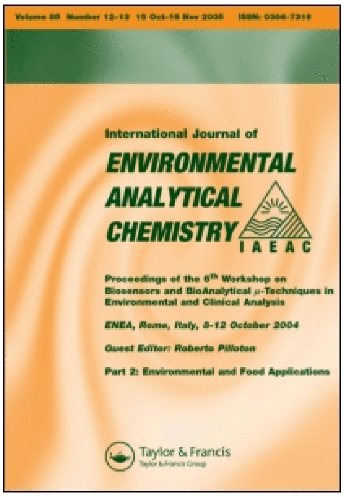

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Moore, R. A. and Karasek, F. W.(1984) 'GC/MS Identification of Organic Pollutants in the Caroni River, Trinidad', International Journal of Environmental Analytical Chemistry, 17: 3, 203 — 221
To link to this Article: DOI: 10.1080/03067318408076973
URL: http://dx.doi.org/10.1080/03067318408076973

Intern. J. Environ. Anal. Chem., 1984, Vol. 17, pp. 203–221
0306-7319/84/1704-0203 $18.50/0

Printed in Great Britain

GC/MS Identification of Organic Pollutants in the Caroni River, Trinidad

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(*Received November 30, 1983*)

Water samples from the Caroni River, Trinidad and other rivers which flow into the Caroni River were qualitatively analyzed for trace organic contaminants by procedures based on XAD extraction followed by GC/MS analysis. Pesticides, polyaromatic hydrocarbons, aliphatic hydrocarbons, phenols and phthalate esters were the main groups of compounds found. Many of the contaminants present in these water samples are known industrial pollutants, and several have been found in waste waters examined by other workers, which suggests that the factories of an industrial complex located upstream of the Caroni/Arena Water Treatment Plant may be the major source of the pollutants. Some compounds identified in the water samples have not been previously reported.

KEY WORDS: Water, contaminants, organic, analysis, gas chromatography–mass spectrometry.

INTRODUCTION

Many organic compounds which originate from industrial, agricultural and other anthropogenic sources are toxic, carcinogenic, and mutagenic in nature, and in many cases these effects are manifest at very low levels of the compounds. The growing awareness of the hazards posed by the ubiquitous occurrence of such compounds in the environment has led to the development of several water pollution monitoring programs in various countries in an effort to permit early detection of potentially dangerous contaminants, and implement corrective measures when necessary. The analytical results of surveys for trace organic compounds in tapwater supplies and environmental water samples have been the subject of many reports. Well waters in Ames, Iowa were analyzed by Burnham.[1] The major compounds in the well water were indene, methyl indene, methyl naphthalene, acenapthalene and acenaphthene. The source of contamination was believed to be residues from a coal gas plant operated in the city of Ames, Iowa, during the 1920's. Tar residues from this plant were buried in a pit that was connected hydrologically to the aquifer supplying the city water.[2] Richard carried out analyses of pesticides in drinking water obtained by treatment of well and river waters from various cities in Iowa and found concentrations of dieldrin and DDE ranging from less than 0.5 mg/L to 50 ng/L and concentrations of atrazine as high as 5000 mg/L.[3] A later publication by Junk reported the presence of much higher concentrations of these pesticides in several Iowa waters at certain periods.[4] Water treatment procedures at one modern treatment plant were shown to be ineffective in reducing the pesticide concentration. The pesticides dieldrin; p,p′ DDT; p,p′ DDE; p,p′ DDD, o,p′ DDT; heptachlor epoxide; lindane; atrazine and several other uncharacterized ones were reported found in the Skunk River near Ames Iowa.[5]

Carbon column extracts of 300,000 gallons tap water of a New Orleans Area Water Supply study in 1974 contained over eighty compounds including atrazine, several phthalate esters and alachlor as major components.[6] In a survey of Athens (Georgia) tap water, Thruston identified several polyaromatic hydrocarbons, biphenyl, dibenzofuran, anthraquinone, dibenzothiophene and other organic compounds in the ng/L range.[7]

Samples of the effluent water from a rapid infiltration system in Phoenix, Arizona contained a broad spectrum of compounds of which alkylbenzenes, alkyl phenols, phthalate esters, and alkanes were the most abundant. Keith identified α-terpineol, dioctyl phthalate, several phenols, and other organic compounds in waste waters from two Kraft paper mills in Georgia.[9] Fatty acids, phenols, benzothiazole and 1-mercaptobenzothiazole were major components of the effluents from a tire-manufacturing plant.[10] Jungclaus analysed the waste water and receiving river waters of a speciality chemicals-manufacturing plant and found concentrations of various anthropogenic compounds to be as high as 15 ppm in waste water and 0.2 ppm in river water.[11] Among the compounds identified were several alkyl phenols, alkyl benzenes, alkanes, substituted triazoles, phthalate esters, and several compounds known to have herbicidal and disinfectant properties.

