

Interim Report

R&D Project 392

Sources and Fates of Synthetic Organics

WRc plc

October 1992

R&D 392/5/NW

ENVIRONMENT AGENCY



102292

SOURCES AND FATES OF SYNTHETIC ORGANICS

I Cousins, C D Watts, H R Rogers and A J Dobbs

Research Contractor:
WRc plc
Henley Rd Medmenham
PO Box 16 Marlow
SL7 2HD

National Rivers Authority
Rivers House Waterside Drive
Almondsbury Bristol BS12 4UD

National Rivers Authority
Rivers House Waterside Drive
Almondsbury Bristol BS12 4UD

Tel: 0454 624400
Fax: 0454 624409

© National Rivers Authority 1992

All rights reserved. No part of this document may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise without the prior permission of the National Rivers Authority.

Dissemination status

Internal: Restricted
External: Restricted

Research contractor

This document was produced under R&D Contract 392 by:

WRc plc
Henley Rd Medmenham
PO Box 16 Marlow
SL7 2HD

Tel: 0491 571531
Fax: 0491 579094

WRc Report N° NR 3232/4101

NRA Project Leader

The NRA's Project Leader for R&D Contract 392:

G Edwards - North West Region

Additional copies

Further copies of this document may be obtained from Regional R&D Co-ordinators or the R&D Section of NRA Head Office.

392/5/NW

CONTENTS	Page
LIST OF TABLES	ii
EXECUTIVE SUMMARY	1
KEYWORDS	1
1. INTRODUCTION	3
2. EXPERIMENTAL	7
2.1 July sampling survey	7
2.2 Analysis of sediments collected 19 February 1992	13
3. RESULTS	15
3.1 Results from the July survey	15
3.2 Results for PCP in sediments collected 19 February 1992	19
4. DISCUSSION OF RESULTS	21
4.1 WRc Positive Ion EI Data	21
4.2 WRc Negative Ion CI Data	21
4.3 WRc PCP Data for water samples	21
4.4 Total Organic Carbon (TOC) Data	22
4.5 NRA Analytical Data	22
4.6 WRc General Survey GC-MS Data	22
4.7 PCP data for sediment samples	23
5. CONCLUSIONS	25
6. RECOMMENDATIONS	27
6.1 Compounds recommended for further detailed study	27
6.2 Recommended work programme for sources and fates study	31
6.3 Timescale for work programme	35
REFERENCES	37

LIST OF TABLES**Page**

1.1	Summary of NRA Red List analytical data for River Alt Catchment between September 1988 and April 1992	4
2.1	Spiking Mixture for Red List Organics Analysis	8
2.2	Spiking Mixture for General Survey GC-MS Analysis	8
2.3	Field Measurements	9
2.4	Statistically derived method limits of detection for analysis of Red List organics in river waters	10
2.4	Pentachlorophenol MID method	11
2.5	Table showing samples analysed and their respective sample codes	12
3.1	WRc Results for Red List Organics in River Alt Catchment 27/28 July Analysis: GC-MS (Positive Ion EI, MID)	15
3.2	WRc Results for Red List Organics in River Alt Catchment 27/28 July Analysis: GC-MS (Negative ion CI, MID)	16
3.3	WRc Results for PCP in River Alt Catchment 27/28 July 1992 Analysis: GC-MS (Positive Ion ET, MID)	16
3.4	WRc Results for Total Organic Carbon (TOC) in River Alt Catchment 27/28 July	16
3.5	Table summarising GC-MS general survey resultsTable 3.5 contined	17
3.6	NRA Results for PCP in River Alt Catchment 27/28 July 1992 Analysis: GC-MS (Positive ion EI, MID)	19
3.7	PCP Results for Bed Sediments Collected from the River Alt catchment 19 February 1992	19
6.1	Physicochemical data for selected compounds	28

EXECUTIVE SUMMARY

Data for the sampling survey carried out on the 28/29 July 1992 are presented. Specific Red List determinand and broad-spectrum GC-MS techniques were used to provide additional information on the range and concentration of organic contaminants in the River Alt catchment. On the basis of the results from this survey and from routine monitoring carried out by the NRA, five priority contaminants are recommended for inclusion in the sources and fates study. Problems with the previously proposed experimental approach are highlighted and a revised approach involving the use of *in situ* mesocosms is described and recommended.

KEYWORDS

Organic contaminants, sources, fates, Red List compounds, River Alt, GC-MS, mesocosm.

1. INTRODUCTION

In the first two sampling exercises carried out on the River Alt catchment in January and February 1992 only three Red List organic compounds were identified; atrazine, simazine and lindane. Furthermore, it was noted that for a river system of such low quality classification the extracts were remarkably uncomplex. It is possible that the dry winter conditions prevalent at the time of sampling may have resulted in reduced contaminant runoff (particularly agricultural pesticides) so giving rise to atypical water quality. However, it was agreed at the progress meeting on 27 May 1992 that the apparent clean state of the river required further investigation.

NRA data for their Red List and Black List monitoring exercises between October 1988 and March 1992 was summarised and tabulated (see Table 1.1). It was clear from a comparison of the NRA data with the results of analysis of Red List compounds from the first two sampling exercises that WRc's data was not atypical for the River Alt. The only Red List organics which the NRA find in 50% or more of their samples of river water or Fazakerley STW effluent are gamma-HCH (lindane), dieldrin, 1,2-dichloroethane and pentachlorophenol (PCP). WRc did not analyse for 1,2-dichloroethane and PCP, but did find lindane in most of the samples analysed. In the NRA's data dieldrin is only present in 75% of the effluent and 5% of the river samples, so it is not unreasonable that WRc did not find this in river water samples collected during both surveys. WRc also found atrazine and simazine in all of the samples and the levels found were within the range of NRA's data, particularly because the higher levels (several micrograms per litre) found by the NRA were in samples collected in the Autumn. Levels of atrazine and simazine in NRA data from winter samples were lower, generally less than a microgram per litre.

The only Red List organic which is consistently present is PCP at levels up to $35 \mu\text{g l}^{-1}$ in the river water samples, with only 5% of the samples not containing detectable levels. It was agreed that WRc should develop a mass spectrometry based method for the quantification of PCP and analytical method development should be carried out for water and sediment samples.

Another sampling exercise was planned for 28/29 July 1992 in which samples taken were split between WRc and NRA. This collaborative exercise was planned to ensure that any Red List organics present in the river were correctly identified and quantified. This progress report presents and discusses results from this survey, recommends several compounds identified in the July survey for inclusion in the sources and fates study and outlines a programme of work.

