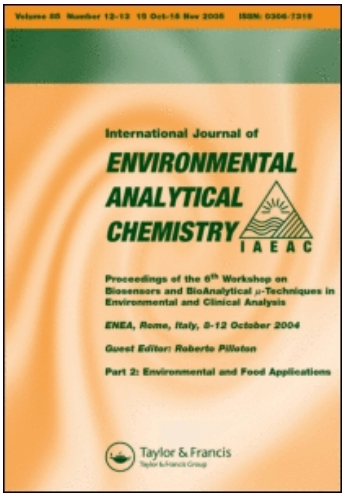

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Pesticides in Effluents and Polluted River Water

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Pesticides in Effluents and Polluted River Water

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A procedure using gas-liquid chromatography has been devised for the simultaneous analysis of a range of pesticides in the River Aire. It was essential to incorporate a clean-up system because the river is so heavily polluted. Analysis of samples showed that α-BHC, γ-BHC and dieldrin were usually present. Malathion, DDT, and DDE were detected occasionally. It is suggested that the pesticides originate in wool-scouring mills, the mill effluents entering the river via the Bradford Corporation Sewage Works.

INTRODUCTION

There is considerable interest in the study of pesticides in river water because of their possible effect on the flora and fauna,[1–7] and because they may contribute to an increase in the amount of pesticides in food-chains.[2, 8–11] The organochlorine pesticides are especially persistent,[12] and, if present in sufficiently high concentrations, are toxic to fish.[13] This effect is likely to be aggravated when there is other contamination in the river which causes a reduction in the dissolved O_2 concentration. The concentrations of pesticides in river water may also be an indication of the general level of pesticide contamination in an area.

Pesticides may accumulate on wool as a result of sheep-dipping, and therefore would be extracted when the wool is scoured. Consequently, the effluents from the woollen mills in this area may contain quite high concentrations of pesticides and could therefore be a prime source of pesticides in river water.

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Normally the concentrations of pesticides in river water are too low to be detected by TLC but the method could be useful for screening effluents and water samples which may contain pesticides in relatively high concentrations. Furthermore, TLC can provide an effective method of clean-up[14-16] for subsequent analysis by GLC, and can also be used for confirmation of the identity of pesticides.[15,16]

The existing methods for the analysis of pesticides in water have been restricted mainly to samples which were relatively uncontaminated, and clean-up procedures have not usually been necessary (see e.g. Croll[17] and Lowden *et al.*[18]). These methods, applied to the effluents from woollen mills and to water from the River Aire, produced unsatisfactory results because of the presence of other compounds which interfered with the analysis. This showed that a clean-up procedure was necessary for these samples. The present work aimed at the simultaneous analysis of a range of pesticides in contaminated water and effluent samples with a view to determining the sources of pesticides in the River Aire.

MATERIALS

Chromogenic reagent of Morley and Chiba[16]

Dissolve 1.7 g silver nitrate in 10 ml water. Add 5 ml ammonia solution (s.g. 0.88) and make up to 100 ml with acetone. Store in a dark glass container.

Chromogenic reagent of Walker and Beroza[19]

Dilute 1 ml of concentrated fluorescein [0.25% (w/v) fluorescein in dimethyl formamide (DMF) to 50 ml with ethanol]. Dissolve 1.7 g silver nitrate in 5 ml water, add 10 ml 2-phenoxyethanol and make up to 200 ml with acetone. Bromine in carbon tetrachloride (5%, w/v) is used as a source of bromine.

Chromogenic reagent of Bates[20]

Dissolve 0.1 g bromophenol-blue in 10 ml acetone and then dilute to 100 ml with a 1% (w/v) solution of silver nitrate in 3:1 (w/v) water:acetone.

Standard solutions of pesticides were prepared in *n*-hexane except for *β*-BHC which was prepared in benzene.

The Pye Panchromatograph (Pye-Unicam Ltd., Cambridge) was equipped with an electron capture detector (code no. 12207) with Tritium source. The columns were 150 cm long and the internal diameter was 5 mm. The stationary phase was either 3% methyl silicone gum (SE–30) or 3% trifluoropropyl methyl silicone (QF–1) supported on celite (mesh size 80–100).

