PHENOLIC WATER POLLUTANTS IN A MALAYSIAN RIVER BASIN

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Abstract. Phenolic chemicals with their very low taste and odour thresholds, high persistence and toxicity, are of growing concern as water pollutants. The compounds are known to exist in raw water as well as in treated water. The level of phenolic priority pollutants in water within the catchment area of the Linggi River Treatment Plant in Negeri Sembilan, Malaysia, which includes the Linggi river basin, was monitored. The 4-aminoantipyrin colourimetric method was used to determine total phenols whereas capillary column gas chromatography was used to determine the individual compounds. The results show that at most sampling stations, particularly those within the Seremban municipality, the level of phenols was found to exceed the recommended Malaysian standard of 2.0 $\mu g/L^{-1}$ for raw water. This is seen as the direct impact of industrial and urbanization of the area and clearly indicates the unhealthy state of the Linggi river. The results also indicate the need to improve the water quality if the river is going to be used as a source of raw water.

Introduction

Phenols are a class of compounds whose common functional group is the hydroxyl group attached to a benzene ring, which may be a single, isolated benzene ring or a part of a condensed ring structure. Besides hydroxyl, many other functional groups, such as halides and alkyl may also be present in a given phenol. Some phenols have very low taste and odour thresholds in water while others are highly persistent and toxic (Giger and Schaffner, 1981).

Phenols are the cause of growing concern as water pollutants, particularly for the fishing industry and for drinking water supply. Eleven phenols have been included in the list of priority pollutants by the U.S. Environmental Protection Agency (Keith and Telliard, 1979).

The existence of phenol in an aquatic environment can be derived, aside from those occurring naturally, from many sources, namely industrial waste water effluents, municipal sewage, bunker fuel, pesticides and many other materials of petroleum origins (Hunt *et al.*, 1977). Natural phenols are formed in aquatic and terrestrial vegetation and can be released as pollutants by the pulp and paper industry. Certain phenolic acids, namely *m*-hydroxybenzoic acid, *m*-hydroxyphenylacetic acid and *m*-hydroxyphenylpropionic acid, have been isolated from liquid manure (i.e. urine) of domestic animals at an average level of 35.8, 27.4 and 40.0 mg/L, respectively (Kump, 1974). This may represent a significant source of naturally occurring phenolic compounds in view of the rather substantial population of farm animals in many countries.

It is well known that chlorinated phenolic compounds, i.e. the chlorophenols, can also be produced during the chlorination of water supplies (Condie, 1986). It was shown that a mixture of 4-chlorophenol, 2, 4-dichlorophenol and 2, 4, 6-trichlorophenols was

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produced when a naturally occurring organic compound, *p*-hydroxybenzoic acid, was chlorinated (Larson and Rockwell, 1979). Since chlorination is part of the water treatment processes used in Malaysian water treatment plants it is imperative that studies be performed to look at this problem, particularly so when the raw water used is highly polluted. One such place is the Linggi river treatment plant in Negeri Sembilan, Malaysia, which utilises the Linggi river water as the source of raw water.

The Linggi river basin consists of Seremban and nearby town districts. Part of the area, which covers approximately the whole of Seremban town and its outskirts, form the catchment areas for the Linggi river treatment plant which supplies 60% and 100% of the water requirements of Seremban and Port Dickson, respectively.

Two reports submitted to the government of Negeri Sembilan in 1961 (Binnie *et al.*, 1961) and in 1979 (Binnie dan Rakan, 1978) had shown that the Linggi river is highly polluted and, by WHO standards, can be classified as "heavily-polluted requiring extensive treatment". The continuing increase in pollution is caused by the development projects in town and industrial areas within the catchment area.

This study is part of a monitoring and analytical method development program which aims to look at the existing levels of phenols and also the dissolved organics in river water within the catchment areas.

Experimental

Materials

All the organic solvents used were of Merck pro analysi grade and used as received. All other chemicals were of analytical-reagent grade and were used without further purification. Phenols standard (USEPA priority pollutants) and tribromophenol (TBP) gas chromatographic standard were supplied by Supelco Inc. USA.

Sampling

Fifteen sampling stations were identified within the study area as indicated in the map given in Figure 1. It covers the main river, i.e. Linggi river and its tributaries including the Linggi river treatment plant.

Water samples, in two one-litre glass bottles (Schott, West Germany) were taken at each station; each was preserved with 1.0 g of $CuSO_4 \cdot 5H_2O$ and 10 g of H_3PO_4 (IHD - WHO, 1978) and kept inside an ice box. All analyses were performed at the laboratory within 48 hours of sampling during which the samples were kept inside a cool-room (4°C).

