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GEOCHEMICAL ASPECTS OF ATMOSPHERICALLY TRANSPORTED TRACE METALS OVER THE GEORGIA BIGHT

A THESIS
Presented to
The Faculty of the Division of Graduate
Studies and Research
by
Ballard M. Mullins

MASTER

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Geophysical Sciences

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Georgia Institute of Technology

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SUMMARY

There has been considerable evidence in recent years that a significant portion of the trace metals reaching coastal waters are transported by the atmosphere. To better understand the significance of contributions to coastal waters, much more study is needed of trace metal concentrations in the nearshore atmosphere. The present study had the following three purposes:

1. To assess trace metal concentrations and enrichment factors in the nearshore atmosphere over the Georgia Bight between Charleston, South Carolina and Jacksonville, Florida
2. To determine the sources of the metals.
3. To evaluate the solubilities of some of the metals in seawater.

Atmospheric trace metal concentrations and enrichment factors generally decrease from Charleston to Jacksonville. Five metals (Cd, Zn, Cu, Ni, and Pb), were found to be anomalously enriched over the Georgia Bight.

Observations from this study suggest that seawater may influence Cu and Zn concentrations in Georgia Bight air.

Solubilities of Zn and Cu in seawater are source dependent, as seen by correlation with EF_{crust}. No

significant solubility of Ni in seawater was observed.

Yearly fluxes of eight trace metals from atmosphere to seawater in the Georgia Bight were estimated. These trace metal fluxes are comparable to fluxes in other areas along the east coast. The fluxes of Cu, Cd, and Zn make considerable contributions to dissolved metal levels in Georgia Bight water.

An attempt to use trace metal concentrations in Spanish mosses as a means of tracing sources of trace metals over the Georgia Bight was inconclusive.

CHAPTER I

INTRODUCTION

Purpose

The objectives of this study were as follows:

1. To determine concentrations and enrichment factors of trace metals in the atmosphere over the continental shelf in the vicinity of four major southeastern cities: Charleston, South Carolina; Savannah, Georgia; Brunswick, Georgia; and Jacksonville, Florida.

2) To determine as closely as possible the sources of the metals (e.g. urban-point sources, general continental sources, sea salt).

3) To evaluate the solubilities of some of the metals in seawater to determine their fate upon entry into the water column, and also to determine if solubility is in any way source related.

The Problem

Trace metals may reach continental shelf waters from several main sources. Among these are atmospheric transport, intrusions of offshore waters, and continental runoff (rivers, sewage outfalls, etc.). Studies in recent years have suggested that, for some metals, atmospheric inputs may be as important as continental runoff, or at least may constitute a significant percentage of continental runoff (Windom and Smith, 1978; Duce, Wallace, and Ray, 1976a). Investigations in the South Atlantic Bight by Windom and Smith (1978), suggested that atmospheric inputs were about equal to river inputs for Cu, Zn, and Ni. The estimates by Duce, et al., (1976), for the New York Bight, indicated smaller but still significant percentages of atmospheric inputs compared to continental runoff. These studies suggest the need for more knowledge of trace metal concentrations in the nearshore marine atmosphere, particularly near urban areas.

Urban areas may be the source of many of the anomalously enriched atmospheric elements in the marine atmosphere due to the influence of industrial emissions, burning of fossil fuels, and automobile exhausts (Rahn, 1975; Lee and von Lehmden, 1973). There have been few studies, however, of trace metal concentrations in the marine atmosphere near coastal urban areas. Besides the studies mentioned above, Lazrus, et al., (1970), analyzed trace metal fluxes due to rainfall at Nantucket, Massachusetts. The Lazrus data will be discussed later in this report. C. C. Patterson of the California Institute of Technology has studied the atmospheric flux of Pb to the Southern California Bight for several years. Some of his data are summarized by Duce, et al., (1974).

The metals analyzed in this study include five of the most common anomalously enriched metals in marine air (Cd, Cu, Zn, Ni, Pb), as well as three metals commonly associated with crustal material (Fe, Al, Mn), and Na, which has a seawater origin. Thus, these metals are all of considerable vlue in determining sources.

Estimates were made in this study of fluxes of trace metals from atmosphere to water, in addition to estimates of solubilities of metals in seawater once they enter the water column. An attempt has also been made to relate concentrations of metals in continental shelf air to concentrations of metals in Spanish mosses in the source areas.

CHAPTER II

EXPERIMENTAL

Sample Collection

Atmospheric samples were collected on four cruises aboard the research vessel R/V Blue Fin, in September, October, and December, 1977, and in January, 1978. One group of samples was also collected on a cruise aboard the research vessel R/V Columbus-Iselin in November, 1977. Exact dates, times, and locations of samples are given in Tables 1-5, and shown later in Figures 1 and 2. The filters used to collect samples were acid-washed 20x25 cm double Whatman #41 filters. The filters were washed in 2 M reagent grade HCl according to the procedure described by Wallace, et al., (1977). Air was vacuum pumped through the filters at a flow rate of approximately 1 m^3/min., for approximately a four hour period. Filters were mounted in a PVC holder which was attached to a pipe extending forward from the bow of the ship. The height of the filter holder was approximately 10 meters above the water on both the Blue Fin and the Columbus-Iselin. The filter holder was connected to the air sampling pump by neoprene coated tubing.

Filters were placed in holders inside the cabin of the ship, and were handled only with clean polyethylene

Table 1. Locations and Times of Air Samples in Vicinity of Charleston, South Carolina (September 19-20, 1977)

Sample Number		Latitude	Longitude	Time	Sample Volume m^3	Wind Direction	Speed
C1	Start	32°25.4'	79°55.5'	1630-9/19	211	SSE	10 mph
	Stop	32°36.8'	79°34.5'	2030-9/19			
C2	Start	32°36.8'	79°34.5'	2233-9/19	205	SSW	15 mph
	Stop	32°53.0'	79°22.9'	0203-9/19			
C3	Start	32°55.5'	79°28.0'	0245-9/20	238	WSW	15 mph
	Stop	32°36.9'	79°40.0'	0645-9/20			
C4	Start	32°36.9'	79°40.0'	0650-9/20	217	WSW	15 mph
	Stop	32°29.5'	79°59.2'	1050-9/20			
C5	Start	32°34.4'	79°53.5'	1135-9.20	265	WSW	15 mph
	Stop	32°49.0'	79°37.0'	1535-9/20			

Table 2. Locations and Times of Air Samples in Vicinity of Savannah, Georgia (December 3-9, 1977)

Sample Number		Latitude	Longitude	Time	Sample Volume m^3	Wind	
						Direction	Speed
S1	Start	31°49.8'	80°50.4'	1010-12/8	262	NE	5-10
	Stop	32°05.0'	80°35.0'	1350-12/8			
S2	Start	32°13.4'	80°29.0'	1510-12/8	227	ENE	5-10
	Stop	31°55.5'	80°39.2'	1855-12/8			
S3	Start	31°55.5'	80°39.2'	1914-12/8	230	ENE	5-10
	Stop	31°43.4'	80°57.4'	2302-12/8			
S4	Start	31°39.5'	80°53.5'	2342-12/8	200	S	5
	Stop	31°51.7'	80°35.0'	0325-12/9			
S5	Start	31°51.7'	80°35.0'	0343-12/9	201	SSW	5
	Stop	32°10.0'	80°25.0'	0735-12/9			
S6	Start	31°58.6'	80°45.1'	0930-12/9	181	SW	5-10
	Stop	32°2.2'	80°52.2'	1141-12/9			

Table 3. Locations and Times of Air Samples in Vicinity of Brunswick, Georgia (January 16-17, 1978)

Sample Number		Latitude	Longitude	Time	Sample Volume m^3	Wind Direction	Wind Speed
B1	Start	31°36.0'	81°53.5'	1145-1/16	224	ESE	5
	Stop	31°16.0'	80°57.2'	1530-1/16			
B2	Start	31°16.0'	80°57.2'	1620-1/16	248	ESE	5
	Stop	30°57.8'	81°06.8'	2010-1/16			
B3	Start	30°57.8'	81°06.8'	2025-1/16	207	ESE-NE	5
	Stop	30°42.5'	81°19.5'	0016-1/17			
B4	Start	30°44.5'	81°25.0'	0055-1/17	252	NE	5-10
	Stop	31°00.0'	81°11.9'	0449-1/17			
B5	Start	31°00.0'	81°11.9'	0455-1/17	202	NE	5-10
	Stop	31°18.2'	81°02.3'	0841-1/17			

Table 4. Locations and Times of Air Samples in Vicinity of Jacksonville, Florida (October 10-12, 1977)

Sample Number		Latitude	Longitude	Time	Sample Volume m^3	Wind	
						Direction	Speed
J1	Start	30°52.3'	81°9.1'	1605-10/10	236	NE	5
	Stop	30°33.3'	81°1.0'	1933-10/10			
J2	Start	30°33.3'	81°1.0	1940-10/10	238	NE	5
	Stop	30°13.5'	81°1.0'	2316-10/10			
J3	Start	30°13.5'	81°1.0'	2345-10/10	222	NE	5-10
	Stop	29°54.0'	81°5.6'	0323-10/11			
J4	Start	29°54.4'	81°11.2'	0430-10/11	232	Calm	5
	Stop	30°13.5'	81°6.5'	0806-10/11			
J5	Start	30°13.5'	81°6.5'	0845-10/11	236	Calm	5
	Stop	30°33.4'	81°6.5'	1213-10/11			
J6	Start	30°33.4'	81°6.5'	1235-10/11	213	NNE	10-15
	Stop	30°53.2'	81°11.0'	1610-10/11			
J7	Start	30°33.0'	81°17.0'	1735-10/11	301	NE	5-10
	Stop	30°23.4'	81°12.2'	2116-10/11			
J8	Start	30°23.4'	81°12.2'	2300-10/11	328	NE-SW	10-15
	Stop	30°04.4'	81°16.6'	0243-10/12			
J9	Start	30°13.5'	81°18.0'	0405-10/12	339	W	10-15
	Stop	30°33.6'	81°17.8'	0755-10/12			

Table 5. Locations and Times of Air Samples Collected Over the Georgia Bight on Columbus-Iselin Cruise (November 5-8, 1977)

Sample Number		Latitude	Longitude	Time	Sample Volume m^3	Wind Direction	Wind Speed
CI1	Start	31°48.2'	80 20.0'	0015-11/6	258	SE	10
	Stop	31°44.7'	80 09.0'	0355-11/6			
CI2	Start	31°32.8'	79 30.6'	1200-11/6	265	SW	10
	Stop	31°3.0'	79 46.0'	1600-11/6			
CI3	Start	30°48.3'	79 54.5'	1950-11/6	230	SW	10
	Stop	30°53.9'	80 11.0'	2330-11/6			
CI4	Start	30°53.9'	80 11.0'	2350-11/6	254	W	10-15
	Stop	30°59.6'	80 27.6'	0340-11/7			
CI5	Start	30°15.0'	80 55.1'	2000-11/7	290	SSE	5-10
	Stop	30°15.0'	80 20.7'	0030-11/8			

