Application of Boron and Tritium isotopes for tracing landfill contamination in groundwater

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Abstract

Groundwater beneath a municipal solid waste landfill area in central Italy has been studied. The study included two sampling events: in June and October 2014. The aim of this study was to determine the quality of groundwater and to test the use of boron and tritium isotopes as tracers of contamination due to the presence of the landfill. The results of chemical analyses indicate that the samples collected from boreholes located downgradient from the landfill are contaminated. The principal contaminants are Cl^- , NH_4^+ , Fe, As, Cr, B, Hg and Zn, which were detected at maximum levels during the June sampling event. The boron and tritium isotopic composition of the collected water samples was analysed to evaluate the source of contamination. The results indicated a $\delta^{11}\text{B}$ value of 19.31‰ for uncontaminated groundwater, while $\delta^{11}\text{B}$ values between 4.37 and 9.41‰ were reported for contaminated groundwater. The correlation between boron and chloride provided a basis for evaluating the plume direction. Tritium (^3H) isotopes were analysed during the second sampling event (October). The results indicate that ^3H values ranging between 2.7 and 3.6 TU were reported for uncontaminated waters; this groundwater has a short residence time in the aquifer. A ^3H value of 34.5 TU was reported for one groundwater sample (Sample 7). This value is indicative of contamination by landfill leachate.

Keywords: Boron Isotope; Groundwater; Landfill; Tritium Isotope;

25 **1 Introduction**

26 Landfill leachate is a serious socio-economic and environmental problem in many European
27 countries (Christensen et al., 2001; Caputo & Vaccaro, 2006; Muhammad & Zhounghua, 2014).
28 Leachate plumes originating in municipal solid waste (MSW) landfills are potential sources of
29 contamination for water resources, including groundwater and surface water, as well as for soil
30 (Barbieri et al., 2014). MSW leachate is a highly concentrated complex effluent that contains
31 dissolved organic matter and inorganic compounds, such as ammonium, calcium, magnesium,
32 sodium, chlorides, as well as heavy metals, such as chromium, copper, lead, iron and nickel (Longe
33 & Balogun, 2010). There have been numerous approaches and methods to evaluate leachate leakage
34 using elemental and isotopic tracing techniques. One tracer is a substance which is either naturally
35 present, occurring in the water (natural tracer) or is introduced artificially to identify the flowpath of
36 water through the subsurface (artificial tracer) (Leibundgut et al., 2009; Tazioli 2011). In the last
37 decades is increasing interest in environmentally friendly tracers (Aquilanti et al., 2013) because of
38 concern has emerged about the application of artificially tracers in aquatic ecosystems due to their
39 potentially negative impact on the environment. A landfill can itself be considered an enormous
40 reservoir of tracers because of it contains a large quantity of chemical compounds with a
41 composition affected by some tracers (Tazioli 2011). Isotopes are natural tracers which allow
42 discriminating pollution sources, what cannot be appreciated merely by elemental chemical
43 concentrations. Furthermore, in the literature the reference values for different isotopic species (as
44 Boron and Tritium) have been listed (for example: Coplen et al., 2002).

45 The aim of this paper is to characterize the groundwater beneath a MSW landfill and to test the use
46 of boron and tritium isotopes as tracers for evaluating contamination of the landfill. Boron (B) has
47 two stable isotopes, namely ^{11}B (80.1%) and ^{10}B (19.9%). The mass difference results in a wide
48 range of $\delta^{11}\text{B}$ values, which are defined as the fractional difference between ^{11}B and ^{10}B , and
49 traditionally expressed in parts per mil. The reported range of $\delta^{11}\text{B}$ in natural waters is from -16 to
50 +59 ‰. Several studies have included the use of $\delta^{11}\text{B}$ values as groundwater tracers. The $\delta^{11}\text{B}$

