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Strontium isotope as tracers of groundwater contamination

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Abstract

Groundwater flowing under a municipal solid waste landfill has been studied to identify potential contamination phenomenon and to test strontium isotopic composition as a natural tracer of contamination. The study was carried on in June 2014 in central Italy. Five selected boreholes were selected and analysed according to their location related to the site. Samples taken from boreholes placed upward to the site were considered as uncontaminated groundwater. One borehole located downward from the site and with major contaminant values has been considered as potentially contaminated end-member. Sr isotope results show that samples located upward from the site present lower Sr concentration and highest Sr isotopic values, which reflects weathered bedrock, while borehole located downward from the site show lowest Sr values and $^{87}Sr/^{86}Sr$ ratio, probably due to pollution by landfill leachate. The mixing calculation highlights the possible mixing phenomenon for the other samples located downward from the site.

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Keywords: Groundwater; Landfill; Strontium Isotope;

1. Introduction

Municipal solid waste landfills are the common method for organized waste disposal in many places around the world. Leachate from these landfills contains a large variety of organic and inorganic pollutants that can migrate into the groundwater.

The use of isotope analyses, as ^{3}H, $\delta^{11}B$ and $\delta^{13}C$, are often applied to identify sources of contamination[1-3]. Strontium isotope can be used as geochemical and environmental tracers. Several authors[4] showed that strontium isotopic analysis could be used to investigate surface and groundwater or leachate contaminated groundwater. The distinctive chemical composition of landfill leachate is a result of the chemical interaction between water, chemical by-products of degrading organic matter in solid wastes, such as organic and inorganic acids, minerals and other

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solids in the fill, and buried cover soils. There are many wastes containing strontium in a landfill, e.g. plastics, concrete, plasters, or others manufactured products. In the landfill leachate plume, strontium concentration will be modified and it will take part in sorption or cation exchange properties. The isotopic fractionation of Sr is very low (0.0115), for this reason it can expect little effect of mass fractionation on the natural distribution, so sorption processes can affect its transport, but will not change the isotopic signature of strontium sources[5]. The aim of this study is to investigate the possible use of Sr isotopic composition as natural tracer of groundwater contamination. Five water samples coming from different hydrogeological locations with respect to landfill site have been analysed to evaluate the existence of different isotopic ratio and the possible relationship with contamination phenomenon.

2. Study area

The studied municipal landfill is open since 1995 and is located in an alluvial plain of the lower Sangro River, Central Italy.

The lower Sangro valley is located between the allochthonous terrigenous units of the Molisan facies[6] and the Plio-Pleistocene marine deposits of the Abruzzo-Molise foredeep[7]. These units, which are primarily clayey deposits, are the basement of the alluvial deposits overlaying on the Aventino-Sangro gravity flow deposits[8], upstream from the confluence of the Sangro and Aventino Rivers, and they overlay marine Plio-Pleistocene deposits downstream from the confluence[9]. 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 places, 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 coarse sands upwards to sands and conglomerates at the top of the formation. Three units influence the hydrogeology of the area: clayey silts (Aquitard), gravels (Aquifer) and grey-blue clay (Aquiclude).

Water samples were selected according their localization in the site: sample 0 is located upward from the landfill, samples 4 and 7 are the boreholes of drainage trench that receive any leachate from the site and sample 5 and 6 are the boreholes of hydraulic barrier that receive any seepage from the drainage trench.

Fig. 1.Study area, water points location

3. Methodology

Five water samples were collected from the landfill site in June 2014. Concentrations of minor and trace elements were measured by an ICP-MS (X Series 2 Thermo Fisher Scientific) in the laboratory of Geochemistry Sapienza University, Italy after filtration (0.45 μm) and acidification in the field (HNO_3 1:1).

For Strontium isotopes, the water samples were filtered through 0.45 μm cellulose sheets. $^{87}Sr/^{86}Sr$ ratios were measured on a Finnigan MAT 261 multi-collector mass spectrometer using a static collection mode, all reported values have been corrected for natural and analytical stable isotope fractionation to $^{88}Sr/^{86}Sr = 8.37521$ and then adjusted to the NBS987 standard value of 0.71024. The values are precise at 0.00002 considering a 95% confidence level. Isotope analyses were conducted in laboratory of USGS of Menlo Park, California.

