Title: Pollutant sources in an arsenic-affected multilayer aquifer in the Po Plain of Italy: implications for drinking water supply

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Abstract: We took an area of ~150 km2 around the town of Cremona to be an analogue for hydrogeological and hydrochemical conditions in arsenic-polluted and arsenic-free groundwaters across the Po Plain of northern Italy. We investigated anthropogenic influences on ground and surface water in the area using Cl/Br ratios, $\delta18O/\delta2H$ and other hydrochemical data from 32 groundwater wells, 9 surface waters, a sewage outfall and a rainwater sample.
The deep aquifer (160-260 m below ground level), which is tapped widely for public supply, is partly recharged by seepage from overlying aquifers (65-150 m below ground level) that are As-polluted (up to 144 µg/L As), producing a trend of increasing As with time. This threatens drinking water quality across the Po Plain where natural As-pollution of groundwater in aquifers at intermediate depth (50-120 m below ground level) is a basin-wide problem.
Groundwater quality in deep aquifers appears free of anthropogenic influences. In contrast, shallow groundwater and surface water are strongly affected by such pollution, although in some areas, quality remains unaffected. Outfalls from sewage-treatment plants and black water from septic tanks firstly affect surface waters, which then locally infiltrate shallow aquifers under high channel stages. Wastewater permeating shallow aquifers carries with it NO3 and SO4 which suppress reduction of iron oxyhydroxides in the aquifer sediments and so suppress the natural release of As to groundwater.

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The Editor,
Science of the Total Environment

Pollutant sources in an arsenic-affected multilayer aquifer in the Po Plain of Italy: implications for drinking water supply
by
Marco Rotiroti, John McArthur, Letizia Fumagalli, Gennaro A. Stefania, Elisa Sacchi and Tullia Bonomi

Dear Sir,

The authors of the script titled above submit it for publication in *Science of the Total Environment* as a research article. The study addresses the issue of human impacts on groundwater in the Po Valley of Italy, where groundwater is the principal source of water used for domestic supply. The paper exploits the developing use of Cl/Br as a tracer of anthropogenic impact, and shows that in some circumstances (that is, in our area) standard interpretations of Cl/Br do not work and need modification before correct conclusions can be drawn.

We find that groundwater pumped for municipal supply is threatened both by salinity and arsenic-pollution, both of which are drawn into the aquifer in response to pumping. Given that close to 10 million consumers in the Po Valley rely on groundwater for domestic supply, we feel a high-impact journal would be a suitable place to publish these results in order to help us alert appropriate national authorities to the problem they face. For these reasons, I think that this manuscript fits the Aims and Scope of *Science of the Total Environment* and thus is suitable for publication as a research article.

The manuscript has been prepared in accordance with the *Science of the Total Environment* guide for authors. It has not been previously published, in whole or in part, and that it is not under consideration by any other journal. All authors are aware of, and accept responsibility for, the manuscript.
All authors disclose any actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations within three years of beginning the work submitted that might inappropriately influence, or be perceived as influencing, their work.

Sincerely,

Marco Rotiroti

For how long will abstraction of deep groundwater be sustainable?
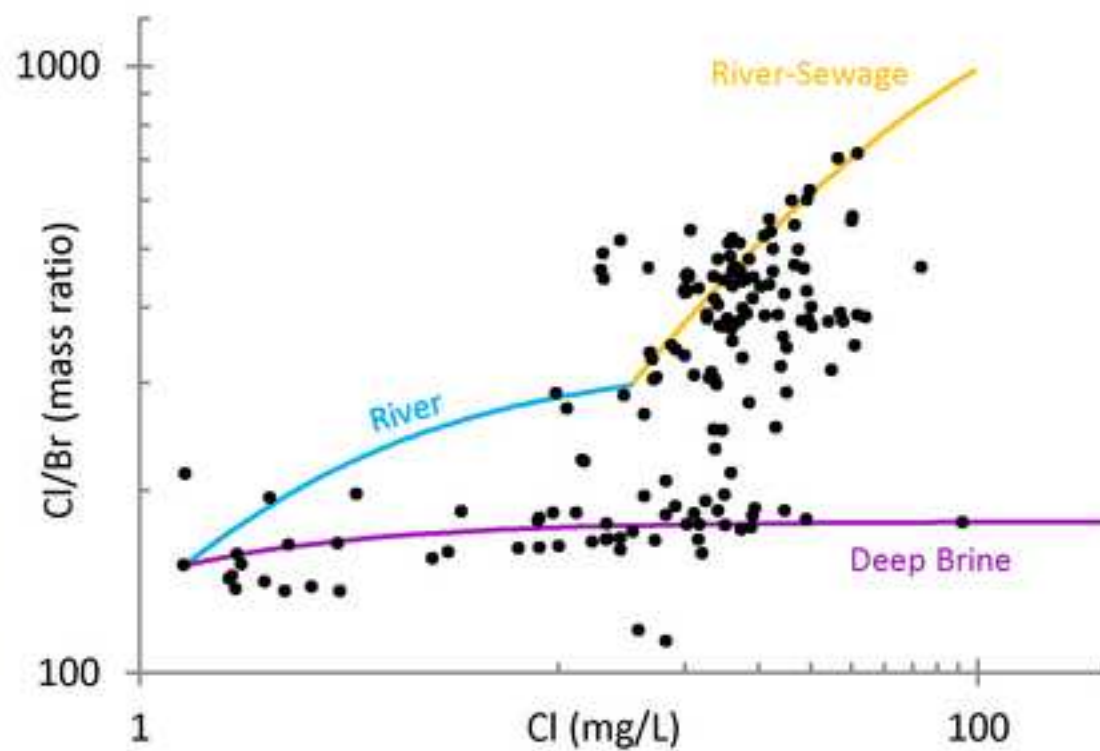
Highlights

Groundwater in the Po Plain is impacted by geogenic As-pollution and human activities

These impacts are evaluated using Cl/Br ratios and stable isotopes as tracers

Shallow aquifers are recharged by surface channels impacted by sewage effluent

Deep aquifers are partly recharged by seepage from overlying aquifers enriched in As

This produces increasing As with time in the deep aquifer tapped for drinking supply

1   **Pollutant sources in an arsenic-affected multilayer aquifer in the Po Plain of Italy:**

2   **implications for drinking-water supply**

3

4   *Marco Rotiroti[1]*, John McArthur[2], Letizia Fumagalli[1], Gennaro A. Stefania[1], Elisa Sacchi[3] and Tullia Bonomi[1]*

5

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12

13   **ABSTRACT**

14   We took an area of ~150 km^2 around the town of Cremona to be an analogue for hydrogeological and

15   hydrochemical conditions in arsenic-polluted and arsenic-free groundwaters across the Po Plain of northern Italy.

16   We investigated anthropogenic influences on ground and surface water in the area using Cl/Br ratios, $\delta^{18}O/\delta^2H$ and

17   other hydrochemical data from 32 groundwater wells, 9 surface waters, a sewage outfall and a rainwater sample.

18   The deep aquifer (160–260 m below ground level), which is tapped widely for public supply, is partly

19   recharged by seepage from overlying aquifers (65–150 m below ground level) that are As-polluted (up to 144 µg/L

20   As), producing a trend of increasing As with time. This threatens drinking water quality across the Po Plain where

21   natural As-pollution of groundwater in aquifers at intermediate depth (50–120 m below ground level) is a basin-

22   wide problem.

23   Groundwater quality in deep aquifers appears free of anthropogenic influences. In contrast, shallow

24   groundwater and surface water are strongly affected by such pollution, although in some areas, quality remains

25   unaffected. Outfalls from sewage-treatment plants and black water from septic tanks firstly affect surface waters,

26   which then locally infiltrate shallow aquifers under high channel stages. Wastewater permeating shallow aquifers

27   carries with it NO_3 and SO_4 which suppress reduction of iron oxyhydroxides in the aquifer sediments and so

28   suppress the natural release of As to groundwater.

30

31   **1. Introduction**

32

33   Human settlements on alluvial plains commonly use groundwater for domestic consumption, industrial use,

34   and irrigation. Natural and/or anthropogenic pollution in such settings may lower groundwater quality and so limit

35   exploitation, as is the case in the Po Plain of northern Italy (Onorati et al., 2006). The Po Plain is Italy's largest

36   alluvial basin and one of the larger in Europe, covering an area of 46,000 km^2. The plain is crossed by the Po River,

37   which flows 652 km from W to E collecting water from 141 total tributaries and hundreds of irrigation channels.

38   These channels discharge into the Po River the excess of irrigation water which is originally diverted from other

39   Alpine rivers that flow from N to S. The Po Plain is home to around 20 million inhabitants and is the most important

40   economic area of Italy. As a consequence, human activities affect both the 75% of its area that is agricultural land

41   and also the 10% that is urban development (Falcucci et al., 2007).

42   Groundwater abstracted from the Po Basin is used for irrigation, domestic supply, and industrial processes

43   (AdBPo, 2006). Irrigation in the Po Plain uses ~10 billion of m^3/y taken from rivers (67%, and distributed to the

44   field by channels), groundwater (22%) and springs (11%) (Zucaro, 2011). In order to avoid human impacts,

45   groundwater for public supply was initially taken from depths > 150 m. In some areas, such deep abstraction

46   encounters natural contamination by As (Carraro et al., 2015; Molinari et al., 2012; Rotiroti et al., 2014b). To avoid

47   this As-pollution, abstractions were deepened 200 – 300 m below ground level (m bgl) where As concentrations are

48   low, possibly because As is sequestered in neoformed sulphide minerals (Carraro et al., 2015; Rotiroti et al., 2014b).

49   Groundwater from depths > 200 m is up to ~54,000 years old and its exploitation may constitute mining of resource

50   that is replenished only slowly (Martinelli et al., 2014) by leakage from overlying aquifers that are As-polluted

51   (Rotiroti et al., 2014b) and/or by upconing from underlying aquifers that are saline (Conti et al., 2000; Martinelli et

52   al., 2014). Such migration is driven only by the hydraulic gradients caused by abstraction (Vassena et al., 2012).

53   Deep abstraction may even induce land subsidence (Martinelli et al., 2014).

54   Given the long-term threat to the sustainability of deep-groundwater posed by groundwater abstraction, we

55   have set out primarily to (a) asses the source of recharge to deep aquifers tapped for domestic supply and (b) for

56   deep groundwater in aquifers used for public supply, to test the potentially adverse effects on water quality in that

57 aquifer posed by influx of As-polluted groundwater and saline groundwater from adjacent. We also examine sources

58 of recharge to shallow aquifers and evaluate, if any, their degree of anthropogenic contamination and develop a

59 conceptual model of As release in the Po Plain.

