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Organochlorine Pesticide Residues in Water and Sediments from the Ovens and King Rivers, North-East Victoria, Australia

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Abstract. Water and sediment samples were taken from five sites on the Ovens and King Rivers (Australia) and analyzed for organochlorine pesticides residues. Residue concentrations were also determined in water samples taken at two hourly intervals during a 32-h storm flow event on the Ovens river. Residues detected in the rivers were most likely transported from surrounding land and upstream sources. The concentrations of DDE, DDT, and dieldrin residues were not different in different depositional areas, although increased proportions of DDD were found in sediments in the quiescent areas of the rivers. More than 70% of the dieldrin residues were found in the unsettled sediment fraction. Changes in flow during the storm event had a marked effect on the residues detected in the water column. DDT was present in largest amounts, which was most likely due to its association with nonfilterable organic matter.

Australian studies have reported detectable levels of pesticide residues in rivers and other waterways (SPCC 1980; Thoma 1988; Bennison *et al.* 1989; Fitzpatrick and Sutherland 1983; McKenzie-Smith 1990; Hill and Nicholson 1992). The detection of organochlorine residues in the aquatic environment led to widespread concern over environmental and human health issues.

In the Ovens and King region in North-East Victoria, Australia, organochlorine pesticides were intensively used to control various pests associated with tobacco cultivation. Tobacco crops are grown on the narrow flood plains extending from the Ovens, Buffalo, Buckland, and King Rivers (Figure 1). The area under cultivation varies, although the crop is generally confined to the river flats. In some cases, crops have extended to the river banks. Up to 4,000 ha were under cultivation during the 1960s and 1970s when organochlorines were being applied intensively in accordance with registered uses for pest control. DDT 1,1′(2,2,2-trichloroethylidene)bis[4-chlorobenzene], and dieldrin 3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,dimethanonaphth[2,3-b]oxirene) were prohibited from use on tobacco crops in Victoria in 1981.

The current study was designed to investigate patterns of occurrence and distribution of organochlorine residues in the sediments and waters of the Ovens and King Rivers.

Methods

Site Location

Three sites were sampled on the Ovens River: Porepunkah (site 1), adjacent to the Ovens Research Station (site 2) and at Myrtleford (site 3). There were two sites on the King River: at Edi (site 4) and Cheshunt (site 5; Figure 1). Between Porepunkah and Myrtleford the Ovens River has a cobble bed with some gravel. The bed and banks are stable with some riparian vegetation along the banks at each site. The King River bed is predominantly small cobbles and gravel. There is a wide riparian strip at site four and some riparian vegetation at site five.

Sediments

Sediments were collected at each of the five sites during February 1990. At each site areas were chosen according to the amount of fine sediment deposited: (i) *depositional* where there was a substantial accumulation of fine material and usually little or no gravel or cobbles, (ii) *non-depositional*, predominantly cobbles and interstitial gravel but no accumulation of fine material (usually in riffles or fast current flow), and (iii) *semi-depositional*, fine sediment between or on the cobble bed (generally backwaters with little or no flow). Three replicate samples were taken in each area using a cylindrical scoop (1905 cm^3) with a 250 μm mesh screen fixed inside the scoop 10 cm above the base with a cap over the end. Sediments were scooped from along the river bed to an average depth of 10 cm. The scoop generally contained 70–80% sediment and water. Samples were processed on site by sieving into stainless steel basins using only the water which was taken at the time of sampling. The <250 μm portion was allowed to settle for 10 min, the supernatant decanted off and the settled material collected (settled sediment fraction). The supernatant was then homogenized and approximately 500 ml was retained (unsettled sediment fraction). Each fraction was analyzed separately. Due to the lack of sediment less than 250 μm in diameter in the non-depositional areas, two samples were collected and combined before processing.

