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Abstract

Iodine is a biophilic element, with one stable isotope, ^{127}I, and one long-lived radioisotope, ^{129}I, which originates in the surface environment almost entirely from anthropogenic activities such as nuclear fuel reprocessing. Very few studies have evaluated the geochemical behavior of iodine isotopes in the subsurface. The concentrations of ^{129}I and ^{127}I were measured in wells fed by a series of artificial recharge ponds in the Forebay Area of the Orange County groundwater basin (California, USA) to evaluate their potential use as hydrological tracers. To substantiate interpretation of ^{129}I and ^{127}I concentration data, the aquifer system was evaluated using literature values of aquifer water mass age based on ^{3}H/^{3}He, Xenon and δ^{18}O tracer data, as well as time-series data of Santa Ana River flow rates over the past decade. The aquifer data demonstrate the nearly conservative behavior of ^{129}I, with ^{129}I/^{127}I ratios likely reflecting variations in source functions as well as climatic conditions, and with inferred particle-water partition coefficients (K_d) of 0.1 cm^3 g^{-1} or less.

Keywords: ^{129}I, iodine, groundwater, tracer, conservative behavior

1. Introduction

1.1. Background

Iodine (I_2) is a biophilic element supplied to the land surface through atmospheric deposition of sea spray, particularly near coastal regions, and from weathering of marine shales where iodine is concentrated in organic matter. It is involved in the geochemical cycling of organic matter through the reductive or oxidative formation of carbon – iodine bonds in aromatic and protein compounds (Summers et al., 1989; Christiansen and Carlsen, 1991; Carlsen et al., 1992; Warwick et al., 1993; Edmonds and Morita, 1998; Warner et al., 2000). Although, iodate (IO_3^-) is the thermodynamically stable form of iodine in the marine environment and is prevalent in alkaline soils and seawater, organic forms of iodine are the dominant forms in air, soils, and in fresh, estuarine and surface ocean waters (Oktay et al., 2001; Schwehr and Santschi, 2003; Santschi and Schwehr, 2004, and references therein).

Iodide (I^-) is the thermodynamically stable form in reducing environments that may also be somewhat acidic. In groundwaters, after infiltration through organic matter - containing and reducing surface soils, the most prevalent species in groundwater generally becomes I^- (Sheppard et al., 1995; Langmuir, 1997; Fabryka-Martin, 2000). I^- exhibits a geochemical behavior that is similar to that of chloride, with weak, outer sphere electrostatic adsorption to positively-charged mineral surfaces and being readily displaced by competitive ligand exchange (McBride, 2000).

Data regarding radioiodine speciation in surface soils and groundwater are limited and quite controversial. The following species have been identified for both stable and radioactive iodine: I^-, IO_3^-, iodine associations with clay silicates, sesquioxides, organic matter, and possibly free iodine (summarized in Von Gunten and Benez, 1995). Because of the mainly anionic nature of iodine species, particle-water distribution coefficients, K_d, of iodine species are generally low, i.e., approximately 1 cm^3/g for I^-, and approximately 10^1 to 10^3 cm^3/g for IO_3^-, depending on the organic content of the soils; for organically bound iodine and/or organic-rich soils (e.g., peats), K_d values are 10^3 cm^3/g or above (e.g., Yoshida et al., 1992; Fukui et al., 1996), and influenced by microbial reactions. This would suggest retention of organo-iodine in surface soils, which typically are more organic matter-rich than aquifer material, where iodine isotopes exhibit greater mobility (e.g., Santschi et al., 1999).

The stable isotope of iodine, ^{127}I, is naturally occurring and has a abundance of 100%. Though most radioisotopes of iodine are short-lived, the isotope ^{129}I has a half-life of 15.6 million years. Radiogenic ^{129}I is produced naturally in the atmosphere by cosmic-ray induced spallation of Xenon, and in the subsurface by spontaneous fission of ^{238}U. The surface inventory of naturally produced ^{129}I is 100 kg (Yiou et al., 1994; Raisbeck et al., 1999). Since the half-life of ^{129}I is much longer than its residence time (τ) in surface environmental compartments, this naturally produced isotope was well-mixed in the surface soil compartment (τ ~1000 y; Kocher, 1982), the surface ocean (τ ~100 y for the mixed layer, depth 0 to ~100 m; Raisbeck et al., 1995), and the atmosphere (τ ~11-18 days; Rahn et al., 1976) before the nuclear age. Anthropogenic sources of ^{129}I include an added 150 kg through atmospheric bomb testing from 1945 –1962 (Eisenbud and Gesell, 1997), and 2360 kg from the discharged waste of nuclear fuel reprocessing at Cap de La Hague, France, and Sellafield, England, from 1966 – 1997 (Raisbeck et al., 1999). In 1990, it was estimated that about 5660 kg of ^{129}I stored in spent reactor fuel had not yet been reprocessed (Finkel and Suter, 1993 as cited in Schmidt et al., 1998). Atmospheric releases by Hanford in Washington, U.S.A. (1944-1972), added another 260 kg (Hanford website, cited in Schnabel et al., 2001). These anthropogenic sources of ^{129}I overwhelm the natural sources, and thus provide a point source of high concentration for tracer applications of the isotopic ratio ^{129}I/^{127}I (Raisbeck et al., 1995; Schink et al., 1995a; 1995b; Santschi et al., 1996; 1999; Moran et al., 1997, 1999a, 1999b; Santschi and Schwehr, 2004; Snyder and Fehn, 2004). A thorough review of recent advances in tracer applications using ^{129}I and ^{129}I/^{127}I can be found in Santschi and Schwehr (2004) and Snyder and Fehn (2004).

The atmospheric input of ^{129}I in surface environments of the USA is mostly from European reprocessing plant emissions (Raisbeck et al., 1995; Moran et al., 1999a; 1999b; Fehn and Snyder 2000), which have been relatively constant in the last decade (Szidat et al., 2000; Schnabel et al., 2001). However, little is known about temporal or spatial variation in this source term, e.g., seasonal changes in transport patterns and deposition patterns. Observed variations in ^{129}I concentrations could also occur due to watershed or aquifer processes. In young groundwaters, ^{129}I concentrations and ^{129}I/^{127}I ratios may also provide information about aquifer processes that ^{127}I and chloride (Cl) alone cannot provide.

^{129}I and ^{127}I studies are important not only because of nuclear proliferation, but also because of iodine deficiency syndrome. This deficiency syndrome is particularly serious in many developing countries where table salt is not iodized or where socioeconomic or environmental factors preclude the use of iodinized table salt (Dai et al., 2004). It appears that the concentration of ^{127}I is not clearly related to the proximity of iodine--rich sea-spray, and thus, studies of iodine in surface and subsurface environments might shed light on its geochemical behavior. Studies of ^{129}I may reveal where stable ^{127}I is tied up in local environments, and why low availability of ^{127}I is more problematic in some areas. Since the speciation of iodine plays a major role in the mobility and residence time of iodine in soils and hydrological systems, consideration of speciation is very important. Selecting areas with relatively young groundwaters is a critical first step before extending the study of this complex isotope to other, older systems.

The objective of this study is to document the mobility and variations in ^{129}I concentrations and ^{129}I/^{127}I ratios in young groundwaters of the aquifer system of Orange County, California, where groundwater flow for recently recharged water is well defined from previous studies.

1.2. Geohydrology of the study site

The Los Angeles-Orange County coastal plain basin is a synclinal structure formed by intense folding and faulting during collision of continental plates. The folded igneous, metamorphic, and sedimentary rock outcrop around the basin as the San Gabriel Mountains to the northwest and the San Bernardino Mountains to the north. Thousands of feet of unconsolidated alluvial sediments fill the basin and an uplift subdivides the basin into effectively two northwest-trending basinal areas, the Upper and Lower Basins. The Santa Ana River drains an area of about 3107 km^2 that comprises the Upper Basin, cuts the uplift between the two adjacent basins and continues through the Lower Basin with little or no natural coastal barrier to the Pacific Ocean (Planert and Williams, 1995). Natural groundwater flow is perpendicular to the long axis of the Los Angeles-Orange County coastal plain basin with discharge to the Pacific Ocean, Fig. 1.

The Lower Basin is encompassed by the Orange County basin and its aquifers. The Orange County groundwater basin, about 906 km^2, is bordered by the Coyote and

Chino Hills to the north, the Santa Ana Mountains to the northeast, and the Pacific Ocean to the southwest (OCWD, 1999). The Orange County basin is further subdivided into the Forebay (recharge) Area to the northeast and the Pressure (confined) Zone to the southwest. The study area, displayed in Fig. 1, is in the Forebay Area.

