

Agrochemical Residue-Biota Interactions in Soil and Aquatic Ecosystems

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AGROCHEMICAL RESIDUE-BIOTA INTERACTIONS IN SOIL AND AQUATIC ECOSYSTEMS

PROCEEDINGS AND REPORT
OF A COMBINED ADVISORY GROUP MEETING
AND RESEARCH CO-ORDINATION MEETING
ON AGROCHEMICAL RESIDUE-BIOTA INTERACTIONS
IN SOIL AND WATER
ORGANIZED BY THE
JOINT FAO/IAEA DIVISION OF ATOMIC ENERGY
IN FOOD AND AGRICULTURE
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IN SOIL AND AQUATIC ECOSYSTEMS

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FOREWORD

Agricultural chemicals (insecticides, herbicides, fertilizers, etc.) play a vital role in enabling modern agriculture to meet growing world food demands. Only a minute fraction of an applied insecticide, for example, actually comes into contact with the pest and, thereby, becomes used for killing it. Rarely is more than half the nitrogen applied as fertilizer usefully recovered in the crop. Large fractions of these applied chemicals thus inevitably find their way into the environment as 'residues'. The fate and significance of these residues depend very largely upon their interactions with the vast range of living organisms (the biota) of the soil and water environment. On the one hand a fertilizer residue may become usefully stored by microbiological action as a potential nutrient for future crops, or it may undergo denitrification and so become lost to agriculture. Similarly, a pesticide residue may undergo desirable degradation to harmless metabolites. On the other hand, on reaching an aquatic system it may poison fish or, by persisting in the soil, it may encourage the emergence of a pesticide-resistant strain of pest. Isotopic tracer techniques provide a most important tool for studying these interactions and assessing the significance of the residue; the related use of radiolabelled substrates provides a very useful tool for studying the effects of residues on biological processes vital to soils and fisheries.

Two research programmes co-ordinated by the Joint FAO/IAEA Division, now called the Joint FAO/IAEA Division of Isotope and Radiation Applications of Atomic Energy for Food and Agricultural Development, are designed to help scientists of developing countries to make safe and effective use of isotope techniques for studying the interactions of agricultural chemicals with the environment under their own conditions. The programmes, which receive generous financial support from the Swedish International Development Authority (SIDA), also provide for research co-ordination meetings among these scientists and others from advanced institutes to discuss problems of mutual interest and recent advances in pertinent research.

The present publication is a report of a first meeting, held in Vienna from 28 August to 2 September 1978, between the participants of the two programmes dealing with agrochemical residue-biota interactions in soil, and in aquatic ecosystems. Particular attention was given to the existing and potential use of labelled substrates as a monitoring tool, e.g. for the capacity of soil to degrade undesirable residues, or for assessing the progress of eutrophication of an inland fishery by excessive nutrients.

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GENERAL

CASE AND COMPARATIVE STUDIES ON XENOBIOTICS IN TERRESTRIAL AND AQUATIC ECOSYSTEMS

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Abstract

CASE AND COMPARATIVE STUDIES ON XENOBIOTICS IN TERRESTRIAL AND AQUATIC ECOSYSTEMS.

Case studies on agrochemical fate in soils, plants, animals and water revealed problems of long-term persistence, bound residues, species diversity, etc. The information obtained from each single experiment brought forward the need for an integrated approach. Each chemical should be characterized by an ecotoxicological profile analysis. Examples are given of such an analysis made in rigorously standardized experiments. The results are used for a comparative ranking of the xenobiotic according to its ecotoxicological risk. For this purpose the experimental data are completed by data regarding the utilization of chemicals, etc. As an example of such a complete analysis, HPMAA (hydrolyzed polymaleic acid anhydride) is given.

1. INTRODUCTION

Many procedures have been designed to assess the behaviour and effects of chemicals in the environment. A 300-page summary of the more feasible ecotoxicological test methods has been recently compiled [1]. These include the use of labelled compounds, in vitro screening, model ecosystems, field experiments and chemical identification procedures.

