NATURAL BACKGROUND LEVEL OF HEAVY METALS IN PIEDMONT GROUNDWATER

ENRICO DESTEFANIS
Dipartimento di Scienze della Terra, Università di Torino, Via Valperga Caluso 35, 10125 Torino, Italy

INTRODUCTION

Heavy metals are naturally present in minerals; many of them, in small amounts, are essential for the biology of living organisms, including human beings. However, their use in industrial cycle, that man developed greatly since XIX century, provoked their anomalous diffusion in many environmental matrices (like oceanic water, continental pedosphere, and hydrosphere) causing an increase of their intake, at different concentration, in the food chain. The growing awareness of their harmful effects, and the consequent damage to health, has prompted several competent organizations to adopt regulations in which the maximum concentrations of these elements are specified, depending on the environmental matrix and the use of the latter.

The aim of this study is to define the so-called "background concentrations" of some heavy metals (Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn) in groundwater, limiting the analysis to the shallow groundwater of the Piedmont Region, little (or not) confined.

This work starts with a general discussion about some natural and industrial sources of selected chemical species and their general behaviour in solution, thus defining the likelihood of their presence and the conditions for their permanence in natural waters.

The next step was the discussion about the definition of "natural background level", through a retrospective and a comparison of the different meanings attributed to this term, since its introduction (Hawkes & Webb, 1962), until the most recent definitions, (Wendland *et al.*, 2008). The definitions have also been linked with the main European standards (2000/60/CE and 2006/118/CE, Parlamento Europeo e Consiglio, 2000) and National standards (D. Lgs. 152/2006 e D. Lgs. 30/2009, Repubblica Italiana) that introduced the values of natural background and other related variables as tools for understanding and assessing the quality of the environmental status.

MATERIAL AND METHODS

The analysis of the main statistical methods was carried on to determine the natural background value, using, as reference models, those proposed by *i)* the U.S. Environmental Protection Agency (EPA, 2006), *ii)* the model BRIDGE of 2005 (regarding the EU member states), and iii) the Institute for Environmental Protection and Research in Italy (Bartolucci *et al.*, 2009).

The comparison among these models allowed to identify the initial parameters needed for the definition of natural background values, and to start the research phase of the data used to define the conceptual model. In general, this model should include and describe some characteristics, as homogeneous as possible, of the water body; the main features for the models definition are relative either to the physical description of the reservoir and to the peculiarity of the hosted aquifer, as well as to the chemical data related to the dissolved ionic species.

Since the chosen study area (*i.e.*, the Piedmont Po Plain) is characterized by considerable lithological heterogeneity and hosts multiple systems of groundwater circulation, it was not considered suitable to be immediately used as a single set. To obtain correct results for the natural background values, as much as possible relevant to the specific features found, the territory has been divided into twenty hydrogeologically homogeneous areas, taking into account the knowledge acquired in the last decade by means of geological and hydrogeological studies made at the Department of Earth Science of the University of Turin.

Some data relative to various areas and to some ionic species were directly acquired by means of chemical analysis, and other information were acquired from the Monitoring Network of the Piedmont Region, with particular attention to the sampled points of the shallow groundwater relative to the period 2001-2010; in particular, in this work about 8200 analyses obtained from about 620 sampling points were processed (Fig. 1).

