

The dissolved organic iodine species of the isotopic ratio of $^{129}\text{I}/^{127}\text{I}$: A novel tool for tracing terrestrial organic carbon in the estuarine surface waters of Galveston Bay, Texas

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Abstract

Variations in $^{129}\text{I}/^{127}\text{I}$ ratios were used to trace terrestrial organic carbon (tDOC) across an estuary because (1) iodine is biophilic, up to 75% of total iodine in fresh and coastal marine waters partitions into organic iodine; (2) $^{129}\text{I}/^{127}\text{I}$ ratios in tDOC are greatly elevated over those from marine systems because atmospheric emissions of ^{129}I from European nuclear fuel reprocessing facilities were mixed more quickly in the surface ocean, up to 500 m in a decade, than the terrestrial system, which mixed approximately 10 cm in 10 to 50 y; and (3) the oceanic contribution of ^{127}I (50 to 65 ppb) to the ratio has a greater dilution effect than ^{127}I from freshwater (0.5 to 40 ppb). Analytical techniques were developed for $^{129}\text{I}/^{127}\text{I}$ ratio determination in dissolved organic iodine (DOI) and the other iodine species, using dehydrohalogenation, anion chromatography, high-performance liquid chromatography, and accelerator mass spectrometry, to be applied to samples from Galveston Bay, Texas. Results indicate that $^{129}\text{I}/^{127}\text{I}$ ratios in DOI from terrestrial sources are elevated in the upper estuary up to salinity of about 20, similar to a behavior previously described for this estuary for stable isotopic signals for dissolved organic matter. $^{129}\text{I}/^{127}\text{I}$ ratios in the other iodine species, e.g., iodide and iodate, did not show this feature, indicating fast isotopic and chemical equilibration between the two isotopes among the different inorganic species in the estuary. These results thus provide proof of concept that $^{129}\text{I}/^{127}\text{I}$ -DOI can serve as a tracer for tDOC in the coastal zone.

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 natural ^{129}I is 100 kg (Yiou et al. 1995; Raisbeck et al. 1999). Because the half-life of ^{129}I is much longer than its residence time (τ) in surface environmental compartments, this isotope was well-mixed in the surface soil compartment ($\tau \approx 1000$ y) (Kocher 1981), the surface ocean ($\tau \approx 100$ y for the mixed layer, depth 0 to ~100 m) (Raisbeck et al. 1995), and the atmosphere ($\tau \approx 11$ -18 d) (Rahn et al. 1976) before the

nuclear age. Anthropogenic sources of ^{129}I include an added 150 kg (Eisenbud and Gesell 1997) through atmospheric bomb testing during 1945 through 1962, and 2360 kg from the discharged waste of nuclear fuel reprocessing at Cap de La Hague, France, and Sellafield, England, during 1966 through 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 (Michel et al. 2002). 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 $^{129}\text{I}/^{127}\text{I}$ (Raisbeck et al. 1995; Schink et al. 1995; Santschi et al. 1996, 1999; Moran et al. 1997, 1999a, 1999b; Santschi and Schwehr 2004).

Anthropogenic ^{129}I is distributed globally (Fehn and Snyder 2000; Snyder and Fehn unpubl. data unref.), leading to the use of ^{129}I concentrations to trace the movement of oceanic water masses in the Atlantic Bight (Santschi et al. 1996), the Gulf of Mexico (Schink et al. 1995), and the Arctic ocean (Raisbeck et al. 1995; Carmack et al. 1997; Smith et al. 1998; Edmonds et al. 1998; Raisbeck and Yiou 1999; Cooper et al. 2001; Yiou et al. 2002). Artificial ^{129}I originates primarily from gaseous waste products released by nuclear fuel reprocessing plants in

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Europe and is transported to North America within approximately 10 to 18 d (Rahn et al. 1976; Moran et al. 1997). Concentrations of ^{129}I and $^{129}\text{I}/^{127}\text{I}$ ratios are used as tracers for surface and groundwater interactions (Santschi et al. 1999; Schwehr et al. 2003).

Concentrations of ^{129}I and $^{129}\text{I}/^{127}\text{I}$ ratios are greatly enriched in organic matter because iodine is biophilic and preferentially partitions into organic matter, wherein organic iodine constitutes about approximately 40% to 75% of the total iodine in fresh and coastal marine waters (Oktay et al. 2001; Alvarado-Quiroz et al. 2002; Schwehr et al. 2003). Also, concentrations of ^{129}I and $^{129}\text{I}/^{127}\text{I}$ values are much higher in terrestrial organic carbon (tDOC) than in marine organic matter because ^{129}I sourced by atmospheric emissions from European nuclear fuel reprocessing facilities are diluted through faster mixing in the surface ocean, approximately 100 m in a decade, than in the terrestrial surface soils, approximately 10 cm in a century. Lastly, ^{127}I concentrations in the ocean (50 to 65 ppb) serve to dilute the $^{129}\text{I}/^{127}\text{I}$ ratio values more effectively than freshwater concentrations (~1 to 40 ppb). For example, in North America, the mean value for $^{129}\text{I}/^{127}\text{I}$ in rain water is 3.8×10^{-9} compared to $^{129}\text{I}/^{127}\text{I}$ values for rivers, which range from 0.1 to 3×10^{-9} (Moran et al. 1997, 1999b, 2002), whereas the $^{129}\text{I}/^{127}\text{I}$ value in the sea surface waters of the Gulf of Mexico is about 65×10^{-12} (Schink et al. 1995).

Riverine transport of tDOC at a rate of approximately 0.25 Pg C y^{-1} is the largest global supply of active carbon to the coastal oceans (Cauwet 2002). According to the United Nations Atlas of the Oceans (2005), in 2001, more than half of the world's population, about 3 billion people, lived within 200 km of the coast. Of the world's 10 largest cities, 8 are located on the coast and in China alone. There are more than 400 million coastal residents with a projected urban increase of more than 125% in the next 25 y. Currently, coastal areas are experiencing the highest growth rate in population, which will result in increased domestic and industrial effluents, more areas of landfill, increased dredging, and erosion from infrastructure construction and coastal development. Anthropogenic pressures on the coastal ecosystem will further increase tDOC export to these waters. The fate and pathways concerning tDOC are poorly understood in terms of the time and space scales of coastal and estuarine removal processes, such as boundary exchange and scavenging (Hansell et al. 2004; Santschi et al. 1999). It is becoming increasingly important to quantify the fluxes and fate of tDOC to elucidate coastal zone impact on global biogeochemistry for climate influences and the cycling of reactive elements and pollutants. Because of its biophilic nature, which is expressed by its tendency toward covalent binding to aromatic moieties in proteins and humic substances, iodine and its isotopes have the potential of tracing and/or dating tDOC, which has an elevated $^{129}\text{I}/^{127}\text{I}$ ratio (Santschi and Schwehr 2004, and references therein).

There are other methods for tracing tDOC. However, this work provides the foundation for dating tDOC as well. Cur-

rently, organic matter in the water column is dated using ^{14}C , ^3H , or ^{234}Th . Each one of these methods provides useful information, yet also has inherent weaknesses. The ^{14}C method requires expensive instruments, i.e., accelerator mass spectrometer (AMS). Additionally, ^{14}C has a very long half-life, approximately 5730 years, and so is an ambiguous geochronometer for short-term processes. Organically bound ^3H can be used as a geochronometer as well, but the method is meticulous, time-consuming, and readily subject to cross-contamination. Most importantly, measured levels of ^3H are close to the detection limit for the method (Pointurier et al. 2003). Studies regarding the use of ^{234}Th , another organic matter tracer for carbon export of particles and colloids, show that this isotope is preferentially bound to acid polysaccharides of about 10 to 15 kDa (Quigley et al. 2002). Therefore, a need exists to find a tracer and/or geochronometer for organic matter in the water column that measures short-term processes. Based on its concentration, anthropogenic ^{129}I from bomb test and reprocessing release fallout has overwhelmed the natural inventory of this isotope for ≤ 50 years, and so has great potential for addressing this need. Different from ^{14}C , which only increased by up to 60% after bomb fallout, ^{129}I in the surface environment increased by 2 orders of magnitude, and thus, provides valuable complementary information for assessing effects of mixing of tDOC from different sources with different ages. This is the first published method to isolate and quantify the species ^{129}I -DOI (dissolved organic radioiodine).

The objective of this study is to test the potential use of $^{129}\text{I}/^{127}\text{I}$ in DOI to trace tDOC in the Galveston Bay estuary. To this end, the goals of this study are to (1) develop the appropriate methods to measure DOI in $^{129}\text{I}/^{127}\text{I}$; (2) to test how far the elevated values of $^{129}\text{I}/^{127}\text{I}$ in DOI can be followed through a transect of salinity in the Galveston Bay estuary; and (3) to compare the results with published data on stable isotopes in dissolved organic matter, i.e., $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, as well as C/N ratios.

