TRACE ELEMENT GEOCHEMISTRY OF THE SOUTH ATLANTIC BIGHT

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INTRODUCTION

During the 1975-76 contract period, emphasis has been on completing collections and analyses of river samples for copper, nickel and zinc to establish the importance of river input to continental shelf waters. In addition shelf waters were analyzed to improve our understanding of the distribution of copper and to obtain estimates of nickel and zinc concentrations. Air sample analyses have allowed us to obtain tentative values for the atmospheric input of trace elements to the South Atlantic Bight. In addition to copper, nickel and zinc we have been studying mercury and arsenic to obtain a more fundamental understanding of transport pathways and processes that effect trace elements in the continental shelf environment.

Ten major rivers of the southeastern United States have been sampled monthly over a year period for copper and for six months for nickel and zinc. One year's data has also been obtained for mercury and arsenic. The locations of continental shelf surface water samples collected during the past year are shown in Figure 1. During the same cruises atmospheric samples were also collected.

A detailed discussion of the results of the past two years' studies and conclusions drawn from them are included in two manuscripts that form the body of this report. The first, "Trace Element Geochemistry of Continental Shelf Waters of the Southeastern United States" will be presented at a joint Soviet-American Symposium on the chemistry of the oceans being held in Odessa, U.S.S.R. The second, "The Geochemistry of Arsenic in the Continental Shelf Environment" was the subject of a Ph.D. Dissertation which was presented and defended during February 1977. All data obtained during the last year are not appended as they will be included in the body of papers being published within the next few months. Tentative

Figure 1.

conclusions from the work done thus far are outlined below.

TENTATIVE CONCLUSIONS

- 1) The most important input mechanism for trace elements to the continental shelf is intrusions with the possible exception of mercury which has an equally important input via the atmosphere.
- 2) The residence times of all the trace elements studied in continental shelf waters are similar (about 0.26 yr) but different from that of water (0.37 yr).
- 3) A portion of trace elements transported to the shelf by rivers may be lost by incorporation onto particles that are swept off the shelf or deposited on the bottom.
- 4) Trace elements are apparently regenerated at depth in the Gulf Stream and off shelf waters, and increased levels may be correlated with nutrient concentrations.
- 5) At present sufficient data exists to suggest that much of the copper in solution is complexed on proton exchangeable (presumably organic) complexes. Arsenic exists primarily as arsenate but may also occur in small amounts as arsenite and dimethylarsenic acid.

TRACE ELEMENT GEOCHEMISTRY OF CONTINENTAL SHELF
WATERS OF THE SOUTHEASTERN UNITED STATES

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TRACE ELEMENT GEOCHEMISTRY OF CONTINENTAL SHELF WATERS OF THE SOUTHEASTERN UNITED STATES

The greatest exploitation of the marine environment by man has occurred on continental shelves. In the future the search for mineral resources and sites for nuclear power plants will focus greater activity in this region. If the continental shelves are to be utilized in a logical way, with minimal environmental impacts, it is important to understand processes that are active there.

Most of the activities related to energy development (e. g., petroleum exploration and production, offshore nuclear power plant siting) may result in releases of stable and radioisotopes of naturally occurring trace elements. To predict the fate of these additions and their ultimate impact on the environment it is necessary to develop a fundamental understanding of the natural processes which govern their behavior. This paper discusses aspects of the geochemistry of trace elements that influence their concentration and distribution in continental shelf waters. The trace elements considered are arsenic, copper, mercury, nickel and zinc. The discussion is based on studies of the continental shelf of the Southeastern United States' coast, which is referred to as the South Atlantic Bight (Figure 1).

The South Atlantic Bight is similar to most continental shelves in that it receives runoff from the adjacent land and is bordered on its deep ocean side by a strong boundary current (Gulf Stream). The hydrographic and chemical characteristics of a typical transect across the shelf are shown in Fig. 2. Middle shelf regions are poor in nutrients while the inner shelf receives inputs from river runoff. Upwelling or intrusions from the Gulf Stream, which occur along the entire South Atlantic Bight

(Blanton, 1971), supply nutrients to the outer shelf.

Trace elements can be delivered to continental shelves by runoff, atmospheric transport and onshore intrusions of deep off-shelf waters (Fig. 3). By determining the magnitude of the trace element fluxes to continental shelf waters and comparing it to their total concentrations it is possible to calculate their residence times. The residence time can then be compared to that of the water (both from intrusions and runoff) to determine whether the elements behave conservatively.

TRACE METAL FLUXES TO CONTINENTAL SHELF WATERS

Rivers. Ten major rivers discharge into the South Atlantic Bight and are responsible for the major portion of continental runoff. These drainage basins are a mixture of crystalline igneous and metamorphic rocks and sedimentary deposits. In general each of the five trace elements studied do not vary considerably in concentration from river to river (Table 1). Observed variations probably relate to differences in the composition in the drainage basins.

Only the dissolved phase of trace elements transported by rivers is important to the continental shelf since the suspended load is deposited in estuaries (Meade, 1969; Windom et al., 1971). The dissolved components of arsenic, copper and mercury have been shown to be conservatively mixed through the estuary (Waslenchuk, 1977; Windom, 1975) and nickel and zinc probably behave similarly. The conservative nature of these elements during their transit through the estuary probably depends on their chemical form. For example, arsenic in river waters primarily exists in the As(V) form and is associated with low molecular weight organic matter (Waslenchuk, 1977). Copper also appears to be complexed with organic matter. Nickel

FIGURE 3. Schematic representation of trace element inputs to continental shelf waters.

TABLE 1
GEOMETRIC MEAN RIVERINE TRACE ELEMENT
CONCENTRATIONS FOR SOUTHEASTERN UNITED STATES

River	-----In solution-----				
	As ²	Cu	Ni	Zn	Hg
	$\mu\text{g}/\ell^1$				
1. Cape Fear	0.39 (0.16-0.60)	1.6 (0.1-3.1)	8.0 (4.0-15)	6.2 (2.9-8.0)	24 (14-36)
2. Pee Dee	0.21 (0.08-0.32)	1.2 (0.1-2.5)	3.6 (2.2-5.8)	3.7 (1.6-4.8)	20 (10-35)
3. Black	0.36 (0.15-0.57)	1.5 (0.2-2.1)	5.8 (3.0-11)	5.2 (2.3-7.9)	20 (10-38)
4. Santee	0.15 (0.04-0.31)	1.5 (0.4-3.9)	4.0 (1.4-8.0)	4.0 (1.4-6.2)	18 (8-38)
5. Cooper	0.27 (0.12-0.47)	1.9 (0.9-3.4)	5.0 (1.4-11)	2.7 (0.6-5.1)	18 (8-28)
6. Savannah	0.30 (0.13-0.47)	1.5 (0.4-3.6)	3.9 (1.0-16)	4.0 (0.5-8.9)	21 (12-38)
7. Ogeechee	0.25 (0.08-0.45)	1.1 (0.2-2.0)	4.1 (1.0-7.5)	2.8 (1.1-4.8)	19 (10-36)
8. Altamaha	0.21 (0.04-0.47)	1.5 (0.3-3.4)	2.7 (1.8-3.2)	3.2 (1.6-6.0)	19 (10-34)
9. Satilla	0.38 (0.25-0.52)	0.9 (0.1-2.6)	2.6 (0.7-3.5)	7.5 (0.7-13)	19 (10-33)
10. St. John	0.49 (0.26-0.72)	1.3 (0.1-2.6)	2.4 (1.6-3.4)	5.9 (1.2-10)	39 (16-61)

¹range given in parentheses

²from Waslenchuk (1977)

and zinc may behave similarly but little is known of the form of mercury in estuaries.

Assuming that trace elements carried in solution by rivers is conservatively mixed through the estuary, the total river input to the continental shelf can be determined by summing the products of the mean concentrations of the elements for each river and its discharge (Table 2). From these calculations the relative importance of river transport for the trace elements considered is $Ni > Zn > Cu > As > Hg$ which is the same general order as their relative abundances.

Atmospheric Transport. Because of their proximity to the continents, continental shelf environments may receive significant trace element inputs due to atmospheric transport. Although it is difficult to measure atmospheric trace element inputs directly, their atmospheric concentrations have been used to deduce input rates (Duce et al., 1976).

Atmospheric concentrations of the five trace elements over the continental shelf of the South Atlantic Bight each vary by about an order of magnitude (Table 3). Much of this variation is undoubtedly due to the trajectory taken by the air parcel sampled. Air transported directly from the continents during offshore winds would clearly be expected to have higher concentrations than that transported during easterly or onshore winds. Some of the variations in atmospheric trace element concentrations may also be due to exchange of trace elements from sea surface to the air (Duce et al., 1976). Even with these uncertainties, however, the mean atmospheric concentrations of the trace elements from air samples collected in the summer and winter can be used to ascertain their annual input. Duce et al. (1976) proposed a model which utilizes observed dry deposition velocities for trace elements and to take into account washout, assumes

TABLE 2

ESTIMATED ANNUAL RIVER TRANSPORT OF
TRACE ELEMENT TO THE SOUTH ATLANTIC BIGHT

<u>Element</u>	<u>River Transport</u> (kg/yr)
Arsenic	1.4×10^4
Zinc	2×10^5
Nickel	2.2×10^5
Copper	8×10^4
Mercury	1.1×10^3

TABLE 3
GEOMETRIC MEAN ATMOSPHERIC TRACE ELEMENT
CONCENTRATIONS AND INPUT TO CONTINENTAL SHELF WATERS³

Element	No. of Samples	Mean ng/SCM	Range ng/SCM	Annual Input ² (10 ⁵ kg)
As ¹	11	1.6	0.2-6.3	0.2
Zn	17	8.9	3.4-24	2.9
Ni	17	1.4	0.2-4.8	0.4
Cu	17	3.0	1.0-16	0.9
Hg	42	2.1	0.3-7.6	0.6

¹Waslenchuk (1977)

²Using a dry deposition velocity of 0.26 cm/sec for As, 0.56 cm/sec for Zn (Cumbray et al., 1975) and 0.5 cm/sec for Cu, Ni and Hg and assuming the total atmospheric flux is 3 times the dry fallout.

