COMPONENT SEPARATION APPROACH TO ESTIMATE NATURAL BACKGROUND LEVELS: A CASE STUDY FROM THE LOWER PO PLAIN (NORTHERN ITALY)

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Introduction

The EU Water Framework Directive (WFD 2000/60/EC) requires Member States to evaluate the "Status" of groundwater bodies, with the aim of achieving good groundwater status within 2015. In the case of naturally high concentrations of undesirable elements, the chemical status must be assessed against threshold values defined on the basis of Natural Background Levels (NBL). The EU research project BRIDGE (Müller et al. 2006) presents a procedure to derive NBL based on two different approaches: (i) pre-selection (PS) and (ii) component separation (CS).
This work presents an application of BRIDGE methodology on the aquifer system of Cremona, in the lower Po Plain (northern Italy), that hosts As, Mn, Fe and NH_4 rich groundwater. These species have a natural origin (Francani et al. 1994; Zavatti et al. 1995) likely related to reductive dissolution of Fe and Mn oxide-hydroxides coupled with oxidation of organic carbon of peat (Rotiroti et al. 2012b). The main aim of this work, which was developed in the framework of a scientific collaboration with the Province of Cremona, is to estimate the NBL for As, Mn, Fe and NH_4 in the Cremona area, using both PS and CS approaches, and then to compare the results.

Methods

The specific study area is located close to the confluence between Adda and Po rivers. It covers a 50 km^2 wide area around the town of Cremona. A subsoil depth of 200-250 m is considered. In the framework of the collaboration with the Province of Cremona, lithostratigraphic and hydrochemical data were collected and field measurements were executed. The interpretation of the lithostratigraphic data together with the measured hydraulic heads leads to the identification of five aquifer units (Rotiroti et al. 2012a): (i) phreatic (F), from 0 to 25 m, (ii) semi-confined (S) from 30 to 50 m, (iii) confined 1 (C1) from 65 to 85 m, (iv) confined 2 (C2) from 100 to 150 m and (v) confined 3 (C3) from 160 to 250 m. Aquifer F has a zone with reduced hydro-facies (F Red) and a zone with oxidised hydro-facies (F Ox) (Rotiroti and Fumagalli 2013), whereas the underlying aquifers have only reduced facies.
The hydrochemical data, collected from the archives of the Province of Cremona, consist of 1˙946 chemical analysis executed for 241 wells/piezometers from 1989 to 2010.
Three sites with possible anthropogenic influences on As, Mn, Fe and NH_4 concentrations (an oil refinery, a municipal solid waste landfill and a group of petrol stations) were identified in the study area. The influences can be occurred due to hydrocarbons and organic leachate spills, which were identified by the analysis of specific chemical parameters (i.e., total hydrocarbons and C.O.D).
Due to missing data, the PS approach was applied using simplified criteria, as described below: (i) subdivision of the dataset for each defined aquifer unit; (ii) exclusion of wells where possible anthropogenic influences could be occurred - for As, Fe and Mn, the data referred to the oil refinery, the landfill and the petrol stations were excluded in aquifer F, whereas only the data of the oil refinery were excluded in aquifer S; - for NH_4, only the data referred to the landfill were excluded in aquifer F; (iii) calculation of a single value representing the whole time series for each sampled well (median) in order to guarantee that all wells contribute equally to the NBL estimation; (iv) subdivision of the aquifer F data in F Red and F Ox; (v) estimation of the NBL on the remaining dataset calculating the 90° percentile.
The CS approach was applied through a MATLAB code. The frequency distribution of the data (chemical concentrations) was modelled with a Maximum Likelihood Estimation (MLE) obtaining a Probability Density Function (PDF). The modelled PDF (PDF_{mod}) is composed of two components: a lognormal PDF (PDF_{logn}), representing the natural component, and a normal PDF (PDF_{nrm}), representing the anthropogenic component (Müller et al. 2006). This two components are multiplied by a mixture parameter (p) as follows (Molinari et al. 2014):
$$PDF_{mod} = (p) PDF_{logn} + (1-p) PDF_{nrm}.$$
Therefore, five parameters identify the PDF_{mod} and are estimated by MLE procedure: p, mean of PDF_{logn} (μ_{logn}), standard deviation of PDF_{logn} (δ_{logn}), mean of PDF_{nrm} (μ_{nrm}) and standard deviation of PDF_{nrm} (δ_{nrm}). The NBL is assumed to be represented by the 90° percentile of the PDF_{logn}, according to Molinari et al. (2014). Since the PDF_{mod} results sensitive to the initial value of p, the MLE is performed varying initial value of p (from 0 to 1, with increments of 0.01) by an iterative algorithm, and the solutions are evaluated considering the goodness of fit (in terms of R^2 and RMSE). Similarly to the PS method, the CS was applied to the median values of the time series of each sampled well, divided for each aquifer. CS was only performed in F Red and aquifer S, since they have a sufficient sample size for

this analysis. Concerning F Red, a re-sampling scheme is here proposed due to the uneven spatial distribution of wells. The re-sampling was performed as follows: (i) creation of a regular grid with cells of 300 m (two times the average distance between wells); (ii) median averaging of the value (median of time series) of each well that is located in the same cell.

Results and discussion

Results presented here regard the example of As. Table 1 shows NBL estimation from PS. NBL results above the reference value (REF) of D.Lgs. 30/09 with the exception of F Ox and aquifer S. NBL estimation from CS is listed in Table 2. Concerning aquifer S, PS and CS approaches lead to similar values (9.6 and 9.64 μg/L, respectively). Conversely for F Red the two results show substantial differences (24.9 and 54.64 μg/L). This difference could be related to the uneven spacing of sampled well (i.e., higher density in the three sites with anthropogenic influences, where the 82% of wells are located; lower density elsewhere), that generates a small ratio (0.18) between the number of wells outside the three sites (27), used for PS, and the total number of wells (147), used for CS. After the re-sampling scheme, the ratio between points outside the three sites (decreased from 27 to 16) and total points (decreased from 147 to 43) increases to 0.37 and the derived NBL becomes 29.10 μg/L, closer to the value obtained from PS.

Conclusions

This work presented an application of BRIDGE method to estimate NBL for undesirable species in groundwater, focusing on CS approach. Both PS and CS approaches lead to comparable results, particularly for uniform data distribution, increasing the reliability of the estimated NBL.

Tab.1 – Estimated NBL for As from PS.

	REF	F Ox	F Red	S	C1	C2	C3
N. of sampled wells		*12*	*147*	*40*	*13*	*7*	*22*
N. of wells after pre-selection		*12*	*27*	*19*	*13*	*7*	*22*
NBL (μg/L)	10	5.7	24.9	9.6	81.4	31.2	27.6

Tab.2 – Estimated NBL for As from CS.

		F Red	S
Original data	*N. of sampled wells*	*147*	*40*
	NBL (μg/L)	54.64	9.64
Data after re-sampling	*N. of points*	43	-
	NBL (μg/L)	29.10	-

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