EXPERIMENTAL

Extraction

Hexane is commonly used for the extraction of organochlorine pesticides,[14, 15, 21–24] but may not be satisfactory for all the organophosphorus pesticides.[25] Consequently, solvents other than hexane are often used to extract organochlorine as well as organophosphorus pesticides from water and other substrates. As part of the present investigation we compared hexane, petroleum ether, benzene, and chloroform as solvents for extraction. Samples (1 l) of river water and effluent were extracted. When hexane was used and the extract was subjected to a clean-up procedure it was shown to contain α-BHC, γ-BHC and dieldrin. A comparison of the results obtained for different extracting solvents (Table I) showed that the most satisfactory chro-

TABLE I

Variation between different extracting solvents in the concentrations obtained for pesticides in river water and sewage effluents (concentrations are expressed in ppb)

		Extracting solvent			
	Pesticide	Hexane	Petroleum ether	Benzene	Chloroform
River water	α-BHC	0.270	0.250	0.090	0.070
	γ-BHC	0.320	0.320	0.320	0.290
	Dieldrin	0.100	0.100	0.100	0.100
Effluent	α-BHC	0.800	0.800	—[a]	—[a]
	γ-BHC	1.740	1.740	—[a]	—[a]
	Dieldrin	0.280	0.280	0.280	0.230

[a] Could not be calculated because of interference on the chromatogram.

matograms and quantitative results were obtained with hexane and petroleum ether. Benzene and chloroform were less satisfactory in that there was much more interference on the chromatogram, although no new peaks were detected. There appeared to be a loss of α-BHC during extraction with either benzene or chloroform. This could have been due to volatility of the extract during evaporation to dryness before partitioning with DMF.

Clean-up

It was immediately obvious that the sample would have to be cleaned up because of the extensive interference observed on both thin-layer plates and

gas-liquid chromatograms. There was some improvement after the extract was passed through an alumina column. Further experiments showed that for both TLC and GLC it was necessary to include a DMF[26] partitioning stage together with the alumina[26, 27] column stage to obtain a satisfactory clean-up. This approach has previously been used for the analysis of organochlorine pesticides in sewage effluents but the effect of this on recovery has not been investigated.[28] We also found that with some of the effluent samples it was necessary to incorporate clean-up on TLC prior to analysis by GLC.

Thin-layer chromatography

Standard preparations of pesticides were used to determine the optimum conditions for separation on TLC. In all these experiments, extracts from river water and effluents were included and the efficiency of separation of the compounds in these extracts was used as one of the criteria for the assessment of optimum conditions.

Comparison of different solvent systems (*Table II*) The chloroform and the benzene-containing solvents each gave a similar R_f value with a number of the organochlorine pesticides. These solvents, with the exception of benzene:methanol (90:10), gave a good separation of the organophosphorus pesticides. Carbon tetrachloride gave very good separation of the organochlorine, but the separation of the phosphorus pesticides was poor, as they scarcely moved from the origin. Hexane and hexane:acetone (90:10) gave a reasonably good separation of the chlorinated pesticides. Although there was no movement of the organophosphorus pesticides in hexane, these compounds were effectively separated in the hexane:acetone (90:10) solvent. The best separation of the compounds present in the river water and effluent extracts was achieved with the hexane:acetone (90:10), and it was decided to use this solvent system routinely. Where appropriate, carbon tetrachloride was also used as a solvent system.

Chromogenic reagents The silver nitrate chromogenic reagent of Morley and Chiba[16] gave very good spots with all the standard organochlorine pesticides, except the BHC isomers, which could not be detected in amounts < 1 mcg. Normally the spots became visible after exposure to u.v. light for 20 min, but with dieldrin an exposure time of more than 30 min was required.

The fluorescein/silver nitrate[19] chromogenic reagent was very effective for the organophosphorus pesticides but was not used routinely because certain of the organochlorine pesticides could not be detected with it.

The silver nitrate/bromophenol-blue chromogenic reagent[20] was satisfactory for all the pesticides under investigation and in particular gave clear spots with the river water and effluent samples.

TABLE II

R_f values for different pesticides in different solvent systems (TLC). The chromogenic reagent of Morley and Chiba[16] was used.