Determination of phenols

Two methods of analysis were used in this study, namely the 4-aminoantipyrine (4-AAP) spectrophotometric method for total phenols (Suess, 1982; APHA, 1971), and the gas chromatographic method for individual compounds.

The 4-AAP method, a generally accepted method for the determination of phenols, does not actually give the total phenol concentration because the 4-AAP does not react

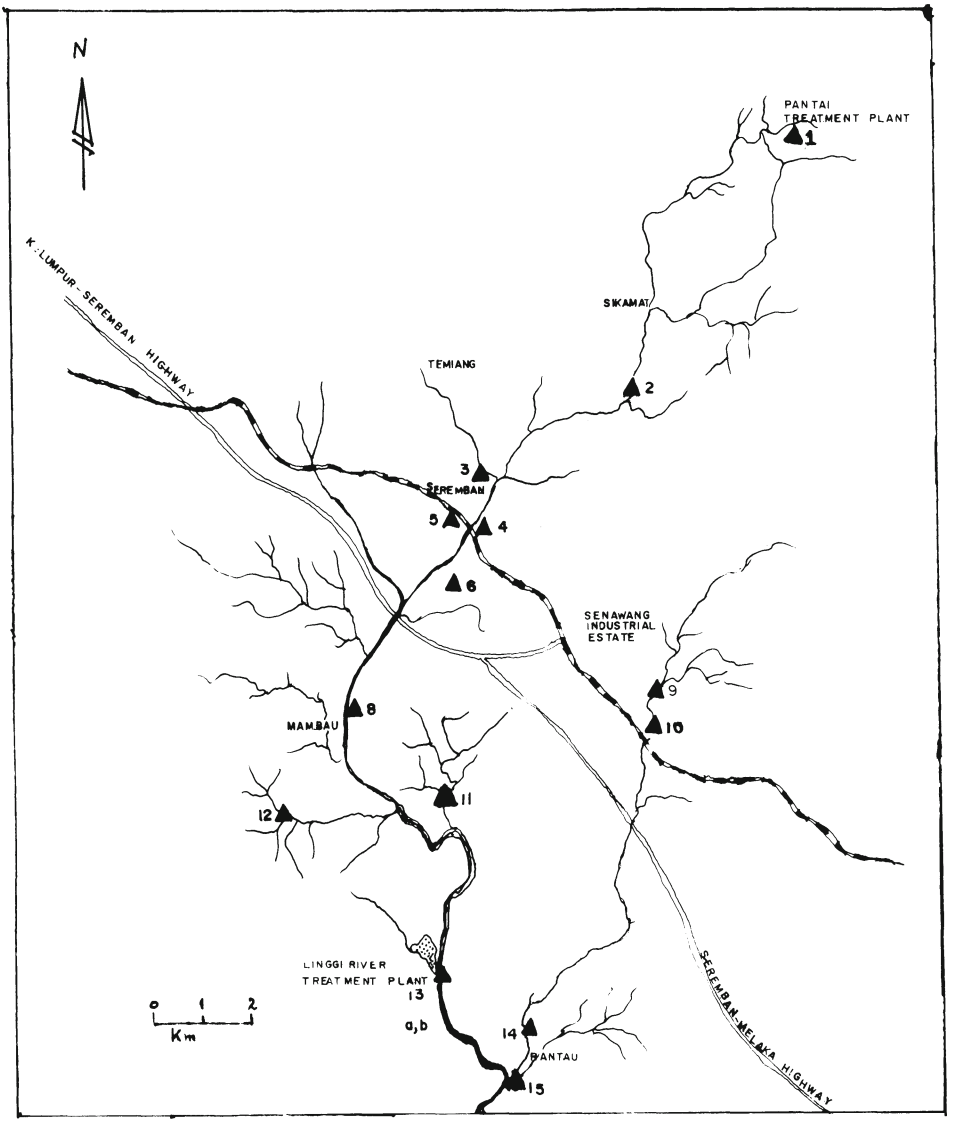

Fig. 1. Map of the Linggi River catchment areas. ▲ indicates the locations of sampling sites.

with many para-substituted phenols. As such the concentration found by this method can be expected to be lower than the actual value.

