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Persistence of Endosulfan and Endosulfan Sulfate in Soil as Affected by Moisture Regime and Organic Matter Addition

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Endosulfan [(1,4,5,6,7,7-hexachloro-8,9,10-trinorborn-5-en-2,3-ylene-bis-methylene) sulfite], a mixture of two stereoisomers α and β at around 2:1 ratio, has been widely used as a broadspectrum cyclodiene insecticide on a wide range of crops including upland cotton and wetland rice systems. It persists in soil and water environments for 3 to 6 months or more (Rao and Murty 1980; Kathpal et al. 1997; Awasthi et al. 2000). However, it is generally less persistent in the environment than other cyclodienes. Endosulfan can undergo degradation to non-toxic or less toxic endosulfan diol or oxidation to equally or more toxic endosulfan sulfate in plants, microbial cultures and soils (Goebel et al. 1982). Formation of endosulfan sulfate is mediated essentially by microorganisms while hydrolysis of endosulfan to endosulfan diol can be chemical, especially under alkaline conditions, and/or microbial. Off-farm transport of endosulfan and toxic and recalcitrant endosulfan sulfate especially from cotton and rice fields to surface and groundwater has caused problems of their toxicity to aquatic life, particularly fish and invertebrates (Leonard et al. 2001). Endosulfan sulfate appears to be the most persistent metabolite of endosulfan in soils, but undergoes rapid degradation in cotton foliage (Kennedy et al. 1998). Almost all studies on soil persistence hitherto were on the fate of endosulfan, and not that of endosulfan sulfate, although the latter has been detected in groundwater in significant amounts in Australia and elsewhere (Kennedy et al. 2001). Despite its off-farm transport to water resources and toxicity to aquatic ecosystem, endosulfan will continue to be used in Australia and other countries on an interim basis under guidelines designed to reduce its inappropriate use and to reduce its off-farm transport to creeks and rivers.

Cotton is grown under non-flooded conditions while rice is preferentially cultivated under submerged soil conditions. Non-flooded soil is predominantly aerobic and lowland soil is predominantly anaerobic. However, in lowland rice a dynamic aerobic-anaerobic interface exists with the surface soil, rhizosphere and flood water in oxidised state while bulk of the soil away from the rice roots is in reduced state. The fate of pesticides applied to non-flooded and lowland soils may not necessarily be the same. Endosulfan sulfate has been detected in cotton field soils after applications of endosulfan to cotton crop (Kennedy et al. 1998, 2001) and in laboratory-incubated soils spiked with endosulfan (Rao and Murty

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1980). There is evidence for slightly faster degradation of endosulfan in wet (non-flooded) soils (moisture level not mentioned) than in flooded soils although no endosulfan sulfate was detected in both water regimes (Awasthi et al. 2000). We studied the relative persistence of endosulfan and endosulfan sulfate in wheat straw-amended and unamended soil under non-flooded and flooded conditions.

MATERIALS AND METHODS

Air-dried, sieved (< 2 mm) soil (organic carbon, 1.6%; total N, 0.13%; clay, 14.1%; silt, 30.1%; sand, 55.8%; pH, 6.6) from the experimental farm of Waite Agricultural Research Station was placed in 10-g portions in 50-ml culture tubes. One set of soil samples was amended with wheat straw [dried in an oven at 60°C for 72 h, pulverised and then sieved (< 1 mm)] at 1% (w/w) level. Unamended and straw-amended soil samples were spiked with 15 μl of 10,000 μg endosulfan ml^{-1} in acetone. After 1 h to allow evaporation of acetone, one set each of unamended and straw-amended soil samples was maintained at 70% water holding capacity to provide non-flooded conditions while another set of corresponding soil samples was flooded with 12.5 ml of distilled water. Soil samples, in duplicate for each treatment, were incubated at 21-23°C for 120 d.

In another experiment, the persistence of endusulfan sulfate was examined following the same procedure as used for endosulfan. To each tube, 20 μl of 10,000 μg endosulfan sulfate ml^{-1} was added. Incubation, extraction and analytical procedures for endosulfan sulfate were as used for endosulfan.

