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Tracers as Essential Tools for the Investigation of Physical and Chemical Processes in Groundwater Systems

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Abstract. In complex environmental systems, tracers are indispensable tools for the investigation of various physical, chemical, and biological processes. From the large variety of tracers employed by EAWAG in the aquatic environment, we present some examples relevant to groundwater research. Some tracers (*e.g.*, ^{222}Rn, ^{3}H/^{3}He, chlorofluorocarbons) allow the time since groundwater infiltration to be determined; this information can be used to quantify process rates such as flow velocities, recharge and reaction rates. Other tracers (*e.g.*, conductivity, isotopes of oxygen or boron) can be used to quantify mixing ratios between waters of different origin, for instance, to study the admixture of leachate from a landfill to an aquifer. In contrast to these inert tracers, chemically reactive tracers (*e.g.*, nitroaromatic compounds) can be used to study subsurface biogeochemical transformation processes, *e.g.* the reduction of contaminants under anaerobic conditions. The successful use of tracers in the study of environmental systems requires highly developed analytical facilities for a broad palette of tracer measurements and a careful choice of appropriate tracers for each specific problem.

Introduction

Parameters such as residence time, mixing ratios, and reaction rates, which can be easily controlled or measured in a laboratory experiment, are often difficult to estimate in environmental systems, such as lakes, aquifers, and disposal sites. Due to its complexity, an environmental system can often only be considered as a black box which responds to a given input signal in a characteristic way. In order to gain an insight into the mechanisms governing a specific system, we use tracers – marker substances whose behavior in the environment is well known and which can be detected even if present only in trace amounts.

Tracers can be divided into several categories according to their behavior in the system or to their source. Substances which have no source or sink within the system are called conservative tracers (*e.g.*, halides, noble gases; SF_6 and chlorofluorocarbons (CFCs) under aerobic conditions). They yield information on the physical structure of the system, whereas reactive tracers (*e.g.*, nitroaromatic compounds, ^{13}C) are needed to study chemical processes. Natural tracers are substances which originate from diffuse geochemical or biogenic sources (*e.g.*, salinity, ^{222}Rn), whereas transient tracers originate from anthropogenic sources (*e.g.*, ^{3}H, CFCs). Since their concentrations may be very small, they often require highly sensitive analytical tools. Artificial tracers are substances which are purposefully released at a specific location and time into the environmental system to be investigated (*e.g.*, dyes, halides, SF_6). The released amount must be chosen such that the tracer concentrations lie above the background concentration. Isotopes, both stable (*e.g.*, ^{18}O, ^{2}H) and radioactive (*e.g.*, ^{3}H, ^{222}Rn) are frequently used as tracers.

Processes to be investigated in aquatic systems are predominantly those involving transport, mixing, dispersion, or chemical or microbiological reactions. These processes can occur in an aquifer, lake, river, soil air, or in a disposal site. Since different processes can influence each other, the use of only one tracer is often not enough to describe the system sufficiently. A combination of different tracers, however, can lead to the desired information.

The selection of a tracer must be adapted to the given problem. Conservative tracers serve for the determination of residence time and mixing in a system, whereas reactive tracers give information on the nature of chemical or biological transformation processes in the system. Besides the chemical and physical properties of the tracer, the timescale of the process to be explored plays an important role. It can vary from seconds up to some ten thousand years. Artificial tracers can be used on short timescales, whereas natural tracers (*e.g.*, ^{14}C) are needed for long timescales.

At EAWAG, a large palette of tracers is used to study complex physical, chemical, and microbiological processes in natural and technical systems. From the simple measurement of conductivity up to the sensitive determination of isotopes, different methods are utilized depending on the specific problem to be tackled. The following examples demonstrate the use of some of these tracers in groundwater studies.

Water Ages and Recharge in Young Groundwaters

In most shallow aquifers, the age of the groundwater (water age or residence time) – defined as the time elapsed since the water parcel was in last contact with the atmosphere – lies between days and decades, but there are old groundwaters that have typical residence times from 10^3 up to 10^7 years. Since 1994, a collaborating team of the Environmental Physics Department of EAWAG, the Physical Institute of the University of Berne, and the Institute of Isotope Geochemistry of ETH has been attempting to use aquifers as archives for environmental and climatic changes in the past [1] and to develop tracer-based dating tools for young and old groundwaters [2].

