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Full Length Research Paper

Evaluating the fate of organic compounds in the Cameroon environment using a level III multimedia fugacity model

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A level III fugacity model was developed to evaluate the fate of chemicals in the Cameroon environment. The model required as input physical-chemical properties, mode and amount of chemical released and environmental characteristics. These were used to predict the distribution of the chemical in the environment, quantify intermedia transfer processes and the major loss mechanisms from the environmental compartments. Five pesticides (endosulfan, chloropyrifos, cypermethrin, deltamethrin and λ-cyhalothrin) representing volatile, water soluble and persistent compounds were selected for model evaluation. Furthermore, a sensitivity analysis was performed to identify the key input parameters. Model simulations indicated significant differences in the fate of the chemicals that could be explained by the variation in physical-chemical properties. The log K_{OW}, emission rate to water (E_W), volume of the water compartment (V_W) and the half-life in water and sediment were identified the as the key parameters influencing the predicted water concentrations. The model developed introduces a cost effective and simple method for screening and identifying priority chemicals. It could also be used to perform baseline exposure and risk assessment of chemicals used in Cameroon where very little data is available for exposure to chemicals due to the huge costs associated with setting up a monitoring program.

Key words: Fate model, fugacity, exposure assessment, chemical fate in Cameroon, persistence.

INTRODUCTION

The use of chemicals and chemical derivatives in agriculture, industry and infrastructure development has contributed to a marked improvement in the standard of living in many developing countries (UNEP, 2008). However, due to poor management practices, lack of resources and poor environmental regulations, much still has to be done to effectively harness the benefits of the chemicals and reduce cost to both humans and the environment. A large number of the chemicals used industrially and in agriculture are toxic to animals and humans; hence information on the volumes discharged, the levels and occurrence in the different environmental matrices (e.g. air, water and biota) is important in developing policy aimed at mitigating the impacts of chemicals, for appropriate monitoring assessment and better management of risk. Oladele (2003) has shown that there is little or no baseline information on application rates of chemicals, levels and impacts on the environment and humans in most African countries. A possible alternative in the absence of monitoring programs is the development and application of environmental fate models because of the predictive and simulation capabilities. Environmental fate models (e.g. EUSES, CalTOX) have been successfully applied by regulatory authorities (e.g. USEPA, EU and Environment Canada) to study the fate of organic chemicals and they now play a central role in the risk assessment of chemicals (e.g. in the EU in the context of the REACH framework). However, environmental fate models have seldom been developed for or applied to tropical or arid environments. In an attempt to fill the gap, this paper describes the development and

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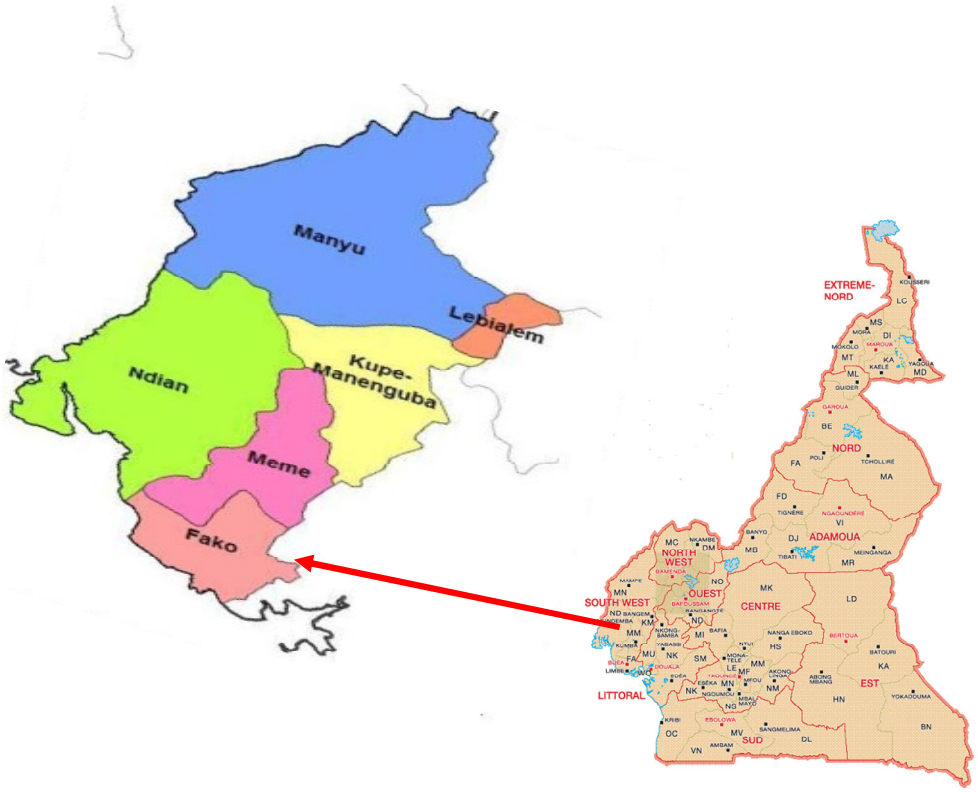

Figure 1. Location of the modeled environment and the boundary regions.

application of a level III multimedia model to evaluate the fate of five agrochemicals in the Cameroon environment. The model was used to predict the fugacity, concentration and mass distribution of the chemicals and quantify the different contaminant removal pathways from the Cameroon environment. The application of the model in risk assessment was also explored and the key parameters that significantly influenced the predicted water concentrations were identified by sensitivity analysis.

