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Geochemical and isotopic evidences for a severe anthropogenic boron contamination: A case study from Castelluccio (Arezzo, central Italy)

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ABSTRACT

In 2009 a deterioration of garden plants watered with domestic wells was related to high boron concentrations (up to 57 mg/L) measured in the shallow aquifer from the industrial area of Castelluccio (Tuscany, Italy), where several factories are or were using boron compounds for their industrial processes. Since 2012 a geochemical and isotopic survey of stream, ground and waste waters, and sediment samples was performed. In addition, monthly geochemical surveys were carried out from January to September 2013, during which concentrations of boron up to 139 mg/L were measured. The geochemical dataset also included raw (borax and sodium boron-hydride) and anthropogenic materials (B-rich slags and muds stored in one of the local factories), the latter being, to the best of our knowledge, analyzed for the first time in this work for bulk and leachate boron concentration and isotopic ratios. The results highlighted that the high concentrations of boron found in the local shallow aquifer had unequivocally an anthropogenic source. It was suggested that prolonged interaction between industrial (presently stored at ground level or buried) by-products and waste and meteoric waters was likely the main process responsible of the groundwater contamination as supported by the analysis of the major solutes. The dispersion of the contaminant could not clearly be observed downward the shallow hydrogeological circuit. Consequently, the presence of other sources of boron in the industrial area of Castelluccio cannot be excluded. This would also explain the reason why no univocal results were obtained by the $^{11}B/^{10}B$ isotopic ratios measured in water, sediment and (bulk and leachate) anthropogenic samples.

To minimize the boron contamination a hydraulic barrier should be constructed where the highest concentrations of boron were measured.

1. Introduction

Boron has recently been classified as a pollutant of drinking water in national and international drinking water legislation (Kloppmann et al., 2005). Despite the fact that boron is an essential micronutrient for plants, high concentrations of boron can affect garden and woods vegetables, e.g. causing off color and stunting of plant growth, leaf edge burning and necrosis (Nable et al., 1997). High concentrations of boron in water can also threaten human health, affecting fertility and pregnancy (e.g. Vengosh et al., 1998). Therefore, boron is classified as a moderate to high toxic element in the aquatic environment (e.g. Goldberg, 1997; Goldberg et al., 2005, 1996; Kistler and Helvaci, 1994; Voutsa et al., 2009). As a consequence, the European Union established a precautionary boron concentration limit for drinking waters of 1 mg/L (Directive 98/83/EC), which was also adopted by the Italian legislation.

The presence of this potentially dangerous element in water systems has natural (e.g. B-rich rock dissolution, volcanic and geothermal activity, seawater, marine spray; e.g. Dotsika et al., 2010, 2005) and anthropogenic (e.g. landfill leachate, industrial effluents, agricultural and sewage runoff; Hasenmueller and Criss,

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2013; Kistler and Helvaci, 1994; Pennisi et al., 2006b) sources. The E.U.-sponsored BOREMED project (http://boremed.brgm.fr) demonstrated that boron contamination has endangered the Mediterranean water resources since >10% of the analyzed ground waters resulted not suitable for human consumption (Kloppmann et al., 2005; Vengosh et al., 2004).

Weinthal et al. (2005) showed that more than 30% of the ground waters from Tuscany (central Italy) have boron contents that exceed the threshold limit of 1 mg/L due to water–sediment interaction processes (adsorption/desorption exchanges) and seawater intrusion (Bianchini et al., 2005; Pennisi et al., 2006a), and mixing with B-rich waters and mud derived by boric acid manufacturing from the Larderello geothermal field (Gonfiantini and Pennisi, 2006; Pennisi et al., 2006b).

The boron isotopic ratio (expressed as $\delta^{11}B = [(^{11}B/^{10}B)_{sample}/(^{11}B/^{10}B)_{standard} - 1] \times 1000$, where the standard is the NBS boric acid 951, whose $^{11}B/^{10}B$ is 4.04362 ± 0.00137; Catanzaro et al., 1970) is considered a good environmental tracer since different sources can be distinguished according to specific isotopic signatures (e.g. Barth, 2000a, 1998, 1993; Chetelat and Gaillardet, 2005; Chetelat et al., 2009; Vengosh et al., 2004, 1994; Voutsa et al., 2009).

In 2009, a significant deterioration of flowers, plants and vegetables watered with domestic wells from the industrial area of Castelluccio (a small urban center near Arezzo, Tuscany) was observed. According to the survey carried out by the local environmental protection agency (ARPAT, *Agenzia Regionale per la Protezione Ambientale della Toscana*), strikingly high boron concentrations (up to 57 mg/L) were measured in several wells pumping water from the shallow aquifer. No clear clues about the contamination source(s) were recognized since a relatively large number of industrial factories, e.g. carpenter, goldsmith, metal refineries, paint and detergent factories, manufacturers of PVC doors and windows, whose activities include the use of boron compounds (e.g. Barth, 1998; EPA, 2008; Kistler and Helvaci, 1994; Vengosh et al., 1994), are or were hosted in the industrial area of Castelluccio. Furthermore, fertilizers and wastewaters (Hasenmueller and Criss, 2013 and references therein) could also have contributed to the observed boron pollution.

In order to recognize the possible source(s) of boron in this complex industrial context an integrated geochemical and isotopic ($\delta^{11}B$) survey of stream, ground (from the three local aquifers) and waste waters and sediment samples was carried out in May–June 2012. The spatial and temporal evolution of dissolved boron in the shallow, most contaminated, aquifer was investigated through monthly geochemical surveys carried out on selected piezometers and domestic wells for 9 months (from January to September 2013), during which amazingly high boron concentrations (up to 139 mg/L, approaching those recorded in spring waters discharging in borate deposits, e.g. Gemici et al., 2008) were occasionally measured. Boron compounds (e.g. borax, $Na_2B_4O_7 \times 10H_2O$, imported from Turkey, and sodium boron-hydride, $NaBH_4$), currently used for industrial treatments, were analyzed for $\delta^{11}B$ values along with waste materials (i.e. pre- and post-flotation slags deriving from the productive cycle, and muds resulting from chemical treatments) stored over a service area. To the best of our knowledge, bulk and leachate boron concentrations and isotopic ratios on such anthropogenic materials were determined for the first time in this work.

2. Geological and hydrogeological setting

Castelluccio (ca. 500 residents) is located along the Arno River at about 8 km NW of Arezzo (Fig. 1S (Supporting Material)). The industrial area, hosting several small-to medium-size factories, is located in the alluvial plain on the right bank of the Arno River, delimited to the west by the Borgo Nuovo Creek and to the north by a slope (about 250 m a.s.l.), which hosts the small Middle-Age center (Fig. 1S (Supporting Material)).

By a geological point of view, the study area is located in the northernmost margin of the Pleistocene Arezzo fluvio-lacustrine basin (Vaselli et al., 2007, and references therein). The basin is filled by continental deposits, which lie on turbiditic sandstones and marls (*Arenarie del Monte Falterona Fm.*), detected at >40 m depths beneath the industrial area (Fig. 1S (Supporting Material)). The continental deposits consist of, from the bottom to the top, lacustrine gray-green clay and silt-to-clay impervious deposits (*Argille di Quarata Fm.*), with lignite beds at the base and calcareous pebble lenses at the top (Vaselli et al., 2007 and references therein). The *Argille di Quarata Fm.* is up to 40 m thick in the industrial area and lies over the *Ciottolami di Laterina Fm.* (mainly constituted by calcareous fluvial pebbles in a sand or silt-to-sand matrix) and *Limi di Latereto e Pian di Tegna Fm.* (silt-sand and sandy–clay deposits), the latter cropping out to the north of Castelluccio (Frattini et al., 2011). The alluvial (mainly gravels and sands) deposits of the Arno River, whose thickness does not exceed 10 m, terminate the stratigraphic succession and widely crop out in the industrial area, where they unconformably lie on the *Argille di Quarata Fm.*

According to Frattini et al. (2011), the hydrogeological setting is characterized by three aquifers, as follows:

- *Deep Aquifer*: hosted in the *Arenarie del Monte Falterona Fm.* at an average depth of 60 m, characterized by secondary permeability.
- *Intermediate Aquifer*: a likely confined or multi-strata aquifer with primary permeability due to interstitial porosity, hosted in the pebbly–sandy layers belonging to the *Argille di Quarata Fm.* It is located at an average depth of 30 m.
- *Shallow Aquifer*: it is a phreatic aquifer with primary permeability, due to interstitial porosity. It is hosted in the *Alluvial Deposits* of the Arno River at an average depth of 10 m. The groundwater outflow under the industrial area is NE–SW oriented and moves from the slope of Castelluccio toward the Arno River.

