AIR-VEGETATION-SOIL PARTITIONING
OF TOXIC CHEMICALS IN ENVIRONMENTAL
SIMULATION MODELING

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ABSTRACT

Accumulation of airborne pollutants in vegetation is an important initial step in the uptake process of the terrestrial food web, providing direct and indirect routes by which biota and, eventually, humans are exposed to chemicals. A set of algorithms for estimating atmospheric pollutant interactions in soil-vegetation-air systems is developed and tested. The model incorporates significant transport pathways with appropriate parameterization and requires a relatively limited number of meteorological input data and pollutant characteristics and vegetation parameters. Testing applications include model comparison to field data in the cases of cadmium in grass and six polycyclic aromatic hydrocarbons (PAH) in maple leaves. Results indicate that the model provides a reasonable compromise between model complexity and the ability to obtain realistic data characterizing model parameters. It is well suited for screening-level assessments; and it can also be used as a component of a management-oriented and multimedia-based environmental assessment of atmospheric pollutants. On-going work is incorporating the model algorithms into a multimedia simulation framework to provide better capabilities.

KEY WORDS: Vegetation, atmospheric environment, air toxics, soil, simulation, modeling

INTRODUCTION

The need for multimedia environmental systems simulation modeling is growing rapidly due to the combination of increasing technical scope and complexity related to questions of risk-based cause and effect and the need to explicitly address cost effectiveness in the development and implementation of environmental regulations. The understanding of pollutant behavior in the environmental media is of particular concern for chemicals that are toxic and are subject to accumulation in environmental compartments where human and ecologic exposure can be important. The multimedia modeling approach involves the simultaneous tracking of environmental stress from an emission source through air, water, and soil to locations where human populations or eco-

logical concerns may be exposed.

An important component of such a multimedia assessment of atmospheric pollutants is the terrestrial food exposure pathway. Until recenlty, the estimation of exposure resulting from atmospheric emissions have only included direct pathways. Recent studies, however, have shown that the food chain can be an important contributor to human and ecological exposure resulting from emissions to air (USEPA, 1994; 1997a, b; 1998). Accumulation in vegetation was found to be an important initial step in the uptake process of the terrestrial food web, providing direct and indirect routes by which biota and, eventually, humans are exposed to chemicals of particular concern, see e.g. Winters et al. (1996) for dioxin-like compounds. Vegetation plays also an important role in the cycling of pollutants, affecting their atmospheric levels both as a source and as a sink, see e.g. Lindberg (1996).

Although several important process-oriented studies have been carried out during the recent years, see e.g. McCrady and Maggard (1993), Bacci et al. (1992), the current understanding of the processes involved in soil-vegetation-air interactions is still limited. In addition, although some simulation models are available (Paterson et al., 1994; Lindstrom et al., 1991), these models may be too difficult to initialize or may require prohibitive amounts of data. On the other hand, other more simple models may be restrictive to support exposure assessments. Recent modeling efforts include the work of Trapp and Matthies (1995), Tsiros and Ambrose (1997), Hung and Mackay (1997), Tsiros et al. (1998b), etc.

In this paper, a set of algorithms for describing atmospheric pollutant dynamics and interaction in air-vegetation-soil systems as a component of a multimedia-based assessment is developed and tested.

ALGORITHMS AND MODEL EQUATIONS

To estimate the chemical concentration in foliage, $C_{pl, f}$ (µg/ cm³), of a plant with leaf volume V_f (cm³), the basic mass balance equation used in the model is:

$$V_f \cdot \frac{dC_{pl,f}}{dt} = N_{dif} + N_{dry} + N_{wet} + N_{trn} - N \quad (1)$$

N_{dif} is the diffusive flux of the vapor phase pollu-

tant between foliage and air (µg/d) and is given as (Trapp and Matthies, 1995):

$$N_{dif} = A \cdot g \cdot \left[C_a^{(g)} - \frac{H \cdot C_{pl,f}}{K_{LW}} \right] \quad (2)$$

where A is the foliar exposed area (cm²); g is the total conductance for the atmosphere-to-leaf transfer of the chemical (cm/d) and includes the stomatal, cuticular and boundary layer conductances; H is the Henry's law constant (dimensionless) of the chemical; $C_a^{(g)}$ is the gas-phase chemical air concentration (µg/L); and K_{LW} is the partition coefficient between foliage and water, which is usually correlated to the octanol water partition coefficient of the chemical, the water and lipid content of the vegetative surface and the plant density.

