ABSTRACT

In this study, a model for the evaluation of the environmental risk of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) for the aquatic organisms has been developed. These compounds are brominated flame retardants (BRFs) used in plastics, electronic devices, textiles and others to prevent fire. The model designed is based on a technical application of the Fuzzy Theory. In particular, three interconnected Fuzzy Inference Systems (FIS) have been created through the use of the Fuzzy Toolbox in Matlab. In order to improve and make the model scientifically robust, several international experts have been questioned about different information needed to build the fuzzy system. Information from 38 questionnaires have been collected and statistically treated. The model has been tested in two case studies, using the data provided by four samples campaigns in two Ebro tributaries in north east of the Spain, the Cinca River (2002 and 2004) and the Vero River (2004 and 2005). Concentrations in biota and sediments obtained in the sample campaigns have been used directly as input for the model. Missing data for HBCD and PBDEs, as BMF factor and toxicity data have been obtained through scientific literature. In both rivers, there exists an industrial park with a widespread use and consequently discharge of flame retardants into the water body. The proposed model evaluates the risk in different points according to the industrial park position. In the Vero River, only PBDEs have been found. The risk of these compounds for the aquatic organisms before the source of pollution has been categorized as LOW (both in 2004 and 2005), with a value of 0.352 (in a range [0-1]). After the industrial park, the risk (0.62) has been considered to be mainly MODERATE in 2004, and mainly HIGH (0.78) in 2005. In Cinca River, four different samples points have been analysed, finding a HIGH risk (0.78) for HBCD in the most contaminated site (near the industrial city of Monzón). Values for PBDEs are much lower in this case study, representing LOW risk in all the analysed points. Concerning the model design, the classic procedure of the FIS has been modified with the aim to give weights or relative importance to the several environmental variables involved in the model. This new insight has been compared with the classic FIS system and has proved to be more conservative and sensitive for all the case studies. The results obtained with the proposed methodology prove that the qualitative environmental risk assessment of PBDEs and HBCD is possible through fuzzy logic. Numerical values and bibliographic data can be translated into fuzzy sets, dealing with the uncertainty and providing a final output easy to understand by the human mind (e.g. LOW, MEDIUM, HIGH risk). This information can be very useful for the decision making processes.
Ringraziamenti

Questo lavoro di tesi, che è coinciso con il mio semestre di Erasmus, è nato e si è svolto interamente presso il CERTEC di Barcellona. Vorrei quindi ringraziare per primi tutte le ragazze ed i ragazzi che in questo periodo mi hanno aiutato, facendomi sentire a casa. In particolare un rangraziamento sentito va a Rosa Mari, Alba, Edgar, Miquel e Sandra che hanno collaborato con me per la realizzazione di questo studio. Vorrei inoltre ringraziare tutte gli esperti che hanno partecipato esternamente rispondendo al nostro questionario, in particolare Ethel Eljarrat del CSIC di Barcellona. Infine desidero ringraziare la mia famiglia, alla quale questo lavoro è dedicato, perchè mi è sempre stata vicina ed anche dopo questa esperienza che si sta concludendo, lo continuerà ad essere.
INDEX

Abstract ........................................................................................................................................... 1

1 Introduction .................................................................................................................................. 7
  1.1 Aim of the project ...................................................................................................................... 8
  1.2 Motivation .................................................................................................................................. 9

2 Brominated flame retardants ....................................................................................................... 10
  2.1 Polybrominated diphenyl ethers (PBDE) .................................................................................. 10
      2.1.1 Physical and chemical properties of PBDEs ..................................................................... 11
      2.1.2 Biotic and abiotic debromination and transformation of PBDEs ...................................... 13
      2.1.3 Bioaccumulation in the aquatic environment ..................................................................... 13
      2.1.4 Human health risk .............................................................................................................. 14
      2.1.5 Legislation ......................................................................................................................... 15
  2.2 Hexabromocyclododecane (HBCD) ......................................................................................... 16
      2.2.1 Physical and chemical properties of HBCD. ..................................................................... 18
      2.2.2 Biotic and abiotic debromination and transformation of HBCD .......................................... 19
      2.2.3 Bioaccumulation in aquatic environment .......................................................................... 19
2.2.4 Human health risk........................................................................................................... 20
2.2.5 Legislation....................................................................................................................... 20

3 Study site and environmental data...................................................................................... 22

3.1 Aquaterra project............................................................................................................... 22
3.2 BFRs in Ebro zone............................................................................................................ 23
  3.2.1 BFRs in Vero River....................................................................................................... 25
  3.2.2 BFRs in Cinca River..................................................................................................... 28

4 Fuzzy theory .......................................................................................................................... 32

4.1 Historical evolution .......................................................................................................... 32
4.2 Fuzzy logic versus classic logic........................................................................................ 33
4.3 Fuzzy sets .......................................................................................................................... 33
4.4 Membership functions ...................................................................................................... 34
4.5 Fuzzy sets versus crisp sets: an example ......................................................................... 35
4.6 Generalization of a fuzzy set ............................................................................................ 37
4.7 Fuzzy approaches and applications .................................................................................. 39
  4.7.1 Fuzzy Inference System (FIS) .................................................................................... 39
  4.7.2 Fuzzy synthetic evaluation (FSE) .............................................................................. 41

5 Methodology ......................................................................................................................... 43

5.1 Introduction......................................................................................................................... 43
5.2 Variables definition ............................................................................................................ 43
5.3 Model design: Fuzzy inference System (FIS)...................................................................... 49
  5.3.1 Fuzzification ................................................................................................................ 50
  5.3.2 Fuzzy rules ................................................................................................................... 54
  5.3.3 Aggregation .................................................................................................................. 61
  5.3.4 Defuzzification ............................................................................................................ 62
5.4 Mamdani-Assilian vs Takagi-Sugeno-Kang ........................................................................ 64
5.5  *The weights* .......................................................................................... 65

5.5.1  Analytic hierarchy process (AHP) ......................................................... 65

5.5.2  Singular value decomposition (SVD) .................................................... 67

5.6  *The questionnaire* .................................................................................. 72

5.6.1  Questionnaire structure ...................................................................... 73

6  Results and discussion ............................................................................... 81

6.1.1  Vero River ......................................................................................... 81

6.1.2  Cinca River ....................................................................................... 84

7  Conclusions ............................................................................................... 88

8  Nomenclature ............................................................................................. 91

Bibliography ..................................................................................................... 93
1 INTRODUCTION

Persistent organic pollutants (POPs) are toxic chemicals that adversely affect human health and the environment around the world. They persist for long periods of time in the environment and can accumulate and pass from one species to the next through the food chain. POPs find their way through the food chain by accumulating in the body fat of living organisms and becoming more concentrated as they move from one creature to another (EPA, 2009). One family of these chemicals are the Brominated Flame Retardants (BFRs). They are used in plastics, textiles, electronic devices and other materials to prevent fire. The most used BFRs are polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and tetrabromobysphenol A (TBBP-A) (Eljarrat et al., 2004). TBBP-A is used primarily in electronic circuit boards and is chemically bound within the resin. In contrast, PBDEs and HBCD are simply mixed with the material that is to be flame-retarded. Therefore, these compounds are more likely to leach out during both product use and disposal (Law et al., 2005). In the last twenty years, the scientific interest about these compounds has increased a lot because several studies have found the presence of these pollutants in almost all the environmental compartments (see Table 1.1).

Table 1.1. Studies focused on BFRs environmental presence

<table>
<thead>
<tr>
<th>Environmental Matrix</th>
<th>Country</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban area and house dust</td>
<td>Spain</td>
<td>Rugeiro et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Sweden</td>
<td>Karlsson et al., 2000</td>
</tr>
<tr>
<td></td>
<td>USA</td>
<td>Wu et al., 2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sjodin et al., 2004</td>
</tr>
<tr>
<td>Sediments and soil</td>
<td>China</td>
<td>Yu et al., 2009</td>
</tr>
<tr>
<td></td>
<td>Spain</td>
<td>Eljarrat et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Portugal</td>
<td>Lacorte et al., 2003</td>
</tr>
<tr>
<td></td>
<td>Korea</td>
<td>Ramu et al., 2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Liang et al., 2010; Wang et al., 2009</td>
</tr>
<tr>
<td>Biota</td>
<td>USA</td>
<td>Tomy et al., 2006</td>
</tr>
<tr>
<td></td>
<td>Germany</td>
<td>Sawal et al., 2004</td>
</tr>
<tr>
<td></td>
<td>Norway</td>
<td>Herzke et al., 2005</td>
</tr>
<tr>
<td></td>
<td>China</td>
<td>Qiu et al., 2010</td>
</tr>
<tr>
<td></td>
<td>Spain</td>
<td>Eljarrat et al., 2004-2005-2007</td>
</tr>
<tr>
<td></td>
<td>UK</td>
<td>de Boer et al., 2004</td>
</tr>
</tbody>
</table>
As shown in Table 1.1, flame retardants can be considered ubiquitously. Moreover, they have been detected in very remote sites in northern Sweden and Finland, suggesting that it undergoes long-range atmospheric transport (Rembersg et al., 2004; de Wit et al., 2004). This has been confirmed by the detection of HBCD, after atmospheric transport from Western Europe and Eastern North America, in polar bears from Greenland and Svalbard in the Arctic Ocean (de Wit et al., 2004). In other studies (de Boer et al, 1998; Ikonomou et al., 2002) PBDEs have been found in whale of deep ocean and in the Arctic. Today some of the congeners belonging to the family of PBDEs are banned in Europe and because of this, the use of others BFRs, like HBCD, are incremented in the last years. Given their long persistence, their capability to bioaccumulate and widespread around the world, as well as, their continued production and use, the necessity of more information and data about their occurrence in biota and environment, is required.

1.1 Aim of the project

Whereas several studies have been conducted by government agencies (EPA, 2008; EPA 2010; EU, 2001; EU, 2002; EU, 2008) and scientists (Roosens et al., 2010; Miyake et al., 2008; Domingo et al., 2008) to evaluate the toxicological properties of these pollutants and impact on human health, not many studies on the environmental risk assessment of BFRs’ widespread exist. This project focuses on the development of a method to evaluate environmental risk of PBDEs and HBCD in the aquatic matrix. The aim of this project is to develop a tool with the following features:

1. Easy to understand and useful for environmental management;
2. Robust and based on scientific literature and experts’ opinion;
3. Able to be adjustable in different environmental conditions and with several compounds of similar behaviour;

In order to attain the main objective of the project and comply with these characteristics, the project has the following targets:

1. Bibliographic research: to gather studies related to BFRs and to select the most suitable methodology to use in this work;
2. Initial Model design using the Fuzzy Toolbox on Matlab;
3. Introduction of weights to the different variables: design of a method compatible with fuzzy logic;
4. Questionnaire design and selection of a relevant number of international experts to consult them;
5. Statistical treatment of the answers obtained from questionnaire;
6. Model review according to the questionnaire information;
7. Model test with some case studies presented in the project;
8. Model optimization and final model design
9. Presentation of the results obtained;
10. Drawing conclusions.

1.2 Motivation

Risk assessment of chemicals is a topic of great interest for me. Before arriving to Barcelona for my Erasmus period, I knew that the topic of my future research was going to be the environmental risk assessment of brominated flame retardants through fuzzy logic. I have to say that during my life, I have never listened a word on fuzzy logic. I did not know what this technique was about. I checked some websites and my interest started to grow on the subject. I saw that fuzzy theory has been used for many years in different fields of the everyday life such as electronic devices. But I could not imagine how I was going to use this tool for risk assessment.

This project has been realized in the CERTEC (Centre d’ Estudis del Risc Tecnològic) in the UPC (Universitat Politècnica de Catalunya). Once in Barcelona, I started to learn more about it and I got involved in the topic. In fact, one of the problems that the research group was dealing with was the assignment of weights to the different variables. This subject was very motivating for me and I started to look for different options to implement this part into the model. As a consequence, a new adaptation of a former method has been implemented in the present project to consider the weight of the variables.

This is just an example to show that the topic of this project, even if unknown for me at the beginning, has helped me to learn lots of new things and to work in a very enthusiastic group of scientists.
2 BROMINATED FLAME RETARDANTS

Advances in polymer science over the past 50 years have led to the introduction of a large number of polymers with different properties and applications. Most of these polymers are petroleum-based and hence, are flammable. In order to meet fire safety regulations, flame retardants are applied to combustible materials such as plastics, wood, paper, and textiles. Flame retardants (FR) are compounds added or applied to a material to increase the fire resistance of that product (EHC-192, 1997). Brominated flame retardants are organobromide compounds which are used to inhibit the inflammability of a material. They are widely used in commercial products like textiles electronics, plastic clothes and furniture.

In this section a general view of two of the most produced BFRs is given: PBDEs and HBCD. Particularly, theyr physical and chemical properties and their fate in the aquatic matrix are explained.

2.1 Polybrominated diphenyl ethers (PBDE)

Polybrominated diphenyl ethers (PBDEs) are added to plastics, polyurethane foam, textiles, and electronic equipment to reduce the likelihood of ignition and to slow the burn rate if the products do catch fire. PBDEs have a common structure of a brominated diphenyl ether molecule that may have from 1 to 10 bromine (Br) atoms attached (see Figure 2.1). Depending on the location and number of Br atoms, there are 209 possible PBDE compounds, termed congeners (EPA, 2010).

![General structure of a PBDE](image)

When fire occurs, the PBDE formulations utilize vapor phase chemical reactions that interfere with the combustion process, thus delaying ignition and inhibiting the spread of fire (D'Silva, 2004). More precisely the PBDE additives interfere with the combustion process by forming bromine gas, which, in turn, displaces the O₂ necessary to sustain the oxidation reactions. In addition, the bromine radicals formed, interfere with the chain reactions of hydrogen and
hydroxyl radicals in the fire. The duality of these processes severely retards and constrains thermal oxidation (EPA, 2010). These characteristics have promoted the widespread use of PBDEs in many objects which are of common use like casings of televisions, personal computers, and other electronic equipment.

The most frequently found PBDE congeners are shown in Table 2.1:

Table 2.1. PBDE congeners commonly found.

<table>
<thead>
<tr>
<th>Congener</th>
<th>Number of bromine atoms</th>
<th>Chemical name</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-28</td>
<td>3</td>
<td>2,4,4′-tribromodiphenyl ether</td>
</tr>
<tr>
<td>BDE-47</td>
<td>4</td>
<td>2,2′,4,4′-tetrabromodiphenyl ether</td>
</tr>
<tr>
<td>BDE-85</td>
<td>5</td>
<td>2,2′,3,4,4′-pentabromodiphenyl ether</td>
</tr>
<tr>
<td>BDE-99</td>
<td>5</td>
<td>2,2′,4,4′,5-pentabromodiphenyl ether</td>
</tr>
<tr>
<td>BDE-100</td>
<td>5</td>
<td>2,2′,4,4′,6-pentabromodiphenyl ether</td>
</tr>
<tr>
<td>BDE-153</td>
<td>6</td>
<td>2,2′,4,4′,5,5′-hexabromodiphenyl ether</td>
</tr>
<tr>
<td>BDE-154</td>
<td>6</td>
<td>2,2′,4,4′,5,6′-hexabromodiphenyl ether</td>
</tr>
<tr>
<td>BDE-183</td>
<td>7</td>
<td>2,2′,4,4′,5,6′-heptabromodiphenyl ether</td>
</tr>
<tr>
<td>BDE-197</td>
<td>8</td>
<td>2,2′,3,3′,4,4′,6,6′-octabromodiphenyl ether</td>
</tr>
<tr>
<td>BDE-206</td>
<td>9</td>
<td>2,2′,3,3′,4,4′,5,5′,6-nonabromodiphenyl ether</td>
</tr>
<tr>
<td>BDE-209</td>
<td>10</td>
<td>2,2′,3,3′,4,4′,5,5′,6,6′-decabromodiphenyl ether</td>
</tr>
</tbody>
</table>

- BDEs 47, 99, 100, 153, 154: they tend to be found in humans, fish and other biota (BDE-47 is dominant).
- BDE-209: it seems to be dominant house dust, sediments and indoor air.