Pesticide	Hexane	Hexane:acetone 90:10	Carbon tetrachloride	Benzene:ethanol 90:10	Benzene:ether 90:10	Benzene:acetone 90:10	Benzene:methanol 90:10	Benzene	Chloroform
p,p'-DDT	0.30	0.60	0.57	0.74	0.78	0.71	0.79	0.69	0.78
o,p'-DDT	0.48	0.62	0.63	0.73	0.75	0.73	0.76	0.65	0.79
p,p'-DDE	0.63	0.67	0.64	0.76	0.78	0.74	0.78	0.66	0.67
p,p'-TDE	0.14	0.51	0.47	—	—	—	—	—	0.80
p,p'-Methoxychlor	0.17	0.36	0.14	0.67	0.73	0.76	0.79	0.55	0.59
γ-BHC	0.19	0.45	0.41	0.66	0.79	0.79	0.78	0.64	0.62
Endrin	0.08	0.57	0.20	0.67	0.75	0.80	0.80	0.57	0.64
Dieldrin	0.02	0.51	0.19	0.66	0.65	0.78	0.81	0.56	0.64
Aldrin	0.67	0.69	0.61	0.75	0.84	0.82	0.82	0.81	0.78
Heptachlor	0.55	0.68	0.60	0.81	0.80	0.82	0.80	0.77	0.75
Heptachlor epoxide	0.12	0.57	0.81	0.72	0.75	0.79	0.78	0.65	0.66
Parathion	0	0.33	0.05	0.67	0.74	0.76	0.76	0.41	0.60
Malathion	0	0.21	0	0.49	0.56	0.65	0.75	0.07	0.37
Endosulfan	0.13	0.59	0.04, 0.29	0.61	0.67	0.70	0.83	0.67	0.70
α-Chlordane	0.27	0.61	0.50	0.77	0.86	0.81	0.87	0.71	0.76

Gas-liquid chromatography

The retention times for the different standard pesticides are shown in Table III. The QF–1 column was more versatile for separating the pesticides being investigated because there is less overlap of neighbouring peaks than with the SE-30 column. With certain groups of pesticides it was not possible to get good separations but the difficulties arising from this could usually be overcome by the complementary use of the two columns. However, in some of the samples analysed it was not possible to obtain a single peak for dieldrin and the quantitative analysis could only be done by peak construction.[27]

TABLE III

Retention time and appropriate response on the electron capture system of the individual pesticides (column temperature, 170°C; detector temperature, 190°C; carrier gas flow rate, 100 ml/min)

Pesticide	Retention time (min)		Response[a]
	SE-30	QF-1	(ng for ½ FSD)
α-BHC	3.3	2.3	0.7
γ-BHC	3.8	3.6	5.0
β-BHC	4.0	2.9	1.0
Heptachlor	7.5	3.2	1.5
Malathion	9.7	11.1	100.0
Parathion	9.8	14.5	22.0
Aldrin	9.9	3.7	1.2
Heptachlor epoxide	12.3	6.9	1.8
α-Chlordane	12.8	6.6	2.4
o,p'-DDE	15.3	5.9	4.0
Endosulphan	15.8	8.9	2.7
β-Chlordane	15.9	7.2	2.8
Dieldrin	19.1	11.0	3.2
p,p'-DDE	19.2	8.0	3.0
Endosulphan	21.8	16.8	5.0
p,p'-DDD	26.8	14.8	8.0
o,p'-DDT	28.2	9.8	8.0
p,p'-DDT	37.7	15.8	12.0

[a] Determined using the QF-1 columns.

METHOD

General

Pyrex glassware was used throughout. All glassware was thoroughly cleaned by the following procedure: an intial soap wash, followed by tap-water rinse and immersion in freshly prepared chromic acid. Finally, the glassware was rinsed sequentially in distilled water, hexane, and acetone, and dried in a drying cabinet. The glassware was checked for contamination prior to analysis by using GLC. Sample bottles were cleaned and checked in the same way.

Solvents were re-distilled if necessary. This was checked by concentrating the solvent from the volume initially used to the intended volume of the final extract. Samples (10 mcl) were then injected on to the GLC column.

Sampling

Samples (2.5 l) were collected from the River Aire and Leeds–Liverpool Canal at Apperley Bridge in Bradford. Effluents were obtained from the sewage works at Esholt and from scouring mills in the Bradford area. All samples were collected in glass containers. Plastic containers were not used because of possible adsorption of pesticides.

Extraction

Samples (1 l) of river water or effluent were acidified to pH 2 with HCl and extracted with 1 × 100 ml and 4 × 50 ml volumes of redistilled hexane on the day of collection. Three drops of ethanol were added to the combined hexane layers to break down the emulsions. If the amount of emulsion was excessive the hexane layer was decanted and the emulsion was centrifuged in a bench centrifuge. The extract was then passed through a column of anhydrous sodium sulphate, which had been pre-washed with hexane. When all the extract had passed through, the column was washed three times with 10 ml of hexane. The volume of the extract was reduced to about 25 ml in the vacuum rotary evaporator at 40°C.