Annual precipitation, from November through March, is about 46 cm in the mountains, decreasing to about 35 cm in the Lower Basin where most is lost to evapotranspiration (ET) (Planert and Williams, 1995). Runoff from precipitation in the surrounding mountains provides flow to the Santa Ana River which is pooled in a reservoir behind the Prado Dam (SARPD). The annual water volume release from the Prado Reservoir is approximately 3300 km^3 (Chino Basin Watermaster, 2003) as an admixture of an average of 740 km^3 from marine-sourced meteoric stormflow (ranging from 120 to 6200 km^3), ~1730 km^3 from baseflow (primarily reclaimed waste waters), and ~ 300 to 900 km^3 of purchased waters from the Colorado River (OCWD, 2004). Estimates for loss to ET in the SAR basin due to Arundo donax, a bamboo-like reed, are about 370 km^3 (SAWPA, 2004). These ET losses may be conservative since they do not include other plant species or irrigation.

Waters from the SARPD are diverted to artificial recharge ponds, such as Anaheim Lake and Kraemer Basin, in the Forebay. Replenishment of the aquifer system is from percolation of the water sources from the recharge ponds and stream bed into permeable sands and gravels. Regionally, groundwater flow is locally impeded by discontinuous lenses of clays and silts, faults, or thinning of aquifer beds along structurally upwarped areas. However, these restrictions do not form complete barriers. Recharge is reported to reach the deepest monitored wells in the Forebay region (about 670 m) (Herndon et al., 1997). The extent of any given layer is not well-defined, but tracer studies suggest that impervious silt and clay layers are thin and discontinuous (Clark et al., 2003; and references therein). Additionally, the study wells (most of which are $\leq$ 200 m depth) typically have long-screened production zones of 60 to 90 m and so do not sample waters from narrow, discrete intervals.

To meet the high water use demands of industry, municipal, and agriculture for about 4 million people, the Orange County Water District (OCWD) annually enhances recharge by 3300 km^3 (270,000 ac-ft), which is nearly the same volume of groundwater pumped from the aquifer system.

1.3. Description of the study site

The study site shows the Forebay recharge area (Fig. 1). Aquifer recharge is through waters diverted from the Santa Ana River at the Prado Dam (SARPD) to the Anaheim Lake and Kraemer Basin spreading ponds then along a flow path from these ponds that includes the wells shown on the cross section (Fig. 2). Previous studies (Davisson et al., 1996; 1998; 1999; summarized in Clark et al., 2003) have used a suite of isotopic tracers and geochronometers throughout an extensive network of wells monitored to determine the flow path and turnover times or ages of groundwaters. The ages of groundwater samples from well water involved in this study are given in Table 1 and depicted in Fig. 2. The $^3H/^3He$ ages were shown to constrain groundwater ages older than 1 year (Davisson et al., 1996; 1999). Ages for waters younger than one year were determined using the measured change in mixing ratios of the $\delta^{18}O$ of the groundwater and the $\delta^{18}O$ of Colorado River water tagged with distinct Xenon (^{124}Xe) isotopes

(Davisson et al., 1999; Clark et al., 2003). Davisson et al. (1999) identified a relatively rapid flow along a path from Anaheim Lake to wells AM 44, AM 9, AM 14, wherein the linear flow velocity averages 5.1 m d^{-1} and the hydraulic conductivity is ~307 m d^{-1}. Tracer tests using $\delta^{18}O$ and Xe also showed that the Orange County Water District OCWD KB 1 well and the AM 10 well are likely recharged preferentially from the Kraemer Basin and not from Anaheim Lake (Davisson, 1998). A tracer study using sulfur hexafluoride (SF_6) released into the SAR at a location in close proximity to the study area (north of the SAR and extending to less than 0.5 km south of Anaheim Lake) demonstrated a similar linear flow velocity of ~ 5.5 m d^{-1} in wells < 60 m depth (Gamlin et al., 2001).

Clemens-Knott et al. (1999) extended the rapid flow path discussed above to beyond AM 33, displaying an average linear flow velocity of 2.7 m d^{-1} with a hydraulic conductivity of ~200 m d^{-1}. High 'preferential' flow is consistent with the steeply dipping aquifers to the west and southwest near the recharge region. With some distance from recharge, the dip decreases and an increase in consolidation of sediments, dispersivity, and diffusivity are expected to occur with an increase in depth. Therefore, it is not surprising that with an increase in depth, there is a correspondent decrease in flow rates and an increase in water age (Clark et al., 2003). However, the study area wells have a relatively shallow completion depth of less than 200 m elevation (Fig. 2) in very heterogeneous, conductive layers that are hydrologically stratified (Tompson et al., 1999, as cited in Clark et al., 2003).

The AMD 9 well is a series of nested wells completed at multiple levels (Fig. 2). Anaheim Lake directly recharges wells AMD 9-1 and AMD 9-2. AMD 9-3 is completed in a low permeability zone, which is recharged with waters from an older source. So, both AMD 9-3 and AMD 9-4 are completed in separate, older aquifer systems, with no apparent recharge from Anaheim Lake or Kraemer Basin during the relatively short time of the isotopic tracer tests (approximately 1 yr). The $^{3}H/^{3}He$ age for water from AMD 9-3 is 6 yrs (Clark et al., 2003) and 25 yrs for AMD 9-4 (Davisson et al., 1999).

In summary, the Upper Santa Ana River catchment waters are pooled in the Prado Reservoir above the Prado Dam, where flow is diverted from the Santa Ana River and mixed with recycled wastewaters. These waters are then spread onto artificial recharge ponds, such as Anaheim Lake and Kraemer Basin. The study wells supplied by this artificial recharge are within a flow path demonstrating high hydraulic conductivity and water turnover of less than ten years, with the exception of AMD 9-3 and AMD 9-4, which are in separate aquifer systems and have a water mass age of 6 yrs and 25 yrs, respectively.

2. Experimental

2.1. Water sample collection

Three to 5 Liters of water were collected from all wells in August and September 1999 (Table 1). The samples were collected by and received through collaboration with the Orange County Water District and the Lawrence Livermore National Laboratory, respectively. Upon receipt, the samples were preserved by the addition of 10 mM $NaHSO_3$ reductant per liter to prevent possible volatilization of elemental gaseous iodine. Aliquots of 5 mL were used for measurement of total ^{127}I by HPLC and ICP-MS (Schwehr and Santschi, 2003). The bulk of the samples were then transferred into acid-cleaned polypropylene bottles, sealed with parafilm, and stored at room temperature in the dark.

2.2. *Processing for $^{129}I/^{127}I$*

The sample processing for $^{129}I/^{127}I$ isotopic iodine ratio determination includes sample pre-concentration (for ease of iodine extraction and subsequent minimization of required reagents), reduction of I_2 and IO_3^- to I^-, recovery of iodine from decomposition of organic iodine forms, liquid-liquid extraction of iodine as the sum of all potential iodine species from the sample, and preparation of AgI targets for AMS measurement.

The first stage of sample preparation was a volume reduction from 3 to 5 L to ~500 mL by distillation by rotary evaporation. The pre-concentrated solutions were placed in Teflon bottles, with the addition of 2 to 4 mg of Woodward iodine, a low ratio carrier (iodine $^{129}I/^{127}I$ ratio of 80 x 10^{-15}). Next, 5 M NaOH was added to adjust the pH to 14. The sample solutions were then oxidized by chlorination with 250 µL of fresh 4 to 6% NaClO, ultrasonicated for 3 hours at 40°C and left in the 40°C bath overnight. Testing of this high pH chlorination treatment for organic matter oxidation yielded recoveries of ~98% iodine from known concentrations of the destruction-resistant L-thyroxine compound. The sample solutions were then cooled to room temperature, treated with 5 mL 1M $NaHSO_3$ and 10 mL 1M $NH_2OH.HCl$, and ultrasonicated again for 1.5 hrs at 40°C, re-cooled, after which the pH was adjusted to 6.5 with HNO_3 (Gabay et al., 1974; Szidat et al., 2000; Schnabel et al., 2001). The Teflon bottles were then sealed with parafilm and refrigerated until extraction.

