CRDC Final Report

A Review of the Dynamics of Endosulfan Partitioning Between Sediments and Water

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TABLE OF CONTENTS

SUMMARY

The cotton industry remains heavily dependent on endosulfan for early season insect control. Endosulfan is particularly effective in Integrated Pest Management programs but it is regularly detected in river water above ANZECC guidelines in greater than 50% of samples during the cotton growing season. The cotton industry has recently agreed to meet reduction targets for endosulfan residues of 25% in three years and 50% in six years in the river systems in cotton-growing areas. The issue of sediment-bound endosulfan and possible adverse effects on macroinvertebrates, particularly benthic organisms, has regularly been raised by regulatory authorities.

This project was designed to:

- Review all available sources of analytical and research data regarding the binding and potential for remobilisation of endosulfan on bottom sediments
- Based on the results of the review and data analysis, make recommendations regarding future research requirements

Based on the survey the following conclusions can be made:

- Contamination of sediments by endosulfan is a normal occurrence where significant residues are transported from sites of application to rivers in runoff. However, there is no compelling evidence available of widespread ecological hazards from storage of endosulfan at high concentrations in sediments. No such cases of long-term storage have been reported.
- Contamination of sediments does occur at a moderate level near application points, with transient ecotoxicological effects, but there are no reports in the literature of major contamination of water resulting from subsequent mobilisation of endosulfan stored in sediments.
- The current concern regarding possible storage of endosulfan in sediments would most effectively be countered if carefully targeted research were conducted.
- It is recommended that research should be conducted to determine the probable size of the pool of residues present in sediments and to measure the rate and extent of partitioning of endosulfan residues in sediments into the water column. This study would best be achieved in farm reservoirs because of the uncertainty of riverine systems.

From this on-farm research to provide quantitative data, convincing modelling of the degree of contamination of the water column possible in river systems could be performed, with targeted field validation. A study of the possibility of reducing river sediment contamination from engineering works on farms designed to reduce flow rates of run-off leading to sedimentation would also be of practical remediation value.

BACKGROUND

The cotton industry remains dependent on endosulfan for early season insect control. Endosulfan is particularly effective in Integrated Pest Management (IPM) programs and there is no direct substitute with similar properties. However, the monitoring program conducted by the Department of Land and Water Conservation (DLWC) on behalf of the irrigation water users regularly detects endosulfan in river water samples in the Namoi, Gwydir and Macintyre Valleys well above ANZECC guidelines of 0.01 µg/L as part of the Central & North West Regions Water Quality Program (CNWRWQP). This monitoring survey, funded jointly by a voluntary levy on waters users and the Department, has provided valuable information for the development of Best Management Practices in the cotton indnstry aiming to reduce its impact on riverine ecosystems. Even in the winter non-spraying season of 1996-97, 17% of the river samples exceeded the guideline (Muschal, 1997; Cooper and Muschal, 1998), because of the persistence of endosulfan sulphate, a more stable metabolic product of the alpha- and beta-isomers contained in endosulfan formulations. On the other hand, there is possibly a trend towards reduced residues in river water since the early 1990s (Cooper and Muschal, 1998), even accounting for the effects of drought. In the early 1990s this trend may have commenced by a reduction of the number of 'leakage'points from cotton farms to the river system. It is logical that discrete work behind the scenes by the DLWC may have resulted in better compliance by cotton farmers with the voluntary retention of contaminated tail waters on farm. We have observed the positive effect of such pressure in a number of cases in the Namoi Valley and no doubt the diligence of DLWC field officers has multiplied this effect elsewhere across all river systems. However, the contribution of 'leakage points' to the contamination of river systems by cotton pesticides cannot be evaluated without a comprehensive audit by DLWC.

The introduction of transgenic Ingard cotton containing the Bt toxin commercially in the 1996-97 season and the expansion in its use since has allowed a reduced number of endosulfan applications, possibly by 25% overall. This factor has no doubt contributed to reduced source pressure for contamination of the river system. Despite these improvements, the negative experience of the 1998-99 cotton growing season with heavy insect pressure and substantial endosulfan use has shown that there is still potential for contamination of the riverine environment.

The cotton industry agreed in 1998 with the National Registration Authority (NRA) to meet reduction targets for endosulfan residues of 25% in three years and 50% in six years in the river systems in cotton-growing areas. Potentially, contamination of river sediments poses a problem for the cotton industry if these endosulfan residues in sediments can be re-mobilised after their initial deposition. As a result of the severe beef contamination problem of the 1998-99 cotton growing season and the recommendations arising from the traceback projects that followed (National Residue Survey, 1999; Kennedy, Hugo and Sanchez-Bayo, 1999), less river contamination can be anticipated as a result of the additional restrictions on the frequency of use of endosulfan and the extended buffer zones required to sensitive areas. However, the role of sediments in storing endosulfan sulphate residues and remobilisation still remains an issue and the possible adverse effects on macroinvertebrates, particularly benthic organisms, has regularly been raised by regulatory authorities.

