MULTIMEDIA TRANSPORT OF ORGANIC CONTAMINANTS AND EXPOSURE MODELING

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SUMMARY

Human exposures to organic contaminants in the environment are a complex function of human factors, physicochemical properties of the contaminants, and characteristics of the environmental media in which the contaminants reside. One subject of interest in the screening of organic chemicals for the purpose of identifying exposure pathways of potential concern is the relationship between exposures and contaminant properties. To study such relationships, a multimedia environmental model termed GEOTOX is used to predict the equilibrium partitioning and transport of "reference" organic chemicals between compartments representing different media (i.e., soil layers, ground water, air, biota, etc.) of a contaminated landscape. Reference chemicals,

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which are added to the surface soil of a landscape, are defined by properties consisting of the Henry's law constant, soil water-soil organic carbon partition coefficient, and bioconcentration factors. The steady-state concentrations of the chemicals in the GEOTOX compartments are then used to estimate lifetime average exposures (in mg/kg-d) to the contaminants for individuals living in the contaminated landscape. Exposure pathways addressed include ingestion, inhalation, and dermal absorption. Local sensitivity analyses are performed to determine which chemical and landscape properties have the greatest effect on the exposure estimates.

INTRODUCTION

Organic compounds released into the environment will distribute to soils, water, and air where various chemical and biological processes act to degrade them. The distribution of organic substances among the different media depends on their physicochemical properties as well as the characteristics of the landscapes where they are released or deposited. Human exposures to the "resident" contaminants in a landscape can subsequently occur through direct contact with various media (e.g., skin contact with soil) or consumption of contaminated foods. Unfortunately, little is known about the relationships between contaminant and landscape properties and potential exposure pathways to humans. To study these relationships, we use a multimedia model termed GEOTOX [1,2] that simulates the simultaneous transport and transformation of a contaminant among different environmental media (e.g., ground water, soils, air, etc.). Human exposures to a contaminant are also estimated by GEOTOX for air-, water-, and soil-based pathways.

The GEOTOX model uses the "fugacity" approach described by Mackay and Paterson [3] to define distributions among the physical phases of each environmental compartment. Transfers between compartments consist of mass transfer and advection. Cohen and Ryan [4] have illustrated the use of multimedia models as screening tools for environmental impacts. GEOTOX has been developed to deal explicitly with a multimedia approach to total human exposure.

As a means of exploring the relationships among contaminant properties, landscape characteristics, and exposure, we have defined a series of reference chemicals with widely varying physicochemical properties (i.e., Henry's law constant, bioconcentration factors, and soil-water partitioning) and a landscape with geohydrologic features that are representative of humid areas in the southeastern U.S. Multipathway exposures to the reference contaminants in the landscape are estimated for an individual who lives an entire lifetime in the landscape and receives all of his/her food from indigenous sources. In the sections that follow, we describe the primary attributes of the compartmental structure of GEOTOX along with the key transport processes between compartments. We also define the contaminant properties that are of primary interest in our analyses as well as the characteristics of the different exposure pathways. We then examine the results of our simulations of the exposures associated with different contaminants in the landscape.

A COMPARTMENTAL VIEW OF THE ENVIRONMENT

The environment can be viewed as a series of distinct, but interconnected compartments, consisting of terrestrial, atmospheric, and aquatic components. We use eight homogeneous compartments to represent a typical landscape unit, which is shown in Figure 1. The terrestrial sub-environment includes an upper soil layer that includes the root zone of plants; a lower soil layer that is the unsaturated or vadose zone above an unconfined aquifer or groundwater component of the landscape. The aquatic environment is represented by a surface water source (i.e., pond, lake) that includes a layer of sediments. The atmosphere is divided into a gas phase and a particulate phase.

A compartment is described by its total mass, total volume, solid-phase mass, liquid-phase mass, and gas-phase mass. Mass flows among compartments include solid-phase flows, such as dust suspension or deposition, and liquid-phase flows, such as surface run-off and groundwater recharge. The transport of individual chemical species among compartments occurs by diffusion and advection at the compartment boundaries. As an example, consider the upper soil layer, which contains solids, liquids, and gases. An organic chemical added to the surface soil distributes itself among these three phases such that it achieves chemical and physical equilibrium. Among the potential transport pathways from the upper-soil compartment are liquid advection (surface run-off), solid-phase advection (soil erosion to surface water or dust stirred up and blown about), and diffusion from the soil-gas phase into the lower atmosphere. Each chemical species is assumed to be in chemical equilibrium among the phases within a single, well-mixed compartment. However, there is no requirement for equilibrium between adjacent compartments. Table 1 lists the pertinent parameters for each of the eight compartments.

