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PhD Thesis

On the development of decision-making systems based on fuzzy models to assess water quality in rivers

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que presenta en William Andrés Ocampo Duque per optar al grau de Doctor per la Universitat Rovira i Virgili, ha estat realitzat sota la seva direcció en els laboratoris del Departament d'Enginyeria Química de la Universitat Rovira i Virgili, i que tots els resultats presentats i la seva anàlisi són fruit de la investigació realitzada per l'esmentat doctorant.

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Tarragona, viernes 01 febrero 2008

Dr. Marta Schuhmacher
Professor Titular d'Universitat

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With the desire that this Contribution allows Cleaner Rivers ...

...Dedicated to mi Wife, Aida Paola Arias Gómez

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Resumen

Existen diversas situaciones en las cuales la descripción en términos lingüísticos de fenómenos complejos permite mejores resultados. Bajo una perspectiva de gestión medioambiental, el manejo de la calidad de las aguas en términos lingüísticos debería proporcionar mejores resultados, que los usuales valores numéricos de los indicadores. A pesar de los volúmenes de información cuantitativa que se manejan actualmente, es bien sabido que la gestión de la calidad del agua todavía obedece fuertemente a juicios subjetivos y de interpretación por parte de los expertos. Por tanto, la pregunta clave es ¿cómo introducir operaciones lógicas que computen con palabras en el análisis de los datos, para producir indicadores auto-interpretables de calidad del agua? De esta manera, los riesgos percibidos en cuanto a los diferentes usos del agua podrían ser mejor estimados.

La lógica difusa es una potente herramienta que permite manipular la incertidumbre, la subjetividad y la imprecisión que están asociadas con las palabras empleadas en el análisis. También, la incertidumbre y la sensibilidad de las variables podrían considerarse mediante conjuntos difusos. Ejemplos de imprecisión lingüística son conceptos tales como “impacto significativo” o “nivel de preocupación”. Cada persona bien puede tener su propio criterio para definirlos. Esta imprecisión refleja la ambigüedad del pensamiento humano para expresar percepciones e interpretaciones. De allí que las variables lingüísticas se presenten como muy atractivas para el manejo de conceptos de la gestión medioambiental, como es el caso de la “calidad del agua”, el “nivel de riesgo” o el “estado ecológico”. En estos casos, las herramientas de la lógica difusa pueden resultar útiles para el desarrollo de mejores métodos clasificatorios y de toma de decisiones.

En la presente Tesis, la flexibilidad de la lógica difusa para computar con palabras se ha adaptado a diversos tópicos en la gestión del agua. Primero, se desarrolló una metodología para evaluar la calidad de las aguas basada en sistemas de inferencia difusos. Así, se diseñó un índice multipropósito de calidad del agua que se obtiene mediante razonamiento difuso. El índice integra un extenso grupo de indicadores que incluyen: contaminación orgánica, nutrientes, patógenos, variables macroscópicas, así

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como sustancias prioritarias micro-contaminantes. El índice es estructurado en forma jerárquica para facilitar la manipulación de la información y el análisis de los resultados. De la misma forma, la importancia relativa de los indicadores de la calidad de las aguas al interior del sistema de inferencia se estimó con un método bien valorado en el área del análisis de decisiones, y que se conoce como el proceso jerárquico analítico. Además, se consideró un método de desarrollo reciente para optimizar la consistencia en la elección subjetiva de los pesos de los indicadores.

Con el índice difuso de calidad de las aguas se estudió el estado global del agua del río Ebro en el último tramo previo a su desembocadura en el Mar Mediterráneo. Los resultados obtenidos con el nuevo índice coinciden significativamente con los reportes oficiales de las agencias regionales de protección de la cuenca y con la opinión de los expertos, en cuanto al estado real del agua del río. El índice difuso logró mejores resultados cuando se comparó con índices tradicionales, primero porque utiliza más información y segundo por el mejor tratamiento de la incertidumbre lingüística. En esta etapa, se concluyó que el diseño de indicadores de calidad de las aguas, soportado en la metodología difusa, es una poderosa alternativa para los tomadores de decisiones encargados de la planeación y gestión sostenible de las cuencas hidrográficas.

En una segunda fase, se utilizó una metodología híbrida que combina los sistemas de inferencia difusos y las redes neuronales artificiales, conocida en el campo de la inteligencia artificial como neuro-fuzzy, para el estudio de la clasificación del estado ecológico de los ríos. Esta metodología permitió un adecuado manejo de la no linealidad y naturaleza subjetiva de las variables involucradas en este problema clasificatorio. Aquí, el estado ecológico resulta de la integración de elementos biológicos, morfológicos y fisicoquímicos, de acuerdo con la reciente Directiva Marco del Agua propuesta en Europa. El modelo clasificatorio se entrenó y validó con información de la cuenca del Ebro.

Con esta base de datos fue posible estudiar la complejidad de los sistemas de inferencia difusos, la selección apropiada del número de reglas lingüísticas requeridas, así como la influencia de la forma de las funciones matemáticas que transforman las variables numéricas en lingüísticas y viceversa. Con los sistemas neuro-fuzzy se lograron excelentes desempeños clasificatorios, por encima del 97%, lo cual resultó

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bastante competitivo si se comparan estos resultados, con los obtenidos con otras herramientas clasificatorias, tales como la redes neuronales probabilísticas y los árboles de clasificación y regresión. Adicionalmente, se obtuvo una mejor capacidad generalizadora con los algoritmos neuro-fuzzy. Por tanto, este método híbrido es apropiado para el diseño de sistemas de inferencia difusos optimizados y capaces de representar situaciones reales.

En la tercera fase de esta Tesis, se desarrolló un modelo conceptual basado en la metodología de evaluación de riesgo ecológico preliminar. Este modelo considera la presencia de sustancias peligrosas, también llamadas micro-contaminantes, en los ríos. El modelo incorpora un sistema innovador para clasificar las sustancias químicas, que está basado en una red neuronal artificial no supervisada, llamada mapa auto-organizativo. Este mapa permitió estimar la peligrosidad ecológica que representa la presencia de determinadas sustancias químicas en el agua. Así, los factores de peligrosidad se estiman mediante el reconocimiento de patrones de las variables de persistencia en el ambiente, potencial de bio-acumulación y toxicidad de las sustancias. Al combinar estos factores de peligrosidad con la concentración (dosis) de dicha sustancia en el medio acuoso, es posible estimar el “potencial de riesgo ecológico”. Debido a la alta imprecisión e incertidumbre lingüística, este potencial se obtiene a partir de un sistema de inferencia difuso.

El modelo así creado, que se conoce como sistema neuro-fuzzy concurrente, involucra un procedimiento consistente para la normalización, lo que facilita una comparación sencilla de los niveles de riesgo entre las sustancias químicas encontradas en el agua. Por tanto, la estimación de los potenciales de riesgo ecológico para cada sustancia en cada sitio de la red de control, es capaz de identificar las sustancias que pueden requerir un estudio más detallado, así como un control más estricto de las emisiones. De esta manera, la integración de potenciales de riesgo ecológico para todas las sustancias, por medio de distribuciones empíricas acumuladas, permite analizar los cambios en la calidad del agua a través del tiempo. Este modelo se utilizó para estudiar la calidad del agua en términos del riesgo ecológico preliminar en la cuenca del Ebro. Los datos se obtuvieron de la red de control de sustancias peligrosas, y se analizó un periodo de cinco años.

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El modelo concurrente neuro-fuzzy para evaluación de riesgo se validó mediante comparación con monitorización biológica. De aquí, se encontró por ejemplo, que la calidad del agua estimada a partir de índices basados en la presencia de comunidades de diatomeas (fitoplancton) ha disminuido, posiblemente como consecuencia de un aumento en la presencia de sustancias químicas en niveles preocupantes. Este modelo resulta entonces de gran utilidad para la evaluación del desempeño en los planes de prevención y control de la contaminación, establecidos por la agencias de protección del medio ambiente.

En la última etapa de esta Tesis, se estudiaron los probables impactos sobre los ecosistemas debidos a las actividades agrícolas, domésticas e industriales en el Bajo Ebro. Para ello, se planteó una evaluación de riesgo ecológico preliminar centrada en el análisis de los sedimentos, ya que con ello se logran resultados complementarios, especialmente en términos de variabilidad temporal. Se llevaron a cabo ensayos eco-toxicológicos de respuesta rápida a los extractos acuosos y orgánicos obtenidos de los sedimentos de ribera. Para ello se utilizó el ensayo de inhibición de la luz producida por la bacteria *Vibrio fischeri*. Estos resultados se contrastaron con los valores de metales pesados y compuestos orgánicos clorados presentes en la zona. Las respuestas toxicológicas mostraron significativas correlaciones con los niveles de los contaminantes. También, en algunos sitios se notó que la toxicidad podría deberse a factores reductores en los sedimentos. Estos resultados, permitieron concluir que el ensayo de toxicidad con *Vibrio fischeri* resultó apropiado para la evaluación de riesgo preliminar.

Se diseñó entonces un sistema jerárquico de inferencia difuso para manejar la información de la evaluación de riesgo en los sedimentos de ribera, con el fin de proporcionar mejores estimaciones del riesgo. De esta manera, los resultados obtenidos en los análisis químicos y eco-toxicológicos se introducen en dos sistemas de inferencia paralelos que estiman el grado de contaminación y toxicidad, respectivamente, en términos lingüísticos. Luego, la caracterización final del riesgo se logra mediante un tercer sistema de inferencia. Finalmente, el riesgo se proporciona en términos lingüísticos, con sus respectivos grados de certeza. Esta nueva metodología resulta muy apropiada para la estimación del riesgo si se compara con los métodos tradicionales.

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Summary

There are many situations where a linguistic description of complex phenomena allows better assessments. Under a perspective of water management, linguistic or narrative statements should be superior to numerical scores in giving risk-based water quality classifications. It is well known that the assessment of water quality continues depending heavily upon subjective judgments and interpretation, despite the huge datasets available nowadays. Therefore, a key question is how to introduce intelligent linguistic operations to analyse databases, and produce self interpretable water quality indicators. Definitions for water indicators and indexes in linguistic terms could be sufficiently rigorous to represent comprehensive assessments. In this way the perceived risks associated with different water uses could be better estimated.

When uncertainty or imprecision are related to the words used in the analysis rather than to the events or variables, these can be conveniently addressed with fuzzy logic. The term fuzzy logic embraces a wide set of diverse methodologies intended to deal with uncertainty and subjectivity. Examples of lexical imprecision are concepts such as: “significant impact” or “level of concern” which are very common in environmental management. This imprecision reflects the ambiguity of human thinking when perceptions and interpretations are expressed. Linguistic variables are ideally suited to express many environmental concepts hard to evaluate, as: “water quality”, “level of risk”, or “ecological status”. In that sense, fuzzy logic tools could result useful to face this sort of decision and classification problems.

In the present Thesis, the flexibility of computing with words offered by fuzzy logic has been considered in water management issues. Firstly, a methodology based on fuzzy inference systems to assess water quality has been developed. A multipurpose water quality index has been designed with fuzzy reasoning. It integrates a wide set of indicators including: organic pollution, nutrients, pathogens, physicochemical macro-variables, and priority micro-contaminants. To facilitate the assessment, the index involves a hierarchical structure. Likewise, the relative importance of the water quality indicators has been dealt with the analytic hierarchy process, a common multi-attribute decision-aiding method. To test the consistency degree in the subjective choice of the

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weights of the indicators, a recent theoretically well founded improvement to this method, based on single value decomposition, has been implemented.

The potential application of the fuzzy water quality index has been tested with a real case study. A dataset collected from the Ebro River (Spain) has been used. The findings clearly agree with official reports and expert opinions about the pollution problems in the studied area. The proposed index has resulted superior to common indexes in estimating the real effects of anthropogenic discharges on water quality. Therefore, the design of water quality indexes based on the fuzzy methodology emerges as suitable and alternative tool to support decision makers involved in effective sustainable river basin management plans.

In a second stage, a methodology based on a hybrid approach that combines fuzzy inference systems and artificial neural networks has been used to classify ecological status in surface waters. This methodology has been proposed to deal efficiently with the non-linearity and highly subjective nature of variables involved in this serious problem. Ecological status has been assessed with biological, hydro-morphological, and physicochemical indicators, as requested by the European Water Framework Directive. A data set collected from the Ebro river basin has been used to train and validate the hybrid classification model.

The complexity of inference systems, the appropriate number of linguistic rules, and the influence of the shape of the mathematical functions that transform numerical variables into linguistic variables (or vice versa), in intelligent neuro-fuzzy based classification systems, have been studied. Up to 97.6% of sampling sites have been correctly classified with neuro-fuzzy models. Such performance resulted very competitive when compared with other classification algorithms. With non parametric classification and regression trees and probabilistic neural networks, the predictive capacities were 90.7% and 97.0%, respectively. Moreover, the superior generalization skills were exhibited by neuro-fuzzy models. Therefore, the hybrid method has resulted useful to search for the optimum structures of the inference systems that better represent the real situations.

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In a third stage, a conceptual model based on screening ecological risk assessment has been developed. It considers the presence of hazardous substances, or micro-pollutants, in river basins. The model incorporates an innovative ranking and scoring system for chemicals, based on a special kind of unsupervised artificial neural network called self-organizing map. It accounts for the likely ecological hazards posed by the presence of chemical substances in freshwater. Hazard factors for chemical substances have been calculated by pattern recognition of persistence, bioaccumulation, and toxicity properties. Due to the high imprecision and linguistic uncertainty in screening risk assessment, a fuzzy inference system has been proposed to compute ecological risk potentials, which are a combination of the hazard to aquatic sensitive organisms, and normalized environmental concentrations.

With the concurrent neuro-fuzzy approach, a consistent normalization procedure has been proposed to compare the levels of concern between chemicals found in water. The estimation of ecological risk potentials for each substance at every site, allows identifying those substances requiring stricter controls and further rigorous risk assessment. Likewise, the aggregation of the ecological risk potentials, by means of empirical cumulative distribution functions, allows estimating those changes in water quality over time. The proposed conceptual model has been applied to a comprehensive dataset of the dangerous substances control network in the Ebro river basin.

The neuro-fuzzy approach for screening risk has been validated by comparison with biological monitoring. It was found for instance that, water quality estimated with diatom community surveys has decreased, in several sampling sites, probably as consequence of higher presence of chemicals at levels of concern. The proposed approach has resulted useful to support decision-makers in the evaluation of the long-term performance of pollution prevention and control strategies in river basins set out by environmental protection agencies.

In the final part of this Thesis, the likely impacts on the ecosystems due to agricultural, human, and industrial activities carried out in an ecologically important area of the Ebro River have been studied. For it, a screening site specific ecological risk assessment was conducted. The study was centered in sediments, since they produce complementary findings to the water quality analysis, especially when temporal trends

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are required. Considering the presence of high levels of potentially toxic substances, such as metals and chlorinated organic compounds, aqueous and organic extracts were used to assess toxicity in sediments by using the photo-luminescent bacteria *Vibrio fischeri* (Microtox®) as screening response variable. Toxic responses have shown strong relationships to the levels of pollutants in the area. Moreover, various sites presented some toxicity level, probably because of other factors associated with reducing environments into the sediments. Results indicated that Microtox® bioassay is an appropriate tool to perform risk assessment studies at screening level.

To manage the information collected in the sediment assessment, and provide better risk estimates, a hierarchical fuzzy inference system has been designed. Results from chemical and eco-toxicological analyses have been used as inputs in two parallel fuzzy inference systems to assess levels of contamination and toxicity, respectively. Results from both inference engines are then treated in a third inference engine which provides a final risk characterization. Finally, the risk is provided in linguistic terms, with their respective degrees of certitude or membership. The method has resulted highly favorable and competitive when compared with current risk assessment methodologies.

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Introductory notes

1. Motivation and hypothesis

Water is a natural resource. It is essential to sustain the life. It also plays a crucial role in the economic development and social welfare. Rivers, lakes, estuaries, seas, and groundwater play a vital role in everyday life. These water bodies are important natural resources for agriculture, industry, recreational use, domestic tasks, and as sources of drinking water. Water also supports ecological habitats and species of paramount importance. Some of the water uses can threaten the water quality. Water pollution in rivers can come from point sources, such as industrial or sewage effluent discharges, or can be diffuse such as agricultural run-off.

Environmental scientists are then motivated to contribute for sustainable water resource management. To do that, diverse technical and conceptual approaches must be developed. In particular, my interest has been the elaboration of rigorous and updated tools to help assess water quality, intended to the protection of aquatic ecosystems. This is the contribution of the present Thesis.

There are many real cases where a linguistic description of complex phenomena allows broad analyses. Under a perspective of water management, linguistic or narrative statements could be superior to numerical values in giving risk-based water quality classifications. It is well known that the assessment of water quality continues depending heavily upon subjective judgments and interpretation, despite the huge databases available nowadays. Rich in data but poor in information seems to be the motto. Even if goodness or badness of water quality could be distinctly identified by a set of critical parameters, the complex interactions of different pollutants and their synergistic effects on aquatic species are unlikely to be reflected accurately in any numerical model. Therefore, the key question is how to introduce linguistic operations

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to analyse water quality statistics, to produce self interpretable and easy-to-use water quality indicators.

For example, the concept of “poor water quality” should be assessed in a way which reflects the perceived risks associated with different water uses. So, if a source contains “high” nitrate concentrations, it may be considered as “poor” for drinking water supply. If this source is also used for irrigation, then its quality should also be “poor”, if the chloride concentration is “high”. Whereas, “medium” levels of both nitrate and chloride would indicate “poor” quality for water supply, but “acceptable” quality for irrigation. The global water quality of the source may be considered “faulty” if it is “quite bad” for water supply and “quite good” for irrigation. In addition, “very bad” quality for irrigation and “quite good” for supply may also be a “failure” condition in a determined situation (Jowitt and Lumbers, 1982). In other scenarios different objectives could be defined and applied according to environmental expert preferences, feelings, and criteria. Definitions for water quality in these terms can be sufficiently rigorous to represent comprehensive assessments.

The use of linguistic variables to describe and assess complex systems has already been extensively elaborated by computer scientists, in an amazing quite mature field: the Fuzzy Logic. Its extension to environmental science is currently matter of study. One of the main advantages of fuzzy logic is the ability to model expert human knowledge, a necessary feature to be considered in the complex process of environmental management. Indeed, computing with linguistic statements has given to fuzzy logic its fame.

The term fuzzy logic embraces a wide set of diverse methodologies intended to deal with uncertainty and subjectivity. Since its introduction in 1965 by Lofti Zadeh, fuzzy logic has been applied to many research areas. The interest in fuzzy is still growing, as depicted in Fig. 1. The number of papers related to “fuzzy” in the Science Citation Index (SCI) for 2006 was 3616. 3.2% of papers also contained the term “water”. Likewise, thirty-three paper contributions in 2006 were associated to the terms “fuzzy”, and “water quality”. Further scientific advances within this field and their widespread acceptance and use are expected to follow.

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Applications of fuzzy logic in the field of water management are then promising given the huge complexity and number of variables involved. Moreover, it is a problem that needs to be faced in a multidisciplinary way. According to the enunciated above, the hypothesis of the present PhD Project has been that "it is possible to improve the environmental assessment and management of water quality in rivers by means of the development of an integrative conceptual framework involving a broad range of interpretable water-quality indicators, able to summarize the real pollution situations that stress aquatic ecosystems in river basins, and helpful for the complex process of decision-making".

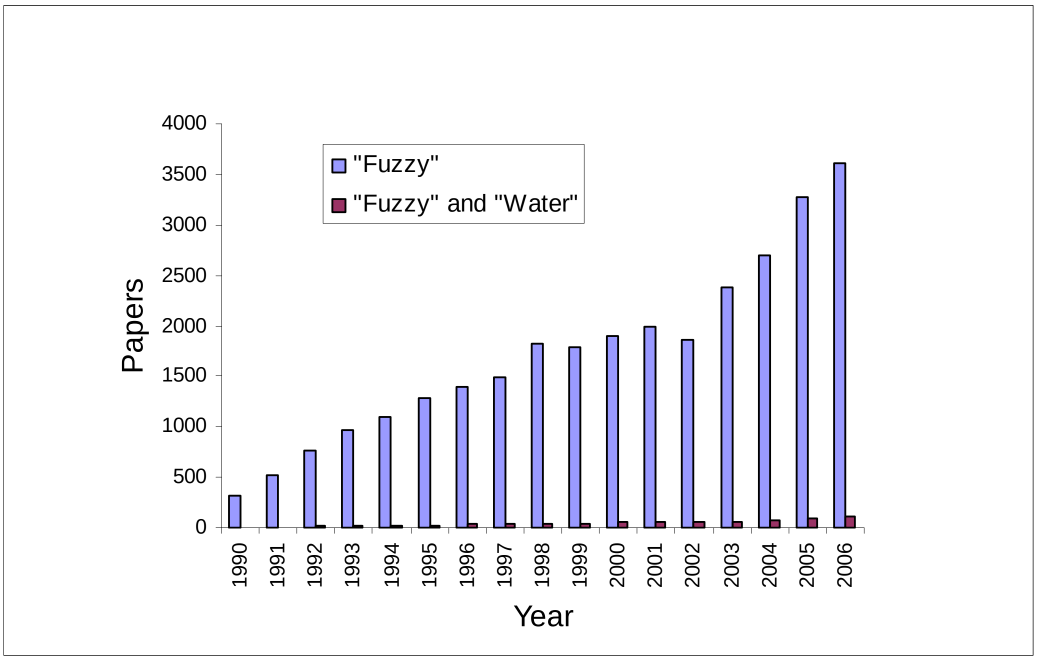

Fig. 1. Evolution of the number of scientific papers, appearing in the Science Citation Index®, related to the terms "Fuzzy" and "Water".

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2. Objectives

2.1. General objective

To develop a conceptual model to assess water quality in rivers from a perspective of environmental risk assessment, including a comprehensive way to manage linguistic uncertainty and subjectivity.

2.2. Specific objectives

1. To design a generalized river water-quality index able to consider the linguistic subjectivity and uncertainty in the assessment.
2. To elaborate an automated model to classify the ecological status in river basins based on the integration of biological, physicochemical, and morphological indicators.
3. To create an intelligent system for water-quality analysis based on the probable ecological risks because of the presence of multiple hazardous substances in river basins.
4. To propose an integrated system to deal with multi-chemical screening risk assessment in river sediments.

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3. Thesis structure

To overcome the proposed objectives, the present document is structured as follows. Every chapter consists on a research paper holding a specific objective. Consequently, each chapter has its own organization: abstract, introduction, methods, results, discussions, conclusions, acknowledgments, and references. According to the hypothesis enunciated above, fuzzy inference systems (FIS) have been selected and validated as appropriate tools to deal with subjectivity and uncertainty in the problem of assessing water quality in river basins. Every chapter reflects therefore a FIS application, to be used in water management. Nevertheless, the connection between chapters is easily established, since a common aim has been followed throughout the Thesis.

First, a global water quality indexing system from selected variables has been proposed to introduce fuzzy models into water management. Then, the interactions between biological, morphological, and physicochemical elements in river basins are explored. After, the likely environmental impacts due to the presence of micro-contaminants are analysed. Finally, a decision support model to manage sediment quality, as necessary extension of water quality protection, has been elaborated.

The development of a multipurpose water-quality index, within a FIS framework, is described in the Chapter 1. It is well known that some water-quality indicators are more important than others. To take into account that, a decision-aiding method that assigns a respective importance to each indicator, has been linked to the FIS. It consists on an improved version of the well known analytic hierarchy process (AHP).

In the Chapter 2, the complexity of the inference engines within FIS has been explored. Consequently, interpretability and accuracy in FIS models have been studied. To take advantage of that, the complex relationships between hydro-morphological, physicochemical, and biological indicators, to provide a classification about the ecological status in river basins, have been considered. An adaptive neuro-fuzzy inference system, the ANFIS algorithm, was selected for the study. Its performance was compared to two state-of-the-art supervised methods, commonly used in classification tasks: the probabilistic neural networks (PNN), and the classification and regression trees (CART).

Chapter 3 proposes a novel screening ecological risk assessment (ERA) methodology to assess water quality because of the presence of hazardous micro-contaminant chemicals in river basins. The method is based on a FIS and supported by a pattern recognition tool called self-organizing-map (SOM). The SOM-FIS structure can be seen as concurrent neuro-fuzzy model. Subjectivity and the uncertain nature of variables involved in risk estimation have conveniently been dealt with. Also, a strong relationship between the chemical pollution analysis with the neuro-fuzzy conceptual model, and biological water quality assessment, carried out with diatom communities in river basins, is also discussed.

Nowadays, sediment quality protection has been viewed as logical and necessary extension of water quality protection. Therefore, the bases for a decision-making system, supported on FIS, to assess river sediments are settled in Chapter 4. Rapid screening toxicity bioassays and concentrations of hazardous chemicals present in river sediments have been collected. These have been used as inputs to a FIS intended to provide screening ecological risk assessment. A methodological procedure to improve the use of rapid screening toxicity bioassays, particularly in the Microtox® test, is described too. Here, multivariate data exploratory analysis was carried out with principal component analysis (PCA). This Chapter is composed by two parts, Part A describing the collection of information, and Part B describing the design of the fuzzy inference system.

Next, a brief description of methods utilized throughout the Thesis is provided. Their application to face the water quality problem is further explained in the respective chapters. All developed tools have been applied and validated with real case studies, usually involving the Ebro river basin, even though their application could easily be extended to other river basins. A Conclusion Chapter is presented as well. Finally, an Annex is presented where a probabilistic risk assessment has been conducted to a highly polluted river located in Colombia, South America. The Annex settles the bases for future research and International Cooperation.

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4. Methods overview

4.1. Ecological risk assessment

During the 1980s, risk assessment emerged as a prominent regulatory tool, and consideration of ecological impacts began to influence regulatory and policy decisions (Hope, 2006). Since then, ecological risk assessment (ERA) has involved the assessment of the risks posed by the presence of substances released to the environment by man, in theory, on all living organisms in the variety of ecosystems which make up the environment (OECD, 2002). ERA methodology was developed from that already established for human health risk assessment (HRA) (USEPA, 2004).

The general principles are widely agreed upon but the application of the process still provokes considerable debate. HRA is concerned with individuals and morbidity and mortality. ERA is concerned with populations and communities, and the effects of substances on mortality and fecundity (Lasinio et al., 2007). ERA has to deal with a multitude of organisms, all with varying sensitivities to chemicals and various groups have distinct exposure scenarios, such as free swimmers and sediment dwellers (EEA, 1998). Many species in aquatic ecosystems are indeed more sensitive to pollution than humans. Therefore, the protection of water quality based on the precept of preserving good ecological status would involve the human health protection as well.

Because of the difficulty in obtaining toxicity data on all organisms in an ecosystem, the recognized practice is to test selected representatives of major taxonomic groups and use these as surrogates for the whole system. This method is questionable as it may not protect the most sensitive species exposed in the environment. Failure to identify the effects of an agent on a potential receptor can result in widespread damage to organisms and ecosystems (EEA, 1998). A common example is the presence of antifouling paints containing tributyltin and the damaging effects on oysters (Alzieu, 2000).

A river basin site with multiple stressors may contain hundreds of chemicals. Therefore, it is important to screen contaminants of potential concern for the ecological risk assessment. Screening is usually accomplished by using a set of toxicological

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benchmarks, or environmental quality standards (EQS). These EQS are helpful in determining whether contaminants deserve further assessment or are at a level that does not require further attention. If a chemical concentration or the reported detection limit exceeds a proposed lower benchmark, further analysis is needed to determine the hazards posed by that chemical. If, however, the chemical concentration falls below the lower benchmark value, the chemical may be eliminated from further study. Concentrations exceeding an upper screening benchmark indicate that the chemical in question is clearly of concern, and that remedial actions are likely to be needed (Jones et al., 1997).

The use of multiple EQS also indicates the likelihood and nature of effects. For example, to surpass only one conservative EQS may provide weak evidence of real effects, whereas surpassing multiple EQS of varying conservatism may provide strong evidence of real effects (Suter II et al., 2000). In practice, EQS are highly subjective and uncertain (Fig. 2). EQS for many chemicals involve large methodological and inherent uncertainties, such as missing or insufficient physicochemical and/or molecular data, very low number of sensitive species tested, etc. In any case, the ERA process involves heavy uncertainties, and the tools to deal with them are still in early development.

In a broad sense, ERA is the characterization of the potential adverse ecological effects resulting from ecological exposures to environmental hazards. The steps in the ERA process are: hazard identification, dose-response assessment, exposure assessment, risk characterization, and risk management (EC, 2003; USEPA, 2007).

Hazard identification is the analysis of an environmental situation to ascertain if there is the potential for an exposure of an organism (including a human) or ecosystem to an environmental stressor that may cause harm. Dose-response assessment is the process of characterizing the relation between the dose of an agent received by a receptor (organism or ecosystem) and the incidence of an adverse effect on that receptor. Exposure assessment is the process of estimating the intensity, frequency, or duration of a human or ecological exposure to agents that are currently in the environment, or may be present in the future. Risk characterization is the process of estimating the incidence of an adverse effect under the conditions of exposure described

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in the exposure assessment. It also includes the description of the meaning of the assessment, including variability and uncertainty in the preceding steps (USEPA, 2007).

The risk assessment establishes whether a risk is present and defines a "magnitude" of that risk. A risk manager must integrate the risk assessment results with other considerations to make and justify risk management decisions. Other considerations in making risk management decisions include existing background levels of contamination, available cleanup technologies, costs of alternative actions, and remedy selections (USEPA, 1997).

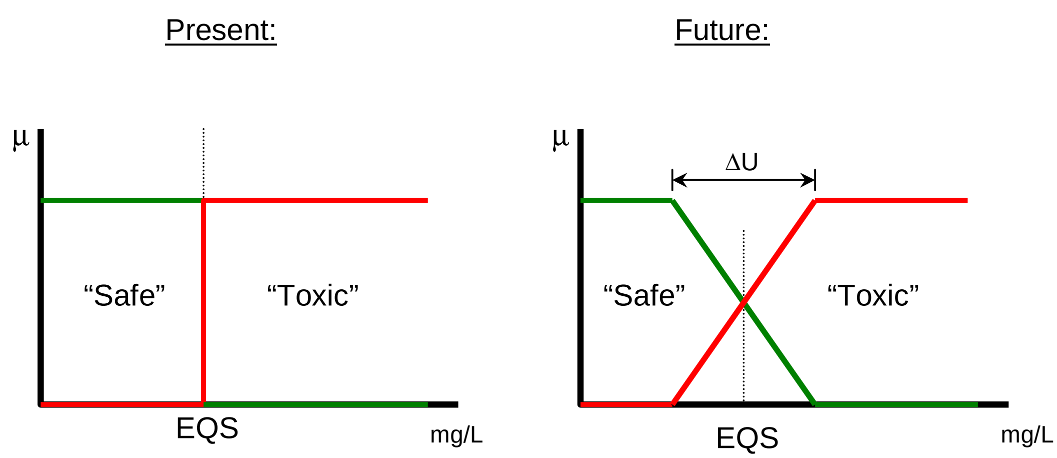

Fig. 2. Need for an appropriate management of uncertainty (*ΔU*) in risk assessment. EQS is Environmental Quality standard.

4.2. Microtox

Microtox toxicity testing technology is a biosensor-based measurement of toxicity, and provides an effective way to monitor either accidental or deliberate water contamination. Microtox tests are based on the use of luminescent bacteria, called *Vibrio fischeri* which produce light as a by-product of normal metabolism. The inhibition of the normal metabolism caused by toxicity may result in a reduction in rate of luminescence. The higher the level of toxicity the lower the production of light is (SDI, 1998). The test provides rapid screening and confirmation results, which are cost-effective, and easy to perform (Parvez et al., 2006). Microtox responds to a very broad range of toxicants and classes of chemical agents including metals, pesticides,

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fungicides, chlorinated solvents, industrial chemicals, etc. (Farre et al., 2006; Hsieh et al., 2004; Muller et al., 2007; Redman et al., 2007).

While chemical analysis can be very sensitive and precise, they are also very narrow and do not detect pollutants for which the analysis is not specifically looking. Chemical specific tests are time-consuming, costly and incomplete tools to screen toxicity. Unanticipated toxicants usually are undetected with chemical analyses in real situations. In addition, even when the chemical constitution of a sample was known in detail, its effective toxicity can not reliably be calculated, since different chemicals in complex samples may work sinergistically (or antagonistically) increasing (or decreasing) toxicity. Chemical analyses should be performed for identifying particular chemicals after a sample is known to be toxic. Therefore, extended monitoring programs in river basins would reduce costs in that way. By using screening toxicity tests, it is also possible to optimize time and costs of chemical sampling in real situations which facilitates the process of screening environmental risk assessment.

4.3. The Water Framework Directive

The European Water Framework Directive (WFD) is one of the most important pieces of environmental legislation produced in recent years, and is likely to transform the way that water quality monitoring is undertaken. It aims to complement a number of other existing legislative instruments including the Bathing (76/160/EEC), Drinking (98/83/EC), Fish (78/659/EEC) and Shellfish (79/923/EEC) Water Directives, as well as those based on specific substances or sources of pollution (i.e. Dangerous Substances (76/464/EC), Groundwater (80/68/EEC), Nitrate (91/676/EEC) and Pesticide (91/414/EEC) Directives). The objectives of the WFD (2000/60/EC) are to improve, protect, and prevent further deterioration of water quality. The term water within the WFD encompasses most types of water bodies, and therefore the legislation applies not only to groundwater but also to all coastal and surface waters (Allan et al., 2006). The WFD is similar in many aspects to the North American Clean Water Act, established in 1977 (USEPA, 2002).

The Directive aims to achieve and ensure the “good ecological quality” status of all water bodies, and this is to be achieved by implementing sustainable management

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plans at the river basin level. Monitoring is required to cover a number of water quality elements including, physical-chemical, hydro-morphological, biological, and chemical parameters (EC, 2000). Design of conceptual decision models for the integration of these elements is therefore mandatory for a better assessment. But, aquatic systems are too complex, and there are many problems associated with "measuring" their ecological quality and their composite elements. These measures are by definition highly subjective and linguistically uncertain. Therefore, advanced methods to manage information intended to provide such measures need to be considered.

4.4. Fuzzy inference systems

When uncertainty or imprecision are related to the words used rather than to the events or variables, these can be addressed with fuzzy logic (Shepard, 2005). Examples of lexical imprecision are concepts such as: "significant impact" or "level of concern". This imprecision reflects the ambiguity of human thinking when perceptions and interpretations are expressed. Linguistic variables are ideally suited to express many concepts found in environmental management, such as water quality, level of risk, or ecological status.

"The aquatic ecosystem in the river is at considerable risk because of high number of wastewater discharges" is a clear example of a statement inherently fuzzy. This sentence is very likely to be found in any water-quality analysis report. Actually, the level of risk contains terms, also called fuzzy sets, or qualifiers that represent a range within the variable. So, the risk for the aquatic ecosystem could include the following qualifiers: very low, low, moderate, high, severe, extreme, or deadly. Usually the number of qualifiers ranges from three to seven which overlap (commonly in a high percentage) in the values that they include. The scale used to measure linguistic variables is determined by convenience. The range from lowest to highest values of all qualifiers is called the universe of discourse. These ranges and qualifiers can be determined by consensus to reflect the local, regional, or national policies or beliefs, within the environmental protection agencies. According to the enunciated above, it is quite obvious that fuzzy logic offers a powerful framework to develop decision models for water management.

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Fuzzy sets theory has been developed for modelling complex systems under uncertain or imprecise environments (Ross, 2004). Fuzzy logic uses sets with dynamic boundaries. An example of fuzzy sets has already been introduced in Fig. 2 (right). The qualifiers defined above for risk are other examples of fuzzy sets. In fuzzy logic for instance, the boundary among “moderate risk” and “high risk” is not a crisp (fixed) number but a range with different levels of membership, or belongingness, to both qualifiers. This is one of the most convenient advantages that fuzzy logic provides. A fuzzy inference system (FIS) is a framework, formulated or designed, to manage information from inputs to produce desired outputs (Mathworks, 2007a). The framework gives a basis to take decisions. The FIS is highly interpretable and somehow quite graphical thanks to commercial available software, but it is strongly dependent of the level of expertise of the modellers about the problem that is being modelled. To design environmental indicators, FIS are demonstrating to be quite appropriate.

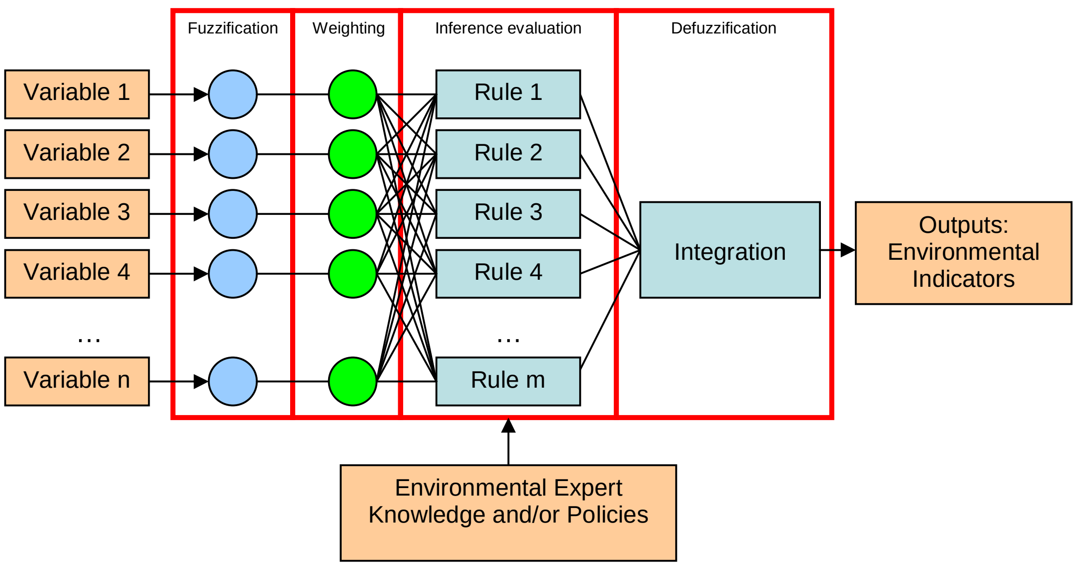

Fig. 3. Fuzzy inference system to design environmental indicators.

Fuzzy logic is a methodology that allows computing with words, and no other modelling method offers such flexibility (Zadeh, 1996). FIS involves three important concepts: membership functions, logical operations, and inference if-then rules (Mathworks, 2007a). Membership functions transform the numerical values to the linguistic world and vice versa. The process is called fuzzification or defuzzification. So, the words (qualifiers) can be computed, with logical operations, into the set of

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inference rules. Such rules reflect the level of expertise of the model. "If the concentration of mercury in water is high then the risk to ecosystems is extreme" is, for example, an if-then rule in a hypothetical FIS intended to "measure" ecological risk.