N_{dry} and N_{wet} are the dry and wet deposition fluxes of particle-bound pollutant, respectively; they can be estimated using the following simple expressions (Tsiros and Ambrose, 1997; Tsiros et al., 1998b).

$$N_{dry} = f_p \cdot r_{dry} \cdot A \cdot V_d \cdot C_a^{(p)} \quad (3)$$

$$N_{wet} = r_{wet} \cdot R \cdot A \cdot C_{wet} - R_w \cdot C_{wet} \quad (4)$$

where f_p is the fraction of particle-bound chemical deposited to the canopy and transferred into the plant interior, r_{dry} and r_{wet} are the interception fractions for dry and wet deposition, respectively; V_d is the dry deposition velocity (cm/d); $C_a^{(g)}$ is the particle-bound chemical air concentration (µg/L); R is the rainfall rate (cm/d), C_{wet} is the pollutant concentration in rain water (µg/cm³), R_w is the washoff water from the vegetation canopy (cm³/d).

N_{trn} is the pollutant flux (µg/d) with the transpiration stream:

$$N_{trn} = q \cdot TSCF \cdot C_{s,w} \quad (5)$$

where q is the transpiration stream flow (cm³ transpiration water/d), $C_{s,w}$ is the soil water concentration of the chemical (µg/cm³ soil water) and TSCF is the concentration ratio between transpiration stream in the xylem and external solution ((µg/cm³ transpiration water)/(µg/cm³ soil water)) which for

organics is usually related to the octanol water partition coefficient (Trapp and Mathiess, 1995).

N is a general term to account for the pollutant mass gains and/or losses:

$$N = \zeta \cdot k \cdot C_{pl,f} \cdot V_L \qquad (6)$$

where ζ signifies source (ζ=-1) or loss (ζ=1) to the specific chemical and k is the kinetic reaction rate constant for chemical transformation (d^{-1}).

ATMOSPHERIC AND SOIL PARAMETER ESTIMATION METHODS

The atmospheric and soil parameters, such as $C_a{}^{(p)}$, $C_a{}^{(g)}$, V_d and $C_{s,w}$ involved in the above model equations, can be estimated via detailed site-specific measurements. Alternative methods coupled with the vegetation model are presented in the following.

Atmospheric deposition

For gaseous chemicals, according to the conventional resistance model, the dry deposition velocity is the inverse of the sum of the resistance of the canopy (R_c), the aerodynamic resistance (R_a), and the boundary layer resistance (R_b). A mechanistic treatment of the resistance terms is given in Wesely (1989). Since the estimation of these resistance terms, however, is sometimes difficult due to limited available data, a more simple approach can be used in which the dry deposition velocity of a vapor-phase chemical is proportional to its molecular diffusion coefficient in air (Cohen, 1997).

Dry deposition velocities of particle-bound chemicals on both vegetative and soil surfaces can be estimated as a function of meteorological conditions, particle-size distribution and soil surface characteristics (Slinn, 1982). Wesely et al. (1983) proposed an approximation of V_d (m/s), which can be used as a preliminary estimate when only wind speed and wind direction data are available.

Advanced models, which account for the effects of meteorological conditions on wet deposition parameters, are available (Walcek and Pruppacher, 1984). Empirically derived washout ratios which represent long-term averages, can also be used. Especially for gases, an upper-limit estimate can be obtained by assuming that raindrops are in equilibrium with the air phase when they reach ground level (USEPA, 1981).

Soil chemical concentrations

The total concentration of the chemical in soil is the result of various mechanisms including surface runoff, soil erosion, volatilization loss and atmospheric deposition. To estimate soil concentrations, hydrologic and transport models or components of models need to be linked to chemical processes submodels. The general soil mass balance equation for a computational soil layer at time t is written (Tsiros and Ambrose, 1997; 1999):

$$M_{soil(t)} = M_{soil(t-1)} + {} + M_{inp(t)} - M_{out(t)} - \zeta M_{transf(t)} \qquad (7)$$

where $M_{soil(t)}$ is the pollutant mass at time t, $M_{soil(t-1)}$ is the mass at time t-1, $M_{inp(t)}$ is the input mass to the soil layer, which for the uppermost surface soil layer accounts for atmospheric wet-and dry-fall, while for a subsurface soil layer is the input mass due to leaching from the upper layer; $M_{out(t)}$ is the output mass, which is due to runoff, erosion, leaching, and volatilization; $M_{transf(t)}$ is the mass transformed due to kinetic reactions; and ζ signifies source (ζ=-1) or loss (ζ=1) to the specific compound.

