Geo-referenced Stream Pollution Modeling and Aquatic Exposure Assessment

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Abstract: The model system GREAT-ER ("Geography-referenced Regional Exposure Assessment Tool for European Rivers") was developed to simulate and assess substance burden of European river basins from point sources. Spatial data sets on river geometry, topography, substance consumption, waste water treatment and discharge are integrated using the geographic information system ArcView to input and visualise data. The whole river network is divided into segments. Discharge from sewage treatment plants to water is simulated via concatenated substance flow models of waste water paths. Using Monte-Carlo simulations the probabilistic distribution of concentration profiles in effluents and river water is calculated as a function of residential sewage water treatment, hydrological flow distribution and chemical substance properties. A transport and elimination model describes downstream fate of the chemical. Temporal concentration distributions of chemicals in each river reach were calculated from variable and uncertain input data. The method was developed for selected pilot areas in the UK using detergents LAS and boron as reference chemicals. GREAT-ER was successfully applied to other chemicals in various German and other European catchments. With the example of the polycyclic musk fragrance HHCB in the Main River, a tributary of Rhine River in Southern Germany, it is illustrated how the concentration pattern in the whole catchment evolves. Monitoring data from a specific program was used to assess the quality of simulations.

Keywords: *River basins; Pollution; Exposure assessment; GIS-model coupling; Modeling*

1. INTRODUCTION

Point as well as non-point sources discharge nutrients, heavy metals, pesticides, and many other industrial and household chemicals into the reaches of a river system. Despite many efforts made to improve water quality, most European rivers (and worldwide) are still far from being in a good chemical and ecological state. The spatial and temporal pattern of waste water discharges and diffuse pollution is determined by the economy operating in the region and the population living there. River basins have a great variety of soil, land-use, climate and ecological factors. Therefore water pollution depicts a highly variable concentration and substance pattern in time as well as in space along the river network. Small streams often have the highest concentration and thus exposure to aquatic communities due to their low dilution of waste water. On the other hand, downstream reaches collect all polluted water from upstream and have therefore high loads which then may enter estuaries. To cope with spatial and temporal variability of polluted river systems a geo-referenced modeling approach has been developed. Socioeconomic and environmental spatial complexity can best be presented in a Geographic Information Systems (GIS), which provides appropriate tools for storage, management, retrieval, analysis and visualization of hydrological, demographic and other spatial data bases. With a simulation model dynamics of substance transport and transformation through the downstream chain of waste water from its use and treatment to receiving water bodies are described. The model takes into account hydraulic, physicochemical and biological processes which affect quantity, structure and properties of the chemical in the waste water as well as in river water. By coupling to a GIS database, the model is provided with spatial heterogeneous properties of the river basin. Furthermore, simulation results can easily be visualized to support water managers and chemical risk assessors with geo-referenced stream pollution information. With the example of the polycyclic musk fragrance HHCB in the Main River, a tributary of Rhine River in Southern Germany, it is illustrated how the concentration pattern in the whole catchment evolves. Monitoring data from a specific program was used to assess the quality of simulations.

2. GEO-REFERENCED MODELLING

2.1. Model system description

The model system GREAT-ER ("Geography-referenced Regional Exposure Assessment Tool for European Rivers") was developed to simulate and assess chemical burden of European river systems by means of a spatially explicit, geography referenced modelling approach (Feijtel et al., 1997, Matthies et al., 2002). Main objective of GREAT-ER is calculation of aquatic exposure concentrations on a regional, river basin level. A modular approach has been developed to keep the implementation open for improvements and new elements:

- river network segmentation
- spatial data processing
- waste water pathway model
- simple hydrological model
- river fate model
- Monte-Carlo simulation
- graphical user interface

From the beginning of GREAT-ER development, comparison of simulated with measured concentrations was an indispensable part to test its validity. In addition, monitoring data can be used to elucidate additional, unreported, unrevelaed or unknown sources (Koormann et al., 1998) or to improve the hydrological model (Schulze and Matthies, 2001). Various catchments all over Europe were investigated with many different chemicals, mainly household chemicals, pharmaceuticals, pesticides, cleaning agents and detergents (see GREAT-ER homepage http://www.great-er.org).

