ELSEVIER

Journal of Chromatography A, 754 (1996) 169–185

JOURNAL OF CHROMATOGRAPHY A

Spatial and temporal trends of pesticide residues in water and particulates in the Mississippi River plume and the northwestern Gulf of Mexico

Debra J. McMillin*, Jay C. Means

Louisiana State University School of Veterinary Medicine, Department of Veterinary Pharmacology and Toxicology, Baton Rouge, LA 70803, USA

Abstract

Selected herbicides, chlorinated pesticides and polychlorinated biphenyls (PCBs) were measured using GC–MS SIM analysis in dissolved, colloidal and particulate phases of sea water samples collected seasonally over a three-year period. Sample preparation used sequential membrane filtration and ultrafiltration prior to solid phase extraction (SPE) of the dissolved phase. Chlorinated pesticides and PCBs were rarely detected. Herbicides were found primarily in the dissolved and colloidal phases. Atrazine was ubiquitous over the entire northwestern Gulf of Mexico coastal shelf area in spring, summer and fall. Highest herbicide concentrations occurred in summer and fall, except for alachlor, which was only detected in spring run-off.

Keywords: Environmental analysis; Water analysis; Extraction methods; Pesticides; Polychlorinated biphenyls

1. Introduction

Several investigators have reported concentration levels and transport of herbicides in the Mississippi River, its drainage basin soils and tributary rivers, showing levels of *s*-triazines that have prompted human health and environmental concerns [1]. Non-point agricultural run-off of pesticides from this vast area of the Mississippi River drainage basin presents a concern for potential impacts upon ecological health in the Gulf of Mexico. Pereira and Rostad [2] estimated annual transport of atrazine, cyanazine, metolachlor and alachlor to the Gulf at less than 2% of applied amounts. Even so, stream loads at Belle Chase, LA, were estimated at up to 2000 kg/day for atrazine in 1989 [2] and 1992 [3]. Goolsby et al. [4] reported increased mass transport of atrazine, peaking at 7110 kg/day, during the summer flooding in 1993, in contrast to expectations that increased discharge rates would tend to dilute herbicide concentrations. Total discharge to the Gulf at this time was estimated to have increased by 80% over that for 1991. These investigators concluded that the transport of these large amounts of herbicides to the Gulf on an on-going basis represents a potential threat to the coastal and estuarine ecosystems. Kemp et al. [5] reported phytotoxicity of atrazine to submerged vascular plants at 5 ppb. In a review of the literature, Stevenson et al. [6] postulated that atrazine, in combination with other factors, could be responsible for a "chronic stressed condition" of submerged aquatic plants.

Chlorinated pesticides, while mostly outlawed, are

*Corresponding author.

0021-9673/96/$15.00
PII S0021-9673(96)00325-1

also still of concern due to their persistence and potential for carcinogenic and reproductive effects. In addition, there is evidence that these chemicals are still used at least occasionally (and illegally) in Louisiana [7]. To date, few data have been obtained on the fate of pollutants discharged into the Gulf of Mexico and their effects on aquatic ecosystems.

An investigation of terrigenous inputs to the Gulf of Mexico coastal shelf waters along the Louisiana and Texas coasts was initiated in 1992. An additional focus was the interaction of pollutants with natural colloids and suspended particulate matter in the possible enhancement of transport in the aqueous phase [8,9]. This required the development and verification of sensitive (parts per trillion range) and compound-specific analytical techniques for application with sea water samples. Methodology included separation of water samples into dissolved, colloidal and particulate phases on board a ship.

Solid phase extraction (SPE) disks were employed for dissolved phase samples to achieve detection limits such that the fate of pollutants could be described quantitatively, to facilitate sample processing and to avoid transport of the large volumes of water required. SPE methodology has been in use for almost two decades, with bonded-phase microparticulate packings housed in various column configurations. More recently (1990), these bonded-phases have been embedded onto PTFE membranes (Empore) or impregnated into glass fiber disks (SPEC) (see Section 2.1). These disks have advantages compared to the cartridge style disks in reduced plugging, elimination of channeling, higher flowrates and improved mass transfer. Other advantages of SPE include the generation of cleaner extracts, potentially improving detection limits, and the ability to store extracted analytes on the SPE material for transport and until further elution and analysis [10], making disks ideal for field sampling. Senseman et al. [11] examined the effects of SPE disk storage, at various temperatures and times, on the recovery of the herbicides and chlorinated pesticides extracted from water samples. They recommended storage at −20°C for up to 90 days, but showed acceptable recoveries for up to 180 days for a range of pesticides. Finally, Hagen et al. [12] suggested that SPE disks could be used with in-line filtration and pressure-induced flow applications, allowing ease of use under difficult conditions, such as moving vessels at sea.

In practice, natural waters may still clog the pores of the SPE disks, however, this was not a consideration in their use for dissolved phase samples, where suspended particulates and colloidal phase material had already been removed. Another consideration is a phenomenon known as "breakthrough", which occurs when analytes are no longer retained by the bonded phase, due to saturation or insufficient retention. Saturation is unlikely with environmental samples where concentrations are in the ppb range. Insufficient retention can be caused by improper conditioning or sample application (such as flowrate) or by improper choice of phase [13].

For this study, several herbicides, pesticides and PCBs were incorporated into GC–MS analytical methodology previously developed for parent and alkylated polynuclear aromatic hydrocarbons (PAHs) [14]. These five classes of organic pollutants were represented by a total of 77 analytes quantified using selected ion monitoring (SIM). GC–MS analysis was the ideal choice for a survey of such a broad range of compounds, where the sensitivity and selectivity of SIM was enhanced through the use of a high resolution capillary column.

The three-year investigation involved collection of water samples at 50 sites and at two depths in each of three seasons. Sampling followed the path of the discharge plume of the Mississippi and Atchafalaya Rivers, known as the "coastal current layer", from Timbalier Bay in Louisiana westward to Aransas Pass, Texas. Cooperating investigators have assembled an extensive database of oceanographic information for this region and time period, including currents, winds, temperature, salinity, turbidity, dissolved oxygen, plant pigments, primary production and phytoplankton/zooplankton taxonomy, in addition to organic and inorganic pollutants [15].

This paper summarizes data for herbicides, chlorinated pesticides and PCBs detected in dissolved, colloidal and particulate phases of water samples and sediment samples. The herbicides were by far the most ubiquitous and abundant pollutants and have become a focal point of this research, both in terms of potentially adverse impacts upon aquatic life and for use in modeling chemical transport processes in the coastal current.

2. Experimental

2.1. Materials

All solvents were of pesticide grade. Other reagents, such as sodium sulfate and glassware were cleaned prior to use with methanol and dichloromethane (DCM) and baked at 180°C overnight. All sample storage containers were pre-cleaned and had PTFE-lined caps. Standards were obtained from Ultra Scientific (North Kingstown, RI, USA). The stock standard (most concentrations at or near 5 ng/μl), from which spiked and calibration standards were prepared, consisted of a mixture of chlorinated pesticides (US-102), PCBs (US CB-681M), six deuterated PAH surrogates (US-108), dibromooctafluorobiphenyl (DBOFBP) (US PPS-170), 1,3-dimethyl-2-nitrobenzene (nitroxylene) (US PPS-100) and other individual components obtained primarily from Ultra Scientific. The instrument internal standard was 2-fluorobiphenyl (US ATS-140).

"Particulate" filters were 0.4 μm, 142 mm membrane filters from Nuclepore (Pleasanton, CA, USA) preceded by glass fiber prefilters (124 mm GF/C) from Whatman (Maidstone, UK). The filtration apparatus consisted of a stainless steel pressure vessel (Cole-Parmer, Niles, IL, USA) connected by PTFE tubing to a 142-mm stainless steel filter holder (Millipore, Bedford, MA, USA). The ultrafiltration apparatus was an Amicon Model DC10L, Model 499 (Amicon, Beverly, MA, USA) equipped with Amicon Spiral-wound ultrafiltration cartridges type S10Y3 (M_r cutoff, 3000).

SPE disks (C_{18}, 47 mm) were obtained from Analytichem International (Harbor City, CA, USA) (Empore), and Spec Corp. (Irvine, CA, USA) (Spec). SPE disks were placed in a 47-mm polycarbonate in-line filter holder (Millipore, Cat. No. XX4304700). A MasterFlex Model 7568-00 ten-channel peristaltic pump equipped with No. 14 heads (Cole-Parmer) was used to pump water onto the SPE disks.

