PB92-209378

EPA/600/R-92/138
June 1992

HIGHER PLANT ACCUMULATION OF ORGANIC POLLUTANTS FROM SOILS

by

Robert M. Bell
Environmental Advisory Unit
University of Liverpool
Merseyside Innovation Centre
131 Mount Pleasant
Liverpool L3 5TF, UK

Cooperative Agreement CR812845

Project Officer

P. R. Sferra
Water and Hazardous Waste Treatment Research Division
Risk Reduction Engineering Laboratory
Cincinnati, Ohio 45268

RISK REDUCTION ENGINEERING LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completi

1. REPORT NO.	2.	3.
EPA/600/R-92/138		PB92-209378

4. TITLE AND SUBTITLE	5. REPORT DATE
Higher Plant Accumulation of Organic Pollutants from Soils	June 1992
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Robert M. Bell	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Advisory Unit University of Liverpool Merseyside Innovation Centre Liverpool L3 5TF, UK	11. CONTRACT/GRANT NO. CR812845
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Risk Reduction Engineering Laboratory--Cincinnati, OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	Final 14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES
Project Officer: P.R. Sferra Telephone: 513-569-7618

16. ABSTRACT The purpose of this work was to determine the effect of higher plants on sites polluted by organic chemicals and to discuss the potential of using plants as an in situ cleanup treatment. This work is based primarily on literature review but also includes greenhouse experiments and field testwork. It is concerned with the behavior of organic pollutants in the plant-soil environment, plant uptake and accumulation of organic pollutants, and variation in uptake by different plant species in different conditions.

The literature review involved keyword searches into suitable databases and review of over 750 scientific publications for information. Within this report greater emphasis was placed on the few reports where sufficient details concerning experimental methods to make comparisons is provided.

The greenhouse experiments were undertaken to investigate the actual extent of plant uptake of pollutants from soils under known environmental conditions. The field testwork was undertaken to quantify natural effects.

This report is not concerned with foodchain effects and is not concerned with effects of the pollutant on the plant itself.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Plant metabolism Plant nutrition Plant physiology Plant tissue Contaminants Soil chemistry Soil dynamics Soil chemistry Soils	Plant accumulation of organic pollutants.	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to public	Unclassified	138
-	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

NOTICE

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement CR812845 to the University of Liverpool. It has been subject to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This final report provides the results of a project funded by RREL through a cooperative agreement with the University of Liverpool to determine the potential of using plants as means of cleaning up hazardous waste sites. The work investigated the fate of organic pollutants as they are affected by the interactions that go on between the plant and the soil, the ability of plants to take up and accumulate these pollutants, and variations in uptake by different plant species in different conditions. Those wishing additional information on this project are urged to contact the author or the EPA Project Officer.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

The purpose of this work was to determine the effect of higher plants on sites polluted by organic chemicals and to discuss the potential of using plants as an *in situ* cleanup treatment.

In situ cleanup systems have many advantages when compared with other cleanup techniques. These systems treat polluted soils, without excavating the bulk of the polluted material, by detoxifying, neutralizing, degrading, immobilizing or otherwise rendering harmless the contaminants where they are found.

The first steps in the development of an *in situ* plant cleanup system for organically polluted soils include the determination of the technical feasibility and cost effectiveness of the method, the determination of the availability of suitable plant species or varieties, the determination of whether the site possesses optimal soil conditions, the conduction of greenhouse scale confirmatory uptake tests, and confirmation that the plant materials that have extracted the contaminants can be disposed of in an environmentally safe manner and that the plant mass and harvesting mechanics are realistically manageable.

This work is based primarily on literature review but also includes greenhouse experiments and field testwork. It is concerned with the behaviour of organic pollutants in the plant-soil environment, plant uptake and accumulation of organic pollutants, and variation in uptake by different plant species in different conditions.

The literature review involved keyword searches into suitable databases (including Water Resources Abstracts, Biosis Previews, Chemical and Biological Abstracts, Agricola, Phytotox) and review of over 750 scientific publications for information. Within this report greater emphasis has been placed on the few reports where sufficient details concerning experimental methods to make comparisons is provided.

The greenhouse experiments were undertaken to investigate the actual extent of plant uptake of pollutants from soils under known environmental conditions. The field testwork was undertaken to quantify natural effects.

This report is not concerned with foodchain effects where the plant may accumulate pollutants and animals feeding on the plant may receive high doses of the pollutant for subsequent effect. Nor does this report address effects of the pollutant on the plant itself. As will be seen, these effects result from interactions between pollutant concentrations and a variety of environmental effects.

CONTENTS

CONTENTS (Continued)

CONTENTS (Continued)

FIGURES

TABLES

TABLES (continued)

TABLES (continued)

TABLES (continued)

TABLES (continued)

SECTION 1

INTRODUCTION

The historical disposal of toxic and hazardous chemicals has caused, in recent years, increased pollution problems and become a threat to our environment and well being. This problem is most acute and has reached large proportions in the industrialised countries. In the United States, for example, a recent estimate includes 25,000 potentially hazardous waste sites (EPA, 1987). In Wales, a survey of potential contaminated sites, based on former use, identified 703 sites, or approximately 0.2% of the total land area (Welsh Office, 1984).

Although many of these contaminated sites contain a wide range of organic and inorganic pollutants, the behaviour and effect of the organic compounds, often the predominant pollutants, have received the least study. This is understandable; inorganic compounds are relatively inexpensive to assess, are quite straightforward to work with, and are few in number. The behaviour of the organic compounds, occurring as pollutants needs to be understood, however, so that successful remedial actions can negate the hazards arising from their presence. The potential health hazard of some of these compounds has been identified (Dacre, 1980).

Organic compounds may have very low water solubility; some do not degrade readily and have long half lives in soil. They may have a very high affinity for lipids, bioaccumulating in tissue, and may accumulate and translocate in the food chain. They can be highly toxic to mammals - many are carcinogenic.

The purpose of this report is to determine the effect of higher plants on sites polluted by organic chemicals and to discuss the potential of using plants as an *in situ* cleanup treatment. Higher plants are those that reproduce by seeds and do not have two conspicuous stages in their life cycle. This definition includes grasses, trees, shrubs, etc., but excludes the ferns, mosses, liverworts, etc.

In situ cleanup systems have many advantages when compared with other cleanup techniques. These systems treat polluted soils, without excavating the bulk of the polluted material, by detoxifying, neutralizing, degrading, immobilizing or otherwise rendering harmless the contaminants where they are found (Stief, 1985). As the polluted materials are not excavated, the workforce is not exposed to the pollutants, and the pollutants do not migrate from the site during excavation.

The first steps in the development of an *in situ* plant cleanup system for organically polluted soils have been identified as

1. determine whether vegetative extraction of pollutants from the contaminated soil has a high probability of being the most technically feasible and cost effective approach at the specific site, realizing that this approach will require a substantial time period and intensive agronomic management over that time,

2. determine whether suitable plant species (or varieties within a species) are available to accomplish the desired contaminant extraction,

3. determine whether the site possesses, or can be readily modified to possess, soil conditions that will support optimal growth of the selected plant materials,

4. conduct greenhouse scale confirmatory uptake tests, and

5. confirm that the plant materials that have extracted the contaminants can be disposed of in an environmentally safe manner and that the plant mass and harvesting mechanics are realistically manageable (Sanning, 1985).

Using vegetation as an *in situ* cleanup technique has received little study although there would appear to be many potential benefits from such a technique were it available. A plant cleanup system for organically polluted soils may prove suitable for a number of different pollutant situations, e.g., when soils are contaminated to shallow depths, i.e., less than 2 meters, which is around the maximum depths plant roots normally penetrate the soil. Such surface situations are commonly encountered from spills or leaks, when the source of the contamination is at, or near, the soil surface. It also occurs on many former tipping (dumping) sites.

Plant cleanup systems, that use the ability of plants to accumulate pollutants and then to metabolize them to simple units, would essentially be inexpensive to establish and maintain. It could, therefore, prove extremely useful when vast volumes of soil and sediment materials are polluted but not to an immediately hazardous extent. These materials may be polluted by dust blow or surface erosion resulting from adjacent contaminated sites.

The ability of plants to remove and accumulate compounds from the soil is an essential function of the plant. Uptake of compounds from land treatment sites, for example, has been recognized as important in the management of these sites for a number of reasons. For example, plants remove much applied nitrogen and phosphorus while they grow and thereby protect the groundwater from these nutrients. Also, plants may be able to extract excessive levels of some microelements from polluted sites and thereby rehabilitate the site for more normal crops (Chaney, 1983).

This report, which is based primarily on literature review but also includes greenhouse experiments and field testwork, is concerned with

1. the behaviour of organic pollutants in the plant-soil environment,

2. plant uptake and accumulation of organic pollutants, and

3. variation in uptake by different plant species in different conditions.

The literature review involved keyword searches into suitable databases (including Water Resources Abstracts, Biosis Previews, Chemical and Biological Abstracts, Agricola, Phytotox) and review of over 750 scientific publications for information on the above topics. Unfortunately, despite this extensive data base, few reported investigations provided sufficient details concerning experimental methods to make comparisons. Within this report, therefore, greater emphasis has been placed on the few reports where such information is provided.

The greenhouse experiments were undertaken to investigate the actual extent of plant uptake of pollutants from soils under known environmental conditions. The field testwork was undertaken to quantify natural effects.

This report is not concerned with foodchain effects where the plant may accumulate pollutants and animals feeding on the plant may receive high doses of the pollutant for subsequent effect. Nor does this report address effects of the pollutant on the plant itself, i.e., stunted growth, delay in germination, enhanced senescence, etc. As will be seen, these effects result from interactions between pollutant concentrations and a variety of environmental effects.

REFERENCES

Chaney, R.L. 1983. Plant uptake of inorganic waste constituents. In: *Land treatment of hazardous wastes*. Parr, J.F., P.B. Marsh, and J.M. Kla (eds.). Noyes Data Corp. Park Ridge, NJ. Pp. 50-76.

Dacre, J.C. 1980. Potential health hazards of toxic organic residues in sludge. In: *Sludge - health risks of land application*. Britton, G., R.L. Damron, G.T. Edds, and J.M. Davidson (eds.). Ann Arbor Sci., Ann Arbor, MI. Pp. 85-102.

EPA, 1987. Superfund: Looking back, looking ahead. April 1987. EPA-87-007. Washington, D.C.

Sanning, D.E. 1985. *In situ* treatment. Chapter 4. In: *Contaminated land. Reclamation and treatment*. M.A. Smith (ed.). Plenum Press. New York and London.

Stief, K. 1985. The long term effectiveness of remedial measures. Chapter 2. In: *Contaminated Land. Reclamation and treatment*. M.A. Smith (ed.). Plenum Press. New York and London.

Welsh Office, 1984. Survey of contaminated land in Wales. Welsh Office, Cathays Park, Cardiff, Wales, UK.

SECTION 2

BEHAVIOUR OF POLLUTANTS IN THE PLANT-SOIL ENVIRONMENT

The behaviour of a compound in the soil depends upon both the physical and chemical properties of the compound and of the soil. As either the soil or the compound varies, so does the eventual fate and effect of the compound and so does the effect on plants growing in the soil.

Once an organic compound, or indeed any other compound, is within the soil, it tends to spread throughout the soil. Once spread within the soil, further processes are known to determine the fate of an organic compound. They include such physical, chemical, and biological processes as leaching, adsorption, desorption, photo-decomposition, oxidation, hydrolysis, and metabolism.

As any number of these processes can be acting on any given chemical at the same time, an assessment of the environmental fate of the compound is extremely complicated. The interrelationships of these processes is shown in Figure 2.1.

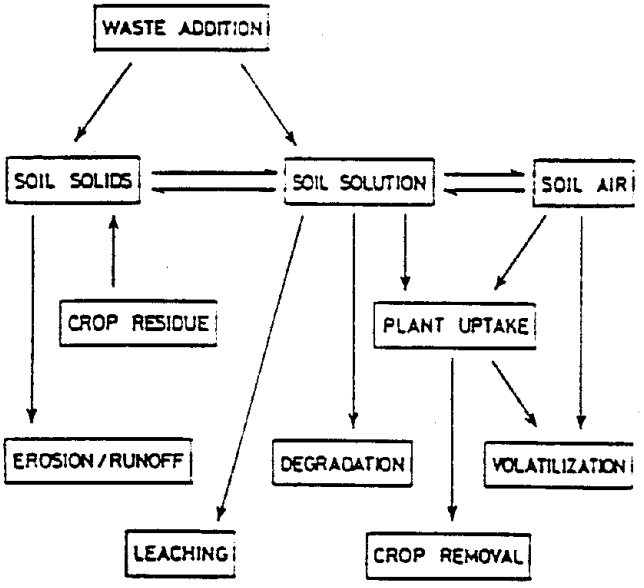

Figure 2.1. Interrelationships and transformations of pollutants in soils.

The migration of any pollutant within the soil is affected by both soil factors and the properties of the compound itself. The processes of spread (excluding mechanical action where man or other animals may pick up the chemical and place it elsewhere) include molecular diffusion and various kinds and combinations of flow.

Molecular diffusion occurs continuously and spontaneously wherever there is a concentration gradient in an attempt to even out that gradient to achieve a uniform distribution. Flow, on the other hand, is not spontaneous but occurs from a combination of external forces.

A compound's solubility and volatility, then, directly control its distribution between undissolved solid, liquid, and vapour phases and controls the extent of its adsorption to the soil matrix. This latter factor is also influenced by the soil itself and is discussed at length below.

Although some of the above factors are influenced by climate, e.g., temperature, soil water content, etc., others are influenced by the very nature of the soil medium itself. Soil is normally heterogeneous and is formed from weathered bedrock. A silt loam surface in good condition for plant growth consists of 20% to 30% by volume of air, 20% to 30% water, 45% minerals, and 1% to 3% organic matter. Soil is generally characterized by three layers referred to, from top to bottom, as the A, B, and C horizons. The A horizon, usually called the topsoil, is normally higher in organic matter than the other horizons and is subjected to leaching of soluble materials. The B horizon, or subsoil, is usually deeper than A, has a greater clay content, and is a zone of accumulated leached material. The C horizon is usually called the substratum and consists of weathered bedrock and other parent materials (Lee et al., 1985).

The way in which compounds partition differently among the different soil horizons depends on their individual constituents and, obviously, the site of their disposal.

Texture, compaction, organic matter, and clay minerals are the major physical soil characteristics affecting chemical behaviour within the soil.

1. Soil texture is a measure of the proportion of different particle size range groups within the soil, e.g., sand, silt, and clay. When sand is the dominant particle, the soil is described as "light" and water infiltrates rapidly. When silts and clays dominate, then the soil is "heavy" and slow to erode.

2. Soil compaction is a measure of the density of the soil. Highly compressed soils have low pore space thereby preventing the movement of air and water within the soil.

3. Soil organic matter is a mixture of plant and animal residues in various stages of decomposition, of chemicals synthesized chemically and biologically from their breakdown products, and of microorganisms and small animals and their decomposing remains (Lee et al., 1985). It is the most active area of the soil. Quantitively it consists of two fractions, humic and

nonhumic. Humic organic matter is the transformed remains of the plants, animals, and microorganisms in the soil; the nonhumic is the unaltered remains. The former includes fulvic acid, humic acid, and humins; the latter includes cellulose, starch, proteins, and fats.

4. Clay minerals are minerals with sheet silicate structures. They are markedly influenced by the time and type of the weathering process of the parent material from which they were derived.

The soil's acidity and cation exchange capacity are major chemical soil constituents affecting chemical behaviour in the soil.

1. Soil acidity, a measure of the hydrogen ion concentration in the soil, influences all soil reactions and biological activity.

2. Cation exchange capacity refers to the capacity of the soil to hold or sorb exchangeable cations. This property arises in the soil's organic matter and clay minerals and influences biological activity and the potential of the soil to be leached.

Vegetation growing on a soil can significantly affect many of these characteristics and reponses. Depending on the nutrient source, for example, plant roots can make the soil near them either more acidic or more alkaline than the soil at a distance from the root. This is because the root exchanges anions or cations with the soil as part of the root's uptake of essential plant nutrients. Smiley (1974) measured the rhizosphere pH (pH_r) of field and container-grown wheat plants and compared it with the nonrhizosphere pH (pH_b). The pH_r was generally lower than pH_b when ammonium was supplied as a fertilizer, higher when nitrate was supplied, and remained relatively unchanged when both forms were added together. Differences in pH_r of up to 2.2 pH units were recorded in laboratory experiments and up to 1.2 units under field conditions.

As a plant root grows into the soil, it will also affect the bulk density of the soil and thus will affect the rate of ion diffusion within the soil. As the plant root grows, it occupies space that was previously occupied by soil pores or soil particles. Since root diameters are of the order 0.1 to 3 mm and soil pores are of the order 0.002 to 0.2 mm, the bulk density of the soil near the plant root automatically increases. Greacen et al. (1968), showed these increases in soil, i.e., an initial density of 1.5 g/cm^3 increased to 1.6 to 1.7 g/cm^3.

When ions within the soil diffuse towards the root, they do so along the concentration gradient, which is measured per unit volume of soil. Hence as the soil is compacted around the root, the concentration of the ion per unit of soil volume is increased and steeper concentration gradients are obtained. In addition, the proportion of clay and organic matter is higher in the volume of soil near the root than at some distance from it. This is because of the differential packing of the soil particles around the root. As clays and organic matter are the prime sites for nutrient and pollutant sorption, the

plant root is directly exposed to higher concentrations of these chemicals than would be found throughout the soil as a whole.

The amount of physical change the root actually exerts on the soil varies with the density of the roots in the soil and with the root morphology.

When it becomes involved with the soil medium, the organic pollutant will distribute between the solid phase (either undissolved particles or adsorbed onto receiving surfaces), the liquid phase (normally dissolved in the soil water), and the vapour phase. In the solid phase, it can be regarded as inert, because it cannot migrate throughout the soil mass and is probably unavailable to plants. Once in the liquid or vapour phase, however, the pollutant can become active and begin to biologically or chemically affect its immediate surroundings. The properties of the pollutant, therefore, influence its effect within the soil environment.

To determine a compound's mobility in the soil, it is essential to know how a given quantity of the applied compound will partition between these three phases. The following discussion is concerned with the various factors acting on an organic pollutant when it is present in the soil. Each section contains a theoretical discussion of what happens in the soil and case studies involving the effect of higher vegetation on the system.

SORPTION AND DESORPTION

Theoretical aspects

Sorption represents the single most important factor affecting behaviour of chemicals in the soil and is an important mechanism for immobilizing soil pollutants. Sorption also reduces the activity of pesticides, retards their movement, and delays their degradation. Sorption has, therefore, been the subject of considerable research.

Adsorption is the accumulation of the pollutant at an interface such as a solute to solid, i.e., on the surface of a solid at the clay colloid/water interface. Absorption is the movement of solutes from one place to another through an interface of a two component mixture, including penetration into plant or animal cells and microorganisms. Desorption is the release of the sorbed molecules.

Once a compound is applied to the environment, a dynamic equilibrium is established between the adsorbed and solution phase, which is known as the partitioning effect. Sorption can be either chemical or physical. Anionic or cationic compounds are chemically sorbed, whereas nonionic compounds are physically sorbed (Kaufman, 1983). Adsorption will affect the rate of volatilization, diffusion, or leaching as well as the availability of the chemical to biological uptake and attack.

Sorption can be specific or nonspecific. The former occurs when specific sites on the surface of soil particles exert forces on a particular unit of a molecule at a certain configuration; the latter is more general and

occurs where any molecule, at any configuration of the soil particle, is sorbed. There are major forces that make sorption possible.

1. Van der Waals forces are weak, but additive, electrostatic forces caused by an uneven distribution of electrons around a molecule. They become significant for large and organic molecules.

2. Hydrophobic bonding is actually a partitioning between a polar solvent (e.g., water) and a nonpolar adsorbent surface (e.g., soil humus). This is related to temperature and is the prime reason for the relationship between the organic carbon content of the soil and the *n*-octanol/water partition coefficient of the soil-borne chemical discussed below.

3. Hydrogen bonding is a weak electrostatic bond that occurs between hydrogen and two atoms of high electronegativity. As with Van der Waals forces, this bonding becomes more significant with larger molecules.

4. Charge transfer is formed between bonds or lone pairs of electrons when there is a partial overlap of the electron orbits of two molecules. It is an important form of bonding for organic chemicals.

5. Ligand exchange is a replacement of one or more ligands of a molecule by a further, stronger chelating, absorbent agent.

6. Chemisorption involves the chemical bonding between adsorbent and adsorbate in an exothermic process.

The adsorbed-liquid partitioning is expressed through an adsorption isotherm, which is often calculated. At low concentrations, the shape of this isotherm may frequently be approximated to a straight line, giving rise to the equation

$$C_s = Kd\ (C_l)$$

where C_s is adsorbed concentration (g/kg soil), C_l is solution concentration (g/m^3 soil solution), and Kd (m^3/kg) is the slope of the adsorption isotherm of the distribution coefficient.

Several workers have reported that adsorption is highly correlated with the organic matter content and cation exchange capacity of the soil (Rhoades et al., 1970; Bailey and White, 1964); whereas it is independent of substrate pH, textural composition, and clay mineralogy (Means et al., 1982). Lambert (1968) goes so far as to suggest classifying soils according to "corrected" or active organic matter content with Ripperdan sandy loam with 1% organic matter as a standard soil.

Since this distribution coefficient (for nonionic pesticides at least) primarily represents adsorption to organic matter, variability between soils may be reduced to an extent by defining an organic carbon distribution coefficient as

$$K_{oc} = \frac{Kd}{f_{oc}}$$

where f_{oc} is the fraction of organic carbon in the soil and K_{oc} represents the adsorption per unit of organic carbon.

Where measured adsorption values are not available, reasonably good correlation has been found between K_{oc} and the *n*-octanol/water partition coefficient (K_{ow}) of the compound or between K_{oc} and the solubility and melting point of the compound (Jury et al., 1983).

The *n*-octanol/water partition coefficient is defined as the ratio of the chemical concentration in octanol to that in water when an aqueous solution is intimately mixed with octanol and then allowed to separate. Dawson et al. (1980) report that this value reflects the bioaccumulation potential of the chemical; this, in turn, is defined as the concentration of the chemical in an aquatic organism compared with the concentration of the chemical in the water to which the organism is exposed (Brown et al., 1983). The bioaccumulation factor is, in fact, a partition of the pollutant between water and the lipid and protein phases of the organism (Briggs, 1981).

The predictive aspects of the *n*-octanol/water partition coefficient with the organic matter content of a soil has resulted in mathematical models describing the plant uptake of organic pollutants from soils (Norton and Chrostowski, 1986). These models present uptake as a simple partitioning process. Norton and Chrostowski's model uses three pollutant specific parameters (organic carbon partition coefficient, the *n*-octanol/water partition coefficient, and Henry's Law constant) and addresses partitioning into the roots, shoots, leaves, and seeds. The authors note that the model is useful only for pollutants that are not products of normal plant metabolism.

These models, although useful for their intended applications of assessing the potential food chain transfer of new and existing chemicals, tend to simplify the living biological system in which plants exist. The use of the *n*-octanol/water coefficient and the other partitioning constants for example should be regarded as a very generalized approach (Dragun, 1986).

The *n*-octanol/water partition coefficient has proved useful as a means to predict soil adsorption, biological uptake, lipophilic storage, and biomagnification. Unfortunately, the partition coefficients of many chemicals are not available. By definition, the partition coefficient expresses the equilibrium concentration ratio between an organic liquid, e.g., *n*-octanol, and water. This partitioning is in essence equivalent to partitioning an organic chemical between itself and water. Chiou et al. (1977) showed a correlation between the partition coefficient and its aqueous solubility covering eight orders of solubility (from 10^{-3} to 10^{4} ppm) and six orders of partition coefficient (from 10 to 10^{7}).

Factors that affect the aqueous solubility of an organic chemical will also affect its partition coefficient. For example, there is about a 25% change in either the partition coefficient or the aqueous solubility for every 10 degree variation in temperature. Temperature can then affect the absorption or accumulation of a pollutant in the roots of a plant.

Goring (1962) also recognized the close correlation between Kd, the soil/water distribution, and the organic matter content of the soil, and proposed a soil organic matter/water distribution, K_{om}, for each chemical

$$K_{om} = \frac{100\ Kd}{\%\ OM}$$

For 2-chloro-6-(trichloromethyl) pyridine, he found K_{om} in the range of 86 to 262, with a mean of 155, for 10 soils with an organic matter content range of 0.3% to 32.2%. Graham-Bryce (1967) and Graham-Bryce and Etheridge (1970) reported similar values of K_{om} in different soils, with mean values of 491 for disulfoton and 5 for dimethoate. As the range of K_{om} values obtained from these experiments with different soils was small, Briggs (1981) suggested that despite the complexities of, and variations in, soil organic matter, K_{om} for a particular chemical is a constant across all soil types.

Briggs (1973) then showed that the behaviour of 30 chemicals, within four different agricultural soils, allowed a relationship between the organic matter/water distribution and the *n*-octanol/ water partition coefficient of the chemical to be obtained. This equation

$$\log K_{om} = 0.52 \log K_{ow} + 0.62$$

follows a linear regression equation where 0.52 and 0.62 are data-fitted coefficients.

Many investigators have since assessed this equation with different groups of environmentally active chemicals and varying soil types (Karickhoff, 1984).

Means et al. (1982) report a broadly similar relationship between the organic matter content of the soil and the *n*-octanol/water partition coefficient of the chemical with

$$\log K_{oc} = \log K_{ow} - 0.317$$

for the sorption of 22 nonpolar compounds (mainly substituted aromatic hydrocarbons) by 14 soils and sediments having an organic matter content range of 0.11 to 2.38%. This equation tended to under estimate the organic matter sorption for two amines tested but could be corrected if the % organic carbon/% montmorillonite clay ratio of the substrate was taken into account. The authors suggest that the enhanced sorption of these two amines must involve specific interactions of the amine functional group with components of

the associated clay minerals, when the ratio of organic matter to clay mineral is low, at less than 0.1. Reactions of this type are known to occur with other aromatic amines.

Schwarzenbach and Westall (1981) reported

$$\log K_{oc} = 0.72 \log K_{ow} + 0.49$$

from their experiments with 13 methylated and halogenated benzenes.

Rao et al. (1982) reported

$$\log K_{oc} = 1.029 \log K_{ow} - 0.18$$

from their experiments with 13 pesticides; and Karickhoff (1981) reported

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346$$

from his work with five polyaromatic hydrocarbons.

Brown and Flagg (1981) investigated the adsorption of nine chloro-s-triazines and dinitroaniline compounds and, by combining other published data, produced the relationship

$$\log K_{oc} = 0.937 \log K_{ow} - 0.006$$

that covered a broad range of compounds within a broad range of soils and sediments. They found that the uncertainty in this equation increased with the addition of data sets on more hydrophobic compounds, where the interaction of specific functional groups with adsorption sites, is not accounted for by the K_{oc} treatment. The addition of data from polar compounds only changed the relationship slightly. They concluded that the practical utility of this form of relationship is maximized when a broad range of chemicals is being investigated. Better precision can be obtained by fitting separate relationships to each distinct group of chemicals.

The above relationships are shown in Figure 2.2. They are surprisingly similar to one another considering they cover the behaviour of over 100 organic chemicals as well as a large number of soils and sediments. Some criticisms, however, have been made of the inappropriate use of these equations.

1. They are valid only with molecular weights of less than 400. Above this figure, van der Waals forces govern soil adsorption of the pollutant and these forces are not dependant upon soil organic matter content.

2. They assume hydrophobicity is the only factor governing adsorption.

3. They ignore the mineral content of a soil and thus any mineral adsorption of a pollutant to a soil. If the % clay/% organic matter is

greater than 30, the mineral surfaces in the soil are significant for pollutant adsorption.

4. They assume K_{oc} or K_{om} for a soil is constant and thereby ignore rhizosphere influences and the difference between top and subsoil.

5. They assume all soil organic matter behaves the same, which it undoubtedly does not.

6. They assume linear isotherms for soil adsorption of pollutants over all pollutant concentrations (Dragun, 1986; Karickhoff, 1984).

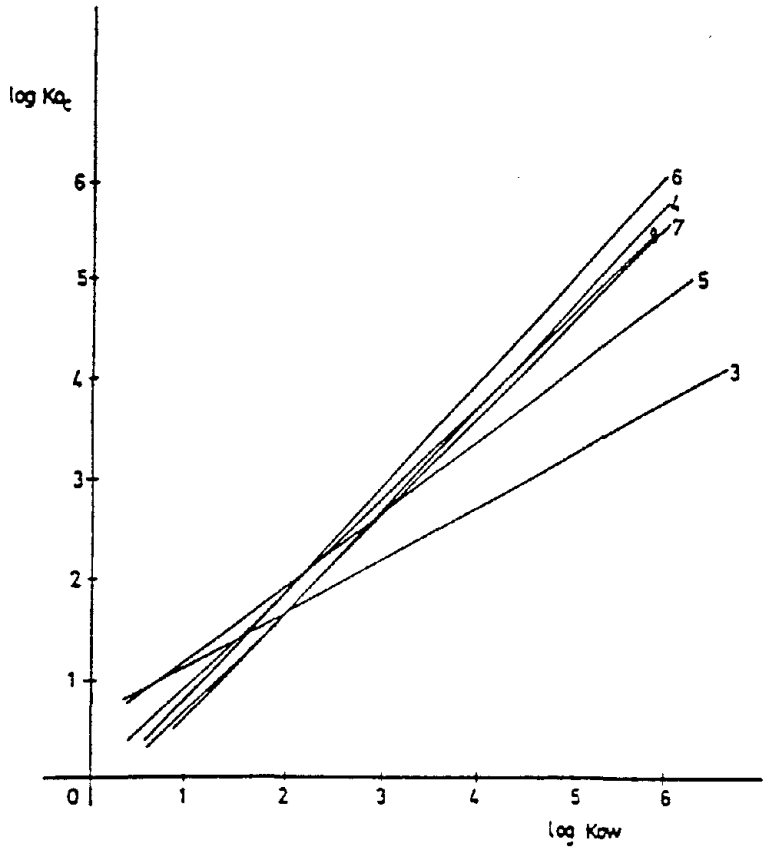

Figure 2.2. The relationship between the organic matter sorption of a soil (K_{oc}) and the *n*-octanol/water partition coefficient (K_{ow}) of the pollutant. (Regressions from 3 - Briggs, 1973; 4 - Means et al., 1982; 5 - Schwarzenbach and Westall, 1981; 6 - Rao et al., 1982; 7 - Karickhoff, 1981; 8 - Brown and Flagg, 1981.)

These linear regression equations relating the organic matter partition to the *n*-octanol/water partition of the organic chemical also have inherent errors that result in variability when observed values are compared with calculated values. These have been discussed by Karickhoff (1984) and are shown in Figure 2.3.

Some efforts have been made to relate the structure of a chemical to its sorptive potential. Hance (1969), for example, related the parachor of a molecule, which is a measure of its volume, and the number of sites on the molecule that could participate in the formation of a hydrogen bond to the adsorption of 29 aromatic compounds by two soils.

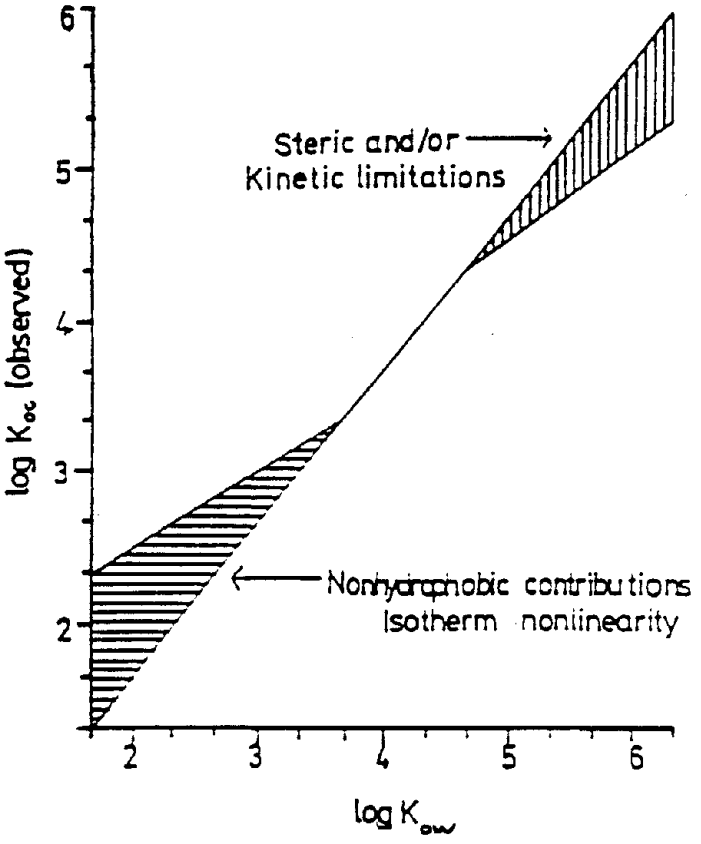

Figure 2.3. Errors in observed values of K_{oc} compared with calculated values. (from Karickhoff, 1984.)

Considerable effort has been expended to determine the relative importance of clay and organic matter in chemical sorption. Both materials sorb chemically and physically and both can exhibit a wide variation in their properties. Wahid and Sethunathan (1978 and 1979) concluded that organic matter was the most important factor governing the sorption of both the isomers of hexachlorocyclohexane (HCH) and parathion by 12 soils. In the absence of organic matter, parathion sorption was correlated with clay content and free iron oxides, whereas the separate isomers of HCH behaved differently.

