GEO-REFERENCED PREDICTION OF ENVIRONMENTAL CONCENTRATIONS OF CHEMICALS IN RIVERS: A HYPOTHETICAL CASE STUDY

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ABSTRACT

For use within environmental risk assessment, a new tool for chemical fate prediction, GREAT-ER (Geography-referenced Regional Exposure Assessment Tool for European Rivers), is being developed. In this paper, the practical applicability of the GREAT-ER simulation methodology is illustrated, by means of a hypothetical but realistic case study. Temporal distributions of predicted environmental concentrations (PEC) were calculated and analyzed. For the analysis of seasonality (i.e. the variability of river flows through the year), the Monte Carlo simulation technique was compared to a discrete ‘flow scenario’ approach. Finally, the scale-independent character of the approach was investigated, by upscaling from a detailed to a larger geographical scale.

INTRODUCTION

The objective of the GREAT-ER project is the development and validation of a powerful and accurate exposure prediction tool for use within the EU environmental risk assessment schemes (Feijtel et al., 1997). This research is carried out on behalf of the European Center for Ecotoxicology and Toxicology of Chemicals (ECETOC). The system will allow to simulate the aquatic fate of individual ‘down-the-drain’ chemicals. These are consumer chemicals which mainly enter the environment via domestic waste water (e.g. detergents). Environmental information and chemical market data will be integrated by means of a Geographic Information System (GIS), ultimately on a pan-European scale. A geographically referenced simulation methodology was developed (Boeije et al., 1997). Real-world input data are used, including their spatial and temporal variability and uncertainty. The simulation results are geo-referenced statistical frequency distributions of predicted environmental concentrations (PEC).

In this paper, first a short description is given of the simulation approach, and the models which were implemented for this hypothetical case study. Next, the case study area is described. The resulting PECs are shown and their statistical distributions are analyzed. The difference between Monte Carlo simulation and discrete simulations is illustrated. Finally, the effect of modeling the case study catchment at a larger geographical scale is investigated..

SIMULATION APPROACH

A hybrid simulation approach is applied, using stochastic and deterministic techniques. The system’s core is formed by a steady-state deterministic fate model. In this model, chemical fate is predicted, based on site-specific environmental conditions and on physical-chemical and biological properties of the substance. A stochastic simulation is applied on top of this, to deal with seasonal variation and parameter uncertainty.

Segmentation

Geographies are divided into interconnected segments, in each of which one or more processes occur. Rivers are represented by a digital river network, of which the segmentation is determined by homogeneous hydrological conditions and by waste water inputs. A geographical segment consists of one river stretch, together with (if a discharge occurs) a Geographic Unit (GU) describing the waste water pathway (Figure 1). The methodology is scale-independent. One can move from a detailed scale to a larger scale by aggregating multiple discharge points and by grouping several river stretches into a single large stretch. Hence, all described processes can be either 'real' or 'hypothetical' (e.g. an aggregated discharge).

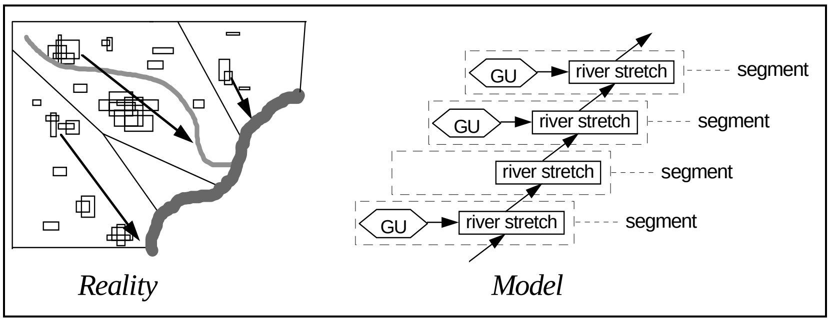

Figure 1. Geographical segmentation

Deterministic Fate Model

The deterministic fate model consists of two main parts. (1) In the waste water pathway model, all processes which occur in the waste water drainage area of a river discharge point are considered. Domestic 'down-the-drain' chemical emissions are predicted from market and population data. These are further processed in sewer and treatment models, resulting in chemical mass fluxes into rivers. (2) In the river fate model, downstream chemical transport and further conversion processes in these rivers are simulated, resulting in PECs for each river stretch.

