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Inventory of heavy metals and organic micropollutants in an urban water catchment drainage basin

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Abstract

The Linggi River drainage basin in Negeri Sembilan Malaysia is the major source of potable water for the townships of Seremban and Port Dickson. Water quality is threatened by industrial and commercial development taking place in the basin. This study investigated the concentrations and distribution of organic micro-pollutants and heavy metals within the catchment. Arsenic, copper, cadmium, lead, mercury and zinc were determined in water and sediment samples. All heavy metal concentrations were increased down the basin; arsenic and copper concentration in particular were elevated probably due respectively to flow in of arsenical herbicides in rubber and oil palm plantations and copper sulphate and an additive in pig food.

Total phenol concentration also increased considerably within the catchment as a result of urbanisation. Five priority phenolic pollutants (2,4-dimethylphenol; 4-chloro-3-methylphenol; 2,4,6-trichlorophenol; 4-introphenol; pentachlorophenol) were found.

Introduction

Organic micro-pollutants such as phenols trihalomethane and hydrocarbons have been given serious attention as pertinent water pollutants in many countries. In the United States, eleven phenols have been included in the list of priority pollutants by the USEPA (Keith & Telliard, 1979). Some phenols have very low taste and odour thresholds in drinking water while others are highly persistent and toxic (Giger & Schaffner, 1981). The presence of phenols in an aquatic environment can be derived from many sources such as industrial waste water effluents, municipal sewage, bunker fuel, and pesticides (Hunt *et al.*, 1977).

Certain phenolic acids such as m-hydroxybenzoic acid, m-hydroxyphenylacetic acid and m-hydroxyphenylpropionic acid have been isolated from liquid manure of domestic animals by Rump (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. Chlorinated phenolic compounds can be produced during the chlorination process of water supplies (Condie, 1986). It was also shown that a mixture of 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenols was produced when a naturally occurring organic compound, p-hydroxybenzoic acid, was chlorinated (Larson & Rockwell, 1979).

Since chlorination is part of water treatment processes in all water treatment plants in Malaysia it is pertinent to study the levels of phenolic compounds in domestic water supplies. It is particularly important for the Linggi river as a previous report showed that the water is highly polluted for domestic water supply when compared to WHO standards (Binnie *et al.*, 1979).

The Linggi river drainage basin is the major source of drinking water for the townships of Seremban (60%) and Port Dickson (100%) serving a total population of 1 million. The quality of this resource is threatened by rapid development taking place in the basin. The Linggi River, the main tributary, passes through the Seremban town while the treatment plant is located down stream.

The aim of this study was to investigate the concentrations and distribution of organic micropollutants and some heavy metals. Instrumental neutron activation analysis was used for the determination of 11 trace elements in sediments, while atomic absorption spectrometry was used for the analysis of lead, cadmium, copper and zinc in the soluble fraction of river water samples.

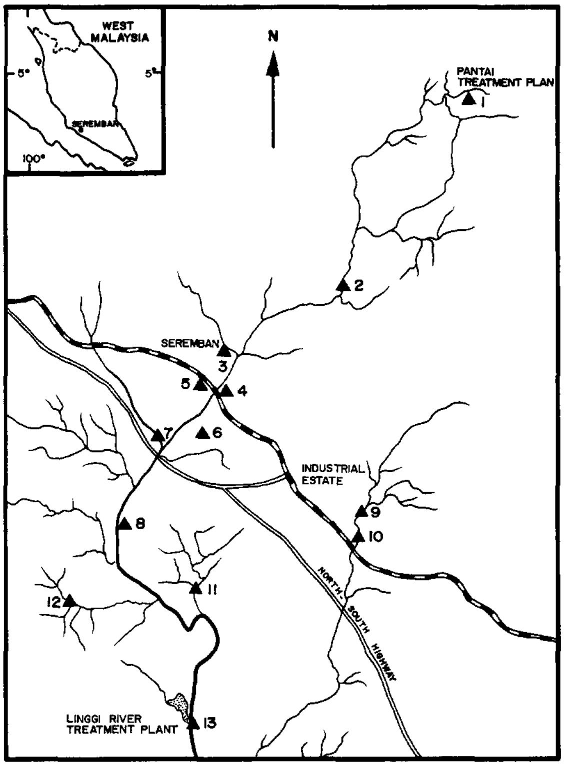

Fig. 1. The Linggi River basin.

