

ORGANIC MICROPOLLUTION INDICES OF EFFLUENTS AND RENOVATED WATERS

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Abstract—Solvent-extractable organics (SEO), representing organic micropollutants, were studied in secondary and tertiary effluents using solvents of different polarity.

Characterization was effected by column fractionation (including adsorption and elution with solvents of ascending polarity) and by gas-chromatographic fingerprinting.

Highest recoveries of SEO were obtained with benzene followed by chloroform, and with diethyl ether as a single solvent.

In secondary effluents the polar fraction accounted for about 45% and the non-polar for 32%, the remaining being of intermediate polarity. Lime treatment and detention in after-lime polishing ponds removed, respectively, about 37 and 68% of the total SEO, 63 and 75% of the (non-polar) pentane fraction, 91 and 96% of the (medium-polarity) dichloromethane fraction, and 53 and 64% of the (polar) methanol fraction.

Gas chromatographic fingerprints were similar for secondary effluents with different sampling periods.

Removal of the total ECD-responding organics in the overall treatment process was about 80%, (similar to the dichloromethane-fraction removal) while that of the FID-responding compounds was about 69%—very close to the total SEO removal.

INTRODUCTION

Solvent-extractable organics in secondary and advanced-treatment effluents derive mostly from the raw wastewater; part of them may be a product of microbial activity and chemical reactions in the treatment processes. As a group, they are characterized by their complexity and by the small concentrations of individual components.

The most important feature of this group is the fact that it comprises the principal objectionable organics—the toxicants (such as synthetic organic chemicals) and the odorants, which are of major concern in use of renovated wastewater and in water quality control; these components are often referred to as "organic micropollutants" and are the main factor in appraising the organic quality of renovated water and effluents.

The characterization methods developed and utilized in this study ranged from determination of total extractables to more specific characterization. They include:

gravimetric determination of total solvent-extractables;

gravimetric determination of extractables in solvents of various polarities;

fractionation of extractables by column chromatography followed by solvent elution in ascending polarity;

gas-chromatographic fingerprinting of specific solvent extracts.

Tracking of the total solvent-extractable content in successive treatment processes provides a simple and

rapid measure of their efficiency in removal of gross organic micropollution. While gravimetric determination of solvent-extractable organics offers a presumptive index of the potentially toxic constituents, fractionation of the group adds to the general information on its composition. In this study the solvent-extractable organics were subdivided into so-called aliphatic, aromatic and polar oxy-compound fractions, each of them associated with a specific degree of detrimental health and environmental effects.

A further, more specific, characterization step consisted in recording the fingerprints of less polar fractions on a gas chromatograph. The assumption was, that gas-chromatographic profile should remain fairly constant in time unless there was a temporary source of pollution which would be recorded as an extra peak or a group of peaks. It also provided a very useful means for tracking the fate of organic compounds through treatment stages without identifying the compounds or groups of compounds represented by individual peaks.

The concentration of organics found by the above methods may serve as an indicator of organic microcontamination and of the toxicological quality of effluents and renovated waters.

EXPERIMENTAL

Samples of secondary- and advanced-treatment effluents of municipal origin were collected from 2 municipal plants:

The Dan Region Sewage Reclamation Plant in Tel-Aviv which comprises stabilization ponds, a lime clarifier and after-lime polishing ponds [see Fig. 1 reproduced from Idelovitch (1978)].

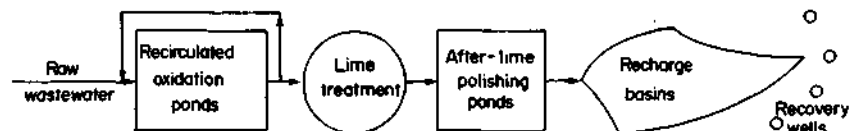


Fig. 1. Dan region wastewater reclamation project, project (DRP)—First Stage schematic flow diagram (Idelovitch, 1978).

The Sewage Purification Plant in Haifa, based on high-rate trickling filters.

Before each determination, the samples were centrifuged for 30 min at 8000 rev/min and filtered through a millipore membrane filter (0.45 μm).

Extraction

The reagent-grade solvents used for extraction included: hexane, benzene, diethyl ether, dichloromethane, chloroform, and a mixture of benzene and chloroform 1:1 v/v. Extraction was initially carried out at pH 2 only, but subsequently the samples were extracted twice—first at pH 2, and then at pH 10—either with the same solvent or with two solvents one after the other (sequential extraction). The pH was adjusted with concentrated hydrochloric acid or a solution of sodium hydroxide.

The diethyl-ether extraction was carried out in a conventional apparatus (Waggott & Saunders, 1976). For the other solvents a cylindrical glass container (Fig. 2) was used provided with 4 internal teflon edgings and equipped with a stirrer passing through a central hole in the glass cover. Occasionally the samples were also extracted in separatory funnels with manual shaking. The effluent samples drawn for extraction ranged from 2 to 10 l, each of them was usually repeated 3 times, the total solvent volume being about 10% of the sample.

The solvent extractables were dried for at least 1 h over anhydrous sodium sulphate, concentrated in a Kuderna Danish evaporator (to 1:1000–5000 for the fractionation series, to 1:200–1000 for the gas-chromatography series), and finally dried in a gentle stream of dry nitrogen for gravimetric procedure.

Fractionation

One millilitre of the concentrate (see above) was transferred to a glass column, 1.0 cm i.d., containing 10 g silica gel (Kieselgel-40, Merck, activated at 275°C for 6 h).

