Journal of Geochemical Exploration 172 (2017) 101–108

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

Application of boron and tritium isotopes for tracing landfill contamination in groundwater

Angela Nigro [a], Giuseppe Sappa [b], Maurizio Barbieri [a,*]

[a] Department of Earth Science, Sapienza University, Piaz.le Aldo Moro 5, 00185 Rome, Italy
[b] Department of Civil Building and Environmental Engineering, Sapienza University, Piaz.le Aldo Moro 5, 00185 Rome, Italy

ARTICLE INFO

Article history:
Received 26 August 2015
Revised 2 February 2016
Accepted 18 October 2016
Available online 20 October 2016

Keywords:
Boron isotope
Groundwater
Landfill
Tritium isotope

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 $\delta^{11}B$ value of 19.31‰ for uncontaminated groundwater, while $\delta^{11}B$ 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.

1. Introduction

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

The aim of this paper is to characterize the groundwater beneath a MSW landfill and to test the use of boron and tritium isotopes as tracers for evaluating contamination of the landfill. Boron (B) has two stable isotopes, namely ^{11}B (80.1%) and ^{10}B (19.9%). The mass difference results in a wide range of $\delta^{11}B$ values, which are defined as the fractional difference between ^{11}B and ^{10}B, and traditionally expressed in parts per mil. The reported range of $\delta^{11}B$ in natural waters is from −16 to +59‰. Several studies have included the use of $\delta^{11}B$ values as groundwater tracers. The $\delta^{11}B$ 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 and Heumann, 1997; Barth, 2000b; Hogan and 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 > 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

* Corresponding author.
E-mail address: maurizio.barbieri@uniroma1.it (M. Barbieri).

http://dx.doi.org/10.1016/j.gexplo.2016.10.011
0375-6742/

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 and Gronow, 1996; Hicks et al., 2000; Fuganti et al., 2003; Tazioli et al., 2004; Mutch and 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 km from the coastline of the Adriatic Sea. It is divided into 3 lots that have a total capacity of >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 (Fig. 1). 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 and 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 and 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 (Fig. 1).

3. Sampling and analytical techniques

Eight water samples were collected in June and October 2014 from boreholes located at the studied landfill of central Italy (Fig. 1) in the aim of controlling geochemical proprerties of groundwater, depending of seasonal changes (Sappa et al., 2015). Water temperature, electrical conductivity (EC), pH and Eh were measured in the field. Bicarbonate was determined by titration with 0.1 N HCl. The chemical composition was determined using standard analytical methods (APHA, 1992). Major ions were analysed with a Chromeleon Dionex (precision ±2%). An ICS 1100 was used for analysing cations, and a Dionex ICS 5000 was used for analysing anions. Concentrations of minor and trace elements were measured using an ICP-MS (X Series 2 Thermo Fisher Scientific) following filtration (0.45 μm) and acidification in the

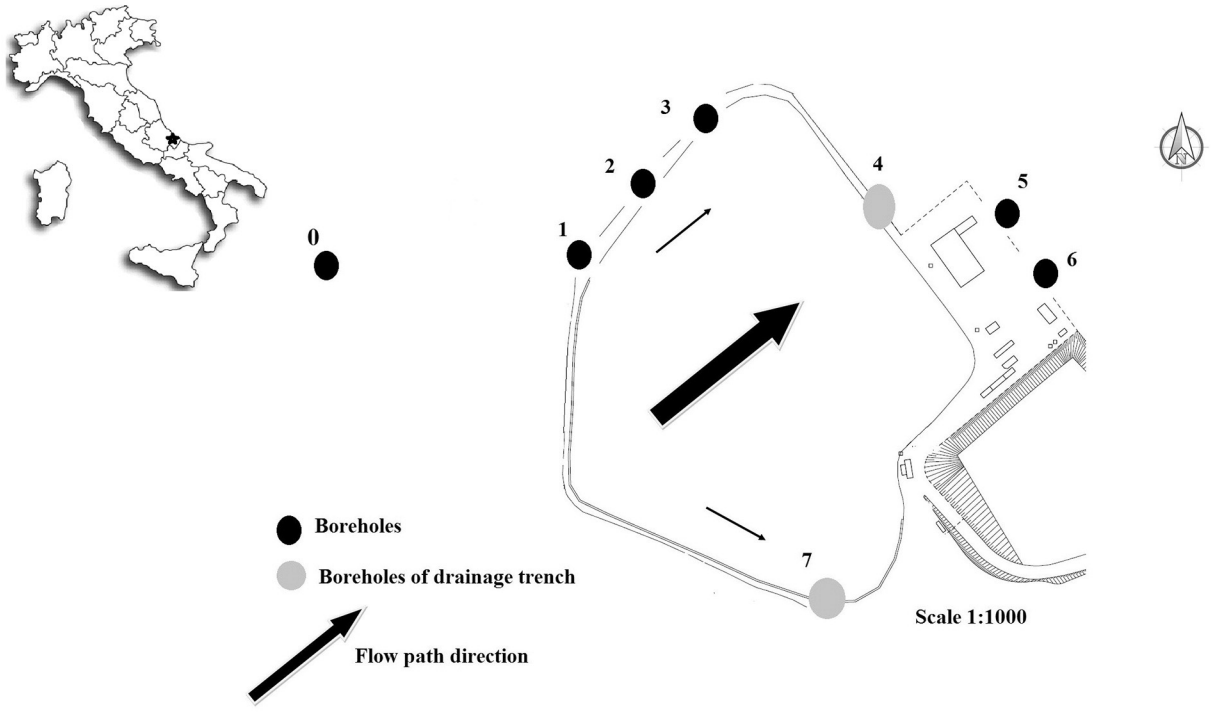

Fig. 1. Groundwater sampling location.