

Landfill investigation using tritium and isotopes as pollution tracers

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Abstract: Some studies of municipal landfills in Italy have pointed out the importance of isotope analysis based tools in evaluating the main source of pollution. Isotope investigations are commonly used especially for defining a hydrogeological conceptual model of a research area but, in some instances, they are useful for locating leachate contamination of groundwater: tritium measures were indicated by some authors for tracing purposes, owing to its stability and sensitivity as a leachate pollution tracer; nitrogen isotopes have been utilized to identify sources of nitrates and ammonium in groundwater; sulphur-34 and carbon-13 were just used in landfill contamination problems.

Tritium (^3H) is a radioactive isotope of hydrogen, occurring in very low quantity in the natural waters. In particular, tritium content in leachate water is still very high in some municipal landfills, due to the presence in the waste of some items containing high levels of tritium (i.e. luminescence paints, watches, etc.). So, with the aid of this tool, it is possible to evaluate a landfill leakage to the surrounding environment, establishing, even better and before chemical signal has been revealed downgradient, whether leakages have migrated through the containment barrier.

It is possible to identify the contamination of groundwater from the tritium increase with respect to the base level, and also to estimate the mixing ratio with the leachate.

The aim of this paper is to show the validity of tritium as a pollutant tracer, with the support of many results in different landfills in Central and Northern Italy. Some indication of the interpretation of results and data of tritium and isotopic content in groundwater,

rainwater and leachate are given. The isotope studies could also include, as supplementary tools, oxygen-18 and deuterium belonging to water molecule, ^{15}N and ^{18}O of NO_3^- , ^{34}S and ^{18}O of SO_4^{2-} , ^{13}C and ^{18}O of CO_3^{2-} .

Riassunto: Alcuni studi effettuati in Italia su discariche di rifiuti urbani hanno evidenziato, in passato, l'importanza degli strumenti basati sulle analisi isotopiche, in particolare per individuare e studiare la principale sorgente di contaminazione. Normalmente però, le ricerche in campo isotopico sono utilizzate specialmente per definire (o meglio approfondire) le caratteristiche idrogeologiche di una data area. In qualche caso esse sono utili a localizzare anche la contaminazione delle acque sotterranee.

Le misure di tritio, ad esempio, sono state indicate da alcuni autori come utili nel definire il percorso delle acque sotterranee, a causa della stabilità della molecola del tritio e della sua sensibilità come tracciante di fuoriuscite di percolato da discariche. Gli isotopi dell'azoto, invece, sono stati utilizzati per identificare le sorgenti di nitrati e ammonio in problemi di contaminazione delle acque sotterranee (Townsend et al., 2003); lo zolfo-34 (isotopo dello zolfo) e il carbonio-13 (isotopo stabile del carbonio) sono già stati utilizzati in problemi di contaminazione da discariche (Tazioli et al., 2005; Walsh et al., 1993).

Il Tritio (^3H) è un isotope radioattivo dell'idrogeno, è presente in bassissime quantità nelle acque naturali. In particolare il suo contenuto nel percolato delle discariche è ancora molto alto in alcuni rifiuti solidi urbani, a causa della presenza (all'interno dei rifiuti stessi) di alcuni oggetti contenenti alti livelli di tritio (ad esempio vernici luminescenti, insegne luminose, orologi fosforescenti, ecc.). così, per mezzo di questo strumento, è possibile valutare un'eventuale perdita di percolato dalle barriere di contenimento di una discarica, con conseguente contaminazione dell'ambiente circostante. Così è possibile stabilire se la contaminazione si diffonde all'esterno della discarica in modo più preciso, e spesso anche prima che a valle vengano rilevate alterazioni nel segnale chimico di alcune sostanze indicatrici.

È possibile identificare l'inquinamento delle acque di falda osservando l'incremento della attività di tritio rispetto al suo valore naturale di base, e così stimare l'eventuale percentuale di mescolamento con il percolato (Tazioli et al., 2004).

Lo scopo di questo lavoro è mostrare la validità del tritio come tracciante di inquinamento da percolato, attraverso la presentazione di diversi risultati relativi ad alcune discariche nell'Italia centrale e settentrionale. Inoltre, vengono fornite alcune indicazioni sull'interpretazione dei risultati e dei dati di tritio e dei contenuti isotopici nelle acque sotterranee, meteoriche e percolato.

Gli isotopi studiati e utilizzati nel presente lavoro sono l'ossigeno-18 e il deuterio (della molecola dell'acqua), l'azoto-15 e l'ossigeno-18 (dei nitrati), lo zolfo-34 e l'ossigeno-18 (dei solfati) e il carbonio-13 e l'ossigeno-18 (di carbonati e bicarbonati).

Keywords: water, leachate, tritium, landfill, groundwater, tracer, isotope

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Introduction

Hydrogeological and geochemical studies of sanitary landfills in Italy, and in Europe more generally, have focused on some aspects regarding, for example, the hydrogeological setting, the monitoring problems, the remediation facilities etc. Few studies focused on the isotope and tritium techniques progress in evaluating main origin of pollution and contaminant fate in the environment (Walsh et al., 1993; Fritz et al., 1996; Fuganti et al., 2003; Townsend et al., 2003; Tazioli et al., 2005). These studies put in evidence the goal of understanding the problem: what is the origin of pollution? Is it the landfill itself or is it some other source?

In Italy, in particular, such techniques are not yet well known and therefore rarely used. This paper does not represent so much innovative research, rather a contribution to improving and expanding the use of isotope techniques in hydrology.