2.1.1 Physical and chemical properties of PBDEs

The physical and chemical properties establish the rules for PBDEs to move into air, soil, water, and sediments, and to exchange among environmental compartments. They also indicate the physical form and phase of the chemical present in air and water. The physical and chemical properties influence the extent to which biotic and abiotic processes may transform or degrade PBDEs in the environment. Bioconcentration properties indicate the relative propensities of brominated diphenyl ether (BDE) congeners to bioaccumulate and biomagnify in ecological food chains. Overall, the most important properties for understanding the environmental behaviour of PBDEs are water solubility ($W_S$), octanol water partition coefficient ($K_{ow}$), octanol air partition coefficient ($K_{oa}$), the Henry’s Law constant ($H$), and vapor pressure ($V_p$) (see Table 2.2).
Table 2.2. Physical and chemical properties of several PBDEs congeners

<table>
<thead>
<tr>
<th>PBDE congener</th>
<th>BDE-47 (1)</th>
<th>BDE-99 (2)</th>
<th>BDE-153 (3)</th>
<th>BDE-209 (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point, °C</td>
<td>79-82</td>
<td>93</td>
<td>183</td>
<td>300-310</td>
</tr>
<tr>
<td>Boiling point, °C</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Decomposes at &gt;320 °C</td>
</tr>
<tr>
<td>Vapour pressure, Pa</td>
<td>$2.5 \times 10^{-4}$ (25 °C)</td>
<td>$5 \times 10^{-4}$ (25 °C)</td>
<td>$5.8 \times 10^{-4}$ (25 °C)</td>
<td>$4.63 \times 10^{-4}$ (21 °C)</td>
</tr>
<tr>
<td>Henry's law constant: Pa m$^3$ mol$^{-1}$ at 25 °C</td>
<td>0.85</td>
<td>0.6</td>
<td>0.26</td>
<td>0.04</td>
</tr>
<tr>
<td>Density, g/cm$^3$</td>
<td>--</td>
<td>2.28</td>
<td>--</td>
<td>3.0</td>
</tr>
<tr>
<td>Water solubility at 25 °C, mg/L</td>
<td>0.001-0.002</td>
<td>0.009</td>
<td>0.009-0.01</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Log $K_{ow}$ at 25 °C</td>
<td>6.01-6.77</td>
<td>6.53-7.66</td>
<td>7.62-7.9</td>
<td>6.3-12.6</td>
</tr>
<tr>
<td>Log $K_{oc}$ at 25 °C</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>6.3</td>
</tr>
<tr>
<td>Log $K_{oa}$ at 25 °C</td>
<td>10.5</td>
<td>11.3</td>
<td>11.9</td>
<td>--</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>485.8</td>
<td>564.7</td>
<td>643.6</td>
<td>959.17</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>$C_{12}H_6Br_4O$</td>
<td>$C_{12}H_5Br_5O$</td>
<td>$C_{12}H_4Br_6O$</td>
<td>$C_{12}Br_{10}O$</td>
</tr>
</tbody>
</table>

(1) US EPA (2010); US EPA (2008a); (2) US EPA (2008b); (3) US EPA (2008c); (4) US EPA (2008d)

Examining all these properties, one can say that:

- Generally, PBDEs have low water solubility. Organic contaminants with low solubility do not readily dissolve in surface water (relatively hydrophobic);
- PBDEs typically have high log octanol water partition coefficients, which suggest a high absorption capacity for organic carbon in soils and sediments and which indicate that they tend to bioaccumulate;
- The rate of volatilization from water to air and the scavenging of the vapour phase of the contaminant in air by precipitation (i.e., wet deposition) are governed by Henry’s Law constant $H$. Usually, $H$ is expressed as atm-m$^3$/mol. Volatilization becomes an important transfer mechanism when the computed $H$ is between $10^{-5}$ and $10^{-3}$ atm-m$^3$/mol (Ritter et al., 1995). Chemicals with $H$ values greater than $10^{-3}$ atm-m$^3$/mol rapidly volatilize into air. PBDEs are low-volatile organic chemicals with $H$ at $10^{-4}$ atm-m$^3$/mol or less, with lower $H$ at higher degrees of bromination;
- The semi-volatile organic compounds tend to have solid phase vapour pressures <1 Pa at 25°C. PBDEs are semi-volatile organic compounds. Vapour pressures of PBDE decrease with increasing molecular weight and degree of bromination;
Brominated flame retardants

- The log($K_{oa}$) is suggestive of the environmental cycling of semivolatile compounds between the air and organic phases such as soil particles, air particles, and vegetation. The greater the log($K_{oa}$) (e.g., ≈10) is, the stronger the propensity of the atmospheric BDE congener to absorb to the organic content of soils and vegetation (Wania et al., 2002);

2.1.2 Biotic and abiotic debromination and transformation of PBDEs

As xenobiotic compounds, PBDEs can be transformed in biota. The most important processes which involve PBDEs are biodegradation, biotransformation, and photolysis. The first two refer to aerobic and anaerobic microorganisms’ action through metabolic pathways, whereas photolysis involves the breakdown of PBDEs by sunlight energy. All of these environmental fate processes can involve the stripping of bromine atoms from the molecule, a process called ‘debromination’. Microorganism can transform organic contaminants presents in soils and sediments because they use them as source of carbon, then they gain energy breaking the chemical bounds and transferring electrons away from the contaminants (Nas, 1993). One possible variation of these transformations is the reductive dehalogenation, in which microorganisms through new catalyst reactions, replace halogen atoms with hydrogen atoms in organic contaminants. Although the higher brominated congeners are debrominated aerobically, the lower molecular weight congeners that are products of this process may be further debrominated by aerobic bacterial degradation via oxidative dehalogenation (Kim et al., 2007). Several recent studies have provided evidence of microbial mediated reductive debromination of decaBDE and octaBDE under laboratory conditions (EPA, 2010). In particular Sulfurospirillum multivorans bacterium has been used for reductive debromination of deca-BDEs and Dehalococcoides ethenogenes 195 bacterium for octa-BDEs, (He et al., 2006).

2.1.3 Bioaccumulation in the aquatic environment

The BDE congeners have a high capacity for bioaccumulation and biomagnification in biota as indicated by their relatively high $K_{ow}$ factors. The behaviour of PBDEs in aquatic environment is of fundamental importance for this work. BDE congeners enter into a water body from atmospheric deposition, air-to-water transfer, or direct discharge from industries and sewage treatment plants (EPA, 2010). Once BDEs enter the aquatic system, they distribute between the
water column and sediments according to their physical-chemical properties. Moreover, within the water column, BDEs distribute between the dissolved phase and the particle phase. Due to their lipophilic and hydrophobic properties PBDEs can bioaccumulate in aquatic organisms. Molluscs and benthic invertebrates live and feed directly on contaminated sediments. These types of organisms are the lower level of food chain, so the BDE congeners move up through food chain from bottom-feeding fish to bigger organisms. Molluscs internally absorb BDEs from the water column through filtering of the water. Fish acquire BDEs through the dietary pathway and also from the water passing through their gills. In this regard, trophic level bioaccumulation in marine and freshwater biota is similar to the bioaccumulation pattern of other classes of lipophilic and persistent compounds such as the PCBs (Evenset et al., 2005; Bragigand et al., 2006; Eljarrat et al., 2004). PBDEs are widely present in the environment (Hites, 2004). Since the first detection in fish in 1981 (Andersson and Blomkvist, 1981), PBDEs have been detected in different environmental matrices, such as air, water, sediment and soil, even in human milk and blood samples (Christensen et al., 2002; Bi et al., 2006; Goel et al., 2006; Voorspoels et al., 2006; Cetin and Odabasi, 2007; Zou et al., 2007).

2.1.4 Human health risk

Whereas no studies have been conducted on the effects of PBDEs on humans, it is sure that PBDEs are stored for a long time in body fat or other tissues. The PBDEs found in human tissue samples are mostly pentaBDEs. Octa- and decaBDEs are also found, but at lower levels (DOH, 2010). BDE-99 and BDE-47, for instance, have been found in human milk, adipose tissue and blood (EPA, 2008), even if no studies currently exist on the potential carcinogenicity of BDE-99 and 47 in humans or experimental animals (EPA, 2005). For decaBDEs several studies have shown that these congeners do not accumulate in tissue, and undergo clearance, largely as a result of the metabolism in the liver and excretion in the bile (EPA, 2008). While PBDs have a low acute toxicity, however, chronic exposure to certain PBDEs (especially in the belly mother) has been associated with abnormal development of brain and skeleton in animals and potential long-term impacts on memory, learning and behavior (Eriksson et al., 2001; Darnerud, 2003). PBDEs also exhibit endocrine disrupting properties in interaction with both estrogen and thyroid hormone systems, either as parent or metabolites (Meerts et al., 1998 and 2001, Legler and Brouwer, 2003). Effects have also been reported on the immune system (Darnerud, 2003; Birnbaum and Staskal, 2004).
2.1.5 Legislation

The European Union (EU) banned the marketing and use of penta and octaBDE in 2/6/2003, with Directive 2003/11/EC of the European Parliament and Counsel (European Parliament, 2003). At that time, the EU exempted decaBDE from the ban. However, in 4/1/2008, the European Court of Justice (the EU’s highest court) ruled that the decision to exempt decaBDE has been flawed and ordered the EU to ban the use of the decaBDE in electrical and electronic equipment (European Court of Justice, 2008). Based on the directive of the court, the ban became effective in 7/1/2008. The ban applies to all EU member countries. Australia banned the use and import of pentaBDE effective 3/6/2007 (Australian Government, 2007). However, it is expected that the use of recycled plastics containing PBDE formulations may continue to incorporate these chemicals in the manufacture of new electronics and information technology (IT) units (Morf et al., 2005). European regulations of commercial PBDEs, are shown in Table 2.3, based on the Bromine Science and Environmental Forum (BSEF, 2010).

<table>
<thead>
<tr>
<th>BFR substance</th>
<th>Content</th>
<th>Legal basis</th>
<th>Deadline for compliance</th>
<th>EU scientific risk assessment status</th>
</tr>
</thead>
<tbody>
<tr>
<td>decaBDE</td>
<td>Separation of BFR plastics from E&amp;E equipment prior to recovery and recycling</td>
<td>WEEE Directive</td>
<td>December 2006</td>
<td>Risk assessment finalized in May 2004. No restrictions on the use of DecaBDE</td>
</tr>
<tr>
<td></td>
<td>Ban of use in E&amp;E applications</td>
<td>RoHS Directive</td>
<td>1 July 2008</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Establishment of controls of emissions, discharges and losses in the Environment and water quality standards</td>
<td>EU Directive establishing the list of priority substances in the field of water policy</td>
<td>Not applicable</td>
<td></td>
</tr>
<tr>
<td>octaBDE</td>
<td>Ban of use in all applications for the EU Market (1)</td>
<td>24th amendment to the marketing and use Directive 76/769/EEC</td>
<td>15 August 2004</td>
<td>Finalized</td>
</tr>
<tr>
<td></td>
<td>Ban of use in E&amp;E applications</td>
<td>RoHS Directive</td>
<td>1 July 2006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Separation of BFR plastics from E&amp;E equipment prior to recovery and recycling</td>
<td>WEEE Directive</td>
<td>December 2006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Establishment of controls of emissions, discharges and losses in the Environment and water quality standards</td>
<td>EU Directive establishing the list of priority substances in the field of water policy</td>
<td>Not applicable</td>
<td></td>
</tr>
</tbody>
</table>

2.1 pentaBDE

<table>
<thead>
<tr>
<th>BFR substance</th>
<th>Content</th>
<th>Legal basis</th>
<th>Deadline for compliance</th>
<th>EU scientific risk assessment status</th>
</tr>
</thead>
<tbody>
<tr>
<td>pentaBDE</td>
<td>Ban of use in all applications for the EU Market (1)</td>
<td>24th amendment to the marketing and use Directive 76/769/EEC</td>
<td>15 August 2004</td>
<td>Finalized</td>
</tr>
<tr>
<td></td>
<td>Separation of BFR plastics from E&amp;E equipment prior to recovery and recycling</td>
<td>WEEE Directive</td>
<td>December 2006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cessation of emissions in the Environment</td>
<td>EU Directive establishing the list of priority substances in the field of water policy</td>
<td>2020</td>
<td></td>
</tr>
</tbody>
</table>

(1) This substance should not be placed on the market or used as a substance or as a constituent of substances or of preparations in concentrations higher than 0.1% by mass. Furthermore, articles should not be placed on the market if they, or flame-retarded parts thereof, contained this substance in concentrations higher than 0.1% by mass.

WEEE: Waste of Electrical and Electronic Equipment
RoHS: Restriction of Hazardous Substances

In Germany, the industrials manufacturers had voluntarily agreed to phase out the PBDE in 1986. Moreover, in 1993 Germany placed official limits on PBDEs used in plastic production, under its Dioxins Ordinance to protect workers’ health because of tendency of PBDE to form brominated dioxins and furan during thermal processing included extrusion of plastic (Fromme et al., 2009).

A recent report of The Bromine Science Environmental Forum (BSEF) estimated the total market demand for the major commercial BFRs in 2001. This report shows the dominance of tetrabromobisphenol-A (TBBPA) (59% of total world usage) and the deca-mix PBDE formulation (27% of total world usage) in volume terms. Recent reports also suggest that usage of hexabromocyclododecane (HBCD) is increasing because the attention is now switching to this compound which is widely used (Eljarrat et al. 2005).

2.2 Hexabromocyclododecane (HBCD)

Hexabromocyclododecane (chemical formula $C_{12}H_{18}Br_6$) is a brominated alicyclic hydrocarbon, and is industrially used as flame retardant in the life cycle steps: production, formulation and industrial use with the aim to increase the flame resistance of different end-products. HBCD was used for the first time by the BASF company in their production of flame-retarded polystyrene foam in the late 1980s; however, the substance has been on the world market since the 1960s (EU Final Draft Risk Assessment HBCD, 2008). World production of HBCD in 2001 totalled 16,700t
Brominated flame retardants (BSEF) and the industrial use of HBCD has increased during the last decade, making it the third most used BFR worldwide at this time (BSEF, 2006; TemaNord, 2008). Today the main downstream uses of HBCD are in the polymer and textile industries, the four principal product types in which is used are:

- Expandable Polystyrene (EPS);
- Extruded Polystyrene (XPS);
- High Impact Polystyrene (HIPS);
- Polymer dispersion for textiles.

As shown in Figure 2.2, HBCD can be found in 16 different isomers. Generally, HBCD is the product of bromination of one of four cyclododecatriene (CDT) isomers (Reyes et al., 1997; American Chemistry Council, 2001), and in the resulting mixture only three different HBCD isomers, named \( \gamma \), \( \alpha \), and \( \beta - HBCD \) are distinguished, even if their absolute stereochemistries are not yet solved (Heeb et al. 2005). Hence, HBCD is generally produced in a mixture, which composition is in a range of about 70 to 95% \( \gamma - HBCD \) and 5 to 30% \( \alpha \) – and \( \beta - HBCD \).

![Figure 2.2. Structure of 6 of 16 possible isomers of HBCD that are present in products at concentrations >1%.

\[\text{Figure 2.2. Structure of 6 of 16 possible isomers of HBCD that are present in products at concentrations >1%}.\]
2.2.1 Physical and chemical properties of HBCD.

Information on the properties for individual diastereomers γ –, α – and β – HBCD are generally scarce, but data about the technical mixture are available (EU Final Draft Risk Assessment HBCD, 2008).

As shown in Table 2.4, HBCD is a slightly soluble compound in water, with a high log octanol water partition coefficient, so it can be considered a hydrophobic compound with high potential to adsorb to soils and sediments and a low potential to leach through soils. Moreover, HBCD has a low vapour pressure and a low Henry’s constant. This indicates that it has a low potential to evaporate from aquatic surface (ECB, 2008).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>641.7</td>
</tr>
<tr>
<td></td>
<td>Ranges from 172-184 to 201-205</td>
</tr>
<tr>
<td>Melting Point (ºC)</td>
<td>• 179-181 α – HBCD</td>
</tr>
<tr>
<td></td>
<td>• 170-172 β – HBCD</td>
</tr>
<tr>
<td></td>
<td>• 207-209 γ – HBCD</td>
</tr>
<tr>
<td>Boiling point (ºC)</td>
<td>Decomposes at &gt;190</td>
</tr>
<tr>
<td></td>
<td>2.38</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.24</td>
</tr>
<tr>
<td>Vapour pressure (Pa), calculated at 21ºC</td>
<td>6.3.10-5</td>
</tr>
<tr>
<td></td>
<td>66 for technical mixture</td>
</tr>
<tr>
<td>Water solubility (µg/L), calculated at 20ºC</td>
<td>48.8 α – HBCD</td>
</tr>
<tr>
<td></td>
<td>14.7 β – HBCD</td>
</tr>
<tr>
<td></td>
<td>2.1 γ – HBCD</td>
</tr>
<tr>
<td>Henry’s Law constant (Pa × m³/mol)</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>5.62 for technical product</td>
</tr>
<tr>
<td>Log Kow</td>
<td>5.07 α – HBCD</td>
</tr>
<tr>
<td></td>
<td>5.12 β – HBCD</td>
</tr>
<tr>
<td></td>
<td>5.47 γ – HBCD</td>
</tr>
</tbody>
</table>
2.2.2 Biotic and abiotic debromination and transformation of HBCD

Like BDEs, the HBCD is a xenobiotic compound and it can be object of different transformations routes in the environment which can change it in other compounds. Hydrolysis is the main process which can affect HBCD through abiotic way. Theoretically abiotic degradation of hexabromocyclododecano is possible; in fact, it is rather easily dehydrobrominated and has a lower thermo-stability than aromatic brominated flame retardants (Kirk and Othmer, 1993). In practice, abiotic degradation is probably of low significance because of the rather rigid ring-structure of HBCD and its low water solubility. For what concerns biodegradation, microorganism can transform organic contaminants presents in soils and sediments (Nas, 1993). To evaluate the aerobic and anaerobic transformation rate of HBCD, water/sediment simulation test have been made (Davis et al., 2003). Results show that γ – HBCD disappears very rapidly from viable anaerobic sediments with half-lives <1 day. This rapid dissipation is due to also to chemical reaction and adsorption over that biotic action. Gerecke et al. (2006) reported that the degradation rates of HBCD stereoisomers vary and β – and γ – HBCD degrade more rapidly than α – HBCD in anaerobic conditions.

2.2.3 Bioaccumulation in aquatic environment

HBCD has been detected in practically all environmental media and is now considered to be a ubiquitous contaminant (Covaci et al., 2006; Law et al., 2008; Ramu et al., 2010). HBCD has been found in river sediments downstream of urban centres or known industrial sources and in marine sediments at substantially higher concentrations than BDEs (Marvin et al., 2006; Ramu et al., 2010). More food web accumulation studies of HBCD have been conducted in areas with diffuse inputs (Bæk et al., 2006; Law et al., 2006a; Tomy et al., 2004; Tomy et al., 2008). These studies have been all indicative of a selective trophic transfer of the α-diastereomer in aquatic food webs. In contrast to the γ-dominated technical mixtures, α-HBCD appears to be the most prominent diastereomer in the majority of biota samples, particularly in higher trophic level species. There have been few studies of food web bioaccumulation of HBCD diastereomers in European marine ecosystems, particularly in urban areas (EU Final Draft Risk Assessment HBCD, 2008). Some of these found HBCD in different level of food chain (Eljarrat et al., 2004; Haukas et al., 2010), indicating biomagnification in different food chains. An EU Risk Assessment submitted HBCD on environmental and human health. Due to the identification of several specific risks to
the aquatic environment, HBCD was classified as phrase R50/53 (very toxic to aquatic organisms, may cause long term adverse effects in aquatic environment).