Clean-up

The extract was partitioned with DMF saturated with hexane[26] to remove all fats, and then the volume was reduced to 2 ml with a gentle jet of clean filtered air at room temperature. It was then passed through a column of 2 g alumina and eluted with 30 ml of hexane. (As difficulties could be encountered in eluting Malathion from the alumina column, this step was omitted when Malathion was present.) The final volume was normally reduced to 0.1 ml for TLC and 10 mcl was spotted on the plate. For GLC a lower concentration was usually required and the volume was reduced to 5–10 ml with 5–10 mcl being injected on to the chromatograph.

Thin-layer chromatography

Plates (20 × 20 cm and 20 × 10 cm) were prepared manually using a Shandon Unoplan applicator. A slurry consisting of 30 g Silica Gel G in 60 ml distilled water was applied to the plates in a spreader. The direction of the spreading was marked. After standing at room temperature for 5 min the plates were transferred to an oven (at 130°C) for 30 min. The oven was opened frequently during the first 10 min to allow moisture to escape and the plates were placed vertically to ensure efficient drying.[29] The sample was spotted on the plate

using the Hamilton microsyringe. A plastic template was used to ensure that the spots were placed in a straight line at regular intervals. The diameter of the spot was restricted to < 0.5 cm.

The plates were transferred to a chromatography tank lined with Whatman chromatography paper No. 1 and containing 200 ml of solvent, which had been allowed to equilibrate for 90 min at room temperature. They were allowed to develop for a pre-marked distance of 10 cm from the sample or standard spot.

The positions of the compounds were established by running standards in parallel. The section of the plate containing the sample to be analysed was covered with aluminium foil to prevent reaction with the chromogenic reagent when it was applied to the plate to show the position of the standard. The silica gel was scraped off in bands which corresponded to the positions of the standards and eluted with about 30 ml of hexane. The volume of hexane was reduced to about 0.1 ml and an aliquot was injected on to the GLC column.

Gas-liquid chromatography

The standing current used for the GLC analysis was attained by applying 12 V. If the voltage was increased beyond this there was no further increase in the standing current. The amplifier was adjusted to give a gain of 10^{-9}A throughout the analysis. The amplifier gain was not increased above this value because of the development of noise and an unsteady base-line.

When a column was changed it was first heated to 220°C for 24 hr with N_2 flowing through. Then it was connected to the detector prior to analysis. The columns were operated at 170°C. The nitrogen flow rate was 100 ml/min. Chart speed was 1 cm/min.

Identification of pesticides

Tentative identification was possible by using TLC to compare the R_f values with those of standards run on the same plate under the same conditions. Provided sufficient pesticide was present in the extract, this was a convenient method of screening samples which were heavily polluted. In this case two different solvent systems were used. Further proof was provided by the use of a specific chromogenic reagent. Subsequent work with GLC almost always confirmed the initial identification by TLC. Conversely the TLC identification was used to reinforce the information obtained by GLC. On GLC the pesticides were identified by comparing the retention times with those of standard pesticides. Confirmation was provided if there was an increase in the peak area, without any distortion, when the suspected pesticide was added to the

extract prior to injection on to the column. The amount added was such that the increase in peak area was small in comparison with the original peak area. This procedure was then repeated with the second column. Final confirmation was provided by extracting the fraction from the TLC place which had the appropriate R_f value for the compound. This fraction was analysed by GLC to determine whether it gave the same R_f as before.

Quantitative analysis

This was done on GLC by relating the peak area of the pesticide to a calibration curve obtained with the standard pesticides. The calibration curve was checked at regular intervals. Peak areas were measured by a planimeter.

Recoveries

Samples (1 l) of river water and effluent were transferred to 2-l separating funnels. Known amounts of standard solutions of pesticides were then added at two different concentrations. The microsyringe needle was kept immersed in the sample during addition. Blank samples were run in parallel. The funnels were shaken and left to stand overnight. The samples were then subjected to the whole of the extraction and clean-up procedure. The pesticides were determined by GLC and the recoveries were calculated (Table IV). For most of the pesticides a satisfactory recovery of $> 85\%$ was obtained for the river water samples. In general, there was a slight decrease in the recovery for the higher amounts of pesticide added. However, this is unlikely to be of great significance since a small volume of intial sample would be used if the pesticide concentrations were much higher.

