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New PEC definitions for river basins applicable to GIS-based environmental exposure assessment

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Abstract

By means of GREAT-ER (Geo-Referenced Regional Exposure Assessment Tool for European Rivers) aquatic chemical fate simulations can be performed for river basins. To apply the resulting digital maps with local (river stretch specific) predicted concentrations in regional aquatic exposure and risk assessment, the output has to be aggregated to a (single) value representative of exposure in the catchment. Two spatially aggregated PEC definitions are proposed for this purpose: $PEC_{initial}$ (unweighted aggregation of concentrations just downstream of wastewater emissions) and $PEC_{catchment}$ (weighted aggregation of all average stretch concentrations). These PECs were tested using simulations for two pilot study catchments (Calder and Went, UK). This confirmed the theoretical considerations which led to the definitions, and it illustrated the need for weighting to resolve scale-dependencies. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Exposure assessment; GIS; GREAT-ER; Predicted Environmental Concentration

1. Introduction

Geo-Referenced Regional Exposure Assessment Tool for European Rivers (GREAT-ER) is a new exposure assessment tool, which links geo-referenced real-world data about environmental properties and chemical emissions with chemical fate models (Feijtel et al., 1997; Boeije et al., 1997). The output of a GREAT-ER simulation for a specific catchment and chemical is a set of geo-referenced local predicted concentrations, linked to a digital river network. This can be visualized as a color-coded GIS map or as a concentration profile along the river (Koormann et al., 1998). Such output is directly applicable for river basin management purposes, it allows model verification by means of site-specific monitoring programs (Holt et al., 1998), and it can be used as a tool to plan such monitoring programs. Moreover, it allows the identification of local high risk areas.

However, for application in a regional environmental risk assessment context, there is a need to aggregate the geo-referenced output to a single value (or at most a frequency distribution) which is representative of chemical exposure within the catchment under study. In this paper, two aggregation methods were developed and examined: aggregation of all predicted concentrations in the catchment, and aggregation of all 'highest' predicted concentrations (occurring immediately below wastewater emission points). The concept of spatially aggregated PECs is illustrated in Fig. 1.

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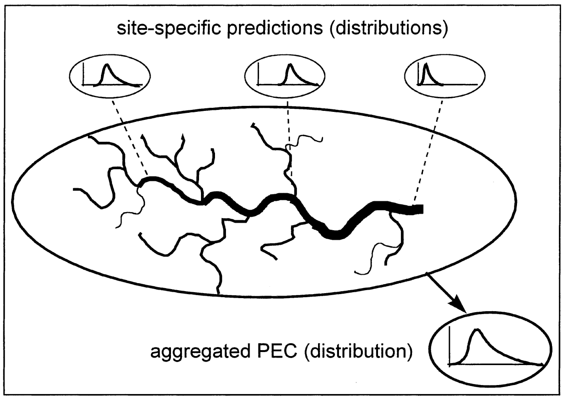

Fig. 1. Aggregated PEC concept.

2. Nomenclature and PEC definitions

Local (frequency distributions of) concentrations are linked to individual river stretches (also called reaches or segments) or to wastewater emission points. As the acronym Predicted Environmental Concentration (PEC) is a regulatory term (e.g. EEC, 1994) which is used in risk assessment for comparison with PNECs or NOECs, a different terminology is recommended for predicted local geo-referenced concentrations. In this paper, the term 'C_{SIM}' (simulated concentration) was used. For each stretch, GREAT-ER simulations produce distributions of the values $C_{\mathrm{SIM,start}}$ (at the beginning of the stretch), $C_{\mathrm{SIM,end}}$ (at the end of the stretch) and $C_{\mathrm{SIM,internal}}$ (average predicted concentration in the stretch). In this paper, aggregated concentration values – which can be used in a risk assessment context – are called 'PEC'. Two aggregated PEC types were defined and tested: $\mathrm{PEC_{initial}}$ and $\mathrm{PEC_{catchment}}$.

2.1. Definition of PEC_{initial}

$\mathrm{PEC_{initial}}$ is the spatial aggregation of concentrations in the river immediately after emission points. In concept, this is roughly comparable to $\mathrm{PEC_{local}}$ as defined in the EU Technical Guidance Documents (EEC, 1994). $C_{\mathrm{SIM,start}}$ was selected as the local basis for spatial aggregation of $\mathrm{PEC_{initial}}$. As no in-stream removal directly below the emission point is considered, $C_{\mathrm{SIM,start}}$ is independent of the river segmentation (length of the stretches) and hence of the river network's scale. Moreover, these values can be validated by monitoring (albeit indirectly), by calculating the mass balance of upstream and wastewater effluent measurements, assuming complete instantaneous mixing. The impact of the uncertainty around in-stream removal and flow velocity is limited to its impact on the upstream concentration – it has no effect on the concentration which is due to the considered wastewater emissions. It can be concluded that $C_{\mathrm{SIM,start}}$ offers the most stable and unambiguous starting point for a $\mathrm{PEC_{initial}}$ aggregation. The fact that in-stream removal is not taken into account for the considered emission points results in the use of the highest C_{SIM} values in the stretches directly below emissions. Note that the $C_{\mathrm{SIM,start}}$ of an emission-receiving river only represents the 'simulated worst-case', predicted in a one-dimensional river model. In reality, higher concentrations may be found close to the emission point due to incomplete mixing.

