

## Article

# Geochemical and Isotopic Evidence for Investigating the Impacts of Landfills on Groundwater: A Case Study in the Campania Region (Southern Italy)

Stefania Stevenazzi <sup>1</sup>, Elena Del Gaudio <sup>2,\*</sup>, Domenico Ruggiero <sup>3</sup>, Ciro D'Aniso <sup>3</sup>, Anna Maria Patelli <sup>4</sup> and Daniela Ducci <sup>1</sup>

<sup>1</sup> Dipartimento di Ingegneria Civile, Edile e Ambientale (DICEA), Università degli Studi di Napoli Federico II, 80138 Napoli, Italy; stefania.stevenazzi@unina.it (S.S.); daniela.ducci@unina.it (D.D.)

<sup>2</sup> Centro Interdipartimentale Ricerca "Ambiente" (C.I.R.A.M.), Università degli Studi di Napoli Federico II, 80138 Napoli, Italy

<sup>3</sup> S.A.P.N.A. S.p.A. (Società a Socio Unico Soggetta al Coordinamento e al Controllo Della Città Metropolitana di Napoli), 80133 Napoli, Italy; domenico.ruggiero@sapnapoli.it (D.R.); ciro.daniso@sapnapoli.it (C.D.)

<sup>4</sup> Freelance Professional, 80129 Napoli, Italy; ampatelli@libero.it

\* Correspondence: elena.delgaudio@unina.it

**Abstract:** In this study, we present the hydrogeological, hydrogeochemical and isotopic characterisation and monitoring activity of a closed landfill located in the northern sector of the Phlegrean Fields groundwater body in the Campania Region (Southern Italy). The aim of the study is to distinguish between natural enrichments (e.g., geogenic sources) and anthropogenic pressures (e.g., leakages from the landfill body) causing anomalously high concentrations of some metals (As, F, Fe, Mn) in groundwater. Major anions, cations, metals, water-stable isotopes, carbon isotopes and tritium were analysed. The results show that high As, F and Fe concentrations are due to adsorption–desorption processes occurring in the aquifer hosted in the volcanic rocks/deposits or the occurrence of upwelling hydrothermal fluids related to the volcanic activity of the Phlegrean Fields, which may cause metal mobilisation. High localised Mn concentrations cannot be solely related to natural processes or to groundwater contamination due to leachate leakage from the landfill body. Instead, we hypothesise a leakage from the landfill gas system. The outcomes of this study show the advantages of the coupled use of physico-chemical and isotopic analyses in improving the comprehension of geochemical processes in areas characterised by the presence of municipal landfills.

**Keywords:** chemical analyses; isotopic analyses; groundwater monitoring; volcanic area; Italy



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## 1. Introduction

Until a few years ago, landfilling was the most usual and economical method for waste disposal. Leachate is the fluid that percolates through landfills; it is generated from liquids present in the waste and from outside water, including rainwater, which percolates through the waste [1]. Leachate composition depends on the nature of the buried solid waste, the chemical and biochemical processes responsible for the decomposition of waste materials, the water content and the age of the landfill [2–4]. Leachate accumulates below the landfill and moves into the subsurface soil, reaching the aquifers beneath the landfill soil and contaminating groundwater. To prevent contamination, the contaminants in leachate can be filtered out and/or absorbed. Geomembranes, geosynthetics and clayey soils are used in controlled landfills to prevent the interaction of leachate with the aquifer. However, membrane leakage and poor maintenance can allow the migration of pollutants from leachate to groundwater [5]. Leachates, mainly derived from the interaction of wastes with rainfall infiltration, are highly contaminating due to the presence of organic and inorganic contaminants, such as ammonia, heavy metals, etc. [6–8]. Moreover, the presence

of the disposed waste also favours negative redox conditions in groundwater. Often, high concentrations of iron, manganese and arsenic are detected due to the reductive dissolution of iron and manganese (hydro)oxides and the consequent desorption of arsenic. The concentrations are also due to the metal-reducing microbial processes in organic matter [9].

Landfill gas is the product of the decomposition of organic material by the action of microorganisms in landfills, and it is a mix of different gases, mainly CH<sub>4</sub> and CO<sub>2</sub> (90 to 98%) but also VOC, H<sub>2</sub>S and <sup>3</sup>H. Normally, these gases cannot contaminate groundwater because they are extracted from landfills using a series of wells that collect gas and are connected to a common point where it can be processed, treated and/or used for energy purposes. The malfunctioning of the gas system can generate groundwater contamination and/or negative redox conditions in groundwater [10].

For all of these reasons, the 'Landfill Directive' 1999/31/EC [11] and its implementation require landfill operators to control landfill gases and to monitor potential leachate leakages from the collecting systems during the entire life of a landfill, i.e., during the active phase and after its closure. For the protection of groundwater, the regulation requires the monitoring of many physico-chemical parameters selected from those derived from the expected composition of the leachate and the groundwater's chemical composition in the area. An appropriate monitoring strategy prior to landfilling has been found to be supportive in assessing the background conditions at a local scale, especially for those inorganic constituents that could be derived from either geogenic or anthropogenic processes [12]. Consequently, groundwater contamination may be more easily detected. Nonetheless, the chemical species required by the regulation are not always sufficient to clearly identify the presence of interactions between leachate and groundwater, especially in geologically and geochemically complex areas. Instead, multidisciplinary approaches have been proposed and proved effective in supplying detailed indications of landfill environmental impacts [4]. In particular, combining chemical and isotopic analyses has been proven to be reliable when distinguishing between natural enrichments (e.g., geogenic sources, seawater intrusion) and anthropogenic pressures (e.g., agricultural activities) and leachate or leakages from landfills [9,13–15].

In this study, we present the hydrogeological, hydrogeochemical and isotopic characterisation and monitoring activity of a closed landfill located in the Campania Region (Southern Italy). The main objectives of this study are: (i) to identify and quantify potential leakages of pollutants from the landfill site affecting groundwater quality; (ii) to distinguish between the natural conditions and anthropogenic pressures causing the anomalously high values of some metals (As, F, Fe, Mn) in groundwater; (iii) to analyse temporal changes and trends of metal content in groundwater. This study makes extensive use of previous geological and geophysical surveys conducted by the landfill operators and hydrochemical analyses derived from six-monthly groundwater sampling, carried out since 2010. Due to the occurrence of concentrations of some metals (As, F, Fe, Mn) being higher than the European and Italian threshold values (Directive 98/83/EC [16] and Italian Legislative Decree 152/2006 [17]), further investigations were required. An ad-hoc sampling campaign was conducted between June and December 2022. Major anions and cations, metals (As, F, Fe, Mn), water-stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ), carbon isotopes ( $\delta^{13}\text{C}$ ) and tritium (<sup>3</sup>H) were analysed in water samples collected from monitoring wells within the landfill and water wells located in the surrounding area.

