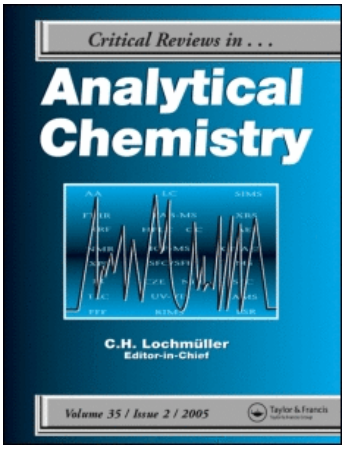

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Modeling of Uptake of Xenobiotics in Plants

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Modeling of Uptake of Xenobiotics in Plants

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Xenobiotics constitute a potential danger to both life and health of humans. The ignorance of properties of xenobiotics used, as well as of the processes they undergo during agrotechnical activities or in plants' inner circulation, may evoke negative effects on the whole ecosystem. Examining the process of sorption of xenobiotics allows us to predict the behavior of pesticides in different systems, to predict the type of processes they undergo, and to determine the main ways of they penetrate plants. The models of pesticides' behavior in plants also allow us to specify management of their microelements. This article points out the basics for determining the process of sorption modeling, describes processes during uptake, and explains the role of phloem and xylem in these processes.

Keywords analytical methods, modeling, plants, sample preparation, uptake, xenobiotics

The use of pesticides had been documented already in 1763 with the application of tobacco extracts to kill the plague of greenfly (1). The continuous use of pesticides over a period of 250 years resulted in their spreading into all elements of the ecosystem. Actually, pesticides can be traced in all parts of Earth. Their nearly ubiquitous presence in the environment necessitates a continuous development of adequate sample preparation and determination methods. Pesticides are used to eliminate "negative" biological factors which are present in the environment. However, many pesticides provide a potential threat to environmental equilibria and therefore they need to be exactly monitored (2).

The presence of xenobiotics in all parts of the ecosystem requires a careful consideration of different analytical strategies for their qualitative and quantitative determination. These strategies will depend on the nature of the sample matrix in which they are to be determined (e.g., atmosphere, water, soil, or plants). According to the complexity of the various sample matrices, all parameters influencing the analytical cycle need to be considered. In order to characterize the migration path of pesticides in nature, all parts of an ecosystem have to be analyzed carefully.

In general, the properties of the pesticides to be determined as well as the characteristics of the sample matrix are the dominating factors for the selection of a proper sample preparation methodology. In the case of an analysis of pesticides in soil, their volatility and solubility in different solvents can be considered as important influential parameters. Thus, for a determination of volatile organochlorine pesticides (OCPs) in soil samples, for example, headspace solid-phase microextraction can be used (3). For the extraction of pesticides that are well soluble in organic solvents, accelerated solvent extraction or other liquid extraction procedures may be used (4). Valuable alternatives to isolate pesticides with high degrees of recovery are supercritical fluid extraction (SFE) and solid-phase extraction (SPE) (5). For an analysis of pesticides in aqueous samples, such as surface or groundwater and rain, SPE is preferentially used to overcome the ecological drawbacks of conventional liquid-liquid extraction (6–9). For the analysis of pesticides in air

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samples, headspace solid-phase microextraction or adsorption of the analytes in sorption tubes or on filter resins can be applied (10–13).

The analysis of pesticides in selected parts of an ecosystem can be shown in representative examples. A typical adaption of an analytical procedure for the determination of OCPs in the environment to the complexity of sample matrices has been described by Mukherjee and Gopal (14). For the analysis of herbicides in river water, soil, and carrot samples, gas chromatography with flame photometric detection was described by Kataoka et al. (15). A thorough investigation of triazine herbizides in environmental samples has been reported by Dean et al. (16); a determination of residual chlorinated pesticides in rainwater has been documented by Ahmed et al. (17).

The diversity of the sample preparation methods and of the final analysis techniques allows one to qualitatively and quantitatively specify the xenobiotics that underwent the uptake process in a plant (18–20).

The purpose of this article is to consider the modeling of the uptake and distribution phenomena of xenobiotics in plants. For this, it is important to take into account the background of uptake processes in plants and to describe the processes taking place during uptake according to construction and chemical composition of a plant. In order to reveal the complexity of the process, the factors influencing the entire procedure are studied by modeling. Consequently, it is possible to display the role of phloem and xylem with respect to the transport of xenobiotics in plants. The intended purpose is a proper consideration of the involved parameters to enable a correct modeling of the uptake of the xenobiotics.

THEORY OF MODELING

Modeling is a set of actions that serve to establish mathematical instructions by the use of which it is possible to describe the real system—the examined systems, to quantitatively characterize the physical, chemical, or biological phenomena that take place in the investigated system. Modeling focuses on investigating real systems in different conditions, both external and internal, and then to draw conclusions from the processes taking place in order to eventually create a mathematical model capable of describing the systems or processes without their being carried out in reality (Figure 1).

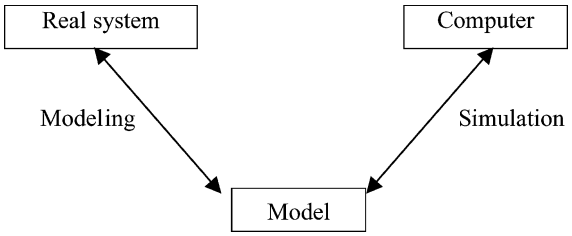

FIG. 1. Relationship and differences between modeling and simulation (21).

A model in that technology is a set of mathematical instructions that serve to generate the data that would describe a given phenomenon or process under examination.

A real system is that part of space in which the phenomena or processes we find interesting take place. Such systems may be natural or artificial. For practical reasons modeling of artificial systems is easier due to elimination of a series of factors that could interfere with the process of model creation. Natural models are characterized by a high degree of complexity and by the multiplicity of factors that influence the final effect, which complicates or even makes it impossible to establish a model for the phenomena or processes examined.

As noted above, the term modeling denotes the interdependence between a model and a real system. In this case, the creation of a model aims at obtaining the compatibility in the following equation:

$$\text{The data received from the real system} = \text{the data received from the model} \quad [1]$$

For Equation 1 to be true for the model created and for the examined real system, it is necessary to apply a series of verifications in order to improve the created model. The improvement mainly involves modification of the mathematical equations in the model so that they reflect the processes and phenomena taking place in the real system with a greater degree of probability. Zeigler distinguished (21) three legitimacies of a model, which are described below according to the degree of probability in reflecting a real state:

replicative legitimacy—the generated data are consistent with the data drawn from the real system;
predictive legitimacy—it is possible to assure the consistency of both data groups before the data from a real system are obtained; and
structural legitimacy—the model reflects the way in which the real system works in order to generate a given reaction.

The interdependence between a model and a real system called modeling is described. Creation of a model describing a given phenomenon aims at using that model in the future for carrying out simulations of selected phenomena on a computer, without the necessity of examining those phenomena taking place in a real system. A series of interdependencies between a model and a computer is called a simulation.

THE ROLE OF PHLOEM AND XYLEM IN UPTAKE

Basic Parts of Plants and Their Functions

Plants are complex organisms and they usually consist of a number of basic parts, such as: root, stem, leaf, and fruit or seed.

Each of these plant parts has specific functions due to which a plant has a chance to survive in certain conditions. The task of a root is to draw water and mineral salts from the soil; it also stores nutritive substances and fixes the plant solidly in the ground. A

stem is responsible for transporting nutritive substances from roots to leaves, and it has certain mechanical functions. The main functions of a leaf are photosynthesis and transpiration. The above description provides only the basic functions of given plant parts. The structure of certain plant parts is different depending on the plant species, which may influence its role in the plant's functioning.

Xylem

Xylem, also called the timber or wood, is the conducting tissue that distributes in a plant water and mineral salts drawn from the soil by the roots. Xylem constitutes heterogeneous tissue containing lignified elements and is composed of: vessels, wood fibers, wood—parenchyma, and coils.

The coils have the shape of elongated cells narrowed at the end. On their walls, there are minute holes through which the transportation of water solutions takes place. Apart from the coils, xylem also contains pipe-shaped vessels. The vessels transport water solutions better than the coils do, as they are not blocked up like the coils (22).