Results of analyses for trace organic compounds in tap water, river water, waste water and marine samples in Japan have also been reported.[12-15] Shinohara found in tap water a large number of alkylbenzenes; odorous components such as menthol, benzaldehyde, acetophenone and its derivatives; plasticisers including dimethyl phthalate, diethyl phthalate, di(2-ethylhexyl) adipate, di(2-ethyl hexyl) phthalate in concentrations ranging from 1–240 parts per billion.[14] Yasuhara analysed water samples from the Hayashida River which is known to be polluted by effluents from leather factories and reported the presence of polyethylene glycols, poly(oxyethylene) alkyl phenyl esters, free fatty acids, and various alkanes.[15]

Waters from the Monatiquot and Merrimack Rivers in New England were found to contain various industrial chemicals which seem to originate from factories located in the vicinity of these rivers.[16] Common plasticisers such as di-(2-ethylhexyl) phthalate, di-isodecyl phthalate, di(2-ethylhexyl) adipate, di-butyl phthalate, and the more uncommon dibutoxyethoxymethane were the major compounds present in the Monatiquot River. Phthalate esters, trichlorobenzene, biphenyl and n-butyl benzoate were identified in the extracts of water from the Merrimack River. The latter three compounds, together with dibutyl phthalate are used as dye-carriers in the dyeing of hydrophobic synthetic-fibers.[17,18] Hites reported that a factory on the Monatiquot river was known to produce some plastic products and several cities located upstream of the Merrimack River had well developed textile industries which included dye shops.[16]

The present research on aquatic pollution in the Caroni River, Trinidad is being undertaken in response to a need for Trinidad to monitor the extent of industrial pollution of its major water systems. An accelerated industrial expansion which this Third World oil-rich country has experienced during the last decade is expected to have a significant impact on the environment. Pollution of the natural water resources is of particular concern since many industries discharge effluents directly into streams, rivers and the ocean. This practice poses a distinct hazard since these waters are used by the local population for domestic and recreational purposes. It is mandatory that harmful and undesirable compounds in these waterways be identified and quantified so that effective control measures can be formulated and implemented.

The Caroni River is one of the most polluted by industry. The river runs in an east-west direction across the capital region and receives drainage from the most industrialized area of the island. Recently, the Caroni-Arena Water Treatment Plant has been commissioned for intake and treatment of water from the Caroni River for redistribution to the population. The water treatment plant is located downstream of the Omeara Industrial Estate. Many factories on this industrial estate are known to discharge effluents directly into streams and smaller rivers, the contents of which eventually flow into the Caroni River at points upstream of the water intake of the treatment plant. To date, no study of the organic contaminants present in these waters has been undertaken. In this work we qualitatively analysed for trace organic compounds in the water samples from the Caroni River and two rivers which receive effluent from the industries before emptying into the Caroni River. Identification of compounds was carried out by computerized gas chromatography-mass spectrometry after preconcentration of water samples using XAD resin columns.[19] In future work methodology for quantitative analyses of organic compounds will be optimized and applied to a study of the concentrations of organic contaminants in river water upstream of the treatment plant and in the treatment plant's finished water. This data will allow the determination of the fate of the pollutants, the effectiveness of the treatment plant in removing undesirable organic compounds from the incoming waters, and will serve as establishing a basis for water quality assurance programs.

EXPERIMENTAL

Instrumental analysis

Gas chromatographic analyses were performed with a Hewlett-Packard (HP) 5880A gas chromatograph equipped with a level 4 integrator, a flame ionization detector, cool on-column injection system and a widebore (0.32 mm × 30 m) DB-1701 fused silica capillary column (J & W Scientific Inc. Rancho Cardova, CA. U.S.A.).

Capillary gas chromatographic/mass spectrometric analysis employing a Hewlett-Packard 5992A GC/MS/Calculator equipped with the same column was used for identification of compounds.

Sorbents and reagents

Amberlite XAD-2 and XAD-7 resins (Rohm and Haas, Philadelphia) were purified by twelve hour sequential Soxhlet extractions with methanol, acetonitrile and diethyl ether. The cleaned resins were stored under methanol.

Purified water was prepared by extracting distilled water sequentially with previously cleaned XAD-2 and XAD-7 resins.

Diethyl ether used for extraction of all but the first three samples was subjected to a clean-up procedure involving four solvent extractions with sodium hydroxide solution (0.05 M) in order to remove a contaminant which was identified in earlier chromatographic analyses of ether extracts. This contaminant was identified as isobutyric acid. Equal volumes of sodium hydroxide and diethyl ether were used in each extraction.

