Uptake of Organic Pollutants in Plants

Litterature survey

by

Anna Hellström

Department of Environmental Assessment
Swedish University of Agricultural Sciences
Box 7050   SE 750 07 Uppsala

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Introduction

Huge amounts of synthetic chemicals are constantly released into our environment. Man-made chemicals are often referred to as anthropogenic (from Gr. *Anthropos* - a man, and *genos* - born of a certain kind) or xenobiotic (from Gr. *xen (o)* - strange, stranger, and *biosis* - way of life) since they are foreign to nature. Distributed into different part of the environment chemicals can be transported long or short distances and can also undergo a variety of reactions and transformations. Because of these many competing interactions the fate of such pollutants is not easy to predict.

Plants are the basal step in the terrestrial food web and are therefore central to both agricultural and natural ecosystems. The same features that account for accumulation and concentration of dilute resources also predispose plants for the accumulation of some anthropogenic substances. This uptake and concentration into a living organism from its environment is called bioconcentration (Bernes, 1998). The bioconcentration factor (BCF) is defined as the ratio of the concentration of a chemical in an exposed biological system to the concentration in the surrounding medium. If the concentration of a chemical in an organism is dependent on both the concentration in the medium and in the food the compound is said to *bioaccumulate*. Transfer of a pollutant from one trophic level to another leading to increased concentration is referred to as *biomagnification.* Although investigations of aquatic systems are more common some studies have been done on bioconcentration of hydrophobic chemicals in terrestrial food chains (McLachlan, 1996; Kelly & Gobas, 2001).

The pathway by which organic pollutants enter the vegetation is a function of chemical and physical properties of each pollutant, such as hydrophobicity, water solubility, and vapour pressure, as well as environmental conditions, such as temperature, organic content of the soil, and plant species. Uptake of organic chemicals into plants can occur from air or soil, depending on the properties of the compounds. Foliage presents the largest plant area for uptake from air. Many of the most problematic pollutants are hydrophobic and the large lipid covered surface of leaves provides an ideal sink for accumulation of these chemicals. Leaves, and to some extent shoots and stems, contain stomata through which gaseous molecules diffuse in and out and interact with a large hydrophobic area.

Water is a key factor in most processes that take place in plants. It delivers mineral nutrients to the shoot, transports photosynthesis products from the leaves, is responsible for turgidity and control of the openings for gas exchange (stomata), serves as substrate for biochemical reactions, and acts as coolant. Water also serves as solvent, transport medium and reactant for uptake, translocation, and degradation of anthropogenic chemicals in plant and soil. Water and solutes moves freely from soils to the interior of roots in the capillary spaces between the outer layers of cells (cortex). The inner of the root (stele), containing the transport vessels, is separated from cortex by a cell layer (endodermis) which in most roots contain the Casparian band; a waxy band acting as a barrier for transport in cell walls and the intercellular space forcing all compounds to pass through the cell membranes of endodermis (Hopkins, 1999). The area outside endodermis plays an important roll in the movement of anthropogenic chemicals since this zone present an extensive surface for the adsorption of pollutants (Trapp & McFarlane, 1995).

Transport in plants takes place in the two-vessel systems xylem and phloem. In the xylem fibrous cells provide support, parenchyma cells storage area for starch and fat, and in the main cells, tracheary elements are responsible for most of the water transport in the plant. In mature plants these tracheids are dead tissue. Water movement across the membrane is most properly described as diffusion although an osmotic gradient also exists, favouring net movement of water in one direction. Main conducting cells of phloem are the sieve elements that have functional membranes and are filled with living protoplasm. There are however no intact nuclei or vacuoles in mature sieve cells. The solutes, which mostly consist of sucrose, are moved into phloem by an active process requiring energy in the form of ATP. Solutes create osmotic gradients. Since no mechanism exists to keep non-ionic anthropogenic chemicals in the phloem sap, the concentration will not exceed the concentration in the xylem (Trapp & McFarlane, 1995).

Plants have several mechanisms to protect them from uptake and transport of toxic substances. Transport of the hydrophobic organic pollutants is limited in phloem by the nature of the chemical. Phloem and membrane transport is often not compatible because a hydrophobic compound that easily cross the membrane are not readily transported in the phloem. Anthropogenic chemicals can also be rapidly degraded by active enzymes (Trapp & McFarlane, 1995). Soil sorption limits the availability of chemicals for plant uptake. Photochemical reactions may degrade chemicals sorbed to the leaves. A rapid flux of water flushes volatile pollutants to locations where they may leave the plant.

Uptake of organic pollutants in plant has been reviewed. Paterson and co-workers (1990) reviewed the mechanisms of uptake of organic chemical contaminants by plants from soil and air, based on a compilation of 150 references documenting the fate of 70 chemicals in 88 species of plant and trees. Simonich and Hites (1994) reviewed the recent studies of organic pollutant accumulation in vegetation. A summary of published literature from the UTAB database pertaining to the uptake/accumulation, translocation, adhesion and biotransformation of organic chemicals by vascular plants was made by Nellessen and Fletcher (1993). Trapp and MacFarlane (1995) have summarised plant contamination by organic contaminants.

Uptake from soil

Organic pollutants can reach the soil by dry or wet deposition after either long-range aerial transport from diffuse sources, or from short-range transport from point sources such as industrial discharges, waste deposits, pesticide spraying etc. The contaminants are partitioned between, soil particles, interstitial water, and interstitial air, and uptake by plants may occur from the water or air phases. The fate of a specific compound in a specific soil depends on the physical and chemical properties of both the compound and the soil. The most important property is hydrophobicity, which usually is expressed as the 1-octanol/water partition coefficient (K_{ow}), or more often log Kow. Log K_{ow} spans over a wide range for different organic compounds as can be seen in figure 1. To describe the distribution of a chemical in soil the soil/water partition coefficient (K_d) is used. K_d is generally proportionally to the hydrophobicity of the compound and to the amount of soil organic matter.