³Samples collected during summer and winter cruises.

that the total atmospheric flux is 3 times the dry fallout. Using this model the trace element input due to atmospheric transport can be calculated for the entire continental shelf area ($6 \times 10^4 \text{ km}^2$) of the South Atlantic Bight (Table 3):

Input due to Intrusions. The intrusion of deep Gulf Stream water onto the shelf occurs frequently in the South Atlantic Bight. Details of these intrusions have been described by Blanton (1971). Along a given transect of the continental shelf intrusions occur about 13 times a year (Blanton and Atkinson, personal communication). The intrusions are identified by nutrient concentrations, salinity and temperature and each excursion apparently displaces 1/5 of the shelf volume. The South Atlantic Bight continental shelf has a volume of $1,920 \text{ km}^3$. Thus the annual volume of intruded waters to this area is $4,980 \text{ km}^3$.

The intrusions originate in the deep slope waters adjacent to continental shelf and show elevated concentrations of the trace elements (Table 4). The enriched trace element concentrations are apparently due to physical transport of plant and animal detritus from the euphotic zone with subsequent degradation and release of trace elements at depth. This process has been described in several studies of deep ocean environments (Boyle and Edmond, 1975; Sclater *et al.*, 1976; Boyle *et al.*, 1976).

An estimate of the annual input of trace elements due to intrusions can be made by multiplying the volume of intruded water by the concentrations of the trace elements (Table 4). It is clear from this calculation that intrusions are the major mechanism of trace element transport to the continental shelf environment.

TABLE 4
ESTIMATE OF TRACE ELEMENT
CONCENTRATION AND ANNUAL INPUT IN INTRUSIONS

	Concentration in Intrusion Waters	Annual Input (10 ⁶ kg)
Arsenic ¹	1.5 µg/ℓ	7.5
Zinc	0.61µg/ℓ	3.0
Nickel	0.61µg/ℓ	3.0
Copper	0.26µg/ℓ	1.3
Mercury	25 ng/ℓ	0.1

TRACE ELEMENT CONCENTRATIONS AND RESIDENCE TIMES IN CONTINENTAL SHELF WATERS

The concentrations of trace elements in continental shelf waters vary relatively little with depths and seasons (Table 5). Most of the As is in the As(V) form with minor amounts existing as As(III) or dimethyl arsenic acid (Waslenchuk, 1977). Little is known of the form of the other trace elements but the relatively high apparent complexation capacity of continental shelf waters suggests that they may exist as complexes.

The mean residence time of a given trace element in continental shelf waters can be determined by the following equation:

$$T = \frac{CV}{I_r + I_a + I_i}$$

where C is the mean trace element concentration, V is the shelf water volume ($1,920 \text{ km}^3$) and I_r , I_a and I_i are the annual inputs due to runoff, atmospheric transport and intrusions, respectively. Using the data from Tables 2 through 5, the residence time for each of the five trace elements can be calculated. The residence times thus obtained (0.22 - 0.29 yrs.) are remarkably similar (Table 6), but are significantly different from that calculated for water (0.37 yrs.). If the trace elements behave conservatively then their residence time should be similar to that of water. The fact that they are all less implies that an excess amount of each element is transported onto the shelf compared to that transported off. Even though the uncertainties in the data used may be considerable, it is of interest to calculate this excess (Table 6) to evaluate possible processes that may result in losses in trace elements from shelf waters.

TABLE 5
TRACE ELEMENT CONCENTRATIONS IN
CONTINENTAL SHELF WATER

	Mean and Standard Deviation	Total Content ² (kg)
Arsenic ¹	$1.04 \pm 0.19 \text{ } \mu\text{g}/\ell$	2×10^6
Zinc	$0.49 \pm 0.08 \text{ } \mu\text{g}/\ell$	9.4×10^5
Nickel	$0.49 \pm 0.06 \text{ } \mu\text{g}/\ell$	9.4×10^5
Copper	$0.16 \pm 0.07 \text{ } \mu\text{g}/\ell$	3.1×10^5
Mercury	$20 \pm 5 \text{ ng}/\ell$	3.8×10^4

¹Waslenchuk (1977)

²Assuming continental shelf area of $6 \times 10^4 \text{ km}^2$ and an average depth of 32 m.

TABLE 6
RESIDENCE TIME OF TRACE ELEMENTS
IN CONTINENTAL SHELF WATERS

Element	Residence Time (yrs)	Excess (mg/m ²)
Arsenic	0.27	13
Zinc	0.27	6
Nickel	0.29	4.3
Copper	0.22	3.5
Mercury	0.24	0.35

Sedimentation on the shelf is clearly a process of potential importance in the removal of trace elements from the water column. The average shelf sedimentation rate of the South Atlantic Bight is probably something less than 0.1 mm/yr. Using this value as an upper limit it is possible to calculate potential sedimentation losses of these elements. Assuming the sediment accumulating has a trace element concentration similar to average carbonate sediments (Turekian and Wedepohl, 1961) and a density of 2.0 g/cc the annual trace element loss would be 0.2, 7, 6, 6 and 0.00x mg/m² for As, Zn, Ni, Cu and Hg, respectively. For zinc, nickel and copper this process accommodates the excess amount delivered to the shelf calculated from the model described above. For arsenic and mercury, however, it appears to be an insignificant removal mechanism.

Primary production on the shelf is the major source of particulate carbon in this environment. The average annual production for the entire shelf has been estimated at 170 gC/m² (Haines and Dunstan, 1975). This would amount to an annual production of approximately 300 g/m² of total particulate organic matter. If the organic matter has concentrations of trace elements approximately equal to that of phytoplankton (20 ppm Zn, 10 ppm As, Cu and Ni and 0.1 ppm Hg), then annually 6 mg Zn/m², 3 mg As, Cu and Ni/m² and 0.03 mg Hg/m² could be removed from the dissolved phase. Assuming the trace elements are not regenerated on the shelf this removal mechanism could be of significance for all but mercury.

A large portion of the trace elements delivered to continental shelf waters by atmospheric transport may be inorganic particulates. Assuming all of the atmospheric input is of this nature, and does not contribute to the soluble trace element content of shelf waters, the amounts of the excesses for which this could account are 0.3, 4.8, 0.6, 1.5 and 1.0 mg/m² for As, Zn, Ni, Cu and Hg, respectively. This mechanism could account for

the apparent excesses in zinc and mercury delivered to the shelf.

Of the five trace elements studied, only arsenic appears anomalous in that its excess cannot be reasonably accounted for by the three possible removal mechanisms. As mentioned earlier, uncertainties in the data used for these calculations are probably quite significant, particularly the uncertainty in the determination of the concentration of trace elements in the intruded waters. Our lack of detailed knowledge of the periodicity and volumes of these intrusions may be the severest limitation on this approach. Even so, the above discussion can give considerable insight into the relative importance of processes that govern trace element concentrations and fates in continental shelf environments.

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THE GEOCHEMISTRY OF ARSENIC IN THE
CONTINENTAL SHELF ENVIRONMENT

A THESIS

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SUMMARY

The concentrations of arsenic species in continental-shelf waters of the southeastern U.S. are controlled mainly by simple physical mixing with intrusions of deep, arsenic-rich waters from the Gulf Stream, and by a biologically-mediated minor arsenic cycle. The riverine and atmospheric arsenic inputs are relatively insignificant. Biological uptake of arsenate in the euphotic zone results in arsenite and methylated arsenic concentration maxima in near-surface waters, and an arsenate concentration maximum at depth.

Arsenic is complexed by organic matter of relatively low molecular weight, and is unreactive in the estuarine environment. Estuarine arsenic concentrations are therefore also primarily controlled by physical mixing.

CHAPTER I

INTRODUCTION

This study concerns the aqueous geochemistry of arsenic in the continental-shelf environment. The determination of the aqueous geochemistry of arsenic is an interesting problem, since, as a metalloid, arsenic should share some characteristics with both the transition metals and the upper group Vb non-metals. One might predict, therefore, that arsenic would participate in the ion-exchange reactions and transport processes typical of the transition metals, and on the other hand, that arsenic would participate in the biological cycle in a manner similar to phosphorous and nitrogen.

Due to its electron configuration (outer shells $4s^2 4p^3$) arsenic can occur in valences of +5, +3, 0, and -3. Arsenic is stable in each of these valence states at oxidation potentials found in the natural aquatic environment (Ferguson and Gavis, 1972). In addition to inorganic species, alkyl-arsenic compounds have also been detected in the environment (Braman and Foreback, 1973). Furthermore, volatile hydrides of both inorganic and organic arsenic compounds (the arsines) are known to occur naturally (Johnson and Braman, 1975). It is therefore evident that arsenic has a complex aqueous geochemistry.

Ferguson and Gavis (1972) have reviewed the subject of the environmental chemistry of arsenic in general, and have indicated that knowledge of the arsenic cycle in natural waters is not adequate to allow

for rational management of the environment. They point out that anthropogenic contributions of arsenic to the oceans are three times that of natural contributions. It is apparent by this that rather large increases of arsenic content may occur in coastal or continental-shelf environments. The extent and effects of the potential accumulation of arsenic in this area are largely unknown, but are of great concern since the preservation of the delicate and vulnerable oceanic ecosystems is of such importance. It is, of course, well known that many arsenic compounds are generally toxic (Christenson *et al.*, 1974).