All solvents were distilled-in-glass grade obtained from Caledon Laboratories, Canada. Sodium hydroxide pellets and hydrochloric acid were ACS grade (J. T. Baker Chemical Co.).

Glasswool preparation

Silanized glasswool (Chromatographic Specialties, Canada) was soaked in purified water for several minutes, placed in a glass column fitted with a teflon stopcock and extracted with several mL of clean ether followed by a few mL of purified water.

Column preparation

Glass columns, 25 cm in length, i.d. 1.0 cm, fitted with teflon stopcocks were employed. A plug of pre-extracted silanized glasswool was inserted at the bottom of the column and a slurry of the resin in methanol added to the column. Approximately 2 g of resin were used to produce a resin column 8 cm long. Another plug of pre-extracted glasswool was inserted into the column at the top of the resin bed and the methanol was drained through the stopcock until the liquid level just reached the top of the resin bed. The resin was then washed with 50 mL of diethyl ether followed by three 20 mL portions of purified water. For each portion the flow was stopped when the liquid level reached the top of the resin bed.

Sample collection

Twelve samples were collected during the period 22/6/82 to 10/5/83. Sampling sites were located on the Manachal River, Mausica River and at three sites on the Caroni River (Figure 1). The first three sample collections were done using 4-litre Van Dorn bottles (M.S.E. Engineering Systems Ltd., Downsview, Ontario, Canada). At each site, two to four grab samples of surface water (depths ≈ 2 m) were taken and these samples were combined to give one sample for each site. The other samples were collected with an automatic sampler capable of collecting up to 12 samples of approximately one-litre volume at preset intervals. At each site a combined sample of 8 to 12 litres of water was collected over a twenty-four hour period using a sampling interval of two hours. The first three samples were collected during the rainy season, April to December, 1982 and the remaining samples were collected during the dry season, January to May, 1983. Sampling sites, periods of sample collection and sample volumes are summarized in Table I. All samples were transferred immediately after collection to clean amber-coloured glass bottles and were refrigerated at 0°C prior to extraction. Extractions were done within 24 hours of sample collection.

Filtration and extraction of samples

Each water sample was filtered through a two-litre Pyrex-glass Buchner funnel fitted with a medium porosity fritted disk (10–15 μm pore size) into a four-litre Pyrex-glass Buchner flask. A two-litre glass reservoir was attached to the top of each column, care being taken to ensure that the quickfit joint between the reservoir column was leakproof. The filtered water sample was carefully added to the reservoir and allowed to pass through the resin by gravity flow at