Materials and Methods

Study area—Galveston Bay is a subtropical estuarine environment where the mean annual precipitation is 132 cm and the mean annual temperature is 21°C (data for Houston, Texas, from NCDC/NOAA 2003). The Galveston Bay is shallow, with a mean depth of 2 m and diurnal tidal changes of less than 40 cm. Consequently, estuarine circulation is primarily wind-driven (Ward 1992, as cited in Santschi 1995; Tang et al. 2002). It is the second largest watershed emptying into the Gulf of Mexico, draining a basin of 46,100 km^2 into an estuarine area of 1432 km^2 , which is adjoined by a wetland area of 526 km^2 (Ward 1992, as cited in Santschi 1995; Pinkney et al. 2002).

Freshwater input to the bay is mainly from the Trinity (83%) and San Jacinto (8%) rivers, which transport moderate to high loads of terrestrial organic carbon (4–7 mg C L^{-1}) (Warnken and Santschi 2004) and suspended particulate matter (4–200 mg L^{-1}) (Guo and Santschi 1997).

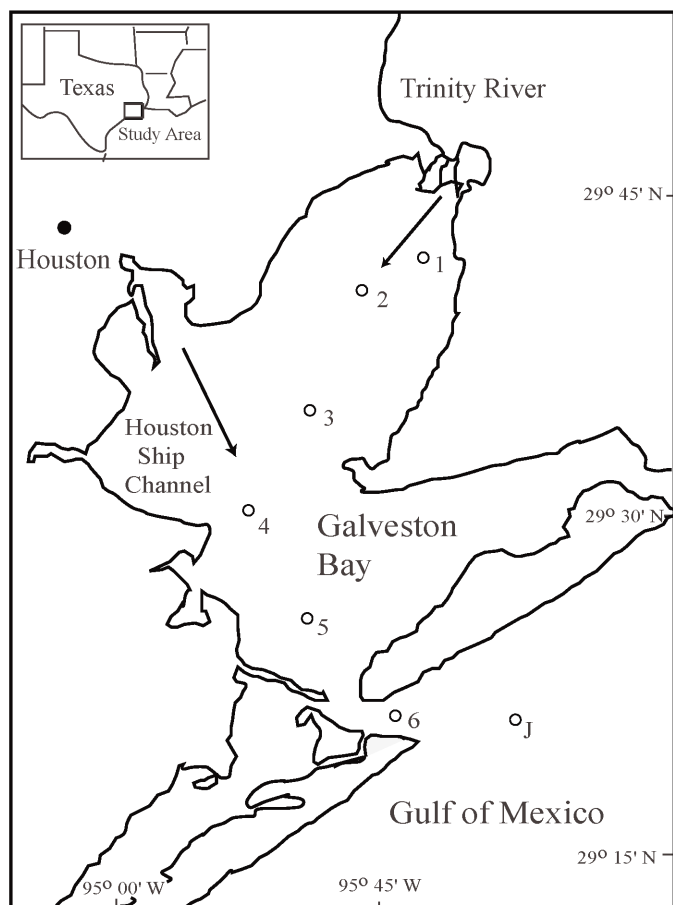


Fig. 1. Sampled locations in Galveston Bay Estuary.

Fig. 1 is a map of Galveston Bay indicating station locations, with the transect beginning at Station 1, nearest the mouth of the Trinity River, and ending with Station J beyond the jetty of Galveston Bay. Samples were collected 14 December 2001.

Sample collection and storage—Containers and tubing were cleaned, and samples prepared as described in Schwehr and

Santschi (2003). Briefly, while wearing polyethylene gloves, acid-cleaned containers were triple-rinsed with 18 M Ω water (deionized water [DIW]), then conditioned with a triple-rinse of sample that was down-current from the collection site. The 10-L sample container was overfilled with surface water, tapped to release any gas bubbles, then overfilled again, and sealed. The sealed containers were immediately stored in a dark, insulated cooler filled with ice. Within approximately 5 h, all samples were collected and transported to the laboratory where they were filtered through a 0.45- μm inline capsule filter assembly.

Table 1 displays the iodine species measured in this study. Each species was determined for both isotopes, ^{127}I and ^{129}I . The methods used for measurement and calculations are indicated in the following sections.

Measurement of [^{127}I] concentration—Immediately after collecting and filtering the sample, the concentrations of stable iodide [$^{127}\text{I-I}^-$], natural total inorganic iodine [$^{127}\text{I-TII}$], and natural iodate [$^{127}\text{I-IO}_3^-$] were determined using the high-performance liquid chromatography (HPLC) method detailed in Schwehr and Santschi (2003) with independent measurements by cathodic stripping square wave voltammetry (CSSWV) using the method of Wong and Zhang (1992).

Briefly, the scheme for measurement of the ^{127}I species concentrations is given here and shown in Fig. 2. Iodide (I^-) was measured directly using HPLC (on Stations 1, 3, 4, and J) and CSSWV (all Stations). Iodate (IO_3^-) concentrations were measured directly using CSSWV and were independently determined using HPLC after acidification and reduction to measure IO_3^- as the difference between total inorganic iodine (TII) and I^- . Organic iodine (DOI) was determined as the difference between total iodine (TI) and TII. The TI was measured by HPLC after the process of dehydrohalogenation (described below), then reduction and acidification, followed by solid phase extraction to remove refractory organics. For TI, three controls were run with the sample set. Controls were a thyroxine standard and a sample each of Galveston Bay and Trinity waters for which TI was previously determined independently

Table 1. Iodine species measured or calculated in this study

Species or Isotope	Symbol	Definition
Total iodine	TI	Sum of all organic and inorganic species; Obtained after reduction and decomposition of all species, $\text{TI} = \text{I}^- + \text{IO}_3^- + \text{DOI}$
Total inorganic iodine	TII	Sum of all inorganic species, $\text{TII} = \text{I}^- + \text{IO}_3^-$ or $\text{TI} - \text{DOI}$
Iodide	I^-	Inorganic species, ^{127}I measured directly by HPLC with independent measurements by voltammetry; Species that is retained on chromatographic resin
Iodate	IO_3^-	Inorganic species, ^{127}I measured by HPLC after reduction to iodide or measured directly using voltammetry; Species that is not retained on chromatographic resin
Dissolved organic iodine	DOI	Sum of all organic species; Obtained by difference $\text{DOI} = \text{TI} - \text{TII}$, Species that is not retained on chromatographic resin
Stable isotope of iodine	^{127}I	Naturally occurring isotope, nearly 100% abundance
Radioisotope of iodine	^{129}I	Anthropogenic concentration is several orders of magnitude greater than natural concentration; Measured using AMS

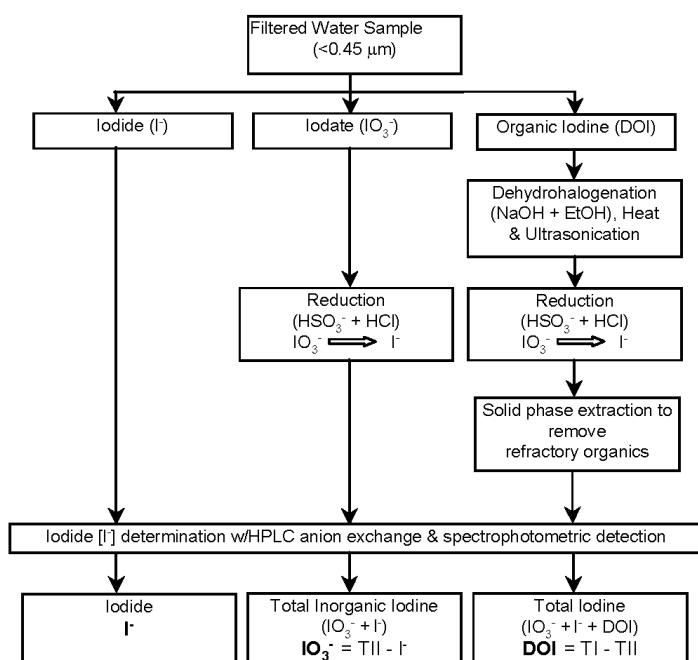


Fig. 2. Process flow chart for the determination of iodine species for the both isotopes ^{127}I and ^{129}I (Schwehr and Santschi 2003).

by inductively coupled plasma-mass spectrometry (ICP-MS).

Each measurement was made using the method of standard additions (Schwehr and Santschi 2003; Wong and Zhang 1992). An I⁻ solution of known concentration was prepared as the working standard for the additions. The sample was diluted to the optimal dynamic range of the instrument, the concentration was measured twice, then the concentration was again measured after a known volume of the working standard was added to the diluted sample. The standard addition was applied to each sample (at least eight measurements per iodine species), with an additional set of measurements by standard additions on the station samples duplicated by HPLC (at least 12 measurements per iodine species).