Sorption-desorption of α-endosulfan and endosulfan sulfate in the soil was studied by the batch method. To 5-g portions of soil in 100-ml Erlenmeyer flasks was added 25 ml of 0.01 M $CaCl_2$ solution of α-endosulfan or endosulfan sulfate. The initial concentration of both compounds ranged between 0.1 $\mu g.ml^{-1}$ and 0.25 $\mu g.ml^{-1}$. The soil-water slurry was shaken for 4 h on a shaker. The soil slurry was centrifuged and the supernatant analyzed for α-endosulfan or endosulfan sulfate. Decrease in the concentration of the compounds in the supernatant after 4-h equilibration was considered as soil-sorbed. Four concentrations of the compounds were used and each was replicated twice. Soil sorption of α-endosulfan or endosulfan sulfate was calculated using the following equation:

$$x/m = K_dC$$

where x/m is the amount of compound sorbed ($\mu g.g^{-1}$); C is the equilibrium concentration of the compound ($\mu g.ml^{-1}$) and K_d is the adsorption constant.

For desorption, after centrifugation of the soil slurry with sorbed compound, the supernatant was decanted and then replaced with fresh 25 ml of 0.01 M $CaCl_2$ solution. This suspension was again shaken for 4 h and then centrifuged. The supernatant was analysed for the compounds to determine desorption.

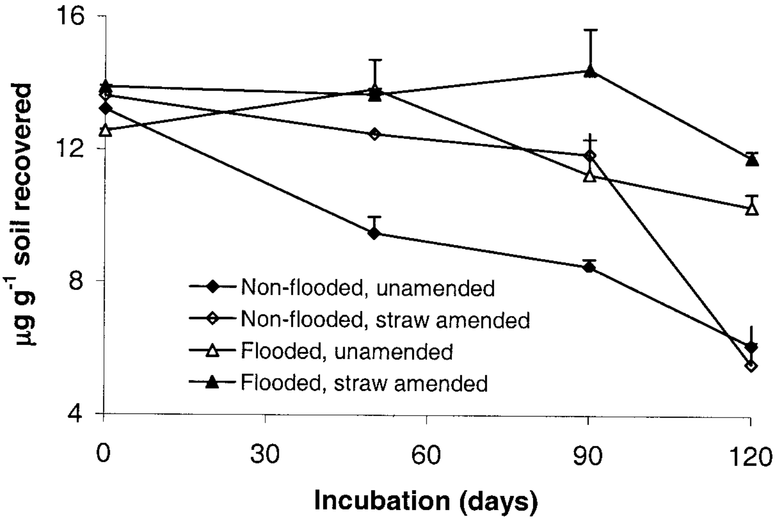

Figure 1. Persistence of α-endosulfan in non-flooded and flooded soil samples, unamended and amended with straw.

Before extraction of endosulfan residues from the soil, 11 ml of water were added to the non-flooded soil samples to provide the same soil-water ratio as in flooded soil. Soil samples were shaken with 20 ml of 1:1 acetone-hexane in a Vortex for 2 min. After adding a pinch of sodium sulfate to the soil samples, the contents in each tube were shaken again for 1 min, centrifuged and the hexane layer analyzed for endosulfan and endosulfan sulfate by gas chromatography.

Gas chromatography was performed with Perkin Elmer Auto System gas chromatograph equipped with autosampler, an on-column, split/splitless capillary inlet system, electron capture detector (ECD) and data processor (Turbochrom Workstation). Injection was made in the split mode at 260°C. A DB-5 column (30 mm x 0.20 mm id, J&W Scientific, Folsom, CA) was held at an initial column temperature of 120°C for 1 min, then at 30°C min^{-1} to 180°C, then at 10°C min^{-1} to 250°C, and finally held at that temperature for 3 min. The injector and detector were held at 260 and 300°C, respectively. The flow rate was 6 ml min^{-1} for carrier gas (helium) and 30 ml min^{-1} for make-up gas (nitrogen). The volume for sample injection was 1 µl. Under these conditions, the retention time (min) was 8.23 for α-endosulfan, 10.1 for endosulfan sulfate and 8.57 for endosulfan diol.