The details of transport processes that take place in xylem are described in the contribution by Bollard (23), who took into consideration the characteristics of the transported substances—nitrogen, phosphorus, iron, and pesticides. Hsu and coworkers studies xylem translocation of cinmethylin in detopped soybean in a pressure chamber (24). Hartung et al. described the transport of abscisic acid in xylem (25).

Phloem

Phloem transports nutritive substances generated in the leaves to other parts of a plant. Phloem consists of (Figure 2): sieve pipes, arranged in vertical chains of cells which have lengthened shape, plastid, cellulose walls, pores, and plasmatic membrane.

The transportation of xenobiotics in a plant may take place from a cell to a cell (short-distance transportation), or in the tissues of two autonomous conduct systems, such as phloem and xylem (long-distance transport). Water plays a very important role in the transportation of various chemical substances in plants. Among the many literature sources dealing with that issue, the contributions of Steudle deserve special attention. Steudle dealt with details about the flow of water through the root system of a plant (27, 28). Patrick and Offler (29) showed the phloem transport of nutrients in plants with regard to the influence of hydrostatic pressure (P source), and osmotic pressure (π source) (Figure 3).

The overall model that considers the function of phloem and xylem was introduced by Boersma, Lindstrom, and Childs in 1991 (30). Those authors indicated in their work that phloem and xylem constitute parallel ways of transportation of water, solutes, or photosynthesis products in a plant. Their model involves the following elements:

- water uptake by roots;
- water transport driven by a gradient of total water potential through roots, stem, and leaves in both xylem and phloem;
- carbohydrate transport in phloem driven by a gradient of positive pressure;
- coupling of xylem and phloem in the source and sink regions;
- water vapor flow from intercellular spaces to the atmosphere; and
- control of water vapor loss and carbon dioxide uptake through stomata.

The foregoing model provides information concerning the influence of water on the transportation of nutrients in plants.

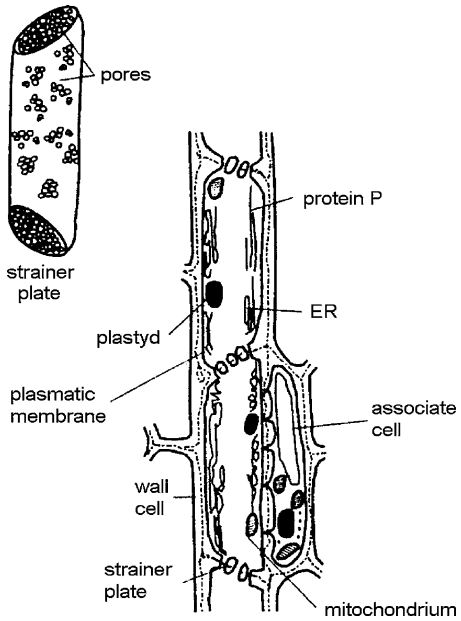

FIG. 2. Structure of phloem (26).

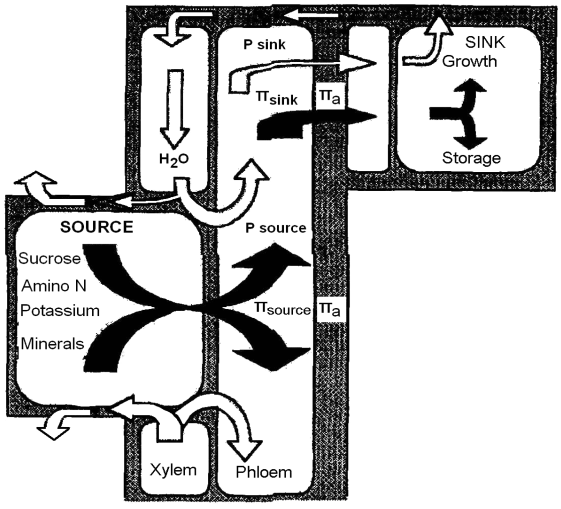

FIG. 3. Model of Patrick and Offler (29).

Among the contributions dealing with the phloem in an overall manner, Wardlaw (31), Fischer and Oparka (32), Hsu and Kleier (33–40), MacRobbie (41), and Van Bell (42) and others (43–49) deserve special attention. The character of transport that takes place in the phloem and xylem was dealt with by Peterson (50), who distinguished between three xenobiotic transportation paths in a plant:

- apoplastic—xenobiotics are unable to pass through a membrane—xylem;
- symplastic—xenobiotics pass through a membrane—phloem; and
- ambimobile—xenobiotics can move in phloem and xylem.

TRANSPORT OF XENOBIOTICS IN PLANTS

Sorption of Xenobiotics from Soil

The size of load in which xenobiotics will undergo changes of sorption from soils to the root system depends on properties of xenobiotics and their relationship to chemical properties of the components included in the roots.

The first law of Fick describes the mass stream of xenobiotics from soil solution to the root system and this mass stream is shown in the following equation (51):

$$N_{dk} = (K_{AW} * D_{P,ef} + D_{W,ef}) * (C_z - C_k/K_{RW} * 2 * l * \pi)/ln\, R_2/R_1 \quad [2]$$

where

N_{dk} = mass stream of xenobiotics adsorpted from soil solution to the root system,
K_{AW} = air/water partition coefficient,
K_{RW} = root/water partition coefficient,
$D_{P,ef}$ = coefficient of effectivity diffusion from air pores of soil [m^2/s],
$D_{W,ef}$ = coefficient of effectivity diffusion in water pores of soil [m^2/s],
C_z = concentration in soil solution [kg/m^3],
C_k = concentration in root [kg/m^3],
L = length of root [m],
R_1 = radius of root,
R_2 = radius of zone enclose root.

The root concentration factor (RCF) has been introduced by Briggs et al. (52) and describes the uptake of nonionized chemicals by plants with nonwoody stems:

$$\text{RCF} = \text{(Concentration in roots)/(concentration in external solution)}$$
$$\log(\text{RCF} - 0.82) = 0.77 \log K_{ow} - 1.52 \quad [3]$$

The RCF is used to describe: concentration factors of the transpiration stream, concentration factors in the roots, and the stem correlated with the octanol/water partition coefficient.

The factors influencing the *o* sorption process are: equilibrium of concentration in the water phase in roots, and concentration in external solution and sorption compounds in lipophilic parts in roots. Briggs investigated the value of RCF for barley. It is evident, that an increase of the K_{ow}-octanol/water partition coefficient also results in an increase of the RCF. Briggs investigated the influence of the pH value on the RCF and found that an increase of the pH value results in a decrease of the RCF.

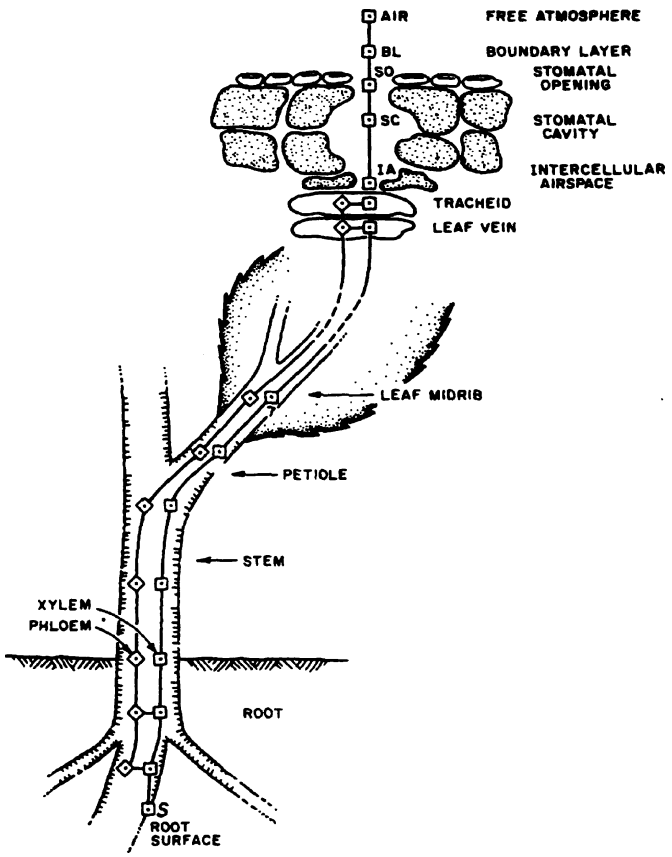

FIG. 4. Xylem and Phloem transport pathways (30).