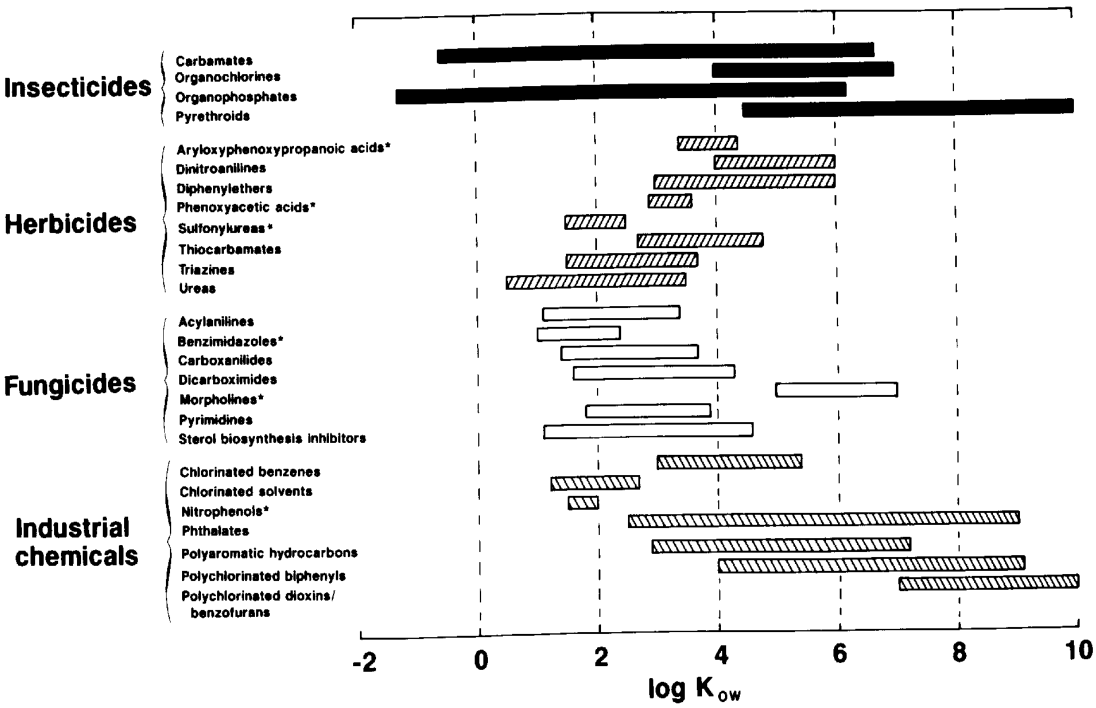

Figure 1 Ranges of octanol/water partition coefficients (as log K_{ow}) for commonly occurring compounds in various classes of pesticides and industrial pollutants. Asterisks indicate ionizable compounds whose log K_{ow} values are plotted for the undissociated molecule. From (Trapp & McFarlane, 1995).

The content of organic carbon in soil is one of the most important environmental factors influencing root-uptake of non-ionic organic compounds from soil into roots. Sorption onto organic carbon K_{oc} can be determined from K_d:

$$Koc = Kd\ 100\ /\ \%\ \text{organic carbon}$$

More hydrophobic compounds, having a higher K_{ow}, are sorbed more strongly to organic particles in the soil. This is described in a linear relationship given by Briggs (1981)

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

Where K_{om} (sorption onto organic matter) is equivalent to Koc. Hydrophobic compounds, $K_{ow}>4$, will be strongly sorbed, $K_d>10$, and moderately hydrophobic compounds, K_{ow} 2-4, moderately sorbed, K_d = 1-10, in soils with organic contents of 1-5% (Trapp & McFarlane, 1995). In most research on the uptake of organic contaminants into plants K_{oc} is used. Dieldrin uptake in carrots from contaminated soil decreased significantly (more than ten times) when 20 % brown coal was added (Bhattacharya & Douglas, 1997).

In soil compounds are also distributed between air and water. This partitioning is dependent on vapour pressure and water solubility and is described by Henry's law (Schwarzenbach, 1993):

$$K_H = P_i/C_w \quad \text{or} \quad K_H' = P_i/(C_w{*}\,RT)$$

Where P_i is the partial pressure, C_w is the concentration in water, K_H is the Henry's law constant, and K_H' is the dimensionless Henry's law constant. A common way to determine K_H' is to calculate it from a compounds vapour pressure and water solubility (Trapp & McFarlane, 1995):

$$K_H' = T/273{*}(v.p{*}10^{-5})/(22.4\ {*}W.S)$$

Where v.p. is the vapour pressure (Pa), W.S is the water solubility (mol/l) and T the temperature (K). Compounds with high Henry's law constant will have a high concentration in the vapour phase and usually a low affinity for water and they are predominately taken up via the vapour phase and are unlikely to be translocated in plants (Trapp & McFarlane, 1995). Pathways for compound with different H' are shown in figure 2.

Polar and anionic compounds move in soil-water and their mobility relative the root affects uptake.

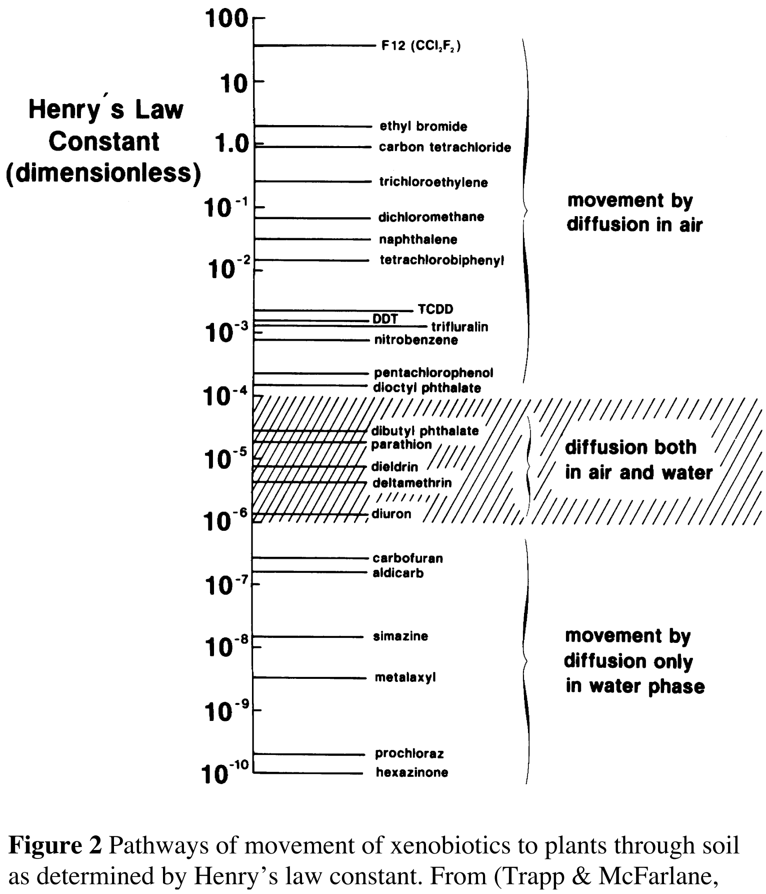

Figure 2 Pathways of movement of xenobiotics to plants through soil as determined by Henry's law constant. From (Trapp & McFarlane,

Cations are more strongly bond in soil, by the process of ion exchange, giving high K_d for simple bases and even several orders higher for doubly-charged organic cations (Trapp & McFarlane, 1995). Therefore uptake of ionised compounds is also affected by pH besides properties such as hydrophobicity and organic matter. Uptake of weak acids normally increases when surrounding pH decrease (Briggs, 1981). The non-ionic acid can pass the membrane dissociate to the anion in the plant compartment of higher pH and be trapped at that side of the membrane.

