

RESIDUES IN GROUND WATER

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ABSTRACT

Ground water is a unique natural resource which is used throughout the world as a supply of drinking water. The detection of pesticide residues in ground water has caused much public concern and precipitated new legislation. The agrochemical industry have the responsibility for producing safe and effective crop protection products together with ensuring the integrity of ground water resources. The establishment of permissible pesticide concentrations in ground water, based upon individual toxicity, are part of a necessary framework for ensuring consumer safety, whilst maintaining crop production.

INTRODUCTION

Ground water represents one of the world's major natural resources and in many countries it is utilised as a vital source of drinking water. In the USA almost 50% of the population rely upon ground water for its sole source of drinking water and in the United Kingdom over 25% of water supplies are of ground water origin. Ground water is relatively cheap to abstract, causes minimal surface disturbance during abstraction, and produces water of consistent quality.

These plentiful supplies of water must however be managed correctly, if they are to continue to meet the needs of industrial, agronomic and domestic consumers. The protection of ground water quality has become a major environmental issue in recent years. Aquifers are prone to contamination which may render the source unsuitable for its desired application. Cleansing of contaminated aquifers can be both expensive and time consuming and so prevention of contamination is far preferable to remediation.

This paper explores the occurrence and significance of pesticide residues in ground water, in the context of crop production and environmental management.

GROUND WATER

In the environment, water continually undergoes physical changes of state and movement, these processes being known as the hydrologic cycle. Water from the seas and oceans of the world evaporate and the condensed vapour falls as rain over the land masses. The precipitation may run-off into streams and rivers, where it ultimately flows back into the seas. Another part of the cycle follows the path of rain water through the soil surface and into the sub-soil. Some of this moisture will be evaporated again and in the root zone some will be transpired by plants, but the

balance will percolate by gravity down through the unsaturated zone, ultimately reaching the ground water beneath. The water cycle is completed by the flow of the ground water and final discharge into rivers or seas.

Ground water formations are, therefore, areas of fully saturated sub-soil and are termed aquifers when sufficiently large in size to supply usable quantities of water. The formation of aquifers through percolating water is caused by the presence of an impermeable or restrictive lower formation (aquitard) upon which the area of saturation can accumulate. There are three types of ground water aquifer, depending upon the sub-surface geology, unconfined, confined and perched (Figure 1).

Unconfined

These aquifers are characterised by highly permeable sub-surface soils overlying impermeable or restrictive layers. The downward percolating water meets the restrictive layer and a saturated region forms, thus the recharge area will be directly above the aquifer. These aquifers may be vast in size and are truly unconfined, having no upper confining surface. The water levels may fall due to evaporation and abstraction, or rise during recharge events and there is no piezometric pressure on the water.

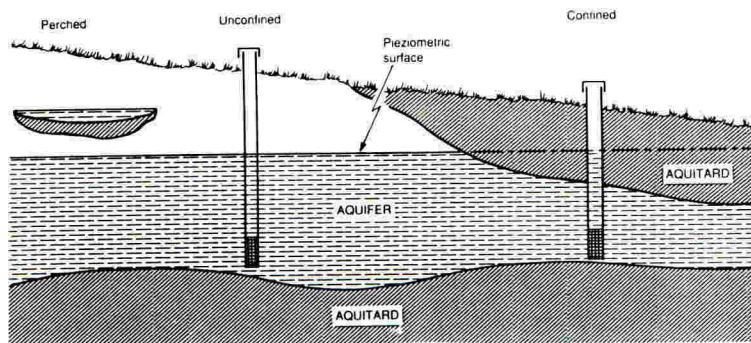
Confined

A confined aquifer is defined by a water bearing formation sandwiched between two impermeable layers. In these cases the recharge area may be located far away from the aquifer. Formations of this type are characterised by a pressure differential between the water in the confined aquifer and the natural unconfined watertable. This pressure is manifest in test borings into the confined regions, where water will rise up the borehole to the piezometric pressure surface.

Perched

Perched water tables are temporary unconfined aquifers formed above permanent unconfined aquifers, their formation being due to a restrictive area causing pooling of the downward travelling water. Perched aquifers may disappear in times of low recharge due to the slow downward percolation of water to the unconfined aquifer beneath.

Figure 1 : Ground Water Aquifers



The flows of ground water are not surprisingly slow, compared to free-flowing streams and rivers. The hydraulic conductivities of ground water are dependent upon the aquifer media. Coarse gravels without fines may exhibit conductivities of greater than 10^{-2} m/s, sand and silts slow down the flows, while clay formations may have conductivities as low as 10^{-12} m/s. Obviously, for a given flow direction in heterogeneous media, ground water will follow preferential flow paths.

Until very recently ground water was considered by many to be pure and plentiful, with little chance of contamination due to the depth at which it was often encountered. However, in 1984 the United States Congress charged the Office of Technology Assessment (OTA) with the responsibility for assessing the status of USA ground water. In this project the OTA identified and classified some 33 possible sources of contamination (OTA, 1984). The contaminants were grouped into categories based on their contamination mechanism. The following table summarises the findings:

Category	Mechanism of Contamination	Examples
I	Deliberate discharge	Septic Tanks, Cesspools, Injection wells, Irrigation.
II	Unplanned discharge during storage of substances	Landfills, Leaking storage tanks, Graveyards.
III	Unplanned discharge during transport or transmission	Leaking pipelines, Spillage.
IV	Discharge through planned activities	Fertiliser, Pesticides, De-salting.
V	Discharge through altered flow patterns	Excavations, Oil and Gas wells.
VI	Naturally occurring discharge	Salt-water intrusion.

The most common sources of ground water pollution were found to include human and animal wastes, industrial wastes, petroleum products (for example leaking fuel storage tanks), heavy metals and microbiological contaminants from landfill leachates, and salt due to salt water intrusion of aquifers along coastal areas. Agricultural products in ground water, whilst emotive, appeared far less significant.

PESTICIDES IN GROUND WATER

Interest in the extent to which pesticides were present in ground water was aroused in 1979, following the detection of the soil insecticide aldicarb, in a domestic well close to potato fields in Long Island, New York (Zaki *et. al.*, 1982). Further monitoring of the area revealed the extent of the problem and subsequent regulatory action eliminated the use of the product on Long Island. Aldicarb was later detected in ground water

in the central plains of Wisconsin and this was soon followed by the detection of DBCP and atrazine residues in other areas of the USA. In 1984, the US Environmental Protection Agency (EPA) reported the occurrence of 12 pesticides in Florida, New York, California and Hawaii (Cohen *et al.*, 1984) and by 1986, a total of 17 pesticides had been found in 23 states (Cohen *et al.*, 1986). In 1985, the US EPA announced a national drinking water survey which would monitor in excess of 60 pesticides.

Pesticides in ground water soon became the focus of attention in Europe. In 1987, monitoring studies were carried out on ground water in the Netherlands and atrazine, simazine, aldicarb and oxamyl were detected (Aharonson *et al.*, 1987). Monitoring studies have since been carried out in many European countries.

In many cases it is difficult to determine whether the presence of a pesticide in ground water is due to spillage, well contamination or genuine leaching, following normal agricultural use. However, it is vital that the origins of ground water contamination are revealed. Pesticides of low mobility may be labelled as 'leachers' and possibly withdrawn, despite the contamination being due to a non-agricultural misuse. Agrochemical companies are striving to develop products of low mobility, but contamination through misuse will always be a problem. The future will bring better products and greater education for the users.

FACTORS AFFECTING PESTICIDE LEACHING

The leaching potential for pesticides can often be predicted from the physico-chemical properties of the compound, coupled with environmental data. Obviously, parameters such as water solubility are key to the leaching potential, although no parameter should be considered in isolation. The strength of adsorption, of a pesticide to soil (K_d), will have great influence on the 'leachability', although even a mobile pesticide would pose little threat to ground water, if its half-life in soil was sufficient to cause degradation faster than leaching.

The following factors could all contribute to mobility and all should be considered when assessing the leaching potential of compounds.

- (i) High water solubility
- (ii) Low adsorption to soil and organic matter ($K_d < 5$ and $K_{oc} < 500$)
- (iii) Low volatility
- (iv) No significant photochemical decomposition
- (v) No significant hydrolytic decomposition
- (iv) Not rapidly degraded in soil
- (vi) Soil type in use area
- (vii) Recharge potential (irrigation and/or rain fall)
- (viii) Anionic charge

Obviously, if all of the above criteria are triggered, then a compound will have a high potential for ground water contamination. The difficulty is in predicting leaching potential of compounds which satisfy only some of these criteria.

In response to the increasing occurrence of pesticide residues in groundwater, government, academic and industrial scientists attempted to produce empirical models to predict 'leachability'. Early data on the potential for products to leach was generated from laboratory studies on soil columns. Indeed, even today there are standard regulatory protocols for laboratory column leaching studies of pesticides. It was not surprising, therefore, that the early models were designed to predict the movement of chemicals in these idealised test systems and to simulate the column leachate concentrations. The models assumed typical piston-flow through the column and included terms for dispersion and adsorption to soil.

With all models, the output data must be interpreted in terms of the input parameters, and so whilst these early models went some way to rank mobility for a given soil, they were unable to predict likely contamination of ground water since they contained no terms for vital parameters, such as degradation. An improved empirical model has been proposed (Gustafson, 1989) which links the adsorption of the pesticide to organic matter (K_{oc}), with the half life for degradation ($t_{1/2}$), where:

$$GUS = \log_{10}(t_{1/2}) \times (4 - \log_{10}(K_{oc})).$$

The Ground water Ubiquity Score ('GUS') can then be interpreted in terms of potential for leaching. GUS indices of <1.8 are attributed to "non-leachers" while compounds with GUS indices >2.8 are potentially "leachers". The author suggests that all compounds with GUS scores >1.8 be considered for further detailed modelling.

More elaborate predictive models have now been produced. The Pesticide Root Zone Model (PRZM) was developed by the US EPA and is able to predict ground water contaminant levels following multiple applications over many years (Carsel *et al.*, 1985). Models of this type require an extensive data input, including very detailed soil characterisation and weather data. Such models are most effective when calibrated against detailed analytical data, where the model can be refined using actual data and predictions made with greater confidence.

With increasing computational power and complexity of models, there is the risk that the model output will be seen as definitive. It must be remembered that whilst the models will give useful indicators for leaching they always work with degrees of idealisation. Soils, however well characterised, are heterogeneous media and therefore channelling, restrictions and preferential flow can always occur. Indeed, no model designed to simulate leaching following normal agricultural pesticide usage will be able to account for ground water contamination due to direct well contamination, through back siphoning from spray tanks, chem-irrigation or spillage of active ingredient. Conversely, pesticides thought to have ground water contaminating potential may not pose a threat in reality if sorptive sub-soil horizons are encountered.

MONITORING STUDIES

Theoretical information, from modelling exercises, obviously provides great insight into the risk of contamination, but only the analysis of field samples will show the real situation. In 1987, the EPA developed protocols for three types of field groundwater study.

The 'Small-Scale Prospective Study' focuses on new active ingredients and was designed to track the movement of the test chemical, from application, through the unsaturated zone, and ultimately into ground water. These prospective studies are designed to be conducted under 'worst-case' conditions, the soils being highly permeable homogeneous sands or loamy sands, the aquifers shallow and the rain fall high. The field results are used to calibrate the PRZM model, so that improved estimates for ground water residues, through repeated applications, varying soil types, and climatic conditions, can be made.

The two other protocols developed by the EPA were Small and Large Scale Retrospective studies. These focused on products already well established in the market. The aims of these monitoring studies were to provide information on the residue levels of a particular pesticide in either a localised area (Small-Scale) or for a wide use product, on a national-scale (Large-Scale).

For these monitoring studies it is not usually practical for the researcher to install new monitoring wells. The monitoring may take place over a very large area and many wells may need to be monitored. The Monsanto Chemical Company recently carried out a national alachlor well survey, in which a total of 1430 wells were sampled in 26 US states (Holden et al., 1990). The use of existing wells is therefore often necessitated, although each well should be thoroughly checked prior to use for monitoring purposes.

DESIGN OF MONITORING STUDIES

Before embarking upon a ground water monitoring programme, the aims of the study should be clearly defined and protocolled. Specific studies required to satisfy regulatory requirements (eg EPA protocols) may follow rigid study guidelines. However, research studies or those aimed at product and environmental stewardship should not be initiated until the aims of the study have been identified. Monitoring studies may be required for many reasons, to calibrate models, to survey residue levels in ground water, to track the movement of chemicals and cost will always be a vital factor to be taken into account in study design.

Ground water surveys are being conducted with increasing frequency their broad aims being to establish the levels of pesticides in ground water. Beyond this aim, one should look to the likely implications of results before sample collection. Sampling wells obviously need to be located or installed, although the installation of new wells over a large area is costly. Any existing wells, to be used for monitoring purposes, should be thoroughly checked prior to use. Old wells may be constructed in iron and may have corroded over the years, wells may be located near chemical storage or handling areas, they may have been used for chem-irrigation or to directly dilute active ingredient in spray tanks.

The detection of pesticide residues in ground water sampled from any one of these wells may be due to well contamination rather than pesticide leaching.

The geology and hydrogeology of the test areas should be investigated. The detail of the investigation will again depend upon the aims of the study. Studies aimed at monitoring movement and calibrating models will require more detailed sub-surface investigations than those aimed solely at residue levels in ground water. However, knowledge of the sub-soils and aquifers of the test areas will help in the interpretation of results. One question that should always be addressed is whether the test areas exhibit typical or extreme conditions for leaching, again the residue data should be interpreted in this light, before extrapolation to the wider environmental impact is considered.

In monitoring studies of any description, consideration must be given to the chemicals being monitored and to the limit of determination of the analyte. Monitoring surveys may be conducted on a single pesticide and perhaps its mobile metabolites, or for a range of pesticides. In each case individual consideration of the target limit of determination (LOD) should be given. Currently, in Europe, monitoring studies may be aimed at compliance with the EEC directive for drinking water standards (EEC, 1980) in which case the target LOD may well be 0.1 ug/l. The monitoring programme may be designed to determine the health consequences of pesticides in ground water and so target LOD's may be individually derived for each pesticide/metabolite based upon toxicity.

SAMPLING TECHNIQUES

There are various ways of taking ground water samples with varying cost and complexity. With every sampling technique it is important that a true aquifer sample is taken and not a static well sample. To achieve this, the sampling well should be purged prior to sampling. Several protocols for sampling have been proposed and are either based upon removal of several casing volumes of ground water prior to sampling or for the removal of ground water until the physico-chemical characteristics of the water (pH, temperature and conductivity) have stabilised.