The described 'blueprint' system can be adapted to the needs of the application. Both the general structure and the interconnections between different processes can be altered. Different fate models and/or solution algorithms can be implemented for each process (or sub-process).

Stochastic Simulation

The input data are statistical frequency distributions, which encapsulate both seasonal variation (e.g. distribution of river flows) and parameter uncertainty. By means of a Monte Carlo simulation, a large number of discrete samples (shots) are taken from these input distributions. The individual shots are used as input for the deterministic model (Figure 2). Afterwards, the discrete model results are statistically analyzed, and are described as PEC frequency distributions for each river stretch.

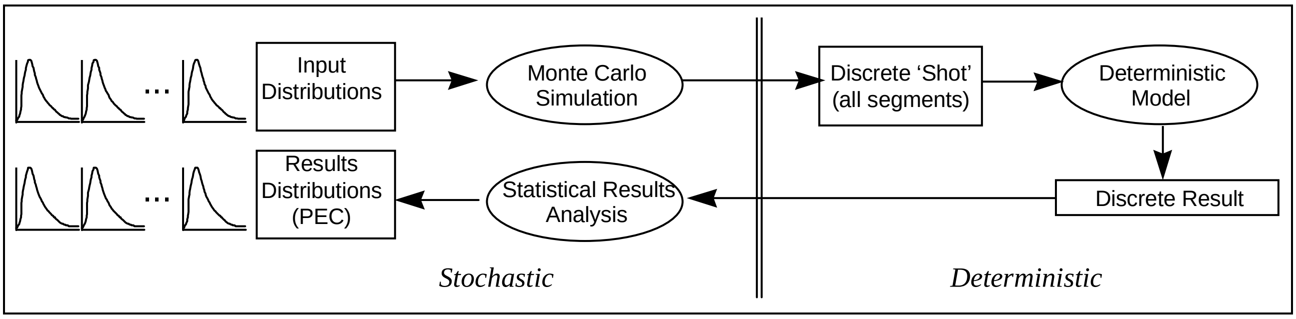

Figure 2. Hybrid simulation approach

IMPLEMENTATION

A simple implementation of the described simulation approach was developed, to perform a hypothetical case study. A simplified waste water pathway structure and low-complexity models were selected, as the objective was to demonstrate the feasibility of the approach and its general behavior, rather than analyze the potential accuracy of the predictions.

Waste Water Pathway Structure

The following processes were considered: domestic emission, combined sewers, waste water treatment, and the river. Within one segment, these processes were interconnected as shown in Figure 3.

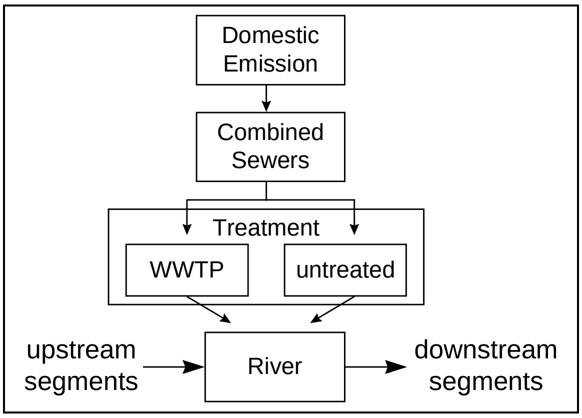

Figure 3. Processes within one segment

Models (Symbols and units: see appendix)

The models' state variables are fluxes: chemical mass fluxes and water flows. At any step, concentrations can be obtained simply through dividing the chemical mass flux by the water flow.

- *Domestic Emission*

Chemical mass fluxes were calculated from market data (product sold per person per year) and population data. Domestic waste water flows (i.e. dry weather flows) were similarly derived from daily water consumption and population.

$$\Phi_{out}^{dom} = M \cdot P \qquad Q_{out}^{dom} = Q_{dwf} = W \cdot P$$

- *Combined Sewer*

No chemical elimination processes in the sewer system were considered. The combined sewer flow was assumed to be related to the (calculated) dry weather flow. A correction factor α was used to derive the sewer flow from this dry weather flow. If $\alpha < 1$, leakages occur; if $\alpha > 1$, the waste water is diluted by rainfall or by infiltration of groundwater. It was further assumed that α can be described by a log-normal distribution. For the given hypothetical case, the mean was set to 1.5, while the 5th percentile was set to 1. This implies that the mean sewer flow is 1.5 times the dry weather flow, while the 5th percentile low sewer flow is equal to the dry weather flow.

