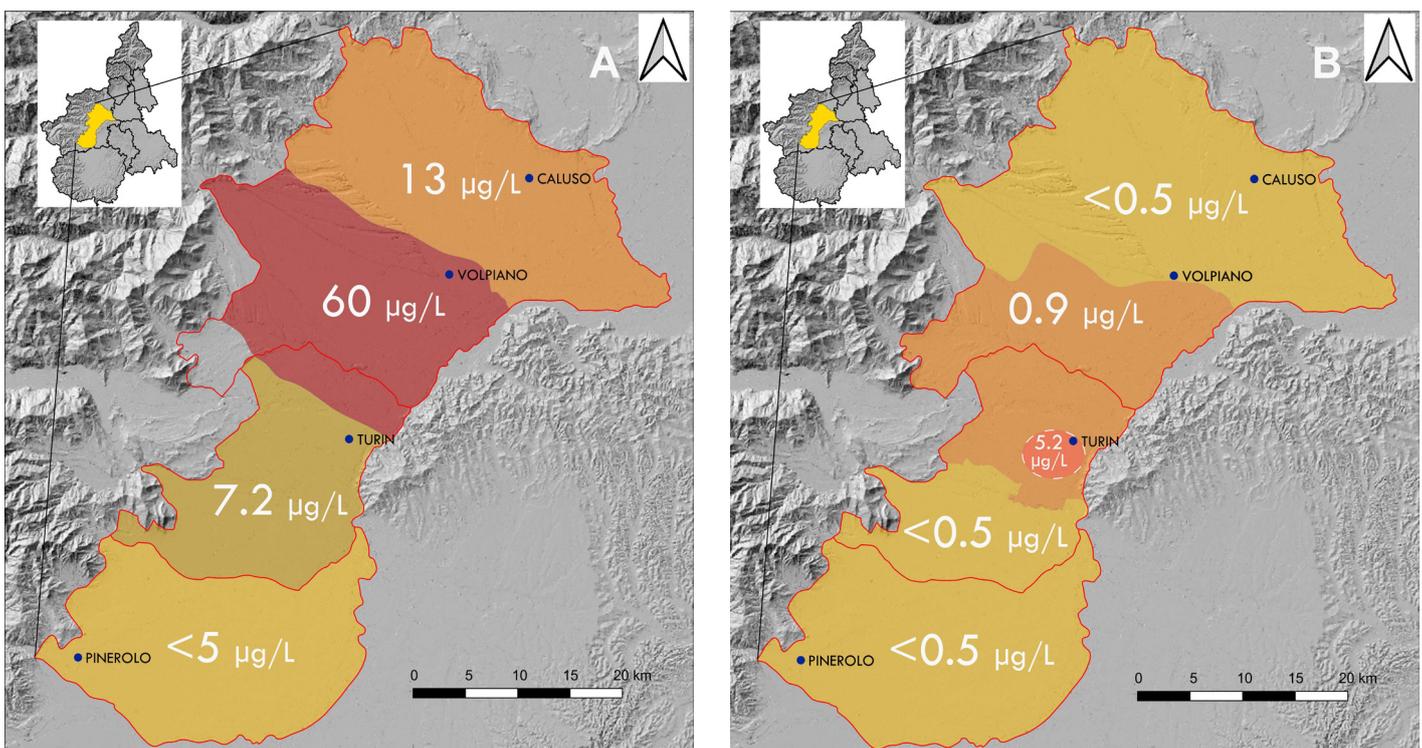


Fig. 4 - BVs determined for nickel (A) and PCE (B).

