Sediments in GREAT-ER

Estimating sediment concentration ranges for European Rivers

Final report
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1. Introduction – Project Plan

Within the river network the movement of a wide range of contaminants often occurs in association with sediment. Contaminants may themselves be particulate in form or may bind to sediment particles at some point in their journey from land to river to estuary. Often, contaminants bound to sediments will form the major part of the contaminant load. It is thus important that sediment concentrations are consistently and accurately represented within any computer models which study contaminant movement and accumulation. This study provides the data to add an enhanced sediment component to an existing software package, GREAT-ER 2.0, the river modelling component of a range of contaminant risk assessment models which look at contaminant transfer to/from the atmosphere and through the land-river-estuary cycle. The study also provides a simple means of assessing likely sediment concentrations for a particular river of interest using river flow and catchment characteristics.

Assessment of chemical exposure in sediments is part of the current TGD and is encapsulated in EUSES. In order to convince regulators that GREAT-ER provides an exposure assessment methodology which is at least equivalent to EUSES (in terms of sophistication) in several environmental compartments, an explicit exposure assessment in sediments is required. Currently GREAT-ER produces a prediction of total (adsorbed and dissolved) concentration but the user cannot assess sediment-associated chemical concentrations (suspended or settled). An explicit prediction of the partitioning of chemical between the dissolved, suspended sediment and bed-sediment phases will also provide enhanced input to the LRI estuary model (GEMCO). More specifically, it will provide a more realistic distribution of the flux of sediment associated pollutants to estuaries. This study defines the form of suspended sediment concentration distributions in rivers in the form of probability distribution functions (pdfs) for inclusion in the GREAT-ER 2.0 software package. Furthermore river flow or other catchment descriptors are linked to expected sediment pdfs to allow users to define pdfs for a particular river in the absence of any monitored sediment data.

Within this study a means of assessing chemical concentrations in suspended and settled sediments was proposed with **three levels of sophistication,** according to the available input data. Development of more than one complexity level is consistent with the approach for the other modules in GREAT-ER. At all levels there will be **four predicted concentrations of chemicals**– (a) dissolved, (b) sorbed to suspended sediment, (c) sorbed to settled sediment and (d) total water column concentration.

Level 1

- Constant suspended sediment (SS) concentration in the water column at all locations in the river network.
- Concentration of chemical adsorbed to SS calculated from equilibrium partitioning.
- Concentration of chemical in settled sediment assumed to be equivalent to SS concentration. Such partitioning is already present in GREAT-ER but is not explicitly visible to the user. It will essentially reproduce the sediment exposure assessment described by the TGD.
- A default SS concentration will be available (i.e. the value in the TGD) but the user will have the option to change this. This work is required in order for following levels to be implemented in the GREAT-ER 2.0 package.

Level 2

- Concentration of chemical adsorbed to suspended sediment (SS) calculated from equilibrium partitioning.
- Concentration of chemical in settled sediment assumed to be equivalent to SS concentration.
- SS concentration in each reach selected from a probability density function (pdf) in each Monte Carlo shot.
- The SS pdf will be the same for all reaches so that the user will simply enter the required parameters (e.g. mean and standard deviation). It is envisaged that a constant SS concentration at all points in the river network in any one shot will be

assumed (i.e. 100% correlation between reaches) and that SS will be imperfectly correlated with river flow. In reality the SS pdf will vary through the channel network so some guidance will need to be written for users to help them choose the most representative SS pdf parameters. Essentially level 1 is a special case of level 2.

Level 3

- An attempt to differentiate catchments with different SS concentrations will be made on the basis of catchment characteristics. It was envisaged that this level would have a user "form" to allow key catchment information (e.g. most prevalent soil type, rainfall characteristics, relief, dominant land use, flow regime) to be entered via "pick lists" and "check boxes". These characteristics will be used to automatically generate SS pdf parameters on the basis of relationships defined by the Cranfield-Durham group.
- Sampling and correlations will be as for level 2.

Level 4

- This is the most sophisticated level and will allow GREAT-ER to receive reach-specific SS inputs and associated dissolved and adsorbed chemical fluxes predicted by a model such as SWAT (the model used in the LRI TERRACE project). Note that SWAT already produces sediment input data which could be changed into pdfs per river reach – but also note that diffuse sources are not the only source of sediment – river bank sediments play a major role in much of Europe and will implicitly be included in (3) and (4) above.
- Input to GREAT-ER will be via an input file generated for the river network containing pdf parameters for the inputs in question as has already been proposed for contaminants.

The estimation of long term average suspended sediment fluxes (and associated contaminants) to the coast have often been calculated using inadequate sediment concentration sampling considering the large variability that exists in space and time (Meybeck *et al*. 2003). The sediment rating curve in the form $C = aQ^b$, (where C = sediment concentration, Q = river flow and a and b are constants for a particular site on a river) has often been used to predict suspended sediment concentration (SSC) in the absence of actual measurements. In the long term this has been shown in some instances to provide long-term sensible estimates of sediment delivery to oceans due to the balancing out of the tendency of the rating curve to over predict low SSC values and under predict high SSC values (Horowitz, 2003), although in other cases the error may be substantially larger. The association of contaminants with suspended sediment however means contaminant fate is highly dependent on the coincident SSC at a particular contaminant concentration, especially for high K_{ow} materials. GREAT-ER 2.0 currently uses a constant SSC, with a default value of 15 mg l^{-1}, in the water column at all locations in the river network to produce a prediction of total (adsorbed and dissolved) chemical concentration. In order to provide a more realistic distribution of the flux or fate of sediment associated pollutants a better representation of suspended sediment is required.

2. Data Availability

In order to achieve the aim of improving the representation of sediment in the GREAT-ER model raw data sets of sediment concentration data and coincident flow measurements were obtained for as many European rivers as possible. These data sets (source, period, frequency, mean SSC, long term average (LTA) or monitored mean flow) are shown in Appendix 1. The LTA discharges (or monitored mean flows) range from 0.92 $m^3 s^{-1}$ to 2235 $m^3 s^{-1}$ the length of record ranges from 3 to 38 years with an average of 16.2 years and the frequency of measurement ranges from two per week to monthly (although some data sets have gaps of more than one month).

Data from 85 monitoring stations have been analysed, these data are from 55 rivers, 30 of the monitoring stations are located within five large river basins in Western Europe: the Rhine, Rhône, Meuse, Ebro and Humber. Figure 1 shows the location of the monitoring points for which data have been analysed.

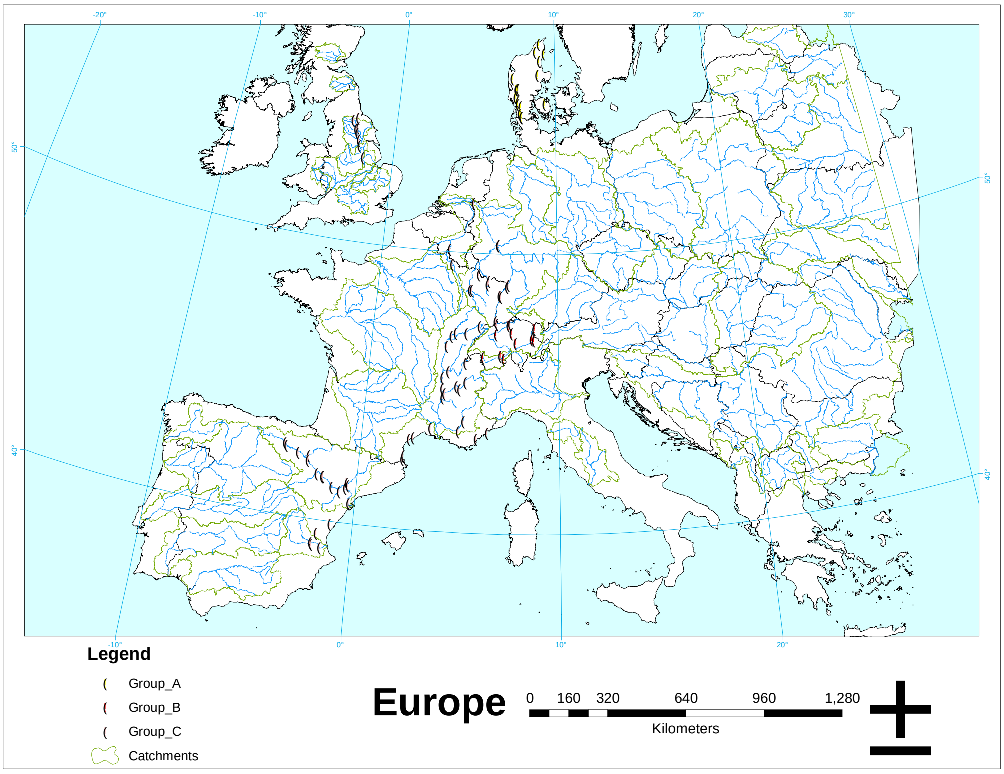

Figure 1: Location of monitoring stations used in analysis

Due to costs or communication difficulties, it proved impossible to obtain data from other river catchments/environments in Europe. Appendix 2 shows the databases known to exist, and gives additional details such as costs and contacts. These data may in the future make a valuable contribution to any further study.

3. Data Analysis

The relationship between flow and SSC often breaks down due to changing or limited supply of sediment, which is often related to anthropogenic factors. This can mean that a high flow is not necessarily accompanied by a high SSC. The SSC and coincident flow data obtained have been analysed and SSC probability distribution functions developed. This allows the provision of a distribution of likely SSC values according to flow characteristics which can be sampled within the GREAT-ER stochastic simulation technique. The data obtained has been split into 3 major groups according to catchment characteristics which show resemblance to a global set of river groupings according to SSC characteristics/statistics made by Meybeck (2003).

3.1. Data groups

Of the datasets that were analysed three distinct groups could be identified:

- **Group A** which is mostly composed of data obtained from Denmark, the obvious characteristics of which are low relief catchments and a high density of lakes. There is only one occasion where SSC in this group exceeds 100 mg l^{-1}. This characteristic has also been shown by Andersen and Svendsen (1997) for the lower Skjern (highest discharge of all Danish rivers), where sampling frequency was every four hours (over 2 years) rather than one to three times per month as seen in the data sets obtained for this study. This grouping should not necessarily be confined to rivers in Denmark. Users assessing rivers outside of Denmark who consider the characteristics of the river in question to be similar (low relief, heavily regulated or groundwater fed) may consider this group more suitable than Group C. For example the Somme (France) that drains a chalk aquifer north of Paris (low relief) is reported to have very low daily variability and the maximum SSC value recorded during high flow was 60 mg l^{-1} (Meybeck *et al*. 2003). Phreatic, or groundwater fed, rivers may be considered to have similar SSC characteristics as heavily regulated rivers or those with a high density of lakes (Meybeck *et al*. 2003). Maneux *et al*. (2001) showed that upstream of dams on the Dordogne (France) SSC in flood conditions would range between 100 and 500 mg l^{-1}, while downstream SSC rarely exceeded 10 mg l^{-1}. Equally, higher order streams in Denmark may be better suited to Group C SSC pdfs. The terminology used for the groupings and how this is presented to the user are discussed further in Section 4.

