ABSTRACT

Chemicals are released to the environment in view of several human activities. These chemicals will distribute in media such as air, water, soil, sediments and biota due to the action of complex physical, chemical and biological processes. Since many of the chemicals are toxic, persistent and subject to accumulation in media where biota and human exposition is significant, it is necessary to control their release. Monitoring programs and remediation of contaminated environments require estimates of concentration levels and persistence of the substance, its fate, transport rates, reactivities and partitioning between media. Multimedia models are low-cost, relatively simple but powerful tools to investigate the fate of released chemicals. These models are a mathematical description of the distribution of the chemicals among the media based on environmental chemistry, thermodynamics, reaction kinetics, transport phenomena and mass conservation. This study encompasses a review of multimedia models developed by Mackay et al. These models adopt fugacity or "equivalent" concentration as equilibrium criteria among the media. A level III model was used to assess the fate of chemical and metallurgical pollutants in a generic environment to illustrate the usefulness of multimedia models. The model determined the concentrations of the chemicals in the media, rates of advective and diffusive transport among compartments, reaction or transformation rates, persistences and accumulation in biota.

INTRODUCTION

The environment has a finite capacity to dilute and degrade chemicals introduced in itself. Certain chemicals persist and accumulate to levels that may cause adverse affects on biota including humans. Some chemicals have the potential to migrate and distribute in several media such as air, water, soil, sediment and biota, reaching unpredicted destinations with unexpectedly high concentrations. Numerous chemicals are naturally present, however with concentrations far below those resulting from human activities. Many of these chemicals are toxic to various organisms, including the human, in case of sufficiently high doses or expositions.

In order to exercise an effective control on the use of chemicals, implement remediation techniques in environments already contaminated and predict the possible behavior of new chemicals it is necessary to determine its concentration, persistence, reactivity and tendency to partitioning between the media. Before indiscriminately discharging chemicals in the environment, it should be done a complete appreciation of its final fate, how they are transported and transformed and where they accumulate, with the purpose of assuring that there is no risk of adverse effects on the living organisms of the ecosystem. To provide a sound scientific basis for managing new and existing substances, it is necessary to understand and predict the fate of releases of these substances to the environment, with the goal of ensuring that there is no risk of adverse effect to humans or other organisms that occupy the environment. The risk of a present or proposed discharge of a substance can be assessed by comparing the concentration of this substance in an environmental compartment to the concentration of the substance that will result in no adverse effects on the organisms in the ecosystem. The evaluation of the fate of chemicals discharged to the environment is conducted with monitoring programs and with multimedia models (Mackay, 1991). These models determine the chemical concentrations under different conditions, help in interpreting the data obtained through monitoring and quantify the relative importance of the various transport and transformation processes (ECETOC, 1992). The usefulness and the potential of the models have been recognized both by the governmental agencies for environmental control as well as the industrial sector. In
fact, it is difficult to conceive how to assess the behavior of a chemical, and therefore to establish appropriate regulations, without the help of a multimedia model. In this regard, the industries have recently begun using these models to predict the environmental fate of new chemicals. Several countries and organizations have also been attracted to their power and relative simplicity. Canada and the European Community are recommending these models to assess the safety of new chemicals to humans and the environment (Cowan et al., 1995). Government researches in the Netherlands have used multimedia models to determine whether their single-media environmental regulations have compatible objectives (Renner, 1995). In the United States, multimedia models have been used to determine priorities for regulation efforts since 1993 and to estimate chemical fate and human exposure near hazardous waste sites since 1995 (USEPA, 1995).

The objective of this work is to demonstrate the application of a level III multimedia model to assess the fate of potentially pollutant chemicals in a generic environment at 25°C.

MUTIMEDIA MODELS DEVELOPED BY MACKAY

Mackay-type or fugacity models are the most widely accepted multimedia fate models. According to Mackay, multimedia models are (best) suited for chemicals chronically discharged in the environment like industrial chemicals. These models operate by simplifying environmental media - air, water, soil, and sediment into homogeneous compartments or boxes and then tracking the flow of and eventual fate of chemicals from box to box. Subcompartments allow for additional complexity. Conservation of mass is the underlying principle of this system. The model requires tree kinds of data: prevailing environmental conditions such as temperatures, flow rates, and accumulation rates; chemical properties that influence partition and reaction tendencies; and emission/discharge data for the chemical (Renner, 1995). Multimedia models must estimate the amounts of the chemicals that will partition in each medium, the relative concentrations in these media, the dominant reactions, the global persistences and the main transport processes between media.