Transport of Xenobiotics from Root System to Stem

The transport of xenobiotics to the stem has been described by Trapp and Mc Farlane (51) in Equation 4:

$$N_{tl} = Q_W * C_{ks} \quad [4]$$

where

N_{tl} = mass stream of xenobiotics to the stem (kg/m^3)
Q_W = transpiration flow of water
C_{ks} = concentration of xenobiotics in xylem.

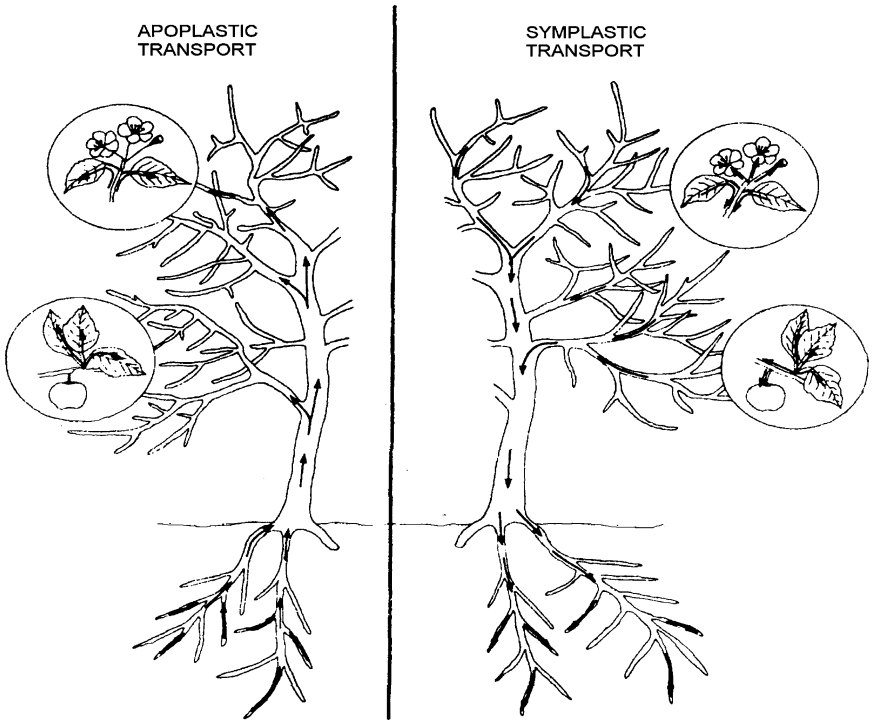

FIG. 5. Apoplastic and symplastic transport (50).

The so-called transpiration stream concentration factor (TSCF) describes translocation of the absorbed chemicals from the roots to the shoots.

$$\text{TSCF} = \frac{\text{(concentration in transpiration stream)}}{\text{(concentration in external solution)}}$$

Briggs investigated relationships between TSCF and log K_{ow} for nondissociated compounds. The result of this investigation is shown in Equation (5).

$$\text{TSCF} = 0.788 - [(\log K_{ow} - 1.78)^2/2.44 \qquad [5]$$

A maximum value of TSCF can be observed at log $K_{ow} = 1.78$. Similar investigations have been conducted for pesticides by Hsu and coworkers (54). The result of their investigations is summarized in Equation 6:

$$\text{TSCF} = 0.7 \exp -(\log K_{ow} - 3.07)^2/2.78 \qquad [6]$$

The TSCF exhibits a maximum at log $K_{ow} = 3.07$.

Transport of Xenobiotics in Stem

Transport of xenobiotics in phloem from leaf to the stem is described as:

$$N_{fl} = Q_f * C_l/K_{\text{lw}} \qquad [7]$$

where

N_{fl} = mass stream of xenobiotic in phloem from leaf to stem [kg/s],
Q_f = flow in assimilation stream (m^3/s),
C_l = concentration in leaf (kg/m^3),
K_{lw} = leaf/water partition coefficient in assimilation stream.

Transport of xenobiotics from stem to fruit can be described as:

$$N_{fo} = Q_f * C_l/K_{lks} \qquad [8]$$

where

N_{fo} = mass stream of xenobiotics from stem to fruit (kg/s),
Q_f = flow in assimilation stream (m^3/s),
C_l = concentration in leaf (kg/m^3).

Transport of Xenobiotics to Fruit-Seed Region

Fujisawa and coworkers (55) proved that the stream of xenobiotics to reach the fruit-seed region is dependent on:

- availability of xenobiotics to the transpiration stream in xylem,
- availability of xenobiotics to the transpiration stream in phloem, and
- decrease in concentration of xenobiotics by degradation and metabolism.

The overall quantity which can reach the fruit-seed region is quantitatively described by the Equation 9:

$$O = \text{UTSCF} * \beta * Q_W * \gamma * C_w \quad [9]$$

where

UTSCF = Upstream Transpiration Stream Concentration Factor,
β = water in transpiration stream,
Q_W = all water to reach the fruit,
γ = concentration of xenobiotics in transpiration stream, which does not undergo changes,
C_w = concentration of xenobiotics in external solution.

PROCESSES THAT TAKE PLACE DURING UPTAKE

It is possible to distinguish the following factors that decide on the proportions of xenobiotic uptake processes in plants, and on their transportation in the plant system (56–59):

- physicochemical properties of active substances;
- the sort of applied sprinkling, the volume and dose of an active substance;
- parameters of the surroundings: temperature, humidity, pressure, direction, and speed of wind, contents of water and mineral salts in the soil; and
- properties and structure of the plant we sprinkle.

While examining the xenobiotic uptake process in plants we should take into consideration the occurrence of the following processes: diffusion, adsorption, absorption, osmosis, etc.

Diffusion

Diffusion is a phenomenon of transportation of one type of substance cells in relation to another type of substance cells in the same phase (e.g., gas, liquid, or solid phase). As a result of diffusion processes, transportation of substance cells from one environment (characterized by a higher concentration rate) to another environment (characterized by a lower concentration rate) takes place. The process of diffusion lasts until the state of balance is reached, that is, the state in which the concentration of a given substance is identical in each location of the surroundings. The speed of diffusion in one direction is illustrated by the first Fick's principle (60):

$$dm/dt = -(Dq * dC)/dx \quad [10]$$

where

dm/dt = speed of substance transfer,
dC/dx = concentration rate of a C substance spread in a direction x,
D = diffusion quotient,
q = cross-section.

Due to a very limited diffusion speed in fluids and solids, while considering the structure of a plant, it is possible to contend that diffusion plays a minimal part in long-distance transport, and that it matters only in the case of short-distance transport within the limits of a couple of adjacent cells. The diffusion process will also have a negligible meaning by the sprinklings, as in these cases other factors—the strength and direction of wind; sprinkling parameters, including the capacity, concentration, and size of drops—will be most important.

Osmosis

Osmosis is a phenomenon independent of the energy expenditure, and it denotes spontaneous movements via the membrane, in accordance with the rate of concentration and pressure on both sides of the water particle's membrane. The membranes of plant cells are selectively permeable. In plants due to the occurrence of osmosis, it is mainly water transportation that is carried out but, apart from this, there is also gas transportation (CO_2). Not only the osmosis phenomenon, but also certain proteins—aquaporin—are responsible for transporting water via the membranes.

Adsorption

Adsorption is an effect of change of concentration of a substance on the surface of another substance. Plants adsorb gas or water solution on the surface of the leaf, stems, or root system. There are two types of adsorption:

1. physical adsorption—caused by forces of intermolecular interaction; and
2. chemical adsorption—caused by the creation of strong bonds between adsorbent and adsorbate.

Freundlich's adsorption isotherm was the first one proposed for adsorption description (59):

$$a = kp^{1/n} \quad [11]$$

where

a = quantity of adsorption matter,
k, n = constants,
p = pressure.

This equation is simple and has been widely used in science, in the character of an empirical equation, for qualitative purposes. However, the equation has no serious theoretical bases.