Table 1.1 Summary of NRA Red List analytical data for River Alt catchment between September 1988 and April 1992

Compound	Limits of detection ug l ⁻¹	Above Altmouth Pumping Station			Fazakerley STW Humus Tank Effluent		
		Concn. range ug l ⁻¹	Mean concn ug l ⁻¹	% 'less thans'	Concn. range ug l ⁻¹	Mean concn. ug l ⁻¹	% 'less thans'
Mercury	0.008 - 0.1	0.008 - 0.36	0.0866	18.5	0.16 - 0.16	0.16	0.0
Cadmium	0.027 - 0.1	0.027 - 1.55	0.2898	6.6	<0.1 - 1.79	0.7646	6.2
Aldrin	0.001 - 0.05	<0.05	0.0025	97.7	<0.007 - <0.007	0.0047	100.0
Dieldrin	0.001 - 0.05	0.001 - 0.135	0.0053	95.5	0.007 - 0.07	0.0305	25.0
Endrin	0.002 - 0.05	<0.05	0.0039	97.8	<0.005 - <0.012	0.0045	100.0
Gamma-HCH	0.05 - 0.61	<0.05 - 2.23	0.2281	12.1 ⊗	<0.006 - 2.03	0.2534	22.2
DDT (p,p')	0.006 - 0.05	<0.05	0.0069	96.6	<0.005 - <0.03	0.075	100.0
Pentachlorophenol	0.06 - 0.1	<0.08 - 35	2.029	4.6 ⊗	0.06 - 15.7	2.068	0.0
HCB	0.003 - 0.05	<0.003 - 0.1	0.0282	72.5	<0.005 - <0.05	0.025	100.0
HCBD	0.003 - 0.05	<0.003 - 0.25	0.0219	92.0	<0.005 - 0.11	0.0293	95.8
Trifluralin	0.005 - 0.1	<0.005 - 0.6	0.0569	77.3	<0.005 - <0.005	0.0033	100.0
Endosulfan	0.002 - 0.04	<0.002 - 0.08	0.0113	71.4	<0.005 - <0.005	0.0033	100.0
Simazine	0.02 - 2.5	<0.02 - 6.16	0.9811	70.0	<0.05 - 10.2	1.85	75.0
Atrazine	0.1 - 2.5	<0.1 - 19.57	2.091	60.0	<0.05 - 10.87	2.827 †	60.0
Tributyltin cmpnd							
Triphenyltin cmpnd							
Azinphos-methyl	0.1	<0.1	0.0667	100.0	<0.05 - <0.5	0.1444	100.0
Fenitrothion	0.1	<0.1	0.0333	50.0	<0.1 - <0.15	0.0778	100.0
Malathion	0.1	<0.1	0.0333	50.0	<0.1 - <0.15	0.0778	100.0
Dichlorvos	0.04 - 2.5	<0.04 - <2.5	0.2804	88.9	<0.04 - <0.15	0.055	100.0
Trichlorobenzene	0.0045 - 2	<0.0045 - <2	0.4555	80.3	<0.005 - <2	0.5215	100.0
1,2-Dichloroethane	0.05 - 500	<0.05 - <500	9.371	43.5 †	<0.61 - <500	39.66	55.0

Table 1.1 continued

Compound	Limits of detection* ug l ⁻¹	Above Altmouth Pumping Station			Fazakerley STW Humus Tank Effluent		
		Concn. range ug l ⁻¹	Mean concn ug l ⁻¹	% "less thans"	Concn. range ug l ⁻¹	Mean concn. ug l ⁻¹	% "less thans"
PCB 28	0.005	<0.005	0.005	100.0	<0.005	0.005	100.0
PCB 52	0.005	<0.005	0.005	100.0	<0.005	0.005	100.0
PCB 101	0.005	<0.005	0.005	100.0	<0.005	0.005	100.0
PCB 118	0.005	<0.005	0.005	100.0	<0.005	0.005	100.0
PCB 138	0.005	<0.005	0.005	100.0	<0.005	0.005	100.0
PCB 153	0.005	<0.005	0.005	100.0	<0.005	0.005	100.0
PCB 180	0.005	<0.005	0.005	100.0	<0.005	0.005	100.0

* The NRA method limits of detection vary considerably, therefore, the table lists the range of detection limits for each determinand.

2. EXPERIMENTAL

2.1 July sampling survey

2.1.1 Sampling and field analyses

A sampling exercise was carried out on the River Alt catchment on the 28/29 July 1992. Samples were taken at the following sites:

1. Fazakerley STW effluent stream - SJ 393968
10-litre, 20 hr composite sample (a 250 ml shot was taken every 30 minutes). Start time 09 45 hrs. 27 July, stop time 05 45 hrs 28 July.
2. Fazakerley STW effluent stream - SJ 393968
10-litre grab sample taken at 12 10 hrs 28 July.
3. Altmouth Pumping Station - SD 293051
10-litre, 20 hr. composite sample (a 250 ml shot was taken every 30 minutes). Start time 11 05 hrs 27 July, stop time 07 05 hrs 28 July.
4. Clockhouse Bridge - SJ 394968
10-litre grab sample taken at 12 10 hrs 27 July.
5. Kirkby Brook - SJ 407979
10-litre grab sample taken at 13 20 hrs 27 July.

Composite samples were taken with an EPIC 1011 Portable Waste Water Sampler. Grab samples were collected by immersing a pre-cleaned 10-litre glass bottle in the river. Each of the 10-litre samples were shaken thoroughly and then divided into a series of seven sub-samples (five to be analysed by WRc and the other two to be analysed by NRA):

1. A 1-litre sub-sample for analysis of Red List organics (WRc).
2. Two 1-litre sub-samples for GC-MS general survey analysis (WRc). One of the sub-samples was basified prior to extraction and the other acidified.
3. A 500 ml sub-sample for analysis of PCP (WRc).
4. A 250 ml sub-sample for Total Organic Carbon (TOC) analysis (WRc).
5. One 2-litre sub-sample for analysis of Red List organics (NRA).
6. A 500 ml sub-sample for analysis of PCP (NRA).

The excess water was used for washing out the sampling bottles.

WRc sub-samples for organic analysis were preserved by acidification using 5M hydrochloric acid and spiked with a mixture of stable isotope labelled and other standards (shown in Table 2.1) immediately after sub-sampling. WRc sub-samples for general

survey GC-MS analysis were also preserved by acidification and were spiked with a separate mixture of stable isotope labelled standards (shown in Table 2.2). WRC sub-samples for PCP analysis were acidified and spiked with $2 \mu\text{g l}^{-1} \text{ }^{13}\text{C}_6\text{-PCP}$.

Table 2.1 Spiking Mixture for Red List Organics Analysis

Compound	Spike level (ng l^{-1})
d_3 -trichlorobenzene	500
d_{14} -trifluralin	500
$^{13}\text{C}_6\text{d}_6\text{-}\gamma\text{-HCH}$	100
d_5 -atrazine	500
$^{13}\text{C}_4$ -dieldrin	100
decachlorobiphenyl	500
d_{10} -malathion	100

Table 2.2 Spiking Mixture for General Survey GC-MS Analysis

Compound	Spike level ($\mu\text{g l}^{-1}$)
d_3 -1,1,1-trichloroethane	1.00
d_5 -chlorobenzene	1.00
d_6 -benzene	1.00
d_{10} -p-xylene	1.00
d_8 -naphthalene	1.00
d_{10} -phenanthrene	1.00
d_{34} -hexadecane	1.00

It had previously been planned to take a sample at Fazakerley Brook and not at Kirkby Brook. However, Fazakerley Brook was not flowing at the time of sampling because of low rainfall in July and also because the brook was dammed in several places as a result of fly-tipping. Therefore, Fazakerley Brook was not likely to be a significant input to the Alt catchment at the time of sampling and Kirkby Brook was chosen as an alternative sampling site.

The manager of Fazakerley STW thought that the composite sample taken at the effluent stream contained an unusually high level of suspended solids. This may have been caused by the EPIC composite sampling nozzle disturbing deposits on the bottom of the effluent channel. This would seem unlikely because deposits disturbed should immediately be washed away by the powerful flow of the effluent. However, in case the composite sample was unrepresentative, as suggested, an additional 10-litre grab sample was taken to compare with the composite sample.

At the two sites where grab samples were taken, the pH, temperature and dissolved oxygen content of the river waters was measured *in situ*.

