INFORMATION ON THE ENVIRONMENTAL SIGNIFICANCE OF THE CHLOROPHENOXYACETIC ACID HERBICIDE MCPA

Paul Johnston, Ruth Stringer,
Greenpeace Exeter Research Laboratory,
University of Exeter,
North Park Road,
Exeter
EX4 4QE

Greenpeace Exeter Research Laboratory
Technical Note 04/94

Introduction

The following is a brief overview of the environmental significance of the chlorophenoxyacetic acid herbicide MCPA. The information in this document is taken from the sources indicated. From the information available, it appears that the behaviour of this herbicide in the environment is relatively poorly understood despite extensive use in a wide variety of applications. In addition, the use pattern is such that considerable impacts may be exerted on non-target species. Accordingly, formulations marketed in the United States must carry label warnings concerning the potential for groundwater contamination, endangerment of rare species, and endangerment of aquatic ecosystems.

The USEPA has, in addition called for a number of studies to be provided on this herbicide and various derivatives, and has also called for the details of the product chemistry to be resubmitted. Major worries are the potential contamination of the products with dioxins and nitrosamines. Given the environmental fate data existing for soils it seems highly likely that wastewater treatment works receiving production effluents from MCPA manufacturing facilities will produce significantly contaminated sludges and also emit degradation products through the effluent. These degradation products are of unknown environmental significance and toxicological data are not available.

1) Manufacture

On the subject of the manufacturing process: MCPA manufacture involves chlorophenol chemistry and The USEPA considers that consequently MCPA may be contaminated with chlorinated dioxins and dibenzofurans. This aspect requires evaluation and the USEPA has indicated that data previously submitted to the Agency under the registration procedure on product chemistry needs to be updated and completed. Likely dioxin content will vary according to the source and degree of refinement of the chlorophenols uses in the manufacturing process. MCPA is used in a number of different chemical forms and the USEPA has noted that the amine salts of MCPA may be contaminated with nitrosamines which are potent carcinogens. The most recent documents published by the USEPA on registration standards for MCPA containing products notes that toxicological information is missing for many of the MCPA derivatives, and that this data gap needs to be rectified.

MCPA is manufactured in the form of a number of derivatives. Some of these are as follows:

MCPA acid, MCPA sodium salt, MCPA diethanolamine salt, MCPA dimethylamine salt, MCPA butoxyethyl ester, MCPA isobutyl ester, MCPA isooctyl ester, MCPA isopropyl ester.

MCPA is otherwise known as (4-chloro-2-methylphenoxy) acetic acid

and is used for post emergence control of annual and perennial broad leaved weeds in cereals, herbage seed crops, flax, rice, vines, peas, potatoes etc. It is a selective, systemic, hormone-type herbicide, absorbed by leaves and roots with translocation. It concentrates in the meristematic regions of plants where it inhibits growth. MCPA is extensively used in Europe as the alkali metal or amine salt

It is formulated as aqueous solution, soluble concentrate, water soluble powder an emulsifiable concentrate. It is formulated in admixture with many other herbicides eg. 2,4 DB, dichlorprop, dalapon-sodium, dicamba, MCPB, mecoprop, bromoxyxnil, ioxynil, benazolin and 2,3,6-TBA.

MCPA is toxic to vines, vegetables, cotton and ornamentals. In mammals, the acute oral LD50 for rats is 700mg/kg body weight. Mice 550mg/kg. In 7 month feeding trial rats receiving 100 mg/kg of diet showed enlargement of the kidneys. The 96H LC50 for rainbow trout is reported at 232 mg/l. The product is not apparently toxic to bees. When used on the common ragwort Senecio jacobea which is highly toxic to cattle and avoided by them, it has the effect of making it more palatable. Another aspect to the use of these and other phenoxyalkanoic herbicides is that they may alter the nutritional quality of the forage.

In soil, according to the Agrochemicals directory, MCPA metabolism involves degradation of the side chain to 4, chloro-2-methyl phenol followed by ring hydroxylation and ring opening. Duration of residual activity in soil is estimated at 3-4 months. A similar metabolic pathway apparently takes place in plants.

2) Human toxicology

The chlorophenoxy-acetic acid herbicides have been subject to a number of studies. The best known are 2,4-D and 2,4,4-T of course. MCPA has been investigated with respect to soft tissue sarcoma and to non-hodgkins lymphoma in Swedish forestry workers and in Danish pesticide workers. No correlation was found for this particular chemical in forestry workers using these herbicides. In a study of Danish pesticide plant workers in two facilities where MCPA was the dominant product of this type revealed an excess of soft tissue sarcomas but no excess of malignant lymphomas. Overall the total cancer risk employed in the manufacture and packaging of these herbicides did not appear to be elevated above that of the normal Danish population. In one factory in the former USSR MCPA was considered responsible for contact dermatitis in the workers (11% of 158) while leukemia was reported in one individual chronically exposed to the compound.

A number of acute poisoning episodes have been described, and exposure to high levels either results in a quick but horrible death, or a long period of unconsciousness followed by a long slow recovery.

There are also some atypical cases of various origins reported in the literature. In one, a condition diagnosed as acute benign

pericarditis 12 hours after applying MCPA. His heart was enlarged under X-Ray examination. After 10 days the pain stopped and five days later the pericardial rub had gone and the heart returned to normal size.No infection was identified by serological studies and there was no recurrence. The problem was attributed to allergic reaction.