- **Group B** is formed from data obtained from Switzerland (Appendix 1), here the mountainous catchments (high relief) and increased erosional processes (e.g. glaciers and landslides) cause high maximum SSC (>10 000 mg l^{-1}). This group may therefore also be suitable for other mountainous catchments (or those rivers heavily affected by mountainous regions and not affected by dams) in southern Europe (younger lithology) where there is substantial glacial activity, snow melt or where the orographic rising of moisture laden air results in high meteorological runoff (Milliman, 2001). This group also provides information on SSC for major rivers whose headwaters are in the Swiss Alps (Rhine and Rhône), upstream of lakes Constance and Geneva respectively. In these lakes a substantial proportion of sediment will settle out of suspension thus reducing concentrations downstream.

- **Group C** lies between the two extremes described by Groups A and B. Here maximum SSC lies between 100 and 8200 mg l^{-1}, although less than 1 % of SSC values in this group are greater than 500 mg l^{-1}. Further division on the basis of catchment characteristics is difficult, firstly because of the limited extent of catchment environments for which data are readily and freely available and secondly because of the complex interactions between a large number of controlling factors (climate, geology, soil, landuse, structural changes (e.g. presence of dams), contribution by bank erosion, antecedent conditions/sediment supply and the influence of urban areas) some of which may change in relatively short timescales. This is further complicated by autochthonous organic matter (OM) production and its interactions with catchment supplied sediment (e.g. floc formation) (Håkanson *et al*., 2005; Schild and Prochnow, 2001; Woodward *et al*., 2002).

  There is the possibility to divide Group C in to central/northern Europe and Southern European catchments. The grounds for so doing are the reported increased variability of SSC and sediment loads during ‘events’ in rivers draining Southern European/Mediterranean catchments (Meybeck *et al.*, 2003), with younger more erodible rocks (Milliman, 2001) and/or semi arid to arid conditions (lack of vegetation) (Kosmos *et al*., 1997) and more intense and variable rainstorms (Serrat *et al.,* 2001). However the division between northern and southern rivers is not always clear cut. In many instances for southern rivers the majority of sediment transported is confined to a smaller flow percentile than for the more northern and central rivers. This has been difficult to assess accurately with the data obtained due to the often infrequent sampling and to the presence of dams which are prevalent in mountainous regions for water storage and power generation. At this point Group C contains all rivers across Europe which are neither dominantly lowland, groundwater fed, or mountainous, snowmelt affected.

By dividing data into these three groups, the establishment of a methodology to achieve the third level of sophistication, the involvement of catchment characteristics, becomes redundant except as a means of distinguishing between the three groups.

3.2. SSC Frequency Distributions

In order to make the sediment concentration data easily usable in GREAT-ER, SSC has been plotted against flow exceedance for each river site and for each Group. Review of the individual river site SSC-flow exceedance curves shows that SSC is fairly constant for flows from Q100 to approximately Q30 (values for this switch to a more constant concentration lie in the range of Q40-Q5). For higher flows (<Q30) SSC tends to rise in a highly non linear fashion, as is illustrated using data from the Rhein at Koblenz (Figure 2).

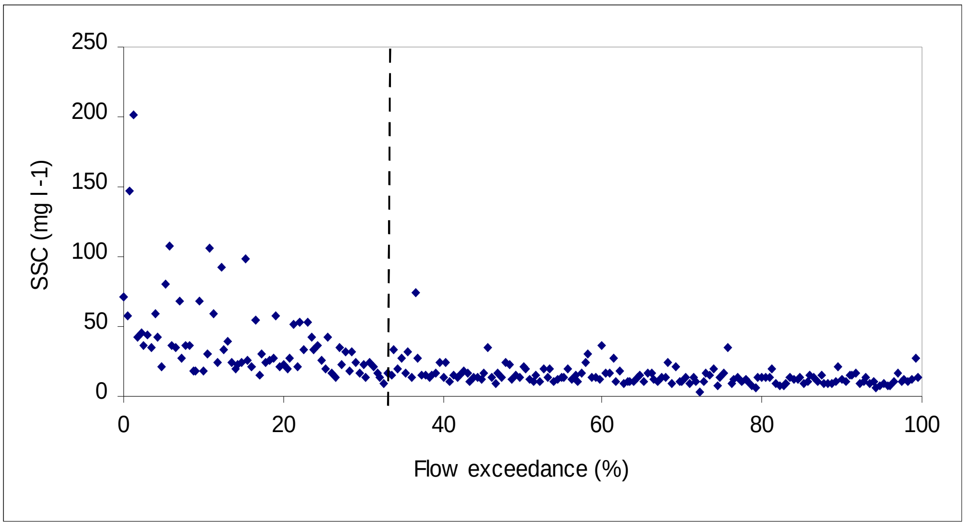

Figure 2: SSC against flow frequency for the Rhein at Koblenz

3.3. Concentration variability at a particular flow exceedance

GREAT-ER is run in a Monte Carlo analysis where flow exceedance is sampled for each run. Therefore it is necessary to understand how sediment concentration varies for a particular flow exceedance in a particular Group. This has been achieved by dividing the flow exceedance axis into a number of classes (bands) and analysing the distribution of monitored data points in each class. Because for flows lower than Q40 sediment concentration shows little variability, flows in this range have been analysed for steps of Q10. For flows greater than Q40 the division is reduced to Q5.

The number of samples and median SSC values for each flow exceeedance band and each group are shown in Figures 3, 5 and 7. The arithmetic mean and maximum SSC concentrations are shown in Figures 4, 6 and 8 (minimum SSC concentrations are not shown, these vary between 0 and 1.8 mg l^{-1} for Groups B and C, and 0.4 and 3 mg l^{-1} for Group A).

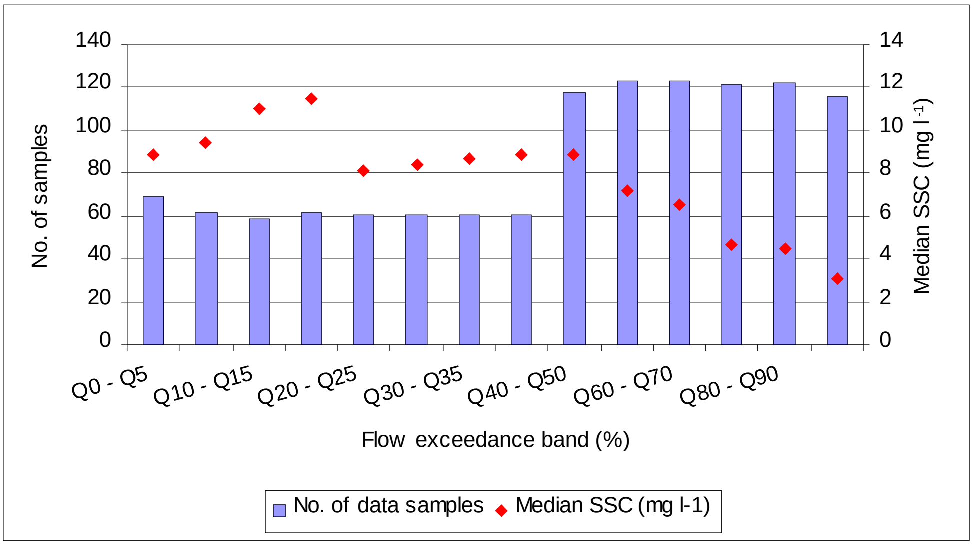

Figure 3: Group A, number of samples and median SSC values (mg l^{-1}) for each flow exceedance band.

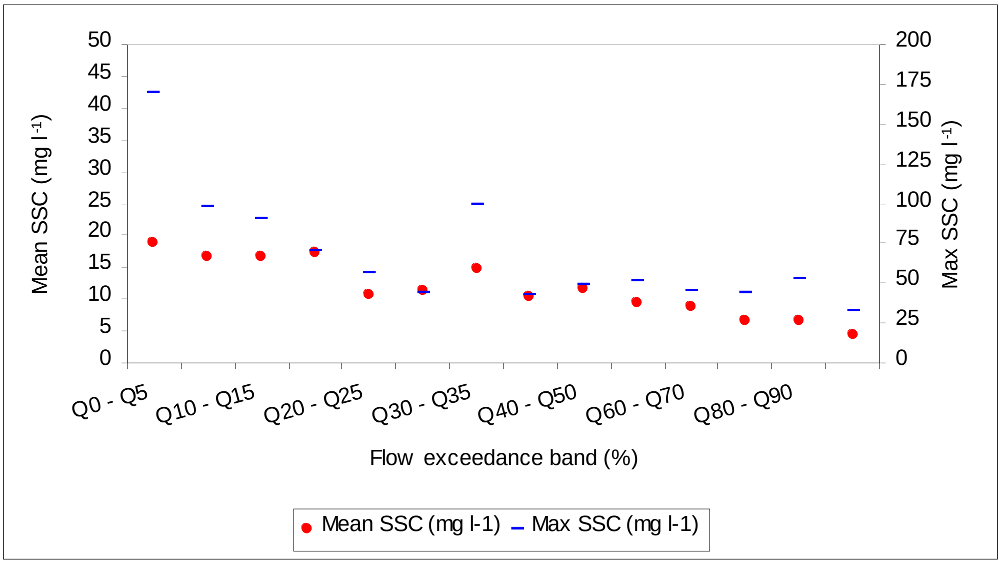

Figure 4: Group A, mean and maximum SSC values (mg l^{-1}) for each flow exceedance band.

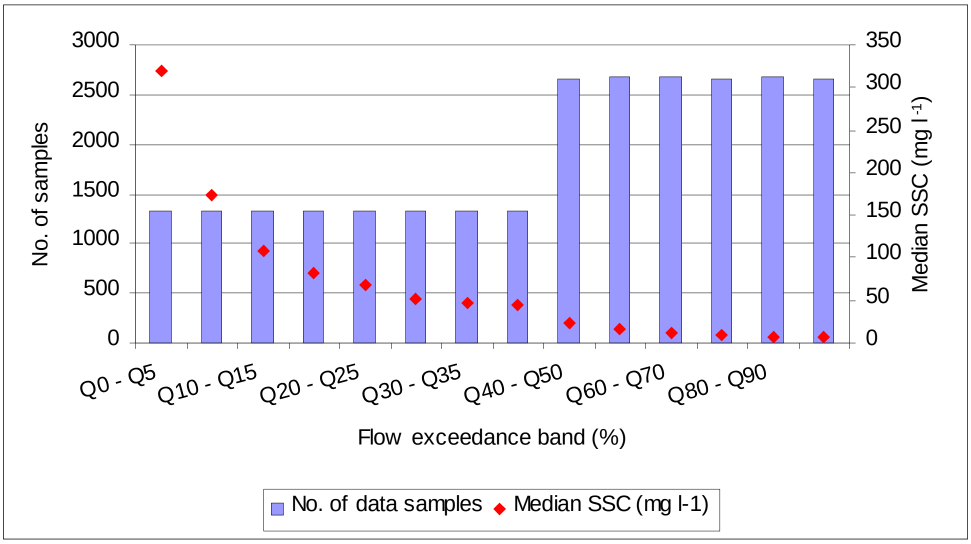

Figure 5: Group B, number of samples and median SSC values (mg l^{-1}) for each flow exceedance band.

