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SimpleTreat: a spreadsheet-based box model  
to predict the fate of xenobiotics in a  
municipal waste water treatment plant

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## SUMMARY

A non-equilibrium steady state box model is reported, that predicts the fate of new chemicals in a conventional sewage treatment plant from a minimal input data set. The model, written in an electronic spreadsheet (Lotus<sup>TM</sup> 123), requires a minimum input: some basic properties of the chemical, its emission rate and a few parameters to account for the scale and mode of operation of the plant. Compound properties necessary as input are air-water and sludge solids-water partition coefficients. If these distribution coefficients are not available but the compound is hydrophobic, default values are calculated from input data such as solubility, vapour pressure and octanol-water partition coefficient. Biodegradability data and the degree of dissociation or protonation are the required input data to account for degradation and speciation changes of the chemical in the water phase. The modelled sewage treatment installation consists of primary sedimentation and the activated sludge technique. The standard output shows the chemical's concentration in effluent and sludge. In addition the output contains the relative amounts degraded and emitted via effluent, sludge and air. The main advantage of this approach is that it provides legislators with a quick insight if a chemical will be an air, water or sludge pollutant when it is discharged into sewage works at a certain rate.

The presented model, SimpleTreat, is an application of a general purpose box modelling system, SimpleBox, which is a spreadsheet-based computational framework developed for environmental fate modelling. Several examples are given to illustrate the influence of volatility, hydrophobicity and biodegradability. Emission patterns as a function of physico-chemical properties (Henry's law constant and the octanol-water partition coefficient) are plotted for degradable and non-degradable compounds. Examples are evaluated and results are compared with measured concentrations. Predicted emissions due to sludge production and volatilization are in good agreement with reported field data.

## SAMENVATTING

In dit rapport wordt een niet-evenwichts steady state boxmodel gepresenteerd waarmee het gedrag en lot van chemicaliën in een conventionele afvalwaterzuivering (rwzi) kan worden voorspeld. Het model, geschreven in een spreadsheet format (Lotus<sup>TM</sup> 123), vereist slechts een gering aantal invoergegevens: enkele basisgegevens van de verbinding, de emissiesnelheid en drie keuzemogelijkheden waarmee de bedrijfsvoering en de schaal van de rwzi kan worden gekarakteriseerd. In principe zijn de lucht-water en de slib-water partitievoëfficiënten de enige stoffeigenschappen die vereist zijn. Indien deze partitievoëfficiënten niet beschikbaar zijn dan kan voor een hydrofobe stof een schatting gemaakt worden op basis van de oplosbaarheid, de dampspanning en de octanol-water verdelingscoëfficiënt. Eventueel zijn nog gegevens vereist m.b.t. de biologische afbreekbaarheid en de basische of zure dissociatiegraad. De gemodelleerde rwzi bestaat uit een voorbezinktank, een beluchtingstank en een nabezinktank. Standaard bevat de output de concentraties van de stof in het effluent en het geproduceerde slib. Daarnaast levert de output de hoeveelheid die afgebroken wordt en geëmitteerd via het effluent, slib en naar de lucht als percentage van de hoeveelheid die op het riool geloosd wordt. Op deze wijze wordt, slechts op basis van stoffeigenschappen, snel een indruk verkregen van de distributie van een continu op een rwzi geloosde stof over water, bodem en lucht.

Het hier beschreven model, SimpleTreat, is gebaseerd op het spreadsheet modellersysteem SimpleBox dat als rekenmodule wordt toegepast in verscheidene boxmodellen voor het schatten van blootstellingsconcentraties.

In dit rapport wordt aan de hand van gevoeligheidsanalyses de invloed van vluchtigheid, hydrofobiciteit en afbreekbaarheid van een stof op het emissiepatroon geschetst. Een aantal voorbeelden worden uitgewerkt en de resultaten worden vergeleken met veldwaarnemingen. Het blijkt dat, voor zowel afbreekbare als persistente stoffen, de emissies via slib en door vervluchtiging goed in overeenstemming zijn met gerapporteerde veldwaarnemingen.

## 1. INTRODUCTION

The Notification Order of the Chemical Substances Act, specifying the notification requirement for manufacturers and importers of so-called "new chemical substances", came into force on January 1987. At the National Institute of Public Health and Environmental Protection (RIVM) in Bilthoven, The Netherlands, methods are being developed to predict the risk for man and environment related to the use of these "new chemical substances" on the basis of data to be provided by the notifier. Currently, an automated risk assessment system is in use in which several tools, e.g. emission models, environmental fate models and extrapolation methods, are combined. In this standard risk assessment, a box model ("Mackay level III") is applied for the steady state emission of chemical substances from a municipal waste water treatment plant (WWTP).

Originally, this WWTP emission model (SimpleTreat 1.0) was written in a spreadsheet format. Later the programme was translated into a computer language in order to form part of the risk assessment system. Together with other spreadsheet-based box models, developed in our institute, SimpleTreat 1.0 has been adopted in 1989 in the OECD compendium of environmental exposure assessment methods for chemicals. Until now, however, neither comprehensive description nor a user manual of SimpleTreat 1.0 has been published.

This report represents a technical description of an updated spreadsheet version of the WWTP emission model, i.e. SimpleTreat 2.0. As such it may serve as useful documentation for updating the risk assessment system. The main differences with respect to the former version are the evaluation of the first order biodegradation rate constant for "readily biodegradable" compounds and the estimation of partition coefficients which has been extended to ionizable hydrophobic chemicals such as weak organic acids and bases. The assumptions upon which the model relies are described in Chapters 3 and how it works is outlined in Chapter 4. Examples of sensitivity analysis in Chapter 5 demonstrate e.g. the relative importance of biodegradability with respect to other removal mechanisms in a WWTP. In Chapter 6 some additional validation results are given. The Annex contains a user manual and a few examples how to apply SimpleTreat 2.0.

## 2. OBJECTIVE

A useful module in a risk assessment system would be a simple procedure to predict the emission of a chemical to the compartments air, surface water and soil (via sludge) from a domestic waste water treatment plant. It is even a prerequisite if exposure scenario's are to be assessed in densely populated industrial area's, where emission is high but usually regulated and the major part of waste water is collected in sewage works. In these area's a xenobiotic compound is likely to enter the sewage system before it reaches the environment. On this route the municipal waste water treatment plant largely determines the relative amounts degraded and distributed over sludge, water and air.

Ideally, only a few base-set data of a chemical would be necessary to predict its relative emission pattern and in case that the emission scenario (loading rate of the chemical and the size of the WWTP) is also known, the concentrations in sludge and effluent. For a general applicability, required input parameters are the sludge solids-water partition coefficient  $K_p$ , the air-water partition coefficient  $K_H$  and the degradation rate constant  $k_{deg}$ . Unfortunately, these parameters do not form part of the base-set data. Although "ready biodegradability" test methods (1) have a high predictive value to a municipal waste water treatment plant (WWTP), it only predicts that the concentration in the effluent is less than 10% with respect to untreated waste water, even when biodegradation is the only possible removal mechanism.

For the important class of hydrophobic chemicals, however, base-set data can be used as model input. Partition coefficients can be evaluated from data as to solubility, vapour pressure, octanol-water partition coefficient ( $K_{ow}$ ) and acid (basic) dissociation constant ( $K_{a(b)}$ ).

A box model seems appropriate to calculate the fate of a chemical in a WWTP. In a multicompartment system a chemical is subject to reaction, media flow and interphase transport, presumably under steady state, non-equilibrium conditions (also known as "Mackay level III"). Along these lines, a WWTP is considered to be composed of three separate basins; each basin represents a specific operating step in a WWTP and consists of several well mixed compartments (boxes) of different media: water, suspended solids or settled solids. The operation of a WWTP, bearing a

close resemblance to a continuous flow reactor where complete mixing occurs, justifies the application of the box modelling concept. As such the model may simplify the operation of a WWTP, however, it satisfactorily accounts for the most relevant processes which determine the fate of a chemical involved in primary sedimentation and the activated sludge technique. Therefore the most relevant compartments and media flows should be included in the model, assuming linear degradation and exchange processes. Thus no attempt is made to fully employ all possible process descriptions or the numerous interactions between the chemical and its engineered environment.



### 3. SYSTEM DEFINITION AND MODELLING ASSUMPTIONS

#### 3.1 Operation parameters

Primary sedimentation, aeration and solids liquid separation are thought to occur in separate basins with a fixed depth of 4, 3 and 3 m, respectively. The area of each basin is proportional to the number of inhabitants of which the waste water is treated. The operation of the installation is simulated with continuous flows of water, suspended solids and settled sludge (see Fig 1a). A separate system of sewage is assumed and therefore no dilution with infiltration water and rainwater occurs. As a consequence the model WWTP receives only 150 L waste water per inhabitant daily. Raw sewage, considered as a well mixed slurry with a composition given in Table 1, enters the primary settler with a flow (Q) proportional to the number of inhabitants.

Fig 1b represents the net daily sludge flow in a municipal waste water treatment plant serving 100,000 inhabitants. This scheme is evaluated from the following assumptions:

- Approximately 2/3 of the solids in raw sewage settles in the primary sedimentation tank and leaves the system as primary sludge.
- In the solids liquid separator, settled sludge is the difference between the inflow of suspended particles from the aeration tank and the outflow via effluent. Part of the settled sludge is wasted leaving the system as excess or surplus sludge at a rate of 35.5 g/d per inhabitant. This figure is typical for an activated sludge reactor operating at a sludge loading rate, k (also known as the food to mass ratio F/M), between 0.2 and 2 kg BOD per m<sup>3</sup> aeration volume per day per kg dry weight activated sludge and a sludge retention time (SRT) between 0.5 and 6 days.
- The difference between the amounts of settled activated sludge and wasted sludge is recycled (return) sludge and is resuspended in the aeration tank.
- The net sludge growth in the aerator is the difference between the actual sludge growth and the rate of degradation of suspended solids which is present in settled sewage. The net sludge growth is calculated as the difference between the flow of activated sludge out of the aerator and the inflows of suspended solids in settled sewage and recycled sludge.

