



Project Summary

Acute Toxicity of Eight Laboratory-Prepared Generic Drilling Fluids to Mysids (*Mysidopsis bahia*)

T.W. Duke, P.R. Parrish, R.M. Montgomery, S.D. Macauley, J.M. Macauley, and G.M. Cripe

Acute toxicity tests were conducted at U.S. Environmental Protection Agency (EPA) Environmental Research Laboratories, Gulf Breeze, Florida, and Narragansett, Rhode Island, with eight laboratory-prepared generic drilling fluids (also called muds) and mysids (*Mysidopsis bahia*). The test material was the suspended particulate phase (SPP) of each drilling fluid. Toxicity of the SPP ranged from a 96-hour LC50 (the concentration lethal to 50% of the test animals after 96 hours of exposure) of 2.7% for a KCl polymer mud to 65.4% for a lightly treated lignosulfonate mud. No median effect (50% mortality) was observed in three drilling fluids — a non-dispersed mud, a spud mud, and a saltwater-freshwater gel mud.

Two of the generic drilling fluids to which mineral oil had been purposely added were also tested at Gulf Breeze. The addition of the mineral oil, even at a concentration as low as 1%, dramatically increased the acute toxicity of both fluids to mysids.

This Project Summary was developed by EPA's Environmental Research Laboratory, Gulf Breeze, FL, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

EPA has permitted the discharge of eight drilling mud types into U.S. Outer

Continental Shelf waters (EPA, 1983) under the National Pollutant Discharge Elimination System (NPDES). This research project was initiated at the Gulf Breeze Laboratory to determine the acute toxicity of these eight generic drilling fluids (Table 1) to representative saltwater crustaceans (*Mysidopsis bahia*). The tests were requested by EPA's Effluent Guidelines Division, Office of Water Regulations and Standards, and were conducted according to methodology prescribed. Two of the drilling fluids were tested at the Narragansett Laboratory to confirm the validity of the tests conducted at Gulf Breeze. Two of the fluids that had been purposely contaminated with mineral oil were tested at Gulf Breeze to determine the toxicity of this additive in representative drilling fluids.

Methods

Test methods followed those proposed by Petrazzuolo (1983) with the following exceptions.

(1) Natural seawater was used instead of artificial seawater, at Gulf Breeze, the natural seawater was pumped from Santa Rosa Sound and filtered through sand and a 5-micrometer fiber filter; salinity was controlled at 20 ± 2 parts per thousand by the addition of deionized water, and temperature was controlled by a commercial chiller;

(2) 5 ± 1 -day-old mysids were used instead of 4 ± 1 -day-old mysids;

Table 1. Source and Reported Composition of Eight Generic Drilling Fluids Received at U S EPA, Gulf Breeze, Florida

Drilling Fluid	Source	Composition	
		Component	Concentration
EPA-83-001, KCl Polymer Mud	Chromalloy	KCl	50.0 grams (g)
		Drispac (Super-Lo)	0.5 g
		X-C Polymer	1.0 g
		Barite	283.2 g
		Starch	2.0 g
		Seawater	257.6 milliliters (ml)
EPA-83-002, Seawater Lignosulfonate Mud	IMCO Services	Attapulgite	30.0 pounds per barrel (ppbb)
		Chrome Lignosulfonate	15.0 ppbb
		Lignite	10.0 ppbb
		Polyanionic Cellulose	0.25 ppbb
		Caustic	To pH 10.5-11.0
		Barite	To bring mud weight to 17-18 pounds per gallon (ppg)
		Seawater	As needed
EPA-83-003, Lime Mud	Hughes	Bentonite	20.06 g
		Lime	5.01 g
		Barite	281.81 g
		Chrome Lignosulfonate	15.04 g
		Caustic	1.00 g
		Lignite	8.02 g
		Distilled water	257.04 ml
EPA-83-004, Non-dispersed mud	Newpark Drilling Fluids	Bentonite	13.0 ppbb
		Acrylic Polymer (for suspension)	0.5 ppbb
		Acrylic Polymer (for fluid loss control)	0.25 ppbb
		Barite	190.7 ppbb
		Deionized Water	299.6 ppbb
EPA-83-005, Spud mud	NL Baroid	Bentonite	12.5 ppbb
		Lime	0.5 ppbb
		Barite	50.0 ppbb
		Seawater/Freshwater	1.0 bbl
		Caustic	To pH 10.0
EPA-83-006, Seawater/Freshwater Gel Mud	Milchem	Bentonite	20.0 ppbb
		Polyanionic Cellulose	0.50 ppbb
		Sodium Carboxymethyl Cellulose	0.25 ppbb
		Barite	20.0 ppbb
		Sodium Hydroxide	To pH 9.5
		Seawater/Freshwater, 1:1	As needed
EPA-83-007, Lightly Treated Lignosulfonate Mud	Magobar Dresser	Bentonite	20.0 ppbb
		Chrome Lignosulfonate	5.0 ppbb
		Lignite	3.0 ppbb
		Soda Ash	1.0 ppbb
		Carboxymethyl Cellulose	0.5 ppbb
		Barite	178.5 ppbb
EPA-83-008, Freshwater Lignosulfonate Mud	Dowell	Bentonite	15.0 g
		Chrome Lignosulfonate	15.0 g
		Lignite	10.0 g
		Carboxymethyl Cellulose	0.25 g
		Sodium Bicarbonate	1.0 g
		Barite	487.0 g
		Deionized Water	187.0 ml