Measurement of ^{129}I concentration—Simultaneously, as samples were being processed for ^{127}I measurements soon after collection, ^{129}I and $^{129}\text{IO}_3^-$ were separated by anion chromatography. The remaining sample portions for both isotopes for IO_3^- and bulk DOI species were frozen in volumes larger than 250 mL, preferably in 1-L containers for ease of processing and storage. Fractions to be analyzed for TI (both isotopes) were stored refrigerated or in a cool, dark room in containers sealed with parafilm, after the addition of a reducing solution (RS). The RS consisted of 2 mL of 1 mol L⁻¹ HSO₃ + 4 mL 1 mol L⁻¹ NH₂OH·HCl, adjusted to pH 6.5, per 1 L sample, to prevent loss of volatile iodine species (Szidat et al. 2000).

The procedure used for measuring the concentration of ^{129}I species was similar to that of ^{127}I (Fig. 2), except that it was

scaled up to allow processing of larger volume water samples (2 to 5 L). The low concentrations of ^{129}I in environmental samples ($\sim 10^7$ atoms L⁻¹) require that measurements be made by an AMS on 1 to 2 mg of AgI derived from the iodine concentration in large volume water samples.

Anion chromatography was used to separate and concentrate $^{129}\text{I-I}^-$ and $^{129}\text{I-IO}_3^-$ according to a modified method of Hou et al. (2001) (Fig. 3). Both isotopes of I⁻ were obtained by passing the filtered sample through a column of strong anion exchange resin, AG1-X4 or AG1-X8 (100-200 mesh). The resin had been pretreated with 2 mol L⁻¹ NaNO₃ solution, then rinsed with DIW until the effluent did not form a white solution after the addition of AgCl (indicating that the resin was in the NO₃⁻ form). The treated resin was slurried into a column using 50 g resin per 1 L seawater with a salinity of 35, or 22 g per 1 L seawater with a salinity of 15. The I⁻ process is shown in Fig. 3 as steps 1 through 6. In step 1, the sample was loaded onto the column at a flow rate of 2 mL min⁻¹. When processed in this fashion, I⁻ was retained on the resin and IO₃⁻ and most DOI fractions passed into the effluent and are saved for step 7. The ^{127}I concentration in the eluant was monitored as a yield tracer for breakthrough and recovery calculations. Alternatively, ^{125}I was added to the sample prior to loading the column to aid in the recovery determination.

In step 2, the resin column was rinsed with 50 mL 18 MΩ DIW, which was added to the IO₃⁻ fraction and RS, then set aside. For step 3, the resin column was then rinsed with 50 mL 0.1 mol L⁻¹ NaNO₃ solution to elute Cl⁻ and Br⁻ retained on the resin (Hou et al. 1999, 2001), and then with 50 mL 1 mol L⁻¹ NaNO₃ solution to elute potentially retained DOI (Reifenhauser and Heumann 1990; Wimschneider and Heumann 1995). These effluents were discarded. Proceeding with step 4, the I⁻ fraction was eluted after soaking the resin column (fitted with a covered reservoir) overnight in a 200-mL 2% NaClO solution. The column was then drained and rinsed with two subsequent 50 mL volumes of DIW. In step 5, all three elutions were combined and reduced with 40 mL of 1 mol L⁻¹ HSO₃ + 0.18 mol L⁻¹ H₂SO₄ that was then stored in a dark, refrigerated container, sealed with parafilm, for the subsequent step 6, liquid-liquid extraction.

To obtain IO₃⁻, RS was added to the sample effluent, and the first DIW rinse to reduce IO₃⁻ species to I⁻ and the solution was allowed several hours to react to completion. The resin was rinsed with DIW then loaded with the reduced IO₃⁻ fraction, step 7. The rinsing and elution processes as outlined for the I⁻ fraction, steps 1 through 6, were repeated and the final elution was also saved as the IO₃⁻ fraction for liquid-liquid extraction.

The concentration of $^{129}\text{I-DOI}$ was obtained as the difference of [$^{129}\text{I-TI}$] - ([$^{129}\text{I-I}^-$] + [$^{129}\text{I-IO}_3^-$]). The general procedure is the same as for ^{127}I , shown in the flow diagram (Fig. 2). The $^{129}\text{I-TI}$ fraction was isolated by adding a measured sample volume to 2.5-L glass bottles fitted with Teflon valves for pressure release. Dehydrohalogenation degrades alkyl and aryl halides.

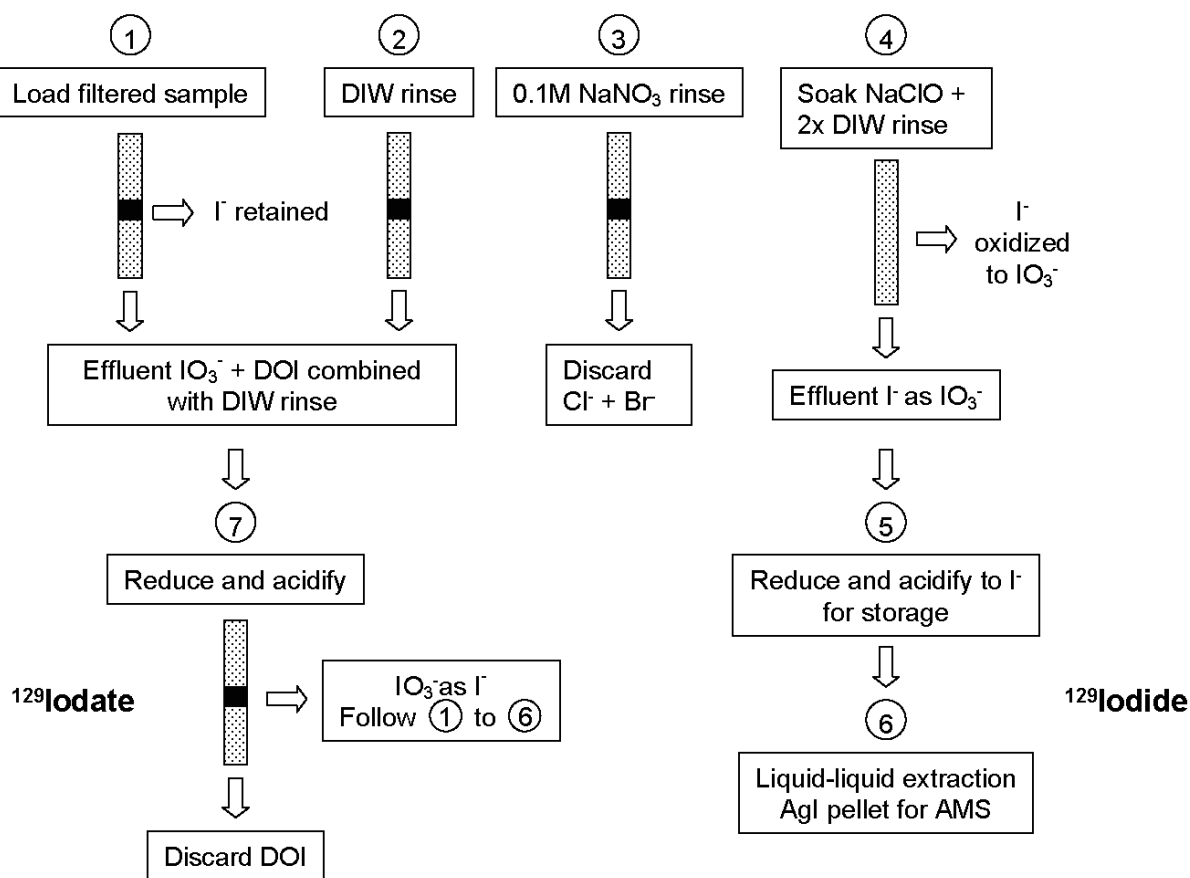


Fig. 3. Flow diagram of anion chromatography process used to separate and concentrate ^{129}I species.

Probably, the majority of DOI, as aryl iodide (such as proteinaceous or complex humic and fulvic acid forms) with some alkyl iodide (Butler 1996), was degraded through acid and alkaline hydrolysis, ultrasonication, heating, and freezing. This combination of physical and chemical processes was designed to uncoil colloidal helices, unfold proteins, break ester bridges, and expose all possible R-I bonds to degradation by dehydrohalogenation.