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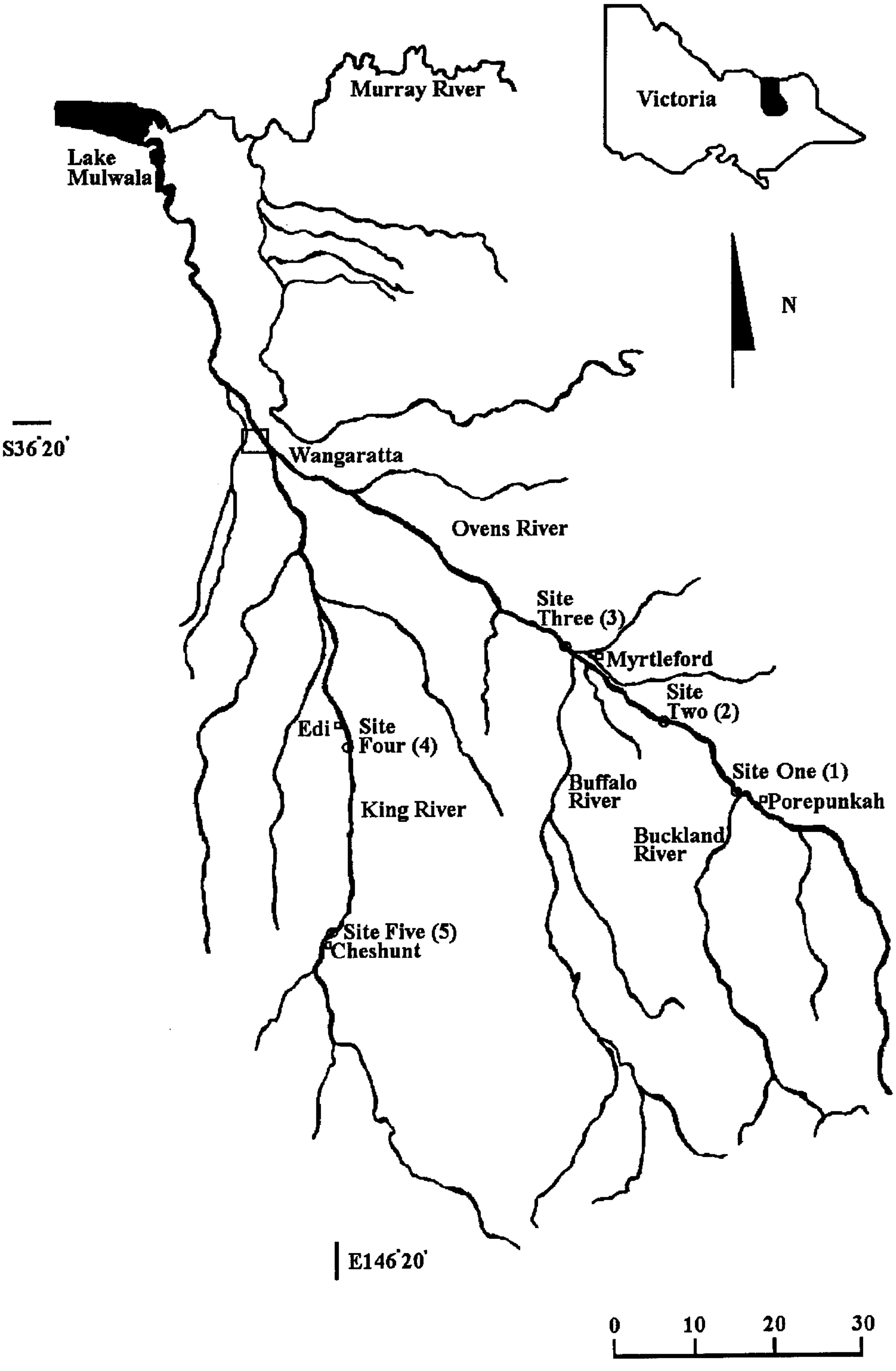

Fig. 1. Map of the Ovens and King rivers region showing site locations for sediment and water samples

Data for DDE, DDD, and DDT were converted to proportions of the total concentration (TDDT), to remove the effect of absolute concentration differences at the sites. These data were compared, using a nonparametric Kruskal-Wallis test.

Seastar™ In Situ *Samplers*

The water column was sampled, using *in situ* Seastar samplers, which pump water through a column of XAD-2 resin. Each sampler was fitted with a filter disc (Whatman 1.2 μm glass fiber filter paper, Green 1986, Seastar Instruments Ltd. 1987). Seastar samplers were deployed at sites 2, 3, and 4 in February 1990. At each site, four Seastar samplers were deployed as follows: (i) in fast current areas, (ii) in an area of little or no current, and (iii) two seastars in slow current areas within the main channel. The Seastar samplers were stationed at each site for an average of 70 hours, pumping at a rate of 150 ml/min. One XAD-2 column was used for the duration of the sampling and filter papers were changed every 24 h. The Seastars pumped an average volume of 177 L of water through each column and 51 L over each filter paper.

The data for Seastar samples were derived from two quantitative analyses: residues recovered from the XAD-2 columns and residues associated with the particulate residue and filter papers. Results were calculated from the total mass of residue recovered from the sample divided by the litres of water pumped for that sample with filter and column results added to give a final result. Data from the filter residue component of Seastar samples were compared using analysis of variance and data from XAD-2 columns compared using a Kruskal-Wallis test.

Storm Event Sampling

A storm event was monitored over 36 h, beginning at 0630 h on June 7, 1991 and concluding at 1430 h on June 8, 1991 at sites 2 and 3 on the Ovens River. Turbidity and total organic carbon (TOC) were measured at both sites every 4 h. Streamline™ automatic water samplers were deployed at both sites to take one 300-ml sample every 40 min. Three consecutive samples were combined to give approximately 1-L samples, each sample representing an integrated sampling time of 2 h. Two Seastar samplers were also deployed at each site. Filter papers were changed every 4 h and XAD-2 columns changed every 8 h. Each unit was in operation continuously over the sampling period at a pumping rate of 150 ml/min. At site 2 an average of 66 L and at site 3 36 L of water were pumped over each column. Site 2 averaged 33 L of water per filter paper compared with site 3, 18.5 L.