The pollutants behaviour prediction plays an essential role in monitoring a complex system such as a landfill. With tritium and isotopic methods it is possible to improve our knowledge of the hydrogeological setting of the site and to establish a potential link between the landfill and its surrounding environment, evaluating any leachate migration through the containment barrier, even better and before chemical signal has produced a downward breakthrough (Fritz et al., 1994; Tazioli et al., 2004).

Being part of the water molecule, tritium travels with water so acting as an ideal tracer in surface water and groundwater systems (Mutch & Mahony, 2008). So the importance of tritium is related to its conservative behavior. Elevated levels of tritium in the leachates occur frequently in municipal landfills throughout the world (Rank et al., 1992; Fritz et al., 1994; Robinson & Gronow, 1996; Hicks et al., 2000; Fuganti et al., 2003; Tazioli et al., 2004; Mutch & Mahony, 2008). Such observation indicates an opportunity to use tritium as a tracer of leachate migration in the surrounding environment.

The paper deals with the results of isotopic measurements performed on rainwater, surface water and groundwater samples, with the aim of investigating the fate of contaminants released from several landfills located in Italy. The main aim of this paper is to confirm the effectiveness of tritium as a contamination tracer. A general review of isotopic tools in pollution problems and some (new and literature) data from different case studies are presented.

The isotope determinations included, besides tritium (^3H), also $\delta^{18}\text{O}$ and $\delta^2\text{H}$ belonging to water molecule, ^{15}N (of NO_3^-), ^{34}S (of SO_4^{2-}).

Background

Tracer concept

One very important concept which is used in pollution issues is that of a *tracer*. A 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). A waste disposal site can itself be considered an enormous reservoir of tracers. In fact it contains, often, a large quantity of chemical compounds with a composition affected by some tracer. It is clear therefore that some of these parameters can be taken as tracers, that is, substances that indicate the possible leakage from the waste disposal site towards the surface water and groundwater.

Base level concentration

In order to consider some chemical substances as tracers, the values in the environment surrounding the landfill must be considerably different when compared with the concentrations found in the

leachate. Also for isotopes it is important to notice a difference (even small) between the isotopic composition of the leachate and the surrounding waters. The first operation which must be done, when using isotopic determinations to trace the contamination, is to define the base environment of the main parameters considered as pollution indicators by performing a series of measurements which are repeated at different times during the year so as to get a picture of time and space variations of chemical species concentrations.

Chemical data and isotope determinations

Isotopes are nuclides of the same element and therefore have the same atomic number (Z) although with a different mass number (A) and a consequent different atomic mass. The difference in mass is due to the different number of neutrons occurring in the nucleus of the atom. The relative percentages of abundance vary among the single natural compounds and even within the same family of compounds. Isotopes are divided into *stable isotopes* (fewer than 300) and non-stable or *radioactive isotopes* (about 1200).

The isotopic data are used to determine some characteristics which cannot be appreciated merely by chemical concentrations, which offer only an indication of the quantitative presence of a certain chemical compound dissolved in water. Isotopes offer, for example, a valuable reference about defining the source of pollution. In the literature the reference values for different isotopic species have already been listed (for example: Clark & Fritz, 1997; USGS, 2002). Within certain limits it is therefore possible to trace, with excellent approximation, the source of contamination which has produced certain concentrations of pollutants, and it is possible to compare different sampling sites.

The water molecule isotopes that are principally used for hydrogeological purposes are deuterium (^2H), oxygen-18 (^{18}O) and tritium (^3H). The first two are stable isotopes, while tritium is a radioactive isotope with a half-life of a bit more than 12.32 years. Natural tritium was firstly detected in natural waters in 1950 (Grosse et al., 1951). It is produced by the interaction of cosmic radiation with the atmosphere (Libby, 1946). Since 1952 the tritium from thermonuclear weapon tests has greatly exceeded the natural production (Fritz & Fontes, 1980). The unit used to measure natural concentration levels of tritium is the Tritium Unit (TU); 1 TU corresponds to an atom ratio of tritium to hydrogen of 10^{-18} , equivalent to a radioactivity of about 3.2×10^{-12} Ci/g of water. The importance of these isotopes is related to their use as tracers of the water cycle (Clark & Fritz, 1997). The altitude, the latitude, the seasonality directly affect the fractionation between oxygen-18 and oxygen-16 and between deuterium and hydrogen-1. Isotopic values are therefore perfect tracers of the original source (recharge) of the groundwater sampled around the landfill. The content of deuterium and oxygen-18 contributes to define the recharge location, but it does not give any indication of the transfer time between that point and the point at which sample is collected. Tritium, on the contrary, is capable of tracking the particle of water which infiltrated at point "x" so defining a range of time occurring to migrate down gradient to the sampling point "y". By taking numerous measurements over time it is also possible to find out exactly after how much time the particle arrives at point "y". This assessment is possible thanks to the fact that tritium is radioactive and its concentration decays in time with a half-life equal to about 4500 days i.e. ≈ 12.32 years, (Lucas & Unterweger, 2000). For this reason it is clear that very low tritium values (0-3 TU) generally refer to groundwater with a long underground life, values between 4 and 8 to water with a short or medium life, values between 9 and 13 TU to

water with a very short life, often only of a few months. The situation is complicated by the mixing by which the water is affected during its flow. Tritium values of more than 13-15 TU in groundwater very probably indicate the presence of external sources of tritium; one of these sources could certainly be waste disposal sites with a content of tritium which is often hundreds of times higher than that naturally present in the environment.

Isotopes involved in pollution problems

The radioactive isotope present in the water molecule (tritium) is used both for dating recent water (less than 50 years) and as a tracer of leakage from waste disposal sites (Rank et al. 1992; Aggarwal et al., 2005; Calestani et al. 1999; Fuganti et al. 2003; Tazioli et al. 2004).

