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ABSTRACT

Two different models have been used to investigate how chemicals present in wastewater from a kraft mill are transported and spread in an aquatic environment. The models, FEQUM (Fugacity EQUilibrium Model) and EXAMS, are presented, their characteristics explained and a comparison of the models is made. In FEQUM the concept of fugacity is considered as the driving force behind chemical transport. The EXAMS dispersion model uses water and sediment flow as the basis for calculating the dispersion of chemicals. FEQUM encompasses the whole environment, water, air, soil, sediments, suspended matter in water and biota, whereas EXAMS includes the aquatic domain only.

Both models have been applied to the Norrsundet area. Norrsundet is a heavily polluted bay on the east coast of Sweden. The pollution is mainly due to a kraft mill located in the area. The models were calibrated using data on chloroform in wastewater and seawater, and then tested on four other pollutants present in the wastewater. Both models give satisfactory results for the compounds investigated, tetrachlorocatechol constituting the only exception. Correlation coefficients between calculated and measured concentrations vary from 0.86 to 0.97. The poor results obtained for tetrachlorocatechol are probably due to the especially high affinity of this compound for suspended particles.

KEYWORDS

Dispersion model, EXAMS, FEQUM, Fugacity model, Kraft bleaching, Fate, Transport, Pollutants.

INTRODUCTION

During the last decades methods in analytical chemistry have been through a revolution. The amount of data which can be obtained on a routine basis has increased drastically as has the accuracy of the data obtainable. This revolution has created a need for developing methods that can handle analytical data in an efficient way and extract from them useful information. One way to utilize the data is to use them as the basis for a mathematical modelling of the processes and reactions occurring in nature. In this work the use of modern computing technology is a necessary prerequisite.

One such type of computer-based models are the chemical fate and transport models. These describe how a compound released to the environment is spread and distributed among different parts of the environment and how it is removed through physical or chemical processes. Some of the models developed comprise the whole environment whereas others consider only certain parts of it, for instance the aquatic domain. Dispersion models can be divided into two main categories, compartment models and continuous models. In a compartment model the physical
environment is divided into a set of segments, each assumed to be homogeneous with respect to the chemical under consideration, and transport of the chemical between these segments is calculated. A continuous model, on the other hand, assumes the chemical concentration to vary continuously both in time and space.

The main objectives of a dispersion model are a) to predict the future situation if the pollution load in the area increases or changes, b) to simulate the effects of control actions aimed at decreasing the pollution, c) to give information on processes which are not easily amenable to experimental determination, such as which of the reactions or processes occurring in the receiving water are the most important ones for the dispersion of the compound, and d) to explain today's situation, i.e. what must have been the main sources of pollution in the past and at what rate has the receiving area been polluted.

There are several ways to adapt a model to a particular part of the physical environment and to test its reliability. A common procedure, and the one we have used in this work, is to calibrate the model and then test its predictive capability. In the calibration phase the parameters of the model are determined such that the model gives the best possible fit to a set of measurements obtained in the area being modelled. One possibility is to use measured concentrations of a specific compound. The second phase, the validation, consists in using the model to predict other results for which there exist experimental data, for instance data on other compounds, while retaining the parameter values determined in the calibration. The models applied in the present work were calibrated by using measured concentrations of chloroform. The validation was based on data available for four other compounds present in the wastewater, one chlorophenol, two chloroguaiacols and one chlorocatechol.

Both models employed in this work are of the compartment type. The main purpose of the work has been to find out how suitable the models are for describing the dispersion in marine waters receiving waste products generated by the forest industry. In particular, we wanted to study how well the models can predict ambient concentrations of the relevant pollutants and how the models compare with respect to various features such as predictive capability and data requirements.