Experimental details

Study sites

Thirteen sampling stations along the Linggi river and its tributaries were identified within the study area (Fig. 1). The drainage basin covers an area of about 1400 km^2. About 15% of the area is still under forest while the rest has been developed for agriculture, urban and mining uses. The average annual rainfall is 2500 mm. Two water treatment plants are situated in the basin, one at station 1 and the other at station 13.

Sample collection and preparation

Samples were collected from each sampling station once a month from January to December 1989. Water samples for organic micropollutants analysis, were collected in two one litre glass bottles (Schott, West Germany) from each station. Each sample was preserved with 1.0 g $CuSO_4$ $5H_2O$ and 10 g H_3PO_4 (IHD-WHO, 1978) and was kept inside an ice box. All analyses were carried out at the laboratory within 48 hours of sampling.

Water samples for heavy metal analysis, were collected in the middle of the river, at a depth of about 50 cm, by using precleaned 2 litre polyethylene bottles. Millipore type HA membrane filters (0.45 μm diam) were used for filtration to separate suspended particulate matter. The filters were washed with dilute Analar nitric acid and demineralised water before filtration to remove any unbound trace elements. Filtration was under pressure using a Sartorius filtration unit. About one litre of the water sample was filtered, and the filtrate was then acidified with dilute nitric acid for storage awaiting analysis.

As some parts of the river were less than 1 m deep it was possible to wade in the river to collect the surface sediment samples. The samples were collected using a plastic scoop, by carefully scraping the top 2 cm directly into precleaned polyethylene containers. At sampling stations with high water levels, sediment samples were collected using a Wildco gravity-type, messenger-activated core sampler (Wildlife Supply Company, Michigan). The sampler was lowered from the bridge across the river. Only the top 2 cm of the core was analysed. Each sediment samples was air dried in a clean hood for several days. After drying, it was disaggregated in a porcelain mortar and sieved through nylon meshes. The fraction >630 μm was discarded. The rest was sieved again and the fraction <200 μm was used. Before analysis, a separate subsample was dried for 2 hours at 105 °C for moisture content determination.

Analysis details

All the organic solvents used were Merck proanalysis grade, used as received. All other chemicals were of analytical reagent grade and were used without further purification. Phenol standards (USEPA priority pollutants) and tribromophenol (TBP) gas chromatographic standard were supplied by Supelco Inc. USA. Standard reference material, lake sediment SL-1, issued by the International Atomic Energy Agency, Vienna, was used as the primary standard for the determination of heavy metals in sediment samples.

Organic micro-pollutants

Total phenols were determined by the 4-aminoantipyrine spectrophotometric method described by Suess (1982). The individual phenols were determined using the procedure developed by Hunt *et al.* (1977). The acidified water samples were distilled and extracted under acidic condition with dichloromethane. The combined organic phase was evaporated to about 1.0 ml. After adding internal standard, the organic phase was then injected into the gas chromatograph.

An HP 5890 capillary gas chromatograph equipped with a flame ionization detector and HP 3392A integrator was employed. A fused silica 30 m x 0.32 mm (diam.) Supelco SPB-5 capillary column was used throughout. The GC parameters employed were initial temperature 50 °C, increased at 8 °C $\min^{-1}$ to 220 °C and maintained at that temperature for 60 min. This allowed the baseline separations of all the eleven phenols. 2,4,6-tribromophenol (TBP) was used as internal standard for quantitative determination.

In addition to the comparison of retention times with phenols standard, an HP 5890 Series II Gas Chromatograph with Mass Selective Detector 5970B equipped with MS ChemStation was used to assist in the peak identifications.

Heavy metals

All water samples were analysed using a Varian Techtron AA-5 Atomic Absorption Spectrophotometer. Lead, copper, cadmium and zinc were determined by the slotted tube atomic trap technique as described by Watling (1977). Mercury was determined by the cold vapour generation method described by Hatch & Ott (1968).

Sediment

About 100 mg of each sediment sample and standard reference material were packed in polyethylene vials for neutron activation analysis as described previously (Sarmani, 1989).

