Journal of Hazardous Materials 263P (2013) 239–247

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Ecological screening indicators of stress and risk for the Llobregat river water

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HIGHLIGHTS

- Ecological risk assessment of fluvial ecosystems.
- Indexes to predict impact on aquatic organisms and terrestrial vertebrates.
- Monthly average risk indexes for a list of metals and organic compounds.
- Risk indexes for a list of pesticides and pharmaceutical compounds.

ARTICLE INFO

Article history:
Received 8 May 2013
Received in revised form 5 July 2013
Accepted 6 July 2013
Available online 13 July 2013

Keywords:
Ecological risk assessment (ERA)
Fluvial ecosystems
Metals
Pharmaceutical compounds
Pesticides

ABSTRACT

The objective of this article is to develop and apply several simple and rough indicators for river aquatic ecosystems assessment in order to screen potential chemical stressors. Several indicators, based on toxicity (PNEC) and on legislation levels (EQS) have been developed. All these indicators are ratios that were calculated by using public and private data of concentrations of a large list of compounds during a period of five years, including metals and organic compounds in the lower part of the Llobregat river basin at the intake of the drinking water treatment plant. Additionally, new campaigns were executed for increasing the information available on the presence of compounds not routinely analyzed, such as some other pesticides and pharmaceuticals. In the case of inorganic pollutants, the indicators obtained in this river section showed significant risk especially for zinc, but also for copper, nickel and barium. For organic pollutants, the pesticides terbuthylazine, diazinon, 2-methyl-4-chlorophenoxyacetic (MCPA), and in a few cases, chlorpyrifos and lindane, also showed indexes above the threshold. Among the pharmaceuticals, the antibiotics clarithromycin and ciprofloxacin were the only ones with risk indicators adverse to ecosystems. The specific values of the indexes obtained rely on the quantity and quality of the data available, so their interpretation should take into account that some values can be high due to the use of too conservative toxicological information.

1. Introduction

Degradation of water bodies has been a key issue in Europe during the last years. Water Framework Directive (WFD, Directive 2000/60/EC) [1] imposes the achievement of good ecological status of water bodies. Environmental objectives should preserve quality of water bodies beyond the potential uses for industry, agriculture, urban and recreational uses, integrating preservation of the health of ecosystems, their functioning and structure. This objective should assure long term preservation of ecosystems and the local biological communities, as well as the absence of dangerous substances that can pose risk to human health.

National administrations, like river basin authorities, should deal with indexes that could be easily used to give an indication of the good chemical, hydromorphological and biological status of each specific water body according to their local characteristics.

Abbreviations: ACA, Catalan Water Agency; AF, assessment factor; BCF, bioconcentration factor; CI, confidence interval; DWTP, drinking water treatment plant; DGT, diffusive gradient thin film; EC_{50}, term half maximal effective concentration; ERA, ecological risk assessment; EQS, environmental quality standards; ES, electrospray; GIS, geographical information systems; $HC_{5\%}$, 5th percentile of the distribution; K_{ow}, octanol–water partition coefficient; IRA, integrated risk assessment; LC, liquid chromatography; LC_{50}, term half maximal lethal concentration; LOEC, lowest observed effect concentration; LOQ, limit of quantification; MS/MS, tandem mass spectrometry; NOEC, no observed effect concentration; PEC, predicted environmental concentration; PNEC, predicted no effect concentration; SGAB, Sociedad General de Aguas de Barcelona; SSD, species sensitivity distribution; SPE, solid phase extraction; TU, toxicity units; WFD, Water Framework Directive; WQI, water quality indexes.

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http://dx.doi.org/10.1016/j.jhazmat.2013.07.008

The threshold for this good status should be established to prevent a significant alteration of water bodies. That means, biological communities should be healthy and physico-chemical and hydromorphological parameters must show that no major changes has been produced compared to the base value in their natural state [2].

Indexes for physico-chemical and biological status are relatively easy to implement. Measurements are based on data that can be obtained by analysis, either in the field, at the laboratory or in real time at monitoring stations, or by identification and counting of species. Concerning specific pollutants, Directive 2008/105/EC [3] establishes environmental quality standards (EQS) for a list of 33 priority substances. These standards have been obtained from toxicological studies that show a clear correlation between chemical and biological response. The monitoring of those substances implies a high cost in laboratory analyses and the information is not always easy to interpret and aggregate. Additionally, proposal for amendment of the above-mentioned directive establishes EQS for biota for some of the legislated compounds [4].

In order to have a clear view of the pollutants posing major stress at a specific site, it should be very helpful to gather information on chemical status for a long period of time and normalize concentrations values according to a reference value, giving an indication of their harmful potential. WFD requirements for achieving a good ecological status do not include guidelines on how to select the most appropriate stressor-specific environmental indicators.

