Derivation of preliminary natural background levels for naturally Mn, Fe, As and NH$_4^+$ rich groundwater: the case study of Cremona area (Northern Italy)

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RIASSUNTO

Derivazione dei valori naturali di fondo preliminari in acque sotterranee naturalmente ricche in Mn, Fe, As e NH$_4^+$: il caso studio dell'area cremonese.

Il presente lavoro riguarda la definizione di valori naturali di fondo preliminari per le specie manganese, ferro, arsenico ed ammonio nelle acque sotterranee del sistema acquifero multistrato della zona di Cremona. La metodologia applicata ha previsto la raccolta dei dati storici e di dati rilevati in campo attraverso una campagna di misure (luglio 2010), la definizione delle caratteristiche del sistema acquifero tramite modellazione tridimensionale dei parametri idrogeologici, la caratterizzazione idrodinamica ed idrochimica del sistema acquifero, la derivazione dei valori di fondo. I valori di fondo sono stati definiti in maniera distinta su due insiemi di dati differenti (campagna di luglio 2010 e serie storiche) considerata la diversa qualità dei dati che i due insiemi presentano. In questo senso i valori naturali di fondo definiti vengono considerati come "preliminari", essendo comunque in grado di fornire indicazioni utili alle Autorità competenti. La proposta di una campagna di monitoraggio dedicata per la derivazione dei valori naturali di fondo definitivi è in fase di valutazione da parte della Provincia di Cremona.

KEY WORDS: *Ammonium, Arsenic, Cremona, Iron, Manganese, Natural Background Levels.*

INTRODUCTION

The problem of naturally elevated concentrations of metals and arsenic in groundwater affects different parts of the world. Natural occurrence of arsenic was exhaustively analyzed in Bangladesh, West Bengal (India) and Vietnam (i.e. MCARTHUR *et alii*, 2001; ROWLAND *et alii*, 2006; POSTMA *et alii*, 2007). In Italy, naturally elevated concentrations of As are documented in the volcanic aquifers of central and southern Italy (i.e. BAIOCCHI *et alii*, 2011) and in the deep alluvial aquifers of northern Italy (i.e. ZAVATTI *et alii*, 1995). The main causes of the As contamination are probably related to the uprising of geothermal deep fluids (BAIOCCHI *et alii*, 2011) for the former, and to reducing environments (ZAVATTI *et alii*, 1995; ROTIROTI *et alii*, 2012) for the latter.

The main aim of this work is to define the preliminary natural background levels (NBLs) for As, Fe, Mn and NH$_4^+$, which affect the multi-layer alluvial aquifer of the Cremona area. Previous studies (Beretta *et alii*, 1992; Francani *et alii*, 1994) registered the presence of high levels of these species generally in the deep aquifers of the area (deeper than 50 m), assuming natural origin. These problem is also underlined by REGIONE LOMBARDIA (2006) which assigned the "particular" environmental status to this area on the basis on the D. Lgs. 152/06.

The specific study area is located near the confluence between the Adda and Po rivers. It covers a 50 km^2 wide area around the urban territory of Cremona (Fig. 1). The considered depth is around 200-250 m.

APPLIED METHODOLOGY

The applied methodology involved the (a) collection of historical data mainly related to water quality and well logs; (b) execution of a field survey of water levels and water quality (July 2010); (c) storage of collected data in specific databases and geographical information systems; (d) implementation of a 3D model of textural distribution, hydraulic conductivity and effective porosity of the multi-layer aquifer, built by means of ordinary kriging interpolation of numerical values which are derived from the coding of well data logs, according to BONOMI (2009); (e) hydrodynamic and hydrochemical characterization of the multi-layer aquifer; (f) derivation of preliminary NBLs according to the BRIDGE methodology (MULLER *et alii*, 2006).

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RESULTS AND DISCUSSION

The 3D model of the hydrogeological parameters of the multi-layer aquifer underlined the presence of an alternation of sandy layers ($K = 10^{-3}$-10^{-5} m/s) and silt-clay lenses ($K = 10^{-7}$-10^{-8} m/s) with a significant presence of peat and lead to the identification of 5 aquifer units. In relation to the hydrodynamic analysis these 5 units are classified as (1) phreatic (F), from 0 to 25 m b. s., (2) semi-confined (S) from 30 to 50 m, (3) confined 1 (C1) from 65 to 85 m, (4) confined 2 (C2) from 100 to 150 m and (5) confined 3 (C3) from 160 to 250 m. The aquifer F can locally assume semi-confined characteristic (Fs) due to the presence of superficial silt-clay lenses, while in the other parts it remains phreatic (Ff).