Table 2.3 Field Measurements

Sample site	Water temp. (°C)	Dissolved Oxygen (mg l ⁻¹)	pH
Clockhouse Br.	17.6	3.0	7.2
Kirkby Brook	17.3	4.9	7.3

2.1.2 Analytical Methodology

WRc Analytical Methodology

Red List Organics

The analytical methodology employed was the same as described in the previous Interim Report (DoE Report N° DoE 3108; NRA Report N° 393/2/NW).

Preliminary work has been carried out to determine statistically derived detection limits for the Red List organics method. Two triplicate batches of 1-litre river water samples were spiked at a low level (10 ng l⁻¹) and then extracted and analysed by positive ion EI and negative ion CI GC-MS. A between batch standard deviation was calculated from the results. This standard deviation was used to calculate a detection limit using the formula below:

$$\text{Limit of detection} = 3.3\sqrt{2}\sigma_r = 4.65\sigma_r \text{ (Cheeseman and Wilson 1989)}$$

where σ_r is the standard deviation of non-blank-corrected results.

Table 2.4 Statistically derived method limits of detection for analysis of Red List organics in river waters

Compound	LOD (ng l ⁻¹)
Positive ion EI	
1,2,4-TCB	57
trifluralin	8
atrazine	6
simazine	6
o,p-DDT	22
p,p-DDT	12
Negative ion CI	
dichlorvos	4
trifluralin	5
HCH	5
aldrin	3
malathion	3
fenitrothion	7
PCB 101	3
PCB 118	11
PCB 138	19
PCB 180	21
α-endosulphan	11
dieldrin	5
endrin	11
o,p-DDT	1
p,p-DDT	5

More detailed experiments are planned by WRc's Analysis Group to verify these detection limits.

Pentachlorophenol

The acidic sample was extracted with n-hexane (1 x 50 ml, 2 x 25 ml aliquots) by vigorous shaking in a glass separating funnel. The solvent layer was separated off and filtered through glass wool to break up emulsions. The extract was dried by freezing out water (-20 °C overnight) and concentrated to 1 ml using a Zymark Turbovap.

The 1 ml hexane extract was diazotised with 1 ml of freshly prepared ethereal diazomethane. The extract and diazomethane were shaken together in a vial and left for

five minutes. Excess diazomethane was then removed under a stream of dry nitrogen gas and the extracts were further concentrated.

The concentrated extracts were analysed by GC-MS using a Hewlett Packard 5890 GC equipped with a cool on-column injector and a Hewlett Packard auto sampler, model number 7673A. The GC was connected to a VG Trio-1 MS via a heated direct interface. The MS was operated with a dedicated EI source in positive ion mode. A Multiple Ion Detection (MID) method was used for detection and quantification of the PCP.

Table 2.4 Pentachlorophenol MID method

	Retention time (min)	Quant. Ion (m/z)	Conf. Ion (m/z)
¹³ C ₆ -pentachlorophenol	24.84	271	286
pentachlorophenol	24.85	265	280

The following operating conditions were employed:

- GC conditions:
 - Column - DB 1, 30m, 0.25 ID
0.25 µm film thickness
 - Column temperature - 30 °C held for four minutes
30-270 °C at 8 °C/min. ramp
held for 10 minutes
 - Injection volume - 1 µl
- MS conditions:

	EI	CI
Filament trap current, µamps	150	350
Electron energy, eV	70	70
Source temperature, °C	200	200

Tuning and mass calibration was carried out using heptacosane (perfluorotributylheptacosamine) which was bled into the source via a heated septum inlet.

- MID conditions:

	EI	CI
Sampling time, ms.	80	80
Stabilisation time, ms.	20	20
MS peak width, amu	1	1

General Survey Analysis

Two separate 1-litre sub-samples were taken at each of the four sampling sites for broad spectrum GC-MS screening. The sub-samples were preserved by acidification and spiked with a mixture of deuterated internal standards on site.

The sub-samples were extracted with dichloromethane (1 x 100 ml, 2 x 50 ml) by vigorous shaking in a glass separating funnel and concentrated to 100 µl. One of the sub-samples was basified to pH 14 (with 5M KOH) and the other acidified to pH 2 (with 5M HCl) prior to extraction. The acidic extract obtained should contain both the acidic and neutral compounds present in the 10-litre bulk-sample whereas the basic extract should contain the basic and neutral compounds. The rest of the methodology was the same as described in the previous Interim Report (DoE Report N^o DoE 3108; NRA Report N^o 393/2/NW).

The extract of the acidified Fazakerley STW sub-sample had very high concentrations of organics which resulted in saturation of the ion current when a 1 µl aliquot was examined on GC-MS. The extract was therefore diluted by a factor of ten and re-examined.

Table 2.5, below, shows the sample codes of the extracts analysed and should be used as a guide for the results table, Table 3.5.

Table 2.5 Table showing samples analysed and their respective sample codes

Sample code	Sample description	Comments
FS1	Fazakerley STW (basic)	Re-analysed x10 dil.
FS2	Fazakerley STW (acidic)	-
CB1	Clockhouse Br. (basic)	-
CB2	Clockhouse Br. (acidic)	-
AP1	Altmouth PS. (basic)	-
AP2	Altmouth PS. (acidic)	-
KB1	Kirkby Brook (basic)	Failed AQC
KB2	Kirkby Brook (acidic)	Failed AQC

Total Organic Carbon (TOC)

The analytical methodology employed was the same as described in the previous Interim Report (DoE Report N^o DoE 3108; NRA Report N^o 393/2/NW).

NRA Analytical Methodology

NRA received the samples from WRc and extracted them as soon as possible after delivery.

Red List Organics

The sample extracts from the survey were analysed by GC-MS (ITS40, positive ion EI) and screened for the following Red List compounds:

alpha-HCH
simazine
atrazine
HCBD
HCB
endosulphan
p,p-DDE
lindane
aldrin
endrin
trifluralin
PCP

Pentachlorophenol

The sample extracts were also screened for PCP by GC-MS (Incos, positive ion EI, MID).

2.2 Analysis of sediments collected 19 February 1992

2.2.1 Red List Organics

Preliminary investigations have been carried out to develop a method to simultaneously analyse for a wide range of Red List organics in sediment samples. A complex multi-step method has been tested (a schematic of the method is included in the previous Interim Report - DoE Report N° 3108; NRA Report N° 393/2/NW). The sediment extracts contained a large amount of interferents (e.g. lipids, fulvic and humic acids) and required a two-stage clean-up using gel permeation chromatography followed by florisil column chromatography. Initial method test results suggest that this method is not suitable for all of the Red List chemicals. The chemicals on the Red List have a wide range of physicochemical properties which makes development of a single method for their analysis in complex sample matrices very difficult. Future sediment method development will therefore focus specifically on the chemicals selected for the detailed sources and fates study.

2.2.2 Pentachlorophenol

PCP has been continually found in water samples analysed by NRA at reasonably high levels (see Table 1.1) and its high literature log K_{ow} of 5.12 (Hansch and Leo 1985) suggests that it would also be present at high levels in the bed sediment. A method was therefore developed for the analysis of PCP in sediments.

Soxhlet extraction has been successfully employed to recover 85% of PCP from sediments (Lee *et al* 1987). However, as steam-distillation has been found to be both a more efficient extraction procedure for certain compounds and to produce a relatively clean extract, it was decided that this technique would form the basis of initial development work.