2.2. Sampling

Field collections were performed on six cruises of ten days duration each; three spring (April 1992, 1993, 1994), two summer (July 1993, 1994) and one fall (October, 1992) cruise. For all cruises, except that of July 1994 (Cruise 5), water samples were collected along up to eight transects perpendicular to the coastline (Fig. 1). Each transect was sampled at two to five points and at surface (1 m) and bottom (1 m up) depths, resulting in the collection of approximately 100 20 l samples per cruise. Cruise 5 in April 1994 followed a course directly west of the mouth of the Mississippi River to Timbalier Bay, the starting transect of the other cruises. The reason for sampling at this location was to study the plume of the river discharge prior to significant dilution by mixing with sea water. Seven longitudinal transects from longitude 89.4°W (the river mouth) to 90.6°W (com-

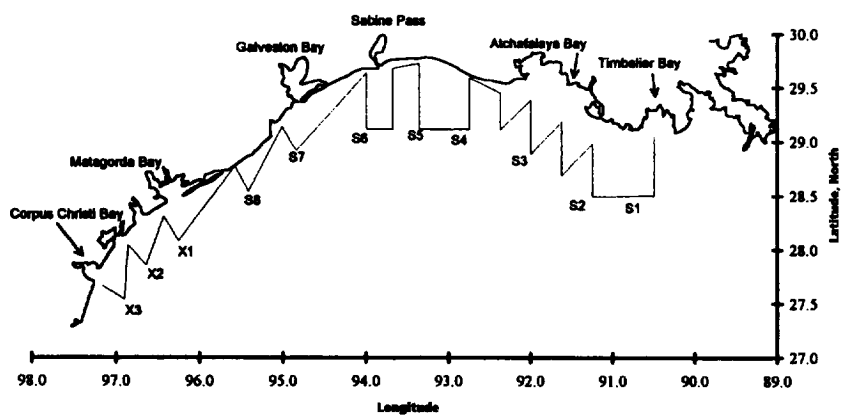

Fig. 1. Cruise track for water sampling sites (transects S1 to S8) for five seasonal cruises (April 1994 cruise sampled along the "plume" at, and to the west of, the mouth of the Mississippi River out towards S1, cruise track not shown).

pared to longitude 90.5°W for transect S1 of the basic cruise track) were sampled at two station points between latitudes of 28.7°N and 29.0°N.

Water samples (20 l) were collected in polypropylene "cubitainers" (Cole-Parmer) and were transferred to a stainless steel pressure vessel. Compressed nitrogen (99.9%) ($1.4 \cdot 10^5$ Pa) was used to facilitate filtration through a 124-mm 0.4 μm Nuclepore membrane filter with a Whatman GF/C glass fiber prefilter. This concentrated the total particulate phase from 20 l on the two filters (samples with high particulate levels required additional filter sets), which were then stored together in small glass jars that were stored at −20°C. Particulate filters were pre-wet with deionized water prior to filtration, and filtration time and surface-area-to-volume ratios were minimized in the filtration apparatus. This reduced the possibility of low concentration estimates due to adsorption. The filtrate was immediately ultrafiltered using the Amicon ultrafiltration system to separate the truly dissolved and enriched colloidal phases. The colloidal fraction was concentrated to 240 or 480 ml (volume adjusted to minimize heat losses) and stored in amber glass jars at 5°C. Dissolved phase (ultrafiltrate) water was collected in clean 4 l cubitainers (further processing on board the ship is described below.)

During the first cruise, bedded sediments were also collected along crossing transects adjacent to the Calcasieu, Sabine and Galveston estuaries, and in a "box" design near the Atchafalaya outflow area. Bedded surficial sediments (0–10 cm) were collected using an Eckman dredge. Sediment samples and filter samples were placed in pre-cleaned specimen jars, sealed with tape in the field and packed on ice for transport to the laboratory. Once in the laboratory, the samples were stored at −20°C.

2.3. Extraction procedures

2.3.1. Particulate phase

The Nuclepore membrane and glass fiber prefilters were placed together in tared PTFE digestion bombs (digestion for trace metal analysis followed organic extraction). Initial extraction was performed with 45 ml of hexane–acetone (2:1, v/v). The surrogates standard was added (120 ng in methanol of deuterated PAH surrogates, nitroxylene and DBOFBP) just prior to the first extraction, and the bombs were placed in an ice-cooled sonicating bath for 6 min. After decanting, extractions were performed two more times using 45 ml of hexane. The extracts were combined and acetone was removed by adding >75 ml of purified water. The top layer of hexane was removed by pipette, filtered through clean anhydrous sodium sulfate and concentrated by rotoevaporation under a nitrogen stream to a final volume of 100 μl. To obtain the particulate fraction mass, the PTFE bombs containing the filter sets were dried at 60°C overnight in an oven modified to exchange the atmosphere with charcoal-filtered air. The masses of the filters and bombs were recorded and the samples were sent to the inorganics sample preparation laboratory for acid digestion. The dry masses of particulate samples obtained from the six cruises averaged 0.54 g and ranged from 0.01 to 15.71 g.

2.3.2. Colloidal phase

Samples (200–500 ml) were transferred to separatory funnels, surrogates standard added (400 ng in methanol of deuterated PAH, nitroxylene and DBOFBP) and extracted with DCM, in triplicate, first at ambient, (neutral) pH, then at acidic pH (2). The extracts from both pH levels were combined and the extract dried and concentrated as described for particulate samples in Section 2.3.1, with solvent exchange to hexane and a final volume of 200 μl.

2.3.3. Dissolved phase

The use of plastic membrane filter housings connected in-line to peristaltic pumps allowed the dissolved phase water samples to be concentrated onto SPE disks on board the ship and made the apparatus capable of withstanding high seas. Prior to SPE extraction on board ship, 20 μl of the deuterated PAH surrogates standard at 40 ng/μl (800 ng total) in methanol was added to 4 l of the ultrafiltrate (dissolved-phase) along with 25 ml of methanol and the solution was mixed thoroughly. SPE disks were conditioned with methanol, DCM and purified water in a standard all-glass filtration apparatus, then placed in the Nuclepore holder. A 2-3 l volume was pumped through a SPE disk using the peristaltic pump set for a flow-rate of 20 ml/min. Extracted volume was determined by measuring the amount of

water that passed through the filtration apparatus. The SPE disk was removed from the filter holder and stored in a small glass vial covered with ~10 ml of methanol and was stored at −20°C while on board the ship, transported on ice and stored again at −20°C. Back in the laboratory, an additional laboratory surrogates standard (120 ng each of DBOFBP and 1,3-dimethyl-2-nitrobenzene in methanol) was added to the vials containing SPE disks, to monitor the laboratory extraction performance. Since the SPE disks are fragile, we chose to extract the disks by sonicating with solvent in the same storage jars, eliminating losses due to excessive drying, weeping of excess water or tearing in reassembling the filtration glassware. The disks were extracted three times with 20, 10 and 10 ml of DCM, sequentially, using a sonicating bath for 1 min per extraction. The extracts were combined in a separatory funnel and the DCM separated from methanol (storage solvent) and residual water by adding excess water (>25 ml) and decanting the DCM layer over clean anhydrous sodium sulfate. Concentration steps for these extracts were similar to those of colloidal phase samples.

2.3.4. Sediments

This extraction method was a modification of that described by MacLeod et al. [16]. Excess water was decanted from sample jars prior to thorough mixing of the sediment sample, and 35 g was weighed into an amber bottle. The sediment was covered with 125 ml of DCM and ~65 g of anhydrous sodium sulfate were incorporated until the sediment mixture was free-flowing. The surrogates standard was added (800 ng in hexane of the deuterated PAH surrogates) just prior to the first solvent aliquot to monitor extraction efficiency. The jars were sealed and placed on a roller mill for 16, 6 and 16 h, sequentially, for a total of three extractions using the modified rock tumbler and rolling times specified by MacLeod et al. [16]. The DCM from each jar was decanted into an amber jar and refrigerated until three extracts were collected. The decanted DCM was filtered through anhydrous sodium sulfate and was concentrated by rotoevaporation and a nitrogen stream to a final volume of 200 μl, with solvent exchange to hexane. Activated fine granular copper was added to reduce sulfur interferences.