Dehydrohalogenation was accomplished by adding NaOH (4 g per L sample) and ethanol (200 mL per L sample), ultrasonicated at 65°C for 3 h, then allowing it to react overnight. These steps were repeated, then the sample was reduced with RS and acidified, ultrasonicated at 45°C for 1.5 h, and cooled in a freezer. Next, the sample was gently warmed to room temperature, uncapped, and placed in a boiling water bath for 2 to 3 h to drive off the ethanol. After cooling, the sample was then passed through Empore C_{18} disks (comparable to the solid phase extraction for the small volumes used for ^{127}I [Fig. 2]) under vacuum to remove any remaining refractory substances, and then processed through a resin column as described for I^- , steps 1 through 6, in the preceding discussion. The Empore C_{18} disks were conditioned before use by soaking in methanol overnight

and rinsing with DIW. The same three controls as described for the ^{127}I -TI procedure were run in parallel with all ^{129}I samples.

The I^- , IO_3^- , and TI (for DOI by difference) fractions were then processed by liquid-liquid extraction by adding a ^{129}I -free carrier solution of $^{127}\text{I}^-$, oxidizing, and acidifying the solution with H_2O_2 to transform all iodine species to I_2 , then shaking in a separatory funnel with CHCl_3 so that all I_2 would partition into the organic CHCl_3 phase. This purified I_2 fraction was then back-extracted into a solution of NaHSO_3 and H_2SO_4 , and precipitated into a pellet of AgI. The detailed version of the extractions and precipitation procedures are described elsewhere (Schwehr et al. 2003). The AgI pellet was cleaned, dried, and mixed with a pure Ag powder in preparation for measurement of the $^{129}\text{I}/^{127}\text{I}$ ratio in the iodine species of I^- , IO_3^- , and TI (DOI by difference), by the AMS facility at the Purdue PRIME Lab.

Assessment

Error calculation for ^{127}I —The TI concentrations measured by HPLC showed standard deviations that were $\leq 3\%$ of the TI values measured by ICP-MS. The IO_3^- concentrations were also indirectly calculated for each sample by the subtraction of I^-

Table 2. Concentration of ^{127}I species in the surface waters of the Galveston Bay, 14 December 2001

Station	Salinity*	Temperature, °C*	Sigma-tau*	[TI] nM	[TII] nM	[I ⁻] nM	[IO ₃ ⁻] nM	[DOI] nM	1 STD for DOI ± nM	% DOI	Chl α^* , $\mu\text{M L}^{-1}$	DOC, $\mu\text{M C}$
1	2.2	14.7	0.87	255	157	97	60	98	8	38	5.6	473
2	7.5	14.8	0.50	237	115	65	50	122	8	52	6.5	353
3	10.7	15.0	7.39	305	193	82	111	112	10	37	10.7	281
4	10.4	16.3	6.89	159	147	66	81	12	6	8	4.7	537
5	14.3	15.8	9.97	297	139	78	61	158	9	53	6.8	443
6	14.2	15.3	9.97	234	151	87	64	83	8	36	9.3	365
J	16	n.r.†	n.r.†	228	220	115	105	8	8	3	n.r.†	403

*Pinckney and Lumsden pers. comm. unref.

† n.r., not recorded.

from TII. DOI was determined as the difference between TI and TII. The maximum standard deviation for any ^{127}I species was less than 11 nmol L⁻¹ standard deviation (SD for one sigma) or less than 10% relative standard deviation (RSD) error. This is important when considering DOI values, which were lower in overall concentrations than the other fractions. The % RSD for values of DOI was $\leq 10\%$ for all stations except Station 4, where it was 12 ± 6 nmol L⁻¹ or approximately 50% error, and Station J, where it was 8 ± 9 nmol L⁻¹ or approximately 125% error.

Error calculation for ^{129}I —The column efficiency was $99 \pm 3\%$ for the recovery of $^{129}\text{I-I}^-$ ($n = 6$) and $^{129}\text{I-IO}_3^-$ ($n = 4$), which is similar to the 97% recovery in the procedure used by Hou et al. (2001) that used an eluant of 800 mL KNO₃. The dehydrohalogenation efficiencies for $^{129}\text{I-TI}$ were $\geq 97\% \pm 3\%$ ($n = 4$). The liquid-liquid extraction recovery was $95\% \pm 5\%$ ($n = 5$). The counting error for $^{129}\text{I}/^{127}\text{I}$ by AMS generally averaged $\pm 10\%$ ($n = 18$). Therefore, the final error for $^{129}\text{I-I}^-$ and $^{129}\text{I-IO}_3^-$ after processing through the column, liquid-liquid extraction, and AMS averaged $\pm 12\%$ ($n = 4$). The counting error by AMS for $^{129}\text{I-TI}$ averaged 6% ($n = 4$). Because $^{129}\text{I-DOI}$ was obtained by difference where $^{129}\text{I-DOI} = ^{129}\text{I-TI} - \{^{129}\text{I-I}^- + ^{129}\text{I-IO}_3^-\}$, the associated propagated error for $^{129}\text{I-DOI}$ ranged from 14% to 25%, and averaged 21% ($n = 4$). The highest error was associated with AMS counting of the $^{129}\text{I-I}^-$ fraction. Because this error was associated with the lowest concentration distributions for the measured ^{129}I fractions, the error could have been decreased by concentrating a larger volume of sample. Optimal sample volumes to decrease the error for the ^{129}I species in Galveston Bay would have been 1 to 2 L for $^{129}\text{I-TI}$, 5 L for $^{129}\text{I-IO}_3^-$, and 6 L for $^{129}\text{I-I}^-$. The actual volumes used were 1 to 2 L for $^{129}\text{I-TI}$, and 2 to 4 L for $^{129}\text{I-IO}_3^-$ and $^{129}\text{I-I}^-$.

Discussion

^{127}I speciation in Galveston Bay—The $^{127}\text{I-TI}$ concentrations in estuarine waters of Galveston Bay, presented in Table 2, are similar to literature values for total inorganic iodine concentrations in other coastal waters (Wong and Cheng 1998, 2001; Abdel-Moati 1999; Cook et al. 2000; Schwehr and Santschi 2003). Fig. 4 shows the distribution of the ^{127}I species concentration in the Galveston Bay relative to salinity. All of the

iodine species, as well as DOC (Table 2), display scatter and deviate from conservative behavior in the estuary. Conservative behavior could be expected because the Trinity River, which accounts for an average of 84% of the fresh water input to the Galveston Bay, was experiencing a relatively high river discharge rate, with a mean value of 586 m³ s⁻¹ for December 2001. (The long-term monthly mean value during the years 1924 through 2002 is 233 m³ s⁻¹ for the USGS station located at Romayor, Texas [USGS 2002]). Using the Trinity River discharge of 586 m³ s⁻¹, an estuarine surface area of 1432 km², and a mean depth of 2.1 m (Ward 1992, as cited in Santschi 1995), the water renewal time for the Galveston Bay during this period would have been about 60 d.

Conservative model for estuarine mixing and ^{127}I —Dissolved, filter-passing (0.45 micron) iodine species data across the salinity gradient were compared to a behavior that is controlled by simple mixing between freshwater and seawater, termed “conservative behavior” (Loder and Reichard 1981; Cifuentes and Eldridge 1998; Truesdale and Jones 2000). End-member values were derived from average literature values for the river and ocean end-members. The resulting end-member concentrations for $^{127}\text{I-TI}$ in the Trinity River (TR_M) and in the Gulf of Mexico (GOM_M) were 295 nmol L⁻¹ and 526 nmol L⁻¹, respectively (Schwehr and Santschi 2003). The concentrations of ^{127}I species from Schwehr and Santschi (2003) were selected because species concentrations for 0 salinity, taken a few months earlier using the same measurement method, were comparable to species concentrations at Station 1, salinity 2.2. No other iodine species concentrations are available for this area. These $^{127}\text{I-TI}$ values were obtained using standard additions, calibrated against the iodine concentration in a certified reference material (SRM 1549, powdered milk), and were measured independently by ICP-MS (Schwehr and Santschi 2003).

