Appraisal of Tests to Predict the Environmental Behaviour of Chemicals
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CHAPTER 5
Predicting the Movement of Chemicals Between Environmental Compartments (air–water–soil–biota)

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5.1 INTRODUCTION

The assessment of the magnitude of transfer of chemicals between air, water, soil and biota and the resulting concentrations in the respective compartments are an indispensable prerequisite for the estimation of probable exposure, accumulation processes and toxicity for organisms including man.

Two kinds of information are usually needed: *relative* information which allows comparison between chemicals tested under similar conditions and

absolute information on process rates and quantities of products under natural environmental conditions. For the first type, standardized experimental conditions often require significant deviations from those of the natural environment in order to obtain relevant results. These experiments include the determination of physico-chemical data and the more simple laboratory tests which provide qualitative or relative information on the transport, transformation and accumulation of chemicals. Absolute information requires more complex laboratory tests under simulated environmental conditions and direct field tests. These tests give results which are representative of the general environment, but are only confirmatory within the specific environmental condition of the test. Since a multitude of factors affects experimental results, comparisons between chemicals should be undertaken only with caution. Both groups of tests are necessary and have specific utility, nevertheless greater insight into environmental behaviour of chemicals is achieved if results are properly synthesized.

To assess the ability of tests to predict the environmental behaviour of a chemical, comparison of results with those obtained by the analysis of environmental samples within monitoring programmes is indispensable. This is true both for comparative laboratory and field tests. Suitability and limits of reported tests of both types will be discussed in this section.

The determination of physico-chemical data is the first step in elucidating the behaviour of a chemical in the environment. However, when evaluating these results one should consider that physico-chemical data yield only partial information and that the role environmental factors play in the respective environmental process should be understood and integrated into a model before any conclusion is drawn. Extensive laboratory work is often needed to clarify these interrelationships. Although it is well known that vapour pressure is related to the occurrence of chemicals in the atmosphere, it would be an error to exclude from consideration the presence of all chemicals with very low vapour pressure when assessing chemical accumulation in the atmosphere and, consequently, global atmospheric transport. DDT (vapour pressure: 10^{-5} Pa; Maier-Bode, 1965), dieldrin (vapour pressure: 10^{-5} Pa; Maier-Bode, 1965) and hexachlorobenzene (vapour pressure: 10^{-3} Pa; Schmidt-Bleek *et al.*, 1982) are well-known examples of compounds with low vapour pressure but significant atmospheric transport.

Computation models to predict the environmental partitioning of a chemical between the media (air, water and soil) have been published recently. Neely (1980) proposed equations based on the substance's physico-chemical properties, like molar mass, vapour pressure, and water solubility. Another approach has utilized the concept of fugacity, which can be defined as the tendency for a substance to escape from a phase, and assumes equilibrium conditions among a set of environmental compartments (Mackay, 1979; Mackay and Paterson, 1981). Both models have been used

for the estimation of environmental compartmentalization of 25 chemicals as a basis for an environmental hazard assessment (Schmidt-Bleek *et al*., 1982).

Because of the complexity of interrelationships between physico-chemical properties of a pure compound and environmental factors, short-term laboratory tests as well as field tests are indispensable for realistic assessment of environmental distribution and transport of the chemical. These tests not only confirm the conclusions or calculated results determined from physico-chemical data, but they are prerequisite to establishing the interrelationship between physico-chemical properties needed for such estimations.

Laboratory tests are either aimed at determining the influence of single environmental factors on the behaviour of chemicals by controlling other major influences from the environment, or at determining the integrated effect of the sum of factors present in a complete environmental system (e.g. simulated ecosystems) without differentiating individual influences. For field tests, a multitude of environmental parameters act in concert on the chemical and such complex interrelationships cannot be easily controlled.

Chemical reactivity is another parameter which complicates the investigation of transfer and transport processes. When chemical reactions occur at rates competitive with distribution or transport processes, distribution pathways will be controlled partially by the parent compound, and partially by its conversion products. The distribution of both the parent compound and its conversion products can be followed and pools and fluxes quantified using radiotracer techniques.

5.2 TRANSFER OF CHEMICALS BETWEEN SOIL AND WATER

Knowledge of the transfer of chemicals between soil and water is necessary to evaluate the migratory tendency of these chemicals, for example, the soil's tendency to take up chemicals from rain, irrigation or waste water spills, or for chemicals to migrate within soils and leach into ground water or run-off in surface water. Physico-chemical properties affecting transfer processes as well as laboratory tests and field trials to quantify chemical movement between water and soil are summarized in Table 5.1.

5.2.1 Physico-chemical Properties

The important influence of soil-sorption properties on all transfer processes between soil and water is generally understood (Furmidge and Osgerby, 1967; Bailey and White, 1970; Jarczyk, 1972; Felsot and Dahm, 1979).

Adsorption models under discussion are the Langmuir and the Freundlich adsorption equations (Bailey and White, 1970). The Langmuir adsorption equation was initially derived for the adsorption of gases by solids; in terms of

Table 5.1 Tests for assessment of the transfer of chemicals between soil and water

Test type	Principles	References (examples)
Determination of physico-chemical properties affecting the transfer	Determination of soil sorption coefficients or constants	OECD Chemical Testing Programme (1981) Felsot and Dahm (1979)
	Correlation with: Water solubility	Felsot and Dahm (1979) Kenaga and Goring (1978) Chiou *et al.* (1979) Briggs (1981b)
	Octanol–water partition coefficient	Felsot and Dahm (1979) Kenaga and Goring (1978) Briggs (1973) Briggs (1981a) Briggs (1981b)
	Parachor	Felsot and Dahm (1979) Lambert (1967) Briggs (1981b)
	Dissociation constants Molecular connectivity indices	Bailey and White (1970) Sabljić and Protić (1982)

Laboratory tests	Leaching experiments in soil columns	Jarczyk (1972) Jarczyk (1978) Biologische Bundesanstalt für Land- und Forstwirtschaft (1973) McCall *et al.* (1980) Lambert *et al.* (1965) Leistra *et al.* (1976)
	Tests of adsorption/desorption, leaching, or run-off in model ecosystems	Best and Weber (1974) Lichtenstein *et al.* (1974) Lichtenstein *et al.* (1978) Liang and Lichtenstein (1980) Virtanen *et al.* (1980) Figge and Klahn (1982)
Field tests	Experiments in large boxes or lysimeters	Moza *et al.* (1972) Kohli *et al.* (1973) Haque *et al.* (1977) Jarczyk (1978)
	Experiments in open fields	La Fleur *et al.* (1973) Caro *et al.* (1974) Willis and Hamilton (1973)

concentrations, it may be written as follows:

$$\frac{x}{m} = \frac{K_1 \cdot K_2 \cdot C_e}{1 + K_2 C_e} \quad (1)$$

where x/m is the amount adsorbed per unit amount of adsorbent, K_1 and K_2 are constants for the system, and C_e is the equilibrium concentration in solution.

The Langmuir isotherm equation implies that the heat of adsorption is independent of surface coverage. This is based on a model which assumes a uniform surface. In contrast to this, the Freundlich isotherm is derived on the assumption that a decrease in heat of adsorption with increasing surface concentration or coverage can occur due to surface heterogeneity. The Freundlich isotherm equation is written as follows:

$$\frac{x}{m} = K \cdot C_e^{1/n} \quad (2)$$

The adsorption constant K can be used to compare sorption of different chemicals on various soils at unit concentration or to study the dependence of adsorption upon other physico-chemical properties of a chemical. $1/n$ provides a rough estimation of the intensity of adsorption (Felsot and Dahm, 1979).

Soil sorption of a chemical from aqueous solution may be characterized in screening tests by the determination of the adsorption coefficient K' for a single concentration, based on oven-dry weight of solid matter (OECD Chemicals Testing Programme, 1981). This test is performed by equilibration of a known amount of chemical dissolved in water or dilute salt solution with a certain amount of soil, followed by centrifugation. The adsorption coefficient K' is then calculated according to (3):

$$K' = \frac{x/m}{C_e} \quad (3)$$

K' is an approximate value of the adsorption constant K in equation (2) .

Whereas, for more polar or ionic chemical molecules, clay minerals play a major role in adsorption effects, for weakly polar non-ionic, organic substances, the amount of organic matter in soils is the most important factor controlling adsorption (Lambert *et al.*, 1965; Spencer *et al.*, 1973; Felsot and Dahm, 1979; Rippen *et al.*, 1982). Therefore, an appropriate adsorption coefficient K'_{oc} would be based on soil organic carbon content:

$$K'_{oc} = \frac{K' \cdot 100}{\%\text{o.c.}} \quad (4)$$

where K'_{oc} is the adsorption coefficient based on organic carbon content in

soil, K' is the adsorption coefficient, and %o.c. is the percentage of organic carbon in soils.

Although adsorption generally is reversible, desorption is not always complete. Therefore, adsorption tests should be followed by desorption tests with the same compounds. Advanced tests, examining the influence of different initial concentrations, provide further information on the adsorption behaviour of a compound (OECD Chemicals Testing Programme, 1981). If a linear line results from plotting the data as $\log (x/m)$ versus $\log C_e$, the log form of the empirical Freundlich adsorption equation (2) is obtained. The adsorption constant K may be based on soil organic carbon content and thus expressed as K_{oc} analogous to K'_{oc} in equation (4).