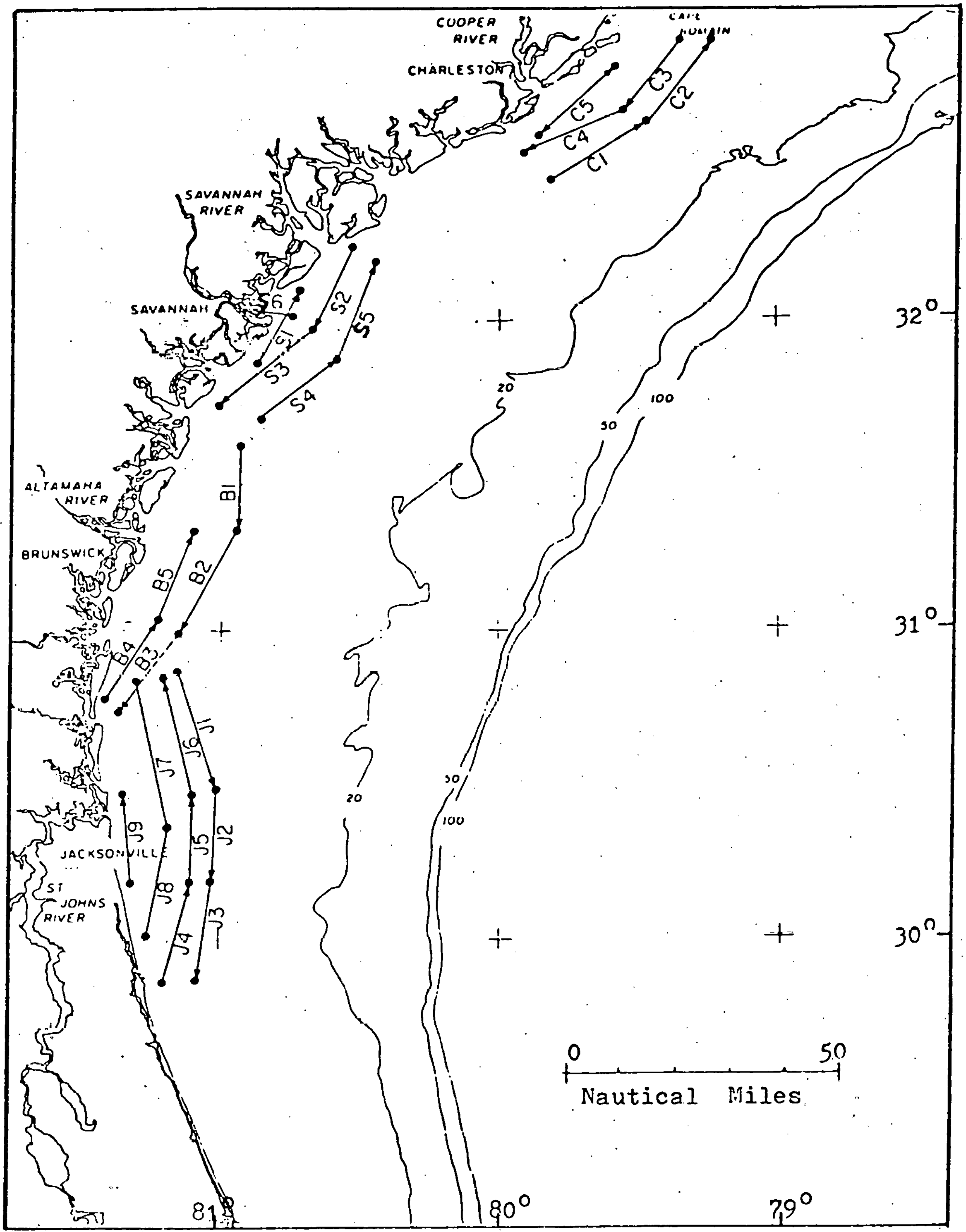


Figure 1. Cruise Tracks of R/V Blue Fin during Air Sampling in Vicinity of Charleston, Savannah, Brunswick, and Jacksonville

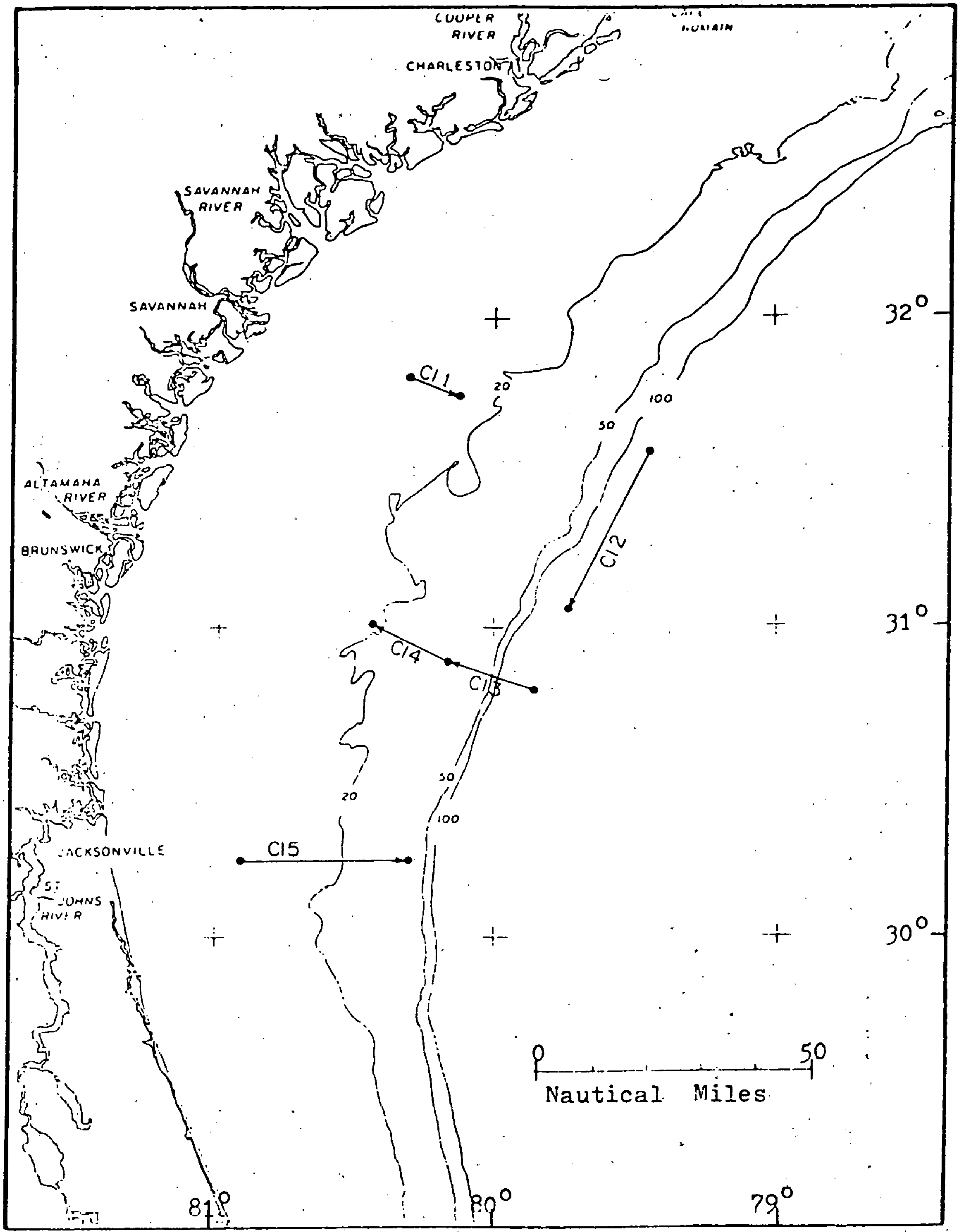


Figure 2. Cruise Tracks of R/V Columbus-Iselin during Air Sampling over the Georgia Bight (Nov. 5-8, 1977)

gloves. After sample collection, the filter holder was dismounted and brought back to the cain, where the filters were folded in quarters, with the sample side inward, and placed in polyethylene bags. These bags were then kept inside another polyethylene bag inside the cabin until they were brought back to the laboratory, where they were then kept in a clean room until analysis.

During the four Blue Fin Cruises, samples of seawater were collected in 250 ml acid-cleaned teflon bottles, for use in the solubility study. The water was collected by peristaltic pumping through polypropylene tubing. The system was thoroughly rinsed with seawater by pumping a considerable volume of water before actually collecting any water in the bottles. The inlet of the tubing through which water was pumped was attached to Kevlar hydrowire, which in turn was attached to a teflon coated weight. The entire water sampling system was designed specifically for trace metal sampling in marine waters.

Spanish mosses were collected from Charleston to Jacksonville on the following basis: three samples were taken from each urban area on the seaward side of the city. Locations are shown in a later section (Figure 8). Samples were stored in polyethylene bags and were kept frozen in the laboratory until analysis.

Sample Analysis

Total Trace Metals

All sample preparation was conducted in a clean room to minimize contamination. Duplicate quarters of each double filter paper were digested in 30 ml reagent grade HNO_3 in teflon beakers. 5 ml of reagent grade HF was added to each sample after the volume of HNO_3 had been reduced to about 10 ml. After adding the HF, the samples were allowed to stand at room temperature for 2 hours, then heated until almost dry. Each sample was then taken up in 5 ml of 10% Ultrex HNO_3, and analyzed by flameless and flame atomic absorption spectrophotometry. Zinc, Al, Fe, and Na were analyzed by flame atomic absorption, and the remainder using a HGA 2200 heated graphite furnace. Acid washed filter blanks were digested in triplicate for each group of samples in the same manner as the sample filters. Mean concentrations of 20 blank analyses are presented in Table 6, with the standard deviation of each mean.

Table 6. Filter Blanks. Mean of 20 Double Filters. ug per Double Filter

Cd	Zn	Cu	Ni	Pb	Mn	Fe	Al	Na
0.044 ±0.02	1.4 ±0.7	0.36 ±0.19	1.2 ±0.4	0.23 ±0.10	0.57 ±0.20	32 ±6.8	6.3 ±2.6	138 ±25

Extracted Trace Metals

Samples were selected from each Blue Fin cruise for solubility analysis. Each was analyzed in duplicate. Quarter filters were placed in the teflon bottles containing 250 ml of seawater which had been collected for this purpose. The bottles were sonicated for 2 minutes and then placed on a mechanical shaker and gently shaken for 3 hours. After the shaking was complete, the filters were removed from the water, and the water was filtered through 0.45 millipore filters which had been previously acid-washed. A teflon filtering apparatus was used which utilizes nitrogen gas to force the water through the filter. The water was divided up into two 100 ml portions for separate analysis by solvent extractions. One was used for Cu analysis and the other for Zn, Cd, and Ni. The extraction procedures used have been described by Smith and Windom (1978). Acid washed filter blanks were leached in triplicate in the same manner as the sample filters. Solubility was calculated as per cent of total metal on the filter paper which was leachable in seawater.

Spanish moss samples were analyzed by digesting 1 gm of moss in 10 ml reagent grade HNO_3, and 5 ml HF in the same manner as described for filter papers. All moss samples were analyzed in duplicate. The residues were taken up in 10 ml of 10% Ultrex HNO_3, and analyzed by flame atomic absorption with the exception of Cd which was analyzed by flameless atomic absorption. A Perkin Elmer 403 atomic absorption spectrophotometer, equipped with a HGA 2200 furnace and a deuterium background corrector, was used for all of the analyses.

Coefficients of variation for the heated graphite furnace analysis of Cd, Ni, Pb, and Mn were determined to be ± 2%, on the basis of replicate flameless atomic absorption signals (n = 3). Replicate values are not available for metals analyzed by flame, because single readings of absorbance were taken for each sample. Replicate analyses of solubility samples gave coefficients of variation of ± 2% for Cd, Cu, and Ni. These also are on the basis of replicate atomic absorption signals. Zinc solubility analyses were done by flame.

CHAPTER III

RESULTS AND DISCUSSION

Cruise tracks of the R/V Blue Fin during the four main sampling cruises, and cruise tracks of the R/V Columbus-Iselin during sampling in November, 1977, are shown in Figures 1 and 2, respectively. Locations, times, and meteorological conditions of all air samples were presented previously in Tables 1-5.

In all of the discussion which follows, the concept of enrichment factor will be used extensively. This concept has been in general use for several years (Duce, et al., 1975; Zoller, et al., 1974). It is very useful in evaluating possible crustal, marine, or anomalous origins of trace metals. There are two commonly used enrichment factors:

$$EF_{crust} = \frac{(X/Al)_{air}}{(X/Al)_{\substack{average\\crustal}}} \qquad EF_{sea} = \frac{(X/Na)_{air}}{(X/Na)_{\substack{average\\sea}}}$$

(Where X = metal of interest)

In each case, reference elements are used, (Al and Na), which are abundant and relatively constant in crustal material or seawater. Average crustal and average seawater abundances of the various metals are available in several published sources (Brewer, 1974: Mason, 1966). An enrichment factor of approximately unity indicates a crustal source ($EF_{crust} = 1$) or seawater source ($EF_{sea} = 1$) for that metal. A very large EF indicates anomalous enrichment for that element, with respect to the given source.

The metals that were found to be anomalously enriched over the Georgia Bight are Cd, Zn, Cu, Ni, and Pb. The metals with a crustal origin are Fe, Mn, and Al. These patterns of enrichment are discussed later and are shown in Table 13 and Figure 4.