Unfortunately, routine monitoring of endosulfan residues in river sediments has not formed a regular part of the the DLWC's Central and North West Regions Water Quality Program (CNWRWQP). This is mainly because of the difficulty and extra cost of obtaining reliable sediment samples. Sampling from the flowing water column is fairly routine if a well defined protocol is followed, except in very adverse weather conditions. Generating a rigorous protocol for sediment sampling is an extremely challenging problem that is currently not solved, even for lagoons, let alone the dynamic zone of a river bed. There are numerous difficulties to overcome, related to various factors such as the choice of depth of sampling, lack of uniformity in the depth of sampling, the location of sampling points on a stream bed, access and even the successful extraction to the surface of samples from the sediment zone. Anyone who has actually attempted to collect such samples can attest to the extreme measures that need to be taken to obtain them. As a result, sediment samples for pesticide analysis tend to taken spasmodically and yield results of low inherent reliability, much less than for samples from the water column.

PROJECT OBJECTIVES

The objectives of this project were given in the grant proposal as:

- Review all available analytical and research data including that generated in the LWRRDC/CRDC/MDBC joint research program from monitoring conducted by the Department of Land and Water Conservation, studies by the EPA and all other sources regarding the binding and potential for remobilisation of endosulfan on bottom sediments

- Based on the results of the review and data analysis, recommendations will be made regarding future research requirements

Thus, there was no experimental work to be conducted in the project.

METHODOLOGY

This short project has been conducted using both literature review and consultation. For various reasons, there are many inadequacies in the database for the report's topic and a degree of uncertainty as a result. To assist in the task of interpreting the data available, the report includes a range of ancillary material considered relevant.

REVIEW

In early work, both the isomers of endosulfan present in commercial formulations and the sulfate metabolite of endosulfan were found to be more persistent when sorbed to soil and sediment (Van Dyk and Van der Linde, 1976; Rao and Murty, 1980). This finding has been confirmed in Australian research projects conducted for the CRDC and LWRRDC since 1990. We have observed that the beta-isomer, in particular, is strongly sorbed to soil, whereas the alpha-isomer is more prone to early volatilisation, particularly when present at high concentration on the leaf surfaces of cotton plants or on the surface of the soil. Subsequent sorption of both isomers into soil organic matter reduces the access of water to endosulfan, so that volatilisation, hydrolysis and biodegradation will all be reduced in rate.

Of more concern in this report is the behaviour of endosulfan when bound to submerged sediments. Before proceeding to examine this situation, several sources of data regarding the environmental fate of endosulfan should be examined.

Sediment analyses for endosulfan residues

A limited number of river sediment samplings and analyses have been carried out by the DLWC. These have been insufficient to allow accurate conclusions to be made about the general extent of contamination of sediments with endosulfan residues. However, these analyses of sediment samples have not indicated clearly that sediments are a major reservoir for endosulfan residues. For example, in the 1997/98 season, endosulfan isomers were detected (limit of detection LOD 0.002 mg/kg) in only two of 15 sediment samples with endosulfan sulphate found in five of these samples (Muschal, 1998). The range of these values was 0.002 – 0.016 mg/kg (2-16 ppb or µg/kg; 2 ppb LOD), with partial indications that the concentration fell several-fold in samples taken at the same site in January and May. In the 1998/99 season (Muschal, 2000), a similar pattern was observed. On the basis of these results involving sampling several times at about 18 sites it is not possible to be confident that contamination of sediments is never a serious problem. On the other hand, the data are consistent with low levels of contamination in river sediments, normally less that 1% of concentrations in soil on farms and insufficient to cause serious problems by remobilisation in the water column. This situation of uncertainty is highly unsatisfactory, because it still allows periodic claims to be made, although usually without any definitive evidence, that incidents such as fish kills may have resulted from disturbance of contaminated sediments and remobilisation of endosulfan.

Peterson and Batley (1993) examined the fate of endosulfan in aquatic ecosystems in the Namoi Valley, suggesting that endosulfan has the potential to accumulate in sediments. They pointed out that in the alkaline waters of the cotton-growing region, hydrolysis is the dominant degradation process for endosulfan. By this mechanism alone, the expected half-lives for the alpha- and beta-endosulfan isomers were found to be 3.6 days and 1.7 days, respectively. In fact, alpha endosulfan usually disappears more rapidly than the beta isomer because of the greater volatility of the former. Half-lives of both isomers in water are quite short, however, less than a week for both in the summer season. Partitioning studies showed, however, that the major proportion of endosulfan could associate with the sediments (log K_{oc}-alpha, 3.6 and log K_{oc}-beta, 4.3). Field studies using some samples taken during the spraying season, mainly from lagoons located nearby, confirmed the presence of high concentrations of endosulfan in sediments. Microcosm experiments in the laboratory showed that loss of endosulfan was slower than predicted from hydrolysis rates. They presented models explaining how sorption and desorption from sediment could limit the loss of endosulfan from a system. While these possibilities were of interest, there was still little evidence about the degree of persistence on sediments since no long term studies were carried out.