2.3.5. Quality control samples

Laboratory reagent blanks and spiked blanks (process) or matrix spikes for sediments were prepared for every ten samples. Spiking solutions were prepared by dilution with methanol of the stock mixture containing all analytes and surrogates to 0.5 ng/μl. Typically, 200 μl of the spiking solution was added to spike the samples. "Ship blanks" consisting of HPLC-grade water that was processed as samples at sea were generated during three cruises.

In an experiment to determine detection levels and the precision of the methodology for SPE extraction and analysis procedures, natural sea water samples from Bodega Bay (CA, USA) were spiked in triplicate at four concentration levels (5, 10, 50 and 100 pg/ml) of all target analytes, with the exception of the herbicides. Samples in this experiment were unfiltered sea water, therefore, a GF/C filter was placed on top of the Empore disk in the in-line holder. After pumping, the GF/C filter was discarded and the SPE disk removed and placed in an all-glass filtration apparatus for elution with 15 ml of DCM.

2.4. Instrumental analysis

Analytical instrumentation consisted of a Hewlett-Packard (HP) (Hewlett-Packard, Wilmington, DE, USA) 5890 GC/HP5970B MS with direct capillary interface maintained at 300°C. The mass spectrometer was tuned prior to calibration every 16 h using perfluorotributylamine (PFTBA) and was operated at 200 V above the tune value. The column was a 30 m×0.25 mm I.D., 0.25 μm film DB-5 capillary column (J&W Scientific, Folsom, CA, USA) operated with UHP helium at 40 cm/s. Injections (2 μl) were accomplished using a HP7673A automatic liquid sampler into a deactivated, glass-wool-plugged liner obtained from Restek (Bellefonte, PA, USA). The injection port temperature was 250°C. Initial column temperature was maintained at 50°C for 3 min, followed by three ramps: 1) 6°C/min to 120°C, 2) 3°C/min to 190°C and 3) 12°C/min to 300°C and then held for 14.5 min. The series of ramps was selected primarily to optimize the separation of alkylated PAHs (data not shown). SIM was performed using fifteen retention time-based windows, containing twelve ions each. Windows for detection of PCBs were determined by the analysis of various

Table 1
Target analyte identification, retention times, GC–MS ions for quantification (Primary) and confirmation, concentration of calibration solution and typical response factors generated from a calibration solution

Analyte	Abbreviation	Peak number	Retention time (min)	Primary ion *m/z*	Confirming ions		Calibration standard concentration ng/μl	Typical response factor
					No. 1 *m/z*	No. 2 *m/z*		
[$^2H_8$]Naphthalene (SS)	d8 NAPH		13.30	136			0.50	1.53E−06
2-Nitro-*m*-xylene (SS)			13.50	134			0.50	1.00E−05
Hexachlorobutadiene			14.27	225	227		0.50	2.63E−06
2-Fluorobiphenyl (I.S.)			18.30	172			5.00	7.78E−07
[$^2H_{10}$]Acenaphthene (SS)	d10 ACE		21.76	164	165[a]		0.50	1.93E−06
Dibromooctafluorobiphenyl (SS)	DBOFBP	1	28.98	456			0.50	2.81E−06
Trifluralin		2	29.05	306	264		0.50	5.65E−06
2,3-Dichlorobiphenyl	CL2-PCB	3	29.30	222	224		0.15	1.95E−06
Hexachlorobenzene		4	29.60	284	286		0.50	3.31E−06
Simazine		5	30.79	201	186	68	0.50	1.05E−05
Atrazine		7	31.17	200	215		0.50	5.60E−06
[$^2H_{10}$]Phenanthrene (SS)	d10 PHEN	8	31.68	188			0.50	1.04E−06
2,4,5-Trichlorobiphenyl	CL3-PCB	11	34.21	256	258		0.15	1.98E−06
2,2′,4,6-Tetrachlorobiphenyl	CL4-PCB	14	35.04	292	290		0.30	2.20E−06
Alachlor		17	36.38	160	188		0.50	5.17E−06
Metolachlor		20	38.68	162	238		0.50	2.59E−06
Cyanazine		21	39.29	225	240	44	0.50	2.57E−05
o,p′-DDE		37	42.76	246	248		0.50	1.25E−06
alpha-Chlordane		38	43.09	373	375		0.50	3.97E−06
trans-Nonachlor		39	43.35	409	407		0.50	3.63E−06
2,2′,3,4,5′-Pentachlorobiphenyl	CL5-PCB	40	44.06	326	324		0.30	2.28E−06
Dieldrin		41	44.05	263	79		0.50	1.69E−05
p,p′-DDE		42	44.19	246	248		0.50	2.13E−06
o,p′-DDD		43	44.48	235	237	318	0.50	1.91E−06
2,2′,4,4′,5,6′-Hexachlorobiphenyl	CL6-PCB	44	44.49	360	362		0.30	2.31E−06
p,p′-DDD (*o,p′*-DDT coelutes)		46	45.62	235	237	318	0.50	1.80E−06
2,2′,3,4′,5,6,6′-Heptachlorobiphenyl	CL7-PCB	47	45.82	394	396		0.50	2.30E−06
p,p′-DDT		48	46.67	235	237	352	0.50	2.76E−06
[$^2H_{12}$]Chrysene (SS)	d12 CHRYS		47.82	240	120		0.50	7.28E−07
[$^2H_{12}$]Perylene (SS)	d12 PERYL		51.54	264			0.50	1.75E−06

Peak number refers to Fig. 2.
SS = surrogate standard.
I.S. = internal standard
[a]Ion used to identify interferences, rather than for use in confirmation of peak identity.

mixtures of arochlors. A 50:50 mix of Arochlor 1242 and 1260 at 10 ppm was determined to be the most useful for producing detectable levels of isomers in the chlorination level-based groups containing two (CL2) to eight (CL8) substituted chlorines.

Calibration standards were prepared at a concentration of 0.5 ng/μl by dilution of the stock mixture containing all analytes and surrogates with DCM–hexane (1:1, v/v). 2-Fluorobiphenyl was added to the calibration standard at a concentration of 5 ng/μl and served as an internal standard that was added to extracts prior to analysis. Table 1 lists the target analytes and the mass fragment used for quantitative evaluation ("primary ion") and for confirmation of identity ("confirming ion") in their order of elution from the GC column. Data were also obtained for thirteen additional pesticides; four isomers of hexachlorocyclohexane (including lindane), heptachlor, heptachlor epoxide, aldrin, endosulfan I and II, and endosulfan sulfate, endrin, mirex and octachlorobiphenyls, for the first two collections. None of these analytes were detected in any phase or in the sediment samples and were subsequently dropped from the target analyte list. The method is nevertheless capable of quantifying these substances as well. Calibration was based on the average of two standard analyses; one prior to analysis of up to ten samples (fifteen for dissolved phase extracts) and one standard following the samples. Data were corrected for recovery of surrogates added in the laboratory at the time of extraction (colloidal- and particulate-phase) or in the field (dissolved-phase) unless recovery fell below 10% (see also Fig. 2).

3. Results and discussion

3.1. Validation of methodology

Linearity and dynamic range of the GC–MS using the SIM method described above was demonstrated by generation of standard curves for each analyte containing five to nine levels of concentration that were analyzed in duplicate or triplicate. Standard