In all cases the sampling equipment should be checked for compatibility with the monitoring chemicals (Chow *et al.*, 1990). The simplest mode of sampling is by plastic or Teflon bailer, its use is labour intensive and the risk of contamination may be high, but the materials are relatively cheap. Other sampling techniques require the use of a pump to bring the water sample to land surface. Pumps may be installed in the well, which reduces the risk of sample contamination, or above ground, which can cause problems with contamination, but does allow flexibility with sampling, when the pump can be transported to each location. Traditional sampling devices with pumping techniques have involved simple bottle collection, although more recently adsorbent filters and cartridges have been used (Hill *et al.*, 1989).

An important consideration prior to sample collection is storage and transportation. Samples should be treated to retain the integrity of the sample from the moment of collection to the time of analysis. If the analysing laboratory is near there may be little problem, although in many

cases it may be necessary to store samples for some time prior to transportation. Storage stability tests should be conducted to prove the integrity of samples. Often freezing and subsequent thawing of ground water samples will cause dissolved organic matter to flocculate and problems can be encountered with adsorption of analytes, at low concentrations to the organic precipitate. Indeed, the US EPA advocate the storage and shipping of samples at 5°C to prevent the adsorption problem. However, the shipping of samples in a chilled state is often more difficult, and costly, than freezing. Cartridge sampling offers a useful alternative where the loaded adsorbents can be frozen during transportation. With all modes of sampling the risk of contamination should always be born in mind. Sampling in windy conditions should be avoided and all sampling staff should be trained in zero-contamination sampling techniques.

ANALYSIS

The analysis of groundwater samples in the analytical laboratory is performed by sample concentration followed by quantitation. Sample concentration can be performed by liquid-liquid or solid-liquid partitioning, although often large sample volumes are required to achieve low limits of determination. Recently, automated systems aimed at the concentration of water samples have become commercially available and these help to increase sample throughput. The advantages of cartridge collection of ground water samples can be seen in the laboratory, where analytes can be eluted in a small volume of organic solvent without further concentration.

The final determination can be carried out using a range of chromatographic techniques with selective detection. The final quantitative technique being governed by the analytes in question. The development of multi-residue methods for pesticides increase the amount of information that can be generated from a single monitoring study. This approach has been used by the US EPA who have monitored a total of 126 analytes using just eight analytical protocols (US EPA, 1990).

SIGNIFICANCE OF RESULTS

There is no doubt that under conspiring circumstances pesticides may be detected in ground water. However, recent large-scale surveys have shown that detections are a rare occurrence and the levels when detected are usually very small. For example, in a study carried out in Germany during 1986, a total of 13,000 water samples were analysed from some 200 sampling wells. Less than 0.5% of the samples analysed contained pesticide residues above 0.1µg/l (IPS, 1987).

The last decade has seen the introduction of quality standards for ground and drinking water in many countries. In 1980, a European Community Directive (EEC, 1980) set out Maximum Admissible Concentrations (MACs) for pesticides in drinking water. These arbitrary maximum permissible levels were set at 0.1µg/l for individual pesticides and 0.5 µg/l for the total pesticide concentration. The levels were set similarly for all pesticides irrespective of use pattern, agricultural benefits and, most importantly, toxicity.

Several attempts have been made to propose MACs that were derived based upon the wealth of toxicity data available for registered pesticides. In 1984, The World Health Organisation (WHO, 1984) proposed that a fraction of the pesticides' acceptable daily intake (ADI) be allocated to residues in drinking water. This move was followed by the establishment of Health Advisory Levels (HALs), for individual pesticides, by the US Environmental Protection Agency (US EPA, 1989). The HALs are concentrations of individual pesticides that if consumed every day for a lifetime would cause no harmful effects. The HALs utilise 20% of the ADI and assume a consumption of 2 litres of drinking water per day. In 1987, GIFAP produced a toxicological evaluation of pesticides in drinking water in which they proposed that at least 10% of the acceptable daily intake (ADI) for a given pesticide be allocated (GIFAP, 1987).

In the United States a National Survey of Pesticides in Drinking Water Wells (NPS) has recently been completed by the EPA. The study was conducted between 1988 and 1990, sampled approximately 1300 community water systems (CWS) and analysed 101 pesticides and 25 pesticide degradates (US EPA, 1990). The survey was statistically designed to represent approximately 95,000 drinking water wells and over 10.5 million rural domestic wells. The results indicated that approximately 10% of CWS wells and 4% of rural domestic wells contained at least one detectable pesticide, although significantly, less than 1% of all wells contained ground water with concentrations above HALs. This monitoring programme was designed to establish the status of United States' ground water in the light of the HALs. The results will help to map those areas with vulnerable aquifers and to determine where pre-treatment of the water may be necessary before consumption.

Pesticides are, and will continue to be, an essential agricultural tool in global crop production. Recent advances in environmental science, mathematical modelling and analytical chemistry, now enable the registration of new, more effective and environmentally benign products. However, pesticides by their very nature, are released into the environment, and despite lower application rates, more biodegradable products and greater operator education, ground water contamination can never be totally eliminated. The vast database of toxicity data that is available for each product, as in the United States, should, however, be used to determine risk to the consumer.

In Europe, it is this part of the environmental and scientific jigsaw that is still missing. Arbitrarily set drinking water standards, often set at the limits of analytical determination are essentially pseudo-zero standards. If enforced, these sometimes unachievable standards will cause a reduction in the range of available products, thus affecting national agricultures, and also cause unnecessary public concerns over water safety.

CONCLUSIONS

Ground water is a unique natural resource and utilised as a supply of drinking water throughout the world. It is vital that water should be available in sufficient quantity and quality for human consumption. The agrochemical industry is charged with the responsibility for producing safe and effective crop protection products and within this lies the responsibility for ensuring that ground water supplies are preserved for

industrial, agricultural and domestic consumers. Ground water will not provide a supply of quality water unless the use of agrochemical products are managed effectively.

The agrochemical industry has taken on the challenge of producing safe and effective products to aid crop production, but the establishment of individual permissible pesticide concentrations, based on sound risk assessment, in ground and drinking water, are essential if crop production can go hand-in-hand with environmental management.

REFERENCES

- Aharonson, N.; Cohen, S.Z.; Drescher, N.; Gish, T.J.; Gorbach, S.; Kearney, P.; Otto, S.; Roberts, T.R.; Vonk, J.W. (1987) 'Potential contamination of ground water by pesticides', Pure and Appl. Chem., 59, 1419-46.
- Carsel, R.F.; Mulkey, L.A.; Lorber, M.N.; Baskin, L.B. (1985) 'The Pesticide Root Zone Model (PRZM): a procedure for evaluating pesticide leaching threats to ground water', Ecological Modeling, 30, 49-69.
- Chow, W.; Jones, R.L.; Norris, F.A.; Romine, R.R. (1990) 'Validation of Hardware Materials Permitted for Groundwater Sampling of Agricultural Chemicals', Poster Presentation 08A-11, Seventh International Congress of Pesticide Chemistry, Hamburg, Germany.
- Cohen, S.Z.; Creeger, S.M.; Carsel, R.F.; Enfield, C.G. (1984) In 'Treatment and Disposal of Pesticide Wastes'; Krueger, R.F.; Seiber, J.N., Eds.; ACS Symposium Series No. 259, pp 297-325, American Chemical Society, Washington, DC.
- Cohen, S.Z.; Eiden, C.; Lorber, M.N. (1986) In 'Evaluation of Pesticides in Ground Water'; Garner, W.Y.; Honeycutt, R.C.; Nigg, H.N., Eds.; ACS Symposium Series No. 315, pp 170-96, American Chemical Society, Washington, DC.
- EEC (1980) 'EEC Directive Relating to the Quality of Water Intended for Human Consumption' (80/778/EEC).
- GIFAP (1987) 'Toxicological Evaluation of Pesticides in Drinking Water', GIFAP, Avenue Albert Lancaster 79A, 1180 Bruxelles, Belgium.
- Gustafson, D. (1989) 'Ground Water Ubiquity Score: a simple method for assessing pesticide leachability', J. Environ. Tox. Chem., 8, 339-57.
- Hill, I.R.; Simmons, N.D. (1989) 'The Advantages of Solid-Phase Extraction Techniques for Water Sampling Under Field Conditions - Part II' Proc. 198th ACS National Meeting, Miami Beach, Florida.
- Holden, L.R.; Graham, J.A. (1990) 'The National Alachlor Well Water Survey', Poster Presentation 08D-12, Seventh International Congress of Pesticide Chemistry, Hamburg, Germany.

- IPS (1987) 'Pflanzenschutzwirkstoffe und Trinkwasser - Ergebnisse einer Untersuchung der Pflanzenschutzindustrie. Industrieverband Pflanzenschutz. V., Frankfurt/Main, 36pp.
- Office of Technology Assessment (1984), 'Protecting th Nation's Groundwater from Contamination', OTA-0-133, U.S. Congress, Washington, DC.
- United States Environmental Protection Agency (1989) 'Health Advisory Summaries' National Pesticide Survey (WH-550A), Office of Pesticide Programs, US EPA, Washington, DC 20460.
- United States Environmental Protection Agency (1990), 'National Pesticide Survey - Project Summary' Office of Pesticide Programs, US EPA, Washington, DC 20460.
- World Health Organisation (1984) 'Guidelines for Drinking Water Quality - Volume 1', Geneva 1984.
- Zaki, M.H.; Moran, D.; Harris, D. (1982) Am. J. Public Health, 72, 1391-5.

THE DETERMINATION OF PESTICIDE LOSSES TO WATER COURSES IN AN AGRICULTURAL CLAY CATCHMENT WITH VARIABLE DRAINAGE AND LAND MANAGEMENT

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ABSTRACT

An experiment was established in a small partly urbanised clay catchment with mixed land use to examine pesticide residue losses to water. By examination of the physico-chemical characteristics of the individual pesticides and the range of formulations applied to the intensively cropped arable areas, a target list of pesticides that it was thought might reach watercourses was identified for study. A water sampling strategy was established, based on automatic and manual sampling, and linked to the hydrologic responses over the drainage season. Water samples were analysed using hplc, gc and ms techniques. In small farm ditches, concentrations of three herbicides were found in excess of 10 µg/l. Elsewhere in the catchment, concentrations were in the range 1 to 3 µg/l. Also occasional concentrations of another three pesticides reached 8 µg/l. The highest concentrations observed were correlated with point source inputs from agricultural areas.

INTRODUCTION

During the last few decades, UK agriculture has become more intensive with increases in the use of agrochemicals and improvements to drainage of clay soils (Raymond, 1984). At the same time there has been an increase in the occurrences of agrochemicals, including pesticides, in watercourses. However, the recent EC Directive for potable waters (Anon., 1980) has led to the need to improve the water supply quality from both groundwaters and surface waters. Although studies have been carried out in the United States and elsewhere on the transport and detection of pesticide residues in water systems (Monke *et al.*, 1989; Hall *et al.*, 1989) knowledge in the UK has until recently been largely confined to large catchment or borehole sources sampled by the River Authorities/NRA (Lees & McVeigh, 1988). As soil type and climatic regime could influence the transport mechanisms of agrochemicals, a number of studies representative of UK conditions have been established to determine the source, rate and implications of pesticide losses. These studies are being conducted in both permeable and impermeable catchments, including sites where soil and crop management strategies are included that might minimise pesticide losses.

One of these studies is located within a small clay-based catchment

in East Anglia, in an area where pesticides have been frequently detected in watercourses (Lees & McVeigh, 1988). The site, although some distance from a potable water supply intake, is particularly interesting since it includes both intensive and non-intensive agricultural areas together with inputs from an adjacent urbanised area. The study forms part of a wider programme, in conjunction with the NERC Institute of Terrestrial Ecology, to examine the effect of land management on the hydrology and ecology of landforms and watercourses. The principal objective of the pesticide study is to determine the transport mechanism and concentrations of key pesticides in drainage water under different land uses and weather patterns.

This paper describes the experimental design and data collection methods, including water sampling. The analytical methodology and quality assurance undertaken are described together with some observations of pesticide residues detected. The significance of the concentrations to the EC Drinking Water Directive for potable waters is discussed.

EXPERIMENTAL DETAILS

The site

The 500ha discrete catchment represents a tributary to the River Great Ouse at Swavesey, Cambridgeshire. The area is subdivided into two principal units with different management systems. The upper part of the catchment has been drained and intensively farmed as grassland and arable units since the early 1970's. The soils are a heavy clay of the Denchworth series (Clayden & Hollis, 1984) typical of many cereal growing areas. In the lower catchment, much of the silty clay floodplain soil has been recently converted to intensively drained arable and grassland following the installation of a pumped drainage scheme. Run-off from several farmyards, the adjacent village and access roads can enter the catchment.

Agricultural management

A comprehensive database has been established for each field within the study area. Detailed farm records have been supplied for each harvest year by the farmers for 80% of the area, covering cropping, nitrogen and agrochemical applications (Table 1). Information on cropping is also collected by ADAS advisers for the majority of fields each year to support estimates of likely agrochemical applications for those fields not covered by the farm records.

The most widely used pesticides are mecoprop, applied in spring to 17-30% of area and isoproturon, applied to 20-34% of the area between autumn and spring. Although only small changes in cropping occurred over the study period (Table 1), a slight trend towards lower usage of some of the target pesticides was seen by the harvest year 1990. The majority of pesticides were applied at label-recommended rates.

Hydrologic studies

Pumping from the catchment was recorded using logged sensors and autographic water level recorders located on the pumped drainage storage lagoon and adjacent carrier drain. Together with Internal Drainage Board records and the pump calibration, run-off was continuously monitored. The hydrologic response to rainfall events and the impact of pumping were

recorded in the catchment, by a range of autographic recorders within the ditch system, and an extensive replicated array of dipwells within fields. Within the upper catchment, a sub-area of 40 hectares was instrumented with a pre-formed calibrated glass fibre flume and dual ultrasonic and pressure transducer head recorders. Rainfall was recorded by two gauges within the catchment and data from an automatic weather station were available from the ADAS Boxworth EHF, located approximately 6 km south.

TABLE 1. Cropping area (%) and the proportion (%) receiving mecoprop (Mec) and isoproturon (IPU) in the catchment, harvest years 1988-90.