A less serious illness in a 34 year old woman was attributed to 3 days of occupational exposure to MCPA without any recognised accident. After the first day she experienced pain, nausea,vomiting and itching and burning of the skin. A serious rash developed which became sever in the underarm region. Upon examination two and a half months later,the liver was found to be enlarged. Similar responses have been reported by other workers, and in some of these allergy tests to MCPA proved positive.

A 64 year old man taking treatment for a heart condition developed haematoma and felt lethargic two weeks after a hand sprayer containing MCPA leaked on his back and wet his clothes. Muscular weakness, haemorrhagic gastritis and slight signs of liver damage were found on examination. After five months of treatment he became free of symptoms. The relationship to MCPA is not understood although a 48 year old farmer who sprayed about 400ml of a mixture of MCPA (34%) and sodium and potassium salts of 2-methoxy-3,6-dichlorobenzoic acid (3%) in 40 litres of water. No accident occurred and the work took around half an hour. The wind blew a light mist of the mixture on the man's face and arms. Intermittent nausea a feeling of fullness and loss of appetite followed after two days and after six days vomiting and severe epigastric pain occurred. Gastroscopy revealed a gastroesphogeal prolapse and erosive haemorrhagic gastro-duodenitis. The lesions had healed after 10 days.

3) Effects on ecosystems

In addition to the microbial degradation that can take place in soil, the chlorophenoxyalkanoic acid herbicides can be readily washed from soil into ground and surface waters. Contamination of groundwater has been observed in the US and this appears to be a problem in Denmark also. Groundwater contamination in the US at least appears to be related to mixing and loading sites for the pesticide. MCPA is regarded as moderately toxic to birds, slightly toxic to freshwater fish, effectively non-toxic to freshwater, estuarine and marine invertebrates. Nonetheless, because of toxicity to non-target species in the US it is regarded as posing a threat to the continued existence of certain endangered species when used on range pastureland. Overall, however the data are regarded as incomplete. In addition there is some evidence that MCPA may be carcinogenic in species of urodele amphibian.

Available data show that MCPA degrades under laboratory conditions with a half-life of less than week, to 50 days. Under anaerobic aquatic conditions, metabolism studies showed that 89% of the parent MCPA remained undegraded after 374 days. Data indicate that

the chemical is stable to hydrolysis and photolysis on soil. MCPA has also been found to be mobile in sandy loam soils, silt loams and silty clay loams. Leaching potential cannot b fully assessed from the data, but there is little doubt that significant leaching could take place. given the extremely high solubility of MCPA salts in water. In flooded soil, MCPA persists unchanged. Further data suggest the MCPA is persistent in leaf litter and soil up to 10 months post treatment.

Identified breakdown products include Phenol, 2,-(2-methyl-4-chloro phenoxy ethanol, 4-chloro-o-cresol, 5-chloro-3-methyl catechol. Aspergillus niger metabolises the compound to 4-chloro-5-hydroxy-2-methyl phenoxy acetic acid together with unidentified polymeric species. There appear to be no toxicological or environmental data for these compounds.

4) Effects on wastewater treatment plant.

There appear to be no specific data on the effect of MCPA on wastewater treatment plants. In the case of the discharge from Esbjerg Chemie, this is a manufacturing effluent containing MCPA, Dichlorprop and Mechlorprop together with phenol and number of substituted phenols, largely methyl phenols and chlorophenols. The analytical reports which have been passed to me show that no analysis for the known degradation products have been carried out. Given the high concentrations of these which have been recorded in the effluent passed to the municipal treatment works it seems likely that interference with treatment plant processes will occur. Phenolic compounds are powerful bactericides. Inhibition of plant treatment processes has been recorded at levels of phenol as low as 50ppm in aerobic reactors.

The removal efficiency for the phenols in the treatment plant in question are very difficult to estimate from the data since the measurements on the input do not coincide with measurements on the output. I would expect, given the nature of the input to the treatment plant, that analysis of effluent be undertaken on at least a weekly basis. Preferably this should be more frequent and should include a wider variety of determinands including the identified degradation products. In addition, given the possibility that chlorinated dioxins may be present in the product and its precursors, monitoring of these in the effluent should be carried out at least monthly and preferably more frequently.

In the case of MCPA itself, based on the data available from the USEPA, the apparent low concentrations in the final effluent do not necessarily indicate that this compound is being broken down. On the basis of physico chemical properties it is highly likely that a great proportion will partition into the sludge. Under anaerobic conditions in the sludge, it is likely to persist and can therefore be mobilised when the sludge is spread on land. Evidence for partitioning to sludge is given by the high concentrations of phenol, an identified MCPA breakdown product in the sludge itself. It is likely that other of the breakdown

products will be present and this needs to be subjected to analytical scrutiny. Finally, the presence of chlorophenols in sewage sludges may lead to de novo synthesis of chlorinated dioxins and this clearly needs to be investigated given the routine application of the sludge to agricultural land..

5) Overview

Overall, there appear to be a number of important data gaps relating to MCPA as evidenced by the USEPA documentation. Its full ecosystem effects are unknown although there is considerable potential to impact aquatic and terrestrial systems.The toxicology of its breakdown products is unknown, and it seems to persist for long periods in anaerobic aquatic environments and in soils. It seems clear that monitoring effort should be extended considerably to include known degradation products, identify new degradation products and monitor the levels of chlorinated dioxins in the sludge and final effluent.

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