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CONTRIBUTION TO THE ENVIRONMENTAL IMPACT ASSESSMENT OF BUILDINGS: NUMERICAL MODELLING OF DANGEROUS SUBSTANCES' RELEASE TO WATER

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Abstract

Any construction product and building undergoing contact with water during its life cycle can release chemical compounds potentially hazardous for the human health and the environment. The release of dangerous substances is presently investigated especially by experimental approaches commonly by laboratory leaching tests while the environmental impacts of construction products and buildings are evaluated by a Life Cycle Assessment (LCA) approach. The dangerous substances release during use stage of construction products (leaching behaviour) is currently very poorly represented in the existing data bases and methods for environmental assessment of construction products and buildings.

In this context, the main objectives of this study were: (i) to develop a methodology for the assessment of the leaching behaviour of various construction products and (ii) to integrate the leaching data in LCA approach at building scale.

The methodology developed for the assessment of the leaching behaviour of construction products is based on: (1) characterisation leaching tests at lab scale, following the horizontal standardised assessment methods for harmonised approaches relating to dangerous substances under the Construction Products Regulation (CPR), (2) modelling and simulation of coupled chemical and transport phenomena at lab and field scale, and (3) utilisation of simulated leaching data for the construction products exposed in natural condition with the LCA method for the characterization of the hazardous effect during the use stage. The proposed methodology was applied and validated on three different classical construction products i.e. CBA (Copper-Boron-Azole) treated wood, fibre-cement sheets and bitumen membranes. The leaching behaviour of CBA treated wood and fibre-cement sheets was simulated over several years under natural exposure conditions, using the geochemical software PHREEQC® . The chemical models consider both the mineral and the organic matrixes and their interaction with treatment compounds. Mass transfer and transport phenomena were modelled. The developed coupled chemical-transport models are able to represent the dynamic leaching behaviour of the respective products in various leaching conditions. For bitumen membranes only experimental characterisation was possible. The leaching data obtained by simulation over the whole use stage of the products were integrated in the life cycle inventory (LCI) and the relevant life cycle impact assessment (LCIA) methods were applied with the enriched inventory. A simplified single-family house was modelled using a software designed to evaluate the intrinsic environmental performances of a building over its entire life cycle. ELODIE software was used in this work. The building scale assessment methodology is based on coupling the methodology developed for the product scale with the Life Cycle Assessment (LCA) at building scale. This methodology allows a proper integration of leaching data in LCA tools and answers several technical questions raised in the field.

Keywords: environmental impact assessment, construction products, building, leaching, chemical-transport modelling, LCA, treated wood, fibre-cement sheets, bitumen membranes

Résumé

Tous les produits de construction ou les ouvrages qui sont en contact avec l'eau de pluie, sont susceptibles de relarguer des composants chimiques potentiellement dangereux pour la santé humaine et l'environnement. Actuellement, le relargage des substances dangereuses dans l'eau est évalué essentiellement par des méthodes expérimentales - généralement des essais de lixiviation réalisées à l'échelle du laboratoire. Par ailleurs, les impacts environnementaux des produits de construction et des bâtiments sont évalués par l'approche Analyse de Cycle de Vie (ACV), réalisées à partir de données propres aux fabricants et de données génériques existantes constituées en bases de données. Or, les émissions de polluants pendant la vie en œuvre des produits de construction sont actuellement mal prises en compte dans ces mêmes bases de données existantes et dans les méthodes utilisées pour l'évaluation des performances environnementales des produits et des bâtiments.

Dans ce contexte, les objectifs de ces travaux ont été : (i) de développer une méthodologie pour l'évaluation du comportement à la lixiviation de différentes matrices de produits de construction et (ii) d'intégrer les données de lixiviation dans les méthodes ACV à l'échelle du bâtiment.

La méthodologie développée pour l'évaluation du comportement à la lixiviation des produits de construction est basée sur : (1) des essais de caractérisation à la lixiviation, selon les méthodes standardisées d'évaluation répondant au Règlement Produits de Construction (RPC), (2) la modélisation et la simulation des phénomènes couplés chimie-transport à l'échelle laboratoire et vraie grandeur et (3) l'intégration des données de lixiviation, obtenues par des simulations numériques en conditions d'exposition naturelle des produits de construction, dans les méthodes ACV, aux échelles produit et bâtiment.

La méthodologie proposée a été appliquée et validée sur trois produits de construction : le bois traité CBA (Cuivre - Bore - Azole), la plaque fibrociment et la membrane bitumineuse. Les comportements à la lixiviation du bois traité CBA et de la plaque fibrociment a été simulé pour des conditions naturelles d'exposition à long terme, en utilisant le logiciel géochimique PHREEQC®. Les modèles chimiques développées permettent de considérer les matrices organiques et minérales et leurs interactions avec les polluants. Les phénomènes de transport des substances ont été également modélisés. Les modèles d'émission développés (couplage chimie-transport) permettent de simuler la lixiviation dynamique des produits considérés, pour différentes conditions d'exposition. Pour la membrane bitumineuse, seule la caractérisation expérimentale a été réalisée. Les données de lixiviation obtenues lors des simulations sur la durée de vie en œuvre des produits ont été intégrées dans les inventaires respectifs du cycle de vie (ICV) des produits. Des méthodes d'impact spécifiques ont été utilisées en association avec les inventaires enrichis pour évaluer les impacts "pollution de l'eau", "toxicité humaine" et "écotoxicité" des produits considérés. L'ACV d'une maison simplifiée a été réalisée en utilisant le logiciel ELODIE. La méthode d'évaluation à l'échelle bâtiment consiste à intégrer les nouvelles données construites sur la base de la méthodologie développée à l'échelle produit aux autres données d'ACV à l'échelle bâtiment. La méthodologie développée au cours de ces travaux permet donc l'intégration des données de lixiviation dans les outils ACV dédiés au bâtiment.

Mots clé : performances environnementales, produits de construction, bâtiment, lixiviation, modèles chimie-transport, simulation numérique, ACV, bois traité, plaque fibrociment, membrane bitumineuse.

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Abbreviations

ANC	Acid/base Neutralisation Capacity test
CBA	Copper-Boron-Azole treatment
CPD	Construction Products Directive
CPR	Construction Products Regulation
DOC	Dissolved Organic Carbon
DSLT	Dynamic Surface Leaching Test
EPD	Environmental Product Declaration
FDES	Fiches de Déclaration Environnementale et Sanitaire
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
Mea	monethanolamine
TC	Total Content
TOC	Total Organic Carbon

Introduction

The environmental impact of construction products and buildings is currently assessed especially by a Life Cycle Assessment (LCA) approach. LCA methods evaluate all stages of the life cycle of the product (or building) via environmental indicators, e.g. energy consumption, resource depletion, water consumption, air pollution, soil pollution, climate change, etc. At the moment, the emissions to water and soil during the use stage of a product are not well evaluated, the impact being either underestimated or overestimated. Underestimation can lead to a wrong evaluation of the environmental impact of buildings and is mainly due to the lack of data (leaching data). On the other hand, overestimation of emissions to water and soil is due to the use of data from generic data bases and can slow down the development of innovative construction products and procedures (e.g. based on secondary raw materials).

The release of pollutants from construction products in contact with water (leaching phenomena) can be evaluated by experimental and numerical methods. Special conceived experimental methods (leaching tests) have already been developed. Leaching from biocide-treated construction products or with waste included has been intensively investigated. However, leaching from classical construction products (without waste included) is a subject that needs to be addressed more deeply in view of a proper assessment of the environmental impact of products and buildings.

Two problematics have been identified: (i) availability of leaching data on construction products and (ii) integration of leaching data in the LCA approach.

Generating leaching data on classical construction products is a recent subject stimulated by the relatively recent European regulation in the construction field. Developments of experimental approaches adapted to any construction material (named horizontal approaches) are strongly encouraged.

Then the integration of the obtained leaching data with LCA tools, especially with the Environmental Product Declaration (EPD) system, is of high interest. Several questions need to be answered and a proper methodology has to be developed.

In this context, two main objectives have been foreseen in the current study:

1. Development of a methodology to assess the leaching behaviour of classical construction products of various matrixes (e.g. porous, non-porous, organic, mineral, treated), based on an experimental, horizontal approach, and application to several widespread construction materials.
2. Proposal for a methodology of coupling LCA and leaching data, i.e. assessment of the environmental impact of leaching from construction products during use stage.

This work was realised essentially with the financial support of Centre Scientific et Technique du Bâtiment (CSTB), with the contribution of Laboratoire dIngénierie des Systèmes Biologiques et des Procédés (LISBP) de Toulouse, BAM Bundesanstalt für Materialforschung und -prüfung Berlin, Berlin and Deutscher Akademischer Austausch Dienst (DAAD).

The present dissertation is structured around four chapters.

Chapter 1 presents the state of the art of the discussed problem. A general methodology for the coupling of leaching and LCA data is presented in chapter 2. The methodology is based on including leaching data in the inventory and further assessing the impact by relevant methods. Leaching data is generated by numerical simulations, based on characterisation leaching tests at lab scale. In chapter 3 the proposed methodology is tested on three preselected construction products. The experimental platforms, the leaching mechanisms developed and the numerical simulation principles are described for: (i) a mineral (non-metallic) porous product (i.e. fibre-cement sheets), (ii) an organic porous product (i.e. treated wood) and (iii) an organic non-porous product (i.e. bitumen membranes).

Chapter 4 presents the methodology for including leaching data within the inventory data over the whole life cycle of the product. Further, the enriched inventory is assessed by specific methods for water pollution, human toxicity and ecotoxicity indicators. Only the case of treated wood is discussed in detail. The second part of this chapter is an exercise for including the enriched inventory at building scale. A simplified house is considered and its environmental performances are assessed.

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Chapter 1

State of the art and rationale

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Actuellement, dans le secteur de la construction l’accent est mis de plus en plus sur les performances environnementales et sanitaires des produits et des bâtiments. En conséquence, des données sont nécessaires pour évaluer et garantir ces performances. En ce qui concerne les émissions des substances dangereuses pendant la vie en œuvre, pour les produits constituant l’enveloppe du bâtiment (utilisation en extérieur), les émissions dans l’eau sont la principale préoccupation, tandis que pour les produits utilisés à l’intérieur du bâtiment, l’accent est mis sur les émissions dans l’air intérieur.

Tous les produits de construction et bâtiments qui sont en contact avec l’eau pendant leur cycle de vie peuvent relarguer des composés chimiques potentiellement dangereux pour la santé et l’environnement. Dans l’évaluation des performances environnementales de produits, il est important d’avoir une estimation représentative des taux d’émission des composés chimiques (exogènes ou endogènes) selon les différents scénarios d’exposition et de comprendre comment ces taux d’émission évoluent dans le temps. Les émissions dans l’eau des produits peuvent être évaluées par des approches expérimentales, ainsi que par des méthodes numériques (simulation numérique). Les phénomènes physico-chimiques et de transfert de masse qui ont lieu au contact produit eau sont regroupés sous le terme “lixiviation”.

A l’heure actuelle, l’impact environnemental des produits de construction et des bâtiments est évalué essentiellement par une approche Analyse du Cycle de Vie (ACV). Malgré l’intérêt actuel pour les phénomènes de lixiviation, l’impact d aux émissions dans l’eau pendant la vie en œuvre des produits est mal pris en compte dans les évaluations, l’impact étant soit sous-estimé, soit surestimé. La sous-estimation peut conduire à une mauvaise évaluation de l’impact environnemental des bâtiments et est principalement due à l’absence des données de lixiviation. La surestimation des émissions dans l’eau et le sol est due à l’utilisation des bases de données génériques, en se basant par exemple sur le contenu total d’une substance dans le produit qui est considéré comme étant complètement lixivié au cours de la phase d’utilisation. Cette hypothèse est fausse pour la plupart des substances. Une telle erreur de calcul peut entraver le développement de certains produits de construction innovants (par exemple à base de matières premières secondaires).

La lixiviation des produits de construction “classiques” (sans déchets inclus) est un sujet qui doit être abordé plus en profondeur afin d’évaluer correctement l’impact environnemental des produits et des bâtiments. Deux problématiques ont été identifiées dans cette étude : (i) la disponibilité des données de lixiviation sur les produits de construction et (ii) l'intégration des données de lixiviation dans l'approche ACV.

La mise à disposition des données de lixiviation sur les produits de construction est un sujet qui peut être résolu par des tests de lixiviation à l'échelle laboratoire et sur le terrain. Néanmoins, les émissions sur plusieurs années d'exposition sont difficiles à obtenir par des méthodes expérimentales, mais pourraient être obtenues par des simulations numériques. Les tests de lixiviation restent indispensables pour construire des modèles fiables à long terme.

L'étape suivante de l'évaluation consiste à intégrer les données de lixiviation dans les outils ACV. Le couplage lixiviation-ACV est une problématique récente. Une méthodologie appropriée doit être développée. L'approche utilisée dans cette étude, est décrite dans le chapitre suivant. Dans le troisième chapitre, la méthodologie proposée est étudié sur trois produits présélectionnés de diverses matrices poreuses, soit organique, minéral (non métallique) poreux et non poreux organique.

1 Introduction

In the construction sector more and more emphasis is put on health and environmental aspects. This means that health and environmental issues must be taken into consideration in the development of both products and services. Consequently, information is needed to prove the health and environmental performance of construction products and buildings. For outdoor use, release of dangerous substances in water is of high concern, while for indoor use focus is on emission to indoor air quality (EC, 2005).

Any construction product and building undergoing contact with water during its life cycle can release chemical compounds potentially hazardous for the human health and environment. In the environmental performance assessment of innovative and common construction products, it is important to have representative estimates of the chemical compounds' (biocides or endogenous substances) emission rates under different exposure scenarios and to understand how these emission rates change with time and other variables. The release can be evaluated by experimental approaches, as well as numerical methods (numerical simulation) and therefore the environmental impact of the product or building could be assessed.

Construction products contain several and various substances which are susceptible of being released to the environment. They can be organic or inorganic (Table 1.1). Organic substances found in construction products are usually pesticides, i.e. biocides added via a treatment in order to increase the product's mechanical and esthetical properties. Among the inorganic, heavy metals are the most common and dangerous, e.g. chromium (Cr), copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), nickel (Ni). They are always present and often highly concentrated, not biodegradable and show a distinct accumulation behaviour on solid surfaces (e.g. soil).

Indeed, heavy metals are commonly found in sewage water and their source is mainly runoff water (Gromaire-Mertz et al., 1999, 2002; Gouman, 2004; Chocat et al., 2007). In Switzerland, for example, roofs represent 69% of copper surfaces in buildings, i.e. ca. $2.5\,\mathrm{m}^2$ copper sheets on roofs / inhabitant (Wittmer, 2006). The rest consists in energy systems, telecommunications, heating systems, water systems. A study carried out in Zürich (Switzerland) showed that the concentration of Cu, Pb, Zn, Cd is up to 75 times higher in roof runoff than in storm water (Mottier et al., 1995). Another study carried out in a central quarter of Paris (France) proved that the concentrations of Cd, Cu, Pb and Zn in runoff water from roofs were 4 to 6

Table 1.1: Pollutants originating from roof, facade, terrace run-off (Boller, 2011)

Source	Substances
roof metal sheets, metal facade metal gutters, drains	copper, zinc, lead, nickel, cadmium, tin, etc.
roof isolation (bitumen, plastics)	biocides/pesticides, flame retardants UV-filters, plasticizers, etc.
facades and terraces	biocides/pesticides, conserving agents UV-filter, synthetic nano-particles, etc.
atmospheric wash-out	copper, pesticides, etc.

times higher than those from drive ways (Gromaire-Mertz et al., 1999, 2002).The contamination of sewage water with heavy metals has been observed in other countries too, e.g. in Holland (Gouman, 2004), in Sweden (Bergbäck et al., 2001; Sörme et al., 2001), in Germany (Förster, 1999).

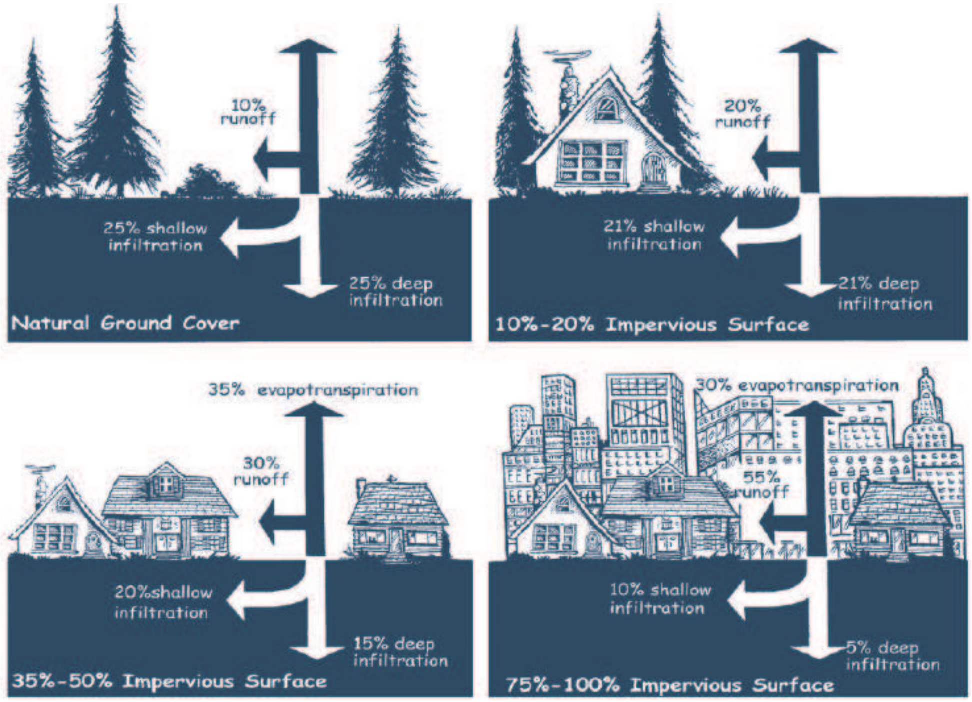

Figure 1.1: Relationship between impervious cover and surface runoff EPA (2003).

In urban and suburban areas, much of the land surface is covered by buildings and pavement, which are impervious surfaces and do not allow rain and snowmelt to soak into the ground. For example, in the United States alone, pavements and other impervious surfaces cover more than 11 mil ha, an area nearly the size of Ohio (Frazer, 2005). Instead, most developed areas rely on storm drains to carry large amounts of runoff from roofs and paved areas to nearby waterways. Thus, pollutants, such as oil, dirt, chemicals and lawn fertilizers are carried directly to streams and rivers, where they might seriously harm water quality. In natural ground covered areas, 50% of the storm water infiltrates (shallow or deep), while in areas with 75–100% impervious surface, only 15% of storm water manages to infiltrate into the soil and 55% is being directed to rivers (see Figure 1.1) (EPA, 2003). Either way, if runoff is directly rejected to the environment by infiltration (e.g. the case of house settlements) or if it is collected and later directed to rivers (e.g. the case of dense buildings or industrial sites), the environmental impact of pollutants released from construction products (and buildings) needs to be assessed.

2 Leaching phenomena

The physico-chemical and mass transfer phenomenon occurring at the product-water contact is called leaching. If the "solid-liquid" system is not in equilibrium, it moves towards a new stable thermodynamic status. Leaching is defined by the following phenomena:

(i) chemical reactions taking place in the structure of the material (pours or fibres),

(ii) precipitation/solubilisation, or other fixation/solubilisation mechanisms,

(iii) diffusion (if the product is porous, from the more concentrated regions, i.e. pores or surface to the more diluted regions, i.e. leachate compartment),

(iv) absorption (of gases, mainly CO_2 which can react with hydroxyl ions in an alkaline environment).

The liquid in contact with the solid phase at moment $t = 0$ is called leachate and at $t > 0$ it is called eluate. The leachate can consist of demineralised water, diluted acids/bases (in lab tests), rain, ground, underground or marine water (in tests under natural exposure conditions). Eluates are leachates containing various concentrations of leached substances (insignificant or high).

From the point of view of leaching, the construction products can be classified as follows:

- granular – "composed of solid particles with a particle size smaller than a specified size or grading" (CEN, 2012a) and

- monolithic – "which has certain minimum dimensions and physical and mechanical properties that ensure its integrity over a certain period of time in the considered intended conditions of use" (CEN, 2012a).

Based on their matrix, construction products can be: (i) organic, (ii) metallic, (iii) mineral and (iv) mixed. The structure of the product can be porous or non-porous, favouring or not the diffusion of substances from the pores to the surface.

Two main types of leaching scenarios are possible (all phenomena described above in (i) (v) may take place):

(a) percolation - water passes through the material,

(b) external mass transfer - water flows around the material.

Historically, the development of leaching tests and methodologies has started as a necessity in the assessment of the environmental behaviour of waste or materials containing recycled waste. Water is considered the main environmental pollution vector responsible for transfer and dispersion of soluble pollutants from solid waste materials placed in real scenarios implying contact with water. Many studies have been reported on leaching behaviour of waste (e.g. (van der Sloot, 1990; van Zomeren and Comans, 2004)) and on the leaching behaviour of construction products containing wastes. It is mainly the case of cement-based materials containing inorganic waste (Gervais et al., 1999; van der Sloot, 2002; Tiruta-Barna et al., 2004; Barna et al., 2005) or asphalt amended with waste ash (Dubey and Townsend, 2007; Chiu et al., 2009). All these studies aimed at describing the leaching behaviour in view of land filling (wastes, stabilized wastes) or recycling (wastes, construction materials containing wastes).

Currently, the leaching behaviour of "classical" construction products (without waste included) is of high interest (EC, 2005). In 2011 the Construction Products Regulation – CPR (EC, 2011) replaced the Construction Products Directive – CPD (EC, 1989). The scope of the new CPR is the regulated issues under seven basic requirements (BRs) for construction works, which have to be assured by the member states:

1. mechanical resistance and stability,
2. safety in case of fire,
3. hygiene, health and the environment,
4. safety and accessibility in use,
5. protection against noise,

6. energy economy and heat retention,
7. sustainable use of natural resources (new requirement compared to CPD).

The BR 3 on hygiene, health and the environment, states that "the construction works must be designed and built in such a way that they will, throughout their life cycle, not be a threat to the hygiene or health and safety of their workers, occupants or neighbours, not have an exceedingly high impact, over their entire life cycle, on the environmental quality or on the climate, during their construction, use and demolition in particular as a result of any of the following: ... (d) the release of dangerous substances into ground water, marine waters, surface waters or soil; (e) the release of dangerous substances into drinking water or substances which have an otherwise negative impact on drinking water; ...". In order to comply with the BR 3 the European Commission mandated CEN/TC 351 to develop methods for the assessment of the leaching behaviour of various construction products (based on wood, concrete, etc.) with the same methods, i.e. horizontal approach. A generic horizontal dynamic surface leaching test (DSLT) for determination of surface dependent release of substances from monolithic or plate-like or sheet-like construction products and a generic horizontal up-flow percolation test for determination of the release of substances from granular construction products have been validated in 2012 (CEN, 2012b). Moreover, an Expert Group on Dangerous Substances (EGDS) was established and has prepared an "Indicative list on dangerous substances" and a database on national regulations in terms of dangerous substances (EC, 2013).

Previous studies concerning the release of potentially hazardous substances to the environment (soil, groundwater, surface water etc.) from "classical" construction products generally report that this is an issue of concern, depending on the type of pollutants and exposure conditions (Lebow, 1996; Schiopu, 2007; Robert-Sainte, 2009; Ahn et al., 2010; van der Sloot and van Zomeren, 2011). For example, metallic roofs are the main source of heavy metal release (Zn, Cu, Cd, Ni, etc.) into the urban sewage water (Förster, 1999; Bergbäck et al., 2001; Sörme et al., 2001; Gouman, 2004; Faller and Reiss, 2005; Robert-Sainte, 2009). Moreover, preservative treatment is currently widely spread in the construction products' industry. Various biocides are applied in surface or core treatment in order to prevent biological attack and increase the products' durability (mechanical properties). Several oil and waterborne treatment solutions have been used on construction products, such as: creosote, pentachlorophenol, terbutryn, mecoprop, ammoniacal copper arsenate (ACA), chromated copper arsenate (CCA) for wood treatment (Lebow, 1996).

Furthermore, surface treatment can be applied during the maintenance phase of the product. Leaching from treatment products has been extensively studied, for example by van der Voorde (2012) who investigated the leaching of biocides. However, this subject is complementary with the scope of the current work.

Biocides added with the treatment solution (before or during the service life of a product), as well as endogenous substances (originating in the material) are susceptible of leaching and might be a threat to people or the environment. Yet, literature data is very scarce concerning leaching data on the "classical" construction products and more knowledge is needed on this topic.

3 Environmental assessment of pollutant release from construction products

Currently, the environmental impact of construction products and buildings is evaluated namely by a Life Cycle Assessment (LCA) approach. LCA is a tool to "assess environmental impacts and potential environmental impacts throughout a product's life cycle" (ISO 14040, 2006), from cradle-to-grave (i.e. from raw material extraction, to disposal and recycling of the final product after use). In LCA, the central objects of analysis are a product function and the industrial and other processes connected to it. Thus, the function of lightning a room can be fulfilled with a lamp, wiring and electricity. The system extends to the transportation of coal from mines to power plants, the production of electric wires and glass, the mining of fossil fuels and metals, the disposal of used lamps, the recycling of copper wires etc. (Heijungs et al., 2004).

The ISO 14040 standard distinguishes four main phases in LCA: (i) goal and scope definition, (ii) inventory analysis, (iii) impact assessment and (iv) interpretation (Figure 1.2).

The first step in a LCA is to define the goal and scope of the study, including the system boundary and level of detail. This depends especially on the intended use of the study. The life cycle inventory (LCI) phase makes an inventory of input/output data necessary to meet the goals of the defined study. The impact assessment phase (LCIA) provides information in order to assess the LCI results of the considered system and to understand their environmental significance. The final phase of an LCA is the interpretation of LCI and LCIA results, as a basis of conclusions, recommendations and decision-making in accordance with the goal and scope definition.

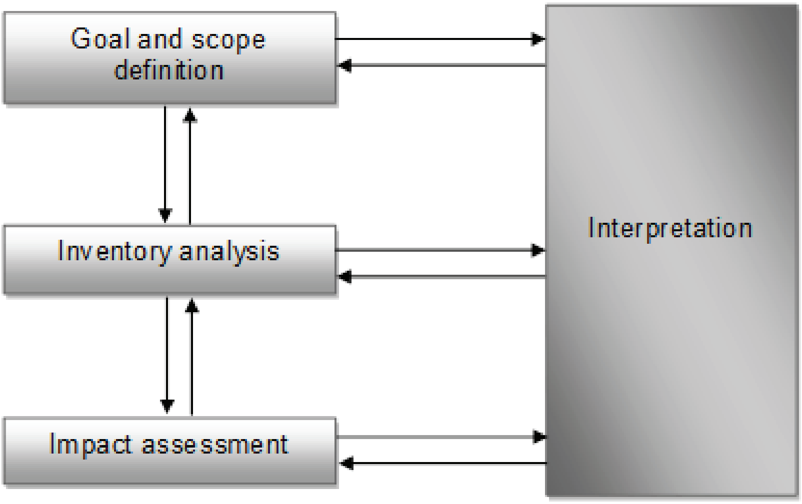

Figure 1.2: LCA phases cf. ISO standards 14040-44 (ISO 14040, 2006; ISO 14044, 2006).

The main advantage of LCA is that it helps to avoid the transfer of impacts between the various stages of the life cycle of a product or a system. The life cycle of a construction product contains the following stages: production, transport, construction process, use and end of life (Figure 1.3).

The environmental impacts associated with a product, for each phase of its life cycle, are evaluated using indicators, such as raw material acquisition, energy use and efficiency, content of materials and chemical substances, waste generation, released substances to air, soil and water. This information, together with the product and company details, is centralised in the so called EPDs (Environmental Product Declarations). An EPD is a standardized, LCA based tool to communicate the environmental performance of a construction product or system, and is applicable worldwide for all interested companies and organizations. EPDs are voluntarily developed information and their purpose is to provide quality-assured and comparable information regarding the environmental performance of products.

EPDs have only recently been harmonised at European level by the standard EN 15804 (CEN, 2011). However, already existing EPDs in European countries are not harmonised. They have been developed according to the European standards ISO 14025 (ISO 14025, 2006), ISO standard series 14040 (ISO 14040, 2006) and 14020 (ISO 14020, 2000) or ISO 21930 (ISO 21930, 2007), but transposed with different specifications according to national standard, e.g. French EPDs based on the national standard NF P 01 010 which are centralised in the national database

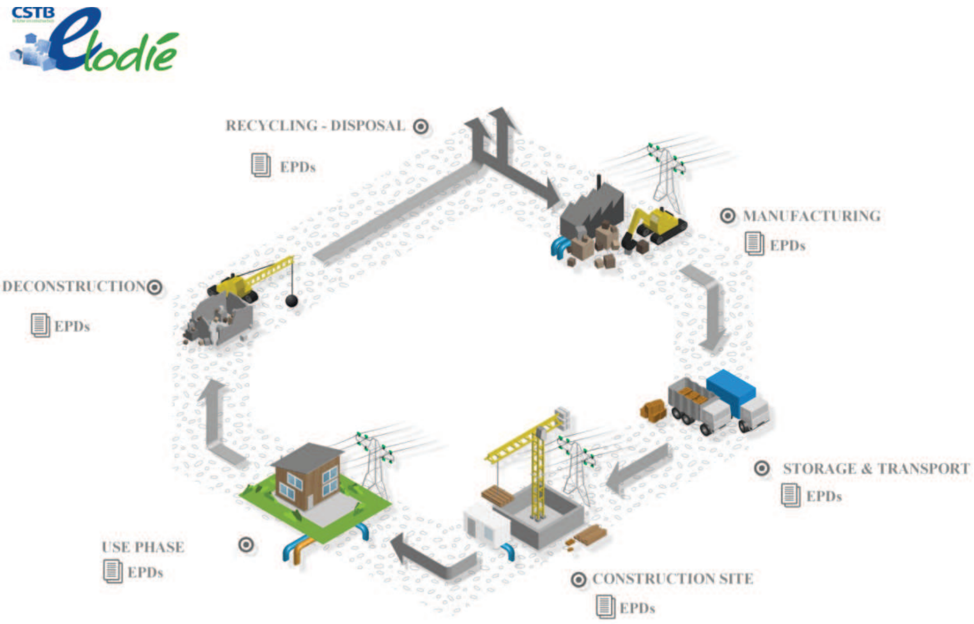

Figure 1.3: Stages of the life cycle of a construction product (CSTB, 2002).

INIES (Association HQE, 2009). In most of existing EPDs the inventory concerns mainly the production stages. Data referring to use of resources (energy and raw materials), emissions to air and water or process waste are mostly regarded during the production and sometimes transport phase. Nevertheless, the French EPDs consider the impact over the whole life cycle of the product, i.e. production, transport, construction process stage, use stage and end of life. Concerning the impact categories (and methods) used at European level, the results presentation vary from country to country (see three examples in Table 1.2). With the publication in 2012 of the harmonised European standard (CEN, 2011), the national standards has been or will be (depending on the country) replaced by it. The European standard provides core product category rules for construction products in order to ensure the harmonisation of all EPDs. More recently, the European guidance document EeBGuide (EeBGuide, 2012), based on standards ISO 14040-44, EN 15978 (CEN, 2010) and the EN 15804 (CEN, 2011), provides information on calculation rules, metrics, provisions and instructions for the preparation of LCA studies for energy-efficient buildings and building products for European research projects, also in view of harmonising the methodology for the construction of EPDs.

At present, the release of potentially hazardous substances towards soil and water are considered only partially in the EPDs. More, several ambiguities have been identified:

Table 1.2: Impact categories in EPDs from three European countries.

Country / Name	Impact categories	Unit/FU
French FDES	Use of energy	MJ
	Consumption of raw materials	kg Sb eq.
	Total water consumption	L
	Waste production	kg
	Climate change	kg CO_2 eq.
	Atmospheric acidification	kg SO_2 eq.
	Air pollution	m^3
	Water pollution	m^3
	Ozone depletion potential	kg CFC eq.
	Photochemical ozone creation potential	kg C_2H_4 eq.
German EPDs	Use of energy	MJ
	Abiotic resource depletion	kg Sb eq.
	Total water consumption	L
	Global warming potential	kg CO_2 eq.
	Ozone depletion potential	kg CFC eq.
	Acidification potential	kg SO_2 eq.
	Eutrophication potential	kg PO_4^{2-} eq.
Finish RT–Environmental declarations	Use of energy	MJ
	Consumption of raw materials	g
	Emissions to air	g of pollutant
	Emissions to water	g of pollutant
	Process waste	g

- Leaching data (i.e. emissions towards soil and water during use stage) are not considered or are very scarce.
- Concerning the inventory phase, if considered, leaching data is included either in the water or the soil emissions indicator, depending on the existence of reference flows in the corresponding list. Nevertheless, for a correct calculation of the impact, the target compartment of pollutant emission needs to be stated clearly.
- The results are given for one year or for all reference service life (RSL), e.g. 50 years of use. The relationship between the two values is linear (obtained either by dividing the all service life emissions by the RSL, respectively, by multiplying the one year emissions with the RSL). Or, it has already been observed in field leaching tests that emissions over longer periods (several years) are not constant in time (Schiopu, 2007; Morsing and Klamer, 2010). This aspect relies on a more fundamental default of the LCA methodology

which is the absence of the temporal dimension.

– Concerning the LCIA phase, in a first step, emissions of pollutants to water and soil during use stage (leaching data) have a local scale but they are summed with emissions during the other phases of the product's life cycle, taking place elsewhere and at different moments. Here again, this shortcoming relies on the fundamental basis of LCA method which loses the spatial location of the environmental burdens. In a next step, the impact of emissions to water and soil is calculated using different methods. For example, in France the pollutant impact in FDES is calculated by the critical volumes method, i.e. the volume of water (in m^3) needed to dilute the emissions from a certain product, in order to meet the thresholds from the ICPE regulation (ICPE, 2008). This method is considered as "user-friendly" but it does not take into consideration the impact mechanisms (e.g. the transport of the pollutants between different compartments such as from soil to groundwater, to freshwater, etc).

At European level, in the EN 15804 standard (from CEN / TC 350), the inventory of the release of dangerous substances to soil and water are considered as mandatory (and data should be obtained according to the standards from CEN/TC 351) but also as additional information. Nevertheless, a specific indicator and a calculation method are not yet defined regarding the assessment of the impact due to these emissions (to water and soil).

In order to evaluate the contribution of different life stages to the total emissions for several pollutants we realised a comparison for cement based products (Lupsea et al., 2012b). Data found in EPDs for water pollution during use stage is compared to leaching data obtained at field scale (1 year of natural exposure). The two products used to build Table 1.3 are not identical, but similar (concrete slabs made of XF1 C25/30 CEM II, respectively XF1 C25/30 CEM I), as we didn't dispose of both kind of data for the same products. The second column (Release during use stage: leaching data) refers to experimental leaching data taken from (Schiopu, 2007), while the third column (Release during use stage – EPDs data) shows data concerning release to water during the use stage of the product, which is at the moment integrated in the EPD (SNBPE, 2008). In the fourth column (Release during whole life cycle – EPDs data)) we have summed up emissions into water over the life cycle, i.e. release during production, construction process, use stage and end of life (data found in the EPD). The latter doesn't refer to leaching phenomena, but to discharge to the environment via other events. If we disposed of leaching data for the concerned product, and it were taken into account, their contribution to

Table 1.3: Release of substances to water from concrete slabs (EPDs and leaching data) during use stage and their contribution in % to the releases during the whole life cycle of the product.

	Release during use stage		Release during whole life cycle	Contribution of release during use stage	
	Leaching data	EPDs data	EPDs data	Leaching data	EPDs data
Unit	mg/m^2/year	mg/m^2/year	mg/m^2/year	%	%
Al	56.0	0	9.25	85.9	0
Cr	16.0	0	0.124	99.2	0
Cu	15.0	0	0.0624	99.6	0
Zn	14.0	0	0.157	98.9	0
DOC	4300	0	3610	54.4	0

emissions during the whole life cycle would be as calculated in the fifth column (Contribution of release during use stage: leaching data), i.e. up to 99%.

Despite the current interest in leaching data, the impact due to emissions to water and soil during the use stage is not well evaluated, the impact being either underestimated, or overestimated. Underestimation can lead to a wrong evaluation of the environmental impact of buildings and is mainly due to the lack of leaching data.

On the other hand, overestimation of release to water and soil is due to the use of data based on the total content of a substance in the construction products, which is considered to completely leach during the use stage. This assumption is false for most substances. Such miscalculation can hinder the development of some innovative construction products (e.g. based on secondary raw materials).

Another problem for the evaluation of leaching data in the EPDs is the fact that the concentrations of hazardous species and other released substances are very low. At a first glance, these values could be considered as insignificant. Nevertheless, to correctly evaluate the environmental impact, the cumulated mass of the substance leached per functional unit (FU) needs to be estimated on appropriate time spans. In reality, the released quantities could be very high and hazardous for different compartments and consequently a significant impact will be obtained.

In a possible attempt of coupling leaching with LCA data, one can run into the dynamic of leaching data. Emissions to the environment from construction products in contact with water are indeed a dynamic process. The release of substances to soil and water occurs over a certain period and is variable in time. This is proved by all leaching curves obtained in several studies carried out on various products and substances. Some influencing parameters are the liquid to solid ratio, i.e. quantity of rain, the kinetics of the reactions taking place in the pores of the solid, the diffusion in pores.

However, current LCA tools do not yet provide a comprehensive and operational approach for the proper consideration of time dependency. In conventional LCA, the human driven systems which are analysed are typically considered to run in steady state conditions. Indeed, conventional LCA models are ideal simplifications of a reality which is, nonetheless, highly dynamic and variable over time. Methodologies and tools for the proper consideration of time in LCA (both in LCI and LCIA) have not been developed yet. The difficulties concern the inventory as well as the impact assessment phases of an LCA approach. Despite the high importance of the dynamic aspect of leaching data and their integration in LCA methods, this subject is beyond the scope of this current work and could be envisioned in a follow-up project.

At building scale, currently, the environmental performances of buildings are also evaluated by a LCA approach. Several European projects dealing with LCA and buildings have been conducted over the past few years. Most of them were aimed at adapting the methodological rules for LCA studies in the construction sector and enabling the development of user-friendly tools that can be used by building stakeholders, who are usually not LCA experts. These projects included, for example, Annex 31 IEA (IEA Annex 31, 2005), PRESCO (PRESCO, 2004), ENSLIC Building (ENSLIC Building, 2009), LoRe-LCA (LoRe-LCA, 2011) and EeBGuide (EeBGuide, 2012). Integrating leaching data in EPDs which are further used in LCA studies on buildings is another subject of interest, which needs to be addressed in detail. It is, however, not one of the main objectives of this work.

4 Conclusions

Leaching from "classical" construction products (without waste included) is a subject that needs to be addressed more deeply in view of a proper assessment of the environmental impact of products and buildings. Two problematics have been identified in the above sections: (i) collection of leaching data on construction products and (ii) integration of leaching data in the LCA approach.

The collection of leaching data on classical construction products is a subject which can be addressed by leaching tests at laboratory and field scale. Nevertheless, the emissions over longer periods of time (i.e. RSL reference service life) are difficult to obtain by experimental methods, but could be characterised by numerical simulations. However, leaching tests are indispensable in order to build reliable long term models.

Once the release from construction products in contact with water during the use stage evaluated, the next step is to integrate them in LCA tools, along with emissions during other stages. The consideration of leaching data with LCA tools is currently a problematic of high interest. Some tentatives of including leaching data in the LCA approach (e.g. EPDs) have been identified. Yet, several questions need to be answered in what the inventory and the impact assessment concerns. A proper methodology has to be developed.

The approach used in order to respond to the main objectives of this study, i.e. development of a methodology to numerically assess the leaching behaviour of various classical construction products and a methodology for coupling LCA and leaching data, is described in the following chapter. Next, the proposed methodology is studied on three preselected products of various matrixes, i.e. organic porous, mineral (non-metallic) porous and organic non-porous.

Chapter 2

Materials and methods

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Ce chapitre présente la méthodologie développée et appliquée pour l'intégration des émissions de polluants au cours de la phase d'utilisation du produit, dans l'approche ACV. La méthodologie proposée dans cette étude est basée sur l'intégration des données de lixiviation dans l'inventaire et l'évaluation ensuite de l'impact par des méthodes appropriées. La méthode la plus pertinente et la moins coûteuse pour l'estimation des émissions des produits de construction à long terme (pendant toute la durée de vie dans l'ouvrage) est de simuler leur comportement à la lixiviation en utilisant des modèles mécanistiques. Dans cette étude, le développement des modèles mécanistiques est basé sur des essais de lixiviation à l'échelle laboratoire, la modélisation et la simulation numérique à l'échelle laboratoire et sur le terrain. Les résultats ainsi obtenus sont ensuite intégrés dans l'approche ACV.

Les principales étapes de la méthodologie générale proposée sont :

1. La génération des données d'entrée pour le développement des modèles contrlant les phénomènes de lixiviation :
    (a) Pour le modèle chimique les données sont obtenues à l'aide des essais de lixiviation statiques à l'échelle laboratoire (dépendance du pH, essais menés dans des conditions favorisant l'attente de l'équilibre dans des délais court – 2 jours).
    (b) Pour le modèle transport les données sont obtenues à l'aide des essais de lixiviation dynamiques à l'échelle laboratoire ; ces essais sont effectués sur des échantillons monolithiques et permettent d'obtenir des informations supplémentaires sur le mécanisme de diffusion dans les pores du produit et/ou sur le transfert de masse (convection) à la surface du monolithe.
2. Développement du modèle chimique : à partir des données d'entrée générées à l'aide des essais de lixiviation statiques, des données de la littérature et à l'aide des logiciels spécialisés incluant des bases de données spécifiques à la modélisation physico-chimique.
3. Développement du modèle de transport des polluants : à partir des données d'entrée générées à l'aide des essais de lixiviation dynamiques, des données de la littérature et à l'aide des logiciels spécialisés incluant des bases de données spécifiques à la modélisation physico-chimique.
4. Couplage modèle chimique et modèle transport : le modèle chimique développé à l'étape 2 est couplé avec les mécanismes de transfert de masse et de transport identifiés à l'étape 3, afin de décrire l'évolution de l'eau des pores et la composition du lixiviat en fonction du temps.

5. Génération / acquisition des données pour la validation du modèle à l'échelle pilote : ces données sont issues des essais à l'échelle pilote menés dans des conditions naturelles d'exposition, i.e. les produits sont exposés à l'eau (à l'occurrence l'eau de pluie) pendant au moins un an.
6. Validation du modèle à l'échelle pilote : le comportement à la lixiviation des produits exposés dans des conditions naturelles est modélisé. Le modèle chimie-transport est enrichi avec des paramètres décrivant l'exposition dans des conditions naturelles.
7. Couplage lixiviation / approche ACV à l'échelle produit : les émissions cumulées déterminées par simulation numérique sont intégrées dans l'inventaire du cycle de vie (ICV) et des catégories d'impact pertinentes et des méthodes d'évaluation sont choisies et appliquées avec l'inventaire enrichi.
8. Couplage lixiviation / approche ACV à l'échelle bâtiment : les impacts calculés à l'échelle produit sont intégrés avec les autres données ACV à l'échelle bâtiment ; l'impact global est calculé à l'aide des outils pour l'évaluation des performances environnementales des bâtiments.