values of many contaminants, including municipal wastewater (Vengosh et al., 1994; Bassett et al., 1995; Eisenhut et al., 1996; Leenhouts et al., 1998), landfill leachate (Eisenhut & Heumann, 1997; Barth 2000b; Hogan & Blum, 2003) and agricultural return flow (Bassett et al., 1995; Leenhouts et al., 1998), have distinct isotopic compositions that reflect their solute source and are often isotopically distinct from native groundwater (Barth, 2000a). However, tritium is a radioactive isotope with a half-life of slightly more than 12.32 years. It is produced by the interaction of cosmic radiation with the atmosphere. It is rapidly incorporated into water molecules and is removed from the atmosphere in meteoric precipitation. The unit used to measure natural concentrations of tritium is the Tritium Unit (TU), where 1 TU corresponds to an atom ratio of tritium to hydrogen of 10^{-18} . On a mass-of-water basis, 1 TU is approximately equal to 0.118 Bq kg^{-1} . Tritium (^3H) is a common groundwater contaminant at sites associated with a range of human activities, such as nuclear power generation, research reactors, nuclear weapons and disposal of radioactive, industrial and urban waste in landfills. The importance of tritium is related to its conservative behaviour, it remaining dissolved in water without fixation onto other constituents of the environment. This element is present in the effluent as tritiated water and cannot be concentrated or eliminated. This attribute and the relatively low levels at which it can be reliably measured (IAEA, 2004) make tritium one of the most widely used tracers in groundwater studies of contaminated and natural sites (Goutal et al., 2008). High levels of tritium in the leachate occur frequently in municipal landfills throughout the world (Fritz et al., 1994; Robinson & Gronow, 1996; Hicks et al., 2000; Fuganti et al., 2003; Tazioli et al., 2004; Mutch & Mahony, 2008; Hughes et al., 2011; Raco et al., 2013). These observations indicate that there are opportunities to use tritium as a tracer of leachate migration in the surrounding environment.

2 Site Characterisation

The municipal landfill studied is located in an alluvial plain of the lower Sangro River, Central Italy, and approximately 10 kilometres from the coastline of the Adriatic Sea. It is divided into 3

lots that have a total capacity of more than 2,000,000 cubic metres, and it has been open since 1995.

The site is adjacent to a drainage trench that drains the waters flowing beneath the landfill to two boreholes (Figure1). The lower Sangro valley is located between the allochthonous terrigenous units of the Molisan facies (Patacca et al., 1992) and the Plio-Pleistocene marine deposits of the Abruzzo-Molise foredeep (Ghisetti & Vezzani, 1996-97). These units, which are primarily clayey deposits, constitute the basement of the alluvial deposits superimposed on top of the Aventino-Sangro gravity flow deposits (Rusi & Tatangelo, 2010) upstream from the confluence of the Sangro and Aventino Rivers, and they overlay marine Plio-Pleistocene deposits downstream from the confluence (Crescenti et al., 1980). The Plio-Pleistocene basement is mainly composed of clays, sandy clays and marly clays, while arenaceous conglomerates are predominant near the coastal areas. In some locations, the arenaceous conglomerates vary to sandy silts and clayey silts that have typical facies of marine-coastal to fluvio-deltaic environments. The area is characterized by a substrate of marine origin (Plio-Pleistocene) formed of clay and sand at the base and coarsens upwards to sands and conglomerates at the top of the formation. Three units characterize the hydrogeology of the area:

- Unit A: Clayey silts - Aquitard
- Unit B: Gravels - Aquifer
- Unit C: Grey-blue clay - Aquiclude

The grey-blue clays (Unit C) represent the Plio-Pleistocene substrate of marine origin, and they are overlain by alluvial deposits (Unit A and Unit B) of the Sangro River. The reconstruction of the groundwater flow was obtained from boreholes and some geological drilling presents in the area (total 20 points) by previous investigations with Spline interpolation method. It indicates primary flow directions from SW to NE and W to E, with local variations (Figure 1).

99 **3 Sampling and analytical techniques**

100 Eight water samples were collected in June and October 2014 from boreholes located at the studied
101 landfill of central Italy (Figure 1). Water temperature, electrical conductivity (EC), pH and Eh were
102 measured in the field. Bicarbonate was determined by titration with 0.1 N HCl. The chemical
103 composition was determined using standard analytical methods (APHA, 1992). Major ions were
104 analysed with a Chromeleon Dionex (precision $\pm 2\%$). An ICS 1100 was used for analysing cations,
105 and a Dionex ICS 5000 was used for analysing anions. Concentrations of minor and trace elements
106 were measured using an ICP-MS (X Series 2 Thermo Fisher Scientific) following filtration (0.45
107 μm) and acidification in the field (HNO_3 1:1). The analyses were performed at the Geochemical
108 Laboratory of Sapienza, University of Rome (Italy). The analytical accuracy of these methods
109 ranged from 2% to 5%. An internal standard, Rh, was used to correct the ICP-MS instrumental drift.
110 Ultrapure water (Millipore, Milli-Q, 16 $\text{M}\Omega$ cm) was used in preparing blanks, standard solutions,
111 and sample dilutions.

112 For boron isotopes, the water samples were filtered through 0.45 μm cellulose sheets. The
113 determination of boron isotopic compositions was performed by negative thermal-ionization mass-
114 spectrometry (TIMS) (Zeininger & Heumann, 1983; Venghosh et al., 1989). A sufficient volume of
115 water to supply 2 ng of boron was loaded directly onto degassed, zone-refined Re filaments. The
116 boron isotopes were measured as the BO_2 species at masses of 42 and 43. Isotope ratios are reported
117 as per mil deviation ($\delta^{11}\text{B}$) in the $^{11}\text{B}/^{10}\text{B}$ ratios relative to the standard NBS SRM 951, and the
118 analytical precision is $\pm 0.5\%$ as $\delta^{11}\text{B}$. Boron isotopes were evaluated at the USGS Metal and
119 Metalloid Isotope Laboratory in Menlo Park, CA.