A sample of wet sediment (25 g) was spiked with 1 μg $^{13}\text{C}_6$ -PCP (the surrogate internal standard), mixed with a spatula and left for one hour. The spiked sediment was then added to 250 ml of double distilled water and the mixture was acidified to pH 2 with concentrated sulphuric acid in a distillation flask. Pre-extracted sodium chloride (2 g) was added and the mixture refluxed with hexane (70 ml) for three hours in a macro-steam distillation apparatus. The extract was then concentrated to 1 ml using a Zymark Turbovap.

The 1 ml hexane extract was diazotised with 1 ml of freshly prepared ethereal diazomethane. The extract and diazomethane were shaken together in a vial and left for five minutes. Excess diazomethane was then removed under a stream of dry nitrogen gas and the extracts were further concentrated. The concentrated extracts were analysed by GC-MS using the method described in Section 2.1.2.

Sediment dry weight determinations were carried out on 25 g aliquots of wet sediment. Sediment concentrations were presented in weight of PCP per kg of dry sediment.

3. RESULTS

3.1 Results from the July survey

3.1.1 WRc Results

Tables 3.1 to 3.4, below, contain WRc results for Red List organics (including PCP) and Total Organic Carbon.

GC-MS general survey results are summarised in Table 3.5 which provides a list of compounds identified in the extracts of the eight sub-samples and an indication of the approximate concentrations and as such cannot be used for accurate quantitative comparisons. The extract of the acidified Altmouth Pumping Station sub-sample and both extracts of the two Kirkby Brook sub-samples produced chromatograms with poor sensitivity, poor peak shapes and low levels of internal standards. These samples were re-run on a new column but the chromatograms showed little improvement and few compounds were subsequently identified in these extracts. One possible reason for the poor chromatograms is the presence of highly polar acidic organics and this possibility could be addressed by methylating the sample and re-analysing.

Table 3.1 WRc Results for Red List Organics in River Alt Catchment 27/28 July Analysis:
GC-MS (Positive Ion EI, MID)

Sampling site	Sample type	Concentrations (ng l ⁻¹)	
		Atrazine	Simazine
Fazakerley STW	Composite	310	38
Fazakerley STW	Grab	280	190
Clockhouse Br.	Grab	130	12
Altmouth P.S.	Composite	700	110
Kirkby Brook	Grab	8100	**

Note

** Simazine ion (m/z=201) cannot be separated from atrazine ion (m/z=201) because of the high level of atrazine in the sample extract and because of poor chromatographic separation. Baseline separation is usually achieved between atrazine and simazine in water sample extracts but was not possible in this extract because of the high level of atrazine relative to simazine and the large number of other compounds present.

**Table 3.2 WRc Results for Red List Organics in River Alt Catchment 27/28 July Analysis:
GC-MS (Negative ion CI, MID)**

Sampling site	Sample type	Concentrations (ng l ⁻¹)			
		Lindane	Malathion	Dieldrin	Fenitrothion
Fazakerley STW	Composite	28	17	ND	ND
Fazakerley STW	Grab	26	12	ND	ND
Clockhouse Br.	Grab	23	17	ND	ND
Altmouth P.S.	Composite	15	ND	4.6	ND
Kirkby Brook	Grab	26	ND	8.0	28

ND = Not Detected

**Table 3.3 WRc Results for PCP in River Alt Catchment 27/28 July 1992 Analysis:
GC-MS (Positive Ion ET, MID)**

Sampling site	Sample type	Concn. (ng l ⁻¹)
Fazakerley STW	Composite	900
Fazakerley STW	Grab	990
Clockhouse Br.	Grab	890
Altmouth P.S.	Composite	500
Kirkby Brook	Grab	580

Table 3.4 WRc Results for Total Organic Carbon (TOC) in River Alt Catchment 27/28 July

Sampling site	Sample type	Concn. (mg C l ⁻¹)
Fazakerley STW	Grab	27
Clockhouse Br.	Grab	34
Altmouth P.S.	Composite	76
Kirkby Brook	Grab	25

Table 3.5 Table summarising GC-MS general survey results

Compound(s)	Concentration/identification in sample extract ($\mu\text{g l}^{-1}$)						AP1	AP2
	FS1	FS2	CB1	CB2	KB1	KB2		
Trimethyloxirane	-	-	1	-	-	-	-	-
Dimethylpentane	-	-	-	-	-	<1	-	-
Toluene	-	-	2	2	-	2	3	20 ⊗
Cyclopentanone	-	-	1	-	-	-	-	-
Dimethylhexane	-	-	-	-	-	-	1	-
C2-C5 Alkylbenzenes	2-20	<1-70	<1-80	<1-60	<1-5	<1-5	-	7
Decane	-	-	-	-	-	5	6	-
Triethylphosphate	-	-	-	-	-	-	<1	-
Atrazine	-	-	-	-	15	10	-	-
Phthalates	-	-	-	-	-	<1	2-4	-
Methylheptanone	-	6	2	4	-	-	-	-
Methylstyrene	1	15	3	2	5	-	-	-
Naphthalene	3	2	7	5	-	<1	-	- ⊗
Methylnaphthalenes	5-7	5-10	5-10	40	-	<1	-	-
Dichlorobenzonitrile	-	-	-	-	-	5	-	-
Siloxanes	-	-	<1	1	-	-	-	-
Biphenyl	10	25	-	20	-	1	-	-
Dimethylnaphthalenes	1-6	15	6	1-6	-	<1	-	- ⊗
C3-alkylnaphthalenes	<1	-	-	-	-	-	-	-
p-toluenesulphonic acid, methyl ester	10	-	-	-	-	-	-	-
Fluorene	2	1	<1	<1	-	-	-	-
Hexadecane	4	-	-	-	-	-	-	-

Table 3.5 continued

Compound(s)	Concentration/identification in sample extract ($\mu\text{g l}^{-1}$)							
	FS1	FS2	CB1	CB2	KB1	KB2	AP1	AP2
C17-C19 Linear alkylbenzenes	1-3	1-2	1	1	-	<1-2	2-8	<1-2
Hexadecanoic acid	-	-	-	-	-	100	-	-
Octadecanoic acid	-	-	-	-	-	90	-	-
Phenanthrene	-	1	-	1	-	-	-	-
Anthracene	-	1	-	1	-	-	-	-
Caffeine	20	1	1	-	-	<1	-	-
Diethylphthalate	30	5	2	40	140	70	10	5
Squalene	-	-	10	-	-	-	-	-
Coprostanol	40	40	40	15	-	14	13	-
Cholesterol	50	60	70	40	-	30	14	-

3.1.2 NRA Results

NRA screened for a range of Red List organics by GC-MS (+EI full-scan) but did not detect any of the compounds in the sample extracts above a detection limit of $0.1 \mu\text{g l}^{-1}$. However, PCP was detected in the sample extracts by positive ion EI using a MID method (a more sensitive technique).

Table 3.6 NRA Results for PCP in River Alt Catchment 27/28 July 1992 Analysis: GC-MS (Positive ion EI, MID)

Sampling site	Sample type	Concn. (ng l^{-1})
Fazakerley STW	Composite	500
Fazakerley STW	Grab	510
Clockhouse Br.	Grab	470
Altmouth P.S.	Composite	130
Kirkby Brook	Grab	260

3.2 Results for PCP in sediments collected 19 February 1992

Table 3.6, below, contains the concentrations of PCP found in the bed sediment samples collected in the February survey.

Table 3.7 PCP Results for Bed Sediments Collected from the River Alt catchment 19 February 1992

Sampling site	Concn. ($\mu\text{g kg}^{-1}$)
Maghull Bridge	30
Golf Course Bridge	140
Kirkby Brook	14
Brookside	15
Downholland Brook	1
Alt Bridge	350
Altmouth P.S.	45

4. DISCUSSION OF RESULTS

4.1 WRc Positive Ion EI Data

Of the eleven Red List organics analysed for by this technique only atrazine and simazine were present in detectable levels in the five samples examined.