For the solvent extraction procedure, the pre-concentrated sample was placed in a 1000 mL separatory funnel. The solution was acidified to a pH of 1 with 6 M HNO_3, equilibrated with ~10 mL CCl_4 and 5 mL 30% H_2O_2, under shaking and venting, until the

CCl_4 turned pink from the dissolution of I_2. Further additions of CCl_4 and H_2O_2 were added to the remaining separatory funnel solution, and each successive pink CCl_4 was added to the reserved solvent beaker until no change of color was noted in the CCl_4 (usually after 3 repetitions of solvent extraction). Then, 20 mL of 1 M $NH_2OH.HCl$ and 10 mL CCl_4 were added to the remaining separatory funnel sample solution, which was shaken and vented, as a final check that no iodine species remained in the sample. All of the reserved, iodinated CCl_4 fractions were combined and back-extracted into ~15 mL of a freshly made-up aqueous solution of 0.1 M $NaHSO_3$ and 0.18 M H_2SO_4. The colorless solvent was drawn-off as waste, and the aqueous solution was placed into a conical 50 mL glass centrifuge tube. Then 2 mg of Cl^- with a low iodine blank was added to the aqueous back-extract to prevent precipitation of sulfo-silver. Tellerium compounds, often found in sulfo-silver, interfere with the accelerator mass spectrometry (AMS) measurement. The addition of Cl^- also provides a more effective co-precipitation of the low concentrations of iodide. A solution of 0.1 M $AgNO_3$ was added drop-wise during agitation of the back-extract to co-precipitate AgCl (white) and AgI (yellow). To maximize precipitation, the solution was refrigerated overnight. The AgCl was redissolved preferentially by addition of 30% NH_4OH solution, vortexed, centrifuged, decanted, then rinsed thoroughly with 18.3 MΩ de-ionized water. The remaining AgI pellet was rinsed in ethanol and dried in a dark oven, after which it was weighed, mixed with Ag powder, and analyzed by AMS at the Purdue PRIME Lab.

Procedure blanks for the rotary evaporation and chemical reagents were within the range of the carrier iodine blank. The AMS analyses for $^{129}I/^{127}I$ ratios were 2 to 3 orders of magnitude higher than the values for the blanks, consequently, no blank corrections were necessary.

Concentration values for ^{127}I have a maximum relative standard deviation of 3% as measured by high performance liquid chromatography (HPLC). Details for the HPLC procedure used are given in Schwehr and Santschi (2003). Briefly, all samples were run in replicate with 3 standard additions of a known iodide standard solution, for a minimum total of 10 measurements per sample. Additionally, 7 of the 12 samples were measured independently by ICP-MS and HPLC; these were within 3% of the HPLC concentrations (Table 1).

The maximum uncertainties (1 standard deviation, SD) of the individual steps in iodine measurement are: 8 % for the $^{129}I/^{127}I$ ratios by AMS; 5 % for the solvent extraction (SE) of $^{129}I/^{127}I$; and 3 % for the HPLC measurement of ^{127}I. The maximum propagated error for $^{129}I/^{127}I$ ratios is 9.4% (involving AMS and SE). The maximum propagated error (1SD) for ^{129}I is 9.9% (involving AMS, SE, and HPLC). Therefore, both $^{129}I/^{127}I$ and ^{129}I have nearly a 10% maximum relative SD. This error is comparable to that of other studies for $^{129}I/^{127}I$ ratios and ^{129}I concentrations (Oktay et al., 2000, 2001; Moran et al., 2002).

3. Results and Discussion

3.1 The ^{129}I and $^{129}I/^{127}I$ data

Concentrations for ^{129}I and ^{127}I, $^{129}I/^{127}I$ ratios, along with water ages, are presented for each well and for the recharge ponds in Table 1. The ^{127}I concentrations range from 18.3 to 41.1 ppb with a median concentration of 28.4 ppb. The ^{129}I concentrations for Anaheim Lake and Kraemer Basin are 3.50×10^7 and 4.80×10^7 L^{-1}, respectively. Although there is no measurement for the Santa Ana River, the concentration for the Colorado River, measured in 1996, is notably close to the ^{129}I concentration of the recharge ponds,

3.20×10^{7} L^{-1} (Moran et al., 2002). Median concentrations for both the ^{129}I concentrations in the surface waters and in the groundwaters is 4×10^{7} L^{-1}, with an approximate range of 1 to 7×10^{7} L^{-1}. Values for the isotopic ratio of $^{129}I/^{127}I$ range from 7 to 64×10^{-11}, with a median of 42×10^{-11} in surface waters and 27×10^{-11} in groundwaters.

The isotopic ratios for $^{129}I/^{127}I$ and ^{129}I concentrations in the study site wells increase with water mass ages of the groundwaters for the southwesterly flow path, as shown in Fig. 3. One of the wells that produces the youngest groundwater, KB 1, has the lowest ^{129}I concentration and $^{129}I/^{127}I$ ratio, while the well producing the oldest groundwater, AM 33, has the highest ^{129}I concentration, as well as the highest $^{129}I/^{127}I$. The AMD 9-1 well with the youngest groundwater age falls slightly above this trend. As discussed earlier, this suggests that AMD 9-1 is comparable to surface water ratio values since AMD 9-1 has the shortest water mass age and tracer data indicating no mixing with other groundwaters. It follows that all of the other groundwater samples are somewhat diluted with by mixing with other groundwater, with a lower $^{129}I/^{127}I$ value, thus the high values in well AM 33 are contrary to expectations. In the absence of alternate sources, the trend in Fig. 3 is in marked contrast to expectations, i.e., 1) due to the biophilic nature of iodine to partition into organic matter, from 50 to 80 % of the initial values for $^{129}I/^{127}I$ ratios or concentrations of ^{129}I in surface waters would not be present in ground waters and 2) due to sorption in the aquifer matrices, the values for $^{129}I/^{127}I$ ratios or concentrations of ^{129}I would decrease with distance from the source or water mass age.

3.2 Variability due to changes in source signal

The $^{129}I/^{127}I$ ratios measured in both surface water and groundwater samples from Orange County fall among the lowest ratios observed in North American rivers (Moran et al., 2002), but are close to those observed in other southwestern U.S. rivers (Santa Cruz River, Arizona; Rio Grande, Texas; Brazos, Texas; and Pecos River, Texas). These watersheds, characterized by low $^{129}I/^{127}I$ ratios and high Iodine concentrations are in areas of high evapotranspiration, made higher by extensive irrigation for agriculture. In comparison to these other 'low ratio' rivers, surface waters and shallow groundwaters from the OCWD sites have similar ratios but lower stable iodine concentrations. While rivers with high stable iodine concentrations and low ratios represent a mix between a meteoric component and a sedimentary, leached, 'dead' component, the OCWD waters are likely low ratio, low concentration because the meteoric signal is strongly influenced by the marine climate that prevails in this western coastal watershed. A greater influence from sea spray in meteoric water would result in decreased $^{129}I/^{127}I$ ratios, since the fuel reprocessing signal is from long-range transport of non-marine iodine, and Pacific Ocean water has a lower ratio (but higher than a subsurface leachate). A significant subsurface, sedimentary component can also be ruled out because neither an increase in stable iodine nor a significant decrease in $^{129}I/^{127}I$ is observed along the groundwater flow path.

Variations in the observed ratios and concentrations along the flow paths (Kraemer and Anaheim) at OCWD are therefore likely due to changes in the source signal. The most significant, and most easily explained observation, is the much lower $^{129}I/^{127}I$ ratio and ^{129}I concentration found at well AMD 9-4. The groundwater from this well recharged some 25 years ago when emissions from the major fuel reprocessing facilities were significantly lower. The measured ratio in AMD 9-4 is about 4 times lower than the ratio in AMD 9-3, which is the closest upgradient well, with a groundwater age of 6 years. The 4 fold difference in $^{129}I/^{127}I$ ratios between these two wells separated by about 20 years travel time, is of the same order as the difference in emissions from the European nuclear fuel reprocessing facilities over the same time period (roughly 50 kg/yr in 1975 to 200 kg/yr in the mid 1990's; Raisbeck et al., 1999). This data point is one piece of evidence that iodine and ^{129}I (in inorganic forms) are behaving near-conservatively in the subsurface, and points to the similarity between transport of ^{129}I and that of other anthropogenic radioisotopes dominated by the aqueous phase, such as ^{36}Cl and ^{3}H.

Possible causes for variation in the ^{129}I input signal with time are related to transport and deposition of ^{129}I from the major fuel reprocessing facilities. Annualized emissions from fuel reprocessing facilities in Europe steadily increased from the 1970's to about 1990, then remained roughly constant throughout the 1990's. However, weekly to monthly emissions to the atmosphere may fluctuate widely due to the pattern of operations at the fuel reprocessing facilities. Furthermore, seasonal changes in wind direction and weather patterns, along with decadal variations, would certainly result in changes in the direction and rate of transport of atmospheric ^{129}I. In addition, variability in the deposition pattern of ^{129}I (and stable ^{127}I) in the Orange County area would be expected given the Mediterranean climate and factors such as El Nino events that bring warmer, wetter winters (as occurred in 1997-98). Periods of high rainfall and infiltration may leach previously sorbed ^{129}I from watershed soils. The expected magnitude in the variations in ^{129}I deposition is not well known, but $^{129}I/^{127}I$ ratios in rainfall vary by about one order of magnitude over a year in a given location (Moran et al., 1999). Because rivers integrate over space and time, less variability is observed in large systems. The ^{129}I concentrations and ^{129}I/^{127}I ratios in the Mississippi River, which drains ~40% if the contiguous United States and encompasses a wide variation in climatic systems (Oktay et al., 2001), varied by a factor of 5 to 10. However, time series data of ^{129}I and ^{127}I in river samples from a basin in a single climate system are not available (Moran et al., 2002). The pattern of change observed in ^{129}I/^{127}I ratios and ^{129}I concentrations in groundwater samples from OCWD is likely a record of change in the input function, since subsurface sources and sinks for iodine and ^{129}I are likely negligible over the relatively short time of transport.