**DESCRIPTION OF THE MODELS**

**EXAMS**

The EXAMS (Exposure Analysis Modeling System) model was developed by the US Environmental Protection Agency (EPA) in the late 1970s and early 1980s. EXAMS handles the aquatic environment (water and benthic sediments) only. It is probably the best known and most widely used model of its kind. A detailed documentation of the model has been given by Burns & al. (1982). EXAMS is based on common modelling principles. Water, suspended sediments and mobile biotic material moving among the system compartments are treated as carriers of the pollutant under consideration. After specifying the relevant flows a mass balance for the pollutant is set up for each compartment. This results in a set of differential equations which can be solved to give the time development of the concentration in each compartment or steady-state concentrations. What makes EXAMS especially powerful is the possibility it offers to account for chemical transformation processes. The types of processes which can be treated by EXAMS include loss to the atmosphere, direct photolysis, hydrolysis, oxidation and microbial degradation.

**FEQUM**

FEQUM (Fugacity Equilibrium Model) was designed at the Center for Industrial Research in Oslo. The model is an extended version of the fugacity model developed by Mackay and co-workers (Mackay, 1979, Mackay and Paterson, 1981, Mackay and Paterson, 1982, Mackay & al. 1985a, Mackay & al., 1985b). The extensions are in four different directions: a) the FEQUM model can handle an arbitrary number of compartments (the original fugacity model was limited to one compartment of each kind), b) the FEQUM model can handle free flow patterns among compartments of the same type, which means the sea currents can be modelled in a realistic way, c) the model allows for the use of time-dependent parameters, i.e. one can alter relevant parameters during a simulation run and d) the integration algorithm used is changed from a simple Euler algorithm to a Runge Kutta algorithm of second order.
FEQUM is based on the concept of fugacity. The fugacity of a substance (which is closely related to its concentration via the so-called fugacity capacity) is a measure of the ability of the substance to escape from one phase to another, e.g. from water to air. There will be a net flow of the substance between two compartments as long as the fugacity is different in the two compartments. Mackay and Paterson (1982) have set up an equation describing steady-state in a compartment in the fugacity model. In FEQUM this equation translates into

$$E + \sum_{i,j} n_{ij} V_{ij} C_{i} + V_{a,i} C_{i} = \sum_{j} n_{j} V_{j} C_{j} + V_{a,j} C_{j} + \sum_{k} n_{k} k V_{k} C_{k} + \sum_{l} n_{l} D_{l} (f - f_{i})$$

(1)

where

- $E_{i}$ = Emission of chemical to comp. i
- $V_{ij}$ = Volume of inflow from comp. j to comp. i
- $C_{i}$ = Chemical concentration in comp. i
- $V_{a,i}$ = Flow from outside model into comp. i
- $D_{ij}$ = Diffusion between comp. i and comp. j
- $C_{i}$ = Concentration in this inflow
- $V_{oij}$ = Flow out of comp. i to comp j
- $V_{s,ij}$ = Volume of flow from comp. i to a sink
- $k_{ij}$ = rate of first order process j
- $V_{i}$ = Volume of comp. i
- $f_{i}$ = Fugacity of comp. i
- $n$ = number of compartments
- $m$ = number of first order processes allowed in each comp.

There is one such equation for each compartment, giving a total of $n$ equations. A corresponding set of differential equations describing the rate of change of the chemical can easily be formulated. As with EXAMS these equations can be integrated to give the time development of the concentrations (or fugacities) in each compartment.

FEQUM and EXAMS.

FEQUM and EXAMS have many features in common. For instance, the models include the same types of degradation processes (even though the chemistry is considerably more elaborate in EXAMS). The models, however, also differ in several respects. Some of the pertinent differences and model-specific features are summarized below.

1) FEQUM can handle the whole environment, that is to say air, soil, water, sediment, suspended aquatic matter and biota in water. EXAMS handles the aquatic environment including benthic sediments only. Apart from mobile plankton, which is considered as a potential carrier of pollutants, EXAMS does not include biota in water. In EXAMS transfer of pollutants to air is treated as a loss process following first-order kinetics on the same footing as for instance chemical degradation.

2) EXAMS takes into account particle transport among water and benthic compartments, which means that a compound can be transported through the system bound to particles in the water or sediments. However, no real deposition or resuspension processes are implemented. In its present state FEQUM cannot deal with particle transport, but can handle stationary suspended matter in water compartments.