A comparison of measured transect data to the calculated conservative linear mixing model between TR_M and GOM_M reveals that [TI] values are depleted (net sinks) relative to conservative mixing. The range of variability for TI is very similar to that of nutrients (*see below*), implying that the same processes affect both quantities. It is therefore suggested that the scatter in iodine species is related to the patchiness in the

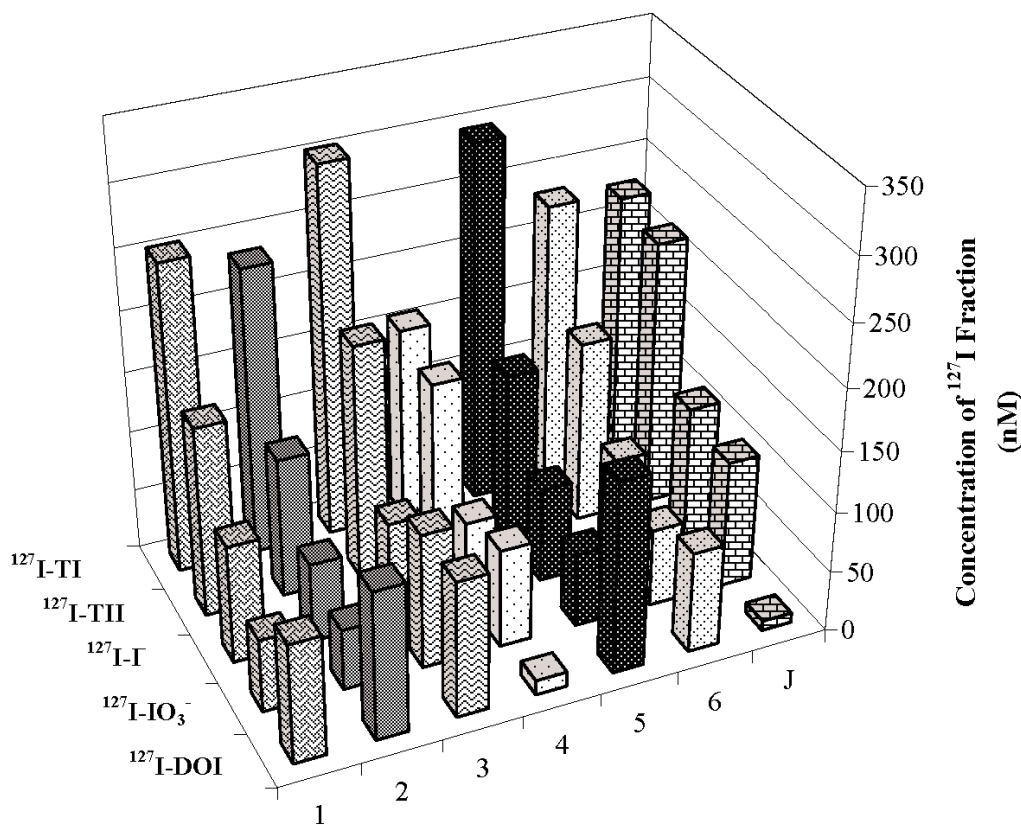


Fig. 4. Distribution of ^{127}I species concentrations in Galveston Bay across a salinity transect from Station 1 at the upper estuary (near the mouth of the Trinity River) to Station J beyond the jetty and into the Gulf of Mexico.

distribution of nutrients (*see below*).

Although the patterns in variability (not shown) are different for TII, I⁻, and IO₃⁻, all three species also show net removal from the Bay water. Station 4 for IO₃⁻ is the exception, suggesting that IO₃⁻ was added as a source at this locale. Unlike the other iodine species, [DOI] has a negative gradient with salinity, indicating a source to the bay at Station 2 and 3, while showing removal at the other transect sampling points.

Deviations from the conservative model—Reasons for deviations from expected conservative mixing include (1) analytical error, or (2) processes that influence iodine speciation, i.e., hydrographic mixing that is nonlinear across the salinity gradient due to riverine variability (Cifuentes and Eldridge 1998; Pakulski et al. 2000; Warnken and Santschi 2004), biotic or abiotic reactions from sediment-water exchange, uptake, release, or remineralization processes. Before one can explore the effects of biogeochemical or hydrological processes, however, one needs to first address the variability due to analytical error.

Variability due to analytical error—The iodine fractions that were measured directly for all samples were TI, I⁻, and TII. The IO₃⁻ concentration was also measured directly at Stations 1, 3, 4, and J. All standard deviations were ≤ 3% RSD for direct measurements. IO₃⁻ was also indirectly calculated for each

sample by the subtraction of I⁻ from TII. DOI was found as the difference between TI and TII. The maximum standard deviation for any iodine species was less than 11 nmol L⁻¹ SD for one sigma or less than 10% RSD error. This is important when considering the DOI values that were lower in absolute concentrations than the other fractions and calculated by difference. However, the RSD error for DOI was generally still acceptable, i.e., equivalent to less than 10%, for all stations except Station 4, where DOI was 12 ± 6 nmol L⁻¹ or approximately 50%, and Station J, where DOI was 8 ± 9 nmol L⁻¹ or approximately 125%. Therefore, the magnitude of the analytical error is not sufficient to account for the variability in the range of iodine species concentrations, with the exception of [DOI] at Stations 4 and J.

Variability due to nutrient patchiness or hydrographic mixing—This interpretation of strong patchiness is supported by the distribution of nitrogen species, phosphate, silicate, and irradiance (K_d) data from the same sampling stations. At Station 4 (salinity 10.36), the nitrogen (NH₄⁺ and sum of NO₂⁻ + NO₃⁻) and orthophosphate concentrations were greatly elevated. This was most likely a patch of water that was more heavily influenced by wastewater inputs from local sources in the Houston Ship Channel (Fig. 1). Deviations from linear mixing are also observed for Stations 4 and 5 in terms of values of

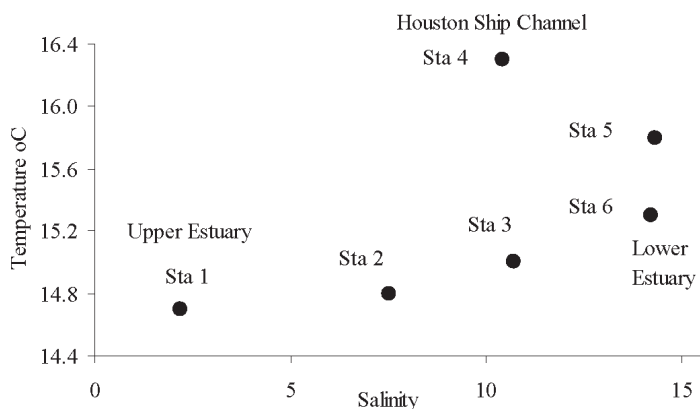


Fig. 5. Temperature versus salinity diagram illustrating nonlinear mixing due to the introduction of a second water mass from the Houston Ship Channel influencing Stations 4 and 5. Data were provided through the courtesy of J.L. Pinckney and S.E. Lumsden.

temperature versus salinity (Fig. 5). For example, there is a relatively conservative, linear mixing trend from Station 1 in the upper estuary near the mouth of the Trinity River across the estuary to Stations 2 and 3, to 6 in the lower estuary near the

Gulf of Mexico. Station 4 shows distinctive admixing of wastewater from the Houston Ship Channel. Station 5 shows intermediate mixing between the confluence of the waters of the Houston Ship Channel and the lower estuary. It should be noted that while “wastewater” refers to effluent from chemical plants, these waters have no relation to the European point sources for ^{129}I .

^{129}I speciation in Galveston Bay—The following notation was used: $^{129}\text{I-TI}$, $^{129}\text{I-TII}$, $^{129}\text{I-I}$, $^{129}\text{I-IO}_3^-$, and $^{129}\text{I-DOI}$, which represent the fractions of ^{129}I in total iodine, total inorganic iodine, iodide, iodate, and dissolved organic iodine, respectively. The distribution for ^{129}I speciation versus station number and salinity is shown in Fig. 6 and Table 3.

Conservative model for estuarine mixing and ^{129}I —The measured $^{129}\text{I-TI}$ value of 6.2×10^7 atoms L^{-1} from a sample taken near the Trinity River is only slightly higher than historical values of the $^{129}\text{I-TI}$ value in the Trinity River of 5.4 to 7×10^7 atoms L^{-1} (Schink et al. 1995; Moran et al. 2002). As for the stable iodine species, a simple model of conservative linear mixing was then used for comparison purposes to measured $^{129}\text{I}/^{127}\text{I}$ and $^{129}\text{I-TI}$ values. The values for the model end-members, TR_M and GOM_M , were not measured and had to be estimated from literature values. These values, $(5.9 \pm 0) \times 10^7$