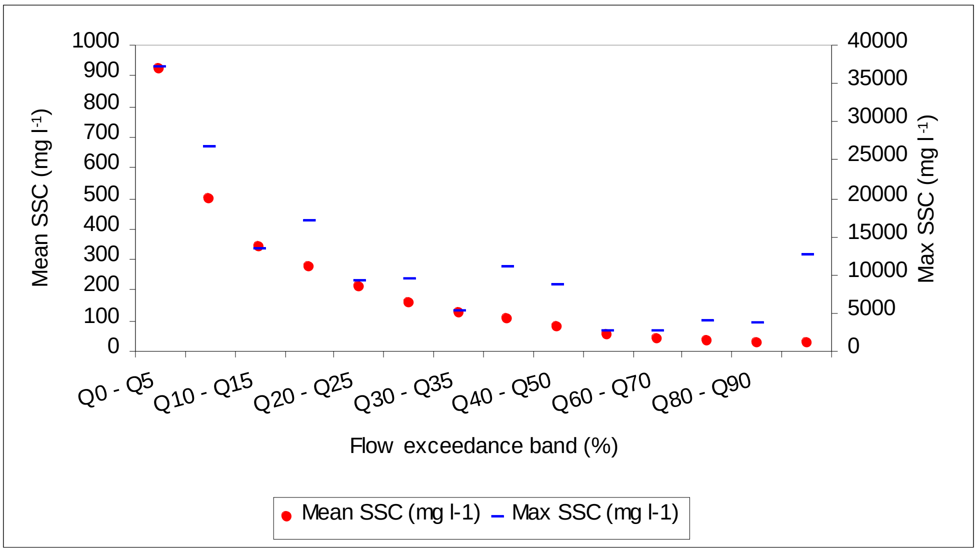

Figure 6: Group B, mean and maximum SSC values (mg l^{-1}) for each flow exceedance band.

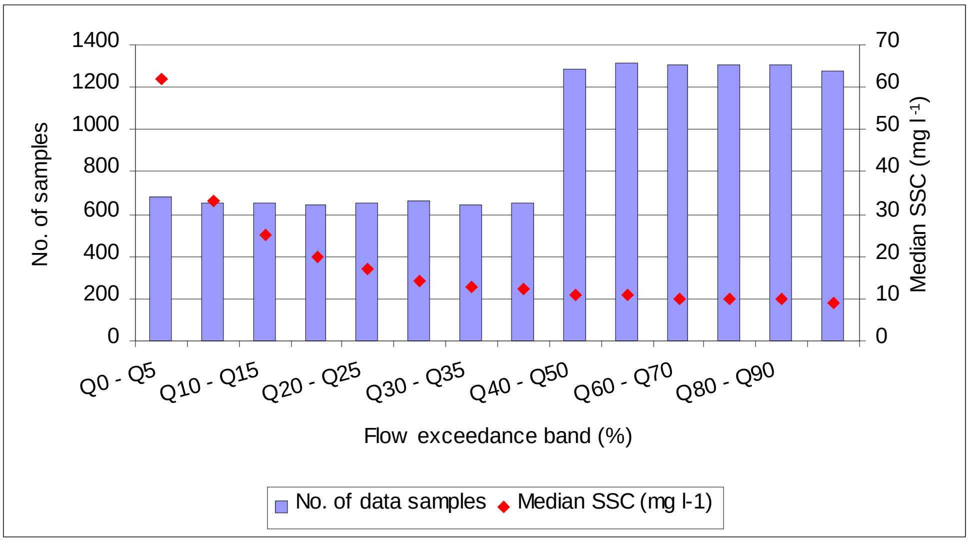

Figure 7: Group C, number of samples and median SSC (mg l^{-1}) for each flow exceedance band.

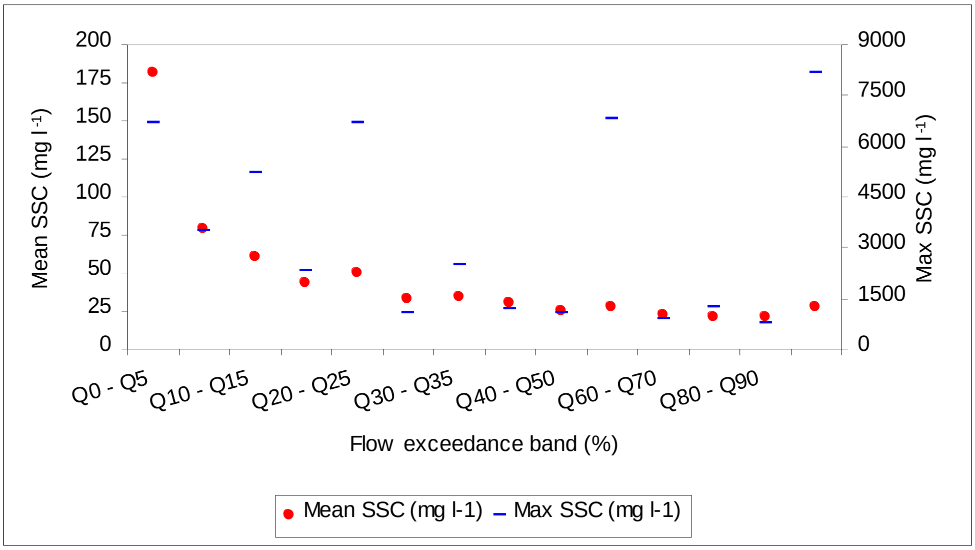

Figure 8: Group C, mean and maximum SSC values (mg l^{-1}) for each flow exceedance band.

For illustrative purposes the distribution of SSC was calculated for each flow exceedance band in increments of 50 mg l^{-1}. Examples from Group C are shown in Figures 9 and 10 which show the distribution of SSC in the Q0-Q5 and Q40-Q50 flow exceedance band respectively.

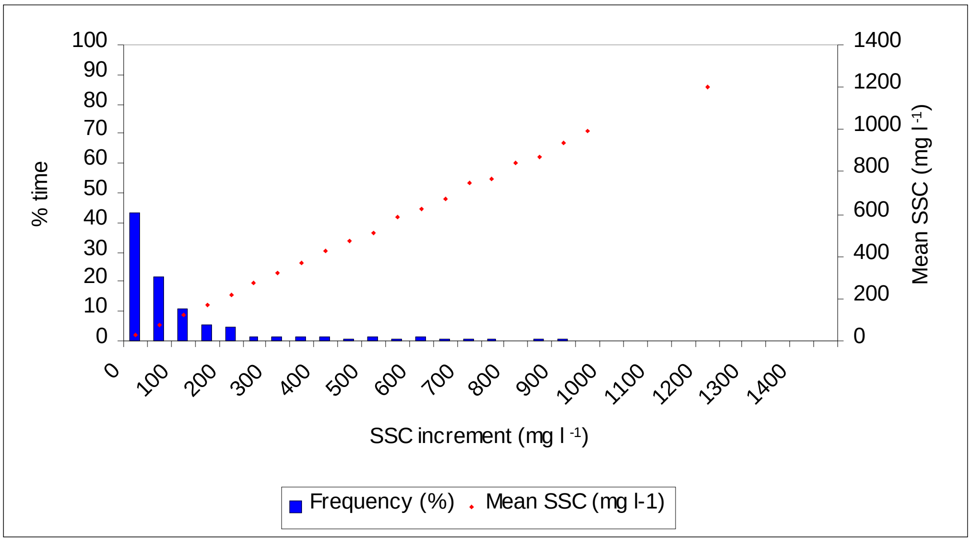

Figure 9: Group C SSC distribution in the Q0 – Q5 flow exceedance band.

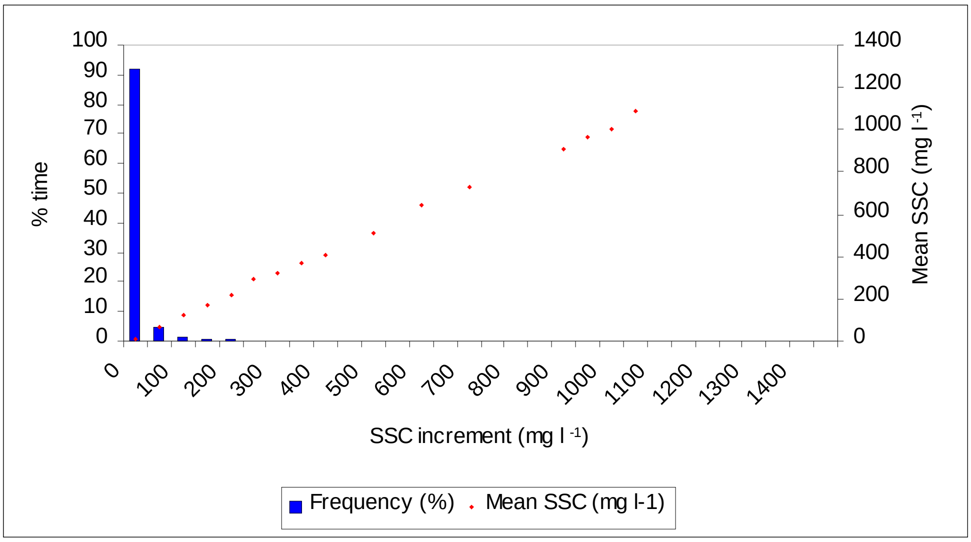

Figure 10: Group C SSC distribution in the Q40 – Q50 flow exceedance band.

The groupings also show major differences in the distribution of SSC across the flow exceedance range. The proportion of time that SSC values are between 0-50 mg l^{-1} is greater than 90 % for flows between Q0-Q100 (all flows) in Group A, Q40-Q100 in Group B and only Q90-Q100 for Group C.

For each Group and each flow exceedance band the resultant distribution has been tested (Goodness-of-fit) to see whether it is significantly different from log-normal, using the Kolmogorov-Smirnov (K-S) statistic. The small number of SSC samples with values of 0 mg l^{-1} were replaced with a value of 0.1 mg l^{-1} in the analysis. The null hypothesis (H_0) is that the observed data follow a log-normal distribution. If the test statistic '**d**' (the distance between the empirical and estimated distribution) is greater than a critical value d the hypothesis of log-normality is rejected. However the K-S test is very sensitive to deviations from the estimated distribution, resulting in the null hypothesis being accepted at low levels of significance in some cases. The results of the log-normality tests are presented in Appendix 3.

