Scientific bases for the development of water quality objectives in Spain. Ecotoxicological criteria

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Abstract

Water Directive Framework (2000/60/CE) deals with the pollution caused by dangerous substances being discharged into the aquatic environment. In accordance with this directive, prevention and control of pollution may be enforced by means of limiting discharges or having water quality objectives (WQOs). The directive is a framework directive, which has to be followed by implementation directives in order to be effective. This study describes the methodology, based on the application of a deterministic model, for the development of WQOs. Following this procedure, national water quality criteria for 7 metals, 15 organic compounds, ammonia, nitrites and fluoride were developed. Finally, WQOs dependant of water hardness were established, between 1 and 10 µg L\(^{-1}\) for Cu and Pb and between 10 and 100 µg L\(^{-1}\) for Ni and Zn. Other WQOs of metals like Sn, Cr and Se ranged from 1 to 10 µg L\(^{-1}\) taking into account the metal oxidation level. WQO for ammonia was established between 0.25 and 10 mg N L\(^{-1}\) depending on the pH. WQO dependant of chloride concentration was established for nitrates, finding a linear relation for waters with chloride concentrations higher than 10 mg L\(^{-1}\). For organic compounds, WQOs for several pesticides (atrazine, simazine, molinate, terbutylazine and metolachlor, \(< 1 \mu g L^{-1}\) respectively), isopropylbenzene \(< 10 \mu g L^{-1}\) and several polycyclic aromatic hydrocarbons (PAHs) (fluoranthene, benzo[a]anthracene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene and indene[1,2,3-cd]pyrene, \(< 0.01 \mu g L^{-1}\) were calculated. The results of this study have been published in the Official Bulletin of the State no. 147 of 20/June/2000.

Key words: water quality objectives (WQOs), deterministic model, copper, ammonia, nitrite.

Resumen

Bases científicas para el desarrollo de objetivos de calidad del agua en España. Criterios ecotoxicológicos

La Directiva Marco del Agua (2000/60/CE) regula la polución causada por la descarga al medio ambiente de sustancias peligrosas. El objetivo de esta directiva está claramente relacionado con la prevención y control de la pollución y puede conseguirse estableciendo valores límite y/o objetivos de calidad del agua (OCAs) que se aplicarán en relación con cada vertido específico. En este estudio se describe una metodología, basada en un modelo determinístico, para la deducción de estos objetivos de calidad del agua. Siguiendo el procedimiento descrito se desarrollaron los criterios de calidad de agua nacionales para 7 metales, 15 compuestos orgánicos, amoníaco, nitratos y cloruros. Finalmente, se establecieron OCAs relacionados con la dureza del agua para el Cu y Pb (entre 1 y 10 µg L\(^{-1}\)), y para el Ni y Zn (entre 1 y 10 µg L\(^{-1}\)). Los OCAs para otros metales como el Sn, Cr y Se se establecieron entre 1 y 10 µg L\(^{-1}\) teniendo en cuenta el estado de oxidación. Para el amoníaco el OCA es dependiente del pH del agua y se estableció entre 0,25 y 10 mg N L\(^{-1}\) y para los nitratos en función de la concentración de cloruros mediante una relación lineal. En el caso de los compuestos orgánicos se calcularon OCAs para varios pesticidas (atrazine, simazine, molinate, terbutylazine y metolachlor, \(< 1 \mu g L^{-1}\) respectivamente), isopropilbenzeno \(< 10 \mu g L^{-1}\) y varios hidrocarburos aromáticos políclicos (PAHs) (fluoranteno, benzo[a]antraceno, benzo[k]fluoranteno, benzo[a]pireno, benzo[g,h,i]períleno e indeno[1,2,3-cd]pireno, \(< 0,01 \mu g L^{-1}\), respectivamente). Los resultados de este estudio han sido publicados en el BOE Nº 147 de 20 de junio de 2000.

Palabras clave: objetivos de calidad del agua (OCAs), modelo determinístico, cobre, amoníaco, nitrito.

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Introduction

Water Quality Objectives (WQOs) are defined as the maximum concentrations of water pollutants that should not be exceeded in order to have a suitable aquatic ecosystem. These objectives are directed not only for the protection of aquatic life in water, but also to safeguard those organisms whose existence is water dependent, or those that might consume any edible portion of such life. The methodology available to deduce WQOs establishes ecotoxicological thresholds (maximum concentration without effects on structure and function of aquatic ecosystems), applying the precaution principle inherent to European environmental policy.

Council Directives 76/464/EEC, 96/61/CE and 2000/60/CE (Water Directive Framework) are related to pollution caused by dangerous substances being discharged onto the aquatic environment. In accordance to their objectives, these directives focus on the pollution prevention and control by means of limit values and/or WQOs.