60

61 **2. Materials and Methods**

62

63 *2.1. Po Plain Aquifer Geology and Architecture*

64 The alluvial systems of the Po Plain are underlain by Pliocene marine deposits and comprise Pleistocene

65 sediments prograded from W to E and were then overlain by Holocene fluvial sediments (Garzanti et al., 2011;

66 Marchetti, 2002). Alpine glaciations significantly increased the rate of glacio-fluvial aggradation and yielded gravel

67 and sand units that are intercalated into units of silt/clay. The thickness of the silt/clay units increases from north

68 (the Alpine foothills) to south (the Po River), reflecting the waning transport energy of glacial rivers (Ori, 1993).

69 This geological setting is particularly evident in Lombardy Region (Figure 1), where monolithic aquifer of gravel

70 and sand in the northern part of the plain (the higher plain) passes southwards into a multilayer system around the Po

71 River (the lower plain) (Bonomi, 2009; Cavallin et al., 1983; Perego et al., 2014).

72 In the multilayer system of lower plain, the deeper aquifers have a sluggish circulation and so longer

73 residence times for groundwater under natural conditions of flow (Martinelli et al., 2014). The long residence times,

74 and confinement of the deeper aquifers, promote reducing conditions and the mobilization of As, Fe, Mn and NH_4

75 driven by degradation of organic matter buried in peat sediments (Carraro et al., 2013; Francani et al., 1994; Rotiroti

76 et al., 2014b; Zavatti et al., 1995).

77

78 *2.2. Study Area*

79 This work refers to a 150 km^2 area around the town of Cremona (lower Po Plain, N Italy; ~70,000

80 inhabitants). The details of aquifer architecture and aspects of groundwater quality, including As-pollution have

81 been presented in Rotiroti et al. (2015a, 2015b, 2014a, 2014b) so only a summary is given here.

82 This multilayer aquifer comprises 5 aquifer units at differing depth ranges, where U means unconfined, S

83 means semi-confined, and C means confined: U (0–25 m); S (30–50 m); C1 (65–85 m); C2 (100–150 m); C3 (160–

84 260 m). Aquifers underlying C3, classified as Aquifer Group B (Carcano and Piccin, 2002), are not exploited in this

85   area since they are saline (Conti et al., 2000). Flow in aquifers U and S is from north to south owing to a strong

86   topographic control. Flow direction in the deeper confined aquifers (C1, C2, C3) is from NW to SE, which is also

87   the direction of regional groundwater flow (Vassena et al., 2012). The minimum hydraulic head is seen in C2

88   (Rotiroti et al., 2014b), resulting in convergent flow into aquifer C2 from both above and below. However, the

89   presence of well-fields for public water supply tapping aquifer C3 locally induces a fall of hydraulic heads (up to 6

90   m) (Cambi et al., 2005) such as to induce a reversal of flow to C3.

91   In aquifer U, redox condition range from reducing to oxidising in response to local factors. In other

92   aquifers, groundwater is anoxic and contains As, Fe, Mn and NH_4 in concentrations that commonly exceed

93   regulatory limits (10, 200, 50 and 500 µg/L, respectively).

94   The Adda and Po Rivers flow across the area (Figure 1). In addition, multiple shallow irrigation channels

95   both direct river water to fields for irrigation and act as drains at times of excess outflow when water tables are high

96   *i.e.* from May to August. Two main collector channels, the Morbasco and Cerca channels (Figure 1) were sampled

97   for this work. The Morbasco is ~32 km long and flows into the Po River. It receives treated sewage from the

98   municipal sewage-treatment plant of Cremona as well as untreated discharges from unsewered sanitation. The Cerca

99   Channel (~6 km long) flows into the Morbasco Channel and is the tail of the Naviglio Civico di Cremona Channel, a

100   ~57 km long canal fed by Adda and Oglio Rivers.

101   The public water supply to Cremona comprises groundwater from two well-fields, one of 9 wells that lies

102   100 m west of Cremona (Figure 1, box B) and another of 10 wells that lies east 200 m of Cremona (Figure 1, box

103   A). Both tap aquifer C3, which is the deepest aquifer. Before addition to the public supply, the groundwater is

104   treated to reduce concentrations of As, Fe, Mn and NH_4 (Sorlini and Gialdini, 2014).

105   Rainfall in the study area is typically 750 mm per year (Bonomi et al., 2008), falling mostly in spring

106   (April/May) and autumn (October/November) (Ginocchi et al., 2016). The study area is mostly agricultural, with

107   prevailing maize cultivation (Bartoli et al., 2012). From May to August maize is grown under surface (border)

108   irrigation. Irrigation water in Lombardy Region derives from rivers (96.8%), feeding an extensive channel network,

109   groundwater (0.7%) and other sources as springs, lakes, etc. (2.5%) and counts a total volume of ~8 billion of m^3/y

110   (Zucaro and Corapi, 2009). This type of irrigation started as early as the 12th Century with the construction of the

111   first important channels (Marchetti, 2002), and it has been practised on its present scale since the 50s/60s. Irrigation

4

112 constitutes an important source of recharge for shallow aquifers, together with precipitation, so much that their

113 hydraulic heads have an increase generally from April to September (Facchi et al., 2004).

114   An important economic activity in the area that could have implications on water quality is livestock

115 farming, in particular, piggery. Pig manure is often used as soil fertilizer, instead of synthetic compounds such as

116 ammonium sulphate, so that this area was classified as nitrate-vulnerable zone (91/676/EEC).

117

118 *2.3. Water Quality Data*

119   We collected 32 groundwaters from private and public supply wells, 9 surface waters (5 river and 4

120 channel), one sample of rainwater and a sample of outfall from Cremona's municipal wastewater treatment plant

121 from July 2012 to October 2014 (Figure 1). In addition, the water supply company of Cremona provided

122 unpublished historical data on water quality (data for 115 groundwaters from 37 wells over the period 2001-2011).

123   Samples were analysed for major ions, trace elements (As, B, Bi, Br, Cd, Cr, Co, Cu, Fe, I, Mn, Mo, Ni, Pb,

124 Se, Sb, V, and U), dissolved organic carbon (DOC), $\delta^{18}O$ and δ^2H in water, $\delta^{13}C$ in dissolved inorganic carbon

125 (DIC) and $\delta^{15}N$ in NH_4. Water sampling and laboratory analyses were performed using standard methods, details are

126 reported in Table S1 together with method quantitation limits and the full list of measured parameters.

127

128 *2.4. End-member Mixing Models*

129   To identify the influence of salt, as a proxy for human influence on ground and surface waters, we use a

130 mixing model of Cl/Br mass ratio against Cl concentration (Alcalá and Custodio, 2008; Davis et al., 2004, 1998;

131 Hoque et al., 2014; Katz et al., 2011; McArthur et al., 2016, 2012; Panno et al., 2006; Vengosh and Pankratov,

132 1998). To investigate whether aquifers were being salinized by deep brine injection or flushed of brine by

133 freshwater, we used the mixing-model approach of Ravenscroft and McArthur (2004), which uses B and Cl to

134 identify ion-exchange of B through these processes. For these models, the end-members were as follows:

135   (a)   uncontaminated groundwater represented by our two most dilute groundwaters, Well 68 with 1.3 mg/L

136   Cl, 19.1 µg/L B, and Cl/Br of 150, and Well 64, with 1.7 mg/L Cl, B 13.8 µg/L and Cl/Br of 151;

137   (b)   river water with 14.8 mg/L Cl and Cl/Br of 297, the average composition of our 10 river samples;

138   (c)   sewage effluent, with 98.2 mg/L Cl and Cl/Br of 981;

139   (d)   road salt from the local highway company, which has 60.4% Cl and Cl/Br of 7545;

140   (e)   domestic salt, with 59.7% Cl and Cl/Br of 3970, the average composition of 14 samples of table,

141   cooking and diswhasher salts obtained from retail outlets in Cremona (Table S2);

142   (f)   a deep brine of Monticelli (Boschetti et al., 2010), with 73,015 mg/L Cl, 17,673 µg/L B, and a Cl/Br of

143   152, and a deep brine of Cremona, end member brine with Cl/Br of 177 and a Cl of 19,500, the Cl/Br

144   being derived from the slope of a linear regression of Br on Cl for aquifer C3 (Figure S1, $r = 0.999$).

145

146   **3. Results**

147

148   *3.1. Water Quality*

149   Measured water quality data are reported in Table S1. The compositions are similar to groundwater

150   compositions from the area reported before (Rotiroti et al., 2014b). In particular, concentrations of As, Fe, Mn and

151   NH_4 are high. Concentrations of B, Ba, Cd, Cr, Co, Cu, Mo, Ni, NO_3, Pb, Se, Sb, SO_4, V, and U are less than WHO

152   and Italian regulatory limits. Depth profiles of conservative and redox-sensitive species measured in October 2014

153   are shown in Figure 2, and other relevant parameters in Figure S2.

154   The EC is higher in shallow aquifers (U and S; mean value of 947 µS/cm) than in deep aquifers (C1, C2

155   and C3; mean of 516 µS/cm) aquifers. Concentrations of Cl and B have similar profiles, with highest concentrations

156   in aquifer U (up to 52 mg/L and 238 µg/L, respectively), a downward decrease to a minimum in C2 with the

157   underlying aquifer C3 having slightly higher concentrations (up to 28.8 mg/L and 87.6 µg/L, respectively).

158   Nitrate is detectable only in aquifer U, with concentrations ≤ 42.8 mg/L. Concentrations of Fe and Mn are

159   highest in reduced parts of aquifer U (≤ 5.41 and ≤ 0.98 mg/L, respectively) and decrease downward to aquifer C3.

160   Concentrations of SO_4 are highest in aquifer U (≤ 171 mg/L) and a decrease downward, being at or below the

161   detection limit (0.05 mg/L) in the deep aquifers. Concentrations of DOC have no clearly identifiable depth-trend and

162   range between 2.8 and 7.6 mg/L, with one outlier of 14.1 mg/L in aquifer U (Well 4).

163   The profiles of Br and I comprise higher values in U (up to 132.8 and 13.1 µg/L, respectively), a downward

164   decrease and a peak in C3 (up to 166.1 and 25.6 µg/L, respectively). Concentrations of As, NH_4 and PO_4 and H_4SiO_4

165   increase downwards to S and C1 (≤ 168 µg/L, 2.0, 1.4, and 42 mg/L, respectively) but decrease downwards

166   thereafter.