120 The tritium measurements were conducted using the method of Cameron (1967). It was analyzed in
121 a proportional counting by β^- counter in the gaseous phase of ethane obtained by reaction of
122 hydrogen with ethylene. The concentrations are reported in tritium units (TU). The analytical

accuracy of the method ranged from ± 0.5 to ± 0.6 TU for these analyses. Tritium isotopes were evaluated at the CNR Laboratory in Firenze, Italy.

4 Results

4.1 Solute chemistry

The chemical-physical data and the major ions for both sampling events are reported in Tables 1 and 2. The pH of all of the groundwater samples was approximately neutral. The EC of the groundwater in the area under study ranged between 1855 and 3202 $\mu\text{S}/\text{cm}$ in June 2014 and between 1533 and 3267 $\mu\text{S}/\text{cm}$ in October 2014. The EC is a notable indicator of the amount of solids dissolved in water, and higher EC values were measured in samples collected from boreholes located downgradient from the landfill, indicating its effect on groundwater chemical composition. The Eh is a measure of the tendency to acquire electrons and thereby be reduced. The Eh shows a positive value with a reduction in samples collected downgradient from the landfill. The results of the analyses indicate that the principal cation in the waters of the study area is Na^+ , which was detected at a maximum concentration in June (304.75 mg/l). In October, the Ca^{2+} concentration increased and the Na^+ concentration decreased compared with the June results. The dominant anion was HCO_3^- with a maximum value of 1617 mg/l. High concentrations of Cl^- (<200 mg/l) were detected in three samples during June, with a maximum value in Sample 6 (707.6 mg/l). In October, only sample 7 shows high Cl^- concentration (416.0 mg/l).

4.2 Trace elements

The data for Li, B, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Cd and Hg are reported in Tables 3 and 4 for both sampling events. Boron was detected at a maximum concentration of 1901 $\mu\text{g}/\text{l}$ in sample 6 (Table 3), and a maximum concentration of Cr was detected in sample 7 (61.42 $\mu\text{g}/\text{l}$, in June). High concentrations of Mn were detected during both sampling events, with a maximum value detected in June (400.6 $\mu\text{g}/\text{l}$). The Italian implementation of the European Water Framework Directive which is the D.Lgs 152/2006 (Italian Republic 2006) sets the maximum Concentration

148 Limit of Contamination (CSC) for some elements in natural waters. The detected Fe concentration
149 exceeds the CSC provided by D.lgs 152/2006 in borehole 0, but it increases in sample 7, where it
150 was detected at a maximum concentration of 1124 µg/l in June and 800 µg/l in October. High
151 concentrations of Co, Ni and As were detected during June in sample 7 (Table 3)

152 4.3 Isotope analyses

153 Boron and tritium isotopes were evaluated in five water samples. The boron isotope composition of
154 water was analysed during June, and the results are reported in Table 3. The data show different
155 values of $\delta^{11}\text{B}$ for water in the study area: the minimum detected value was 4.37‰ (sample 7), and
156 the maximum detected value was 19.31‰ in sample 0. The results of the tritium analyses (October)
157 are reported in Table 4. A tritium level of 34.5 TU was reported for sample 7, while the values
158 ranged from 2.7 to 3.6 TU in other samples.

159 5 Discussion

160 5.1 Major and trace elements

161 The principal cation in groundwater in the study area is Na^+ . Sodium is a natural constituent of the
162 groundwater because it is derived from the leaching of rocks, but it is also present in landfill
163 leachate. The samples show an enrichment of Na^+ downgradient from the site, probably due to the
164 landfill leachate. An excess of Cl^- in water is usually considered to be an indication of pollution,
165 and Cl^- is utilized as a tracer for evaluating groundwater contamination (Mor et al., 2006).
166 Furthermore, many studies show that leachate has high Na, NH_4 and Cl^- concentrations and that the
167 plume of contamination may be delimited by Cl^- concentrations (Statom et al., 2004; Srivastava &
168 Ramanathan, 2008). A high Cl^- content in groundwater is likely to originate from pollution sources
169 such as domestic effluents, fertilizers, and septic tanks because the element has long been used as a
170 disinfectant or biocide. Organic solutes are attacked also, as are other easily oxidized species, and
171 the biological sterility of the solution after the reactions have been completed is readily
172 ascertainable by testing for the presence of free chlorine (Hem, 1985). A high chloride

