

Modeling of the Sorption and Diffusion Processes of Volatile Organic Air Pollutants in Grape Fruits

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A mathematical model for the description of the sorption and diffusion processes of gaseous toluene and *p*-xylene in fruits of grape has been proposed. This model is based on the Fick's II law regarding a particle with a spherical shape (such as the berry of grapevine) and describes changes of air pollutant concentrations in different layers of the fruit, that is, the wax, peel, and pulp, during an exposure to contaminated air. The mass transfer coefficient and diffusion coefficients in the respective layers can be estimated using the experimental values. The theoretical data and the results from the exposure under steady-state laboratory conditions were compared and showed a good applicability of the proposed model for the prediction of volatile air pollutant partitioning in grape berries.

Keywords: Toluene; xylene; fruits; sorption; diffusion; computer modeling

INTRODUCTION

Aerial contamination of vegetation is potentially an important source of human exposure to some toxic chemicals. Whether contaminants present in the atmosphere can be taken up by plants, accumulate, and ultimately enter the human food chain is an important question for determining health risks and safe levels of air-pollutant emissions. With recent public concerns over pollutants in foods, greater attention is being given to the process of chemical uptake by plants (1–3). Our previous studies were also connected with this matter (4, 5). They concerned the investigations of toluene sorption in different fruits and also in an artificial material used as a surrogate for the natural one (comparison study). Special emphasis was placed on the description of the sorption process, with regard to recent knowledge on this topic, as well as on the sorption kinetics. The latter issue was done by correlation to the mathematical models.

Factors affecting chemical uptake and distribution within plants are physical–chemical properties of the compound (vapor pressure, water solubility, and octanol/water partition coefficients), environmental characteristics (e.g., temperature), and plant characteristics (shape, biological structure, and chemical composition of the organs, especially lipid content) (6, 7). With knowledge of these factors, a number of models have been developed to give estimates of how chemicals are partitioned and transported into and between various plant tissues (7–9).

In this paper, we provide a brief review of these models, listing some of their features. We then demonstrate our model for the description of volatile organic

air pollutants partitioning (toluene and *p*-xylene as test cases) between different parts (layers) of grape berries. This model could help to predict bioaccumulation of a given xenobiotic in the respective layers of a spherically shaped fruit at a constant concentration of this pollutant in the air. It may be also helpful in the assessment of the protective role of waxes covering fruit peel.

THEORY: MATHEMATICAL MODELS

Fugacity Models. The first widely used compartment models were the *fugacity* models proposed by Mackay (10) and Mackay and Paterson (11, 12). Fugacity models have been used extensively for modeling transport and transformation of nonionic organic chemicals in complex environmental systems. Fugacity is a way of representing chemical activity at low concentrations, such as those typical in the environment. This kind of model was also developed to estimate air–vegetation bioconcentration factors (13). The controlling factors for a fugacity-based model are octanol–water and air–water (the Henry's law constant) partition coefficients.

Partitioning properties of compounds in the environment can be expressed in terms of fugacity capacities (*Z* values). Fugacity *f* (Pa) is related to concentration *C* (mol/m³) through a fugacity capacity *Z* (mol/m³·Pa), where *C* is *fZ*. Partition coefficients between air and water (*K*_{AW}) and octanol and water (*K*_{OW}) can be described in fugacity terms as

$$K_{AW} = Z_A/Z_W \quad (1)$$

and

$$K_{OW} = Z_O/Z_W \quad (2)$$

where subscripts A, O, and W refer to air, octanol, and water phases, respectively.

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One major advantage of fugacity models is their ability to represent diffusive and advective intermedia transport processes.

Plant Uptake Models. Plants generally have contact with two environmental media—air and soil. Plant interactions with these media are not understood well enough to define an accurate method of predicting chemical uptake. In the absence of complete information, there has been a reliance on simple bioconcentration factors (BCFs) that relate either a soil or air concentration to a plant concentration. What is meant by the *concentration in plant* is difficult to understand in larger plants where roots, stems, and leaves each may have different chemical concentrations. It is now common to see BCFs relating chemical concentrations in leaves to concentrations in air.

Bioconcentration factor BCF_V can be expressed as follows:

$$BCF_V = Z_L/Z_A = C_L/C_A [(g/m^3 \text{ of wet leaf}) / (g/m^3 \text{ of air})] \quad (3)$$

Recent studies on the bioconcentration of organic chemicals has focused on correlations between BCFs and known chemical properties such as Henry's law constant and octanol/water partition coefficients (7, 13). On the basis of azalea leaf experiments with five chemicals, Bacci et al. have developed a correlation of air-leaf bioconcentration factors with air/water and octanol/water partition coefficients (13). McFarlane et al. (14) have demonstrated experimentally that chemicals with similar values of K_{OW} can have drastically different long-term partitioning, again pointing out a lack of understanding of the mechanisms determining plant uptake and partitioning.