(3) Test mixtures were aerated, and
 (4) For the mineral oil tests, glassware was washed with petroleum ether to assure removal of the oil.

To prepare the suspended particulate phase of each drilling fluid, 800 milliliters of chilled seawater were added to a 2-liter Erlenmeyer flask. Then, 200 milliliters of the well-stirred drilling fluid were added to the flask. More seawater (1,000 milliliters) was added to bring the contents of the flask to the 2-liter mark. This 1-part fluid:9-part seawater slurry was placed on a magnetic stirrer and mixed for at least 5 minutes. The pH and dissolved oxygen were measured and, if necessary, adjusted.

The number of animals exposed to a drilling fluid and the number of replicates varied. For range-finding tests, 10 mysids were added to each of 4 concentrations and a control, none of which was replicated. For definitive tests, 20 mysids were added to each of 5 concentrations and 3 replications were maintained; a seawater control and a reference toxicant (positive control) were also maintained. The reference toxicant was sodium lauryl sulfate.

Results and Discussion

Generic Drilling Fluids

The range of toxicity of eight laboratory-prepared generic drilling fluids to mysids was considerable. The 96-hour LC50's were from 2.7% suspended particulate phase (fluid #1) to 65.4% (fluid #7). An LC50 could not be calculated for three fluids — #4, #5, and #6 — because no median effect (50% mortality) occurred (Table 2). It should be noted that these tests were not designed to identify the constituents in drilling fluid #1 that caused it to be more toxic than the other fluids.

The response of the mysids to the reference toxicant, sodium lauryl sulfate, showed that the test animal populations were in suitable condition for the toxicity tests. In five tests, the 96-hour LC50's were from 3.4 ppm to 7.5 ppm. These are in accord with the literature and with unpublished data from Gulf Breeze and a commercial testing laboratory. The reference toxicant LC50's obtained at Gulf Breeze and Narragansett were similar, even though the brood stocks and natural seawater were different.

The interlaboratory agreement of drilling fluid test data from Gulf Breeze and Narragansett was equally good. To assure the validity of the Gulf Breeze tests, two of the drilling fluids (#1 and #5) were tested at Narragansett. The 96-hour LC50 for fluid #1 was almost exactly the same at both laboratories (Table 3). The results of the tests with fluid #5 were similar: Narragansett observed no mortality in 100% suspended particulate phase, whereas Gulf Breeze recorded 12% mortality in that concentration. Considering the nature of the test material, this represents a more than satisfactory duplication of test results.

Mineral Oil-Contaminated Drilling Fluids

The addition of mineral oil to generic drilling fluids #2 and #8 dramatically increased their acute toxicity to mysids. When 1% mineral oil was added, the 96-hour LC50 changed from 51.6% to 13.4% for fluid #2 and from 29.3% to 7.1% for fluid #8. Addition of 5% and 10% mineral oil further increased toxicity (Table 4).