173 concentration in groundwater can be due also to natural sources as brines and seawater intrusion.
174 An increase in Cl^- levels is dangerous for people suffering from heart or kidney diseases (WHO,
175 1997). The maximum Cl^- concentration during this study was detected in sample 6 throughout the
176 June sampling event and in sample 7 during the October sampling event. Both samples were located
177 downgradient from the landfill. Correlations among the different chemical elements may then be
178 indicative of the water behaviour in the subsoil (Tazioli et al., 2012). Figure 2 shows relationship
179 between Cl^- and SO_4 for both sampling events. In June (Graph A) water are divided in two groups:
180 group 1, includes also borehole 0 located upgradient from the site, the amount of Cl^- may be
181 connected to SO_4 content; Group 2, water collected downgradient from landfill, the Cl^-
182 concentrations are not related to SO_4 values. In October, all samples were fairly well-aligned except
183 for borehole 7. The well relationship for group 1 indicates that the chemical composition of the
184 spring water is related to leaching phenomena coming from rocks. Cl^- and SO_4 are often associated
185 with sedimentary rocks (Hem, 1985). For others samples (i.e. sample 7) the high Cl^- contents may
186 indicate contamination phenomena. A high value of ammonium (180 mg/l) and the maximum Br
187 concentration (3.32 mg/l) were also detected in sample 7 in October, and their origin was likely
188 from the leachate. The location of sample 7 is in an area that is highly influenced by waste disposal
189 site.

190 Heavy metals are the major indicators of anthropogenic impact and have various sources, such as
191 traffic activities, dry ash deposition from incineration plants, industrial effluents, road runoff and
192 landfill leachate (Singh et al., 2008). Thus, the monitoring of heavy metals contamination could be
193 important in assessing the impact from the landfill on groundwater quality. The analytical data
194 indicate that elevated Mn concentrations were detected in all samples during both sampling events.
195 Therefore, Mn is likely a naturally occurring metal in the geological substrate of the area, and it
196 could not be used to evaluate the contamination of groundwater in the area. High levels of Fe were
197 detected in all samples but were highest in sample 7. This observation indicates that the elevated Fe
198 concentration in sample 7, which was located downgradient from the landfill, was due to leachate.

199 The predominant oxidation state of chromium in rock minerals is Cr^{3+} . Dissolved chromium,
200 however, may be present as trivalent cations or as anions with an oxidation state of Cr^{6+} . Six
201 different ionic forms of chromium are considered to be stable in aqueous systems. The reduced
202 forms are Cr^{3+} , CrOH^{2+} , $\text{Cr}(\text{OH})_2$, and $\text{Cr}(\text{OH})_4$. Chromate anions are the dominant species in
203 solutions that are alkaline and mildly oxidizing. Chromium is one of the most common groundwater
204 contaminants at industrial sites and military facilities due to its widespread use as a metal corrosion
205 inhibitor (Melitas et al., 2001). Industrial applications of chromium may also produce waste
206 solutions containing chromate anions. (Eary & Ral, 1988; Cabatingan et al., 2001)

207 In June, samples 6 and 7 show As concentrations that exceed limit provided by Dlgs 152/2006
208 (table 3). Because small amounts of arsenic can be toxic to humans, this element is considered a
209 highly undesirable impurity in water. The stable forms of arsenic in solution in water are arsenate
210 (AsV) and arsenite (AsIII) oxyanions. Arsenic has been used as a component of pesticides and may
211 thus enter streams or groundwater through waste disposal or agricultural drainage. An important
212 factor in the natural circulation of arsenic, however, is the volatility of the element and some of its
213 compounds. The limit of arsenic in groundwater established by D.lgs 152/2006 is 10 $\mu\text{g/l}$.

214 All samples, except for borehole 0, indicate detected Hg concentrations that exceed the limit of 1
215 $\mu\text{g/l}$ established by Dlgs 152/2006. Mercury is a hazardous environmental contaminant (Wang et
216 al., 2004). The stable form of mercury in most natural water systems is the free metal, Hg
217 (aqueous). Mercury may form chloride or hydroxide complexes depending on pH and the total
218 chloride concentration. Organic complexes, such as methyl mercury, HgCH_3 , and other similar
219 forms can be produced by methane-generating bacteria in contact with metallic mercury in lake or
220 stream sediment (Hem, 1985). In the Mercury Study Report to Congress (USEPA, 1997), sources of
221 mercury emissions were placed in three categories: natural, anthropogenic, and re-emitted sources.
222 The anthropogenic emission sources of mercury mostly result from solid waste incineration
223 (municipal and medical wastes), coal and oil combustion, pyrometallurgical processes (iron, lead,
224 and zinc), production of mercury and gold and by fluorescent bulbs (Wang et al., 2004; Aucott et

225 al., 2012). Mercury in municipal waste originates from the disposal of mercury-containing products,
226 such as batteries, fluorescent bulbs, and paints. The efficiency of removing mercury by municipal
227 waste incineration is generally quite low, from 30 to 45% (Chang et al., 2000). It is estimated that in
228 the United States, the release of 43 metric tons of mercury from municipal waste incineration is
229 approximately 30% of the total mercury emissions per year (USEPA, 1997). Consequently, mercury
230 is generally readily leached by percolating water in solid waste landfills and is easily transferred to
231 groundwater.