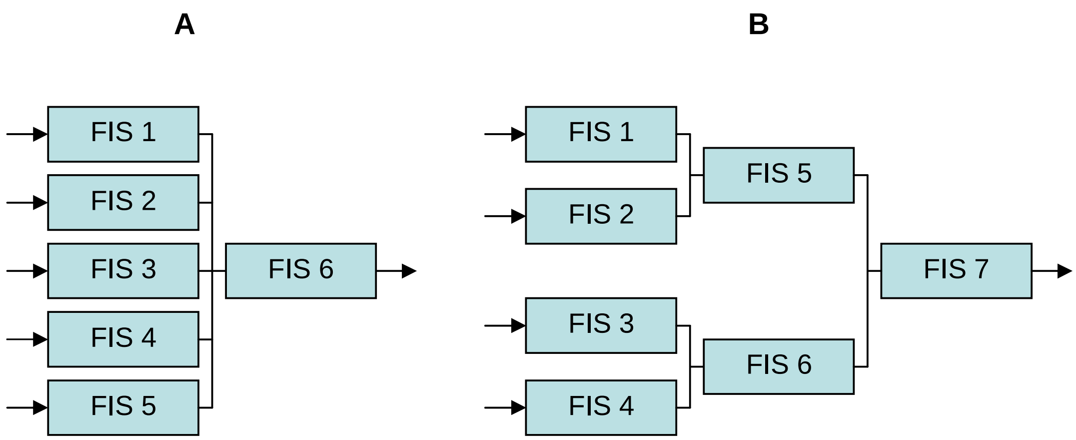

Fig. 4. Examples of hierarchical fuzzy inference systems for complex systems.

A FIS may be conveniently used to design environmental indicators. It is displayed in Fig. 3. A FIS is roughly divided into four parts: fuzzification, weighting, inference rules, and defuzzification (Mathworks, 2007a). The fuzzification process involves the definition of inputs, as well as their respective membership functions that transform the numerical value of a variable into a membership grade to a fuzzy set, which describes a level of the variable (e. g. low, high). Since not all variables have the same importance, it is necessary to guide, into the rules, the influence of each variable to the final score. The evaluation of inference rules includes the application of logic operations into each rule, and the use of aggregation methods to join the decisions (outputs) of every rule. It produces an integrated output fuzzy set that preserves the knowledge of the whole inference engine. Finally, defuzzification returns the fuzzy output to the numerical world. When a problem is complex, as those faced in the present Thesis, a structured hierarchy to interconnect various partial FIS can be developed. It facilitates the complete analysis and management of information (Gentile et al., 2003). Examples of hierarchical FIS are provided in Fig. 4.

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4.5. Neuro-fuzzy systems

Neuro-fuzzy systems are intelligent structures containing artificial neural networks and fuzzy logic systems. The hybridization produces systems that combine the human-like if-then reasoning style of fuzzy systems with the connectionist structure of neural networks. The main strength of neuro-fuzzy systems is that they can be seen as approximators with the ability to solicit interpretable rules (Paiva and Dourado, 2004). Neuro-fuzzy systems involve two contradictory requirements: interpretability versus accuracy. In practice, one of the two properties prevails (Ang and Quek, 2005). So, the neuro-fuzzy modelling research can be divided into two areas: linguistic modelling, focused on interpretability; and precise modelling, focused on accuracy. Linguistic fuzzy modelling would have application to environmental decision models. Precise fuzzy modelling would help to improve the performance of traditional environmental models already in use.

The term neuro-fuzzy may describe several configurations involving fuzzy systems and neural networks. In Chapter 2 an integrated model is presented. In turn, a concurrent neuro-fuzzy model is developed in Chapter 3. In a concurrent model, the neural network assists the fuzzy system continuously to determine the required parameters, especially if the input variables of the FIS cannot be measured directly (Fig. 5a). Such combinations do not optimize the fuzzy system but only aid to improve the performance of the overall system. Learning takes place only in the neural network and the fuzzy system remains unchanged during this phase (Abraham, 2001).

In integrated models, neural network learning algorithms are used to determine the parameters of fuzzy inference systems. Integrated neuro-fuzzy systems share data structures and knowledge representations (Abraham, 2001). Fuzzy systems are characterized by being highly interpretable but the knowledge must be available. In turn, neural networks are able to “learn” from data, but their interpretation is not easy. To a large extent, the drawbacks pertaining to these two approaches seem complementary. Therefore, it seems natural to consider building integrated systems combining the concepts of FIS and neural networks. To do that, it is common to represent a FIS in a structure appropriate to apply neural network learning algorithms. It

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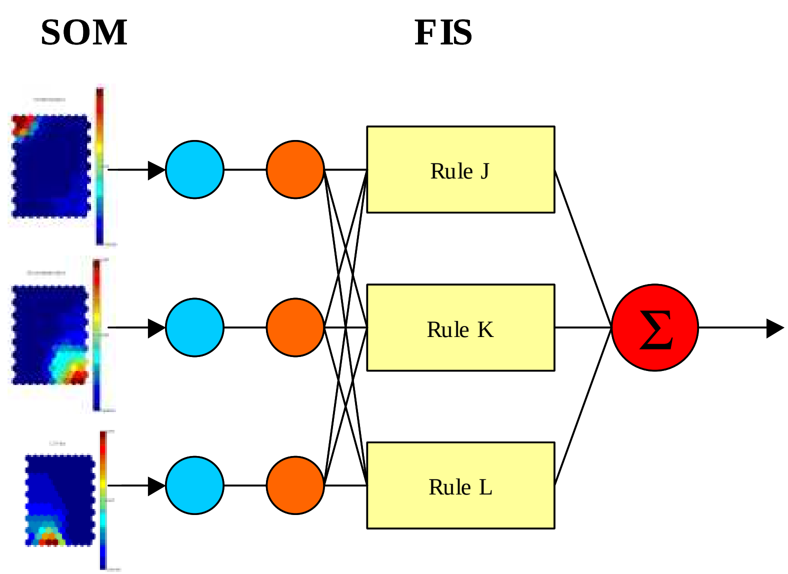
can be observed in Fig. 5b. The list of integrated neuro-fuzzy models is widespread. The ANFIS algorithm is a very well known member of that family (Jang, 1992).

a. Concurrent neuro-fuzzy system:



b. Integrated neuro-fuzzy system:

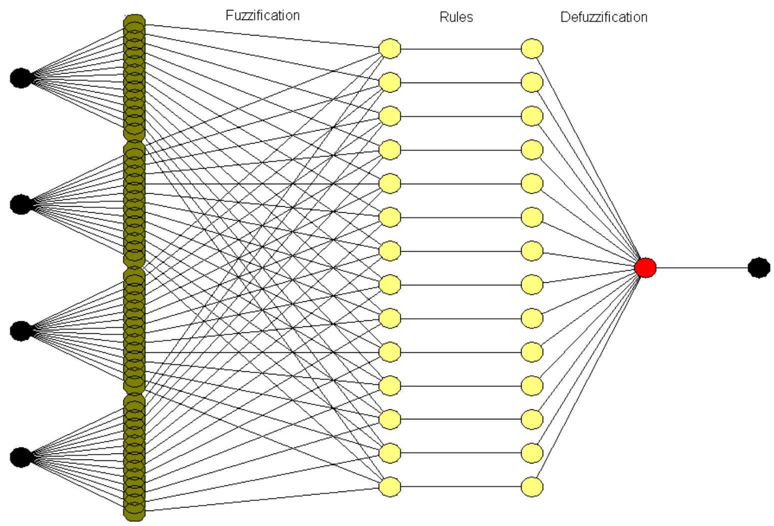


Fig. 5. Some structures of neuro-fuzzy systems.

As enunciated above, FIS models consider membership functions that are fitted at judgment of the decision-maker. Moreover, the inference engine structure must be predetermined with settings from expert knowledge about the modelled system. With ANFIS models, it is possible to discern directly from data, the shape of the membership functions and the structure of the inference engine (Firat and Gungor, 2007). Thus,

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rather than arbitrarily choosing the membership function parameters, and the FIS structure, these could be tailored to the input/output data space, in order to better account for uncertainties and variability in data. A practical application of ANFIS is discussed in Chapter 2. In ANFIS, the learning process is only concerned with parameter level adaptation within fixed structures. For large scale problems, it would be very complicated to determine the optimal antecedent consequent structures, number of rules, etc. (Abraham, 2001). Also, the computational requirements in ANFIS dramatically increase in problems with high number of input variables. It is commonly called “curse of dimensionality”.

4.6. The analytic hierarchy process

The analytic hierarchy process (AHP) is a structured tool to deal with complex decisions (Ho, 2008). It is used throughout the world in a wide variety of decision-making problems. It was proposed by Thomas Saaty in the 1970s and has extensively been improved since then (Vaidya and Kumar, 2006). The AHP provides a framework to structure a decision problem, to represent and quantify its elements, to relate elements to goals and evaluate alternatives. A decision problem is decomposed into a hierarchy of more easily understandable sub-problems, each of which can be analyzed independently.

Once the hierarchy is conceived, the decision makers may systematically evaluate its various elements, comparing them by pairs. In making the comparisons, the decision makers can use concrete data about the elements, and/or their judgments about the relative importance of the elements. The essence of the AHP is that human judgments, and not just the underlying information, can be used in performing the evaluations (Saaty, 2003). The AHP converts these evaluations into numerical values that can be processed and compared over the entire range of the problem. A numerical weight is derived for each element of the hierarchy, allowing diverse elements to be compared to another in a rational way.

AHP is based on pair-wise comparisons. The relative importance of the different attributes is given on a 1 to 9 scale. These values are assigned by verbal elicitation of decision makers (Saaty and Ozdemir, 2003). For example, if a person says attribute *A* is

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"moderately more important" than attribute *B*, *A* would have a relative weight 3 times that of *B*. In turn, if *A* is "extremely more important" than *B*, the weight of *A* would be 9 times that of *B*. The 0-9 scale is arbitrary and alternative scales have been proposed. However, the main drawback of the AHP is that the perceived meaning of the verbal expressions varies from person to person, and also depends on the set of elements involved in the comparison. However, this trouble is correctable as many proposals are currently emerging in the field of decision theory.

4.7. Probabilistic neural networks

The PNN is in essence a combination of neural networks and Bayesian statistics. A PNN implements a practical solution (based on Parzen kernels, and spheres of influence) for the mathematical problem of approximating the unknown distribution of a given population based on a learning set consisting of multivariate sample data, and without making any assumptions on the nature of the distribution itself. Once the estimator is built, the predictions are generated via the well known Theorem of Bayes. The most common choice of kernel is the basic Gaussian kernel, which involves only the Gaussian function, and therefore one sphere of influence parameter. As Bayesian approximators, PNN may be used for both mapping and classification tasks (Mathworks, 2007b). According to their purpose, the architecture of the PNN follows very precise rules. The learning phase of the PNN involves only one pass through the training data, and there is no need for a training validation set. Judging a PNN generalization performance is handled through external validation. It is possible to validate the model using full cross-validation experiments based on random selection (Niculescu, 2003).

The PNN training is so fast that for the case of a small number of input and output variables it can be performed in real time. In addition, the PNN is very robust, learning only the essential information from outliers, and being able to handle sparse samples. The basic Gaussian kernel mapping PNN performance is comparable to that of the best back-propagation neural networks. A major drawback of the PNN is that as the number of training cases grows, the same happens with the memory requirements associated with the network layers and their connections. It is appropriate to use PNN only for moderately large training sets. Large size of the training set impacts negatively

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on the computational speed of the resulting PNN. Therefore, the use of the principal components analysis (PCA) to reduce the model inputs could be highly convenient in these cases. Selecting the appropriate kernel is a very delicate and complex experimental process. There is a strong connection between the kernel choice and the PNN learning and generalization performance. A common drawback of PNN is its black box structure (Niculescu, 2003).

4.8. Classification and regression trees

CART is a non parametric statistical methodology to analyze classification issues (Mathworks, 2007c). If the dependent variable is categorical, CART produces a classification tree. When the dependent variable is continuous, it produces a regression tree. In CART, the major aim is to produce an accurate set of classifiers by discovering the predictive structure of the problem under consideration. That is, CART helps in understanding the variables and their interactions that are responsible for a given phenomenon (Yohannes and Webb, 1999).

The purpose of CART classifiers is to enable one to predict the class of any future observations from the profile of characteristics submitted for analysis. In brief, the construction of a CART classification rule centres on the definition of three major elements: the sample-splitting rule, the goodness-of-split criteria, and the criteria for choosing an optimal tree for analysis. CART builds trees by applying predefined splitting rules and goodness-of-split criteria at every step in the node-splitting process. In a highly condensed form, the steps in the tree-building process involve: growing a tree with a large number of nodes, combining some of the branches of this large tree to generate a series of sub-trees of different sizes, and selecting an optimal tree via the application of measures of accuracy of the tree (Yohannes and Webb, 1999). CART is a competitive classification algorithm (Kurt et al., 2008).

4.9. Self organizing maps

The self-organizing map (SOM) is a recent tool used for clustering, visualization, and abstraction. The basic concept behind the SOM is preservation of topology (relationships among data) (Vesanto et al., 2000).

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A SOM is a one active layer neural network consisting of a multidimensional array of neurons. Each neuron in the grid is also an output neuron. The neurons are connected only with their closest neighbours in the array according to a prescribed topological scheme. The local feedback has the result that topologically close neurons react similarly when they receive similar input. In other words, if a particular neuron represents a given pattern, then its neighbours represent similar patterns. The SOM is trained through unsupervised competitive learning using a "winner takes it all" policy (Niculescu, 2003).

All neurons in the active layer obtain the same multidimensional input and at the same time. A training case is presented to the network, and the winning neuron is found. That winner has its weights updated using the current learning rate, while the learning rate for the neighbours is scaled down proportional to the distance to the winner. Consequently, the knowledge of that pattern will be localized in the area of the winner. Any number of inputs may be used as long as the number of inputs is greater than the dimensionality of the grid space. Each training cycle involves one pass through the data and the training is stopped when changes to the network weights become insignificant. A new case is classified to the cluster associated with the corresponding winner neuron of the grid. SOM are strictly linear in their response, therefore, their use as classifiers is limited to situations that tolerate it. They train relatively fast and are easy to interpret. Furthermore, SOM layers may be combined with other neural network type layers (Niculescu, 2003).

4.10. Principal component analysis

Principal components analysis (PCA) is a statistical technique widely used to reduce multidimensional data sets to lower dimensions for analysis (Mathworks, 2007c). PCA is a powerful tool to exploratory data analysis and for making predictive models. PCA calculates the eigenvectors of the singular value decomposition of a dataset, usually after mean centring the data for each attribute. The results of PCA are component scores and loadings. They preserve the main features of the original dataset. PCA is an orthogonal linear transformation that converts the data to a new coordinate system such that the greatest variance by any projection of the data comes to lie on the

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first coordinate (first principal component), the second greatest variance on the second coordinate, and so on. In theory, PCA is the optimum transformation for a given dataset in terms of least squares.

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Chapter 1

Assessing water quality in rivers with fuzzy inference systems: A case study[1]

Abstract

In recent years, fuzzy-logic-based methods have demonstrated to be appropriate to address uncertainty and subjectivity in environmental problems. In the present study, a methodology based on fuzzy inference systems (FIS) to assess water quality is proposed. A water quality index calculated with fuzzy reasoning has been developed. The relative importance of water quality indicators involved in the fuzzy inference process has been dealt with a multi-attribute decision-aiding method. The potential application of the fuzzy index has been tested with a case study. A data set collected from the Ebro River (Spain) by two different environmental protection agencies has been used. The current findings, managed within a geographic information system, clearly agree with official reports and expert opinions about the pollution problems in the studied area. Therefore, this methodology emerges as a suitable and alternative tool to be used in developing effective water management plans.

Keywords: Water quality standards; Fuzzy inference systems; Analytic hierarchy process; Water management

[1] William Ocampo-Duque, Núria Ferré-Huguet, José L. Domingo and Marta Schuhmacher. Assessing water quality in rivers with fuzzy inference systems: A case study. *Environment International, Volume 32, Issue 6, August 2006, Pages 733-742*

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1. Introduction

The number of pollutants compromising the health of river ecosystems can be very notable, depending on the economic and social characteristics of the riparian societies beneficiated with the water (Lekkas et al., 2004). Environmental protection agencies define comprehensive sets of indicators to monitor water quality. In order to protect the ecological status, as declared in the Water Framework Directive (EC, 2000), not only environmental concentrations of chemicals in rivers are being used to assess water quality, but also their effects on trophic chains. Much work is currently done in order to implement biological monitoring (Allan et al., 2006). However, chemical monitoring will continue being an important source of data.

Water quality indicators have generally been grouped into three broad categories: physical, chemical and biological, each of them containing a significant number of water quality variables (CCME, 2004). The acceptability of water quality for its intended use depends on the magnitude of these indicators being often governed by regulations (EPA, 1994). In relation to this, for example, the Catalan Water Agency (Catalonia, Spain) uses more than 150 chemical indicators to survey the condition of freshwaters (ACA, 2005).

Traditional reports on water quality tend to be too technical and detailed, presenting monitoring data on individual substances, without providing a whole and interpreted picture of water quality. To resolve this gap, various water quality indexes have been developed to integrate water quality variables worldwide ([SAFE] Strategic assessment of Florida's environment, 1995; Mitchell and Stapp, 1996; [WEP] Lower Great Miami watershed enhancement program, 1996; Cude, 2001; Liou et al., 2004; Said et al., 2004). Most of these indexes are based on the Water Quality Index (WQI) developed by the U.S. National Sanitation Foundation (NSF, 2005).

The WQI is obtained by adding the multiplication of the respective weight factor by an appropriated quality-value for each parameter. The WQI index consists of nine parameters: dissolved oxygen (0.17), fecal coliforms (0.16), biochemical oxygen demand (0.11), pH (0.11), temperature change (0.1), phosphates (0.10), nitrates (0.10), turbidity (0.08), and total solids (0.07). In parentheses are given the weight factors

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according to the importance of the parameters. Other indexes are also used at regional level to evaluate water quality. The Simplified Water Quality Index (ISQA) is currently applied by the Catalan Water Agency (ACA, 2005). It is mainly a correlation of dissolved oxygen, total organic carbon, suspended solids, and conductivity, with a weight vector of 0.30, 0.25, 0.25, and 0.20, respectively.

However, WQI, ISQA, and other similar indexes exhibit a number of weak points, which enable the assignation of a quality value using a limited number of parameters. Most indexes do not consider toxic pollutants such as heavy metals, hydrocarbons, or pesticides. In turn, some parameters in the index equations can influence dramatically the final score without valid justification, while their formulations are rather elementary, and the number of variables involved is too limited. However, the most critical deficiency of these indexes is the lack of dealing with uncertainty and subjectivity present in this complex environmental problem (Chang et al., 2001; Mpimpas et al., 2001; Silvert, 2000).

The need for more appropriate techniques to manage the importance of water quality variables, the interpretation of an acceptable range for each parameter, and the method used to integrate dissimilar parameters involved in the evaluation process is clearly recognized. In this sense, some alternative methodologies have emerged from artificial intelligence. These methodologies, mainly fuzzy logic and fuzzy sets, are being tested with real environmental problems. The final aim is to reduce the uncertainty and imprecision in criteria employed in decision-making tools (Chang et al., 2001; McKone and Deshpande, 2005).

Fuzzy sets, characterized to be conceptually easy of understanding, and based on natural language, have been successfully used to model non-linear functions, to build inference systems on top of the experience of experts, and to deal with imprecise data (Zadeh, 1996; Pham and Pham, 1999; Romano et al., 2004; Ross, 2004). These advantages have been applied to face water related complex environmental problems (Sadiq and Rodriguez, 2004; Vemula et al., 2004; Liou and Lo, 2005; McKone and Deshpande, 2005; Ghosh and Mujumdar, 2006). In the present study, the fuzzy logic formalism has been used to assess water quality by developing a water quality index

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based on fuzzy reasoning. Advantages and disadvantages of fuzzy logic over traditional methodologies are discussed.

2. Methods

2.1. Fuzzy inference systems

Fuzzy set theory has been developed for modeling complex systems in uncertain and imprecise environment (Ross, 2004). Fuzzy logic uses sets with unclear boundaries. Fuzzy logic can be used for mapping inputs to appropriate outputs. Fig. 1 shows an input–output map for the water quality classification problem: "Given a comprehensive set of water quality indicators, what is the water condition in a river?" Water quality indicators and river condition are fuzzy definitions, since they do not present clearly defined boundaries.

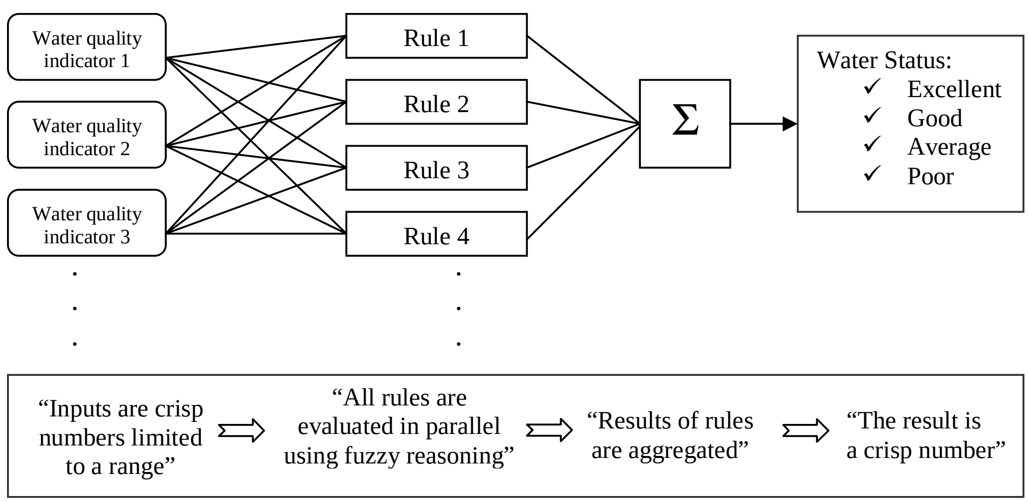

Fig. 1. Input–output map for the river water quality problem in a fuzzy inference system.

Fuzzy inference is the process of formulating the mapping from a given input to an output using fuzzy logic. This mapping provides a basis from which decisions can be made, or patterns discerned. The fuzzy inference process involves three important concepts: membership functions, fuzzy set operations, and inference rules. Although these are briefly described below, a wide description can be found in Ross (2004).

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A membership function is a curve that defines how each point in the input space is mapped to a membership value between 0 and 1. The input space is called the universe of discourse. The output-axis is called the membership value μ. If X is the universe of discourse and its elements are denoted by x, then a fuzzy set A is defined as a set of ordered pairs

$$A = \{x, \mu_A(x) \mid x \in X\} \quad (1)$$

where $\mu_A(x)$ is the membership function of x in A. A membership function is an arbitrary curve whose shape is defined by convenience.

The standard fuzzy set operations are: union (OR), intersection (AND) and additive complement (NOT). They manage the essence of fuzzy logic. If two fuzzy sets A and B are defined on the universe X, for a given element x belonging to X, the following operations can be carried out:

Intersection, AND: $$\mu_{A \cap B}(x) = \min(\mu_A(x), \mu_B(x)) \quad (2)$$

Union, OR: $$\mu_{A \cup B}(x) = \max(\mu_A(x), \mu_B(x)) \quad (3)$$

Additive complement, NOT: $$\mu_{\bar{A}}(x) = 1 - \mu_A(x) \quad (4)$$

The third concept is the inference rule. An if–then rule has the form: "If x is A then z is C", where A and C are linguistic values defined by fuzzy sets in the universes of discourse X and Z, respectively. The if–part is called the antecedent, while the then–part is called the consequent. The antecedent and the consequent of a rule can have multiple parts.

A fuzzy inference system (FIS) can be divided into four parts: fuzzification, weighting, evaluation of inference rules, and defuzzification. The fuzzification process involves the definition of inputs, outputs, as well as their respective membership functions that transform the numerical value of a variable into a membership grade to a fuzzy set, which describes a property of the variable. Since not all variables have the same importance, it is necessary to establish a way to guide the influence of each variable in the final score. The methodology suggested in this work for weight

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assignment is the Analytic Hierarchy Process, which is described in Section 2.3. The evaluation of inference rules includes the application of fuzzy operations to multiple-part antecedents, the application of implication methods from the antecedent to the consequent for every rule, and the use of an aggregation method to join the consequents across all the rules. Finally, defuzzification consists in transforming the fuzzy output into a non-fuzzy numerical value which can be used in non-fuzzy contexts (Silvert, 2000). These steps are explained with the following example, in which the aim has been to assign a water quality score using just two variables: organic matter and dissolved oxygen managed within a FIS.

2.2. Fuzzy inference systems, step by step

The procedure carried out within a FIS is here described. We have hypothesized that the levels of dissolved oxygen (DO) and organic matter (BOD_5) are sufficient to evaluate water quality (WQ) by means of an aggregated index called the Fuzzy Water Quality (FWQ) index. We have chosen “low”, “medium”, and “high” fuzzy sets for inputs, and “good”, “average”, and “poor” fuzzy sets for the output. Trapezoidal membership functions define these fuzzy sets (Fig. 2).

In water quality assessment, expressions as the following are frequently used by the experts: “if the levels of organic matter in a river are low, and the levels or dissolved oxygen are high, then the expected water quality is good”. In fuzzy language, it could be enunciated as follows:

Rule 1: If BOD_5 is low and DO is high then WQ is Good.

In the same way, other rules can be enunciated. Robustness of the system depends on the number and quality of the rules. In this example, we enunciate two more rules:

Rule 2: If BOD_5 is medium and DO is medium then WQ is Average.

Rule 3: If BOD_5 is high and DO is low then WQ is Poor.

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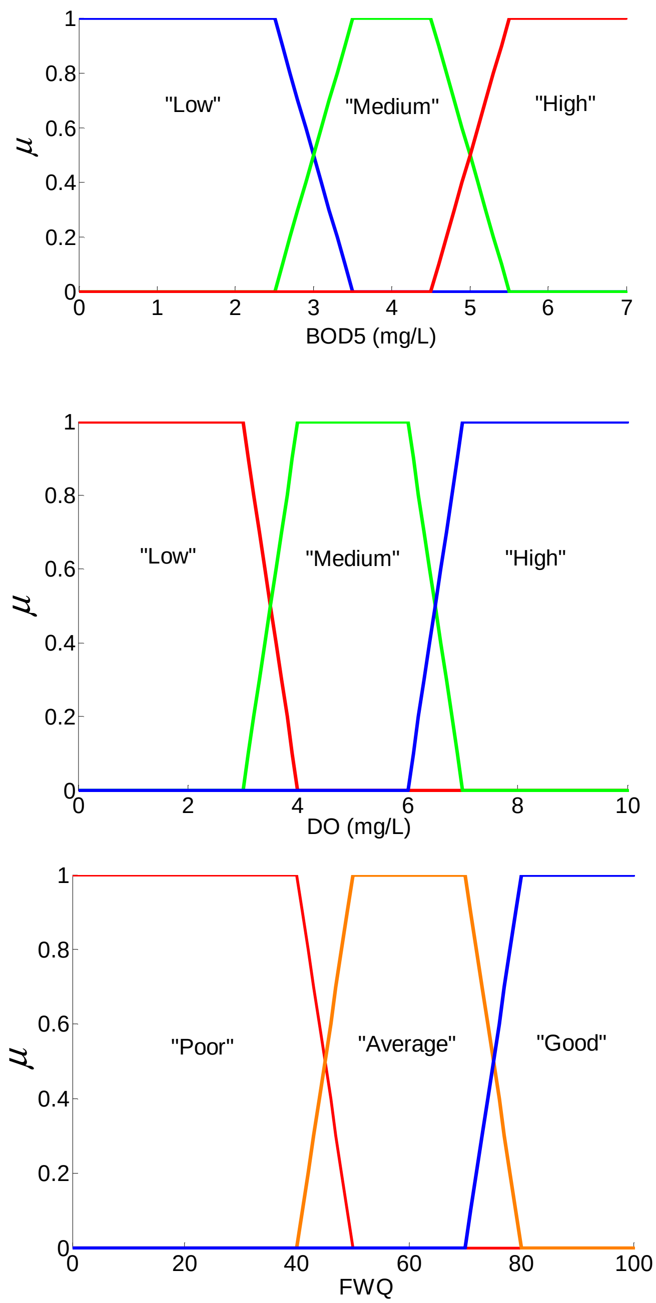

Fig. 2. Membership functions for BOD_5, DO and FWQ parameters.

If we assume that it is necessary to evaluate water quality in two river points: "R1" and "R2", having BOD_5, DO values of 1.0, 9.0, and 3.3, 6.5, respectively, before any calculation, an expert would infer the water quality status in the R1 point by

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applying the first rule. However, when input values are close to boundaries between a fuzzy set and another one, as in R2 point, the output is not so direct, and fuzzy operations should be carried out.

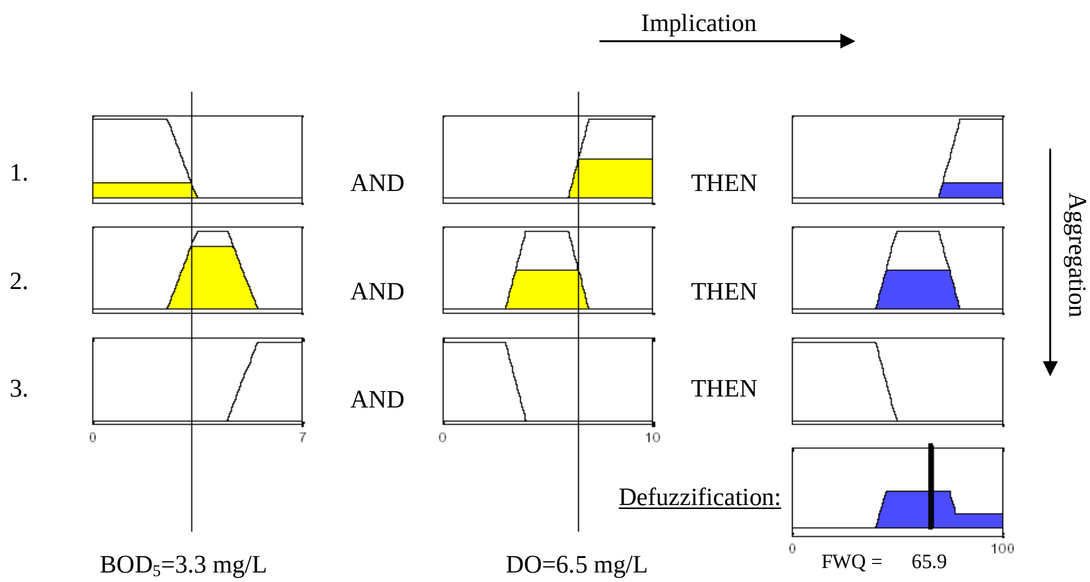

Fig. 3. Fuzzy inference diagram for the water quality scoring problem with two variables and three rules.

We must fuzzify the inputs for R2 point. According to membership functions in Fig. 2, we find that a value of 3.3 for BOD_5 belongs to “low” and “medium” fuzzy sets, with membership degrees of 0.2, and 0.8, respectively. Similarly, a value of 6.5 for DO belongs to “high” and “medium” fuzzy sets, with membership degrees of 0.5, and 0.5, respectively. Thus, a variable could belong to more than one set.

As there are multiple parts in the antecedents of the rules, fuzzy logic operations are applied to give a degree of support for every rule. Applying Eq. (2) to the antecedents of the three rules, we get 0.2, 0.5 and 0.0 degrees of support, respectively.

The degree of support for the entire rule is used to shape the output fuzzy set. The consequent of a fuzzy rule assigns an entire fuzzy set to the output. This fuzzy set is represented by a membership function that is chosen to indicate the qualities of the consequent. If the antecedent is only partially true, having a value lower than 1, the

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output fuzzy set is truncated at this value. This procedure is called the minimum implication method (Ross, 2004). As we got degrees of support lower than 1 for the example rules, we applied the implication method, obtaining that WQ belongs to "Good" fuzzy set, truncated at μ = 0.2, and WQ belongs to "Average" fuzzy set, truncated at μ = 0.5. This is shown in Fig. 3, where columns refer to the input/output fuzzy sets, and rows are the fuzzy rules.

Since decisions are based on the testing of all the rules in the system, these must be aggregated to make a decision. As depicted in Fig. 3, output fuzzy sets for each rule are aggregated to a single output fuzzy set. The aggregation procedure used here is the maximum method (Ross, 2004), which is the union of all truncated output fuzzy sets.

The final step is the defuzzification. The input for the defuzzification process is the aggregated output fuzzy set. As much as fuzziness helps the rule evaluation during intermediate steps, the final desired output is a numeric score. The defuzzification method preferred is the centroid, which is the most prevalent and physically appealing of all available methods (Ross, 2004). The centroid method returns the center of area under the curve formed by the output fuzzy set:

$$z^* = \frac{\int \mu(z) \cdot zdz}{\int \mu(z)dz} \tag{5}$$

By replacing the corresponding membership functions (shown in Fig. 2) in Eq. (5), the water quality index for the "R2" point is:

$$FWQ^* = \frac{\int_{40}^{45}(0.10z-4)zdz + \int_{45}^{75}(0.5)zdz + \int_{75}^{78}(-0.10z+8)zdz + \int_{78}^{100}(0.2)zdz}{\int_{40}^{45}(0.10z-4)dz + \int_{45}^{75}(0.5)dz + \int_{75}^{78}(-0.10z+8)dz + \int_{78}^{100}(0.2)dz} = 65.9$$

The above describes the procedure used to deal with information in a FIS. In Section 2.4, we describe the use of a fuzzy inference system to classify water quality in the Ebro River. A comprehensive set of 27 water quality indicators and 96 rules has been used.

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2.3. The analytic hierarchy process

The successful application of a FIS depends on an appropriate weight assignment to the variables involved in the rules. Weight assignment defines the relative importance and influence of the input parameters in the final score. For that reason, its definition should be carefully done. A good FIS could lead to erroneous simulations due to mistaken weights. In this study, a comprehensive multi-attribute decision-aiding method based on the Analytic Hierarchy Process (AHP) (Vaidya and Kumar, 2006) is proposed to estimate the relative importance of water quality variables. The AHP is a leading methodology to solve decision problems by the prioritization of alternatives. The basis of the AHP is the Saaty's eigenvector method (Saaty, 2003) and the associated consistency index. It is based on the largest eigenvalue and associated eigenvector of $n \times n$ positive reciprocal matrix $\boldsymbol{A}$. a_{ij} elements of $\boldsymbol{A}$ are the decision maker's numerical estimates of the preference of n alternatives with respect to a criterion when they are compared pair-wise using the 1–9 AHP comparison scale. One means that both alternatives are equally preferred, while the preference of an alternative with respect to another could diminish until nine.

Saaty's eigenvector method has a weak point in the methodology applied to measure the consistency of the weight vector formed. A consistency measure is necessary to test the approach degree in the subjective choice of the weights. Recently, a theoretically well-founded improvement to Saaty's method by using the singular value decomposition (SVD) has been proposed (Gass and Rapcsak, 2004). In the AHP-SVD method, the priority of the decision maker could be approximated by the uniquely determined, normalized positive weight vector $\boldsymbol{w}$ with the values:

$$w_i = \frac{u_i + \frac{1}{v_i}}{\sum_{j=1}^{n} u_j + \frac{1}{v_j}} \qquad i = 1, \ldots, n \tag{6}$$

where, $\boldsymbol{u}$ and $\boldsymbol{v}$ are the left and right singular vectors belonging to the largest singular value of matrix $\boldsymbol{A}$, respectively, and n is the number of variables. The consistency measure (CM) of the weight vector is determined on an absolute scale by using the Frobenius norm:

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$$CM = \frac{\left\| \boldsymbol{A} - \tilde{\boldsymbol{A}} \right\|_F}{\left\| \boldsymbol{A} \right\|_F + (41/9)n} \tag{7}$$

where matrix $\tilde{\boldsymbol{A}}$ is formed by setting (w_i/w_j) for every pair (i, j). If $CM < 0.10$ the matrix $\boldsymbol{A}$ is considered to be consistent else decision maker should pair-wise compare again. More details about AHP-SVD methodology can be found in Gass and Rapcsak (2004).

2.4. Development of the Fuzzy Water Quality (FWQ) index

A fuzzy index for the water quality assessment has been developed. Ranges and weights of the variables in the inference system have been optimized to match the predicted fuzzy scores with ISQA and WQI indexes for the case study (Table 1). The right prediction of the fuzzy model strongly depends on the number of fuzzy sets used in the mapping process, since it facilitates to give more continuity to the universe of discourse. However, three fuzzy sets to split the inputs and outputs have been considered suitable for the scope of this study.

Table 1. Optimized predictions of current water-quality indexes with fuzzy inference systems

Index	**Variables**	**Value**	**Fuzzy-Value**
ISQA	TOC (0.32), SS (0.32), DO (0,32), CON (0,04)	83 ± 2	82 ± 2
WQI	BOD_5 (0.1362), DO (0.2029), FC (0.0800), NO_3(0.1251), pH (0.1362), PO_4 (0.0917), SS (0.1251), TUR (0.1028)	74 ± 3	75 ± 4

Optimized weights are in parentheses. ISQA is a simplified index used by the Catalan Water Agency. WQI is the index developed by the American National Sanitation Foundation.

Twenty-seven parameters divided into 5 groups have been selected to cover the whole space of possible pollutant sources. Toxic substances (pesticides, heavy metals, aromatic hydrocarbons and organochlorines) were chosen in order to get representation of the list of priority substances included into the European Water Framework Directive (EC, 2000), as well as to add substances reported in the European Pollutant Emission Register (EC, 2005) for the studied zone. The groups of indicators are the following:

• Primary: dissolved oxygen (DO), conductivity (CON), pH, and suspended solids (SS).

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• Organic matter: biochemical oxygen demand (BOD_5) and total organic carbon (TOC).

• Microbiology: total coliforms (TC), fecal coliforms (FC), salmonellas (Sa), and fecal streptococci (FS).

• Anions and ammonia: phosphates (PO_4), nitrates (NO_3), sulphates (SO_4), chlorides (Cl), fluorides (F) and ammonia (NH_4).

• Priority substances: atrazine (Atr), benzene–toluene–ethylbenzene–xylenes (BTEX), nickel (Ni), simazine (Sim), trichlorobenzenes (TCB), chromium (Cr), hexachlorbutadiene (HCBD), polycyclic aromatic hydrocarbons (PAH), arsenic (As), lead (Pb) and mercury (Hg).

Trapezoidal membership functions were used to represent "low", "medium", "high", "poor", "average", and "good" fuzzy sets. They are represented as:

$$\mu(x;a,b,c,d) = \max\left(\min\left(\frac{x-a}{b-a},1,\frac{d-x}{d-c}\right),0\right) \tag{8}$$

where *a, b, c,* and *d* are membership function parameters. A list of these parameters is summarized in Table 2. For the purposes of the present study, the shape of the membership functions is secondary. However, linear fuzzy sets facilitate the defuzzification. Ranges for fuzzy sets were based on European trend concentrations in river waters (EEA, 2003), guidelines for drinking-water quality (WHO, 2004), toxicity and ecotoxicity parameters, and Spanish available regulations for classifying water in river basins, and setting objectives. These ranges are also shown in Table 2.