MODEL APPLICATION AND RESULTS
Vegetation exposure to cadmium

In this application, data were taken from two different field studies in which the contamination of soils and grass with cadmium and other metals has been investigated. In the first study, soil and plant species of *Lolium sp.* from several roadside sites in the area of Gipuzkoa, Spain, were investigated (Garcia and Millan, 1998). The second study focused on elevated cadmium and lead levels in both soils and plant species of *Cynodon dactylon* in the downtown area of Athens, Greece (Chronopoulou-Sereli et al., 1998). In both studies traffic emission was confirmed as the contamination source. For the model testing, the soil concentration values reported in these studies were used as inputs to the model. Additional important parameters and the assigned values are shown in Table 1. Cadmium concentrations due to diffusion exchange between atmosphere and leaves was not consid-

Table 1. Selected model parameters and assigned values for the case of cadmium in grass

MODEL PARAMETER	INPUT VALUE	COMMENTS - REFERENCES
Transpiration stream flow, L/d	1	typical value
Leaf density, g/mL	0.77	typical value for grass (McCrady and Maggard, 1993)
Loss rate constant, d^{-1}	0.08	typical value
Exposure period, d	100	typical value
TSCF	0.45	estimated based on reported range of values
Partition coefficient, L/kg	120	lack of site-specific data; value selected from a range of estimated values based on data (USEPA, 1998).
$C_a^{(p)} \cdot V_d$, $\mu gm^{-2}d^{-1}$	2	"conservative" estimate based on extensive data on metal atmospheric deposition (Lindberg and Turner, 1988)

ered since cadmium is not present in the vapor, Table 2. Error statistics summary for comparison between measured and predicted cadmium concentrations in vegetation for the two different data sets examined in the study phase. The total cadmium concentration in plants then is estimated due to root uptake and atmospheric deposition of particle-bound cadmium. Results are shown in figure 1. For model evaluation, typical error statistics was also performed (Tsiros et al., 1998a; Ambrose and Roesch, 1982; WMO, 1975). The values for the average error, the relative error, the standard error of estimate, and its coefficient of variation, were calculated and the results are shown in Table 2. These values imply a fair agreement of predicted and observed data for the case of *Lolium sp.* (Garcia and Millan, 1998) and a good agreement

for the case of *Cynodon dactylon* (Chronopoulou-Sereli et al., 1998).

Vegetation exposure to PAH

In this application, the airborne contamination of *Acer saccharum* (sugar maple) with several polycyclic aromatic hydrocarbons (PAH) is investigated. Extensive field data are available from a site located in the downtown area of Bloomington, Indiana (USA), which is surrounded by moderately heavy traffic on four sites at all times of the year (Simonich and Hites, 1994). For model testing purposes, the air concentrations of six different PAH as reported in the field study were used as inputs to the model. The examined PAH are: benzo(a)pyrene (B[a]Py), chrysene (Chry), benzo(a)anthracene (B[a]An), benzo(e)pyrene (B[e]Py), pyrene

Table 2. Error statistics summary for comparison between measured and predicted cadmium concentrations in vegetation for the two different data sets examined in the study

	Average Error (mg/kg)	Relative Error	Standard Error (mg/kg)	Coeff. of Variation
(1)	0.039	0.194	0.153	0.76
(2)	-0.008	-0.014	0.06	0.104
(1) Field data from Garcia and Millan (1998)				
(2) Field data from Chronopoulou-Sereli et al. (1998)				

Cd in vegetation (mg/kg dry wt)
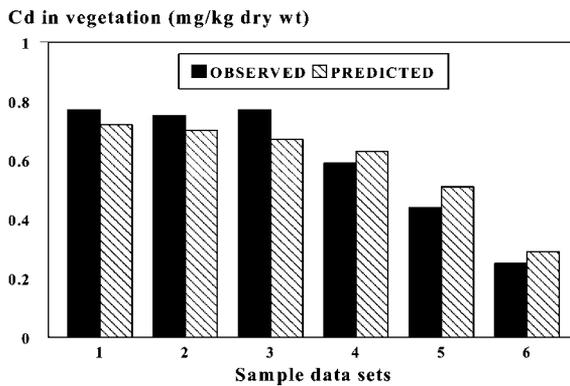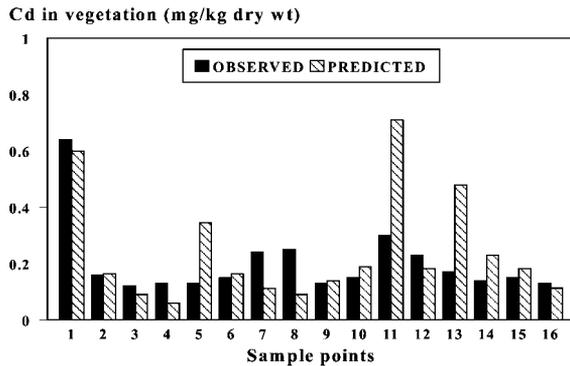