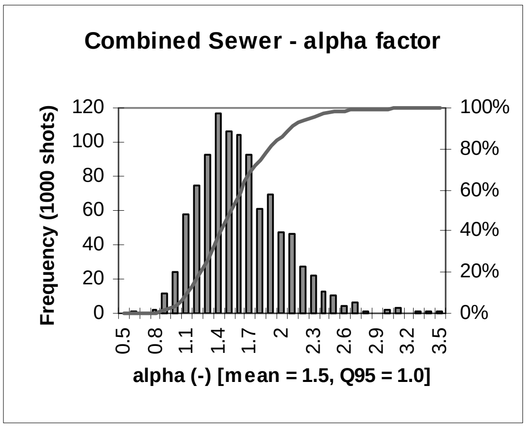

Figure 4. Combined Sewer - α

$$\Phi_{in}^{sewer} = \Phi_{out}^{sewer} = \Phi_{out}^{dom} \qquad Q_{in}^{sewer} = Q_{out}^{sewer} = \alpha \cdot Q_{dwf}$$

- *Waste water treatment*

The treatment process consists of an untreated discharge model and a waste water treatment plant (WWTP) model. The inflows were calculated as shown below:

$$\Phi_{in}^{untreat} = \Phi_{out}^{sewer} \cdot f_{untreat} \qquad Q_{in}^{untreat} = Q_{out}^{sewer} \cdot f_{untreat}$$

$$\Phi_{in}^{wwtp} = \Phi_{out}^{sewer} \cdot f_{wwtp} \qquad Q_{in}^{wwtp} = Q_{out}^{sewer} \cdot f_{wwtp}$$

In the untreated discharge model, no chemical elimination or changes in flow were assumed.

$$\Phi_{out}^{untreat} = \Phi_{out}^{untreat} \qquad Q_{out}^{untreat} = Q_{in}^{untreat}$$

The WWTP consists of a bypass model and an actual treatment model. In the bypass model, a plant's maximal hydraulic capacity is assumed to be $3 \cdot Q_{dwf}$. The treated fraction is calculated as:

$$\text{if } Q_{in}^{wwtp} > 3 \cdot Q_{dwf} \quad \text{then} \quad f_{treated}^{wwtp} = 1 - \frac{Q_{in}^{wwtp} - 3 \cdot Q_{dwf}}{Q_{in}^{wwtp}} \quad \text{else} \quad f_{treated}^{wwtp} = 1$$

The actual treatment model describes chemical elimination based on a given (chemical-specific) removal percentage. Flow is assumed constant through the plant.

$$\Phi^{wwtp}_{out} = \Phi^{wwtp}_{in} \cdot \left[1 - f^{wwtp}_{treated} \cdot R_{wwtp}\right] \qquad Q^{wwtp}_{out} = Q^{wwtp}_{in}$$

- *River*

The chemical mass flux into a river was calculated as the sum of the different inputs. Flows were not calculated, but were taken as such from the hydrological dataset (which was assumed to be hydraulically consistent). Hence, no flow mass balancing was required.

$$\Phi^{river}_{in} = \Phi^{river}_{upstream} + \Phi^{wwtp}_{out} + \Phi^{untreat}_{out} \qquad Q^{river}_{in} = Q^{river}_{out} = Q^{river}$$

A 1st order elimination model was applied to describe chemical in-stream removal. The river stretch travel time was calculated from length and flow velocity. The latter was estimated from actual and mean river flow, according to the method for English catchments by Round & Young (1997).

$$\Phi^{river}_{out} = \Phi^{river}_{in} \cdot e^{-k_{river} \cdot HRT} = \Phi^{river}_{in} \cdot e^{-k_{river} \cdot \frac{l}{v} \cdot \frac{1}{3600}} \qquad v = 10^{-0.599} \cdot \left(Q^{river}_{actual}\right)^{0.286} \cdot \left(\frac{Q^{river}_{actual}}{Q^{river}_{mean}}\right)^{0.165}$$

Next to this, so-called ‘internal’ values were also calculated for each river stretch. These were defined as the average value of the exponential decay curve between the maximal and the minimal value in the stretch.