## 2. Materials and Methods

### 2.1. Geological and Hydrogeological Setting of the Study Area

The object of this study was the Settecainati-Cava Bianco Landfill, which is located in the northern sector of the Phlegrean Fields groundwater body (GWB; Figure 1). The morphology of the GWB (about 200 km<sup>2</sup>) consists of a topographic high that slopes southward towards the sea and northward towards the Volturno-Regi Lagni Plain. The Phlegrean Fields GWB is an active volcanic field formed after two significant eruptions: the Campanian Ignimbrite (~39 ky [18]) and the Neapolitan Yellow Tuff (~15 ky [19]). The map

in Figure 1 shows the hydrogeological units cropping out in the study area, while the hydrogeological cross sections of Figure 2 (the section traces are in Figure 1) show a profile view of the subsurface deposits. Due to the alkali-potassic volcanism of southern Italy, with explosive and subordinately effusive styles of activity, pyroclastic deposits and pyroclastic rocks (ranging from trachybasalts to phonolitic alkali-trachytes [20]) predominate the lavas [21]. From the younger to the older units, the hydrogeological succession comprises the following:

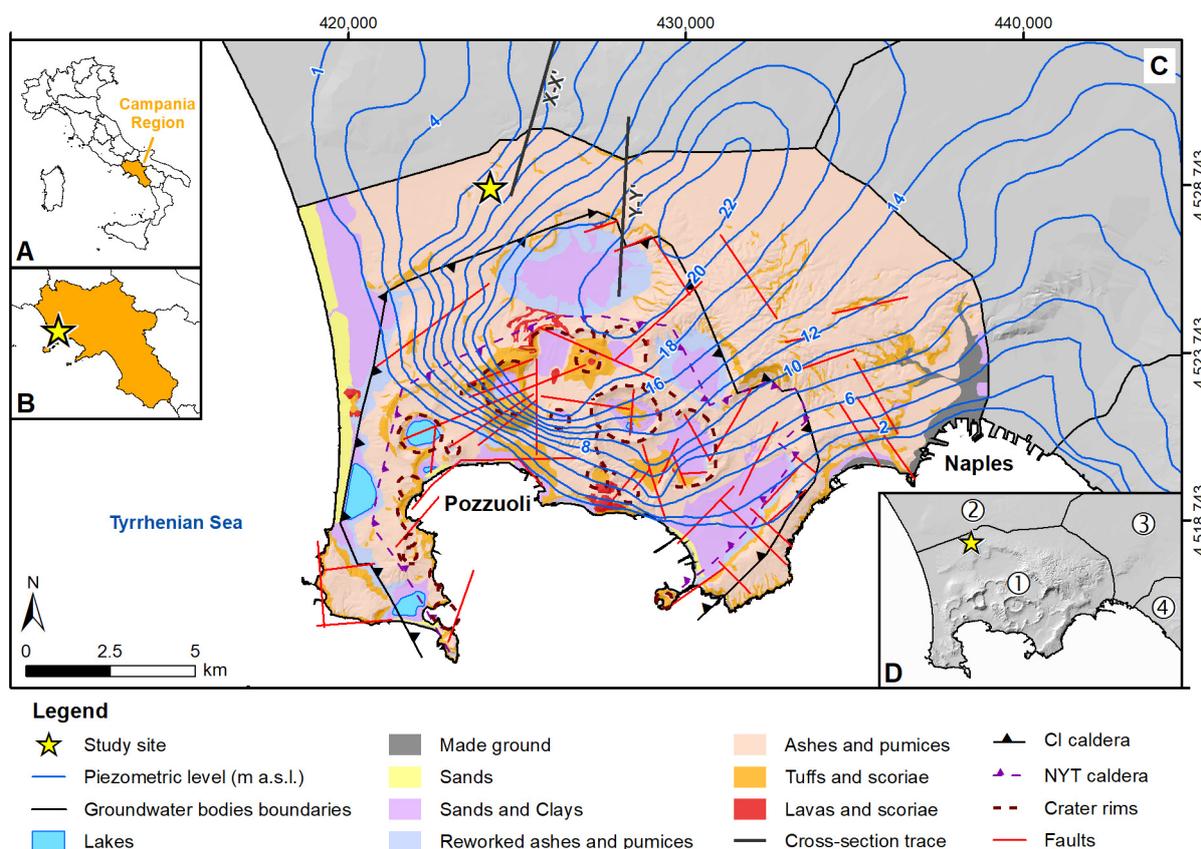
- Upper pyroclastic deposits related to the eruptions subsequent to those of the Campanian Ignimbrite and the Neapolitan Yellow Tuff are loose to soft pyroclastics, mainly from fallout (e.g., pumice, ash, lapilli), with a prevalent medium grain size (PSc) and a prevalent fine grain size (PSf), and reworked material (PSr). Due to the widespread presence of fine materials and the frequent interruptions in the coarser levels, this pyroclastic unit is characterised by a permeability degree ranging from medium to low.
- Neapolitan Yellow Tuff (NYT) are the tuffs associated with the ~15 ky eruption of the Phlegrean Fields. The tuffs have a mixed permeability for fracturing and porosity; the permeability degree is generally low, and higher permeability is due to intense fracturing.
- Campanian Ignimbrite (CI) are greyish cinerites associated with black scoriae and lava shreds associated with the ~39 ky eruption of the Phlegrean Fields, lithoid facies (CI-L), incoherent facies (CI-I) and scoriaceous facies (CI-Sc). The permeability degree is variable, ranging from low to high as a function of the fracture setting and, for the incoherent facies, of the grain size; scoriae are characterised by high permeability.
- Lower pyroclastic deposits (PS-old) are silt to sandy volcanic sediments related to volcanic eruptions older than the CI. These unwelded pyroclastic deposits have a permeability for porosity; the permeability degree ranges from low to high as a function of the grain size.
- Marine deposits, mainly clays with sandy layers (Ag). Due to the fine grain size of the materials, this unit has very low permeability.

The groundwater flow is characterised by a piezometric high of around 20 m a.s.l., probably associated with the rising of deep fluids [22], followed by a radial trend directed toward the sea to the south and west, towards the alluvial-pyroclastic Volturno-Regi Lagni Plain GWB to the north, and towards the Plain east to Naples GWB to the east [21,23]. The Phlegrean Fields GWB has a net recharge due to rainfall (estimated at 171 mm/y [24]), plus minor amounts due to seawater intrusion and deep fluids rising along the major tectonic lineaments. The geological-stratigraphical characteristics of the northern sector of the Phlegrean Fields GWB are similar to the contiguous Volturno-Regi Lagni Plain GWB, considering that the boundary between the two GWBs does not coincide with a 'physical' subsurface watershed (i.e., a tectonic or lithostratigraphic element) but is determined by the piezometric setting (Figure 1).

In the past, the examination of the numerous chemical analyses available in the GWB [25] revealed that Phlegrean groundwater is bicarbonate-alkaline water, salinised near the coast [26,27] and has a chemical profile typical of thermal waters in the inland areas of the Phlegrean caldera. Arsenic and fluoride contents are high, especially within the caldera, whereas high iron and manganese contents were found along the eastern coastal sector. These high values of As and F ions and, in some areas, Fe and Mn ions are often much higher than the European and Italian reference values (Directive 98/83/EC [16] and Italian Legislative Decree 152/2006 [17]). The raised values have been highlighted for a long time [23], and they are due to the volcanic origin of the area and the persistence of endogenous phenomena (thermal waters, fumaroles, bradyseism, etc.). The Regional Council of Campania, taking into account the above-cited studies and internal reports carried out by the University of Naples Federico II, indicated that the natural background levels (NBLs) for these ions are significantly higher than the Italian and European reference values and set new threshold values (see Table 1) for the entire GWB (Campanian Regional Decree 371/2020 [28]).