Chemical Analysis

Water samples were extracted with dichloromethane (3 × 100 ml). The combined extracts were dried over anhydrous sodium sulphate prior to concentration and inversion into hexane in Kuderna-Danish concentrators for clean-up by Florisil® column chromatography. Residues were determined by gas chromatography with electron capture detection (GC-EC) on a Perkin Elmer 8500 gas chromatograph with a pre-column split to allow for dual column–dual detector operation. Columns used were (i) DB17 15 m × 0.32 mm ID 0.25 μm (ii) DB225 15 m × 0.32 mm ID 0.25 μm. Sediments and filter papers were air dried, moistened with water, and extracted with acetone/hexane (20/80) prior to work-up and analysis as described for water extracts. XAD-2 columns were eluted according to the procedure described in "Trace organic extraction columns," File SR-16 Seastar Instruments Ltd. (1987). The analytical procedures used would have detected organochlorine residues eluting between HCB and methoxychlor. Reagent blanks and spiked recovery samples were analyzed with each batch of samples extracted. Reagent blanks were generally clear, except for a low background interference for dieldrin in the filters, for which a blank correction was applied. Recoveries for DDE, DDD, DDT, and dieldrin were generally greater than 90% for all sample matrices; the results presented are uncorrected for percentage recovery. The limits of detection obtained were: sediments, 1 ng/g dry weight basis; XAD-2 columns, <0.02 μg (dependent on interferences from individual columns); filters, <0.005 μg and water samples.

Results

Sediments

Residues of dieldrin and total DDT (DDT and its metabolites DDE and DDD) were detected in sediment samples at all sites (Total DDT (TDDT) N = 84, dieldrin N = 84). No other organochlorine residues were detected. For all results, only *p,p*-isomers of DDT and its metabolites were detected. Site two had the highest mean concentration of TDDT (31.9 ng/g) and site one the lowest (6.3 ng/g). The mean concentration of TDDT residues at site three was 24 ng/g and site four 25 ng/g. Dieldrin was found at levels considerably lower than TDDT but in the same order of magnitude. The maximum dieldrin concentration (42 ng/g) was measured at site 1 (mean 6 ng/g). Sites 2 and 4 averaged approximately 5 ng/g and sites 3 and 5, 3 ng/g (Figure 2).

There were no significant differences ($p > 0.05$) between DDD, DDE, or DDT concentrations measured in the two fractions of sediment samples. Forty-five percent, 44%, and 46% of DDD, DDE, and DDT residues, respectively, were found in the unsettled material (Figure 2). The ratios of the metabolic breakdown products of TDDT in settled and unsettled fractions were also similar: Settled: DDD 14%, DDE 45%, DDT 41%. Unsettled: DDD 14%, DDE, 47%, DDT 39%. There was a significant difference ($p < 0.01$) for dieldrin between sediment fractions with the unsettled material accounting for 79% of the dieldrin detected in sediments (Figure 2).

There were no significant differences ($p > 0.05$) in the proportion of DDE and DDT to TDDT between the three types of depositional areas sampled (Figure 2). There was a significant difference ($p < 0.01$) in proportion of DDD between the three areas. DDD was a greater proportion of the total concentration in depositional areas. There were no significant differences ($p > 0.05$) between any of the sites for proportions of DDD, DDE, and DDT. For dieldrin there were no significant differences ($p > 0.05$) between concentrations detected in each of the depositional areas (Figure 2).

Seastar Samples

Dieldrin and TDDT were detected in Seastar samples at each of the three sites sampled (TDDT N = 12, dieldrin N = 12). No other organochlorine residues were detected. Site 2 had the highest concentrations of TDDT (maximum 1.4 ng/L, mean 1.27 ng/L), measured in a sample from an area of slow current flow. Sites 3 and 4 had mean TDDT concentrations of 0.95 ng/L and 0.73 ng/L, respectively. The highest dieldrin concentrations were also measured at stie 2 (maximum 1.21 ng/L in the fast current area, mean 0.98 ng/L). Sites 3 and 4 had similar dieldrin concentrations with means of 0.77 ng/L and 0.60 ng/L, respectively. The ratios of the metabolic products of TDDT from Seastar samples were similar to those found in sediments, although there was some increase in the amount of DDD and DDT compared to DDE (DDD 18%, DDE 40%, DDT 42%). DDD varied as a percentage of TDDT associated with filter residue compared to that collected on the XAD-2 columns. The metabolic composition of the filter residue was DDD 13%, DDE 41%, and DDT 46% while for XAD-2 columns it was DDD 24%, DDE 32%, and DDT 43%. The proportion of residue concentrations from Seastar samples which were associated with filter residue were DDD 52%, DDE 72%, DDT 72%, and dieldrin 73% (N = 37).

A comparison of DDD, DDE, DDT, and dieldrin residue concentrations was made between the areas of different current velocities where the Seastar samplers were deployed. There were no significant differences ($p > 0.05$) found between areas with different current velocities for any of the residues detected on either XAD-2 columns or filter residue.