However variable or short term, the climatic fluctuations in the input function of ^{129}I/^{127}I ratios and ^{129}I concentrations would be included in the catchment response. The catchment response is expected have low ^{129}I/^{127}I values and ^{129}I concentrations during wet seasons due to the strong influence of stormflow from marine iodine-enriched meteoric rains (Baker et al., 2000; Huang et al., 2001; Sturgis and Barrie, 1988; and Landsberger, 1988). During baseflow conditions the anticipated catchment response is through high ^{129}I/^{127}I values and ^{129}I concentrations from the evaporative concentration of solutes mixed with reclaimed wastewater and a small percentage of Colorado River Water. This general trend is observed in the data as higher ^{129}I/^{127}I values and ^{129}I concentrations during the extended drought of the southwestern U.S. (Cook et al., 2004) and in lower values and concentrations during the wet years of 1997-98 influenced by El Nino.

Since both marine-sourced meteoric rainfall and ET can play a major role in solute concentrations in this watershed, changes in patterns observed in ^{129}I/^{127}I and ^{129}I concentrations along flow paths likely represent changes in both the input function and in climatic factors such as ET.

3.3 Sorption described by the soil-water partition coefficient, K_d

The isotope ^{129}I in surface waters can exist as IO_3^-, I-, or organo-iodine, with IO_3^- being the thermodynamically stable form in oxic waters (e.g., Schwehr and Santschi, 2003; Santschi and Schwehr, 2004; Schwehr et al., 2004, and references therein). Soil-water partition coefficients, K_d, for both IO_3^- and organic forms of iodine are 10^1 cm^3 g^{-1} or higher, while those for I^- are of the order of 1 cm^3 g^{-1} or below (e.g., Sheppard et al., 1995; Fukui et al., 1996; Fuhrman et al., 1998; Santschi et al., 1999; Kaplan et al., 2000).

The retardation factor, R, defined as the ratio of the residence time of the isotope to the water residence time, is related to the K_d value as follows

$$R = 1 + K_d (1-Ø)\rho/Ø \qquad (1)$$

with Ø = porosity and ρ = density of particles (g cm^{-3}).

The probable range of K_d values can be calculated using values for Ø = 0.3, and ρ = 2.5 taken from Davisson et al. (1998) and a range of R values of 1.5 to 2.2. The more likely R value of 1.5 was calculated using the year of fallout from atmospheric bomb testing, 1962, subtracted from the year of well water sampling, 1999, divided by the longest well water residence time, 25 yrs. The less likely R value of 2.2 was determined using the year of the onset of release from the Hanford facility, 1944. The inferred range of K_d values calculated using equation (1) are the maximal K_d value of 0.2 cm^3 g^{-1} (Hanford release), and the more probable K_d of ≤ 0.08 cm^3 g^{-1} (atmospheric bomb testing). Since the atmospheric release of ^{129}I from the European nuclear reprocessing facilities of Sellafield and La Hague began in 1966, the K_d due to ^{129}I groundwater residence time from this source would be ≤ 0.08 cm^3 g^{-1}. These K_d values are at the lower range of those published in the literature (Sheppard et al., 1995; Fukui et al., 1996; Fuhrman et al., 1998; Santschi et al., 1999; Kaplan et al., 2000). Low values of K_d are thus a reflection of the near-conservative behavior of iodine isotopes in the Orange County groundwater basin.

The observed differences among the other wells, which produce younger groundwater, cannot easily be explained, and likely point to shorter-term variation in the input signal of ^{129}I. These shorter-term fluctuations of ^{129}I concentrations are likely dampened by dispersion during transport and infiltration. The ^{127}I and chloride (Cl^-) concentrations appear to fluctuate randomly as well, and do not significantly correlate with each other nor with ^{129}I concentrations.

3.4 Macromolecular retention of dissolved organic iodine (DOI)

The recently observed organic nature of ^{129}I in surface waters explains the 50% to 70% decrease in ^{129}I concentrations from the surface waters to the nearest wells. This decrease suggests that macromolecular organic iodine is more strongly sorbed than inorganic iodine forms and is removed upon infiltration into subsurface waters (Santschi and Schwehr, 2004; Santschi et al., 1999). A notable exception to the decrease in ^{129}I concentration from surface to infiltrated waters is from Anaheim Lake to AMD 9-1. Since AMD 9-1 has the shortest groundwater mass age and a 100% tracer value, the ^{129}I concentration in AMD 9-1 can be directly compared with surface water. This suggests that the other groundwater samples are somewhat diluted with 'older' groundwater, with a lower ^{129}I/^{127}I value, discussed in Section 3.1. An alternate explanation is that the higher concentrations may result from infiltration of colloidal organic matter through coarser gravels.

The ^{129}I fraction removed from the recharge to well waters agrees with the ~ 50% surface retention in ^{129}I reported by Santschi et al. (1999) between infiltrating river water and the nearest well in the Glatt River Aquifer observation system, Switzerland. The observed groundwater mobility of ^{129}I and ^{127}I in the Santschi et al. (1999) study was consistent with a K_d value of about 1 cm^3 g^{-1}. The 50 % removal observed in that study, as well as in ours, is also consistent with the observations by Oktay et al. (2001), who reported that about 50% of the ^{129}I in Mississippi River water was associated with macromolecular organic matter. Furthermore, the study of ^{129}I and ^{127}I partitioning in sandy, glaciofluvial soils on the Canadian Shield also found 43 to 73% of the ^{129}I was organically-bound or in residual mineral fractions, with a K_d for iodine of 1.6 cm^3 g^{-1} (Quiroz et al, 2002). Also, 50 to 90% retention of ^{129}I in the top 15 cm of vertical soil profiles was observed in the West Valley, New York (Rao and Fehn, 1999), in Martin, Texas (Santschi and Schwehr, 2004), and in Japan (Muramatsu et al., 2004). However, in samples from the present study, ^{127}I concentrations did not appear to have noticeably decreased from the source water to the nearest wells, suggesting that ^{129}I and ^{127}I are not in the same chemical form or that the isotope ^{129}I is not yet equilibrated in the surface environment.

3.5 Analogy between TOC and DOI

Concentrations of total organic carbon (TOC) demonstrate the same trend as the ^{129}I concentrations. TOC in Anaheim Lake and Kraemer Basin at the time of the sample collection was 4.53 and 3.74 mg L^{-1}, respectively (Table 1). These TOC concentrations are close to the expected value of macromolecular organic matter previously observed in fresh waters in arid climates (e.g., the mean DOC in rivers located in arid regions is 3 mg L^{-1}, (Thurman, 1985)). Values for TOC in the wells at the time of the sample collection averaged 1.46 mg L^{-1} (median of 1.37 mg L^{-1}) which infers retention of 60 to 70% of TOC in surface waters. Also, Davisson et al. (1998) documented 50% TOC removal from a one-month old water mass (1.5 mg L^{-1} TOC at < 91 m depth) as dated by the $\delta^{18}O$ tracer (Colorado River water) that was introduced into Anaheim Lake (with TOC of 3.0 mg L^{-1}). The same study also showed ~50% decrease in TOC from recharge water from the Santa Ana River in Anaheim Lake (8.4 mg L^{-1}, < 1.0 μm) when sampled in a well (4.1 mg L^{-1} from ~64 m depth, < 0.2 μm) after one month. The surface water TOC was larger in size (0.2-1μm fraction) and younger (7 % higher in percent modern ^{14}C) than the well water TOC (< 0.2 μm). This suggests that the TOC in surface waters is higher molecular weight and more labile towards microbial reactions than the lower molecular weight, refractory TOC in groundwaters. By design the artificial recharge to the sandy aquifer system is used as a natural 'filter' to aid in elimination of macromolecular halogen organic colloids, which increase the formation potential of carcinogenic trihalomethanes when the waters are disinfected with chlorine compounds (Leenheer et al., 2001).