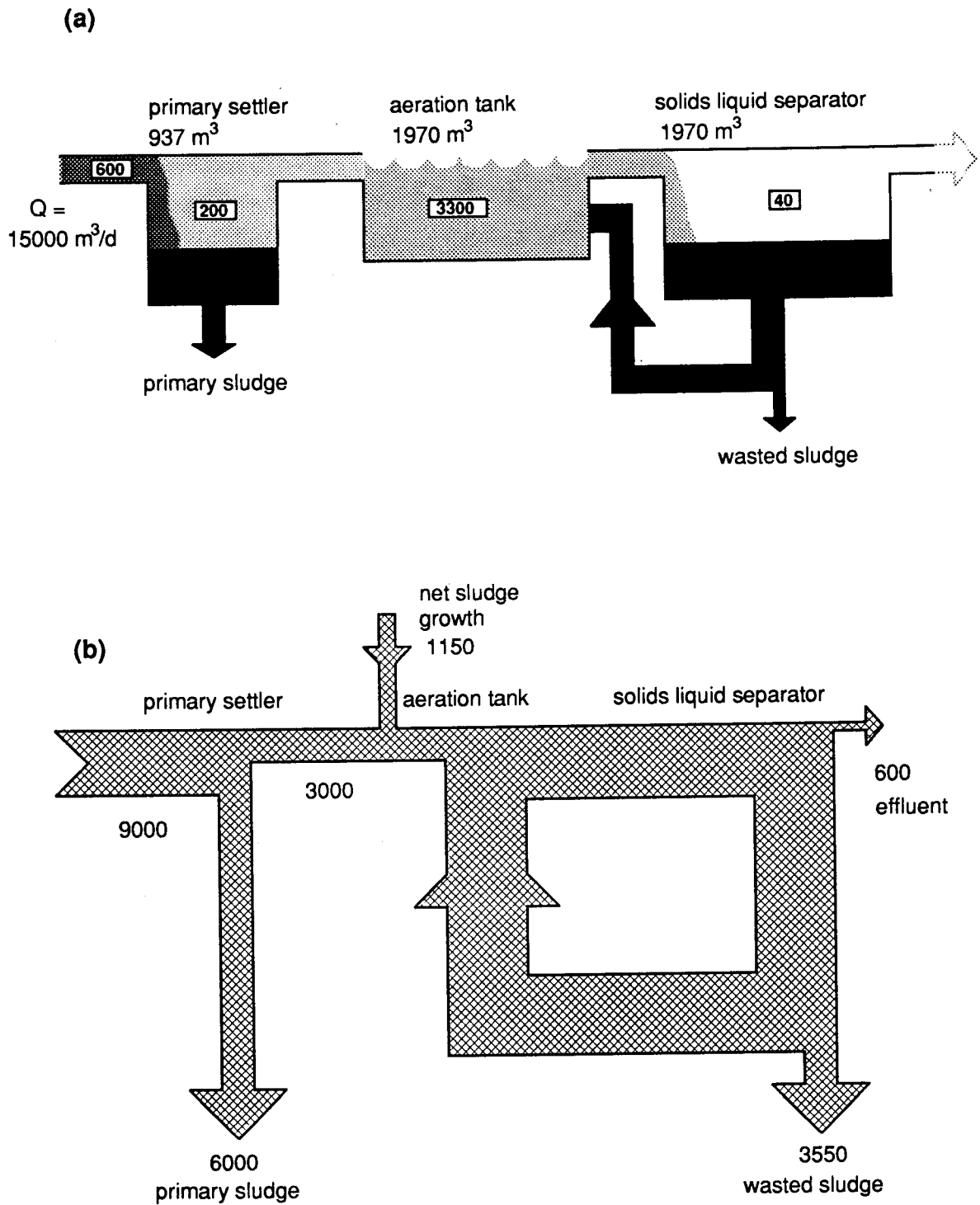


Fig 1. (a) Schematic representation of a municipal waste water treatment plant, equipped with a primary settling tank, treating the waste water of 100,000 inhabitants. Inserted numbers indicate steady state concentrations of suspended solids (mg/L dry matter).  
(b) Assumed daily sludge flow (kg dry matter/d).

According to the size of the plant and the assumed densities of the solids (Table 2), all flows of dry solids are converted into volume flow rates ( $\text{m}^3/\text{s}$ ). The operational conditions, given in Table 3, pertain to a conventional activated sludge reactor operating at an intermediate sludge loading rate while serving 100,000 inhabitants.

### 3.2 Intercompartment mass transfer

#### 3.2.1 Equilibrium partitioning

Partition coefficients for air-water ( $K_H$ ) and sludge solids-water ( $K_p$ ) are input parameters unless the chemical is hydrophobic. In that case default values are generated from base-set data such as solubility, vapour pressure and octanol-water partition coefficients.

$K_H$  for hydrophobic compounds. The ratio of equilibrium concentrations in the gas phase ( $C_{\text{air}}$ ) and the water phase ( $C_w$ ) is given by :

$$K_H = C_{\text{air}}/C_w = H/RT \quad (1)$$

in which R is the gas constant and T is the absolute temperature. If solute speciation changes (due to acid dissociation, protonation etc.) are neglected, it is presumed that Henry's law constant, H, can be estimated from the ratio of the vapour pressure and the solubility of a chemical.

$K_p$  for hydrophobic compounds. It has been determined by Karickhoff et al. (3) that, if the pollutant concentration is below  $10^{-5}$  mol/L or less than one half of its water solubility, sorption isotherms are linear for natural aquatic systems. It has also been shown that concentrations in sediments are positively correlated to the fraction of organic carbon ( $f_{\text{oc}}$ ) of the sorbent. However, waste water usually contains higher amounts of pollutants than the water column of natural aquatic systems. Still a "low-loading" isotherm linearity is assumed since the high content of suspended solids in raw and settled sewage and in particular in activated sludge can accommodate a higher amount of pollutant per volume waste water. Moreover, the organic carbon content of sludge is at least ten times higher than in

particulate matter of natural aquatic systems. Thus the volume ratio organic matrix/water is at least two orders of magnitude greater than in surface water. Therefore, the sorbed concentration ( $X_s$  mg/kg dry matter) is proportional to the dissolved concentration ( $C_w$  mg/L) according to  $X_s = K_p C_w$ , where  $K_p$  (L/kg) is the linear adsorption coefficient or the sludge solids-water partition coefficient.  $K_p$  is equal to the product of  $f_{oc}$  and  $K_{oc}$ , which is the sorption coefficient normalized to the fraction of organic carbon of the sorbent.  $K_{oc}$  has been shown to be largely independent of the properties of the different types of suspended or settled particles (3, 4, 5). Many different empirically derived relationships between  $K_{oc}$  and  $K_{ow}$  have been published for different classes of chemicals (6). For general purposes, without prior knowledge of the structure of the chemical, we prefer to use the formula  $K_{oc} = 0.5 K_{ow}$  since the factor 0.5 is in between previously reported values ranging from 0.4 to 0.6. Thus the partition coefficient is estimated from a compound parameter,  $K_{ow}$ , and the fraction of organic carbon of the sludge:

$$K_p = 0.5 f_{oc} K_{ow} \quad (2)$$

$K_H$  and  $K_p$  for hydrophobic ionizable compounds. For some organic chemicals the dominant sorption mechanism depends on the degree of their ionization (i.e. the ratio of neutral species to the total species). Such compounds include weak organic bases such as amines and weak organic acids such as carboxylic acids and phenols. The aforementioned relationships pertain only to the neutral chemical. However, a relation between the concentration in the nonaqueous phase (neutral species) in equilibrium with the total concentration in water (neutral and ionized species) would be of more practical use. In order to obtain the overall partition coefficients, the ionization constants  $K_a$  or  $K_b$  and the pH must be known. Therefore, if  $[H^+] = 10^{-7}$  mol/L, the total concentration ( $C_T$ ), being the sum of the neutral and ionized species, is written as:

$$C_T = [\text{neutral species}](1 + K_{a,b}/10^{-7}) \quad (3)$$

Equilibrium partitioning between air and water is evaluated as the ratio of the concentration of the neutral (authentic) form in the gas phase and the *total* concentration  $C_T$  in the aqueous phase (pH=7):

$$K_H = C_{\text{air}}/C_T = (H/RT)/(1 + K_{a,b}/10^{-7}) \quad (4)$$

where  $K_{a,b}$  is either the acid or base dissociation constant if the neutral species is a weak acid or a base, respectively. Assuming that  $K_{ow}$  pertains to the neutral species, combination of equations (2) and (3) gives an expression for the *overall* solids-water partition coefficient:

$$K_p = 0.5 f_{oc} K_{ow}/(1 + K_{a,b}/10^{-7}) \quad (5)$$

Equation (5) neglects sorption of ionized species which may occur upon formation of a neutral ion-pair. Lee et al. (7) recently described the distribution of pentachlorophenol, accounting for sorption of both the neutral and ionized forms. For the present study, however, it is assumed that sorption of the ionized species can be neglected.

### 3.2.2 Non-equilibrium exchange

*Irreversible transfer* plays a dominant role as a "transport sink" in the system and strongly affects the fate of a chemical in a waste water treatment plant. Water and suspended solids continuously move from one basin to another or out of the system, carrying the chemical in each phase with it. In the two sedimentation basins, continuous settling is responsible for irreversible transport of the pollutant from suspended solids to the settled sludge. Irreversible transfer also occurs through recycled sludge, carrying the chemical from settled activated sludge in the solids liquid separator into the suspended solids phase in the aeration tank.

