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Response to UK Water Framework Directive Technical Advisory Group Updated Recommendations for Environmental Standards

UK WFD TAG has issued a consultation on proposed EQS's for zinc and copper. The consultation lasts from 26th April to 8th June 2012.

Length of consultation

1- NFA view is that this is too short a time period (6 weeks) and given that the proposals are for WFD River Basin Management 2015-2021 with potentially significant financial implications it is of greater benefit to ensure a thorough review of the proposals rather than a swift review. The length of time of the consultation period should follow Government guidelines of 12 weeks.

There is a considerable amount of academic expertise available, some of which was used in earlier Environment Agency science reports relevant to this consultation and it is important that these experts are specifically consulted on the proposals in the consultation. [reports SC030194 & SC080021]

There are also other academics with relevant expertise and it is NFA's view that they too should be consulted on aspects of the consultation. However the period of the consultation falls into the end of the academic year with exams and dissertations to review and therefore, for a number of these other experts, the time frame of the consultation is very inconvenient Extending it for another 6 weeks would be of great benefit in order to allow their input.

The Society of Environmental Toxicology and Chemistry has its major World Congress 20-24th May 2012 and many experts are preparing for this and attending it. A number of these scientists who have relevant knowledge should have had the opportunity to comment on this consultation.

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Derivation of EQS's for zinc

2- The EU SCHER has commented specifically on the zinc EQS (22 March 2012) but it has to be noted that its comments are based solely on data presented to the SCHER. The zinc EQS is presented on an Added Risk basis. The finding of risk or otherwise will therefore depend on the 'natural background level of dissolved metals' to which any proposed EQS is to be added.

Adaptation and Acclimation of biota to background metals levels in water

It is now clearly established that aquatic organisms adapt and acclimate to background zinc in water.
Refs:- *Zinc resistance in chironamus riparius – evidence in physiological and genetic components, Miller & Hendricks in J.N.Am.Benthol.Soc Vol 15, 2007*

- *Copper & zinc tolerance of tropical micro-algae after copper acclimation by Johnson et al in Environ.Toxicol Vol 22 2007*
- *Multigenerational zinc acclimation and tolerance in daphnia magna by Muyssen & Janssen in Env.Tox & Chem Vol 20,9, 2001*
- *Effects of stream water contaminated with zinc and cadmium to juvenile cut-throat trout by Harper et al in Arch.Environ.Contam.Tox Vol 54 2008*
- *Importance of Acclimation to environmentally relevant zinc concentrations of sensitivity of daphnia magna to zinc- by Mussens & Janssen in Env.Toxicol.Chem Vol 24 2005*
- *Kinetics and mechanism of tolerance induction on acclimation of villorita cyprinoides to copper and zinc-by Sathyanathan in J.Biosci Vol 21 1996*
- *Acclimation and response of algal communities from different sources of zinc toxicity -by Wang in Water, Air & Soil Pollution Vol 28 1986*
- *Plasma clearance of Cadmium and zinc in non-acclimated and acclimated trout- by Chourdhry et al in Aquatic Toxicology Vol 64 2003*

Organisms from very low background levels of zinc in water are exceptionally sensitive to additions of zinc. It is very important that in selecting the No Effect Concentrations of zinc for species determined by laboratory eco-tox tests that these species originate from metal backgrounds concentrations that are relevant to the real environment levels of zinc. The consequence of including data from organisms cultivated in a zinc or other metal deficient background skews the distribution curve thus resulting in a very low PNEC being derived.

It should be noted that in the EU Zinc Risk Assessment Report eco-tox data from the mid to upper ranges of DOC and hardness typical of the EU were excluded from the data set used in the SSD approach in calculating the PNEC.

Adoption of Biotic Ligand Model

3- NFA is very pleased to have the validity of the BLM (Biotic Ligand Model) recognised in determining the bio-available fraction of metals in the aquatic environment for regulatory purposes. NFA is of the opinion that this is a very major step forward in a regulatory approach based on science.