	1988			1989			1990		
	Area	Mec	IPU	Area	Mec	IPU	Area	Mec	IPU
TOTAL	-	30	34	-	17	23	-	21	20
Winter Wheat	40	14	26	47	14	20	34	15	16
Spring Wheat	0	0	0	2	2	0	4	2	2
Winter Barley	14	11	8	9	1	3	9	4	2
Spring Barley	5	5	0	0	0	0	0	0	0

Water Sampling

Water samples for pesticide analysis were collected from both ditches and drainage pipes. Samples were taken to be representative of both run-off following rainfall events and of quieter flow recession periods. Sampling was intensified to cover the initial run-off following autumn pesticide applications but continued throughout some years to cover also spring applications and the run-off response from early summer thunderstorms.

Manual water sampling

Manual samples were taken by immersing 2.5 l darkened glass bottles into the watercourses or by direct collection from field pipe drains. For new bottles, the manufacturer's dust cap was removed shortly before sampling; recycled bottles underwent a comprehensive washing programme which included repeat rinses and pressure washing. All bottles were also prior rinsed in situ with the sample water and then sealed with a plastic cap with inert inner seal, coded against location, time and date of sampling and then delivered within 24 hours to the laboratories for subsequent analysis.

Automatic water samples

Samples were also taken using three programmable water samplers located in the catchment. The sampler type used was chosen after investigation of the range of water samplers suitable to support pesticide studies. The system operated utilised a battery source to pump approximately 350 ml of stream water into a glass canister immediately prior to taking each sample. This was then run to waste through a silicon manifold and distributor arm to a discrete tube. This process acted to flush the canister and inlet tube prior to the rotor arm moving to the appropriate sample bottle.

Each sample routine followed this procedure with seven further 'shots' delivered through a discrete silicon tube to provide the required 2.5 l

sample. When the required number of samples had been taken, the glass sample bottles were sealed with a plastic cap with inert inner seal, coded against location and date of sampling and then delivered to the laboratories for subsequent analysis, usually within 72 hours of the sampler operation.

Although, to avoid contamination, it was desirable that the manifold and bottle tubing were made of teflon, there was insufficient flexibility in teflon tubing to provide a manifold to feed the 24 sample bottles. However, it was considered that water would pass rapidly through this part of the system with minimum exposure time to the silicon parts. The teflon coated sampler inlet tube was fixed to an adjustable metal bracket driven into the stream bed. An adjacent water level recorder defined the relationship between the sequential water samples and the catchment hydrologic response.

The water samplers were initiated automatically using pre-set level triggers with variable sensitivity depending on location and frequency of sampling required. Sampling within the flume was triggered by a sensitive electronic prong switch where the rising water formed a connection between two electrodes. Elsewhere, particularly where debris might be a problem, a float switch trigger was mounted in a small plastic chamber sump. At each location, an environmentally sealed Newlog 32K data logger was linked to the water sampler to record sampling times. The logger data were regularly downloaded using a hand-held Psion computer and transferred to a datapak.

PESTICIDE RESIDUE ANALYSIS

Active Ingredients

The active ingredients selected for analysis in this study were the aryloxyalkanoic acid herbicide mecoprop, (widely used in the catchment), the urea herbicides isoproturon and chlorotoluron (also widely used), linuron, the triazine herbicides atrazine and simazine (frequently reported in water sources) and the insecticide dimethoate. Indicators of mobility and persistence of the pesticides selected are given in Table 2.

Analytical Methods

The sample volume was sufficient for a replicate analysis if required.

Extraction Procedure

A one l aliquot of unfiltered water was placed in a 2 l separating funnel, 30 g NaCl was added and the mixture shaken until the NaCl dissolved. 25 ml, 2N HCl was added, followed by 100 ml dichloromethane, and the funnel shaken for 2 minutes. The dichloromethane was runoff into a 500 ml bottle containing 25 g anhydrous Na_2SO_4 . The water was then re-extracted with a further 100 ml dichloromethane. The dichloromethane extracts were combined and filtered through either a Whatman No. 1 filter paper or a funnel containing anhydrous Na_2SO_4 into a Florentine flask. The volume was reduced to approximately 5 ml using a rotary evaporator. The flask contents were transferred to a 7 ml vial, the flask was rinsed with small amounts of dichloromethane and the washings combined in the vial. The vial contents were evaporated to dryness under a stream of dry nitrogen. The residue was dissolved in 1 ml of methanol and then divided into two 0.5 ml portions.

The extracts were stored at -18°C prior to analysis. The extract was used directly for the determination of isoproturon, chlorotoluron, linuron,

dimethoate, atrazine and simazine. For the determination of mecoprop, a 0.5 ml portion of the extract was evaporated to dryness and then derivatised to form a pentafluorotoluene derivative (Anon., 1986).

TABLE 2. Indicators of mobility and persistence - active ingredients

	Octanol-water ¹ partition coefficient Kow	Water ¹ solubility (mg/l)	Approximate soil persistence ² of active amounts for weed control (months)
Mecoprop	1	620	0.5-1
Isoproturon	177	55	2-4
Chlorotoluron	195	70	3-6
Atrazine	219	30	4-18
Simazine	91	5	4-8
Linuron	1010	81	3-6
Dimethoate	5	25000	Not applicable

¹ Source - Worthing & Hance (1991), ² Source - Riley & Eagle (1990)

Determination of the Pesticides

The concentrations of isoproturon, chlorotoluron, linuron, atrazine and simazine were determined by reverse phase hplc using a photodiode array detector. Dimethoate and mecoprop concentrations were determined by gc using a nitrogen/phosphorus detector and an electron capture detector, respectively. The limit of detection was 0.1 µg/l (the EC maximum permitted concentration for a single pesticide in potable water (Anon., 1980) or less, except for mecoprop where the limit of detection ranged from 0.2-0.5 µg/l.

For results above the limit of detection, the identity of the pesticide(s) was confirmed in one of several ways. For those pesticides determined by hplc using photo-diode array detector, the identity could be confirmed by comparing the u.v. spectrum with that of a known standard. Alternatively, the extract was re-analysed using a normal phase hplc system with a fixed wavelength u.v. detector. For those pesticides determined by gc, the identity was confirmed by re-analysis of the extract using a column of different polarity to that used for the initial analysis.

Mass Spectrometry

Some of the most important results were confirmed by mass spectrometry. For those pesticides amenable to gc analysis, gc-ms provided a qualitative and quantitative confirmation of the results. An ms interfaced to an hplc system was not available. However, it was possible to provide qualitative and semi-quantitative confirmation of some relatively high concentrations of isoproturon by using direct insertion-ms.

Analytical Quality Assurance

In order to ensure the validity of the analytical data, two types of quality assurance work were performed: recovery experiments and storage

stability experiments.

In the early phases of the work, the recovery experiments consisted of adding known amounts of pesticide (equivalent to 2 µg/l in the sample) to sample replicates. These spiked replicates were analysed and the amount of added pesticide determined and expressed as a percentage of the known amount added. This procedure proved to be inadequate where the samples contained concentrations many factors greater than 2 µg/l. Therefore the recovery procedure was refined so that the water sample was retained after initial extraction and then spiked and re-extracted. Recovery data were typically between 58 and 94%.

Shortly after the initiation of the experimental programme, a bulk sample of water was spiked with four of the target pesticides - mecoprop, isoproturon, atrazine and dimethoate, one from each chemical class. The sample was then mixed, and sub-divided into aliquots. Some of these were extracted and analysed immediately, those remaining were stored in a cold-room for three months and were extracted and analysed at monthly intervals. This storage time was typical of the early stages of the experiment. The results showed little reduction (less than 20%) in the concentration of isoproturon after three months but, for atrazine and dimethoate, the reductions in concentrations were 60% and 50% respectively.

The data for mecoprop were incomplete due to analytical difficulties with the method. This means that those results above the limit of detection could be underestimated by as much as 50% and that the true limit of detection may have been 0.2 µg/l. However, this does not greatly affect the overall conclusions based on the results which were uncorrected for both recovery and storage stability.

The laboratory procedures have been considerably improved; samples are currently stored in a cold-room for not more than 14 days before they are extracted. Storage stability experiments are being conducted under these conditions. The concentration of pesticides so far examined (isoproturon, chlorotoluron, linuron, atrazine and simazine) declined by less than 20%.

RESULTS

Rainfall/Run-off

The hydrology of the catchment was strongly influenced in the study period by very contrasting weather. The winter, 1988/89 was relatively mild and dry and was followed by a very warm and dry spring and summer producing lower than average drainflow. Autumn/winter 1989/90 was again relatively mild but was characterised by very high rainfall in December 1989 which produced rapid water movement within the catchment. The remainder of 1990 was again particularly dry with little flow after late spring 1990. Although some water movement through gravel bands in the silty clay soil was possible, the discreteness of the catchment was demonstrated by a water balance close to 100% over the hydrologic year from August 1989 to 1990.

Pesticide losses

Water samples for analysis of the target pesticides were collected from Swavesey from spring 1989. Analysis has been completed and confirmed on samples up to spring 1990 only.

Pesticide residues were identified in watercourses throughout the catchment in 1990, with the highest detections following heavy spring or summer rainfall, in small farm ditches in the upper catchment. In 1990, simazine was detected at nearly 100 µg/l compared with similar data for 1989 for the same area when the highest concentrations detected for simazine were 35 µg/l, mecoprop at 40 µg/l and isoproturon at 240 µg/l. Examination of the likely sources for these high concentrations suggested that they originated from point sources rather than diffuse leaching, either as run-off from farmyards where application chemicals were mixed or as the result of accidental spillages.

Diffuse losses were detected throughout the catchment with concentrations in the lower catchment ditches typically in the range 1-3 µg/l for simazine, atrazine and isoproturon. Isoproturon was regularly detected in winter 1989/90 following the onset of regular drainflow. Occasional higher concentrations, up to 8 µg/l, were detected for linuron, chlorotoluron and dimethoate in late spring. Atrazine was found regularly in the Swavesey catchment, despite no known agricultural usage. Sub-sampling within the catchment indicated two principal sources - urban run-off in the upper catchment and from railway ballast in the lower catchment. Mecoprop was rarely detected, although some difficulties occurred with the initial analysis for this chemical.

DISCUSSION AND CONCLUSIONS

There are few similar studies in the literature with which to compare the losses reported here. However, in studying the pathways of pesticide movement into streams in Canada, Frank *et al.* (1982) reported 22% of the total load could be attributed to spills. Atrazine concentrations from field drains were reported by Monke *et al.* (1989) ranging from 1-10 µg/l in Indiana and Southwick *et al.* (1988) found concentrations up to 3.5 µg/l in Louisiana field drains.

The high concentrations found in ditches in the Swavesey study and attributed to point sources demonstrates the importance of careful practice by operators when handling pesticides. It also suggests that some relatively large inputs to water could quite easily be reduced.

The diffuse losses were lower in concentration but remained for longer duration. As the catchment is some distance from potable water sources, some dilution would be expected to take place before reaching abstraction points. However, if the diffuse losses recorded at Swavesey are the result of normal farm practice, it seems likely that pesticide loss could occur along much of the course of the river and its tributaries in intensively farmed areas and that there might not be sufficient dilution available. The EC Drinking Water Directive (Anon., 1980) refers to the concentration found in water consumption at the tap. Contaminating the raw supply, with insufficient dilution from the rest of the catchment, will affect the ability of the Water Undertaker to provide potable water in compliance with the Directive without further treatment. This has been demonstrated in the large catchment Granta study (Clark *et al.*, 1991), where mecoprop, isoproturon, chlorotoluron and simazine, amongst others, have been recorded in raw river water at concentrations above the EC drinking water limit.

The results of this study and future work should be brought to the attention of the MAFF Pesticide Safety Division for the appropriate

regulatory action.

Future work at Swavesey aims to identify the mechanisms involved in pesticide loss, determine the mass load of pesticide leaving the catchment and, in conjunction with the Institute of Terrestrial Ecology, assess the ecological impact of these losses.

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REFERENCES

- Anon. (1980) EC Council Directive relating to the quality of water intended for human consumption (80/778/EEC). Off. Journal European Community, No. L229/11-29.
- Anon. (1986) Chlorophenoxy Acid Herbicides, Trichlorobenzoic Acid, Chlorophenols, Triazines and Glyphosate in Water 1985. Methods for the Examination of Waters and Associated Materials. The Standing Committee of Analysts. The Department of the Environment. HMSO 1986.
- Clark, L.; Gomme, J.; Hennings, S. (1991) Study of pesticides in waters from a chalk catchment in Cambridgeshire. Pesticide Science. 32, 15-33.
- Clayden, B.; Hollis, J.M. (1984) Criteria for differentiating clay soils. Soil Survey Technical Monograph No. 17, p99. Harpenden, UK.
- Frank, R.; Braun, H.E.; van Hove Holdrinet, M.; Sirons, G.J.; Ripley, B.D. (1982) Agriculture and water quality in the Canadian Great Lakes Basin: V. Pesticide use in 11 agricultural watersheds and presence in stream water, 1975-1977. Journal Environmental Quality, 11, 497-505.
- Hall, J.E.; Murray, M.R.; Hartwig, N.L. (1989) Herbicide leaching and distribution in tilled and untilled soil. Journal Environmental Quality, 18, 439-445.
- Hance, R.J. (1989) Accuracy and precision in pesticide analysis with reference to the EC 'water quality' directive. Pesticide Outlook. 1, 23-26.
- Lees, A.; McVeigh, K. (1988) An investigation of pesticide pollution in drinking water in England and Wales. Friends of the Earth Report, London. 151pp.
- Monke, E.J.; Kladvivko, E.J.; Van Scoyoc, G.E.; Martinez, M.; Huffman, R.L.; (1989) Movement of pesticides and nutrients in drainage water. In: Land and Water Use, Dodd & Grace (Eds), Balkema, Rotterdam, 297-304.
- Worthing, C.R.; Hance, R.J. (Eds) (1991) Pesticide Manual, 9th Edition. Published by BCPC.
- Raymond, W.F. (1984) Trends in agricultural land use: the lowlands. In Agriculture and the Environment. Proceedings of ITE Symposium, Monks Wood Experimental Station, UK, Feb. 1984, 7-12.
- Riley, D.; Eagle, D. (1990) Herbicides in soil and water. In: Weed Control Handbook-Principles. R.J. Hance and K. Holly (Eds), 8th Edition. 243-259. Issued by BCPC. Published by Blackwell Scientific Publications.
- Southwick, L.M.; Willis, G.H.; Bengston, R.L.; Lormand, T.J. (1988) Atrazine in subsurface drain water in southern Louisiana. In: Proceedings on Planning Now for Irrigation and Drainage, IR Div/ASCE, 580-586.