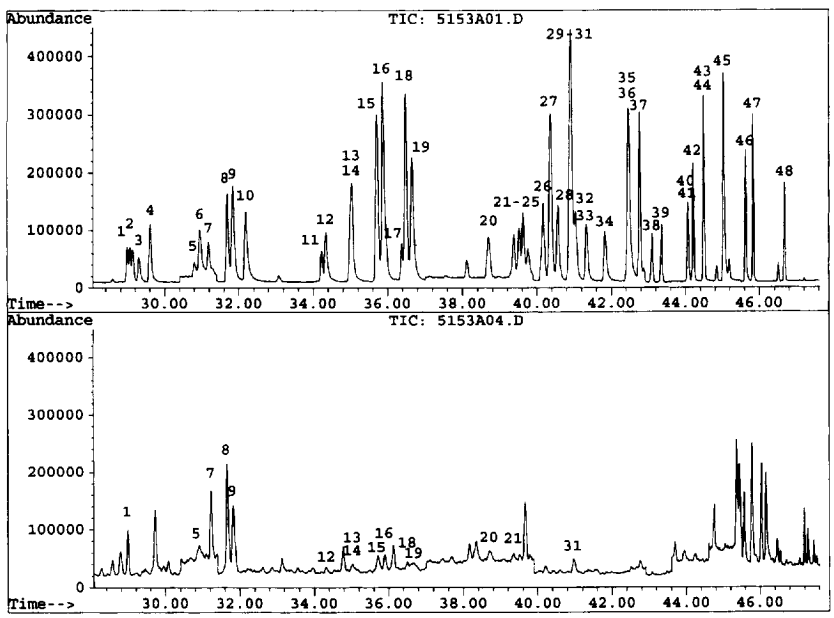

Fig. 2. Total ion chromatograms from GC–MS SIM analyses of a standard solution (top) and a colloidal phase sample extract (bottom), showing the retention time range (28–47 min) where most herbicides, chlorinated pesticides and PCBs elute. Peak numbers refer to Table 1, additional numbered peaks not identified in the table are (6) dibenzothiophene, (9) phenanthrene, (10) anthracene, (12) and (13) methyldibenzothiophene isomers, (15) 3-methylphenanthrene and 1-methyldibenzothiophene, (16), (18) and (19) methylphenanthrene isomers, (22)–(29) dimethylphenanthrene isomers, (31) fluoranthene, (32)–(35) dimethylphenanthrene isomers, (36) pyrene and (45) 1,2,8-trimethylphenanthrene.

deviations for calculation of method detection limits (MDLs) were calculated from five replicate injections of the daily calibration standards at 0.5 ng/μl, and converted to ng values using response factors generated from the regression statistics. The limit of detection (LOD) [17] was calculated as three times the standard deviation and this was used to calculate the MDLs for each of the four sample types, by correcting for sample size and extract volumes. The MDLs for sediments (averaging 1.6 ng/g) and the particulate phase (averaging 32 ng/g) were the highest, in the ppb range, while the large sample size used for dissolved and colloidal phase samples contributed to achieving MDLs in the parts per trillion range (averaging 8.6 pg/ml and 61 pg/ml, respectively). The field data were subjected to blank subtraction, where necessary, and therefore were not corrected for detection limits.

Table 2 shows recoveries of the spiked analytes. Recovery data for sea water spiked at 5, 10, 50 and 100 pg/ml did not show any significant trends between concentration levels; the mean values for all spiked samples are shown. Herbicide analytes had not been added to the target analyte list at the time of

Table 2
Mean recovery of spiked analytes from natural sea water enriched at 5, 10, 50 or 100 pg/ml and extracted using SPE disks from process spikes for three-phase water extraction procedures (dissolved, colloidal and particulate) and from spiked sediment samples

Analyte	Spiked sea water mean (SD) $n=12$	Process spikes			Spiked sediment mean (SD) $n=6$
		Dissolved mean (SD) $n=6$	Colloidal mean (SD) $n=11$	Particulate mean (SD) $n=7$	
d8NAPH	37% (12%)	81% (33%)	73% (23%)	53% (18%)	174% (67%)
Nitroxylene	15% (17%)	87% (35%)	74% (28%)	63% (26%)	NA
Hexachlorobutadiene	15%[a]	79% (33%)	61% (18%)	55% (19%)	NA
d10 ACE	40% (6%)	92% (25%)	85% (26%)	80% (10%)	186% (57%)
DBOFBP	24% (4%)	114% (34%)	88% (26%)	121% (9%)	NA
Trifluralin	47%[a]	109% (36%)	103% (38%)	173% (59%)	NA
CL2-PCB	52% (14%)	100% (29%)	87% (22%)	113% (23%)	76% (31%)
Hexachlorobenzene	29% (6%)	105% (30%)	93% (26%)	93% (17%)	78% (19%)
Simazine	55%[a]	106% (46%)	128% (30%)	99% (15%)	NA
Atrazine	146%[a]	103% (45%)	118% (28%)	101% (43%)	NA
d10 PHEN	50% (8%)	106% (28%)	95% (25%)	104% (15%)	183% (45%)
CL3-PCB	42% (9%)	114% (25%)	94% (22%)	110% (20%)	69% (47%)
CL4-PCB	32% (5%)	112% (30%)	92% (22%)	103% (19%)	73% (19%)
Alachlor	71%[a]	124% (36%)	111% (30%)	127% (38%)	NA
Metolachlor	NA[a]	133% (47%)	121% (32%)	140% (50%)	NA
Cyanazine	135%[a]	80% (36%)	173% (52%)	94% (71%)	NA
o,p'-DDE	35% (6%)	114% (29%)	95% (23%)	110% (27%)	NA
Chlordane	58% (12%)	119% (30%)	102% (29%)	125% (24%)	191% (94%)
trans-Nonachlor	56% (14%)	121% (29%)	103% (28%)	126% (20%)	197% (98%)
CL5-PCB	36% (7%)	116% (29%)	100% (23%)	106% (36%)	155% (70%)
Dieldrin	68% (17%)	113% (30%)	95% (21%)	103% (42%)	208% (108%)
p,p'-DDE	36% (10%)	113% (30%)	97% (23%)	107% (30%)	153% (63%)
o,p'-DDD	52% (9%)	120% (31%)	104% (26%)	120% (32%)	NA
CL6-PCB	25% (6%)	113% (28%)	97% (24%)	108% (23%)	144% (63%)
p,p'-DDD/*o,p'*-DDT	55% (13%)	122% (31%)	103% (26%)	110% (39%)	112% (41%)
CL7-PCB	19% (7%)	114% (29%)	98% (23%)	114% (25%)	132% (55%)
p,p'-DDT	41% (11%)	128% (38%)	111% (37%)	143% (60%)	53% (78%)
d12 CHRYS	45% (10%)	106% (29%)	101% (28%)	86% (28%)	69% (48%)
d12 PERYL	38% (14%)	88% (28%)	98% (29%)	13% (9%)	153% (64%)

NA-not available due to variations in data acquisition methods.
[a]Data obtained from a single sample spiked at 50 pg/ml.

this experiment, so data shown for these compounds in the first column consist of data from a single sample of dissolved phase sea water spiked at 50 pg/ml and concentrated using a Spec SPE disk. Metolachlor recovery could not be calculated due to the high (9 ng/ml) levels present in the unspiked sample. Recovery from the natural sea water samples was acceptable, but generally low for most analytes, due to the use of a glass fiber filter ahead of the SPE disk, to prevent plugging.

Because the entire amount of three-phase samples generated at sea were used for extraction, laboratory duplicate extracts were not possible. Instrument duplicates and laboratory reagent blanks and process spikes (Table 2) produced good results. Particulate filters were not pre-washed prior to use at sea, and did generate some contamination, which was limited to low levels of certain alkylated PAHs. Ship blanks also showed contamination with alkylated PAH, and some carryover of atrazine and metolachlor, at sample concentration levels of 3 and 6 pg/ml, respectively, for two out of three blanks. Field surrogate recoveries from 68 dissolved phase samples (Cruise 1) processed through SPE disks at sea averaged 69%, while laboratory surrogate recoveries averaged 140%. For six laboratory spikes of SPE disks extracted by sonication, recovery of herbicides, pesticides and PCBs averaged 113%, ranging from 79% to 143% and with a mean R.S.D. of 33%.

3.2. Field data

Table 3 shows summary data for six cruises representing three seasons over the period from 1992 through 1994. Mean concentrations are shown for each of the three phases in water samples and for sediment cores (Cruise 1, April 1992, only). Herbicides were not measured in the bedded sediments, and were detected most frequently in the dissolved phase, followed by the colloidal phase, and only rarely in the suspended particulate phase. These observations are consistent with those made in the Chesapeake Bay estuary [8]. Chlorinated pesticides and PCBs were found primarily in the suspended particulate phase and in bedded sediments and were also detected at highest concentrations in these matrices (ppb levels as opposed to parts per trillion). Nearly all dissolved phase samples contained levels of herbicides well above the MDLs. Since the herbicides were the most ubiquitous and abundant of the pollutant classes measured, they are the primary focus of this report and efforts to elucidate sources, fates and on-going investigations of impacts upon aquatic life, as well as modeling of transport processes in the coastal current.