232 In June, Zinc shows high values in samples 6 and 7 (Table 3). Zinc has only one significant
233 oxidation state, Zn^{2+} , and it is widely used in metallurgy, principally as a constituent of brass and
234 bronze, or for galvanizing in which it is applied as a coating to inhibit corrosion of steel. White
235 pigment in paint and rubber is generally rich in Zinc. These applications tend to disperse the
236 element widely in the environment, and its availability for solution in water has been greatly
237 enhanced by industrial civilization (Hem, 1985). A comparison of the chemical composition of
238 groundwater sampled upgradient from the landfill (borehole 0) with waters downgradient from the
239 landfill indicates an increase in the concentrations of analysed constituents in the downgradient
240 groundwater. Whereas metals and metalloids can be released from metallic (batteries, electronics),
241 plastic and textile compounds in municipal solid waste (Mor et al., 2006), alkali metals and alkali-
242 earth elements such as Li, Rb, Cs, Ba and Sr tend to originate from admixtures of salts. The Al, Fe
243 and Mn detected in groundwater may have resulted from the weathering of building materials that
244 were disposed of in the studied landfill (Mor et al., 2006).

245 According to Dotsika et al., 2006, the B and Cl^{-} concentrations can be used for evaluating the origin
246 of boron contents in water resources. Boron concentrations in seawater range between 4.5 and 5
247 mg/l, and the B/Cl ratio is 2×10^{-4} . In groundwater contaminated by domestic wastewater and other
248 anthropogenic sources (derived from Na- or Ca-borates), the concentrations of boron is
249 significantly higher and B/Cl ratio is much higher than that of seawater. Figure 3 shows the
250 relationship between B and Cl for samples collected during the June sampling event. Three samples

(1, 2 and 3) indicate B/Cl ratios lower than the B/Cl ratio for seawater, and other samples including sample 0 indicate B/Cl ratios greater than that of seawater, with values ranging from 2.69×10^{-3} to 5.03×10^{-3} . As also indicated in the results from the study discussed above (Dotsika et al., 2006), these results could indicate contamination of the waters, including groundwater in borehole 0. Isotope analyses were performed to evaluate the source of contamination in groundwater. The boron isotope composition was analysed in five samples collected during the June sampling event, and the tritium isotope composition was analysed in the same number of samples collected during the October sampling event.

5.2 Boron Isotope- End member Selection

Natural boron (B) has two stable isotopes, namely ^{11}B and ^{10}B , with an approximate $^{11}\text{B}/^{10}\text{B}$ ratio of 4. Variations in the ratio of the two isotopes are normally expressed as parts per thousand deviations. The $\delta^{11}\text{B}$ notation is defined as:

$$\delta^{11}\text{B} = [(^{11}\text{B}/^{10}\text{B})_{\text{sample}} / (^{11}\text{B}/^{10}\text{B})_{\text{NBS 951-1}}] \times 1000$$

Boron is a ubiquitous trace element, and it is present in aqueous solutions such as the $\text{B}(\text{OH})_4^-$ ion, undissociated boric acid $\text{B}(\text{OH})_3$, and borates $(\text{Na,Ca,Mg})\text{B}(\text{OH})_4^+$ (Barth, 2000b).

Boron is also notably common in man-made components such as chemical fertilizers and detergents. In Europe, boron is mostly derived from California and Turkish borate deposits (Barth, 1998). Anthropogenic boron in wastewater is isotopically distinct from natural boron in groundwater and can thus be utilized to identify the source of contamination. The isotope ratio of synthetic boron products reflects the source of boron and the type of products. For example, synthetic Na-borate products from California contain $\delta^{11}\text{B} = -0.4$ to 7.5‰ , while Turkish products (Na-Ca borates) indicate a negative value for $\delta^{11}\text{B}$ (Vengosh, 1989). Leachate also contains high concentrations of boron, as discussed in the literature (Davidson and Bassett, 1993; Vengosh et al., 1994; Hogan and Blum, 2003). Some of the reported values of boron isotopes ($\delta^{11}\text{B}$) in leachate at MSW landfills are approximately 3-10‰ (Eisenhut & Heumann, 1997; Barth, 2000; Hogan &