Atmospheric Concentrations

The ratios of metals in samples to metals in blanks ranged from about 2:1 to greater than 10:1. The lower ratios occur in many cases because of the relatively low volume of air sampled. Air volumes generally ranged between 200-300 m^3, and in the case of metals with low atmospheric concentrations, this is not enough volume to produce a high sample to blank ratio. The lower sample volumes evidently also produced some problems with agreement between duplicate quarters of the same filter papers (Tables 7-11). Since the metals sampled in this study are associated with particulate matter, a large volume of air sample is needed to produce a uniform distribution of all types of particles on the filter paper. This effect produced fairly large uncertainties for some samples, but the concentrations generally are in good agreement with previous values obtained by Windom and Smith (1978) over the Georgia Bight for much larger sample

Table 7. Trace Metal Concentrations and Enrichment Factors of Atmospheric Samples Collected over the Continental Shelf in Vicinity of Charleston, South Carolina (September 19-20, 1977)

Sample Number	Cd		Zn		Cu		Ni		Pb		Mn		Fe		Al	Na
	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	ng/m^3
C1 A	1.3	8800	--	230	--	620	1.4	33	20	1900	--	3	46	2	--	3200
B	0.6		9.0		19		1.4		8.1		1.6		62		45	2600
C2 A	1.3	7600	--	320	--	220	--	87	12	1500	--	3	--	2	--	3600
B	0.4		13		7.0		3.9		9.8		1.5		59		46	3000
C3 A	6.9	11000	--	380	--	130	--	11	--	3100	--	3	100	1	--	7700
B	4.1		62		18		1.3		96		7.2		88		190	4200
C4 A	0.4	2000	--	120	--	59	--	43	--	690	--	4	79	1	--	1100
B	0.4		8.3		2.9		3.2		9.0		4.1		60		80	1500
C5 A	--	2800	--	190	--	29	--	33	28	1100	--	3	93	1	--	1300
B	1.1		25		3.2		4.5		21		5.1		79		150	1200
Mean	1.8	6440	23	248	10	212	2.9	41	31	1660	4.0	3	74	1	102	2940
S.D.	±2.1	±3895	±23	±103	±8	±240	±1.5	±28	±37	±922	±2.4	+.5	±17	±.5	±65	±1919

Table 8. Trace Metal Concentrations and Enrichment Factors of Atmospheric Samples Collected over the Continental Shelf in Vicinity of Savannah, Georgia (December 8-9, 1977)

Sample Number	Cd		Zn		Cu		Ni		Pb		Mn		Fe		Al	Na
	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	ng/m^3
S1 A	0.3	440	11	52	3.3	21	3.8	23	19	430	5.2	1	120	1	430	1760
B	0.4		17		5.4		9.1		24		2.1		230		200	1600
S2 A	1.2	1900	---	110	6.7	47	8.4	61	15	620	5.1	2	110	1	170	1600
B	0.4		15		3.5		9.5		17		1.1		120		150	1900
S3 A	0.1	600	2.1	59	1.7	59	1.3	40	12	730	ND	ND	45	1	170	3000
B	0.3		11		8.8		8.5		18		ND		96		100	3500
S4 A	0.1	960	13	200	2.1	44	ND	28	15	1100	ND	ND	67	2	110	4300
B	0.4		22		4.1		5.5		22		ND		130		97	4800
S5 A	0.2	720	---	100	---	31	---	68	31	1700	4.8	2	---	1	150	3800
B	0.3		13		2.8		8.5		41		1.6		57		120	4700
S6 A	0.8	2000	21	240	4.2	53	30	290	36	2100	11	6	140	2	130	5300
B	0.5		33		5.0		39		49		7.0		200		120	4400
Mean	0.4	1103	15	128	4.3	42	11	85	25	1113	3.2	2	120	1	162	3390
S.D.	+0.2	±678	±6.7	±76	±1.0	±14	±11	±102	±11	±660	±3.2	±2	±48	±.5	±77	±1404

Table 9. Trace Metal Concentrations and Enrichment Factors of Atmospheric Samples Collected over the Continental Shelf in Vicinity of Brunswick, Georgia (January 16-17, 1978)

Sample Number	Cd		Zn		Cu		Ni		Pb		Mn		Fe		Al	Na
	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	ng/m^3
B1 A	0.1	400	20	93	2.5	15	0.9	1	62	1300	3.9	1	100	1	260	540
B	0.2		19		1.5		0.9		35		2.4		85		200	450
B2 A	0.4	400	10	47	1.5	15	ND	0.5	40	940	2.9	1	85	0.5	270	650
B	0.4		12		1.9		0.8		37		0.5		85		260	650
B3 A	0.4	800	11	81	2.0	15	ND	ND	43	1400	2.0	1	72	1	190	820
B	0.4		15		2.3		ND		43		1.7		82		180	970
B4 A	0.7	1200	12	93	2.4	29	ND	2	52	1400	2.1	1	75	1	150	2400
B	0.3		13		2.7		4.0		17		1.7		150		---	1200
B5 A	---	1200	12	128	1.9	29	ND	ND	14	1200	2.8	3	45	1	110	3300
B	0.4		15		2.5		ND		32		3.6		35		130	3100
Mean	0.4	800	14	88	2.1	21	0.7	0.7	38	1248	2.4	1	81	1	175	1408
S.D.	±0.1	±400	±3	±29	±0.3	±11	±0.8	±0.7	±10	±191	±0.8	±0.8	±27	±0.2	±61	±1122

Table 10. Trace Metal Concentrations and Enrichment Factors of Atmospheric Samples Collected over the Continental Shelf in Vicinity of Jacksonville, Florida (October 10-12, 1977)

Sample Number		Cd		Zn		Cu		Ni		Pb		Mn		Fe		Al	Na
		ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	ng/m^3
J1	A	0.3	310	15	33	12	37	ND	4	26	690	---	1.3	240	0.8	380	3400
	B	0.3		7.0		7.0		3.0		59		6.2		140		390	3000
J2	A	0.2	320	8.0	28	9.0	46	9.0	32	24	750	---	1.7	110	0.7	240	4300
	B	0.2		4.0		7.0		5.0		37		5.0		94		270	3800
J3	A	0.4	440	8.0	31	5.0	21	8.0	22	23	810	---	1.6	100	0.7	180	3200
	B	0.3		4.0		1.0		0.7		34		4.2		69		270	4000
J4	A	0.5	800	10	43	3.0	10	ND	ND	17	880	---	2.0	97	0.7	180	3600
	B	0.3		4.0		ND		ND		39		4.8		66		220	3100
J5	A	0.2	400	6.0	37	ND	1	ND	3	16	880	---	2.1	83	0.6	170	3700
	B	0.1		4.0		0.3		0.9		31		4.1		36		170	3400
J6	A	0.1	400	7.0	63	3.0	18	ND	8	31	1800	---	2.8	92	1.0	99	11000
	B	0.2		5.0		ND		2.0		34		3.9		58		130	7000
J7	A	0.1	680	8.0	120	ND	3	ND	ND	15	1800	---	3.3	65	1.0	50	3100
	B	0.1		6.0		0.3		ND		25		2.7		21		89	2800
J8	A	0.1	380	6.0	40	2.0	10	ND	2	8.0	690	---	1.7	59	0.6	91	2700
	B	0.2		4.0		ND		0.5		23		2.8		57		180	2100
J9	A	0.2	760	9.0	81	4.0	26	7.0	53	17	1900	---	2.8	89	0.9	120	3100
	B	0.2		5.0		0.2		4.0		45		3.4		25		93	1700
Mean		0.2	500	7.0	53	3.0	20	2.2	14	28	1133	4.1	2.1	83	0.8	184	3833
S.D.		±0.1	±193	±2.0	±31	±3.3	±15	±2.7	±18	±7.8	±530	±1.1	±0.7	±44	±0.03	±64	±2012

Table 11. Trace Metal Concentrations and Enrichment Factors of Atmospheric Samples Collected over the Georgia Bight on Columbus-Iselin Cruise (November 5-8, 1977)

Sample Number	Cd		Zn		Cu		Ni		Pb		Mn		Fe		Al	Na
	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	EF	ng/m^3	ng/m^3
CI-1 A	0.3	3120	15	390	16	690	5.0	170	16	2394	1.4	2	300	8	55	2030
B	0.4		16		---		10		20		0.7		180		41	---
CI-2 A	0.2	680	13	95	1.6	16	4.0	34	28	1000	1.5	1	340	3	160	2300
B	0.3		12		1.9		5.4		22		2.1		140		150	
CI-3 A	0.2	1080	16	210	14	220	0.7	9	28	1994	0.4	0.4	280	5	88	2900
B	---		---		---		---		---		---		---		---	
CI-4 A	0.2	1040	16	200	9.4	160	7.0	83	24	1688	ND	0.5	140	2	80	4300
B	0.2		14		9.2		6.0		23		1.0		90		93	
CI-5 A	0.3	1040	20	190	14	230	2.3	43	16	1181	6.2	5	85	2	98	700
B	0.2		11		16		5.4		21		5.0		100		96	
Mean	0.3	1400	15	240	11	270	4.6	68	22	1650	2.0	1.8	195	4	95	2400
S.D.	±0.1	±980	±1.5	±110	±5.9	±256	±2.7	±63	±4.3	±574	±2.2	±1.9	±34	±3	±38	±1315

volumes (about 500 m^3).

Mean atmospheric concentrations of Cd, Zn, and Cu are greater in the Charleston samples than in the other three nearshore areas (Tables 7 - 10, Figure 3). This pattern is most obvious when the mean values for samples collected during easterly and westerly winds are used (Table 12). Westerly winds blowing off Charleston produce nearshore atmospheric concentrations of Cd, Zn, and Cu that are higher than those encountered in the other areas for these metals. It is not possible to tell from the limited amount of data available in this study if Charleston really is the source of greater amounts of trace metals than the other cities. However, the data strongly indicate that Charleston could be a major source of enriched Cd, Zn, and Cu over the Georgia Bight, and Savannah and Brunswick could be the source of a relatively large amount of Zn. It also appears from Table 12 and Figure 3 that a major source of Ni over the Georgia Bight is Savannah. The mean Ni concentrations observed during westerly winds off Savannah are several times greater than those encountered elsewhere. Lead concentrations are generally uniform in each study area, perhaps reflecting the influence of automobile exhausts in all areas.

Columbus-Iselin samples were collected at five different locations over the Georgia Bight, ranging from about 50 to 100 km offshore (Figure 2). It is interesting to note that mean concentrations of Cd, Zn, Cu, and Ni in the Columbus-Iselin samples are generally within the range of the mean nearshore values and in many cases are actually higher (Table 12 and Figure 3). This suggests that continental influences extend out at least to the edge of the continental shelf and probably farther. It is also interesting to note that in many cases, trace metal concentrations resulting from easterly winds are greater than those resulting from westerlies. This is reflected in the Brunswick, Jacksonville, and Columbus-Iselin mean values. This is not surprising, considering the above observation that Columbus-Iselin samples frequently have higher trace metal concentrations that nearshore samples.