RESULTS AND DISCUSSION

In a laboratory-incubation study, the relative persistence of α-endosulfan and endosulfan sulfate in unamended and wheat straw-amended soil samples was examined under non-flooded (to represent cotton soil) and flooded (to represent

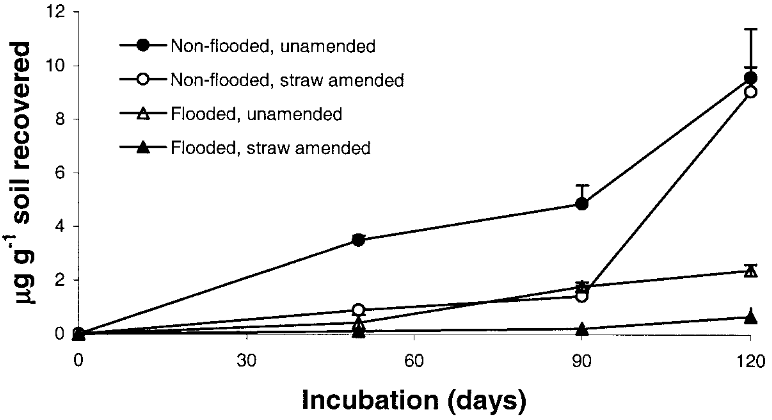

Figure 2. Endosulfan sulfate recovered from unamended and straw-amended soil samples under non-flooded and flooded conditions.

wetland rice soil) conditions. α-Endosulfan decreased more rapidly under non-flooded conditions than under flooded conditions in both unamended and straw-amended soil samples during the 120-day incubation (Fig. 1). Thus, endosulfan decreased to less than 45% of the original level under non-flooded conditions irrespective of organic addition as compared to a decrease of 15-18% under flooded conditions during the same period. Addition of straw retarded the degradation of endosulfan under both water regimes. Half-life values of endosulfan were 137 d under nonflooded, unamended conditions, 125 d under nonflooded, straw-amended conditions, 430 d under flooded unamended conditions and 501 d under flooded straw-amended conditions.

During the degradation of α-endosulfan, endosulfan sulfate accumulated as a major metabolite under both non-flooded and flooded conditions, although in distinctly greater amounts in unamended non-flooded soil, almost in stoichiometric amounts (Fig. 2). In non-flooded soil amended with straw, endosulfan sulfate, formed from endosulfan, was not considerable until 90 d, and increased sharply between 90 and 120 d, reaching almost the same level as in non-flooded soil not amended with straw. The formation of endosulfan sulfate, though in small amounts, even in predominantly anaerobic flooded soil, unamended or amended with straw is surprising. Generally, soil submergence and organic additions increased the persistence of endosulfan and decreased its conversion to endosulfan sulfate. In an earlier study, Shalini-Singh et al. (1999) found that degradation of endosulfan was more pronounced in flooded soils than in non-flooded soils. Endosulfan sulfate, formed from endosulfan was recalcitrant to further degradation under both water regimes irrespective of organic amendment.

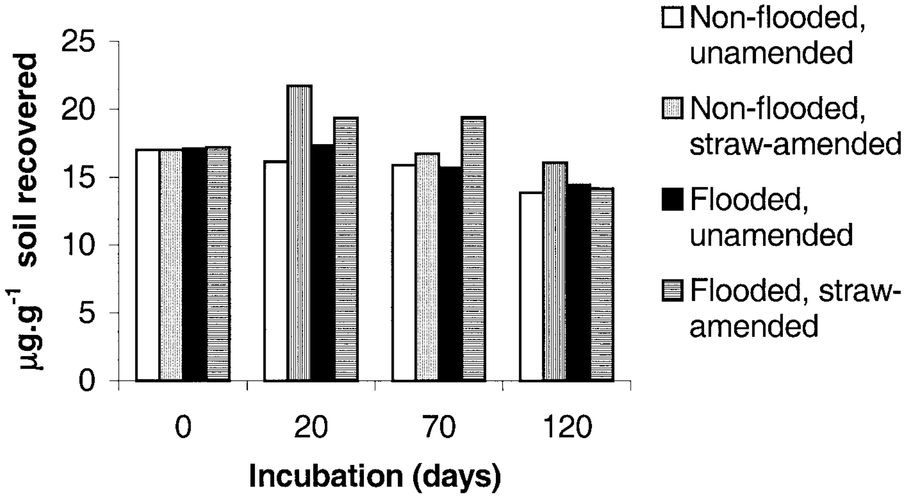

Figure 3. Persistence of endosulfan sulfate in non-flooded and flooded soil samples, unamended or amended with straw.