In contrast to the determination of more simple physico-chemical parameters, the determination of sorption coefficients or constants involves problems which are, on the one hand, due to the difficulties in standardizing natural soils, and on the other, due to interferences by competitive environmental processes, primarily the biotic degradation of the chemical during the required adsorption and/or desorption period. The difficulties in data interpretation encountered because of the large variations in adsorption behaviour of natural soils, may be overcome by replacing natural soils by standard mixtures. A mixture of sand, kaolinite, and peat, as used by La Fleur (1979), however, may lead to difficulties similar to those with natural soils, due to the non-homogeneous structure of peat. Therefore, Rippen *et al.* (1982) proposed to replace the natural soils by synthetic adsorbents. The authors showed that inorganic adsorbents like silica gel, kieselguhr or alumina had only low K-values for non-polar chemicals, whereas cellulose exhibited high adsorption constants. They demonstrated also that a correlation of K-values for cellulose with K_{oc}-values of natural soils is possible. A mixture of cellulose and inorganic absorbents could, therefore, take into account both adsorption on mineral and on organic soil constituents.

Since the determination of adsorbed portions of chemicals is usually carried out indirectly, i.e. by measuring the unadsorbed portions left in solution, losses by biotic degradation or conversion in natural soils may be misinterpreted for adsorption. Biotic degradation may be prevented by sterilization; however, this may result in alterations of the adsorbing surfaces, especially for those soils high in organic matter. There is also the possibility to include a determination of biotic degradation within the adsorption test, by measuring the amount of CO_2 formed from the xenobiotic during the adsorption or desorption period (Vockel, 1981). This method provides optimal gain for the experimental effort but requires the use of ^{14}C-labelled chemicals. Another means to overcome the difficulties related to biodegradation losses is the use of model adsorbents rather than natural soils.

A simple, rapid, and reproducible method to determine soil sorption, which

essentially involves filtration rather than centrifugation as in the conventional method, was reported by Wahid and Sethunathan (1978) for γ-BHC and parathion. It uses a hypodermic syringe fitted with a filter paper disc and permits quantification of the two chemicals sorbed at extremely short time intervals down to 5 sec.

Soil sorption has been shown to be correlated to more simple physico-chemical parameters. Empirical equations have been obtained experimentally for non-ionic chemicals relating soil adsorption to water solubility (Kenaga and Goring, 1978; Felsot and Dahm, 1979; Chiou *et al.*, 1979; Briggs, 1981b), and octanol–water partition coefficients (Briggs, 1973; Kenaga and Goring, 1978; Felsot and Dahm, 1979; Briggs, 1981a). Dissociation constants play a role for ionizable chemicals (Bailey and White, 1970).

Parachor is a temperature-independent substance parameter which relates surface tension to the liquid and vapour density. Quayle (1953) suggested an additive scheme to correlate this parameter with chemical structure. Lambert (1967) derived the following expression relating the parachor to the partition coefficient, neglecting any interactions

$$\log K_p = aP\Delta U \tag{5}$$

where P is the parachor, K_p the partition coefficient, a a constant and ΔU the difference in internal pressure between the two phases. Where water is one of the phases, the ΔU term is dominated by the internal pressure of water which is ~10 times that of immiscible organic solvents. Therefore, for solvent water partitions, the ΔU term is similar for all solvents and, in the absence of solute solvent interactions, all partitions should be similar except where the organic phase itself contains much water (>5 M water). If the presence of water in the organic phase increases the internal pressure in the organic phase, it will decrease the difference between the two phases and hence decrease the partition coefficient. If we assume that the difference in internal pressure ΔU is proportional to the difference in the water concentrations in the aqueous and organic phases, ΔW, equation (5) becomes

$$\log K_p = a'P\Delta W \tag{6}$$

(Briggs, 1981b).

The Collander equation (7)

$$\log K_{p1} = a \cdot \log K_{p2} + b \tag{7}$$

relating partition coefficients of any pair of solvents to each other (Collander, 1950), and equation (6) were used by Briggs (1981b) to calculate, for non-ionic chemicals, relationships between soil adsorption, octanol–water partition coefficients, water solubility, bioconcentration factors, and the parachor, if the water concentrations in the respective organic phases in

equilibrium with water are known. These theoretical relationships were shown to be comparable to those obtained experimentally. For the calculation of soil adsorption constants, the only additional information needed is the water concentration in soil organic matter at equilibrium.

The parachor offers a very rapid way to calculate approximate values of the octanol–water partition coefficient and hence also of soil adsorption constants from chemical structure characteristics alone without the use of experimental data (Briggs, 1981b). A relationship between parachor and adsorption constants has also been found experimentally (Lambert, 1967; Felsot and Dahm, 1979).

Molecular connectivity indices are numerical characteristics of a molecule, which depend on the number and types of atoms and bonds as well as their spatial considerations. Each index is a quantitative representation of molecular structure at different levels of complexity. For the calculation of second-order valence molecular connectivity indices, atoms of molecular subgraphs are described by their valence delta values, which include the number of valence electrons in the atom and the number of hydrogen atoms bound to it. Molecular connectivity indices have been shown to be linearly correlated to the octanol–water partition coefficients for a variety of monofunctional chemical classes including esters, alcohols, ketones, carboxylic acids, amines, and hydrocarbons (Murray *et al.*, 1975). The relationship between molecular connectivity indices and soil sorption coefficients reported by Sabljić and Protić (1982) offers another possible means of estimating soil sorption coefficients without experimental data. However, this means relationship has been shown, thus far, only for polycyclic aromatic hydrocarbons.

The information available today on the relationship of physico-chemical properties to adsorption/desorption processes is helpful in assessing transfer rates of chemicals between soil and water, but all estimates should be accompanied by confirmatory laboratory and/or field tests.

5.2.2 Laboratory Tests

In most cases, laboratory tests do not produce data which is quantitatively predictive of chemical behaviour in the environment, but they give, by relatively simple means, comparative data for various chemicals.

The migratory behaviour of chemicals in soils and their transfer to leaching water usually is determined by soil column studies in the laboratory (Lambert *et al.*, 1965; Jarczyk, 1972; Biologische Bundesanstalt für Land- und Forstwirtschaft, 1973; Leistra *et al.*, 1976; Jarczyk, 1978; McCall *et al.*, 1980). The chemical is applied on the top of the column which is then percolated with water. The eluation is analysed for the chemical at appropriate time or volume intervals. Similarly, the upward movement of chemicals in soil

is tested in columns where the chemical is applied to the deepest soil layer. The column is set into a container, and water is added so that the column is subirrigated. The units are placed in a hood with the fan operating. At the end of the experimental time, the columns are sliced and the different layers analysed for the chemical (Harris, 1969). A relationship between results of leaching experiments in soil columns and sorption coefficients was confirmed by McCall *et al.* (1980) who demonstrated decreasing leaching distances in soil columns with increasing sorption coefficients. Leistra *et al.* (1976) reported the relationship of sorption coefficients with leaching behaviour for aldicarb and its metabolites. The sorption coefficients, together with diffusion coefficients and various soil and column parameters, were combined in a mathematical model

A simple but reliable test methodology to assess the migration behaviour of chemicals in soils is chromatography. McCall *et al.* (1980) demonstrated a correlation of soil adsorption coefficients with liquid chromatographic retention times. Since adsorption coefficients have been correlated with soil column leaching distances, a correlation between retention times and column leaching distances is evident. A general correlation between *Rf*-values of partition thin-layer chromatograms and partition coefficients was established by Lambert (1968). The R_m-value, defined by equation (8)

$$R_m = \log\left[\frac{1}{Rf} - 1\right] \tag{8}$$

is related to the partition coefficient of the respective TLC-system. If soil is used as a thin-layer coating and water as a developing solvent (Helling and Turner, 1968; Helling, 1971a–c; Helling *et al.*, 1971; Helling *et al.*, 1974; Lord *et al.*, 1978), the R_m-value can be correlated to the adsorption coefficient and the organic matter content of the soil (Briggs, 1981b).

Tests for the migration of chemicals from soil into water are indispensable for hydrophilic chemicals. For lipophilic pesticides, it may be more appropriate to study the leaching behaviour of readily formed conversion products, rather than that of the parent compound. The conversion products usually are more hydrophilic and thus more susceptible to leaching and run-off. With radiolabelling techniques, both parent compound and conversion products can be monitored in experimental systems (Scheunert et *al.*, 1981).

The environmental relevance of results from laboratory leaching experiments can be evaluated by comparison with field test data and by monitoring the occurrence of the respective chemical in natural ground water at locations where known releases have occurred. The predictability of laboratory leaching results to behaviour under environmental conditions may

be improved by using undisturbed soil cores instead of disturbed or sifted soils (Jarczyk, 1978). However, the variations in adsorption capacity of natural soils are so large, that the differences between disturbed or undisturbed soils might be less important than the utilization of a soil type consistent with that of the natural environment for which the predictions are being made.

The prediction of leaching behaviour in an ecosystem from results of laboratory column studies as well as from mathematical models based on two-phase equilibria is complicated by the fact that many unaccountable variables influence field behaviour. For example, downward leaching may be accompanied by lateral migration, upward movement may be initiated as a consequence of volatilization, transport may occur along fractures, etc. If mathematical or laboratory models are based on two-phase equilibria (chemical in dissolved and adsorbed phase), the occurrence of three-phase equilibria (including undissolved chemical), after high dosing rates under field conditions, may prevent realistic predictions (NRCC), 1980). Hamaker (1975) concluded from available laboratory and field data that in the field there is less movement of chemical than indicated by laboratory leaching tests and recommended the use of laboratory test results to compare the leachability of one chemical with others of known leaching behaviour.

Laboratory model ecosystems are generally designed to determine chemical transfers between all media and the biota, in addition to the examination of intracompartmental accumulation, conversion and degradation. However, some model systems are especially suitable for the determination of chemical transfers from soil into water or vice versa.