A better-reasoned equation of the isotherm of adsorption finds additional support in a theory published by Langmuir (60). On the surface of an adsorbent, a definite number of active places is found. On every active place, only one particle of adsorbate can undergo sorption. The chemical bond with the adsorbate is strong enough for the particles to not shift places on the surface. On the surface of adsorbent, a monomolecular

layer of adsorption is created. This phenomenon as well as Equation 12 is accounted for in (62).

$$\theta = kp/1 + kp \qquad [12]$$

where

θ = degree of covering of the adsorbent's surface,
k = constant,
p = pressure.

According to Langmuir the adsorption rate increases at first in proportion to pressure, next this growth gradually lessens and, with the pressure high enough the gas adsorption attains constant size due to the lack of free active centers.

Langmuir's theory assumes the monomolecular character of the adsorption layer. The theory taking into account multimolecular layers on the surface of adsorbent is called the potential adsorption theory, which was introduced by Eucken (63) and Polanyi (64).

This theory assumes that multimolecular layers have a diffusive character and their density depends on their distance from the surface of adsorbent. Potential theory of adsorption does not propose definite equations of isotherms of adsorption. Such equations are substituted by characteristic curves of adsorption.

The succeeding theory of adsorption is the theory of multimolecular adsorption introduced by Brunauer, Emmett, and Teller (BET) (65). In this theory of adsorption on the surface of an adsorbent there is a layer of adsorbate created, on which another layer of adsorbate is created, and so forth. As a result of this process on the surface of adsorbent, a complex of many adsorbate layers potentially may be created. The BET equation takes the following form (65):

$$\theta = [Cp/p_s]/(1 - p/p_s)[1 + (C - 1)p/p_s] \qquad [13]$$

where

θ = degree of covering,
p = external pressure,
p_s = pressure of the saturated vapor over the flat surface,
C = constant.

Harkins and Jura (66) proposed an isotherm of adsorption based on the creation of an adsorbate membrane on the surface of adsorbent, which is considered to be monomolecular or characterized by constant thickness. The equation of adsorption isotherm by Harkins-Jura (HJ) (66) follows:

$$\log p/p_s = B - A/v^2 \qquad [14]$$

where

p = external pressure,
p_s = pressure of saturated vapor over the flat surface,
A, B = constants,
v = volume of the adsorbed vapors.

Absorption

Absorption is a phenomenon in which the penetration of a substance to a phase of another substance in the process of diffusion takes place. The process of absorption consists of two main stages: during the first stage the adsorption takes place, and during the second stage the diffusion inside the adsorbent takes place.

Accumulation

The processes of accumulation are the excessive accumulation of selected components in certain parts of a plant. These processes have different courses depending on the sorption properties of given parts of plants, which can absorb and accumulate selected components to which they later show greater affinity.

Metabolic Processes

Metabolic processes embrace the whole of chemical transformations which the absorbed xenobiotics in a plant undergo. As a result of a metabolic process, xenobiotics undergo transformations into other compounds. Metabolic processes are characteristic to a certain group of compounds, characterized by definite chemical properties. It is necessary to point out that numerous products of metabolic processes of transformations are more toxic than the substrates. Rouchaud and coworkers studied, for example, the metabolic pathway for benomyl and its metabolics in melon plants (67).

Uptake

Among the contributions dealing with uptake in an overall manner, Burt and Corbin (68) investigated uptake, translocation, and metabolism of propham by wheat, sugar beet, and alfalfa. Similar investigations of ions were conducted by Chandler et al. (69) for uptake and translocation of alachlor in wheat and soybean. Peterson and Edgington (70) examined uptake of fungicides and the fluorescent dye PTS in onion roots. A study of the dynamic uptake and translocation of thiabendazole and methyl-2-benzimidazolecarbamate in pepper and tomato was presented by Ben-Aziz and Aharonson (71). An interesting study by of Price and coworkers (72) also dealt with the problem of uptake and translocation of 1-methylpyridinium and related compounds in wheat. The role of epicuticular waxes and compartmentation on uptake of pesticides in barley leaves was investigated by Schreiber and Schonherr (73). The physical-chemical studies by Thompson (74) on diffusion of chemical vapor from target areas deserve special attention. A review was published by Nissen (75), in which the author specified the role of organic and inorganic compounds in the uptake process.

MODELING OF UPTAKE OF XENOBIOTICS BY PLANTS

Numerous models describing the uptake of xenobiotics by plants can be found in literature. All these models differ with

respect to the degree of complexity, parameters they take into account, or to the plant parts they describe. Some of these models are intended for simulation of the behavior of certain groups of xenobiotics only.

The model created by Bacci and Gaggi (76, 77) supposes a homogeneous structure of plant matrix. This is 1-element model in which sorption of xenobiotics occurs until the moment equilibrium between air and plant is reached. The process of sorption in this model can be described by Equations 15–16, the change of concentration of xenobiotics in a homogeneous plant being:

$$dC_M/dT = k_1 * C_A - k_2 * C_M \qquad [15]$$

Concentration of xenobiotics in plant material with $t \to \infty$

$$C_M(t\infty) = C_A k_1/k_2 \qquad [16]$$

where

C_M = concentration of xenobiotics in plant material,
C_A = concentration of xenobiotics in air,
k_1 = rate constant of sorption,
k_2 = rate constant of desorption.

A graphic presentation of the model of Bacci and Gaggi is shown in Figure 6. A serious drawback of this model is the supposed homogeneous structure of a plant matrix and the simplification of sorption and desorption processes. Consequently, this model was developed further and a new model supposing a heterogeneous structure of the plant matrix and a change of volume of a xenobiotic during the time of the sorption process has been created. This model has the capability of many variations, allowing for a number of elements to be entered. An adequate model to describe the sorption of xenobiotics in plants is a three-element system supposing that a plant (fruit) is built from three elements: pulp, peel, and wax. However, this model has not found wide application. Another model describing the sorption of xenobiotics in fruits has been presented by Górna-Binkul and coworkers (78). This model describes sorption and diffusion of gaseous toluene and *p*-xylene in fruit of grapes. It is based on Fick's second law and supposes a partition of xenobiotics between the spherical zones (parts of fruit). A confirmation of the proposed model is shown in Figure 7, indicating an active uptake until equilibrium has been reached.

Modeling of uptake of xenobiotics in fruits was also the subject of work by Ligor and Buszewski (79). They investigated the sorption and distribution of volatile organic compounds (VOC) in fruits by means of a setup for dynamic exposure which allows us to show the place of accumulation of xenobiotics. The corresponding apparatus for dynamic exposure of plant material is depicted in Figure 8. This apparatus allows us to control sorption temperature as well as the stream of gas flow containing the volatile xenobiotics. The control of these conditions permits us to simulate different weather conditions in the laboratory.

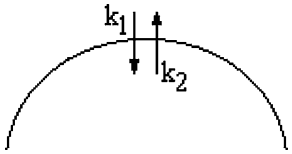

FIG. 6. Model of Bacci and Gaggi (76, 77).

In order to examine the flow of liquids through the root system of a plant, a model of water and solute transport through root systems has been created by Fiscus (80). According to Fiscus, the root system of a plant constitutes the most important resistance point which makes it difficult for the water and solutes to penetrate the plant. Despite these difficulties, the root system also constitutes the main water supply organ in a plant. The model built by Fiscus (80) is composed of the following parts (Figure 9): pressure transducer, temperature-controlled chamber, conductivity cell, and balance.

The water, situated in the temperature-controlled chamber, penetrates the root system in the conditions of controlled temperature and pressure. The water and solutes are transported along the roots and by a tube to the conductivity cell, and next to the balance. Due to the specific model construction, it is possible to qualitatively (in the conductivity cell) and quantitatively (on the balance) indicate the substances transported through the root system. In his model, Fiscus did not take into account the processes involved in the water movement that take place on a cellular level and differentiated only three methods of transport: by convection, by diffusion, and by active components of the solute flux.