This research is directed towards the determination of the reactivity of arsenic in estuarine and continental-shelf waters. A trace element's reactivity governs, to a great extent, its environmental concentration and residence time, and hence the extent of transfer through the marine ecosystem. In order to estimate the residence time and reactivity of arsenic, one must determine the concentrations and forms of arsenic occurring in interacting waters from on and off the continental shelf, in the atmosphere, and in rivers. With such data, it becomes possible to evaluate the various transportational pathways of arsenic, and to ascertain the processes and mechanisms by which the various arsenic species are interrelated. Furthermore, it may be possible to predict potential variations in shelf-water arsenic concentrations due to changes in anthropogenic arsenic input.

A consideration of the thermodynamics of arsenic in natural water systems (Ferguson and Gavis, 1972) reveals that the predominant dissolved arsenic species in oxygenated river and ocean waters are the arsenic acids (As^{5+}), H_2AsO_4^- and HAsO_4^{2-} . The highly soluble, crystalline

arsenic oxides, As_2O_5 and As_2O_3 , do not occur in natural waters. The arsenious acids (As^{3+}) and the organic arsenicals are thermodynamically stable only at low Eh levels. The presence of significant environmental concentrations of As^{3+} (Johnson and Pilson, 1975), methyl arsonic acid and dimethylarsinic acid (Braman and Foreback, 1973) have been explained by biologically-mediated processes (Braman, 1975). The work with cultures by McBride and Wolfe (1971) supports this hypothesis.

Little information exists concerning arsenic geochemistry in environments similar to that of the study area. However, Wedepohl (1969) reports total-aqueous arsenic in the Pacific and Indian Oceans, and the English Channel to range from 0.15 to 6 $\mu\text{g/liter}$. For rivers in Sweden, the arsenic concentrations vary from 0.2 to 0.4 $\mu\text{g/liter}$, in Japan, from 0.25 to 7.7 $\mu\text{g/l}$, for the Elbe River, Germany, from 20 to 25 $\mu\text{g/l}$, and for the Columbia River, they average 1.6 $\mu\text{g/l}$. Braman and Foreback (1973) report 0.25 and 0.16 $\mu\text{g/l}$ As^{5+} for two Florida rivers, with one of the rivers containing 0.06 $\mu\text{g/l}$ (as As) methylarsonic acid and 0.30 $\mu\text{g/l}$ (as As) dimethylarsenic acid. For saline bay waters, they report values of from 0.06 to 0.12 $\mu\text{g/l}$ As^{3+} , from 0.35 to 1.45 $\mu\text{g/l}$ As^{5+} , from <0.02 to 0.07 $\mu\text{g/l}$ methylarsonic acid, and from 0.20 to 1.00 $\mu\text{g/l}$ dimethylarsenic acid. Johnson and Pilson (1972) determined that Western North Atlantic surface waters contain an average of 2.1 $\mu\text{g/l}$ As^{5+} , with Gulf of Mexico surface waters somewhat higher (2.25 to 4.5 $\mu\text{g/l}$). For the same areas, waters beneath the thermocline averaged 3.3 $\mu\text{g/l}$ arsenate. Johnson and Pilson also report that arsenate comprises 80% of the total arsenic.

Duce *et al.* (1976) have shown that atmospheric particulates are

enriched with arsenic. By using various models, they have estimated the flux of atmospheric, particulate arsenic to the oceans in remote areas (for instance, Bermuda) to be 0.06×10^{-15} to 0.5×10^{-15} g/cm²sec. Over a one year sampling period at Bermuda, Duce *et al.*, found a mean atmospheric arsenic concentration of 0.17 ng/m³. These investigators conclude that the atmospheric arsenic is derived either from volcanic or from sea-spray activity. Little is known about the fate of the arsenic subsequent to its deposition on the sea surface. Johnson and Braman (1975) have reported total atmospheric arsenic concentrations at a coastal Florida location to be approximately one order of magnitude higher (1.7 ng/m³) than those reported by Duce *et al.* (1976) for Bermuda.

Walsh *et al.* (1977) have shown that the atmospheric arsenic is almost entirely associated with the particulate phase, whereas Johnson and Braman (1975) have found volatile (gaseous) methylated arsenicals in rural, coastal, atmospheric samples. Johnson and Braman tentatively attribute the presence of the volatile alkyl-arsenical compounds to unnamed terrestrial biological processes.

Peirson *et al.* (1974) and Duce *et al.* (1976) have noted the importance of rain to the flux of atmospheric arsenic to the sea. Peirson *et al.* (1974) found rain to contain about 1 to 4 µg/l As at several coastal locations around the United Kingdom. Kanamori and Sugawara (1965) found an average arsenic content of 1.6 µg/l for 39 rain-water samples in Japan, and 0.6 µg/l for five rain-water samples from the open ocean.

The small amount of information available on the aqueous

geochemistry of arsenic is primarily concerned with either open-ocean or terrestrial environments, and contains only a few results of speciation analyses. Therefore, the nature of arsenic in the dynamic and productive coastal environment is essentially unknown.

This dissertation presents the results of an investigation into the marine geochemistry of arsenic in the Georgia Bight. The goals of the investigation were:

- (i) to determine the rates and pathways of arsenic inputs to the continental-shelf waters,
- (ii) to reveal the speciation of arsenic in the various environmental compartments,
- (iii) to ascertain the processes and mechanisms by which the various species are interrelated, and
- (iv) to determine the factors controlling the concentration of arsenic in the continental-shelf waters.

Study Area

This investigation is concerned with the Georgia Bight, which is that continental shelf area extending from Cape Canaveral, Florida, to Onslow Bay (Fig. 1). The Bight is a discreet water mass, bounded seaward by the Gulf Stream and the continental slope, and covering an area of approximately $6.4 \times 10^4 \text{ km}^2$. Average depth of the Bight is approximately 30 meters, yielding a water volume of 1915 km^3 . In the discussions which follow, the terms Bight, Georgia Bight, shelf, and study area are synonymous, and describe the area just defined. The area has also been called the South Atlantic Bight by others, but will not be so named here.

Ten major rivers, the St. Johns, Satilla, Altamaha, Ogeechee, Savannah, Cooper, Santee, Black, Pee Dee, and Cape Fear Rivers, debouch into the Bight, and comprise the great proportion of the total fresh water input. Several smaller streams together make up about 18% of the total fresh water inflow. The rivers drain both the igneous-metamorphic terrain of the Piedmont, and the swampy, sedimentary province of the Coastal Plain. Diverse industries are located adjacent to some of the rivers, and the drainage basins of all contain cultivated land.

Approximately 50 inches of rain per year fall directly on the Bight waters. During the summer months onshore winds prevail, whereas offshore winds prevail during the rest of the year.

STUDY AREA

CHAPTER II

METHODS

Arsenic Speciation Analyses

The measurements of the various arsenic-species concentrations were made on aqueous sample preparations by the plasma-emission spectrophotometric technique of Braman *et al.* (1973 and 1976). Briefly, this technique involves the following. An aliquot of up to 40 ml is placed in a reaction vessel, and acidified to either pH 1-2 (for As⁵⁺ and methylarsenical analyses) or pH 4-5 (for As³⁺ analyses). The sample is purged with helium for several minutes. A strong reducing reagent (NaBH₄) is injected through a septum, and reacts with the arsenic to form gaseous arsine and methylarsines from the arsenic and methylarsenical ions, respectively. The arsines are trapped in a U-tube cooled by liquid nitrogen. At the completion of the reaction (approximately 5 minutes), the liquid nitrogen is removed, and the U-tube is allowed to warm, assisted by a wire-coil heater mounted on the tube. The various arsines are selectively volatilized as their boiling temperatures are reached, and are swept by a helium-gas carrier into a D.C.-arc, discharge cell mounted on a spectrophotometer. The spectrophotometer monitors an arsenic-emission wavelength, and the relative amount of arsenic in each successive arsine pulse is measured.

The detection limit (the amount of arsenic giving a signal twice that of background) is about 0.5 ng for As³⁺ analyses, and 1 ng for As⁵⁺

and methylarsenical analyses. This yields respective minimum analysable concentrations of about 0.02 $\mu\text{g/l}$ and 0.04 $\mu\text{g/l}$.

There are no known matrix interferences other than high concentrations of organic carbon compounds, which evolve CO_2 , causing a depression of the signal. CO_2 , however, is effectively separated from the arsines by passing the gases from the cold trap through a NaOH (CO_2 -adsorbing) bead-packed tube.

By replicate analyses, a 7% coefficient of variation was determined for samples containing 5 - 20 ng arsenic (the usual working range). The accuracy of the method was found to be $\pm 5\%$, based on replicate analyses of digested National Bureau of Standards Orchard Leaf samples in the same arsenic range as above.

Sampling and Sample Preparation

Natural Waters

A variety of methods for collecting seawater have been used, and each has been tested against the others to ensure freedom from contamination. For deep samples, either clean Niskin bottles or a non-metallic pumping system was used. Surface seawater samples were obtained either by the pumping system, or by lowering sample bottles in a weighted, all-Teflon sampler from the bow of the ship. Care was taken always to sample water not contaminated by the ship itself.

River samples were also taken by lowering a Teflon sampler to the surface. This was accomplished from the upstream side of highway bridges. Estuarine samples were taken by hand from the bow of a small boat.

All aqueous samples were collected in acid-washed and rinsed

polypropylene or Teflon bottles. Samples which were to be stored before analysis were quickly frozen with dry ice, and maintained in this state until the analysis was performed. Tests of this preservation method indicated that samples can be stored for several weeks without change.