**Table 1.** Reference values indicated by Directive 98/83/EC [16] and the Italian Legislative Decree 152/2006 [17] and threshold values (natural background level) set by the Campanian Regional Decree 371/2020 [28] for the Phlegrean Fields GWB.

Chemical Parameter	Reference Value ( $\mu\text{g/L}$ )	Natural Background Level ( $\mu\text{g/L}$ )
As	10	32
F	1500	15,000
Fe	200	200
Mn	50	62

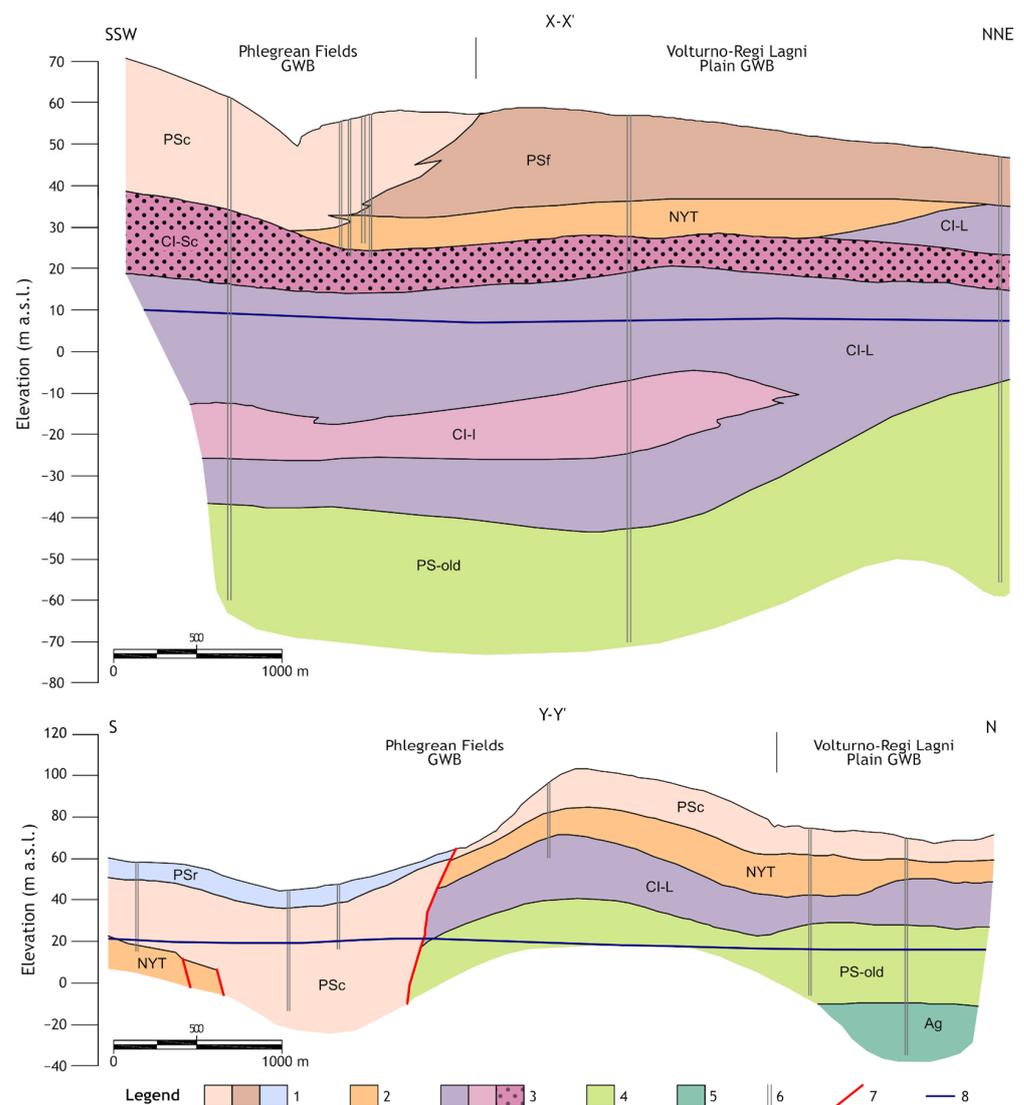


**Figure 1.** (A,B) Location of the study site in the Campania Region, Southern Italy. (C) Hydrogeological setting of the Phlegrean Fields GWB (simplified and modified after [25]) and location of the study site. Piezometric levels after [21]. Onshore fault distribution after [29,30]. CI: Campanian Ignimbrite; NYT: Neapolitan Yellow Tuff. GWBs delineation according to [31]. Coordinates refer to the WGS 1984—UTM Zone 33 N projection. (D) (1) Phlegrean Fields GWB, (2) Volturno-Regi Lagni Plain GWB, (3) Plain east to Naples GWB, (4) Somma-Vesuvius GWB. In the basemap in (C,D), the hill shading was derived from the TINITALY digital elevation model [32].

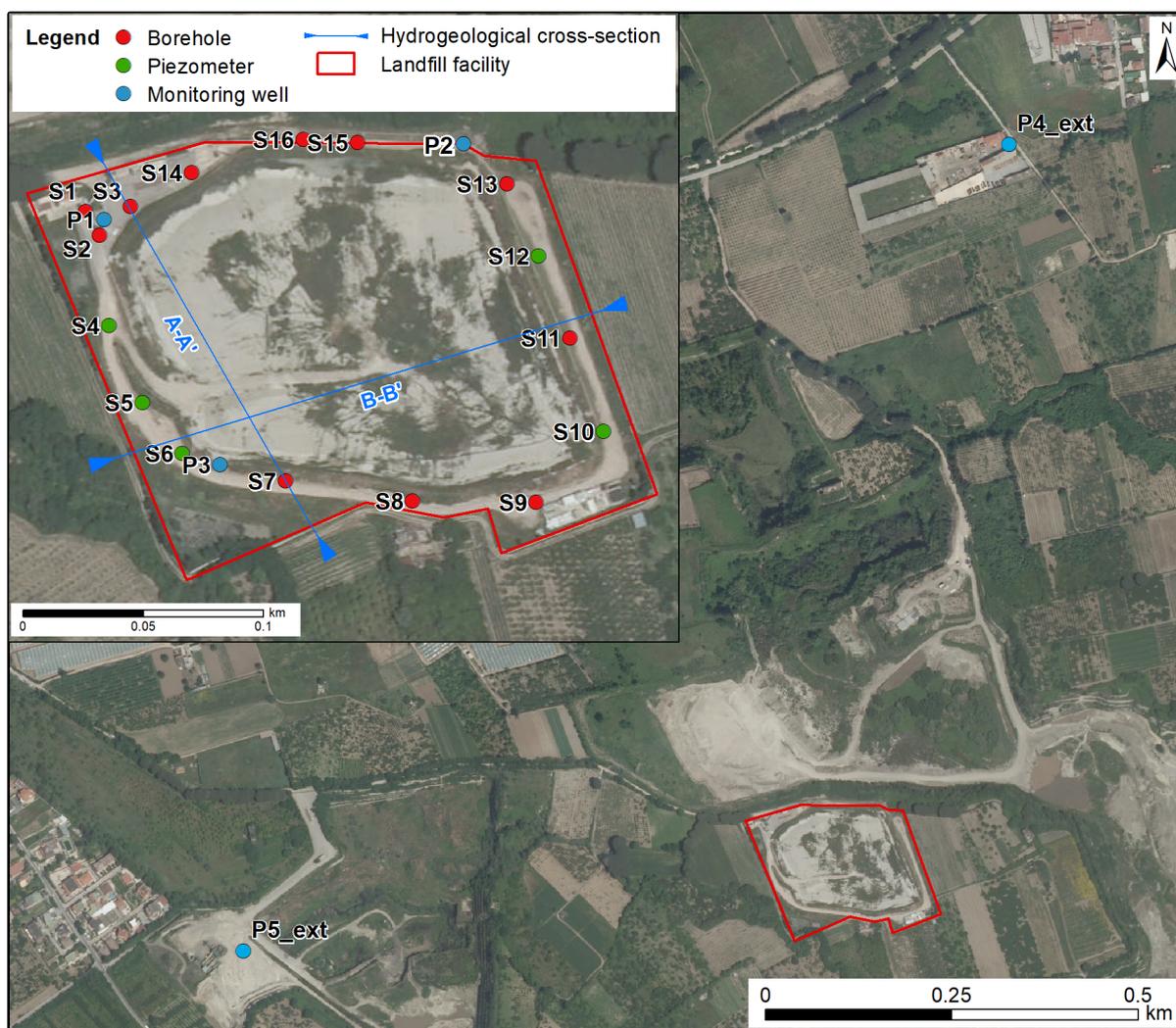
## 2.2. Study Site, Field and Laboratory Analysis Procedures