$\mathrm{PEC_{initial}}$ is described by the spatial mean and standard deviation of the local $C_{\mathrm{SIM,start}}$ values. As $C_{\mathrm{SIM,start}}$ values are independent of scale, weighting to resolve scale-dependencies is not required. This approach ensures that all emission points are given equal importance.

2.2. Definition of $PEC_{\mathrm{catchment}}$

$\mathrm{PEC_{catchment}}$ is the spatial aggregation of concentrations representative of the entire catchment. This is a new concept typical for geo-referenced exposure assessment, which can roughly be compared to $\mathrm{PEC_{regional}}$ in the EU Technical Guidance Documents (EEC, 1994).

As $\mathrm{PEC_{catchment}}$ aims to provide a measure for the 'representative' concentration all over a catchment, it is based on the average local concentrations $C_{\mathrm{SIM,internal}}$. For chemicals which undergo in-stream removal, these concentrations are scale dependent, as their calculation depends on the stretch length. The longer a stretch is, the more residence time is available for in-stream removal. Hence the average concentration will be lower in long stretches compared to short stretches (assuming all other conditions are identical). This scale-dependency needs to be neutralized in the aggregation process.

2.2.1. Stretch selection

There are two plausible options for the selection of stretches which are included in the aggregation: (1) selection of all stretches in the digital river network, or (2) selection of only those stretches which are downstream of pollution sources. Option (1) is the most comparable with the current regional exposure assessment approach ('unit world' models, e.g. Mackay et al., 1992), in which all surface waters in a region are considered for the dilution of the chemical mass loading. It allows to compare the degree of chemical-specific pollution between catchments, and it also allows a quantitative evaluation of chemical-related water quality in a catchment, which is especially useful from a water quality management point of view. Option (2) is clearly different from the currently used methods. However, this concept may also be appropriate: risk assessment of the aquatic environment should mainly focus on rivers that are potentially at risk (i.e. downstream of pollution points), and need not necessarily deal with pristine environments. A practical reason in favor of this option is the fact that data on upstream unpolluted rivers (headwaters) are generally scarce and/or of low quality, especially when large-scale databases and maps are used.

2.2.2. Scale-dependency

An unweighted spatial aggregation of predicted river concentrations can be scale-dependent in two ways: (α) related to the level of geographical detail of the river network, and (β) related to the applied river stretch length.

(α) *River network geographical detail.* The unweighted aggregated $PEC_{catchment}$ is influenced by the number of upstream unpolluted rivers which are included in the digital river network. The more unpolluted headwaters are present, the lower the aggregated $PEC_{catchment}$ will be. The number of headwaters in the river network depends not only on the digitization but also on the type of catchment: mountainous catchments will typically have more (but smaller) sources than lowland catchments. This scale-dependency is illustrated by means of the example river network in Fig. 2. If all headwater stretches are included (situation 1A), the unweighted average $PEC_{catchment}$ is 0.15. If on the other hand only the most downstream unpolluted stretch is considered (situation 1B), the unweighted average $PEC_{catchment}$ is 0.50. This scale-dependency is resolved when headwater stretches are not considered (situation 2): in this case the unweighted average $PEC_{catchment}$ is 0.75, independent of the upstream river network's level of detail.

(β) *Stretch length.* In practice, river stretch length cannot be fixed for modeling purposes, e.g. due to the presence of confluences. Because of this, the unweighted aggregated $PEC_{catchment}$ is influenced by the river segmentation. If the most downstream stretch of the river network in Fig. 2 would be split up into two stretches, the concentrations would be 0.59 and 0.41. It follows that the unweighted average $PEC_{catchment}$ (based on the selection of only the loaded stretches, situation (2) would be 0.67 instead of 0.75.

2.2.3. Weighting

Because of both potential scale-dependencies (α) and (β), an unweighted spatial aggregation of $C_{SIM,internal}$ values cannot be used for $PEC_{catchment}$ calculations. Resulting $PEC_{catchment}$ values would not be comparable between catchments that were digitized at a different scale or using different stretch lengths, and would not be a constant within a single catchment if it would be modeled using different scales or river segmentations. Moreover, it would be possible to direct the value of $PEC_{catchment}$ by modifying the number of considered headwaters, or by modifying the segmentation.

Weighting by stretch length. Weighting by stretch length obviously solves scale-dependency (β). However, it does not solve scale-dependency (α). Hence, this approach can only be applied in combination with option (2) for stretch selection, only considering the stretches downstream of pollution sources. The ecological interpretation is that equal importance is attached to rivers with equal length. Small rivers are considered equally valuable as large rivers. This attaches importance to the entire aquatic ecosystem (the bulk water as well as the river's edges), and also the terrestrial environment near the river which is influenced by it. The weights w_i for each stretch i can be calculated as given in Eq. (1) (with l_i the length of stretch i)

$$w_i = \frac{l_i}{\sum_{j=1}^{n_{\text{stretches}}} l_j}. \qquad (1)$$

Weighting by flow increment. Weighting by flow increment in a stretch can solve both scale dependencies (α) and (β). For the PEC analysis, the flow increment (i.e., the increase of flow) in a stretch is defined as the difference in mean flow between the considered stretch and the upstream stretch. After a confluence, the sum of both upstream flows is used. For the most upstream