Trois produits sont sélectionnés pour les études de cas à l'échelle produit et l'étude de cas d'une maison individuelle simplifiée est considéré pour l'application de la méthodologie à l'échelle bâtiment. Les problèmes rencontrés dans cette procédure sont discutés.

1 Introduction

This chapter presents the methodology developed and applied for the integration in LCA approaches of pollutant emission during the use stage of the product. First, the general methodology is presented. It is based on leaching tests and numerical simulations of the leaching behaviour of construction products. Three products are selected for case studies. The performed leaching tests and the principles of the modelling (and simulation) are described. Leaching data thus obtained is used to enrich the inventory of the LCA methods (LCI). The next step is to choose a suitable impact method, in order to assess the environmental impact due to emissions to water and soil during the use stage. The problems encountered in this procedure are discussed.

2 General methodology

We have seen in section chapter 1 §3 that the impact of emissions from construction products to water and soil can be assessed by a LCA approach. Currently, this is a difficult and yet not elucidated problem. The methodology proposed in this study is based on including leaching data in the inventory and further assessing the impact by relevant methods. The most pertinent and less expensive method for the prediction of release from construction products over long exposure periods is to simulate their leaching behaviour using mechanistic models. The development of reliable leaching models applied in this study is based on characterisation leaching tests at lab scale, modelling and numerical simulation at lab and field scale.

Given the importance of what we called “monolithic materials” (see chapter 1 §2) in the construction industry (the construction products are utmost consolidated materials), this work is dedicated to this type of products.

The general methodology proposed for coupling the leaching assessment of monolith construction products with LCA methods follows several steps (Figure 2.1):

1. Equilibrium (pH dependency) leaching tests at lab scale are performed on crushed samples in view of determining the chemical stability of the material, the pollutants’ behaviour and the leaching mechanisms.
2. Based on information obtained from the pH dependency test (and literature data, if existent), a chemical model is developed.

3. Dynamic lab tests performed on monolith samples (validated as horizontal leaching test) offer supplementary information about the diffusion mechanism taking place in the pores of the product and/or about the external mass transfer (convection) at the monolith surface.
4. The chemical model developed in tier 2 is coupled with mass transfer and transport mechanisms identified in tier 3, in order to describe the pores' water evolution and the leachate composition in function of time.
5. Pilot scale tests are envisioned in natural exposure conditions on products exposed to rain over at least one year.
6. The leaching behaviour of the products exposed in natural conditions is modelled. The chemical-transport model is enriched with parameters describing the exposure over 1 year in natural conditions.
7. The cumulative release determined by numerical simulation is included in the life cycle inventory (LCI), along with the release over the other stages of the product's life cycle.
8. Relevant impact categories and evaluation methods (LCIA) are chosen and applied with the enriched inventory.

3 Studied materials

In a first step we have identified the main construction products used for the buildings' envelope, which come into contact with water (products used for the roofing, façade, terraces and in foundations). A classification in function of their structure and nature is shown in Table 2.1.

In the next step we have reduced the list of products, according to several criteria:

- main products used in Europe (common products on the market or increased trend),
- products containing a priori dangerous substances for the environment,
- products which are susceptible of leaching when brought in contact with water.

These criteria and results from previous studies (e.g. (Schiopu et al., 2009; Burkhardt et al., 2011; Tiruta-Barna and Schiopu, 2011)) allowed the selection of five

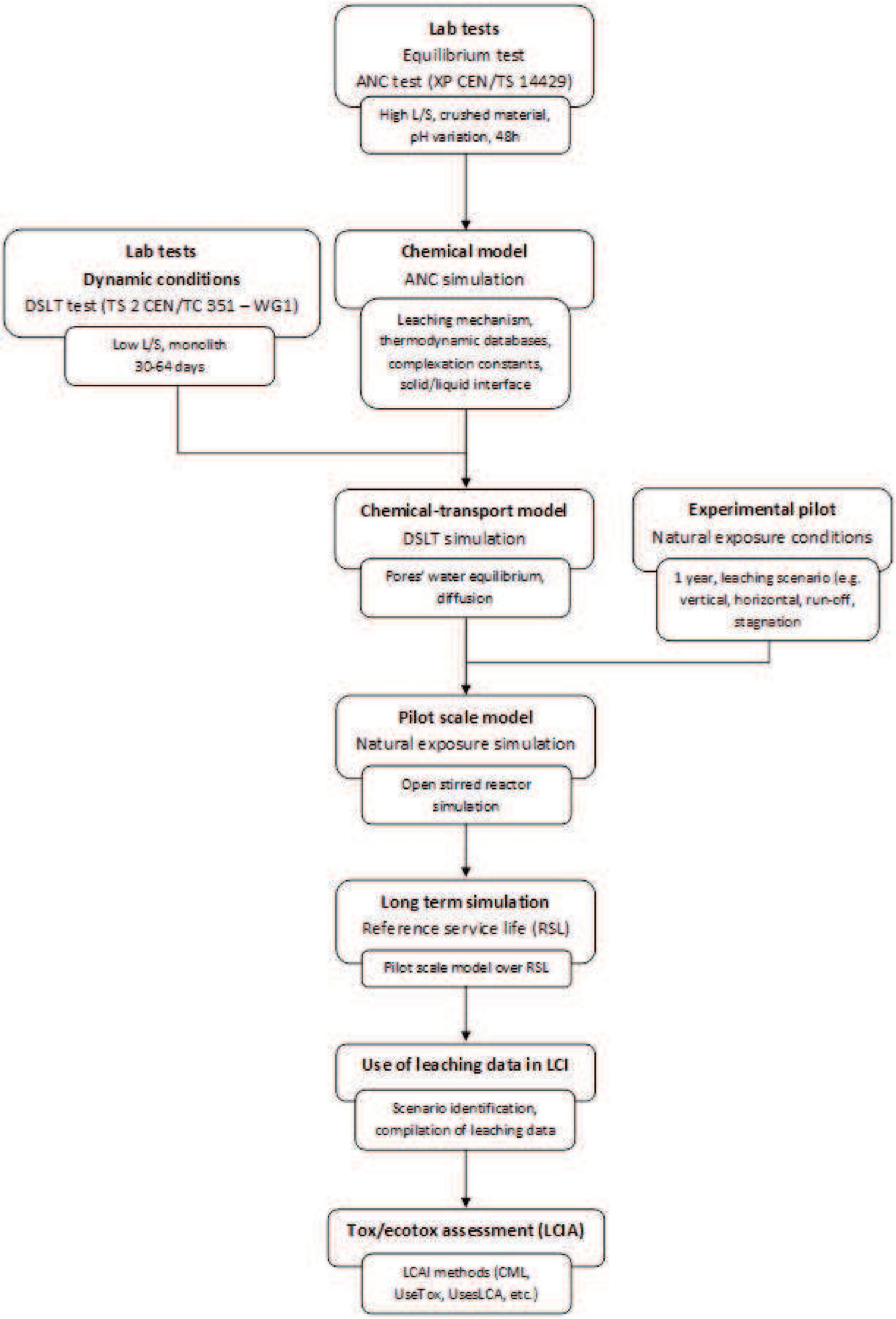

Figure 2.1: Scheme of the methodological approach for the assessment of the tox/ecotox impact of monolith construction products in contact with water.

Table 2.1: Classification of construction products used in the envelope of buildings.

Organic	Natural	Wood
		Bituminous
	Synthetic	Based on polymers
Mineral (non-metallic)	Based on cement	Fibre-cement
		Mortar, concrete
	Based on clay	Terracotta tiles
	Based on glass	Photovoltaic tiles
	Natural	Ardoise, stones
Metallic	Ferrous	Steel
	Nonferrous	Zinc, copper

products (i.e. fibre-cement sheets, treated wood, bitumen membrane, photovoltaic panel and steel roofing sheets) for preliminary leaching tests.

The screening carried out on eluates from the preliminary leaching tests (see below), restricted our choice for further testing to three construction products: fibre-cement sheets, treated wood and bitumen membrane (Figure 2.2).

Figure 2.2: Fibre-cement sheets (left), treated wood (middle) and bitumen membrane (right).

3.1 Fibre-cement roof sheets

Fibre-cement roof sheets are a composite material, made of cement, sand (silica) and reinforcing fibres. After the 80s, the asbestos fibres were replaced with cellulose or synthetic fibres, e.g. polyvinyl alcohol (PVA) fibres. The usual composition is a mixture between cellulose and synthetic fibres, thus: 2% PVA fibres, 5% cellulose fibres, 80% cement (sometimes the formulation contains $10-30\%$ inert fillers such as silica or limestone) (Merkley and Luo, 2004). Cellulose fibres are susceptible to bio-decay or rot attack when incorporated into fibre reinforced cement composite materials which are in contact with water. Thus, a technology of making reinforced cementations composite materials using biocide treated cellulose fibres has been developed. Nevertheless, in high humidity environments, the pore spaces in the fibre-cement sheets facilitate water transport to the fibres and biocides could leach from the product. A commercial product "fibre-cement profiled roofing sheet natural grey" with blinded composition was used in this study. The experimental leaching assessment has been carried out at CSTB (Centre Scientifique et Technique du Bâtiment), Grenoble - more details in chapter 3 §3.

3.2 CBA treated wood

Being an economical, durable and aesthetically pleasing building product, treated wood is a frequent choice for construction projects. Previous studies generally report high leaching rates from treated wood, depending on the type of preservative and exposure conditions (Lebow, 1996; van der Sloot and van Zomeren, 2011). During the years, different classes of biocides have been used in wood treatment, due to legislative constraints imposing increasingly strict conditions. Nowadays, the most common wood biocides are based on boron, copper and various synthetic organic substances such as propiconazole or tebuconazole. The product studied in this research consists of *Pinus sylvestris* treated with copper-boron-azole (further called "CBA"), containing tebuconazole as main organic biocide. The wood samples were treated by vacuum pressure with an aqueous solution (2.1 %) of a commercial preservative (as described in the EN 113 standard). The commercial wood preservative consisted of copper carbonate (22.5 %, i.e. 12.9 % Cu), boric acid (4.9 %, i.e. 0.65 % B), tebuconazole (0.53 %), monoethanolamine (MEA) and 2-ethylhexanoic acid. The treatment process and the experimental leaching assessment have been carried out at the German Institute BAM (Bundesanstalt für Materialforschung und prfung), Berlin more details in chapter 3 §2.

3.3 Bitumen membrane

Bitumen membrane is a type of roofing product for buildings with flat or nearly flat roofs. They are composite sheet membranes a mixture of bitumen, mineral fillers and polymers (e.g. styrene-butadiene-styrene copolymer SBS, atactic polypropylene APP) (Partl et al., 1996). Several authors have investigated the leaching behaviour of bitumen membranes (Brandt and de Groot, 2001; Burkhardt et al., 2011). Different biocides have been identified, e.g. mecoprop, terbutryn, diuron, irgalol, etc. (Burkhardt et al., 2011). A commercial product "polymer-modified bitumen sheet membrane" blinded composition, was used in this study. The experimental leaching assessment has been performed at CSTB, Grenoble more details in chapter 3 §4.

4 Material characterisation

Characterisation assays have been carried out on the tested products in order to determine parameters needed for development of the mechanistic leaching models, i.e. the porosity and the total content of the materials. The open porosity is a key parameter in the transport-chemical model. It was measured cf. NF P 18-459 standard on fibre-cement sheets and cf. standard DIN 66133 for CBA treated wood.

The total content of the samples is a parameter used in the chemical model development. For CBA treated wood it was determined by mass balance calculations (see chapter 3 §2.1), while for fibre-cement sheets by analytical methods (see chapter 3 §3).

In what bitumen membranes concerns, no parameters for the material characterisation were measured.

5 Characterisation leaching tests

In this section the principles of the characterisation leaching tests used in the experimental work are described. A preliminary leaching test was firstly used for screening of pollutant release from preselected construction materials. Secondly, the leaching study strictly speaking applied to the three selected materials was based on the static ANC test and the dynamic DSLT test described below. We propose these two leaching tests to be included in a horizontal approach for leaching assessment of construction products.

5.1 Preliminary static test

The aim of this test is to bring additional information for the product selection and to help identifying the target substances for further analysis. The preselected products (according to the above mentioned criteria) in monolith form were brought in contact with demineralised water during 48 h, with a liquid to solid ratio (mL/g or mL/cm^2) as low as possible (minimum solution volume necessary for analytical procedures and complete immersion of the product). A screening analysis on about

30 metals and more than 700 organics was performed on the collected eluates. The tests have been carried out at CSTB and the analyses have been performed by the LaDrome Laboratories. The analytical methods used are centralised in Appendix A.

5.2 Static test – ANC

This test, called ANC (Acid/base Neutralisation Capacity test – based on XP CEN/TS 14429 (CEN, 2006)) aims to describe the pH dependency of leaching for different components. It provides information on the influence of pH on pollutant release, acid/base neutralisation capacity and physico-chemical stability of the material. It was intended for the characterisation of the leaching behaviour of waste. Nevertheless, it is more and more used on construction products (Esser et al., 2001; Schiopu, 2007; van der Sloot and van Zomeren, 2011). A similar method is under development in the USA Draft US EPA Method 1313 (EPA, 2009a). However, for the coherence of the results, we chose to use here the European standard. Crushed material is brought in contact with demineralised water and acid or alkaline solutions (NaOH, HCl or HNO_3) of various concentrations, such that the pH of the obtained eluates varies between 2 and 14. The product in contact with the solutions is shaken for 48 h (or longer, depending on the product), until equilibrium is reached, i.e. the pH and conductivity of the eluates are stable.

5.3 Dynamic test – DSLT

The dynamic surface leaching test (DSLT) has been carried out on fibre-cement sheets and bitumen membranes cf. TS 2 from CEN/TC 351 (CEN, 2012b) and on treated wood cf. OECD 313 (OECD, 2007). These tests are used to describe time dependency of leaching of different components. The corresponding standard in the USA is the US EPA Draft Method 1315 (EPA, 2009b). The products in monolith form are immersed in demineralised water for 64, respectively 30 days. Eluates are collected for analysis and replaced with fresh demineralised water at fixed time intervals, e.g. after 6 hours, 1 day, 2 days, 5 days etc. A stirrer has been used in tests on bitumen membranes and fibre-cement sheets, in order to homogenise the leachate.

Concerning the experimental protocols of the ANC tests, for the cement based products we used PVC recipients/containers of 0.5 L in volume, filled up to maximum 80% of the capacity. The tests on organic products, i.e. treated wood and bitumen membrane, were carried out in glass bottles of 1L in volume. Sets of 6 to

12 recipients were stirred for 48 h (or longer in the case of bitumen membrane) in an overhead shaker (Figure 2.3 left).

Figure 2.3: ANC installation (left); DSLT reactors (right).

DSLT tests on fibre-cement sheets and bitumen membrane were performed in special conceived leaching reactors (Figure 2.3 right). These reactors were designed during the current study. One leaching cell is built up from: (1) a bed and a cover made of polypropylene; (2) a cylindrical body made of borosilicate glass; (3) one supply and one evacuation valve; (4) 8 short lower and one long upper supports for the samples. The technical scheme of the reactors is presented in Figure 2.4. The diameter of the reactor is 30 cm and its load volume is 20 L (80% from the total volume). The reactors are compliant with magnetic stirrers and heaters up to 200 C. Due to the special system of supports, dynamic tests can be carried out on heavy and dense materials, such as concrete slabs or on light floating materials, such as wood boards. The reactors are built in accordance with the practical issues presented in CEN/TS 351 robustness validation for dynamic surface leaching tests on monolith samples in horizontal scenario. Moreover, a continuous recirculation system can be attached (using the supply and evacuation valve and a pomp), in order to perform CMLT leaching tests (Continuous Monolithic Leaching Test), e.g. based on (ADEME, 2005).

The fibre-cement sheets and the bitumen membranes have been tested at CSTB, Grenoble (France). The analytical analysis of the eluates has been performed by the LaDrome Laboratories (France). Leaching from treated wood has been the subject of the collaboration between the CSTB, Grenoble (France) and the BAM Institute, Berlin (Germany). The leaching tests and the analytical background concerning this product have been performed at BAM.

Eluates from the static and dynamic leaching tests carried out on the three products were collected, filtered and analysed for inorganic and organic compounds.

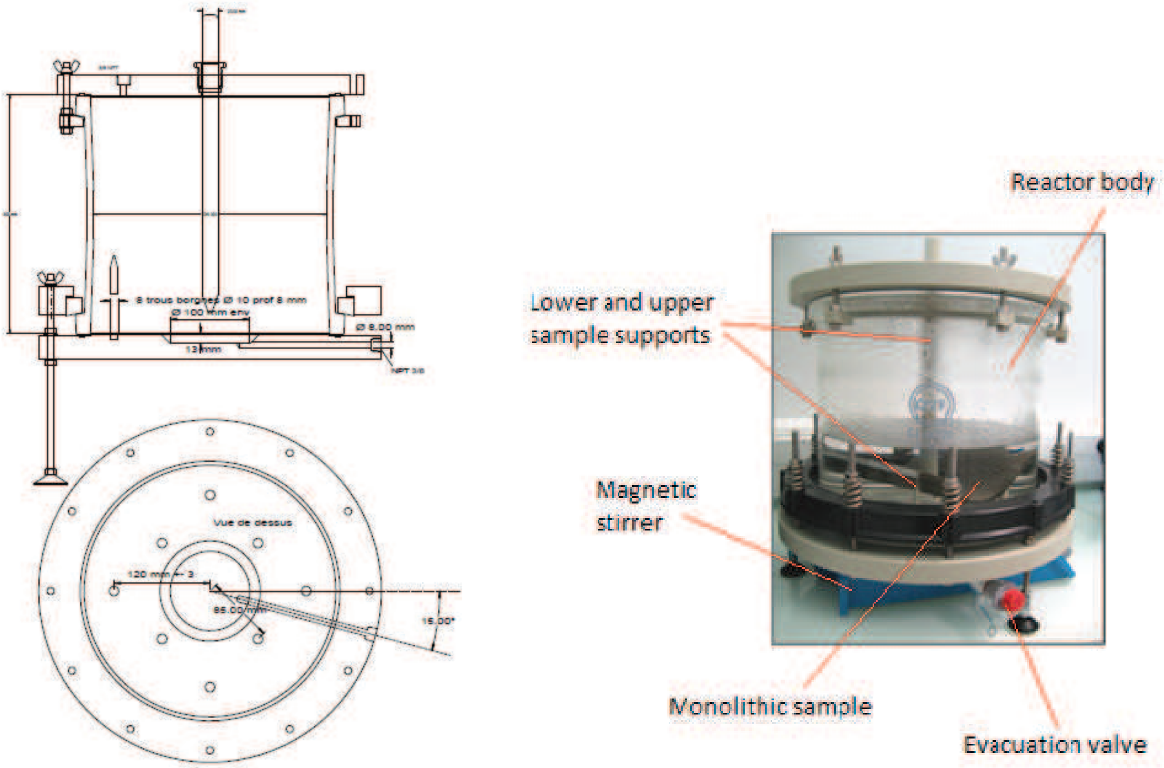

Figure 2.4: Scheme of the DSLT leaching reactor - front view (right); top view (down); in service (left).

More details concerning the tests performed and the analytical methods used on each studied product are given in chapter 3 (see §2 for CBA treated wood, §3 for fibrecement sheets and 4 for bitumen membranes).

6 Pilot experiments

Pilot experiments have not been performed in the current work for time and pecuniary reasons. Leaching tests in natural exposure conditions have been carried out in a previous research project at CSTB Grenoble, and described extensively in (Schiopu, 2007). The parameters defining the natural exposure conditions (i.e. exposure between July 2005 and July 2006, with a total rainfall 800 mm/year) have been used in the development of models which simulate the leaching behaviour of the products over longer periods (e.g. 1 year) in real exposure scenarios.

The experimental results obtained in pilot tests have been used to validate the models developed to simulate leaching in real exposure scenarios. More details on the used methodology (i.e. development of models for simulation of the leaching behaviour over 1 year in natural exposure conditions) are presented in chapter 4 §2.2.1.

7 Modelling principles

The methodological steps following the experimental works are dedicated to the mathematical modelling and numerical simulation of the leaching mechanism at laboratory and pilot scales.

At laboratory scale, the pH dependency test (ANC) is used to assess chemical speciation issues of the product in contact with water. The results of the pH dependence test are used in mechanistic geochemical speciation modelling to quantify the chemical phases (minerals and sorptive phases) controlling the release. The dynamic leaching test (DSLT) allowed the characterisation of the diffusion processes from the pores towards the surface of the product and the convection with the leachate. As a result, coupled chemistry-transport mathematical model have been developed, able to simulate numerically the leaching tests' results.

A further step in the modelling approach is the evaluation of pollutant release at long term exposure under natural conditions. For this task, the experimental parameters characteristic of the pilot studies previously realised on treated wood have been used together with a proper definition of a realistic leaching scenario. The principles of modelling at pilot scale are detailed in chapter 4 §2.2.1.3.

In the current study the numerical implementation of the leaching models has been realised using the free version of PHREEQC® software (Parkhurst and Appelo, 1999). Its efficiency in solving similar types of applications has been tested and confirmed in previous studies (Ettles et al., 2005; Halim et al., 2005; Tiruta-Barna, 2008).

The modelling principles and simulation protocol are explained in details for each case study in chapter 3.

8 Including leaching data in LCA

This part of the study is based on the four steps of the LCA approach, which we recall here: (i) goal and scope definition, (ii) inventory analysis (LCI), (iii) impact assessment (LCIA) and (iv) interpretation.

8.1 Goal and scope definition

The step of goal and scope definition largely deals with formulating the precise questions to be answered, e.g. what is the exact function of the system and where do its boundaries lie. This phase also involves setting some *a priori* restrictions. For our specific case, i.e. buildings in contact with meteoric water, the aim is the assessment of environmental impact of construction products or buildings. As for the boundaries of the system, we focus only on the system product in contact with rain water. This phenomenon corresponds to the use phase of a product or building.

8.2 Inventory analysis (LCI)

LCI focuses on outlining the structure and interdependency of the processes in relation to the product function analysed. Quantification of emissions per process finally leads to the overall emissions for the entire product system.

As mentioned in the first chapter, currently the emissions to water during the use stage of the product (i.e. leaching data) are not (or not correctly) considered in the inventory analysis. In order to do a proper LCA for building products which come in contact with water, it is important to include in the calculus the leaching data. Two methodological steps should be considered:

1. Identification of the emission scenario to be considered with LCA framework, i.e. in which compartment the pollutants are directly emitted by the product during its utilisation (emission scenarios);
2. Compilation of the leaching and material properties data aiming to evaluate the pollutant quantities released in real exposure conditions (leaching data).

Different leaching/exposure scenarios for the construction products have been defined (Schiopu, 2007), in function of the leaching mechanisms (type of water contact) involved. They are listed here below:

1. Sloping plane corresponds to a slope higher than 15% and is characteristic for pitched roof, generally roofing and covering products for which the main water contact type is the runoff.
2. Horizontal plane corresponds to the same construction products as in (1) but in a horizontal configuration, products for terrace (concrete, pavement bricks and asphalt, wood, metal slabs, different granulates, etc.), products used in public works like road (with different layers exposed directly or indirectly to water infiltration). Rain water in contact with horizontal surfaces can either

form stagnant layers, or runoff, or infiltrate and percolate the product if it is porous.

3. Vertical corresponds to façade type products exposed to rain water (bricks, concrete, wood, etc. with their surface treatments). Rain waters runoff and in a certain degree infiltrate if the product is porous.
4. Contact with soil corresponds to foundations for all categories of civil works. All contact types are possible: water runoff, stagnation, infiltration, percolation.
5. A fifth category could be introduced corresponding to works completely immersed in water like dikes, piles, basins, made generally of concrete based products, granulates, wood, etc.

Leachates from the exposure scenarios ((1)-(5)) can follow certain routes towards the environment:

1. Leachates going directly into the soil (beneath or surrounding the product) as in scenarios (1) – (4), then spreading within the connected compartments (water bodies, soils);
2. Leachates going directly into water bodies (groundwater, river, sea, ...) as in scenario (5), then spreading within connected compartments;
3. Leachates going to water bodies after treatment in a sewer system: it is the case of rain water collected in sewer systems, treated and then released (note that the treatment systems are not actually dimensioned for specific pollutants like biocides).

Once the emission scenario identified and the corresponding emissions evaluated, the leaching data can be included in the LCI. The key point to be determined is the pollutant emission dynamics from the construction, i.e. its concentration in the leachate in function of time over the product life spread. As discussed in section chapter 1 §3, it is important to include relevant leaching data in the inventory, i.e. data characterising the leaching behaviour of the product over the whole RSL.

8.3 Impact assessment (LCIA)

The third phase in an LCA approach, impact assessment, aims at aggregating and interpreting the results of the inventory analysis. For example, emissions of acidifying substances are converted into one score for acidification. At this phase, LCA takes into consideration the global and local scale issues (Flemström et al., 2004) by using standardised environments for given time periods and geographic scales, applying generalised modelling tools and data bases. Therefore, the toxic/ecotoxic effects' assessment overlaps at local scale with Environmental Risk Assessment (ERA) and obviously gives different results.

In order to do a proper LCIA, relevant impact categories need to be identified and defined. The CML Handbook (Guinée et al., 2002) provides an overview of baseline impact categories and associated baseline characterisation methods, such as: depletion of abiotic resources, impact of land use, climate change, stratospheric ozonedepletion, human toxicity, ecotoxicity, acidification, eutrophication, etc.

Because pollutant substances leached from construction products get in contact either with soil or directly with water (e.g. freshwater, groundwater, sea water etc.), in this study we will focus on indicators characterising these compartments, such as human- and eco-toxicity. These impact categories are also relevant with regard to the harmful effect of the substances leached from construction products. Well known models in this field are IMPACT 2002+ (Jolliet et al., 2003), USES-LCA (Huijbregts et al., 2000), Eco-Indicator 99 (Goedkoop et al., 1998), CalTOX (McKone et al., 2001), EDIP (Hauschild and Wenzel, 1998), USEtox (Rosenbaum et al., 2008). These models attempt to estimate the damages to ecosystems of a defined chemical in a defined amount. Such models are built up of:

- the fate model (for estimating the pathway of the chemical through the environment);
- the exposure model (for estimating the exposure of target organisms to the chemical) and
- the effect model (for estimating the dose-response characteristics).

Traditionally, the characterisation is calculated with Equation 2.1

$$IR_c = \sum_s m_s \times CF_{c,s} \tag{2.1}$$

where IR_c is the indicator result for impact category c, $CF_{c,s}$ the characterisation factor that connects intervention s with impact category c, and m_s the size of intervention s (i.e. the mass of substance s emitted).

This equation reflects some fundamental principles of characterisation:

(i) no space-time characteristics are provided

(ii) distinction between potential and actual impacts

(iii) linearity of the effects (non-linearities contained in the dose-response curve are excluded)

(iv) mass loading term expressed in kg (while fate models require the specification of a mass flow rate expressed in kg/s).

Concerning the assessment of toxic substances, the ways the impact was calculated has evolved during the years a historical overview of the tox/ecotox approaches used in LCIA is presented by (Heijungs et al., 2004). Thus, the oldest form of life cycle impact assessment for toxic substances is to lump the mass release (Equation 2.2), all characterisation factors being equal to 1.

$$IR_c = \sum_i m_i \tag{2.2}$$

An improvement came with the so-called critical-volume approaches (Mekel and Huppes, 1990). The characterisation factors are calculated as in Equation 2.3.

$$CF_i = \frac{1}{TV_i} \tag{2.3}$$

where TV_i is the threshold value for substance i. The critical-volume method is currently used for the determination of the "emissions to water" indicator in the French EPDs (FDES - Fiches de Déclaration Environnementale et Sanitaire), which are included in the Inies database (Association HQE, 2009).

The incorporation of a fate model (pollutant spreading) and of an effect model (pollutant effect on environmental targets) marks a revolution in LCIA (Guinée and Heijungs, 1993). Characterisation factors are now obtained by multiplying a fate factor (FF) and an effect factor (EF) (Equation 2.4).

$$CF_{i,j,k} = EF_{i,j} \times FF_{i,j,k} \tag{2.4}$$

Here, $CF_{i,jk}$ denotes the characterisation factor for substance i affecting target ecosystem j, which was initially emitted to compartment k. Thus, substances released to air may deposit to soil or water where they affect terrestrial or aquatic ecosystems. More sophisticated models include the multimedia transport between compartments.

The choice of one or other method for impact calculation is a matter of current knowledge and also of compatibility with the current approach in the field of construction products and building, as will be detailed in chapter 4.

8.4 Interpretation

Finally, the interpretation of the LCIA provides an array of possibilities for investigating the solidity and consequences of the results. This phase can include uncertainty and sensitivity analyses, comparison of the results with previous results, decomposition into contributing parts etc.

For the selected case studies we evaluated the impact of leaching process and its weight in the total impact over the whole life cycle of the products. We also compared the impact due to different horizontal leaching scenarios, i.e. stagnation and run-off. The impact of leaching process was then analysed at building scale (for details see chapter 4).

9 Conclusions

In this work a methodology is proposed for assessing the environmental impacts of the construction products and buildings during the use stage. Leaching phenomena are responsible for the emission of potentially hazardous substances in the surrounding soils and water bodies. The proposed methodology is based on an in deep investigation of the leaching process, based on leaching tests at laboratory scale, modelling and simulation of leaching behaviour in natural exposure conditions.

The selected leaching tests are proposed for a horizontal approach: an equilibrium test (ANC) and a dynamic test (DSLT), both supplying a minimum of information necessary to understand the material specific leaching behaviour.

The leaching data are used for the development of mechanistic models considering the main chemical and physical processes, the aim being a realistic evaluation of the pollutant emission through the water contact.

The proposed evaluation method is in line with the general LCA methodology and is based on coupling leaching models (long time leaching behaviour) with toxicology tools. It should provide more realistic results than the current estimations (when they exist) and can feed EPDs as well as more general LCI data bases. The obtained inventory data is a total mass of pollutant emitted from a unit of construction product (FU) during its use period. This data is further used in a LCA approach as any other common LCI data, by applying characterisation factors from appropriate LCIA methods. However, the knowledge of the leaching behaviour (by experimental and modelling tools) allows in perspective a more complete and realistic evaluation. At the level of LCA, time dependent evaluations could then be possible.

Three construction products have been selected for further testing: (i) a porous cement based product, i.e. fibre-cement sheets, (ii) an organic porous product, i.e. CBA treated wood and (iii) a non porous, organic product, i.e. bitumen membranes. These products are further used in case studies for the proposed methodology, in order to assess the environmental impact of construction products, considering the leaching behaviour during the use phase of the product/building.

The following chapters present the two main steps of the proposed methodology:

- Chapter 3 studies the leaching behaviour of the three selected products. The experimental investigations (static and dynamic leaching tests) are used to develop a mechanistic model, in order to simulate the leaching behaviour of the three different materials, i.e. porous/non porous, cimentitious/organic matrix, at long term exposure under natural conditions.
- Chapter 4 describes the actual integration of leaching data with the LCA methods, i.e. an inventory enriched with data regarding the emissions to water and soil during the use phase of the product, and the eco- and human toxicity assessment applied on this inventory with adequate impact methods.

Chapter 3

Horizontal leaching assessment

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Dans ce chapitre il est présenté l'étude sur le comportement à la lixiviation de trois produits de construction. Les produits sélectionnés en fonction de la représentativité sur le marché, la typologie de la matrice et le relargage des substances dangereuses (identifiées à l'aide des essais préliminaires) sont : le bois traité CBA (matrice poreuse organique, échantillon de *Pinus sylvestris* traité avec un produit de préservation à base de cuivre bore - azole - amine), la plaque fibrociment (matrice poreuses minérale non métallique, produit à matrice cimentaire avec des fibres cellulosiques) et la membrane bitumineuse (matrice non poreuse organique, matrice bitumineuse avec une couche supérieure de gravier).

La méthodologie présentée dans le chapitre précédent a été appliquée. Des essais de lixiviation à l'échelle laboratoire ont été menés en vue de caractériser les principaux mécanismes chimiques et le transport de masse responsable du relargage des substances. Les essais de lixiviation (nommés ANC et DSLT, présentés dans le chapitre 2) sont des outils pertinents pour une "approche horizontale" (i.e. l'évaluation du comportement à la lixiviation des divers produits de construction avec les mêmes méthodes) conformément aux travaux du Comité Européen de Normalisation CEN / TC 351 (Produits de construction - évaluation de l'émission des substances dangereuses réglementées. WG1 relargage dans le sol et l'eau). Les résultats de lixiviation sont ensuite utilisés pour la construction du modèle couplé chimie-transport capable de représenter le comportement à la lixiviation à l'échelle laboratoire, et capable d'être adapté aux conditions correspondant à une échelle plus large.

La première section présente une étude approfondie du bois traité CBA. Afin de mieux identifier les mécanismes de relargage, des échantillons de bois non traité (avant traitement) ont été également étudiés. L'originalité de notre travail consiste dans l'élaboration d'une approche mécanistique et d'un modèle numérique basé sur les processus chimiques et physiques, ce qui est une nouveauté dans le domaine du bois traité.

Les principales conclusions de l'étude expérimentale peuvent être résumées comme suit :

- Les éléments endogènes inorganiques tels que Ca et K et des ions comme le sulfate et le phosphate sont émis à partir du bois traité et non traité en contact avec l'eau à différents pH. Ils sont liés à la phase solide ou solubilisés dans l'eau des pores et sont les principaux électrolytes régissant la force ionique.
- Des composés organiques sont libérés du bois non traité. La quantité du carbone organique total (COT) relargué ainsi que les substances contenant des

groupes carboxyle et phénolique augmentent avec le pH. Ce constat s'explique principalement par des réactions d'hydrolyse sur les polymères du bois.

- La composition chimique du bois change pendant le stockage des échantillons après le traitement (pour la fixation des biocides). Cela affecte non seulement le relargage des substances pendant le test ANC, mais y compris la disponibilité de sites de liaison pour les biocides dans la phase solide.
- Dans le cas de produits contenant du Cu et des amines, le traitement ne consiste pas seulement en réactions de liaison des complexes Cu-amines sur la matrice du bois, mais aussi en modifications des composants du bois en raison des réactions directes avec les amines. Un certain nombre de composés contenant de l'azote sont libérés du bois traité CBA, probablement due à un excès d'amines et aux réactions des amines avec les éléments endogènes au bois.
- Les émissions de Cu sont relativement élevées par rapport à son contenu initial (i.e. 30%). Cu est relié aux sites carboxyliques et phénoliques et forme des complexes solubles avec les composants extractibles. Le faible relarguage au pH neutre (i.e. entre 7 et 8) s'explique par la distribution de Cu entre les composants solides et les extractibles, ainsi que par les propriétés acide/base des sites de liaison.
- Le bore est relargué à un niveau élevé (i.e. 30% du contenu total). Même si certains phénomènes de fixation sont possibles, leur efficacité est faible (démontré par la non-dépendance du pH).
- Le tébuconazole est relargué en moindre pourcentage par rapport à son contenu initial dans les échantillons de bois (i.e. 17%). Sa fixation sur la structure du bois massif semble être influencée par le pH, ce qui suggère des liaisons hydrogène avec les groupes OH sur le bois.

Le modèle couplé chimie-transport considère les biocides et la chimie du bois en fonction des connaissances actuelles (données thermodynamiques) et de l'étude expérimentale. Les résultats obtenus conduisent aux conclusions suivantes concernant le comportement à la lixiviation des biocides :

- Le cuivre est lié principalement par des mécanismes de complexation sur les groupes phénoliques et carboxyliques de la lignine et de l'hémicellulose, même en présence de la monoéthanolamine. Son relargage dépend fortement la nature chimique des produits d'extraction et de la valeur du pH. Le rôle de la monoethanolamine est de fournir un pH d'environ 7.5 de l'eau des pores, quand la solubilité du cuivre est la plus faible. Cependant, lors des essais dynamiques, le pH dans l'eau des pores tend vers le pH natif et la fixation de cuivre devient plus faible.

- Le bore interagit faiblement avec la cellulose et présente un comportement diffusionnel proche de celui d'un traceur.
- Le tébuconazole est fixé par des liaisons hydrogène aux polymères de bois et son relargage augmente avec la valeur du pH.

La section 2 présente l'étude expérimentale et la modélisation du comportement à la lixiviation de la plaque fibrociment. à l'échelle du laboratoire, les essais de lixiviation ont permis d'identifier les principaux mécanismes chimiques et de transport. Ces données ont ensuite été utilisées pour le développement d'un modèle de transport de produits chimiques. Toutefois, le dispositif expérimental n'était pas suffisant pour élucider les mécanismes de fixation/mobilisation des composés organiques spécifiques (biocides ou autres composés dangereux). La plaque fibrociment présente globalement un comportement à la lixiviation de type ciment, en ce qui concerne les espèces minérales. Des espèces potentiellement dangereuses sont relarguées en quantités importantes si on les compare à la teneur totale, même si elles sont présentes en trace. La simulation d'un scénario vrai grandeur permet d'évaluer les effets des émissions cumulées sur de longues périodes, puis l'intégration des données de lixiviation avec des méthodes d'évaluation environnementale. Cette étude est la première consacrée à des produits de construction à base de fibres-ciment.

Dans la section 3, le comportement à la lixiviation d'une membrane bitumineuse a été étudié partiellement. L'étude a été limitée à des travaux expérimentaux. A cause de la structure non poreuse du bitume, nous n'avons pas été en mesure d'obtenir des échantillons adéquats pour l'essai statique de dépendance du pH. Cependant, le test ANC réalisé sur une petite quantité de matériau broyé a montré un comportement indépendant de pH pour toutes les espèces organiques analysées. L'équilibre a été atteint après 7 jours (versus 2 jours pour les produits poreux), ce qui s'explique par les processus de diffusion lente qui ont lieu à partir du cœur vers l'extérieur des échantillons, étant donné que le produit est non poreux. Comme supposé, la membrane bitumineuse relargue des faibles quantités d'espèces inorganiques, e.g. de Al, Fe, Mg, Ca, Na. La source primaire peut être le gravier dans la couche supérieure, utilisée pour offrir une protection contre les UV. En ce qui concerne les substances organiques, même si les essais préliminaire et l'ANC ont permis d'identifier certains biocides organiques (MCPP, fenuron et le naphtalène), ces espèces n'ont pas été trouvées dans les éluats de DSLT. Cela pourrait s'expliquer par le ratio liquide-solide plus élevé (de 2,5 à 5 fois plus élevé que dans le test ANC). En effet, même pendant les essais préliminaires les concentrations étaient proches de la limite de détection. Par conséquent, la dilution les rend indétectable. D'autre part, la concentration du carbone organique dissous (COD) a été mesurée dans tous les éluats DSLT et des quantités légèrement plus élevées ont été observées lorsque le rapport éluat/produit était plus élevé pendant les deux DSLT, soit $10\,\mathrm{cm}^3/\mathrm{cm}^2$ en comparaison avec le $5\,\mathrm{cm}^3/\mathrm{cm}^2$. Plusieurs conclusions peuvent être soulignées :

- Pour ce type de produit à matrice non poreuse et hydrophobe, comme le bitume, le paramètre le plus important est la surface de contact avec l'eau. En conséquence, le ratio liquide/surface est un paramètre important ;
- Idéalement, un protocole d'essai spécifique à ce type de matrice doit être élaboré, afin de permettre l'identification des principaux mécanismes de relargage ;
- Ce travail démontre qu'une procédure de lixiviation horizontale est difficilement applicable pour tout produit de construction et que pour certains produits les essais de lixiviation doivent être adaptés en fonction du matériau, de manière à fournir des informations pertinentes.

Dans la dernière section de ce chapitre une question opérationnelle à court terme concernant les données de lixiviation des produits de construction est présentée. Une base de données appelée LixiBat a été développée, pour intégrer différents types de données caractérisant le comportement à la lixiviation des produits de construction, i.e. données expérimentales (à partir des essais à l'échelle laboratoire, pilote et vraie grandeur) et des données de simulation (à partir de la modélisation numérique). LixiBat peut être utilisé pour : (i) valider de nouveaux résultats expérimentaux ou de simulation, ou (ii) pour intégrer de données sur le comportement à la lixiviation de produits de construction dans les outils d'évaluation environnementale.

1 Introduction

In this chapter the leaching behaviour of three construction products is studied extensively. The chosen products are: CBA treated wood (organic porous), fibre-cement sheets (mineral, non-metallic porous) and bitumen membranes (organic non-porous).

The methodology presented in the previous chapter was applied. At laboratory scale, leaching tests were used in view of the characterization of main chemical mechanisms and mass transport responsible for the pollutant release. These leaching tests (named ANC and DSLT, presented in chapter 2) are potentially relevant tools for a "horizontal approach" (i.e. the assessment of the leaching behaviour of various construction products with the same methods) as those envisioned by the European Commission – CEN/TC 351 (CEN, 2012b) . The leaching results were then used for the building of coupled chemical-transport model able to represent the leaching behaviour at laboratory scale, and capable to adapt for up-scaled field conditions.

The first two sections present an extensive study of CBA treated wood, which is the main material investigated in this work. The originality of our work consists in developing a mechanistic approach and a numerical model based on chemical and physical processes, which is a novelty in the field of treated wood.

Sections 3 and 4 present the experimental and modelling study on fibre-cement and bitumen membrane materials.

In the last section of this chapter, a practical issue concerning leaching data for construction products is presented. A database called LixiBat has been developed in the current study, for various types of data characterising the leaching behaviour of construction products, i.e. experimental data (from lab, pilot and field scale tests) and simulation data (from numerical modelling). LixiBat can be used for: (i) validating new experimental or simulation results, or (ii) for integrating data on the leaching behaviour of building products in the environmental assessment tools.

2 Organic porous product: CBA-amine (Copper-Boron-Azole) treated wood

2.1 A mechanistic interpretation

This section has been published in the *Science of the Total Environment Journal*, with the following reference (cited in this manuscript as (Lupsea et al., 2013a)):

Lupsea, M., Mathies, H., Schoknecht, U., Tiruta-Barna, L., Schiopu, N., Biocide leaching from CBA treated wood - a mechanistic interpretation, Science of the Total Environment, 444 (2013), 522-530.

2.1.1 Introduction

Pollutant release from construction products in contact with water is currently a research subject receiving attention from the European regulation and standardisation authorities (CEN, 2005). Being an economical, durable and aesthetically pleasing building material, treated wood is a frequent choice for construction projects. However, we need to ensure that biocides used for the treatment do not pose a threat to people or environment. Previous studies generally report high leaching rates from treated wood, depending on the type of preservative, exposure conditions and wood specimen (Lebow, 1996; Schoknecht et al., 2005; Ahn et al., 2010; Schiopu and Tiruta-Barna, 2012).

Understanding the leaching process is crucial for the management of wood products over their whole life cycle, especially during their use stage and end of life (wastes), but also for developing new treatment methods and products. So far, leaching from wood has been investigated for inorganic and a few selected organic preservatives, and factors that influence their release have already been summarised by several authors (Schoknecht et al., 2005). However, most of these studies only report on results of experimental leaching tests, but do not investigate the chemical mechanisms involved.