Mackay-type or fugacity models encompass four types of increasing complexity.

Level I model provides a first look at a chemical fate by partitioning chemicals among compartments according to fugacity, a thermodynamic quantity that determines how a substance will diffuse between compartments to reach equilibrium.

Level II models also account for transformations and reactions within a compartment using a rate constant, which can also be expressed as a residence time or half-life.

Level III models allow for no-non-equilibrium distribution and require additional expressions for the rates of transfer between compartments. Level III models are non-conservative, steady state and introduce resistance to chemical migration between environmental compartments. These models are built around a system of equations, one for each compartment, which describe all inputs and outputs for each compartment (ECETOC, 1992). They present a more accurate estimate of chemical distribution, quantities and concentrations in each environmental compartment and its lifetime. The data required for Level 3 models are: Henry's law constant, the adsorption coefficients for soil and sediment and the bioconcentration factor, if the biota is included in the model. For common hydrophobic chemicals, only data on solubility and vapor pressure would suffice as the other parameters may be calculated from these data. However, the use of experimentally determined partition coefficients should be preferred. Additional data include transformation rate constants, emission or discharge rates for each compartment, rates of transfer between compartments which are generally estimated (ECETOC, 1992). A review of Level 3 models and a discussion of their features, performance, and desired outputs may be found in (Cowan et al., 1995).

Level IV models are non-equilibrium, non-conservative and non steady-state. These models allow predictions of the time required for the chemical to disappear from the environment once its use has ceased or, alternatively, the time needed to reach steady-state when chemical releases are continuing. Level IV models are built around the same set of equations as Level III models but, because they assume no steady-state, solving this set becomes more complicated, especially, if the variability in the release with time is complex.

It is important to strike a balance between simple models, which do not represent reality, and models which are difficult to use. Level I models with an air/water/solids "unit world" present, on a basis of limited number of data, the major feature of the environmental fate and behavior of chemicals, i.e., the "target" compartment(s) where they are expected to accumulate. Level 2 models usually are of minor interest. Level 3 models are of value to assess the distribution of a chemical in the environment in a more realistic manner. Level IV models should be used only for estimating the estimating the disappearance of chemicals.
from the environment. Recently it was concluded that a Level III multimedia model that includes at least four compartments (air, water, soil and sediment) is the preferred type for regulatory contexts since this type of model incorporates sufficient complexity to gain a quantitative prediction of chemical distribution, pathways and relative concentrations (Mackay et al. 1996). In certain cases, a Level IV, unsteady-state or dynamic evaluation, may be required. Such a formulation has been employed by (Cohen et al., 1990; Mackay, 1989; and Wania and Mackay, 1993). Some models that focus on the long-term effects of hazardous waste sites and contaminated soils also use a Level 4 unsteady-state approach (Mackay et al. 1996).

APPLICATION OF A LEVEL III MULTIMEDIA MODEL

A level III multimedia was applied to analyze the fate of potentially pollutant chemicals in a generic environment at 25°C. Evaluative or generic environments are hypothetical environments keeping, however, the main characteristics of a real environment. They basically consist of homogeneous volumes of air, water, soil, sediment and, sometimes, biota, being an alternative to real environments and presenting scientific, educational and regulatory merits (Renner, 1995).

There are three reasons for conducting an evaluative fate assessment. First, it reveals general features of chemical behavior and focuses efforts on obtaining information on the most important characteristics of the chemical, rather than the environment. Second, this assessment may be sufficient to demonstrate that the chemical is of no concern, or is of definite concern. Third, the assessment can be undertaken, compared, and communicated internationally.

The adopted model is a "fugacity model". Fugacity is a thermodynamic quantity related to the chemical potential and to the activity, which characterizes the escaping tendency of a chemical from a phase. In these models the fugacity is used instead of the concentration as the controlling variable. The fugacity is also employed as the equilibrium criterion of the model. The environment will be in equilibrium if the fugacity of the chemical is the same in all compartments. In addition, there is a linear relationship between concentration and fugacity. Furthermore, the rates of all processes involved are directly proportional to the fugacity.