No pretreatment of natural water samples is necessary, as the analytic technique is sufficiently sensitive to measure ambient concentrations. To distinguish between dissolved and total arsenic, the samples were filtered through 0.45 μ membranes.

Particulates

The acid/ NaBH_4 reduction reaction discussed above allows direct analysis of the labile fraction of arsenic species associated with inorganic and humic type organic-matter particulates. For these analyses, a slurry of a known amount of filterable solids and distilled water was made, and was then treated as an aqueous sample. In this manner, the natural concentration of the arsenic species were measured.

Atmospheric Samples

Atmospheric particulate samples were collected on two thicknesses of Whatman #41 filter paper using high-volume air samplers similar to those described by Duce *et al.* (1976). Total arsenic content was determined of a nitric-acid digest of the filter paper and particulates by adding an aliquot of the solution to distilled water in the reaction vessel, and following the procedures for aqueous samples.

Drawing a high volume of air through a glass tube packed with silver-plated glass beads also allows collection of atmospheric arsenic. Although this technique is primarily for the collection of volatile arsenicals (Johnson and Braman, 1975), it may also be used to collect

gaseous and particulate arsenicals together, to determine the speciation of the arsenicals. The adsorbed and filtered arsenic compounds are dissolved in a mildly alkaline rinsing solution, and analysed as an aqueous sample.

Sampling Program

The investigation was made during the period from September 1975 through September 1976. The selected rivers were sampled at monthly intervals. The Satilla River estuary was sampled in November 1975, and the Ogeechee and Savannah River estuaries were sampled in March and June, 1976, respectively. The upper reaches of the St. Johns River, from Lake Monroe, Florida to Jacksonville, Florida, were sampled in March, 1976, from the seven highway bridge crossings over the St. Johns.

Two sampling cruises were made in the Georgia Bight and adjacent oceanic waters; the R/V Columbus-Iselin cruise of March, 1976, and the R/V Blue Fin cruise of September, 1976.

Dissolved Organic Carbon (DOC) Analyses

DOC was determined by the method of Menzel and Vaccaro (1964), on 0.45 micron membrane-filtered samples. Precision, based on replicate analyses, is $\pm 10 \mu\text{g C}$ in the range of 0 - 500 $\mu\text{g C}$.

Fractionation of Organic Matter (Ultrafiltration)

Amicon Corporation's ultrafiltration cells and membranes were used to fractionate the dissolved organics in natural-water samples. Amicon's recommended procedures were followed. It should be noted that the molecular-weight cut-off values assigned by Amicon to their various membranes are operational definitions only. The molecular-weight range retained or passed by any membrane is dependent on the type and shape of the molecular structure; hence the assignments are necessarily nominal.

CHAPTER III

RESULTS AND DISCUSSIONS

Arsenic in the Riverine Environment

Figure 2 and Table 1 contain the dissolved arsenic concentration data for samples from ten major southeastern rivers, obtained at approximately one month intervals during the period September 1975 to September 1976. Arsenate, As^{5+} , is the only detectable dissolved arsenic species in the river waters. The most notable feature of the arsenic variation over the year is the low concentration in most rivers during the months November to January. Aside from that feature the arsenic concentration is generally constant about a mean, for each river.

The occurrence of low arsenic concentration during the late fall and early winter months is similar to the occurrence of low iron concentrations in southeastern rivers observed by Windom (1975) for the same season. Seasonally lowered metal concentrations have also been observed by Troup and Bricker (1975), in the Susquehanna River. Such a feature suggests that riverine metal concentrations are regulated by the seasonally variable, interrelated factors of precipitation, runoff, and river discharge. For the Satilla River, there exists a loose positive relationship between river discharge rate and arsenic concentration (Figure 3). The relationship supports the idea that high dissolved metal concentrations occur in rivers subsequent to periods of high precipitation. High precipitation and runoff conditions probably

Figure 2. Dissolved Arsenate Concentrations in Major
Southeastern Rivers

RIVERINE ARSENIC CONCENTRATIONS

Figure 3. Relationship Between Satilla River Discharge
and Arsenic Concentration

ARSENIC LEVEL AND RIVER DISCHARGE RATE
SATILLA RIVER — '75-'76

TABLE 1. Dissolved Arsenate Concentration in Major Southeastern Rivers (ug/l)

River	1975					1976						
	S	O	N	D	J	F	M	A	M	J	J	A
St. Johns	.52	.40	.26	.28	.31	.63	.55		.42	.42	.56	.65
Satilla	.52	.36	.25	.28	.33	.51	.32	.37	.30	.44	.36	.55
Altamaha	.31	.23	.04	.16	.21	.47	.22	.24	.14	.15	.14	.22
Ogeechee	.41	.45	.08	.19	.22	.20	.18	.25	.28	.28	.22	.30
Savannah	.47	.43	.13	.17	.33	.46	.36	.36	.21	.19	.22	.20
Cooper	.41	.47	.12	.15	.18	.19	.35	.27	.22	.26	.24	.42
Santee	.04	.08	.08	.17	.16	.31	.18	.17	.17	.16	.15	.18
Black	.53	.31	.20	.25	.15	.40	.36	.50	.40	.47	.35	.74
PeeDee	.19	.13	.07	.25	.11	.32	.24	.25	.20	.32	.20	.23
Cape Fear	.24	.20	.16		.32	.36	.49	.56	.46	.39	.47	

TABLE 2. RIVER DISCHARGE DATA

RIVER		MEAN ANNUAL DISCHARGE ^(c) km ³ /year	ARSENIC CONCENTRATION ug/l	ARSENIC DISCHARGE (ug x 10 ¹¹ /yr)
St. Johns	*(b)	6.4 (1.4)	.45	28.8 (6.3)
Satilla	*(b)	2.2 (0.2)	.38	8.2 (0.8)
Altamaha	*(a)	12.0	.21	25.2
Ogeechee	*(a)	2.1	.25	5.3
Savannah	(a)	13.0	.29	37.7
Cooper	*(a)	13.2	.27	35.6
Santee	(a)	0.6	.15	0.95
Black	(b)	0.9	.39	3.7
Pee Dee	(a)	16.1 (7.6)	.21	33.8 (16.0)
Cape Fear	(a)	<u>5.6 (1.8)</u>	.37	<u>20.7 (6.7)</u>
TOTAL		72.1 (11.0)		200 (30)

* Mean annual discharges are long term averages (18-42 years) since current water year records are not available; all other figures are for the 1975-1976 water year (taken from current unpublished and past published water records (Water Resources Data) of the U.S. Geological Survey, U.S. Dept. of the Interior).

(a) Piedmont Plateau rivers

(b) Coastal Plain rivers

(c) Includes flows of unsampled tributaries and adjacent small streams.

Values in parentheses gives the flow attributed to these.

NOTE: 1 km³ = 10¹² liters

result in more efficient flushing of soils, than do dryer conditions. However, the correlation between discharge and arsenic content is poor for the other non-dammed rivers.

For purposes of flux calculations, an average yearly arsenic concentration was calculated for each river (Table 2). It is evident that rivers with drainage basins primarily in the crystalline Piedmont terrain (Piedmont Plateau) have lower arsenic concentrations (average 0.23 $\mu\text{g/l}$) than those having drainage basins restricted to the Coastal Plain sedimentary terrain (average 0.41 $\mu\text{g/l}$). The Cape Fear is the only river which does not fit into this scheme. Although it is a Piedmont river, the arsenic concentration is high (0.37 $\mu\text{g/l}$). The Cape Fear flows through a rather heavily and diversely industrialized area, and the high arsenic levels, therefore may be anthropogenic. In general, though the riverine arsenic concentrations reported here are similar to the lowest values found in the literature for other world rivers.

Total dissolved organic carbon (DOC) concentrations of the river samples (Table 3) vary similarly to arsenic concentrations through the year, although marked low winter values occur only in the Cape Fear, Pee Dee, Black, and Santee Rivers. More marked are the exceptionally high values in the Satilla, Altamaha, Ogeechee and Savannah Rivers during the summer of 1976 (values marked by * in Table 3). With the exception of these high concentrations, the DOC values correlate highly with the corresponding arsenate concentrations of Table 1. The positive relationship, described by the equation

$$\{\text{DOC}\} = 10.6 \{\text{As}\} + 5.7$$

Table 3. DOC Concentrations in River Waters

(mg/liter)

River

St. Johns	8.2	12.0	15.0	12.0	10.0	7.5	7.6	7.0	16.0	8.1	20.0	15.0
Satilla	23.0	18.0	16.0	12.0	-	7.0	9.0	11.0	6.0	-	23.0*	45.0*
Altamaha	11.0	8.5	4.4	7.8	-	8.0	5.2	5.2	21.0*	15.0*	5.0	10.0
Ogeechee	11.0	10.0	8.5	7.2	-	8.5	7.1	6.1	80.0*	25.0*	13.0*	25.0*
Savannah	4.6	5.4	5.4	6.0	-	9.0	9.2	8.0	21.0*	7.6	12.0	10.0
Cooper	8.3	-	2.4	5.4	4.0	4.8	-	5.4	7.1	12.0	5.4	7.6
Santee	10.0	-	3.7	6.0	8.0	11.0	15.0	7.5	9.2	13.0	13.0	1.5
Black	15.0	-	13.0	2.8	2.1	11.0	4.4	8.0	6.0	17.0	16.0	15.0
Pee Dee	9.5	-	6.5	5.0	2.1	-	6.6	9.8	9.6	13.0	9.2	9.6
Cape Fear	-	13.0	13.0	6.6	3.5	4.8	11.0	11.0	-	12.0	9.2	8.0

* see text for comment

has a correlation coefficient of .39, and is significant at the .001 level. The covariance of DOC and arsenate concentrations is also strong for contemporaneously sampled waters from various locations along the upper, fresh-water reaches of an individual river, the St. Johns (Figure 4). The data points are numbered, increasing upstream, according to sample location. In general, the swampy, uppermost reaches of the river have the highest arsenic and organic-matter concentrations.