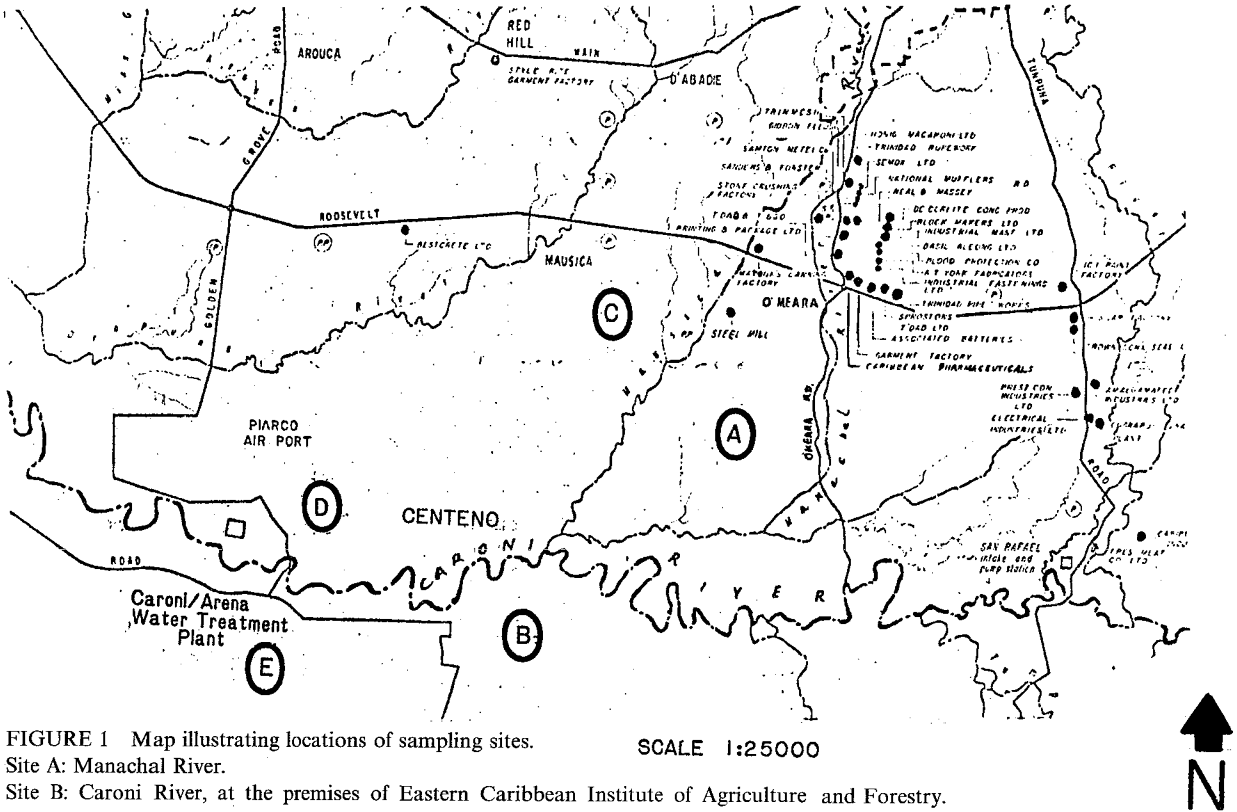

FIGURE 1 Map illustrating locations of sampling sites.
Site A: Manachal River.
Site B: Caroni River, at the premises of Eastern Caribbean Institute of Agriculture and Forestry.
Site C: Mausica River at Churchill Roosevelt Highway.
Site D: Caroni River at St. Helena Bridge.
Site E: Caroni River at Intake of Caroni/Arena Water Treatment Plant.
● represents industries.

TABLE I

Sample volumes, sampling locations and sampling periods.

Sample No.	Sampling site	Period of collection	Volume of water collected
I	D	22/06/82	8L
II	E	01/09/82	8L
III	A	01/09/83	4L
IV	B	01/09/83	4L
V	C	07/09/83	4L
VI	C	31/01/83 to 01/02/83	12L
VII	A	07/02/83 to 08/02/83	8L
VIII	B	08/02/83 to 09/02/83	9L
IX	C	22/03/83 to 23/03/83	9L
X	A	23/03/83 to 24/03/83	8L
XI	B	28/03/83 to 29/03/83	8L
XII	C	10/04/83 to 11/05/83	10L

$\approx$30 mL/min. When the solution level reached the top of the resin bed the wall of the reservoir was washed with three 25 mL portions of purified water, each portion being allowed to drain through the column to the top of the resin bed. The last wash was allowed to drain completely through the column.

The sorbed organics were then eluted with 25 mL of purified diethyl ether. The reservoir wall was washed with two 10 mL portions of diethyl ether and each wash was allowed to drain into the resin but not through the column, by opening the stopcock of the column briefly until a trace of ether escaped. The reservoir was removed, the column capped and left to stand for fifteen minutes. The ether was then allowed to drain through the column and the eluate collected into a 25 mm diameter thick-walled test-tube. A further 5 mL of ether was added to the column and allowed to flow through immediately into the receiving test-tube.

Residual water was removed from the diethyl ether by immersing the test tube in liquid nitrogen or in a dry ice–acetone freezing bath for several seconds to freeze the water (lower layer). The supernatant diethyl ether solution was decanted into the concentration vessel of the Kuderna–Danish (K–D) evaporator. The ice in the test-tube was washed with 5 mL of ether, the test-tube briefly re-immersed in the freezing bath and the ether decanted into the concentration vessel.

The organic extract was concentrated to 1.5 mL using the K–D evaporator. The volume was then adjusted to 0.1 mL with a stream of nitrogen and the resultant concentrated extract analysed by capillary GC and GC/MS. All of the extracts were kept refrigerated at 0°C prior to analysis.

All samples from the first three sampling sessions were subjected to the complete treatment outlined in Figure 2. The acidification step was not done for samples of the later sampling sessions, since studies of the extraction efficiencies of the resins showed that recoveries were best at pH 7 and acidification to pH 2 provided no advantage.[19] In all cases, blanks were prepared by subjecting an equal amount of purified water to the same treatment as the samples.