Log-normality has been assumed for groups B and C as the skewness and kurtosis are consistently smaller than 0.5 (Tables 2 and 3) and after visual inspection of the percentile plots. However, log-normality cannot be assumed for Group A, and data do not follow any obvious mathematical distribution. Here it is suggested that values are selected randomnly from the minimum to maximum observed values in each flow exceedance class. Tables 1 to 3 present the values required for implementation of these distributions within GREAT-ER, results are summarised in Figures 11-13.

Table 1: Number of samples (N), mean, minimum (Min), maximum (Max), standard deviation (Sdev) of sediment concentration and skewness and kurtosis of the transformed distribution for Group A by flow percentile band (note that all results are given in terms of the natural logarithm, ln (SSC mg l^{-1})).

Flow percentile band	N	Mean	Min	Max	SDev	Skewness	Kurtosis
Q0 - Q5	69	2.433	0.993	5.136	0.909	0.925	0.457
Q5 - Q10	62	2.375	0.470	4.585	0.873	0.680	0.029
Q10 - Q15	59	2.407	0.833	4.500	0.868	0.513	-0.358
Q15 - Q20	62	2.584	0.875	4.263	0.710	0.478	0.232
Q20 - Q25	61	2.180	1.099	4.025	0.607	0.580	0.497
Q25 - Q30	61	2.196	-0.916	3.784	0.726	-0.810	4.665
Q30 - Q35	61	2.301	1.030	4.605	0.787	1.006	0.853
Q35 - Q40	61	2.199	1.030	3.761	0.520	0.538	0.759
Q40 - Q50	118	2.224	0.693	3.892	0.643	0.349	-0.084
Q50 - Q60	123	2.036	0.642	3.951	0.637	0.389	0.168
Q60 - Q70	123	1.911	0.000	3.807	0.687	0.309	0.575
Q70 - Q80	121	1.558	0.000	3.784	0.761	0.513	0.368
Q80 - Q90	122	1.539	-0.693	3.970	0.846	0.016	0.430
Q90 - Q100	116	1.136	-0.511	3.497	0.769	0.405	0.341

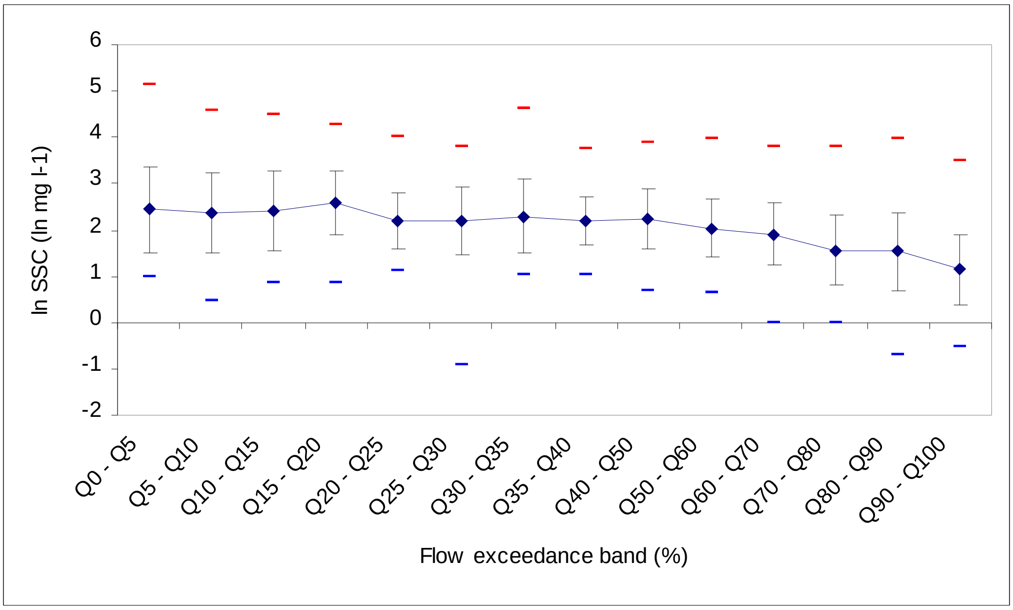

Figure 11: Group A: Natural log (mean SSC) versus flow exceedance showing minimum (blue), maximum (red) and +/- one standard deviation (bar around mean)

Table 2: Number of samples (N), mean, minimum (Min), maximum (Max), standard deviation (Sdev) of sediment concentration and skewness and kurtosis of the transformed distribution for Group B by flow percentile band (note that all results are given in terms of the natural logarithm, ln (SSC mg l^{-1})).

Flow percentile band	N	Mean	Min	Max	SDev	Skewness	Kurtosis
Q0 - Q5	1338	5.597	0.588	10.524	1.680	-0.119	-0.540
Q5 - Q10	1335	4.956	-0.916	10.196	1.678	-0.141	-0.421
Q10 - Q15	1333	4.599	-0.105	9.501	1.655	-0.069	-0.533
Q15 - Q20	1334	4.344	-2.303	9.746	1.612	0.016	-0.228
Q20 - Q25	1334	4.149	-0.511	9.134	1.584	-0.002	-0.486
Q25 - Q30	1335	3.934	-1.204	9.142	1.497	0.075	-0.218
Q30 - Q35	1334	3.772	-2.303	8.557	1.477	0.005	-0.297
Q35 - Q40	1334	3.542	-0.693	9.313	1.447	0.109	-0.187
Q40 - Q50	2667	3.199	-2.303	9.058	1.467	0.252	-0.074
Q50 - Q60	2668	2.811	-1.609	7.904	1.569	0.103	-0.515
Q60 - Q70	2670	2.523	-2.303	7.859	1.614	-0.015	-0.369
Q70 - Q80	2667	2.316	-2.303	8.260	1.561	-0.007	-0.120
Q80 - Q90	2669	2.142	-4.605	8.229	1.499	0.078	-0.114
Q90 - Q100	2664	2.036	-2.303	9.442	1.293	0.309	0.368

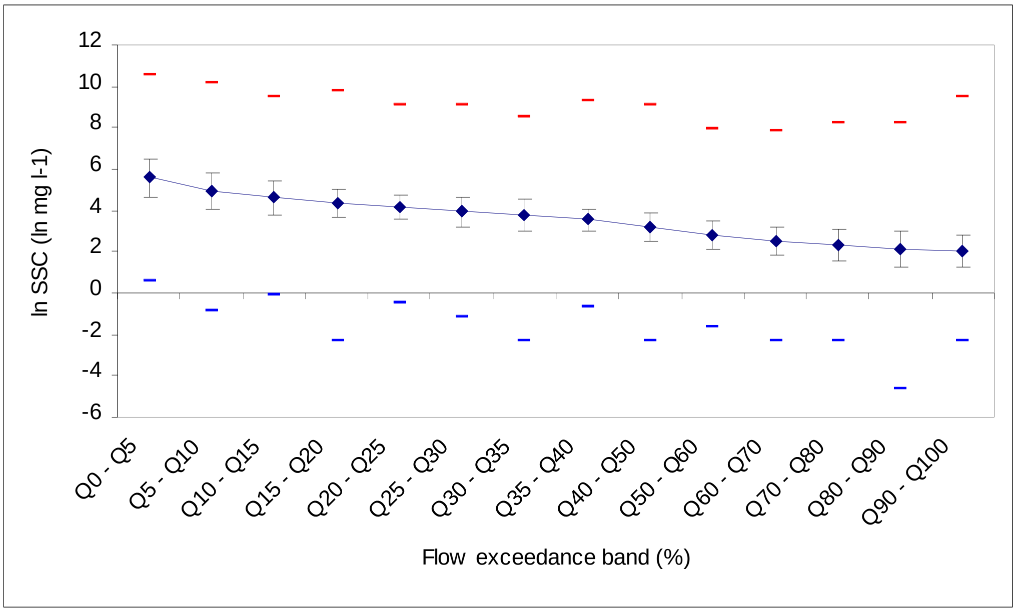

Figure 12: Group B: Natural log (mean SSC) versus flow exceedance showing minimum (blue), maximum (red) and +/- one standard deviation (bar around mean)

Table 3: Number of samples (N), mean, minimum (Min), maximum (Max), standard deviation (Sdev) of sediment concentration and skewness and kurtosis of the transformed distribution for Group C by flow percentile band (note that all results are given in terms of the natural logarithm, ln (SSC mg l^{-1})).

Flow percentile band	N	Mean	Min	Max	SDev	Skewness	Kurtosis
Q0 - Q5	677	4.232	0.000	8.807	1.299	0.231	0.581
Q5 - Q10	653	3.539	-2.303	8.152	1.194	-0.162	2.907
Q10 - Q15	651	3.246	-2.303	8.560	1.104	0.498	2.252
Q15 - Q20	646	2.960	-2.303	7.741	1.172	-0.217	3.206
Q20 - Q25	652	2.895	-2.303	8.810	1.128	0.208	4.434
Q25 - Q30	660	2.722	-2.303	6.966	1.196	-0.274	3.006
Q30 - Q35	647	2.630	-2.303	7.824	1.122	0.301	3.396
Q35 - Q40	652	2.605	-2.303	7.082	1.190	-0.338	3.247
Q40 - Q50	1291	2.439	-2.303	6.994	1.153	-0.498	4.431
Q50 - Q60	1316	2.431	-2.303	8.826	1.134	-0.168	3.692
Q60 - Q70	1306	2.380	-2.303	6.791	1.116	-0.095	3.443
Q70 - Q80	1307	2.323	-2.303	7.142	1.145	-0.345	3.506
Q80 - Q90	1304	2.303	-2.303	6.631	1.124	-0.088	2.840
Q90 - Q100	1277	2.278	-2.303	9.012	1.153	-0.087	3.892

