

## **Proposals for Reference Thresholds of selected chemical parameters for the Central-Baltic GIG intercalibration.**

***Work paper for the CB GIG***

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### **I – Rationale**

The aim of this document is to propose realistic and WFD compliant “reference thresholds” for some important chemical parameters, in order to harmonise the criteria to be applied for the selection of reference samples used in the Intercalibration (IC) process, at the level of the Central Baltic GIG.

These chemical reference thresholds are complementary to the general reference criteria previously established for the CB GIG.

The thresholds were principally derived from datasets linking invertebrates to general chemical elements, but other values taken from national water quality classifications, diatoms datasets, specific studies and expert opinions were also considered.

Different methods used to establish chemical values corresponding to “no or very minor impact on biological quality elements” are listed below.

#### *Definition of “no impact thresholds”*

This method used by France involves undertaking a regression between ICMi (of samples in high, good, and moderate status) and concentration of a given PC parameter, reducing the range of concentration included in the regression step-by-step until no significant relationship is observed between ICMi and concentration. The chemical values correspond to the mean and 90-percentiles of the data observed during the year (12 monthly samples) preceding the biological sample.

This method was first presented during the CB GIG Steering Group meeting in Mallorca (28-29 November 2005). The corresponding work paper (*Proposals for deriving “No effect thresholds” of selected chemical parameters on the Invertebrate ICM index for the Central-Baltic GIG intercalibration.* Wasson et al., January 23th, 2006) was circulated to the CB GIG Steering Group, and is given in annex II.

#### *Observed values in High Status sites*

The values proposed by UK correspond to the 75<sup>th</sup> percentile of the distribution of chemical values characterising samples considered to be in high status based on macro-invertebrates. The chemical values characterising each site corresponds to the mean and/or 90-percentile of all the chemical data observed at this site during the 3 year period preceding the sample.

The corresponding work paper (*Chemical Concentrations for defining reference condition for Central-Baltic river intercalibration*. John Murray-Bligh et al., 3 February 2006) was examined during the CB GIG meeting in Paris, 23-24 February 2006, and is given in annex III.

#### Observed values in reference sites

Some data corresponds to chemical values observed in the reference sites included in the IC datasets by various MS (e.g. France, Poland, Spain, UK). These sites were selected on the basis of “very low pressure” criteria, following the REFCOND Guidance.

#### National Water quality classification

The limit of the “high quality” class corresponding to some national classification (France, SEQ Eau; Italy, DL 152; Germany, LAWA 1998) was also considered as representative of “very minor” biological impact.

#### Other values of interest

Some values resulting from scientific papers, expert opinions, or ongoing work of the REBECCA project were also considered.

The information available is summarized in the Excel file “CBGIG\_REFCOND\_Chemical.xls” given in Annex I.

## **II – Definition of Chemical Reference Thresholds**

### ***General considerations***

- First of all, we must consider that the information collected so far is rather scarce, and the analysis of biotic responses in the range of very low chemical contamination did not received a great attention from the scientific community. The value proposed here below are thus tentative ones, and could be challenged by stronger scientific works.
- The proposed values correspond to the “**reference threshold**” as defined in the general REFCOND criteria table and the corresponding flow chart circulated to all MS. It was not possible to derive “rejection criteria” with the information available so far.
- We propose both mean values and 90-percentile values for some parameters. The mean is the most robust statistic when few data are available, as it is frequently the case for new reference sites. The 90-percentile should be used only when a sufficient data chronicle is available (at least 12 monthly chemical samples).
- In general, the available information was not sufficient to derive type-specific reference thresholds for all types.

### ***Comments***

#### ***BOD5***

The proposed reference values are **2.4 mg/l** for the mean and **3.6 mg/l** for the 90-percentile for all types except R-C3; values for R-C3 are respectively **2 and 2,75 mg/l**.

For lowland types, these values are just below the proposal of France, and slightly higher than UK proposal (2.2 and 3.4 mg/l), but 25% of the high status sites exceed in fact these thresholds in UK. The mean value correspond to the no-impact threshold for the most sensitive type (C6) in France, and the threshold for disappearance of *Leuctra* (Plecoptera) in Denmark.

The higher sensitivity towards BOD5 of the types C2, C3 and C4, as suggested by the UK proposal, is not confirmed by the “no impact thresholds” derived in France for these types. Germany too gives the same value for C4 and C5.

For C3, although the no-impact threshold in France is much higher than the observed values, we follow the range of observed values (France, UK, Austria) to propose the 2 and 2,75 mg/l thresholds.

*Note : when BOD5 data are not available, TOC values in the range proposed by Germany should be used : **5 mg/l** for all types except C3 : **3 mg/l**.*

As the major effect of BOD5 is the oxygen depletion, this impact should be in fact more pronounced in lowland streams, with higher temperature and lower flow velocity. The proposed values seem thus protective for all CB types. If the BOD5 level is close to the threshold, the absence of impact must be validated with the dissolved oxygen concentration.

### ***Dissolved Oxygen***

The reference values for DO are expressed as % saturation, so as to compensate the thermal effect. Both 10<sup>th</sup> and 90<sup>th</sup> percentiles are used because eutrophication can lead to over-saturation during daylight.

The proposed values are differentiated by types, as slow flowing streams can have naturally lower DO values. We follow the view of Germany considering R-C4 as lowland rivers.

The proposed reference values are in the range **95% - 105% as mean value for all types**; for the 10<sup>th</sup> and 90<sup>th</sup> percentiles, values are differentiated by types : **90% - 110%** for small siliceous lowland and mountain types (C2 and C3), and **85% - 115%** for the other types.