Monte Carlo Simulation

By means of a 1000 shot Monte Carlo simulation, the variability of the parameters mentioned in Table 1 was incorporated into the simulation. The correlation between the river flow and the factor α (and hence also combined sewer flow) was assumed to be 0.6. This was taken from the defaults used in the SIMCAT model (NRA, 1990).

Table 1. Parameters used in Monte Carlo simulation

Parameter	Description	Distribution	Correlation to river flow
Q^{river}	river flow	lognormal	1
R_{wwtp}	chemical elimination percentage in a WWTP	normal	0
α	combined sewer flow correction factor	lognormal	0.6

Only the variability of flows and the uncertainty on chemical elimination in WWTPs was taken into account. Hence, this exercise was not a complete uncertainty analysis, and the resulting PEC distributions had relatively narrow uncertainty boundaries. In simulations including all possible uncertainty factors, much wider PEC distributions are expected.

DESCRIPTION OF THE HYPOTHETICAL CASE STUDY

Hypothetical Catchment

A hypothetical but realistic catchment was constructed, which consists of a main river and one tributary. Along the main river, there are two large cities (A and B), which discharge their waste water into the river, after treatment or untreated. The tributary runs through a rural area with disperse population, which discharge their untreated waste water directly into the tributary. A representation of this catchment is given in the left half of Figure 5. The right half of the same Figure shows the applied segmentation. A schematic representation, including segments identification numbers (Segment ID), is given in Figure 6. Segments containing a waste water input were labeled with ‘D’.

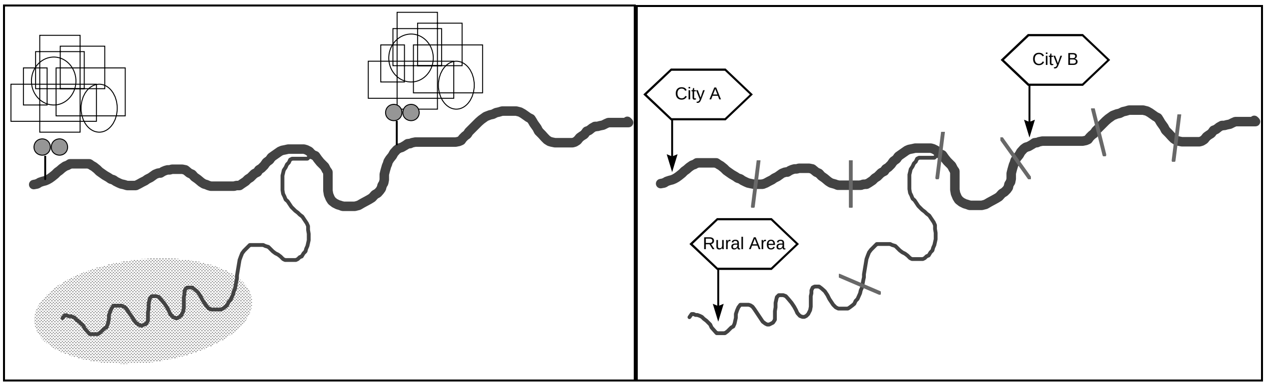

Figure 5. Hypothetical catchment

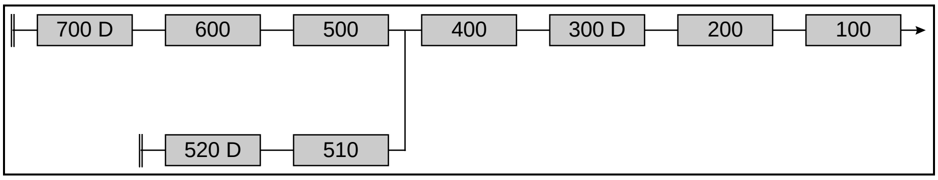

Figure 6. Hypothetical catchment - schematic representation

The river stretches and waste water discharge properties are shown in Table 2. For all discharges, the per capita water consumption was assumed to be 200 L/cap.day.