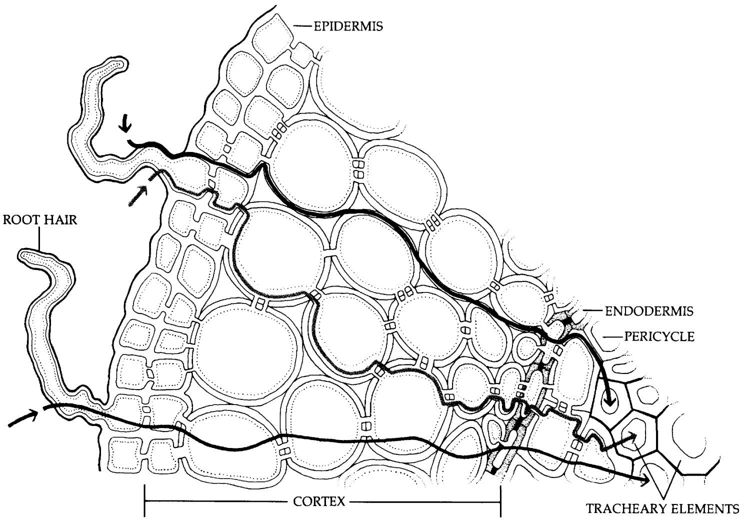

Figure 3 Pathways for the movement of water from soil into the trachery elements. From (Raven *et al.*, 1992).

When entering the root with the water stream a compound can follow three possible pathways. The apoplastic pathway, via the cell walls, the symplastic pathway in the protoplasm via the plasmodesmata, or the transcellular pathway, from vacuole to vacuole (Raven *et al.*, 1992). This is illustrated in figure 3 showing a root in section. The compound can move in the, apoplast, and thereby avoid entering the cells, until reaching the endodermis, a cylindrical sheet of cells that are tightly connected by the waxy, water impermeable Casparian band. There all molecules are forced to traverse the plasma membranes and the protoplasts of the tightly packed endodermal cells and enter the symplast to reach the xylem where they can be translocated. This barrier requires an active transport for hydrophobic compounds (Trapp & McFarlane, 1995). There is also a possibility of transport with resin or latex flows.

The efficiency of uptake by roots can be described as the ratio between concentration of chemical in roots and the concentration in the surrounding medium. This is called the root concentration factor (RCF). Brigg and co-workers (1982) showed that uptake of nonionised compounds consists of two components (1) an equilibration of the concentration in the aqueous phase inside the root with the concentration in the surrounding solution (0,82 of RCF) and (2) sorption on hydrophobic root solids. The latter component seems to become important above log K_{ow} of 1.5. In barley, Brigg's et. al. established the following relationship for carbamoyloximes and phenylureas:

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

This relationship was found to hold for uptake of a range of non-ionised compounds by a variety of plant species (Briggs *et al.*, 1982).

Many studies have been performed to investigate the plant uptake of hydrophobic compounds like polychlorinated biphenyls(PCBs), dioxins (PCDD), furanes (PCDF) and polycyclic aromatic hydrocarbons (PAHs) from soil. Most of the studies in greenhouse (O'Connor *et al.*, 1990), and in field (Fries & Marrow, 1981; Sawhney & Hankin, 1984; Webber *et al.*, 1994) of uptake of PCB, dioxins, DDT and other hydrophobic compounds from soil have shown that the only root uptake that can be seen are accumulation in the lipid-rich peels of e.g. carrot, beet and turnip. There is almost no strong evidence of transport in plants to above ground parts. No translocation of either phenols or PAHs to grain of barley grown on soil treated with two kinds of contaminated fertilisers was found by Kirchmann & Tengsved (1991). Plant uptake 2,4,6-trichlorophenol is probably no matter of concern in soils contaminated with low concentrations according to a study by Sceunert and co-workers BCR was lower than 1 for carrot, cress, maize, and beans and 2.5 for barley (Scheunert *et al.*, 1989). Roots of hydroponically grown soybean and corn adsorbed 70 % of added labelled TCDD in a laboratory study, but no translocation was detected (McCrady *et al.*, 1990). Thus, contamination of leaves and shoots seems to be due to uptake from air in most cases (Fries & Marrow, 1981; Bacci & Gaggi, 1986; O'Connor *et al.*, 1990; Webber *et al.*, 1994; Heinrich & Schulz, 1996).

There is, however, one interesting exception. Hülster and co-workers found active transport of dioxins in two members of the genus *Cucurbita*, zucchini (*Cucurbita pepo* L. cv. Giromontiina) and pumpkin (*Cucurbita pepo* L. cv Gelber Zentner) (Hülster *et al.*, 1994). Cucumber (*Cucumis sativus* L. cv Delikatess), which, like zucchini and pumpkins, belongs to the family of Cucurbitaceae did not show any uptake of dioxins from soil. This behaviour is not yet fully understood. Some more studies on uptake of chloro-organic compounds in *Curcubita* (White *et al.*, 2003) and other crops

(Mattina *et al.*, 2000) has been published. The case is different with many “modern” pesticides. These are often more polar than the classical persistent environmental pollutants and can be transported in the vascular system after having entered the plant. They are defined as systematic pesticides. Binding of pesticides in the apoplastic pathway of stems showed, in a laboratory experiment, to be related to their degree of lignification and to the hydrophobicity of the pesticides (Barak *et al.*, 1983).

The main concern for human health regarding uptake of organic pollutants from soil is the risk of contamination of agricultural fields and accumulation in crops. There are some studies of uptake of environmental contaminatns present in sludge or compost (Beck *et al.*, 1996; Kolb & Harms, 1996). These studies point in the same direction as earlier mentioned studies, no translocation through the plant to edible parts above ground, but edible roots and tubers such as carrots can be contaminated. However, volatile compounds may contaminate edible leafs and fruits after volatilisation and transport through the air. There is also the possibility that fruits and shoots near soil can be contaminated directly by soil.

Roots provide anchorage and energy storage and undergo both physical and chemical interaction with the soil. It is in many cases accurate to imagine as much of the plant below ground as above. Considering differences between species and environmental conditions most roots actively modify their environment in one way or another. The rhizosphere bacteria and fungi are nourished by organic nutrients exuded from roots, some micro-organism contribute to plant health by modifying soil acidity, adding chelating agents, producing antigens to ward of pathogens, and expanding the effective absorption area resulting in increased water and nutrient uptake. Currently the information regarding the mycorrhizal influence on uptake and chemical metabolism is insufficient.