In the GC method the acidified water samples were distilled and extracted with dichloromethane under acidic conditions. The combined organic phases were concentrated using a Kuderna – Danish evaporator to about 1.0 mL. After adding the internal standard (TBP), the concentrate was then injected into the gas chromatograph. This is a simplified method involving a single extraction under acidic conditions unlike the one suggested by Hunt *et al.* (1977), which involves double extractions under basic and acidic conditions.

GAS CHROMATOGRAPHIC ANALYSIS

An HP 5890 capillary gas chromatograph equipped with a flame ionization detector and HP 3392A integrator was employed. A fused silica 30 m × 0.32 mm I.D. Supelco SPB-5 capillary column was used throughout. The GC parameters employed were: initial temperature 50°C, increased to 220°C at 8°C/min and held there for the next 60 min. This allowed the baseline separations of all the eleven phenols, although phenol and 2-chlorophenol were eluted very close together. Direct on-column injection was employed. The detector temperature was 310°C. An example of a gas chromatogram generated for a mixture of priority pollutant phenols is given in Figure 2.

2, 4, 6-Tribromophenol (TBP) was used as internal standard for quantitative determination.

In addition to the comparison of retention times with standard phenols, an HP 5890 Series II gas chromatograph with mass selective detector 5970B equipped with MS ChemStation was used to assist in the identification of peaks separated by the GC.

Results and Discussion

Table I shows the levels of total phenols at the various stations for the year 1989 at monthly intervals. In the table '0' means that the sample absorbance is lower than the

TABLE I

The levels of total phenols determined at various sampling stations for the year 1989.

Stations	Level of total phenols (4-aminoantipyrine reagent method) (μg/L)											
	Date of sampling (year 1989)											
	19 Jan	14 Feb	07 Mar	06 Apr	17 May	26 June	18 July	16 Aug	13 Sep	18 Oct	15 Nov	20 Dec
1	0	0.6	0.5	0.9	0.7	0	0.8	4.0	0.5	0	0	0.6
2	9.4	6.5	7.9	11.1	0.5	6.3	8.1	5.1	4.5	1.0	2.0	1.8
3	4.4	10.0	6.3	11.1	8.9	9.0	0.9	6.7	15.3	8.3	1.4	9.6
4	4.7	5.2	15.5	8.5	6.1	53.6	30.4	9.3	23.2	26.2	9.3	21.3
5	23.4	8.6	8.0	4.7	7.4	3.8	6.6	8.8	1.5	10.4	34.9	11.0
6	11.2	9.2	30.0	4.1	3.1	19.5	37.6	12.0	2.4	18.6	37.3	13.2
7	9.5	6.7	12.6	1.3	2.1	10.4	8.6	20.5	22.0	3.5	35.7	23.3
8	10.2	3.2	9.0	8.5	3.5	3.8	1.0	8.4	14.0	4.8	36.1	4.6
9	8.4	6.3	8.8	27.7	7.4	6.9	1.8	5.1	2.4	3.8	2.0	1.5
10	26.9	12.1	5.5	29.6	0.5	4.7	3.6	13.9	4.3	12.0	26.1	2.8
11	9.2	5.4	4.4	3.5	4.3	1.6	6.2	2.3	6.4	18.1	2.6	1.8
12	6.8	9.2	36.4	3.8	2.6	0.8	4.4	1.8	8.4	9.6	2.0	1.0
13a	3.1	8.5	5.2	12.3	5.8	4.1	2.9	0.7	2.6	3.3	1.1	0.8
13b	0.6	0.6	0.6	3.1	0	0	0.6	0.5	0	0.7	0.6	0
14	20.4	33.1	41.4	17.5	0.6	8.2	8.4	11.1	9.8	30.0	2.7	3.5
15	10.7	8.5	16.3	7.3	6.8	1.0	9.8	6.4	11.4	18.1	12.1	23.6