TABLE I. MATERIAL BALANCE IN PLANTS
AND SOIL FIVE YEARS AFTER APPLICATION
OF ALDRIN- ^{14}C TO SOIL

Applied in 1969	103 mg	(100%)
Residue in soil 1973		34.5%
Taken up by plants 1969		0.1%
Taken up by plants 1970		0.2%
Taken up by plants 1971		0.1%
Taken up by plants 1972		0.1%
Taken up by plants 1973		0.1%
Leaching water 1969		1.6%
Leaching water 1970		4.9%
Leaching water 1971		2.4%
Leaching water 1972		1.3%
Leaching water 1973		0.4%
Recovery after 5 years		45.7%
Volatilization within 5 years		54.3%

Some examples are given here to illustrate the problems of data interpretation and of assessing the significance of xenobiotic chemicals.

It is the opinion of the authors that, when appropriately classified, the information and data from individual case studies provide a comparative ranking of chemicals according to ecotoxicological risk. The experimental approach, which involves tests that meet certain criteria, is illustrated by a specific example (Section 4.2)

2. CASE STUDIES IN SOIL AND PLANTS

2.1. Long-term balance studies

Lysimeter experiments were begun in 1969 to assess the total long-term fate of ^{14}C -labelled chemicals under field conditions. Results and conclusions have

TABLE II. COMPARISON OF DISAPPEARANCE AND RESIDUAL BEHAVIOUR OF ALDRIN AND BUTURON WITHIN ONE VEGETATION PERIOD AFTER USE

Values are percentage of applied radioactivity

	Aldrin	Buturon
Total residues in top 10 cm soil layer based on applied ^{14}C	55.5	42.4
Parent compound in total residue of top 10 cm soil layer	22.5	13.5
Methanol non-extractable portion of residues of top 10 cm soil layer	4.2	22.7
Residues in leaching water	1.9	0.3

TABLE III. UNEXTRACTABLE RESIDUES^a IN SOIL (0–10 cm DEPTH) FOLLOWING SOIL TREATMENT WITH ^{14}C -CHEMICALS (IN % RADIO-ACTIVITY RECOVERED)

Chemical applied	Unextractable after 1 vegetation period	Unextractable after 2 vegetation periods
Dieldrin	1	3
Kepone	2	2
Kelevan	8	12
Aldrin	11	18
Imugan	32	68
2,2'-Dichlorobiphenyl	42	74
3,4-Dichloroaniline	84	89
Allylalcohol	91	Not analysed
p-Cl-aniline	95	92

^a Unextractable by 48-h extraction with methanol, acetone or chloroform in a Soxhlet.

been published [2-6]. Some 20 chemicals have been investigated in this model system. The chemicals were applied in one single dose and analysis of the radioactivity remaining in the soil, plants and in the lysate were made continually for at least nine years. The residue was, when possible, also chemically identified. By way of example, the material balance of 103 mg ^{14}C -aldrin added to the system is given in Table I [7]. It is shown that within five years half the radioactivity applied was lost by volatilization. It is seen that volatilization may be considered as being a major pathway of residue loss in the soil ecosystem, and the uptake by plants and leaching by water are of minor importance.

2.2. Persistence of a metabolite

Relative rapid disappearance of the parent compound does not necessarily indicate a complete degradation. A metabolite may be accumulated which is much more persistent than the parent compound. This has been demonstrated for compounds containing a chlorinated aromatic ring, and isotopically labelled in the ring. In Table II, data are given on the behaviour of the urea herbicide buturon and of the cyclodiene insecticide aldrin in the soil-plant system. The large portion of unextractable residue of buturon was attributed to the primary metabolite p-chloroaniline. Experiments with [^{14}C]-p-chloroaniline in the soil-plant system confirmed this view: more than 90% of the added radioactivity became 'unextractably' bound to the soil and plant tissue. Upon alkaline hydrolysis of the bound residues a significant portion was solubilized and identified as p-chloroaniline. This behaviour of the bound residual radioactivity would therefore be consistent with the presence of the parent compound in some bound form (see below).

2.3. Bound residues

The 'bound residue' problem has been discussed for several years. An important question is whether the residue is available for uptake by crops. Therefore studies of the bound residues, including their chemical identification and changes in the course of time, are of importance for the assessment of their availability. However, it is often a difficult analytical procedure to demonstrate the chemical nature of the bound residue unequivocally. Only recently, the successful identification of carbamate-derived bound residues in plants was described [8].