2.2. River network segmentation

The whole digital river network is divided into segments (Fig. 1). A new segment (or reach) starts at a confluence, location of a gauging station, a discharge site, a weir or any other location where hydrological, hydro morphological, chemical or other river properties change. A division is made such that uniform conditions can be assumed within each reach. A reach can receive a discharge from an industrial or municipal waster water input. Downstream reaches transport, dilute, transform and degrade discharged chemicals. Any other discharge or confluence overlays upstream loads leading to a longitudinal variability of substance concentrations. A tree-walking algorithm guarantees correct topological representation of the river network (Koormann et al., 1998).

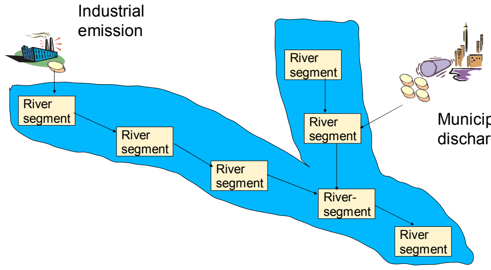

Figure 1. Segmentation of a river network.

2.3. Spatial data processing

All reaches of a catchment are attributed with spatial data on hydrological flow, river bed geometry, flow velocity and other properties. Discharge sites are waste water treatment plants (WWTP) which are spatially related to corresponding receiving reaches. Maps with demographic, topographic and background data are processed to visualize the catchment under investigation (Fig. 2). Chemical market data are used to estimate average per-capita consumption of 'down-the-drain' chemicals. GREAT-ER is implemented under Windows-NT using ArcView as GIS-based graphical user interface. In a first step, all spatial data are transformed manually or semi-automatic into a predefined data format. In the next step, they are automatically converted into a consistent geo-referenced data set.

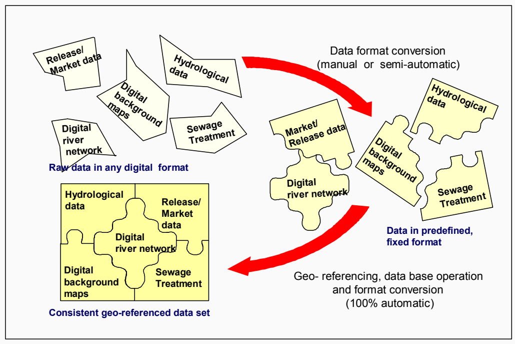

Figure 2. Spatial data processing.

2.4. Simulation models

GREAT-ER is designed to calculate emission data of a chemical from average consumption figures, population connected to the waste water system and specific industrial discharges. A chain of coupled simulation models was developed to describe down-the-drain transport from use in households or industry through sewer and treatment systems to the receiving water body (Fig. 3). Depending on available information different complexity modes for each sub-model can be selected. Mode 1 only consists of basic data on average consumption, sewage treatment efficiency and lumped first-order degradation rates in the river. Different treatment methods (mechanical, trickling filter, activated sludge) are distinguished in their elimination efficiency. Mode 2 models the behaviour of a chemical in a standard treatment plant with SimpleTreat, which is also used in EUSES software package, developed for chemical risk assessment in the EU (EC 1996). During the last few decades a lot of experience was gained which enabled a better understanding of the processes governing fate of chemicals in aquatic ecosystems (Van Leeuwen and Hermens, 1995; Trapp and Matthies, 1998). This knowledge was used in mode 3 to model the various processes in river reaches. Dilution, advective transport, sorption to suspended matter, volatilization, abiotic and biotic degradation is taken into consideration. Hydrological flow data are derived from long-term historic time series of gauging stations. Discharges are interpolated between gauging stations by using a non-linear regression equation (Schulze and Matthies, 2001).

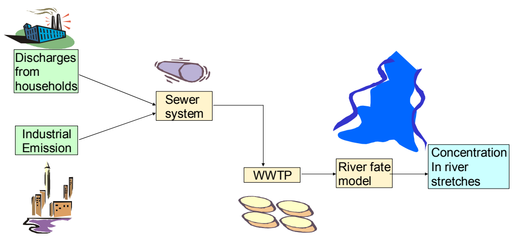

Figure 3. Coupled models for down-the-drain chemicals.