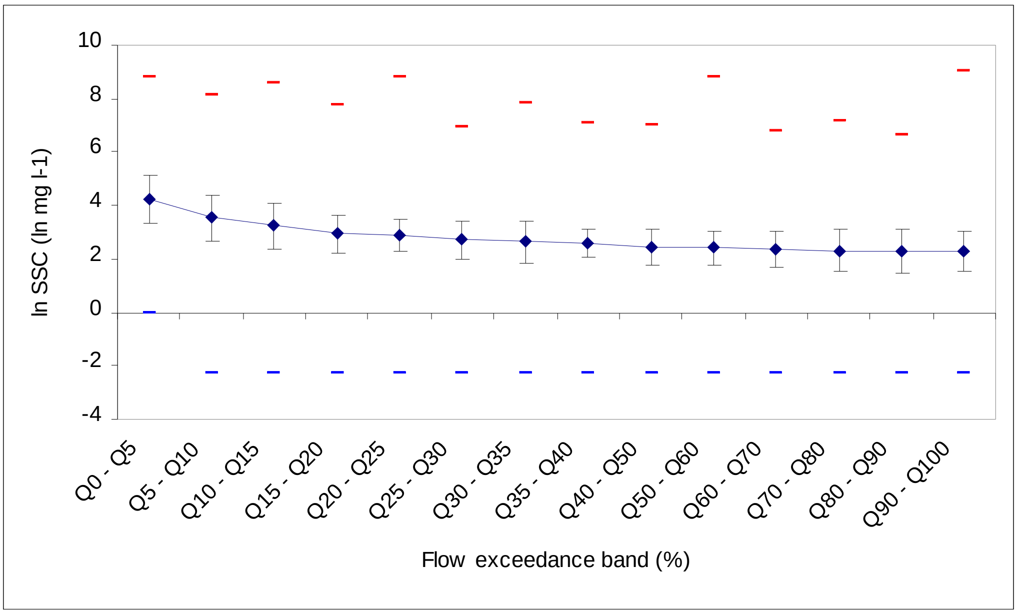

Figure 13: Group C: Natural log (mean SSC) versus flow exceedance showing minimum (blue), maximum (red) and +/- one standard deviation (bar around mean)

4. Using the new sediment concentration options in GREAT-ER

The suggested procedure for use of these grouped data in GREAT-ER is as follows:

- The user is asked to select a Group for their river – text boxes will be provided to guide this choice. The user also has an option to input site specific data. In this case they will be asked to provide statistics for flow exceedance bands as described above.
- GREAT-ER is run and samples a flow frequency
- That flow frequency is classified according to the exceedance band (used for sediment analysis) in which it lies
- For that Group and exceedance band a distribution of possible sediment concentrations exists – For Groups B and C these distributions are considered log-normal.
- GREAT-ER will sample a sediment concentration from the appropriate log-normal distribution for Groups B and C (by Group and flow exceedance value). For Group A values should be selected randomnly from the observed range.
- Partitioning between soluble and sorbed phases will be carried out
- The next Monte Carlo run will commence and the process will be repeated

What the user will see:

In order not to confuse the users a naming system for the Groups should be agreed. This could, for example relate to river type, or may remain as A, B and C where further explanation is given in an accompanying text box. Suggested text is given below:

Group A: Rivers which are predominantly groundwater fed, with low topography and/or frequent lakes
Examples: Danish rivers, Somme (France), Pang (UK)

Group B: Rivers draining high mountain areas with glacial activity and or high snow cover in winter. Strong relief. Not impacted by major lakes.
Examples: Upper reaches (within Switzerland) of Rhine and Rhone, Reuss, Lonza

Group C: All rivers not included in Groups A or B
Examples: Ebro + Jucar (Spain), Rhine, Rhone, Meuse, Moselle, Ouse system + Tees (UK)

5. Methodology to use catchment characteristics (Level three)

In an MSc study alongside the Sediments in GREAT-ER study, methods to estimate sediment concentration in rivers based on catchment characteristics have been developed. Here the best freely available spatial data set has been found to be the recent PESERA soil erosion map (Figure 14), which covers the majority of the EU countries.

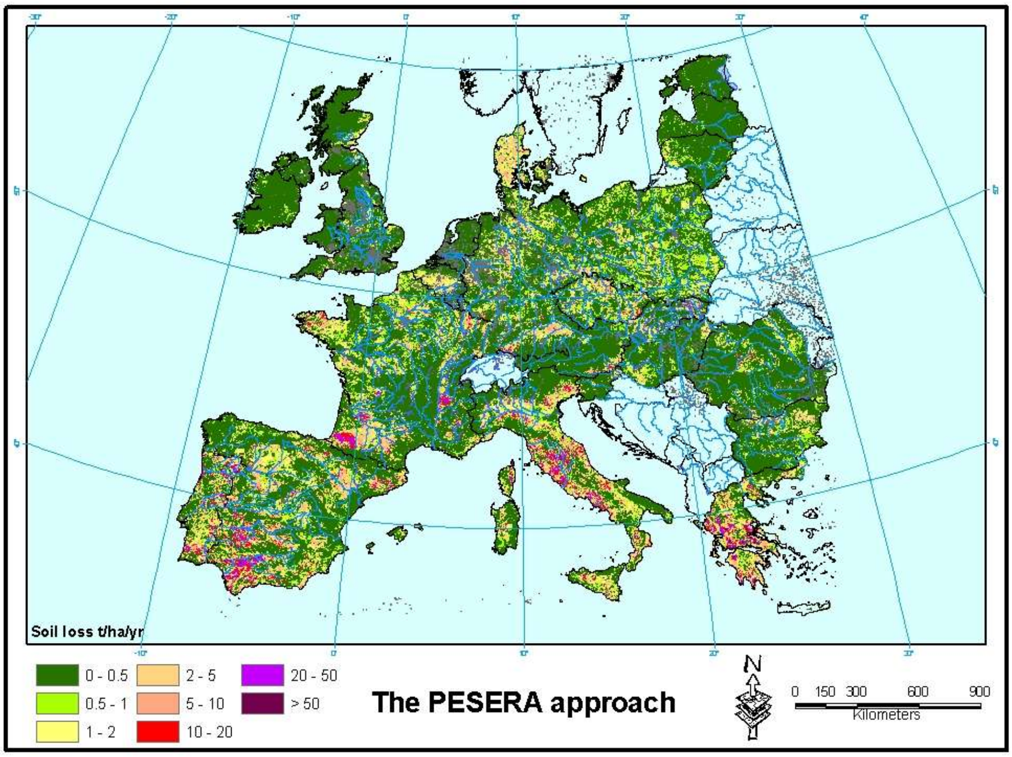

Figure 14: PESERA soil erosion map

In this study, the first step has been to derive relationships between PESERA values in a catchment and sediment yield (t yr^{-1}) at the catchment outlet. Other relationships for prediction of sediment yield based on catchment area and an equation for a sediment delivery ratio (the ratio of catchment erosion to sediment yield) from literature have also been tested. Here the observed relationship between SSC and flow exceedance was again used with a constant mean value for SSC being assumed for all rivers for Q < Q30. For each flow exceedance range the long-term percentage of sediment moved at that flow was calculated (Table 3). Then, knowing the total amount of sediment leaving a catchment in a year (from the sediment yield estimates), the flow exceedance curve for the site and the general relationship between SSC and flow exceedance, sediment can be distributed into flow exceedance classes and mean concentration can be calculated for each class.

Table 4: Percentage of sediment transported in different flow exceedances for major European rivers

Flow exceedance range	% of material transported
Q0-Q10	62.9
Q10-Q20	14.3
Q20-Q30	7.7
Q30-Q40	4.6
Q40-Q50	3.2
Q50-Q60	2.3
Q60-Q70	1.9
Q70-Q80	1.4
Q80-Q90	1.0
Q90-Q100	0.7

Work is on-going to refine and validate this sediment concentration methodology. It should be noted that this method will only be applicable to very large river basins because of the inherent inaccuracies in sediment delivery formulae for small areas.

6. **Organic Matter – Carbon**

The amount of organic matter, or organic carbon, in sediment is thought to be important in controlling the partitioning of contaminants between water and sediment phases as carbon provides a binding site for chemicals. Here a review of typical organic carbon contents in SSC for European rivers is presented. It is not possible with the data available to define an organic carbon content per flow exceedance range, as seen for SSC above.

6.1. Reported values in literature

Typically suspended sediment is a complex mixture of inorganic and organic particles (Walling and Webb, 1981; Walling and Kane, 1984; cited in Hillier (2001)). Similarly to SSC organic carbon has historically been sampled at inappropriate frequencies with respect to its variability in time and space. Many studies have shown an inverse relationship of the fraction of particulate organic carbon (POC) with SSC (Ernstberger *et al.*, 2004; Ittekkot and Laane, 1990; Veyssy *et al.,* 1999).

With respect to allocthonous POC this relationship may be because mineral material is supplied in higher proportions in higher flows (Meybeck, 1982), which may also indicate a function of particle size, density and therefore availability (Hillier, 2001). With respect to autochthonous POC increased SSC decreases the photic depth and primary production therefore highest POC fractions are likely to occur in lower flows where SSC is likely to be at a minimum. Although the fraction of POC tends to increase with decreasing SSC the majority of total POC may be transported in flood conditions (Kempe *et al*., 1990; Meybeck, 1982; Veyssy *et al.*, 1999). The relationship between SPM concentration, flow and the proportions of allochthonous and autochthonous organic matter also therefore have implications on the quality of organic matter (labile fraction) (Ernstberger *et al.*, 2004; Hillier, 2001). Some of the highest fractions of OC in SSC (>15 %) (maximum value reported by Ittekkot and Laane (1990)) have been reported for rivers with very low SSC's or eutrophic rivers. The ranges of POC fractions reported for European rivers are shown in Table 5 and range between 1.3 % and 25 %.

Ankers *et al.* (2003) investigated the influence of catchment characteristics on SSC properties using data collected from 60 small catchments grouped in to 10 study areas, catchments which were selected to provide a representative range of topographic, land use, soil and geological characteristics. Mean OC contents of SSC samples ranged from 4.5-12.2% (Table 5). Despite the differences between the study areas nine showed no significant difference in mean OC content of SSC. One study area had significantly higher mean OC contents of SSC and this was attributed to the characteristically high organic matter (OM) content of the dominate soil type of the area (redzinas). Variability between the small catchments within each study area was also shown to be limited. Similarly Hillier (2001) also indicated that the organic matter was primarily soil derived in the river Don (Scotland) (Table 5) and Tipping *et al.* (1997) found POC in 11 rivers feeding into the Humber to be mainly derived from surface soil horizons in high flows while autochthonous inputs became important in the summer. The differences in POC concentrations for the Garonne and Dordogne rivers, mean values of 2-3.8 % and 4.5 – 6 % respectively presented by Schafer (2002) (Table 5) were also explained by differences in the organic matter content of soil (upper horizons) but also the proportion of forested areas in the catchment. The Dordogne catchment has a greater coverage of forest than the Garonne, 40 and 25% respectively (contributing seasonal inputs), the upper soil horizon in the Dordogne typically contains twice the organic matter of the Garonne soils (5 and 2 - 2.5 % respectively). Thus the European soil map may provide the basis for a method to better define typical organic carbon fractions in river sediments. However in the case of rivers with high inputs from sewage treatment plants or eutrophic rivers a different approach would be required.

