

A comprehensive monitoring approach to evaluate the impact of an urban landfill on a naturally reducing aquifer

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Abstract The processes leading to high levels of arsenic, iron, and manganese in a naturally reducing aquifer beneath a landfill are investigated. Traditional groundwater monitoring (physical-chemical parameters, major and trace inorganic compounds, organic compounds) has been complemented with the analysis of environmental isotopes of groundwater and of the dissolved gases (e.g., CH₄ and CO₂). The results suggest that landfill gas circulating in the aquifer (as demonstrated by ¹⁴C dating of methane) enhanced the naturally reducing conditions of the aquifer, eventually resulting in the observed high concentrations of redox-sensitive elements. At the same time, high pressure of CO₂ at some piezometers locally lowers pH, hence increasing the dissolution of sedimentary carbonates and alkalinity. In addition, the reuse of water from leachate treatment to meet circular economy requirements was invoked to explain the high levels of tritium and ²H, associated with strongly significantly negative ¹³C, observed in a production well and in a nearby piezometer. Environmental isotopes can fruitfully complement traditional monitoring when the comprehension of processes is desired, but expert judgment is required.

Keywords: groundwater, methane, environmental isotope, urban waste, pollution

1. Introduction

Modern urban landfills are useful instruments for the safe disposal of everyday waste, especially when associated to a correct separate waste collection and circular economy best practices. Nevertheless, environmental pollution in the surrounding of the disposal area is always a major threat. The leachate and gas produced during the waste maturation must be carefully collected and transferred to appropriate treatments or uses e.g., for energy production, in order to avoid harmful pollutants from migrating to groundwater or other natural matrices.

Appropriate monitoring practices are required to take immediate actions when the protective barriers start to fail. Groundwater monitoring procedures attempt to detect the passage of specific contaminants or pollution indicators, such as inorganic compounds and organic contaminants. Traditional monitoring is based on the respect of fixed

thresholds for selected parameters. The evaluation of these indicators can be fruitfully complemented by the use of environmental isotopes, both in groundwater and gas-phase. ³H and ^δ²H are well known tracers of leachate pollution due to the typical fingerprint (Hackley et al., 1996; Mutch and Mahony, 2008). Carbon isotope analysis is useful to assess a landfill impact on the groundwater contamination (Porowska, 2015).

Negative redox conditions in groundwater trigger the reductive dissolution of iron and manganese (hydro)oxides resulting in the release of these metals and sorbed elements, such as arsenic (Wang and Mulligan, 2006; Parrone et al., 2022). This is caused by natural conditions of the aquifer, leachate pollution, interaction of groundwater with plant-emitted landfill gas (Kerfoot, 1994; Kerfoot et al., 2004; Whitlock and Kelly, 2010).

In this study, we investigate the processes leading to high concentration of arsenic, iron, and manganese in a naturally reducing aquifer beneath a landfill. Traditional groundwater monitoring (physical-chemical parameters, main and trace inorganic compounds, organic compounds) has been combined with the analysis of groundwater environmental isotopes and dissolved gases (e.g., CH₄ and CO₂).

2. Data and methods

2.1. Case study description

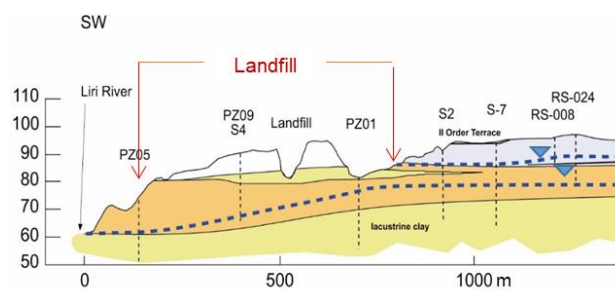


Figure 1. Schematic cross section of the study site showing the location of the landfill facility. Light blue: fluvial terrace; yellow and orange: lacustrine sequence; dotted blue lines: piezometric head

The landfill started operations in 2002 and is equipped with liners and a leachate collection system. The geology consists of a fluvial terrace with gravel and sands that lies above a lacustrine sequence of Middle Pleistocene including clay, silt and sandy levels rich in geogenic organic matter (peat), as well as volcanic products (Preziosi et al., 2019). The waste basins are located in the silty-clayey horizons of the lacustrine succession beneath the above-mentioned fluvial deposits (Fig.1). There are two distinct aquifers, one located in the fluvial terrace and the other in the lacustrine alluvial levels below, which are separated by a thick clay layer. The fluvial terrace ends at the entrance of the plant so in the site only the lower aquifer occurs (Fig.1). The depth to the water table aquifer ranges between 5 and 15 m, while the piezometric head of the lower aquifer ranges between 5 and 45 m of depth.