Ninety-six rules were enunciated, three for each indicator, and three for each partial score into groups. Each rule had only one antecedent in order to facilitate the weight assignment. The structure of fuzzy rules was: if indicator *i* is "Low" then FWQ is "Good", if indicator *i* is "Medium" then FWQ is "Average", and if indicator *i* is "High" then FWQ is "Poor". There were exceptions for DO and pH, in whose case rules were: if DO is "Low" then FWQ is "Poor", if DO is "Medium" then FWQ is "Average", if DO is "High" then FWQ is "Good", if pH is "Low" or pH is "High" then FWQ is "Average", and if pH is "Medium" then FWQ is "Good".

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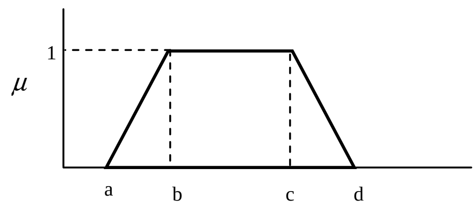
Table 2. Parameters for membership functions used in the fuzzy inference system



Group	Indicator	Units	"Low"			"Medium"				"High"			Range
			a=b	*c*	*d*	*a*	*b*	*c*	*d*	*a*	*b*	*c=d*	
Primary	DO	mg/L	0	3	4	3	4	7	8	7	8	12	0-12
	pH	-	0	6	7.5	6	7	8	9	7.5	9	14	0-14
	CON	µS/cm	0	600	700	600	700	800	900	800	900	1400	0-1400
	SS	mg/L	0	8	11	8	11	14	17	14	17	24	0-24
Organic matter	DBO_5	mg/L	0	2.5	3.5	2.5	3.5	4	5	4	5	10	0-10
	TOC	mg/L	0	2	3	2	3	4	5	4	5	9	0-9
Microbiology	TC	MPN/100 mL	0	50	100	50	100	1000	2000	1000	2000	10000	0-10000
	FC	MPN/100 mL	0	25	50	20	40	400	800	400	800	4000	0-4000
	Sa	Presence=1, Absence=0 in 1 L	0	0.2	0.4	0.2	0.4	0.6	0.8	0.6	0.8	1	0-1
	FS	MPN/100 mL	0	20	40	20	40	200	400	200	400	2000	0-2000
Anions and ammonia	PO4	mg/L	0	0.2	0.4	0.2	0.4	0.6	0.8	0.6	0.8	1	0-1
	NO3	mg/L	0	10	20	10	20	30	40	30	40	50	0-50
	NH3	mg/L	0	0.07	0.14	0.07	0.14	0.18	0.24	0.18	0.24	0.5	0-0.5
	SO4	mg/L	0	75	100	75	100	125	150	125	150	250	0-250
	Cl	mg/L	0	50	100	50	100	150	200	150	200	250	0-250
	F	mg/L	0	0.3	0.6	0.3	0.6	0.9	1.2	0.9	1.2	1.5	0-1.5
Priority Substances	Atr	ng/L	0	80	160	80	160	240	320	240	320	500	0-500
	BTEX	µg/L	0	40	80	40	80	120	160	120	160	200	0-200
	Ni	µg/L	0	10	15	10	15	20	25	20	25	50	0-50
	Sim	ng/L	0	80	160	80	160	240	320	240	320	500	0-500
	TCB	µg/L	0	4	8	4	8	12	16	12	16	20	0-20
	Cr	µg/L	0	10	20	10	20	30	40	30	40	50	0-50
	HCBD	µg/L	0	0.4	0.8	0.4	0.8	1.2	1.6	1.2	1.6	3	0-3
	PAH	ng/L	0	20	40	20	40	60	80	60	80	100	0-100
	As	µg/L	0	15	25	15	25	35	45	35	45	60	0-60
	Pb	µg/L	0	15	25	15	25	35	45	35	45	60	0-60
	Hg	µg/L	0	0.2	0.4	0.2	0.4	0.6	0.8	0.6	0.8	1	0-1
FWQ Indexes			**"Poor"**			**"Average"**				**"Good"**			**Range**
		-	0	40	50	40	50	70	80	70	80	100	0-100

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2.5. Study area

The Ebro River flows mainly through the Northeast of Spain and flows into the Mediterranean Sea after covering more than 900 km. The whole Ebro basin covers an area of 85 362 km^2. When crossing Catalonia, the Ebro River takes the name "Low Ebro". It starts at the village of Ribarroja and extends up to the Delta mouth, going through 134 km length. In 2004, the mean annual flow was 415 m^3/s, but as all Mediterranean rivers, heavy fluctuations ranging from 127 to 962 m^3/s have been recorded depending on the dry and wet seasons. An important human, agricultural and industrial activity is developed along its riparian zone (Navas and Lindhorfer, 2003). Some big chemical industries and a nuclear power plant are located in the riparian zone. Good water quality in the Low Ebro is crucial to preserve ecologically sensitive ecosystems, especially those settled in the Delta area.

The Ebro Delta is one of the most important wetland areas in the western Mediterranean. It is valuable both economically and ecologically, highlighting rice agriculture, and bird habitats for more than 300 species. Part of the Delta was designated as a Natural Park with some special protected areas. It is considered of international importance for breeding and dwelling of endemic and endangered birds (DOGC, 2004). Ecosystems in the Low Ebro are facing a number of problems, mainly produced by water necessities for irrigation and supplying in dry zones, affecting the natural hydrological regime. Nowadays, the unsustainable management of the Ebro basin is acknowledged (Day et al., 2006) and the development of analytical tools to assess the present and future ecological condition of the water, as required in the European Water Framework Directive, is clearly necessary.

Water quality in the Low Ebro is monitored by two Environmental Protection Agencies: the Catalan Water Agency (ACA) and the Confederación Hidrográfica del Ebro (CHE). Therefore, data from both agencies can be compared. Five periodic sampling points (SP) are located in the area (Fig. 4). ACA sampling points are: SP1 (Flix), SP3 (Xerta), and SP5 (Tortosa, close to the Delta). In turn, CHE sampling points are: SP2 (after the Ascó nuclear power plant) and SP4 (Tortosa).

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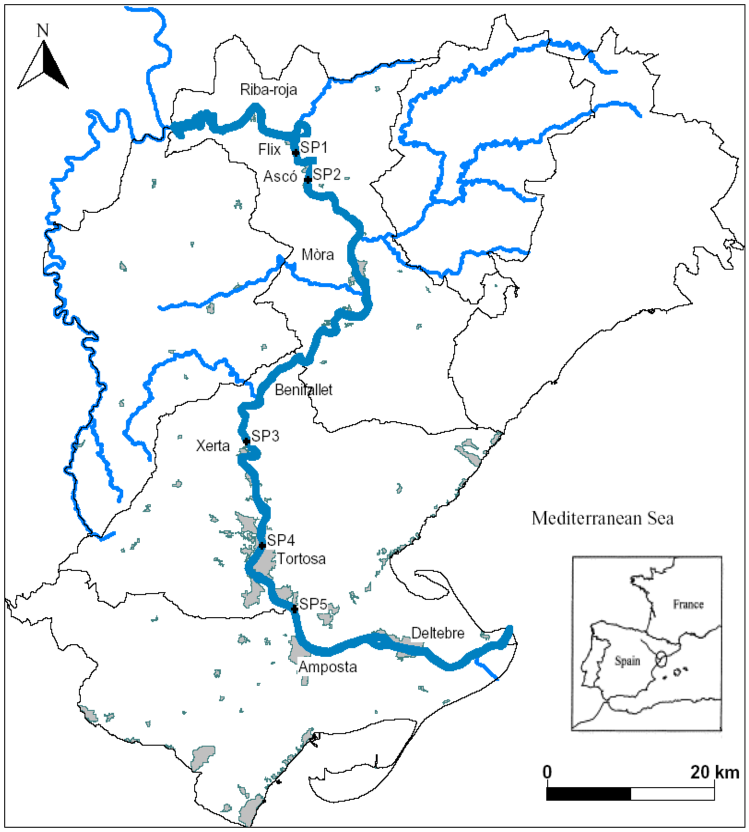

Fig. 4. Sampling sites in the studied area.

3. Results

The water condition for the Ebro River when crossing Catalonia has been assessed with the FWQ index. Input data extracted from public databases (ACA, 2005 and CHE, 2005) have been used to assess water quality between 2002 and 2004. Weights for water quality indicators calculated with the AHP–SVD-method, which is described in Section 2.3, are shown in Fig. 5. The pair-wise comparison was conducted with risk quotients for the substances. These quotients were calculated in the way of characterization factors for use in Life Cycle Impact Assessment regarding to the emissions of pollutants to river streams. Multimedia fate transport and exposure models, particularly CalTOX and USES-LCA models were used for risk estimation. More details about this methodology were recently reported (Ocampo-Duque and Schuhmacher, 2005). In addition, some experts were consulted about the results of the weight assignment. It is important to remark that indicators here chosen have a very different nature.

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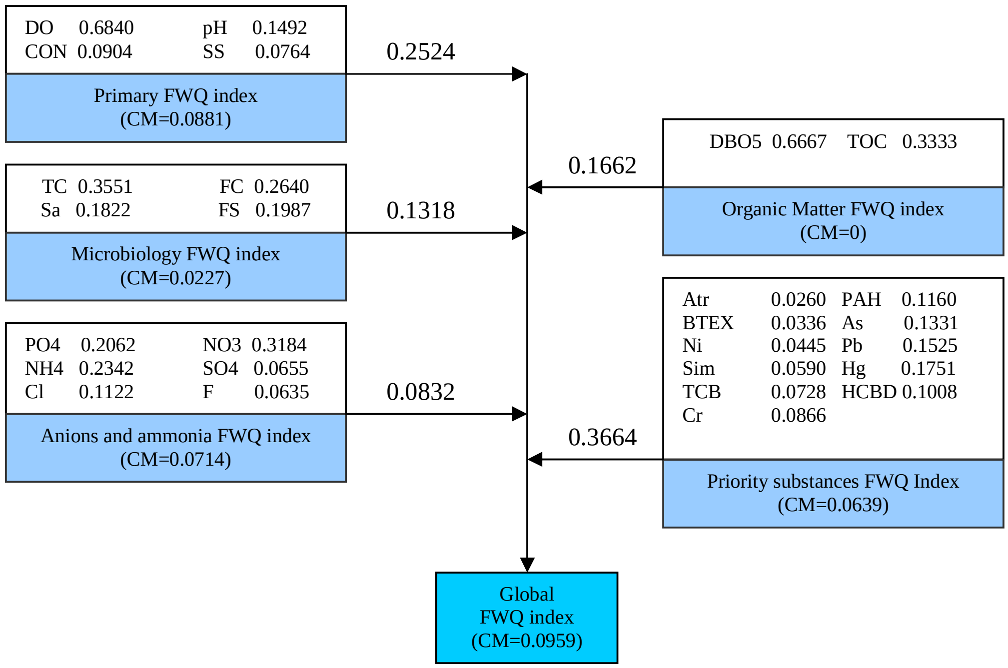

Fig. 5. Optimized weights for indicators included in the fuzzy water quality index (FWQ) estimated with the AHP–SVD methodology. Consistency measures in parentheses.

The results for the global FWQ index calculated according to the FIS are shown in Fig. 6. In turn, the comparative contribution to the global index for groups of indicators is depicted in Fig. 7. On the other hand, a comparison between the proposed FWQ index, the reputed WQI index, and the regional regulatory ISQA index is shown in Fig. 8.

4. Discussion

4.1. Evaluation of the water status in the Low Ebro with the FWQ index

An index-based framework to assess water quality in the Low Ebro has been developed. Annual mean values of currently monitored indicators have been used to test this fuzzy index. In general, primary and organic matter parameters led to high values for FWQ indexes, indicating a relative good condition, mainly affected by conductivity values. However, low values for microbiology FWQ indexes drove to results of concern. The presence of coliforms, salmonellas and streptococci at high concentrations

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indicate that the Ebro River is receiving discharges without an adequate treatment. Likewise, agricultural run-off might also increase these indicators. Microbiology scores are lower in sampling sites located after cities. It can be observed in Fig. 7 for SP2, SP4 and SP5.

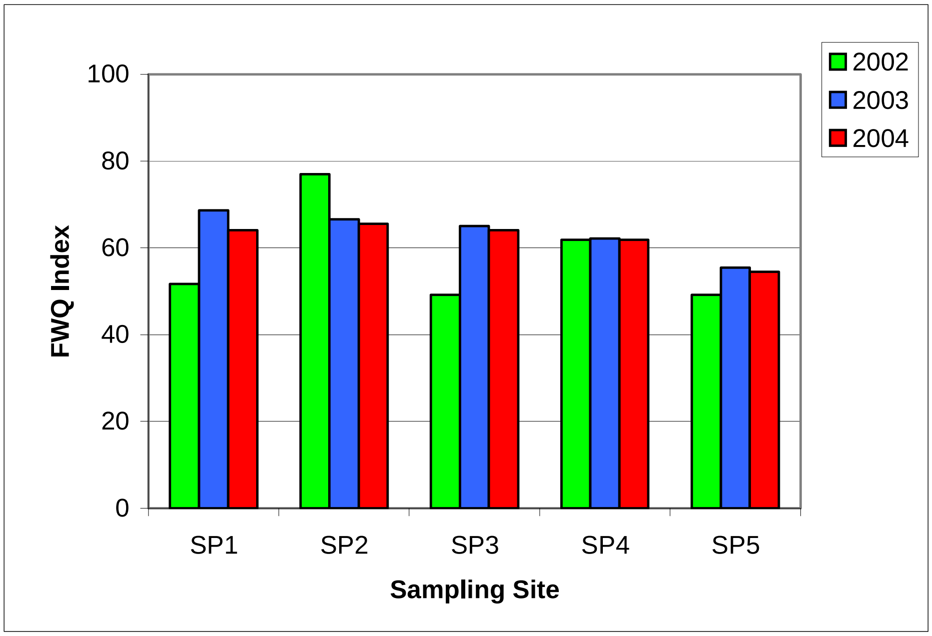

Fig. 6. Results for the global fuzzy water quality index in the "Low Ebro".

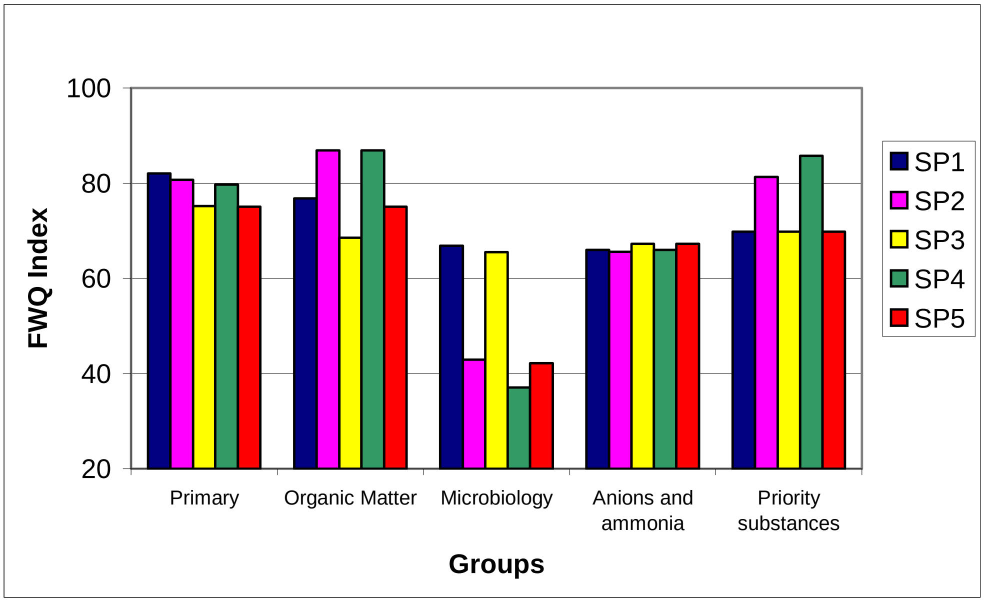

Fig. 7. Contribution of groups of indicators to the global fuzzy index in the studied area (year 2003).

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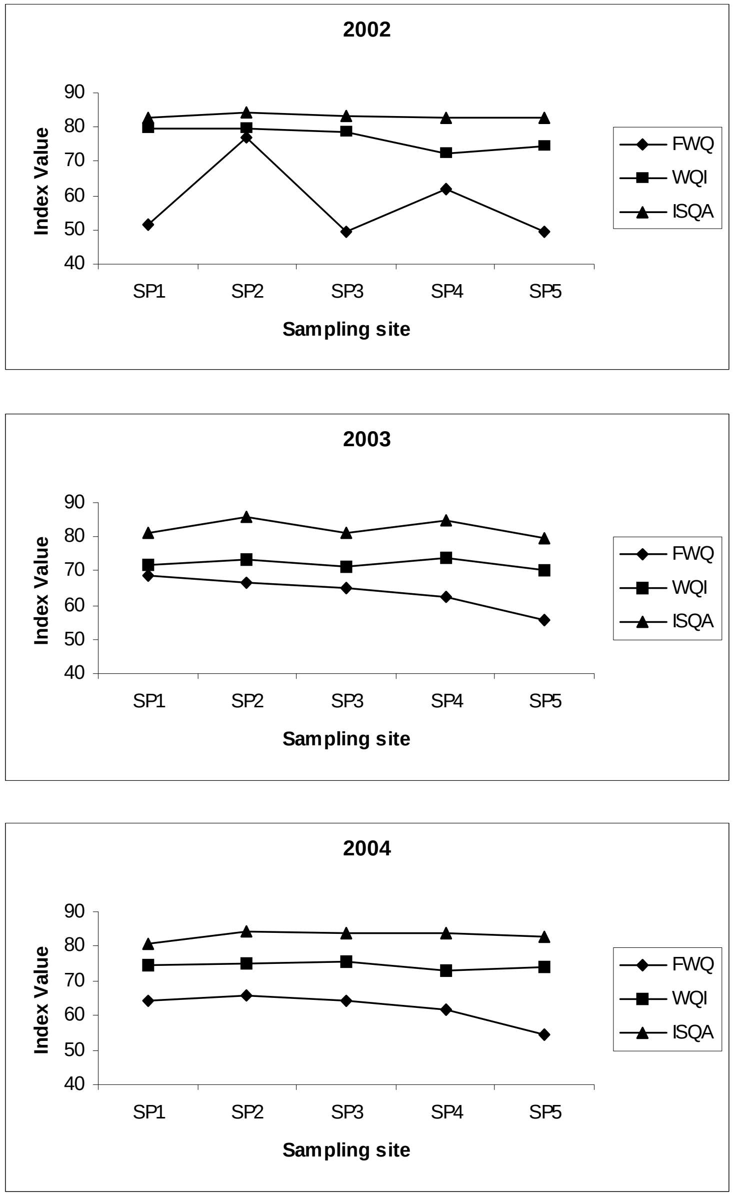

Fig. 8. Results for water quality indexes in the "Low Ebro" river.

We found that anions and ammonia FWQ indexes have been mainly reduced by the presence of high chloride and sulfate concentration. Sulfates are due to the presence of high natural gypsum concentration in the basin soils (Elorza and Santolalla, 1998), while high chloride levels are due to the presence of industrial facilities emitting more than 80 000 tones per year in the zone (EC, 2005). Consequently, the Ebro River has

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high salinity due to the combination of both natural and anthropogenic reasons. High salinity levels in water are detrimental not only for urban uses, but also for agrarian systems threatened by salinization in the Delta. For priority substances, the score is mainly affected by the presence of mercury in concentrations very close to acceptable limits. However, low index scores are not perceived because of the nature of data used, representing annual means. Other values reported for priority substances are notably below the regulatory limits.

An analysis of variance (ANOVA) over the fuzzy global results has shown that there are not significant ($p < 0.05$) differences between years assessed. It indicates that policies to diminish pollution are not giving optimistic results. On the other hand, ANOVA shows that there are significant differences between sampling sites. The SP2 exhibits a marked good water quality, while SP5 shows the worst score. Differences between SP2 and the other sampling sites are due to the fact that this sampling site is located just after a big dam (Flix dam). The dam modifies the solute transport phenomena allowing sedimentation processes and the consequent reduction of pollutant concentrations in the stream.

A global FWQ index of 67 ± 6 has been estimated for the period January-2002 to December-2004. This estimation has been 74 ± 3 and 83 ± 2 with WQI and ISQA indexes, respectively. These values are far from appropriate water quality standards to be fulfilled by European rivers as declared in the Water Framework Directive (EC, 2000). Global results show that water quality along Low Ebro River is deteriorated as it approaches to the Delta (Fig. 6). The lowest fuzzy scores have been found for SP5, located few kilometers from rice crops which are irrigated with river water. These results agree with those of environmental experts and official reports, which clearly declare the non-compliance of European precepts (CHE, 2004) appointed in the Water Framework Directive (EC, 2000). According to FWQ index results, many efforts in planning and control should be carried out by industries, farmers, citizens and stakeholders to enhance Low Ebro water quality in coming years. The current situation clearly endangers the river ecosystems and regional sustainability.

The FIS has been optimized with WQI and ISQA scores. Since a more comprehensive set of indicators has been used, a lower score and higher variability have

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been obtained with the fuzzy index. It has been found that one output fuzzy set differing from the normal results for the majority of the output fuzzy sets penalizes the final aggregated score much more than current scoring systems. This behavior observed in the defuzzification centroid method, normally used in Mamdani inference systems, could be avoided by defining more ranges and rules. However, the classification performance of the model probably would not significantly improve. This weakness could be also avoided with Sugeno inference systems, where singletons are used instead of output fuzzy sets. However, it is still under investigation by our research group.

4.2. Validation of the proposed FWQ index

The validation of an index such as FWQ index is not an easy task. Indexing processes suffer from the risk to miss information. Although indexing processes have many limitations, their benefits are significant when measuring sustainable development or environmental impacts. FWQ index does not aim at describing the variation of the concentration of a single pollutant or the alteration of a physical parameter. It is used to estimate the state of ecosystems generated by diverse driving forces and pressure agents. FWQ index represents the global stress exerted on the water body taking into account both natural and anthropogenic factors.

The most relevant aspect to highlight here is the methodology applied to produce the index. The most important advantage of the fuzzy methodology is that the inference system is built with words. None equation is used to represent the inference model, which is characterized to be highly non-linear. Equations have been only used to map variables. This is especially valuable in water management decision processes, in which individuals without a mathematical background are involved.

A comparison of the performance for the proposed index and some indexes currently employed by environmental protection agencies could address some interesting remarks. In Fig. 8, the FWQ index is compared to the ISQA index, which is used by the Catalan Water Agency for current reporting, and to the benchmarking WQI index (Said et al., 2004). The treatment of the information within the FIS directly influences the final score. WQI and ISQA scores are always over 70, giving a “good water quality” score in a non-fuzzy environment. ISQA scores are higher because they

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do not consider microbiological pollution. FWQ scores give a water condition in the Low Ebro as “some portion is average and some portion is good”. FWQ outputs better agree with the real condition reported by the Confederación Hidrográfica del Ebro for the studied zone (CHE, 2004). This regional environmental protection agency reports that water quality decreases as it comes closer to the sea. It matches with the fuzzy index prediction.

Anyhow, the best way to validate the performance of this index is comparing it with impact indicators in the trophic chain. Fish has been widely used as a model for determining the effects of environmental pollutants on living organisms (Lacorte et al., 2006). In fact, some researchers (Lavado et al., 2004 and Lavado et al., 2006) have recently revealed that some biochemical responses in carps from the Ebro river show endocrine-disrupting effects, which are associated to exposure to domestic, agricultural and industrial effluents. These results match with FWQ index spatial data. In particular, variations in some biochemical marker activities measured in fish collected from the Delta region (close to SP5) have shown high differences when compared to those measured in fish collected from a “relative clean region” (Table 3). Unfortunately, the number of data reported by these researchers is limited to draw vast conclusions. Although the sampling campaigns corresponded to a period prior to FWQ index calculations, we have demonstrated that water quality has remained unchanged for a sufficient time.

Table 3. Comparison between impact indicators (biochemical markers) and FWQ index for some sites in the “Low Ebro”

Indicator	Unit	Sampling Site: Clean area	SP1	SP5	Reference
Global FWQ index	-	62	65	63	This study
Priority substances FWQ index	-	86	62	63	This study
EROD activity in carps	pmol/min/ mg protein	69	416	689	Lavado et al. (2006)
AChE activity in carps	pmol/min/ mg protein	55	32	33	Lavado et al. (2006)
UDPGT -T activity in male carps	pmol/min/ mg protein	368	273	198	Lavado et al. (2004)
UDPGT -E2 activity in male carps	pmol/min/ mg protein	539	450	356	Lavado et al. (2004)

EROD: 7 ethoxyresorufin O-deethylase, AChE: acetylcholinesterase,
UDPGT: uridine diphosphate glucuronosyl-transferase, T: Testosterone, E2: Estradiol

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5. Conclusions

In this paper, we present a robust decision-making tool for water management in the form of the fuzzy water quality (FWQ) index. A suitable environmental application of inference systems based on fuzzy reasoning to integrate water quality indicators has been shown. The methodology developed in this research clearly improves methods used to date. The flexibility of fuzzy logic to develop classification models with a simple framework, built with natural language, should be recommended in the development of similar environmental indexes in which highly subjective information must be correlated. It has been demonstrated that computing with words within the FIS improves the tolerance for imprecise data. The FIS is also able to predict scores obtained with current indexes using the same number of parameters. Moreover, the necessity to link fuzzy inference systems and weighting methodologies to deal with the relative importance of input variables has been also shown.

We have assessed water quality in the Ebro River with physicochemical indicators. Although the Water Framework Directive highlights the need to use biotic components in the global assessment of European waters, chemical monitoring networks will continue being a comprehensive source of information for decision making in water management. In this sense, the use of fuzzy logic has demonstrated that water quality in the Low Ebro is below sustainable expected scores.

6. Acknowledgements

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Chapter 2

A neural-fuzzy approach to classify the ecological status in surface waters[2]

Abstract

A methodology based on a hybrid approach that combines fuzzy inference systems and artificial neural networks has been used to classify ecological status in surface waters. This methodology has been proposed to deal efficiently with the non-linearity and highly subjective nature of variables involved in this serious problem. Ecological status has been assessed with biological, hydro-morphological, and physicochemical indicators. A data set collected from 378 sampling sites in the Ebro river basin has been used to train and validate the hybrid model. Up to 97.6% of sampling sites have been correctly classified with neural-fuzzy models. Such performance resulted very competitive when compared with other classification algorithms. With non-parametric classification–regression trees and probabilistic neural networks, the predictive capacities were 90.7% and 97.0%, respectively. The proposed methodology can support decision-makers in evaluation and classification of ecological status, as required by the EU Water Framework Directive.

Capsule: Fuzzy inference systems can be used as environmental classifiers.

Keywords: Ecological status; EU Water Framework Directive; Fuzzy inference systems; Neural networks; Ebro river

[2] William Ocampo-Duque, Marta Schuhmacher and José L. Domingo. A neural-fuzzy approach to classify the ecological status in surface waters. *Environmental Pollution, Volume 148, Issue 2, July 2007, Pages 634-641.*

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1. Introduction

Water pollution is one of the main environmental issues on which European citizens are seriously concerned (EC, 2005). The Water Framework Directive (WFD) was created as a response to such public concern (Achleitner et al., 2005). It constitutes a key mandatory document to establish good water quality across the European continent (Vighi et al., 2006). Its central requirement is that the environment must be protected to a high level in its entirety, emphasizing on ecological protection (Dodkins et al., 2005). This good ecological status should involve the values of the biological quality elements for surface water bodies which show low levels of distortion resulting from human activities (EC, 2000). In fact, to set boundaries among good, moderate, and/or bad ecological status has resulted in a highly subjective task.

Because of ecological variability, the controls to preserve ecological conditions are regionally specified. Consequently, the ecological ranking is applied by comparing all water streams within a river basin against reference conditions specified for each river basin (Moreno et al., 2006; Munne and Prat, 2004).

The Confederación Hidrográfica del Ebro (CHE) has established interesting mechanisms to rank the ecological status of surface waters (CHE, 2005). They are based on several environmental indexes. The overall evaluation system is somewhat complex. However, it is inevitable given the extent of uncertainty, subjectivity, and variability in ecological assessment, as well as the large number of parameters that must be dealt with. Moreover, it is practically impossible to measure inputs for all water bodies. For that reason, the development of appropriate models to simulate ecological status in data-poor environments, based on well documented areas, is a current necessity.

However, traditional equation based techniques to model this real world problem are hardly suitable to face the non-linearity, subjectivity, and complexity of the cause–effect relationships among ecological variables (Marsili-Libelli, 2004). In order to classify ecological status, we here propose an emerging frame that combines the virtues of fuzzy inference systems to model expert human knowledge, with the proved adaptive learning capabilities of artificial neural networks. Inputs were selected to follow WFD

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suggestions about river classification. The main objective has been to deal efficiently with uncertainty and subjectivity of the variables involved in the assessment of ecological status in rivers.

2. Methods

2.1. Study area and model variables

The Ebro river basin (NE Spain) covers an area of 85 362 km^2. It supports an important human, agricultural, and industrial activity. Various big chemical industries and nuclear power plants are located near to the flow channel. Consequently, many pollutants are released to the surface waters, stressing sensitive ecosystems, especially those located in the Delta.

In this study, a representative index for each biological, hydro-morphological, and physicochemical component has been used to produce an ecological classification system for the Ebro river basin. A parameter to consider geographic variability is also included. A data set covering 378 sampling sites (Fig. 1) has been used to train and validate the models (CHE, 2004). Monitoring values corresponding to the summer 2001–2002 periods have been used. The measured outputs (meaning: high, good, moderate, poor, or bad) are based on the ECOSTRIMED method (Bonada, 2003; Prat et al., 2000). These variables are described here:

2.1.1. Ecotype

Ecotypes are regions with similar environmental, structural, and ecosystemic characteristics identified according to the distribution of macroinvertebrates and their frequencies of appearance. River basins are subdivided into ecotypes to set reference conditions and establish quality objectives. Six ecotypes have been defined in the Ebro river basin (Munne and Prat, 2000). They are: (1) wet mountain, (2) great rivers, (3) depression, (4) Mediterranean mountain, (5) Ebro axis, and (6) high mountain (Fig. 1).

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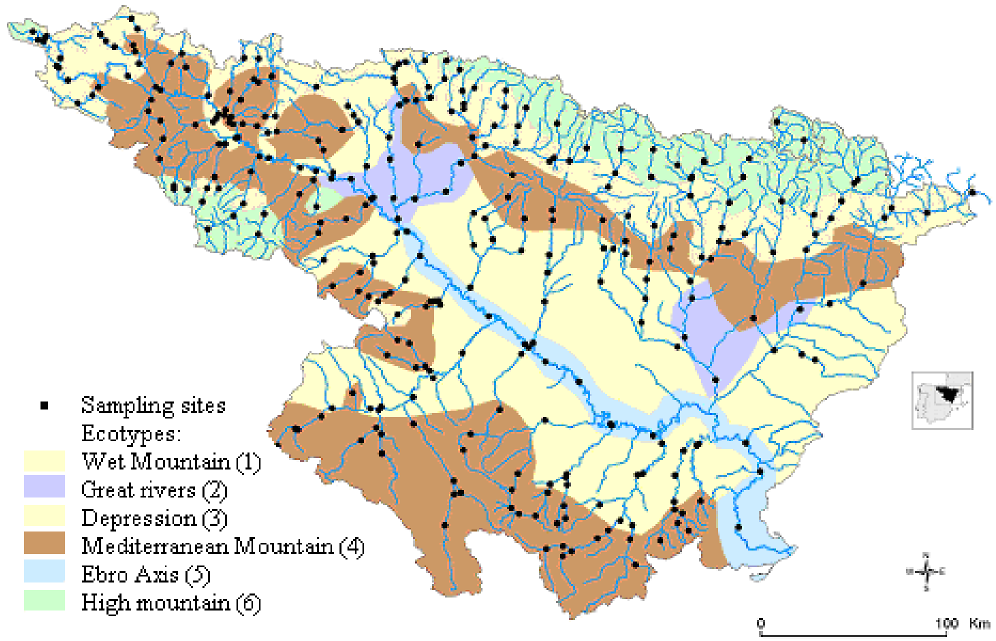

Fig. 1. Sampling sites and ecotypes in the studied area.

2.1.2. QBR index

Riparian habitat is a key element to preserve biodiversity (Ward et al., 2002). The QBR protocol is a simple method to evaluate riparian habitat quality (Munne et al., 2003). In Spain, it is becoming popular in studies related to the implementation of the WFD (CHE, 2005). For QBR determination, the river is divided into three sections: the main channel, the floodplain zone, and the riparian area. Four components are surveyed: total riparian vegetation cover, cover structure, cover quality, and channel alterations. Differences in the river geomorphology are also considered. Table 1 shows the QBR scoring system which varies from 0 to 100. The higher the score the better the riparian quality.

Table 1. Scoring system for the IBMWP and QBR indexes in the Ebro river basin[a]

			IBMWP			
Status	**Description**	**QBR**	**Ecotype 1**	**Ecotypes 2,3,5**	**Ecotype 4**	**Ecotype 6**
High	Pristine condition	≥ 95	≥ 100	≥ 65	≥ 90	≥ 110
Good	Slight disturbance	75 - 90	81 - 100	56 - 65	71 - 90	86 - 110
Moderate	Important modification	55 - 70	61 - 80	41 - 55	55 - 70	66 - 85
Poor	Strong alteration	30 - 50	31 - 60	20 - 40	25 - 54	35 - 65
Bad	Extreme degradation	≤ 25	≤ 30	≤ 20	≤ 25	≤ 35

[a](CHE, 2004).

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2.1.3. IBMWP index

The Iberian Biomonitoring Working Party (IBMWP) index (Alba-Tercedor et al., 2002) is the Spanish adaptation of the original British BMWP protocol (Hawkes, 1998). The BMWP is a widely accepted biotic index to monitor water pollution. The IBMWP index surveys river water quality as a function of the abundance and diversity of aquatic invertebrates, since they are a key component of the food chain (Metcalfe, 1989; Swaminathan, 2003).

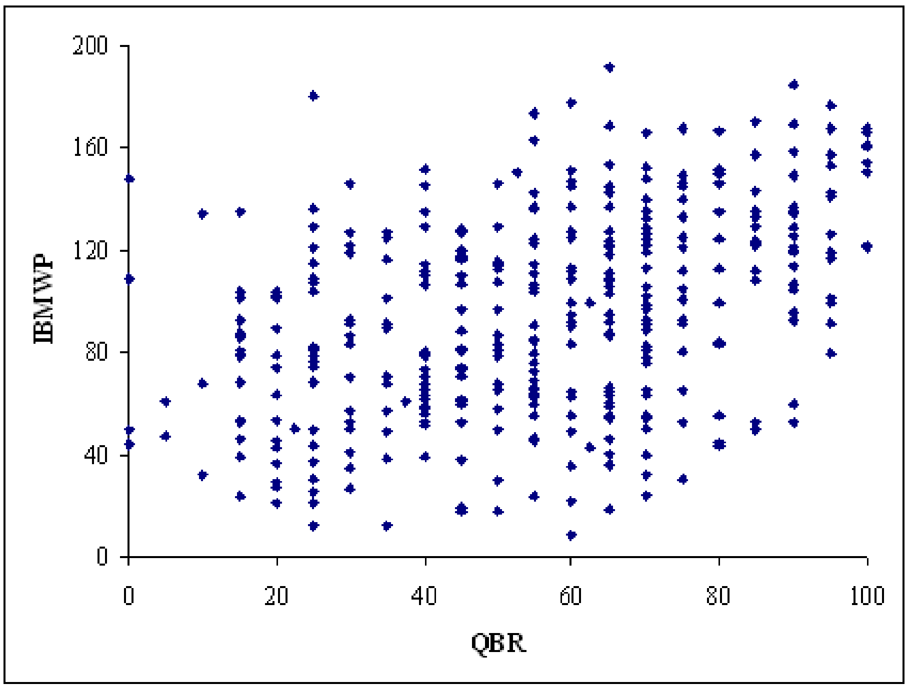

Fig. 2. QBR and IBMWP values in the studied area.

The IBMWP index is based on two hypotheses. First, changes in abundance and biodiversity of macro-invertebrates community are caused by reduction in dissolved oxygen level that could be due to pollution. Second, some invertebrates are more sensitive to pollution than others. Based on this, the presence of highly sensitive species gives higher scores than highly tolerant species. The IBMWP index is obtained by adding the scores for all species found in a determined site. The higher the IBMWP the better the biological quality. As the IBMWP strongly depends on the ecotype, since there are regions where it is easier to find more abundance of invertebrates, the

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boundary values to classify the status are set as in Table 1. For instance, in high mountain ecotype the minimum IBMWP for high status is 110, while the same status is attained with an IBMWP of 65 in great rivers ecotype. In Fig. 2, it can be observed the high spectrum of QBR and IBMWP values in the studied area, which is appropriate for the training steps of the neural-fuzzy models.

2.1.4. FWQ index

In spite of the maturity of physicochemical monitoring in rivers, current water quality indexes lack consistent ways to deal with uncertainty and subjectivity (McKone and Deshpande, 2005). In this study, a methodology based on fuzzy logic is used to integrate the most relevant (and available) physicochemical parameters in a unified score, known as the Fuzzy Water Quality (FWQ) index. A similar procedure to that reported by Ocampo-Duque et al. (2006) has been used. The FWQ index is obtained by applying a Fuzzy Inference System (FIS) to water quality variables. A typical FIS mainly consists of membership functions and fuzzy rules within an inference engine.

Five variables were used: conductivity (0.25), dissolved oxygen (0.33), ammonia (0.14), nitrates (0.14), and phosphates (0.14). In parentheses are given the weights according to the importance of the parameters. Weights were adapted from those used by other water quality indexes (Ocampo-Duque et al., 2006). A FIS composed by 20 inference rules, with trapezoidal membership functions (MF) has been created. MF are represented as:

$$\mu(x;a,b,c,d) = \max\left(\min\left(\frac{x-a}{b-a},1,\frac{d-x}{d-c}\right),0\right) \qquad (1)$$

where *a*, *b*, *c*, and *d* are the MF parameters reported in Table 2. For dissolved oxygen (DO) rules were: if DO is “very high” then FWQ is “high”, if DO is “high” then FWQ is “good”, if DO is “medium” then FWQ is “moderate”, if DO is “low” then FWQ is “poor”. For the other variables rules were: if variable is “low” then FWQ is “high”, if variable is “medium” then FWQ is “good”, if variable is “high” then FWQ is “moderate”, if variable is “very high” then FWQ is “poor”. Ranges for classes are also reported in Table 2. Finally, defuzzification is produced with the bisector method. FWQ scores vary from 0 to 100. The higher the score the better the physicochemical quality. More details about FWQ and FIS can be consulted in Ocampo-Duque et al. (2006).