3) In FEQUM arbitrary flows in water or air can be defined. This means that advection flows can start in any compartment, pass through any other compartment of the system, branch to several compartments and terminate in several different sinks. It is also possible to define circular flows including two or more compartments. EXAMS takes into account two types of water transport, advective flows and turbulent dispersion. This gives a high degree of flexibility in defining the flow pattern. Unlike FEQUM, however, EXAMS presumes that each advective flow has an external source.

4) EXAMS can treat the neutral and ionized forms of acids or bases as separate chemical species. FEQUM does not offer this possibility but assumes that the chemical exists only in its unionized form. Ionization reactions, in EXAMS, are treated as equilibrium processes. The data to be provided by the user are the relevant ionization constants.
Both EXAMS and the fugacity model of Mackay were developed primarily for application to rivers, lakes and ponds. For such systems the model parameters that specify the water flow, in particular the turbulent diffusion coefficients, have a well defined physical interpretation and can be determined experimentally. The water movements in estuaries and coastal areas are much more complex, being driven by tidal waves, wind induced currents and the occurrence of water density gradients as well as by more stable large scale currents. By applying EXAMS and FEQUM to a coastal area it is implicitly assumed that the combined effect of these mechanisms can be lumped into a specific set of water flow parameters, an assumption which, of course, needs to be verified. Therefore, both models, as applied in the present work, are to be considered as essentially empirical models.

THE NORRSUNDET AREA

General description

The Norrsundet area is a heavily polluted bay on the east coast of Sweden about 230 km north of Stockholm (Fig. 1). The main source of pollution is a kraft mill (Norrsundet Bruk) which discharges wastewater into the nearby coastal water at a rate of about 1 m³/s. The effluent is mostly uncharacterized. However, a few individual compounds have been identified, including chloroform, chlorophenols, chloroguaiacols and chlorocatechols. Generally, the whole Gulf of Bothnia has a high background level of these compounds (Xie et al., 1986), due to a series of pulp and paper mills located around the gulf.

Data from Norrsundet

Measurements of the above compounds have been carried out in water and sediments of Norrsundet on four occasions between September 1982 and November 1983 (Xie et al., 1986). The sampling points were well distributed over the investigated area, but the vertical resolution (in the water column) was rather poor. Pollutant concentrations in the effluent have been measured in two of the cases, chloroform in only one, on November 3, 1983.

Xie et al. (1986) do not give any information on the number of samples taken at each station.

Fig. 1. The Norrsundet area about 230 km north of Stockholm
or on the precision of the measured concentrations presented. Such information would have been of great value in the calibration and validation of the models investigated. It is particularly unsatisfactory to have at hand only a single concentration value of chloroform in the effluent without any uncertainty estimate associated with it.

The effluent from the kraft mill is discharged into a shallow pond where it is mixed with seawater. In this pond seawater flows from the south and is pumped to the north at a rate of about 20 m/s. The main current in the Gulf of Bothnia moves from the north to the south along the Swedish coast with an average speed of about 0.5 knot (Falkenmark, 1986; Jonsson, 1986). Besides being influenced by this large scale current, water motion and pollutant transport in Norrsundet, in particular that occurring in the top layer, is heavily dependent upon the wind direction, which is predominantly from the southwest.

Apart from the above information, there seems to exist few quantitative data on the flow pattern in Norrsundet. Using an empirical method derived by Håkanson & al. (1984), Jonsson (1985) has calculated the water residence time in four different areas of Norrsundet. Being the only site-specific data available, these residence times (given in Table 2 below) have played an important role in the present work.

**MODEL INPUT DATA**

**Chemical data**

The fate and behaviour of a chemical in the environment is to a large extent dependent on its physico-chemical properties. Table 1 shows some relevant data for chloroform and the four compounds used in validating the investigated models.

In addition to the data given in Table 1, EXAMS and FEQUM also can utilize information on degradation processes, when relevant. All reactions are assumed to follow (pseudo) first order kinetics. In the present calculations the following oxidation rate constants were used: Cl: 0.7·10^{-2} h^{-1}; 2,4,6-TrCP: 1.0·10^{-2} h^{-1}; 3,4,5-TrCG: 0 h^{-1}; TeCG: 0.5·10^{-2} h^{-1}. The rate constants for the first two compounds were obtained from Mabey & al. (1982) assuming an oxidant concentration of 1·10^{-3} M. For TeCC the constant was estimated from data given by Abrahamsson and Xie (1983). In the case of Cl, base-promoted hydrolysis also plays a significant role. The rate used for this reaction was 0.23·10^{-1} h^{-1} assuming the pH to be 7.