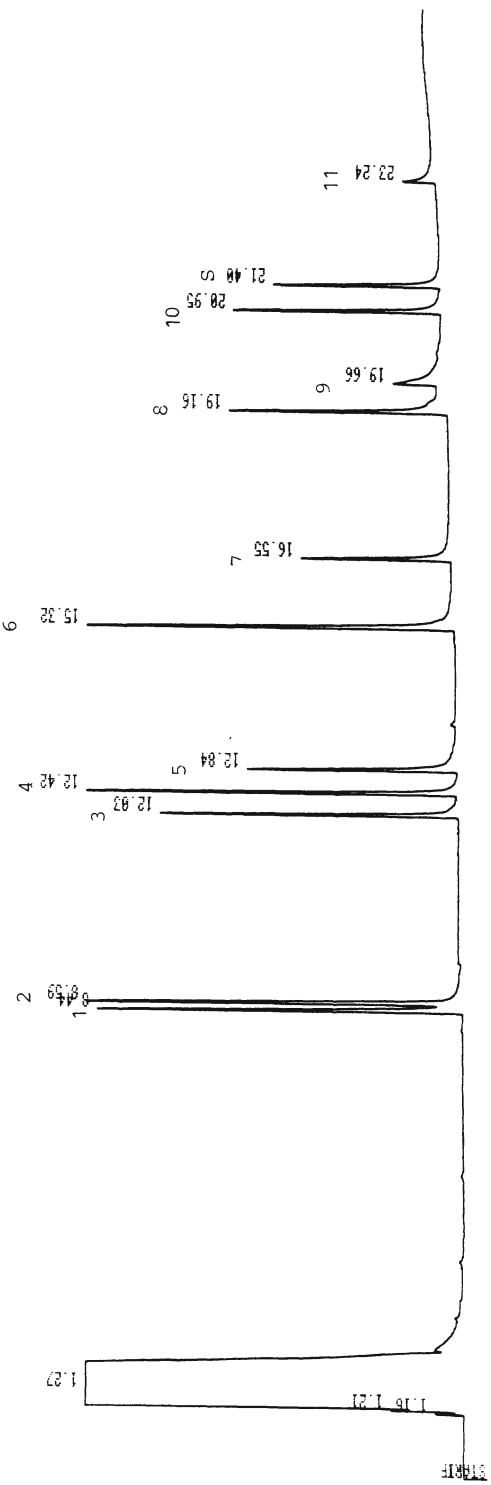

Fig. 2. Gas chromatogram of phenols priority pollutants. (1) Phenol, (2) 2-chlorophenol, (3) 2-nitrophenol, (4) 2, 4-dimethylphenol, (5) 2, 4-dichlorophenol, (6) 4-chloro-3-methylphenol, (7) 2, 4, 6-trichlorophenol, (8) 2, 4-dinitrophenol, (9) 4-nitrophenol, (10) 2-methyl-4, 6-dinitrophenol, (11) pentachlorophenol and (S) internal standard (2, 4, 6-tribromophenol).

blank absorbance indicating the absence or the very low concentration of phenols (i.e. in the order of less than 0.5 $\mu g\ L^{-1}$). Station 1, at Pantai Treatment Plant, is selected as the reference point due to its undisturbed and clean river. Stations 13a and 13b are at Linggi river treatment plant, where 13a is the intake raw water (Linggi river water) and 13b is the treated water. All other stations are along the main river, Linggi river or its tributaries. Stations numbers 3 to 7 are directly in the Seremban town area while stations 9 and 10 are near the Senawang Industrial Estate. The main sources of pollution in the study areas have been identified as wastewaters or effluents from rubber processing factories, timber sawmills, motor and battery workshops, engineering workshops, pig farming and other agricultural uses and squatters' areas.

The Malaysian Ministry of Health has recommended the required maximum level of phenols in raw water to be 2 $\mu g\ L^{-1}$ and that of treated water to be 1 $\mu g\ L^{-1}$ (Malaysian Ministry of Health, 1987). Except for station 1, which is the cleanest station, the level of phenols detected at all stations monitored on most occasions far exceeded the recommended value. The worst stations seemed to be stations 4, 5, 6, 7, 8, 10 and 14. These stations are located either directly in Seremban town area or near the pollution sources e.g. rubber factory (station 6), motor and battery workshops (stations 7 and 8), agricultural and squatters' areas (stations 10 and 14). It is possible that the pollution emitted contributed to the higher level of phenols detected.

It is observed that the levels of phenol fluctuate throughout the year depending on the month of sampling or the condition of the river. An example of this variation can be seen in Figure 3 for stations number 4 to 7. The higher value was normally observed when the river flow was significantly low i.e. during the dry spell as encountered during the March, June and November sampling trips.

Although the levels of phenols in river water in most upstream stations are higher, (as high as 53.6 $\mu g\ L^{-1}$ as detected for station 4) by the time the water reaches the intake point (i.e. station 13a) the level is significantly lower, with the lowest value detected for December at 0.8 $\mu g\ L^{-1}$. This can be attributed to a dilution effect and perhaps also to microbial degradation. However, the mean concentration at this station is significantly higher than the recommended value of 2.0 $\mu g\ L^{-1}$.