2.5. Probabilistic approach

A comprehensive risk assessment requires estimation of the probability of an adverse effect on man, animals or ecological communities from possible exposure to substances. Often a 90th or 95th percentile is taken for risk assessment. GREAT-ER provides users with a probabilistic approach. All input data, in particular hydrological data, can be expressed as time-dependent frequency distributions. By a Monte-Carlo simulation joint probabilities of output, i.e. concentrations in all reaches can be determined instead of one deterministic value. GREAT-ER calculates temporal variability and uncertainty for each reach, from which any percentile can be derived. Moreover, mean concentrations in all reaches (or any percentile) can be statistically analyzed to give the spatial frequency distribution of the catchment. Thus a two-dimensional frequency distribution of concentrations in a catchment is calculated representing spatial and temporal probability distribution in a catchment.

3. PILOT STUDIES WITH DETERGENTS

GREAT-ER was developed by a European consortium consisting of five institutions sponsored by ERASM/CEFIC (ECETOC, 1999). Two pilot areas were selected to develop the methodology. One study area was Ouse River in Yorkshire (UK), the other upper Lambro in Northern Italy. A comprehensive monitoring campaign was carried out to test model quality for which detergent ingredients LAS (n-dodecylalkylbenzene sulfonate) and boron were chosen. The arbitrary chosen quality objective was to stay below a factor of three between average simulated and measured concentrations without any fitting or calibrating the model. Fig. 4 shows the graphical user interface of GREAT-ER with the color coded map of mean simulated concentrations of LAS in Calder River (UK). The user can immediately see the pattern of LAS concentrations along the whole river network together with locations of WWTPs, cities and any other information. Moreover, he/she can depict the profile in a chart with mean and 90th percentile of simulated concentration distributions in each reach. Figure 5 shows simulated values for LAS in Calder River (UK) with none of the model parameters fitted. The 90th percentile demonstrates simulated spread. A 2-year monitoring campaign was carried out with a 2-week sampling period. Simulated and measured means were in good agreement. Measured spread was lower than the simulated one indicating that uncertainty of input parameters is higher than actual variability depicted by the monitoring campaign. Figure 6 shows that measured and simulated means for the whole investigated catchment in Yorkshire are well within a factor of three, which was the objective of the pilot study.

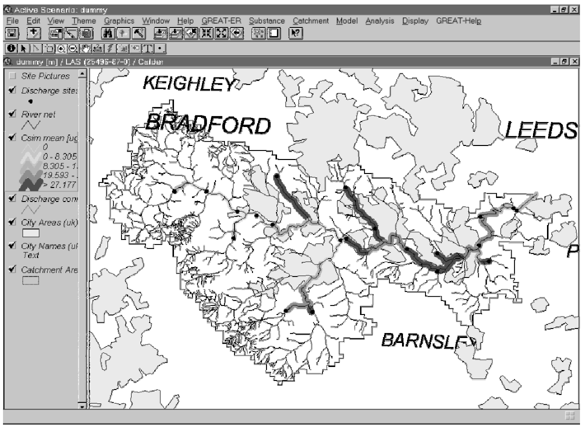

Figure 4. Visualization of the LAS concentration in Calder River (UK).

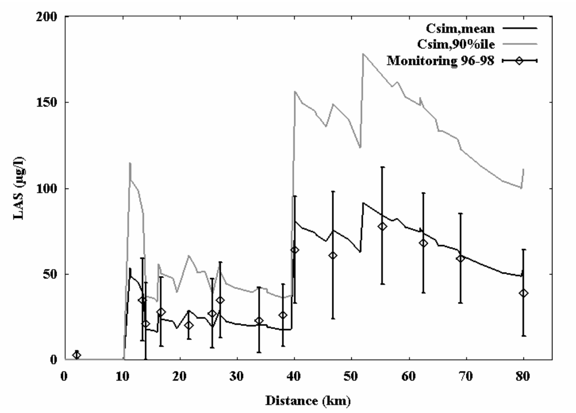

Figure 5. Chart of mean and 90th percentile of LAS concentration in Calder River (UK).