The other isotopes involved in pollution problems vary according to the type of substance that is considered as a pollutant for the area being examined.

In areas with high levels of sulphate or sulphide pollution at the source sulphur isotopes could be used (above all sulphur-34; expressed as $\delta^{34}\text{S}$ difference per mil, ‰, compared to a standard reference) and oxygen-18 of the sulphates (expressed as difference per mil, ‰, compared with a standard reference sample). Other isotopes of sulphur, less utilized for hydrological purposes, are sulphur-32, sulphur-33 and sulphur-36.

In areas with high levels of nitrogenous components at the source, oxygen-18 as reference isotopes together with nitrogen-15 ($\delta^{15}\text{N}$ ‰) could be used. The adopted reference for ^{15}N is atmospheric nitrogen (Nair). Other isotopes of nitrogen are ^{14}N and fourteen radioactive isotopes with atomic masses ranging from ^{10}N to ^{25}N . ^{15}N is used to trace the origin of those compounds containing nitrogen, such as nitrates (NO_3^-) and ammonium (NH_4^+). In fact, on the basis of these values it is possible to trace the source and evaluate whether it is of natural or anthropic origin and, in the latter case, if it is due to chemical fertilisers rather than to organic sewage. From data found in the literature we can deduce that nitrate molecules dissolved in groundwater with values lower than +8‰ are typical of agricultural areas, since $\delta^{15}\text{N}$ coming from chemical fertilisers is about 0 (Clark & Fritz, 1997) whereas higher values are generally the result of the nitrification of the nitrogen contained in animal waste, manure or sewage (USGS, 2002). Other authors specify that waste of animal origin has nitrates with nitrogen-15 values of between +10‰ and +23‰ while for organic sewage the values are between +10‰ and +20‰ (Aggarwal et al., 1998).

The $\delta^{13}\text{C}$ in dissolved carbonates (CO_3^{2-}), bicarbonates (HCO_3^-) and carbon dioxide (CO_2) is useful in identifying the physical origin of these compounds. In groundwater the values of $\delta^{13}\text{C}$ are approximately between -15 ‰ and -10‰ compared with the standard PDB (Pee Dee Belemnite) while values are slightly higher for surface water, owing to some processes occurring in an open system. In reducing environments, such as sanitary landfill sites, bacterial activity creates an intense isotopic fractionation, leading to strongly positive $\delta^{13}\text{C}$ values ($\delta^{13}\text{C} > +15\text{‰}$). Such fractionation affects especially methane; most landfills, in fact, where strong methane production occurs, have coexisting carbon dioxide or DIC (dissolved inorganic carbon) that is enriched in ^{13}C (Lansdown et al., 1992). For this reason, once the local base environment is known, it is possible to verify whether or not pollution is present.

Tritium as leachate tracer

Tritium is just one of the substances available in the environment as a tracer. Even if present in very low quantities in natural water it is an integral part of the water molecule, therefore not subject to

any kind of chemical reactions and it is not absorbed by the soil, but travels together with the groundwater, since it is itself water. For each atom of tritium there are 10^{18} atoms of hydrogen, that is to say an infinitely higher quantity; in order to identify tritium highly accurate instruments must be utilized. Its use as a tracer is connected with the fact that, in a great number of waste disposal sites, the relative concentration of tritium is considerably higher than that which occurs naturally in the groundwater. The ratio may even be several hundreds of times higher, as several studies carried out on similar cases have been shown (Fritz et al., 1994; Hicks et al., 2000; Fuganti et al., 2003; Mutch & Mahony, 2008).

It is therefore clear that where there occurs a minimum leakage from the landfill site, whereas it could be difficult to identify it with chemical analysis, analysing the tritium content could make it possible to trace this leakage. In fact only small variations of tritium in the groundwater (much greater, however, than the values normally present in the environment) are needed to be able to ascertain external contamination. For example, if the tritium content in the leachate is higher than 1000 TU, it is possible to trace even a leachate leakage of less than 10 L.

Sources of tritium

There are some studies which detected elevated tritium levels in municipal landfill leachate, (Egboka et al., 1983; Tazioli, 1993; Robinson & Gronow, 1996; Fuganti et al., 2003; Tazioli et al., 2004; PADEP, 2006;).

In the past, the high levels of tritium in the leachate were linked to the presence in the atmosphere of high tritium contents (due to the thermonuclear experiments in 1950s and '60s). These high contents in the atmosphere suggested to hydrogeologists the possible use of tritium as a good tracer for groundwater age determination. The IAEA (International Atomic Energy Agency) encouraged experts around the world to monitor tritium content in rain water, in order to have a spatial and temporal variation of tritium content (IAEA-WMO, 2004). Now (as the effects of these experiments have completely disappeared) we can state that the high levels found in some municipal landfills have another source. In fact, the tritium level in the atmosphere after the thermonuclear bombs reached a peak value of 2000 TU in the northern hemisphere, 250 TU in the Tropical regions and 120 TU in the southern hemisphere. Nowadays, the tritium level in the precipitations is almost under 15 TU in the whole hemisphere (IAEA_WMO, 2004).

Luminescent paint in solid waste materials (Hackley et al., 1996; Robinson & Gronow, 1996), gaseous tritium lighting devices, exit signs, sealed glass tubes filled with tritium gas, military-style compasses, watches, shooting ranges, key chains: all these items contain a high level of tritium. It is suspected that a significant percentage of these items find their way into municipal solid waste.

In any case, the main source of higher levels found in landfill leachate probably originates from the improper disposal of self-luminescent emergency exit signs found in waste. A single exit sign has the potential to cause observed tritium levels up to 5000 TU (PADEP, 2006). Luminescent items often contain, in fact, tritiated hydrocarbons.