167   Duplicated sampling of groundwater for some wells after 27 months shows little difference in composition

168   (Figure S3). Concentrations of As, Fe, Mn and NH_4 from July 2012 are slightly higher than those from October

169   2014 but not statistically difference at the 5% significance level (Mann-Whitney U test; p-value of 0.21, 0.67 and 1

170   for As, Fe and Mn, respectively). A small but significant difference in NH_4 (p-value of 0.03) might reflect the fact

171   that samples collected in October 2014 were filtered through 0.2 μm whilst those collected in July 2012 were not.

172   For surface waters, Br and I apart, all concentrations were higher in channel waters than in river water

173   (Table S1 and Figure 2). For Br and I, the converse was true, with Br being 50 μg/L in rivers and 37 μg/L in

174   channels whilst I was 4.0 in rivers and 1.6 in channels.

175   No surface-water sample exceed the Italian regulatory limits for surface waters (D. Lgs. 152/06). River

176   water quality results quite stable over the two monitoring dates (July and October 2014) whereas channel waters had

177   higher mean concentrations for all measured species in October 2014 with respect to July 2014.

178   Rainfalls in Cremona during 3 days before the surface water sampling were 3.6 mm in July 2014 and 0.0 in

179   October 2014; the daily average stage of Po River at Po3 location during the sampling was 28.56 m above sea level

180   (a.s.l.) in July (22/07/14) and 28.26 m a.s.l. in October (07/10/2014) (ARPA Lombardia). On the basis of these data

181   and visual observation in the field, it can be considered that channels had higher stages in July 2014 and lower

182   stages in October 2014 whereas the Po River had comparable stages during the two sampling dates.

183

184   *3.2. Stable Isotopes*

185   Values of δ^2H *vs* $\delta^{18}O$ (Figure 3a) plot on or close to the local meteoric water line (LMWL) of northern

186   Italy (Longinelli and Selmo, 2003) and of Cremona (Francani et al., 1994) showing that evaporation has not affected

187   our groundwaters during their time as recharge. The groundwaters cluster between the more enriched values for

188   local precipitation and the more depleted values for the Po River, the latter reflecting the strong influence of water

189   from the Western Alps (Marchina et al., 2015). Depth profiles of $\delta^{18}O$ show little by way of trends (Figure 3b), with

190   groundwaters from shallow and deep aquifers having similar values, except for 3 shallow wells (5, 11 and 26) that

191   are more enriched. The $\delta^{18}O$ values of shallow groundwaters fall between those of the Po River (-10.1 to -9.2;

192   Marchina et al., 2016, 2015) and local precipitations (-7.73 to -5.95 ‰; Longinelli and Selmo, 2003). Values of $\delta^{18}O$

193   for deep groundwaters fall within the range reported for deep aquifers of the Po Plain by Pilla et al. (2006) of -9.0 to

194   -8.2 ‰ and nearby sites at Lodi (-8.93 to -8.33 ‰; Guffanti et al., 2010), Pavia (~ -8.7 to ~ -8.5 ‰; Pilla, 1998),

195   Milano (~ -9.8 to ~ -8.3 ‰; Avanzini et al., 1994), Piacenza (-9.42 to -7.38 ‰; Martinelli et al., 2014) and Parma (-

196   9.86 to -7.05 ‰; Martinelli et al., 2014).

197   Measured $\delta^{13}C$ values range from -9.3 to -14.9 ‰, an interval that reflects supersaturation with respect to

198   calcite and dolomite (Rotiroti et al., 2015b). The values of $\delta^{15}N$ measured in NH_4 range from 4.09 to 7.81 ‰. These

199   data fall within the range of NH_4 produced by the mineralization of soil organic nitrogen and peat (from ~ +2 to ~ +8

200   ‰; Kendall, 1998), of sewage and septic tanks (~ +4‰; Gooddy et al., 2016) and of wastewaters outfalls (~ +4 to ~

201   +16 ‰; Hood et al., 2014), but are distinct from the NH_4 isotopic composition of synthetic fertilizers (-7.4 to

202   +3.6‰; Vitòria et al., 2004b), of pig manure (+8 to +15‰; Vitòria et al., 2004a) and of landfill leachate (from ~ +7

203   to ~ +10 ‰; Gooddy et al., 2014).

204

205   *3.3. Cl/Br Ratio*

206   On a cross-plot of Cl/Br against Cl (Figure 4) that includes both our data and historical, most groundwaters

207   from the shallow aquifers (U and S) fall close the river-sewage mixing line or are more enriched in Cl. One sample

208   (Well 3) is enriched in Br. Only one groundwater (Well 32) plots towards the unpolluted field marked by low Cl/Br

209   and low Cl (McArthur et al., 2012 and reference therein).

210   Deep groundwaters show no anthropogenic influences. The deep aquifers (C1, C2 and C3) mostly plot

211   along a mixing line between our dilute groundwater end-member and a deep brine end-member. At lower Cl

212   concentrations, some addition of Br from organic decay may have pulled many of the more dilute groundwaters

213   below brine-mixing lines. The Cl/Br value of 177 is consistent with the Cl/Br of 152 measured in the Monticelli

214   brine (Boschetti et al., 2010), substantiating the hypothesis that salinity in aquifer C3 can be mainly governed by a

215   mixing between dilute groundwater and deep brine. The sample from Well 50, and in a minor way that from Well

216   66, shows higher Cl/Br with respect to the others measured in deep aquifers.

217   River and channel data cluster separately, the former having lower Cl/Br. Po River waters (Po1, Po3 and

218   Po4) are similar and show little difference between sampling dates (average Cl/Br of 327). Waters Ad1 and Po2

219   have similar Cl/Br (mean of 280 in July 2014 and 223 in October 2014). Water Po2 likely reflects the composition

220   of the Adda rather than the Po as it was collected ~500 m downstream of the confluence of the Adda and Po Rivers

221   before the rivers mixed fully. Channel samples plot close to the river-sewage mixing-line. Those collected in

222   October 2014 have an average Cl/Br of 451 that overlaps values for the shallow aquifers. Those collected in July

223   2014 have an average Cl/Br of 478 and plot slightly apart from shallow aquifers.

224   The sample of rainwater plots at low Cl but has a highish Cl/Br of 213. Similar high values were found for

225   rain in south-eastern France at Gard (Cl/Br 201) and Hérault (Cl/Br 269) (Ladouche et al., 2009). The sample

226   collected from Cremona's sewage-treatment plant has a Cl/Br of 981; this is slightly higher than values for sewage

227   effluent from Israel (410 – 873; Vengosh and Pankratov, 1998) and the USA (300 – 600; Davis et al., 1998) but is

228   within the range of septic-tank effluent in West Bengal, India (690 – 2530; McArthur et al., 2012).

229

230   **4. Discussion**

231

232   *4.1. Recharge to shallow aquifers*

233   Groundwater quality of most shallow groundwaters are contaminated by human activity as shown by the

234   high EC and Cl/Br values up to 1174 µS/cm and 624, respectively. Nevertheless, rare instances of uncontaminated

235   groundwater occur *e.g.* Well 32, with Cl/Br of 197, a value close to that of 214 found in our spot rainwater sample.

236   Such rare exceptions apart, the high Cl/Br of most shallow groundwater and channel waters arises from inputs of

237   raw and treated sewage effluents with Cl/Br up to 981 (Figure 4). The Morbasco Channel, in particular, receives the

238   outflow of 3 wastewater treatment plants and some untreated effluents from domestic unsewered sanitation.

239   Shallow groundwaters do not fall on the mixing line between effluent and uncontaminated groundwater, a

240   fact that suggests direct contamination of groundwater by effluent is uncommon, rather, shallow groundwaters fall

241   on a mixing line between channel waters and sewage effluent, a concordance that suggests effluent recharge aquifers

242   indirectly as a component of channel water after dilution with natural channel flow. Our Cl/Br data therefore

243   confirms the findings (Facchi et al., 2004; Pilla et al., 2006) that irrigation channels in the Po Plain mainly act as

244   loosing streams and are an important source of recharge to shallow aquifers. Notwithstanding that, point-source

245   contamination by untreated domestic sewage has been reported from parts of the Po Plain (Delconte et al., 2014;

246   Sacchi et al., 2013).

247   The tendency of some shallow groundwater $\delta^{18}O/\delta^2H$ values toward those of local precipitation (Figure 3)

248   suggests that rainfalls are also an important source of recharge for shallow aquifers.

249   A minority of shallow groundwaters plot in a scatter array towards the low Cl/Br of groundwater from Well

250   3. These lower Cl/Br suggest inputs of Br from organic degradation may locally contribute Br preferentially to Cl

251   and so lower Cl/Br. Groundwater from Well 3 contains 4.0 mg/L of Fe, which attests to the reducing capacity of

252   aquifer U at this point and supports the suggestion that, locally, degradation of buried peat may be driving redox

253   (Rotiroti et al., 2015b, 2014b). Such degradation would contribute additional Br to groundwater. Conformation of

254   this suggestion derives from the TANGRAM$^©$ database (Bonomi et al., 2014) which shows that 4 m of the total 6-m

255   screen-length of Well 3 straddles a peaty sand unit. Nevertheless, given the strong human impact on shallow

256   groundwaters, we cannot say definitively that street runoff (Vengosh and Pankratov, 1998) and/or brominated flame

257   retardants (Winid, 2015) are not the cause of the lower Cl/Br array in shallow groundwaters.

258   The generally higher Cl in shallow groundwaters than in channel water is probably not due to evaporation

259   of channel water before and during infiltration because the $\delta^{18}O$ and δ^2H of shallow groundwaters show no

260   evaporative trend (Figure 3). The data fall within a narrow range (–9.1 and –8.4 for $\delta^{18}O$; –58.9 to –55.5 for δ^2H)

261   and plot close to the LMWL for the area (Figure 3). The higher Cl concentrations in groundwaters compared to

262   channel waters is therefore attributed to time-biased sampling of channel water that vary their Cl concentration

263   through the year in response to changing inputs of sewage effluent and its dilution by natural flow.