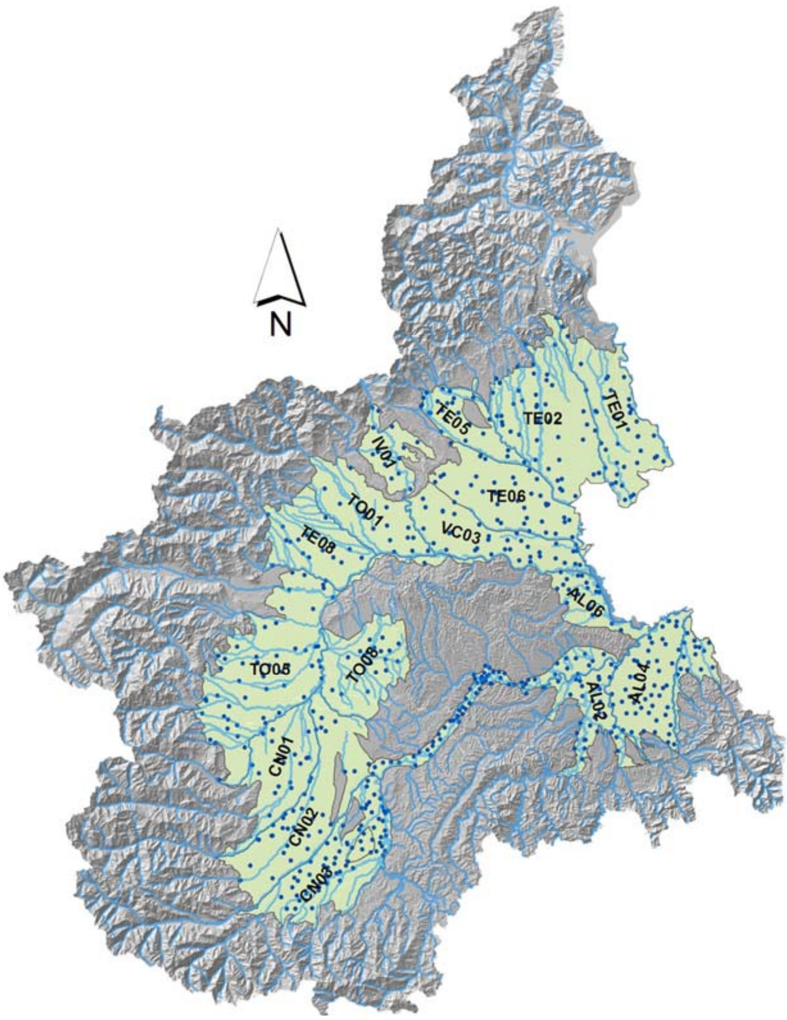

Fig. 1 - Distribution of the sampling points distributed on homogeneous areas.

These information were assigned to homogeneous areas as defined in the previous phase, and were used as different data sets, trying to respect the prescription of the methods cited above. Owing to the large number and diversity of information, concerning not only the presence of heavy metals studied in the shallow aquifer but also in the deep aquifer, and including information such as basic chemistry (major ions), the presence of some organic pollutants and other characteristics of groundwater (depth, *p*H, temperature), a huge database was created; starting from this database, it was possible to obtain smaller data sets appropriately extracted and filtered as required.

The chosen data sets were finally verified with various statistical tests, proposed by different authors (Garret, 1991; Matschullat *et al*., 2000; NAVFAC, 2004), in order to define the suitability of subsequent processing steps and their statistical description. The calculation of the natural background value assumes indeed that data are representative of pristine conditions of the water body; unfortunately, due to the strong anthropization of the investigated areas and to the lack of information relative to the period before the industrial age for the sampling points chosen on the basis of this criterion, this requirement were satisfied through the identification of some values undoubtly related to anthropogenic pollution, and their consequent exclusion from the dataset. For some metals such discrimination was easier because of their industrial origin (lead, copper, zinc); for some others (such as iron, manganese, and nickel), whose presence can be attributed to several different origin, statistical tools were applied for the identification of anomalies and were called outliers.

Another typical feature of the datasets related to trace elements, as the heavy metals studied in this work, is the lack of data relative to many sampling points where the metals concentration, was below the detection limits (DL). Besides the traditional approaches that suggest to assign dummy values to the data (*e.g.*, ½ DL), a statistical approximation was applied for their evaluation, (Regression Order Statistic method - ROS) that, although with caution, allowed us to apply the methods for the determination of natural background values.

At last, natural background values were calculated referring primarily to what is proposed by Wendland *et al*., (2008) who suggests the use of percentiles for the distributions of data. To compare the values obtained in this way, also other methods have been applied, for the "cumulative frequency diagrams" as proposed by Bauer & Bor, (1993, 1995).

We finally observed that the values obtained using the different methods were in pretty good agreement, and they allowed us to define in our region (we believe for the first time in an organized and motivated way) the natural background values in almost all of the homogeneous areas previously identified in this study; we also tried to define the so-called threshold values, as provided by the European directive and Italian law (2006/118/CE and D. Lgs. 30/2009, respectively).

RESULTS

For a more simple use of the data elaborated in this work, maps drawn on the base of calculated natural background values were made, to represent these values in every different area (see for example the map in Fig. 2 showing the background values distribution of nickel).