2.2.4 Human health risk

There is a scarcity of relevant toxicity studies for HBCD. Studies have documented that HBCD may affect biotransformation enzymes, lipid metabolism and also the endocrine system by interfering with thyroid or reproductive hormone homeostasis (Canton et al., 2008; Chengelis, 2001; Germer et al., 2006; Palace et al., 2008). HBCDs are commonly used in expanded and extruded polystyrene foams for thermal insulation of buildings, upholstery textiles and to a lesser extent in high-impact polystyrene (BSEF, 2004). Products containing HBCDs, such as building materials, upholstery textiles, are common in urban regions, thus, diffuse leaching of HBCDs from the products can be expected to be higher in the urban areas, where population density and consumption of such products is higher. Yu et al. (2008) found atmospheric HBCD concentrations in urban areas of China to be substantially higher than those in industrial areas, suggesting that urban areas are the source of HBCDs. Similarly, a study on the occurrence of HBCDs in Sweden by Remberger et al. (2004) revealed that elevated concentrations of HBCDs are found not only near point sources (e.g., textile or polymer industry) but also in rural areas, indicating diffuse sources of HBCDs. In regard to toxicity data, whereas chronic toxicity in the liver, (considered for some time as the main target organ) seems to occur after exposure to relatively high doses, impacts on the hormone thyroid levels in the blood with significantly lower doses have been reported, raising the possibility that HBCD has properties to encourage endocrine disorders (Birnbaum and Staskal, 2004). Fundamental changes in neurological and behavioral characteristics (spontaneous behavior, learning and memory) associated with impacts on certain receptors of the nervous system in mice exposed to HBCD in the early days of their lives have been found (Eriksson et al., 2002). There exists few information on their potential carcinogenic properties.

2.2.5 Legislation

In 2008, the European Chemicals Agency (ECHA) decided to include HBCD in the SVHC list (Substances of Very High Concern). In May 2009, HBCD has been included in the ECHA recommendation list of priority substances to be subject to authorisation under REACH
(Registration, Evaluation, Authorisation and Restriction of Chemicals framework) *(Wikipedia, HBCD)*. The 1st June of 2009 ECHA’s recommendation list was sent to the Commission, who will take the final decision on which substances should be submitted to Authorisation at this stage.

Two legal obligations result from the inclusion of a substance on the candidate list. These obligations are not linked only to the listed substance on its own or in preparations but also to its presence in articles.

- First, any producer or importer of an article containing HBCD has to notify ECHA of the presence of HBCD by June 2011;
- Second, the inclusion of a substance in the candidate list involves a “duty to inform”. In particular suppliers of product containing HBCD must provide sufficient information to their consumers.

In USA, Environmental Protection Agency has launched a review of HBCD that should be published in 2012.
3 STUDY SITE AND ENVIRONMENTAL DATA

This chapter presents the sites in which this study evaluates the environmental risk of PBDEs and HBCD. The data have been collected in different sampling campaigns in Ebro River Basin, within the framework of a European project called Aquaterra explained next.

3.1 Aquaterra project

AquaTerra (Integrated modelling of the river-sediment-soil-groundwater system; advanced tools for the management of catchment areas and river basins in the context of global change (PL 505428)) is an Integrated Project from the EU 6th Framework Programme. This five-year project began in 2004 and finished in March 2009, with its final conference in Tubingen, Germany. The project was aimed to produce high-quality scientific information on the interactions between soil, sediment, water, groundwater and air in the context of global change. AquaTerra involved 45 partners from 22 countries and during the course of the work, it produced a large volume of information, ranging from scientific publications and conference presentations to project deliverables and reports.

In the 20th century, manufactured chemicals for many industrial, agricultural and household purposes have been released into the environment in large quantities. Some of the most prominent groups include halogenated compounds that are for instance used as pesticides (DDT, lindane, PCP), flame retardants (PCBs later PBDE), solvents (TCE, PCE, etc.). These manmade compounds are inherently stable in most environments and therefore occur now at a global scale and throughout the food web. Meanwhile, there is no doubt that these pollutants produced a chemical footprint on the whole planet, which is an often overseen but important aspect of global change. With comprehensive sampling in various European river basin, the project Aquaterra could show that many manmade compounds can be found ubiquitously in all compartments, in air, in soil and sediments, in surface water as well in groundwater. Fate and transport of these compounds in the environment is highly dynamic and numerous physical, chemical as well as biological processes govern the pathway of pollutants in the environment. This includes complex input functions into soils and surface waters, migration in soil, groundwater, surface waters and sediments as well as redistribution processes from soil and water into the atmosphere. Following the "chemocycle" of pollutants, AquaTerra made integral
efforts to identify and parameterize the biological, chemical and physical processes relevant for the prediction of the long-term fate and impact of man-made pollutants in the environment. AquaTerra’s work was based on strong stakeholder involvement; regarding knowledge production, scientific results were presented in a manner that allowed their use for a wide range of potential end users (Aquaterra Final Report, 2010). The project was divided in nine subprojects. One of them: ‘Basin: Integration of research in Aquaterra Rivers basin’, considered practical research cases of five European river basins differing in climate, size functioning and pollution profile. The five rivers were: Brevilles, Ebro, Meuse, Elbe, Danube. The data available form Basins were analysed in the subproject ‘Monitoring: Data Analysis, Monitoring and Analytical Protocols and Sampling Devices’, in which the targets compounds (priority pollutants), emerging compounds and relevant metabolites were identified in environmental samples and degradation products for emerging contaminants. In the case of the proposed project, data from the Ebro River Basin was used.

3.2 BFRs in Ebro zone

The Ebro is the most voluminous river in Spain, with an average flow of 426 m³/s (CSIC-Spanish National Research Council). Its source is in Fontibre (Cantabria), and flows through Cantabria, Castilla y Leon, La Rioja, Navarra, Aragon and Catalonia where it discharges in Mediterranean Sea (in the province of Tarragona) (see Figure 3.1). This river was the object of study in Aquaterra EU project and many analysis and sampling campaigns were made in the last years. Within a monitoring programme at different risk zones in this river, two high contaminated areas were detected.
As shown in Figure 3.2, the study area for this project is located in the northeast of Spain, along the Cinca and Vero rivers (two Ebro tributaries), in the Ebro River basin. Four different sampling stations have been selected at the Cinca River: site C1 (Puente de las Pilas) and C2 (La Boquera), 20 and 12 Km respectively upstream from Monzón; site C3, just downstream from Monzón, a heavily industrialized town with a very important chemical industry; and site C4 (Chalamera), 30 Km downstream of site C3. Moreover, three sampling stations have been selected at the Vero River: site V1 (Castillazuelo), 11 km upstream from an industrial park; site V2 (Barbastro), just 1 km downstream from the industrial park, and site V3 (La Boquera), 4 km downstream of site V2. Different fish species have been sampled: barbels (*Barbus graellsii*), bleaks (*Alburnus alburnus*), south-western nases (*Chondrostoma toxostoma*) and carps (*Cyprinus carpio*). The first data on BFRs in the Ebro basin were obtained thanks to a study based on a sampling campaign on October 2002. In this study fishes and sediments sampling were analysed (Eljarrat et al., 2004; Eljarrat et al., 2005). Other following samplings were made in November 2004 and November 2005 (Eljarrat et al. 2007).
These analyses were made by the Environmental Chemistry Department of the Spanish National Research Council (CSIC). Gas chromatography coupled to mass spectrometry using negative ION chemical ionization (GC-NICI-MS) analyses were performed for the determination of congeners from mono to deca-BDEs (see Figure 3.3).

Figure 3.3. Left: ASE 200 System (Dionex, Sunnyvale, CA) for selective pressurized liquid extraction (SPLE); middle: Agilent 6890 Gas Chromatograph; right: Agilent 5973 Network mass spectrometer; in CSIC of Barcelona.

CSIC provided the data used to develop this project. In the following section, the results of the campaigns for the Vero River and Cinca River are presented as the basis for the model developed to evaluate the BFRs environmental risk.

3.2.1 BFRs in Vero River

Vero River is a tributary of Cinca, River in the Ebro basin. The position of three samples zones have been yet presented in section 3.2, but they are better shown in Figure 3.4. Two samples campaign were made, the first one on November 2004 and the second one on November 2005 (Eljarrat et al., 2007).

Figure 3.4. Positions of sampling sites along Vero River.
The Vero River basin is not subjected to a high industrial activity; however, a small industrial area discharges their effluents to this river. Due to the applications and uses of BFRs in industrial activities, some industries in this area are suspected to cause river contamination. The first one, a textile industry, which produces polyester-based fibres, some of them treated with flame retardants. The second one produces epoxy resins, and the third one is focused on the polyamide polymerization. During the first sampling campaign in November 2004, surface sediments (0-2 cm) were collected from the middle river bed at each selected site. Six benthivorous barbel (Barbus graellsii) specimens have been collected from the site V1, and 8 barbel and two carps (Cyprinus carpio) were collected from the site V3. During the second sampling campaign in November 2005, additional sediments and fish were collected: eight barbel specimens were collected from site V1, and 5 barbels from site V3. It was not possible to find fish at site V2 due to the high degree of pollution on this stretch of the river. The result and concentrations find in the two campaigns are reported in Table 3.1 and Table 3.2.

<table>
<thead>
<tr>
<th></th>
<th>November 2004</th>
<th>November 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V1</td>
<td>V2</td>
</tr>
<tr>
<td>%TOC</td>
<td>2.4</td>
<td>5.6</td>
</tr>
<tr>
<td>BDE-47</td>
<td>0.23</td>
<td>43.8</td>
</tr>
<tr>
<td>BDE-100</td>
<td>0.26</td>
<td>22.5</td>
</tr>
<tr>
<td>BDE-154</td>
<td>0.58</td>
<td>nq</td>
</tr>
<tr>
<td>BDE-153</td>
<td>0.84</td>
<td>nq</td>
</tr>
<tr>
<td>BDE-183</td>
<td>1.19</td>
<td>69.8</td>
</tr>
<tr>
<td>BDE-209</td>
<td>7.46</td>
<td>5395</td>
</tr>
<tr>
<td>TOTAL³</td>
<td>11.10</td>
<td>5531</td>
</tr>
</tbody>
</table>

nd: below limit of detection; nq: not quantified; na: not included in the analytic determination; a: the total PBDE values was found considering nd=0.

The site V2 was found to be the most contaminated zone followed by site V3 > site V1. As expected, PBDE levels were greater near the site of industrial impact. Sediments affected by the industrial park contamination (sites V2 and V3) showed a congener pattern clearly dominated by the BDE-209, which was present at concentrations varying from 1910 to 12500 ng/g dw (dry weight).

Similar to the findings in sediments, fish samples from the site downstream of the industrial park (V3) were found to be much more contaminated than those collected at the site upstream of the factory (V1). The comparison between the two sampling campaigns showed that levels during
Study site and environmental data

2005 were slightly higher than those found in 2004, probably reflecting the same situation observed for sediment samples with an increase of contamination with time.

The most relevant finding is the presence of significant concentrations of BDE-209 in fish samples collected downstream of the factory, its bioavailability was questioned due to its large molecular size resulting in decreased uptake rates (Allchin et al., 1999). Another possible explanation of low BDE-209 concentrations in aquatic biota may be due to relatively rapid biotransformation.

In Table 3.3, the ratios between lipid weight concentrations in biota and concentrations in sediments normalized with organic carbon are reported. This table shows that levels of BDE-47 in fish were higher than levels in sediments, indicating the high bioavailability of this congener. It was also seen that the bioavailability decreases with increase in bromination degree, with a fish-to-sediment ratio around 0.1 for the hepta-congener BDE-183.

Table 3.2. PBDEs concentrations in fishes samples ng/g (lipid weight) (Eljarrat et al., 2007).

<table>
<thead>
<tr>
<th></th>
<th>V1 November 2004</th>
<th>V1 November 2005</th>
<th>V3 November 2004</th>
<th>V3 November 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barbel (n = 6)</td>
<td>Mean 12.6</td>
<td>Mean 11.2</td>
<td>Mean 8.27</td>
<td>Mean 3.25</td>
</tr>
<tr>
<td>Barbel (n = 8)</td>
<td>Mean 36.7</td>
<td>Mean 63.8</td>
<td>Mean 221</td>
<td>Mean 367</td>
</tr>
<tr>
<td>Barbel (n = 8)</td>
<td>Mean 2.85</td>
<td>Mean 3.46</td>
<td>Mean 137</td>
<td>Mean 306</td>
</tr>
<tr>
<td>Barbel (n = 8)</td>
<td>Mean 5.38</td>
<td>Mean 4.50</td>
<td>Mean 102</td>
<td>Mean 123</td>
</tr>
<tr>
<td>Barbel (n = 2)</td>
<td>Mean 2.35</td>
<td>Mean nd</td>
<td>Mean 34.0</td>
<td>Mean 114</td>
</tr>
<tr>
<td>Barbel (n = 5)</td>
<td>Mean nd</td>
<td>Mean nd</td>
<td>Mean 66.5</td>
<td>Mean 79.5</td>
</tr>
<tr>
<td>Carp (n = 2)</td>
<td>Mean 3.25</td>
<td>Mean 4.50</td>
<td>Mean 102</td>
<td>Mean 123</td>
</tr>
<tr>
<td>Barbel (n = 5)</td>
<td>Mean nd</td>
<td>Mean nd</td>
<td>Mean 66.5</td>
<td>Mean 79.5</td>
</tr>
</tbody>
</table>

% lipid | V1 | V2 | V3 | V4 |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Barbel (n = 6)</td>
<td>Mean 12.6</td>
<td>Mean 11.2</td>
<td>Mean 8.27</td>
<td>Mean 3.25</td>
</tr>
<tr>
<td>Barbel (n = 8)</td>
<td>Mean 36.7</td>
<td>Mean 63.8</td>
<td>Mean 221</td>
<td>Mean 367</td>
</tr>
<tr>
<td>Barbel (n = 8)</td>
<td>Mean 2.85</td>
<td>Mean 3.46</td>
<td>Mean 137</td>
<td>Mean 306</td>
</tr>
<tr>
<td>Barbel (n = 8)</td>
<td>Mean 5.38</td>
<td>Mean 4.50</td>
<td>Mean 102</td>
<td>Mean 123</td>
</tr>
<tr>
<td>Barbel (n = 2)</td>
<td>Mean 2.35</td>
<td>Mean nd</td>
<td>Mean 34.0</td>
<td>Mean 114</td>
</tr>
<tr>
<td>Barbel (n = 5)</td>
<td>Mean nd</td>
<td>Mean nd</td>
<td>Mean 66.5</td>
<td>Mean 79.5</td>
</tr>
</tbody>
</table>

Table 3.3. Ratios (mean values) between the concentrations of PBDEs found in barbel specimens (ng/g lipid weight) and the concentrations found in sediment (ng/g organic carbon) (Eljarrat et al., 2007)

<table>
<thead>
<tr>
<th></th>
<th>V1 November 2004</th>
<th>V1 November 2005</th>
<th>V3 November 2004</th>
<th>V3 November 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-47</td>
<td>3.83</td>
<td>1.82</td>
<td>4.91</td>
<td>0.67</td>
</tr>
<tr>
<td>BDE-183</td>
<td>0.05</td>
<td>-</td>
<td>0.09</td>
<td>0.13</td>
</tr>
<tr>
<td>BDE-209</td>
<td>-</td>
<td>-</td>
<td>0.0013</td>
<td>0.0011</td>
</tr>
</tbody>
</table>

nd: below limit detection; a: total PBDE value was calculated considering nd=0.
3.2.2 BFRs in Cinca River

In a sampling campaign of October 2002, a total of 23 specimens of barbel (*Barbus graellsi*) were collected, muscle tissues and liver tissue were preserved (frozen at $-20^\circ C$) until analysis. PBDEs have been detected in all the sediment samples at concentrations ranging from 2 to 42 ng/g dw (dry-weight). HBCD has been detected only in two samples, corresponding to the site near the chemical industry (site C3) (514 ng/g dw) and downstream (site C4) (90 ng/g dw) (see Table 3.4). In these samples, HBCD contamination was greater than that observed for PBDEs. This is the first time HBCD has been found in environmental samples in Spain (Eljarrat et al., 2004).

Table 3.4. Concentrations (expressed in ng/g dry weight) of PBDEs and HBCD$^*$ in the river, sediment samples of the 4 sites studied. nd$^a$=not detected (Eljarrat et al., 2004).

<table>
<thead>
<tr>
<th></th>
<th>Site C1</th>
<th>Site C2</th>
<th>Site C3</th>
<th>Site C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-47</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>BDE-100</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>BDE-118</td>
<td>nd$^a$</td>
<td>Nd</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>BDE-154</td>
<td>nd</td>
<td>0.1</td>
<td>0.3</td>
<td>2.9</td>
</tr>
<tr>
<td>BDE-153</td>
<td>0.1</td>
<td>0.1</td>
<td>0.5</td>
<td>7.8</td>
</tr>
<tr>
<td>BDE-183</td>
<td>0.1</td>
<td>0.1</td>
<td>0.6</td>
<td>22.8</td>
</tr>
<tr>
<td>BDE-209</td>
<td>2.1</td>
<td>2.1</td>
<td>39.9</td>
<td>5.7</td>
</tr>
<tr>
<td>Total BDEs</td>
<td>2.4</td>
<td>2.6</td>
<td>41.7</td>
<td>39.8</td>
</tr>
<tr>
<td>HBCD</td>
<td>nd</td>
<td>nd</td>
<td>513.6</td>
<td>89.7</td>
</tr>
</tbody>
</table>

*a*: concentrations expressed in ng/g dry weight, b: nd=not detected.

Regarding fishes samples (see Table 3.5), PBDEs were detected in all the muscle and liver samples at concentrations ranging from 0.2 to 436 and 0.1 to 446 ng/g ww (wet-weight), respectively. HBCD was detected only in samples corresponding to sites C3 (215-1127 ng/g ww for muscles, and 161-1172 ng/g ww for livers) and 4 (42-135 ng/g ww for muscles, and 49-180 ng/g ww for livers). In these samples, HBCD contamination was similar or greater than that observed for PBDEs.
Study site and environmental data

Table 3.5. Mean concentrations of PBDEs and HBCD\(^a\) in the muscle tissue and liver samples of the 4 sites studied (Eljarrat et al., 2004).

