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**Environmental risk evaluation of difficult
substances in USES 2.0**

P. van Beelen

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RIVM, P.O. Box 1, 3720 BA Bilthoven, telephone: 31 - 30 - 274 91 11; telefax: 31 - 30 - 274 29 71

Abstract

This report gives an inventory of the problems which arise when difficult substances are evaluated with the Uniform System for the Evaluation of Substances (USES). It gives an indication about the different classes of chemicals which can give problems in USES. Further, it describes the problems which occur when the physicochemical properties of these compounds are entered into USES. Many default estimations of sorption or bioaccumulation in USES are not valid for these compounds. In comparison with neutral molecules the speciation, bioaccumulation, and toxicity of these compounds are more strongly dependent upon a number of environmental parameters like pH and the presence of salts. This leads to larger uncertainties in the risk evaluation, which might be counterfeited by larger safety margins or a more extended data set.

Samenvatting

Het “Uniform System for the Evaluation of Substances” (USES) wordt gebruikt om de risico's van aangemelde stoffen te evalueren op basis van een beperkte set gegevens. Het computermodel USES is ontworpen om de risico's van neutrale organische verbindingen te analyseren. De toxiciteit, het risico op bioaccumulatie en de verdeling van de stof over vaste en vloeibare fases, kan worden geschat via de octanol/water partitie-coëfficiënt (Kow) van deze verbindingen. Deze schattingen zijn alleen geldig voor neutrale organische verbindingen die een minimum toxiciteit vertonen, maar niet voor andere typen verbindingen zoals organische kationen, anionen, surfactanten en anorganische verbindingen.

Dit rapport geeft een overzicht van de problemen die ontstaan wanneer deze moeilijke stoffen worden geëvalueerd met USES. Eerst wordt er een indicatie gegeven van de verschillende klassen van chemicaliën die problemen kunnen geven in USES. Vervolgens worden de problemen beschreven die optreden wanneer de fysisch-chemische eigenschappen van deze verbindingen in de inputmodule van USES worden gebracht. Smeltpunt, kookpunt, dampspanning en Kow van moeilijke stoffen zijn vaak niet beschikbaar en de Kow van deze stoffen mag niet worden toegepast in USES. Veel standaardschattingen van sorptie of bioaccumulatie in USES zijn niet geldig bij deze stoffen. Dit betekent, dat alle sorptie- en bioconcentratiefactoren in USES moeten worden geschat vanuit de literatuur. Normalisatie van deze factoren naar het organisch koolstofgehalte van grond en sedimenten is alleen mogelijk, als er bewijs is dat de sorptie wordt veroorzaakt door de organische fractie. Vergeleken met neutrale moleculen zijn speciatie, bioaccumulatie en toxiciteit van geladen moleculen sterker afhankelijk van een aantal milieuparameters zoals pH en de aanwezigheid van zouten. Dit veroorzaakt bij de risico-evaluatie van deze moleculen grotere onzekerheden, die kunnen worden verminderd door grotere veiligheidsmarges of een uitgebreidere dataset.

Summary

The Uniform System for the Evaluation of Substances (USES) is used to evaluate the risks of notified substances on the basis of a limited data set. The computerized USES model was designed to evaluate the risks of neutral organic compounds. The toxicity, risk of bioaccumulation and the partitioning of the compound between solid and aqueous phases, can be estimated from the octanol/water partitioning coefficient (K_{ow}) of these compounds. These estimations are only valid for neutral organic compounds showing baseline toxicity but not for other types of compounds like organic cations, anions, surfactants and inorganic compounds.

This report gives an inventory of the problems which arise when these difficult substances are evaluated with USES. First, it gives an indication about the different classes of chemicals which can give problems in USES. Secondly, it describes the problems which occur when the physicochemical properties of these compounds are entered into the USES input module. The melting point, boiling point, vapor pressure and the K_{ow} of difficult substances are often not available and the K_{ow} should not be used in USES. Many default estimations of sorption or bioaccumulation in USES are not valid for these substances. This implies that all sorption and bioconcentration factors in USES have to be estimated from literature. Normalization of these factors to the organic carbon content of soils and sediments is only possible when there is evidence that the compound is preferentially sorbed to the organic fraction.