3.6 Microbial influence

In contrast to studies that show reducing and anoxic conditions which lead to microbially-enhanced desorption of iodine from rice paddy soils during stormflow (Yoshida et al., 1992; Muramatsu et al., 2004, and studies therein), conditions at this site are different. In the SAR basin, while stormflow waters do show a marked increase in microbe concentrations (Izbicki et al., 2004), these waters have a neutral to slightly basic pH (7 to 7.5 average in groundwaters and ~ 8.5 in surface waters) and are highly oxygenated

(Leenheer, 2002). Aerobic biodegradation and infiltration remove most colloidal organic matter with the first 10 to 30 cm of infiltration (Leenheer, 2002). Further, in experiments with river water conducted by Radlinger and Heumann (2000), ^{129}I-spiked humic substances were transformed from labile low molecular weight (LMW) fractions to refractory high molecular weight (HMW) fractions within hours to days.

Significantly, these combined findings suggest that anthropogenic ^{129}I concentrations and ^{129}I/^{127}I values may be used as a biomarker and tracer of refractory HMW organic matter, or possibly in refractory LMW fulvic acids and terpenoids. Also, since most of the ^{129}I is retained as HMW fractions in the surface, the remaining fraction is likely inorganic and in the form of the iodide as exhibited by the low K_d values.

4. Conclusions

Hypothetically, with a relatively constant annualized atmospheric input of ^{129}I from European nuclear fuel reprocessing facilities, the trends for ^{129}I/^{127}I ratios and ^{129}I concentrations in groundwaters were anticipated to decrease with water mass age as per published K_d values for iodide. However, from measurements of ^{129}I and ^{127}I in wells from the Orange County groundwater basin fed by the Anaheim Lake and Kraemer Basin recharge ponds, literature values of aquifer water mass ages times based on ^{3}H/^{3}He and δ^{18}O data with Xenon tracers, we conclude that iodine and its isotopes behave near-conservatively in this aquifer, with maximal K_d values of the order of 0.1 cm^3 g^{-1}, which are at the low range of observed K_d values for iodide. The observed 50 to 80% decrease in ^{129}I concentrations from surface waters to groundwaters due to the retention of macromolecular organic iodine in surface soils further suggests that the species of iodine in these groundwaters is iodide. Further studies are needed to assess the anthropogenic source of ^{129}I and its species and mobility in watersheds.

The ^{129}I/^{127}I ratios as well as ^{129}I concentrations in well water vary with aquifer water mass age within an order of magnitude, likely as a result of changes in the input function. During stormflow, the recharge waters to the aquifer system are strongly influenced by marine, iodine-enriched, meteoric precipitation as seen in the wet El Nino years of 1997-98. During the extended drought conditions seen in the early 1990's, the high ^{129}I/^{127}I ratios and ^{129}I concentrations reflect baseflow conditions in the Santa Ana River wherein recharge waters are from an admixture of concentrated salts from evapotranspiration effects, reclaimed waste waters, and a low percentage of imported Colorado River water.

This study demonstrates the potential for using iodine isotopes as hydrological tracers for past river flow conditions in this recharge area, which is situated in a semi-arid drainage basin with high water demand and with a recharge area affected by evapotranspiration. However, the following criteria or assumptions need to be addressed in future studies in order to develop ^{129}I further as a tracer for riverine flow and transport processes: 1) establishment of the input function of ^{129}I into the region; 2) relationship between concentration of ^{129}I in the river water of the and flow rate; 3) better characterization of the relative contributions of ^{129}I and ^{129}I/^{127}I from all input waters, including time-series variations in input from the SARPD, spreading ponds, and meteoric precipitation.

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References

Baker, A.R., Thompson, D., Campos, M.L., Parry S.J., & Jickells, T.D., 2000. Iodine concentration and availability in atmospheric aerosol. Atmos. Environ. 34, 4331-4336.

Carlsen, L., Lassen, P., Christiansen, J.V., Warwick, P., Hal, A., & Randall, A., 1992. Radio-labelling of humic and fulvic materials for use in environmental studies. Radiocimica Acta 58/59, 371-376.

Chino Basin Watermaster, 2003. Optimum Basin Management Program: Chino Basin Dry Year Yield Program Model Report, prep.by Wildermuth Environmental, Inc., Lake Forest, Cal. Vol. III, 6-1-6-4. http://www.cbwm.org/docs/engdocs/dryyearyieldreport/DYY.htm

Christiansen, J.V. & Carlsen, L., 1991. Enzymatically controlled iodination reactions in the terrestrial environment. Radiochimica Acta 52/53, 327-333.

Clark, J.F., Hydson, G.B., Davisson, M.L., Woodside, G., & Herndon, R., 2003. Geochemical imaging of flow near an artificial recharge facility, Orange County, CA. Groundwater, Accepted.

Clemens-Knott, D., Foster, J.H., Yoshiba, G., Davisson, M.L., Hudson, G.B., & Beiriger, J., 1998. Hydrogeochemical study of waters on the lower Forebay region of the Santa Ana River---Coastal Groundwater Basin, Orange County, CA., pp. 16.

Cook, E.R., Woodhouse, C.A., Eakin, C.M., Meko, D.M., & Stahle, D.W., 2004. Long term aridity changes in the western United States. Science 306, 1015-1018.

Dai, J.L., Zhang, M., Zhu, Y.G., 2004. Adsorption and desorption of iodine by various Chinese soils I. Iodate. Environment International 30, 525-530.

Davisson, M.L., Hudson, G.B., Herndon, R., Niemeyer, S., & Beiriger, J., 1996. Report on the feasibility of using isotopes to source and age-date groundwater in Orange County Water District's Forebay region, Orange County, California, In Lawrence Livermore National Laboratory UCRL-ID-123953 (pp. 31).

Davisson, M.L., 1998. Final results of Anaheim Lake tracer study, In *Report to OCWD*, Orange County Water District, California, pp. 5.

Davisson, M.L., Hudson, G.B., Moran, J.E., & Niemeyer, S., 1998. Isotope tracer approaches for characterizing artificial recharge and demonstrating regulatory compliance. Annual UC Water Reuse Res. Conf., June 4-5, Monterey, Calif., In Lawrence Livermore National Laboratory UCRL-JC-129656 (pp.9). URL website: http://www.llnl.gov/tid/lof/documents/pdf/233183.pdf.

Davisson, M.L., Hudson, G.B., Herndon, R., & Woodside, G., 1999. Report on isotope tracer investigations in the Forebay of the Orange County Groundwater Basin: Fiscal years

1996 and 1997, In Lawrence Livermore National Laboratory UCRL-ID-133531 (pp. 44). URL website: http://www.llnl.gov/tid/lof/documents/pdf/235457.pdf.

Edmonds, J.S. & Morita, M., 1998. The determination of iodine species in environmental and biological samples (Technical report). Pure Appl. Chem. 70 (8), 1567-1584.

Eisenbud, M. & Gesell, T., 1997. In Environmental Radioactivity, Boston: Academic Press, p.656.

Fabryka-Martin, J. (2000). Iodine-129 as a groundwater tracer. In Environmental Tracers in Subsurface Hydrology (pp. 504-510), Boston: Kluwer Acad. Publ.

Fehn, U. & Snyder, G., 2000. ^{129}I in the southern hemisphere: global redistribution of an anthropogenic isotope. Nuclear Instruments Methods B 172, 366-371.

Finkel, R.C. & Suter, M., 1993. AMS in the earth sciences: techniques and applications. Adv. Anal. Chem 1, 1-114.

Fukui, M., Fujikawa, Y., & Satta, N., 1996. Factors affecting interaction of radioiodide and iodate species in soil. J. Environ. Radioactivity, 31 (2), 199-216.

Gabay, J.J., Paperiello, C.J., Goodyear, S., Daly, J.C., & Matuszek, J.M., 1974. Method for determining Iodine-129 in milk and water. Health Physics, 26, 89-96.

Gamlin, J.D., Clark, J.F., Woodside, G., & Herndon, R., 2001. Large-scale tracing of groundwater with sulfur hexafluoride, Jour. of Environ. Eng., 127 (2), 171-174.

Herndon, R.L., Brukner, D., & Sharp, G., 1997. Groundwater systems in the Orange County Groundwater Basin, In TIN/TDS (Total inorganic nitrogen/ total dissolved solids) Task Force 2.2 Report, Orange County Water District (pp. 11).

Huang, S., Arimoto, R., & Rahn, K.A., 2001. Sources and source variations for aerosol at Mace Head, Ireland. Atmos. Environ. 35 (8), 1421-1437.

Izbicki J.A., Pimentel, M.I., Leddy, M., & Bergamaschi, B., 2004. Microbial and dissolved organic carbon characterization of stormflow in the Santa Ana River at Imperial Highway, Southern California, 1999-2002. U.S. Geological Survey Scientific Investigations Report 2004-5116., 71p.