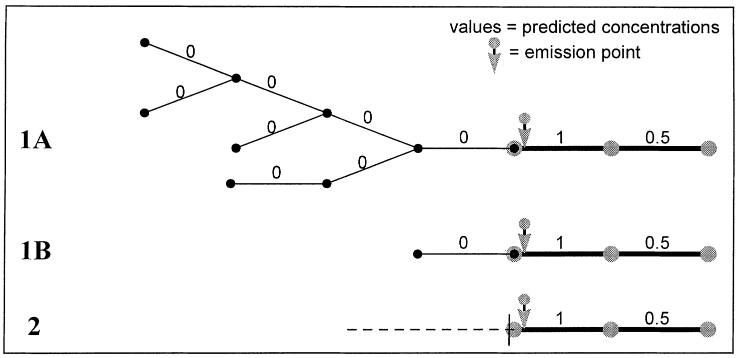

Fig. 2. Scale-dependency: example river network.

stretches in the digital river network (i.e., which do not have upstream stretches), the flow increment is equal to the flow itself. Hence, the flow increment in these most upstream stretches is equal to the flow increment in the entire headwaters subcatchment which, in reality, feeds into them. This concept is illustrated in Fig. 3.

The flow increment $\Delta Q3$ in stretch 3 is calculated as the difference of the flow in stretch 3 with the upstream flow (= the sum of flows in stretches 1 and 2). For stretches 1 and 2, there are no upstream stretches: the 'upstream' flows are zero, and consequently the flow increments $\Delta Q1$ and $\Delta Q2$ are equal to the flows in stretches 1 and 2. For stretch 1, which in reality receives the outflow of an upstream headwaters subcatchment, the flow increment $\Delta Q1$ corresponds with the entire headwaters catchment, rather than with the drainage area of only stretch 1 itself.

Weighting by flow increment assigns the weight of all headwaters, which are in reality at more upstream locations, to the stretches which are most upstream in the digital river network. This way, scale-dependency (α) is resolved: the weight of the unpolluted headwaters is independent of how detailed these headwaters have been digitized. Note that it is crucial that these most upstream stretches be free of pollution. If not, the concentration of such single polluted upstream stretch is given the weight of the entire (unpolluted) headwaters subcatchment feeding into this stretch, and hence the $\mathrm{PEC}_{\mathrm{catchment}}$ would be a gross overestimation of the true situation. As flow increment is correlated with the drainage area of a stretch and hence also with stretch length, scale-dependency (β) is also resolved. If a stretch is split into two sub-stretches, the sum of the flow increment in both stretches is equal to the flow increment in the original stretch.

The ecological interpretation of this weighting approach is similar to the 'weighted by stretch length' approach. However, stretches receiving emissions may have a somewhat higher weight, because the wastewater emission adds to the flow increment in a stretch. The weights w_i for each stretch i can be calculated as follows in Eq. (2) (with ΔQ_i the flow increment in stretch i). Note that the total flow increment in a catchment (i.e. the sum of the flow increments in all stretches) must necessarily be equal to the flow at the end of the catchment Q_{end}.

$$w_i = \frac{\Delta Q_i}{\sum_{j=1}^{n_{\mathrm{stretches}}} \Delta Q_j} \equiv \frac{\Delta Q_i}{Q_{\mathrm{end}}}. \tag{2}$$

Weighting by stretch volume. The volume of a river stretch can be calculated from its flow, flow velocity and length (Eq. (3)). Hence, this approach implicitly contains a weighting by length and solves scale-dependence (β). Although this weighting decreases the importance of individual headwater stretches (due to the implicit weighting by flow) it does not solve scale-dependency (α): a large number of headwater stretches will, together, still contribute significantly to the weighted average. Hence, this approach can only be applied in combination with the stretch selection (2) (only the stretches downstream of pollution sources). Weighting by stretch volume focuses on large rivers (because these have the largest volume). This may be of less ecological relevance, as smaller rivers are often more ecologically valuable or vulnerable than large ones. Also, weighting by volume stresses the importance of 'bulk water' organisms rather than the benthic or river edge ecosystem. From an exposure point of view, weighting by volume focuses on high dilution situations, where exposure (and risk) levels may be lower than what is representative for the entire catchment. The weights w_i for each stretch i can be calculated as given in Eq. (3) (with $V_{\mathrm{stretch}\ i}$, Q_i, l_i, v_i the volume, flow, length and flow velocity of stretch i):

$$w_i = \frac{V_{\mathrm{stretch}\ i}}{\sum_{j=1}^{n_{\mathrm{stretches}}} V_{\mathrm{stretch}\ j}} = \frac{Q_i\, l_i / v_i}{\sum_{j=1}^{n_{\mathrm{stretches}}} (Q_j\, l_j / v_j)}. \tag{3}$$

Calculation of weighted average and standard deviation. A weighted average is calculated as follows ($\bar{x}_{\mathrm{w}}$ = weighted averge, x_i = individual values, n = number of values):

$$\bar{x}_{\mathrm{w}} = \sum_{i=1}^{n} x_i w_i \quad \text{with} \sum_{i=1}^{n} w_i = 1. \tag{4}$$

The weighted variance σ_{W}^2 is an estimator of the population's true variance, just like the unweighted