Cd in vegetation (mg/kg dry wt)

Figure 1. Predicted vs. measured cadmium concentration in grass for sixteen different sampling sites in the area Gipuzkoa, Spain (field data by Garcia and Millan, 1998), and for six different data sets in the downtown area of Athens, Greece (field data by Chronopoulou et al., 1998)
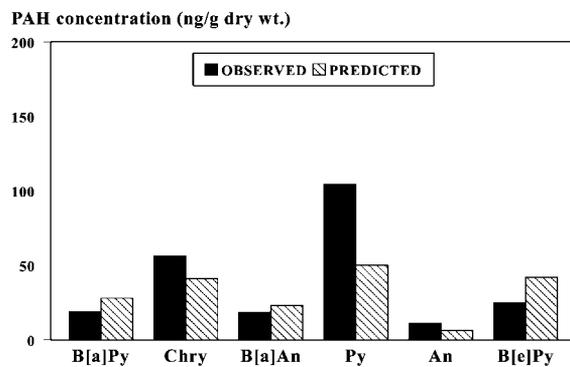
PAH concentration (ng/g dry wt.)

Figure 2. Comparison of observed and model predicted PAH concentrations in maple leaves. Observed data by Simonich and Hites (1994)

(Py) and anthracene (An). Although in the field study air and vegetation samples were collected every three weeks throughout the growing season, average values of air concentrations were used for the examined PAH in the model simulations. Model results were also evaluated on an average basis. Air concentrations were reported as vapor-phase, particle-phase and total. Selected important parameters and the assigned values used in the simulations are presented in Table 3. Dry deposition velocities to the vegetation surface were predicted according to Slinn (1982) for typical values of canopy characteristics and long term average meteorological data (wind, temperature) derived from a NOAA (National Oceanic and Atmospheric Administration) database. PAH concentrations due to root uptake and translocation to the plant foliage was not considered, since for highly lipophilic chemicals such as PAH and PCDD/F, the contamination of plant foliage via airborne deposition is the most important mechanism. The total PAH concentration in plants then is estimated due to air-to-vegetation transfer and atmospheric deposition of particle-bound chemical. Results are shown in figure 2. Generally, the model gives reasonable results, with simulations to be most accurate for the cases of benzo(a)anthracene and chrysene. Results for benzo(a)pyrene and benzo(e)pyrene are in tolerable good agreement with the observed data. The poorest predictions are for pyrene and anthracene (underestimation by a factor of 2), which are present in the atmosphere almost entirely in the vapor phase (average observed vapor fractions for anthracene and pyrene: 0.99 and 0.95, respectively).

DISCUSSION

The evaluation of model simulation results showed, in general, that the model provided a plausible description of air-vegetation-soil dynamics available from the monitoring studies on cadmium in grass and several PAH in maple leaves. The current use of the model is oriented to site-specific studies with only limited data available for testing and verification. In such cases, the model can be used to support tentative hypotheses, which point to additional data and process studies that are needed to confirm or contradict these conclusions. The model can be typically used for performing screening-level analyses of potential exposures and risks and also site-specif-

Table 3. Selected model parameter values for the case of PAH in maple leaves

MODEL PARAMETER	INPUT VALUE	COMMENTS - REFERENCES
Leaf density, g/mL	0.8	typical value
Leaf area index	5.0	typical value
Leaf water content, % wet weight	48	average value based on measured values (Simonich and Hites, 1994)
Lipid content, % dry weight	1.5	average value based on measured values (Simonich and Hites, 1994)
Loss rate constant, d^{-1}	0.05	typical value
V_d , cm/s	2.2	predicted by the dry deposition model by Slinn (1982) for typical values of canopy characteristics and long-term average meteorological data (wind, temperature) derived from NOAA database
Octanol-water partition coefficients for the examined chemicals		several references as quoted in Cohen et al. (1997)

ic predictive assessments. In these cases, the numerical estimates of the model should be typically interpreted as a measure of the potential magnitude of exposure and risk and not as specific numerical estimates.