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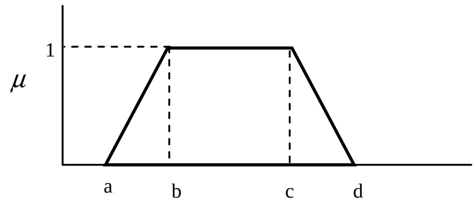
Table 2. Parameters of trapezoidal membership functions for the FWQ index



		Low			**Medium**				**High**				**Very high**		
Indicator	**Units**	***a=b***	***c***	***d***	***a***	***b***	***c***	***d***	***a***	***b***	***c***	***d***	***a***	***b***	***c=d***
Conductivity	μS/cm	0	800	1000	800	1000	1200	1400	1200	1400	1600	1800	1600	1800	2500
Oxygen	% O_2	0	20	30	20	30	45	55	45	55	70	80	70	80	100
Ammonia	mg/L NH_4	0	0.2	0.4	0.2	0.4	1.2	1.4	1.2	1.4	2.2	2.4	2.2	2.4	4
Nitrates	mg/L NO_3	0	8	12	8	12	22	26	22	26	36	40	36	40	50
Phosphates	mg/L PO_4	0	0.12	0.18	0.12	0.18	0.26	0.32	0.26	0.32	0.46	0.52	0.46	0.52	0.80
		Poor			Moderate				Good				High		
FWQ index	-	0	40	50	40	50	60	70	60	70	80	90	80	90	100

μ is the membership value, *a, b, c,* and *d,* are the parameters for the membership functions (equation 1).

2.2. Adaptive Neural Fuzzy Inference Systems (ANFIS)

FIS models focus on the use of heuristics in the system description. They can be seen as logical models that use "if–then" rules to establish qualitative and quantitative relationships among variables. Their rule-based nature allows the use of information expressed in the form of natural language statements, making the model transparent for interpretation (Vernieuwe et al., 2005). However, this approach is weak when there is a need of adjusting the linguistic knowledge of the expert with available data.

FIS models as the described above consider membership functions that are fitted at judgment of the decision-maker. Moreover, the inference engine structure must be predetermined with settings from expert knowledge about the modeled system. In the problem described here regarding ecological classification, it is proposed to discern, directly from data, the shape of the membership functions and the structure of the inference engine. Thus, rather than arbitrarily choosing the MF parameters, and the FIS structure, these have been tailored to the input/output data, in order to account for uncertainties and variability in data, with an optimization technique called ANFIS.

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Since its introduction (Jang, 1993), ANFIS benefits have successfully been proved in many engineering applications. However, its use in environmental issues is currently increasing. Recently, ANFIS was used to construct water level forecasting systems in reservoir management (Chang and Chang, 2006; Chau et al., 2005). ANFIS for prediction of pesticide occurrence in rural domestic wells with limited information has been explored (Sahoo et al., 2005). Recently, an ANFIS model was presented to predict groundwater electrical conductivity based on the concentration of positively charged ions (Tutmez et al., 2006). ANFIS has also been used to model nutrient loads in watersheds (Marce et al., 2004).

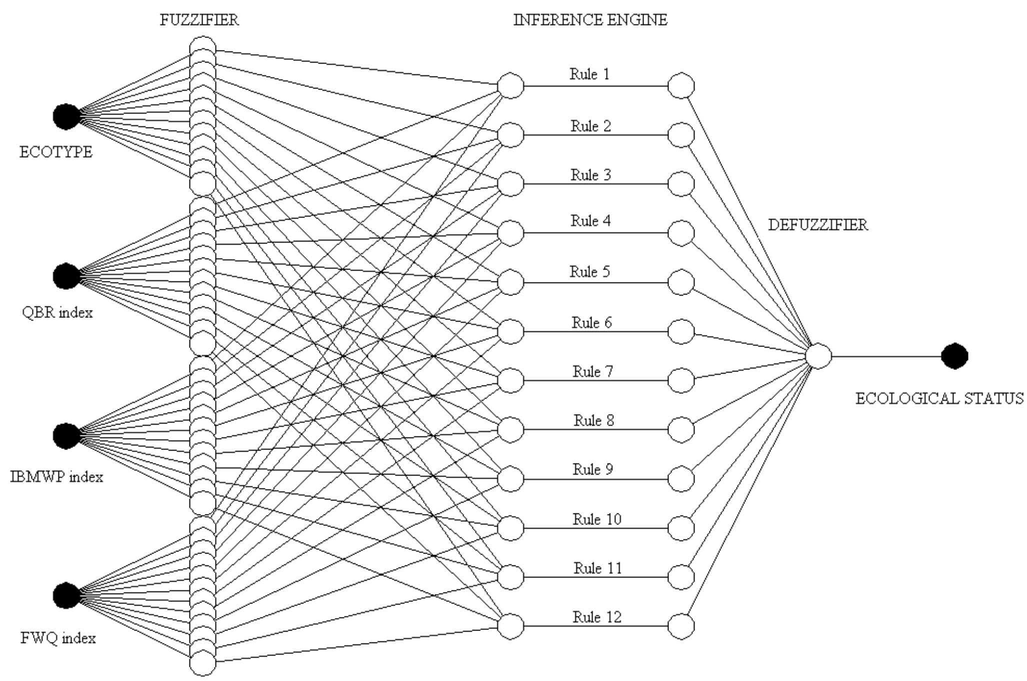

Fig. 3. Fuzzy inference system for ecological classification in the studied area.

First, ANFIS generates an initial structure with a subtractive clustering algorithm. After, MF parameters are optimized with a hybrid algorithm which uses the steepest descent method (back-propagation) for input MF parameters, and the least squares estimation for output MF parameters. Finally, a methodology is applied to control over-fitting enhancing the generalization capability.

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Fig. 3 shows the FIS model built for the ecological status classification problem. Ecotype, QBR, IBMWP, and FWQ indexes are integrated with FIS to represent the ecological status. Model parameters and structure have been optimized with the ANFIS algorithm.

To compare the performance of the FIS against other classification tools, we selected two methods: the classification and regression tree (CART), and the Probabilistic Neural Network (PNN).

2.3. Classification and regression trees (CART)

CART is a method based on a binary recursive partitioning technique to identify important cause–effect relationships within variables (Razi and Athappilly, 2005). CART is an alternative technique to using multiple regression that automatically sifts large, complex databases, searching for and isolating significant patterns and relationships. This discovered knowledge is then used to generate reliable, easy-to-grasp predictive models (Breiman et al., 1993). It is non-parametric, and does not require any assumptions about data distributions. Recently, CART was found to be competitive to multiple regression and to artificial neural networks (Bennett et al., 2006; Garzon et al., 2006). To our knowledge, comparative studies between ANFIS and CART are not available yet.

2.4. Probabilistic Neural Networks (PNN)

PNN is a class of neural network suitable for classification problems (Beltran et al., 2006; Xue et al., 2005). A PNN is a three layer network. The pattern layer represents an implementation of the Bayes classifier, where the class dependent probability density functions are approximated using a Parzen estimator. This approach provides an optimum pattern classifier in terms of minimizing the expected risk of wrongly classifying an object. The pattern layer operates competitively, where only the highest match to an input vector wins and generates an output. Thus, only one classification category is generated for any given input vector (Niwa, 2004).

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3. Results

Optimum initial FIS structure, determined with subtractive clustering algorithm, has resulted in 12 rules and 12 MF for each input. For each rule, an output MF was obtained. It has the form:

$$\mu_{O,j} = k_{1,j} * \text{ecotype} + k_{2,j} * \text{FWQ} + k_{3,j} * \text{QBR} + k_{4,j} * \text{IBMWP} + k_{5,j} \quad (2)$$

where $\mu_{O,j}$ is the output MF of the rule j, $k_{i,j}$ are the linear parameters for the rule j.

The ecological status (ES) is obtained as:

$$ES = \frac{\sum_{j=1}^{R} w_j * \mu_{O,j}}{w_j} \quad (3)$$

where w_j, is the firing strength for the rule j, and R is the number of rules. The firing strength is calculated as:

$$w_j = \mu_{1,j}(\text{ecotype}) * \mu_{2,j}(\text{QBR}) * \mu_{3,j}(\text{IBMWP}) * \mu_{4,j}(\text{FWQ}) \quad (4)$$

with $\mu_{k,j}$ being the MF of the input k in the rule j (k = 1 for ecotype, k = 2 for QBR, k = 3 for IBMWP, and k = 4 for FWQ).

Table 3. Performance of the neural-fuzzy models

Model	Membership Function	Parameters: Linear	Parameters: Nonlinear	RMSE	Well classified points	DEV-1	DEV+1
1	Gaussian	60	96	0.2747	350	12	16
2	Trapezoidal	60	120	0.2973	337	17	24
3	Generalized Bell	60	144	0.1898	369	5	4
4	Composite Gaussian	60	192	0.3284	329	19	30
5	Sigmoidal	60	99	0.2566	356	11	11
6	Asymmetric Sigmoidal	60	190	0.2623	259	93	17

RMSE: Root Mean Square Error.
DEV-1: Predicted ecological status has resulted one grade lesser than real
DEV+1: Predicted ecological status has resulted one grade higher than real
Total points: 378

Different MF types including Gaussians, trapezoidals, bells, and sigmoidals were tested. The number of linear and non-linear parameters to be optimized is displayed in Table 3. During optimization, 10% of the data, randomly chosen, were

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used for model checking in order to control the over-fitting. Optimum parameters were found once checking data error reached the minimum.

The Root Mean Square Error (RMSE) and the number of correctly classified points have served to check the performance of the models. It is shown in Table 3. In turn, Table 4 shows the comparative performance of ANFIS versus other classification techniques. RMSE and percentage of correctly predicted points with ANFIS models were in the ranges 0.1898–0.3284, and 68.5–97.6%, respectively. The best fitting was obtained with the FIS composed by generalized bell MF. These functions are expressed as:

$$\mu_{k,j}(x; a_{k,j}, b_{k,j}, c_{k,j}) = \frac{1}{1 + \left| \frac{x - c_{k,j}}{a_{k,j}} \right|^{2b_{k,j}}} \tag{5}$$

where $a_{k,j}$, $b_{k,j}$, and $c_{k,j}$ are non-linear MF parameters, for the input k and the rule j. Both, linear and non-linear parameters in Eqs. (2) and (5), have been optimized with the hybrid algorithm described in Section 2.3. A response surface, calculated with the Generalized bell ANFIS model for ecological classification, considering two independent variables, is depicted in Fig. 4. Finally, the twelve rules within the inference engine had the following structure:

“If ecotype is $\mu_{1,j}$ and QBR is $\mu_{2,j}$ and IBMWP is $\mu_{3,j}$ and FWQ is $\mu_{4,j}$, then ECOLOGICAL STATUS is $\mu_{O,j}$”.

Table 4. Comparative performance of classification models

Model	**Well classified**	**DEV-1**	**DEV+1**
Generalized Bell ANFIS	369	5	4
Sigmoidal ANFIS	356	11	11
Classification and Regression Tree (CART)	343	12	23
Probabilistic Neural Network (PNN)	367	4	7

DEV-1: Predicted ecological status has resulted one grade lesser than real
DEV+1: Predicted ecological status has resulted one grade higher than real
Total points: 378

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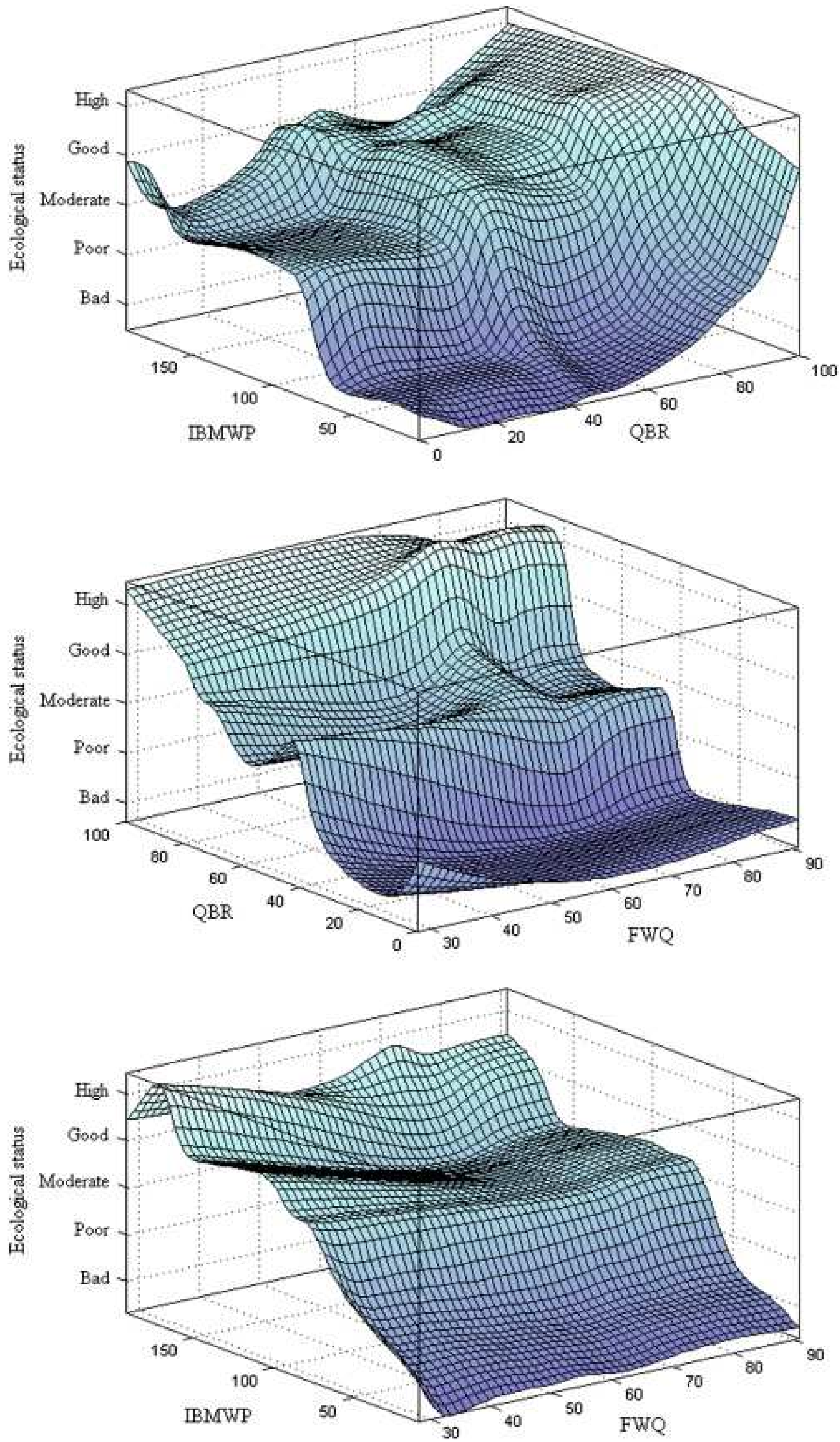

Fig. 4. Response diagrams with the generalized bell ANFIS model.

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A CART for the input–output data set has been developed. It is depicted in Fig. 5. Ten percent of data has been used for testing. The best tree size was obtained with a re-substitution and cross-validation procedure. About 90.74% of total points have been well classified with CART. As shown in Table 4, the performance of the ANFIS models is competitive with the CART method. In fact, bell and sigmoidal FIS models resulted to be superior to the classification tree. However, the simplicity of CART over ANFIS must be remarked.

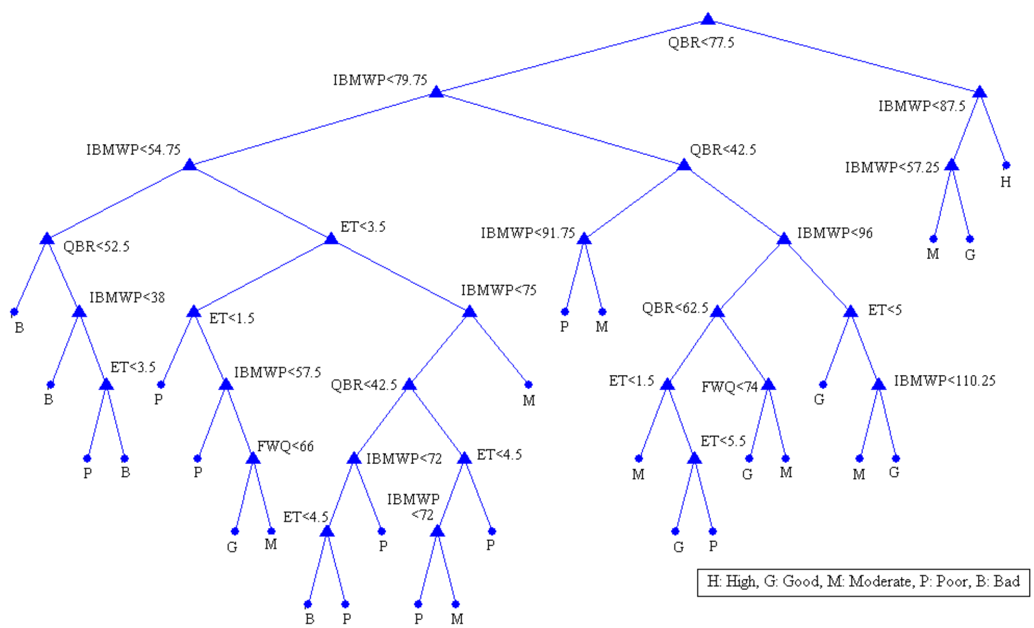

Fig. 5. Classification tree for ecological status in the studied area.
ET: ecotype, QBR: riparian quality index, IBMWP: biological index, FWQ: physicochemical fuzzy index.

A PNN has also been developed with the same input/output data set. As shown in Table 4, high predictive capacities produced the PNN. However, the weak point of this approach occurred during the validation stage. When PNN was asked for predicting the ecological status for a validation data set composed by 38 sites, only 71.05% were correctly classified. In turn, CART and generalized bell ANFIS correctly classified the 78.95% and 92.11% of validation points, respectively. It demonstrates the higher generalization skills of the neural-fuzzy models.

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4. Discussion

In general, high predictive capacities have been found with ANFIS as classifier for ecological status in surface waters. A clear influence of the shape of the MF is observed in Table 3. The best results were obtained with generalized bell MF. As shown in Table 3, in most sites FIS outputs agree with real values. Points in the DEV − 1 column are those whose predicted ecological status has been ranked one grade lesser than real ones. In contrast, points in the DEV + 1 column received one grade higher than real ones.

Misclassified points could be attributable to noise within variables. However, some patterns help explain misclassifications. In most of such situations the scores fell close to class boundaries among moderate, poor, and/or bad status. Also, there were cases where one indicator has given a classification quite different to the others. These patterns have resulted imprecise to the inference engine, and therefore difficult to predict.

The subtractive clustering algorithm has allowed the use of few inference rules to get high predictive power. However, to maintain the model accuracy, a considerable number of MF, and non-linear parameters, were necessary. This high non-linearity comes from the very diverse nature of variables, representing states and impacts within the ecosystems. Fig. 4 depicts the non-linear structure of the modeled classification system. From a view over this Figure, it can be noticed that the IBMWP is the main indicator to decide the final ecological class. IBMWP defines the curvature over the other indicators. Likewise, QBR handles over FWQ.

Looking into the produced inference engine, the capacity of the fuzzy model to extract knowledge from data with interpretability and transparency can be demonstrated. Thus, some automatic rules extracted from the optimized FIS could be put in verbal form as:

1. If physicochemical quality is medium and riparian quality is low and biological quality is low then ecological status is bad.
2. If riparian quality is high and biological quality is medium then ecological status is moderate.

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The CART (Fig. 5) partitions the learning dataset in nodes (triangles) formed automatically. By continuously posing and answering binary yes/no questions, every data point flows down to next level of nodes. Left branches are for negative answers. Finally, each data point attaches to a terminal node that classifies the ecological status. IBMWP is the governing indicator for the ecological classification since it appears in more nodes. The QBR is the second discriminatory criterion being present in the upper nodes of the tree. The ecotype (ET) is also important to give the final class, but it is in the lower nodes. The FWQ is the least determinant indicator, since it only appears in two nodes. CART results agree with those from ANFIS, regarding the importance of the biological element over the others in the assessment of the ecological condition.

In general, the high influence of the IBMWP over the final classification can be well predicted with ANFIS, and CART. It agrees with the ECOSTRIMED protocol, where it is enunciated that the biological element must receive more weight over other elements (CHE, 2004). Perhaps, the same conclusion could be got from PNN, given its demonstrated accuracy. But, its black-box structure hinders to draw a conclusion.

With the FIS model, we have found that 54.76% of the sites within the Ebro river basin were below good ecological status for the assessed period. The main factor to get such results has been the low QBR score. A 76.72% of QBR data presented moderate, poor, or bad status. In turn, 35.19% of FWQ data, and 27.78% of IBMWP data were below expected scores.

Therefore, important efforts should be carried out by citizens, stakeholders, and river protection agencies to improve the overall quality of waters. In that direction, we strongly suggest the use of the FIS classifiers to support decision-makers in evaluation and classification of ecological status, as required by the WFD. Moreover, for a better assessment, the use of more biotic, morphological, and chemical inputs is highly recommended. These could easily be inserted in a FIS model. Finally, the ability to classify ecological status by means of fuzzy boundaries is a valid advantage to deal with subjectivity and uncertainty. Therefore, it would be possible to classify a site as partially good, or partially moderate, which is more adjusted to the reality, taking into account that boundaries are usually hard to fit.

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5. Conclusion

A decision-making tool for water management in the form of an ecological status classification system based on morphological, biological, and physicochemical inputs is presented. A suitable environmental application of fuzzy logic to integrate water quality indicators is shown. The FIS classifier developed here has been competitive when compared with other statistical methods. The flexibility of fuzzy logic to develop classification models with a simple framework, built with natural language, is recommended in the development of similar environmental indexes, where highly subjective information must be correlated. The FIS classifiers allowed dealing efficiently with uncertainty and non-linearity, being appropriate for integration of qualitative and quantitative data. The main advantage of the FIS approach has been that correlations among variables were causally determined. The FIS models learned from data, and interpretable inference rules were automatically created. Although the FIS classification system has been optimized with information from a particular river basin, the methodology could be adapted to other studies regarding the WFD.

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Chapter 3

A concurrent neuro-fuzzy inference system for screening ecological risk assessment in rivers[3]

Abstract

Because of the presence of hazardous substances in river basins, in this study a conceptual model to assess water quality has been developed. The model incorporates a novel ranking and scoring system, based on a special kind of artificial neural network called self-organizing map, to account for the likely ecological hazards posed by the presence of chemical substances in freshwater. Hazard factors for chemical substances have been calculated by pattern recognition of persistence, bioaccumulation, and toxicity properties. Due to the high imprecision and uncertainty in screening ecological risk assessment, a fuzzy inference system has been proposed to compute ecological risk potentials (*ERP*), which are a combination of the hazard to aquatic sensitive organisms, and normalized environmental concentrations. By aggregating the *ERP*, changes in water quality over time can be estimated. The proposed concurrent neuro-fuzzy model has been applied to a comprehensive dataset of the dangerous substances control network in the Ebro river basin (Spain). The *ERP* approach has been validated by comparison with biological monitoring. Diatom based water quality has decreased in four years, at least in 38% of studied sites, probably as consequence of higher presence of chemicals at levels of concern. The proposed approach can support decision-makers in the evaluation of the long-term performance of pollution prevention and control strategies in river basins set out by environmental protection agencies.

Keywords: Fuzzy inference systems; Self organizing maps; Screening ecological risk assessment; Water quality; Ebro River

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1. Introduction

Chemical pollution in rivers can alter aquatic ecosystems, causing loss of habitats and biodiversity (Lyons, 2006). Some pollutants may remain in the environment for a long time. They may bio-accumulate through the food chain and be dangerous to aquatic organisms. Developing reliable methods for estimating the risks due to these substances in aquatic environments has therefore become a priority (Camusso et al., 2002). Because of the growing number of potentially hazardous chemicals identified in water and other river compartments, there is a recognized need to create integrated risk-based systems to facilitate decision-making processes. Such systems must consider the concentration of most chemicals in field, and also their likely hazard to aquatic ecosystems. By extracting information from properties of toxicity, fate and transport, persistence, and potential for bioaccumulation, the hazard of a chemical substance can be quantified (Juraske et al., 2007).

A number of difficulties have to be faced to design multi-substances risk-based systems for ecological protection. Firstly, owing to the need to integrate dissimilar criteria, and to manage large and diverse datasets, ranking and scoring methodologies require consistent ways to deal with subjectivity. Secondly, to estimate potential risks usually involves high methodological and inherent uncertainties. Fortunately, a step forward has been given by the progress in Artificial Intelligence (AI) to deal with such challenges. Skills to recognize non-linear patterns by means of self-learning and the easiness to deal with subjectivity, uncertainty, and imprecision, have considered AI tools to be appropriate to support water quality management (Chau, 2006).

In particular, artificial neural networks (ANN) and fuzzy inference systems (FIS) have been consistently introduced into environmental modelling and data analysis. Self-Organizing-Maps (SOM) have been pointed out as a suitable methodology to cluster heterogeneous data (Ferré-Huguet et al., 2006; Nadal et al., 2006; Stanimirova et al., 2005). In turn, the use of fuzzy systems has recently been extended to assess water quality (Chang et al., 2001; Giusti and Marsili-Libelli, 2006; Karmakar and Mujumdar, 2006; Ocampo-Duque et al., 2006, 2007; Sadiq and Rodriguez, 2004). One of the main advantages of fuzzy logic is the ability to model expert human knowledge, a necessary feature to be considered in the complex process of environmental management.

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Because of the presence of hazardous substances in river basins, the purpose of the present study was to design a system to assess the potential screening risks. A concurrent neuro-fuzzy model, which integrates SOM and FIS, has been used to create the system which is intended to aquatic ecosystem protection, as requested by the European Water Framework Directive (WFD). The model has resulted useful to manage both uncertainty and subjectivity in risk estimation.

2. Methods

In ecological risk assessment, the risk is usually a function of damage and dose. Ideally, the damage would be an integrated measure of all adverse ecological health effects associated with acute and chronic exposures to a chemical. However, to provide useful information, the assessment needs to be forced to rely on available and reliable data. It must be noted that the number of chemicals in the environment is huge, and the efforts required for complete risk assessment are prohibitive. This has motivated to the development of multiple ranking and scoring methods in order to simplify and provide screening hazard values (Swanson and Socha, 1997). From scores produced by these methodologies, it would be suitable to design generalized risk indexing systems. Often, ranking systems have been based on three characteristics to quantitatively assign a score to each chemical substance: persistence, bioaccumulation and toxicity, commonly known as PBT properties (Knekta et al., 2004). The management of the subjectivity in those ranking methodologies is still a pending task. To overcome that, in this study a pattern recognition algorithm, the SOM, has been applied to PBT properties.

Given the complexity in aquatic ecosystems for screening and indexing purposes, the dose can conveniently be replaced by environmental concentrations. Moreover, the variability in orders of magnitude of concentrations requires a consistent normalization procedure. The use of the Environmental Quality Standards (*EQS*) seems to be appropriate. However for real situations, a boundary standard below which the presence of a hazardous substance in the environment can be considered safe for ecosystems is uncertain, since *EQS* are fitted after extended analyses of eco-toxicity databases and experts' opinion. In the present study, ecological risk potentials (*ERP*) are defined as alternative approaches to common risk assessment methodologies. *ERP*

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combine the hazard to aquatic organisms, posed by the presence of toxic substances, and the concentration of the chemicals measured in field, within a FIS. The hypothesis has been that fuzzy arithmetic helps to manage uncertainty and subjectivity.

2.1. Case study

The Ebro river basin is located at the NE of Spain, covering an area of 85 362 km^2. It is formed by a river network of approximately 12000 km, and is drained toward the Mediterranean Sea. Population density in the basin is 33 inhabitants/km^2. 7370 Hm^3 of water are annually used: 86% for agriculture, 7% in urban supplies, 6% for industrial activities, and 1% in cattle raising. Due to the large quantity of agricultural activities carried out in the basin, the considerable domestic uses, and the presence of important industrial processes in riparian zones, a comprehensive set of diverse pollutants is released to the river.

Pollution control in the Ebro river basin is managed by the Confederación Hidrográfica del Ebro (CHE). The CHE has established a network, called red de control de sustancias peligrosas (RCSP), to control hazardous substances. Since there is clear evidence that most of these sites are heavily impacted by considerable releases of a number of toxic compounds, RCSP has been selected as case study. A map locating the network sites is depicted in Fig. 1. Data corresponding to the period 2002-2006 have been used to test the *ERP* approach. Moreover, a geographic information system (GIS) has allowed to analyze spatial variability. Mean annual concentrations in water for heavy metals, pesticides, and other hazardous substances (Table 1) were extracted from the RCSP database, and normalized according to:

$$NoC = \frac{C_w}{EQS} \tag{1}$$

where *NoC*, and C_w, are normalized concentration, and concentration of the chemical in water, respectively. The *EQS* here used are those recently defined by the WFD (EC, 2006). Unfortunately, the WFD list lacks of *EQS* for many hazardous substances of concern in regional environments. Consequently, when these were unavailable, the median value of a comprehensive survey of freshwater benchmarks to protect aquatic organisms, currently applied by diverse environmental protection agencies (MMA,

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2000; RAIS, 2007; SEPA, 2004; USDOE, 1999; USEPA, 2007a; USGS, 2004), was used as normalizing criterion. The list of *EQS* for equation 1 is given in Table 1.

Table 1. Selected environmental quality standards (*EQS*)

Substance	CAS #	*EQS* (µg/l)	Substance	CAS #	*EQS* (µg/l)
1.1.1-Trichloroethane	71-55-6	1.50E+02	d-HCH	319868	1.90E+03
1.2-Dichloroethane*	107-06-2	1.00E+01	Heptachlor	76-44-8	6.90E-03
3.4-Dichloraniline	95-76-1	3.00E-01	Heptachlor epoxide	1024-57-3	3.80E-03
Alachlor*	15972-60-8	3.00E-01	Hexachlorobenzene*	118-74-1	1.00E-02
Aldrin*	309-00-2	1.00E-02	Hexachlorobutadiene*	87-68-3	1.00E-01
Ametryn	834-12-8	3.00E-01	Indeno[1,2,3-cd]pyrene*	193-39-5	2.00E-03
Anthracene*	120-12-7	1.00E-01	Isodrin*	465-73-6	1.00E-02
Arsenic	7440-38-2	1.90E+02	Isoproturon*	34123-59-6	3.00E-01
Atrazine*	1912-24-9	6.00E-01	Lead*	7439-92-1	7.20E+00
Benzene*	71-43-2	1.00E+01	Mercury*	7439-97-6	5.00E-02
Benzo(a)pyrene*	50-32-8	5.00E-02	Metolachlor	51218-45-2	4.40E+00
Benzo[g,h,i]perylene*	191-24-2	2.00E-03	Methoxychlor	72-43-5	2.45E-02
Benzo[k]fluoranthene*	207-08-9	3.00E-03	Molinate	2212-67-1	3.00E-01
Cadmium*	7440-43-9	2.50E-01	Naphthalene*	91-20-3	2.40E+00
Chlorfenvinphos*	470-90-6	1.00E-01	Nickel*	7440-02-0	9.35E+01
Chlorobenzene	108-90-7	1.07E+01	Parathion-ethyl	56-38-2	1.30E-02
Chloroform*	67-66-3	2.50E+00	Parathion-methyl	298-00-0	8.00E-03
Chlorpyriphos*	2921-88-2	3.00E-02	Pentachlorobenzene*	608-93-5	7.00E-03
Copper	7440-50-8	1.62E+01	Pentachlorophenol*	87-86-5	4.00E-01
Chromium	7440-47-3	1.30E+02	Prometon	1610-18-0	3.00E-01
DDT*	50-29-3	2.50E-02	Prometryn	7287-19-6	3.00E-01
opDDT	789-02-6	1.00E-03	Propazine	139-40-2	3.00E-01
ppDDD	72548	1.10E-02	Selenium	7782-49-2	5.00E+00
ppDDE	72559	1.05E+01	Simazine*	122-34-9	1.00E+00
ppDDT*	50293	1.00E-02	Terbutryn	886-50-0	1.00E+00
Dichlorobenzene	95-50-1	1.70E+01	Tetrachloroethylene*	127-18-4	1.00E+01
Dichloromethane*	75-09-2	2.00E+01	Tetrachloromethane*	56-23-5	1.20E+01
Dicofol	115-32-2	1.98E+01	Tetradifon	116-29-0	3.00E-01
Dieldrin*	60-57-1	1.00E-02	Toluene	108-88-3	1.20E+02
Dimethoate	60-51-5	6.20E+00	Trichlorobenzene*	87-61-6	4.00E-01
Diuron*	330-54-1	2.00E-01	Trichloroethylene*	79-01-6	1.00E+01
Endosulfan*	115-29-7	5.00E-03	Trifluralin	1582-09-8	3.00E-02
Endosulfan-sulfate	1031-07-8	1.14E+00	Xylenes	1330-20-7	3.00E+01
Endrin*	72-20-8	1.00E-02	o-xylene	95-47-6	1.00E+01
Ethylbenzene	100-41-4	1.10E+02	m+p-xylenes	108-38-3	2.00E+01
Fluoranthene*	206-44-0	1.00E-01	Zinc	7440-66-6	2.13E+02
Hexachlorocyclohexane*	608-73-1	2.00E-02	4-nonylphenol	104-40-5	3.00E-01
a-HCH	319846	1.92E+01	4-(tert-octyl)phenol	140-66-9	1.00E-01
b-HCH	319857	2.34E+05			

* Values from the Water Framework Directive (EC, 2006).

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Fig. 1. Map of the network of selected sites to monitor hazardous substances in the Ebro river basin (Spain).

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2.2. Self organizing maps and the ecological hazard index

SOM are unsupervised neural networks inspired in the self-organizing capacity of the human brain. They are appropriate to cluster high-dimensional data (Vesanto and Alhoniemi, 2000). The method utilizes non-linear mapping of inputs onto a honeycomb map that preserves the most important topological relationships between the variables. The output map is an array of nodes. Each node contains a characteristic weight, which can appropriately be used in normalization tasks. More details of the algorithm are available from Vesanto et al. (2000). SOM has been recently applied as convenient tool for clustering of environmental data (Ferré-Huguet et al., 2006; Nadal et al., 2006; Stanimirova et al., 2005).

In the present study, the SOM algorithm has been used to calculate the Ecological Hazard Index (*EHI*), a screening number to account for potential hazards posed by the presence of toxic substances to living aquatic organisms. The *EHI* is a slight modification of the Waste Minimization Prioritization Tool developed by the USEPA (2000). The methodology follows that recently proposed by Nadal et al. (2006). SOM outputs, called component planes are depicted in Fig. 2a. Each node of the map represents a normalized PBT value. This value, ranging between 0 and 1, has been found useful for scoring purposes. Fig. 2b shows the integrated SOM. Thus, the *EHI* is calculated as:

$$EHI = 3 * S_{Pov} + 3 * S_{BCF} + 2 * S_{tox-fish} + 2 * S_{tox-daphnia} \tag{2}$$

where S_{Pov}, S_{BCF}, $S_{tox\text{-}fish}$, and $S_{tox\text{-}daphnia}$ are the individual node scores after SOM application to overall persistence (P_{ov}), calculated from half-lives of the chemicals in air, water and sediments, bio-concentration factor (BCF), LC50 to sensitive fish (*tox-fish*), and LC50 to *Daphnia magna* (*tox-daphnia*).

Physical-chemical properties for the calculation of the overall persistence were obtained from the USES-LCA 2.0 database (Huijbregts et al., 2005). Sources for experimental data used in this database were obtained from Howard et al. (1991), Linders et al. (1994), Mackay et al. (2000), and Tomlin (2002). If no experimental data were found, the estimation method for biodegradation half-lives described by Aronson

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et al. (2006), and the physical/chemical property and environmental fate estimation model EPI Suite™ (USEPA, 2007b), were used. Data on the bio-concentration factor in fish were taken from the USES-LCA 1.0 database (Huijbregts et al., 2000) and from Linders et al. (1994) and Meylan et al. (1999). In turn, ecotoxicological parameters regarding to LC50 to *Daphnia magna* and fish were taken from DEPA (2004), Linders et al. (1994), and Payet (2004). PBT data are summarized in Table 2. The scores and the *EHI* are shown in Table 3.