Cameroon is located in the Gulf of Guinea at the intersection of West Africa and Central Africa. The country covers an area of approximately 475000 km^2 is home to a diversity of ecological zones and habitats, ranging from a Sahel-like climate in the northern-most part of the country to dense rainforest in the south. Agriculture is the mainstay of Cameroon's economy and agricultural needs account for more than 75% of the land use and more than 50% of total exports. Some of the major crops cultivated include cocoa, coffee, sugar cane, potatoes, tomatoes, corn and plantains. In addition to the favorable agricultural conditions, the high temperature, humidity and rainfall also offer favorable conditions for weed and pest growth, with a negative impact on crop yields which is translated into economic as well as financial loss to the farmers. To off set this effect and increase productivity, a wide variety of agricultural inputs, especially pesticides, are used for weed and pest control both by agro industrial giants and subsistence farmers (Mbiapo and Youovop, 1993; Mathews et al., 2003; Sonwa et al., 2008). Also, organic pollutants such as polychlorinated biphenyls (PCB) and dioxins are released into the Cameroon environment from obsolete transformers discarded into refuse dumps and incineration facilities with poor emission controls (Sama 1999; IPEN, 2005). Despite the pressures from these discharges, Cameroon still lacks the basic mechanisms allowing an efficient chemical monitoring program and evaluating the (IPEP, 2005). Also, very little research has been done on quantifying the relationship between chemical loadings and the prevailing concentrations in air, water, soil, sediments and biota in the Cameroon environment. Environmental fate models can play a pivotal role in addressing these deficiencies because of the predictive capabilities especially in assessments for which there is no actual environmental experience. Furthermore, fate models have value in research and chemical management purposes, as well as addressing policy and management questions of concern.

METHODS

The model environment selected for this study is a subsection of the Cameroon environment scaled to represent Fako Division in the Southwest province of Cameroon (Figure 1). The region was considered to be homogenous in climatic and weather conditions (e.g. temperature, rainfall, soil characteristics) and extends from the Atlantic Ocean to Mount Cameroon. It is bounded to the North by

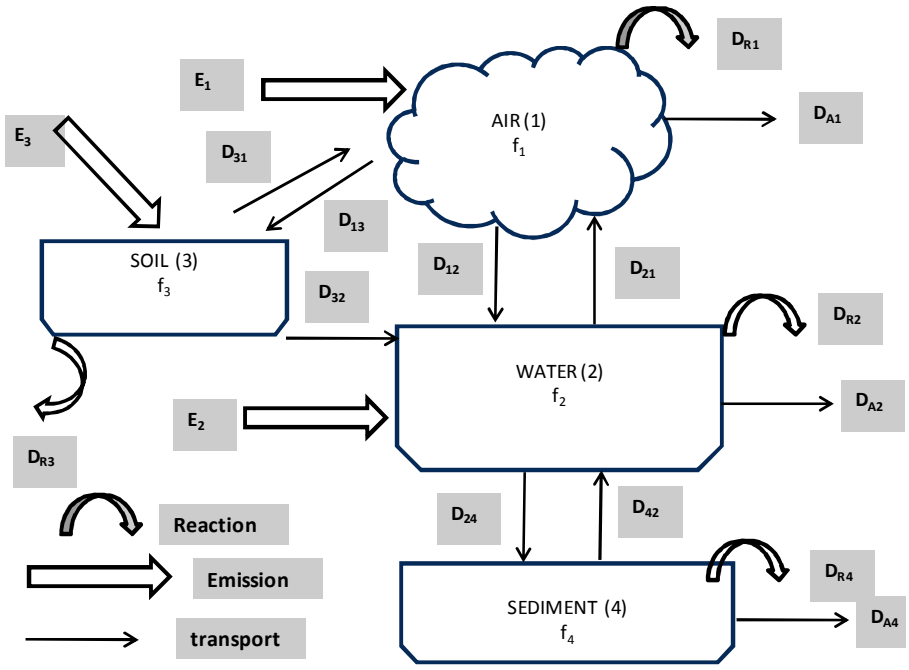

Figure 2. Schematic representation of environmental compartments indicating intermedia transfer processes.

Meme division, to the West by Ndian division, to the East by the Littoral province and to the South by the Atlantic Ocean. The selected region was segmented into four bulk compartments (air (1), water (2), soil (3) and sediment (4)) linked together by inter-compartmental fluxes (Figure 2). The four bulk compartments are further subdivided into a number of sub-compartments: air (air, aerosols), water (dissolved phase, suspended particles), soil (air, water, solids) and sediment (pore-water and solids).

The water compartment was assumed to cover approximately 60% of the total area of Fako Division (8.5E09 km^2) and the area of the sediment compartment was assumed equal to the area of the water compartment. The air compartment was reduced to an arbitrary height of 1000 m and the area of the soil compartment was determined as the difference between the areas of the air and the water compartments as suggested in Mackay (2001). The selected model domain is typical of tropic conditions with reported mean temperature of 28°C (Wanji et al., 2003) and an estimated rainfall rate of 3200 mm/year (Tingem et al., 2007) and wind speed of 3 m/s (Tchinda et al., 2000). The physical dimensions of compartments as well as other parameters used to characterize the Fako environment are listed in Table 1.

Model development – The fugacity concept

The fugacity concept has been thoroughly described in various papers by Mackay and co-authors (Mackay and Paterson, 1981; Mackay et al., 1996; Mackay, 2001) and only a summary is provided here. Fugacity is defined as chemical activity of a gas and expresses the escaping or fleeing tendency from a phase or compartment. It has units of pressure (Pa) and for dilute solutions is linearly related to concentration via the expression:

$C = Zf$

Where; C (mol/m^3) is the concentration, Z (mol/m^3Pa) is the fugacity capacity of the phase and *f* (Pa) is the fugacity.