According to 76/464/EEC Directive, the Council will lay down WQOs for the substances within List 1 (priority pollutants), selected mainly on the basis of their toxicity, persistence and bioaccumulation in living organisms and in sediments, taking into account the differences in characteristics between salt water and fresh water.

Therefore, such WQOs are derived from scientific data obtained from experimental or in situ observations for a specified period of time.

Although the first WQO was proposed in 1980, the criteria to set quality objectives were developed 11 years later (Bro-Rasmussen, 1994) by the Scientific Committee on Toxicity and Ecotoxicity of Chemicals (CSTE), today replaced by the Scientific Committee on Toxicology, Ecotoxicology and Environment (CSTE).

In accordance with council directive 76/464/EEC and in order to be implemented in the Spanish legislation, the Ministry of Environment required the Department of Environment of INIA to develop WQOs in Spain. Each member country must establish WQOs, at least, for a priority of substances included in the so-called List 1 of the 76/464/EEC Directive.

The present paper describes the procedures followed to establish WQOs in Spain, which were finally published in the Official Bulletin of State (BOE, 2000).

Procedures

It is clear from 76/464/EEC Directive that WQOs should be based principally on toxicity, persistence and bioaccumulation of substances. For the majority of List 1 chemicals (see 76/464/EEC Directive), the Scientific Advisory Committee has tended to emphasize toxicity with information on persistence and bioaccumulation acting as modifying factors.

The general procedure can be summarised as follows: 1) study of all toxicity data in aquatic organisms, 2) selecting the most sensitive species and 3) application of safety factors to obtain the final WQO.

There are two main methodologies: 1) using probabilistic models (USEPA, 1984), and 2), using deterministic procedures (Bro-Rasmussen, 1994). The probabilistic model is based on the study of all toxicity available data, establishing the probabilistic distribution and selecting the acceptable effect level (generally percentile 95%) to ensure the protection of all species with an uncertainty of 5%.

The deterministic model consists of the study of available toxicity data and the selection of the most sensitive organism; the water quality objective is established applying several factors in order to obtain a margin of safety (MOS) to protect aquatic ecosystems. These factors are applied on the lowest toxicity range, approaching the closer order of magnitude. This procedure assumes the division of the selected toxicity data by 10 to assure the protection of more sensitive unknown species, by 10 if data set do not cover all taxonomic groups, by 100 if the selected toxicity data is obtained from an acute test, and by additional multiples of ten to cover persistence, biomagnification, carcinogenesis, etc.

The probabilistic model supplies a realistic point of view about toxicological behaviour of different species, because the probabilistic curve is made using all available toxicological data. The amount of toxicological data needed is the main disadvantage of this model; in order to reduce the uncertainty of the model, we need a great quantity of toxicological data covering all types of species.

On the other hand, the deterministic model supplies a more protective level because WQOs are obtained applying the security factors on the toxicity data of the most sensitive organisms. This model have as disadvantage the uncertainty about the sensitivity of analysed and available data.

When there is a relationship between toxicity and a water quality parameter, we need data covering
different ranges representing the variability of the related parameter. In Spain there is a great variability of water quality and in the probabilistic approach we need different toxicity probabilistic curves covering different ranges of the water quality parameter; in this case is better the deterministic approach.

The WQOs published by Bro-Ramussen (1994) and the Canadian Water Quality guidelines for the protection of aquatic life (CCREM, 1987) are two examples of this deterministic procedure.

Later, the technical meeting on risk assessment (EU, 1996), and within the program to assess the environmental risk of chemicals, in the European Union, has developed a new procedure to obtain aquatic ecotoxicological thresholds. This procedure is based on the predicted no effect concentration (PNEC) founded on the criteria established by CSTE, with some modification when the precaution principle is applied. This point of view is taken into account in the new Framework Directive of Water (2000/60/CE).

Development of water quality objectives of inorganic pollutants

Most of water quality criteria have been developed for organic pollutants; however, the toxicity of inorganic compounds to aquatic living organisms is also related to water quality parameters (Wan, 1987; Welsh et al., 1993) and therefore the already described general procedure needs of some adaptations.

For inorganic substances we have four alternatives:
1. Selection of water conditions in which the toxicity is the highest.
2. Creation of the toxicity distribution curve related to the affecting water quality parameter, and to select the 95% percentile.
3. Distribution of toxicity data in different ranges of the affecting water quality parameter.
4. To study the quantitative relationship between the affecting water quality parameter and toxicity.

Each of these alternatives offers different protection levels, realism and require different toxicological information. These differences can be summarised in Table 1.