*Reversible transfer* or diffusive transfer between two adjacent phases is driven by the non-equilibrium concentrations. The transfer rate is linearly related to the deviation from the equilibrium concentration of the chemical. It is presumed that reversible transfer of an organic pollutant

to air, suspended and settled solids can only take place from the aqueous phase.

In the two sedimentation basins, air-water transfer is simulated with a two layer model. This approach, applied by Liss and Slater (8) and extended by Mackay and Leinonen (9), leads to an expression for the flux in terms of mass transfer coefficients (see Table 4) for air ( $K_{air}$ ) and water ( $K_{water}$ ).

Air-water exchange of volatile organic substances in the aeration tank is dependent on the mode of aeration. The overall transfer rate constant during surface aeration,  $k_s$ , is obtained from the assumption that it is proportional to the liquid phase transfer rate constant of oxygen,  $K_L a$ :

$$k_s = 0.6 K_L a \quad (6)$$

This has been shown valid if  $H$  of a chemical exceeds 250 Pa m<sup>3</sup>/mol, i.e. when the liquid layer resistance controls the rate of interface mass transfer. The proportionality factor accounts for the ratio of liquid phase diffusivity of the volatile compound and oxygen. Roberts et al. (10) have shown that this factor is rather constant (0.5-0.7) for chlorinated hydrocarbons with one or two carbon atoms. The overall mass transfer rate constant for oxygen,  $K_L a$ , is estimated from the amount of oxygen required per m<sup>3</sup> waste water treated ( $R_o$ ), the hydraulic retention time  $\tau_a (= V_a/Q)$  and  $\Delta O_2$ , which is the difference between the oxygen saturation and the actual  $O_2$  concentration in the aeration tank (see Table 3). From mass balance considerations Roberts et al. (10) derived that

$$K_L a = R_o / (\tau_a \cdot \Delta O_2) \quad (7)$$

If bubble or diffuse aeration is applied the overall transfer rate constant,  $k_b$ , is obtained from a relationship reported by Blackburn et al. (11):

$$k_b = 0.0005 G_a V_a^{-1} H^{1.045} \quad (8)$$

where  $G_a$  is the air flow rate which is assumed to be 7±2 times the waste water flow rate  $Q$ , depending on the oxygen requirement.

It is assumed that water-suspended solids transfer rates can be expressed in terms of half-lives for uptake or clearance listed in Table 4.

### 3.3 Degradation

It is postulated that degradation may occur in the water phase of the aeration tank exclusively according to first order kinetics. It is assumed that the degradation rate constant can be estimated from positive results of some of established biodegradability test methods. It is generally accepted that a compound that has passed one of the stringent OECD tests for "ready biodegradability" (1) will also be mineralized in a WWTP, even if biodegradation is the only possible removal mechanism. Although according to the OECD test hierarchy (1) these tests are not meant to simulate biodegradation in a WWTP, there is a wide consensus on its predictive value to a WWTP. Thus if other removal processes are negligible, mineralization alone is responsible for at least 75% elimination, depending on the sludge loading rate of the aeration tank (see Table 5).

The first order degradation rate constant ( $k_{deg}$ ) for "readily biodegradable" compounds is derived from a simple mass balance calculation.  $C_i$  and  $C_e$  are the concentrations in the water phase of the inflow and the flow out of the aeration tank, respectively. Steady state conditions are achieved if the input ( $QC_i$ ) is balanced by the output ( $QC_e$ ) and the mass per time degraded ( $k_{deg} C_e V_a$ ):

$$QC_i = QC_e + k_{deg} C_e V_a \quad (9)$$

This equation can be rewritten as:

$$C_i/C_e = 1 + k_{deg} \tau_a \quad (10)$$

In Table 5 three operating regimes of an activated sludge reactor are related to assumed elimination efficiencies for non-sorbing, non-volatile compounds. If the ratio of  $C_i$  and  $C_e$  is related to the retention time,  $\tau$ , according to Table 5, it follows from equation (10) that the first order rate constant for mineralization during the aeration process,  $k_{deg}$ , is equal to 3/hr.

#### 4. THE FATE OF A CHEMICAL IN A WWTP REPRESENTED BY A NINE BOX MODEL

##### 4.1 Transport and transformation

According to these assumptions, all processes affecting the fate of a chemical in each particular phase in each basin of a WWTP can be included schematically in a nine box model (Fig 2). Box 1 represents the air compartment above the WWTP and has a volume equal to the sum of the area's of the three basins multiplied by a presumed height of 4 m. Wind advection is calculated from the assumed wind speed (3 m/s), the total surface of the plant and the height of box 1. The primary settler consists of box 2 (water), 3 (suspended solids) and 4 (settled solids). The aeration tank contains mixed liquor of water (5) and suspended particulate matter (6). The solids liquid separator contains three compartments: water (7), a relatively small volume of suspended solids (8) and settled activated sludge (9). Raw sewage is considered as an equilibrated two phase system transporting the pollutant into box 2 and 3. The fraction of the chemical sorbed onto the particulate phase of raw sewage is obtained from equation (2):

$$\text{fraction sorbed} = R K_p / (R K_p + 1) \quad (11)$$

where  $R$  is the *total* concentration of solids in raw sewage in kg/L (see Table 1). The chemical concentration in each phase of the raw waste water slurry,  $C(\text{in},2)$  and  $C(\text{in},3)$ , is calculated from discharge data, the size of the plant and equation (11).

Irreversible or advective transport is represented by an open arrow whereas reversible transfer or diffusive (dispersive) exchange is indicated by a two-headed solid arrow. Degradation as a disappearance mechanism exclusively occurs in box 5 and is presented by a curved open arrow pointing out of the system.



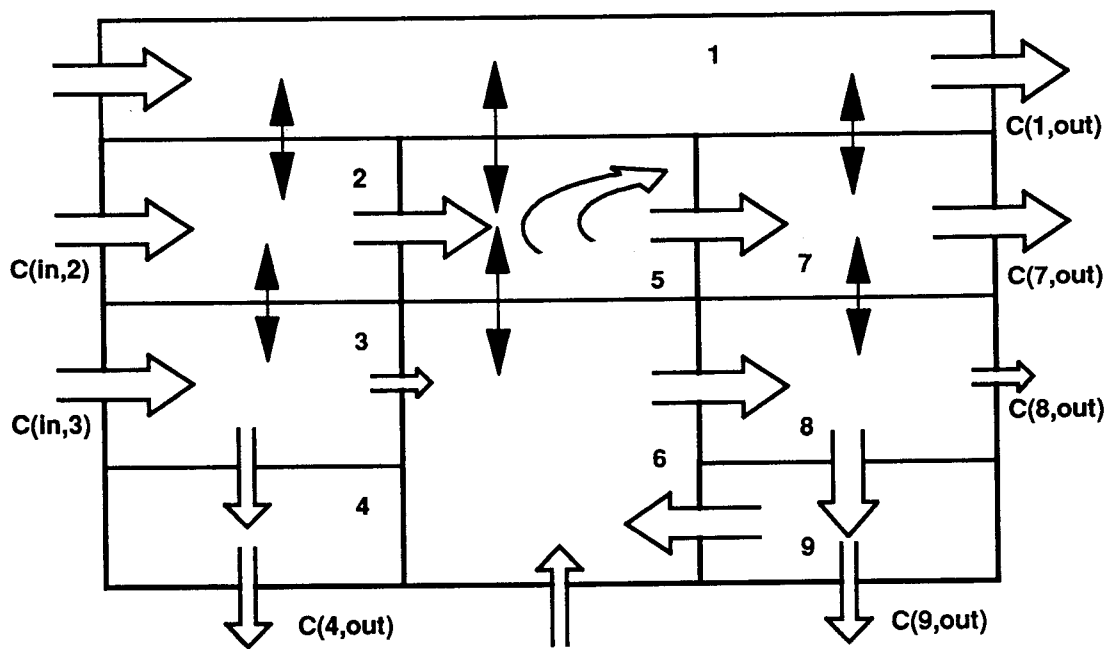


Fig 2. Steady state box model representation of the fate of a chemical in a municipal waste water treatment plant.

#### 4.2 Standard input for SimpleBox

In order to provide the general-purpose box modelling system SimpleBox (2) with standard input, the volume of each box is evaluated ( $\text{m}^3$ ) from the chosen scale of the plant and system definition. In SimpleBox mass transfer ( $\text{mol/s}$ ) between two boxes is expressed as the product of a "media volume flow rate" ( $\text{m}^3/\text{s}$ ) and the concentration ( $\text{mol}/\text{m}^3$ ) in the source box. This "media volume flow rate" can either represent an actual advective flow (irreversible exchange, open arrows) or dispersion (reversible exchange, solid arrows). These are the coefficients of the unknown steady state concentrations in all boxes which are necessary to perform a multiple mass balance computation. All irreversible media volume flow rates are simply evaluated from the scale and definition of the system and are denoted as  $\text{ADV}(i,j)$  in which  $i$  is the source box and  $j$  is the acceptor box. The dispersive exchange rate between two boxes is to be evaluated for both directions:  $\text{XCH}(i,j)$  and  $\text{XCH}(j,i)$ . The most straightforward way to obtain values for  $\text{XCH}(i,j)$  appears the employment of Mackay's concept of fugacity capacity  $Z_i$  ( $\text{mol}/\text{m}^3/\text{Pa}$ ) and interphase transfer coefficient  $D_{i,j}$  ( $\text{mol}/\text{Pa}/\text{s}$ ). It can easily be shown (Mackay and Patterson, 1982), that

$$\text{XCH}(i,j) = D_{i,j}/Z_i \quad (12)$$

Expressions for  $Z_i$  and  $D_{i,j}$  are given in Tables 6 and 7 (see also lit. ref. 12). The standard input, consisting of  $\text{ADV}(i,j)$ ,  $\text{XCH}(i,j)$ , 9 box volumes, two inflow concentrations of the chemical and a first order decay constant in box 5, is processed by SimpleBox in solving a steady state set of nine linear mass balance equations by means of the built-in matrix inversion routine of the Lotus<sup>TM</sup> 123 spreadsheet programme.