Residues in sediments of tail drains on cotton farms

As part of the program on "Minimising the impact of pesticides on the riverine environment using the cotton industry as a model", funded by LWRRDC, CRDC and the MDBC, sediments in tail drains were examined. Obviously, deposited sediments in tail-drains and return drains will contain endosulfan soon after runoff. Thus, endosulfan residues in the tail drain of field 4 of Auscott, Warren, were significantly higher than in the field immediately after the first two irrigations, declining later until they reached values similar to those in the field. Apparently pesticide was deposited from runoff accumulating to some degree in the tail drain. Later, storm and irrigation waters redistributed the layer of tail drain deposits more heavily loaded with endosulfan. However, when sampled in winter or just before the spraying season from sediments exposed to air, endosulfan residues in the associated return tail-drain of field 21 on Auscott Narrabri were not significantly different from those in the field. There was also no apparent increasing trend of concentration with distance along the drain. A similar correlation of drain sediments with field concentrations was found in tail drain deposits the following year. Clearly, under conditions where sediments are exposed to drying over a period of several months as occurs in return drains on cotton farms, endosulfan residues completely disappear.

Dissipation from a pond

In the concluding stages of the LWRRDC project "Transport and fate of pesticides in cotton production systems: NSW field site and degradation study (USY3)" (Kennedy *et al.*, 1997), a study was conducted of ponded tailwater runoff to analyse the rate of degradation and sedimentation of endosulfan residues. The ponded water initially contained about 200 mg of endosulfan. Three weeks later (13/1/96) the amount of endosulfan in the water column had decreased to about 60 mg, reflecting disappearance of the alpha- and beta-isomers almost entirely. Dissipation followed a two stage process, each phase following first order kinetics with half lives of 1.5 and 7.8 days respectively. A rapid initial dissipation corresponded with the disappearance of alpha- and beta-endosulfan, while the second, slower phase, of the dissipation was dominated by the presence of the more chemically stable endosulfan sulphate remaining in the runoff. Total endosulfan on colloidal and suspended sediment (> 0.7 μm) decreased from 30 mg to 5 mg in that period. At the same time, a sedimentation process was observed to occur on the floor of the pond, with pesticide loads in bottom sediment rising to about 100 mg, almost half of load in the initial runoff (Kimber *et al.*, 1996). The majority of the residues in this sedimented material was endosulfan sulphate. Initially, it was thought that endosulfan sulphate formation occurred mainly on cotton fields, either on foliage or in soil. However, a special study commissioned later by the joint LWRRDC/CRDC/MDBC program has clearly shown (Kennedy *et al.,* 1998) that endosulfan sulphate can be formed directly in water, apparently as a result of the activity of aquatic bacteria. Similar organisms capable of forming endosulfan sulphate have been isolated from soil (Shivaramaiah, 2000). While most of both isomers will be expected to dissipate by volatilisation or hydrolysis, about 15% of the endosulfan residues may be converted to endosulfan sulphate in the water column. As a result of this finding, contamination of river water by endosulfan sulphate cannot be ascribed completely to runoff water in storms. Although this is likely to be the major source of such river contamination, at least a part must now be the result of direct conversion in rivers following aerial drift.

This study clearly indicates a potential for sediments to concentrate residues from the water column, particularly of endosulfan sulphate. Given a half-life of endosulfan sulphate in soil of more than two months (Kennedy *et al.,* 1997) there would appear to be the possibility of similar persistence of endosulfan sulphate in river sediments.

Particle fractionation

Application of a split thin channel fractionation procedure (SPLITT) to Namoi River sediments contaminated with endosulfan allowed the collection of four particle size fractions (Leonard *et al.,*2000) . Endosulfan sorption was significantly concentrated on the large (>63 nm) particle fraction of all sediments, although there was no significant difference in the total organic carbon content of the fractions. The endosulfan isomer ratio (alpha/beta) declined rapidly after its direct application to sediment, mainly due to loss of the alpha-isomer. Laboratory toxicity assessment of endosulfan-spiked sediment using nymphs of the mayfly *Jappa kutera* gave no observable effect in a concentration of 42 μg L^{-1} and a lowest observable effect concentration of 76 μg L^{-1} (wet weight). During a 10-day sediment toxicity test, sediment concentrations of alpha-endosulfan declined, whereas endosulfan sulfate concentrations increased after initially being absent. There were significant linear regressions of total endosulfan and endosulfan sulfate concentrations in the water column after 10 days, with total endosulfan in the bottom sediment. These two concentrations of total endosulfan in the bottom sediment after 10 days corresponded to total endosulfan concentrations in the water column of 0.13 μg L^{-1} and 0.18 μg L^{-1}, respectively. Pulse water-only exposures of *J. kutera* separately to technical grade endosulfan, the alpha-isomer and endosulfan sulfate in Namoi River water gave similar 96-hour values of 0.3 μg L^{-1}, while beta-endosulfan gave a value of 0.9 μg L^{-1}. Changes in the composition of endosulfan compounds measured in sediments and the *in situ* passive samplers placed in the Namoi River adjacent to cotton fields indicated that alpha-endosulfan (somewhat surprisingly) and endosulfan sulfate were the most mobile endosulfan compounds during field run-off events. Presumably, this reflects experience soon after application when this isomer remains in significant quantities. The beta-isomer is recognised as more strongly bound to soil and more persistent there.