3. Materials and methods

3.1. Stream and ground waters

After the survey carried out by the local environmental protection agency (ARPAT, *Agenzia Regionale per la Protezione Ambientale della Toscana*) in 2009 and repeated in 2010 during which 10 out of the 20 wells analyzed showed concentrations of boron >1 mg/L (Conti, 2011), a detailed geochemical investigation was carried out in the study area between May and June 2012, when 54 waters were sampled (Fig. 1) and analyzed. Four waters were collected from the Arno River (upstream and downstream the industrial area and in between) and Borgo Nuovo Creek (before the confluence into the Arno River) from the mid-stream. Ground waters from 50 wells and old- and new-drilled piezometers (Fig. 1) were sampled using a tubing reel connected to a double valve pump supplied by a 12 V battery. Three samples were collected from the deep aquifer, 29 from the shallow aquifer, 7 from the intermediate aquifer and 11 from fenestrated wells, which intercepted both the shallow and the intermediate aquifers.

Seventeen water samples from the shallow aquifer (PZ01, PZ02, PZ04, PZ05, PZ07, PZ08, PZ09, PZ10, PZ11, P02, P03, P04, P06, P09, P16, P18, P20) and two from both the shallow and the intermediate aquifers (P22, P26) were collected on a monthly basis from January to September 2013. Seven samples (AS1, PZ03, PZ06, P08, P10, P19 and P24), an intermittent spring water (SP) located along the main

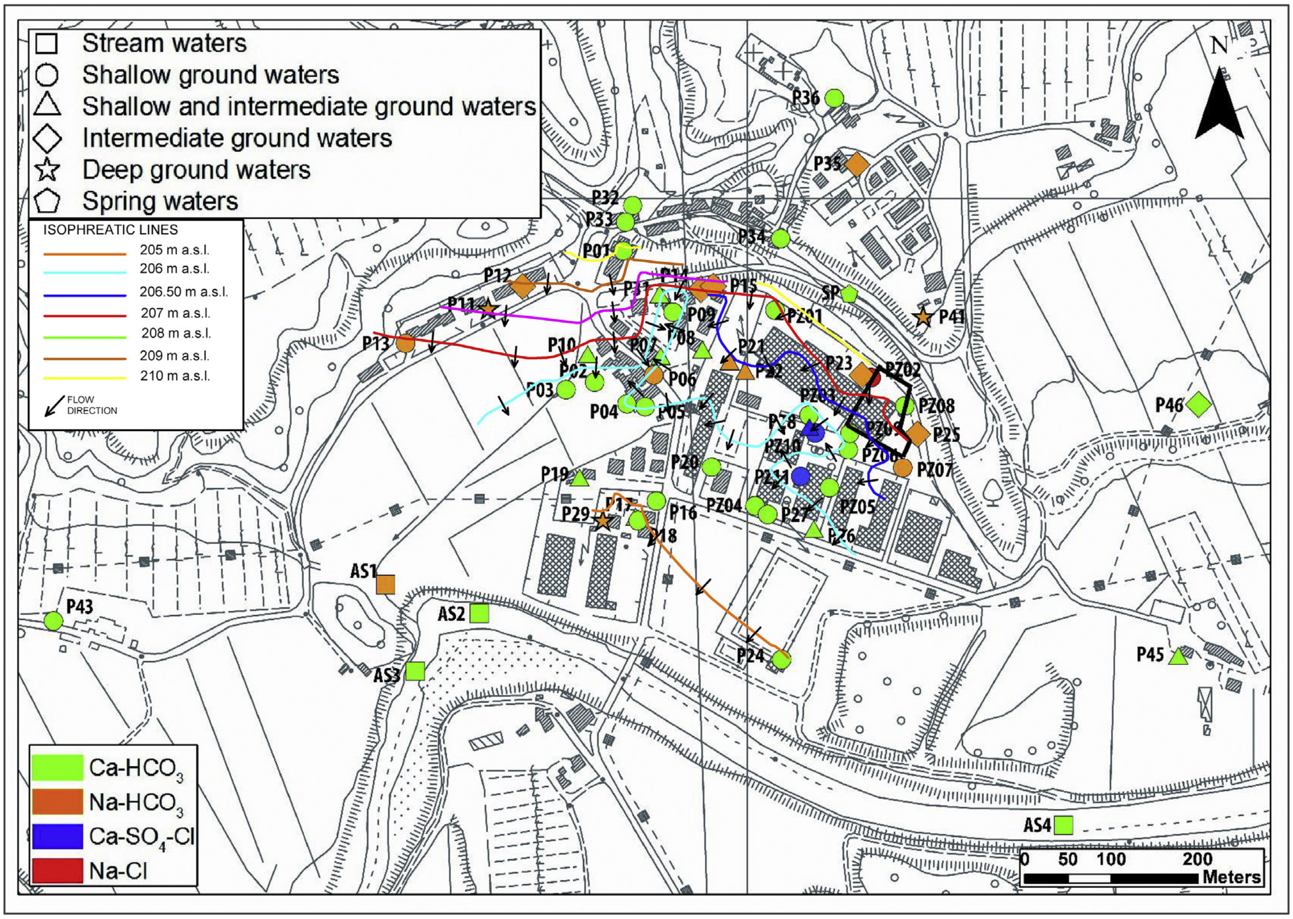

Fig. 1. Location of the sampling points (squares = stream waters; circles = shallow aquifer; triangles = fenestrated wells into the shallow and the intermediate aquifers; diamonds = intermediate aquifer; stars = deep aquifer; pentagon = spring). The colors indicate the geochemical facies of the waters collected in May–June 2012 (green = Ca–HCO$_3$; orange = Na–HCO$_3$; blue = Ca–SO$_4$–Cl; red = Na–Cl). The black polygon defines the area where the boron-rich industrial materials (slags and muds) are stored. Isophreatic lines of the shallow water table and groundwater outflow direction (black arrows) are reported (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

road that connect the industrial area to Castelluccio, and the P05 well (Fig. 1) were collected in January 2013, May 2013, and August 2013, respectively.

Temperature (°C), pH and electrical conductivity (normalized to 20 °C and expressed as mS/cm) were measured in the field. The water table depth (in meters) was measured prior to the water sampling with a portable Universal phreatimeter reel. Two aliquots filtered at 0.45 μm were collected in polyethylene bottles, one for the analysis of anions and the other, acidified with 0.5 mL of Suprapur HCl, for the analysis of cations. A third filtered (0.45 μm) aliquot was collected for the determination of the boron concentration and the isotopic composition. A fourth aliquot was sampled during the first sampling campaign in 1 L polyethylene bottles from one piezometer (PZ07) and two wells (P04 and P22) for the analysis of ^{3}H content. Moreover, two cumulated meteoric water samples (from February to March 2013 and from May to July 2013) were collected using two rain gauges (situated in two different sites) for the determination of ^{3}H contents.

Major ionic species were determined by ion chromatography using an 861 Advanced Compact IC-Metrohm for cations (Na, K, Mg, Ca) and a 761 Compact IC-Metrohm for anions (Cl, SO$_4$). HCO$_3$ was analyzed within 24 h from the sampling collection by titration (Basic Titrino 794-Metrohm). The analytical errors was <5%. The ^{3}H content (expressed as TU, Tritium Units) was determined by Liquid Scintillation Counting (LSC) (analytical error: 1%) at the Geoisotopical Unit of Public Health, Department of Chemistry (Koper, Slovenia). Boron content in waters was determined by using three different methods at the laboratories of the CNR-IGG and two Italian private companies (T.C.A. Ltd. and C.S.A. Research Group), as follows: i) molecular absorption spectrometry (Pye Unicam SP6-350; instrumental detection limit: 20 μg/L; analytical error <10%), according to the method proposed by Bencini (1985), ii) ICP-AES (720 Series; instrumental detection limit: 5 μg/L; analytical error <5%) and iii) ICP-MS (7500ce Agilent Technologies; instrumental detection limit: 0.1 μg/L; analytical error <5%). The analytical results obtained using the three different methods were comparable ($R^2 = 0.996$ for both ICP-MS and ICP-AES vs. molecular absorption spectrometry). δ^{11}B was analyzed on selected samples by MC-ICP-MS (NEPTUNE, Thermo Scientific; $2\sigma \leq 0.83‰$) at ALS Laboratories (Sweden). Prior to the isotopic analysis, 100–150 mL of water were pre-concentrated using the boron specific ion-exchange resin Amberlite IRA 743 in order to have about 100 μg/L of boron in solution (Aggarwal et al., 2009).