**TABLE 1 Chemical/Physical Parameters Used**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviation</th>
<th>Mol. weight g/mole</th>
<th>Vapour pressure Pa</th>
<th>Water Solubility ppm</th>
<th>Henry's law constant atm. mol</th>
<th>log Pow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>Cl</td>
<td>119.38</td>
<td>150.5</td>
<td>8200.0</td>
<td>2.88·10^{-3}</td>
<td>1.97</td>
</tr>
<tr>
<td>2,4,6-Trichlorophenol</td>
<td>2,4,6-TrCP</td>
<td>197.5</td>
<td>1.59</td>
<td>800.0</td>
<td>4.0·10^{-6}</td>
<td>3.61</td>
</tr>
<tr>
<td>3,4,5-Trichloroguaiacol</td>
<td>3,4,5-TrCG</td>
<td>227.47</td>
<td>0.64</td>
<td>9.10**</td>
<td>-</td>
<td>4.13</td>
</tr>
<tr>
<td>Tetrachloroguaiacol</td>
<td>TeCG</td>
<td>261.92</td>
<td>0.138</td>
<td>4.20**</td>
<td>-</td>
<td>4.42</td>
</tr>
<tr>
<td>Tetrachlorogatechol</td>
<td>TeCC</td>
<td>247.89</td>
<td>5.3·10^{-4}**</td>
<td>2.70</td>
<td>-</td>
<td>4.19</td>
</tr>
</tbody>
</table>

1 Pow: octanol-water partition coefficient

**TABLE 2 Geographical Data, Norrsundet area**

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Name</th>
<th>Number</th>
<th>Area 10^6 m²</th>
<th>Volume Water 10^3 m³</th>
<th>Water depth m</th>
<th>Water residence time days</th>
<th>Air Volume 10^3 m³</th>
<th>Sediment Volume 10^3 m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milgrund</td>
<td>1</td>
<td>4.4</td>
<td>11.5</td>
<td>2.6</td>
<td>0.5</td>
<td>4.4</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>Svartgrund</td>
<td>2</td>
<td>3.7</td>
<td>20.5</td>
<td>5.5</td>
<td>-</td>
<td>3.7</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Klinken</td>
<td>3</td>
<td>10.1</td>
<td>60.7</td>
<td>6.0</td>
<td>-</td>
<td>10.1</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>Klackarna</td>
<td>4</td>
<td>36.4</td>
<td>581.0</td>
<td>16.0</td>
<td>-</td>
<td>36.4</td>
<td>3.64</td>
<td></td>
</tr>
<tr>
<td>Rödhällan</td>
<td>5</td>
<td>17.8</td>
<td>147.0</td>
<td>8.2</td>
<td>0.9</td>
<td>17.8</td>
<td>1.78</td>
<td></td>
</tr>
<tr>
<td>Utosten</td>
<td>6</td>
<td>7.9</td>
<td>200.0</td>
<td>25</td>
<td>0.8</td>
<td>7.9</td>
<td>0.79</td>
<td></td>
</tr>
</tbody>
</table>
Geographical data

The division of the receiving area was chosen to closely follow that employed by Jonsson (1965). One of the compartments was merged with an adjacent one, another was subdivided into two new compartments, and a new compartment was placed outside the original receiving area. The chosen partitioning is given in Fig. 2. The compartment names and their geometrical dimensions are given in Table 2. The volumes, areas, mean depths and residence times were taken or calculated from Jonsson (1965), except for "Utposten" and "Klunken", where data were obtained from a sea chart of the Norrsundet area.

Each subarea was split horizontally into two layers, a water and a sediment layer. In FEGUM an air layer is also needed. The depths of the sediments are set to 0.1 m in all cases and the height of the air column to 1 m. The layers will be denoted as X-A (Air), X-W (Water) and X-S (Sediment), where X is the compartment name or number given in Table 2.