The combined (acidic and basic) ether extractables were eluted with isoctane, benzene, and a chloroform-methanol mixture 1:1. The acidic dichloromethane extractables were correspondingly eluted with pentane, dichloromethane and methanol. The separated fractions were concentrated, dried and weighed.

Gas-chromatography

Two to five microlitres of the concentrate (see above) were chromatographed isothermally at 190°C in a Packard model 417 gas-chromatograph on 15% QF1 + 10% DC200 (1 + 1), Gas chrom Q 110/120; the carrier gas was nitrogen at a flow rate of about 30 ml min⁻¹. Aldrin (0.01 $\mu\text{g ml}^{-1}$) was added to some of the samples just prior to injection. A flame ionization detector (FID) or an electron capture detector (ECD) was used.

RESULTS

The results of the extractions are presented in Figs 3 and 4. It appears, on the strength of the recoveries, that the sequential extraction (benzene followed by chloroform) is the most efficient one, followed by the mixture of benzene and chloroform, which yielded slightly better recoveries than benzene and ether used separately (whose recoveries are quite close). Compared to their chloroform and dichloromethane counterparts (which are also almost identical), the benzene and ether recoveries are about 1.5 times higher for secondary effluents and about twice higher for lime-clarifier and after-lime polishing pond effluents. The poorest recoveries were obtained with hexane.

Figure 3 indicates that the bulk of the effluent organics is of medium polarity, being preferentially extracted with benzene (dielectric constant $\epsilon = 2.3$) and ether ($\epsilon = 4.8$) and only to a very small extent by hexane ($\epsilon = 1.9$). At the same time, the polarity is not the only factor affecting the recoveries, as no difference was found between chloroform ($\epsilon = 4.8$) and dichloromethane ($\epsilon = 9.1$), whereas the ether recoveries were significantly higher.

Except for the hexane extractables, whose concentration, (about 1.0 mg l⁻¹) approaches the value

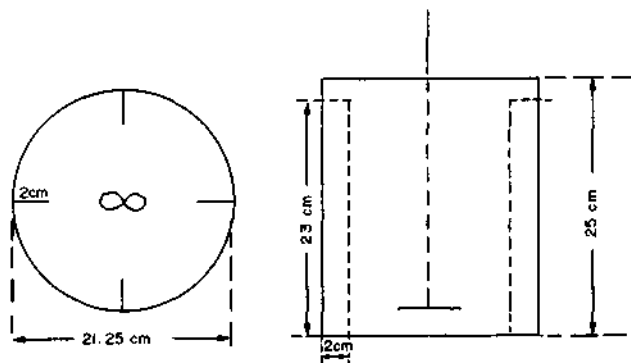


Fig. 2. Liquid-liquid extractor.

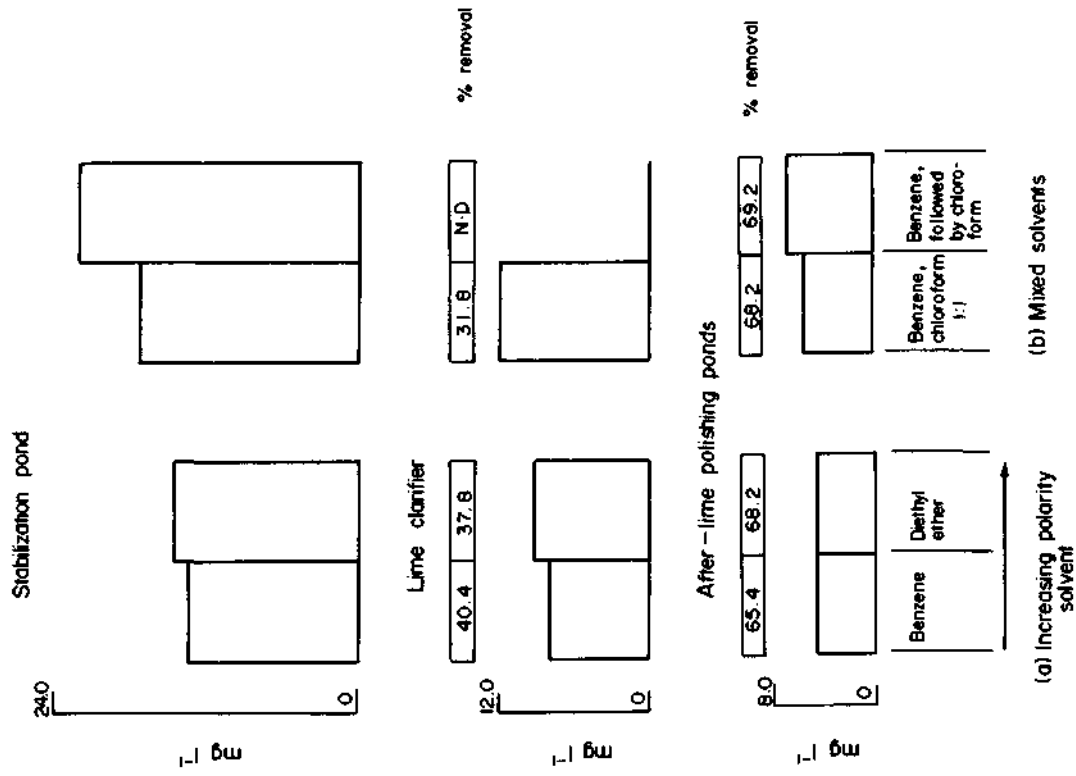


Fig. 3. Concentration of acidic pH solvent extractables in effluents of successive treatment stages (DRP).