#### 4.3 Output

From the obtained standard output of SimpleBox, i.e. the steady state concentrations in all boxes, emission rates are obtained and converted into customized output. Emission to the receiving water is the resultant of advective flows out of box 7 and 8, i.e. the chemical dissolved and adsorbed to suspended matter in the effluent. The model output contains the

concentration in the effluent, specified as purely dissolved and associated with the suspended particles. Further output processing includes the removal rate by degradation and emission to the atmosphere. The emission rate via sludge is the sum of the advective fluxes out of box 4 and 9. The average concentration of the chemical in combined primary and wasted sludge is calculated in mg/kg dry matter.

If there is no information on the scale of the WWTP and the discharge rate of a particular chemical but only properties of the compound are available as input data, yet model calculations provide a quick insight into the distribution by a WWTP. From default values for the operation of the plant and disposal rate of the compound into the sewage system, SimpleTreat computes relative emissions to the environmental compartments.

## 5. SENSITIVITY ANALYSIS

### 5.1 Non-degradable compounds

The influence of hydrophobicity on the emission to the atmosphere is shown in Fig 3a. The relative emission to air of compounds with  $H > 10 \text{ Pa m}^3/\text{mol}$  significantly decreases if  $\log K_{ow}$  is higher than 4. The gas stripping rate constant for surface aeration is assessed using oxygen as a reference compound. Although this has been shown valid for chemicals with  $H > 250 \text{ Pa m}^3/\text{mol}$ , when mass transfer is governed by the liquid phase resistance (13,14), we assume that the expression for  $k_s$  holds for all chemicals. The surface aeration volatilization curve for non-adsorbing chemicals ( $K_{ow} = 10$  in Fig 3a) declines from 85 % at  $H = 250 \text{ Pa m}^3/\text{mol}$  (water phase resistance prevails) to about 45 % at  $H = 25 \text{ Pa m}^3/\text{mol}$  (both air and liquid phase resistance) and further to 10 % at  $H = 2.5 \text{ Pa m}^3/\text{mol}$  (air phase resistance prevails). The last figure seems rather high, however, it should be noted that a half life as short as 7.8 days (or 10 % volatilization within 28 hr) has been reported for DDT ( $H = 2.8 \text{ Pa m}^3/\text{mol}$ ) in 1 m deep natural waters which are not aerated (13). Therefore we believe that this approach does not lead to an overestimation of the water-air transfer during the aeration process.

It has been inferred by Roberts et al. (10) and Matter-Müller et al. (14) that volatilization due to surface aeration is more efficient than bubble or diffuse aeration. In Fig 3b the difference between surface and bubble aeration is shown for non-adsorbing persistent chemicals. Also this model predicts that surface aeration causes a greater transfer of organic compounds to the air than bubble aeration. The lower efficiency of the latter has been ascribed to limitations due to saturation of the gas phase in the bubbles of the exit gas (10,14).

Emission of low volatile compounds ( $H < 10 \text{ Pa m}^3/\text{mol}$ ) to water is strongly reduced if the hydrophobicity increases from  $\log K_{ow} = 3$  to 4 (see Fig 4), whereas removal due volatilization is dominant if  $\log K_{ow} < 3$  and  $H > 100 \text{ Pa m}^3/\text{mol}$ . Fig 4 also indicates that an increase of the volatility from 1 to  $100 \text{ Pa m}^3/\text{mol}$  does not dramatically affect the trend in % emission via wasted sludge if  $\log K_{ow}$  increases from 3 (<10%) to 5 (>75%).

## % EMISSION TO AIR

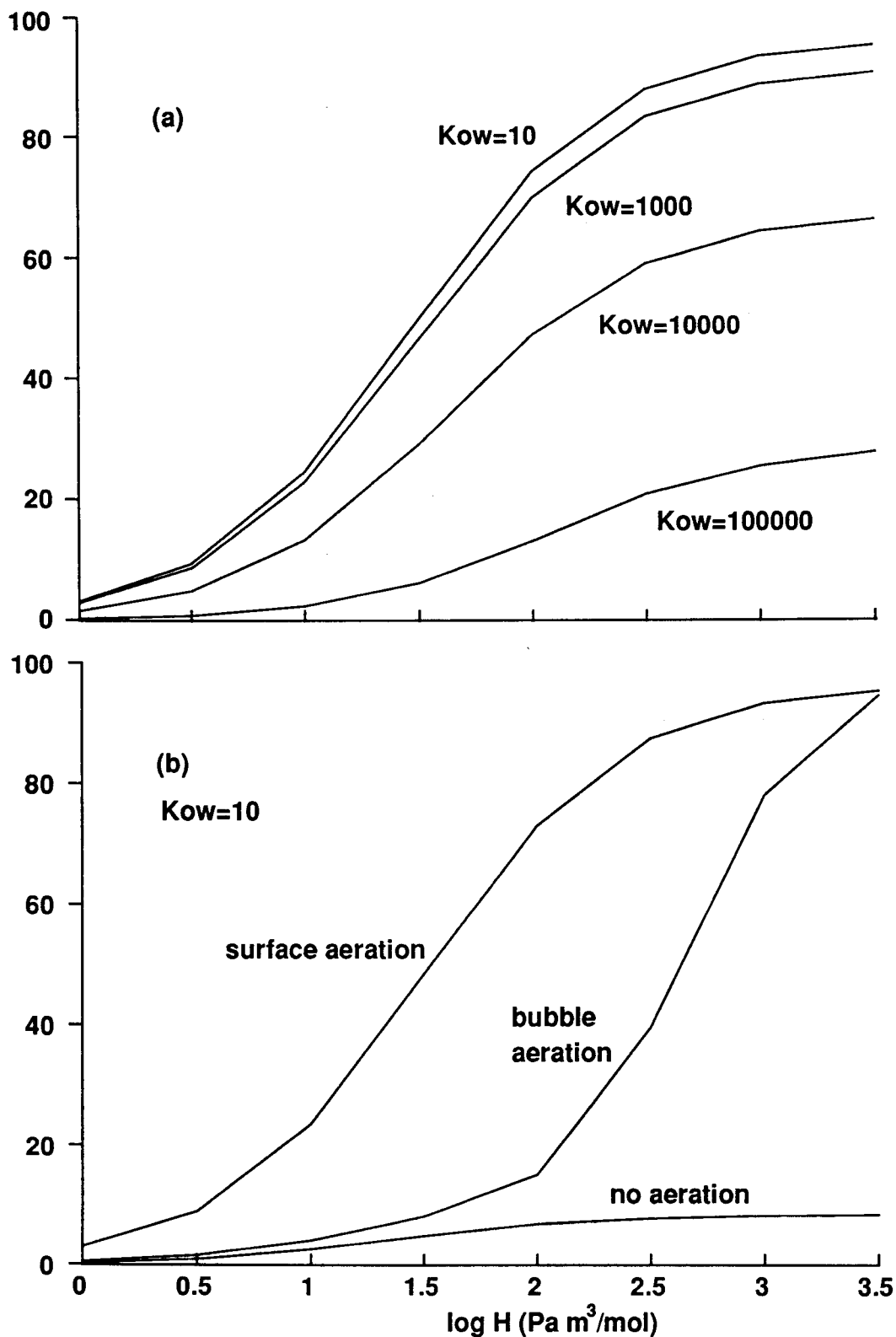


Fig 3. (a) Relative emission to the air (surface aeration) vs volatility for varying  $K_{ow}$ .  
 (b) Influence of the mode of aeration on volatilization ( $K_{ow} = 10$ ).