Fiscus pointed out a series of equations in which he included, among others, the following data: the three methods of water transport in the root system, volume fluxes, and osmotic pressure. The equation below is a final product of Fiscus' calculations and it reflects the total model of water and solute circulation in the root system:

$$J_v^2 + J_v[\omega RT - L_p(\Delta P - \sigma^2\pi^0 - \pi^*)] - L_p RT(\omega\Delta P + \sigma J_s^* - \omega\pi^*) = 0 \qquad [17]$$

where

J_v = Total volume flux,
L_p = Root system hydraulic conductances coefficient,
J_s, J_s^* = Total and active solute fluxes,
σ = reflection coefficient (osmotic efficiency),
ω = tissue solute mobility coefficient,
R = universal gas constant.

The model by Fiscus is a simplified one, and it describes only the flow of water and the substances dissolved within the root system. The very idea of examining the flow within a root is correct, as it is through the root that numerous minerals and

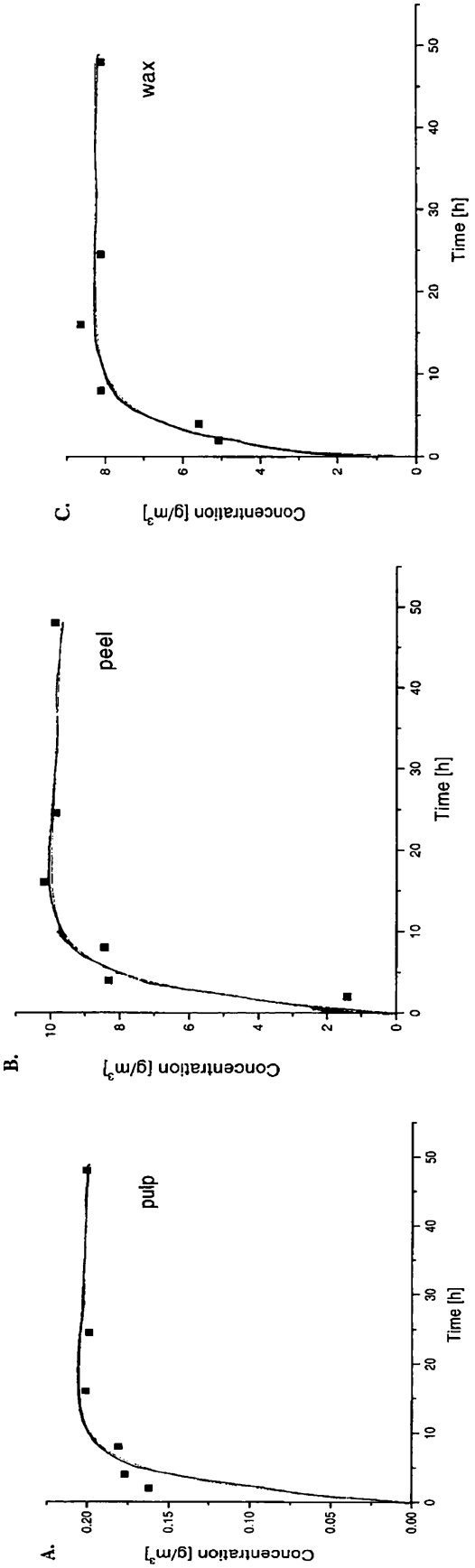

FIG. 7. Sorption course of *p*-xylene in respective layers of a grape berry (A-pulp, B-peel, C-wax) (78).

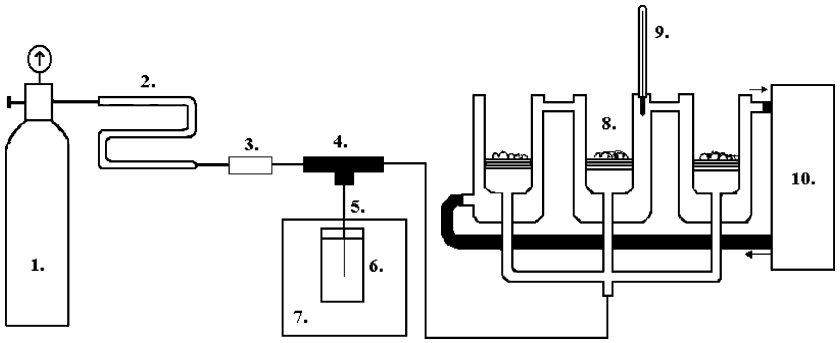

FIG. 8. Apparatus for dynamic exposure of plant material (79): 1, Gas cylinder; 2, Dryer; 3, Flow regulator; 4, T-joint; 5, Capillary; 6, Vial; 7, Water bath; 8, Exposure Vessels; 9, Thermometer; 10, Temperature controller.

water reach a plant. However, the lack of connection to the models describing the flow of water within the stem, or within other plant parts, diminishes the use of Fiscus' model in broader-spectrum research. The decisive parameter in this model is the water flow tension/pressure in a root; if too strong, it may cause washing out of the chemical ingredients of a root, which in turn unsettles the balance of the process.

Chiou and coworkers (81) proposed a partition-limited model for the plant uptake of organic contaminants from soil and water. In their theoretical assumptions, they started from studying a simpler uptake model in which the nonionic contaminants were passively transported into the root system of a plant, and thus into a plant itself, from a soil-free nutrient solution in which water constituted not only a solvent for the contaminants but also a medium for transportation. In the partition-limited model, the uptake of contaminants and other solutes takes place from the soil to the root system. Those authors examined the uptake in chosen plants (carrot, radish, crops, etc.), considering different types of soils: sandy soil, clay soil, and muck. The study focused on investigating the effective concentration of a contaminant in the soil for the sorption to take place. The effective concentration in the soil pore water can be estimated from the calculated C_{som} (som = normalized contaminant concentration in soil) and K_{som} (contaminant partition coefficient between som and water). Contaminants within a plant are assumed to be in a state of equilibrium with various plant organic components and water (however, the equilibrium state with the external water may not be kept up, especially if the contaminant is relatively water insoluble).

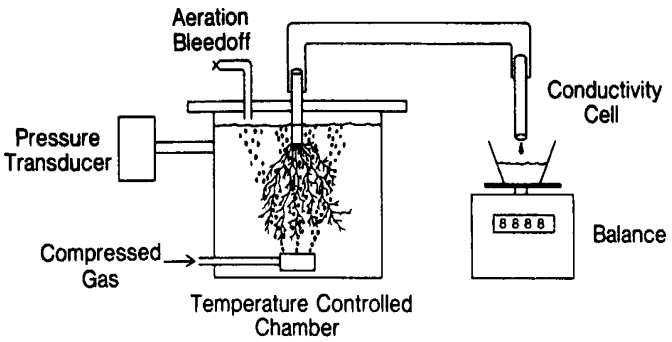

FIG. 9. A model of Fiscus (80).

Equally as in the case of Fiscus' model, the disadvantage of the model by Chiou lies in its simplification; boiling down to examining the process of sorption of organic substances from water and soil. Those authors assumed a passive transport from water and soil to a root. Yet, soil is a very active and changeable system, reacting with the rest of ecosystem. A plus of this model is the taking into account of different types of soil and plants.

Behrendt and Bruggemann (82, 83) applied a model study of root uptake of pesticides (Simulation Model Network Atmosphere-Plant-Soil, SNAPS) to the examination of wheat and barley under the changing climate conditions. The crops were growing on different soil types, and were observed along the whole vegetation period. In the course of research, Behrendt and Bruggemann calculated the chemical root uptake, assumed to be a passive process, and water-soluble contaminant concentration in plant compartments for such pesticides as terbuthilazine, isoproturon and carbofuran. SNAPS consists of a soil model (calculating the soil water dynamic and the chemical uptake) and a plant model. The graphic representation of both models is shown by Figure 10.