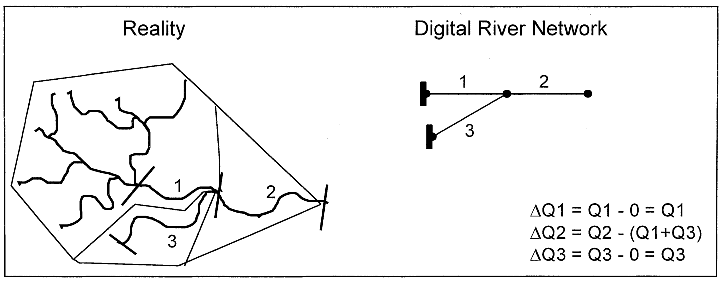

Fig. 3. Flow increment: concept.

variance σ^2 is one. However, a different porbability function $f(x)$ is used, reflecting a non-aselective sampling approach of the population. For the 'traditional' calculation of variances, an aselective sampling is represented by assigning equal probability to each x_i: $f(x_i) = 1/n$. For the weighted calculation, the probability for each x_i is equal to its weight: $f_W(x_i) = w_i$. When the number of sampled values is finite, the variance can be calculated as given in Eq. (5). Note that estimators for the variance using a finite number of samples n are only unbiased asymptotically with n going to infinity; hence, a correction to the probability function is required (multiplication by $n/(n-1)$).

$$\begin{aligned}\sigma^2_W(x) &= \int_{-\infty}^{+\infty} (x - E(x))^2 f(x)\,dx \\ &\cong \sum_{i=1}^{n} \left((x - \bar{x}_W)^2 w_i \frac{n}{n-1} \right) \\ &= \frac{\sum_{i=1}^{n} ((x - \bar{x}_W)^2 w_i)\, n}{n-1}. \end{aligned} \tag{5}$$

3. Case studies

3.1. Method: Model, chemicals, catchments

A simple chemical fate model was applied. A percentage elimination was used to describe removal in the sewer system and in wastewater treatment, and a fixed first-order in-stream removal rate coefficient was used to calculate fate in rivers. A Monte Carlo simulation (1000 shots) was applied for combined uncertainty and variability analysis. Only mean C_{SIM} values were used for spatial aggregation.

A fate simulation was conducted for the surfactant Linear Alkylbenzene Sulphonate (LAS). Next to this, a simulation was conducted for the hypothetical substance CONS (a completely conservative inert chemical with the same emission as LAS). The chemical properties and market data used for LAS were based on chemical industry data (ECETOC, 1998) (Table 1).

Table 1
Chemical parameters

	LAS	CONS
Product consumption	1 kg/(cap. year)	1 kg/(cap. year)
In-stream removal rate	0.006–1.71 h^{-1} [a]	0 h^{-1}
Removal in primary treatment	45%	0%
Removal in activated sludge treatment	98%	0%
Removal in trickling filter treatment	85%	0%
Removal in the sewer	25%	0%

[a] Uniform distribution.

The PEC calculations were applied to two Yorkshire (UK) catchments: the Went and the Calder. The datasets were not completely quality-controlled, and may still have contained minor errors. Therefore, it is stressed that the analysis presented here should not be interpreted as a reliable exposure assessment, but only as a test of the proposed PEC definitions and calculation methodologies.

For the $PEC_{catchment}$ calculations, three different stretch selection options were used: 1A = all stretches; 1B = a reduced catchment containing all polluted stretches plus one stretch for each unpolluted subcatchment; and (2) = a reduced catchment containing only polluted stretches (Fig. 4). 1A and 1B are two cases representing the same concept ('all stretches'), but applied at a different level of geographical detail. A description of both catchments and the effect of the applied stretch selection is given in Table 2.

The Went catchment is much smaller than the Calder. In the Calder, the flow at the end of the catchment is ~20 times higher than in the Went; its total cumulative stretch length is a factor 10 higher, its cumulative volume is 30 times higher; and the total population is 30 times bigger. Still, the Calder only has three times more wastewater emission points, which can be explained by the (on average) larger size of the emissions. The total population divided by the river flow at the end of the catchment is 1.5 times higher in the Calder than in the Went. In other words, the total domestic pollution load in the Calder receives (in total) 1.5 times less dilution than that in the Went.

Pollution in the Calder is concentrated in the most downstream 6% of the stretches (i.e., the 'main' rivers), while in the Went more than 25% of the stretches is influenced by pollution (including smaller tributaries). Hence, the number of stretches and the total stretch length was highly reduced when instead of all stretches (of the 1:50 000 river network) only the polluted stretches plus one unpolluted stretch per headwater subcatchment (selection 1B), or strictly only the polluted stretches were used (selection 2). This effect was stronger in the Calder than in the Went. The reduction in total river volume was much more limited, and was similar in both catchments. This can be explained by the smaller volume of unpolluted headwater stretches compared to the more downstream parts of the rivers.

3.2. Results

An illustration of the geo-referenced simulation results for LAS in the Calder is given in Fig. 5 (concentrations quartiles were color-coded, black circles represent emission points).