Kaplan, D.I., Serne, R.J., Parker, K.E., & Kutnyakov, I.V., 2000. Iodide sorption to subsurface sediments and illitic minerals. Environ. Sci. Technol., 34, 399-405.

Kocher, D.C., 1982. On the long-term behaviour of iodine-129 in the terrestrial environment. In Environmental Migration of Long-lived Radionuclides (pp. 669-679), Vienna: IAEA.

Landsberger, S., Drake, J.J., & Vermette, S.J., 1988. Enriched concentrations of bromine, chlorine, and iodine in urban rainfall as determined by instrumental neutron activation analysis. Chemosphere. 17 (2), 299-307.

Langmuir, D., 1997. The redox behavior of natural systems, In D. Langmuir, Aqueous Environmental Geochemistry (pp. 403-430), New Jersey: Prentice Hall.

Leenheer, J.A., Rostad, C.E., Barber, L.B., Schroeder, R.A., Anders, R., & Davisson, M.L., 2001. Nature and chlorine reactivity of organic constituents from reclaimed water in groundwater, Los Angeles County, California. Environ. Sci. Technol. 35, 3869-3876.

Leenheer, J.A., 2002. Processes controlling attenuation of dissolved organic matter in the subsurface, In G. R. Aiken and E.L. Kuniansky, U.S. Geological Survey Artificial Recharge Workshop Proc., Sacramento, Calif., USGS Open-File Report 02-89.

McBride, M.B., 2000. Chemisorption and precipitation reactions, In M.E. Sumner, Handbook of Soil Science, (pp. B-265-302). Boca Raton: CRC Press.

Moran,J.E., Oktay, S., Santschi, P.H., & Schink, D.R., 1997. Surface ^{129}Iodine/^{127}Iodine ratios: Marine vs. terrestrial, Applications of Accelerators, In J.L. Duggan & I.L. Morgan, Research and Industry, (pp. 807-810). New York: AIP Press.

Moran, J.E., Oktay, S.D., Santschi, P.H., & Schink, D.R., 1999a. Atmospheric dispersal of ^{129}Iodine from European nuclear fuel reprocessing facilities. Environ. Sci. Technol. 33 (15), 2536-2542.

Moran, J.E., Oktay, S., Santschi, P.H., Schink, D.R., Fehn, U., & Snyder, G., 1999b. World-wide redistribution of ^{129}Iodine from nuclear fuel reprocessing facilities: Results from meteoric, river, and seawater tracer studies. IAEA-SM-354/101.

Moran, J.E., Oktay, S.D., and Santschi, P.H., 2002. Sources of Iodine and ^{129}Iodine in Rivers. Wat. Resour. Res., 38(8), 24-1 to 24-10.

Muramatsu, Y., Yoshida, S., Fehn, U., Amachi, S., & Ohmomo, Y., 2004. Studies with natural and anthropogenic iodine isotopes: iodine distribution and cycling in the global environment. J. Environ. Radioactivity 74, 221-232.

Oktay, S.D., Santschi, P.H., Moran, J.E., & Sharma, P., 2001. ^{129}I and ^{127}I transport in the Mississippi River. Environ. Sci. and Technol., 35, 4470-4476.

Oktay, S.D., Santschi, P.H., Moran, J.E., & Sharma, P., 2000. The ^{129}Iodine Bomb Pulse Recorded in Mississippi River Delta Sediments: Results from Isotopes of I, Pu, Cs, Pb, and C, Geochim. Cosmochim. Acta, 64 (6), 989-996.

OCWD, 1999. Orange County Water District, Master Plan Report for 2020, http://OCWD 2020 rpt\OCWD Online - Year 2020 Master Plan Study.htm .

OCWD, 2004. Orange County Water District, Groundwater recharge operations, http://www.ocwd.com/_html/recharge.htm.

Planert, M. & Williams, J.S., 1995. Los Angeles-Orange County coastal plain aquifer system, In HA 730-B: California, Nevada; USGS Groundwater Atlas of the United States, http://capp.water.usgs.gov/gwa/ch_b/B-text4.html.

Quiroz, N.G.A., Kotzer, T.G., Milton, G.W., Clark, I.D., & Bottomley, D., 2002. Partitioning of ^{127}I and ^{129}I in an unconfined glaciofluvial aquifer on the Canadian Shield. Radiochim. Acta 90, 1-10.

Radlinger & Heumann, 2000. Transformation of iodide in natural and wastewater systems by fixation on humic substances. Environ. Sci. Technol. 34, 3932-3936.

Rahn K.A., Borys, R.D., & Duce, R.A., 1976. Tropospheric halogen gases –inorganic and organic components. Science 192, 549-550.

Raisbeck, G.M., Yiou, F., Zhou, Z.Q., & Kilius, L.R., 1995. ^{129}I from nuclear fuel reprocessing facilities at Sellafield (U.K.) and La Hague (France); potential as an oceanographic tracer. J. Marine Systems 6, 561-570.

Raisbeck, G.M. & Yiou, F., 1999. I-129 in the oceans: origins & application. Sci. Total Environ. 237/238, 31-41.

Rao, U. & Fehn, U., 1999. Sources and reservoirs of anthropogenic iodine-129 in Western New York. Geochim. Cosmochim. Acta 63, 1927-1938.

SAWPA, 2004. Sant Ana Watershed Project Authority, Team Arundo, http://www.sawpa.org/arundo/

Santschi, P.H., Schink,, D.R., Corapcioglu, O., Oktay-Marshall, S., Sharma, P., & Fehn, U., 1996. Evidence for elevated levels of Iodine-129 in the deep Western Boundary Current in the Middle Atlantic Bight, Deep-Sea Res., 43, 259-265.

Santschi, P.H., Moran, J.E., Oktay, S., Hoehn, E., & Sharma, P., 1999. ^{129}Iodine: A new tracer for surface water/groundwater interaction. IAEA-SM-361/10.

Santschi, P.H., and Schwehr, K.A. 2004. ^{129}I/^{127}I as a new environmental tracer or geochronometer for biogeochemical or hydrodynamic processes in the Hydrosphere and Geosphere: The central role of organo-iodine. Sci. Tot. Environ., 321, 257-271.

Schink, D.R., Santschi, P.H., Corapcioglu, O., Oktay, S., & Fehn, U., 1995a. Prospects for "iodine-129" dating of marine organic matter using AMS, Nucl. Instr. and Methods in Phys. Res. B, 99, 524-527.

Schink, D.R., Santschi, P.H., Corapcioglu, O., Sharma, P., & Fehn, U., 1995b. ^{129}I in Gulf of Mexico waters, Earth. Plant. Sci. Lett., 135, 131-138.

Schmidt, A., Schnabel, C., Handl, J., Jakob, D., Michel, R., Synal, H. A. Synal, Lopez, J.M., & Suter, M., 1998. On the analysis of iodine-129 and iodine-127 in environmental materials by accelerator mass spectrometry and ion chromatography. Sci. Total Environ. 223, 131-156.

Schnabel, C., Lopez-Gutierrez, J.M., Szidat, S., Sprenger, M., Wernli, J., Beer, J., & Synal, H.A., 2001. On the origin of I-129 in rain water near Zurich, Radiochim. Acta 89, 815-822.

Schwehr, K.A. & Santschi, P.H., 2003. A sensitive determination of iodine species, including organic iodine, for fresh water and seawater samples using high performance liquid chromatography and spectrophotometric determination. Analytica Chim. Acta 482, 59-71.

Sheppard, M.I., Thibault, D.H., McMurry, J., & Smith, P.A., 1995. Factors affecting the soil sorption of iodine. Water Air and Soil Pollution, 83, 51-67.

Snyder, G., and Fehn, U. 2004. Global distribution of ^{129}I in rivers and lakes: implications for iodine cycling in surface reservoirs. Nucl. Instr. Methods Phys. Res. B, 223-224, 579-586.

Sturges, W.T. & Barrie, L.A., 1988. Chlorine, bromine and iodine in Arctic aerosols. Atmos. Environ. 22 (6), 1179-1194.

Summers, R.S., Fuchs, F., & Sontheimer, H., 1989. The fate and removal of radioactive iodine in the aquatic environment. Am. Chemical Society, Symposium Series 219, 623-636.

Szidat, S., Schmidt, A., Handl, J. Jakob, D., Botsch, W., Michel, R., Synal, H.-A., Schnabel, C., Suter, M., Lopez-Gutierrez, J.M., & Stade, W., 2000. Iodine-129: sample preparation, quality control and analyses of pre-nuclear materials and of natural waters from Lower Saxony, Germany, Nuclear Instruments Methods B 172, 699-710.

Thurman, E.M., 1985. Organic carbon in natural waters: amount, origin, and classification (p. 1-65), In Organic Geochemistry of Natural Waters, Boston: Kluwer Academic.