Remediation

Plants and the associated microbial communities in the rhizosphere offer a potentially important treatment strategy for biological remediation of chemically contaminated soils. Most experiments show degradation in soil by micro-organisms rather than uptake in plants as the main cause of dissipation of organic chemical from the soil. Bioremediation is often facilitated in the rhizosphere probably because of the ability of the roots to modify their environment (Todd et. al. 1993). There is, however, also possibility of bioaccumulation in plant that can be used to enhance remediation of contaminated soils. Burken and Schnoor showed both uptake and metabolism of the herbicide atrazine in poplar trees (*Populus*) grown in bioreactor, but the seedlings were taken from 3-4 years old trees (Burken & Schnoor, 1997). Adsorption of naphthalene by roots of two plant species (tall fescue, *Festuca arundinacea* Schreber and alfa-alfa, *Medicago sativa* L.) with different lipid content has been quantified in a greenhouse experiment indicating that lipid content is a controlling factor in adsorption of naphthalene onto plant roots (Schwab *et al.*, 1998). Greenhouse experiment investigating the use of vegetation to increase degradation of anthracene and pyrene in soil (Reilley *et al.*, 1996).

Uptake from air

The waxy layer of cuticle serves as a barrier to water loss and a rate-limiting barrier for uptake of xenobiotics into plant leaf cells. The cuticle consists predominantly of lipid material, synthesised by epidermal cells and deposited on the outer surface. The cuticular membrane consists of an outer region of soluble and polymerised aliphatic lipids and an inner layer containing large amount of various cell-wall polysaccharides. A pectin-rich layer attaches the cuticular membrane to the cell wall. More or less all plant species also have an outer epicuticular wax layer. Principal component of the cuticle membrane is the lipid polyester cutin. Cutin is an insoluble polyester of cross-linked hydroxy-fatty acid and hydroxyepoxy-fatty acids and waxes the precise intermolecular structure is still uncertain. Incorporated in the cutin are structures of fibrillae and lamellae. The fibrillae are composed of polysaccharides, which may exhibit a distinctive reticulate pattern while lamellae may contain wax compounds (Kirkwood, 1999).

Organic compounds can reach plant surface as free gas molecules, dissolved in water droplets, or sorbed to particles. Deposition from the gas phase or sorbed to particles is called dry deposition, while deposition of contaminants dissolved in water is called wet deposition. The deposited compounds can be incorporated in cuticular lipids, diffuse through the lipid layer and eventually be translocated by phloem, or contaminants may enter the plant through stomata as a gas. It has been suggested that beside the lipid component of the cuticle there also exist an aqueous route consisting of pores, carbohydrate strands and lipid interfaces (Price, 1982; Paterson *et al.*, 1990). Welsch-Pausch and co-workers (1995) found that dry gaseous deposition was the principal pathway of Cl_4-Cl_6 dioxins and furanes (PCDD/F) in greenhouse and out-door experiments with welsh ray grass (*Lolium multiflorum*). Two similar field studies were made by Simonich and Hites and Nakajima and co-workers(1994; 1995) concerning deposition of polycyclic aromatic hydrocarbons (PAH) to a number of plant surfaces (needles, leaves, seeds, and bark from sugar maple (*Acer saccarum*) and white pine trees (*Pinus strobus*) and azalea leaves (*Rhododendron oomuraski*)

Uptake from air into plants will be influenced by temperature, air pollutant concentration, plant species and properties and content of lipids content, time of exposure, whether the pollutant is in the gas or particle phase and properties of the compound such as hydrophobicity, molar volume and volatility.

Hydrophobicity is, as for other uptake routes, a very important factor for foliar uptake. In general compounds of intermediate hydrophobicity, log K_{ow} = 1-3, are taken up and translocated more easily through the cuticle than compounds outside this range, according to Trapp and McFarlane (1995) Unlike in roots there are no endodermis for molecules to pass before reaching the transport stream when compounds are applied to foliage and shoot thus allowing a more efficient movement of polar compounds. Translocation of hydrophobic compounds is limited by their sorption onto plant solids including the cuticle itself. They are also less readily translocated via phloem transport because of low or non-solubility. On the contrary is the large lipophilic surface that the plant foliage constitutes an ideal collector for hydrophobic compounds. Surface sorption and uptake into needles increased with hydrophobicity according to Schreiber and Schönherr (1992).

There is also some evidence for the influence of molar volume on uptake through plant leaves. Bauer and Schönherr (1992) have correlated the solutes molar volume with the mobility in the outer layer of the cuticle. The rate constants of desorption and the molar volume showed good correlation. How size of solutes and temperature affect diffusion in plant cuticle was also investigated by Baur and co-workers (1997).

The uptake rate and mobility of chemicals in cuticles from different plant species differ considerably (Riederer & Schönherr, 1984; 1985; Keymeulen *et al.*, 1993; McCrady, 1994; Baur *et al.*, 1997). The experiments of Riederer and Schönherr on the accumulation and transport of 2,4-dichlorophenoxy acetic acid (2,4-D) in enzymatically isolated plant cuticles shows a wide variation between species (Riederer & Schönherr, 1984; 1985). Content and composition of lipids and foliage area can be species-specific properties influencing uptake. Some studies has suggested that pollutant concentration and rate constants should be normalised to the lipid concentration of the vegetation or its surface area, especially when directly comparing different species and tissues (Schreiber & Schönherr, 1992; McCrady, 1994; Simonich & Hites, 1994). A problem with this is the difficulties to correctly determine lipid content in vegetation. Some lipophilic compounds in plants are volatile, others are hard or impossible to extract quantitatively. There is also to little knowledge which lipids are important for uptake of organic pollutants. Uptake can of course also be affected by the condition of the plants. Uptake of the herbicide 2,4-D in soybean is, e.g., influenced by plant water status (Kogan & Bayer, 1996).

Temperature has in laboratory experiments shown to influence the partition coefficient for uptake in foliage (Baur *et al.*, 1997; Keymeulen *et al.*, 1997). However partitioning of PCB between air and rye grass (*Lolium multiflorum*) in laboratory (using fugacity meter) showed that under environmental conditions the temperature dependence of the partitioning coefficient did not influence the plant concentration of most semivolatile organic compounds (SOC:s). The slow uptake/clearance kinetics prevents the plant/air system from reacting quickly to the new equilibrium state resulting from the temperature-induced change in the partitioning coefficient. Simonich and Hites (1994) defined a vegetation-atmosphere partition coefficient (K_v) that account for vegetation concentration of semivolatile compounds (SOCs), the lipid content of vegetation and the atmospheric gas-phase SOC concentration. They believe that the long-term partitioning is governed by gas-phase concentration and temperature and that there exists an annual cycle of partition of SOCs into the waxy layer at low temperatures (in spring and fall) and a volatilisation back in the summer. Also, Franzaring points out the temperature as the most important factor governing accumulation of gas-phase organic air pollutants (Franzaring, 1997).