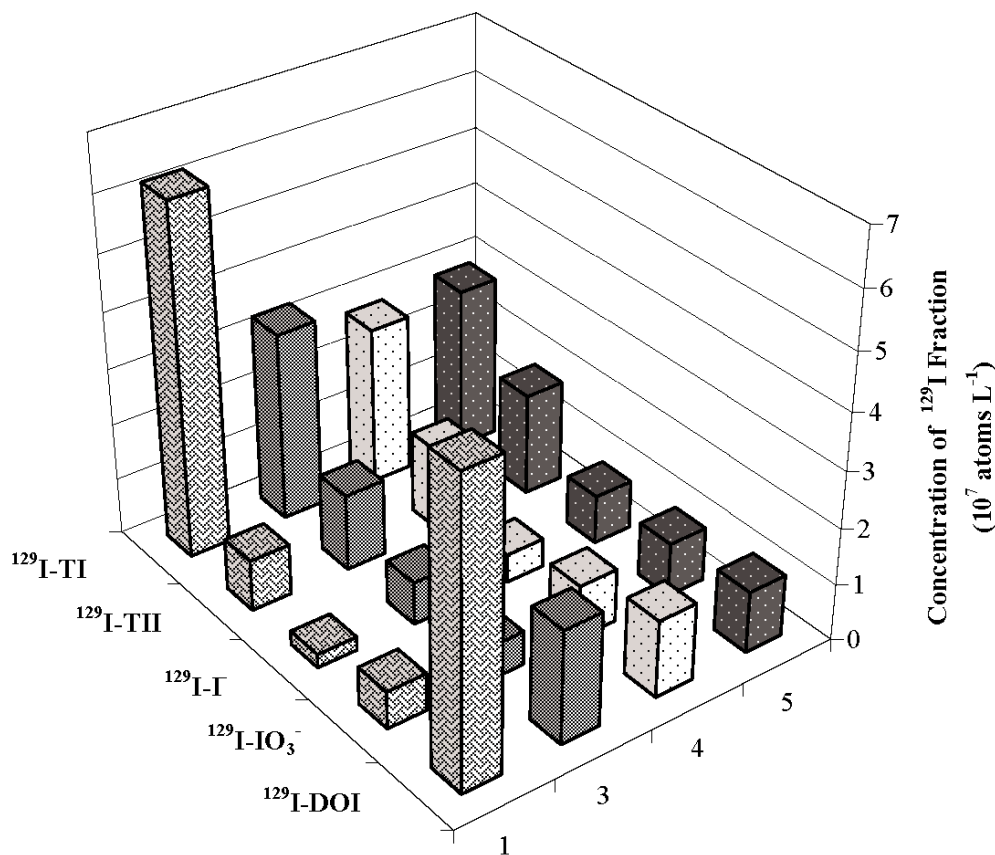


Fig. 6. Distribution of ^{129}I species concentrations in Galveston Bay across a salinity transect from Station 1 at the upper estuary (near the mouth of the Trinity River) to Station 5 in the lower estuary.

Table 3. Concentration of ^{129}I species in the surface waters of the Galveston Bay, Dec 2001

Station	Salinity	$^{129}\text{I-TI}$ (10^7 at L^{-1})*	$^{129}\text{I-TII}$ (10^7 at L^{-1})†	$^{129}\text{I-I}$ (10^7 at L^{-1})*	$^{129}\text{I-IO}_3^-$ (10^7 at L^{-1})*	$^{129}\text{I-DOI}$ (10^7 at L^{-1})†
1	2.2	6.2	0.86	0.24	0.62	5.4
2	7.5	N.M.	N.M.	0.55	N.M.	N.M.
3	10.7	3.4	1.3	0.76	0.52	2.1
4	10.4	2.8	1.4	0.51	0.90	1.4
5	14.3	2.9	1.8	0.87	0.91	1.1
J	16	N.M.	N.M.	0.72	N.M.	N.M.

*Measured directly; N.M., not measured.

†Calculated by difference; N.M., not measured.

atoms L^{-1} for TR_M and $(1.6 \pm 0) \times 10^7$ atoms L^{-1} for GOM_M (Schink et al. 1995; Schwehr and Santschi 2003) are assumed to be representative for the end-member $^{129}\text{I-TI}$ concentrations. Little variability in the input ^{129}I is expected because (1) point source atmospheric inputs of anthropogenic ^{129}I from European nuclear reprocessing facilities have been nearly constant over the past decade (Santschi and Schwehr 2004; Szidat et al. 2000; Schnabel et al. 2001) and (2) the measured concentration is within the range of the historical $^{129}\text{I-TI}$ values for the Trinity River of 5.4 to 7×10^7 atoms L^{-1} (Schink et al. 1995; Moran et al. 2002). Regarding variability in the input ^{127}I concentration, (1) it has been reported by Warnken and Santschi (2004) that the DOC concentration in the Trinity River is proportional to flow, and (2) it has been reported by Cook et al. (2000) that the proportion of organic ^{127}I increases with increasing DOC. We, therefore, propose that our $^{127}\text{I-DOI}$ is proportionally high for the year because our sampling period was during a relatively high discharge rate. It follows that high $^{127}\text{I-DOI}$ concentrations cause effectively lower $^{129}\text{I}/^{127}\text{I-DOI}$ ratio values. Furthermore, variability in riverine ^{127}I input from our measured values at high discharge would be expected to be at lower concentrations and,

therefore, the $^{129}\text{I}/^{127}\text{I-DOI}$ ratio values will likely be at a higher contrast to $^{129}\text{I}/^{127}\text{I-TI}$ values than reported here. Also, in the GOM_M , both ^{129}I and ^{127}I values have been relatively constant over the past decade (Schink et al. 1995; Moran et al. 1997; Schwehr and Santschi 2003). Therefore, Fig. 7 was constructed using $^{129}\text{I}/^{127}\text{I}$ values along the mixing line between TR_M and GOM_M that were derived by dividing each $^{129}\text{I-TI}$ value by its corresponding $^{127}\text{I-TI}$ value for a particular salinity (diamonds). Then measured values for $^{129}\text{I}/^{127}\text{I-DOI}$ (Table 4), shown as squares, were compared with those of the conservative mixing model. Whereas isotope ratios in DOI at Station 5 are predicted by conservative mixing, those at the stations with lower salinity are not. $^{129}\text{I}/^{127}\text{I-DOI}$ concentrations are significantly elevated at these stations. These elevated values likely trace tDOC through the upper reaches of the Bay, at salinities less than 20, e.g., at Station 1 and 4, possibly enhanced through wastewater input from the Houston Ship Channel at Station 4. This salinity zone of 0 to approximately 20 ppt is the zone most strongly dominated by terrestrial species, as previously demonstrated through C/N ratio values by Guo and Santschi (1997) (Fig. 8A). Additionally, Guo et al. (1997) reported that macromolecular organic matter = 10 kDa

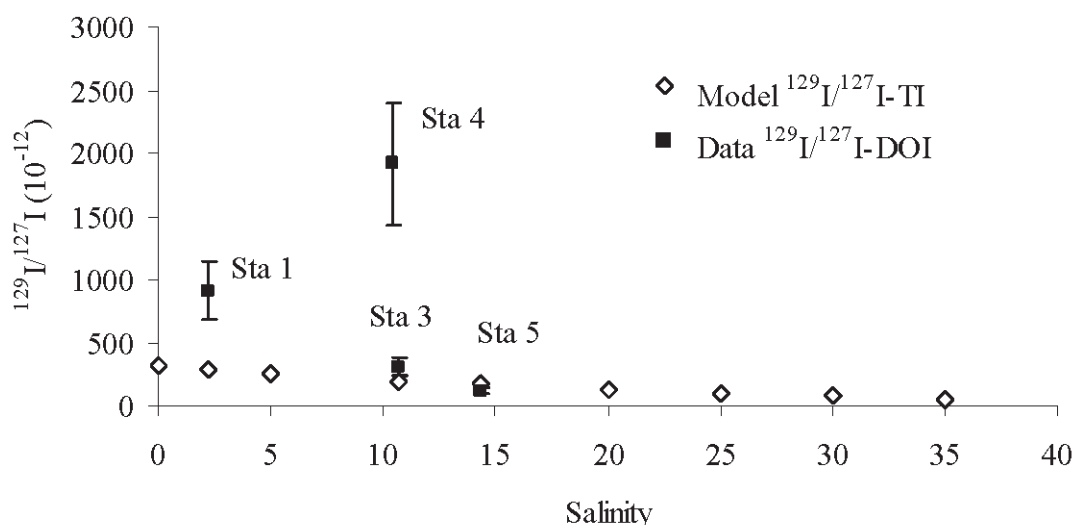
**Fig. 7.** Comparison of observed (squares) $^{129}\text{I}/^{127}\text{I-DOI}$ data values with modeled (diamonds) $^{129}\text{I}/^{127}\text{I-TI}$ ratio values.

Table 4. Concentration of $^{129}\text{I}/^{127}\text{I}$ species in the surface waters of the Galveston Bay, Dec 2001

Station	Salinity	$^{129}\text{I}/^{127}\text{I}\text{-TI}$ (10^{-12})*	$^{129}\text{I}/^{127}\text{I}\text{-TII}$ (10^{-12})†	$^{129}\text{I}/^{127}\text{I}\text{-I}^-$ (10^{-12})*	$^{129}\text{I}/^{127}\text{I}\text{-IO}_3^-$ (10^{-12})*	$^{129}\text{I}/^{127}\text{I}\text{-DOI}$ (10^{-12})†
1	2.2	406	91	41	170	912
2	7.5	N.M.	N.M.	142	N.M.	N.M.
3	10.7	183	110	153	78	309
4	10.4	295	159	128	184	1913
5	14.3	163	212	184	248	119
J	16	N.M.	N.M.	105	N.M.	N.M.

