

Stepwise approach for the derivation of sediment quality criteria at different spatial scales: case study of mercury contamination in river basins from North Spain

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Introduction: The Environmental Quality Standards (EQS) directive [1] was an important improvement of long-term water quality monitoring at the European level, pointing towards the use of sediments and biota as matrices for the assessment of priority substances under the WFD [2]. Different approaches exist that can be used by water managers for sediment quality assessment and monitoring, including the development of regional background and threshold levels or the application of Sediment Quality Guidelines (SQGs). But are they comparable? The main objective of the present work was to determine and compare sediment *background* or reference values, *thresholds*, and guidelines derived using different methodologies and various types of data on biological effects related to the levels of Hg in freshwater sediments. The study region comprises several catchment areas and distinct metallo-regions in North Spain. A previous study in the Nalón River basin, which included several mining districts [3], revealed that background geological levels in the study area might naturally contribute to higher metal levels in sediments than other basins in North Spain. However, the absence of SQGs in Spain precludes the development of a sound Ecological Risk Assessment (ERA) and water quality protection plans in the area. Thus, first, Predicted No Effect Concentrations (PNECs) were calculated from data on spiked sediment toxicity tests from the literature. Second, we calculated Hg *background* levels (metal concentration in the sediment not due to local anthropogenic sources) and *threshold* levels (the upper limit of normal background fluctuation related with no-effects) using a reference condition approach in North Spain (a spatial network of minimally disturbed sites) and, in a third tier, SQGs for Hg were developed using field community effect-based approaches in the case of Nalón River basin.

Methods: The derivation of guidelines followed the EU Technical Guidance for Deriving Environmental Quality Standards (EU TGD [4]), using reliable and relevant sediment-spiked toxicity data. To identify *background* levels in North Spain, first an appropriate selection of the reference sites that could be used to obtain the Hg sediment *background*

concentration in the study area was done (n=56). *Threshold* concentrations were obtained from the *background* values, once ecological status was validated by macroinvertebrate community metrics (Good or Very Good) or the absence of toxicity with *Tubifex tubifex* chronic bioassay according to the criteria by Rodríguez et al. [5]. Upper percentiles (P90, P95) or upper confidence limits of the mean, the median, and the Tukey's inner fence method were used to determine *Threshold* values. Field data from the Nalón River basin (with rivers affected by different degrees of Hg concentrations) included chronic bioassays with *T. tubifex* performed on field collected sediments and benthic community multimetric indexes to estimate low and high SQGs.

Results and discussion: The *background* Hg levels varied mainly due to local differences in the river basin geology, with a median value of 0.11 mg/kg dw (range= 0.01-2.92). Threshold concentrations varied depending of the statistics or method used. The most conservative values tend to be given by P90s (0.38 mg/kg dw) while the values were 7 times higher with the Tukey's inner fence method (2.80 mg/kg dw). The PNEC values were only calculated using spiked-sediment toxicity data with the deterministic approach. The limited set of effect-data available required the application of assessment factors, which resulted in unreliable PNEC values far below the *background* concentrations in the study area. In comparison, *T. tubifex* EC₂₀ provided a low range of SQGs that were within the range of the calculated *background* concentrations, whereas EC₅₀ values could be considered as high range SQGs and were in agreement with the SQGs calculated from effects measured by the benthic community multimetric indexes.

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References: [1] EC, 2008; [2] EC 2000; [3] Méndez-Fernández et al, 2015 Arch Environ Contam Toxicol 68:107-123; [4] EC, 2011; [5] Rodríguez et al, 2011 Aquatic Toxicol 10 :207-213.