Now, however, it is generally accepted that organic matter is more important than clays except in dry soils or where the organic carbon content of the soil is low (Kaufman, 1983).

Soil pH and moisture are further critical factors affecting sorption of some chemicals in soils. The pH affects the dissociation constant of the chemical, which, in turn, affects its chemical bonding potential. All chemicals are adsorbed strongly at low pH; anionic compounds are adsorbed negatively at slightly basic conditions and nonionic compounds are moderately adsorbed. Sorption of organic chemicals is more complete in dry soils than in wet soils because surfaces that would normally preferentially adsorb water become available to the chemical. Yaron and Saltzman (1972) demonstrated this experimentally with the organophosphorus insecticde, parathion. As their soil water content increased, so parathion sorption decreased.

Temperature may also influence adsorption both through its effects on the solubility and vapour pressure of the compound and because adsorption processes are exothermic (Harris and Warren, 1964). Generally, an increase in soil temperature leads to decreased adsorption; however, there are exceptions where higher temperatures result in lower soil water conditions.

To obtain many of the above relationships, it is necessary to assume that pollutant adsorption to soil is reversible, i.e., the pollutant will be released from the organic fraction of the soil into the soil solution in the direction of the concentration gradient. The ease of desorption appears to depend on the actual strengh of the adsorption process. Harris and Warren (1964) found that various herbicides could be recovered from soils and sediments with low organic fractions more readily than they could from muck soils. Graham-Bryce (1967) found that the adsorption of the systemic herbicide disulfoton was fully reversible if desorption took place immediately after uptake when the sorbing soils were still wet. Desorption, or release of the herbicide from the sorbing soils, was modified if the soils were allowd to dry thoroughly between adsorption and desorption (Sims et al., 1984).

Error is introduced into the relationships via the formation of irreversibly bound residues, which occur in soils, plants, and animals. Although the presence of these residues has been known for some time, only the increasing recent use of radiolabelling techniques has led to a quantification of their extent (Klein and Scheunert, 1982). These bound, or non-extractable residues are defined as chemical species that are unextracted by methods that do not significantly change the chemical nature of the compound. They exclude fragments recycled through metabolic pathways leading to natural products. Table 2.1 gives a few examples to demonstrate the significance of these bound residues.

TABLE 2.1. PESTICIDE RESIDUES BOUND IN SOIL, MEASURED IN PERCENT OF APPLIED AMOUNT. (Adapted from Klein and Scheunert, 1982.)

Chemical class	Time of exposure	% Residue bound
Free phenols	1 vegetation period	50-58
Anilines	1 vegetation period	31-58
Triazines	4-12 months	56-65
Urea herbicides	1 vegetation period	28-41
Carbamates	30-32 days	17-57
Organophosphates	7-84 days	18-80
Cyclodiene	1 vegetation period	1-8

Di Toro and Horzempa (1982) also reported the concept of irreversibly bound residues from their sediment sorption studies with 2,4,5,2′,4′,5′-hexachlorobiphenyl. They suggested that it may be inappropriate to treat this and PCB isomer adsorption reactions as either completely reversible or totally irreversible.

In most instances, sorption can be regarded as advantageous, because sorbed compounds in the soil are environmentally less active. Fairbanks and O'Connor (1984) concluded that adding sludge containing PCBs to soil did not increase the environmental hazard of the PCBs because of the additional sorptive capacity of the added sludge.

Case studies

The actual type of soil, and thus its sorptive capacity and characteristics, highly influences plant uptake of pollutants from soil. This is because pollutants are sorbed more tightly, become biologically inactivated, and thus less available to the plant roots as the organic matter content of the soil increases (Finlayson and MacCarthy, 1973). Adams (1971), for example, reported tenfold differences in the bioactivity of pesticides in soils with different organic matter contents.

Attempts to relate the extent of adsorption of a given herbicide to soil properties have shown a correlation between adsorption and organic matter content, clay content, and cation exchange capacity of the soil. Harrison et al. (1976) investigated the effects on oats of atrazine, chloramben, fluometuron, propachlor, and trifluralin in 10 North Carolina soils. Some 15 soil properties were measured and correlated with fresh weight inhibition levels. Organic matter content of the soils was the soil variable most closely related to the herbicide phytotoxicity, and there was an inverse relationship between the herbicide water solubility and its inactivation by this organic matter.

VOLATILIZATION AND DIFFUSION

Theoretical aspects

Volatilization and diffusion are further processes by which organic compounds can be spread throughout the soil. The vapour partitioning of a compound is important because this spread is considerably greater than that by the solution phase. Even for chemicals with relatively low vapour densities, this transport route has been shown to be significant (Mayer et al., 1974).

The rate at which a compound vapourizes in the soil, and from a soil, will be influenced by its inherent volatility, the ambient and soil temperature, dilution with inert biological material, and any restraints placed on the compound by the soil. The vapourized molecules will tend to diffuse outward primarily through the air spaces in the soil and, while diffusing, will tend to dissolve in the soil water. The partition of a chemical between the soil water and soil air is in a constant flux or equilibrium. The diffusion within the soil is best described by Fick's Law; the liquid-vapour partition is generally represented through Henry's Law.

Goring (1967) suggested that Fick's first law of diffusion was probably applicable to all diffusion processes in soil, including movement of organic chemicals through air, water, and organic matter. This means that the rate of movement of a chemical is directly proportional to the concentration of the chemical and its diffusion coefficient, which is a quantitative expression of the diffusion rate through different media.

Fick's Law is expressed

$$\frac{F}{A} = - D\left(\frac{dC}{dX}\right)$$

where F is the amount of substance diffusing per unit of time across area, A, normal to the direction, X, and dC/dX is the concentration gradient in that direction. The negative sign is required because diffusion takes place in the direction of decreasing concentration (Hartley and Graham-Bryce, 1980).

The diffusion rate of a gas is influenced by molecular weight, temperature, presence of other diffusing gases, continuity of soil air spaces, and the distribution of the chemical into the different phases of the soil. Because this distribution depends on the characteristics of the soil, the extent of volatilization and diffusion of a particular chemical is site specific. Insecticides diffuse more slowly in soil than in air because the pathway through the soil pores is restricted and because the chemical may be sorbed by the soil. The exact geometry of the soil pathway depends on the nature of the pore space formed by the particles in a given soil and on the soil moisture content (Graham-Bryce, 1969).

The division of a compound between the soil solution and the air spaces in the soil is often described by Henry's Law and the extent of partitioning is described by Henry's Constant. Henry's Law is expressed

$$C_g = Kh\ (C_l)$$

where C_g is the concentration of chemical in the vapour phase (g/m^3 soil air); Kh is Henry's Law Constant, which has no dimensions; and C_l is the solution concentration (g/m^3 soil solution) (Jury et al., 1983).

Those compounds with a high vapour pressure, which would be reflected in a high Henry's Constant, will easily move from the soil solution into the soil air, and will be quickly spread throughout the soil. There have, unfortunately, been no all- embracing studies to determine the level at which Henry's Constant describes the predominant transport route. Graham-Bryce (1984) reports that a partition between vapour and aqueous phase of 10^{-4} is normally sufficient to ensure vapour effects when working with pesticides. This is based on experience with particular compounds rather than broad-ranged, detailed investigations. It remains uncertain what level of Henry's Constant for organic priority pollutants should be taken to be descriptive of vapour phase transport.

Volatilization, itself, is the loss of the compound to the air mass. It is influenced by many soil and compound parameters. The position of the compound in the soil will, for example, affect its chance of being volatilized and, thereby, of leaving the soil. For example, only 3% of applied heptachlor was recovered from surface-treated soil, 3 to 4 months after application compared with 15% of the insecticide incorporated into the soil after 5 months (Saha and Stewart, 1967).

Soil type also affects the degree of potential volatilization of a chemical from the soil. Guenzi and Beard (1970) report that volatilization rates for DDT and lindane from soil containing moisture greater than 15 bar tensions were dependent on temperature, adsorptive characteristics of the soil, and concentration of the chemical. For DDT and lindane at 30°C, the rate of volatilization from soil was in the order of Valentine loamy sand > Hand loam > Raber silty clay loam > Promise clay, which had 0.6%, 1.63%, 3.06%, and 3.57% organic matter contents, respectively.

Harris and Lichtenstein (1961) showed an increase in the rate of aldrin volatilization from soil, with increases in aldrin concentrations in the soil and increases in the rate of air movement over the soil surface. The soil surface and air over the soil are connected by a layer or boundary of stagnant air through which water vapour and chemical vapour move by diffusion.

Guenzi and Beard (1970) also found higher losses of both DDT and lindane at temperatures of 55°C than at 30°C. Haque et al. (1974) investigated the vapour behaviour of the PCB Aroclor 1254. They found that the loss of the chemical, via its vapour phase, was negligible from soil but quite significant from sand. As temperature increased, vapour loss increased, and isomers with fewer chlorine atoms showed greater loss than those having more chlorine atoms.

The loss of Aroclor 1254 from itself is shown in Figure 2.4. Although the loss is rather small at 26°C, it is substantial at 60°C.

Farmer et al. (1972) reported that the vapour density of a chemical in soil is the main factor controlling volatilization, and that the vapour density increases with increasing soil concentrations until a peak is reached. Their laboratory studies gave maximum volatilization rates from Gila silt loam of 202, 22, and 5 Kg/ha/year for the pesticides lindane, dieldrin, and DDT, respectively. These rates decreased rapidly with decreasing pesticide concentrations, but they suggested the decrease could account for a significant proportion of these applied chemicals that are lost under normal field conditions.

In fact, losses of organic chemicals from soil surfaces through volatilization have been reported for the s-triazines and phenylureas, which have very low vapour pressures (Kaufman, 1983).

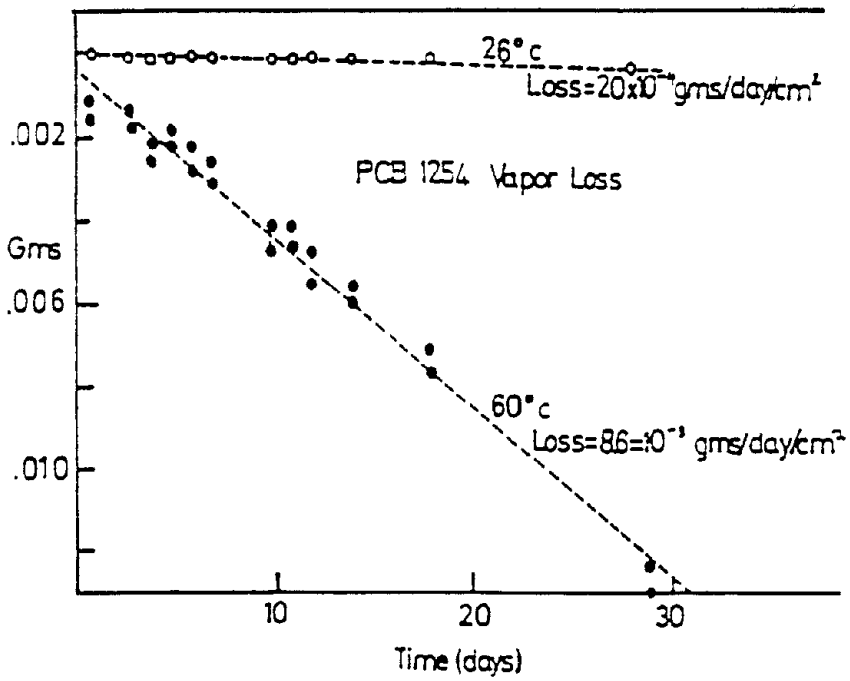

Figure 2.4. The loss of Aroclor 1254 from itself at different temperatures. (From Haque et al. 1974.)

Case studies

Investigations have aimed at assessing the rate of volatilization, and thereby loss, of chemicals from the soil. Much of this work has been carried out with soil fumigants, or herbicides that act through their vapour phase. These compounds normally have high vapour pressures and low water solubilty (Harvey, 1974; Goring, 1962).

Harvey (1974) investigated the soil adsorption and volatility of 12 dinitroaniline herbicides in a Plano silt loam and their respective effects on the growth of foxtail millet, *Setaria italica*. High correlations between the effects of the herbicide vapours on growth of the millet under laboratory conditions and the relative effectiveness of seven of the herbicides under field conditions suggested that absorption of the vapours of the

dinitroaniline herbicides by plants may be more important than absorption of the herbicides from soil solutions.

DEGRADATION

Theoretical aspects

Degradation of a compound in the soil can occur by biological or nonbiological processes and can occur whether the compound is in a solid, liquid, or vapour phase. The concentration of most organic compounds in the soil, therefore, decreases with time providing that no further additions are made and that the compound is not being synthesized via the degradation of other compounds. The rate at which degradation occurs is generally considered to be first order and can be described as

$$M(t) = M(0) \exp. (-ut)$$

where M(t) is the quantity of the compound remaining in the soil at time, t, (Jury et al., 1983). The rate of degradation of individual compounds is normally described by half life, i.e., the time taken for one half of the initial concentration of the compound to be degraded.

The half lives of many compounds have been published (Ryan, 1976; Smith and Dragun, 1984; Jury et al., 1983). Actual half lives are, however, very dependent on local environmental conditions and published material can only be taken as a guide. Half lives of many organic pollutants are included in Section 5.

Nonbiological transformations of compounds are more numerous than biological transformations. They include those brought about by light as well as reactions such as hydrolysis, oxidation, or reduction, which may be catalyzed by soil colloids. Photodegradation is the action of sunlight chemically altering and degrading an organic chemical in the soil. It usually depends on the absorption spectrum of the compound.

Biodegradation is generally defined as the molecular degradation of an organic substance resulting from the complex action of living organisms. A substance is said to be biodegraded to an environmentally acceptable extent when its undesirable environmental properties are lost (Rochkind et al., 1986).

Many biological agents with the capacity to directly degrade, or otherwise change organic compounds, are in the soil.

1. Bacteria, of which there are many different groups and species, are normally classified according to their energy source for survival. The heterotrophs, which decompose organic materials, are thereby more important in degrading organic pollutants than are the autotrophs which use light as their energy source either through photosynthesis or the oxidation of inorganic materials.

2. Fungi, which constitute a large fraction of the microbial biomass of a soil, also depend on heterotropic metabolism. They are very resistant to unfavourable environmental conditions and many grow at temperatures below 10°C.

3. Algae, which need oxygen, are usually restricted to the soil surface. At the surface they may be present in appreciable numbers and may enhance the photodecomposition of some organic chemicals.

4. Higher life forms, include the protozoa, nematodes, insects, and worms who graze on the other life forms in the soil or feed on detrital matter. They may directly degrade organic compounds or assist in their degradation by mixing the soil and contributing to its aeration.

5. Higher plants, which often form the soil surface cover and through plant roots may reach soil depth of up to 3m (Foxx et al., 1984), are discussed at length in Section 3.

There are, of course, many interactions between and within each of these life forms and between them and the various soil constituents including organic compounds. Microbial activity, for example, may cause desorption of a compound from the soil organic matter and thus may increase chemical mobility and the potential for degradation within a soil. Perhaps the greatest interactions among the life forms results from competition for readily assimilable substrates, so that growth rates are generally restricted. This encourages those life forms that can use substrates other organisms cannot use.

Although biological degradation refers to degradation that occurs from all biological agents in the soil, the literature indicates that by far the larger volume of research has been carried out with micro, rather than macro, biological agents. Generally, degradation seems related to the overall level of microbiological activity rather than the presence of any one particular agent. Biological degradation tends to occur more in soils with relatively high organic matter contents, (providing soil sorption does not protect the target compound), than in those with low organic matter content. Adding nutrients often increases the rate of degradation and this is now referred to as "enhanced degradation." It is of potential interest as a soil cleanup technique.

Some herbicides actually induce microbial populations with particular ability to degrade them (Audus, 1964). Most herbicides,however, do not induce this sort of behaviour and it is assumed that they are degraded incidently in the rapidly metabolizing soil environment. Lower concentrations of herbicides in the soil are normally degraded faster than higher concentrations.

Microorganisms in soils and soil water convert many synthetic organic chemicals to inorganic products. Other compounds are transformed only by cometabolism. Microbial processes may lead to environmental detoxication, the formation of new toxicants, or the biosynthesis of persistent products. Some organic chemicals are resistant to microbial attack.

The soil environment is, by its very nature, heterogeneous, with soil particles ranging from meters to nanometers. It is within this environment that many of the biological agents of degradation have to work, and therefore, results tend to vary considerably.

Components of the microscopic population are affected to different degrees when exposed to pollutants (Alexander, 1969). The compound may exert a general depressive effect on most or essentially all components; on the other hand, it may act upon a very limited group. This normally depends on both the type and concentration of the compound and the nature of the population.

Case studies

Microorganisms are more abundant in the soil surrounding plant roots than in soil remote from the root (Table 2.2) (Rovira and Davey, 1971). This zone of soil in which the microorganisms are influenced by the root is called the "rhizosphere." This normally poorly defined zone has a microbiological gradient (Table 2.3) where the greatest numbers of microorganisms occur directly adjacent to the root and decline with distance away from it. Direct microscopy of roots grown in soil show that over the older root portions bacteria can be 10 to 40 cells deep, whereas the younger root tip is often bacteria free. Other organisms, e.g., the mycorrhizal fungi, actually penetrate the root cortex several cells while also remaining in the soil.

The root associated microorganisms, i.e., the bacteria, fungi, and actinomycetes of the rhizosphere affect their host plant through their effect on such factors as the availability of plant nutrients and subsequent nutrient uptake. Their presence also causes an increased rate of decomposition of soil organic matter.

TABLE 2.2. EXTENT AND DESCRIPTION OF THE RHIZOSPHERE OF 18-DAY-OLD BLUE LUPIN (*Lupinus angustifolium*) SEEDLINGS. (From Rovira and Davey, 1971)

Distance from root, mm.	Microorganisms (1000s/g oven-dried soil) Bacteria	Streptomycetes	Fungi
0	159,000	46,700	355
0-3	49,000	15,500	176
3-6	38,000	11,400	170
9-12	37,400	11,800	130
15-18	34,170	10,100	117
80	27,300	9,100	91

TABLE 2.3. COMPARISON OF THE COLONY COUNTS OF BACTERIA IN THE RHIZOSPHERE OF VARIOUS CROP PLANTS AND IN ROOT FREE SOIL (From Rovira and Davey, 1971)

Crop		Colony Counts, 10^6/g soil Root free	Rhizosphere
Red Clover	*Trifolium pratense*	143	3,255
Oats	*Avena sativa*	184	1,090
Flax	*Linum usitatissimum*	184	1,015
Wheat	*Triticum aestivum*	120	710
Corn	*Zea mays*	184	614
Barley	*Hordeum vulgare*	140	505

The rhizosphere microflora can be adapted by inoculation of the seeds or roots of the plant by the required microorganism. Much more basic research is needed, however, before the inoculated population will automatically develop into the dominant component of the microflora in what is an extremely competitive environment.

Chemicals, such as pollutants or herbicides, applied to the soil, either accidentally or deliberately, bring about changes not only in the soil microflora but also in the relationships between plants and rhizospheric organisms (Taleve and Stoimenova, 1984). The nature of these changes has not received much study. Sandman and Loos (1984) found that the most probable number of 2,4-D degrading organisms in the rhizosphere of African clover was greater than the number within the rhizosphere of sugarcane. They suggest that this increased rhizosphere population could play a part in protecting various types of plants against soil-applied chemicals.

EFFECTS OF WATER

Theoretical aspects

The impact of water on a site containing hazardous chemicals can be effectively managed by man, and adverse effects through off-site transfer of pollutants need never occur. Mass flow of pollutants however often occurs by surface runoff and water infiltration of the soil mass causes leaching of chemicals to the underlying groundwater.

Surface runoff is an effect of rainwater on the soil surface. As the slope of the soil surface increases, there is a corresponding rise in the velocity of surface water runoff, which in turn results in greater erosion. Long, unbroken slopes allow surface runoff to build up and concentrate in narrow channels producing rill and gully erosion. Land grading techniques are required to arrest this runoff and subsequent erosion and are commonly used on a variety of sites.

Leaching is of major importance in determining the fate of any compound when it is in the soil. Leaching is the rapid removal of the soil water component of the soil sorbed/soil water equilibrium, which thereby moves the equilibrium towards the desorption of the compound.

Chemicals are moved through the soil by rainfall or irrigation, or both. This is governed by three processes: desorption of the chemical from the soil, diffusion of the chemical through water, and hydrodynamic dispersion. The net result of these processes is the increased spread of the organic chemical throughout the soil, moving with the concentration gradients.

The rate of water flow through the soil is, on the microscopic scale, very heterogeneous and is controlled by the size of the soil pores. Within the soil pore, flow rate increases concomitantly with distance from the pore wall, but may be almost zero in pores away from the continuous pathways of flow. Differences in flow rate result in the gradual spread of the pollutant in a band through the soil, called convective dispersion.

In temperate regions, the movement of pollutants through soils via leaching shows a seasonal distribution (Leistra, 1980). In the spring much of the rainfall evaporates from the soil surface or is taken up from the upper layers of the soil by plant roots. In the winter, both rainfall is larger and plant usage less, so that leaching may become more significant. Complications in this may be experienced when soils containing much clay show large cracks on drying. When intense rain falls on such a soil, part may rapidly enter the deeper reaches of the soil before the upper soil layers are fully moistened. This water may carry with it some of the pollutant to these deeper layers, but the main portion of the compound would leach less then would be expected.

Although the movement of pollutants with the mass flow of water may be significant as far as their environmental effects are concerned, as a pathway of loss this appears insignificant. Herbicides, for example, are rarely found beneath the plough layer of a soil.

Water moves both upward (Bailey and White, 1970) and downward in the soil, and thus any pollutant within the soil water follows the same route. Vegetation on the soil surface with its associated water requirement for transpiration can draw considerable quantities of water to the soil surfaces from great depth, especially in those areas where high evapo-transpiration ratios are prevalent. This influence of vegetation on the movement of a compound in the soil increases as the mass of the crop increases (Leistra, 1980).

Bell and Parry (1984) have reported on the upward transport of heavy metal and various anions, including sulphates and complex cyanides, from polluted soils that were overlaid by 600 mm of clean soils, primarily through the translocation pull of overlying vegetation.

The potential of any chemical to be leached from the soil is influenced by its own persistence. Some chemicals are rapidly broken down in the soil and are, therefore, unlikely to be present long enough in the soil to be leached.

Case studies

There is evidence from pot experiments that herbicides enter plants more or less concomitantly with water. Therefore it would be expected, and indeed was the case, that increasing the water dose always resulted in a higher total insecticide residue in beets grown on sandy loam or sandy clay loam soils and a greater plant weight. Uptake of the insecticide by the plant was also increased if more of the compound was available in the active root zone for the plant to take up. If there is not enough water, then not enough chemical may reach the root; if there is too much water, then polar metabolites in particular will be leached away from the active rhizosphere and result in less uptake (Dejonckheere et al., 1982).

Wax and Behrens (1965) investigated the effects of temperature and relative humidity on the root and foliar uptake of radiolabeled atrazine in quackgrass (*Agropyron repens*). They found that uptake and translocation increased as temperature increased but also as relative humidity decreased. This follows the response of transpiration to these environmental factors.

The phytotoxicities of atrazine, simazine, linuron, lenacil, and aziprotryne were increased as the moisture content of the soil increased. These increases were a result of differences in the concentration of the herbicides that were accumulated by the plants, with total uptake being directly proportional to water uptake (Walker, 1971).

Moyer et al. (1972) began with the premise that herbicide uptake by a plant was related to the volume of water transpired, as shown by Sheets (1961) and Shone and Wood (1972). They established a system containing soil on which the herbicide diuron was adsorbed to see if plants are able to take up equivalent amounts of herbicide from media having different quantities of adsorbed herbicide but equal concentrations of herbicides in solution. After 7 days growth in the system, the amount of herbicide supplied to the exposed barley plants by mass flow was calculated. The values obtained from the different media were all similar, indicating that 50 to 60% of the diuron supplied to the root was accumulated by the shoot, whether the root was in contact with amended nutrient solution, with solution plus peat having approximately 7.7 μg/g adsorbed diuron, or with solution plus loam soil having about 1.3 μg/g of adsorbed diuron. Diuron uptake seems, therefore, to be controlled by the soil solution concentration and the volume of water transpired.

Transpiration rates for crops are commonly in the order of 200 to 270 kg water per kg dry matter yield and some crop yields are as great as 2000 kg dry matter/ha. This indicates the vast quantity of water that actually passes through plants that are growing on soils and suggests the potential for plant accumulation of soil-borne pollutants. Walker (1983), however, concludes that this uptake by plants will only make a minor contribution to herbicide loss from the soil.

WIND BLOW AND MASS TRANSFER

The movement of organic chemicals over the soil surface can be as important as their movement through the soil, especially in terms of pollution potential and environmental effect. There are two main types of overland flow: where the chemical is in solution in water and where the chemical is adsorbed onto particulate matter being carried along in the overflowing water. Good management of a site area will considerably reduce the potential for these transport processes to occur.

Abandoned or inactive hazardous waste sites have been recognised as candidates for vegetative stabilization to reduce fugitive emissions (Turner et al., 1984). The primary control mechanism is direct stabilization of the soil surface by the plant roots binding the soil and the stems and leaves forming a protective cover preventing particles from becoming airborne.

CONCLUSIONS

The above factors (sorption and desorption, volatilization and diffusion, degradation, water, and wind) that determine the behaviour of a compound applied to the soil, make identifying the role of vegetation difficult. Each factor interacts not only with one another but with other processes that naturally occur in the soil. Without carefully considering many factors, the environmental fate of any one compound can not be determined. An even more complex situation occurs when a range of compounds are present within a soil and the compounds are competing with one another for, say, sorption sites.

The sorptive capacity of soils and sediments and response of many compounds, albeit primarily complex organic herbicides, to sorption has been well described. The organic matter content of the soil best describes the soil's ability to sorb compounds, whereas the *n*-octanol/water partition coefficient best describes the ability of the compound to be sorbed. The greater the soil's organic matter content and the higher the K_{ow} of the compound, then the more sorbed and the less environmentally active will be the compound.

Vapour transport in soils and sediments has received less study. Transport will be affected by both physical and chemical aspects of the soil as well as of the compound. A need still exists to understand the relationships between the physicochemical properties of a compound and potential for vapour phase transport.

Other factors and processes affect a compound in the soil and in the region of the soil affected by the plant root. Degradation of compounds, through biological, physical, and chemical means, is continually progressing, and the concentration of a particular chemical in the soil reduces with time, regardless of the action of higher plants. The spreading of compounds through wind or water erosion also reduces concentrations in one area but increases them in another. Further work is needed on all of these processes,

particularly those related to the behaviour of organic compounds that occur as pollutants on many of our uncontrolled hazardous waste sites, so that remedial actions can be properly designed.

REFERENCES

Adams, R.S. 1971. Effect of soil organic matter on the movement and activity of pesticides in the environment. In: *Trace substances in environmental health - V* Proc. Univ. Mo. 5th Ann. Conf. Hemphill, D.D. ed. June 29-July 1. pp 81-93.

Alexander, M. 1969. Microbial degradation and biological effects of pesticides in soil. In *Soil Biology*. Reviews of Research, UNESCO, Belgium. pp. 209-240.

Audus, L.J. 1964. Herbicide behaviour in the soil; II Interaction with microorganisms. In: *The physiology and biochemistry of herbicides* Audus, L.J., ed. Academic Press, London & N.Y.

Bailey, G.W., and J.L. White. 1964. Review of adsorption and desorption of organic pesticides by soil colloids with implications concerning pesticide bioactivity. *J. Agric. Food Chem.* 12(4):324-332.

Bailey, G.W, and J.L. White. 1970. Factors affecting the adsorption, desorption, and movement of pesticides in soil. *Res. Revs.* 32:29-92.

Bell, R.M., and G.D.R. Parry. 1984. Upward migration of contaminants through covering systems. In: *Proc. Conf. Management of Uncontrolled Hazardous Waste Sites*. HMCRI, Washington DC.

Briggs, G.G. 1973. A simple relationship between soil adsorption of organic chemicals and their octanol water partition coefficients. *Proc. 7th Br. Insect. Fung. Conf.*, Nottingham, U.K. pp. 83-86.

Briggs, G.G. 1981. Theoretical and experimental relationship between soil adsorption, octanol water partition coefficients, water solubilities, bioconcentration factors, and the parachor. *J. Agric. Food Chem.* 29:1050-1059.

Brown, D.S., and E.W. Flagg. 1981. Empirical prediction of organic pollutant sorption in natural sediments. *J. Environ. Qual.* 10(3):382-386.

Brown, K.W., G.B. Evans, and B.E. Frentrup. 1983. *Hazardous waste land treatment*. Ann Arbor Sci., Ann Arbor, MI.

Chiou, C.T., V.H. Freed, D.W. Schmedding, and R.L. Kohnert. 1977. Partition coefficients and bioaccumulation of selected organic chemicals. *Environ. Sci. and Technol.* 11(5):475-478.

Dawson, G.W., C.J. English, S.E. Petty. 1980. Physical and chemical properties of hazardous waste constituents. Attachment 1, Appendix B in background document (RCRA subtitle C) identification and listing of hazardous waste. Office of Solid Waste, EPA May 2, 1980.

Dejonckheere, W., G. Melkebeke, W. Steurbaut, and R.H. Kips. 1982. Uptake and residues of aldicarb in sugarbeet leaves. *Pestic. Sci.* 13:341-350.

Di Toro, D.M., and L.M. Horzempa. 1982. Reversible and resistant components of PCB adsorption-desorption. *Environ. Sci. Technol.* 16:594-602.

Dragun, J. 1986. The soil chemistry of hazardous materials; basic concepts and principles. *Proc. Conf. Superfund*, HMCRI. pp. 453-454.

Farmer, W.J., K. Igue, W.F. Spencer, and J.P. Martin. 1972. Volatility of organochlorine residues from soil: Effect of concentration, temperature, air flow and vapor pressure. *Soil Sci. Soc. Amer. Proc.* 36:443-447.

Foxx, T.S., G.D. Tierney, J.M. Williams. 1984. Rooting depths of plants as related to biological and environmental factors. Los Alamos Nat. Lab. LA 10254.

Goring, C.A.I. 1962. Theory and principles of soil fumigations. In: *Advanced Pest Control Research*. R.I. Metcalf, ed, 5:47-84. Interscience Publishers, New York.

Goring, C.A.I. 1967. Physical aspects of soil in relation to the action of soil fungicides. *Ann. Rev. Phytopath.* 5:285-318.

Graham-Bryce, I.J. 1967. Adsorption of disulfoton by soil. *J. Sci. Food Agric.* 18:73-77.

Graham-Bryce, I.J. 1969. Diffusion of organophosphorous insecticides in soils. *J. Sci. Food Chem.* 20:489-494.

Graham-Bryce, I.J. 1984 Optimization of physicochemical and biophysical properties of pesticides. In *Pesticide synthesis through rational approaches.* Magee, P.S., G.K. Kohn, and J.J. Menn, eds., Amer. Chem. Soc., Washington DC.

Graham-Bryce, I.J., and P. Etheridge. 1970. *Abstr. 7th Int.Congr. Plant Prot.* pp. 137-139.

Greacen, E.L., D.A. Farrell, and B. Cockroft. 1968. Soil resistance to metal probes and plant roots. *Trans. 9th. Int. Congr. Soil Sci.* 1:769-779.

Guenzi, W.D., and W.E. Beard. 1970. Volatilization of lindane and DDT from soils. *Soil Sci. Soc. Amer. Proc.* 34:443-447.

Hance, R.J. 1969. An empirical relationship between chemical structure and the sorption of some herbicides by soils. *J. Agric. Food Chem.* 17(3):667-668.

Haque, R., D.W. Schmedding, and V.H. Freed. 1974. Aqueous solubility, absorption, and vapour behaviour of PCB, Aroclor 1254. *Environ. Sci. Technol.* 8(2):139-142.

Harris, C.I., and G.F. Warren. 1964. Adsorption and desorption of herbicides by soil. *Weeds*. 12:120-126.

Harris, C.R., and E.P. Lichtenstein. 1961. Factors affecting the volatilization of insecticidal residues from soil. *J. Econ. Entomol.* 54:1038-1045.

Hartley, G.S., and I.J. Graham-Bryce. 1980. *Physical principles of pesticide behaviour.* Academic Press, London.

Harvey, R.G. 1974. Soil adsorption and volatility of dinitroaniline herbicides. *Weed Sci.* 22(2):120-124.

Jury, W.A., W.F. Spencer, and W.J. Farmer. 1983. Behaviour assessment model for trace organics in soil; 1. Model description. *J. Environ. Qual.* 12(4):558-564.

Karickhoff, S.W. 1981. Semi empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere* 10:833-846.

Karickhoff, S.W. 1984. Organic pollutant sorption in aquatic systems. *J. Hydraulic Eng.* 110(6):707-735.

Kaufman, D.D. 1983. Fate of toxic organic compounds in land applied wastes. In: *Land treatment of hazardous wastes.* Parr, J.F., P.B. Marsh, and J.M. Kla, eds., Noyes Data Corp., Park Ridge, NJ

Klein, W., and I. Scheunert. 1982. Bound pesticide residues in soils, plants and food with particular emphasis on the application of nuclear techniques. In: *Agrochemicals: Fate in food and the environment.* IAEA-SM-263/38 Vienna. pp. 177-205.

Lambert, S.M. 1968. Omega, a useful index of soil sorption criteria. *J. Agric. Food Chem.* 16(2):340-343.