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Although 85% of Switzerland's drinking-water supply originates from young groundwaters, information on the mean residence time within the aquifers is often scarce. Commonly it is assumed that the extraction of groundwater for drinking-water supply or irrigation does not severely affect the aquifer, and that after some time a new steady state is reached which allows sustainable exploitation of the aquifer. However, such extraction can lead to severe changes in the aquifer and, in some cases, even cause permanent disturbance (*e.g.*, by intrusion of salt water) which may inhibit any further use of the aquifer. Therefore, any rational groundwater management has to be based on conclusive information concerning the aquifer dynamics, *i.e.*, on residence time and recharge rates.

Methods based on the analysis of conservative tracers, such as rare gases (^3H/^3He [3][4]) and CFCs [5][6], which were originally developed in oceanography, have recently been applied to date young groundwater. Two different sets of dating methods can be distinguished.

i) The first set utilizes the fact that certain atmospheric trace components, such as CFCs and tritium, have a time-dependent input function. The atmospheric partial pressures of CFCs have increased steadily over the last 50 years as a result of industrial production, whereas tritium concentrations in precipitation reached a sharp maximum in the early 1960s due to nuclear bomb tests and have declined since then. Gas and vapor exchange imprint the changing atmospheric conditions on newly forming groundwater during its infiltration. Comparison of the measured tracer concentrations with the input functions allows the time of infiltration of a groundwater sample to be determined.

ii) The second set of methods relates to radioactive decay, *e.g.*, the decay of tritium to ^3He with a half-life of 12.4 years. In a closed system in which all isotopic changes only result from radioactive decay, the ratio of the stable daughter (^3He) and radioactive mother (^3H) is a direct measure of the time elapsed since the water was last in contact with the atmosphere. As this so-called ^3H-^3He method relies only on radioactive decay, ^3H-^3He dating does not require knowledge of the atmospheric tritium input function.

Using a combination of dating methods makes the computation of mean residence times of groundwaters more reliable than using just one technique which, as a consequence, allows mixing processes in groundwater to be addressed. Since the tracers used are both chemically and biologically inert, they take part only in the physical processes in the groundwater. Thus, the chemical and biological alterations in the aquifer can be separated from the common physical processes of the moving groundwater (advection and diffusion).

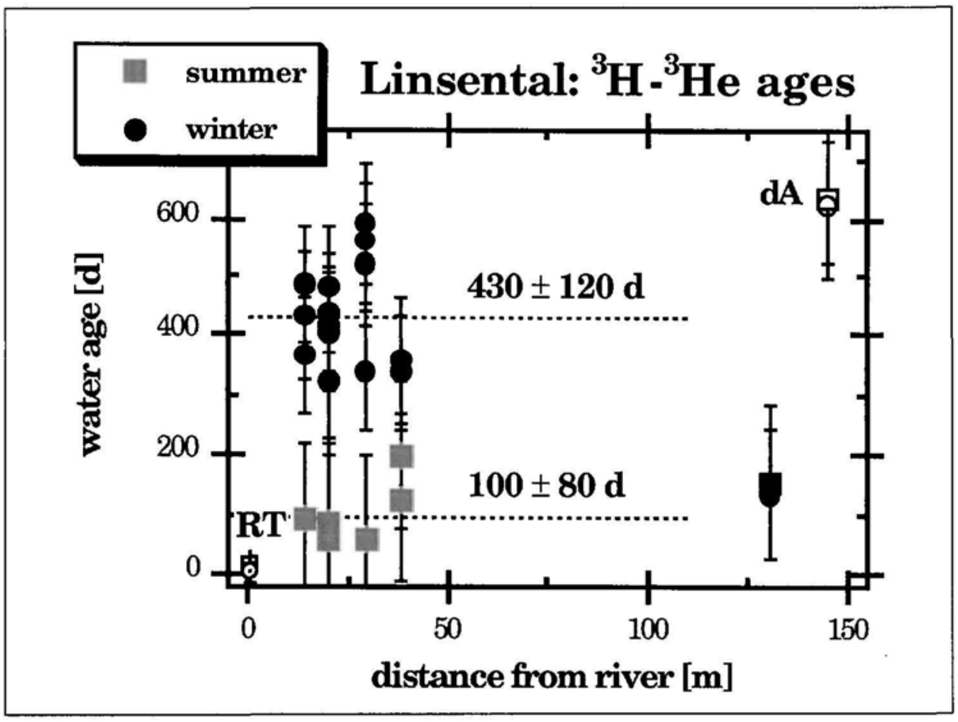

Fig. 1. *Temporal distribution of ^3H-^3He water ages in the Linsental aquifer along the presumed direction of groundwater flow from the recharge area of the River Töss (RT) towards a sampling site of the deep aquifer (dA).* In summer, the groundwater, except for samples from the deep aquifer, is much younger than in winter.