It will be shown in the next section that organic matter-arsenic complexes exist in riverine (and estuarine) waters. This result, together with the observed covariance of arsenate and DOC, suggests that riverine arsenate concentration is an imposed quality. Furthermore, complexation with organic matter apparently maintains arsenate at the observed dissolved concentration. If arsenate concentration is an imposed parameter, then the high springtime DOC values in some rivers, which correspond to relatively low arsenate concentrations, must reflect either excess organic matter or preferential organic matter - metal complexation.

Another implication of the apparent causal relationship between organic carbon and arsenate concentrations is that some process other than precipitation of the least soluble, crystalline, arsenic compound is most important in controlling the upper limit of dissolved arsenate concentration. The observed dissolved arsenate concentrations are far below saturation with respect to the least soluble compound (Ferguson and Gavis, 1972). Hence it is likely that processes such as coprecipitation with, and adsorption to, other solid species (iron hydroxides, for instance) remove arsenate from solution at concentrations below

Figure 4. Relationship Between DOC and Arsenic in
St. Johns River

ARSENIC vs. DOC
- ST. JOHNS RIVER

saturation.

From the mean annual discharges of the ten major rivers which were sampled and analysed monthly, and their average arsenic concentrations, the total river transport of this element to the study area can be determined (Table 3). Assuming that arsenic behaves conservatively as it passes through the estuaries, the annual input to the Georgia Bight is 20×10^{12} $\mu\text{g/yr}$ arsenic. The assumption of conservative behavior of arsenic at the salt-water interface is discussed in the following section.

Arsenic in the Estuarine Environment

The reactive nature of dissolved arsenic in the estuarine environment must be determined in order to estimate the net riverine arsenic flux to the Georgia Bight. The mixing behavior of arsenic was examined in the Ogeechee, Savannah, and Satilla River estuaries.

Reactivity

Arsenic is apparently unreactive in the estuarine environment. This is evident from the relationship between dissolved arsenate ion (As^{5+} , the predominant arsenic species in river waters) and salinity in the Ogeechee, Satilla, and Savannah River estuaries (Figure 4 and Table 4). The salinities plotted on the horizontal axis are indicative of the extent of mixing of riverine and oceanic waters, and represent progressively seaward locations from left to right.

The linearity of the curves indicate that dissolved arsenic is subject only to simple physical mixing of two end-member water types; fresh water, with an arsenic concentration of about $0.2 \mu\text{g/l}$, and saline, coastal waters, with an arsenic concentration of 0.7 to $1.0 \mu\text{g/l}$. Note

Figure 5. Estuarine Mixing Curves for Arsenic

ESTUARINE MIXING OF ARSENIC

Table 4. Estuarine Dissolved-Arsenate Data

<u>Estuary</u>	<u>‰ Salinity</u>	<u>Organic Molecular Weight Fraction</u>	<u>µg/l Arsenate</u>	<u>mg/l DOC</u>
Ogeechee	0	whole sample	.19	55
		>100,000 M.W. isolated	nd	7
		>10,000 M.W. removed	.19	40
		>2,000 M.W. removed	.15	35
	2	whole sample	.29	49
		>10,000 M.W. removed	.29	--
		>2,000 M.W. removed	.19	--
	6	whole sample	.44	43
		>100,000 M.W. isolated	nd	nd
		>10,000 M.W. removed	.44	35
		>2,000 M.W. removed	--	30
	10	whole sample	.59	39
		>100,000 M.W. isolated	nd	nd
		>10,000 M.W. removed	.59	--
		>2,000 M.W. removed	--	27
	14	whole sample	.72	37
		>100,000 M.W. isolated	nd	nd
		>10,000 M.W. removed	.72	27
		>2,000 M.W. removed	.35	24
	18	whole sample	.84	30
		>100,000 M.W. isolated	nd	nd
		>10,000 M.W. removed	.84	25
		>2,000 M.W. removed	--	21
	22	whole sample	1.00	26
		>100,000 M.W. isolated	nd	nd
		>10,000 M.W. removed	1.00	20
		>2,000 M.W. removed	.45	17

NOTE: (--) = not tested

(nd) = not detected (i.e. <0.02 µg/l for As, <1 mg/l for DOC)

(Table 4 is continued on next page...)

Table 4. Estuarine Dissolved-Arsenate Data (continued)

<u>Estuary</u>	<u>Salinity</u>	<u>Organic Molecular Weight Fraction</u>	<u>µg/l Arsenate</u>
Savannah	0	whole sample	.15
	2		.19
	4		.27
	6		.34
	8		.39
	10		.45
	12		.51
	15		.61
	18		.72
	20		.78
Satilla	0	whole sample	.11
	2		.17
	4		.22
	6		.29
	8		.35
	10		.41
	12		.46
	15		.56
	22		.74

the inset, which shows, schematically, the types of curves indicative of non-conservative mixing (Boyle *et al.*, 1974). If dissolved arsenic were lost to the sediments in the estuary, a loss-type curve would obtain; alternatively, if arsenic dissolved from the sediments in the estuary, a gain-type curve would prevail.

Conservative mixing of arsenate through the estuaries is somewhat contradictory to what might be expected, since removal mechanisms are known to influence other dissolved elements in the estuarine environment. In particular, precipitation of ferric hydroxides and organic matter, and potential uptake by suspended particles (including micro-organisms) are unimportant with regard to the distribution of arsenic. Each of these removal mechanisms was considered to determine how they are rendered ineffective, as discussed below.

The Ogeechee River estuary was chosen for further investigation because it is the least complex, and hence most ideal for a study of mixing phenomena, as Boyle *et al.* (1974) and Sholkovitz (1976) have pointed out.

Potential Removal Mechanisms

Precipitation of Ferric Hydroxides. It is well documented that iron precipitates as ferric hydroxide or hydrated oxide-organic complexes at the salt-water interface (Windom, 1975; Boyle *et al.*, 1974). It is also well known that arsenate ion is actively scavenged by ferric hydroxide (*cf.* the coprecipitation technique for concentrating arsenic prior to analysis). If arsenate were present in estuarine waters as the free ion, coprecipitation with iron should occur.

Arsenic undergoes no significant complexing interactions with

any inorganic radicals other than OH^- (Ferguson and Gavis, 1972), and organic matter - arsenic complexes have not been previously documented.

Evidence that organic matter - arsenate complexes do exist, however, was obtained by use of ultrafiltration. With this technique, it is possible to remove successively various size fractions of dissolved organic matter. If arsenic is complexed by any of the organic fractions, it will be removed along with the organics, leaving the filtrate deficient. Figure 6 shows the results of the arsenic analyses performed on fractionated and unfractionated Ogeechee River estuary samples. The lower curve was derived by analysing the filtrates of a 2,000 (nominal) molecular weight cut-off membrane. The filtrates of >10,000 molecular weight membranes were not deficient in arsenic. The difference between the two curves apparently reflects the complexation of arsenic by dissolved organic matter of low molecular weight, nominally less than 10,000 molecular weight units.

The DOC levels in the Ogeechee estuary at the time of sampling were very high compared to the bulk of the values reported in Table 2. However, the arsenic complexing behavior itself is probably not atypical. The above results suggest that arsenic is not present as the uncomplexed, free metal ion. It follows, then, that arsenic may remain unreactive with respect to ferric hydroxide colloids and floccules by virtue of its complexation with light organic matter.

Alternatively, one may consider the possibility that ferric hydroxide colloids are somehow rendered non-reactive towards dissolved ionic constituents (including arsenate). Koenings and Hooper (1976) have shown that in lake water, the presence of colloidal organic matter

Figure 6. Estuarine Mixing Curve for Arsenic in Fractionated
Ogeechee River Samples

ARSENIC IN ORGANIC-FRACTIONATED
OGEECHEE ESTUARY
WATERS

reduces the ionic activity of ferric colloids. This in turn reduces the extent of interaction between ferric colloids and phosphate. Assuming that the largely chemically similar orthophosphate and arsenate ions behave similarly in this respect, Koenings and Hooper's results may apply to the present study. Colloidal organic matter is certainly present in the southeastern estuaries (Beck *et al.*, 1974). It is unknown whether or not the differing ionic strengths, pH, and major-ion chemistries of lake and estuarine environments would modify the colloidal organic matter interference. Colloidal organic matter (COM) undergoes essentially complete flocculation and precipitation in the estuaries, quite unlike COM in lakes. However, due to physical forces, organic matter is repeatedly resuspended, maintaining a variable concentration of suspended organics in the water column. It is perhaps reasonable to assume that both COM interference with ferric hydroxide ionic activity, and low-molecular-weight organic matter - arsenate complexation act in concert to effect a mutual ferric hydroxide - arsenate nonreactivity.

Precipitation of Organic Matter. The above argument leads directly into consideration of the estuarine mixing behavior of dissolved organic matter. It can be demonstrated that some organic matter flocculates and is lost from the dissolved state in the estuary, in like manner to iron. The uppermost curve of Figure 7 (data is tabulated in Table 4) represents the mixing behavior of total DOC in the Ogeechee estuary. The statistically significant regression is a loss-type curve, indicating removal of DOC. The lowermost curve, just above the horizontal axis, represents the concentration of large (greater than 100,000 molecular weight) organic matter as a function of salinity. It is evident that

Figure 7. Estuarine Mixing Curves for Ogeechee River Organic-matter Fractions

DOC IN ORGANIC FRACTIONS

-OGEECHEE ESTUARY

this fraction undergoes essentially total loss at low salinity. If the lowermost curve is subtracted from the upper curve, the result is a linear (conservative) curve. The two intermediate curves, also linear, are derived from the filtrates of 10,000 and 2,000 molecular weight membranes. These results imply that DOC is unreactive in the estuary, except for the very heaviest fraction. Since arsenic is complexed only by much lighter organics, it is not affected by the precipitation of the heavy fraction.