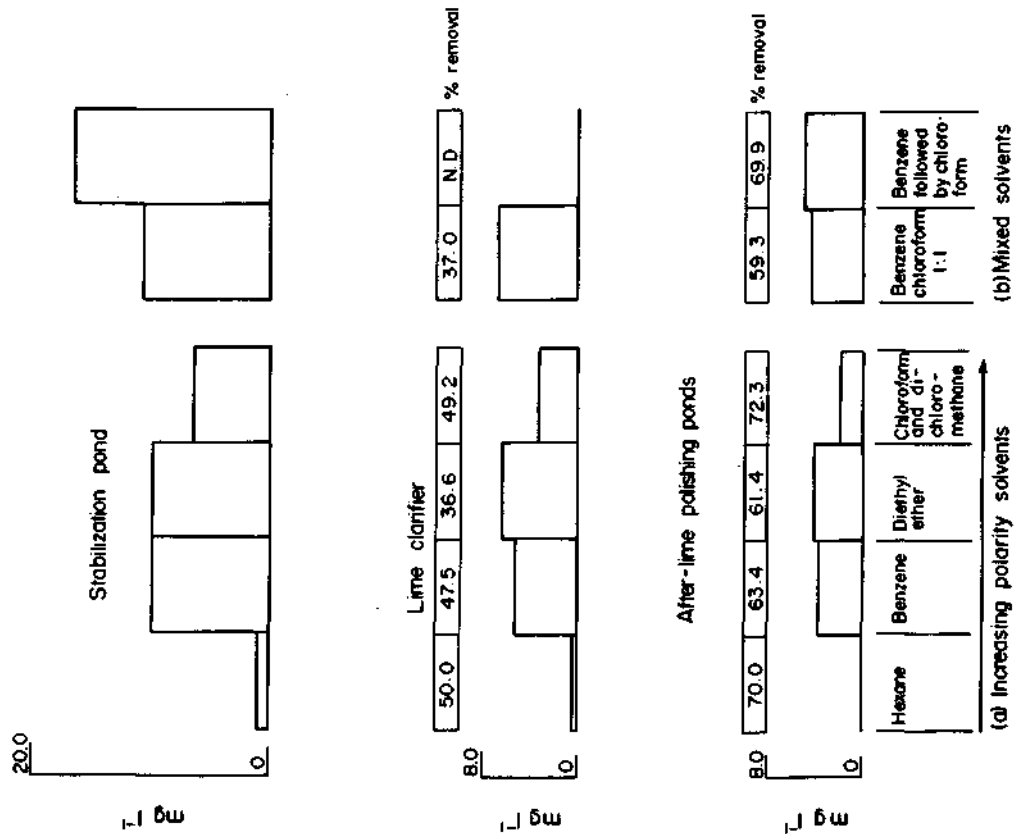


Fig. 4. Concentration of total solvent extractables in effluents of successive treatment stages (DRP).

Table 1. Concentration of solvent extractables in secondary effluents

Extractant	Reported solvent extractables concentration (mg l ⁻¹)	Reference
Sequential, hexane followed by chloroform	9.3*	American effluents (Levins, 1971)
Sequential, benzene followed by chloroform	22.4	Our results
Diethyl ether	0.8-5.2	American effluents (Bunch <i>et al.</i> , 1961)
	3.9-6.8	English effluents (Painter, 1971)
	7.3-22.6	Our results
Dichloromethane	2.0	Swiss effluents (Giger <i>et al.</i> , 1976)
	6.5	Our results
	~0.9*	American effluents (Levins, 1971)
Hexane	~1.1*	English effluents (Waggott & Saunders, 1976)
	~1.0*	Our results

* Calculated according to data in the paper.

reported by Waggott & Saunders (1976) and by Levins (1971), the concentrations of solvent extractables in local secondary effluents appear to exceed the values reported by some investigators for municipal secondary effluents (Table 1), probably due to lower water consumption and higher wastewater strength.

Lime treatment and detention in after-lime polishing ponds make for a significant reduction of the concentration of solvent extractables: the average acid solvent-extractables removal was about 44% in the lime clarifier and about 66% in the polishing ponds, while the corresponding figures for average total sol-