The fugacity capacity Z expresses the affinity of a medium to dissolve or sorb a chemical and depends on the nature of the chemical, temperature, pressure and sorption characteristics of the medium. Different expressions are available for calculating Z-values depending on the media (Mackay, 2001) and these are summarized in Table 2. In the fugacity approach, both diffusive and non-diffusive processes are used to describe the movement of chemicals between phases in contact. The diffusive flux (N_D, mol/h) between two phases with fugacities f_1 and f_2 is described by:

$N_D = D (f_1 - f_2)$

Where; D (mol/Pa h) is a transfer coefficient or transport parameter and the magnitude of f_1 and f_2 determine the direction of flux that generally occurs from high to low fugacity. Non-diffusive (or advective) transport processes such as sediment deposition are also described by a flux N_A such that:

$N_A = GC$

Where; G (m^3/h) is the volumetric flow rate and C is the concentration (mol/m^3). By substituting C= Z*f*, the non-diffusive or advective flux (N_A) can be described in fugacity format as:

$N_A = (G Z) f = D_A f$

Where; D_A = GZ (mol/Pa h) is the D value for advective transfer and f (Pa) is the fugacity of the compartment.

Assuming that the contaminant is present at low concentrations, transformation or degradation reactions are characterized using first order kinetics (Mackay, 1991; Ince and Inel, 1989) such that:

$N_R = VCk = (V Z k) f = D_R f$

Where; D_R = (VZk) (mol/Pa h) is the D value for reaction, k ($time^{-1}$) is the first order rate constant and V is the volume of the compact-

Table 1. Dimensions of environment and Physical – chemical properties of the evaluated chemicals.

Environmental parameters					
Compartment	Air	Water	Soil	sediment	
Area (m^2)	5.08E+10	5.08E+09	4.57E+10	5.08E+09	
Depth (m)	1000	20	0.1	0.01	
Sub compartments (volume fractions)					
Particulates	2E-11	1.04E-05			
Air			0.2		
Water			0.2	0.8	
Solids			0.6	0.2	
OC mass fractions (g/g)					
Soil Solids			0.02		
Sediment Solids				0.04	
particulates	0.2				
Chemical properties					
	cyhalothrin	cypermethrin	chloropyrifos	endosulfan	deltamethrin
MWT (g/mol)	449.9	416.3	350.57	406.96	505.24
S_W (g/m3)	5.21E-03	4.16E-03	2.08	3.33E-01	2.08E-03
V_P (Pa)	2.49E-07	4.99E-07	3.04E-03	1.63E-03	2.45E-06
log K_{OW}	7.02	6.62	4.84	3.57	5.45
ΔH_{sol} (J/mol)	10000	10000	10000	10000	10000
ΔH_{vap} (J/mol)	50000	50000	50000	50000	50000
H (Pa m3/mol)	2.89E-12	4.99E-12	1.81E-05	1.33E-06	1.01E-11
Half-lives (h)					
Air	5	17	5	17	5
Water	170	170	550	55	17
Soil	1700	550	5500	550	550
Sediment	5500	1700	1700	170	170
Suspended particulates	5500	1700	1700	170	170

MWT is the molecular weight; S_W is the solubility in water, VP is the vapour pressure; log K_{OW} is the octanol-water partition coefficient; ΔH_{sol} and ΔH_{vap} are the heats of solution and vaporization respectively. We assumed 60% of the area of Fako Division is covered by water; the area of the air compartment was ten times the volume of the water compartment and the area of the sediment compartment was assumed to be equal to the area of the water compartment. The area of the soil compartment is the difference between the area of the air and water compartment (Mackay, 2001).
Properties of cypermethrin, chloropyrifos, endosulfan and cyhalothrin are from the Hazardous Substance databank (HSDB). (http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB) and for deltamethrin from International Programme on Chemical Safety Environmental Health Criteria 97: Deltamethrin. (http://www.inchem.org/documents/ehc/ehc/ehc97.htm). All degradation rate constants for all chemicals are from Mackay 2001.

Table 2. Definition of Z-values (mol/m^3Pa) (Mackay, 2001).

Compartment	**Expression**	**Definition of symbols**
Air	Pure Air $Z_A = 1/RT$ Aerosols $Z_Q = Z_A\ 6x10^6/P^S_L$	T = absolute temperature (K) R = gas constant (8.314 Pa m^3/mol K) P^S_L = vapour pressure of liquid
Water	Pure phase $Z_W = 1/H$	H = Henry's law constant (Pa m^3/mol)
Soil and sediment	$f_{OC}\ K_{OC}\ Z_W\ \rho_S/1000$	f_{OC} - fraction of organic carbon K_{OC} = organic carbon water partition coefficient ($K_{OC} = 0.41K_{OW}$) ρ_S - soil and sediment solids density 2500 kg/l

ment.

Equilibrium is assumed within each compartment (e.g. between gas phase and aerosols in air) but not between compartments (e.g. between air and water). Chemicals enter the model environment by direct emissions and chemical transfer between compartments occurs by (a) bulk one-way transfer associated with transport of material from one compartment to another (e.g. runoff from soil to water D_{32}, in Figure 2) and (b) diffusive process which is associated with molecular motion of pollutant across interface from one compartment to another (e.g. diffusion from water to sediment /desorption from sediments into water (D_{24} and D_{42} in Figure 2). A set of key input parameters termed mass transfer coefficients (units m/h) are required in the determination of the D-values of the different processes and these are listed in Table 3.

Irreversible loss of pollutant from the model environment is by degradation reactions in air (D_{R1}), water (D_{R2}), soil (D_{R3}) and sediment (D_{R4}) which were modeled by specifying compartmental degradation rate constants.