Leaching processes can be simulated in relatively simple terrestrial model ecosystems. Water is percolated through a soil–plant system after treatment of the soil with the chemical. The percolated water is collected and checked for chemical residues (Lichtenstein *et al.*, 1974). Besides leaching, plant uptake, volatilization and degradation may be determined in another, relatively simple apparatus reported by Best and Weber (1974). A highly complicated plant metabolism box has been constructed by Figge and Klahn (1982) enabling measurements of leaching as well as total mass balance studies under controlled climatic conditions.

The simulation of soil run-off also requires more complicated microcosm designs. These experimental systems are compartmentalized and consist of terrestrial and aquatic components. Rain is simulated, and the run-off from the soil into the water is measured (Lichtenstein *et al.*, 1978; Liang and Lichtenstein, 1980; Virtanen *et al.*, 1980).

Such microcosms should be used instead of tests with soil and water alone whenever potential influences of biota on transfer processes are to be assessed. For instance, after application of fonofos-^{14}C to a soil–plant–water microcosm, the amount of ^{14}C transported in run-off decreased drastically in

response to the presence and nature of cover crops (Liang and Lichtenstein, 1980).

5.2.3 Field Tests

Field tests are appropriate whenever environmental conditions need to be closely approximated due to the importance of the test compound. Field experiments to determine the transfer of chemicals from soil to water are carried out in large boxes (Moza *et al.*, 1972; Kohli *et al.*, 1973; Haque *et al.*, 1977) or lysimeters (Jarczyk, 1978) or in open fields (La Fleur *et al.*, 1973; Willis and Hamilton, 1973; Caro *et al.*, 1974). The comparability of experiments in boxes or lysimeters to open field conditions should be considered. In contrast to open field tests, experiments in boxes or lysimeters permit the use of radioactive labelled compounds and, therefore, the leaching behaviour of conversion products can also be assessed. Aldrin (Moza *et al.*, 1972), dieldrin (Kohli *et al.*, 1973) and buturon (Haque *et al.*, 1977) were not found in leaching water at a depth of 60 cm but their hydrophilic conversion products were detected. Any test for the determination of organic chemical behaviour, which examines only transfer of the parent compound without analysing changes in conversion products, should be considered as generally inconclusive.

5.3 TRANSFER OF CHEMICALS BETWEEN WATER AND AIR

Information on the transfer of chemicals between water and air is important primarily to assess volatilization rates of chemicals from water into the air, which, in addition to direct emission, is one of the most important pathways of chemicals into the atmosphere and, consequently, of their global distribution.

Table 5.2 presents physico-chemical substance parameters relevant to transfer processes between water and air, as well as laboratory and field tests for the determination of these processes.

5.3.1 Physico-chemical Properties

The role physico-chemical data play in predicting the flux of chemicals through the air–water interface in both directions has been described by several models. The two-film boundary layer model of Lewis and Whitman (1924) is the most useful to work with, although physically it is somewhat unrealistic. The model assumes the bulk of the two phases, water and air, to be homogeneously mixed. The interfacial transport is hindered only by the two laminar boundary layers through which transport occurs, exclusively by diffusion. The flux of a chemical through the boundary layers is proportional

to the concentration difference:

$$F = K \cdot \Delta c \tag{9}$$

where F is the flux in mass per unit of time and per unit of area, Δc is the concentration difference, and the factor K the interfacial mass transfer coefficient which has dimensions of velocity (usually expressed in $m \cdot sec^{-1}$ or $m \cdot h^{-1}$). Assuming an initial concentration C_0 of a chemical in water and a concentration of nearly zero in the air (i.e., the situation of a single chemical pollutant in a water body or of a laboratory volatility experiment), the decrease in concentration C in water as a function of the time t is exponential in accordance with first order kinetics:

$$C = C_0 \exp\left(-\frac{K}{L} \cdot t\right), \tag{10}$$

where L is the depth of the water body.

The reciprocal of the mass transfer coefficient K is called the overall mass transfer resistance and is the sum of the liquid-phase resistance $1/k_l$ and the gas-phase resistance $R \cdot T/k_g \cdot H$, where R is the gas constant, T the absolute temperature, k_l the liquid film mass transfer coefficient, k_g the gas film mass transfer coefficient, and H the Henry's Law constant. H, assuming limited water solubility and ideal behaviour, can be approximated as follows:

$$H = \frac{p}{S} \tag{11}$$

where p is the partial pressure of the compound at saturation and S is the maximal solubility of the compound in the liquid phase at the respective temperature.

Thus, according to the two-film boundary layer model, the overall mass transfer coefficient K may be defined as follows:

$$K = \left[\frac{1}{k_l} + \frac{R \cdot T}{k_g \cdot H}\right]^{-1} \tag{12}$$

If the value of H is greater than $5 \cdot 10^{-3}$ atm m^3 mol^{-1}, which implies a compound of high vapour pressure and/or low water solubility, the resistance lies almost totally in the liquid phase, and the second term in equation (12) is relatively unimportant; i.e., the volatility is liquid-phase controlled. If the Henry's law constant is below $5 \cdot 10^{-6}$ atm m^3 mol^{-1}, which implies a compound of low vapour pressure and/or high water solubility, the first term of equation (12) is unimportant, and the volatilization is vapour-phase

Table 5.2 Tests for assessment of the volatilization of chemicals from water to the air

Test type	Principles	References (examples)
Determination of physico-chemical properties affecting the transfer	Calculation of transfer from physico-chemical substance properties (water solubility, vapour pressure, diffusion coefficients) and environmental parameters according to models	Liss and Slater (1974) Mackay and Leinonen (1975) Schulz (1980) Wolff and van der Heijde (1982) Southworth (1979) Rathbun *et al.* (1982)
Laboratory tests	Determination of air–water Henry's law constants	Mackay *et al.* (1979)
	Indirect determination of volatility by concentration decrease in open vessels	Dilling *et al.* (1975) Dilling (1977) Hill *et al.* (1976) Smith *et al.* (1980) Smith *et al.* (1981) Metcalfe *et al.* (1980) Rathbun and Tai (1981) Southworth (1979) Rathbun *et al.* (1982)

	Indirect determination of volatility by concentration decrease in wind tunnels	Cohen *et al.* (1978) Slater and Spedding (1981)
	Indirect or direct determination of volatility in a closed aerated system	Klöpffer *et al.* (1982)
	Direct determination of volatility in a closed system	Kilzer *et al.* (1979)
Field tests	Indirect determination of volatility in flowing channels	Ruf and Scherb (1977)
	Indirect determination of volatility in natural ponds	Klein *et al.* (1981) Lay *et al.* (1982) Salonen and Vaajakorpi (1974)
	Direct determination of volatility over flooded fields	Cliath *et al.* (1980)

controlled. For chemicals with Henry's constants between these two limits, both liquid and gas-phase resistance is of varying importance.

Test guidelines available today to calculate the volatility of a chemical dissolved in water in terms of the flux through the interface at a given water concentration (expressed in mass per unit of time and per unit of area), or in terms of the half-life time in water, which is independent of the initial concentration, are based upon the calculation of H according to equation (11) and the liquid and gas mass transfer coefficients.

The calculation of H according to equation (11) gives inexact results if either the vapour pressure, or the water solubility of the chemical, or both are so low that their experimental determination is difficult. Although the vapour pressure can be estimated from the boiling point and melting point (Mackay *et al.*, 1981), and water solubility can be estimated from molecular structure characteristics via the parachor (Briggs, 1981b; see Section 5.2.1), the use of such data in equation (11) followed by calculation of volatility according to equations (9), (10), and (12) would give inaccurate data. Therefore, for such substances the experimental determination either of H according to Mackay *et al.* (1979) or of volatilization rates (see Section 5.3.2) are preferable to calculation methods.

Furthermore, equation (11) is not applicable to substances with infinite water solubility, which, nevertheless, are volatile from aqueous solutions due to their high vapour pressure, e.g., acetone (Rathbun *et al.*, 1982). For these substances, H may be estimated according to Mackay *et al.* (1979) (13):

$$H = 18 \cdot 10^{-6} \cdot \gamma \cdot p_s \qquad (13)$$

where γ is the activity coefficient and P_s the vapour pressure of the pure solute. Some correlations for γ as a function of molecular properties can be used to estimate H (Mackay and Shiu, 1977). However, also in such cases it is recommended to determine either H or the volatilization rates experimentally.

For the calculation of liquid and gas mass transfer coefficients, it should be taken into account that these parameters are strongly dependent on environmental conditions. Two approaches to the approximation of these parameters have been proposed:

1. Liss and Slater (1974) and Mackay and Leinonen (1975) propose estimated values for the annually and globally averaged gas and liquid film mass transfer coefficients based on water and CO_2 fluxes for the oceans. A gas-phase mass transfer coefficient, 30 m/h, is estimated for water where resistance to interfacial transport lies in the gas phase. The liquid phase mass transfer coefficient, 0.2 m/h, is estimated for carbon dioxide where resistance lies in the liquid phase. For other compounds, the values for water or carbon dioxide are multiplied by the ratio of the square roots of the molecular weights of water or carbon dioxide and the

respective compound. No further properties of the substance are needed for the calculation.