Also in Italy, the effects of thermonuclear experiments are almost exhausted; in fact, tritium levels in the rain water currently range between 3 and 13 TU. An example of such trend is reported in Fig. 1, where the results of Pian dell'Elmo rain gauge station (Central Italy, province of Ancona) put in evidence the descending trend from 1992 to 2010. In particular, from an analysis of the seasonal variation of

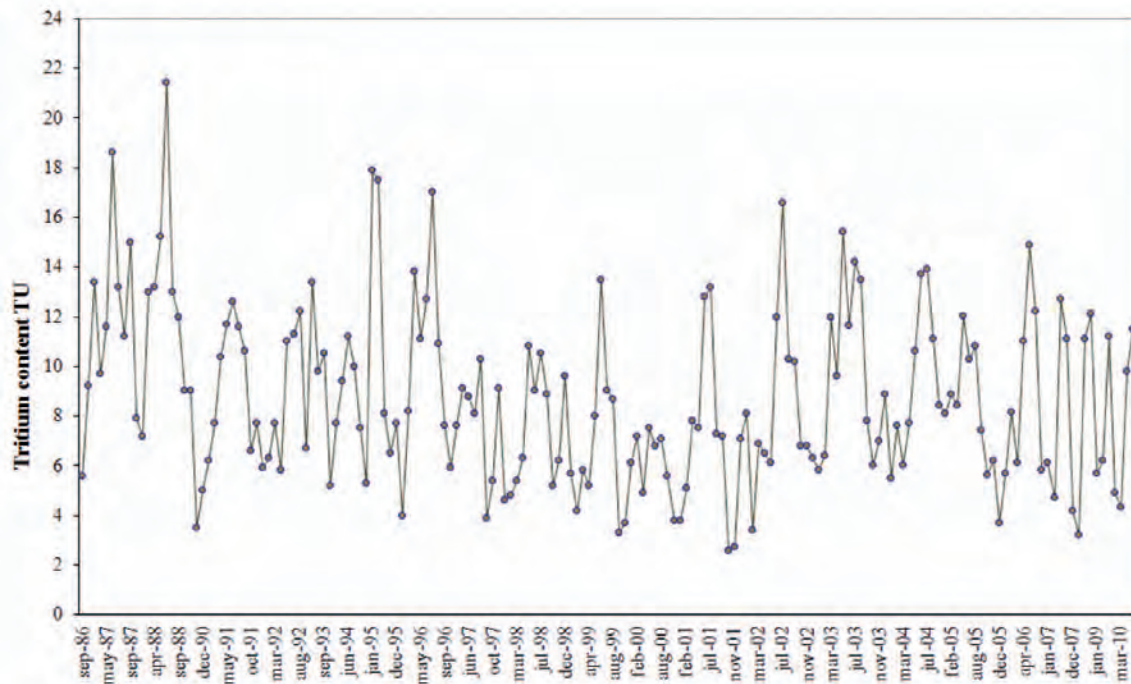


Fig. 1: Historical trend of tritium content in rain water (Pian dell'Elmo gauging station, located in Marche Apennine at 950 m a.s.l.).

the tritium composition (Tab. 1), it's apparent that the average calculated each 10 years tends to decrease. The lowest average values are around 6 TU (winter months), the highest are around 12 TU (summer months), over the entire period of sampling. So, the only sources of high tritium levels found in municipal landfill are those cited. Some previous works (Tazioli, 1993; Calestani et al., 1999; Fuganti et al., 2003) also reported studies of municipal landfills in Italy with high tritium levels in the leachate.

Tab. 1: Average of tritium data from Pian dell'Elmo gauging station (Central Italy).

		TU
average values in different seasons	spring	8,96
	summer	11,64
	autumn	6,44
	winter	6,19
full period average		8,71
'80 average		12
'90 average		8,5
'00 average		8,2

Tritium activity anomalies method

The first objective in this kind of investigation is to establish the background values of the main environmental parameters related to contamination. The method used to detect groundwater and/or surface water pollution originating from a landfill is based on the occurrence of tritium activity anomalies (Tazioli et al., 2004). Once we have established the tritium and other isotopes base concentration levels, it is possible to compare the values measured in piezometers,

wells and surface water to the base concentration levels, in order to detect if a contamination leakage from the landfills occurs.

This method is based on the analysis of environmental tritium content and isotopic composition of water in the region and on the subsequent groundwater sampling and analysis in the area surrounding the landfill and in the leachate. It is possible to identify the contamination of groundwater from the tritium increase with respect to the base level and, in this case, also to estimate the mixing ratio with the leachate (Tazioli et al., 2004).

The tritium content, in fact, is unaffected by bacterial activity as well as chemical processes (Fuganti et al., 2003).

In order to estimate the regional base level of environmental tritium in shallow groundwater, the tritium activity of rainwater samples collected on a monthly basis from local rain gauge stations must be analysed. Furthermore, the results of a global network for investigating isotopic trends in precipitation all around the world, performed in cooperation between IAEA and WMO (World Meteorological Organisation), must be taken into account. Since 1961, in fact, a worldwide survey of the isotopic composition of monthly precipitation began, in which tritium, oxygen-18 and deuterium have been measured in hundreds of sampling stations; the programme is called GNIP (Global Network of Isotopes in Precipitation (IAEA/WMO, 2004).

From the aforementioned investigations it is possible to know the local variability of the parameters in the region of interest. Such variability - still very low - depends on the natural distribution of water in the environment, and in the different pathways along which groundwater moves; in fact, there may be different residence times even in the same groundwater body. This fact produces the observed variability in tritium values. In recent years, the tritium concentration in Italy ranged from 3 to 6 TU in winter months and reached the maximum values (up to 14 TU) in spring and summer months (Fig. 1). Generally the tritium activity in water samples is measured with liquid scintillation analysers.