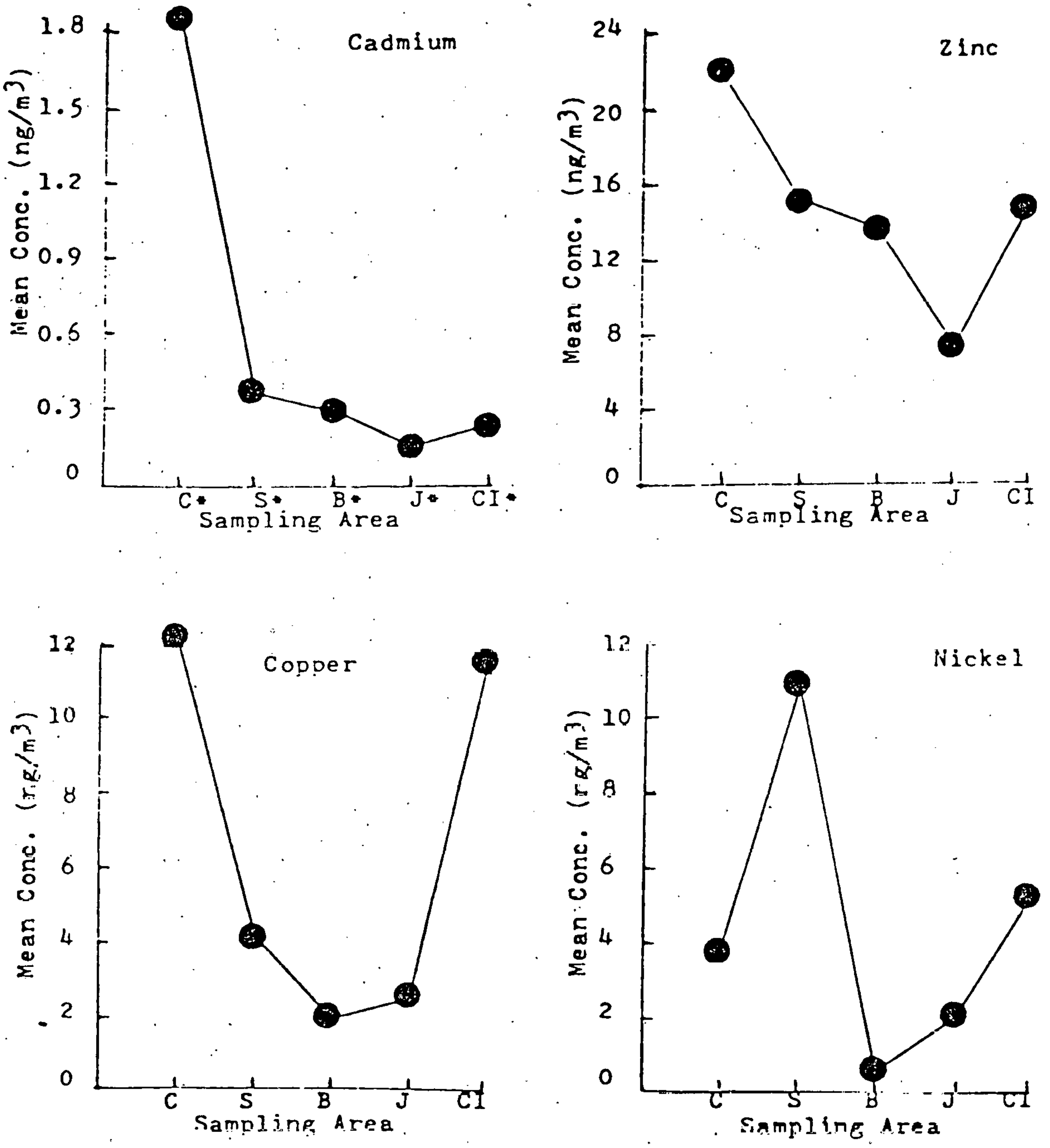
The atmospheric concentrations of trace metals observed over the Georgia Bight generally fall within the range of values found by Duce (1976) in Bermuda, but most of the concentrations of Cd, Zn, Cu, Ni, and Pb over the Georgia Bight are similar to the highest concentrations of these metals observed in Bermuda. In general, the Georgia Bight mean concentrations of these five metals are much higher than the mean concentrations observed in Bermuda. These observations suggest that continental influences cover the Georgia Bight and may reach Bermuda.

Enrichment Factors

A comparison of mean EF_{crust} values in the four nearshore areas with Columbus-Iselin and Bermuda samples

Table 12. Mean Atmospheric Trace Metal Concentrations vs Wind Direction

	Cd	Zn	Cu	Ni	Pb	Mn	Fe	Al	Na
	ng/m^3								
					Charleston				
Westerly	2.1	27	7.8	3.2	35	4.5	80	116	2900
Easterly	0.95	9.0	19	1.4	14	1.6	54	45	2900
					Savannah				
Westerly	0.38	19	3.6	21	32	4.1	109	121	4500
Easterly	0.45	11	4.9	6.8	18	2.3	120	102	2200
					Brunswick				
Westerly	0.22	15	9.3	6.5	23	0.5	118	86	4303
Easterly	0.40	14	2.1	0.7	38	3.5	81	190	1400
					Jacksonville				
Westerly	0.18	6.0	1.6	2.9	23	3.1	57	120	2400
Easterly	0.28	6.9	3.4	2.0	29	4.4	91	203	4200
					Columbus-Iselin				
Westerly	0.24	14	8.2	4.0	25	0.9	214	114	3160
Easterly	0.32	16	19	5.7	18	3.3	167	72	1360
					Bermuda Samples (Duce, 1976)				
All Wind Direction	0.19	3.2	0.9	0.08	3.5	1.2	94	140	1500



* C = Charleston, S = Savannah, B = Brunswick,
J = Jacksonville, CI = Columbus-Iselin

Figure 3. Mean Atmospheric Trace Metal Concentrations by Area

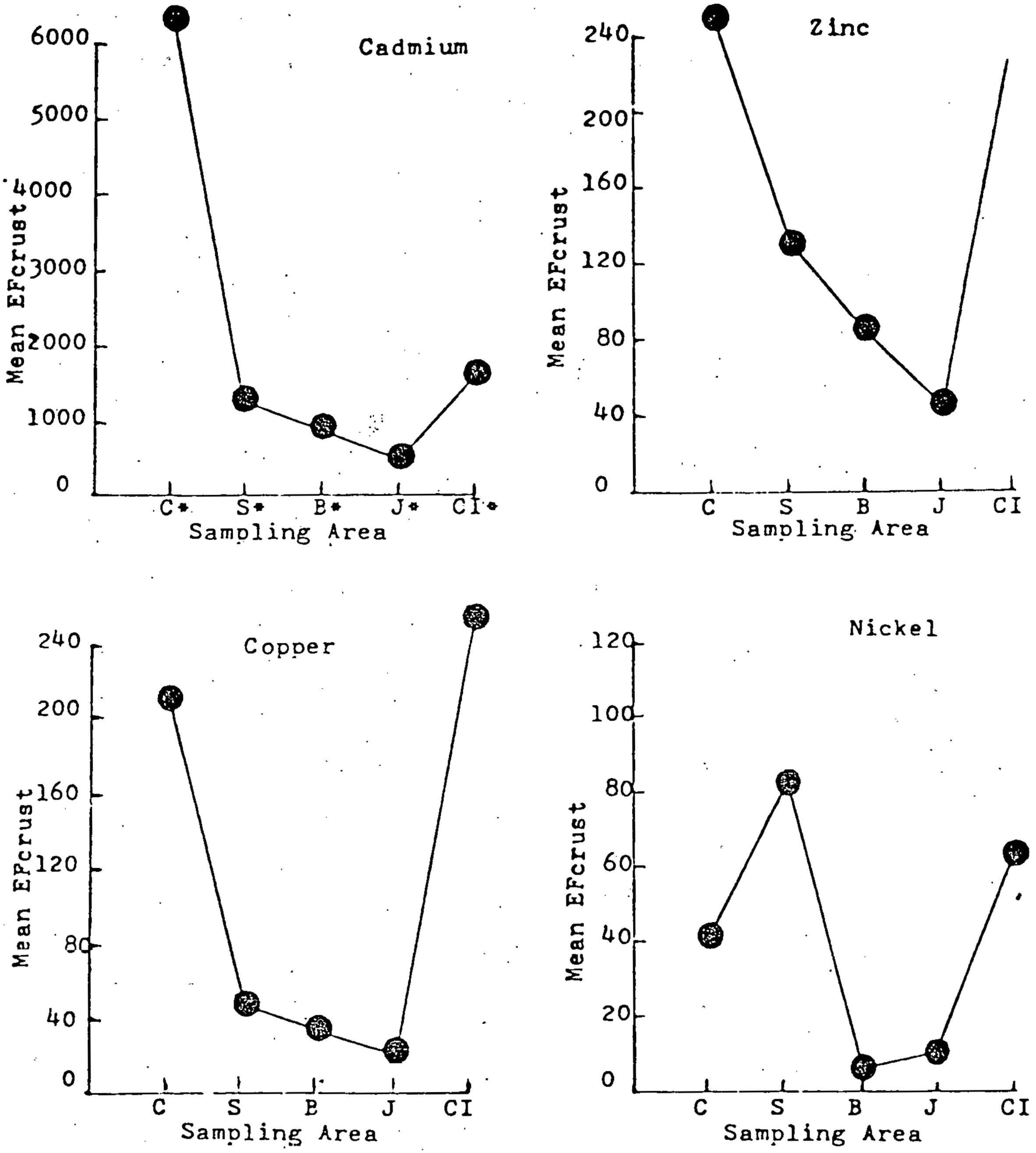
supports the conclusions based on observations of trace metal concentrations in air samples. Once again, discreet patterns can be seen in the four nearshore areas (Table 13 and Figure 4). The Charleston and Savannah samples have the highest EF_{crust} values for Cd, Zn, Cu, and Ni, while Jacksonville samples have the lowest values. Lead EF_{crust} values are fairly uniform throughout the nearshore samples. The Columbus-Iselin mean EF_{crust} values for Cd, Zn, Cu, and Ni compare reasonably well with Charleston and Savannah, but are generally greater than Brunswick and Jacksonville. This is the same pattern observed for atmospheric concentrations of these four metals. The Bermuda EF_{crust} values are substantially lower than observed over the Georgia Bight for all metals except Mn and Fe. In general, the mean EF_{crust} data in Table 13 indicate that Cd, Zn, Cu, Ni and Pb are anomalously enriched over the Georgia Bight, while Mn and Fe are predominantly of crustal origin.

Inter-element Correlation Coefficients

Inter-element correlation coefficients for all metals in the four nearshore areas are presented in Tables 14-17. The number of samples involved in the calculations and levels of confidence are also given in the tables. The Charleston correlation coefficients are the most interesting to analyze for purposes of this study because the area was under the influence of strong westerly winds for virtually the entire sampling period. As a result, the trace metals

Table 13. Mean EF_{crust} Values vs Wind Direction

	Cd	Zn	Cu	Ni	Pb	Mn	Fe	Al	Na
					Charleston				
Westerly	5850	252	110	43	1598	3	2	---	---
Easterly	8800	230	620	33	1900	3	2	---	---
					Savannah				
Westerly	1200	180	43	129	1600	3	2	---	---
Easterly	980	74	42	41	590	1	1	---	---
					Brunswick				
Westerly	1040	200	160	83	1700	0.5	2	---	---
Easterly	800	88	21	1.1	37	1	1	---	---
					Jacksonville				
Westerly	570	60	18	28	1300	2	1	---	---
Easterly	480	51	19	10	1100	2	1	---	---
					Columbus-Iselin				
Westerly	930	170	130	42	1600	1	3	---	---
Easterly	2100	290	460	107	1800	3	5	---	---
					Bermuda Samples (Duce, 1976)				
All Wind Directions	570	26	9.6	1.1	170	1	1	---	---



* C = Charleston, S = Savannah, B = Brunswick,
J = Jacksonville, CI = Columbus-Iselin

Figure 4. Mean Atmospheric EF_{crust} Values by Area

Table 14. Interelement Trace Metal Correlation Coefficients-Charleston

	Zn	Cu	Ni	Pb	Mn	Fe	Al	Na
Cd	+0.96	+0.56	-0.70	+0.98	+0.69	+0.61	+0.86	+0.71
Zn		+0.42	-0.49	+0.97	+0.84	+0.84	+0.88	+0.81
Cu			-0.98	+0.50	+0.05	-0.04	+0.10	+0.80
Ni				-0.61	-0.31	-0.49	-0.29	-0.58
Pb					+0.86	+0.77	+0.83	+0.85
Mn						0.60	+0.98	+0.38
Fe							+1.0	+0.32
Al								+0.04

n = 5

At 95% level of confidence, r = 0.81

At 99% level of confidence, r = 0.92

Table 15. Interelement Trace Metal Correlation Coefficients - Savannah

	Zn	Cu	Ni	Pb	Mn	Fe	Al	Na
Cd	+0.63	+0.60	+0.87	+0.23	+0.80	-0.39	0.00	-0.34
Zn		-0.01	+0.88	+0.69	+0.81	+0.66	-0.49	+0.38
Cu			+0.23	-0.30	+0.18	-0.13	+0.31	-0.45
Ni				+0.81	+1.0	+0.28	+0.21	+0.45
Pb					+0.83	-0.09	-0.21	+0.62
Mn						+0.51	+0.13	+0.25
Fe							+0.20	-0.59
Al								-0.74

n = 6

At 95% level of confidence, r = 0.75

At 99% level of condifence, r = 0.87

Table 16. Interelement Trace Metal Correlation Coefficients - Brunswick

	Zn	Cu	Ni	Pb	Mn	Fe	Al	Na
Cd	-0.05	-1.0	+0.14	-1.0	-1.0	-0.30	-0.96	+0.44
Zn		-0.53	+0.08	+0.39	+0.42	-0.04	+0.14	-0.26
Cu			+0.33	-1.0	-1.0	-0.81	-1.0	+0.12
Ni				+0.14	-0.25	+0.84	-0.07	-0.09
Pb					-0.53	+0.53	+0.61	-0.91
Mn						-0.38	-0.29	+0.29
Fe							+0.36	-0.60
Al								-1.0

n = 5

At 95% level of confidence, r = 0.81

At 99% level of confidence, r = 0.92

Table 17. Interelement Trace Metal Correlation Coefficients - Jacksonville

	Zn	Cu	Ni	Pb	Mn	Fe	Al	Na
Cd	+0.35	+0.35	+0.12	+0.47	+0.73	+0.49	+0.92	-0.17
Zn		+0.60	-0.02	+0.65	+0.62	+0.73	+0.87	-0.13
Cu			+0.51	+0.73	+0.84	+0.90	+1.0	-0.06
Ni				+0.34	+0.22	-0.51	-0.50	-0.57
Pb					+0.83	+0.78	+0.99	+0.28
Mn						+0.92	+1.0	+0.11
Fe							+1.0	+0.02
Al								-0.19

n = 9

At 95% level of confidence, r = 0.63

At 99% level of confidence, r = 0.77

sampled were relatively fresh from the source area and relationships between metals should better reflect sources. Also, winds were much stronger during the Charleston sampling than during any of the other three sampling periods (Tables 1-4). With stronger winds, there is increased production of whitecaps, and increased injection of sea salt into the atmosphere from seawater (Woodcock, 1953). Among the metals which are transferred from sea to air, Na would be expected to have the greatest flux because of its large concentration in seawater. Thus, if any trace metals correlate strongly with Na, seawater can be suspected as a significant source.