There was a significant negative correlation between mineral oil content

Table 2. Results of Acute Toxicity Tests with Eight Generic Drilling Fluids and Mysids (*Mysidopsis bahia*). The Tests Were Conducted at U.S. EPA, Gulf Breeze, Florida, During August-September 1983

Drilling Fluid	Range-finding Test (median effect)	Definitive Test ^a (96-h LC50 & 95% CL)	Positive Control ^a (96-h LC50 & 95% CL)	Definitive Test ^b (96-h LC50 & 95% CL)
#1	>1% <10% SPP ^c	2.7% SPP (2.5-2.9)	5.8 ppm ^d (4.3-7.6)	3.3% SPP (3.0-3.5)
#2	>50% <100% SPP	51.6% SPP (47.2-56.5)	7.5 ppm (6.9-8.1)	62.1% SPP (58.3-65.4)
#3	>10% <50% SPP	16.3% SPP (12.4-20.2)	7.3 ppm (6.6-8.1)	20.3% SPP (15.8-24.3)
#4	No median effect in 100% SPP	12% mortality in 100% SPP	3.4 ppm (2.8-4.1)	---
#5	100% SPP	12% mortality in 100% SPP	Same as for #1	---
#6	No median effect in 100% SPP	20% mortality in 100% SPP	6.0 ppm (5.4-6.6)	---
#7	>50% <100% SPP	65.4% SPP (54.4-80.4)	Same as for #6	68.2% SPP (55.0-87.4)
#8	>10% <50% SPP	29.3% SPP (27.2-31.5)	Same as for #3	30.0% SPP (27.7-32.3)

^aCalculations by moving average, no correction for control mortality unless stated.

^bCalculations by SAS® probit; correction for all control mortality. Analyses performed by R. Clifton Bailey, U.S. EPA Program Integration and Evaluation Staff, WH-586, Office of Water Regulations and Standards, Washington DC 20460

^cThe suspended particulate phase (SPP) was prepared by mixing 1 part drilling fluid with 9 parts seawater. Therefore, these values should be multiplied by 0.1 in order to relate the 1:9 dilution tested to the SPP the whole drilling fluid.

^dCorrected for 13% control mortality

and the 96-hour LC50 for each fluid; Spearman's $r = -0.976$ with a probability ≤ 0.0001 (Steel and Torrie, 1980).

Literature Cited

Petrazzuolo, G. 1983. Proposed Methodology: Drilling Fluids Toxicity Test for the Offshore Subcategory; Oil and Gas Extraction Industry. Technical Resources, Inc., Bethesda, MD 20817. Draft dated May 19, 1983.

Steel, R.G. and J.H. Torrie. 1980. Principles and Procedures of Statistics, 2nd ed. McGraw-Hill, New York, NY. 633 pp.

U.S. Environmental Protection Agency. 1983. Issuance of Final General NPDES Permits for Oil and Gas Operations on the Outer Continental Shelf (OCS) of Alaska; Norton Sound and Beaufort Sea. Federal Register Vol. 48, No. 236, December 7, 1983, pp. 54881-54897.

Table 3. Results of Acute Toxicity Tests with Mysids (*Mysidopsis bahia*) and Two Generic Drilling Fluids Conducted at U.S. EPA, Gulf Breeze, Florida, and Narragansett, Rhode Island, During August-September 1983

Test Location	Drilling Fluid	96-hour SPP ^a LC50	95% Confidence Limits
Gulf Breeze	#1	2.7%	2.5-2.9%
	#5	No Median Effect ^b	---
Narragansett	#1	2.8%	2.5-3.0%
	#5	No Median Effect ^b	---

^aThe suspended particulate phase (SPP) was prepared by mixing 1 part drilling fluid with 9 parts seawater. Therefore, these values should be multiplied by 0.1 in order to related the 1:9 dilution tested to the SPP of the whole drilling fluid.

^bNo median effect (50% mortality) occurred in 100% SPP.

