

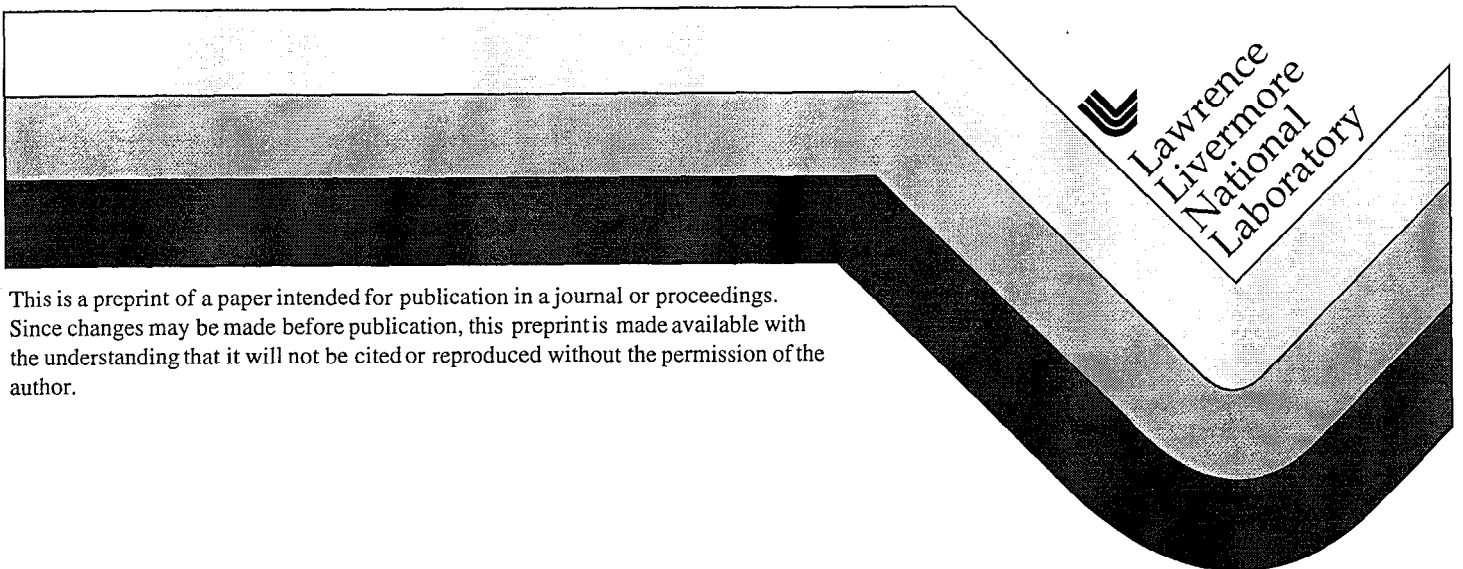
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¹²⁹Iodine: A New Tracer for Surface Water/Groundwater Interaction

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The use of isotopic tracers for age dating and tracing recently recharged groundwater has gained credibility from traditional hydrogeologists and water resource managers in recent years. Given that the use of polluted surface water that has been artificially or naturally recharged for public water supply is likely to continue to increase, geochemical tools for tracing surface water/groundwater interaction will become increasingly relied upon for prediction of water quality. Anthropogenic ¹²⁹Iodine has the potential to join the established isotopic water tracers such as ³H/He, ¹⁴C, $\delta^{18}\text{O}$ and δD , in tracking the movement and chemical evolution of surface water from infiltration to subsurface flow.

¹²⁹Iodine was produced in nuclear bomb tests, which raised the ratio of ¹²⁹I ($T_{1/2} = 15.6$ my) to stable iodine, ¹²⁷I, by several orders of magnitude in the surface environment. Subsequent emissions of ¹²⁹I from European nuclear fuel reprocessing facilities, have resulted in a steady increase in ¹²⁹I/¹²⁷I ratios for the past 30 years in reservoirs in exchange with the atmosphere. The highly sensitive analytical technique of accelerator mass spectrometry allows measurement of ¹²⁹I/¹²⁷I ratios in surface water and shallow groundwater from anywhere in the Northern Hemisphere, on sample sizes of one to four liters. The unique biogeochemical behavior of iodine provides information about the role of biota and degrading organic matter in fate and transport scenarios during infiltration.