Case Histories

An overview of some case histories concerning isotopic data from some landfill sites in Central and Northern Italy are given. In particular, tritium contents and isotopic data concerning either polluting or non-polluting landfill will be presented.

Generally speaking tritium content in the leachates of investigated landfills range from a minimum of 20 TU (for an old sanitary landfill) to a maximum of some thousands of TU. Values from 10 to 100,000 TU have also been reported (Fuganti et al., 2003).

Case History 1 (Northern Italy)

The landfill was constructed within a 10 m thick silty-clayey layer. This landfill covers older waste accumulations dumped without bottom lining. The average thickness of soil between the bottom of the landfill and the top of the aquifer is about 2 m. In this landfill a migration of leachate towards the underground environment has been verified. From a geological point of view (Fig. 2), the sub-soil is characterized by an alternance of alluvial Holocene clay and silty-sandy clay (down to about 10 m b.g.l.) and by an alternance of alluvial Holocene and Pleistocene gravel-sandy and silty-clay sedi-

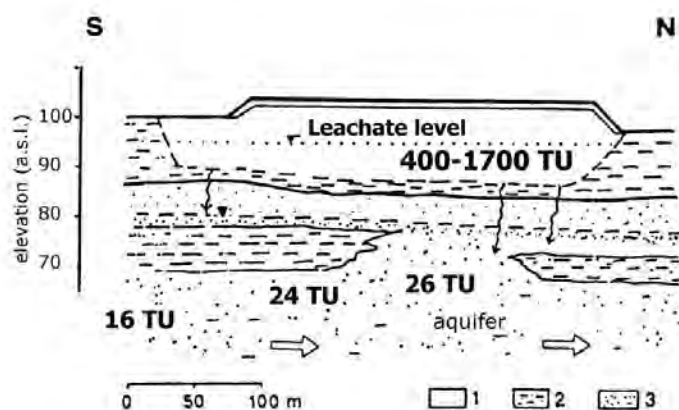


Fig. 2: Hydrogeological cross section of the landfill 1. 1: wastes. 2: silty and sandy-clayey layer. 3: gravel and sandy sediments. Values of tritium activities in TU are reported for leachate and phreatic groundwater (after Calestani et al., 1999).

ments from 10-13 m to over 40 m in depth (Calestani et al., 1999). The gravel-sandy sediments host groundwater, recharged by local rainfall (about 100 m a.s.l.) and rivers located between 100 and 800 m a.s.l. Around the landfill, in fact, there are rivers at a distance between 400 and 800 m (Fig. 3); river Taro, the main one, has a riverbed incised in the ground about 7 m, while the other streams around the landfill have less incised riverbeds (1-2 m). From isotopic contents (tritium content about 10-15 TU) it is clear that groundwater has a short residence time in the aquifer.

The geochemistry of unconfined groundwater is of calcium-bicarbonate type with a slightly negative redox potential (-20 to -30 mV) and electrical conductivity between 700 and 1100 $\mu\text{S}/\text{cm}$ (compensated at 25 °C). Tritium values are sketched in hydrogeological cross section in Fig. 2. It can be seen that tritium values of the leachate vary between 400 and 1700 TU whereas in the unconfined aquifer values between 16 and 26 TU have been measured. Groundwater tritium activity allowed leachate leaching to be monitored along flow direction as far as 2.5 km from the waste disposal site (Fig. 3). Tritium values of contaminated groundwater are low with respect to those

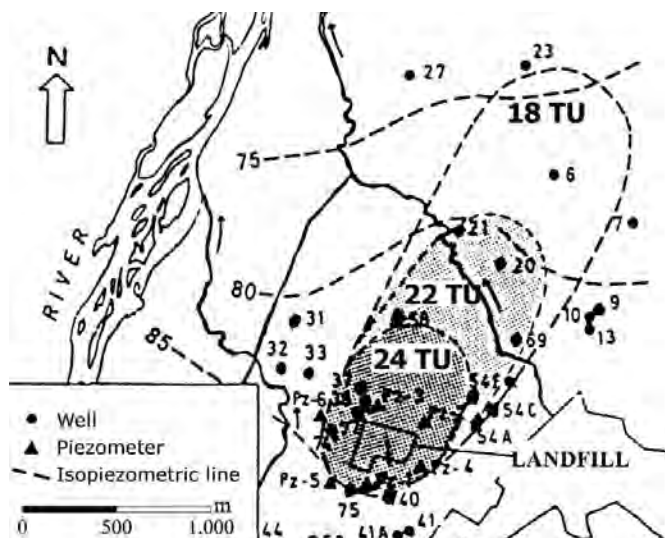


Fig. 3: Leachate migration downgradient from the landfill 1. Grey zones indicate the pollutant plume discovered by means of tritium content (after Calestani et al., 1999).

of leachate, but slightly above the local tritium background (6-15 TU) even at a considerable distance from the landfill. For this kind of groundwater pollution the chemistry values indicate a variation of some chemical parameters only at a very short distance from the landfill, whereas the anomalous tritium values are distributed downstream for a long distance (Calestani et al., 1999).

Case History 2 (Central Italy)

The landfill is located in Central Italy, near the Adriatic Sea, on a hilly zone characterized by layers of marine blue marly clays of Plio-Pleistocene age, interbedded with silty sand with a maximum thickness of 15 m. Eluvial and colluvial deposits cover clays with a thickness ranging between 2 m and 17 m. Groundwater flowing inside the sandy aquifer has a calcium bicarbonate chemistry, with high concentrations of sulphate and chloride. The TDS were often up to 3 $\text{g}\cdot\text{l}^{-1}$. The landfill caused a severe contamination of soil and groundwater downstream (Tazioli, 1993). The tritium content of leachate has been utilized as tracer of groundwater pollution caused by the waste disposal site. This was possible because tritium activity, measured on the leachate, displays values up to 500 TU, whereas the local base concentration in groundwater is around 10-15 TU. The contamination appears evident by observing tritium values in boreholes (dug wells) placed downstream (with values up to 260 TU; Fig. 4).