In comparison with neutral molecules the speciation, bioaccumulation, and toxicity of charged molecules are more strongly dependent upon a number of environmental parameters like pH and the presence of salts. This leads to larger uncertainties in the risk evaluation of these molecules, which can be reduced by larger safety margins or a more extended data set.

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1. Introduction

The assessment of the risks resulting from environmental release of a multitude of chemicals, is a difficult task. In addition to the more than 100 000 chemicals which are on the European market today, a lot of new chemicals are put on the market each year (Van Leeuwen et al. 1996). The new chemicals have to be notified to the regulatory authorities, which have to assess the environmental risk involved with the use of these chemicals. The Uniform System for the Evaluation of Substances (USES) has been developed to evaluate the potential hazards and risks of notified substances on the basis of a specified data set (Vermeire et al. 1994). Based on USES 1.0 and an European Union Technical Guidance Document (EC 1996) for the risk assessment of new and existing substances, the European Union System for the Evaluation of Substances (EUSES) has been developed (EC 1996; Vermeire et al. 1997). EUSES is not suited for the evaluation of the use of pesticides since, as yet, there are no fully harmonized rules for the European Union available. The European Union Directive on the Uniform Principles for the evaluation and authorization of plant protection agents (EC 1994) has not been adopted at this moment. Recently USES 2.0 (Linders J.B.H.J and Jager D.T. (eds.) 1997) was developed as an update of USES 1.0 comprising both EUSES and the risk assessment system for pesticides. This risk assessment system is based EC Uniform Principles and on Dutch legislation on the use of pesticides (Linders J.B.H.J and Jager D.T. (eds.) 1997). The risk assessment of new and existing substances with USES and EUSES is performed using the so-called Base Set required for the notification of new substances (Vermeire et al. 1994). Since this is a limited data set, extrapolation procedures are used to predict the risk of a substance to man and the environment. This risk is expressed as the PEC/PNEC ratio (Predicted Environmental Concentration / Predicted No Effect Concentration). These estimation and extrapolation methods are based on a number of assumptions which make them unsuitable for inorganic chemicals, surfactants or ionized chemicals (Vermeire et al. 1994). This created problems with the environmental risk assessment of organic non-agricultural pesticides with USES 1.0 (Tas et al. 1996). A number of problems can occur when the USES is applied in the risk assessment of such "difficult" chemicals. For different classes, different properties might be missing in the base data set because they can not be obtained experimentally. For cations and anions for example, the vapor pressure will usually be low and might not have been reported. The ready biodegradability test is not useful for inorganic compounds since the biodegradation rate will be zero for most of these compounds. Also the Kow of inorganic compounds is rarely measured since it has no meaning for predicting sorption or bioaccumulation from these compounds.

Inorganic chemicals, surfactants and ionized chemicals have in common that there is a charge distribution over the molecule. This charge distribution can be small, like with neutral surfactants which have a hydrophilic part and a hydrophobic part. The hydrophilic part has a charge distribution which facilitates dissolution in water. Many surfactants, and most inorganic chemicals have a large charge distribution and form cations or anions when they are