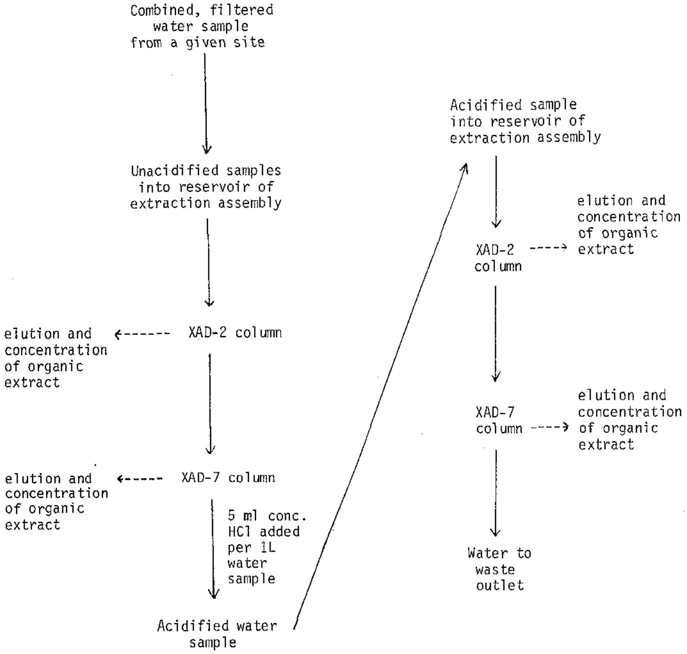

FIGURE 2 Flow diagram of treatment of water samples.
——→ pathway of water.
---—→ pathway of extracted organics.

IDENTIFICATION OF COMPOUNDS

The compounds were identified by mass spectral matching techniques from the GC/MS data. The internal search system of the HP 5992, the PBM/STIRS search system of Cornell University and all the available data in our atlases of mass spectra (8 Peak Index, MSDC; EPA/NIH Mass Spectral Data, Mass Spectrometry Centre of Nuclear Studies–Registry of Mass Spectral Data compiled by Stenhajen, Abrahamson and McLafferty) were utilized. Many of the compounds gave such unambiguous spectral matches that the identifications are quite certain. In others, where the mass spectral match was unclear, or no reference spectra were available, the assignments are less certain. Some compound identifications were verified by matching the GC and GC/MS data with that of authentic standards. For a limited number of compounds, no identification could be assigned.

RESULTS AND DISCUSSION

Sample I–IV

The compounds identified in these samples are summarized in Table II. All samples contained 1,6 dimethyl-4-isopropyl naphthalene. Sample 1 contained a compound tentatively identified as bis(2-hydroxy-5(1,1,3,3-tetra-methyl-butyl)-phenyl) sulphide (spectrum No. 217, Figure 3) and an unidentified compound with major ions of m/z values 69, 113 and 41 (spectrum No. 165, Figure 3). Extracts of sample II were relatively free of contaminants. Several chromatographic peaks of the extracts from the Mausica and Manachal River samples (III and IV respectively) represented compounds whose mass spectra had as major ions m/z values of 41, 69, 113 (spectra No. 37 and No. 75, Figure 4). Mass spectral computer matching by the Cornell University PBM/STIRS system failed to reveal reliable spectral matches for these compounds. The Manachal River extract contained a series of unidentified hydrocarbons. The pesticide 1-napthyl n-methyl carbamate, commonly known as carbaryl, was found in the extract from the Mausica River sample (spectrum No. 47, Figure 4).

TABLE II

Compounds present in samples I to V

Compounds	I	II	III	IV	V
			Sample No.		
α-terpineol	X				
Dibutyl formamide	X				
Diethyl phthalate	X		X	X	
1,6 dimethyl-4-isopropyl naphthalene	X	X	X	X	X
Dodecylcyclohexane	X				
Dibutyl phthalate	X	X	X		
1-naphthyl n-methyl carbamate					X
Bis(2-hydroxy-5(1,1,3,3,-tetramethylbutyl)-phenyl) sulphide (tentative)	X				
Di-(2 ethylhexyl) phthalate	X		X		
Unidentified alkanes	X		X		
Unidentified (spectrum No. 165, Figure 3)	X				
Unidentified (spectrum No. 37, Figure 4)		X	X		X
Unidentified (spectrum No. 75, Figure 4)		X	X		X
Unidentified (major ions m/z 223, 135, 57)					X