*Measured directly; N.M., not measured.

†Calculated by difference; N.M., not measured.

in Galveston Bay is mostly removed in this salinity zone. Furthermore, Guo et al. (2003) showed that terrestrial influence of colloidal macromolecular organic compounds, as traced by $\delta^{13}\text{C}$ and $\delta^{14}\text{N}$ (Fig. 8B and 8C), extended to a salinity of about 20 ppt, in agreement with our data (Fig. 8D).

While isotopic ratios of DOI showed distinctive enhancements at the low salinity stations, this was not true for the other iodine species. $^{129}\text{I}/^{127}\text{I}$ ratios in iodide and iodate did not show this feature, indicating fast isotopic and chemical equilibration between the two isotopes among the different inorganic species in the estuary. Therefore, it appears that iodine isotope ratios in DOI trace tDOC into the coastal zone, similarly to carbon isotopes.

Conclusions

Values for $^{129}\text{I}/^{127}\text{I}$ in tDOC are greatly elevated over those from marine systems. The question in this research was if isotope ratios of iodine, a biophilic element, can be used to trace tDOC across an estuary, similar to carbon isotopes. Novel analytical techniques of $^{129}\text{I}/^{127}\text{I}$ ratio determination in DOI and the other iodine species, using dehydrohalogenation, anion chromatography, HPLC, and AMS techniques, were developed and applied to samples from a transect across Galveston Bay, Texas. Results indicate that elevated $^{129}\text{I}/^{127}\text{I}$ values in DOI from terrestrial sources are significant up to salinity of about 20, similar to previously described stable isotope signals of DOM ($\delta^{13}\text{C}$, $\delta^{14}\text{N}$, and C/N ratios) in this estuary (Guo and Santschi 1997, Guo et al. 2003). $^{129}\text{I}/^{127}\text{I}$ ratios in the other iodine species, e.g., iodide and iodate, did not show this feature, indicating fast isotopic and chemical equilibration between the two isotopes among the different inorganic species in the estuary. Results thus demonstrate the proof of concept for using isotope ratios of DOI as novel tracers for the presence of tDOC in the coastal zone. Future research should include measurement of the end-member values during the same collection period as the estuarine transect sampling, and direct comparison to carbon isotopic ratios of DOC.

References

Abdel-Moati, M. A. R. 1999. Iodine speciation in the Nile River estuary. *Mar. Chem.* 65:211-225.

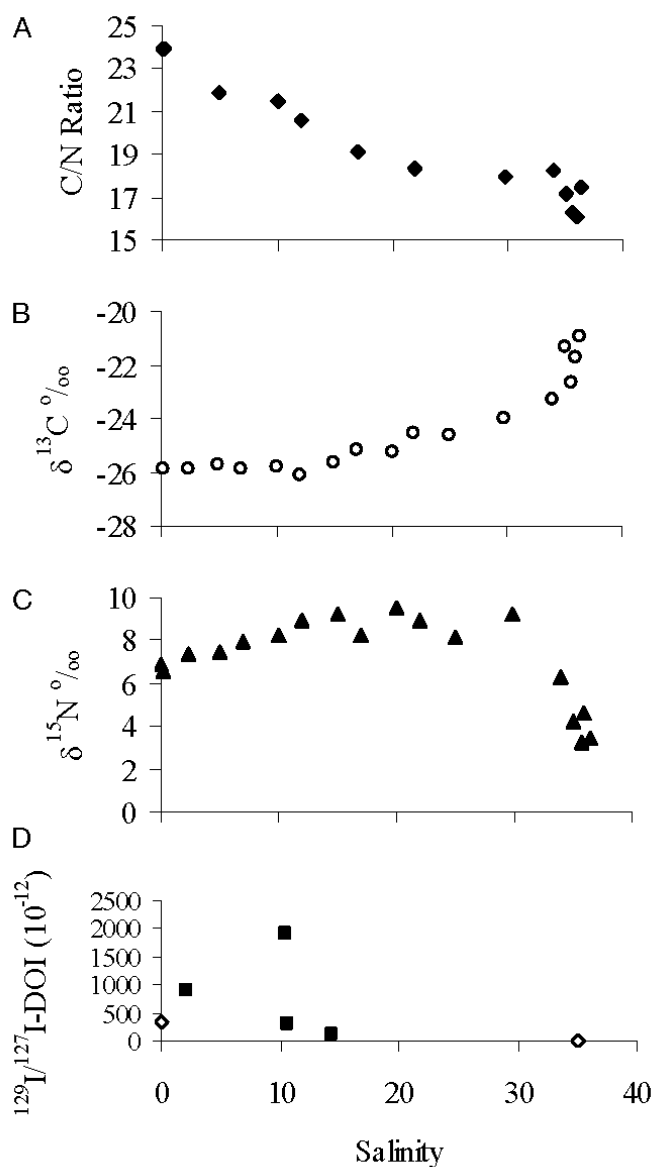


Fig. 8. Comparison of (A) C/N ratios, (B) $\delta^{13}\text{C}$, and (C) $\delta^{14}\text{N}$ for high molecular weight colloidal material (1 to 200 nm) (Guo et al. 1997, 2003) with (D) $^{129}\text{I}/^{127}\text{I}$ -DOI data (squares) and published endpoint values (diamonds) along a salinity gradient in the Galveston Bay.