PESTICIDE RESIDUES IN WATER SUPPLIES

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ABSTRACT

The paper describes the current UK drinking water standards for pesticides and an overview of the pesticide levels currently found. The results of monitoring by Anglian Water Services are used for illustrative purposes. Actions to comply with standards are discussed briefly and views offered on the way forward.

BACKGROUND

Drinking water quality is a subject which has been given extensive attention by the media in recent years. Initially it formed part of the publicity associated with privatisation of the water industry in England and Wales, but following privatisation the high profile of drinking water quality has been maintained. Water customers are now much more aware of quality issues and are asking far more questions of the water companies than ever before. Some quality aspects have received greater publicity than others and pesticide residues have received greater attention than most. In the debate about pesticide residues the EC Drinking Water Directive (EEC, 1980) has figured prominently.

CURRENT DRINKING WATER STANDARDS

The EC Drinking Water Directive was adopted by the Community on 15 July 1980 and Member States were required to take the necessary steps to ensure compliance with the directive by 1985. It set standards for "pesticides and related products" which were defined as insecticides, herbicides, fungicides, PCBs and PCTs. The standards were described as maximum admissible concentrations (MACs) in drinking water of 0.1 $\mu\text{g/l}$ for individual pesticides and 0.5 $\mu\text{g/l}$ for total pesticides.

Thus all pesticides were treated as equal and compliance with the total pesticides limit became in large part a function of the number of pesticides included in the analytical suite. These standards were criticised as unscientific and clearly not related to toxicological considerations. They arose, however, from an approach which is somewhat different from that traditionally adopted in the UK. The political view was taken that there should be no pesticides in drinking water and the 0.1 $\mu\text{g/l}$ standard was adopted as a "surrogate zero" related to the analytical limits of detection at the time.

Despite the concern of the water industry and UK government about the EC approach adopted to setting standards for pesticides, the standards were explicitly incorporated as MACs into UK law in the Water Supply (Water Quality) Regulations 1989. Furthermore the Regulations set monitoring requirements which meant that more samples had to be analysed

for pesticides than had generally been the case previously.

Upon the incorporation of the EC pesticide standards in the Regulations water companies had to take action to meet them. Where they could not be met companies were obliged to offer formal undertakings to the Secretary of State for the Environment under Section 20(5)(b) of the Water Act 1989. In this way the companies gave a firm commitment to action by a specified date.

However, Government recognised that non-compliance with the pesticide standards *per se* did not threaten the safety of water supplies. DoE therefore published advisory limits for individual pesticides based upon toxicological data and World Health Organisation methodology. (Department of the Environment/Welsh Office, 1989). These limits are provided for guidance pending compliance with the UK statutory limit of 0.1 µg/l. It is worth noting that whilst most advisory limits are higher than 0.1 µg/l, the advisory limit for aldrin and dieldrin are 0.03 µg/l, i.e. less than the EC standard. Examples of the advisory limits for some of the more widely occurring pesticides are:-

atrazine	2 µg/l
simazine	10 µg/l
mecoprop	10 µg/l
MCPA	0.5µg/l
isoproturon	4 µg/l

No advisory limit for total pesticides has been proposed and the view taken widely in the UK is that it is the concentration of individual pesticides which are of primary significance. Nevertheless compliance with the EC total pesticides limit will become increasingly difficult as the range of pesticide analyses extends.

The UK government has asked the European Commission to review the pesticide standards to provide individual standards based on toxicology.

CURRENT PESTICIDE CONCENTRATIONS

So what pesticide residues are finding their way into drinking water?

Intensive arable farming is practised over much of Eastern England. So one might expect this to be an area where pesticide residues are found most frequently. About 50% of Anglian Water supplies come from rivers and reservoirs and about 50% from ground water sources. The surface waters are subjected to extensive treatment which includes granular activated carbon treatment at all works to remove organic substances. Despite this pesticide residues are found in treated water at concentrations in excess of 0.1 µg/l and the position for the year ended 31 December 1990 is summarised in Table 1.

Anglian Water's normal suite of pesticide determinations during 1990 extended to 43 active ingredients. During that year 15 different pesticides were detected at concentrations above 0.1 µg/l. Eleven of these were found in surface water derived supplies. Atrazine, isoproturon, mecoprop and propyzamide at > 0.1 µg/l were common to both surface and ground water supplies demonstrating their widespread occurrence.

Some 37% of samples from surface water derived supplies and 12% from groundwater derived supplies contained pesticides above the standard of 0.1 µg/l. the population which received water containing pesticides above this figure was 2.4 million out of a total population served (for water supply) by Anglian Water of 3.8 million. However, no water supplied has exceeded the DoE advisory values for pesticides.

Elsewhere in England and Wales fewer values have been found in excess of 0.1 µg/l. In the report of the Chief Inspector of the Drinking Water Inspectorate for 1990 it was reported that 2.1% of the 540,000 pesticide determinations made in England and Wales were above 0.1 µg/l. (Department of the Environment/Welsh Office, 1991). Thirty four different pesticides were detected above 0.1 µg/l during the year.

The principal messages coming from the Chief Inspector's report are that

- (a) a very wide range of individual substances (approximately 450) are used as pesticides in the UK
- (b) the use of pesticides should be limited to the minimum necessary for effective control of pests compatible with the protection of public health
- (c) the published DoE advisory values for pesticides in drinking water include a wide margin of safety and provide signals for initial action by water companies
- (d) the amounts of pesticides swallowed from drinking water, in every case, were for smaller than the amounts which are known to be harmful or are likely to cause harm.

ACTIONS TO REDUCE PESTICIDE CONCENTRATIONS IN DRINKING WATER

The water companies, in offering undertakings to the Secretary of State under the Water Act 1989, had to specify the actions they would take to comply with the pesticides standards. Many companies were concerned that the treatment technology to achieve <0.1 µg/l for any pesticide was unproven. Whilst treatment processes are available to reduce pesticide concentrations, their performance at these very low concentrations and across a wide spectrum of compounds has not been fully evaluated. Consequently some undertakings were to investigate treatment methods. Other companies undertook to install specific treatment whilst recognising the novelty of the technology to achieve this particular objective.

Anglian Water's undertakings are to install by various dates up to 1995 ozone treatment and granular activated carbon filters at surface water treatment works and, for ground water works, granular activated carbon filters. In all cases, however, the undertaking also promises to notify the National Rivers Authority of the exceedance so that pollution control measures can be considered. These notifications were made shortly after the undertakings had been accepted by the Secretary of State.

Anglian Water has continued its R & D work in the field of pesticide removal. This has been directed largely towards optimising granular activated carbon (GAC) treatment with respect to carbon type, contact

times and regeneration intervals. (Croll et al, 1991). The overall conclusions are that generally, 0.1 µg/l can be achieved for the most widely occurring herbicides (atrazine, simazine, mecoprop and isoproturon) providing concentrations in the untreated water do not exceed 0.3 µg/l. Where herbicide concentrations are higher (0.5 to 2 µg/l) with peaks up to 5 µg/l more extensive GAC treatment is required and even at 30 minutes contact time occasional exceedances of 0.1 µg/l occur in the treated water.

These results confirm that the strategy of GAC and ozone adopted by the company is the correct one. Support for the use of ozone for the control of pesticide residues comes particularly from the French experience where both ozone and ozone/hydrogen peroxide have been evaluated (Duquet et al, 1991). Anglian Water's own preliminary assessments confirm the findings of the French in the use of ozone for pesticide removal

However, in addressing the question of pesticides in drinking water increasing attention is being given to the use of pesticides. The importance of the proper use of pesticides has been re-emphasised recently by the publication of the Code of Good Agricultural Practice for the Protection of Water (Ministry of Agriculture Fisheries and Food/Welsh Office, 1991). However, it is clear that use in strict accordance with the Code will still result in residues in water sources in large part because of the properties of some of the compounds used. Calls for a strategy of placing restrictions upon the use of the more persistent materials have been made by several Member States in the Community and are also now being addressed by the UK government. Some important users of atrazine (which is almost exclusively non-agricultural in use in the UK) have already voluntarily discontinued its use in favour of non persistent materials such as glyphosate. This is in advance of the completion of a review currently being undertaken at the request of DoE by the Advisory Committee on Pesticides of the uses of atrazine, simazine and isoproturon.

THE OUTLOOK

A water treatment strategy to remove pesticide residues is emerging which centres on the use of granular activated carbon. However, R & D work will continue to identify removal performance for a wide variety of pesticides under differing conditions to achieve the extremely low levels required in the treated water.

Increasing attention will be given to the responsible use of pesticides and to the properties of individual active ingredients in the environment. More stringent control of use is likely to bring relatively quick responses in reducing pesticide concentrations in water sources. Whilst the situation has some similarities to the nitrate problem the analogy should not be taken too far.

However, in adopting alternatives to the more persistent herbicides currently found in water supplies we must ensure that we do not replace them with others which will quickly appear in water. Those who market alternatives such as imazapyr and triclopyr must satisfy themselves, the water industry and Government that their products do indeed offer a way forward.

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REFERENCES

- Croll, B.T. ; Chadwick, B. ; Knight, B. (1991) The removal of atrazine and other herbicides from water using granular activated carbon, Paper to be presented at IWSA Conference on Atrazine and Other Pesticides, Florence, Italy, 21-24 October 1991, 13 pp.
- Department of the Environment/Welsh Office (1991). Drinking Water 1990. A report by the Chief Inspector,.Drinking Water Inspectorate, H.M.S.O. July 1991, 194 pp.
- Department of the Environment/Welsh Office (1989). Guidance on Safeguarding the Quality of Public Water Supplies, H.M.S.O., 108 pp
- Duguet, J.P. ; Wable, O. ; Bernazeau, F. ; Mallevalle, J. (1991) Removal of atrazine from the Seine River by the ozone-hydrogen peroxide combination in a full scale plant, Proceedings of the Tenth Ozone World Congress, Monaco, March 1991, 301-312
- European Economic Community (1980). Directive relating to the quality of water intended for human consumption (80/778/EEC), Official Journal of the European Communities 30.8.80, L229/11 - L229/29
- Ministry of Agriculture Fisheries and Food/Welsh Office (1991). Code of Good Agricultural Practice for the Protection of Water, MAFF publications, (1991), 80 pp.

TABLE 1. Anglian Water Services Ltd. Pesticide Residues in Drinking Water 1990

Pesticides	Pesticides		
	measured	detected	
Urea herbicides	Isoproturon	+	+
	Chlorotoluron	+	+
	Linuron	+	+
Acid herbicides	Mecoprop	+	+
	Dicamba	+	
	MCPA	+	
	2,3,6-TBA	+	+
	2,4-D	+	+
	Dichloroprop	+	+
	2,4,5-T	+	
	MCPB	+	+
Organo-phosphorus	Azinphos-methyl	+	
	Carbophenothion	+	
	Dimethoate	+	
	Chlorfenvinphos	+	
	Dichlorvos	+	+
	Diazinon	+	+
	Malathion		
	Fenitrothion		
	Pirimiphos-methyl		
	Parathion	+	
	Chlorpyrifos	+	
	Mevinphos	+	
Triazines	Atrazine	+	+
	Simazine	+	+
	Propazine		
Other Pesticides	Aldicarb		
	Propyzamide	+	+
	Bromoxynil	+	+
	Ioxynil	+	+
Organo-chlorines	Hexachlorobenzene		
	Alpha-HCH		
	Gamma-HCH	+	
	Heptachlor		
	Aldrin	+	
	Isodrin	+	
	Heptachlor epoxide		
	Endosulphan		
	Dieldrin	+	
	pp' DDE		
	Endrin		
	pp' TDE		
	pp' DDT		

NB: No water supplied exceeded DoE advisory limits.

DIETARY INTAKES OF RESIDUES OF HERBICIDES AND PLANT GROWTH REGULATORS

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ABSTRACT

The dietary significance of any herbicide or plant growth regulator residue in food or water is a function of the toxicity of the chemical and dietary exposure to it. Dietary intakes can be estimated from the amounts of foods and water consumed and levels and incidences of residues in food and water. These estimates range from crude overestimates incorporating unrealistic assumptions about residue levels in foods to more realistic estimates based on data on actual residue levels in food. Comparison of dietary intake estimate for a number of herbicides and plant growth regulators with acceptable intakes shows that residue levels in food and water arising from currently approved uses lead to dietary intakes which are very much lower than maximum acceptable levels.

INTRODUCTION

The application of herbicides and plant growth regulators to crops and stored products may result in small amounts of the pesticide used (or various metabolites or degradation products) being present as residues in food and/or water. In the UK approval for use of a pesticide in a particular situation will only be granted if the likely levels of dietary exposure to these residues are considered to be acceptable.

The approach to prediction of dietary intake of pesticide residues adopted by the Advisory Committee on Pesticides (ACP) has been described (HMSO, 1990). The modelling techniques used by the ACP reflect the philosophy of the WHO, who have recently published guidelines for predicting dietary intakes of pesticide residues (WHO, 1989). Once a pesticide has been approved and is being used it is possible to obtain information on incidences and levels of its residues in food and water. This information can be used to make more realistic predictions of dietary exposure.

This paper presents a number of estimates of dietary intakes of herbicide and plant growth regulator residues and compares them with acceptable daily intakes (ADIs) to assess the toxicological significance of these residues in food and water.

ESTIMATING INTAKES OF PESTICIDE RESIDUES

The dietary intake of a pesticide residue can be considered as the product of the amount of food or water consumed and the concentration of residue in that food or water. Since pesticides typically have a range of uses which will lead to varying amounts of residue in a number of foods, this can be expressed as $\sum F_i M_i$ where F_i represents consumption of a particular commodity (eg apples or water) and M_i represents the concentration of the particular pesticide residue in that commodity.

Data on food consumption are available from a number of sources. The ACP bases its dietary intake estimates on a survey of 2197 adults commissioned by MAFF and DH and carried out by the Office of Population Censuses and Surveys (OPCS) and on a survey of 488 infants carried out by MAFF. Since it is important that exposure of individuals with unusual dietary habits should be considered, the ACP's 'worst case' estimates are generally based on 'unusually high' (97.5th percentile) intakes of commodities, however average intake data may also be used.

There are a number of ways in which residue levels in foods may be estimated. For a pesticide to be approved there must be enough experimental evidence available to judge the highest residue level which is likely to occur if the pesticide is used properly; this is the Maximum Residue Limit (MRL), which may be used as a statutory limit. This figure is used in the most crude intake estimates, the Theoretical Maximum Daily Intakes (TMDIs). For each commodity,

$$\begin{aligned} \text{TMDI} &= F_i \times M_i \text{ (mg)} \\ \text{where } F_i &= 97.5\text{th percentile daily food consumption for the} \\ &\quad \text{relevant commodity (kg);} \\ M_i &= \text{MRL for the relevant commodity (mg/kg)}. \end{aligned}$$

TMDIs are clearly overestimates because they assume that all food that can be treated is treated, that all treated food contains highest likely residues and that no residues are lost during storage, preparation, processing or cooking of the food before consumption.