3.2.1. Spatial distribution

Concentrations of all analytes were generally highest near the shore along the transects and they were inversely correlated with salinity gradients. Samples from Cruise 5 in April 1994 showed highest concentrations of analytes at the site closest to the Mississippi River discharge to the Gulf of Mexico (Southwest Pass). Pesticides and PCBs were detected only in the particulate phase, with sporadic distribution. All herbicides were present in the dissolved and colloidal phases, with the exception of trifluralin, which was most frequently detected in the particulate phase. Concentrations in dissolved and colloidal phase samples at Southwest Pass were maximal for atrazine (140 and 220 pg/ml) and metolachlor (79 and 130 pg/ml). Fig. 3 shows the spatial distribution of atrazine in the colloidal phase in the river plume to the west of the Southwest Pass. Concentrations of atrazine decreased rapidly to the west and were consistently lower in bottom waters. The spatial distribution of atrazine in the dissolved phase was similar to that of the colloidal phase except that lower concentrations were detected in this phase. The results for the plume cruise (No. 5, April 1994) differed in this respect from all of the other cruises in that colloidal phase herbicides showed higher concentrations than in the dissolved phase. Means et al. [8] and Sigleo and Means [9] discussed the behavior of atrazine binding to colloidal phases in estuarine environments. They showed that binding of atrazine to colloidal phases was dependent upon the pH and salinity of the solution phase. They measured higher partition coefficients of atrazine with colloids at low salinity than in environments with a higher saline content. The field observations made here are consistent with these earlier laboratory results. Furthermore, the field observations made by Means et al. [8] that the highest binding potential to colloids in the Chesapeake Bay estuary was found in the "turbidity maximum" of

Table 3
Mean concentrations of pollutants from six sample collections (1992–1994) of water (three-phase analysis) and sediments. Total number of samples analyzed was 293 dissolved phase, 272 colloidal phase, 266 particulate phase and 51 sediments (sediments collected on April 1992 cruise only)

Analyte	Dissolved phase				Colloidal phase				Particulate phase				Sediments			
	Mean pg/ml	Range		Frequency of detection	Mean pg/ml	Range		Frequency of detection	Mean pg/ml	Range		Frequency of Detection	Mean pg/ml	Range		Frequency of Detection
		Min.	Max.			Min.	Max.			Min.	Max.			Min.	Max.	
Herbicides																
Trifluralin	1.8	0.96	2.8	4	2.0	0.84	3.4	5	4.4	0.088	22	13	NA	NA	NA	NA
Simazine	19	0.010	160	128	17	1.1	50	75	18	17	19	2	NA	NA	NA	NA
Atrazine	199	1.1	1682	289	109	4.0	822	243	16	16	16	1	NA	NA	NA	NA
Alachlor	23	4.6	68	11	nd	na	na	0	1.4	1.4	1.4	1	NA	NA	NA	NA
Metolachlor	24	1.6	147	276	26	2.0	155	199	8.6	3.6	33	11	NA	NA	NA	NA
Cyanazine	93	0.60	523	102	77	5.6	460	49	88	45	181	3	NA	NA	NA	NA
Chlorinated pesticides																
Hexachlorobutadiene	nd	na	na	0	nd	na	na	0	4.0	0.56	23	6	NA	NA	NA	NA
Hexachlorobenzene	nd	na	na	0	3.1	0.81	6.0	4	3.3	0.23	7.1	14	0.28	0.23	0.36	4
Chlordane	9.4	2.6	17	5	2.3	1.1	5.7	9	0.81	0.26	2.6	8	nd	nd	TR	0
trans-Nonachlor	0.50	0.50	0.50	1	1.7	0.74	4.3	5	0.46	0.27	0.9	4	nd	nd	TR	0
Dieldrin	11	11	11	1	19	2.3	62	9	nd	na	na	0	3.1	3.0	3.1	2
o,p'-DDE	2.1	0.33	5.4	3	nd	na	na	0	6.0	6.0	6.0	1	NA	NA	NA	NA
p,p'-DDE	3.5	2.0	8.3	9	8.1	1.9	13	5	nd	na	na	0	0.64	0.17	1.8	31
o,p'-DDD	nd	na	na	0	nd	na	na	0	1.7	0.011	2.7	3	0.84	0.20	1.6	13
p,p'-DDD/*o,p'*-DDT	nd	na	na	0	nd	na	na	0	nd	na	na	0	1.2	0.21	2.5	3
p,p'-DDT	nd	na	na	0	3.8	3.8	3.8	1	10	10	10	1	nd	nd	nd	0
Polychlorinated biphenyls																
CL2-PCB	6.5	2.4	22	5	17	0.64	70	27	5.8	0.58	111	28	0.63	0.24	1.3	6
CL3-PCB	33	0.45	209	21	33	3.6	196	33	73	0.37	946	41	1.0	0.71	1.4	2
CL4-PCB	78	1.8	324	20	51	8.7	313	32	53	0.11	523	38	nd	nd	TR	0
CL5-PCB	nd	na	na	0	22	3.6	130	34	30	0.059	149	28	1.7	0.37	6.3	13
CL6-PCB	nd	na	na	0	6.4	1.0	22	11	4.9	0.13	54	43	1.2	0.21	3.7	9
CL7-PCB	nd	na	na	0	nd	na	na	0	4.8	0.90	9.9	3	0.46	0.46	0.46	1

nd = not detected, NA = Not analyzed, Tr = trace level, not quantitated.

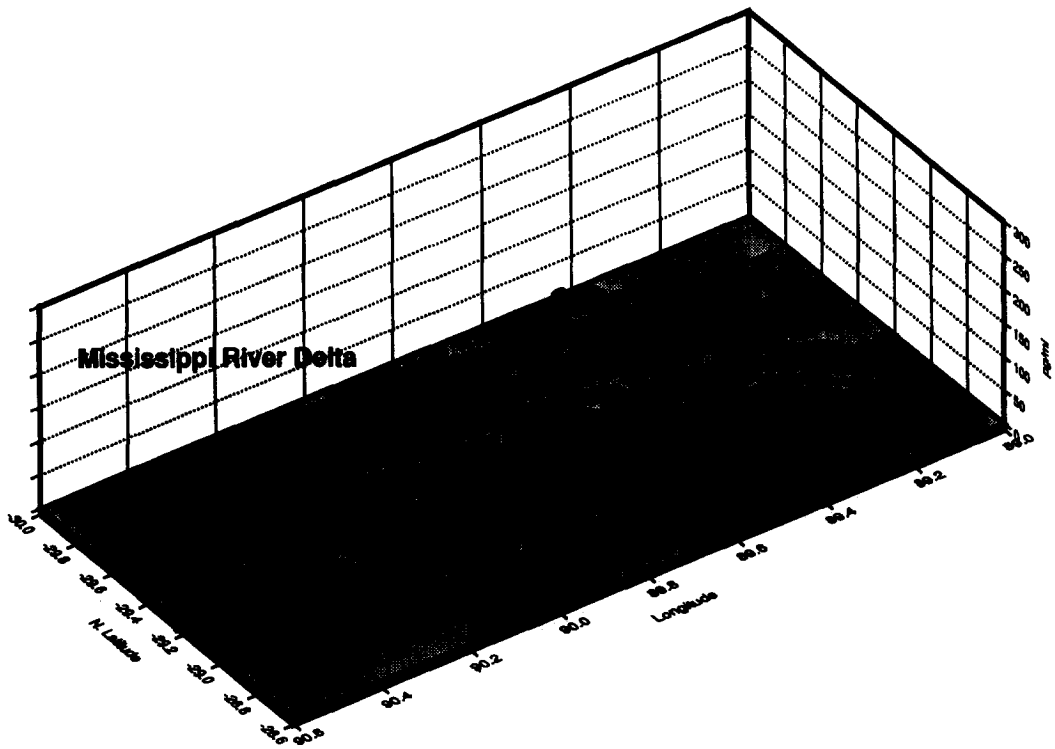

Fig. 3. Spatial distribution of colloidal phase atrazine in water samples (both surface and bottom shown) collected west of the Mississippi River Southwest Pass discharge in April 1994.

the estuary is also consistent with the present findings.