Results and discussion

Table 1 shows the range and mean concentration levels of some organic micropollutants such as dissolved organic, total phenols and aromatic hydrocarbons for the year 1989. Analysis of the water samples revealed the presence of a number of phenolic priority pollutants, such as 2,4-dimethylphenol, 4-chloro-3-methylphenol, 2,4,6-trichlorophenol, 4-nitrophenol and pentachlopehnol. Station 1, at Pantai Treatment Plant, was selected as the reference point due to its upstream location (Fig. 1). All other stations are located

Table 1. Concentration of micropollutants in water from the Linggi River (see Fig. 1 for location).

Station	Dissolved organics (mg l^{-1})		Total phenols ($\mu g\ l^{-1}$)		Aromatic hydrocarbons (mg l^{-1})	
	Range	Mean	Range	Mean	Range	Mean
1	0.1–1.1	0.61	0.5–4.0	1.07	0.1–0.6	0.36
2	0.6–3.5	2.10	0.5–11.1	5.35	0.0–1.2	0.56
3	0.3–2.6	1.68	0.9–15.3	7.66	0.1–0.8	0.50
4	1.7–9.6	5.17	4.7–53.6	17.88	0.0–1.6	0.76
5	0.6–4.3	1.92	1.5–34.9	10.85	0.0–0.9	0.30
6	0.9–8.1	4.19	2.4–37.3	16.50	0.0–1.8	0.87
7	0.3–5.1	2.07	1.3–35.7	13.00	0.1–1.4	0.50
8	0.5–3.9	1.88	1.0–36.1	8.93	0.1–1.0	0.47
9	0.1–4.9	1.10	1.5–27.7	6.84	0.2–1.8	0.41
10	0.9–5.1	2.48	0.5–29.6	11.80	0.0–1.4	0.63
11	0.5–2.5	1.28	1.6–18.1	5.48	0.1–1.1	0.51
12	0.5–3.4	1.54	0.8–36.4	7.23	0.0–0.9	0.29
13	1.0–4.3	2.21	0.7–12.3	4.20	0.0–1.3	0.64

along the Linggi river or its tributaries. Stations 3 to 7 are situated directly in the Seremban town area, while the stations 9 and 10 are within the Senawang Industrial Estate zone. The likely main sources of pollution in the study areas have been identified as wastewaters or effluents from rubber processing factories, timber saw mills, engineering workshops, pig farming and other agricultural uses, and domestic wastes. The Linggi treatment plant at station 13 receives water containing a high load of pollutants from these sources.

The recommended maximum level of phenols in raw water in Malaysia has been set at 2 $\mu g\ l^{-1}$ and for the treated water at 1 $\mu g\ l^{-1}$ (Malaysia, 1987). Except for station 1, the level of phenols detected at all other stations monitored far exceeded the recommended value on most occasions. The worst seemed to be stations 4, 5, 6, 7, and 10, which are located within the Seremban municipality. It was observed that the levels of phenol fluctuate throughout the year depending on the month of sampling and the condition of the river. The higher values were normally observed when the river flow was low during the dry spelt in March, June and November.

Table 2 shows the range and mean concentrations of lead, cadmium, copper and zinc in the river water samples over the twelve month sampling period. The Linggi river water contained approximately higher metal concentrations six times than in the Langat river. This is not surprising as the Linggi river basin is heavily urbanised. Of interest are the elevated levels of copper in the river water, probably caused by pig farming in the basin. Copper is normally added to the animal feed to control certain diseases.

The water treatment process carried out at the Linggi River Treatment Plant involving 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 mean level of phenols to less than 1.0 $\mu g\ l^{-1}$. This was in line with the general agreement that the activated carbon treatment is the most effective barrier against organic micropollutants (Van Hoof, 1986). Table 3 shows the general water quality improvement of the treated water as compared to the raw water. The organic micropollutant levels in the treated water were within the recommended drinking water standard. However, the mean levels of cadmium and lead were three times higher than the recommended standard. This indicated that the treatment process is not efficient enough to reduce the heavy metal concentrations to the acceptable limits.

The range, means and standard deviations of all elements analysed in the sediment samples are given in Table 4. These data give some indication

Table 2. Concentration of heavy metals in water from the Linggi River (see Fig. 1 for location).