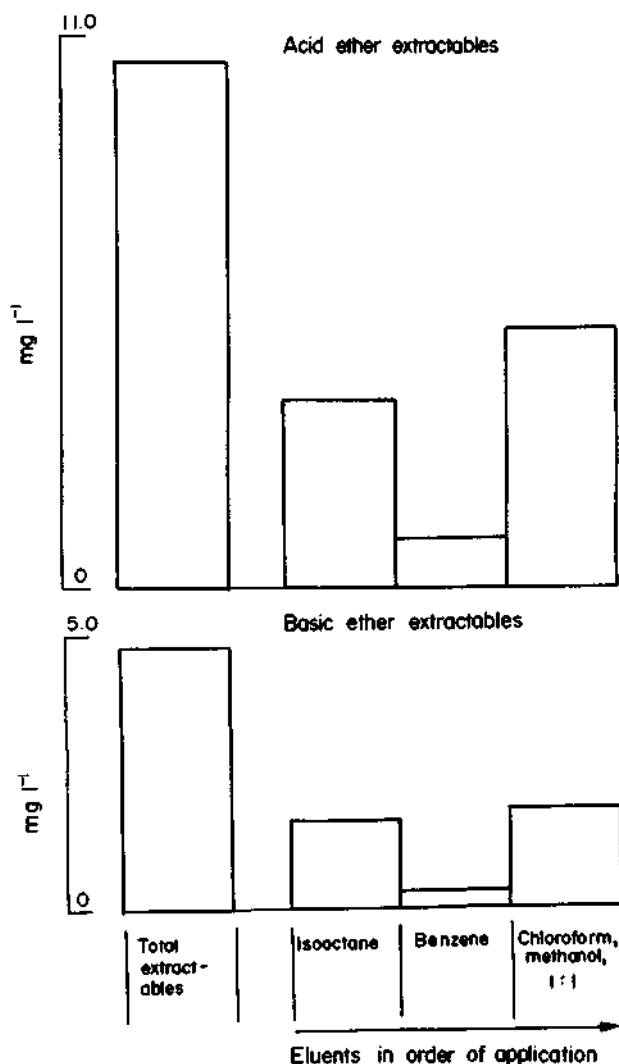


Fig. 5. Fractionation of ether extractables from secondary-trickling filter effluents.

vent-extractables were 37 and 68% respectively. The overall percent removal of different solvents extractables was quite similar throughout all the experiments.

Fractionation

Results are presented in Figs 5 and 6. The polar organics apparently constitute the major fraction of solvent extractables in secondary effluents: 45% of the ether extractables and 55% of the dichloromethane extractables. The non-polar pentane and isooctane eluates account for about 32% of the ether extractables and about 12% of the dichloromethane extractables, respectively. This may indicate that ether extracts a wider spectrum of organics. The benzene and dichloromethane eluates, which are of intermediate polarity constitute 9% of the ether extractables and 17% of the dichloromethane extractables.

Dichloromethane is possibly more efficient as an eluent where organics extracted by the same solvent are concerned.

There is no significant difference in the distribution of the acid and basic ether extractables.

Figure 6 shows that the lime clarifier and the overall treatment remove the dichloromethane fraction to the large extent 91 and 96% respectively. Next comes the non-polar pentane fraction (63 and 75%) and finally the polar methanol fraction (53 and 64%).

The distribution in dichloromethane extracts from advanced-treatment effluents shows increasing contribution of the polar methanol fraction: 63% in the lime clarifier as against the 72% in after-lime polishing ponds, and decreasing percentage of the intermediate dichloromethane fraction: about 4 and 0.3% respectively. The percent of the non-polar pentane fraction remains fairly the same throughout all treatment stages, including oxidation pond effluents: 11–12%.

Chromatographic fingerprints

Some of the fingerprints obtained are shown in Figs 7–9. Numerical values over particular peaks rep-

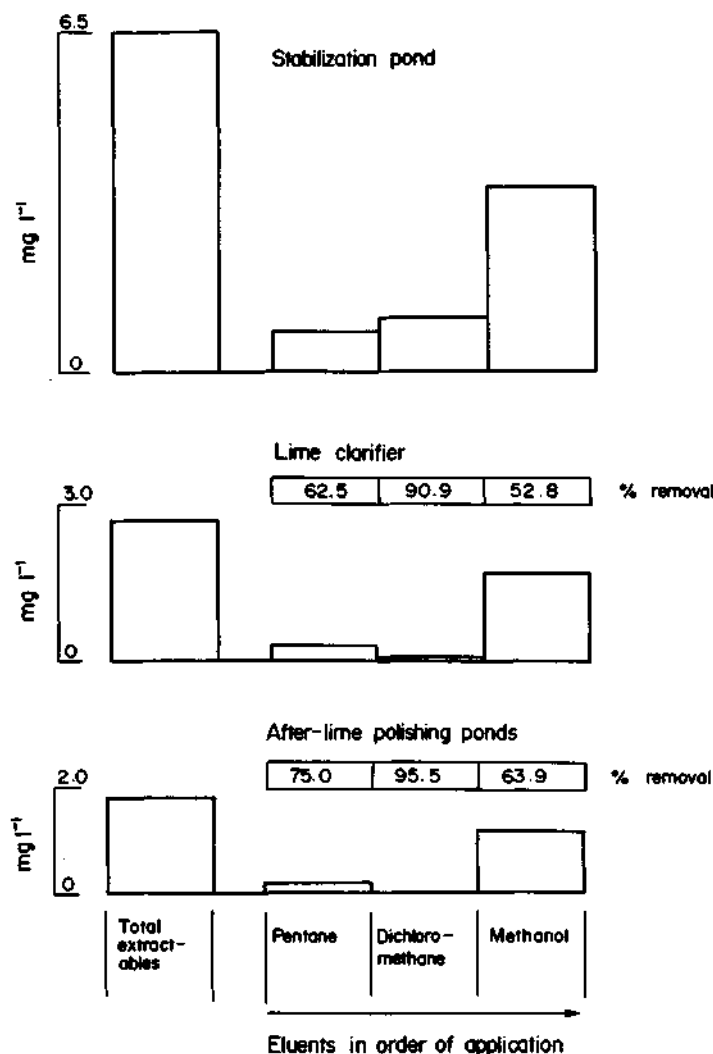


Fig. 6. Fractionation of dichloromethane extractables from successive treatment stages effluents (DRP).