S.A.P.N.A. S.p.A. is a public company owned by local authorities, and it currently manages the Settecainati-Cava Bianco Landfill. The landfill facility is located in an almost plain area, sloping towards the west, and characterised by the presence of agricultural fields, orchards and scattered buildings. Pit quarries, for the extraction of pozzolan soil [33], are present on the northern and western sides of the landfill. The landfill itself occupies the area of a previous pit quarry (for the extraction of pozzolan soil). The landfill was active for about one year (2004–2005), and it was closed immediately after. A total of about 617,000 tons of municipal solid waste (MSW) were stored in the landfill during its active phase. According to 2014/955/EU [34], the wastes were classified as ‘E.E.R.

19.05.03' (off-specification compost) and 'E.E.R. 19.12.12' (other wastes, including mixtures of materials, from the mechanical treatment of wastes not containing hazardous substances, i.e., not containing explosives, flammable gases/aerosols/liquids/solids, self-reactive or self-heating substances, substances corrosive to metal or substances hazardous to the ozone layer). Geological, geognostic and geophysical surveys conducted in the landfill area in the 2010s were used for the geological and hydrogeological reconstruction of the area and the landfill body. Sixteen borehole logs (to depths of 50–55 m) were used for the lithostratigraphic reconstruction, and the results of permeability tests (Lefranc and slug tests) were used for the hydrogeological parametrisation of lithological materials (i.e., pyroclastic deposits); six geoelectric tomographic profiles were used for the delineation of the landfill body. Piezometers were installed in five out of the sixteen boreholes, to depths of 90 m, to measure groundwater levels and to enable the collection of groundwater samples for chemical analyses (Figure 3).

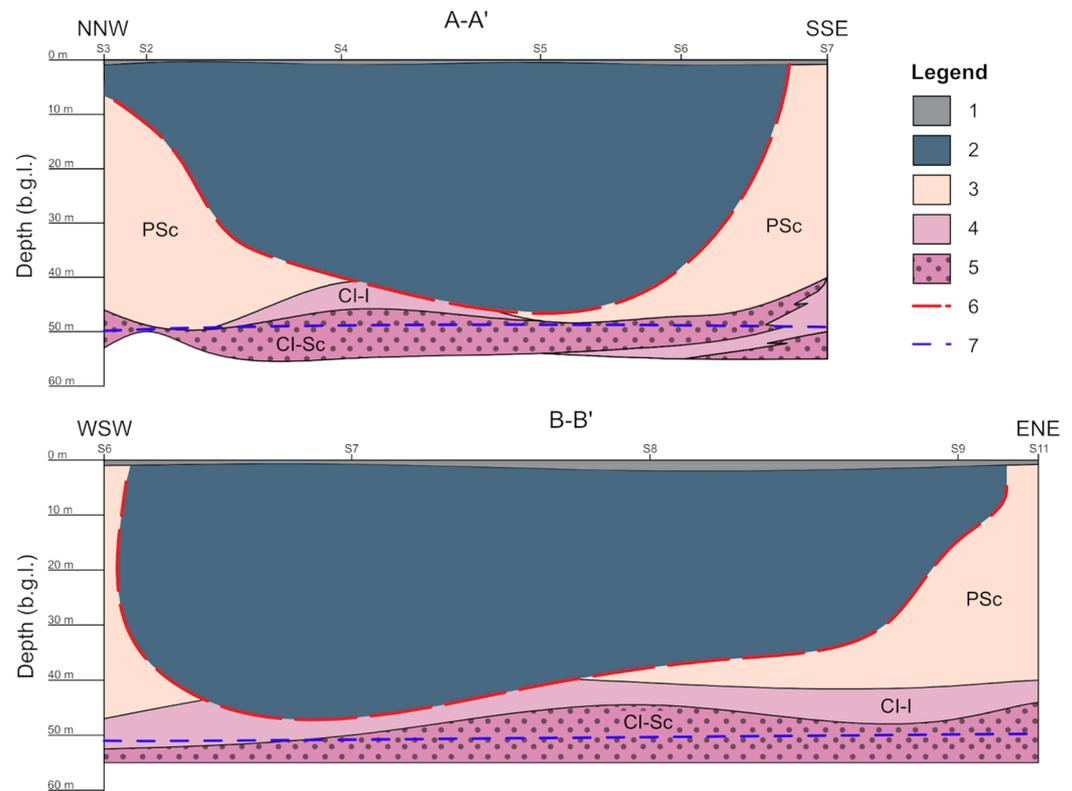


**Figure 2.** Hydrogeological cross sections (modified after [24]). Legend, from left to right: (1) upper pyroclastic deposits of prevalent medium grain size (PSc) and of prevalent fine grain size (PSf), and reworked pyroclastic material (PSr); (2) Neapolitan Yellow Tuff (NYT); (3) Campanian Ignimbrite: lithoid facies (CI-L), incoherent facies (CI-I), scoriaceous facies (CI-Sc); (4) lower pyroclastic deposits (PS-old) of silt to sandy grain size; (5) marine deposits, mainly clays with sandy layers (Ag); (6) borehole logs; (7) faults; (8) piezometric level after [21].



**Figure 3.** Groundwater monitoring network, location of the geognostic surveys (borehole/piezometer logs) and the litho-stratigraphic cross-sections reported in Figure 4. The red polygon delineates the perimeter of the Settecainati-Cava Bianco landfill. Basemap: 2012 aerial photo from <http://www.pcn.minambiente.it/mattm/> (accessed on 8 September 2023).

The hydrochemical analyses of water samples collected at three monitoring wells (from 70 m depth), located upgradient (P2) and downgradient (P1 and P3) of the landfill body, were used for the physical and chemical characterisation of groundwater in the landfill area (Figure 3). Water samples were mostly collected every six months since 2010. Water sampling and chemical analyses are conducted by the ECORICERCHE S.r.l. Laboratory, under the supervision of S.A.P.NA. S.p.A. The main physico-chemical parameters (temperature, electrical conductivity, pH), major anions and cations (except  $\text{HCO}_3^-$ ), minor elements (e.g., metals) and contaminants (e.g., solvents and hydrocarbons) were monitored. Metal concentrations were obtained through mass spectrometry following the EPA 6020B:2014 protocol [35]. As, F, Fe and Mn concentrations were considered in this study to identify significant changes over time.