Paterson and Mackay (15) have proposed a multicompartment fugacity model for plants that includes not only leaves, stem, and roots (as in models mentioned above) but also xylem, phloem, and cuticle. This model was validated against experimental results obtained by Bacci et al. (16), who found that foliage concentrations were not directly dependent on the pollutant concentration in soil but rather on concentration in the air. On the basis of efforts to construct more comprehensive plant uptake models, Paterson and Mackay suggested that intermedia transport processes in the air-soil and air-plant interface should be regarded (15). Riederer proposed a fugacity-based equilibrium model that treats only the leaf-air interface but includes more details on the composition of leaves (17). Riederer (17) reports that a full description of steady-state partitioning within plant foliage requires a model that includes rates of uptake from and loss to aqueous and solid phases at the surface of the cuticle and the rates of translocation, metabolism, and dilution due to growth.

The current literature reveals that in order to advance beyond simple equilibrium models, knowledge of the rate constants at the boundary between compartments is essential.

EXPERIMENTAL PROCEDURES

To give some estimates for our model, the laboratory experiments based on the exposure of fruits to a polluted air stream were performed using a specially designed system. Its scheme, exposure conditions, and contaminant determination procedure are described in detail in our previous papers (4, 5). Generally, the system consists of a dynamic vapor generat-

ing part (producing air with a constant level of pollutant) connected with a set of thermostated exposure vessels in which plant material was placed. Fruits of the grapevine, bought at a local market, were exposed to a stream of air contaminated with ubiquitous in the environment and toxic pollutants such as toluene and xylene. These compounds were purchased from J. T. Baker, Deventer, The Netherlands (purity > 99%) and their concentrations in the produced air stream were as follows: 2.18 and 7.55 $\mu\text{g}/\text{dm}^3$ for toluene and *p*-xylene, respectively. Grape berries were put in the exposure vessels (one in each). After a certain time of sorption, the berry was removed from the vessel and subjected to the extraction. Separate parts of a berry were extracted with dichloromethane (for GC, J. T. Baker). The extracts were filtered and gas chromatographically analyzed. Using the data from the analyses, the average concentrations of the tested compounds in wax, peel, and pulp of the fruit were calculated on the basis of the following typical values: equivalent radius of berry, 0.0125 m; wax layer thickness, 0.00001 m; and peel (without wax) thickness, 0.00075 m.

PROPOSED SORPTION AND DIFFUSION MODEL

Model Assumptions. (1) Adsorption and absorption of contaminant can be approximated by effective absorption.

(2) A grape berry is a sphere. The volume of the berry can be divided into three layers: pulp (layer 1), peel (layer 2), and cuticular wax (layer 3). Contaminant diffuses inside each layer with a velocity determined by apparent diffusion coefficient D_1 , D_2 , or D_3 (m^2/h). The layers are spherical, and the radii of the layers are R_1 , R_2 , and R_3 (m).

(3) The concentration of contaminant at layer boundaries fulfills the relationship $C_1 = C_2/K_{12}$, $C_2 = C_3/K_{23}$, $C_3 = C_f/K_{3f}$, where C_i is the concentration (g/m^3) at layer $i = 1-3$, C_f is the concentration in the air at the berry surface, and K_{ij} and K_{3f} are partition coefficients. Equilibrium distribution of pollutant in the fruit (constant ratios of contaminant concentrations in the respective layers) is assumed to be achieved. Pollutant concentrations on both sides of the layer boundary change with time.

Due to gradual losses of water and aroma and flavor compounds (evaporation processes) by a grape berry along the exposure experiment, some changes of contaminant solubility in pulp (layer 1) and peel (layer 2) can be expected. These kinds of processes are not observed in the case of wax (layer 3) because it is nonliving structure and thus does not change its properties with time. A possible decrease of the solubility of contaminants (lower concentrations in the peel and pulp) during the experiment can be allowed for in the model by the introduction to it of an apparent partition coefficient (K_{23}) that is time dependent according to the formula $K_{23} = A + Bt$. Parameter A describes the equilibrium of the pollutants between layers 2 and 3 for a fresh berry, and parameter B describes changes of this equilibrium as a result of the changes of the properties of these internal layers. In the model, it was assumed that layers 1 and 2 change their properties in the same manner, and hence the partition coefficient K_{12} is time constant. Additionally, diminishing of the volume of a berry connected with fluid evaporation was neglected.