3.2. Sediment samples and anthropogenic materials

Seven 10 m deep drillings (named PZ01 to PZ09) were carried out in the industrial area of Castelluccio. From each core, sediments were collected at three different depths, as follows: i) at 1 m depth (PM), ii) in the capillary fringe (FC) (at about 5 m depth) and iii) at an intermediate depth between the two (INT) (at about 2.50 m depth). One sample (DP) was collected from clay-rich layers at the base of the PZ02 and PZ09 sediment cores. Sediment samples were gently crushed, homogenized and sieved in the field to remove the granulometric fraction >2 cm, and stored in polyethylene bags. Then, they were dried at 40 °C, sieved at 2 mm and grinded with a planetary agate ball mill. The sediment pH values were measured with a Crison micropH 2000 pH-meter, after adding 10 mL of MilliQ water to 1 g of powdered sample and stirring periodically for 24 h. The organic carbon content was determined according to the method proposed by Springer and Klee (1954).

Preflot (pre-flotation) and Postflot (post-flotation) slags and muds were collected, after homogenization, in polyethylene bags. In the factories, these materials were stored to form separated cumulus up to 5 m high, each covering areas of about 50–70 m^2. About 1 kg from different sites of each cumulus was transferred to a plastic container until about 15–20 kg of material was collected. Then, the material was homogenized by hand with latex gloves for about 10 min. About 2 kg of sample from each container was collected and dried at 40 °C and quartered until about 100 g of material were obtained. The samples were grinded as for the sediments to get an impalpable powder. About 200 g of borax (from Turkey) were collected directly for the original container and transferred to a plastic bag. Sodium boron-hydride was sampled in a 250 mL polyethylene bottle from the barrel in use.

Boron contents in sediments, slags and muds were analyzed on powdered samples by ICP-AES (720 ES, Varian) at C.S.A. Research Group after HNO_3–HF–HCl dissolution (total boron, B_{tot}) and after leaching test in CO_2-saturated water (available boron, B_{av}). The leaching tests were performed by adding 100 mL of CO_2-saturated MilliQ water (pH < 4.5) to 5 g of powdered sample. The final solution was obtained by filtering (0.45 μm) the leachate after about 12 h. This test was used to mimic in the laboratory the sample leaching by meteoric and runoff waters.

GXR-1 and GXR-4 standards were used during the analytical runs, whose boron contents were of 13.5 (expected value: 15 mg/kg) and 4 (expected value: 4.5 mg/kg) mg/kg, respectively. Boron contents in the blanks for bulk and leaching analyses were negligible with respect to those found in the solid and liquid samples.

The main solutes (Na, K, Mg, Ca, Cl, SO_4) and HCO_3 in the leachates and wastewaters were determined by ion chromatography (861 Advanced Compact IC-Metrohm for cations and a 761 Compact IC-Metrohm for anions) and titration (Basic Titrino 794-Metrohm), respectively (analytical error <5%).

The boron isotopic composition ($\delta^{11}B$) was analyzed by MC-ICP-MS (NEPTUNE, Thermo Scientific; $2\sigma \leq 1.19‰$) at ALS Laboratories (Sweden) on sediments ($\delta^{11}B_{tot}$) and slags and muds (both on solid samples, $\delta^{11}B_{tot}$, and leached samples, $\delta^{11}B_{lct}$), and on borax and sodium boron-hydride.

4. Results

4.1. Natural waters

Temperature (in °C), pH, electrical conductivity (in mS/cm), concentrations of the main and minor compounds (in mg/L), the boron contents (in mg/L) and isotopes ($\delta^{11}B$ ‰ NBS951) and Tritium Units (^3H) for stream and ground waters collected in May–June 2012 are reported in Table 1 and 1S (Supporting Material), respectively. The analytical results of the geochemical monitoring carried out on 19 wells from January to September 2013 are reported in the supplementary material (SM1), along with those of (i) AS1, PZ03, PZ06, P08, P10, P19 and P24, (ii) SP and (iii) P05 collected in January, May and August 2013, respectively; the boron contents (in mg/L) and the $\delta^{11}B$ values determined on the analyzed samples are reported in Table 2.

Table 1
Location (in UTM), electrical conductivity (in mS/cm), TDS (in mg/L), temperature (in °C), pH, concentrations of the main and minor compounds (in mg/L), boron contents (in mg/L), $\delta^{11}B$ values (NBS boric acid 951 in ‰) of the stream waters collected in May–June 2012. The geochemical facies for each sample is also reported.

Sample ID	AS1	AS2	AS3	AS4
E	1,728,582	1,728,690	1,728,616	1,729,366
N	4,822,554	4,822,520	4,822,453	4,822,275
EC at 20 °C	1.682	0.432	0.438	0.465
TDS	1117	343	342	336
T	14	15.1	14.5	18.4
pH	7.75	8.1	8.25	8.49
HCO_3^-	653	229	220	215
F^-	0.35	0.09	0.12	0.09
Cl^-	111	9	10	10
Br^-	0.19	0.03	0.02	0.02
SO_4^{2-}	39	24	25	25
Ca^{2+}	67	61	66	65
Mg^{2+}	14	8	8	8
Na^+	98	9	9	9
K^+	31.5	1.6	2.3	1.7
B	0.11	0.02	0.02	0.02
$\delta^{11}B$	−6.0			
Facies	Na–HCO_3	Ca–HCO_3	Ca–HCO_3	Ca–HCO_3

As clearly shown in Fig. 2, the boron contamination was restricted to the alluvial plain east of Borgo Nuovo Creek, where the industrial activities are located. In particular, the highest boron concentrations, up to >100 mg/L, were found in the shallow aquifer and sporadically in the waters collected from the intermediate aquifer or from those fenestrated wells that connect the shallow and intermediate aquifers (Fig. 2), suggesting a shallow or superficial origin of the contamination. Accordingly, boron concentrations in the groundwater samples collected from the deep aquifer were <1 mg/L, both outside (P11, P41) and inside (P29) the industrial area, ranging from 0.12 (P11) to 0.43 (P29) mg/L in May–June 2012 (Table 1S (Supporting Material); Fig. 2). These deep ground waters displayed a Na–HCO_3 composition (Fig. 1), with TDS (Total Dissolved Solids) values ranging from 917 (P41) to 1214 mg/L (P29) and pH from 7.47 (P41) to 7.88 (P11) (Table 1S (Supporting Material)). The rather impervious *Argille di Quarata Fm.*, overlying the deep aquifer (Fig. 1S (Supporting Material)), represented an effective protection that prevented seepage of contaminants from the shallower depths. Similarly, most waters collected from the intermediate aquifer in May–June 2012 were characterized by a Na–HCO_3 geochemical facies (Fig. 1), with TDS and pH ranging from 786 to 1017 mg/L and from 7.41 to 7.85, respectively (Table 1S (Supporting Material)), and boron concentrations from 0.03 (P46) to 0.11 (P15) mg/L. Only the P25 well (situated in the eastern part of the industrial area) showed a content of boron of 2.7 mg/L (Fig. 2), i.e. higher than the recommended E.U. value for drinking waters.

A higher compositional variability was recognized for waters collected from the fenestrated wells. The majority of these waters collected in May–June 2012 had a Ca–HCO_3 composition (Fig. 1), with TDS and pH values ranging from 545 to 1227 mg/L and from 6.97 to 7.75, respectively (Table 1S (Supporting Material)). Waters from P21 and P22 had a Na–HCO_3 composition, with relatively high TDS (1467 and 1413 mg/L) and pH (7.12 and 8.82) values. One sample (P28) had a Ca–SO_4–Cl composition, whereas its TDS (1263 mg/L) and pH (7.02) values were in the range observed for the fenestrated wells. Except for P17, P31 and P45 samples (collected from wells located in south- and north-western peripheral zones of the industrial area and SE of the study area; B ≤ 0.24 mg/L), waters from the fenestrated wells collected in May–June 2012 and located within the alluvial plain had concentrations of boron exceeding 1 mg/L (Fig. 2). In particular, values of

Table 2
Boron contents (in mg/L) and $\delta^{11}B$ values (in ‰) of the natural waters collected from January to September 2013.