Table 2. River and discharge properties

Segment ID	river stretches				discharges	
	length (km)	distance* (km)	mean flow (m^3/s)	Q95 flow (m^3/s)	# people (cap)	% treated (-)
main river						
100	10	10	66.00	49.50	-	-
200	10	20	65.00	48.75	-	-
300	10	30	64.00	48.00	750000	50 %
400	10	40	63.00	47.25	-	-
500	10	50	52.00	39.00	-	-
600	10	60	51.00	38.25	-	-
700	10	70	50.00	37.50	500000	75 %
tributary						
510	25	65	10.00	6.00	-	-
520	25	90	8.00	4.80	100000	0 %

* distance from the most upstream point of the stretch to the end of the catchment

Hypothetical Chemicals

Two hypothetical chemicals were defined: a conservative chemical A and a degradable chemical B. The chemical properties and market information are given in Table 3. It is stressed that these chemicals are not related to any existing or new substance.

Table 3. Chemical properties and market data

	chemical A	chemical B
product consumption	2 kg/cap.year	2 kg/cap.year
in-stream removal rate	$0\ h^{-1}$	$0.069\ h^{-1}$ ($t_{0.5} = 10$ h)
WWTP elimination percentage	0 % ± 0 %	95 % ± 5 %

RESULTS & DISCUSSION

Predicted Environmental Concentrations (PEC)

- *Main River PEC Profiles* (Figure 7)

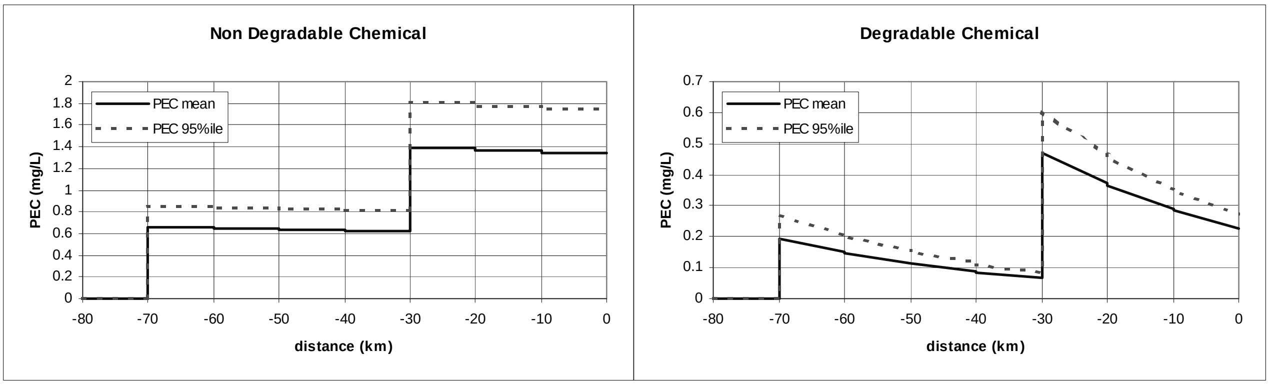

Figure 7. Main river PEC profiles

Discussion:

The impact of the discharges of both cities is obvious. The tributary (at 40 km) results in a slight PEC decrease, which suggests that the tributary has a slight dilution effect on the main river. The PEC decrease after both cities is caused by increasing dilution and by in-stream-removal (for Chemical B only). The uncertainty boundaries in this experiment are very narrow. This is due to the fact that only a limited uncertainty analysis was performed.

- *Tributary* (Table 4)

Table 4. Tributary: PECs at the tributary mouth (and in main river at same location)

	Chemical A		Chemical B	
	Tributary	Main River	Tributary	Main River
PEC_{mean} (mg/L)	0.699	0.627	0.082	0.085
$PEC_{95\%ile}$ (mg/L)	1.082	0.816	0.086	0.109

Discussion:

The tributary’s dilution is sufficient to reduce its relative impact on the main river PEC, as is shown for Chem. A. For Chem. B, PECs are further reduced by in-stream removal, and - even though the tributary receives the untreated waste water of 100,000 people - the tributary dilutes the main river.