Table 4. Comparative Acute Toxicity of Two Generic Drilling Fluids without and with Mineral Oil Tested with Mysids (*Mysidopsis bahia*) at U.S. EPA, Gulf Breeze, Florida, During August-October, 1983

Drilling Fluid ^a	96-hour SPP ^b LC50	95% Confidence Limits
#2	51.6%	47.2-56.5%
#2-01	13.4%	11.1-16.9%
#2-05	1.08%	1.4-2.2%
#2-10	0.49%	0.39-0.62%
#8	29.3%	27.2-31.5%
#8-01	7.1%	5.7-9.0%
#8-05	0.90	0.74-1.1%
#8-10	0.76%	0.63-0.87%

^aThe two digits following the generic drilling fluid number indicate the percentage of mineral oil in the fluid.

^bThe suspended particulate phase (SPP) was prepared by mixing 1 part drilling fluid with 9 parts seawater. Therefore, these values should be multiplied by 0.1 in order to relate the 1.9 dilution tested to the SPP of the whole drilling fluid.

The EPA authors, **T. W. Duke** (also the EPA Project Officer, see below), **P. R. Parrish**, **R. M. Montgomery**, **S. D. Macauley**, **J. M. Macauley**, and **G. M. Cripe** are with Environmental Research Laboratory, Gulf Breeze, FL 32561. The complete report, entitled "Acute Toxicity of Eight Laboratory-Prepared Generic Drilling Fluids to Mysids (*Mysidopsis bahia*)," (Order No. PB 84-199 850; Cost: \$8.50, subject to change) will be available only from:

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Project Summary

Partitioning of Cadmium, Copper, Lead and Zinc Among Particulate Fractions and Water in Saginaw Bay (Lake Huron)

Kenneth R. Rygwelski, Jill M. Townsend, and V. Elliott Smith

An intensive study of toxic metals in Saginaw Bay (Lake Huron) during 1976-1979 has resulted in a large data base on the temporal and spatial variability of Cd, Cu, Pb and Zn concentrations in both the water and suspended solids. Generally, a trend of decreasing concentrations of both the total and dissolved metals from the inner to the outer bay was observed. Partition coefficients of all the metals studied were not constant with respect to time or space. Particles in the 10-74 μm range were found to contain the majority of the particulate metal mass in the water, and they sorbed metals to a higher degree than the other size fractions considered.

This Project Summary was developed by EPA's Environmental Research Laboratory, Duluth, MN, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Objectives

The distribution of four trace metals, cadmium, copper, lead, and zinc, was studied in Saginaw Bay (Lake Huron) in order to establish a large data base suitable for future assessment of water quality trends and the development of mass balance models for metallic toxins. A major objective was to determine the importance of various size fractions of suspended solids in concentrating trace metals in the water column.

Methodology

During 1976-78, Cranbrook Institute of Science carried out an intensive survey of cadmium, copper, lead, and zinc in Saginaw Bay. A total of 33 cruises were conducted by sampling up to 27 stations on the bay at approximately two-week intervals during the months of April-November. Table 1 lists the numbers and types of samples collected for the laboratory analysis of these metals. In addition to these samples, other param-

Table 1. Sampling Program

Sample Types	Year Sampled With Number Collected		
	1976	1977	1978
<i>Saginaw Bay Cruises</i>			
Whole Water	374	562	313
<.45 μm (dissolved)	336	522	313
.45-10 μm (particulate)	-	-	92
10-74 μm (particulate)	-	-	92
74-210 μm (particulate)	-	-	138
210-1000 μm (particulate)	-	-	138
<i>Saginaw River Loadings</i>			
Whole Water	160	208	228
<i>Precipitation</i>			
Whole Water	11	93	122
<.45 μm (dissolved)	11	56	56

eters measured included chloride, conductivity, non-filterable chlorophyll *a*, pH, Secchi disc depth, temperature, total alkalinity, total non-filterable residue, and transmittance

A serial filtration system designed for this study was used to fractionate whole water into various particle size fractions (listed in Table 1) to be analyzed for metals. A separate filtration system was used to filter whole water through a 45 μm filter to obtain the dissolved fraction.

No special pre-treatment was necessary for water samples analyzed for metals, but particulate samples were prepared by using a nitric acid digestion method. Samples were then analyzed using flame and flameless atomic absorption spectrophotometry.