Time-dependent changes in the molar inventory of a contaminant in a compartment are defined by the following mass-balance equation:

$$\frac{dN_i^a}{dt} = \lambda_i^a N_i^a(t) - \sum_{\substack{j=1\\ j\neq i}}^{m} T_{ij}^a N_i^a(t) - T_{io}^a N_i^a(t) + \sum_{\substack{j=1\\ j\neq i}}^{m} T_{ji}^a N_j^a(t) + S_i^a(t) \qquad (1)$$

where

N_i^a = molar inventory of species a in compartment i at time t, moles;

λ_i^a = decay constant for species in a compartment i accounting for radioactive decay, chemical decomposition, etc., y^{-1};

T_{ij}^a = transfer rate of species a from compartment i to compartment j, y^{-1};

T_{io}^a = transfer rate of species a from compartment i to some external system o, y^{-1};

S_i^a = source term for the rate of introduction of species a into compartment i, moles/y; and

m = the number of compartments.

The transfer rates between compartments are a function of the diffusive and advective fluxes between the compartments. The steady-state solution to Eq. (1) is obtained by setting the derivatives equal to zero and solving the system of simultaneous equations for a constant source, S_i. The partitioning of a contaminant between the solid, liquid, and gas phases of a compartment is determined by the soil/sediment partition coefficient, K_d, and the Henry's law constant, H, which represents the equilibrium partitioning of a contaminant between air and water (which can be estimated as the ratio of vapor pressure to aqueous solubility). The K_d value for a neutral organic compound in a particular soil can also be estimated as the product of its organic carbon/water-partition coefficient, K_{oc}, and the weight fraction of organic carbon in the soil. To estimate transfers of a contaminant to foods, three additional partition coefficients are used in GEOTOX. The plant/soil partition coefficient, K_{sp}, is the ratio of contaminant concentration in vegetation (dry weight) to concentration in soil. Contaminant transfers from media and feed to milk and meat are estimated with the partition coefficient, K_{fd}, which is the ratio of contaminant concentration in animal fat to contaminant concentration in animal diet. The third partition coefficient is the bioconcentration factor for fish, K_{fw}. This factor is calculated as the ratio of the contaminant concentration in fish at steady state to the contaminant concentration in water.

Reference Chemicals

For the purpose of illustrating the effect of the physicochemical properties of a contaminant on exposure estimates, we have chosen low and high values for H and K_{oc}, and the bioconcentration factors, K_{fd} and K_{fw}, denoted collectively as B. Table 2 presents the values chosen for the different properties. A reference chemical is defined by a unique combination of property values. As an example, H(h)K(h)B(h) represents a substance with high values for the properties; low values are designated by an "l". There are eight unique combinations of the properties, each of which defines a different reference chemical (the reference chemical combinations are denoted HlKlBl, HlKhBl, HlKlBh, HlKhBh, HhKlBl, HhKhBl, HhKlBh, and HhKhBh). All of the reference chemicals have a gram-molecular weight of 100 and diffusion constants for air and water of 5×10^{-6} and 5×10^{-10} m/s [5], respectively. Because little is known about the potential range of K_{sp} values for organic chemicals, we simply assume that the concentration of a contaminant in plant biomass is equal to the concentration of the contaminant in soil water.

Reference Landscape

The landscape for which we have chosen to simulate the equilibrium partitioning and transport of the reference chemicals among the eight compartments shown in Fig. 1 is indicative of the southeastern U.S., a humid region with annual rainfall of about 100 cm. The salient characteristics of the atmospheric compartments are a mixing height of 1000 m and an annual average wind speed of about 4 m/s. The dust load of the air (particles) compartment is 100 $\mu g/m^3$ and the average deposition velocity of the particles is 330 m/d. The upper and lower soil layers are 0.25 and 2 m thick, respectively, with organic carbon contents of 2 and 0.1 wt%. The surface soil layer supports an annual average standing biomass (dry) of 3×10^7 kg/km^2. Surface runoff amounts to 35 cm/y and evapotranspiration is 60 cm/y. Erosion of surface soil is estimated at 3×10^5 kg/km^2-y. The groundwater compartment, with a thickness of 46 m, has a porosity of 0.1 and a density of 2.3 kg/L. Recharge to the aquifer is 5 cm/y and irrigation withdrawals are the equivalent of 2 cm/y. The organic carbon content of the aquifer is 0.01 wt%. The area of the surface-water compartment is 2% of the total land surface and the underlying sediments are 0.05 m thick. Estimates of all the landscape parameters are summarized in McKone and Layton [1] and the derivation of the parameter estimates are contained in Layton et al. [2].

