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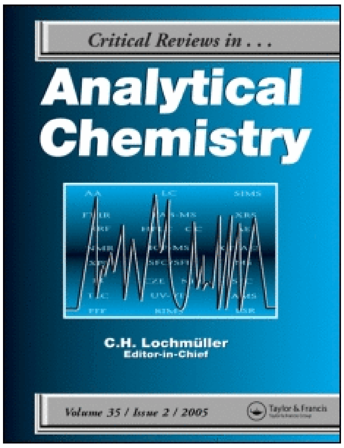

Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

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Online publication date: 18 June 2010

To cite this Article Miljevic, Nada(2003) 'Application of Environmental Isotopes in Evaluation of Pollutants', Critical Reviews in Analytical Chemistry, 33: 4, 307 — 310

To link to this Article: DOI: 10.1080/714037682

URL: http://dx.doi.org/10.1080/714037682

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Critical Reviews in Analytical Chemistry, 33(4):307–310 (2003)

ISSN: 1040-8347
DOI: 10.1080/10408340390272467

Application of Environmental Isotopes in Evaluation of Pollutants

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INTRODUCTION

Environmental isotopes, isotopes of light elements (hydrogen, carbon, nitrogen, oxygen, sulfur, chlorine) are used as a modern, specific, and reliable technique for studies of global element cycles [1], hydrology [2], authentication of food and drinks [3], medical research [4], and pollution monitoring. Some of them, such as tritium (^{3}H) and radioactive carbon (^{14}C) are radioactive, while the others are stable (^{2}H, ^{13}C, ^{15}N, ^{18}O, ^{34}S and ^{37}Cl). The former spontaneously undergo decay with time, the latter do not. Due to energy considerations, the lighter isotopic species will react slightly faster than the heavier (although there are exceptions), resulting in a change in isotopic composition going from reactant to product compounds. The application of environmental isotopes is based on the different and distinct isotopic composition of the given molecules, due to isotopic fractionation caused by their origin and any transformation process the products underwent. They can be used at either their natural abundance or artificially enriched abundance, in labeled compounds at tracer levels.

Pollution of surface water may be remedied by concerted prevention and controls, but it is more serious when pollution enters the groundwater. Polluted groundwater may remain in aquifers for centuries, even millennia, and is very difficult, if not impossible, to be cleaned. Therefore, the studies of the interaction of groundwater and surface water are of a great interest in developing control policy on land close to groundwater sources in preventin the pollution of public supplies derived from aquifers.

WATER RESOURCES MANAGEMENT

In addition to classical geologic/hydrologic methods, the isotopic abundance of ^{2}H, ^{3}H^{13}C, ^{14}C, and ^{18}O is widely applied for the investigation of the history and pathway of water in different parts of the hydrological cycle. Isotopic content has been employed to determine the following:

- the origins and ages of different water bodies;
- the location and proportion of water recharge;
- the degree of mixing;
- velocity of groundwater flow.

Based on the tritium content in precipitation, river (the Sava), and groundwater in the area of the Makis aquifer, the infiltration rate and mean residence time of shallow groundwater body that serves as the drinking water supply of Belgrade were determined [5]. The significant vertical age structure was found, where the upper layer, average thickness of about 10 *m* with a small infiltrance on local recipient, and lower layer, average thickness between 10–15 *m*, characterized by fast turnover, exist. The spatial origin of groundwater with the predominance (about 80%) of the Sava River water infiltration through the pumped well was discovered. An efficient groundwater pathway could cause a non-acceptable contamination of the main aquifer. These findings were used in setting optimum strategies for a sustainable management of groundwater resource in this basin.