For the development and testing of these dating methods for young groundwaters, we have chosen an aquifer in the Linsental, located in the valley of the River Töss near the city of Winterthur. In this system, we study the dynamics and spatial distribution of groundwater infiltration from the river and its catchment area. Quantification of the mean residence time along the direction of presumed groundwater flow provides objective criteria for assessing the possible impacts of the planned natural rehabilitation of the River Töss on the recharge dynamics of the Linsental aquifer (*Fig. 1*).

The ^3H-^3He water ages in the Linsental aquifer show a distinct difference between summer and winter. In summer, all water samples, except the one from the far deep aquifer (dA), have approximately constant water ages of *ca.* 100 days. In winter, the samples from the deep aquifer close to the river have water ages of *ca.* 430 days, which agrees with the age of the far deep aquifer that remains constant with time. The greater water ages in winter indicate that river water infiltrates locally into the deep aquifer only in summer. Since the riverine water (River Töss: RT) has zero water age, the relatively young groundwater close to the river in summer is interpreted as being a mixture of deep groundwater and river water. In winter, local infiltration is cut off, and, therefore, the composition of the groundwater is comparable to the composition of the far deep aquifer, which seems to be in steady state.

Determination of Mixing Processes in Waste Materials

One of the main environmental concerns with regard to landfilling is the leaching and transport of contaminants from the landfill into groundwater. The leaching process is dependent upon the landfill hydrology and the geochemistry and reactivity of the landfill material. Landfill hydrology obviously depends on the permeability, the homogeneity, and the physical characteristics of the landfilled material. A landfill can be seen as a spatially heterogeneous, porous, and, by design, unsaturated system. The flow paths and interaction times determine the extent of the leaching process. Rainwater, *e.g.*, which passes by preferential flow paths through a landfill, will only have limited interaction with the waste material. It is the aim of a hydrological investigation to determine these parameters.

Due to the complexity of any landfill system, hydrological studies can best be conducted with tracers. Flow paths through a landfill can be determined by the addition of a tracer at a specific location. Alternatively, a substance homogeneously distributed in the landfill material may be used to distinguish between rainwater and retained water in the leachate. A further and elegant method to distinguish different origins of water in leachate is the determination of oxygen isotope ratios ($^{18}O/^{16}O$). This method has the advantage that the tracer is the water molecule itself, which avoids tracer retardation or kinetic problems of diffusion. The relatively simple concept behind these methods is that of mixing. It is assumed that there are two end members of constant composition, retained landfill water measured in the leachate prior to a rain event and rainwater, and that the leachate composition is a function of the mixing of these two end members. Details of these methods can be found in [7][8].

Together with *Tomas Vitvar* from the Department of Geography and *Gerald Richner* from the Institute of Terrestrial Ecology, both ETH-Zürich, and with the assistance of Canton Aargau, an investigation of the hydrological properties of a municipal solid waste incinerator (MSWI) bottom-ash landfill (Landfill Lostorf, AG, Switzerland) has been carried out. For a period of 22 months discharge, electrical conductivity and rainfall were monitored in the oldest compartment (1991, 6000 m^2 × 6 m) [9]. Changes in the usually high salt content of the leachate (ionic strengths of up to 0.2) were employed to estimate the proportion of rainwater in the leachate. In addition, $^{18}O/^{16}O$ measurements were made during a number of rain events. The results have been compared.