Octanol-air partition coefficient, K_{oa}, is a parameter used to understand the sorption of a pollutant to leaf surfaces. K_{oa} can be calculated from Henry´s law constant, H´, and K_{ow} (Paterson *et al.*, 1991) or measured (Harner & MacKay, 1995; Keymeulen *et al.*, 1997). Harner made these measurements by passing air saturated with octanol through a glass wool column coated with a solution of the compound in octanol and measured the compound in the outlet air by collecting it on an absorbent trap. The authors suggest that K_{oa} be measured directly, especially for highly hydrophobic organic compounds. They also showed that K_{oa} is strongly dependent on temperature. Keymeulen and co-workers used a headspace method to determinate cuticle-air partition coefficient (K_{ca}) for four monocyclic hydrocarbons (benzene, toluene, ethylbenzene, *m*-, *p*-, and *o*-xylen) and showed good correspondence between log K_{ca} and log K_{oa}. A laboratory study supports that plant-air partition coefficient is linearly correlated with K_{oa} (Tolls & McLachlan, 1994).

Difference between measured (Riederer & Schönherr, 1984) and from determined permeance (Riederer & Schönherr, 1985) calculated leaf-air partition coefficient gave the conclusion that the cuticle membrane is not homogenous. According to Schönherr and Riederer cuticles are heterogeneous membranes and may be looked at as composite membranes made up of a thin outer skin which is the barrier limiting rate of uptake and transport and an inner compartment which is responsible for its sorptive properties (Schönherr & Riederer, 1989). Kinetics of uptake has been described as a one-compartment model for the entire leaf. Bacci et. al has described uptake and clearance of organic contaminants into azalea leaves in greenhouse experiments in a one-compartment model: the so called "azalea model" (Bacci *et al.*, 1990b). More recent experiments indicate that needle uptake are better described by a two-compartment model (Reischl *et al.*, 1987; Schreiber & Schönherr, 1992; Hauk *et al.*, 1994; Tolls & McLachlan, 1994). Many authors have noted that equilibrium may never be reached during the length of experiment (Paterson *et al.*, 1991; McCrady & Maggard, 1993; Hauk *et al.*, 1994; Tolls & McLachlan, 1994; Umlauf *et al.*, 1994; Hung *et al.*, 2001). Selective solvent extraction methods have been developed to separate these two compartments (Reischl *et al.*, 1987; Hauk *et al.*, 1994; Strachan *et al.*, 1994; Umlauf *et al.*, 1994). A fast response to temperature and initial exposure has been found by Simonich et. al. and Nakajima et. al. and are presumed to be due to accumulation by the outer leaf or needle compartment (Simonich & Hites, 1994; Nakajima *et al.*, 1995). Keymeulen and co-workers exposed virgin pine trees to toluene, ethylbenzene, and xylen under field conditions for several years (Keymeulen *et al.*, 1993). It took 5-6 month to reach equilibrium in most cases. This can be due to slow partitioning into an inner leaf compartment .

Biomonitoring

Many studies have been made on using pollutant concentration in vegetation as indicators of atmospheric contamination levels. This has been reviewed in some papers (Paterson *et al.*, 1990; Kylin, 1994; Simonich & Hites, 1995; Smith & Jones, 2000)

There are advantages to use plants instead of ordinary air sampling. Vegetation integrates contamination over time and is much easier and cheaper to collect than air samples. The use of vegetation to qualitatively indicate organic pollutant atmospheric contamination is valid as long as the mechanism of plant uptake is considered. Different species have been used for biomonitoring persistent organic pollutants within cities, countries, continents, and on global basis. Scots pine (*Pinus sylvestris*) (Eriksson *et al.*, 1989; Calamari *et al.*, 1991; Jensen *et al.*, 1992,Tremolada, 1996 #448; Safe *et al.*, 1992; Strachan *et al.*, 1994; Juuti *et al.*, 1995), spruce (*Picea abies*), (Reischl, 1988; Weiss, 1998) Saxifrage (*Saxifraga oppositofolia*) (France *et al.*, 1997) are example of species used and also for identifying point sources. Most studies on uptake from air are done on leaves or needles but there are some studies on bark (Simonich & Hites, 1994).

Evergreen plants such as conifers are well suited for biomonitoring of persistent organic pollutants both on local, regional and global level. They can be sampled all year around and several year-classes of needles can be found on the individual trees. Biomonitoring of organic contaminants with conifers has been used to observe geographic and temporal patterns of atmospheric organic pollutants (Eriksson *et al.*, 1989; Jensen *et al.*, 1992; Tremolada *et al.*, 1996; Weiss, 1998). Conclusion drawn from those are that higher concentration in needles of the pesticides DDT and lindane (γ-hexachlorohexane [γ-HCH]) are found closer to spraying areas, α-hexachlorohexane (α-HCH) is uniformly spread throughout Europe probably because of long-range transport and PCB and HCB in needles seems to be indicators of industrial activities. The accumulation of polycyclic aromatic hydrocarbons (PAHs) in vegetation has been investigated in several studies (Kylin, 1994; Simonich & Hites, 1994; Wagrowski & Hites, 1997; Bakker, 2002). A preliminary Swedish investigation of 24 PAHs at 9 sites near Stockholm and two Estonian sites was performed in 1993 showing elevated concentration near roads and industries (Kylin, 1994). PAH burdens on a mass per total leaf area were determined in urban, suburban and rural vegetation in northeastern USA to quantify the ability to remove PAHs from air. PAH burdens in rural areas were on average 10 times lower than in urban areas. The calculated PAH flow was 160 t /year from the atmosphere to vegetation. Vegetation scavenged about 4 % of the total amount of emitted PAH (Simonich & Hites, 1994).