The analysis of water quality data underlined the general presence of reduced hydrochemical *facies*, characterized by high concentration of ammonia, manganese, iron and arsenic. Concerning the aquifer F, the Ff zone presents oxidized *facies*, while the Fs zone presents reduced *facies*. In particular, the survey of July 2010 registered high ammonia concentrations (1-5 mg/L, up to 18.9 mg/L) from aquifer S to C3. High concentrations of iron and manganese were also measured, they range respectively from 100 to 6000 μg/L and from 10 to 1200 μg/L. The higher levels were found in the upper aquifers: in Fs for Mn and in Fs & S for Fe. Arsenic was also found with high concentrations, ranging from 1 to 180 μg/L, especially in the 30-100 m depth range, corresponding to aquifers S & C1. The measurements of July 2010 can represent the natural background because no direct sources of Mn, Fe and As or indirect human influences were found. In the analysis of the hydrochemical historical data, a separation between the data referred to the natural background and to indirect human influences was done. Pollutions by hydrocarbons and organic matter in general were considered as indirect human influences on Mn, Fe and As concentrations (BURGESS & PINTO, 2005). The analysis of historical chemical data referred to the natural background generally confirmed the hydrochemical characterization emerged from the data of July 2010 survey.

The pre-selection approach (WENDLAND *et alii*, 2006) was applied to derive the NBLs for As, Fe, Mn and NH_4^+. The NBLs were separately derived from two different datasets, July 2010 and historical data, due to their different quality: the July 2010 dataset is characterized by a homogeneous methodology of sampling and analysis but it is referred to a short time period, while the historical dataset is referred to a longer time period (2000-2010) but it is characterized by different methodologies of sampling and analysis.

In the derivation of the NBLs from the July 2010 dataset the following criteria were applied: (a) exclusion of samples influenced by human activities, the criteria were NaCl content of more than 1000 mg/L, $[NO_3^-] > 50$ mg/L (modified from BRIGDE as PREZIOSI *et alii*, 2010) and $[SO_4^{2-}] > 500$ mg/L (as D. Lgs. 152/06); (b) exclusion of samples with incorrect ion balance (exceeding 10%); (c) subdivision of the dataset for each defined aquifer unit, the samples from multiaquifer wells were excluded; (d) subdivision in reduced and oxidized groundwater within the dataset of each aquifer, the criterion was $[Fe^{2+}] < 0.2$ mg/L, $[Mn^{2+}] < 0.05$ mg/L for oxidized groundwater and $[Fe^{2+}] \geq 0.2$ mg/L & $[Mn^{2+}] \geq 0.05$ mg/L for reduced groundwater (e) derivation of the NBLs on the remaining dataset calculating the 97.7° percentile (BRIGDE allows the use of 97.7° instead of 90° percentile in the case of well defined aquifers are available and no human influence exists). The derived NBL values are reported in Table 1. It should be noted that for the aquifer F a separation between reduced (F red) and oxidized (F ox) groundwater resulted. Figure 1 shows the extent of F ox and F red zones with the respective sampled wells. The limits of the zones were defined following hydrogeological criteria. In the southern part of the study area the F red zone corresponds to the Po river valley, characterized by peat and superficial clay deposits that allow semi-confined and reductive condition. In the northern part of the area the F red zone correspond to a superficial clay layer that allows semi-confined and reductive condition too. The remaining

TABLE 1 - Derived NBL values from the July 2010 dataset.

	REF	F Ox	F Red	S	C1	C2	C3
N. of samples		*4*	*8*	*11*	*3*	*10*	*8*
Ammonium (mg/L)	0.5	0.05	3.36	6.47	4.68	4.20	4.57
Iron (μg/L)	200	608	4665	3890	1015	698	718
Arsenic (μg/L)	10	5	42	171	149	54	37
Manganese (μg/L)	50	107	1197	537	136	140	125

TABLE 2 - Derived NBL values from the historical dataset.