<table>
<thead>
<tr>
<th>Site</th>
<th>Muscle mean</th>
<th>Liver mean</th>
<th>Muscle mean</th>
<th>Liver mean</th>
<th>Muscle mean</th>
<th>Liver mean</th>
<th>Muscle mean</th>
<th>Liver mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>BDE 47</td>
<td>Nq 0.1</td>
<td>0.8</td>
<td>0.8</td>
<td>11.5</td>
<td>32.8</td>
<td>12.8</td>
<td>18.5</td>
</tr>
<tr>
<td></td>
<td>BDE100</td>
<td>Nd nd</td>
<td>Nq nd</td>
<td>0.7</td>
<td>4.2</td>
<td>Nq</td>
<td>12.4</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>BDE 118</td>
<td>Nd nd</td>
<td>0.3</td>
<td>nd</td>
<td>3.2</td>
<td>1.1</td>
<td>1.5</td>
<td>nd</td>
</tr>
<tr>
<td></td>
<td>BDE 154</td>
<td>Nq Nq 0.8</td>
<td>Nq</td>
<td>76.5</td>
<td>96.9</td>
<td>56.5</td>
<td>85.2</td>
<td>30.4</td>
</tr>
<tr>
<td></td>
<td>BDE 153</td>
<td>0.3 0.2</td>
<td>0.3 0.2</td>
<td>110</td>
<td>141</td>
<td>106.5</td>
<td>147.5</td>
<td>40.9</td>
</tr>
<tr>
<td></td>
<td>BDE 183</td>
<td>1 nd</td>
<td>1.4 nd</td>
<td>58.9</td>
<td>9.8</td>
<td>70.1</td>
<td>4</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td>BDE 209</td>
<td>Nd nd</td>
<td>Nd nd</td>
<td>Nd Nd</td>
<td>Nd Nd</td>
<td>Nd Nd</td>
<td>Nd Nd</td>
<td>Nd Nd</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>1.3 0.2</td>
<td>4.5 0.4</td>
<td>263.4</td>
<td>297.9</td>
<td>236.5</td>
<td>279.2</td>
<td>96.3</td>
</tr>
<tr>
<td></td>
<td>BDEs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HBCD</td>
<td>Nd nd</td>
<td>Nd nd</td>
<td>Nd Nd</td>
<td>309</td>
<td>750.4</td>
<td>483.9</td>
<td>624.8</td>
</tr>
</tbody>
</table>

|        |            |            |             |            |             |            |             |            |
|        |            |            |             |            |             |            |             |            |

\(a\): concentrations expressed in \(\mu g/g\) dry weight, b:nd=not detected.

One interesting result is that the BDE 209 (the most produced of deca-BDE congener (BSEF)), was not found in biota was the most present in sediments of the all PBDEs. When sediment concentrations were compared to those in barbel collected at the same sites along the Cinca River, high fish-to-sediment ratios were obtained (see Table 3.6).

Table 3.6. Ratios between the concentrations of PBDEs and HBCD found in fish (\(\mu g/g\) dry weight) and the concentrations found in sediment (\(\mu g/g\) organic carbon) from site C3 (Eljarrat et al., 2004)

<table>
<thead>
<tr>
<th>BFRe</th>
<th>Muscle to sediment</th>
<th>Liver to sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE 47</td>
<td>16.6</td>
<td>13.4</td>
</tr>
<tr>
<td>BDE 100</td>
<td>1.2</td>
<td>5.7</td>
</tr>
<tr>
<td>BDE 118</td>
<td>0.6</td>
<td>nd</td>
</tr>
<tr>
<td>BDE 153</td>
<td>16.7</td>
<td>18.9</td>
</tr>
<tr>
<td>BDE 154</td>
<td>20.7</td>
<td>20.0</td>
</tr>
<tr>
<td>BDE 183</td>
<td>4.3</td>
<td>0.5</td>
</tr>
<tr>
<td>BDE 209</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>HBCD</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Such comparisons are best made using lipid weight concentrations in the fish compared to the concentrations in sediment normalized to organic carbon (Bierman, 1990). However, all the muscle and liver material were used for BFR determinations, and no extra sample has been available for the determination of lipid content. Specially, levels of BDE-47, BDE-153, and BDE-154 in fish were high compared with levels in sediment (13-21-fold) indicating the high
bioavailability of these congeners. These large fish-to-sediment ratios indicate that these contaminants are bioavailable and are taken up readily by the fish. This is also supported by the fact that for some BDE congeners detectable were found in fish but not in the corresponding sediments: 17 different PBDEs were detected in fish samples, whereas only 8 PBDE congeners were found in sediments. Solely BDE-209, the main BDE congener found in sediments from the area, was not found in biota samples. The main reason for their absence in biota seems to be its relatively low bioaccumulation potential. This may be due either to a low uptake rate for this very large molecule or a relatively rapid excretion after biotransformation. The low bioconcentration hazard of BDE-209 was also reported by other authors (Yu et al., 2009; Mizukawa et al., 2009).

In November 2004, another sampling campaign was conducted. In Table 3.7, the sediment concentrations of the four sites are reported. HBCD results the most present pollutant after the industrial park of Monzon.

<table>
<thead>
<tr>
<th>Site</th>
<th>TOC</th>
<th>BDE 47</th>
<th>BDE100</th>
<th>BDE 154</th>
<th>BDE 153</th>
<th>BDE 183</th>
<th>BDE 209</th>
<th>total BDEs</th>
<th>HBCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>2.21</td>
<td>0.089</td>
<td>0.051</td>
<td>nd</td>
<td>nd</td>
<td>0.274</td>
<td>13.614</td>
<td>14.144</td>
<td>nd</td>
</tr>
<tr>
<td>C2</td>
<td>1.28</td>
<td>0.074</td>
<td>0.070</td>
<td>0.503</td>
<td>nd</td>
<td>0.416</td>
<td>35.981</td>
<td>37.171</td>
<td>9.075</td>
</tr>
<tr>
<td>C3</td>
<td>1.19</td>
<td>0.277</td>
<td>0.468</td>
<td>9.722</td>
<td>31.404</td>
<td>70.222</td>
<td>17.767</td>
<td>131.317</td>
<td>1613.105</td>
</tr>
<tr>
<td>C4</td>
<td>1.73</td>
<td>0.152</td>
<td>0.273</td>
<td>6.557</td>
<td>19.514</td>
<td>39.928</td>
<td>21.089</td>
<td>86.742</td>
<td>865.606</td>
</tr>
</tbody>
</table>

Table 3.7. Sediment concentrations of BFRs, expressed in ng/g dry weight.

The new sampling contains new biota samples of south-west European Nase (*Chondrostoma toxostoma*). As shown in Table 3.8, BFRs concentration increase significantly after site C3, the site corresponding to industrial park of Monzon. It also can be noted that the concentrations remains at high levels in site C4, probably because the low flow of the river.
### Table 3.8. Biota concentrations in ng/g lipid weight.

<table>
<thead>
<tr>
<th>BFRs</th>
<th>Site C1</th>
<th>Site C2</th>
<th>Site C3</th>
<th>Site C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE 47</td>
<td>1.44</td>
<td>3.74</td>
<td>64.3</td>
<td>37.17</td>
</tr>
<tr>
<td>BDE100</td>
<td>0.7</td>
<td>4.72</td>
<td>119</td>
<td>21.58</td>
</tr>
<tr>
<td>BDE 154</td>
<td>1.9</td>
<td>76.43</td>
<td>203.78</td>
<td>262.25</td>
</tr>
<tr>
<td>BDE 153</td>
<td>1.79</td>
<td>29.93</td>
<td>1716.6</td>
<td>225</td>
</tr>
<tr>
<td>BDE 183</td>
<td>0.37</td>
<td>1.55</td>
<td>212.88</td>
<td>114.25</td>
</tr>
<tr>
<td>BDE 209</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>total BDEs</td>
<td>7.59</td>
<td>143</td>
<td>4586.6</td>
<td>756.5</td>
</tr>
<tr>
<td>HBCD</td>
<td>nd</td>
<td>344.27</td>
<td>37552</td>
<td>10926</td>
</tr>
</tbody>
</table>

*nd* = not detected

With a new available technique (liquid chromatography), it has been possible to evaluate the distribution of the three HBCD isomers which are produced in mixture. In Figure 3.5 it is shown this distribution of sample sediment in site C4. The new analysis enables to understand the different behaviour of these molecules in environment, showing that of the three isomers the $\gamma$ – *HBCD* is the one with highest bioavailability and bioaccumulation.

![Liquid Chromatograph in CSIC](image1)

![Distribution of three commercial isomers of HBCD in site 4](image2)

*Figure 3.5. Left: Liquid Chromatograph in CSIC; right: distribution of three commercial isomers of HBCD in site 4. Sampling campaign of November 2004.*
4 FUZZY THEORY

Fuzzy logic is a type of multi-valued logic that represents a way to deal with uncertainty and vagueness opposed or alternative to classic or Aristotelian logic. Systems based on fuzzy logic are particular useful to solve complex problem in which the involved parameters are numerous and, in some cases, qualitative, vague and imprecise. It allows representing the uncertainty of a measure, or size, expressed in human language, like risk, hazard and quality. Fundamental components and tools of this theory are presented in this section. First, a historical introduction about the development of fuzzy logic in 20th century is given, then the main concept and features of this theory are described with a clarifying example, and finally the most common application of fuzzy theory are presented.

4.1 Historical evolution

The birth of Fuzzy Theory is based on the fact that traditional two-valued logical systems, classic set theory and probability theory are inadequate for dealing with imprecision, uncertainty and the complexity of the real world. It is generally agreed that an important point in the evolution of the modern concept of uncertainty has been the publication of a seminal paper by Lofty Zadeh named Fuzzy Sets (Zadeh, 1965). However, some ideas presented in the paper were envisioned some 30 years earlier, by the British-American philosopher Max Black and by the Polish philosopher Jan Łukasiewicz. The features of this new logic were developed both in USA and Japan in 1960s and 1970s, and it is generally agreed that the first application was made in 1974 in U.K. where Sito Assilian and Ebrahim Mamdani built the first boiler with a fuzzy system control (Wikipedia-Fuzzy Logic). In 1980s, there was a real boom of fuzzy applications in Japan, where the word fuzzy assumed the meaning of ‘intelligent’. In 1987, Hitachi made the first control system based on fuzzy logic for the Sendai subway. Today fuzzy logic is introduced in software systems like Fuzzy Logic Toolbox for MATLAB (1994), and it has provided consistent and proven means to model many real world system as industrial plants, electrical devices, risk assessment and, recently, occupational accidents analysis (Darbra et al., 2008). Fuzzy logic has at the same time many applications in environmental risk management; Lehn and Temme (1996) developed a fuzzy tool to classify potentially contaminated sites in Germany; Van der Werf and Zimmer (1998) proposed a fuzzy indicator of the environmental impact of pesticides used in agriculture; Mohamed and Cotè (1999) developed a decision analysis-based model to assess the
risk posed to human health from polluted sites; Hu et al. (2003) developed a tool for the selection of remediation techniques for petroleum contaminated site; Uricchio et al. (2004) proposed a decision support system based on fuzzy logic for groundwater pollution risk evaluation; Ocampo et al. (2006) calculated a water quality index with a fuzzy logic based system.

4.2 Fuzzy logic versus classic logic

Fuzzy logic (FL) is a type of multi-valued logic, this means that admits more than two truth values. In fact, as multi valued logic it denies the law of excluded middle, one of the fundamental principles of classic, or Aristotelian logic, according to which a proposition is necessarily true or false, so its truth degree belongs to the discrete set [True, False], represented by Boolean logic with values [0,1] (Klir and Yuan, 1995). Hence, no intermediate truth statuses are allowed in classic logic. So as multi valued logic FL can be considered a generalization, or more properly an extension of classic logic.

It can be said that the transition of the two logics born on the concept of fuzzy sets and on the difference with the classic concept of set. In classic logic if a class of object is considered, it can be divided in a set A and set non-A, and no object can belong both to A and non-A. A is a crisp set. Ordinary sets, also named crisp sets, are defined to divide the individuals in some given space into two groups: members (those that certainly belong to the set) and non-members (those that certainly do not). A well-defined and unambiguous separation exists between members and non-members, because crisp sets have a clear and well defined boundary. The characteristic function of a crisp set assigns a value of either 1 or 0 to each individual, according to the membership of each individual to the set considered. If an object falls into this crisp set, it is characterized by value 1; if an object is not member of this crisp set the function assigns a value of 0. In fuzzy logic, the concept of set is different from the one presented. This is explained in details in the following section.

4.3 Fuzzy sets

Fuzzy logic is built around the central concept of a fuzzy set and membership function, in fact, it is more properly called ‘fuzzy set theory’. The most important difference between fuzzy sets and crisp sets are the boundaries, which in fuzzy sets are not net and well defined. Hence, objects
can belong to a fuzzy set with a membership degree (from 0 to 1), assigned by a characteristic function, called membership function (MF). In others words it can be said that: a fuzzy set (FS) is a class of objects with continuum grades of membership (Zadeh, 1965). In practical application, fuzzy sets represent linguistic values, used to define a state of a variable or input of the problem. Generally these linguistic variables that involve fuzzy sets are words like ‘LOW’, ‘MEDIUM’, ‘HIGH’. A variable value can belong to two different fuzzy sets, in the same way. In terms of linguistic variables a parameter in a problem, can be LOW with its own membership degree to this fuzzy set, and at the same time it can be MEDIUM, with another membership degree to this fuzzy set.

After a preliminary introduction on the concept of fuzzy sets, now the standard definition can be given. Let $X$ be a space of points or objects, also called universe of discourse. A general element of $X$ is denoted by $x$. Then a fuzzy set $A$ is characterized by membership function $\mu_A(x)$ which associates each point in $X$ with a real number in the range between $[0,1]$, representing the grade of membership of $x$ in $A$. A fuzzy set $A$ can be considered as an ordered set of pairs:

$$A = \{x, \mu_A(x) | x \in X\}$$  \hspace{1cm} Eq. [4.1]

Where:

$$\mu_A : X \rightarrow [0,1]$$  \hspace{1cm} Eq. [4.2]

### 4.4 Membership functions

As said before, the concept of fuzzy sets is strictly related with the concept of membership function. Typically, the values which the membership function assigns to the inputs fall in the range $[0,1]$. This type of functions transforms the numerical value of a variable into a membership degree to a fuzzy set. The shape of the membership functions can be very different (see Figure 4.1), but trapezoidal and triangular shapes are the most common in current applications. For example, if a membership function is of trapezoidal type (see Figure 4.1 (d)); it is characterized by four parameters ($a_1, a_2, a_3, a_4$). The membership degree linearly increases from 0 to 1 for values between $a_1$ and $a_2$, is equal to 1 for values between $a_2$ and $a_3$ and decreases linearly to 0 for values between $a_3$ and $a_4$. 
4.5 Fuzzy sets versus crisp sets: an example

Considering, for instance, the problem about “how old is a person?” and a crisp set $A = \textit{set of old ages}$, and assuming a boundary of this set at 35 years, it can be said that if a person is 36 years old, he belongs to the crisp set $A$; else if the person is 34 years old, he does not belong to the crisp set of old ages. Figure 4.2 shows this concept.
The strong distinction across the boundary 35 years old seems to be too restrictive according to human language and thought.

This problem is now studied through fuzzy logic approach. The fuzzy sets related to the variable ‘age’ can be, for instance, individuated by linguistic variables or categories ‘YOUNG’, ‘MIDDLE AGE’, ‘OLD’, and one of the possible representation of this division is reported in Figure 4.3.

It can be noted that the transition between two fuzzy sets is gradual, and that there are intersection of the boundaries of the sets. This intersection is described by membership
functions shape and trend. The degree of overlapping between two fuzzy sets is proportional to the amount of uncertainty included in the description of a variable (Marchini et al., 2009). According to Figure 4.3, if the subject is 7 years old, surely it can be included in the young set and there is not the necessity to use fuzzy logic. But if the subject is 25 years old, he could be included in the set of “young” people and in the “middle age” set too. In this case fuzzy logic can be very useful to provide degrees of membership to each fuzzy set. In practice, Figure 4.4, shows how the degree of membership to each of the sets for a person of 40 years.

![Figure 4.4. The problem ‘how old is a person?’, using membership functions.](image)

Therefore, the person of 40 years belongs to two fuzzy set, with a two different membership degree: to the MIDDLE AGE set with a certain degree next to 0.9, to OLD set with degree approximately of 0.2. Hence it can be noted that the sum of membership degrees of the same variables (in the example the age) does not have to be equal to one. This property is based on the membership functions shapes and trends, which are context-dependent features. The capability to construct appropriate membership functions for given various concepts in various contexts is the base usefulness of a fuzzy system (Klir and Yuan, 1995).

### 4.6 Generalization of a fuzzy set

Fuzzy sets like those given by Eq. [4.1] are the most common in literature and are also called ordinary fuzzy sets or type-1 fuzzy sets. More generalized sets were introduced in 1975 by Zadeh.
(Zadeh, 1975). The reason to generalize fuzzy sets is that designing well-defined membership functions seems to be in contrast with the word ‘fuzzy’, that means lots of uncertainty. The first generalization of an ordinary fuzzy set is named *interval valued fuzzy sets*. In this case, membership functions are not as specific as their counterpart of ordinary fuzzy sets, but this lack of specificity makes them more realistic in some applications. Their advantage is that allows to express the uncertainty in identifying a particular membership degree and this uncertainty is involved in an interval-value also named *footprint of uncertainty (FOU)*, representing a blurring of classic MFs characterized by the lower and upper membership functions, LMF and UMF respectively. This concept is shown in Figure 4.5.

![Figure 4.5. Interval-valued fuzzy set (\(\tilde{A}\)) with a triangular membership function.](image)

FOU represents new features of fuzzy set theory, which contain other information useful to make a more realistic evaluation of the fuzzy phenomena. A further generalization can be made on the *interval valued fuzzy sets* if the interval is considered as a fuzzy set. Therefore the MF is three-dimensional and its third dimension represents the value of membership for each point of its domain, which is FOU. This type of sets is called *type-2 fuzzy sets* (see Figure 4.6).
According type-1 fuzzy sets have a grade of membership that is crisp, whereas type-2 fuzzy sets have a grade of membership that is fuzzy, so they can also called “fuzzy-fuzzy sets” (Mendel, 2007). The generalization can go on until type-n FS. The most significant disadvantage of this type of fuzzy set is that computational complexity increases considerably for each higher type of fuzzy sets, but at this time several works have been published on the application of type-2 fuzzy sets and interval valued fuzzy sets (Mendel, 2007; Chen, 2010; Ramirez, 2011; Acosta et al., 2010).

4.7 Fuzzy approaches and applications

Fuzzy theory has different application thanks to practical system developed on its features. The two most common techniques based on fuzzy logic are now described in broad terms.