As discussed in a recent paper (Tiruta-Barna and Schiopu, 2011), a leaching process implies complex chemical and physical phenomena: biocide interactions with the solid wood structure (fixation), distribution between the solid and liquid phase (mobilisation), and transport processes (mainly diffusion inside the wood porous system). The fixation mechanism of copper on the wood structure has been intensively studied (Jiang, 2000; Lee, 2011; Mettlemary, 2011). This is not the case for other compounds, especially organic biocides, for which the fixation mechanisms have not been elucidated so far. Irrespective of the biocides, very few reaction constants exist in literature allowing a quantitative estimation of the fixation level. Also the mobilisation mechanisms are hardly investigated. What is the role of the wood/water chemistry in terms of pH and extractives on the biocide leaching? No studies have been reported on the composition of the organic matrix in eluates, and no leaching mechanism that includes the role of these extractives has been proposed so far.

The intention of this study was to investigate the leaching behaviour of treated wood and to propose leaching mechanisms for inorganic and organic compounds. The product studied here is sapwood of *Pinus sylvestris* treated with copper-boron-azole (further called CBA), containing tebuconazole as organic biocide, and monoethanolamine as major constituent. Copper is an essential micronutrient for most living cells, but in larger doses it acts as an algicide, bactericide, fungicide, insecticide, and moldicide (Freeman and McIntyre, 2008); boron is used as insecticide and fungicide (Lebow, 1996); tebuconazole is a fungicide that is added to copper containing wood preservatives to act against copper-tolerant fungi (Grundlinger and Exner, 1990). These properties are hazardous when the biocides are controlees released in surrounding environment.

Experiments based on the leaching procedure of the European standard XP CEN/TS 14429 ("pH dependence leaching test" or "Acid Neutralisation Capacity test" - further called "ANC") (CEN, 2006) were performed to determine the acid/base properties of samples from untreated and treated wood and investigate the pH influence on the release of elements, ions and organic compounds. The ANC test is in line with the Construction Products Regulation (EC, 2011). In order to comply with the Basic Requirement BR 3 "Hygiene, health and the environment" of the CPR, the European Commission mandated CEN/TC 351 to develop methods for the assessment of the leaching behaviour of various construction products (based on wood, concrete, etc.) with the same methods, i.e. horizontal approach (CEN, 2012a). Other leaching procedures were developed specifically for wood products (e.g. CEN/TS 15119 (CEN, 2007)). Nevertheless, these specific methods are suitable for some regulatory purposes but not for chemical modelling. The method applied in our research was chosen because it is more suitable for a mechanistic model development (equilibrium conditions are reached at different pH values and therefore chemical mechanisms can be identified).

2.1.2 Properties of biocides in treated wood – a review

Wood is a heterogeneous, hygroscopic, cellular and anisotropic material. It is composed of cells, and the cell walls are composed of micro-fibrils of cellulose, hemicellulose, lignin, other minor polysaccharides and a small fraction of extractives (Rowell, 2005). Treatment of wood causes a series of reactions between wood components and constituents of the wood preservative, e.g. complexation, ion exchange, adsorption, hydrolysis.

2.1.2.1 Fixation of biocides in wood

Complexes of copper, monoethanolamine and wood Copper fixation in wood has been intensively investigated and several mechanisms have been suggested, depending on the biocide formulation. It can be characterised as chemisorption accompanied by physical precipitation.

Cu−Mea complex. In the treatment solution Mea coordinates with Cu to form monovalent, divalent and neutral Cu−Mea complexes with different metal-ligand stoichiometry (Jiang, 2000; Zhang and Kamdem, 2000; Lee, 2011; Mettlemary, 2011) (see selected complexes in Figure B.1 in the appendix).

Cu−Wood complexes. Binding sites for Cu^{2+} are weak dissociating groups mainly situated on lignin and hemicellulose, i.e. carboxyl and phenolic hydroxyl groups, which dissociate according to the ambient pH. Complexation of Cu on wooden materials was studied by several authors (Ravat et al., 2000; Guo et al., 2008) and complexation constants have been calculated. The surface complexation model for Cu−Wood is based on stoichiometric reactions between ligand site and metal ion (ligand/Cu^{2+} $= 1/1$).

Cu−Mea−Wood complexes. Several fixation mechanisms of Cu−Mea complexes have been proposed depending on pH conditions (see Equations 3.1 to 3.6–binding sites of wood were symbolised by $-COO^{-}$ and $-Ph-O^{-}$ and Mea_{-H} refers to deprotonated Mea $H_2N-CH_2-CH_2-O^{-}$). Equations 3.1 and 3.2 (see also Figure B.2 in the appendix) suggest ligand exchange reactions that dominate at pH above 10, i.e. soluble neutral Cu−Mea complexes exchange one of the deprotonated ligands (Mea_{-H}) with wood (Thomason and Pasek, 1997; Craciun et al., 1997). Equations 3.3–3.6 present cation exchange reactions that occur at pH below 10. Monovalent Cu−Mea complexes bind to one wood site, while divalent Cu−Mea complexes require two sites for the bonding reaction (Lee, 2011) Complexes between Cu and Mea are not formed at pH below 5 (Lee and Cooper, 2010).

Ligand exchange reaction of neutral Cu$-$Mea complexes, dominant at pH > 10:

$$-\mathrm{COO}^- + [\mathrm{Cu(Mea{-}H)(Mea_{-H})}]^0 \longrightarrow [-\mathrm{COO}{-}(\mathrm{CuMea_{-H}})^+]^0 + [\mathrm{Mea_{-H}}]^- \tag{3.1}$$

$$-\mathrm{Ph}{-}\mathrm{O}^- + [\mathrm{Cu(Mea{-}H)(Mea_{-H})}]^0 \longrightarrow [-\mathrm{Ph}{-}\mathrm{O}{-}(\mathrm{CuMea_{-H}})^+]^0 + [\mathrm{Mea_{-H}}]^- \tag{3.2}$$

Complexation of charged Cu$-$Mea complexes; possible at pH < 10:

$$-\mathrm{COO}^- + [\mathrm{Cu(Mea)(Mea_{-H})}]^+ \longrightarrow [-\mathrm{COO}{-}(\mathrm{CuMeaMea_{-H}})^+]_0 \tag{3.3}$$

$$-\mathrm{Ph}{-}\mathrm{O}^- + [\mathrm{Cu(Mea)(Mea_{-H})}]^+ \longrightarrow [-\mathrm{Ph}{-}\mathrm{O}{-}(\mathrm{CuMeaMea_{-H}})^+]_0 \tag{3.4}$$

$$2\,({}^-\mathrm{COO}{-}) + [\mathrm{Cu(Mea)(Mea)}]^{2+} \longrightarrow [(-\mathrm{COO}{-})_2(\mathrm{CuMea_2})^{2+}]_0 \tag{3.5}$$

$$2\,({}^-\mathrm{Ph}{-}\mathrm{O}{-}) + [\mathrm{Cu(Mea)(Mea)}]^{2+} \longrightarrow [(-\mathrm{Ph}{-}\mathrm{O}{-})_2(\mathrm{CuMea_2})^{2+}]_0 \tag{3.6}$$

The quantity of complexing sites of wood was determined in different studies and the values were in the same order of magnitude: 0.1 mmol/g wood (Balaban and Uçar, 2001), 0.75 mmol/g of lignin (Guo et al., 2008) and 0.57 mmol/g straw lignin (Merdy et al., 2002), i.e. 0.1 mmol/g to 0.2 mmol/g of wood if the data are related to wood. Regarding the structure of the formed complex, Lee (2011) found that at pH near 9.5, Cu was adsorbed in wood up to the CEC level by the reaction of [CuMea$_{\text{-H}}$]$^+$ complexes.

Moreover, fixation of Cu in wood can be supported by the addition of carboxylic acids like 2-ethylhexanoic acid. Two effects are suggested in literature: (i) 2-etylhexanoic acid forms complexes with either wood components or Mea that influence Cu fixation; (ii) 2-etylhexanoic acid decreases the pH of the treatment solution and thus, favours the complexation of Cu on wood in more stable forms (Humar et al., 2005).

Mea-Wood complexes. Not only Cu$-$Mea complexes react with active groups on wood, but also the amine itself. Humar et al. (2003) found by FTIR (Fourier Transformed InfraRed spectroscopy) that Mea can react with $-$COOH groups of hemicellulose and C_1, C_3, and C_4 positions of benzene rings in lignin. At low and moderate pH values, ion exchange reaction is considered the most likely bonding mechanism between MeaH$^+$(HO$-$CH$_2-$CH$_2-$NH$_3^+$) ions and dissociated groups of wood. A correlation of the ion exchange reaction of Mea with the CEC of wood was observed. As the pH increases above the pKa value of protonated Mea (pKa $= 9.5$) the concentration of neutral Mea increases. Under these conditions the ion exchange reaction with acidic functional groups of wood decreases, whereas neutral Mea can interact with lignin through the formation of hydrogen bonds between its hydroxyl group and hydroxyl and carbonyl groups present in the lignin (Spencer et al., 1985; Rodrigues et al., 2001). However, sorption of Cu is dominant and is not competing with Mea (Lee and Cooper, 2010).

Boron in wood Boron is introduced in wood as boric acid or borate. It is considered to be only weakly bound to components of wood. Very few studies exist on eventual bonding mechanisms. Obanda et al. (2008) affirm that B forms organic complexes in which it is linked to active sites in wood components by O-bridges. A reaction between the negatively charged hydroxocomplex $B(OH)_4^-$ and hydroxyl groups of polysaccharides with formation of a bidentate complex has been proposed (Ramos et al., 2006). If proteins are present in the treatment solution, B retention on cellulose but not on lignin is enhanced due to a triple interaction that has not been fully elucidated resulting in boron hydroxycomplex-protein-cellulose (Ratajczak and Mazela, 2007).

Tebuconazole in wood Binding of tebuconazole to wood components has been very little investigated. However, several authors studied the complexation between various azoles and transition metals, including Cu and tebuconazole (Zhang and Wu, 2005; Dytrtová et al., 2011). A Cu : tebuconazole : acetate complex with a ratio of 1 : 2 : 2 has been obtained in vitro (Evans and Schmalzl, 2007, 2008). In such a structure, the Cu(II) atom is coordinated to the triazole groups of two tebuconazole ligands and two acetate ligands.

To our knowledge, the formation of complexes of tebuconazole and Mea has not been described yet. However, it has to be expected from the stability constants of Cu−Mea complexes (Mettlemary, 2011) that Mea binds Cu and other metals stronger than tebuconazole. It seems to be likely that wood treated with Mea-based formulations predominantly contains free tebuconazole (Evans and Schmalzl, 2008).

2.1.2.2 Wood in contact with water When wood comes in contact with water small molecules are solubilized. The so called "extractives" belong to several classes: fats, fatty acids, fatty alcohols, phenols, terpenes, polyphenols, tannins, lignans, steroids, resin acids, waxes (Sjöström, 1993). Acetic acid–originating from acetylated hydroxyl groups of cellulose (Arni et al., 1965)–and formic acid are degradation products of wood polymers. These carboxylic acids are mainly emitted to the air (Balaban and Uçar, 2003), but are also expected to occur in eluates of wood. In alkaline solutions, a series of hydrolysis reactions take place on wood polymers resulting in the elimination of small molecules related to lignin monomers (Evstigneev, 2010) or to hemicellulose (Xiao et al., 2001).

The role of extractives on the biocide leaching was neglected so far, while it is evidence that these molecules can interfere with the solid matrix and with biocides by at least two main properties: acid/base reactions (pH regulation) and binding by different mechanisms (complexation, precipitation). Interactions with Cu have been investigated for several types of native organic substances. Interactions of Cu with polyflavonoids (Teixeira et al., 2005), vanillin (Ruddick et al., 2001) and other natural molecules containing acidic groups were described (Teresa et al., 1997). Mixed complexes of Cu with different ligands can also be formed, for example with both Mea and an extractive compound. Studying the reactions of taxifolin and chrysin with the Cu−Mea complex, Jiang (2000) found in both cases a green extensive precipitation, suggesting that hydroxyl and ketone groups of the extractives are the major sites for Cu chelation–one mole of Cu is coordinated to two moles of amine in the Cu−Mea−taxifolin or Cu−Mea−chrysin complexes.

No stable complexes with extractives have been suggested for B and tebuconazole.

2.1.3 Materials and methods

2.1.3.1 Wood samples and treatment Two types of *Pinus sylvestris* samples were used in the leaching tests: wood that was cut off 9 years ago (later called "conditioned") and shavings collected from different trees in carpentry ("fresh"). A description of the samples is given in Table 3.1.

Table 3.1: Codification of samples of untreated and treated wood.

Sample code	Description	Treatment[a]
UF	Up to 1 year old shavings[b]	Without
UA	Cut off 9 years ago[c]	Without
BF	Up to 1 year old shavings[b]	16 kg/m^3
BA	Cut off 9 years ago[c]	16 kg/m^3

[a] Amine based preservative CBA
[b] Shavings from *Pinus sylvestris* collected at BAM's carpentry
[c] Trees (*Pinus sylvestris*) were cut off 9 years ago and conditioned at 20 ± 2 °C and 65 ± 5% relative humidity (cf. EN 113)

A wood preservative consisting of copper carbonate (22.5%, i.e. 12.9% Cu), boric acid (4.9%, i.e. 0.65% B) and tebuconazole (0.53%) was used to treat both types of wood ("conditioned" and "fresh"). In addition, the preservative contained a mixture of amines with Mea as the main component and carboxylic acids. In the following, the preservative will be called CBA. BA-samples were obtained by treating monolithic (15 mm × 25 mm × 50 mm) test specimens (UA) by vacuum pressure impregnation with a 2.1% solution of the concentrated preservative in water (described in (EN 113, 1996)). The final concentration in wood samples (assuming that the treatment solution has been homogenously adsorbed) was 16 kg/m^3 CBA, i.e. 2 kg/m^3 copper, 0.1 kg/m^3 boron and 0.085 kg/m^3 tebuconazole. After the treatment, the test specimens were kept for 4 weeks at 20 ± 2°C and 65 ± 5% relative humidity to allow evaporation of water and reactions of the preservative with wood (fixation). BF-samples were obtained by treating shavings (UF) with a 2.1% solution of CBA in a mixture of acetone and water (16 kg/m^3 CBA). After immersion in the treatment solution, the shavings were conditioned for two weeks at room conditions, until they reached a constant mass.

2.1.3.2 Leaching tests The Acid Neutralisation Capacity (ANC) test was based on the method described in XP CEN/TS 14429 (CEN, 2006). Crushed material (≤ 1 mm) was brought in contact with NaOH and HCl solutions of different concentrations, forcing the pH of the eluate to vary between 4 and 12. In these tests we replaced HNO_3 solutions, as advised in the standard, with HCl solutions, because of the strong oxidation character of HNO_3. The liquid to solid ratio was 10 L/kg and the solutions were stirred for 48 hours, until the final pH of the eluate was stabilised. Filtered eluates (595 1/2S& S folded filter) were prepared for different analytical methods in order to identify or quantify cations, anions and organic substances.

2.1.3.3 Analytical methods Substances of interest were chosen in accordance with former studies and after an inorganic and organic screening of the eluates. An analytical approach was developed in order to identify substances released from CBA treated wood. Therefore we divided the eluates from ANC tests into two parts:

1. Eluate samples were directly used to determine TOC (total organic carbon), formic and acetic acid, inorganic species (Cu, K, Ca, Cr, Zn, B, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}), total phenols and acid number;

2. Eluate samples that were lyophilised to quantify tebuconazole, carbon and nitrogen, and identify Mea, functional groups and a series of organic extractives.

An overview on the methods used to analyse eluates from ANC tests is presented in Figure 3.1. The limits of quantification for all quantitative determinations are presented in Table B.1 in the appendix.

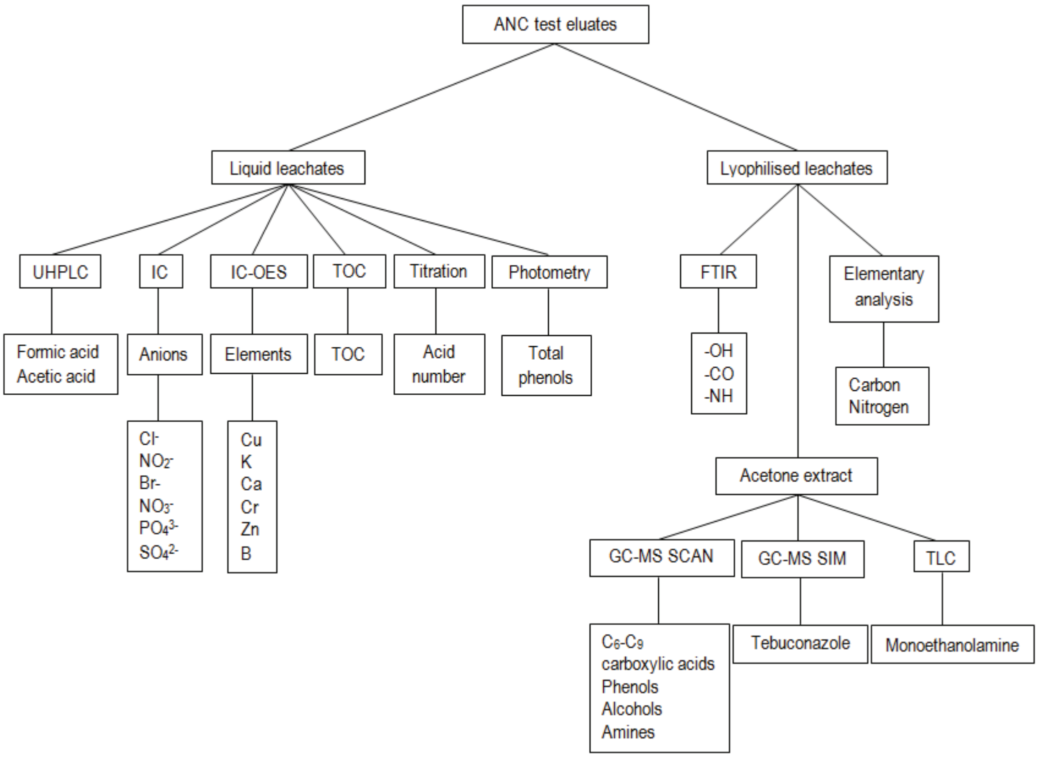

Figure 3.1: Strategy for the analysis of eluates from ANC tests and target parameters.

Analysis of liquid eluates TOC was measured cf. DIN EN ISO 1484 standard, elemental analysis was performed by ICP-OES (Optical Emission Spectrometry) cf. DIN EN ISO 11885 standard and anions were quantified by IC (Ion Chromatography) cf. DIN EN ISO 10304-4 standard.

Formic and acetic acid were identified and quantified in eluates by UHPLC (Ultra High Performance Liquid Chromatography).

Total concentration of carboxyl groups was estimated by titration with a 0.1 M NaOH solution in presence of phenolphthalein. Alkaline eluates were first neutralised with 0.1 M HCl in order to protonate all carboxyl groups. Since concentrations of inorganic acids were negligible compared to the total amount of acid groups, the acid groups determined with this test were considered as carboxyl groups.

A photometric method was used to quantify the total content of phenols, namely the modified Prussian Blue Assay for Total Phenols (Hagerman, 2002). In presence of $FeCl_3$ and $K_3Fe(CN)_6$, the colour of the ANC eluates turned to different shades of green to blue. The total concentration of phenolic groups was calculated from the measured absorbance at 700 nm. The method was calibrated with pyrogallol.

Analyse of lyophilised eluates After filtration, ANC eluates with alkaline pH were first neutralised with a 0.1 M HCl solution. Then the acid, neutral and neutralised (former alkaline) samples were lyophilised to remove water in order to be able to identify functional organic groups (−COOH, −OH, R−N, −NO, etc.) in the solid samples by FTIR. Parts of the lyophilised samples were extracted by acetone and analysed by GC-MS (Gas Chromatography coupled with Mass Spectrometry) and TLC (Thin Layer Chromatography). An elemental analysis for carbon and nitrogen was also performed using a Macro-Elementary Analyser.

2.1.4 Results

ANC tests deliver two types of results: (i) amount of H^+ moles added per L solution, as a function of final pH of the eluate and (ii) variation with pH of the concentration of target substances in the eluates. Such curves were obtained for both untreated and treated wood, "conditioned" and "fresh", as seen in Figure 3.2. Concentrations obtained in mg/L were converted to mol/L.

The graph at top-left of Figure 3.2 is a titration-like curve; it represents the pH of the system as a function of the acid or base added. The added acid is expressed as mol H^+/L of eluate, while the base added was represented as negative mol H^+/L. The point of zero acid and base addition is called the "native pH" of the wood eluates. The native pH was between 4 and 5 for untreated wood, and between 7 and 8 for the treated wood.

Copper, boron and tebuconazole were only found in eluates from treated wood. The concentration of Cu and B in eluates from "conditioned" and "fresh" samples have similar curve shapes and values. While the B concentration was almost constant, the Cu concentrations varied up to one order of magnitude over the pH range, with a minimum at neutral pH. At native pH (7.5) the emissions were smaller than in acid or alkaline eluates. Tebuconazole concentrations in eluates increased

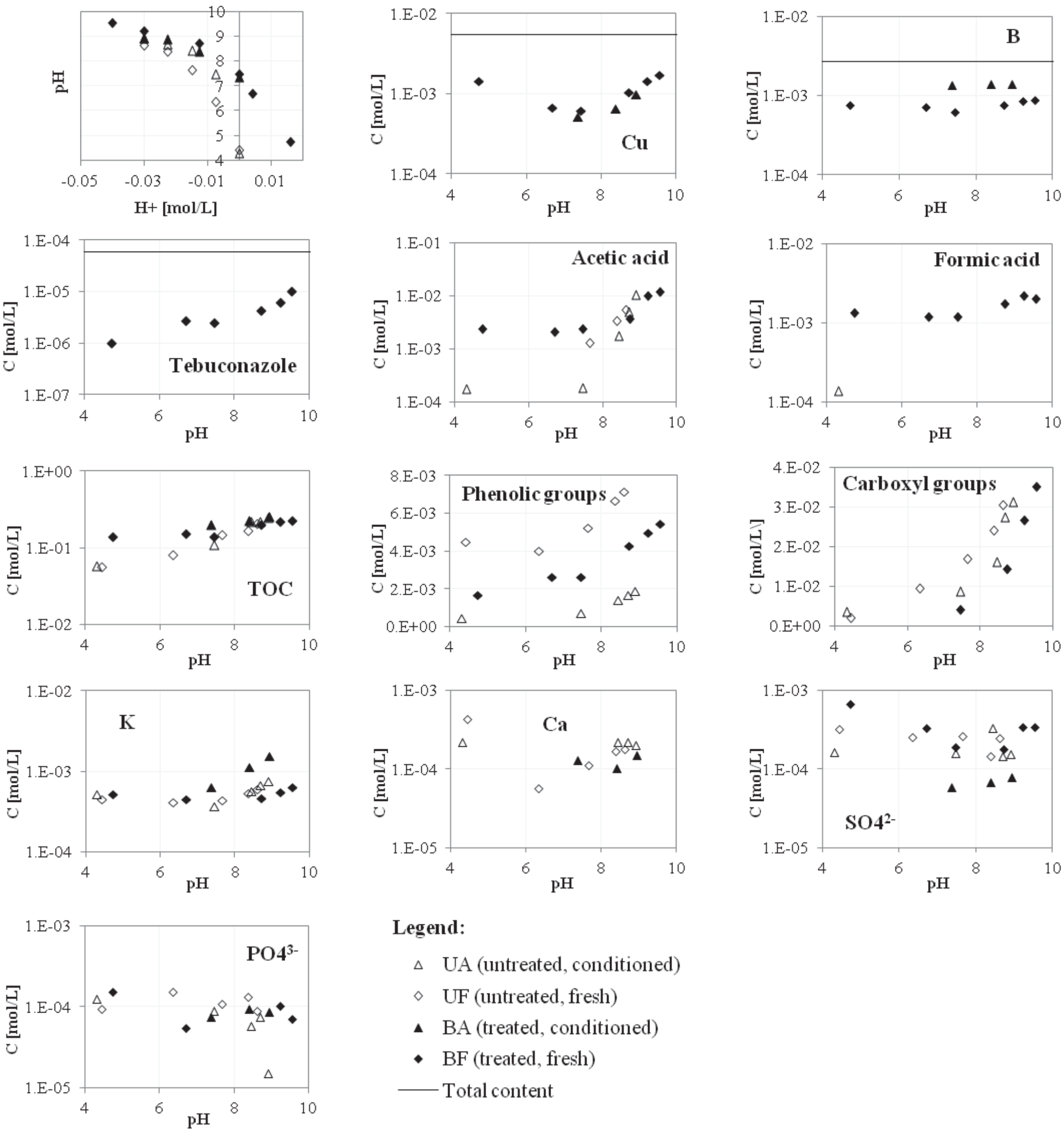

Figure 3.2: pH of eluates depending on acid or base addition and pH dependency of leaching of different substances in ANC tests.

with pH. About 30% of the initial content of Cu and B, and up to 17% of the initial content of tebuconazole were eluted under the ANC test conditions.

Concentrations of total organic carbon, carboxylic acids and phenols increased with pH. The concentrations were higher in eluates from untreated "fresh" compared to "conditioned" wood. All eluates contained less phenolic than carboxyl groups. The release of acetic acid from untreated samples increased with pH, almost 1000 times higher at alkaline pH compared to acid conditions. Formic acid was mainly detected in eluates from treated wood. Its concentrations in eluates were only slightly higher under alkaline conditions than under native and acid conditions.

The concentration of potassium was almost constant with pH. Calcium exhibited a minimum of solubilisation at neutral pH for untreated samples and was hardly detectable in part of the eluates from treated wood (and therefore not presented for BF-samples). Sulphate and phosphate were also present at relatively low concentrations that were similar for the different pH conditions.

The concentrations of the other metals (Cr, Zn) and anions (Cl^-, Br^-, NO_2^-, NO_3^-) were very low and the data were not further considered.

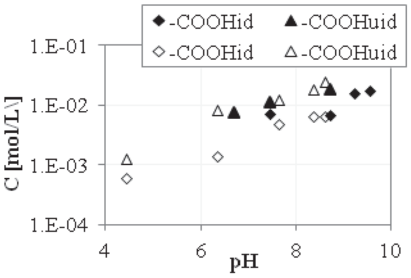

Figure 3.3: Concentration of carboxyl groups from carboxylic acids identified and quantified by UHPLC "$-COOH_{id}$" compared to the concentration of unidentified carboxyl groups "$-COOH_{uid}$" in eluates from treated (BF, filled icons) and untreated (UF, empty icons) samples of "fresh" wood.

Figure 3.3 illustrates the pH dependent elution of formic and acetic acid (calculated sum of $-COOH$ groups) compared to the amount of unidentified carboxyl groups (difference between the total amount of $-COOH$ groups determined by titration and the sum of $-COOH$ groups corresponding to formic and acetic acid). Carboxyl groups from formic and acetic acid represent only a fraction of the total amount of carboxyl groups in eluates.

Carbon and nitrogen were quantified in lyophilised eluates of untreated and treated samples. Figure 3.4 summarises data for the pH dependency of the global parameters TOC in liquid eluates, and elemental carbon and nitrogen in lyophilised eluates. At neutral pH the concentration of TOC in eluates is almost equal to the concentration of carbon from the solid residues of eluates. Slightly lower carbon concentrations compared to TOC concentrations in some lyophilised samples with acid and alkaline pH can be explained by the volatilisation of small molecules (such as acetic acid) during the lyophilisation process. However, for both measurements the concentration of organic carbon increases from acid to alkaline conditions. TOC concentrations were higher in eluates from treated than from untreated wood at pH between 4 and 7, but this difference vanishes with increasing pH. The nitrogen content in eluates from treated wood was up to 15 times higher than in eluates from the untreated samples.

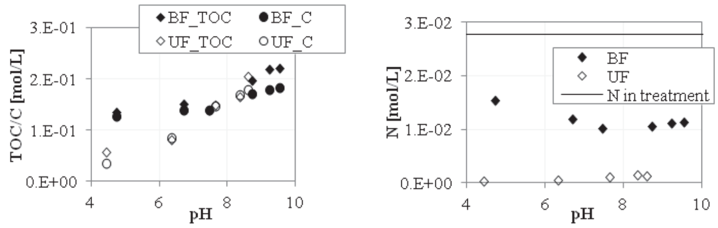

Figure 3.4: pH of eluates depending on acid or base addition and pH dependency of leaching of different substances in ANC tests.

Data from the element analysis (C, N) for the lyophilised eluates, titration of acid groups and photometric assay of phenolic groups in eluates are presented in Table 3.2 as empiric stoichiometric formulae for the organic matter released from the different wood samples. At equivalent carbon content, untreated wood released higher amounts of phenolic groups under acidic compared to alkaline conditions, whereas the release of nitrogen and carboxyl groups did not show clear pH dependency. Treated wood releases about ten times more nitrogen than untreated wood, but less carboxyl and phenolic groups. The amount of released nitrogen decreased, whereas the amount of phenolic and carboxyl groups increased with the pH of eluates. C_{uid} represents TOC in eluates minus carbon from tebuconazole and the quantified carboxylic acids (formic and acetic acid). $-\text{COOH}_{\text{uid}}$ represents carboxyl groups determined by titration minus carboxyl groups from quantified carboxylic acids (formic and acetic acid). For example, in the case of treated wood, at alkaline pH (8.72), the empiric formula for the organic matrix of the eluate is $\text{C} : \text{N} : (-\text{OH}) : (-\text{COOH}) = 100\ : 5 \cdot 91\ : 2 \cdot 36\ : 4 \cdot 26\,.$

Table 3.2: Empiric stoichiometric formula for the organic matter found in lyophilised eluates from untreated and treated wood at different pH values.

pH	C_{uid}	N	$-OH$	$-COOH_{uid}$
UF untreated "fresh" wood				
4.43	100	0.84	8.40	2.52
6.34	100	0.54	5.41	10.81
7.65	100	0.80	4.00	9.20
8.37	100	0.90	4.50	12.16
8.61	100	0.74	3.70	12.59
BF treated "fresh" wood				
4.73	100	13.29	1.45	–
6.70	100	9.00	2.00	–
7.46	100	8.40	2.20	0.00
8.72	100	5.91	2.36	4.26
9.22	100	6.06	2.75	6.06
9.54	100	6.25	2.98	9.82

The presence of Mea in eluates from treated wood was confirmed by TLC. FTIR spectra were measured for lyophilised eluates that were obtained from ANC experiments at native pH. Spectra for untreated and treated "fresh" wood are shown in Figure 3.5 as an example. Usually, samples from untreated wood exhibit higher absorption bands at wavelength of about $3300\,cm^{-1}$ ($-OH$). Differences between untreated and treated samples were mainly observed in the ranges of $1560\,cm^{-1}$ to $1730\,cm^{-1}$ ($-C{=}O$ and $-COO$) and $1070\,cm^{-1}$ to $1460\,cm^{-1}$ ($R-NH_2$, $R-NH^{-}R$), Signals for amines are higher in the samples from treated wood. Characteristic absorption bands are summarized in Table B.3 in the appendix.

Qualitative GC-MS analysis indicated that the composition of acetone extracts from lyophilised eluates depends on the origin of the samples, but also on the pH during the ANC tests. A series of substances containing various functional groups and structures (hydroxyl, keto and carboxyl groups, esters, ethers, and cyclohexane, benzene and benzofuran rings) were identified both in samples from untreated and treated wood. Many of them can be considered as degradation products of lignin, like vanillin and coniferyl alcohol. Samples of untreated and treated wood also contain C_6-C_9 carboxylic acids and the terpene derivative terpin hydrate. However, there are also substances that were identified either in untreated or in treated wood, in some cases also depending on the pH during the ANC test. Only eluates from treated wood contained 2-ethylhexanoic acid (included in the wood preservative).

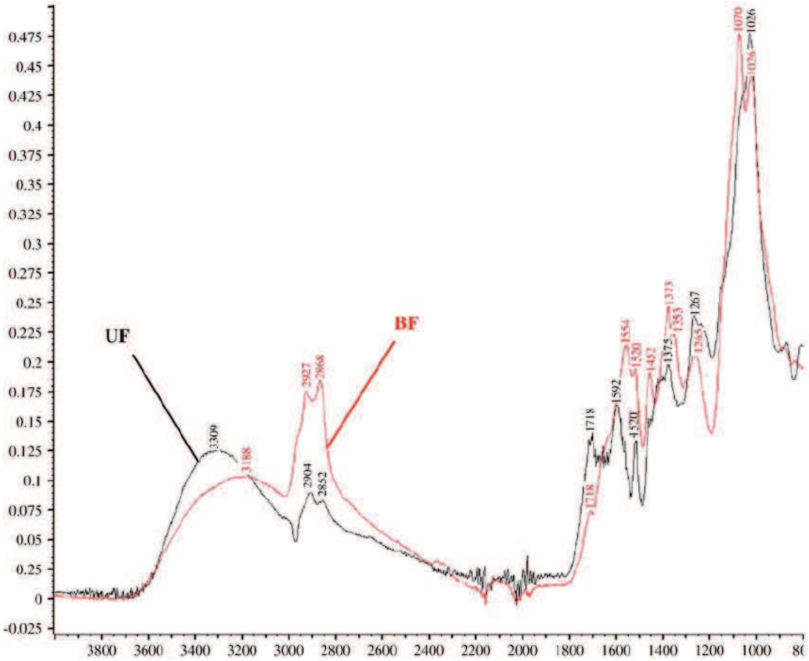

Figure 3.5: FTIR spectra from lyophilised eluates from untreated (UF) and treated "fresh" wood (BF).

In addition, a series of substances with different types of nitrogen bonds, like amines, amides, heterocyclic rings (pyrrol, piperidine, imidazole, isoindol) were only identified in samples from treated wood. A list of identified substances is given in Table B.2 in the appendix.

2.1.5 Discussion

During the ANC test, samples from "conditioned" wood respond more sensitively to the addition of NaOH than the "fresh" shavings (Figure 3.2), i.e. the buffering capacity is higher for "fresh" than for "conditioned" samples of *Pinus sylvestris*. The difference of about 3 pH units between the native pH of untreated and treated wood can be explained by modification of the reactivity of wood due to the preservative treatment. The pKa values of carboxyl groups of hemicellulose and lignin in wood range between 3 and 5. This pKa value interval is also common for soluble carboxylic acids. So, at native pH of untreated wood (pH=4.5), both dissociated and undissociated carboxyl groups occur with similar amounts. At pH above 5, most of the carboxyl groups of hemicellulose and pectins are dissociated and capable of complexing with Cu. At pH above 8, the phenolic groups of lignin are significantly dissociated and are essentially completely dissociated at pH above 10.5 (Cooper, 1991).

Addition of acid to wood samples causes protonation of carboxyl groups and compensates the neutralisation effect of the preservative components in treated wood. Addition of 0.016 mol H^+/L (or 0.16 mmol/g wood) to samples of treated wood, caused a drop in pH from 7.6 to 4.5 (4.5 is in the range of the native pH of eluates from untreated wood). This means that the majority of complexing sites (i.e. 0.1 mmol/g to 0.2 mmol/g) was occupied by components of the wood preservative (Mea, Cu, Cu−Mea−). The same reasoning also applies for the binding sites of extractives (carboxylic and phenolic groups) from treated samples. Acid addition also neutralises the excess of Mea and other derived amino-compounds in liquid phase.

Addition of base has the same effect on untreated and treated wood, i.e. deprotonation of carboxyl and phenolic groups. Excess of OH^- supports hydrolysis of polymers within wood and therefore an increase of soluble decomposition products. Solubilisation mechanism is also plausible at high pH, especially for heavy acids (e.g. resin, octanoic acid, etc.) present in the wood structure. A confirmation of the hydrolysis mechanism is the identification in eluates of compounds akin to the coniferyl alcohol/guaiacyl monomer unit of soft wood lignin. An increased release under alkaline conditions was observed for several parameters related to organic substances that originate from wood, i.e. TOC, carboxyl and phenolic groups and acetic acid. The amounts of TOC and acetic acid released from "fresh" and "conditioned" wood did not differ considerably, whereas the concentrations of phenolic and carboxyl groups were higher in eluates from "fresh" compared to "conditioned" wood (Figure 3.2). This supports the assumption that the reactivity of wood changes with the duration of storage due to release of substances, but also due to chemical reactions within wood, favouring precipitation.

As the pH of the CBA treatment solution was 9.63, which favours neutral and monovalent Cu-Mea complexes' formation, it can be assumed that complexation reactions with monovalent Cu-amine dominate (see Figure B.2 in the appendix).

The content of Cu added by the treatment solution was estimated to be about 0.06 mmol/g wood. This is lower than the reported quantity of binding sites in wood of 0.1 mmol/g to 0.2 mmol/g wood (see chapter 3, §2.1.2.1). So there are sufficient binding sites to bind the whole amount of Cu according to the described reactions. The quantity of Mea added with the CBA solution was estimated to be 0.24 mmol/g wood. This quantity could be distributed as follows: 0.06 mmol/g wood linked in Cu−Mea−Wood, 0.18 mmol/g wood bound to remaining binding sites by mechanisms cited in §2.1.2 (up to the maximum site capacity) and transformed by reactions with wood extractives. However, it has to be expected that an excess of free amine either evaporates or is still available in the pores' liquid – as shown by detection of Mea by TLC and high concentrations of nitrogen in eluates from treated wood (Figure 3.4).

Differences in organic substances in eluates were observed between untreated and treated wood. Higher TOC concentrations in eluates from treated wood are probably caused by organic substances originating from wood that became extractable after treatment with the CBA solution (see calculation in Table B.4 in the appendix). This observation can be explained by hydrolysis of wood components caused by the alkaline pH of the CBA solution and demonstrates that treatment irreversibly modifies the reactivity of wood. Another source of organic carbon is the presence of constituents of the preservative solution, i.e. Mea. The empirical formula in Table 3.2 shows that Mea cannot be the major organic compound in eluates.

Results for the determination of total carbon are similar for the TOC analysis in eluates and element analysis for lyophilised samples. Somewhat lower values for a few lyophilised samples can be caused by losses during the evaporation procedure. That means that element analysis confirms the results obtained from TOC quantification. In addition, element analysis shows that the amount of nitrogen is very low in eluates from untreated wood, and considerably higher in eluates from treated wood.

Carboxyl groups originate from wood, but partly also from the wood preservative, like 2-ethylhexanoic acid which was included in the CBA solution and was only identified in eluates from treated wood. However, the quantity of 2-ethylhexanoic acid added with the CBA solution was about 0 · 007 mmol/g wood, which, if totally released during ANC experiments, represents only a very small part of the total amount of carboxyl groups in eluates.

Phenolic groups, acetic and formic acid can only originate from wood since they are not included in the wood preservative. Acetic acid represents a considerable part of extractable substances containing carboxyl groups. The pH-dependency of the elution of acetic acid from untreated wood is similar to that of the total amount of substances with carboxylic acids, whereas formic acid was only found in the sample with low pH (Figure 3.2). Data on acetic acid support the assumption that hydrolysis is generally increased under alkaline conditions. Compared to untreated wood, acetic acid was released in considerably higher amounts from treated wood under neutral and acid conditions.

About 1 to 10% of the original amount of tebuconazole is released during the ANC test, whereas the release is about 10 times higher at alkaline compared to acid pH (Figure 3.2). The water solubility of tebuconazole is relatively low, i.e. about $36\,\mathrm{mg/L}$ (at pH 5-9, $20\,^{\circ}\mathrm{C}$) (FAO, 2004), which is equivalent to about $1.2 \times 10^{-4}\,\mathrm{mol/L}$. The concentrations observed in eluates indicate that water solubility was not limiting for the tebuconazole release. The pH dependency suggests binding to wood via hydrogen bonds, since deprotonation under alkaline conditions limits the availability of hydrogen binding sites. Release of tebuconazole may also be explained by molecular associations and co-elution with extractives that show similar pH-dependency. Another possible interaction can be the formation of soluble complexes with Cu, e.g. a Cu-tebuconazole-acetate complex (see §2.1.2). However, the large differences in concentrations of Cu and tebuconazole, different pH-dependency and missing data on the stability of such complexes do not allow conclusions on the occurrence and stoichiometry of such complexes.

Potassium, calcium, sulphate and phosphate were quantified at relevant concentrations in the ANC leachates (Figure 3.2). All these components originate from natural wood. Interestingly, calcium was hardly detected in leachates from treated wood. It is assumed that calcium reacts with carbonate from $CuCO_3$ in the preservative solution and forms insoluble calcium carbonate but this hypothesis must be verified.

The concentrations of B did not show pH dependency and were higher in eluates from "conditioned" samples. It can be assumed that this is caused by chemical reactions within wood that cause a decrease of sites in wood polymers that weakly bind B (see §2.1.2) during storage of wood. However, this assumption cannot be supported by further data obtained during this study.

Cu is released to about 10% of its initial content, with a minimum under neutral conditions. Leaching of Cu from treated wood is determined by its competitive distribution between solid wood matrix and extractives and Mea in the liquid phase. The equilibrium of this distribution depends on the availability of binding sites and on the pH. An increase of pH causes hydrolysis of wood components and therefore an increase of extractives that support binding sites in the liquid phase. Binding of Cu decreases when less deprotonated binding sites are available–under acid conditions.

Cu oxide can also precipitate on wood components. However, the water solubility of these oxides is too low to contribute considerably to the Cu detected in leachates from the ANC test. It was also observed that higher amounts of Cu are released from "fresh" compared to "conditioned" wood, which can be explained by higher amounts of binding sites of extractives observed in leachates from "fresh" wood.

The amount of nitrogen extracted under acid conditions was higher compared to neutral and alkaline conditions. This can be caused by a decrease of deprotonated binding sites ($-COO^-$, $-Ph-O^-$) for protonated Mea ($MeaH^+$) and monovalent $Cu-Mea$ complexes.

The FTIR spectra represent the sum of functional groups in these complex mixtures. The spectra of eluates from untreated and treated wood at native pH indicate that the ANC eluates are complex mixtures of substances containing a variety of different substance classes (e.g. hydrocarbons, esters, alcohols, polysaccharides), and that eluates from untreated wood contain higher amounts of substances with ester bonds, whereas eluates from treated wood contain higher amounts of substances containing primary and secondary amino groups.

Information obtained by GC-MS analysis of acetone extracts of lyophilised eluates is restricted to substances that are eluted during the ANC test, resist the lyophilisation procedure and can be extracted by acetone. Many of the identified substances are related to the decomposition of wood polymers (e.g. vanillin, coniferyl alcohol). GC-MS analysis confirmed that the lyophilised eluates contain complex mixtures of substances that contain a series of functional groups as also observed by FTIR analysis. Differences in the composition of samples from untreated and treated wood are obvious. A series of substances that include nitrogen groups were only identified in samples from treated wood. That means that Mea does not only form complexes with Cu and wood, but also reacts with wood components forming nitrogen containing extractable substances.

2.1.6 Conclusions

Leaching from CBA treated wood was investigated with the aim to identify chemical mechanisms of fixation and mobilisation of biocides based on a pH dependency leaching test (ANC test) that has been already widely applied for waste and concrete construction materials. Despite the fact that it is an aggressive test (test conditions are unlikely to occur under service conditions), ANC results, in combination with a suitable set of analytical methods, provide manifold information about the studied system and chemical reactions that occur in this system, information which is indispensable for the interpretation of leaching processes. However, in the case of CBA treated wood it proved to be difficult to describe the entire composition of the eluates without investing great effort for molecule identification and set up of methods for quantification.

The main conclusions from this study can be summarised as follows:

– Inorganic endogenous elements like Ca and K, and ions like sulphate and phosphate are released from untreated and treated wood in contact with water at different pH. They are linked to the solid phase (e.g. Ca in treated wood) or solubilised in wood pore water (e.g. K) and are the main electrolytes that regulate the ionic strength.