Care was taken in choosing equipment made of materials that would minimize contamination in all phases of the sample collection, filtration, digestion, and analysis. Routine blank checks were made on sample bottles, the filtering process, and on particulate filters and screens.

Accuracy of the metal analysis was determined through participation in interlaboratory comparison studies and by analysis of standard reference samples and use of the standard addition method. Results of between-run analyses of standards and samples were used to determine precision.

Results

The full report contains an overview of the data and describes the spatial and temporal distribution of zinc, copper, lead and cadmium in Saginaw Bay. Partition coefficients of all the metals studied were not constant with respect to time or space. Two types of partition coefficients were determined, a K_{pg} (general K_p) and a K_{ps} (specific K_p). For all four metals, the K_{ps} calculated for each of the specific size fractions (10-74 μm , 74-210 μm , and 210-1000 μm) were within the range of the K_{pg} values calculated using total non-filterable residue data. Particles in the 10-74 μm range were found to contain the majority of the particulate metal mass in the water and exhibited the highest K_{ps} of these metals.

Partition coefficients (K_{ps} and K_{pg}) in Saginaw Bay increased as the suspended solids concentration decreased. This trend held for cadmium, copper, zinc, and lead (Figures 1-4). Segment 4 was chosen to represent the largely oligotrophic outer bay, and segment 1 was typical of the eutrophic inner bay.

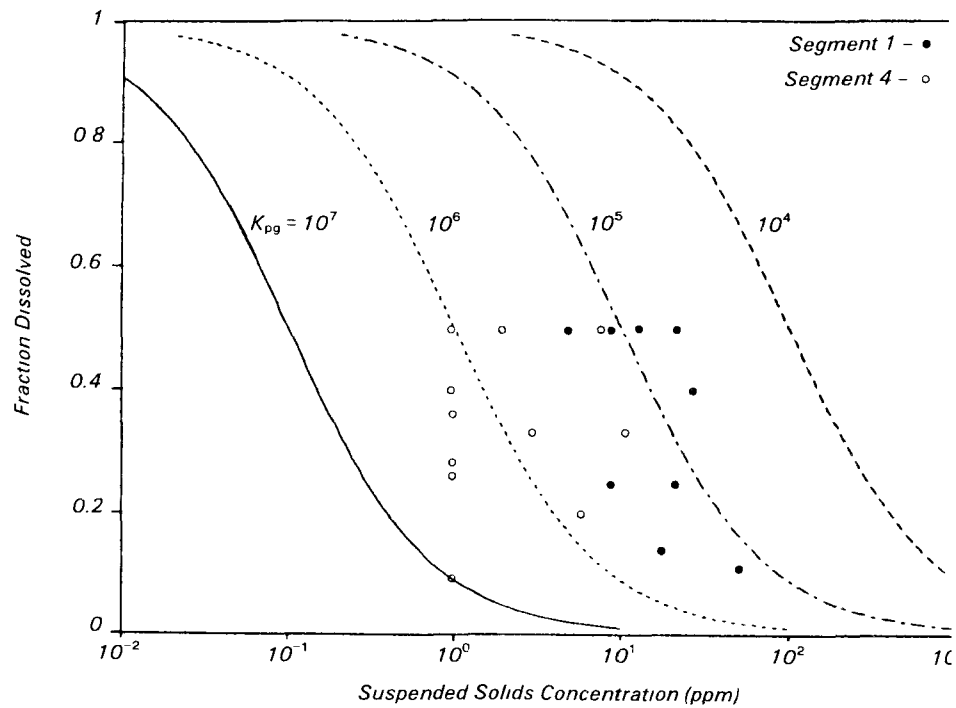


Figure 1. General partition coefficients for cadmium, 1976.