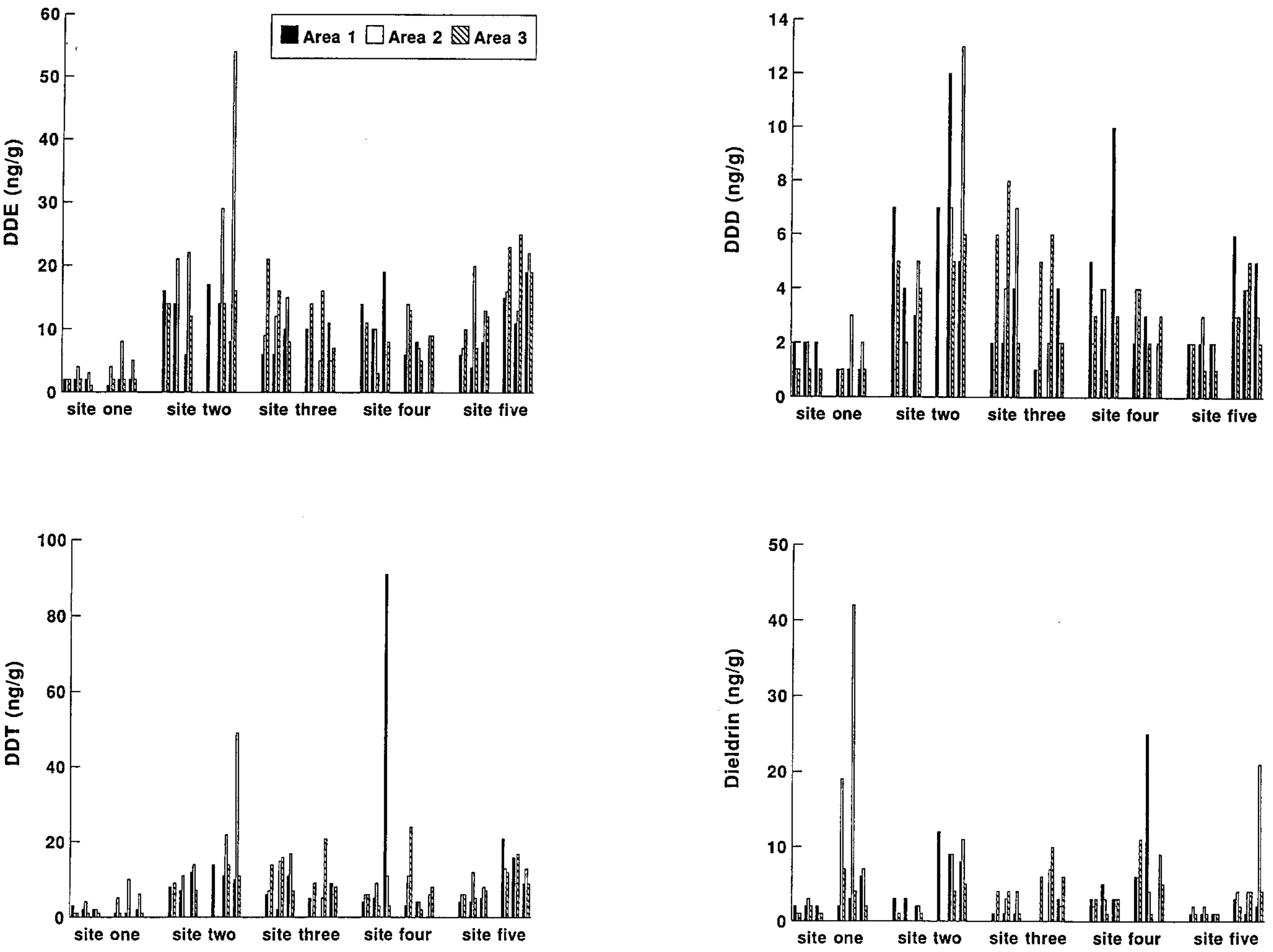

Fig. 2. Concentrations of DDE, DDD, DDT and dieldrin residues in the sediments (<250 μm) from five sites. Samples are from areas with different amounts of deposited sediment within a reach at a site. Area 1 = depositional, area 2 = non-depositional, area 3 = semi-depositional. For each site the first cluster of bars represents the concentration of residues in the settled material of the processed sediment sample and the second cluster are from the unsettled material

Storm Event

The mean daily flows measured during the storm event at Myrtleford, upstream of site three, were 186 Ml (06/06/91), 275 Ml (07/06/91), 446 Ml (08/06/91) and 383 Ml (09/06/91). Turbidity was lower at site 2 than at site 3. Turbidity rose at site 3 to a maximum of 15 nephelometric turbidity units (NTU) at 12 h and gradually fell to 5.7 NTU. At site 2, turbidity peaked at 5.1 NTU at 16 h and declined to 4 NTU (Figure 3). Sites 2 and 3 had similar levels of TOC, although site 3 was consistently higher for up to 28 h. Site 3 had a maximum TOC concentration of 5 mg/L on three occasions. A maximum of 4 mg/L TOC was recorded on four occasions at site 2 in the latter 16 hours of the storm event (Figure 3). There were detectable levels of TDDT and dieldrin residues in all water samples collected from both sites during the storm event (Table 1). No other organochlorine residues were detected. With the exception of one outlier, the data show the residues at site 2 to be generally lower than at site 3 (Table 1). At site 2, between 6 and 16 h, the mean concentration of TDDT was 5.0 ng/L (N = 5 outlier excluded). An anomalous high concentration (342 ng/L TDDT) was detected at 8 h. Notably, this was the only water sample which contained metabolic residues of DDT (Table 1). The maximum residue concentration measured at site three was 16 ng/L of DDT in one sample at 6 h. The mean concentration of TDDT residues (8.6 ng/L) detected in the first 16 h of the storm event at site 3, was higher than in the latter 16 h (6.0 ng/L; N = 8, Table 1). Dieldrin was detected only once at site 2, at 10 h (Table 1). At site 3, dieldrin was detected in each sample in the first 12 h of sampling.