According to the assumptions discussed above, a mathematical model can be expressed as follows:

differential mass balance for contaminant

$$\frac{\partial C_i}{\partial t} = D_i \left(2 \frac{\partial C_i}{\partial r} + \frac{\partial^2 C_i}{\partial r^2} \right) \quad i = 1, 2, 3, i \text{ (layer index)} \quad (4)$$

To simulate the sorption process, initial and boundary conditions must be formulated.

initial conditions

$$C_i(t = 0, r) = 0 \quad i = 1, 2, 3 \quad (5)$$

boundary conditions

for $r = R_3$

$$\beta(C_{f,b} - C_f) = -D_3 \frac{\partial C_3}{\partial r}; \quad C_3(r = R_3)K_{f3} = C_f \quad (6)$$

where β is the mass transfer coefficient (m/h) and C_f and $C_{f,b}$ are contaminant concentrations in the air at the berry surface and inside the air phase;

for $r = 0$

$$\frac{\partial C_1}{\partial r} = 0 \quad (7)$$

for $r = R_1$

$$D_1 \frac{\partial C_1}{\partial r} = D_2 \frac{\partial C_2}{\partial r}; \quad C_1(r = R_1)K_{12} = C_2(r = R_1) \quad (8)$$

for $r = R_2$

$$D_2 \frac{\partial C_2}{\partial r} = D_3 \frac{\partial C_3}{\partial r}; \quad C_2(r = R_2)K_{23} = C_3(r = R_2) \quad (9)$$

MODEL SOLUTIONS AND PARAMETER ESTIMATION

The model (eqs 4–9) was solved numerically using the method of orthogonal collocation on finite elements. The orthogonal collocation on finite elements method applied here is the same as described in the literature (18, 19). The set of ordinal differential equations obtained after discretization due to orthogonal collocation on finite elements was solved with the VODE procedure (20) using the relative and absolute error equal to 10^{-6} . The VODE procedure automatically chooses the appropriate time increment to fulfill assumed error conditions. In each calculation the number of internal collocation points in subdomains (elements) was equal to 9. The number of subdomains was equal to 3—one subdomain for one layer.

The calculation of model parameters was based on the measured average pollutant concentration inside each layer (4). Model parameter K_{12} was calculated from experimental data for times >7 h. Other parameters, D_1 , D_2 , D_3 , A , B , β , and K_{3f} , were estimated through minimization of a sum of the squared differences between the experimental and the theoretical average

layer concentration. The minimization was performed with the use of the least-squares Marquardt method as modified by Fletcher (21).

The theoretical average layer concentration was calculated from

$$C_{av}(t) = \frac{1}{V} \int_V C(t) dV \quad (10)$$

where V is the layer volume.

All of the obtained values are presented in Table 1.

RESULTS OF CALCULATIONS

Comparisons of the experimental and theoretical data concerning the course of sorption of tested substances in grape berries, separately for each layer, are presented in Figures 1 and 2.

DISCUSSION

Vapor-Phase Uptake. The volatile pollutants can be transported in gaseous form to aboveground parts of plants, and the compound molecules can take two different routes—cuticular and stomatal pathways. The vapor-phase transport of contaminants at the interface between the atmosphere and fruits has not been reported yet. A network of parallel and serial conductances and resistances can describe that transport at the atmosphere/foilage interface. Conductances (meters per second) are equivalent to mass transfer coefficients. Adjacent to the leaf surface there is an unstirred air layer called the boundary layer, the conductance of which depends on wind speed and leaf surface topography (17). The mass transfer coefficient to a sphere from the boundary air layer is theoretically equal to $\beta = D_m/R$, where D_m is the molecular diffusion coefficient of pollutant in air and R is the radius of the sphere. In our case D_m is ~ 0.02 m²/h and $R \sim 0.0125$ m, which gives $\beta = 1.6$ m/h. The mass transfer coefficients from a turbulent atmosphere (such as a stream of air in the experiments) are a fewfold higher than in the case of stagnant air. Thus, the estimated β values seem to be too low. However, it must be taken into account that in the model one stage of the mass transport process to a grape berry interior was neglected, that is, the adsorption process on the waxy surface. This stage, in reality, does not proceed with an infinitive rate, and due to this process some resistances of mass transfer occur. These resistances could influence the obtained values of effective mass transfer coefficients.