2.2 Methods

A network of piezometers screened in the lower aquifer has been used for groundwater monitoring campaigns at the site since 2016. (Fig.2). Groundwater sampling have been performed with low flow pumping to minimize sample disturbance. Field parameters (T, EC, pH, DO, ORP) have been measured with probes in a flow-through cell. Laboratory analysis (IC, ICP-EOS and ICP-MS) have been performed for major and trace elements. Organic compounds include DOC, PAH, PCB, VOC. Ammonia and sulphide have been measured in the field with a portable UV-Vis spectrophotometer. Dissolved gases in the head space of groundwater samples have been analyzed by gas chromatography. Environmental isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$, tritium, $\delta^{13}\text{C}$) in groundwater and $\delta^{13}\text{C}$, ^{14}C of dissolved CH_4 and CO_2 have been also analyzed.

3. Results

A piezometric high within the plant may be related to a connection between the water table aquifer and the lower one, and groundwater flows from NNE to SSW in the southern end of the site (Fig.2). They are predominantly anoxic (DO 1 mg/L), pH is close to neutral and the facies is calcium-bicarbonate. Iron, manganese and arsenic are often above national standards for groundwater (200 $\mu\text{g/L}$ for Fe, 50 $\mu\text{g/L}$ for Mn, 10 $\mu\text{g/L}$ for As) (Tab. 1). PAH, PCB and VOC were below the standards, except benzene occasionally exceeding its standard at one piezometer (PZ11, between PZ17 and PZ12, not shown in Fig.1 because it is no longer active). Dissolved CH_4 (Fig. 3) and CO_2 show a scattered distribution in groundwater, with the highest concentration in the southern end of the site and, for CO_2 only, in the production well. Results of ^{14}C dating confirmed that methane is modern and likely produced by methyl fermentation within the waste. Further, alkalinity and sulfates are locally high. Isotope fingerprint reveals significant variations from the background at some piezometers and at the production well for $\delta^2\text{H}$, tritium, $\delta^{13}\text{C}$.

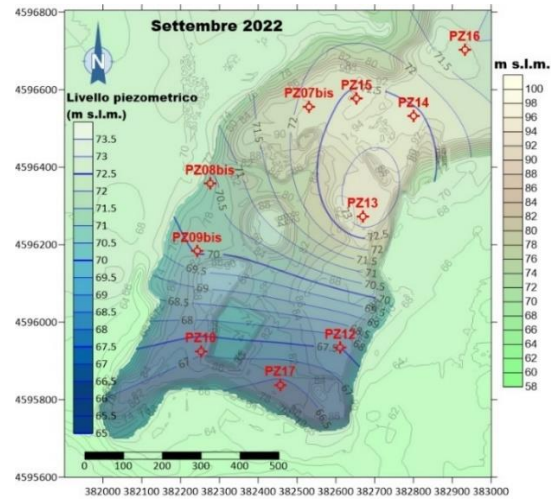


Figure 2. Active monitoring network and piezometric head contours (m a.s.l.) (September 2022)

	Mn ($\mu\text{g/L}$)	Fe ($\mu\text{g/L}$)	As ($\mu\text{g/L}$)
PZ07b	391,5	1844,0	39,7
PZ08b	192,8	886,7	9,4
PZ09b	119,6	466,2	15,7
PZ10	563,0	2910,0	10,4
PZ12	170,5	1228,0	71,7
PZ13	1925,0	190,7	11,7
PZ14	146,9	782,7	23,1
PZ15	160,8	902,4	58,0
PZ16	237,2	448,3	40,8
PZ17	392,1	2404,0	48,6