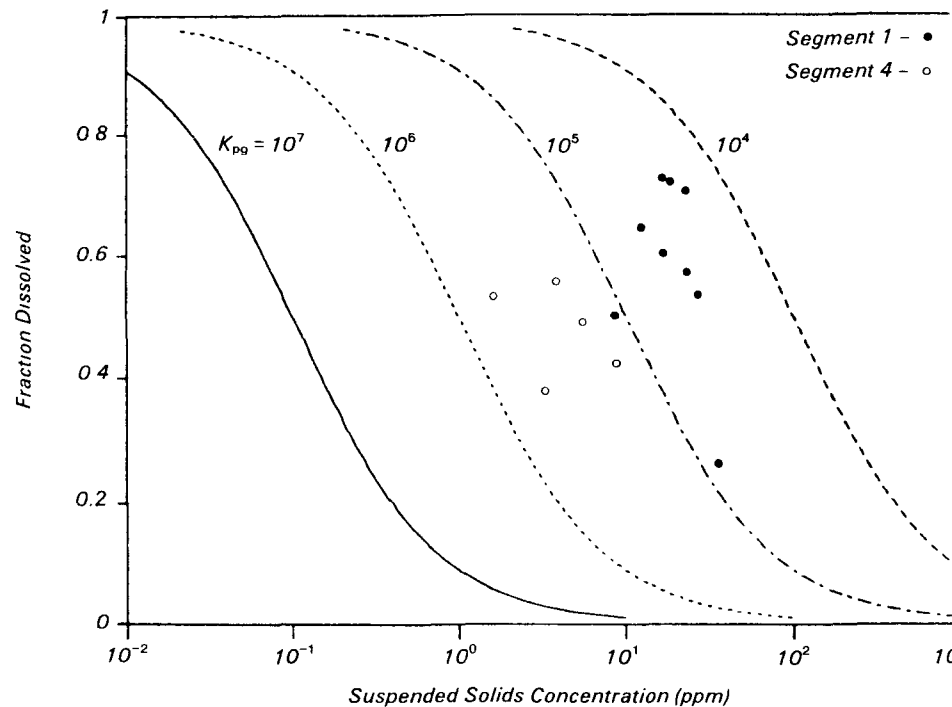


Figure 2. General partition coefficients for copper, 1978.