**Figure 4.** NW–SE and SW–NE litho-stratigraphic cross-sections. Traces are taken from Figure 3. Legend: (1) made ground; (2) landfill material; (3) upper pyroclastic deposits (PSc); (4) Campanian Ignimbrite, incoherent facies (CI-I); (5) Campanian Ignimbrite, scoriaceous facies (CI-Sc); (6) bottom of the landfill body reconstructed from geoelectric tomographic profiles; (7) piezometric level (October 2022).

A specific groundwater monitoring campaign was conducted from June to December 2022 to deepen the hydrogeological knowledge of the landfill area and the surroundings and to distinguish between the natural conditions and anthropogenic pressures causing high anomalous values of some metals (As, F, Fe, Mn) in groundwater. The groundwater monitoring network was defined by considering: (i) the three monitoring wells and five piezometers located inside the landfill facility; (ii) a private well located parallel to the landfill, representing the ‘blank’ sample; (iii) a private well located downgradient from the landfill, to verify potential contamination outside the borders of the landfill area (see Figure 3). These wells capture the same shallow aquifer. No other wells were available in the surroundings of the landfill facility. Groundwater levels were measured with a manual water level meter (PASI Measuring Instruments) in June and October 2022, at the end of the wet and dry periods, respectively. Four sampling campaigns were conducted in the summer and autumn of 2022 to analyse the physico-chemical parameters. A total of 17 water samples were collected. Before sampling, the wells and piezometers were purged to remove stagnant water. Raw (i.e., non-filtered) waters were pre-washed and stored using: (i) polyethylene bottles for chemical (i.e., major anions and cations and nitrogen compounds) and isotopic analyses; (ii) a polyethylene bottle pre-washed with 2% nitric acid for metals; (iii) a dark-glass bottle for dissolved gases. Physico-chemical parameters (pH, electrical conductivity, temperature) were measured both on site using a portable pH-conductivity meter (Hanna Instrument) and then again in the laboratory. Water samples were stored at 4 °C in a refrigerator until delivery to the laboratory. Chemical analyses for determining CO<sub>2</sub>, major anions and cations, nitrogen compounds, As, F, Fe and Mn were executed by the Laboratory of Analytic Chemistry for the Environment (ACE) of the Department of Chemical Sciences of the University of Naples Federico II. Testing involved titration, ion chromatography and

mass spectrometry on unfiltered samples. Chemical analyses were carried out following the protocols described in APAT-IRSA/CNR [36], ISO 10304-1:2007 [37], ISO 17294-2:2016 [38] and APHA [39]. The error in the ionic balance (BAL) always resulted in values lower than  $\pm 5\%$  ( $-1\% < \text{BAL} < +3.8\%$ ). With regard to undetected data, the detection/quantification limit was assumed. Five of the samples collected in July 2022 were also analysed for water-stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ), carbon isotopes ( $\delta^{13}\text{C}$ ) and tritium ( $^3\text{H}$ ). Isotopic analyses were executed by the ISO4 Laboratory of the University of Turin. The water samples for the measurement of  $\delta^{13}\text{C}$  were prepared following the protocols described in McCrea [40]. The analyses of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  were carried out through WS-CRDS (wavelength-scanned cavity ring down spectroscopy) technology. The results are expressed according to the standard PDB [41] and V-SMOW2 [42], following the international convention defined by the International Atomic Energy Agency. The analytical error was  $\pm 0.2\%$  for  $\delta^{18}\text{O}$  and  $\pm 1\%$  for  $\delta^2\text{H}$ . Measurements of tritium were obtained following the LSC (liquid scintillation counting) protocol.

Descriptive statistics (arithmetic mean, minimum and maximum values), diagrams (i.e., the Schoeller–Berkaloff diagram), bivariate plots (e.g., the  $\delta^2\text{H}$ – $\delta^{18}\text{O}$  plot) and spatial distributions (e.g., piezometric surface) were evaluated to characterise the groundwater chemistry and to reconstruct the hydrogeological setting of the study area. The piezometric surface was obtained by applying the natural neighbour spatial interpolation technique [43], considering the monitoring wells and the piezometers present within the landfill area.

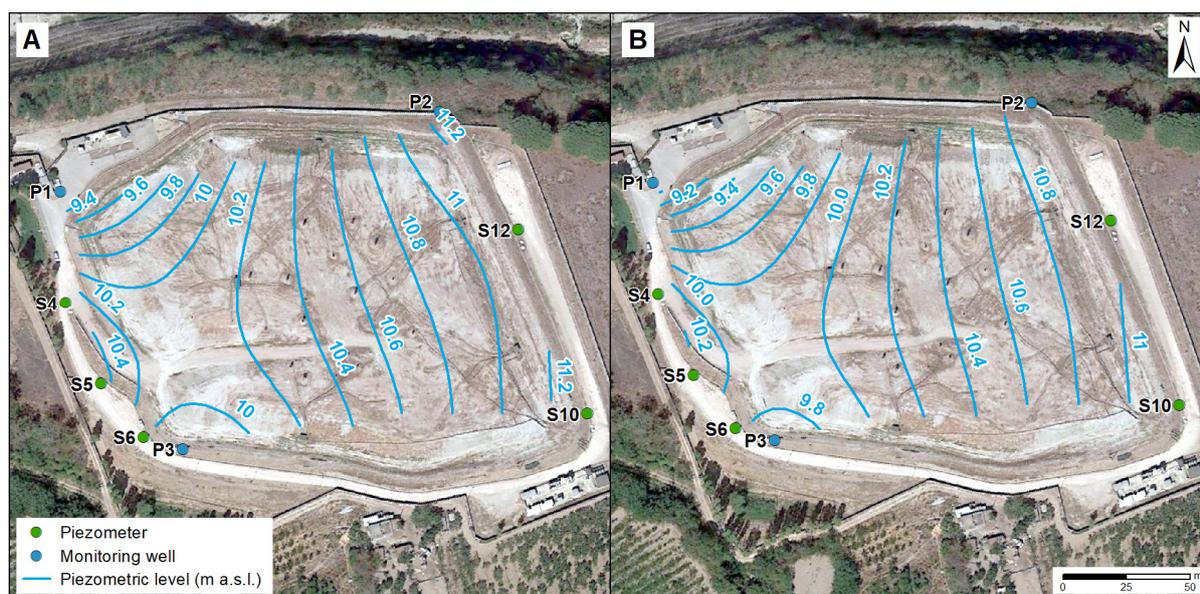
### 3. Results

#### 3.1. Geological and Hydrogeological Setting of the Landfill Site

The subsurface of the landfill area is characterised by the presence of pyroclastic deposits from the Phlegrean Fields and Somma-Vesuvius eruptions (Figure 4):

- Upper pyroclastic deposits (PSc) from the surface to about 40 m below ground level (b.g.l.) are related to the eruptions subsequent to those of the Campanian Ignimbrite (~39 ky [18]). These deposits consist of loose to soft pyroclastics, mainly from fallout, of medium to fine grain size (e.g., pumice, ash, lapilli). They present medium–low hydraulic conductivity.
- Campanian Ignimbrite (CI) from about 40 m b.g.l. to the borehole maximum depth (55 m b.g.l.). This consists of greyish cinerites associated with black scoriae and lava shreds. Within the landfill area, the CI has a maximum thickness of 12 m, without identifying the bottom of the layer. The degree of diagenesis is highly variable spatially, influencing the hydraulic conductivity of the layer. The incoherent facies (CI-I) presents a hydraulic conductivity similar to that of the upper PSc, whereas the scoriaceous layers (CI-Sc), which are diffusely present in the landfill area, present a medium hydraulic conductivity.
- Lower pyroclastic deposits (PS-old) are located below the CI and relate to volcanic eruptions older than the CI itself, mainly constituting silt to sandy volcanic sediments. These PS-old deposits were identified through borehole logs located in the surroundings of the landfill area, as shown in Figure 2, but are not reported in Figure 4.