Sample ID	Jan13		Feb13		Mar13		Apr13	May13		Jun13		Jul13		Aug13	Sep13
	B	$\delta^{11}B$	B	$\delta^{11}B$	B	$\delta^{11}B$	B	B	$\delta^{11}B$	B	$\delta^{11}B$	B	$\delta^{11}B$	B	B
AS1	0.4														
PZ01	0.2		0.03		0.07		0.37	0.11		0.08		0.2		0.11	0.09
PZ02	139	−8.7	60	−2.9	17.4	−4.4	18.7	20.8	−2.6	22.1	−3.5	20.0		25.6	30
PZ03	15	+5.1													
PZ04	14		7.7		4.2		5.1	1.9		2.5		2.9	−6.1	2.5	3.03
PZ05	1.6	+14.5	1.3		2.6		2.6	0.98		0.86		0.6		0.38	0.47
PZ06	9.1														
PZ07	21	−3.9	3.5		0.73		0.52	0.29		0.32		1.0		0.79	1.48
PZ08	119		2.8		0.64		0.92	0.7		0.48		1.9		8.6	12.3
PZ09	18	+2.6	3.7		1.4		7.3	2.9		2		2.4		2.5	2.88
PZ10	11		6.2		2		2.8	1.11		0.87		1.0		1.1	1.05
PZ11	2.1		1.1		1.7		3.4	1.16		0.87		0.7		0.67	3.36
P02	5.3	−5.7	3.8		4.5		6.2	4.2		3.8		4.5		4.9	4.55
P03	0.2		0.05		0.8		2.2	0.17		0.32		1.0		1.3	1.89
P04	5.9	−4.5	6.5		11		18.3	11.3		9.6		10.1		8.1	6.18
P05														7.8	
P06	9.2	−4.5	6.8	−2.7	8.2	−0.6	12.2	7.3	−4.2	3.8	−7.1	5.7		6.2	5.51
P08	5														
P09	0.8		1.2		0.64		1.7	0.71		0.34		0.2		0.21	0.26
P10	2.6														
P16	5.5	+9.4	6.7		6.6		8.1	4.1		3.23		2.9		2.2	1.82
P18	4		5.8		5.2		8	4.3		3.7		3.8		2.6	1.99
P19	3.5														
P20	4	+4.1	3.9		3.3		4.2	2		1.7		1.8		1.5	1.56
P22	19		29		16.7		16	7.7		6.9		8.0		7	6.12
P24	0.1														
P26	0.1		2.4		3.1		2.3	0.31		0.61		0.8		0.55	0.64
SP								0.07							

boron >20 mg/L were measured in the P21, P22 and P28 wells, P22 showing a $\delta^{11}B$ value of −0.9‰ (Table 1S (Supporting Material)). Boron contents >1 mg/L were also measured in the P08, P10, P19 and P22 samples in January 2013 (Table 2). In particular, P22 waters showed high concentrations of boron during the whole monthly monitoring survey, ranging from 6.12 to 29 mg/L in September 2013 and February 2013, respectively (Fig. 3). The highest concentration of boron detected in the water sample P22 coincided with a change in the geochemical facies from Na–HCO_3 to Na–Cl and an increase in the SO_4 content (SM1). The P26 waters sampled during the monthly monitoring survey showed boron contents >1 mg/L from February to April 2013, with concentrations up to 3.1 mg/L (March 2013). The phreatic level in P26 (Fig. 3) occasionally presented anomalous values, likely induced by well pumping before the sampling.

Among the shallow ground waters, no boron anomalies were found in those wells drilled above and north of the slope delimiting the alluvial plain. These water samples (i.e. P01, P32, P33, P34, P36) were characterized by Ca–HCO_3 composition (Fig. 1) with TDS, pH and boron concentrations ranging from 681 (P01) to 820 mg/L (P32), from 7.08 (P01) to 7.25 (P34), and from 0.02 (P34) to 0.14 mg/L (P36), respectively (Table 1S (Supporting Material)). Similarly, as reported by Cabassi et al. (2012) and Vaselli et al. (2007), boron contents from ground waters collected on the left bank of Arno River, adjacently to the study area and not affected by any industrial settlement, were comprised between 0.02 and 0.2 mg/L, i.e. similar to those measured outside the contamination halo at Castelluccio. In May–June 2012 the shallow ground waters collected in the northern (PZ01, P09), southern (P24) and western (P03) margins of the industrial area displayed boron concentrations <1 mg/L and Ca–HCO_3 composition (Figs. 1 and 2), as also showed by the intermittent spring water (SP) collected in May 2013, whose boron content was of 0.07 mg/L. These waters were characterized by TDS and pH values ranging from 498 to 869 mg/L and from 6.81 to 7.68, respectively, during the whole sampling period. PZ01 waters were constantly characterized by boron concentrations ≤0.11 mg/L, whereas P03 and P09 waters occasionally exceeded the threshold for drinking water. In particular, P09 showed concentrations of 1.2 and 1.7 mg/L in February and April 2013, respectively, whereas the highest boron content in P03 was of 2.2 mg/L in April 2013, although high concentrations were also measured in August and September 2013: 1.3 and 1.89 mg/L, respectively (Table 2). In May–June 2012 (Table 1S (Supporting Material)), the $\delta^{11}B$ values of PZ01, P03 and P09 were −10.9, +11.0 and −4.4‰, respectively.

In the alluvial plain, shallow ground waters flowed from NE to SW with a relatively fast hydrological circulation, as suggested by the tritium values measured in the shallow aquifer (6 TU) and in one sample collected from a fenestrated well located in the shallow and the intermediate aquifer (7 TU). We may estimate a residence time of <4 years, since the local meteoric water, though only collected as cumulated precipitation in two periods of 2013, was characterized by TU values ranging from 7 to 9. The phreatic level of all the monitored wells and piezometers (Figs. 3 and 4) had a progressive increase from January to March 2013 (during which time the highest boron contents were generally measured), while from April to September 2013 it slowly, though constantly, decreased.

Independently by the sampling period, the highest concentrations of boron were found in the piezometer PZ02, with a value of 121.6 mg/L in May–June 2012 and a maximum of 139 mg/L in January 2013 (Tables 1S (Supporting Material) and 2), with $\delta^{11}B$ values ranging from −8.7 to +0.3‰ with no temporal trend (Table 2). It is noteworthy to point out that in March 2013, when the highest phreatic level was measured, the lowest boron concentration was observed (17.4 mg/L) (Table 2; SM1; Fig. 4) and that from April to September 2013 the boron content remained ≤30 mg/L (Table 2; Fig. 4). The waters from the piezometer PZ02 (located in the NE margin of the alluvial plain and adjacently to the industrial muds and slags; Fig. 1) were characterized by a Na–Cl composition, high TDS (from 1568 to 3293 mg/L), and pH ranging from 8.19 to