EXPOSURE PATHWAYS

For the purposes of our analysis we assume that a lifelong resident of the reference landscape receives all of her/his food and water from the landscape. The landscape has a surface area of 1 km^2, and we further assume that each reference chemical is continuously added to the surface-soil layer. There are seven pathways by which an individual can be exposed to a reference chemical: (1) inhalation; (2) water consumption, (3) fruit and vegetable ingestion; (4) meat and dairy-food ingestion; (5) fish ingestion; (6) soil ingestion; and (7) dermal absorption of contaminants adsorbed to soil particles. In order to estimate lifetime exposure to a reference chemical via these pathways, we calculate a time-weighted exposure (in mg/kg-d) based on childhood (0 to 10 y) and adult (10 to 70 y) exposures. Table 3 lists the appropriate physiologic characteristics of the two age groups. Another assumption related to the exposure scenario is that half the drinking water comes from the surface-water compartment and half comes from ground water. Because of a general lack of data on the biotransfer of organic compounds from contaminated soils to crops and meat, we have adopted a simplified approach for calculating exposures to contaminants via the consumption of fruits/vegetables and meat/dairy products [1,2]. We calculate exposures via the fruit/vegetable pathway as the product of the contaminant concentration in edible biomass and the daily intake of fruits, vegetables, and grains (see Table 3 for daily intakes). For the meat- and dairy-food-based pathways, exposures are computed as the product of the ingestion of milk or beef fat and the concentration of a contaminant in fat. The contaminant concentration in fat is calculated by multiplying the weighted-average concentration in contaminated media and feed by the bioconcentration factor, K_{fd}. The concentration of a contaminant in fish is calculated as the product of the contaminant concentration in surface water and K_{fw}. Exposures to contaminated soils occur via direct ingestion and dermal absorption. Daily intakes are calculated as the product of contaminant concentration in soil and soil intakes by each exposure route.

DISTRIBUTION OF REFERENCE CHEMICALS AMONG THE EIGHT ENVIRONMENTAL COMPARTMENTS

To examine the effect of chemical properties on the compartmental distributions of the chemicals, we used GEOTOX to calculate the percentage breakdown of the total mass of each reference chemical among the eight compartments under steady-state conditions (calculations were based on the annual addition of one g-mole of each chemical to the surface soil of the 1 km^2 landscape, no subsequent chemical or biological degradation, and transport out of the landscape via advection from the surface water and air compartments). The primary parameters influencing the compartmental distributions were H and K_d. The bioconcentration factors did not significantly affect the distribution of the reference chemicals among the compartments. In Figure 2 we show graphically the distributions of four reference chemicals (expressed as percents of the total mass in the landscape) among the eight landscape compartments. The four chemicals represent four different combinations of the low and high values of H and K_d. Significant percentages of the reference chemicals with the high Henry's law constants reside in the atmospheric (gas) compartment; however, with a low value of that parameter, essentially none of the chemicals reside in the atmosphere at steady-state conditions. As the value of K_d increases for both the low and high Henry's law compounds, more of the compounds reside in the subsurface compartments (i.e., the two soil layers and ground water) due to the greater sorption to solids contained in those compartments.

