Extraction of Petroleum Hydrocarbons from Oil-Contaminated Sediments

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Petroleum degradation occurring in situ in Chesapeake Bay is an important aspect of the ecology of this region. To assess the degradative capabilities of the naturally-occurring microorganisms in Chesapeake Bay, several areas, including Colgate Creek in Baltimore Harbor, are sampled on a regular basis. Colgate Creek is heavily contaminated with a variety of petroleum compounds, including cosmoline (a wax used to protect automobiles during transport across the Atlantic), kerosine (used to wash wax from the automobiles), motor oil and tanker fuels. Thus, Colgate Creek is continuously exposed to petroleum and petroleum by-products. Recently, 17,000 gallons of fuel oil, in an accidental spill, were released into Colgate Creek. The point of study in our research is to determine if a correlation exists between numbers of petroleum-degrading microorganisms with amount of petroleum-like material routinely extracted from sediment and water collected in Colgate Creek (WALKER and COLWELL, 1973). At the present time, only a few techniques are available for extracting oil from water (GRUENFELD, 1973; HUGHES et al., 1973). The extraction procedures used to obtain petroleum-like compounds from estuarine and marine sediments have not been compared. Hence, in this paper we examine several methods and solvents for extraction of estuarine water and sediments.

Sediment samples (1 kg) were collected using a Ponar grab and stirred to provide a homogeneous sample. Each sample (100 g) was extracted with 400 ml benzene using: i) the Soxhlet method, ii) mixing with a magnetic stirrer and teflon magnetic stirring bar, iii) sonication of the sediment prior to and during mixing and iv) shaking the sediment using a reciprocal shaker with a horizontal stroke of 1" and a speed of 150 - 200 strokes per min. Employing the use of a reciprocal shaker proved to be the most efficient method in terms of greater yield of extracted material.

Using the reciprocal shaker, several solvents for recovery of extractable material were compared, including hexane, benzene and chloroform. Sediment (100 g) was added to 1 liter screw-cap flasks containing 100 ml of each solvent. Nitrogen was bubbled into each flask prior to sealing to prevent excessive oxidation. The extraction was carried out for 12 - 24 h with shaking, at which time the solvent was removed and transferred to a second 1 liter flask containing ca. 25 g Na_2SO_4. This step was repeated three times, using 100 ml of solvent in each case to provide quantitative recovery of extractable material. The benzene extracts yielded the largest net

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recovery of extractable material. See Table 1. Benzene is more polar than hexane, which provides additional extraction efficiency. Furthermore, benzene is less dense than water (unlike chloroform), also a factor in the recovery procedure.

TABLE 1

Comparison of solvents in recovery of extractable compounds from sediments.

	Dry weight (mg)		
	Hexane	Benzene	Chloroform
1st replicate	147	334	241
2nd replicate	156	317	222
3rd replicate	160	325	216
4th replicate	138	320	229
Average	150 ± 4	324 ± 3	227 ± 4

The quantitative and qualitative differences, according to solvent used, were determined by analysis using low-resolution computerized mass spectrometry (Table 2). The data given in Table 2 were obtained by loading each of the extracts into a 3/4-inch capillary tube closed at one end. Samples were tared prior to, and after, analysis. A CEC 21-103C mass spectrometer with scanning capability to about m/e 500 was employed. Comparison of the amount and proportional representation of each component present in the extracts with the crude oil provided good evidence that the extracted material contained the hydrocarbons found in petroleum. Differences in proportional representation of each of the hydrocarbon components compared with the data for oil can be attributed to weathering and microbial degradation (WALKER and COLWELL, 1974). Analysis of the chloroform extract carried out in triplicate indicates the relatively good reproducibility of both the extraction procedures and the mass spectrometric analytic method.

From the data obtained in this study, it is concluded that benzene is the most effective solvent of the three solvents tested for extracting petroleum hydrocarbons. The mass spectrometer results, combined with results from total recovery of petroleum hydrocarbons, (Table 1), indicate that benzene or benzene-methanol azeotrope is the solvent of choice for extracting hydrocarbons from oil-contaminated sediments. Thus, a method of reciprocal shaking, employing benzene as the solvent, will provide the most efficient extraction of petroleum hydrocarbons from estuarine or marine sediments.

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TABLE 2

Classes of hydrocarbons extracted from samples of sediment.[1]

Hydrocarbon class	Hexane extract	Benzene extract	Chloroform extract				Crude oil[2]
			1	2	3	Average	
Paraffins	21.1	20.0	19.9	20.1	21.0	20.3 ± 0.2	41.1
Monocycloparaffins	21.1	26.0	25.4	26.6	26.1	26.0 ± 0.2	19.6
Dicycloparaffins	6.6	8.5	7.7	8.1	8.5	8.1 ± 0.1	4.3
Tricycloparaffins	6.4	7.2	6.7	7.5	7.6	7.2 ± 0.2	0.8
Tetracycloparaffins	0.3	2.4	0.2	-	-	0.2 ± 0	0.2
Pentacycloparaffins	0.4	0.5	0.2	0.2	-	0.2 ± 0	-
Hexacycloparaffins	0.1	-	-	-	-	-	-
Alkylbenzenes	22.1	28.8	22.8	23.3	26.3	24.1 ± 0.8	23.8
Benzcycloparaffins	5.7	0.6	5.0	3.7	2.9	3.8 ± 0.4	5.2
Benzdicycloparaffins	7.4	0.2	5.1	2.8	1.9	3.2 ± 0.7	2.4
Alkylnaphthalenes	5.2	3.1	3.7	4.0	2.8	3.5 ± 0.2	1.3
Alkylacenaphthenes	1.9	1.0	1.6	1.7	1.2	1.5 ± 0.1	0.5
Fluorenes	0.8	1.0	0.8	0.8	0.8	0.8 ± 0	0.4
Phenanthrenes	0.6	0.5	0.5	0.5	0.5	0.5 ± 0	0.2
Cyclopentaphenalenes	0.4	0.4	0.4	0.4	0.4	0.4 ± 0	0.1
Sample size (mg)	1.84	0.84	1.28	2.25	0.74	1.42 ± 0.4	1.2
Percent vaporized	93.0	83.3	89.9	81.3	81.1	84.1 ± 2.4	100.0

[1] Figures are % of yield.

[2] Reference for comparison with material extracted from natural samples and a control in the mass spectrometry analysis.

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