- *Discharges of Cities A and B* (Table 5)

Table 5. Discharges of Cities A and B: concentrations and chemical mass fluxes

	Chemical A		Chemical B	
	City A	City B	City A	City B
PEC_{mean} (mg/L)	27.379	27.379	7.686	13.944
$PEC_{95\%ile}$ (mg/L)	62.303	62.303	17.749	31.999
Φ_{mean} (g/s)	31.710	47.56	9.429	25.284
$\Phi_{95\%ile}$ (g/s)	31.710	47.56	12.046	27.901

Discussion:

For the conservative Chemical A, the PEC distributions are identical for both cities, as these values only depend on - assumed identical - market data and domestic water consumption. For Chemical B, the uncertainty of the mass fluxes can be explained by the variability of WWTP removal and plant bypassing.

- *Extremely High Flow Events*

Plant bypassing occurred in 82 of the 1000 Monte Carlo shots. As this is above the 5% threshold, the 95th percentile PECs were influenced by these extreme flow events.

Analysis of PEC Distributions (degradable Chemical B)

For 3 locations in the study area, an analysis of the PEC distributions of Chemical B was made: the discharge (effluent) from City A, the mixing zone of this discharge in the river, and the end of the catchment (segment 100) (see Figure 8).

- *Description of PEC Distributions*

PEC distributions are described by their mean and 95th percentile values. The latter was obtained (1) by assuming log-normality (using the method of moments) and (2) by complete statistical analysis of the results dataset. Skewness of the distributions was also determined (Table 6). These distributions are illustrated by the histograms in Figure 8, together with their geographical locations.

Table 6. Description of PEC distributions

	City A discharge	City A mix. zone	End of Catchment
PEC_{mean} (mg/L)	7.69	0.193	0.226
$PEC_{95\%ile}$ assuming log-normality (mg/L)	17.75	0.269	0.271
$PEC_{95\%ile}$ from statistical analysis (mg/L)	18.22	0.278	0.275
skewness -	2.37	0.76	0.39