Blum, 2003). We analysed the boron isotope composition of five samples collected during the June sampling event to evaluate the source of contamination and the direction of the contaminant plume. The samples were selected depending on their locations within the landfill site and the chemical analysis results. The boron isotope data (Table 3) show different values between the borehole 0, located upgradient from the landfill, and water downgradient from the site. Specifically, borehole 0 has high $\delta^{11}\text{B}$ values (19.31 ‰) and B concentration of 777.6 $\mu\text{g/l}$. In this sample B concentrations can be related to water-rock interaction processes. Boron can easily enrich clayey sediments (Palmucci and Rusi, 2014), which are abundant within the geological context of the study area and thus represent a potential source of its. Therefore, for hydrogeological considerations (sample location) isotopic value and chemical characteristics (as relationship Cl/SO_4 , figure 2), borehole 0 can be considered as representative of uncontaminated groundwater. Additional investigation is required to define the $\delta^{11}\text{B}$ range of the natural baseline; nevertheless, any deviation of the isotopic composition from the natural value, especially if coupled with an increase in B content, is suspected to be contaminated. Water from the drainage trench (boreholes 4 and 7) indicates low $\delta^{11}\text{B}$ values (9.41 - 4.37 ‰) similar to non-marine evaporites, which are the major industrial sources of B (Davidson and Bassett, 1993; Vengosh et al., 1994). Man-made boron products are manufactured from natural borate minerals predominantly mined in non-marine evaporite deposits related to Tertiary volcanism in California, U.S.A., and western Turkey (Barth, 2000). For the isotopic value, location and contaminants presence, sample 7 can be considered the contaminated end-member. The $\delta^{11}\text{B}$ values suggest that landfill leachate is enriched in boron with a low $\delta^{11}\text{B}$ signature, relative to those of natural contamination sources. Figure 4A shows the relationship between $\delta^{11}\text{B}$ and B, which indicates that there is a trend from sample 0 (uncontaminated groundwater) to sample 7. Samples 5 and 6 show intermediate isotopic composition respect to two end-members (Figure 4). These waters have high values of B, Cl and others trace elements (see table 2). The isotopic values highlight reduction respect background water especially for sample 5; therefore we can suppose that there was a contamination phenomenon. Probably these waters are affected by mixing between

landfill leachate and uncontaminated groundwater. When the meteoric precipitation is higher (e.g., in June), the contamination reaches the boreholes located downgradient (e.g., 5 and 6) from the site, because of the drainage trench fails to collect the leachate from the landfill. The plume of contamination may have formed within the transect between boreholes 4 and 7 (lower $\delta^{11}\text{B}$) and advanced in the direction of boreholes 5 and 6, where high values of chloride and same traces elements as (B, Cu and Ni) were reported as major indicators of contaminated water, but these values were lower compared with uncontaminated water (sample 0).

5.3 *Tritium Isotope*

Tritium is a radioactive isotope with a half-life of slightly more than 12.32 years. It is produced by the interaction of cosmic radiation with the atmosphere and is used both for dating recent water (less than 50 years) and as a tracer for leakage from waste disposal sites (Fuganti et al., 2003; Aggarwal et al., 2006; Tazioli et al., 2004; Tazioli, 2011; Hughes et al., 2011). The tritium levels currently detected in precipitation in both hemispheres are almost under 15 TU (IAEA_WMO, 2004). In Italy its level in rainwater ranges between 3 and 13 TU. Some studies reported ^3H analytical data for municipal landfill leachate (Fuganti et al., 2003; Tazioli et al., 2004; Mutch & Mahony, 2008; Hicks et al., 2000) that indicate values higher than the natural levels of groundwater. Solid waste materials such as sealed glass tubes filled with tritium gas, watches, key chains, and luminescent paint contain high levels of tritium; therefore, it can be found in municipal solid waste. Values reported for leachate are higher, e.g., 500-1700 TU, while contaminated groundwater contains lower levels of tritium compared to leachate but higher levels compared to uncontaminated water (Tazioli, 2011). In this study, the ^3H level has been analysed in five groundwater samples collected at the landfill during the October sampling event (Table 4). Table 4 shows that a tritium level of 2.7 TU was reported for uncontaminated groundwater (borehole 0) and a tritium level lower than 4 TU was reported in boreholes 4, 5 and 6, while a tritium level of 34.5 TU was reported for sample 7. These results indicate that there is groundwater contamination

327 beneath the landfill in the vicinity of borehole 7 because the tritium level in sample 7 is higher than
328 the levels reported for the other water samples and is also higher than reported levels in rainwater
329 (from 3 to 13 TU). Furthermore, we know that the isotopes in the groundwater have a short
330 residence time in the aquifer. If the tritium data are compared with the results of the chemical
331 analyses (Tables 2 and 4), it becomes apparent that during October, borehole 7 was the only sample
332 with high Cl^- and Fe concentrations (416.0 mg/l and 800.3 $\mu\text{g/l}$, respectively). Furthermore, sample
333 7 is the water sample with the lowest Eh value (69 mV). The analytical data for this sample also
334 indicate a high concentration of NH_4 , which is a typical leachate contaminant.