It is interesting to note that for Charleston, Fe and Al are perfectly correlated (r = 1.0). This is not surprising since stronger winds might be expected to transport significant crustal material. Cadmium and Zn are both strongly correlated with Al and Fe, indicating that strong westerly winds off Charleston are transporting anomalously enriched metals along with crustal material.

An aspect of the inter-element relationships in the Charleston samples which is potentially very significant is the correlation of Zn and Cu with Na, suggesting a seawater source. There is some evidence that seawater could in fact be a significant source of Zn and Cu. The sea surface microlayer is enriched in trace metals compared to subsurface water (Duce, et al., 1972; Piotrowicz, et al., 1972;

Hoffman, et al., 1972) and this enrichment should be reflected in the sea salt particles produced when bubbles break through this microlayer (Hoffman and Duce, 1974; Piotrowicz, 1972). Duce et al., (1976) found significant enrichment of Zn, Cu, and Fe on sea salt particles in Narragansett Bay generated by a device known as a Bubble Interfacial Microlayer Sampler (BIMS), (Fasching, et al., 1974). Duce, et al., (1976) calculated that the flux of Zn and Cu to the atmosphere from marine waters could be as great as crustal and anthropogenic sources. The flux of Fe, according to these calculations, was of the same order of magnitude as Zn and Cu, but was swamped by crustal and anthropogenic sources. If the sea surface microlayer composition in the Georgia Bight waters is similar to the waters studied by Duce (1976), then the correlation of Zn and Cu with Na in the present study could indicate significant fluxes of these metals from water to air. Unfortunately, there is no way to quantify the seawater contributions to the Zn and Cu concentrations in Georgia Bight air with existing data. The advantage of the BIMS device is that it samples trace metals very close to the surface of the water, thus making it possible to separate seawater contributions from continental contributions. However, the indication is that this problem would be well worth further investigation in the future.

During sampling in the vicinity of Savannah, Brunswick, and Jacksonville, the areas were under the influence of weak easterly winds most of the time. Inter-element correlations for samples from these areas are thus not as meaningful as those for samples collected in the vicinity of Charleston. It is true that there are a considerable number of significant positive correlations in the Jacksonville data, but this does not reflect anything significant about Jacksonville air due to the predominant easterly winds.

Trace Metal Solubilities in Seawater

Since the metals analyzed in this study are associated with particular material, a significant proportion may be relatively nonreactive in the water column. To evaluate the fate of the metals after entering the water, the solubilities of Cd, Zn, Cu, and Ni in seawater were determined for selected samples in each area. The solubilities were calculated as per cent of total metal on the filter papers which was soluble in seawater.

The per cent solubilities, together with EF_{crust}, wind direction and speed are presented in Table 18 for the four main areas. The solubilities of metals in five samples which were collected at the Skidaway Institute Dock during a dust storm in February 1977 (Windom and Chamberlain, 1978), are also discussed. The uncertainties in many of the solubility figures in Table 19 are quite high. This is because the uncertainties in the blank values are taken into account in calculating these uncertainties of sample values. As a result, the samples which have the

Table 18. Trace Metal Solubilities Compared Against EF_{crust}, Wind Direction, and Speed

Sample	Cd		Cu		Zn		Ni		Wind	
Number	% Sol.*	EF	% Sol.*	EF	% Sol.*	EF	% Sol*	EF	Dir.	Speed
					Charleston					
C2	28±1	8800	61±5	620	90	230	10	33	SSE	10
C3	10	7600	65±4	220	90	320	10	87	SSW	15
C4	83±8	11000	49+5	130	80±4	380	10	11	WSW	15
C6	24±2	2800	---	---	90	190	---	---	WSW	10-15
	(r = 0.59)		(r = 0.55)		(r = -0.72)					
					Savannah					
S1	17±7	440	10	21	90	52	10	23	NE	5-10
S4	90	960	10	44	10	200	10	28	S	5
S5	36±18	720	10	31	10	110	10	67	SSW	5
S6	10	2000	10	53	16±12	240	10	290	SW	5-10
	(r = -0.28)				(r = -0.78)					
					Brunswick					
B2	---	---	---	---	44±16	93	10	1	ESE	5
B3	90	400	---	---	67±23	47	10	0.5	ESE	5
B4	90	800	---	---	59±24	81	10	ND	ESE	5
B5	21±3	1200	---	---	67±19	93	10	2	NE	5-10
B6	20±6	1200	---	---	---	---	10	ND	NE	5-10
	(r = -0.40)				(r = -0.49)					

*Solubilities above 90% or below 10% are expressed as greater than or less than values due to uncertainties in solubility calculations.

Table 18 (Continued)

Sample Number	Cd % Sol.	Cd *EF	Cu % Sol.	Cu *EF	Zn % Sol.	Zn *EF	Ni % Sol.	Ni *EF	Wind Dir.	Wind Speed
					Jacksonville					
J2	23±5	310	42±9	37	77±23	33	---	---	NE	5
J3	57±14	320	27±10	46	90	28	---	---	NE	5
J4	10	440	70±28	21	90	31	---	---	NE	5-10
J5	10	800	10	10	89±33	43	---	---	Calm	
J9	45±13	380	10	10	90	40	---	---	SW	10-15
J10	21±5	760	10	26	90	81	---	---	W	10-15
	(r = -0.58)		(r = 0.55)		(r = 0.25)					
					Skidaway Dock (Dust Storm)					
DS1	24±2	32	29±6	0.5	10±1	2	10	1		
DS2	30±3	20	19±5	0.5	12±1	2	10	1		
DS3	10	ND	10	1.4	13±.4	2	10	2		
DS4	30±2	230	10	162	11±0	44	20±.1	2		
DS5	77±11	4.0	17±3	3.7	15±.4	2	20±.1	1		

lowest amounts of metals on the filter papers have higher uncertainties. This means, however, that the high uncertainties are associated with relatively small absolute amounts of metals.

Solubilities were compared with EF_{crust} and wind direction to determine if they vary in any significant way with source. Results of regression analysis of EF_{crust} on per cent solubility are also presented in Table 19. Coefficients for these analyses are only calculated within each area. None of the correlations within areas are significant at the 95% level of confidence. This suggests that solubility does not vary directly with EF_{crust}. There are probably not enough samples, however, within each group for this to be significant, considering the uncertainties in both EF_{crust} and solubility.

To further investigate the relationships between EF_{crust} and solubilities in each area, they were plotted against each other for each area (Figures 5 - 7). Nickel was not evaluated in this way because it showed negligible solubility for all samples (Table 18).

Some interesting patterns can be seen in these plots, especially those for Zn and Cu. It is clear that Zn solubilities in each area cluster together in definite groupings (Figure 5). With the exception of the Charleston data, higher EF_{crust} values of Zn tend to be associated with lower solubilities. When a correlation coefficient relating