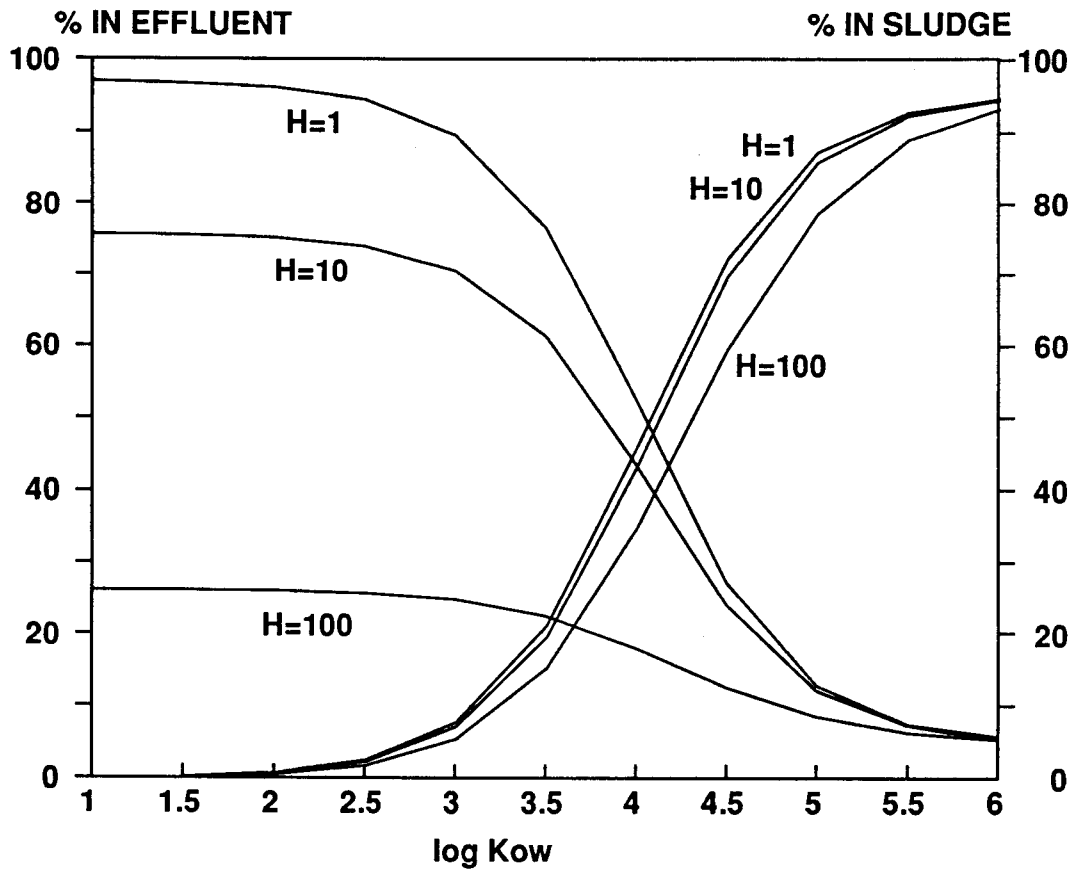


Fig 4. Relative emission to surface water (left) and sludge (right) vs  $\log K_{ow}$  for varying volatility.

## 5.2 Relative importance of biodegradation

Apparently neither Henry's law constant below  $100 \text{ Pa m}^3/\text{mol}$  nor the degradation rate constant in the range of  $0-3 \text{ h}^{-1}$  (see Fig 5) is a key parameter for the prediction of the emission via sludge production. Fig 5 shows that  $K_p$  (for hydrophobic compounds:  $K_{ow}$ ) is the most important compound property if the emission via sludge solids is to be estimated. In the model it is assumed that eventual biodegradation is first order in the compound concentration ( $k_{deg} = 3/\text{hr}$  for readily biodegradable compounds) and occurs only in the water phase of the aeration tank. In Fig 5 the removal via primary sludge and via combined primary and wasted sludge is plotted as a function of the partition coefficient for non-volatile compounds, either non-degradable or readily biodegradable. These curves pertain to a sewage treatment plant operating with an aeration time of 3 hr and a sludge retention time equal to 1.7/d. Removal due to biodegradation decreases from 70% to less than 10% if the sorption coefficient increases from  $10^3$  to  $10^5 \text{ L/kg}$ . In this range, removal via combined sludge is so strongly dependent on the sorption coefficient that biodegradation has only a minor influence on this emission route. The role of primary sedimentation is here of course the explanation as approximately 2/3 of the raw sewage solids, carrying the adsorbed chemical with it, is removed by the primary settler before any biodegradation in the aerator can take place. In the range between  $10^3$  and  $10^4 \text{ L/kg}$ , which is typical for sorption coefficients of surfactants, a considerable shift in the elimination pathways is observed. Removal due to adsorption onto combined primary sludge and wasted sludge is substantial in this range; even if a compound is readily biodegradable it accounts for 20 to 60% elimination. It should be emphasized, however, that these results only pertain to sewage works equipped with a primary sedimentation basin.

In Fig 6 it is shown that even for  $H$  values up to  $300 \text{ Pa m}^3/\text{mol}$ , removal due to microbial degradation plays a key role. This is in fair agreement with results reported by Namkung and Rittmann (15) who assigned rate constants which correspond first order rate constants equal to  $7.4 \text{ h}^{-1}$  or higher to volatile degradable compounds. However, the relative importance of biodegradation sharply diminishes if hydrophobicity increases from  $\log K_{ow} = 3$  to 5.

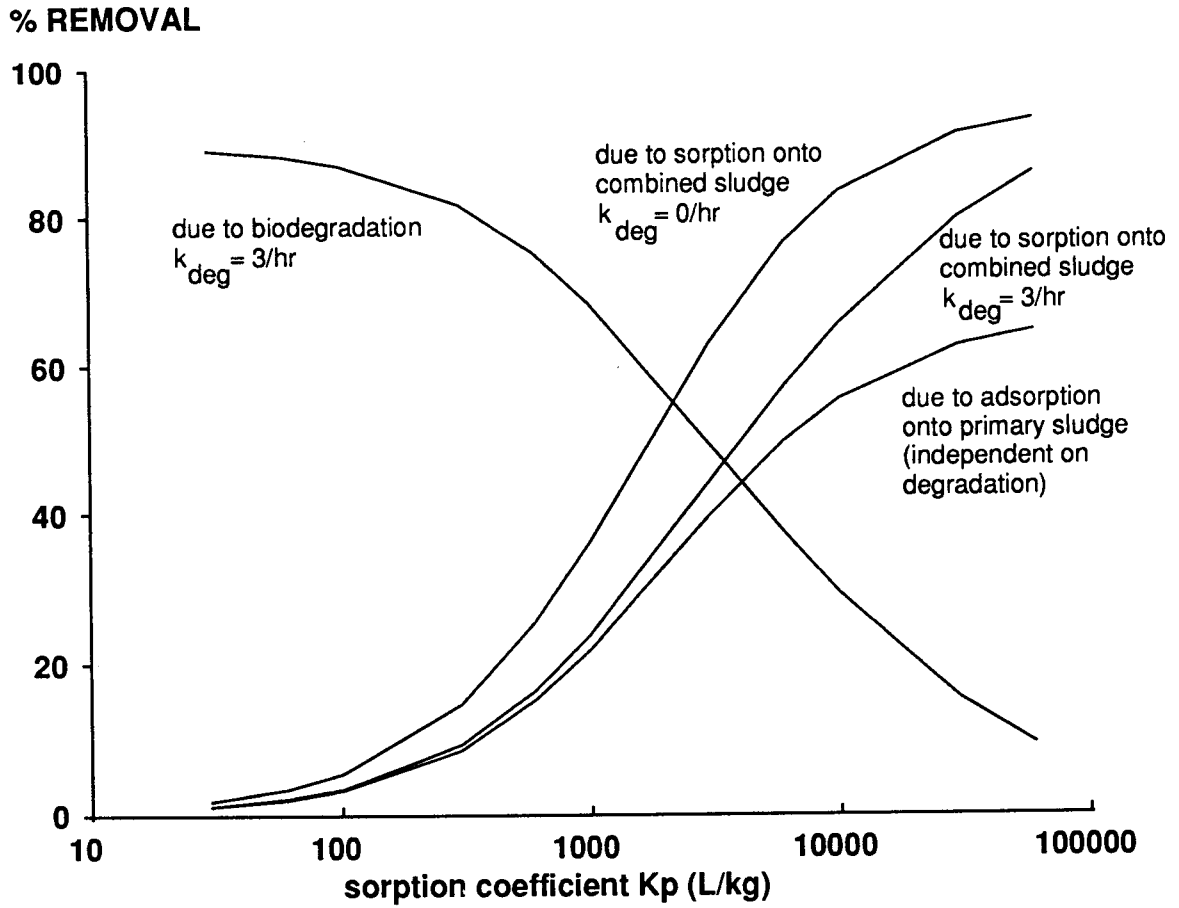


Fig 5. Increasing relative emission via sludge solids for increasing hydrophobicity both for non-degradable and biodegradable compounds.



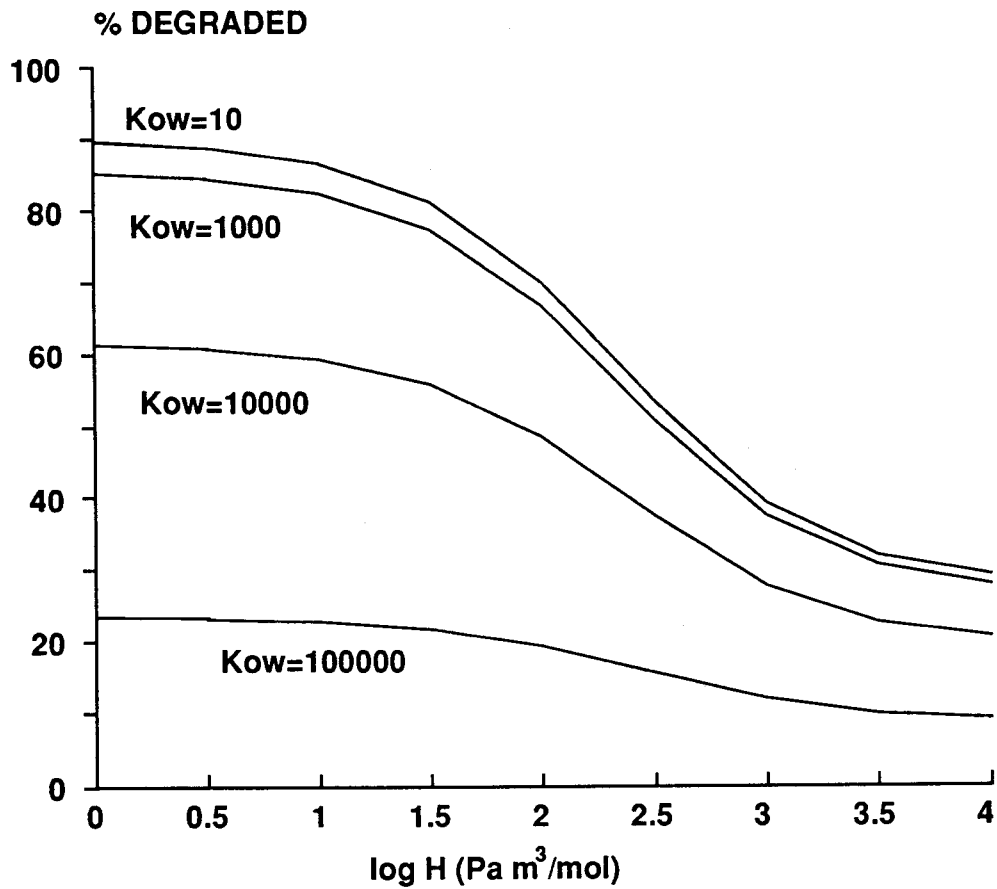


Fig 6. Relative importance of biodegradation ( $k_{deg} = 3/hr$ ) of hydrophobic compounds vs Henry's law constant for varying  $K_{ow}$  values. Mode of operation: surface aeration,  $k = 0.6 \text{ kg/kg/d}$ .