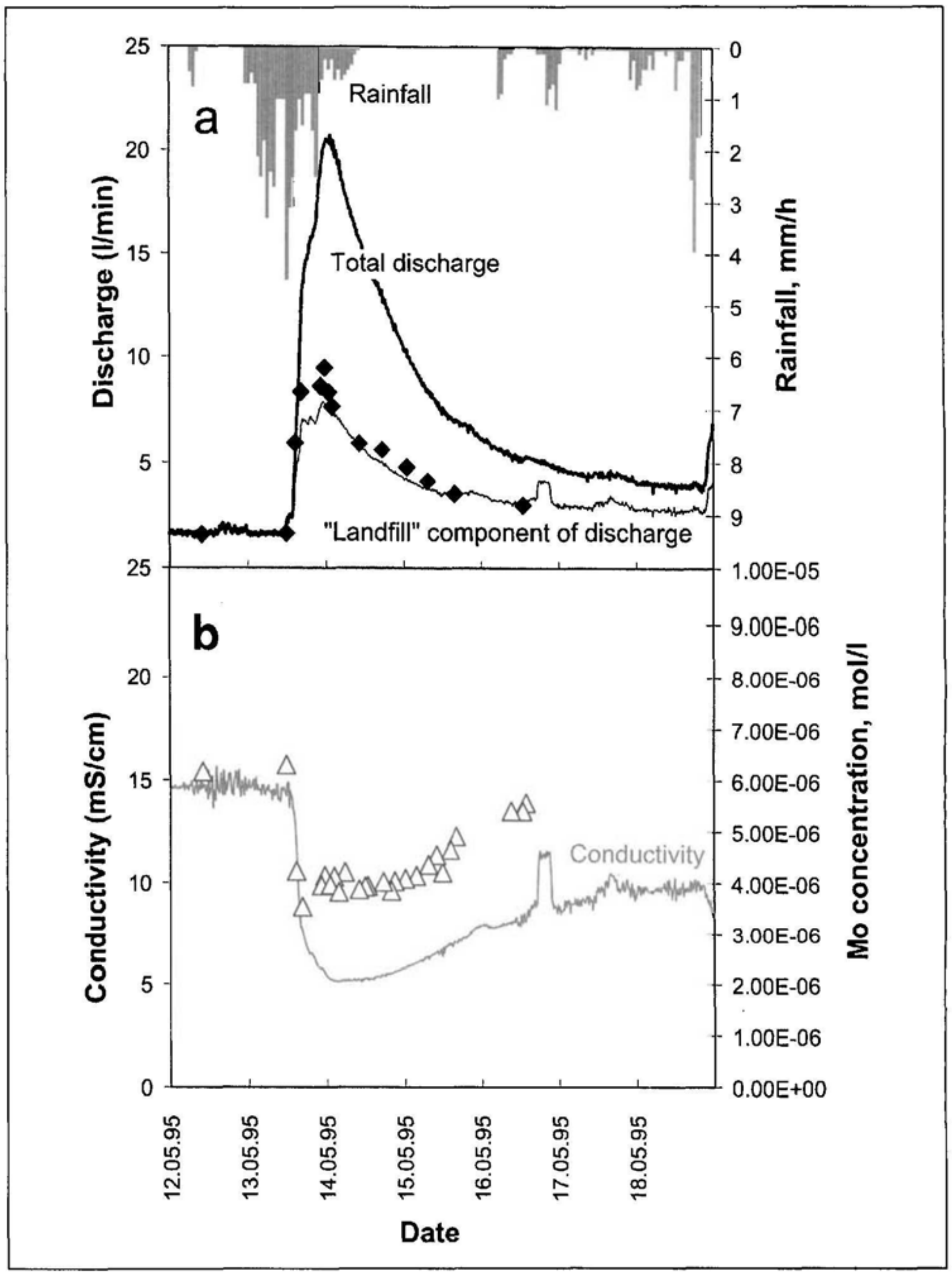

Fig. 2. *Rainfall, discharge, conductivity, and source apportionment as a function of time after a rain event in Landfill Lostorf. a)* The lower curve represents the landfill component of the discharge estimated from conductivity. The filled diamonds represent the same parameter estimated from $^{18}O/^{16}O$ measurements. Note the rapid response of the discharge to rainfall. *b)* Conductivity and Mo concentrations (triangles).

Fig. 2 illustrates the relationship between the different components of the discharge and leachate composition as a function of a rain event. The inverse relationship between total discharge and conductivity can be explained by the dilution of landfill water with rainwater. The landfill component of the leachate is shown in *Fig. 2, a*. It appears that landfill water is entrained with rainwater after rain events. Both conductivity measurements and $^{18}O/^{16}O$ tracer tests show this phenomenon and are in good agreement in this example. These results indicate that a part of the rainfall passes into the leachate drainage without interacting with the landfill material, but that at the same time, the load of dissolved substances in the leachate increases significantly. The extent of these phenomena depends on the saturation of the landfill and rainfall intensity.