There were particularly high levels of atrazine in the samples taken at Altmouth Pumping Station (700 ng l^{-1}) and Kirkby Brook (8100 ng l^{-1}). These sample extracts are being diluted and re-analysed in order to confirm the atrazine results.

The concentrations of the compounds in the composite sample taken from the STW effluent stream compare well with the concentrations in the grab sample taken at Clockhouse Bridge. This is expected because the flow of the river at Clockhouse Bridge comprises over 90% STW effluent. The concentration of simazine in the grab sample taken from the STW effluent stream is significantly different from the concentration of simazine in the composite sample but it is possible that a slug of simazine was leaving the works when the grab sample was taken.

It was not possible to quantify simazine in the sample taken at Kirkby Brook because of the high level of atrazine in this sample. The atrazine ion ($m/z=201$) overlapped the simazine quantitation ion ($m/z=201$) causing interference.

4.2 WRc Negative Ion CI Data

Of the 21 Red List organics analysed for by this technique only lindane, malathion, fenitrothion and dieldrin were present at detectable levels.

Lindane was detected in all the River Alt samples at similar levels ($15 - 28 \text{ ng l}^{-1}$). Negative ion CI was used in preference to positive ion EI for quantification of lindane because of the higher sensitivity of negative ion CI for analysis of organochlorine compounds.

Malathion was detected at low level in the samples taken from the STW effluent and at a similar level in the sample taken at Clockhouse Bridge.

Dieldrin and fenitrothion were detected at low level in Kirkby Brook. Dieldrin was also detected in the samples taken upstream of Altmouth Pumping Station.

4.3 WRc PCP Data for water samples

PCP was detected in all of the water samples at similar levels ($0.5 - 0.9 \mu\text{g l}^{-1}$) and these results are of the same order of magnitude as NRA data (Table 3.5). In order to provide further statistical analysis of results a more extensive intercomparison exercise would be required which would involve the analysis of a large number of replicated samples.

4.4 Total Organic Carbon (TOC) Data

The concentrations of TOC in the samples are higher than those measured in the February survey with a particularly high TOC concentration (76 mg l^{-1}) found in the composite sample taken at Altmouth Pumping Station.

4.5 NRA Analytical Data

NRA did not detect any Red List organics by their general screening (full scan) GC-MS method. This is not unexpected because of the relatively low sensitivity of this screening technique when compared to -CI methods. However, it is unusual that atrazine was not detected in the samples taken at Kirkby Brook and Altmouth Pumping Station as it was found at a very high level in these samples by WRc.

The NRA reported PCP concentrations ($0.1 - 0.5 \text{ } \mu\text{g l}^{-1}$) are a little lower than the WRc reported concentrations ($0.5 - 0.9 \text{ } \mu\text{g l}^{-1}$). However, the trends observed in NRA PCP results are the same as those observed in the WRc PCP results with highest concentrations being found in the Fazakerley STW effluent samples.

4.6 WRc General Survey GC-MS Data

In contrast to the previous survey the sample extracts contained large amounts of organic material and produced complex and poorly resolved chromatograms which made interpretation very difficult. All sample extracts contained a large background 'hump' believed to be a mixture of branched and cyclic hydrocarbons which was not quantified. The high background in the sample extracts gave rise to a relatively high practical detection limit of $1 \text{ } \mu\text{g l}^{-1}$. Contaminants identified above this $1 \text{ } \mu\text{g l}^{-1}$ level include linear alkyl benzenes (LABs), polycyclic aromatic hydrocarbons, solvent residues, alkanolic acids, steroids and notably atrazine. Atrazine was identified in both extracts of the Kirkby Brook sub-sample at approximate concentrations of 10 and $15 \text{ } \mu\text{g l}^{-1}$ respectively which compares well with the concentration of atrazine ($8 \text{ } \mu\text{g l}^{-1}$) detected in the sub-sample analysed for Red List organics.

Most of the compounds identified in the Fazakerley STW effluent sample extracts were identified at similar levels in the Clockhouse Bridge sample extracts. This is as expected because the flow of the river at Clockhouse Bridge comprises over 90% STW effluent. Natural organic chemicals (e.g. the steroids; cholesterol and coprostanol) and synthetic organic chemicals (e.g. C_{17} - C_{19} linear alkyl benzenes) indicative of STW effluent were found at all of the four sampling sites. However, although useful data has been obtained from this broad screening exercise there are undoubtedly a wide range of contaminants in the extracts which were not identified because they were obscured by the background hydrocarbon 'hump'. In order to identify these compounds further information is required on potential chemical pollutants discharged/used in the River Alt catchment. Analytical methods can then be devised, with dedicated clean-ups, to screen specifically for these compounds.

4.7 PCP data for sediment samples

The highest sediment concentration ($350 \mu\text{g kg}^{-1}$) of PCP was found at Alt Bridge, an area of particularly thick bed sediment. Downstream near the pumping station the concentration is somewhat surprisingly much lower ($45 \mu\text{g kg}^{-1}$). The sediment PCP concentration at Golf Course Bridge, downstream of Fazakerley STW, was also reasonably high ($140 \mu\text{g kg}^{-1}$). This is expected because the STW is thought to be the major source of PCP in the River Alt catchment. Sediment concentrations of PCP at the other sampling sites were relatively low.

5. CONCLUSIONS

1. Results from the Red List screening exercise confirm that atrazine and PCP are important priority contaminants in the River Alt and its main tributaries and should therefore be considered for inclusion in the sources and fates study.
2. Only low or undetectable levels of other Red List determinands were present in the water samples collected during the July survey.
3. PCP was also found to be present in high levels in sediments collected from the River Alt catchment during the February survey.
4. Several of the chemicals identified by GC-MS general survey are candidate EC List I chemicals (i.e. naphthalene, methyl- and dimethylnaphthalenes, toluene, biphenyl, fluorene, phenanthrene and anthracene) and should also be considered for inclusion in the sources and fates study.
5. There are probably further chemicals present in the River Alt catchment suitable for further study which were not identified by the broad screening technique employed. In order to identify these compounds further information is required on potential chemical pollutants discharged/used in the River Alt catchment. Analytical methods can then be devised, with dedicated clean-ups, to screen specifically for these compounds.

6. RECOMMENDATIONS

6.1 Compounds recommended for further detailed study

The River Alt catchment has been selected for the study by the steering committee and sampling and analysis exercises have been carried out. On the basis of these and information from the routine monitoring carried out by NRA the following chemicals have been recommended for further study: atrazine, biphenyl, 1,2-dichloroethane, naphthalene and pentachlorophenol. *tatime?*

These compounds all meet the following four selection criteria, which are derived from the project objectives:

1. They are all priority pollutants.
2. They are all present in the River Alt catchment at suitably high levels to enable adequate fate studies to be carried out.
3. They encompass a wide range of physicochemical properties, potential degradation rates and reactions (see Table 6.1).
4. They are all widely found in UK rivers.

The following sections briefly outline the known uses and possible sources of the selected compounds and their expected behaviour in the aquatic environment is discussed.