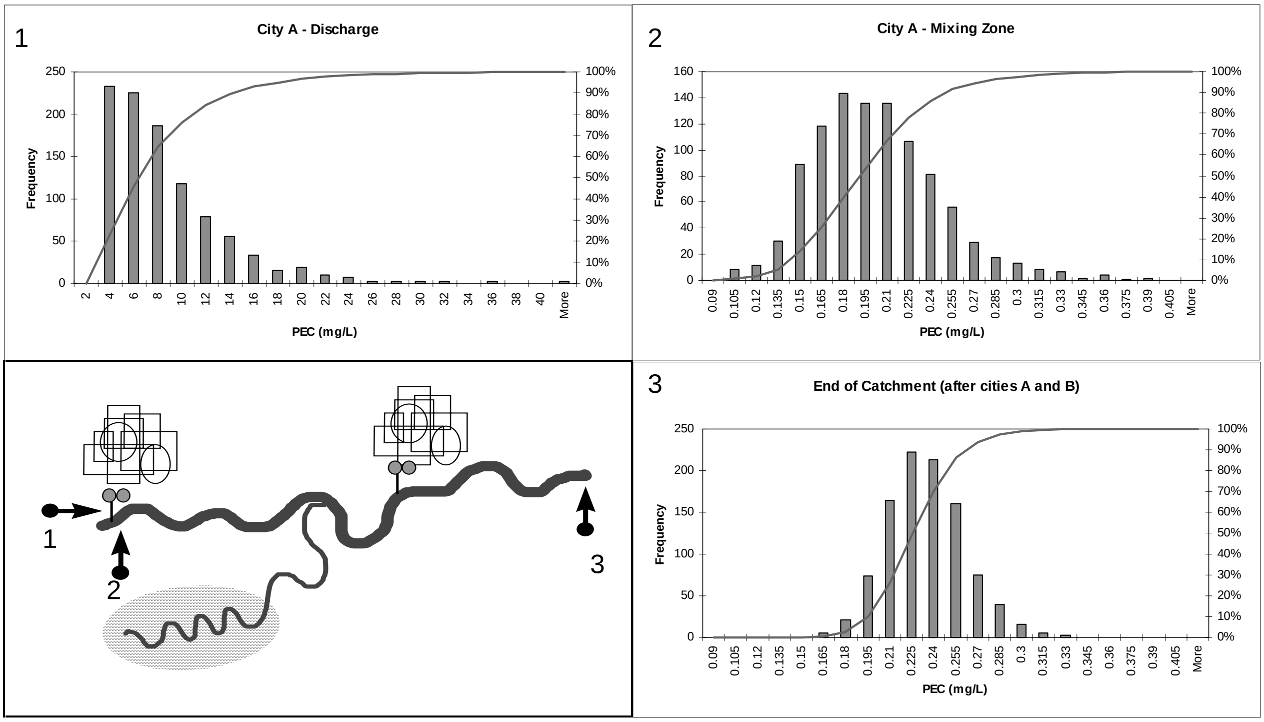

Figure 8. PEC distributions

Discussion:

The 95th percentile PECs calculated using the log-normality assumption corresponded well with the true 95th percentiles. The skewness in the river was lower than in the discharge, due to leveling out of high sewage PECs by high river flows (the correlation between river and sewer flows was 0.6). The lower skewness at the end of the catchment can be explained by leveling out due to multiple discharges and the effect of in-stream removal.

- *Log-Normality Test*

A one-sample Kolmogorov-Smirnov test (on the logarithms of the PECs), using a significance threshold $\alpha = 0.05$, showed that the log-normality assumption for all three PEC distributions was valid.

Monte Carlo Simulation versus Flow Scenario Approach

An alternative to Monte Carlo simulation for dealing with flow seasonality, is the calculation of PECs from discrete Flow Scenarios. In this case, one obtains a PEC from a single simulation at mean flow: PEC(Qm). From another simulation, at the 5th percentile flow, one obtains PEC(Q95). Both calculation approaches were compared (using ‘internal’ PECs). The relative difference of the discrete PECs at these two Flow Scenarios and the corresponding Monte Carlo simulation PECs are shown in Figure 9.

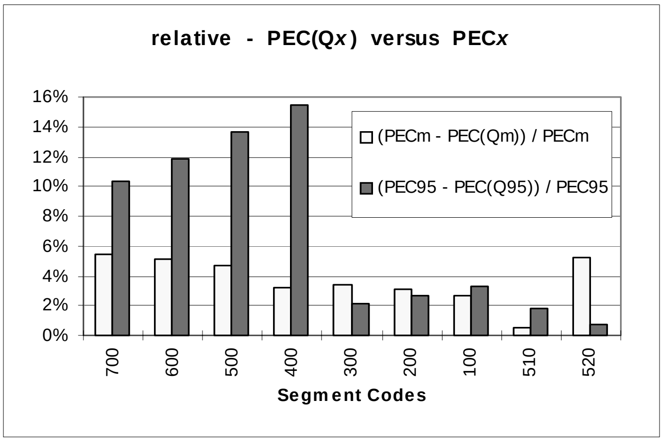

Figure 9. Flow Scenario vs. Monte Carlo

<u>Discussion</u>:
Mean PEC and PEC at mean flow were very similar for all segments. In some cases, the PEC at Q95 significantly under-estimated the 95th percentile PEC (10 - 15 % deviation). From this, one can derive that the Flow Scenario approach can provide quick initial results (especially for mean PECs). For more detailed simulations, and especially for 95th percentile PECs, Monte Carlo approach was better-performing. Note that for a complete uncertainty analysis, Monte Carlo simulation is also required.

Spatial Aggregation

In another exercise, the entire catchment was represented by a single (aggregated) segment (Table 7). The river flow was taken from the final stretch in the detailed approach (segment 100). The aggregated stretch length was calculated as the weighted average (by population) of the distances from each discharge to the end of the catchment. For the aggregated discharge, the number of people was equal to the sum of all three discharges, and the WWTP connection degree was calculated as the average of the discharges, weighted by population.