Table 2. Persistence, bioaccumulation, and toxicity (PBT) properties used as inputs to the SOM*

Substance	**SOM code**	**Pov (days)**	**BCF fish (-)**	**LC50 fish (mg/l)**	**LC50 daphnia (mg/l)**
1,1,1-Trichloroethane	TCE	1.00E+03	1.50E+01	2.27E+01	2.55E+01
1,2-Dichloroethane	DCE	1.01E+03	2.00E+00	1.06E+02	1.12E+02
3,4-Dichloraniline	DCA	1.72E+03	3.00E+01	2.60E+01	8.80E-01
Alachlor	ALA	1.10E+01	3.90E+01	5.20E-01	2.30E-01
Aldrin	ALD	2.25E+02	3.72E+03	6.00E-02	3.00E-02
Ametryn	AME	1.05E+02	4.60E+01	9.00E+00	1.10E+01
Anthracene	ANT	3.06E+02	9.12E+02	1.19E-02	2.00E-02
Arsenic	As	1.00E+05	1.50E+02	5.60E-01	4.80E-01
Atrazine	ATR	1.99E+02	8.20E+00	1.17E+01	3.60E+00
Benzene	BEN	1.36E+02	6.00E+00	5.90E+01	6.30E+01
Benzo(a)pyrene	BPY	7.83E+02	5.69E+03	2.50E-02	5.00E-03
Benzo[g,h,i]perylene	BPE	2.17E+03	2.54E+04	8.00E-03	1.20E-02
Benzo[k]fluoranthene	BFL	4.81E+03	1.01E+04	2.60E-02	3.60E-02
Cadmium	Cd	1.00E+05	2.02E+02	1.10E-01	1.30E-01
Chlorfenvinphos	CFV	1.28E+02	3.17E+02	4.00E-02	2.50E-04
Chlorobenzene	CBZ	2.08E+02	2.70E+01	2.09E+01	2.34E+01
Chloroform	CFM	4.82E+02	4.00E+00	4.38E+01	2.89E+01
Chlorpyriphos	CPF	5.40E+01	1.70E+03	3.00E-03	1.70E-03
Copper	Cu	1.00E+05	1.20E+02	2.20E-02	5.00E-03
Chromium	Cr	1.00E+05	4.00E+01	1.60E+00	2.00E+00
DDT	DDT	6.54E+03	7.43E+04	9.00E-03	1.00E-03
opDDT	opDDT	6.54E+03	3.72E+04	9.00E-03	2.00E-03
ppDDD	ppDDD	5.60E+03	2.95E+04	4.50E-03	2.00E-04
ppDDE	ppDDE	6.39E+03	5.13E+04	1.60E-02	8.00E-03
ppDDT	ppDDT	6.54E+03	7.43E+04	9.00E-03	1.00E-03
Dichlorobenzene	DCB	8.98E+02	1.32E+02	6.82E+00	7.99E+00
Dichloromethane	DCM	1.61E+02	1.00E+00	2.62E+02	2.68E+02
Dicofol	DIC	2.16E+02	5.03E+03	1.83E-01	1.40E-01
Dieldrin	DIE	1.29E+03	7.61E+03	3.00E-02	6.00E-03
Dimethoate	DIM	6.80E+01	3.00E-01	6.20E+00	4.60E-01
Diuron	DIU	2.41E+02	6.00E+01	5.90E+00	1.40E+00

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Endosulfan	EDS	1.10E+01	6.01E+02	8.77E-01	4.73E+00
Endosulfan-sulfate	ENS	4.02E+02	2.19E+02	7.40E-01	3.32E+00
Endrin	END	9.12E+03	1.87E+03	1.00E-02	1.00E-03
Ethylbenzene	ETB	1.20E+01	5.30E+01	8.46E+00	9.74E+00
Fluoranthene	FLU	7.43E+02	4.92E+03	2.64E-01	3.46E-01
Hexachlorocyclohexane	HCH	1.07E+02	6.63E+02	1.62E+00	2.03E+00
a-HCH	aHCH	2.50E+02	3.03E+02	1.40E+00	8.00E-02
b-HCH	bHCH	2.15E+02	3.32E+02	1.00E+00	6.00E-02
d-HCH	dHCH	1.07E+02	6.63E+02	1.00E+00	5.00E-02
Heptachlor	HEP	1.00E+00	7.43E+03	2.30E-02	6.00E-03
Heptachlor epoxide	HEE	4.42E+02	6.63E+03	1.70E-01	2.30E-01
Hexachlorobenzene	HCB	8.02E+03	1.53E+04	5.00E-02	7.00E-02
Hexachlorobutadiene	HBU	6.78E+02	2.41E+03	9.00E-02	1.00E-01
Indeno[1,2,3-cd]pyrene	INP	2.32E+03	2.86E+04	8.00E-03	1.20E-02
Isodrin	ISO	2.59E+02	2.02E+04	6.00E-03	4.60E-04
Isoproturon	ISP	1.65E+02	5.50E+01	9.00E+00	5.07E+02
Lead	Pb	1.00E+05	3.28E+02	6.50E-01	9.00E-01
Mercury	Hg	1.00E+05	3.03E+03	1.40E-02	9.00E-03
Metolachlor	MET	2.22E+02	6.50E+01	2.00E+00	2.50E+01
Methoxychlor	MTO	4.33E+02	2.17E+03	5.20E-02	7.80E-04
Molinate	MOL	1.20E+01	7.80E+01	1.94E+01	2.21E+01
Naphthalene	NAP	5.10E+01	3.98E+02	4.50E+00	8.60E+00
Nickel	Ni	1.00E+05	8.70E+01	4.70E-01	5.20E-01
Parathion-ethyl	PAR	8.90E+01	1.59E+02	5.70E-01	2.50E-04
Parathion-methyl	MPA	8.50E+01	5.40E+01	2.70E+00	7.30E-03
Pentachlorobenzene	PCB	1.72E+03	5.75E+03	1.74E-01	2.34E-01
Pentachlorophenol	PCP	2.27E+02	6.95E+02	8.00E-01	1.08E+00
Prometon	PRO	6.10E+01	4.70E+01	1.20E+01	7.70E+00
Prometryn	PRT	1.06E+02	1.55E+02	2.50E+00	1.27E+01
Propazine	PRZ	1.05E+02	4.10E+01	1.75E+01	1.77E+01
Selenium	Se	1.00E+05	5.00E+02	1.35E+00	2.46E-01
Simazine	SIM	2.00E+02	1.40E+01	4.90E+01	9.21E+01
Terbutryn	TER	1.06E+02	2.63E+02	3.00E+00	2.66E+00
Tetrachloroethylene	PER	4.12E+02	1.80E+01	8.00E-01	8.50E+00
Tetrachloromethane	TCM	3.37E+03	3.00E+01	4.40E+01	4.86E+01
Tetradifon	TDF	9.75E+02	8.50E+02	1.01E+01	2.10E+00
Toluene	TOL	1.90E+01	2.40E+01	2.13E+01	2.36E+01
Trichlorobenzene	TCB	2.27E+02	8.81E+02	2.06E+00	2.52E+00
Trichloroethylene	TET	1.97E+02	3.90E+01	1.35E+00	2.74E+01
Trifluralin	TFL	1.35E+02	5.62E+03	1.47E+00	4.20E-01
Xylenes	XYL	2.60E+01	6.20E+01	7.43E+00	8.59E+00
o-xylene	OXY	2.60E+01	6.80E+01	8.00E+00	3.10E+00
M+p xylenes	MPX	2.50E+01	7.60E+01	9.20E+00	9.60E+00
Zinc	Zn	1.00E+05	1.00E+03	1.20E+00	1.50E+00
4-nonylphenol	NON	1.60E+01	9.16E+02	1.13E-01	2.77E-01
4-(tert-octyl)phenol	TOP	5.50E+01	5.73E+03	2.90E-01	5.10E-01

* *Pov*: overall persistence, *BCF fish*: Bio-concentration factor in sensitive fish, *LC50 fish*: lethal concentration 50% to sensitive fish, and *LC50 daphnia*: Lethal concentration 50% to *Daphnia magna*.

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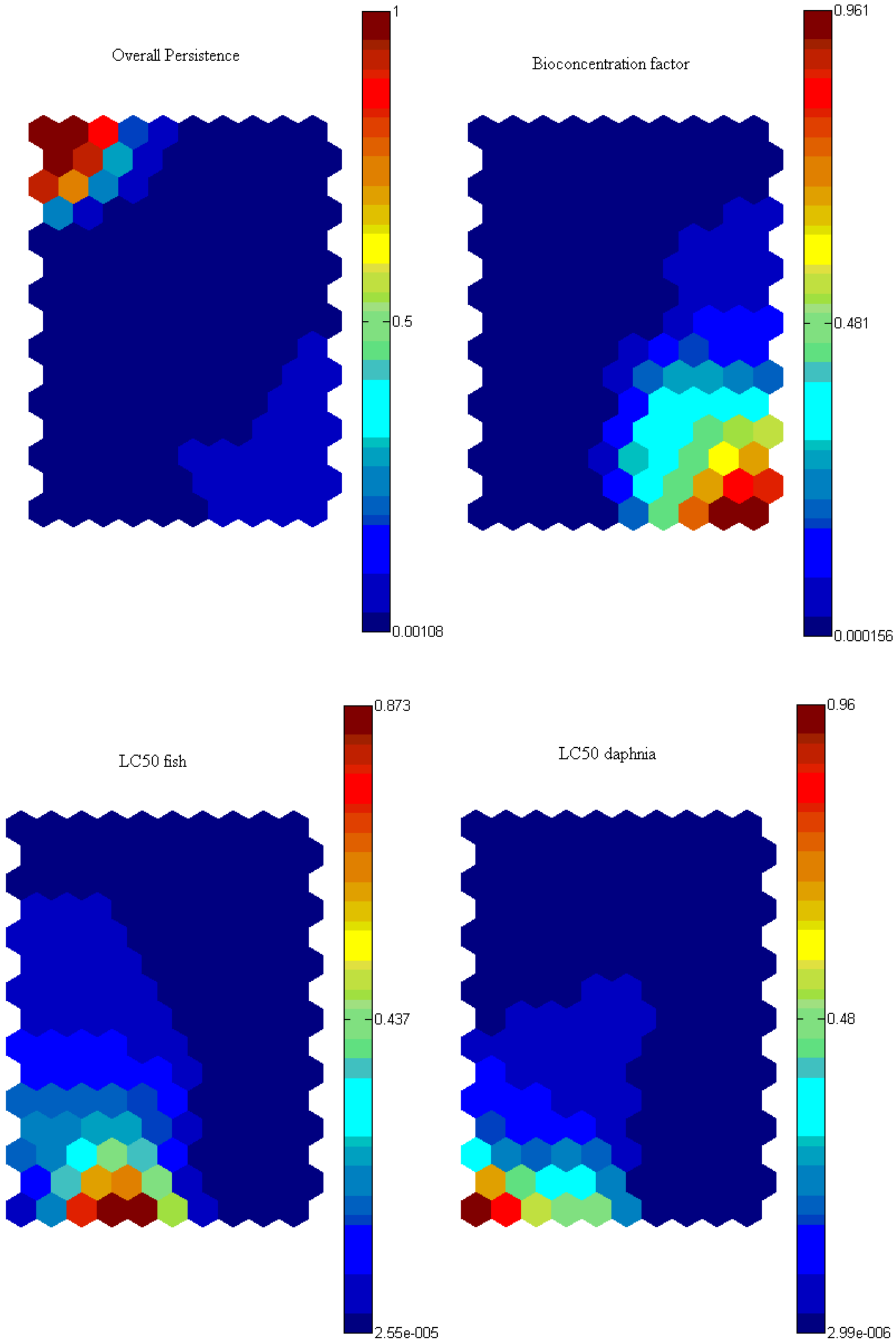

Fig. 2a. Component planes (c-planes) obtained with the SOM to PBT properties for all pollutants under study.

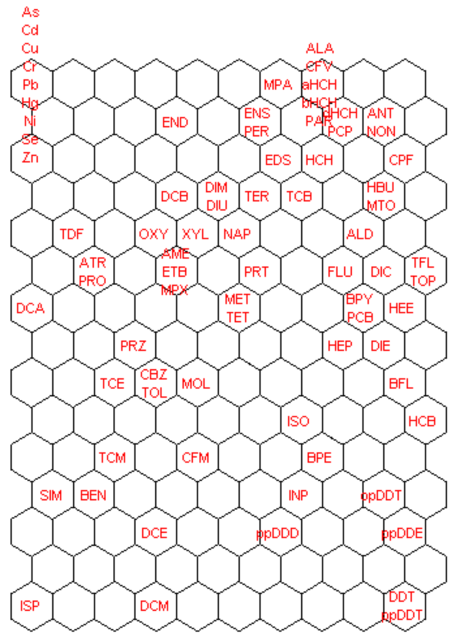

Fig. 2b. Self-organizing-map obtained to cluster PBT properties of the pollutants under study. Meaning of abbreviations is given in Table 3.

Table 3. Individual *S* scores of PBT properties as outputs after SOM application, and the ecological hazard index (*EHI*) calculated with equation 2

Substance	SOM code	S_{Pov}	S_{BCF}	$S_{tox\text{-}fish}$	$S_{tox\text{-}daphnia}$	*EHI*
DDT	DDT	7.13E-01	9.57E-01	1.00E+00	1.00E+00	9.01E+00
PpDDT	ppDDT	7.13E-01	9.57E-01	1.00E+00	1.00E+00	9.01E+00
PpDDE	ppDDE	7.05E-01	6.54E-01	1.00E+00	1.00E+00	8.08E+00
OpDDT	opDDT	7.02E-01	4.73E-01	1.00E+00	1.00E+00	7.52E+00
PpDDD	ppDDD	6.33E-01	4.17E-01	1.00E+00	1.00E+00	7.15E+00
Endrin	END	8.95E-01	1.50E-01	9.99E-01	1.00E+00	7.13E+00
Hexachlorobenzene	HCB	8.95E-01	1.50E-01	9.99E-01	1.00E+00	7.13E+00
Arsenic	As	1.00E+00	8.16E-03	9.97E-01	9.99E-01	7.02E+00
Cadmium	Cd	1.00E+00	8.16E-03	9.97E-01	9.99E-01	7.02E+00
Copper	Cu	1.00E+00	8.16E-03	9.97E-01	9.99E-01	7.02E+00
Chromium	Cr	1.00E+00	8.16E-03	9.97E-01	9.99E-01	7.02E+00
Lead	Pb	1.00E+00	8.16E-03	9.97E-01	9.99E-01	7.02E+00
Mercury	Hg	1.00E+00	8.16E-03	9.97E-01	9.99E-01	7.02E+00
Níkel	Ni	1.00E+00	8.16E-03	9.97E-01	9.99E-01	7.02E+00
Selenium	Se	1.00E+00	8.16E-03	9.97E-01	9.99E-01	7.02E+00
Zinc	Zn	1.00E+00	8.16E-03	9.97E-01	9.99E-01	7.02E+00
Benzo[k]fluoranthene	BFL	5.74E-01	1.87E-01	9.97E-01	9.98E-01	6.28E+00
Indeno[1,2,3-cd]pyrene	INP	2.56E-01	3.77E-01	1.00E+00	1.00E+00	5.90E+00
Benzo[g,h,i]perylene	BPE	2.41E-01	3.44E-01	1.00E+00	1.00E+00	5.76E+00
Isodrin	ISO	3.60E-02	2.25E-01	9.99E-01	1.00E+00	4.78E+00
Pentachlorobenzene	PCB	1.82E-01	8.13E-02	9.86E-01	9.90E-01	4.74E+00
Dieldrin	DIE	1.47E-01	8.94E-02	9.97E-01	9.98E-01	4.70E+00
Benzo(a)pyrene	BPY	8.22E-02	7.26E-02	9.98E-01	9.98E-01	4.46E+00
Fluoranthene	FLU	8.22E-02	7.26E-02	9.98E-01	9.98E-01	4.46E+00

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Heptachlor epoxide	HEE	4.26E-02	8.10E-02	9.98E-01	9.98E-01	4.36E+00
Heptachlor	HEP	1.20E-02	9.89E-02	9.92E-01	9.98E-01	4.31E+00
Hexachlorobutadiene	HBU	6.94E-02	3.76E-02	9.90E-01	9.98E-01	4.30E+00
Dicofol	DIC	2.82E-02	6.81E-02	9.97E-01	9.99E-01	4.28E+00
Trifluralin	TFL	1.13E-02	8.40E-02	9.86E-01	9.97E-01	4.25E+00
Methoxychlor	MTO	4.13E-02	3.18E-02	9.96E-01	9.99E-01	4.21E+00
Aldrin	ALD	2.34E-02	4.37E-02	9.98E-01	9.99E-01	4.20E+00
Chlorpyriphos	CPF	1.61E-02	2.18E-02	9.96E-01	9.99E-01	4.10E+00
Anthracene	ANT	2.64E-02	1.30E-02	9.91E-01	9.98E-01	4.10E+00
Chlorfenvinphos	CFV	1.73E-02	1.09E-02	9.92E-01	9.98E-01	4.06E+00
a-HCH	aHCH	2.48E-02	8.20E-03	9.80E-01	9.95E-01	4.05E+00
b-HCH	bHCH	2.48E-02	8.20E-03	9.80E-01	9.95E-01	4.05E+00
Pentachlorophenol	PCP	1.93E-02	7.25E-03	9.86E-01	9.94E-01	4.04E+00
Alachlor	ALA	1.42E-02	6.31E-03	9.89E-01	9.95E-01	4.03E+00
d-HCH	dHCH	1.42E-02	6.31E-03	9.89E-01	9.95E-01	4.03E+00
Parathion-ethyl	PAR	1.42E-02	6.31E-03	9.89E-01	9.95E-01	4.03E+00
Dichlorobenzene	DCB	8.98E-02	1.41E-02	8.98E-01	9.52E-01	4.01E+00
Endosulfan-sulfate	ENS	2.16E-02	6.17E-03	9.80E-01	9.70E-01	3.98E+00
Parathion-methyl	MPA	1.99E-02	5.22E-03	9.62E-01	9.91E-01	3.98E+00
Hexachlorocyclohexane	HCH	1.85E-02	6.79E-03	9.73E-01	9.73E-01	3.97E+00
Trichlorobenzene	TCB	1.85E-02	6.79E-03	9.73E-01	9.73E-01	3.97E+00
Terbutryn	TER	1.61E-02	5.46E-03	9.60E-01	9.79E-01	3.94E+00
Endosulfan	EDS	2.07E-02	6.20E-03	9.75E-01	9.54E-01	3.94E+00
Tetrachloroethylene	PER	2.47E-02	3.97E-03	9.75E-01	9.26E-01	3.89E+00
Tetradifon	TDF	8.92E-02	7.08E-03	8.12E-01	9.68E-01	3.85E+00
Dimethoate	DIM	2.10E-02	1.52E-03	8.95E-01	9.79E-01	3.81E+00
Diuron	DIU	2.10E-02	1.52E-03	8.95E-01	9.79E-01	3.81E+00
o-xylene	OXY	1.95E-02	1.10E-03	8.62E-01	9.68E-01	3.72E+00
Naphthalene	NAP	8.57E-03	2.99E-03	9.10E-01	9.03E-01	3.66E+00
Prometryn	PRT	1.67E-02	1.98E-03	9.57E-01	8.43E-01	3.65E+00
Atrazine	ATR	2.12E-02	1.35E-03	8.27E-01	9.53E-01	3.63E+00
Xylenes	XYL	4.60E-03	1.77E-03	8.73E-01	9.03E-01	3.57E+00
3,4-Dichloraniline	DCA	1.72E-01	1.93E-03	5.52E-01	9.45E-01	3.52E+00
Prometon	PRO	1.14E-02	7.19E-04	8.15E-01	9.22E-01	3.51E+00
Ethylbenzene	ETB	4.63E-03	1.05E-03	8.48E-01	8.93E-01	3.50E+00
M+p xylenes	MPX	4.63E-03	1.05E-03	8.48E-01	8.93E-01	3.50E+00
Ametryn	AME	6.70E-03	9.67E-04	8.44E-01	8.80E-01	3.47E+00
Metolachlor	MET	2.15E-02	8.53E-04	9.68E-01	7.34E-01	3.47E+00
Trichloroethylene	TET	2.15E-02	8.53E-04	9.68E-01	7.34E-01	3.47E+00
Propazine	PRZ	9.05E-03	6.90E-04	7.19E-01	8.06E-01	3.08E+00
Molinate	MOL	1.53E-02	6.07E-04	6.69E-01	7.66E-01	2.92E+00
Chlorobenzene	CBZ	2.80E-02	4.49E-04	6.43E-01	7.43E-01	2.86E+00
Toluene	TOL	2.80E-02	4.49E-04	6.43E-01	7.43E-01	2.86E+00
1,1,1-Trichloroethane	TCE	5.31E-02	3.57E-04	6.21E-01	7.25E-01	2.85E+00
1,2-Dichloroethane	DCE	9.44E-03	2.91E-03	5.88E-01	7.77E-01	2.77E+00
Chloroform	CFM	1.68E-01	2.12E-04	2.75E-01	6.20E-01	2.30E+00
Tetrachloromethane	TCM	1.98E-01	2.48E-04	2.30E-01	4.79E-01	2.01E+00
Isoproturon	ISP	1.68E-03	7.04E-04	9.48E-01	3.97E-02	1.98E+00
Dichloromethane	DCM	3.26E-03	8.29E-04	1.27E-01	5.28E-01	1.32E+00
Benzene	BEN	5.39E-02	1.59E-04	1.16E-01	2.08E-01	8.11E-01
Simazine	SIM	5.39E-02	1.59E-04	1.16E-01	2.08E-01	8.11E-01

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2.3. Fuzzy inference systems and the ecological risk potential

FIS use heuristic rules to establish qualitative and quantitative relationships among variables. The rule-based nature allows managing information in the form of natural language statements. It is highly convenient in environmental modeling and management. FIS are supported on three concepts: membership functions, fuzzy operations, and inference rules. A membership function is a curve that defines the membership of a variable to a fuzzy set, which acts as a qualifier (e.g. "low" or "high"). Fuzzy operations used in this study were: intersection (AND) and union (OR). If two fuzzy sets *A* and *B*, with membership functions μ_A and μ_B, defined on a universe of discourse *X*, then for a given element *x*, we have:

Intersection: $$\mu_{A\cap B}(x) = \min(\mu_A(x), \mu_B(x)) \quad (3)$$

Union: $$\mu_{A\cup B}(x) = \max(\mu_A(x), \mu_B(x)) \quad (4)$$

Finally, a rule may have the form: "If *x* is *A* AND *y* is *B* THEN *z* is *C*", where *A*, *B*, and *C*, are linguistic qualifiers defined by fuzzy sets in the universes of discourse *X*, *Y*, and *Z*, respectively.

Table 4. Sets of the fuzzy inference system and membership function parameters to be used in equation 5*

	EHI		*NoC*		*ERP*	
Fuzzy set	σ	*c*	σ	*c*	σ	*c*
Low	1.0	1.0	0.38	0.000	17.0	0.0
Moderate	1.0	3.0	0.38	0.675	17.0	30.0
High	1.0	5.0	0.38	1.350	17.0	60.0
Very High	1.0	7.0	0.38	2.025	17.0	90.0
Extreme	1.0	9.0	0.38	2.700	17.0	120.0
Range	0 - 10		0 - 2.7		0 - 120	

* *EHI*: Ecological hazard index, *NoC*: Normalized concentration, *ERP*: Ecological risk potential.

2.3.1. Design of the membership functions

A FIS was used to compute the *ERP* defined above. FIS inputs are the *EHI* and the *NoC* also described in previous sections. Gaussian membership functions were used to represent all the fuzzy sets. They are convenient because of the low number of parameters, having the shape:

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$$\mu(x,\sigma,c) = \exp\left(\frac{-(x-c)^2}{2\sigma^2}\right) \quad (5)$$

where σ and *c* are parameters shown in Table 4.

Table 5.Matrix of fuzzy sets used in equation 6*

Number of Rule *i*	*EHI* *j=1*	*NoC* *j=2*	*ERP* *j=3*
1	low	low	low
2	low	moderate	low
3	low	high	moderate
4	low	very-high	high
5	low	extreme	very-high
6	moderate	low	low
7	moderate	moderate	moderate
8	moderate	high	moderate
9	moderate	very-high	high
10	moderate	extreme	very-high
11	high	low	low
12	high	moderate	moderate
13	high	high	high
14	high	very-high	very-high
15	high	extreme	extreme
16	very-high	low	moderate
17	very-high	moderate	high
18	very-high	high	very-high
19	very-high	very-high	very-high
20	very-high	extreme	extreme
21	extreme	low	moderate
22	extreme	moderate	high
23	extreme	high	very-high
24	extreme	very-high	extreme
25	extreme	extreme	extreme

* *EHI*: Ecological hazard index, *NoC*: Normalized concentration, *ERP*: Ecological risk potential.

Ranges to distribute fuzzy sets were defined as follows. For the *EHI*, the range was 0-10, since these are the minimum and maximum values that could be obtained after SOM mapping of PBT properties. In turn, for *NoC* the range was fitted to include 96% of field data. Consequently, a maximum value of 2.7 was found in water. The maximum value of the FIS output (*ERP*=100) has been calibrated to be obtained after computing maximum values for *EHI* and *NoC*. For simplicity, *ERP*=100 was set for *NoC*>2.7 (i.e., 4 % of field data considered outliers). Consequently, five fuzzy sets were

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symmetrically distributed into the universes of discourse of inputs and outputs. Membership functions of all variables are displayed in Fig. 3.

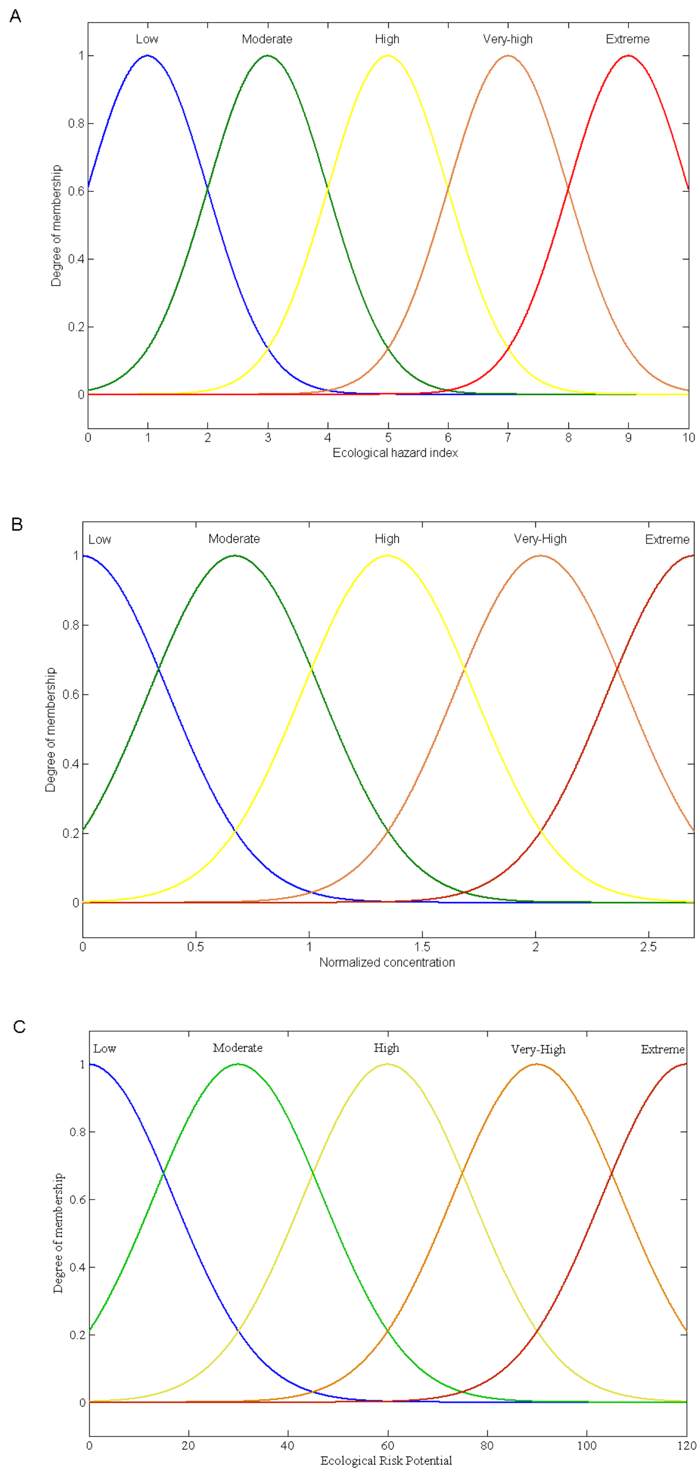

Fig. 3. Membership functions. Parameters are provided in Table 4.

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2.3.2. Design of the inference engine

After fuzzification, which means to compute the degrees of membership of inputs to each fuzzy set, the next step was the computation with words. For it, each rule had the following structure:

IF *EHI* is "set (i, 1)" AND *NoC* is "set (i, 2)" THEN *ERP* is "set (i, 3)" (6)

where "set (i, j)" are those defined in the matrix of the Table 5. These were defined by an expert panel. The evaluation of the 25 rules involves the application of three sequential operations: integration of antecedents, implication, and aggregation. As antecedents are composed by two sets linked with the operator AND, a degree of support for every rule was calculated with equation 3. Then, an implication operation is applied to modify the output fuzzy set to the degree of support specified by the antecedent. With the implication method here used, the output fuzzy set of every rule is chopped off by the degree of support. Subsequently, all truncated output fuzzy sets are aggregated. Finally, the operation is translated back to the numerical world by using centroid defuzzification. For more details on fuzzy arithmetic the reader is referred to Ocampo-Duque et al. (2006).

3. Results and discussion

3.1. Ecological hazard index

We hypothesized that the potential hazard to ecosystems posed by a pollutant depends mainly on PBT properties. The application of the self-organizing map algorithm to PBT data of pollutants considered in this study is depicted in Fig. 2b. The output SOM map structure looks like a honeycomb grid with 150 hexagons (15 × 10). The learning phase was broken down with 10 000 steps, and the tuning phase consisted on 10 000 additional steps. All chemicals were spread over the grid according to similarities of overall persistence (given by half-lives in water, sediments, and air), bio-concentration factors in fish, and LC50 for sensitive fish and *Daphnia magna*. Four main clusters could be identified. (a) Heavy metals were grouped up in the left corner; (b) DDTs appeared down in the right corner; (c) many organochlorine pesticides were situated up in the right corner of the map, with the higher number of chlorines into the molecule seems leading toward the right boundary); (d) the remaining hazardous

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substances form a widespread cluster with low molecular weight substances located down, and the rest overlapping with the pesticides cluster.

According to the *EHI* determined by SOM and equation 2, DDTs were identified as the most hazardous pollutants, with values ranging from 7.15 to 9.01. This is due to their high values onto the three branches: toxicity, bioaccumulation, and persistence. All heavy metals also appeared in the upper ranking of the hazard index. This can be explained since there is no scientific consensus about the values to be used for their half-lives. Therefore, an overall persistence of 1E+05 days has been assumed for all metals. Secondly, all listed metals presented toxicities and bio-concentration factors quite similar as to be clustered in the same node.

Heavy PAHs appeared below metals, with values ranging from 6.28 for benzo(k)fluoranthene to 4.46 for benzo(a)pyrene. These results were similar to those obtained in a recent study on human health (Nadal et al., 2006). Ranking positions in Table 3 are strongly influenced by the number of chlorine atoms in the molecules. BTEX (down in Table 3) have received scores ranging from 3.72 for o-xylene to 0.81 for benzene. Simazine and isoproturon seem to be the least hazardous pesticides in this ranking. According to the data shown in Table 3, it is clear that toxicity was the governing factor in the scoring system.

3.2. The ecological risk potential

The *ERP* is the output of the concurrent neuro-fuzzy model. The term concurrent was introduced by Wang et al. (2005). The higher the *ERP* the greater the level of concern is in terms of screening-risk. *NoC*=1 and *EHI*=7 yield *ERP*=50. These hypothetical values provide an idea about the significance of the *ERP* scores presented in subsequent paragraphs. Actually, *NoC* can be interpreted as risk characterization ratios (*RCR*) (EC, 2003). Likewise, Fig. 3 (bottom) may help to decide the membership of an *ERP* to a risk level in linguistic terms. Ideally, *ERP* should be as low as possible.

A view on *ERP* would allow identifying sites and substances of concern. Therefore, model results are managed with a Geographic Information System (GIS). An example, in which the analysis of aldrin in water can be carried out, is depicted in Fig.

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4. Next, some findings in sites and substances at levels showing some degree of concern to preserve freshwater ecosystems are briefly reported. Regarding to heavy metals, *ERP* values below 40.0 were estimated for As, Cr, Ni, Se, and Zn. *ERP* for Cu were relatively low in most sites, even though a maximum value (48.1) was found in SP-23 during 2004. For Pb, *ERP* in most sites were around 42.0 excepting a maximum score (65.1), which coincides in year and site with the maximum score for Cu. For Hg, most sites showed *ERP* values in the range 40.0-53.0, meaning *NoC* close to 1.0. Some *ERP* scores over 60.0 in SP-1, and SP-16 were also found for Hg. Very high scores were computed for Cd in many sites.

In relation to persistent organic pollutants in water, *ERP* values, increasing with time, for aldrin, dieldrin, endrin, and isodrin were found in SP-1, SP-2, SP-4, SP-5, SP-6, SP-7 and SP-8. For these pesticides peaks over 70.0 were obtained. Also, very high *ERP* were computed at different sites for op-DDT, pp-DDD, and pp-DDT, with paramount scores of 100.0, 78.1, and 90.5, respectively. Repeated worrying values for hexachlorobenzene were computed in the entire basin. Values of *ERP* increasing with time were also estimated in nine sites (SP-1 to SP-9) for pentachlorobenzene. Relative high *ERP* have resulted for 3,4-dichloroaniline, a by-product of degradation of original pesticides, in SP-24. For atrazine, an isolated maximum *ERP* of 54.6 in SP-21 was found during 2005. *ERP*>60.0 were calculated for chlorpyriphos in SP-21 and SP-23. Moreover, high *ERP* for endosulfan, heptachlor, heptachlor epoxide, molinate, lindane, parathion, and methyl-parathion were estimated at different sites and years. For PAHs, a number of very high *ERP* scores were found for benzo[g,h,i]perylene, benzo[k]fluoranthene, and indeno[1,2,3-cd]pyrene at various sites during the period assessed.

Although the presence of just a chemical at levels of concern should be a necessary and sufficient condition to go on controls, for risk management purposes would be more convenient to count the number of chemicals that surpass some concern levels. Thus, empirical cumulative distribution functions (CDF) can be plotted with the calculated *ERP* of all substances. The results of the CDF to the entire river basin are depicted in Fig. 5. A raise in levels of concern over time is clearly observed. Data in Fig. 5 explain, for instance, that assuming levels of concern when *ERP*>50, the number

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of worrying substances increased from 10% in 2002 to 22% in 2006. In other words, the cumulative distribution (y-axis) has decreased from 90% in 2002 to 78% in 2006.

3.3. Sensitivity analysis

ERP values depend on the membership function parameters and the inference engine structure (i. e., number, weight, and complexity of the rules). Since the SOM converges to a unique solution, and the inference engine operates with linguistic variables, sensitivity analysis should only be done to membership function parameters. Gaussian functions require two parameters: σ and c as expressed in equation 5. c parameters are constant unless the number of fuzzy sets, symmetrically distributed into the universes of discourse of all variables (Fig. 3), was modified. Therefore, a partial-derivative sensitivity analysis to σ parameters, which represent the width of the fuzzy sets and express their overlaps, has been carried out. The FIS has been run for a full and real domain of *EHI* and *NoC* inputs. Maximum 2.3% variation in *ERP* was obtained for 10% perturbation in both inputs. In turn, maximum 4.6% variation in *ERP* has been obtained for 20% perturbation in both inputs. The low degree of sensitivity in outputs is highly favorable, and demonstrates the convenient management of uncertainty by computing with fuzzy arithmetic.

3.4. Model validation

The validation of a methodology such as the *ERP* approach is not an easy task. Screening risk-based indexing models suffer from the risk to miss information, having many limitations because of their necessary assumptions. However, their benefits are significant when measuring state and impacts, to give responses before undesired conditions, according to the DPSIR (Drivers-Pressure-State-Impact-Response) conceptual model (Bunke and Oldenburg, 2005). The *ERP* approach can be used to estimate the likely stress on aquatic ecosystems generated by diverse drivers and pressure agents. In this sense, it is not a methodology to quantify impacts, but impact indicators help to check its performance. A simpler way to test its usefulness is by comparing it with current screening risk assessment methodologies. Both ways have been explored to give confidence about *ERP* benefits.

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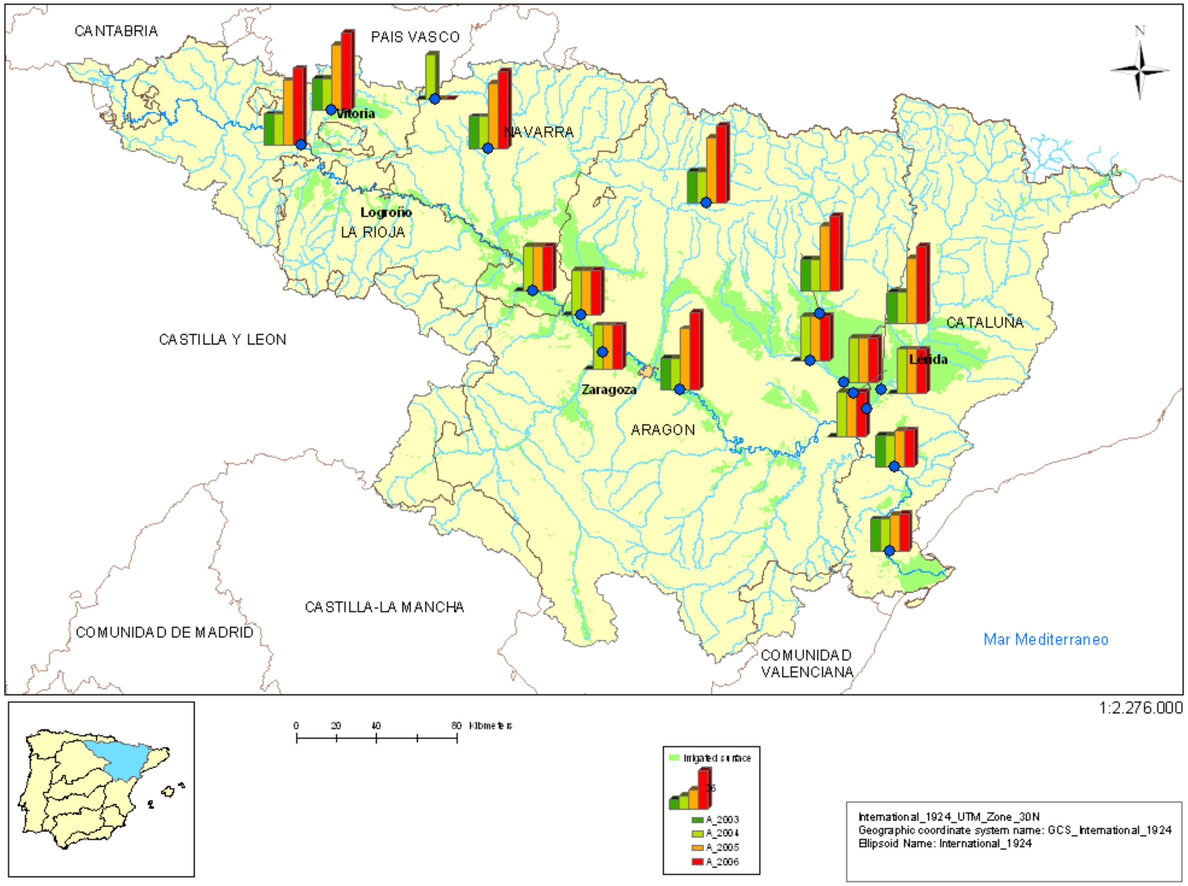

Fig. 4. Geographic information system displaying ecological risk potentials (*ERP*) for aldrin in water (bars correspond to years).

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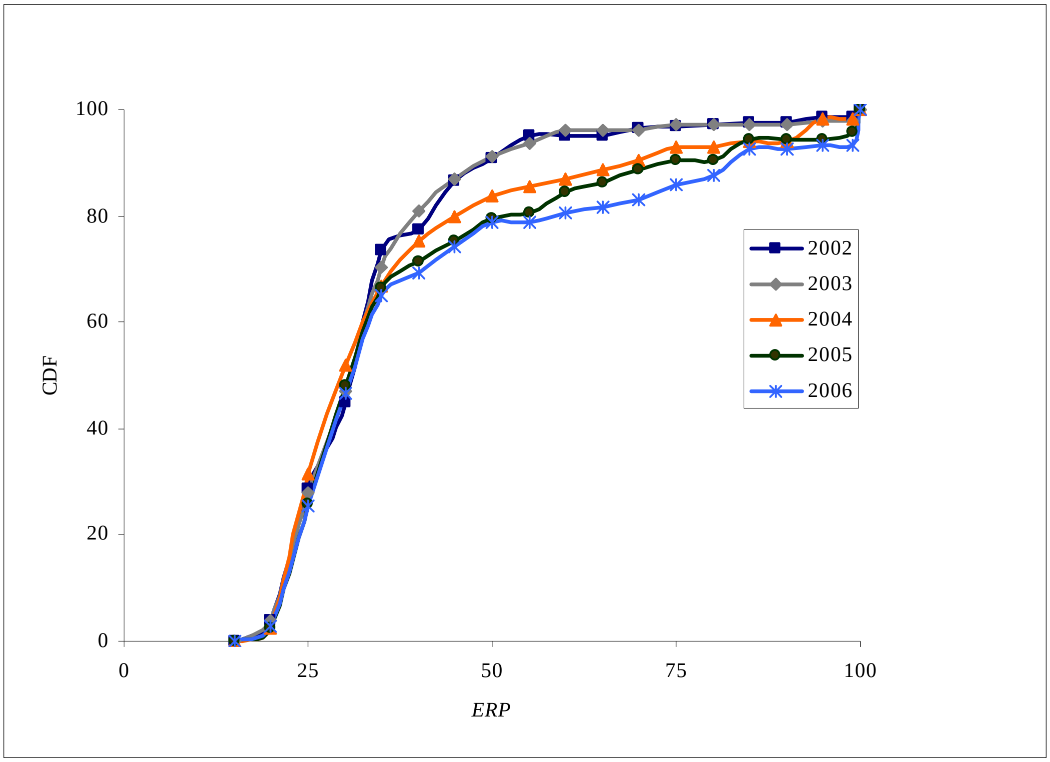

Fig. 5. Empirical cumulative distribution function (CDF) of *ERP* in the Ebro river basin.