– Organic compounds are released from natural wood. The quantity of released TOC as well as substances with carboxyl and phenolic groups increases with pH. This observation is mainly explained by hydrolysis reactions on wood polymers.

– The chemical composition of wood changes during storage, at least for sapwood from *Pinus sylvestris*. This affects not only binding and release of substances in the ANC test, but also the amount and composition of extractives, including the availability of binding sites in the solid as well as the liquid phase.

– Wood is modified by the treatment with preservatives. In the case of products containing Cu and amines, this does not only involve binding reactions of Cu−amine complexes, but also modifications of wood components due to reactions with amines. A number of compounds containing nitrogen are released from wood treated with a CBA solution, probably due to an excess of amines and reactions of amines with wood components. It can be expected that these reactions depend on the identity of the amines, the ratio between Cu and amines and the pH conditions in the preservative solution and in wood.

– Cu release is relatively high with respect to its initial content. Cu is bound on carboxyl and phenolic sites and forms soluble complexes with extractives. The balance between binding to solid and extractable components, as well as the acid/base properties of the binding sites, result in the lower release at neutral pH.

- B is released at a high level. Even if some fixation phenomena are possible, their effectiveness is weak (demonstrated by the non-dependency on pH) and cannot effectively hinder the leaching.
- Tebuconazole is released in lesser extent if compared to its initial content in wood samples. Its fixation on solid wood structure seems to be influenced by pH, suggesting hydrogen bond interactions with OH groups on wood.

This work is preliminary to a modelling approach, aiming at a semi-quantitative description of the leaching process in ANC test. The modelling of chemical processes identified in ANC test is a key step for the development of a coupled chemical–transport model for leaching of treated wood, and constitute a future work.

2.2 Modelling inorganic and organic biocide leaching

This section has been published in the *Science of the Total Environment Journal*, with the following reference (cited in this manuscript as (Lupsea et al., 2013b)):

Lupsea, M., Tiruta-Barna, L., Schiopu, N., Schoknecht, U., Modelling inorganic and organic biocide leaching from CBA-amine treated wood, Science of the Total Environment, accepted.

2.2.1 Introduction and approach

Treated wood is a common construction product in building projects. Despite its characteristics: economical, sustainable and aesthetically pleasing building material, we need to ensure that the chemical compounds (inorganic and organic, endogenous and biocides) released during its contact with water (through leaching phenomena) do not pose a threat to people or environment.

The most pertinent and less expensive method for estimating the pollutants' release from treated wood is by numerical simulation of the leaching behaviour of the product. Very few studies have been carried out so far in this direction. Waldron and Cooper (2010) applied generic 1st order reaction kinetics in order to explain the time dependency of biocide release, but no chemical properties and reactions were considered. Schoknecht et al. (2005) modelled the metal release from treated wood in standard leaching tests, however, without considering the biocide fixation or other wood properties (acid/base behaviour, complexation and hydrolysis of wood fibres). A geochemical model was developed by Postma et al. (2009), considering partitioning between particulate and dissolved organic matter taking the fraction of reactive organic matter into account. In this work the wood properties and reactivity were not considered per se but rather represented by a generic natural organic matter with generic properties. Using the semi-empirical adsorption models on generic organic matter (humic/fulvic models) could not explain the intimate mechanism governing the interactions of biocides (metals and organics) with the distinct wood components. An alternative chemical model was developed by Tiruta-Barna and Schiopu (2011), which describes the leaching behaviour of several inorganic biocides in wood. In their model the authors considered the fixation on wood components and interaction with extractives (native wood compounds released in contact with water), albeit the nature of the organic soluble matrix was not investigated but rather regarded as total Dissolved Organic Carbon (DOC).

The aim of this study is to develop a quantitative chemical-transport model able to simulate the leaching of biocides from CBA-amine treated wood, as experimentally observed in laboratory leaching tests. The product studied here consisted in *Pinus sylvestris* treated with a commercial preservative based on amine- Copper-Boron-Azole (further called "CBA"), with tebuconazole as main organic biocide. CBA treatment is a water borne, organometallic pressure treatment, widely used in the wood products' industry nowadays. The current study describes a reliable modelling approach for assessing the biocides' release at laboratory scale, bringing together the experimental observations of the leaching behaviour (obtained in laboratory leaching tests, i.e. controlled leaching conditions) and fundamental knowledge about the wood/biocide chemistry. Compared to previous modelling attempts, the originality of the presented model consists in taking into consideration the fixation mechanisms for inorganic and organic biocides on the wood structure, their interactions with wood extractives and the transport mechanisms. The modelling of wood leaching behaviour in natural exposure conditions is beyond the scope of this work; it represents a further step, currently in work in the authors' team.

The development of the coupled chemical-transport model is based on a methodology combining:

1. Experimental investigation of the leaching behaviour of treated wood by using laboratory characterization leaching tests associated with a panel of analytical methods (as discussed in a previous paper Lupsea et al. (2013a)). Current available information was also used concerning the chemistry of natural materials.
2. Chemical model of biocides' interaction with the wood's solid structure (lignin, hemicellulose, cellulose) and with the liquid matrix (wood extractives).
3. Transport model describing mass transport in porous structure, in leachate and mass transfer between these compartments.

2.2.2 Materials and methods

2.2.2.1 Experimental data used for the model development The model development is based on experimental observations and data obtained at laboratory scale, by characterisation leaching tests performed on treated wood. This work previously performed is presented in Lupsea et al. (2012a, 2013a). The main principles of the experimental work are resumed hereafter; more details are given in appendix C.

Treated samples of *Pinus sylvestris* sapwood were obtained by vacuum pressure impregnation EN 113 (1996) of $15\,\mathrm{mm} \times 25\,\mathrm{mm} \times 50\,\mathrm{mm}$ pieces, with a commercial wood preservative, consisting of copper carbonate (22.5%), boric acid (4.9%), and tebuconazole (0.53%). In addition, the preservative contained a mixture of amines with monoethanolamine (hereafter noted "MeaH") as main component and carboxylic acids. The final concentration in the wood samples was determined by mass balance calculations: $16\,\mathrm{kg/m^3}$ CBA, i.e. $2\,\mathrm{kg/m^3}$ copper, $0.1\,\mathrm{kg/m^3}$ boron and $0.085\,\mathrm{kg/m^3}$ tebuconazole. After treatment, test specimens were conditioned for 4 weeks at 20 ± 2°C and $65 \pm 5\%$ relative humidity to allow evaporation of water and reactions of the preservative with wood (fixation). The open porosity was determined on wood samples by mercury intrusion porosimetry Plötze and Niemz (2011), cf. standard DIN 66133.

Two standard leaching tests were performed on the treated wood samples. ANC test (Acid Neutralisation Capacity, based on CEN (2006)) provides information on the influence of pH on pollutant release, acid/base neutralisation capacity and physico-chemical stability of the material. Initially developed for the assessment of the leaching behaviour of wastes, the pH dependency test is widely used for the characterisation of construction products (van der Sloot and Dijkstra, 2004; Schiopu et al., 2009; Król, 2011; Tiruta-Barna and Schiopu, 2011; van der Sloot and van Zomeren, 2011). In this study, the purpose of the pH dependency test is to help at characterising the chemistry in the pores of the product.

DSLT (Dynamic Surface Leaching Test OECD (2007)) is used to investigate time dependency of leaching of different components from block samples. This test was initially developed for treated wood characterisation. A similar protocol is under development at European level for the assessment of the dangerous substances release from construction products to soil, surface water and groundwater (CEN, 2012b). Various analytical methods (qualitative and quantitative) were carried out on eluates obtained from the leaching tests, in liquid or lyophilised form (a global overview of the experimental work is presented in Figure C.1 in the appendix). The following compounds have been quantified: total organic carbon (TOC), mineral species (Cu, K, Ca, B, Cl^-, PO_4^{3-}, SO_4^{2-}), tebuconazole, organic acids (formic, acetic, maleic and total carboxylic groups) and total phenols. Details on the test protocol and application to treated wood samples are given in Lupsea et al. (2012a) for DSLT and Lupsea et al. (2013a) for ANC test.

In this work, the results obtained in the experimental program (i.e. the quantitative eluates' composition (species cited above) and qualitative information on extractives detected in eluates) were used for the model development. These experimental data are represented in Figure 3.6 for ANC test, and Figure 3.7 for DSLT test.

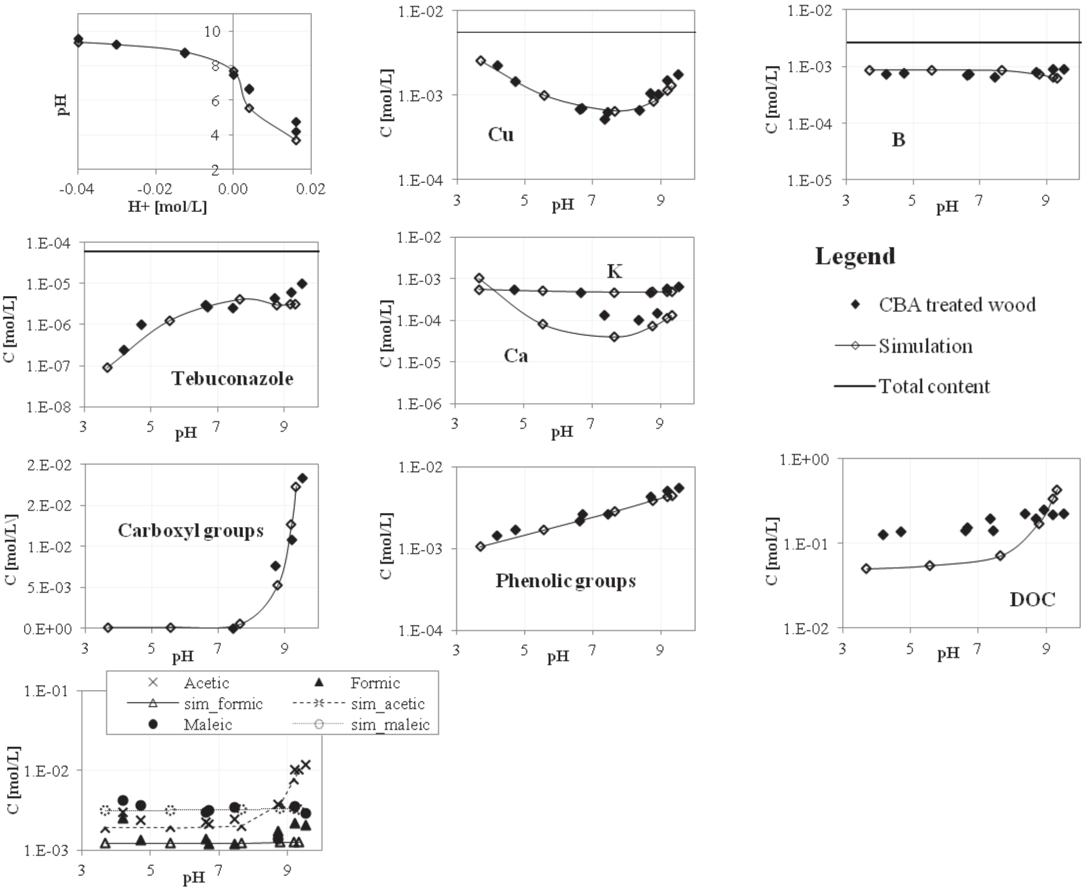

Figure 3.6: Experimental and simulated results for ANC test.

2.2.2.2 Modelling tools The geochemical modelling software PHREEQC® was used with the Lawrence Livermore National Laboratory (LLNL) thermodynamic database. Original LLNL reactions and equilibrium constants were supplemented with constants from literature and the MINTEQ database. All parameters used in the model and the corresponding references are presented in Tables 3.3 and 3.4. Data from literature has been used as much as possible for equilibrium constants. Missing values were determined by model adjustment on experimental leaching results from ANC test (i.e. “concentration-vs-pH”, and “pH-vs-acid or base added”). The process was iteratively conducted until the error (differences between simulated and experimental concentrations) was minimized. The diffusion coefficients

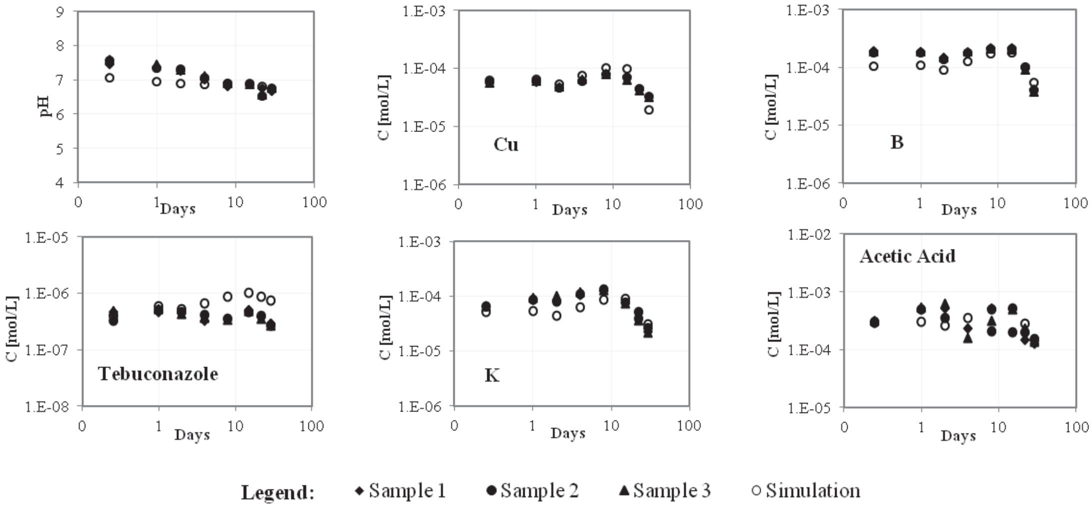

Figure 3.7: Experimental and simulated results for DSLT.

necessary for the transport modelling have been determined by adjustment on DSLT experimental data (explained in §3).

2.2.3 Model development

2.2.3.1 Chemical model The chemical model is based on the approach developed in (Tiruta-Barna and Schiopu, 2011) for treated wood. However, the present study is different in the following points:

- A different treatment product was used, i.e. CBA with amine as major constituent of the solution.
- An organic biocide, tebuconazole, was considered for the first time and included in the model.
- A thorough investigation of the eluates allowed more detailed input data concerning the organic matter (extractives).
- The previous modelling study regarded the organic soluble matrix as a global DOC, whereas the present study takes in consideration each class of organic substances, identified by the analytical platform (see 2.1 and the supplementary document for more details).

The main hypotheses for the development of the chemical model are detailed hereafter:

Table 3.3: Parameters for reactions used in model (in addition to LLNL data base).

Reaction	log K	Reference
$\mathrm{H^+ + Octanoic^- = OctanoicH}$	4.89	(zir, 2012)
$\mathrm{H^+ + Abietic^- = AbieticH}$	7.26	(Buckingham and Macdonald, 1995)
$\mathrm{H^+ + Formic^- = FormicH}$	3.745	MINTEQ
$\mathrm{H^+ + Acetic^- = AceticH}$	4.757	MINTEQ
$\mathrm{H^+ + Vanillin^- = VanillinH}$	8.75	(Buckingham and Macdonald, 1995)
$\mathrm{H^+ + Maleic^{2-} = HMaleicH^+}$	1.83	(zir, 2012)
$\mathrm{H^+ + HMaleic^- = H_2Maleic}$	6.07	(zir, 2012)
$\mathrm{Cu^{2+} + 2\,H_2O = Cu(OH)_2^{2+} + 2\,H^+}$	-16.19	MINTEQ
$\mathrm{Cu^{2+} + 3\,H_2O = Cu(OH)_3^- + 3\,H^+}$	-26.88	MINTEQ
$\mathrm{Cu^{2+} + 4\,H_2O = Cu(OH)_4^{2-} + 4\,H^+}$	-39.98	MINTEQ
$\mathrm{2\,Cu^{2+} + 2\,H_2O = Cu_2(OH)_2^{2+} + 2\,H^+}$	-10.60	MINTEQ
$\mathrm{Cu^{2+} + Vanillin^- = CuVanillin^+}$	6.3	(Mubarak et al., 2010)
$\mathrm{Cu^{2+} + 2\,Vanillin^- = Cu(Vanillin)_2}$	11.2	(Mubarak et al., 2010)
$\mathrm{Cu^{2+} + Octanoic^- = CuOctanoic^+}$	2	deduced from MINTEQ
$\mathrm{Cu^{2+} + Abietic^- = CuAbietic^+}$	2	deduced from MINTEQ
$\mathrm{Cu^{2+} + Formic^- = CuFormic^+}$	2	MINTEQ
$\mathrm{Cu^{2+} + Maleic^{2-} = CuMaleic}$	4.47	(Navon et al., 1997)
$\mathrm{Cu^{2+} + HMaleic^- = CuHMaleic^+}$	4.08	(Navon et al., 1997)
$\mathrm{Cu^{2+} + H_2Maleic = CuH_2Maleic^{2+}}$	3.36	(Navon et al., 1997)
$\mathrm{H^+ + MeaH = MeaH_2^+}$	9.5	(Tauler et al., 1986)
$\mathrm{MeaH = Mea^- + H^+}$	-17	(Scheiman, 1962)
$\mathrm{Cu^{2+} + MeaH = (CuMeaH)^{2+}}$	4.5	(Mettlemary, 2011)
$\mathrm{Cu^{2+} + 2\,MeaH = (Cu(MeaH)_2)}$	8.4	(Mettlemary, 2011)
$\mathrm{Cu^{2+} + 3\,MeaH = (Cu(MeaH)_3)^{2+}}$	10.8	(Mettlemary, 2011)
$\mathrm{Cu^{2+} + 4\,MeaH = (Cu(MeaH)_4)^{2+}}$	11.5	(Mettlemary, 2011)
$\mathrm{Cu^{2+} + 2\,MeaH = (CuMeaH(Mea)) + H}$	1.5	(Mettlemary, 2011)
$\mathrm{Cu^{2+} + 2\,MeaH + OH^- = (Cu(MeaH)_2OH)^+}$	15.42	(Mettlemary, 2011)
$\mathrm{Cu^{2+} + 2\,MeaH = Cu(Mea)_2 + 2\,H^+}$	-8.4	(Mettlemary, 2011)
$\mathrm{Cu^{2+} + 2\,MeaH + 2\,OH^- = Cu(MeaH)_2(OH)_2}$	19.58	(Mettlemary, 2011)
$\mathrm{H^+ + Lig\_acO^- = Lig\_acOH}$	3.37	(Ravat et al., 2000)
$\mathrm{H^+ + Lig\_phO^- = Lig\_phOH}$	8. 34	(Ravat et al., 2000)
$\mathrm{(CuMeaH(Mea))^+ + Lig\_acO^- = Lig\_acO(CuMeaH(Mea))}$	0	this study
$\mathrm{(CuMeaH(Mea))^+ + Lig\_phO^- = Lig\_phO(CuMeaH(Mea))}$	0	this study
$\mathrm{Cu^+2 + Lig\_acO^- = Lig\_acOCu^+}$	3.58	(Ravat et al., 2000)
$\mathrm{Cu^+2 + Lig\_phO^- = Lig\_phOCu^+}$	7.56	(Ravat et al., 2000)
$\mathrm{Cel\_alO^- + H^+ = Cel\_alOH}$	15	deduced from (van der Sloot and Dijkstra, 2004)
$\mathrm{BO_2^- + 2\,Cel\_alOH = (Cel\_alOH)_2BO_2^-}$	0.7	(Tiruta-Barna and Schiopu, 2011)
$\mathrm{Lig\_phOH + Tebuconazole = Lig\_phOH(Tebuconazole)}$	4	this study
$\mathrm{Lig\_acOH + Tebuconazole = Lig\_acOH(Tebuconazole)}$	5.8	this study
$\mathrm{VanillinH(s) = VanillinH(aq)}$	-50	this study
$\mathrm{Cu(OH)_2 + 2\,H^+ = Cu^{2+} + 2\,H_2O}$	8.674	MINTEQ
$\mathrm{OctanoicH(s) = OctanoicH(aq)}$	-7	this study
$\mathrm{AbieticH(s) = AbieticH(aq)}$	-4	this study
$\mathrm{H^+ + X^- = HX}$	3.4	(Ravat et al., 2000)
$\mathrm{Ca^{2+} + 2\,X^- = CaX_2}$	2.5	(Tiruta-Barna and Schiopu, 2011)

Table 3.4: Other parameters used in model.

Surface and kinetic parameters		
Specific surface area	100 m^2/g	(Tiruta-Barna and Schiopu, 2011)
Site density carboxyl	0.05 mol/kg wood	this study
Site density phenol	0.06 mol/kg wood	this study
Site density hydroxyl (cellulose)	0.5 mol/kg wood	(Tiruta-Barna and Schiopu, 2011)
Kinetic constant for vanillin	0.0159 mol/L	this study
Kinetic constant for acetic acid	1711 mol/L	this study
Parameters used in transport model		
Effective diffusion coefficient, D_R m^2s^{-1}	1.6×10^{-11}	this study
Effective diffusion coefficient, D_T m^2s^{-1}	1.0×10^{-11}	
Open porosity, %	67	this study

1. The main processes at the wood/liquid interface are: (i) surface complexation of Cu and Cu−MeaH complexes with phenol and carboxyl groups lying on wood polymers; (ii) precipitation of Cu and Cu- MeaH with wood extractives; (iii) interaction of tebuconazole and carboxyl and phenol groups on wood by hydrogen bonds; (iv) ion exchange by carboxyl groups involving Ca and MeaH; (v) B weak complexation by cellulose; (vi) solubilisation of several extractives.
2. In the aqueous phase: (i) equilibrium reactions of mineral species; (ii) Cu complexation with MeaH and dissolved organic matter; (iii) dissolution/precipitation of inorganic solids like oxides, carbonates, silicates, and organic compounds.

The wood compartment and wood/liquid interface. The following composition was considered for the *Pinus sylvestris* samples: 27% lignin, 28% hemicelluloses, 40% cellulose and 4% extractives and minerals (Sjöström, 1993). In accordance with literature (Thomason and Pasek, 1997; Jiang, 2000; Zhang and Kamdem, 2000; Lee, 2011; Mettlemary, 2011) Cu is being complexed on the wood structure via phenol and carboxyl groups from the lignin and hemicellulose structure. Two complexation mechanisms were considered: (i) a direct surface complexation of Cu ions, and (ii) complexation of Cu−MeaH complexes on the same sites. In Table 3.3, "Lig_acO−" and "Lig_phO−" correspond to total carboxyl, respectively phenol groups in wood ("Lig_" is the generic name for both lignin and hemicellulose).

For surface complexation modelling, Dzombak and Morel diffuse double-layer model with the Donnan diffuse layer model was used (implemented in PHREEQC® with default thickness). This model requires the following input parameters: intrinsic complexation constants, site density and specific surface area of the material, data which are very scarce in literature. Site density for carboxyl and phenyl groups was taken from (Ravat et al., 2000; Guo et al., 2008) and adapted to our wood composition (see Table 3.4). For the specific surface area of wood fibres we considered the mean value used by (Tiruta-Barna and Schiopu, 2011), i.e. $100\,\mathrm{m}^2/\mathrm{g}$ wood.

The first type of reactions required monodentate complexes to be considered in the model. Intrinsic complexation constants for Cu were taken from (Ravat et al., 2000). For the second type, Cu−MeaH complexes are bound to one wood site, i.e. carboxyl (noted $-\mathrm{acO}^-$) or phenol (noted $-\mathrm{phO}^-$) (Lee, 2011). For pH ≤ 10, (Zhang and Kamdem, 2000) propose a cation exchange mechanism involving monovalent Cu−MeaH complexes $[\mathrm{Cu(MeaH)(Mea)}]^+$, as described in Equations 3.7 and 3.8.

$$-\mathrm{acO}^- + [\mathrm{Cu(MeaH)(Mea)}]^+ \longrightarrow [-\mathrm{acO}-(\mathrm{Cu(MeaH)(Mea)})^+]^0 \tag{3.7}$$

$$-\mathrm{phO}^- + [\mathrm{Cu(MeaH)(Mea)}]^+ \longrightarrow [-\mathrm{phO}-(\mathrm{Cu(MeaH)(Mea)})^+]^0 \tag{3.8}$$

In Equations 3.7 and 3.8 and Table 3.3, "MeaH" represents neutral monoethanolamine (i.e. $\mathrm{HO-CH_2-CH_2-NH_2}$), "Mea" stands for deprotonated monoethanolamine (i.e. $\mathrm{H_2N-CH_2-CH_2-O^-}$) and "$\mathrm{MeaH_2^+}$" represents protonated monoethanolamine (i.e. $\mathrm{HO-CH_2-CH_2-NH_3^+}$). Thus, a reaction of protonation and one of deprotonation for MeaH were considered, with the equilibrium constant given in Table 3.3. Both MeaH and Mea participate in complexation reactions with Cu.

Unlike the first type of reactions (Cu complexed directly on the wood surface), no formation/stability constants exist in literature concerning the complexation of Cu−MeaH compounds on wood. These values were therefore adjusted such that the simulated Cu concentrations fit the experimental curve concentration-vs-pH. The obtained stability constants have small values, pointing out that reactions 3.7 and 3.8 are secondary, compared to the direct complexation of Cu on wood.

Binding of tebuconazole on wood components has been very little investigated. Only complexation between tebuconazole and Cu has been studied in vitro (Evans and Schmalzl, 2007; Dytrtová et al., 2011). However, the large difference in concentrations of Cu and tebuconazole in eluates, different pH-dependency shapes, and missing data on the stability constants do not allow conclusions on the occurrence and stoichiometry of such complexes. Moreover, the formation of complexes of tebuconazole and MeaH has not been described yet. However, from the stability constants of Cu−MeaH complexes (Mettlemary, 2011) it can be expected that MeaH binds Cu and other metals stronger than tebuconazole. So tebuconazole-MeaH or Cu-tebuconazole complexes were excluded. Nevertheless, ANC results show that tebuconazole is released in about 10 times higher concentrations at alkaline compared to acidic pH (Figure 3.6). The water solubility of tebuconazole is relatively low, i.e. $36\,\mathrm{mg/L}$ (at pH 5 to 9, $20\,°\mathrm{C}$) (FAO, 2004), or $1.2 \times 10^{-4}\,\mathrm{mol/L}$. The concentrations observed in eluates (between 10 to 7 and $10\,\mathrm{mol/L}$ to $5\,\mathrm{mol/L}$) indicate that water solubility was not limiting for the tebuconazole release. The pH dependency suggests binding to wood via hydrogen bonds, since deprotonation under alkaline conditions limits the availability of hydrogen binding sites (Lupsea et al., 2013a). Constants for these reactions have been adjusted with experimental data. Phenol sites seem to bind tebuconazole stronger than carboxyl groups on wood.

As already experienced by Tiruta-Barna and Schiopu (2011), ion exchange reaction with low affinity sites was considered to explain Ca behaviour. The exchange sites were carboxyl groups of hemicellulose. Ion exchange involving MeaH and carboxyl groups of hemicellulose and lignin has been suggested by Humar et al. (2003). However, sorption of Cu on the same sites is dominant and is not competing with MeaH (Lee and Cooper, 2010). Moreover, no constants were found to define this mechanism, so it was not considered in our model.

Boron is introduced in wood as boric acid. Few studies exist on eventual bonding mechanisms. B release was modelled considering weak organic complexes in which B is linked to active sites in wood components by O-bridges (Obanda et al., 2008). The reaction has been described by (Ramos et al., 2006) as the formation of a bidentate complex between B and the cellulose substrate "Cel_alOH". The complexation constant has been adjusted using experimental ANC results concentration-vs-pH. For modelling it was considered that $2/3$ of cellulose hydroxyl groups are in favourable position (i.e. adjacent) for reaction (site density given in Table 3.4).

Equilibrium in aqueous phase. In aqueous phase equilibrium reactions have been considered for all mineral constituents (K^+, Ca^{2+}, Na^+, Cu^{2+}, Cl^-, PO_4^{3-}, SO_4^{2-}) and all quantified organic compounds (see below), interfering for pH and ionic strength calculation and for biocides" aqueous speciation. All corresponding equilibrium constants were taken from the LLNL and MINTEQ databases. No saturation was observed from saturation index calculation, which demonstrates that at least in the considered experimental conditions (ANC test), leaching of mineral compounds, including Cu and B, was not governed by precipitation/dissolution reactions. One of the main results previously reported (Lupsea et al., 2013a) concerns the chemical nature of the extractives, here resumed: substances containing various functional groups and structures (hydroxyl, ketone and carboxyl groups, esters, ethers, and cyclohexane, benzene and benzofuran rings) were identified by qualitative GC-MS (Gas Chromatography coupled with Mass Spectrometry) on lyophilised eluates. Many of them can be considered as degradation products of lignin, like vanillin and coniferyl alcohol. Eluates also contained C_6–C_9 carboxylic acids and terpin hydrate, 2-ethylhexanoic acid (included in the wood preservative) and substances with different types of nitrogen bonds like amines, amides, heterocyclic rings. For modelling proposes, an equivalent compound was chosen for each class of extractives. The choice for these equivalent compounds was also based on the existing literature data. Thus, all fatty acids identified (i.e. C_6–C_9 carboxylic acids) have been considered as octanoic acid (noted "OctanoicH"); extractible resins have been allocated abietic acid (noted "AbieticH") and finally, all lignin-borne soluble compounds have been regarded as vanillin (noted "VanillinH").

The following complexes of Cu with organic compounds were considered in solution: (i) complexes of Cu with MeaH, suggested by (Mettlemary, 2011); (ii) Cu complexation with all quantified carboxylic acids i.e. formic, acetic and maleic acid; (iii) Cu complexation with resin acids, i.e. abietic acid; (iv) Cu complexation with fatty acids, i.e. octanoic acid and (v) complexation of Cu with phenolic compounds, i.e. vanillin. The release of phenolic compounds (alias VanillinH) and acetic acid (AceticH here below) increases with pH by a supposed hydrolyse mechanism. This behaviour was modelled by irreversible reactions of organic -macromolecules with OH (Equations 3.9 and 3.10). There are no quantitative information in literature concerning equilibrium or kinetics of such hydrolyse reactions. Therefore the reactions were considered to have a certain degree of advancement during the ANC test, depending on pH conditions. The kinetics must depend only on OH^- if the solid surface does not evolve significantly during the reaction (wood structural components don't disappear). Kinetic constants were determined by statistical regression from the experimental data (Table 3.3).

$$\mathrm{R{-}(VanillinH) + OH^- = R + Vanillin^- + H_2O} \tag{3.9}$$

$$\mathrm{R'{-}(AceticH) + OH^- = R' + Acetic^- + H_2O} \tag{3.10}$$

In Equation 3.9 and 3.10, R and R' are solid organic polymers containing labile fragments of VanillinH, respectively AceticH, able to be released in alkaline solutions.

The initial composition of the system (for $100\,\mathrm{g}$ of wood in $1\,\mathrm{L}$ pure water – the ratio used in ANC test) used in the simulation is presented in Table 3.5. The composition for boron (as boric acid), copper (as hydroxide), tebuconazole and monoethanolamine was calculated from the initial content of the treatment solution. The quantity of soluble mineral species (K^+, Na^+, Cu^+2, Cl^-, PO_4^{3-}, SO_4^{2-}) and Ca (as wollastonite) was estimated from the plateau concentration observed in ANC test, for each species. By the same method were estimated the initial quantities of formic and maleic acids.

Table 3.5: Initial composition of the system, for 100 g of wood in 1 L pure water.

Solid species	mol/L
Boric acid ($B(OH)_3$)	0.001[a]
$Cu(OH)_2$	0.005[a]
Tebuconazole	5.85e-5[a]
Octanoic acid	0.0007[b]
Abietic acid	0.03[b]
Vanillin	0.006[d]
Wollastonite ($CaSiO_3$)	0.0008[c]
SiO_2	Possible to precipitate[f]
Azurite ($Cu_3(CO_3)_2(OH)_2$)	Possible to precipitate[f]
Malachite ($Cu_2(CO_3)(OH)_2$)	Possible to precipitate[f]
Aqueous species	**mol/L**
Cl	0.00015[c]
K	0.00065[c]
S(6)	0.0003[c]
Na	8.4e-5[f]
C(4)	1.4e-5[e]
P(5)	0.0001[c]
Acetate	0.0022[c]
Formate	0.0014[c]
Maleate	0.0036[c]
MeaH	0.013[a]

[a] from total content
[b] from acid number (total concentration of carboxyl groups)
[c] from ANC experimental results
[d] from total phenols' concentration
[e] CO_2 uptake in eluates from atmosphere
[f] following literature information, e.g. (Lee, 2011; Tiruta-Barna and Schiopu, 2011)

The sum of the initial composition of "OctanoicH" and "AbieticH" was considered in accordance with the concentration of carboxyl groups in eluates, after subtracting the concentrations of all quantified carboxylic acids (i.e. formic, acetic and maleic acid). For more details regarding these calculations, see (Lupsea et al., 2013a). The initial composition of "VanillinH" was calculated from the concentration of total phenols in eluates.

2.2.4 Coupled transport-chemical model

Wood is a porous product, and thus the diffusion could be considered as the main mechanism of substances' transport into the matrix and at solid / liquid interface. Figure 3.7 shows DSLT results (Lupsea et al., 2012a) used in this modelling section. The observed concentrations (at the moment of the eluate's renewal) are the result of chemical changes and diffusion occurring during wood/water contact. The cumulative emissions in mg/m^2-vs-time are represented in Figure 3.8, accompanied by the line with 0.5 slope, which proves – in accordance with the diffusional transport model (Crank, 1975) – that the leaching process was controlled by diffusion during the first 8 days; afterward the process slowed down. The observed diffusional regime confirms also that the wood sample was homogenous in composition (no significant gradient of biocides or other species in wood block); without this condition, a 0.5 slope could not be observed at the beginning of the test (more explanation in supplementary document).

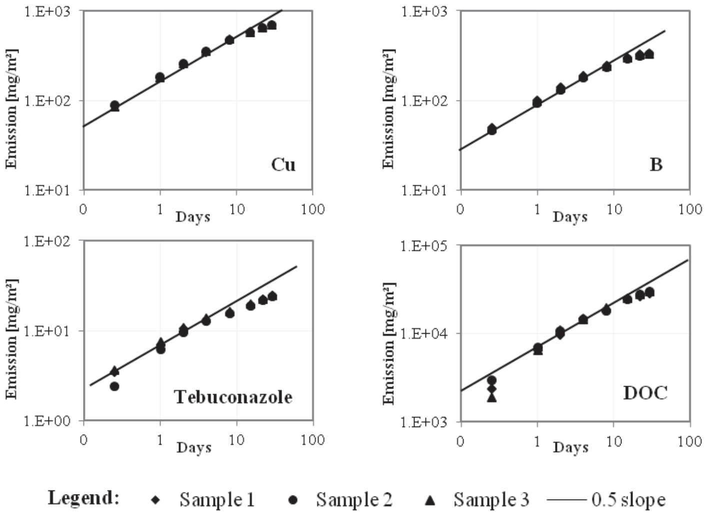

Figure 3.8: Cumulative emissions in mg/m^2 during DSLT and 0.5 slope representation for leaching mechanism controlled by diffusion.

The progressive release of MeaH determines a continuous and slight decrease of pH. At the end of DSLT (30 days), only 8% of Cu and 10% of tebuconazole were released, while 45% of B was lost. The high release and almost depletion of B was also observed by Schoknecht et al. (2004). This result suggests that the slope change after 8 days is not due to Cu and tebuconazole depletion but instead to a limiting process like the evolution of the complex chemical equilibrium. Regarding DOC behaviour, the slope is slightly different proving that the chemical processes control the release. A slowdown is observed again after 8 days. This particular trend can be explained by the depletion of amine resulting in the pH modification inside the porous structure (Figure 3.6 shows a pH decrease for about 1 unit after 8 days) and consequently the reinforcing of the biocides' fixation on wood, in parallel with a decrease of DOC solubilisation. In this pH region, the pH and DOC decrease result in a lesser Cu and tebuconazole release.

In this part of the study, the DSLT experimental results were used for fitting an effective diffusion coefficient and at the same time for validating the chemical model. The chemical model developed in §2.1 for representing the ANC test results was used here with the same reactions and the local equilibrium hypothesis for pore water/solid system. The transport-chemical model aims at simulating the dynamic leaching in the test experimental conditions, thus the diffusion mechanism was considered in the porous system and leachate compartment was modelled as a stirred reactor (i.e. the leachate composition is homogenous). The resolution with PHREEQC® of the diffusion-convection-chemistry model simulating a monolithic leaching test is presented in (Tiruta-Barna, 2008).

Wood is an anisotropic material, with three principal axes of diffusion (longitudinal – D_L, radial – D_R, tangential – D_T). For *Pinus* species, it was found that D_R and D_T are quite similar while DL is much larger (Waldron and Cooper, 2010), e.g. $D_T : D_R : D_L$ = 1 : 1.5 : 22 for southern pine, or $D_T : D_R : D_L$ = 1 : 1.6 : 31 for red pine.

In DSLT carried out in this study, the longitudinal diffusion was blocked, diffusion being possible only in radial and transversal directions. The mathematical method used by (Waldron and Cooper, 2010) and (Rabia et al., 1996) for diffusion resolution was used, considering the ratio $D_T : D_R$ = 1 : 1.6, common for *Pinus* species. The effective estimation of the diffusion coefficients was performed by fitting the simulated curve concentration-vs-time on the experimental data, for a tracer species (i.e. only the transport model was simulated, without any chemical background). Among the elements released by wood in ANC test, K^+ exhibits a pH independent leaching behaviour and thus it was considered as a tracer. After evaluation of the diffusion coefficients (Table 3.4), the complete chemical-transport model was used for simulating of DSLT dynamic leaching, with similar diffusion coefficients for all chemical species.

2.2.5 Results and discussions

2.2.5.1 Model validity For the model development, reaction constants and parameters from literature were used as much as possible. However, a certain number of key parameters are currently missing, especially thermodynamic constants for complexation reactions involving MeaH. These values were estimated for the most important reactions, by adjustment of the simulated concentrations to the experimental ones (see also Table 3.3). These values seem to be coherent with regard to the order of magnitude of similar type of reactions, and were also validated by a sensitivity analysis.

Concerning the transport model, the effective diffusion coefficient is in the range of figures reported in literature (Ra et al., 2001; Mukam Fotsing and Tchagang, 2005; Schoknecht et al., 2005; Waldron and Cooper, 2010).

Simulation results are presented in Figures 3.6 and 3.7 for ANC and DSLT respectively and compared with experimental data. The pH in the simulation of ANC in the acid area is slightly lower than the experimental values. However, the mean relative error is less than 4%. This might be due to the initial composition for the equivalent compounds containing carboxyl and phenol groups (e.g. OctanoicH, AbieticH, VanillinH) and their associated pKa (see Table 3.5). However, the calculated total carboxylic and phenolic groups as well as the individual small acids agree with the experimental data. The sum of all organic carbon contained in the different compound groups is close to the measured DOC in eluates (Figure 3.6). The chemical simulation fails for tebuconazole at alkaline pH, probably due to a more complex interaction pathway with wood structure. The adjustment of the complexation constant of tebuconazole with wood by hydrogen bonds was sensitive for a $\log(K)$ variation of ± 0.1 (Table 3.3).

The chemical-transport model fails for representing rigorously several experimental points in DSLT. Copper release is very well represented without any special adjustment. When similar errors occur for many species, we can expect that the transport model is not perfect. In Figure 3.7, the first points show some differences for K, B, pH, probably due to inhomogeneity and anisotropy of the porous structure. In view of ANC and DSLT results for tebuconazole, an incomplete chemical model is rather offending. However, the errors are acceptable for such a complex system (the overall mean error is less than 25%); this is merely the first coupled chemical-transport model for treated wood and it is an important step for further developments. The completion of the chemical model could be discussed in the sense that not all possible reactions were taken into account. The model was based on confirmed mechanisms and on the most possible reactions pointed out by the literature survey. It could be supposed, for example, that Cu forms mixed complexes with various extractives and MeaH, but the combination of such complexation possibilities leads to an even higher number of reactions. Another limiting aspect was the lack of data for equilibrium constants. As the number of possible reactions is very high, the number of model unknown parameters could explode and the adjustment results would become irrelevant. All these aspects are reasons why in the model, groups of compounds were represented by equivalent compounds (i.e. total phenols, total carboxylic acids) and literature unconfirmed reactions were left behind. Tentative to include more reactions with different classes of extractives is discussed in the supplementary document.

2.2.5.2 Biocide behaviour The model allows speciation calculations and the simulation of species' distribution between different compartments (on wood, in pore water, in leachate). As such, the model represents a useful tool for a better understanding of biocide leaching. Figure 3.9 shows the distribution of Cu between the liquid and solid phases, i.e. in solution (graph on the left) and complexed on wood (graph on the right). The simulations were carried out considering the experimental condition of ANC test. In solution, Cu is complexed with MeaH, deprotonated phenolic compounds and carboxylic acids, and hydroxyl ions. At acid pH we observe a strong complexation with fatty acids, which decreases with the pH increase, due to competing reactions with phenolic extractives (alias VanillinH) and wood deprotonated sites (all being weaker acids than fatty acids). At pH near native (between 7 and 8) Cu is linked preferentially to phenolic extractives. For pH ≥ 9, copper complexes with MeaH become dominant.

On wood, Cu is complexed on phenolic and carboxyl sites of lignin and hemicellulose by two mechanisms: directly or via MeaH. Figure 3.9 (right) shows that the first mechanism is prevalent under all pH conditions (by seek of homogeneity, concentrations of fixed Cu were reported as mol/L of leachant). Thus, we might consider the second complexation mechanism (wood$-$Cu$-$MeaH) as negligible. A sensitivity study realised by removing from the model the direct wood$-$Cu mechanism shows that Cu amount fixed by this second mechanism strongly rises with pH

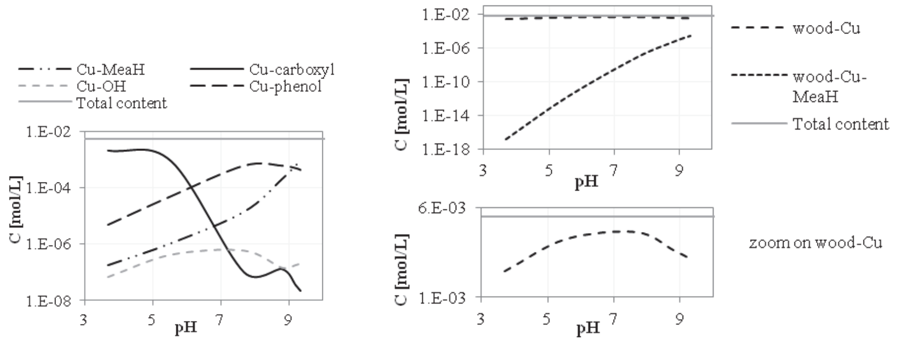

Figure 3.9: Variation of copper distribution with pH in solution (left) and on wood (right). In solution complexes with: (i) monoethanolamine (Cu−MeaH), (ii) free Cu^{2+} and hydroxyl complexes (Cu−OH), (iii) phenolic compounds (Cu−phenol), (iv) carboxylic acids (Cu−carboxyl). On wood fixed by: (i) direct complexation (wood−Cu), (ii) via MeaH complexes (wood−Cu−MeaH).

and aqueous Cu diminishes correspondingly; the shape of copper concentration-vs-pH didn't fit the experimental data for any values assigned to the respective equilibrium constants (for more details see supplementary document). The observation that wood−Cu−MeaH complexation isn't the main mechanism of copper complexation on wood is an important outcome of this study. As observed, the most favourable pH region for Cu fixation corresponds to native pH ≈ 7.5 of samples. The native pH of untreated wood was 4.5 (Lupsea et al., 2013a). Figure 3.6 shows that at this acidic pH, Cu solubility is more important. Thus, it can be stated that the role of monoethanolamine is to neutralise the natural acidity of wood, enabling by this way Cu binding on deprotonated sites. A higher pH induces reactions on wood like hydrolyses, the release of more extractives and consequently a higher mobility of Cu. Concerning boron, even if some fixation phenomena are possible, their effectiveness is weak (demonstrated by the non-dependency on pH) and cannot effectively hinder the leaching. The mechanism in which B is linked to active sites in wood components (cellulose) by O-bridges was used in this study and satisfactory simulate both leaching tests. Nevertheless, its total loss counted in both tests is the highest among the studied biocides and confirms the weak binding capacity with the wood structure.