dissolved in water. The cations can react with OH^- to form neutral molecules which predominate at pH values above their pKa and anions can react with H^+ to form neutral molecules which predominate below their pKa. Therefore it is important to know whether a chemical has a pKa between the environmentally relevant range of 2-10. The pH(H_2O) range of a number of Dutch soils ranged from 4 - 8 (Janssen et al. 1997). The environmentally relevant pKa range of chemicals has to be wider because a partial dissociation of a chemical can also be important. For example, an acid with a pKa of 2 is for 1% undissociated at pH 4. Therefore an environmentally relevant pKa range of 2-10 can be estimated. A compound usually has different physical, chemical and (eco)toxicological properties above and below its pKa. Information is needed to determine whether the above mentioned properties were measured with a neutral or charged form of the molecule. If, for example, the pure chemical is an acid, the octanol/water partition coefficient (K_{ow}) will be determined using the acid form. This K_{ow} will be used by USES 2.0 to predict sorption to soil and bioaccumulation in the field where the pH might be higher so that the anionic form of the chemical is present. This anionic form will often show less sorption and less bioaccumulation compared to the neutral acid.

In this report an inventory is made of the problems associated with the use of charged molecules in EUSES and USES 2.0. At first this report will describe the different classes of chemicals which give problems within the environmental risk assessment in USES. Secondly the problems with the use of physiochemical properties will be described. These problems affect the chemical distribution and the effect assessment of these compounds. Finally, this report will give recommendations about the handling of difficult substances in USES 2.0 and it will indicate which research is needed to improve the handling of difficult substances in future versions of USES.

1.1 The different classes of chemicals

Before the data of a new notified chemical can be incorporated into USES it is important to determine what kind of chemical is notified. The environmental pollutants were divided into four broad categories based on their toxic mode of action: Narcosis type chemicals, polar narcotic chemicals, reactive chemicals, and specifically acting chemicals (Verhaar, Urrestarazu Ramos, and Hermens 1996). Other toxic modes of action are: Oxidative phosphorylation uncouplers, respiratory inhibitors, electrophiles, acetylcholinesterase inhibitors, or central nervous system seizure agents (Russom et al. 1997). For the environmental distribution of pollutants, other properties are also important. Chemicals can be classified according to their partitioning in different environmental compartments (Mackay et al. 1996). Five different types were described: Type 1 substances partition into all phases, Type 2 substances are involatile, Type 3 substances are insoluble, Type 4 substances are both involatile and insoluble, Type 5 substances speciate into different chemical forms (Mackay et al. 1996). The cutoff values proposed were a vapor pressure of 10^{-7} Pa and a solubility of 10^{-9} g per liter. This classification can give problems when the vapor pressure or the solubility are

extremely low and are therefore not known accurately. Therefore a classification scheme based on the structural formula is proposed here. Cations, anions and neutral compounds behave differently. Inorganic compounds cannot be mineralized completely as in the case of organic compounds. Acids and bases can behave as neutral compounds or as charged compounds, depending on the pH in the environmental compartment they reside in. The notified chemicals can be distinguished into 10 classes based on environmental distribution and toxicity:

1. Inorganic cations
2. Inorganic anions
3. Neutral inorganic compounds
4. Organic cations
5. Organic anions
6. Organic acids with a pKa of the neutral molecule between 2 and 10
7. Organic bases „ „ „ „ „ „ „
8. Organic surfactants, which can be cationic, anionic or neutral.
9. Neutral organic compounds with a slightly polar substituent which exhibits polar narcosis (Urrestarazu Ramos et al. 1997).
10. Neutral organic compounds.

At first the question emerges which class of chemical is used. A detailed knowledge of organic chemistry is required to decide whether a compound has charged forms or reactive structures on the basis of the structural formula (Verhaar, van Leeuwen, and Hermens 1992). It may be possible in the near future to perform molecular orbital calculations based on the structural formula which can predict charge distributions over a molecule. When these calculations are automatically incorporated into USES, then it might be possible to determine automatically what kind of chemical is notified.

At the moment the users of USES have to study the data of the notified compounds to determine which class of chemical is used. Most of the inorganic compounds are charged molecules which dissociate when dissolved in water. Many organic compounds have carboxylic acid, amino, phenol or other groups which can either pick up or release a H⁺ ion. An estimation of the pKa is less straightforward. Nevertheless information about the pKa is needed to decide whether a compound is a neutral or charged molecule. QSARs for a crude estimation of the pKa for acidic groups in specific classes of organic compounds are available (Karickhoff and McDaniel 1991) and may be incorporated in future versions of USES. When the pKa of the compound has been measured or calculated it is possible to determine whether a cationic, neutral or anionic form was used for the determination of the properties of the molecule.