If sufficient data are available on the distribution of residues between edible and inedible portions of the food or the effects on residue levels of storage, processing or cooking prior to consumption it is possible to produce a more realistic estimate, the Estimated Maximum Daily Intake (EMDI). For each commodity,

$$\begin{aligned} \text{EMDI} &= F_i R_i P_i \\ \text{where } R_i &= \text{the residue level in the edible portion of the} \\ &\quad \text{commodity (eg in banana pulp), when the whole} \\ &\quad \text{commodity residue is } M_i \text{ (mg/kg);} \\ P_i &= \text{the proportion of the residue which survives} \\ &\quad \text{processing or cooking.} \end{aligned}$$

Since only a portion of any crop will be treated and treated crops will not always contain the highest likely residues, more realistic estimates (Estimated Daily Intakes, EDIs) may incorporate reduction factors based on the proportion of the crop treated and the ratio of the amounts of homegrown to imported food (EDI_{calc}) or may be based on known residue levels as determined by a surveillance programme (EDI_{mon}). For each commodity,

$$\text{where } \begin{array}{l} EDI_{calc} \\ T_i \end{array} = F_i R_i P_i T_i$$

= the proportion of produce in circulation which is treated;

$$\text{or } EDI_{mon} = F_i S_i$$

where S_i = the 'actual' residue level as measured in a surveillance programme (mg/kg). Since the majority of results in such programmes are negative, ie residue levels are less than the reporting limit or the limit of determination, the 'actual' residue may be estimated in a number of ways, for example the mean with 'negative' residues expressed as zero or the reporting limit or limit of determination.

Consumption of water is assumed to be 2 litres/day. It is not possible to predict precisely the likely concentrations of pesticides in ground- and surface-waters following use according to the label recommendations. However, the physico-chemical properties, the application rates, timing and frequency, degradation rates, adsorption potential and transport under the likely worst case climatic conditions are used to estimate the potential to contaminate waters. Pesticides with a short halflife or those applied at very low rates are unlikely to enter water, whereas those used in processes involving an aqueous effluent could contaminate surface-water. In cases where pesticides have been found in raw water, some treatment may be necessary to ensure that the limit of 0.1µg/l is not exceeded to comply with the EC Directive on Drinking Water. For the purposes of assessing the likely contribution of such contaminated water to the overall intake of pesticides in the total diet, residues are taken as unlikely to exceed the EC limit of 0.1µg/l.

All these estimates are based on single commodities, however in practice a number of commodities may be treated and total dietary intakes will be composed of elements contributed by each of these commodities and by water. One approach to total dietary intake estimation is to use food consumption data to construct a number of 'standard diets' to represent eating habits of one or more sections of the population and then to calculate $ETMDI_i$, $EEMDI_i$ or $EEDI_i$. An objection to this method of estimating exposures is that 'standard diets' do not represent real eating patterns. An alternative approach is to use a sample of individual diets (such as the OPCS survey sample) to prepare individual exposure estimates. Statistical measures of the distribution of exposures may then be used in risk assessment.

THEORETICAL MAXIMUM DAILY INTAKES OF HERBICIDES AND PLANT GROWTH REGULATORS

TMDIs for individual foods and 'total diet' TMDIs have been calculated for a number of herbicides. The chemicals chosen for consideration are those approved since 1986 and tecnazene, which is currently under review. Highest likely residues and ADIs have been taken from ACP evaluations (MAFF 1987, 1988 a & b, 1990 a-c, 1991). For tecnazene, the UK advisory MRL (5 mg/kg) and the ACP's advised ADI (0 - 0.03 mg/kg bw) have been used. Regarding contamination of water by the chemicals chosen for consideration, quizalofop-ethyl, fenoxaprop-ethyl, fenoxaprop-p-ethyl and fluazifop-p-butyl have very short half-lives and high adsorption coefficients and therefore are unlikely to contaminate water. DPX M6316 is also unlikely to contaminate water because of its low application rate and relatively high degradation rate in agricultural soils. For these five chemicals, therefore dietary intakes resulting from contamination of water have not been considered. The approvals for glufosinate-ammonium and cycloxydim limit the use of these chemicals to crops and timings on soils unlikely to be the most vulnerable to solute transport. Approved uses of tecnazene can lead to contamination of surface-waters, however in compliance with the EC Directive residues in drinking water should not exceed 0.1 µg/l. For these three chemicals, dietary intake calculations have been based on drinking water containing <0.1 µg pesticide/l. An example of a set of TMDI calculation, for cycloxydim can be found in Table 1. The results are represented in Figure 1.

Calculations for quizalofop-ethyl, fenoxaprop-ethyl, fenoxaprop-p-ethyl, fluazifop-p-butyl, DPX M6316, glufosinate-ammonium, cycloxydim and tecnazene are summarised in Table 2. It should be noted that these calculations incorporate yet another conservative assumption. Where residues are not determinable they are assumed to be at the limit of determination.

TABLE 1. Theoretical Maximum Daily Intakes of Cycloxydim-derived residues

(Acceptable Daily Intake (ADI) = 0 - 0.07 mg/kg bw)

a) Single commodities

Commodity	97.5th Percentile Intake (kg/day)	Highest Likely Residue (mg/kg)	Theoretical Maximum Daily Intake 60 kg consumer		
			(mg)	(mg/kg bw)	%ADI
potatoes	0.216	2	0.4	0.007	10
peas	0.065	5	0.3	0.005	8
swedes	0.052	0.5	0.03	0.0004	0.6
Brussels sprouts	0.063	1	0.06	0.001	2
cabbage	0.069	1	0.07	0.001	2
cauliflower	0.072	1	0.07	0.001	2
rapeseed oil	0.013	<0.05	0.0006	0.00001	0.02
sugar	0.125	<0.05	0.006	0.0001	0.1
water	2 litres	<0.0001	0.0002	0.000003	0.004

b) Total diet

97.5th percentile total intake = 0.7mg/day
 = 0.01 mg/kg bw/day
 = 14% ADI

Figure 1. Dietary Significance of Herbicides and PGR Residues in Food and Water - Cycloxydim

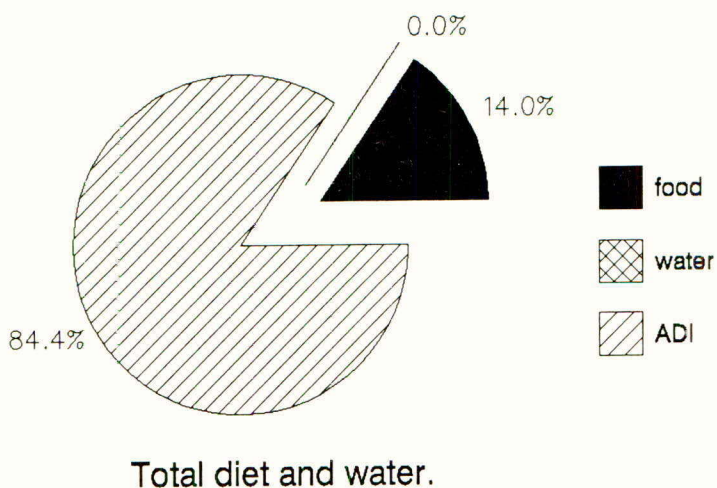
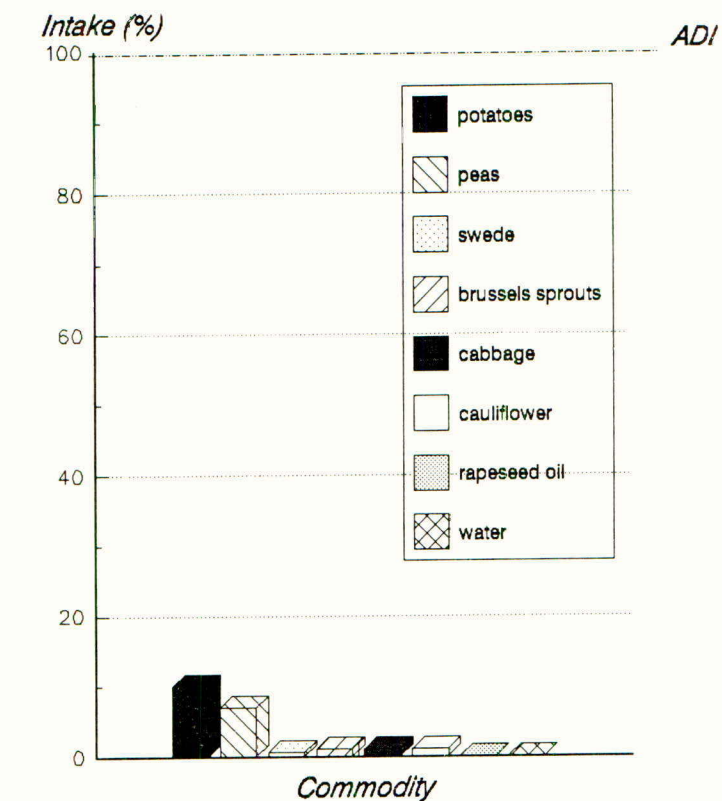


TABLE 2. Dietary Significance of PGR and Herbicide Residues in Food and Water.

Chemical	ADI (mg/kg bw)	Commodity	TMDI (mg/kg bw)	%ADI
quizalofop-ethyl	0-0.01	beetroot	0.00006	0.6
		rapeseed oil	0.00004	0.4
		sugar	0.0002	2
		total diet	0.0002	2
fenoxaprop-ethyl	0-0.003	wheat	0.00008	3
		total diet	0.00008	3
fenoxaprop-p-ethyl	0-0.003	wheat	0.00008	3
		total diet	0.00008	3
fluazifop-p-butyl	0-0.005	soft fruit	0.00008	2
		rapeseed oil	0.00004	0.8
		sugar	0.0002	4
		carrots	0.00009	2
		onions	0.0001	2
		peas	0.0002	4
		total diet	0.0004	8
DPX M6316	0-0.2	wheat	0.00008	0.04
		barley	0.00008	0.04
		total diet	0.00009	0.04
glufosinate-ammonium	0-0.02	apples	0.0002	1
		vegetables	0.0002	9
		potatoes	0.004	18
		dried peas	0.003	16
		rapeseed oil	0.0001	0.5
		wheat	0.0004	2
		total diet	0.005	25
		water	0.000003	0.02
cycloxydim	0-0.07	potatoes	0.007	10
		peas	0.005	8
		swedes	0.0004	0.6
		Brussels sprouts	0.001	2
		cabbage	0.001	2
		cauliflower	0.001	2
		rapeseed oil	0.00001	0.02
		sugar	0.0001	0.1
		total diet	0.01	14
		water	0.000003	0.005
tecnazene	0-0.03	potatoes	0.02	60
		water	0.000003	0.01

For all 8 compounds theoretical maximum intakes resulting from residues in water are much less than 1% of the upper limit of acceptable intakes and can therefore be considered insignificant in terms of dietary risk. Turning to dietary risk arising from exposure to residues in food none of the TMDIs exceed ADIs, indeed for 5 of these compounds even these first tier TMDIs which seriously overestimate intakes from food are less than 10% of acceptable intakes. Exposures to cycloxydim, glufosinate-ammonium and tecnazene residues appear more significant, however the conservative assumptions on which TMDI estimates are based must be remembered. Intakes of tecnazene are considered in more detail below, to illustrate how the preparation of more realistic estimates leads to more accurate measures of the dietary significance of pesticide residues.

ESTIMATING INTAKES OF TECNAZENE

A number of intake estimates for tecnazene are represented in Figure 2.

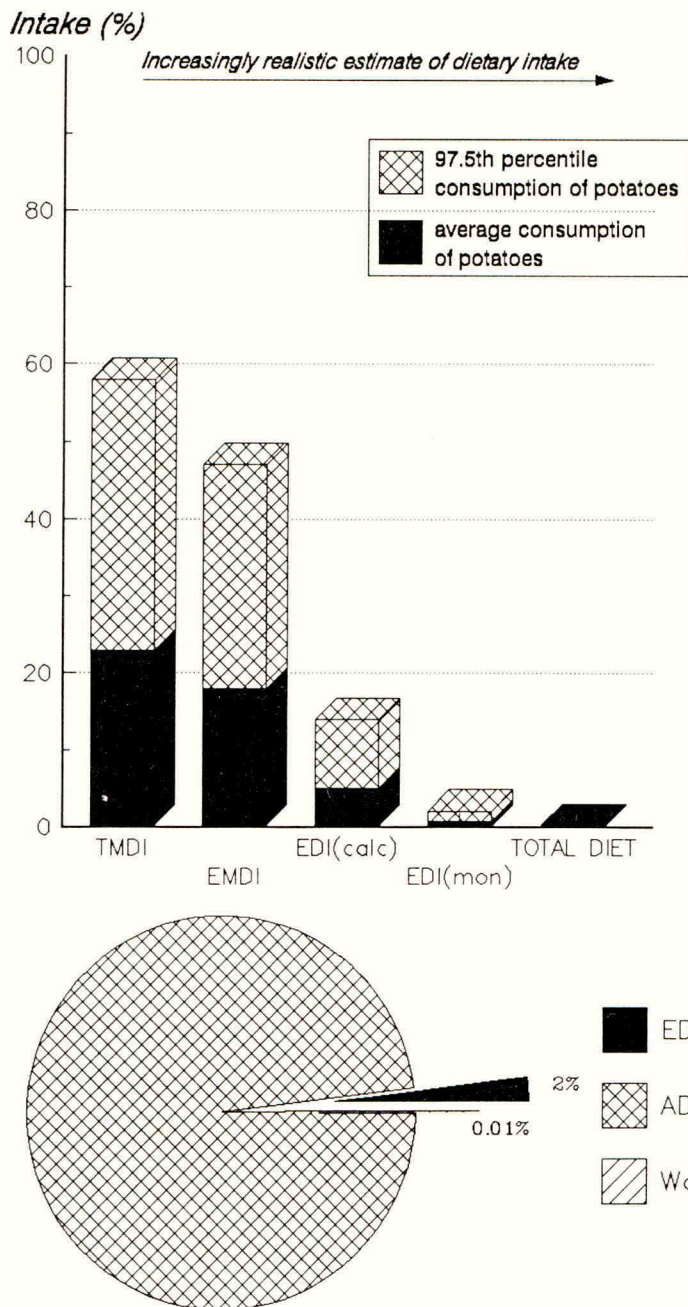
The TMDI arising from residues of tecnazene in potatoes is 60% (97.5th percentile consumption) or 20% (average consumption) of the acceptable intake. Since all potato is cooked before consumption and there is some loss of residue (at least 20%) on cooking, the EMDI is 50% (97.5th) or 20% (average) of the ADI.