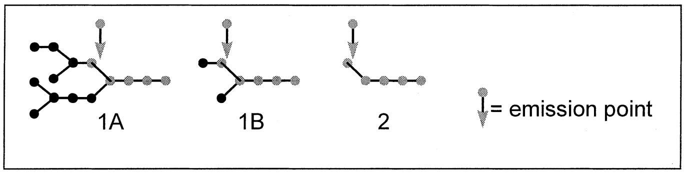

Fig. 4. Stretch selection options for $PEC_{catchment}$.

Table 2
Test catchment description and stretch selection

	Went	Calder
Mean river flow at the end of the catchment	0.98 m^3/s	19 m^3/s
Number of waste water emission points	7	21
Total population	28 053	798 458
Population per unit of flow at the end of the catchment (cap/(m^3/s))	28 625	42 024
Stretch selection 1A		
Number of stretches	105	1562
Cumulative stretch length	112 km	1103 km
Cumulative mean river volume	78.6×10^3 m^3	2400×10^3 m^3
Stretch selection 1B		
Number of stretches	46	164
Cumulative stretch length	52 km	215 km
Cumulative mean river volume	64.4×10^3 m^3	1900×10^3 m^3
Stretch selection 2		
Number of stretches	28	93
Cumulative stretch length	36 km	118 km
Cumulative mean river volume	55.8×10^3 m^3	1800×10^3 m^3

3.2.1. $PEC_{initial}$

$PEC_{initial}$ was defined as the unweighted spatial aggregation of $C_{SIM,start}$ for all stretches in the catchment which directly receive an emission of wastewater. The results of the $PEC_{initial}$ calculation are given in Table 3.

3.2.2. $PEC_{catchment}$

$PEC_{catchment}$ was defined as the spatial aggregation of $C_{SIM,internal}$ values over the entire catchment, or over the polluted section of the catchment. As discussed above, for the first option weighting by flow increment is required, while for the second option weighting by length or by volume is needed. For LAS, the spatial variability of $C_{SIM,internal}$ values is shown in Fig. 6. These histograms were weighted by flow increment ('all stretches' case) or by stretch length ('only polluted stretches' case). The left part of Fig. 6 illustrates the dominance of unpolluted headwaters in the 'all stretches' case (peak at concentration zero).

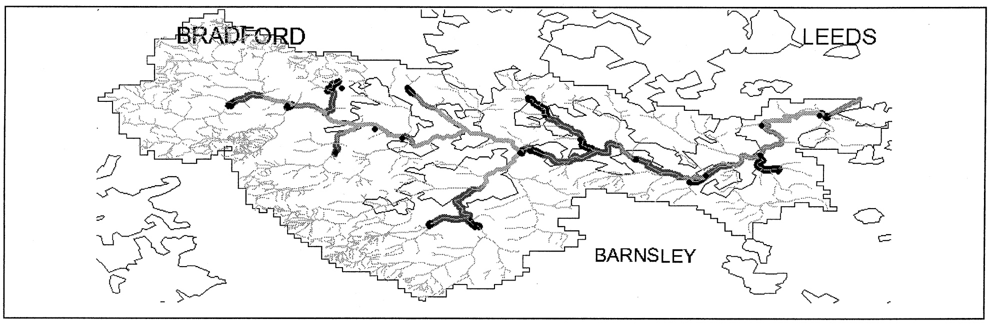

Fig. 5. Calder simulation: LAS (geographical projection).

Table 3
$PEC_{initial}$ calculations (in mg/L)

	Went		Calder	
	Mean	Std. dev.	Mean	Std. dev.
LAS	0.65	1.44	0.089	0.178
CONS	8.3	17.3	2.2	3.6

In the $PEC_{catchment}$ calculations presented here (Table 4), four different weightings of C_{SIM} values (unweighted, by length, by flow increment and by volume) were used in combination with the three different stretch selection approaches. Only the weighting techniques described higher in the definitions are considered relevant; the results obtained with the other techniques are given to illustrate their scale-dependency and hence their limitations. $PEC_{catchment}$ values are listed in Table 4. Results obtained with scale-dependent calculations were printed in italics.

3.3. Discussion

3.3.1. Scale dependencies in $PEC_{catchment}$ calculations

Effect of reduction in catchment detail (*1A versus 1B*). The type-(α) scale-dependency (linked to the number of unpolluted headwater stretches) of the unweighted, weighted-by-length and weighted-by-volume calculation approaches can be observed by comparing $PEC_{catchment}$ for stretch selection 1A and 1B. When the number of unpolluted headwater stretches in the network was reduced (i.e., when the level of detail was decreased), $PEC_{catchment}$ increased in all cases. The volume-weighted $PEC_{catchment}$ was least affected because the total volume of the headwater stretches has a relatively low weight compared to the entire catchment's volume: the reduction of the considered headwater stretches only caused a 25–30% decrease in total volume.

$PEC_{catchment}$ weighted by flow increment was independent of the number of considered unpolluted headwaters. The minor differences between stretch selection 1A and 1B for the Calder were due to inconsistencies in the flow data, which caused a negative flow increment for some stretches. This also led to the not strictly monotonous behavior of the weighted cumulative frequency distribution curves for the Calder in Fig. 6.

The simulation results confirm the theoretical considerations about scale dependency. It can be concluded that for a $PEC_{catchment}$ calculation which aims to consider the entire catchment (both the polluted and the unpolluted parts), weighting of $C_{SIM,internal}$ by flow increment is the recommended approach to obtain a stable and meaningful result.