Also in this case tritium were revealed before chemical concentration changes occurred.

Case History 3 (Northern Italy)

The landfill is located in a wide alluvial plain. It is located above an alternance of continental deposits of marine origin, made of silty clay and silty gravel and sand. Silty gravel and silty sand layers contain several aquifers, fragmented by clay lenses. The shallowest one is unconfined with the water table at a few metres depth; immediately below there is a confined aquifer, at a depth between 8-9 m b.g.s. and 17-18 m b.g.s. (Tazioli et al., 2005).

The unconfined groundwater is characterized by a rapid renewal, being recharged by local precipitation, whereas the confined ground-

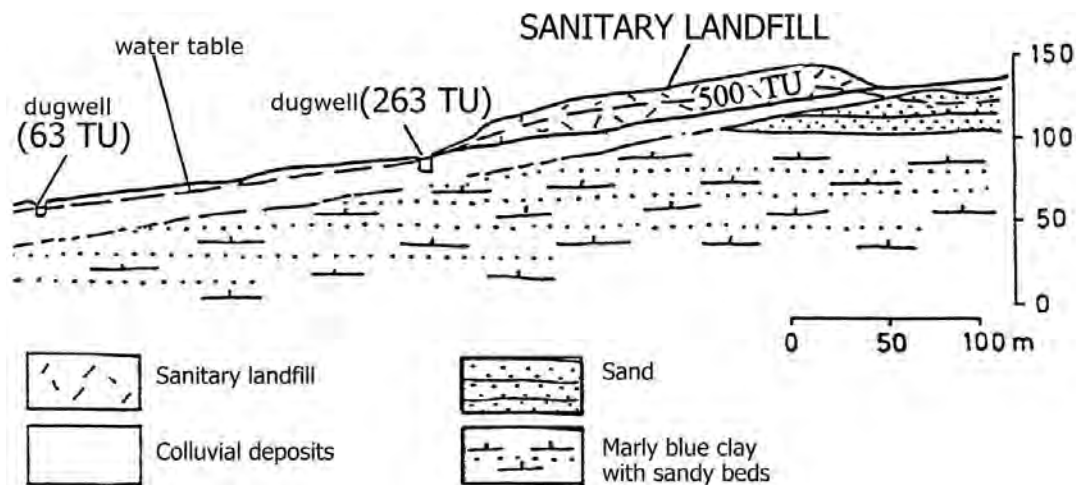


Fig. 4: Geological section of the landfill 2. Tritium values show the occurrence of leakage from the landfill to the surrounding environment (after Tazioli G.S., 1993).

water (with a residence time of at least 30 years) is recharged upstream by rainfall at higher elevation in the mountains. Ground and surface waters are strongly polluted by nitrates and ammonium, so the common thought was that the landfill had been responsible for this kind of pollution. In order to verify this hypothesis isotopic and tritium analyses were made; such analyses established that no connection existed between the landfill and the surrounding environment. In fact, from nitrogen-15 isotopic data, it's apparent that (Fig. 5) the values obtained in piezometers are in the range typical of fer-

tilizers and organic input from soils. Leachate from landfill generally shows values of nitrogen-15 much more to the right of the graph in Figure 5, having values similar to those relevant to manure and septic waste (being nitrogen from organic matter). Tritium analyses endorse such observation (Fig. 6). In fact, tritium values both in unconfined and confined aquifers are within the range of recent atmospheric values (1-3 TU in confined groundwater, 8-11 TU in unconfined groundwater). Isotopic and tritium values have therefore ruled out any link between the aquifers and between landfill and aquifers.