The proportion of homegrown to imported potatoes in the UK is 6.1, and 35% of homegrown potatoes are treated. Therefore

$$\begin{aligned}
 EDI_{\text{calc}} &= (0.216 \text{ or } 0.082) \times 5 \times 0.8 \times 0.85 \times 0.35 \\
 &= 0.3 \text{ mg/day (97.5th)} \text{ or } 0.1 \text{ mg/day (average)} \\
 &= 14\% \text{ ADI (97.5th)} \text{ or } 5\% \text{ ADI (average)}
 \end{aligned}$$

The rolling cycle of surveys of the Working Party on Pesticide Residues (HMSO 1989 and 1990) includes a programme of continuous monitoring of potatoes and tecnazene is one of the analytes.

Figure 2: Estimating Dietary Intakes of Tecnazene from potatoes



¹ based on unusually high (97.5th percentile) consumption of potatoes.

The average residue level found in these surveys is 0.2 mg/kg (1987, 120 samples). Therefore,

$$\begin{aligned} \text{EDI}_{\text{mon}} &= (0.216 \text{ or } 0.082) \times 0.2 \\ &= 0.04 \text{ mg/day (97.5th) or } 0.02 \text{ mg/day (average)} \\ &= 2\% \text{ ADI (97.5th) or } 0.7\% \text{ ADI (average)}. \end{aligned}$$

The most realistic intake estimates, the EDI_{mon}'s, are in good agreement with estimates of dietary intake of tecnazene obtained from total diet studies (HMSO 1989, see Figure 2). These studies are based on randomly purchased commodities prepared as if for eating. The proportions of foodstuffs reflect dietary consumption patterns. Average intakes of tecnazene were 0.0029 mg/day in 1981 and 0.0043 mg/day (0.2% ADI) in 1984-85, both representing 0.2% of the ADI.

CONCLUSION

Regulatory controls exist to ensure that residues in food and water resulting from the use of approved pesticides do not pose unacceptable risks to consumers. Estimates of intakes for all the herbicides and plant growth regulators considered in this paper are well within acceptable levels.

ACKNOWLEDGEMENTS

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REFERENCES

- HMSO (1990a) *Advisory Committee on Pesticides Annual Report 1988, Appendix IV.*
- WHO, Geneva (1989) *Guidelines for Predicting Dietary Intake of Pesticide Residues.*
- MAFF (1987) *Pesticide Safety Division, Evaluation on Quizalofop-ethyl.*
- MAFF (1988a) *Pesticide Safety Division, Evaluation on DPX M6316.*
- MAFF (1988b) *Pesticide Safety Division, Evaluation on fluazifop-P-butyl.*
- MAFF (1990a) *Pesticide Safety Division, Evaluation on fenoxaprop-p-ethyl.*
- MAFF (1990b) *Pesticide Safety Division, Evaluation on fenoxaprop-ethyl.*
- MAFF (1990c) *Pesticide Safety Division, Evaluation on cycloxydim, 1990.*
- MAFF (1991) *Pesticide Safety Division, Evaluation on glufosinate-ammonium, 1991.*
- HMSO (1989) *Report of the Working Party on Pesticide Residues: 1985-88. Food Surveillance Paper No. 25.*
- HMSO (1990) *Report of the Working Party on Pesticide Residues: 1988-1989, Issue No. 8, 1990 of the Pesticides Register.*

THE IMPACT OF CONSUMER ATTITUDES ON THE
FRESH PRODUCE INDUSTRY

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In the United Kingdom today consumers have become more aware of the direct links between health and diet and have, as a consequence, become concerned about the effects of agro-chemical residues in fresh produce.

Their worry has extended beyond that of personal health to a concern about the impact of agro-chemicals and intensive systems of agriculture on the environment.

The produce industry has responded to these changes in consumer attitudes by introducing its own "Code of Practice for Pesticide Control". At the same time producers have been quick to introduce effective management systems to control and limit the use of agro chemicals.

This action, which has been taken with the full cooperation and involvement of both retail and Government organisations, has enabled the produce industry to face its customers, the consuming public with confidence.

The produce industry can say today, with authority and integrity that fresh fruit and vegetables are good for our health and any chemical residues which do exist do not constitute a health hazard.

To fully understand the impact of consumer attitudes on the fresh produce industry and its relevance to agro-chemicals it is necessary to review some of the changes that have affected the industry during the last 10 years.

In the United Kingdom the late '70's and '80's saw the social environment and attitudes of the British people being fundamentally altered.

People were living longer at a time of falling birth rates. Progressively more women entered full or part-time employment and there was a marked increase in single person households.

Economic growth led to higher disposable incomes across all stratas of the socio-economic structure and improving standards of living raised the aspirations and expectations of society.

Consumers displayed a growing demand for convenience stimulated by informal and unstructured life styles and traditional formal meals were progressively replaced by snacking habits.

There was a demand for improved quality and greater variety from a public which had become more sophisticated, better educated and more travelled.

Multiple retailers recognising these attitudinal changes in their customers became not only the catalysts but also the instruments of change.

They offered new shopping experiences with a wider choice in more convenient locations. They improved the quality of their offer to meet the aspirations of their customers not only in terms of the products on sale but also the store environment in which they were sold.

It had become manifestly evident by the early '80's, that for fresh produce, the traditional chain of distribution using poor cultural practices at source, ill equipped wholesale markets and old fashioned independent retailers had become a wholly inadequate conduit through which to satisfy emerging market demands.

It was becoming recognised that from the orchard in some distant country to the market place in Europe, producer, importer and retailer had an important role to play in getting fresh produce to the market and, ultimately, to the consumer, safely, efficiently and with the minimum loss of product quality.

In the United Kingdom it was the recognition of the mutual interdependence of each link which led to the development of a new and dedicated system of distribution that had as its objective, satisfaction of consumer needs, its prize was to be market development, the facilitator was to be product quality.

It was a market that expanded not only in volume but displayed a much faster rate of growth in value outstripping the index of retail food prices by 30% over 5 years. A total market enhancement of £900m turning the UK from a discount dumping ground for poor quality fresh produce into a market for high quality produce selling at a premium.

The Retail Market for Fresh Produce

	Value £ bn	Index	Food Price Index
1985	3.0	100	100
1986	3.4	115	103
1987	3.7	122	106
1988	3.9	131	110
1989	4.2	141	116
1990	4.7	156	126

It was this opportunity coupled with a desire to meet a consumer demand for fresh produce that was both a pleasure to eat, convenient to buy and healthy that was seized upon by a new type of retailer in association with a new type of produce distribution company establishing their own dramatic growth patterns.

The Distribution Channels for Fresh Produce

	% Share	
	1976	1990
Supermarkets	22	50
Greengrocers	37	27
Market Stalls	25	17
Others	16	6

The share of the UK produce market, now 50%, captured by some 6 national multiple organisations, has undoubtedly been one of the crucial enabling features encouraging a traditional producer orientated trade to become a modern market led industry.

This growth in supermarkets spurred on by changing shopping habits with more emphasis on one stop shopping and large out of town superstores has meant that the supply of produce is becoming increasingly channelled through large and sophisticated produce handling companies involved in all aspects of importation and distribution.

In the UK there followed investment in refrigerated vessels, port facilities, temperature controlled vehicles, modern produce handling centres, prepacking and ripening facilities with more sophisticated pre and post harvest practices being established at source.

Environmental management from harvest to retail store coupled with extensive quality assurance resources have become the tools of the produce industry today. These UK patterns of change will emerge as a vigorous underlying feature of the European produce market during the 1990's.

It is an economic fact of life that any chain of distribution establishes and maintains common standards throughout its length.

The adoption of the latter system focusing as it does on quality and making extensive use of technical expertise in the supply chain has made UK food retailing organisations such as J Sainsbury, Tesco and Safeways world leaders in their field.

These companies have now realised that consumers regard their fresh produce offer as one of the most critical indicators of their competence as food retailers.

It was into this background that in the late '80's the environmentally health conscious consumer was born. Today they, the majority of the population, display a growing concern about the potentially detrimental effects of food additives and chemical residues on health and the impact of intensive methods of agricultural production on the environment.

In February 1989 a survey carried out by the Natural Resources Defence Council, an American pressure group, claimed that cancer causing chemicals were being sprayed onto fruit and vegetables and putting young children at risk. They highlighted Alar on apples as being the most dangerous of these chemicals.

Panic ensued in the US and American housewives stopped purchasing apples. Meryl Streep launched Mothers and Others for Pesticide Limits and here in the United Kingdom Pamela Stephenson of Parents for Safe Food advised the public that "our children are being used as guinea pigs, and I feel that if only one child is affected by the spray it is every reason to suspend its use."

In the UK the produce industry industry has made a careful and measured response to this type of exposure and pressure.

We were aware that Government policy within Europe would place a greater educational focus on the care of and respect for ones body. The thrust of this policy will be to improve the health of the population by encouraging those products and habits which are beneficial and discouraging those which are detrimental.

At the same time consumers have a growing awareness of the links between diet and health and in particular their relevance to heart disease and the carcinogenic properties in food.

This has encouraged the consumption of healthier foods in general and brought with it authoritative recommendations to eat more fresh fruit and vegetables.

As a result of this the European Community is making available funds to support the generic advertising of domestically produced European fresh produce to improve the health of the population.

To support these encouraging signals our industry took action on two fronts. We established an active consumer educational programme involving not only housewives but also school children and we established our own Code of Practice for Pesticide control. A code of practice that was drawn up with the full cooperation and involvement of not only our major customers but also the Government regulatory authorities.

When our industry refers to the use of chemicals it is a description which embraces insecticides, fungicides, herbicides and plant growth regulators. Properly used in accordance with our Code of Practice and manufacturers recommendations we have no scientific evidence that approved chemicals present any threat to human health.

The Independent Advisory Committee on Pesticides which studies the long and short term toxicity of each product, its effect on livestock, domestic animals and the environment base their judgments on toxological information produced in line with the agreed protocol of "Good laboratory practice."

We are satisfied that it is only when they are totally convinced of a chemicals safety that they will advise the Government Minister to approve its use.

The message we are now getting across to consumers is that the official Government approval system which investigates the possible effects on human health, notably cancer, birth and inheritance defects as well as effects on the nervous and immune systems do provide the consumer with the protection they demand, require and deserve.

The majority of chemicals used in the horticultural industry break down leaving no residue before the produce reaches the consumer. Where residues are present the levels are so small they present no risk to health and are easily excreted by our bodies.

The chemicals used by the horticultural industry today are designed to target particular pests leaving others unharmed and correctly used the impact on the environment is limited to reducing wild creatures food supply of insects and weed seeds in the field in which they are used.

The main thrust of our Code of Practice and Pesticide Policy is that crop protection programmes must be geared to minimal use of chemicals to achieve the standard of pest, disease and weed control required.

Growers must now provide the produce distribution company with details of the trade products and active ingredients they propose use. It is then up to the distribution company to determine whether its use is to be restricted or terminated.

Manufacturers recommended dosage must be strictly adhered to. Harvest intervals must be observed at all times and only one product may be used for each target on each occasion.

All personnel involved in the application of crop protection chemicals must be suitably trained and the equipment they use must be properly maintained.

Comprehensive written records of all crop protection and post harvest treatments must be available for inspection by the technical staff of the distribution company.

Residue monitoring at source, in the distribution system and in retail samples is carried out to determine whether or not pesticide residues are present, their nature and level.

We believe that the action we have taken meets the criticisms made in the media by consumer pressure groups and we can as an industry face our customers with confidence and with nothing to hide.

The opinion of the Government Working Party on Pesticide Residues is that the exposure to chemical residues in the average national diet does not constitute a hazard to health.

We have also anticipated the legislative impact of the Food Safety Act which was introduced on the 1st January 1991. Under this act distributors of fresh fruit and vegetables are obliged to take all reasonable precautions and exercise all due diligence to ensure that:

- their products comply with food safety requirements
- they are not injurious to health
- that they are not selling, to the purchasers prejudice, a product which is not of the nature, substance or quality demanded
- they do not falsely or misleadingly describe or present their products

This legislation departs from the common law principal of caveat emptor, let the buyer beware, and seeks to protect the buyer, in our case the public, from technically incompetent producers trying to supply potentially unhealthy and inferior quality products.

The results of all our efforts are that we have seen a greater application of integrated pest management techniques leading to a genuine reduction in the use of agro-chemicals. We as an industry are very supportive of this practice.

We have also seen much greater care and attention with the use of agro chemicals. The horticultural industry is now much more aware of manufacturers recommendations and conscious of the profound importance of strict adherence to them. The agro-chemical industry will be pleased to hear this.

Finally with regard to organically grown products we believe that because of the demonstrable safety of conventionally grown fresh produce the consumer proposition for organics will have to shift from an offer of health protection to one of an environmentally acceptable system of production. Organics will grow but it will not take over from conventional systems of production.

The agro-chemical industry and the fresh produce industry share a common interest and its one of education and management. It is absolutely vital that the agro-chemical industry ensures that its customers properly understand how to use their products and have the right equipment so to do.

At the same time it is absolutely vital that the general public know and understand why agro-chemicals are being used, what regulatory systems are in place to control their use and receive a meaningful assurance that when they purchase fresh produce it does not contain any latent health hazard caused by chemical residues.

The issue of chemical residues is here to stay. It should not however become a major problem if the public is properly educated and their use is strictly regulated. It is an area in which we will exercise extreme vigilance but we have taken heart from the scientific evidence published by the Government that fruit and vegetables are good for our health and any chemical residues which do exist do not constitute a hazard to our health.

SIGNIFICANCE OF CHLORPROPHAM/PROPHAM RESIDUES IN THE ENVIRONMENT

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ABSTRACT

Modern agricultural practice impinges directly on environmental issues and is considered responsible for many of today's pollution problems. Pesticides are a case in point. To illustrate this, the potato crop, its production and storage and its dependence on pesticides is considered. The significance of post-harvest treatments in particular and the central position of chlorpropham/propham in the maintenance of tuber quality for processing are emphasised. Aspects covered for chlorpropham/propham in this context are application methods, possible alternatives, distribution problems, metabolism, balance studies, environmental implications and overall safety. These factors are assessed in line with their position as backlog chemicals facing re-registration in 1992-1993.