Four equations were developed to describe the mass balance for the major compartments in the model. At steady state (input = output):

For the air compartment (1):

$$E_1 + f_2D_{21} + f_3 D_{31} - f_1 (D_{12}+D_{13}+D_{A1}+D_{R1}) = 0 \quad (1)$$

For the water compartment (2):

$$E_2 + f_1 D_{12} + f_4 D_{42} + f_3 D_{32} - f_2 (D_{21}+D_{24}+D_{R2}+D_{A2}) = 0 \quad (2)$$

For the soil compartment (3):

$$E_3 + f_1 D_{13} - f_3 (D_{32} + D_{31} + D_{R3}) = 0 \quad (3)$$

For the Sediment compartment (4):

$$E_4 + f_2 D_{24} - f_4 (D_{42} + D_{R4} + D_{A4}) = 0 \quad (4)$$

The subscripts are 1 for air, 2 for water, 3 for soil and 4 for sediment, R for reaction, A for advection and E for emission. The f's represent fugacities and D's represents D values for transport and transformation processes (Table 4). The set of equations were then solved by algebra to yield the fugacities, concentrations, mass distributions and transport and transformation rates for individual and combined processes in all compartments. A particularly useful metric is the overall persistence or residence time (τ_O) of the chemical in the model domain calculated from the amount of chemical emitted (E mol/h) and the amount of chemical present in the environment (M, mol) as:

$$\tau_O = M/E$$

The overall persistence is generally a combination of the reaction (τ_R) and advection (τ_A) residence times calculated from:

$$\tau_R = M/\sum D_{Ri} f \text{ and } \tau_A = M/\sum D_{Ai} f$$

Where; D_{Ri} and D_{Ai} are the reaction and advection D-values for compartment i and f is the fugacity. Valuable information on the relative importance of the process to deplete the compartment of the chemical can be gained by comparing the residence time. A short residence time indicates a fast and dominating the process. The overall persistence is related to the advection and reaction residence times by:

$$1/\tau_O = 1/\tau_R + 1/\tau_A$$

Chemical parameters

Five 5 pesticides that are commonly used in this region based on previous studies (Mathews et al., 2003; IPEP, 2005) were selected for evaluation. These include cypermethrin, chloropyrifos, endosulfan, deltamethrin and λ-cyhalothrin. Physical-chemical properties for the selected chemicals at 250°C are listed in Table 1. The chemical properties were converted to values at the prevailing conditions using Arrhenius and Van't Hoff type equations (Schwarzenbach et al., 2003).

Emission scenarios assumed

This study is evaluative and the focus is to understand how the physical-chemical properties control the environmental fate characteristics such as partitioning, transport, transformation and persistence. An emission rate of 1000 kg/h to air, water and soil individually with no advection from neighboring regions was assumed in all simulations. These different scenarios were chosen since it is commonly accepted that the chemical fate characteristics (for example persistence) in the environment is usually not only determined by chemical property but also by the mode of discharge (Mackay et al., 1996).

Sensitivity analysis

A sensitivity analysis was performed to identify the key input parameters and quantify the influence on predicted concentrations of the chemicals in the water compartment. Sixteen input parameters representing environmental characteristics (e.g. temperature, rain rate, volume of compartments), the physical-chemical properties (Henry's law constant (H), octanol-water partition coefficient (log K_{OW}), degradation half-lives) were selected for this evaluation. These parameters were varied within reasonable limits (± 10% of their initial values) using a Monte Carlo analysis technique. A uniform distribution was selected for the sampling of values within this range. This ensures that all values are equally likely to occur within the range and the Monte Carlo analysis technique randomly selects values within the range without applying any weighting factors. The model predicted water concentration of the different chemicals was selected as the output to be monitored. One thousand simulation trials were run using the Crystal Ball® software package for Microsoft Excel® (Crystal Ball, 2002).

RESULTS AND DISCUSSION

Mass distribution and removal processes

The model output for endosulfan emitted to air, water and soil respectively are shown in Figures 3 - 5. In the emission to air scenario (Figure 3), approximately 46 and 49% are found in air and soil respectively and 6% in water. The most significant removal mechanisms for endosulfan are reaction in air (756 kg/h, approximately 76% of the total removal) and advection in air (188 kg/h, approximately 20% of the total removal). Intermedia transport results in a net transfer of 30 kg/h of endosulfan from air to water and of 25 kg/h from air to soil.

In the emission to water scenario (Figure 4), 97% is found in water and 1% in air and 1% in soil. The significant removal mechanisms for endosulfan are reaction in water (886 kg/h, approximately 88% of the total removal)

Table 3. Intermedia mass transfer coefficients (m/h) used in model equations.

	Symbol	m/h	Reference
Air side air-water MTC	U_1	5	Mackay, 2001
Water side air-water MTC	U_2	0.04	Mackay, 2001
Rain rate	U_3	0.0004	calculated
Aerosol dry deposition velocity	U_4	6E-10	Mackay, 2001
Air side MTC over soil	U_7	0.02	Mackay, 2001
Soil water phase diffusion MTC	U_6	0.00001	Mackay, 2001
Soil air boundary layer MTC	U_5	5	Mackay, 2001
Sediment-water MTC	U_8	0.0001	Mackay, 2001
Sediment deposition velocity	U_9	5E-07	Mackay, 2001
Sediment resuspension velocity	U_{10}	2E-07	Mackay, 2001
Soil water runoff rate	U_{11}	0.000146	Mackay, 2001
Soil solids runoff rate	U_{12}	7.31E-08	Mackay, 2001

MTC is the mass transfer coefficient a rate constant that relates the mass transfer rate, mass transfer area and concentration gradient as driving force.

Table 4. Equations used to determine D- values for transport processes.

Compartments	Process	Equation
From Air (1) to Water (2)	absorption	$D_{VW} = A_W/(1/U_1Z_1 + 1/U_2Z_2)$
	Rain dissolution	$D_{RW} = U_3 A_W Z_2$
	Wet deposition	$D_{QW} = U_3 A_W Z_Q Q v_Q$
	dry deposition	$D_{QD} = U_4 A_W Z_Q v_Q$
	Total	$D_{12} = D_{VW} + D_{RW} + D_{QW} + D_{QD}$
From Water (2) to Air (1)	Volatilization	$D_{21} = D_{VW}$
From Air (1) to Soil (3)	Absorption	$D_{VS} = 1/[1/ U_7A_SZ_1 + 1/(U_6A_SZ_2 + U_5A_SZ_1)]$
	Rain dissolution	$D_{RS} = U_3A_SZ_2$
	Dry Deposition	$D_{QS} = U_4A_SZ_6$
	Total	$D_{13} = D_{VS} + D_{RS} + D_{QS}$
From Soil (3) to Air (1)	Volatilization	$D_{31} = D_{VS}$
From Water (2) to Sediment (4)	Diffusion	$D_{WS} =U_8A_WZ_2$
	Deposition	$D_D = U_9A_WZ_5$
From Sediment (4) to Water (2)	Diffusion	$D_{WS} = U_8A_WZ_2$
	Resuspension	$D_R = U_{10}A_WZ_4$
From Soil (3) to Water (2)	Water runoff	$D_{SW} = U_{11}A_SZ_2$
	Soil runoff	$D_{SS} = U_{12}A_SZ_3$

and advection in water (70 kg/h, approximately 7% of the total removal). Intermedia transport is dominated by volatilization from water to air that result in a net transfer of 40 kg/h from water to air.