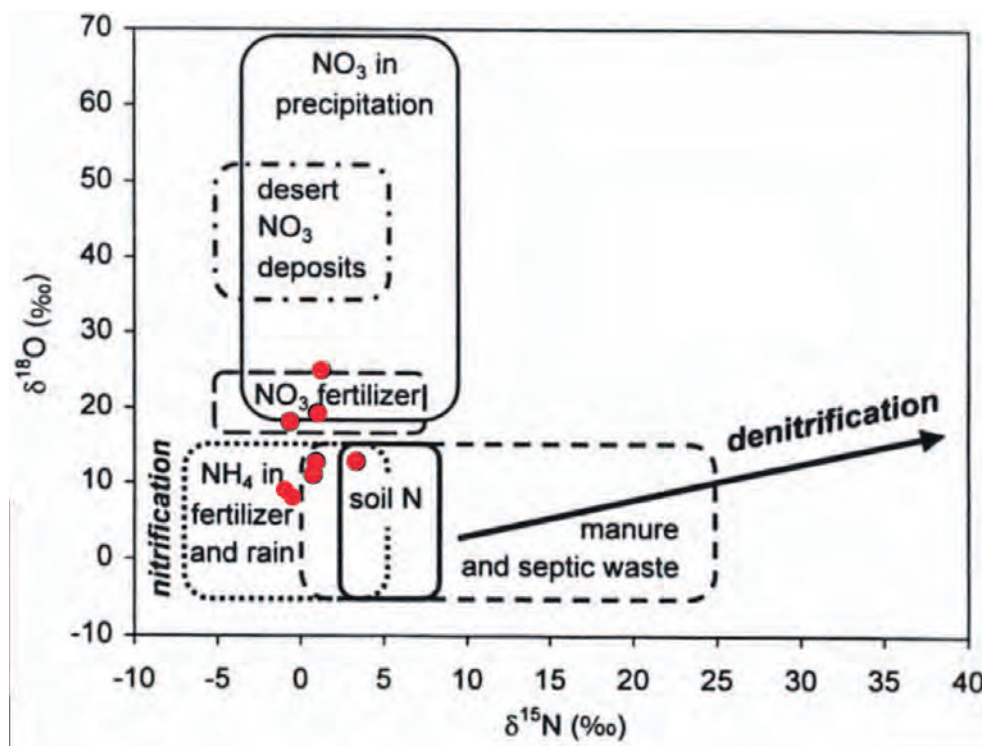


Fig. 5: Typical ranges of oxygen-18 and nitrogen-15 values (after Kendall, 1998). In this plot isotopic values measured in groundwater around landfill n.3 have been added (solid circles).

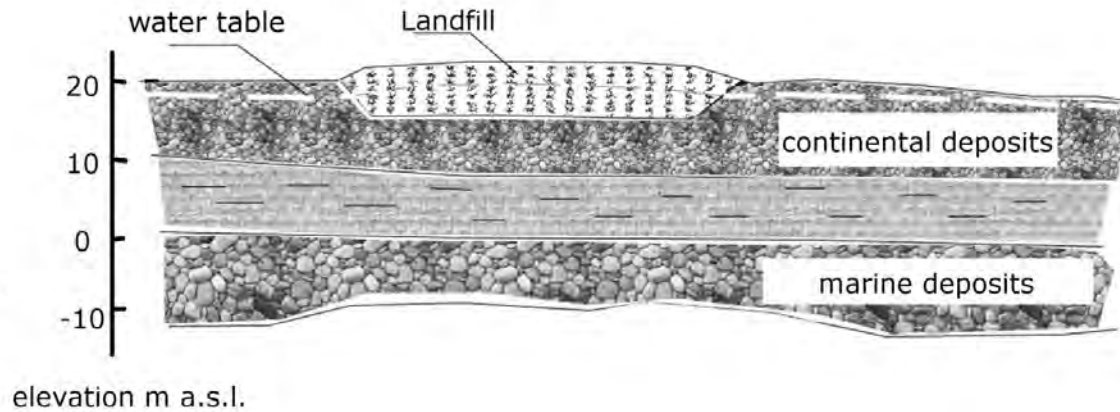


Fig. 6: Cross section of the area around the landfill n.3. Tritium values in confined aquifer ranged between 1 and 3 TU; in unconfined aquifer tritium values are between 8 and 11 TU. Leachate has 800-1000 TU (Tazioli et al., 2005).

Discussion

By analyzing isotopic data (Tazioli, 1993; Tazioli, 1996; Calestani et al., 1999; Tazioli et al., 2004; Tazioli et al., 2005) from different landfill sites (referring to about 15 landfills in Northern and Central Italy), some considerations can be made.

First of all, it is clear that the hydrogeological knowledge of isotopes base level concentrations and concentration variations (seasonal effects) are required, in particular, relative to the different aquifers in each of the studied sites. It is often possible to note a linear correlation between tritium values in different groundwaters and $\delta^{18}\text{O}$ (Fig. 7). From this correlation it's possible to locate leachate contaminating groundwater (points above the line are referred to piezometers and wells polluted by leachate).

This is not absolute evidence of the occurring pollution but it can

be considered as a good indication about the necessity to investigate the anomalies with more accuracy.

Some other types of isotopic analysis may also be useful tools in targeting contamination source location:

- carbon-13 data collected (Calestani et al., 1999; Tazioli et al., 2004) in several landfills (Fig. 8) clearly show the difference between contaminated groundwater, leachate and uncontaminated groundwater;
- sulphur-34 values too, in some instances, could show a good differentiation (Fig. 9); if the values of oxygen-18 (relative to SO_4^{2-}) are plotted against SO_4^{2-} content (Fig. 10), a nearly steady trend of oxygen-18 can be noted wherever any eventual lower value could be due to a probable mixing with leachate.

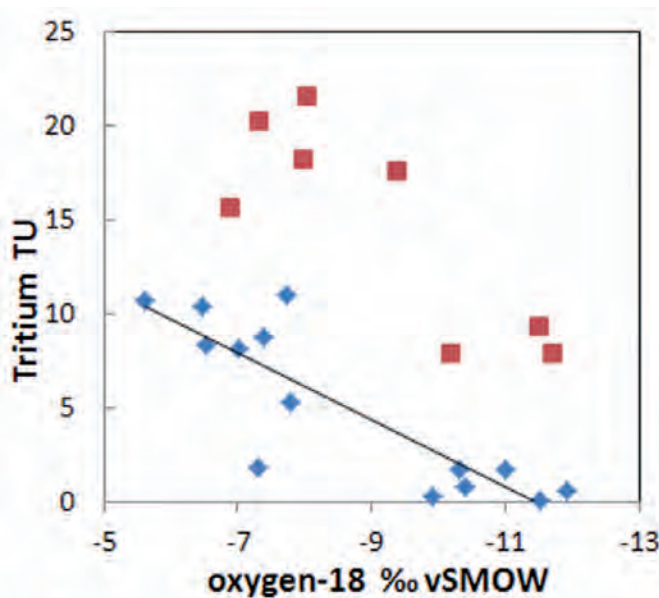


Fig. 7: Comparison between tritium contents and oxygen-18 contents of groundwater in over 10 landfill sites (Central and Northern Italy, from Tazioli, 1993; Tazioli et al., 2004; Tazioli et al., 2005). The square symbols indicate groundwater polluted by leachate. Values around -7 ‰ vSMOW are referred to shallow (unconfined) groundwater, values around -12 ‰ vSMOW are referred to deep (confined) groundwater.