Seastar samples contained TDDT and dieldrin residues. No other organochlorine residues were detected. DDT, as in the water samples, was predominant (Table 1). The maximum residue concentration (59 ng/L TDDT) was detected at site 3 during the first 8 h of the event. Only this sample had an appreciable concentration of metabolic residue (Table 1). At site 2, a maximum concentration of 31 ng/L TDDT was also detected during the first 8 h. A second DDT peak of 22 ng/L was observed between 16 and 24 h (Table 1). At this site, with the exception of a result at 8 h, data are available for one seastar only due to equipment failure. Dieldrin was detected in all Seastar samples from both sites at concentrations higher than those found using Seastar samplers during base flow conditions. With two exceptions, the concentrations at site 3 were

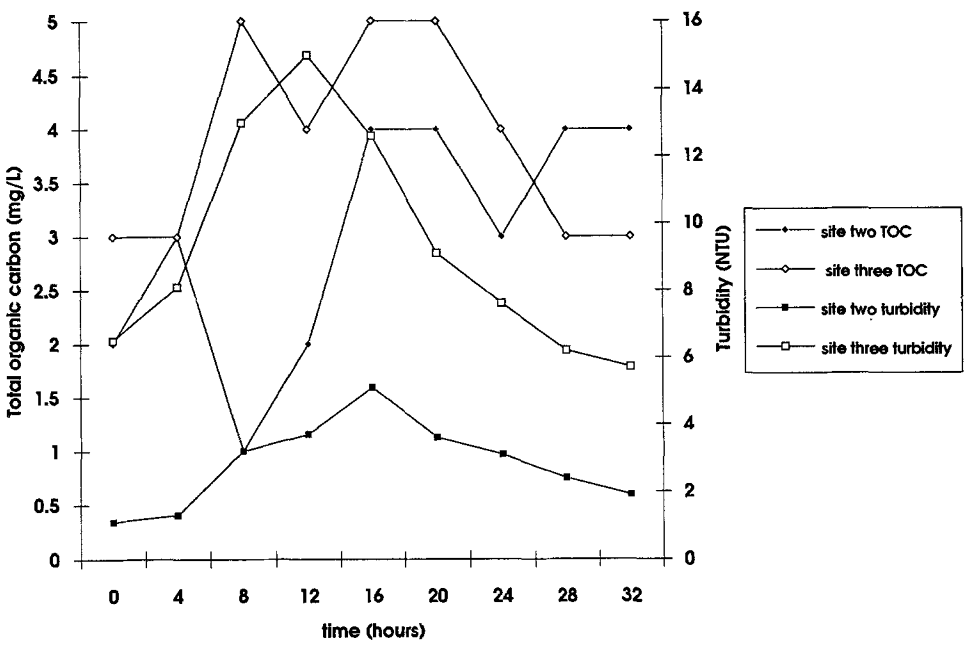

Fig. 3. Four hourly measurements of total organic carbon (TOC) and turbidity at sites 2 and 3 during the storm event

Table 1. Concentrations of DDD, DDE, DDT, total DDT, and dieldrin residues (ng/L) in water and Seastar samples during the storm flow event

	Time (h)	DDD	DDE	DDT	Dieldrin		DDD	DDE	DDT	Dieldrin
Site **two**	2	NA^a	NA	NA	NA	Site **three**	ND	ND	5.3	1.0
	4	NA	NA	NA	NA		ND	ND	4.0	2.3
	6	ND^a	ND	6.1	ND		ND	ND	16	2.4
	8	ND	2.0	340	ND		ND	ND	11	1.6
	Seastar	ND	1.4	1.99	1.09		0.40	0.46	6.69	1.92
	Seastar	1.97	2.37	26.22	0.45		2.86	5.2	50.79	2.01
	10	ND	ND	3.0	ND		ND	ND	14	2.3
	12	ND	ND	2.2	1.8		ND	ND	2.2	1.0
	14	ND	ND	1.9	ND		ND	ND	13	ND
	16	ND	ND	5.1	ND		ND	ND	3.1	ND
	Seastar	NA	NA	NA	NA		ND	0.35	2.16	1.81
	Seastar	0.42	ND	5.61	0.36		ND	0.83	8.35	2.66
	18	NA	NA	NA	NA		ND	ND	12	ND
	20	NA	NA	NA	NA		ND	ND	6.1	ND
	22	NA	NA	NA	NA		ND	ND	3.7	ND
	24	NA	NA	NA	NA		ND	ND	4.0	ND
	Seastar	NA	NA	NA	NA		ND	0.3	1.38	1.86
	Seastar	ND	NA	22.38	0.70		ND	0.15	2.11	1.44
	26	NA	NA	NA	NA		ND	ND	3.8	ND
	28	NA	NA	NA	NA		ND	ND	3.0	ND
	30	NA	NA	NA	NA		ND	ND	11	ND
	32	NA	NA	NA	NA		ND	ND	4.4	ND
	Seastar	NA	NA	NA	NA		ND	ND	1.67	1.30
	Seastar	ND	NA	2.05	NA		ND	NA	2.22	0.89

^{a}NA = not available, ND = not detected

three to four times higher than at site 2 (Table 1). This contrasts with base flow conditions where site 2 concentrations were markedly higher than site 3 (Figure 2). The amount of DDT associated with filter residue was 17% at site 2, and 61% and 29% at site 3. For dieldrin, 100% of the residue was associated with the filter at site 2 and at site 3 (a) 62% and (b) 64%.