Surfactants lower the surface tension of water which is 72 Newton/km. The surface tension of a saturated solution of the test substance is required in the base data set. Therefore it is relatively easy to determine whether the substance is a surfactant. With ordinary detergent type surfactants the surface tension is in the range of 25 - 35 Newton/km and the concentration in the range of 50 - 200 mg/liter when the critical micelle concentration is reached (Swisher 1987).

2. Physicochemical properties

2.1 Problems with the octanol/water partition coefficient

The octanol/water partition coefficient of ionized chemicals and surfactants is often not measured. The estimation of this coefficient from molecular fragment method programs is not possible for ionic substances (Richner and Weidenhaupt 1997). Organic surfactants will not distribute homogeneously between octanol and water but will accumulate in the octanol/water interface. This makes the measurement of the K_{ow} very difficult. The octanol/water partition coefficient is used in the distribution module to predict sorption (Jager, Visser, and van de Meent 1994) and in the effects module to predict bioaccumulation (EC 1996). The relationships used in USES, are only valid for non-polar organic compounds (Vermeire et al. 1994). The K_{ow} of ionized chemicals and surfactants should therefore not be inserted in the input module of future versions of USES. Instead of the K_{ow} the specific partition coefficients of these chemicals should be used.

2.1.1 Problems with the use of the K_{ow} for organic acids and bases

For organic acids and bases the K_{ow} will usually be determined on the neutral molecule. Since the charged form of the molecule will have a much lower hydrophobicity, the "effective" K_{ow} of a mixture of the neutral and the charged forms of the molecule will be lower than the measured K_{ow} of the neutral form. This can result in an overestimation of the sorption and the bioaccumulation in the distribution and in the effect module of USES 2.0 and an underestimation of the toxicity for aquatic organisms.

Four different types of acids can be distinguished:

1. $AH^- \rightleftharpoons A^{2-} + H^+$
2. $AH \rightleftharpoons A^- + H^+$
3. $AH^+ \rightleftharpoons A + H^+$
4. $AH^{2+} \rightleftharpoons A^+ + H^+$

Categories 1 and 4 will stay in the ionic form so that the pK_a does not have a large effect on the apparent K_{ow} . Category 3 acids are positively charged (like many organic amines), but become neutral at a pH above their pK_a . Here the pH can have a marked influence on sorption, solubility and toxicity. The AH^+ form might sorb to clay particles and the A form might sorb to organic material. The effect of a pH change is not easily predicted with these acids.

2.1.2 The use of an effective Kow for organic acids and bases

For organic acids of the type AH the situation is more simple because the corresponding base A^- is not expected to show much sorption or bioaccumulation. For these acids an effective Kow can be calculated which can be used to estimate sorption (Lee et al. 1990) and bioaccumulation in the usual way (Van Beelen and Fleuren Kemilä 1997).

Kow might be calculated using:

$$Kow = Kow_n * F + Kow_i (1-F)$$

with F is the fraction undissociated $F = 1/(1+10^{(pH-pKa)})$

$Kow_n =$ The octanol/water partition coefficient of the neutral molecule

$Kow_i =$ The octanol/water partition coefficient of the ion.

The default estimate of the Kow_i might be 0.1. This is the lowest Kow that EUSES will accept (see EUSES appendix II Page 3).

The correction for the fraction undissociated F is equal to the correction factor CORR at Page 502 of the Technical Guidance Documents (EC 1996). For organic bases in the form A the corresponding form AH^+ will only have a low contribution to the total sorption and the Kow can also be calculated with the above formula. The use of an effective Kow for acids of the type AH and bases of the type A makes it possible to incorporate these acids and bases into EUSES and predict bioaccumulation and sorption from the Kow.