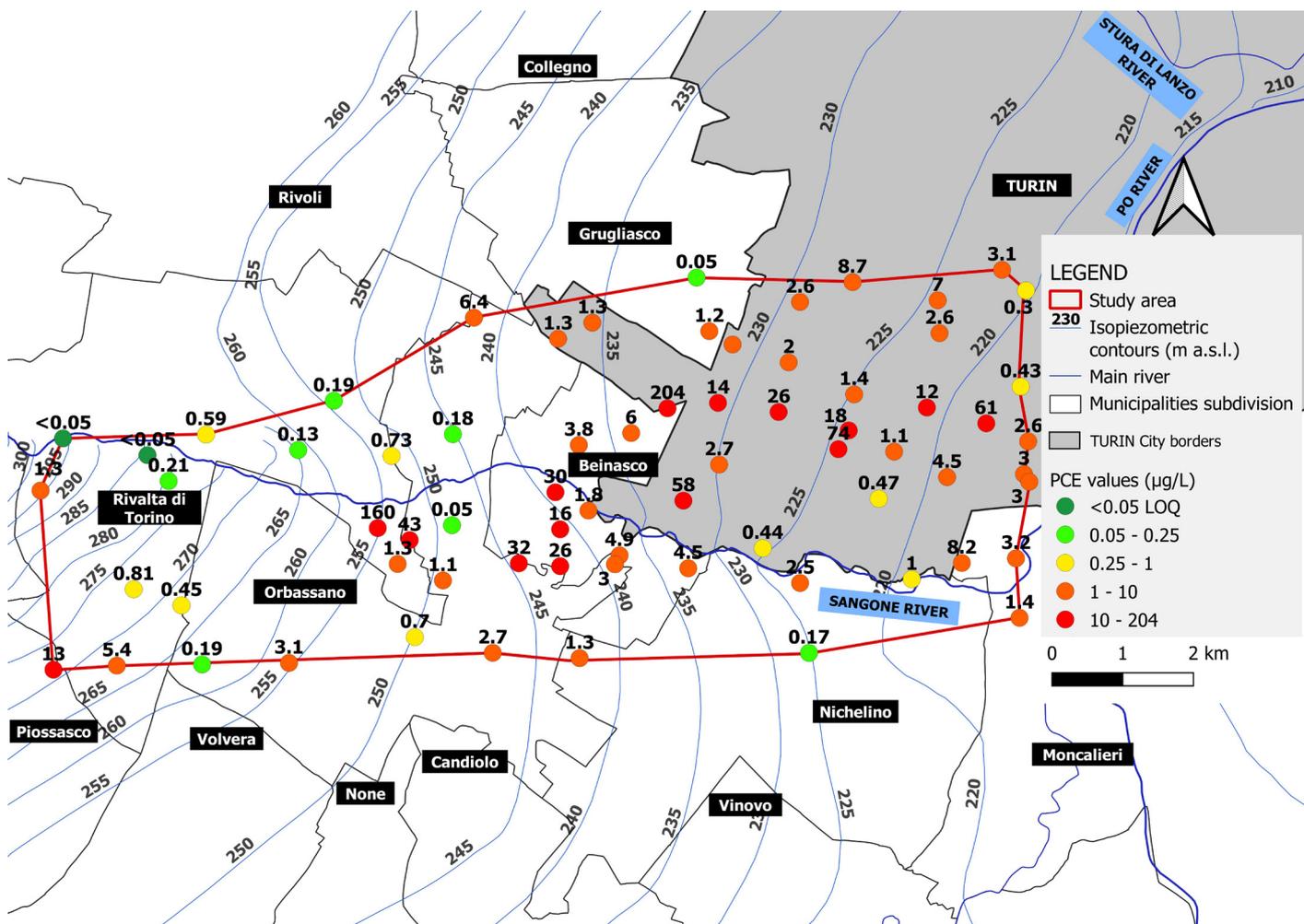


Fig. 5 - PCE distribution in the Turin site.

Table 1 - BVs and CSC of the chlorinated solvents in the Turin site.

	PCE	TRICHLOROETHYLENE	TRICHLOROMETHANE	1,1-DICHLOROETHENE	1,2- DICHLOROETHENE
BVs	9.1	0.45	0.61	0.14	0.96
CSC	1.1	1.5	0.15	0.05	60

connected to the identification of a possible correlation between punctual contamination and observed concentrations.

In the statistical analysis, a correlation emerged between the outliers and the data of the second population identified (numerically higher values), suggesting a punctual contamination origin. The first population data (numerically smaller values) are linkable to diffuse contamination and, therefore, used in the subsequent statistical elaboration.

Comparison between local and provincial sites

Different results emerged linked to a different data availability in relation to the provincial and local case studies present in the Turin area. The reference value choice, which corresponds to the value to be imposed if the dataset requirements for applying the statistical procedure are not described, is not indicated with

sufficient attention by the Guideline, given the dual possibility of choosing the higher punctual observation or the higher mean value.

The provincial-scale study seems to be insufficient to define the ABVs, opting for the imposition of a reference value corresponding to the maximum value of the average of the annual averages, while on a local scale, it has been possible to obtain an ABV of 9.1 µg/L.

CONCLUSIONS

BV determination for the groundwater matrix includes a series of unique issues for this matrix. The characterization of diffuse pollution requires a high level of knowledge to discriminate this phenomenon from punctual pollution. This type of study is essential for the correct comprehension and management of existing contaminations.

The previous contamination level of the investigated areas has been defined. The subsequent procedure application in different contexts and conditions allowed us to verify their robustness and to obtain these values.

The studied areas are represented by a similar industrial past that saw the proliferation of activities that employed chlorinated solvents with a consequent presence of environmental issues linked to incorrect management.

The study of larger sectors is possible; however, numerous monitoring points are needed, as is an optimal geological and hydrogeological characterization. For these reasons, the use of the regional monitoring network does not appear sufficient for this type of study, deeming additional necessary points.

Regarding the BV determination methodology, the ability of the statistical analysis to distinguish the concentrations affiliated or not affiliated with the punctual contamination must be highlighted. Furthermore, any differences in using or not using the monitoring points correlated to the contaminated sites can be evidenced; however, it is necessary and mandatory to exclude this type of concentrations from the statistical processing.

BV determination based on a single sampling campaign makes it possible to refer this indicator to a specific moment; therefore, the transposition and use of this value for different periods appears to be invalid. Some difficulties emerged in the procedure application for concentrations lower than 0.5 µg/L and, comparing the PCE case studies, different values that were related to the different data availability were observed.

Although the identified concentrations are low, a PCE “large-scale diffuse source” is not present due to the concentrations below the LOQ at several monitoring points. Furthermore, every identified concentration higher than the LOQ can be correlated to punctual sources being derived exclusively from anthropic origin, considering the inexistent impact of diffuse sources.

The BVs reveal 3 previously unknown punctual contaminations not linkable to the diffuse origin.

In conclusion, the BVs defined are considered indicative, keeping these sectors among those that need to be further investigated and revealing that a regional monitoring network not suitable for this type of study.

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