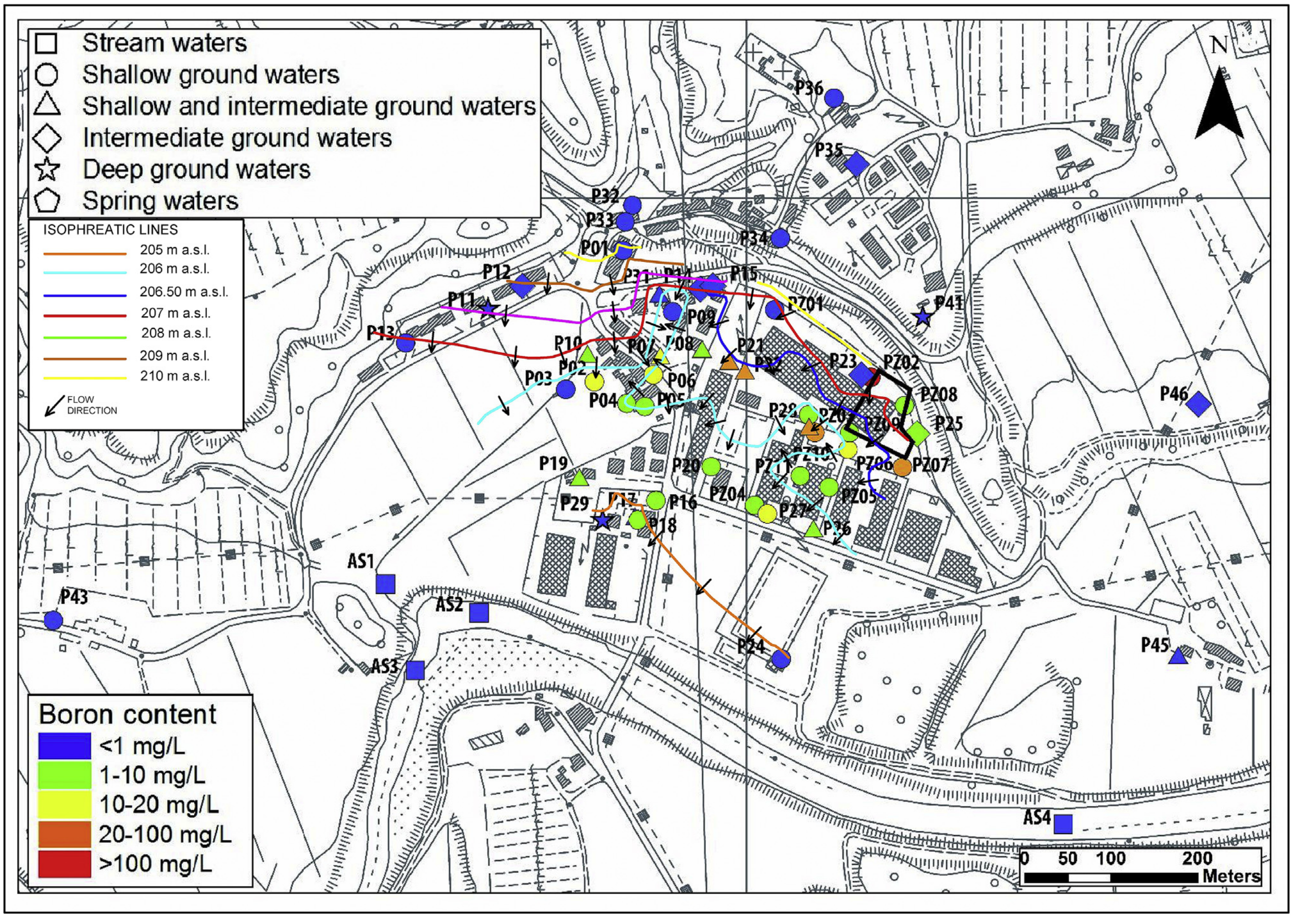

Fig. 2. Dot-map of boron concentrations (blue = <1 mg/L; green = 1–10 mg/L; yellow = 10–20 mg/L; orange = 20–100 mg/L; red = >100 mg/L) in the waters collected in May–June 2012 from the study area. Isophreatic lines of the shallow water table and groundwater outflow direction (black arrows) are reported (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

8.94 in May–June 2012 and January, February and September 2013, i.e. when the highest boron concentrations were measured (Tables 1S (Supporting Material) and 2; SM1). The geochemical facies changed to Na–HCO_3 from March to August 2013, concurrently the boron concentrations decreased (17.4–25.6 mg/L) as well as TDS (974–1366 mg/L), whereas the pH values showed a remarkable alkaline character (8.25–8.81).

High boron concentrations were also measured in those water samples collected close to PZ02. In May–June 2012, PZ07 had a boron content of 31 mg/L, whilst that of PZ06, PZ10, and P27 was >10 mg/L. The shallow ground waters collected in this sector of the alluvial plain showed a relatively high variability of their geochemical composition, which also changed during the monthly survey. In May–June 2012, PZ10 and PZ11, and PZ07 showed a Ca–SO_4–Cl and a Na–HCO_3 composition, respectively, but PZ07 turned to be Ca–HCO_3 in January 2013. The PZ10 and PZ11 waters were characterized by a Ca–HCO_3 composition during the whole monitoring survey and from January to August 2013, respectively, PZ11 showing again a Ca–SO_4–Cl facies in September 2013. These shallow groundwater samples were characterized by δ^{11}B values ranging from −11.5 (PZ11) to +6.6‰ (PZ06) (Tables 1S (Supporting Material) and 2). No specific spatial distribution was observed.

In January 2013, a dramatic increment in the boron content was measured in the waters from PZ08, located in the nearby of PZ02, with a concentration of 119 m/L, whilst in February 2013 a sharp decrease (2.8 mg/L) occurred (Fig. 4). Concurrently with the increase in the boron content, the chemical composition of PZ08 waters changed to Na–Cl and TDS increased up to 2348 mg/L in January 2013. In February 2013 a Ca–HCO_3 composition and lower salinity (SM1) was restored.

In the western sector of the industrial zone, high boron concentrations (>10 mg/L) were also observed in the shallow groundwater samples: P02 in May–June 2012, P04 in March to May and July 2013, P06 in May–June 2012 and April 2013 (Tables 1S (Supporting Material) and 2). The δ^{11}B values showed a large variability, being comprised between −7.1 (P06) and +13.7 (P16) ‰ (Tables 1S (Supporting Material) and 2), with no specific behavior in terms of spatiality and temporality.

Generally, δ^{11}B values were varying from −11.5 (PZ11) to +14.5 (PZ05) ‰ in the shallow ground waters collected during the whole sampling period (Tables 1S (Supporting Material) and 2). No particular areal distributions were observed and furthermore, domestic wells and piezometers were characterized by abrupt δ^{11}B variations even when located at few tens of meters from each other, e.g. PZ05 (+14.5‰), PZ07 (−3.9‰) and PZ09 (+2.6‰; Fig. 1), markedly differing from boron isotopic values measured in May–June 2012 in the same samples (e.g. PZ02 and PZ05).

Monthly variations of the δ^{11}B values were measured for the PZ02 and P06 waters from January to June 2013. The boron isotopic composition of PZ02 and P06 ranged from −8.7 (January 2013) to ±2.6‰ (May 2013), and from −7.1 (June 2013) to −0.6‰ (March 2013), respectively.

Stream waters showed no boron anomalies. Water samples from the Arno River (i.e. AS2, AS3, AS4) were characterized by a Ca–HCO_3

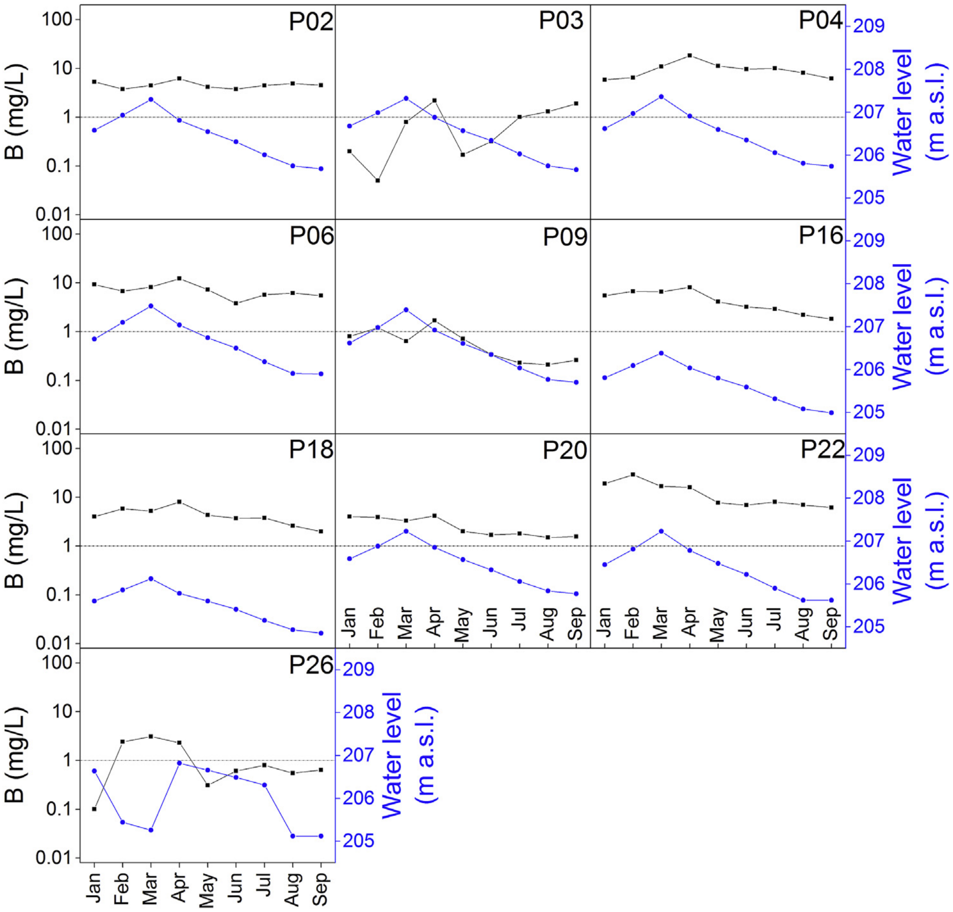

Fig. 3. Boron concentrations (in mg/L) (black line) and phreatic level (in meters) (blue line) from wells sampled during the monthly monitoring period of January to September 2013 (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

composition, with TDS varying from 336 to 343 mg/L and slightly alkaline pH (8.10–8.49) and boron concentrations of 0.02 mg/L. The Borgo Nuovo Creek sample (AS1) collected in May–June 2012 had a Na–HCO_3 composition (Fig. 1), with TDS and pH values of 1117 mg/L and 7.75, respectively, whilst in January 2013 it had a Ca–HCO_3 composition with lower TDS (682 mg/L) and a pH value of 8.06. The boron contents in the Borgo Nuovo Creek samples collected in May–June 2012 and January 2013 were <1 mg/L, with a $\delta^{11}B$ value of −6.0‰ in May–June 2012 (Tables 1 and 2).