International studies

Even in the international data, there is no definitive analysis of the degree of persistence of endosulfan residues in sediments, and their subsequent migration to the water column as a result of resuspension. A number of studies indicate that endosulfan residues are present in sediments, usually as a minor component of a range of other organochlorines.

Miles and Pfeuffer (1997) found that, although endosulfan was often found in the water columns in Florida canals, it was not notably a persistent residue in the canal sediments. Atrazine, ametryn, bromacil, simazine and norflurazon were the most frequently detected pesticides in surface water samples and DDE, DDD and ametryn were the most frequently detected pesticides in sediment samples collected over the period November 1991 to June 1995 in a monitoring network that includes 27 stations in south Florida canals. The 744 pesticide detections during this time period represent about 2% of the total number of analytical determinations. Many of the most frequently detected compounds were used in large amounts in the monitoring area based on pesticide usage estimates. Spatial trends in pesticide detections followed use patterns. The maximum atrazine detections occurred in winter to late spring and were associated with usage on turfgrass and agricultural products. Endosulfan residues above the Florida water quality criterion were occasionally observed in surface water in the Homestead area and most of the exceedences occurred in confined waters. Methods with higher sensitivity were being developed, and were expected to increase the number of detections in future sampling. Pesticides which bind strongly to soil, pesticides that are highly persistent and those used in large amounts were some of the more frequently found pesticides in sediments.

In South America, Rubero *et al.* (1997) monitored residues of organochlorine pesticides in water, in the water hyacinth *Eichhomia crassipes* and in the sediments of three subsystems of the high Parana river, Colombo, during the period of August 1992 to August 1994. The Baia river-Guarana lake subsystem presented the greatest content and frequency of contamination by organochlorines. Also, sediments in this subsystem have shown higher levels of contamination than water and water hyacinth. The pesticides detected in higher concentration in these subsystems were lindane (HCH), aldrin, heptachlor, endosulfan, *p,p'*-DDE and *p,p'*-DDT. A screening for persistent chlorinated hydrocarbons was carried out in December 1995 in the main coastal region Nicaragua, where use has been taking place for decades (Carvalho *et al.,* 1999). Results for a wide range of organochlorine pesticides in lagoon sediments show levels that generally were very low in various estuaries of San Juan del Sur. For example, total DDTs in these lagoons averaged 4.5 ± 3.4 μg kg^{-1} dry weight, which may be considered a baseline level for the region. Other compounds such as HCHs, BHC, endosulfan, heptachlor, endrin, toxaphene, and aroclors were present in concentrations even lower, generally below 1 μg kg^{-1} dry weight. However, sediments of the Esteros Naranjo-Paso Caballos system at Chinandega district contained pesticide residues in much higher levels, attaining maximum values of 1,420 μg kg^{-1} and 270 μg kg^{-1} dry weight, respectively, for toxaphene and total DDTs. Other compounds such as aroclors, chlordane, endosulfan, and dieldrin were also present in the sediments of this lagoon system, but in lower concentrations. Thus, no special mention of endosulfan as a major contaminant was found necessary consistent with a transient presence. In the absence of data regarding use patterns and times of sampling, it is difficult to draw conclusions of strong significance from such a study.

In Greece, Angelidis *et al.* (1997) collected water and sediment samples from several stations along the Evrotas river, for a one year period, from August 1991 to August 1992, and analysed these for nutrients (Total N, NO_3-N and Total P) and pesticides. Higher nutrient concentrations were detected in the part of the river which is flowing through the plain of Sparta and is receiving industrial and domestic effluents, as well as the runoff from the agricultural land of the area. The industrial effluents (orange juice plants) and the agricultural land runoff, seem to play the major role during winter and spring, while the discharge of domestic septage (cesspools contents) in the reduced water flow, appears to be an important source of nutrient pollution during summer, In the water and sediments of the river were detected the herbicides alachlor, atrazine, amitrol and simazine, the insecticides azinphos ethyl, carbofuran, diazinon, dicofol, endosulfan, fenthion, methyl parathion, as well as the fungicide captan. In the river water, the highest concentrations of herbicides atrazine, simazine and alachlor were found in summer (August 1991). The same herbicides as well as the insecticides azinphos ethyl, iazinon, dicofol, fenthion and methyl parathion, were found in significant amounts in the riverine sediments. Thus, endosulfan was also not of special significance in sediments.

