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4.10 2,4-D AND ITS SALTS AND ESTERS

EVALUATION OF EFFECTS ON THE ENVIRONMENT

2,4-D, 2,4-dichlorophenoxyacetic acid, is a selective herbicide available as the free acid, salts and esters. 2,4-D has low volatility and is not expected to be lost by evaporation after application. Amine salt formulations of 2,4-D are less volatile than butyl, ethyl, or isopropyl ester formulations.

The 2-ethylhexyl (EH) ester is hydrolysed under alkaline conditions (half-life 48 days at pH 7 and 2.2 days at pH 9). 2,4-D may be degraded slowly by photolysis. The half-life of 2,4-D in aqueous solution was 4.5 days under aerobic conditions and 312 days under anaerobic conditions. The major breakdown product was CO_2, with 2,4-dichlorophenol, 2,4-dichloroanisole, and 4-chlorophenoxyacetic acid also being formed as intermediates. The half-lives of 2,4-D determined in natural waters after aerial application of its dimethylamine (DMA) salt ranged from 1.1 to 20 days. 2,4-D formulations were found to be rapidly hydrolysed or biodegraded in ponds and lakes.

There was no evidence of bioaccumulation of 2,4-D in aquatic organisms.

The behaviour of 2,4-D salts and esters in soils is greatly influenced by the organic matter content and pH. 2,4-D is more strongly adsorbed in soils with higher organic matter content and/or lower pH. The rapid biodegradation of 2,4-D in soil prevents significant downward movement under normal field conditions. Run-off from treated soil has been estimated at between 0.01 and 1% of the applied 2,4-D; the maximum recorded concentrations following run-off were about 0.2 µg/l. Under non-sterile conditions various esters of 2,4-D are hydrolysed very rapidly in soils (>72% within 72 h). A number of microbial organisms rapidly degrade 2,4-D, which has half-lives of 1.25 h to 40 days, usually between 3 and 10 days. The DMA salt rapidly dissociates, leaving 2,4-D which then undergoes further degradation.

Field trials in the USA using the DMA salt or the EH ester at 2.24 kg acid-equivalent/ha on grass resulted in maximum initial residues at day 0 of 120 or 153 mg acid-equivalent/kg, respectively. These initial residues decreased by a half to a third by day 7.

In general, populations of aerobic bacteria, actinomycetes, and fungi in soils were not affected by 2,4-D at 25 ppm. At an application rate of 0.95 kg/ha, populations of bacteria, fungi, and actinomycetes were reduced by 26.3%, 19.5% and 30%, respectively, by the iso-octyl (IO) ester, but approximately half as much by the DMA salt.

2,4-D at the maximum recommended application rate has a growth-stimulating effect (10%) on *Skeletonema costatum*, whereas it inhibits the growth of *Navicula pelliculosa,* (24%) and *Lemna gibba* (75%). The 5-day EC_{50} for the acute toxicity of 2,4-D and its salts and esters differs widely among algal species and compounds, ranging from 0.23 mg ai/l (EH ester for *Skeletonema costatum*) to 153 mg ai/l (DMA salt for *Anabaena flosaquae*). The acute toxicity of 2,4-D to the aquatic higher plant *Lemna gibba* also depended upon the salt or ester used, with 14-day EC_{50} values of 3.3, 0.58 and 0.5 mg/l for 2,4-D, the DMA salt and the EH ester respectively.

At concentrations ranging from 0.001 to 100 mg/l, 2,4-D had no effect on chlorophyll production in several algal species. *Anabaenopsis raciborskii* was found to tolerate up to 800 µg/ml of 2,4-D in liquid culture media.

Many studies have been performed on invertebrate fresh water and estuarine or marine species, including *Daphnia*, *Gammarus*, *Macrobranchium*, *Crassostrea*, *Palaemonetes*, *Panaeus,* and *Uca*. Many forms of 2,4-D have been evaluated: 2,4-D itself, the DMA, diethanolamine (DEA), isopropylamine (IPA), tri-isopropanolamine (TIPA), and sodium salts, and the EH, butoxyethyl (BE), and isopropyl (IP) esters. 2,4-D and its salts are generally less toxic to these organisms than the ester forms. Acute toxicity (48-h LC_{50} values) to *Daphnia magna* ranged from 5.2 mg ai/l (IO ester) to 184 mg ai/l (DMA salt) and 21 day NOECs ranged from 0.0015 mg ai/l (EH ester) to 27.5 mg ai/l (DMA salt) and 79 mg ai/l (acid).

At concentrations of 1.0 and 10.0 mg BE ester/l, grass shrimp were observed to avoid water containing these levels. In a life-cycle study on *Daphnia magna*, the NOEC was 23.6 mg ai DEA salt/l. In a chronic toxicity study on *Daphnia magna* using the BE ester, the Maximum Acceptable Toxicant Concentration (MATC) ranged between 0.70 mg/l and 0.29 mg/l.

Frog and toad tadpole 96-hour LC_{50} values ranged from 8 mg/l for the free acid to 477 mg/l for the DMA salt.