Results of an experiment with nine ^{14}C -labelled chemicals [9] added to soil have shown that in general the amount of soil-bound radioactivity increases with time (Table III). From this, the uptake of radioactivity by plants in the field was usually found to be very small: less than 1% of the total added radioactivity. However, the amount of the radioactivity taken up during the second vegetation

TABLE IV. COMPARISON OF ALDRIN/DIELDRIN RESIDUES IN PLANTS AFTER ALDRIN SOIL APPLICATION IN FIELD TRIALS AND ^{14}C EXPERIMENTS

Crop	Field Trials (ppm)			^{14}C Experiments ^a (mean ppm)
	Application rate (kg/ha)	Mean value or range	Highest value	
Potatoes, whole	2-4 ^b	0.04-0.06	0.10	0.17
	2-4 ^b	0.08	0.24-0.27	
Potatoes, peeled	2-4 ^b	0.01-0.03	0.03	0.06
	3-4 ^c	0.01	0.14	
Potatoes, whole (treated 1 year before planting)	2.5 ^b	0.04	0.11	0.10
Sugar beets, whole	2-4 ^b	<0.01-0.05	0.05	0.04
	2-3 ^d	0.06	0.06	
Sugar beets, whole (treated 1 year before planting)	2-4 ^b	<0.01	0.02-0.03	0.02
	2-3 ^d	0.01	0.01	
Sugar beet leaves	1-6 ^b	≤0.01	0.01	≤0.01
Maize kernels	1-6 ^b	<0.01-0.02	0.02	<0.01
Maize leaves, dry	1-6 ^b	0.01-0.07	0.07	0.04
Wheat grains	1-6 ^b	<0.01-0.01	0.01	<0.01
Wheat straw	2-4 ^b	<0.01-0.16	0.16	0.10

^a Application for ^{14}C experiments was 3 kg/ha.

^b Shell, private communication.

^c Lee, U.K. Ministry of Agriculture (1969).

^d Ref. [11].

period was not as much reduced as was lost by evaporation. Binding increases persistence and prevents the disappearance of residues through evaporation and leaching. Unextractability of the bound residue depends on the nature of the matrix. Soils rich in organic matter usually have a higher binding capacity. Upon soil treatment with sewage and waste compost smaller portions are bound, however, this may have been due to shorter exposure times.

TABLE V. INSECTICIDE RESIDUE UPTAKE BY PLANT SPECIES GROWN IN POTS

Insecticide	Plants	% of the appl. radioactivity in plants	Average % in plants
Aldrin	Spinach	1.66–6.66	3.3
	Carrots		
	Cabbage		
Dieldrin	Spinach	1.75–7.74	5.0
	Carrots		
	Cabbage		
Chlordan	Carrots	3.56	3.56
Technical heptachlor	Wheat	0.6	0.6
Isodrin	Carrots	3.1–4.0	3.6

2.4. The value of laboratory investigations for predicting chemical behaviour in the field

Well-designed experiments supply reproducible results that are correct in themselves but which may not be correlated easily with the situation in the field. In Table IV, results of a series of experiments are given which indicate a uniformly lower aldrin/dieldrin residue level in plants grown in the field compared with the respective lysimeter- ^{14}C experiments [10]. The values of the latter experiment are above the mean of the field trials, but generally within the same range. In field trials only the parent compounds, aldrin and dieldrin, are usually determined. The ^{14}C -data of Table IV also have been calculated as residue of aldrin or dieldrin equivalent. Similar careful interpretation of data as in the lysimeter and field trials of residue uptake by plants should be made in the analysis of ^{14}C residues in soils.

As indicated under field conditions, absorption of chemical residues by plants is generally less than 1% of the applied amounts. Reproducible greenhouse experiments with various plant species grown in pots revealed a higher percentage uptake (Table V). In the lysimeter experiment, aldrin uptake in carrot leaves was only 5% and in the carrots it was less than half compared with the uptake of plants grown in small pots. These findings indicate that when extrapolating experimental results to environmental situations, plant species must also be taken into account.