Lee, C.R., J.G. Skogerboe, K. Eskew, R.A. Price, and N.R. Page. 1985. Restoration of problem soil materials at Corp Of Engineers construction sites. US Army Corp. of Engineers. Waterways Experimental Station. Vicksburg, Mississippi.

Leistra, M. 1980. Transport in solution. Ch. 2. *Interactions between herbicides and the soil.* Academic Press, NY. pp. 31-57.

Mayer, R., J. Letey, and W.J. Farmer. 1974. Models for predicting volatilization of soil incorporated herbicides. *Soil Sci. Soc. Amer. Proc.* 38:563-568.

Means, J.C., S.G. Wood, J.J. Hassett, and W.L. Banwart. 1982. Sorption of amino and carboxy-substituted polynuclear aromatic hydrocarbons by sediments and soils. *Environ. Sci. Technol.* 16:93-98.

Moyer, J.R., R.B. McKercher, and R.J. Hance. 1972. Influence of adsorption on the uptake of diuron by barley plants. *Con. J. Plant Sci.* 52:668-670.

Norton, S.B., and P.C. Chrostowski. 1986. Plant uptake of organic pollutants from contaminated soil; A conceptual model. *Proc. of Soc. of Environ. Toxicol. Chem.* Paper 292.

Rao, P.S.C., J.M. Davidson, V.E. Berkheiser, L.T. Ou, et al. 1982. Retention and transformation of selected pesticides and phosphorous in soil-water systems. A critical review. USEPA 600/3-82-060.

Rhoades, R.C., I.J. Belasco, H.L. Pease. 1970. Determination of mobility and adsorption of agrochemicals on soils. *J. Agric. Food Chem.* 18(3):524-528.

Rochkind, M.L., J.W. Blackburn, and G.S. Sayler. 1986. Microbial decomposition of chlorinated aromatic hydrocarbons. EPA/600/2-86/090.

Rovira, A.C., and C.B. Davey. 1971. *The plant root and its environment. Biology of the rhizosphere*, University Press of Virginia, Charlottesville, VA. pp 153-204.

Ryan, J.A. 1976. Factors affecting plant uptake of heavy metals from land application of residuals. *Proc. Conf. Disposal of residues on land.* St Louis. pp. 98-105.

Saha, J.G., and W.W.A. Stewart. 1967. Heptachlor, heptachlor epoxide, and gamma-chlordane residues in soil and rutabaga after soil and surface treatments with heptachlor. *Can. J. Plant Sci.* 47:79-88.

Sandmann, E.R.I.C., and M.A. Loos. 1984. Enumeration of 2,4-D degrading microorganisms in soils and crop plant rhizospheres using indicating media; High populations associated with sugarcane (*Saccharum officinarum*). *Chemosphere* 13(9):1073-1084.

Schwarzenbach, R.P., and J. Westall. 1981. Transport of non polar organic compounds from surface water to groundwater. *Environ. Sci. Technol.* 15(11):1360-1367.

Sheets, T.J. 1961. Uptake and distribution of simazine by oat and cotton seedlings. *Weeds* 9(1):1-13.

Shone, M.G.T., and A.V. Wood. 1972. Factors responsible for the tolerance of blackcurrents to simazine. *Weed Res.* 12:337-347.

Sims, R.C., D.L. Sorensen, J.L. Sims, J.E. McLean, R. Mahmood, R.R. Dupont, and K. Wagner. 1984. Review of in place treatment techniques for contaminated surface soils. EPA-540/2-84-003b November, 1984.

Smiley, R.W. 1974. Rhizosphere pH as influenced by plants, soils and nitrogen fertilizers. *Soil Sci. Soc. Amer. Proc.* 38:795-799.

Smith, L.R., and J. Dragun. 1984. Degradation of volatile chlorinated aliphatic priority pollutants in groundwater. *Environ. Intern.* 10:291-298.

Taleva, A., and I. Stoimenova. 1984. Effect of some herbicide combinations on rhizosphere microflora of sunflower. In: *Soil biology and conservation of the biosphere*, Szegi, J., ed., pp. 287-296.

Turner, J.H., M.R. Branscome, R.L. Chessin, A.S. Damle, R.V. Kamath, C.M. Northeim, and C.C. Allan. 1984. Fugitive particulate emissions from hazardous waste sites. Research Triangle Inst. EPA contract 68-03-3149, Research Triangle Park, NC.

Wahid, P.A., and N. Sethunathan. 1978. Sorption-desorption of parathion in soils. *J. Agric. Food Chem.* 26(1):101-105.

Wahid, P.A., and N. Sethunathan. 1979. Sorption-desorption of a, b and g isomers of hexachlorocyclohexane in soils. *J. Agric. Food Chem.* 27(5):1050-1053.

Walker, A. 1971. Effects of soil moisture content on the availability of soil applied herbicides to plants. *Pestic. Sci.* 2:56-59.

Walker, A. 1983. The fate and significance of herbicide residues in soil. *Sci. Hortic.* 34:35-47.

Wax, L.M., and R. Behrens. 1965. Absorption and translocation of atrazine in quackgrass. *J. Weed Soc. Amer.* 13(2):107-109.

Yaron, B., and S. Saltzman. 1972. Influence of water and temperature on adsorption of parathion by soils. *Soil Sci. Soc. Amer. Proc.* 36:583-586.

SECTION 3

PLANT UPTAKE OF ORGANIC POLLUTANTS

Chemicals in the soil enter plants through at least four main pathways.

1. Root uptake into conduction channels and subsequent translocation by the transpiration stream.

2. Uptake from vapour in the surrounding air.

3. Uptake by external contamination of shoots by soil and dust, followed by retention in the cuticle or penetration through it.

4. For oil containing plants, e.g. cress, carrot, and parsnip, uptake and transport in oil cells (Topp et al., 1986).

In nearly all cases, a combination of all of these pathways or events will reflect the total pollutant concentration in the plant.

THE PLANT TRANSPORT SYSTEM

In general, plant roots are the most important site of uptake of chemicals from the soil (Finlayson and MacCarthy, 1973). This is the logical point of chemical entry since the actual function of the roots is to give support to the plant and to absorb water and mineral salts. The most active site for such uptake is 20 to 40 mm above the root cap in the zone of the root hairs.

The transport or conduction of liquids within the plant is known as translocation. It may occur upwards or acropetally, downwards or basipetally, or laterally, within specialized transport vessels, the xylem and phloem.

The function of the young roots is to absorb water and solutes and the protective covering to these absorbing zones offers little resistence to water flow to the transport system, or apoplast, within the plant. The main absorbing regions are relatively restricted and may extend only a few centimeters from the root tip. The branching of most root systems, however, ensures a multiplicity of absorbing points. Older roots are suberised and thereby impervious to water.

In the absorbing zone, the surface area to volume ratio of the root may be greatly increased by the presence of many thousands of root hairs, which

grow out of the epidermal cells of the root. In a classical study of rye (*Secale cereale*), Dittmer (1937) showed that a single rye plant exposed 4300 ft^2 of surface to the soil and estimated the number of root hairs on a 4-month rye plant at 14 million.

Any chemical taken up by a plant root, or conversely taken in through the plant leaf, and transported throughout the plant passes along the path provided by the symplast and apoplast. The path provided by the symplast consists of the living plant tissue that is bounded by the plasmalemma and connected via plasmodesmata. It is a reactive environment that places chemicals in proximity to enzymes and other reactants. Movement within the conductive portion of the symplast or phloem occurs by mass flow and diffusion. It is a slow process, with rates of a few millimeters or, at best, a few centimeters per hour. It is responsible for movement of sugars, hormones, metabolic solutes, and in some instances pollutants, to the growing and storage tissues.

The apoplastic system includes all the dead portions of the plant. Cell walls and xylem form a water-permeable continuum through which both short- and long-distance solute transport occurs by diffusion and mass flow, respectively. The system often works under positive pressure or under tension created from the leaf's need for water, which can result in quite fast rates of water transport of up to 100 m/hr. All substances that enter the plant do so via the apoplast, which also protects the symplast from the destructive forces of desiccation, abrasion, and even pressure sufficient to cause its collapse.

Any pollutant entering the plant through the roots initially enters into the free space of the root tissue, followed by movement across the plasmalemma into the endodermis. Entrance into the stele, and the vascular tissues within, then occurs through the cellular membranes. Movement within the xylem is determined by diffusion, which is being controlled by the energy potential of the solute, and mass flow, which is controlled by the energy potential gradient of the continuous solvent system. Movement within the phloem depends on diffusion, membrane transport, and cytoplasmic streaming, and requires metabolic energy.

Some chemicals appear to be restricted to either transport in the apoplast or in the symplast, whereas others termed, ambimobile, move in both systems. Presently, chemicals can not be classified according to their mode of transport.

Although the most common pathway by which nutrients, other solutes, and pollutants enter the plant is through the roots, another possible route of entry of pollutants into plants is through the stomata of the leaves and stems in the form of gasses (Table 3.1). Little research has been done on this route of pollutant entry, partly because most systemic herbicides are not very volatile (Edgington and Peterson, 1977).

Two processes precede the penetration of chemicals in the soil into leaf tissue via the air; firstly, volatilization from the soil itself which is

dependent on the soil type (see section 4.1); secondly, deposition from the air onto the leaf surfaces. Uptake via vapour is, therefore, related to both the volatility of the pollutant itself and its deposition velocity from the air to the plant surface (Topp et al., 1986).

TABLE 3.1. PREVALENCE OF STOMATA ON THE SURFACES OF LEAVES OF SOME REPRESENTATIVE CROP PLANTS

Plant	Number per cm^2 Leaf Surface	
	Upper leaf	Lower leaf
Bean	40	281
Plum	0	253
Oat	25	23
Corn	94	158
Pea	101	216

The initial barrier to the penetration of volatilized chemicals into the leaves and other aerial parts of the plant is the cuticle and its associated structures. The cuticle, which is composed of four regions (the epicuticular wax, the cutin, the pectin, and the outer wall of the epidermal cell), can be described as a nonliving, noncellular membrane that covers all the outer aerial plant surfaces. Its main function is to control the loss of water from the leaves of the plant, a function achieved by wax platelets imbedded in the upper surfaces of the cutin matrix. The area available for water loss, and thus the area available for the entry of aqueous solutions depends on the spacing of the wax platelets in the leaf.

Plants can regulate this spacing; if the loss of water from the leaf surface exceeds the supply from the roots, the cutin will contract to bring the platelets closer together and reduce the area available for water exchange (Crafts, 1964).

Certain regions of the cuticle may act as sites of preferential entry for gaseous pollutants, i.e., stomata, trichomes, the cuticle over leaf veins, anteclinal walls, leaf bases, etc. The cuticle varies not only in thickness and chemical composition according to species, leaf maturity, and surface and position on the leaf, but also according to environmental conditions, e.g., temperature, relative humidity, and light. Vapour phase uptake of organic pollutants is, therefore, likely to vary considerably between species. The ecotoxicological importance of plant cuticles as a lipophilic sorption agent has recently been pointed out (Riederer and Schonherr, 1985). Cuticular material occurs in considerable amounts in both natural and agricultural plant communities (180 to 1500 kg/ha.).

The older parts of plants, particulary perennials, are normally covered with bark. This is a heavily suberized multicellular layer that provides an

impervious covering except where the surface is damaged or is penetrated by specialized structures like the lenticels. Although aqueous solutions can enter uninjured bark to a small extent, it seems unlikely that this form of entry is in any way significant when compared with root and shoot entry.

ROOT UPTAKE AND TRANSLOCATION OF POLLUTANTS

Uptake of most chemicals by plant roots from polluted soils is a passive process. At its simplest, then, movement of pollutants from soil to plant leaves can be regarded as a series of consecutive partitions between soil solids and soil water, root and soil water, and then the transpiration stream and the tissues of the plant root, plant stem and plant leaves. At any stage in this transport, the chemical can be bound within the plant or metabolized.

Uptake has been seen to occur in two phases: firstly, chemical partitioning onto the external root surfaces with rapid accumulation into the free space of the root, and secondly, the slower process of moving across the living cells of the cortex to reach the vascular system of the plant (Crowdy and Jones, 1956).

Factors affecting the translocation of the chemical from root to shoot, although being influenced by the water potential gradient created by the leaves, are poorly understood (Brown et al., 1983). The effect of many herbicides on plants is known, however, to depend on transpiration rate (Sheets, 1961).

Polar chemicals may pass through the lipid membranes in the root with difficulty, whereas the unhindered passage of water results in the selective rejection of these chemicals at the membrane barriers. Lipophilic chemicals, on the other hand, being reversibly sorbed by the root solid, might be expected to pass to the xylem unhindered once equilibrium is reached.

Plant roots are, additionally, not discriminating towards small organic molecules with a molecular weight of less than 500, except on the basis of polarity. If the molecule is nonpolar, it tends to adsorb to the roots' surfaces rather than pass through the epidermis. The more polar the molecule the more readily it will reach the root, pass through the epidermis, and be translocated.

Because the first stage of uptake into the root is a passive process, it can occur in both living and dead root tissue to equal degrees. Tames and Hance (1969) investigated the extent of root sorption of herbicides by freshly killed roots of a number of plant species. With atrazine, diuron, linuron, monolinuron, and GS14260, bean roots showed the greatest adsorptive capacity on both a dry and fresh weight basis. There was variation among the other tested plant species, including oat, pea, cucumber, and radish, with some species adsorping more of different types of herbicides than did others. There was no relationship between the adsorptive capacity of the roots and the susceptibility of the plants to the tested compounds.

This variation in compound uptake was shown earlier by Crafts (1964). He investigated the uptake and translocation of several labeled herbicides and, using autoradiographs, concluded that this probably resulted from some organic chemicals being bound within the roots and, therefore, not available for translocation.

Crowdy et al. (1956) reported that translocation of a chemical continued even after the plant had been removed from the chemical so that the root must be providing a reservoir of the chemical. No measurement of the new equilibrium between the root concentration and the outside solution concentration was made however, and this possibly was the cause of the recorded uptake.

Crowdy (1973) then demonstrated an inverse relationship between translocation of a number of grisofulvin derivatives to the shoots of broad beans and the partition coefficients of these compounds between hexane and water. Crowdy concluded that there may be an optimum lipid/water partition coefficient for maximum translocation, which is likely to vary between different compounds, species of plant, and pathways of entry into the plant.

Shone et al. (1973) undertook similar research into herbicide uptake and thus its effect. They investigated the absorption and translocation of the herbicide simazine by 6 day old barley plants, in either 24- or 48-hour experiments in water culture. To describe the relationship between simazine transport and water uptake, they calculated the Transpiration Stream Concentration Factor (TSCF), which was defined as

$$\text{TSCF} = \frac{\mu\text{g simazine in shoots per ml water transpired}}{\mu\text{g simazine per ml uptake solution}}$$

In these experiments, water was taken up preferentially to simazine, since the TSCF was always less than unity and there was no evidence of loss of, or breakdown of, the parent compound. The concentration of simazine in the plant roots, on a fresh weight basis, however rapidly reached a value greater than unity probably as a result of physical adsorption of the herbicide on the root tissue.

TSCF was assessed indirectly from the mass of chemical accumulated in the shoots for a known volume of water transpired. TSCF is, therefore, affected by those environmental conditions that directly affect translocation, e.g., temperature, light intensity, and humidity, and if required, could be increased or decreased by changing these environmental conditions.

For a nonpolar solute, which should not be affected by gradients of electrical potential, values of the TSCF greater than unity would imply a direct dependence of transport of the solute on metabolism.

In line with the definition of the TSCF, Shone and Wood (1974) proposed that the uptake of a chemical into roots can be described by its Root Concentration Factor. This is simply defined as

$$RCF = \frac{\text{concentration in root}}{\text{concentration in external solution}}$$

Briggs et al. (1983) proposed the Stem Concentration Factor (SCF) as

$$SCF = \frac{\text{concentration in stem}}{\text{concentration in external solution}}$$

Shone and Wood (1974) undertook a series of investigations using radiolabeled herbicides in solution culture with barley seedlings. They showed that the quantity of the herbicide transported to the shoots could not be inferred from the extent to which it is bound in the roots (Table 3.2). In addition, although the RCF of some of the tested herbicides exceeded 1, actual uptake was not affected by temperature, this suggests that the root retained the compounds by physical sorption. Translocation from the roots to the shoots did not then take place until the root was saturated by the compound.

TABLE 3.2. TYPICAL VALUES FOR TSCF* AND RCF† FOR BARLEY FROM A SERIES OF HERBICIDES (Abbreviated from Shone and Wood, 1974)

Herbicide	TSCF	RCF
2,4-D at pH 4	3.12	88.4
Simazine	0.90	4.5
Diuron	0.81	3.1
Atratone	0.78	1.3
Atrazine	0.75	1.9
Hydroxyatrazine	0.26	2.2
2,4-D at pH 6.5	0.14	8.1
Ethirimol	0.09	0.7

*Transpiration stream concentration factor.
†Root concentration factor.
Herbicides in solution culture at pH 5 to 6.5 unless otherwise stated. For atratone, atrazine and hydroxyatrazine, the uptake solution contained 1 ppm. For the remainder, the solution concentration was 0.2 ppm.

This also worked in reverse. Shone et al. (1974) transferred the barley seedlings from solution culture containing the herbicides under test to unpolluted cultures and found that RCF was decreased before TSCF was affected by the change (Table 3.3). This suggests that the lipophilic herbicides, which

appear to penetrate the cortical cells of the root, tend to reach the shoots more readily than do the lipophobic herbicides, which may be largely confined to the free space in the roots. With the exception of 2,4-D, the uptake and translocation of all the tested herbicides was passive and was compatible with passive movement in the transpiration stream. Uptake of 2,4-D at pH 4 appeared related to the metabolic activity of the plant.

TABLE 3.3. LABELED HERBICIDES IN ROOTS AND SHOOTS OF BARLEY SEEDLINGS (Adapted from Shone et al., 1974)

	After 24 hrs in 0.2 ppm labeled herbicide solution		After a further 24 hrs in clean solution	
Herbicide	Shoots	Roots	Shoots	Roots
Simazine	0.23	0.08	0.22	0.03
Diuron	0.25	0.08	0.25	0.01
2,4-D at pH4	1.49	1.92	1.35	1.10
Ethirimol	0.07	0.02	0.09	0.01

Concentrations are given as μg herbicide in shoots and roots.

Hawxby and Basler (1976) reported that the more water soluble herbicide dinitramine was translocated within the plant to a greater extent than the less soluble profluralin. This is expected on the basis of the relationship between water solubility and the *n*-octanol/water partition coefficient. Uchida et al. (1982) found that the mobility of different classes of pesticides in rice plants also correlated well with water solubility and *n*-octanol/water coefficients.

These attempts at relating root uptake to some physicochemical parameter of the test compound continued with Briggs et al. (1982) working with barley roots. Root accumulation of different herbicides was directly related to *n*-octanol/water coefficient of the tested compound whereas transpiration stream concentrations showed a bell shaped dependence on K_{ow} with a broad maximum around 1.8 (Table 3.4). The general explanation of this is probably that at K_{ow} values below optimum, translocation is limited by root concentration; at K_{ow} levels higher than optimum, translocation is limited by the rate of release of the chemical into the transpiration stream.

All the TSCF in this experiment were below unity; this indicated that the tested chemicals moved passively into the shoot with the transpiration water and were not taken up against a concentration gradient. There appeared an optimum lipophilicity for maximum uptake to shoots by translocation centered on a log K_{ow} of around 1.8.

TABLE 3.4. THE RELATIONSHIP BETWEEN THE *n*-OCTANOL/WATER PARTITION COEFFICIENT (K_{ow}) AND RCF* AND TSCF† FOR THE UPTAKE OF *o*-METHYLCARBAMOLYOXIMES AND SUBSTITUTED PHENYLUREAS BY BARLEY FROM NUTRIENT SOLUTION (Adapted from Briggs et al., 1982)

Chemical	Log K_{ow}	RCF	TSCF
o-Methylcarbamoyloximes			
	-0.57	0.66	0.19
	-0.47	0.91	0.21
	-0.13	0.95	0.28
	1.08	0.94	0.54
	1.49	1.48	0.67
	2.27	2.8	0.94
	2.89	5.61	0.51
	3.12	8.72	0.26
	4.6	81.1	0.06
Substituted phenylureas	Log K_{ow}	RCF	TSCF
	-0.12	0.73	0.05
	0.80	1.20	0.47
	1.04	1.10	0.47
	1.57	0.94	0.22
	1.80	2.00	0.50
	1.98	3.17	0.55
	2.64	5.86	0.37
	2.80	7.08	0.47
	3.7	34.9	0.11

*Root concentration factor
†Transpiration stream concentration factor

If the *n*-octanol/water partition coefficient and the RCF are logarithmically regressed against each other, then equations similar to those describing pollutant sorption in soils are obtained for the methylcarbamoyloximes:

$$\log RCF = 0.559 \log K_{ow} - 0.833$$

with a correlation coefficient of 0.96.

For the substituted phenylureas

$$\log RCF = 0.589 \log K_{ow} - 0.812$$

with a correlation coefficient of 0.85.

If the data sets are combined, then

$$\log RCF = 0.57 \log K_{ow} - 0.814$$

with a correlation coefficient of 0.917.

Briggs et al. (1982) report

- $\log RCF \text{ (macerated roots)} = 0.77 \log K_{ow} - 1.52$

for the best fit from seven chemicals, which were sorbed to a measurable extent, with a correlation coefficient of 0.981. They continued by assuming that RCF can be explained by a partitioning to lipophilic root solids and some compound being translocated, the amount of which was taken to be constant for all compounds tested. This gave

$$\log (RCF - 0.82) = 0.77 \log K_{ow} - 1.52$$

where the mechanism of the small uptake, contributing 0.82 to the RCF value, arises from the equilibrium of the chemical between the external solution and the water contained in the roots, both within the free space and within the cells. If such an equilibrium were complete, a contribution of about 0.9 to the RCF value would be expected for roots containing 90% water by weight. The measured value of 0.82, therefore, suggests that the equilibrium was nearly complete.

Unfortunately, few other attempts have been made to relate plant uptake to either physical or chemical properties of the pollutant. Topp et al. (1986) also related log RCF to log K_{ow} following the exposure of barley seedlings for 7 days to various pollutants with a log K_{ow} range from 2 to 6. Their equation

$$\log RCF = 0.63 \log K_{ow} - 0.959$$

with a regression coefficient of 0.896, is very similar to that of Briggs et al. (1982) above.

Much of this early work, primarily designed to improve the performance of herbicides, has not been repeated with those organic chemicals that currently exist as pollutants. This is urgently needed so that the environmental behaviour of new organic chemicals, or those currently existing as pollutants, can be determined without the need for complex and time consuming investigations.

The above discussion is concerned with uptake from nutrient solution. Walker (1972) highlighted the problems of measuring plant uptake of chemicals from the soil. He found that the concentrations of the herbicide atrazine in the shoots of wheat plants growing in 12 different soils were directly

proportional to the soil solution concentration of the herbicide estimated from slurry adsorption measurements. A large discrepancy existed between the total uptake of herbicide and the amount theoretically supplied by mass flow in reponse to transpiration, since only the nonadsorbed portion of the pollutant dissolved in the soil water was available to the plants. In an experiment where only one soil was used, and the half life of the chemical was taken into account, Walker could make a much closer prediction of atrazine uptake.

The potential for uptake of a chemical from the soil solution is then the same as that from a nutrient or hydroponic solution. Moyer et al. (1972) started out with the premise that a plant's herbicide uptake was related to the volume of water transpired (as shown by Sheets, 1961, and Shone and Wood, 1972) and, in turn, showed this reponse with the herbicide diuron.

Uptake from the soil is, therefore, related to the pollutant concentration in the soil solution and not to the concentration in the soil, per se. Since, for nonionic compounds, adsorption is largely on the organic matter in soil, the uptake of chemicals into plant roots should be dependant also on the organic matter content of the soil.

Modelling

If the above is taken at face value, to cover the behaviour of all nonionic organic pollutants, then the behaviour of a pollutant in the soil can be related to its behaviour in the plant.

For a given compound, the organic matter/water distribution (see Section 2.1) which is relatively constant from soil to soil, is related to the *n*-octanol/water distribution by;

$$\log K_{om} = 0.52 \log K_{ow} + 0.62$$

As $\log K_{ow}$ increases, adsorption increases and, hence, soil solution concentration decreases for a given concentration of pollutant (Briggs et al. 1976). For a soil with a given organic matter and water content, the fraction of the pollutant in the soil solution can be calculated from its $\log K_{ow}$. The product of this fraction and the TSCF appropriate to the value of $\log K_{ow}$ gives the relative ease of translocation from soil. This is shown in Table 3.5 for a soil with 2% organic matter and 15% water content.

The optimum for uptake from soil is given by compounds with a $\log K_{ow}$ around 0.5, which is lower than the optimum $\log K_{ow}$ value of 1.7 for uptake from solution (Briggs et al., 1976).

TABLE 3.5. A COMPARISON OF THE POTENTIAL FOR ROOT AND SHOOT UPTAKE OF DIFFERENT POLLUTANTS FROM THE SOIL SOLUTION OF A SOIL OF 2% ORGANIC MATTER AND 15% WATER CONTENT AS MEASURED BY THE TSCF* AND THE RCF†
(From Briggs et al., 1976).

log K_{ow}	TSCF	RCF
0	0.65	1.0
1	0.95	2.6
2	1.00	5.7
3	0.70	13.8
4	0.05	33.0
5	0.01	79.0
6	<0.01	190.0

*Transpiration stream concentration factor
†Root concentration factor

If the calculations are continued, the effects of increasing log K_{ow} can be determined, i.e., the effects of increasing lipophilicity upon the net root or shoot uptake from a particular soil. This is shown in Tables 3.6 and 3.7.

TABLE 3.6. THE EFFECT OF LIPOPHILICITY ON RCF* AND NET ROOT UPTAKE FOR A SOIL†
(Calculated from Briggs et al., 1976.)

log K_{ow}	RCF	% chemical in water	net uptake
			(RCF x % in water)
0	1	65	65
1	2.6	35	84
2	5.7	14	80
3	13.8	5	70
4	33.1	1	33
5	79.4	0.25	20
6	190	0.10	19
7	457	0.04	18

*Root concentration factor.
†Soil containing 2% organic matter with a 15% water content.

TABLE 3.7. THE EFFECT OF LIPOPHILICITY ON TSCF* AND NET UPTAKE FOR A SOIL† (From Briggs et al., 1976.)

log K_{ow}	TSCF	% chemical in water	net uptake (TSCF x % in water)
-0.5	0.2	80	16
0	0.65	65	42
0.5	0.85	50	43
1	0.95	35	33
2	1.0	14	14
3	0.7	5	3.5
4	0.05	1	0.05
5	ca 0.01	0.25	0.0025
6	<0.01	0.1	<0.001

*Transpiration stream concentration factor.
†Soil containing 2% organic matter with a 15% water content.

Achieving these values would take time because they are the end points of various equilibria. For example, there is an equilibrium between the pollutant concentration adsorped on the soil organic matter and that in the soil solution. The pollutant concentration of the soil solution is, in turn, in equilibrium with that within the plant. These equilibria will move toward the plant as the pollutant is translocated away from the root and soil and into the shoot.

Topp et al. (1986) reported that, under environmental conditions, an equilibrium of chemical concentration between soils and plants is reached only very slowly or not at all. Figure 3.1 shows the time course of the uptake by barley of two chlorinated benzenes from soil in outdoor boxes under field conditions.

Figure 3.1 illustrates that the two chemicals reach an equilibrium, i.e., a constant concentration factor, only after 100 days or more, at the time of harvest when growth stops and the plants become dry. In the earlier growth stages, concentration factors decrease due to dilution by the increase in plant mass and through the loss of the chemical to transpiration exceeding continuing uptake from the soil.

PLANT UPTAKE BY VAPOUR

For some of the more volatile herbicides and pollutants, diffusion in the vapour phase and subsequent uptake by the shoot, both before and after emer-

gence, may be an important route of chemical entry to the plant (Parker 1966; Prendeville 1968). Barrows et al. (1969), for example, said that aerial contamination explained the differences found in their experiments with dieldrin uptake by corn grown in either the field or the greenhouse.

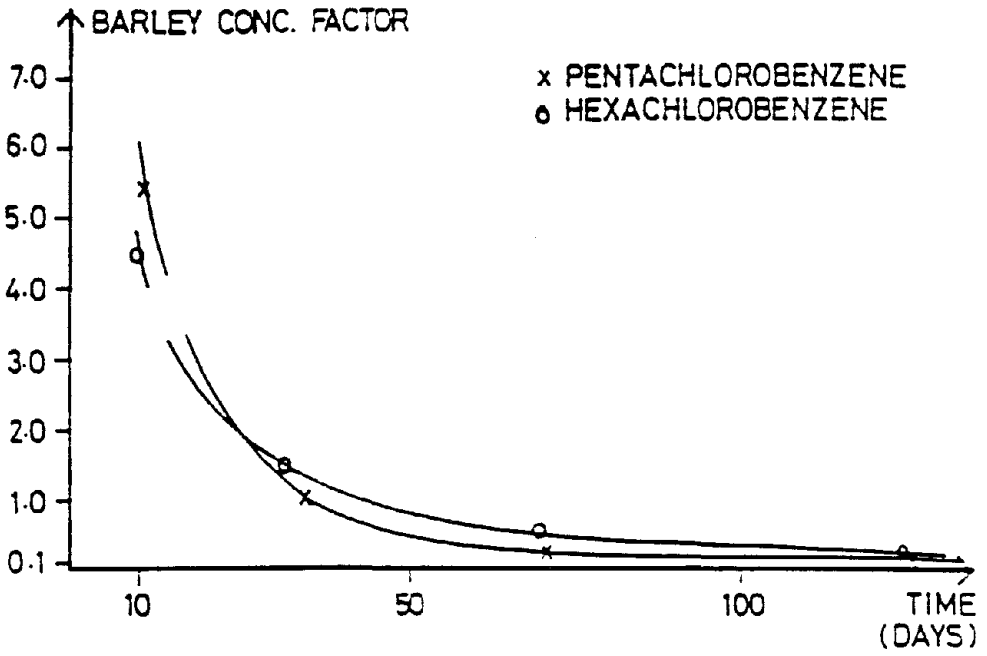

Figure 3.1. The time course of uptake of two chlorinated benzenes by barley. (From Topp et al., 1986.)

Beall and Nash (1971) developed a method to discriminate between a pesticide's movement through the plant vascular system and a vapour phase movement. They found soybean shoots were contaminated by soil-applied dieldrin, endrin, and heptachlor largely via root uptake and subsequent translocation. Vapour phase movement, however, dominated for DDT and was nearly seven times greater than for root sorption. Foliar contamination from vapour sorption of residues from all four insecticides was of the same order of magnitude, about 6.5 ppm plant dry weight, whereas contamination from root sorption varied from 38 ppm to 1 ppm, depending upon the insecticide.

Using a similar method Fries and Marrow (1981) found that PCBs reached the shoots of plants via the vapour phase rather than from root uptake and translocation.

In a laboratory greenhouse study investigating the uptake of 16 organic chemicals into barley, Topp et al. (1986) found that foliar uptake of the volatilized chemical from the air far exceeded translocation of the substance taken up by the roots to the shoots. The relationship between barley foliar uptake and volatilization from soil after 7 days exposure was

$$FU = 46.11 - 28.95 \log VOL$$

where FU was foliar uptake in percent of total ^{14}C-uptake, and VOL was the organic ^{14}C trapped from the air plus that sublimated on the exposure chamber walls in percent of ^{14}C originally applied. The correlation coefficient for this relationship was 0.988 (Figure 3.2). Eleven of the tested chemicals fitted the curve; four did not. These latter chemicals were substances whose ^{14}C was taken up preferably after mineralization to $^{14}CO_2$.

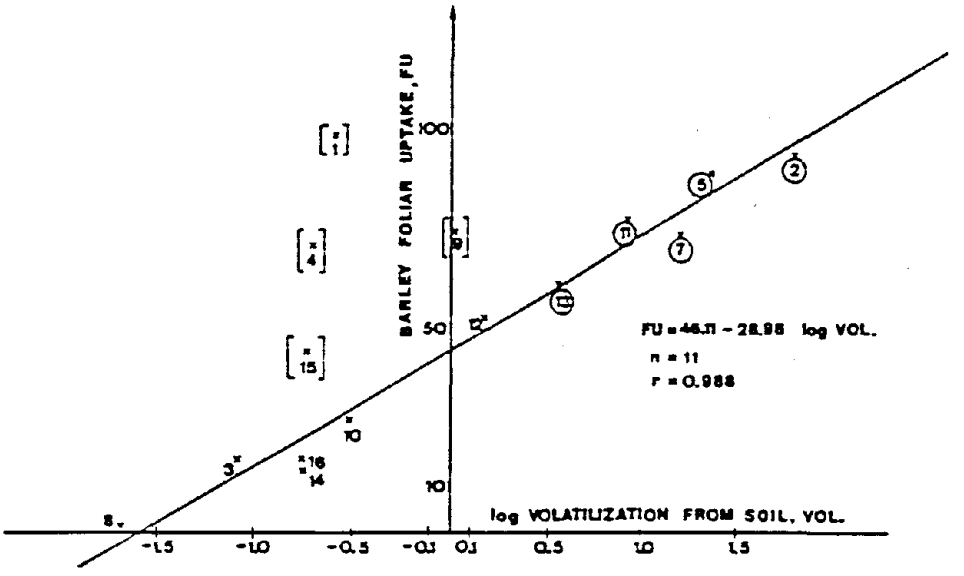

Figure 3.2. Correlation of barley foliar uptake after 1 week exposure with volatilization from soil. (From Topp et al., 1986).