2. The mass transfer coefficients can be calculated from diffusion coefficients and environmental conditions. Instead of obtaining estimates of the average half-life for chemicals in water, half-life estimates for specific environmental situations can be obtained. Diffusion coefficients are available from literature, as measured values, or can be calculated according to various methods (Reid *et al.*, 1977), with only the knowledge of molecular weight and molecular volume. The critical environmental parameters are the turbulence of air for the gas-phase mass transfer coefficient and the turbulence of water for the liquid phase mass transfer coefficient. Good correlations have been found between the gas-phase mass transfer coefficient and wind speed (Mackay and Matsugu, 1973; Mackay, 1980; Wolff and van der Heijde, 1982).

   The quantitation of the liquid-phase mass transfer coefficient, however, is more complex since the turbulence of water usually is due to more than one environmental factor, for example flow of a river or current, influence of the wind, or mechanical stirring as in the laboratory, etc. Schulz (1980) proposed the assessment of the liquid-phase mass transfer coefficient from the flow velocity of rivers; however, according to Wolff and van der Heijde (1982), an appreciable error can be made if the influence of wind on this parameter is disregarded. These authors propose a calculation model for the liquid-phase mass transfer coefficient based solely on wind speed, to be used for aquatic systems with the exception of turbulent rivers where stream velocity should be taken into account. However, it has been shown that at very low wind speeds (<2 m/sec) weak water movements, for example stirring in the laboratory, have a considerable effect on the liquid-phase mass transfer coefficient (Cohen *et al.*, 1978; Southworth, 1979; Rathbun and Tai, 1981; Rathbun *et al.*, 1982). In these specific situations, the model of Wolff and van der Heijde (1982) is not applicable.

Southworth (1979) reported a method to calculate the liquid-phase mass transfer coefficient based on the current velocity of water, but regarding also wind velocity. Similarly, he calculated gas-phase mass transfer coefficients based on the wind velocity, regarding also the influence of current velocity of water. In order to compare calculated volatilization rates with those obtained from laboratory experiments, he proposed to establish, for a hypothetical substance with a molecular weight of 100, 'apparatus-specific' mass transfer coefficients for given stirring rates and wind velocities.

Some uncertainty remains in the calculation of the liquid-phase mass transfer coefficients. Furthermore, the exact dependence of k_1 and k_g on chemical substance properties is not fully understood. The uncertainties both in calculating H discussed above and in calculating mass transfer coefficients

suggest not relying on calculation methods alone. Additionally, interactions between several chemicals in aqueous solution or suspension are not regarded in calculation models although it has been reported that, for example, detergents (Smith *et al.*, 1980) or humic acids (Mackay *et al.*, 1979) do affect volatilization rates. The influence of water impurities in general on volatilization rates has been shown by Singmaster III (1977). Comparative laboratory experiments with distilled and three environmental waters showed, for four chlorinated hydrocarbons, a 2–3 fold prolonged half-life in the environmental waters. In view of these limitations of calculation models, and in view of the importance of volatilization rates which are the limiting factor for the half-lives of many environmental chemicals in aquatic systems, it is recommended that theoretical methods should be used for the determination of the volatility of chemicals from aqueous solutions only as a preliminary step until more information becomes available on the complex physico-chemical interactions. Calculations should be followed by laboratory experiments and a combined evaluation of results from both methods.

5.3.2 Laboratory Tests

Laboratory tests quantifying transfer phenomena between water and air include the determination of the air–water Henry's law constants, volatility measurements, and the determination of the uptake of chemical from the air by water. Henry's law constants can be determined in the laboratory by a simple method (Mackay *et al.*, 1979) where nitrogen is bubbled through an aqueous solution of the chemical. Henry's constant is calculated from the decrease in the concentration of a chemical in the stripping vessel after equilibrium conditions have been achieved. This method is recommended when the calculation of H from vapour pressure and solubility data is inaccurate due to very low water solubility and/or very low vapour pressures, and when more complicated laboratory tests are unwarranted. The authors have compared calculated and experimental results for five substances of high and medium volatility ($H = 10^{-3}$–10^{-4} atm m^3/mol) and found a good agreement. For two substances of low volatility ($H = 10^{-7}$–10^{-8} atm m^3/mol) agreement was also satisfactory (Metcalfe *et al.*, 1980). However, another group reported difficulties using this method for substances of low volatility (Smith *et al.*, 1981).

A good correlation between Henry's law constants and molecular weight was reported by Southworth (1979) for polycyclic aromatic hydrocarbons.

Laboratory measurements of chemical volatility from aqueous solutions include indirect and direct detection and quantification of volatilized compounds. With indirect methods, volatilization is estimated as the concentration decrease in the original aqueous solution. Assuming the absence

of other major losses such as biotic or abiotic degradation, indirect methods are acceptable for highly volatile substances for which volatilization losses can be detected within a short experimental time. Relatively simple methods (Dilling *et al.*, 1975; Hill *et al.*, 1976; Dilling, 1977; Southworth, 1979; Metcalfe *et al.*, 1980; Smith *et al.*, 1980, 1981; Rathburn and Tai, 1981; Rathburn *et al.*, 1982) use open beakers with stirred aqueous solutions. Their limits are reached when the concentration decrease (within a reasonable time period) equals the standard deviation of the analytical determination procedure. In some cases, the reaeration constant of oxygen and/or the volatilization rate of water are measured simultaneously to assess the liquid and/or gas phase mass transfer coefficient, and to aid in extrapolation of the volatilization rates obtained in the laboratory to those occurring under environmental conditions (Hill *et al.*, 1976; Smith *et al.*, 1980, 1981; Metcalfe *et al.*, 1980; Rathbun and Tai, 1981).

Large scale laboratory experiments in wind tunnels have been conducted to investigate the gas exchange between the air–water interface. The experience gained from such studies with natural gases, like carbon dioxide (Hoover and Berkshire, 1969; Liss, 1973; Broecker *et al.*, 1978), oxygen (Downing and Truesdale, 1955; Liss, 1973) and water vapour (Liss, 1973) have been used to facilitate similar experiments with xenobiotic chemicals, for example, benzene and toluene (Cohen *et al.*, 1978) or dieldrin (Slater and Spedding, 1981). Although, in principle, the direct measurement of the rate of volatilized substances is possible, volatilization is usually determined indirectly.

Using direct methods, the volatilized substance is trapped and then loss rates are determined. In this case other factors contributing to decreases in the parent compound in solution need not be considered; furthermore, even very small losses can be determined within relatively short time periods. For highly volatile compounds, however, there is the risk of incomplete trapping. Such unaccounted for trapping losses result in volatilization rate estimates which are much lower than actually occur. Therefore, trapping methods should be used only for compounds with medium or low volatility, and mass balance measurements should be included as part of the experimental design.

A small laboratory apparatus which may be used to determine the chemical volatility either indirectly or directly, depending on the properties of the chemical in question, has been developed by Klöpffer *et al.* (1982). It consists of a volatilization chamber, filled with an aqueous solution of the chemical, which is stirred, and a system of cold traps in Dewar flasks filled with an acetone–dry-ice mixture. Alternately, samples may be taken from the volatilization chamber to determine the decrease of initial concentration, or from the traps to measure volatilized amounts directly. The half-lives obtained in this apparatus differ from those calculated according to Mackay

and Leinonen (1975) by a factor of 3–4 (Scheunert, 1982a). This means that the overall mass transfer coefficient in this apparatus is within the range of average environmental conditions.

In a short-term, direct laboratory screening method (Kilzer *et al.*, 1979), the volatilized substance is trapped with the aid of a cold finger. This apparatus has been designed primarily to determine the volatility of chemicals from soils (see Section 5.4.2). For the determination of volatility from aqueous solution, this method is useful only as a short-term screen for comparative purposes. It is limited to substances whose volatility can be determined within 8 hours, since the cold finger has to be changed at least every hour and the test cannot be run overnight without observation.

The process opposite to the volatilization of chemicals from aqueous solution—*the uptake of chemicals from the air by water*—has been measured for dieldrin in the laboratory by using a wetted-wall column (Slater and Spedding, 1981).

Double-distilled water was pumped through an all-glass pump to the top of a glass column 152 cm in height and 2.5 cm in internal diameter. Water level fluctuations were minimized by the use of a surge tank from which the water flowed down the inner walls of the column at a velocity of 0.25 m s^{-1}. Air containing ^{14}C-dieldrin vapour at about 3×10^{-7} mgl^{-1} was passed up the column, the average concentration being obtained by sampling the air at the top and the bottom of the column. Measured volumes of air were drawn through Dreschel bottles containing toluene, and the ^{14}C-activity in the solvent at the end of the experiment was determined by liquid scintillation spectrometry. The water reaching the bottom of the column was passed through a polyurethane plug which was shown by a preliminary experiment to completely remove ^{14}C-dieldrin from solution. The dieldrin-free water then passed through the pump back to the top of the column. At the completion of the experiment, the radioactivity in the polyurethane plug was determined by liquid scintillation counting. Thus, the amount taken up by the water was determined both directly in the water and indirectly by analysing the air.

5.3.3 Field Tests

The transport of chemicals from water to air under field conditions has been measured by indirect and direct methods. The residue decline in natural waters depends on a multitude of variables; a simple computer model as a screen for persistence of chemicals in aquatic ecosystems has been presented by Roberts *et al.* (1981). The measurement of concentration declines in natural waters generally is a good estimate of volatilization only if other sources for loss including adsorption into sediments and biotic or abiotic degradation are negligible.

Measurement of concentration declines has been applied to the flowing channels of waste water from treatment plants (Ruf and Scherb, 1977). In most experiments in natural ponds (Salonen and Vaajakorpi, 1974; Klein *et al.*, 1981) the decline in concentration of chemicals in water is due to volatilization, adsorption into the sediment, degradation, and uptake by organisms; thus, little specific information on volatilization rates can be obtained from just the measurement of a concentration decline in the water. Three-phase equilibria in the sediment–water system may result in measured half-lives of residues in water, which are not independent of initial concentrations (Lay *et al.*, 1982).