The composition of the metabolic breakdown products of TDDT measured in samples collected during the storm event were different compared with those measured during base flow. DDT made up 99% of TDDT detected in water at site 2 and 100% at site 3. For Seastars DDT was 91% at site 2 and 88% at site 3 of the total residues detected.

Discussion

Residues Occurring in the River Environment

The occurrence of TDDT and dieldrin residues in the Ovens and King Rivers is to be expected given the previous widespread intensive use of organochlorine pesticides and the levels of residues which have been detected in soils from the region (Victorian Department of Agriculture and Rural Affairs 1991, pers. comm.; McKenzie-Smith 1990). The concentrations of TDDT in the sediment are in the same order of magnitude as those measured in previous Ovens and King Rivers studies. Dieldrin residues were detected with greater frequency in this study than in previous studies although, the few historical data available show that they are of the same order of magnitude (Fitzpatrick and Sutherland 1984; McKenzie-Smith 1990). The differences in the frequency of detection of dieldrin residues is most likely a result of inclusion of the unsettled material in sediment samples for analyses. Seventy-nine percent of dieldrin was found in this fraction (Figure 2).

The position of a site with respect to upstream land use influenced the concentrations detected due to instream transport of residues. Site 5 has a riparian zone, and the adjacent land is grazing pasture which would minimize runoff. Upstream, however, there are extensive areas used for tobacco farming. There is a riparian zone at site 3 with adjacent land being used for pondage on the right bank and predominantly forestry on the left bank. At this site, the major source of organochlorine residues would be expected to have come from upstream, *i.e.*, from site 2. The low concentrations of TDDT detected in sediments at site 1 reflect its position, upstream of all major tobacco farming areas. The high dieldrin concentration detected at this site cannot be explained.

Sediment samples from sites 2 and 4 had the highest detected concentrations of TDDT. Historically, organochlorine pesticides were applied to the land immediately adjacent to these sampling sites. Site 4 had the highest average concentrations of dieldrin in sediments. This site was adjacent to a property which was previously a tobacco farm. Dieldrin was used on this property while it was under cultivation and dieldrin residues in the soil and stock were of particular concern when the property was turned over to grazing (property owner, confidential pers. comm., 1990).

Distribution of Residues Within the River Environment

Sediments: Sediments contained >99% of the residues detected during this study which is comparable with other studies of residues in water and sediments (Miles and Harris 1973; Frank *et al.* 1974; Colombo *et al.* 1990; Gilliom and Clifton 1990). While there have been many studies which correlate residues with fine sediments, there have been few reports showing that these residues correspond specifically with depositional areas in rivers (Routh 1972; Lopez-Avila and Hites 1980). The majority of work contrasting sediment deposition areas has involved lakes (Frank *et al.* 1981a; Allan 1986; Eadie and Robbins 1987). In this study, residues in sediments (<250 μm) from areas within a reach of the river which differed in the quantity and composition of deposited material were compared. The DDE and DDT proportions and dieldrin concentrations in sediments from different depositional areas were not significantly different. However, there was a significant difference in the proportion of DDD to TDDT between the areas, with DDD found in greatest proportions in the depositional areas. This result suggests that either preferential deposition or breakdown of DDD, compared with DDE and DDT, occurs in depositional areas. The highest proportion of DDD was found at site 1. Residues at this site may have been transported further than at other sites as there is no potential for contamination apparent upstream. If the residues had been transported some distance, then an increase in the proportion of DDD could be explained by the longer residence time in the river. Miles (1976) found an increase in the ratio of DDD to DDT from source to river mouth and attributed this increase to longer contact time of adsorbed DDT residues with anaerobic organisms. Other workers have attributed higher proportions of DDD to TDDT compared with DDE to TDDT to the presence of anaerobic conditions (Harris and Miles 1975; Colombo *et al.* 1990; Ramesh *et al.* 1991).

Concentrations of DDD in filter residue (Seastar samples) accounted for approximately 50% of the DDD measured compared with 65% for DDE, DDT and dieldrin. This suggests that DDD, when compared to DDE and DDT in the aqueous phase, was being preferentially transported in <1.2 μm filtrate. Miles (1976) found an average of 47% of the DDD was sorbed to particulate matter in whole water samples. This may have resulted in an increased proportion of DDD in the depositional area where finer material is known to settle preferentially.

Seastars: The data obtained using Seastar samplers were consistent with the sediment data. Overall differences in the concentrations of dieldrin compared with TDDT were similar for both matrices as were the ratios of the metabolic products of TDDT. The highest concentrations of TDDT detected in sediments and using Seastar samplers were from site 2.

It was hypothesized that within a reach of river, sampling different current velocities could yield varying amounts of pesticide residue. The results show there were no significant differences for any compound found in the filter residue or on columns in areas of different flow characteristics. This could have been due to a more homogeneous distribution of particulate matter than expected since the reaches sampled were relatively small and the differences in flow characteristics localized.

The distribution of dieldrin residues between the columns and filter residues was different from expected. Miles (1976) reported that an average of 13% of dieldrin in unfiltered water samples was associated with particulate matter, although there was a considerable range in the data. Miles (1976) also found an average of 47% of DDD and >60% DDE and DDT were associated with particulate matter which is consistent with results from the Seastars. Considering Miles' (1976) data, and that dieldrin has the smallest octanol-water partition coefficient of the compounds detected, it was expected that a considerable proportion of the dieldrin residue would be found on the XAD-2 column. This was not found as 73% of the dieldrin residues were detected in the filter residue. Without further investigation there is no apparent explanation for the discrepancy between these results.