We measured ¹²⁹I/¹²⁷I ratios in about 30 major rivers and found a strong signal of anthropogenic ¹²⁹I in all of them (Moran et al., 1998). The effect of local point sources such as the Savannah River Facility and Hanford Facility are easily observed in the Savannah and Columbia Rivers, respectively. Likewise, the Rhine and Rhone rivers in Switzerland, have ratios well above "background" due to their proximity to the main global source in northwest Europe. Away from local point sources, one observes a mixing trend between atmospherically-delivered ¹²⁹I from European nuclear fuel reprocessing facilities, and low-ratio iodine derived from soil weathering (Moran et al., 1998). This anthropogenic ¹²⁹I should be easily observable in soil water and shallow groundwater anywhere in the northern hemisphere.

Data on radioiodine speciation in surface soils and groundwater are limited and quite controversial. The following species were found for stable and radioactive iodine: I⁻, IO₃⁻, iodine associations with clay silicates, sesquioxides, organic matter, and possibly free iodine (summarized in Von Gunten and Benes, 1995). Because of the mainly anionic nature of iodine species, particle-water distribution coefficients of iodine species are low, i.e., approximately 1 cm³/g for I⁻, and approximately 10 cm³/g for IO₃⁻, while for organically bound iodine, they are considerably larger. This would suggest retention in surface soils, which typically are more organic matter rich than aquifer material.

Results of ¹²⁹I and ¹²⁷I analyses from the Glatt River and Glattfelden aquifers (Switzerland), which are situated at 2-7 m away from the Glatt River, are given in Table 1. Values of temperature, dissolved oxygen, and pH in the different samples ranged from 11-16 °C, 0.2-2.5 mg/l, and 7.3-7.8, respectively. These data are quite encouraging because of the very strong ¹²⁹I signal observed, the large range in ¹²⁹I concentrations over a short distance, and the strong correlation between ¹²⁹I and ¹²⁷I. ¹²⁹I and ¹²⁷I, as well as the ¹²⁹I/¹²⁷I ratios decrease from the river into the closest groundwater well, and from there on more slowly with increasing water residence time (Table 1). Water residence times in these aquifers are known from ²²²Rn (Hoehn and von Gunten, 1989) and ³H pulse dating (Santschi et al., 1987). The ³H dating was carried out after an accidental release of ³H in the Glatt River by a manufacturing plant. The fact that ¹²⁹I/¹²⁷I ratios also decrease from the river into the groundwater, and in the groundwater with increasing water residence time, agrees with the conceptual model that would predict that these ratios

would decrease with increasing water or iodine residence time, in accordance with the approximately linear increase in the recent decades from the atmospheric discharge rates of the European reprocessing plants (Yiou et al., 1995).

Table 1. Results from the Glattfelden Aquifer, Switzerland

Sample#	Water residence time (d)*	^{129}I (10^8 atoms/l)	^{127}I (ppb)	$^{129}\text{I}/^{127}\text{I}$ atom ratio (10^{-8})
1	1.8	8.9	2.9	6.9
2	2.8	6.3	2.8	5.0
3	3	6.4	2.5	5.7
4	5	5.9	2.6	5.1
5 (deep)	550	0.69	1.6	0.96
6 (river)	0	20	4.0	11

*) According to Hoehn et al., 1989; Santschi et al., 1987.

The behavior of ^{129}I is consistent with a two box model. The first region is situated right near the river-aquifer interface, extending over less than 1 m, and retains all (or most) organically bound species of iodine. Evidence from the Mississippi River indicates that approximately 50% of the ^{129}I is bound to macromolecular organic matter, and 10% or less is in a particle-bound form. If this is the case for the Glatt River, this would be consistent with the approximately 50% decrease in ^{129}I concentration from the river water to the first groundwater sample (with 1.8 days water residence time). The second region comprises the rest of the aquifer, and is where iodine species are slightly retarded in proportion to the ratio of the residence time of the tracer to the water residence time, according to the particle-water partition coefficient of the iodine species present.

Our preliminary data from the Swiss site suggests that in the very near field redox conditions and organo-iodine retardation are important, while in the far field, changes in ^{129}I related to changes in its input function dominate. Given that the source for anthropogenic ^{129}I has been increasing for the past 30 years with a steep increase since 1990, (Yiou et al., 1994) it may be possible to match a ^{129}I level with a date, as is done for fuel-reprocessing ^{85}Kr . Here, ^{129}I enjoys two advantages over the tritium-helium method and the ^{85}Kr method: the much greater magnitude of the anthropogenic signal relative to the background, and the much smaller sample size needed.

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