Shone and Wood (1976) investigated the reverse, that is, the potential for triazine herbicides to be lost from the leaf surface by volatilization. They applied labeled simazine, atrazine, and atraton to the hypocotyls of radish plants. After 24 hours, a negligible quantity had been translocated to the roots and over 95% of all three compounds could be recovered from within the plant. A similar experiment, under the same conditions and using the same concentration of atrazine, showed that over 85% applied to a glass rod was lost, presumably by volatilization.

If vapour phase uptake of volatilized chemicals is related to cutin and wax composition and to cuticle thickness, then vapour phase uptake will be species dependent as these factors are variable among different species. Such differences in the foliar absorption characteristics of different species have been reported. Riederer and Schonherr (1985) investigated the diffusion of 2,4-D across plant cuticles from 10 species and found it to vary. Leece (1976) related the foliar absorption of chemicals by peach, apple, and orange to cuticle thickness, weight, surface wax, and embedded wax content, and to surface wax wettability, ultrastructure, and composition (Table 3.8).

Peach surface waxes were more difficult to wet than were orange waxes, and although more polar than orange waxes, they may be more resistant to water penetration because they are rich in hydrocarbons and triterpenoids.

TABLE 3.8. THICKNESS, WEIGHT AND WAX CONTENT OF CUTICLES ISOLATED FROM PEACH, APPLE, AND ORANGE LEAVES*. (Adapted from Leece, 1976.)

Cuticle	Peach	Apple	Orange
Thickness, μm			
adaxial	1.6	2.1	4.1
abaxial	2.0	2.9	3.9
Weight, μg/cm^2			
adaxial	238	347	448
abaxial	270	560	430
Surface wax, μg/cm^2			
adaxial	35	31	18
abaxial	71	47	12
Embedded wax, μg/cm^2			
adaxial	70	65	43
abaxial	50	68	48

*Peach leaf area was 61 cm^2; apple, 40 cm^2; orange 29 cm^2

Topp et al. (1986) reported results showing that qualitative composition is probably more important than thickness for cuticle penetration, cutin, and wax. Surface wax concentration correlated well with resistance to foliar absorption.

In general, any modification of the molecular structure that results in increased lipid solubility will tend to enhance cuticular or membrane penetration; however, this is not always the case. Normally, the nonpolar derivatives of a variety of chemicals penetrate the cuticle or other membranes more readily than do polar ones.

WHOLE PLANT UPTAKE

Any plant part exposed to an organic pollutant has the potential of sorbing and or translocating that pollutant to other parts of the plant. This is also the case with the seed of the plant. Much work has been done on both the uptake of chemicals from the soil by the seed coat and the transfer of the chemical from the parent plant to the seed to ultimately affect the development of the offspring (Edgington and Peterson, 1977).

However, many chemicals apparently are significantly phytotoxic when applied to the seed; the concentration is too high for the germinating seedling. Thus, it is very difficult, if not impossible, for the seed to accumulate enough pollutant to make any significant difference to the total

soil loading. Any chemical that is sorbed by the seed will, in turn, be diluted by the plant mass as the plant grows.

As both root and foliar uptake of pollutants actually implies membrane penetration by the pollutant, a process related to molecule size, it should also be possible to relate uptake to pollutant molecule size. Topp et al. (1986) reported

$$\log CF = 5.943 - 2.385 \log M$$

with a correlation coefficient of 0.949, and where CF is the whole plant Concentration Factor from barley seedlings being exposed to the pollutants for 7 days, and M is the molecular weight of the pollutant. This relationship (Figure 3.3), applied to volatile as well as nonvolatile compounds including extremely complex pigments, was good enough for the authors to conclude that molecular weight is probably more suitable for predicting plant uptake than is log K_{ow}. This relationship was, however, based on compounds with a relatively narrow range of molecular weights, from 400 to 800; further investigation with a wider range of chemicals is needed.

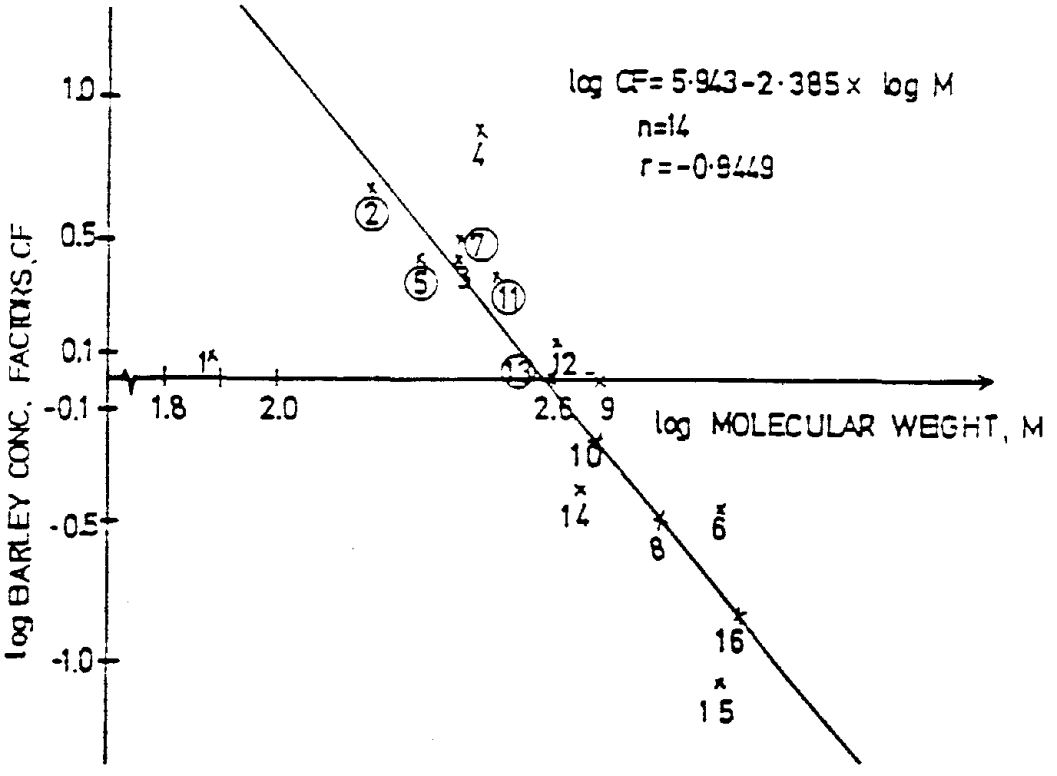

Figure 3.3. Correlation of barley concentration factors (based on soil concentration) with molecular weights after 1 week exposure. (From Topp et al., 1986.)

BEHAVIOUR OF POLLUTANTS IN PLANTS

Partitioning

Pollutants or pollutant residues absorbed and translocated in plant tissues may be present in three possible forms: freely extractable residues, extractable conjugates bound to natural components of plants, and unextractable or bound residues incorporated into the plant constituents. The latter may be considered analogous to the bound residues in soil (Khan 1982) and could be the cause of many underestimates of herbicide uptake by plants when inefficient extraction procedures were used (Lichtenstein, 1980; Wheeler et al., 1969).

Haque et al. (1978), for example, planted rice seedlings into soil containing radioactive pentachlorophenol and found that after 1 week, the plants had absorbed about 3% of the applied radioactivity, of which half was bound within the plant and could not be removed by normal extraction procedures. In fact, when these plants were fed to mammals the residues were excreted nearly quantitatively, which suggests that the residues were also unavailable to the mammals.

Klein and Scheunert (1982) concluded that plant growth conditions are an important factor affecting the formation rate of bound pesticide residues in plants. Optimum growth conditions which gave high growth yields, resulted in high levels of bound residues; conversely, poor growth conditions resulted in low levels of bound residues. Most of these bound residues were located and localized in the lignin.

Examples of the extent of bound residues are shown in Table 3.9.

TABLE 3.9. PESTICIDE RESIDUES BOUND IN PLANTS, IN PERCENT OF TOTAL RESIDUES IN THE PLANT. (Adapted from Klein and Scheunert, 1982.)

Chemical class	Time of exposure	% Residue bound
Free phenols	1 vegetation period	29 - 38
Anilines	1 vegetation period	87 - 90
Triazines	20 - 100 days	20 - 63
Urea herbicides	48 - 105 days	46 - 72
Cyclodiene	1 vegetation period	1 - 2

Once uptake of a chemical is under way it can occur at quite a rapid rate. Sheets (1961), for example, reported that because of root uptake and translocation, the herbicide simazine was found throughout seedling oat plants only 3 hours after being placed within a simazine-amended nutrient solution. Actual accumulation of the herbicide in the leaf tips of the plants began within 48 hours of exposure and depended on the translocation rate of the plants.

Briggs et al. (1983) proposed the concept of the Stem Concentration Factor as

$$SCF = \frac{\text{concentration in stem}}{\text{concentration in external solution}}$$

to assist in explaining their results following uptake, over 96 hours, of four nonionized chemicals in nutrient solution into barley shoots. The four chemicals were selected to span a wide range of lipophilicity. They found that, with the exception of the most lipophilic chemical studied, the amount of chemical in the basal and central stem section remained constant after 24 to 48 hours, whereas the chemical concentration in the top portion of the shoots continued to increase for all compounds up to 72 to 96 hours (Figure 3.4).

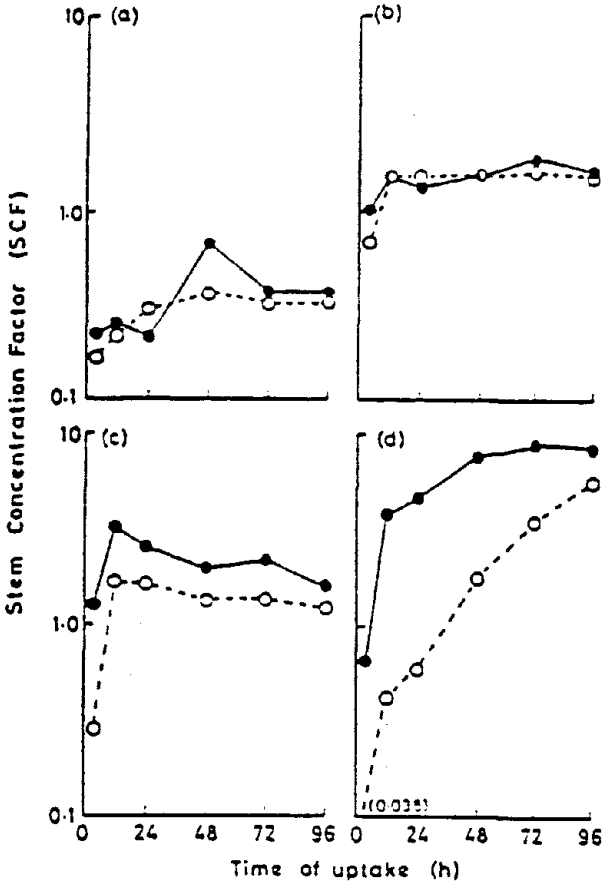

Figure 3.4. Time course for Stem Concentration Factor. The compounds were (a) oxamyl, (b) 4-chlorobenzaldehyde-*o*-methylcarbamoyloxime, (c) 3-phenoxybenzalde-*o*-methylcarbamoyloxime, and (d) 4-(4-bromophenoxy) phenylurea; ● = stem bases, o = centre of stems. (From Briggs et al., 1983.)

When the plants grown in chemical-amended nutrient solution for 48 hours were transferred to an unamended solution, the amount of chemical in the stem base declined after a further 24 hours. This decline appeared to be

positively related to lipophilicity, i.e., the more lipophilic chemical took longest to start to decline.

These results suggest that the barley stem is acting as "a rather inefficient chromatography column," with the concentration of the chemical in the lower portions of the stem being determined by a reversible partition between the xylem sap and the adjacent stem. Although small amounts of chemical reach the tops of the leaves before the stem chemical concentration reaches a constant maximum, it is only after the partition requirements of the stem are filled that the chemical being translocated from the roots really begins reaching the tops of the leaves and accumulating there as water is transpired. Although water is also transpired by the leaf sheaths, the translocated chemical does not appear to accumulate there, probably because the chemical equilibrium between stem and xylem sap is rapid.

In a further experiment Briggs et al. (1983) related the SCF of macerated stem material to the *n*-octanol/water partition coefficients of 15 chemicals by

$$\log SCF \text{ (macerated stems)} = 0.95 \log K_{ow} - 2.05$$

with a regression coefficient of 0.98. This equation is similar to that discussed earlier within this report for absorption by macerated roots.

For the more lipophilic chemicals, absorption by the stem solids increases rapidly with increasing lipophilicity. The time taken for the whole of the stem to equilibrate with the concentration of the chemical entering in the transpiration stream is also positively related to increasing lipophilicity. Although the TSCF determines the chemical concentration in the transpiration stream it does not affect the time taken to reach equilibrium as this is independent of concentration. If SCF is plotted against log K_{ow} (Figure 3.5), a maximum of 6 for the SCF is reached at a log K_{ow} of around 4.5. This arises as the increasing absorption potential for the more lipophilic chemicals is balanced out against their decreasing potential to be translocated.

Very few studies have been carried out to determine whether a pollutant within a plant is adsorbed onto the cell surface or is collected internally within the cell. Ware et al. (1968) found high concentrations of DDT and its related degradation products in alfalfa roots grown in the field. On further inspection, they found that the thin epidermal layer of the root contained nearly five times the level found in the whole roots and approximately six times that found in the cortex. This suggests that the DDT or its degradation products, or both, reach the root surface and either become bound to the epidermis and thus cannot be moved inward, or that the root structure is such that it actually filters or screens out the pollutant.

Similar results were found by Saha and Stewart (1967) who reported that the peel of rutabaga contained 98% of the total plant residue resulting from soil-applied heptachlor. In addition, Smith et al. (1967) showed that Dursban is not absorbed into the root but accumulates on the root surface.

Beestman et al. (1969) investigated the translocation and sites of accumulated radiolabeled dieldrin in corn. They found the stalks below the fifth node were the primary site of dieldrin localization and contained 70% to 90% of the total dieldrin. Accumulation was in the order: lower stalk > lower leaves > upper stalk > upper leaves > ears.

When ^{14}C-dieldrin was translocated up from the roots into the shoots, it was found to be located in the apoplast tissues (i.e., mechanical tissue cells or on their cell walls) and in the xylem tissue. None of the soil-applied carbon labeled dieldrin was found in the phloem vessels or symplast. In addition, the dieldrin concentrations increased as the edge of the leaf was approached (Cotner et al., 1968).

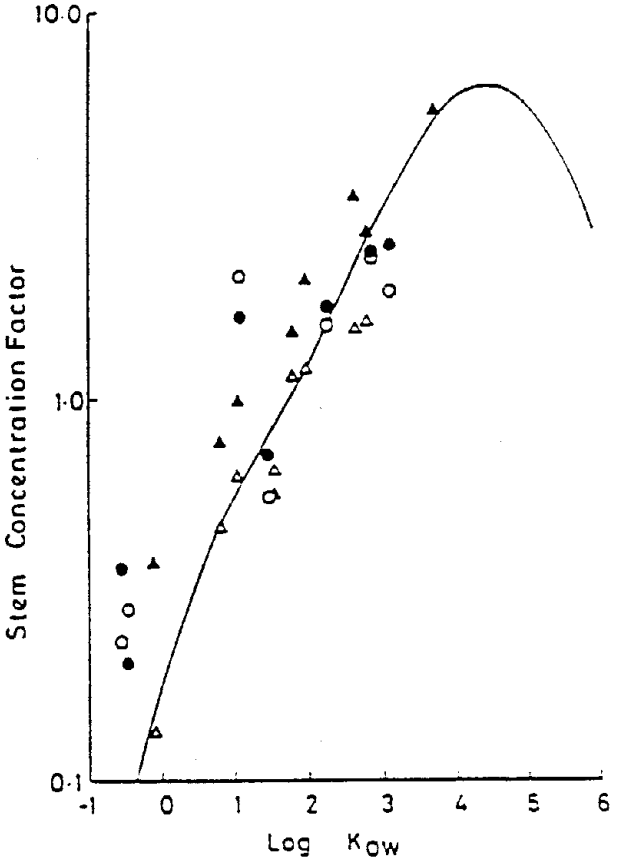

Figure 3.5. The relationship between the Stem Concentration Factor of chemicals in barley and their *n*-octanol/water partition coefficients (as log K_{ow}). Values are the mean of 24 and 48 hour measurements. (From Briggs et al., 1983.)

O'Donovan and Vanden Born (1981) used a microautoradiographic technique to determine the distribution of ^{14}C-labeled picloram in soybean tissue following root uptake. Little radioactivity was retained in the roots and this appeared to be mainly associated with the protoplasm of the root cortical

cells. In the stem, radioactivity was primarily present in both the xylem and phloem.

Considerably more radioactivity was found in the young apical leaves, both in the xylem and phloem, than in the older primary leaves, where radioactivity was present only in the xylem.

McFarlane (1986, personal communication) investigated the distribution of four ^{14}C ring-labeled test chemicals in soybeans grown under amended hydroponic conditions for 3 days. Bromacil was originally distributed in the plant roots and then, with time, moved into the stems and leaves. Its concentration in the leaves and roots then remained approximately equal and was probably in equilibrium. A similar early pattern was found for diclobenil, but with time the chemical concentration in the root decreased whereas that in the leaves increased. This indicates movement of the chemical from the roots for deposition in the leaves. Nitrobenzene and dinitrobenzene, the other two chemicals, remained primarily associated with the plant roots and, possibly because of the short time period available for translocation, were not moved upwards to any significant extent (Figure 3.6).

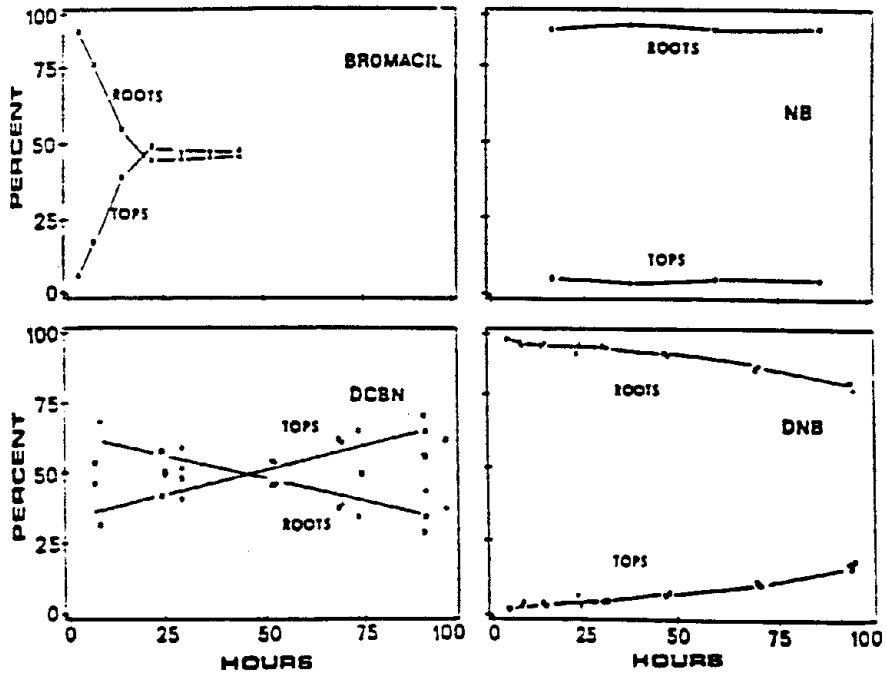

Figure 3.6. Chemical distribution patterns within whole soybean plants, shown as a percent of total chemical in the plants with time. The compounds were bromacil, DCBN - dichlorobenzonitrile, DNB - dinitrobenzene, and NB - nitrobenzene. (From McFarlane, 1986, personal communication.)

Degradation

Because knowledge of the metabolism of herbicides within plants has been of great importance in ensuring the efficiency of herbicides (Geissbuhler et al., 1963), much basic research has been undertaken to investigate this. Unfortunately because there has been little impetus for research into pollutant metabolism by plants, there is a corresponding lack of information.

Research into herbicide metabolism goes back many years. Nash (1968), for example, reported diuron was metabolized within a plant to its monomethyl derivative 3-(3,4-dichlorophenyl)-1-methylurea. Hamilton and Moreland (1961) reported that simazine is converted to a detoxified hydroxysimazine in vivo by corn plants and in vitro by corn extracts. Ware et al. (1968) reported DDT metabolism to DDE by plant tissue, and Smith et al. (1967) showed that 3,5,6-trichloro-2-pyridinol undergoes metabolism in cranberry plants with the liberation of chlorine and the formation of several decomposition products.

Freed and Montgomery (1963) and Crafts (1964) have reviewed the metabolism of herbicides in plants under sections of the major herbicide types, phenoxy acids, the carbamates, and symmetrical triazines.

1. The phenoxy acids are some of the earliest commercial herbicides and have a wide range of weed control in grains and grasses. There is much evidence that the 2,4-D molecule, the most common member of this group, can be metabolized in plants, and in many cases, the evolution of $^{14}CO_2$ has been shown after treatment of plants with radiolabeled 2,4-D. Differences in response to 2,4-D in red and black currants and varieties of apples and strawberries were strongly correlated with differences in the abilities of the plants to oxidize the carboxyl and methylene carbons from the side chain of the molecule. Red currant which is tolerant of 2,4-D, oxidized up to 50% of the carboxyl carbon and 20% of the ethylene carbon of the 2,4-D, whereas the nontolerant black currant only oxidized 2%, under the same conditions. The tolerant apple variety, Cox, could decarboxylate 57% of the applied 2,4-D in 92 hours, whereas the sensitive Bramley Seedlings metabolized only 2%. Similar studies have shown that bean stems, peas, and cucumber species are able to metabolize 2,4-D probably along metabolic lines similar to those of bacteria, which partially degrade the benzene ring without cleaving the phenol ether linkage. Plant roots are generally more efficient in the decarboxylation of phenoxyacetic acids than are shoots.

2. The carbamates, recognised as mitotic poisons, inhibiting the Hill reaction of photosynthesis, have their lethal action in root meristems. The herbicide EPTC was rapidly taken up by resistant plants and metabolized so that an applied radiolabel was incorporated into various plant constituents, e.g., cystine.

3. Symmetrical triazines, simazine and atrazine being the most popular, have a wide spectrum of selective biological activity. Again, there appears to be a metabolic difference between resistant and susceptible plant species, with the resistant species having a metabolic pathway that effectively detoxifies the herbicide. This pathway may result from the presence of a

cyclic hydroxamate that reacts with the triazine in the sap of resistant plants. Montgomery and Freed (1961) reported that appreciable amounts of $^{14}CO_2$ were given off by intact corn plants after being exposed to the radiolabeled herbicide. In addition, the corn was able to rupture the benzene ring, where the label had been applied, to completely oxidize the fragments.

In summary, both groups of workers concluded that metabolism of most of the major groups of herbicides occurs within plants following their uptake and that such metabolism may play a major part in the biological activity of such compounds.

Finlayson and MacCarthy (1973) have compiled the metabolic and other degradation products of pesticide residues in plants and soils (Table 3.10). Eastin and Basler (1977) reviewed the techniques available for assessing the absorption and translocation of pesticides.

The potential of different plant species to degrade herbicides seems to be related to their tolerance or susceptibility to the herbicide, with tolerant species generally having some form of metabolic protection (Mottley and Kirkwood, 1978).

Shimabukuro (1968) compared the metabolism of the herbicide atrazine in the two resistant species, corn (*Zea mays*) and sorghum (*Sorghum vulgare*), and found even different metabolic pathways. In corn, atrazine was metabolized via both the 2-hydroxylation and N-dealkylation pathways; in sorghum, only the latter pathway was used. Considerably more research is needed in these areas of breakdown and associated plant protection through genetic tolerance to the herbicide.

Plants also use a variety of reactions to reduce more complex aromatic structures to simpler units. Typical steps include demethylation, β oxidation, and decarboxylation, (Ellis 1974). Plants are known to accumulate large quantities of aromatic compounds, principally phenolics, ranging in structure from simple phenols to polymers such as lignins; some are known to be ring cleavage substrates in microbial metabolism. Ellis and Towers (1970), using sterile cultures, showed that *Ruta graveoleus* and *Melilotus alba* were able to cleave the aromatic ring of both phenylpropanoid and indole compounds but this cellular reaction may not be typical of that occurring in the intact plant (Berlin et al., 1971).

Many disagree on the role of polyaromatic hydrocarbons in plants. As early as 1966, Graf and Diehl published results showing the existence of several polyaromatic hydrocarbons in various plants. They suggested that these compounds were naturally synthesized in the plants and may even act as growth hormones. Wagner and Siddiqi (1970, 1971), however, do not believe that plants can form benzo(*a*)pyrene or benzo(*b*)fluoranthene. They did not find any aromatic compounds in lettuce, rye, soybean, or tobacco grown in carefully filtered air, but did find these compounds in plants grown in the field. They suggested, therefore, that these chemicals were taken from the air.

TABLE 3.10. METABOLIC AND OTHER DEGRADATION PRODUCTS FROM PESTICIDE RESIDUES IN PLANTS AND SOILS. (From Finlayson and MacCarthy, 1973.)

Pesticide	Substrate Plants	Soil	Products
Aldicarb	+	+	sulfoxide, sulphone, oxime
Aldrin	+	+	dieldrin
Amitrole	+	+	several
Captan	+	?	thiophosgene
Carbaryl	+	+	a-naphthol
Carbofuran	+	?	3-hydroxy, 3-keto, others
DDT	+	+	DDE and others
Disulfoton	+	?	sulphoxide, sulphone
Endosulfan	+	?	sulfate, others
Fensulfothion	+	+	sulfone, oxygen analog
Heptachlor	+	+	epoxide
Hexachlorocyclohexane	+	+	pentachlorocyclohexane
Linuron	+	?	3,4-dichloroaniline
Pentachloronitrobenzene	+	+	pentachloroaniline
Phenoxyacetic compounds	+	?	several
Phorate	+	+	sulfoxide, sulfone
Trifuralin	+	+	several
Vegadex	+	+	lactic acid
Zectran	+	?	several

Avocado fruit has also been shown to metabolize the relatively inert hydrocarbons benzene and toluene, both of which occur naturally within the fruit. Toluene is metabolized to a greater extent than benzene by fruit exposed to hydrocarbon vapour, but both were metabolized, to a small but significant extent, to CO_2 (Jansen and Olsen, 1969). Durmishidze and Ugrekhelidze (1969), quoted in Sims (1982), demonstrated the cleavage of the carbon atoms in the benzene ring into organic and amino acids. The first stable products of benzene metabolism in tea plants were organic acids, which accumulated in the plant part where the benzene was introduced (roots and stems). A pathway for benzene metabolism in plants was proposed as

benzene-->phenol-->pyrocatechol-->*o*-benzoquinone-->muconic acid.

Durmishidze et al. (1973), also quoted in Sims (1982), studied the assimilation and conversion of 3,4-benzpyrene-1,2-^{14}C with 14 day old, sterile corn and bean seedlings in a sterile nutrient solution. When the radiolabeled compound was introduced into the leaves or roots of the plants, approximately 50% of the label was assimilated into organic acids, which were concentrated at the site of assimilation. In a follow-up experiment with a wider range of plant species, also quoted in Sims (1982), organic acid radioactivity ranged from 5.4% to 56.5% of the total radioactivity of the root biomass and from 2.1% to 62.2% of the total radioactivity in the leaf biomass. Radioactivity

was also incorporated into amino acids (up to 18% of the total radioactivity) and into carbon dioxide (up to 9%).

A series of investigations at the Cold Regions Environmental Engineering Labs investigated the response of terrestrial plants to 2,4,6-trinitrotoluene (TNT). Following the growth of yellow nutsedge, *Cyperus esculentus*, in hydroponic solution containing various concentrations of TNT, TNT and its metabolites 4-amino-2,6-dinitrotoluene (4-ADNT) and 2-amino-4,6-dinitrotoluene (2-ADNT) were found throughout the plants. Since TNT was the only compound in the nutrient solution, the metabolites must have been formed within the plant. Levels of 4-ADNT exceeded those of 2-ADNT and TNT itself, ranging up to 2200 mg/kg in the roots of plants grown in 20 mg/l of TNT. Increasing the solution concentration of TNT increased the concentrations of all three compounds in the plants (Palazzo and Leggett, 1986).

There is little good evidence that plants can degrade organo-chlorine chemicals. Davis (1984), however, suggests that this is a possibility and that there may be many more chemicals available for degradation than was once considered. He concluded the following.

1. Plants can sometimes transform chemicals more extensively than can other organisms, possibly because of longer exposure periods than other organisms.

2. Dechlorination has been listed as a mechanism of metabolism for several pesticides, although specific pathways involved have not been elucidated.

3. Dehalogenation bond cleavages have been attributed to peroxidases in plant tissues. Peroxidases are ubiquitous in the plant kingdom and are found throughout the plant cell. This enzyme has also been found in increased quantities in cells selected for increased tolerance to paraquat.

4. Plants synthesize many aromatic compounds and are also capable of degrading them. Plants are capable of the ring fusion reactions required to complete catabolism of aromatic nuclei to CO_2.

5. Cell suspensions of purple cockle, carrot, clover, tobacco, lettuce, and parsley were found to metabolize lindane. Carrot cultures metabolized up to 6.8% in 12 to 68 days. The main metabolite was tentatively identified as a glucoside of trichlorophenol.

Harms and Langebartels (1986) reported on a rapid bioassay technique designed to investigate plant cell breakdown of various chemicals in cell suspension culture. Their results from the bioassay (Table 3.11) showed that even the most persistent chemicals were catabolized and metabolized in suspensions of either soybean or wheat cells. The predominant fractions found were polar conjugates and nonextractable, i.e., bound residues, and there were differences between the species. From this, it can be seen that if a chemical enters the plant, either by the roots or shoots, and then enters a plant cell, it will be changed.

TABLE 3.11. THE BEHAVIOUR OF ORGANIC CHEMICALS APPLIED* TO CELL CULTURES OF SOYBEAN AND WHEAT (Adapted from Harms and Langebartels, 1986.)

Chemical	% of recovered radioactivity Soybean		Wheat	
	Cell-Total†	Changed‡	Cell-Total†	Changed‡
2,4-dichlorophenoxy-acetic acid	31	16	97	90
4-chloroaniline	21	19	86	83
3,4-dichloroaniline	24	19	90	81
pentachlorophenol	59	40	93	93
diethylhexylphthalate	63	12	92	20
perylene	55	52	91	10
benzo(a)pyrene	39	36	91	37

*Applied at 1 mg/l, for 48 hours to the logarithmic growth phase
†'Cell Total' refers to the amount of radioactivity recovered from the cell mass within the suspension culture, as a percent of the total recovered from cell mass plus nutrient solution.
‡'Changed' refers to the percent of the total recovered that was not present in the cell in its original applied form, i.e., the percent that had been metabolized or catabolized by the cells.

A common criticism of much of this plant degradation work is that there is virtually no assured method of eliminating microorganisms from the experimental system and this could lead to false conclusions (Ellis and Towers, 1970). Many chemicals, however, are liable to degradation if they can be collected within a plant cell. Such degradation could be a valuable technique in destroying long-lived pollutants and deserves considerable further research investigation.

REFERENCES

Barrows, H.L., J.H. Card, W.H. Armiger, and W.M. Edwards. 1969. Contribution of aerial contamination to the accumulation of dieldrin by mature corn plants. *Environ. Sci. Technol.* 3(3):262-3.

Beall, M.L., and R.G. Nash. 1971. Organochlorine insecticide residues in soybean plant tops: Root uptake vs. vapour sorption. *Agron. J.* 63:460-464.

Beestman, G.B., D.R. Keeney, and G. Chesters. 1969. Dieldrin translocation and accumulation in corn. *Agron. Jour.* 61:390-393.

Berlin, J., W. Barz, H. Harms, and K. Haider. 1971. Degradation of phenolic compounds in plant cell cultures. *FEBS Letters*. 16(2):141-146.

Briggs, G.G., R.H. Bromilow, R. Edmondson, and M. Johnston. 1976. Distribution coefficients and systemic activity. *Chem. Soc. Spec. Publ.* 29:129-134.

Briggs, G.G., R.H. Bromilow, and A.A. Evans. 1982. Relationship between lipophilicity and root uptake and translocation of non-ionized chemicals by barley. *Pestic. Sci.* 13:495-504.

Briggs, G.G., R.H. Bromilow, A.A. Evans, and M. Williams. 1983. Relationships between lipophilicity and the distribution of non-ionised chemicals in barley shoots following uptake by the roots. *Pestic. Sci.* 14:492-500.

Brown, K.W., G.B. Evans, and B.E. Frentrup. 1983. *Hazardous waste land treatment*. Ann Arbor Sci., Ann Arbor, MI.

Cotner, R.C., R.H. Hamilton, R.O. Mumma, and D.E.H. Frear. 1968. Localization of dieldrin in wheat tissue. *J. Agr. Food Chem.* 16(4):608-609.

Crafts, A.S. 1964. Herbicide behaviour in the plant. In: *The physiology and biochemistry of herbicides*, L.J. Audus (ed), Academic Press, London & N.Y. Pp. 75-110.

Crowdy, S.H. 1973. Patterns and processes of movement of chemicals in higher plants. *Proc. 7th Br. Insect. Fung. Conf.*, Nottingham, U.K. Pp. 831-839.

Crowdy, S.H., J.F. Grove, H.G. Hemming, and K.C. Robinson. 1956. *J. Exp. Bot.* 7:42-64.