Direct measurement of the volatility of chemicals from waters, such as a flooded field, is possible by utilizing aerodynamic techniques to estimate the vapour flux in the atmosphere above the water (Cliath *et al.*, 1980). This procedure is similar to those used to measure volatilization over terrestrial fields (see Section 5.4.3).

As in the case of other field studies, field tests on the volatility of chemicals from water should be used only for selected reference substances since these procedures are expensive.

In Table 5.3, half-lives of chemicals with different volatilities (one liquid-phase controlled chemical, one partly liquid-phase controlled chemical, and two gas-phase controlled chemicals), as calculated and determined experimentally under laboratory and field conditions, are presented. The table shows half-lives comparable within an order of magnitude for the liquid-phase controlled and the partly liquid-phase controlled chemical, with the exception of trichloroethylene in a pond compartment where only very low water movement occurred. Due to relatively rapid volatilization, the losses due to competitive processes seemed to be low. However, more confirmatory field data is necessary to generalize the extrapolation of theoretical and laboratory data to field conditions.

Poor agreement between calculated and laboratory data on the one hand and field data on the other is evident for the two gas-phase controlled chemicals. Their half-lives under field conditions are much shorter even when conversion products for pentachlorophenol were included in the analysis. The reason for this discrepancy is not the test method but the fact that chemical decomposition of both substances under field conditions is faster than volatilization. *p*-Chloroaniline is decomposed by autoxidation from the second day after application. This fact is reflected by the decrease in the concentration curve for the pond water, which is clearly exponential only for 3 days. Pentachlorophenol, in its ionized form, is photolysed by sunlight in water (pH 7.3) after 5–7 days (Wong and Crosby, 1977). It is assumed that for many chemicals with low volatility there are elimination mechanisms in natural waters, which occur at much higher rates than volatilization. It may be

Table 5.3 Half-lives of chemicals volatilized from water as calculated or determined experimentally according to different methods (in h/m depth)

Chemical	Trichloroethylene	Hexachlorobenzene	*p*-Chloroaniline	Pentachlorophenol
Resistance in the liquid phase (in per cent of the overall resistance)[a]	94% (liquid-phase-controlled)	86% (partly liquid-phase-controlled)	0.3% (gas-phase-controlled)	0.3 (gas-phase-controlled)
Half-life calculated, 20 °C (assording to Mackay and Leinonen, 1975)	**6.4**	**10**	**2183**	**3165**
Half-life in laboratory tests	20 °C, aerated closed system: **5.5–18** (Klöpffer *et al.*, 1982; Schmidt-Bleek *et al.*, 1982)	20 °C, aerated closed system: **31–41** (Klöpffer *et al.*, 1982; Schmidt-Bleek *et al.*, 1982)	20 °C, aerated closed system: **3633** (Klöpffer *et al.*, 1982; Schmidt-Bleek *et al.*, 1982)	20 °C, aerated closed system: **2984** (Klöpffer *at al.*, 1982; Schmidt-Bleek *et al.*, 1982)
	25 °C, open beaker: **4.5–6** (Dilling, 1977)			
Half-life in field tests	15–26 °C, channel: **4.4–43.6** (Ruf and Scherb, 1977)	20 °C, pond: **31** (Schauerte *et al.*, 1982)	20 °C, pond: **72 for 3 days** (Schauerte *et al.*, 1982)	15 °C, pond: **264** (Krieger, 1981)
	14 °C, pond compartment: **65** (Lay *et al.*, 1982)			

[a]This percentage is not constant but depends on environmental conditions. The figures given in this line are based on averaged k_l- and k_g-values according to Liss and Slater (1974)

concluded that volatility testing is relevant for less volatile substances only if they are chemically persistent, and that further research on volatility testing should be focused mainly on liquid-phase controlled chemicals.

5.4 TRANSFER OF CHEMICALS BETWEEN SOIL AND AIR

Numerous data are available for the transfer of chemicals from soil into the air. Besides contributing to atmospheric contamination, this transfer is important to the assessment of chemical residues in soil and their uptake by food plants. Information available on the opposite process—the adsorption of chemicals from the air by soils—is limited to low molecular weight atmospheric compounds.

5.4.1 Physico-chemical Properties

The role physico-chemical properties play in the transfer process of chemicals between soil and air is complex. The factors and mechanisms involved are different between free and adsorbed chemicals, between chemicals on surfaces and incorporated chemicals, between dry and moist soils. Before considering volatilization mechanisms of chemicals from soils, the volatilization of pure, free chemicals is discussed briefly.

The volatilization of *pure compounds* may be described by a model similar to that for the volatilization from water. The volatility of pure substances can be derived from equations for the volatility from aqueous solutions (9), (10) and (12) with the liquid phase resistance ($1/k_l$) equal zero, the 'water solubility' (S, expressed in moles/m^3) equal $10^6/M$, and the 'concentration difference' (Δc, expressed in g/m^3) equal 10^6. The volatility of a pure substance is then:

$$F = \frac{k_g \cdot p}{R \cdot T} \cdot M \qquad (14)$$

where k_g is the gas-phase mass transfer coefficient, p is the vapour pressure, R is the gas constant, T is the absolute temperature, and M is the molecular weight (Schulz, 1980; Sleicher and Hopcroft, 1982).

For the transfer of chemicals *from soil to air*, relevant physico-chemical substance properties and laboratory and field tests are listed in Table 5.4.

For the calculation of volatility of chemicals *adsorbed on dry surfaces*, equation (14) is applicable if, instead of the vapour pressure of the pure substance, the vapour pressure as reduced by soil sorption is used (Spencer *et al.*, 1973). It has been shown that the substance loss from the surface is constant provided the surface remains completely covered (Hartley, 1969; Taylor, 1978) and provided the decrease in concentration does not result in a decrease of vapour pressure (see Section 5.4.2).

Table 5.4 Tests for assessment of the transfer of chemicals from soil to the air

Test type	Principles	References (examples)
Determination of physico-chemical properties affecting the transfer	Assessment of transfer from vapour pressure, soil sorption coefficients or constants, diffusion coefficients, and water solubility	Spencer *et al.* (1973) Hartley (1969) Sleicher and Hopcroft (1982) Burkhard and Guth (1981)
Laboratory tests	Determination of vapour pressure reduced by soil adsorption	Spencer and Cliath (1969) Spencer and Cliath (1972) Cliath and Spencer (1972) Spencer and Cliath (1974)
	Indirect determination of volatility from soil	Haque *et al.* (1974)
	Direct determination of volatility from soil	Burt (1974) Kearney and Kontson (1976) Atallah *et al.* (1979) Kilzer *et al.* (1979) Burkhard and Guth (1981)
	Direct determination of volatility of chemicals incorporated into moist soils	Spencer and Cliath (1973) Spencer and Cliath (1974)

	Direct determination of volatility from laboratory ecosystems after soil treatment	Kloskowski *et al.* (1981) Gillett and Gile (1976) Beall *et al.* (1976) Schuphan (1977) Ebing and Schuphan (1979) Cole *et al.* (1976) Figge and Klahn (1982) Best and Weber (1974)
Field tests	Indirect estimation of volatility in large boxes by mass balance studies	Moza *et al.* (1976) Moza *et al.* (1979a and b)
	Indirect estimation of volatility in open fields by determination of soil concentration decrease	Sleicher and Hopcroft (1982) Elgar (1975) Talekar *et al.* (1977) Lichtenstein *et al.* (1970) Freeman *et al.* (1975) Ware *et al.* (1977) Edwards (1966) El Zorgani (1976)
	Direct determination of volatility over open fields	Caro and Taylor (1971) Willis *et al.* (1972) Taylor *et al.* (1976) White *et al.* (1977) Cliath *et al.* (1980) Turner *et al.* (1977)

For standardized conditions (dry soils in the laboratory), a more simple relationship has been reported. The evaporation rate (F, mass per unit of time and per unit of area) is proportional to vapour pressure and the square root of molecular weight (Hartley, 1969; Spencer *et al.*, 1973). Consequently, if the volatility of a reference compound is known, the volatility of a test compound may be calculated according to (15):

$$F_2 = \frac{p_2}{p_1} \cdot \frac{M_2}{M_1} \cdot F_1 \qquad (15)$$

where, F_2 is the volatility of the test chemical, F_1 is the volatility of the reference chemical, p_2 is the vapour pressure of the test chemical, p_1 is the vapour pressure of the reference chemical, M_2 is the molecular weight of the test chemical, and M_1 is the molecular weight of the reference chemical.

This equation which applies under laboratory conditions, however, is not valid under field conditions, except perhaps for compounds of low volatility for which residues may persist for extended periods (Taylor, 1978). The main reason for this inapplicability may be the irregular changes in moisture contents of soils in open fields.

Volatilization from *moist soil surfaces* is much higher than that from dry soils. It has been well established today that this phenomena is not due to 'codistillation' but to an increased vapour pressure of the chemical in moist soils, resulting from displacement of the chemical by water from adsorption sites (Spencer *et al.*, 1973). It is assumed that volatilization from a moist soil takes place mainly from the aqueous phase and, thus, is subjected to the rules of volatilization from aqueous solutions, as reported in Section 5.3 (Hamaker, 1972).

In case of *soil-incorporated chemicals*, the two-film model (see Section 5.3.1) is discussed mainly in the context of transfer of chemicals, preferably sulphur dioxide, from air to soils. The deposition velocity k_g is comparable to the mass transfer coefficient k between water and air (see equations (9), (10) and (12)). The value reciprocal to k_g is the overall resistance to the transfer and is the sum of the gas-phase and soil resistance (Klöpffer, 1981).