Hydrological data

As mentioned previously, information on the flow pattern in Norrsundet is scarce. The pond into which the effluent is discharged prevents the water in "Milgrund" from being mixed with the water in "Klunken". We have made the assumption that except for the minor amount that is pumped from the south into this pond, the replacement of the water in "Milgrund" takes place exclusively via "Svartgrund". This, of course, is an approximation to the real situation. We believe, however, that the approximation may be a good one, as the border zone between "Milgrund" and "Klunken" is characterized by several islands and skerries and the water depth is everywhere less than 3 m. An overview over the flows adopted in the present model calculations is given in Fig. 3.

Using the residence times and compartment volumes quoted in Table 2, one can estimate the total in-out flux of water across the various segment boundaries. By further invoking the assumption on flow directions mentioned above, it is possible to estimate the rates of the flows indicated in Fig. 3. The result of this estimation is given in Table 3. The flow W-7, between "Klunken" and "Klackarna", was determined by a rough interpolation between the values for W-2 and W-5.
Air flows

In FEQUM air flows can also be specified. The prevailing wind direction in the area under consideration is from southwest to northeast. Based on experience from previous studies (Aschjem, 1987) the height of the air columns have been set to 1 m. An average residence time of 1 hour was used for each compartment. This corresponds to the air flows given in Table 4.

Input of pollutants to the receiving water

Chemical concentrations measured in the effluent on November 3, 1983 (Xie & al., 1986) are given in Table 5. Combining these data with information on effluent flow rate enables one to estimate the discharge rate of the compounds considered. The flow rate is somewhat uncertain but was probably in the range 68-86 000 m³/day at the time in question. This gives the discharge rates shown in Table 5. There is a possibility that the values for chloroform are too low as an estimate of the real amount of chloroform flowing into the receiving area since additional chloroform may be formed after the effluent has left the plant.

Background levels of the relevant compounds are uncertain. Assumed values, based on the work of Xie & al. (1986), are listed in Table 5. It should be emphasized that the concentrations obtained by use of the models, especially those obtained in the inner parts of the receiving area, are relatively insensitive to the choice of background level.

Measured concentrations in the Norrsundet Area

Mean values of the pollutant concentrations measured in the water column in Norrsundet on November 3, 1983 (Xie & al., 1986) are shown in Table 6. Concentrations were averaged over the whole compartment area. All samples were taken 5 m below the sea surface and can be said to represent the mean vertical concentration.
Table 6: Mean water concentrations in Norrsundet on 3rd of November 1983

<table>
<thead>
<tr>
<th>Compound</th>
<th>Milgrund</th>
<th>Svartgrund</th>
<th>Klunken</th>
<th>Klackarna</th>
<th>Rödhellan</th>
<th>Utposten</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>4500</td>
<td>2800</td>
<td>1000</td>
<td>360</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>2,4,6-TrCP</td>
<td>235</td>
<td>52</td>
<td>60</td>
<td>31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3,4,5-TrCC</td>
<td>1050</td>
<td>360</td>
<td>161</td>
<td>22</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>TeCG</td>
<td>850</td>
<td>290</td>
<td>119</td>
<td>13</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>TeCC</td>
<td>119</td>
<td>110</td>
<td>97</td>
<td>79</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

-= unknown concentrations

RESULTS

Results of calibration

The models were calibrated to give the best possible fit to water concentrations of chloroform measured in the receiving area. Chloroform was used as a tracer by Xie et al. (1986) to determine the dilution of the effluent from Norrsundet Bruk. The compound is relatively inert and has little tendency to adsorb to sediments. This makes it well suited for calibration purposes.

The flows W-2, W-5, W-6 and W-7 (see Fig. 3) were chosen as the basic adjustable parameters in the calibration process, the rates given in Table 3 being used as a starting point. The flows W-1, W-3 and W-4 were fixed at the values shown in Table 3.