Table 5: POC content of European rivers

Reference	River	Low	High	Notes
Cauwet 1985, cited in Kempe, Pettine and Cauwet (1990)	Loire (France)	3 % (high flow)	15 % (low flow)	
Schafer (2002)	Garonne (France)	1.3 %	23 %	Mean of 2 - 3.8 %
Schafer (2002)	Dordogne (France)	3.7 %	25 %	Mean of 4.5 - 6 %
Veyssy *et al*. (1999)	Garonne (France)	2 -5 % associated with high SSC (>50 mg l^{-1})	3 - 24 % associated with low SSC (<50 mg l^{-1})	Reported lability of OM in the autochthonous dominated period (low flows) to be very high.
Hillier (2001)	Don (Scotland)	7 % (high flows)	13 % (low flows)	Wax and proteins at higher concentration in base flow, humate / fulvate material more identifiable in high flows.
Ankers *et al*. (2003)	SW England (10 study areas)	4.5 % (mean)	12.2 % (mean)	No significant difference between nine of the areas.
Cauwet and Sidorov (1996)	Lena river (Siberia)	4 %	20 %	Higher fractions seen in higher flows and SSC's due to snow/ice melt in June.

6.2. Conclusions relating to proportion of organic matter in suspended sediment

For European rivers reported organic carbon content of suspended sediment is always less than 25% by weight. High values tend to be associated with heavily human impacted rivers and low flow conditions (low dilution). For higher flow conditions, when higher SSC values are seen, OC content of SSC varies between approximately 2 and 7% by weight. The following section looks at the implications of varying OC in SSC for partitioning of contaminants.

7. Partitioning of contaminant between dissolved and sorbed phases

The objectives of this part of the study are:

- to assess the importance of suspended sediment in transporting contaminants
- to estimate the partitioning of contaminant in streams
- to establish the role of colloids

The approach was to develop a model of equilibrium partition in streams and then sequentially add components to this system to assess their significance and so build the most practical model of stream partition.

7.2. The role of partition in a three phase system

The three phase system modelled assumes that partition can occur between all three phases (suspended sediment, bed sediment, and the dissolved phase – Figure 15). Each transfer has its own adsorption coefficient but only one Koc is considered reasonable and therefore the adsorption coefficient for each pair of phases is dictated by the organic carbon content of the sediment.

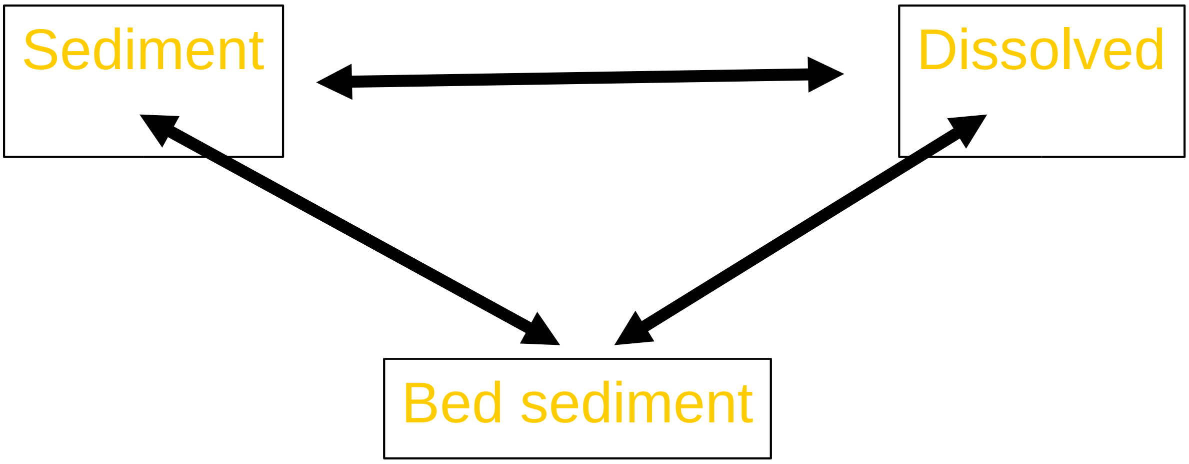

Figure 15: Schematic diagram of the three phase model used in this study.

The form of the equation used is:

$$P_s = \left(\frac{W_p[sedt]}{1000000}\right) \Big/ \left(\frac{W_p[sedt]}{1000000} + \frac{2\rho d_D}{1000} + 2 f_{oc} K_{oc}\right)$$

where:

P_s = the proportion of contaminant adsorbed to the suspended sediment
[sedt] = concentration of suspended sediment (mg l^{-1})
W_p = wetted perimeter
r = density of the sediment (g cm^{-3})
d_D = effective diffusion distance
f_{oc} = fraction of suspended sediment that is organic carbon
K_{oc} = the organic carbon content normalised adsorption coefficient

The river is assumed to have a wetted perimeter of 2m, and [sedt] = 50 mg l^{-1}, this sediment having a density of 1.6 g cm^{-3} and assumed to have a fraction of organic carbon of 25%. The river bed is assumed to have an effective interaction depth of 10mm.

The results show that if the three phase system is at equilibrium then the proportion that is bound to suspended sediment is negligible and decreases as K_{oc} increases (Figure 16). The reason for this is that in a river channel with a wetted perimeter of 2m and an effective interaction depth of 10mm then there is so much more adsorptive surface in the bed than suspended in the flow itself.

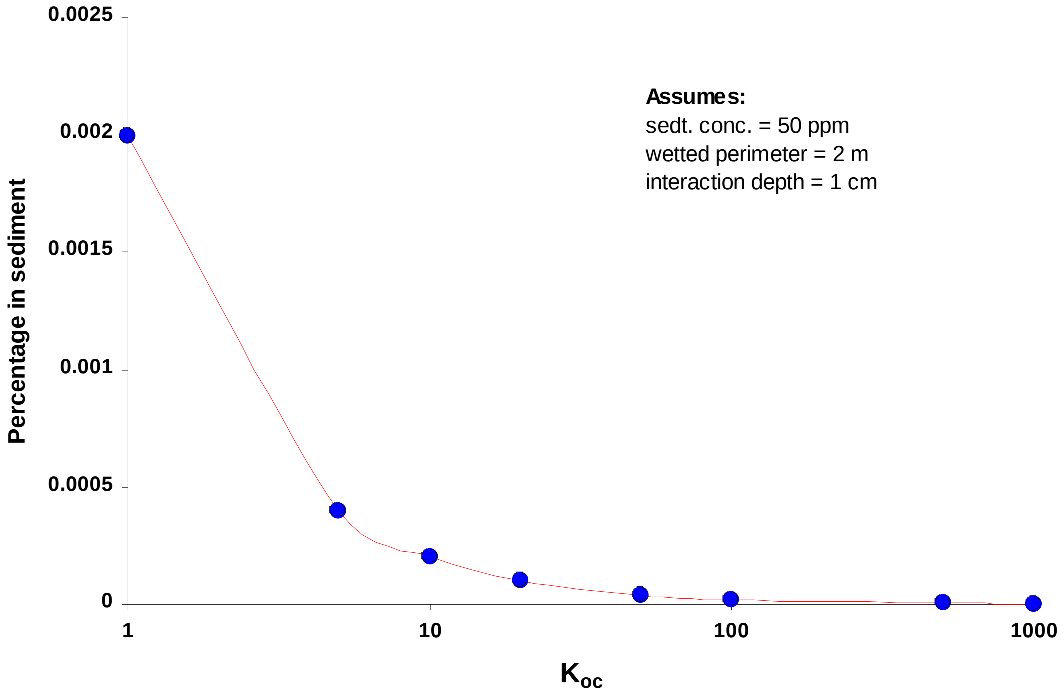

Figure 16: The proportion of contaminant bound to suspended sediment in a three phase system.

7.3. The role of colloids within the fluvial system

To the system modelled above a fourth phase is now added, that is a colloidal phase where colloid is defined as particles that are too small to settle out of suspension. A single K_{oc} is assumed for each of the four phases but it is assumed that colloidal matter is 100% organic carbon; this is a very conservative estimate. Several model runs have been carried out as follows:

a) How important is colloid in a 4-phase system?

In the 4 phase system, i.e. including bed sediment, the importance of all the adsorptive phases (suspended sediment + colloidal phase) is no more than 2.5% even with up to 100 ppm colloid (Figure 17) and this proportion drops as the K_{oc} increases and is unaffected by changes in the colloid concentration.

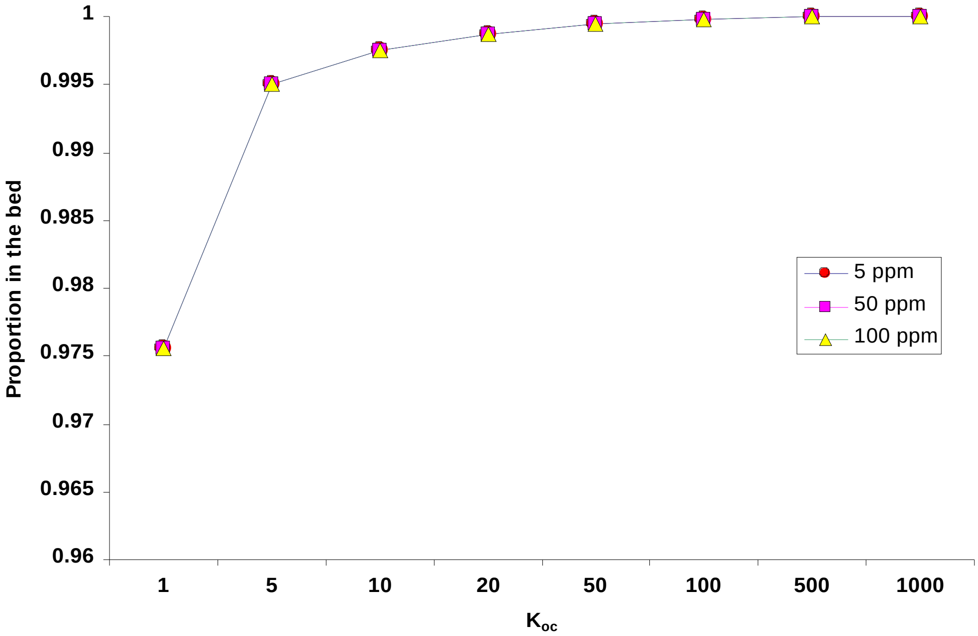

Figure 17: The proportion of contaminant bound to the bed sediment in a four phase system

b) How important is colloid in the water column?
If colloid makes no difference in terms of partition compared to the bed sediment, how important is colloid in comparison to the suspended sediment. A three phase model is run comparing only: suspended sediment, colloid and solution. In order to give the best possible comparison between suspended sediment and colloid concentration, values for both were selected from the records of the harmonised monitoring network for the UK (HMS). In total 500 model runs were conducted with 500 suspended sediment concentrations and colloid concentrations being selected at random from all the samples analysed from all British rivers in the year 2002. The K_{oc} is taken as 100 and the fraction of organic matter on the suspended sediment is kept as 14% even though the average observed value for the samples from the HMS is 6%.

The average suspended sediment concentration for the HMS sites is 15 ± 27 mg l^{-1}, while that for colloid is 5 ± 2.5 mg C l^{-1}. The proportion bound to the suspended and colloidal phases is very small but in general more is bound to colloid than suspended sediment (Figure 18). The average proportion bound to colloid is 69%. The reason for this is relatively simple, the average concentration of colloid is a third of that for the suspended sediment but the proportion of organic carbon is 6 times as great.