4.7.1 Fuzzy Inference System (FIS)

The Fuzzy inference system has many applications in several fields, like risk assessment, water quality evaluation and environmental risk assessment. In Figure 4.7, the main steps that constitute the system are presented.
The steps to be done to apply inference processes include:

- Identification of representative, rational and accurate input and output variables
- Selection of level categories (or sets) for each input and output variable (e.g. low, medium, high)
- Establishment of membership functions (triangular, trapezoidal, Gaussian, etc.) for each input and output variable at each level
- Applying an inferring process (box named ‘FUZZY INFERENCE’). This step includes several elements and processes and it is based on a rules system. These rules are linguistic propositions which link the inputs, in the form of linguistic variables, with the outputs, linguistic or quantitative as well. There are two principal ways in which fuzzy rules can be determined:
  1. Eliciting them from experienced human operators;
  2. Obtaining them from empirical data by suitable learning methods, usually with the help of neural networks.

There are two types of fuzzy inference systems that are commonly implemented: Mamdani-type and Sugeno-type. These two types of inference systems vary somewhat in the way outputs are determined. Mamdani’s fuzzy inference method, which is the most commonly used fuzzy methodology, expects the output membership functions to be fuzzy sets. On the other hand, Sugeno-type systems are used to model any inference system in which the output membership functions are either linear or constant (The Mathworks, 2010). This fuzzy approach will be explained in more details in the methodology section, since it is the one implemented for risk assessment in this project.
4.7.2 Fuzzy synthetic evaluation (FSE)

If raw data have to be grouped into several categories according to predetermined criteria, fuzzy synthetic evaluation (FSE) can be applied. Two concepts from crisp and fuzzy logic theory are used in this type of evaluations: relation between finite sets and composition of relations. A brief and clear description of these two concepts is given in Buckley and Eslami (2002). The steps described below have to be followed when applying this technique:

- Select \( n \) assessment parameters which are representative, rational and accurate in order to form an assessment factor set \( U = \{ u_1, u_2, \ldots, u_n \} \);
- Select \( m \) assessment criteria categories in order to form an assessment criteria set \( V = \{ v_1, v_2, \ldots, v_m \} \) (e.g. \( V = \{ \text{low, medium, high} \} \));
- Establish membership functions of each assessment parameter to assessment criteria at each level;
- Replace monitoring data of each assessment parameter into the membership functions to get the fuzzy relation matrix \( \bar{R} \), which can be expressed as:

\[
\bar{R} = \begin{bmatrix}
    r_{11} & r_{12} & \cdots & r_{1m} \\
    r_{21} & r_{22} & \cdots & r_{2m} \\
    \vdots & \vdots & \ddots & \vdots \\
    r_{n1} & r_{n2} & \cdots & r_{nm}
\end{bmatrix}
\]

Where \( r_{ij} \) (\( i = 1, 2, \ldots, n; j = 1, 2, \ldots, m \)) means the membership degree of the \( i^{th} \) assessment parameter to the assessment criterion at the \( j^{th} \) level.
- Establish or compute the weights of each assessment parameter, i.e. their relative importance, to get a matrix of weights, such as:

\[
\bar{W} = [w_1 \quad w_2 \quad \cdots \quad w_n]
\]

This can be done by applying several methods: the superscale method, the entropy method, the Analytic Hierarchy Process (AHP), etc. The superscale method refers to the computation of the ratio of the value of every assessment parameter at each monitoring point over corresponding water quality standards (Shen et al., 2005). The entropy method entails the measurement of the amount of useful information within the data provided (Zou et al., 2006) and the AHP method deals with the estimate of the importance of a given set of parameters when they are compared pair-wise using a comparison scale developed by Saaty (1990).
• Carry out the composition of fuzzy relations \( \overline{W} \) and \( \overline{R} \) (\( \overline{B} = \overline{W} \circ \overline{R} \)). This can be computed similar to matrix multiplication (i.e. \( b_j = \sum_{i=1}^{n} w_i r_{ij} \)) or by replacing addition and multiplication by the appropriate operations of fuzzy sets intersection and union, respectively.

• Assign an assessment criterion level to evaluate the resulting \( \overline{B} \) matrix. For example, the maximum value of \( \overline{B} \) may determine the level.
## 5 METHODOLOGY

### 5.1 Introduction

The methodology developed to evaluate the risk due to BFRs contamination in aquatic organisms is described in this chapter. The model has been built using fuzzy logic. More specifically, several interconnected Fuzzy Inference System (FIS) have been defined (see section 4.7.1). Information from experts has been required to define the whole system. In order to get this information a questionnaire has been designed and proposed to a wide group of international experts. Experimental data from the study area, as well as, from scientific literature have been used to test the model.

In the following subsections, the structure of the model is presented. Then specific characteristics of the FIS are explained and finally the questionnaire structure (sent to international experts) is described. Moreover, with the aim to consider the different weight or importance of several variables involved, an adaptation of the Analytic Hierarchy process is proposed.

### 5.2 Variables definition

Generally, the environmental risk evaluation of a substance is made following the plan:

- Hazard Identification;
- Effect assessment (relationship between dose and response);
- Exposure assessment;
- Risk characterization.

Several adaptations to this traditional process are found. One of them, is the comparison between the substance concentration in a specific environmental matrix (PEC) and the concentration under which no effects occur for the organisms present in this matrix (PNEC), created by European Commission (EC), according to the Technical Guidance Document on Risk Assessment (EU, 2003). However, this methodology may not be adequate to ensure the protection of all the environmental targets or compartments. Considering persistent organic pollutants (POPs), it is needed to identify the substance hazard related to their capacity to persist in environment and accumulate in biota. A model able to evaluate and quantify the
Environmental risk of PBDEs / HBCD, and more generally, hydrophobic compounds, is presented in this section. As seen in Figure 5.1, the risk for the aquatic organism depends on substance toxicity properties, on its bioaccumulation in the organism and on the environmental matrix properties. At the same time, each one of these macrovariables depends on several microvariables (e.g. intrinsic toxicity, biomagnification, chemical and physical degradation).

![Figure 5.1. General scheme of aquatic organism risk.](image)

Due to the complexity of getting information on all these microvariables, an adaptation of the original scheme has been made. This is based on the BFR’s properties and behaviour in aquatic matrix. This model takes into consideration the central role of the sediment and biota since BFR’s are lipophilic substances therefore are mainly found in these two compartments and not in water. As shown in Figure 5.2, this model consists of three interconnected FIS, each FIS having several inputs (group of factors) and one output.

![Figure 5.2. General scheme of the three groups which constitute the system.](image)
Each factor included in the model has been represented by the associated variable indicator listed in Table 5.1. The three outputs (Risk, Hazard and Accumulation) have been defined as real numbers included in the range [0,1]. Data availability and the necessity to implement the risk evaluation with PBT (Persistence-Bioaccumulation-Toxicity) evaluation has been the criterion for variables choice.

<table>
<thead>
<tr>
<th>FACTOR</th>
<th>INDICATOR VARIABLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioavailability</td>
<td>Total Organic Content (TOC)</td>
</tr>
<tr>
<td>Bioaccumulation</td>
<td>Biota-Sediment Accumulation Factor (BSAF)</td>
</tr>
<tr>
<td>Biomagnification</td>
<td>Biomagnification Factor (BMF)</td>
</tr>
<tr>
<td>Persistence</td>
<td>Degradation Half-Life</td>
</tr>
<tr>
<td>Toxicity</td>
<td>Non-Observed Effects Concentration (NOEC)</td>
</tr>
<tr>
<td>Exposure</td>
<td>Concentration of the Chemical in Sediment</td>
</tr>
</tbody>
</table>

Next each of the three groups with their inputs/outputs is discussed:

- **Group 3**: as explained in section 2.1.1 and in 2.2.1, PBDEs and HBCD are both hydrophobic pollutants. Thus, they bioaccumulate in aquatic matrix, especially, in sediments and suspended solids. The fate of these hydrophobic chemicals is largely determined by sorption to suspended particulates and sediments (Loonen et al., 1994). Sorption of these pollutants in aquatic organisms depends on the characteristics of both the sediments and the chemicals involved (Ron van der Oost et al., 1996). Among other factors, sorption is determined by the sediments’ organic matter content and particle size. The affinity of non-polar compounds for sediment is primarily dependent on its hydrophobicity (Ron van der Oost et al., 1996). Relative to the water column, sediment is a more appropriate environmental compartment to be related to levels of pollutants in biota (Connor, 1984). Moreover, sediment characteristics are fewer dependants on seasonal variations. In addition, sediments may serve as a storage compartment for long-term release, reflecting the history of discharges to an area (Connor, 1984). Group 3 has three inputs (Bioavailability, Bioaccumulation, Biomagnification) and all of these are related with the sediment; whereas the output provides information about the accumulation level in biota.
Bioavailability is defined as the contaminant flux, which is function of the local environment conditions, including contaminant interactions with the solid matrix, concentration gradients, pH, redox potential, solution composition and TOC. Considering this, TOC has an important role on the bioavailability of organic contaminants, because it represents the organic matter present in the sediment in which the contaminant enters in the biological process (EPA-1999). Therefore, it has been selected as indicator variable for bioavailability.

Biomagnification is the process in which, the chemical concentration in an organism achieves higher level, than that of a lower step in trophic chain (Veltman et al., 2005). Molluscs and benthic invertebrates live and feed directly on contaminated sediments. These types of organisms are at lowest level of food chain, so the BDE congeners move up through food chain from bottom-feeding fish to bigger organisms. The indicator used to evaluate this variable is the BMF (Biomagnification Factor):

$$BMF = \frac{C_u}{C_i}$$  \hspace{1cm} Eq. [5.1]

Where:

- $C_u$ is the pollutant concentration in the organism of upper level in food chain;
- $C_i$ is the pollutant concentration in the organism of lower level in food chain.

The data needed to calculate the BMF factor according to Eq. [5.2] are not available. Therefore, BMF values used have been obtained from the literature. In particular both for PBDEs and HBCD the most conservative values met have been selected. These are for HBCD 1.2, whereas for PBDEs 3.2. For what concern PBDEs, in each sample, more than one congeners have been detected, and the value of 3.2 refers to the lowest brominated congener, BDE-47.
Bioaccumulation is defined as the net process in which the contaminant concentration in an organism achieves a level exceeding that in environmental matrix (Veltman et al., 2005). This variable has been associated to Biota to Sediment Accumulation Factor (BSAF):

\[
BSAF = \frac{C_B}{C_S}
\]

Where:

- \( C_B \) is the pollutant concentration in biota normalized to lipid fraction;
- \( C_S \) is the pollutant concentration in the sediment normalized to organic carbon fraction (Veltman et al., 2005).

As previously shown in the section 3.2, experimental data available for this FIS are concentrations of PBDEs and HBCD in biota and sediments and TOC. Hence it has been possible to calculate the BSAF values for the specific cases of study reported in this project. For PBDEs, a BSAF value for each congener present in the samples has been calculated and the highest, hence the most conservative, has been elected.

- **Group 2**: as PBT pollutants, PBDEs and HBCD cannot be removed at rates adequate to prevent their bioaccumulation in aquatic species (EPA 1999). Group 2 provides the hazard of the substance, related to the biota, processing three inputs: Persistence, Accumulation in Biota (the output of Group 3) and Toxicity.

  - **Persistence** is the residential time, at steady state, in multimedia environment. Degradation half-life (\( T_{1/2} \)) has been selected as indicator variable, and data on it were taken from, ecotoxicology data base, literature and performed under similar conditions (aerobic conditions).

  - **Toxicity** is the degree to which a substance can damage an organism. No Observed Effect Concentration (NOEC) in the water has been chosen as indicator for the toxicity. This is a risk assessment parameter that represents a concentration of a pollutant that will not harm the species involved and derives from toxicity tests (OECD, 2006). Generally, two types of NOEC exist, acute and
chronic. In this work, chronic NOEC values have been considered and they have been obtained from literature. As for other indicators, also for the NOEC the most conservative values have been chosen and they are $2 \mu g/l$ for PBDEs and $3.1 \mu g/l$ for HBCD.

- **Accumulation** is a value between $[0,1]$ and represent the chemical quantitative accumulated in the organism.
- **Group 1**: provides information about final levels of risk for biota. It has only two inputs: the hazard (output of Group 2) and the exposure.
  - **Exposure** refers to the chemical concentration that can occur in any environmental matrix, in this case the sediment. The indicator variable selected to represent exposure is simply the pollutant concentrations in sediment normalized to the organic carbon fraction (PEC); in this model exposure is calculated as:
    
    $$
    Exposure = \frac{PEC}{PNEC}
    $$

    Eq. [5.3]

    Where $PEC$ is the total PBDEs concentration in sediment and $PNEC$ is the Predicted No Effect Concentration. Different ways to calculate the PNEC exist, but in this study the method advised from the Technical Guidance Document (TGD) (EU, 2008) has been chosen. According to this, the PNEC in the sediment is the NOEC in the sediment divided by 10. The most conservative values met in literature belong to the lower brominated congeners (i.e. tetra and penta brominated), and is equal to $1.55 \ mg/kg \ dw$. This PNEC is normalized at 5% of TOC, hence, for each singular case the PNEC is:

    $$
    PNEC^* = 1.55 \ast \frac{TOC^*}{5}
    $$

    Eq. [5.4]

    Where, $PNEC^*$ and $TOC^*$ are the specific values for each study case. For HBCD the most conservative value of PNEC in sediment is $0.86 \ mg/kg \ dw$.

- **Hazard**, is the output of Group 2, and belong to the range $[0,1]$.

Each of the three steps is connected to others with a FIS (Fuzzy Inference System). The choice to use fuzzy logic is based on different reasons; first the scarcity of data about flame retardants, in
particular HBCD, seconds the need to handle controversial, sensitive and subjective parameters, like toxicity and risk (Darbra et al., 2008).

5.3 Model design: Fuzzy inference System (FIS)

As commented before, the model designed for this study uses one of the main applications of fuzzy theory, the Fuzzy Inference System (FIS). In this section, an explanation of each one of the steps of the FIS will be given. The system has been built using the Fuzzy Toolbox presented in Matlab. Hence, the process applied to this study will be explained using this tool as basis.

Fuzzy inference is the process of formulating the mapping from a given input to output using fuzzy logic. In Figure 5.3, a general scheme is presented.

As shown in the scheme, first the inputs or numerical values are transformed into fuzzy values or numbers, then this fuzzy numbers are treated with fuzzy rules to generate a fuzzy output. Finally, a numerical output is obtained through a defuzzification process. In the following section, a description of all these parts with their own applications is given.

The Fuzzy Toolbox allows to act on every step in the inference process and even to modify it. The starting window (see Figure 5.4) is divided into two parts: the upper one, in which it is possible to insert input variables (left side) and output variables (right side); the lower one where there are the commands which can be used to modify all the steps that constitute the inference
Environmental Risk Assessment of PBDE and HBCD in Ebro River Basin

process, discussed in following section. Hence the first action is to insert variables system; for instance, considering the Group 3 (see Figure 5.2), the starting point is reported in Figure 5.4.

![Image of FIS Editor: Group3](image)

**Figure 5.4. The Fuzzy Toolbox on Matlab.**

### 5.3.1 Fuzzification

The fuzzification is the process in which numerical values or inputs are converted into fuzzy numbers; to do this, numbers and names of the fuzzy sets are needed (see section 4.3 for more details). Moreover it is necessary to establish the type and parameters of membership functions.

For instance, two input variables, $X_1$ and $X_2$, can be considered. A possible fuzzification of these parameters is shown in Figure 5.5.
In the present study the fuzzy sets or linguistic variables used, for all of the parameters of the system are: LOW, MODERATE, HIGH.

Only for the final output, Risk, five different fuzzy sets have been used: NEGLIGIBLE LOW, MODERATE, HIGH, VERY HIGH.

Membership functions relate values of the variables with the fuzzy sets (see section 4.4). The parameters of the function have been established thanks to the experts’ opinion gathered through the questionnaire (explained in section 5.6). In this study three types of membership functions have been used:

- **Z-shape** used in the case of study of lower fuzzy sets, like LOW and NEGLIGABLE; for this function, it is necessary to know two parameters \(a\) and \(b\) which locate the extreme of sloped portion of the curve as given by

\[
f(x,a,b) = \begin{cases} 
1, x \leq a \\
1 - 2\left(\frac{x-a}{b-a}\right)^2, a \leq x \leq \frac{a+b}{2} \\
2\left(\frac{x-b}{b-a}\right)^2, \frac{a+b}{2} \leq x \leq b \\
0, x \geq b 
\end{cases}
\]

Eq. [5.5].
Figure 5.6. An example of Z-shape membership function.

- **S-shape** used in the case of study for upper fuzzy sets, like HIGH and VERY HIGH, in which two parameters are also needed,

\[
f(x,a,b)=\begin{cases} 
0, & x \leq a \\
2 \left(\frac{x-a}{b-a}\right)^2, & a \leq x \leq \frac{a+b}{2} \\
1-2 \left(\frac{x-b}{b-a}\right)^2, & \frac{a+b}{2} \leq x \leq b \\
1, & x \geq b 
\end{cases} \quad \text{Eq. [5.6]}
\]

Figure 5.7. An example of S-shape with two parameters.
The Π-shape used in the case of study for intermediate fuzzy sets, like MODERATE and as well as for the final risk, LOW and HIGH. For this function four parameters are needed and it is represented be equations:

\[
f(x, a, b, c, d) = \begin{cases} 
0, & x \leq a \\
\frac{2(x-a)^2}{b-a}, & a \leq x \leq \frac{a+b}{2} \\
1-\frac{2(x-b)^2}{b-a}, & \frac{a+b}{2} \leq x \leq b \\
1-\frac{2(x-c)^2}{d-c}, & c \leq x \leq \frac{c+d}{2} \\
\frac{2(x-d)^2}{d-c}, & \frac{c+d}{2} \leq x \leq d \\
0, & x \geq d
\end{cases}
\]

Eq. [5.7]

Figure 5.8. An example of Π-shape function.

Functions can be modified or added in the opposite window. As seen in Figure 5.9, the different membership functions for the Group 1 are reported. The previous functions shapes have been selected because they allow:

- To pass form one fuzzy sets to others in gradual way;
- To define them with few parameters.
5.3.2 Fuzzy rules

Fuzzy rules are used in fuzzy systems to connect the input with the output, and normally they are based on propositions like: if...then.... One of the most important features of fuzzy logic is that this proposition, therefore human language, can be used when data and measures available are affected by errors and uncertainty. The if... part of a rule is called ‘antecedent part’, which states conditions on the input variable(s); the then... part is called ‘consequent part’ and describes the corresponding state of the output variable(s).