Crowdy, S.H., and D. Rudd Jones. 1956. Partition of sulphonamides in plant roots: A factor in their translocation. *Nature* 178:1165-1167.

Davis, M.E. 1984. Development of photosynthetic plants genetically adapted to degrade organochlorine compounds. Battelle Columbus Laboratories, Columbus, OH. Contract number 68-02-3169.

Dittmer, H.J. 1937. A quantitative study of the roots and root hairs of winter rye (*Secale cereale*). *Amer. J. Bot.* 24:417-420.

Eastin, E.F., and E. Basler. 1977. Absorption, translocation, and degradation of herbicides by plants. *Res. Meth. in Weed Sci.* 2nd ed., Southern Weed Science Society. Pp 90-96.

Edgington, L.V., and C.A. Peterson. 1977. Systemic fungicides: Theory, uptake and translocation. In: *Antifungal Compounds*. Vol. 2. Siegel,M.R., and H.D.Sisler (eds.). Vol 2. Marcel Dekker, New York and Basel. Pp. 51-89.

Ellis, B.E. 1974. Degradation of aromatic compounds in plants. *Lloydia* 37(2):168-184.

Ellis, B.E., and G.H.N. Towers. 1970. Degradation of aromatic compounds by sterile plant tissues. *Phytochem.* 9:1457-1461.

Finlayson, D.G., and H.R. MacCarthy. 1973. Pesticide residues in plants. In: *Environmental pollution by pesticides* C.A. Edwards (ed.), Plenum Press, London & N.Y. Chapter 2.

Freed, V.H., and M.L. Montgomery. 1963. The metabolism of herbicides by plants and soils. *Residue Rev.* 3:1-17.

Fries, G.F., and G.S. Marrow. 1981. Chlorobiphenyl movement from soil to soybean plants. *J. Agr. Food Chem.* 29:757-759.

Geissbuhler, H., C. Haselback, H. Aebi, and L. Ebner. 1963. The fate of N'-(4-chlorophenoxy)-phenyl NN-dimethylurea (C-1983) in soils and plants. *Weed Res.* 3:277-297.

Gortz, J.H., and J.L.P. van Oorschot. 1984. Uptake and translocation of 14C asulam and 14C bromacil by roots of maize and bean plants. *Pestic. Biochem. Physiol.* 21:45-52.

Graf, W., and H. Diehl. 1966. Concerning the naturally caused normal level of carcinogenic polycyclic aromatics and its cause. *Arch. Hyg.* 150:49.

Hamilton, R.H., and D.E. Moreland, 1961. Simazine: Degradation by corn seedlings. *Science.* 135:134-135.

Haque, A., I. Scheunert, and F. Korte. 1978. Isolation and identification of a metabolite of pentachlorophenol-14C in rice plants. *Chemosphere* 1:65-69.

Harms, H. and C. Langebartels. 1986. Standardized cell suspension test systems for an ecotoxicologic evaluation of the metabolic fate of xenobiotics. *Plant Sci.* 45:1-9.

Hawxby, K., and E. Basler. 1976. Effects of temperature on absorption and translocation of profluralin and dinitramine. *Weed Sci.* 24(6):545-548.

Jansen, E.F., and A.C. Olsen. 1969. Metabolism of ^{14}C-labelled benzene and toluene in avacado fruit. *Plant Physiol.* 44:786-787.

Khan, S.U. 1982. Studies on bound ^{14}C prometryn residues in soil and plants. *Chemosphere* 11(8):771-795.

Klein,W., and I. Scheunert. 1982. Bound pesticide residues in soils, plants and food with particular emphasis on the application of nuclear techniques. In: *Agrochemicals: Fate in food and the environment.* IAEA-SM-263/38 Vienna. Pp. 177-205.

Leece, D.R. 1976. Composition and ultrastructure of leaf cuticles from fruit trees, relative to differential absorption. *Aust. J. Plant Physiol.* 3:833-847.

Lichtenstein, E.P. 1980. Bound residues in soils and transfer of soil residues in crops. *Residue Rev.* 76:147-153.

Montgomery, M., and V.H. Freed. 1961. The uptake, metabolism and translocation of simazine and atrazine by corn plants. *Weeds.* 9:231.

Mottley, J., and R.C.Kirkwood. 1978. The uptake, translocation and metabolism of dichlorbenil in selected aquatic species. *Weed Res.* 18:187-198.

Moyer, J.R., R.B. McKercher, and R.J. Hance. 1972. Influence of adsorption on the uptake of diuron by barley plants. *Con. J. Plant Sci.* 52:668-670.

Nash, R.G. 1968. Plant uptake of ^{14}C diuron in modified soil. *Agron. Jour.* 60:177-179.

O'Donovan, J.T., and W.H. Vanden Born. 1981. A microautoradiographic study of ^{14}C labelled picloram distribution in soybean following root uptake. *Can. J. Bot.* 59:1928-1931.

Palazzo, A.J., and D.C. Leggett. 1986. Effect and deposition of TNT in a terrestrial plant. *J. Environ. Qual.* 15(1):49-52.

Parker, C. 1966. The importance of shoot entry in the action of herbicides applied to the soil. *Weeds* 14:117-121.

Prendeville, G.N. 1968. Shoot zone uptake of soil applied herbicides. *Weed Res.* 8:106-114.

Riederer, M., and J. Schonherr. 1985. Accumulation and transport of (2,4-dichlorophenoxy) acetic acid in plant cuticles; Permeability of the cuticular membrane. *Ecotoxicol. Environ. Safety* 9:196-208.

Saha, J.G., and W.W.A. Stewart. 1967. Heptachlor, heptachlor epoxide, and gamma-chlordane residues in soil and rutabaga after soil and surface treatments with heptachlor. *Can. J. Plant Sci.* 47:79-88.

Sheets, T.J. 1961. Uptake and distribution of simazine by oat and cotton seedlings. *Weeds.* 9(1):1-13.

Shimabukuro, R.H. 1968. Atrazine metabolism in resistant corn and sorghum. *Plant Physiol.* 43:1925-1930.

Shone, M.G.T., D.T. Clarkson, J. Sanderson, and A.V. Wood. 1973. A comparison of the uptake and translocation of some organic molecules and ions in higher plants. In: *Ion transport in plants*, W.P. Anderson(ed.). Academic Press, London & N.Y. Pp 571-582.

Shone, M.G.T., B.O. Barlett, and A.V. Wood. 1974. A comparison of the uptake and translocation of some organic herbicides and a systemic fungicide by barley; ii Relationship between uptake by roots and translocation to shoots. *J. Exp. Bot.* 25(85):401-409.

Shone, M.G.T., and A.V. Wood. 1976. Uptake and translocation of some pesticides by hypocotyls of radish seedlings. *Weed Res.* 16:229-238.

Shone, M.G.T., and A.V. Wood. 1974. A comparison of the uptake and translocation of some organic herbicides and a systemic fungicide by barley: I Absorption in relation to physico-chemical properties. *J. Exp. Bot.* 25(85):390-400.

Sims, R.C. 1982. Land treatment of polynuclear aromatic compounds. Ph.D. Thesis, N. Carolina University, Raleigh, N.C.

Smith, G.N., B.S. Watson, and F.S. Fisher. 1967. Investigations on Dursban insecticide. Metabolism of O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate and 3,5,6-trichloro-2-pyridinol in plants. *J. Agric. Food Chem.* 15(5):870-877.

Tames, R.S., and R.J. Hance. 1969. *Plant Soil* 30:221-226.

Topp, E., I. Scheunert, A. Attar, and F. Korte. 1986. Factors affecting the uptake of ^{14}C-labelled organic chemicals by plants from soil. *Ecotoxicol. Environ. Safety* 11:219-228.

Uchida, M., H. Nishizawa, and T. Suzuki. 1982. Hydrophobicity of buprofezin and flutolanil in relation to their soil adsorption and mobility in rice plants. *J. Pesticide Sci.* 7:397-400.

Wagner, K.H., and I. Siddiqi. 1971. Die speicherung von 3,4-benzfluoranthen im sommerweizen und sommerroggen. *Z. Pflanzenernahr. Bodenkd.* 130:241-243.

Wagner, K.H., and I. Siddiqi. 1970. Der stoffwechsel von 3,4-benzpyren und 3,4-benzfluoranthen im sommerweizen. *Z. Pflanzenernahr. Bodenkd.* 127:211-219.

Walker, A. 1972. Availability of atrazine to plants in different soils. *Pestic. Sci.* 3:139-148.

Ware, G.W., B.J. Estesen, and W.P. Cahill. 1968. An ecological study of DDT residues in Arizona soils and alfalfa. *Pestic. Monit. Jour.* 2(3):129-132.

Wheeler, W.B., H.A. Moye, C.H. van Middenlem, and N.P. Thompson. 1969. Residues of endrin and DDT in turnips grown in soil containing these compounds. *Pestic. Monit. Jour.* 3(2):72-76.

SECTION 4

VARIATIONS IN POLLUTANT UPTAKE BY DIFFERENT PLANT SPECIES

Just as different pollutants are sorped in soils and accumulated in plants to different degrees, so will different plant species accumulate the same pollutant to different degrees. This variation in reponse has great significance in the selection of plants to use in any *in situ* plant cleanup system of polluted soils. Obviously, if one species accumulates a greater quantity of pollutant from the soil in a shorter time period than do other plant species, it has many benefits and could be used to optimize a cleanup system.

Any organic compound or pollutant in the soil affects vegetation in two broad ways.

1. At low concentrations, the compound partitioned into the soil solution or into the gaseous phase is available for uptake by the vegetation.

2. At high concentrations, a phytotoxic response may occur.

The magnitude of both of these plant responses depends on both the organic chemical and the vegetation species.

Phytotoxicity can occur (a) when the foliar portion of the vegetation is exposed to the organic compound either directly through its application or indirectly through its volatilization from the soil, or (b) when the root system contacts the compound. The applied concentrations at which phytotoxicity occurs is typically different for foliar versus root contact, as well as different for different vegetation species.

Phytotoxicity can influence the effectiveness of a plant cleanup system. If the plant is killed, or its growth is restricted, then it is likely that pollutant accumulation and metabolism by the plant, will be reduced. The level of a pollutant within a particular soil that causes a phytotoxic response could therefore be used to identify materials that may be suitable for this system.

The longer the plant is exposed to the pollutant, the greater is the accumulation of the pollutant (Section 3 and Section 6). On polluted soils, vegetation may be permanently present (e.g., forest or grassland), or it may be planted and harvested in cycles (e.g., crops), or it may just be present as undesirable volunteer or weed species to be disposed of when site cleanup

occurs. It would be expected that each of these different types of vegetation would accumulate different amounts of pollutants from the soil.

The amount of a pollutant that each plant species can accumulate must, in some way, be related to the efficiency of the pollutant collecting system, i.e., the plant root system. This efficiency would, in turn, be a factor of both the total root mass available for pollutant sorption and the extent of the root penetration throughout the soil. Only limited information is available on this.

Russel (1969) includes figures for the fresh weights of roots in the top 10 cm of soil -- figures that range from 6000 kg/ha for *Agropyron cristatum* to 1500 kg/ha. for wheat. Foxx et al. (1984a, 1984b) investigated the maximum rooting depths of a number of plant species growing on low level waste sites (Tables 4.1 and 4.2).

TABLE 4.1. AVERAGE MAXIMUM ROOTING DEPTHS OF PLANT SPECIES OF THE PINEYWOODS AND PRAIRIES (Adapted from Foxx et al.,1984a.)

Species	Common name	Depth cm.
Trees		
Acer spp.	Maple	113.8
Carya spp.	Hickory	152.0
Juglans spp.	Walnut	173.8
Pinus rigida	Shortleaf pine	78.1
Pinus spp.	Pine	181.6
Quercus spp.	Tree oaks	672.1
Grasses and forbs		
Andropogon gerardii	Big bluestem	207.1
Andropogon scoparius	Little bluestem	165.4
Axonopus spp.	Carpet grass	76.0
Cynodon dactylon	Bermuda grass	126.6
Eragrostis spp.	Love grass	127.4
Lespedeza spp.	Bush clover	244.0
Medicago spp.	Alfalfa	
Panicum spp.	Panic grass	220.7
Paspalum spp.	Dallis grass	143.4
Sorgastrum nutans	Indiangrass	159.0
Sporobolus spp.	Dropseed	241.1

The earlier sections indicated at least four routes by which chemicals in the soil can enter a plant: root uptake into conduction channels, uptake from vapour, uptake by external contamination, and uptake and transport in oil cells. If uptake between different plant species is to be compared, it is important that this should occur within one uptake route. Unfortunately, there are extremely few reports of plant uptake of soil-borne organic pollutants where each uptake route has been considered separately, or even

where the influence of the separate routes has been noted. This type of information is urgently needed.

TABLE 4.2. AVERAGE MAXIMUM ROOTING DEPTHS FOR DIFFERENT PLANT TYPES. DATA LISTED ARE PERCENT OF PLANTS HAVING ROOTING DEPTHS, IN CM, OF LESS THAN THE INDICATED DEPTHS (Adapted from Foxx et al., 1984.)

VEGETATION	DEPTH				
	90	180	275	360	450
Annual grasses	75	100			
Biennial forbs	65	100			
Annual forbs	65	88	97	100	
Perennial forbs	42	71	85	93	97
Subshrubs	41	85	96	96	96
Perennial grasses	40	79	94	99	99
Evergreen trees	33	80	86	86	86
Deciduous grasses	7	52	70	78	80
Shrubs	10	47	60	72	77

Investigations into plant uptake of organic chemicals from soils, and comparisons between different plant species, go back many years. Beall and Nash (1969) grew soybean, wheat, corn, alfalfa, bromegrass, and cucumber for 3 to 4 weeks in a variety of soils polluted with the herbicides endrin, DDT, dieldrin, and heptachlor. If the concentration in the plant leaf is expressed as a ratio to the soil concentration (that is, as a Concentration Factor, CF), then bromegrass had the highest CF for endrin and heptachlor whereas wheat had the highest for DDT and dieldrin. The highest CF from this experiment was 2.43 for the aerial shoots of bromegrass growing on soil polluted by 5 ppm heptachlor.

Harris and Sans (1969) found that sugar beet roots took up more dieldrin from a clay soil containing 1.2 ppm dieldrin than did carrots, potatoes, and sugar beet tops. The uptake by corn, oats, and alfalfa were all less than the other crops, with approximately 0.2 ppm dieldrin in them. Davis et al. (1964) found that soybean took up more atrazine per gram of fresh weight from nutrient solution than did corn or cotton. Conversely, Nash et al. (1970) reported that cotton took up a greater amount of heptachlor from soils than did soybean, although they note that there were considerable differences in biomass produced and that this would have affected their results.

Hermanson et al. (1970) reported that carrots normally take up more organochlorine insecticide residues than do other root crops such as potatoes, radish, turnip, and beet.

Walker and Featherstone (1973) investigated the absorption and translocation of atrazine and linuron by carrot, parsnip, lettuce, and turnip seedlings in culture solutions. They found marked differences between the species in the distribution of the herbicides within the plants. A high

proportion of the linuron absorbed by the carrot and parsley seedlings was retained in their root systems, whereas in lettuce and turnip over 60% was translocated to the shoots (Table 4.3). With atrazine, differences were also apparent but were less marked. Examination of the extracts of the different plant species showed that up to 45% of the linuron translocated in parsnip and carrot was present as metabolites, but that little metabolism had occurred in the shoots of lettuce and turnip or in the roots of any of the species. They suggested that the tolerance of parsnip and carrot seedlings to linuron resulted from a combination of root fixation and metabolism in the shoot.

TABLE 4.3. LINURON AND ATRAZINE ABSORPTION* BY DIFFERENT PLANT SPECIES (Adapted from Walker and Featherstone, 1973.)

Vegetation	Plant part	Concentration in plant tissue in μg/g. Linuron	Atrazine
Parsnip	shoot	0.219	0.749
	root	2.267	0.590
Carrot	shoot	0.379	0.544
	root	1.218	0.328
Lettuce	shoot	0.769	0.909
	root	0.660	0.405
Turnip	shoot	1.338	2.128
	root	0.739	0.382

*After 12 days in a nutrient solution containing 0.05 μg/ml of the radiolabeled herbicide.

Bristow et al. (1972) grew cotton, soybean, bean, pea, corn, cucumber, muskmelon, onion, oat, and wheat on a sandy loam polluted by 25 ppm of pentachloronitrobenzene for seven days. The CFs, based on fresh weight of roots, ranged from 0.75 for cotton to 0.08 for wheat. The order of CFs was as the species are listed above.

Overcash (1983), in a review, quoted maximum CFs of 26 for grass; 9.9, lettuce; 2.9, radish; 2.6, parsley; 1.9, carrot; 0.72, potato; 0.39, sugarbeet; and 0.12, watercress grown in hexachlorobenzene-polluted soils. No information was given on the plant part analyzed.

Many further attempts have assessed uptake by different plant species. Some 150 data sets have been assessed to produce Table 4.4. This table compares the maximum CFs of various plants grown on soils polluted by various

pollutants, as decribed by their *n*-octanol/water partition coefficient. The variation in results and lack of pattern highlight the need for further work.

TABLE 4.4. MAXIMUM REPORTED PLANT CF* FOLLOWING GROWTH ON SOILS POLLUTED BY A RANGE OF ORGANIC COMPOUNDS†

log K_{ow}	Max. CF	Plant	Part	Authors
-0.14	22.4	Pea	root	Lichtenstein et al., 1967
1.83	7.4	Barley	shoot	Klosowski,et al., 1981
2.72	8.1	Barley	shoot	Klosowski, et al., 1981
2.9	42.6	Corn	root	Beestman, et al., 1969
2.9	396.0	Pea	root	Lichtenstein, et al., 1968
3.2	648.0	Pea	root	Lichtenstein, et al., 1967
3.72	8.7	Ryegrass	root	Voerman and Besemer, 1975
5.2	2.7	Barley	shoot	Klosowski, et al., 1981
5.57	2.6	Bean	root	Bristow, et al., 1972
6.04	17.0	Wheat	stem	Sims and Overcash, 1983
6.18	39.0	Grass		Smelt and Leistra, 1974

*Concentration Factor
†Described by their *n*-octanol/water partition coefficients (log K_{ow}).

Some of this work must investigate the role and extent uptake plays in the four possible uptake routes described earlier. Perhaps the least investigated uptake and transport route is that within the oil cells of adapted plants. In this group of plants with high root lipid contents are plants like cress, carrot, and parsnip. The relationships outlined above in Section 3 are probably not completely valid for these plants because, for lipophilic chemicals, additional effective uptake mechanisms result from the root lipids.

Topp et al. (1986) compared the uptake of hexachlorobenzene, which has a low water solubility, by an oil containing plant, cress, with that of a non oil containing plant, barley (Figure 4.1). The uptake by cress was higher throughout the experimental period. It is quite possible that increased uptake of lipophilic chemicals is related to the root lipid concentration of the plant, but there is no work to substantiate this.

Not only are these variations in the extent of pollutant accumulation between plant types and species, there are also reported differences between cultivars and individuals of the same species. In an experiment to investigate the effects of maturity and varietal differences in carrot on the uptake of endrin residues from soil, Hermanson et al. (1970) found that, in general, endrin residues in the root appeared to decline with increasing maturity. Although the actual carrot variety exposed to the endrin could

affect CFs by as much as four times, 50 to 80% of this endrin was always removed by peeling the carrot.

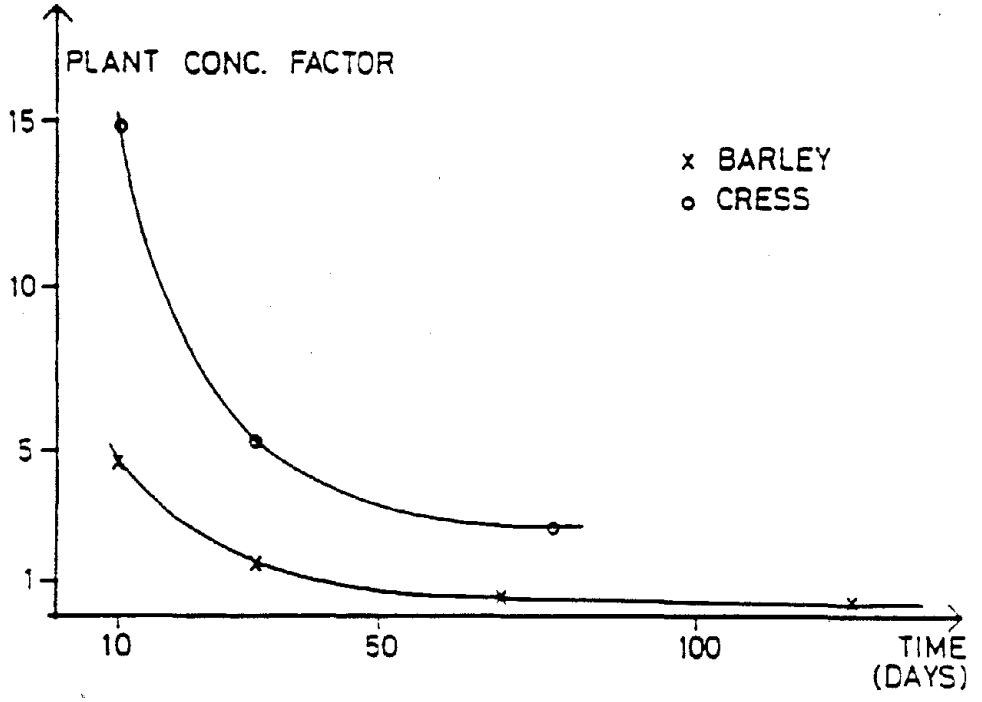

Figure 4.1. Time course of uptake of hexachlorobenzene from soil by barley and cress. (From Topp et al., 1986.)

Various attempts have been made to utilize genetic variation within plants by selecting for tolerance for environmental stresses. Davis (1984) reported on a program design to obtain plants that could degrade organochlorine molecules via cell tissue-culturing techniques. The experiments were only partially sucessful; cell lines of milkweed could be selected for tolerance to up to 7.5 ppm pentachlorophenol and 5 ppm lindane, but the plants could not be regenerated.

In conclusion, the use of plants to collect and degrade pollutants is still in its infancy. The potential for this technique is, however, vast; in one reported instance, pea roots contained over 600 times the soil concentration of the pollutant under study. If this collection system could be harnessed to a plant able to degrade the pollutant, then cleanup would be achieved. Considerable further work is needed, and in some cases is under way, to assess the full potential of the variation between plant species, cultivars, and indeed individuals so that the optimum use of plants on polluted soils can be made.

REFERENCES

Beall, M.L., and R.G. Nash. 1969. Crop seedling uptake of DDT, dieldrin, endrin and heptachlor from soils. *Agr. Jour.* 61:571-575.

Beestman, G.B., D.R. Keeney, and G. Chesters. 1969. Dieldrin uptake by corn as affected by soil properties. *Agronomy J.* 61:247-250.

Bristow, P.R., J. Katan, and J.L. Lockwood. 1972. Control of *Rhizoctonia solani* by pentachloronitrobenzene accumulated from soil by bean plants. *Phytopath.* 63:808-813.

Davis, D.E., J.V. Gramlich, and H.H. Funderburk Jr. 1964. Atrazine absorption and degradation by corn, cotton, and soybeans. *Weeds*. 252-255.

Davis, M.E. 1984. Development of photosynthetic plants genetically adapted to degrade organochlorine compounds. Batelle Columbus Laboratories, Columbus, OH, Contract number 68-02-3169.

Foxx, T.S., G.D. Tierney, and J.M. Williams. 1984a. Rooting depths of plants as related to biological and environmental factors. Los Alamos Nat. Lab. LA 10254 MS.

Foxx, T.S., G.D. Tierney, and J.M. Williams. 1984b. Rooting depths of plants on low level waste sites. Los Alamos Nat. Lab. LA 10253 MS.

Harris, C.R., and W.W. Sans. 1969. Absorption of organochlorine insecticide residues from agricultural soils by crops used for animal feed. *Pestic. Monit. J.* 3(3):182-185.

Hermanson, H.P., L.D. Anderson, and F.A. Gunther. 1970. Effects of variety and maturity of carrots upon uptake of endrin residues from soil. *J. Econ. Entomol.* 63(5):1651-1654.

Kloskowski, R., I. Scheunert, W. Klein, and F. Korte. 1981. Laboratory screening of distribution, conversion and mineralization of chemicals in a soil-plant system adn comparison to outdoor data. *Chemosphere*. 10(10):1089-1100.

Lichtenstein, E.P., T.W. Fuhremann, and K.R. Schulz. 1968. Use of carbon to reduce the uptake of insecticidal soil residues by crop plants; effects of carbon on insecticide adsorption and toxicity in soil. *J. Agr. Food Chem.* 16(2):348-355.

Lichtenstein, E.P., T.W. Fuhremann, N.E.A. Scopes, and R.F. Skrent. 1967. Translocation of insecticide from soils into pea plants; Effects of the detergent LAS on translocation and plant growth. *J. Agr. Food Chem.* 15(5):864-869.

Nash, R.G., M.L. Beall, and E.A. Woolson. 1970. Plant uptake of chlorinated insecticides from soils. *Agron. Jour.* 62:369-372.

Overcash, M.R. 1983. Land treatment of municipal effluent and sludge : Specific organic compounds. Utilization of Municipal Wastewater and Sludge. Pp. 199-231.

Russel, E.J. 1969. *Soil condition and plant growth*. Longmans, London.

Sims, R.C., and M.R. Overcash. 1983. Fate of polynuclear aromatic compounds (PNAs) in soil-plant systems. *Residue Reviews*. 88:2-68.

Smelt, J.H., and M. Leistra. 1974. Hexachlorobenzene in soils and crops after soil treatment with pentachloronitrobenzene. *Agric. and the Environ*. 1:65-71.

Topp, E., I. Scheunert, A. Attar, and F. Korte. 1986. Factors affecting the uptake of ^{14}C-labelled organic chemicals by plants from soil. *Ecotoxicol. Environ. Safety*. 11:219-228.

Voerman, S., and A.F.H. Besemer. 1975. Persistence of dieldrin, lindane, and DDT in a light sandy soil and their uptake by plants. *Bull. Environ. Contam. Toxicol*. 13(4):501-505.

Walker, A., and R.M. Featherstone. 1973. Absorption and translocation of atrazine and linuron by plants with implications concerning linuron selectivity. *J. Exp. Bot*. 24(79):450-458.

SECTION 5

PLANT UPTAKE OF POLLUTANTS

Within each of this Section's subsections the cited literature deals directly with plant accumulation of particular pollutants within pollutant groups, rather than the more general concepts of pollutant behaviour in the soil or higher plant uptake of pollutants as discussed earlier. In many instances, the route of the pollutant into the plant part has not been reported and no attempt has been made to distinguish between plant accumulation by different uptake routes. Some contradictory data are, therefore, evident. Each subsection also includes a listing of typical pollutants within a group from "The water related environmental fate of 129 priority pollutants" (U.S. EPA, 1979).

The listings include various data that will assist in determining the potential environmental fate of the compound. These data include the *n*-octanol/water partition coefficient of the compound (K_{ow}), its Henry's Constant (Hc), its organic carbon partition coefficient (K_{oc}), and its half life ($T_{1/2}$).

By definition, for example, the higher the log K_{ow} for a particular pollutant, the more water insoluble it is and the less of it that is likely to be present in the soil solution. In turn, a high log K_{ow} also infers that less of the compound is likely to be translocated from the plant roots to the plant shoots and more of it is likely to be physically sorbed to the plant root.

The higher the Henry's Constant for a particular compound, the more it will partition from the liquid phase to the vapour phase. As vapour phase transport through the soil is considerably faster than liquid movement, it would be expected that these compounds will be the first to be accumulated by a plant. Vapour transport and the loss of compounds from the soil means that the plant leaves are exposed to gaseous compounds that can then be accumulated.

To be available for plant uptake, the compound must remain in the soil long enough to come into contact with the plant roots or must be volatilized from the soil to come into contact with plant leaves. From this, one would expect more information would be available on plant uptake and accumulation of organic compounds with long half lives than actually exists.

The following discussion reveals that contradictory data and conclusions have been reported. Much of this arises from not recognizing that four quite distinct uptake routes are available for a compound to enter a plant. There are also many pollutants whose accumulation into plants has not been studied. This leaves many large gaps in the available data and thus, large gaps in the conclusions from this data base.

PESTICIDES

For discussion purposes, pesticides can be divided into the targets they are used to control, i.e., insecticides, herbicides, and fungicides. Insecticides can then be further divided on the basis of their chemical structure into the halogenated hydrocarbons, the organophosphates, the carbamates, and the inorganic insecticides like lead, arsenic, and mercury. The inorganic insecticides will not be discussed here; the former will be discussed according to their chemical structures. A description of some physical and chemical parameters of pesticides recognized as priority pollutants is included in Table 5.1.

TABLE 5.1. THE PHYSICAL AND CHEMICAL PARAMETERS OF PESTICIDES RECOGNIZED AS PRIORITY POLLUTANTS

Compound	log K_{ow}*	$t_{1/2}$†	Hc‡	log K_{oc}§	Report $t_{1/2}$θ
Acrolein	-0.09	B	3.3720	-0.273	nd
Aldrin	-0.14	C	0.0022	-0.324	1-4y,a
Chlordane	2.78	C	0.0001	2.681	2-4y,a
DDD	5.99	C	0.0000	5.984	nd
DDE	5.69	B	0.0009	5.675	nd
DDT	4.89	C	0.0190	4.852	3-10y,a
Dieldrin	2.9	C	0.0003	2.804	1-7y,a
Endosulfan	3.55	C	1.2222	3.473	nd
Endrin	5.6	C	0.0000	5.582	4-8y,a
Heptachlor	3.9	A	0.3410	3.833	7-12y,a
Heptachlor epoxide	3.9	C	nd	3.833	nd
Hexachlorocyclohexane	3.8	B	0.0003	3.370	2y,a
Lindane	3.72	C	0.0006	3.648	nd
Isophorone	1.70	nd	nd	1.569	nd
TCDD	6.14	C	nd	6.138	1y,a
Toxaphene	2.9	C	1.2518	2.804	10y,a

*Log K_{ow} are taken from U.S. EPA (1979).
†Half lives are assessed as A = less than 10 days, B = 10-50 days, and C = greater than 50 days, based on the prinicipal fate process in the environment (EPA, 1979).
‡Henry's Constant (dimensionless) has been calculated according to Thibodeaux (1979) from data supplied within U.S. EPA (1979).
§Log K_{oc} has been calculated according to Rao et al. (1982).
θReported half lives are in days unless followed by y = years, followed by a = Dacre (1980); b = Jury et al. (1984); c = Ryan (19860); e = U.S. EPA (1979), which is based on the predominant environmental process thought to determine fate.

Biological magnification of halogenated hydrocarbons has been well documented and is of great concern. Most research exists on plant sorption of DDT, probably because it is one of the oldest of the chlorinated insecticides and has had very wide use. The amounts of DDT found in plant material range from not detectable to 7.5 ppm in root crops and from "not detectable" to 10 ppm in the leaves of crop plants. These figures will result from the sum of the possible uptake routes, as previously discussed (Nash, 1974). Several researchers have observed that DDT is distributed throughout the plant, and this primarily results from vapour phase uptake (Beall and Nash, 1971).

Aldrin and heptachlor, two chlorinated cyclodiene insecticides, have also received considerable attention. Both are readily converted to their more stable epoxides, i.e., dieldrin and heptachlor epoxide, in soils and

plants. Plant residues have ranged from 0 to 150 ppm for aldrin plus dieldrin, and 0 to 10 ppm for heptachlor plus heptachlor epoxide. The high values were obtained from the fibrous roots of plants. A few experiments have demonstrated clearly that both aldrin and heptachlor and their epoxides are sorbed by plant roots and translocated throughout the plant even to the seeds.

Plant species and varieties affect the amount of pesticides residues found within a plant. Lichtenstein et al. (1965) reported differences in absorption of aldrin and heptachlor by five carrot varieties -- differences of 22% to 80% of the soil concentration. Residues of the same pesticides in peanut, soybean, oat, barley, and corn seeds were directly related to the fat content of the seed (Bruce et al., 1966). Residues also vary within the plant, with the top half of the stem normally containing much less residue than the lower half of the stem, as the distance for translocation is decreased (Beall and Nash, 1971).

Soil pH, temperature, organic matter, and clay affected the amount of diuron and its metabolites in the roots and shoots of 14-day-old oat seedlings grown in a modified Lakeland sandy loam soil. An increase in soil pH resulted in greater amounts of diuron in the shoots. To a lesser extent, increased soil organic matter and reduced soil temperature also influenced herbicide content of shoots. In contrast, herbicide content of roots was independent of pH, organic matter, or temperature. The compounds actually identified in the shoots included both the parent compound and monomethyl derivatives (Nash, 1968).

To study the transfer of soil residues to crops, a sandy soil and a silt loam were each treated with one of six insecticides of different water solubilities (0.001 ppm to 320 ppm) and plants were grown in the soil. The amounts of ^{14}C compounds that penetrated into the plant tissue depended on the water solubility of the insecticide and the soil type, i.e., most of the ^{14}C compounds were picked up from a sandy soil that had been treated with the most water soluble insecticide. The amount of ^{14}C recovered from soils and plants was similar with DDT (water solubility 0.001 ppm) and carbofuran (water solubility 320 ppm) recovered. With DDT, however, most of the insecticide remained in the soil; with carbofuran most of the recovered insecticide residues plus metabolites were associated with the greens. The amounts of ^{14}C bound to plant tissue as well as the amounts of detoxification products in plant tissue increased with increasing water solubilities of the insecticides (Lichtenstein, 1980).