Biological monitoring to support water quality has gained more relevance since the implementation of the WFD in Europe. Due to the interesting features of diatom communities to support the water quality analysis (Prygiel et al., 2002), impact indicators based on diatom surveys in freshwaters have been recently adopted in the Ebro river basin (CHE, 2005). Moreover, diatoms have been found useful to identify water pollution because of toxic substances (Legrand et al., 2006; Schmitt-Jansen and Altenburger, 2005). Therefore, three diatom indexes (the IPS index, the IBD index, and the CEE index), calculated with Omnidia software (Goma et al., 2004) and estimated in those sites where the *ERP* approach was also applied, were used for comparison. At each site, the mean of the three diatom indexes was used to give biological water quality in linguistic terms. Five classes, as requested by the WFD, were used: high, good, moderate, poor, and bad. More details about the diatom surveys and the biological water quality classification can be found in CHE (2002, 2005).

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Table 6. Comparison between the analysis of chemical pollution estimated with the *ERP* approach and the biological water quality estimated with diatom indexes

Site	2002			2005		
	ERP>50*	*ERP*>75*	Diatom mean index**	*ERP*>50*	*ERP*>75*	Diatom mean index**
SP-1	4.1%	2.0%	Good (16.2)	32.7%	16.3%	Good (15.7)
SP-2	1.3%	1.3%	Bad (4.7)	25.3%	9.3%	Poor (6.8)
SP-3	9.3%	4.0%	Good (13.8)	14.7%	5.3%	-
SP-4	2.0%	2.0%	Moderate (11.7)	30.0%	14.0%	-
SP-5	2.0%	2.0%	Moderate (12.3)	30.6%	14.3%	Good (15.2)
SP-6	2.0%	2.0%	Poor (8.5)	30.6%	14.3%	Poor (8.6)
SP-7	2.0%	2.0%	Good (15.4)	30.6%	14.3%	-
SP-8	2.0%	2.0%	Poor (5.8)	30.6%	14.3%	Poor (8.9)
SP-9	6.7%	4.0%	Moderate (9.3)	14.7%	5.3%	Poor (8.6)
SP-10	0.0%	0.0%	Moderate (11.4)	12.9%	9.7%	Poor (8.7)
SP-11	6.5%	3.2%	Good (15.8)	12.9%	9.7%	Poor (8.4)
SP-12	3.2%	3.2%	Moderate (11.9)	12.9%	9.7%	Moderate (10.5)
SP-13	0.0%	0.0%	Good (14.4)	15.4%	11.5%	Good (14.5)
SP-14	0.0%	0.0%	Moderate (9.2)	12.9%	9.7%	Bad (4.7)
SP-15	0.0%	0.0%	Bad (2.1)	10.3%	6.9%	Poor (6.3)
SP-16	7.1%	0.0%	Good (14.0)	15.7%	7.1%	Good (14.0)
SP-17	0.0%	0.0%	Good (13.7)	10.3%	6.9%	Bad (4.6)
SP-18	0.0%	0.0%	Moderate (11.2)	13.3%	10.0%	Poor (5.3)
SP-19	15.2%	2.2%	Poor (7.3)	19.6%	6.5%	Poor (8.4)
SP-20	13.0%	2.2%	Moderate (10.7)	17.4%	6.5%	Poor (8.6)
SP-21	10.9%	0.0%	Poor (8.6)	21.7%	6.5%	Poor (6.0)
SP-22	11.5%	1.9%	Moderate (10.7)	19.2%	9.6%	Moderate (10.3)
SP-23	2.2%	0.0%	Poor (7.5)	19.6%	8.7%	Poor (8.0)
SP-24	0.0%	0.0%	Moderate (9.5)	17.4%	6.5%	Poor (7.4)

* *ER*P>50 and *ERP*>75 columns provide the percentages of toxic substances that surpass the respective level of concern.

**Diatom mean index is the mean of three indexes (the IPS index, the IBD index, and the CEE index). Numerical scores are provided in parentheses. These are transformed to linguistic values, to give biological water quality, according to the following ranges: High (17-20), Good (13-17), Moderate (9-13), Poor (5-9), and Bad (0-5). More details about the diatom monitoring survey, in the Ebro river basin, can be found in CHE (2005).

As shown in Table 6, the agreement between the screening ecological risk outputs, and the biological water quality analysis determined with diatom indexes, is quite satisfactory. During the period 2002 to 2005, the percentage of *ERP* of concern, that is *ERP*>50 or *ERP*>75 (worst case), has increased in all studied sites. Likewise, the biological water quality decreased, at least in 38% of sites. This reduction could be due to the higher stress by toxic substances. It is important to remark that changes in diatom communities could be consequence of a number of environmental factors, toxic substances included. In any case, the presence of toxic substances at levels of concern seems to have incidence in the high number of sites with “poor” and “bad” biological diatom quality (29% in 2002, and 63% in 2005). Although the comparative results are

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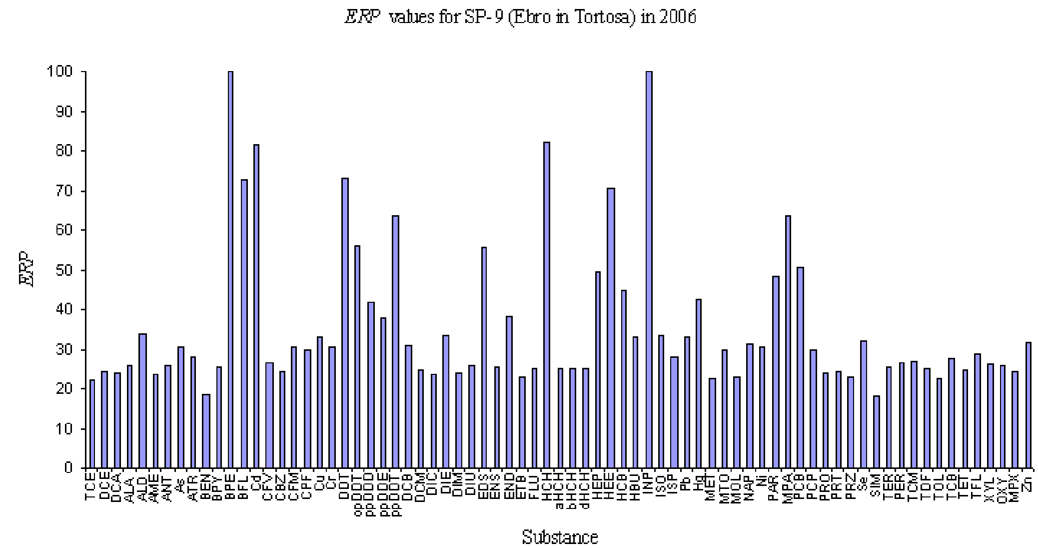
fairly conclusive, more research is necessary about the complex relationships between chemical pollution and biological indicators.



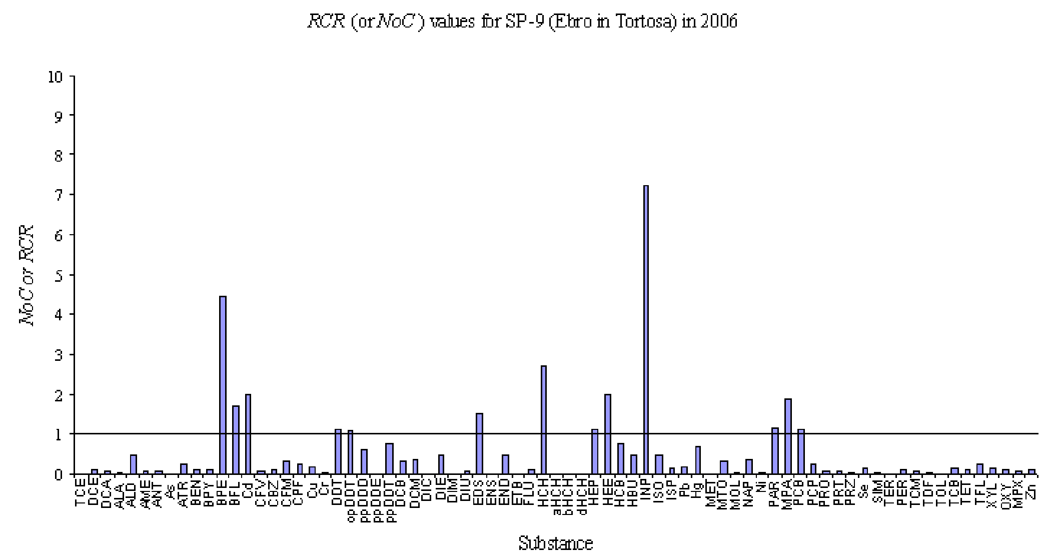


Fig. 6. Ecological risk potentials (*ERP*) versus risk characterisation ratios (*RCR*).

The most common methodology to assess chemical risks in aquatic ecosystems is the risk quotient method. Recently, species sensitivity distributions (SSD) to estimate potentially affected fractions have been also proposed (Posthuma and De Zwart, 2006). SSD give better statistical confidence, because they consider a number of species instead of only the most sensitive ones. However, SSD are methods to deal with variability in risk quotients, by using more eco-toxicological data rather than a way to

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manage their uncertainty. Uncertainty and variability are different concepts usually applied as synonyms by risk assessors. Uncertainty is more appropriate to manage subjectivity and/or "unknown" variability. The concept of risk is subjective and linguistically uncertain in nature. For that reason, it is here computed with fuzzy arithmetic.

To test the performance of the *ERP* approach, a comparison versus the *RCR* method has been carried out. *ERP* and *RCR* (or *NoC*) in one of the most important sampling sites are depicted in Fig. 6. The *ERP* approach has identified a considerable number of concerning chemicals. The identification of some chemicals of concern is also possible with *RCR*. However, the "level" or "degree" of concern is better explained by FIS outputs, since they are conveniently normalized in a 0-100 scale after linguistic management of information. In fact, *ERP* can be also expressed in linguistic terms by using Fig. 3 (bottom). Certainly, the *ERP* approach is a modification of the *RCR* method.

4. Conclusion

A conceptual model to help decision-makers involved in sustainable river basin management, based on artificial intelligence tools, has been proposed. SOM have provided a convenient insight to cluster PBT properties. FIS have allowed dealing with subjectivity and uncertainty in risk estimation, and computing with words has given more sense to numerical outputs. The model generates a suitable indicator to search for levels of concern of pollutants that may mean potential threats to freshwater ecosystems. The *ERP* approach is suitable to analyze overall trends by anticipating the probable impacts from multiple substances, identifying those sites requiring enhanced protective measures. Although the *ERP* approach is built on multiple substances assessment, it is far of accounting for synergies among pollutants.

The *ERP* approach has been useful to study chemical pollution in the Ebro river basin. Several *ERP* scores of concern have been estimated throughout the basin. Among them, overall and substance specific assessment were performed. The most polluted sites have been identified in the high Ebro (sites SP-7 and SP-8), with concerning high levels especially for heavy metals. It coincides with the findings recently reported by

Terrado et al. (2006). On the other hand, important stresses because of the presence of persistent organic substances released by industrial processes and agriculture have been easily identified in many sites. In conclusion, results show that water quality in the Ebro river basin is below expected scores to fulfill the WFD.

5. Acknowledgements

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Chapter 4

Part A. Estimating the environmental impact of micro-pollutants in the low Ebro: An approach based on screening toxicity with *Vibrio fischeri* [4]

Abstract

The aim of this study was to assess the likely impacts on the ecosystems due to agricultural, human, and industrial activities carried out in an ecologically important area of the Ebro River (Spain). For it, a screening site specific ecological risk assessment was conducted. Considering the presence of high levels of potentially toxic substances, such as metals and chlorinated organic compounds, aqueous and organic extracts were used to assess toxicity in sediments by using the photo-luminescent bacteria *Vibrio fischeri* (Microtox®) as screening response variable. Sediment samples collected during 2005-2006 in the last course of the Ebro River and its Delta have been analyzed. Toxic responses have shown strong relationships to the levels of pollutants in the area. Moreover, various sites presented some toxicity level, probably because of other factors associated with reducing environments into the sediments. Results indicate that Microtox® bioassay is an appropriate tool to perform risk assessment studies at screening level.

Keywords: Sediments; Ecological risk assessment; *Vibrio fischeri*; Ebro River (Spain)

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1. Introduction

Nowadays, the control of sediment quality is being considered as a necessary extension of the control of river water quality (Borja et al., 2004). The protection of river sediments is necessary since they are both sink and potential source of contaminants to the water column (Chau, 2006). In turn, sediments integrate pollutant concentrations over time, pollutant levels in water are more variable and dynamics (Ayyamperumal et al., 2006), while sediment pollutants may affect benthic and other food-chain organisms (Moreno-Garrido et al., 2007). Finally, sediments are also an integral part of the aquatic environment, providing habitat, feeding, and breeding areas for a number of organisms. Recently, sediments' protection has become mandatory to preserve the ecological status in rivers, as requested by the Water Framework Directive.

Although chemical analysis provides data about environmental pollutant concentrations, it gives little information about bioavailability and/or toxicity at the site. Therefore, biological analyses combined to chemical analyses are essential to infer probable adverse biological effects (Chapman, 2007). Different bioassays are currently in use, being most of them often expensive and time consuming. The need for cost effective and rapid screening methodologies to assess chemical toxicity has led to the development of tests based on microorganisms. Sediment microbial communities, especially bacteria, play an important role in nutrient cycling, organic matter decomposition, and pollutant fate in aquatic sediments. Microbial toxicity tests seem also to be more sensitive than those with animals or plants. Moreover, sediment quality guidelines derived from animal toxicity data are not always low enough to protect sediment microorganisms (van Beelen, 2003).

The *Vibrio fischeri* luminescence inhibition test seems to be one of the most promising screening toxicity tests. It is able to detect toxicity for a wide spectrum of chemicals and has shown good correlation with other standard acute toxicity assays (Parvez et al., 2006). It poses few ethical problems being highly reproducible (Fulladosa et al., 2007). Microtox® toxicity testing for sediment samples can be performed with pore water, sediment elutriates, organic extracts, and bulk solid samples in solid phase tests. Pore water and sediment elutriates are useful in exposing the bacteria to water soluble substances, which provides a realistic estimation of bioavailability to pelagic

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communities (Demuth et al., 1993). Organic extracts allow exposing the bacteria to non-polar substances, whereas solid phase tests are useful to expose the bacteria to the whole sediment. However, some studies indicate that solid-phase assays can be affected by silt-clay contents due to the adsorption of bacteria to fine-grained sediments, resulting in false increase of toxicity (Ringwood et al., 1997).

In this study, we conducted a screening site specific ecological risk assessment based on a riparian sediment survey for the last 134 km of the Ebro River (NE Spain) prior arriving to the Delta at the Mediterranean Sea. In this area, the river has historically been stressed by riparian industrial and agricultural activities (Ocampo-Duque et al., 2006). Therefore, high concentrations of metals and persistent organic pollutants (POPs) in sediments have been reported (Lacorte et al., 2006), while evidence of endocrine disrupting effects in local fish has been also found (Lavado et al., 2006). Consequently, the objectives of the present investigation were the following: (1) to perform a screening toxicity study by using the *Vibrio fischeri* toxicity test bacteria for sediment samples, and (2) to search for the potential relationships between the presence of pollutants, compartmental characteristics, and toxic responses in the frame of a screening ecological risk assessment.

2. Materials and methods

2.1. Study area and sampling

The Ebro River flows through the Northeast of Spain to the Mediterranean Sea. When crossing Catalonia, the river takes the name of “Low Ebro”. An important number of human, agricultural, and industrial activities are developed along its riparian zone. In recent years, historical releases from a chlor-alkali process to the Flix reservoir (SP4 in Fig. 1) have concerned regional environmental protection agencies, stakeholders, and general population (Lavado et al., 2006). Elevated concentrations of metals, organochlorine compounds, and pesticides were recently reported for different environmental compartments downstream (CHE, 2006). In order to contribute to the knowledge about the ecological status in the Low Ebro, two sampling campaigns were carried out in 2005-2006. Twenty sampling sites were selected (Fig. 1). Site selection was done according to the proximity to potential emission sources. At each site, a

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composite sediment sample was prepared by mixing 3 sub-samples collected at 0-5 cm depth. Samples were stored at 4 ºC prior to analyses.

Fig. 1. Sampling sites.

2.2. Chemical analyses

Details on the analytical procedure were previously reported (Nadal et al., 2004). In brief, 0.5 g of dried sediment samples was treated with 5 ml of nitric acid in Teflon vessels for 8 h at room temperature. Subsequently, they were heated at 80 °C in a stove for 8 h. After cooling, solutions were filtered and made up to 25 ml with ultrapure water. Metal concentrations were determined by ICP-OES (Mn, Ni, Zn), ICP-MS (Cd, Cr, Cu, Hg, Pb), and ICP-HG (As). A rigorous internal and external quality control was

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performed by using certified reference material MESS-3-Marine Sediment Reference Materials for trace elements and other constituents (NRC-CNRC, Canada). Detection limits (mg/kg of dry weight) were the following: 0.1 for As, 0.03 for Cd, 0.25 for Cr, 0.10 for Cu, 0.01 for Hg, 50 for Mn, 1.00 for Ni, 0.03 for Pb, and 5 for Zn.

Compartmental characteristics of the sediments were also determined. Ammonia was determined on 2% NaCl aqueous extracts. These extracts were distilled in alkali media, and ammonia was trapped by boric acid solution, and subsequently titrated with sulfuric acid. Total organic matter was oxidized at 550ºC and loss of ignition was measured by gravimetric analysis. The pH values were measured on aqueous extracts at a ratio 1:1 (w:v). Finally, texture was also determined by a current particle-size analysis according to the Bouyoucos method (Bouyoucos, 1927).

As the measured metal concentrations in sediments for the studied area were similar to those recently reported by regional environmental protection agencies (CHE, 2005, 2006; ACA, 2006), in order to get a more comprehensive data set for sediment characterization, sediment concentrations for POPs (mainly PCBs, DDTs, HCHs, and hexachlorobenzene (HCB)) were obtained from those reports, as well as from the scientific literature (Fernandez et al., 1999; Pastor et al., 2004). They were also integrated to the assessment.

2.3. Ecotoxicological analyses

To assess the sediments toxicity, Microtox® acute bioassay was conducted on aqueous and organic extracts of the samples. Basic test and 90% basic test for aqueous extracts were performed with determination at 15 minutes contact (Azur, 1999). Aqueous elutriates were obtained by mixing 10 g of wet sediment with 20 ml of 2% NaCl solution, shaking during 12 h, and finally filtered. This solution is isotonic to *Vibrio fischeri* and sodium has dispersive properties that allow the extraction of the soluble fraction and weakly adsorbed soluble pollutants to the sediment. These elutriates can give information about the possible transfer of pollutants from sediment to surface waters.

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Organic extraction was done by adding 5 g of anhydrous sodium sulphate and 30 ml of acetone:hexane (1:1) to 2 g of wet sediment. The mixture was treated for 20 minutes in a microwave closed digester (Mars X) with controlled temperature (115ºC). Extracts were then filtered and evaporated, and the remaining residue dissolved in 4 ml of dimethyl sulphoxide (DMSO). 0.5 mg of wet sediment yielded a volume of 1 μl of DMSO. DMSO extracts were added to Microtox® vials to give a final concentration equivalent to 1%. DMSO, a polar aprotic solvent that dissolves both polar and non-polar compounds, is suitable for bioassays due to its low toxicity. An organic extraction blank was performed to assess the likely toxicity of the used solvents. EC50 results are expressed in mg of dry sediment per ml of extract, as well as in percentage of extract dilution.

Table 1. Sediment characteristics for samples collected in the “Low Ebro” river (Spain)

Sampling site	Location	Sediment type	Sediment texture	pH	% TOM	mg N-NH_4^+/kg
SP1	Riba-Roja	Reservoir	Clay loam	7.60	0.30	74.80
SP2	Riba-Roja	Reservoir	Clay loam	7.70	0.62	34.20
SP3	Flix	Reservoir	Clay loam	7.70	0.29	20.85
SP4	Flix	Reservoir	Clay loam	7.69	0.56	24.48
SP5	Ascó	Fluvial	Clay loam	7.62	0.47	70.56
SP6	Garcia	Fluvial	Clay loam	7.30	0.43	223.18
SP7	Mora d’Ebre	Fluvial	Clay loam	7.50	0.68	285.09
SP8	Miravet	Fluvial	Clay loam	7.64	0.38	31.40
SP9	Benifallet	Fluvial	Clay loam	7.99	0.07	18.73
SP10	Xerta	Fluvial	Clay loam	8.00	0.03	37.98
SP11	Xerta	Fluvial	Clay loam	8.02	0.09	24.60
SP12	Tortosa	Fluvial	Sandy clay loam	8.18	0.21	13.91
SP13	Punta Banya	Marsh	Sandy clay loam	7.45	0.28	16.71
SP14	Palma Marina	Marsh	Sandy clay loam	7.52	0.46	39.50
SP15	La Tancada	Marsh	Sandy clay loam	7.50	0.22	38.65
SP16	Regants la Cinta	Fluvial	Sandy clay loam	7.42	0.29	28.12
SP17	Fangal	Marsh	Clay loam	7.52	0.48	129.82
SP18	Far de l’Arenal	Marsh	Sandy loam	7.51	0.27	7.21
SP19	Pont dels Moros	Fluvial	Silty clay loam	7.94	0.56	5.89
SP20	El Garxal	Fluvial	Silty clay loam	8.32	0.05	7.07

TOM: total organic matter.

3. Results and discussion

Table 1 shows sampling location and sediment characteristics. In general, sediments were fine textured except for marsh samples with a high sand content. Sediments were alkaline with a low content of organic matter and variable concentration of ammonia. Table 2 summarizes metal concentrations for the sites included in the

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current study. Data for POPs in various zones of the Low Ebro are given in Table 3. US EPA freshwater sediment benchmarks have been used for comparative analysis (US EPA, 2007).

Table 2. Measured concentrations (mg/kg of dry weight) of metals in sediments

Site*	**Cd**	**Cu**	**Hg**	**Pb**	**Zn**	**As**	**Cr**	**Ni**	**Mn**
SP 1-05	0.13	8.80	0.03	11.12	25.53	5.79	0.52	0.05	254.99
SP 1-06	0.12	9.10	0.15	11.16	53.42	4.05	8.61	18.29	158.20
SP 2-05	0.19	28.58	0.06	19.90	45.27	8.40	0.72	0.05	461.46
SP 2-06	0.09	100.65	0.09	16.55	34.90	4.49	7.32	12.88	184.88
SP 3-05	0.13	11.51	0.02	14.65	29.25	6.36	0.42	0.05	185.82
SP 4-05	0.67	17.32	3.03	34.80	62.69	6.57	0.87	0.05	412.75
SP 4-06	0.24	8.05	1.82	11.20	37.22	5.93	10.38	22.81	198.97
SP 5-05	0.37	18.82	4.20	28.72	65.95	11.17	1.11	24.64	529.37
SP 5-06	0.50	22.82	4.92	19.78	95.33	9.61	18.79	26.52	2316.04
SP 6-05	0.33	14.80	1.08	31.20	63.40	6.21	0.79	19.39	546.28
SP 6-06	0.35	20.93	2.56	108.50	80.32	8.86	15.04	29.46	1570.96
SP 7-05	0.30	15.03	1.26	13.84	54.36	6.86	0.85	23.82	1268.95
SP 8-05	0.31	14.10	0.57	37.92	60.88	6.03	0.61	18.54	376.14
SP 8-06	0.71	22.48	1.36	193.06	176.49	8.87	17.78	23.36	525.16
SP 9-05	0.50	21.66	1.40	31.25	60.35	6.03	0.68	22.90	434.38
SP 10-05	0.14	4.78	0.21	10.23	29.97	2.74	0.26	10.98	223.43
SP 11-05	0.16	8.33	0.27	13.30	34.71	4.28	0.45	13.74	307.41
SP 11-06	0.19	3.71	0.25	34.07	48.74	3.68	7.12	18.10	179.60
SP 12-05	0.35	13.96	0.64	21.00	53.23	5.03	0.77	18.73	492.44
SP 12-06	0.12	5.22	0.11	22.95	39.08	4.24	5.78	15.20	137.75
SP 13-05	0.08	5.03	0.04	7.96	25.14	6.97	0.40	0.05	256.15
SP 13-06	0.10	3.03	0.04	11.61	32.75	6.48	8.17	18.83	259.00
SP 14-05	0.08	3.93	0.03	5.95	17.36	6.15	0.41	10.20	229.35
SP 14-06	0.13	2.80	0.04	7.50	31.80	8.98	8.55	17.94	274.13
SP 15-05	0.09	6.44	0.03	9.48	22.86	6.44	0.41	14.36	279.08
SP 16-05	0.05	3.51	0.03	4.09	12.61	4.05	0.25	10.04	129.80
SP 16-06	0.17	9.03	0.10	10.26	36.77	15.88	10.33	16.40	255.70
SP 17-05	0.25	17.22	0.11	16.86	41.82	7.05	1.05	19.51	349.53
SP 17-06	0.16	6.72	0.08	12.16	37.53	8.22	18.41	17.18	272.07
SP 18-05	0.08	3.11	0.03	5.15	14.74	7.18	0.31	10.63	200.86
SP 18-06	0.09	0.89	0.02	4.37	29.13	7.18	5.75	14.45	210.16
SP 19-05	0.25	18.61	0.15	32.84	57.86	8.56	0.73	27.92	376.18
SP 19-06	0.10	3.13	0.06	9.34	39.34	2.98	7.67	18.98	130.37
SP 20-05	0.17	7.28	0.14	10.56	27.37	6.24	0.37	13.69	190.34
SP 20-06	0.05	2.36	0.01	3.90	23.10	3.04	4.11	14.68	119.74
Benchmark**	0.99	31.6	0.18	35.80	121.00	9.80	43.40	22.70	460.00

* Samples have been coded as SPXX-YY, XX: sampling site, YY: year
** Values correspond to US EPA freshwater sediment benchmarks (US EPA, 2007).

Table 4 shows the results for eco-toxicological analyses. Results from both extracts, inorganic and organic, are provided. Toxicity classification is expressed according to Bombardier and Bermingham criteria (Bombardier and Bermingham, 1999). According to these criteria, four levels should be used to classify toxicity. EC50

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dilution percentages and EC50 dilution levels (expressed as µl DMSO per ml Microtox® solvent) are used for aqueous and organic extracts, respectively. Selected ranges in both extracts are: non-toxic (≥100%, ≥1 µl/ml), marginally toxic (10-99%, 0.1-0.9 µl/ml), moderately toxic (1-9%, 0.01-0.09 µl/ml), and highly toxic (<1%, <0.01 µl/ml).

Table 3. Concentrations (µg/kg of dry weight) of persistent organic pollutants (POPs) in sediments for various sites of the studied area

Site	Statistic	PCBs	DDTs	HCHs	HCB	References
SP4	Max	665.40	17941.00	255.00	6323.50	(ACA, 2006)
	Mean	496.51	7521.65	57.81	1530.89	
SP5	Max	-	28.60	5.60	38.00	(CHE, 2006)
	Mean	-	19.46	2.65	16.60	
SP8	Mean	203.00	390.00	14.10	480.00	(ACA, 2006)
SP12	Max	98.00	240.53	6.00	68.40	(CHE, 2006;
	Mean	28.42	101.51	4.03	18.75	ACA,2006)
SP16	Max	10.60	55.00	2.80	11.90	(Pastor et al., 2004)
	Mean	5.90	15.70	0.20	1.80	
SP19	Mean	87.65	63.50	10.10	42.00	(ACA, 2006)
SP20	Mean	39.00	31.95	5.70	17.00	
Benchmark		59.80	5.28	3.00	20.00	(US EPA, 2007)

Evidence of toxic responses has been identified in the Low Ebro with the Microtox® bioassay. For extracts soluble in water (i.e. elutriates), and according to the Bombardier and Bermingham criteria, 55.6% of samples were classified as "non-toxic", while 41.7% were "marginally toxic". Likewise, 2.7% of samples resulted to be "moderately toxic". For organic extracts, most samples were classified as "marginally toxic" (52.8 %) and "moderately toxic" (41.7 %). Most pollutants appeared in organic phases. Lower toxicities in elutriates versus organic extracts could be due to washing effects in superficial sediments, and the subsequent lower soluble fraction of toxic substances. Thus, non-washed pollutants would be adsorbed by organic and solid sediment particles.

The current results could also suggest a higher sensitivity in Microtox® bioassays when DMSO extracts are used compared to aqueous extracts. It was also noted in a recent study by Grant and Briggs (2002). According to this, it seems clear that testing sediment toxicity using organic extracts with Microtox® bioassay provides better numerical estimates than using elutriates (Demuth et al., 1993).

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Table 4. Results of ecotoxicity basic tests with *Vibrio fischeri* for sediments collected in the "Low Ebro" river (Spain)

	Aqueous extracts EC50			**Organic extracts EC50**		
Site*	**mg dry sediment / ml**	**% v/v**	**Criterion****	**mg dry sediment / ml**	**µl DMSO/ml Microtox solvent**	**Criterion****
SP1-05	538.9 (448.8-602.7)	>100.0	NoTox	3.31 (3.01-3.76)	0.331 (0.301-0.376)	MaTox
SP1-06	>1000.0 (-)	>100.0	NoTox	1.16 (1.03-1.32)	0.230 (0.204-0.261)	MaTox
SP2-05	301.8 (199.3-415.4)	60.4 (39.9-83.1)	MaTox	2.22 (1.67-3.02)	0.264 (0.198- 0.359)	MaTox
SP2-06	441.7 (394.6-516.2)	88.3 (78.9-103.2)	MaTox	0.64 (0.57-0.74)	0.105 (0.093-0.123)	MaTox
SP3-05	>1000.0 (-)	>100.0	NoTox	6.42 (6.33-7.15)	0.679 (0.669-0.756)	MaTox
SP4-05	151.9 (120.1-165.5)	30.4 (24.0-33.1)	MaTox	0.06 (0.06-0.07)	0.014 (0.014-0.016)	MoTox
SP4-06	169.1 (133.4-184.0)	33.8 (26.7-36.8)	MaTox	0.07 (0.06-0.08)	0.016 (0.014-0.019)	MoTox
SP5-05	22.2 (17.1-27.4)	4.4 (3.4-5.4)	MoTox	0.20 (0.14-0.32)	0.060 (0.042-0.096)	MoTox
SP5-06	229.1 (181.9-288.3)	45.8 (36.4-57.6)	MaTox	0.08 (0.07-0.10)	0.020 (0.018-0.023)	MoTox
SP6-05	97.6 (76.8-124.1)	19.5 (15.3-24.8)	MaTox	0.07 (0.05-0.08)	0.028 (0.021-0.032)	MoTox
SP6-06	154.0 (75.1-185.7)	30.8 (15.0-37.2)	MaTox	0.38 (0.33-0.44)	0.104 (0.093-0.122)	MaTox
SP7-05	98.0 (12.3-171.3)	19.6 (2.5-34.3)	MaTox	0.72 (0.66-1.09)	0.206 (0.189-0.312)	MaTox
SP8-05	>1000.0 (-)	>100.0 (-)	NoTox	1.86 (1.41-2.19)	0.165 (0.125-0.193)	MaTox
SP8-06	>1000.0 (-)	>100.0 (-)	NoTox	3.65 (3.48-4.16)	0.567 (0.538-0.645)	MaTox
SP9-05	>1000.0 (-)	>100.0 (-)	NoTox	5.02 (4.39-5.74)	0.595 (0.456-0.723)	MaTox
SP9-06	>1000.0 (-)	>100.0 (-)	NoTox	5.36 (4.77-6.26)	0.599 (0.52-0.699)	MaTox
SP10-05	279.1 (205.5-417.1)	55.8 (41.1-83.4)	MaTox	1.83 (1.40-2.41)	0.194 (0.148-0.256)	MaTox
SP11-05	558.1 (452.2-762.2)	>100.0 (-)	MaTox	2.05 (1.79-2.80)	0.265 (0.231-0.360)	MaTox
SP11-06	>1000.0 (-)	>100.0 (-)	NoTox	6.12 (5.70-6.57)	0.718 (0.669-0.7719	MaTox
SP12-05	>1000.0 (-)	>100.0 (-)	NoTox	0.14 (0.14-0.14)	0.020 (0.020-0.020)	MoTox
SP12-06	>1000.0 (-)	>100.0 (-)	NoTox	12.96 (12.07-13.91)	1.358 (1.265-1.458)	NoTox
SP13-05	>1000.0 (-)	>100.0 (-)	NoTox	0.74 (0.67-0.85)	0.063 (0.057-0.072)	MoTox
SP13-06	586.3 (276.0-812.4)	117.3 (55.2-162.5)	MaTox	0.10 (0.10-0.11)	0.012 (0.012-0.013)	MoTox
SP14-05	340.2 (293.0-399.1)	58.6 (50.5-68.8)	MaTox	0.04 (0.03-0.05)	0.007 (0.005-0.009)	HiTox
SP14-06	>1000.0	>100.0 (-)	NoTox	0.41 (0.41-0.45)	0.059 (0.059-0.064)	MoTox
SP 15-05	>1000.0 (-)	>100.0 (-)	NoTox	4.76 (3.88-6.15)	0.559 (0.456-0.723)	MaTox
SP16-05	>1000.0 (-)	>100.0 (-)	NoTox	0.42 (0.32-0.56)	0.050 (0.038-0.067)	MoTox
SP16-06	339.2 (276.4-389.5)	67.8 (55.2-77.8)	MaTox	0.10 (0.09-0.12)	0.016 (0.014-0.019)	MoTox
SP17-05	121.4 (85.4-183.1)	24.3 (17.1-36.7)	MaTox	0.27 (0.27-0.27)	0.071 (0.071-0.071)	MoTox

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SP17-06	155.4 (111.3-195.3)	31.1 (22.3-39.1)	MaTox	0.18 (0.12-0.20)	0.025 (0.017-0.029)	MoTox
SP18-05	>1000.0 (-)	>100.0 (-)	NoTox	0.16 (0.14-0.22)	0.014 (0.012-0.019)	MoTox
SP18-06	>1000.0 (-)	>100.0 (-)	NoTox	2.69 (2.00-3.76)	0.335 (0.249-0.468)	MaTox
SP19-05	>1000.0 (-)	>100.0 (-)	NoTox	7.65 (3.57-15.95)	0.806 (0.376-1.679)	MaTox
SP19-06	>1000.0 (-)	>100.0 (-)	NoTox	2.48 (2.21-2.90)	0.307 (0.272-0.358)	MaTox
SP20-05	>1000.0 (-)	>100.0 (-)	NoTox	0.60 (0.56-0.68)	0.061 (0.056-0.069)	MoTox
SP20-06	>1000.0 (-)	>100.0 (-)	NoTox	1.88 (1.59-2.69)	0.220 (0.186-0.315)	MaTox

*Samples have been coded as SP XX-YY, where XX is the site and YY is the year. EC50: 50% effect concentrations of sediment aqueous and organic extracts. 95% confidence limits in parenthesis.

** NoTox: Non-toxic, MaTox: Marginally toxic, MoTox: Moderately toxic. HiTox: Highly toxic. These criteria have been defined by Bombardier and Bermingham (1999).

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The area exhibiting higher sediment toxicity, coincides in both extracts with the area influenced by significant industrial activities. A chlor-alkali plant is located close to SP4 (Fig. 1). As observed from chemical analyses, the concentrations of organic pollutants (mainly PCBs, DDTs, HCHs, and HCB), and Hg in this site substantially exceeded the benchmarks protective for aquatic ecosystems. However, and fortunately for the ecological community welfare downstream, most pollutants remain trapped in sediments because of a dam located in that zone. It can be noticed in Table 3. Nowadays, the need to dredge those sediments, stored along many years, is clearly acknowledged by local stakeholders.

Higher toxicities also coincide with the area of influence of a Nuclear Power Plant, which is located close to SP5. Although in this site, concentrations of POPs are still high, they have been dramatically reduced when compared with concentrations in SP4 (Table 3). Likewise, the levels of metals in this site also exceeded the US EPA benchmarks (Table 2). In fact, measured concentrations of metals were higher in SP5 than in SP4. In SP5, metal levels were 25-fold and 3-fold higher than the benchmarks for Hg and Mn, respectively. The high presence of Mn could be due to geochemical features of the river basin (Ferre-Huguet, 2007). High values, close to benchmarks, for As and Ni were also detected. The concentrations of these elements remain high for the sites SP6, SP7 and SP8. Values up to 5-fold higher than the benchmark for Pb were also detected at these sites. It could be attributable to a natural presence of Pb in soils, as well as to the presence of lead pellets resulting from hunting, which is frequent in the area (Ferre-Huguet, 2007). Moreover, lower river slopes, and a meandering behavior contribute to settle pollutants in sediments. It is important to point out that the presence of radionuclides has not been considered in the analysis. However, the water concentration of artificial radionuclides due to this nuclear power plant seems to be negligible (Pujol and Sanchez-Cabeza, 2000).

Downstream the industrial area (from SP9 to SP12), the toxicity degree seems to be reduced (Table 4). In fact, metal concentrations in sediments appeared below the benchmarks, excepting Hg. Each metal and persistent organochlorines have tended to decrease downstream these affected points. For instance, in SP12, mean values for PCBs, DDTs, HCHs, and HCB were 0.5-fold, 20-fold, 0.9-fold and 0.77-fold the

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benchmarks. In Spain, policies to control DDT river releases are still weak, and DDT production and trade are still permitted (Greenpeace, 2004).

In the Ebro Delta, Microtox® results have revealed moderate toxicity, especially for DMSO organic extracts. In this area, isolated concentrations upper than the benchmarks have been only detected for As (1.6-fold higher than the benchmark in SP16), and Ni (1.2-fold higher than the benchmark in SP19). In this zone is also common reaching total DDTs concentration between 1 and 10 times the benchmarks. In particular, macro-invertebrate species living in Delta sediments have exhibited high DDT concentrations (Pastor, 1995). In addition, the impact of agricultural activities releasing a considerable number of agrochemicals used in intensive rice crops (Terrado et al., 2007), covering the 66% of the Delta area, could be also responsible for such toxicity responses. However, further studies should be conducted to assess this issue.