A precondition for the two-film model is the homogeneous mixing of both phases. This is rather unrealistic for water and even more so for soils, and therefore the model is applied only for gases with relatively high diffusion coefficients (e.g., sulphur dioxide). Normally, the transport of the chemicals within the soil is the limiting factor both for volatilization from soil and for uptake into soil.

The volatilization of soil-incorporated chemicals is dependent, in addition to the factors affecting the volatility from soil surfaces, upon the rate of transport of the chemicals from deeper soil layers to the evaporating surface. Aside from molecular diffusion which is of minor importance, the upward mass flow of aqueous solutions of the chemicals by capillary forces

('wick-effect') is the most important factor in this process. Water-solubility and sorption properties play an important role, as well as the water content of the soil in the upward transport of chemicals. Where a 'wick-effect' operates, it increases evaporation of chemicals from moist soils as compared to dry soils. However, the fact that chemicals may move downward in percolating water as well as upward due to the 'wick-effect' complicates prediction of chemical volatilization from water loss rates. The occurrence of three-phase equilibria is another problem which renders more difficult the extrapolation from simple models to field conditions. Even though volatilization rates from soil-incorporated chemicals cannot be estimated accurately because of the many variables involved, the atmospheric vapour concentration ratios of closely related compounds volatilized from *dry soil* can be calculated from relative saturation vapour pressures and adsorption isotherms (Cliath and Spencer, 1972; Spencer *et al.*, 1973). Desorption isotherms for weakly polar chemicals on soil, relating relative vapour density, d/d_0, to soil concentration usually follow the Freundlich equation:

$$\frac{x}{m} = K' \cdot \left(\frac{d}{d_0}\right)^{1/n} \tag{16}$$

where d is the observed vapour density, d_0 is the saturation vapour density without soil, x is the weight of chemical taken up by a weight m of solid, K' is the vapour phase desorption coefficient, and $1/n$ is a constant. If $1/n$ is very close to unity, i.e., at low concentrations, adsorption isotherms are closely approximated by assuming a linear relationship between x/m and d/d_0. Consequently, assuming linear adsorption isotherms between soil concentration, x/m, and relative vapour density, d/d_0, the ratio of the vapour density of two closely related chemicals can be calculated with the equation (17):

$$\frac{d_2}{d_1} = \frac{K'_1}{K'_2} \cdot \frac{\left[\frac{x_1}{m_1}\right]}{\left[\frac{x_2}{m_2}\right]} \cdot \frac{d_{0_2}}{d_{0_1}} \tag{17}$$

The magnitudes of K'_1 and K'_2 will change with soil properties and the nature of the chemical, but the ratio of K'_1/K'_2 should be relatively constant for any pair of 'closely related' compounds in any soil.

Another measure of relative volatility of soil-applied pesticides is a simple distribution coefficient, k_d, expressing the ratio between the actual vapour density, d, in ng/l, and the soil chemical concentration, x/m in μg/g. Such a distribution coefficient is related to the vapour pressure of the pesticide and its adsorption by the soil, but it is not a measure of vapour flux from the surface (Spencer *et al.*, 1973). Vapour flux is a function of distribution

coefficients and mass transfer coefficients, including diffusion coefficients and is dependent on environmental conditions.

Burkhard and Guth (1981) have proposed the calculation of the distribution ratio between *wet soil* and air from the distribution ratio between water and air and the soil/water adsorption coefficient, assuming that volatilization from a moist soil surface is volatilization from water modified by soil adsorption. The distribution ratio between water and air was calculated from water solubility and vapour pressure at saturation. The calculated chemical concentration in the air above wet soil has been compared with that obtained experimentally in a volatility measurement apparatus. Experimental and calculated results showed a linear correlation when plotted on logarithmic scales. However, it should be noted that the five test chemicals all had very low volatility from water ($H = 10^{-7} - 10^{-10}$ atm m^3 mol^{-1}) and, consequently, this transfer would be completely gas-phase controlled. The utility and interpretability of such tests with more volatile compounds seem questionable.

All theoretical approaches to estimate the volatility of organic chemicals from soil should be followed by experimental laboratory and/or field tests.

5.4.2 Laboratory Tests

Volatilization of pure, unadsorbed substances probably does occur in the environment only under exceptional conditions. As discussed in Section 5.4.1, it is related to the vapour pressure. Laboratory methods to determine the vapour pressures of pure substances either by direct pressure measurement or by gas saturation techniques will not be discussed in this chapter. A gravimetric method to determine the volatility of pesticides from glass plates by measuring the weight losses by means of a highly accurate, self-recording electric balance has been reported by Gückel *et al.* (1973; 1982). Although these tests were carried out under conditions which occur only rarely in the environment, they are suitable for a comparative evaluation of chemicals. If various carrier substances used for formulating pesticides are included in the measurements, adsorption effects and other interactions relevant to the agricultural environment can be considered (Gückel *et al.*, 1974).

Volatility of chemicals from soils may be assessed in the laboratory by different methods. The vapour pressure as reduced by soil adsorption may be determined by gas saturation techniques, passing nitrogen through the soil at a very slow rate approximating equilibrium conditions. The vapour pressure is then calculated from the amount of volatilized chemical trapped and determined by appropriate methods (Spencer and Cliath, 1969; Spencer and Cliath, 1972, 1974; Cliath and Spencer, 1972). The extent of vapour pressure decrease, due to adsorption, is related to the concentration on the soil surface.

The vapour pressure of an adsorbed chemical reaches that of the pure chemical at relatively low soil concentrations (Spencer and Cliath, 1975). The determination of reduced vapour pressure may be standardized by using a standard adsorbent (e.g., silica gel) instead of a natural soil (Politzki *et al.*, 1982). The ability to compare and rank different chemicals under experimentally reproducible conditions compensates for the disadvantage of having to use a standard adsorbent.

Measurements of volatility from soils by indirect methods, i.e., determination of concentration decrease in soil (e.g., Haque *et al.*, 1974) are applicable only to persistent compounds which do not undergo significant abiotic or biotic changes during the period of volatilization. With direct methods, air or nitrogen is passed over the soil surface and the volatilized substances trapped, identified and quantified by appropriate methods (Burt, 1974; Kearney and Kontson, 1976; Atallah *et al.*, 1979; Burkhard and Guth, 1981). Volatilized substances may be trapped also by a cold finger apparatus without the use of an air stream (Kilzer *et al.*, 1979), as described in Section 5.3.2. Although this experimental design does not simulate environmental conditions, the ranking of volatility for different chemicals is similar to that for residue losses occurring under field conditions.

For the determination of volatility of soil-incorporated chemicals, methods have been developed, which permit the soil surface to remain relatively moist during evaporation and facilitate the transport of the chemical to the soil surface with the water movement (Spencer and Cliath, 1973, 1974). This method should be used when the determination of surface evaporation alone does not give sufficient information.

Some closed aerated laboratory ecosystems are fitted with equipments to trap and determine chemical products volatilized from the whole system, thus, providing volatilization data not only for bare soil but accounting for the influences of plants and/or animals (Best and Weber, 1974; Gillett and Gile, 1976; Cole *et al.*, 1976; Beall *et al.*, 1976; Schuphan, 1977; Ebing and Schuphan, 1979; Kloskowski *et al.*, 1981; Figge and Klahn, 1982). Results from these systems should be considered better approximations of volatile behaviour for natural environmental conditions than those obtained by the volatilization studies with pure environmental media. However, these data are quantitatively predictive only if the air flow lies within the range of those occurring under field conditions; for example, the air flow in the agroecosystem chamber of Beall *et al.* (1976) simulated a wind speed of about 1 m/sec, representing a very calm wind, which, however, is within the natural range of wind velocities. If, in smaller laboratory ecosystems, only low wind speeds can be achieved, then the extrapolation of volatility data to outdoor conditions should be made only on a comparative basis (Kloskowski *et al.*, 1981).

Laboratory tests to determine the process opposite to the volatilization

from soil—*dry deposition of chemicals on to soil*—have been reported mainly for sulphur dioxide. Payrissat and Beilke (1975) measured the decrease of SO_2-concentrations in air moving over soil as a function of time in a 720 l chamber built in hard PVC which has low SO_2-adsorption properties. Terraglio and Manganelli (1966) passed air–SO_2 mixtures through glass columns filled with soils, and analysed the gas mixtures leaving the soils. Judeikis and Stewart (1976) used a cylindrical flow reactor with a concentric Pyrex cylinder coated with soil or other solids, and passed a carrier gas mixed with a small amount of nitrogen containing traces of SO_2, which was then analysed. Precondition for an effective transfer of chemicals from the air into soil is the adsorption on the mineral components, on the organic matter, or dissolution in the soil liquid (Klöpffer, 1981). In moist soils, all three mechanisms may be effective. Terraglio and Manganelli (1966) reported the variation of SO_2-transfer to soil, depending on soil properties and moisture content. The adsorption could be plotted as a Freundlich isotherm.

5.4.3 Field Tests

Field experiments on volatility of chemicals from soil to air are performed in large boxes, lysimeters or under actual field conditions. In most cases, plants are included in the test system. In boxes, the use of ^{14}C-labelled chemicals in mass balance studies permits the portion of chemical 'volatilized' within a certain time period to be quantified. This 'volatilization' loss also includes volatile conversion and mineralization products. A design of this experimental set-up is given in Section 5.5.1 (Moza *et al.*, 1976, 1979a and b). Such box studies are recommended when the identity of the volatilized portion is less important than the remaining residue, for example for agricultural problems.