- Alvarado-Quiroz, N. G., T. Kotzer, G. Milton, J. D. Clark, and D. Bottomley. 2002. Partitioning of ^{127}I and ^{129}I in an unconfined glaciofluvial aquifer on the Canadian Shield. *Radiochim. Acta* 90:469-478.
- Butler, E. C. V. 1996. The analytical chemist at sea: Measurements of iodine and arsenic in marine waters. *Trends Anal. Chem.* 15:45-52.
- Carmack, E. C., and others. 1997. Changes in temperature and tracer distributions within the Arctic Ocean: Results from the 1994 Arctic Ocean section. *Deep-Sea Res. II* 44:1487-1493.
- Cauwet, G. 2002. DOM in the coastal zone, p 579-609. *In* D. A. Hansell and C. A. Carlson [eds.] *Biogeochemistry of marine dissolved organic matter*. Academic.
- Cifuentes, L. A., and P. M. Eldridge. 1998. A mass- and isotope-balance model of DOC mixing in estuaries. *Limnol. Oceanogr.* 43:1872-1882.
- Cook P. L. M., P. D. Carpenter, and E. C. V. Butler. 2000. Speciation of dissolved iodine in the waters of a humic-rich estuary. *Mar. Chem.* 62:179-192.
- Cooper, L. W., G. H. Hong, T. M. Beasley, and J. M. Grebmeier. 2001. Iodine-129 concentrations in marginal seas of the North Pacific and Pacific-influenced waters of the Arctic Ocean. *Mar. Poll. Bulletin* 42:1347-1356.
- Edmonds, H. N., J. N. Smith, H. D. Livingston, L. R. Kilius, and J. M. Edmond. 1998. ^{129}I in archived seawater samples. *Deep-Sea Res. I* 45:1111-1125.
- Eisenbud, M., and T. Gesell. 1997. *Environmental radioactivity*. 4th ed. Academic Press.
- Fehn, U., and G. Snyder. 2000. ^{129}I in the southern hemisphere: Global redistribution of an anthropogenic isotope. *NIMB* 172:366-371.
- Guo, L., and P. H. Santschi. 1997. Isotopic and elemental characterization of colloidal organic matter from Chesapeake Bay and Galveston Bay. *Mar. Chem.* 59:1-15.
- , P. H. Santschi, and T. S. Bianchi. 1999. Dissolved organic matter in estuaries of the Gulf of Mexico, p. 269-299. *In* T. S. Bianchi, J. R. Pennock, and R. Twilley [eds.], *Biogeochemistry of Gulf of Mexico estuaries*, Wiley.
- , N. Tanaka, D. M. Schell, and P. H. Santschi. 2003. Nitrogen and carbon isotopic composition of HMW dissolved organic matter in marine environments. *Mar. Ecol. Progr. Ser.* 252:51-60.
- Hansell, D. A., D. Kadko, and N. R. Bates. 2004. Degradation of terrigenous dissolved organic carbon in the western Arctic Ocean. *Science* 304:858-861.
- Hou, X. L., H. Dahlgard, B. Rietz, U. Jacobsen, S. P. Nielsen, and A. Aarkrog. 1999. Determination of chemical species of iodine in seawater by radiochemical neutron activation analysis combined with ion-exchange pre-separation. *Anal. Chem.* 71:2745-2750.
- , ———, and ———. 2001. Chemical speciation of ^{129}I in seawater and a preliminary investigation to use it as a tracer for geochemical cycle study of stable iodine in seawater. *Mar. Chem.* 74:145-155.
- Kocher, D. C. 1981. A dynamic model of the global iodine cycle and estimation of dose to the world population from releases of iodine-129 to the environment. *Environ. Int.* 5:15-31.
- Loder, T. C., and R. P. Reichard. 1981. The dynamics of conservative mixing in estuaries. *Estuaries* 4:64-69.
- Michel, R., T. Ernst, D. Jakob, S. Szidat, H. A. Synal, and C. Schnabel. 2002. Long-lived radionuclides in the environment: the case of iodine-129. *In* Proceedings EUROSAFE, Berlin. <http://www.eurosafe-forum.org/ipsn/pdf/euro2_4_2_iodine129.pdf>
- Moran, J. E., S. D. Oktay, P. H. Santschi, and D. R. Schink. 1997. Surface ^{129}I / ^{127}I ratios: Marine vs. terrestrial, p. 807-810. *In* J. L. Duggan and I. L. Morgan [eds.], *Applications of accelerators in research and industry*, AIP Press.
- , ———, ———, and ———. 1999a. Atmospheric dispersal of ^{129}I from European nuclear fuel reprocessing facilities. *Environ. Sci. Technol.* 33:2536-2542.
- , ———, ———, ———, U. Fehn, and G. Snyder. 1999b. World-wide redistribution of ^{129}I from nuclear fuel reprocessing facilities: Results from meteoric, river, and seawater tracer studies. IAEA-SM-354/101.
- , ———, ———. 2002. Sources of iodine and ^{129}I in rivers. *Water Resour. Res.* 38:24.1-24.10.
- NCDC, NOAA. 2003. National Climate Data Center of the National Oceanographic and Atmospheric Administration Web site for Houston, Texas. <<http://lwf.ncdc.noaa.gov/oa/climate/research/cag3/v1.html>>
- Oktay, S. D., P. H. Santschi, J. E. Moran, and P. Sharma. 2001. ^{129}I and ^{127}I transport in the Mississippi River. *Environ. Sci. Technol.* 35:4470-4476.
- Pinkney, J. L., E. B. Ornlodottir, and S. E. Lumsden. 2002. Estuarine phytoplankton group-specific response to sub-lethal concentrations of the agricultural herbicide, atrazine. *Mar. Pollution Bull.* 44:1109-1116.
- Pakulski, J. D., and others. 2000. Microbial metabolism and nutrient cycling in the Mississippi and Atchafalaya River plumes. *Est. Coast. Shelf Sci.* 50:173-184.
- Pointurier, F., N. Baglan, G. Alanic, and R. Chiappini. 2003. Determination of organically bound tritium background level in biological samples from a wide area in the south-west of France. *J. Environ. Radioact.* 68:171-189.
- Quigley, M. S., P. H. Santschi, and C. C. Hung. 2002. Importance of acid polysaccharides for ^{234}Th complexation to marine organic matter. *Limnol. Oceanogr.* 47:367-377.
- Rahn, K. A., R. D. Borys, and R. A. Duce. 1976. Tropospheric halogen gases: Inorganic and organic components. *Science*. 192:549-550.
- Raisbeck, G. M., F. Yiou, Z. Q. Zhou, and L. R. Kilius. 1995. ^{129}I from nuclear fuel reprocessing facilities at Sellafield (UK) and La Hague (France): potential as an oceanographic tracer. *J. Mar. Syst.* 6:561-570.

- and ———. 1999. ^{129}I in the oceans: origins and applications. *Sci. Tot. Env.* 237/238:31-41.
- Reifenhauser, C., and K. G. Heumann. 1990. Development of a definitive method for iodine speciation in aquatic systems. *Fresenius J. Anal. Chem.* 336:559-563.
- Santschi, P. H. 1995. Seasonality in nutrient concentrations in Galveston Bay. *Mar. Environ. Res.* 40:337-362.
- , D. R. Schink, O. Corapcioglu, S. Oktay-Marshall, P. Sharma, and U. Fehn. 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.
- , L. Guo, I. D. Walsh, M. S. Quigley, and M. Baskaran. 1999. Boundary exchange and scavenging of radionuclides in continental margin waters of the Middle Atlantic Bight: implications for organic carbon fluxes. *Cont. Shelf Res.* 19:609-636.
- and K. A. Schwehr. 2004. $^{129}\text{I}/^{127}\text{I}$ 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., P. H. Santschi, O. Corapcioglu, P. Sharma, and U. Fehn. 1995. ^{129}I in Gulf of Mexico waters. *Earth Planet. Sci. Lett.* 135:131-138.
- Schnabel, C., J. M. Lopez-Gutierrez, S. Szidat, M. Sprenger, H. Wernli, J. Beer, and H. A. Synal. 2001. On the origin of ^{129}I in rain water near Zurich. *Radiochim Acta* 89:815-822.
- Schwehr, K. A., and P. H. Santschi. 2003. A sensitive determination of iodine species, including organic iodine, for fresh water and seawater samples using high performance liquid chromatography and spectrophotometric determination. *Anal. Chim. Acta*, 482:59-71.
- , ———, and J. E. Moran. 2005. ^{129}I Iodine: A new hydrologic tracer for aquifer recharge conditions influenced by river flow rate and evapotranspiration. *Appl. Geochem.* 20:1461-1472.
- Smith, J. N., K. M. Ellis, and L. R. Kilius. 1998. ^{129}I and ^{137}Cs tracer measurements in the Arctic Ocean. *Deep-Sea Res.* I 45: 959-984.
- Szidat, S., and others. 2000. Iodine-129: sample preparation, quality control and analyses of pre-nuclear materials and of natural waters from Lower Saxony, Germany. *Nucl. Instrum. Methods Phys. Res. B* 172:699-710.
- Tang, D., K. W. Warnken, and P. H. Santschi. 2002. Distribution and partitioning of trace metals (Cd, Cu, Ni, Pb, Zn) in Galveston Bay waters. *Mar. Chem.* 78:29-45.
- Truesdale, V. W., and K. Jones. 2000. Steady-state mixing of the iodine in shelf seas off the British Isles. *Cont. Shelf Res.* 20:1889-1905.
- United Nations Atlas of the Oceans. 2005. Human settlements on the coast. <<http://www.oceansatlas.org/servlet/CDSServlet?status=ND0xODc3JmN0bl9pbmZvX3ZpZXdfc2l6ZT1jdG5faW5mb192aWV3X2Z1bGwmNj1lbiY1NT0yMSYzMz0qJjM3PWtvcw~~>>
- USGS. 2002. United States Geological Survey water data for Trinity River gauging station #08066500 (Romayor, Texas). <<http://tx.waterdata.usgs.gov>>
- Ward, G. H. 1992. The prediction problems for salinity intrusion, p 315-326. *In* R. W. Jensen, R. W. Kiesling, and F. S. Shipley, [eds.], *Proceedings of 2nd State of the Bay Symposium, Galveston Bay National Estuary Program Publication GBNEP-23.*
- Warnken, K. W., and P. H. Santschi. 2004. Biogeochemical behavior of organic carbon in the lower Trinity River downstream of the Lake Livingston reservoir (Texas, USA). *Sci. Tot. Env.* 329: 131-144.
- Wimschneider, A., and K. G. Heumann. 1995. Iodine speciation in size fractionated atmospheric particles by isotope dilution mass spectrometry. *Fresenius J. Anal. Chem.* 353:191-196.
- Wong, G. T. F., and L. S. Zhang. 1992. Chemical removal of oxygen with sulfite for the polarographic or voltammetric determination of iodate or iodide in seawater. *Mar. Chem.* 38:109-116.
- and X. H. Cheng. 1998. Dissolved organic iodine in marine waters: determination, occurrence and analytical implications. *Mar. Chem.* 59:271-281.
- and ———. 2001. The formation of iodide in inshore waters from the photochemical decomposition of dissolved organic iodine. *Mar. Chem.* 74:53-64.
- Yiou, F., G. M. Raisbeck, Z. Q. Zhou, L. R. Kilius, and P. J. Kershaw. 1995. Improved estimates of oceanic discharges of ^{129}I from Sellafield and LaHague. *In* *Proceedings of the International Conference on Environmental Radioactivity in the Arctic, Oslo, Norway.*
- , ———, G. C. Christensen and E. Holm. 2002. I-129/I-127, I-129/Cs-137 and I-129/Tc-99 in the Norwegian coastal current from 1980 to 1998. *J. Env. Radioact.* 60: 61-71.

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