The proposed model incorporates significant transport pathways with appropriate parameterization, while it requires a relatively limited number of routinely collected meteorological data and parameters concerning pollutant and vegetation chararacteristics. Other currently available models use similar data but they are more appropriate for long-term assessments since they are based on steady-state approaches, i.e. USEPA (1990; 1993a, b), Buck et al. (1995). Also, in some of these models (USEPA, 1993b; Buck et al., 1995) only the transfer of chemicals to plants via atmospheric deposition and root uptake from the soil is simulated; air-to-foliage transfer, which can be an important dominant contamination pathway for several pollutants, is not included. In addition, in these models the soil concentration used in the uptake from soil is representative of a steady-state or a close-to-steady-state system. The model

presented in this study includes both atmospheric deposition and diffusion, while the soil concentration term accounts for the temporal variation of accumulation, transport, environmental degradation and transformation of chemicals over a multi-year period.

Furthermore, as more data from research on air-vegetation dynamics processes becomes available, appropriate model extension can occur, with more mechanistic and process-based functional dependencies. Model limitations due to the uncertainty associated with some transfer parameters and incomplete field data for testing need to be addressed via experimental and field studies.

SUMMARY AND CONCLUSIONS

The current understanding of the processes involved in air-vegetation-soil dynamics of atmospheric pollutants is limited and the modeling technology tools are, in general, not well developed. In this paper, a set of algorithms for estimating atmospheric pollutant interactions in soil-vegetation-air systems was developed and tested. The model incorporates significant transport path-

ways with appropriate parameterization, while it requires a relatively limited number of parameters and input data, providing, therefore, a reasonable compromise between model complexity and the ability to obtain realistic data characterizing model parameters. Testing applications included model comparison to field data in the cases of cadmium in grass and several PAH in maple leaves. Based on the evaluation of the results for the examined cases, the numerical estimates of the model in its present status should typically be interpreted as a measure of the potential magnitude of exposure and not always as specific numerical estimates. The model can, therefore, be used to support tentative hypotheses, which point to additional data and

process studies that are needed to confirm or contradict these conclusions. The model was also found to be well suited for screening-level assessments as a component of a management-oriented and multimedia-based assessment. On-going work is incorporating this vegetation model into an integrated multimedia simulation framework to provide better model capabilities.

DISCLAIMER

Although the information in this document has been funded wholly or in part by the U.S. EPA, it does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

Ambrose, R.B. and Roesch, S.E. (1982). Dynamic Estuary Model Performance. *J. Environ. Engin. Div. ASCE* **108,** 51-71.

Bacci, E., Cerejeira, M., Caggi, C., Chemello, G., Calamari, D. (1992). Chlorinated dioxins: volatilization from soils and bioconcentration in plant leaves. *Bull. Environ. Contam. Toxic.* **48,** 401-408.

Buck, J., Whelan, G., Droppo, G., Strenge, D., Castleton, K., McDonald, J., Sato, C., and Streile, G., (1995). Multimedia Environmental Pollutant Assessment System. PNL-10395, Pacific Northwest Laboratory, Richland, Washington.

Chronopoulou-Sereli, A., Haidouti, C., Chronopoulos, J. and Massas, I. (1998). Microclimatic conditions and levels of pollution in public squares in Athens, Greece. *Toxicol. Environ. Chemistry* **68,** 1-9.

Cohen, Y., Winer, A.M., de Water, R.V., Pan, F., Vohra, R., Zhou, L., Hernandez, L. (1997). Development of predicted capabilities for intermedia transfer factors for toxic air pollutants. Final Report. University of California, Los Angeles, CA.

Garcia, R., Millan, E. (1998). Assessment of Cd, Pb and Zn contamination in roadside soils and grasses from Gipuzkoa (Spain). *Chemosphere* **37,** 1615-1625.

Hung, H. and Mackay, D. (1997). A novel and simple model of the uptake of organic chemicals by vegetation from air and soil. *Chemosphere* **35,** 959-977.

Lindberg, S.E. (1996). Forests and the global biogeochemical cycle of mercury: the importance of understanding air/vegetation exchange processes. In *Global and regional mercury cycles: sources, fluxes, and mass balances*, W. Baeyans et al. (ed.), pp. 359-380, NATO ASI Series, The Netherlands.

Lindberg, S.E. and Turner, R.R. (1988). Factors influencing atmospheric deposition, stream export, and landscape accumulation of trace metals in forested watersheds. *Water, Air and Soil Pollut.* **39,** 123-156.