Similar results are reported by Sholkovitz (1976) who shows that only a few percent of the dissolved organic matter present in Scottish river water undergoes removal (flocculation) when mixed with seawater. Reuter and Perdue (1977) state that dissolved organic matter in river waters is mainly comprised of material resembling soil fulvic acids, and that the remaining few percent consists of higher molecular weight material resembling soil humic acids. This high-molecular-weight fraction, which probably corresponds to the largest organic matter fraction in the present study, and to the flocculable material of Sholkovitz, is intimately related with iron colloids. The removal of the combined product, termed "iron-humates", at the estuary, was proposed by Sholkovitz (1976) to be an important factor in the non-conservative behavior of manganese, aluminum, and phosphorous, and possibly other trace elements. The apparent conservative behavior of arsenate, however, indicates that not all trace elements behave similarly in this respect.

Particle Uptake. In order to rigorously establish the mixing behavior of arsenic, both the reactant and product approaches of Sholkovitz (1976) have been taken in analysing the Ogeechee River estuary samples.

That is to say, both the reactants (dissolved species) and the products (particulate species) of the potential removal processes have been examined. In the estuary, suspended particulates and plankton are potential sites of arsenic uptake, and hence these were studied.

For this study, no attempt was made to separate biota from particulates. Rather, total suspended materials collected on 0.45 micron filters were analysed. The combined effects of biological uptake, adsorption, and coprecipitation with both iron and organics, therefore, determine the nature of arsenic associated with this mixed solid phase.

In addition to inorganic arsenic, a methylated form of arsenic was found to be present (Table 5). The existence of methylated arsenic indicates that uptake and biomethylation probably has occurred, dimethylarsenious acid being the product (Braman, 1973). Braman has pointed out however, that dimethylarsenic is very resistant to oxidation, and hence once formed, could have a considerable residence time in natural waters. The lack of trend of dimethylarsenic with increasing salinity (Figure 8) therefore suggests that the methylation occurs upstream, and the methylated form simply persists through the estuary.

The amounts of dimethylarsenious acid associated with the particulates are only a few percent of the total dissolved arsenic load. It is therefore clear that processes resulting in methylarsenic formation are quantitatively unimportant during estuarine transport.

The constancy of inorganic arsenic levels shown in Figure 9 suggest that, on the whole, arsenic associated with particulate matter is non-labile in the estuary. These data are therefore in agreement with the conservative behavior indicated by the mixing curves shown in Figure 5.

Table 5. Arsenic in Particulate Material, Ogeechee River Estuary

<u>‰ Salinity</u>	<u>µg Arsenate-As/gram</u>	<u>µg Dimethylarsenic-As/gram</u>
0	9.2	1.1
2	9.0	3.5
6	7.8	0.8
10	8.2	3.6
14	12.6	1.4
18	9.3	1.9
22	7.2	0.4

Figure 8. Arsenic Species Associated with the Solid Phase
in the Ogeechee River Estuary

OGEECHEE ESTUARY

ARSENIC IN PARTICULATE MATERIAL (SUSPENSIDS)

The total arsenic concentrations associated with the particulate phase in the estuary fall within the range observed by Crecelius (1975) for two Washington State rivers which have dissolved arsenic concentrations and suspended particulates similar to the Ogeechee River. This would again tend to indicate that no arsenic is exchanged between the solid and dissolved phases at the estuary.

Atmosphere-to-Ocean Arsenic Flux

Duce *et al.* (1976) have shown that arsenic, as well as a number of other elements, is introduced to the sea surface from an atmospheric reservoir *via* particulate fallout and rain. They formulated a model, partly based upon the atmospheric studies of Cambray *et al.* (1975), who have assigned an effective particle deposition velocity to several elements. For arsenic, this deposition velocity is 0.26 cm/sec, which means that 0.26 cm³ of air is swept clean of arsenic-containing particulates due to fallout each second, over each cm² of ocean surface. This allows estimation of the arsenic contribution to the sea surface by dry fallout, if the atmospheric arsenic concentration is known. The model also provides for the removal rate increase due to rain washout; the dry fallout flux is multiplied by 3, on the empirically derived assumption that rainfall removes particulates from the atmosphere at twice the yearly dry fallout rate. This model was used to estimate atmospheric transport of arsenic to the waters of the study area. The treatment is crude, because many variables cannot be taken into account. The result should therefore be looked upon only as an order-of-magnitude estimate. As will become evident later, the atmosphere-to-ocean arsenic

flux is relatively unimportant, thus the lack of precision in the estimate is not serious.

Atmospheric particulate samples were taken along the southeast coast during September, 1976. The total particulate arsenic concentrations of the atmosphere along the ship's tracks (Figure 9) are given in Table 5. Zinc and iron analyses of the samples were also performed (by R. Smith, Skidaway Institute) and are reported.

Arsenic correlates with both zinc (coefficient of determination, $r^2 = 0.75$) and iron ($r^2 = 0.50$) at the .002 and .02 significance levels, respectively. The covariences suggest that the elemental concentrations are controlled by a common factor. Duce *et al.* (1976) have concluded that the atmospheric iron, and probably a significant fraction of the atmospheric zinc in the Bermuda area are derived from the North American continent. Hence, the correlations of these metals with arsenic may indicate that the arsenic in the Georgia Bight atmosphere is also derived from continental sources.

Air samples were also collected using silvered beak-packed tubes and no pre-filtering during the periods in which filter samples W.F. 2, W.F. 3, W.F. 4, W.F. 5, W.F. 6 and W.F. 11 were obtained in order to examine the speciation of the atmospheric arsenic. Analyses of these samples yield atmospheric arsenic concentrations of 1.1, 1.4, 0.81, 1.3, 0.13, and 0.13 ng/m^3 inorganic arsenic, respectively. The absolute arsenic concentrations of these samples are not significant because of the poor particle collection efficiency of the tubes, compared to the Whatman filter technique. However, the analyses do reveal that all the collected arsenic was inorganic. Further studies are required to determine

Figure 9. Atmospheric Sample Locations

Table 6. Atmospheric Concentrations of Arsenic and some Trace Metals

<u>Sample #</u>	<u>ng/m³</u> <u>Arsenic</u>	<u>ng/m³</u> <u>Zinc</u>	<u>ng/m³</u> <u>Iron</u>
W.F. 1	0.2	4.6	63
2	4.3	15	460
3	2.2	12	500
4	*	3.7	330
5	1.1	5.7	370
6	0.16	7.2	310
7	6.3	15	510
8	0.48	3.4	220
9	0.48	6.0	150
10	0.46	8.5	150
11	<u>1.2</u>	<u>10</u>	<u>140</u>
average	1.7	8.3	291

*insufficient sample for arsenic analysis

the phase distribution of atmospheric arsenic.

The study area atmospheric arsenic concentrations (W.F.'s 1, 2, 10, and 11) vary over an order of magnitude, from 0.2 ng/m^3 to 4.3 ng/m^3 , and average 1.5 ng/m^3 . The average of all samples in Table 7 is 1.7 ng/m^3 . For more isolated oceanic regions, Duce *et al.* (1976) find a yearly variation of from 0.03 to 0.96 ng/m^3 , with an average value of 0.17 ng/m^3 , or approximately one order of magnitude less arsenic than that of the study area. The Bight-atmosphere iron and zinc concentrations also average higher than the Bermuda concentrations; at Bermuda, iron averages 100 ng/m^3 , and zinc averages 2.5 ng/m^3 . Although the winds were largely from the northeast during the sampling period, it again appears that continental proximity influences the atmospheric chemistry of arsenic over the continental shelf.

Assuming that the arsenic-containing particulates are soluble, every second the arsenic in $1.7 \times 10^{14} \text{ cm}^3$ of air is added to the Bight waters (*ie.* $0.26 \text{ cm}^3/\text{cm}^2\text{sec}$ fallout rate, over $6.4 \times 10^4 \text{ km}^2$). Annually then, $5.4 \times 10^{21} \text{ cm}^3$ of atmosphere is effectively swept clean of particulates due to fallout. Hence, if the atmospheric arsenic concentration is 1.5 ng/m^3 ($1.5 \times 10^{-9} \text{ } \mu\text{g/cm}^3$), $8.1 \times 10^{12} \text{ } \mu\text{g}$ are introduced yearly to the shelf waters by dry fallout alone. Then adjusting for washout according to Duce's model (3 times the dry fallout), the total atmospheric transport to the Bight is $24.3 \times 10^{12} \text{ } \mu\text{g/year}$.

It is interesting to compare the above rate with the atmospheric transport rate calculated using a different approach. Rain water was collected at the beginning and at the end of a week of rainy weather from 10/19/76 to 10/26/76 at Skidaway Island. The weather had been dry

for more than two weeks preceeding the collections. Analyses of the two samples yielded arsenic concentrations of 0.33 $\mu\text{g/l}$ (10/19/76) and 0.03 $\mu\text{g/l}$ (10/26/76), As^{5+} being the only detectable species. If one assumes that the average of these two concentrations, 0.18 $\mu\text{g/l}$, represents the mean arsenic concentration of rain water in the study area, and that 90 km^3/yr of rain falls on the shelf (or 136 cm/year over $6.4 \times 10^4 \text{ km}^2$), then approximately $16.2 \times 10^{12} \mu\text{g}$ is the annual arsenic contribution to the Bight due to washout. Now, according to Duce *et al.* (1976), arsenic in rain comprises only 2/3 of the total atmosphere-to-ocean flux. Therefore, by adjusting for the dry fallout component (multiplying by 1.5), a total flux of $24.3 \times 10^{12} \mu\text{g/year}$ arsenic is obtained. This rate is in perfect agreement with that derived in the preceeding paragraph. However, the degree of the agreement is somewhat fortuitous, since the average rainwater arsenic concentration used in the calculation is based on only two samples. For instance, Kanamori and Sugawara (1965) found rainwater-arsenic concentrations of 0.6 $\mu\text{g/l}$ on the open ocean, indicating that this parameter can vary considerably. Nevertheless, the two methods probably yield a significant order-of-magnitude estimate of the atmospheric arsenic input to the Bight waters.