The landfill component can have a sufficiently long residence time in the landfill (*ca.* 1–3 years for Landfill Lostorf) for the landfill water component to be in equilibrium with the solid phase. The leachate obtained under dry conditions, which is not diluted with rainwater, can provide an insight into geochemical processes occurring in the landfill. Molybdenum serves as a good example. Concentrations run parallel to conductivity during the rain event shown in *Fig. 2, b*. Thermodynamic calculations [10] have indicated that this element may be in equilibrium with $CaMoO_4$ in the landfill water. During the rain event undersaturation is encountered. Other elements have different behaviors which, however, all depend on the hydrology of the landfill in question. Tracer tests have provided the key to understanding leaching processes in landfills and can be regarded an essential tool.

Mixing of Groundwaters Downgradient of Old Unlined Landfills

High boron concentrations have been reported in groundwaters contaminated by old landfills with predominantly domestic wastes (*e.g.*, [11][12]). A major source of anthropogenic boron is its use as a sodium perborate-monohydrate ($Na_4B_4O_7 \cdot 10H_2O$), an oxidation-bleaching agent in domestic and industrial cleaning detergents. Sodium perborate is formed when sodium-borate minerals are treated with hydrogen peroxide. Boron is present in aqueous solutions as boric acid (pK = 9.2), with two dominant species near neutral pH, as follows:

$$H_3BO_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+ \quad (1)$$

Boron is known to be retarded to some degree only in groundwater environments with a high clay content [13]. Boron isotope ratios can be employed as a new tool to assess mixing ratios of groundwater of various origins [13][14]. Two stable isotopes of boron exist, ^{11}B and ^{10}B. A large relative mass difference between the two isotopes leads to significant variations in the $^{11}B/^{10}B$ ratio in nature. The boron isotope fractionation can be explained by the crystal chemistry of the various boron-containing minerals; sodium borates are enriched in ^{11}B, while, *e.g.*, calcium borate-minerals are depleted in ^{11}B [13][14]. Throughout time, raw materials of detergents may originate from sources with different boron isotope ratios. Boron isotope values are given in conventional d notation (per mil deviation from a standard). For further details on boron isotope fractionation, see [13] and [14].

One of the goals of EAWAG's subproject 'Contaminated Sites' within the research project 'Sustainable Water Resources Management, Töss Region, Switzerland' was to characterize the groundwater contamination downgradient of various old unlined compartments with mainly household wastes in Landfill Riet, Winterthur [15]. In this study, boron isotope ratios were measured three times in various shafts of leachate drains and groundwater observation wells [16]. A newly developed analytical technique, Negative Thermal Ionization Mass Spectrometry (NTIMS), was used for measuring boron isotope ratios in water samples from Landfill Riet [16]. The NTIMS technique is characterized by high analytical sensitivity, allowing the measurement of boron samples in the ng/l range. By adopting the refined NTIMS technique of [17], samples were analyzed (3–4 replicates per sample) by a direct loading procedure with an analytical uncertainty of 0.4 per mil ($2s_{mean}$), determined on sample replicates.

We found a considerable variation in the isotope ratios between –7.0 and 16.6 per mil. *Fig. 3* shows the areal distribution of the values for boron isotope ratios. Shaft S15 is leachate from a compartment of 1925–1935 (contaminated site II), and the observation well G3 is groundwater downgradient from this compartment. These two sampling stations revealed boron isotope ratios of less than –3. Shaft S13 is leachate from landfill compartments younger than 1960, and wells KB1 and KB2 are groundwater from a compartment of 1950–1960 (contaminated site III). These sampling positions revealed boron isotope ratios between 3 and 9. The wells RS65, RS68, and 92–23, are groundwater partly from upgradient of the landfill site. These sampling positions revealed boron isotope ratios of more than 9. The result of groundwater well RS69 with its value of *ca.* zero points to mixing between the S15/G3 leachate and other groundwaters. This assumption is supported by the result of a flow-model simulation at high water-table flow conditions [18], where areal groundwater flows from WNW to ESE. The values of the groundwater in 'contaminated site III' could originate from a plume of the compartments younger than 1960. The results showed that boron isotope ratios are a promising tool for the assessment of mixing rates of groundwaters contaminated by leachate from various compartments of old unlined landfills with predominantly domestic wastes.