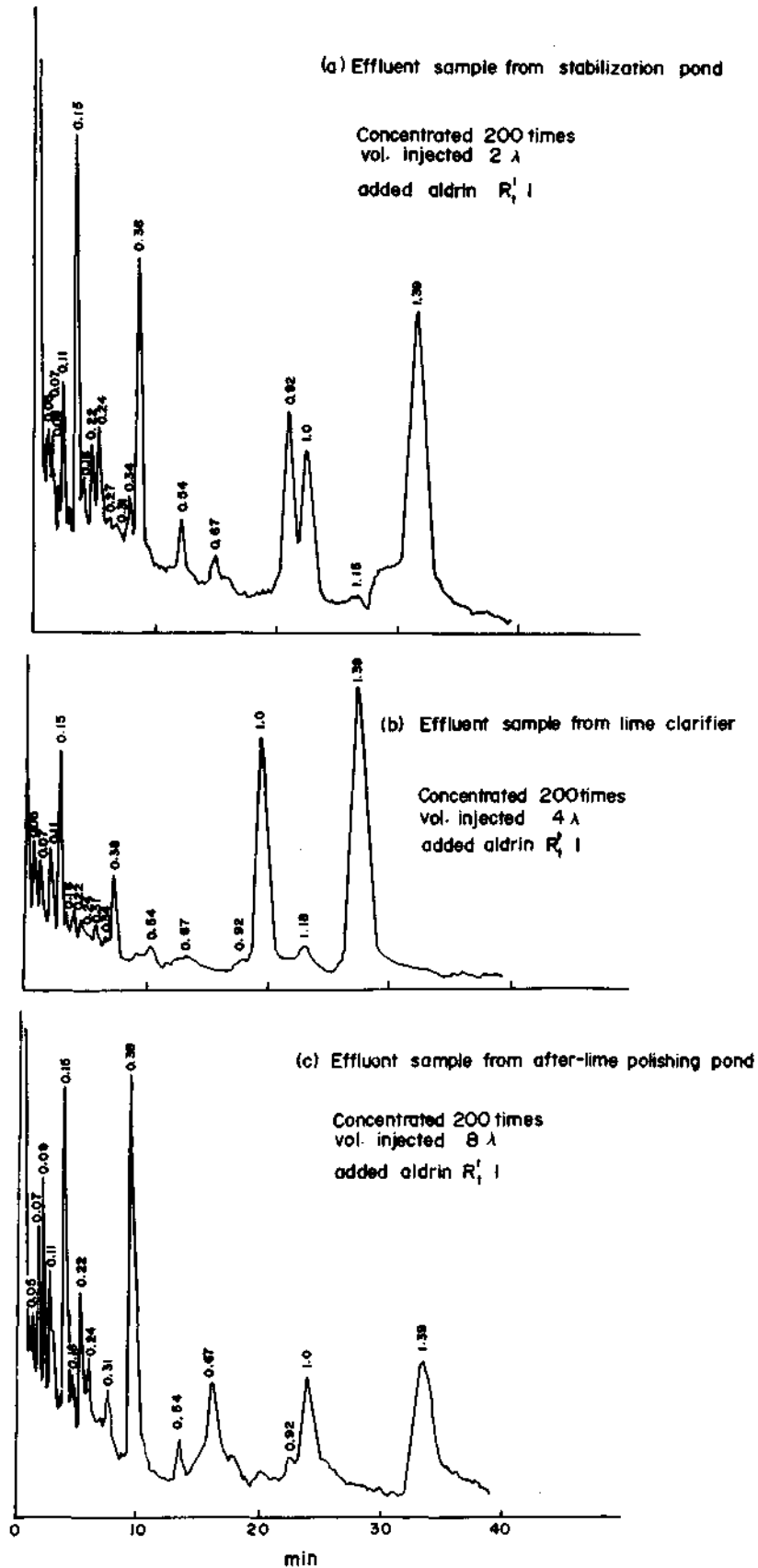


Fig. 7. GC-ECD fingerprints of benzene extractables from DRP effluents; sampling date 15/9/76.