Pollutant Distribution among Fruit Layers. In the course of the exposure of grape fruits to a contaminated air stream, the concentrations in all of the layers decrease after reaching a maximum value. This is most probably connected with contaminant solubility changes due to water and lipid component losses (5, 22). Average concentrations of *p*-xylene and toluene in all of the layers had reached maximum values at ~ 15 – 16 h (an exception can be noted for toluene in pulp taking into account the experimental data). It should be noted that

Table 1. Values of Model Parameters

contaminant	partition coefficients				effective diffusion coefficients			mass transfer coefficient
	K_{12} (–)	$K_{23} = A + Bt$ (–)		K_{3f} (–)	D_1 (m ² /h)	D_2 (m ² /h)	D_3 (m ² /h)	β (m/h)
toluene	133	0.5497	0.002253	0.0003388	0.0001911	8.903×10^{-5}	8.603×10^{-9}	1.306
<i>p</i> -xylene	49	0.8128	0.0008177	0.0009152	0.000897	0.000307	7.168×10^{-9}	0.5713

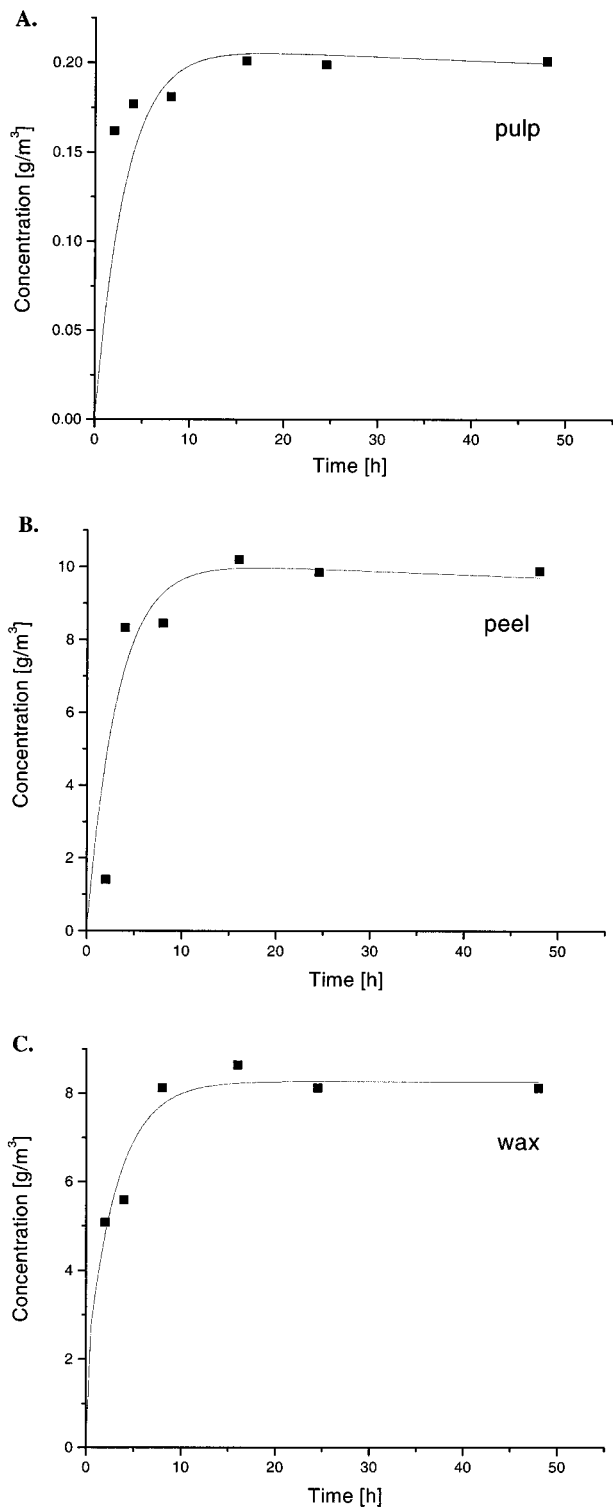


Figure 1. Sorption course of *p*-xylene in the respective layers of a grape berry: (A) pulp; (B) peel; (C) wax; solid line, theoretical curve; points, experimental values.

in the case of wax the concentrations of *p*-xylene and toluene were growing much faster during the first hour of exposure than in the other layers, which can be explained by the very good sorption properties of the wax layer.