6.1.1 Atrazine

Atrazine is a systemic herbicide which acts by inhibiting photosynthesis in the target plants. Typical agricultural application rates are in the range 0.5 to 2.5 kg per hectare although higher application rates are used for total plant control on railway tracks, roadside verges and industrial sites. Atrazine is not now manufactured in the UK and its usage in non-agricultural situations has recently been restricted. Its major release to river systems will undoubtedly be from diffuse sources. Atrazine is moderately water soluble (28 mg l^{-1} ; Kidd and James 1991) and has a low affinity for natural suspended solids ($\log K_{oc} \sim 2$; Pereira and Rostad 1990; Apte and Rogers 1992). River concentrations of atrazine are likely to increase considerably after storm events and higher river concentrations of atrazine would be expected in the summer and autumn when application rates of the chemical are likely to be greatest.

Atrazine was found in most of samples from all three WRC surveys of the River Alt catchment. In the July survey atrazine was found at $8 \mu\text{g l}^{-1}$ in a grab sample taken at Kirkby Brook. Residues of atrazine are widely found in surface waters in both the UK and the rest of Europe.

Atrazine can be degraded by micro-organisms (Erickson and Lee 1989) but only undergoes hydrolysis under acidic conditions ($\text{pH} < 5$) and it is not particularly

photolytically labile. It therefore seems likely that atrazine will only slowly be removed from the aquatic environment and long surface water half lives of 10 to 200 days (Howard *et al.* 1991) have been reported under various conditions.

Water samples can be analysed for atrazine by WRC's method for semi-volatile Red list organics. Quantification is carried out by GC-MS (MID, positive ion EI). Analysis of sediment samples can be carried out by Soxhlet extraction, extract clean-up by column chromatography and quantification by GC-MS.

Table 6.1 Physicochemical data for selected compounds

Contaminant	H (Pa.m ³ mol ⁻¹)	log K _{ow}	Estimated t _{1/2} in surface water*	Potential sources to River Alt
atrazine	3.1 x 10 ^{-4a}	2.63 ^b	10 - 200 days ^c	Land runoff
biphenyl	2.0 x 10 ^{1d}	4.01 ^e	1.5 - 7 days ^c	Landfill site leachate to STW, Hydrocarbon residues
1,2-dichloroethane	9.2 x 10 ^{1f}	1.48 ^g	5.8 days ^h	Intermediate in vinyl chloride manufacture, solvent usage
naphthalene	4.9 x 10 ¹ⁱ	3.59 ^j	20 days ^c	Hydrocarbon residues
pentachlorophenol	4.9 x 10 ^{-2g}	5.12 ^k	1 hr - 4.6 days ^c	Landfill site leachate to STW

Notes:

* Data represent overall decay rates. The wide spread of values for some contaminants reflects the variability of field data

a Kidd and James (1991)
b Isnard and Lambert (1988)
c Howard *et al* (1991)
d Fendinger and Glofelty (1990)
e De Bruijn and Hermens (1990)
f Volskay and Grady (1988)

g WHO (1987)
h Ambrose (1987)
i Shorten *et al* (1990)
j Travis and Arms (1988)
k Hansch and Leo (1985)

6.1.2 Biphenyl

Uses of biphenyl include: as a dye carrier; as a heat transfer agent; as an impregnate in citrus fruit manufacture where it acts as a mild fungicide; in the manufacture of plasticisers; and in optical brighteners (Weaver 1979). Biphenyl is also a by-product of several important industrial processes, notably in: the manufacture of high octane motor fuels; catalytic cracking to form lighter gasoline components; and as a high boiling point component of coal tar, a component which is often used in the manufacture of creosote.

Biphenyl's range of uses suggest that release to the aquatic environment, from both point and diffuse sources, will be of concern. However, few data exist to quantify biphenyl's presence therein. A potential source to the Alt catchment is the leachate from the landfill site in Kirkby. Also, biphenyl in Fazakerley STW may have originated from local petrochemical companies as biphenyl is present as a by-product, in the wastewater produced during the manufacture of hydrocarbon fuels.

Mackay (1975) investigated the evaporation of low-solubility contaminants from water bodies to the atmosphere. The half-life of biphenyl in water 1 m deep was estimated to be 7.5 hours. Baily (1983) investigated the ability of river water to biodegrade biphenyl. The times required to biodegrade 50% of biphenyl from various starting concentrations were reported as $1 \mu\text{g l}^{-1}$, 1.5 days; $10 \mu\text{g l}^{-1}$, 2 days; and $100 \mu\text{g l}^{-1}$; 3 days. Overall half-lives in surface water of 1.5 days to 7 days have been reported (Howard *et al.* 1991). Biphenyl has an intermediate partition coefficient ($\log K_{ow}$ of 4.01; De Bruijn and Hermens 1990) and therefore has a moderate tendency to accumulate in sediments and biota.

Analysis of biphenyl in water and sediment samples can be carried out by solvent extraction, extract clean-up by column chromatography and quantification by GC-MS (MID, positive ion EI).

6.1.3 1,2-Dichloroethane

1,2-Dichloroethane, one of several volatile organochlorines on the Red List, is manufactured in very large quantities (ca. 5 million tonnes per year). It is mainly used as an intermediate, particularly in vinyl chloride manufacture, so production volume in this case is misleading as an indicator of environmental release. Other uses of the chemical are as a solvent and as a fumigant for stored grain and these are likely to be the major diffuse sources to the environment (Crathorne and Dobbs 1990).

1,2-Dichloroethane has been regularly found by NRA in samples taken from Fazakerley STW and Altmouth Pumping Station (see Table 1.1). Mean concentrations of this compound in samples taken by NRA are as high $40 \mu\text{g l}^{-1}$ at Fazakerley STW and $9 \mu\text{g l}^{-1}$ at the downstream Altmouth Pumping Station.

The major properties determining its environmental fate are its high vapour pressure (8.53 kPa at 20 °C; WHO 1987) and its moderate water solubility (8.69 g l^{-1} ; Volskay and Grady 1988) which together result in a high volatilisation rate from water. Biodegradation is slow and sediment sorption is low so the dominant loss processes in rivers is likely to be volatilisation.

Analysis of samples of water for dichloroethane can be undertaken by solvent extraction and gas chromatography but its high volatility can cause problems with the extraction and concentration stages. A better approach is to exploit its high volatility and utilise head space or purge and trap techniques coupled with analysis with GC-MS. WRc have a purge and trap GC-MS based method for the analysis of dichloroethane.

6.1.4 Naphthalene

Naphthalene is a constituent of crude and refined oil-water mixtures and pulverised coal, and it is acutely toxic to fish and other aquatic life at relatively low concentrations (Rodgers *et al.* 1983). GC-MS general survey analysis of samples from Fazakerley STW and Clockhouse Bridge (immediately downstream) indicate that naphthalene is input from the STW into the River Alt catchment at $\mu\text{g l}^{-1}$ levels.

The principle loss of naphthalene from river waters is due to volatilisation. Naphthalene is resistant to hydrolysis and oxidation but other minor degradation pathways include biodegradation and photolysis (Rodgers *et al.* 1983). A surface water half-life of 20 days (Howard *et al.* 1991) has been reported. Naphthalene has an intermediate partition coefficient ($\log K_{ow}$ of 3.59; Travis and Arms 1988) and will therefore sorb weakly to suspended particulates and bed sediment.

Analysis of naphthalene in water and sediment samples is similar to biphenyl. A deuterated analogue (d_8 -naphthalene) is commercially available which would be an ideal surrogate internal standard for the analysis.