264   Shallow groundwaters have higher Cl/Br than river waters (Figure 4), and a different $\delta^{18}O/\delta^2H$ (Figure 3),

265   proving that the study area's main rivers, the Po and the Adda, do not directly recharge shallow aquifers. This

266   finding confirms similar conclusions of others (Marchina et al., 2016; Martinelli et al., 2014; Rotiroti et al., 2014b)

267   that the Po River is mainly a gaining river fed by groundwater in the study area, rather than a losing river sourcing

268   groundwater, despite widespread abstractions of groundwater for industrial and domestic use.

269   The high concentrations of SO_4 found in shallow groundwater ($\leq$ 171 mg/L) must have an anthropogenic

270   source, given the human impact on shallow groundwater revealed by Cl/Br values and SO_4/Cl mass ratios up to 7.2

271   and may derive from the use of manure fertilizer (Menció et al., 2016). Concentrations of NO_3 are generally low,

272   owing to the prevalence of reducing conditions, and so nitrate reduction, in much of the shallow aquifers (U and S)

273   around Cremona, as is the case for most of the lower Po Plain (Balestrini et al., 2016; Sacchi et al., 2013). In rare

274   oxic parts of the shallow aquifers nitrate persists at high concentrations (Well 5, 43 mg/L NO_3) in association to high

275   SO_4, further confirming its anthropogenic source.

276

4.2. Recharge to deep wells

Deep groundwaters with $\delta^{18}O$ in the range -9.0 to -8.2 ‰, a range similar to ours, have been traced to recharge areas in the high Po Plain and Alpine foothills (Pilla et al., 2006), with elevations of 150-250 m asl, so our deep groundwaters likely are also recharged at similar locations.

Concentrations of Cl in the deep aquifer C3, the most exploited for public supply, range up to 90 mg/L. With the exception of groundwater from Well 66, the fresher groundwater samples with Cl < 10 mg/L plot below the mixing line for brine with Cl/Br of 177 (Figure 4). This suggests excess Br from organic decay may be influencing these dilute samples. The suggestion is confirmed by a close co-variance of excess Br with both NH_4 (Figure S4a) and DOC (Figure S4b), all three of which are products of microbial fermentation of sedimentary organic matter, which is known to increase Br in groundwater at the expense of Cl: degradation of lignite and peat gave groundwaters in the Hula Valley of Israel values of Cl/Br as low as 4 (Nissenbaum and Magaritz, 1991). Degrading organic matter in soils of Western Australia were reported with Cl/Br between 6 and 10 (Gerritse and George, 1988), with similar low values in peats from Chile and Germany (Biester et al., 2012; Biester et al., 2006). A quantification of the relation between excess Br and DOC was achieved by Desbarats et al. (2014).

Deep groundwaters from aquifer C3 with Cl concentrations above 10 mg/L plot close to a mixing line with Cl/Br of 177 (Figure 4). Deep brines are common in the Po Plain, *e.g.* the Monticelli brine with a Cl/Br of 152 (Boschetti et al., 2010). Monticelli is located on the same buried thrust that underlies the study area of Cremona (Bonini, 2007). Buried thrust may channel uprising deep brines (Pilla et al., 2015) and impose a degree of uniformity to their composition. The higher Cl concentrations in our C3 groundwater therefore are assumed to come from minor mixing with such deep brines, which have Cl/Br considerably below the seawater value of 288.

This mixing appears to have been historical, and is now in reverse, as aquifer C3 is being flushed of brine. Six indicators attest to this flushing: (a) the high concentrations of B in groundwater from aquifer C3 ($\leq$ 87 µg/L) release by ion-exchange; (b) mass ratios of Na/Cl mostly above 2 and ranging up to 8.9, compared to 0.54 for seawater, showing the presence of excess Na over Cl; (c) a strong correlation between B and Na (Figure S5a); (d) a strong inverse correlation between Ca and Na (Figure S5a); (e) groundwater compositions that plot along the exchange line as defined by Re et al. (2013) (Figure S5b), and (f) compositions that plot in the freshwater–flushing field of a B *vs* Cl cross plot (Ravenscroft and McArthur, 2004) (Figure S5c).

11

304   Iodine concentrations in aquifer C3 range up to 26 μg/L, giving Cl/I mass ratios between 890 and 2020

305   (Table S1; mean 1258). These values are well below the marine value of ~300 000 (Skinner and Berger, 2003). Such

306   low Cl/I have been reported before for deep groundwater of the Po Plain (Boschetti et al., 2010; Conti et al., 2000)

307   and must result from the input to groundwater of I from organic degradation.

308   The above discussion points out that at least part of groundwater abstracted from C3 seems to be replaced

309   from underlying aquifers in Wells 67 and 110 and from overlaying aquifers in Well 66.

310

311   *4.3. Temporal trends of groundwater composition*

312   Our discussion above shows that aquifer C3 is being flushed of saline contamination but not at what rate.

313   Development of aquifer C3 for most public supply in the area raises the question as to how sustainable the resource

314   might be, how quickly groundwater composition is changing with time, and whether the quality is increasing or

315   decreasing *i.e.* flushing is continuing now.

316   Our repeat-sampling interval of 27 months is too short to do other than place an upper limit on rate of

317   change of groundwater composition. Nevertheless, we attempt to do so using the average concentration of As and Cl

318   in C3 over the sampling dates available. These are reported in Figure 5. We use average concentration, rather than

319   the time-series for each well because the available sampling dates are a few, and wells were not all sampled on the

320   same dates. The average compositions suggest that no discernible trend is shown by Cl concentrations, but that As

321   concentrations show a slight increase with time. The increase of As in C3 cannot result from upward leakage of As-

322   rich groundwater in underlying aquifers (Conti et al., 2000) as that would be accompanied by Cl, which is not seen;

323   indeed, the aquifer is freshening. The change in As concentration may result from continuing slow reduction of

324   sedimentary iron oxyhydroxides with concomitant release of As to groundwater (Rotiroti et al., 2015b). Such an

325   hypothesis is compatible with the near absence of SO_4 in groundwater in aquifer C3, reduction of which had it been

326   present might have sequestered As from solution in neoformed pyrite. Anyhow, the As release via iron

327   oxyhydroxides reduction coupled to organic matter degradation seems to have a minor contribution to As-pollution

328   in C3 since here excess Br and As are uncorrelated (Figure S4c). Finally the increase in As concentrations might

329   result from leakage downwards of As-polluted groundwater from overlying aquifers C1 and C2 in response to

330   abstraction. This seems confirmed by the October 2014 data since Well 66, which has the highest As concentration

331   in C3 (59.8 μg/L), is the sole from C3 that plots above the mixing line for brine.

332

4.4. Strengthening the conceptual model for As release

In anoxic aquifers worldwide, natural pollution by arsenic arises from the reductive dissolution of sedimentary iron oxyhydroxides. This mechanism has been invoked to explain such pollution in the USA (Korte, 1991; Korte and Fernando, 1991; Matisoff et al., 1982), the Bengal Basin (Nickson et al., 1998, 2000 et seq.), the Red River Basin, Vietnam (Berg et al., 2001; Postma et al., 2007), alluvial aquifers in Pakistan (Husain et al., 2012; Nickson et al., 2005), the Po Plain of Italy (Carraro et al., 2013; Rotiroti et al., 2014b), the Mekong River Basin of Cambodia (Rowland et al., 2007 et seq.) and other worldwide locations (see Gulens et al., 1979; Ravenscroft et al., 2009 for reviews). The reduction of sedimentrary iron oxyhydroxides is driven by microbial metabolism of organic matter (Banfield and Nealson, 1997; Chapelle and Lovley, 1992; Chapelle, 2000; Lovley, 1997; Nealson, 1997). In the multilayer aquifers around Cremona, the reduction has been postulated to be driven by the degradation of peat incorporated into semi-permeable silty and clayey aquitards (Rotiroti et al., 2015b; Rotiroti et al., 2014b).

In groundwaters that show little anthropogenic influence (aquifers C1, C2, C3 and well 32 tapping aquifer S) concentrations of As, PO_4, and NH_4 co-vary, albeit weakly (Figure S6). The covariance provides confirmation of the strong co-absorption onto iron-oxyhydroxides of As and PO_4 and their concomitant release on its reduction (Ravenscroft et al., 2001). Microbial metabolism of organic matter in anoxic waters not only reduces iron oxyhydroxides but also generates NH_4 from amino acids, so the positive correlation between As and NH_4 (Figure S6b) although weak, provides some confirmation that these process co-occur. Moreover, the measured values of $\delta^{15}N$, together with other indicators (Francani et al., 1994; Rotiroti et al., 2015b), suggest that NH_4 derives from natural organic matter. Therefore, the assumption that peaty aquitards are probably the main source of organic matter driving As release in this system seems reasonable.

Reduction of SO_4 can generate neoformed pyrite that sequesters As. Concentrations of As are highest in aquifers S and C1 but their concentrations of SO_4 differ markedly (Table S1). These observations suggest that the process of SO_4-reduction, if it occurs at all in these aquifers, does not to reduce As concentrations to zero.

The release of As to shallow aquifers in Cremona is suppressed by anthropogenic inputs of NO_3 and possibly SO_4 from wastewater, as occurs in the Bengal basin. (McArthur et al., 2016, 2012). Reduction of iron oxyhydroxides is suppressed by NO_3 because NO_3 is reduced more easily than Fe^{3+} by microbial processes. In addition, the presence of SO_4 allows co-precipitation of As in sulphides formed by SO_4-reduction. A weak negative

360   correlation between Cl/Br, indicative of wastewater discharges high in NO_3 and SO_4 and concentrations of As

361   (Figure S7) appears to confirm the suppressant effect of waste waters on As-pollution in the study area. Increasingly

362   stringent regulations on the use of N-based fertiliser in the Po Plain (91/676/EEC), and so the designation of large

363   areas of the Po Plain as nitrate-vulnerable zones (Sacchi et al., 2013) therefore has the potential to decrease NO_3

364   inputs to the shallow aquifers, thereby allowing the wider development of anoxia and so an increase in As-pollution.