Surface and core sediments were collected from the main body of Lake Huron in 1969 and from Georgian Bay and North Channel in 1973 (Frank *et al.*, 1979). These were analyzed for organochlorine insecticides and PCB (polychlorinated biphenyls). Residues of organochlorines were higher in the 12 depositional basins in Lake Huron and Georgian Bay than in sediment in the nondepositional zones. Residues of PCB varied from 9-33 μg/kg in the 12 basins. Both parent DDT and its two metabolites were present in sediment at a mean residue of 7.8 μg/kg for the whole lake. The main lake had residues of 10.2 μg/kg while Georgian Bay had 5.8 μg/kg and North Channel 4.1 μg/kg, in keeping with use pattern since 1943. HEOD (dieldrin) was present in only 5.7% of sediment samples from main Lake Huron, 30% from Georgian Bay and 15% from North Channel. The highest residues 1.7 μg/kg occurred in the North Channel. No chlordane was detected; heptachlor epoxide was identified in 8.5% of sediments collected in Lake Huron, 23% from Georgian Bay and 14% in North Channel.

Endosulfan appeared in 4% of samples from both Georgian Bay and North Channel.

Suspended sediment samples were collected approximately every two weeks from the Niagara River at Niagara-on-the-Lake (Canada) between April 1979 and April 1980 (Warry and Chan, 1981). Three other samples were collected from the Fort Erie (Canada) end of the river during July 1979. All samples were analyzed for organochlorine pesticide residues. PCB (polychlorinated biphenyl) was the most prevalent residue, followed by DDT, mirex, chlordane, methoxychlor and endosulfan. The Niagara River was apparently the largest single source of PCB to Lake Ontario. Comparison with other work indicated that the loadings of total PCB from this source had more than doubled since 1968. Most suspended sediment contaminated with PCB, mirex and *p,p'*-DDT emanated from sources which entered the Niagara River between Grand Island and Niagara-on-the-Lake. Thus, endosulfan was not singled out for notice in these mobile sediments.

A further monitoring survey was conducted in Canada for 1985 to 1987 (Wan, 1989) to determine the levels of agricultural pesticides azinphosmethyl, diazinon, dinoseb, endosulfan, and fensulfothion in selected farm ditches leading to the Lower Fraser, Nicomekl, and Sumas rivers in British Columbia, Canada. In ditch water, azinphosmethyl, diazinon, endosulfan, and fensulfothion were not detected (limit of detection, 1 μg/L). However, dinoseb was consistently found in ditch water for one year after the spray season at levels varying from 0.3-18.6 μg/L, averaging 4.9 μg/L. The endosulfan level in ditch water of one farm reached 1530 μg/L shortly after a spray application, even though it was not found at other times of the year. In ditch sediments, low levels, i.e., 2.7, 4.0, 22.9 and 10.3 μg/kg respectively of azinphosmethyl, diazinon, dinoseb, and fensulfothion were sporadically found. Endosulfan was, however, consistently found in sediments at all study sites at levels varying from 2-150 μg/kg, averaging 18.8 μg/kg.

Another Canadian study (Wan *et al.*, 1995) also showed the presence of high concentrations of endosulfan residues on-farm, but no significant evidence of persistence in sediments. Farm ditches flowing into three rivers important to fisheries in the Lower Fraser Valley of British Columbia, Canada, were sampled periodically at seven locations from July to December in 1991, to determine the distribution of total residues of endosulfan including endosulfan sulfate, in ditch water and sediment. Residues were detected at levels ranging from 77.8 mg/kg in crop soils collected close to the sites for sampling ditch water and sediments. Endosulfan concentrations in ditch water varied from 0.01 μg/L to 13.4 μg/L, whereas those in ditch sediments ranged from 5 μg/kg to 2,461 μg/kg. Of the two stereoisomers monitored, the concentration of beta-endosulfan was detected at 8, 7 and 6 times higher than alpha-endosulfan in soils, sediments and water, respectively. The transformation product, endosulfan sulfate, was also found in the three substrates, with mean concentrations of 1,015 μg/kg, 218 μg/kg, and 0.30 μg/L for soils, sediments and water, respectively. None of these data are surprising with similar results being found on Australian cotton farms. By far the highest concentrations of endosulfan are at the site of application, with dissipation ensuring that even the highest concentrations in sediments observed close to the site of application are at least two orders of magnitude lower in endosulfan content than in soil at the point of application.