The total number of possible non-conflicting fuzzy inference rules is (Klir and Yuan, 1995):

\[ N_{rules} = n_{fs}^{n_{e}} \]  

Eq. [5.8]

Where:

- \( N_{rules} \) is the number of rules;
- $n_f$ is the number of fuzzy sets;
- $n_v$ is the number of variables in input.

There are two principal ways in which fuzzy rules can be determined. One way is to elicit them from experts on the topic. The other way is to obtain them from empirical data by suitable learning methods, usually with the help of neural networks. In this study, the first option has been selected. The total possible combinations of the inputs in the antecedent part have been considered. The consequent part has been established thanks to the opinion of several international experts on the topics. Hence, for this particular study it can be said that there are:

- 27 rules for Group 2 and 3, $3^3$;
- 9 rules for Group 1, $3^3$.

In Figure 5.10, the rules editor of Group 2 is presented (i.e. inputs: persistence, fish accumulation and toxicity; output: hazard).

![Figure 5.10. Rules editor for Group 2.](image)
5.3.2.1 **Operators**

Generally it is necessary to deal with more than one input variable. In this case the antecedent part is built with fuzzy operators. Hence, the multiple variables can be related through logic operators based on the fuzzy sets operations according to the following relationships:

- Logic operator **NOT** → fuzzy complement;
- Logic operator **AND** → fuzzy intersection;
- Logic operator **OR** → fuzzy union.

Operations with fuzzy sets are extensions of those corresponding to ordinary sets. Considering two fuzzy sets \( A \) and \( B \), it can be said that:

- \( A \) and \( B \) are **equal** \( (A = B) \) if and only if \( \mu_A(x) = \mu_B(x) \) for all \( x \) in \( X \).
- A fuzzy set \( A \) is **empty** if and only if its membership function is identically zero in \( X \).
- The **complement** of a fuzzy set \( A \) denoted as \( \bar{A} \), is defined as:
  \[
  \mu_{\bar{A}}(x) = 1 - \mu_A(x) \quad \text{Eq. [5.9]}
  \]
- The **union** \( A \cup B \) is defined as:
  \[
  \mu_{A \cup B}(x) = \max[\mu_A(x), \mu_B(x)] \quad \text{Eq. [5.10]}
  \]
  The union \( A \cup B \) is the smallest set containing both \( A \) and \( B \).
- The **intersection** \( A \cap B \) is defined as:
  \[
  \mu_{A \cap B}(x) = \min[\mu_A(x), \mu_B(x)] \quad \text{Eq. [5.11]}
  \]

As in the union operation, the intersection of \( A \) and \( B \) is the largest set which is contained in both \( A \) and \( B \).

It is clear that if the interval \([0,1]\) is considered, classical and fuzzy operations are the same, just as it is shown in the following figures (Figure 5.11 and Figure 5.12).
The fuzzy complement, intersection and union are not unique operations. Contrary to their crisp counterparts different functions may be appropriate to represent these operations in different contexts. Therefore, not only membership functions of fuzzy sets but also operations on fuzzy sets are context-dependent. The capability to determine appropriate membership functions and meaningful fuzzy operations in the context of each particular application is crucial for making fuzzy set theory practically useful.

A desirable feature of the standard fuzzy operations is their inherent prevention of the compounding of operands errors. If any error \( e \) is associated with the membership degrees \( \mu_A(x) \) and \( \mu_B(x) \), then the maximum error associated with the membership grade of \( x \) in any operations remains \( e \) (Klir and Yuan, 1995).

To illustrate an example of fuzzy operator, the case in which \( X_1 = 3 \) and \( X_1 = 2.75 \) can be considered; taking only the rule, ‘If \( X_1 \) is LOW and \( X_2 \) is MEDIUM than \( Z \) is AVERAGE’, the membership degree to the LOW set for \( X_1 \) and MEDIUM set for \( X_2 \) are:

- \( \mu_{LOW}(X_1 = 3) = 0.5 \)
Given particular values of the input variables, the degree of fulfilment of a rule is determined by aggregating the membership degrees of these input variables into the respective fuzzy sets. The fuzzy output is obtained by degrees of fulfilment and the consequent part of the rules. As commented before, the operators used to connect several fuzzy sets are the AND and OR operators. The complement NOT, is not considered because it refers to the same fuzzy sets and it is not able to operate on more fuzzy sets. In this study the And operator has been used, therefore the two main methods to apply it will be explained: Minimum and Product.

Recovering the previous example, from the two membership degree, an output can be obtained using the “minimum” method:

$$\mu_{OUT} = \min(\mu_{X_1}, \mu_{X_2}) = \min(0.5, 0.25) = 0.25$$

The other possibility is to use the “product” method between the two membership degrees:

$$\mu_{OUT} = \mu_{X_1} \times \mu_{X_2} = 0.125$$

In the minimum and product method, variable weights have been considered to be equal. However, in this study the importance of these variables wanted to be reflected on the system. A different operator in the inference system has also been used. This is possible in the Fuzzy Toolbox modifying the And button as shown in the next figure. Therefore, a different operator for the inference system has been introduced in the Fuzzy Toolbox. As it can be seen in Figure 5.14, the And method has been changed to AHP_weight method. The comparison of these three methods will be made in the results section.
This method is an adaptation of the original AHP method explained in section 5.5.1. Just to understand the AHP_weights method works, a brief description is given. This operator is a function built in Matlab which allows inserting the weights derived from questionnaire. The function that constitutes a new operator is the following.

```matlab
function y = AHP1_and(x)
    w_var=[0.5 0.5];
    if min(x)==0
        y=0;
    else
        y=w_var.*x;
    end
```

Figure 5.14. The new fuzzy operators used in the Group 3.

Figure 5.15. Matlab function used to insert the weights in the model.
As shown in the reported Matlab script, the function has, as inputs, the vector $x$, which components are the membership degree of the antecedent part. The output is the sum of the products between these degree (values in the range $[0,1]$) with the corresponding weights.

$$y = \mu_1 \cdot w_1 + \mu_2 \cdot w_2 + \mu_3 \cdot w_3$$  \hspace{1cm} \text{Eq. [5.12]}

Where:

- $\mu_1, \mu_2$ and $\mu_3$ are the membership degree of three variable, for instance, in Group 3 they are the membership degrees of bioavailability, bioaccumulation and biomagnification;
- $w_1, w_2, w_3$ are the weights associated to variables;
- $y$ is the membership degree of the consequent part of the specific rule.

The obtainment of these weights comes from the questionnaire and the application of the AHP. This is explained in section 5.5.

The condition: \textit{if $\min(x) = 0$ \hspace{0.5cm} then $y = 0$}; it is needed because the inference rules are only activated if all degrees, in antecedent parts, are more than zero.

5.3.2.2 Implication

Implication is a graphical process in which for each rule involved in the system, the membership degree of the consequent part (i.e. the output of the Operators part) is transformed in an area. The extension and shape of this area depend on both the fuzzy sets representing the consequent part of the rule and the implication method. In fuzzy toolbox, two ways for this step are reported:

- \textit{The minimum}, which truncates the output fuzzy set
- \textit{The product}, which scales the output fuzzy set.

Taking the value of previous example 0.25 in previous example, the two ways of implication to calculate the area are shown in Figure 5.16.
The implication method chosen in this study is the minimum. The decision has been based on the extended use of these in literature (Ocampo et al., 2006).

5.3.3 Aggregation

To find an output value, all the rules used in the system have been considered. Aggregation is the process by which the fuzzy sets of the output provided by each rule are combined in one single fuzzy set representing the fuzzy output of the system. In the previous example, only one rule has been used for simplicity, but to represent meaningful outputs, all the rules that are involved in the problem have to be taken in consideration. Practically, the different areas obtained across the different rules have to be overlapped. For example, if the two outputs shown in Figure 5.17(a) and Figure 5.17(b) are considered, from to two different rules, the aggregated output would be that shown in Figure 5.17(c).
Defuzzification is the process used to obtain a final crisp number that represents the output. Different methods can be used:

- **Centroid method**: It is also named *center of the area* or *center of gravity*. It gives the value within the range of output variables for which the area under the graph of membership function is divided into two equal subareas. This value is calculated by the formula shown in Eq. [5.13] (Klir and Yuan, *Fuzzy sets and Fuzzy logic*). An example is given in Figure 5.18

\[
z^* = \frac{\int \mu(z) \cdot zdz}{\int \mu(z)dz}
\]

Eq. [5.13]

Where:

- \(z^*\) is the final numerical output;
- \(\mu(z)\) is the membership function of the output
- \(z\) is output value under the membership function graph.
As like shown in Figure 5.18, the defuzzified value is:

\[ z^* = 73.8 \]

- **Smallest, middle, and largest of maximum (SOM,MOM, LOM):** These three methods refer to the maximum value assumed by the aggregate membership function. This means that from the maximum value of the function, the smallest point is taken for \( SOM \), the medium \( MOM \) and the largest for \( LOM \). In the example given in Figure 5.18, MOM, SOM and LOM values would be: 90, 80 and 100.
As reported in Figure 5.19, centroid method represent a more gradual way to obtain a numerical values respect others methods. According to this, and also because centroid is the most used in literature, this method of defuzzification has been used in this study. But the centroid method has a flaw, it can never reach the highest values in the output range, for instance, in the first group of the study model, it is impossible to set a risk equal to one. In this study, this issue is resolved representing the final result not only as a crisp number, which is obtained after defuzzification, but also in term of membership degree of outputs. In this way a final RISK output of 0.8 or 0.9 has a membership degree to the fuzzy sets HIGH or VERY HIGH close or even equal to 1. This option seems to be the best and is consistent with the principles of fuzzy logic.

### 5.4 Mamdani-Assilian vs Takagi-Sugeno-Kang

The system presented until now follows Mamdani-Assilian method, the most commonly used for fuzzy inference. Takagi Sugeno-Kang is an alternative way, to infer very similar to the first one. The first two parts of the Sugeno system are the same: (fuzzification and application of the rules). The main difference between these two systems is then in the output membership function. In Sugeno inference, the output function is either linear or constant. For instance if two input variables $X_1$ and $X_2$ are considered, the output of a given rule might be:
Methodology

\[ Z = AX_1 + BX_2 + C \quad \text{Eq. [5.14]} \]

Where \( A, B \) and \( C \) are constants.

The output of each rule \( z_i \) is related with the weight of the rule and finally the output number is obtained as:

\[ Z = \frac{\sum_{i=1}^{N} w_i z_i}{\sum_{i=1}^{N} w_i} \quad \text{Eq. [5.15]} \]

Where:

- \( w_i \) is the degree of fulfillment of the \( i \)-th fuzzy rule;
- \( N \) is the total number of fuzzy rules;
- \( Z \) is the fuzzy output.

Sugeno system is suited for modelling nonlinear systems by interpolating between multiple linear models. Inference systems used in this study, are Mamdani-Assilian type built on Fuzzy Toolbox in Matlab. This type of model has been preferred to Sugeno type because is more commonly used and is well suited to human input (Matworks). Moreover Sugeno type is preferable in problems with a lot of available data, this is not the case of environmental studies in general.

5.5 The weights

The acknowledgment of the different importance of the variables involved in a system is a quite new aspect in fuzzy systems developed to environmental risk assessment. Therefore, in this study introducing weights to the different inputs has been of special relevance. In practice, the aim has been not only to establish, for instance, if bioavailability is more important than biomagnification, but also to quantify their relative importance. In this section, the mathematical method used to establish these weights will be explained. It consists of two parts, the matrix construction (5.5.1) and the weights and consistency obtainment (5.5.2).

5.5.1 Analytic hierarchy process (AHP)

AHP is a tool used to facilitate the solution of complex problems in which numerous and conflicting information is involved (Saaty, 1980). When it is necessary to work with different
parameters in a problem, it could be very important to establish if some of these parameters are more important than others and quantify their importance. The first step to deal with this problem is to build a positive and reciprocal matrix in which the elements are numerical values, representing a pair comparison of the parameters involved in the problem. From this matrix a vector representing the importance or weights of each parameter to the others is calculated. Finally a consistency index for the original matrix is defined. In this section, the process of building a matrix is explained and the comparison criteria are presented. The matrix algebra tool used to calculate the weights is also detailed.

5.5.1.1 Building comparison matrix A

In AHP methodology the first step is the pair wise comparison of the parameters. This comparison is based on a set of numerical values (generally integers) representing the importance that each parameter can assume in relation to others. The following definition for the matrix $A$ is given:

$$A = (a_{ij}), i, j = 1, \ldots, n$$  \hspace{1cm} \text{Eq. [5.16]}

Where:

- $n$ is the parameters number;
- $a_{ij}$ are the element of matrix that represent pair wise comparison factor based on the range $[m, \ldots, M]$.

Therefore on the diagonal of the matrix $A$ the element $a_{ii} = 1$. Then matrix elements satisfy others two conditions:

1. $a_{ij} > 0$;
2. $a_{ij} = 1/a_{ji}, i, j = 1, \ldots, n$

Hence, considering for instance, three parameters general representation of $A$ could be:

$$A = \begin{pmatrix}
1 & a_{12} & a_{13} \\
1/a_{12} & 1 & a_{23} \\
1/a_{13} & 1/a_{23} & 1
\end{pmatrix}$$  \hspace{1cm} \text{Eq. [5.17]}
5.5.1.2 Choosing a comparison scale

Generally, in literature comparison scale range from 1 to 9 (Gass, 2004; Ocampo, 2006) and the relative explications are reported in Table 5.2.

<table>
<thead>
<tr>
<th>Importance</th>
<th>Definition</th>
<th>Explication</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Equal importance</td>
<td>Two element contribute equally to the objective</td>
</tr>
<tr>
<td>3</td>
<td>Moderate importance</td>
<td>Experience and judgement slightly favour one element to another</td>
</tr>
<tr>
<td>5</td>
<td>Strong importance</td>
<td>Experience and judgement strong favour one element to another</td>
</tr>
<tr>
<td>7</td>
<td>Very strong importance</td>
<td>One element is favoured very strongly over another and this is demonstrated by practice</td>
</tr>
<tr>
<td>9</td>
<td>Extremely importance</td>
<td>The evidence favouring one element over another is of the highest possible order of affirmation</td>
</tr>
</tbody>
</table>

Although, numbers 2, 4, 6, 8 are not present in the table, but they can be used to represent middle states. In the presented study, to simplify the problem a [1, 5] comparison scale has been chosen, because nine options for the comparison between two variables have seemed too complicated when asking to experts and unsuitable to this study. Moreover, a comparison scale with 5, 6 or 7 numbers are more commonly used than 8 or 9 numbers (Standard, 2000).

5.5.2 Singular value decomposition (SVD)

Once the matrix of comparison is built, an algebra matrix tool can be used to establish both the weights and the consistency of the matrix. The singular value decomposition of a general matrix $A$ is a transformation into a product of three matrices, each of which has a simple special form and geometric interpretation (Gass, 2004). This SDV representation is given by following theorem:

**Theorem:** Any real matrix $(m \times n)$ $A$ of rank $k$ ($k \leq \min(m, n)$), can be expressed in the form of:

$$A = UDV^T$$

Eq. [5.18]

Where:

- $D$ is a diagonal matrix whit positive diagonal elements $\alpha_1, \ldots, \alpha_k$.
- U is a \((m \times k)\) matrix and \(U^TU = 1\);
- V is an \((n \times k)\) matrix and \(V^TV = 1\).

An equivalent form of Eq. [5.18] in terms of diads is:

\[ A = \sum_{i=1}^{k} \alpha_i u_i v_i^T \]  

Eq. [5.19]

Where:
- Diagonal numbers \(\alpha_i\) of D are called singular values, they are the absolute values of eigenvalues of \(A\);
- The vectors \(u_i\) and \(v_i\) are the columns of \(U\) and \(V\) and are called left and right singular vectors respectively. They form an orthonormal basis for the columns and rows of \(A\) in \(m\) dimensional and \(n\) dimensional spaces.

### 5.5.2.1 Calculating weights by SVD in AHP

Now the priority of parameters as a uniquely and normalized positive weight vector is defined:

\[ w_i = \frac{u_i + \frac{1}{v_i}}{\sum_{j=1}^{n} \left(u_j + \frac{1}{v_j}\right)}, i = 1, ..., n \]  

Eq. [5.20]

Where:
- \(u\) and \(v\) are the left and right singular vector belonging to the largest singular value of \(A\), which is a matrix \((m \times n)\) having singular values \(\alpha_1 \geq \alpha_2 \geq \cdots \geq \alpha_n\).

In this study the matrix \(A\), used to establish the weights, derives from experts’ opinions, but only the consistent answers have been used.

### 5.5.2.2 Measure of consistency based on SVD

This section will show that the consistency of pair wise comparison matrices can be effectively measured on an absolute scale based on the SVD approach and by using the Frobenius norm. This norm could be defined, for a \((m \times n)\) matrix \(A\), as:
Methodology

\[ ||A||_F = \left( \sum_{i=1}^{n} \sum_{j=1}^{n} a_{ij}^2 \right)^{1/2} \]

Eq. [5.21]

Or, using singular values as:

\[ ||A||_F^2 = \alpha_1^2 + \cdots + \alpha_n^2 \]

Eq. [5.22]

To find an expression for an index of consistency two theorems are used:

1. **The SVD of a positive, consistent matrix A is the diad:**

\[ A = \frac{c_1}{c_2} \begin{pmatrix} c_2 w_1 \\ c_2 w_2 \\ \vdots \\ c_2 w_n \end{pmatrix} \left( \begin{array}{cccc} 1 & 1 & \ldots & 1 \\ c_1 w_1 & c_1 w_2 & \ldots & c_1 w_n \end{array} \right) \]

Eq. [5.23]

Where:

- \( w = (w_i) \in R^n \);
- \( c_1 \) and \( c_2 \) are positive constant such that \( c_1^2 = \sum_{i=1}^{n} \frac{1}{w_i^2}, \ c_2^2 = 1/\sum_{i=1}^{n} \frac{1}{w_i^2} \);
- \( \frac{c_1}{c_2} \) is the only singular value of \( A \);
- In AHP, the values \( w_i, \ i = 1, \ldots, n, \) belong to the interval which represent our comparison scale, and are integers.