### ***N-NH4***

The proposed values are differentiated by types, following the findings of UK, Germany, and the results of no impact thresholds in France. The view of Germany considering R-C4 as lowland rivers is coherent with the no impact thresholds observed in France for this type.

The proposed values are **0.05 and 0.1 mg/l** for the mean, and **0.12 and 0.25 mg/l** for the 90<sup>th</sup> percentile, in between the values proposed by France, UK, and Germany. These values are consistent with the proposals from Ireland, but only for the types C2 and C3.

### ***P-PO4 (or SRP)***

Original values were provided as Soluble Reactive Phosphorus (SRP) for UK, Total Phosphorus (Total-P) for Italy, and Orthophosphates Phosphorus (P-PO4) for the other countries. SRP is approximated to P-PO4, and Total-P was converted as P-PO4 with an approximate ratio of 0.5.

As Phosphorus is a nutrient with no acute toxic effect, we follow the view of UK to give reference thresholds only for the **mean values**. To convert in mean values the 90<sup>th</sup> percentile provided by some countries, we used an average ratio of 0.59 derived from the French reference sites dataset (33 sites).

UK proposes lower values for the siliceous types C2 and C3, and Germany also for C3. But no impact thresholds in France are lower for C3 (and C4) than for C2 and C6.

The no impact thresholds in France are much higher than the observed values in reference sites, but the invertebrates are not the quality element most sensitive to phosphorus. The values proposed by UK are derived from high status sites based on phytobenthos.

The proposal of Germany is about twice the UK proposal for lowlands (C1, C4, C5).

As a synthesis of these proposals, C3 appears as the most sensitive type, C1, C4, C5 and C6 are less sensitive, and C2 lies in between.

The proposed reference values are **20 µg/l** for C3, **30 µg/l** for C2 and **40 µg/l** for the other types. These values are slightly higher than the UK proposal, but below the values from France and Germany.

### ***N-NO3***

The impact of nitrates on invertebrate communities is by far the less obvious in streams and rivers. In France, it was not possible to determine significant or realistic regressions models between ICMi and NO3 with the whole dataset, or by type. In all cases, the relationships could be related to changes in the physical environment linked to agricultural landscapes and practices, more than to a direct effect of the NO3 itself. UK recognise the same problem and suggested a protective value of 6 mg/l for N-NO3.

For diatoms, some ongoing works of the REBECCA project seemed to demonstrate a significant impact of nitrates on the IPS index, but of much lower intensity than for phosphorus. In France, this relationship is evident for the type C3, but not obvious at all for the lowlands, even for the type C2. There is no significant relationship between IPS and N-NO3 in the range 0 – 6 mg/l, for high alkalinity lowland streams (C4, C5, C6), and for low alkalinity lowlands (C2) the relationship is very weak.

Moreover, the relationship between diatoms (IPS index) and N-NO3 could be largely biased by the correlation between nitrates concentrations and other impacting elements such as BOD5, NH4 and phosphorus. In the French dataset, when filtering first the samples with the proposed reference thresholds of these three elements, no relationship is observed for the remaining samples between IPS and N-NO3 in the range 1 to 8 mg/l for C2, and 1 to 10 mg/l for C6.

UK proposed conservative values for screening diatom reference sites, respectively 2 and 4 mg/l of N-NO3 for low alkalinity/upland types and high alkalinity/lowland types. However, a significant number of sites can be encountered in high status (as EQR values for Diatoms) above these thresholds, although the impact appears more pronounced for the C2 and C3 types.

Toxicological effects: In a review paper based on toxicological data, Camargo *et al.* (2005) stated that long term exposures to 10 mg/l N-NO3 can adversely affect some invertebrates and fishes (mainly salmonids in low alkalinity water), and suggest a protective threshold at 2 mg/l N-NO3 for the most sensitive freshwater species. The lowest NOEC or LOEC values for invertebrates are around 3 to 6 mg/l N-NO3.

### ***Proposal for nitrates:***

Due to the weak relationships evidenced with biological quality elements in lowland streams and rivers, this parameter can be considered with a certain flexibility in the corresponding types.

As for phosphorus, we suggest to use only **mean** values.

For invertebrates, the proposed values are **6 mg/l N-NO3**, except for C3 (**2 mg/l**).

Following the suggestion from UK, thresholds can be differentiated for diatoms. We suggest to consider the UK proposal (except for the type C2): **2 or 4 mg/l N-NO3**, according to the type.

However, due to the general diffuse contamination in agricultural lowlands, it could be difficult to find reference sites matching the nitrate criteria in some regions.

We suggest in this case to follow a two step procedure :

- 1 – to screen first the sites with BOD5, N-NH4 and P-PO4;

2 – on the remaining sites, to derive a type specific relationship between N-NO<sub>3</sub> and the biological element to identify a possible “no impact” threshold, or to validate the absence of impact from nitrates.

### **III – Concluding remarks**

The thresholds proposed in this document should not be interpreted as regulatory standards; the aim is only to allow the comparability of reference conditions for the Intercalibration exercise in the Central Baltic River GIG. These values cannot be used without carefully checking the other general pressure criteria.

We tried to match in a pragmatic way the WFD requirement of “very minor anthropogenic impact” for the definition of these reference conditions, in order to ensure the feasibility of the IC exercise. In most cases, the proposed thresholds are rather “protective” and should allow selecting true reference samples.

A drawback of fixing more stringent and “over protective” thresholds for some types, could be to eliminate sample that could actually be used for reference. This drawback has to be evaluated according to the difficulty of selecting reference samples.

### **Reference**

Camargo J.A, Alonso A. & Salamanca A. 2005 : Nitrate toxicity to aquatic animals: a review with new data for freshwater invertebrates. *Chemosphere*, 58: 1255-1267.