Corresponding with the landfill facility, a shallow, unconfined aquifer is hosted in the CI layer. Groundwater depth is assessed to be about 50 m b.g.l., which corresponds to a piezometric level of around 9–11 m a.s.l., with a hydraulic gradient equal to 9‰. Groundwater flow is oriented from east to west, with S10 and P1 being the local maximum and minimum, respectively. The groundwater flow direction and hydraulic gradient remained constant over the two sampling campaigns (Figure 5). A lowering of the piezometric levels by about 20 cm was observed at the end of the dry period (October 2022) compared to the end of the wet period (June 2022).



**Figure 5.** Piezometric level of the shallow, unconfined aquifer in June (A) and October (B) 2022. Basemap: Orthophoto of the landfill area in 2021, provided by S.A.P.NA. S.p.A.

The landfill body is mainly hosted in the PS deposits, and it covers an area of about 2.3 ha with a maximum depth of about 40 m. The distance between the bottom of the landfill body and the water table is sometimes less than 10 m (Figure 4).

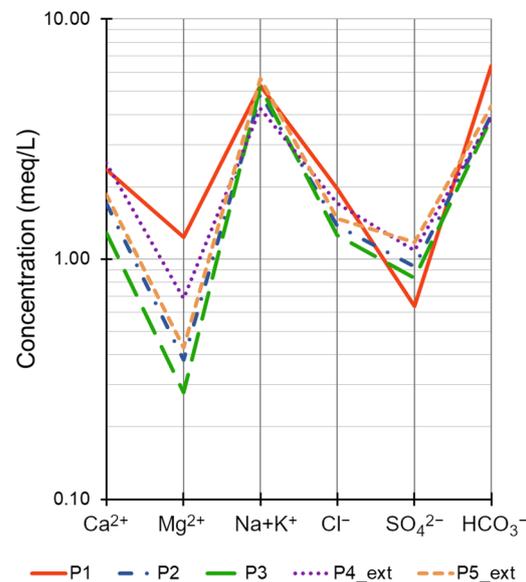
### 3.2. Hydrochemical and Isotopic Characterisation

The chemical composition of the water samples is of a bicarbonate-alkaline type (Figure 6), which is typical of Phlegrean Fields groundwaters not affected by seawater intrusion [25]. The water sample collected in P1 differs from the other samples by showing a higher concentration of calcium, magnesium and bicarbonates and a lower concentration of sulphates. Nitrogen compounds are generally present in low concentrations, despite the occurrence of agricultural fields in the surroundings of the landfill area. Nitrate concentrations range between 2.7 and 28.2 mg/L, with an average of 20.3 mg/L. The lowest  $\text{NO}_3^-$  concentrations occur in P1 (5 mg/L and 2.7 mg/L being measured in the summer and autumn sampling campaigns, respectively). Ammonium was detected at a few sampling points: (i)  $\text{NH}_4^+$  concentration is about 0.12 mg/L in P2, P3 and P4\_ext; (ii)  $\text{NH}_4^+$  concentrations equal to 8.1 mg/L and 5.9 mg/L were measured in samples collected in P1 during the summer and autumn sampling campaigns, respectively.

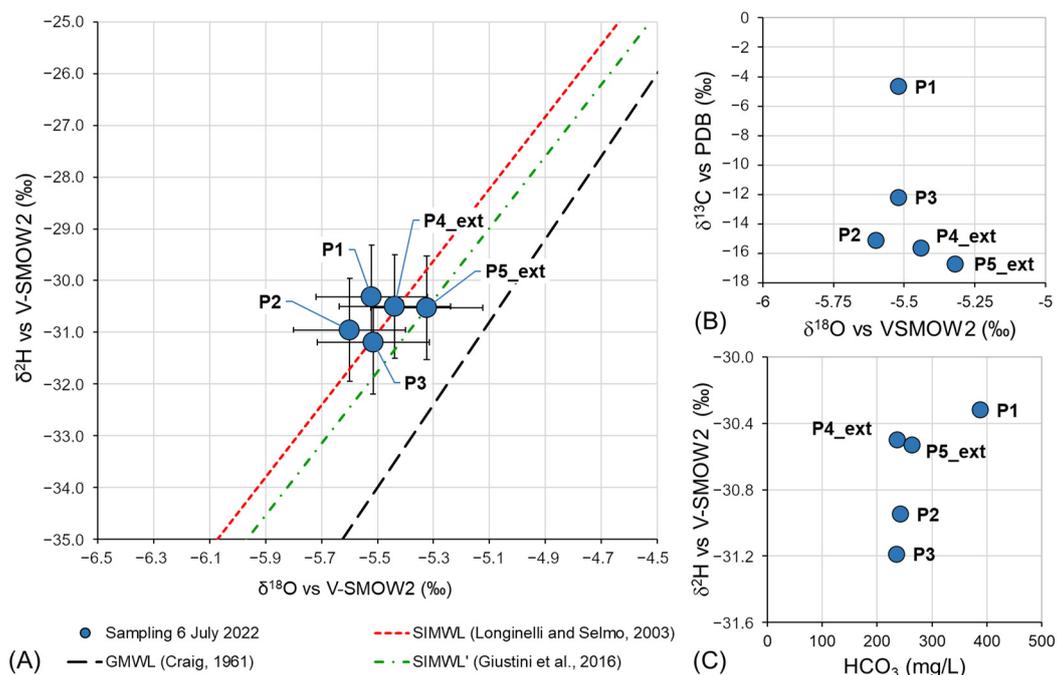
The electrical conductivity summarises the concentration of the major anions, as high electrical conductivity values correlate to high concentrations of bicarbonates and magnesium ( $R^2 = 0.7$ ) and, subordinately, chlorides ( $R^2 = 0.6$ ), and vice versa. EC values measured in the period June–December 2022 ranged between 559  $\mu\text{S}/\text{cm}$  and 1098  $\mu\text{S}/\text{cm}$ , with the highest values measured in P1. The pH indicates slightly basic waters, showing values in the range of 6.3–8.1. About 75% of the water samples collected in the period June–December 2022 showed carbon dioxide content in the range of 40–70 mg/L; the remaining 25% (four samples) showed values of 80–100 mg/L. The highest  $\text{CO}_2$  contents were measured in P1.