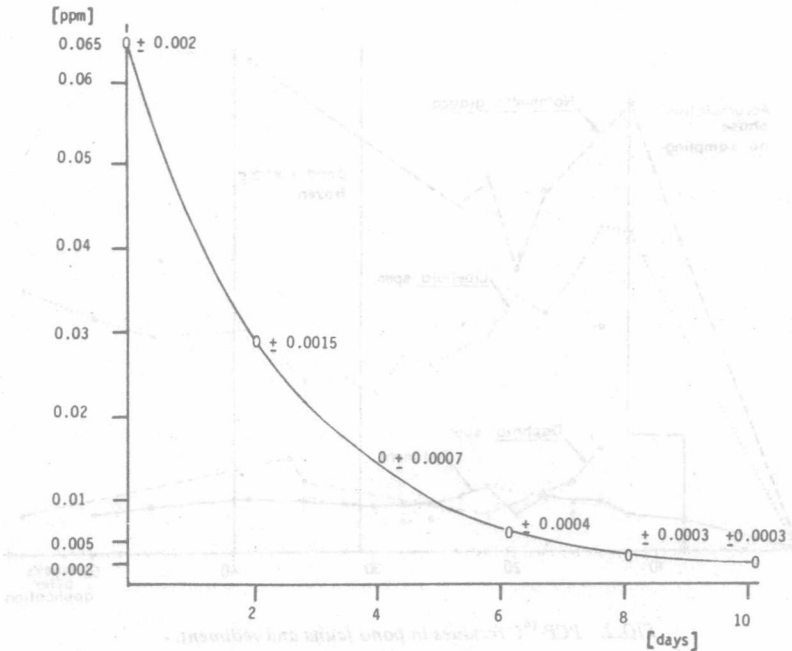


FIG.1. Decline of PCNB concentration in pond water.

3. Case studies in a pond system [12]

An open air aquatic ecosystem that has been used in the experiments is described below. Six units, each containing about 6 m³ of water, were dug in a marshy meadow and filled from a nearby natural pond. Within three weeks the experimental ponds had developed an ecosystem similar to that of the original pond. The only species artificially introduced were carp and golden orfe.

For the assessment of a long-term balance and ecotoxicological effects, three of the ponds were contaminated daily with 50 ppb of either ¹⁴C-labelled HCB (hexachlorobenzene), PCNB (pentachloronitrobenzene) or PCP (pentachlorophenol) for a period of three weeks. The three untreated ponds served as controls.

3.1. Fate of the chemicals in water and sediment

Total doses of 1200 mg HCB, 1500 mg PCNB and 2100 mg PCP, equivalent to concentrations of 0.2 to 0.3 ppm, were applied to the ponds. After three weeks, the applications were discontinued, and levels of ¹⁴C-radioactivity were found to decline rapidly, following first order kinetics, e.g. as is shown for PCNB in Fig.1. The half-life value for PCNB in pond water is about two days.