Choosing a set of values for the flow rates W-1 to W-7 establishes a water flow regime in Norrsundet. Due to infrequent measurements of chloroform we were not in a position to model the regime as function of time, nor could a long term average be established. However, concentration data for chloroform were available both for the effluent and the receiving water on November 3, 1983. Therefore, a consistent determination of flow conditions at that particular time was feasible. The calibration was thus performed with respect to the data reported for November 3, 1983.

With the estimated discharge of chloroform (Table 5) it proved impossible to reproduce the measured ambient concentrations of this compound, as given in Table 6. Both models invariably predicted too low concentrations in "Milgrund" and "Svartgrund". Therefore, in the first place emphasis was put on reproducing the relative magnitude of the chloroform concentrations in the various compartments, rather than their absolute values. To achieve this the flow rates had to be modified, some rather drastically. Thus, the flows W-2 and W-7 were both reduced to 20% of their initial values (given in Table 3), W-5 to 50%, while W-6 could be left unchanged. These changes might appear quite large. One should bear in mind, however, that there is a definite uncertainty associated with the initial values as they are based on a regression relationship developed for the whole east coast of Sweden rather than on on-site measurements. Furthermore, the initial flow rates must be expected to represent a long-term average of the flow condition in Norrsundet, whereas the calibration will describe the situation prevailing at the time when the concentration measurements were made.

Keeping the flow rates at the levels specified above, one could reproduce the observed chloroform concentrations with a reasonable accuracy by increasing the discharge rate relative to the experimental values (Table 5). With EXAMS a two-fold increase, giving a rate of 2490 g/h, was required. With FEQUM the corresponding value was 2050 g/h. Even though the validity of the models must be considered uncertain, these results do indicate that the reported discharge rate of chloroform from Norrsundet Bruk underestimates the real load. A possible explanation why this might be so was provided above. At this point it is worth mentioning that no such explanation had to be invoked in the case of the test compounds investigated (see below).

The final results of the calibration are shown in Table 7.

The poor fit in the compartment "Rödhellan" is related to the fact that, with the flow pattern assumed in the model calculations, the concentration in "Rödhellan" is bound to be almost the same as that in the neighbouring compartment, "Klackarna". Consequently, as long...
The flows used are: 20%: W-2, W-7. 50%: W-5. 100%: W-1, W-3, W-4, W-6 and air flows as given in Table 4.

**TABLE 8 Measured and calculated concentrations of four chlorinated phenols in Norrsundet**

<table>
<thead>
<tr>
<th>Compartment</th>
<th>2,4,6-TrCP</th>
<th>3,4,5-TrCG</th>
<th>TeCG</th>
<th>TeCC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min max</td>
<td>min max</td>
<td>min max</td>
<td>min max</td>
</tr>
<tr>
<td>Milgrund</td>
<td>150 320 161 158</td>
<td>500 1600 749 821</td>
<td>400 1300 665 650</td>
<td>38 200 1570 1550</td>
</tr>
<tr>
<td>Svartgrun.</td>
<td>7 1 101 98</td>
<td>320 420 458 510</td>
<td>250 340 419 405</td>
<td>63 160 988 967</td>
</tr>
<tr>
<td>Klunken</td>
<td>43 74 37 38</td>
<td>120 237 156 194</td>
<td>45 214 152 155</td>
<td>97 356 371</td>
</tr>
<tr>
<td>Klackarna</td>
<td>46 17 17 17</td>
<td>36 64 87</td>
<td>4 25 68 69</td>
<td>97 157 168</td>
</tr>
<tr>
<td>Rødhällan</td>
<td>17 17 17 15</td>
<td>62 86</td>
<td>16 68 69</td>
<td>156 168</td>
</tr>
<tr>
<td>Utposten</td>
<td>6 6</td>
<td>15 21 28</td>
<td>8 8 22 23</td>
<td>- 52 55</td>
</tr>
<tr>
<td>Hackgr.</td>
<td>44 63 0 0</td>
<td>8 21 0 0</td>
<td>2 12 0 0</td>
<td>- 48 0 0</td>
</tr>
</tbody>
</table>

min = minimum measured concentration in the compartment (Xie et al., 1986)
max = maximum measured concentration in the compartment
EXAMS = concentration calculated by EXAMS.
FEQUM = concentration calculated by FEQUM.
As the models are calibrated to give good agreement with the average concentration in "Klackarna", which is much higher than that in "Rødhällan", an overestimation of the concentration in "Rødhällan" is unavoidable.