For the other cruises, atrazine concentrations were highest at near-shore sampling stations off the Atchafalaya Basin outlet in the summer and fall, while high near-shore concentrations were also noted off the Sabine River estuary in the spring. Figs. 4 and 5 show the spatial distribution of atrazine in samples collected in October 1992 for dissolved and colloidal phases, respectively. Metolachlor spatial distributions showed remarkable similarity for both spring or summer samplings from different years. For both April collections, a single high point (120 pg/ml each) was noted both in 1992 and 1993 at the near-shore point in the transect along longitude 95.5°W, west of Galveston Bay. The fall and summer distributions generally showed maximal concentrations for metolachlor along the eastern transects, S4 in October 1992, S3 in July 1993 and S1 in July 1994. Cyanazine distributions showed greatest frequencies and highest concentrations primarily along transects 1–3, with the exception of the October 1992 collection, when it was detected over a wider spatial range, at 34 of 59 sites at concentrations averaging 140 pg/ml, and ranging up to 520 pg/ml. Simazine concentrations tended to be highest near the Atchafalaya estuary (transects S3 and S4) regardless of sampling season, and was rarely detected in samples west of the Sabine Pass.

3.2.2. Temporal distribution

Table 4 shows mean concentration values and detection frequencies for herbicides by collection period (cruise) for all three phases in water samples. Fig. 6 shows mean concentrations by collection date for herbicides in the dissolved phase. Dissolved phase, atrazine concentrations were both highest in concentration and the most frequently detected of all of the compounds measured. Cyanazine showed the next highest average concentrations for all sample periods, however, metolachlor was the second most frequently detected herbicide. Colloidal phase mean

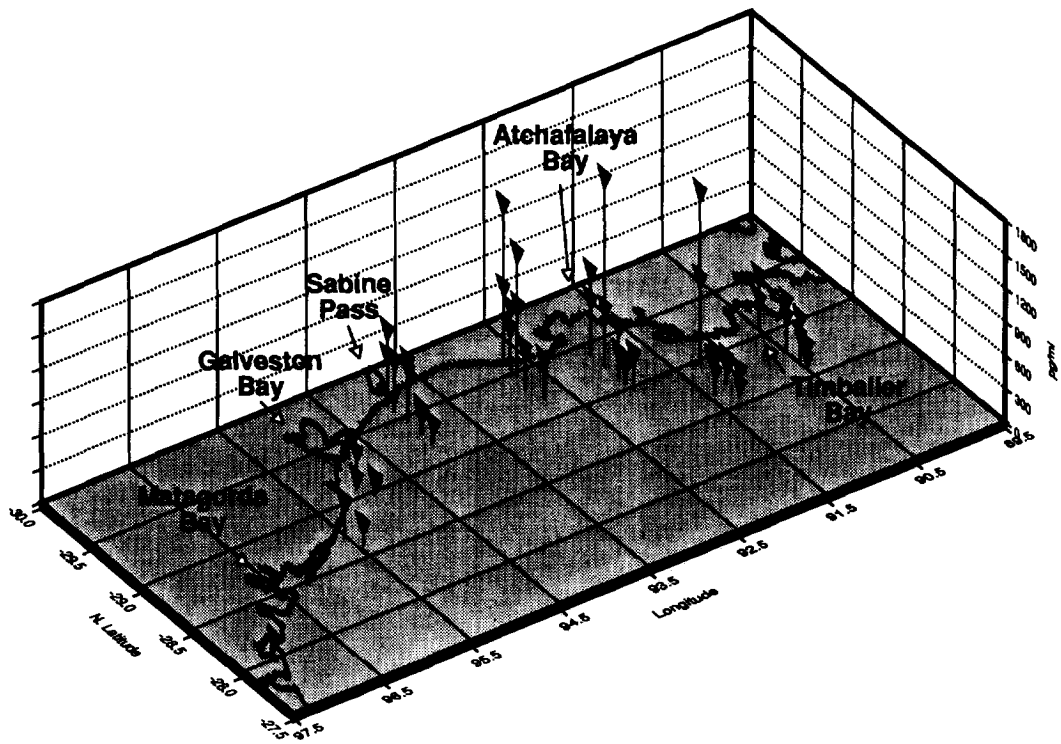

Fig. 4. Spatial distribution of dissolved phase atrazine in water samples (both surface and bottom shown) collected along the coastal shelf region of the Northwestern Gulf of Mexico in October 1992.

concentrations showed the same trends. Concentrations of herbicides tended to be highest during the low discharge volume periods (summer and fall cruises), with the exception of alachlor, which was detected only in samples taken during the April cruises. Fig. 7 shows concentrations for atrazine in surface samples collected along transect S1, adjacent to Timbalier Bay for each of the five seasonal basic cruises. Again, it can be seen that summer concentration profiles were much higher than in samples from the spring collections, with the fall, 1992 cruise profile yielding intermediate concentrations. This figure also shows the trend of decreasing concentrations away from shore (with decreasing North latitude), with predominant gradients seen in April samples. The exception was the pattern observed in July 1994, where higher atrazine concentrations were observed at stations further from shore. Correlation of salinity data to herbicide concentration profiles yields information on the nature of such trends. Fig. 8 shows salinity data for the same transect stations and sampling times. High discharge volumes during spring flooding lead to more intense salinity gradients, while in early summer, southerly and southeasterly winds push low salinity water easterly and offshore [15]. This appears to allow herbicide concentrations to remain relatively undiluted at further distances from shore, as was observed in July 1994 (Fig. 7).

Atrazine concentration profiles for the other transects are similar to those seen in the first transect, but the trends become less pronounced along the more westerly transects, as increased mixing and dilution occur. Temporal and spatial patterns for other herbicides are less clear due to their lower concentrations, but generally show the same trends as noted for atrazine; highest concentrations in summer samples and at near-shore sampling stations.

While true end-member analysis for the herbicides cannot be performed since samples were not collected in the fresh (zero salinity) portions of each estuary, local dilution trend analysis against salinity

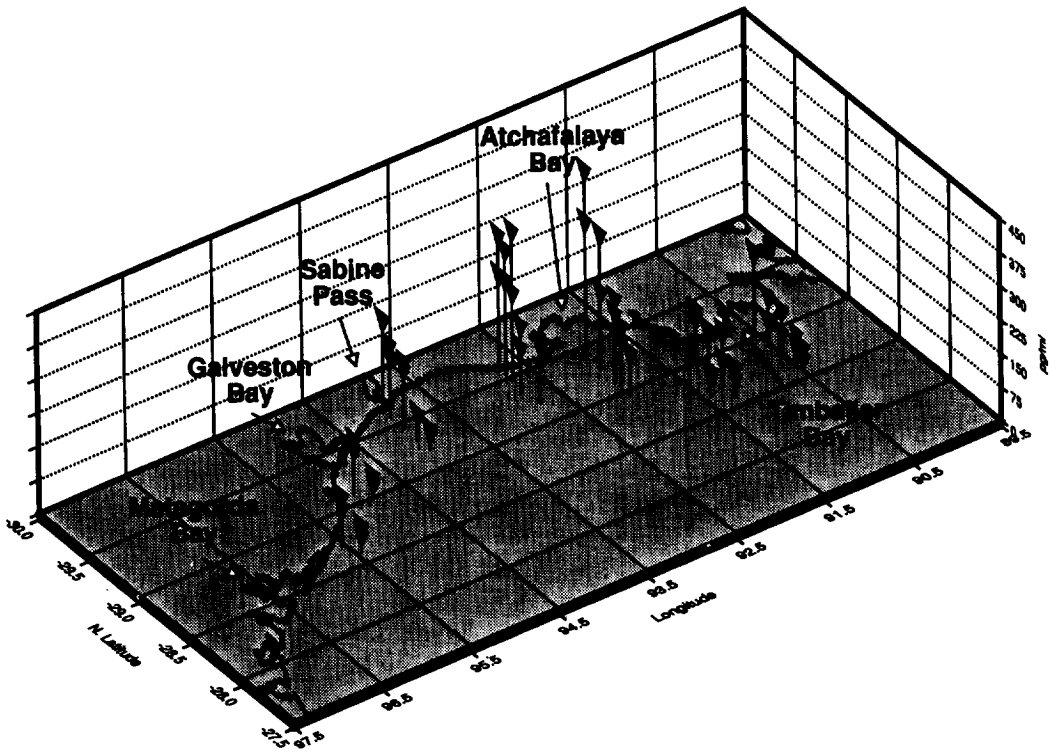

Fig. 5. Spatial distribution of colloidal phase atrazine in water samples (both surface and bottom shown) collected along the coastal shelf region of the Northwestern Gulf of Mexico in October 1992.

can yield information on the conservative or non-conservative behavior of compounds entering and being transported through the coastal shelf current. In general, removal of atrazine and other herbicides and chlorinated organics shows non-conservative trends with respect to simple dilution (estimated from salinity). This suggests that removal processes such as sorption to particulates and subsequent removal by sedimentation and/or microbial degradation are active in the coastal shelf current. Estimates of the depositional flux rates to bedded sediments in the shallow shelf region for refractory compounds, such as DDT and its metabolites, or PCB congeners, may be possible using average sedimentation rates measured during this study corrected for resuspension. For less refractory compounds, such as herbicides, such estimates are not possible, since deposition appears to be in the form of metabolites rather than parent compounds.