6.1.5 Pentachlorophenol

PCP and its derivatives (sodium pentachlorophenoxide and PCP laurate) are potent, non-selective biocides used extensively in the pulp and paper and wool textile industries, as agricultural pesticides and as intermediates in herbicide production (Wild *et al.* 1992). However, about 80% of the PCP produced is used in the timber industry where it is employed as an as a wood preserver, as a remedial treatment for timber at risk from fungal attack in buildings and as a biocide to treat masonry. The main source in the River Alt catchment is thought to be the leachate from a landfill site in Kirkby.

PCP was found in all of the water samples collected during the July sampling survey and the sediment samples collected in the February sampling survey at high levels. NRA data (Table 1.1) showed that PCP was present in more than 95% of water samples taken weekly, over a three year period, from Fazakerley STW and Altmouth Pumping Station.

In water PCP is expected to be found in the anionic form due to its weak acid (pK_a 4.74) properties. This anionic form (pentachlorophenate anion) absorbs ultraviolet radiation and can thus be photolytically degraded. Fox and Joshi (1984) reported partial degradation of PCP to 2,3,4,6- and 2,3,5,6- tetrachlorophenol by photolytic reductive chlorination. Some PCP may be lost from water by volatilisation, while a small proportion may be microbially degraded (Wild *et al.* 1992). However, most PCP in water will be removed by adsorption onto suspended particles which settle out and are incorporated into the bed

sediment. Surface water half-lives from one hour to 4.6 days (Howard *et al.* 1991) have been reported.

WRC have already developed methods for the analysis of PCP in water and sediment samples. Quantification is carried out by GC-MS (MID, positive ion EI).

6.2 Recommended work programme for sources and fates study

6.2.1 Review of Objectives

The objectives of this contract can be considered as the study of three aspects of pollutant behaviour in water:

- their sources;
- their behaviour;
- their fate.

The field surveys completed so far have provided information relevant to the identification of sources. Further surveys will provide more information and there does not appear to be a problem with meeting the contract objectives on the 'sources' aspect of the contract. The behaviour and fate aspects are more difficult.

The original planning assumption for this study was that we would identify a river with a fairly well established point source of Red List or other priority substances and a downstream run with no significant additional inputs. This would have allowed an in-situ study of the behaviour and fate of the selected chemicals as set out in the contract objectives by following a body of water downstream. This concept was always recognised as being rather idealistic because of difficulties associated with downstream sources and tracing problems. Nevertheless, the strategy has been used successfully in previous studies of this kind carried out for the DoE and NRA.

It was envisaged that a similar approach would be suitable for the River Alt, however, this catchment has turned out to be so far from the conceptual ideal with significant downstream diffuse sources that some other experimental approach is required to address the behaviour and fates aspects of the objectives. Before outlining the approach we would recommend to overcome this difficulty it may be useful to expand on the objectives of the behaviour and fate issues with the aim of providing more generic data that could be applied in other river systems.

The behaviour and fate of chemicals in natural waters can be predicted quite easily using physicochemical constants and simple laboratory experiments. However, there is not a great deal of field derived evidence to support such laboratory predictions and there are many environmental processes which could confound them such as slow equilibration

between environmental compartments, association with natural colloids etc. If we consider the 'behaviour' of chemicals we need answers to the following major questions:

1. Are environmental releases of the chemicals in forms which equilibrate rapidly on release to water bodies? There is some evidence that particulate bound forms may be significant.
2. Is the flowing water essentially at a steady state equilibrium with the bed sediment?
3. Will contaminated sediment reach an equivalent steady state condition if it re-equilibrates with uncontaminated water, and if so over what timescale?
4. Do field K_{oc} values agree with those predicted from K_{ow} or water solubility?

In relation to 'fate' the questions are similar:

5. Do the laboratory predictions of controlling processes match what happens in the field?
6. Can field rates be reasonably predicted? If so, what and how much supporting information is needed?

In order to address these questions we propose field experiments in which changes in concentration with time of the selected chemicals can be followed under realistic conditions but with no possibilities of additional inputs. This will involve isolating large samples of water under *in situ* conditions (mesocosm containers) and monitoring concentration changes.

Samples will be taken periodically from these mesocosms for analysis of the selected compounds. This will be carried out over a timescale appropriate for the time of travel in the River Alt from the Fazakerley STW to the 'estuary' at Altmouth Pumping Station. The sampling frequency would largely depend on the estimated persistence of the contaminants of interest, obtained using physicochemical or available literature information.

This approach will provide information on the fate of selected compounds during transport in the river which can be compared with predicted and published data. A suitable and secure site for the mesocosms would be upstream of the Pumping Station and access to this site would need to be arranged via the NRA with the MoD. Special care will be needed to avoid the mesocosm water transferring to or mixing with external river water when the river level is adjusted by pumping to the estuary. In addition the environmental conditions within the mesocosm and in the river (such as pH, dissolved oxygen, turbidity, wind speed above surface and redox) will be monitored and consideration will be given to problems associated with the collection of representative samples, maintenance of particles in suspension and possibility of sorption losses to containment vessels.

The use of the mesocosm approach where the experimental system is physically isolated from the river, but is subjected to the same environmental conditions means that the range of compounds selected for study can be widened by artificially enriching the water column. Consideration will be given to the addition of selected priority pollutants to the mesocosms to increase the compounds for which fate and behaviour information is obtained. Possible compounds for addition would be γ -hexachlorocyclohexane, PCB 128 and malathion or fenitrothion.

6.2.2 Direction/Revision of Work Programme

1. Select a list of chemicals in collaboration with NRA and DoE for the proposed mesocosm study which are: i) naturally present in the Alt at sufficiently high levels for study; and ii) to be added to the mesocosms.

It is important that the selected chemicals are naturally present/introduced at a sufficiently high level to the mesocosms to produce reliable behaviour and fate information. For example, it is important that the minimum change in concentration which can be detected by the analytical method is not a significant proportion of the total concentration present.

2. Complete a thorough literature review for the selected compounds and collate physicochemical and persistence data. Any gaps in physicochemical data and fate information will be identified and if necessary supplemented with laboratory studies.
3. Use the collated physicochemical data to calculate the partitioning and fate of the selected chemicals using simple models.
4. Carry out field mesocosm experiments using the following experimental design:

Mesocosms will consist of plastic tanks containing 100 litres or more of water. The plastic tanks will be cleaned and leached in the laboratory and installed in the River Alt in metal support cages which will be anchored to the river bed or banks. The containers will be filled with river water on site and stirred intermittently for a period of a couple of hours to equilibrate the container surfaces. The containers will then be emptied and experiments will be performed on: i) natural river water; (ii) enriched natural river water; and synthetic river water with added surficial bed sediment collected from the Alt.

(i) The container will be filled with river water, stirred and a sample taken for analysis of selected compounds present in River Alt water. A further four samples will be taken for analysis at intervals over a period equivalent to the time of travel of river water in the Alt. The container will be stirred immediately prior to each sampling event and samples will be preserved in a way appropriate to the subsequent analysis.

The results will be used to determine field half-lives for the selected compounds which will be compared with calculated or published half-lives.

(ii) The container will be prepared and filled as for (i) and additional chemicals will be added. This enrichment will be carried out using concentrated solutions of the chemicals dissolved in a small volume of a water soluble (or miscible), volatile solvent to provide appropriate concentrations in the water to enable their fate to be monitored. The container will be stirred and a sample taken for analysis of the added chemicals. Further samples will be taken as in (i) and all samples will be preserved in a way appropriate to subsequent analysis.

The results will be used to determine half-lives for the added chemicals and these field values will be compared to calculated or published half-lives.