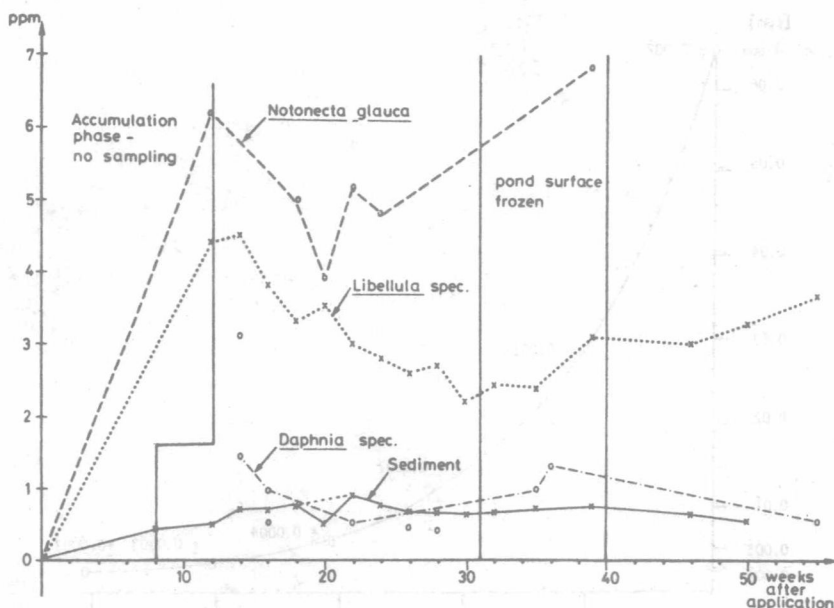
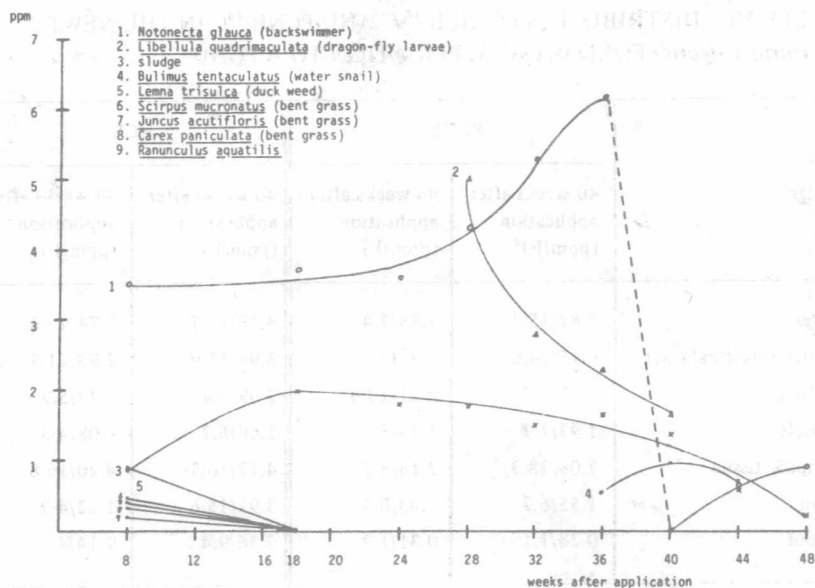
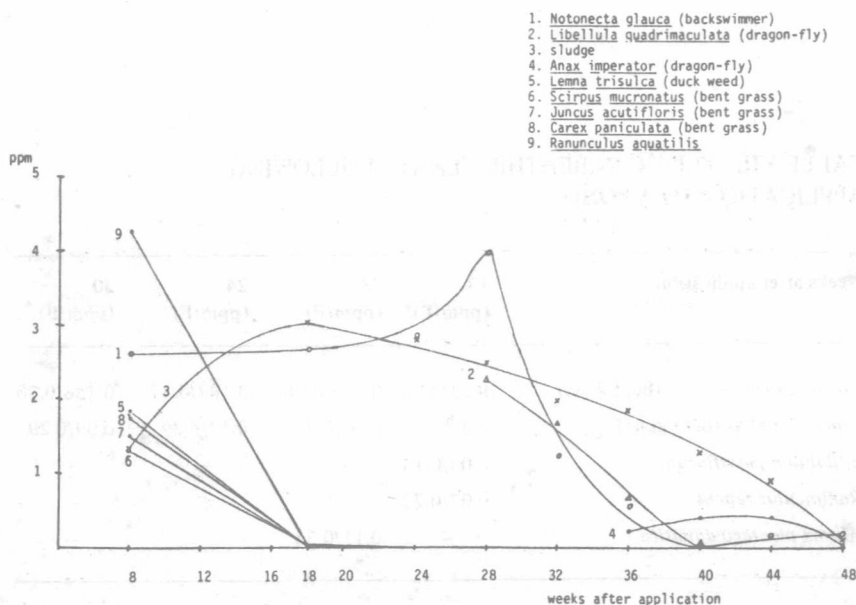


FIG. 2. PCP- ^{14}C residues in pond fauna and sediment.

The radioactivity of the added chemicals was found to accumulate mainly in the bottom sediment. HCB and PCNB concentrations reached a maximum value of 2.0 ppm and 3.0 ppm sediment fresh weight respectively within 18 weeks and then declined slowly to 12% and 5% respectively of the maximum within 30 weeks after application was stopped. The radioactivity remained in the first few centimetres of the soil around and at the bottom of the pond, and it was concluded that the residues do not leach out of the system.

3.2. Fate of the chemicals in flora and fauna

Residue levels recovered in various pond biota, based on radioactivity measurements, are given in Figs 2–4 respectively for PCP, HCB and PCNB. The time given is after termination of dosing. The data show that body burdens may increase even after the application was interrupted (e.g. in *Notonecta*). The values obtained with this organism demonstrate also that one has to be very careful in interpreting single analytical data. The curves for the three chemicals show similar qualitative accumulation patterns. Such observations suggest the possibility of developing general principles.

FIG. 3. HCB-¹⁴C residues in pond biota and sludge.FIG. 4. PCNB-¹⁴C residues in pond biota and sludge.