EXPOSURES TO REFERENCE CHEMICALS

We predicted lifetime average exposures to each of the reference chemicals and found that the four compounds with the high values for the Henry's law constant (i.e., HhKlBl, HhKhBl, HhKlBh, and HhKhBh) resulted in exposures that were dominated by inhalation. In fact, the inhalation pathway ranged from 93 to 98% of the lifetime exposure. The next important pathway for those chemicals was meat/dairy-food ingestion, which amounted to no more than 4% of total exposure. The low Henry's law compounds, in contrast, produced annual average exposures that were about a factor of 40 higher than the low Henry's law compounds. The main reason for the difference is that the residence time of the volatile chemicals in the atmospheric (gas) compartment is quite short because of advective losses, and therefore the ambient concentration did not reach levels that produced elevated exposures. The principal exposure pathways for the low Henry's law compounds is shown in Figure 3. When the bioconcentration factors were low, ingestion of water and grains/vegetables (i.e., denoted as biota) were the dominant pathways, but when the bioconcentration factors were high, fish and meat/dairy-food ingestion became important. The ingestion of contaminated ground water from the landscape, however, may be unimportant for short-term inputs, as opposed to steady-state inputs, because of the long residence times associated with the groundwater compartment. Dermal absorption and soil ingestion were never significant pathways for any of the eight reference chemicals considered. Nevertheless, we note that we are simulating an idealized exposure scenario (i.e., an individual receives all food, air, and water from the contaminated landscape), and therefore under other exposure scenarios skin absorption and soil ingestion could actually constitute the primary or sole exposure pathways to a contaminant at a given location.

To study further the relationship between the Henry's law constant and the total exposure to a compound, we varied this parameter over six orders of magnitude. At values less than 0.1 torr-L/mol, there was essentially no changes in the calculated exposures because the concentrations of the various contaminants in soils and water were not significantly changing and hence the associated noninhalational exposures were also unchanging (see Figure 4). We also completed a differential sensitivity analysis by sequentially reducing each variable by 1% and determining the percent change in total exposures. For a compound with a low Henry's law constant (i.e., HlKlBl), the most important parameters were those that directly affected the hydrologic balance of the landscape and chemical partitioning between soil and soil water. A 1% decrease in rainfall increased total exposure by 1.9% and similar decreases in evapotranspiration, runoff, organic carbon content of the surface soil layer, and K_{OC} changed total exposures by -1.12, +0.26, +0.30, and +0.30%, respectively. For a high Henry's law compound (i.e., HhKhBh), exposures were most sensitive to changes in parameters affecting the atmospheric concentration of a chemical. The height of the atmospheric compartment and average wind speed had the greatest effect on total exposure (i.e., both increased exposure by +1.01%), followed by rainfall (-0.04%), evapotranspiration (+0.02%), and the Henry's law constant (+0.02%).

CONCLUSIONS

We have used the GEOTOX multimedia transport model to investigate how reference chemicals distribute in a humid landscape consisting of eight compartments. A key parameter affecting the compartmental distributions of the reference chemicals continuously added to surface soil is the Henry's law constant, H. With low values of this parameter (~ 10^{-3} torr-L/mol), chemicals distributed primarily to ground water and soils. When the soil water/soil organic carbon partition coefficient, K_{OC}, was raised from low (10) to high (10^3) values, the amount of reference chemical sequestered in soils increased, which meant that smaller amounts of each chemical were available for transport to the atmosphere or surface water. Changes in H also had an important effect on the predicted exposures. As H decreased, total exposures increased, with ingestion exposures dominating total exposures at low values of H. Skin absorption of chemicals adsorbed to soils and ingestion of contaminated soil were never important exposure pathways in our idealized scenario of exposures to reference chemicals in the landscape. One important data gap that stands out is the absence of data on plant-uptake factors for organic compounds. Additional studies are needed to quantify these uptake factors for different food-chain crops and chemicals with varying physicochemical properties.

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Table 1. Parameters that define the primary attributes of the eight compartments used in GEOTOX.

Compartment	Parameter
Air (gas)	Height
	Absolute humidity
	Precipitation
	Ambient temperature
	Yearly average wind speed
Air (particles)	Height
	Dust load
	Deposition velocity of dust particles
	Resuspension velocity of soil particles
Biomass	Dry-mass inventory
	Dry-mass production
Upper and lower soils	Thickness
	Bulk density
	Water content
	Air content
	Organic carbon fraction
	Evapotranspiration (surface soil)
	Surface runoff (surface soil)
	Mechanical erosion (surface soil)
Ground water	Water inventory
	Rock porosity
	Rock density
	Irrigation withdrawal
	Recharge
	Organic carbon fraction
Surface water	Fraction of land surface
	Average depth
	Suspended-sediment load
	Sediment-deposition rate
	Precipitation
	Evaporation
Sediments	Thickness
	Bulk density
	Porosity
	Sediment resuspension rate
	Sediment deposition rate
	Organic carbon fraction

Table 2. Primary properties selected to represent reference contaminants. A reference chemical is defined by a unique combination of properties. For example, H(h)K(h)B(h) stands for a reference chemical with high values for each of the three properties.