4.2. Sediment cores

To assess whether the rock reservoirs were potential candidates of the high boron concentrations in the shallow aquifer, total (B_{tot}) and available boron (B_{av}) contents (in mg/L) and $\delta^{11}B_{tot}$ values on selected drill cores are reported in Table 3. The analytical dataset was implemented with the clay + silt fraction (in % by wt.) and organic carbon (C_{org}) content (in % in wt.), which were recognized to influence the presence of boron and its availability in soil (Chaudhary et al., 2005; Goldberg, 1997; Goldberg and Su, 2007; Goldberg et al., 2008).

B_{tot} concentrations ranged from 9.4 (PZ06-FC) to 197 (PZ01-PM) mg/kg. B_{av} concentrations were lower than the detection limit (0.20 mg/L) in PZ01, PZ03-INT, PZ03-FC and PZ06-INT, whereas in the remaining samples they varied from 0.79 (PZ06-FC) to 8.99 (PZ02-FC) mg/L, representing less than 19% of B_{tot} in all the samples. A higher B_{av} concentration (28.02 mg/L) was found in PZ02-DP, corresponding to 49% of B_{tot}. $\delta^{11}B_{tot}$ values were negative in all sediment samples, being from −14.2 (PZ01-FC) to −4.8 (PZ03-INT) ‰.

4.3. Anthropogenic materials and wastewaters

The contents of B_{tot} and B_{lct} were higher in the slag than in the mud samples (Table 4). The highest concentrations of B_{tot} were measured in the Preflot 1 (18,268 mg/kg) and Postflot 2 (17,550 mg/kg) samples. The concentration of B_{lct} had the highest value in the Preflot 1 (12,550 mg/L) and Preflot 2 (4160 mg/L) samples, representing up to 69% of B_{tot}. The mud samples showed relatively lower B_{tot} and B_{lct} contents ranging from 863 to 3358 mg/kg and from 421 to 683 mg/L, respectively. The $\delta^{11}B_{tot}$ values were ranging from −4.9 (Mud 1) to +0.6 (Preflot 2) ‰ while those from the leached samples were ranging from −3.4 (Mud 1) to −1.3 (Postflot 1) ‰.

The chemical composition of the slag and mud leached solutions is reported in Table 5. The pH values resulted to be alkaline, as they were from 8.86 (Mud 2) to 9.91 (Preflot 1). Relatively high concentrations of Na, Cl and SO_4 were recorded, while those of the (bi) carbonate species were partially related to the adopted leaching procedure, during which CO_2-saturated MilliQ water was used.

Industrial borax had $\delta^{11}B$ value of −5.1‰, accordingly with the isotopic range reported by Palmer and Helvaci (1997) for that exploited from the western Turkish borate deposits (i.e., from −1.6 to −25.3‰). Sodium boron-hydride ($NaBH_4$) had a more strikingly negative $\delta^{11}B$ value, i.e. −22.8‰.

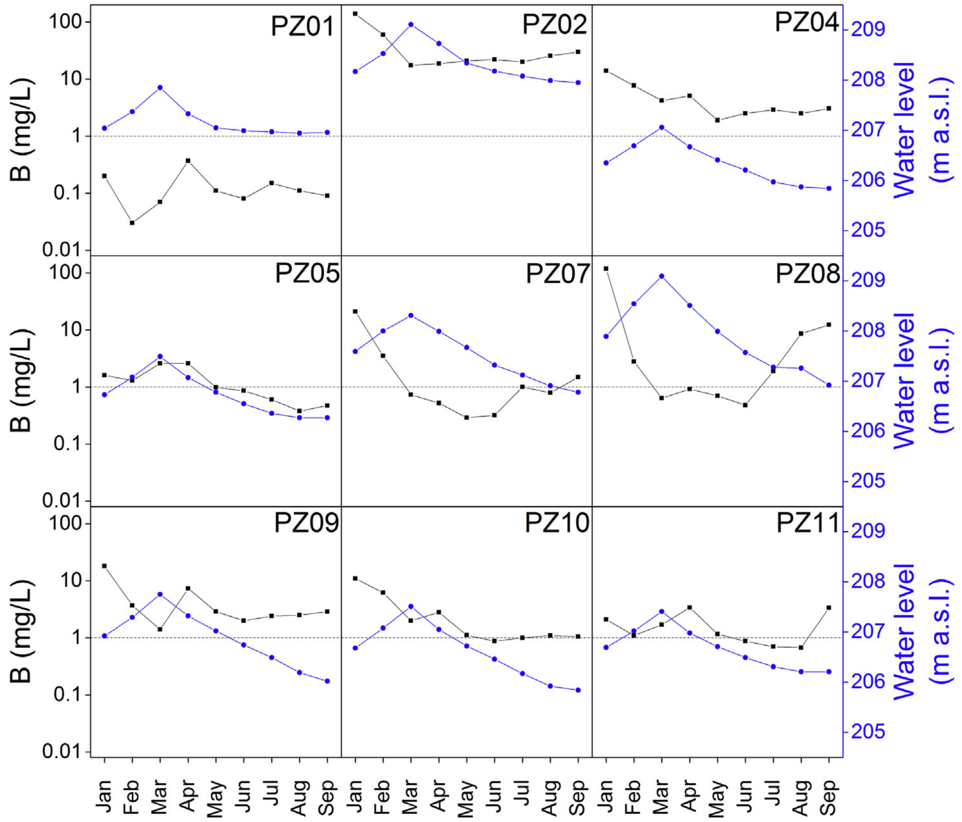

Fig. 4. Boron concentrations (in mg/L) (black line) and phreatic level (in meters) (blue line) from piezometers sampled during the monthly monitoring period of January to September 2013 (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Wastewaters collected in January–February 2013 from the industrial sewers were characterized by weakly alkaline pH (from 7.24 to 8.25) and low TDS values (<260 mg/L). The geochemical facies varied from Na–HCO_3 (AR1 and AR3) to Ca–SO_4–Cl (AR2 and AR4), while boron concentrations were <1 mg/L (Table 6), with the exception of AR3 (1.7 mg/L), which was collected from a sewage well connected to toilets.

Table 3
Depth (in meters), silt + clay fraction (in %), organic carbon content (in %), pH, concentrations of total boron (B_{tot}, in mg/kg), available boron resulting from leaching test with CO_2-saturated water and referred to sediment to water ratio of 1:20 (B_{av}, in mg/L) and $\delta^{11}B_{tot}$ values (in ‰) of the sediment core samples.

Sample ID	Depth	Silt + Clay fraction	C_{org}	pH	B_{tot}	B_{av}	$\delta^{11}B_{tot}$
PZ01-PM	0.60	25.1	0.08	8.21	196.86	<0.20	−11.0
PZ01-INT	2.50	61.2	0.33	7.79	150.01	<0.20	−10.5
PZ01-FC	4.85	47.4	0.28	7.67	106.47	<0.20	−14.2
PZ02-PM	0.50	36.1	0.22	7.62	54.79	1.15	−7.5
PZ02-INT	2.50	53.1	0.45	7.59	75.27	3.79	−7.1
PZ02-FC	4.55	32.2	0.08	8.66	47.98	8.66	−7.1
PZ02-DP	5.50				57.20	28.02	
PZ03-PM	0.63	65.5	0.55	7.82	42.57	1.77	−5.4
PZ03-INT	2.55	68.6	0.45	7.59	52.17	<0.20	−4.8
PZ03-FC	4.93	38.6	0.11	7.89	18.15	<0.20	−12.1
PZ05-PM	0.60	17.5	0.16	7.65	16.21	2.16	−12.2
PZ05-INT	2.50	19.3	0.11	8.15	29.26	4.26	−11.6
PZ05-FC	5.00	33.5	0.23	8.39	35.03	5.07	−10.1
PZ06-PM	0.55	31.8	0.43	8.10	25.13	4.12	−7.8
PZ06-INT	2.50	25.6	0.13	8.18	17.80	<0.20	−8.8
PZ06-FC	5.50	12.9	0.09	7.13	9.41	0.79	−5.6
PZ09-PM	0.43	22.5	0.10	8.33	16.46	0.98	−8.7
PZ09-INT	2.50	49.4	0.44	7.85	44.10	1.76	−6.1
PZ09-FC	5.00	20.7	0.07	7.20	11.22	1.02	−7.1
PZ09-DP	7.50				44.70	6.48	
PZ11-PM	0.63	14.1	0.11	8.23	13.02	2.02	−6.1
PZ11-INT	2.53	46.4	0.24	8.34	32.19	2.77	−8.1
PZ11-FC	4.70	28.5	0.12	8.17	15.68	1.29	−6.4

5. Discussion

The boron contamination in the shallow ground waters from the industrial area of Castelluccio appeared to be severe and persistent during the January to September 2013 monitoring survey with highly variable boron concentrations across sites. Sharp, though temporary, increments in boron contents were sporadically measured (e.g. in January 2013 PZ07 and PZ08 showed boron concentrations of 21 and 119 mg/L, respectively), suggesting the occurrence of temporary contamination events rather than a continuous release of the contaminant in the shallow aquifer.