Effect of stretch selection: all stretches (*1A*) *versus only polluted stretches* (*2*). $PEC_{catchment}$ increased when only polluted stretches were used instead of the entire catchment. This is evident, as average exposure levels are necessarily higher in the polluted sections of a catchment

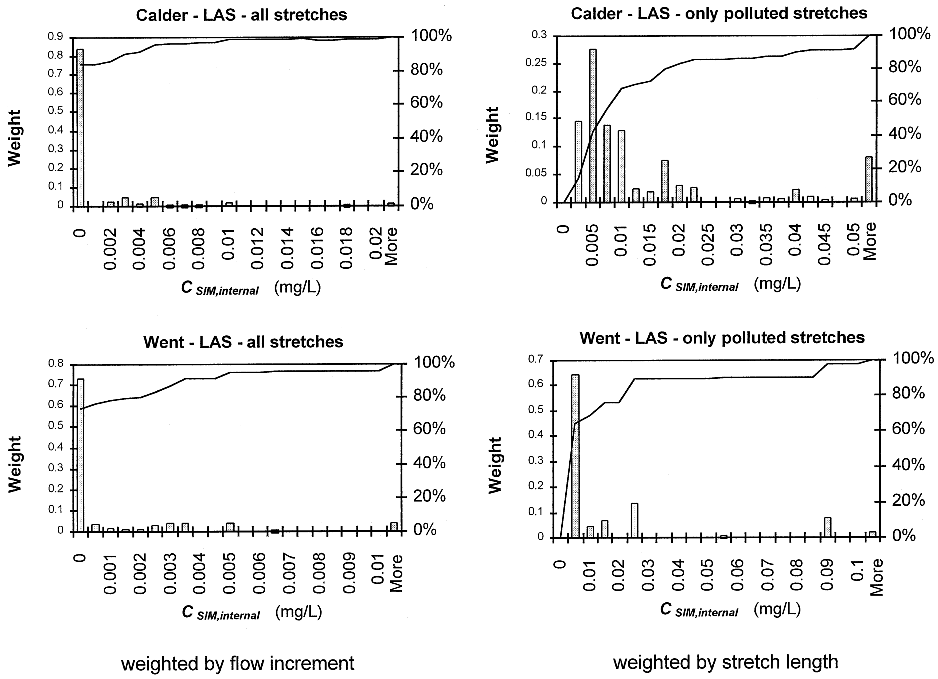

Fig. 6. Spatial variability of $C_{SIM,internal}$ values (LAS) (weighted histograms).

Table 4
$PEC_{catchment}$ calculations (in mg/L)

	Went		Calder	
	Mean	Std. dev.	Mean	Std. dev.
LAS				
Stretch selection 1A				
Not weighted	0.036	0.32	0.00130	0.0137
Weighted by length	0.0088	0.103	0.0021	0.0159
Weighted by flow increment	0.0030	0.0136	0.00147	0.0138
Weighted by volume	0.0075	0.041	0.0023	0.0117
Stretch selection 1B				
Not weighted	0.083	0.49	0.0124	0.041
Weighted by length	0.0189	0.151	0.0105	0.035
Weighted by flow increment	0.0030	0.0136	0.00151	0.0140
Weighted by volume	0.0094	0.046	0.0073	0.0121
Stretch selection 2				
Not weighted	0.136	0.62	0.022	0.052
Weighted by length	0.027	0.182	0.0191	0.045
Weighted by flow increment	0.032	0.26	0.0190	0.040
Weighted by volume	0.0105	0.049	0.0075	0.0123
CONS				
Stretch selection 1A				
Not weighted	0.72	4.6	0.081	0.60
Weighted by length	0.40	1.67	0.162	0.91
Weighted by flow increment	0.28	0.72	0.144	0.73
Weighted by volume	0.74	0.94	0.184	0.81
Stretch selection 1B				
Not weighted	1.64	7.0	0.77	1.72
Weighted by length	0.86	2.4	0.82	1.93
Weighted by flow increment	0.28	0.72	0.158	0.73
Weighted by volume	0.93	0.97	0.89	0.55
Stretch selection 2				
Not weighted	2.7	8.8	1.37	2.1
Weighted by length	1.23	2.8	1.51	2.4
Weighted by flow increment	1.09	3.85	0.73	1.00
Weighted by volume	1.04	0.98	0.94	0.52

compared to the zero-exposure in the unpolluted sections. In all cases, the $PEC_{catchment}$ increase was higher in the Calder than in the Went. This is explained by the catchment structure: as there are more unpolluted headwater stretches in the Calder compared to the Went, dropping these headwaters from the calculations has a stronger impact in the Calder.

For the flow-increment weighted case, the $PEC_{catchment}$ increase was by more than a factor 10 for LAS and by a factor 4–5 for CONS. However, this calculation method is considered irrelevant in combination with stretch selection 2. Indeed, when only polluted stretches are considered, the flow increment weight of entire unpolluted headwater sub-catchments is assigned to the situation of the most upstream polluted stretches into which these headwaters feed (cf. Fig. 3, assuming that stretch 1 would be polluted). Hence, such calculations result in a strong overestimation of true exposure levels.

The spread of the spatial distributions decreased. This can be ascribed to the reduction in spatial variability when a large number of 'extreme' cases (zero concentration) are removed from the population (see also Fig. 6).