Table 1. Iron, manganese and arsenic concentration ($\mu\text{g/L}$) in groundwater (September 2022)

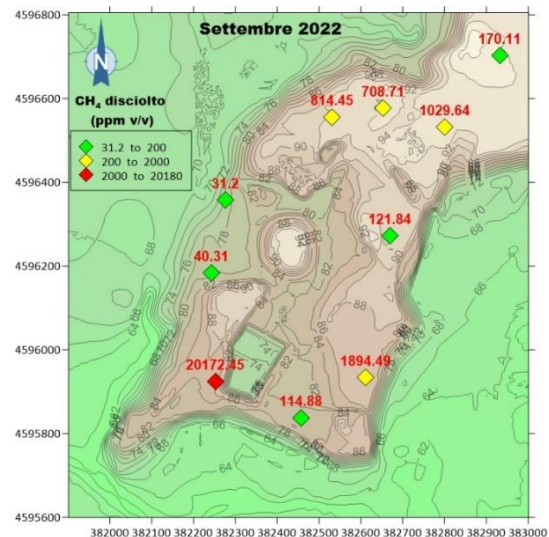


Figure 3. CH_4 concentration (ppm v/v) in groundwater (September 2022)

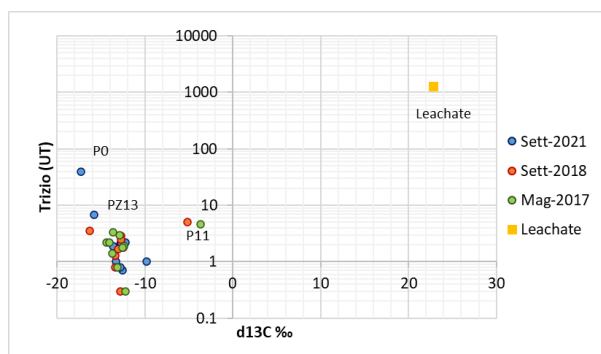


Figure 4. Tritium versus $\delta^{13}\text{C}$ of DIC in samples from 2017 to 2021

4. Discussion

Tritium, $\delta^2\text{H}$ and $\delta^{13}\text{C}$ in groundwater are within the expected range for natural groundwater, except when dissolved gas pressure is significant. The high concentration of CH_4 and CO_2 at some piezometers, associated with more negative $\delta^{13}\text{C}$ of DIC, supports the hypothesis of a gas-phase contributing to dissolved organic carbon (from CH_4), which enhances the naturally reducing conditions of the aquifer, eventually causing the observed high levels of redox sensitive elements. While CO_2 decreases pH locally, increasing alkalinity from sedimentary carbonate dissolution, as evident by less negative $\delta^{13}\text{C}$ at one piezometer (PZ11, Fig. 4). High tritium and $\delta^2\text{H}$ observed at the production well (P0) and in a nearby piezometer (PZ13, Fig. 4) may suggest leachate contamination. However, the ratio tritium versus $\delta^{13}\text{C}$ show that these samples are not aligned towards the leachate but in an opposite direction (Fig. 4). For this reason, infiltration of water from leachate treatment, which is reused within the plant to meet circular economy requirements, was invoked to explain high tritium and $\delta^2\text{H}$, associated to strongly negative $\delta^{13}\text{C}$, observed therein. Indeed, the water molecule of the recovered water derived from leachate is strongly enriched in both deuterium and tritium.

5. Conclusions

The integrated monitoring of geochemical, isotope and dissolved gas data shed light on the diverse processes that lead to the high levels of As, Mn and Fe observed in groundwater. The naturally reducing environment in the lacustrine sediments is the main cause of the dissolution of these elements in groundwater. However, the variable concentration of methane observed may locally enhance reducing conditions, thereby increasing the concentration of these elements.

Observed anomalous levels of tritium and deuterium upgradient of the plant may have been caused by water from leachate treatment. Finally, dissolved CO_2 from the landfill gas could have decreased the pH and increased the alkalinity locally.

We conclude that a complex set of physical and chemical parameters, including environmental isotopes, can fruitfully complement traditional monitoring when process understanding is desired; however, expert judgment is needed to avoid making hasty decisions.

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