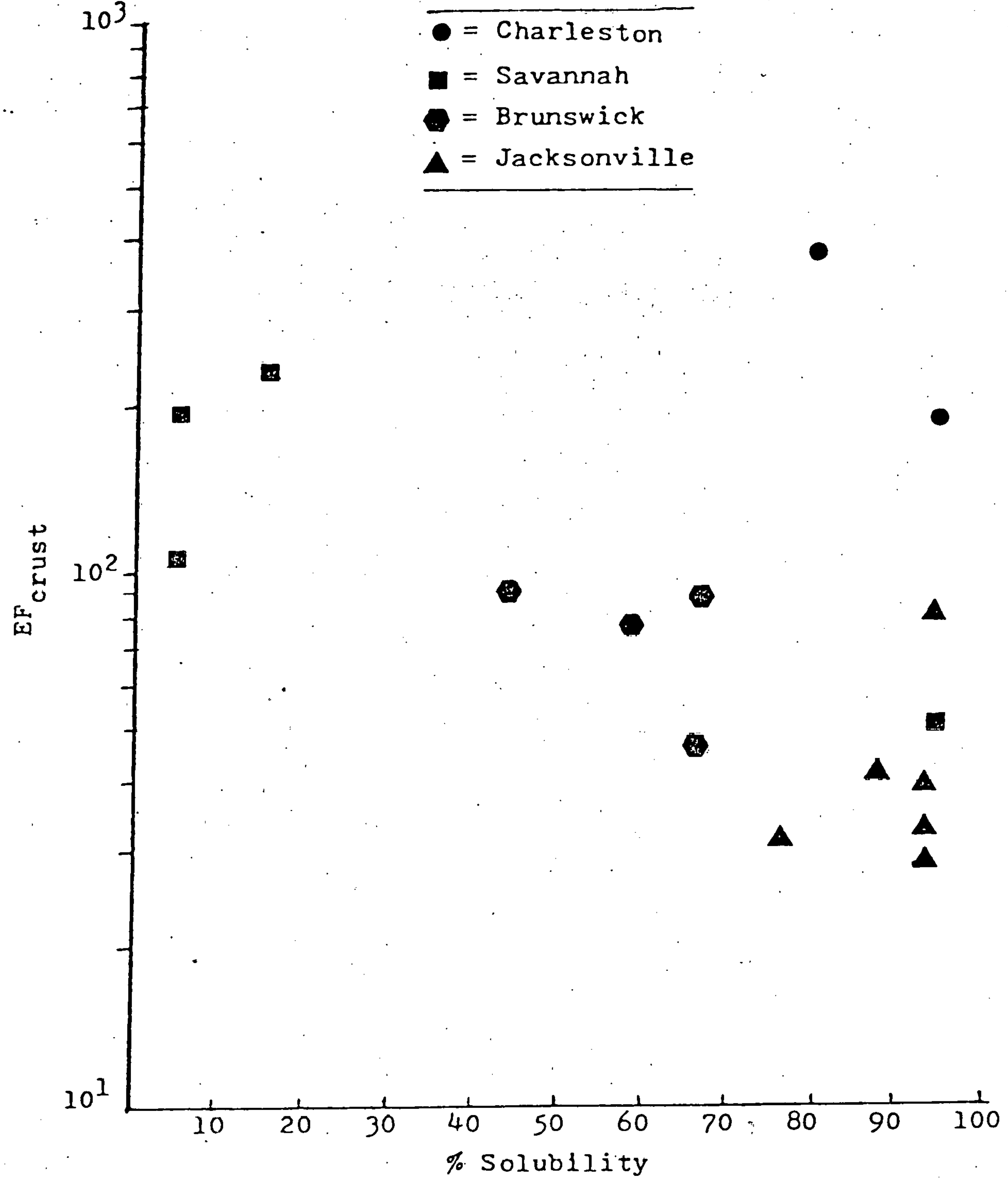


Figure 5. Plot of % Solubility of Zinc vs. EF_{crust}

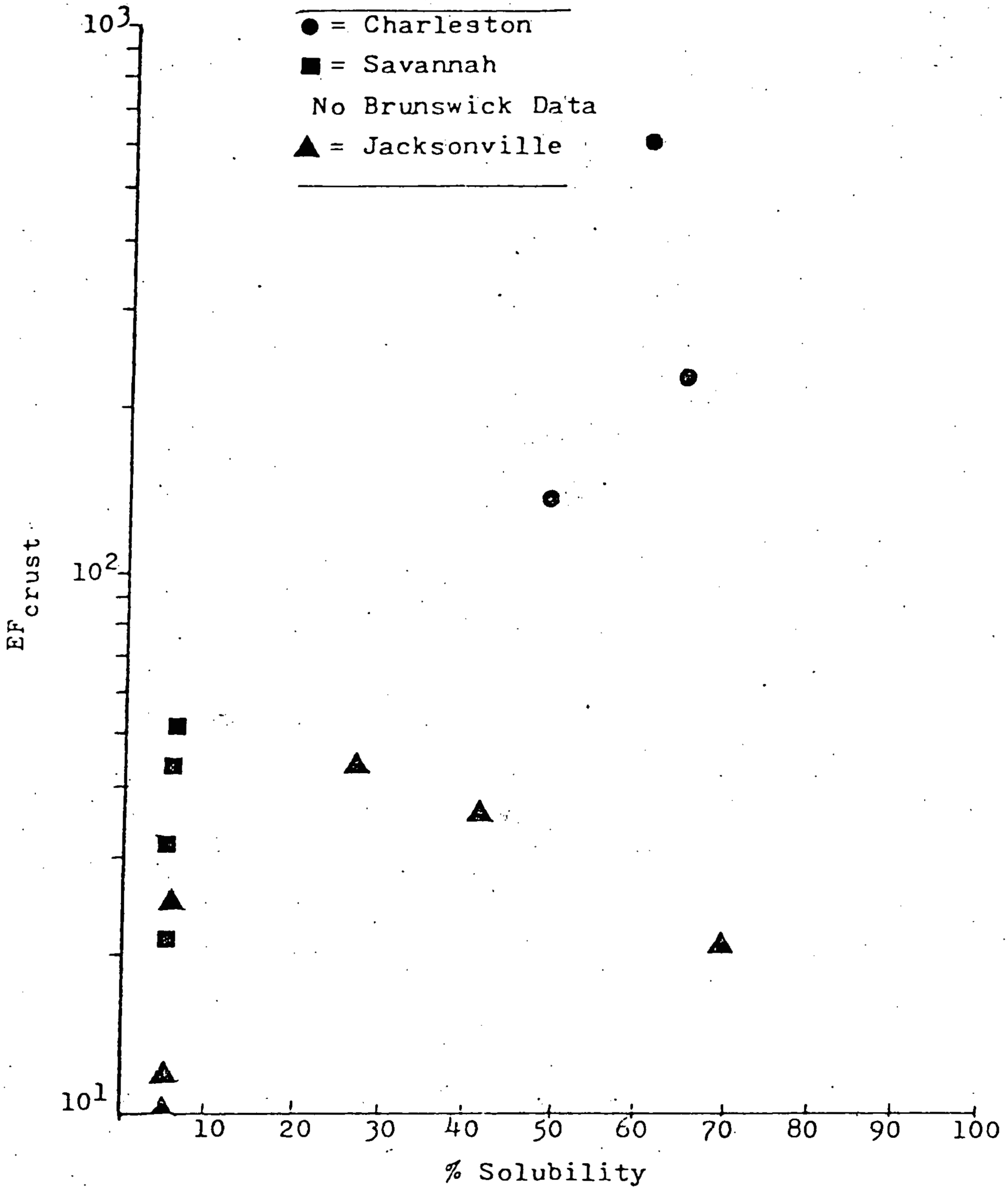


Figure 6. Plot of % Solubility of Copper vs. EF_{crust}

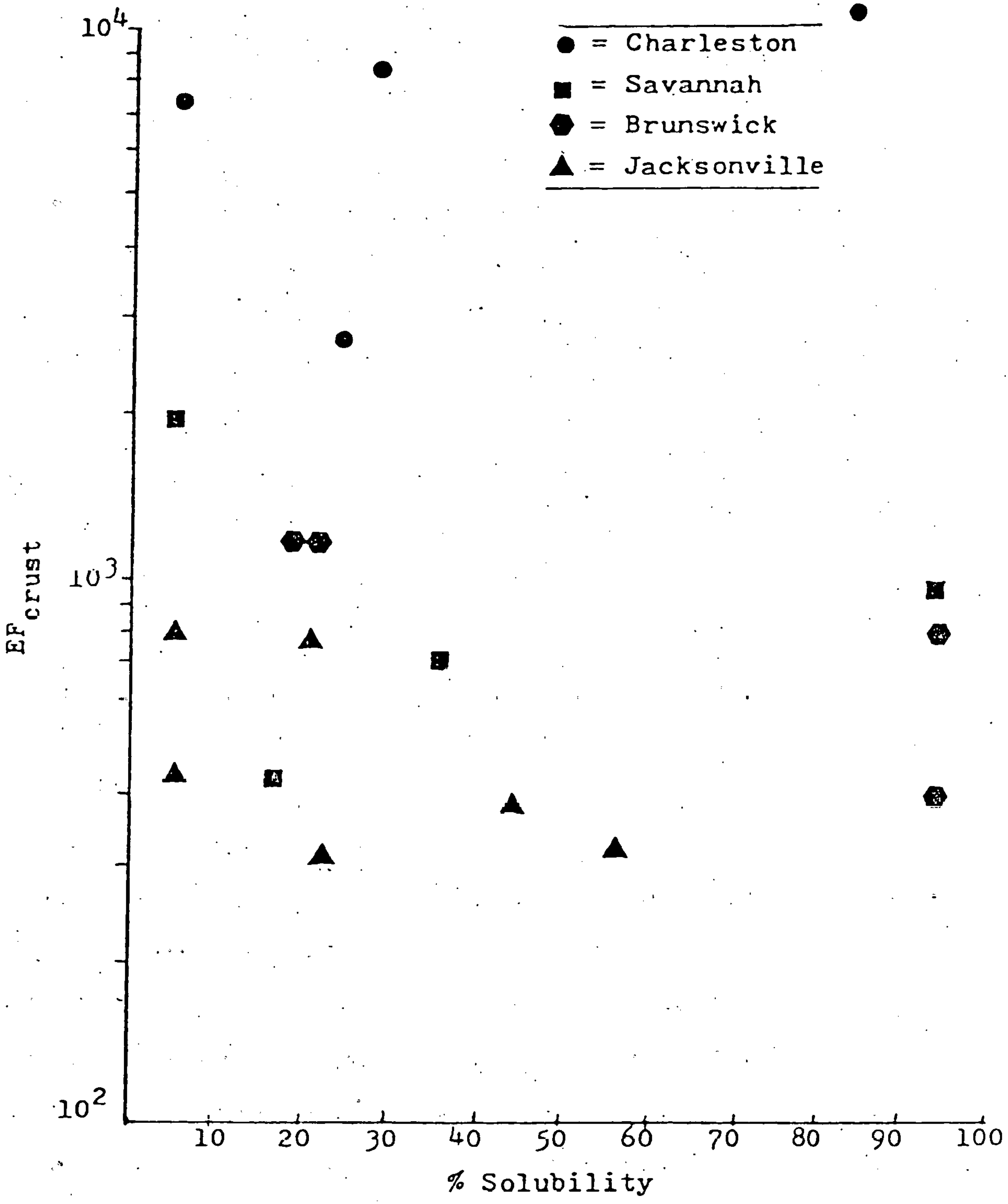


Figure 7. Plot of % Solubility of Cadmium vs. EF_{crust}

solubility and EF_{crust} is calculated for Savannah, Brunswick, and Jacksonville samples, excluding Charleston samples, a coefficient of r = -.64 (n = 18), is obtained. This is a significant negative correlation at the 99% level of confidence. There is a possible explanation for the semmingly anomalous Charleston data in Figure 5. As pointed out earlier, Zn is strongly correlated with Na in the Charleston samples, thus it is possible that EF_{crust} and solubility data for Zn are significantly affected by seawater contributions. Whether or not this is true, there is a strong indication that Zn solubility is negatively correlated with EF_{crust}. It is also clear that Zn solubility varies over a considerable range.

Copper solubilities also tend to be grouped together by area, although the groupings are not as pronounced as with Zn (Figure 6). Once again, there seems to be a relation between EF_{crust} and solubility, although, in this case, higher Cu enrichment factors are associated with higher solubilities. The correlation coefficient for data plotted in Figure 6 is r = +0.54 (n = 13), and is significant at the 95% level of confidence. Copper solubility, then, also appears to be source related as was Zn. Savannah Cu solubilities are lowest as they were for Zn, while Charleston Cu solubilities are highest and Jacksonville are intermediate. Brunswick Cu solubilities were not used due to excessively large differences in duplicate analyses.

There are no clear patterns in the Cd solubility data (Figure 7). The only trend that can be seen is that most solubilities cluster below about 30%. Source dependence is not evident for Cd as it is for Zn and Cu.

An interesting aspect of solubility is that it frequently changes radically with drastic changes in wind direction (Table 18). Specific examples of this are the Cd and Zn results of samples S1 and S4 when wind direction changed from NE to S. The Cd solubility increased about 70% while Zn solubility decreased about 80%. Again, between samples B4 and B5, wind direction whifted from ESE to NE, and the Cd solubility dropped by about 70%. Another example was in the interval between samples J4-J5-J9. Wind direction shifted from NE to calm to SW. Both Cd and Cu solubilities changed during these shifts. It is not surprising that solubility should change with wind direction, considering the above observations about dependence of solubility on source.

There seem to be no obvious relationships between enrichment factor and solubility in the dust storm data. The EF_{crust} values for these samples are quite low with the exception of sample DS 4. This indicates a dominant crustal source for the material. Correlations between EF_{crust} and solubility which were observed previously for Zn and Cu do not hold here. Zinc has low EF_{crust} values and low solubility, which is the reverse of the pattern previously observed.

Copper has generally low EF_{crust} and low solubility values, but sample DS4 has a very high enrichment factor and low solubility. This also does not hold with the previous pattern. Cadmium shows the same general range of solubilities as seen previously. Nickel solubilities are generally low, as they were with the other samples. It is not evident why there should be differences in solubility behavior for Zn and Cu, from that observed for continental shelf samples, but these differences suggest that further study of solubilities would be well worthwhile.

In general, several conclusions seem obvious from the solubility study. Zinc and Cu solubilities are clearly source dependent. Cadmium solubility may also be source dependent, but it is not evident from this study. The only indication of source dependence for Cd is the change in solubility with wind direction. Zinc solubility in the Savannah, Brunswick, and Jacksonville samples is negatively correlated with EF_{crust}, while Cu solubility of all samples is positively correlated with EF_{crust}. These patterns do not hold for the dust storm samples. In atmospheric samples collected over the continental shelf, solubility of atmospheric Cu and Zn in seawater is apparently a function of the source of the aerosol. The variability of trace metal solubility in seawater is obvious from this study. This fact emphasizes the need for long term sampling if one wishes to accurately evaluate metal inputs to marine waters.

Atmospheric Fluxes of Trace Metals to Georgia Bight Waters

Some rough estimates of atmospheric input of trace metals to the Georgia Bight can be made using the atmospheric data obtained in this study together with a model for fluxes of various sized particles to the water. The flux model used here is the same used by Duce (1975), and Duce and Hoffman (1976), to estimate fluxes of metals to the ocean in the Bermuda area. These authors made use of three different models, but their model #3 will be used here because it yielded results intermediate between the other two. Briefly, this model uses mean dry deposition velocities (Vd) obtained at four stations in the North Sea by Cambray, et al., (1975). The mean dry deposition velocity for each metal is then multiplied by the mean atmospheric concentration for that metal to obtain a flux to the water. To account for precipitation removal of particles, the assumption is made that rainfall accounts for twice the flux of dry fallout, and the total flux is three times the dry fallout. This model #3 does not give fluxes for Cu, Cd, or Ni since the data by Cambray (1975) did not include these metals. For these metals, model #1 (Duce, 1975) was used. This model assumes that atmospheric particles are distributed uniformly to a height of 5000 meters and there are 40 rainfalls/year which remove these particles.