In the emission to soil scenario (Figure 5), 99% is found in soil and very negligible amounts in water and air. The significant removal mechanisms are reaction in soil (963 kg/h, approximately 97% of the total removal) and reaction in water (28 kg/h, approximately 3% of the total removal).

The results for the other compounds in the emission to air scenario, indicated approximately 80 - 98% of cypermethrin, λ-cyhalothrin, chloropyrifos and deltamethrin partition into the soil compartment. Only λ-cyhalothrin and cypermethrin are found in the sediment compartment (approximately 16%) and the air and the water compartments (6%). Reaction in air was the major removal mechanism for chloropyrifos (894 kg/h, 89% of the total), whereas reaction in soil was the major removal mechanism for cyhalothrin, deltamethrin and cypermethrin.

In the emission to water scenario, approximately 87 - 94% of cyhalothrin and cypermethrin are found in sediment and 5 - 12% in water, whereas 60 - 75% of chloropyrifos and deltamethrin are found in the water compartment and 18 – 3 6% in sediments. Reaction in

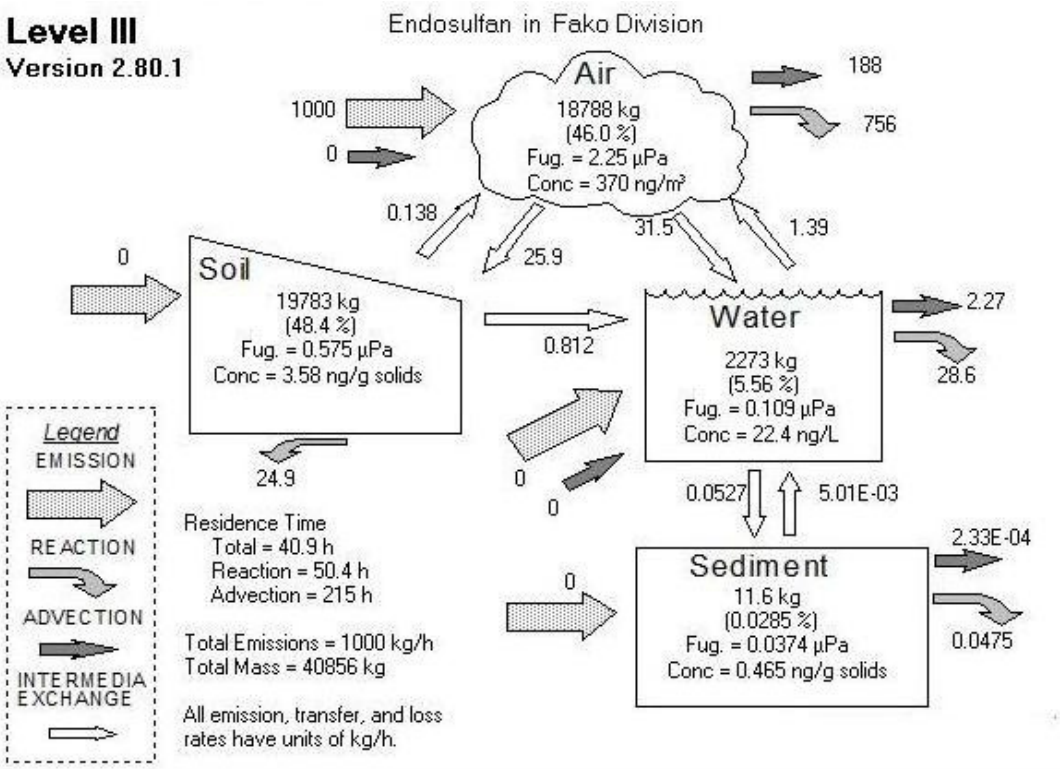

Figure 3. Schematic representation of model predicted results for endosulfan emitted to air.