Influence of Intrusions on the Arsenic

Content of Continental-Shelf Waters

Intrusions of extra-continental shelf waters are a major mechanism of water exchange between the continental shelf and the open ocean. Figure 11, taken from Blanton (1971), schematically depicts the intrusion process. Blanton and Atkinson (personal communication) have estimated

that the intrusions occur about every two weeks for 6 months of the year, or 13 intrusions occur per year. The intrusion volumes are apparently on the order of one-fifth the shelf water volume, based on measurements of density, salinity and temperature. The water mass exchange, then, is $1/5 \times 1915 \text{ km}^3 \times 13 \text{ intrusions/year}$, or $4980 \text{ km}^3/\text{year}$.

The intruded water is derived from deep water in the Gulf Stream, adjacent to the continental slope, where the total dissolved arsenic concentration is about $1.5 \text{ } \mu\text{g/l}$ (discussed in the following section). The arsenic input to the Bight waters due to intrusions is therefore $4980 \text{ km}^3/\text{year} \times 10^{12} \text{ liters/ km}^3 \times 1.5 \text{ } \mu\text{g/l}$, or $7.5 \times 10^{15} \text{ } \mu\text{g/year}$.

Concentration and Distribution of Arsenic in Continental-Shelf and Adjacent Waters

The distribution of some distinct water masses in the Georgia Bight are revealed by the temperature-contrast enhanced, satellite photo (figure 11) and by the derived line drawing (Figure 12). The presence of warm Gulf Stream and cool coastal waters are clearly seen. Some features of the Gulf Stream are notable, especially the partial entrainment of a lens of cooler intermediate water midway between Jacksonville, Florida and Wilmington, N.C., and the pronounced semi-permanent seaward deflection of the Stream just south of Wilmington. Other similar photos taken at different times show that the Gulf Stream has marked variations in position, migrating in an east-west sense.

Extensive sampling of Georgia Bight and adjacent oceanic waters was accomplished from the R/V Columbus-Iselin during March, 1976, and from the R/V Blue Fin during September, 1976 (Figure 13). The results

Figure 11. Temperature-contrast Enhanced, Satellite-photo
of the Study Area

ENHANCED SATELLITE IMAGERY

FOR GEORGIA BIGHT WATER TEMPERATURE CONTRAST

(DECEMBER 74)

- COOL
- INTERMEDIATE
- WARM (GULF
STREAM)

Figure 13. Study-area (Oceanic) Sampling Stations

OCEAN - SAMPLE STATIONS

the analyses of these samples (Table 7) were used to establish the As^{5+} distribution in the study area surface waters (Figure 14). In general, the arsenic species concentrations reported here are in accord with those found in the literature. Arsenate predominates with concentrations around 1 $\mu\text{g/l}$ (as As), while arsenite and dimethylarsenic concentrations are approximately an order of magnitude less. The pattern of arsenic distribution has features similar to those of the water mass distribution (Figure 12), suggesting that the arsenic concentrations are largely controlled by simple physical mixing. Gulf Stream waters apparently contain the highest arsenic concentrations, and are diluted by the low arsenic content of river-influenced coastal waters. Although somewhat different here than in the temperature-contrast photo, partial entrainment of inshore water into the Gulf Stream, and the pronounced seaward deviation of the Gulf Stream are reflected.

Vertical profiles of arsenic concentration were obtained by analyses of samples collected at selected Gulf Stream and Sargasso Sea locations. Samples were collected from the surface (approximately 30 cm. depth), from near the lower boundary of the mixed layer (as defined by a bathythermograph trace), and at one or two deeper positions (200 m to 500 m). Due to the shoal nature of the shelf (average depth 30 m), and to the significant wave and current activity, shelf waters are only occasionally stratified. More commonly, as was the case for all sampling excursions during this investigation, the Bight waters were vertically homogeneous (*ie.* isothermal), and hence the arsenic concentrations are constant with depth.

Concentration profiles (Figure 15) indicate that As^{5+} concentrations

Table 7. Concentrations of Arsenic Species in Oceanic Waters

Sample # ^(a)		$\mu\text{g/l}$ <u>Arsenate</u>	$\mu\text{g/l}$ <u>Arsenite</u>	$\mu\text{g/l}$ <u>Dimethylarsenic</u>
C.I.	1	1.13 (s)	.04 (s)	nd ^(b)
	2	1.43 (s)	.04 (s)	nd
	3	1.13 (s)	.14 (s)	nd
		0.99 (250 m)	.09 (250 m)	nd
		1.13 (500 m)	.09 (500 m)	nd
	4	1.18 (s)	.06 (s)	.05 (s)
	5	1.27 (s)	.06 (s)	.05 (s)
	6	1.14 (s)	.05 (s)	.19 (s)
		1.17 (200 m)	.05 (200 m)	.08 (200 m)
		1.38 (500 m)	.03 (500 m)	nd
	7	1.28 (s)	.02 (s)	.18 (s)
		1.37 (500 m)	.02 (500 m)	nd
	8	1.11 (s)	.03 (s)	.29 (s)
	9	1.16 (s)	.07 (s)	.06 (s)
	10	1.05 (s)	.06 (s)	.06 (s)
	11	1.10 (s)	.05 (s)	.19 (s)
	12	1.32 (s)	.05 (s)	nd
		1.54 (250 m)	.03 (250 m)	nd
		1.55 (500 m)	.03 (500 m)	nd
	13	1.20 (s)	.07 (s)	.06 (s)
	14	1.18 (s)	.06 (s)	.05 (s)
	15	1.13 (s)	.05 (s)	.23 (s)
		1.59 (500 m)	.04 (500 m)	.13 (500 m)
	16	0.98 (s)	.05 (s)	.05 (s)
	17	0.62 (s)	.03 (s)	.15 (s)
	18	1.14 (s)	.07 (s)	.06 (s)
	19	1.13 (s)	.15 (s)	.04 (s)
		1.13 (40 m)	.15 (40 m)	nd (40 m)
		1.06 (250 m)	.14 (250 m)	nd (250 m)
		1.60 (500 m)	.13 (500 m)	nd (500 m)
	20	1.23 (s)	.07 (s)	.06 (s)
	21	1.21 (s)	.06 (s)	.05 (s)
	22	1.06 (s)	.04 (s)	nd (s)
		1.04 (40 m)	.04 (40 m)	nd (40 m)
	23	1.29 (s)	.06 (s)	.29 (s)
		1.50 (500 m)	.07 (500 m)	.24 (500 m)
	24	1.20 (s)	.06 (s)	nd (s)
		1.41 (40 m)	.05 (40 m)	nd (40 m)
		1.79 (250 m)	.02 (250 m)	nd (250 m)
	25	1.29 (s)	.07 (s)	.05 (s)
	26	0.70 (s)	.04 (s)	.06 (s)
	27	1.16 (s)	.04 (s)	nd (s)
		0.97 (40 m)	.02 (40 m)	nd (40 m)

(continued)

Table 7. Concentrations of Arsenic Species (continued)

<u>Sample #</u>	<u>µg/l</u> <u>Arsenate</u>	<u>µg/l</u> <u>Arsenite</u>	<u>µg/l</u> <u>Dimethylarsenic</u>
C.I. 28	1.12 (s)	.07 (s)	nd
	1.15 (40 m)	.06 (40 m)	nd
	1.34 (250 m)	.04 (250 m)	nd
	1.31 (500 m)	.04 (500 m)	nd
29	1.19 (s)	.07 (s)	.06 (s)
30	1.13 (s)	.04 (s)	nd
	1.33 (250 m)	.04 (250 m)	nd
	1.34 (500 m)	.03 (500 m)	nd
31	0.82 (s)	.04 (s)	.05 (s)
32	0.95 (s)	.04 (s)	.04 (s)
33	1.12 (s)	.04 (s)	.04 (s)
34	1.16 (s)	.05 (s)	.04 (s)
35	1.27 (s)	.05 (s)	.04 (s)
36	1.17 (s)	.07 (s)	.06 (s)
37	1.18 (s)	.09 (s)	nd
	1.15 (40 m)	.07 (40 m)	nd
	1.14 (250 m)	.03 (250 m)	nd
	0.97 (500 m)	.04 (500 m)	nd
38	1.26 (s)	.06 (s)	nd
	1.65 (250 m)	.05 (250 m)	nd
	1.55 (500 m)	.05 (500 m)	nd
39	0.85 (s)	.04 (s)	.05 (s)
B.F. 1	0.79 (s)	nd	.06 (s)
2	0.68 (s)	nd	.08 (s)
	0.99 (9 m)	nd	nd
3	0.99 (s)	.06 (s)	.18 (s)
	0.96 (40 m)	.04 (40 m)	.20 (40 m)
	1.22 (200 m)	.03 (200 m)	.09 (200 m)

(a) C.I. = R/V Columbus-Iselin cruise samples

B.F. = R/V Blue Fin cruise samples

(b) nd = not detected

(s) = surface

Figure 14. Contour Plot of Arsenate Distribution in
Surface Waters.