335 **6 Conclusions**

336 The chemical composition of groundwater beneath a MSW landfill site in central Italy has been
337 studied. The geology of the area is characterized by Plio-Pleistocene basements primarily composed
338 of clays. A small aquifer composed of gravels and alluvial deposits of the Sangro River represents
339 the hydrogeological framework. Water samples were collected during two sampling events (June
340 and October 2014) from 8 boreholes located at the waste disposal site. The results of chemical
341 analyses show that the samples located downgradient from the landfill are contaminated. The
342 principal contaminants are Cl^- , NH_4^+ , Fe, As, Cr, B, Hg and Zn. For the June sampling event, more
343 samples indicated contamination when compared with uncontaminated water located upgradient
344 from the site. Therefore, we analysed the boron isotopes for five samples to evaluate the source of
345 contamination. The results indicate that the $\delta^{11}\text{B}$ values are very different for uncontaminated
346 (19.31‰) and contaminated groundwater (4.37 and 9.41‰), thus suggesting that the source of
347 pollution for boreholes 4 and 7 is leachate from the landfill site. When the meteoric precipitation is
348 higher (e.g., in June), the contamination reaches the boreholes located downgradient (e.g., 5 and 6).
349 Lower levels of contaminants were detected in the downgradient water samples during the October
350 sampling event. Only borehole 7 indicated high concentrations of the chemical constituents
351 previously mentioned. In addition, we analysed the ^3H isotopes. The results show different values

352 for uncontaminated groundwater, with values ranging from 2.7 to 3.6 TU, and borehole 7
353 (contaminated water) with a values of 34.5 TU. This value is indicative of groundwater
354 contamination by landfill leachate.

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508 **Figure 1:** Groundwater sampling location.

509 **Figure 2:** The sulphate content and dissolved chloride ratio expressed in meq/l. Graph A shows
510 results for June sampling events, graph B shows results for October. Group A well correlation
511 between elements, group B probably Cl^- contamination.

512 **Figure 3:** Boron concentrations vs. Chlorine in June sampling event; Black triangle: seawater;
513 Line: seawater dilution line; Rhombus: boreholes of site; Rhombus below the dilution line are
514 boreholes 1, 2 and 3.

515 **Figure 4:** A, $\delta^{11}\text{B}$ vs. B for five water points. B, $\delta^{11}\text{B}$ vs. Cl. Sample 0 is uncontaminated
516 groundwater, Sample 7 is groundwater contaminated by leachate.

517 **Figure 5:** $\delta^{11}\text{B}$ vs. B/Cl ratio in five water points. Sample 0 is uncontaminated

518 **Figure 6:** ^3H vs. Cl in October sampling event. Sample 7 is the only water point that shows high
519 level of ^3H and high Cl^- concentration.

520 **Table 1:** Chemical-physical data for boreholes in June sampling event. Ion are expressed in mg/l; T
521 ($^{\circ}\text{C}$); pH (pH unit); EC ($\mu\text{S}/\text{cm}$); Eh (mV)

522 **Table 2:** Chemical-physical data for boreholes in October sampling event. Ion are expressed in
523 mg/l; T ($^{\circ}\text{C}$); pH (pH unit); EC ($\mu\text{S}/\text{cm}$); Eh (mV)

524 **Table 3:** Minor- Trace elements expressed in $\mu\text{g}/\text{l}$ and $\delta^{11}\text{B}$ (‰) in June sampling event

525 **Table 4:** Minor- Trace elements expressed in $\mu\text{g}/\text{l}$ and ^3H (TU) isotopes in October sampling event
526