General remarks

The general procedure to develop WQOs is the following:

Table 1. Different characteristics of the alternatives to WQOs development for inorganic pollutants

<table>
<thead>
<tr>
<th>Alternative</th>
<th>Level of protection</th>
<th>Reality</th>
<th>Required information</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>***</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>2</td>
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<tr>
<td>3</td>
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</tr>
<tr>
<td>4</td>
<td>***</td>
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<td>***</td>
</tr>
</tbody>
</table>

* Lower requirements than ***.

1. Toxicological data compilation. Bibliographic data could be obtained from all kind of data sources. Information on ambient concentration levels as well as environmental levels related to point source contamination in various compartments of aquatic ecosystems should be provided. The toxic parameters relevant to aquatic environment, i.e., acute, subacute, and chronic effects, including reproduction, should be reported for flora, microbial systems, and fauna. On-line databases (EPA, IUCLID, POLTOX, MEDLINE, AGRIS, CAB, etc.) and other WQOs published, are the principal data sources.

2. Taxonomic groups and species more relevant and/or sensitive. All taxonomic groups must be represented in the data set. For the aquatic environment, we need ecotoxicological data in algae, invertebrates and fishes.

3. Physic-chemical properties of pollutant. There are several inherent pollutant properties that can affect its toxicity. We need to know the speciation capacity, toxicokinetic properties, and the relationship between toxicity and water quality parameters (pH, hardness, chloride concentration, etc.).

4. Data selection and classification. The compiled toxicity data must be selected and classified according to their quality, end-point (50% lethal or effect concentration, L(E)C50; no observed effect concentration, NOEC; etc.) and guarantees (standardised and good laboratory practices studies).

5. Safety factors. Finally, the WQO is obtained applying the following factors on the selected toxicity data: 1/100 of L(E)C50 value, 1/10 of NOEC value, 1/10 additional to cover the lack of relevant species, 1/10 additional to cover persistence and/or biaccumulation capability, and 1/10 additional to cover genotoxicity capability.

Examples

1. WQO for copper. The WQO established for total dissolved copper is based on the following:
— For aquatic organisms copper toxicity is related to physicochemical characteristics determining the chemical speciation. We think that the best approach to establish ecotoxicological thresholds is to express the toxicity as a function of total concentration of dissolved copper and to state WQO taking into account the relationship with water hardness, as has been described (USEPA, 1984).

— The acute toxicity of copper to aquatic organisms is well known and there is plenty of information available covering the main taxonomic groups of fish and invertebrates, however, information about algae is poor (ECOTOX, USEPA 2000). Acute toxicity data is summarised in Table 2 getting the lowest for the most sensitive groups. Cladocera and salmonids are the most sensitive groups to copper.

— The information about chronic toxicity is fewer than acute data and its ratio is lower than 10. According to this fact the acute data were taking as base to derive the WQO.

— Copper is an essential element and its absorption is controlled by the homeostasis. There is not a relationship between copper toxicity and its bioaccumulation in aquatic organisms through waterborne sources (Carbonell et al., 1993); the bioaccumulation was taken as irrelevant for this metal.

— Copper is a natural element found in marine and freshwaters at different concentrations according with the geologic and physicochemical properties. This fact forces establishment WQO according with the anthropogenic loading of copper, subtracting the background geologic levels. This approach is quite conservative, but in specific areas with high background levels and/or hardness, could be admitted higher concentrations than the established by the WQO.

— Figure 1 shows the graphic of toxicity data on fish versus water hardness; we can see a clear relationship between toxicity and hardness, but there is not a good regression function. For this reason, our proposal is to fix four WQOs depending on calcium carbonate concentration range.

According with these items, the WQO for copper was established as shows Table 3.

Other heavy metals (Zn, Ni, Pb) show similar behaviour and their WQOs were established according to the water hardness range (see Table 3).

2. WQO for ammonia.

The toxicity of ammonia depends on water pH. Until now, water quality criteria for aquatic ecosystems protection followed the EIFAC (European Inland Fisheries Advisory Commission) recommendations, assuming the un-ionized form as responsible of toxicity; however, since 1998 USEP A recommend a quality criteria for total ammonia, variable with pH, showing that ionized form has also toxicity. Taking into account this point of view our proposal is based on the following items:

— There are a lot of information about acute toxicity in different aquatic organisms (West, 1985; Dabrowska and Sikora, 1986; Arthur et al., 1987; Snell and Persoone, 1989) being salmonids the most sensitive specie, ranging L(E)C₅₀ from 2.5 to 100 mg

Table 2. Lowest acute toxicity data for the most sensitive groups*

<table>
<thead>
<tr>
<th>Hardness (mg CaCO₃ L⁻¹)</th>
<th>L(E)C₅₀ invertebrates (µg L⁻¹)</th>
<th>L₅₀ fish (µg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 50</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>50-100</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>&gt; 100</td>
<td>50</td>
<td>250</td>
</tr>
</tbody>
</table>

* Data from ECOTOX database (USEPA, 2000).