Von Gunten, H.R., and Benes, P. 1995. Speciation of Radionuclides in the Environment. Radiochim. Acta, 69 1-29.

Warner, J.A., Casey, W.H., & Dahlgren, R.A., 2000. Interaction kinetics of I_2 (aq) with substituted phenols and humic substances. Environ. Sci. Technol. 34, 3180-3185.

Warwick, P., Zhao, R., Higgo, J.J.W., Smith, B., & Williams, G.M., 1993. The mobility and stability of iodine-humic and iodine-fulvic complexes through sand. Sci. Total Environ. 130/131, 459-465.

Yiou, F., Raisbeck, G.M., Shou, Z.Q., & Kilius, L.R., 1994. ^{129}I from nuclear fuel reprocessing; potential as an oceanographic tracer. Nucl. Instrum. Methods B 92, 436-439.

Yoshida, S., Y. Muramatsu, and S. Uchida. 1992. Studies on the sorption of I^- (iodide) and IO_3^- (iodate) onto andosols. Water Air Soil Pollut. 63:321– 329.

List of Figures

Fig. 1. Map showing (a) the general location of the study area, the Santa Ana River Basin; (b) the Santa Ana River Basin indicating the unconfined Forebay recharge area, the Santa Ana River, Prado Dam, Anaheim Lake and Kraemer Basin, and the location of the cross section shown in Fig. 2; and (c) a detailed map showing the cross section location.

Fig. 2. Cross-section showing the study wells and the artificial recharge ponds. Contours represent groundwater age as determined from ^{3}H/^{3}He for waters (>1 yr) and δ^{18}O with Xe tracer tests. All groundwaters are < 10 yrs old and are recharged from the recharge ponds with the exception of AMD 9-3 and AMD 9-4 which are in a separate aquifer system.

Fig. 3. (a)The ^{129}I/^{127}I (10^{-11}) values and (b) ^{129}I (10^{7} L^{-1}) concentrations for groundwaters, as a function of groundwater mass age. The surface waters of the recharge ponds, Anaheim Lake and Kraemer Basin, are shown as contrasting symbols with ‘0’ age. The surface waters and AMD 9-4 (25 yr water mass age) are not included in the trend.

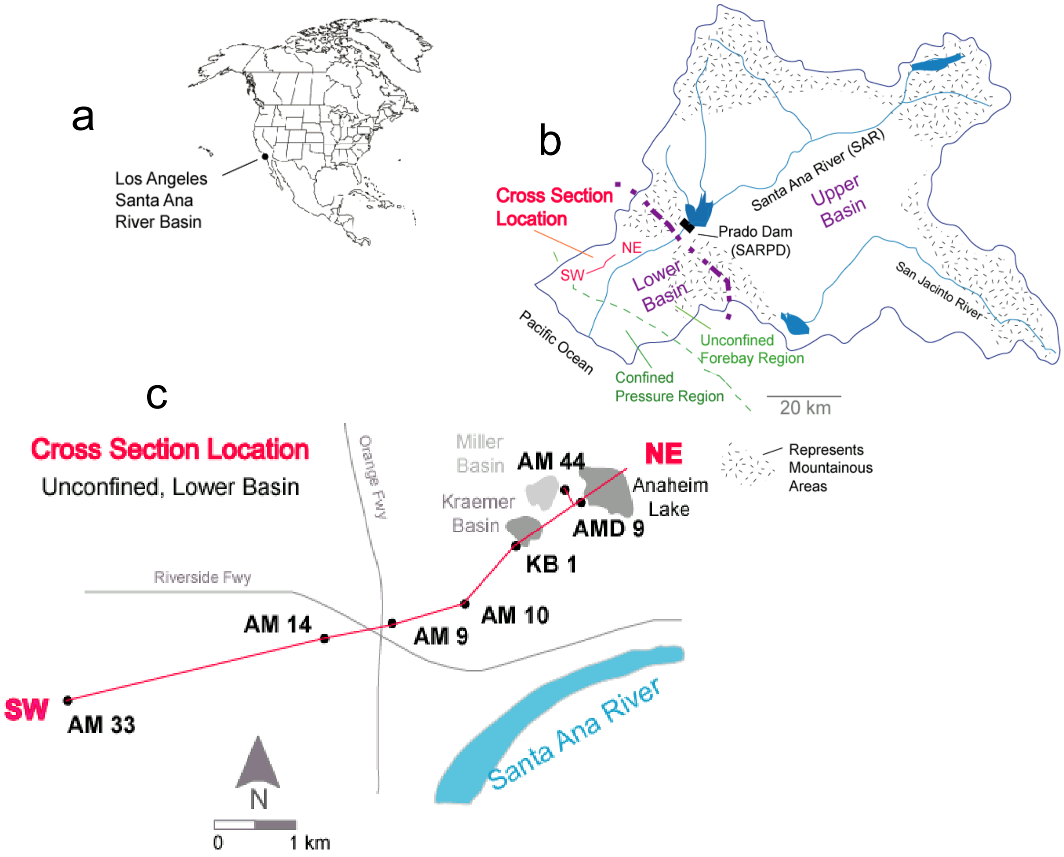
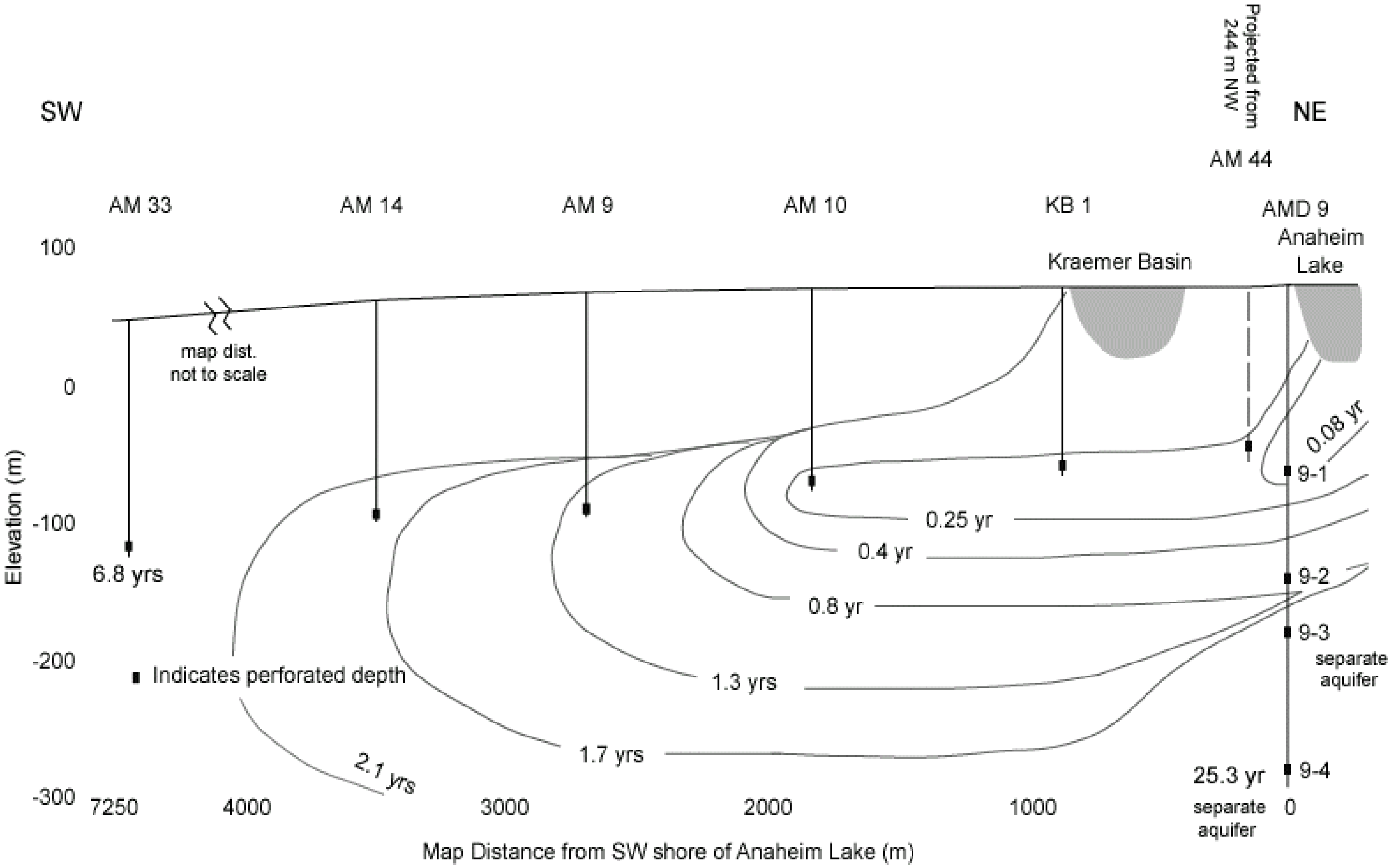
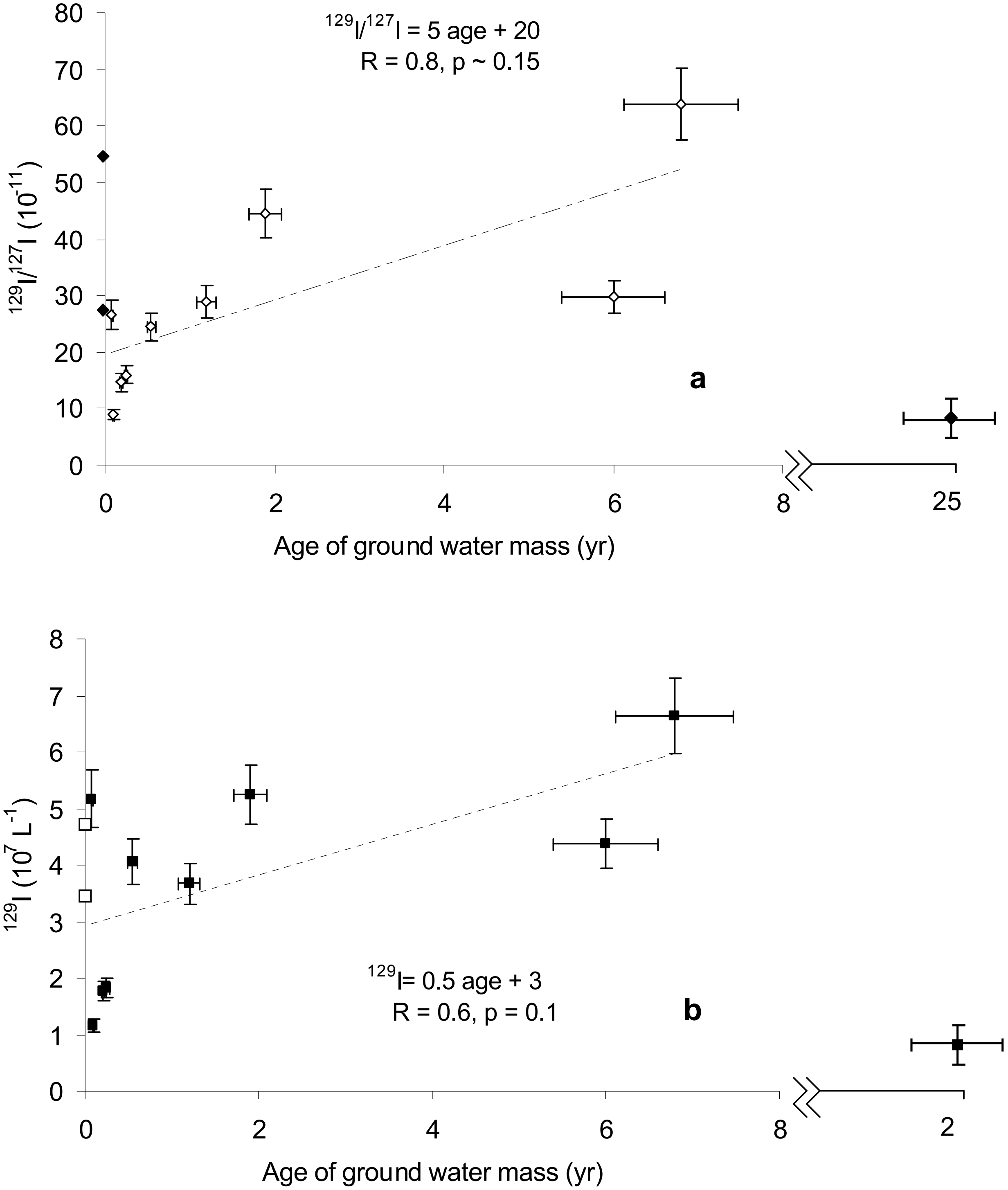