Analyses of the isotope ratios  $\delta^{18}\text{O}$ – $\delta^2\text{H}$  show that the selected monitoring point distribution fits well with the two local meteoric water lines valid for Southern Italy [44,45], highlighting the meteoric origin of groundwater (Figure 7A). Waters collected from the five monitoring wells show similar  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values; thus, they originate from the same recharge area, without mixing with other types of water (e.g., the upwelling of deep fluids, seawater intrusion, etc.). P1 differs from the other monitoring wells because its water shows a higher  $\delta^{13}\text{C}$  content and a higher  $\text{HCO}_3^-$  concentration with respect to the

other samples (Figure 7B,C). Moreover, the tritium content in P1 is slightly higher than in the other monitoring wells, being equal to  $1.0 \pm 0.5$  T.U., whereas the tritium content in the other monitoring wells is lower than 0.6 T.U.



**Figure 6.** Schoeller–Berkaloff diagram of water samples located in Figure 3 collected in June–July 2022.

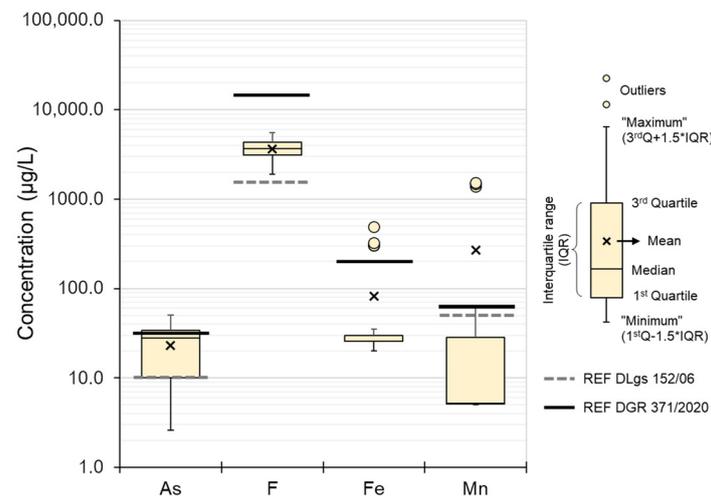


**Figure 7.** (A)  $\delta^{18}\text{O}$ – $\delta^2\text{H}$  diagram for the selected monitoring points with the global meteoric water line (GMWL, [46]) and two local meteoric water lines valid for Southern Italy: LMWL [44] and LMWL' [45]. (B)  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  diagram. (C)  $\text{HCO}_3^-$ – $\delta^2\text{H}$  diagram.

### 3.3. Recent and Long-Term Monitoring of As, F, Fe, Mn in Groundwater

At least 75% of the samples collected in the period June–December 2022 show an As concentration above the Italian regulatory limit of  $10 \mu\text{g/L}$ , and more than 40% of the samples show As concentrations slightly higher than the Campanian regional regulatory limit for the Phlegrean Fields GWB of  $32 \mu\text{g/L}$  (Figure 8). As concentrations higher

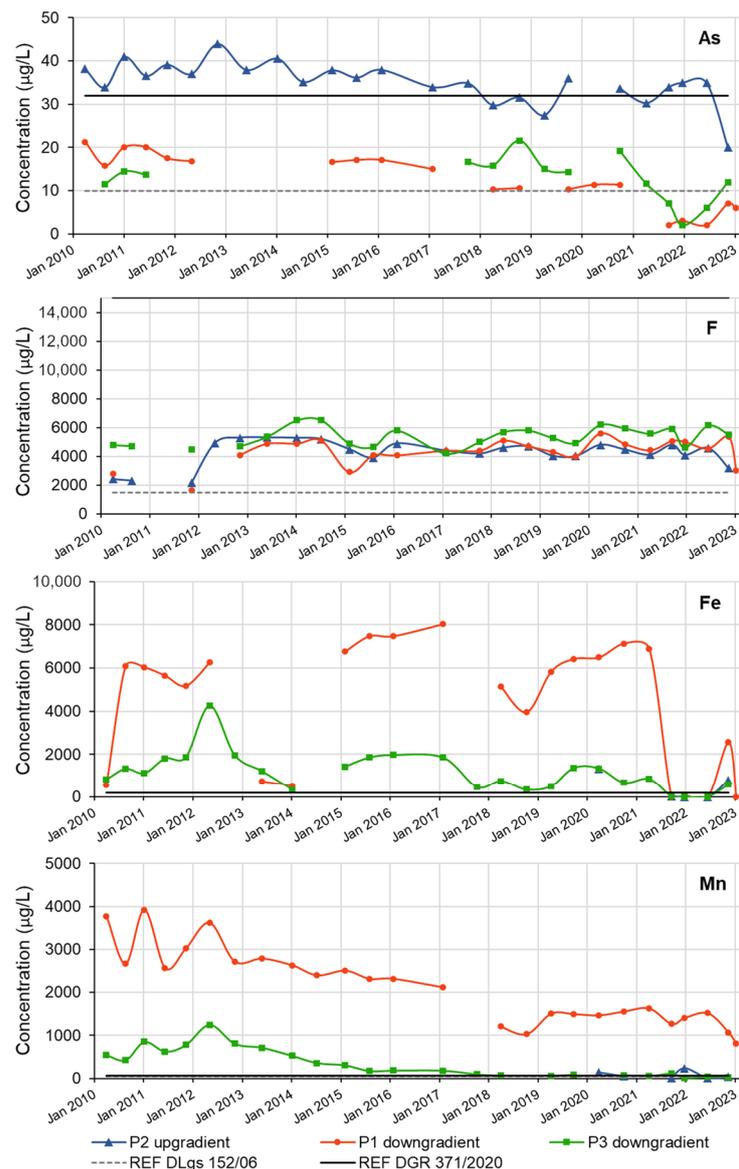
than 32 µg/L were measured in P2 and S12 (located within the landfill area, upgradient and downgradient with respect to the landfill body, respectively) and in P5\_ext, located outside the landfill area. Despite the lack of some measurements, long-term monitoring activity shows As concentrations lower than 32 µg/L in the two monitoring wells located downgradient from the landfill area (P1 and P3 in Figure 9). Instead, As concentrations higher than 32 µg/L were measured in P2, located upgradient from the landfill body, although a decreasing trend is identifiable (Figure 9).



**Figure 8.** Boxplot representation of As, F, Fe, Mn concentrations in water samples located in Figure 3 and collected in the period June–December 2022 (total number of samples = 17). For the purpose of this representation, below-detection limit values were set equal to the limit value. Each boxplot is compared with the corresponding regulatory reference values (REF) at the Italian level (Legislative Decree 152/06 [17]) and Campanian regional level (Regional Decree 371/2020 [28]) for the Phlegrean Fields GWB.

Both the recent and long-term monitoring activities show F concentrations in groundwater samples higher than the Italian regulatory limit but a lot lower than the Campanian regional regulatory limit for the Phlegrean Fields GWB (Figures 8 and 9). Similar F concentration values were measured in wells located inside and outside the landfill area. Moreover, the long-term monitoring activity in the three monitoring wells within the landfill facility shows a stationary trend of F concentration values.