The water treatment process carried out at the Linggi River Treatment Plant involves the use of activated carbon in addition to the normal flocculation and sedimention processes. This study shows that the treatment process used was effective in reducing the level of phenols to less than 1.0 $\mu g\ L^{-1}$. Only on a single occasion was the treated water found to be in excess of the recommended level (i.e. 3.1 $\mu g\ L^{-1}$), as indicated by the April value at station 13b (Table I). This may be due to the very high level of phenolic pollutants in the raw water for the particular month (i.e. 12.3 $\mu g\ L^{-1}$). This is in line with the general belief that the activated carbon treatment is the most effective barrier against organic micropollutants (Van Hoof, 1986).

The gas chromatographic analysis of water samples from some selected stations reveals the presence of certain phenolic priority pollutants.

Table II lists the type and amount of phenolic components identified in water samples from station 7 for the months of August, September, October and November. Only five

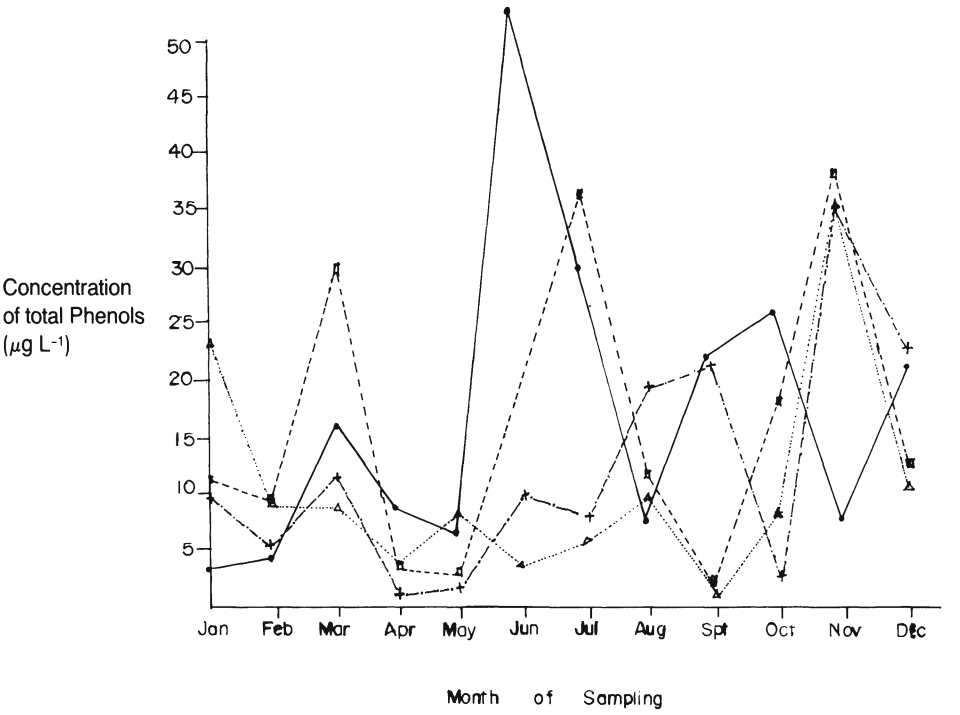

Fig. 3. The monthly variations in the levels of phenols at stations 4, 5, 6 and 7. ● station 4, △ station 5, □ station 6, + station 7.

TABLE II

The amount (in μg/L) of phenols priority pollutants detected at Station 7.

Type of phenolic component	Retention time / min	Date of Sampling 16 Aug.	13 Sept.	18 Oct.	15 Nov.
Phenol	8.44	–	–	–	–
2-Chlorophenol	8.59	–	–	–	–
2-Nitrophenol	12.03	–	–	–	–
2, 4-Dimethylphenol	12.42	–	–	–	9.2
2, 4-Dichlorophenol	12.84	–	–	–	–
4-Chloro-3-metholphenol	15.32	0.3	–	–	–
2, 4, 6-Trichlorophenol	16.55	0.2	2.6	3.7	–
2, 4-Dinitrophenol	19.16	–	–	–	–
4-Nitrophenol	19.66	0.2	–	–	35.1
2-Methyl-4, 6-dinitrophenol	20.95	–	–	–	–
Pentachlorophenol	23.24	25.8	20.4	13.6	–
Total phenols		26.5	23.0	17.3	44.3

components, namely 2, 4-dimethylphenol, 4-chloro-3-methylphenol, 2, 4, 6-trichlorophenol, 4-nitrophenol, and pentachlophenol were detected in the samples. The absence of other phenolic components may not necessarily indicate that they are not present in the water, but it is more likely that the method used to extract them is not efficient enough. The concentration technique using a Kuderna–Danish as used here may contribute to the loss of low-boiling components, particularly phenol and 2-chlorophenol.