When experiments in open fields are conducted, the residue losses in the upper soil layer include volatilization of parent compounds and of organic metabolites, mineralization losses as well as leaching to deeper layers (Edwards, 1966; Lichtenstein *et al.*, 1970; Freemann *et al.*, 1975; Elgar, 1975; El Zorgani, 1976; Ware *et al.*, 1977; Talekar *et al.*, 1977; Sleicher and Hopcroft, 1982). Therefore, field results are relevant to volatility only for persistent lipophilic chemicals like DDT or dieldrin with low conversion rates, low mineralization rates, and low leaching rates (Edwards, 1966; El Zorgani, 1976; Talekar *et al.*, 1977; Ware *et al.*, 1977; Sleicher and Hopcroft, 1982). An exponential representation of loss is an inappropriate description of chemical losses from fields by volatilization, as the volatilization from a smooth flat area with a uniform chemical deposit occurs at a constant rate (see Section 5.4.1). However, since the soil surface is rough and of complex geometry, the chemical layer non-uniform, and since a decrease in soil concentration can result in a decrease in vapour pressure (see Section 5.4.1),

residue loss decreases with time, even if competitive processes like leaching or decomposition are only of minor importance. Therefore, the half-life concept is generally used for chemical residue losses from soil, at least for estimates within limited (defined) time spans. Often different half-lives are obtained for subsequent time periods (Elgar, 1975; Scheunert, 1981).

In spite of all these limitations on the interpretation of residue losses from field tests, these methods are essential to the evaluation of the environmental significance of laboratory or outdoor experiments in boxes. By comparing the residue decline in the upper soil layer in the open field, with that occurring in box systems, the environmental significance of volatile loss estimates from box experiments can be ascertained. When box experiments on the behaviour of chemicals have been demonstrated to simulate the natural environment to an acceptable degree, these experiments may be employed as a tool to evaluate the environmental significance of laboratory data.

Direct measurements of the volatilization of chemicals and their conversion products from open fields have also been reported (Caro and Taylor, 1971; Willis *et al.*, 1972; Taylor *et al.*, 1976; White *et al.*, 1977; Turner *et al.*, 1977; Cliath *et al.*, 1980). The flux rate into the air is measured by collecting the air samples at various heights over the field and extracting the volatile chemical. In most cases, the fields are covered with plants so that the evaporation loss from a whole ecosystem is estimated.

The vertical flux of chemical vapour ($F\uparrow$) through a horizontal plane at height z above the soil is given by equation (18)

$$F\uparrow = K_z(d_c/d_z) \tag{18}$$

where d_c/d_z is the gradient of vapour concentration with height and K_z is the vertical eddy diffusivity coefficient at the height z. Since K_z is a function of the meteorological conditions only and not of any physico-chemical property (provided that the chemical behaves as a molecular vapour), K_z may be calculated from water flux data if available.

In the 'aerodynamic method', the eddy diffusivity coefficient is determined from the gradient of the wind profile over the surface. The vertical flux intensity is then calculated directly from the equation (19):

$$P\uparrow = K^2 \cdot \frac{(c_1 - c_2)(u_2 - u_1)}{\ln\left(\frac{z_2}{z_1}\right)^2 \phi^2} \tag{19}$$

where c_1 and c_2 are chemical concentrations and u_1 and u_2 are windspeeds at the heights z_1 and z_2 above the surface, K is van Karman's constant (0.4) and ϕ is the thermal stability correction term obtained by measurements of temperature lapse rates in the atmosphere (Taylor, 1978).

These kinds of field studies are expensive, difficult and, thus, cannot be recommended as a routine test for a large number of chemicals. However,

since these procedures represent the only means to obtain quantitative environmental data on volatilization, they should be used for reference chemicals to calibrate and evaluate laboratory data.

5.5 TRANSFER OF CHEMICALS BETWEEN SOIL, AIR AND BIOTA

The transfer of chemicals from water to organisms, from soil to animals, and within food chains is discussed in Chapter 4. In this section, the transfer of chemicals between soil, air and higher plants will be discussed. Since higher plants contain by far the largest portion of organic carbon in the biosphere, they contribute considerably to the transport of chemicals between environmental media and to their global distribution. The uptake and bioaccumulation of chemicals by plants from soil will be discussed in Section 5.5.1. The opposite process, the transfer of chemicals applied to plants via roots to the soil, is usually less important since plant treatment is accompanied by unintended soil contamination. Contamination of soil by the plant roots, in fact, has been shown to be very low (Weisgerber *et al.*, 1968 and 1970). The transfer of chemicals from plants to the air is discussed in Section 5.5.2; the opposite process, the uptake of chemicals by plants from the air, is indirectly part of the uptake of chemicals from soil by plants and, thus, is included in Section 5.5.1.

5.5.1 Uptake and Bioaccumulation of Chemicals by Plants

The assessment of mechanisms and factors affecting the uptake of chemicals from soil by plants is of great importance, especially for the nutrition and health of man. Besides the direct effect on unwanted chemical residues in food, the uptake of chemicals by plants can be regarded as a starting point of food web bioaccumulation or possible biomagnification of toxic chemicals in terrestrial animals.

The role physico-chemical data play in predicting the uptake of chemicals from soil by higher plants is not clear although data on plant uptake under a multitude of experimental conditions are available. Plant uptake is a complex process which includes not only the normal root uptake into conduction channels but also uptake and transport through oil channel systems (for oil-containing plants; Hulpke and Schuphan, 1970), from vapour in the surrounding air (Hulpke, 1970; Nash and Beall, 1970; Nash, 1974; Harvey, 1974; Kloskowski., 1981) and through external contamination by soil or dust followed by dissolution in the waxes of the cuticle (Grimmer, 1979).

Two mechanisms are involved in the uptake of chemicals into plants via roots: uptake into roots and subsequent translocation into shoots. For plants with 'normal' lipid content and with non-woody roots, the *uptake* of

non-ionized chemicals into the roots *from aqueous solution* is positively related to the logarithm of the *n*-octanol–water partition coefficient (log K_{ow}; Briggs *et al.*, 1982). The root concentration factor (defined as concentration in roots divided by concentration in external solution) is generally independent of concentration for dilute solutions (Leroux and Gredt, 1977) and was shown to increase with increasing log K_{ow} and to decrease to a limiting value of less than unity for polar compounds (Briggs *et al.*, 1982). Assuming that the root concentration factors can be explained by a partitioning to lipophilic root solids and a small uptake taken to be constant for all compounds, the mechanism of the small uptake can be ascribed most simply to equilibration of the chemical between the external solution and the water contained within the roots, both within the free space and the cells.

The efficiency of translocation of a chemical to shoots after root uptake is described by the transpiration stream concentration factor (defined as concentration in transpiration stream divided by concentration in external solution (Shone and Wood, 1974). For 18 chemicals, the translocation to the shoots was shown to be a passive process and was most efficient for compounds of intermediate polarity (centred at log K_{ow} = 1.8). The factors affecting the translocation of chemicals from roots to shoots are poorly understood. Polar chemicals may pass through the lipid membranes in the root with difficulty, whereas the passage of water is presumably not hindered, resulting in selective rejection of these chemicals at the membrane barriers. Lipophilic molecules on the other hand, being reversibly sorbed by the root solids, might be expected to pass to the xylem unhindered once equilibrium is reached, resulting in a transpiration stream concentration factor of unity. However, very lipophilic molecules are not readily transported in plants even after long exposure to the chemical. Thus, no relationship between the uptake by the root and the subsequent translocation to the shoot could be discerned (Briggs *et al.*, 1982).

When regarding the *uptake* of chemicals by plants *from soil*, it should be considered that not all the chemical applied to soil is in solution because of adsorption on to the soil phase, adsorption of non-ionic compounds being largely on the organic matter in soil. For a soil with given organic matter and water content, the fraction of chemical in soil solution can be calculated from the adsorption coefficient. The product of this fraction and the transpiration stream concentration factor appropriate to the value of log K_{ow} gives the relative ease of translocation from soil. The optimum, log K_{ow}, for uptake from soil is around 0.5, which is much lower than the value of 1.8 for optimum uptake from solution (Briggs *et al.*, 1977).

The relationships discussed probably are not fully valid for plants with 'higher' lipid content or with oil channels (cress, carrot), since additional uptake mechanisms due to the lipids are effective (Scheunert, 1982b).

The uptake via vapour in the air is related to the volatility of the chemical

or its degradation products. In the laboratory, for DDT and some cyclodiene insecticides, this pathway has been shown to contribute more to the total plant residue than root uptake (Nash, 1974). Under field conditions, vapour uptake is less important (Scheunert, 1982b). Thompson (1983) calculated deposition velocities of chemical vapours from the air to plant surfaces, regarding a total of seven surface and aerodynamic resistances. Typical values of the deposition velocities calculated on these bases were found to be around 5×10^{-3} m sec^{-1} in the case of vapours with molecular weights around 300.

For the uptake and translocation of chemicals reaching the plant surface either by deposition via vapour or by deposition via soil or dust particles, the same mechanisms are effective as for the uptake of foliage-applied pesticides. The efficiency of cuticle penetration, adsorption into the symplast, and short- and long-distance transport within the plant play a major role. In general, any modification of the molecular structure which results in increased lipid solubility will tend to enhance cuticular or membrane penetration; however, this is not always the case. Normally, the non-polar derivatives of a variety of chemicals penetrate the cuticle or other membranes more readily than polar ones (Kirkwood, 1976).