Natural Background/Ambient background level of zinc and copper in UK waters *And* Recognition that the UK consists of a number of metallo-regions or metallo-catchments

4- Several proposals are made in the consultation on how the 'natural environment' or 'pristine environment' may be determined.

That UK is mineral rich in certain areas and that the flux of metals from former mines is of concern is well documented. The flux of metals in the aquatic environment in the UK due to anthropogenic activity has been in existence for circa two thousand years, primarily due to various periods of mining. This flux of zinc should not be considered as wholly anthropogenic for two reasons.

Natural outflows of waters with high levels of metals from fractured metal rich seams also occur.

E.g. 'Metals in Water, Determining Natural Background Concentrations in Mineralized Areas' by Runnells, Shepherd and Angino in Environ.Sci.Technol 1992.

And 'Physico-chemical surface water conditions of catchments with metallogenic origin: A contribution to the establishment of the EC Water Framework Directive 2000/60/EG in Germany' by Neitzel,Schneider,Schlumprecht (2002)

Work by *Huffmeyer,Klausmeir & Matthies in Science of the Total Environment, 2009* shows that of the zinc loading in the River Ruhr some 1/3rd originates from geochemical strata and former mines.

In the UK, *Mayes, Potter & Jarvis in Science of the Total Environment, Vol 408, 2010* propose that the flux from geochemical strata and former mines in the UK accounts for some 190+tonnes of zinc and 19+ tonnes of copper in river systems. This originates from 338 discharges from 4923 mines that are recorded. Many areas of

the UK have not been analysed in the same manner as there are not sufficient records. Areas of mineralization that were not exploited, due to being judged as not commercially viable, may still be a significant source of metals into the aquatic environment due to natural emergence of waters through fractured rocks. Mayes et al also propose that the loadings of metals first offered may be significantly under estimated, an underestimate of some 40 %.

Naturally contaminated waters are identified in *'Metals in Water: Determining natural background concentrations in mineralized areas' by Runnells, Shepherd and Angino in Environ.Sci.Technol 1992.*

The conclusions drawn in this paper can be considered equally relevant to the UK.

The range of zinc in UK topsoils is shown in the Advanced Soil Geochemical Atlas of England & Wales by British Geological Survey 2012 on p220. Silting from the soils through which rivers run will transfer varying amounts of zinc in water.

Areas of high rates of deposition from the air as the result of historical coal burning and industry metallurgy emissions e.g. around Manchester and Sheffield, have left a legacy of elevated metals levels that still continue to leach zinc and other metals into upland waters.

It is clear therefore that the UK has varying levels of metals and sources of these metals in river catchments.

All in all the proposal of a pristine i.e. low zinc/ other metals aquatic environment, with the background concentrations proposed in the consultation, seems unrealistic for the UK as a whole.

From the above references the natural origin zinc loading is substantially higher that may be envisaged and therefore a proposal for a 5 or 10^{th}%-ile of the concentrations of zinc and other metals identified in UK waters as the natural background is without statistical substantiation or scientific justification. The 10^{th}%-ile of the distribution curve of measured concentration values is the 10^{th}%-ile but this cannot be said to be the natural background level.

The 'natural' background concentration at any point on a river is in fact a range of concentrations. The loading from natural sources appears to be in the same order of magnitude as discharges into controlled waters by IPPC processes as recorded in the UK PRTR. Other diffuse sources of natural and anthropogenic origins also contribute to the flux of the metals.

Variations in measured concentrations are caused by a number of factors. The prime one of which is rainfall and therefore the cause of variations of flows in UK rivers.

Rainfall not only causes changes in flux of mobilized zinc from all sources, anthropogenic and natural but also variances in concentration by dilution.

Data held in the Centre for Ecology & Hydrology, Wallingford, UK for river flow rates shows that the flow rates may vary 10 fold and more. This variation is not predicable on a daily or annual basis.