2. **The upper bound of Frobenius norm of an n-dimensional, positive and consistent matrix A is:**

\[ ||A||_F^2 \leq \frac{(M + m)^2}{4Mm} n^2 \]

Eq. [5.24]

Where:

- \( M \) and \( m \) are the parameters from Schweitzer inequality:

\[ \left( \frac{1}{n} \sum_{j=1}^{n} a_j \right) \left( \frac{1}{n} \sum_{j=1}^{n} \frac{1}{a_j} \right) \leq \frac{(M + m)^2}{4Mm} \]

Eq. [5.25]
By Eq. [5.22], the square of Frobenius norm, can be defined for a n-dimensional positive and consistent matrix $A$ as:

$$\|A\|^2_F = \frac{c_1^2}{c_2^2} = \sum_{j=1}^{n} \frac{1}{w_j^2} \sum_{j=1}^{n} w_j^2$$

Eq. [5.26]

Where $0 < m \leq a_j \leq M$, for $j = 1, ..., n$. If $a_j = w_j^2$, by the Schweitzer inequality,

$$\|A\|^2_F = \sum_{j=1}^{n} \frac{1}{w_j^2} \sum_{j=1}^{n} w_j^2 \leq \frac{(M + m)^2}{4Mm}^{-n^2}$$

Eq. [5.27]

If the comparison scale [1,5] is considered, $M = 25, m = 1$ and:

$$\|A\|^2_F \leq \frac{26^2}{4 \times 25} n^2$$

Eq. [5.28]

From which:

$$\|A\|^2_F \leq \frac{26}{10} n$$

Eq. [5.29]

A basic property of Frobenius norm is:

$$\left|\|A\|^2_F - \|A\|^2_F\right| \leq \|A - \tilde{A}\|^2_F \leq \|A\|^2_F + \|\tilde{A}\|^2_F$$

Eq. [5.30]

If weight vector given by Eq. [5.20] is considered to generate a positive, consistent and reciprocal matrix $\tilde{A}$ by setting $(w_i/w_j)$ for every pair $(i, j)$ the measure of consistency for $A$ can be represented as:

$$\|A - \tilde{A}\|^2_F$$

Eq. [5.31]

For this problem the ratio used is:

$$CM = \frac{\|A - \tilde{A}\|^2_F}{\|A\|^2_F + \left(\frac{26}{10} n\right)}$$

Eq. [5.32]

Where:

- $CM$ is the consistency measure;
- $\left(\frac{26}{10} n\right)$ is the upper bound of Frobenius norm for the consistent matrix $\tilde{A}$, considering [1, 5] comparison scale.
Methodology

- $\tilde{A}$ is consistent matrix in which the element are the ratios $\left(\frac{w_i}{w_j}\right)$ for every pair $(i,j)$.
- If $CM < 0.1$ the chosen decision is acceptable and it can be said that $A$ is a consistent judgement matrix.

This method has been used for each of the expert answer; the ones that resulted consistent have been processed to calculate the final matrix from which the variable weights have been obtained. The rest of the answers have been discarded. In practice, this calculation has been made in Matlab with the script shown below:

```matlab
function [w,IM,CM] = ProbA1(A)
[U,S,V]=svd(A);
LSV=S(1,1);
u=U(:,1);
v=V(:,1);
Denom=zeros(1,1);
for i=1:size(A,1)
    Denom=Denom+(u(i,1)+1/v(i,1));
end

for i=1:size(A,1)
    w(i,1)=(u(i,1)+1/v(i,1))/Denom;
end

for i=1:size(A,1)
    for j=1:size(A,1)
        $A_{\text{consistent}}(i,j)=\frac{w(i,1)}{w(j,1)}$;
    end
end

IM=norm(A-$A_{\text{consistent}}$,'fro')
Scale_range=norm(A,'fro')+(26/10)*size(A,1);
CM=IM/Scale_range
```

Figure 5.20. Matlab function for consistency and weights calculation.

With this tool it has been possible to select only the consistent answers to determine the final matrix $A$ and the final weights. In practice, about a half of thirty eight experts’ answers have been resulted consistent.
5.6 The questionnaire

To build an inference system several information are required. More precisely, once input and output are established, it is essential to know:

- The ranges in which vary the fuzzy or linguistic variables (see section 5.3.1);
- The output or consequent part of every rule included in the system (see section 5.3.2).

To obtain this information a questionnaire has been designed and has been sent to a large number (170) of international experts on the topic. With the aim of assigning weights on the variables (according to AHP (see section 5.5.1)) a part dedicated to evaluation and comparison between these variables has been included. This questionnaire has, at the same time, the aim to give scientific validity and robustness to this study. As commented before fuzzy system is context-dependent. The capability to construct appropriate membership functions, for given various concepts in various contexts, is the base usefulness of a fuzzy system. To pursue this goal, international expert on environmental chemistry, toxicology and risk assessment have been consulted. In a letter sent with the questionnaire, the experts have been asked to respond within two weeks. At the end of this period, a reminder to those who have not responded has been sent, to solicit the answer. One hundred and seventy questionnaires have been sent and after one month thirty eight filled questionnaires have been recollected and used as basis of this study. A first statistical result is presented in Figure 5.21, in which it can be seen that the majority of the answers are from Spain, Holland, Switzerland, Canada and Italy, respectively. These answers have been analysed and summarized with a common and coherent method.
5.6.1 Questionnaire structure

In this section all of the questionnaire parts will be explained. The results obtained from questionnaire will be presented and to see more details on all the experts answers and opinion, see the Annex.

The questionnaire has been built on an excel file, in different sheets. In the first of them, a general explanation on the project is given. Then, in each section, has been replaced by specific instructions to be easily filled by the experts. Moreover, buttons which allow moving between the sheets (see Figure 5.22) have been inserted. There are three parts which constitute the questionnaire:

- The study of variables weights involved in the system;
- Study of the ranges or fuzzy sets for each parameters that represent the variables;
- Consequent part of rules.

![% Countries answers](image)

*Figure 5.21. Countries provenience of collected questionnaires.*

![Next Step](image)

*Figure 5.22. An example of the button used in the questionnaire.*
At the end of each section, a space for observations has been placed. These comments have been used to correct and improve the system.

### 5.6.1.1 Study of weights

The first section has been dedicated to compare the variables in pairs (see Figure 5.23). The expert could choose the option thanks to a drop down list between the two parameters. In this study, the comparison scale chosen, has been in based on the range [1;5], following AHP method. However, in the questionnaire linguistic expressions have been presented in order to not confuse the expert with the numbers.

<table>
<thead>
<tr>
<th>VARIABLE</th>
<th>IMPORTANCE (click on the cell and choose one option)</th>
<th>ANOTHER VARIABLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIOAVAILABILITY IS</td>
<td>Than BIOACCUMULATION</td>
<td></td>
</tr>
<tr>
<td>a) Extremely less important</td>
<td>b) Less important</td>
<td>Equal important</td>
</tr>
<tr>
<td>d) More important</td>
<td>e) Extremely more important</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.23. Pair wise comparison in the questionnaire.

Hence, the expert should choose only one of the precedent options. Each of these, represents an integer number in the comparison scale (see Table 5.3), used in the AHP methodology to calculate the weights (see section 5.5.2.1) and to establish the consistency of the answers of each expert (see section 5.5.2.2). The consistent answers have been used to obtain a final matrix for the determination of the variable weights.

<table>
<thead>
<tr>
<th>Linguistic judgement</th>
<th>Numerical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equal important</td>
<td>1</td>
</tr>
<tr>
<td>More important</td>
<td>3</td>
</tr>
<tr>
<td>Extremely more important</td>
<td>5</td>
</tr>
<tr>
<td>Less important</td>
<td>1/3</td>
</tr>
<tr>
<td>Extremely less important</td>
<td>1/5</td>
</tr>
</tbody>
</table>

Table 5.3. Linguistic expression and corresponding numerical values.

Taking only the consistent answer, (verified according to Eq. [5.32])) three final matrices for the three groups have been built. In these matrices each component is the median of all the values indicated by the experts. Considering for instance, the matrix $G2$ shown in Figure 5.24, the value $1/3$ in the first row, represents the relative importance between Fish Accumulation and Toxicity.
This means that according to the most of the experts Fish Accumulation was three time less important than toxicity.

\[
G3 = \begin{pmatrix}
1 & 1 & 1 \\
1 & 1 & 1 \\
1 & 1 & 1 \\
\end{pmatrix} \quad G2 = \begin{pmatrix}
1 & 1/3 & 1 \\
3 & 1 & 3/2 \\
1 & 2/3 & 1 \\
\end{pmatrix} \quad G1 = \begin{pmatrix}
1 & 1 \\
1 & 1 \\
\end{pmatrix}
\]

Figure 5.24. Left: pair wise comparison matrix for the Group 3; middle: matrix for Group 2; right: matrix for Group 1.

In Table 5.4 the final weights, calculated according to Eq. [5.20], are reported. It can be observed that only in the second group a difference between the three parameters has come out, with a significant importance (0.51) of toxicity respect to persistence and fish accumulation (0.29 and 0.2 respectively).

<table>
<thead>
<tr>
<th>Table 5.4. The weights of the variable involved in the system.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Group 2</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Group 3</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

### 5.6.1.2 Study of variables range

To build the inference system it is necessary to know, for each variable, where the boundaries of fuzzy sets must be allocated. The numerical values of each fuzzy set have been asked to the experts. An example of the three parameters is shown in Figure 5.25.

![Figure 5.25. Section of the questionnaire dedicated to the study of the ranges.](image)

In this example, it can be noted that if the expert wanted to add other values a part from those in the drop-down list, he could do it in an appropriate lateral column (COLUMN 2 in Figure 5.25). As it has been done in the weights section, the median has been used to summarize the different...
answers. An example of the distribution of experts’ opinion concerning TOC is reported in Figure 5.26.

![Figure 5.26. Results for the establishment of ranges for TOC.](image)

The values resulted from the median of all the answers, have been proposed as quantitative corresponding values for the fuzzy sets related with the variables (the third column in Table 5.5). Considering the previous example of the TOC, reported in Figure 5.26, the median of experts’ opinion results:

- 0.1 for a “LOW” TOC;
- 3 for a “MODERATE” TOC;
- 25 for a “HIGH” TOC.

These numbers represents in the fuzzy logic, the numerical values of the indicator (in this case the TOC) in which the variable (in this case the bioavailability) belong to the fuzzy set with the highest membership degree (i.e. 1). These values are reported in Table 5.5, in the third column, whereas in the fourth column the ranges of each fuzzy set are presented. It can be noted that in correspondence of the highest membership degree to a fuzzy sets the membership degrees to the others sets is equal to zero.
It can be noted that according to experts’ opinion, the variable persistence can be considered HIGH when its indicator (i.e degradation half-life) is equal or more than 160 days. Both for PBDEs and HBCD, the degradation half-life met for this indicator exceeds this value. Hence degradation half-life of 160 days has been selected as the input number for PBDEs and HBCD because the membership degree to fuzzy sets “HIGH PERSISTENCE” is the maximum (i.e 1), in correspondence of $T_{1/2} = 160$ days.

### Table 5.5. Fuzzy sets, MF-type and parameters get form questionnaire.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Fuzzy Set</th>
<th>Values</th>
<th>Range</th>
<th>MF-type</th>
<th>MF-parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TOC</strong></td>
<td>Low</td>
<td>0.1</td>
<td>0 – 3</td>
<td>Z-shape</td>
<td>(0; 0.1)</td>
</tr>
<tr>
<td></td>
<td>Moderate</td>
<td>3</td>
<td>0.1 – 25</td>
<td>Pi-shape</td>
<td>(0.1; 3; 3; 25)</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>25</td>
<td>25 -</td>
<td>S-shape</td>
<td>(3; 25)</td>
</tr>
<tr>
<td><strong>BSAF</strong></td>
<td>Low</td>
<td>1</td>
<td>0 – 10</td>
<td>Z-shape</td>
<td>(0; 1)</td>
</tr>
<tr>
<td></td>
<td>Moderate</td>
<td>10</td>
<td>1 – 500</td>
<td>Pi-shape</td>
<td>(1; 10; 10; 500)</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>500</td>
<td>10 -</td>
<td>S-shape</td>
<td>(10; 500)</td>
</tr>
<tr>
<td><strong>BMF</strong></td>
<td>Low</td>
<td>1</td>
<td>0 – 10</td>
<td>Z-shape</td>
<td>(0; 1)</td>
</tr>
<tr>
<td></td>
<td>Moderate</td>
<td>10</td>
<td>1 – 300</td>
<td>Pi-shape</td>
<td>(1; 10; 10; 300)</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>300</td>
<td>10 -</td>
<td>S-shape</td>
<td>(10; 300)</td>
</tr>
<tr>
<td><strong>Deg. half-life</strong></td>
<td>Low</td>
<td>2</td>
<td>0 – 40</td>
<td>Z-shape</td>
<td>(0.2)</td>
</tr>
<tr>
<td></td>
<td>Moderate</td>
<td>40</td>
<td>2 – 160</td>
<td>Pi-shape</td>
<td>(2; 40; 40; 160)</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>160</td>
<td>160 -</td>
<td>S-shape</td>
<td>(40; 160)</td>
</tr>
<tr>
<td><strong>NOEC</strong></td>
<td>Low</td>
<td>43.93</td>
<td>0 – 1.7</td>
<td>Z-shape</td>
<td>(0; 43.93)</td>
</tr>
<tr>
<td></td>
<td>Moderate</td>
<td>1.7</td>
<td>43.93 – 0.03</td>
<td>Pi-shape</td>
<td>(43.93; 1.7; 1.7; 0.03)</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>0.03</td>
<td>1.7 -</td>
<td>S-shape</td>
<td>(1.7; 0.03)</td>
</tr>
<tr>
<td><strong>PEC</strong></td>
<td>Low</td>
<td>0.5*PNEC</td>
<td>0 – 1*PNEC</td>
<td>Z-shape</td>
<td>(0; 0.5*PNEC)</td>
</tr>
<tr>
<td></td>
<td>Moderate</td>
<td>1*PNEC</td>
<td>0.5<em>PNEC – 3</em>PNEC</td>
<td>Pi-shape</td>
<td>(0.5<em>PNEC; 1</em>PNEC; 1<em>PNEC; 3</em>PNEC)</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>3*PNEC</td>
<td>1*PNEC -</td>
<td>S-shape</td>
<td>(1<em>PNEC; 3</em>PNEC)</td>
</tr>
<tr>
<td><strong>Fish Accumulation</strong></td>
<td>Low</td>
<td>0.2</td>
<td>0 – 0.5</td>
<td>Z-shape</td>
<td>(0; 0.2)</td>
</tr>
<tr>
<td></td>
<td>Moderate</td>
<td>0.5</td>
<td>0.2 – 0.8</td>
<td>Pi-shape</td>
<td>(0.2; 0.5; 0.5; 0.8)</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>0.8</td>
<td>0.8 - 1</td>
<td>S-shape</td>
<td>(0.5; 0.8)</td>
</tr>
<tr>
<td><strong>Hazard</strong></td>
<td>Low</td>
<td>0.2</td>
<td>0 – 0.5</td>
<td>Z-shape</td>
<td>(0; 0.2)</td>
</tr>
<tr>
<td></td>
<td>Moderate</td>
<td>0.5</td>
<td>0.2 – 0.8</td>
<td>Pi-shape</td>
<td>(0.2; 0.5; 0.5; 0.8)</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>0.8</td>
<td>0.8 - 1</td>
<td>S-shape</td>
<td>(0.5; 0.8)</td>
</tr>
<tr>
<td><strong>Risk</strong></td>
<td>Negligible</td>
<td>0</td>
<td>0 – 0.25</td>
<td>Z-shape</td>
<td>(0; 0.25)</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>0.25</td>
<td>0 – 0.5</td>
<td>Z-shape</td>
<td>(0; 0.25; 0.25; 0.5)</td>
</tr>
<tr>
<td></td>
<td>Moderate</td>
<td>0.5</td>
<td>0.25 – 0.75</td>
<td>Pi-shape</td>
<td>(0.25; 0.5; 0.5; 0.75)</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>0.75</td>
<td>0.5 – 1</td>
<td>S-shape</td>
<td>(0.5; 0.75; 0.75; 1)</td>
</tr>
<tr>
<td></td>
<td>Very High</td>
<td>1</td>
<td>0.75 - 1</td>
<td>S-shape</td>
<td>(0.75; 1)</td>
</tr>
</tbody>
</table>
5.6.1.3 The output of the rules

The proposed system consists of three levels, one with two inputs and the others two with three inputs (see Figure 5.27).

![Figure 5.27. Proposed model diagram.](image)

The fuzzy sets, or linguistic variables considered in the system are three: LOW, MODERATE and HIGH. Only for the final output (risk) five fuzzy sets has been considered: NEGLIGIBLE, LOW, MODERATE, HIGH, VERY HIGH. Considering Eq. [5.8] the number of the rules is:

- $3^2$ for the first level;
- $3^3$ for second and third levels.

For a total of 27+27+9=63 rules. The experts have been asked to select for each rule an output. In Figure 5.28, an example for the GROUP 1 is presented, in which the expert had to choose between 5 possible outputs.

![Figure 5.28. The output for the first group of variables.](image)
As shown in Figure 5.29, for GROUP 2 and 3 the possible choices are 3: LOW, MODERATE and HIGH.

For all of the 63 rules considered, the experts have been indicated the more appropriate output, or consequent part (explained in section 5.3.2), according to their opinion. In this case the consequent parts indicated by more than 50% of the experts have been selected as the outputs of the rules. This method has allowed to have no unclear situations for any rules. The example of Group 1 it can be seen in Figure 5.30.

The summarized answers are reported for this group in Figure 5.31.
Other 54 consequents have been selected for the second and third group. The summarized answers can be seen in the Annex.
6 RESULTS AND DISCUSSION

The developed model has been applied to different monitoring points of two rivers from the Ebro basin, the Vero River and Cinca River. Risk assessment results are presented in this section. The risk of BFR’s in the Vero River has been assessed based on experimental data from 2004 and 2005. On the other hand, the risk of BFR’s in the Cinca River has been evaluated in 2002 and 2004. Monitoring points were previously shown in Figure 3.2 in the section 3.