Investigating the effect of flooding on endosulfan degradation using two soils, Awasthi et al. (2000) found accumulation of endosulfan diol, a less toxic hydrolysis product in flooded soils and no endosulfan sulfate was detected in non-flooded soils. In our study, endosulfan sulfate was detected under both water regimes, but in distinctly greater amounts in non-flooded soil and no endosulfan diol was detected in flooded soil, even when amended with straw.

In another experiment, the soil persistence of added endosulfan sulfate was examined in non-flooded and flooded soil samples, unamended and amended with straw. There was no appreciable decrease in the concentration of endosulfan sulfate in any of the treatments during 120-day incubation (Fig. 3). Evidently, endosulfan sulfate persisted under both moisture regimes, even after organic addition.

The sorption of α-endosulfan (K_d: 78.9) to the soil was more pronounced (Fig. 4) than that of endosulfan sulfate (K_d: 65.1). Endosulfan sulfate (9.5%) was desorbed faster than α-endosulfan (5.0%) during 4-h equilibration. Evidently, because of its relatively low sorption and high desorption, endosulfan sulfate, once formed in agricultural soils after application of endosulfan to cotton or rice, can be more mobile than its parent compound and therefore is more prone to off-site migration to groundwater and rivers.

Endosulfan diol is formed readily and is the major metabolite of endosulfan in predominantly anaerobic flooded soil (Awasthi et al. 2000) and in cultures of indigenous microorganisms from low-oxygen soils and sediments (Guerin 1999). Likewise, a mixed bacterial culture enriched from a soil with a history of endosulfan use could (i) oxidise endosulfan to endosulfan sulfate as the terminal metabolite and (ii) also hydrolyse endusulfan to endosulfan monoaldehyde

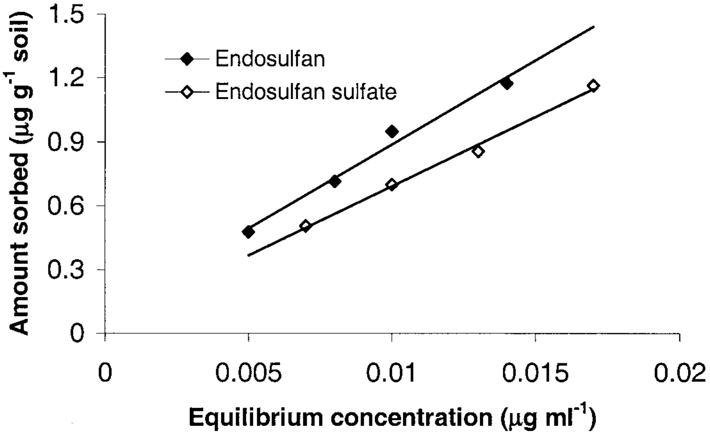

Figure 4. Sorption isotherms for α-endosulfan and endosulfan sulfate in soil.

(Sutherland et al. 2000). In the present study, hydrolysis of endosulfan to endosulfan diol and endosulfan monoaldehyde was negligible even under soil conditions that favor anaerobiosis, as in flooded soils especially amended with straw. Addition of organic sources is known to hasten the reduction of a soil. Interestingly, even in flooded soil, some oxidation of endosulfan to endosulfan sulfate occurred, probably at the oxic sites of the flooded soil viz., surface soil and water. Formation of endosulfan sulfate in non-flooded aerobic soils as in cotton soils is not desirable, because of its high toxicity and long persistence.

Certain soil amendments, as noticed in our study with straw addition, appear to retard or delay the formation of endosulfan sulfate even in aerobic soils. Efforts should be directed toward developing practices to prevent or at least retard the formation of endosulfan sulfate from endosulfan applied to aerobic soils.

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