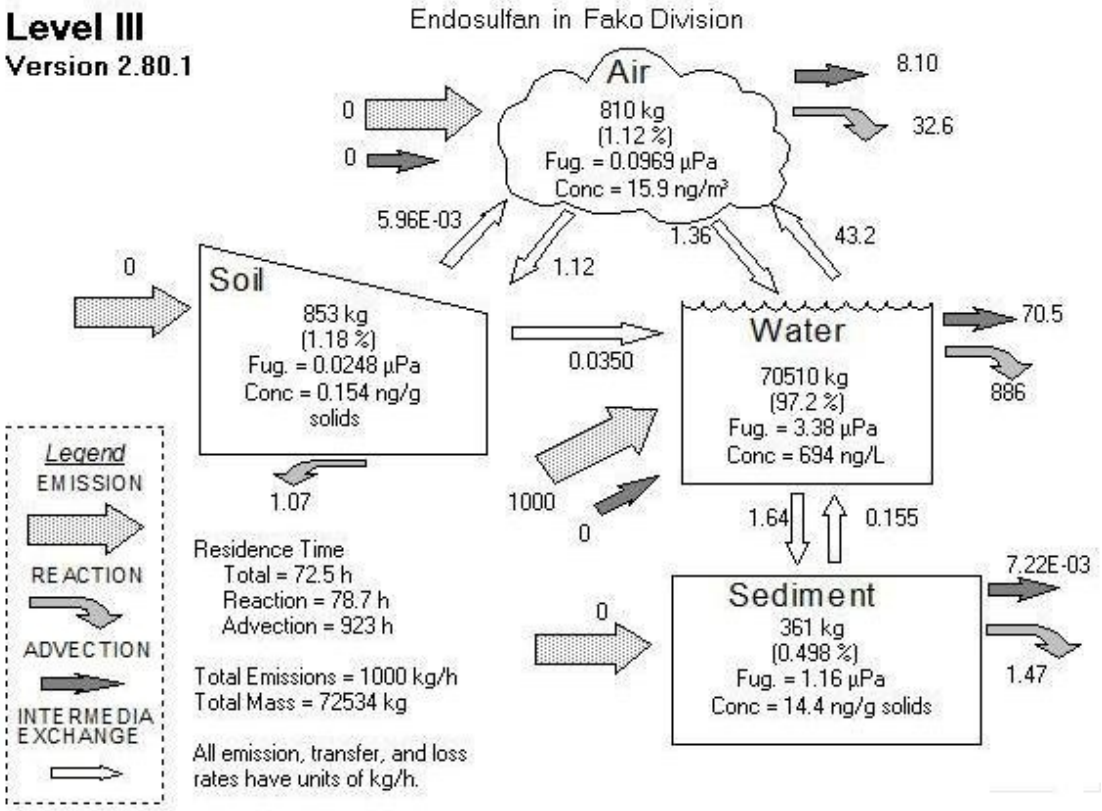

Figure 4. Schematic representation of model predicted results for endosulfan emitted to water.

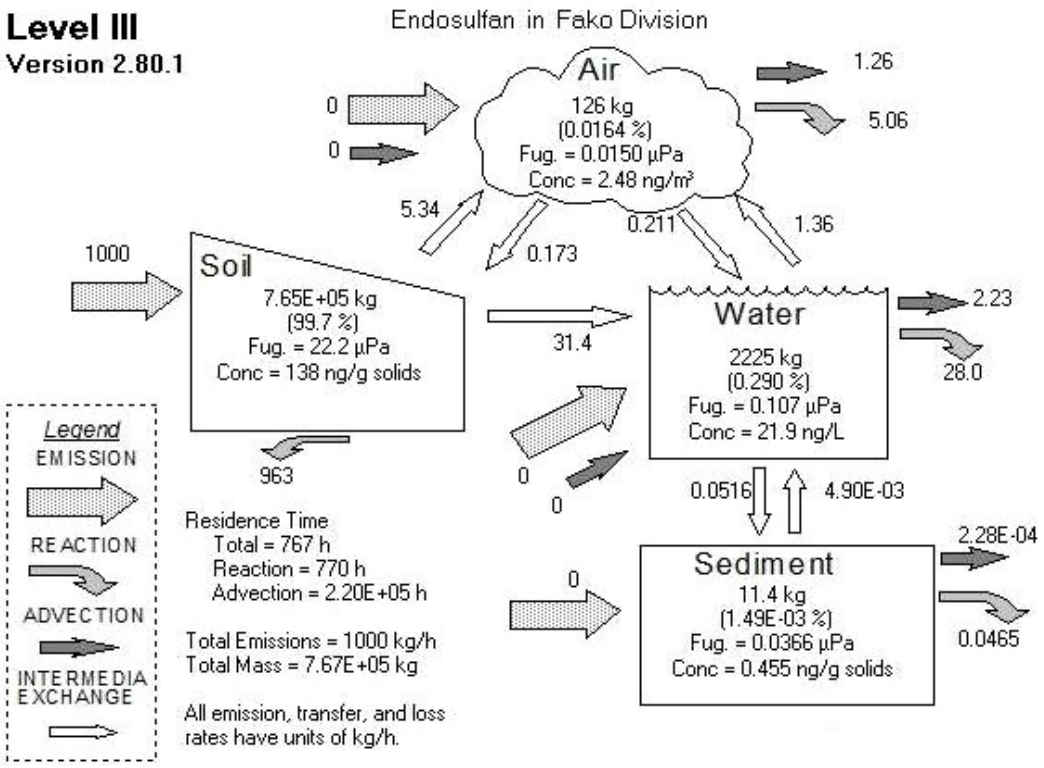

Figure 5. Schematic representation of model predicted results for endosulfan emitted to soil.

water is the major removal mechanism for deltamethrin (94%) and chloropyrifos (46%), while reaction in sediment is the major removal mechanism for cyhalothrin (53%) and cypermethrin (57%).

In the emission to soil scenario the results indicated a similar fate picture for all compounds with > 99% of the chemical found in the soil compartment and negligible amounts in air, water and sediment compartments. Generally, net transfer from air to soil and air to water dominated the intermedia transport with very high net transfer rates (687 - 795 kg/h) from air to soil observed for cyhalothrin, deltamethrin and cypermethrin. Significant net transfer of chemical from water to sediment was observed for cyhalothrin (600 kg/h) and cypermethrin (590 kg/h).

Variation in predicted concentrations

The model predicted bulk concentrations and fugacities of endosulfan are also shown in Figures 3 - 5. The highest concentrations in air (370 ng/m^3) and water (694 ng/l) are predicted in the emission to air and water scenario, respectively. Similarly, the highest concentrations in sediments (15 ng/g solids) and soils (8138 ng/g solids) are predicted in the emission to water and soil scenarios, respectively.

The model predicted bulk concentrations in air, water, soil and sediments for the other compounds are shown in Table 5. In general, the highest concentrations in air (131 - 219 ng/m^3) water (280 - 3720 ng/l) and soil (138 - 1404 ng/g solids) are observed in the emission to air, water and soil scenarios. However, sediment concentrations are highest in the emission to water scenario for chloropyrifos, cypermethrin and deltamethrin and the emission to air scenario for cyhalothrin.