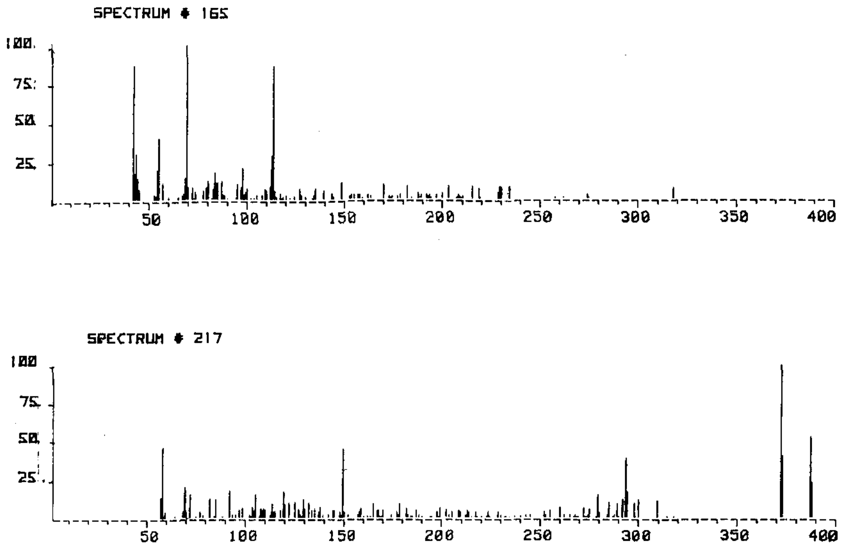

FIGURE 3 Mass spectra of compounds present in sample I. Spectrum 165 represents an unidentified component while spectrum 217 was tentatively identified as bis(2-hydroxy-5(1, 1, 3, 3, tetramethylbutyl)-phenyl) sulphide.

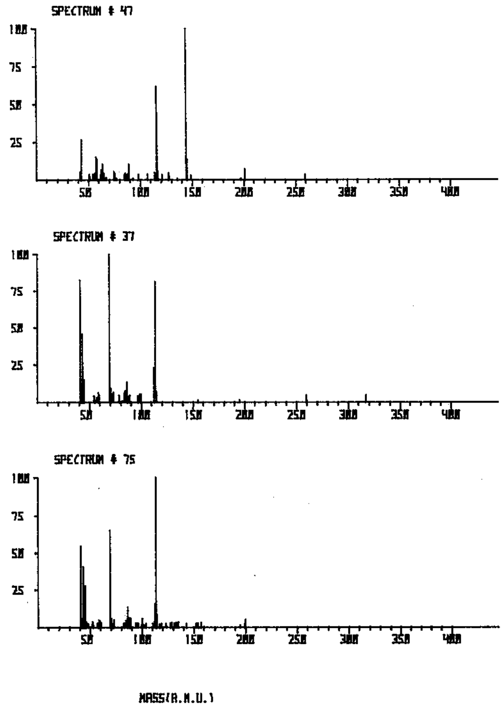

FIGURE 4 Mass spectra of compounds present in samples III, IV and V. Spectrum No. 47 was identified as 1-naphthyl n-methyl carbamate (common pesticide name, carbaryl). Spectra No. 37 and No. 75 were unidentified.

Samples VI–XII

The pollutant profiles of these samples were considerably more complex than previous samples. The compounds identified in the extracts are listed in Table III. More than thirty different compounds were identified in these samples, many of them being known industrial pollutants. The water samples from the Mausica River were generally the most heavily polluted, both in terms of number of compounds and their concentration levels. The extracts of samples VI, VII, VIII and XII all contained terpineol. Several of the pollutants identified in extracts from Mausica River were phenolic compounds which were not very well resolved on the chromatographic column. Figure 5 shows a chromatographic trace of the extract of sample VI taken from the Mausica River. Improvement of the chromatographic resolution and reliability of mass spectral identifications was facilitated by the application of fractionation procedures based on low pressure column chromatography and high pressure liquid chromatography.[21]

Spectra of some unidentified components of samples VI to XII are shown in Figure 6. The increased complexity of samples VI to XII as compared to that of earlier samples is attributable to two factors. Samples VI to XII were taken during the dry season when dilution effects are likely to be minimal; secondly, the use of the automatic sampler greatly extended the period over which the samples were collected, thus increasing the chances of intercepting pollutant discharges.

It is noteworthy that the profile of trace-organic compounds found in the Trinidad river waters resembled more closely those of waste waters that have been characterized by several workers[8-11] than those reported for well waters and drinking water supplies.[1,7] Alkyl

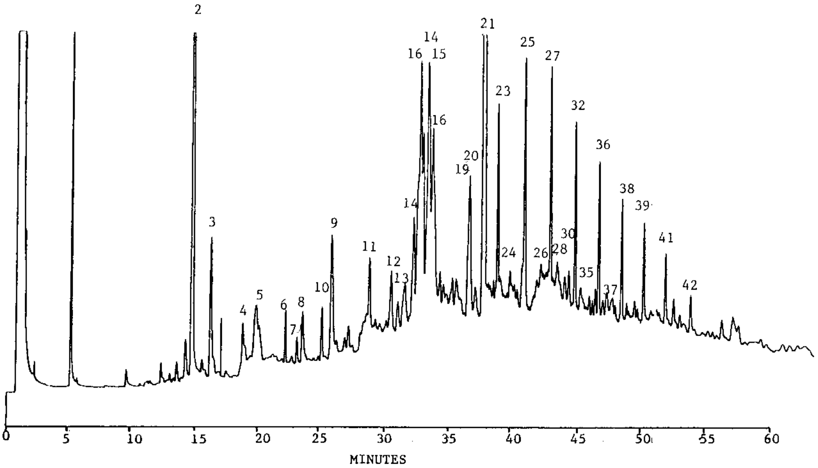

FIGURE 5 Gas chromatogram of extract from Mausica River sample VI. See Table II for compound identification.