The deposition velocities used in this study, adjusted for total fallout including rainfall, are presented in

Table 19. Estimated Trace Metal Fluxes from Atmosphere to Georgia Bight

Metal	Vd cm/sec	Charleston	Savannah	Brunswick	Jacksonville	Columbus-Iselin
		ng/m^3				
			Weighted Averages*			
Cd	0.6	1.7	0.41	0.31	0.24	0.27
Zn	1.7	21	16	14	6.5	15
Cu	0.58	12	4.1	5.7	2.6	12
Ni	0.62	2.5	15	3.6	2.4	5.1
Pb	0.79	28	26	30	26	22
Mn	1.3	3.5	3.3	2.0	3.9	2.0
Fe	2.5	71	114	100	77	185
Al	4.5	93	113	138	168	95

Fluxes (kg/yr)***

Metal	Total Flux	Charleston**	Savannah	Brunswick	Jacksonville	Rest of Bight
Cd	2.0x10^{3}	8.7x10^{2}	2.0x10^{2}	1.4x10^{2}	1.1x10^{2}	7.0x10^{2}
Zn	2.4x10^{5}	3.1x10^{4}	2.4x10^{4}	1.8x10^{4}	0.9x10^{4}	1.6x10^{5}
Cu	5.9x10^{4}	5.8x10^{3}	2.0x10^{3}	3.4x10^{3}	1.2x10^{3}	4.7x10^{4}
Ni	3.0x10^{4}	1.3x10^{3}	7.8x10^{3}	1.5x10^{3}	1.1x10^{3}	1.8x10^{4}
Pb	1.8x10^{5}	1.6x10^{4}	2.0x10^{4}	1.8x10^{4}	1.7x10^{4}	1.1x10^{5}
Mn	2.9x10^{4}	3.7x10^{3}	3.7x10^{3}	1.9x10^{3}	4.1x10^{3}	1.6x10^{4}
Fe	4.0x10^{6}	1.5x10^{5}	2.6x10^{5}	1.9x10^{5}	1.6x10^{5}	3.2x10^{6}
Al	4.6x10^{6}	2.0x10^{5}	4.3x10^{5}	4.5x10^{5}	5.9x10^{5}	2.9x10^{6}

Table 19 (Continued)

* See text for explanation.

** The Flux areas in the vicinity of each city were taken to be 2500 km^2, (50 km by 50 km).

*** Yearly flux calculation = (Vd) x (Weighted Avg.) x (kg/ng) x (area) x (sec/yr).

Table 19, together with the calculated fluxes in kg/yr to each of the study areas, as well as to the entire 3×10^4 km^2 Georgia Bight. Each individual study area was taken to be 2500 km^2 (50 km x 50 km). The weighted average atmospheric concentrations used in the flux calculations (Table 19), were calculated from information in Table 12 in which wind data were separated into easterly and westerly components. The part of the year that the particular wind direction prevailed was obtained from local NOAA climatological reports for each of the study areas. Thus, the flux calculations are weighted for dry deposition, rainfall input, wind direction, and atmospheric concentration by area. It must be kept in mind, of course, that these are order of magnitude estimates. Actual measurement of deposition velocities due to dry fallout and rainfall over the Georgia Bight would remove a considerable amount of uncertainty from the calculations. There is, however, good reason to think that dry deposition velocity should not vary greatly from area to area. Different metals tend to always be associated with particular particle sizes (Lee and Von Lehmden, 1973; Rahn, et al., 1971; Gladney, et al., 1974), and the deposition velocity of any particular particle size should be about the same in any area. Rainfall input, of course, could be quite variable, but the estimate used here is an intermediate value between estimates made by several observers of rainfall inputs to marine waters

(Duce, et al., 1976).

There have been few studies of atmospheric trace metal fluxes to nearshore marine waters with which to compare these data. Some of the available data are listed in Table 20. The data of Windom and Smith (1978) are most relevant here, because they are from the same study area. Their estimates were for the entire South Atlantic Bight (6×10^4 km^2), based on earlier data gathered from the same general sampling area. The estimates in this study cover an area half as large, but there is good agreement between results, taking the area discrepancy into account. Other results in Table 21 are from the New York Bight, (Duce, et al., 1976a), and Nantucket, Massachusetts (Lazrus, et al., 1970). The New York and Nantucket data have been normalized to a 10^4 km^2 area by Duce, et al., (1976a). These other studies did not report as many metal fluxes as the present study, but the data available for comparison show good order of magnitude agreement, considering all the assumptions made and the different approaches to the problem in each study. The New York Bight fluxes for three anomalously enriched metals (Zn, Cd, and Pb) are several times greater than in this study. The Nantucket fluxes for Zn and Pb are also several times greater than this study. If these differences are real, they probably reflect the generally greater anthropogenic inputs to the atmosphere in the northeast United States.

Table 20. Comparison of Atmospheric Trace Metal Fluxes to Various Nearshore Marine Waters

	Cd	Zn	Cu	Ni	Pb	Fe	Al
				kg/yr x 10^3			
South Atlantic Bight	---	910	190	370	---	---	---
Windom, et al. (1978) (6×10^4 km^2)							
New York Bight	12	810	---	---	600	3720	4290
Duce, et al. (1976) (10^4 km^2)							
Nantucket, Mass.	---	760	---	---	850	110	---
Lazrus, et al. (1970) (10^4 km^2)							
This Study (3×10^4 km^2)	2	240	59	30	180	4000	4600

The contributions that the fluxes of Cd, Cu, and Zn make to the dissolved content of Georgia Bight waters were estimated by making use of per cent solubilities for these metals as reported earlier (Table 18), and the fluxes for each metal (Table 19). Per cent solubility was multiplied by yearly fluxes to obtain the contribution to the soluble fraction. This calculation was made for each sampling area, as well as for the overall bight (Table 21). The volume of water in the vicinity around each city was calculated on the basis of a 50 km by 50 km area, and an average depth of 10 m. The overall bight was taken to be 3 x 10^4 km^2 in area having an average depth of 30 m. Dissolved seawater concentrations of Cd, Cu, and Zn were analyzed in each of the four urban areas as a part of the solubility study (Table 21).

It is interesting to note that in most cases, seawater concentrations are several times greater than the annual soluble metal contribution. In the case of Cu and Zn for the Charleston data, however, contributions are disproportionately high compared to seawater concentrations. This could again indicate that migration of Cu and Zn from seawater to air is significantly affecting flux values. One other apparent discrepancy in the data in Table 22 is in the Zn data for Jacksonville. The annual contribution appears high compared to ambient concentration. The concentration value used is very likely low. In a series

Table 21. Atmospheric Contributions to Dissolved Cu, Cd, and Zn in the Georgia Bight

Study Area	Mean[a] % Sol.	Flux (kg/yr)	Amount Dissolved (ug/l/yr)	Ambient Seawater Conc. (ug/l)*
		Cadmium		
Charleston	35	8.7×10^{2}	0.012	0.045
Savannah	38	2.0×10^{2}	0.003	0.005
Brunswick	58	1.4×10^{2}	0.003	0.005
Jacksonville	26	1.1×10^{2}	0.001	0.004
Total Bight	39**	2.0×10^{3}	0.001	---
		Copper		
Charleston	58	5.8×10^{3}	0.13	0.36
Savannah	5	2.0×10^{3}	0.004	0.32
Brunswick	30**	3.4×10^{3}	0.04	0.37
Jacksonville	26	1.2×10^{3}	0.01	0.28
Total Bight	30**	5.9×10^{4}	0.02	0.16**
		Zinc		
Charleston	91	3.1×10^{4}	1.1	1.6
Savannah	30	2.4×10^{4}	0.29	1.0
Brunswick	59	1.8×10^{4}	0.42	1.1
Jacksonville	91	0.9×10^{4}	0.32	0.44
Total Bight	68**	2.4×10^{5}	0.18	1.4***

Volume of water used in calculations of individual areas = 2.5×10^{13} liters.

Volume of water in total bight = 9×10^{14} liters.

* = Measured in this study.

** = Mean of all calculated solubilities for that metal in that area.

Table 21 (Continued)

*** = Mean of 12 values from Windom and Smith (1978)

a = Mean of all solubilities for that metal for that area. Solubilities greater than 90% were taken to be 95%, and those less than 10% were taken to be 5%.

of 16 seawater samples taken throughout the Georgia Bight, Windom and Smith (1978), did not find any Zn concentration below 1.0 ug/l. Also, the other ambient concentrations of Zn for other areas are above 1.0 ug/l, suggesting the given value of 0.44 ug/l in Table 22 may be erroneous.

Trace Metals in Spanish Mosses

An attempt was made to use Spanish mosses as an additional indicator of sources of metals. Over the past several years, many investigators have reported using mosses of various kinds as indicators of heavy metal deposition (Goodman and Roberts, 1971; Little and Martin, 1974; Ruhling and Tyler, 1973; Martinez, et al., 1971). Mosses evidently possess considerable ion-exchange properties (Knight, et al., 1961; Clymo, 1963). Moss shoots readily retain particular matter from the air, and then provide a large surface area for ion exchange phenomena to proceed. The above investigators have discovered relatively greater concentrations of heavy metals in mosses near industries and around urban as compared to non-urban areas. It was therefore felt that analysis of metals in mosses in this study might be helpful in tracing sources. Spanish moss samples were collected on the seaward side of each of the four cities. The seaward side of the cities was chosen specifically because it was felt that mosses there would be more likely to reflect trace metal concentrations of air moving out over the continental shelf. Locations are shown in Figure 8. Mean concentrations of metals in mosses for each city, along with the standard deviations of each mean are given in Table 22. Mean EF_{crust} values for each set of samples are also given in Table 22. Plots of the concentrations and EF_{crust} data for Cd, Cu, Ni, and Zn by area are presented in Figures 9 and 10. These four metals were plotted for a comparison with the plots for atmospheric data (Figures 3 and 4).

Results from these analyses do not correspond with the atmospheric data. In fact, the moss data do not vary from area to area. Considering the uncertainties, all four areas are identical with regard to EF_{crust}. Concentrations change slightly from area to area, but not to the degree that the atmospheric samples changed. For example, by far the highest Ni concentrations occurred in Savannah air samples, but Ni is lowest in Savannah mosses.

In order to further explore any possible relationships between continental shelf air and moss samples, inter-element correlations were performed for the Charleston mosses. The Charleston mosses were selected for the same reasons discussed previously, (i.e. strong westerly winds prevailed during the sampling period). In comparing Charleston moss and air correlation coefficients (Tables 14 and 23), a few interesting patterns can be seen. Cadmium is correlated with Fe and Al in both cases. Iron and Al are also correlated with each other in both cases. For the most part, however,