For both catchments, the LAS $PEC_{catchment}$ based on only polluted stretches (selection 2) and weighted by volume was a factor 2.5 lower than the corresponding $PEC_{catchment}$ weighted by length. This is in line with the expectation that weighting by volume focuses the attention to larger rivers with higher dilution and after more in-stream removal has taken place. For CONS a similar effect was seen (factor 1.6 for the Calder, factor 1.2 for the Went). The effect was less extensive because CONS is only affected by dilution, not by in-stream removal. The spread of the volume-weighted $PEC_{catchment}$ was also lower for both chemicals and catchments, which can be explained by the leveling out of very high or low concentrations in the more downstream rivers.

Effect of river segmentation. The type-(β) scale-dependency (linked to the variable stretch length) of the unweighted $PEC_{catchment}$ calculation could not be illustrated with a calculation example in this work, because the river network segmentation itself was not modified.

3.3.2. Comparison of PEC calculations and catchments

$PEC_{initial}$. For LAS, $PEC_{initial}$ was a factor 7 higher in the Went compared to the Calder. For CONS, the difference between $PEC_{initial}$ in both catchments was smaller (a factor 4). The higher $PEC_{initial}$ of CONS in Went versus Calder cannot be due to a different wastewater treatment infrastructure as the chemical is conservative. Also for LAS this is not probable, as in both catchments the sewage is mainly treated by trickling filter plants. A plausible explanation is the difference in catchment structure. On average, the emission points in the Went are at a more upstream location than those in the Calder. Hence, they generally receive a lower dilution.

For LAS, the spread of the spatial $PEC_{initial}$ distribution was similar in both catchments (standard deviation/mean ≅ 2). For CONS, the spread of the distribution in the Went was similar to the LAS case, while for the Calder it was more narrow (std. dev./mean ≅ 1.6).

The $PEC_{initial}$ for CONS was much higher than for LAS, which is obvious as CONS is not eliminated in wastewater treatment. Furthermore, as CONS undergoes no in-stream removal, $C_{SIM,start}$ values associated with more downstream emission points also contain a major component of upstream pollution, which further increases $PEC_{initial}$.

$PEC_{initial}$ versus $PEC_{catchment}$. As expected, $PEC_{initial}$ was always higher than $PEC_{catchment}$. Compared to the weighted-by-flow-increment $PEC_{catchment}$ considering all stretches, this difference was by more than a factor 200 for LAS and 30 for CONS in the Went. In the Clader it was by a factor 60 for LAS and 15 for CONS. The spread of the $PEC_{initial}$ distributions was a factor 2–5 lower for LAS and a factor 1–3 lower for CONS than the spread of $PEC_{catchment}$. This is caused by the relative similarity of concentrations immediately after emissions compared to the much larger variability of concentrations all over the catchment.

When only the polluted stretches are considered, the difference between $PEC_{initial}$ and $PEC_{catchment}$ is less spectacular. In the Went, $PEC_{catchment}$ values were lower than $PEC_{initial}$ by a factor 24 (LAS) or 7 (CONS) (weighted-by-length) and 60 (LAS) or 8 (CONS) (weighted-by-volume). In the Calder, the difference was limited to a factor 5 (LAS) or 1.4 (CONS) and 12 (LAS) or 2.3 (CONS), respectively. The difference between Went and Calder indicates that the pollution in the Calder is more concentrated in the downstream sections of the catchment, resulting in a 'polluted-only' $PEC_{catchment}$ which is closer to $PEC_{initial}$. In the Went, pollution is more widely distributed in space, hence relatively more in-stream removal (for LAS) and extra dilution can take place, resulting in a 'polluted-only' $PEC_{catchment}$ which is farther away from $PEC_{initial}$. The difference between LAS and CONS is due to the absence of in-stream removal for the latter. For CONS, the difference between $PEC_{initial}$ and the 'polluted-only' $PEC_{catchment}$ is only due to additional dilution downstream of the emission points.

$PEC_{catchment}$ weighted by length, considering only polluted stretches. A neutral view on the situation in the polluted parts of a catchment (assuming equal importance for all locations in the river) is represented by $PEC_{catchment}$ weighted by length, considering only polluted stretches.

LAS exposure levels calculated for the polluted part of the Went are a factor 1.4 higher than those in the Calder. This can mainly be explained by the higher $PEC_{initial}$ in the Went. The fact that the ratio between $PEC_{catchment}$ values of the Went and the Calder is much lower than the ratio between their $PEC_{initial}$ values (factor 7), is mainly due to the different dilution properties in both catchments. Contrary to LAS, the exposure to CONS in the polluted parts of the Went was slightly lower than in the polluted parts of the Calder – even though $PEC_{initial}$ was higher in the Went by a factor 4. This can only be ascribed to the different dilution in both catchments.

$PEC_{catchment}$ weighted by volume, considering only polluted stretches. When stretch volume is used for weighting instead of stretch length, the aggregated exposure level dropped by a factor 2.5 for LAS and 1.2–1.6 for CONS. As already mentioned higher, this is due to the fact that weighting by volume attaches most attention to downstream stretches with high dilution and after more in-stream removal. Note that in this weighting case, the exposure to CONS in the Calder was slightly lower than in the Went (contrary to the weighted-by-length case presented above).