Interesting findings have been obtained after applying principal component analysis (PCA) to the results concerning the monitored pollutants, including the eco-toxicological outputs and the compartmental characteristics (ammonia concentration ($N\text{-}NH_4^+$), and total organic matter (TOM)). Previous to PCA, environmental concentrations were normalized dividing them by their respective benchmark. Spearman correlation analysis was also performed to help identify possible relationships among variables. PC1 contains organic compounds (PCBs, DDTs, HCHs and HCB), Hg, and toxicity in organic phase (TU_{org}) (Table 5). PC1 explains 50.8% of the variance. It agrees with the fact that most of these compounds have been identified as released at the same point (Flix reservoir). This finding would also presume the presence of organic mercury compounds. PC2 explains 13.8% of the variance. It assembles heavy metals with similar oxidation numbers which behave as cations (Cd, Cu, Pb, Zn). In turn, PC3 explains 8.4% of the variance, grouping Cr, Ni, $N\text{-}NH_4^+$, Mn, and toxicity in aqueous phase (TU_{aq}). This group may contain soluble species, such as Cr^{6+}, ammonia and Ni cations. Finally, PC4 explains 6.6% of variance, mainly groups toxicity in organic phase (TUorg), TOM, and As. The PCA has classified both toxicity outputs in different PCs. However, a significant correlation between both, aqueous and organic, toxicity outputs was found (Spearman´s rho = 0.558, $p<0.01$). It indicates that both tests overlap responses, being complementary in the screening assessment of toxicity. The presence

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of TOM and TU_{org} in the same PC is also remarkable, despite the low variance explained by it. PCA Figures are presented as supplementary data.

Table 5. Matrix of rotated principal components*

	Principal Component			
	1 (50.84%)	2 (13.85%)	3 (8.37%)	4 (6.62%)
Cd	0.493	0.770	0.134	0.208
Cu	0.350	0.660	0.516	0.175
Hg	0.766	0.310	0.377	0.177
Pb	0.037	0.919	0.070	0.019
Zn	0.215	0.921	0.176	0.183
As	-0.008	0.164	0.321	0.727
Cr	0.323	0.405	0.573	0.430
Ni	-0.023	0.389	0.658	0.114
Mn	0.360	0.339	0.574	0.155
$N\text{-}NH_4^+$	0.173	0.037	0.766	0.064
TOM	0.209	0.174	0.096	0.713
PCBs	0.922	0.257	0.215	0.081
DDTs	0.950	0.062	0.140	0.210
HCHs	0.897	0.313	0.240	0.038
HCB	0.937	0.215	0.207	0.118
TUaq	0.443	-0.125	0.578	0.145
TUorg	0.647	-0.138	-0.123	0.617

$N\text{-}NH_4^+$: Ammonia. TOM: Total organic matter. HCB: Hexachlorobenzene. TU_{aq}=100/EC50(mg/ml) for aqueous extract. TU_{org}=100/EC50(mg/ml) for organic extract.
*Rotation method: Normalization Varimax with Kaiser. Explained variance in parenthesis.

As expected for aqueous extracts, high Spearman correlations were found between metal concentrations (Hg, Cd, Zn, Mn and Cr) and toxicity. Metals are present in water-soluble fraction and/or would remain weakly adsorbed onto the sediment matrix. Therefore, they may become bio-available and easily contaminate water. The presence of organic pollutants is probably the main responsible of toxicity results for DMSO organic extracts, since few metals have shown some correlation with Microtox® outputs. Particularly, correlations of TU_{org} with Mn and As are notable. It indicates that some of those metals could be bound to water insoluble organic compounds, as humic substances, or being present as organometallic compounds. Recently, organic arsenic has been found toxic to *Vibrio fischeri* (Fulladosa et al., 2007). Likewise, As-containing molecules are widely employed in poultry and other animals farming and agriculture. Arsenic concentrations resulted high in agricultural sites. In any case, the toxicity levels

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found in both extracts, and the high levels of POPs and metals for many sites in the studied area could negatively affect benthic communities.

It is important to remark that toxicity in sediments, evaluated by bioassays, can often be strongly influenced by natural factors known as "confounding factors". Clearly, there are multiple natural factors which contribute to the potential toxicity of sediments. A reference toxic could exhibit different toxicity responses depending on the pH, grain size, ammonia, salinity, total organic carbon, pore-water volume, and ratio of simultaneously extracted metals/acid volatile sulfide (SEM/AVS) (Lapota and Word, 2000). Between them, ammonia seems to show a significant influence in creating a reducing environment that may pose a risk of adverse effects to benthic organisms (Delistraty and Yokel, 2007). The correlation between $N\text{-}NH_4^+$ and toxicity in aqueous phase is highly significant (Spearman´s rho = 0.59, $p<0.01$). Indeed, most samples exhibiting marginal toxicity in aqueous phase showed high $N\text{-}NH_4^+$ concentration. The alkaline nature of waters in the Ebro, pH close to 8, could contribute to increase the toxicity to *Vibrio fischeri* because of the presence of unionized ammonia. No correlation between $N\text{-}NH_4^+$ and toxicity in organic phase could be detected. On the other hand, the biological effects of sulfide in sediments are poorly understood, while the influence of sulfur compounds to *Vibrio fischeri* is controversial (Salizzato et al., 1998; Delistraty and Yokel, 2007).

The organic matter has shown some relationship with toxic responses due to both, the presence of metals bound onto this sediment fraction, and the inclusion of POPs. High organic matter levels are commonly associated with fine grain sediment. Bacteria feed on organic matter and cause a chain of events, which include oxygen depletion and elevated levels of sulfide and ammonia. These are natural processes and should not be confused with contaminants of concern. It is obvious that in sediments, final toxic effects are probably a consequence of synergistic relationships between multiple pollutants present in concentrations close to protective values, as well as other factors associated to compartmental characteristics, which can not be avoided. The low matter content in the samples of the current study (<0.7%) could minimize the importance of the confounding factors in the toxicity. However, further research is necessary to elucidate the contribution of confounding factors.

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In the present investigation, it has been demonstrated that Microtox® bioassay applied to sediments provides complementary information to current analytical techniques. Additionally, Microtox® has been used to detect overall effects produced by the presence of multiple pollutants and natural contamination, which is common when conducting ecological risk assessment in real scenarios. This study also illustrates that sediments are convenient compartments to test the impact of micro-pollutants in aquatic ecosystems. Therefore, the setting of European sediment quality standards within the context of the Water Framework Directive is an urgent necessity. With regard to the studied area, an evidence of "marginal to moderate" risk to aquatic ecosystems has been found from both, chemical and screening toxicity analyses, especially downstream industrial releases, and in the area of intensive agriculture.

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6. Supplementary material

Fig. S1 shows the Principal Component Analysis of samples collected in the Low Ebro. It can be observed that most polluted sites are clearly identified by the PC1. It gives the highest PC score to the site located in the Flix reservoir (SP4). Sampling sites downstream SP4 appear ordered when going down toward the cluster, which is mainly composed by the sampling sites located in the Delta (Fig. S1 A). PC1 groups organic compounds (PCBs, DDTs, HCHs and HCB), mercury, and toxicity in organic phase. PC2 assembles heavy metals with similar oxidation numbers that behave as cations (Cd, Cu, Pb, Zn). The Figure S1 B shows that toxicity is conveniently classified by PC3 and PC4 scores, for aqueous and organic extracts, respectively. In both cases, higher PC scores are given to more toxic sites. PC3 groups Cr, Ni, N-NH_4^+, Mn, and toxicity in aqueous phase. PC4 mainly groups toxicity in organic phase, TOM, and As, even though it only explains 6.62% of the variance.

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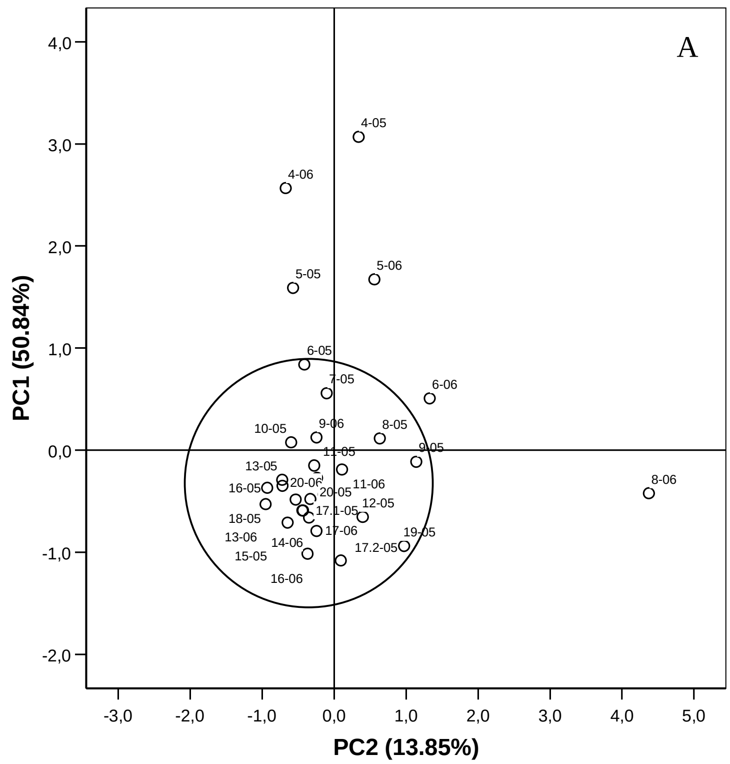

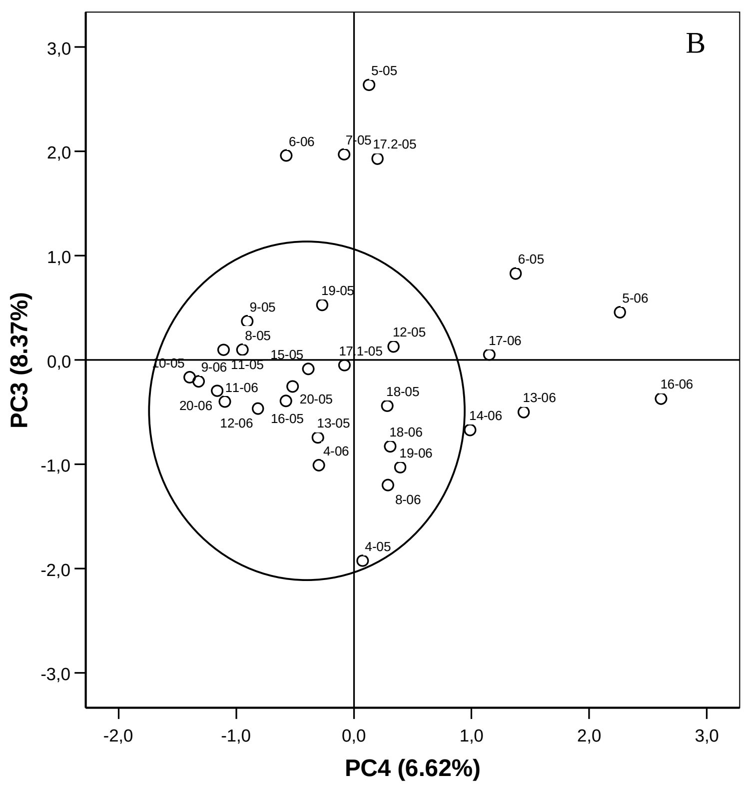

Fig. S1. Principal component analysis.

Part B. Sediment based risk assessment for rivers: A chemical and ecotoxicological fuzzy approach[5]

Abstract

Nowadays, the need to include sediment compartments in the assessment of impacts produced by anthropogenic activities stressing river ecosystems is clearly acknowledged. Sediments produce complementary findings to water compartment, specially when temporal trends are required. In this work, a methodological model has been proposed to deal with site-specific environmental risk assessment based on sediment analysis. The model uses fuzzy logic tools to manage the information and establish the relationships between the different variables. In that sense, a survey of physical-chemical, inorganic, organic, and toxicological indicators has been collected in the Ebro river, in order to test the fuzzy approach. Results suggest a clear relationship among the increased levels of pollutants and eco-toxic responses (measured as inhibitory reductions of light for photo-luminescent bacteria *Vibrio fischeri*, due to overall reduction in water and sediment quality). The model has resulted useful to estimate the likely environmental risks specially in sites located downstream important industrial releases and in areas with intensive agriculture.

Keywords: Environmental risk assessment, *Vibrio fischeri*, Ebro river, Hierarchical fuzzy inference systems.

[5] William Ocampo-Duque, Jordi Sierra, Núria Ferré, Marta Schuhmacher, José L. Domingo. Sediment based risk assessment for rivers: A chemical and ecotoxicological fuzzy approach. *Proceedings of the International Meeting on Soil and Wetland Ecotoxicology (SOWETOX 2007), Barcelona, Nov. 26-27, 2007. ISBN: 978-84-475-3247-6.*

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1. Introduction

Nowadays, the control of sediment quality is being considered as a necessary extension to the control of river water quality [1]. The protection of river sediments is needed since: sediments are both sink and potential source of contaminants to the water column [2], sediments integrate pollutant concentrations over time, whereas pollutant concentrations in water are more variables and dynamics [3], some toxic pollutants found as traces in water may accumulate in sediments to elevated levels, sediment pollutants may affect benthic and other food-chain organisms [4], and sediments are an integral part of the aquatic environment, providing habitat, feeding, and breeding areas for many organisms.

Chemical analysis provides information about contaminant concentrations, but gives little insight about bioavailability or toxicity at the site. Therefore, biological analyses combined to chemical analyses are mandatory to infer probable adverse biological effects. Different bioassays are currently in use, and most of them are often expensive and time consuming. The need for cost effective and rapid screening methodologies to assess chemical toxicity has led to the development of tests based on micro-organisms. The *Vibrio fischeri* luminescence inhibition test seems to be one of the most promising screening toxicity tests. It is able to detect toxicity for a wide spectrum of chemicals, has shown good correlation with other standard acute toxicity assays, poses few ethical problems, and is highly reproducible [5].

In a previous study (this Chapter Part A), a screening site specific ecological risk assessment based on a riparian sediment survey was conducted for the Low Ebro [6]. In this region, the river has historically been stressed by riparian industrial and agricultural activities; therefore, high concentrations of heavy metals and persistent organic pollutants in sediments have been reported, and evidence of endocrine disrupting effects in local fish has also been found. In that study, the purposes were: (1) to perform a screening toxicity study by using the *Vibrio fischeri* toxicity test bacteria for sediment samples, and (2) to search for the probable relationships among the presence of organic and inorganic pollutants, compartmental characteristics, and toxic responses in the frame of a screening ecological risk assessment. Based on the results of the previous study, the present paper introduces the use of fuzzy logic as a suitable tool for risk

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management. A hierarchical fuzzy inference system has been built to manage the collected information and to provide a final status of the probable adverse effects caused by the presence of toxic substances in sediments.

2. Methods

Fuzzy models focus on the use of heuristics for systems description. They can be seen as logical models that use "if–then" rules to establish qualitative and quantitative relationships among variables. Their rule-based nature allows the use of information expressed in the form of natural language statements. It provides a convenient basis for environmental decision-making, since models are transparent for interpretation. Fuzzy inference is supported on three concepts: membership functions, fuzzy operations, and if-then rules. A membership function (MF) is a curve that defines the degree of belongingness of a variable to a fuzzy set, which acts as a qualifier. Gaussian membership functions have been used in this work. They have the shape:

$$\mu(x,\sigma,c) = \exp\left(\frac{-(x-c)^2}{2\sigma^2}\right) \tag{1}$$

where (σ, c) are the MF parameters and μ is the membership degree. MF parameters used in this work are defined below.

The fuzzy operations used in this work were: intersection (AND), and union (OR). If two fuzzy sets *A* and *B*, are defined on a universe of discourse *X*, with membership functions μ_A and μ_B, for a given element *x* belonging to an universe of discourse *X*, then:

Intersection: $$\mu_{A\cap B}(x) = \min(\mu_A(x), \mu_B(x)) \tag{2}$$

Union: $$\mu_{A\cup B}(x) = \max(\mu_A(x), \mu_B(x)) \tag{3}$$

Finally, an if–then rule has the form: "If *x* is *A* AND *y* is *B* THEN *z* is *C*", where *A, B,* and *C* are linguistic values (or qualifiers) defined by fuzzy sets in the universes of discourse *X, Y* and *Z*, respectively. The if–part and the then–part are called antecedent and consequent, respectively.

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To design a fuzzy inference system (FIS), two parts are clearly separated: the membership functions and the inference engine (the set of rules). When designing membership functions, the ranges of the qualifiers of the inputs and outputs (i.e., fuzzy sets like: "low", "moderate", or "high"), and the shape of these qualifiers is adjusted. For the inference engine, a simultaneous process to evaluate all rules is defined. It includes the application of fuzzy operations to antecedents, the use of implication methods to transfer information from antecedents to consequents, and the employment of an aggregation method to join the consequents across all the rules, in order to make a final decision. Finally, a defuzzification process is applied to transform fuzzy outputs into numerical values. Recently, benefits of FIS have been extended to environmental science with promising results, particularly in the development of environmental indicators for water quality management [7, 8].

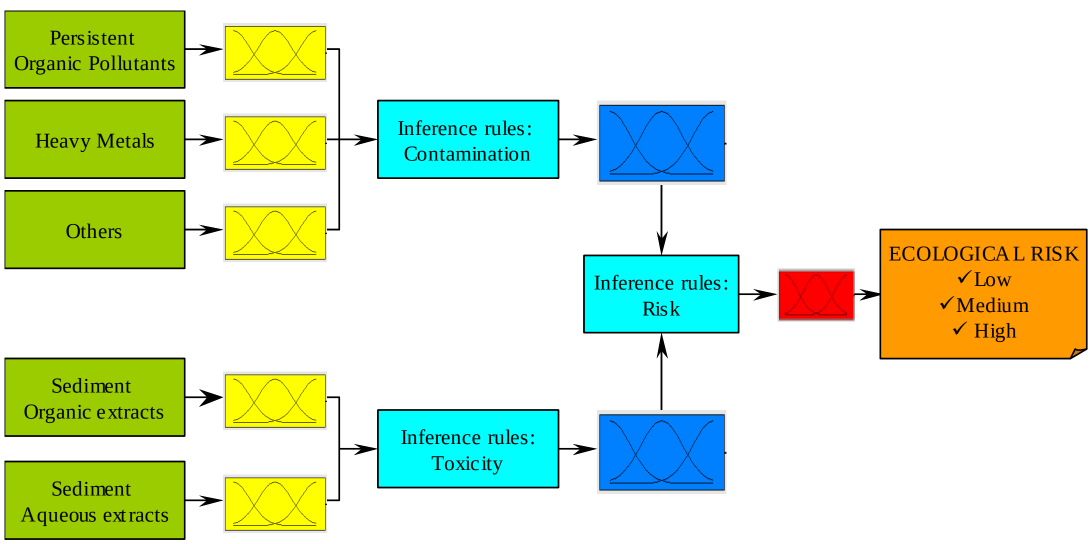

Fig. 1. Hierarchical fuzzy inference system for ecological risk assessment in river sediments.

In this work, a hierarchical FIS arrange is proposed to deal with the estimation of risk values in sediment based risk assessment. Results from chemical and eco-toxicological analyses are used as inputs in two parallel FIS to assess levels of contamination and toxicity, respectively. Results from both inference engines are then treated in a third inference engine which provides a final risk characterization. The Fig. 1 depicts the hierarchical FIS.

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In the contamination inference engine, concentrations of persistent organic pollutants, heavy metals and other relevant water quality indicators are used to provide a degree of contamination. To do so, sediment concentrations are normalized dividing them by the subsequent USEPA sediment quality benchmark [9]. Normalized concentrations are then fuzzified with Gaussian membership functions (MF). Fuzzy sets and MF parameters have been: Low (σ = 0.528, c = 0), Moderate (σ = 0.528, c = 1.2), and High (σ = 0.528, c = 2.4). The parameters σ and c were defined in equation 1. Input fuzzy sets are then used in the inference engine to give a degree of contamination. Rules within the contamination inference engine were:

If concentration is low then contamination is low
If concentration is moderate then contamination is moderate
If concentration is high then contamination is high.

Fuzzy sets and MF parameters for contamination variable were: Low (σ = 22, c = 0), Moderate (σ = 22, c = 50), and High (σ = 22, c = 100). Defuzzification is operated with the bisector method to provide a contamination score. Since each substance or indicator receives a contamination score, then the degree of contamination in a sampling site is defined as the highest contamination score between all available contamination indicators.

Results from Microtox® acute bioassays conducted on aqueous and organic extracts are used in the toxicity inference engine to give a screening toxicity score. EC50 dilution percentages and EC50 dilution levels (expressed as µL DMSO * mL^{-1} Microtox solvent) are used for aqueous and organic extracts, respectively. Details about these indicators can be consulted in [6] (this Chapter Part A). These inputs are also fuzzified with Gaussian MF. Fuzzy sets and MF parameters have been: Low (σ = 22, c = 0), Moderate (σ = 22, c = 50), and High (σ = 22, c = 100) for aqueous EC50s. In turn, fuzzy sets and MF parameters have been: Low (σ = 0.22, 0), Moderate (σ = 0.22, c = 0.5), and High (σ = 0.22, c = 1.0) for organic EC50s. Rules within the toxicity inference engine were:

If EC50 is low then toxicity is high
If EC50 is moderate then toxicity is moderate
If EC50 is high then toxicity is low.

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Fuzzy sets and MF parameters for the toxicity variable were similar to those for the contamination variable. The third inference engine integrates results from contamination and toxicity inference engines to give a risk score. Nine rules have been used:

If contamination is low and toxicity is low then risk is low
If contamination is low and toxicity is moderate then risk is moderate
If contamination is low and toxicity is high then risk is high
If contamination is moderate and toxicity is low then risk is moderate
If contamination is moderate and toxicity is moderate then risk is moderate
If contamination is moderate and toxicity is high then risk is high
If contamination is high and toxicity is low then risk is high
If contamination is high and toxicity is moderate then risk is high
If contamination is high and toxicity is high then risk is high

After rules evaluation, the risk score is calculated by defuzzification. Again, the method used has been the bisector. Likewise, fuzzy sets and MF parameters for the risk variable were similar to those used for contamination and toxicity variables.

3. Results and discussion

Table 1 displays the results after applying the hierarchical FIS model to data from the ERA study in the Low Ebro. Table 1 shows that all sites monitored in the low Ebro have shown evidence of “Moderate” and “High” risk. Cleaner sites have received a “Moderate” fuzzy score with belongingness (or certitude) equal to 1.0. Also, more polluted sites have received scores belonging to the “High” fuzzy set with an important degree of membership (or certitude) to this set (close to 0.4), leaving a possibility (close to 0.7) of the risk to belong to the “Moderate” fuzzy set.

For the sake of simplicity, in this study we have used just three fuzzy sets for all variables (i.e. low, moderate and/or high). However, the conceptual model could use a higher number of qualifiers, considering other fuzzy sets (like very low, very high, marginal, etc.) to provide a better assessment. Results exhibited here, and extracted from the hierarchical FIS agree enough with those described in [6] (this Chapter, Part A), where the overall conclusion has been “an evidence of marginal to moderate” risk to aquatic ecosystems in the studied area. Critical results, those with higher membership degrees in the high fuzzy set, coincide with industrial releases and areas of intensive agriculture.

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Table 1. Risk values (as degrees of membership) for different sites in the studied area

Site	**2005**			**2006**		
	Low	**Moderate**	**High**	**Low**	**Moderate**	**High**
SP1	0.076	1.000	0.076	0.076	1.000	0.076
SP2	0.076	1.000	0.076	0.006	0.662	0.395
SP3	0.076	1.000	0.076	ND	ND	ND
SP4	0.006	0.662	0.395	0.006	0.662	0.395
SP5	0.007	0.689	0.371	0.006	0.662	0.395
SP6	0.008	0.716	0.347	0.006	0.662	0.395
SP7	0.006	0.662	0.395	ND	ND	ND
SP8	0.006	0.662	0.395	0.006	0.662	0.395
SP9	0.006	0.662	0.395	ND	ND	ND
SP10	0.076	1.000	0.076	ND	ND	ND
SP11	0.076	1.000	0.076	0.076	1.000	0.076
SP12	0.006	0.662	0.395	0.006	0.662	0.395
SP13	0.076	1.000	0.076	0.076	1.000	0.076
SP14	0.076	1.000	0.076	0.076	1.000	0.076
SP15	0.076	1.000	0.076	ND	ND	ND
SP16	0.006	0.662	0.395	0.006	0.662	0.395
SP17	0.068	0.999	0.084	0.068	0.999	0.084
SP18	0.076	1.000	0.076	0.076	1.000	0.076
SP19	0.008	0.716	0.347	0.006	0.662	0.395
SP20	0.006	0.662	0.395	0.006	0.662	0.395

It is important to point out that in relation to the risk perception, the hierarchical FIS outputs are similar to those reported in [6] (this chapter Part A), despite the low number of qualifiers. In any case, the purpose of this paper has been to describe the advantages and the inputs required in such a novel methodology, rather than defining an optimized model. To optimize a FIS model, the nature and number of rules, as well as the most convenient shape of the membership functions, must be defined by a panel of experts in a consensus way. Furthermore, the FIS model could be fitted from field observations and expert judgment in order to develop a more robust tool. Some algorithms are already available for this task [8].

The hierarchical FIS model described above allows carrying out an Environmental Risk Assessment (ERA) from a heuristic point of view. Since "risk" should be defined as a subjective and uncertain variable which integrates a number of observations, rather than as deterministic quotient between contamination and effects of single pollutants. Therefore, the integration of fuzzy logic and ERA is promising. The flexibility of fuzzy logic to develop classification models with a simple framework, built with natural language, is timely for the development of risk indexes in which highly subjective information must be correlated. Moreover, computing with words within FIS improves the tolerance for imprecise data, a common scenario in risk assessment.

In this paper, we have described a convenient application of fuzzy logic to environmental risk assessment. The methodology adopted in this research clearly improves methods used to date. The use of fuzzy sets provides an alternative approach to current deterministic risk quotients. The approach is closer to human judgment, because of computation based on words (used as qualifiers). Moreover, the fuzzy approach takes into account the subjective nature of risk variables, a fact that is closer to real assessments at which expert opinion is conclusive. Although risk indexing processes may have many limitations, since they may suffer from the risk to miss information, their benefits are significant for decision making. In that sense, a good model should preserve the most important features of the inputs, and the fuzzy frame is appropriate to such task. Therefore, the most relevant aspect to highlight here is the methodology applied to produce the risk index, rather than the numerical or linguistic findings. The most important advantage of the fuzzy methodology is that the inference system is built with words. None equation is used within the inference engine, which is characterized to integrate high non-linear data. This is especially valuable in water management decision processes, in which variables from a very diverse nature have to be integrated.

4. Acknowledgements

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General Conclusions

In this Thesis, a suitable set of applications for decision making in water management, based on modern paradigms for environmental protection, has been designed and validated. The key success factor in methodologies here developed has been the appropriate management of the information through hierarchical and heuristic structures built with fuzzy inference systems. The flexibility of fuzzy logic for computing with simple words, expressing the expert knowledge in natural statements, to provide consistent environmental evaluations under anthropogenic driving forces, have allowed dealing easily with subjectivity and linguistic uncertainty. It has made easier to face concepts such as water quality, ecological status, or environmental risk, which are usually hard to classify and assess. It has been demonstrated that computing with words within fuzzy systems improves significantly the tolerance for the ambiguity of human thinking when perceptions and interpretations on water management issues need to be expressed and integrated. Therefore, the use of fuzzy inference systems, especially to produce self interpretable water management indicators, has resulted highly promising, and therefore strongly recommended to design conceptual models for environmental asssessment.

Interpretability has been perhaps the main feature to consider the applicability of fuzzy logic in the development of risk based water quality composite indicators. However, these artificial intelligence systems are not infalible. Some of the drawbacks of the fuzzy inference systems were clearly identified, and resolved linking them to other methodologies. These linkages have given more power to the tools here developed. The use of methods from decision theory has provided consistent ways to take into account the importance of the diverse variables considered in the assessments. In turn, learning algorithms from artificial neural networks have been so useful in building automated inference engines starting from experimental evidence. Likewise, pre-processing algorithms, such as the self organizing maps, have allowed deciphering patterns from original data prior to their presentation to the inference systems which supply the final outcomes.

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With the advantages and disadvantages of fuzzy inference systems, several appropriate indicators for water management have been designed and validated throughout this Thesis:

(1) A composite water quality index for multipurpose analysis in rivers, which integrates diverse pollution indicators, such as macrovariables, nutrients, organic pollution, local priority micro-contaminants, and pathogens.

(2) An automated classification model to integrate physicochemical, morphological and biological indicators, to estimate the ecological status in rivers.

(3) A conceptual methodology for screening ecological risk assessment in rivers, based on the estimation of ecological risk potentials, which give an idea about the likely hazards posed by the presence of dangerous substances in aquatic ecosystems. These risk potentials are conveniently integrated by means of empirical cumulative distributions to assess the evolution in water pollution in river basins over time. Likewise, the ecological risk potentials help finding those substances which need stricter control of emissions, in order to prevent impairment of ecosystems.

(4) A sediment-based screening risk assessment methodology based on linguistic risk estimation, which delivers the level of risk in catchments through the monitoring of chemicals of concern, such as metals and persistent organic pollutants, and the application of ecotoxicity tests using biological responses to measure toxic effects which provide integrated information about the significance of chemical contamination. In that sense, the tests based on *Vibrio fischeri* bioluminescence inhibition have offered rapid, easy-to-use and cost effective responses for the toxicity assessment in real complex situations.

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Annex

Desarrollo de un modelo para la gestión de cuencas hidrográficas basado en evaluación de riesgo ambiental: Experiencias europeas y aplicación a ríos colombianos[6]

Resumen

Un recurso natural cuyo valor ha cobrado gran importancia mundial es la diversidad biológica. En Latinoamérica, este recurso se está perdiendo a una tasa acelerada debido principalmente a la desaparición de los ambientes naturales como consecuencia del incremento de la actividad industrial y de un desarrollo mal planificado. Actualmente se reconoce que la protección de ambientes naturales, se sustenta en una apropiada gestión integral del agua, como se reconoce en la legislación Europea, conocida como "Directiva Marco del Agua". En esta se manifiesta que todas las aguas deben protegerse para garantizar un estado ecológico bueno. Ante esta visión, se hace necesario establecer herramientas y modelos de gestión fundamentados en la protección y recuperación de ecosistemas acuáticos, principalmente aquellos que se destacan por su riqueza biológica, con el propósito de conservar y fomentar la diversidad biológica. Al conservar estas zonas se garantiza la continuidad de los procesos vitales de poblaciones naturales de un número importante de organismos.

La cuenca del río Cauca, que se caracteriza por una alta heterogeneidad ambiental debido a sus características geológicas y climáticas que garantizan alta disponibilidad de nichos ecológicos y buena oferta de biodiversidad, requiere de adecuadas herramientas para sus modelos de gestión de los recursos naturales. Además, la demanda actual del agua para diversos usos: doméstico, industrial y agrícola, requiere de una gestión eficiente del recurso hídrico. De forma particular, en el entorno colombiano existe una carencia de metodologías adecuadas para gestionar los riesgos por presencia de sustancias químicas peligrosas en las aguas y sus probables efectos

[6] William Ocampo-Duque y Marta Schuhmacher. Desarrollo de un modelo para la gestión de cuencas hidrográficas basado en evaluación de riesgo ambiental: Experiencias Europeas y aplicación a ríos colombianos. *Memorias del 50º Congreso de la Asociación Colombiana de Ingeniería Sanitaria y Ambiental(ACODAL) y 12º Congreso Bolivariano de AIDIS. Santa Marta (Colombia), 12-14 septiembre de 2007*

sobre la salud de las personas y los ecosistemas. A nivel Europeo, se están estableciendo mecanismos para la gestión sostenible de las cuencas, fundamentados en conceptos de gestión y análisis de estos riesgos. En el presente proyecto, se ha desarrollado un modelo metodológico que permite una evaluación del riesgo ambiental por presencia de agentes contaminantes en el río Cauca. Esta herramienta se fundamenta en reglamentaciones internacionales vigentes y en procedimientos ampliamente aceptados para la evaluación del riesgo. En este trabajo se presentan algunos resultados del modelo conceptual que se está proponiendo para analizar la contaminación en el río Cauca en la zona del Departamento del Valle del Cauca. Los resultados demuestran que se deben proponer mecanismos para reducir la presencia de sustancias micro-contaminantes que pueden afectar seriamente la salud de las personas y los ecosistemas.

Palabras clave: Evaluación de Riesgo Ambiental, Análisis Monte Carlo, Pesticidas, Microtox®, río Cauca.

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1. Introducción

La Directiva Marco del Agua (DMA), establecida en el año 2000 en la Unión Europea (Correlje et al., 2007), se ha convertido en un documento rector que ha despertado muchas esperanzas para las personas interesadas en la protección y conservación de la calidad medio ambiental de los ríos. La DMA pretende establecer una regulación de todo el ciclo hidrológico para poder garantizar en el futuro la conservación y recuperación de todos los ecosistemas acuáticos, dando una importancia fundamental a la situación de las comunidades biológicas que viven en los diferentes ecosistemas. La directiva ha acuñado el concepto de estado ecológico que está llamado a ser un elemento fundamental para la mejora de los ecosistemas acuáticos.

De acuerdo con el profesor Narcís Prat, de la Universidad de Barcelona, con el advenimiento de la DMA debe generarse una "Nueva Cultura del Agua", en la que se garantice que el agua sea utilizada por todas las especies, de tal manera que las funciones ecológicas de los ecosistemas no queden alteradas a la vez que se usa el agua en beneficio propio. Hoy en día una sola especie, la humana, utiliza de forma directa o indirecta una gran parte del agua dulce del planeta (hasta un 50% de los recursos fácilmente utilizables) para sus intereses, sea para beber, para regar, para producir electricidad o para navegar. Pocos rincones quedan sin su intervención, y en algunos casos el 100% del agua que circula por una cuenca está siendo empleada para usos humanos. Hay ríos en España, en los cuales debido a la inapropiada gestión, se ha conseguido que este no llegue al mar, que toda el agua sea usada por el hombre sin que circule por el lecho del río (Prat, 2001). La nueva cultura del agua no es otra cosa que la observación del respeto por los recursos naturales que han promulgado las grandes culturas de la humanidad a través de la historia. Es la misma visión de los pueblos indígenas latinoamericanos, ajustada a las necesidades actuales.

La conservación del funcionalismo de los ecosistemas acuáticos es el aspecto clave que implica la nueva Directiva Marco del Agua (DMA) de la Unión Europea. Pero a fin de que los ecosistemas acuáticos mantengan su funcionalismo próximo a un sistema sin afección humana, o en el caso de los sistemas muy modificados llegar al máximo potencial ecológico, son necesarios cambios profundos en los actuales modelos de gestión del agua, cambios que afectan a cómo se gestiona el recurso de forma

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cuantitativa, cómo se gestiona la calidad del agua por los diferentes usos, la manera como los sistemas de ribera son gestionados, y en general la política de ordenamiento territorial. La Nueva Cultura del Agua se tiene que aplicar a cada uno de estos aspectos para alcanzar los objetivos de la conservación o restauración de los ecosistemas acuáticos. Hay que reconocer que los ríos, los lagos, los embalses y las marismas pueden mantener un buen estado ecológico, con una comunidad biológica que conserve su funcionalismo cercano a las condiciones que existían cuando el ser humano no era tan omnipresente en el territorio, solamente si se logra conservar la cantidad y la calidad del agua. Este capítulo anexo trata de la Calidad del Agua en el río Cauca.

El río Cauca en su recorrido por el Departamento del Valle presenta serios problemas de polución. Estos se encuentran asociados con el uso inadecuado del suelo, las descargas de aguas de uso doméstico de los centros urbanos, entre los que se encuentra la ciudad de Cali, los aportes de aguas residuales de las industrias, la explotación minera, los procesos de deforestación y la contaminación por el inadecuado manejo de los residuos sólidos procedentes de los municipios. Esto ha producido un deterioro creciente de la calidad del agua del río. En el área de jurisdicción de CVC (corporación autónoma regional del valle del Cauca, entidad de protección ambiental regional), se cuenta con alto conocimiento, al menos de las variables macroscópicas, de la calidad del agua en la cuenca y de los vertimientos generados en las diferentes actividades, debido a que se realizan monitoreos sistemáticos desde 1980, a lo largo de 19 estaciones (Figura 1).

En estos puntos se determinan periódicamente variables tales como: pH, Temperatura, Color, Turbiedad, Sólidos, DBO, DQO, Oxígeno Disuelto, Durezas, Calcio, Magnesio, Alcalinidades, Sulfatos, Fosfatos, Fósforo Total, Nitrógeno Total, Nitrógeno Amoniacal, Nitratos, Nitritos, Hierro, Manganeso, Sodio, Potasio, Cobre, Zinc, Cadmio, Cromo, Níquel, Plomo, Cloruros, Coliformes Totales y Coliformes Fecales. La contaminación por materia orgánica, la alta presencia de patógenos, la gran carga de sólidos y las preocupantes bajas concentraciones de oxígeno disuelto en un trayecto importante, son las variables que ha tenido en cuenta CVC para establecer objetivos de calidad hacia el año 2015 (CVC, 2006). Sin duda, todos los esfuerzos de la entidad ambiental y de los usuarios del agua y de la población en general, deberán destinarse a cumplir estas metas. Un número importante de familias se benefician del

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agua del río, la bocatoma de la planta de potabilización que suministra gran parte del agua de Cali, se encuentra en un punto de alta contaminación del río, lo que incrementa sustancialmente el costo del tratamiento. También, la salud de los trabajadores que extraen arena, la calidad del agua para el riego agrícola y para los diversos usuarios y la salud de las familias ribereñas se ven comprometidas por causa de la contaminación.

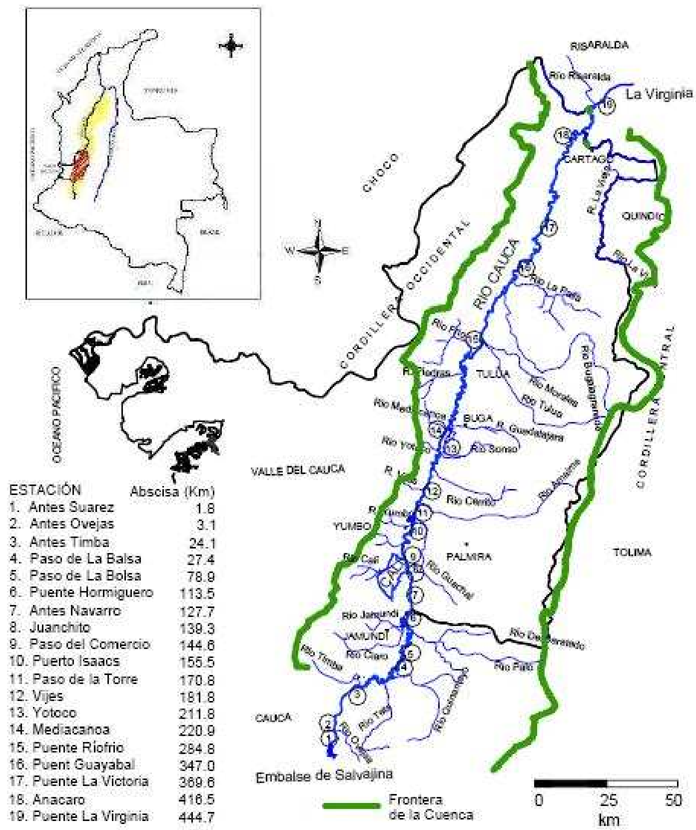

Figura 1. Estaciones de monitoreo de CVC en el río Cauca.