However, if the total amount of phenols detected by the GC (Table II) is compared with the value of total phenols determined by means of the 4-AAP method (Table I) for the same samples, the two results agree quite well. Similar agreements were also reported by Folke and Lund (1983) and Kopecni *et al.* (1989). In addition to the expected lower value of the 4-AAP method as compared with the GC method, the slightly lower value of the 4-aminoantipyrine reagent method can also be ascribed to incomplete steam distillation of nitrophenols (Nortwitz *et al.*, 1987).

Conclusion

The level of phenolic water pollutants in the catchment area of Linggi river treatment plant were generally found to be very much higher than the maximum recommended level of 2.0 $\mu g\ L^{-1}$. This can be attributed to the present unhealthy state of the river basin. Of all the eleven phenols priority pollutants only five components were identified namely 2, 4-dimethylphenol, 4-chloro-3-methylphenol, 2, 4, 6-trichlorophenol, 4-nitrophenol and penta-chlorophenol. However the extensive treatment processes carried out at the treatment plant at present are very effective, to the extent that the level of phenol in the treated water was within the required value of 1.0 $\mu g\ L^{-1}$.

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References

APHA: 1971, *Standard Methods for the Examination of Water and Wastewater*, 13th Edition, New York, pp. 508–510.

Binnie, Deacon and Gourley: 1961, *Report on Proposed Water Supply to Seremban and Port Dickson – Linggi Scheme.*

Binnie dan Rakan: 1979, *Report on Development Plan for Seremban and Port Dickson Water Supply.*

Condie, L. W.: 1986, 'Toxicological problems associated with chlorine dioxide', *J. Am. Water Works Assoc.* **78**, 73–78.

Folke, J. and Lund, U.: 1983, 'Occurrence of low- and high-chlorinated phenols in municipal sewage before and after passing through biological treatment plant', *J. Chromatogr.* **279**, 189–198.

Geiger, W. and Schaffuer, C.: 1981, 'Determination of phenolic water pollutants by glass capillary gas chromatography' in Keith, L. H. (ed.), *The Identification and Analysis of Organic Pollutants in Water Vol. 1*, Ann Arbor Science Publishers, Michigan, Chapter 8, pp. 141–154.

Hunt, G. T., Clement, W. H. and Faust, S. D.: 1977, 'An evaluation of technique for the recovery and identification of trace quantities of phenolic compounds in natural waters' in Ewing, G. W. (ed.), *Environmental Analysis*, Academic Press, pp. 57–78.

IHD - WHO Working Group on Quality of Water: 1978, *Water Quality Survey*, Unesco/WHO.

Keith, L. H. and Telliard, W. A.: 1979, 'Priority pollutants I: A perspective view', *Environ. Sci. Technol.* **13**, 416–423.

Kopecni, M. M., Tarana, M. V., Cupic, S. D. and Comor, J. J.: 1989, 'Gas chromatographic determination of phenols in waste water – oil emulsions', *J. Chromatogr.* **462**, 392–397.

Larson, R. A. and Rockwell, A. L.: 1979, 'Chloroform and chlorophenol production by decarboxylation of natural acids during aqueous chlorination', *Environ. Sci. Technol.* **13**, 325–329.

Malaysia Ministry of Health: 1987, *National Guidelines for Drinking Water Quality*.

Norwizt, G., Nataro, N. and Keliher, P. N.: 1987, 'Steam distillation of phenolic compounds in the presence of a large amount of sodium chloride', *Nicrochem. J.*, **35**(2), 240–243.

Rump, O.: 1974, 'Phenolic acids as indicators of pollution with liquid manure. A method for their detection; *Water Res.* **8**, 889–894.

Suess, M. J.: 1982, *Examination of Water for Pollution Control*, Vol. 2, Pergamon Press, Oxford, Chapter 4, pp. 451–470.

Van Hoof, F.: 1986, 'Formation and removal of organic micropollutants in drinking water treatment', in Bjorseth, A. and Angeletti, G. (eds.), *Organic Micropollutants in the Aquatic Environment*, D. Reidel Pub. Co., Dordrecht, 1986, pp. 364–372.