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A new hazard index of complex mixtures integrates bioconcentration and toxicity to refine the environmental risk assessment of effluents

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Abstract

A new methodology to evaluate the overall environmental hazard of unknown mixtures, based on bioconcentration potential and toxicity, was developed using a combination of two methodologies: 1) the estimation of the octanol–water partition coefficient (K_{ow}) using reverse-phase high performance liquid chromatography (RP–HPLC) and 2) the toxicity identification evaluation (TIE).

Forty seven compounds with known K_{ow} and different molecular structures where used for the calibration of the log K_{ow} in relation to the retention time in reverse-phase high performance liquid chromatography (RP–HPLC). A linear regression with an $R^2=0.81$ and an $sd=0.69$ was established between log K_{ow} and RP–HPLC retention time. This K_{ow} estimation method was furthermore validated using seven additional compounds, showing acceptable estimations of the log K_{ow} of unknown substances.

Two different mixtures were tested, one containing 3,4 Dichloroaniline, Diazinon and 4-Nonylphenol and another one containing a mixture of 16 pesticides. Both mixtures were first tested as a whole effluent and then fractionated and tested, using a miniaturized *Daphnia magna* test.

An equation is presented, that combines both methodologies and establishes a relative hazard index RHI, ranging from 1 to 10 for any particular mixture of chemicals.

The results show how the method presented can refine the security factors that could be included in the environmental risk assessment of effluents in the future.
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1. Introduction

Effluents present a very complex and variable mixture of compounds making very expensive, time consuming, and sometimes impossible to perform a complete chemical characterization.

The impact of effluents discharged into aquatic environment should take into account the persistence, the bioconcentration potential and the toxicity of the components (Hynning, 1996). There are several methods to evaluate the toxicity of the effluents such as the Whole Effluent Toxicity Test (WETT), Toxicity Identification Evaluation (TIE) or Effect Directed Analysis (EDA) but, there is a lack of validated methods to evaluate persistence or bioconcentration potential of these complex matrices.

The environmental risk assessment (ERA) protocols have been developed for single substances to reduce the spilling from its source but, there are yet no simplified risk assessment protocols to evaluate a whole effluent poured into the environment or influents entering waste water treatment plants (WWTP).

Considering the environmental quality standards (EQS) in the European Water Framework Directive (EC, 2000) and the European Directive on Integrated Pollution Prevention and Control (Directive 96/61/CE) the principles for a simplified Environmental Risk Assessment of effluents is highly desirable.

Here, we apply a combination of two methodologies. On one hand, the K_{ow} estimation and in the other hand, the extraction, fractionation and ecotoxicity testing of the fractions.

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Toxicity test of the fractions, and subsequent chemical analysis of the toxic fractions, can reduce analysis cost by focusing on relevant toxic compounds (Hartnik et al., 2007). For this purpose non-polar sorbents (e.g., C18-phases) are frequently used in many bioassay-directed fractionations (Brack, 2003; Hewitt and Marvin, 2005).

For the K_{ow} estimation chemical methods of assessing potentially bioacumulating substances (PBS) all rely on the relationship between hydrophobicity of a compound and its tendency to bioacumulate, expressed as a bioconcentration or bioaccumulation factor (De Maagd 2000).

For the calculation of the K_{ow}, many methods have been used, "shake-flask method" (OECD, 1981; He et al 1995), "slow stirring method" (Haelst et al., 1994), theoretical calculation (Leo et al., 1971) but the only one that can be used, so far, for multiple unknown substances is Reverse Phase High Performance Liquid Chromatography (RP–HPLC) (OECD 117).

Established protocols mentioned above like EDA and TIE aims to establish a relationship between the chemical substances present in effluents and the biological effects they produce, trying to provide the stakeholders a higher amount of information in order to make a better assessment. Both systems apply an extraction procedure, followed by a fractionation of the sample. Then, a toxicity test is applied to each fraction and a chemical characterization is performed to those fractions that are toxic. EDA was shown to be a powerful, and in many cases, successful tool to identify and confirm previously unknown or unexpected pollutants in the environment, (Brack, 2003).

