



Research papers

Hydrogeochemical characterization and Natural Background Levels in urbanized areas: Milan Metropolitan area (Northern Italy)



Mattia De Caro*, Giovanni B. Crosta, Paolo Frattini

DISAT – Department of Earth and Environmental Sciences, University of Milano Bicocca, Piazza della Scienza, 4, Milan 20126, Italy

ARTICLE INFO

Article history:

Received 23 November 2016
 Received in revised form 30 January 2017
 Accepted 13 February 2017
 Available online 16 February 2017
 This manuscript was handled by Corrado Corradini, Editor-in-Chief, with the assistance of Barbara Mahler, Associate Editor

Keywords:

Natural Background Level
 Groundwater quality status
 Hydrogeochemical modelling
 Urban areas
 Pre-selection
 Component Separation

ABSTRACT

Although aquifers in densely populated and industrialized areas are extremely valuable and sensitive to contamination, an estimate of the groundwater quality status relative to baseline conditions is lacking for many of them. This paper provides a hydrogeochemical characterization of the groundwater in the Milan metropolitan area, one of the most densely populated areas in Europe. First, a conceptual model of the study area based on the analysis of the spatial distribution of natural chemical species and indicator contaminants is presented. The hydrochemical facies of the study area depend on the lithology of catchments drained by the main contributing rivers and on the aquifer settings. The anthropogenic influence on the groundwater quality of superficial aquifers is studied by means of probability plots, concentration versus depth plots and spatial-temporal plots for nitrate, sulfate and chloride. These allow differentiation of contaminated superficial aquifers from deep confined aquifers with baseline water quality. Natural Background Levels (*NBL*) of selected species (Cl, Na, NH₄, SO₄, NO₃, As, Fe, Mn and Zn) are estimated by means of the pre-selection (*PS*) and the component separation (*CS*) statistical approaches. The *NBLs* depend on hydrogeological settings of the study area; sodium, chloride, sulfate and zinc *NBL* values never exceed the environmental water quality standards. *NBL* values of ammonium, iron, arsenic and manganese exceed the environmental water quality standards in the anaerobic portion of the aquifers. On the basis of observations, a set of criteria and precautions are suggested for adoption with both *PS* and *CS* methods in the aquifer characterization of highly urbanized areas.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The European Water Framework Directive (WFD 2000/60/EC) and Groundwater Directive (GWD 2006/118/EC) require Member States to evaluate the status of groundwater bodies against EU-wide quality standards for nitrates and pesticides and threshold values (*TVs*) established by Member States for other compounds. The groundwater *TVs* should be based on (Annex II-part A, GWD 2006/118/EC): the interactions between groundwater and associated aquatic and dependent terrestrial ecosystem, the interference with actual or potential legitimate uses or functions of groundwater, and the hydrogeological characteristics including Natural Background Levels and water balance. In practice, *TVs* are mainly derived by Member States considering standards for water consumption, Natural Background Levels and, in a few cases, environmental water quality standards (Scheidleder, 2012). For instance, Italian *TVs* (D.Lgs. 30/2009) are based on environmental quality standards (D.Lgs. 152/2006) that also correspond to drinking water

standards (D.Lgs. 31/2001). However, when the Natural Background Level of undesirable elements is higher than these quality standards, the *TVs* should correspond to Natural Background Levels. Therefore, a preliminary step for defining the status of groundwater bodies consists in the definition and evaluation of the *NBLs*. The *NBL* or Baseline level is defined as “the range of concentration of a given element, isotope or chemical compound in solution, derived entirely from natural, geological, biological or atmospheric sources, under conditions not perturbed by anthropogenic activity” (Edmunds and Shand, 2009). Groundwaters from aquifers that are part of the active water cycle have been influenced for decades by human activities. Water changes chemistry from the moment water enters the system through rainfall infiltration, river water, or other sources, until it leaves through runoff, evaporation or withdrawal (Vázquez-Suñé et al., 2005). Consequently, superficial aquifers rarely reflect true natural concentration levels, whereas deep aquifers can be free from anthropogenic impacts (Müller et al., 2006). Groundwater status in highly urbanized and farm areas is especially affected by anthropogenic influence due to diffuse pollution from agricultural practices and wastewaters (Appelo and Postma, 1994). This makes

* Corresponding author.

E-mail address: m.decaro@campus.unimib.it (M. De Caro).

difficult to determine whether the observed groundwater condition reflects a natural chemical status according to the WFD directive (Wendland et al., 2005).

Several approaches are used to derive *NBL* (Matschullat et al., 2000). Some parametric approaches use statistics under the assumption that a natural element distribution is described via a normal or lognormal distribution (Reimann and Filzmoser, 2000). Different approaches, such as the mode analysis (Carral et al., 1995), the 4 σ -outlier test and the iterative 2 σ -technique, aim to identify positive anomalies (i.e. anthropogenic influences) from the normal data distribution. They evaluate the *NBL* as different confidence intervals of the normal distribution (e.g. 95% confidence interval, mean \pm 2 σ). Other statistical methods, such as the Component Separation (CS) method (Wendland et al., 2005), involve the separation of the distribution function of a given element into a lognormal and a normal distribution (Ahrens, 1957) related to natural and anthropogenic concentrations, respectively. Finally, different non-parametric approaches, such as the Relative cumulative frequency analysis (Bauer and Bor, 1995) or the Pre-Selection (PS) approach (Müller et al., 2006), are available. The latter separates the natural component by excluding anthropogenic data from the dataset by using some indicator chemical species such as NO₃, Cl or SO₄ (Müller et al., 2006; Hinsby et al., 2008). The natural background is determined as a fixed percentile value (e.g. 90th or 97th) of the data distribution (Müller et al., 2006). Recently, the EU BRIDGE research project (*Background cRiteria for the IDentification of Groundwater thrEsholds*, 2006) proposed different methods to derive *NBLs* considering the degree of knowledge about geology and availability of chemical data. In particular, it suggested the use of PS or CS approaches based on knowledge about geochemical processes and abundance of monitoring data (Müller et al., 2006).