Generally, the distributions of both pollutants among the layers look similar; that is, the highest concentrations (expressed as pollutant mass per volume of layer) were observed for peel and the smallest for pulp. However, amounts of the tested contaminants sorbed

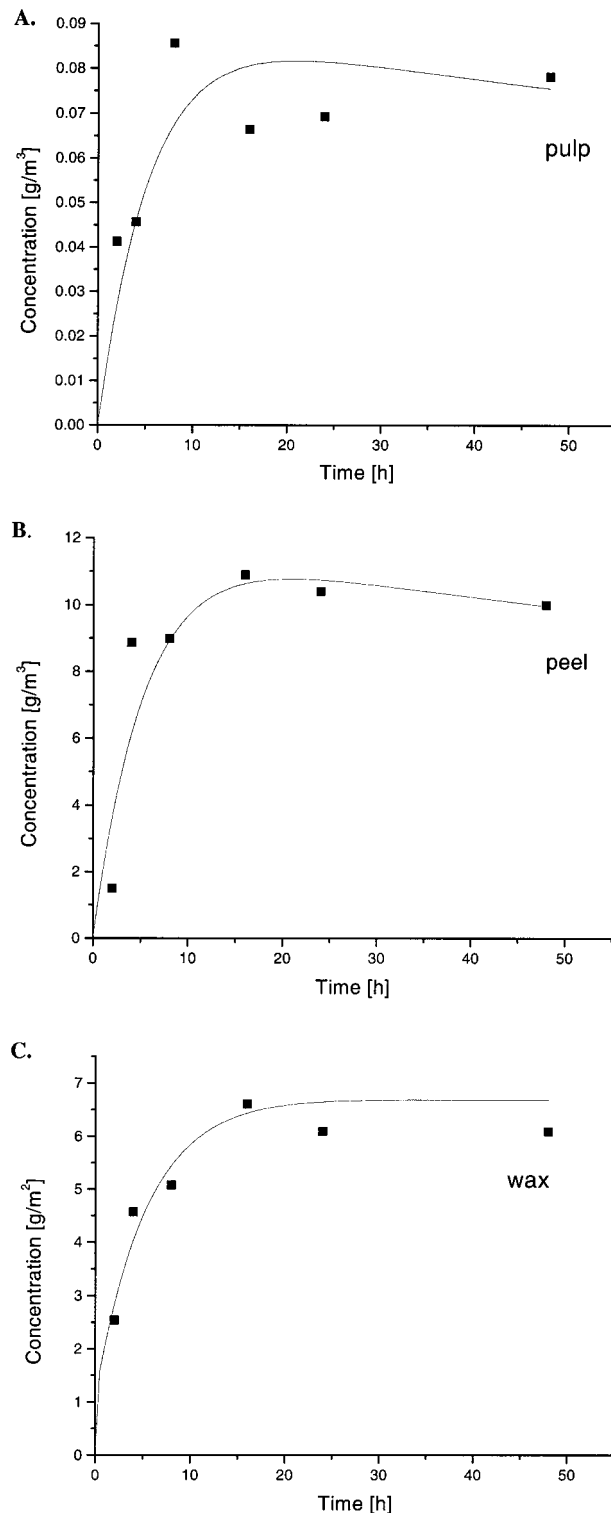


Figure 2. Sorption course of toluene in the respective layers of a grape berry: (A) pulp; (B) peel; (C) wax; solid line, theoretical curve; points, experimental values.

in pulp differ significantly (maximum concentration of *p*-xylene is ~2.5 times higher than that of toluene).

Model Output. The presented model is simplified (the adsorption of pollutant on the fruit wax is neglected; a berry structure is not considered in detail), so the obtained diffusion coefficients are not real but calculated values (apparent diffusion coefficients). They are dependent on the tortuosity and shape of pores, through which diffusion occurs, and on the topography of the surface of diffusion. However, this simple ap-

proach gave diffusion coefficients comparable to the literature data (23) with regard to their order of magnitude (waxes are solids and diffusion coefficients are smaller up to 6 orders of magnitude than in liquids). Despite the above-mentioned simplifications, the proposed model enables the description of the distribution of concentrations of volatile air pollutants between the layers of a spherically shaped fruit (assuming that contaminant equilibrium is established). Initial tests of this model, with *p*-xylene and toluene as contaminants and grape berries as the examined fruits, show a good agreement with the experimental results (Figures 1 and 2). Thus, it can be presumed that the model might work satisfactorily and give correct data for other pollutants (present in the atmosphere in the gaseous state) and fruit species.

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