The aim of this study is to develop an equation capable of assessing the hazard of a mixture and consequently make a further step in the environmental risk assessment of effluents. The methodology presented combines the RP–HPLC system to estimate the log K_{ow} of mixtures of unknown chemical compounds with the Effect Directed Analysis techniques to finally estimate a hazard index of effluents. The proposed method is simple and robust, which makes it applicable for screening and monitoring purposes.

2. Theoretical approximation

Simplified environmental assessments are mostly based on risk quotients, expressed as the ratio between exposure and effects. The European TGD (Technical Guidance Document on Risk Assessment of Chemical Substances following European Regulations and Directives, 2003) and the definitions of EQS (Environmental Quality Standards) interpreted this quotient as the PEC/PNEC ratio, where PEC expresses the Predicted Environmental Concentration and the PNEC is the Predicted No Effect Concentration obtained through the application of a "safety factor" to the lowest toxicity value.

For the case of effluents, the concentration may be expressed as the percentage of dilution instead of concentration, using the acronym PNED.

Analysing the principles for setting water quality standards (Tarazona, 1997; Bro-Rasmussen et al., 1994), the Water Framework Directive and the TGD, an adaptation of the PNEC value can be established as:

$$\mathrm{PNEC} = \frac{\mathrm{EC}_{50}}{\text{Safety Factors}} \quad \text{or alternatively,} \tag{1}$$

$$\mathrm{PNED} = \frac{\mathrm{ED}_{50}}{\text{Safety Factors}}.$$

The value of the EC_{50} introduced in the PNEC equation is taken from the lowest toxicity data, obtained from the most sensitive specie tested. Dealing with effluents, the concentration is normally expressed as percentage of dilution. The safety factors of Eq. (1) can be understood differently depending on the document. For the case of effluents, an adaptation has been made and is explained as follows:

A) 100 value for the percentage correction since the EC_{50} value is expressed as a percentage of dilution in which 50% of the individuals are affected.
B) 10 value to assess the variability between species and test conditions. Theoretically, some species may be sensitive to some of the chemicals while some other species may be sensitive to other chemicals present in the mixture. For the case of complex mixtures Pedersen and Petersen (1996) published some safety factors ten times below the OCED factors based on bioassays with mixtures of 26 different compounds and 5 different test organisms. Nevertheless this feature won't be discussed throughout this work.
C) A 10 value to assess the persistence. The value can be refined by the use of chronic tests or adaptations of standardised test (OECD 301a–f). The refinement of this security factor could be discussed elsewhere.
D) A 10 value to assess the bioaccumulation. This value will be refined with the methodology presented.

Considering this approximation, the research project presented here, is focused on the refinement of this 10 value to achieve a more realistic PNEC value.

3. Experimental

3.1. Chemical mixture preparation

Two different mixtures (M1 and M2) were studied. The characteristics of each one and the preparation processes are described below:

> The mixture M1 consist of three different compounds, Nonylphenol (NP), 2,4 Dichloroaniline (DA) and Diazinon (DZ) mixed in milliQ water. These compounds were selected in base of their high toxicity to *Daphnia magna*, their different modes of action and their octanol–water partition coefficient. Concentrations of the individual substances were chosen so all fractions had toxicity to *Daphnia magna* for themselves and contribute to the general toxicity. The mixture M2 was prepared using a 16 pesticides, see Table 1 (EPA 625/ CLP Pesticide Mix; Supelco, USA). In this case, all the compounds interfere in the transmission of nerve impulse which represents a different case than M1. Also, working with a higher amount of compounds, represents a higher level of complexity and a better approach of reality.

In order to establish the initial concentrations of M1 and M2, previous toxicity test with *Daphnia magna* were carried out.

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