In 1974, Nash summarized the state of knowledge on plant uptake of pesticides from soils, their translocation, and their metabolism within the plant (Table 5.2). The list is short, and remains short, considering the vast number of pesticide formulations currently used. The results indicate that plants sorb and can metabolize most pesticides.

TABLE 5.2. PLANT UPTAKE, TRANSLOCATION, AND METABOLISM OF PESTICIDES FROM SOILS. (Adapted from Nash, 1974.)

Compound	Root uptake	Translocation	Metabolism
Aldrin	yes	yes	yes
Dieldrin	yes	yes	probable
Isodrin	yes	probable	yes
Endrin	yes	yes	yes
Heptachlor	yes	yes	yes
Heptachlor epoxide	yes	yes	unknown
Chlordane	yes	improbable	unknown
Endosulfan	yes	yes	unknown
Toxaphene	probable	improbable	unknown
BHC	yes	yes	yes
Lindane	yes	yes	yes
DDT	yes	probable	yes
Diazinon	yes	yes	probable
Dimethoate	yes	probable	probable
Disulfoton	yes	yes	yes
Phorate	yes	yes	yes
Parathion	yes	probable	unknown
Chloroneb	yes	yes	yes

Lindane, DDT, and aldrin are absorbed into crops; the degree depends on the crop, the soil type in which the crop had grown, and its concentration within the soil. Carrots absorbed more insecticide than any other crop (Iwata et al., 1974) and, in the case of lindane, accumulated more than was in the soil. The insecticides were most readily absorbed from a sandy loam and least from a muck. The amounts absorbed by the same crop from the same soil were not in direct proportion to the concentration recovered from the soil; relatively less was recovered from the more polluted soils.

No comprehensive reported investigations relate plant uptake and accumulation of pesticides with their physical and chemical parameters although this may be expected because of the economic/confidential nature of this information. The actual efficiency of herbicides depend on their characteristics and their ability to affect the growth of plants and, in some cases, to be accumulated.

POLYHALOGENATED BIPHENYLS

Discussions of PCBs are often complicated by differences in the chemical and biological terms that describe them. In the chemical industry, PCBs are normally described by their Aroclor number, where the first two digits represent the carbon number of the hydrocarbon and the last two digits are the mean percent chlorine on the carbon molecule. Aroclors are, therefore, mixtures of

chemicals. Aroclor 1254 is a mixture of chemicals with 12 carbon atoms and 54% chlorine. Plants and other biological systems, however, see the Aroclor mixture as its individual congeners. Some physical and chemical parameters of PCBs recognized as priority pollutants are included in Table 5.3.

The fate of PCBs in soil and their potential for uptake by plants has received little attention, partly because their use did not involve application to agricultural land. In recent years, however, they have gained research popularity because of their detrimental effect upon the environment.

TABLE 5.3. THE PHYSICAL AND CHEMICAL PARAMETERS OF THOSE POLYCHLORINATED BIPHENYLS RECOGNIZED AS PRIORITY POLLUTANTS.

Compound	log K_{ow}*	$t_{1/2}$†	Hc‡	log K_{oc}§	Report $t_{1/2}$θ
2-chloronaphthalene	4.12	C	0.0221	4.060	14y,a;i,b
Arochlor 1016	5.58	C	0.0132	5.562	4y,a;i,b
Arochlor 1221	4.09	C	0.0048	4.029	4y,a;i,b
Arochlor 1232	4.54	C	0.0350	4.492	4y,a;i,b
Arochlor 1242	5.58	C	0.0172	5.562	4y,a;i,b
Arochlor 1248	6.11	C	0.1477	6.107	4y,a;i,b
Arochlor 1254	6.72	C	0.1134	6.735	4y,a;i,b
Arochlor 1260	6.11	C	0.3038	6.107	4y,a;i,b

*Log K_{ow} are taken from U.S. EPA (1979).
†Half lives are assessed as A = less than 10 days, B = 10-50 days, and C = greater than 50 days, based on the prinicipal fate process in the environment (EPA, 1979);
‡Henry's Constant (dimensionless) has been calculated according to Thibodeaux (1979) from data supplied within U.S. EPA (1979).
§Log K_{oc} has been calculated according to Rao et al. (1982).
θReported half lives are in days unless followed by y = years, followed by a = Dacre (1980); b = Jury et al. (1984); c = Ryan (19860); e = U.S. EPA (1979), which is based on the predominant environmental process thought to determine fate. If more than one reference occurs for the half life they are separated by ;. nd = no data, i = infinity.

Iwata et al. (1974) evaluated PCB uptake by carrots from a low-organic-matter sandy soil. Aroclor 1254 was applied at 100 ppm to the top 15 cm of soil in the field. "Goldinhart" carrots were grown using normal agricultural practices. For the persistent 5 and 6 chlorine isomers, unpeeled fresh carrots contained about 5% of the soil level. Peeling the root removed 14% of the carrot fresh weight but 97% of the PCBs, leaving the peeled carrot with only 0.16% of the PCB soil level. Chromatographic analysis showed a preferential uptake of isomers of low chlorination which is in line with their K_{ow}. Iwata et al. concluded that carrots are outstanding in scavanging organochlorine pesticide residues from soil.

Suzuki et al. (1977) showed that PCBs in soil can be transferred to a plant via plant roots. When they grew soybean sprouts for 14 days in soil containing 100 ppm PCB, they found maximum concentrations of 150 μg/kg. Translocation rates of PCB isomers differ, largely depending on the degree of chlorination with related degrees of water solubility. Their experiments were primarily designed to test their methods rather than to obtain accurate uptake concentrations.

Moza et al. (1979) found that the uptake of a radiolabeled tri- and pentachlorobiphenyl was greater in the high-oil carrot than the low-oil sugar beet. For the trichlorobiphenyl, only 32.5% of the applied radioactivity was recovered in the plants and soil after the first exposure season; volatilization loss was 67.5%, carrot plant uptake was 3.1%, and sugar beet uptake was 0.2%. For the pentachlorobiphenyl, total recovery was 58.5%; volatilization loss was 41.5%, crop uptake was 1.4%, and conversion was less than 1%.

Mrozek and Leidy (1981) collected and transplanted *Spartina alterniflora* plants into Aroclor 1254-amended soils under estuary-like conditions. After a 90 day growth period, the plants were harvested and separated into aerial and below-ground portions. Following analysis, a comparison of the increasing absence of the higher chlorinated congeners in the aerial tissue with those in the below ground tissue and those in the soil suggested that uptake was selective for the lesser chlorinated congeners. This has also been shown by Iwata et al. (1974). The mean CFs across the various congener peaks, and with a mean soil concentration of 0.039 ppm, were 14.4 for the below-ground tissue and 0.56 for the aerial tissue.

As a result of their review, Fries and Marrow (1981) concluded that no study demonstrated beyond doubt that plant root uptake and subsequent translocation of PCBs do actually occur. The residues that were reported in many of the reviewed papers could have arisen from direct adsorption to the roots or surface adsorption to the aerial parts by volatilized PCB. This is one of the first experiments where the authors recognized different uptake routes. Fries and Marrow, therefore, grew soybean plants in specially constructed pots to determine the residue concentrations in the plant tops from either surface or subsurface soil-applied tri-, tetra-, or pentachlorobiphenyls. The plants were harvested at 52 days and divided into top stem, bottom stem, top leaves, bottom leaves and seed pod for analysis. They found that the concentration of residue in the plant increased with increasing chlorination and that detectable residues were only found in the lower leaves of plants where the biphenyl was in the surface soil.

Some of this literature on PCB uptake by higher plants is reviewed and placed into an environmental context by Strek and Weber (1982). They do not, however, attempt to resolve the root uptake versus vapour uptake arguments.

Sawhney and Hankin (1984) then found the reverse of most other workers in that the leaves of beet grown on Aroclor-amended soil contained higher concentrations of the pollutant than did the roots. Beet roots contained 15, 16, and 35 μg/kg, repectively, of the Aroclor 1248, 1254, 1260, whereas the leaves contained 22, 94, and 52 μg/kg, respectively, (Table 5.4). Similar

results were also found with turnips also grown on the amended soil. CFs reached a peak of 0.4 for turnip leaves with the least chlorinated Aroclor, 1248. In line with other authors, greater plant tissue contamination occurred with the lesser chlorinated Aroclors giving a ranking for uptake of 1248 >1254 >1260. Sawhney and Hankin, however, make no attempt to separate potential vapour uptake from root uptake and translocation.

TABLE 5.4. PCBs (Aroclors) IN SOIL AND IN VEGETABLES GROWN IN SOIL AMENDED WITH CONTAMINATED SEDIMENTS. (From Sawhney and Hankin, 1984.)*

Aroclor	Soil	Beet root		Beet leaf		Turnip root		Turnip leaf	
	µg/kg	µg/kg	CF	µg/kg	CF	µg/kg	CF	µg/kg	CF
1248	80	15	.187	22	.275	30	.375	32	.400
1254	1880	16	.008	94	.050	16	.008	40	.021
1260	14440	35	.002	52	.004	20	.002	27	.002
Total	16400	66		168		66		99	

*CF = Concentration Factor calculated by dividing the amount in the plant part by the amount in the soil.

Jacobs et al. (1976) amended a loamy sand, having an organic matter content of 1.1%, with various concentrations of PBBs to investigate uptake into Nordstem orchard grass (*Dactylis glomerata*) and Spartan Delite carrot (*Daucus carota*) in a greenhouse. No PBBs were detected in repeated clippings of the tops of the grass, either in the grass roots or in the carrot tops. CFs in the carrot roots did not exceed 0.002 and they concluded that PBBs are unlikely to be taken up into vegetation to any significant degree.

The same authors continued their work (Chou et al., 1978) and found that when soybean and corn seedlings were grown in a nutrient solution containing radiolabeled PBBs for about 7 days, plant root contained PBB residues but none was found in the leaves.

These compounds all have high log K_{ow} values and would therefore be expected to be sorbed to plant roots to concentrations many times those in the surrounding soil or sediment media. This has not been reported.

The time scale of many of these investigations has been short. When a PCB is within the soil, it is partitioned between the organic content of the soil and the liquid phase. The plant root can only sorb the compound in the liquid phase. Attachment to the organic faction is strong, however, and considerable time is needed to adjust the equilibrium of the compound to the liquid phase. Further work on longer term experiments is therefore required.

HALOGENATED ALIPHATICS

No relevant information on plant uptake and accumulation of this large group of compounds was found in the literature searches. Most of the compounds have low log K_{ow} and short half lives, as shown in Table 5.5. They are unlikely, therefore, to be present in the soil environment for long periods, but if they were, they would be translocated within plants.

HALOGENATED ETHERS

No information was found on this group of compounds other than the chemical and physical parameters described in Table 5.6. They exhibit a range of log K_{ow} and log K_{oc} and so would be expected to be both accumulated by the plant root and translocated within a plant following uptake.

MONOCYCLIC AROMATICS

These cyclic compounds, described in Table 5.7, have multiple double bonds. Plants appear to be able to metabolize the benzene ring to organic acids, which then accumulate in the plant part where the benzene was introduced (Sims, 1982).

Toluene, for example, has been reported to be absorbed and detoxified by roots, foliage, and fruits, with organic acids being the primary products of cleavage of the toluene aromatic ring. The oxidation of toluene and its metabolites to CO_2 was more rapid in corn and bean seedlings than in perennial plants. Regardless of how the toluene was taken up by plant roots or leaves, however, the same metabolites were found in all species. An enzyme system in plants is thus capable of degrading the benzene ring and transforming aromatic into aliphatic compounds. The toluene that enters the plant is not bioaccumulated or translocated as such, but it is readily metabolized and assimilated into the plant cell components and CO_2 (Overcash et al., 1982).

Although this is a large group of compounds with a wide range of physical and chemical properties, most have relatively short half lives and would, therefore, not present a long-term pollution problem.

PHTHALATE ESTERS

Again, little information is available on these compounds other than that described in Table 5.8. They would be expected to be sorped to plant roots and may also be transported via the vapour phase. Considerably more investigations are needed to determine the potential for plant accumulation of the phthalate ester group of chemicals.

Overcash et al. (1982) reported on the effects of di-*n*-butyl phthalate on the plant mass and height of soybean, corn, and fescue. Unfortunately, no uptake concentrations were assessed.

POLYCYCLIC AROMATICS

The chemical and physical parameters of the polycyclic aromatic compounds are included in Table 5.9. Many research efforts have centered on the risk arising from plant accumulation of polycyclic aromatic hydrocarbons (PAHs) because some of these compounds have been shown to be carcinogenic. Polyaromatic compounds are composed of multiple fused benzene rings and include compounds such as naphthalene and anthracene.

Some of the earliest experiments to investigate the uptake of PAHs added to soil were undertaken in Germany by Wagner and Siddiqi (1970, 1971). They observed that, at high concentrations, soil-borne PAH contamination of wheat, rye, maize, barley, and carrot affected the development of both roots and shoots. Their results, however, were not consistent because the control plants also became contaminated, possibly by aerial contamination. CFs for both roots and shoots were generally less than 0.1 on a dry matter basis.

Higher CFs for PAHs have been reported by Ellwardt (1977) and Muller (1976) from their work with potato tubers and radish and carrot roots. In these instances, the PAH remained in the outer portion of the root and concentrations in the leaves of the plants remained very low, again suggesting that aerial contamination is the only method by which plant leaves become contaminated by soil-borne PAHs.

Harms and Sauerbeck (1984) found PAH contamination of potato tuber, radish, and carrot when direct contact with the soil allowed transfer of the compound. Concentrations in the above ground portions of the plants remained low, however.

In Muller's study (1976), 3,4-benzopyrene was taken up and translocated in both carrot and radish. If the composted solid town waste and soil mix contained 2 ppm, red radish tubers contained 3.5 ppb, and the leaves contained 20 ppb. In other experiments using pure quartz sand as the substrate, much more pollutant was taken up but actual concentrations in the carrot roots declined with successive crops. Uptake of benzopyrene, however, strongly depends on the chemical composition and physical nature of the substrate.

When, in a study by Sims and Overcash (1983), the soil concentration of B(*a*)P was increased, the plant concentration remained approximately the same. Biomagnification of B(*a*)P for seed, stem, and straw was demonstrated. With 3,4-benzfluoranthene, the pattern was not the same. Plant concentrations were generally much higher with smaller differences between the plant parts. Also an increase in plant 3,4-benzfluoranthene content correlated with an increase in soil content. Thus the two PNAs exhibited different behaviour under similar soil and crop conditions but both showed biomagnification.

A quantitative determination of the uptake and plant effects of all PAHs is practically impossible and many researchers have restricted their work to the most toxic compounds, e.g., benzo(*a*)pyrene. Tracer experiments have confirmed that this compound can be taken up by the roots and translocated

upwards and, if shoot-applied, can move basipetally and disappear from the plant (Grosse, 1978).

Harms (1975) proposed that the uptake rate of PAHs into plants depended on their molecular size. The highly condensated ring structures of benzo(*a*)pyrene and dibenz(*a*,*h*)anthracene resulted in low CFs whereas the lower ring numbers of benzanthracene and anthracene resulted in higher CFs. Topp et al. (1986) proposed molecular size as a major influence on plant uptake. In turn, molecular size is broadly related to water solubility and *n*-octanol/water partition coefficients.

Data provided in Sims (1982), described the assimilation and conversion of 3,4-benzpyrene-1,2-^{14}C with 14-day-old sterile corn and bean seedlings in a sterile nutrient solution. When the radiolabeled PAH was introduced into the leaves or roots of the plants, approximately 50% of the label was assimilated into organic acids, which were concentrated at the site of assimilation. In a follow-up experiment, also described in Sims (1982), with a wider range of plant species, organic acid radioactivity ranged from 5.4% to 56.5% of the total radioactivity of the root biomass, and 2.1% to 62.2% of the total radioactivity of the leaf biomass. Radioactivity was also incorporated into amino acids, up to 18% of the total radioactivity, and carbon dioxide, up to 9%.

Plants can use a variety of reactions to reduce more complex aromatic structures to simpler units. Typical steps include demethylation, β oxidation, and decarboxylation. Recently, plants have been shown to be capable of the ring-fission reactions needed to permit complete catabolism of aromatic nuclei to carbon dioxide. The existence of such catabolic routes makes it likely that the accumulation of secondary metabolites in plants is a dynamic process of definite significance in the life of the plant (Ellis, 1974). Experiments with sterile plants and with plant cell suspension cultures have shown that benzo(*a*)pyrene can be metabolized into oxygenated derivatives (Harms et al., 1977). Although some of these derivatives are known to be more toxic than the original compound, they appear to be polymerized into the insoluble plant lignin fraction, which may be an important mechanism for their detoxification.

TABLE 5.5. THE PHYSICAL AND CHEMICAL PARAMETERS OF THOSE HALOGENATED ALIPHATIC HYDROCARBONS RECOGNIZED AS PRIORITY POLLUTANTS

Compound	log K_{ow}*	$t_{1/2}$†	Hc‡	log K_{oc}§	Report $t_{1/2}$θ
Chloromethane	0.91	C	1.619	0.756	120,e
Dichloromethane	1.25	B	0.1276	1.106	100,e
Trichloromethane	1.9	B	0.1200	1.775	i,b;50,e
Tetrachloromethane	2.64	nd	0.96	2.537	i,b
Chloroethane	1.54	B	0.6152	1.405	nd
1,1-Dichloroethane	1.79	B	0.1774	1.662	45,e
1,2-Dichloroethane	1.48	B	0.0380	1.343	90,e
1,1,1-Trichloroethane	2.17	nd	1.4606	2.053	1-8y,e
1,1,2-Trichloroethane	2.17	nd	0.0308	2.053	nd
1,1,2,2-Tetrachloroethane	2.56	A	0.1580	2.454	nd
Hexachloroethane	3.34	nd	0.1037	3.257	nd
Chloroethene	0.60	A	151.69	0.437	i,b;1,e
1,1-Dichloroethene	1.48	A	7.8377	1.343	1,e
1,2-Trans-dichloroethene	1.48	A	1.7682	1.343	1,e
Trichloroethene	2.29	A	0.3739	2.176	4,e
Tetrachloroethene	2.88	A	0.8471	2.784	10,e
1,2-Dichloropropane	2.28	nd	0.0962	2.166	nd
1,3-Dichloropropene	1.98	A	0.0563	1.857	nd
Hexachlorobutadiene	3.74	C	1.0708	3.668	nd
Hexachlorocyclopentadie	3.99	A	1.5027	3.926	nd
Bromomethane	1.10	B	8.1969	0.952	i,b
Bromodichloromethane	1.88	nd	nd	1.755	nd
Dibromochloromethane	2.09	nd	nd	1.971	nd
Tribromomethane	2.30	nd	0.0434	2.187	nd
Dichlorodifluoromethane	2.16	C	109.36	2.043	30y,e
Trichlorofluoromethane	2.53	nd	4.5637	2.423	10y,e

*Log K_{ow} are taken from U.S. EPA (1979).
†Half lives are assessed as A = less than 10 days, B = 10-50 days, and C = greater than 50 days, based on the prinicipal fate process in the environment (EPA, 1979).
‡Henry's Constant (dimensionless) has been calculated according to Thibodeaux (1979) from data supplied within U.S. EPA (1979).
§Log K_{oc} has been calculated according to Rao et al. (1982).
θReported half lives are in days unless followed by y = years, followed by b = Jury et al. (1984); e = U.S. EPA (1979), which is based on the predominant environmental process thought to determine fate. If more than one reference occurs for the half life they are separated by ;.
nd = no data, i = infinity.

TABLE 5.6. THE PHYSICAL AND CHEMICAL PARAMETERS OF THOSE HALOGENATED ETHERS RECOGNIZED AS PRIORITY POLLUTANTS

Compound	log K_{ow}*	$t_{1/2}$†	Hc‡	log K_{oc}§	Report $t_{1/2}$θ
Bis(chloromethyl)ether	-0.38	A	0.0086	-0.571	1,e
Bis(2-chloroethoxy)methane	1.26	C	0.0000	1.117	0.5-2y,e
2-Chloroethyl vinyl ether	1.28	A	0.0104	1.137	1,e
Bis(2-chloroethyl)ether	1.58	nd	0.0005	1.446	nd
Bis(2-chloroisopropyl)ether	2.58	nd	0.0047	2.475	nd
4-Chlorophenyl phenylether	4.08	nd	0.0101	4.018	nd
4-Bromophenyl phenyl ether	4.28	nd	nd	4.224	nd

*Log K_{ow} are taken from U.S. EPA (1979).
†Half lives are assessed as A = less than 10 days, B = 10-50 days, and C = greater than 50 days, based on the prinicipal fate process in the environment (EPA, 1979).
‡Henry's Constant (dimensionless) has been calculated according to Thibodeaux (1979) from data supplied within U.S. EPA (1979).
§Log K_{oc} has been calculated according to Rao et al. (1982).
θReported half lives are in days unless followed by y = years; e = U.S. EPA (1979), which is based on the predominant environmental process thought to determine fate.
nd = no data.

TABLE 5.7. THE PHYSICAL AND CHEMICAL PARAMETERS OF THOSE MONOCYCLIC AROMATIC HYDROCARBONS RECOGNIZED AS PRIORITY POLLUTANTS

Compound	log K_{ow}*	$t_{1/2}$†	Hc‡	log K_{oc}§	Report $t_{1/2}$θ
Phenol	1.46	A	0.0000	1.322	i,b;2,c
Nitrobenzene	1.85	C	0.0005	1.724	i,b
2,4-Dinitrotoluene	2.01	nd	0.0000	1.888	nd
2,6-Dinitrotoluene	2.05	nd	nd	1.929	nd
Benzene	2.13	A	nd	2.012	2,e
2-Chlorophenol	2.17	nd	0.0005	2.053	nd
Toluene	2.69	A	0.2703	2.588	2-7,c;1,e
2,4-Dichlorophenol	2.75	A	0.0002	2.667	3-28,c;6,e
Chlorobenzene	2.84	nd	nd	2.742	i,b
2,4,6-Trichlorophenol	3.38	nd	0.0135	3.298	nd
Ethylbenzene	3.15	A	0.2672	3.061	1,e
1,2-Dichlorobenzene	3.38	nd	0.0832	3.298	nd
1,3-Dichlorobenzene	3.38	nd	0.1505	3.298	nd
1,4-Dichlorobenzene	3.39	nd	nd	3.308	nd
1,2,4-Trichlorobenzene	4.26	A	0.1387	4.204	nd
Hexachlorobenzene	6.18	C	0.0251	6.179	nd
Pentachlorophenol	5.01	A	0.0001	4.975	nd
2-Nitrophenol	1.76	C	0.0036	1.631	nd
4-Nitrophenol	1.91	B	0.0010	1.785	16,c
2,4-Dinitrophenol	1.53	C	nd	1.394	nd
2,4-Dimethylphenol	2.50	nd	0.0000	2.393	1-2,c
p-Chloro-*m*-cresol	2.95	nd	nd	2.856	30,c
4,6-Dinitro-*o*-cresol	1.85	nd	nd	2.753	nd

*Log K_{ow} are taken from U.S. EPA (1979).
†Half lives are assessed as A = less than 10 days, B = 10-50 days, and C = greater than 50 days, based on the prinicipal fate process in the environment (EPA, 1979).
‡Henry's Constant (dimensionless) has been calculated according to Thibodeaux (1979) from data supplied within U.S. EPA (1979).
§Log K_{oc} has been calculated according to Rao et al. (1982).
θReported half lives are in days unless followed by y = years, followed by b = Jury et al. (1984); c = Ryan (1986); e = U.S. EPA (1979), which is based on the predominant environmental process thought to determine fate. If more than one reference occurs for the half life they are separated by ;. nd = no data, i = infinity.

TABLE 5.8. THE PHYSICAL AND CHEMICAL PARAMETERS OF THOSE PHTHALATE ESTERS RECOGNIZED AS PRIORITY POLLUTANTS

Compound	log K_{ow}*	$t_{1/2}$†	Hc‡	log K_{oc}§	Report $t_{1/2}$θ
Dimethyl phthalate	2.12	B	0.0000	2.001	nd
Diethyl	3.22	B	0.0006	3.133	4,c
Di-*n*-butyl	5.20	B	0.0884	5.171	nd
Di-*n*-octyl	9.21	B	0.9884	9.287	nd
Bis(2-ethylhexyl)	8.73	B	0.5351	8.803	14,c
Butyl benzyl	5.80	B	nd	5.788	nd

*Log K_{ow} are taken from U.S. EPA (1979).
†Half lives are assessed as A = less than 10 days, B = 10-50 days, and C = greater than 50 days, based on the prinicipal fate process in the environment (EPA, 1979).
‡Henry's Constant (dimensionless) has been calculated according to Thibodeaux (1979) from data supplied within U.S. EPA (1979).
§Log K_{oc} has been calculated according to Rao et al. (1982).
θReported half lives are in days unless followed by y = years, followed by c = Ryan (1986), which is based on the predominant environmental process thought to determine fate. If more than one reference occurs for the half life they are separated by ;. nd = no data.

TABLE 5.9. THE PHYSICAL AND CHEMICAL PARAMETERS OF THOSE POLYCYCLIC AROMATIC HYDROCARBONS RECOGNIZED AS PRIORITY POLLUTANTS.

Compound	log K_{ow}*	$t_{1/2}$†	Hc‡	log K_{oc}§	Report $t_{1/2}$θ
Acenaphthene	4.33	C	0.0025	4.276	nd
Acenaphthylene	4.07	C	0.0021	4.008	nd
Fluorene	4.18	C	0.0032	4.121	nd
Naphthalene	3.37	C	0.0100	3.288	i,b;0.1-125,c
Anthracene	4.45	C	0.0434	4.399	nd
Fluoranthene	5.33	C	0.0004	5.305	44-182,c
Phenanthrene	4.46	C	0.0045	4.409	i,b
Benzo[*a*]anthracene	5.61	C	0.0000	5.593	15-6250,c
Benzo[*b*]fluoranthene	6.57	nd	nd	6.581	67-130,c
Benzo[*k*]fluoranthene	6.84	C	nd	6.858	nd
Chrysene	5.61	C	0.0006	5.593	5-10,c
Pyrene	5.32	C	0.0005	5.294	nd
Benzo[*ghi*]perylene	7.23	C	0.0000	7.260	nd
Benzo[*a*]pyrene	6.04	C	0.0000	6.035	2-694,c
Dibenzo[*a*]anthracene	5.97	C	0.0000	5.963	21-190,c
Indeno[123-*cd*]pyrene	7.66	C	nd	7.702	200-600,c

*Log K_{ow} are taken from U.S. EPA (1979).
†Half lives are assessed as A = less than 10 days, B = 10-50 days, and C = greater than 50 days, based on the prinicipal fate process in the environment (EPA, 1979).
‡Henry's Constant (dimensionless) has been calculated according to Thibodeaux (1979) from data supplied within U.S. EPA (1979).
§Log K_{oc} has been calculated according to Rao et al. (1982).
θReported half lives are in days unless followed by y = years, followed by b = Jury et al. (1984); c = Ryan (1986), which is based on the predominant environmental process thought to determine fate. If more than one reference occurs for the half life they are separated by ;.
nd = no data, i = infinity.

MISCELLANEOUS COMPOUNDS

The physical and chemical parameters of other compounds are described in Table 5.10. Because nitrosamines are another group of chemicals found in sewage wastes they have been investigated for plant contamination. Although plants can accumulate nitrosamines from nutrient solution and soil (Brewer et al., 1980; Dean-Raymond and Alexander, 1976), nitrosamines appear to be rapidly degraded in both environments. Sander et al. (1975) cultivated cress plants (*Lepidium sativum*) over nutrient solutions containing the nitrosamines, nitrosodiethylamine, nitrosomorpholine, and dinitrosopiperazine. They found that the plant roots quickly absorbed each of the nitrosamines but that the

concentration within the plant was quickly depleted. The losses in the plant could have resulted from the effect of sunlight on the chemicals, vapourization, or metabolic breakdown within the plant.

TABLE 5.10. THE PHYSICAL AND CHEMICAL PROPERTIES OF MISCELLANEOUS COMPOUNDS RECOGNIZED AS PRIORITY POLLUTANTS

Compound	log K_{ow}*	$t_{1/2}$†	Hc‡	log K_{oc}§	Report $t_{1/2}$θ
Dimethyl nitrosamine	0.06	nd	nd	-0.087	nd
Diphenyl nitrosamine	2.57	nd	nd	2.465	nd
Di-*n*-propylnitrosamine	1.31	nd	nd	1.168	nd
Benzidine	1.81	A	nd	1.683	1,e
3,3-Dichlorobenzidine	3.02	A	nd	2.928	1,e
1,2-Diphenylhydrazine	3.03	nd	nd	2.938	nd
Acrylonitrile	-0.14	A	0.0040	-0.324	nd

*Log K_{ow} are taken from U.S. EPA (1979).
† Half lives are assessed as A = less than 10 days, B = 10-50 days, and C = greater than 50 days, based on the prinicipal fate process in the environment (EPA, 1979).
‡ Henry's Constant (dimensionless) has been calculated according to Thibodeaux (1979) from data supplied within U.S. EPA (1979).
§Log K_{oc} has been calculated according to Rao et al. (1982).
θ Reported half lives are in days unless followed by y = years, followed by e = U.S. EPA (1979), which is based on the predominant environmental process thought to determine fate. If more than one reference occurs for the half life they are separated by ; nd = no data.

Kearney et al. (1980) investigated the uptake and translocation of ^{14}C-labeled *N*-nitrosodipropylamine (NDPA) and *N*-nitrosopendimethalin (NP) in soybeans grown in the field in Matapeake silt loam amended with the pollutants. No residues of NDPA were found in the beans or other plant parts. Low levels of ^{14}-C were found in plants grown on NP amended soil but, again, not in the beans.

Another group of chemicals investigated because of their carcinogenic properties are the aflatoxins. Mertz et al. (1980) exposed 12-day-old maize seedlings to Hoagland's solution adulterated with aflatoxin B1. After 7 days, the seedlings were transferred to aflatoxin-free solution or soil to determine the concentration of the toxin absorbed and retained within the plant tissue. Two days after transfer, there was a 75% and 50% reduction in root and leaf-stem concentration. After four days, the tissue concentrations appeared to increase slightly, probably as a result of reabsorption of previously desorbed

toxin. After 13 days, the concentration of the toxin had been reduced to 80% and 96% of the original in the root and leaf stem tissue, respectively.

In a follow up experiment, Mertz et al. (1981) transplanted 2-day-old lettuce seedlings to a clay loam adulterated with the aflatoxin B1. Following a growth period of 7 to 12 days, the aflatoxin recovered from leaf stem and root tissue represented less than 1% of the original soil addition.

CONCLUSIONS

At the start of this rather extensive collation and review of reported plant uptake experiences, it was anticipated that much useful information concerning levels of uptake, differences between liquid and vapour phase uptake, and differences between pollutants could be obtained. This has not been the case.

Because many authors approached uptake from one specific point of view, all the experimental details or plant details, etc., are not included in their reports. This has made a broader interpretation of the collected data almost impossible.

The above data do illustrate one rather major point: no research on plant accumulation has been undertaken for large groups of chemical compounds.

REFERENCES

Beall, M.L., and R.G. Nash. 1971. Organochlorine insecticide residues in soybean plant tops: Root uptake vs. vapour sorption. *Agron. J.* 63:460-464.

Brewer, W.S., A.C. Draper, and S.S. Wey. 1980. The detection of dimethylnitrosamine and diethylnitrosamine in municipal sludge applied to agricultural soils. *Environ. Pollut.* 1B:37-43.

Bruce, W.N., G.C. Decker, and J.G. Wilson. 1966. The relationship of the levels of insecticide contamination of crop seeds to their fat content and soil concentration of aldrin, and heptachlor. *J. Econ. Entomol.* 59(1):180-182.

Chou, S.F., L.W. Jacobs, D. Penner, and J.M. Tiedje. 1978. Absence of plant uptake and translocation of polybrominated biphenyls(PBBs). *Environ. Health Perspectives.* 23:9-12.

Dacre, J.C. 1980. Potential health hazards of toxic organic residues in sludge. In: *Sludge - Health risks of land application.* Britton, G., R.L. Damron, G.T. Edds, and J.M. Davidson (eds.). Ann Arbor Sci., Ann Arbor, MI

Dean-Raymond, D., and M. Alexander. 1976. Plant uptake and leaching of dimethylnitrosamine. *Nature.* 262:394-396.

Ellis, B.E. 1974. Degradation of aromatic compounds in plants. *Lloydia.* 37(2):168-184.

Ellwardt, P. 1977. Variation in content of polycyclic aromatic hydrocarbons in soil and plants by using municipal wastes composts in agriculture. *Proc. Series - Soil organic matter studies.* 2:291-298.

Fries, G.F., and G.S. Marrow. 1981. Chlorobiphenyl movement from soil to soybean plants. *J. Agr. Food Chem.* 29:757-759.

Grosse, B. 1978. Zur analytik von 3,4 benzpyren und dessen aufnahme uber wurzel und sprob hoherer pflanzen. Dissertation TU, Munich.

Harms, H. 1975. Metabolisierung von benzo(a)pyren in pflanzlichen zellsuspensionskulturen und weizenkeimpflanzen. *Landbauforsch* 25:83-90.

Harms, H., and D. Sauerbeck. 1984. Toxic organic compounds in municipal waste materials: Origin, content, and turnover in soils and plants. *Angew. Botanik.* 58:97-108.