## 6. VALIDATION

De Nijs et al. (16) have validated the model by comparing measured effluent and sludge concentrations of 9 hydrophobic compounds with calculated values. The measured influent concentrations have been utilized to calculate the effluent and sludge concentrations with SimpleTreat for a medium sludge loading rate ( $k = 0.6$  kg/kg/d) and surface aeration. Calculated values are in good agreement to concentrations found in effluent being within an error interval of a factor three. Predictions for sludge differed less than a factor ten from measured concentrations, although the concentration of toluene was underestimated by one order of magnitude.

Table 8 includes assumed input data and predictions for the fate of linear alkylbenzene sulphonates (LAS) in a WWTP, compared to reported data of concentrations measured in sludge. The model predicts that about 2/3 is eliminated due to biodegradation and that the concentration in sludge is 8.3 g/kg. The model would predict a concentration beyond the range of reported field data if the biodegradation rate of LAS is set to zero. However, LAS is readily biodegradable and reported elimination percentages in the effluent exceed 95% both in laboratory scale plants and in the real world, thus a degradation rate of  $3 \text{ hr}^{-1}$  may be rather conservative. This may explain why concentrations lower than 8.3 g/kg (but higher than 3 g/kg) are normally found. The assumption that waste water received by the treatment plant is undiluted domestic is another reason. Such waste water has a higher concentration of surfactants than if it would contain a share of infiltration water or industrial discharges which usually are low in surfactants. Taking this into account, predictions are in good agreement with measured data.

In Table 9 predicted emission to air of five persistent volatile compounds are compared to values estimated on the basis of average concentrations measured in the influent and effluent of two WWTP's near Chicago (15). The reported Henry's Law constants,  $K_{ow}$  values and operating parameters of the WWTP's (15), have been used for model calculations. Their best estimates for volatilization are remarkably close to predicted values. These results are consistent with data of Petrusek et al. (17) who found that volatilization of chemicals may account for the removal of at least 25% if the Henry constant is  $100 \text{ Pa m}^3/\text{mol}$  or higher.

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## TABLES

**Table 1.** Assumed composition of raw waste water (mg/L) entering the primary settler of a conventional activated sludge plant.

	inorganic	organic	800
solids (settleable)	140	260	130
solids (suspended)	60	140	100
dissolved	330	330	150
total	530	730	380

**Table 2.** Parameter values of suspended and settled solids in the primary settler (p) and the aeration tank/solids liquid separator (a,s).

symbol	meaning	value
$d_o$	density of organic solids	1 (kg/L)
$d_i$	density of inorganic solids	2.5 (kg/L)
$d_p$	mean density of solids in p	1.5 (kg/L)
$d_{a,s}$	mean density of solids in a and s	1.3 (kg/L)
$f_{oc}(p)$	organic C fraction of raw sewage and solids in p	0.30 (-)
$f_{oc}(as)$	organic C fraction of solids in a and s	0.37 (-)

**Table 3.** Summary of operation parameters of the simulated waste water treatment plant (scale: 100,000 inhabitants). Primary settler, aeration tank and solids-liquid separator are denoted by p, a and s respectively.

parameter	units	meaning	value
$\tau_p, \tau_a, \tau_s$	$\frac{h}{2}$	hydraulic retention time	1.5(p);3.1(a);3.1(s)
$A_p, A_a, A_s$	$m^2$	area	234(p);657(a);657(s)
k	$kg \cdot kg^{-1} \cdot d^{-1}$	sludge load	0.6
$\theta_a$	d	sludge retention time	1.7
$R_o$	$kg \cdot m^{-3}$	oxygen requirement	0.216
Q	$m^3 \cdot d^{-1}$	waste water flow rate	15000

**Table 4.** Assumed parameter values for deriving reversible exchange rates. Except for  $t_a$ , values reported by Mackay et al. (1985) are used.

symbol	meaning	value
$K_{air}$	mass transfer coeff.(air)	$2.78 \cdot 10^{-3} \frac{m}{s}$
$K_{water}$	mass transfer coeff.(water)	$2.78 \cdot 10^{-5} \frac{m}{s}$
$K_{p.water}$	mass transfer coeff.(pore water)	$2.78 \cdot 10^{-6} \frac{m}{s}$
$t_p$	uptake/clearance $t_{1/2}$ solids (p)	$3.6 \cdot 10^3 s$
$t_a$	uptake/clearance $t_{1/2}$ solids (a)	$3.6 \cdot 10^2 s$
$t_s$	uptake/clearance $t_{1/2}$ solids (s)	$3.6 \cdot 10^3 s$

**Table 5.** Assumed elimination levels of a readily biodegradable, non-adsorbing and non-volatile compound in a municipal waste water treatment plant for the three operating modes which can be selected in SimpleTreat.

operating regimes assumed in the model			max. elimination solely due to biodegradation	
aeration time, $\tau_a$ (hr)	sludge retention time (d)	sludge loading rate (kg BOD/kg/d)	% elimination	$C_e/C_i$
1	0.5	2.0	75	0.25
3.1	1.7	0.6	90.5	0.095
10.2	5.5	0.18	97	0.030

**Table 6.** Expressions for  $Z(i)$  in mol/m<sup>3</sup>/Pa in box  $i$ .  $K_p$  in L/kg both for primary sludge and activated sludge.

box (i)	general	hydrophobic chemicals
Z(1)	$(RT)^{-1}$	$(RT)^{-1}$
Z(2),Z(5),Z(7)	$H^{-1}$	$H^{-1}$
Z(3),Z(4)	$K_{pp} d_p H^{-1}$	$0.5 f_{oc(p)} K_{ow} d_p H^{-1}$
Z(6),Z(8),Z(9)	$K_{pa,s} d_{a,s} H^{-1}$	$0.5 f_{oc(a,s)} K_{ow} d_{a,s} H^{-1}$

**Table 7.** Definition of interphase transfer coefficients.  $k_{s,b}$  in the expressions for  $D_{15}$  and  $D_{51}$  pertains either to surface aeration (eqn 6) or bubble aeration (eqn 8).

$D_{i,j}$	expression (mol/s/Pa)
$D_{12}, D_{21}$	$A_p / (1/(K_{air} Z_1) + 1/(K_{water} Z_2))$
$D_{17}, D_{71}$	$A_s / (1/(K_{air} Z_1) + 1/(K_{water} Z_7))$
$D_{15}, D_{51}$	$k_{s,b} / (1/(V_1 Z_1) + 1/(V_5 Z_5))$
$D_{23}, D_{32}$	$(\ln 2/t_p) / (1/(V_2 Z_2) + 1/(V_3 Z_3))$
$D_{56}, D_{65}$	$(\ln 2/t_a) / (1/(V_5 Z_5) + 1/(V_6 Z_6))$
$D_{78}, D_{87}$	$(\ln 2/t_s) / (1/(V_7 Z_7) + 1/(V_8 Z_8))$



**Table 8.** Reported concentrations of LAS measured in sludge from municipal waste water treatment plants compared to predicted values. Model calculations pertain to a sludge loading rate equal to 0.2 kg/kg/d.

Assumed input parameters for model calculations		Concentration in sludge (g/kg dry matter)		predicted emission pattern
compound properties	emission scenario	measured	predicted	
solubility: 62 mg/L vapour pressure: 0.01 Pa mol weight: 348	2.58 g/inhabitant/d (Rapaport & Eckhoff, 1990)	3-12 (McEvoy & Giger, 1986)	8.3 (13.1 if	sludge production: 30.8%
	waste water: 150 L/d per inhabitant concentration	7 (De Henau et al., 1989)	$k_{deg} = 0)$	degradation: 66.9%
$K_p = 1660$ L/kg (De Henau et al., 1989)	solids in raw sewage: 600 mg/L dry matter	3.6-4.4 (Brunner et al., 1988)		effluent: 2.3%

**Table 9.** Percentage of removal of 5 persistent and volatile compounds by volatilization as predicted by SimpleTreat in comparison with best estimates from field data reported by Namkung and Rittmann (1987). Operation mode: diffused aeration.

compound	Calumet WWTP (Chicago)	SimpleTreat
	$\theta_a = 5.5$ d; $G_a/Q = 5.5$ $k = 0.2$ kg/kg/d	$\theta_a = 5.5$ d; $G_a/Q = 5.3$ $k = 0.2$ kg/kg/d
trichloromethane	43.6	33.3
1,2-dichloroethane	20.6	30.4
tetrachloroethylene	83.6	83.4
trichloroethylene	69.4	65.6
1,1,1-trichloroethane	44.9	33.3

APPENDIX User manual

SimpleTreat 2.0 runs on any IBM-compatible personal computer loaded with the spreadsheet programme LOTUS-123, Release 2.0 or higher. A little experience with LOTUS-123 is required to perform model calculations and to have the input and output tables printed. It is essential that the spreadsheet programme has matrix calculation facilities such as matrix multiplication and matrix inversion.