Simulation results for tebuconazole leaching show acceptable coherence with experimental data, even if this is the first attempt to model organic biocide chemistry in treated wood. Tebuconazole complexation with Cu and MeaH or other possible interactions with extractives were not considered in this model. The model is very sensitive to acid/base properties of the fixation sites (pKa of carboxyl and phenol sites), that could explain its weakness in alkaline domain. Nevertheless, the fixation mechanism of tebuconazole needs to be validated by analytical methods and constants for the corresponding reactions need to be deduced.

2.2.6 Conclusions

This is a first coupled chemistry-transport model for treated wood leaching, aiming at understanding the intimate leaching mechanism of mineral and organic biocides. It considers biocides and wood chemistry based on the current knowledge (thermodynamic data) and experimental investigation. The capability of the developed model to simulate the chemical and transport behaviour is the main result of this study. The results obtained lead to the following conclusions concerning the biocide leaching behaviour. Copper is bound mainly by complexation mechanisms on phenolic and carboxylic groups on lignin and hemicellulose, even in the presence of monoethanolamine. Its leachability strongly depends on the chemical nature of extractives and on the pH value. Therefore the role of monoethanolamine is to provide a pore-solution pH of about 7.5 when the copper solubility is the weakest. But during dynamic leaching, the pore solution pH turns back to native pH and copper fixation becomes weaker.

Boron interacts weakly and exhibits a diffusional behaviour close to those of a tracer. Tebuconazole is captured by hydrogen-bound interactions on wood polymers and its leachability rises with the pH value. Further testing of the distribution of tebuconazole (trapped on the wood structure and leached or trapped on fractions dissolved from wood polymers) could confirm the mechanism used in the model. This work proved that the characterization leaching tests like ANC and DSLT, combined with appropriate analytical methods, are useful experimental tools. It is thus demonstrated that knowledge of main extractives' behaviour is a necessary step for the understanding of biocide leaching mechanisms. The presented model was developed and validated on the basis of laboratory leaching tests, considering the main chemical and transport mechanisms governing the biocides' behaviour. The complex nature of the material makes impossible the consideration of all properties, reactions, phenomena (inhomogeneity, polymers and pore evolution in time,...). Despite its limits, the interest of such model resides in its flexibility for representing and simulating various leaching conditions. Based on the chemical-transport model, the leaching behaviour of CBA treated wood could be simulated at larger scales and in natural exposure conditions. The consideration of temperature variation (including frost periods), distribution of preservatives in real wood samples or larger time spans could make the model adaptable for simulation of leaching behaviour of wood in real exposure scenarios. It is subject of current and future investigations. These capabilities make the leaching model an interesting tool for generating useful data for environmental risk and life cycle assessments of treated wood based materials and wastes.

3 Mineral (non-metallic) porous product: fibre-cement sheets

3.1 Introduction

Fibre-cement sheets are construction products used to cover the exterior of buildings in both industrial and domestic applications. They are manufactured for various use-situations: wet areas, acoustic, fire rated, structural and decorative purposes as well as flooring requirements. Fibre-cement sheets are a composite material, made of cement, sand (silica) and reinforcing fibres.

Fibre-reinforced cement-products were invented in the late 19th century by the Austrian Ludwig Hatschek, by mixing 90% cement with 10% asbestos fibres (St John et al., 1998). For over 100 years, this form of fibre-cement was extensively used for roofing, pipe and walling products in external use. After the discovery in the 70s that asbestos produced lung cancers years after professional or occasional exposure, asbestos use was progressively prohibited. Starting with the 80s, asbestos fibres were replaced with cellulose or synthetic fibres, e.g. polyvinyl alcohol (PVA) fibres.

Long-term performance and durability of fibre-cement composites have been research subjects worldwide, particularly after the replacement of asbestos with natural or synthetic fibres. It has been observed that cellulose fibre-cement materials can have performance drawbacks such as lower rot resistance and poorer long-term durability compared to asbestos cement composite materials. Cellulose fibres (cellulose and hemicellulose) are highly hydrophilic and porous, which makes them susceptible to bio-decay or rot attack when incorporated into cement composite materials (also porous) which are in contact with water. Thus, a technology of making reinforced cementations composite materials using biocide treated cellulose fibres has been developed (Merkley and Luo, 2004). Nevertheless, in high humidity environments, the pore spaces in the fibre-cement sheets facilitate water transport to the fibres and biocides could leach from the product. Fibre-cement sheets are very thin (4-10 mm), and even shallow depths of corrosion can generate significant impact on the bending strength.

Indeed, it has been observed that asbestos reinforced fibre-cement sheets that have undergone the effects of leaching can release asbestos fibres to the environment. Though the leaching behaviour of cement has been widely studied (Taylor, 1997; Faucon et al., 1996; Carde and Francois, 1999; van der Sloot, 2000, 2002; Engelsen et al., 2009, 2010), little is known about leaching from fibre-cement sheets (Babic, 2006). More precisely, there exists no information yet concerning the leaching behaviour of fibre-cement sheets based on synthetic fibres (not asbestos).

The objective of this study was to investigate and simulate the leaching behaviour of fibre-cement sheets and the release of potentially hazardous substances (organic biocides and heavy metals). The assessment is based on static and dynamic leaching tests. A numerical approach was also developed in view of simulating the long-term leaching behaviour of fibre-cement sheets based on synthetic fibres.

3.2 Materials and methods

Samples. The composition of fibre-cement sheets is usually: 2% PVA fibres, 5% cellulose fibres, 80% cement (Merkley and Luo, 2004) (sometimes the formulation contains $10 - 30\%$ inert fillers such as silica or limestone). The samples used in this study consist of a commercial product (fibre-cement profiled roofing sheet natural grey), bought on the market. For static leaching tests, the product was crushed (1mm), while the dynamic leaching tests were performed on monolith samples ($184\,\text{mm} \times 220\,\text{mm} \times 6\,\text{mm}$), with an exposure surface of $809.6\,\text{cm}^2$. In order to evaluate the leaching only by the surfaces which are in contact with water in real exposure conditions (not by the thickness of the product) the transversal sides were blocked by using an inert glue to cover the cut areas of the samples.

Target substances. A screening analysis (about 30 metals and more than 700 organics - see Appendix A) performed on eluates obtained from the preliminary static test (see protocol in chapter 2 §5.1) helped at defining the list of substances of interest, i.e. toxic species (heavy metals, biocides, organics) and other species necessary for developing a modelling approach. Besides different metals and anions that normally leach from the cement matrix, a wide range of organic substances was also detected in eluates from fibre-cement sheets (see Table 3.6). Many of these organic substances are known as biocides (pesticides, herbicides, fungicides, etc.) and need a deeper analysis. The list of target organic substances was limited to four organics: naphthalene, anthraquinone, terbutryn and fenuron. The rest of organic substances identified in the screening test were not selected for further analyses. They are either found in very small quantities (near to the detection limit, e.g. 2-nitrophenol), or identified in small concentrations only at pH below 4 (e.g. para-tert-octylphenol), or are biodegradable (e.g. DNOC), or are volatile (e.g. ethylbenzene, formaldehyde, acetaldehyde), or are not toxic (e.g. methylphenols).

Among the detected organic substances, naphthalene and octylphenol are found on the list of priority substances in water (EC, 2012a). However, because octylphenol was analysed in concentrations close to the detection limit, it was not further considered as a target substance.

Table 3.6: Substances from fibre-cement sheets detected in preliminary leaching tests.

Inorganic *	Ca, Na, K, Al, B, Fe, Si, Cr, Cu, Mo, Ni, Sr, Cl^-, SO_4^{2-}
Organic *	*naphthalene*, ametryne, dinitro-ortho-cresol (DNOC), propiconazole, *terbutryn*, 2-methylphenol, 4-methylphenol, acetone, *anthraquinone*, *fenuron*, ethylbenzene, meta+para xylene, acetaldehyde, formaldehyde, para-tert-octylphenol, 2-nitrophenol

* in *italics* the elements selected as target substances for ANC and DSLT tests (after preliminary testing).

Leaching tests. A static pH dependency leaching test was carried out (further called ANC), based on the TS 14429 (CEN, 2006) standard (see chapter 2 §5.2 of this manuscript). The principle of this test is to assess the pH leaching behaviour of all leached species in terms of equilibrium concentrations at different pH values. Crushed material was brought in contact with different concentrations of nitric acid, in order to force the pH of eluates to vary between 2 and 14, at fix liquid-to-solid ratio (10 L/kg). The suspensions were stirred for 48 h in an end-over-end roller. The pH measured in eluates on fibre-cement sheets with no acid addition (only demineralised water) is referred to as the natural pH of the material. To prevent microbial activity and thus, the deterioration of the concerned organic substances, an inhibitor (NaN_3) was used in concentration of 0.2 g/L (Jouannin, 2004; Hansen et al., 2005; Hansen and Andersen, 2006). The ANC test was performed on triplicate.

The dynamic surface leaching test (DSLT) was carried out in triplicate in specific reactors (see chapter 2 §5.3), based on the Technical Specification TS 2 from CEN/TC 351 (CEN, 2012b). The observed concentrations are the result of chemical changes and transport phenomena (e.g. diffusion processes in the pores) occurring during product/water contact. The objective of this test is to evaluate the coupled chemistry-transport processes. NaN_3 was used as inhibitor, in order to prevent the deterioration of the tracked organic pollutants. The ratio liquid to exposed surface of product was $10\,cm^3/cm^2$. In order to study the possible leaching from the applied glue, a blank test was carried out. The blank sample consisted in a glass sample covered with the same surface ($48.5\,cm^2$) of glue as the one used to block the longitudinal leaching from the original samples. Also, agitation was used over the whole duration of the DSLT test, i.e. 35 days.

Analytical methods. For all experimental assays (chemical characterisation of the material, equilibrium and dynamic leaching tests) the pH and the concentration of each target substance in eluates were analysed. Eluates were first vacuum filtered and then analysed for inorganic and organic species by standardised methods and with the corresponding detection limits, as seen in Table 3.7.

Table 3.7: Analytical methods used for the quantification of target elements.

Substance	Method[*]	Standard	Detection limit
DOC	DOC analysis	NF EN 1484	0.1 mg(C)/L
Heavy hydrocarbons	GC EQHYT		50 µg/L
Ca	IC	NF EN ISO 14911	1 mg/L
Na			1 mg/L
Mg			1.0 mg/L
Chlorides	IC	NF EN ISO 10304-1	1.0 mg/L
Nitrates			1.0 mg(NO_3)/L
Sulphates			1.0 mg/L
Al	ICP-OES	NF EN ISO 11885	5 µg/L
B			5 µg/L
Fe			5 µg/L
Sr			5 µg/L
Si			0.1 mg/L
Cr	ICP-MS	NF EN ISO 17294-2	0.2 µg/L
Cu			0.2 µg/L
Mo			0.2 µg/L
Ni			0.2 µg/L
Naphthalene	CMO MT02	Internal method	0.02 µg/L
Terbutryn			0.040 µg/L
Anthraquinone			0.020 µg/L
Fenuron			0.040 µg/L

[*] HPLC = High Plasma Liquid Chromatograph
ICPOES = Inductively Coupled Optical Emission Spectrometry
IC = Ion Chromatography
ICP-MS = Inductively Coupled Plasma Mass Spectrometry
CMO MT02 = liquid/liquid extraction: 1 L of sample is extracted in a mixture dichloromethane/ethyl acetate (80/20) at several pH values; the extract is analysed by a systematic multi detection in gaseous and liquid chromatography (HPLC/DAD, HPLC/MS/MS, GC/ECD/NPD, GC/MS)

The elemental total content of the material was determined by extraction with aqua regia followed by analysed by ICP/AES methods cf. NF EN ISO 11885. The inorganic species quantified are: Al, B, Ca, Cr, Cu, Fe, Mo, Ni, K, Si, Na, Sr.

The porosity of the monolith samples is a key parameter in the transport-chemical model. The open porosity of fibre-cement sheets was determined experimentally cf. NF P 18-459 standard, which describes the methods for the testing of porosity and density of hardened concrete.

3.3 Experimental results

The total content for the analysed elements is given in Table 3.8. The open porosity obtained by the experimental method is 38%, which is slightly higher than the porosity of cement based products.

Table 3.8: Total content of fibre-cement sheets in mg/kg of dry matter.

Al	B	Ca	Cr	Cu	Fe	Mo	Ni	Si	Na	Sr	K
10700	23.1	352000	42	31.9	22400	1.92	21.4	1070	1240	192	4920

Based on the quantitative results from ANC and DSLT test, we reduced the list of elements retained for the modelling approach, by eliminating those elements which were constantly released in quantities close to or less than the detection limits, i.e. Ni, naphthalene, anthraquinone and fenuron. The list of species used in the model is:

(i) highly soluble elements: Na, K, Cl

(ii) major elements in cement: Ca, Si, Al, Fe

(iii) pollutants potentially hazardous in natural leaching conditions: Cr, Cu, Mo, Sr, B, SO_4^2

(iv) organic biocide: terbutryn.

ANC tests delivered results under two forms: (i) final pH value of the eluate in function of H^+ moles added per L solution and (ii) variation of the concentration of target substances with pH (Figure 3.10).

The native pH is imposed by the mineral matrix of the product, between 12 and 13. By acid addition the pH decreases up to 10, corresponding to the depletion of C−S−H (calcium silicate hydrate) and portlandite. A high amount of acid is needed to descend towards pH 4 proving a strong capacity of acid neutralisation, mainly

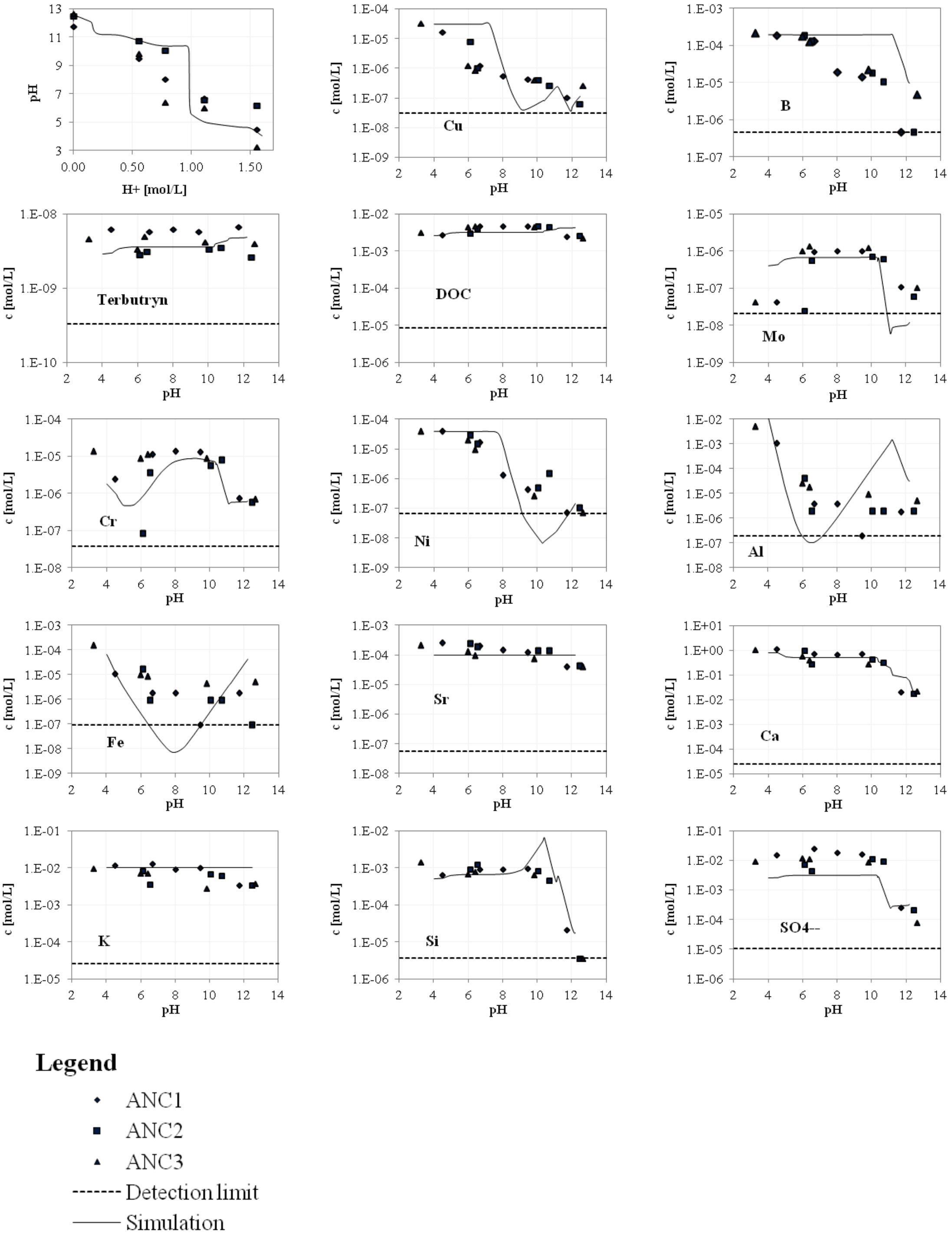

Figure 3.10: ANC results: experimental and simulation.

due to the buffering character of the carbonates. All major elements (Ca, Si, Al, K) and minor elements (Fe, Cl^-, SO_4^{2-}) are those typically found in cement matrixes and their leaching behaviour is identical with the one observed for concretes, i.e. in the most acid pH region all elements approached maximum leachability (van der Sloot, 2000; Barna et al., 2005; Engelsen et al., 2009; Schiopu et al., 2009).

Concerning the release of potentially hazardous species, several typical behaviours are encountered. Mo and Cr show a maximum release at neutral pH, a decrease at acid and alkaline pH. Along with Cu, these elements exhibit a leaching behaviour commonly encountered for cement based materials. B solubilisation increases with pH decrease, while Sr concentration remains constant. Terbutryn solubility and total dissolved organic matter DOC (organic compound originated probably in the fibres) don't depend on the chemical context (pH, mineral species' concentrations).

DSLT results are presented as curves of concentration in function of time (Figure 3.11). The observed concentrations are the result of chemical changes and transport phenomena (e.g. diffusion processes in the pores) occurring during product/water contact. The objective of this test is to evaluate the coupled chemistry-transport processes.

The differences between the triplicates in the ANC experimental data could be explained by the inhomogeneity of the samples. Because of the presence of fibres in the product, during the crushing procedure, the samples exhibited a certain heterogeneity (some contained more fibres, others more cement matrix). These differences are not visible in the DSLT test, where the samples were monolithic and thus at this scale homogenous and almost identical.

3.4 Model development and modelling results

The leaching behaviour of cement based products has been modelled by different authors. We used here an approach based on ANC and dynamic leaching tests, developed and presented elsewhere (Schiopu et al., 2009) mechanistic model that couples chemical aspects and transport phenomena specific for the interactions of the cement products with water. The geochemical code PHREEQC® (Parkhurst and Appelo, 1999) coupled with MINTEQ thermodynamic data base was used for the model implementation because of its capabilities on chemical modelling and for the facilities to add the transport components of the coupled model. The data base was completed with specific reaction constants taken from literature.

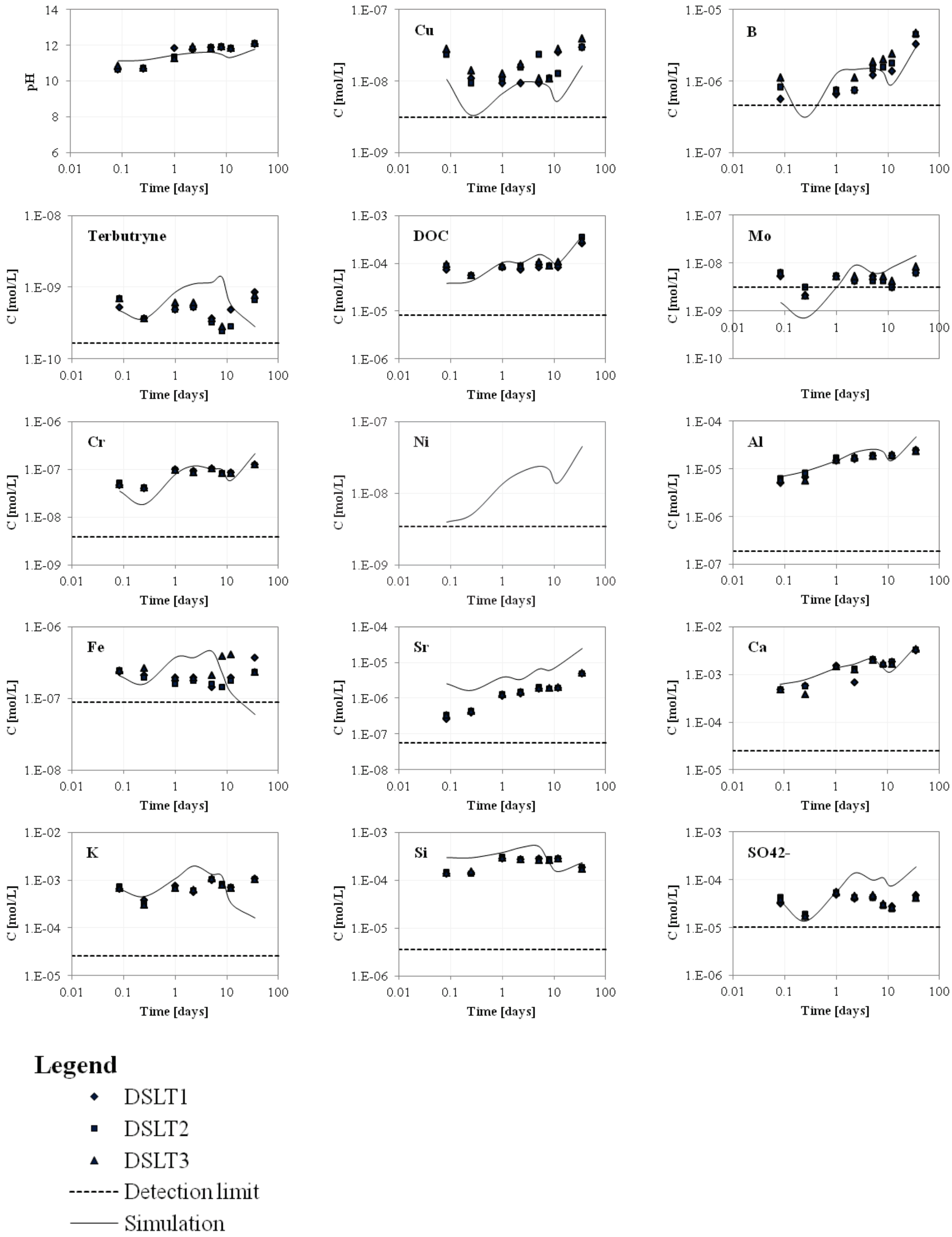

Figure 3.11: DSLT results: experimental and simulation.

The system product/water is characterised by two compartments which exchange flows, i.e. the pore-water in the pores of the product and the leachate compartment. Once the product brought in contact with water the system tends towards a new equilibrium state by transport process (composition of leachate different from that of the pore-water). Different processes take place:

(i) in the porous matrix: dissolution/precipitation processes, chemical reactions (acid/base, complexation, redox) in liquid phase, diffusion of soluble chemical species through the pores (from the core to the surface of the product) and transfer to the liquid;

(ii) in the leachate: chemical reactions between species, dissolution/precipitation reactions at the product/leachate interface (corrosion of the material surface), transport with the leachate and possibly interaction with a gas phase.

The model describing the leaching behaviour of a solid product is composed of: (1) a chemical model which considers all chemical reactions taking place in the pore-water of the product and (2) a transport model which takes into account the most important specific mass transfer and transport phenomena occurring in each compartment and between the compartments. Such a complex chemical-transport model was already considered for the modelling of leaching from cement based materials containing wastes and from construction products (Réthy, 2001; De Windt and Badreddine, 2007; Tiruta-Barna, 2008; Schiopu et al., 2009). Particularly the ANC test was essential for the chemical model development allowing identification and quantification of reactive mineralogical phases controlling the element release. The dynamic test DSLT allows the transport model development (mainly diffusion in pores) and finally the model calibration. The parameters for the model (mineralogical phases, diffusion coefficients) were fitted with the whole experimental data obtained.

The chemical model. The chemical model must describe the mineralogical phases and the chemical reactions occurring in the system product/water. The model developed by Schiopu et al. (2009) on concrete slabs was used, enriched with data referring to the organic background (synthetic fibres) and to the organic substances identified in eluates, which were not included in the above mentioned model. Moreover supplementary inorganic pollutants detected in eluates were considered in the model like boron, strontium, molybdenum.

In the chemical model information from literature about the mineralogical composition of cement based materials was considered. Calculation of saturation indexes (PHREEQC® - (Parkhurst and Appelo, 1999)) for eluates composition allowed the selection of those phases (initial and neoformed in contact with water) susceptible to control the element release in the laboratory test conditions. The developed geochemical model must simulate the neutralisation curve and buffering capacity of the product, the principles of such model have been described in detail elsewhere (Schiopu et al., 2009; Hareeparsad et al., 2011). The concrete materials are constituted mainly by amorphous CSH (hydrated calcium silicates) and contain portlandite, calcite, sulfoaluminates (e.g. ettringite), quartz and other silicates in different proportions. The components of concrete included in the model are: portlandite ($Ca(OH)_2$), CSH-gel-1.8 ($Ca_{1.8}SiO_{3.8}H_2O$), calcite ($CaCO_3$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_2 \cdot 26\,H_2O$), quartz ($SiO_2$), calcium aluminates ($Ca_3Al_2(OH)_{12}$). Soluble elements, i.e. Na, K, Cl (from soluble salts like NaCl, KCl) have been considered solubilised in the porewater at the beginning of the leaching process.

Other mineralogical phases were included in the model in order to explain the release of minor and trace elements observed in ANC eluates. Cu, Ni, Cr and Mo presented two different release patterns: (i) metal cations (Cu, Ni), which leach in high concentrations under acidic conditions and their release decreases with pH increase, and (ii) elements that form oxyanions (Cr, Mo) which present a solubility minima at pH 4-6 and a maxima at pH 8-11. Thus, copper behaviour was modelled by the dissolution and precipitation of its hydroxide ($Cu(OH)_2$) and tenorite (CuO). Nickel release is controlled by its hydroxide $Ni(OH)_2$. Ferrihydrite ($Fe(OH)_3$) was considered to be the solubility controlling mineral phase around neutral pH for Fe. The unleached content of Fe at pH 4.6 is present mainly as ferrihydrite. The model is in agreement with other studies on cement based materials, for example (Engelsen et al., 2010).

Molybdenum and chromium have a similar behaviour, typical for the substituted calcium aluminate-sulphates like ettringite and monosulphate by oxyanions, at alkaline pH. A chromium substituent of ettringite, Cr(IV)-ettringite ($Ca_6Al_2(CrO_4)_3(OH)_{12} \cdot 26\,H_2O$) (Gougar et al., 1996; Zhang and Reardon, 2003; Chrysochoou and Dermatas, 2006) was considered in the model. Molibdate ion in cement also forms substituted ettringite and monosulphate, as reported in literature (Kindness et al., 1994; Klemm, 1998). These are solid solutions phases with ettringite or monosulphate and powellite as end-members. In this model substituted monosulphate ($Mo-AFm$) was considered, calculated as solid solution. In neutral and acid conditions these phases are dissolved and powellite ($CaMoO_4$) precipitates. The behaviour of Mo and Cr at pH 5-6 was modelled considering surface complexation of respective anions (MoO_4^{2-}, CrO_4^{2-}) on sorbent surfaces like ferrous hydroxides. The diffuse two-layer model of Dzombak and Morel implemented in PHREEQC® and the complexation constants supplied with MINTEQ database were used. The combination of these 2 mechanisms explains the shape of the ANC concentration curve. Boron exists probably as substitution in ettringite like ($Ca_6Al_2O_4(B(OH)_4)_2(OH)_8 \cdot 26\,H_2O$) (Csetenyi and Glasser, 1993; Gougar et al., 1996; Zhang, 2000; Sun and Wang, 2010), explaining its low availability in alkaline solution. Adsorption on iron hydroxides could be expected in neutral conditions.

Strontium may occur as a metasilicate (SrSiO3), with possible interaction with solubilized SO_4^{2-} as celestite ($SrSO_4$). New phases can form by dissolution of the material constituents at neutral or acid pH: gibbsite ($Al(OH)_3$), gypsum ($CaSO_4 \cdot H_2O$), SiO_2 amorphous.

Concerning the organic matrix, terbutryn and global DOC leaching was modelled. Because no information on the binding of terbutryn on the cement or fibre structure was found in literature, the leaching was modelled by a solubilisation mechanism. Similarly was modelled also the leaching of DOC (dissolved organic carbon).

The reactions considered in the model and the corresponding constants are given in Table 3.9. The initial concentration of each phase in the solid matrix was evaluated based on the concentrations of each species in the ANC eluates and on experimental investigations of the elemental mineral total content.

The coupled chemical-transport model. DSLT curves showed the variation of the concentrations of each species with time, in leachates on monolith samples. The chemical model presented above (and validated by ANC experimental results) was used, with transport parameters.

The diffusion coefficient was firstly estimated by fitting the diffusion model to the release data for soluble ions Na, K and Cl considered as tracers. A diffusion coefficient of 8×10^{-12} m^2/s was estimated, which is a common value for cement matrixes.

Table 3.9: Parameters used in the model.

Mineralogical phase	Dissolution/precipitation reaction	log K	Initial concentration mol/L	References
B-Ettringite	$Ca_6Al_2O_4(B(OH)_4)_2(OH)_8 \cdot 26\,H_2O + 18\,H^+ = 2\,Al^{3+} + 6\,Ca^{2+} + 40\,H_2O + 2\,H_3BO_3$	120.87	0.0001	(Csetenyi and Glasser, 1993)
$Ca_3Al_2(OH)_12$–cement	$Ca_3Al_2(OH)_{12} + 12\,H^+ = 2\,Al^{3+} + 3\,Ca^{2+} + 12\,H_2O$	80.33	0.05	(Lothenbach and Winnefeld, 2006)
Calcite	$CaCO_3 = Ca^{2+} + CO_3^{2-}$	-8.475	0.3	MINTEQ
Cr-Ettringite	$Ca_6Al_2(CrO_4)_3(OH)_{12} \cdot 26\,H_2O + 12\,H^+ = 2\,Al^{3+} + 3\,CrO_4^{2-} + 6\,Ca^{2+} + 38\,H_2O$	60.54	3e-006	MINTEQ
Csh−gel−1.8	$Ca_{0.8}SiO_{2.8} \cdot H_2O + 1.6H^+ + 2.2H_2O = 0.8Ca^{2+} + 2\,H_2O + H_4SiO_4$	11.08	0.13	Stronach and Glasser (1997)
DOC(s)	$DOC = DOC$	-2.35	0.01	This study
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_12 \cdot 26\,H_2O + 12\,H^+ = 2\,Al^{3+} + 6\,Ca^{2+} + 38\,H_2O + 3\,SO_4^{2-}$	62	0.006	LLNL
Ferrihydrite	$Fe(OH)_3 + 3\,H^+ = Fe^{3+} + 3\,H_2O$	4.891	0.0002	(Engelsen et al., 2009)
Portlandite	$Ca(OH)_2 + 2\,H^+ = Ca^{2+} + 2\,H_2O$	22.675	0.08	MINTEQ
Strontium metasilicate	$SrSiO_3 + 2\,H^+ + H_2O = H_4SiO_4 + Sr^{2+}$	14.8438	0.0001	LLNL
Tenorite	$CuO + 2\,H^+ = Cu^{2+} + H_2O$	7.62	3e-005	(Engelsen et al., 2009)
Terbutryn(s)	Terbutryn = Terbutryn	-8.3	1e-006	This study
Mo-AFm0.5	$Ca_{2.5}(MoO_4)_{0.5}Al(SO_4)_{0.5}(OH)_6 \cdot 3\,H_2O + 4\,H^+ =$ $Al^{3+} + 2.5Ca^{2+} + 7\,H_2O + 0.5MoO_4^{2-} + 2\,OH^- + 0.5SO_4^{2-}$	-4	6e-006	This study
$Ni(OH)_2$	$Ni(OH)_2 = Ni^{2+} + 2\,OH^-$	10.8	3.8 e-5	MINTEQ
Powellite	$CaMoO_4 = Ca^{2+} + MoO_4^-$	-7.94	-	MINTEQ
Silica	$SiO_2 + 2\,H_2O = H_4SiO_4$	3.018	-	MINTEQ
Gypsum	$CaSO_4 \cdot 2\,H_2O = Ca^{2+} + SO_4^{2-} + 2\,H_2O$	4.848	-	MINTEQ
Gibbsite(C)	$Al(OH)_3 + 3\,H^+ = Al^{3+} + 3\,H_2O$	-7.77	-	MINTEQ
$Cu(OH)_2$	$Cu(OH)_2 + 2\,H^+ = Cu^{2+} + 2\,H_2O$	-8.64	-	MINTEQ
Celestite	$SrSO_4 = Sr^{2+} + SO_4^{2-}$	6.465	-	MINTEQ
Na^+			0.006	
K^+			0.013	
Cl^-			0.002	
Ferrihydrite sites	$AfhOH + H^+ = AfhOH_2^+$	7.29	0.002	MINTEQ
(AfhOH)	$AfhOH = AfhO^- + H^+$	-8.93		MINTEQ
	$AfhOH + CrO_4^{2-} + H^+ = AfhCrO_4^- + H_{2O}$	10.85		MINTEQ
	$AfhOH + CrO_4^{2-} = AfhOHCrO_4^{2-}$	3.9		MINTEQ
	$AfhOH + SO_4^{2-} = AfhOHSO_4^{2-}$	0.79		MINTEQ
	$AfhOH + MoO_4^{2-} = AfhOHMoO_4^{2-}$	2.4		MINTEQ
	$AfhOH + H_3BO_3 = AfhOHH_3BO_3$	0.62		MINTEQ

3.5 Discussions

Material leaching behaviour. The studied product exhibits a cement-like behaviour during leaching, as shown in Figure 3.10 and Figure 3.11. The neutralisation curve and the buffering capacity obtained in ANC test are explained by the presence of typical cement phases: portlandite, C-S-H and calcium carbonate.

The behaviour of high soluble elements (i.e. K, Cl) is independent of the pH. The major elements Ca, Si, Al behaviour is controlled by the different mineralogical phases shown in Table 3.9, i.e. CSH and portlandite, calcium-aluminate, gibbsite, ettringite in alkaline media, amorphous SiO_2 and gypsum in neutral media. The sulphate behaviour was controlled by ettringite at alkaline pH, by gypsum at neutral pH and thus indirectly by the Ca release as well. The Cu, Ni and Fe release is controlled by their oxides/hydroxides. Mo, Cr and B release is determined by substituted ettringite and monosulphate phases in alkaline conditions and by adsorption on iron hydroxides in neutral conditions when ettringite and monosulphate are dissolved. Sr was also detected in leachates coming probably from silicates present in cement matrix.

If compared to the total content (see Table 3.8) during ANC, Cu and Mo leached up to approximately 60% (the maximum corresponds to the most acid pH, i.e. 3.26). B leached approximately 98% from its total content (at pH 3.26), whereas Cr leached only 17% at acid pH. Other studies which observed the leaching behaviour of cement based materials under the same experimental conditions, i.e. ANC test, report similar leaching ratios, compared to the total content. For example, Schiopu et al. (2009) observed the leaching behaviour of concrete slabs during pH dependency tests and found that all major pollutants (Cu, Mo, Cr, B) leach in maximum quantities at acid pH and in concentrations similar to those observed in the current study. Engelsen et al. (2010) characterised the leaching of minor and trace elements released from recycled concrete aggregates. van der Sloot (2002) studied the leaching behaviour of concrete mortars. Both studies showed a similar release pattern for major and trace elements.

Concerning leaching during dynamic tests, a high release was observed for B and Sr (approx. 6% from total content). Cu and Mo release was up to 2% after 35 days. These results are also in line with previous studies made on concrete.

In what concerns the organics released, a possible source for the DOC is the degradation of cellulose fibres. Previous studies show that the high alkalinity of pore-water in the cement matrix weakens the cellulose fibres, induces their decomposition (Tolêdo et al., 2000) and, consequently, leads to the decay of the composite tenacity in the long term exposure. On the other hand, the constant presence of the organic biocide terbutryn (CAS 886-50-0) in eluates from fibre-cement was unexpected. This biocide belongs to the class of triazines. It was of interest to include it on the list of target substances as it has not been detected before in eluates from fibre-cement products without core or surface treatment, or added coatings. Nevertheless, it is widely used in the construction products' industry in renders, in order to protect the building's envelope against growth of grasses and aquatic algae (PPDB, 2007) and in the core or surface treatment of construction products (Bagda et al., 2000; Menge et al., 2005; Paulus, 2005). Moreover, several studies reveal its presence in receiving waters of urban water catchments (Quednow and Püttmann, 2007; Schoknecht et al., 2009; Burkhardt et al., 2011). The only valid explanation for its presence in eluates from fibre-cement sheets (in both ANC and DSLT tests) could be that it was previously used in the treatment of the cellulose fibres, which were later embedded as reinforcement in the final product (mixed with cement), in order to prevent the biological attack of the fibres and thus, the mechanical degradation of the product. The leaching of terbutryn and total dissolved organic matter DOC was modelled as solubilisation process and diffusion in porewater. The highest release of terbutryn 0.016 mg/kg was at alkaline pH in ANC test.

As mentioned in section §3.2, four organics have been traced in eluates from ANC tests. However, only terbutryn was identified above the detection limit in all eluates. The solubility of the traced organics (napthahalene, anthraquinone, terbutryn and fenuron) is given in Table 3.10, along with the highest measured quantities in eluates. We notice a very high discrepancy between the two values. For naphthalene, for example, the released quantity is 105 times smaller than its solubility in water. So, either their presence in the material was very small (traces) or these organics were strongly adsorbed on other organic (or, less probable, mineral) phases.

The adsorption of the herbicide fenuron (CAS 101-42-8) has been very little investigated. Aguer et al. (2000) studied the adsorption of fenuron on smectites (which belong to the clay minerals' class) and observed that fenuron was adsorbed as neutral molecule on uncharged siloxane surface by hydrophobic bonding, with some contribution of polar bond. Nevertheless, its adsorptivity remains low (one fenuron molecule for each 2000-200 exchange sites), which suggest a high mobility of fenuron in natural soil and water systems. We concluded that fenuron cannot be

Table 3.10: Solubility of organic trace elements.

Substances	Highest release ANC mg/L	Solubility in water at 20°C mg/L
Naphthalene	1.70e-04	32
Anthraquinone	1.90e-04	0.12 0.60
Terbutryn	1.60e-03	20
Fenuron	4.00e-04	3.85

significantly fixed by the matrix but instead it is little present in the material, only traces, and it was therefore not included in the leaching mechanism of the studied fibre-cement sheets.

Terbutryn complexation on soil has been intensively investigated, as reviewed by (Daho, 2006). The adsorption/desorption studies indicate that the mobility in soil ranges between low and medium in the different soils tested. Barriuso et al. (2000) observed that decreasing soil pH generally increases herbicide adsorption. We notice that the leaching from fibre-cement sheets presented a rather independent pH behaviour. Also, the soil organic matter is the most important factor controlling the adsorption of terbutryn on oxisols. This could lead to the assumption that a possible adsorption of terbutryn on the cellulose fibres from the fibre-cement sheets may be considered. However, no studies were made on the possible adsorption of this herbicide on the components of construction products and thus, no mechanisms are yet defined and no complexation constants exist. For modelling we assumed that the solubility law governed terbutryn behaviour and that it was found in small quantities in the product.

For the validation of these assumptions, further analytical tests need to be performed.

Because the fibre-cement sheets are used in the buildings' envelope, their surface area is an important scenario parameter. The released quantities of hazardous species, expressed in mg of substances per kg and per m of product, are presented in Table 3.11. The release during ANC tests is up to 30 times higher than during the dynamic test, explained by the aggressive experimental conditions (pH, high contact product-water and high liquid-solid ratio). A high release of DOC is observed, which could be the consequence of the decomposition of fibres in the alkaline environment in the pores, induced by the cement matrix. If compared to their initial content (see Table 3.8), B, Cu, Mo, Ni and Sr leach in high quantities in the ANC test. Still, Ni has not been detected in eluates from DSLT tests, which is in coherence with the measured concentrations at natural pH (alkaline pH) in ANC eluates.

Table 3.11: Maximum and total release of pollutants, in mg per kg and per m^2 of product, in ANC and DSLT tests (experimental data).

Substance	ANC mg/kg	ANC % of TC	DSLT mg/kg	DSLT % of TC	DSLT mg/m^2
DOC	573	ND	110	ND	1146
B	22.6	97.84	1.27	5.49	13.64
Cr	7.2	17.15	0.36	0.85	3.49
Cu	19.9	62.38	0.09	0.29	0.94
Mo	1.27	66.09	0.04	1.90	0.37
Ni	1.68	78.79	ND	ND	ND
Sr	218	113.54	12.8	6.65	128
Terbutryn	0.016	ND	0.009	ND	0.09

Model. The main limitations of the developed model concern the chemistry of organic compounds in the cement matrix and the possible interactions with DOC and fibres. Concerning specific organic compounds in cement matrix, the issue is rather recent and there is no specific literature investigating their leaching release and modelling. More accurate modelling of this complex system is not possible without deeper experimental investigations e.g. equilibrium solubility in pore-water, sorption on fibres and cement phases supported by structural analysis, etc. Other limits inherent to geochemical modelling concern the availability of thermodynamic data for specific phases containing minor elements.

Despite the model limitations and the uncertainties in the experimental measurements, in general the developed model was able to predict the measured pollutant concentration over the entire pH range. Also, a good agreement between experimental and simulated results was observed for dynamic scenarios. The chemical model represents satisfactorily the ANC test results for the major elements and for trace elements. It is in agreement with other previously reported models for cement based materials, the same kind of mineralogical phases are considered. Also, it has been shown that a significant amount of information can be drawn from the pH dependent leaching characterisation test.

Long term leaching behaviour. The leaching behaviour of a fibre-cement product has been numerically simulated for long term exposure to rain water. The coupled chemical-transport model was developed and validated at laboratory scale. This model was used together with information concerning natural exposure conditions to simulate the leaching behaviour over 1 year. A run-off scenario was considered (for more details see chapter 4 §3), such that the product stays in contact with meteoric water over 1 year. The exposure conditions are taken from (Schiopu, 2007). An average constant flux was considered for the leachate, i.e. rain water. The simulation was performed on a real-scale sample, i.e. $1.1\,\text{m} \times 0.918\,\text{m} \times 0.0067\,\text{m}$. The scenario parameters used in the simulation are given in Table 3.12 while the chemical and transport parameters are presented in Table 3.9.