Behrendt and Bruggemann used the following equations in this model:

$$S_R(z,t) = -\text{TSCF}\ \text{S}(z,t)\ C(z,t) \qquad [18]$$

where

C = dissolved concentration in soil water,
z = depth in soil,
t = time,
S = root uptake rate,
S_R = chemical uptake in transpiration stream,
TSCF = empirical reflection coefficient.

$$\text{TSCF} = 0.784 \exp[-(\log K_{ow} - 1.78)^2/2.44] \qquad [19]$$

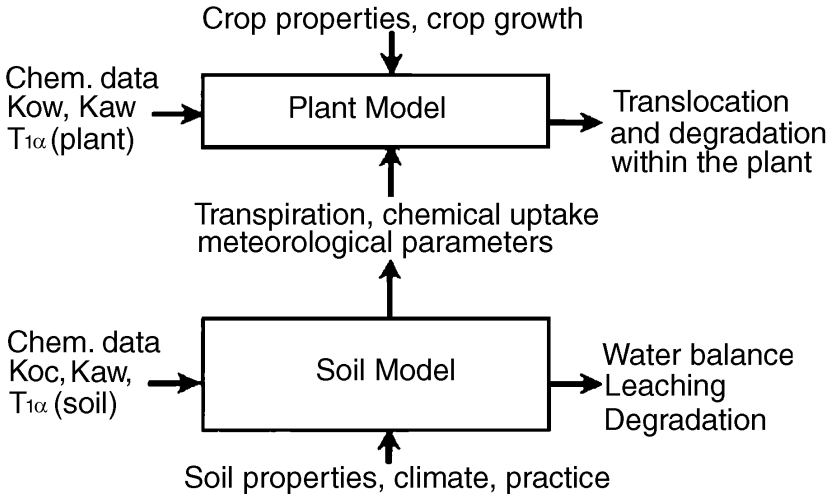

FIG. 10. The graphic representation of both models (82).

where

K_{ow} = octanol/water partition coefficient.

An auxiliary plant compartment model (Figure 11), consisting of stem, leaves, and fruit, calculates the translocation and degradation of pesticides in a plant and plant parts (first-order process), as well as the chemical's diffusive exchange with the atmosphere.

$$K_{LA} = (WC + L_p(K_{ow})^b)p_L/(p_w K_{aw}) \qquad [20]$$

where

L_p = lipid fraction leave,
WC = water content leave,
B = empirical correcion coefficient
K_{aw} = air/water partition coefficient.

In the course of research the effectiveness of uptake from sandy and loamy soils has been shown and proven, especially for the pesticides with a groundwater contamination potential, which seem to penetrate the crops most easily.

The major advantage of the SNAPS model is that it postulates a three-element system: air–plant–soil. Taking into consideration differences between soil types in this modeling process broadens the possible scope of applications of the model. Another advantage is the illustration of mutual influence patterns between certain elements.

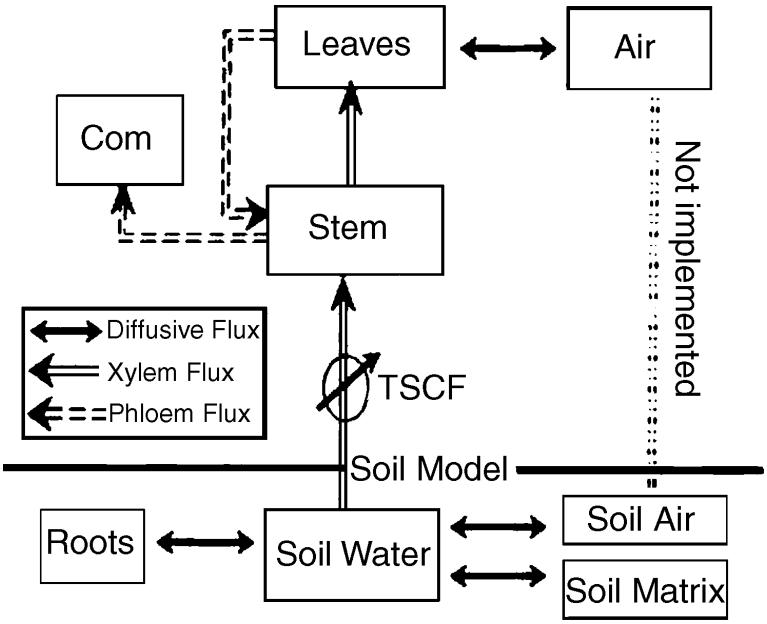

FIG. 11. Plant compartment model (82).

The plant compartment model has also been used as a base for the PLANTX model (84), developed by Trapp and coworkers which considers the following processes:

- diffusive exchange in soil water and air pores to roots,
- transfer into roots with the transpiration stream,
- translocation into stems and leaves via the transpiration stream,
- partitioning into the stem,
- transport into fruits via the assimilation stream,
- diffuse exchange between air and leaves via stomata and cuticle;
- metabolism, and
- dilution by growth.

Trapp used the following relationship in this model:

Roots

$$\begin{aligned}\text{Mass change} = &\pm \text{diffusion from/to soil}\\ &+ \text{mass flow within the transpiration stream}\\ &- \text{metabolism}\end{aligned}$$

Stem

$$\begin{aligned}\text{Mass change} = &+ \text{mass flow with transpiration stream from soil}\\ &- \text{mass flow within the transpiration stream to leaves}\\ &+ \text{mass flow within the phloem from leaves}\\ &- \text{mass flow within the phloem to fruits}\\ &- \text{metabolism}\end{aligned}$$

Leaves

$$\begin{aligned}\text{Mass change} = &+ \text{mass flow within the transpiration water from the stem}\\ &\pm \text{diffusive flux from/to air}\\ &- \text{mass flux within the phloem into the stem}\\ &- \text{Metabolism}\end{aligned}$$

Fruits

$$\begin{aligned}\text{Mass change} = &+ \text{mass flow within the phloem from the stem}\\ &- \text{metabolism}\end{aligned}$$

The validation of the PLANTX model has been carried out with bromacil. The model is applicable for simulations of the uptake from soil or solutions, it is numerically stable and needs few input parameters (such as partition coefficients and exchange rates), and its functioning is based on the minimal data (K_{ow}, Henry's law constant, K_{aw}, molecular weight, MW).

An advantage of the PLANTX model is that it considers the dynamic uptake of compounds from soil, which corresponds more directly to the real systems existing in nature. It is also worth paying attention to the fact that the model takes into account the role of phloem and xylem in the transport of xenobiotics in a plant. Also the including of individual processes, such as metabolism, indicates quite a detailed imitation of natural processes that take place during the intake of xenobiotics and the complementary processes.

As far as the uptake of airborne organic chemicals is concerned, according to Sabljic and coworkers (85), the aboveground parts of a plant may absorb the pollutants from the atmosphere in a twofold pattern: either via penetrating the surface and the cuticle of a plant before reaching the inner tissues (in case of the nonvolatile substances), or via entering the internal parts of a plant through open stomata (in case of the volatile substances and gases).

The same assumption has been used by Riederer (86) in the creation of his fugacity-based model, which illustrates the partitioning and transport of organic chemicals in the plants' foliage. Riederer pointed out three possible uses of the model: in predicting the equilibrium concentration in leaf tissues, in estimating the air-to-leaves bioconcentration equilibria, and in identifying the places of chemical accumulation in foliage tissues.

Bacci and coworkers (87) focused, in turn, on the uptake of organic chemical vapors in a plant's leaves. In their azalea model, the concentration and release of contaminant vapors in and from the azalea leaves were calculated. The plants were exposed to constant vapor levels of such chemical substances as the herbicide alachlor and the insecticide dieldrin. For both substances leaf/air bioconcentration factors have been calculated. The selected chemicals were introduced into the fortified soil aliquots, and placed in glass containers—each chemical substance and its soil bed in a separate glass greenhouse. The greenhouses were maintained in a constant temperature and continuously illuminated; air circulation and regular water supplies were guaranteed. Each greenhouse contained two azalea plants in pots with original soil, pots being further fixed in the oil bed containing a contaminating substance. Bacci and his coworkers studied first the sorption from air to leaves, and then the release from leaves to air after the removal of contaminated soil and increasing the air circulation in glasshouses.

The kinetic studies with the use of the above-mentioned chemicals allowed authors to indicate the interdependence between the azalea leaf/air bioconcentration factor, and the K_{ow} and the K_{aw} (where K_{ow} = partition coefficients 1-octanol/water, and K_{aw} = partition coefficients air/water).