Harms, H., W. Dehren, and W. Monch. 1977. Benzo(*a*)pyrene metabolites formed by plant cells. *Z. Naturforsch.* 32:321-326.

Iwata, Y., W.E. Gunther, and F. A. Westlake. 1974. Uptake of a PCB (Aroclor 1254) from soil by carrots under field conditions. *Bull. Environ. Contam. Toxicol.* 11(6):523-528.

Jacobs, L.W., S.F. Chou, and J.M. Tiedje. 1976. Fate of polybrominated biphenyls (PBBs) in soils. Persistence and plant uptake. *J. Agric. Food Chem.* 24(6):1198-1201.

Jansen, E.F., and A.C. Olsen. 1969. Metabolism of ^{14}C-labelled benzene and toluene in avocado fruit. *Plant Physiol.* 44:786-787.

Jury, W.A., W.F. Spencer, and W.J. Farmer. 1983. Behaviour assessment model for trace organics in soil; 1. Model description. *J. Environ. Qual.* 12(4):558-564.

Jury, W.A., W.J. Farmer, and W.F. Spencer. 1984. Behavior assessment model for trace organics in soil; 2. Chemical classification and parameter sensitivity. *J. Environ. Qual.* 13:567-572.

Kearney, P.C., J.E. Oliver, A. Kontson, W. Fiddler and J.W. Pensabene. 1980. Plant uptake of dinitroaniline herbicide related nitrosamines. *J. Agric. Food Chem.* 28:633-635.

Lichtenstein, E.P. 1980. Bound residues in soils and transfer of soil residues in crops. *Residue Rev.* 76:147-153.

Lichtenstein, E.P., G.R. Myrdal, and K.R. Schulz. 1965. Absorption of insecticidal residues from contaminated soils into five carrot varieties. *J. Agr. Food Chem.* 13(2):126-131.

Mertz, D., T. Edward, D. Lee, and M. Zuber. 1981. Absorption of aflatoxin by lettuce seedlings grown in soil adulterated with aflatoxin B1. *J. Agric. Food Chem.* 29:1168-1170.

Mertz, D., D. Lee, M. Zuber, and E. Lillehoj. 1980. Uptake and metabolism of aflatoxin by *Zea mays*. *J. Agric. Food Chem.* 28:963-966.

Moza, P., I. Scheunert, W. Klein, and F. Korte. 1979. Studies with 2,4,5-trichlorobiphenyl-^{14}C and 2,2',4,4',6-pentachlorobiphenyl-^{14}C in carrots, sugarbeets, and soil. *J. Agric. Food Chem.* 27(5):1120-1124.

Mrozek, E., and R.B. Leidy. 1981. Investigation of selective uptake of PCB by *Spartina alterniflora*. *Bull. Environ. Contam. Toxicol.* 27:481-488.

Muller, V.H. 1976. Aufnahme von 3,4-benzpyren durch nahrungspflanzen aus kunstlich angereicherten substraten. *Z. Pflanzenernaehr. Bodenkd.* 6:685-695.

Nash, R.G. 1968. Plant uptake of ^{14}C diuron in modified soil. *Agron. Jour.* 60:177-179.

Nash, R.G. 1974. Plant uptake of insecticides, fungicides and fumigants from soils. In: *Pesticides in soil and water*. W. Guenzi (ed.) Chapter 11. Pp.257-313.

Overcash, M.R., J.B. Weber, and M.L. Miles. 1982. Behaviour of organic priority pollutants in the terrestrial system: Di-*n*-butyl phthalate ester, toluene and 2,4-dinitrophenol. *Water Resources Research Inst.* 171:94.

Rao, P.S.C., and J.M. Davidson. 1982. Retention and transformation of selected pesticides and phosphorous in soil-water systems. A critical review. U.S. EPA. 600/3-82-060. 341 pp.

Ryan, J. 1986. The land treatment of appendix VII organics presented in petroleum industry wastes. In: *Land treatment- A hazardous waste management alternative*. Loehr, R.C., and J.F. Malina (eds.).

Sander, J., M. Ladenstein, J. Labar, and F. Schweinsberg. 1975. Experiments on the degradation of nitrosamines by plants. In: *N-Nitroso compounds in the environment*. Bogovski, P., and E.A. Walker (eds.). Pp. 205-210.

Sawhney, B.L., and L. Hankin. 1984. Plant contamination by PCBs from amended soils. *J. Food Prod.* 47(3):232-236.

Sims, R.C. 1982. Land treatment of polynuclear aromatic compounds. Ph.D. Thesis, N. Carolina University, Raleigh, N.C.

Sims, R.C., and M.R. Overcash. 1983. Fate of polynuclear aromatic hydrocarbons (PNA's) in soil-plant system. *Residue Revs.* 88:2-68.

Strek, H.J., and J.B. Weber. 1982. Behaviour of polychlorinated biphenyls (PCB's) in soils and plants. *Environ. Pollut.* 28:291-312.

Suzuki, M., N. Aizawa, G. Okano, and T. Takahashi. 1977. Translocation of PCBs in soil into plants: A study by a method of culture of soybean sprouts. *Arch. Environ. Contam. Toxicol.* 5:343-352.

Topp, E., I. Scheunert, A. Attar, and F. Korte. 1986. Factors affecting the uptake of ^{14}C-labelled organic chemicals by plants from soil. *Ecotoxicol. Environ. Safety.* 11:219-228.

U.S. EPA. 1979. The water related environmental fate of 129 priority pollutants. PB80-204373. Office of Water Planning and Standards, Washington, D.C.

Wagner, K.H., and I. Siddiqi. 1971. Die speicherung von 3,4-benzfluoranthen im sommerweizen und sommerroggen. *Z. Pflanzenernahr. Bodenkd.* 130:241-243.

Wagner, K.H., and I. Siddiqi. 1970. Der stoffwechsel von 3,4-benzpyren und 3,4-benzfluoranthen im sommerweizen. *Z. Pflanzenernahr. Bodenkd.* 127:211-219.

SECTION 6

EXPERIMENTAL INVESTIGATIONS

INTRODUCTION

A range of experiments was designed to investigate some of the hypotheses previously reported on plant uptake of nonionic hydrocarbons from soils. The experiments can be described simply as assessments of plant uptake under a range of conditions, using different soil types and different plant species. Uptake has been generally taken to include both root uptake and translocation and vapour uptake following volatilization from the soil surface.

Each of the experiments can be related to one another through controls so that climatic variations, occurring through the use of a greenhouse without air conditioning, could be assessed. The experiments were not designed to be definitive statements of uptake but descriptions of potential.

The following experiments were conducted.

1. An introductory experiment for familiarization with the greenhouse and operational conditions and to assess the potential for plant uptake of hexachlorobenzene (HCB), phenol, toluene, and trichloroethane (TCE).

2. An assessment of plant uptake of HCB from different soil media.

3. An assessment of plant uptake of HCB with plant age.

4. An assessment of the effects of volatilization of HCB on total plant uptake concentrations.

5. An assessment of the uptake of HCB from soil by different plant species.

Each of the experiments was similar in a number of respects.

1. Pollutants were mixed within the soil and the plants were sown as seed and harvested as adults from each pot.

2. The 5-inch-diameter plastic pots were completely lined with aluminium foil so that the polluted soil did not come into contact with the sides of the pot.

3. The soil medium consisted of a mixture of cactus soil (Franks Nursery) and silica sand (Wedron Silica Co.) to achieve various soil organic matter levels.

4. Each pot contained 600 g of dry soil material to which analytical grade chemical was added to achieve the desired pollutant concentrations.

5. The pots were watered to excess so that water collected in saucers beneath each pot.

6. The pots were spaced apart from one another.

7. Fertilizer was added at various intervals throughout experiments as a liquid feed.

8. At harvesting, watering stopped and actual harvesting did not begin until all excess water in the saucer beneath each pot had been drawn back into the pot.

9. Harvesting consisted of collecting plant roots and plant tops as separate items and taking fresh weights.

10. Polluted soil was carefully removed from plant roots.

11. All treatments were replicated at least three times.

Analyses were conducted according to U.S. Environmental Protection Agency approved methods (U.S. Environmental Protection Agency, 1982).

Time constraints may have reduced the overall value of these investigations. Although the results would have been more complete without the limitations, the experimental strategy was to assess the potential for plant uptake. It is unlikely, then, that the limitations listed below are highly significant.

1. Biological activity within the experimental pots was not assessed. Although sterilized soil materials were used in setting up the pots, there were visual signs of fungal growth towards the end of some experiments. No doubt bacterial activity occurred in the pots. This activity could have reduced the concentration of the pollutant under test through biological degradation and may not have occurred equally throughout all test pots.

2. The biological variation of the plant material under test and individual plant and species variation remain unassessed. For example, the variation in germination rate between one batch of seeds of a particular species could vary significantly from a further batch of the same seed purely through genetic difference. This difference becomes more important in the experiment where many different species are used. Wherever possible, replicates were used to attempt to overcome this variation.

3. Because harvesting both soil and plant material was destructive and thereby terminated the investigation, there was no monitoring of uptake with time.

4. No analytical scans investigated degradation products arising from biological breakdown of the pollutant under test. This may cause underestimates of soil and plant concentrations.

The experiments were all conducted in the greenhouses at the U.S. Environmental Protection Agency's T & E Facility in Cincinnati, OH. The environmental conditions in the greenhouses were monitored for temperature (°F) and relative humidity; results throughout the experimental investigations are outlined below (Table 6.1).

TABLE 6.1. ENVIRONMENTAL CONDITIONS WITHIN THE EXPERIMENTAL GREENHOUSES

Week commencing	Temperatures			Relative Humidity
	Mean	High	Low	Mean
10 Aug 1986	80	100	60	65
17 Aug	85	100	68	60
24 Aug	75	102	50	50
31 Aug	75	100	52	55
07 Sep	75	102	54	55
14 Sep	70	95	52	65
21 Sep	75	100	64	60
28 Sep	80	115	66	60
05 Oct	75	98	55	65
12 Oct	70	100	45	45
19 Oct	65	93	55	60
26 Oct	65	100	50	50
02 Nov	--	--	--	--
09 Nov	65	95	33	45
16 Nov	65	83	55	45
23 Nov	65	83	55	45
30 Nov	--	--	--	--
07 Dec	65	95	55	35
14 Dec	70	100	55	45
21 Dec	65	90	55	45
28 Dec	70	95	55	35
04 Jan 1987	65	93	57	35
11 Jan	70	80	55	35
18 Jan	65	90	53	35
25 Jan	65	88	50	20
01 Feb	70	100	55	25
08 Feb	75	105	50	25
15 Feb	75	100	53	15
22 Feb	75	100	58	20
01 Mar	70	93	58	30
08 Mar	75	105	55	15
15 Mar	75	105	60	15
22 Mar	75	100	60	15
29 Mar	70	85	60	25
05 Apr	75	100	60	25
12 Apr	75	105	60	40
19 Apr	75	110	55	35
26 Apr	75	105	60	40
03 May	70	110	55	25
10 May	80	110	60	25
17 May	80	105	55	25
24 May	85	105	65	30
31 May	85	110	70	30
07 Jun	85	110	65	30
14 Jun	85	110	70	40

EXPERIMENT TO DETERMINE THE ACCUMULATION AND PHYTOTOXICITY OF HEXACHLORO-BENZENE (HCB) IN RADISH AND CARROT GROWN IN HCB POLLUTED SOIL

Methods

A growth medium (1:1 weight ratio of cactus soil [Frank's Nursery] and silica sand [Wedron Silica Co.] resulting in an organic matter content of 5.70%) was placed in aluminum foil-wrapped 5 inch pots. Analytical grade HCB (Fischer Scientific) was mixed with the soil medium to give soil-borne concentrations of 0, 1, 10, 100, 250, 500, 1000, 2500, 5000, and 10000 mg HCB/kg of dry growth medium.

Ten radish seeds and 15 carrot seeds were planted per pot in growth medium containing a range of HCB concentrations.

The experiment began on August 12, 1986. On September 29, after 48 days of growth, the radishes were harvested, and on October 31, after 80 days of growth, the carrots were harvested. Each treatment had three replicates.

During harvesting, the vegetation was cut from the roots and vegetation samples were analyzed. The pots were allowed to stand for 3 days to allow the soil to dry sufficiently to separate the roots and tubers from the soil.

Results

TABLE 6.2. GERMINATION OF THE SEED TYPES, PER SOIL CONCENTRATION OF HCB, 30 DAYS AFTER SOWING

Proposed Soil concentration mg HCB /kg	% Seeds germinated	
	Radish	Carrot
0	77.0	91.3
1	47.0	--
10	27.0	--
100	33.0	28.7
250	3.0	--
500	17.0	--
1000	13.0	42.0
2500	47.0	--
5000	3.0	48.7
10000	10.0	62.0

TABLE 6.3. SOIL AND RADISH CONCENTRATIONS* OF HCB FOLLOWING RADISH GROWTH WITHIN THE POLLUTED SOIL FOR 50 DAYS

Concentrations in soil		Concentrations in vegetation		
Initial	Final	Root	Leaf	Radish (edible part)
0.00	0.03	0.28	0.00	0.00
5.15	0.41	6.03	0.07	0.62
2.01	1.54	8.10	0.02	0.02
2188	6.81	19.97	0.03	0.63
3994	13.08	26.7	0.01	3.09
7216	35.30	37.5	0.12	381.00
10150	56.60	24.5	0.05	665.00
5770	91.70	21.3	0.67	776.00
18200	119.90		0.28	508.00
18890	101.00	46.6	0.08	604.00

*All concentrations in mg HCB/kg soil.

TABLE 6.4. SOIL AND CARROT CONCENTRATIONS* OF HCB FOLLOWING CARROT GROWTH WITHIN THE POLLUTED SOIL FOR 50 DAYS

Concentration in soil		Concentration in vegetation		
Initial	Final	Root	Leaf	Carrot (edible part)
2188	51.8	140.9	5.16	27.18
10150	88.4	328.6	33.43	27.08
18200	2396.6	6957.0	19.23	76.22
18890	3668.0	6440.0	7.50	93.52

*All concentrations in mg HCB/kg soil.

Conclusions

This simple experiment highlighted many of the problems associated with work of this nature.

1. The germination rates of both radish and carrot seeds varied greatly, from only 3% to 77% for radish and 28.7% to 91.3% for carrot,

suggesting that the greater the number of seeds grown, the greater experimental reproducibility would be achieved.

2. This variation in germination masks any effects of the pollutant on germination, but it appears that HCB concentrations up to 1% in soil of 5.7% organic matter content do not affect radish or carrot seed germination.

3. The analytical testwork had poor reproducibility; the concentrations measured at the beginning of the experiment were not verified by the analysis. The final soil concentrations appeared unrelated to the initial.

4. When radish was grown in HCB-polluted soils, the highest concentrations (7216 mg/kg) of HCB occurred in the edible portion of the radish, with least being found in the plant leaves. Generally, concentrations in the plant tissue increased with increasing soil concentrations.

5. When carrot was grown in HCB-polluted soils, the highest HCB concentrations occurred in the root of the carrot as distinct from its edible portion, and, again, lowest concentrations were found in the plant leaves.

6. HCB concentration in the carrot root reached a maximum of 6957 mg HCB/kg following growth in soil, whose initial concentration was 18,200 mg HCB/kg and whose final soil concentration of 2396.6 mg HCB/kg.

7. This experiment highlights one of the problems in using the Root or Leaf Concentration Factor as a term describing plant accumulation of pollutants from soil. Soil concentrations of pollutants rarely remain stable, and in this experiment, a consistent trend was shown with the concentration of HCB in soil being reduced throughout the experiment, probably as degradation occurred.

HCB is a long lived pollutant, with a log *n*-octanol/water partition coefficient of 6.18 and a Henry's Constant of 0.0251. Therefore HCB would be expected to be strongly sorbed to the organic matter in the soil, and in due course to the plant root, and migrate through the soil pores in the vapour phase. Controlling the vapour migration of HCB wastes has been addressed in U.S. Environmental Protection Agency (1980).

EXPERIMENT TO DETERMINE THE ACCUMULATION AND PHYTOTOXICITY OF TRICHLOROETHANE (TCE) IN RADISH GROWN IN TCE POLLUTED SOIL

Methods

The methods outlined in the Section above, were replicated to establish this experiment. Soil concentrations of TCE were 0, 500, 1000, 2500, 5000, and 10000 mg/kg, and 5% and 10%. The soil organic matter content was 9.4% by weight.

The experiment began on August 29, 1986. On October 22, 1986, after 54 days of growth, the radishes were harvested.

Results

TABLE 6.5. GERMINATION OF RADISH SEED, PER SOIL CONCENTRATION OF TCE, 30 DAYS AFTER SOWING

Proposed soil concentration	% Seed germination
0	83
500	97
1000	87
2500	100
5000	87
10000	87
5%	83
10%	73

TABLE 6.6. SOIL AND RADISH CONCENTRATIONS OF TCE (mg/kg FRESH WEIGHT) FOLLOWING RADISH GROWTH IN THE POLLUTED SOIL FOR 55 DAYS

Concentration in soil		Concentration in vegetation	
Initial	Final	Leaf	Roots
43.1	0.086	0.713	0.274
236.0	0.084	0.484	0.174
323.0	1.316	0.180	0.094
481.0	1.576	0.153	0.374
----	0.839	1.003	1.533
1373.0	1.652	0.330	4.792
957.0	9.995	0.162	4.457
4104.0	9.473	0.122	2.685

Conclusions

TCE is not an ideal pollutant to investigate under these experimental conditions. It has a log K_{ow} of 2.17 and a high Henry's Constant of 1.46, indicating its volatility. TCE is known to be degraded by various systems (Wilson and Wilson, 1985). The experiment indicated:

1. Even soil concentrations of TCE up to 10%, in a soil of organic matter content of 9.4%, did not affect the germination rate of the radish seeds. Possibly higher concentratins of TCE than these would prove toxic to germinating seeds but these concentrations actually delayed germination until the soil concentrations had been reduced to a level that did not prove toxic.

2. The soil concentration of TCE throughout the 55 day experiment was drastically reduced so that maximum concentrations experienced by the plants at the end of the experiment were only up to 10 mg/kg.

3. TCE was found in both the leaves and roots of radish grown in the polluted soils. There was no trend of increasing plant concentrations with increasing soil concentrations, probably because of the drastic reduction in soil concentrations discussed above and TCE's volatility that allowed all plants to be exposed to TCE to a similar extent.

EXPERIMENT TO DETERMINE THE ACCUMULATION AND PHYTOTOXICITY OF PHENOL IN RADISH AND CARROT GROWN IN PHENOL POLLUTED SOIL

Methods

The methods outlined above were replicated to result in a wide range of soil concentrations of phenol. The soil organic matter content was 9.4% by weight.

The experiment began on November 3, 1986. On January 22, 1987, after 80 days of growth, the radishes were harvested, and on February 16, 1987, after 112 days of growth, the carrots were harvested.

Results

TABLE 6.7. GERMINATION OF THE SEED TYPE, PER SOIL CONCENTRATION OF PHENOL, 30 DAYS AFTER SOWING

Presumed soil concentration	Radish	Carrot
0	83	58
50	93	45
100	90	40
500	70	42
1000	53	9
2500	0	0
5000	0	0
10000	0	0

TABLE 6.8. FRESH WEIGHT* OF CARROT GROWN FOR 112 DAYS, AND RADISH GROWN FOR 80 DAYS IN PHENOL-POLLUTED SOIL

Initial soil concentration	Carrot, total production Leaf	Root	Radish, total production Leaf	Root
5.7	18.4	33.1	34.3	6.4
25.6	15.2	26.2	32.7	9.9
6.5	18.5	26.0	40.7	6.3
193.5	16.7	25.8	28.6	7.8
587.0	4.9	12.3	24.5	10.9
1408.0	0	0	0	0
1232.0	0	0	0	0
13823.0	0	0	0	0

*Fresh weight in g, concentration in mg/kg.

Conclusions

Phenol has not appeared to be the ideal pollutant to investigate under these environmental conditions. Its log *n*-octanol/water partition coefficient is 1.46, indicates a water solubility and it is degraded relatively easily by a variety of routes. Detailed conclusions follow.

1. Germination of both plant species was reduced as concentrations of phenol in the soil reached 1000 mg/kg. No seeds of either species germinated at concentrations above 2500 mg phenol/kg soil.

2. Total production, assessed as fresh weights of both species, was determined at harvesting. Carrot produced more root than leaf during its 112-day exposure, whereas radish produced more leaf than root. Overall production of both species per pot was remarkably similar at approximately 40 mg fresh material per pot.

3. Due to analytical problems, which could not be overcome, phenol concentrations in vegetation were not determined and so uptake rates could not be assessed.

EXPERIMENT TO DETERMINE THE ACCUMULATION AND PHYTOTOXICITY OF TOLUENE IN RADISH AND CARROT GROWN IN TOLUENE POLLUTED SOIL

Methods

The methods outlined were replicated to establish this experiment. Soil concentrations of toluene were 0, 50, 100, 500, 1000, 2500, 5000, and 10000 mg/kg. The soil organic matter content was 9.4% by weight.

The experiment began on November 4, 1986. On January 22, 1987, after 81 days of growth, the radishes were harvested, and on February 20, 1987, after 116 days of growth, the carrots were harvested.

Results

TABLE 6.9. GERMINATION OF CARROT AND RADISH, % OF APPLIED SEEDS, PER SOIL CONCENTRATION, mg/kg, OF TOLUENE

Presumed soil concentration	Radish	Carrot
0	87	35
50	87	25
100	73	45
500	87	47
1000	83	40
2500	90	29
5000	67	49
10000	30	2

TABLE 6.10. FRESH WEIGHT OF CARROT GROWN FOR 116 DAYS AND RADISH GROWN FOR 81 DAYS IN TOLUENE-POLLUTED SOIL

Presumed soil concentration	Carrot Total production Shoot	Carrot Total production Root	Radish Total production Shoot	Radish Total production Root
0	13.7	36.5	23.5	19.0
50	10.3	27.5	21.4	13.6
100	15.7	32.2	25.2	11.0
500	12.7	32.8	23.6	9.2
1000	16.9	37.2	22.6	8.7
2500	18.3	40.1	25.1	8.1
5000	13.9	24.8	17.2	6.8
10000	1.6	6.7	13.7	7.6

*Fresh weight in g, presumed concentration in mg/kg.

Conclusions

Analysis of soils and vegetation for toluene was also very difficult and no analytical results were obtained. The experiment has shown that the germination rate of both carrot and radish was affected by concentrations of toluene between 5,000 and 10,000 mg/kg in soil containing 9.4% organic matter. These concentrations did not prove totally phytotoxic.

EXPERIMENT TO ASSESS THE EFFECT OF DIFFERENT SOIL ORGANIC MATTER CONTENTS ON THE ACCUMULATION OF HCB IN RADISH GROWN IN HCB POLLUTED SOIL

Methods

This experiment used five growth media: pure silica sand, pure cactus soil, pure peat (Transcontinental Peat Moss Co.), and various mixtures of these materials to give a range of soil organic matter contents. These were

pure sand	0.0 %
5% peat, 95% sand	3.1 %
5:1 sand:peat	10.2 %
pure cactus soil	16.7 %
pure peat	96.1 %

Each of these soil media was treated with five concentrations (0, 100, 250, 500, and 1000 mg HCB/kg) of HCB, with three replicates of each treatment. Each treatment was sown with 10 seeds.

The experiment began on December 6, 1986, and on January 13, 1987, after radish growth of 67 days in sand and 80 days in the other growth media, radishes were harvested on February 11 and 22 and on March 10, 1987.

Results

TABLE 6.11. GERMINATION RATES* OF RADISH TAKEN AT HARVEST TIME, AFTER BEING SOWN IN HCB POLLUTED SOILS OF VARYING ORGANIC MATTER CONTENTS

Presumed soil concentrations	Organic matter contents 96%	17%	10%	3%	0%
0	47	83	50	77	30
100	33	83	50	60	67
250	47	90	53	43	27
500	47	87	30	60	40
1000	60	87	23	80	33

*At maturity, 67 days after sowing in sand and 80 days after sowing in the other growth media

TABLE 6.12. INITIAL AND FINAL SOIL CONCENTRATIONS* OF HCB FOLLOWING RADISH GROWN TO MATURITY IN SOIL OF DIFFERENT ORGANIC MATTER CONTENTS

Percent Organic Matter Contents									
0%		3%		10%		17%		96%	
Init	Final	Init	Final	Init	Final	Init	Final	Init	Final
0.5	2	4	2	3	1	0.6	1	4	0.2
203	385	74	155	158	150	207	150	335	190
270	644	340	231	233	251	495	252	243	249
457	697	598	489	532	277	670	280	514	668
456	859	1167	---	692	328	589	327	1060	1242

*Concentrations as mg HCB/kg.

TABLE 6.13. ACCUMULATION* OF HCB IN RADISH ROOTS AND LEAVES AFTER BEING GROWN TO MATURITY IN SOILS OF DIFFERENT ORGANIC MATTER CONTENTS

Organic Matter Contents									
0%		3%		10%		17%		96%	
Root	Leaf	Root	Leaf	Root	Leaf	Root	Leaf	Root	Leaf
0.6	0.00	0.01	0.00	0.03	0.00	0.1	0.00	0.1	0.00
39.2	0.00	3.9	0.01	5.6	0.00	5.0	0.00	1.5	0.00
26.8	0.02	5.4	0.03	6.0	0.01	6.4	0.01	2.3	0.00
31.8	0.01	10.1	0.01	10.8	0.01	17.4	0.01	3.1	0.00
31.2	0.01	9.2	---	7.4	0.01	10.4	0.00	4.4	0.00

*Accumulation as mass by concentration in mg.

Conclusions

This successful experiment highlights the importance of soil organic matter in sorping pollutants within the soil. Such sorption reduces the amount of any soil borne pollutant available for plant uptake and accumulation.

Detailed conclusions include the following.

1. As established previously, HCB concentrations of up to 1000 mg/kg had no effect upon the germination rate of the test species. This is the case even when the pollutant is present in pure sand or pure peat, with soil organic matter contents ranging from 0 to 100%.

2. When the presumed soil concentrations of HCB (i.e., those attempted by carefully weighing out and mixing of materials) were compared with those actually found at the start and termination of the experiment, several problems became apparent.

   a. Some HCB added to the soils could not be found in the soil after just 2 hours, i.e., the estimated time between establishing the pots and sampling the soil. This could be explained by the concept of irreversibly bound residues, as discussed in Section 2 of this report.

   b. Generally, HCB concentrations in all soils decreased with time, so that at the end of the experiment, when plant mass would be greatest, pollutant concentrations available for plant uptake would be least.

3. When the accumulation of HCB, calculated as the plant-part mass times its concentration, in the radish roots and leaves are considered, the following are concluded.

   a. Considerably more HCB accumulated in the plant root than in the plant leaf.

   b. The plant root accumulated more HCB as HCB concentrations in the soil medium increased.

   c. Considerably more HCB was accumulated in plant roots grown in pure sand, with a soil organic matter of 0%, than in pure peat, with a soil organic matter content of 100%. In sand, sorption of HCB by soil organic matter would be absent.

   d. A maximum of 39.2 mg of HCB was accumulated by radish roots grown in sand polluted by an initial soil concentration of 202 mg/kg. In a pot containing 600 g of soil, this approximates 33% of the total soil borne pollutant. If the attempted soil concentration of 250 mg/kg was, in fact, achieved, this percent changes to 26%. If the final soil concentration of 385 mg/kg is used, plant root accumulation accounted for 17% of the HCB in the pot.

EXPERIMENT TO DETERMINE THE EFFECT OF PLANT AGE ON THE ACCUMULATION OF HCB IN RADISH GROWN IN HCB POLLUTED SOIL

Methods

Two concentrations of HCB (1000 and 5000 mg/kg) were made up in soil with an organic matter content of 5.7%. Each pot was sown with 10 radish seeds on March 19, 1987, and each treatment had four replicates. Plants were harvested every 2 weeks for 14 weeks, with the final harvest being taken on May 7, 1987.

Results

TABLE 6.14. SOIL, PLANT ROOT, AND PLANT LEAF CONCENTRATIONS OF HCB, (mg/kg), WITH TIME; SEED SOWN IN SOIL CONTAINING 5.7% ORGANIC MATTER AND AN ESTIMATED 1000 mg HCB/kg.

Time, days after sowing	Soil	Root	Leaf
14	1034 (222)*	778 (164)	233 (159)
22	1889 (314)	1054 (84)	75 (45)
31	1126 (242)	1453 (184)	88 (15)
37	2059 (271)	4782 (866)	44 (11)
43	2347 (363)	3342 (485)	103 (41)
49	2398 (159)	4095 (1088)	147 (46)

*Mean of 4 replicates (Standard Error)

TABLE 6.15. SOIL, PLANT ROOT, AND PLANT LEAF CONCENTRATIONS OF HCB, (mg/kg), WITH TIME; SEED SOWN IN SOIL CONTAINING 5.7% ORGANIC MATTER AND AN ESTIMATED 5000 mg HCB/kg

Time, days after sowing	Soil	Root	Leaf
14	3193 (839)*	1103 (57)	155 (47)
22	4742 (1015)	3215 (900)	186 (63)
31	4407 (605)	2707 (339)	115 (14)
37	6987 (592)	9004 (1064)	195 (72)
43	7174 (817)	5032 (413)	52 (36)
49	5912 (765)	13249 (3498)	622 (183)

*Mean of 4 replicates (Standard Error)

TABLE 6.16. PLANT ROOT ACCUMULATION* OF HCB (mg) WITH TIME; GREENHOUSE GROWN IN A SOIL CONTAINING 5.7% ORGANIC MATTER

Time, days after sowing	Soil concentration mg HCB/kg 1000		5000	
	Root	Leaf	Root	Leaf
14	3.7 (0.7)**	0.7	5.9 (0.8)	0.5
22	3.4 (0.3)	0.6	13.3 (2.9)	1.5
31	10.8 (0.8)	1.2	29.2 (3.0)	1.7
37	108.0 (9.9)	1.2	131.6 (10.0)	4.3
43	269.2 (41.9)	3.6	421.9 (60.9)	1.6
49	264.9 (42.6)	3.3	634.0 (131)	12.9

*Accumulation as mass by concentration in mg.
**Mean of four replicates (Standard Error)

TABLE 6.17. SOIL CONCENTRATION OF HCB (mg/kg) AFTER BEING EXPOSED FOR VARIOUS TIME INTERVALS, WITH OR WITHOUT ESTABLISHED VEGETATION, IN A GREENHOUSE

Time, days after sowing	With vegetation	Without vegetation
14	1034 (222)*	1640 (145)
22	1889 (314)	2505 (462)
31	1126 (242)	861 (187)
37	2059 (271)	1834 (230)
43	2347 (363)	1771 (189)
49	2398 (159)	2432 (371)

*Mean of 4 replicates (Standard Error)

Conclusions

This was another successful experiment investigating the changes in plant accumulation of soil-borne pollutants with actual time of exposure. Detailed conclusions follow.

1. Unfortunately, soil concentrations appeared to have increased with time for both the pots with 1000 and those with 5000 mg HCB/kg soil. This is obviously not possible and must result from some analytical problem. The

concentration in the 1000 mg/kg pots had increased to 2398 mg/kg after 49 days and the 5000 mg/kg pots had increased to 5912 mg/kg.

2. Plant root concentrations also increased with time in both sets of pots. There was a 5-fold increase in the 1000 mg HCB/kg pots and a 12-fold increase in the 5000 mg/kg pots, from 14 days to 49 days exposure.

3. Plant leaf concentrations of HCB remained low throughout the experiment.

4. A large variation in the replicate pots of each treatment, as assessed by the standard error, suggests that more replicates should have been used.

5. The concentration of HCB in soil that was not planted with radish generally reflected the changes in HCB concentration found in the corresponding pots sown with radish. At harvesting, the corresponding soil concentrations were 2398 mg/kg in the pots with radish and 2432 mg/kg in the pots without.

6. Of most significance is the fact that both plant roots and leaves, grown in 1000 or 5000 mg HCB/kg soil, accumulated more HCB with increasing time of exposure. HCB mass within the radish root increased approximately 70 times, from 14 days to 49 days exposure in soil containing 1000 mg HCB/kg. The corresponding increase in the 5000 mg/kg pots was 110 times.

7. The maximum plant root accumulation of the pollutant was apparently reached after 49 days' growth in the 1000 mg/kg pots; the accumulation after 43 and 49 days' exposure remained relatively constant. That this was not the case for the 5000 mg/kg pots could reflect the equilibrium between the soil sorbed and plant available pollutant. In the 1000 mg/kg pots, all pollutant available for plant uptake had in fact been taken up by the 49th day. In the 5000 mg/kg pots, because of the larger concentration available for uptake, this position had not been reached.

8. The maximum accumulation of the pollutant by the plant roots in the 1000 and 5000 mg/kg pots, based on the corresponding soil concentration, accounted for 19% and 18%, respectively, of the added HCB.

EXPERIMENT TO ASSESS THE EFFECT OF VOLATILIZATION OF HCB FROM HCB POLLUTED SOIL ON THE ACCUMULATION OF HCB IN RADISH PLANTS

Methods

Two concentrations of HCB (0 and 1000 ppm) and nine replicates of each concentration were established. Radish seeds were sown into the polluted soils through 3/8-inch plastic tubing for all the pots, to isolate the lower leaves from the soil. The pots were then covered with aluminium foil so that only the upper portions of the tubes were exposed. Each pot was sown with four radish seeds. The experiment began on March 3, 1987, and radishes were harvested after 35 days. The pots were kept adjacent to one another.