Table 3.12: Parameters specific for the long term simulation.

Total rain	$800\,\text{L/m}^2\text{/year}$
Monthly rain flux	$66.67\,\text{L/m}^2\text{/month}$
Sample surface	$1.1475\,\text{m}^2$
Open porosity	0.38 %
Diffusion coefficient	$8 \times 10^{-12}\ \text{m}^2\text{/s}$

The numerical simulation results over 1 year exposure at field scale in run-off scenario are shown in Figure 3.12.

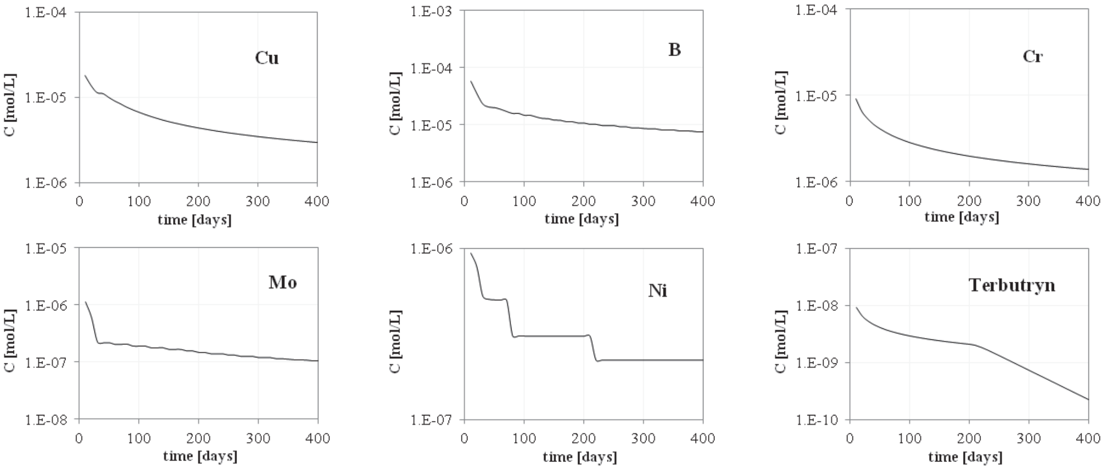

Figure 3.12: Leaching behaviour of hazardous species of fibre-cement sheets over 1 year in natural exposure conditions - simulation results.

The pH and concentration of monitored species in leachates was represented as function of time. Variations over at least one order of magnitude are observed for almost all chemical species. The cumulative release after 1 year of exposure is calculated in Table 3.13. It is rather high if compared to the initial total content of the target elements.

Table 3.13: Cumulative emissions for potentially hazardous species from fibre-cement sheets after 1 year in natural exposure conditions - simulation results.

Chemical species	Cumulative emission $g/m^2/year$	% TC
Al	5.17	3.7
B	0.132	44.0
Cr	0.117	21.4
Cu	0.319	77.0
Ni	0.0166	6.0
Mo	0.0160	64.1
Sr	0.639	25.6
Terbutryn	4.60×10^{-4}	TC not determined
DOC	21.1	TC not determined

The obtained leaching data can be further used for environmental assessment of the fibre-cement sheet product. The integration of leaching data in a LCA approach at building scale is presented in chapter 4 §3.

3.6 Conclusions

The methodology for the leaching behaviour assessment was applied to a fibre-cement sheet product. At laboratory scale, the use of the proposed leaching tests allowed the identification of the main chemical and transport mechanisms and parameters of the leaching process. These data were then used for the development of a chemical-transport model. However, the experimental setup was not sufficient for elucidating the mechanisms of fixation/mobilization of specific organic compounds (biocides or other hazardous compounds). The knowledge of the intimate mechanisms requires specific investigations like the determination of adsorption isotherms.

The studied material exhibits globally a cement-type leaching behaviour with respect to the mineral species. Even if present in trace proportions, potentially hazardous species are released in significant quantities if compared to the total content. The simulation of upscaled scenarios allows the evaluation of the cumulative release over long periods and then the integration of leaching data in appropriate environmental assessment methods. This study is the first one dedicated to fibre-cement construction products.

4 Organic non-porous product: bitumen membranes

4.1 Introduction

Bitumen membranes are used on flat or nearly flat roofs, most commonly in commercial application, though they are becoming increasingly more common in residential application too.

Membrane roofs are made from synthetic rubber, thermoplastic (PVC or similar material), or modified bitumen. Modified bitumen sheet membranes were developed in the early 1960s. They are composed of multiple layers of reinforcing fabrics (polyester, fibreglass or a composite carrier) that serve as carriers for the hot polymer-modified bitumen as it is manufactured into a roll material. The modified bitumen sheets are usually coated with a gravel layer to provide UV protection.

Unlike older roof coverings, which contained coal tar, modern bitumen roof coverings are made entirely of mineral oil bitumen. Coal tar consists largely of PAH (Polycyclic Aromatic Hydrocarbon) 10^4 times more PAH per kg of product than mineral oil bitumen products. Products containing coal tar have been prohibited since 1989 and their use declined sharply from the beginning of the 80s when roof insulation increased.

Besides leaching of PAH, biocides are also susceptible of leaching from bitumen membranes. Bituminous sealing membranes may be protected against root penetration by the addition of herbicides (i.e. Mecoprop (Bucheli et al., 1998)), which might leach at contact with rain water.

The objective of this study was to investigate the leaching behaviour of bitumen membranes. The difficulties encountered concerned the applicability of the classical leaching tests (pH dependency and dynamic tests) on the considered product, i.e. organic, non porous, bituminous, dense.

4.2 Materials and methods

4.2.1 Samples

Two types of leaching tests were performed on a commercial product: a pH dependency test (ANC) and a dynamic leaching test (DSLT). The ANC test is normally carried out on crushed material (≤ 1 mm) cf. protocol described in TS 14429 standard. In the case of bitumen products, the crushing procedure led to the melting of the bitumen and the impossibility of effectively crushing the product. An attempt to crush the bitumen product was made by using dry ice (carbon dioxide in solid phase), however without success. The friction in the mill rapidly heated the product and caused the melting of the bitumen. Nevertheless, a small quantity of crushed product could be recovered and used in a simplified pH dependency test.

However, in order to better explain the pH dependency of the bitumen membranes, small samples ($1\,\mathrm{cm}^2$) were cropped and used in an ANC test; nevertheless, the contact surface product/leachate is much smaller than for crushed samples.

Monolith samples for the dynamic surface test ($18.5\,\mathrm{cm} \times 18.5\,\mathrm{cm}$) were cut out in order to fit the reactor dimensions. The gravel layer was not removed from the samples.

4.2.2 Target substances

The preliminary tests, based on the protocol described in chapter 2 §5.1 helped at defining the list of substances of interest, which were further analysed in the ANC and DSLT test. The screening analysis (about 30 metals and more than 700 organics see Appendix A) restricted the target substances to a couple of minerals and organics, as shown in Table 3.14.

Table 3.14: Target substances for bitumen membrane analysed in preliminary leaching tests.

Inorganic	*Al, Ca, Fe, Mg, Na,* SO_4^{2-}
Organic	DOC, *heavy hydrocarbons*, *naphthalene*, para-tert-octylphenol, *mecoprop (MCPP)*, 2-methylnaphthalene, *fenuron*, ethylbenzene, xylene (ortho, meta, para), *formaldehyde*, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2-nitrophenol, *nonylphenols*, trinexapac-ethyl

DOC (Dissolved Organic Carbon) and the heavy hydrocarbons' amount have been analysed in order to evaluate the total organic release. Other organics identified during the screening can be classified as follows: substances with low toxicity (e.g. 2-methylnaphthalene), BTEX (e.g. ethylbenzene, xylene), organics with small solubility in water (e.g. methylphenols) and pesticides (e.g. MCPP, fenuron). Several organics mentioned above have been detected only in traces or were not persistent in all eluates (e.g. trinexapac-ethyl, 2-methylnaphthalene), which is why they were excluded for further testing.

Found on the list of priority substances under the Water Framework Directive (EC, 2012a), naphthalene and nonylphenols have been analysed in eluates from ANC and DSLT tests. The biocides Fenuron (CAS No: 101-42-8) and Mecoprop –

Table 3.15: Analytical methods used for the quantification of target elements.

Substance	Method	Standard	Detection limit
DOC	DOC analysis	NF EN 1484	0.1 mg(C)/L
Heavy hydrocarbons	GC EQHYT		50 µg/L
Ca	IC	NF EN ISO 14911	1 mg/L
Na			1 mg/L
Mg			1.0 mg/L
Sulphates	IC	NF EN ISO 10304-1	1.0 mg/L
Al	ICP-OES	NF EN ISO 11885	5 µg/L
Fe			5 µg/L
Naphthalene	CMO MT02	Internal method	0.02 µg/L
Fenuron			0.040 µg/L
Mecoprop			0.020 µg/L
Nonylphenols	GC/MS		0.040 µg/L
Formaldehyde			1 µg/L

MCPP (CAS No: 7085-19-0) have been detected in all eluates. MCPP and fenuron are specific herbicides used in several treatment products, which are applied on bitumen membranes against root growth (Burkhardt et al., 2011). Formaldehyde was selected because its presence in eluates could increase the solubility of other organics.

4.2.3 Analytical methods

The pH and the concentration of each target substance were analysed for eluates from both equilibrium and dynamic leaching tests. Eluates were first vacuum filtered and then analysed for inorganic and organic species by standardised methods and with the corresponding detection limits, as seen in Table 3.15.

4.2.4 Leaching tests

A static pH dependency leaching test (ANC test – Acid/base Neutralisation Capacity test) based on XP CEN/TS 14429 (CEN, 2006) was performed on crushed samples (see explications above concerning the crushing). This test provides information on the influence of pH on pollutant release, acid/base neutralisation capacity and physico-chemical stability of the material. For alkaline solutions we used NaOH, while for acid solutions we replaced HNO_3 solutions, as advised in the standard, with HCl solutions (because of the strong oxidation character of HNO_3 and given the organic nature of the product). Also, in order to prevent microbial activity and thus, the deterioration of the concerned organic substances, an inhibitor ($HgCl_2$) was used (Jouannin, 2004; Hansen et al., 2005; Hansen and Andersen, 2006). Due to the lack of crushed material, we could not perform the ANC test in triplicate, as advised in the standard. Moreover, the leaching behaviour of the product was studied only at 4 different values of the pH. The ratio liquid/solid (L/S) was 10 L/kg. The pH stabilisation was achieved only after 7 days (Figure 3.13).

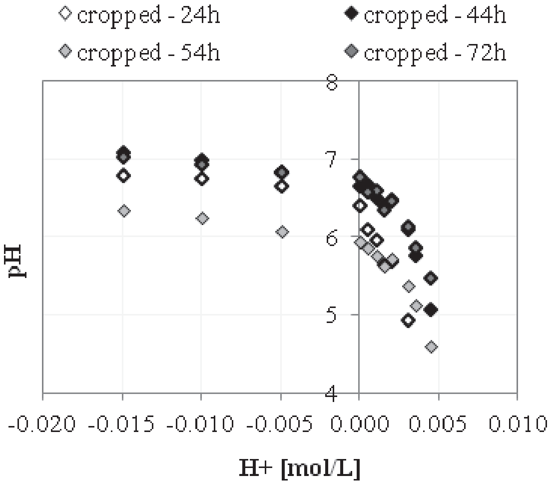

Figure 3.13: pH dependency of cropped bitumen samples at different contact times.

Using the same L/S, we performed an ANC on small cropped samples (1 cm^2), and analysed the pH of the leachates during 72 hours in 10 acid/alkaline solutions and one native pH solution, i.e. demineralised water, without acid or base added.

The dynamic test (DSLT – Dynamic Surface Leaching Test) was carried out cf. TS 2 from CEN/TC 351 (CEN, 2012b) in special conceived leaching reactors (see description in chapter 2 §5.3). This test is used to describe time dependency of leaching of different components. NaN_3 was used as inhibitor to prevent microbial activity. Seen the results from the ANC test and the nature of bitumen (non-porous, dense monolith), two situations were simulated in duplicate: (i) a high ratio liquid/solid (L/A) of 10 cm^3/cm^2 and (ii) a small ratio liquid/solid (L/A) of 5 cm^3/cm^2.

4.3 Experimental results

The evolution of the pH of cropped samples, i.e. 1 cm^2, is shown in Figure 3.13. The native pH stabilises after 3 days at around 7. The ANC performed on crushed samples (equilibrium reached after 7 days) shows a slightly different pH dependency than cropped samples (see Figure 3.14). The native pH of crushed bitumen membranes is around 8. Between pH 11 and 6, the pH curve descends very sharp, followed by a smooth descent till pH 4. A higher buffering capacity was observed for the crushed product in alkaline conditions, than for the cropped samples. The phenomenon is opposite under acid conditions.

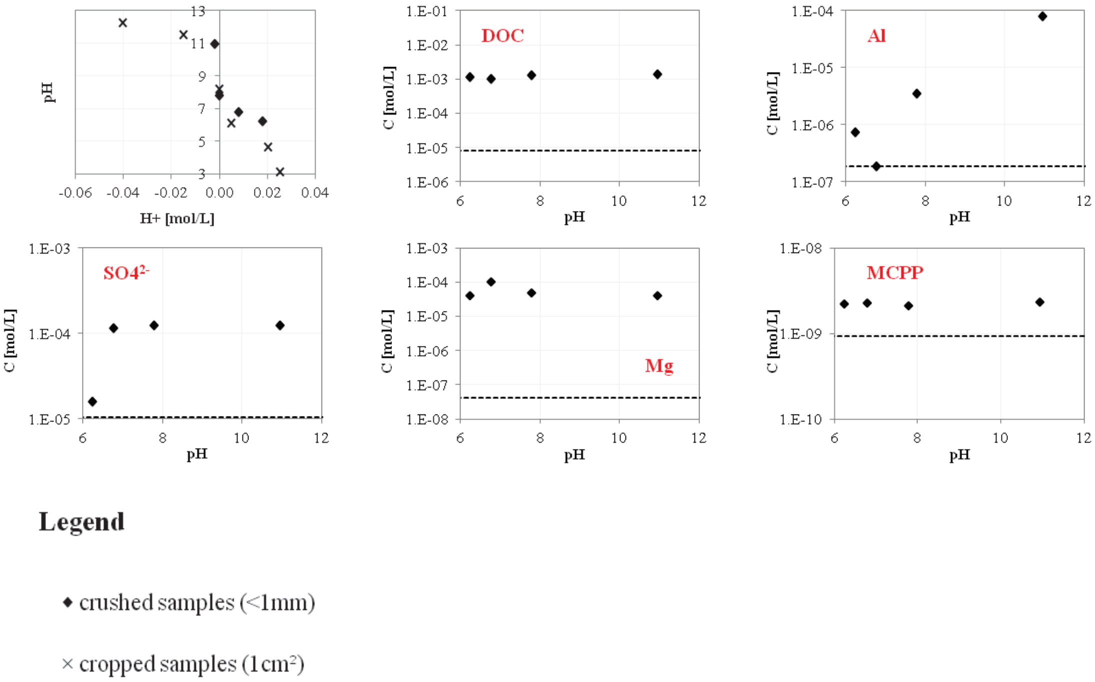

Figure 3.14: ANC results on crushed samples (≤ 1 mm) at equilibrium after 7 days.

During ANC tests, bitumen membrane released small quantities of DOC, namely 0.012 gC/L, 5 times more than the fibre-cement sheets, but 30 times less than treated wood. This is surprising because the product is based on organic matter. The release doesn't, however, depend on the pH. The leaching of MCPP is also pH independent. The same pH-independent behaviour was observed for several other substances (e.g. Mg, Fe). Nevertheless, it should be noted that the pH in the performed ANC tests on crushed samples ranges between 6 and 12. No information was obtained for acid pH values.

Eluates from DSLT were analysed only for organic species. The emissions in two different leaching scenarios, i.e. L/A = 5 cm^3/cm^2, respectively 10 cm^3/cm^2, are presented in Figure 3.15 as variation of concentration with time. Only DOC was observed in eluates. The other organics, i.e. naphthalene, MCPP and formaldehyde were not detected (close to the detection limit).

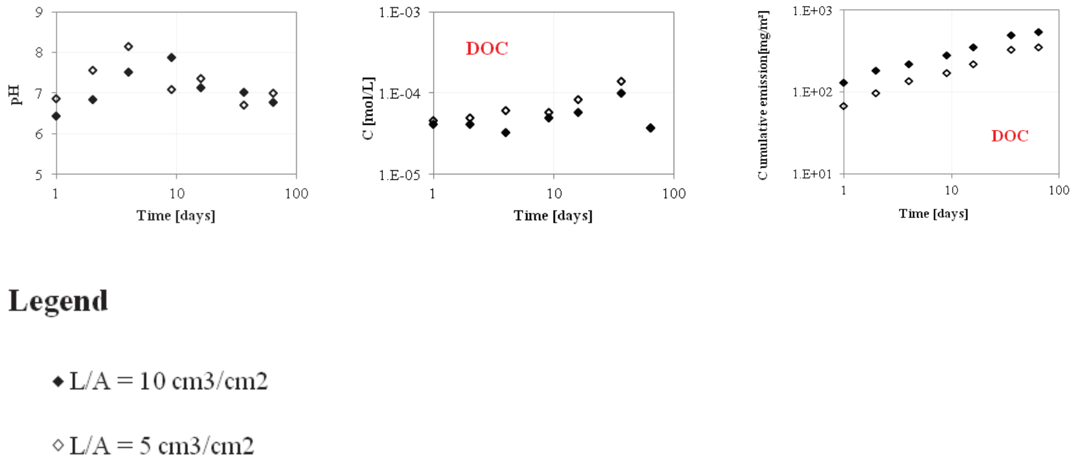

Figure 3.15: DSLT results.

4.4 Discussion and conclusions

The leaching behaviour of bitumen membranes was investigated only partially. The study was limited to experimental investigations. Because of the organic structure of bitumen, we were not able to obtain proper samples for the pH dependency test, i.e. crushed product. However, the ANC test performed on a small quantity of crushed material showed a pH independent behaviour for all organic potentially hazardous species. The second ANC performed on small cropped samples showed a smaller native pH.

The equilibrium in the case of crushed samples was reached after 7 days, which is explained by the slow diffusion processes which might take place from the inner to the exterior of the small crushed samples, considering that the product is non-porous. For the cropped samples, an equilibrium state was observed after 3 days. Nevertheless, diffusion might be an influent parameter, given the size of the samples and we expect that the observed results represent rather a wash off process than a core dissolution /diffusion one. In the case of crushed samples, the carrier structure (polyester, fibreglass or a composite carrier) was destroyed, while the cropped samples might be considered as miniature monolith samples, thus, the diffusion remains a rate controlling step.

As assumed, bitumen membranes released small quantities of inorganic species, i.e. Al, Fe, Mg, Ca, Na. The primary source might be the gravel in the upper layer, meant to offer UV protection.

In what the organic release concerns, although preliminary leaching and ANC tests permitted to identify some organic biocides (e.g. MCPP, fenuron and naphthalene), they have not been found in eluates from DSLT. This could be explained by the higher liquid to solid ratio (2.5 to 5 times higher than in ANC test). Indeed, even during ANC tests the concentrations were close to the detection limit. Hence, dilution makes them undetectable. The concentration of DOC, on the other hand, has been measured in all eluates from DSLT samples and a slightly higher release is observed when the ratio leachate/product is higher, i.e. $10\,\mathrm{cm}^3/\mathrm{cm}^2$ (see Figure 3.15).

From this study several conclusions could be underlined.

For this type of products non porous, water repulsive material, such as bitumen, the most important parameter is the contact surface with water. The leaching is reduced at wash off since the internal diffusion is expected to be very slow. Consequently the L/A ratio is an important parameter. In order to observe a relevant release the leaching test should be adapted by using lower L/A ratios, and possibly microbial inhibitor when labile organic compounds are involved. Finally, the difference between ANC and DSLT tests is not obvious since for both the samples are consolidated pieces. Ideally, a protocol must be developed for an efficient crushing of such kind of material in order to ensure an intimate contact and dissolution in ANC test.

This work demonstrates that a horizontal leaching procedure is difficult to apply for any construction product and that some test adaptations must be foreseen depending on the material, in order to provide relevant information.

5 A database for leaching data – LixiBat

This section has been published in the proceedings of the *World Sustainable Building Conference* (18 – 21 October, 2011 Helsinki, Finland), with the following reference:

Lupsea, M., Schiopu, N., Tiruta-Barna, L., Laurent, N., LixiBat - A Database for the Leaching Characteristics of the Building Products, World Sustainable Building Conference, 2011, Helsinki, Finland

5.1 Introduction

The building during its life stage is responsible for multiple environmental impacts at local scale (indoor air quality air as transfer vector, water and soil pollution water as transfer vector). The pollution transfer vector of concern in this paper is water. The demand regarding the assessment of the environmental performances of building products placed in real scenarios implying contact with water is continuously growing. At European scale, this problem has been raised by the European Commission mandating the European standardisation Committee (Mandate M/366) in 2005 to start the work on defining experimental methods for characterising emissions from building products during the stage of service life (CEN, 2012a).

Recent researches have shown that a large typology of pollutants originated in building materials is present in the environment's compartments. Biocidal active substances are often used in renders and paints for exterior façade coatings to avoid growth of fungi and algae (Schoknecht et al., 2009); afterwards they are found in surface water (Skark et al., 2004; Chevre et al., 2006). The latest research on the Zürich (Switzerland) sewage show a three times higher concentration than admitted in biocidal substances (Burkhardt et al., 2011). In Paris (France) the high level of heavy metals present in the roof runoff water is due to the great number of metallic roofs (Robert-Sainte, 2009). Many similar results have been proved in other European countries, such as Netherlands (Gouman, 2004), Sweden (Sörme et al., 2001) or Germany (Förster, 1999).

Started more than 30 years ago, the study on the leaching behaviour of different building products has provided quite poor exploitable data until now, mainly due to the difficulty to properly understand the leaching mechanisms and to predict its long term behaviour. Current literature offers experimental data at laboratory, pilot and field scale (Schiopu, 2007), as well as numerical data (Schiopu et al., 2009), coming from modelling and simulation. Unfortunately these data are hardly exploitable, being very heterogeneous. Moreover, recent research (Laurent et al., 2010) showed that the release due to leaching could represent up to 90% of the whole life cycle water emissions of products. Nevertheless, presently these data are little or not at all taken into account in the environmental assessment tools, such as the LCA - Life Cycle Assessment, which are largely used in the construction sector in order to produce the EPDs Environmental Product Declarations.

Databases and software have already been created to characterise the leaching behaviour of waste or polluted soil, but none focuses on the leaching phenomenon of the building products. An example of such a database is LeachXS, created by the Energy research Centre of the Netherlands (ECN). It is a data base but at the same time an expert system for characterising and evaluating the environmental impact of the leaching phenomenon (LeachXS, 2011). The data refers to leaching experiments mainly made on wastes, in the context of their use as secondary raw materials (SRM) in the Netherlands.

The objective of our work is to help exploiting the data on the leaching behaviour of construction products by creating a specific database - LixiBat. This database should permit an easy access and use, as well as the integration of its content in different environmental assessment tools, such as LCA or environmental and health risk assessment methods (see Figure 3.16).

5.2 Methods

The work has started with the collection of data on the leaching behaviour of different building products in order to cover a wide domain of application and construct a flexible database. Investigating the gathered data has showed a high diversity in the type of experiments, exposure conditions, or representation of results. The building products analyzed can come from different parts of a building, the results can be expressed in various measuring units (e.g. mg/L, g/kg, mol/L) and characterize experiments at different scales, under different exposure conditions. Also, the concerned data can come from numerical models and simulations of the leaching behaviour of building products. The bibliographic study showed the existence of a whole variety of leaching data:

- Studies at various scales: laboratory, pilot, field and also numerical simulations;
- Products of different structures: organic, mineral and metallic;

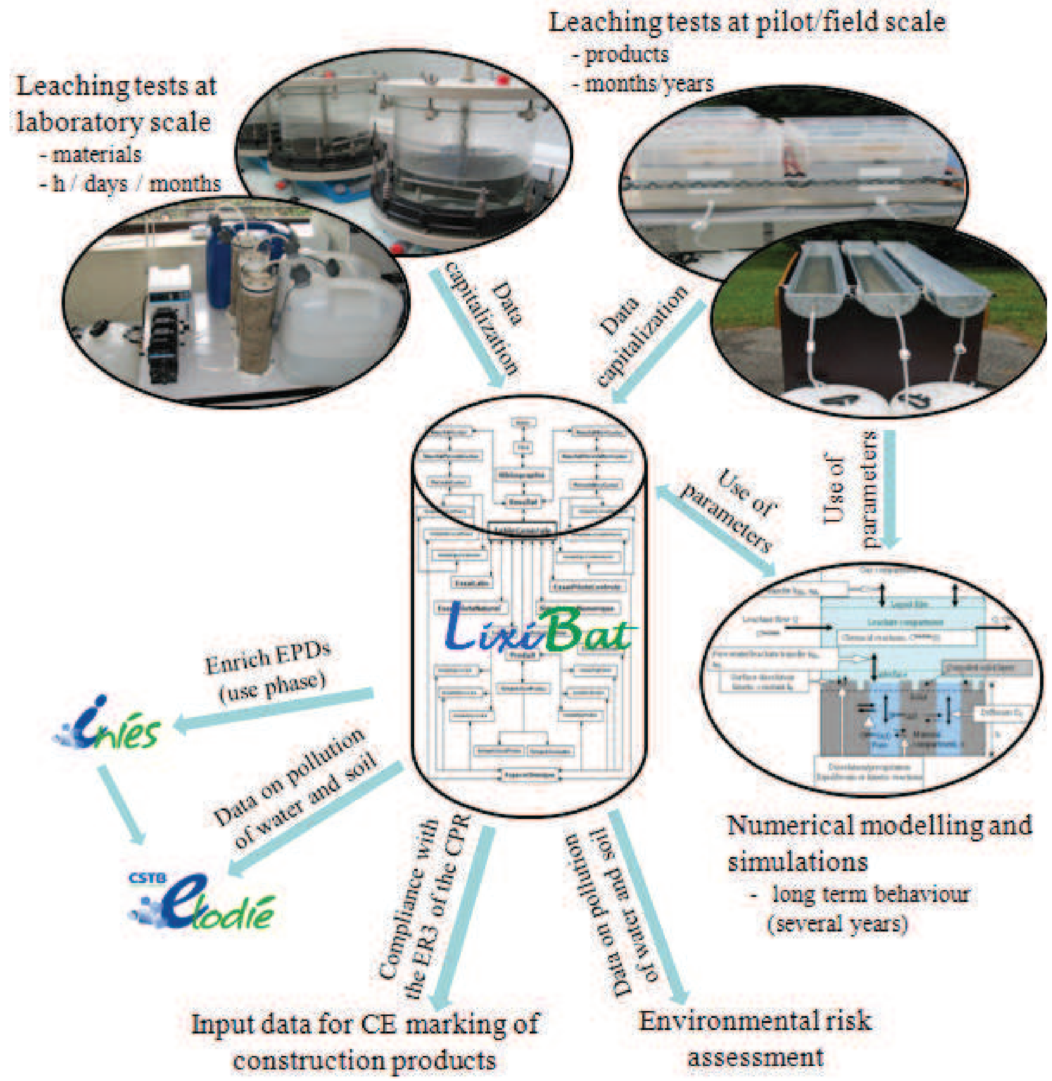

Figure 3.16: LixiBat and its applications.

- Various functionalities for the construction products: facade, roof, terrace, foundation.

Thus, we have classified the source data by:

- building product,
- type of experiment and
- form of results.

Classifying and reusing this data set rises up quite many problems and confronts difficulties. Taking into consideration the complexity of data that comes from leaching experiments, we have decided to group this information using a relational scheme, i.e. to construct a relational database. Such a construction matches data by using common characteristics found within the data set. The data are organized in a collection of relations, the so called tables. A relation is defined as a set of tuples that have the same attributes. A tuple represents an object and the information about this object. A relation is described as a table, which is organized into rows and columns. All the data referenced by an attribute are in the same domain and conform to the same constraints (EC, 2012b). The software used to do the grouping of a relational database is called a database management system (DBMS). We have developed the LixiBat database under Microsoft Office Access 2007 as DBMS in French. Furthermore, we have conceived a graphical user interface to feed the database and to search information in it, developed in Microsoft Visual C ♯ 2008.

5.3 LixiBat database: an overview

The first step in the construction of LixiBat was to identify all the parameters that need to be integrated in the database, a stage which is based on the bibliographic research mentioned here above. We have retained the pertinent data for the characterization of an experiment. Thus, we have organized these parameters in the following categories: Product, Experiment, Result and Reference. These categories are briefly described hereafter.

5.3.0.1 Product The building products have numerous characteristics of which we are interested to define the most relevant for: i) identifying the product, and ii) interpreting the leaching results. We have decided to associate to the object “Product” the following attributes: name, shape (i.e. granular or monolith), structure’s matrix (i.e. mineral, metallic, organic or composite), function, fabricant, age, type of aging, porosity, permeability, density, moisture and chemical composition. The data on the product's chemical composition allows us to better identify the product and it gives information about the substances susceptible for emission by leaching. There are several options to express the chemical composition data such as: elementary, mineral and organic composition, registered by mass of wet matter (mg/kg), or mass of dry matter (mg/kg DM), or concentration in the pore water (mg/L). Information about the methods for the chemical analysis can also be stored in this section. With each new product introduced in the database, the list of chemical substances grows, considering a full name, the CAS number, the chemical formula and the molar mass of the substance. The same list of chemical substances will be used later for the detailed results, offering the possibility to enlarge it, if the concerned substance doesn't yet exist in the database.

5.3.0.2 Experiment This part is the widest section in the LixiBat database. The information referred to, describes the experimental conditions in detail – data that is essential for the interpretation of the results. All these parameters have been classified in the next sub-sections: leachate, atmosphere, sample, experimental conditions and numerical simulation.

The leachate plays an important role in the leaching phenomenon and therefore we have characterized it by attributes that can influence the leaching: pH, conductivity, oxidation/reduction potential and chemical composition.

The bibliographic research proved the importance of the air quality involved in the experiment. For example, different pollutants (e.g. SO_2, NO_2, O_3) can contribute to the acidification of rainwater, which is the main leachate in natural conditions. In consequence, the chemical composition of the atmosphere is an interesting parameter for the leaching phenomenon and therefore it has been included in LixiBat at the section "Atmosphere".

Once used in an experiment, the building product is reshaped at particular dimensions or is changed in different ways (crushed, compacted ...), becoming a sample. The parameters characterizing the sample, essential for the leaching behaviour are: a binary parameter to define the shape of the sample, i.e. crushed or monolith, the geometrical surface of contact, the geometrical shape and the compaction.

The experiment itself is characterized by other parameters, depending on the scale, i.e. laboratory, pilot or field. The laboratory experiments are defined by the following attributes: total duration, contact time, temperature, leachate volume,

volume/surface ratio, liquid/solid ratio, agitation. More specific, for the dynamic, static and percolation experiments at laboratory scale, we have the attributes: static or dynamic, standard and flow rate of the leachate. On the other hand, for the pilot experiments in controlled conditions, we can add values for the runoff flow and the inclination angle. The outdoor experiments, in natural conditions, at pilot or field scale, have also specific parameters, like: the geographic site, total duration, period of contact, rainfall, temperature, UV intensity, direction of the wind, inclination angle of the sample. In case of leaching data coming from numerical simulations, we need to store the information concerning the numerical model and simulation. As each simulation is based on a real experiment, the parameters taken in account are the same as for the corresponding experiment. Still, some extra information needs to be added: the duration of the simulation (the numerical simulation can predict the leaching behaviour on a larger time scale than the experiments do), the type of simulation (static or dynamic), the simulation tool used (e.g. the name of the software), the simplifications considered in the model.

5.3.0.3 Results Being the target of our study, the information concerning the results needs to be as complete as possible. First of all, we observe that the results from laboratory experiments in static conditions are taken only at one moment of time, while others are taken in more steps, which introduces the term "period". Among these results, some are taken under a cumulative form, while others are pinpointed results (see Figure 3.17).

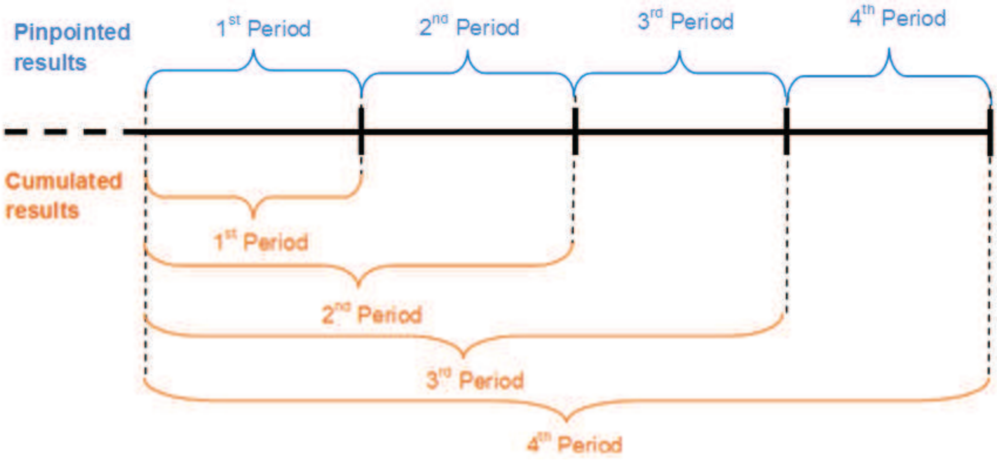

Figure 3.17: Representation of cumulative and pinpointed periods.

Cumulative results allow measuring the total quantity of substance that has leached from the beginning of the experiment up to a certain sampling moment. The pinpointed results show the evolution of a substance's concentration in the leachate, as a function of time. In the studied references, the leaching results are presented either in the cumulative or noncumulative form. According to this, the attributes used to define the results differ. Cumulative results are characterized in LixiBat by the following attributes: surface mass concentration (mg/m^2), mass composition (mg/kg), percentage of the total mass (%), mass and molar concentration for each substance (µg/L, mol/L), cumulated duration (days), cumulated volume of the leachate and rainfall for each period (L, mm). On the other hand, noncumulative (or pinpointed) results are defined by the next parameters: mass and molar concentration for each substance found in the leachate; duration, leachate volume, rainfall and liquid/solid ratio in L/kg and cm^3/cm^2 for each period; pH, conductivity and oxidation/reduction potential for the leachate.

5.3.0.4 References To prove the pertinence of the data introduced in LixiBat, and to offer the possibility to search for more details about the concerned data, the section "References" contains bibliographic references. The attributes characterizing this section are: author(s), editor (magazine, conference, etc.), title, type of publication (article, book, report, etc.), volume and year of publication.

To sum up, LixiBat is composed of 35 tables and 225 attributes, defining a complex database, adaptable to many types of existing leaching experiences (see Figure 3.18).

5.4 Conclusions and perspectives

LixiBat is a complex database, when regarding its structure, but it is also a simple to use database, where one can track back a wide range of details concerning a certain type of leaching behaviour. Covering the experimental, as well as the numerical aspect of the leaching phenomenon, LixiBat offers exploitable data. The main advantage of this database is that it is focused on the leaching behaviour of building products, which makes it more reliable and precise (its structure takes into account the specificities of the various construction products). Although its structure is rigid and implies a deep knowledge of the leaching phenomenon, LixiBat is a flexible database, allowing the introduction of various types of experimental data, coming from both standardized and non-standardized tests.

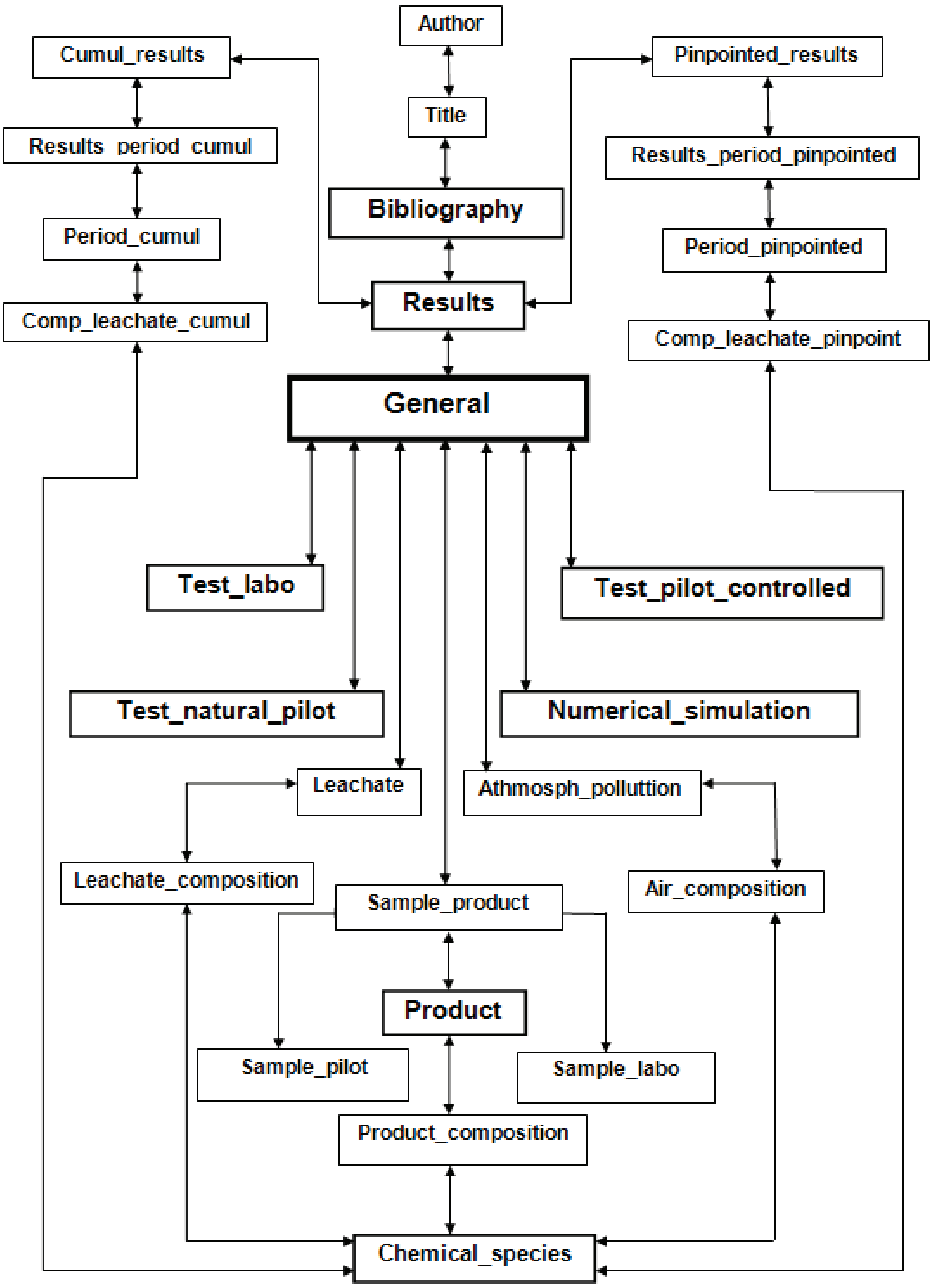

Figure 3.18: LixiBat diagram.

LixiBat can be used not only for validating new leaching results, but also for integrating data on the leaching behaviour of building products in the environmental assessment tools or environmental and health risk assessment methods. Starting from experimental data from leaching tests in laboratory or natural conditions, one can use a numerical model to simulate the leaching behaviour of the concerned building product throw out its service stage period and use the obtained results in LCA tools for instance. This approach can help, for example, improving the quality of the EPDs of building products, by providing reliable data, where it is mostly missing nowadays.

Until now, LixiBat is summing up a total of 226 parameters, assembled into 35 tables from experiments and numerical simulations. Its structure makes it flexible and adaptable to a wide range of data. At the moment, LixiBat contains leaching data on more than 50 different building products, data coming from all types of experiments and simulations. The database is continuously updated, in order to assemble more and more data about different leaching behaviour of building products. Our target is to integrate as much leaching data as possible in LixiBat and to make it a reliable database in its domain, for specific leaching studies and for integration in the environmental assessment tools like LCA or environmental and health risk assessment methods.

Chapter 4

Including leaching data in the environmental assessment of products and buildings

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Ce chapitre traite de l'évaluation de l'impact environnemental des produits et bâtiments, en prenant en compte les données de lixiviation. Le défi consiste à intégrer les émissions dans l'eau et le sol pendant la vie en œuvre dans les calculs d'impact. Une méthodologie est décrite dans ce sens.

La première partie consiste en une étude de cas sur le bois traité CBA à l'échelle produit. La méthodologie proposée pour inclure les données de lixiviation dans les méthodes ACV est basée sur des simulations à long terme, c'est à dire des simulations numériques intégrant des modèles mécanistiques chimie-transport pour l'évaluation des émissions dans des conditions naturelles d'exposition. Les données de lixiviation ainsi obtenus sont incluses dans l'inventaire du cycle de vie (ICV) du produit concerné. L'impact est évalué par une méthode qui dispose des indicateurs d'écotoxicité et toxicité humaine, i.e. le modèle USEtox$^{\text{TM}}$. La méthode fournie par la norme française NF P 01-010 pour l'indicateur pollution de l'eau (i.e. basée sur l'approche "volume critique") a été également utilisée. Cette norme fournit les règles harmonisées pour la réalisation des études d'analyse de cycle de vie des produits de construction conduisant à l'établissement des Fiches de Déclaration Environnementale et Sanitaire (FDES). Les données relatives aux étapes de la production, transport, fin de vie du produit sont issues d'une FDES d'un produit équivalent à celui considéré dans cette étude.

La deuxième partie de ce chapitre poursuit l'exemple en incluant les données de lixiviation dans l'évaluation de l'impact environnemental des bâtiments d'une étude à l'échelle du bâtiment. Une maison individuelle simplifiée a été considérée, avec l'enveloppe constituée de : (i) toiture en plaques fibrociment, (ii) façade en bois traité CBA et (iii) terrasse en bois traité CBA. La maison est modélisée à l'aide d'un logiciel conçu pour évaluer les performances environnementales intrinsèques d'un bâtiment durant tout son cycle de vie. Le logiciel ELODIE est utilisé dans ce travail. La méthodologie d'évaluation à l'échelle bâtiment est basée sur le couplage de la méthodologie décrite dans la première partie de ce chapitre (i.e. échelle produit) avec l'Analyse du Cycle de Vie (ACV) à l'échelle bâtiment – actuellement la méthode la plus utilisée pour l'évaluation environnementale des bâtiments.

Plusieurs conclusions peuvent être tirées des études à l'échelle produit et bâtiment :

- L'évaluation environnementale des produits de construction, actuellement basée sur l'ACV, peut être enrichie en considérant l'impact des phénomènes de lixiviation pendant la phase de vie en œuvre. Un exemple détaillé a été donné pour le bois traité CBA.