4. Results and discussion

4.1. Water chemistry

Heavy metals are the major indicators of anthropogenic impact and have various sources, such as traffic activities, dry ash deposition from incineration plants, industrial effluents, road runoff and landfill leachate[10]. Thus, the monitoring of heavy metals contamination could be important in assessing the impact from the landfill on groundwater quality.

Chemical composition of groundwater have been analysed during June 2014. The major contaminants are Cl, NH_4^+, B, Cr, Ni, As and Zn[11]. These elements reach maximum values in sample 7 which is the borehole of drainage trench, while they show minimum concentrations in sample 0 which is located upgradient from the site. Samples 0 and 7 can be considered as end-members in the study area. Sample 0 is the uncontaminated end-member while sample 7 is the contaminated end-member. Sample 4, 5 and 6 show intermediate values respect to two end-members.

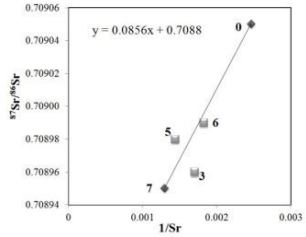

Figure 2: A: $^{87}Sr/^{86}Sr$ versus 1/Sr for groundwater samples and mixing line

4.2. Natural vs. anthropogenic sources

Strontium-isotope ratios ($^{87}Sr/^{86}Sr$) vary in nature, because one of the strontium isotopes (^{87}Sr) is formed by the radioactive decay of the naturally occurring element rubidium (^{87}Rb). The $^{87}Sr/^{86}Sr$ ratios are used mainly as tracers of water–rock interaction[12-14]. It reflects the different Sr sources (water rock interaction and pollution) and the Sr isotopic signature can provide constraints on the mixing from these sources. The introduction of leachate into groundwater results in a mixing of two distinct water masses in terms of composition. These two sources of water have different isotopic signatures. In Figure the $^{87}Sr/^{86}Sr$ ratios are *vs.* Sr contents. The upgradient borehole has a specific isotopic signature (0.70905) which reflects the weathered bedrock. This value may corresponds to a marine signal (0.70905-0.70910)[15], according to the nature of the geological substrate of the study area. The borehole 7, which is the contaminated end-member, shows a minimum $^{87}Sr/^{86}Sr$ value (0.70895). These waters are characterized by fresh waters which interact with minerals and wastes in the landfill, therefore their isotopic values reflect the impact of leachate in groundwater. The mixing equation between two end-members, were calculated as given by[16] and reported in Fig. 2. The contaminated end-member presents the higher Sr concentration, probably due to interact with wastes containing Sr, and minor $^{87}Sr/^{86}Sr$ ratio, while borehole 0 (uncontaminated end-member) shows minor strontium concentration and major isotope value. Sample 6 plots on the straight line, showing intermediate composition with respect to the end-members. Its characteristics are probably due to mixing phenomenon between leachate and fresh groundwater. Samples 3 and 5 also present high Sr value respect to borehole 0 and an isotopic value intermediate with respect to the end-members. The graph shows that samples located downgradient from the site present a different isotopic composition suggesting the existence of a contamination phenomenon in sample 7 and, in samples 5 and 6, a probably mixing phenomenon between the two end-members.

5. Conclusion

The groundwaters collected from boreholes of a landfill of central Italy were analysed during June 2014. The major contaminants identified are Cl, NH_4^+, B, Cr, Ni, As and Zn. We have analysed strontium isotopic composition in five water samples selected in the study area. $^{87}Sr/^{86}Sr$ ratio was used to identify sources of potential

contamination. The results show that borehole located upgradient from the site, represents uncontaminated end-member, with high isotope value and low Sr concentration, while borehole considered as a contaminated end-member, for hydrogeological consideration (location and high contaminants values), shows low $^{87}Sr/^{86}Sr$ ratio and high Sr concentration. The calculated mixing line shows that the other samples, particularly sample 6, present intermediate composition with respect to the end-members. These results confirm the possibility of the $^{87}Sr/^{86}Sr$ ratios for monitoring groundwater pollution.

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