3.2.3. Depth distribution

The spatial distributions (Figs. 3–5) show herbicide concentrations for both surface and bottom water samples at each point along the transects. Generally, the highest concentrations were found at the surface. This is consistent with the observation that more buoyant fresh waters entering the Gulf override more dense saline Gulf waters in the shelf zone. However, this pattern was reversed in samples collected in October, 1992 (Fig. 9). Surface samples consistently showed the highest herbicide concentrations in the spring and summer samples, while bottom samples showed the highest concentrations in the fall, 1992 samples. This latter phenomenon may be associated with dilution of surface water concentrations with local freshwater inputs after Hurricane Andrew or with some other, unknown, phenomenon. Metolachlor and cyanazine showed similar, but less distinct, trends as compared to atrazine.

Table 4
Mean concentrations and detection frequency for target analytes in three-phase water samples colected on six cruises. Concentrations in pg/ml for dissolved and colloidal phases and in ng/g for particulate phase

Phase		April 1992	October 1992	April 1993	July 1993	April 1994	July 1994
Dissolved	Number analyzed:	68	58	70	34	32	30
Trifluralin	Mean	nd	nd	1.8	nd	nd	nd
	Frequency	0	0	4	0	0	0
Simazine	Mean	17	23	11	30	5.3	30
	Frequency	20	34	34	17	12	11
Atrazine	Mean	110	407	98	302	33	246
	Frequency	68	56	69	34	32	30
Alachlor	Mean	38	nd	25	nd	5.4	nd
	Frequency	6	0	2	0	3	0
Metolachlor	Mean	22	30	18	29	18	24
	Frequency	58	58	67	34	30	29
Cyanazine	Mean	87	140	34	156	8.6	135
	Frequency	29	34	11	13	1	14
Colloidal	Number analyzed	68	58	48	34	32	30
Trifluralin	Mean	nd	3.4	0.84	nd	nd	1.8
	Frequency	0	1	1	0	0	3
Simazine	Mean	nd	9.9	7.4	22	23	22
	Frequency	0	21	20	15	9	10
Atrazine	Mean	82	124	54	176	82	138
	Frequency	46	58	42	34	32	31
Alachlor	Mean	nd	nd	nd	nd	nd	nd
	Frequency	0	0	0	0	0	0
Metolachlor	Mean	23	10	10	22	55	33
	Frequency	9	56	43	33	27	31
Cyanazine	Mean	nd	52	11	186	nd	57
	Frequency	0	32	2	9	0	6
Particulate	Number analyzed	68	58	38	34	32	36
Trifluralin	Mean	nd	nd	11	1.9	0.79	3.8
	Frequency	0	0	2	5	5	1
Simazine	Mean	nd	nd	nd	nd	nd	18
	Frequency	0	0	0	0	0	2
Atrazine	Mean	nd	nd	nd	nd	16	nd
	Frequency	0	0	0	0	1	0
Alachlor	Mean	nd	nd	nd	nd	1.4	nd
	Frequency	0	0	0	0	1	0
Metachlor	Mean	5.6	5.7	nd	nd	14	nd
	Frequency	2	6	0	0	3	0
Cyanazine	Mean	130	nd	nd	nd	45	nd
	Frequency	2	0	0	0	1	0

Results from the plume cruise also showed higher concentrations of herbicides in surface samples as compared to bottom samples.

3.2.4. Mass transport estimates for herbicides

Mass transport of four *s*-triazine herbicides across five transects in the northwestern Gulf of Mexico was calculated for the October 1992 cruise, using average net volume transport (cu.m./s) values calculated from acoustic doppler current profile (ADCP) measurements acquired continuously during all sampling cruises [15], and using the formula:

$$\text{Mass transport} = \text{volume transport} \cdot \text{concentration} \cdot 8.64 \cdot 10^{-5},$$

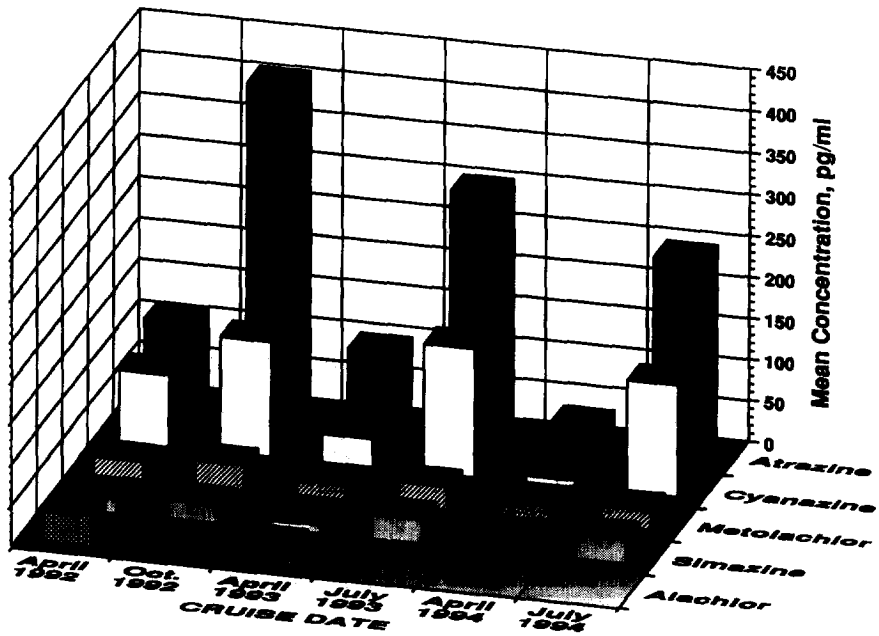

Fig. 6. Summary of mean dissolved phase herbicide concentrations in water samples from six seasonal collections, 1992–1994.

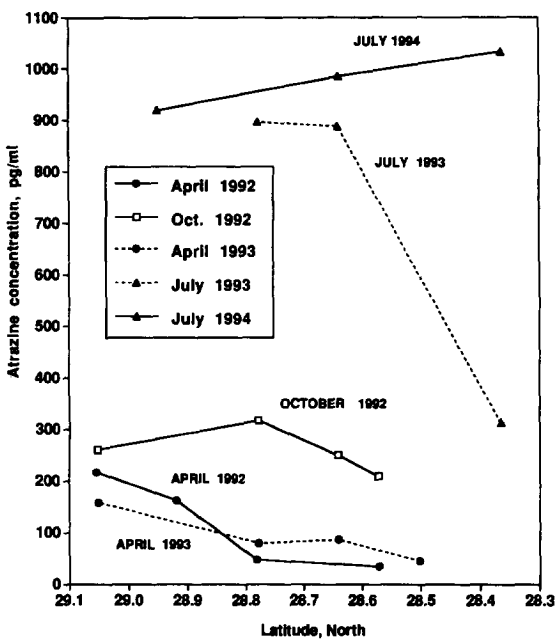

Fig. 7. Temporal and spatial distribution of dissolved phase atrazine in surface water samples off Timbalier Bay, LA, transect (S1).

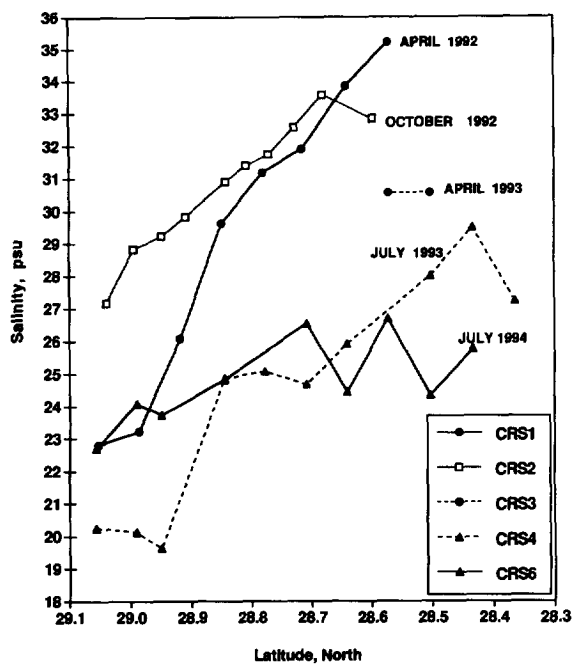

Fig. 8. Salinity variation along Timbalier Bay transect (S1) at a depth of 2 m for six cruises.