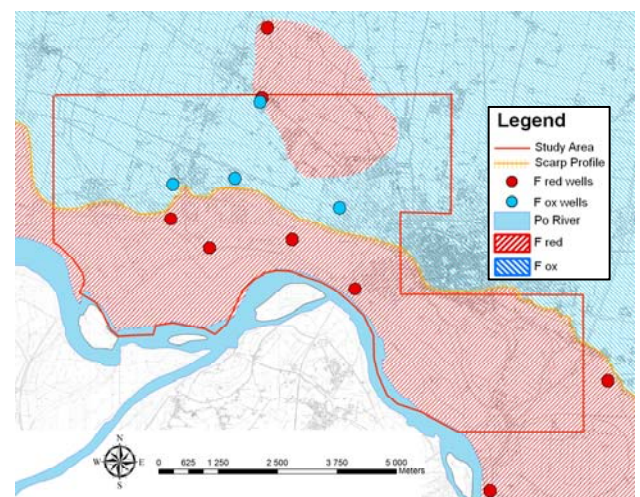|	REF	F Ox	F Red	S	C1	C2	C3
N. of sampled wells		*7*	*56*	*18*	*5*	*9*	*27*
Ammonium (mg/L)	0.5	0.10	2.30	2.45	2.01	1.72	2.01
N. of sampled wells		*15*	*23*	*19*	*19*	*10*	*27*
Iron (μg/L)	200	105	3924	3083	1050	548	149
N. of sampled wells		*12*	*27*	*19*	*13*	*7*	*22*
Arsenic (μg/L)	10	8	35	21	106	34	28
N. of sampled wells		*15*	*24*	*19*	*19*	*10*	*28*
Manganese (μg/L)	50	130	1350	425	376	147	71

Fig. 1 – Extent of F red and F ox zones and location of the sampled wells used in the NBLs derivation from July 2010 dataset.

zone was considered as F ox due to the presence of sandy deposits. This is confirmed by the sampled wells in the central part of the study area but it will be verified with new sampling in the zone with no measurements.

The derivation of NBLs from the historical dataset followed a simplified methodology due to missing information. The applied criteria were: (a) exclusion of wells where possible indirect human influences could be occurred, the occurrence of indirect influences was tested by the analysis of specific chemical parameters (i.e. total hydrocarbons, C.O.D.); (b) calculation of a unique value representing the whole time series for each sampled well (90° percentile) in order to guarantee that all wells contribute equally to the NBL derivation; (c) subdivision of the aquifer F data in F red and F ox on the basis of the zonation showed in figure 1; (d) derivation of the NBLs on the remaining dataset calculating the 90° percentile. The derived NBL values are reported in Table 2.

The two types of derived NBL values (from July 2010 and historical data) results comparable for Mn and Fe. Also for As the two type of values are comparable, with the exception of aquifer S. This difference is probably related to the historical dataset which is only referred to two sites and it could be non-representative of the whole aquifer. Considering the ammonium, the two NBL values considerably differ, with the exception of aquifer F. The NBL values from the July 2010 dataset result always higher. These differences could probably be related to specific conditions occurred in the survey of July 2010.

Considering the reference values (REF in Table 1 & 2) for As, NH_4^+ (D. Lgs. 30/09) and Fe, Mn (D. Lgs. 152/06), the derived NBLs are higher respect to REF up to more than one order of magnitude, with the exception of F ox zone. Comparing these results with the NBLs derived in Emilia-Romagna Region (MARCACCIO *et alii*, 2012) for As and NH_4^+ in the aquifer with an average depth of 75 m, the NBLs are similar for NH_4^+ (4.6 mg/L in Emilia-Romagna) but they differ for As (33 μg/L in Emilia-Romagna).

CONCLUSIONS

This work concerned the derivation of natural background levels for As, Fe, Mn and NH_4^+ in the multi-layer aquifer of the Cremona area. This derivation was based on a hydrochemical and hydrodynamic characterization combined to a modelling of the hydrogeological parameters of the aquifer. The NBLs was derived on the basis on two different datasets, related to a field survey and to historical data. In both cases this derivation could be considered a preliminary calculation due to the short time period of the measurements for the former and to the poor quality of the data (different methodologies of sampling and analysis) for the latter. The derivation of definitive NBLs requires a dedicated monitoring along a minimum time period of one year. A specific dedicated monitoring for the derivation of definitive NBLs has been proposed to the Province of Cremona.

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