GC conditions: 30 m × 0.32 mm i.d. DB-1701 fused silica capillary column; flame ionization detector; cool on-column injection at 40°C; temperature programmed from 40°C; temperature programmed from 40°C to 250°C at 2°C/min; carrier gas–helium, 2 ml/min @ 40°C.

TABLE III
Compounds identified in samples VI to XII

Compounds	Sample No.						
	VI	VII	VIII	IX	X	XI	XII
1. 2-ethyl-1-hexanol		X					
2. α-Terpineol	X	X	X	X			X
3. Benzothiazole	X	X	X	X	X		X
4. Unidentified (spectrum No. 149, Figure 6)	X			X			
5. Unidentified	X						
6. Unidentified	X						
7. Unidentified	X						
8. 1 (3H) Isobenzofuranone		X		X		X	X
9. 6 chloro-3,4 dimethyl phenol n-methyl carbamate	X	X	X	X	X	X	X
10. 2,4 dimethyl, 6 t-butyl phenol (or isomer)	X						
11. Diethyl phthalate	X	X	X	X	X	X	X
12. p-propoxy phenol		X		X	X	X	X
13. Unidentified	X			X	X		X
14. p-nonyl phenol or isomers	X			X			X
15. Unidentified (Spectrum No. 181, Figure 6)	X						
16. 4-(2,2,3,3 tetramethyl butyl)-phenol or isomers	X			X			X
17. Dodecyl phenol or isomer				X			
18. Eicosane				X	X		X
19. 1,6 dimethyl 4-isopropyl naphthalene	X	X	X		X	X	X
20. S-Hydrindacene 1,1,4,5,6,8-hexamethyl	X			X			
21. Dibutyl phthalate	X		X	X			X
22. 2 hydroxy-benzothiazole							X
23. Heneicosane (C_{21} alkane)	X			X			
24. 1-naphthyl-n methyl carbamate	X						X

25. Docosane	X			X		X
26. Unidentified (Spectrum No. 201, Figure 6)	X					
27. Tricosane	X			X		
28. 2,6 di-t-butyl-4 mercaptophenol	X					
29. Unidentified	X					X
30. 2,6 dinonyl phenol or isomers	X					
31. 2,6,10 trimethyl tetradecane				X		
32. Tetracosane	X			X		X
33. 11 cyclohexyl heneicosane			X			
34. 9 cyclohexyl heptadecane		X				
35. 1-phenanthrene carboxylic acid, 1,2,3,4,4a,9, 10,10a-octahydro 1, 4a dimethyl-7-(1 methyl ethyl)-, methyl ester	X					X
36. Pentacosane	X			X		X
37. 3 hydroxy 4-isopropyl 5,10 dimethyl decalone-1	X					
38. Hexacosane	X			X		X
39. Heptacosane	X			X		X
40. Di(2-ethylhexyl)phthalate					X	X
41. Octacosane	X					
42. Unidentified	X					X

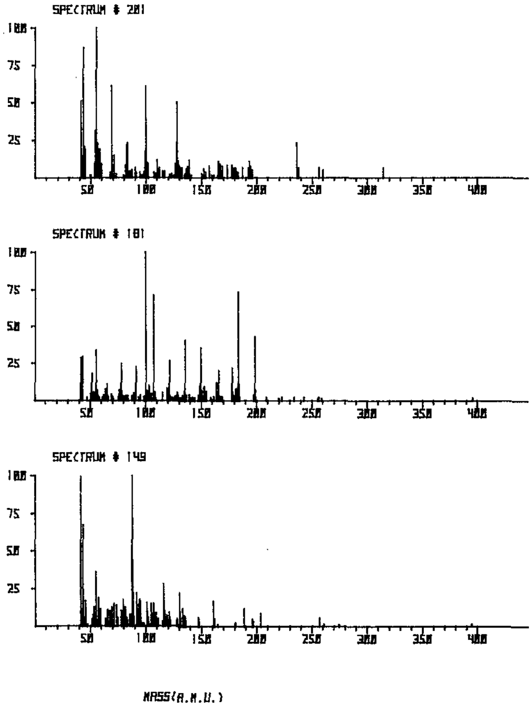

FIGURE 6 Mass spectra of some unidentified components of samples VI to XII. Spectra 201, 181 and 149 refers to listings 26, 15 and 4, respectively, of Table III.