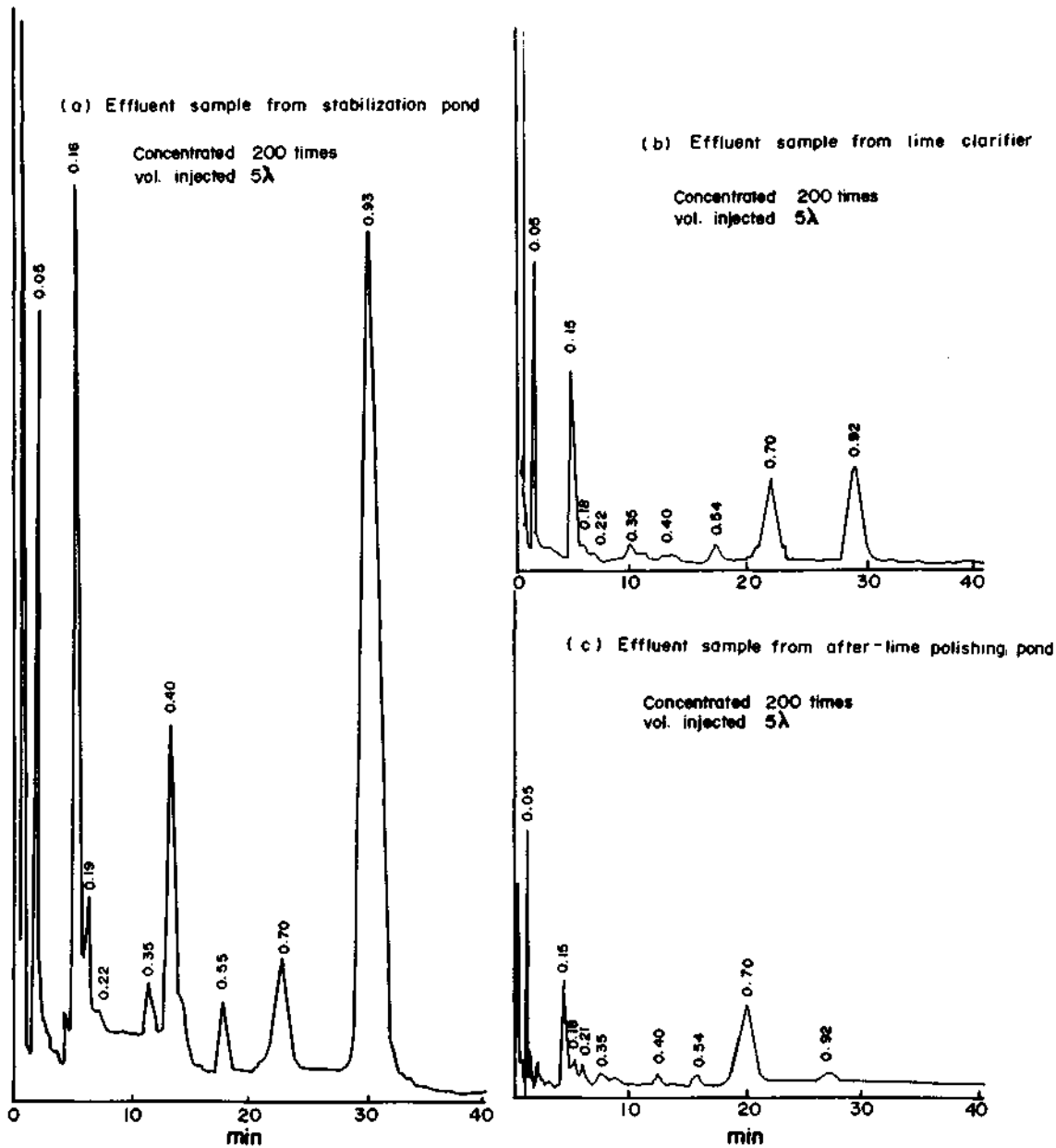


Fig. 8. GC-ECD fingerprints of ether extractables from DRP effluents: sampling date 14/12/76.

represent their relative retention times (R'_i) relative to that of aldrin (taken as unity). The peaks in Figs 8 and 9 are also listed in Table 2 according to R'_i and height (the latter suitability recalculated for an equal injection volume of 5 μ l).

Removals of particular R'_i compounds in the treatment processes were calculated from the changes in peak height following the treatment, on the assumption that the peak height is directly proportional to the amount of compound it represents.

With the peaks arranged in order of height, it is possible to evaluate the contribution of particular R'_i peaks in the examined fingerprints (Table 3). It appears that major peaks (≥ 100 mm) are few. Among

them, the R'_i 0.15 recurs in 3 samples of the oxidation pond effluents, and the R'_i 0.92 and R'_i 1.39, in 2 samples each. The R'_i 0.38 appears as a major peak only in 1 sample but recurs as a minor one in the remaining two. On the average, the major peaks in secondary effluents cover about 64% of the total chromatographed organic compounds.

Table 2 indicates that the major peaks are, in general, effectively removed by lime clarification alone. The removal of total GC-ECD detectable compounds calculated from the summed peak heights was 60–75% for the lime clarifier treatment and 80–85% for the overall process. By calculating the percent removal of total GC-FID detectable compounds