Persistence and residence time in the environment

The shortest τ_O of approximately 2 days was observed for endosulfan and the longest τ_O of approximately 322 days was observed for chloropyrifos. The reaction residence times (τ_R) ranged from 2 to 325 days with endosulfan and deltamethrin showing the shortest τ_R and cyhalothrin and chloropyrifos the longest τ_R. Similarly, the advection residence times τ_A ranged from 10 days for endosulfan to 7E05 days (1800 years) for deltamethrin.

The capacity for a given compartment to accumulate the chemical is determined by the product of the volume (V, m^3) and the fugacity capacity of the compartment (Z).

The fugacity of endosulfan in air (Figure 3) is approximately 4 times that in soil however, the VZ (soil) is 8.46E04 and VZ air is 2.04E04 that is, soil has approximately 4 times the capacity of the air to accommodate endosulfan as shown in Figure 3. Furthermore, Figure 3 also indicates the different loss mechanisms from the soil namely soil-air diffusion, soil run-off and reaction in soil.

Table 5. Model predicted concentrations in the bulk compartments.

	Compartment	Units	Chloropyrifos	Cyhalothrin	Cypermethrin	Deltamethrin	Endosulfan
Emission to air	Air	g/m^3	131	218	219	206	370
	Water	ng/l	61	213	167	22.2	22.4
	Soil	ng/g solids	149	15716	5100	23.7	0.47
	Sediment	ng/g solids	35.3	355	115	99.2	3.58
Emission to water	Air	g/m^3	9.4	0.04	0.173	1.06	15.9
	Water	ng/l	3719	2332	1869	280	694
	Soil	ng/g solids	9138	1.72E05	56995	300	14.4
	Sediment	ng/g solids	2.5	0.07	0.09	0.51	0.15
Emission to soil	Air	g/m^3	0.5	5.7E-04		0.010	2.5
	Water	ng/l	103	8.4	2.2	0.44	21.9
	Soil	ng/g solids	254	621	67.7	0.47	0.46
	Sediment	ng/g solids	1404	446	144	144	138

From the D values for these processes we can determine the half time (0.693 VZ/D) which is defined as the time required for the process to clear the compartment of the chemical. The calculated half times for soil air diffusion (12 years), soil-water runoff (2 years) and soil reaction (22 days). It is immediately clear from these figures that reaction in soil is the most important loss mechanism for the soil compartment. For the air compartment, the half times for deposition from air to soil and air to water were 17 and 20 days respectively and the half times for reaction and advection from air were 3 and less than 1 day respectively. However, advection merely transfers the endosulfan to the neighboring regions (e.g. to Meme division) and does not solve the contamination problem hence it is evident that the reaction half time of 3 days is the important loss process from the air compartment. A similar analysis of the fate of chloropyrifos and cyhalothrin emitted to water indicated a half time for water air transfer of 151 days for chloropyrifos and 100 years for cyhalothrin; for water to sediment transfer 90 days for chloropyrifos and 7 days for cyhalothrin; for reaction 24 days for chloropyrifos and 8 days for cyhalothrin. Thus reaction in water is the most important loss mechanism from the water column for both compounds followed by water-sediment transfer. However, the effect of differences in physical-chemical properties on fate is evident in the differences in the magnitude of the water-air and water-sediment transfer half times. The higher log K_{OW} of cyhalothrin indicates a compound that is tightly bound to suspended particulates and thus rapidly removed by particulate deposition, whereas the higher vapour pressure for chloropyrifos indicates a chemical that rapidly volatilizes from the water column. A similar analysis can be carried out for the other compounds to reveal the important sources and sinks as well as the important environmental characteristics.

Key parameters identified by sensitivity analysis

The influence of the varied input parameters on the predicted water concentration and the overall residence time (persistence) is presented in Table 6. The values (%) represent the contribution of the varying parameter to the variance of the selected output parameter. For example, log K_{OW} contribute 44 and 70% to the variance in the predicted concentration in water and overall persistence of cypermethrin. Generally, four input parameters namely the log K_{OW}, the emission rate to water (E_W), the volume of the water compartment (V_W) and the half-life in water ($t_{1/2}W$) contributed more than 95% of the variance in the predicted water concentration for all the compounds. Three of these parameters (log K_{OW}, V_W and the $t_{1/2}W$) together with the half-life in sediment ($t_{1/2}S$) and the volume of the sediment compartment (V_S) were the top five most sensitive input parameters that contributed more than 98% in the variance in the predicted overall persistence of the chemical in the model environment.

DISCUSSION

Generally the fate of a chemical in the environment depends to a large extent on the mode of entry, physical-chemical properties (e.g. the octanol water partition coefficient (K_{OW}), solubility in water (S_W) and the Henrys law constant), as well as the properties of the media (e.g. the fraction of organic carbon, mass transfer coefficients) within which the chemical exists. These properties provide very important insights as to the preferred migration pathways and ultimate fate of a chemical in the environment. The influence of the mode of entry is immediately obvious from the results shown Figures 3 - 5 and Table 5 that indicates different fate and partitioning properties of

Table 6. Summary of the results of the sensitivity analysis.

chemical	OBS Parameter	V_W	E_W	log K_{OW}	$t_{1/2}W$	$t_{1/2}S$	V_S
Cypermethrin	τ_O	3.2		70.1	9.9	15.0	
	C_W	17.0	32.7	43.5	6.0		
Chloropyrifos	τ_O			93.1	5.1		
	C_W	28.2	32.1	34.4	4.7		
Deltamethrin	τ_O			69.8	28.2		
	C_W	35.10	32.7	1.9	29.2		
Cyhalothrin	τ_O	12.5		49.1	16.3	16.9	4.2
	C_W	24.2	47.7	14.1	12.0		
Endosulfan	τ_O				97.5		
	C_W	35.4	35.2		28.0		