Sampling along a latitudinal transect on Ellesmore Island in the Canadian High Arctic (76°-83° N) was undertaken to determine the most likely influx pathways of OC pollution to this region. At seven sites the sums of six organchlorine groups (toxaphene, HCHs, CBz, Chlordane-related compounds, DDT, PCB) was determined in saxifrage. The authors claim that they found a close relationship between the OC concentrations and the plant cesium-137 activities. The r_ for the relationships between OC concentrations and caesium activity ranged from 0.42 to 0.82 (France *et al.*, 1997)

Transport and metabolism

With exception of hormone-like chemicals, there is no evidence of active uptake and transport for anthropogenic chemicals (Trapp & McFarlane, 1995). Passive uptake and transport is controlled by diffusion, solubility in water and in the cuticular membrane. Generally, this can be explained by physical properties such as hydrophobicity and acid strength affecting the reversible partitioning of nonionised compounds onto the plant solids of the stem or the ion trapping in for example the phloem for weak acids. Partitioning of chemicals to materials in the stem increases with increasing K_{ow} (McCrady *et al.*, 1987). Metabolism is more difficult to predict and may differ markedly between species unlike the transport processes. Live cells, especially near the cambium and phloem, may provide an area for rapid metabolic degradation of anthropogenic chemicals (Trapp & McFarlane, 1995)

The most important property for transport of nonionised chemicals in plants is the hydrophobicity. It determines the ease of movement across membranes. Partitioning of compounds onto plant solids limits the long-distance transport and is also a function of hydrophobicity. Movement of nonionised compounds is analogous with column chromatography. Briggs and co-workers defined a stem concentration factor, SCF (Briggs *et al.*, 1983)

SCF=conc in stem/conc in external solution

He found the relationship:

$$\log \mathrm{SCF}_{\mathrm{macerated}}\ \mathrm{stems} = 0.95 \log K_{ow} - 2.05$$

Movement of 17 substituted benzenes , under pressure through stem segment of soybean, with transpiration stream gave rice to accumulation at sites with the greatest transpiration in the shoot (McCrady *et al.*, 1987).

Movement from root to shot is described with the transpiration stream concentration factor TSCF (Briggs *et al.*, 1982) Determined analogous with RCF:

TSCF=conc in xylem sap/conc in external solution

usually estimated from measurements of the amount of compound accumulated for a known amount of transpiration if necessary corrected for the degradation rate of the compound

$$\mathrm{TSCFcorrected}=(\mathrm{TSCFapparent}*t*k)/[1-\exp(-kt)]$$

Briggs and co-workers have measured TSCF for two series of nonionised compounds (O-methylcarbamoyloximer and phenylureas in barley) spanning over a wide range of K_{ow} showing an optimum at log K_{ow} 1.8 (Briggs *et al.*, 1982).

Other literature data also fit the curve reasonably well. Sicbaldi and co-workers also found a Gaussian curve relationship when studying pesticides from different chemical classes in soybean although with the maximum at a K_{ow} of approximately 3.0 (Sicbaldi *et al.*, 1997). To reach the vascular system compounds must pass the barrier between the apoplastic and symplastic system and TSCF is a measure of the ability to do this. Polar compound should have difficulties passing the lipophilic membrane of endodermis and indeed TSCF is reduced as log K_{ow} decrease. Why TSCF also decrease when log K_{ow} raise is not fully understood (Trapp & McFarlane, 1995). Partitioning onto lipid-like phases can be one explanation. Apparently more hydrophobic compounds cross the endodermis much less efficient than water.

Nonionised compounds move more easily in the greater water flow in the xylem thus they can move freely between the phloem and xylem tissue. The uptake of weak acids is pH dependent and the polarity increases markedly for the ionised form of a compound. Therefore, the movement of weak acids across the membranes can change with pH. Carboxylic acid having pK_a values between 3 and 6 produce anions typically 3 to 4 log K_{ow} units more polar than the undissociated parent acids. Therefore, the SCF for weak acids depends not only on K_{ow} but also on pK_a, the permeability ratio (PAH/PA-) and on the pH of the xylem sap and the adjacent plant compartments and also TSCF for those compounds is dependent on pH of the surrounding medium. For example Uptake of 2,4-D with surrounding pH 4 gave a TSCF = 4.14 and at pH 7 TSCF = 0.04 (Briggs *et al.*, 1987).

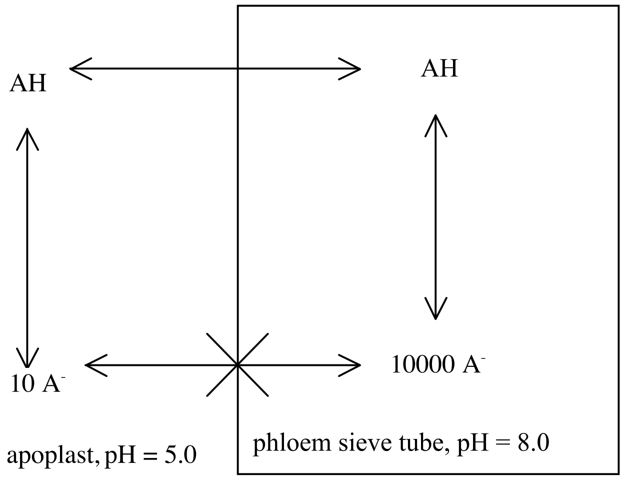

Figure 4. Accumulation of weak acids within cells by the ion trap effect. From (Trapp & McFarlane,

Because of the lipophilic membrane between xylem and phloem and the much greater volume of flow (50- to 100-fold) in the xylem the majority of phloem-mobile xenobiotics are weak acids. Polar nonionised compounds do not cross the membrane and the hydrophobic compounds cross the membrane but diffuse back into the greater volume of xylem. Weak acids accumulate in the phloem by ion trapping in the more basic phloem (pH~8) relative to the apoplast (pH ~5.5) (fig 4). Transport in the phloem depending on two processes first the compound need to enter the phloem through the membrane and then be transported effectively in the phloem. For optimal diffusion into phloem the acid should be as undissociated as possible (high pKa) and the undissociated molecule ought to have log K_{ow} ~1.8. But to remain and be transported long distances in the phloem, the compounds should have a low pK_a and the small amount of undissociated molecules should be very polar log $K_{ow} < 1$ to remain in the phloem.

One of the compounds shown to be transported most efficiently is maleic hydrazide (Trapp & McFarlane, 1995). The pK_a of maleic hydrazide is 5.65, which is almost optimum for accumulation. On the other hand, the log K_{ow} is -0.63, optimal for remaining in phloem. Glyphosate, a common herbicide, is also translocated extremely well in the phloem. This is a complex compound with three acidic functions and one basic amino group.

Metabolism in plants resembles liver metabolism in many ways and oxidation is the most frequently observed transformation reaction. Reductive processes are less common, hydrolytic reactions may also occur. Conjugation takes place in two ways. Soluble conjugates can be formed introducing glucoside, gluthatione, amino acid or malonyl to the functional group existing in the xenobiotics or formed in the transformation reaction. Incorporation in biomolecules gives insoluble or bound conjugates. Many aromatic or heteroaromatic compounds with hydroxyl, carboxyl, amino or sulfhydroxyl groups are known to be deposited into lignin or other cell wall components. The basic different between plant and liver metabolism is that conjugates are predominantly excreted in animals but in plants they are compartmentalised and stored within plant tissue (Trapp & McFarlane, 1995).

