

Procedure for estimating chemical properties and chemical concentrations in different media of an environmental fate model

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1 Estimation of chemical property data with Epi Suite

Chemical property data required for a three-box model such as the Small World Model¹ include two partition coefficients and three degradation half-lives:

octanol-water partition coefficient, K_{ow} or $\log K_{ow}$ (logarithm of K_{ow})

air-water partition coefficient, K_{aw}

degradation half-life in air, $t_{1/2,a}$

degradation half-life in water, $t_{1/2,w}$

degradation half-life in soil, $t_{1/2,s}$

The partition coefficients are dimensionless, because they represent the ratio of the chemical's concentration in one medium (air or octanol) to the concentration in the second medium (water); all concentrations are, for example, in mol/m³ (these are the units used in the Small World Model; in general, it could also be kg/L or any other units of concentration).

The degradation half-lives have units of time, often seconds, hours or days.

Epi Suite can be downloaded from

<http://www.epa.gov/opptintr/exposure/pubs/episuite.htm> and runs on Windows computers. It contains a wide range of individual property estimation methods. Here we use AOPWIN (degradation in air), BIOWIN (degradation in water and soil), KOWWIN (K_{ow}) and HENRYWIN (K_{aw}). For all methods, the CAS number is easiest to be used as input (open the estimation method selected from the list on the left of Epi Suite, enter CAS number, and click "calculate").

1.1 AOPWIN for degradation in air

AOPWIN yields rate constants of the chemical's reaction with OH radicals in air. The output is a 2nd-order rate constant in units of cm³/(molecules·s)². This rate constant describes the "speed" of a reaction of two components, the chemical of interest and the OH radical in air. The concentration of OH radicals can be assumed to be constant; a typical average value for this concentration is $c_{OH} = 7.5 \cdot 10^5$ molecules/cm³. We can multiply the 2nd-order rate constant by c_{OH} and obtain thereby a 1st-order rate constant in units of 1/s:

$$k_{2nd} \cdot c_{OH} = k_{1st}$$

From this 1st-order rate constant, k_{1st} , we obtain the degradation half-life in air, $t_{1/2,a}$, as

$$t_{1/2,a} = \ln 2 / k_{1st}.$$

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² Epi Suite says "cm³/molecules-sec", but this is somewhat sloppy notation.

This is now in units of seconds; after conversion in units of hours, it is the value that we need as input to the Small World Model.

If the chemical's rate constant for reaction with OH radicals has been determined experimentally, the experimental value will also be reported by AOPWIN, because the method contains both the estimation model and a database of measured values. The measured value is labeled "exp".

1.2 BIOWIN for degradation in water and soil

For degradation in water and soil, we assume that it mainly takes place as aerobic biodegradation, i.e. by oxygen-consuming microorganisms in the soil and in the water (more precisely, at the ground of a river or lake and on the surface of suspended particles). This process is described by the BIOWIN method contained in Epi Suite (again, enter the chemical's CAS number and then click "calculate").

BIOWIN yields output from six individual sub-methods or sub-models. The third one, BIOWIN3, estimates the time span that is required for ultimate biodegradation, i.e. complete breakdown of the chemical. (BIOWIN4 only addresses primary biodegradation, i.e. disappearance of the initial chemical structure, but not complete breakdown. The other methods, 1, 2, 5 and 6 provide estimates of the likelihood of ready biodegradability.) BIOWIN3 yields a score between 0 and 5. The higher this score, the shorter the biodegradation half-life; the conversion of scores into half-lives is approximately: 5 – hours, 4 – days, 3 – weeks, 2 – months, 1 – years. The authors of the BIOWIN method have recently published the following more detailed conversion scheme (Aronson et al. 2006, p. 1957):

| BIOWIN3 score | aerobic biodegradation half-life (days) |
|---------------|-----------------------------------------|
| > 4.75 | 0.17 |
| 4.25–4.75 | 1.25 |
| 3.75–4.25 | 2.33 |
| 3.25–3.75 | 8.67 |
| 2.75–3.25 | 15 |
| 2.25–2.75 | 37.5 |
| 1.75–2.25 | 120 |
| 1.25–1.75 | 240 |
| < 1.25 | 720 |

These half-lives need to be converted into hours and can then be used as input to the Small World Model.