	Parameter value	
Parameter	Low	High
Henry's law constant, torr-L/mol (H)	10^{-3}	10^{3}
K_{oc} (K)	10	10^{3}
Bioconcentration factors (B)		
K_{fw}	10	10^{3}
K_{fd}	10^{-2}	1

Table 3. Physiologic, food, and soil intake parameters for a child and adult (based on data in Snyder [6], US NRC [7], Hawley [8], and Lepow et al. [9]). Adapted from McKone and Layton [1].

Parameter	Units	Child	Adult
Age	y	0–10	10–70
Weight	kg	17	70
Surface area of skin	m^2	0.79	1.7
Inhalation rate	m^3/d	10	22
Water intake	L/d	0.7	2
Intake of fruits and vegetables[a]	kg (fresh)/d	0.6	0.5
Intake of milk and dairy products	kg (fresh)/d	0.5	0.3
Intake of meat and poultry	kg (fresh)/d	0.1	0.3
Intake of fish	kg (fresh)/d	0.002	0.0065
Soil ingestion	mg/d	100	58
Dermal absorption of soil	mg/d	8	5

[a] For vegetation the ratio of fresh mass to dry mass is assumed to be approximately 5.

FIGURE CAPTIONS

Fig. 1. Compartmental structure of the GEOTOX multimedia model.

Fig. 2. Percentage breakdowns of the steady-state mass inventories of four reference chemicals among six of the major compartments.

Fig. 3. Major components of the daily exposures to four reference chemicals added to the GEOTOX landscape.

Fig. 4. Total daily exposures resulting from the steady-state release of chemicals with different Henry's law constants, but with fixed values of K_{oc} (100), K_{fw} (1000), and K_{fd} (1). Releases are to the surface-soil layer.