2.2 Problems with water solubility

The relationship between the octanol/water partitioning coefficient and the solubility described at p. 74 in the USES 1.0 directory does not hold for charged molecules. This relationship is therefore not used in EUSES and USES 2.0. It is not necessary since both the octanol/water partitioning coefficient and the water solubility are in the base data set for compounds with an annual production volume above 0.1 ton per year. Even when the solubility is measured there are still some problems. The solubility of cations and anions is strongly dependent on the chemical composition of the natural water, groundwater or soil pore water. Anionic surfactants can precipitate with calcium ions in hard river water (Zhu et al. 1998). When acids or bases are dissolved in water for the experimental determination of the solubility, these compounds will strongly affect the pH of the water. The pH of the water phase has a strong influence on the solubility. The solubility of these compounds at extremely high or low pH values will therefore have little predictive value for their solubility under natural conditions in water.

2.3 Problems with vapor pressure and the Henry coefficient

The boiling point, vapor pressure and melting point are physical constants which describe the tendency of the molecules of a chemical to stay together. Charged molecules often precipitate in crystal lattices which firmly hold the positively and negatively charged molecules by electrostatic interactions. Therefore many of these compounds have a low vapor pressure, a high boiling point and a high melting point. The organic acids and bases however, can be converted into uncharged molecules at a specific pH value. These uncharged molecules will have a much higher vapor pressure, a lower melting point and a lower solubility compared to their charged counterparts. In analogy with the use of the effective K_{ow} , an effective Henry coefficient (H) can be calculated for organic acids and bases which is strongly dependent on the environmental pH. This was earlier described for chlorophenols (Slooff et al. 1991). H might be calculated using:

$$H = H_n * F + H_i (1-F)$$

with F is the fraction undissociated $F = 1/(1+10^{(pH-pK_a)})$

H_n = The Henry coefficient of the neutral molecule

H_i = The Henry coefficient of the ion.

The default estimate of the Henry coefficient of the ion might be 10^{-9} . This is almost the lowest Henry coefficient that EUSES will accept (see EUSES appendix II Page 5).

3. Environmental distribution

This chapter follows the EUSES and USES 2.0 documentation and describes in which chapters problems can occur with difficult substances.

3.1 Adsorption to aerosol particles

The fraction of the chemical associated with aerosol particles will not be correctly described by the Junge equation for charged molecules (see EUSES chapter Adsorption to aerosol particles p.III-20). Specific measurements of the fraction sorbed to aerosol particles are needed. When no data are available this fraction can be set to 1 for charged molecules because these molecules are bound tightly to particles by electrostatic interactions.

3.2 Partitioning coefficients between water and soil, sediment or biota

Water molecules have a dipole moment which give them the tendency to surround charged molecules. Therefore most charged molecules will have a very low Henry coefficient and will not evaporate from water. A low default Henry coefficient (like 10^{-9} see EUSES appendix II Page 5) will have to be set for these molecules (See EUSES p. III - 21). From this Henry coefficient the dimensionless Henry coefficient $K_{air-water}$ can be calculated. The solid phase/air partitioning coefficient $K_{soil-air}$ can be calculated from the solid phase/water coefficient ($K_{soil-water}$) which has to be determined experimentally and the estimated $K_{air-water}$ using:

$$K_{soil-air} = K_{soil-water} / K_{air-water}$$

For charged molecules often no K_{ow} is available. Even a correctly measured K_{ow} of a charged molecule or surfactant should not be entered in USES because it will not give correct estimations. The bioaccumulation of charged molecules is not governed by the K_{ow} . When an experimentally determined K_{ow} of compounds like Cs, Cd or Hg is entered in USES the strong bioaccumulation and sorption of these compounds (Slooff et al. 1995) will not be predicted. It is difficult to predict the sorption of charged molecules to soil. Cations tend to sorb to clay particles whereas anions can be mobile in soil.