It is noted that the partitioning of residues on Seastar samplers, compared to actual partitioning in the aqueous phase, may be spurious. Aggregation of particles may result in desorption as a function of the *solids concentration effect* (Elzerman and Coates 1987). The importance of aggregation on filters has not been determined for Seastar samplers.

Storm Event: For both water and Seastar samples, the concentrations of residues detected during the storm event confirm the importance of these high flow events in transporting pesticide residues (Allan 1986). Cooper *et al.*, (1987), Frank *et al.*, (1981b), and Trulhar and Reed (1976) observed higher concentrations of TDDT during periods of runoff. Associated with these events was a marked increase in the amount of suspended particulate matter. Cooper *et al.* (1987) and Truhlar and Reed (1976) found, however, only limited correlation between particulate matter and residue concentrations with no correlation at all in some streams.

In this study, the higher average concentrations of both dieldrin and TDDT detected in water samples and Seastar samples at site 3 during the first 16 h of the high flow event coincided with peaks in turbidity. However, two further peaks of TDDT occurred at site 3 after 16 h, and these were not related to turbidity. At site 2, the TDDT peaks which occurred in the Seastar and whole water samples were not related to the turbidity measured as there was only a minor increase in turbidity from background levels, even though the river level had risen measurably. The anomalous concentration of DDT (340 ng/L) measured at site 2 at 8 h may be attributable to a flushing effect (SPCC 1980). A comparable slug occurred at this site during storm flow conditions in 1989 (3,800 ng/L DDT; McKenzie-Smith 1990).

The residues detected at times of low turbidity may have been associated with dissolved organic material or other forms of organic matter including colloidal material, humic substances, and macromolecules. These, collectively referred to as nonfilterable organic matter (NOM), may form an association with residues analogous to their association with particulate material (Carter and Suffet 1982; Gschwend and Wu 1985; McCarthy and Black 1988); NOM are normally included as part of the solution phase as they are not necessarily removed by centrifugation or filtration (Gschwend and Wu 1985).

Assuming NOM are in dynamic equilibrium (Riley 1970 and Sheldon *et al.* 1973 cited in Gschwend and Wu 1985) conditions of high flow may have caused a flux in NOM. The variation in TOC measured during the event supports this suggestion, although no direct relationship can be implied. Observations of the river during the storm event showed variation in discharge which could account for the peaks in residues not associated with turbidity. With the exception of the DDT peak which occurred at 30 h (site 3), the residue peaks observed in both whole water and Seastar samples occurred while the river was rising at site 2. Although the river had not measurably risen after 16 h at site 3, it was noted that there was an increase in width and the current was markedly stronger. This is supported by the hydrographic data.

The proposition of an association between DDT and NOM is supported by the distribution of DDT residues from Seastar columns compared to filter residue and the frequency with which DDT was detected. From Seastar samplers operating in normal flow conditions an average 28% of DDT residues were measured on the column compared with 83%, 71%, and 39% when operating in high flow. Although some of the residues detected on the columns may have initially been sorbed to particulate matter <1.2 μm, the contrast in DDT distributions between base flow and high flow could suggest that there was a greater association with NOM.

The predominance of DDT residues measured during high river flows has been observed in other studies (Frank *et al.* 1981b; Gilliom and Clifton 1990; McKenzie-Smith 1990). The ratios of metabolic products of TDDT detected during the storm event were different from those detected in sediments and by using Seastars during base flow. Of the total residues detected, DDT was 99% and 100% of TDDT in unfiltered water samples from sites 2 and 3, respectively, and 93% and 90% from Seastar samplers at sites 2 and 3, respectively. DDT was approximately 40% of residues in sediments and 45% of residues in Seastar samples during base flow. DDT, because of its greater partition coefficient, may have become more readily associated with the NOM than other compounds. Gschwend and Wu (1985) and others (McCarthy and Black 1988) demonstrated that NOM accounted for the solids concentration effect. This effect is an inverse relationship between sediment concentration and partition coefficient most pronounced for compounds with large partitioning (O'Conner and Connolly 1980). It could be reasoned that DDT having a greater partition coefficient, compared to the other compounds measured in this study, would be detected most frequently.

In conclusion, this study has shown TDDT and dieldrin, are widespread in the Ovens and King rivers. Concentrations detected in the water column and in sediments generally reflected upstream and adjacent land use practices. At base flow the results suggest sediments would be the most useful matrix for the determination of concentrations and distribution of residues within the river environment, although this study has highlighted the potential for inacurracy in residue measurement depending on the sampling method. Storm event flow represented a major contrast to base flow in the distribution of residues. These differences should be emphasized where concentrations in the water column and impact of residues on the environment are being assessed. This information should be useful in determining sampling methods in field studies and in the interpretation and modelling of pesticide residue data derived from a river environment.