1.3 KOWWIN for K_{ow}

KOWWIN yields an estimate of the K_{ow} that is derived from the structural fragments present in the structure of the chemical. Again, if measured K_{ow} values are available, these are also reported. The logarithm of the K_{ow} can directly be used as input to the Small World Model.

1.4 HENRYWIN for K_{aw}

HENRYWIN yields an estimate of the Henry's law constant (HLC) that is derived from the structural fragments present in the structure of the chemical. Again, if measured HLC values are available, these are also reported. The HLC is given in units of $\text{atm}\cdot\text{m}^3/\text{mol}$ or $\text{Pa}\cdot\text{m}^3/\text{mol}$, because it represents the ratio of vapor pressure (in atm) and water solubility (in mol/m^3). To convert it into a dimensionless air-water partition coefficient, K_{aw} , we need to convert the vapor pressure into a concentration in air. This can be done by assuming the chemical in the gas phase behaves like an ideal gas. The ideal gas law is $p\cdot V = n\cdot R\cdot T$, with p for vapor pressure (in atm or Pa), V for volume (in m^3), n for number of moles (dimensionless), R for gas constant (in $\text{J}/(\text{mol}\cdot\text{K})$ if p is in Pa and in $\text{atm}\cdot\text{m}^3/(\text{mol}\cdot\text{K})$ if p is in atm), and T for temperature (in K). Rearrangement gives: $n/V = c_{\text{air}} = p/RT$, which means that we need to divide the vapor pressure by $R\cdot T$ to obtain a concentration in air in mol/m^3 .

Accordingly, we also need to divide the HLC in by $R\cdot T$ to obtain the dimensionless air-water partition coefficient, K_{aw} . From the K_{aw} , we take the logarithm and can use this number as input to the Small World Model.

Note that the value of the gas constant depends on the units. If we use HENRYWIN output in $\text{atm}\cdot\text{m}^3/\text{mol}$, we need to use the gas constant in units of $\text{atm}\cdot\text{m}^3/(\text{mol}\cdot\text{K})$: $R = 8.206\cdot 10^{-5} \text{ atm}\cdot\text{m}^3/(\text{mol}\cdot\text{K})$. With $T = 298 \text{ K}$, $R\cdot T$ is equal to $0.0245 \text{ atm}\cdot\text{m}^3/\text{mol}$, and $K_{aw} = \text{HLC}/(R\cdot T)$ is dimensionless, as intended. If we use HENRYWIN output in $\text{Pa}\cdot\text{m}^3/\text{mol}$, we need to use the gas constant in units of $\text{J}/(\text{mol}\cdot\text{K})$: $R = 8.3145 \text{ J}/(\text{mol}\cdot\text{K})$. $R\cdot T$ is then equal to 2478 J/mol and K_{aw} is again dimensionless.

2 Adjustment of the Small World Model and Estimation of Chemical Concentrations

Background information on multi-compartment models is provided by MacLeod et al. (2010). In the Small World Model, chemical property data derived as described above are entered in cells C9 to C14.

2.1 Bulk environmental properties

The bulk environmental properties are set in cells C17 to C23 in the model. They include temperature, total surface area, fractions of surface area covered by water and soil, and the height and depth of the air, water and soil compartment.

In its base case, the model is parameterized for the global system (this is why it is called the "Small World Model"): the total surface area is $5.1\cdot 10^{14} \text{ m}^2$, which is the surface area of the earth; the fraction of ocean water is 0.71, and the fraction of soil is 0.29, which are the global averages. The default temperature, however, is 298 K (25°C) in the base case, which is higher than the global average of approximately 285 K. This is because most chemical property data are available for 298 K and it was decided that no adjustment of chemical property data to lower temperatures should be performed automatically by the model. It is, however, possible to do this manually, but this requires additional work and background knowledge of the users. In that case, the temperature in cell C17 would have to be changed accordingly. Always enter the temperature in units of K, not in °C.

In the base case, the air compartment represents the troposphere up to a height of 6 km, the water compartment represents the oceanic surface water down to a depth of 100 m, and the soil compartment represents the top soil with a depth of 10 cm. The organic carbon content of the soil is 2% (this is set in cell C35).