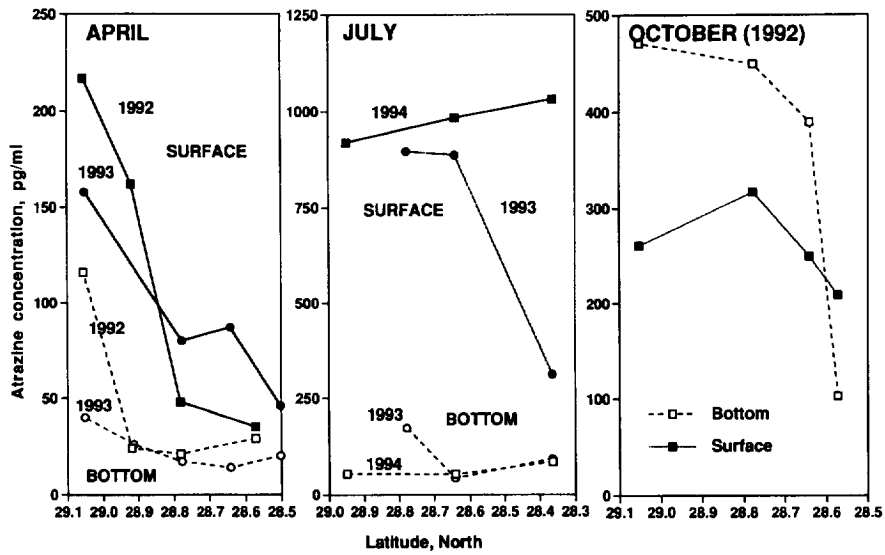

Fig. 9. Variation in dissolved phase atrazine concentrations with depth and season along Timbalier Bay transect (S1).

where mass transport is expressed as kg/day, volume transport is expressed as cu.m/s and concentration is given in ng/l [3].

Mass transport values (east-to-west flux) for atrazine ranged from 800–3000 kg/day. The data for all four herbicides are shown in Fig. 10. Low flux values for the transect at longitude 92.0°W were attributed to a wind shift from a predominantly east–west vector to a north–south vector during sampling at this transect only, resulting in an offshore flux that was not estimated. These values for atrazine compare well to the value of 2000 kg/day for April 1992, reported for the Mississippi River at Belle Chase, LA [3].

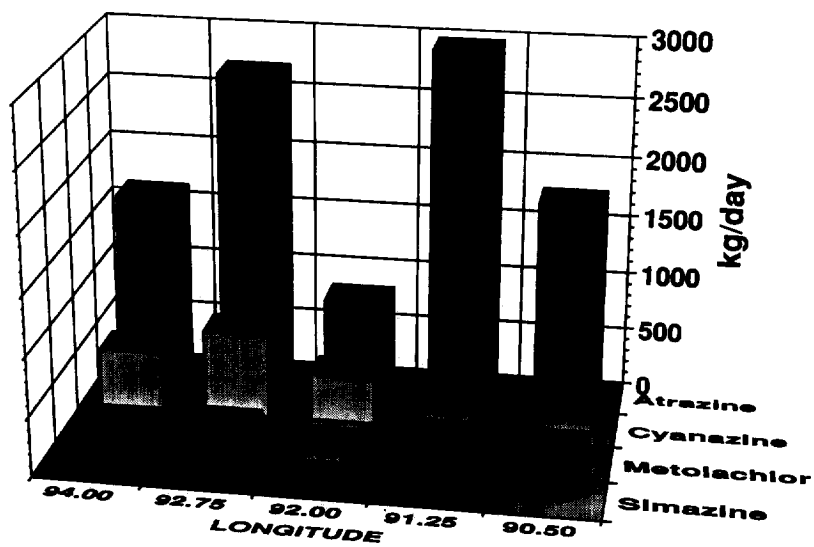

Fig. 10. Calculated dissolved phase herbicide transport across five coastal current transects, October 1992.

4. Conclusions

A sensitive multi-component GC–MS SIM method was applied to the analysis of selected pesticides in sea water samples separated into dissolved, colloidal and particulate phases on board a ship. The method was able to detect and show trends for several components over a large spatial range.

Concentrations of all herbicides were highest near the shore and at the surface for both dissolved and colloidal phases, and the data showed observable concentration gradients away from shore and with depth. These trends can be correlated with dilution with Gulf of Mexico waters as well as with advection of water masses to the west along the coastal shelf.

The presence of herbicides, even at the low concentrations detected in this study, nevertheless represent transport of huge amounts of material from riverine systems into the ocean on a continuing (year-round) basis and further investigation of these types of large-scale phenomena, particularly of conserved material, such as refractory organics and trace metals, is warranted. The local concentrations and estimates of total mass transport of the parent materials reported here represent only a fraction of the total metabolites and degradative compounds that have the potential to cause adverse affects on aquatic ecosystems.

Acknowledgments

This study was funded by the Minerals Management Service, US Department of the Interior, through the Texas–Louisiana Shelf Physical Oceanography Program under contract No. 14-35-0001-30632 (Mississippi River Plume Hydrography).

References

[1] USEPA, Federal Register Notice (OPP-300C10-60 FRL-4919-5), November 23, 1994.
[2] W.E. Pereira and C.E. Rostad, Environ. Sci. Technol., 24 (1990) 1400.
[3] USGS, U.S. Geological Survey Open File Report 94.376, 1994.
[4] D.A. Goolsby, W.A. Battaglin and E.M. Thurman, U.S. Geological Survey Circular 1120-C, 1993.
[5] W.M. Kemp, W.R. Boynton, J. Cunningham, J.C. Stevenson, T. Jones and J.C. Means, Mar. Env. Res., 16 (1985) 255.
[6] J.C. Stevenson, T.W. Jones, W.M. Kemp, W.R. Boynton and J.C. Means, in J.D. Costlow, L.E. Cronin, T.B. Duke and W. McClellan (Editors), Agrichemicals and estuarine productivity, John Wiley, New York, 1983, p. 195.
[7] J.C. Means, Report to the Louisiana Department of Agriculture, 1995.
[8] J.C. Means, R.D. Wijayaratne and W.R. Boynton, Can. J. Fish Aquat. Sci., 40 (1983) 337.
[9] A.C. Sigleo and J.C. Means, Rev. Environ. Contam. Toxicol., 12 (1990) 123.
[10] C. Markell, D.F. Hagen and V.A. Bunnelle, LC·GC, 9 (1991) 332.
[11] S.A. Senseman, T.L. Lavy, J.D. Mattice, B.M. Myers and B.W. Skulman, Environ. Sci. Technol., 27 (1993) 516.
[12] D.F. Hagen, C.G. Markell and G.A. Schmitt, Anal. Chim. Acta, 236 (1990) 157.
[13] M.-C. Hennion and V. Pichon, Environ. Sci. Technol., 28 (1994) 576A.
[14] J.C. Means and D.J. McMillin, Final Report USMMS OCS Study MMS-93-OO18, U.S. Dept. of the Interior, Minerals Mgmt. Service, Gulf of Mexico OCS Regional Office, New Orleans, LA, 1993, p. 153.
[15] S.P. Murray, Annual report, OCS Study/MMS 94-0028, U.S. Dept. of the Interior, Minerals Mgmt. Service Gulf of Mexico OCS Regional Office, New Orleans, LA, 1994, p. 229.
[16] W.D. MacLeod, D.W. Brown, A.J. Friedman, D.G. Burrows, O. Maynes, R.W. Pearce, C.A. Wigren and R.G. Bogar, NOAA Technical Memorandum NMFS F/NWC-92, 1985, p. 121.
[17] L.H. Keith, W. Crummett, J. Deegan, R.A. Libby, J.K. Taylor and G. Wentler, Anal. Chem., 55 (1983) 2210.