The OH- derivatives of atrazine seems to represent the greater part of the metabolites developed by corn seedlings The parent compound transformed very readily after entering the seedling (Raveton *et al.*, 1997). An outdoor pot study by Nakagawa et. al. also concluded that hydroxyatrazin was the main metabolite (Nakagawa *et al.*, 1996). The pyrimidyl moiety of the fungicide cyprodinil (4-cyclaopropyl-6-methyl-2-(phenylamino)pyrimidin was shown to be taken up more readily then the phenyl part when studying soil-bound residues of ^{14}C-labelled compound in methanol-extracted soil (Dec *et al.*, 1997). Harms (1992) compared the phytotoxicity and metabolic fate of pesticides in cell cultures of plants and seedlings grown under aseptic conditions and concluded that the metabolites were qualitatively the same. A study of uptake and transformation of benzene and toluene by plant leaves with a similar method was made by Ugrekehelidze (1997).

Methods

The focus of research on plant uptake has been on laboratory studies and comparatively fewer field studies have been done. There are methods developed for cell cultures and ground plant parts (Langebartels & Harms, 1985; Harms, 1992; Raveton *et al.*, 1997), and separate plant parts like cuticles or leaves (Barak *et al.*, 1983; Riederer & Schönherr, 1984; Langebartels & Harms, 1985; Riederer & Schönherr, 1985; Schönherr & Riederer, 1989; Bauer & Schönherr, 1992; Keymeulen *et al.*, 1997; Kömp & McLachlan, 1997). Other have developed advanced laboratory system to study whole plants (Topp *et al.*, 1989; McCrady *et al.*, 1990; Trapp *et al.*, 1990; Schroll & Scheunert, 1992; Hauk *et al.*, 1994; Tolls & McLachlan, 1994; Sicbaldi *et al.*, 1997), or greenhouse and outdoor pot and lysimeter experiment (Fries & Marrow, 1981; Bacci & Gaggi, 1985; 1986; Bacci *et al.*, 1990a; Bacci *et al.*, 1990b; Bacci & Calamari, 1991; Bacci *et al.*, 1992). Cell cultures is often used for studies of metabolism in plant cells (Harms, 1992; Raveton *et al.*, 1997). Harms made a comparing study of phytotoxicity and metabolic fate of pesticides in cell cultures of plants and seedlings grown under aseptic conditions. Advantages of using cell cultures are the cost counted in time and equipment compared to growing whole plant under controlled conditions. It is easy to make repeated experiments and the answers are quick and rather free from disturbing factors. There is no competing metabolism by micro-organism and it is easy to control photodegradation. The major drawback is that we do not get the whole picture. Metabolism in a mature plant or a seedling can differ greatly from that in a cell culture. Langebartel et.al.(1985) used a fractionating procedure with both chemical and enzymatic method to investigate residues of pentachlorophenol bound to different cell wall compartments. Barak and co-workers used ground stems to relate binding of pesticides to lignification and to hydrophobicity of the pesticides (Barak *et al.*, 1983).

Riederer and co-workers using enzymatically isolated cuticles to investigate adsorption transport and permeability in plant leaves. Some of the experiments are repeated with the polymer matrix left after extraction of the soluble cuticular lipids (Riederer & Schönherr, 1984; 1985). Schönherr and

Bauer presented a technique to measure the unilateral sorption from the outer face of an isolated cuticle (Schönherr & Baur, 1996). The apparatus used was a desorption chamber and a lid between which the cuticular membrane was sandwiched (Schönherr & Riederer, 1989). Determination of the plant cuticle-air partitioning coefficients with enzymatically isolated cuticles was made by (Keymeulen *et al.*, 1997). The method was based on gas phase equilibrium of target compound in closed vials and their analysis by headspace gas chromatography.

The fugacity meter described by Kömp and McLachlan measures the concentration of a chemical in air in equilibrium with a solid phase (Kömp & McLachlan, 1997). It consists of a glass column in which the plant material is packed. An air stream is then passed through the column in such a way that equilibrium between the surface of the vegetation and the air is established. In this way the equilibrium partitioning can be measured after only brief periods of contamination since the equilibrium of SOCs within the plant is much more rapid than the transport to the plant .

Many studies have been made on uptake by the roots of the whole plant and subsequent translocation in the xylem and the strategy usually are to apply the xenobiotics in nutrient solution and measure the amount collected in different parts of the plant. Sicbaldi and co-workers measured concentration of pesticides directly in xylem sap collected from stem or leaf bases using pressurised root chamber (Sicbaldi *et al.*, 1997).

When investigation the pathways of organic pollutant into plants it is often needed to separate the air movement from soil to foliage from the systemic transport from root to leaf. Schroll et. al. present a closed laboratory system consisting of a modified desiccator that make it possible to separate determination of both plant pathway as well as a complete mass balance of ^{14}C (Schroll & Scheunert, 1992). It is a further development of the, by Topp and co-workers, earlier used equipment (Topp *et al.*, 1986). McCrady and co-workers separated shoots from the roots and the hydroponic solution in exposure chambers consisting of two canning jars one inverted over the other (1990).

Something in between laboratory and field studies are outdoor lysimeter experiments including simulation of climate soil and biotic parameters. Bacci and co-workers (1985; 1986; 1990a; 1990b;

1991; 1992) used greenhouse with controlled air flux temperature and light for study of uptake and release kinetics organic compounds in azalea leaves. Outdoor pot experiments with contaminated soils have for instance been done by Nakagawa and co-workers and by Fries and Marrow (1981; 1996). Hülster and co-workers designed field experiment on contaminated soil with conventionally grown zucchini, fruits grown without soil contact, plants grown in pots with uncontaminated soil buried in the contaminated soil so that fruits and low growing leaves are in contact with contaminated soils, and plant grown in uncontaminated soil 1.5 m above ground (1994)

Studies of seedling can be misleading and caution should therefore be observed when modelling and considering seedling experiments for verification of modelling results. In growing seedling most development occurs in the roots, materials and energy are derived from the seed, photosynthesis and transpiration are often very limited, biochemical reaction differ dramatically from those of mature plants.

Photodegradation and volatilisation on plant surface should be taken into consideration when studying plant uptake. Volatilisation chambers can be used for determining the volatility of pesticides from plant surfaces (Starr & Johnson, 1968; Dörfler *et al.*, 1991)

The distribution is normally measured by autoradiography following application of radiolabeled compounds (Fries & Marrow, 1981; Briggs *et al.*, 1982; Briggs *et al.*, 1983; Langebartels & Harms, 1985; Topp *et al.*, 1986; Scheunert *et al.*, 1989; Schroll & Scheunert, 1992; Dec *et al.*, 1997). One disadvantage with this technique is that it shows only the position of the radiolabel and does not identify the compound. A way to achieve more information is to labelling different parts of the molecule as Dec did when studying cyprodinil uptake from soil into barley (Dec *et al.*, 1997).