**Test runs on 2,4,6-TrCP, 3,4,5-TrCG, TeCG and TeCC**

To test the calibrated models calculations were performed for 2,4,6-TrCP, 3,4,5-TrCG, TeCG and TeCC using the flow pattern established in the calibration phase. The only changes made in the model input were the chemical-specific data and the pollutant load. The relevant parameters are given in Tables 1 and 5. The results of the test runs are summarized in Table 8.

As can be seen from Tables 6 and 8, calculated and measured concentrations agree quite well for most of the compounds. The only notable exception is TeCC, for which calculated values in the innermost compartments are almost ten times larger than those measured. This discrepancy can be explained, at least in part, by TeCC's high lipophilic character. Although not reflected in its octanol-water partition coefficient (Table 1), TeCC has been shown to have a
particularly high affinity to suspended particulate matter (Martinsen et al., 1987). The wastewater from Norrsundet Bruk contains a large amount of fibres and other types of organic matter which will tend to settle on the bottom and, consequently, act as a sink to TeCC. Neither FEQUM nor EXAMS can account for this kind of loss process in a proper way. In addition to this, TeCC is also more easily oxidized than the other chlorophenolics and is generally more difficult to analyse.

The model output also includes information on how the studied chemicals are removed from the system. The main sinks for the different compounds and their relative importance are given in Table 9. One important thing to notice is that, according to the calculations, the input of chlorophenolics to the Norrsundet area is to a large extent transported with the water across the system boundary.

**DISCUSSION**

When disregarding tetrachlorocatechol, both models give a reasonably good prediction of the water concentrations of the investigated chlorophenolics. In most cases the predicted values lie between the minimum and maximum concentration measured in the respective compartment. To obtain a numerical measure of the goodness of fit, linear regressions on observed and calculated concentrations were performed. The results are shown in Table 10.

As can be seen from Table 10, the correlation coefficients are quite close to 1, the smallest one being 0.87. This, however, merely demonstrates a linear relationship between measured and calculated concentrations. If the regression equations are considered, the picture is changed. In broad outlines, TeCC then differs from the other compounds by a large slope and y-axis intercept value. This shows that the models are unable to give correct predictions for TeCC. In contrast, with the other compounds the slopes are close to 1 and the y-axis intercepts almost at 0. The main reason why the intercepts are not exactly zero is the inability of the models to separate the concentrations in "Klackarna" and "Rödhällan". The calculated concentration in "Rödhällan" is too high, leading to a too high y-axis intercept.

Considering the coarse nature of the models themselves and the uncertainty surrounding many of the model parameters and parts of the chemical data one can hardly expect much better agreement than that obtained for 2,4,6-TrCP, 3,4,5-TrCG and TeCG. One should also recall that the measurements themselves are somewhat uncertain. This uncertainty, however, is likely to be less than that associated with the model parameters.

As can be seen from Table 8, the two models give quite similar results when applied to the present case, which is in agreement with previous experience (Aschjem 1987, Kolset et al. 1986). In fact, there is no basis for saying that one model is significantly better than the other with regard to predictive ability.

As already noted EXAMS partitions acids and bases into the relevant ionized and unionized forms whereas FEQUM does not. Since only the neutral form of the chemical can volatilize one would expect FEQUM to predict higher (total) concentrations than FEQUM for those compounds that exist predominantly in their ionic form. Of the substances studied here this applies to 2,4,6-TrCP, TeCG and TeCC. However, the effect of disregarding ionization is relatively small and tends to be masked by the other differences between EXAMS and FEQUM.