Kingston Harbour, a 50-km^2 bay in Jamaica connected to the Caribbean sea only through a 3.5 km channel, is contaminated with residues of at least 7 insecticides (Mansingh and Wilson, 1995), which are introduced by the Rio Cobre. Weekly sampling of the harbour for a month in July 1992 revealed the following maximum and mean residue levels in water (µg/litre) and sediments (µg/kg; data in parentheses), respectively: alpha-endosulfan, 8.56 and 2.18 (1 and 0.52); beta -endosulfan, 15.7 and 7.86 (0.76 and 0.4); endosulfan sulfate, 0.0003 and 0.0003 (0); *p,p'*-DDT, 7 and 7 (0.04 and 0.35); dieldrin, 3.75 and 1.88 (0.001 and 0.001); aldrin, 0 (36.7 and 9.2); endrin, 0.93 and 0.26 (0.006 and 0.006); lindane, 0 (0.8 and 0.5); and diazinon, 0.1 and 0.05 (0.007 and 0.045). Oysters and fish were also contaminated with alpha -endosulfan, diazinon and aldrin.

A better understanding of chemical routing through complex watersheds is needed for development and improvement of models to predict the transport of pesticides in runoff from agricultural lands. Methoxychlor (2.8kg/ha) and endosulfan (5.6kg/ha) were applied to a 3.1-ha soybean field at the upstream end of a 2144-ha watershed in the loess hill area of the Yazoo River basin in north-central Mississippi. Runoff was measured and sampled from the soybean field and at six sites along the watershed's main channel.The insecticides were detectable in channel flow (ephemeral) for about 3 weeks following the last appication; they were detected as far as 3.5 km downstream. Nearly all (97%) the methoxychlor was transported from the soybean field on suspended sediment, whereas about 60% of the endosulfan transport was in the water phase. About 1.6 and 0.6% of the applied methoxychlor and endosulfan, respectively, were lost from the soybean field in runoff and sediments during the study period. Insecticide yields were related to runoff volume, sediment yield, sediment organic matter yield, and time after the last application. Methoxychlor concentrations in channel flow tended to decrease more than would be expected from dilution, whereas most endosulfan concentration decreases could be explained by dilution. The decreases in methoxychlor and endosulfan concentration with downstream distance agreed well with those reported for other pesticides.

What ecotoxicological significance are endosulfan-contaminated sediments? Muddy sediments were collected from a tidal creek bottom in South Carolina after rain runoff from an agricultural watershed and tested for their effects on larval settlement/growth, survival and reproduction of cultured meiobenthic polychaetes and copepods. Endosulfan strongly inhibited larval colonization and early juvenile growth of the cosmopolitan, euryhaline polychaete *Streblospio benedicti*. In laboratory microcosms, concentrations as low as 50 µg/kg sediment significantly reduced the number of larval colonists by > 50% relative to endosulfan-free control sediments. Higher concentrations closer to actual field levels suppressed *Streblospio benedicti* colonization completely. Early growth of newly metamorphosed juveniles was depressed 36 and 40% relative to controls at endosulfan concentrations of 50 and 100 µg/kg, respectively. In contrast, when the common benthic harpacticoid copepod *Pseudobradya pulchella* was chronically exposed to sediment endosulfan as high as 200 µg/kg, survival and egg production were unaffected despite many examples of high endosulfan toxicity to other crustaceans. Of more than 1,600 *Pseudobradya pulchella* tested, more than 95% survived endosulfan concentrations of at least 200 µg/kg, and over 98% of 1,200 females produced normal clutches of eggs. Similarly, survival of another common benthic copepod, *Nannopus palustris*, was not significantly affected below a threshold concentration of 200 µg/kg endosulfan. At 200 µg/kg, however, *Nannopus palustris* survival was significantly reduced relative to control and 50 µg/kg endosulfan treatments. These results are similar to those noted above with Australian species of benthic organisms (Leonard *et al.*, 2000).

DISCUSSION

Distribution and transport of endosulfan in sediments

The presence of endosulfan residues in river water may be as a component of the non-sedimentable fraction, either directly in solution or bound to colloidal material such as humic substances. A CRDC project (US39C) on "Remediation of endosulfan on cotton farms" with Angus Crossan as a CRDC PhD fellow is examining such binding, using the technique of field flow fractionation. This enables separation of different colloidal fractions by generating more than one force field and by using the ELISA technique, we expect to be able to determine the distribution of pesticides such as endosulfan and diuron on these fractions and larger sedimentable particles. This analysis will provide the ability to calculate distributions of endosulfan and to determine the likely load carried in each form.

The likely transport behaviour of endosulfan on sedimentable fractions presents a complex problem. The sediment load is strongly dependent on the stream velocity. As the stream velocity increases the load increases dramatically. This effect is an example of an inertial force, which Kennedy's (2000) new book on "Action in Ecosystems" explains in some detail, showing how such potential energy is real, depending on momentum exchange by the transmission of energy quanta between molecular surfaces. This effect can be taken advantage of in remediation of storm runoff by providing engineering works designed to slow down stream flow (i.e. by expanding the space available for the stream to travel through).