(iii) A mesocosm will be established in the Alt using surficial bed sediment and synthetic river water. Sufficient bed sediment to form a settled layer of approximately 2 cm depth in the container will be mixed with the water and then left to settle. After settling, the water will be sampled and analysed for the selected compounds. The mixing/settling sampling regime will be repeated a further two times. The concentration present in the mesocosm water column after mixing will be compared with that measured in the river water.

The results will provide information on the desorption of chemicals from contaminated sediments and indicate whether the bed sediment and water column concentrations are at equilibrium in the river water.

5. Bed sediment and equivalent river water samples will be collected and analysed for the selected compounds (where this information has not already been produced). The bed sediment concentrations expected under equilibrium partitioning conditions will be calculated from the measured water column concentrations and published values for $\log K_{ow}$ (or $\log K_{oc}$ if available). Comparison of the measured and calculated sediment concentrations will establish whether the water and sediment concentrations are in equilibrium.
6. Partitioning experiments will be carried out in the laboratory subject to the availability of ^{14}C -radiolabelled analogues of the selected compounds. Water and bed sediments will be collected from the Alt and will be mixed to provide model samples with different solids loadings. Labelled contaminants will be added and samples taken periodically and the radioactivity in the 'dissolved' phase measured. This approach will provide complementary information on the rate of attainment of partitioning equilibrium as this aspect would not be readily addressed in the mesocosm experiments.
7. Compare laboratory predictions and field values and where possible rationalise any differences. If necessary, revise field and laboratory protocols and perform further experiments.
8. An overall assessment of the fate and behaviour of the selected compounds in the Alt will be made using the field and experimentally derived data and predictions from simple models. A comparison of these approaches will be made to determine the feasibility of using simple predictions based on contaminant concentrations and

published physicochemical data as an alternative to field measurements to provide realistic estimates of the fate of organic chemical pollutants.

9. Report findings.

6.3 Timescale for work programme

November 1992

DoE and NRA to consider recommendations and advise WRc as to acceptability of the strategy to achieve revised objectives. DoE, NRA and WRc to consider the new work programme in contract terms and make contract revisions if necessary.

November 1992

Complete physicochemical and persistence data compilation and identify gaps in/or limitations of information.

November 1992 - August 1993

Establish mesocosm experiments in the Alt catchment. Carry out *in situ* partitioning and fate studies on selected priority pollutants. Identify gaps in physicochemical data and fate information and if necessary supplement field measurements with laboratory studies.

August - September 1993

Assess the utility of simple modelling approaches for contaminant fate prediction with consideration for other types of contaminant and or/river system.

REFERENCES

- Ambrose, R.B. Jr. (1987) Modelling volatile organics in the Delaware estuary, *Journal of Environmental Engineering, ASCE*, **113**, 703-721.
- Apte, S.C. and Rogers, H.R. (1992) Speciation and partitioning of atrazine and gamma-hexachlorocyclohexane in estuarine waters, *Science of the Total Environment* (in press).
- Baily, R.E., Gonsior, S.J. and Rhinehart, W.L. (1983) Biodegradation of monochlorobiphenyls and biphenyl in river water, *Environmental Science and Technology*, **17**, 617-621.
- Cheeseman, R.V. and Wilson, A.L. (first published 1976; revised June 1989 by Gardner, M.J.) A manual on analytical quality control for the water industry. WRC Technical Report (NS 30), WRC plc, Medmenham, PO Box 16, Marlow, Buckinghamshire SL7 2HD.
- Crathorne, B. and Dobbs, A.J. (1990) Chemical pollution of the aquatic environment by priority pollutants and its control. Chapter 1 In: *Pollution: causes, effects and control - 2nd edition*, edited by R.M. Harrison, The Royal Society of Chemistry, Thomas Graham House, Science Park, Cambridge CB4 4WF.
- Erikson, L.E. and Lee, K.H. (1989) Degradation of atrazine and related s-triazines, *Critical Reviews in Environmental Control*, **19**, 1-14.
- De Bruijn, J. and Hermens, J. (1990) Relationship between octanol/water partition coefficients and total molecular volume of hydrophobic organic chemicals, *Quantitative Structure-Activity Relationships*, **9**, 11-21.
- Fendinger, N.J. and Glotfelty, D.E. (1990) Henry's law constants for selected pesticides, PAHs, and PCBs, *Environmental Toxicology and Chemistry*, **9**, 731-735.
- Fox, M.E. and Joshi, S.R. (1984) The fate of pentachlorophenol in the Bay of Quinte, Lake Ontario, *Journal of Great Lakes Research*, **10**, N^o 2, 190-196.
- Hansch, C. and Leo, A.J. (1985) *Medchem Project*. Claremont, CA: Pomona College. Issue No. 26.
- Howard, P.H., Boethling, R.S., Jarvis, W.F., Meylan, W.M. and Michalenko, E.M. (1991) *Handbook of environmental degradation rates*. Lewis Publishers, Inc. 121, South Main Street, Chelsea, Michigan 48118, USA.
- Isnard, P. and Lambert, S. (1988) Estimating bioconcentration factors from octanol-water partition coefficient and aqueous solubility, *Chemosphere*, **17**, N^o 1, 21.

Kidd, H. (Ed.) and James, D.R. (Ed.) (1991) *The Agrochemicals Handbook - Third Edition*. The Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 4WF.

Lee, H., Stokker, Y.D. and Chau, A. (1987) Analysis of phenols by chemical derivatisation, V. Determination of pentachlorophenol and 19 other chlorinated phenols in sediments, *Journal of Associated Official Analytical Chemists*, **70**, N° 6, 40-44.

Mackay, D. and Leinonen, P.J. (1975) Rate of evaporation of low-solubility contaminants from water bodies to the atmosphere, *Environmental Science and Technology*, **9**, 1178-1180.

Pereira, W.E. and Rostad, C.E. (1990) Occurrence, distributions and transport of herbicides and their degradation products in the lower Mississippi River and its tributaries, *Environmental Science and Technology*, **24**, 1400-1406.

Rodgers, J.H., Dickson, K.L., Saleh, F.Y. and Staples, C.A. (1983) Use of microcosms to study transport, transformation and fate of organics in aquatic systems, *Environmental Toxicology and Chemistry*, **2**, 155-167.

Shorten, C.V., Elzerman, A.W. and Mills, G.L. (1990) Methods for the determination of PAH desorption kinetics in coal fines and coal contaminated sediments, *Chemosphere*, **20**, (1-2), 137-159.

Travis, C.C. and Arms, A.D. (1988) Bioconcentration of organics in beef, milk, and vegetation, *Environmental Science and Technology*, **22**, 271-274.

Volskay, V.T. Jr. and Grady, C.P.L. Jr. (1988) Toxicity of selected RCRA compounds to activated sludge microorganisms, *Journal of the Water Pollution Control Federation*, **60**, 1850-1856.

Weaver, W.C., Simmons, P.B. and Thompson, Q.E. (1979) Diphenyl and terphenyl, *The Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Ed, vol 7, New York, Wiley-Interscience, 782-789.

World Health Organisation (WHO) (1987) Environmental Health Criteria 62 on 1,2-dichloroethane, *International Programme on Chemical Safety*, World Health Organisation, Geneva 1987.

World Health Organisation (WHO) (1987) Environmental Health Criteria 71 on pentachlorophenol, *International Programme on Chemical Safety*, World Health Organisation, Geneva 1987.

Wild, S.R., Harrad, S.J. and Jones, K.C. (1992) Pentachlorophenol in the UK environment I: A budget and source inventory, *Chemosphere*, **24**, N° 7, 833-845.