- Une connaissance approfondie des mécanismes de lixiviation est nécessaire afin d'obtenir des données de lixiviation fiables.
- Des méthodes adéquates sont indispensables à l'évaluation de l'impact. Nous avons utilisé ici le modèle USEtox™ pour le calcul des indicateurs écotox et toxicité humaine et la méthode NF P 01-010 pour l'indicateur pollution de l'eau. Le modèle Usetox™ est considéré par la communauté scientifique comme le meilleur disponible actuellement. La méthode NF P 01-010 est la méthode normalisée en France et utilisée largement dans les outils d'évaluation environnementale des produits de construction et des bâtiments.
- Les données d'inventaire doivent être en corrélation avec les bases de données utilisées par le modèle d'impact choisi, en ce qui concerne la nomenclature, e.g. les flux d'inventaire exprimés sous forme ionique ou métallique, des composés organiques définis individuellement ou par classes de substances. Les flux simplifiés (actuellement utilisé dans les FDES françaises) sont utiles pour des raisons pratiques, mais difficilement utilisables pour le calcul d'impact.
- Comme déjà mentionné dans le chapitre 1, faisant la somme des émissions de polluants dans l'eau et le sol pendant la phase d'utilisation, i.e. les données de lixiviation (qui ont un impact local), avec des émissions pendant les autres phases du cycle de vie du produit (qui concernent les différents compartiments d'émission et différentes périodes), est peu pertinent. Néanmoins, les méthodes ACV actuelles sont restrictives, ne tenant pas compte de la localisation spatiale des contraintes environnementales.
- L'impact sur toute la durée de vie du produit pourrait être évalué par simulation numérique. Néanmoins, la simulation numérique sur plusieurs années (par exemple 50 ans de durée de vie) nécessite du temps, des machines informatiques puissantes et avancées.

Les deux études, à l'échelle produit et bâtiment, ont montré que les données de lixiviation (correspondant à la phase d'utilisation) ont un impact significatif sur les indicateurs globaux écotoxicité, toxicité humaine et pollution de l'eau, qui sont évalués au cours du cycle de vie complet du produit.

1 Introduction

This chapter deals with the assessment of the environmental impact of products and buildings by taking into account the leaching data. The challenge is to include the emissions to water and soil during use stage in the impact calculations. A methodology is described in this sense.

The first part considers a case study on CBA treated wood a product scale study. The proposed methodology for including leaching data in LCA methods is based on long term simulations, i.e. numerical simulations integrating mechanistic chemical-transport models for the assessment of the emissions over 1 year in natural exposure conditions. Leaching data thus obtained is included in the inventory of the concerned product, along with information characterising all stages of the product's life cycle. The impact is assessed by methods considering eco- and human toxicity indicators, i.e. USEtox™ model. Data regarding the production, transport, end of life stages of the product are taken from the corresponding EPD file.

The second part of this chapter pursues the example by including the leaching data in the environmental impact assessment of buildings a building scale study. A simplified single-family house is modelled using a software designed to evaluate the intrinsic environmental performances of a building over its entire life cycle. ELODIE software is used in this work. The building scale assessment methodology is based on coupling the methodology described in the first part of this chapter (i.e. product scale) with the Life Cycle Assessment (LCA) at building scale – currently the most used methodology of environmental assessment of buildings.

2 Product scale study

2.1 Introduction and approach

Pollutant release from construction products in contact with water is a current research subject. The environmental impact of products and buildings is evaluated by a LCA (Life Cycle Assessment) approach. LCA takes into consideration the global and local scale issues by using standardised environments for given time periods and geographic scales, applying generalised modelling tools and data bases. However the question of a realistic local impact assessment remains open.

At the moment, the emissions to water and soil during the use phase of a product are not well evaluated, the impact being either underestimated (because of lack of leaching data), or overestimated (using data from generic data bases).

The aim of this study is to assess the leaching behaviour of construction products based on treated wood, in view of including leaching data within a LCA approach. The proposed methodology is studied on *Pinus sylvestris* treated with copper-boron-azole (further called "CBA").

Wood is widely used in the construction industry. Because it is a natural organic product susceptible of biodecay and rot attack, a core or surface treatment needs to be stipulated depending on its application (i.e. in/outdoor exposure, contact with water, contact with soil, etc.). Previous studies generally report high leaching rates from treated wood, depending on the type of preservative and exposure conditions (Lebow, 1996; Schoknecht et al., 2005; Ahn et al., 2010; van der Sloot and van Zomeren, 2011). This is why the leaching behaviour of treated wood needs to be evaluated and furthermore included in the LCA approaches of construction products (based on wood) and at a larger scale, i.e. buildings.

The methodology developed in this study addresses two main aspects: (i) evaluation of leaching data on treated wood and (ii) coupling of leaching data with LCA data over the whole use stage of the product. The global methodology is presented in chapter 2 (see also Figure 2.1).

2.2 Assessment of leaching data on treated wood

As explained in chapter 2 (Figure 2.1), the evaluation of leaching data at real scale has been carried out through the following steps:

- pH dependency leaching test at lab scale for the definition of the physico-chemical stability of the material and the pollutant leaching mechanisms,
- development of a chemical model able to describe the pollutant partitioning between material and water,
- dynamic leaching test performed on monolith samples for the investigation of the time evolution of the leaching process,
- development of the chemical-transport model able to simulate the leaching behaviour at lab scale,
- pilot scale tests in which the material is exposed to natural leaching conditions,
- modelling of the leaching behaviour at pilot scale and extrapolation for other possible exposure conditions, time horizons, etc. - this step should supply the necessary data for long term leaching behaviour of the product, data which are compatible with an LCA-type environmental evaluation.

The first 4 steps have been described in detail in chapter 3 §2.1 and §2.2. The tests and models carried out at pilot scale (natural exposure conditions) will be presented here after.

2.2.1 Materials and methods

The purpose of this study is the development of mechanistic models in order to perform numerical simulations of the leaching behaviour of CBA treated wood at field scale (i.e. natural exposure conditions and samples at real scale) and long term (i.e. 1 year). The modelling is based on experimental investigation presented in detail (samples, leaching tests and pilot experiments) elsewhere (Schiopu, 2007). However, for a better understanding we recall in a succinct description the materials and experimental methods previously used by (Schiopu, 2007).

2.2.1.1 Samples and field tests The experimental investigations considered in this study were performed on *Pinus sylvestris* samples treated with copper-boron-azole (CBA). The samples consisted of a commercial wood duckboard, industrially treated for outdoor use (class 4 corresponding to wood placed horizontally outside, in contact with the ground or fresh water), bought on the ordinary market. The treatment of wood was based on copper, boron and an organic biocide – the total content in preservative compounds was determined by chemical analysis: 1244 mg/kg copper, 93 mg/kg boron, 12.5 mg/kg azole. This material is noted "A" in the following.

Field tests were performed at pilot scale samples consisting of slabs of a commercial CBA treated wood product ($9.8\,\mathrm{mm} \times 40\,\mathrm{mm} \times 4\,\mathrm{mm}$) material A were exposed outdoor to rain for one year. Two scenarios for horizontal exposure have been considered as representative for wood products' usages during service life: (i) stagnation and (ii) run-off scenario. The run-off scenario corresponds to a quick draining of the rainwater whereas in the stagnation scenario rain water remains in contact with the product for longer periods of time. Despite the fact that the meteorological conditions are the same for both scenarios, the product-leachate contact conditions are different, i.e. bigger contact surface and longer contact duration in the stagnation scenario than in the run-off.

We recall here the main parameters of the field test (more details on the experimental protocol and exposure conditions are given in (Schiopu, 2007)):

- Total duration of the test: 1 year (July 2005 July 2006)

- Location: test field at the CSTB in Grenoble, France
- Total rainfall: 800 mm/year.

2.2.1.2 Leaching model at lab scale As mentioned before, the simulation of the leaching behaviour of CBA treated wood during field tests is based on a coupled chemical-transport model developed to simulate leaching at lab scale. The chemical model used for this material is described by (Tiruta-Barna and Schiopu, 2011). It is based on experimental data from characterisation leaching tests (pH dependency tests) (Schiopu, 2007). The pH dependency test, or ANC (Acid Neutralisation Capacity), is performed on crushed material, under aggressive conditions (agitation, acid and alkaline leachates, high liquid to solid ratio L/S) cf. XP CEN/TS 14429 (CEN, 2006). It provides information on the influence of pH on pollutant release, acid/base neutralisation capacity and physico-chemical stability of the material. The chemical model described in (Tiruta-Barna and Schiopu, 2011) considers Cu, Cr and Zn complexation on the wood surface (via phenol and carboxyl groups of the lignin and hemicelluloses). Boron release is modelled by the bidentate complex of boric acid with cellulose. The organic matter in eluates (extractives) is characterised by a general parameter, i.e. dissolved organic carbon (DOC), which is considered to participate in acid/base reactions and metal complexation.

The leaching mechanism thus described is used to characterise the chemical phenomena taking place in the pore water of a monolith sample of the considered product at contact with water. The transport parameters (diffusion coefficient) are determined by means of dynamic surface leaching tests (DSLT) performed at lab scale on monolith samples (according to EN 7375), over 64 days. The transport model describing mass transport in porous structure was modelled using an effective diffusion coefficient of 1×10^{-11} m^2/s.

2.2.1.3 Development of the leaching model at pilot scale For the development of the long-term model (simulation of the leaching behaviour over 1 year in natural exposure conditions), data from the field test obtained with CBA - commercial samples (material A) were used and the chemical-transport model developed at lab scale was adapted, considering real exposure parameters. Each scenario (i.e. stagnation and run-off) was treated separately. For both scenarios (performed under the same exposure conditions), 34 rainy events were registered. This leaching model at pilot scale was developed in the current work.

Stagnation scenario In the stagnation scenario carried out over 1 year, 8 alternating stagnation and rain periods were identified among them 4 consecutive freeze periods. The diffusion coefficient associated to these 4 periods was replaced with a smaller value (diffusion in pores of a frozen body is slowed down). The rain periods correspond to long rain duration or intense rain, when the stagnant leachate overflows into the collector. The stagnation periods correspond to longer periods, when no or only short showers were registered and is characterised by stagnation and partial evaporation of the leachate.

Run-off scenario In the run-off scenario were modelled 34 rainy events, followed each by 34 stagnation periods. Each period depends only on meteorological parameters, i.e. rain or evaporation. The run-off scenario was modelled considering a film layer consisting of water, which covered the surface of the product.

Simulations on amine-CBA treated wood This material (noted B in the following) is the one extensively studied in the current work (see chapter 3 §2.1 and §2.2). The introduction of leaching data in an LCA approach requires the knowledge of the mass fluxes of the released pollutants at real scale. Field leaching measurements are not available for this second material. Simulations of leaching process were performed for material B considering the exposure conditions of the pilot setup described here above. By this way the total release of hazardous substances was evaluated.

More, the simulation results obtained for material B were compared with the pilot data obtained for material A in order to validate qualitatively (through orders of magnitude) the developed model at lab scale and to prove its adaptability for up-scaling.

The main differences between the two types of materials are:

- the treatment was performed at laboratory scale (based on EN 113 standard) for samples B (see chapter 3 §2.1) and industrially (unknown method) for samples A,
- the composition of the treatment solution (concentration of active biocides) was different (the final concentration in wood samples B treated at lab scale was 3481 mg/kg copper, 289 mg/kg boron and 179 mg/kg tebuconazol),
- the B samples were treated with a formulation based on amines (see details in chapter 3 §2.1), which it seems not to be the case for material A (material slightly acid).

We recall here that the leaching behaviour at laboratory scale of the amine-CBA treated wood (material B) was investigated and modelled in the current work (chapter 3 §2.1, (Lupsea et al., 2013a,b)). It takes into account biocides' interaction with the wood's solid structure (lignin, hemicellulose, cellulose) and with the liquid matrix (wood extractives). Cucomplexation on the wood structure is considered, as well as complexation with several extractives, e.g. vanillin, carboxylic acids (octanoic, formic, acetic, maleic). The tebuconazole release is modelled by pH dependent binding on polarized OH moieties on wood.

The long-term model is based on the same pattern for both materials; the parameters for the composition of the product (density, chemical composition, leaching mechanism) were distinct for each material, while the parameters concerning the field pilot, i.e. type of water contact, sample geometry, rain events, were the same.

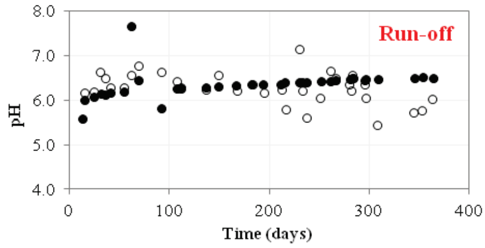
In all scenarios the leachate was modelled as an open stirred reactor with continuous or discontinuous inflow (rain) and outflow (leachate overflow). For all scenarios, the geochemical modelling software PHREEQC® was used with the Lawrence Livermore National Laboratory (LLNL) thermodynamic database and additional reactions for specific chemical mechanisms.

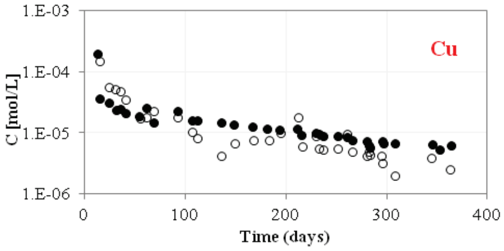
2.3 Results and discussion

The simulation results of the leaching from CBA treated wood material A, at field scale in both scenarios (stagnation and run-off) are shown in Figure 4.1. The pH and concentration of monitored species in leachates was represented on function of time. Variations over several orders of magnitudes are observed for almost all chemical species.

Figure 4.1 shows a good correlation between simulation and experimental data on material A at pilot scale for both scenarios, i.e. run-off and stagnation. This proves that the modelling approach combining chemistry and transport, lab and field scales is reliable.

Simulation results for material B (pH and hazardous substances only) are presented in Figures 4.1 and 4.2, and compared with those of material B. We notice in Figure 4.2 that there is a significant difference between the pH in eluates for material A and B (in simulation results). This can be explained by the alkalinity induced by the treatment method in case of material B (because of the presence of amines in the treatment solution and their contribution to the fixation mechanisms of biocides, e.g. Cu, on the wood structure - see (Lupsea et al., 2013a) for more details on the leaching mechanisms). In the run-off scenario the pH of eluates from both types


Run-off
pH
8.0
7.0
6.0
5.0
4.0
0
100
200
300
400
Time (days)


Cu
C [mol/L]
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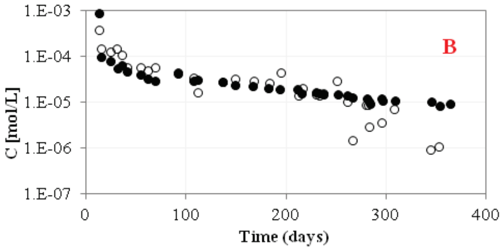
1.E-04
1.E-05
1.E-06
0
100
200
300
400
Time (days)


B
C [mol/L]
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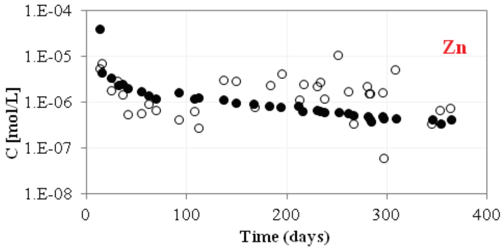
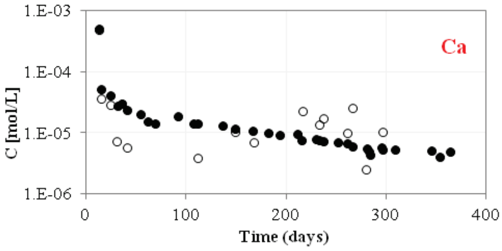
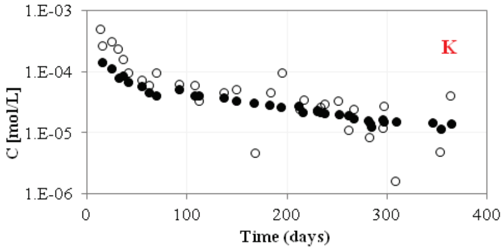
1.E-04
1.E-05
1.E-06
1.E-07
0
100
200
300
400
Time (days)


Zn
C [mol/L]
1.E-04
1.E-05
1.E-06
1.E-07
1.E-08
0
100
200
300
400
Time (days)


Ca
C [mol/L]
1.E-03
1.E-04
1.E-05
1.E-06
0
100
200
300
400
Time (days)


K
C [mol/L]
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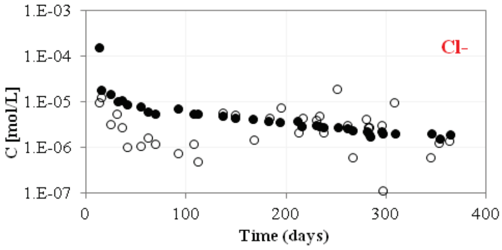
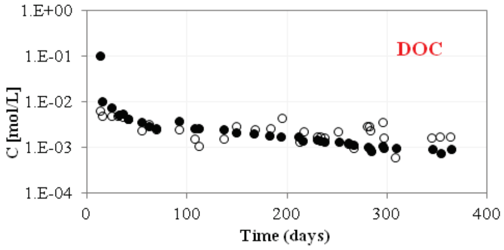
1.E-04
1.E-05
1.E-06
0
100
200
300
400
Time (days)


Cl-
C [mol/L]
1.E-03
1.E-04
1.E-05
1.E-06
1.E-07
0
100
200
300
400
Time (days)


DOC
C [mol/L]
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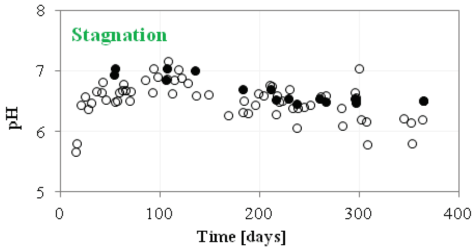
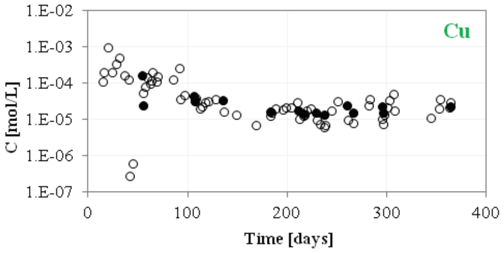
1.E-01
1.E-02
1.E-03
1.E-04
0
100
200
300
400
Time (days)


Stagnation
pH
8
7
6
5
0
100
200
300
400
Time [days]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C [mol/L]
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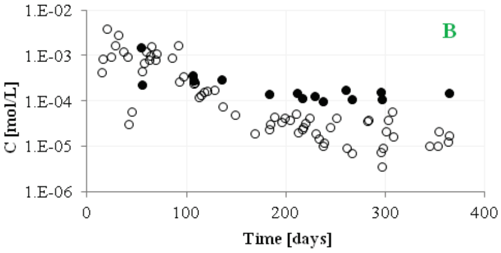
1.E-03
1.E-04
1.E-05
1.E-06
1.E-07
0
100
200
300
400
Time [days]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C [mol/L]
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1.E-03
1.E-04
1.E-05
1.E-06
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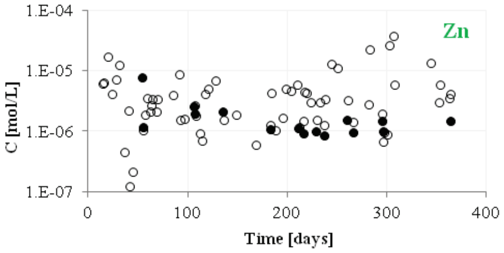
200
300
400
Time [days]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1.E-06
1.E-07
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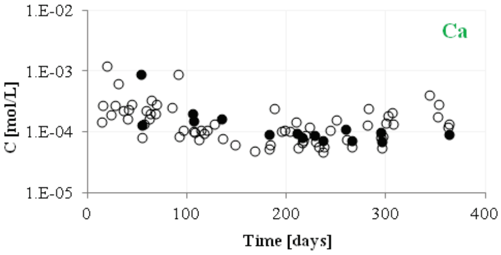
200
300
400
Time [days]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1.E-04
1.E-05
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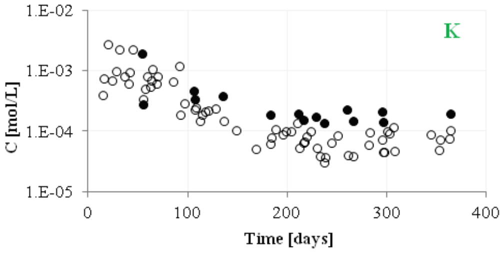
Time [days]


K
C [mol/L]
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1.E-05
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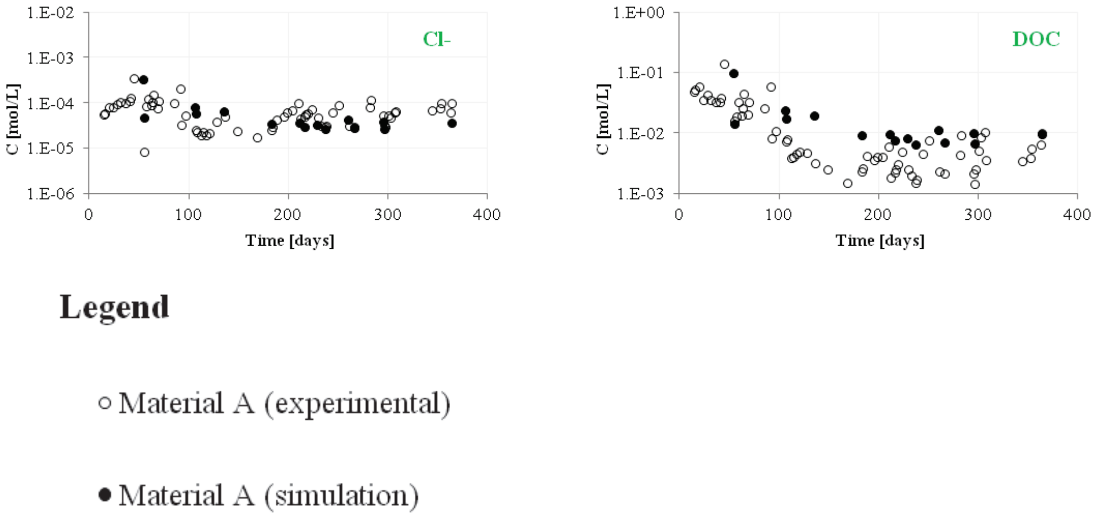

Figure 4.1: Simulation and experimental results for material A during runoff (in red) and stagnation (in green) scenarios.

of treatment show a constant value after approximately 300 days of exposure. The pH for both samples reaches a similar value, around 6.5. This behaviour could be explained by the complete release with time of free amines from material B and of fatty acids from A and B along with other endogenous compounds and biocides. The same pH value was observed in eluates from untreated wood, washed with diluted acids (corresponding to the slight acidity of natural rain water) (Lupsea et al., 2013a).

Table 4.1 shows the cumulative emissions obtained from simulation of leaching over one year in stagnation and run-off scenario for both types of treatment.

For both materials, boron leaching during stagnation scenario is more intense than during run-off, because of the product-leachate contact duration - in run-off scenario the product is in contact with water only during the rainy event and up to the evaporation of the film layer from its surface, while in the stagnation scenario the product is almost constantly in contact with the leachate. Moreover, the contact surface is higher (double) in the stagnation scenario. Nevertheless, the behaviour in the first 50 days is opposite, i.e. more B leaches in the run-off scenario. This could be explained by the fact that the first overflow (collection and measurement) during the stagnation scenario took place only after 45 days. Boron is only slightly fixed by the wood structure (as demonstrated by the leaching tests results and modelling at lab scale).

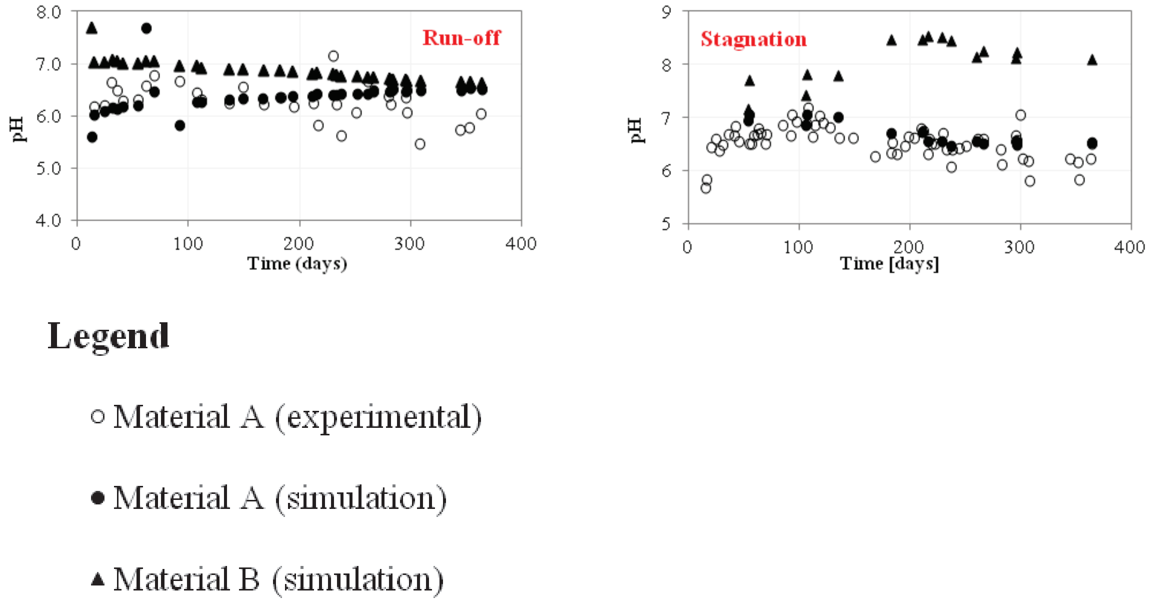

Figure 4.2: pH of eluates from field scale leaching tests over 1 year in stagnation and run-off scenarios – experimental and simulation for both types of wood treatment.

Copper exhibits opposite behaviours for materials A and B. The emission in stagnation scenario for material B is particularly high (more than 1 g/m^2) if compared to the other cases. At the same time, the leachate pH is also higher for this scenario (pH above 8). The explanation could be that in the stagnation scenario the wash off of alkaline and extractive species is more important than in runoff (for the same reasons as above - case of boron). The behaviour of Cu is strongly dependent on the pore water pH and extractive concentration. If the total loss of alkaline and extractives species of pore water is important, especially at the beginning of the pilot, then Cu mobilization and its release change in time. The concentration gradient between leachates and porewater at the material interface seems to play an important role which is difficult to foresee only by qualitative suppositions. Here the importance of a mechanistic and quantitative model is fully demonstrated.

The cumulative emissions for the active biocides from material B in run-off scenario and stagnation are given in Table 4.1. These values will be further used in the assessment of the environmental impact of CBA treated wood products due to leaching during use stage.

Table 4.1: Cumulative emissions from CBA treated wood (material B).

	Stagnation $mg/m^2/year$	% from TC	Run-off $mg/m^2/year$	% from TC	$mg/m^2/50$ years
Cu	2499	13.14	460	2.42	1033
B	666	42.19	172	10.87	362
Tebuconazole	166	17.02	160	16.40	427

2.4 Integration with LCA

Once the leaching behaviour of a product defined, the next step is the application of the proposed methodology (chapter 2 §8) to assess the environmental impact of the potentially hazardous substances released during leaching, i.e. improvement of the inventory and the impact evaluation methods. We will further discuss both steps and present a practical application.

We considered for this work the EPD file based on the French standard NF P 01-010 (FCBA, 2011) for a CBA treated *Pinus sylvestris* product used in exterior facade works (selections from the FDES file are attached in appendix E).

2.4.1 Inventory analysis in the EPD

The EPD data are used as ground information which is analysed and further enriched. The methodology proposed in this study for including leaching data in the EPD (enriching the LCI) implies:

(i) identifying the emission scenario to be considered with LCA framework, i.e. in which compartment the pollutants are directly emitted by the product during its utilisation, and

(ii) compiling the leaching and material properties data which aim to evaluate the pollutant quantities released in real exposure conditions.

Table 4.2 presents an analysis of the inventory data found in the considered EPD file (FCBA, 2011) for a CBA treated *Pinus sylvestris* product used in exterior facade works. Data found in this EPD for water pollution indicator during use phase is compared to leaching data obtained in this study by numerical simulation, based on a mechanistic model developed from experimental leaching data obtained at field scale - see §2.2 in this chapter. From the structural point of view, i.e. type of wood, treatment composition, density, geometry, we can consider the two products

Table 4.2: Emissions to water from CBA treated wood (EPDs and leaching data) during use phase and their contribution in % to the emissions during the whole lifecycle of the product.

	Yearly emissions during use phase[c]			Yearly emissions during whole lifecycle[c]	Contribution of emissions during use phase[c]		
	Leaching data				Leaching data		
	Stagnation	Run-off	EPDs	EPDs	Stagnation	Run-off	EPDs
Unit	mg/m^2/year			mg/m^2/year	%		
Cu	2499	460	80.9	85.3	99.99	99.99	94.84
B	665	172	NC[a]	NC[a]	—	—	—
Teb[d]	166	160	23.7[b]	24.2[b]	99.99	99.99	97.93

[a] NC = not considered

[b] Value corresponding to the entire class "biocides", counted in the EPD at the indicator "emissions to soil"

[c] values per function unit (FU), i.e. g/m^2/year

[d] Teb = Tebuconazole

as being similar. Only biocidal release is considered, with the observation that data for boron is completely missing from the EPD although it is a biocide contained in the treatment formulation. Also, in the EPD file, azole (tebuconazole) release is considered in the "soil pollution" indicator and is calculated in the "biocides" flow. The first two columns in Table 4.2 refer to simulated data from this study, based on mechanistic models for leaching under natural exposure conditions over 1 year (material B stagnation and run-off scenario - see §2.2 in this chapter), while the third column shows data concerning emissions to water during the use phase, which is currently integrated in the EPD (FCBA, 2011). In the fourth column we have summed up emissions to water over the lifecycle, i.e. emissions during production, transport, construction stage, use stage, end of life - only original data found in the EPD, expressed on mg/m^2/year. Notice that leaching data found in the EPD is taken from literature (FCBA, 2005; Morsing and Klamer, 2010) corresponding to experiments performed at field scale on similar products. No leaching tests or simulations have been performed on the concerned product. The weight of leaching data in the total emissions to the environment via water, i.e. over the whole lifecycle of the product, is calculated in columns five, six and seven. For Cu, this means that emissions currently considered in the EPD during use stage represent 94.84% if compared to the sum of the emissions during the whole life cycle of the product (i.e. production, transport, use stage end of life). If however, leaching data obtained by numerical simulation over 1 year in natural exposure conditions on a similar product (i.e. CBA treated wood material B) was considered, emissions during use stage would represent 99.99%. The 5% difference (between calculation including and not leaching data) means that the release considered in the EPDs is up to 16 times smaller than the cumulative emissions obtained by numerical methods (based on field test leaching data). Moreover, if data on copper behaviour (a common and often studied element) is available, organic biocides, e.g. tebuconazole, are little referenced and other compounds, such as boron, are completely neglected in the inventory. More, in the EPD file, the target compartment is not well defined: the inventory data corresponding to emissions to water are summed with data for emissions to soil.

In the following, we try to overcome some of the identified shortcomings and apply the methodology for including the leaching data in the LCI of the chosen product.

Different leaching/exposure scenarios for the construction products have been defined in chapter 2 §8, in function of the leaching mechanisms (type of water contact) involved: (1) sloping plane, (2) horizontal plane, (3) vertical, (4) contact with soil and (5) works completely immersed in water. We recall here that these exposure scenarios lead to leachates which are emitted:

- directly into the soil beneath or surrounding the product, or
- directly or indirectly (after treatment) into water bodies (groundwater, river, sea, ...).

Depending on the architecture and type of building, water comes in contact with the product in different ways, e.g. stagnation, run-off. The chosen EPD corresponds to the run-off scenario. For the definition of target compartments, we will consider only the leaching scenario in which the stormwater goes directly into the soil. Storage at household is not considered here, the following calculations will be based on the maximizing hypothesis that the entire quantity of released substances during rainwater-product contact (in run-off scenario) is rejected directly in soil.

An impediment in the process of enriching the EPD inventory file is the nomenclature of existing data, defined in (AIMCC, 2009). For practical issues the flows have been simplified, i.e. substances have been grouped in categories, e.g. polycyclic aromatic hydrocarbons, heavy metals, copper and its compounds, etc., and associated conversion factors. For example, the category “nitrogen compounds (in N)” contain (the conversion factor in N is marked in parenthesis): ammonia (0.82), nitrite (0.31), nitrate (0.23), methylamine (0.45), etc. Nevertheless, reducing the number of input variables in the inventory (the fluxes) involves difficulties in the following step which is the impact evaluation. For example, the simplified flux "polycyclic aromatic hydrocarbons" covers a wide range of substances (e.g. anthracene, naphthalene, phenanthrene, benzo(a)pyrene, pyrene, etc.), each being characterised by a certain toxicity factor, some more, others less toxic e.g. the characterisation factor for anthracene is 100 times smaller than the one for benzo(a)pyrene. Thus, if no specifications are given in the inventory considering the exact constituent identified in the emissions to water and soil, the evaluation of the impact can be mistaken. Another aspect concerns the speciation of metals. The neutral metallic form and ionic forms are not equivalent with respect to toxic and ecotoxic effects and therefore the impact calculation methods require more precision in the flux definition. We translated the inventory in the EPD with the nomenclature imposed by the chosen impact assessment method, USEtox™ for instance (see below). The EPD and the enriched inventory, with the new nomenclature are given in Table 4.3. The inventory is translated in EPD terms and in USEtox™ terms in the first two columns. The flows considered for the maximising and the minimising scenarios are marked in third, respectively fourth column. Several flows are considered in both scenarios (there was no ambiguity in the nomenclature used in the EPD). The emissions to water and soil during production, transport, use phase and disposal, expressed in g of substances per functional unit (FU), i.e. 1 m^2 of product over 1 year, are presented for all flows considered in the EPD file, along with the corresponding USEtox™ nomenclature. Because no data was found in the EPD for this stage of the life cycle of the product, it was not included in the calculations, nor in Table 4.3.

Table 4.3: Inventory data for emissions to water and soil during production, transport, use phase and disposal, expressed in g of substances emitted per FU, i.e. 1 m^2 over 1 year.

EPD flows	USEtox^{TM} flows	MAX[a]	MIN[b]	Production		Transport		Use phase[**]		Disposal	
				Water em.	Soil em.	Water em.	Soil em.	Soil em. 1yr	Soil em. 50yr	Water em.	Soil em.
Al and compounds	Fosetyl-aluminium	x		3.03e-02	0	2.15e-06				6.36e-05	0
As and compounds	Arsenic (III)		x	4.42e-05	7.90e-08	1.80e-07	7.20e-10			5.84e-07	4.74e-10
Cd and compounds	Cadmium (II)	x	x	5.60e-06	1.26e-08	3.00e-07	3.26e-13			2.52e-07	2.14e-13
Cr and compounds	Chromium (III)		x	1.25e-03	3.71e-06	1.05e-06	9.02e-09			3.65e-06	5.94e-09
	Chromium (VI)	x									
Cu and compounds	Copper (II)		x	4.36e-03	9.78e-07	6.08e-07	1.66e-12	4.60e-01	2.07e-02	4.54e-07	1.09e-12
Sn and compounds	Stannane, tetrachloro-	x		8.05e-06	2.25e-09	6.74e-12				1.28e-10	0
Fe and compounds	Sulf. ac., iron (2+) salt	x		7.09e-02	1.27e-03	5.30e-05	3.60e-06			2.32e-04	2.37e-06
Hg and compounds	Mercury (II)	x	x	1.93e-06	2.79e-10	1.79e-09	6.00e-14			1.51e-08	3.96e-14
Ni and compounds	Nickel (II)	x	x	1.89e-03	9.60e-08	1.04e-06	2.48e-12			5.86e-07	1.64e-12
Pb and compounds	Lead (II)	x	x	6.71e-05	1.14e-07	2.08e-07	7.56e-12			2.08e-06	4.98e-12
Zn and compounds	Zinc (II)		x	2.61e-04	5.86e-06	1.81e-06	2.70e-08			1.28e-05	1.78e-06
Cl compounds - organic	Allyl chloride	x	x	3.54e-06		1.06e-08				1.28e-06	
-CN and compounds[*]				1.33e-04		9.42e-07				4.02e-07	
Cl compounds - inorganic[*]				9.62e-01		2.21e-01				1.20e-01	
Cl compounds (not specified)[*]				2.01e-04						2.68e-06	
F compounds - inorganic[*]				1.36e-03		4.55e-06				1.65e-06	
P compounds	Phosphate, trimethyl-	x	x	4.65e-03		1.79e-06				8.27e-05	
N compounds	Hydrazine	x		1.06e-02		5.34e-04				5.64e-03	
	Methyl amine		x								
PAH	Anthracene		x	1.50e-05		5.55e-06				1.51e-06	
	Benzo(a)pyrene	x									
Heavy metals (not specified)	Barium (II)		x		6.86e-05		7.20e-08				5.32e-05
	Berillium (II)	x									
Biocides	Cypermethrin				5.62e-04		6.96e-06				2.57e-06
	Teflubenzuron	x									
Suspended solids[*]				5.58e-02						1.39e-03	
Hydrocarbons (not specified)	Benzene	x		2.12e-02						1.21e-03	
Metals (not specified)[*]				2.12e-01						1.07e-03	
	Tebuconazol	x	x					1.60e-01	8.53e-03		

[*] Flows in EPD which did not have a correspondent in the USEtoxTM data base

[**] Leaching data, i.e. emissions to soil during use stage: data from 1 year simulation, and average data for 1 year calculated from cumulated emission at 50 years

[a] Flows selected for the maximising scenario (highest characterisation factor between substances from the same category)

[b] Flows selected for the minimisation scenario (smallest characterisation factor between substances from the same category)

Another aspect is the life span considered in the EPD and its coherence with the emission data. In the studied case, the EPD considers a RSL of 50 years. The LCI includes data over the entire RSL, reduced to the FU which can be "1 m^2 and 1 year" or "1 m^2" (over RSL).

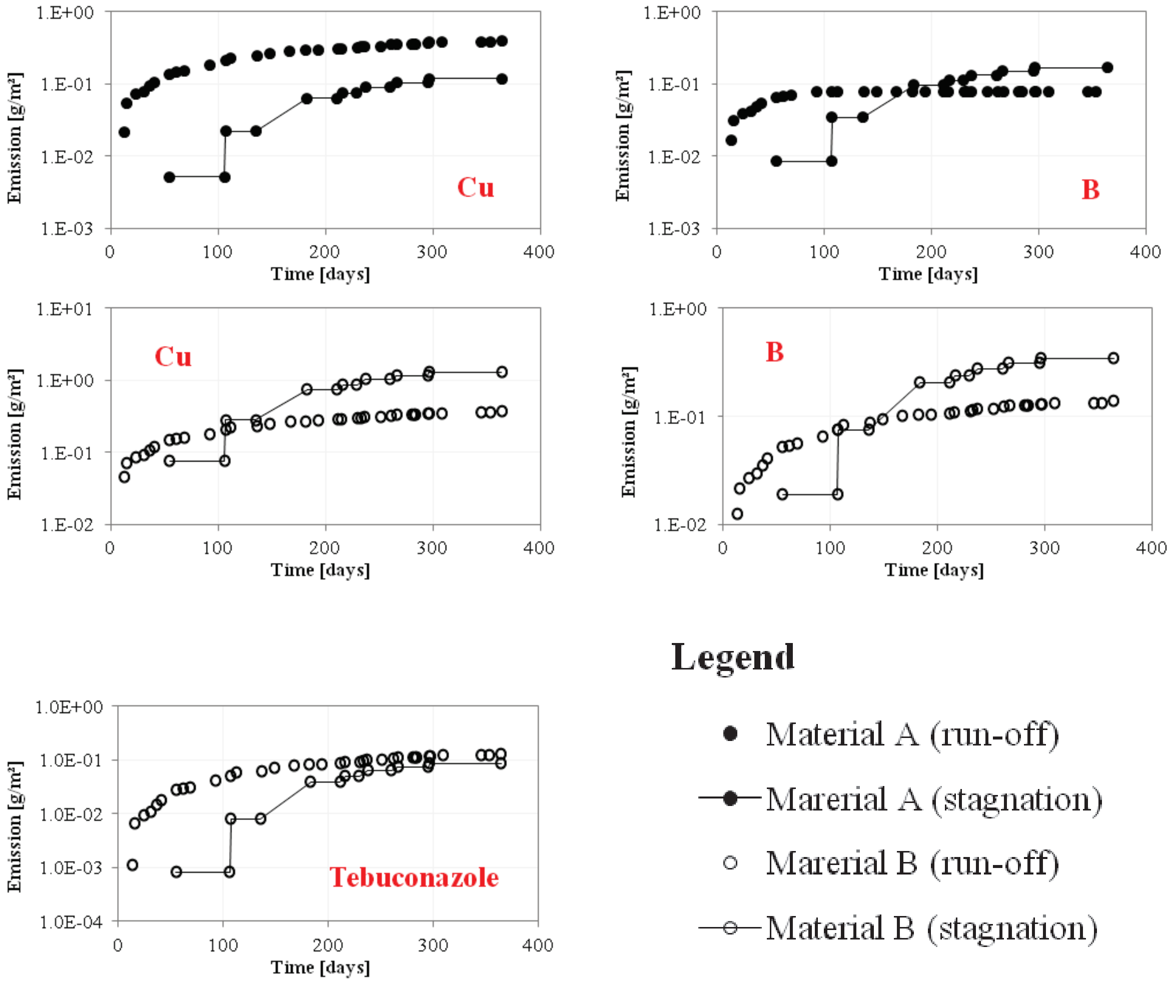

Figure 4.3: Cumulative emissions from CBA treated wood at field scale over one year in stagnation and run-off scenario simulation for treatment type A and B.

As already discussed in chapter 1 §3, emissions from construction products over several years (e.g. RSL) are not constant in time - depending on the product, the release is more significant during the first days/months of contact and it decreases after several months/years. Moreover, in the current discussed case study on treated wood we notice that the emissions (in run-off and stagnation scenario) after 1 year are significant (see Table 4.1), e.g. 40% from the total content in boron is released in the stagnation scenario after 1 year. Multiplying these emissions by 50 years would largely exceed the initial total content. For this reason, including in the inventory the cumulative emission over 1 year and multiplying it by the RSL (e.g. 50 years) is a maximising hypothesis rather incorrect. Numerical simulations over the RSL should provide more precise information concerning the total release. Nevertheless, it was not possible to run simulations over 50 years in the case of CBA-amine treated wood due to the duration and convergence problems encountered in the numerical simulation. The complexity of the chemical model proved to be a determining factor. However, in Figure 4.3 the cumulated release tends to stabilize after ca. 250 days, the increase is rather limited or follows a constant slope. Thus, we used extrapolation on the simulated leaching data in order to evaluate the cumulated release at 50 years. The values determined by this method are presented in the last column in Table 4.1. This data was included in the inventory divided by the RSL, corresponding to an average release per FU (i.e. 1 year).

For resume: in our scenario, the emission compartments are: the soil for all life cycle stages of the construction product (data from EPD and our leaching simulation for the use stage), and water for production, transport, construction and end of life stages. For the use stage, the released quantity of pollutant to the environment corresponds to the calculated cumulative emissions over the RSL (by extrapolation from 1 year simulated data) reported to the FU.