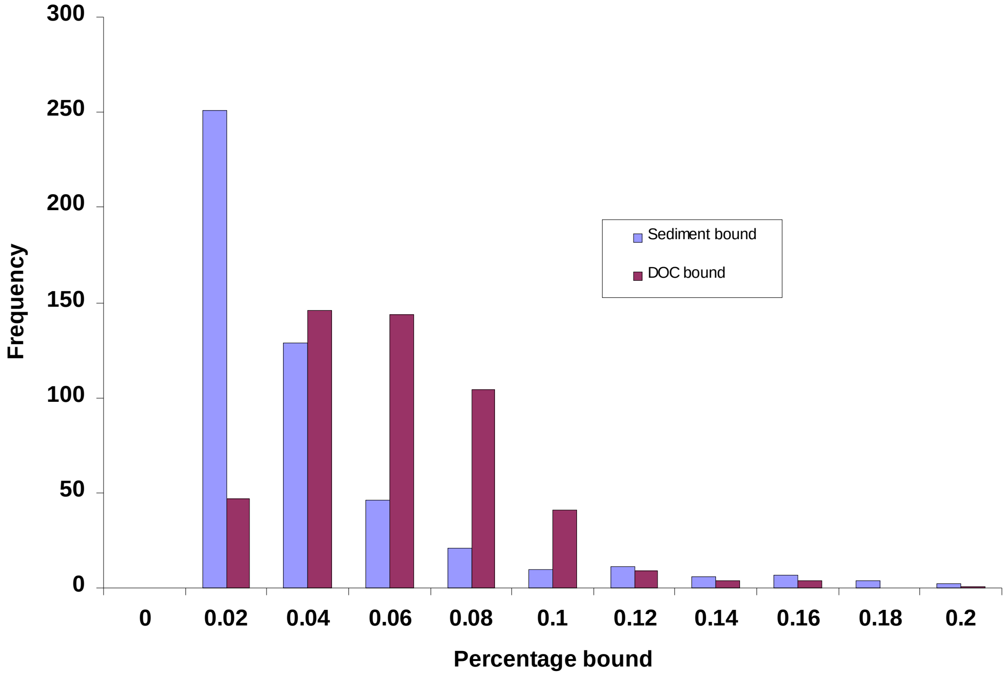

Figure 18: The percentage of contaminant bound to suspended sediment and colloid for all 500 model runs

7.4. Is the river at equilibrium?

The above models assume that the adsorptive phases in the river are at equilibrium. In order to test this assumption the river was modelled using the Damkoehler number. The Damkoehler number is a dimensionless parameter that measures the balance of adsorption to the walls of a conduit in comparison with the advection along the conduit. It is possible to formulate the Damkoehler number in a number of ways, for this case it is assumed that the river is an absorptive conduit and that interaction between the bed and the flow is by means of diffusion into a porous bed sediment. The Damkoehler number is:

$$N_D = \frac{D_{eff}\, l}{Q}$$

where:

N_D = the Damkoehler number
D_{eff} = the effective diffusion coefficient into or from the bed
l = the effective length of the river; and
Q = the river discharge

For examining the behaviour of rivers the D_{eff} is taken to be 0.00001 $m^2\ s^{-1}$, a value typical of a pyrene in river sediment, the effective length is taken to be between 1 and 100 km and Q is taken as being between 0.01 and 100 $m^3\ s^{-1}$. In this formulation the Damkoehler number is independent of the magnitude of the wetted perimeter, however, it is assumed that all of the wetted perimeter of the river is interacting with the flow.

The dimensionless Damkoehler number can be interpreted relative to critical limits. The balance between advection along the conduit and absorption to the walls of the conduit is considered to be $N_D = 1$, where $N_D > 1$ implies a dominance of absorption over advection, while values of $N_D > 100$ imply that the wall of the conduit is at equilibrium with the flow. The results show that even given the conservative assumptions under which the calculation is performed equilibrium could only be assumed for a river over 100 km in length with flows less than 0.01 $m^3\ s^{-1}$, i.e. under very unrealistic conditions (Figure 19). Furthermore, absorption to the walls of the conduit only dominates at very low flows. Therefore, we must conclude that contaminant in solution in a river is unaware of the river bed and does not interact with it. Therefore, contaminant in the river bed sediment can only have got there by settling from the flow and not from adsorption or absorption from the flow.

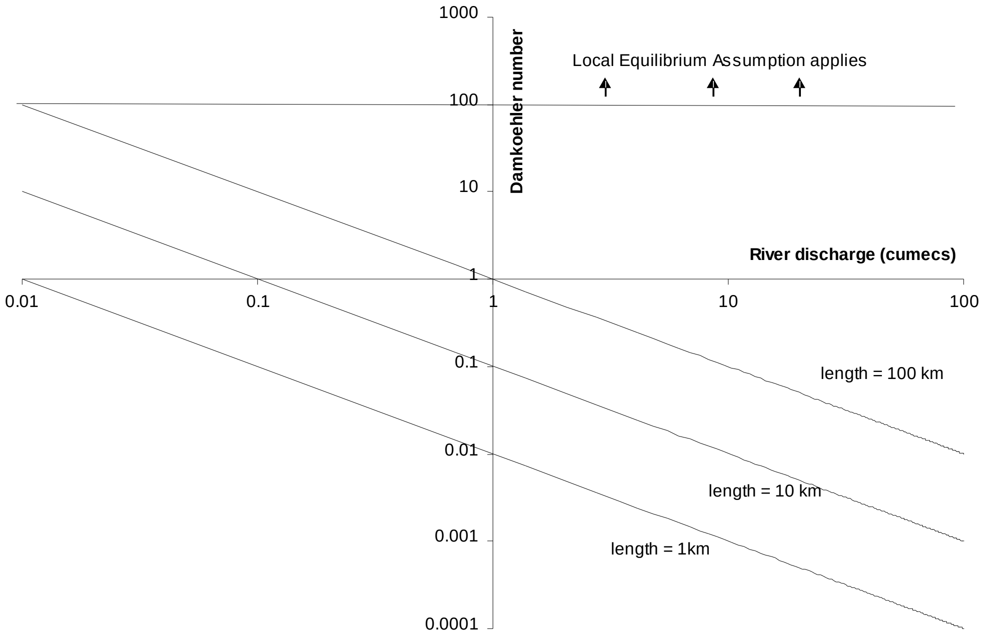

Figure 19: The Damkoehler number (N_D) in comparison to river discharge and the local equilibrium assumption

7.5. Conclusions relating to partitioning

The river system is not at equilibrium, this implies that:

a. All contaminant on the river bed is there due to the settling out of contaminated particles

b. Any contaminant on the suspended sediment must have been transported with the sediment and been acquired in the source area or in transit, or it is the resuspension of contaminated bed sediments

ii) In the presence of a colloidal phase, this will dominate over a suspended sediment phase, although the suspended sediment is not at equilibrium with the river bed it is likely to be at equilibrium with the water column.

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Appendix 1 Suspended sediment data used in this study

Table A1:1 Group A rivers

River	Station	Source	Period	Frequency	LTA Q ($m^3 s^{-1}$)	Mean Q ($m^3 s^{-1}$)	Mean SSC ($mg l^{-1}$)	Catchment area (km^2)
Skjern	Gjaldbæk Bro	DMU	2000 - 2003	monthly	14.66	17.26	7.2	1055
Skjern	Alergård	DMU	2000 - 2003	1-3/month	29.30	26.09	6.7	1550
Stor	Skærum Bro	DMU	2000 - 2003	2-1/month	16.02	18.19	6.2	1097
Omme	Sønderskov Bro	DMU	2000 - 2003	2-1/month	8.26	8.98	6.7	612
Varde	V. Vagtborg	DMU	2000 - 2003	1-3/ month	11.97	12.92	6.4	814
Ribe	V. Stavnager Bro	DMU	2000 - 2003	1-3/ month	8.57	10.57	6.1	675
Guden	Motorsvejbro	DMU	2000 - 2003	2-3/ month		34.30	8.1	
Konge	V. Vilslev Spang	DMU	2000 - 2003	2-1/month	6.87	7.89	6.9	427
Grøn	Rørkær	DMU	2000 - 2003	2-1/month	6.98	7.54	10.2	563
Uggerby	NS Ransbæk	DMU	2000 - 2003	2-1/month	3.44	4.58	24.1	347
Voer	Fæbroen	DMU	2000 - 2003	2-1/month	2.46	3.18	31.9	239
Ry	Manna	DMU	2000 - 2003	2-1/month	2.85	3.52	15.8	285
Lindenborg	Ved Møllebro	DMU	2000 - 2003	monthly	3.40	4.05	11.9	318
Sneum	V. Nørå Bro	DMU	2000 - 2003	2-1/month	3.21	3.75	8.8	223
Brede	Bredebro	DMU	2000 - 2003	2-1/month		4.35	7.3	
Vid	Emmerske	DMU	2000 - 2003	2-1/month	3.50	3.63	10.2	248
Odense	NS Ejby Sluse (9.45)	DMU	2000 - 2003	monthly		4.72	11.4	

DMU Danish National Environmental Research Institute

Table A1:2 Group B rivers

River	Station	Source	Period	Frequency	LTA Q ($m^3 s^{-1}$)	Mean Q ($m^3 s^{-1}$)	Mean SSC ($mg\ l^{-1}$)	Catchment area (km^2)
Rhein	Diepoldsau, Rietbrücke	BWG	1966 - 2003	2/week	238.00	251.68	206.6	6119.0
Reuss	Seedorf	BWG	1979 - 2003	2/week	44.60	45.02	37.7	832.0
Reuss	Mühlau, Reussbrücke	BWG	1977 - 2003	2/week	130.00	131.62	28.2	2904.0
Lonza	Blatten	BWG	1966 - 2003	2/week	4.68	5.62	88.1	77.8
Rhône	Porte du Scex	BWG	1965 - 2003	2/week	183.00	189.60	207.1	5220.0
Landquart	Felsenbach	BWG	1979 - 2003	2/week	24.70	25.52	580.8	616.0
Emme	Wiler, Biberist	BWG	1984 - 2003	2/week	19.20	18.96	47.7	940.0
Aare	Untersiggenthal	BWG	1962 - 1993	2/week	561.00	559.97	32.2	17625.0
Rhein	Bad Ragaz	BWG	1979 - 1991	2/week	166.00	176.24	239.1	4455.0
Rhone	Brig- oberhalb Saltinamündung	BWG	1992/3 & 2003	2/week	42.00	42.72	696.2	913.0

BWG Bundesamt für Wasser und Geologie (Switzerland)