The K_{ow} of surfactants is not easily determined experimentally. Surfactants with long hydrophobic alkyl chains show a higher bioconcentration factor and exhibit higher toxicity (Tolls 1998). This correlation between toxicity and hydrophobicity is only valid in a certain class of surfactants. Generally, it is observed that surfactant toxicity increases from anionics via nonionics to cationics (Versteeg et al. 1997). Therefore the hydrophobicity of a surfactant cannot be used to predict toxicity in general because it depends on the specific class of surfactant.

When no experimental data on bioaccumulation of a charged molecule are available, then it is not possible to predict bioaccumulation. The default biota to solid phase accumulation factor might be set to something like a 100 kg soil per kg biota dry weight assuming a moderately strong bioaccumulation of charged molecules. The default biota to water accumulation factor might be set to something like 1 million liter per kg biota dry weight. These latter two estimates are just a first crude guess of the author of this report and should be replaced by better estimates.

When a single partitioning coefficient of a charged molecule is available all solid phase/water partitioning coefficients can be estimated to be equal to this value. When the biota to water accumulation factor and the partitioning coefficient between water and soil are known, the biota to soil or sediment accumulation factor can be calculated according to:

$$K_{\text{biota-soil}} = K_{\text{biota-water}} / K_{\text{soil-water}}$$

This also means that the default soil/water or sediment/water partitioning coefficient is $1000\ 000 / 100 = 10,000$ liter per kg soil or sediment. This is the ratio of the above two very crude guesses of the author and should be replaced by better estimates. A literature search on the partitioning coefficients and the accumulation factors of the different classes of charged molecules, surfactants and organic acids or bases will make it possible to derive much better default values than the ones proposed in this paragraph. When sufficient data are available, safety factors should be derived from the probability distribution of the available data (Chapman, Fairbrother, and Brown 1998).

3.3 Degradation and transformation of inorganic compounds

Inorganic compounds cannot be mineralised but (bio) transformation will often occur. In a sewage treatment plant and in soil and sediment reduction, oxidation, complexation or precipitation of inorganic compounds have a profound influence on the fate of inorganic compounds in the environment. There are no general rules which describe the fate of inorganic compounds in a sewage-treatment plant. When no information is available it should be assumed that inorganic compounds are not removed in a sewage-treatment plant and are not degraded in soil, water or sediment. Risk assessment with USES can be improved when these processes are accounted for by manually incorporating experimentally determined transformation rates, precipitation constants and sorption constants into the program. When the solids-water partition coefficients in sewage sludge are not available they can be estimated from the sediment-water partition coefficient or the soil-water partition coefficient.

3.4 Calculation of the dissolved concentration in surface water after a pesticide application

In USES 2.0 the sorption of pesticides is calculated using the K_{om} which is derived from the K_{ow} . This can give problems when the applied pesticide is not a neutral organic compound. When a fraction of a pesticide spray reaches a ditch the concentration in the water can be decreased by sorption of the pesticide to the suspended matter in the water (See USES 2.0 p. III -- 22). In formula P. -- 16:

$$F_{diss_{ditch}} = 1 / (1 + F_{om_{ditch}} * K_{om} * SUSP_{ditch})$$

the sorption constant of the compound to the suspended matter in the ditch water has to be used instead of $F_{om_{ditch}} * K_{om}$. The sorption constant of the compound to soil or sediment might be used as a surrogate.