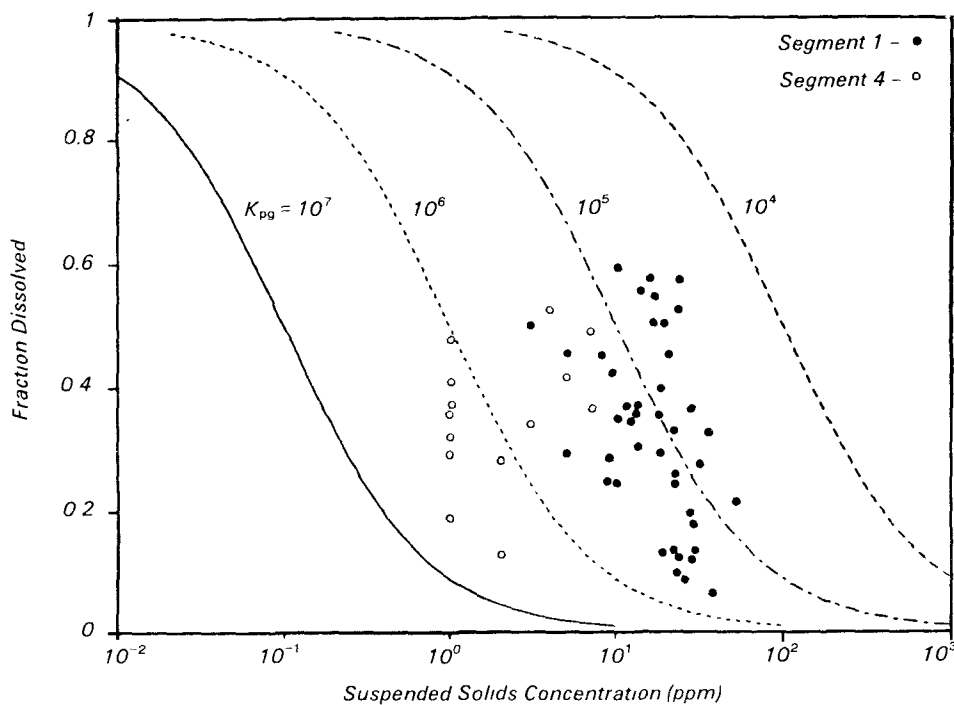


Figure 3. General partition coefficients for zinc, 1976-1978

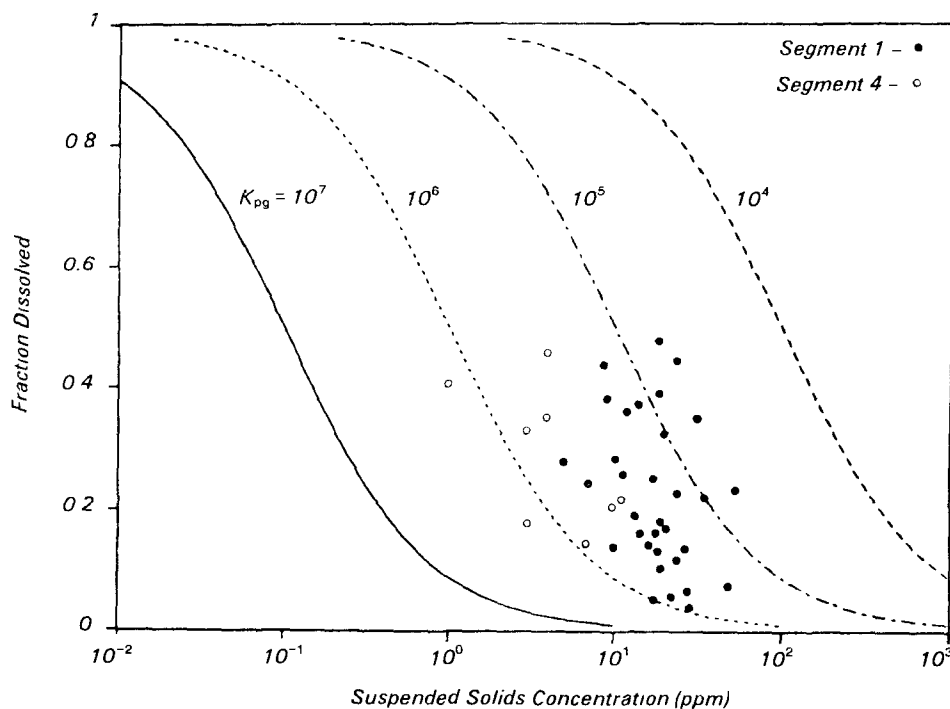


Figure 4. General partition coefficients for lead, 1977-1978.

The figures also show that the fraction of metal dissolved increases within a given segment as the suspended solids concentration decreases. This trend is predicted by theory if constant partition coefficients can be assumed within a given segment.

Data for cadmium, copper, lead, and zinc as total metal, dissolved metal, particulate metal mass in the water, and the concentration of metal in the particles are presented in figures and tables contained in the full report.

Gradients of decreasing concentration from the inner to outer bay segments were noted for total and dissolved metals studied and for other non-metal parameters, including total non-filterable residue, conductivity, chloride, alkalinity, and non-filterable chlorophyll *a*. Quarterly and annual summaries of all non-metal parameters are presented by bay segments.

Recommendations

These results indicate an inverse relationship between the solids concentration and partition coefficients of these metals in Saginaw Bay. Such a "mass effect" has been noted elsewhere. However, it is possible that the chemical nature of particulates and of adsorbing metal species also plays an important role in partitioning. If all of these variables were well defined in Saginaw Bay, in both space and time, then it would be possible to predict partition coefficients in other fresh water systems. Complete characterization of these variables was not possible in this study, until such data are available, an empirical approach such as the one used here is probably most appropriate to define partitioning.

Quality control measures are an important consideration in any study, particularly one involving analysis of trace metals. Determining blank levels for equipment and processes used in the study was crucial to providing accurate results. Results of such quality control programs should be used in establishing analytical strategies and determining the reliability of the data generated.

It was difficult to compare these data to those of previous studies, as little partitioning data on metals exists. It is hoped that these results will provide a needed base of information on trace metal partitioning in waters of the Great Lakes.

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The complete report, entitled "Partitioning of Cadmium, Copper, Lead and Zinc Among Particulate Fractions and Water in Saginaw Bay (Lake Huron)," (Order No. PB 84-209 899; Cost: \$16.00, subject to change) will be available only from:

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