365

366   **5. Conclusions**

367

368   This study dealt with the assessment of the recharge to shallow aquifers and the source of water to deep

369   wells used for drinking water supply in the As-affected multilayer aquifer in Cremona, considered as an analogue

370   for the aquifers of the lower Po Plain. Our findings are that:

371   a)   shallow aquifers receive considerable recharge from irrigation/drainage channels that are polluted by

372   sewage effluent, giving rise to high Cl/Br values in shallow groundwaters. Nevertheless, in some areas

373   shallow aquifers are still free from such an influence;

374   b)   shallow groundwater is not much affected by As-pollution because of the high NO_3 and SO_4 concentrations

375   in channel water due to sewage effluents. Reduction of NO_3 suppresses As-pollution by suppressing

376   reduction of iron oxyhydroxides. Reduction of SO_4 generates pyrite that can sequester As from solution and

377   so lower concentrations of pollutant As;

378   c)   deep groundwater abstractions from aquifers C2 and C3 supply much of the regions domestic supply,

379   especially for the town of Cremona. The supplies are unaffected by anthropogenic pollution but have

380   concentrations of Cl that are increased by historical mixing with deep brines. The deep aquifers are

381   currently being flushed of this Cl-contaminated water by fresher water, as evidenced by strong ion-

382   exchange loss of Ca from recharging waters, with concomitant increase in B and Na;

383   d)   the As-pollution of deep aquifers is likely;

384   e)   over a 27-month period, As-pollution in the deep aquifers may have increased slightly as a result of

385   drawdown of As-rich groundwater from overlying aquifers. If confirmed, the increases pose some threat to

386   the treatment plants currently dealing with purification of groundwater for public supply, since treatment

387   may be based on an assumed constant composition of groundwater;

388   f)   to assess this risk, routine monitoring for As on a monthly basis should be instituted.

389   These findings related to the Cremona area could have implications on drinking supply management in the whole

390   lower Po Plain (5-10 million inhabitants) since here natural As contamination in intermediate aquifers is a regional

391   problem and many wells that serve drinking supply are tapped in deep aquifers underlying the peak of As

392   concentration.

393

401

402   **Appendix A. Supplementary material**

403   Additional tables (Tables S1-S2) and figures (Figures S1-S7) are the supplementary material related to this article.

404

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Figure Captions

Figure 1. Study area with rivers, channels and sampling points labelled with ID number; wells are classed for each tapped aquifer; total 14 groundwater and 1 surface water samples were collected in July 2012, 9 surface water and 1 rain samples were collected in July 2014 and 28 groundwater, 9 surface water and 1 sewage samples were collected in October 2014; Uox: zone with oxidising conditions in aquifer U; Ured: zone with reducing conditions in aquifer U; Umix: zone with mixing conditions in aquifer U; S: aquifer S; C1: aquifer C1; C2: aquifer C2; C3 aquifer C3.

Figure 2. Groundwater and surface water concentrations of conservative and redox-sensitive species measured in 2014 over depth; symbol length corresponds to well screen interval; Uox: oxidized zone of aquifer U; Ured: reduced zone of aquifer U; S: aquifer S; C1: aquifer C1; C2: aquifer C2; C3: aquifer C3.

Figure 3. (a) Plot of measured and reference δ^2H vs $\delta^{18}O$ in groundwater, Po River water and precipitation; LMWL: local meteoric water line by [a]Longinelli and Selmo (2003) and [b]Framcani et al. (1994); also plotted are weighted-means of precipitation by [c]Longinelli and Selmo (2003) in 4 stations at Mantova, Milano, Parma and Piacenza, all near Cremona and values of the Po River in Cremona by [d]Marchina et al. (2015, 2016). (b) Measured $\delta^{18}O$ over depth; symbol length corresponds to well screen interval; sampling points labelled with ID number are cited in the text; dashed boxes represent reference range values (see Section 3.2 for range values). U: aquifer U; S: aquifer S; C1: aquifer C1; C2: aquifer C2; C3: aquifer C3.

Figure 4. Plot of Cl/Br vs Cl for our data and legacy data, together with mixing lines between end-members given in Section 2.4; sampling points labelled with ID number are cited in the text; percentages indicated on mixing lines represent the fraction of the high-Cl end-member over the low-Cl end-member; Uox: oxidized zone of aquifer U; Ured: reduced zone of aquifer U; S: aquifer S; C1: aquifer C1; C2: aquifer C2; C3: aquifer C3.

Figure 5. Average concentration of As and Cl in C3 over the sampling dates available (May 2006, October 2006, November 2007, April 2010 and February 2011 from unpublished historical data provided by the water supply company of Cremona and October 2014 from this study).

Figure size

Fig. 1: 1.5 columns fitting image.

Fig. 2: 1 column fitting image.

Fig. 3: 1 column fitting image.

Fig. 4: 1 column fitting image.

Fig. 5: 1 column fitting image.