Station	Lead (mg l^{-1})		Cadmium (µg l^{-1})		Copper (mg l^{-1})		Zinc (mg l^{-1})	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
1	0.01–0.38	0.23	2.0–22	12	0.01–0.73	0.17	0.12–0.69	0.30
2	0.01–0.37	0.19	0.4–27	9.9	0.01–0.88	0.19	0.18–2.13	0.66
3	0.12–0.65	0.32	0.1–42	15	0.11–0.92	0.35	0.01–0.81	0.54
4	0.01–0.48	0.27	1.0–46	17	0.02–0.26	0.13	0.01–1.68	0.62
5	0.02–1.32	0.52	2.0–46	18	0.04–0.53	0.24	0.01–1.88	0.68
6	0.02–0.65	0.29	4.0–35	20	0.07–0.31	0.20	0.04–2.16	0.76
7	0.02–0.60	0.34	11–52	22	0.01–0.41	0.18	0.08–2.63	1.24
8	0.07–0.32	0.23	4.6–55	20	0.02–0.30	0.12	0.08–1.96	0.68
9	0.06–0.45	0.22	2.2–32	13	0.06–0.92	0.25	0.05–2.17	0.84
10	0.07–0.64	0.22	5.8–49	22	0.02–0.84	0.18	0.03–2.11	0.87
11	0.16–0.42	0.28	4.0–27	17	0.01–0.61	0.20	0.11–2.30	1.22
12	0.06–0.53	0.22	4.9–32	24	0.01–0.31	0.11	0.02–2.73	0.77
13	0.11–0.53	0.25	3.7–52	20	0.02–0.75	0.19	0.07–2.23	0.79

Table 3. Improvements in the water quality of Lingii River water after water treatment.

Parameter	Raw water		Treated water	
	Range	Mean	Range	Mean
Micro-organics				
Dissolved organic (mg l^{-1})	1.0 –4.3	2.21	0.7 –3.3	1.39
Total phenols (µg l^{-1})	0.7 –12.3	4.20	0.0 –3.1	0.66
Aromatic hydrocarbon (mg l$^{-1)}$	0.1 –1.3	0.64	0.0 –1.8	0.43
Heavy metal				
Cd (µg l^{-1})	12–52	24	3.7 –56	15
Cu (mg l^{-1})	0.04–0.75	0.24	0.02–0.23	0.1
Pb (mg l^{-1})	0.11–0.53	0.28	0.04–0.35	0.1
Zn (mg l^{-1})	0.07–2.05	0.84	0.07–2.23	0.7

Table 4. Heavy metal concentrations in sediments (mg kg^{-1}) from the Linggi River.

Element	Range	Mean	Standard deviation
As	5.2–82.5	40.6	22.2
Ce	56.1–167	99.3	35.1
Co	23.0–0.147	58.8	35.5
Cr	10.1–129	66.2	39.1
Cs	8.5–49.4	19.4	10.9
Eu	0.2–1.6	0.5	0.3
La	13.4–36.5	21.8	6.8
Sb	0.4–4.3	2.2	1.2
Sc	4.1–25.6	13.3	5.2
Th	17–59	32	12
Zn	80–253	150	57

of the average values in the stretch of river surveyed, rather than for each sampling station. The levels of arsenic in most of the sediment samples were elevated; arsenical herbicide is widely used in the rubber and oil palm plantations within the river basin. About 72% of the drainage area is used for agriculture. The arsenic residue may have found its way into the river system through surface run off.

Conclusions

The total level of phenolic water pollutants in the catchment area was 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. Only five components were identified, namely 2,4-dimethylphenol, 4-chloro-3-methylphenol, 3,4,6-trichlorophenol, 4-nitrophenol and penta chlorophenol. The extensive treatment processes carried out at the treatment plant at present is very effective in reducing the levels of phenol in the treated water to less than 1.0 $\mu g\,l^{-1}$. However, the process is not efficient enough to reduce the levels of heavy metals to the accepted standards. The source of copper pollution was from pig farming activities in the basin, where copper sulphate is used as a food additive. The high arsenic levels in the sediments was caused by extensive use of arsenical herbicide in the rubber and oil palm plantations in the study area.

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