A review on environmental factors affecting plant uptake of chemicals from soil (plant species, growth stage, application rates, soil properties, etc.) has been given by Nash (1974).

Test methods to assess the uptake and bioaccumulation of chemicals from soils by plants are summarized in Table 5.5. Chemical uptake rates by higher plants obtained from open (Weisgerber *et al.*, 1970; Wallnöfer and Königer, 1974; Mittelstaedt and Führ, 1975; Cheng *et al.*, 1975) or aerated closed (Best and Weber, 1974; Kloskowski, 1981; Kloskowski *et al.*, 1981) laboratory tests are not representative of environmental conditions since rates from small laboratory pots are higher than those from large boxes or fields. For closed systems with a low air flow rate, the difference is even higher due to increased uptake from the gaseous phase. Thus, it is difficult to correlate laboratory and field data. This applies to plant data obtained within laboratory microcosms. However, laboratory or microcosm experiments are important to determine mineralization rates and to establish the complete mass balance of chemicals which is not possible in field tests.

Field tests for the bioaccumulation of chemicals from soil by plants include outdoor experiments in large boxes (Kohli *et al.*, 1973; Moza *et al.*, 1976, 1979a and b; Scheunert *et al.*, 1977) or in open fields (Onsager *et al.*, 1970; Lichtenstein *et al.*, 1970; Talekar *et al.*, 1977). These tests provide information which is relevant to environmental behaviour but quantitatively extrapolatable only for the specific conditions of the respective experiment. Variation of results with different environmental conditions (soil type, climate, plant species) is considerable.

In order to include conversion products in the investigation of chemical

Table 5.5 Tests for assessment of the transfer of chemicals from soils into higher plants

Test type	Principles	References (examples)
Laboratory tests	Open plant–soil tests	Weisgerber *et al.* (1970) Wallnöfer and Königer (1974) Mittelstaedt and Führ (1975) Cheng *et al.* (1975)
	Aerated closed plant–soil tests	Kloskowski (1981) Kloskowski *et al.* (1981) Best and Weber (1974)
	Open terrestrial ecosystems	Lichtenstein *et al.* (1974) Liang and Lichtenstein (1980) Virtanen *et al.* (1980)
	Aerated closed terrestrial ecosystems	Schuphan (1977) Ebing and Schuphan (1979) Gillett and Gile (1976) Beall *et al.* (1976) Cole *et al.* (1976) Figge and Klahn (1982)
Field tests	Experiments in large boxes	Kohli *et al.* (1973) Scheunert *et al.* (1977) Moza *et al.* (1976, 1979a and b)
	Experiments in open fields	Onsager *et al.* (1970) Talekar *et al.* (1977) Lichtenstein *et al.* (1970)

uptake by plants, ^{14}C-labelling of the chemical is indispensable. This, however, is generally not acceptable in open fields. Therefore, an outdoor experimental set-up using boxes has been designed to permit the use of radioactive labelled substances and to avoid problems associated with the increased uptake rates observed in laboratory pots. This model (Kohli *et al.*, 1973; Moza *et al.*, 1976, 1979a and b; Scheunert *et al.*, 1977) includes boxes of $60 \times 60 \times 60$ cm, filled with soil and kept under outdoor conditions with the upper surface of the soil at the same level as the surrounding ground, therefore meteorological conditions equal those of the surroundings. The boxes have holes at the bottom, permitting the drainage of excess leachate which is collected in a splash tray.

Although experiments in these boxes give uptake rates which are still somewhat higher than the average measured in open field conditions, rates are within the range measured in field experiments (Scheunert *et al.*, 1977). These experiments are, therefore, suitable to calibrate and evaluate laboratory data.

5.5.2 Volatilization of Chemicals from Plants

The volatilization of chemicals from plants into air represents an important pathway of atmospheric contamination. This is true both for the volatilization of chemical deposits from leaves, and the evaporation of chemicals taken up from the soil through the transpiration stream. Methods for the assessment of volatilization from leaves are presented in Table 5.6. The latter process occurs continuously during the uptake, and is included in the determination of plant residues, as discussed in Section 5.5.1, and in the determination of volatility of chemicals from plant–soil systems after soil treatment, as discussed in Section 5.4. This process may be assessed separately from other factors by injection of chemicals into plant stems while growing the plants in a closed aerated system, and then analysing the air for release of the chemical (Ebing and Schuphan, 1979).

Laboratory tests to assess the volatilization of chemicals from plant surfaces are nearly identical to those for determining volatilization from soil surfaces. Volatility is a function of vapour pressure which, as in the case of soil, is reduced by adsorption or by dissolution in leaf waxes. Results from indirect methods utilizing the application of chemicals on leaf surfaces in the laboratory and the determination of residues on the leaves after defined time periods (e.g., Weisgerber *et al.*, 1968, 1969 and 1970), include losses other than volatilization, for example metabolic degradation. Thus, these methods are applicable as volatility tests only for persistent chemicals which do not undergo significant chemical changes during the experimental period. In cases where only the residue loss is of interest, for example if potential residues in food shall be predicted, these methods produce sufficient information.

Table 5.6 Tests for assessment of the transfer of chemicals from plants to the air

Test type	Principles	References (examples)
Laboratory tests	Indirect determination of volatility from plant surfaces	Weisgerber *et al.* (1968, 1969, 1970)
	Direct determination of volatility from plant surfaces	Burt (1974) Que Hee *et al.* (1975)
	Direct determination of volatility from laboratory ecosystems after plant treatment	Nash *et al.* (1977) Schuphan (1977) Ebing and Schuphan (1979) Figge and Klahn (1982) Harvey and Reiser (1973)
Field tests	Indirect estimation of volatility in large boxes by mass balance studies after plant treatment	Haque *et al.* (1976) Sandrock *et al.* (1972)
	Indirect estimation of volatility in open fields by determination of plant residue decrease after plant treatment	Sleicher and Hopcroft (1982) Stringer *et al.* (1975)
	Direct determination of volatility over open fields	Cliath *et al.* (1980) Turner *et al.* (1977) Taylor *et al.* (1977)

With direct methods (Burt, 1974; Que Hee *et al.*, 1975), air is passed over the treated plant surfaces, the volatilized substances are trapped by appropriate equipment, and determined by specific analytical methods. In theses cases, misinterpretation of decomposition for volatility will not occur. The volatility from dried plant material was shown to be higher than that from soil (Burt, 1974).

The determination of chemical volatility from plant in laboratory ecosystems (Nash *et al.*, 1977; Schuphan, 1977; Ebing and Schuphan, 1979; Figge and Klahn, 1982) is performed in the same type of microcosm as used for the determination of volatility from soils. Harvey and Reiser (1973) reported a special trap system to collect also volatile metabolites, acidic, neutral, and basic substances being trapped separately. The results obtained from such ecosystems include the influences of soil, and, thus, are closer to environmental conditions than experiments with excised or dried leaves alone. Their direct predictability to environmental conditions, however, depends on the meteorological conditions in the system, especially on wind speed, as discussed in Section 5.4.2.

The extrapolation of results of short-term experiments to long-term environmental behaviour is possible only when the kinetics during the early experimental periods approximate those at later stages. This should apply to volatilization from flat, non-adsorbing, completely covered surfaces, as discussed in Section 5.4.1. However, under real conditions this does not seem to be true for plant volatilization. The volatilization losses of toxaphene and DDT from an agroecosystem chamber containing soil and cotton plants (Nash *et al.*, 1977) were found to follow log concentration with log time during the first week and then log concentration with linear time thereafter. The occurrence of several stages of volatiiization may be explained by the fact that regular surface volatilization will be followed by a volatilization of residues entrapped in surface irregularities on the leaves and of residues which have penetrated the leaf tissue (Taylor, 1978).

Field tests for chemical volatilization from plants are the same as those reported in Section 5.4.3 for the volatilization from soils, except that the chemical is sprayed on the growing plants. The 'volatility' as assessed indirectly from mass balance studies in large boxes, as described in Section 5.4.3, is significantly higher after foliar application of the chemical than after soil application (Sandrock *et al.*, 1972). According to direct volatility measurements in the laboratory (Burt, 1974), higher volatilization rates of parent compounds from plant surfaces are one reason for this phenomenon. However, higher total degradation rates by plants than by soils may also contribute significantly to the higher residue loss from leaves than from soil.

In experiments in open fields, the chemical is sprayed on plants, and the volatility is determined either indirectly by monitoring the residue loss from the plants (Stringer *et al.*, 1975; Sleicher and Hopcroft, 1982) or directly by

measuring volatile compounds over the field as described in Section 5.4.3 (Turner *et al.*, 1977; Taylor *et al.*, 1977; Cliath *et al.*, 1980). In the former case, the residue loss is determined only for plants alone, and the inclusion of soil losses is avoided. However, these residue losses are not only caused by volatilization but also by metabolic processes, as mentioned earlier. In the latter case, volatility is determined as a single factor, values not only include that from plant surfaces but also that from soil. Thus, the choice of method depends on the information needed in a specific case. Usually, the indirect method is preferred since it is easier to perform and since in most cases, especially in agricultural research, more information is required on the residual chemicals on the plants than on atmospheric contamination.

5.6 CONCLUSIONS

Theoretical approaches from physico-chemical parameters as well as laboratory and field tests yield good partial information on single factors affecting the intermedial transport of chemicals in the environment. The interaction between these factors in the ecosphere is complex and sometimes not well understood. Field tests give results which are relevant for a specific environment, but which are difficult to interpret. Basic research is needed to develop tests which are designed to elucidate the fundamental relations that permit laboratory observations to be interpreted in terms of field situations.

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