Para la protección efectiva del medio ambiente, se deben controlar tanto los indicadores macro-contaminantes, como los micro-contaminantes (Ocampo-Duque et al., 2006). El Valle del Cauca, por ser una región eminentemente agrícola, con 200.000 hectáreas sembradas de caña, puede presentar cantidades significativas de pesticidas en sus aguas, sedimentos y biota. Asimismo, la presencia de grandes asentamientos industriales en la región, destacando la producción de pulpa y papel, las artes gráficas, la industria química y la metalmecánica, sugieren una posible presencia de sustancias peligrosas, que debe ser perjudicial para el estado ecológico del río. Los impactos

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negativos por la presencia de sustancias peligrosas (micro-contaminantes) se evalúan apropiadamente, siguiendo la metodología de evaluación de riesgo (Laenge et al., 2006).

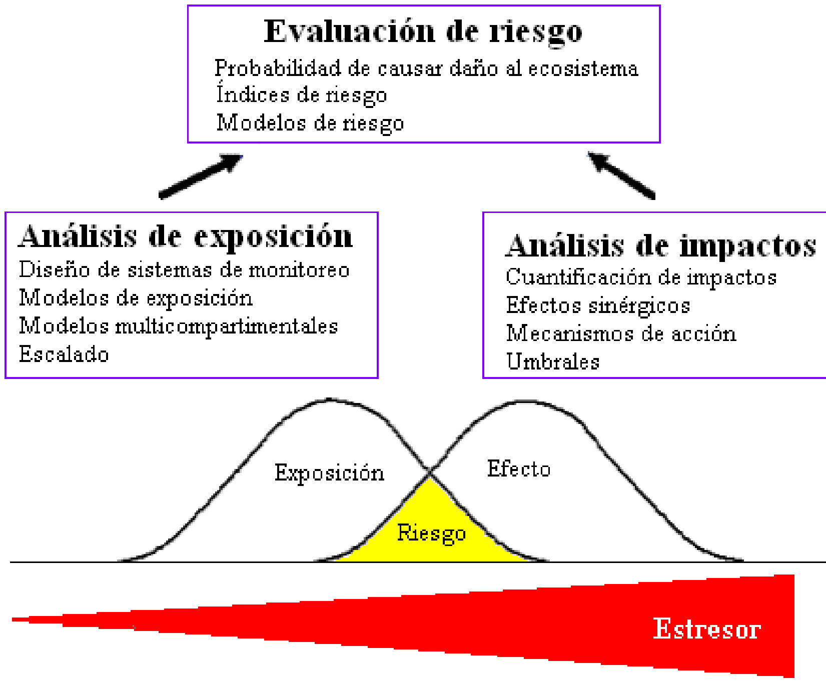

Figura 2. Marco conceptual para la gestión del riesgo ambiental.

2. Metodología

El marco conceptual de las evaluaciones de riesgo ambiental (Figura 2) utilizadas para la toma de decisiones en la gestión de ríos y sus ecosistemas consta de las siguientes etapas:

a. Identificación de la naturaleza del problema. Después de seleccionar las áreas de interés (ecosistemas estratégicos, como es el caso de la Laguna de Sonso, en el Valle del Cauca, o los bosques de ribera), se bosquejan los posibles impactos por presencia de productos químicos presentes en las aguas y sedimentos, como consecuencia de las emisiones de las industrias locales, se colecta e integra la información sobre las características de movilidad, toxicidad y persistencia de los presuntos contaminantes y la probable cuantificación de fuentes de emisión.

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b. Análisis de la exposición. Se estiman los efectos producidos por procesos de transporte y degradación de los contaminantes y el posible destino hacia los ecosistemas del río. Para complementar la información de campo, se puede recurrir a modelos de simulación de múltiples medios. También se aplican índices de contaminación o alteración de la calidad de las aguas y se formulan estrategias de monitoreo necesarias para completar los análisis.

c. Análisis de impactos. Se evalúa el impacto desfavorable en el ecosistema, mediante la cuantificación de parámetros indicadores de la contaminación con énfasis en la protección de ecosistemas acuáticos. Se buscan impactos químicos mediante el análisis de concentraciones ambientales de compuestos orgánicos e inorgánicos presentes. Finalmente, se correlacionan con bio-ensayos eco-toxicológicos y con estándares máximos permisibles de calidad para el agua, establecidos por agencias ambientales internacionales y por la comunidad científica.

d. Evaluación del riesgo. Integra los resultados de la evaluación de los potenciales de exposición con los impactos, a fin de estimar el potencial de daño ecológico y hacia la salud humana. Hay diversas técnicas para estimar los riesgos. El procedimiento normal consiste en comparar los niveles de exposición a los cuales está expuesta o puede estar expuesta una población con los niveles a los cuales no se espera que ocurran efectos tóxicos. Actualmente, se están utilizando métodos de la teoría de la probabilidad y de la posibilidad para el tratamiento de la variabilidad y la incertidumbre de las variables, con el fin de estimar los umbrales del daño. Finalmente, los estimativos de riesgo se pueden gestionar mediante sistemas de información geográfica.

La evaluación de riesgo ambiental se divide en dos grandes ramas: la evaluación del riesgo para la salud humana y la evaluación del riesgo ecológico. El riesgo para la salud humana está a su vez subdividido en: riesgo cancerígeno y riesgo no-cancerígeno. Este último es el riesgo potencial para la salud y se expresa como un cociente de peligrosidad *HQ* (hazard quotient). En términos generales, el riesgo se produce como una combinación de la dosis y de la peligrosidad de la sustancia. La dosis debe estimarse a partir de mediciones en campo de las concentraciones de los contaminantes en las diferentes matrices (agua, sedimentos, biota, aire) o mediante modelos de

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transporte, en el caso de que se quieran estimar los riesgos aguas abajo de una fuente puntual de emisión.

La peligrosidad es una función de parámetros tales como la persistencia, el potencial de bio-acumulación y la toxicidad. En el caso del riesgo carcinogénico, la peligrosidad se determina a partir del factor de cáncer *CSF* (cancer slope factor). Para la estimación del *HQ*, el indicador de peligrosidad que se utiliza, se conoce como la dosis de referencia, *RfD* (Reference dose). Para estimar el cociente de riesgo ecológico (*EcoRisk*), se utilizan benchmarks, los cuales son valores para los cuales existe la certeza de que los efectos sobre las poblaciones biológicas pueden ser mínimos. Generalmente, los benchmarks se fijan para proteger las especies más sensibles a la polución, es decir, se fijan teniendo en cuenta el principio de precaución (EPA, 2001).

De acuerdo con lo anterior, los valores de riesgo en cada caso, se pueden estimar mediante:

$$CDI = \frac{C * IR * EF * ED}{BW * AT}, \quad Risk = CDI * CSF, \quad HQ = \frac{CDI}{RfD}, \quad EcoRisk = \frac{C}{BM}$$

donde, *CDI*: ingesta crónica del contaminante (mg/kg/día), *C*: concentración del contaminante en agua (mg/L) *IR*: velocidad de la ingestión (L/día para agua), *EF*: frecuencia de la exposición (días/año), *ED*: duración de la exposición (año), *AT*: tiempo promedio (días), *BW*: peso medio de un individuo (kg), *RfD*: dosis de referencia (mg/kg/día), *CSF*: factor de cáncer $(mg/kg/día)^{-1}$, *Risk*: nivel de riesgo cancerígeno, *BM*: benchmark protectivo para ecosistemas acuáticos (mg/L).

3. Resultados y discusión

En el año 2006, la CVC ha realizado una campaña para el monitoreo de la presencia de algunos pesticidas en las aguas del río Cauca. En total se han determinado 4 pesticidas organo-fosforados y 16 organo-clorados. Algunas de las sustancias detectadas corresponden a sub-productos de la descomposición de los pesticidas originales (como la endrin-cetona que se produce por descomposición fotoquímica del Endrin). A continuación se presentan los resultados de la evaluación del riesgo ambiental que se ha llevado a cabo para dichos pesticidas. La evaluación de riesgos se

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ha llevado a cabo utilizando simulación Monte Carlo. Este es un método probabilístico sugerido por la Agencia de protección Ambiental Americana (EPA)(EPA, 2001).

Con este método se emplean distribuciones de probabilidad para caracterizar las variables dentro de las ecuaciones del riesgo, en vez de utilizar estimaciones puntuales. De esta manera, el valor resultante en el cálculo del riesgo es un rango y no un valor puntual. Así, los valores resultantes dentro del rango calculado para el riesgo tienen unas probabilidades asignadas, conocidas como percentiles. Con este método se manejan adecuadamente tanto la variabilidad como la incertidumbre de las variables, con lo que se pueden obtener mejores estimaciones del riesgo, ya que se consideran los valores más (y/o menos) probables a la hora de la toma de decisiones ambientales.

En este trabajo se han utilizado los resultados de la campaña de monitoreo de CVC para estimar los riesgos hacia la salud y hacia los ecosistemas por la presencia de pesticidas. Los *CSF* y las *RfD* fueron tomadas de la base de datos IRIS de la EPA. Se tomaron los *BM* sugeridos por EPA, algunos de los cuales aparecen en la Tabla 1. Se estimó un margen de incertidumbre de un 10% en el valor central sugerido por EPA, para llevar a cabo las simulaciones. Las otras variables se tomaron como funciones probabilísticas usando valores sugeridos por agencias internacionales y por criterios expertos. Así: *IR lognormal*(0.25,0.025) , *ED lognormal*(71.14, 7.11), *EF triangular*(0, 182.5, 365), *BW* lognormal(70, 7) y *AT* se tomó como valor puntual igual a 25 550 días.

Riesgos de cáncer: De las pruebas realizadas con animales, existe suficiente evidencia científica para decir que los pesticidas organoclorados con más de cinco cloros en su molécula presentan efectos carcinogénicos. El riesgo carcinogénico admisible según la EPA, es del orden de 1.0E-06 para cualquier sustancia tóxica. Este valor implica que una persona en un millón, tendría probabilidades de desarrollar cáncer como consecuencia de la exposición crónica a dicha sustancia. De acuerdo con las estimaciones llevadas a cabo en este trabajo, se han encontrado estimaciones de riesgo del orden de 1.0E-04 para aldrin, y 1.0E-05 para alfa-lindano y heptacloro epóxido, en aquellos sitios en los que se encontraron las concentraciones más elevadas. Los resultados obtenidos mediante simulación Monte Carlo se muestran en la Figura 3, para estos tres pesticidas, en los sitios con máximas concentraciones reportadas. Se exhiben como distribuciones de probabilidad y/o como funciones de probabilidad acumulada.

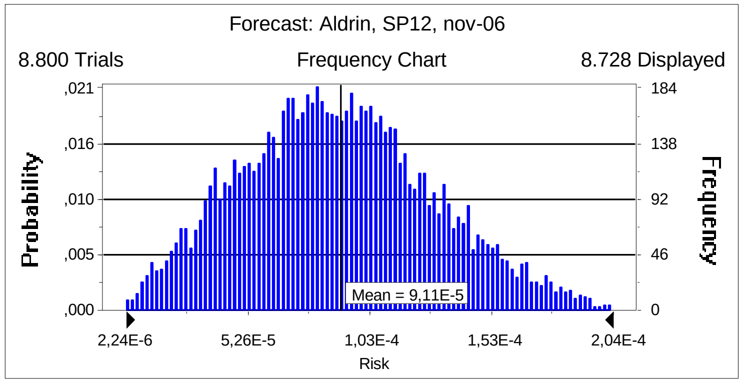

Figura 3a. Valor de riesgo cancerígeno para Aldrin en la estación SP12 (Vijes) durante el muestreo de noviembre 2006.

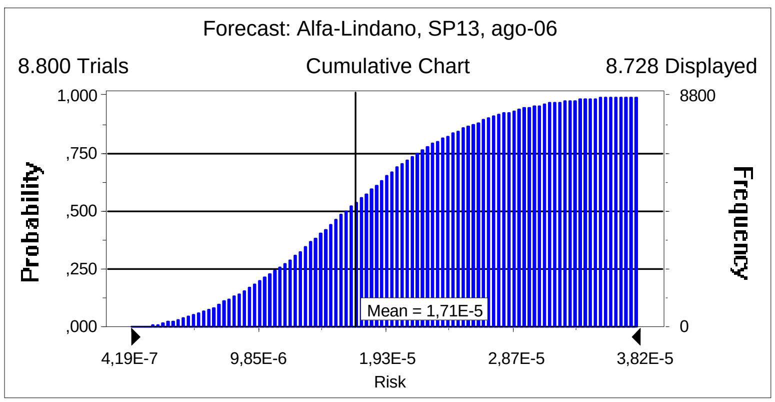

Figura 3b. Valor de riesgo cancerígeno para alfa-lindano en la estación SP13 (Yotoco) durante el muestreo de agosto de 2006.

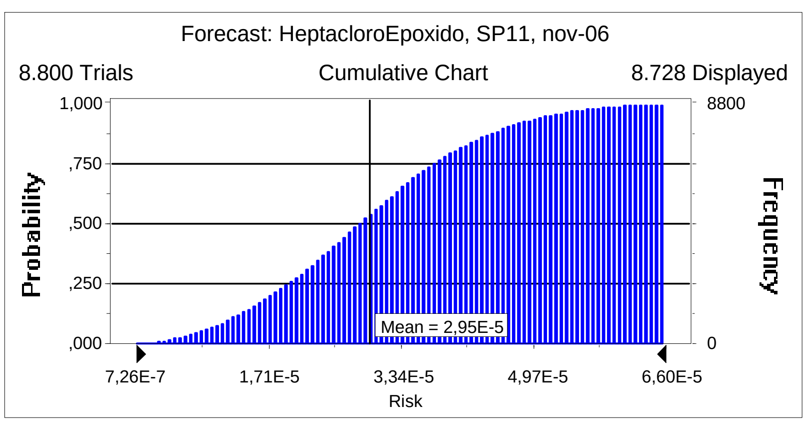

Figura 3c. Valor de riesgo cancerígeno para heptacloro epóxido en la estación SP11 (Paso de la Torre, Yumbo) durante el muestreo de noviembre de 2006.

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De acuerdo con los resultados anteriores, se puede decir que los tres pesticidas se han encontrado en concentraciones preocupantes en algunas zonas del río Cauca. También hay áreas con bajas concentraciones, que pueden suponen valores de riesgo bajos. La gran variabilidad geográfica hace suponer que los contaminantes provienen de fuentes difusas (agricultura). En términos de salud humana, la situación es preocupante ya que en el área existe una buena cantidad de empresas de extracción de arena en las que laboran muchas personas, por tratarse de un proceso altamente artesanal. También muchos niños son expuestos al agua del río ya que viven en las riberas y se bañan en él, así que la exposición dérmica puede incrementar el riesgo.

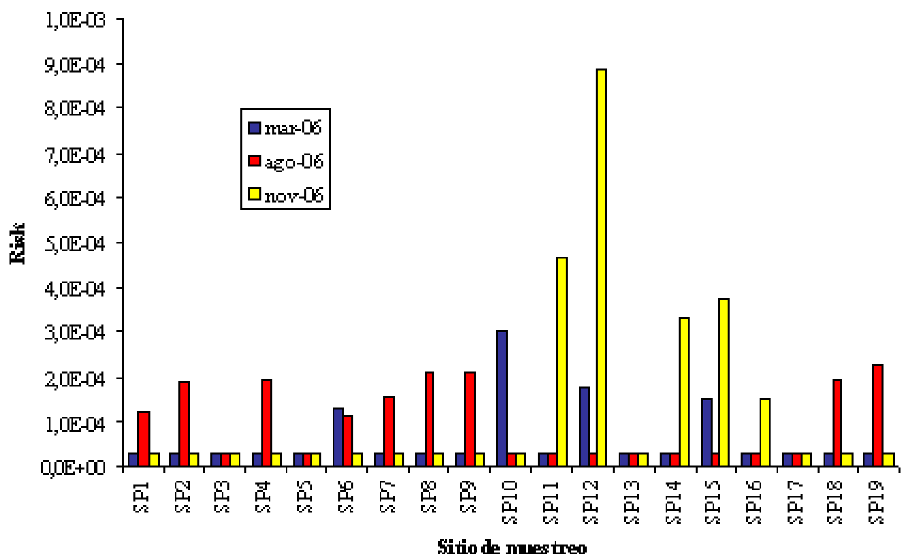

Figura 4. Valores de riesgo cancerígeno (percentil 95) para aldrin en las estaciones de monitoreo de CVC durante 2006. Valores de fondo corresponden a la mitad del límite de detección reportado.

En este estudio se han tomado los resultados de los monitoreos en tres meses marzo, agosto, noviembre. Se debe esperar que las concentraciones sean más elevadas durante los meses de verano porque el caudal del río se reduce sensiblemente. En la Figura 4 se muestran la variabilidad temporal y geográfica para el pesticida aldrin. La zona con mayor valor de riesgo corresponde a la SP12 (Vijes), para el mes de noviembre. También, existen otras zonas con valores de riesgo preocupantes. En agosto aparece un mayor número de sitios (9 de 19) con valores de riesgo superiores a 1.0E-05. En noviembre de 2006 aparecen 4 sitios de muestreo con valores de riesgo del orden de

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1.0E-5, y un valor en el orden de 1.0E-04. El aldrin es una sustancia de uso prohibido según la Agencia de protección ambiental de los Estados Unidos. Valores similares se obtienen para los otros pesticidas clorados.

Riesgo no-cancerígeno: A diferencia de los valores presentados anteriormente, en la zona de estudio los *HQ* alcanzan siempre valores menores que la unidad. Se considera seguro para la salud humana un $HQ<1$, pero este valor tiene en cuenta efectos diferentes a los cancerígenos. Los valores máximos de *HQ* corresponden nuevamente a los pesticidas organoclorados, aldrin y heptacloro epóxido, con valores (percentiles 95) del orden de 0.636 y 0.848. En este caso, considerando sólo las concentraciones de los pesticidas se puede asegurar que las concentraciones encontradas en el río Cauca no presentarían efectos negativos hacia la salud humana.

Tabla 1. Cocientes de peligrosidad *HQ* para los pesticidas monitoreados en el río Cauca, región Valle del Cauca

Sustancia	***HQ***			**Localidad**	**Fecha**
	percentil 10	**percentil 50**	**percentil 95**		
Diazinon	3.48E-03	8.65E-03	2.96E-02	SP14, Mediacanoa	ago-06
Metil paratión	6.84E-04	1.70E-03	5.71E-02	SP8, Juanchito	ago-06
Malatión	4.80E-05	1.16E-04	3.23E-04	SP12, Vijes	ago-06
Clorpirifos	6.04E-03	1.47E-02	4.01E-02	SP14, Mediacanoa	ago-06
Heptacloro	8.62E-04	2.20E-03	7.84E-03	SP6, Puente Hormiguero	nov-06
Aldrin	7.22E-02	1.75E-01	6.36E-01	SP12, Vijes	nov-06
Heptacloro epóxido	1.00E-01	2.44E-01	8.48E-01	SP11, Paso de la Torre	nov-06

Riesgo ecológico: En el caso del análisis de riesgo ecológico, se han tomado los valores de referencia (o benchmarks) sugeridos por la EPA para aguas de ríos y se han utilizado funciones probabilísticas triangulares para parametrizar la incertidumbre del benchmark, con una incertidumbre del 10% para cada benchmark. La Tabla 2 muestra los valores máximos obtenidos para el parámetro *EcoRisk* en la zona del Valle del Cauca. Como se puede ver en la Tabla, se han encontrado concentraciones máximas de pesticidas que sobrepasan en varios órdenes de magnitud los valores de referencia sugeridos por la comunidad internacional. Siendo los casos más críticos aquellos localizados entre Yumbo y Mediacanoa, para los pesticidas clorpirifos, heptacloro y heptacloro epóxido, con valores *EcoRisk* del orden de 800, 320 y 930, respectivamente. Los valores del parámetro *EcoRisk* deberían ser menores que uno para que no exista

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ningún nivel de alerta, por tanto los niveles de alerta aquí tienen que ser máximos. Según la Tabla, los valores máximos se han obtenido en el mes de agosto. Estos valores tan significativamente altos ponen en riesgo la salud de los ecosistemas del río, tanto las comunidades de invertebrados como los peces y las aves que se benefician del agua del río, poniendo en peligro la alta biodiversidad de la zona. En realidad, muchas especies biológicas son considerablemente más sensibles a la contaminación que los humanos, de allí que los valores para proteger las comunidades biológicas se consideren seguros también para los humanos, y se haga actualmente tanto énfasis por parte de la comunidad científica en el buen estado ecológico de los ríos. Como se muestra más adelante, el uso de varias de estas sustancias se ha prohibido en algunos países por el alto nivel de riesgo ambiental que representan.

Tabla 2. Cálculos estocásticos del índice *EcoRisk* para las concentraciones máximas de pesticidas monitoreados en el río Cauca, región del Valle del Cauca

Pesticida	**Benchmark (µg/L)***	*EcoRisk* **Percentil 10**	**Percentil 50**	**Percentil 95**	**Localidad**	**Fecha**
Diazinon	0.043	9.52	10.05	10.78	SP 14, Mediacanoa	ago-06
Metil Paration	0.008	28.20	29.77	31.90	SP 8, Juanchito	ago-06
Malation	0.097	14.45	15.26	16.37	SP12, Vijes	ago-06
Clorpirifos	0.0035	761.23	803.59	863.09	SP14, Mediacanoa	ago-06
Heptacloro	0.0019	301.88	318.39	341.79	SP 6, Jamundí	nov-06
Aldrin	3.000	0.92	0.97	1.05	SP 12, Vijes	nov-06
Heptacloro epóxido	0.0019	882.58	930.99	998.92	SP 11, Yumbo	nov-06

*Valores sugeridos por USEPA, Fuente: http://www.epa.gov/

El esfuerzo de CVC por monitorear pesticidas es valioso pero limitado. La cantidad de sustancias tóxicas emitidas por la agricultura debe ser sustancialmente mayor, por lo que muchos compuestos no se monitorean. Además, algunas sustancias peligrosas son adsorbidas por los sedimentos y el material particulado. La presencia de sustancias peligrosas en la biota (invertebrados, peces y aves) también debería ser monitoreada, ya que los efectos sobre los ecosistemas deben vigilarse. Estas matrices no hacen parte de las campañas de monitoreo todavía, y deberían ser incluidas en los años venideros. Muchas sustancias peligrosas presentan riesgos significativos para la salud humana debido a la capacidad de persistir en el medio ambiente y de migrar a través de la cadena trófica. Con urgencia, a nivel nacional (en Colombia) se debe emprender la tarea de establecer los valores de referencia (benchmarks) protectivos para los ecosistemas acuáticos tanto marinos como de aguas dulces, con el fin de tomar medidas

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para reducir los peligrosos efectos de la contaminación sobre los ecosistemas y sobre la salud humana.

Asimismo, los límites de detección que se han usado para estas determinaciones son relativamente altos (200 ng/L, para la mayoría de pesticidas) considerando la peligrosidad de las sustancias que se están analizando. En España, se han establecido límites de 100 ng/L para las sustancias prioritarias de la DMA y 1000 ng/L cuando el pesticida reviste poca peligrosidad. Igualmente, cuando se carece de estándares de calidad ambiental, como en el caso de los valores permisibles para proteger la fauna bentónica, es decir, valores benchmarks para sedimentos, el objetivo se fija como la reducción anual, o al menos que los valores no incrementen en el tiempo. En el caso de cultivos estacionales, los muestreos se hacen durante cierta época del año, este no es el caso colombiano, ya que se cultiva caña de azúcar durante todo el año. Asimismo, la lista carece de pesticidas ampliamente usados en cultivos de caña, tales como: glifosato (round-up), captano, carbofurano (Furadam 5G), Aldicarb (Temik 10G), o benomil (benlate) (Victoria et al., 1995). Pesticidas como atrazina, diuron, dieldrin, ametrina, y simazina, también han sido detectados en sedimentos de canales de irrigación de cultivos de caña (Muller et al., 2000) y por tanto deberían monitorearse.

La Tabla 3 muestra los niveles de riesgo genérico para algunos pesticidas asociados con cultivos de caña de azúcar en diferentes partes del mundo. El riesgo genérico se ha establecido en nuestro grupo de investigación a partir de diversos indicadores: dosis, persistencia en el medio ambiente, capacidad de bio-acumulación y toxicidad a humanos, mamíferos, abejas y peces, así como el potencial de transporte hacia zonas remotas (Juraske et al., 2007). La *ADI* en la Tabla 3 corresponde a la *Acceptable Daily Intake*, es decir a la cantidad diaria que una persona podría recibir por vía oral, sin que se presenten problemas para la salud. Este parámetro lo ha establecido la Organización Mundial de la Salud.

4. Propuesta para el control de la contaminación por sustancias peligrosas

Los daños causados por la contaminación de las aguas son enormes y generan altos costos sociales y privados. Sin embargo, evitar estos daños debe hacerse de manera efectiva y con el mínimo costo posible para una economía que necesita tasas de

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crecimiento sostenidas. Las tasas retributivas por vertimientos puntuales, establecidas por la Ley 99 de 1993 y reglamentadas en el Decreto 901 de 1997, son un instrumento económico diseñado para minimizar el costo total de cumplimiento de una meta regional concertada con la comunidad. El objetivo es inducir a quienes vierten contaminantes a las aguas a implementar su opción de descontaminación menos costosa e incentivar la innovación tecnológica en opciones de mínimo costo. Se cobran por los vertimientos puntuales de carga contaminante de Demanda Bioquímica de Oxígeno (DBO_5) y de Sólidos Suspendidos Totales (SST). A Diciembre de 2003, las tasas retributivas tenían un costo de 74.24 \$COP/kg y 31.75 \$COP/kg, para DBO_5 y SST, respectivamente. Sin embargo, estos dos parámetros son insuficientes para "penalizar" de manera efectiva el "costo de la contaminación".

Tabla 3. Niveles de riesgo para pesticidas asociados con cultivos de caña

#	**Pesticida**	**Riesgo genérico***	**Uso**	**ADI (mg/kg/día)**	**Observaciones**
1	Aldicarb	Muy alto	Insecticida	3.00E-03	
2	Aldrin	Muy alto	Insecticida	1.00E-04	Prohibido en USA
3	Ametrina	Bajo	Herbicida	1.50E-02	
4	Atrazina	Muy alto	Herbicida	5.00E-03	
5	Benomil	Moderado	Fungicida	3.00E-02	
6	Captano	Moderado	Fungicida	3.00E-01	
7	Carbofurano	Alto	Insecticida	2.00E-03	
8	Clorpirifos	Muy alto	Insecticida	3.00E-03	
9	DDT	Muy alto	Insecticida	2.00E-03	Prohibido en USA
10	Diazinon	Muy alto	Insecticida	1.00E-03	
11	Dieldrin	Muy alto	Insecticida	1.00E-04	Prohibido en USA
12	Diuron	Muy alto	Herbicida	1.00E-02	
13	Endosulfan sulfato	Moderado	Insecticida	8.00E-03	
14	Endrin	Muy alto	Insecticida	2.00E-04	Prohibido en USA
15	Glifosato	Moderado	Herbicida	3.00E-01	
16	Heptachlor epoxide	Muy alto	Insecticida	5.00E-04	Prohibido en USA
17	Heptacloro	Muy alto	Insecticida	5.00E-04	Prohibido en USA
18	Lindano	Muy alto	Insecticida	3.00E-03	
19	Malatión	Alto	Insecticida	5.00E-02	
20	Metil Paratión	Muy alto	Insecticida	2.00E-04	
21	Simazina	Muy alto	Herbicida	5.00E-03	

*Definido de acuerdo con (Juraske et al., 2007)

Se deberían entonces utilizar parámetros adicionales con los que se puedan determinar los efectos de los contaminantes sobre la salud de los ecosistemas. La Toxicidad a una especie sensitiva, como tercer parámetro dentro de las tasas

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retributivas, podría ser un indicador razonable y apropiado para gestionar los costos de la contaminación. Además de la cantidad de los vertidos, su grado de peligrosidad (toxicidad) puede generar un mayor (o menor) deterioro de la calidad ecológica. Es claro que una sustancia muy tóxica que se encuentre presente aún en bajas concentraciones puede producir más daños ambientales que una sustancia poco tóxica que se descargue en cantidades importantes. Tal es el caso de las dioxinas y los furanos (Mari et al., 2007). Así, sería necesaria la inclusión de, al menos, una variable que cuantifique la "toxicidad hacia los ecosistemas" dentro de las tasas retributivas nacionales. Asimismo, se hace fundamental el establecimiento de tasas retributivas por contaminación de otras fuentes, como es el caso de los contaminantes que aparecen en las aguas subterráneas y aquellos contaminantes que surgen como producto de la actividad agrícola (contaminación por fuentes difusas). Es bien sabido que la contaminación difusa es mayoritariamente responsable por la contaminación de los ríos.

Tabla 4. Tasas retributivas utilizadas en Cataluña (España)

Parámetro	**Costo**
Materias en suspensión (MES)	0.24 €/kg
Materias inhibidoras (MI)	4.78 €/equitox
Materias oxidables (MO)	0.48 €/kg
Sales solubles (SOL)	3.8 €/S/cm
Nitrógeno (N)	0.30 €/kg
Fósforo (P)	0.61 €/kg

Fuente: (GENCAT, 1999)

Un estado óptimo de las aguas de una región requiere unas infraestructuras difícilmente financiables bajo asignación presupuestaria nacional. La creación de un tributo ecológico como un canon de saneamiento podría permitir el cumplimiento de la premisa de "quien contamina paga", lo que a su vez permitiría subvencionar los gastos del tratamiento de las aguas residuales. Este canon de saneamiento ha sido recientemente implementado en algunas comunidades en España. Para gravar la toxicidad potencial de los efluentes industriales, se utilizan las unidades de Toxicidad (equitox).

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El valor de la EC50 se determina mediante el ensayo estándar de bacterias luminiscentes, conocido comercialmente como microtox® y/o el ensayo de inhibición de la movilidad de *Daphnia magna*, de acuerdo con la legislación vigente (Gibert, 2004). Luego se calculan los equitox mediante la siguiente expresión, equitox = 100/EC50. Finalmente, los equitox medidos para un efluente industrial o urbano permiten determinar el coste variable que la compañía debe asumir por el peligro ambiental de su emisión.

La Tabla 4 muestra los costos del canon de saneamiento de Cataluña (España). De manera similar en Uruguay, se ha propuesto el uso del índice SEDTOX, para la determinación de la toxicidad de efluentes industriales. Este índice ha sido desarrollado en Canadá y representa un valor integrado producto de una batería de bio-ensayos, ya que las respuestas biológicas de estos bio-ensayos tienen gran variabilidad (Bombardier and Bermingham, 1999). Cabe destacar que los bio-ensayos propuestos aquí, presentan muchas ventajas, ya que constituyen pruebas directas del efecto de los vertidos tóxicos sobre los organismos, presentan un protocolo relativamente sencillo y son en general de bajo costo operativo.

Actualmente estamos llevando a cabo bio-ensayos con Microtox® a muestras colectadas en el río Cauca. En junio de 2007, se colectaron muestras de sedimentos en diversos sitios de la cuenca. El monitoreo de los sedimentos permite conocer el estado de la contaminación a largo plazo, ya que los sedimentos presentan menor movilidad y facilidad para acumular sustancias tóxicas. Adicionalmente, muchas sustancias peligrosas tienden a ligarse a las fases sólidas, por lo que no serían detectables en las muestras acuosas. Las sustancias ligadas a los sedimentos son igualmente peligrosas para la fauna acuática, especialmente para aquellos organismos que se alimentan en la zona béntica.

Se han tomado muestras en el río Cauca, en las cercanías a la desembocadura de los principales ríos tributarios y en la Laguna de Sonso, que ejerce como zona protegida. La Tabla 5 muestra los resultados de la valoración con Microtox® para las muestras analizadas, siguiendo los criterios del índice SEDTOX (Bombardier and Bermingham, 1999). Se observan valores significativamente altos para toxicidad tanto por sustancias acuosas como por sustancias orgánicas. Una vez más la gran variabilidad

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en el comportamiento puede deberse al hecho de la alta contaminación difusa en la zona.

Tabla 5. Resultados cualitativos del análisis de toxicidad de diversas muestras colectadas en Junio de 2007 para el río Cauca y tributarios*

Sitio de Muestreo	Tipo	Toxicidad extracto orgánico	Toxicidad extracto acuoso
Río Palmira	Tributario	Altamente tóxico	No tóxico
Río Fraile	Tributario	Marginalmente tóxico	Altamente tóxico
Canal CVC en Laguna de Sonso	Tributario	Marginalmente toxico	No tóxico
Río Cerrito	Tributario	Altamente tóxico	Marginalmente tóxico
Río Amaime	Tributario	No tóxico	Marginalmente tóxico
Río Bolo	Tributario	Marginalmente toxico	No tóxico
Río Yumbo	Tributario	Altamente tóxico	Marginalmente tóxico
Laguna de Sonso	Zona protegida	Marginalmente tóxico	No tóxico
SP5, Jamundí	Río principal	No tóxico	No tóxico
SP6, Jamundí	Río principal	Moderadamente tóxico	No tóxico
SP7, Navarro	Río principal	Marginalmente tóxico	Marginalmente tóxico
SP8, Juanchito	Río principal	Moderadamente tóxico	No tóxico
SP10, Yumbo	Río principal	Marginalmente tóxico	Moderadamente tóxico
SP11, Paso de la Torre	Río principal	Marginalmente tóxico	Marginalmente tóxico
SP12, Vijes	Río principal	Marginalmente tóxico	Marginalmente tóxico
SP14, Mediacanoa	Río principal	Marginalmente tóxico	Marginalmente tóxico

*El grado de toxicidad debe interpretarse como Altamente tóxico > Moderadamente tóxico > Marginalmente tóxico > No tóxico.

Todos los tributarios del río Cauca que fueron analizados presentaron algún grado de toxicidad. Esta toxicidad es probablemente debida a la presencia de fuentes difusas, aunque también muchos tributarios reciben efluentes de plantas industriales de la zona, así como descargas de las aguas residuales de las poblaciones que atraviesan. En el río Cauca también los valores de toxicidad han resultado altos, especialmente aguas abajo de la zona industrial de Yumbo, donde los extractos acuosos presentan toxicidad moderada y los extractos orgánicos presentan toxicidad marginal. Dicha toxicidad también se ve reflejada en las muestras tomadas en la Laguna de Sonso, zona protegida distante más de cuarenta kilómetros de la ciudad de Cali y de Yumbo, en la que la evidencia de contaminación por sustancias orgánicas puede afectar la salud del ecosistema.

Los efectos combinados de la toxicidad en las aguas por sustancias provenientes de la agricultura, por efluentes domésticos y por actividades industriales se estudian muy apropiadamente, y a menor costo, mediante bioensayos, ya que la detección del

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número significativo de sustancias contaminantes que se envían a los ríos incrementa notablemente los costos del control de la contaminación y dificulta el establecimiento de planes de mejoramiento de la calidad ambiental, para las autoridades ambientales. Por esta razón, en este trabajo se ha propuesto el uso de bioensayos para controlar efluentes tanto industriales como domésticos y agrícolas, ya que estos pueden reflejar de una mejor manera, y a menor costo, las posibles consecuencias de la polución.

La vigilancia de las sustancias micro-contaminantes en el Valle del Cauca es prioritaria, y se debe incluir en los planes de control de la contaminación. La toma de decisiones de las autoridades ambientales no debe reducirse sólo a criterios macroscópicos, como actualmente se acostumbra. Variables como la carga orgánica (DBO_5), los niveles de oxígeno disuelto y la presencia de sólidos son insuficientes para la toma de decisiones en la mejora de la calidad del medio ambiente. En este trabajo, se ha demostrado que en la región del Valle del Cauca, la presencia de micro-contaminantes reviste peligrosidad tanto para la salud, debido al uso de pesticidas organoclorados que son precursores de cáncer, como para la vida acuática, llegando en muchos casos a encontrarse concentraciones de sustancias tóxicas de dos y tres órdenes de magnitud superiores a las concentraciones normalmente aceptadas por la comunidad científica internacional. Asimismo, la evidencia de efectos adversos para la salud de los ecosistemas ha sido probada mediante bio-ensayos de ecotoxicidad.

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List of Publications of the Thesis

Chapter 1
William Ocampo-Duque, Núria Ferré-Huguet, José L. Domingo and Marta Schuhmacher. Assessing water quality in rivers with fuzzy inference systems: A case study. *Environment International, Volume 32, Issue 6, August 2006, Pages 733-742.*

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The article was included in Top 25 Hottest articles list of the Journal: Position 3 (July-September 2006), and Position 25 (April – June 2006).

Chapter 2
William Ocampo-Duque, Marta Schuhmacher and José L. Domingo. A neural-fuzzy approach to classify the ecological status in surface waters. *Environmental Pollution, Volume 148, Issue 2, July 2007, Pages 634-641.*

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Chapter 3
William Ocampo-Duque, Ronnie Juraske, Vikas Kumar, Marti Nadal, Marta Schuhmacher, and José L. Domingo. A concurrent neuro-fuzzy inference system for screening ecological risk assessment in rivers. *Submitted to Journal of Environmental Management.*

Chapter 4 Part A
William Ocampo-Duque, Jordi Sierra, Núria Ferré-Huguet, Marta Schuhmacher, José L. Domingo. Estimating the environmental impact of micro-pollutants in the low Ebro: An approach based on screening toxicity with *Vibrio fischeri. Chemosphere (Accepted).*

Journal Impact Factor 2006: 2.442, Aggregated Impact factor 2006 for Environmental Sciences: 1.892. Journal Rank: 27 out of 144.

Chapter 4 Part B
William Ocampo-Duque, Jordi Sierra, Núria Ferré, Marta Schuhmacher, José L. Domingo. Sediment based risk assessment for rivers: A chemical and ecotoxicological fuzzy approach. *Proceedings of the International Meeting on Soil and Wetland Ecotoxicology (SOWETOX 2007), Barcelona, Nov. 26-27, 2007. ISBN: 978-84-475-3247-6.*

Annex
William Ocampo-Duque y Marta Schuhmacher. Desarrollo de un modelo para la gestión de cuencas hidrográficas basado en evaluación de riesgo ambiental: Experiencias Europeas y aplicación a ríos colombianos. *Memorias del 50º Congreso de la Asociación Colombiana de Ingeniería Sanitaria y Ambiental (ACODAL) y 12º Congreso Bolivariano de AIDIS. Santa Marta, Colombia, 12-14 septiembre de 2007.*