Bioaccumulation of chemical contaminants

Sediments are significant contaminants in themselves, and many contaminants are readily adsorbed on to the sediment and are transported with them. The primary sources of sediment in a river system are river inflows, bank erosion, storm events run-offs and disposal of waste by man. Wave action and currents disperse sediments. The sediments deposit on the bottom and are resuspended, dispersed and transported. This process continues till the sediment is out of the system or become a permanent part of the bed. A knowledge of particle sizes, settling speeds, the effects of flocculation on these parameters is important in determining (a) settling rates (b) deposition rate at the sediment water interface, (c) the release of contaminants to the surrounding waters. Through these processes, the concentration of sediment and contaminants at the air-water and sediment-water interface are greatly influenced. If the particle is spherical with known density, the two are related by the well-known Stokes" Law $w_s = gd^2/18\mu\ (p_s-p)$ where w_s is the settling speed of the particles; g is the acceleration due to gravity; d is the diameter of the particle; p is density of the particle; μ is density of water; and μ is molecular viscosity of water . The formula is valid for settling speeds such as that the Reynold's number ($Re = pw_sd/u$) is less than 0.5 with a diameter of less than 100 µm. Particles are not spherical and tend to floc and individual particles of 1 µm are closely clumped together. Because of this behaviour the diameter and settling speed are not well related by Stokes' law. As noted above, settling speed is strongly affected by inertial forces generated by high stream velocity.

In studies of the fate of pesticides, herbicides and other chemicals in pond and flooded soil the losses of parent compounds due to dilution, sorption, hydrolysis diffusion and photolysis have not been distinguished. Most of the losses have been attributed to biodegradation. In some studies it has been indicated that microbial communities associated with sediment may be active in biodegradation. Several pure cultures have been isolated from sediment that degrade various halogenated chemicals showing that microbial communities associated with sediment have significant metabolic capabilities for variety of chemicals. Once a chemical becomes associated with the sediment, the chances for biodegradation may be enhanced. Adding sediment to a water sample is essentially the same as inoculating with a mass of microorganisms. As a general rule the total biomass of bacteria is 100 to 10,000 higher in the top 0.2 to 0.3 cm of the sediment than in the water column. The higher activity in sediment could a consequence of increased availability through sorption on the sediment surface. Characterisation of the biodegradation capabilities of microbial communities associated with the sediment is important for understanding the residence time of the chemical in the river system.

Bioavailability of neutral lipophilic organics chemicals contained in sediment.
The problem is complex because of the numerous type of chemicals and the wide variety of sediment that exist in the environment.. The fact that overlying water is brought into the sediment by the benthic invertebrates indicate that they are exposed to a mixture of interstitial water and surface water. The actual exposure is then the rate of pumping, Koc of the chemical, the organic carbon content of the sediment, concentration of chemical on the sediment, in the interstitial water and overlying water and the feeding habits of the organisms. A wide variety of invertebrates with diversity of living habits and different feeding habits are associated with the sediments. The primary food source for most benthic invertebrates is associated with the particulate organic matter. There is enough evidence to suggest that the sediment interstitial water is a key route exposure for

benthic population. A comparison of the uptake of chemicals from food versus water has show that water was the principal route of exposure.

Bioavailability as a function of organic carbon

For neutral organic lipophilic chemicals, organic carbon in the sediment is very important in controlling their bioavailability. The use of organic carbon (OC) to predict soil adsorption for many chemicals has become widely accepted. The ability of OC to normalise the differences observed in the soil partition coefficients (K_p) for a given for different soils or soil fractions usually expressed as: $K_p = K_{oc} * F_{oc} = C^s / C^w$ where $K_{p\ is}$ = soil/water partition coefficient, K_{oc} = the organic carbon normalised, $K_{o,}$ F_{oc} = fraction organic carbon = % oc/100, C^s = the concentration of chemical on the sediment phase, C^w = the chemical concentration in the water phase. This equation can be used in a number of ways to assess the bioavailiblity of chemicals in natural surface waters or sediment interstitial waters. Most natural waters do not contain high levels of dissolved organic carbon (DOC) They are typically in the range of microgram to lower mg/L. Small lake and farm pond may approach to 100 mg/L and some streams in coniferous forest may contain 200-300 mg/L. The existing data of binding of chemicals to DOC is meagre. Organic carbon levels need to be measured when assessing the significance of lipophilic organics on sediments.

Bioaccumulation is the accumulation of a chemical within animal tissue to the extent that the organism or its predator becomes unsuitable for human or animal consumption. The testing procedures using octanol/water partitioning coefficient though quite reliable for predicting bioaccumulation in fish becomes unreliable for organisms with the water only. If the water contains the sediment, then the prediction of bioaccumulation of the contaminants within aquatic organisms may be highly unpredictable. This is because the sediments compete with the organisms for the contaminants. The accumulation by the organisms is a function of the affinity of the contaminant for the sediment and the amount of sediment present in the system.