Some field studies are made on uptake mechanism. Reischl et. al. analysed distribution of DDT DDE α-and γ-HCH, HCB in spruce needles sampled in northern Bavaria. They compared the content in the wax with that in the remaining of the needle concluding that DDT and DDE stays in outer of the needle and HCH an HCB are also found inside the needle (Reischl *et al.*, 1987). Umlauf et. al. confirmed this by exposing spruce needles with PCBs DDT, DDE, tetra- penta- and hexachlorobensen, and α-and γ-HCH in laboratory chambers (Umlauf *et al.*, 1994). Compounds with higher molecular weights (PCBs, DDT and DDE) were easily extracted from the needles while the compounds with lower molecule weight (chlorobenzenes and HCHs) seem to penetrate into the interior of the needle and took longer time to extract. Kylin et. al. evaluated a method with longer extraction time for the outer compartment (Kylin *et al.*, 1996). However, it should be remembered that the definition of the outer and inner compartments of needles or leaves can only be made operationally and that no absolute definition is, as yet, possible. One possible biochemical definition of three compartments is, 1) the epicuticular wax 2) the cuticle lipids 3) the inner lipids of the needle .

Strachan and co-workers sampled pine needles along a transect from northern Norway to southern West Germany (Strachan *et al.*, 1994). They compared calculation of concentration on area basis with calculation on fresh weight basis. Water content was almost the same in all samples and the two calculations gave similar interpretations. They also studied sampling methodology and found that the number of sampled trees and the age of the trees are not important factors, the facing direction might be of concern if local sources exist but the sample height of the trees is an important factor. A comparison of using dry weight or lipid weight as basis for PAH concentrations in a number of plant parts, among them pine needles, during the growing season showed that the lipid concentration had a large effect on PAH concentration, especially in needles (Simonich & Hites, 1994). On the other hand the lipids in needles and other plant parts are very diverse regarding physical and chemical properties. Therefore, measuring the amount of them can be difficult and also to know which of them that are important for the uptake.

Models

Because of the large number of organic compounds present in the environment there are tools needed for interpretation and prediction of the fate of chemicals in plants. One possibility to achieve this is mathematical models that combine the physiochemical properties of chemicals with anatomical and physiological properties of plants. Models have been developed to integrate available knowledge of the complex interactions and to aid in presentation of plant functions and help make predictions about chemical fate. There is everything from simple mathematical relationship to advanced models consisting of several compartments. There are model taking the whole plant into consideration (Trapp *et al.*, 1990; Dowdy D & McKone T, 1997; Hung & Mackay,

1997) and those modelling specific parts, for instance uptake in cuticle/leaves (Paterson *et al.*, 1991; Tolls & McLachlan, 1994; Deinum *et al.*, 1995)

Ryan et.al presents a procedure to group chemicals for their relative potential for plant uptake on their chemical and physical properties (Ryan *et al.*, 1988). Dowdy and McKone predicts plant uptake from calculated molecular connectivity index (Dowdy D & McKone T, 1997).

Many models are based on fugacity. Fugacity is a compounds tendency to "flee" a system (from Latin *fugere*, to flee) (Schwarzenbach, 1993). It is a way to describe a relative chemical potential of a compound in a system. When a compound is in equilibrium between two phases in the environment the concentration differ in the two media but the fugicity is the same. Fugacity quotients are used to studying food chain bioaccumulation (McLachlan, 1996). The approach is to divide the fugicity of a compound in the organism by the fugicity of the surrounding phase. Fugacity f, with unit of pressure (Pa), is an equilibrium criterion which is linearly related to concentration C (mol*m^{-}3) through a fugacity capacity Z (mol*m^{-}3*Pa^{-}1), where:

$$C=Zf$$

The difference between using partitioning coefficient and fugacity is only the formulation.

A three-compartment (leaf, stem and root) fugacity model applied on bromacil in soybean under hydroponic conditions was presented by Hung and McKay (1997). The model is believed to give acceptable accurate prediction for risk assessment of exposure to contaminants consumed either directly from vegetation or indirectly in natural and agricultural food chains.

A methodology for assessing congener-specific vapour-particle partitioning and photolytic degradation rates of dioxin and dioxin-like compounds and to assess environmental concentration associated with uptake of vapour phase chemicals by plants was presented by Chrostowski and co-workers (1996).

Reflections and future research

Uptake of organic compounds in plants is a large area of research with many aspects to consider. Contamination of agricultural crops and the possible accumulation in the food chain is the risk scenario most people find alarming because it concerning human health directly. There is also the ecotoxicological aspect. Organic pollutant can affect plants when taken up. Accumulated chemicals can reach soil when the plant wilt and disturb the microbial ecosystem or reach the ground water. Plants probably play an important roll in long rang air transport of semivolatile organic compounds over terrestrial areas.

Bioconcentration in plants can be of use for other purposes. Remediation of contaminated soils can be achieved to some extent by uptake in plants even if most of the effect seen is due to microbiological degradation. Plants, and especially evergreen conifers, can be used for biomonitoring concentration and movement of semivolatile organic compounds in air.

The large amount of chemicals and plant species make it impossible to analyse every combination especially taking different environmental factors into account. The large diversity of species concerning such as lipid content, foliage and root area, metabolism and other biochemical properties and the large diversity of chemical properties among the organic pollutant make it hard to find generally applicable relationships to predict the fate of organic compounds in plants. Upon that the diversity of the whole environment must be taken into account. However with our knowledge about physical and chemical properties of different chemical classes and physiology and biochemistry of plants in combination with experimental experience we can make some predictions about possible scenarios.

It seems that most effort has been put on laboratory experiments and in most research areas concerning uptake in plants more field studies are needed. Details of mechanism are often better studied in controlled laboratory experiments, but the experience of field studies is needed to fully understand the broad relationships.

In the field of uptake from soil one of the most interesting research result is the discovery of translocation of dioxins in members of the genus *Cucurbita*. The uptake and possible translocation of hydrophobic compounds in pumpkins and zucchini and related species should be further studied. Both if there is some genus specific transport system and if other species or other hydrophobic compounds show the same behaviour.

An interesting research area according to uptake from air is the use of plants as biomonitors. Large continuous programs to monitor organic air pollutants are expensive. A great deal of the cost is field-sampling equipment. If it were possible to use the natural sampling surface that evergreen conifers constitutes it would be feasible to monitor larger areas. There is, however, a need to study the mechanisms more thorough to know if we get a momentous picture or a long-term sampling when we analyse the plants.

Furthermore it is necessary to keep up with the release of new chemicals. The brominated flame retardants are, among others, a new source of alarm. Those are for instance found in sludge spread on the fields and it is easily claimed that those hydrophobic compounds are not taken up in the crops. There are, as we have seen, possible that some plants translocate even very hydrophobic compounds to eatable parts and there are several evidences that lipid-rich roots like carrots accumulate hydrophobic compounds.

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