After running LOTUS-123 and loading the spreadsheet WWTP2\*0.WK1 the following will appear on the screen:

```
#####
#
#          SIMPLETREAT version 2.0 (910304)          #
# CHEMICAL FATE MODEL FOR A MUNICIPAL WASTEWATER TREATMENT PLANT #
#                                     by                #
#               J. Struijs, RIVM, Bilthoven, The Netherlands        #
#####
#
# SimpleTreat is a box model of the so-called "Mackay-type"; it only #
# can be run in the steady state, non-equilibrium ("level 3") mode.  #
# SimpleTreat is designed to estimate the relative emission of a     #
# chemical to air, surface water and sludge. Standard output shows  #
# concentrations in effluent and sludge if the emission rate of the  #
# chemical and the size of the wastewater treatment plant are given. #
#
#           Information: Netherlands 030-742001; Jaap Struijs      #
#                                 [RETURN]                         #
#####
```

Press ENTER or RETURN to display the following screen:

```
#####
# MODEL INPUT                     SIMPLETREAT version 2.0 (91-03-04)
#####
# -----
# PROPERTIES OF THE COMPOUND (IN NEUTRAL FORM IF Ka,Kb GIVEN)
# -----
# COMPOUND NAME           :
# FORMULA                 :
# MOLECULAR WEIGHT        :           ( 100 ) g/Mol    =
# SOLUBILITY              :           ( 1E+02 ) mg/L    =
# VAPOUR PRESSURE        :           ( 1E+00 ) Pa      =
# KP OCTANOL-WATER       :           ( 1E+03 ) -       =
# Ka (IF NEUTRAL FORM IS ACID):          ( 1E-20 ) -       =
# Kb (IF NEUTRAL FORM IS BASE):          ( 1E-20 ) -       =
#
# BIODEG. (OECD) Y or N   :           ( N   )           =>
#                                     k-deg =
# HENRY'S LAW CONSTANT    :           ( 1E+00 ) Pa m3/Mol =
# KP SOLIDS-WATER        :           ( 2E+02 ) L/kg      =
```

The cell pointer highlights cell D8, behind the colon of "COMPOUND NAME", which form part of the block "PROPERTIES OF THE COMPOUND". Only column D of the input block is unprotected; other cells in the spreadsheet are protected against unintended erasing or overwriting. After the name of the compound has been typed in, the cell pointer is moved one down, to D9, for entering the formula of the compound (also alpha-numeric). These entries are only important for administrative reasons, not for calculations. Note that if these entries begin with a number, for example 4-nitrophenol, the prefix (' ) should be typed in first.

In cell D10, the molecular weight of the compound (g/Mol) should be typed in. If D10 remains empty, the value between brackets, i.e. 100 g/L, being the default value will be chosen by the programme. Also for other entries in the input blocks PROPERTIES OF THE COMPOUND, METEO DATA and EMISSION DATA, default values between brackets in the spreadsheet can only be overruled by entering values in the D column.

The SOLUBILITY, VAPOUR PRESSURE and KP OCTANOL-WATER ( $K_{ow}$  not  $\log K_{ow}$ ), in units as indicated, are the following data to be entered in cell D11, D12 and D13, respectively. If the compound is an organic acid or base, values for solubility and  $K_{ow}$  are assumed to pertain to the neutral, thus unionized, species and either  $K_a$  (=  $K_a$ , the acid dissociation constant, not  $pK_a$ ) or  $K_b$  (=  $K_b$ , the basic dissociation constant, not  $pK_b$ ) should be specified in cell D14 or D15. If the compound is not ionizable, these cells should remain empty and the programme will choose the default values which are virtually zero ( $10^{-20}$ ).

Move the cell pointer to D17 if the compound is "readily biodegradable" according to the OECD Guidelines for Testing Chemicals or Annex Part C (Methods for the determination of ecotoxicity) of the EC Directive 84/449/EEC. Entering **Y** will cause the first order biodegradation rate constant in the aeration tank to be equal to  $8.33E-4 \text{ s}^{-1}$  (= 3 /hr). Any other entry will set the degradation rate equal to zero which is also the default value.

Press **F9** (CALC) to recalculate the worksheet and move the cell pointer to D19. The default values for HENRY'S LAW CONSTANT (=  $K_H \times RT$ , see subparagraph 2.2.1) and KP SOLIDS-WATER (=  $K_p$ ) are shown between brackets. These values are derived from the compound properties in cells D10..D15, according to the assumptions for equilibrium partitioning, described in

sub-paragraph 2.2.1. of this report. Thus cells D19 and D20 usually remain empty for a hydrophobic chemical. However, if either cell D19 or D20 or both contain input data, these *calculated default* values are overruled. In general, H and  $K_p$  are required input data for non-hydrophobic chemicals such as surface active compounds. The complete MODEL INPUT block consists of the following:

```

#####
# MODEL INPUT                               SIMPLETREAT version 2.0 (91-03-04) #
#####
#
# -----#
# PROPERTIES OF THE COMPOUND (IN NEUTRAL FORM IF Ka,Kb GIVEN) #
# -----#
# COMPOUND NAME           : #
# FORMULA                 : #
# MOLECULAR WEIGHT       :      ( 100 ) g/Mol      = 1.00E-01 kg/Mol #
# SOLUBILITY             :      ( 1E+02 ) mg/L      = 1.00E+00 Mol/m3 #
# VAPOUR PRESSURE        :      ( 1E+00 ) Pa        = 1.00E+00 Pa #
# KP OCTANOL-WATER       :      ( 1E+03 ) -         = 1.00E+03 - #
# Ka (IF NEUTRAL FORM IS ACID):      ( 1E-20 ) -     = 1.00E-20 - #
# Kb (IF NEUTRAL FORM IS BASE):      ( 1E-20 ) -     = 1.00E-20 - #
#
# BIODEG. (OECD) Y or N   :      ( N )              =>NO DEGRADATION #
#                               k-deg = 0.00E+00 s-1 #
# HENRY'S LAW CONSTANT    :      ( 1E+00 ) Pa m3/Mol = 1.00E+00 Pa m3/Mol #
# KP SOLIDS-WATER         :      ( 2E+02 ) L/kg      = 1.52E+02 L/kg #
#
# -----#
# METEO DATA #
# -----#
# TEMPERATURE AIR         :      ( 14 ) centigr.    = 2.87E+02 dgr. Kelvin #
# TEMPERATURE WATER      :      ( 14 ) centigr.    = 2.87E+02 dgr. Kelvin #
# WINDSPEED               :      ( 3.0 ) m/s        = 3.00E+00 m/s #
#
# -----#
# EMISSION DATA #
# -----#
# DISCHARGE RATE COMPOUND :      ( 1E+00 ) kg/d      = 1.00E+00 kg/d #
# NUMBER INHABITANTS      :      ( 6667 ) -         = 6.67E+03 - #
# WASTE WATER/INHABITANT  :      ( 150 ) L/d        = 1.50E+02 L/d #
# CONC. OF SOLIDS IN INFLUENT :      ( 600 ) mg/L     = 6.00E-01 kg/m3 #
#
# ==> AQUEOUS CONCENTRATION 9.31E-01 mg/L dissolved = 9E-04 kg/m3 #
#                               93.1 % #
# ==> SOLIDS CONCENTRATION 1.72E-01 kg/m3 solids #
#                               6.9 % #
# ==> TOTAL CONCENTRATION 1.00E+00 mg/L raw wastewater #
# -----#
# MODE OF OPERATION OF THE PLANT #
# -----#
# AERATION MODE (Surf./Bubb.) : S          INPUT S or B #
# LOADING OF THE PLANT        : M          INPUT L,M or H #
#
#####

```

Depending on the available input data, model calculations can be performed in two fashions:

- 1.) the prediction of relative emission of a chemical from a standard WWTP. Only data in block "PROPERTIES OF THE COMPOUND" are required as input.
- 2.) the relative emission pattern and concentrations in effluent and sludge. At least two entries in the block EMISSION DATA are necessary in addition to the properties of the compound.

#### 1.) CALCULATION OF RELATIVE EMISSION

Only data in the block PROPERTIES OF THE COMPOUND are required to calculate the relative distribution of a chemical by a conventional WWTP operating at a moderately low sludge loading rate ( $k = 0.2 \text{ kg/kg/d}$ ) and surface aeration. Press **MACRO C** (hold down the **MACRO** key and press **C**) to invoke a macro which executes the model calculation. The following will appear on the screen:

```
#####
# MODEL OUTPUT                SIMPLETREAT version 2.0 (91-03-04)
#####
#                               RESULTS FOR           0
# -----
# EMISSION DISTRIBUTION
# -----
# VIA PRIMARY SLUDGE          = 4.59E-02 kg/d = 4.6 %
# VIA SURPLUS SLUDGE         = 3.20E-02 kg/d = 3.2 %
# VIA WATER EFFLUENT         = 8.88E-01 kg/d = 88.8 %
# VIA SUSP. SOLIDS EFFLUENT  = 5.41E-03 kg/d = 0.5 %
# VIA AIR                     = 2.86E-02 kg/d = 2.9 %
#                               SUM = 1.00E+00 kg/d = 100.0 %
#
# TO TOTAL SLUDGE            = 7.8 %
# TO RECEIVING WATER         = 89.4 %
# TO THE AIR                  = 2.9 %
# DEGRADED                    = 0.0 %
#                               SUM = 100.0 %
```

This emission distribution would be obtained if the programme is executed on the basis of default values exclusively.