6.1.1 Vero River

As explained in section 3.2.1, three points (V1, V2 and V3) of the Vero River were monitored (see Figure 3.4). However, no biota samples were found at point V2, probably due to the high level of PBDEs contamination that killed most of the aquatic fauna. As a consequence, no risk assessment has been possible in this point. As consequence no assessment has been possible in this point.

In order to assess the environmental risk for the other two sample points (V1 and V3), several input data were required to be introduced in the model (see Table 6.1). Some of these data have been obtained experimentally (e.g. TOC, exposure) and others have been gathered from the scientific literature (e.g. BMF, NOEC)

<table>
<thead>
<tr>
<th>Year</th>
<th>Sample point</th>
<th>TOC (%)</th>
<th>BSAF (-)</th>
<th>BMF (-)</th>
<th>NOEC (µg/l)</th>
<th>half-life (days)</th>
<th>Exposure (PEC/PNEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vero River</td>
<td>V1</td>
<td>2.4</td>
<td>3.83</td>
<td>3.2</td>
<td>2</td>
<td>160</td>
<td>0.015</td>
</tr>
<tr>
<td>2004</td>
<td>V3</td>
<td>3.6</td>
<td>4.88</td>
<td>3.2</td>
<td>2</td>
<td>160</td>
<td>1.73</td>
</tr>
<tr>
<td>Vero River</td>
<td>V1</td>
<td>1.8</td>
<td>1.79</td>
<td>3.2</td>
<td>2</td>
<td>160</td>
<td>0.05</td>
</tr>
<tr>
<td>2005</td>
<td>V3</td>
<td>4.4</td>
<td>0.78</td>
<td>3.2</td>
<td>2</td>
<td>160</td>
<td>5.69</td>
</tr>
</tbody>
</table>

Risk assessment results obtained after introducing these data into the fuzzy model implemented with the Matlab Fuzzy Toolbox are shown in Table 6.2. In this table, the final risk results are shown according to the AND operator (see section 5.3.2.1) used to combine the rules: Minimum, Product and the adaptation of the AHP method proposed in this project.
Table 6.2. Risk values associated to PBDEs obtained at two sample points of the Vero River (V1 and V3) in 2004 and 2005.

<table>
<thead>
<tr>
<th>AND operator</th>
<th>2004</th>
<th>2005</th>
<th>2004</th>
<th>2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHP method</td>
<td>0.352</td>
<td>0.62</td>
<td>0.35</td>
<td>0.784</td>
</tr>
<tr>
<td>Min</td>
<td>0.25</td>
<td>0.58</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td>Prod</td>
<td>0.25</td>
<td>0.57</td>
<td>0.25</td>
<td>0.75</td>
</tr>
</tbody>
</table>

As it can be seen in Figure 6.1, risk value ranges from 0 to 1. The risk output (present in Table 6.2) depends directly on two variables: Hazard and Exposure. However, it is important to remember that Hazard is the output of a lower-level FIS which has three inputs (Persistence, Fish Accumulation and Toxicity). At the same time, Fish accumulation depends on three other variables: Bioavailability, Bioaccumulation and Biomagnification. To see more details on the calculation of the risk and on all the three interconnected FIS, see the Annex.

Figure 6.1. Output calculation in Fuzzy Toolbox

Risk values seem to be in accordance with the expected results, since a lower risk has been obtained at point V1, before the industrial park located near V2, and a higher risk has been assessed at point V3, after the industrial park.

At point V1 differences between 2004 and 2005 are not observed. On the contrary, at V3 an increase of the risk is evident. This might be due to uninterrupted industrial discharge to the
river and as a consequence increasing the accumulation of this compound on the sediment and fish. It is important to note that from 2004 octa- and penta-brominated diphenyl ethers have been banned in Europe. However, the observed risk increase might be due to the fact that decabrominated diphenyl ethers, in particular BDE-209, have not been restricted.

Results presented in Table 6.2 have been given as single quantitative values. However, since fuzzy logic allows assigning values to more than one category, risk results can also be given together with the degree of membership to the risk sets. An example is given in Figure 6.2. Here a risk value of 0.78 can be expressed as ‘The risk is HIGH with a certainty level of 96% and VERY HIGH with a certainty level of 4%’. Thus, final risk values can also be represented as shown in Table 6.3.

<table>
<thead>
<tr>
<th>AND operator</th>
<th>2004</th>
<th>2005</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V1</td>
<td>V3</td>
</tr>
<tr>
<td>AHP method</td>
<td>67% LOW</td>
<td>46% HIGH</td>
</tr>
<tr>
<td></td>
<td>33% MODERATE</td>
<td>54% MODERATE</td>
</tr>
<tr>
<td>Min</td>
<td>100% LOW</td>
<td>21% HIGH</td>
</tr>
<tr>
<td></td>
<td>79% MODERATE</td>
<td></td>
</tr>
<tr>
<td>Prod</td>
<td>100% LOW</td>
<td>17% HIGH</td>
</tr>
<tr>
<td></td>
<td>83% MODERATE</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6.2. Fuzzy categories for risk. Example of degrees of membership for a risk value of 0.784.
This way of presenting the results seems to be in accordance with one of the objectives of the project, i.e. to build a model easy to interpret and useful for environmental managers. Moreover, within the context of the fuzzy logic, results presented as fuzzy numbers are more coherent. In Figure 6.3, the results obtained by using the AHP method are presented in a visually-friendly format.

![Visually-friendly presentation of risk values associated to PBDEs in the Vero River: 2004 (left); 2005 (right).](image)

### 6.1.2 Cinca River

As it has been explained in section 3.2.2, four sample points of the Cinca River (C1, C2, C3 and C4) were monitored during several campaigns (see Figure 3.2). Both PBDEs and HBCD were found at several points. The proposed model has been tested with samples from 2002 and 2004. Results from 2004 include all the sample points. HBCD was not found at site C1, 20 km upstream of industrial park of Monzon. However, it was found at site C2, just 3 km upstream of Monzon, and at very high concentrations at sites C3 and C4, downstream the industrial park. On the contrary, results from 2002 refer only to C3 because TOC values were not available at the other sample points. Input data necessary to be introduced into the model are reported in Table 6.4 for 2004. As in the Vero River cases, the values of BMF, NOEC and half-life have been gathered from the scientific literature, whereas BSAF, TOC and exposure have been obtained from experimental data.
Table 6.4. Input data used to calculate environmental risk of PBDEs and HBCD in the Cinca River in 2004 (NA: Not applicable).

<table>
<thead>
<tr>
<th>Sample point</th>
<th>BFRs</th>
<th>TOC (%)</th>
<th>BSAF (-)</th>
<th>BMF (-)</th>
<th>NOEC (µg/l)</th>
<th>Half-life (days)</th>
<th>Exposure (PEC/PNEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>PBDEs</td>
<td>2.21</td>
<td>0.359</td>
<td>3.2</td>
<td>2</td>
<td>160</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>HBCD</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>C2</td>
<td>PBDEs</td>
<td>1.28</td>
<td>1.94</td>
<td>3.2</td>
<td>2</td>
<td>160</td>
<td>0.090</td>
</tr>
<tr>
<td></td>
<td>HBCD</td>
<td>0.49</td>
<td>1.2</td>
<td>3.1</td>
<td>160</td>
<td>0.040</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>PBDEs</td>
<td>1.19</td>
<td>1.08</td>
<td>3.2</td>
<td>2</td>
<td>160</td>
<td>0.355</td>
</tr>
<tr>
<td></td>
<td>HBCD</td>
<td>0.78</td>
<td>1.2</td>
<td>3.1</td>
<td>160</td>
<td>7.88</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>PBDEs</td>
<td>1.73</td>
<td>4.23</td>
<td>3.2</td>
<td>2</td>
<td>160</td>
<td>0.162</td>
</tr>
<tr>
<td></td>
<td>HBCD</td>
<td>0.22</td>
<td>1.2</td>
<td>3.1</td>
<td>160</td>
<td>2.910</td>
<td></td>
</tr>
</tbody>
</table>

Risk values associated to PBDEs in the Cinca River are reported in Table 6.5. It is possible to note that there is not an increase of the risk along the river, according to the fact that in the industrial park of Monzon PBDEs are not used as largely as HBCD. As in the Vero River, the AHP method has given for PBDEs more conservative results than the Minimum or the Product AND operators.

Table 6.5. Risk values for PBDEs obtained at four sample points of the Cinca River (C1, C2, C3 and C4) in 2004.

<table>
<thead>
<tr>
<th>AND operator</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHP method</td>
<td>0.352</td>
<td>0.351</td>
<td>0.351</td>
<td>0.353</td>
</tr>
<tr>
<td>Min</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.264</td>
</tr>
<tr>
<td>Prod</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.262</td>
</tr>
</tbody>
</table>

HBCD is widely used in the industrial park near site C3. HBCD risk results are shown in Table 6.6. According to the values shown in this table, an increase of the risk is observed due to the presence of the industrial park (C2 risk values < C3 risk values), then, a decrease is observed. The same trend is observed by using the three AND operators. However, the AHP method seems to be more sensitive, given that risk values of 0.782 and 0.694 in C3 and C4, respectively, have been computed, whereas the Minimum operator shows no significant differences between C3 and C4, and the Product operator does not show any difference at all. The high risk at point C4, 30 km downstream of C3, is probably due to the low flow of the river that favours the pollutant to accumulate in the sediment.
Table 6.6. Risk values for HBCD obtained at three sample points of the Cinca River (C2, C3 and C4) in 2004 (NA: Not applicable).

<table>
<thead>
<tr>
<th>AND operator</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHP method</td>
<td>NA</td>
<td>0.349</td>
<td>0.782</td>
<td>0.694</td>
</tr>
<tr>
<td>Min</td>
<td>NA</td>
<td>0.249</td>
<td>0.742</td>
<td>0.739</td>
</tr>
<tr>
<td>Prod</td>
<td>NA</td>
<td>0.249</td>
<td>0.742</td>
<td>0.742</td>
</tr>
</tbody>
</table>

As in the Vero River case, the HBCD risk can also be reported in terms of degree of membership to the several risk categories. Results expressed this way are shown in Table 6.7. These results are also shown in Figure 6.4.

Table 6.7. Risk associated to HBCD in the Cinca River expressed as degree of membership to several risk categories (2004) (NA: Not applicable).

<table>
<thead>
<tr>
<th>AND operator</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHP method</td>
<td>NA</td>
<td>69% LOW</td>
<td>97% HIGH</td>
<td>90% HIGH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31% MODERATE</td>
<td>3% VERY HIGH</td>
<td>10% MODERATE</td>
</tr>
<tr>
<td>Min</td>
<td>NA</td>
<td>100% LOW</td>
<td>100% HIGH</td>
<td>100% HIGH</td>
</tr>
<tr>
<td>Prod</td>
<td>NA</td>
<td>100% LOW</td>
<td>100% HIGH</td>
<td>100% HIGH</td>
</tr>
</tbody>
</table>

Figure 6.4. The HBCD risk in Cinca River.

Finally, results associated to the sampling campaign that was carried out in 2002 near the industrial park of Monzon (site C3) are presented. These results allow for the comparison of the risk associated to PBDEs and HBCD at a given point in 2002 and 2004. Input data necessary to be
Results and discussion

Introduced into the model are reported in Table 6.8. Assessment risk results are reported in Table 6.9.

<table>
<thead>
<tr>
<th>BFRs</th>
<th>TOC (%)</th>
<th>BSAF (-)</th>
<th>BMF (-)</th>
<th>NOEC (µg/l)</th>
<th>Half-life (days)</th>
<th>Exposure (PEC/PNEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDEs</td>
<td>1.5</td>
<td>75.8</td>
<td>3.2</td>
<td>2</td>
<td>160</td>
<td>0.09</td>
</tr>
<tr>
<td>HBCD</td>
<td>1.5</td>
<td>0.33</td>
<td>1.2</td>
<td>3.1</td>
<td>160</td>
<td>1.99</td>
</tr>
</tbody>
</table>

Table 6.8. Input data used to calculate environmental risk of PBDEs and HBCD in the Cinca River at site C3 in 2002.

<table>
<thead>
<tr>
<th>AND operator</th>
<th>Risk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PBDEs</td>
</tr>
<tr>
<td>AHP method</td>
<td>0.393</td>
</tr>
<tr>
<td>Min</td>
<td>0.368</td>
</tr>
<tr>
<td>Prod</td>
<td>0.348</td>
</tr>
</tbody>
</table>

Table 6.9. Risk values for PBDEs and HBCD obtained at point C3 of the Cinca River in 2002.

Concerning PBDEs there has been a slight decrease of the risk from 2002 to 2004, probably due to the fact that penta-BDEs and octa-BDEs were banned in 2004. Therefore the total concentration of these compounds in the sediment and fish has decreased. On the contrary, the risk for HBCD has increased from 2002 to 2004. This also can be explained due to the aforementioned ban of PBDEs that would probably increase the use of HBCDs.
7 CONCLUSIONS

In the present work a model to assess the risk of PBDEs and HBCD to aquatic organisms has been developed using fuzzy logic. The results obtained through the application of the model to several case studies in the Cinca and the Vero Rivers (at the Ebro River basin) show the reliability and sensitivity of the proposed model.

Fuzzy logic has been used for the last years in different technical and scientific areas (control devices, statistical analysis, etc.), but currently very few applications exist in the environmental risk assessment of chemicals. With the implementation of the proposed system, fuzzy logic and, in particular, Fuzzy Inference Systems (FIS) have been proved to be excellent tools to be used for environmental risk management. The final output of the risk assessment can be understood by environmental managers and the decision-makers, and this was one of the main features that the model had to comply with.

Concerning the other characteristics that were required for this tool, they have also been implemented. In first place, the model has a scientific base. A questionnaire has been filled in by an important group of experts on the topic and their answers have been used to build up the model. Moreover, an intensive bibliographic research has been conducted to gather information about those variables which were not available from experimental data. In second place, the model can be adjustable to other environmental situations and compounds. For example, the present model is easily adaptable to other substances with high hydrophobicity and persistence, such as most of the persistent organic pollutants (POPs). These substances, according to their physical and chemical properties, distribute both in sediment and water column. Thus, the general risk for the aquatic organisms could be evaluated using this model provided that this model focuses on sediment concentration values and fish contamination. Finally, as required, the model is easy to use and improve.

Another relevant topic of the model was the introduction of weights for the variables included in the system. Not all the variables have the same importance but this fact has been hardly reflected in the bibliographic studies reviewed. Therefore, one of the main objectives of the project was to reflect this issue into the final model. After considering different possibilities, an adaptation of the Analytical Hierarchy Process (AHP) has been implemented.
obtained, it can be said that this new approach has proved to be more conservative and sensitive than the classic AND operators used in FIS.

With regard to the risk assessment results, in the Vero River a *Moderate to High* risk has been found for PBDEs after a textile industrial site in 2004. One year later, at the same sample point, the risk has been observed to increase to *High to Very high*. Two reasons may explain this increase: (1) the continuous discharge in the water body of BDEs by textile industries (in particular deca-BDEs); (2) the low flow of the river. Both facts favoured PBDEs to accumulate in the sediment.

In the Cinca River four different sample points have been analysed. PBDEs and HBCD have been found in all the points, except for a point (C1) located 20 km upstream of an industrial area, where HBCD was not present. A net prevalence of HBCD both in biota and sediments samples was in general observed. As in the Vero River, at the Cinca River there is also an industrial park characterized by an important chemical industry. This area is located near the city of Monzón. The level of risk associated to PBDEs in 2004 has been assessed to be *Moderate to Low* at the four points along the river. This is due to the fact that in the industrial park of Monzón PBDEs are not used as largely as HBCD. In the case of HBCD, the risk at the most polluted point (C3) was *High to Very High*. This is quite logic since it was located just after the industrial site. Thirty kilometres downstream this site, the risk related to HBCD has been computed to reduce to *Moderate to High*.

The last case study has focused only on the site near Monzón (C3). This case study has been used to compare the risk associated to both flame retardants before many congeners of the PBDEs family were banned in 2004 in the European Union. In this case it can be observed that from 2002 to 2004, the risk associated to HBCD increased, while that of PBDEs decreased, probably due to the fact that HBCD used was not restricted.

The model proposed for environmental risk assessment has worked well. However, since there is always room for future improvements, several issues that could be pursued in the near future are mentioned. One of them refers to data availability. In fact, several parameters in this work have been obtained from the scientific literature. This is due to the fact that complete environmental studies (i.e. studies in which biomagnification and bioaccumulation ratios, chemicals concentrations, toxicity values, etc. are altogether determined) are to date practically
unfeasible. Moreover, in particular for HBCD and PBDEs, there are currently few studies and environmental data available. Therefore, if more data were available the results would be more adjusted. Another improvement could be related with the evaluation of the sensitivity of the model to changes in all the input parameters.
8 NOMENCLATURE

PBDE  Polybrominated diphenyl ether
$\alpha, \beta, \gamma$ – HBCD  Hexabromocyclododecane diastereoisomers
WS  Water Solubility
$K_{ow}$  Octanol-water partition coefficient
H  Henry’s law constant
$V_p$  Vapour pressure
$K_{oa}$  Organic-air partition coefficient
$K_{oc}$  Organic carbon normalised distribution coefficient
dw  Dry weight
lw  Lipid weight
$\mu_A(x)$  Membership grade of $x$ in fuzzy set $A$
$a,b,c,d$  Membership function parameters
$N_{rules}$  Number of the rules
$n_f$  Number of fuzzy sets
$n_v$  Number of variables
$\bar{A}$  Fuzzy complement
$A \cap B$  Fuzzy intersection
$A \cup B$  Fuzzy union
$\mu_{OUT}$ or $\mu(z)$  Membership degree of fuzzy output
$w_1, w_2, w_3$  Weights of variable
SOM  Smallest Of the Maximum
MOM  Middle Of the Maximum
LOM  Largest Of the Maximum
CM  Consistence Measure
TOC  Total Organic Carbon
BSAF  Biota-Sediment Accumulation Factor
BMF  Bio-Magnification Factor
NOEC  No Observed Effect Concentration
PEC  Predicted Environmental Concentration
PNEC  Predicted No Effect Concentration
$T_{1/2}$  Degradation half-life


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