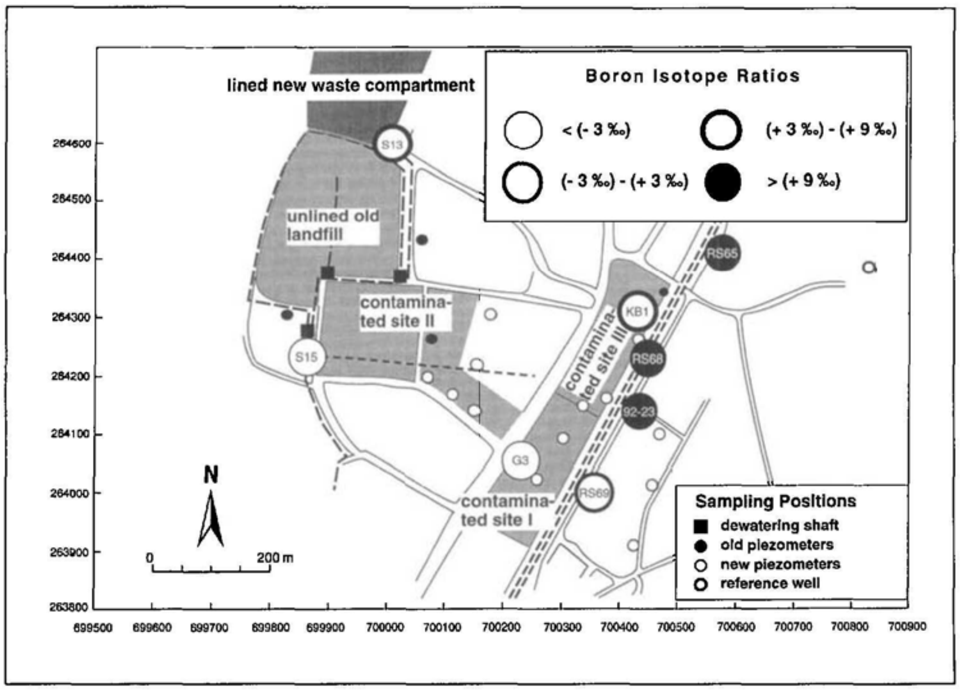

Fig. 3. *Plan view of Landfill Riet, Winterthur*. Numbers in circles: sampling stations with data on boron isotope ratios.

In Situ Characterization of Subsurface Reductants Using Reactive Tracers

Knowledge of reactants and reaction mechanisms with regard to pollutant transformation is essential to assess the need for possible remediation measures of contaminated aquifers. Often in anaerobic groundwaters, several biogeochemical redox processes take place in parallel, giving rise to numerous potential reductants for subsurface contaminants. Typical abiotic reductants in such systems include various species of reduced sulfur (*e.g.*, H_2S/HS^-, polysulfides), ferrous iron (*e.g.*, Fe^{II}_{aq}, FeS(s), magnetite, and other minerals containing structural Fe^{II}), or reduced moieties of natural organic matter (*e.g.*, hydroquinone structures). Such species may be present in aqueous solution, as colloids, or as sorbates or precipitates at solid surfaces, which complicates their identification by chemical analyses. However, reactive tracers applied as *in situ* probes may help to identify those reductants that dominate the transformation of contaminants in complex natural systems [19].

Here, we illustrate how nitroaromatic compounds (NACs) can be used as reactive tracers for the study of reductive transformation processes in aquifers. Knowledge about the reactivity of such compounds with various subsurface constituents has become available in recent years as groundwater pollution by NACs was recognized as a widespread problem (*e.g.*, [20]). NACs are used as pesticides, explosives, and solvents, but they are also important intermediates in the synthesis of dyes, pharmaceuticals, or polymers [21].

Depending on the type of reductants involved, the rates of NAC reduction may be more or less sensitive to substituent effects. If the transfer of the first electron to the nitro group is the only rate-determining step in the overall reduction of NACs to the corresponding anilines, rate constants for the reduction of substituted nitrobenzenes may vary by many orders of magnitude due to the strong impact of NAC substituents on the stabilization of the resulting nitroaryl radical-anion intermediate. This is the case for dissolved natural organic matter as reductant [22] (see left-hand panel in *Fig. 4, b*). If other processes contribute to the rate-limiting reaction steps, *e.g.*, precursor complex formation of the reductant with NACs, the patterns of substituent effects on NAC reduction are different [23] (illustrated by the middle panel in *Fig. 4, b* for adsorbed Fe^{II} as reductant). Thus, the effects of NAC substituents on reduction rates may be very different and, therefore, characteristic for certain subsurface reductants. The following example illustrates how the concept of analyzing the relative *reactivity* of a suited set of NACs may be used to infer the active reductant(s) present in an anaerobic aquifer.