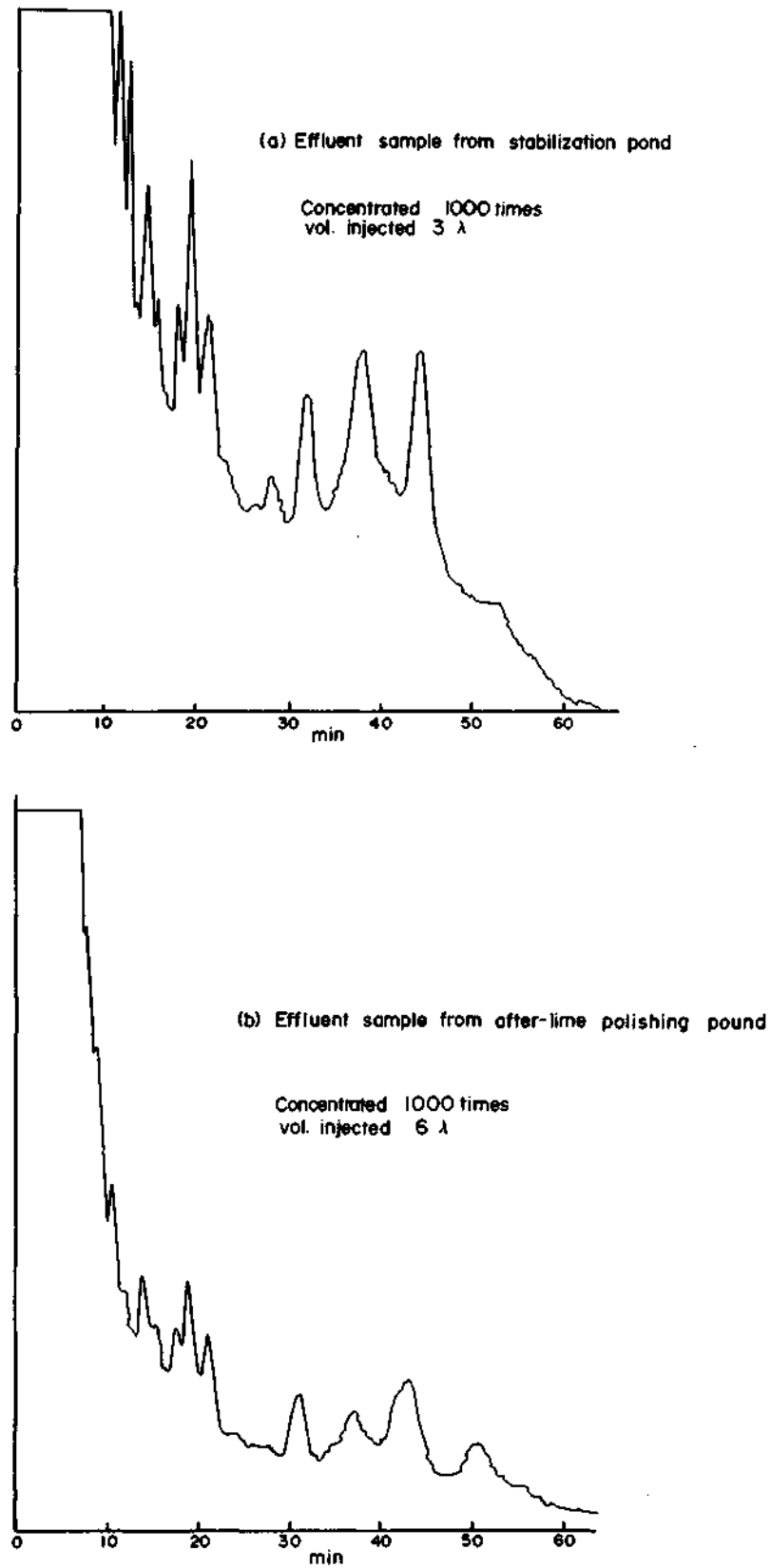


Fig. 9. GC-FID fingerprints of ether extractables from DRP effluents; sampling date 30/6/77.

Table 3. Distribution of peak heights in stabilization pond effluents

Peak height (mm)	R_i		
	Sampling date		
	30/6/76	15/9/76	14/12/76
> 200	1.39;	0.15; 0.38; 1.39	
199-150	0.15;		0.05; 0.15; 0.92
149-100	—	0.92	—
99-50	0.11; 0.21; 1.15	0.11; 0.24	0.38
49-20	0.07; 0.09; 0.18	0.05; 0.21; 0.34; 0.54;	0.18; 0.67
	0.38; 0.54	0.67; 1.81; 2.09	
19-10	0.24; 0.30; 0.67	0.30;	0.34; 0.54
	2.09; 2.89;		

(Fig. 9) from the total peak area, it was found that the overall treatment process removed about 64% of the organics.

REMOVAL OF CHLORINATED PESTICIDES IN THE SUCCESSIVE TREATMENT STAGES

While analysing the treated effluents for chlorinated pesticides, we found that one of the most frequently occurring was lindane, whose average concentration in oxidation pond effluents was about $0.3 \mu\text{g l}^{-1}$, in lime clarifier effluents about $0.1 \mu\text{g l}^{-1}$, and in after-lime polishing ponds about $0.03 \mu\text{g l}^{-1}$. Because of its persistence under chemical treatment reflected in relatively high levels in the lime-treated effluents, we used it in investigating the extent of removal of chlorinated pesticides in a controlled, advanced-treatment system. The second pesticide representative was aldrin. A sample of oxidation pond effluents was spiked with acetone solutions of those pesticides (at a final concentration of $4 \mu\text{g}$ lindane and $2.5 \mu\text{g}$ aldrin l^{-1} effluent sample), lime flocculated, kept for 10 days in a rectangular tray (in simulation of the lime clarifier and the after-lime polishing pond treatment) and finally analysed according to *Standard Methods* (1975).

The chromatograms obtained for each treatment step are included in Fig. 10, and the results are listed in Table 4. It appears, that under the simulated treatment conditions, starting with about 10 times greater pesticide concentration in secondary effluents, the

overall removal was close or equal to 100%. Lime flocculation did not suffice for complete removal of lindane, which confirmed the data obtained on effluents from the advanced-treatment renovation system.

DISCUSSION

Recovery and concentration of trace organics in water by liquid-liquid extraction is a widely-used procedure. The best recoveries are obtained by applying sequential polarity extraction at acid and basic pH. Waggott & Saunders (1976) studied secondary effluents by a sequence consisting of hexane, benzene, neutral ether, acid butanol and basic butanol, in that order. The last two solvents recovered about 48% of the total extractable matter, apparently consisting largely of high molecular-weight humic substances.