Figure 1 Color
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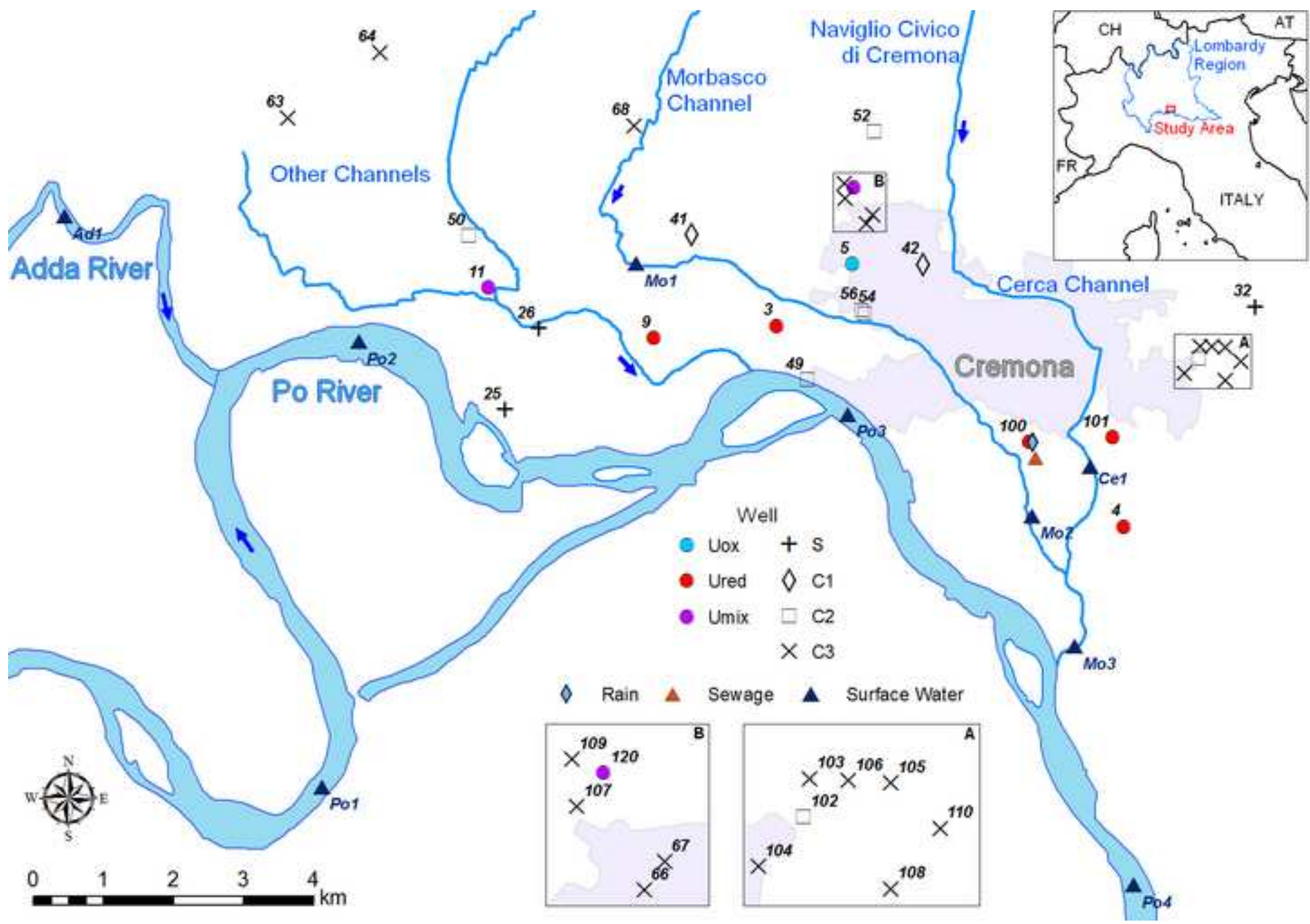
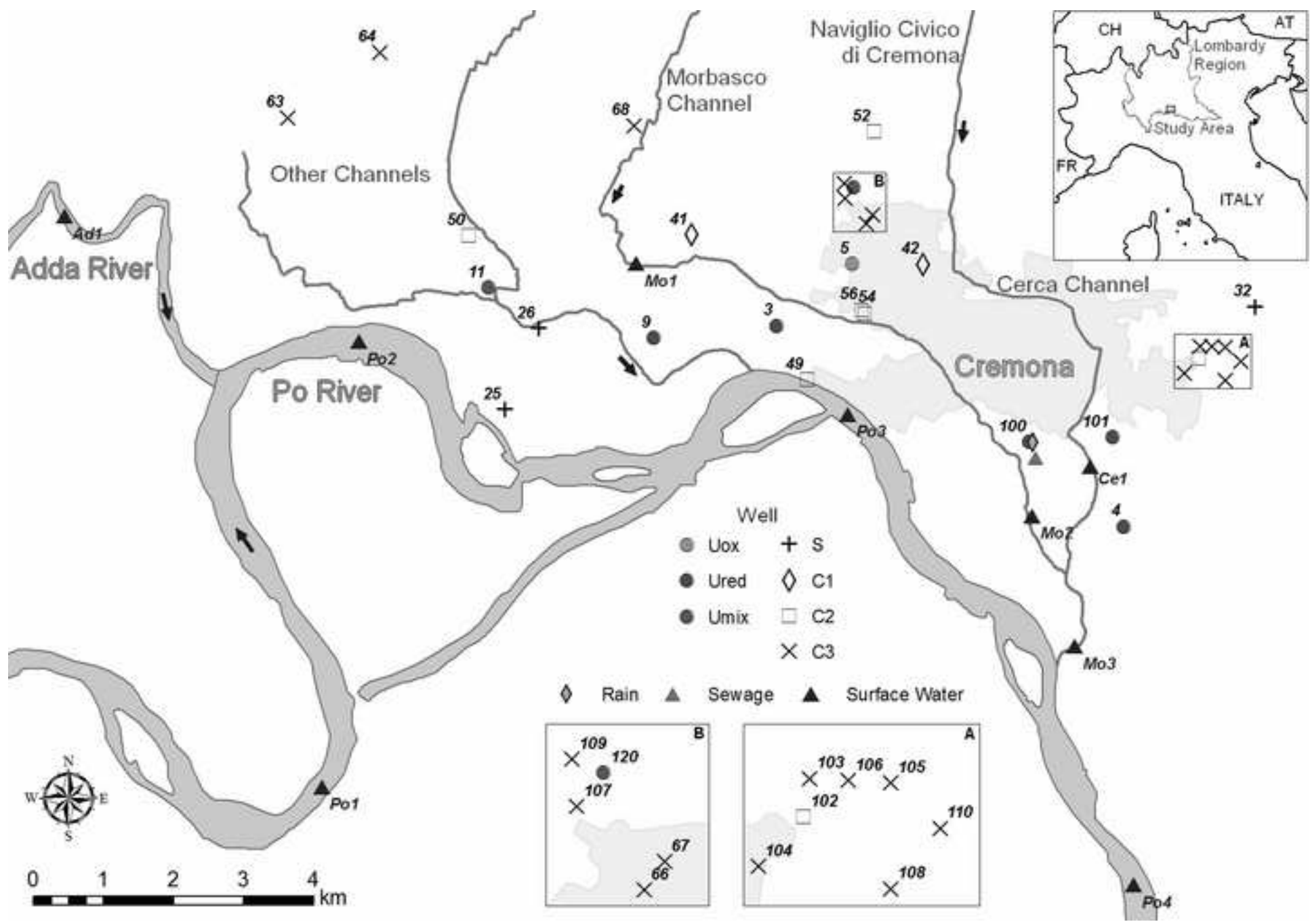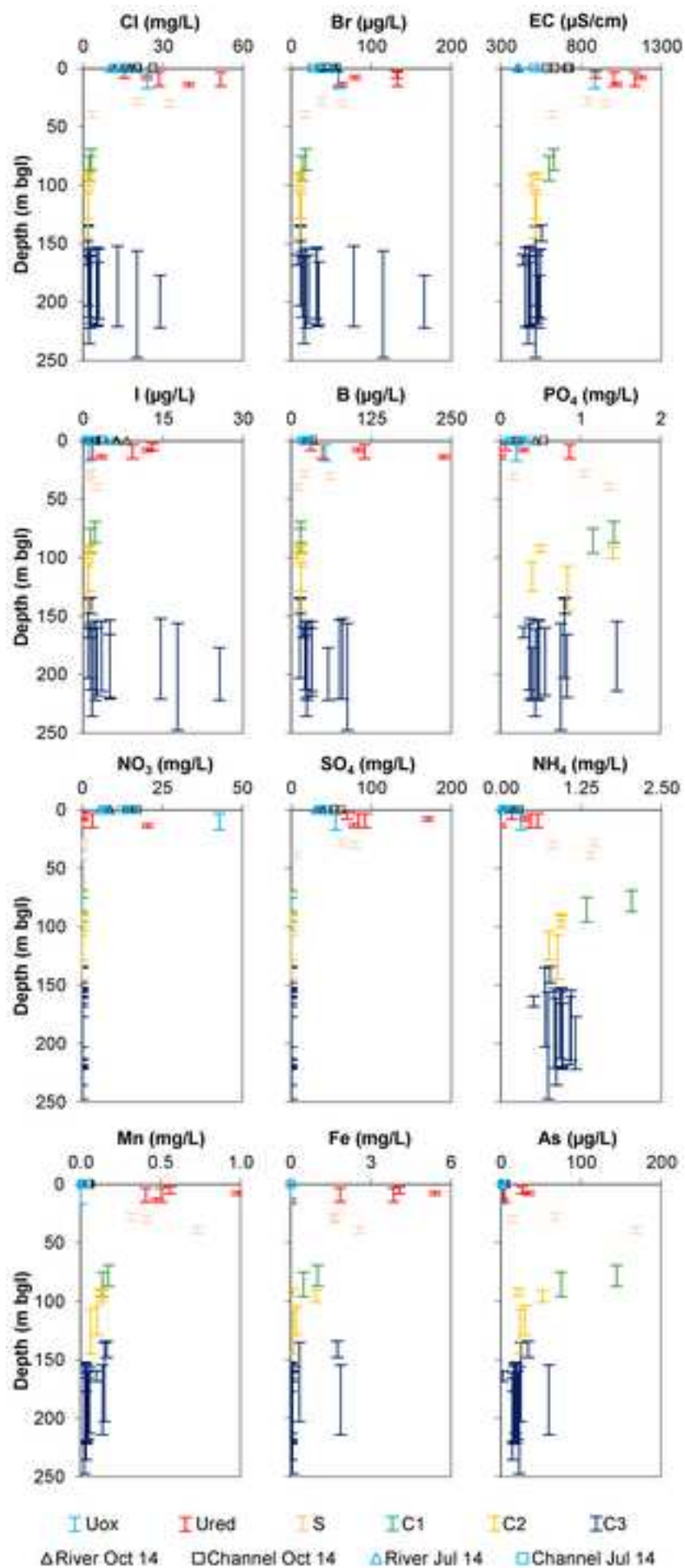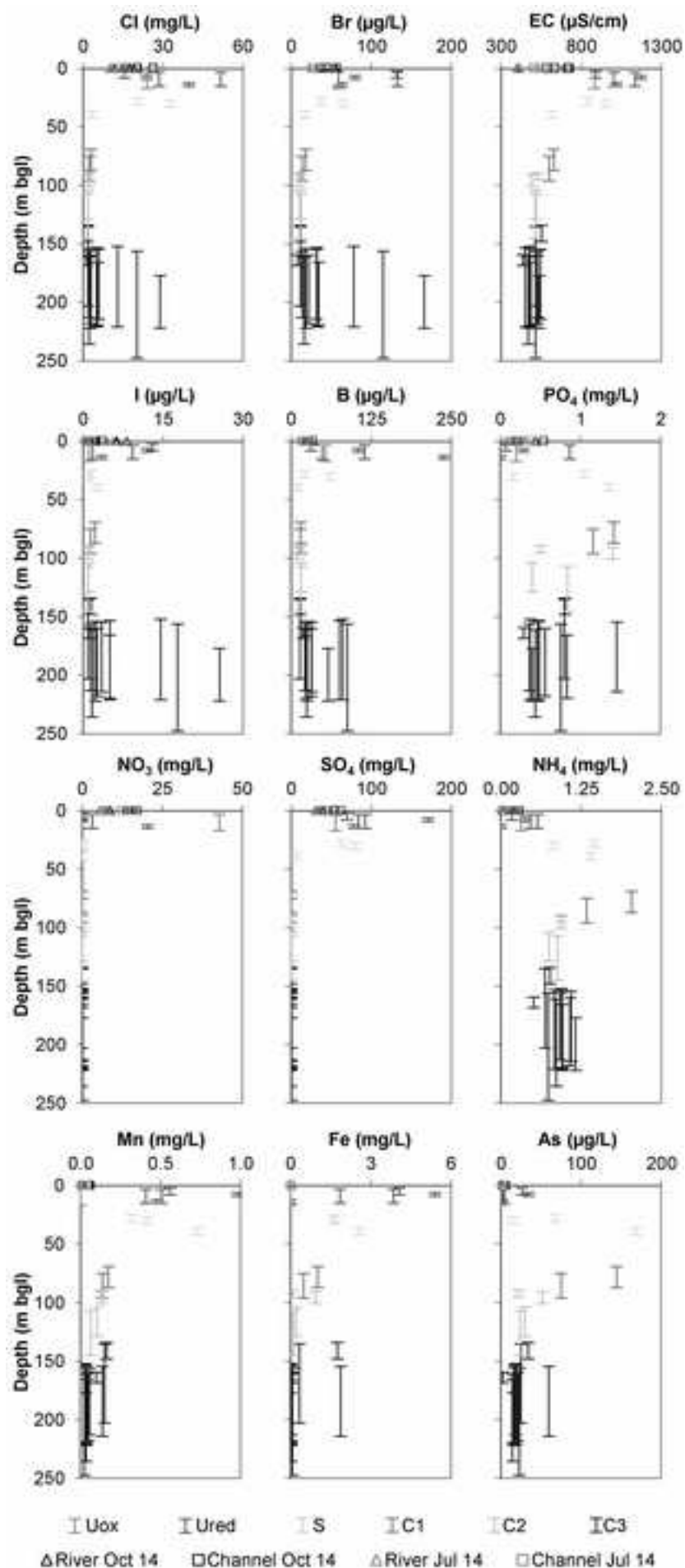**Figure 2 Color**
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