Table 3. WQOs dependant of water hardness

<table>
<thead>
<tr>
<th>CaCO₃ (mg L⁻¹)</th>
<th>Ni and Zn (µg L⁻¹)</th>
<th>Cu and Pb (µg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 50</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>50-100</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>100-200</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>&gt; 200</td>
<td>100</td>
<td>10</td>
</tr>
</tbody>
</table>
N L⁻¹ according with water pH (USEP A, 1998). Table 4 shows a summary of acute toxicity data range from pH 6 to 9.5.

— Chronic toxicity has been less studied. The lower NOECs ranged from 1 to 10 mg N L⁻¹ according with water pH (USEP A, 1998).

— Bioaccumulation and persistence of ammonia in water ecosystems is taken as irrelevant.

WQO was established applying a factor of 10 on the acute toxicity data for the most sensitive species (100 mg N L⁻¹ pH < 7.0; 10 mg N L⁻¹ 7.0 < pH < 8.0; 2.5 mg N L⁻¹ pH > 8.0). This proposal agrees with EIFAC criteria (see Table 4), but shows differences with PNEC obtained from Technical Guidance Document (EU, 1994).

Figure 2 shows the graphic for toxicity data versus pH value, comparing USEPA and Canada criteria with the INIA proposal.

3. WQO for nitrite.

It is well known that nitrite toxicity is a function of chloride concentration, decreasing when chloride arises. The bibliographic review is in agreement with EIFAC criteria, 0.06 mg N L⁻¹, taking salmonid as the most sensitive species. The relationship between nitrite toxicity and chloride concentration is linear with a slope of 0.3, being the Y-axis intercept negligible at chloride concentrations higher than 10 mg L⁻¹.

Chronic toxicity has been less studied and WQO was established from acute data, taking bioaccumulation and persistence as irrelevant. Our proposal take EIFAC recommendation (< 0.06 mg N L⁻¹) in freshwater with low chloride concentration (< 10 mg L⁻¹); for higher chloride concentration, WQO increases following a straight relationship with a slope of 0.03, as shows Figure 3.

In addition to the explained examples, WQOs for fluoride, cyanide, chromium, selenium and 13 organic compounds were also established. Tables 3, 5 and 6 show the final developed WQOs.

Following the described procedure, WQOs for several pesticides (atrazine, simazine, molinate, terbuthylazine, metolachlor) isopropyl-
benzene and several polycyclic aromatic hydrocarbons (PAHs) (fluoranthene, benzo[a]anthracene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene and indene[1,2,3-cd]pyrene). Table 7 shows the obtained values.

Water quality objectives for total phosphorous and nitrogen were not developed. The principal environmental risk of total phosphorous and nitrogen in surfaces waters is related with its capability to develop eutrophication processes. In this case, procedures based in Directive 76/464/CEE are not suitable. The eutrophication process is more related with conditions and hydrodynamic characteristics of receiving water than a specific concentration (Daniel, 1998). Several authors (Vollenweider, 1968; Sawyer, 1974) consider concentrations of 0.01-0.02 mg L\(^{-1}\) (total phosphorous) as trigger values in the eutrophication process. In 1976, USEPA recommended concentrations lower than 0.025 mg total P L\(^{-1}\) in lakes and basins, but in 1998 WQO were not developed to surface waters (Parry, 1998).

In Spain, due to the geoclimatic diversity, and regarding an enough protection level to all ecosystems, we need to establish a WQO of about 10 µg L\(^{-1}\) (total phosphorous) lower than basal levels in some places without eutrophication problems. We think that in this case a probabilistic model using loads (not concentrations) will be more useful.

## Conclusions

The proposed methodology is based on the application of the deterministic model. This model is more protective than the probabilistic, because WQO is established from toxicity data of the most sensitive species, covering the whole aquatic ecosystem. Applying the probabilistic model there is a 5% of uncertainty of damage in a more sensitive species.

In WQOs dependant of water quality parameters, the best option is to establish a quantitative relationship between toxicity and water parameter; when it is not possible, we could establish WQOs according with several ranges of the water parameter or select the worst conditions in order to guarantee the protection of the ecosystem.

The use of WQOs according with several ranges could be the best option when the most sensitive taxonomic group changes with the variation of conditions.

The protection ecosystems policy must be in agreement with sustainability. Ecotoxicology supplies the knowledge to deduce scientific laws, but also civil laws that govern management decisions. Human health and ecosystem status must be considered to select which level of risk can be accepted, taking into account the degree of uncertainty. This aspect is essential for Sustainable Development concept, when environmental decisions are intended to avoid pollution by setting an acceptable level of contamination.

The final results of this study were published in the Official Bulletin of the State number 147 (995/2000) of 20/Jun/2000.

## Acknowledgements

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