**EXAMPLE 1** The relative emission pattern of 1,4-dichlorobenzene from the following compound properties:

molecular weight = 147 g/mol  
 solubility = 83 mg/L  
 vapour pressure = 90 Pa  
 log  $K_{ow}$  = 3.5

As Henry's law constant, H, or the partition coefficient directly related to H, (i.e.  $K_H = H/RT$ ), and the solids-water partition coefficient ( $K_p$ ) are not known, only these properties of 1,4-dichlorobenzene are required to calculate its distribution. In this example the data have been derived from "Integrated Criteria Document Chlorobenzenes" (Slooff et al., 1991). As 1,4-dichlorobenzene is considered a borderline case of "ready biodegradability" calculations are performed twice, both for BIODEG. (OECD) specified as **Y** and **N** in cell D17. After **F9** (CALC) the input block (default is no degradation) would read:

```
# -----
# PROPERTIES OF THE COMPOUND (IN NEUTRAL FORM IF Ka,Kb GIVEN)
# -----
# COMPOUND NAME           : 1,4-dichlorobenzene
# FORMULA                 : C6H4Cl2
# MOLECULAR WEIGHT        :      147 ( 100 ) g/Mol   =
# SOLUBILITY              :      83 ( 1E+02 ) mg/L   =
# VAPOUR PRESSURE        :      90 ( 1E+00 ) Pa     =
# KP OCTANOL-WATER       : 3162.2776 ( 1E+03 ) -    =
# Ka (IF NEUTRAL FORM IS ACID):      ( 1E-20 ) -    =
# Kb (IF NEUTRAL FORM IS BASE):      ( 1E-20 ) -    =
#
# BIODEG. (OECD) Y or N   : N      ( n      )      =>
#
#                               k-deg =
# HENRY'S LAW CONSTANT    :      ( 2E+02 ) Pa m3/Mol =
# KP SOLIDS-WATER        :      ( 5E+02 ) L/kg     =
#
# -----
```

Note that between brackets default values for H and the  $K_p$  are already calculated from the input compound properties in D10..D15 typed in previously. These default values are correct if the compound is hydrophobic

and no data have to be introduced into cells D19 and D20. After the command **MACRO C** the screen will display the distribution of 1,4-dichlorobenzene which is assumed not to degrade in a standard WWTP operating at a moderate sludge loading rate ( $k = 0.6$  kg/kg/d) under a surface aeration regime:

```
#####.
# MODEL OUTPUT          SIMPLETREAT version 2.0
#####
#                      RESULTS FOR 1,4-dichlorobenzene
# -----
# EMISSION DISTRIBUTION
# -----
# VIA PRIMARY SLUDGE      = 1.26E-01 kg/d = 12.6 %
# VIA SURPLUS SLUDGE     = 2.14E-02 kg/d = 2.1 %
# VIA WATER EFFLUENT     = 1.69E-01 kg/d = 16.9 %
# VIA SUSP. SOLIDS EFFLUENT = 3.61E-03 kg/d = 0.4 %
# VIA AIR                 = 6.80E-01 kg/d = 68.0 %
#                          SUM = 1.00E+00 kg/d = 100.0 %
#
# TO TOTAL SLUDGE        = 14.7 %
# TO RECEIVING WATER     = 17.3 %
# TO THE AIR              = 68.0 %
# DEGRADED                = 0.0 %
#                          SUM = 100.0 %
```

Press **HOME** and move the cell pointer to D17 in order to replace **N** with **Y** and repeat the calculation (**MACRO C**). The following output will appear on the screen:

```
#####
# MODEL OUTPUT          SIMPLETREAT version 2.0
#####
#                      RESULTS FOR 1,4-dichlorobenzene
# -----
# EMISSION DISTRIBUTION
# -----
# VIA PRIMARY SLUDGE      = 1.26E-01 kg/d = 12.6 %
# VIA SURPLUS SLUDGE     = 7.54E-03 kg/d = 0.8 %
# VIA WATER EFFLUENT     = 5.57E-02 kg/d = 5.6 %
# VIA SUSP. SOLIDS EFFLUENT = 1.27E-03 kg/d = 0.1 %
# VIA AIR                 = 2.40E-01 kg/d = 24.0 %
#                          SUM = 4.30E-01 kg/d = 43.0 %
#
# TO TOTAL SLUDGE        = 13.3 %
# TO RECEIVING WATER     = 5.7 %
# TO THE AIR              = 24.0 %
# DEGRADED                = 57.0 %
#                          SUM = 100.0 %
```

This example shows that biodegradation has only little effect on the emission via combined sludge but reduces the emission to the receiving water and to the air by a factor 3 compared to *non-degradable* 1,4-dichlorobenzene.

## 2. CALCULATION OF RELATIVE EMISSION AND CONCENTRATIONS IN EFFLUENT AND SLUDGE

At least the blocks PROPERTIES OF THE COMPOUND and EMISSION DATA have to be specified in order to obtain relevant concentration in effluent and sludge. If DISCHARGE RATE COMPOUND and NUMBER INHABITANTS in the block EMISSION DATA are not specified calculations are performed for the default values 1 kg/d and 6667 respectively, however, the following message will appear in part CONCENTRATIONS in EFFLUENT, SLUDGE and AIR of the MODEL OUTPUT block:

"CAUTION: CONCENTRATIONS BELOW ARE NOT RELEVANT, EMISSION NOT SPECIFIED!"

Input data as to METEO DATA and MODE OF OPERATION OF THE PLANT are not necessary if the user accepts that calculations are performed pertaining to water-air temperatures equal to 14 °C, a wind speed of 3 m/s, surface aeration (S) and an intermediate sludge loading rate (M) equal to 0.6 kg/kg/d.

**EXAMPLE 2** Predicted effluent and sludge concentrations of trichloromethane from the following compound properties and emission scenario:

$$K_{ow} = 100$$

$$\text{Henry's law constant} = 340 \text{ Pa m}^3/\text{mol}$$

$$\text{discharge rate into the sewage system} = 375 \text{ g/d}$$

$$\text{number of inhabitants the plant is serving} = 100,000$$

In this example no data on the solubility and vapour pressure are given, however, these compound properties are only used by the programme to calculate a default value for Henry's law constant (H) of trichloromethane





Note that the input block lists the total concentration in raw waste water and the distribution over the aqueous and solids phase for this specific emission scenario. Apparently less than 1% of trichloromethane resides in the suspended solids of raw waste water. In absence of emission data the distribution would be correct but not the concentration as it is based upon the default emission scenario. Press **MACRO C** to obtain the model output:

```

#####
# MODEL OUTPUT                SIMPLETREAT version 2.0                #
#####
#                               RESULTS FOR trichloromethane           #
# -----#
# EMISSION DISTRIBUTION                                             #
# -----#
# VIA PRIMARY SLUDGE         = 1.82E-03 kg/d = 0.5 %                #
# VIA SURPLUS SLUDGE         = 1.85E-04 kg/d = 0.0 %                #
# VIA WATER EFFLUENT         = 4.62E-02 kg/d = 12.3 %               #
# VIA SUSP. SOLIDS EFFLUENT  = 3.13E-05 kg/d = 0.0 %                #
# VIA AIR                     = 3.27E-01 kg/d = 87.2 %              #
#                               SUM = 3.75E-01 kg/d = 100.0 %      #
#                               #                                     #
# TO TOTAL SLUDGE            = 0.5 %                                #
# TO RECEIVING WATER         = 12.3 %                               #
# TO THE AIR                  = 87.2 %                               #
# DEGRADED                    = 0.0 %                               #
#                               SUM = 100.0 %                       #
#                               #                                     #
# CONCENTRATIONS in EFFLUENT, SLUDGE and AIR                       #
# -----#
#                               #                                     #
#                               #                                     #
#                               #                                     #
# CONCENTRATION IN EFFLUENT  = 3.08E-03 mg/L DISSOLVED             #
# CONCENTRATION IN EFFLUENT  = 2.09E-06 mg/L ADSORBED              #
# TOTAL CONC. IN EFFLUENT    = 3.08E-03 mg/L TOTAL                 #
#                               #                                     #
# CONC. IN SLUDGE PRODUCED   = 0.21 mg/kg (dry matter)            #
# CONC. AIR AT WATER WORKS   = 8.02E-06 g/m3                       #
#####
#                               #                                     #
# CHARACTERISTICS OF THE SEWAGE TREATMENT PLANT                   #
# -----#
# k (biodegradation)         = 0.00E+00 s-1 = 0.0 d-1              #
# k (stripping)              = 1.78E-03 s-1 SURFACE AERATION      #
#                               #                                     #
# number inhabitants         = 100000                               #
# sludge loading rate (k)    = 0.60 kgO2/kg dry matter/d          #
# sludge retention time (SRT) = 1.7 d                               #
# surplus sludge production  = 35.5 g/d/inhabitant                 #
# total sludge production    = 95.5 g/d/inhabitant                 #
# aeration time              = 3.2 h                                #
# BOD_load                   = 1.79 kgO2/m3/d                     #
# BOD-REMOVAL (total per day) = 2.8E+03 kgO2/d                    #
# reduced k --> k'           = 0.48 kgO2removed/kg dry matter/d   #
# FACTOR; fraction BOD removed= 0.80 -                             #
#####

```

The model output indicates that trichloromethane is for the major part removed from a WWTP by stripping: 87.2% which is much higher than the figure in Table 9 of this report. The explanation is that results of model calculations in Table 9 pertain to plant operating conditions which simulate the Calumet plant in Chicago. For volatile compounds like trichloromethane the emission to air strongly depends on the aeration mode which SimpleTreat defaults surface aeration. However simulating the behaviour of trichloromethane in the Calumet plant, bubble aeration was assumed. The latter has been shown less effective in stripping chemicals from the aeration tank than surface aeration.

A two page report is obtained by **MACRO R** which will start the matrix printer to print the complete model input and output sheet.