Lindstrom, F.T., Borsma, L. and McFarlane, C. (1991). Mathematical model of plant uptake of organic chemicals: development of the model. *J. Environ. Qual.* **20,** 129-136.

McCrady, J.L. and Maggard, S.P. (1993). Uptake and photodegradation of 2,3,7,8-Tetrachlorodibenzo-pdioxin sorbed to grass foliage. *Environ. Sci. Technol.* **27,** 343-350.

Paterson, S., Mackay, D. and McFarlane, C. (1994). A model of organic uptake by plants from soil and the atmosphere. *Environ. Sci. Technol.* **28,** 2259-2266.

Simonich, S.L. and Hites, R.A. (1994). Vegetation-atmosphere partitioning of polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* **28,** 939-943.

Slinn, W.G.N. (1982). Predictions for particle deposition to vegetative canopy. *Atmos. Environ.* **16,** 1785-1794.

Trapp, S. and Matthies M,. (1995). Generic one-compartment model for uptake of organic chemicals by foliar vegetation. *Environ. Sci. Technol.* **29,** 2333-2338.

Tsiros, I.X. and Ambrose, R.B. (1997). South Florida Mercury Screening Study. Part 2. Mercury in Everglades Agricultural Area. EPA-600/x-97-xxx, US Environmental Protection Agency, Athens, GA.

Tsiros, J., Elmaloglou, S., Ambrose, R. (1998a). Comparative study of two methods for modeling soil water regime

in agricultural fields. *Water Resour. Manage.* **12,** 285-293.

Tsiros, I.X.,. Haidouti, K., and Chronopoulou-Sereli, A. (1998b). Airborne fluoride contamination of soils and olives trees near an aluminum plant. Measurements and simulations. *J. Environ. Sci. Health* **A33,** 1309-1324.

Tsiros, I.X. and Ambrose, R.B., (1999). An environmental simulation model for mercury transport and fate in small rural catchments. *Chemosphere* **39,** 477-492.

US EPA (1981). The potential atmospheric impact of chemicals released to the environment. EPA 560/5-80-001, US Environmental Protection Agency, Washington, DC.

US EPA (1990). Methodology for assessing health risks associated with indirect exposure to combustor emissions. Interim Final Report. EPA 600/6-90-003, US Environmental Protection Agency, Washington, DC.

US EPA (1993a). Addendum to methodology for assessing health risks associated with indirect exposure to combustor emissions. Interim Final Report. EPA 600/AP-93/003, Exposure Assessment Group, Office of Health and Environmental Assessment, Washington, DC.

US EPA (1993b). Multimedia contaminant fate, transport, and exposure model. US Environmental Protection Agency, Office of Research and Development, Washington, DC.

US EPA (1994). Estimating exposure to dioxin-like compounds, Vol. II. Properties, sources, occurrence and background exposure. Draft, Office of Research and Development, Washington, DC.

US EPA (1997a). Protocol for Screening Level Human Health Risk Assessment. Region 6, Multimedia Planning and Permitting Division. Center for Combustion Science and Engineering. Office of Solid Waste, Washington, DC.

US EPA (1997b). Mercury study report to congress. Volume III. An assessment of exposure from anthropogenic mercury emissions in the United States. Office of Air Quality Planning and Standards, Office of Research and Development. Research Triangle Park, NC.

US EPA (1998). Human health and ecological risk assessment support to the development of technical standards for emissions from combustion units burning hazardous wastes. Draft Report, EPA Contract Number 68-W6-0053. Office of Solid Waste, Washington, DC.

Walcek, C.J. and Pruppacher, H.R., (1984). On scavenging of SO_2 by clouds and raindrops: I. A theoretical study of SO_2 washout by rain falling through a pollution plume. *J. Atmos. Chem.* **1,** 307-324.

Wesely, M.L. (1989). Paramerization of surface resistances to gaseous dry deposition in regional-scale numerical models. *Atmos. Environ.* **23,** 1293-1304.

Wesely, M.L., Cook, D.R. and Hart, R.L. (1983). Fluxes of gases and particles above a deciduous forest in wintertime. *Boundary-Layer Meteorol.* **90,** 237-255.

Winters, D., Cleverly, D., Meier, K., (1996). A statistical survey of dioxin-like compounds in United States beef: A progress report. *Chemosphere* **32,** 469-478.

World Meteorological Organization. (1975). Intercomparison of conceptual models used in operational hydrological forecasting. *Operational Hydrol.* Report No 7.