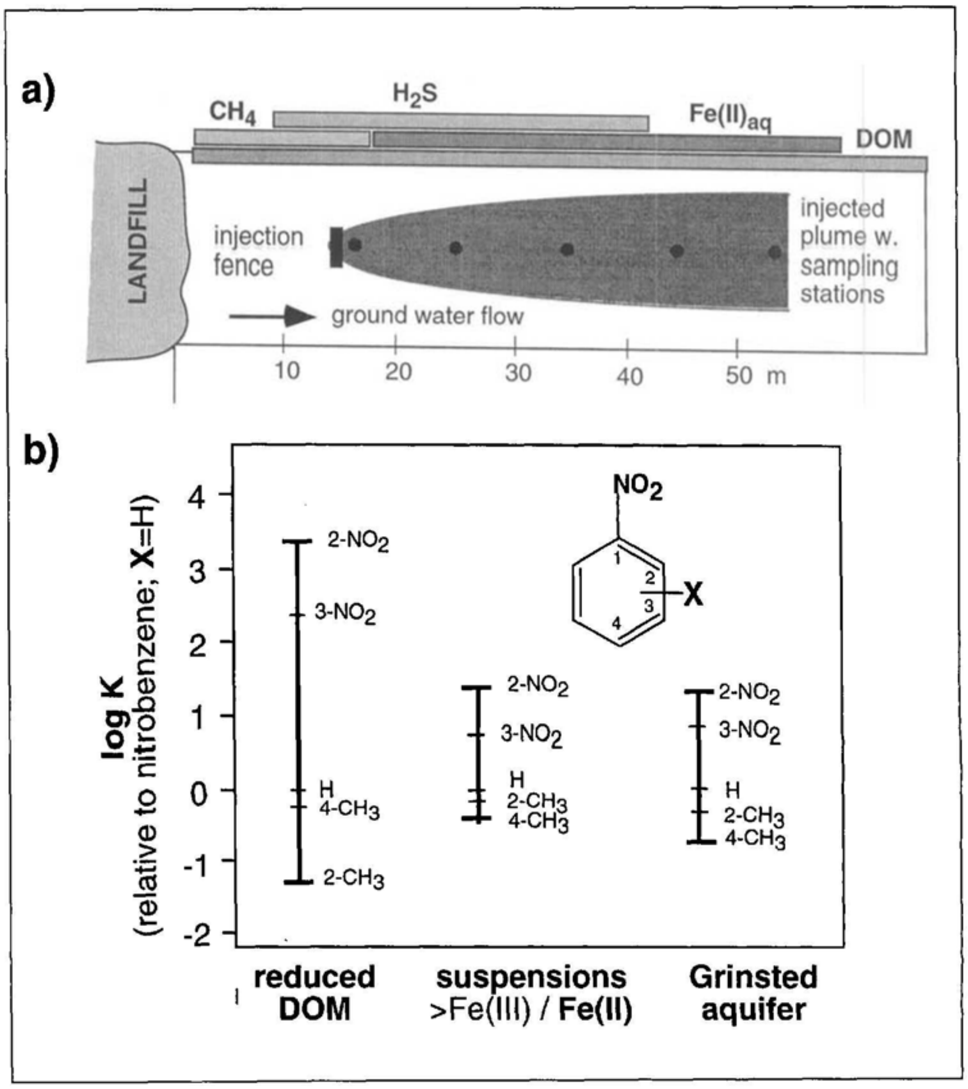

Fig. 4. a) *Schematic representation of a field injection experiment conducted in the anaerobic part of a landfill leachate plume.* Possible reductants along the flow line are depicted as bars. The reactivity patterns of nitroaromatic tracers injected into the aquifer were used to characterize the active reductants present. b) *Comparison of the reactivity of the tracers within the aquifer and in model systems exhibiting only DOM or surface bound Fe^{II} as reductants.* Pseudo-first-order rate constants of the NACs are normalized to the respective rate constant of nitrobenzene (k_{rel} = k(NAC)/k(nitrobenzene); [h^{-1}/h^{-1}]).

The reactivity pattern of five nitroaromatic probe compounds was studied in an anaerobic leachate plume of a landfill at Grindsted, Denmark, by means of injection experiments in the plume area, and by laboratory batch experiments containing groundwater and aquifer sediment (*Fig. 4, a*) [24]. The reactivity of the compounds in the aquifer was compared to their reactivity in well-defined model systems to delineate processes and reductants that were active in the leachate plume. The distribution of soluble redox-sensitive compounds in the plume is shown schematically in *Fig. 4, a*. Closest to the landfill, methane production and sulfate reduction prevailed, followed by sulfate and iron reduction. Generally, the groundwater was rich in dissolved or colloidal organic matter (DOM = 50–120 mg C_{org}/l) and in dissolved Fe^{II} (> 1.4 mM). Since reduction of NACs by dissolved H_2S and Fe^{II} is relatively slow, the major processes determining the reactivity of NACs expected under these conditions include biotransformation and abiotic reduction by DOM and Fe^{II} associated with iron-(hydr)oxide surfaces.