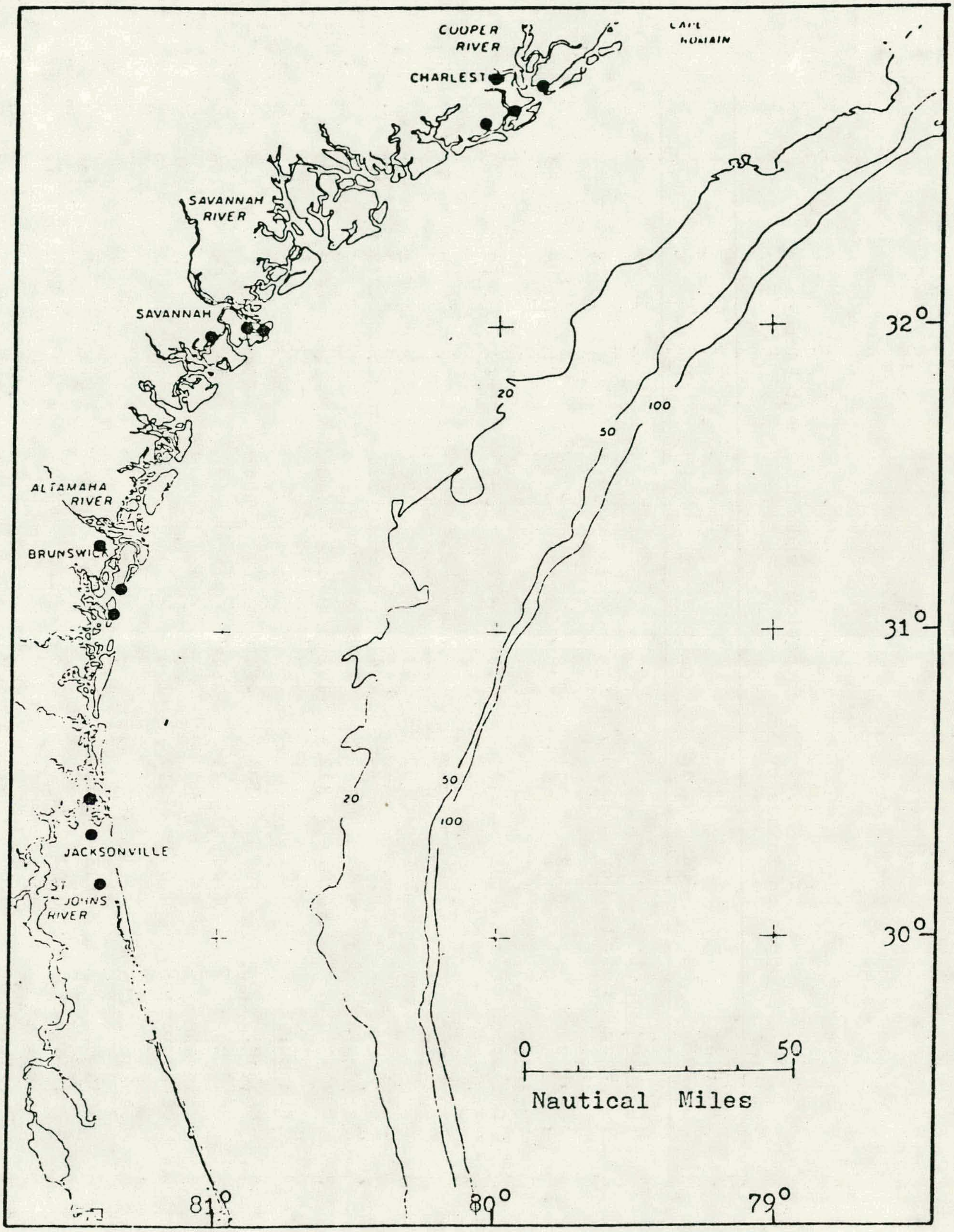
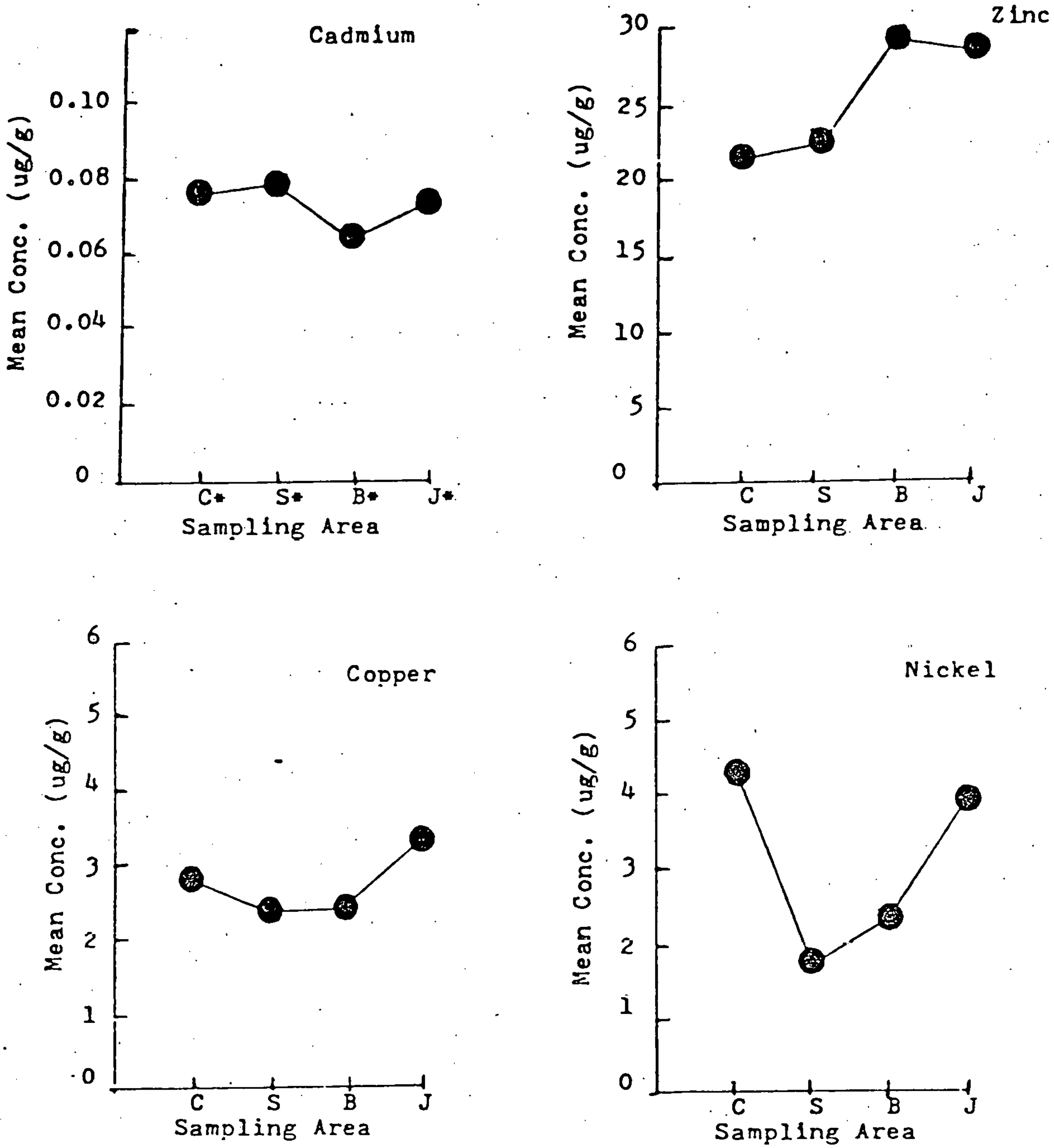


Figure 8. Locations of Spanish Moss Samples around each Urban Area

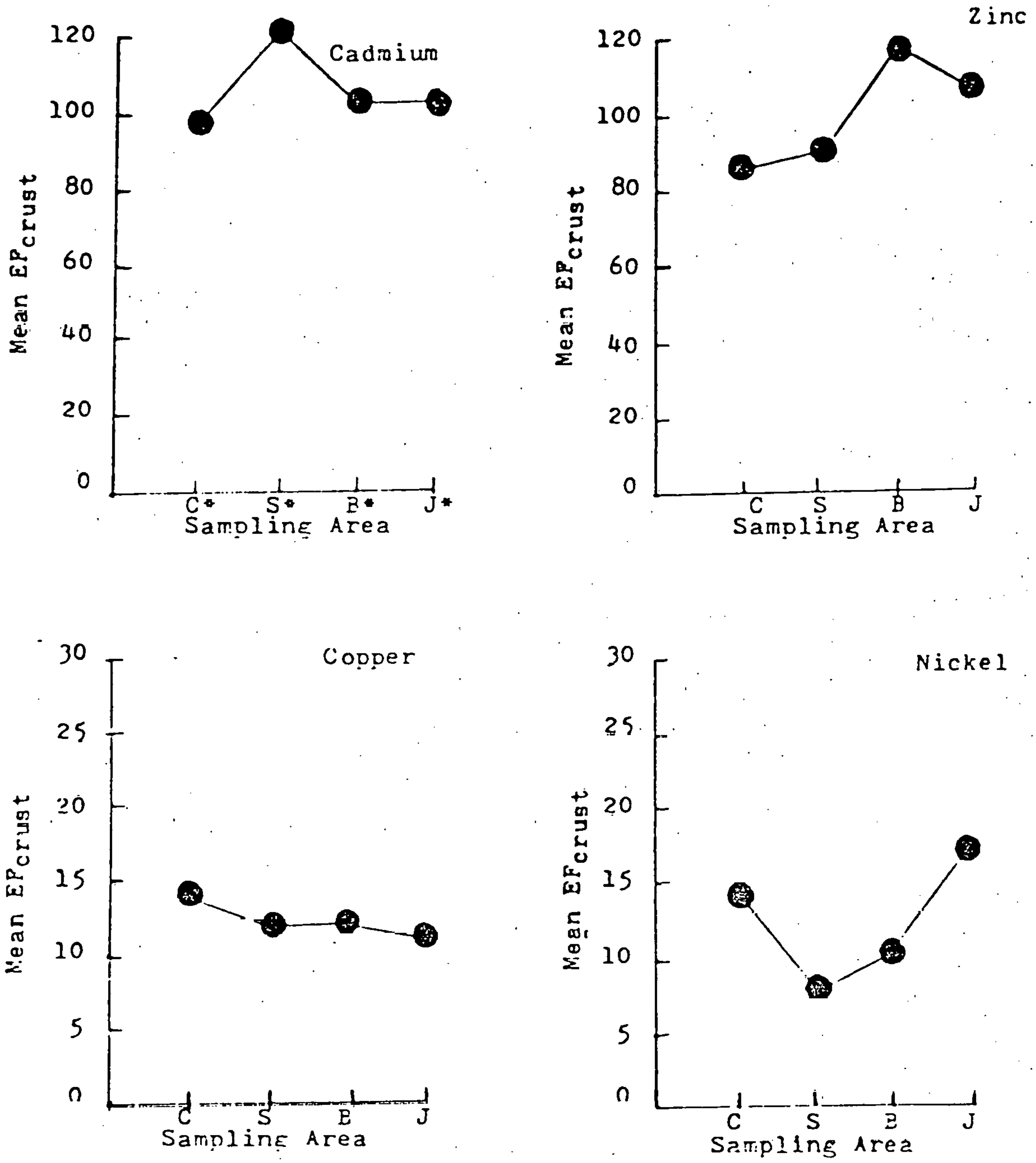
Table 22. Mean Trace Metal Concentrations and Enrichment Factors in Spanish Mosses by Area

Sample Area	Cd	Zn	Cu	Ni	Pb	Mn	Fe	Al
Charleston								
Mean EF_{crust}	97	87	15	14	1869	8.5	1	---
Mean ug/g	0.08	21	2.8	4.2	89	37	200	310
Standard Deviation	±0.01	±11	±0.9	±1.2	±68	±18	±69	±87
Savannah								
Mean EF_{crust}	121	92	13	7.5	1767	8.9	1	---
Mean ug/g	0.08	22	2.4	1.6	128	25	242	274
Standard Deviation	+0.01	±12	-1.2	±1.3	+134	±11	±98	±97
Brunswick								
Mean EF_{crust}	103	134	14	10	3041	7.4	1	---
Mean ug/g	0.06	29	2.4	2.2	121	22	165	246
Standard Deviation	±0.03	±17	±1.0	±1.0	±62	±3.5	±23	±20
Jacksonville								
Mean EF_{crust}	102	106	13	17	2372	8.6	1	---
Mean ug/g	0.07	27	3.3	3.8	107	25	221	279
Standard Deviation	±0.05	±20	±1.9	±0.9	±65	±10	±145	±148



* C = Charleston, S = Savannah, B = Brunswick,
J = Jacksonville, CI = Columbus-Iselin

Figure 9. Mean Spanish Moss Trace Metal Concentrations by Area



* C = Charleston, S = Savannah, B = Brunswick,
J = Jacksonville, CI = Columbus-Iselin

Figure 10. Mean Spanish Moss EF_{crust} Values by Area

the coefficients in the two tables are so greatly different that this comparison does not really help.

On the basis of the limited amount of air data available in this study, it does not seem that the mosses are of much value in tracing sources. It may be, however, that concentrations of metals in mosses represent long term average atmospheric concentrations, while the samples in this study are single points in the annual cycle. If the mosses are in fact better long term indicators of trace metal concentrations in the atmosphere, then the indication is that the four urban areas studied do not vary much in their contributions to Georgia Bight air.

Table 23. Interelement Trace Metal Correlation Coefficients Charleston-Spanish Mosses

	Zn	Cu	Ni	Pb	Mn	Fe	Al
Cd	+0.61	+0.22	+0.61	+0.20	-0.31	+0.91	+0.90
Zn		+0.80	-0.34	+0.90	-0.78	+0.62	+0.37
Cu			-0.42	+0.68	-0.89	+0.67	+0.45
Ni				-0.38	-0.20	+0.25	+0.43
Pb					-0.45	+0.45	+0.20
Mn						-0.65	-0.44
Fe							+0.90

n = 4

At 95% level of Confidence, r = 0.95

At 99% level of Confidence, r = 0.99

CHAPTER IV

CONCLUSIONS

This study has evaluated atmospheric trace metal concentrations and enrichment factors over the Georgia Bight. Both generally decrease southward from Charleston to Jacksonville. Anomalously enriched metals over the Georgia Bight are Cd, Zn, Cu, Ni, and Pb.

Atmospheric trace metal concentration patterns can be seen around each nearshore urban area, while further offshore, these patterns break down but continental influences are still evident throughout the Bight.

Observations from this study suggest that seawater may influence Cu and Zn concentrations in Georgia Bight air.

Solubilities of Zn and Cu in air samples are source dependent. Nickel shows negligible solubility in all samples collected in this study.

Fluxes of trace metals from atmosphere to seawater in the Georgia Bight are comparable to other areas along the east coast. These fluxes make considerable contributions to dissolved metal levels in Georgia Bight water.

Spanish mosses were not useful in this study in tracing sources of atmospheric trace metals, but the mosses may be good long term indicators of relative atmospheric trace metal concentrations.

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