ARSENIC (V) DISTRIBUTION
IN SURFACE WATERS
MARCH '76

■ <1.1 $\mu\text{G/LITER}$

▤ 1.1-1.2

□ 1.2-1.3

▥ >1.3

Figure 15. Vertical Profiles of Concentrations of Arsenic Species.

increase with depth, whereas As^{3+} concentrations decrease. This relative variation is shown clearly in a summary of the data (Figure 17), where surface- and deep-water (250 to 500 m) sample concentrations are plotted for three water masses.

Whereas Johnson and Pilson (1972) report that arsenite may comprise up to 20% of the total inorganic arsenic, the results of this investigation indicate that arsenite usually comprises less than 10% of the total. Furthermore, the average arsenate concentration of Sargasso Sea waters reported by Johnson and Pilson to be 2.1 $\mu\text{g/l}$, here is found to be less than 1.5 $\mu\text{g/l}$.

Thermodynamic considerations indicate that the ratio $\text{As}^{3+}:\text{As}^{5+}$ should be about 20 orders of magnitude less than that observed in this investigation (Woolson, in press). However, the observed profiles are consistent with the distribution of an element involved in the biological cycle, and hence suggests the following possible explanation for the observed distribution: (i) in the euphotic zone, As^{5+} (oxidized) is taken up by microorganisms (presumably phytoplankton), and during the process of metabolism, some unstable As^{3+} (reduced) is produced. In this way, a high concentration (by thermodynamic considerations) of As^{3+} is maintained in the mixed layer; (ii) at depth, productivity rapidly decreases, hence As^{3+} concentrations decline; (iii) upon its death, an organism sinks and undergoes bacterial destruction, such that oxidized As^{5+} is released to the water column, concentrating As^{5+} at depth.

Johnson (1972) has shown that bacterial reduction of arsenate to arsenite is possible in seawater, but further work is required before this process can be confirmed. The distribution of arsenic species with

Figure 16. Summary of Profile Data .

ARSENIC (V) vs ARSENIC (III)

MARCH '76

The distribution of arsenic species with depth in areas of high and of low production should be compared to determine the importance of the biological cycle.

In order to estimate the arsenic flux to the Bight *via* intrusions, an average value was required for the arsenic content of water at about 100 meters depth adjacent to the continental slope, whence the intrusions are derived. For this purpose, the total arsenic concentrations at 200 to 500 meters depth at stations adjacent to the slope (C.I.'s 6, 7, 12, 15, 19, 23, and 24) were averaged, yielding 1.58 $\mu\text{g/l}$. The 100 meter arsenic concentration would be less than this, yet higher than the surface concentration (average 1.41 $\mu\text{g/l}$), or approximately 1.5 $\mu\text{g/l}$.

Dimethyl arsenic is not everywhere detectable. However, when present it occurs usually at concentrations near the detection limit (approximately 0.04 $\mu\text{g/liter}$) and hence it is difficult in most cases to make meaningful interpretations concerning its distribution. However, dimethylarsenic concentrations of up to 0.30 $\mu\text{g/liter}$ are observed occasionally in surface waters, with lower concentrations in corresponding deep waters. Hence the methylated arsenical behaves similarly to As^{3+} , being more highly concentrated in the productive euphotic zone than at depth. Again the influence of the biological cycle is suggested.

Arsenic Residence Time in the Georgia Bight

It is now possible to determine the approximate residence time for arsenic in the Georgia Bight waters, and to describe the quantitatively most important transfer mechanisms. The residence time, τ , of arsenic is given by the equation:

$$\tau = \frac{\text{total mass of arsenic in Bight waters}}{\text{rate of arsenic input to the Bight}}$$

The calculation is of course crude, but the results are useful, nevertheless.

The total mass of arsenic in Bight waters is estimated by multiplying the average arsenic concentration by the volume (1915 km^3). The average Bight arsenic concentration is obtained simply by averaging the 14 (presumably typical) surface total-arsenic concentrations ($1.04 \text{ } \mu\text{g/l}$) measured for the shelf waters during the R/V Columbus-Iselin cruise (samples C.I. 7, 8, 9, 10, 11, 16, 17, 18, 22, 26, 27, 31, 32, and 39). Hence, the total mass of arsenic residing in the shelf waters is approximately $2 \times 10^{15} \text{ } \mu\text{g}$.

The rate of arsenic input is obtained by summing the riverine, atmospheric, and intrusive inputs discussed earlier. These are respectively $20 \times 10^{12} \text{ } \mu\text{g/year}$, $24 \times 10^{12} \text{ } \mu\text{g/year}$, and $7.5 \times 10^{15} \text{ } \mu\text{g/year}$. It becomes evident that only the input due to intrusions is significant, and that the rate of arsenic input is therefore on the order of $7.5 \times 10^{15} \text{ } \mu\text{g/year}$. Hence, the residence time of arsenic in the Bight waters is $\tau = 0.27 \text{ year}$.

Preliminary calculations for copper, mercury, nickel, and zinc, based on as yet incomplete data from ongoing research by H.L. Windom, yield residence times of 0.22, 0.31, 0.29, and 0.28 years, respectively. These results would tend to support the validity of the arsenic residence time calculation.

Calculation of the residence time of the Bight water mass itself will allow, by comparison with the arsenic residence time, an estimation of the reactivity of arsenic in continental-shelf waters. Water inputs

are rivers, rain, and intrusions. Total riverine water input (Table 2) is $72 \text{ km}^3/\text{year}$; total rainfall is $90 \text{ km}^3/\text{year}$, based on an average yearly rainfall of 136 cm (from U.S. Weather Bureau Statistics) over the Bight area; and the total volume of intruded water is $4980 \text{ km}^3/\text{year}$. This gives a total water-mass input of $5142 \text{ km}^3/\text{year}$. Again, the predominance of intrusions over other input processes is apparent. The water mass residence time is therefore 0.37 year, which is in fair agreement with the arsenic residence time. This suggests that arsenic is largely unreactive in shelf waters. However, the approximate 40% deviation between the trace-element residence times and the water-mass residence time may indicate that a portion of the introduced elements is lost from the water column. Direct examination of continental-shelf particulate matter is required to determine the importance of uptake processes.

The riverine and atmospheric arsenic contributions are very similar, and both are unimportant compared to the input due to intrusions. In contrast, Windom *et al.* (1975) found that atmospheric mercury transport to the continental shelf waters was much greater than riverine transport. Furthermore, they conclude that variations in the mercury concentration of continental-shelf waters can be explained by seasonal variations in atmospheric input from continental sources. Although arsenic has, like mercury, some highly-volatile forms, atmospheric-arsenic contributions are less influential than atmospheric-mercury contributions in determining the composition of the Bight water. This is so, because aqueous-arsenic concentrations are about two orders of magnitude greater than aqueous-mercury concentrations. Hence, it is obvious that atmospheric input of a trace element will be important only if the ratio of atmospheric

concentration to aqueous concentration is high, as is the case for Hg,
but not for arsenic,

CHAPTER IV

CONCLUSIONS

The dissolved-arsenic content of rivers is apparently controlled by arsenic availability and by complexation with dissolved organic matter of low molecular weight. In the southeastern United States, Piedmont Plateau rivers generally contain less arsenic (average 0.23 μg arsenate-As per liter) than do Coastal Plain rivers (average 0.41 $\mu\text{g}/\text{l}$). The occurrence of complexes between dissolved organic matter and arsenate, together with the covariance of arsenate and dissolved organic carbon concentrations indicates that arsenate concentration is an imposed parameter in these fresh waters. The seasonal variations in arsenic concentrations are related to river discharge fluctuations, and probably reflect seasonal variations in the flushing efficiency of soils.

Arsenic, in all phases, species, and compartments, is largely unreactive in the estuarine environment. Arsenic is apparently prevented from coprecipitating with flocculating iron hydroxide by (i) the reduction of ferric-hydroxide ionic activity by interfering colloidal-organic matter, and by (ii) the non-availability of arsenate as a free ion due to complexation with dissolved-organic matter of low molecular weight.

Whereas the larger dissolved-organic fractions are lost to the sediments at the fresh-water/salt-water interface, the smaller organic-matter fractions are unreactive and pass through the estuary conservatively, with the complexed arsenic. Biological interaction with arsenic may

occur in the estuary, but it is unimportant from a mass balance point of view. Arsenic associated with particulate matter does accumulate in the sediments as the suspended matter settles, but little or no exchange between particulate and dissolved phases occurs.

Arsenic concentrations in the maritime atmosphere of the Georgia Bight are similar to those in non-urban coastal areas of Florida, but are one order of magnitude greater than those in remote oceanic regions, due to the proximity of continental sources. The contributions of atmospheric and riverine arsenic to the study area are similar, but both are unimportant compared to the influence of Gulf Stream intrusions.

The overwhelmingly important pathway of arsenic to the continental shelf waters is *via* mixing with intruded deep Gulf Stream water, originating from seaward of the continental slope. It is evident by this that cultural contributions would have to be increased by several orders of magnitude to significantly affect overall continental shelf arsenic concentrations. Similarities between the residence times of arsenic and of the water mass itself, as well as similarities between major features of the arsenic-distribution pattern and that of the water-mass distribution pattern indicate that dissolved arsenic is largely conservative in the Bight. Concentrations are controlled by simple physical mixing, with a superimposed, biologically-mediated, minor arsenic cycle.

The relationships among the oceanic arsenic species are consistent with a biologically-mediated minor cycle, involving uptake of arsenate in the euphotic zone, and the production of arsenite and dimethylarsenic. The deep-water release of arsenate upon the decomposition of pelagic, organic detritus produces a deep-water arsenate concentration maximum.

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