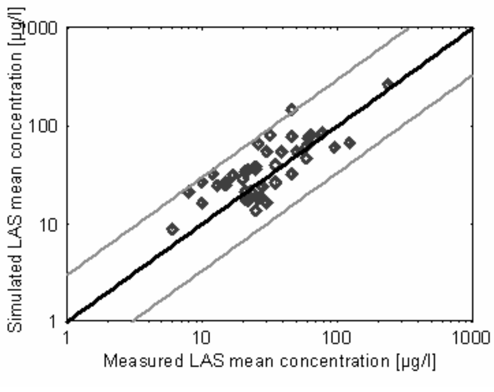

Figure 6. Quality check of simulation with LAS concentrations in Ouse catchment (UK); upper and lower line give range of 3 and 1/3.

4. APPLICATION WITH THE MUSK FRAGRANCE HHCB IN MAIN RIVER CATCHMENT

4.1. Substance Characteristics

Synthetic musk fragrances are essential ingredients in numerous perfumes, cosmetics and personal care products, soaps, detergents, and other cleaning agents (Ohloff, 1990). Since the early 1990s not only nitro musk compounds, but also polycyclic musk fragrances have been detected in rivers and the sea, fish, human adipose tissue and human milk (Rimkus and Wolf, 1996). Seven single compounds are involved, of which HHCB (1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-[g]-2-benzopyran; CAS-No. 1222-05-5; trade name: e.g. Galaxolide®) occurs with highest concentrations in the environment. Due to its ubiquitous occurrence in the aquatic environment, its bioaccumulation and neurotoxic effects potential, it has recently returned to the public eye.

Despite its versatile usage, a consumption rate of up to 2,400 t/a in Europe, and environmental concentrations of up to 1.2 µg/l in rivers, 63 mg/kg (dry weight) in sewage sludge and 63.6 mg/kg in fat tissue of fish (Plassche and Balk, 1997), these chemicals have not yet been investigated in sufficient detail. This situation hampers the comprehensive assessment of ecological risks posed by these compounds. In addition to data concerning the effects of these substances, information on their fate and environmental exposure is also necessary.

Table 1: Selected properties of HHCB

CAS number	1222-05-5
Molar mass	258.4 g/mol
Log K_{ow}	5.9
Water solubility	1.75 mg/L
Vapor pressure	0.073 Pa
Henry's law constant	11.3 Pa m^{-3} mol^{-1}
Estimated per-capita consumption	4.015 g/a
Volatilization rate constant	0.008 - 0.040 h^{-1}
WWTP elimination efficiencies [1]	
Trickling filter plants	83 % ± 4 %
Activated sludge	92 % ± 4.6 %

[1] data from Simonich et al., 2000

The synthetic polycyclic musk fragrance HHCB was detected in many German river basins with variable concentrations. Environmental standards have not been issued so far. Here, Main River which is a tributary of Rhine River in Southern Germany was investigated with GREAT-ER.

4.2. Catchment characteristics

The catchment map of the Main River is shown in Fig. 7. It has an area of 27,230 km². The total length of the river is 524 km. About 6.7 million inhabitants are living in the area discharging their waste water via more than 1,150 municipal sewage treatment plants. Agriculture, vineyards, metal industry and other industrial branches are also located there. They are mostly connected to industrial treatment plants of which more than 750 discharge directly into Main River and its tributaries. Hydrological flow is routinely measured at about 200 gauging stations. A monitoring campaign of river-borne organic substances was carried out which also involved the musk fragrance HHCB.

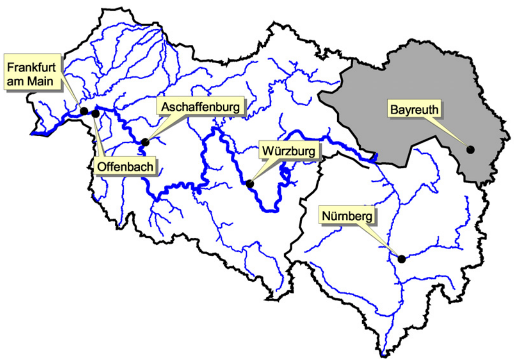

Figure 7. Map of Main River catchment.