a
Los Angeles
Santa Ana
River Basin
b
Cross Section
Location
NE
SW
Santa Ana River (SAR)
Upper
Basin
Prado Dam
(SARPD)
Lower
Basin
San Jacinto River
Pacific Ocean
Unconfined
Forebay Region
Confined
Pressure Region
20 km
Represents
Mountainous
Areas
c
Cross Section Location
Unconfined, Lower Basin
Orange Fwy
Miller
Basin
AM 44
NE
Anaheim
Lake
Kraemer
Basin
AMD 9
KB 1
Riverside Fwy
AM 10
AM 14
AM 9
SW
AM 33
Santa Ana River
N
0
1 km

Fig. 1



SW
NE
Projected from 244 m NW
AM 44
AM 33
AM 14
AM 9
AM 10
KB 1
AMD 9
Anaheim Lake
Kraemer Basin
100
0
-100
-200
-300
Elevation (m)
map dist. not to scale
6.8 yrs
0.08 yr
9-1
0.25 yr
0.4 yr
9-2
0.8 yr
9-3
separate aquifer
1.3 yrs
▮ Indicates perforated depth
1.7 yrs
2.1 yrs
25.3 yr
9-4
separate aquifer
7250
4000
3000
2000
1000
0
Map Distance from SW shore of Anaheim Lake (m)

Fig.2



$^{129}I/^{127}I = 5$ age + 20
R = 0.8, p ~ 0.15
$^{129}I/^{127}I\ (10^{-11})$
80
70
60
50
40
30
20
10
0
a
0
2
4
6
8
25
Age of ground water mass (yr)
$^{129}I\ (10^{7}\ L^{-1})$
8
7
6
5
4
3
2
1
0
$^{129}I = 0.5$ age + 3
R = 0.6, p = 0.1
b
0
2
4
6
8
2
Age of ground water mass (yr)

Fig. 3

Table 1. Iodine and water age data for the Orange County study wells.

	AM 33	AM 14	AM 9	AM 10	KB 1	Kraemer Basin	AM 44	Anaheim Lake	AMD 9-1	AMD 9-2	AMD 9-3	AMD 9-4
^{129}I/^{127}I (10^{-11}) [a]	63.8	44.5	29.0	14.6	9.0	55.2	16.0	28.5	26.6	24.5	29.7	7.1
^{129}I (10^{7} L^{-1}) [b]	6.6	5.3	3.7	1.8	1.2	4.8	1.8	3.5	5.2	4.1	4.4	0.9
^{127}I (ppb) [c]	22.0 [d, e]	25.0 [d]	26.8 [d]	25.7 [d]	27.2 [d]	18.3 [d]	24.2 [e]	26 [e]	41.1 [e]	35.1 [e]	31.2 [e]	27.3 [e]
Groundwater mass age (yr)	6.8 [f, h]	1.9 [g, h]	1.2 [g, h]	0.2 [g, h]	0.1 [g, h]		0.25 [h]		0.08 [h]	0.55 [h]	6 [f]	25.3 [g, h]
Sample collection date	Aug 99	Aug 99	Aug 99	Sep 99	Aug 99	Aug 99	Aug 99	Sep 99	Sep 99	Sep 99	Sep 99	Sep 99
TOC (mg L^{-1}) [i]	0.89	1.13	0.9 [k]	0.89	1.88	3.74	1.19	4.53	2.44	1.76	1.52	1.37
Cl (mg L^{-1}) [i]	86.9	73.8	78.8	89	91.6	87.9	103	89.2	105	98.9	86.9	121

[a] Maximum uncertainty for ^{129}I/^{127}I (10^{-11}) ratios is 9.4%; [b] Maximum uncertainty for ^{129}I (10^{7} L^{-1}) is 9.9%; [c] Maximum uncertainty for ^{127}I (ppb) is 3%; [d] Independently analyzed by ICP-MS and by HPLC; [e] analyzed by HPLC (Schwehr & Santschi, 2003); [f] based on ^{3}H/^{3}He data (Clemens-Knott et al., 1998, Clark et al., 2003), uncertainty ± 1 yr (Davisson et al., 1998); [g] based on ^{3}H/^{3}He data (Davisson et al., 1999; Clark et al., 2003), uncertainty ± 1 yr (Davisson et al., 1998); [h] based on data from δ^{18}O and ^{124}Xe tracer studies (Davisson,1998; Davisson et al., 1999; Clark et al., 2003), uncertainty for δ^{18}O and ^{124}Xe tracers is ± 1% dilution (Davisson et al., 1998); [i] aqueous geochemical data from G. Woodside; [lk] interpolated from monthly measurements preceding and proceeding sample collection.