INTRODUCTION

Agriculture can be considered a victim of its own success having attained an increase in production averaging a constant 3% per annum over the period 1950-1984.

As agriculture is a complex industry closely interacting with the environment a price has to be paid for such success. Criticism is made in the form of bad press covering soil erosion, pollution etc. Obviously the above increases cannot be maintained. In 1988 an increase in production of 1% was recorded and as the number of mouths to feed is increasing by 1.7% per year, the challenge facing food producers is becoming much greater, coupled with less available farm land and more environmental restrictions (MacKenzie, 1990).

As much of the above success in productivity has been credited to the use of pesticides, aspects of environmental restrictions are particularly pertinent. Much more interest now exists in the total environment rather than just the narrow aspects of crop and animal production. Universities courses have been modified to take these factors into account where agriculture, food and the environment is unified into a single course structure.

Agriculture and the chemical industry are blamed for many environmentally sensitive issues e.g. nitrates and triazine residues in ground water: anxieties expressed by the EMA (British Medical Association) regarding ubiquitous trace levels of pesticides in drinking water: the targetting of Red List chemicals in water courses and pesticide build up in animal fats etc.

It is not easy to answer/solve many of these criticisms, particularly bearing in mind the poor public perception of agrochemicals.

Attempts are being made. In the case of organochlorines which have largely been banned, levels reported in monitoring surveys are continuing to drop in spite of the introduction of more sensitive methods of detection (Yess, 1988).

Much more open recording of residue levels in food and water samples is now being adopted and details of chemicals looked for and not found above reporting limits are all steps in the right direction if public confidence is to be built up in this area. More attempts should be made to educate the public at large on definitions of MRL's (Maximum Residue Limit), ADI's (Acceptable Daily Intake) and GAP (Good Agricultural Practice) etc. if further progress is to be made.

Looking to the future, a point of concern is the introduction of crops with genetically engineered resistance to herbicides. Apart from public disquiet on the use of such techniques, the problem of residue build up and/or metabolite production in these resistant plants would need to be assessed. Confusion could arise in the case of a pesticide operator who must decide which chemical to use, not only on the basis of crop type but also on whether the particular crop variety has been modified.

What now follows is a look at a particular food crop - potatoes, a staple food item which is kept under regular analytical surveillance for pesticide residues.

As can be noted from table 1, the potato crop is submitted to a diverse range of agrochemicals throughout the growing and subsequent storage periods. This list contains only main classes of chemicals and excludes accidental contamination by spray drift e.g. by glyphosate or contamination through volatility e.g. 2,4 D etc. or chlorpropham in the case of seed potatoes.

From chemical surveillance monitoring both in this country and in North America the one group of chemicals that does stand out in terms of residues is the storage chemicals, in particular, chlorpropham. From available information on pesticide residues in food in the USA, human intake for the 70 most ingested chemicals averages 0.15 mg/day and most (0.105 mg) of this intake is composed of three chemicals (ethylhexyldiphenylphosphate, malathion and chlorpropham) (Ames, 1989).

TABLE 1. Possible agrochemical treatments applied to potatoes during growth and storage.

Nematacides	aldicarb oxamyl disulfoton	applied to the seed bed
Herbicides	linuron monolinuron paraquat metribuzin	applied at or shortly after field emergence
Blight control chemicals	mancozeb metoxuron metalaxyl benalaxyl maneb	applied to foliage often at 14 day intervals
Defoliant	sulphuric acid metoxuron diquat	applied 2-3 weeks prior to harvest
Storage chemicals		
Sprout suppressants	tecnazene chlorpropham propham maleic hydrazide	applied at time of store loading or afterwards as required a sprout suppressant applied in the field prior to harvest (restricted use)
Fungicides	thiabendazole carbendazim	applied at time of store loading

Chlorpropham and propham

The background to chlorpropham/propham will now be considered in detail. Firstly the need for sprout suppressant chemicals will be discussed. After potatoes are harvested and put into storage, sprouting can occur following a short period of dormancy (cv. dependent). The storage temperature will control the onset and amount of sprouting. At 4°C potatoes can be stored for 6-9 months without appreciable sprouting but unfortunately, low temperature sweetening occurs and results in an increase in reducing sugar concentration which is unacceptable to the processing industry and crispers in particular. The processing section of the potato market has steadily increased and now comprises over 25% of U.K. production. For processing, potatoes must be stored at 8-10°C and a sprout suppressant must be applied.

TABLE 2. A summary of published information on chlorpropham and propham residues in foods.

Country	Author and Year	Type of sample	Number analysed	chlorpropham/ propham found- mean and/or range (mg kg ⁻¹)
Canada	Frank et al, 1987	unwashed, unpeeled	33 (only 2 above MDA ^a)	0.18
Germany	Schumann et al, 1983	washed, unpeeled	-	1.65-3.15
Holland	De Vos et al, 1984	peeled, cooked	12 (11 positive for chlorpropham) (5 positive for propham)	0.061 (0.003-0.23) 0.018 (0.01-0.10)
Sweden	Andersson, 1986	domestic potatoes	384 (1 positive)	1 sample in range 2-5 mg kg ⁻¹
		imported potatoes	553 (29 positive)	24 samples in range 2-5 mg kg ⁻¹
				5 samples in range 5-10 mg kg ⁻¹
Switz- erland	Wuthrich et al, 1985	cereals, bread, potatoes	10 (5 positive)	0.036 (ND ^b to 0.140)
USA	Cartrell et al, 1988	washed, unpeeled	27 (22 positive)	0.145 (0.006-0.947)
		total food classes	27 (25 positive)	(0.003-0.947)
UK	MAFF, 1989	washed, unpeeled	75	0.02 (ND to 0.8)

^a Minimum Detectable Amount, ^b Not Detected

Chlorpropham and propham are members of the phenylcarbamate group of herbicides and chlorpropham was first used commercially in 1951 (Witman and Newton, 1951). As slightly volatile mitotic inhibitors, both compounds have been used world wide as potato sprout suppressants for forty years. Early toxicological studies and residue data obtained from storage trials do not stand up to present day more demanding scrutiny.

Backlog chemicals which were given clearance for use when regulations were less strict are gradually being re-assessed by various Government and International bodies. The Codex Alimentarius Commission is due to review chlorpropham/propham in 1992/93.

In spite of being used as potato sprout suppressants for forty years there is still a decided lack of knowledge available in the public domain on the toxicity and possible carcinogenic nature of chlorpropham/propham (Anon, 1976; Anon, 1987). This is obviously not a unique situation and has not gone unnoticed by the potato processing industry which is making strenuous efforts throughout the EC, in Scandinavia and in North America to pull resources in the form of a database covering all aspects of these chemicals. However, the agrochemical industry, for well recognised reasons i.e. patent protection etc., is not prepared to release information too readily on the toxicological packages completed or in the process of being completed to satisfy USA Environmental Protection Agency/Codex requirements. The re-registration of backlog chemicals which is necessary in this case does highlight the difficulties involved in an independent group working with published data and attempting to come to some conclusions on the relevance and significance of residues.

Chlorpropham and propham are normally applied to potatoes at a rate of 10-20 mg kg⁻¹ after wound healing i.e. 3-4 weeks after going into store. Applications can be in the form of granules, dusts or fogs (most common among processors). Re-application is possible and can lead to total chlorpropham/propham applications in the region of 50-100 mg kg⁻¹ /storage season. Even distribution of the chemicals is a challenge with large variability being recorded on many occasions (0.5-80 mg kg⁻¹) (Duncan et al, 1986). With mean chlorpropham/propham residues measured soon after application estimated at approx. 5 mg kg⁻¹, it is difficult to account for the remaining 25-75% applied. Some obviously is adsorbed by the fabric of the store itself, some lost through volatilisation (Boyd and Duncan, 1986) but anxieties have been expressed within the potato industry about the possibility of breakdown both during application and in the tuber and studies have been initiated to answer these questions. No evidence of breakdown during fog application has been found. The determination of chlorpropham/propham in potatoes is reasonably straightforward, but much more difficult in processed material, particularly crisps and frying oil (Ritchie et al, 1983).

TABLE 3. Example of current chlorpropham/propham MRLs (mg kg⁻¹) in force in European countries.

Netherlands	5	Germany	5
Belgium	5	Luxembourg	5
France	0.5 ^a	Spain	5
Portugal	5	Greece	5
Italy	0.5 ^a	Austria	5
Switzerland	5	United Kingdom	- ^b
Denmark	0 ^c	Sweden	2 ^d

^a in peeled potatoes

^b proposed MRL only

^c in ware potatoes

^d chlorpropham only

Approximately 10% of potato material is lost during processing in the form of peel, starch and waste water and the fate of sprout suppressant residues associated with these fractions has not been fully investigated. Tecnazene, an alternative sprout suppressant allowed in the UK but not in Europe has resulted in the build up of metabolites in fish and sediments downstream from a number of potato processing plants (Whale et al, 1988). Presumably the more persistent nature of tecnazene as well as higher application rates to control sprouting enhanced the problem. Chlorpropham/propham which degrade more readily in soil and water would not present the same problem.

To date, 4-methoxychlorpropham, 3,3'-dichloroazobezene and 3-chloroaniline are the only reported metabolites of chlorpropham identified in potato tubers in spite of the absence of metabolites reported in earlier radiolabelled chlorpropham studies (Heikes, 1985; Worobey and Sun, 1987; Worobey et al, 1987). It should be emphasised that 90% of chlorpropham/propham residues can be removed by peeling and, therefore, crisps made from whole (i.e. unpeeled) potatoes will contain higher residues of chlorpropham/propham than conventional crisps (Ritchie et al, 1983).

Processors world-wide are aware of their dependence on chlorpropham/propham for sprout suppression and in the last 10-15 years have made strenuous efforts to improve their information on these chemicals and to investigate possible alternatives.

Plant breeding to produce potato cultivars with long dormancy characteristics is already underway but will take some time before commercial cultivars appear on the market and there is no guarantee that they will satisfy other processing criteria.

International efforts are being made to characterise the enzymes responsible for low temperature sweetening in the hope of manipulating the control systems through genetic engineering. As discussed earlier, genetic engineering of crops has met with considerable consumer resistance. Because of the innovative techniques used, this project is already behind schedule.

Natural chemical alternatives e.g. carvone, pulegone and dimethylnaphthalene, have been investigated with some success, but the relatively small size of the potato sprout suppressant market makes further development of these chemicals questionable purely on economic grounds.

Maleic hydrazide is used in North America, in particular, as a sprout suppressant. Trials in the UK have produced variable results thought to be due to climatic conditions at time of application. However, in the USA where application is considered successful, distribution of the chemical among tubers is not always uniform resulting in uneven control of sprouting.

Estimated costs of controlled atmosphere (CA) storage have tended to rule out this option at present although new technology may make it feasible in the future.

Irradiation of potatoes (10 kGy) will prevent sprouting. Customer

resistance to irradiated foods and the difficulty of treating potatoes economically makes this option unviable.

Over the next 5-10 years, at least, the potato industry will have to rely on chlorpropham/propham for sprout control of potatoes intended for processing. Bearing that point in mind, and the fact that these chemicals have been used for forty years on a staple food, it is disturbing that gaps still exist in our knowledge particularly in terms of precise mode of action and environmental fate.

This emphasises the difficulty of the industry in defending its use of pesticides as even with current legislation, most studies are retroactive rather than proactive in response to criticism from pressure groups.

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REFERENCES

- Ames, B.N. (1989) Pesticide residues and cancer causation. *ACS Symposium series* 414, 223-237.
- Andersson, A. (1986) Monitoring and biased sampling of pesticide residues in fruits and vegetables. *Methods and results, 1981-1984. Var Foeda* 38 (suppl 1), 8-55.
- Anon., (1976) IARC monographs on the evaluation of carcinogenic risk of chemicals to man. *Some carbamates, thiocarbamates and carbazides. Vol 12 WHO/IARC*
- Anon., (1987) IARC monographs on the evaluation of carcinogenic risks to humans. *Overall evaluations of carcinogenicity: an updating of IARC monographs volumes 1 to 42. Supplement 7 WHO/IARC.*
- Boyd, W.D.; Duncan, H.J. (1986) Studies on potato sprout suppressants. 7. Headspace and residue analysis of chlorpropham in a commercial box potato store. *Potato Research* 29, 217-223.
- De Vos, R.H.; Van Dokkum, W.; Olthof, P.D.A.; Quirijns, J.K.; Muys, T.; Van Der Poll, J.M. (1984) Pesticides and other chemical residues in Dutch total diet samples (June 1976-July 1978) *Food Chemistry Toxicology* 22, 11-21.
- Duncan, H.J.; Beglan, M.; Boyd, I.M.G. (1986) Optimising the use of sprout suppressant chemicals. *Aspects of Applied Biology* 13, 473-479.
- Frank, R.; Braun, H.E.; Ripley, B.D. (1987) Residues of insecticides, fungicides and herbicides on Ontario-grown vegetables, 1980-1985. *Journal of the Association of Official Analytical Chemists* 70, 1081-1086.
- Gartrell, M.J.; Craun, J.C.; Podrebarac, D.S.; Gunderson, E.L. (1986) Pesticides, selected elements, and other chemicals in adult total diet samples, October 1980- March 1982. *Journal of the Association of Analytical Chemists* 69, 146-161.

- Heikes, D.L. (1985) Mass spectral identification of a metabolite of chlorpropham in potatoes. *Journal of Agricultural And Food Chemistry* 33, 246-249.
- MacKenzie, D. (1990) Famines before floods? *New Scientist* 125, 28-29.
- Ministry of Agriculture, Fisheries and Food (1989) Report of the Working Party on Pesticide Residues: 1985-1988. HMSO, London.
- Ritchie, W.; Boyd, I.M.G.; Duncan, H.J. (1983) A method for the determination of chlorpropham residues in crisps and crisp frying oil. *Potato Research* 26, 73-77.
- Schumann, G.; Mehlfeldt, G.; Levy, R. (1983) Untersuchungen von Speisekartoffeln aus Grosslagerhausern auf Chlorpropham-Ruckstande. *Zeitschrift fur die Gesamte Hygiene und ihre Grenzgebiete* 29, 260-263.
- Whale, G.; Sheahan, D.; Matthiessen, P. (1988) The toxicity of tecnazene, a potato sprouting inhibitor, to freshwater fauna. *Chemosphere* 17, 1205-1217.
- Witman, E.D.; Newton, W.F. (1951) Chloro-IPC- a new herbicide. *Proceedings of the North eastern Weed Control Conference* 1951 45-46.
- Worobey, B.L.; Sun, W.F. (1987) Mass spectral characterisation of chlorpropham and two of its metabolites. by GC-MS. *Chemosphere* 16, 1457-1462.
- Worobey, B.L.; Pilon, J.C.; Sun, W.F. (1987) Mass spectral characterisation of a halogenated azobenzene (dichloroazobenzene) from potato peels. *Journal of Agricultural and Food Chemistry* 35, 325-329.
- Wuthrich, C.; Muller, F.; Blaser, O.; Marek, B. (1985) Die Belastung der Bevolkerung mit Pesticiden und anderen Fremdstoffen durch die Nahrung. *Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene* 76, 260-276.
- Yess, N.J. (1988) Food and Drug Administration program. Residues in foods-1987. *Journal of the Association of Official Analytical Chemists* 71, 156A-174A.