Previous studies worked on the effort of establishing water quality indexes (WQI) to give an indication of water quality bodies beyond individual parameters concentrations. Those indexes can be based on a fixed list of parameters or they can be case dependent, considering specific pollutants according to the most common impacts in every case. The main problem associated with these indexes is the limited range of parameters to be integrated, which can underestimate the ecological impact. A long list of applications of WQI is found in literature, applying or customizing most common ones in different countries around the world like Turkey [5], Iran [6], Chili [7], Zimbabwe [8], Argentina [9], etc.

More advanced studies are conducted for combining bioassessment and modeling techniques, like the one performed in Denmark [10]. Some of the efforts to create new indexes also include application to geographical information systems (GIS) [11] and web-based approaches [12]. Studies about dealing with the uncertainty of environmental risk prediction have been undertaken [13]. Gottardo et al. [14,15] proposed a methodology for integrated risk assessment (IRA) based on a fuzzy inference system in order to hierarchically aggregate a set of environmental indicators. Fuzzy logics have been applied in the recent years for developing risk indicators [16,17].

The study published by von der Ohe et al. [18] presents a more similar approach to the study hereinafter presented as a prioritization of a list of chemicals is done, according to a decision tree, for their monitoring based on the information available for 500 organic substances in four European basins.

The idea of establishing a comprehensive index is to provide a unique indicator on water quality for the environmental managers. This effort of simplicity can be very useful but the information on the impact on single parameters is lost. Present work is focusing on giving a simple indicator on the impact on every pollutant that can be found in Llobregat river waters, considering its effect on aquatic and vertebrate organisms and considering its relation to legislative thresholds, referred as EQS.

2. Methodology

2.1. Risk indexes determination methodology

Legislation has been developed applying the concept of aquatic ecosystem protection and establishing EQS for priority substances [3]. Further biota EQS have been proposed for future amendments [4]. The methodology for deriving these standards is based, among others, on the concepts of ecological risk assessment (ERA) based on PNEC (predicted no effect concentration) and PEC (predicted environmental concentration) [19].

New indexes have been created for the calculation of environmental risk for a series of compounds. Those indexes are based on analytical results on the concentration of these compounds on surface water (PEC) and reported effects (PNEC). For those compounds with no PNEC reported, calculations for obtaining PNEC values have been performed based on available data.

Taking PEC_j as the concentration of a contaminant j measured in water, a risk indicator of aquatic organisms, $I_{ao,j}$, is defined as follows:

$$I_{ao,j} = \frac{PEC_j}{PNEC_j}. \tag{1}$$

$PNEC_j$ is derived from toxicological values in water, basically NOEC (no observed effect concentration) of crustaceans, algae, and fishes, and the proper safety factor (assessment factor, AF).

For priority substances, EQS give a concentration that supposedly impact on aquatic media, $C_{REF,j}$. In these cases, where threshold concentration for pollutants is legislated, similar indicator to the one given in expression (1) could be derived, replacing the PNEC by the legislative value of EQS:

$$I_{am,j} = \frac{PEC_j}{C_{REF\ ,j}}, \tag{2}$$

where $I_{am,j}$ is an indicator of aquatic impact.

Protection of terrestrial vertebrates (mammals and birds) that are predators of aquatic organisms are also part of the aquatic ecosystem and could be assessed by comparing concentration of contaminants in aquatic organisms (PEC_{food}) with the value of PNEC expressed on food basis ($PNEC_{food,j}$) [19].

$PEC_{food,j}$ could be expressed by using the transference bioconcentration factor (BCF) that measures the ratio concentration of contaminant in small aquatic organisms (considered food) ($PEC_{food,j}$) divided by the concentration of contaminant in water (PEC_j). In this way, an indicator of terrestrial vertebrates risk, $I_{tv,j}$, could be obtained with the following expression:

$$I_{tv,j} = \frac{PEC_j}{PNEC_{food,j}/BCF_j}. \tag{3}$$

BCF_j values could be obtained from empirical studies or, in case of organic compounds, from correlations with $\log K_{ow}$ (octanol–water partition coefficient).

The above-mentioned expressions show that, having the concentration of the contaminants in water (PEC_j), the calculation of all the exposed indicators can be performed. For all these indicators, a target value of 1 was taken as the limit of correct environmental situation.

Every risk assessment process should consider the potential effect of a given substance and its exposure level [20], but certain aspects should be considered when creating and calculating indexes based on environmental concentration and exposure of pollutants. On one hand, the use of maximum or average concentrations in a given period of time and the treatment of data below the limit of quantification (LOQ) are needed to be taken into account. On the other hand, there is a tendency of equaling concentration of