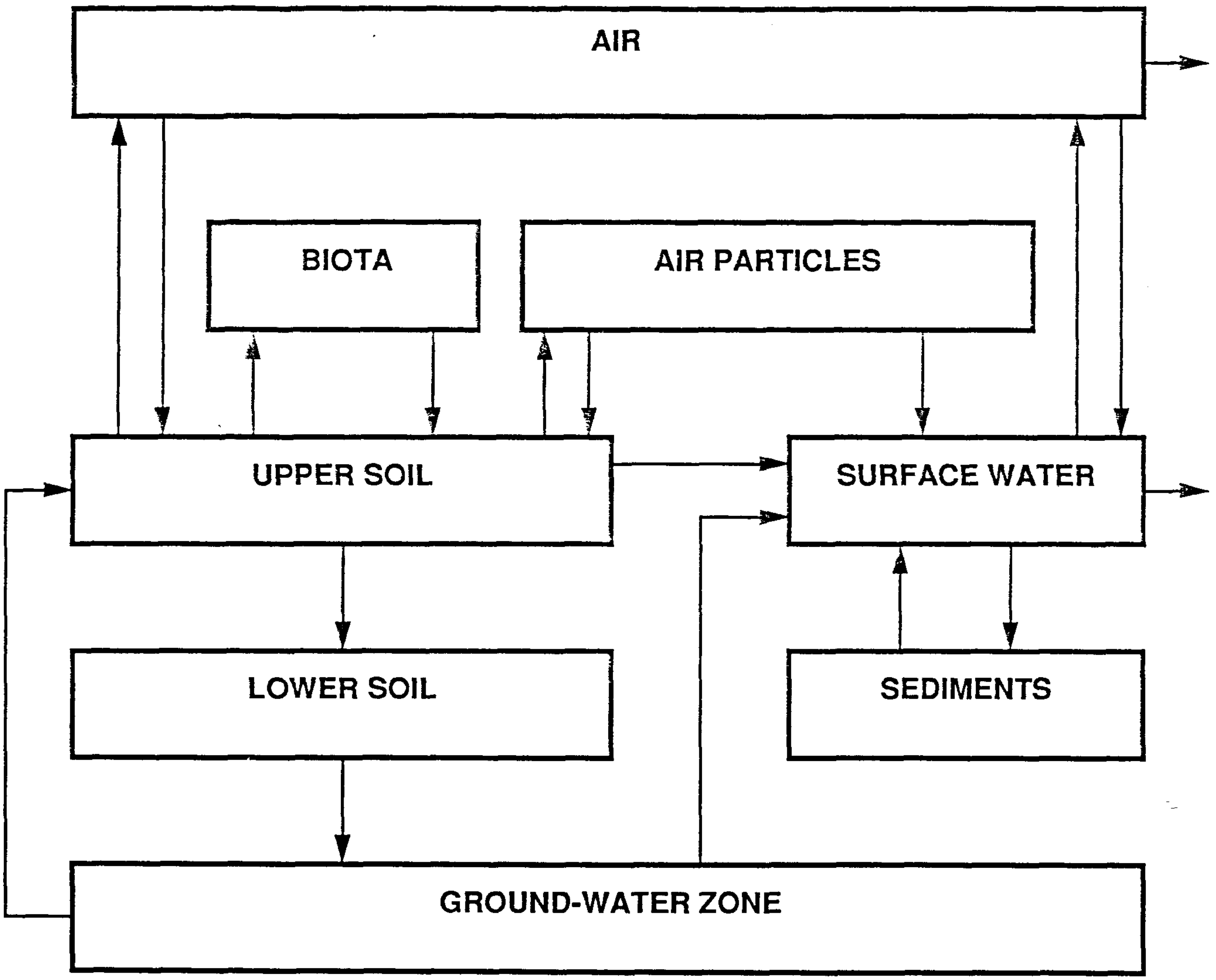

AIR
BIOTA
AIR PARTICLES
UPPER SOIL
SURFACE WATER
LOWER SOIL
SEDIMENTS
GROUND-WATER ZONE

Figure 1

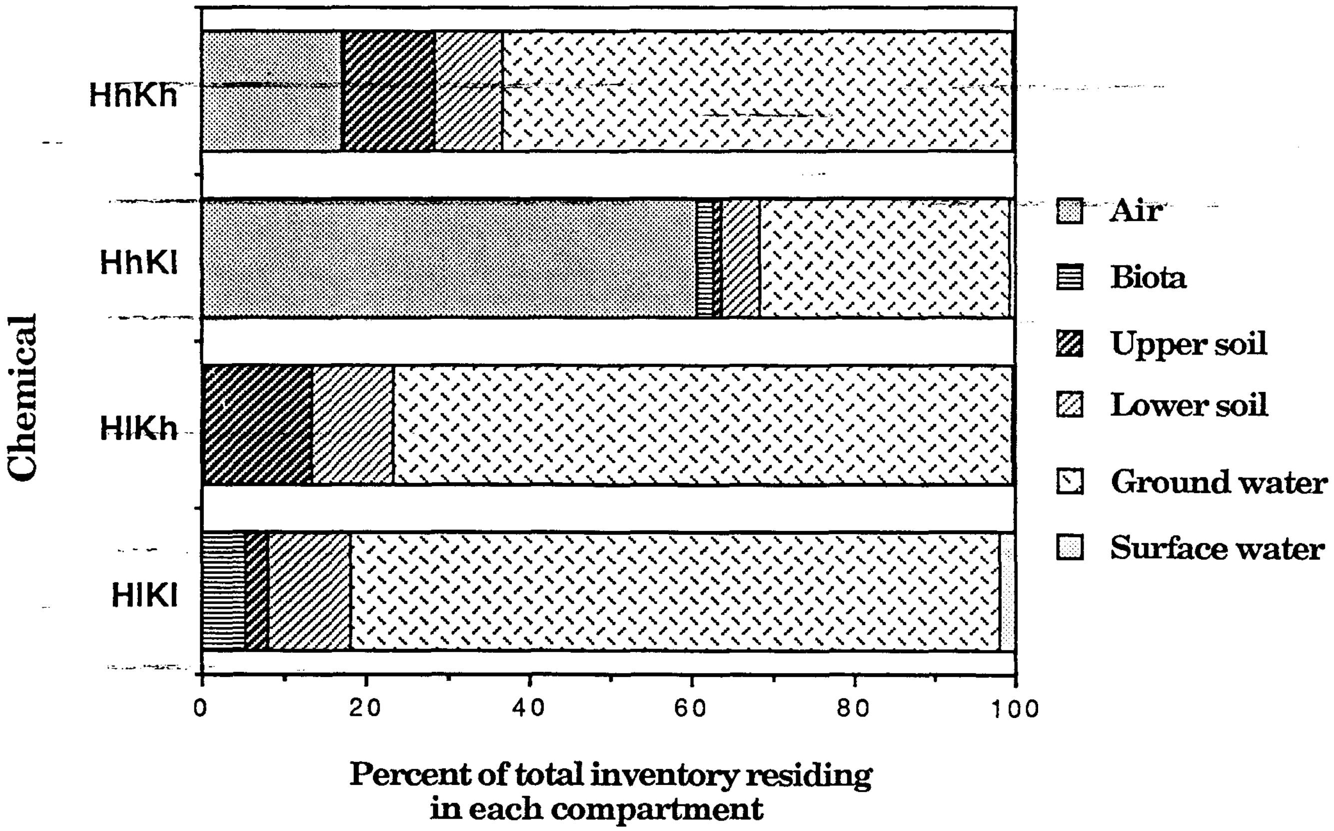
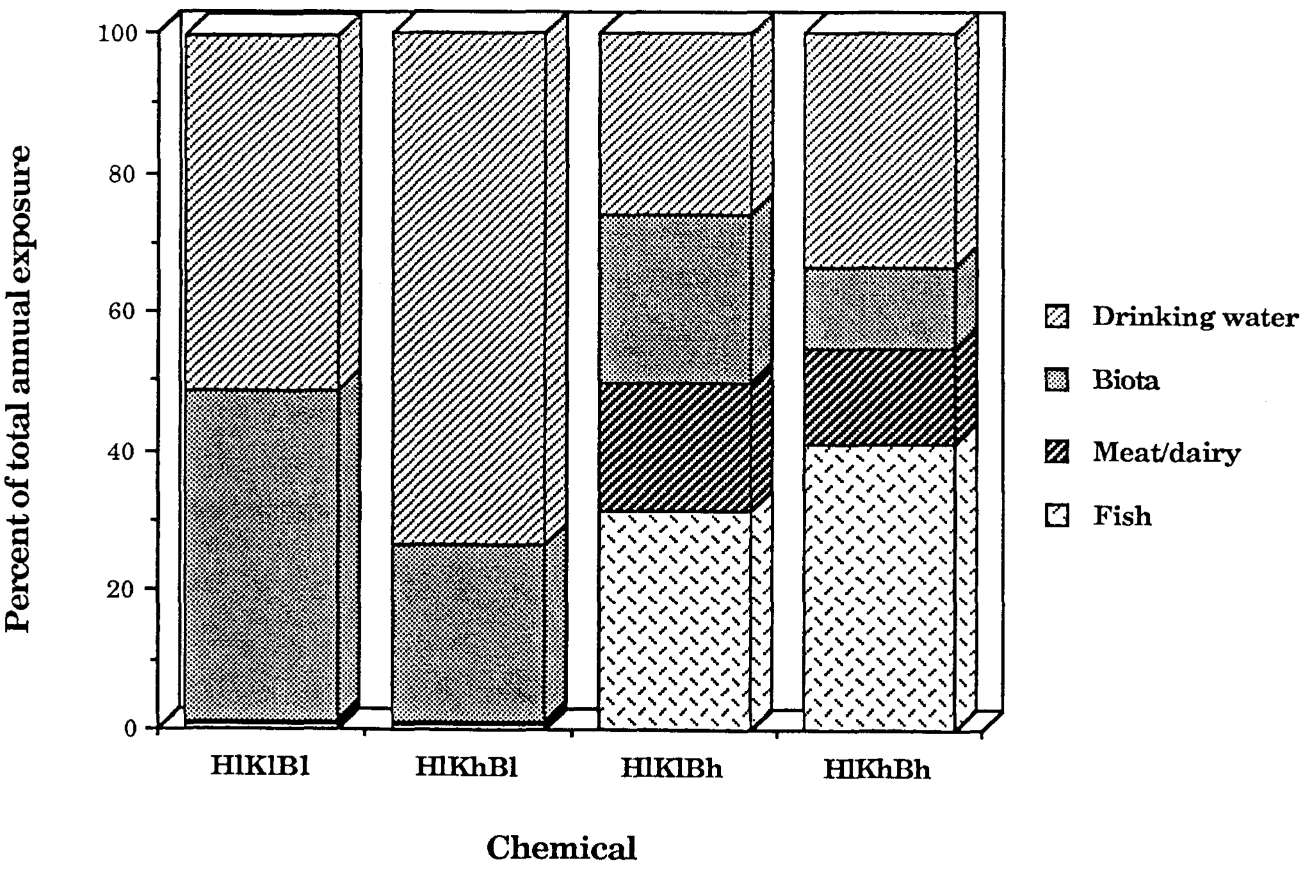
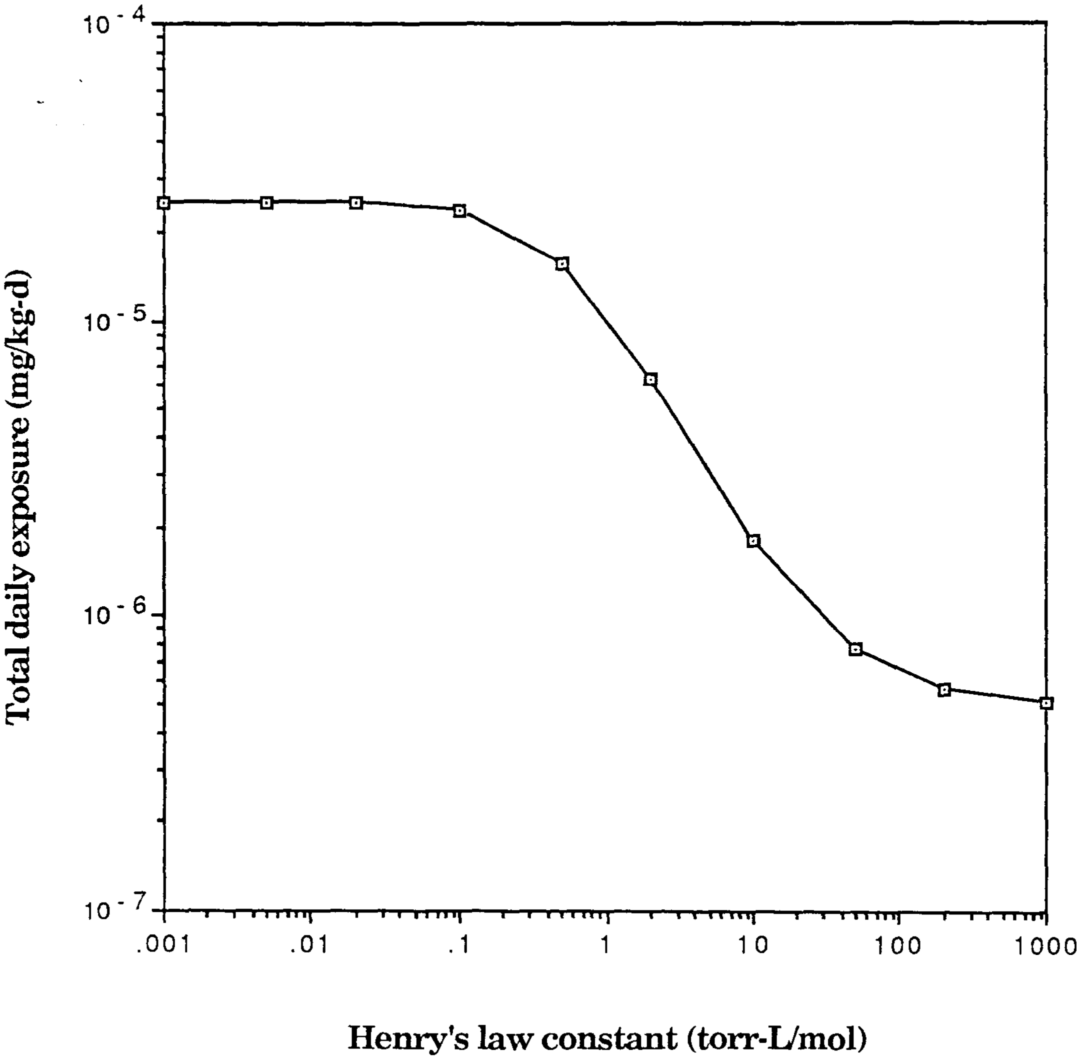

HhKh
HhKl
HlKh
HlKl
Chemical
0
20
40
60
80
100
Percent of total inventory residing in each compartment
Air
Biota
Upper soil
Lower soil
Ground water
Surface water

Figure 2



100
80
60
40
20
0
Percent of total annual exposure
HlKlBl
HlKhBl
HlKlBh
HlKhBh
Chemical
▨ Drinking water
▨ Biota
▨ Meat/dairy
☐ Fish

Figure 3



10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
Total daily exposure (mg/kg-d)
.001
.01
.1
1
10
100
1000
Henry's law constant (torr-L/mol)

Figure 4