The input data for the model includes the description of the environment, the physical chemical, kinetic and transport properties of the chemical, rates of admission of the chemical in the environment by emissions, discharges and by advection with the background concentrations. Background concentrations determine the extent to which advection and dispersion from the model boundaries contributes to the overall mass balance of a chemical in the unit world.

The chemicals tested were the benzo(a)pyrene (BaP) and the trichloroethylene (TCE). The BaP is a non-polar organic chemical produced when a fuel is burned with insufficient oxygen, existing, for instance, in the effluents generated by the coke making process. This chemical has been proved to be highly toxic since it presents both carcinogenic and mutagenic action (Mackay, 1991). The TCE is an important industrial solvent. The model results are given in Figures 1 and 2.

The model provides the likely concentrations of the chemical prevailing in the different media and establishes the relative importance of the various routes of the environment contamination. The results also allow identifying the media where the chemical reaches the highest concentrations. For these media, complementary specific models should be employed. Another relevant information of the model is the chemical persistence in the environment as, obviously, the more persistent chemicals cause more awareness. The persistence is clearly an important data to any environmental regulation thus deserving being strictly defined.

At steady state (Level III) when the amount of chemical is constant with time, the total input and output rates on the environment should be equal. The overall persistence of the chemical is then the ratio of its mass to the total input or output rate. The total output rate is the sum of the advective rate, due to the advective fluxes usually in the air or in the water, with the degradation reaction rate. If the total advection rate is large compared to the overall reaction rate, most of the chemical exits the system by advection, being able to contaminate other regions. Hence, from the local point of view, the persistence calculated as stated above, is of utmost interest. On the other hand, from the global point of view, the persistence based only on the reaction rate is more important.

Finally, for an assessment of chemical fate based on models to have credibility, it must be demonstrated that the model gives adequate predictions for a variety of chemicals that differ in behavior. This requires applying the models to actual regions for which discharge data and monitoring information (usually concentrations) exist and demonstrating a level of agreement between the model results and reality.
Clearly, it is expected that the multimedia models be validated by comparing the predicted concentrations with measured concentrations in real environments. Generally, the agreement between these concentrations is, at the best, of order of magnitude. Actual concentrations are hardly obtained with accuracy since they possess large spatial and temporal variability, as do the other environmental parameters. Practical experience shows that for many chemicals usually show large temporal and spatial variations. Reliable, critically evaluated chemical data are lacking. A further complicating factor is the difficulty of translating laboratory derived rate constants into environmental rate constants. Environmental parameters usually show large temporal and spatial variations. For practical purposes, average values are used in most model calculations. Data on emissions or discharge into the different environmental compartments are often not known accurately. In many cases emissions are not constant and may be discontinuous. Again for practical purposes, averaged values are normally used.

The models are probably more reliable to persistent and widely dispersed chemicals in the environment and in sites far away from the sources of emissions/discharges. As the actual concentrations vary considerably even in a single medium, ideally the models should provide concentration spectra with a mean and a variance instead of a unique value only. Chemicals with similar properties may then have similar variances.

It is important to let it clear that in the present work, the model was applied to a generic environment and does not have the pretension of simulating a specific real environment. This will be the next step of the research, particularly to regions in the state of Rio de Janeiro following the procedure adopted in Canada, USA, France and the Netherlands.

Figure 1 - Model results for BaP.
ChemCAN v. 4.0
Chemical: Trichloroethylene
Region: Generic

Air
- 0.114 kg/h
- 14.2 kg (29.1 %)
- Fug. = 1.29e-3 μPa
- 0.071 ng/m²
- 0.197 kg/h
- 0.098 kg/h

Soil
- 0.111 kg/h
- 5.585 kg (11.4 %)
- Fug. = 1.130 μPa
- 4.14e-4 ng/g

Water
- 1.29e-4 kg/h
- 28.9 kg (59.3 %)
- Fug. = 0.979 μPa
- 0.145 ng/L

Sediment
- 9.33e-5 kg/h
- 2.12e-5 kg/h
- 9.39e-6 kg/h

Legend:
- EMISSION
- REACTION
- ADVECTION
- INTERMEDIATE EXCHANGE

Total Emissions = 0.342 kg/h
Total Mass = 48.8 kg
Persistence = 143 h = 5.938 days

Figure 2 – Model results for TCE

REFERENCES