The sorption of organochlorines on sediment is related to the organic carbon content of the solid phase. Many of the pesticides show little or no mobility in soils or systems containing large amounts of organic carbon. On the other hand, they are fairly mobile in sandy systems. The key component in hazard assessment is the expected mobility of a chemical in contact with sediment or soil of the region, equating chemical persistence in soil and sediment with the availability of the chemical aquatic life should be avoided.

Dynamics of water/sediment interactions

The difficulty in assessing whether sediment-associated contaminants will cause toxicity or will bioaccumulate is based on determining the bioavailability of these chemicals to aquatic organisms. The holistic nature of various environmental compartments that determine the bioavailability of sediment-associated chemicals to aquatic organisms. Sediments are important in controlling the concentration of toxic chemicals in water column because sediment acts as sink and source. Aquatic sediments (top 10-20 cm) represent relatively a small volume of the entire ecosystem, and high concentration of sediment bound chemicals tend to be localised. Once a chemical enters the water column, it remains in the dissolved state or it partitions to the suspended particulate matter. In either state, the chemical may be available to pelagic and benthic organisms. Sorbed chemicals are exchanged between sediments and animal tissue depending on the residence time of the particulate matter in the organisms, the equilibrium partition of the chemical, the dissolved organic carbon associated with the particles, and possibly other surface characteristics. Concentration of the chemicals are subject to fate processes such as photolysis and biodegradation.

Transport of the contaminants to the sediment bed is influenced by the system hydrodynamics. The concentration of the chemical in the aqueous phase may be reduced by sorption, whereas in pore water concentration depends on the surface characteristics of the particulate material and the existing chemical gradients. Accumulation by benthic biota depends on the distribution of chemical gradients among sediments, pore water and animal tissue. The distribution of dissolved or sorbed chemicals in the sediment bed, including release back into the water column is determined by sediment resuspension, biological activity, interstitial mixing, sediment reworking, and burial.

MANAGEMENT & RESEARCH IMPLICATIONS

This review has indicated that sediments contaminated with endosulfan are of concern, although evidence regarding serious effects other than as a transient phenomenon without long-term implications is sparse, even at the toxicological level. There is no evidence indicating species extinction is a probable outcome of contamination of sediments at the levels observed. There are also means of limiting off-farm transport of sediments, particularly by ensuring low cross-surface velocities wherever possible. However, there is insufficient evidence available to be confident that contaminated sediments and their partitioning to the water column does not sometimes occur, without deleterious effects. New research is the only means by which this question can be answered. With respect to the need and practicability of this research, the following conclusions can be made:

- There is no strong or consistent evidence indicating that persistent endosulfan residues are likely to be a major problem associated with contamination of river sediments. On the contrary, the transient nature of endosulfan is confirmed in nearly all field studies, although the potential for accumulation of residues of endosulfan sulphate in sediments at moderate levels (but still at a concentration with ecotoxicological effects) on a time scale of several months is amply shown by the data. Despite this effect, it seems unlikely that large quantities of endosulfan are being stored, that can raise the endosulfan concentration in the water column globally to levels of concern, should these be mobilised.

- Nevertheless, a question mark remains on whether accumulation might not occur in some circumstances, where sediments remain well submerged and undisturbed for a long period. The lack of long-term accumulation may reflect the normal rate of disturbance of sediments at the top of the river bed, and exposure to air or drying out. The effect of factors such as pH, temperature and soil type has not been resolved. For example, sediments are likely to be anaerobic and therefore often alkaline, accelerating the rate of hydrolysis. This may be an important factor in the longevity of endosulfan residues since the rate of hydrolysis increase ten-fold for each pH unit above 7 so that hydrolysis to endosulfan diol is quite rapid above pH 9.

- The question of whether the water column can be seriously contaminated from sediments on the stream bed has also not yet been seriously examined. The concentrations observed in sediments are usually moderate, except in on-farm situations, and these levels would be diluted significantly if sediments are mobilised. A full assessment of the possible role of sediments in river contamination would need to provide a model of the extent of contamination of the water column possible by desorption.

- Because sediments accumulate endosulfan in the organic fraction, the concentration in sediments will always be much higher than that dissolved in water above (see Leonard *et al.*, 2000). As an approximation, the K_{OC} or K_{OW} values for endosulfan isomers and endosulfan sulphate would enable this to be calculated. However, there is a need for experimental assessment of the process of desorption from sediments and to estimate the maximum extent that the water column can be contaminated when at equilibrium with endosulfan in sediments. The presence of organic material (e.g. humic substances, etc.) in the water column may drastically modify the equilibrium distribution but we have no experimental data to assess this effect.

A study of the relationship between runoff flow velocity and the settling rate of sediments, together with the distribution of pesticide residues on sediment fractions would also yield data of practical value to cotton farms. It is suggested that engineering works to control flow rates on cotton farms could be of value in controlling pesticide runoff carried on sediments.

Any new research commissioned by the CRDC would need to address these questions.

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