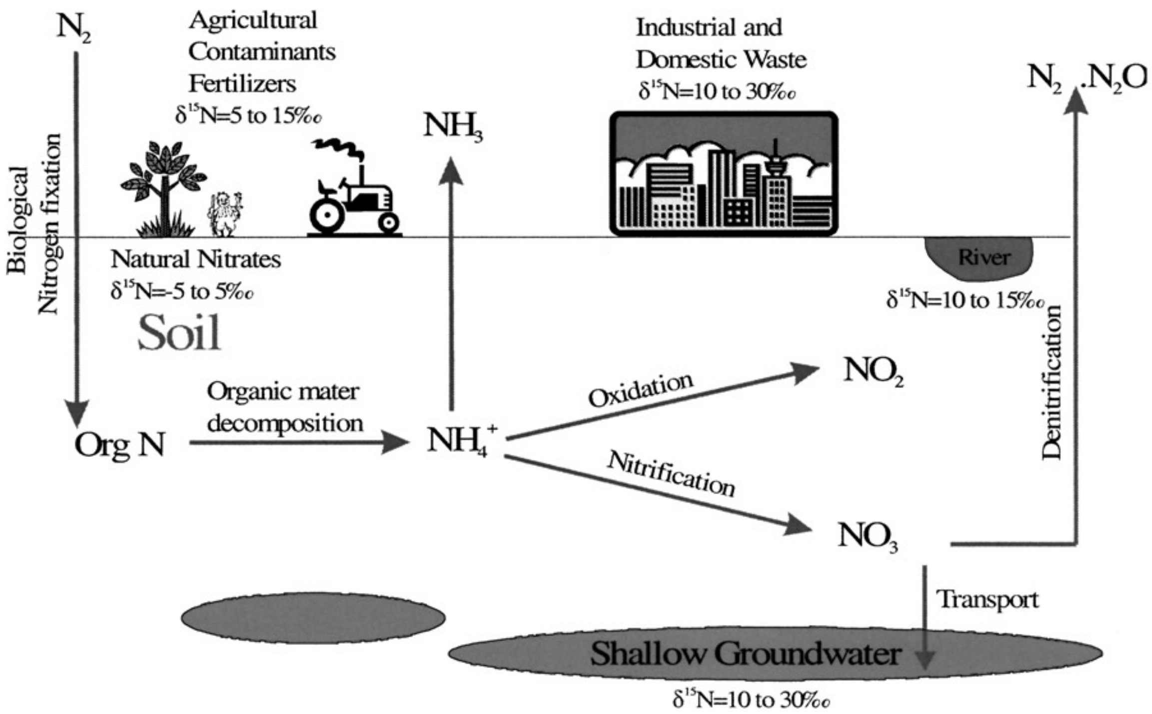

FIGURE 1. Natural cycling of nitrogen isotopes in the environment.

IDENTIFICATION OF ORIGIN CONTAMINANTS

After the identification and quantification of pollution, the problem of interest is the characterization of the sources and determination, whether the pollution is locally derived or transported over long distances. Surface sources of pollution can be designated as natural, industrial, agricultural, or domestic. Environmental isotope methods are a powerful tool used to:

- follow the contributions from different sources and over time;
- see the effects of efforts to limit the diffusion of a pollutant;
- identify the isotopic fingerprints of pollutants.

Based on mass balance and, using linear mixing models, the proportions from the different sources could be estimated, and the relative importance of various sources of pollutants determined.

Nitrogen (NO_3 and NH_4) pollution in groundwater is an important environmental problem in shallow aquifers in many countries. A preliminary condition for prevention is to determine the origin of nitrogen dissolved in groundwater, due to approximately 80% of the antropogenic nitrogen inputs, which are either stored or denitrified in the catchments. The nitrogen content, expressed as $\delta^{15}N$ value (deviation from the standard, ‰), is characterized by its different sources (fertilizer, natural soil, animal waste, or sewage). The $\delta^{15}N$ values for natural nitrates are in the range of -5 to $+5$‰ (Figure 1). The increase of the value between 10 and 30‰ is related to the main role of human and animal origin in unscrewed settlements. The effect of artificial fertilizer in the shallow groundwater of agricultural regions can be recognized by $\delta^{15}N$ values of approximately $+5$‰. The leaching of nitrate from soil into groundwater depends on the soil and fertilizer type. Using mineral fertilizer, $\delta^{15}N$ value increases up to 15.5‰, while the application of manure or sludge results in much higher $\delta^{15}N$ values, up to 33.8‰, indicating denitrification effects [6].

The appropriate method for tracing the sources of NO_3 contamination is the combination of nitrogen ($^{15}N/^{14}N$) and oxygen ($^{18}O/^{16}O$) isotopic fingerprints in NO_3 (^{15}N-NO_3, ^{18}O-NO_3), which allows us to make some deductions concerning the identification of nitrate sources and the degree of their denitrifaction [7]. This process is combined with the significant isotope fractionation, with a characteristic enrichment of $\delta^{15}N$ (10 to 15‰) and $\delta^{18}O$ (13 to 16‰) in the residual nitrate. In combination with the exact determination of groundwater age (tritium or ^{14}C dating), it is possible to deduce outlines for NO_3 sanitation concepts. Once

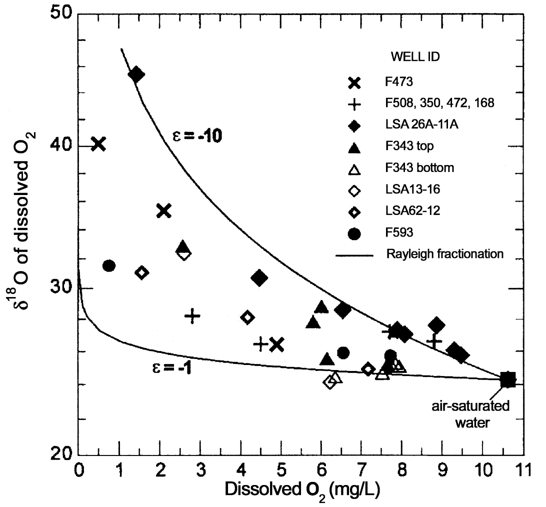

FIGURE 2. Isotopic composition of the diminishing O_2 reservoir in the mixing zone as a function of the remaining O_2 concentration (pressurized air used as a reference gas) [8].

the origin of nitrate in drinking water is understood, corrective measures may be taken to prevent or minimize further contamination.