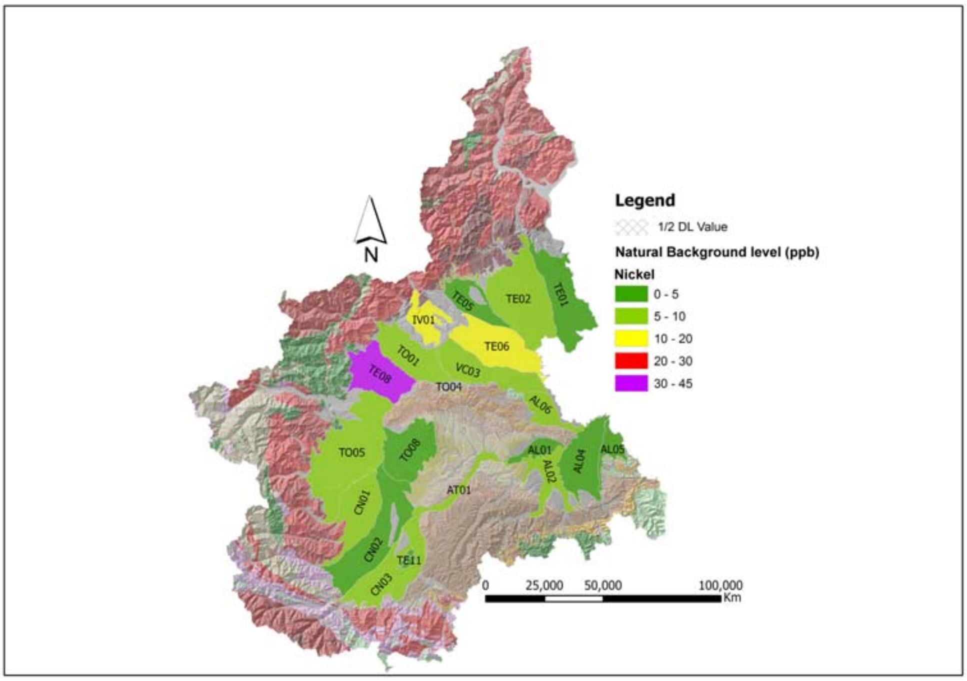

Fig. 2 - Map of natural background level of nickel.

The maps indicates a certain concentration homogeneity for some species, with the exception of iron and manganese; in fact these two transition metals are very widespread in the Piedmont plain soils and are very sensitive to chemical and physical conditions of the water body. Other species, such as cadmium and mercury, are virtually absent in the geological matrices of our region, and their presence, in the study area, is almost exclusively due to anthropogenic inputs.

Maps of exceedances were also made to compare data from the regional monitoring network and the obtained threshold values.

We also applied factor analysis to explain what has been enhanced by processing data; this approach evidenced some correlations existing between different ionic species in many of the identified areas. For example, is very common the occurrence of correlations between the following three couples of elements: Fe-Mn, Ni-Cr and Cu-Zn (Fig. 3).