RESULTS AND DISCUSSION

Samples of water from the River Aire and the Leeds–Liverpool Canal, and effluents from the Bradford Sewage Works at Esholt and from wool-scouring mills in the Bradford area have been analysed (Table V). The results show that α-BHC, γ-BHC and dieldrin are usually found in all of these samples. DDT, DDE and Malathion were detected in the river water occasionally and this always corresponded with the presence of the pesticide in the sewage effluent if it was analysed at the same time. The results show that there is a close relationship between the pesticide in the river and in the sewage effluent. Invariably, the concentration of a given pesticide was higher in the sewage effluent than in the river water. The concentrations of pesticides in the river water above the sewage outfall were negligible. This demonstrates that at the

point where the samples of river water were taken (just below the sewage outfall) the main source of pesticides is the sewage effluent. The presence of the pesticides in the mill effluents suggests that these effluents may contribute to the pesticides in the sewage effluent. Scouring-mill effluent in this area is directed to the Sewage Works for treatment.

TABLE IV

Recovery of pesticides added to water and to effluent samples

Pesticide	Amount added to 1 l (ng)	Water, % recovery	Effluent, % recovery
α-BHC	100	92	75
	200	84	63
γ-BHC	100	100	100
	200	88	88
Aldrin	100	68	75
	200	59	75
o,p'-DDE	100	93	45
	200	88	75
p,p'-DDE	100	85	45
	200	80	45
α-Chlordane	100	100	83
	200	60	53
Endosulfan I	100	95	73
	200	66	73
Dieldrin[a]	100	> 80	> 80
	200	> 80	> 80
Malathion[a]	5,000	> 80	> 80
	10,000	> 80	> 80
p,p'-TDE	500	100	100
	1,000	98	100
p,p'-DDT	500	100	100
	1,000	100	100
o,p'-DDT	500	75	60
	1,000	55	50

[a] Values for Malathion and dieldrin can only be calculated by difference, and so accurate recovery could not be obtained.

The method of analysis which we have used for this work consists of a number of different procedures. It is clearly necessary to include a rigorous clean-up system in order to analyse the pesticides satisfactorily. Our investigations show that one river which is heavily contaminated with pesticides is also heavily polluted with other substances which can interfere with the analysis of pesticides. This may mean that rivers and effluents with high concentrations of pesticides present the most difficult analytical problems.

TABLE V

General survey of pesticides found in different samples. (Concentrations are expressed as ppb[a])

Sample	Date	pH	α-BHC	γ-BHC	Dieldrin	*p,p'*-DDT	*p,p'*-DDE	M
re								
rley Bridge)	28.1.1969	7.1	0.120	0.260	1.200	0.500	0.530	
	4.4.1969	7.0	0.040	0.091	0.022	—	—	
	15.5.1969	7.1	0.014	0.014	—	0.107	0.007	
	15.6.1970	7.1	0.250	0.350	0.180	—	—	
	27.7.1970	7.1	0.033	0.200	0.240	—	—	
	2.10.1970	7.0	0.250	0.320	0.100	—	—	
fluent	15.5.1969	6.0	0.180	0.200	0.110	3.000	0.110	
rd Corporation	15.6.1970	6.2	2.650	3.750	0.675	—	—	
e Works—Esholt	27.7.1970	6.9	0.875	1.000	0.360	—	—	
	2.10.1970	6.8	0.800	1.740	0.280	—	—	
erpool Canal	28.1.1969	7.3	0.014	0.020	—	—	—	
ley Bridge)	4.4.1969	7.0	0.008	0.012	—	—	—	
	15.5.1969	7.1	0.004	0.005	—	—	—	
ouring mill	24.10.1969	8.0	—	—	0.160	1.000	0.140	
ts	30.10.1969	8.5	0.100	0.160	1.560	—	—	
	5.11.1970	7.6	1.400	1.950	0.630	—	—	

are not corrected for recovery.
s indicate that the pesticide could not be detected.

As these are the rivers which are likely to be subjected to the most intensive investigations it is important that these considerations are recognised.

Since our experimental work was completed a review on methods for the analysis of pesticides and herbicides in water has been published.[30]

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