Many data were available on the effects of 2,4-D and its salts and esters on various growth stages of fish such as *Oncorhynchus*, *Lepomis*, *Pimephales*, *Gambusia*, *Micropterus*, and *Salmo*. Generally, 2,4-D and its salts are less toxic to fish than are the esters. Typical 96-h LC_{50} values for adult fish ranged from 5 to 10 mg a.i./l for the IO ester, from 200 to 400 mg a.i./l for 2,4-D, and from 250 to 500 mg a.i./l for the DEA salt, although lower figures have been reported. Early life stages appear to be more sensitive, with 32-day NOECs ranging from 0.12 mg a.i./l (EH ester) to 17.1 mg a.i./l (DEA salt) and 63.4 mg a.i./l (acid).

Embryos and larvae of the fathead minnow (*Pimephales promelas*), were exposed to up to 416.1 μg/l of the BE ester for 32 days. The NOEC was 80.5 μg/l, with the MATC estimated to be 96.0 μg/l. The sodium salt of 2,4-D had no inhibitory effect on the hatching of carp eggs at 25 mg/l, but at a concentration of 100 mg/l none hatched. At 50 mg a.i./l the sodium salt was not harmful to carp embryos but induced behavioural changes, some morphopathological changes, and ultimately death in carp larvae.

Honeybee oral and contact LD_{50} values for the DMA salt and EH ester were all >100 μg/bee. Toxic effects have not been noted for bees in the field.

2,4-D (in combination with MCPA) did not harm *Trichogramma cacoeciae* at 1.5% in water or *Aleochara bilineata* at the label recommended rate. 2,4-D mixed amine salts and mixed isopropyl esters were toxic to coccinellid larvae and to sawflies. No reproductive effects were observed in European cockroaches reared on food containing 1000 mg/kg of 2,4-D (unspecified).

Application of 2,4-D at 1250 g a.i./l in field crops did not affect staphylinids, carabids, or spiders during a 20-month observation period. Mortality of adult millipedes exposed to 2,4-D at a rate of 33.6 kg/ha was noted on the first day and exceeded 50% of control mortality by day 7.

The 14-day LC_{50} for earthworms exposed to the DMA salt was 350 mg/kg soil, with no mortality noted at concentrations less than or equal to 100 mg a.i./kg. A 48-hour LC_{50} of 61.6 $\mu g/cm^2$ has been reported for earthworms exposed on filter paper.

Acute avian LD_{50} values range from 200 to >2000 mg/kg bw for mallards, bobwhite quail, Japanese quail, pheasants, chukar partridges, and rock doves. Dietary LC_{50} values exceed 4640 mg/kg diet for mallards, bobwhite quail, Japanese quail, and pheasants for the acid, salt, and ester. At doses greater than the recommended application rate, the acid, salt, and ester did not adversely affect the reproductive performance of pheasants, quail, partridges, or chickens.

Oral LD_{50} values for rats and rabbits range from 699 to 2322 mg/kg bw for the acid and its salts and esters. Dermal LD_{50} values for the rabbit exceed 2000 mg/kg bw and inhalation LC_{50} values range from 1.8 to 10.7 mg/l.

Risk assessment

The information on use and application rates used for this risk assessment is derived from the agricultural use of 2,4-D within the European Union and the USA. It should be noted that 2,4-D can be formulated as a variety of different salts (e.g. DMA, sodium, DEA, TIPA, and IPA) and esters (EH, IO, and BE). However of all these different forms, the DMA salt and EH ester account for approximately 95% of the global use of 2,4-D. This risk assessment is therefore restricted to the use of these compounds. It should be noted that both of them are rapidly hydrolysed to 2,4-D. The major uses of 2,4-D include application to cereals, corn, sorghum, soya beans, sugar cane, rice, pasture, top fruit, turf, non-cropland, fallow, forestry, and aquatic weeds. Applications can be made by either conventional tractor-mounted or drawn hydraulic sprayers or by aerial application (e.g. in forestry use) at rates varying from 0.25-4.48 kg acid-equivalent/ha.

This risk assessment is based on the principle of calculating Toxicity:Exposure Ratios (TERs) and follows the EPPO/CoE Environmental Risk Assessment models and trigger values.

Aquatic environment

The main risk to aquatic organisms from the use of 2,4-D is from overspray during aerial use, spray drift from ground-based hydraulic applications, or use to control aquatic weeds.

The EPPO/CoE risk assessment scheme for aquatic organisms showed a low acute risk (TERs >10) to fish, aquatic invertebrates, and algae from both spray drift contamination arising from ground-based hydraulic applications and from overspray contamination arising from aerial applications. A potential acute risk (TERs <10) to both aquatic higher plants and amphibians from overspray contamination during aerial applications was identified. The use of 2,4-D to control aquatic weeds also presented a potential acute risk (TERs <10) to algae as well as amphibians and aquatic higher plants. However, the risk to algae and aquatic higher plants can be ignored as these organisms are the targets when 2,4-D is used in this way. A potential acute risk to amphibians still remains from the use for aquatic weed control. It should be noted, however, that such a risk to amphibians needs to be balanced against the risks associated with alternative aquatic weed control practices such as not conducting weed control (e.g. algal bloom leading to water deoxygenation) or the potential damage caused by manual weed control, both of which may pose a higher risk to fish and other aquatic organisms. The EH ester is not recommended for aquatic weed control.