Controls, containing no HCB and left uncovered to the atmosphere, were also established.

Results

TABLE 6.18. THE EFFECTS OF COVERING THE SOIL SURFACE ON CONCENTRATIONS OF HCB IN RADISH GROWN IN A GREENHOUSE FOR 35 DAYS IN A SOIL OF 5.7% ORGANIC MATTER AND POLLUTED BY 1000 mg HCB/kg

Plant part/ Soil	1000 mg HCB/ kg Covered	1000 mg HCB/ kg Uncovered	0 mg HCB/kg Control
Leaf	157 (33)*	242 (49)	117 (30)
Root	1045 (215)	1610 (340)	97 (114)
Soil	1553 (189)	1289 (149)	26 (6)

*Results from 9 Replicates (Standard Error)

TABLE 6.19. THE EFFECTS OF COVERING THE SOIL SURFACE ON THE ACCUMULATION (mg) (CONCENTRATION BY MASS) OF HCB IN RADISH GROWN IN A GREENHOUSE FOR 35 DAYS IN A SOIL OF 2% ORGANIC MATTER AND POLLUTED BY 1000 mg HCB/kg

Plant part	Covered	Uncovered
Leaf	0.997 (0.23)	0.896 (0.17)
Root	9.02 (1.15)	6.36 (1.23)

Conclusions

This experiment was specifically designed to quantify the volatilization of HCB from the experimental pots and to investigate the significance of the tranlocation of HCB from the plant roots to the leaves. The experimental design should have stopped gaseous pollutant uptake by the plant leaves. It was expected that the leaves of plants grown isolated from the soil surface would contain less HCB than those where gaseous uptake may have occurred. Detailed conclusions include the following.

1. The plant leaf contained higher concentrations of HCB when the soil surface was left uncovered than when it was covered. This was expected as the uptake of volatilized pollutant was stopped by the aluminium foil in those covered pots. This indicated that gaseous phase uptake by plant leaves is significant for HCB.

2. The plant root concentration was highest in the pots with uncovered soil surfaces. Reasons for this are uncertain. Possibly vapour phase transport in the soil is also significant for root sorption of the pollutant, and volatilized pollutant has been kept in the vicinity of the root, available for uptake, by the presence of the soil surface cover.

3. The soil concentration at the end of the experiment was, as expected, lowest in those pots with uncovered soil surfaces. Volatilization of the pollutant had reduced soil concentrations where the vapour phase pollutant had been allowed to leave the soil.

4. Surprisingly, large concentrations of pollutant were recovered in soil, plant roots, and leaves from pots that originally had received no pollutant loading. This clearly demonstrates the importance of vapour phase transport of HCB. Plant leaves, the first surface to be exposed to gaseous HCB from adjacent pots, showed highest concentrations.

5. The plastic tubing around the plant increased both plant root and leaf yield and the trends discussed above are reversed when accumulation of the pollutant is considered.

EXPERIMENT TO ASSESS THE UPTAKE OF HCB BY DIFFERENT PLANT SPECIES WHEN GROWN IN HCB POLLUTED SOIL

Methods

Two concentrations of HCB (1000 and 5000 ppm) with five replicates of each concentration were sown with 12 different plant species. The experiment began on March 19, 1987. Plants were harvested at various dates depending on the growth of the crop, which, in turn, partially depended on its suitability for greenhouse growth. The plants used and their harvest or exposure times were

Festuca ovina (Sheeps fescue)	97 days
Kentucky Bluegrass (Argyle)	77 days
Taraxacum officinale (dandelion)	63 days
Lathyrus latifolius (perennial sweet pea)	89 days
Sweet corn (Golden hybrid blend)	36 days
Medicago sativa Ladak (Alfalfa)	82 days
Green bean (Tendergreen)	36 days
Carrot (Danver)	82 days
Radish (Crimson Giant)	36 days
Trifolium pratense (red clover)	63 days
Beet (Early Wonder Green Top)	63 days
Fescue/Clover mix	77 days

Results

TABLE 6.20. FINAL PLANT ROOT CONCENTRATIONS (mg/kg dry weight), GREENHOUSE GROWN IN SOIL CONTAINING 2% ORGANIC MATTER AND TWO CONCENTRATIONS OF HCB

	600 mg HCB/kg		3000 mg HCB/kg	
Initial soil	1243	(41)*	4581	(170)*
Bean	3291	(166)	4614	(406)
Fescue	1101	(144)	3880	(336)
Clover	3089	(625)	4184	(353)
Radish	3479	(684)	8792	(821)
Bluegrass	1228	(92)	5366	(421)
Corn	2471	(143)	4468	(359)
Dandelion	883	(80)	2897	(991)
Alfalfa	1253	(246)	4048	(492)
Carrot	1974	(693)	5827	(892)
Beet	3372	(410)	4358	(290)
Pea	807	(60)	4506	(208)
Fescue/Clover	950	(73)	4629	(500)
Radish (no foil)	2217	(365)	6366	(656)

*Five replicates (Standard Error)

TABLE 6.21. PLANT ACCUMULATION (mg) OF HCB, GREENHOUSE GROWN IN A SOIL CONTAINING 2% ORGANIC MATTER AND 600 OR 3000 mg HCB/kg

	600 mg HCB/kg		3000 mg HCB/kg	
	Root	Leaf	Root	Leaf
Bean	36	0.7	52	0.7
Fescue	5	0.0	10	0.6
Clover	44	0.1	46	1.2
Radish	46	0.6	106	0.8
Bluegrass	10	0.0	39	0.1
Corn	37	0.3	56	1.0
Dandelion	26	0.8	60	1.0
Alfalfa	12	0.0	34	0.2
Carrot	7	0.1	15	0.2
Beet	36	0.2	46	0.4
Pea	7	0.0	41	0.0
Fescue/Clover	12	0.0	25	0.1
Radish (no foil)	31	0.2	81	0.9

*Five replicates

TABLE 6.22. FINAL SOIL CONCENTRATIONS (mg/kg) OF HCB AFTER THE GROWTH AND HARVESTING OF VARIOUS PLANT SPECIES IN A GREENHOUSE

Initial soil	1243	(41)*	4581	(170)*
Bean	1162	(118)	3699	(241)
Fescue	805	(30)	4143	(161)
Clover	655	(43)	3628	(257)
Radish	1172	(74)	3812	(129)
Bluegrass	786	(58)	4532	(128)
Corn	1111	(173)	5212	(303)
Dandelion	667	(37)	3632	(326)
Alfalfa	637	(37)	4012	(191)
Carrot	688	(47)	4314	(211)
Beet	668	(29)	4094	(224)
Pea	775	(28)	4631	(262)
Fescue/Clover	720	(30)	5582	(170)
Without vegetation	737	(35)	4330	(104)
Without foil	1075	(40)	4523	(120)

*Five replicates (Standard Error)

Conclusions

This successful experiment was designed to assess plant species differences in both concentrations and accumulation of soil-borne pollutants in plant leaves and roots. Detailed conclusions are as follows.

1. Species response to growing in HCB polluted soil varied widely. For example, after 89 days of exposure, the roots of perennial sweet pea still had a lower HCB concentration than either of the surrounding soil media. Dandelion and the fescue/clover mix were similar. On the other hand, radish root, after 36 days of exposure, contained significantly higher HCB concentrations than did the surrounding soil. Bean and carrot were similar.

2. The majority of the roots of the vegetation under test finished the experiment with higher concentrations of HCB than did the surrounding soil medium. The roots in the more polluted soils tended to finish the experiment with less HCB than did the surrounding soil.

3. When the accumulation of HCB by the different plant species is considered, radish and clover roots accumulated most from the soil where 600 mg HCB had been added; radish and dandelion roots accumulated most from the soil where 3g HCB had been added. Maximum plant root accumulation accounted for 8% of the added pollutant.

4. Plant leaves also accumulated some of the added HCB although this was always less than that accumulated by the plant roots. There were different trends between the two pollutant levels; bean, dandelion, and radish leaves accumulated most from the soil containing 1000 mg HCB/kg, whereas clover, corn, and dandelion accumulated most from the soil containing 5000 mg HCB/kg. There is no obvious reason for this. Plant leaf accumulation was always less than 1% of the pollutant added to the soil.

5. The soil concentrations after vegetation growth and removal also show a wide range. An initial soil concentration of 1243 mg HCB/kg was reduced to 655, 637, and 667 mg HCB/kg by the growth and removal of clover, alfalfa, and dandelion, respectively. Similarly, the initial soil concentration of 4581 mg/kg was reduced to 3699, 3628, and 3632 mg/kg by bean, clover, and dandelion. The comparative control concentrations, where the soil was left unvegetated within the greenhouse, were 737 and 4330 mg HCB/kg. This reduction is likely to arise from a combination of factors including degradation and volatilization of the HCB.

CONCLUSIONS

For each experiment, detailed conclusions have been given. The aim of this subsection is to present some of the broader conclusions from the experimental work.

It should be recognized that working in a greenhouse environment and not in the field presents many drawbacks. Uptake rates from microecosystems, as

in a greenhouse, have been reported up to 50 times those actually experienced in the field under normal climate conditions (Fuhr and Mittlestaedt 1982; Kloskowski et al., 1981). This is partially because the plant root is in constant contact with the pollutant and is not able to grow away from it, as would occur in the field.

In this Section, the investigation of the potential for plant accumulation of HCB from soils with different organic matter contents is reported. Because pollutants in soils are sorbed to the organic fraction of the soil and, thereby, made environmentally unavailable (Karickhoff, 1984), those soils with most organic fraction should allow least plant uptake of the pollutant. This was demonstrated. Radish accumulation of HCB decreased with increasing organic matter contents of the soil, all other environmental factors being equal. There was a substantial decrease in accumulation with a modest increase in organic matter content, from 0 to 3%. Accumulation did occur in all soils, even in those containing 96% organic fraction, but this was extremely low.

After a growth period of 67 days, maximum plant accumulation of HCB represented approximately 33% of that measured in the soil at the start of the experiment.

This investigation followed radish accumulation of the soil-borne HCB with time. There have been few similar investigations although Topp et al. (1986) showed that plant CFs decreased with time when barley was grown in HCB and pentachlorobenzene polluted soils. Because the concept of the CF includes a measure of plant mass, as the plant grows, the concentration of the pollutant within the plant becomes increasingly less.

The reported investigation showed that accumulation of the pollutant from the soil by the plant increased with time and that, even after reaching maturity, (about 49 days for radish), there was still further potential for root sorption of the pollutant. This accumulation with time probably reflects the time taken for the equilibrium in the soil (between the sorbed and liquid phases) to shift to the liquid phase and depends on the concentration of the pollutant in the soil. Plant leaf accumulation of HCB from the soil also increased with time.

Although HCB has been identified as primarily moving through soils in its vapour phase (USEPA, 1980), plant leaf accumulation of HCB was extremely low in all experiments. It would be expected that volatilization of the compound from the soil surface would cause it to accumulate in the lower leaves of the plant. This was not investigated because of the insufficient mass of lower leaves produced during the experiments.

The difference between radish accumulation of HCB when the soil surface was covered with that when it was left uncovered is reported. Leaf concentration was higher in those plants where the soil surface was left uncovered, suggesting that volatilization of the pollutant and subsequent uptake by plants actually does occur. Surprisingly, however, these plants also contained the highest root concentrations. The only obvious explanation for this is that more of the pollutant was being kept in the vicinity of the plant root for possible sorption.

In the study that investigated uptake of HCB from soil by a range of different plant species, the species were selected for being able to grow in the experimental greenhouse conditions rather than on the basis of other reported experiences of uptake. The plants under test showed a wide range in both their abilities to accumulate the pollutant and to clean up the soil in which they were growing. Alfalfa, for example, reduced a soil concentration of 1243 mg/kg to 637 mg/kg after 82 days growth.

Greater variation could be shown if further plant species were tested for their abilities to clean up soil. It remains possible, and indeed likely, that further test species could show greater affinity for soil cleanup.

These experiments have highlighted many areas where further work is needed to understand the behaviour of pollutants in soils and the influence of plants on the soil. They have also shown that the use of plants to clean up soils remains a valid concept. In one experiment, the plant accumulated about 33.3% of the applied pollutant from the soil within 67 days.

As was discussed at the initiation of this investigation, the greenhouse facilities were not ideal for the experiments but this has not prevented the collection of extremely valuable information.

REFERENCES

Fuhr, F., and W. Middlestaedt. 1982. Influence of experimental and certain environmental factors on the uptake of soil applied herbicides. *Proc. Int. Pestic. Chem.* 29:757-759.

Karickhoff, S.W. 1984. Organic pollutant sorption in aquatic systems. *J. Hydraulic Eng.* 110(6):707-735.

Kloskowski, R., I. Scheunert, W. Klein, and F. Korte. 1981. Laboratory screening of distribution, conversion, and mineralization of chemicals in a soil plant system and comparison to outdoor data. *Chemosphere*, 10(10):1089-1100.

Topp, E., I. Scheunert, A. Attar, and F. Korte. 1986. Factors affecting the uptake of ^{14}C labelled organic chemicals by plants from soil. *Ecotoxicol. Environ. Safety* 11:219-228.

U.S. Environmental Protection Agency. 1980. *Land disposal of Hexachlorobenzene waste. Controlling vapour movement in soil*. EPA-600/2-80-119.

U.S. Environmental Protection Agency. 1982. *Test methods for evaluating solid waste. Physical/chemical methods*. SW846.

Wilson, J.T., and B.H. Wilson. 1985. Biotransformations of trichloroethylene in soil. *App. Environ. Microbiol*. 49(1):242-243.

SECTION 7

FIELD TESTWORK - AN INVESTIGATION INTO PLANT UPTAKE OF 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN IN THE FIELD

INTRODUCTION

Considerable research has investigated the behaviour of pesticides in the environment and the interactions between pesticides in soil and plants (Talekar et al., 1983; Dejonckheere et al., 1976). From the work of Briggs and others (Briggs et al., 1976, 1982; Shone and Wood, 1974; Shone et al., 1974), vegetation apparently accumulates organic chemicals from nutrient solutions via root uptake, and translocation can be related to, and assessed from, the *n*-octanol/water coefficient of the chemical. This coefficient is defined as the ratio of the chemical concentration in octanol to that in water when an aqueous solution is well mixed with octanol and then allowed to separate.

Plant root accumulation of organic chemicals from solution increases as the log *n*-octanol/water coefficient (log K_{ow}) of the chemical increases and can reach many times unity. Plant shoot accumulations following root uptake and translocation reach their maximum at a log K_{ow} of around 1.8, and, as they never reach unity, this indicates passive movement of the chemical with the transpiration water (Briggs et al., 1982).

In the field, plant accumulation can be related to the concentration of the chemical in the soil solution rather than in the soil as a whole. This results from sorptive effects of the soil organic matter (Karickhoff, 1981), which can also be related to the log K_{ow} of the chemical, with the more water insoluble (or lipophilic) chemicals being sorbed to the greatest extent. The quality of soil solution is dependent upon both the water holding capacity of the soil (and, thus, the amount of water in the soil) and the amount of time the water is in contact with the sorbed pollutant.

Plant root and soil organic matter thereby compete as sites for pollutant sorption within the soil. Although it is known that pollutant sorption to soil organic matter is in equilibrium and can, therefore, be reversed (Graham-Bryce, 1967), similar information is not available concerning the behaviour of pollutant sorbed to plant roots. Therefore, with time, pollutant sorption to plant roots will possibly increase whereas that to soil organic matter will decrease.

This section is concerned with higher plant uptake of TCDD from dioxin polluted soil in the field. The aim of the investigation is to assess the extent of species variation and the degree of plant uptake of TCDD from soil under field conditions. This knowledge is essential in understanding the environmental cycling of soil borne pollutants and thus in designing remedial actions to limit their impact.

The actual concentration of any chemical in the soil does not remain constant over any length of time. Various forces remove the chemical from its immediate sphere of influence (e.g., dust blow, volatilization, and leaching) and forces that break the chemical into a simpler unit (e.g., bio- and photodegradation). Pollutant concentrations in the soil, therefore, generally decrease with time if no further pollutant additions are made. The methods most likely to be responsible for the disappearence of TCDD from soil include photodegradation, wind and water movement of contaminated particles, volatilization, microbial degradation, and biomass removal (Young, 1981).

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) is a member of the dioxin group of chemicals and is one of the most water insoluble or lipophilic chemicals found as a pollutant on hazardous waste sites. It has a log K_{ow} of 6.14 (EPA, 1979) and is one of the most long-lived pollutants with an estimated half life of 10 years (EPA, 1985). Its effect on the environment through suspected animal health effects is great and has caused much concern (Kimbrough et al.,1984; Tucker et al., 1981).

Few investigations have assessed the potential for plant uptake of TCDD from soil. Young (1981) reported typical data for TCDD concentrations in grasses, (roots = 710 ppt; crown = 270 ppt; leaves = 10 ppt) and broadleaves (roots = 760 ppt; stem and leaves = 75 ppt) when grown outside in soil containing approximately 0.6 ppb (600 ppt) of TCDD. The levels of TCDD in roots and in soil are broadly similar. Although the above ground portions of vegetation were contaminated, the test species were perennial species and the levels of TCDD may reflect soil particle contamination.

Helling et al. (1972) undertook further investigation of plant uptake of dioxins. Lakeland sandy loam with a low adsorptive capacity was treated with radiolabeled pollutants at the rates of 0.07 ppm 2,4-dichlorophenol (DCP), 0.10 ppm DCDD, and 0.06 ppm TCDD. Oats and soybean were grown in this soil and their tops were harvested at intervals to maturity. Maxima of 0.21% of the DCP and 0.15% of the DCDD and TCDD present in the soil were translocated to oats or soybean tops. Mature oats and soybean tops contained 10 and 20 ppb DCP, and less than 1 ppb DCDD or TCDD. Concentrations in oat grain or soy bean were undetectable.

The tissue content of DCP, DCDD, and TCDD decreased as the age of soybeans and oats increased. Total content increased for 15 to 20 days and then remained relatively constant. Tissue dilution (due to growth) could account for this relationship and indicated that no further uptake occurred after 15 to 20 days. Several other processes, however, such as metabolism, volatilization from the tissue, and translocation back into the roots, could

also be occurring. It is impossible to determine from this experiment which, if any, of these processes are actually taking place.

METHODS

Field Sampling

Plants growing on dioxin-polluted soil at the Minker Site, St. Louis, Missouri, were collected on November 24, 1986. The safety precautions taken during the plant and soil sampling included the use of Tyvek suits, inner and outer boots and gloves, and full-face respirators. These precautions follow normal EPA procedures.

The plants were excavated from the dioxin-polluted soil using a stainless steel trowel, which was steam-cleaned between each use. The upper portions of the plant, including stems, leaves, and shoots were carefully cut from the lower root portions of the plant with the use of stainless steel scissors, which were also steam cleaned between each use. The roots were separated from the polluted soil so that the plant root sample contained only adsorbed soil particles. The soil associated with the plant roots, i.e., that in the rhizosphere, was sampled for analysis and represented the collected soil sample.

Wherever possible, three individuals were collected to represent each different plant species sampled from the site. The individuals were collected at some distance from one another in an attempt to obtain different plant genotypes, as well as different soil concentrations from the heterogeneous site. Some 10 different plant species were assessed, which resulted in a total of 90 samples (30 plant shoots, 30 plant roots, and 30 soil samples) being forwarded for analysis.

Plant species were identified according to Steyermark, 1977.

Analytical methods

Samples were analyzed at the TMS Analytical Laboratories, Indianapolis, according to EPA QA/QC procedure. The analysis procedure was modified from one used as EPA Region VII to determine TCDD in soil and sediment samples with the use of gas chromatography and tandem mass spectrometry.

Five grams of anhydrous sodium sulfate was placed in a 10 ml serum vial with cap and septum and weighed. Approximately 5 grams of a soil sample was added and the vial reweighed. The sample was then spiked with internal and surrogate standards of isotopically labeled 2,3,7,8-TCDD. Following mixing by shaking, and extracting with acetonitrile/dichloromethane in the closed vial, an aliquot of the extract was taken and, after separation from acetonitrile, the dichloromethane was used directly for GC/MS/MS analysis.

A cleanup procedure was included for those samples that did not meet quality assurance criteria. The extract may concentrate to reduce the minimum detectable concentration. Quantification of the TCDD was based on the

response of native TCDD relative to the isotopically labelled TCDD internal standard. Performance was assessed based on the results for surrogate standard recoveries, EPA performance evaluation samples, spike recovery tests, and method and field blanks. The procedure was varied for analysis of the vegetation samples. For these samples, the extraction was carried out by Soxhlet extraction, to scale up the option A column cleanup step by a factor of 3. Solvent washes of the Option D column cleanup step before eluting the TCDD was also used.

RESULTS

Table 7.1 relates the rhizosphere soil concentration of TCDD to that in the plant root and plant shoot associated with that in the soil.

DISCUSSION

As can be seen from Table 7.1, there was a wide range of concentrations of the dioxin TCDD in soil, plant root, and plant leaf. Unfortunately, the sampling area was not as polluted as was originally believed and some samples did not contain TCDD. This reduced the value of the set of data.

The Concentration Factors (CF) of the different parts of the different plant species, as defined by Shone and Wood (1972), are given (Table 7.2).

These results show TCDD being accumulated in the plant root from the surrounding soil, in one case up to 15 times. In addition, on five occasions TCDD was recovered from the plant root but not from the soil surrounding the plant root.

Plant leaf CFs were generally zero; this showed that TCDD was usually not recovered or accumulated in the plant leaf. In two cases, TCDD was recovered from the plant leaf of *Allium vineale*, the crow garlic, although not recovered from the surrounding soil. It is not known whether this resulted from contamination or whether this fleshy, stalk like leaf of the plant related to the common onion actually showed TCDD accumulation.

As no real history of the vegetation of the site is known, e.g., seeding dates, the variation in TCDD accumulation between different plant species can not be accurately discussed, other than to say that such differences in both root and leaf accumulation existed. Plant accumulation of these long-lived pollutants depends on the time of exposure (Topp et al., 1986) as well as the local soil conditions.

The results show conclusively that plant roots sorb high levels of lipophilic pollutants from the soil. Such sorption is in competition with that occurring on the soil organic matter and could, eventually, collect all the pollutant from within the soil. From a sample size of 30, this occurred on five occasions. The use of plant root sorption as a positive soil cleanup technique through the ability of the root to collect and hold pollutants, and

the environmental fate of TCDD, needs and warrants considerable further investigation.

TABLE 7.1. THE CONCENTRATION OF TCDD FOUND IN THE SOIL AND VEGETATION COLLECTED FROM THE MINKER SITE*

Sample	Plant species	Concentration, ppb† Soil‡	Root‡	Leaf‡
1	*Festuca elatior*	2.710	7.857	0.775
2	*Festuca rubra*	0.234	0.575	ND§
3	*Festuca rubra*	ND	0.201	ND
4	*Festuca rubra*	0.393	6.06	ND
5	*Allium vineale*	ND	0.255	0.784
6	*Allium vineale*	ND	1.554	0.344
7	*Festuca elatior*	0.884	3.274	1.218
8	*Festuca elatior*	0.449	0.867	ND
9	*Carex blanda*	0.402	1.088	ND
10	*Carex blanda*	0.281	0.673	ND
11	*Carex blanda*	0.530	0.894	ND
12	*Glachoma hederacea*	ND	ND	ND
13	*Glachoma hederacea*	ND	0.426	ND
14	*Glachoma hederacea*	1.307	4.884	ND
15	*Taraxicum officinale*	8.340	10.081	ND
16	*Taraxicum officinale*	0.287	0.295	ND
17	*Taraxicum officinale*	7.208	0.168	0.495
18	*Daucus carota*	0.384	4.743	ND
19	*Daucus carota*	0.175	0.295	ND
20	*Rosa multiflora*	ND	0.063	ND
21	*Rosa multiflora*	0.384	0.395	ND
22	*Rubus* spp.	0.044	0.033	ND
23	*Geum canadense*	0.044	ND	ND
24	*Geum canadense*	ND	ND	ND
25	*Geum canadense*	ND	ND	ND
26	*Setaris viridis*	ND	ND	ND
27	*Juniperus virginiana*	ND	ND	ND
28	*Acer saccharinum*	0.764	0.409	ND
29	*Acer saccharinum*	0.466	0.898	ND
30	*Acer saccharinum*	0.135	0.363	ND

*St. Louis, Missouri, Nov. 24, 1986
†Detectable limit varied, about 0.3 ppm
‡Dry weight
§Not detectable

TABLE 7.2. THE RANGE OF ROOT AND SHOOT CONCENTRATION FACTORS FOUND FOR TCDD FOR DIFFERENT PLANT SPECIES*

Plant species	Range of root CF†	Range of shoot CF†
Festuca elatior	2.9, 3.7, 1.9	0.29, 1.38, 0.00
Festuca rubra	2.5, ∞‡, 15.4	0.00, 0.00, 0.00
Allium vineale	∞, ∞,	∞ ∞
Carex blanda	2.7, 2.4, 1.7	0.00, 0.00, 0.00
Glachoma hederacea	0, ∞, 3.7	0.00, 0.00, 0.00
Taraxicum officinale	1.2, 1.0, 0.1	0.00, 0.00, 0.07
Daucus carota	12.4, 1.7,	0.00, 0.00,
Rosa multiflora	∞, 1.0,	0.00, 0.00,
Rubus spp.	0.8,	0.00,
Geum canadense	ND§, ND, ND	0.00, 0.00, 0.00
Setaria viridis	ND,	0.00,
Juniperus virginiana	ND,	0.00,
Acer saccharinum	0.5, 1.9, 2.7	0.00, 0.00, 0.00

*Collected from a dioxin-polluted site in St. Louis.
†Concentration Factor defined as root/shoot concentration divided by corresponding soil concentration (Shone and Wood, 1972)
‡Infinity, meaning dioxin was found in the plant material but not in the corresponding soil sample
§No data, i.e., no dioxin was recovered in either plant or soil sample

REFERENCES

Briggs, G.G., Bromilow, R.H., Edmondson, R., and M. Johnston. 1976. Distribution coefficients and systemic activity. Chem. Soc. Special Publ. no 29. 129-134.

Briggs, G.G., Bromilow, R.H., and A.A. Evans. 1982. Relationship between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. *Pestic. Sci.* 13:495-504.

Dejonckheere, W., Steurbaut, W., and R.H. Kips, 1976. Residues of quintozene, its contaminants and metabolites in soil, lettuce and Witloof chicory, Belgium 1969-1974. *Pestic. Monit. J.* 10(2):68-73.

Graham-Bryce, I.J. 1967. Adsorption of disulfoton by soil. *J. Sci. Fd. Agric.*, 18:73-77.

Helling, C.S., Isensee, A.R., Woolson, E.A., Ensor, P.D.J., Jones, G.E., Plimmer, J.R., and P.C. Kearney. 1972. Chlorodioxins in pesticides, soils and plants. *J. Environ. Qual.* 2(2):171-178.

Karickhoff, S.W. 1981. Semiempirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere*, 10:833-846.

Kimbrough, R.D., Falk, H., Stehr, P., and G. Fries. 1984. Health implications of 2,3,7,8-tetrachlorodibenzodioxin (TCDD) contamination of residential soil. *J. Toxicol. Environ. Health* 14:47-93.

Shone, M.G.T., and A.V. Wood. 1972. Factors affecting absorption and translocation of simazine by barley. *J. Exp. Bot.* 23(74):141-151.

Shone, M.G.T., and A.V.Wood. 1974. A comparison of the uptake and translocation of some organic herbicides and a systemic fungicide by barley. I Absorption in relation to physicochemical properties. *J. Exp. Bot.*, 25(85):390-400.

Shone, M.G.T., Barlett, B.O., and A.V. Wood. 1974. A comparison of the uptake and translocation of some organic herbicides and a systemic fungicide by barley. II Relationship between uptake by roots and translocation to shoots. *J. Exp. Bot.* 25(85):401-409.

Steyermark, J.A. 1977. *The Flora of Missouri.* Iowa State University Press.

Talekar, N.S., Chen, J.S., and H.T. Kao, 1983. Long term persistence of selected insecticides in subtropical soils; their adsorption by crop plants. *J. Econ. Entomol.*, 76(2):207-214.

Topp, E, Scheunert, I., Attar, A., and F. Korte. 1986. Factors affecting the uptake of 14-C labelled organic chemicals by plants from soil. *Ecotoxicol. Environ. Safety* 11:219-228.

Tucker, R.E., Young, A.L., and A.P. Grey (eds.). 1981. *Human and environmental risks of chlorinated dioxins and related compounds.* Plenum Press, New York and London.

U.S. EPA, 1979. Water related environmental fate of 129 priority pollutants. Volume 1. PB80-204373.

U.S. EPA, 1985. Health assessment document for polychlorinated dibenzo-*p*-dioxins. EPA/600/8-84/014F.

Young, A.L. 1981. Long term studies on the persistence and movement of TCDD in a natural ecosystem. In *Human and environmental risks of chlorinated dioxins and related compounds.* Tucker, R.E., Young, A.L., & A.P. Gray (eds.). Plenum Press, New York.

SECTION 8

DISCUSSION

This project investigated the behaviour of organic pollutants in soils and plant uptake and accumulation of these soil-borne pollutants. The overall aim was to assess the potential of higher plants to clean up polluted soil.

Sanning (1985) identified the first steps in developing an *in situ* plant cleanup system for organically polluted soils.

1. Determine whether vegetative extraction from the contaminated soil has a high probability of being the most technically and cost effective approach at the specific site, realizing that this approach will require a substantial time period and intensive agronomic management over that time.

2. Determine whether suitable plant species (or varieties within a species) are available to accomplish the desired contaminant extraction.

3. Determine whether the site possesses, or can be readily modified to possess, soil conditions that will support optimal growth of the selected plant materials.

4. Conduct greenhouse-scale confirmatory uptake tests.

5. Confirm that the plant materials that have extracted soil contaminants can be adequately disposed of in an environmentally safe manner and that the plant mass and harvesting mechanics are realistically manageable.

From the work discussed in this report such a cleanup system, although requiring considerable further investigation, has much merit and has a high potential. Unfortunately, the time and resources required to realize the goal of soil cleanup by higher plants is likely to be great.

This report has collated much information showing that higher plants do accumulate many times the concentration of some pollutants that actually occur within the soil. There is strong evidence to suggest that those pollutants with high log *n*-octanol/water partition coefficients (log K_{ow}) are sorbed to the plant root in direct relationship to their K_{ow}. From a nutrient solution, plants can sorb up to 600 times the concentration of the pollutant occurring in the solution. Plant leaf concentrations appear to increase as the log K_{ow} of the pollutant approaches 1.8. The concentration of the pollutant in the leaf, however, never reaches that in the nutrient solution.

Evidence from soil studies is much more complex, partly because the soil system itself is much more complex. Only limited evidence is reported that plant roots accumulate more pollutant, as a concentration, than exists in the soil within which it is growing. The evidence from the simple experimental investigations undertaken as part of this project, however, collaborate the relationship between root sorption and K_{ow}. In many cases, plant roots contained four to five times the concentration of hexachlorobenzene than existed within the soil. From field data collected from a dioxin-polluted site in St. Louis, on two occasions plant root contained over 10 times the amount of dioxin found in the adjacent soil. On five more occasions, dioxin was found in the plant root but not in the adjacent soil. These results, from a total of 30, indicate that plant root accumulation of almost any pollutant can occur if time is allowed.

Higher plants can also accumulate pollutants that move in the vapour phase within and from the soil. This ability is described by Henry's Constant. Almost no data from compounds other than that from pesticides describe the importance of this mode of soil transport. Vapour phase transport is estimated to be some 30 times faster than is aqueous phase transport, so that the pollutant should reach the plant root or lower plant leaf much faster in the vapour phase than in the liquid phase. No research has been undertaken to assess plant root uptake of chemical vapours.

Once within a plant, a pollutant can be transported to many places, although some pollutants probably never leave the plant root. The extent of pollutant transport within a plant also appears related to the K_{ow} of the pollutant. Increasing evidence suggests that a wide range of compounds can be degraded by plant cells; to what extent and with what compounds this actually occurs, however, remains uncertain. Considerable further effort is needed to understand routes of plant degradation and routes of transport of pollutants within plants.

From the experimental research undertaken here, those sites likely to prove most amenable to the use of a higher-plant-accumulation system can be described.

- They would have sandy soil with low organic fractions.
- They would have high water tables so that the soils are often saturated.
- They would be polluted by long lived pollutants, with high K_{ow}s.
- They would be amenable to a long-term solution because the plant's accumulation of the pollutant increases with increasing time.

Although the species selected would depend on the site, etc., having the species able to degrade the pollutant would be desirable. The range of plant species from which selection can occur is vast.

The aim of this project has suffered throughout from a basic lack of other reported work. Many recognized priority pollutants have not been investigated for their potential to be accumulated or degraded by plants. Much of the published material is old, originating in the 1960s, and refers to the behaviour of pesticides. The dearth of information on this subject is an anomaly in our modern society.

In view of this, further research is needed:

- to determine the importance of vapour phase transport and investigate plant root uptake of vapours,
- to investigate the relationship between RCF, TSCF, and K_{ow} for compounds that occur today as pollutants,
- to investigate plant degradation of pollutants following both root uptake and translocation and vapour phase collection,
- to undertake further greenhouse trials aimed at identifying species, cultivar and individual variation in uptake and accumulation to enable selection of optimums, and
- to undertake field trials on polluted sites.

REFERENCES

Sanning, D.E. 1985. In situ treatment. Chapter 4. In *Contaminated Land. Reclamation and treatment*. M.A. Smith (ed.). Plenum Press. New York and London.