For Fe and Mn, the exceedances of regulatory limits (both Italian and Campanian regional regulations) only concern a small percentage of the samples, resulting in outliers (Figure 8). Outliers were only measured in P1. Below detection limit values represent 65% and 47% of the samples collected in June–December 2022 for Fe and Mn, respectively. The highest Fe concentrations range between 300 and 489 µg/L, similar to the outlier values of the Phlegrean Fields GWB [25]. Instead, the highest Mn concentrations range between 1396 and 1526 µg/L, which are even higher than the outliers of the Phlegrean Fields GWB [25]. Fe concentrations are highly variable in the long term, without showing a clear trend (Figure 9). Mn concentrations, mainly measured in P1 and P3 during the long-term monitoring activity, show a decreasing trend (Figure 9). In particular, Mn concentrations measured in P3 show values close to the regulatory limits (50 and 62 µg/L for the Italian and Campanian regional regulations, respectively). Despite the decreasing trend, Mn concentrations measured in P1 remain elevated, with an average value of 1469 µg/L in samples collected in the period June–December 2022.



**Figure 9.** Concentrations of As, F, Fe, Mn in the monitoring wells located within the landfill facility from 2010 to 2023. Each plot is compared with the corresponding regulatory reference values (REF) at the Italian level (Legislative Decree 152/06 [17]) and Campanian regional level (Regional Decree 371/2020 [28]) for the Phlegrean Fields GWB.

#### 4. Discussion

The results of the recent and long-term hydrochemical monitoring activity conducted at the Settecainati-Cava Bianco landfill show the following:

- The chemical composition of the water samples is typical of Phlegrean Fields groundwaters not affected by seawater intrusion. Despite the presence of agricultural fields in the surroundings of the landfill area, nitrogen compounds are generally present in low concentrations. Nitrate concentrations hardly exceed the value of 25 mg/L, this value being a sort of guideline defined by EU regulation [47] to identify critical areas concerning nitrate pollution. It is possible that the deep groundwater depths (down to 50 m b.g.l.), the medium–low hydraulic conductivity of the unsaturated zone material and the presence of vegetated soil contribute to groundwater protection against contamination from the ground surface.
- As concentrations slightly higher than the Italian and/or Campanian regional threshold values are generally present in groundwater in the studied area, both inside

and outside the landfill facility. The long-term trend shows slightly decreasing As concentrations over the last ten years in the monitoring wells inside the landfill facility. Nonetheless, the presence of arsenic in groundwater is natural and related to adsorption–desorption processes occurring in the aquifer hosted in volcanic rocks and deposits (pyroclastics and tuffs) or due to the upwelling of hydrothermal fluids enriched in metals from the Phlegrean Fields area. This origin was also confirmed by previous local studies [23,48].

- Despite F concentrations being higher than the Italian threshold value, they have never exceeded the natural background levels identified for the Phlegrean Fields GWB [25] in the monitoring period (2010–present). As for arsenic, the presence of high F concentrations in groundwater could be due to the volcanic origin of the deposits (i.e., the occurrence of adsorption–desorption processes) or to the occurrence of upwelling hydrothermal fluids (which are enriched in metals) related to the volcanic activity of the Phlegrean Fields [23,48].
- Fe concentrations are highly variable in the long-term monitoring period, with the highest concentrations in the same range of the outliers identified for the Phlegrean Fields GWB [25]. The occurrence of anomalous Fe concentrations in groundwater could be due to metal mobilisation. In fact, the mobility of Fe in groundwater is facilitated near fault zones in active volcanic areas [49,50], which are close to the landfill facility and favour the upwelling of deep gas inputs (e.g., CO<sub>2</sub> or H<sub>2</sub>S). Moreover, anoxic conditions may occur underneath the landfill body, thus creating a reducing environment that may cause metal mobilisation. Negative redox conditions in groundwater may also be favoured by the presence of waste disposal (i.e., leachate leakage) [9].
- The presence of high Mn concentrations in groundwater in the studied area is extremely localised in monitoring well P1, located downgradient from the landfill body. Despite the decrease in Mn concentrations in the last ten years, it currently exceeds the natural background values identified for the Phlegrean Fields GWB [25]. Therefore, solely natural processes (i.e., metal mobilisation due to the presence of dissolved gases of volcanic origin in groundwater [49,50]) do not completely explain the occurrence of localised elevated Mn concentrations.

Despite the fact that the  $\delta^{13}\text{C}$  content in P1 may suggest contamination of the groundwater due to leachate [14,15], the  $\delta^2\text{H}$  content in P1 is similar to the other sampling points, contradicting this hypothesis, as verified in other landfill facilities [9,10]. Contamination due to leachate can also be excluded when considering the low tritium content in P1 [10]. Thus, besides the natural factors that influence the carbon isotopic content (atmospheric CO<sub>2</sub> and CO, dissolution of carbonates, deep fluids enriched in CO<sub>2</sub>), excluding the leachate contamination, it could be hypothesised that there is leakage from the landfill gas system (CO<sub>2</sub>, CH<sub>4</sub>). In fact, the presence of CO<sub>2</sub> in groundwater can result in the dissolution of carbonates (e.g., calcite, magnesium), ion exchange reactions, and adsorption/desorption reactions related to changes in pH. These reactions are reflected in a decrease in pH, an increase in alkalinity (i.e., bicarbonate content) and electrical conductivity and a change in carbon  $\delta^{13}\text{C}$  content [10,51]. High values of electrical conductivity, bicarbonates, CO<sub>2</sub> and  $\delta^{13}\text{C}$  content were measured in P1. Such a hypothesis may explain the elevated Mn concentration in P1 because gases enriched in methane and carbon dioxide, such as landfill gases, can change the redox conditions in the soil, reduce Mn(IV) to Mn(II) from sediments in the vadose or saturated zone and lead to increased Mn concentrations in groundwater [51,52]. Localised reducing conditions can also cause denitrification processes, which lead to decreased NO<sub>3</sub><sup>−</sup> concentration in groundwater and favour the ammonification process (dissimilatory nitrite reduction to ammonium [53]), which leads to increased NH<sub>4</sub><sup>+</sup> concentrations in groundwater, as observed in P1.

## 5. Conclusions

This study demonstrated the efficacy and reliability of combining chemical and isotopic analyses to distinguish between natural enrichments (i.e., geogenic sources) and leachate or gas leakages from landfills and other anthropogenic pressures (e.g., agricultural activities), which may cause anomalous concentrations of major and minor chemical compounds in groundwater. The key findings can be summarised as follows:

- Establishing an ad hoc monitoring network enabled the characterisation of groundwater chemistry and the identification of potential contamination due to the presence of the landfill body.
- Despite the lack of some measurements, the long-term monitoring activity of groundwaters within the landfill facility allowed us to recognise trends in the concentration of major and minor compounds, with a focus on As, F, Fe and Mn.
- The continuous upwelling of hydrothermal fluids from the active volcanic Phlegrean Fields system causes a natural enrichment of arsenic and fluoride in groundwater. The upwelling of deep gases (e.g., CO<sub>2</sub> or H<sub>2</sub>S) also facilitates the mobilisation of iron and manganese in groundwater.
- A reducing environment favouring metal mobilisation may also be related to local anoxic conditions due to the presence of the landfill body itself, which acts as a barrier and limits the gas exchange with the atmosphere.
- The presence of waste disposal underneath the landfill body (i.e., the occurrence of leachate leakage) can be excluded. Instead, leakage from the landfill gas system is found to be the most probable cause for localised high manganese concentrations in groundwater. The next steps of this study will be an inspection of the landfill gas collection system and a repetition of the groundwater sampling campaign for chemical and isotopic analyses.
- The Settecainati-Cava Bianco landfill case study can represent a reference for similar studies for the assessment of groundwater quality and the identification of potential sources of contamination in areas affected by the presence of municipal landfills.

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