$PEC_{catchment}$ weighted by flow increment, considering all stretches. The overall exposure situation in a catchment can be measured by means of $PEC_{catchment}$ weighted by flow increment, considering all stretches (polluted as well as unpolluted).

Both for LAS and CONS, $PEC_{catchment}$ weighted by flow increment in the Calder was a factor 2 lower than in the Went. This is due to two factors: it is directly determined by the lower $PEC_{initial}$ in the Calder, and it is also influenced by the location of the emission points. As most emissions are situated in the downstream regions, most of the Calder's upstream sections are unpolluted, which significantly reduces the average exposure over the entire catchment. This explains why the ratio between the 'all stretches' $PEC_{catchment}$ values in the Went and Calder is higher than the ratio between the 'polluted-only' $PEC_{catchment}$ values. The difference in catchment structure also explains why $PEC_{catchment}$ for CONS based on all stretches is lower in the Clader than in the Went, while $PEC_{catchment}$ based on only the polluted stretches has a similar value in both catchments.

3.3.3. Impact on data requirement

The $PEC_{catchment}$ calculation methodologies using stretch selections 1B or 2 do not require data about the entire river network that is being studied. When only polluted stretches are considered (2), no data is needed about the unpolluted sections of the catchment. When the entire catchment is considered, only the most downstream unpolluted stretches (1B) are required to obtain a $PEC_{catchment}$ weighted by flow increment. Hence, for these recommended $PEC_{catchment}$ calculations, fate simulations, flow data collection and river network digitization are not required for the entire catchment, but only for a limited (downstream) part. This may reduce the effort needed to apply the GREAT-ER methodology for new regions, and it will strongly decrease the required simulation time.

4. Conclusions

- Two spatially aggregated PEC types were defined, tested and built into the GREAT-ER system:
  - $PEC_{initial}$ was defined as the spatial aggregation of initial river concentrations after each wastewater emission in the catchment, by means of an unweighted average.
  - $PEC_{catchment}$ was defined as the spatial aggregation of all 'internal' river concentrations (i.e., the average value in a stretch), by means of a weighted average. To obtain an aggregated exposure value representative of the entire catchment, all stretches (polluted and unpolluted) have to be considered. In this case, weighting by flow increment is needed to resolve scale-dependency. To produce an aggregated exposure value representative of the polluted parts of the catchment, only the polluted stretches should be considered. In this case, weighting by stretch length or by stretch volume is required to resolve scale-dependency. Weighting by length results in a 'neutral' aggregation which attaches identical importance to all locations in the river network. Weighting by volume stresses the importance of downstream parts of the river with a higher dilution and after more in-stream removal, hence resulting in a lower exposure estimate.
- A higher $PEC_{catchment}$ in the polluted part of the catchment compared to the entire catchment is obvious, and inherently part of the concept. It must be stressed that a $PEC_{catchment}$ based on only polluted stretches is not representative of the entire catchment, and this should be taken into account when such a PEC is applied in a risk assessment framework.
- The irrelevance due to scale-dependency of an unweighted $PEC_{catchment}$ was illustrated. The need for an adequate stretch selection as a function of the selected weighting technique was also shown. It is stressed that the use of an inappropriate stretch selection/weighting combination results in an aggregation which depends on the level of detail of the digital river network or on the geographical scale. Such aggregations are irrelevant because they cannot be compared between catchments or between different digital versions of a single catchment. Consequently, as such values are not unambiguously determined, they cannot be compared with effects levels, and hence they cannot be used in environmental risk assessment.
- For the two recommended $PEC_{catchment}$ calculations, data collection and chemical fate simulations are not required for the entire catchment but only for a limited (downstream) part. This may highly reduce the effort needed to apply GREAT-ER to new catchments. Moreover, it also decreases the required simulation time.

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References

Boeije, G., Vanrolleghem, P., Matthies, M., 1997. A geo-referenced aquatic exposure prediction methodology for 'down-the-drain' chemicals. Wat. Sci. Tech. 36 (5), 251–258.

ECETOC, 1998. European Center for Ecotoxicology and Toxicology of Chemicals, Brussels, Personal Communication.

EEC, 1994. Technical Guidance Documents in support of the risk assessment directive (93/67/EEC) for substances notified in accordance with the requirements of Council Directive 67/548/EEC, Brussels.

Feijtel, T.C.J., 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., Niessen, H., 1997. Development of a geography-referenced regional exposure assessment tool for European rivers – GREAT-ER. Chemosphere 34, 2351–2374.

Holt, M., Fox, K., Daniel, M., Morris, G., McEvoy, J., Buckland, H., 1998. GREAT-ER validation by monitoring UK catchments. In: Proceedings of the Eighth annual SETAC Europe meeting, Bordeaux, France.

Koormann, F., Matthies, M., Trapp, S., 1998. Simulation and visualization of spatial exposure patterns: intermediates in the river Rhine system. In: Pugh, D.M., Tarazona, J.W. (Eds.), The Use of Ecotoxicology and Human Toxicology in the Regulation of Chemical Safety in the European Union. Kluwer Academic Publishers, Dordrecht.

Mackay, D., Paterson, S., Shiu, W.Y., 1992. Generic models for evaluating the regional fate of chemicals. Chemosphere 24, 695–717.