4.3. Simulation results

Besides elimination in wastewater treatment plants volatilization from water is the only important loss process for HHCB. As can be seen from Table 1 estimated volatilization rates vary within almost one order of magnitude due to temporal and spatial variability of environmental parameters like water depth, flow rate and wind speed. A mean volatilization rate constant of 0.015 h^{-1} was estimated for the river reaches of the main channel where the transport of HHCB mainly takes place. Temporal variability of volatilization is represented by the probabilistic approach assuming a coefficient of variation of 33%.

Figure 8 shows a typical graphical representation of mean simulated HHCB concentrations in the Main catchment using this rate as in-stream removal rate in mode 1 (lumped approach). It can be clearly seen that highest concentrations (dark orange lines) are located in the highly urbanized area of Frankfurt/Main and in some tributaries where dilution of polluted wastewater is low due to small volume flows of water.

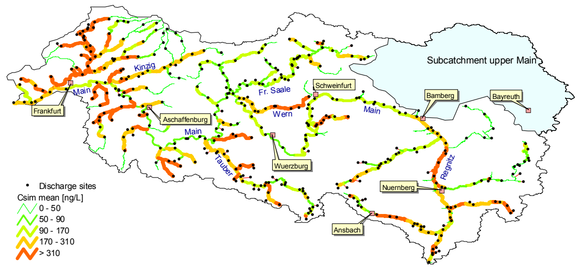

Figure 8. Mean simulated concentrations of HHCB in the Main catchment classified into five concentration classes.

Calculated concentrations in the main channel of Main River are in the intermediate range. In Figure 9, these concentrations are compared to monitoring data taken in May, 1998 to provide a better picture of the concentration profile in the Main River itself and to verify model results.

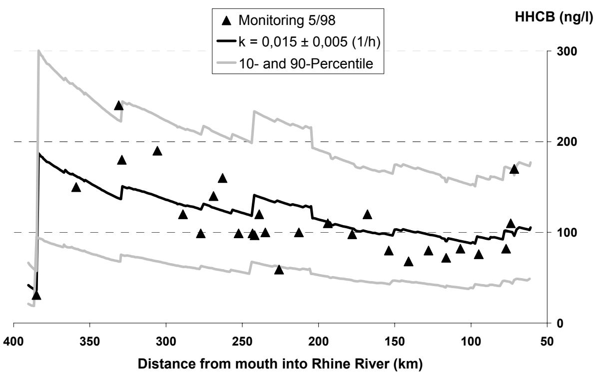

Figure 9. Measured and simulated concentration profile of HHCB along Main River.

Mean simulated concentrations agree well within the arbitrarily defined target value of factor three with monitoring data. All data points are within the interval given by the 10th and 90th percentile (gray lines in Figure 9), respectively. Moreover, relative profiles along Main River are very similar indicating that dominating processes are correctly mirrored by the model.

Additionally, it has to be pointed out that measured data represent actual concentrations from May, 1998 whereas GREAT-ER simulates longtime mean steady-state concentrations. Besides ignoring spatial variability of volatilization this is a probable reason for observed deviations between monitoring and simulation results. However, results demonstrate general applicability of the model for household chemicals like HHCB in larger catchments.

5. CONCLUSIONS AND OUTLOOK

The application of GREAT-ER to the musk fragrance HHCB in Main River demonstrates that the geo-referenced simulation methodology can be transferred to other catchments and simultaneously to other substances. Simulation runs with higher complexity modes could provide more insight into the effect of the dominating processes, but also require more detailed input data which are often not available. Nevertheless, a more detailed analysis of the fate of HHCB in various catchments using complexity mode 3 is in progress. Ongoing projects extend GREAT-ER to Rhine and Elbe River basins. GREAT-ER was selected for integration into the DSS-Elbe (decision support system) to evaluate measures to achieve a good chemical state according to management objectives of EU Water Framework Directive (Matthies et al., 2003).

6. ACKNOWLEDGEMENTS

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