When the model is adjusted to a region such as the southern part of Ghana, this requires the following steps:

- The total surface area is $2.39 \cdot 10^{11} \text{ m}^2$.
- The air compartment mainly represents the planetary boundary layer up to a height of 1 to 2 km; at the workshop on December 2, 2010, we used a height of 1000 m. In addition, the air compartment would need to be open, i.e. it should exchange air with the surrounding environment at a rate that is determined by average wind speeds in the region. In the base case, the model does not have this feature, i.e. the version we created at the workshop in Accra still has a closed air compartment. I am working on a version of the model where inflow and outflow of air can be switched on and off by the users.
- The water compartment mainly represents freshwater bodies such as Lake Volta. The fraction of surface area covered by water is available as geographical information (3.5%), and the depth of the water compartment can be obtained by division of the volume of Lake Volta by the surface area covered by water. At the workshop, we used 20 m. A conceptual limitation of the water compartment as it is in the current version of the model is that there is no sediment underneath. This is not a problem if the water compartment represents oceanic surface water (and was the reason why no sediment was implemented), but if the water compartment is interpreted as a freshwater body of 20 m depth, a sediment compartment would be required. This can only be solved by an extension of the model, which requires new coding.
- The soil compartment covers 96.5% of the surface area and its depth was set at 10 cm. The organic carbon content of the soil was increased to 3% (cell C17). This parameter can also be used to represent the waxy surface of leaves, i.e. the sorptive capacity of vegetation.

In conclusion, it is simple and straightforward to adjust the dimensions of the three compartments and the entire model domain according to local or regional data. However, there are a few inconsistencies caused by the basic structure of the model that require changes in the model code (air compartment open for exchange with surrounding air; sediment compartment).

2.2 Emission data

The emissions of the chemical considered are set in cells K58 to K60. Emissions can be to a single compartment only or to two or all three compartments in any combination. In the case of atrazine in Ghana, we used the amount of 2000 metric tons that is imported annually to the country as an estimate of (potential) emissions, converted this to an emission rate of $1.06 \cdot 10^5 \text{ mol/h}$ and assigned 90% of this to soil and 10% to air.

2.3 Model output

The model yields so-called Level-I and Level-III results. Level I describes the partitioning of the chemical that is determined by the two partition coefficients, K_{aw}

and K_{ow} . This means that the ratio of concentration in air and concentration in water is exactly equal to K_{aw} ; the ratio of concentrations in soil and water is equal to the soil-water partition coefficient, K_{sw} , which is derived from the K_{ow} in cell G14. At level I, nothing else happens in the model except this equilibrium partitioning dictated by K_{aw} and K_{ow} . Level-I results are displayed in the pie chart in cells E-F-G34 to E-F-G52.

Level III, in contrast, displays a considerably more complex picture. At level III, the equilibrium partitioning determined by K_{aw} and K_{ow} is overlaid by various additional processes, including: degradation in each of the compartments; deposition from air to surface media by precipitation and settling aerosol particles; runoff from soil to water by particles carried by rivers; and some more. All of these processes are expressed by first-order rate constants and are in competition. The faster processes have a stronger impact on the distribution of the chemical than the slower ones. For example, if a chemical is released to air only and rapidly degraded in air (but not deposited very rapidly), it “does not have enough time” to be deposited to soil and water in such amounts that the concentrations in soil and water build up to the levels defined by K_{aw} and K_{ow} . In other words, the ratio of the concentration in air to the concentration in water is then higher than the value given by the K_{aw} , because the concentration to water is “too low”.

Level III results are displayed in the pie chart in cells I-J-K73 to I-J-K91 and in the flow chart in cells M10-AC10 to M40-AC40.

For the example of atrazine in Ghana, we obtained level-III results of 90.8% in soil, 9.2% in water, and 0.01% in air. Division of the amount in water by the volume of water yielded a concentration of $9.63 \cdot 10^{-5} \text{ mol/m}^3$, equivalent to $2.08 \cdot 10^{-5} \text{ g/L}$. This is 20.8 $\mu\text{g/L}$, which is probably too high as a background concentration in surface water. Possible improvements of this result may be achieved by:

- using a lower emission rate; it is possible that the 2000 tonnes/yr are not entirely released to the environment
- adding a sediment compartment, which would take up some of the chemical
- making the air compartment of the model open, which would lead to removal of some chemical with outflowing air.

The key point of the modeling exercise is not to generate “the right number” in the first attempt, but to establish a first view of the “big picture” consisting of the environmental system, the properties of the chemical, and the emission data. Even a result that is not (yet) in agreement with the field data helps to establish and refine our understanding of the system.

Acknowledgment

Thanks to Jana Weiss for comments on the document.

References

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