AUTHOR INDEX

- Abbas, H. K. 3B-2
 Adamidis, T. 7C-2
 Adams, R. 8B-7
 Agamalian, H. 5B-5
 Akinyemiju, O. A. 4D-3
 Ali, E. 6A-6
 Allen, R. 8A-5
 Andreasen, C. 4B-4
 Arissian, M. 7C-8
 Arnold, G. M. 8A-5
 Arsenovic, M. 8C-4
 Askew, M. F. 3C-4, 6B-4
 Atkins, P. 5B-1
 Atkinson, D. 6B-1

 Bahr, J. T. 2-9
 Bailey, S. W. 9B-2
 Bakos, J. 2-10
 Baloch, R. I. 4D-8
 Banks, V. E. 6A-8
 Barber, D. 3A-2
 Barnes, C. J. A. 3A-1
 Barreda De, 4D-7
 Barta, I. C. S. 8B-6
 Baylis, A. D. 3C-3
 Baylis, J. M. 3A-5
 Bell, A. R. 6C-3
 Bellinder, R. 5B-2
 Benoit, D. L. 4B-5
 Benyamini, Y. 8B-3
 Beraud, J. M. 2-5
 Beyer, E. M. 1-1
 Binney, R. 4D-4
 Bihari, F. 2-10
 Birley, M. A. 5C-3
 Black, I. A. 3C-5, 5B-6
 Blouet, A. 7C-8
 Boatman, N. D. 4B-6, 5C-8
 Bodeux, C. 5C-3
 Bond, W. 5B-3
 Boyd, I. M. G. 9B-6
 Boyette, C. C. 3B-2
 Brooke, D. N. 4D-6
 Brown, H. 9A-4
 Brown, H. M. 7A-2
 Brown, V. K. 7B-4
 Bryan, R. 7C-9
 Buckley, D. C. 3D-4
 Burn, A. J. 5B-1
 Bussler, B. H. 2-3
 Butler, R. C. 5C-7

 Campbell, J. 4D-10
 Capri, E. 4D-9
 Carlton, R. R. 4D-10
 Carter, A. D. 4D-2, 4D-4
 Caseley, J. C. 8A-5, 8A-9
 Chandler, K. 4B-5

 Chida, T. 2-7
 Chisholm, C. 4C-3
 Clarke, J. H. 7C-6, 8A-6
 Claument, J. 2-5
 Claus, J. S. 2-6, 4C-3
 Clay, D. V. 4C-5, 8C-1
 Cobb, A. H. 8B-2
 Collins, J. L. 8C-2
 Cooke, A. S. 5C-1
 Cornes, D. W. 3C-2, 4C-2, 4D-11
 Coupland, D. 7A-1
 Courtney, A. D. 8A-3, 9A-3, 9A-5
 Cousins, R. 6C-5
 Crosby, G. A. 2-9
 Cruz, R. De La, 8A-11
 Cussans, G. W. 6C-5

 Danielou, V. 8A-7
 Darmency, H. 8A-4
 Davies, D. H. K. 4B-3, 6B-1, 9A-3, 9A-4, 9A-7
 De'Ath, M. R. 8C-2
 Delpeuch, I. 3C-3
 Del Re, A. M. 4D-9
 Dempster, J. P. 7B-1
 Derksen, D. A. 4B-5
 Dietrich, R. F. 7A-2
 Dixon, F. L. 3C-1
 Downey, S. 4D-10
 Drennan, D. S. H. 3C-11
 Duke, S. O. 3B-2
 Duncan, H. J. 9B-6
 Dutka, F. 8B-6
 Du Rieu, A. G. 4D-11

 Eadsforth, C. V. 3D-3
 Edwards, C. A. 7B-2
 Efthimiadis, P. 7C-2
 Eifert, G. 2-10
 Evans, B. E. 5C-4

 Fageiry, K. H. E. 3C-11
 Ferris-Kaan, R. 8A-2
 Feucht, D. 4A-4
 Fielder, A. G. 7C-9
 Firbank, L. G. 3A-6, 6C-1
 Fisher, N. M. 4B-3, 6B-1
 Fitzpatrick, D. A. 3D-1
 Forche, T. 4B-2
 Fowler, S. V. 8C-6
 Fox, G. 3A-2
 Frost, A. J. 7B-3
 Froud-Williams, R. J. 3B-1, 4B-6, 8A-2
 Gange, A. C. 7B-4

 Garcia-Baudin, J. M. 4D-1
 Garnett, R. P. 6A-6, 8C-5
 Garro, J. E. 8A-11
 Garstang, J. R. 7C-10
 Gasquez, J. 8A-4
 Gauvrit, C. 4A-5, 9A-2
 Ghebbioni, C. 4D-9
 Gilbert, A. J. 6A-2
 Gill, J. P. 3D-3
 Giltrap, N. J. 7C-10
 Glass, C. R. 6A-2
 Glendinning, P. J. 4D-6
 Gohbara, M. 3B-2
 Gorski, S. F. 4A-6
 Graham, K. 2-1
 Grant, R. K. 4D-8
 Green, J. H. 4A-3
 Green, J. M. 4A-3
 Groeneveld, R. M. W. 9A-8
 Groot, de N. A. 9A-8
 Grosjean, O. 3C-9
 Grothaus, G. D. 3D-1
 Grundy, A. C. 4B-6
 Guckert, A. 7C-8
 Gullner, G. 8B-4

 Haggard, R. J. 5C-2
 Hall, J. C. 8B-1
 Hargett, L. T. 2-11
 Harr, J. 2-11
 Harris, D. A. 6A-5
 Harris, G. L. 9B-2
 Hemmen, C. 4C-4
 Henderson, D. W. 9B-5
 Henderson, E. J. C. 3C-2
 Hewson, R. T. 3C-5
 Hignett, R. R. 9B-4
 Hill, A. L. 8A-3
 Holden, A. N. G. 8C-6
 Hollis, J. M. 4D-4
 Holtum, J. A. 8A-10
 Hooker, J. E. 5C-3
 Horton, P. 7A-4
 Howard, C. L. 6C-5

 Iwane, Y. 7C-1
 Iwanzik, W. 4D-11

 Jeffrey, W. A. 6A-4
 Jensen, J. E. 4B-4
 Jensen, P. 4C-3
 Jepson, P. 7B-5
 Joenje, W. 4B-1
 Johnson, G. 7A-4
 Johnson, K. S. 6A-5
 Jones, A. T. 5C-2
 Jones, D. 5C-2
 Jones, N. E. 4B-7

- Joy, D. N. 6C-3
Jung, B. 4C-1
- Kanzaki, M. 7C-1
Keen, B. W. 3A-3
Kenyon, W. H. 7A-2
Kennedy, P. J. 4B-7
Kerber, E. 8B-7
Kerlan, M.-C. 8A-7
Kimenia, J. K. 3C-12
Kiralý, L. 8B-4
Kirkwood, R. C. 5C-9
Kittl, R. 4A-4
Klevorn, T. B. 2-7
Klinker, 4A-4
Komives, T. 8B-4
Konradt, M. 4C-4
Kreidi, M. 4C-3
- Landes, M. 4C-1
Lawrie, J. 4C-5
Lawson, H. M. 3C-6, 3C-7,
3C-8
Leah, J. 8B-2
Leake, C. R. 4D-10
Lefol, E. 8A-7
Lichtner, F. T. 7A-2
Lindell, S. D. 7A-3
Lintel-Smith, G. 3A-6
Lorenzo, E. 4D-7
Lotz, L. A. P. 9A-8
Lunis, P. 7B-3
Lutman, P. J. W. 3C-1
- Majek, B. A. 3C-10
Marrs, R. H. 7B-3
Marshall, E. J. P. 5C-6
Mason, A. 8C-5
Mason, D. J. 9B-2
Mathiessen, P. 4D-6
Matienzo, M. T. 4D-1
Matsuzawa, M. 7C-7
Maurer, W. 3C-2, 4C-2, 4D-11
McCloskey, M. 6C-1
McMinn, A. L. 5A-3
Menendez, J. 8A-9
Merwin, I. A. 5B-2
Miller, P. C. H. 9A-9
Millington, S. 3B-6
Mills, M. J. 4D-6
Misselbrook, J. 4A-1
Miyazawa, T. 7C-7
Moll, S. 6A-3
Montury, A. 2-5
Moon, M. P. 2-1
Mortimer, A. M. 5C-4, 6C-5
Moss, S. R. 8A-6
Müller-Schärer, H. 5B-4
Murphy, G. J. 4A-8
Murphy, M. 6B-3
- Nagy, M. 2-10
- Nau, K.-L. 6A-7
Navas, M.-L. 8A-8
Nawamaki, T. 2-2, 2-4
Naylor, R. E. 4B-7
Neal, J. C. 5B-2
Neary, P. E. 3C-10
Newton, J. E. 4A-7
Nezu, M. 2-6
Nixon, C. J. 5C-3
Njoroge, J. M. 3C-12
Noctor, G. 7A-4
Nowakowski, M. 5C-5, 5C-6
- Oakes, D. B. 4D-4
Obrador, A. 4D-1
Ogilvy, J. M. E. 6A-5
Okada, M. 7C-1
O'Keeffe, M. G. 2-7
Orson, J. H. 3A-4, 6C-6
- Pallett, K. E. 8B-5
Palmer, J. J. 7C-4
Peebles, K. A. 2-1
Perkins, J. M. 3D-2
Perrissin Fabert, D. 7C-8
Pessala, B. 4A-7
Peters, N. C. B. 3B-4
Petzold, R. 5A-2
Pfister, K. 8B-7
Picton, J. 9A-3
Pillmoor, J. B. 7A-3
Pinthus, M. J. 7C-5
Plant, R. A. 7B-3
Policello, G. A. 4A-8
Porter, K. 5C-5
Potter, C. A. 5B-4
Powles, S. B. 8A-10
Prado, R. de 8A-9
Price, D. R. H. 9B-3
Pritts, M. P. 5B-2
Proven, M. J. 9A-3
Putwain, P. D. 5C-4
- Raffel, H. 6A-7
Rasmussen, J. 3B-5
Read, M. A. 5B-6, 7C-4
Reboud, X. 8A-7
Rees, D. 7A-4
Rees, L. 7C-3
Reinke, H. 2-1, 4C-3
Richards, M. C. 9A-7
Rickard, S. 6B-2
Rittenburg, J. 3D-1
Romano, M. L. 8B-1
Rubin, B. 7C-5, 8B-3
Ruckle, R. E. 4A-8
Rule, J. S. 6C-2
Ryan, P. J. 3C-2, 4C-2, 4D-11
- Sakaki, M. 2-8
Sansome, G. 9A-6
Sato, R. 2-8
Schär, H. P. 8B-7
- Schonfeld, M. 8B-3
Schroeder, D. 8C-6
Scott, T. A. J. 4C-2
Seckinger, K. 2-11
Shannon, P. J. 8A-11
Sherratt, T. N. 7B-5
Sherratt, A. P. 7C-3
Shida, T. 2-7
Shigematsu, S. 2-6, 7C-7
Shirakawa, N. 7C-1
Sholl, J. 4A-7
Sibony, M. 7C-5
Simmons, N. 9B-1
Skorda, E. A. 7C-2
Sovljanski, R. 8C-4
Stafford, J. V. 9A-9
Stephens, R. J. 8C-1
Stephenson, G. R. 8B-1
Stock, D. 4A-2
Stocker, D. R. 3D-1
Stopes, C. 3B-6
Strathmann, S. 3C-9, 4C-1
Streibig, J. C. 4B-4
Suzuki, K. 2-2, 2-4
Swanton, C. 4B-5
- Taberner, A. 8A-9
Tadeo, J. L. 4D-1
Takahashi, S. 2-6
Takeuchi, M. 7C-1
Tal, A. 8B-1
Teasdale, R. 3D-2
Tenne, F. D. 6A-8
Thain, N. B. 8C-3
Thomas, B. 5A-3
Thompson, T. R. 4D-4
Thonke, K. E. 9A-1
Tomkinson, J. K. 8B-5
Tooby, T. 5A-1
Townsend, G. M. 6C-6
Trevisan, M. 4D-9
Turnbull, A. 4D-6
- Ummel, E. 2-11
Urvoy, C. 4A-5
- Vallee, P. 8A-7
Van Saun, W. A. 2-9
Voon, C. H. 3C-3
- Wakeham, A. C. 5C-9
Walker, A. 4D-5
Walz, A. W. 6C-3
Warwick, S. I. 8A-1
Watsnabe, S. 2-2, 2-4
Waters, S. 3B-3
Watkinson, A. R. 3A-5, 3A-6,
6C-1
Watson, C. A. 5C-3
Weiler, E. W. 8B-7
Wells, B. H. 2-2
West, T. M. 3B-4, 5C-7
White, R. H. 2-3

White, R. M. 6A-1
Whiting, A. J. 9A-3, 9A-4
Whytock, G. P. 9A-4
Williams, E. L. 2-3
Williams, R. J. 4D-6
Williamson, A. R. 4D-2
Wilson, B. J. 6C-4
Wirth, W. 4A-4

Wiseman, J. S. 3C-6, 3C-7,
3C-8
Woodbridge, A. P. 3D-3
Woolley, E. W. 7C-9
Worrall, T. L. 8B-2
Wright, E. 6C-6
Wright, K. 7A-3
Wright, K. J. 6C-4

Yaacoby, T. 8B-1
Yamamoto, S. 2-2, 2-4
Yanagisawa, K. 7C-7
Yoshida, R. 2-8
Young, A. J. 7A-4, 8B-5
Young-Hee Moon 4D-5
Zivanovic, M. 8C-4