The sequential extraction process used—benzene followed by chloroform—was similar to Levins (1971) who used hexane followed by chloroform, and is useful in recovering the non-polymeric organic material, i.e. with the molecular weight cut off below 1000. Since the organic species belonging to this fraction comprise the majority of known toxic organic micro-pollutants and are the principal source of disposal and odour problems, our sequence seems especially suitable for gravimetric determination of microorganic pollution. Moreover, although different solvents and solvent sequences make for different recoveries, the per cent removal of particulate extractables in the successive treatment stages are in the same range. In these circumstances, one-step single-solvent extraction

Table 4. Removal of lindane and aldrin in successive treatment steps

Pesticide	Concentration found ($\mu\text{g l}^{-1}$)			% Removal	
	Spiked ox. pond effluent	After-lime floccul.	After-lime floccul. and detention	After-lime floccul.	After-lime floccul. and detention
Lindane	3.46	0.90	0.09	74.0	97.4
Aldrin	2.40	0.06	0	97.5	100

may be used to evaluate the efficiency of the effluent treatment system.

Column fractionation permits rough classification of the organic matter into so-called aliphatic, aromatic and oxy fractions. Results of qualitative identification analysis of these fractions were reported by several investigators. Rosen & Middleton (1955), and Lively & Mashini (1965), found that the aliphatic and aromatic fractions eluted from the column with pentane and benzene respectively, contained petroleum waste products responsible for odour in polluted water. Examining the aliphatic hydrocarbon fractions isolated from primary and secondary effluents, Giger *et al.* (1976) found mixtures of *n*-alkanes close to the petroleum-derived hydrocarbons. The aromatic hydrocarbon fraction in primary and secondary effluents was found to contain chlorinated and alkylated benzenes, the latter in the form encountered in gasoline and diesel fuel. Among the polynuclear aromatic hydrocarbons in municipal wastewaters were identified compounds with up to four rings such as naphthalene, diphenyl, anthracene, phenanthrene, fluorene, pyrene, fluoranthene (higher-ring molecules being very poorly water soluble and strongly adsorbing to solid particles) (Giger *et al.*, 1974). The final-polar methanol-fraction isolated from primary and secondary effluents contained cyclic and higher aliphatic and aromatic alcohols, phenols and alkylated phenols, and assorted phthalates and adipates (Giger *et al.*, 1976). Sproul & Ryckman (1961) found that the methanol fraction was relatively available for biological oxidation.

The literature cited above demonstrate the water-quality significance of the groups of compounds included in the fractions separated by column chromatography. Our own findings regarding removal of these fractions in the successive treatment stages provide an indication of the treatment efficiency that may be expected for each fraction. In this context, the excellent (almost 100%), removal of the aromatic dichloromethane fraction in the after-lime polishing ponds (Fig. 6) is of extreme importance! This fraction possibly includes, i.e., polynuclear aromatic compounds known to be carcinogenic, as well as chlorinated aromatics. In addition, high removals of both, aromatic and aliphatic fraction compounds in the overall treatment system means elimination of hydrocarbons causing odour and taste problems in water and having a general environmental significance.

The polar methanol fraction, which appears to be the least removable, is probably enriched by products of hydrolysis or of degradation of high molecular-weight compounds in the course of treatment (Rebhun & Manka, 1979), the new compounds replacing, in the total fraction balance the organics originally present in the effluent. They are not known to be of significant water-quality importance, being readily biodegradable.

The advantage of fingerprinting for evaluating the efficiency of sewage treatment was pointed out by

many researchers. Katz *et al.* (1972) compared the organics of primary and secondary effluents, using anion exchange chromatography and u.v. detection. Caruso *et al.* (1968) recorded gas chromatographic fingerprints at four points: raw sewage influent, primary settling-basin effluent, digester supernatant liquor, final clarifier effluent; finally, Roberts *et al.* (1977) compared the gas chromatographic fingerprints of domestic wastewaters before and after activated carbon treatment.

Our own investigation referred to the secondary effluents as the starting point for evaluating the efficiency of further, advanced treatment. The fingerprints of the secondary effluents investigated showed several substantial peaks, both with flame-ionization and with electron-capture detectors. As the former responds to most organics, FID fingerprints characterize the solvent-extractables content except for those organics which are too polar— or have too high molecular weights—for chromatography. The total percent removal of all FID peaks in the overall treatment process was actually found very close to the percent removal of benzene- and ether extractables: about 64% as against the average 67% (Fig. 4). On the other hand, removal of the ECD fingerprint peaks which represent the halogens and other electron absorbing compounds, was much higher: about 80% (Table 2) close to removal of the dichloromethane fraction (Fig. 6).

Examination of particular ECD fingerprint peaks showed general recurrence of the same major peaks in the secondary effluents. As they account for most of the chromatographed matter, their removal determines the total EC-detectable organics. If an individual peak is found to persist throughout the treatment process, it can be isolated and possibly identified by mass spectroscopy. Peaks failing to fit into the normal chromatographic profile of a given secondary effluent indicate an additional pollution source.

An interesting and important conclusion of our findings concerns the similarities in the extent of removal of different organic indices. For example, removal of solvent extractables was found close to that of total FID-responding organics; removal of the dichloromethane fraction obtained by column chromatography was similar to that of ECD-amenable compounds and very close to that of chlorinated pesticides, (in this case, lindane and aldrin). This leads to another conclusion, namely that the quantitative indices developed and used in this study may serve as rapid and representative indicators of organic quality (organic micropollutants) of effluents and renovated waters. Work is continuing on effluents of advanced treatment and renovated waters, with particular emphasis on confirming and refining the use of these quality indicators.

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