The azalea model (Figure 12) focuses merely on the sorption of xenobiotics in leaves, the source of xenobiotics being the glass containers filled with it. This situation imitates the use of pesticides in soil, from which the contaminants vaporize and permeate a plant, thus fulfilling their protective function. A constant temperature in the glass container synchronizes the whole

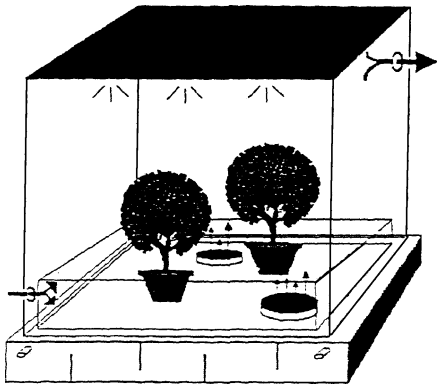

FIG. 12. Azalea model (77).

intake process but, in the natural environment, the situation of temperature stability is not frequently observed.

A similar experiment was conducted by Trapp and coworkers (87) on barley, although in that laboratory model ecosystem the uptake of contaminants—C^{14}-labeled chemicals—took place directly from the polluted soil as well as from the air. Trapp observed that a plant's foliage absorbed mainly the chemicals with high K_{ow} and with relatively high Henry's law constant, while the chemicals with medium K_{ow} were mainly transported along the transpiration stream. Transfer rates and the K_{ow} and K_{oc} (partition constant between soil organic carbon and water) values were reported as important factors influencing the bioconcentration in a plant.

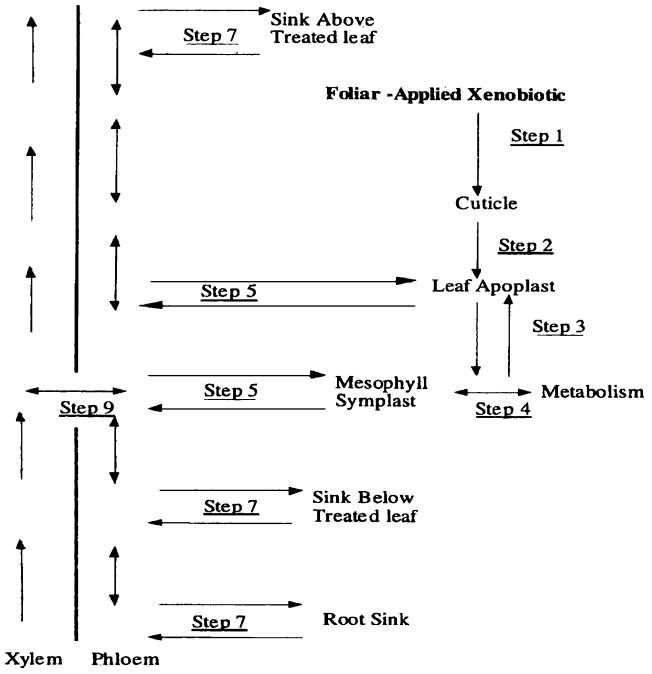

FIG. 13. Block diagram describing the pathway of xenobiotics transport (89).

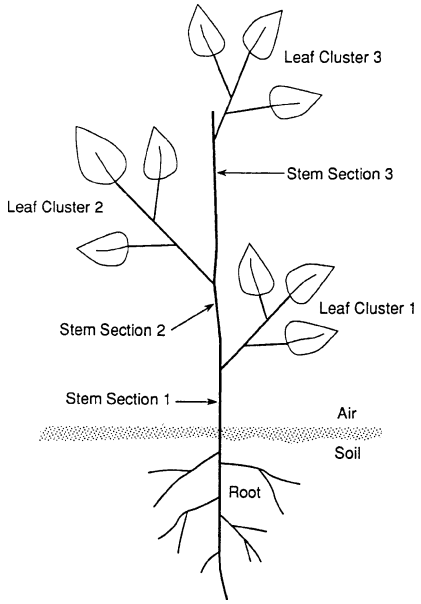

FIG. 14. Schematic diagram of a generic plant (94).

Also Paterson, Mackay, and McFarlane (88) described a chemical uptake model, using the property of fugacity as a core criterion in the equilibrium partitioning process between different plant compartments. Their fugacity model of chemical uptake concentrates not only on the air-leaf system, but on the organic substances' absorption from both soil and atmosphere. The authors pointed to the importance of such factors as molecular weight, aqueous solubility, vapor pressure, octanol/water partition coefficient, atmosphere and/or soil characteristics,

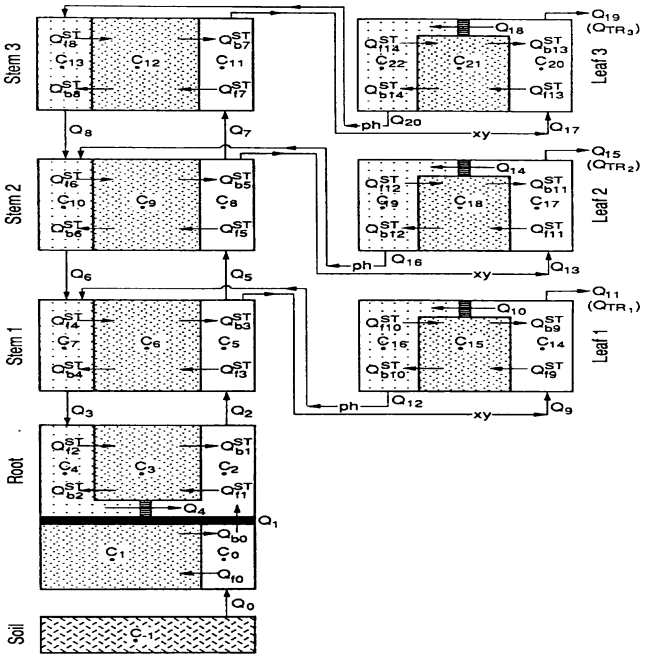

FIG. 15. Conceptualisation of a plant (94).

TABLE 1
Examples for the Determination of Xenobiotics in Plants

Sample	Compounds	Extraction	Clean-up	Determination	Ref.
Wheat Beans Onion Radishes	Delthametrin Pirimiphosmethyl Fonofos	SFE		GC-ECD	(94)
Fruits Vegetables	ONP, OPP	LLE		GLC with termoionic detector	(95)
Fruits Vegetables	OCP	LLE	Florisil clean-up	GLC-ECD	(95)
Medicinal plants	OCP	LLE	SPE, Florisil	GC-ECD	(96)
Fruits Vegetables	79 Pesticides	LLE		GC-FPD	(97)
Fruits Vegetables	143 Pesticides	LLE	LLE	GC-ECD, TLC	(98, 99)
Grapes	Benzoylurea Insectides	LLE	SPE	HPLC	(100)
Crops	72 Pesticides	LLE	GPC	GC-ECD, GC-FPD	(101)
Potato Orange Peach	40 Pesticides	SFE		GC/MS	(102)
Fruits Vegetables	48 Pesticides	LLE		GC-FPD, GC-ECD, GC-FTD	(103)
Crops	Pesticides	LLE	SPE	GC-NPD	(104)
Apples Tomatoes Lettuce	Herbicides Insecticides Fungicides	LLE		GC-ECD,GC-NPD	(105)
Fruit juices	9 Pesticides	MSPD	Florisil	GC/MS	(106)
Vegetables	9 Pesticides	MSPD		GC-ECD	(107)
Citrus fruits	5 Pesticides	MSPD		HPLC-UV	(108)
Celery	Volatile constituents	HS-SPME		GC/MS	(109)
Aromatic plants	Volatile constituents	HS-SPME		GC-FID, GC/MS	(110)
Vegetables	7 Pesticides	LLE		GC-ECD	(111)
Plant	28 Pesticides	LLE	SPE	GC-ECD, GC/MS	(112)

Abbreviations: ONP, organonitrogen pesticides; OPP, organophosphorus pesticides; OCP, organochlorine pesticides; SFE, supercritical fluid extraction; LLE, liquid-liquid extraction; MSPD, matrix solid-phase dispersion; GPC, gel permeation chromatography; GC, gas chromatography; ECD, electron capture detection; GLC, gas-liquid chromatography; FPD, flame photometric dectection; TLC, thin-layer chromatography; HPLC, high-performance liquid chromatography; MS, mass spectrometry; FTD, flame thermoionic detector; NPD, nitrogen phosphorus dectection; UV, ultraviolet; HS, headspace; SPME, solid-phase microextraction; FID, .

temperature, and plant species and physiology in the uptake of organic chemicals and their distribution in plant compartments. Paterson and Mackay's model was first tested with the sorption of C^{14}-labeled bromacil. The chemical was injected into the soil (root environment), placed in an exposure chamber and divided from the atmosphere (shoot environment) by a plastic support disc, in order to eliminate the probability of circulation of the pollutant between the air and soil. Thus, the introduced chemical substance reached all the plant compartments (root, stem, and leaf) only through the root uptake and xylem translocation. The patterns and paths of the compound translocation were reported to be dependent on its chemical properties. Other experiments have shown that the main source of a pollutant for a plant foliage is the atmosphere/evaporation from soil, but it is the root that is the main accumulating plant compartment.