Owing to the very rapid degradation of the salts and esters of 2,4-D in water, the long-term risk to aquatic organisms from these compounds was considered to be low. However the primary breakdown product, 2,4-D acid, is more persistent in water and therefore the long-term risk assessment is based on it. Measured levels of 2,4-D in surface waters associated with approved uses (ranging from 0.00008 mg/l in small watersheds in Saskatchewan to 0.0021 mg/l in ground and surface waters in the UK) indicate that the long-term risk to fish and water-column- and sediment-dwelling invertebrates is low (TERs >10).

Terrestrial environment

Micro-organisms

The most significant routes of exposure of soil micro-organisms to 2,4-D are likely to be from its use by ground or aerial applications. Data from laboratory studies indicate that the risk to soil micro-organisms from the use of 2,4-D should be low at application rates of 7.5 and

18.75 kg 2,4-D/ha, which are higher than the maximum recommended application rates. In another study, application of the DMA salt and the IO ester at rates corresponding to 0.95 kg 2,4-D/ha resulted in 10-30% reductions in populations of soil bacteria, fungi, and actinomyces, with the ester producing greater reductions. As the trigger for concern in the CoE/EPPO micro-organism risk assessment scheme is an effect of >30%, it can be concluded that the risk to soil micro-organisms from the use of 2,4-D should be low.

Plants

2,4-D is a translocated selective herbicide that is used to control a variety of broad-leaved weeds. Consequently, although 2,4-D may pose a risk to broad-leaved non-target plants, this is to be expected from its mode of action and consequent use.

Invertebrates

Bees

Bees may be exposed to 2,4-D by foraging flowering weeds present in treated crops. At the maximum individual application rate of 4.48 kg acid-equivalent/ha, the hazard quotients for both contact and oral toxicity were >45 for both the DMA salt and the EH ester. As the EPPO/CoE trigger for concern is a hazard quotient of >50, the acute risk to honeybees from the use of 2,4-D at this application rate should be low. This is supported by the fact that 2,4-D has never been implicated in any honeybee poisoning incidents in the UK Wildlife Incident Investigation Scheme (WIIS).

Other arthropods

Arthropods may be exposed to 2,4-D from its many agricultural and non-agricultural uses. On the basis of the EPPO/CoE triggers for concern with regard to effects on non-target arthropods in laboratory studies (effects >30%), 2,4-D may pose a risk to arthropods at high application rates, but the laboratory data were either generated with a joint formulation with MCPA, or were old and may be unreliable. Limited field data at the lower and more typical range of application rates (up to 1.25 kg/ha) indicate that this risk may not be realized in the field.

Earthworms

Earthworms may be exposed from either single or multiple applications of 2,4-D to a wide variety of crops but in particular from its use on grass, fallowland, and stubble. The TER from a maximum application rate of 5.37 kg DMA salt/ha is above the EPPO/CoE trigger value of 10, which indicates that the acute risk to earthworms from the use of 2,4-D should be low.

Vertebrates

Vertebrates are likely to be exposed to 2,4-D either from grazing on treated or contaminated vegetation or consuming contaminated insects. For this risk assessment the estimation of residues on food items represents the maximum value determined immediately after application and does not take into account the rapid degradation in the environment. It further assumes that all food consumed contains 2,4-D at the level of the MRL.

Birds

The short-term dietary TERs based on measured initial residues on short grass arising from the application of 2.24 kg acid-equivalent/ha, indicate a potential medium risk (10 <TER <100) to grazing birds from both aerial and ground-based applications. The initial residues declined to a half or a third by 7 days after application. It should be noted that 2,4-D has never been implicated in any bird-poisoning incidents as a result of normal use. This suggests that the risk to grazing birds from 2,4-D is unlikely to be high. The short-term dietary TERs based on initial residues on large insects predicted by the EPPO/CoE vertebrate risk assessment scheme indicate a low acute risk (TER >100) to small insectivorous birds from both aerial and ground applications (4.48 kg acid-equivalent/ha and 2.24 kg acid-equivalent/ha respectively). Large insects are likely to constitute a higher proportion of both bird and mammalian diets than small insects during early growth stage or pre-emergence use.

Mammals

The acute oral TERs based on measured initial residues on short grass arising from application at 2.24 kg acid-equivalent/ha indicate a potential high risk (TER <10) to grazing mammals from both aerial and ground-based applications, but the initial residues declined to a half or a third by 7 days after application. The acute oral TERs based on predicted initial residues on large insects however indicate a medium acute risk (10 <TER <100) from aerial applications, and a low acute risk (TER >100) from ground-based applications, to small insectivorous mammals. It should be noted however that 2,4-D has never been implicated in any mammal-poisoning incidents as a result of normal use. This suggests that the risk to mammals from 2,4-D is unlikely to be high.