Table 7. Aggregated Segment Properties

river flow	(m^3/s)	mean = 66.0 5th %ile = 49.5
river length	(km)	49.25
population	(cap)	1350000
% connected to treatment	(-)	55.56 %

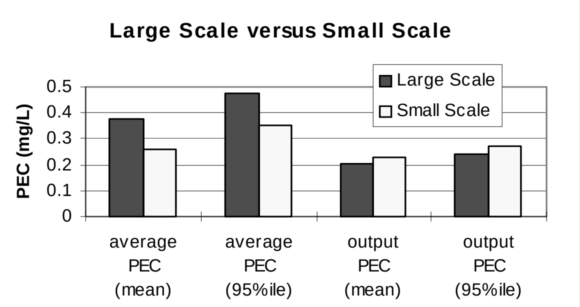

Figure 10. Large scale vs. small scale

In Figure 10, the ‘internal’ and output PEC values are shown for the large scale approach, as well as the corresponding small scale results. The small scale average values were calculated as the weighted average (by stretch length) of the ‘internal’ PECs.

<u>Discussion</u>:
The large scale prediction for the catchment’s output PEC approximated the more detailed small scale value within 12% (under-estimation). For the average PEC of the entire catchment, on the contrary, the large scale approach over-estimated the mean PEC by 45% and the 95th percentile PEC by 36 %.

CONCLUSIONS

The GREAT-ER simulation approach allowed to analyze the impact of different discharges and tributaries on the temporal and spatial distributions of PECs in a hypothetical (but realistic) catchment. The resulting PEC distributions were log-normal. For the prediction of 95th percentile PECs, Monte Carlo simulation was superior to the discrete Flow Scenario approach. Also for a complete uncertainty analysis, Monte Carlo simulation is needed. However, to quickly obtain initial results, the Flow Scenario approach may be useful. Finally, it was found that the GREAT-ER methodology allowed spatial aggregation of the simulated hypothetical catchment, from a small detailed scale to a larger scale.

REFERENCES

Boeije, G., Vanrolleghem, P. and Matthies, M. (1997). A geo-referenced aquatic exposure prediction methodology for 'down-the-drain' chemicals. IAWQ - WATERMATEX '97, Quebec, June 17-20, 1997 (Proceedings).

Feijtel, T., Boeije, G., Matthies, M., Young, A., Morris, G., Gandolfi, C., Hansen, B., Fox, K., Holt, M., Koch, V., Schröder, R., Cassani, G., Schowanek, D., Rosenblom, J. and Niessen, H. (1997). Development of a Geography-referenced Regional Exposure Assessment Tool for European Rivers - GREAT-ER. Chemosphere (34), 2351-2374..

NRA (1990). SIMCAT consent setting model - User guide. The National Rivers Authority's R&D Programme. Project No. 022, Output ref. P-61. NRA, Bristol.

Round, C. & Young, A. (1997). Velocity estimation at ungauged sites. Final Report. GREAT-ER Working Note no. 5. Institute of Hydrology, Wallingford.

APPENDIX: SYMBOLS AND UNITS

$\Phi_{in/out}^{p}$	chemical mass flux into / out of process p	g/s
$Q_{in/out}^{p}$	water flow into / out of process p	m^3/s
M	chemical market (sales) data	$g/cap\cdot s$
W	per capita water use	$m^3/cap\cdot s$
P	population in geographical segment	cap
Q_{dwf}	dry weather waste water flow	m^3/s
α	ratio actual flow to dry weather flow	–
$f_{untreat}$	sewer flow fraction which receives no treatment	–
f_{wwtp}	sewer flow fraction which is sent to the WWTP	–
$f_{treated}^{wwtp}$	WWTP influent fraction which is treated	–
f_{bypass}^{wwtp}	WWTP influent fraction which is bypassed	–
R_{wwtp}	WWTP chemical elimination percentage	–
$\Phi_{upstream}^{river}$	chemical mass flux from upstream river stretches	g/s
Q^{river}	river flow taken from database	m^3/s
k_{river}	1^{st} order chemical in-stream removal rate	h^{-1}
HRT	travel time in river stretch	h
l	river stretch length	m
v	river flow velocity	m/s
Q_{mean}^{river}	mean river flow	m^3/s
Q_{actual}^{river}	actual river flow	m^3/s

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