To arrive at a firm conclusion about the validity of the calibrated models, one would have to look at more compounds than those investigated in the present work. As there is a limited amount of information available on the ambient concentration of the relevant compounds such a task is difficult to accomplish. However, we feel that present results justify a reasonable

**TABLE 10 Regression And Correlation Coefficients**

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Cf</th>
<th>2,4,6-TrCP</th>
<th>3,4,5-TrCG</th>
<th>TeCG</th>
<th>TeCC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EXAMS</td>
<td>FEQUM</td>
<td>EXAMS</td>
<td>FEQUM</td>
<td>EXAMS</td>
</tr>
<tr>
<td>Y-axis Intercept ( (A) )</td>
<td>-0.01</td>
<td>0.1</td>
<td>22.6</td>
<td>22.5</td>
<td>63.4</td>
</tr>
<tr>
<td>Slope ( (B) )</td>
<td>1.02</td>
<td>0.96</td>
<td>0.60</td>
<td>0.58</td>
<td>0.70</td>
</tr>
<tr>
<td>Corr. Coeff. ( (R) )</td>
<td>1.0</td>
<td>1.0</td>
<td>0.86</td>
<td>0.87</td>
<td>0.97</td>
</tr>
</tbody>
</table>

\* Regression equation defined by: (Predicted conc.) = A + B \cdot (measured conc.)
Pollution of the Norrsundet Bay

degree of confidence in the calibrated models. More specifically, the results indicate that
the flow pattern arrived at may be a fairly good approximation to the stream condition which
existed in Norrsundet on November 3, 1983. The chemicals investigated in this work show a
considerable variation with respect to physicochemical properties (see Table 1). This fact
increases our confidence in the models.

It might be tempting to apply the established models to project the future development of
pollutant concentrations in Norrsundet under various discharge scenarios, e.g. a 50% 
reduction in the present load. Both EXAMS and FEQUM allow for this possibility. However, as
the time constants are likely to be several years (due to the presence of polluted
sediments), using the models for this purpose presupposes that the flow pattern determined in
the calibration is close to annual average flow conditions. As we have no indication whether
this is the case, an application such as that suggested would be uncertain. It might be better
to employ the flow data of Jonsson (1985) if the development of pollutant concentrations is
to be investigated.

There are a number of parameters in the models which we had to estimate or simply leave out.
Several of these, including currents and amounts of suspended particulate and biotic (i.e.
planktonic) matter in the receiving water, could have been determined relatively easily
through field measurements. This suggests that one should start the work with dispersion
models at an early stage in the investigation of a receiving area, when the measurement
programme is being planned. Taking due account of the data required by the models will give a
better likelihood of high quality results, and a much better model of the receiving area.

SUMMARY AND CONCLUSIONS

The results presented in this work show that the models EXAMS and FEQUM are both capable of
predicting the concentrations of some selected chlorophenolics in the Norrsundet area as
accurately as one can reasonably expect. Thus, the predicted values for the test compounds
were mostly between the maximum and minimum values measured in the relevant compartments.
These findings give some indication that the calibrated models give a roughly correct picture of
the flow pattern at the particular time of concern and that, except for sedimentation, all
important chemical transformation and loss processes are reasonably well described by the
models. It is noticeable, however, that a considerable increase in the reported discharge of
chloroform had to be assumed in order to reproduce the concentrations of that compound. Also,
a substantial modification of the initial estimated flow conditions in the area had to be
made. The concentrations of one compound, tetrachlorocatechol, were greatly overestimated by
both models. This can be explained by the high affinity of this compound for particles
together with the fact that neither of the models investigated can properly account for
sedimentation processes.

In the present work we were somewhat hampered by the fact that much of the data needed to
adapt the models to the studied environment in a satisfactory way were unavailable. In
particular, information on water currents was very scarce. This experience suggests that if
dispersion models are to be a really useful tool in the investigation of coastal waters
receiving industrial waste, the modelling work and field measurements should be closely
coordinated.

This work was meant as a preliminary investigation of the Norrsundet area and as part of a
study aimed at elucidating the usefulness and relative merits of EXAMS, FEQUM and similar
models in describing pollutant dispersion in bounded coastal areas such as bays and
estuaries. Much work has still to be done in this field. We feel, however, that the results
obtained are encouraging enough to warrant further investigations along the lines pursued
here.

ACKNOWLEDGEMENT

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REFERENCES