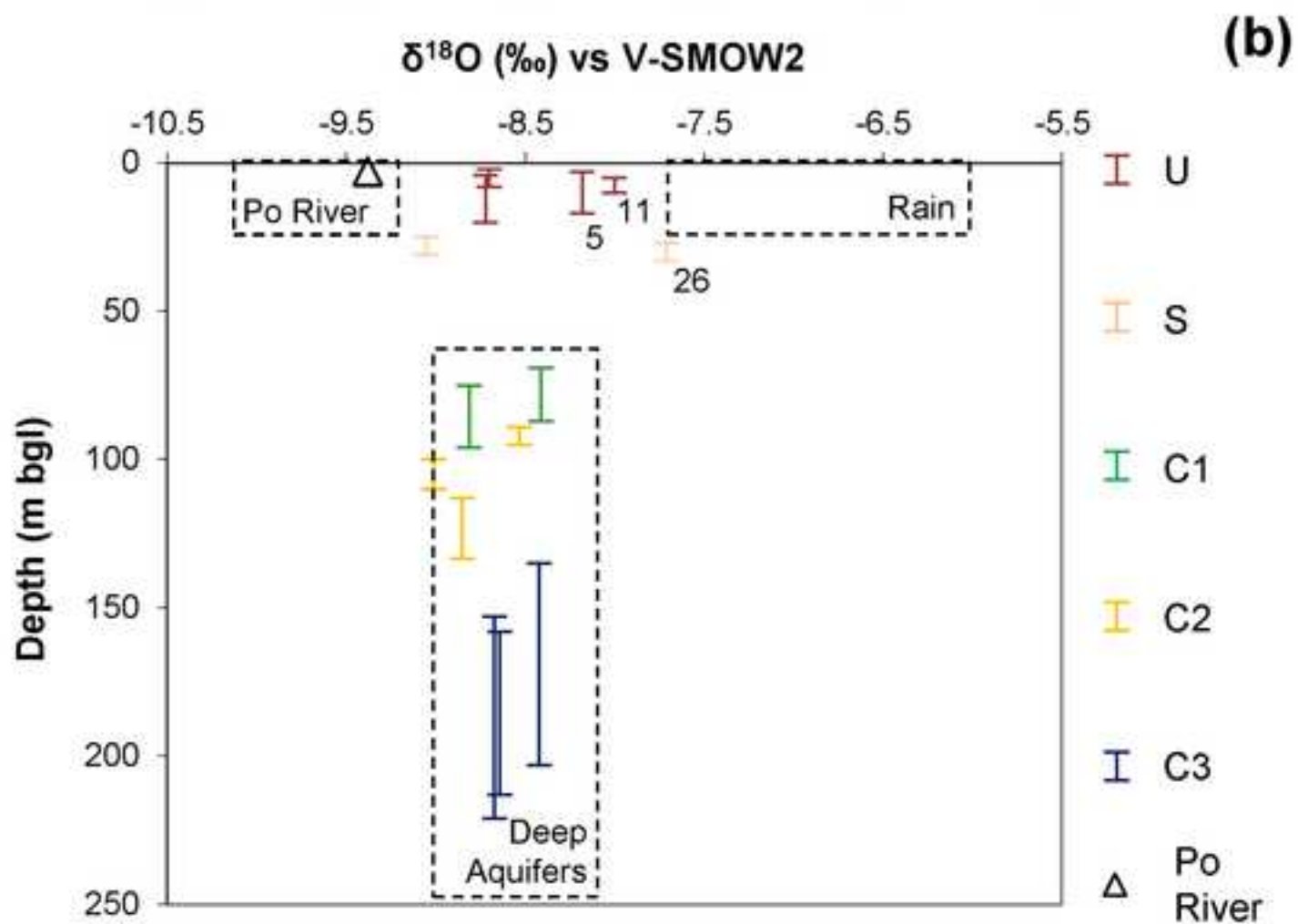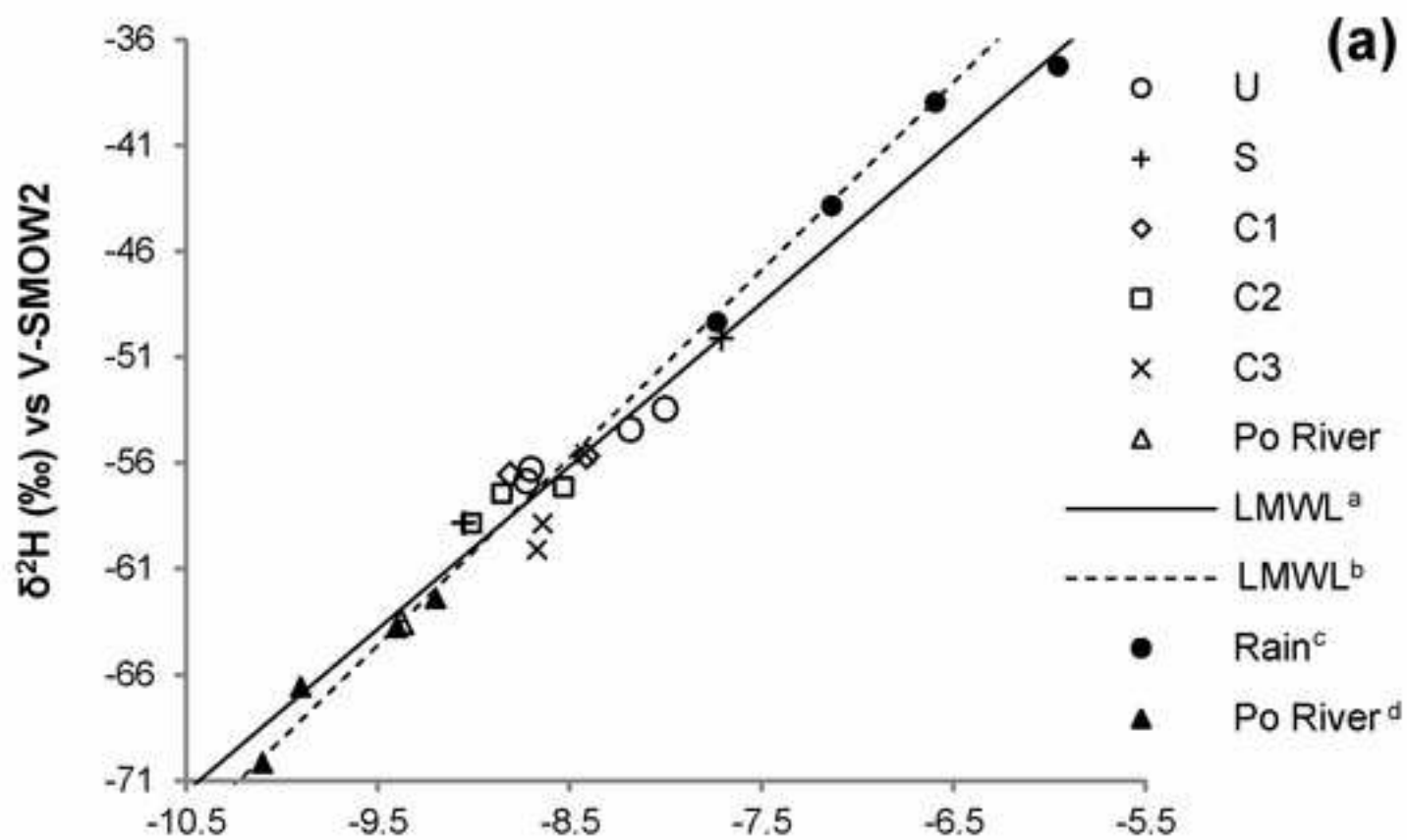
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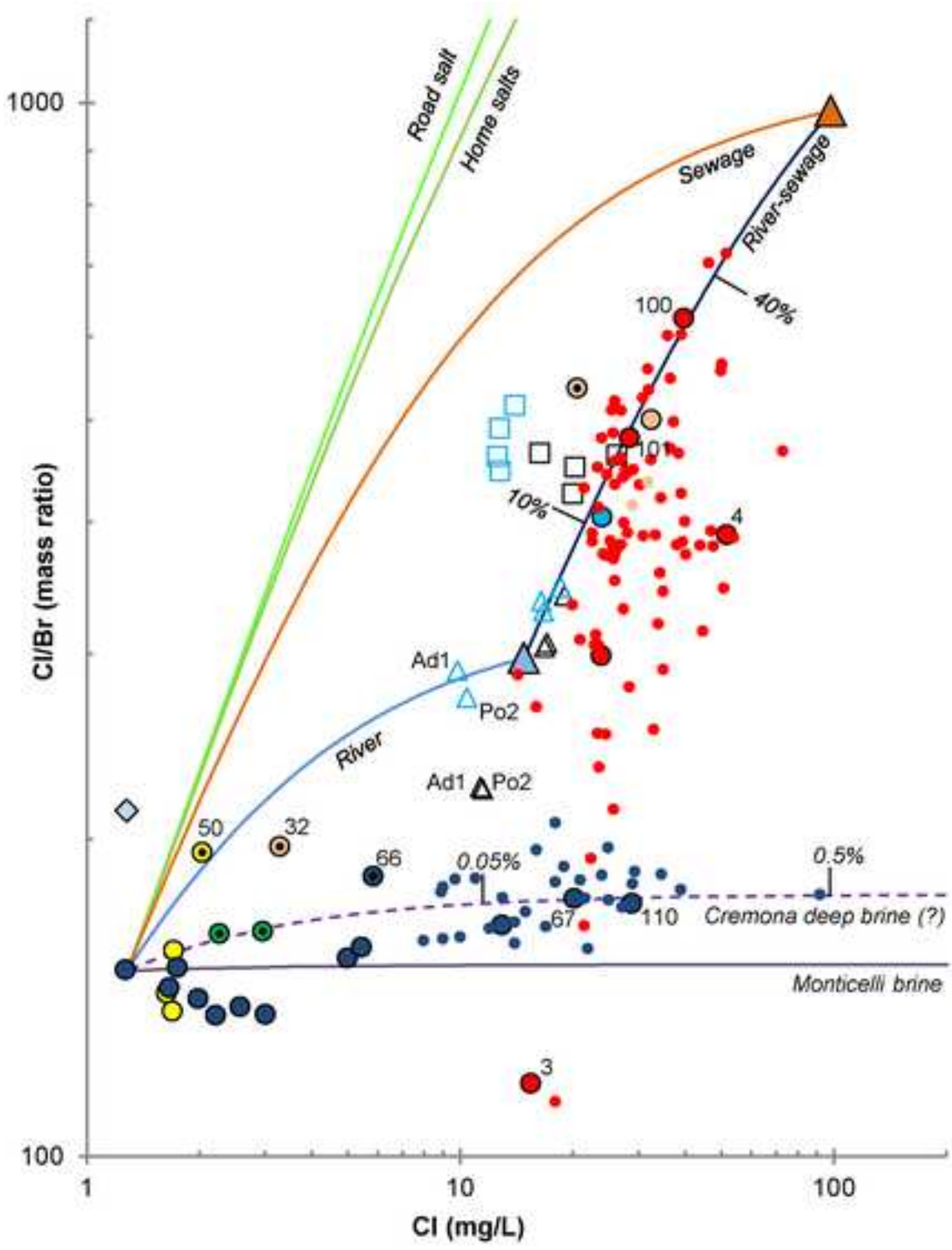
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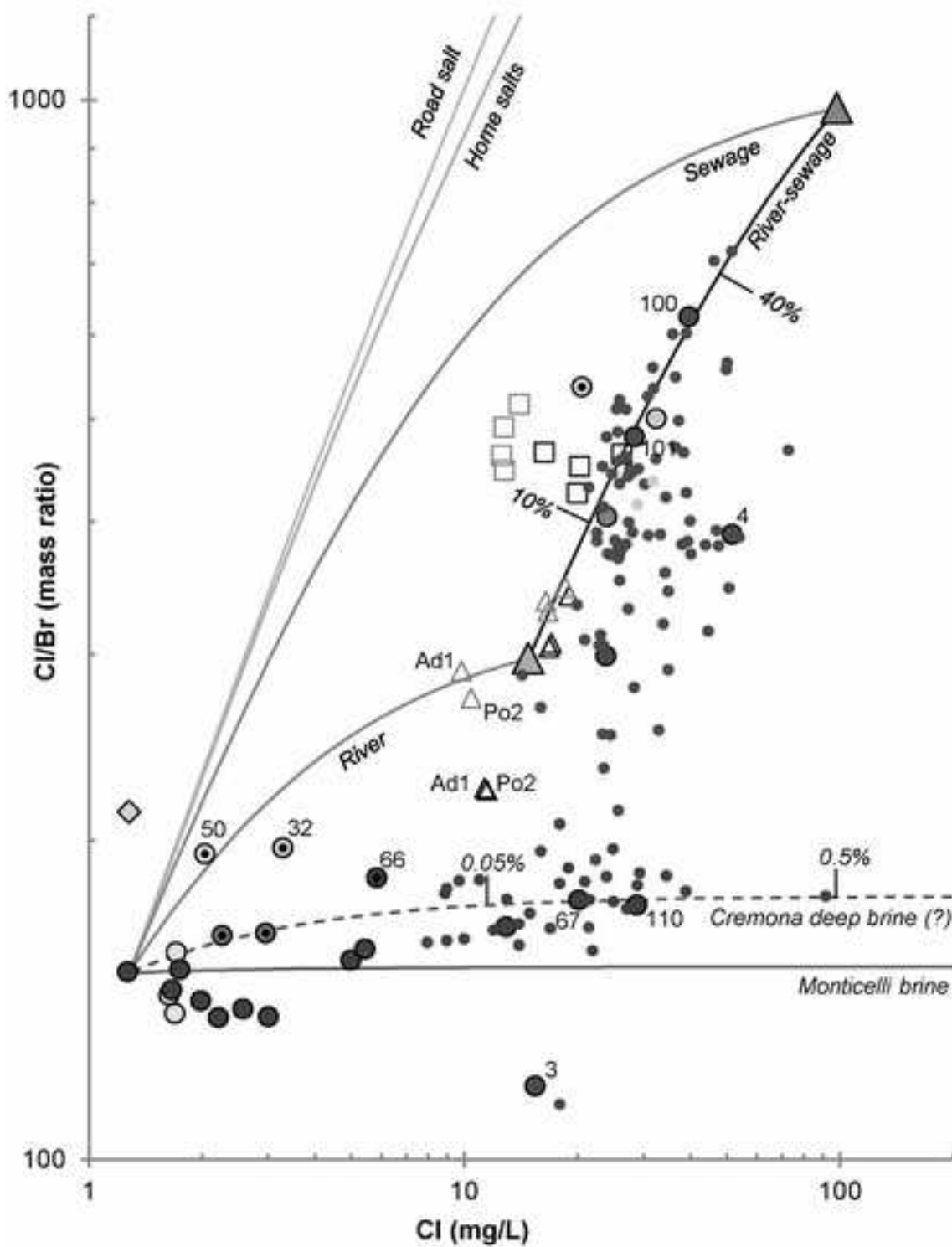