Table1

June	Ca	Mg	Na	K	Cl	SO4	HCO3	Br	F	NO2	NO3	T	pH	EC	Eh
0	82.08	55.50	304.75	12.57	154.5	253.2	695.6	n.d	0.58	n.d	35.52	18	6.89	2075	171
1	98.03	79.38	170.10	7.12	92.23	100.1	1056	0.48	0.63	0.04	19.72	19	6.74	1877	116
2	100.38	74.44	157.49	6.07	90.46	151.7	918.4	n.d	0.32	0.06	45.35	21	6.59	1855	186
3	96.08	81.90	124.08	5.20	66.33	79.12	948.9	1.09	0.57	n.d	6.56	22	6.60	1636	125
4	96.21	73.33	192.66	5.26	125.0	159.2	884.8	0.69	0.50	0.06	15.46	21	6.51	1914	132
5	60.43	87.60	499.93	9.93	453.0	135.6	1056	n.d	n.d	n.d	n.d	22	7.30	2622	119
6	68.03	69.12	770.80	9.88	707.6	118.9	768.9	n.d	0.63	n.d	n.d	21	7.00	3202	178
7	78.64	70.18	303.03	68.11	229.2	92.21	948.9	n.d	0.07	n.d	1.12	27	7.23	2876	102

Table2

Oct.	Ca	Mg	Na	K	NH4	Cl	SO4	HCO3	Br	F	NO3	PO4	T	pH	EC	Eh
0	209.0	73.77	284.9	12.7	n.d	175.7	212.6	1001	n.d	0.63	21.52	n.d	17	6.70	1888	105
1	210.5	84.23	145.7	3.63	n.d	94.26	96.08	1214	0.16	0.52	18.67	0.15	19	6.45	1731	242
2	230.3	82.25	159.5	7.94	n.d	102.3	133.0	1126	0.78	0.42	27.99	0.45	19	6.34	1829	188
3	226.3	85.47	81.11	3.70	n.d	67.89	61.09	1211	0.72	0.55	0.080	2.23	19	6.05	1533	102
4	216.2	77.55	199.9	6.49	n.d	129.6	151.9	1196	0.40	0.59	0.440	0.66	21	6.38	1877	85
5	229.3	85.87	236.1	5.55	n.d	181.8	142.0	1193	n.d	0.51	36.79	0.55	21	6.80	1971	224
6	236.0	81.91	144.3	4.08	n.d	115.6	151.9	1129	0.29	0.41	41.99	n.d	22	6.95	1797	222
7	223.3	92.34	342.4	93.6	180	416.0	148.3	1617	3.32	0.92	n.d	0.61	22	7.10	3267	69

Table3

June	Li	B	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Rb	Sr	Cd	Hg	δ11B
0	16.47	777.6	0.120	194.5	6.00	2.768	2.493	0.548	11.01	0.366	<0.001	406.0	0.590	0.740	19.31
1	28.98	1.480	0.772	239.7	125.0	3.649	10.88	1.655	36.89	3.322	<0.001	771.5	0.667	1.150	n.d
2	19.49	0.523	0.206	85.16	11.0	2.501	7.296	1.691	23.32	1.007	<0.001	485.5	0.531	1.289	n.d
3	24.62	1.263	0.866	237.2	206.0	4.995	17.51	2.125	64.27	2.903	<0.001	749.2	0.845	1.170	n.d
4	22.81	627.0	0.270	358.6	63.0	4.400	14.24	6.421	82.42	1.399	<0.001	587.5	0.548	1.104	9.41
5	27.20	1313	1.245	159.1	15.0	4.061	43.75	34.43	92.45	4.395	<0.001	696.2	1.947	4.280	14.36
6	16.41	1901	1.206	359.8	112.0	4.310	45.87	42.23	166.9	13.58	<0.001	548.2	2.166	2.355	17.11
7	27.34	999.6	61.42	400.6	1124	14.28	76.82	9.317	160.4	20.83	8.731	772.0	1.443	1.648	4.37

Table4

Oct.	Li	B	Cr	Mn	Fe	Co	Ni	Cu	As	Rb	Sr	Cd	Hg	3H
0	26.76	487.1	0.131	80.30	215.9	1.290	5.09	0.520	0.728	1.905	426.2	0.567	0.271	2.7
1	40.50	371.6	0.085	164.6	6.956	0.628	4.80	0.602	1.069	1.588	699.2	0.804	0.557	n.d
2	40.41	432.4	<0.001	186.4	23.43	0.669	0.54	0.769	<0.001	2.524	681.1	0.983	0.132	n.d
3	34.27	174.9	0.098	161.3	343.1	1.574	7.01	<0.001	1.695	1.121	544.3	0.415	0.794	n.d
4	44.52	555.8	<0.001	158.7	136.2	2.566	1.56	0.761	<0.001	4.246	660.8	0.829	0.119	3.6
5	39.70	513.4	0.192	30.58	1.441	0.440	7.85	2.247	1.195	1.696	657.6	0.751	0.703	3.0
6	37.43	360.2	0.067	39.56	<0.001	0.496	13.21	3.550	0.273	1.461	672.4	0.887	0.601	3.4
7	9.105	167.6	9.625	61.84	800.3	1.819	8.90	<0.001	1.422	10.17	164.9	<0.001	<0.001	34.5

Figure1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6