The highest concentration of boron detected in the shallow groundwater samples were always found in the PZ02 waters, though showing a substantial decrease from January (139 mg/L) to September (30 mg/L). The lowest boron content in PZ02 waters was

Table 4
Concentrations of total boron (B_{tot}, in mg/kg), available boron resulting from leaching test with CO_2-saturated water and referred to solid to water ratio of 1:20 (B_{lct}, in mg/L), $\delta^{11}B_{tot}$ and $\delta^{11}B_{lct}$ values (in ‰) of slag and mud samples.

Sample ID	B_{tot}	B_{lct}	$\delta^{11}B_{tot}$	$\delta^{11}B_{lct}$
Preflot 1	18,268	12,550	−1.4	−2.3
Preflot 2	9745	4160	+0.6	−2.8
Postflot 1	8259	4146	−2.0	−1.3
Postflot 2	17,550	2516	−0.4	−1.8
Mud 1	863	421	−4.9	−3.4
Mud 2	3358	683	−1.4	−2.5

Table 5
TDS (in mg/L), pH and concentrations of the main solutes (in mg/L) of the slag and mud leachates (referred to solid to water ratio of 1:20).

Sample ID	Preflot 1	Preflot 2	Postflot 1	Postflot 2	Mud 1	Mud 2
TDS	258,565	439,207	96,238	91,144	315,342	408,623
pH	9.91	9.76	9.62	9.56	9.14	8.86
HCO_3^-	88,470	112,034	46,550	45,528	16,076	16,947
CO_3^{2-}	35,450	31,781	9566	8149	1094	605
Cl^-	29,960	60,540	2720	2520	33,940	117,840
SO_4^{2-}	10,420	65,680	5020	4880	74,300	86,560
Ca^{2+}	1680	2480	1804	2200	9700	16,660
Mg^{2+}	872	376	498	509	382	1030
Na^+	88,720	141,640	29,080	26,240	85,680	117,040
K^+	1058	6000	424	600	4660	9340

recorded in March 2013 (17.4 mg/L) and it coincided with the highest phreatic level measured in the PZ02 piezometer, suggesting a dilution effect induced by the uprising of the phreatic level.

5.1. *Natural water–rock interactions*

The origin of the strikingly high boron contents measured in the groundwater system is unlikely related to interaction processes with geological materials. The low B_{av} fraction resulted from the leaching tests on sediment samples suggested that boron in the studied sediments is mainly allocated in the minerals structures, particularly in the fine fraction (silt and clay) of sediments (Barth, 2000b; Chaudhary et al., 2005; Goldberg, 1997; Goldberg and Su, 2007; Goldberg et al., 2008; Gonfiantini and Pennisi, 2006; Lemarchand et al., 2007; Mather and Porteous, 2001; Simon et al., 2006; Tirez et al., 2010; Vengosh et al., 1994). This is also supported by the fact that no significant correlations between the B_{av}/B_{tot} ratio and the organic carbon content and pH (not shown) were observed. The $\delta^{11}B_{tot}$ values were negative, suggesting a preferential incorporation of the lighter boron isotope (^{10}B) as observed for adsorption of $B(OH)_4^-$ by clay minerals interacting with B-rich solutions (Chaudhary et al., 2005; Goldberg, 1997; Goldberg and Su, 2007; Goldberg et al., 2008; Pennisi et al., 2006a). Similarly, the enrichment in ^{10}B in the analyzed sediments was likely related to adsorption/desorption exchanges between sediments and B-rich waters. Accordingly, the highest B_{av} concentrations were found on the drill cores at the phreatic level with particular reference to the PZ02-FC and PZ02-DP whose waters (PZ02) showed the highest boron concentrations.

5.2. *Anthropogenic sources*

An anthropogenic source of boron was the most probable cause of contamination for the Castelluccio ground waters. As the permeability of the shallowest (sandy silt to gravel with sand) sediments is high, seepage of B-rich anthropogenic sources from the surface cannot be excluded as a possible pollution mechanism. The high permeability and the shallow depth of the unsaturated zone favor the seepage rate and reduce the sediment auto-depuration capability, making the shallow aquifer highly vulnerable. Since wastewaters showed negligible boron contents (≤1.7 mg/L) compared to shallow groundwater samples, the contamination was unlikely related to possible losses from the sewer pipes. The most B-enriched ground waters were characterized by peculiar geochemical facies (Figs. 1 and 2) with high concentrations of Na, Cl and SO_4 (Tables 1 and 1S (Supporting Material); SM1). The highest concentrations of boron were systematically measured in the PZ02 waters. These samples were collected in the most proximal site to the slag and mud deposits, whose B-rich leachates were actually characterized by a chemical composition dominated by Cl, Na and SO_4 (Table 5).

Table 6
Electrical conductivity (in mS/cm), TDS (in mg/L), temperature (in °C), pH, concentrations of the main solutes (in mg/L) and boron contents (in mg/L) of the wastewater samples are reported.

Sample ID	AR1	AR2	AR3	AR4
EC at 20 °C	0.05	0.16	0.33	–
TDS	38.9	99.2	256.5	90.3
T	5	5	7	–
pH	8.25	7.59	7.96	7.24
HCO_3^-	17	38.4	155	20
Cl^-	4.34	13.85	20.01	14
SO_4^{2-}	4.18	12.42	8.93	21
Ca^{2+}	3.66	12.15	18.39	14
Mg^{2+}	0.23	1.21	2.7	1.5
Na^+	3.55	8.87	23.7	8
K^+	3.06	2.55	7.01	1.4
B	0.2	0.4	1.7	0.6

A schematic reproduction of the industrial cycle of a local factory, which operates by using the studied slags and muds from raw products, whose melting and physical–chemical processes are covered by industrially patents, is shown in Fig. 5 along with the respective boron isotopic ratios.

The heavy boron isotope tends to increase along the industrial processing chain since the $\delta^{11}B$ values cluster around 0‰ in the pre-flotation slags and post-flotation wastes and between −4.9 and −1.4‰ in the industrial muds (Fig. 5). Slightly negative values were also measured in the slag and mud leachates (−3.4 to −1.3‰,

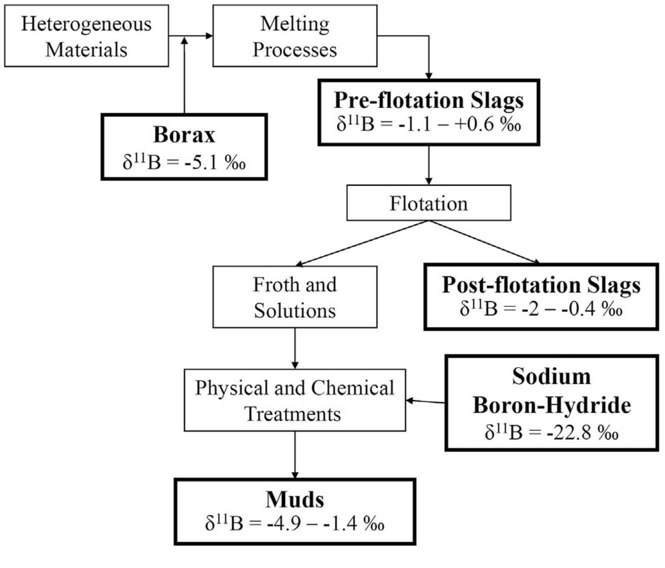

Fig. 5. Schematic reconstruction of the industrial cycle during which slag and mud by-products are produced.

respectively), whereas those of the raw products were more negative δ^{11}B values (i.e. borax and sodium boron-hydride −5.1 and −22.8‰, respectively). Raw products were stored in safe areas to prevent any leakage; hence, borax and sodium boron-hydride can unlikely be introduced in the groundwater system. This is also supported by the high Cl and SO_4 concentrations, not present in raw materials, associated with increments of boron in the groundwater samples. Contrarily, the chemical composition of the PZ02 waters showed clear analogies with that of slag and mud leachates (alkaline pH, high Na, Cl and SO_4 contents). Accordingly, as shown in the Na/Cl vs. B/Cl binary diagram (Fig. 6a), groundwater samples plot along a mixing line between low-B natural waters and industrial leachates. In particular, the most contaminated shallow ground waters showed Na/Cl and B/Cl ratios close to those of leachates from pre- and post-flotation slags, which were stored close to the PZ02 piezometer.