The aim of this study is to analyse the hydrogeochemistry of groundwater in the Milan metropolitan area (Lombardy, Italy) and to estimate the *NBLs* of selected species using PS and CS approaches. Although numerous studies regarding the geological and hydrogeological characterization of the area are available (Lombardia and Eni Division Agip, 2002; Piccin, 2009; Francani et al., 2010; Garzanti et al., 2011), a comprehensive hydrogeochemical characterization is still lacking. Several local studies examined isotopic composition of groundwater bodies (Olivero et al., 1987; Pilla et al., 2006; Conti et al., 2000), nitrate and arsenic occurrence (Pilla et al., 2006; Arduini et al., 2008; Masetti et al., 2008; Rotiroti et al., 2014) and contamination risk (ARPA Lombardia 2012, 2013). Additionally, several studies about the estimate of pollutant threshold values for groundwater bodies in large urban area exist (Edmunds et al., 2003; Wendland et al., 2005; Gałuszka, 2007; Griffioen et al., 2008; Tueros et al., 2009; Gemitzi, 2012; Rodríguez et al., 2006; Rotiroti et al., 2014; Preziosi et al., 2010, 2014; Rotiroti et al., 2015; Ducci and Sellerino, 2012; Ducci et al., 2016) showing the importance of evaluating the groundwater quality status to baseline conditions in extremely valuable areas. The approach presented in this paper includes: (i) a geochemical characterization of the study area based on mapping of naturally controlled species, a detailed mapping of the indicator contaminants pattern, and the identification of contamination trends through space and time; (ii) a simple statistical method (PS) for determining *NBLs* over large regions; and (iii) a statistical method (CS) to evaluate *NBLs* for detailed scale problems and to identify the relationship between anthropogenic inputs and land uses. The application of PS and CS approaches to a very large dataset, in a complex environmental framework (with extremely complex patterns of urban, industrial and farming areas), and the comparison of the results obtained for several groundwater bodies are among the novel elements of this study. The adoption of the different methods is critically reviewed in the discussion

and the use of the results for the identification of the most probable source of contamination is suggested.

1.1. Study area

The Milan metropolitan area (Fig. 1) is located in the Po Plain (Lombardy region, northern Italy) and covers 1575 km² (population density: 2036 inhabitants/km²) of the study area (4300 km²). The entire study area hosts about 8.5% of the whole Italian population (5,181,192 people, 3,208,509 of which in the Milan province, ISTAT, 2014). The area is bounded by the Po River to the south, the Adda and the Ticino rivers to the east and west, respectively, and to the north by the Prealps foothills. The elevation ranges between 40 and 280 m asl and the average topographic gradient is about 0.003. The climate is continental and the mean annual precipitation ranges from 600 to 800 mm/year in the lower plain. The valleys of the main rivers (Ticino, Adda, Lambro) are deeply incised due to erosion of post-glacial deposits, leading to several orders of fluvial terraces, with the river bed lower than the regional groundwater level. For this reason, the main rivers play a dominant draining action and keep the water table quite shallow permitting only small oscillations in time (Giudici et al., 2007). According to the distribution of the main superficial hydrological features (rivers and lowland springs), and of the Milan metropolitan area, the study area can be geographically subdivided into ten zones (Fig. 1).

The Milan – Po plain aquifer system (Fig. 2) is composed of three main aquifers made up of Pliocene - Pleistocene continental sediments overlying marine depositional sequences (Lombardia and Eni Division Agip, 2002). The unconfined (P) aquifer consists of coarse lithology, mainly gravel with a sandy matrix (gravel-sand unit in Fig. 2c). The aquifer, 20–100 m thick, overlays a clayey-silty aquitard. This shows a good continuity in the southern portion of the study area (South of Milan), whereas (Fig. 2) it disappears moving northward. The underlying semi-confined (SC) aquifer consists of succession of sands and sandy gravels 50 to 150 meter thick. The base of the semi-confined aquifer consists of clay and silt layers and locally of conglomeratic units. The deep confined aquifer (C) consists of sandy lenses within clay and silt units representing the lower Pleistocene continental-marine transition facies. The occurrence of lowland springs called *fontanili* (Figs. 1 and 2) is observed across the Po Plain (E-W for about 600 km) along the transition between high and lower plain and in a 20-km-wide belt. This is related to a decrease of the grain size, passing from coarse sandy gravel to medium-fine sand, and in transmissivity (De Luca et al., 2014). The constant temperature (ca. 12–15 °C) and flow rate of the *fontanili* has enabled their use since ancient times for irrigation, preventing fields from freezing during winter.

2. Material and methods

2.1. Data collection and pre-processing

Five independent geochemical datasets, provided by local and regional agencies, and covering the period 1980–2014 were merged into a single database after homogenization and multiple quality checks. A total of 120,655 chemical analyses from 5075 sampling wells (Fig. 1) are available. The database includes sampling point coordinates, depth and a code indicating the aquifer to which each record belongs. In order to exclude low quality samples two consistency checks have been performed (Wendland et al., 2005; Müller et al., 2006) by considering: (i) incorrect ion balance (IB) and (ii) absence of depth or aquifer information. For samples with the complete cation and anion series, a 10% threshold

Download English Version:

<https://daneshyari.com/en/article/5771059>

Download Persian Version:

<https://daneshyari.com/article/5771059>

[Daneshyari.com](https://daneshyari.com)