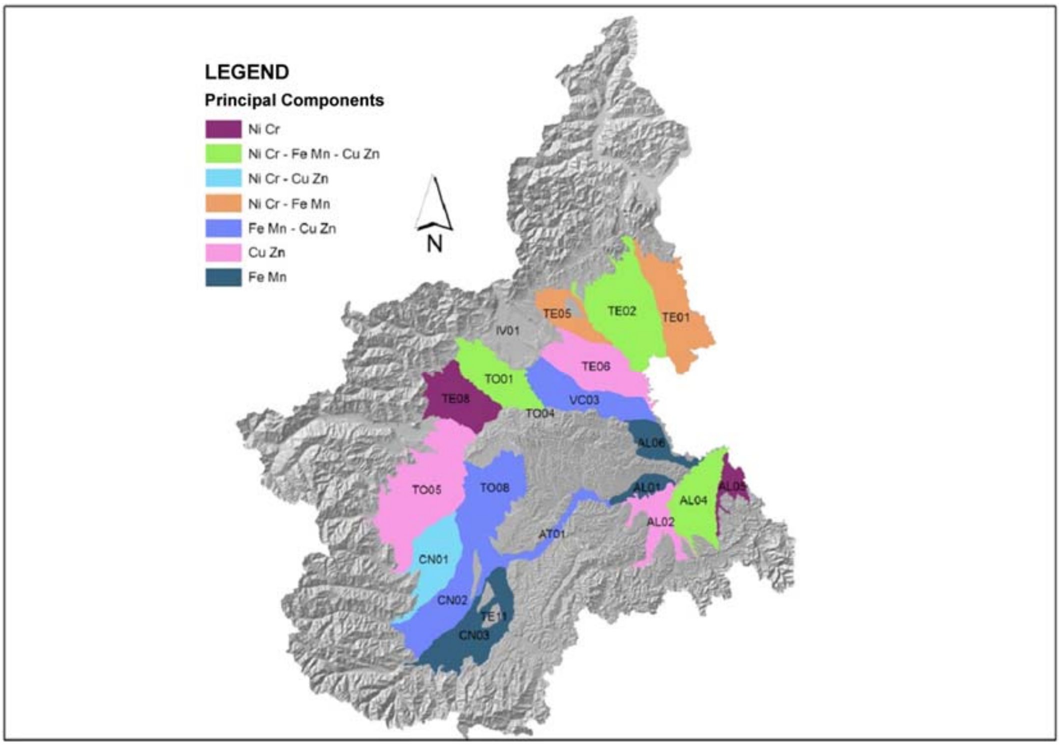

Fig. 3 - Principal components identified with factor analysis.

Due to some peculiarities arising from the definition of background values and factor analysis, two case studies has been chosen (the alluvial fan of the Stura di Lanzo River and the Orba River basin) to confirm what was suggested by the statistical approach. In these localities high concentration of nickel was detected in the water, even in the tap water for human drinking. For this purpose, specific sampling campaigns were carried out, and the samples were analyzed by means of ICP/OES spectrophotometry and voltammetry. The results confirmed the hypothesis already suggested by factor analysis, *i.e.*, the existence of a close correlation between the composition of the supply basins (containing high amount of basic and ultrabasic rocks debris, hosting nickel -bearing femic minerals) and high level of nickel in the waters.

CONCLUSIONS

The realization of this work helped us to apply to the Piedmont Po plain some of the main methods for the definition of natural background levels of heavy metals in groundwater, allowing us to apply and compare different approaches to the problem. Moreover, the obtained results represent the first data of background levels of heavy metals in Piedmont groundwaters. Finally, forecasting the deadlines scheduled for 2015 (2000/60/CE, Parlamento Europeo e Consiglio, 2000), were EU member States should provide parameters values in order to define the environmental quality status, it was possible to test the Piedmont Region groundwater monitoring network as suitable or not suitable for the previously described purposes.

REFERENCES

2000/60/CE (2000): Direttiva 2000/60/CE del Parlamento Europeo e del Consiglio, del 23 ottobre 2000, che istituisce un quadro per l'azione comunitaria in materia di acque (Direttiva "acque"). *G. U.*, **L327**, 1-73.

2006/118/CE (2006): Direttiva 2006/118/CE del Parlamento Europeo e del Consiglio del 12 dicembre 2006 sulla protezione delle acque sotterranee dall'inquinamento e dal deterioramento. *G. U.*, **L372**, 19-31.

Bartolucci, E., Bussettini, 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. ISPRA, Roma, 40 p.

Bauer, I. & Bor, J. (1993): Vertikale Bilanzierung von Schwermetallen in Böden – Kennzeichnung der Empfindlichkeit der Böden gegenüber Schwermetallen unter Berücksichtigung von lithogenem Grundgehalt, pedogener An- und Abreicherung sowie anthropogener Zusatzbelastung, Teil 2. Texte 56, Umweltbundesamt, Berlin.

Bauer, I. & Bor, J. (1995): Lithogene, geogene und anthropogene Schwermetallgehalte von Lößböden an den Beispielen von Cu, Zn, Ni, Pb, Hg und Cd. *Mainzer Geowiss. Mitt*., **24**, 47-70.

D. Lgs. 152/06 (2006): Decreto Legislativo 3 aprile 2006, n. 152. Norme in materia ambientale. Gazz. Uff. n. 88 del 14 aprile 2006, Suppl. Ord. n. 96.

D. Lgs. 30/09 (2009): Decreto Legislativo 16 marzo 2009, n. 30. Attuazione della direttiva 2006/118/CE, relativa alla protezione elle acque sotterranee dall'inquinamento e dal deterioramento. (09G0038). Gazz. Uff. n. 79 del 4 aprile 2009.

EPA (2006): Data Quality Assessment: Statistical Methods for Practitioners - EPA QA/G-9S. U.S. Environmental Protection Agency, Washington, U.S.A., 190 p.

Garrett, R.G. (1991): The management, analysis and display of exploration geochemical data. *In*: "Exploration geochemistry workshop", Geological Survey of Canada, Open File 2390, 9-1–9-41.

Hawkes, H.E. & Webb, J.S. (1962): Geochemistry in mineral exploration. Harper and Row, New York, 415 p.

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

NAVFAC (2004): Guidance for environmental background analysis - Volume III: Groundwater. Engineering Service Center, Port Hueneme, California, 203 p.

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.