Figure 4. Cl/Br (mass ratio) versus Cl (mg/L) diagram showing mixing trends between river, sewage, road salt, home salts, Monticelli brine and Cremona deep brine (?) end-members.
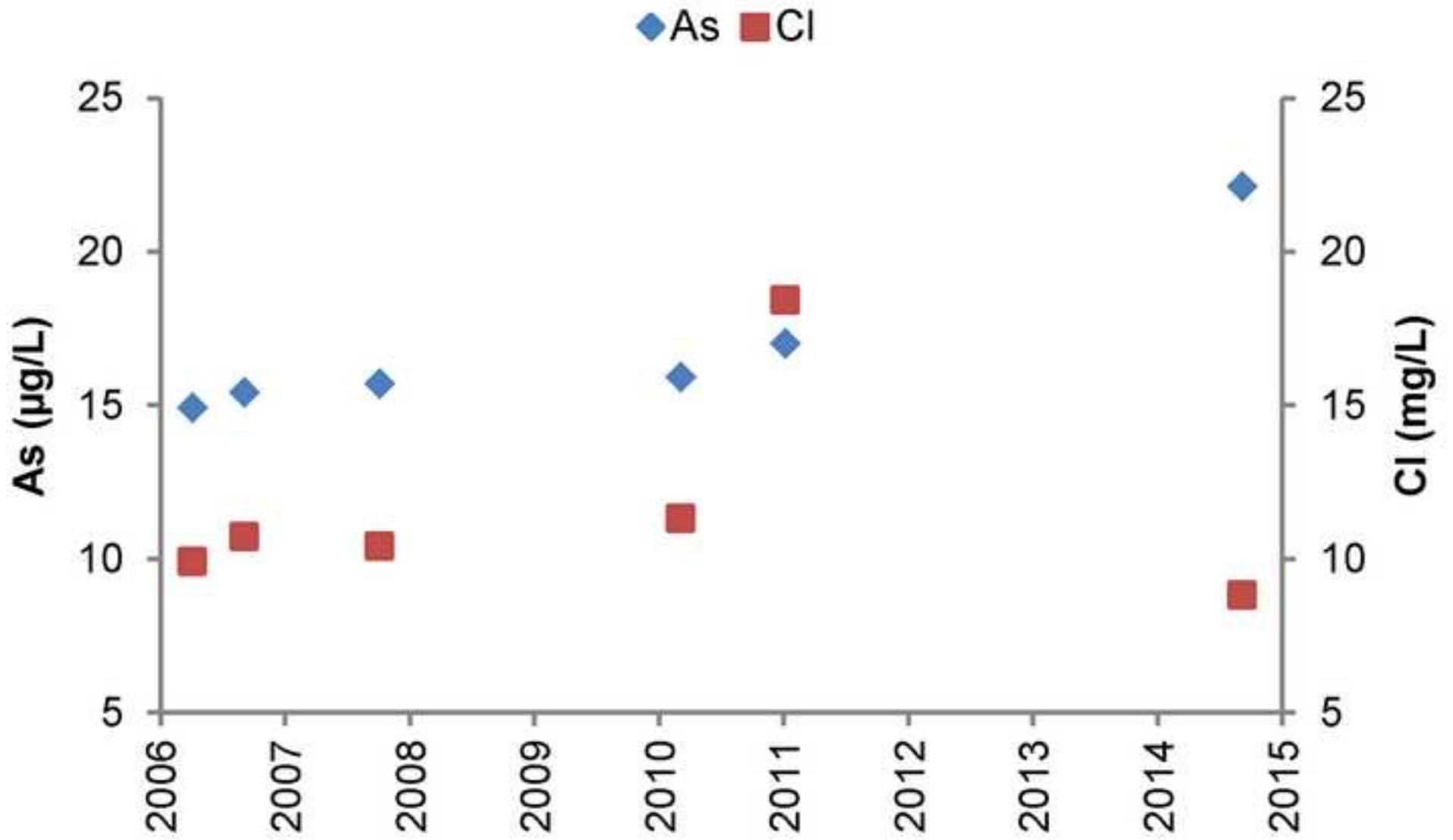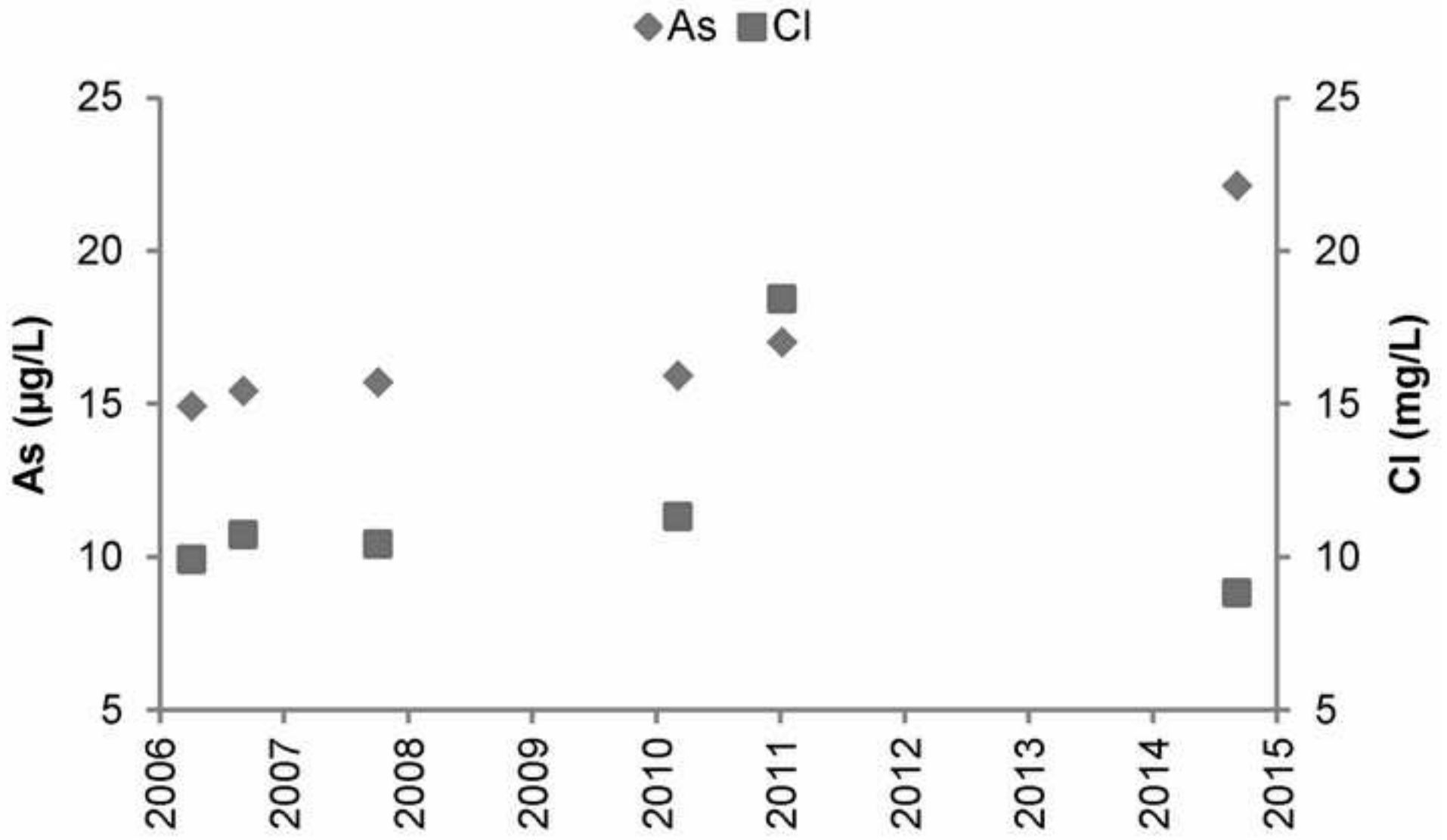
Supplementary material for on-line publication only