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References

Allan RJ (1986) The role of particulate matter in the transport and burial of contaminants in aquatic ecosystems. In: Hart BT (ed) The role of particulate matter in the transport and fate of pollutants. Water Studies Centre Chisholm Institute of Technology, Melbourne, Australia

Bennison GL, Hillman TJ, Suter PJ (1989) Macroinvertebrates of the Murray River (Survey and Monitoring 1980–85). Murray-Darling Basin Commission Canberra, Australia

Carter CW, Suffet IH (1982) Binding of DDT to dissolved humic materials. Environ Sci Technol 16:735–740

Colombo JC, Khalil MF, Arnac M, Horth AC, Catoggio JA (1990) Distribution of chlorinated pesticides and individual polychlorinated biphenyls in biotic and abiotic compartments of the Rio de La Plata. Environ Sci Technol 24:498–505

Cooper CM, Dendy FE, McHenry JR, Ritchie JC (1987) Residual pesticide concentrations in Bear Creek, Mississippi, 1976 to 1979. J Environ Qual 16:69–72

Eadie BJ, Robbins JA (1987) The role of particulate matter in the movement of contaminants in the Great lakes. In: Hites RA, Eisenrich J (eds) Sources and fates of aquatic pollutants. American Chemical Society, Washington, DC

Elzerman AW, Coates JT (1987) Hydrophobic organic compounds on sediments: Equilibria and kinetics of sorption. In: Hites RA, Eisenrich SJ (eds) Sources and fates of aquatic pollutants. American Chemical Society, Washington, DC

Fitzpatrick CR, Sutherland PD (1983) Pesticide transport from intensive agricultural catchments. Paper presented at Hydrology and Water Resources Symposium 1983, Hobart Australia, November 8–10

Fitzpatrick CR, Sutherland PD (1984) Pilot survey of pesticide residues in rivers in the tobacco growing regions of North-East Victoria. EPA 83/1296, unpublished data. Environment Protection Authority, Victoria, Melbourne, Australia

Frank R, Montgomery K, Braun HE, Berst AH, Loftus K (1974) DDT and dieldrin in watersheds draining the tobacco belt of Southern Ontario. Pest Monitor J 8:184–201

Frank R, Thomas RL, Braun HE, Gross, DL, Davies TT (1981a) Organochlorine insecticides and PCBs in the surficial sediments of Lake Michigan (1975). J Great Lakes Res 7:42–50

Frank R, Braun HE, Holdrinet MVH (1981b) Residues from past uses of organochlorine insecticides and PCB in waters draining eleven agricultural watersheds in Southern Ontario, Canada 1975–77. Sci Total Environ 20:225–276

Gilliom RJ, Clifton DG (1990) Organochlorine pesticide residues in the bed sediments of the San Joaquin River, California. Water Resources Bull 26:11–24

Green DR (1986) An advanced water sampling system for *in situ* concentration of trace compounds from water. Available from Seastar Instruments Ltd, PO Box 2430, 2045 Mills Road, Sidney, British Columbia, Canada, V8L3S1

Gschwend PM, Wu S (1985) On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. Environ Sci Technol 19:90–96

Harris CR, Miles JRW (1975) Pesticide residues in the Great Lakes region of Canada. Residues Rev 57:27–79

Hill HS, Nicholson BC (1992) Pesticides in the River Murray. Report to the Murray-Darling Basin. Australian Centre for Water Treatment and Water Quality Research Canberra, Australia

Lopez-Avila V, Hites RA (1980) Organic compounds in industrial wastewater. Their transport into sediments. Environ Sci Technol 14:1382–1390

McCarthy JF, Black MC (1988) Partitioning between dissolved organic macromolecules and suspended particulates: Effects on bioavailability and transport of hydrophobic organic chemicals in aquatic systems. In: Adams WJ, Chapman GA, Landis WG (eds) Aquatic toxicology and hazard assessment: 10th Volume. American Society for Testing and Materials, Philadelphia, PA

McKenzie-Smith FJ (1990) Biocide contamination in the aquatic environment. A study of the Ovens and King Rivers region. Scientific Report Series SRS 90/004 Environment Protection Authority, Victoria, Melbourne, Australia

Miles JRW (1976) Insecticide residues in stream sediments in Ontario, Canada. Pest Monitor J 10:87–91

Miles JRW, Harris CR (1973) Organochlorine residues in streams draining agricultural, urban-agricultural and resort areas of Ontario, Canada 1971. Pest Monitor J 6:363–368

O'Connor DJ, Connolly JP (1980) The effect of concentration of adsorbing solids on the partition coefficient. Water Res 14:1517–1523

Ramesh A, Tanabe S, Murase H, Subramanian AN, Tatsukawa R (1991) Distribution and behaviour of persistent organochlorine insecticides in paddy soil and sediments in the tropical environment: A case study in South India. Environ Pollut 74:293–307

Routh JD (1972) DDT residues in Salinas River sediments. Bull Environ Contam Toxicol 7:168–177

Seastar Instruments Ltd (1987) Seastar *in situ* water sampler Model A300 operations and maintenance manual. Seastar Instruments Ltd, PO Box 2430, 2045 Mills Road, Sidney, British Columbia, Canada, V8L 3S1

SPCC (1980) Namoi Environmental Study. State Pollution Control Commission New South Wales. Issued under the authority of the Hon. Eric Bedford, BA, MP, Minister for Planning and Environment

Thoma K (1988) Pilot survey of pesticide residues in streams draining a horticultural catchment, Picadilly valley, South Australia. Technical Paper No. 131, Department of Agriculture, South Australia

Truhlar JF, Reed LA (1976) Occurrence of pesticide residues in four streams draining different land-use areas in Pennsylvania, 1969–71. Pesticides Monitoring J 10:101–110