This means that sampling for metals, dissolved and total, carried on a once per month basis, cannot reflect the dynamic variations in flux of metals in water or the variations in the abiotic factors such as DOC, hardness and others that affect bio-availability of the metals zinc and copper as Specific Pollutants.

NFA believes that the 5^{th} or 10^{th} %-ile of the distribution curve of measured dissolved concentrations of zinc and copper does not reflect the natural background level of zinc and copper in UK waters and that the natural background levels are considerable higher, probably in the range of 25 to 30% of the range of values.

Ref - *Predictions of river quality across NW England using catchment characteristics by Rothwell et al in Journal of Hydrology Vol 395 2010*

- *A spatial and seasonal assessment of river chemistry across NW England by Rothwell et al in Science of the Total Environment Vol 408 2010*

In order to have a more comprehensive understanding of the variability of bio-available fractions of zinc and copper in the UK aquatic environment NFA proposes that an exercise of deploying passive samplers such as DGT on a daily basis at a number of flow measuring points in a couple of river basins should be undertaken. This would be cost effective and very helpful in understanding the dynamic fluxes of bio-available fractions of metals.

Ref- ' In Situ Speciation Measurement of Trace Metals in Headwater Streams' by Warken, Lawlor, Lofts, Tipping, Davison & Zhang in Environ Sci Technol Vol 43 2009 and several other related papers on DGT as a technique and measurements of labile metal in aquatic systems with Davison, Zhang and Warken amongst others as authors (8+ papers)

Finally, extensive research for example by Prof Macklin of University of Aberystwyth and by Dr Hudson-Edwards, Birkbeck College, London on metal levels in sediments in many UK rivers shows that the levels vary significantly over the last 2,000 years and that the levels vary in manner that is not obviously time related. The work of these and other researchers show that the distribution of zinc from the mineralogically rich areas and from anthropogenic use of metals such as zinc, copper

and others has altered metals loadings for such a length of time (over 2,000 years) that these ambient levels may be taken as 'natural levels'.

There is much evidence that aquatic organisms have adapted as well as acclimated to high levels of dissolved metals, levels far in excess of those proposed in the consultation of background + EQS,

NFA is of the view that despite a conservative EQS proposed for both zinc and copper, the greatest concern is that unrealistic proposals for a natural background level for each of these metals may give rise to a concern of risk from the metals whereas this risk not may exist.

NFA proposes that the natural variances of bio-available levels of these metals in UK waters should be determined in order to guide regulatory thinking and guidance.

NFA is of the view that there is sufficient evidence in the press that both acclimation and adaption exist across several trophic levels and that an over-precautionary approach to the EQS and unrealistic proposed determination of background is not scientifically justified.

NFA recognises that there are however historical legacy issues on certain water bodies where the loading of metals is in excessive of what is tolerable by the environment and that these exceptional cases should be resolved individually.

Summary

All the evidence points to the fact that there is no scientific justification for a single background value for natural or pristine background value of dissolved zinc and copper in UK waters derived from the 10^{th}%-ile from the distribution curve of measured concentrations. Likewise there is no justification for derived the natural background value in water from sediment values and partition coefficients.

Natural levels or ambient levels of both metals have a substantial mass contribution from natural sources that are significant with respect to current anthropogenic fluxes.

A suitable background value (the highest ambient level measured where no adverse effects on biota are observed) for the Added Risk Approach should be judged from the database of newly generated data from passive samplers, for example DGT devices.

This exercise should be extended to determine catchment relevant data and hence an appropriate range of ambient background levels of dissolved metals in water for the catchment.

UK WFD TAG should take greater scientific input from the extensive knowledge base in academia in response to this consultation.

In particular is strongly recommended that scientists with great skills and background in modelling uncertainty and fluxes in the environment, for example Professor Keith Beven of University of Lancaster Environment Science Dept, and others, should be consulted.

29 May 2012
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On behalf of Non Ferrous Alliance