Within the aquifer, dinitrobenzenes were generally reduced at very high rates and without any noticeable lag phase. These compounds were always reduced first within the mixture of NACs studied. These results and the very similar pattern of NAC reduction under original and microbially deactivated conditions suggest that NAC reduction was dominated by abiotic reactions rather than by biotransformation. Reduction of all NACs proceeded orders of magnitude faster in the presence of aquifer sediment compared to filtrated groundwater. This suggests that the most reactive reductants were associated with the solid matrix of the aquifer. Throughout the plume, a very similar pattern of NAC reduction was found, indicating that the same type of reactions occurred throughout the entire anaerobic part of the aquifer.

The reactivity pattern of the NACs within the aquifer was very similar to the pattern observed in model systems where Fe^{II} associated with Fe^{III} (hydr)oxides was the only reductant (*Fig. 4, b*). In these two systems, the range of relative reactivities of NACs and their sequence reduction were similar. Furthermore, NACs present in mixtures exhibited similar competition effects for reaction sites in both systems (data not shown). If DOM is the predominant reductant in a system, NACs present in mixtures are reduced without any competition effects. Dinitrobenzenes react 2–3 orders of magnitude faster than mono-NACs, and 4-CH_3-NBs are reduced at the lowest rate (*Fig. 4, b*). The results suggest that ferrous iron adsorbed to Fe^{III}(hydr)-oxides was the dominating reductant of the NACs throughout the plume.

This case study demonstrates that biogeochemical processes controlling the reductive transformation of pollutants in anaerobic aquifers can in fact be inferred from the relative reactivity patterns of NACs used as redox-sensitive probe compounds. Despite the presence of various potential abiotic reductants (*e.g.*, H_2S/HS^-, Fe^{II}_{aq}, reduced organic matter) as well as microbial activity, ferrous iron associated with Fe^{III}-(hydr)oxide surfaces appeared to be the dominant reductant throughout the entire anaerobic part of the plume. The high reactivity of surface-bound Fe^{II} can be maintained over long periods of time, since such species may be continuously regenerated by the uptake of Fe^{II} from solution [23] or by the activity of iron-reducing microorganisms [25]. Since ferrogenic conditions are widely found in anoxic aquifers, Fe^{II} associated with iron-(hydr)oxide minerals may be regarded as a fairly ubiquitous reductant in such systems. Such species are able to react with a series of reducible pollutants including certain halogenated solvents, azo compounds, sulfoxides, chromate, or arsenate (for a compilation see [26]).

Conclusions

The presented case studies of tracer-based groundwater research show how tracer methods allow quantitative description of system parameters that are very difficult to estimate by other means. In the Linsental aquifer, groundwater residence times of some hundreds of days were directly quantified by ^3H-^3He dating, and a seasonal change in river infiltration could be identified. Based on combined measurements of conductivity and $^{18}O/^{16}O$ ratio in leachate from the Landfill Lostorf, the dilution of the leachate with rainwater after rain events could be quantified. In the groundwater downgradient of the Landfill Riet, boron isotope measurements allowed the identification of water components of different origin and the quantification of mixing between them. The predominant reductant controlling the reductive transformation of pollutants in an anaerobic leachate plume of a landfill at Grindsted could be inferred from the relative reactivity patterns of NACs used as redox-sensitive probe compounds.

These are only a few examples demonstrating the potential of tracer approaches in the environmental sciences. Tracers are tools that allow us to visualize, analyze, and quantify specific processes in complex systems. As such, they are essential to the endeavor of deepening our understanding of environmental systems. Besides groundwater, EAWAG researchers are using tracer methods in other aquatic systems, particularly in lakes and rivers. Analytical equipment and experience of a wide range of tracers is available at EAWAG; this is further supplemented by close collaboration with specialized laboratories at ETH-Zürich and at other research institutions. In the attempt to obtain an integrated understanding of complex environmental systems, one may in future expect more multitracer studies to be conducted to examine simultaneously the physical, chemical, and biological processes occurring within such systems.

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