The boron isotopic ratios in the slag and mud leachates were within the variation interval of those measured for the PZ02 waters, although the latter varied over a wider range (from +0.3 to −8.7‰), being occasionally either higher or lower than those measured in the leachates (Tables 1 and 1S (Supporting Material) and 3). As a consequence, differently to what suggested by the chemical composition, the isotopic data provided no clear clues to support whether the boron contamination was caused by the interaction of meteoric water with the industrial materials. However, the variations of the δ^{11}B values measured in the PZ02 waters during the monitoring period could be related to a heterogeneous composition of the contaminant source. Such heterogeneity would also support the apparently not univocal isotope fractionation observed during the leaching tests carried out on the anthropogenic materials, which showed either ^{11}B enrichment, i.e. Postflot 1 and Mud 1, or ^{11}B depletion, i.e. Preflot 1, Preflot 2, Postflot 2 and Mud 2. Nevertheless, it is noteworthy to point out that, to the best of our knowledge, investigations on boron isotopic variations induced by water-industrial by-products interaction processes are not available in literature. Thus, both chemical and isotopic data in such materials represent remarkable information to be added to the boron isotope systematics.

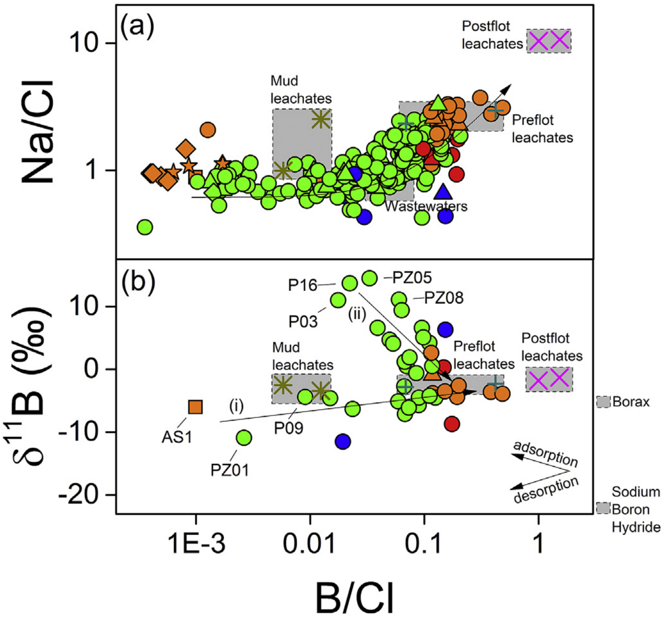

Fig. 6. (a) Na/Cl and (b) δ^{11}B (in ‰) vs. B/Cl binary diagrams. Symbols for natural waters as in Fig. 1 and industrial material leachates: cyan cross (+): pre-flotation slag, pink cross (×) = post-flotation slag, dark yellow stars = mud. Trends are highlighted with black arrows. Variation ranges for industrial material leachates, wastewaters and raw products (borax and sodium boron-hydride) are shown (gray areas). In Fig. 6(b) two end members are indicated as (i) and (ii) (see text for description) and adsorption/desorption theoretical trends are reported (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

The δ^{11}B values in the investigated waters ranged from −11.5 to +14.5‰, showing large spatial and temporal variations as well as the boron concentrations. In the δ^{11}B vs. B/Cl diagram (Fig. 6b), the analyzed waters are distributed along two different trends, which appear deriving from two distinct end-members: (i) a component with a low B/Cl (<0.01) ratio and δ^{11}B values <−5‰, and (ii) a component with a higher B/Cl (ca. 0.02) ratio with δ^{11}B values >+10‰. Whatever the end-members, the two trends are approaching the fields depicted by the industrial pre- and post-flotation leachates. The former component was likely related to desorption processes from sediments ($\delta^{11}B_{tot}$ values ≤−4.8‰), affecting waters with low boron contents (i.e. AS1, PZ01 and P09 waters in May–June 2012, showing boron concentrations and δ^{11}B values of 0.11, 0.1 and 0.38 mg/L and −6.0, −10.9 and −4.4‰, respectively). The latter component could be produced by either adsorption processes on clay minerals (leading to an increase in the δ^{11}B values and a decrease in the B/Cl ratios) or a distinct anthropogenic source, although neither the spatial distribution of the waters characterized by δ^{11}B values >+10‰ (i.e. PZ08, P03 and P16 waters, in May–June 2012 and PZ05 water, in January 2013) nor their proximity to waters with negative δ^{11}B values clearly support these hypothesis.

The isophreatic lines and the groundwater outflow direction, reported in Figs. 1 and 2, indicate that boron from the PZ02 (red circle) waters can affect the downstream ground waters. However, it is more difficult to explain the relatively high boron concentrations measured in the ground waters located westward the industrial area of Castelluccio, thus suggesting that a multiple boron source cannot be ruled out. Nevertheless, the contribution by industrial wastes to the contamination of the shallow ground waters appears to be most the probable source of contamination. Sporadic spilling events detected in other piezometers located near PZ02 and the slag and mud deposits, as highlighted by changes in the geochemical facies (e.g. PZ07 in January 2013 and P22 in February 2013) and sharp increments of boron content (e.g. PZ08 in January 2013), are apparently supporting this hypothesis.

5.3. Prevention and remediation strategies

Some strategies to minimize and/or remediate the boron contamination of the groundwater system in the industrial area of Castelluccio were adopted by the local industry in order to verify whether the slag and deposits were the effective source of boron. A roofing sheet was built, few months before the first sampling campaign, over the industrial waste deposits to avoid the interaction with the meteoric waters, whereas the by-products were moved to verify the presence of fissures in the reinforced-concrete pavement. Moreover, an inspecting video-camera survey was installed in the industrial sewer network to check the integrity of the sewer pipes. However, so far these mitigation procedures did not produce evident results.

A pump-and-treat system for the hydraulic containment is planned shortly to prevent the migration of the contaminated groundwater towards the residential zone situated to the west of the industrial area. The hydraulic barrier will be realized by pumping two wells (PZ02 and PZ10), which are located along the western side of the industry (Figs. 1 and 2). An extended bi-to tri-weekly monitoring of water levels and boron concentrations is planned to test the efficiency of the hydraulic barrier and to ascertain the (expected) natural decrease of the boron concentrations in the ground waters in those wells located outside the industrial area. Furthermore, if a significant drop of the boron concentrations will be observed after these actions, a direct responsibility of the industry could also be implied. Nevertheless, it is likely that before achieving boron concentrations lower than 1 mg/L, a relatively long period of time (months to years?) might be required since the decrease boron concentrations can be expected to be slowed down by adsorption/desorption processes on clay minerals.

6. Conclusions

This work has highlighted the presence of a severe boron contamination of ground waters in the industrial area of Castelluccio town, near the city of Arezzo (Tuscany, Central Italy). The boron contamination markedly affected the shallow aquifer, hosted in the alluvial deposits of the Arno River, whereas the deep aquifer (located in the sandstone formation, at about 60 m depth) showed no boron anomalies. The intermediate aquifer, hosted in pebbly–sandy levels inside clay deposits at about 30 m depth, only occasionally displayed boron content >1 mg/L and limited to those fenestrated wells that connect this aquifer with the shallowest one.

Since the geological setting does not allow to explain the high boron concentrations measured in the local groundwater system, the origin of the contamination was then ascribable to anthropogenic source(s). The groundwater chemistry has allowed to identify the PZ02 water as the proxy of the anthropogenic source. Some important analogies between the PZ02 chemical compositions and the leachates of the anthropogenic material (industrial slags and muds, resulting by melting and physical and chemical processes were borax and sodium boron-hydride are used) were recognized. Moreover, some abrupt increases in the boron concentrations, detected during the monitoring period in the ground waters situated close to the industrial site where slags and muds are stored, were associated with significant variations of the chemical composition of the groundwater samples, which tended to geochemically approach those of the industrial slag leachates as the B/Cl ratio increased. This may imply that the interaction between industrial materials and meteoric waters is possibly representing one of the possible sources of contamination, the seepage of pollutants from the surface being enhanced by the high permeability of the shallow alluvial deposits.

For the first time, bulk and leachate boron isotopic investigations were carried out in industrial materials such as slags and muds, which can be considered as useful reference values for further studies where waters contaminated by industrial by-products occur. Nevertheless, the isotopic imprinting of the industrial materials was not clearly detected in the groundwater samples, which showed significant spatial and temporal variations of $\delta^{11}B$ values.

Remediation actions such as a hydraulic barrier are expected to restore the pre-contamination conditions or at least minimize the dispersion halo of boron to the groundwater system of Castelluccio.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apgeochem.2015.08.008.

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