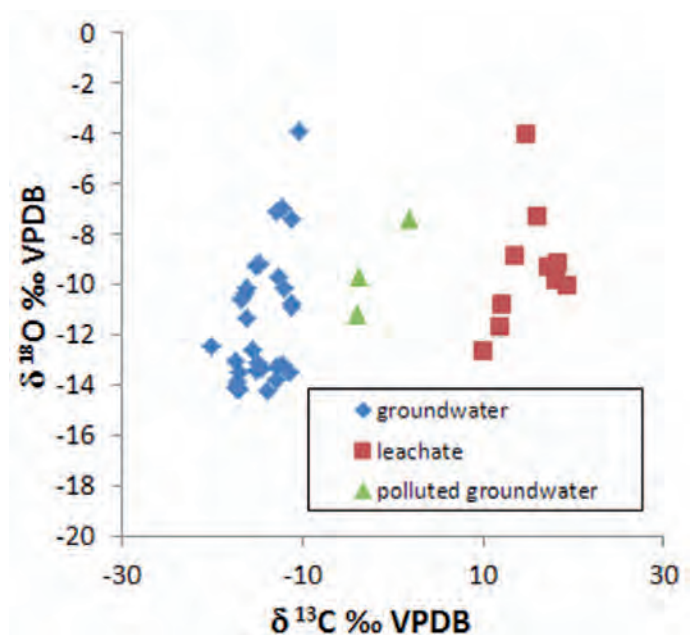


Fig. 8: Plot of oxygen-18 water values against carbon-13 values of dissolved carbon (DIC) in groundwater and leachate.

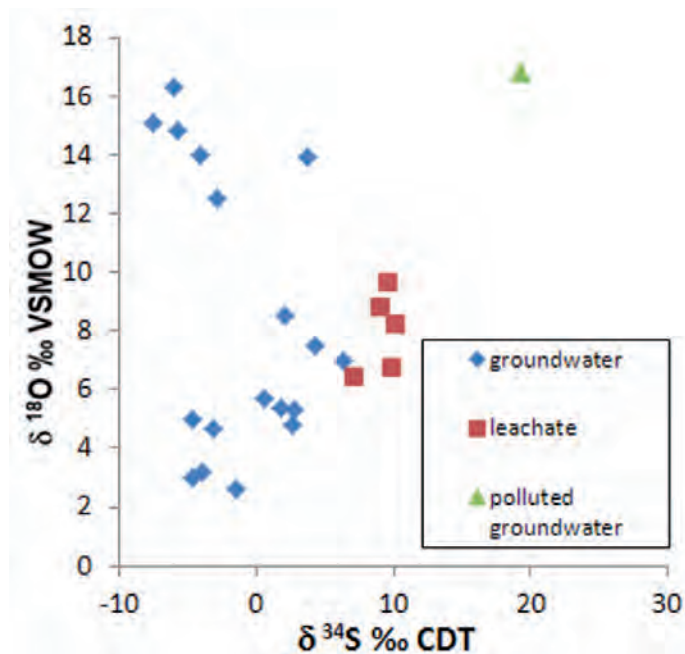


Fig. 9: Plot of oxygen-18 water values against sulphur-34 values of dissolved sulphates in groundwater and leachate (Tazioli, 1993; Calestani et al., 1999; Tazioli et al., 2005).

Conclusion

In this paper some case studies of isotopic tools to define groundwater contamination by landfill have been presented. The paper outlines the importance of isotope investigations, generally used for defining hydrogeological conceptual models of investigated area, as a very useful tool to evaluate the potential occurrence of leachate leakages from a landfill to its surrounding environment. Tritium measures are strongly recommended for tracing purposes, owing to its stability and sensitivity as leachate pollution tracer, and to a notable difference in concentration between values in leachate and environmental base levels. The results show that tritium values distribution may give information about the occurrence of leachate pollution also if standard chemical pollution parameters do not show any peculiar anomaly.

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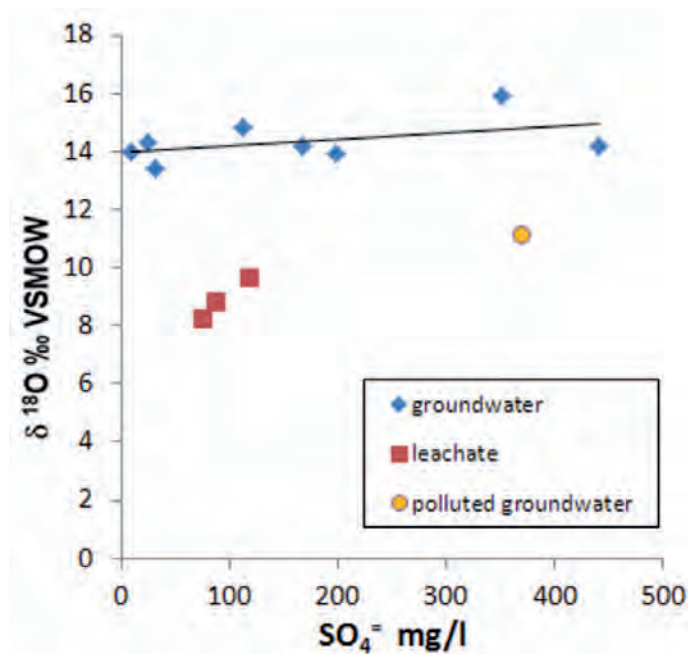


Fig. 10: Oxygen-18 values in the sulphate against sulphate content in groundwater and leachate.

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