The numbers indicate the contribution (%) of the parameter to the variance in overall persistence (τO) and water concentration (CW). For example, log KOW contribute 44%, emission rate to water (EW) contribute 33%, volume of the water compartment (VW) contribute 17% and the half life in water (t1/2W) contribute 6% of the variation in predicted water concentration (CW) for cypermethrin. Only parameters that contributed more than 5% were selected. OBS parameter is the parameter than was monitored in the sensitivity analysis. VW volume of water compartment, VS volume of sediment compartment; EW emission to water; t1/2W is the half life in water; t1/2W is the half life in sediment.

endosulfan depending on the media into which the chemical was emitted. Furthermore, the predicted mass distributions and differences in the environmental fate of the chemicals followed the variation in the hydrophobicity (as indicated by the log K_{OW}) and the volatility (Henry's law constant, H). For example, for cyhalothrin (log K_{OW} = 7.02) emitted to air, 99% in the bulk air compartment is associated with aerosols, 87% in the bulk water is associated with suspended particulates in water and 95% in bulk sediment is associated with sediment solids. The corresponding figures for deltamethrin (log K_{OW} = 5) is 90% associated with aerosols in air, 22% associated with suspended particulates in water and 99% in soil and sediment solids. Similarly, increasing the H of a chemical favors partition to air compared to water and soil. Chloropyrifos and endosulfan with relatively higher H values (10^{-5}-10^{-6} Pa m^3/mol) were found in relatively higher amounts in air. However, it is important to distinguish between compartments with an appreciable amount of chemical and compartments where the concentration is high. For example 97% of endosulfan emitted to water remains in the water column and < 1% is found in sediment; however the sediment concentration is 10 times higher than the concentration in water. This distinction is important and has implications in the assessment of the exposure of aquatic species and humans that feed at the top of aquatic food webs to the different compounds. For example, in the EU guidelines for risk assessment of pesticides (EU 2002), a worst case exposure (CF_{max}, mg/kg) of fish eating birds and mammals is determined as the product of the bioconcentration factor (BCF) and the dissolved concentration in water (C_W, mg/L) (that is, CF_{max} = BCF*C_{Wi} where BCF = L_F*K_{OW}, L_F is the lipid fraction). Thus for a fish with L_F of 0.05 and assuming the predicted concentration in water column as C_{Wi}, the calculated CF_{max} for cyhalothrin and cypermethrin were between 800 - 1000 times higher than for endosulfan and between 20 - 30 times higher than for deltamethrin. However, only 6 - 12% of cyhalothrin and cypermethrin was found in water. These concentration levels can be compared to concentration levels published as guidelines by regulatory agencies that may produce adverse effects in an initial risk assessment for these compounds.

A general comment refers to the results of the sensitivity analysis. In all simulations, a similar amount of chemical was emitted into the same environment. It is obvious that changes in partitioning properties significantly affect the predicted water concentrations and the overall environmental persistence. Such results are expected since the chemicals span a range in variation of physical-chemical properties. The variance in the overall persistence of chloropyrifos, deltamethrin and endosulfan are influenced by the octanol-water partition coefficient (log K_{OW}) and the half life in water ($t_{1/2}W$) due to the large amounts present in water, whereas the overall persistence of cyhalothrin and cypermethrin are influenced by the log K_{OW} and the sediment half life ($t_{1/2}S$) due to the large amounts present in sediments.

Generally, concentrations in water are mainly influenc-ed by water emissions together with the log K_{OW} and the water half-lives ($t_{1/2}W$). When endosulfan is compared to chloropyrifos, it is interesting that the influence of log K_{OW} is important only for chloropyrifos (35%) while the influence of $t_{1/2}W$ is higher in endosulfan than for chloropyrifos. While the difference in log K_{OW} is very small between these compounds, the half-life in water ($t_{1/2}W$) for endosulfan is ten times shorter than for chloropyrifos, thus the predicted water concentration of endosulfan is significantly influenced by the $t_{1/2}W$ than the log K_{OW}.

The predicted water concentration of deltamethrin is

significantly affected by the half life in water that contributes approximately 30% of the variation, whereas the results for cyhalothrin indicated the octanol water partition coefficient contributed 14% and the half life in water contributed 12% of the variation in predicted water concentration. Considering there are two orders of magnitude difference in log K_{OW} and an order of magnitude difference in $t_{1/2}$W between cyhalothrin and deltamethrin, these results reveal the importance of reaction in water in determining the overall persistence and the predicted water concentration

Concluding remarks

A level III fugacity model was developed and applied to evaluate the fate of chemicals with a range in physical-chemical properties in Fako Division of Cameroon. It was not possible to evaluate the model predictions because of the lack of monitoring data. Nevertheless the model played a valuable role in improving the general understanding of the behavior of the selected chemicals in the Cameroon environment because of the large amount of information generated regarding for example the major transport and removal processes and the potential exposure of aquatic organisms. Mechanistic models of the type described in this paper can be very useful to environmental managers, regulatory agencies and chemical manufacturers because of their predictive and simulation capabilities. In principle, such mechanistic models could also be used as an initial screening tool to evaluate the environmental fate of chemicals for which there are no measurements, to estimate the potential human exposure and risk resulting from consumption of fish contaminated with chemicals.

A major shortcoming in this study was the lack of accurate input data for model parameterization as well as analytical data for model evaluation. Although complete parameterization of the model with accurate and site specific data is neither possible nor required, the most reliable values for key chemical properties (e.g. K_{OW}, solubility in water) were selected from the best sources currently available so model error due to using unreliable values has been limited as much as possible. The largest model error may well be related to the selected water and sediment degradation rate constants, which can be highly variable depending on actual field conditions. However, little can currently be done to improve the input values for these parameters. We suggest that the focus of future efforts aimed at improving the model and increasing confidence in the model predictions should be on acquiring accurate degradation rate constants for the chemicals. The developed model is available in excel format and can be made available to interested persons by the authors upon request. We also welcome any initiatives aimed at improving the model and/or application to other environments and/or chemicals.

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