3.5 Purification of drinking water

In EUSES page III-72 the purification factor of drinking water is calculated using the K_{ow} . This estimation is only valid for neutral organic compounds. For the other classes of compounds the limits of $\log K_{ow} = 4$ and $\log K_{ow} = 5$ can be recalculated to a soil-water partitioning coefficient K_p in m^3/kg using the formula described in the EUSES documentation page III-21.

$$K_p = \frac{F_{oc} * 1.26 * K_{ow}^{0.81}}{1000}$$

the fraction organic carbon is estimated to be $F_{oc} = 0.05$

Filling in $K_{ow} = 10^4$ yields $K_p = 0.1 m^3/kg$

and filling in $K_{ow} = 10^5$ yields $K_p = 0.7 m^3/kg$

So for difficult substances the limits in the purification factor are 0.1 and 0.7 m^3/kg for the K_p instead of 4 and 5 for the $\log K_{ow}$.

4. Effects assessment

4.1 Toxicity data

Toxicity data can only be interpreted with the physicochemical properties of the chemical in mind. During aquatic toxicity tests many problems with precipitation, sorption to the vessel, evaporation and complexation with media components can occur. Surfactants even have some extra problems. The toxicity of surfactants has to be tested below their critical micelle concentration (Sherrard et al. 1996). When the surfactant concentration increases above the critical micelle concentration the toxicity does not increase (Sherrard et al. 1996).

The toxicity of charged compounds like the anion pentachlorophenolate and the cation Zn^{2+} is dependent on the pH and the concentrations of buffers and salts in the test medium (Van Beelen and Fleuren Kemilä 1997). The interpretation of toxicity tests with difficult compounds like surfactants, anions and cations is not simple. For these substances the influence of environmental conditions like pH, dissolved organic carbon, and salts on toxicity can be very significant. The toxicity tests which are more representative for the natural situation in surface water, sediments and soils should be preferred.

4.2 Micro-organisms effects data

The toxic effect of a chemical on the micro-organisms in a sewage treatment plant is often reported as $EC50_{slurry}$ in g chemical/liter slurry. USES recognizes the input in kg chemical/m³ aqueous phase of the slurry. The effect of a chemical on a microorganism is dependent on the internal concentration of the chemical in the microorganism. This internal concentration is in equilibrium with the external concentration in the aqueous phase in the slurry (Van Beelen and Fleuren Kemilä 1997). The equilibrium between the concentration in the aqueous and in the solid phase of the slurry is determined by the sorption coefficient K_p . At the $EC50_{slurry}$ the concentration in the aqueous phase is C_w and the concentration in the solid phase is C_s . The total amount of water in the slurry is W and the total amount of solid is S . A mass balance equation gives:

$$EC50_{slurry} = C_w * W + C_s * S$$

$$K_p = C_s / C_w$$

This means that:

$$C_w = EC50_{slurry} / (W + K_p * S)$$

At the overall concentration of the chemical $EC50_{slurry}$ the concentration in the aqueous phase $C_w = EC50_{micro}$

When one litre of a not very thick slurry is used $W = 1$

The EC50_{micro} in the aqueous phase can be estimated from the total EC50_{slurry} using the sorption coefficient Kp in m³/kg and a mass balance equation in a slurry with S g solid /l sediment.

$$EC50_{micro} = EC50_{slurry} / (1 + (Kp * S))$$

4.3 Terrestrial compartment

When in the EUSES documentation page III-107 the PEC soil is calculated via the equilibrium partitioning method an extra safety factor of 10 is used for substances with a log Kow > 5. This safety factor accounts for the uptake of soil by organisms. For charged molecules no Kow is given and the Kp can be used as an alternative.

A log Kow = 5 corresponds with a Kp of 0.7 m³/kg soil.

This means that a safety factor of 10 must be used for a PEC local soil which is calculated from aquatic data using the equilibrium partitioning method for charged chemicals with a Kp > 0.7 m³/kg.