A number of factors influencing effectiveness of a xenobiotic application was identified by Satchivi and coworkers (89, 90) in their presentation of a nonlinear dynamic simulation model for xenobiotic transport (Figure 13). Satchivi concentrated on foliar application of a xenobiotic, and its transport and allocation in a plant. In this model the authors paid special attention to

the chemical's physiochemical parameters (e.g., molar volume, acid dissociation constant): anatomical, physiological, and biochemical features of a plant; and so forth. It was observed that, in the case of the foliage application, xenobiotic molecules' permeation took place first through the leaf cuticle, and then through the phloem and xylem (long-distance transport). On these physiological bases, the authors developed mathematical relationships to describe the processes of permeation and xenobiotic transportation, and finally to develop a computer simulation model concerning the allocation of xenobiotics in plants. In the process of model validation (90), in which herbicides (such as, bentazon, chlorimuron, prosulfuron) were used, it has been noted that this kind of computer simulation is able to aid in prediction of the xenobiotic absorption rate, the accumulation of a chemical substance in certain plant compartments, as well as the metabolic processes the xenobiotic undergoes.

In developing their mathematical model for the evaluation of the uptake, transport, accumulation, and biodegradation (UTAB) of organic chemicals by plants, Boersma and Lindstrom (91–93) assumed plant division into adjacent compartments (root, stem, and leaves), each compartment further divided into organs responsible for transport (xylem and phloem) and a part in which accumulation and storage take place. Compartments were assumed to function simultaneously and in operational consolidation, each being characterized by a uniform concentration and separated by certain barriers from another compartment. The physical and chemical characteristics of both compartments (e.g., volume, sorption coefficient, areas of contact) and barriers (e.g., hydraulic conductivity, reflection coefficient) as well as the properties of penetrability of different barriers were taken into account.

In the course of research a series of mass balance equations describing the uptake were formulated, in which chemical mass in each of the compartments is shown as a function of time. In the initial stadium of the experiments, Boersma and Lindstrom assumed a one leaf–one stem–one root plant model. The validation process of the UTAB model was performed with bromacil on the soybean plant. The subject of these experiments was a

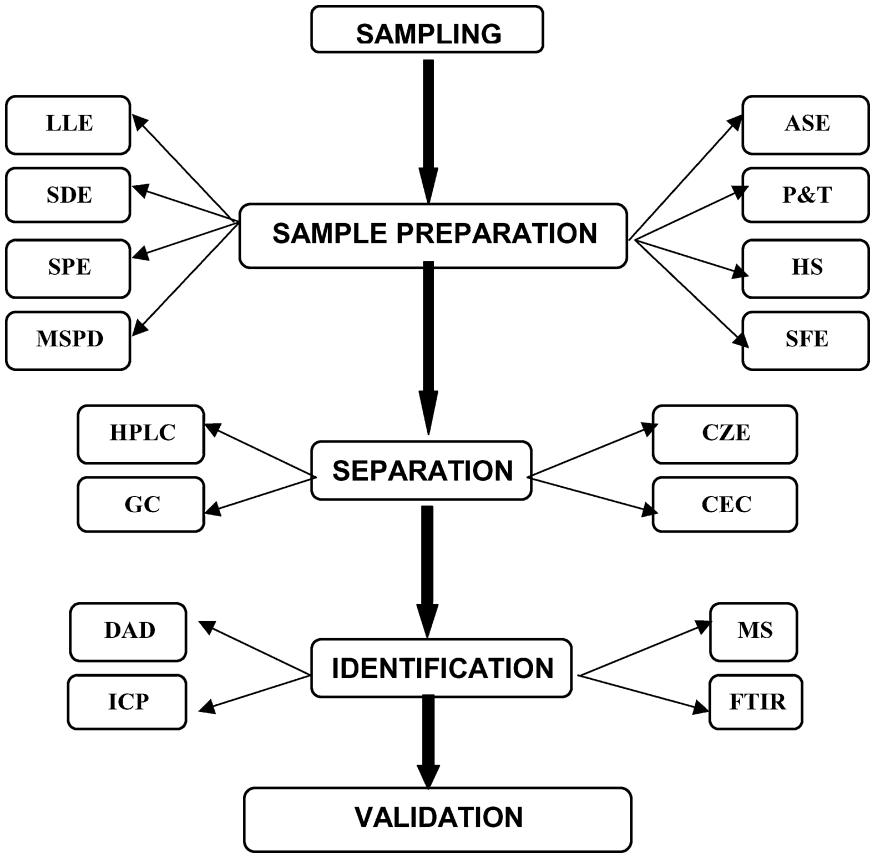

FIG. 16. Methods of analysis of a plant. Abbreviations: LLE, liquid-liquid extraction; SDE, single-drop extraction; SPE, solid-phase extraction; MSPD, matrix solid-phase dispersion; ASE, accelerated solvent extraction; P&T, purge and trap; HS, headspace; SFE, supercritical fluid extraction; GC, gas chromatography; HPLC, high-performance liquid chromatography; CZE, capillary zone electrophoresis; CEC, electrochromatography; DAD, diode-array detector; ICP, inductively coupled plasma; MS, mass spectrometry; FTIR, infrared spectrometry with Fourier transformation.

plant with three stems and three leaf compartments. The hierarchy of leaves on the stem is shown in the Figure 14.

The conceptual plant scheme has been transferred into a figurative model of compartments, which illustrates the processes examined, constituting the bases for further mathematical calculations (Figure 15).

In this model, authors took into account a pathway of xenobiotics in a plant. The plant was divided into sections (leaf, stem). Each section had three parts. Between parts and sections is transport of xenobiotics by phloem and xylem. The validation process with the use of bromacil proved the effectiveness of UTAB model in simulating the uptake and distribution mechanisms. The UTAB model successfully aids in predicting xenobiotic contamination in plants (95).

Among the contributions dealing with modeling of uptake of xenobiotics in an overall manner, Schroll and Scheunert (96), Hung and Mackay (97) deserve special attention.

ANALYTICAL METHODS

The various physicochemical properties of xenobiotics require dedicated chemical analyses to obtain reliable qualitative and quantitative information about individual compounds (Table 1). It has been stated that xenobiotics in plants undergo different processes, such as, migration, diffusion, accumulation, and metabolic processes. These processes necessitate the use of specific sample preparation techniques and exceptional selectivity in reference to the final analysis methods (Figure 16).

The diversity of the sample preparation methods and of the final analysis techniques allows us to qualitatively and quantitatively specify the xenobiotics that underwent the uptake process in a plant.

SUMMARY

This contribution discusses the theory of modeling, specifies its elements, and details legitimacies of a model. The basic structure of a plant has been characterized with special reference to describing certain plant compartments and their functions as well as organs that are involved in the processes of uptake, substance transportation, and accumulation. The role of xylem and phloem in sorption has been specifically indicated. The contribution gives an account of certain chemical and metabolic processes that uptake involves. The correlations between parameters describing the sorption process have been demonstrated. Successive sections illustrate different models of sorption, either by taking into account separate plant compartments as process location places or by presenting overall uptake models. An account of analytical methods is given. The article refers to numerous literary sources on the modeling of uptake, giving a general insight into the theory of modeling and constituting a broad-spectrum compilation of the available scientific and experimental data on sorption modeling.

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