Table A1:3 Group C rivers

River	Station	Source	Period	Frequency	LTA Q ($m^3 s^{-1}$)	Mean Q ($m^3 s^{-1}$)	Mean SSC ($mg l^{-1}$)	Catchment area (km^2)
Swale	Catterick Bridge	CEH	1994 - 1997	Weekly	12.87	16.04	57.6	499.0
Swale	Leckby Grange	CEH	1994 - 1997	Weekly	19.58	27.15	52.7	1350.0
Ure	Westwick Lock	CEH	1994 - 1997	Weekly	21.97	23.85	43.0	914.0
Nidd	Cowthorpe	CEH	1994 - 1997	Weekly	7.42	9.55	27.6	484.3
Aire	Beal Weir	CEH	1994 - 1997	Weekly	35.83			1932.0
Don	Doncaster	CEH	1994 - 1997	Weekly	16.35	15.16	33.2	1256.0
Trent	North Muskham	CEH	1994 - 1997	Weekly	90.87	76.02	35.0	8231.0
Meurth	Bouxiers	RNDE	1990 - 2001	2-1 /month	40.20	44.63	30.4	2980.9
Moselle	Liverdun	RNDE	1990 - 2001	2-1 /month	66.50	68.12	16.7	3461.4
Rhine	Strasbourg	RNDE	1993 - 2002	Monthly	1075.00	1091.34	17.4	39650.0
L'ill	Strasbourg	RNDE	1992 - 2002	Monthly	53.70	53.69	16.6	4600.0
Sarre	Kekastel	IKSMS	1998 - 2004	2/month		14.80	21.1	
Sarre	Sarreinsming	IKSMS	1998 - 2004	2/month		22.95	24.8	
Sarre	Kanzem	IKSMS	1998 - 2003	2/month		93.99	28.2	
La nied	Heckling - Saare	IKSMS	1998 - 2003	2/month		11.95	29.8	
Rhein	Weil am Rhine	IKSR	1995 - 2003	2/month	1050.00	1155.23	14.5	35370.0
Rhein	Lauterbourg	IKSR	1994 - 2003	2-1 /month	1255.00	1333.35	18.6	49300.0
Rhine	Koblenz	IKSR	1994 - 2003	2/month		1893.37	23.2	
Rhein	Lobith	IKSR	1994 - 2000	2-1 /month	2235.12	2523.33	34.2	160800.0
Mosel	Koblenz	IKSR	1994 - 2003	2/month		392.05	21.4	
Argens	Roquebrune sur Argens	RNDE	1971 - 2003	Monthly (with gaps)		15.05	22.2	
Rhône	Chasse sur Rhône	RNDE	1969 - 2004	Monthly (with gaps)		1043.12	25.8	
Rhône	Charmes sur Rhône	RNDE	1980 - 2003	Monthly (with gaps)		1472.74	36.4	

River	Station	Source	Period	Frequency	LTA Q	Mean Q	Mean SSC	Catchment area
Doubs	Avanne Aveney	RNDE	1969 - 2003	Monthly (with gaps)		90.18	14.8	
Doubs	Colombier Fontaine	RNDE	1969 - 2003	Monthly (with gaps)		70.78	10.3	
Drac	Fontaine	RNDE	1982 - 2003	Monthly (with gaps)		111.81	66.2	
Isere	Chateauneuf sur Isere	RNDE	1980 - 2003	Monthly (with gaps)		363.52	66.9	
Rhône	Saint Vallier	RNDE	1971 - 2003	Monthly (with gaps)		1085.48	21.9	
Rhône	Pougny	RNDE	1971 - 2003	Monthly (with gaps)		400.76	19.2	
Durance	Les Mees	RNDE	1971 - 2004	Monthly (with gaps)		8.71	83.4	
Durance	Saint Paul les Durance	RNDE	1970 - 2004	Monthly (with gaps)		132.91	72.8	
Tech	Elne	RNDE	1971 - 2003	Monthly (with gaps)		7.67	14.4	
Herault	Florensac	RNDE	1971 - 2003	Monthly (with gaps)		28.91	11.9	
Rhône	Jons	RNDE	1969 - 2003	Monthly (with gaps)		636.54	22.7	
Orb	Villeneuve les Beziers	RNDE	1981 - 2003	Monthly (with gaps)		23.17	16.3	
Isere	Pontcharra	RNDE	1971 - 2003	Monthly (with gaps)		140.96	177.5	
Tet	Sainte Marie la Mer	RNDE	1982 - 2003	Monthly (with gaps)		10.30	21.7	
Isere	Tullins	RNDE	1971 - 2003	Monthly		295.75	90.1	
Var	Saint Laurent du Var	RNDE	1972 - 2003	Monthly		46.35	230.0	
Saone	Ouroux sur Saone	RNDE	1982 - 2003	Monthly		313.35	14.5	
Saone	Auxonne	RNDE	1971 - 2003	Monthly (with gaps)		136.46	16.9	
Saone	Charrey sur Saone	RNDE	1984 - 2003	Monthly		148.23	17.1	
Mijares	Ribesalbes	CHJ	1994 - 2004	Monthly (with gaps)		1.02	9.8	2467.3
Turia	Ictiofauna	CHJ	1994 - 2004	Monthly		2.63	11.4	4939.8
Cabriel	Cofrentes	CHJ	1994 - 2004	Monthly (with gaps)		12.03	47.2	4697.8
Jucar	Cofrentes	CHJ	1994 - 2004	Monthly (with gaps)		0.92	25.5	11830.4
Ebro	Mendavia	CHEBRO	1980 - 2004	Monthly	115.76	95.52	34.2	
Ebro	Castejon	CHEBRO	1980 - 2004	Monthly	255.80	180.30	38.1	
Ebro	Zaragoza	CHEBRO	1980 - 2002	Monthly	255.60	173.58	74.3	40434.0
Ebro	Sastago	CHEBRO	1980 - 2004	Monthly	264.60	191.79	65.3	

River	Station	Source	Period	Frequency	LTA Q	Mean Q	Mean SSC	Catchment area
Ebro	Mequinenza	CHEBRO	1980 - 2004	Monthly	343.70	202.34	6.4	
Ebro	Tortosa	CHEBRO	1980 - 2001	Monthly	425.20	259.73	10.9	84230.0
Ebro	Miranda	CHEBRO	1980 - 1994	Monthly	57.50	50.60	10.0	
Aragon	Caparroso	CHEBRO	1980 - 2005	Monthly	74.59	50.95	64.2	
Gallego	Zaragoza	CHEBRO	1999 - 2005	Monthly	12.44	17.45	26.9	
Cinca	Fraga	CHEBRO	1980 - 2004	Monthly	94.34	52.79	70.1	
Segre	Seros	CHEBRO	1980 - 2005	Monthly	96.31	71.07	42.8	
Jalón	Grisen	CHEBRO	1980 - 2005	Monthly	7.09	3.48	90.5	

CEH	Centre of Ecology and Hydrology (UK)
RNDE	French Water Data Network
IKSMS	International Commission for the Protection of the Mosel and Saar
IKSR	International Commission for Protection of the River Rhine
CHJ	Confederacion Hidrografica del Jucar
CHEBRO	Confederación Hidrográfica del Ebro

Appendix 2: Suspended sediment data identified but unavailable for this study

Table A2:1 Data sources identified but data not obtained

Source	Data	Cost	Contact
DANUBS	Unknown	Unknown	http://danubs.tuwien.ac.at/ Professor Helmut Kroiss [hkroiss@iwag.tuwien.ac.at]
French Water Data Network - RNDE	Data for the remaining 5 river basin databanks.	Free	Yves Gouisset [Yves.GOUISSET@rhone-alpes.ecologie.gouv.fr]
Hungarian Water Management - VITUKI	Monitoring stations on the Danube, Tisza and their tributaries(5-10 measurments a year) periods of 30 – 50 years.	Unknown	Szekeres@vituki.hu
Bulgarian National Institute of Meteorology and Hydrology - NIMH	Suspended sediment data in Bulgarian rivers is stored in the CIBSD database.	Available for scientific research.	Professor George Gergov [g_gergov@internet-bg.net]
Norwegian Water Resources and Energy Directorate - NVE	Hydra II database – long term flow and sediment transport.	Unknown	
Polish Institute of Meteorology and Water Management - IMGW	13 stations	365 Euro per station	Agnieszka.Juskowiak@imgw.pl (Applied Hydrological Division)
Polish State Hydrological Survey	Daily SSC measurements at 16 monitoring stations (50 year period) on the Vistula (Lajczak 2003).	Unknown	
Swedish Meteorological and Hydrological Institute - SMHI	10 stations with monitoring periods of approximately 25 years.	450 Euro	Flarup Marcus [Marcus.Flarup@smhi.se]

N.B. Links to Web sites of National Hydrological and Hydrometeorological Services, or other national bodies in charge for operational hydrology and water resources assessment activities in Europe and around the world can be found at <http://www.wmo.ch/web/homs/Links/linksnhs.html#RAVI>. This includes the RNDE, VITUKI, NVE, IMGW, NIMH and SMHI from above.

Appendix 3

Table A3:1 Results of the Kolmogorov-Smirnov test of significance for log-normal distributions

Flow exceedance range	Group A	Group B	Group C
Q0 - Q5	d = 0.14940, p < 0.10	d = 0.05039, p < 0.01	d = 0.03925, p = n.s.
Q5 - Q10	d = 0.10681, p = n.s.	d = 0.04953, p < 0.01	d = 0.05630, p < 0.05
Q10 - Q15	d = 0.08946, p = n.s.	d = 0.04282, p < 0.05	d = 0.06915, p < 0.01
Q15 - Q20	d = 0.13966, p < 0.20	d = 0.03108, p < 0.20	d = 0.05285, p < 0.10
Q20 - Q25	d = 0.10426, p = n.s.	d = 0.03905, p < 0.05	d = 0.06828, p < 0.01
Q25 - Q30	d = 0.11179, p = n.s.	d = 0.03165, p < 0.15	d = 0.06841, p < 0.01
Q30 - Q35	d = 0.15568, p < 0.15	d = 0.03464, p < 0.10	d = 0.08254, p < 0.01
Q35 - Q40	d = 0.09413, p = n.s.	d = 0.03821, p < 0.05	d = 0.08492, p < 0.01
Q40 - Q50	d = 0.06122, p = n.s.	d = 0.04555, p < 0.01	d = 0.09495, p < 0.01
Q50 - Q60	d = 0.06194, p = n.s.	d = 0.04658, p < 0.01	d = 0.07359, p < 0.01
Q60 - Q70	d = 0.10265, p < 0.20	d = 0.03362, p < 0.01	d = 0.07410, p < 0.01
Q70 - Q80	d = 0.09137, p = n.s.	d = 0.03652, p < 0.01	d = 0.07354, p < 0.01
Q80 - Q90	d = 0.06281, p = n.s.	d = 0.04982, p < 0.01	d = 0.06861, p < 0.01
Q90 - Q100	d = 0.05464, p = n.s.	d = 0.03787, p < 0.01	d = 0.07750, p < 0.01