phenols, a number of which were found in the Trinidad waters, were also major components of samples analyzed by Jungclaus[11] and Tomson.[8] The origin of these compounds, in both cases, appeared to be industrial waste water. The influent water to the infiltration system studied by Tomson was actually sewage from an activated sludge plant, while Jungclaus directly sampled the waste water from a chemical-manufacturing plant in addition to the plant's receiving water. Several industrial applications of phenols are documented; 2,6 di-tert-butyl-4-methyl phenol is a known antioxidant[10] while p-nonyl phenol, usually in the form of a technical-grade mixture of isomers, is used in the preparation of lubricating oil additives, resins, plasticizers and surface-active agents.[20] Several alkyl naphthalenes were found in waters examined by Tomson and Jungclaus[10, 11] but

1,6 dimethyl-4-isopropyl napthalene, which was present in most of the samples analyzed in our study was not reported. Burnham did not identify the specific alkyl naphthalenes found in well waters.[1] Alkyl naphthalenes reported by Jungclaus were components of naphthenic oil used to extend and soften rubber formulations for tire manufacture.[10] Benzothiazole, which was identified in six of our samples, was found to be a major component of the waste waters of the tire-manufacturing facility[10] and was also present in the effluent water from a chemical-manufacturing plant.[11] It is used in the tire-manufacturing industry as a vulcanization accelerator. The compound α-terpineol was identified in waste waters samples by Tomson and in Kraft paper mill waste water by Keith.[9] It is known to be used in the manufacture of perfumes and in the denaturing of fats for soap manufacture.[20] Yashuhara reported 2 ethyl-1-hexanol in the waters of the Hayashida River. This compound is used in industry for mercerizing textiles and as a solvent for dyes, resins and various oils.[20] The presence of aliphatic hydrocarbons and alkyl phthalate esters in the Trinidad water samples is not surprising since these two groups of compounds have been found to occur in many water samples. Phthalate esters are used extensively as plasticizers and lubricants and in the manufacture of dyes and various resins. We have found no previous report of compounds 8, 9, 28, 35 and 37 (Table III) in environmental water samples.

The lack of toxicological data on many industrial chemicals, including several found in this study, makes it difficult to assess their relative importance to environmental concerns. Aliphatic hydrocarbons generally pose no danger to humans unless ingested in huge amounts. Most alkyl phenols do not seem to be particularly toxic; they generally have LD_{50} values $\simeq 2500\,\text{mg/kg}$.[11] Similar toxicity data has been reported for α-terpineol and many phthalate esters.[20] Alkyl naphthalenes reportedly show acute and chronic toxic effects at high concentrations.[9] The pesticide carbaryl is rated as "slightly hazardous"; it's LD_{50} value for rats is $\simeq 675\,\text{mg/kg}$, while its LC_{50}, defined as the concentration of toxicant necessary to kill 50% of a species being tested, is 2.0 ppm for fish.[22] It is readily degradable (half-life in soil $\simeq 2$ weeks) and therefore not expected to show significant bioaccumulation. The presence of benzothiazole in these waters is of some concern since its LD_{50} for mice is said to be about 100 mg/kg when administered via intravenous route, indicating fairly high toxicity.

The results of this study show that the river waters upstream of the Caroni/Arena water treatment plant are polluted by organic chemicals. However, the degree of pollution and the possible health and environmental hazard posed by the contaminants cannot be ascertained until results of an extensive quantitative survey are obtained and toxicological information on the effect on human health of low level chronic ingestion of industrial chemicals becomes available. The fact that many of the compounds identified have known industrial applications suggests that factories located upstream of the treatment plant are the most likely source of the pollutants.

A monitoring program employing analytical methodology based on preconcentration of organics on resin columns followed by gas chromatographic analysis with flame-ionization detection is feasible for quantification of the classes of compounds identified in these water systems. GC detection should be supplemented by GC/MS analyses on a periodic basis for the identification of new pollutant species which can be expected to arise as industrial activities expand and diversify.

Acknowledgements

This work was supported by a grant from the International Development Research Centre, Canada. The authors wish to express their appreciation to the personnel of the Caribbean Industrial Research Institute, Trinidad for their contribution to the research program. The assistance of the Water and Sewage Authority, Trinidad is also gratefully acknowledged.

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