The fractionation of dissolved oxygen isotopes can be used to identify respiration in aquatic systems. Microbial respiration consumes oxygen and alters its concentration, which controls groundwater redox conditions. In contaminated environments, oxygendemand and aerobic versus anaerobic pathways of degradation largely determine whether remediation of a particular set of contaminants occurs, and what kind of additional *in situ* reclamation approaches might be possible (Figure 2) [8]. Decreasing the ^{18}O content in dissolved oxygen indicates a reduction of dissolved oxygen concentrations in the mixing zone.

Contamination of groundwater by organic compounds is one of the major environmental problems affecting water resources worldwide. The major sources of organic contaminants in them are petroleum hydrocarbons BTEX (benzene, toluene, ethylbenzene, and xylenes) at a gasoline-contaminated site and chlorinated solvents, such as perchloroethylene (PCE), trichloroethylene (TCE), and 1,1,1-trichloroethane (TCA).

The development of new analytical techniques, specifically gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS), makes possible the exploration of the use of environmental isotopes (^2H, ^{13}C, ^{37}Cl) as fingerprints to evaluate sources and transformation processes that affect organic contamination in groundwater [9] and new possibilities for the application of stable isotopes to assess natural attenuation of organic compounds in groundwater and remediation technologies.

Abiotic and biotic degradation of chlorinated solvents is accompanied by a large isotopic fractionation [10]. The preferential degradation of enriched ^{13}C hydrocarbons is occurring during bioventing, and analysis of CO_2 is a monitoring tool for the effectiveness of bioremediation contaminant remediation. The compound-specific carbon isotope analyses on organic contaminants show a large isotope fractionation during biodegradation of trichloroethylene (TCE) (Figure 3) [11].

Although the chlorine stable isotope variation in nature is minimal (range of 3.5‰), the

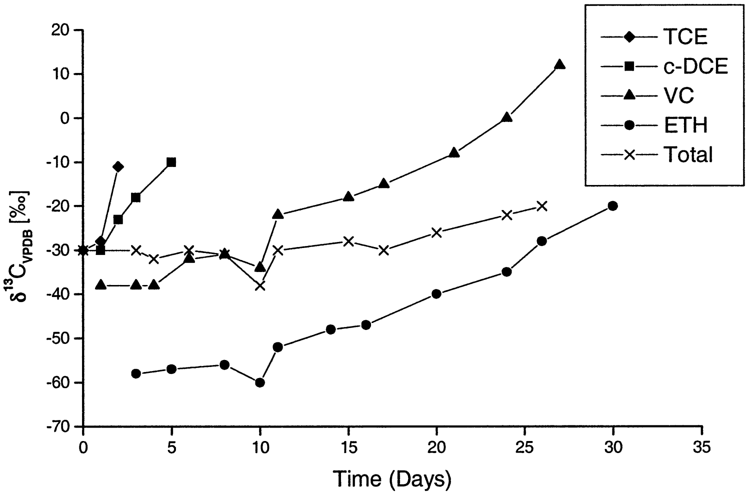

FIGURE 3. $\delta^{13}C$ patterns for trichloroethylene (TCE), cis-1,2-dichlorothene (cDCE), vinyl chloride (VC) and ethane (ETH) during biodegradation of TCE [11].

interpretation of the isotopic fingerprints of chlorinated solvents is based on the knowledge of their production (isotopic composition results from the individual manufacturing practices) and of the biological degradation in water and soil. Residual chlorinated aliphatic hydrocarbons (CAHs), during evaporation, generally become depleted in ^{13}C and enriched in ^{37}Cl, contrary to residual CAHs during microbial degradation which, become enriched in both ^{13}C and ^{37}Cl [12]. In addition, the δ^{37}Cl parameter is valuable for the quantitative evaluation of mixing different sources of chloride in brines and aquifers.

CONCLUSIONS

An increasing threat to groundwater supplies and surface water quality requires a determination of the origins of specific compounds or tracing the flow of effluents in the natural environment. The isotope techniques can assess the vulnerability of groundwater to pollution from the surface, by determining how rapidly it moves, and where it is being recharged and determine sources and degradation and pathways of contaminant compounds from the site.

Environmental isotopes can also identify incipient pollution, providing an early warning when the chemical or biological indicators do not give cause for concern that makes their essential contributions to management concepts on groundwater resources protection. They can help to guide remedial strategy and can lead to large cost savings in clean-up efforts.

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