5. The approach for different classes of compounds

Table 1 The approach for different classes of compounds

§		1	2	3	4	5	6	7	8	9	10
2.1	effective Kow useful	-	-	-	-	-	+	+	-	+	+
2.2	pH and salts dependent solubility	+	+	+	+	+	+	+	+	-	-
2.3	effective Henry coefficient	-	-	-	-	-	+	+	-	+	+
3.1	tightly bound to aerosol	+	+	+	+	+	-	-	+	-	-
3.2	default Henry and Kp	+	+	+	+	+	-	-	+	-	-
3.3	mineralisation possible	-	-	-	+	+	+	+	+	+	+
4.1	toxicity pH and salts dependent	+	+	+	+	+	+	+	+	-	-

Table 1 gives an overview of the different approaches that might be used for different classes of compounds. The numbers on the upper row are numbers of the different classes of chemicals which are described in paragraph 1.1. The numbers 1-3 are the inorganic compounds, 4 and 5 are the organic ions, 6 and 7 are organic acids and bases, 8 are surfactants and 9 and 10 are neutral organic compounds. The first column gives the paragraph numbers of this report where the different approaches are described. A + indicates that the approach mentioned in column 2 is suitable for a class of compounds and a - indicates that the approach is not suitable. The row marked 2.2 for example, indicates that the solubility of neutral organic compounds (class 9 and 10) is not very dependent on the pH and the presence of salts. The rows marked 2.1 and 2.3 indicate that an effective Kow or Henry coefficient can be used for organic acids and bases (class 6 and 7). For the neutral organic compounds (class 9 and 10) the normal Kow and Henry coefficient can be used. Therefore these are also marked with a + at the rows marked 2.1 and 2.3. The compounds marked with a - at row 2.3 show hardly any evaporation from the water phase. In the air these compounds are tightly bound to aerosol particles. Therefore these compounds are marked with a + and the row 3.1. The use of the Kow and the vapor pressure from the base data set for notified substances make it possible to calculate partitioning for organic acids and bases and for neutral organic compounds (class 6, 7, 9 and 10). For the other classes of compounds, a default Henry and Kp has to be used as is indicated in row 3.2. The last row indicates that the toxicity of most classes of compounds is dependent on the presence of salts and on the pH. The toxicity of neutral organic compounds (class 9 and 10) is less dependent on the pH and the presence of salts.

6. Conclusions

The Uniform System for the Evaluation of Substances (USES) can be modified to accommodate inorganic compounds and organic ions and surfactants. These charged molecules show a more complex environmental behavior than neutral organic compounds. The sorption and toxicity of these compounds are often strongly dependent on the environmental conditions like the pH and the presence of counter ions.

The melting point, boiling point, vapor pressure and the octanol/water partitioning coefficient are required by the EC council regulation 793/93 in the base set but not useful for the risk evaluation of many charged molecules. The measurement of the above physical properties is very difficult and sometimes impossible for a number of charged molecules.

The absence of information on the partitioning and bioaccumulation of charged molecules in the base data set must lead to rather extreme worst case estimates both for the predicted environmental concentration and the predicted no effect concentration. When more data on partitioning and bioaccumulation are available a more realistic risk assessment can be performed.

7. Recommendations

- The incorporation of an automatic system to calculate the charge distribution in a molecule into the USES program might automatically detect the charged molecules which give problems with the current version of USES. A feasibility study can be performed to estimate both the cost and the benefits of such change in USES.
- Methods can be developed to estimate all required partitioning and bioconcentration factors from a single partitioning coefficient of a charged molecule. A literature search might come up with a realistic worst case safety factor for certain classes of charged molecules. This study can also give information about reasonable worst case estimates when no partitioning or bioaccumulation factors are available.
- A number of QSARs for different classes of chemicals which determine whether a structural formula represents a charged molecule at a certain pH can be obtained by literature search.
- The melting point, boiling point, vapor pressure and the octanol-water partitioning coefficient might not be required in the base data set for the evaluation of charged molecules in USES. Instead the appropriate intermediate partitioning coefficients might be required.

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Mailing list

1	Directoraat-Generaal Milieubeheer, Directeur Stoffen, Veiligheid en Straling, t.a.v. dr. C. Plug
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