2.4.2 Impact categories and evaluation methods (LCIA)

In the French EPD, the impact is assessed by applying the critical volume method on the obtained flows. Finally an impact indicator called “water pollution” gives the volume of water (m^3) needed to dilute the emissions to water and soil down to the ICPE limits (ICPE, 2008). In soil, the mobility of the leached substances (including hazardous ones) depends on multiple physicochemical and biological factors. By different transport mechanisms in soil, the pollutants can reach groundwater or surface waters (Lebow, 1996). The bioavailability and the effects of the pollutants on leaving organisms have to be considered. It is clear that the “critical volume” method is not proper for the assessment of the environmental impact of leaching from construction products. More reliable indicators which account for the effects of the target pollutants could be eco- and human toxicity indicators, developed in recent impact assessment methods. Thus, the next step is to choose the relevant impact categories and evaluation methods.

Life Cycle Impact Assessment (LCIA) aims to improve the understanding of the relative importance of the individual emissions in lifecycle inventories. The toxic/ecotoxic impact is obtained by using a weighted summation of the released pollutants of a product system with help of characterisation factors, i.e. multiplying the released mass with the corresponding damage or characterization factor as in (Equation 4.1):

$$IS = \sum_i \sum_x m_{x,i} \times CF_{x,i} \tag{4.1}$$

where IS represents the impact score, e.g. for human toxicity expressed in [cases]; $CF_{x,i}$ the characterisation factor of substance x released to compartment i [cases/kg] and $m_{x,i}$ the emission quantity of x to compartment i (the quantities listed in Table 4.3).

The question which remains is which method to apply for the calculation of the characterisation factors. A characterisation model calculates substances-specific characterisation factors that express the potential impact of each elementary flow (in the inventory) in terms of the common unit of the category indicator.

Several methodologies have been published that account for fate, exposure and effects of substances and provide cardinal impact measurements. Among these methods used with the LCA method we recall: IMPACT 2002 (Jolliet et al., 2003), CML (Guinée et al., 2002), Eco-Indicator 99 (Goedkoop et al., 1998), EDIP (Hauschild and Wenzel, 1998). In 2005, a comprehensive comparison of life cycle impact assessment toxicity characterisation models was initiated by SETAC (Society for Environmental Toxicology and Chemistry) (Rosenbaum et al., 2008). The programme within this initiative aimed to establish recommended methodologies and guidelines for the different impact categories and consistent sets of characterisation factors. A quantitative comparison has been conducted on seven existing LCIA models to identify the most influential parameters and reasons for differences between models finally, USEtox™ model was developed. A recent study (Hauschild et al., 2013) performed for the Joint Research Centre of the European Commission (JRC) has identified USEtox™ as being the preferred choice for the evaluation of eco- and human toxicity impact of released substances to the environment. This method calculates characterisation factors for human toxicity and freshwater ecotoxicity. A database of chemical properties was set up for as many chemicals (inorganic and organic) as possible for which characterisation factors can be computed. It includes data concerning physico-chemical properties, toxicological data on laboratory animals as a surrogate to humans and ecotoxicological effect data for freshwater organisms. We recall some of its features:

- It uses nested multimedia models to model chemical fate and human exposure, considering urban, continental and global scales.
- USEtox™ offers the largest substance coverage (more than 1250 human toxicological characterisation factors).
- The USEtox™ model considers three impact indicators: (i) human toxicity cancer, (ii) human toxicity non-cancer and (iii) ecotoxicity for chemical emissions to urban air, rural air, freshwater, sea water, agricultural soil and/or natural soil. The unit of the characterisation factor for freshwater aquatic ectoxicity is PAF/m^3/day/kg emission (Potentially Affected Fraction) and for human toxicity is “cases/kg emission” both summarised as Comparative Toxic Unit (CTU).

For the assessment of the impact of the considered product in the before mentioned leaching scenario (emissions to water and soil) we used the SimaPro® LCA sofware with the USEtox™ (v1.01) model for the calculation of the characterisation factors.

As explained in the previous paragraph, the EPD inventory contains categories of substances (see Table 4.3, first column). Their direct use with the LCIA methods is impossible. In order to overcome this fault, categories which covered a wide range of substances were represented by the substances with the highest, respectively the smallest characterisation factor. For example, in the case of “heavy metals (not specified)” (nomenclature in the EPD), the value of the flow was associated to barium for the minimising case simulation (barium has the smallest characterisation factor in USEtox™) and to beryllium for the maximising case simulation. So, a sensitivity analysis was realised allowing to obtain the maximum and the minimum impact.

The graphs in Figure 4.4 show the evaluation results for our material (CBA-amine treated wood): the contribution of emissions to water and soil for each phase (production, transport, construction stage, use stage and end of life) in the considered impact indicators. Both calculation methods are compared, (i) “1 year simulation”, i.e. inventory data corresponding to use stage per FU is taken from numerical simulation over 1 year in natural exposure conditions and (ii) “1 year average”, i.e. inventory data for the use stage is obtained by an average of the emissions over 50 years of use, obtained extrapolation of the release simulated over 1 year. As explained in §2.4.1 (in this chapter), the use phase is characterised only by leaching data, while production, transport, construction stage and end of life were

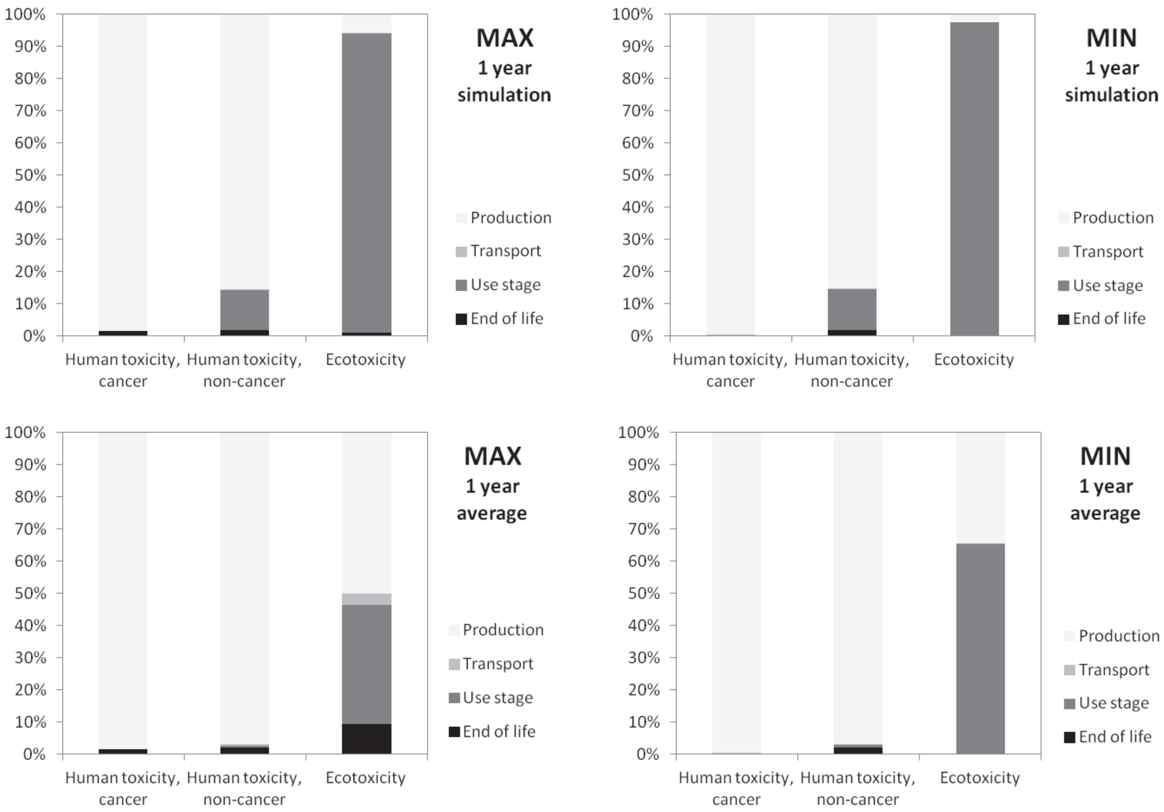

Figure 4.4: Impact assessment results for maximising and minimising simulations (leaching data is calculated from (i) simulation over 1 year – noted 1 year simulation; (ii) average data, i.e. extrapolation of simulation data over 50 years of use - noted 1 year average).

considered with the original EPD data. Emissions during the construction stage were all null in the original document, thus the impact of this stage is zero. For both simulations (maximising and minimising the impact), the human toxicity cancer and non-cancer impact is highest during the production phase, while the impact due to the use stage, transport and end of life is null or very small. On the other hand, the ecotoxicity impact is the highest during the use stage ($\approx 93\%$, respectively 60% for “1 year average”, data compared to the other stages). This is due to the high characterisation factor and high release of copper, i.e. 100 times more than during production phase. The production, transport and end of life have a small ecotoxicity impact. An important difference is observed between the maximising and minimising simulations, which accounts only for the production, transport and end of life stages, given that the flux corresponding to the use stage was not subject to nomenclature changes (the inventory for use stage corresponds to our leaching data and was precisely translated in the USEtox nomenclature). Human toxicity (cancer) and ecotoxicity indicators are up to 10^3, respectively 10^2 higher in the maximising scenario than in the minimizing scenario.

2.5 Conclusions

The proposed methodology enriches the current EPDs considering the impact of leaching process during the product use phase. We showed how it could be applied on French EPDs (built based on the NF P 01-010 standard). However, it could be also used for EPDs based on, for example, the European standard EN 15804.

Integrating leaching data in the inventory flows is based on leaching tests and simulations. A deep knowledge of the leaching mechanisms is necessary. In the test bed case presented (CBA-amine treated wood - material B), the leaching data were obtained through the following steps : (i) laboratory leaching tests ANC and DSLT; (ii) chemical and transport model developed at labscale; (iii) real leaching scenario simulation. We considered here only the run-off scenario. Other exposure scenarios could also be stipulated (e.g. vertical exposure, products in contact with soil or groundwater) depending on the product utilization. The assessment of the impact needs proper tools. We used here the USEtox™ model for the eco- and human toxicity evaluation. For the calculation of eco- and human toxic impact a thorough nomenclature needs to be used (in what concerns organic and inorganic emissions). The considered flows should be correlated with the databases used by the chosen impact model. Simplified flows as currently used in the EPDs are useful for practical reasons, but rather inappropriate for impact calculation, as shown in the example above. Depending on the impact method used, the inventory needs to be detailed (as in the case of USEtox™) or could be simplified (as in the case of the critical volume method). In order to solve this problem, a detailed and a simplified inventory should be available.

In what the NF P 01-010 EPDs concerns, new indicators should be assessed. The currently used indicator "water pollution" is useful for the harmonisation of exiting EPDs. However, it is not relevant for a proper assessment of eco- and human toxicity impacts, as it does not take into consideration the pollutants fate and effects. The emission scenario (target compartment) needs to be well defined in order to choose a suitable impact model.

Finally, we observed that the leaching process dynamics is specific for a substance and a product and consequently the emissions to the target compartment (e.g. soil in the considered scenario) are dynamic over long time periods. The dynamic aspect should be accounted in the impact modelling as well. The existing impact models used in LCA methodology do not yet take into account the dynamic features of the coupled emission, fate, exposure and effect phenomena. This is a subject that needs further investigation.

3 Building scale study

3.1 Introduction

The assessment of environmental building performances is of high interest in the construction sector. As for product level, Life Cycle Assessment (LCA) is the most used method to address the environmental impacts at building level too. It models a product's life cycle, documenting energy and material flows entering or leaving the product system, and assessing the associated environmental burdens. As stated before, see chapter 1, several European projects dealing with LCA and buildings have been conducted over the past few years; the most recent is the EeBGuide project (EeBGuide, 2012), which provides rules and instructions on how to conduct LCA studies of construction products and energy-efficient buildings.

Several LCA-based tools have been already developed in this direction, e.g. ECOSOFT (Austria) (ECOSOFT, 2012), Eco-bat (Switzerland) (ECO-BAT, 2013), GaBi-Build-IT (Germany) (GaBi, 2013), SBS (Germany) (SBS, 2013), ELODIE (France) (CSTB, 2002), EQUER (France) (EQUER, 2010), COCON (France) (EQUER, 2007), GreenCalc+ (The Netherlands) (GreenCalc+, 2010), EcoEffect (Sweden) (EcoEffect, 2008), envest 2 (UK) (everest, 2013), BEES (USA) (BEES, 2009).

The objective of this study is to develop a methodology for the integration of leaching data in the environmental assessment at building scale. The building scale assessment methodology is based on coupling the methodology described in the first part of this chapter (i.e. product scale) with the Life Cycle Assessment (LCA) at building scale - currently the most used methodology of environmental assessment of buildings. The methodology is applied on a simplified single-family house by using ELODIE software.

3.2 Approach and methods

Developed by the CSTB, ELODIE (CSTB, 2002) is a tool based on the Life Cycle Approach (LCA), built for the assessment of the environmental impacts of buildings. ELODIE uses Environmental Products Declarations (EPDs) provided by manufacturers in the INIES database (Association HQE, 2009), integrating contributory elements, such as energy and water consumptions, transport of users (in line with the French standards NF P01-010 (AFNOR, 2000) and NF P01-020 (AFNOR, 2005)). The output of the tool is an environmental multicriteria profile of the building.

The calculation model used in ELODIE is based on the quantification of the flow's balance (contributory elements). The model considers the sum of the impacts of various flows as material and products, as energy and water consumptions (see Figure 4.5) (Chevalier et al., 2010).

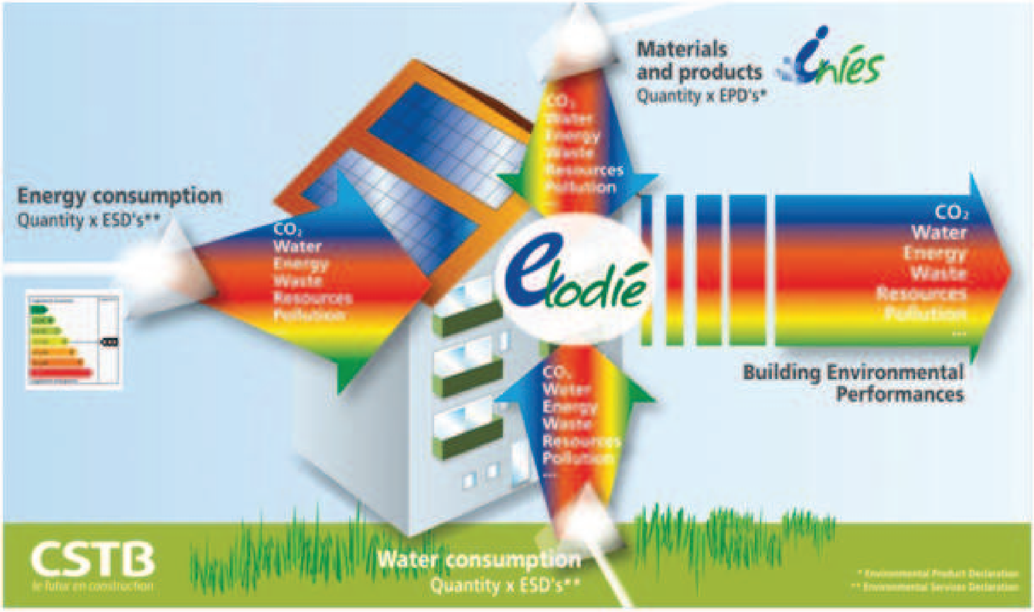

Figure 4.5: Scheme of the model used in ELODIE for the evaluation of the environmental performance of buildings (CSTB, 2002).

The quantification of the contributory element "product and materia" is based on the French EPDs, i.e. FDES, hosted by the free access database INIES (Association HQE, 2009). FDES files contain 10 environmental indicators to evaluate the environmental impact of a product, as shown in chapter 1, Table 1.2.

Leaching data (if present) concerns only the indicator "water pollution" used in the FDES. This indicator is calculated using the critical volume method conform the NF P01-010 standard.

Nevertheless, ELODIE includes additional indicators (see Table 4.4) for eco- and human toxicity. For more explanation why these indicators are the most adequate for the assessment of the impact due to emissions to water and soil, see §2 and the case study on CBA treated wood. Moreover, the EPDs and the LCA tools (at product and building scale) are in a constant development. For example, currently the European standards EN 15804 and EN 15978, at product, respectively building scale, consider eutrophication potential (expressed in kg PO_4^{3-}eq.) as mid-point indicator. This indicator is also included in ELODIE (Table 4.4).

Thus, the final results in ELODIE, concerning water and soil emissions (including leaching data during use stage) are expressed by the following indicators:

- water pollution in m^3 and calculated by the critical volume method, c.f. NF P01-010),
- ecotoxicity in PAF/m^3/day and calculated by the USEtox method, considering characterisation factors for chemical emissions to urban air, rural air, freshwater, sea water, agricultural soil and/or natural soil),
- human toxicity, cancer and non-cancer expressed in DALY and considering the human exposure model used by the USEtox method).

The midpoint characterisation is expressed in Comparative Toxic Unit (CTU), i.e. cases (/$kg_{emission}$) for human toxicity and PAF/m^3/day (/$kg_{emission}$) for ecotoxicity. (Hauschild et al., 2013) suggest that the transition from midpoint to endpoint characterization can be done by applying average severities for cancer and non-cancer, as proposed by (Huijbregts et al., 2005), i.e. an adjustment of 11.5 disability life years for cancer, expressed in DALY/case and 2.5 DALY/case for non-cancer. This method is, however, not mature yet. Still, according to (Hauschild et al., 2013) this is the best suggested method up to now. In what the ecotoxicity indicator concerns, no characterisation model has been already proposed for the midpoint/USEtox to endpoint characterisation.

Table 4.4: Input parameters for ELODIE, regarding the indicators for the considered products, with and without leaching data included.

			Fibre-cement sheets			CBA treated wood		
Indicator	Source/Method	Unit/FU	Total with		Total	Total with		Total
			min	max	without	min	max	without
Energy consumption	FDES	MJ	311			10.9		
Resource depletion	FDES	kg Sb eq	36			0.000885		
Water consumption	FDES	L	80			1.07		
Hazardous waste	FDES	kg	0.03			0.000494		
Climate change	FDES	kg CO_2 eq.	25			-0.375		
Atmospheric acidification	FDES	kg SO_2 eq.	0.108			0.00102		
Air pollution	FDES	m^3	1 358			26.7		
Water pollution	SimaPro/MatFrance	m^3	3.87		3.65	0.51		0.29
Human toxicity, cancer	SimaPro/USEtox	DALY	3.66e-08	3.84e-08	6.03e-13	9.05e-11	1.39e-08	9.05e-11
Human toxicity, non-cancer	SimaPro/USEtox DALY	1.86e-10	1.92e-10	5.70e-11	1.66e-09	1.68e-09	1.65e-09	
Ecotoxicity	SimaPro/USEtox	PAF/m^3/day	0.92	0.99	0.02	0.94	1.66	0.33
Eutrophisation	SimaPro/MatFrance	kg eq. PO_4^{3-}	0.99			0.03		
Destruction of stratospheric ozone layer	FDES	kg CFC eq.	0			3.47e-11		
Formation of photochemical ozone	FDES	kg ethylene eq.	10.6			0.000139		

Figure 4.6 presents the method for integrating leaching data at product scale into ELODIE framework at building scale.

The proposed methodology was studied on a simplified individual single-family house. The house was modelled using the ELODIE software, with the parameters presented in Table 4.5. In the simplified simulation, only the envelope (outdoor use components) of the building was considered in order to evaluate the impact of leaching data.

Table 4.5: Parameters characterising the building modelled with ELODIE tool.

Parameter		Value
Reference service life		100 years
Outdoor use components	Terrace in CBA treated wood	$74.12\,m^2$
	Roof in fibre-cement sheets	$166.87\,m^2$
	Facade in CBA treated wood	$332.15\,m^2$

The environmental impact calculations, based on the methodology developed in this study (see Figure 4.6) followed several steps:

- The cumulative emissions per FU for the considered products were calculated from leaching data obtained in this study by extrapolation over the whole RSL. Leaching data was obtained by numerical simulation over 1 year in natural exposure conditions (for CBA treated wood see chapter 3 §2, for fibre-cement sheets see §3). The FU used in the corresponding FDES files is $1\,m^2$ over 1 year for treated wood and $100\,m^2$ over 1 year for fibre-cement (wood boards have an effective surface smaller than $1\,m^2$, while one fibre-cement sheet covers more than $1\,m^2$).
- The inventory given in the FDES files (i.e. (Eternit, 2003) for fibre-cement sheets and (FCBA, 2011) for CBA treated wood, both attached in appendix D and E) was enriched with emissions to water and soil during use stage, for both products, i.e. cumulative emissions calculated in the previous step (over the RSL of the products) were divided by the RSL and an average release per FU (1 year) was integrated with FDES inventory data.
- The impacts were calculated using the SimaPro™ tool, i.e. the USEtox™ model for eco- and human toxicity impacts and the critical volume method (also used in the EPD and known as MatFrance in SimaPro™) for the water pollution indicator. Two scenarios were considered: (i) with leaching data included and (ii) without leaching data. Moreover, as discussed in §2, taking into consideration the lack of information concerning the nomenclature of

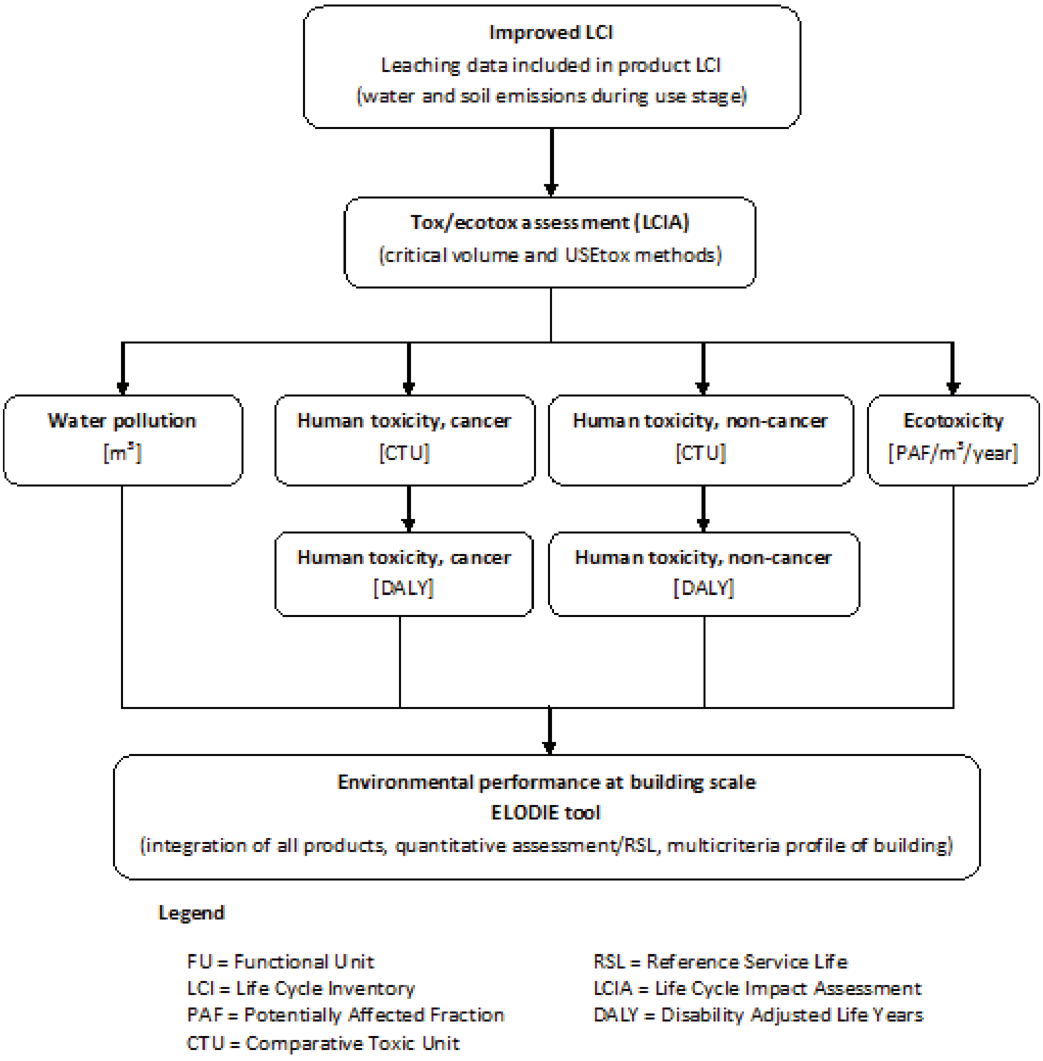

Figure 4.6: Methodological scheme for including leaching data in the assessment of the environmental performances of buildings with ELODIE.

pollutants in the inventory, two subscenarios were considered in the first scenario (i.e. with leaching data included): a maximising and a minimising scenario.

- The human toxicity (cancer and non-cancer) indicators were expressed in DALY, as discussed before.
- The final values for the four indicators concerning the emissions to water and soil during use stage, i.e. water pollution, ecotoxicity, human toxicity cancer and non-cancer, were included in ELODIE for the three considered scenarios: (i) with leaching data included maximising scenario, (ii) with leaching data included minimising scenario and (iii) without leaching data. The other indicators, e.g. energy consumption, resource depletion, water consumption, climate change, etc, were considered from the associated FDES files for each product.

The values included in ELODIE for all indicators and per product are given in Table 4.4.

3.3 Results and discussion

The impacts at building scale simulated with ELODIE are presented in Figure 4.7 and Table 4.6. As expected, the emissions to water and soil during the use stage have an important weight in the overall process comparing the orange and blue lines with the red line in Figure 4.7. For example, leaching data increases the impact in ecotoxicity and water pollution with approximately 91 %, if considered in the inventory. If comparing the maximising and the minimising scenarios (orange and blue lines in Figure 4.7) a high discrepancy is noticeable for the human toxicity cancer impact, i.e. in the maximising scenario the impact due to leaching data represents 99 % from the impact due to emissions during the whole lifecycle of the product and 62 % in the minimising scenario. This is explained by the difference in the characterization factors of different pollutants considered in the inventory, namely: chromium (Cr^{6+} has a higher impact factor than Cr^{3+}), arsenic, PAH (anthracene has a smaller characterisation factor than benzo(a)pyrene), biocides and hydrocarbons On the other hand, the differences between the maximising and minimising scenario corresponding to human toxicity non-cancer impacts have similar values the evaluation of the human toxicity non-cancer impact considered mainly fluxes which didn't suppose a minimising or maximising scenario (e.g. copper, which is included in the inventory of the FDES as ionic copper and in the same

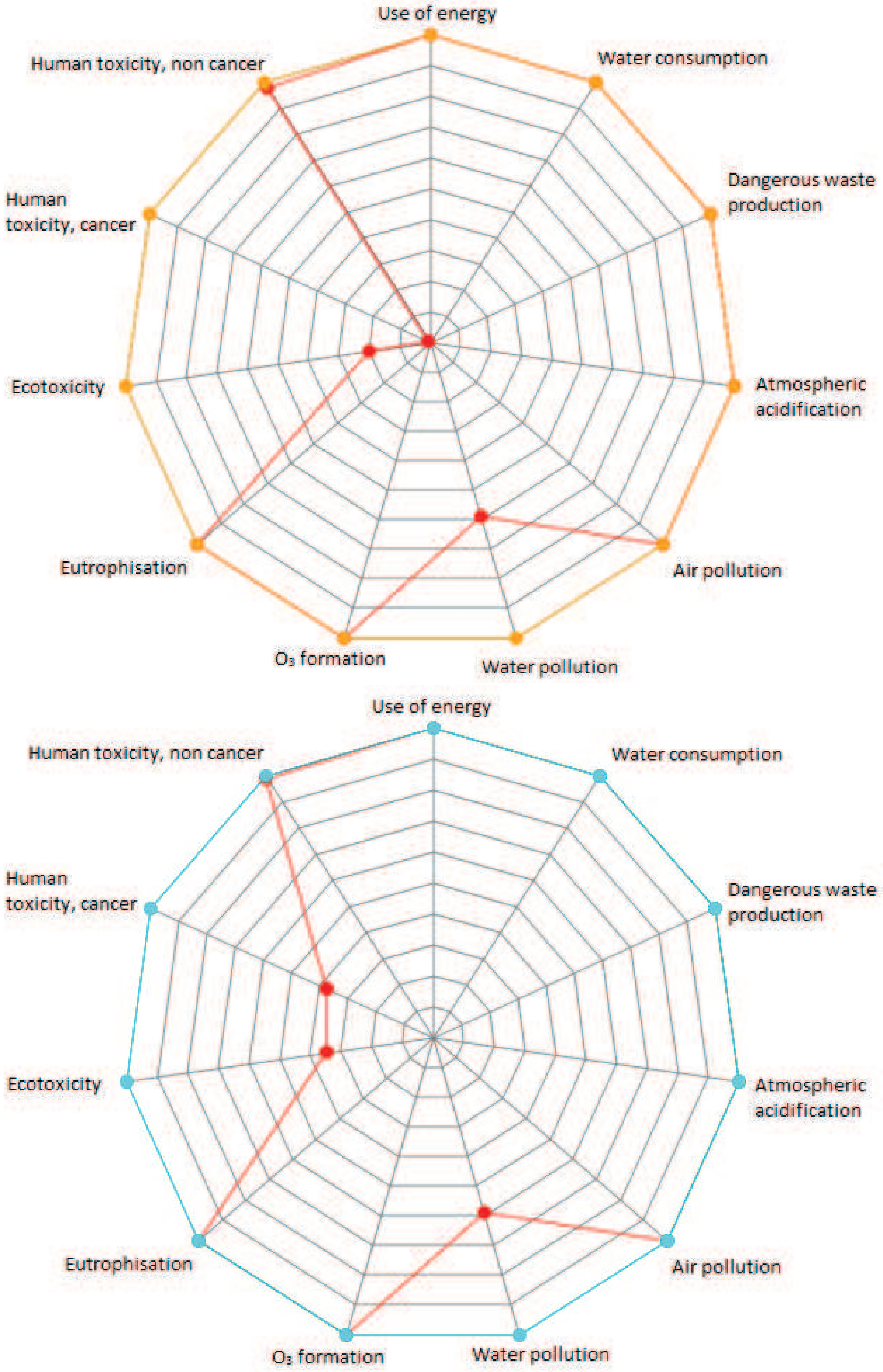

Figure 4.7: Environmental impact of the modelled house comparison of three simulations with ELODIE: (1) in red without leaching data, (2) in orange with leaching data included maximizing scenario and (3) in blue with leaching data included minimising scenario.

Table 4.6: Impact of emissions to water and soil at building scale and weight of leaching data in the global impact.

Indicator	Unit	With		Without	Leaching data %	
		MIN	MAX		MIN	MAX
Water pollution	m^3	1.6	1.6	9.70e-01	39.38	39.38
Human toxicity, cancer	DALY	7.60e-10	4.40e-08	2.90e-10	61.84	99.34
Human toxicity, non-cancer	DALY	5.23e-09	5.30e-09	5.20e-09	0.57	1.89
Ecotoxicity	$PAF/m^3/day$	3	5.2	1	66.67	80.77

form in the USEtox inventory). Nevertheless, other products, implying a different inventory, might have a different behaviour.

The comparison between the two scenarios at building scale, i.e. with and without leaching data included is given in percentage in Table 4.6.

A sensitivity analysis was performed on the leaching data considered in the inventory. The impact was evaluated in two cases:

1. Emissions per FU were allocated the cumulative release over 1 year, obtained by numerical simulation,
2. Average emissions per FU were calculated by dividing the cumulative release over the RSL (calculated by extrapolation of the release during 1 year).

The two scenarios (with both maximising and minimising inventory) are presented in Figure 4.8. As expected, the impact is higher when using an inventory based on leaching data over 1 year, than when using an inventory which considers average emissions. Indeed, if the emissions over 1 year are multiplied by the RSL, the release of all pollutants largely exceeds the total content of the product. A particularly high difference is observed for the ecotoxicity and water pollution indicators, where the impact calculated using the emissions after 1 year is 10 times higher than when using average leaching data.

3.4 Conclusions

The environmental impact at building scale was assessed on a single family house using the simulation tool ELODIE. The impact was evaluated for the envelope of a simplified house model (outdoor use components), in order to study the influence of the emissions to water and soil during the use stage, characterised by leaching data. The used methodology is based on leaching data obtained by numerical simulations of mechanistic chemical-transport models, which were developed using experimental characterisation leaching tests. Four impact indicators

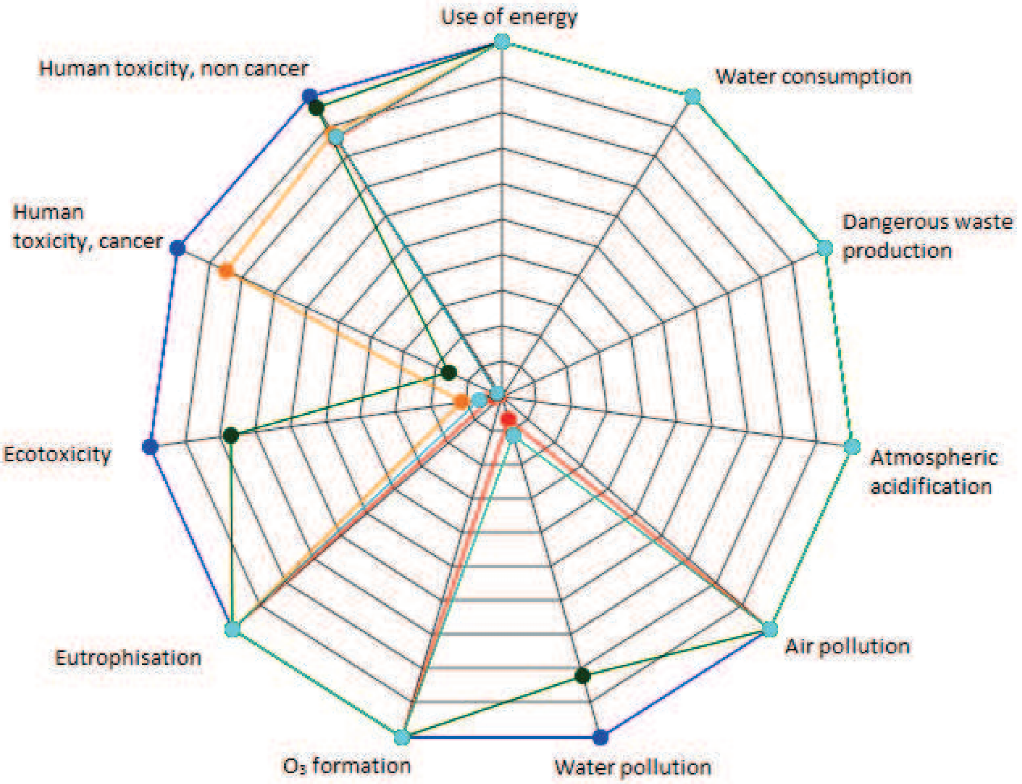

Figure 4.8: Sensitivity study on inventory data in ELODIE : (1) in red without leaching data, (2) in orange with average leaching data included maximizing scenario, (3) in light blue with average leaching data included minimising scenario, (4) in green with leaching data after 1 year minimising scenario and (5) in blue with leaching data after 1 year maximising scenario.

have been calculated to assess the impact due to emissions to water and soil during use stage, i.e. water pollution, ecotoxicity, human toxicity cancer and non-cancer. In order to study the sensitivity of the inventory data (in what the nomenclature regards), two scenarios have been considered: (i) a maximising scenario and (ii) a minimising scenario. The comparison of the results for the minimising and maximising scenarios shows that a correct and proper inventory is important. The overall results prove that the contribution of leaching data in the global tox/ecotox impact can represent up to 99%.

4 Conclusions

The objective of this chapter was to include leaching data in the environmental impact of products and buildings. The proposed methodology is based on numerical simulations of the leaching behaviour of construction products. The assessment at building scale considers the sum of the impacts of all considered products. At product scale the methodology was studied on CBA treated wood. At building scale a simplified single-family house was considered, with the envelope consisting of: (i) roof in fibre-cement sheets, (ii) facade in CBA treated wood and (iii) terrace in CBA treated wood.

Several conclusions could be drawn from the case studies at product and building scales:

- The environmental assessment of products currently based on LCA could be enriched considering the impact of leaching process during the product use phase. A detailed example was given for CBA treated wood.
- A deep knowledge of the leaching mechanisms is necessary in order to obtain proper leaching data.
- Adequate methods are indispensable for the assessment of the impact. We used here the USEtox™ model for the eco- and human toxicity evaluation, presently considered as the best available.
- The inventory data needs to be correlated with the databases used by the chosen impact model from the point of view of the nomenclature, e.g. inventory flows expressed in ionic or metallic form, organic compounds defined individually or in classes of substances. Simplified flows (currently used in the EPDs) are useful for practical reasons, but rather inappropriate for impact calculation.
- As already mentioned in chapter 1, summing up emissions of pollutants to water and soil during use stage, i.e. leaching data (which have a local impact), with emissions during the other phases of the product's life cycle (which concern different emission compartments and different time spans) is rather incorrect. Nevertheless, current LCA methods are restrictive, not considering the spatial location of the environmental burdens.
- The impact over the whole reference service life (RSL) of the product could be assessed by numerical simulation. If the study focuses on the impact of emissions to water and soil, or on pollution during use stage, or if the emissions to water and soil during use stage are significant, the methodology developed in this study, based on numerical simulations of the leaching behaviour of products in natural exposure conditions, is more adequate. Nevertheless, a numerical simulation over several years (e.g. 50 years of service life) is time demanding and powerful and advanced computing machines are necessary.

- Both studies, at product and building scale, showed that leaching data (corresponding to the use stage) has a significant impact in the global eco- and human toxicity indicators, evaluated over the whole life cycle of the product.

Conclusions and perspectives

Conclusions

Any construction product undergoing contact with water during its use stage is susceptible of pollutant release. However, these emissions to water and soil are not well evaluated in the current assessment procedures.

The current study had two main objectives:

(I) Evaluation of the leaching behaviour of some classical construction products (without waste included);

(II) Development of a methodology for the integration of leaching data in the LCA approach of construction products and buildings.

In order to respond to the first objective, a study methodology was proposed based on laboratory leaching tests and mechanistic modelling applied on selected construction materials.

The main construction products, used for the buildings' envelope, which come into contact with water (products used for the roofing, façade, terraces and in foundations) were identified and classified in function of the structure and nature of the material. Preliminary leaching tests helped at identifying three interesting products (widely used, different matrix types, containing potentially hazardous substances) for the methodology application: CBA treated wood, fibre-cement sheets and bitumen membrane.

The experimental work was based especially on two laboratory leaching tests representative for a horizontal approach compatible with monolithic materials. These tests are:

1. The static pH-dependency leaching test (ANC): it helps at characterising the leaching chemical mechanisms.
2. The dynamic surface leaching test (DSLT): it supplies information concerning the time dependency of leaching of different pollutants (transfer, kinetic mechanisms).

The experimental work showed that their application to treated wood and fibre-cement materials is appropriate, while the application to bitumen membrane encountered practical difficulties due to the material properties (impossibility to thinly crush the material and achieve dissolution equilibrium).

These tests together supply the necessary information for the leaching mechanism understanding and modelling. A coupled chemical-transport model was developed for CBA treated wood and fibre-cement sheets. The main achievement in this part of the study was the development of a leaching mechanism for CBA treated wood and fibre-cement sheets, taking into consideration the inorganic and organic compounds. In the case of treated wood, biocide (copper, boron, tebuconazole) dynamic leaching was modelled for the first time considering a coupled chemistry-transport model, aiming at understanding the intimate leaching mechanism of mineral and organic compounds. Concerning the fibre-cement sheets, the experiments revealed the leaching of the pesticide terbutryn, believed to be added as a treatment for the cellulose fibres included in the product. Bitumen membranes proved to be an atypical product, due to its mechanical properties: high density, non porous, temperature dependent structure. No numerical simulation could be performed for this product.

The second objective of the study was to develop a methodology for the integration of the leaching data in LCA tools. The proposed methodology requires the following steps:

1. Identification of the emission scenario to be considered within LCA framework, i.e. in which compartment are the pollutants directly emitted by the product during its use (emission scenarios).
2. Improvement of the Life Cycle Inventory (LCI) with leaching data, i.e. considering leaching data with the inventory flows corresponding to emissions to water and soil during use stage.
3. Life Cycle Impact Assessment (LCIA) using the new enriched inventory and appropriate methods, i.e. calculation of water pollution, eco- and human toxicity indicators.

The methodology was applied for the environmental impact assessment of a simplified individual single-family house. Two of the selected products were used for the case study, i.e. CBA treated wood and fibre-cement sheets. Leaching data obtained from simulations over 1 year under natural exposure conditions were used in the LCI and further interpreted by impact calculation. The respective

French EPDs were used for the individual product evaluation (for other impact indicators during the other phases of the life cycle). The impact of leaching data at building scale was assessed using the ELODIE software. The construction products addressed in this study were included with enriched inventory concerning the emissions of pollutants during use stage. The USEtox™ model was used to assess the impact for ecotoxicity and human toxicity (cancer and non-cancer), which are the main consequences of the pollutant emissions by leaching. Also, the method proposed by the French standard NF P 01-010 was used for the indicator "water pollution".

The main conclusion of this part is that the impact of leaching data can represent up to 90% of the impact due to emissions to water and soil during the whole life cycle. This was observed for both eco- and human toxicity indicators. Moreover, the same study was performed on the "water pollution" indicator, widely spread in current EPDs (e.g. the French FDES) and the same trends were observed. The global contribution of the use stage to the product or building life cycle impacts cannot be generalized or extrapolated from a material to another since it strongly depends on the material's physical-chemical properties. These properties have crucial repercussions on the leaching behaviour and pollutant emission. Therefore, the long term leaching behaviour should be carefully assessed and for doing this, powerful tools like modelling and simulation could be used.

Concerning the feasibility of the use stage integration in the French EPDs (FDES), several limitations were identified:

- an ambiguous consideration of the emission compartment (water or soil) for all life cycle stages of a product;
- too generic classes of substances (metals, biocides, etc), making impossible a proper evaluation of the environmental impacts;
- eco- and human toxicity indicators are missing; they should be considered in addition to or instead of more general categories like "water pollution" (expressed in m^3).

Perspectives

The perspectives raised by this study concern: (i) leaching tests, (ii) innovative construction products, (iii) dynamic LCA approach and (iv) building scale assessement.

Leaching from classical construction products has not been extensively considered up to now. Once the horizontal test methods proposed by CEN TC 351 validated, a higher interest in leaching evaluation of construction products is expected. This study showed that modelling of the leaching behaviour is of high importance in environmental assessment (or risk assessment) of construction products and buildings. In this sense, the chemical background of the leaching phenomena taking place in the pores of the material is fundamental. The development of the leaching mechanism for each type of matrix is based on pH dependency tests. In this study we performed the experiments based on the XP CEN/TS 14429 standard which describes experimental approaches for the evaluation of the leaching behaviour of waste. Nevertheless, construction products have various types of matrixes and difficulties might come up in some particular cases (e.g. crushing of bitumen membranes). For leaching mechanism identification, a useful approach would be the standardisation of specific tests for different types of construction products taking into consideration their specificities (porous/nonporous, metallic, composites, etc.).

Besides the products tested in this study, many other construction products need to be regarded. As in the case of the release of terbutryn from fibre-cement sheets, potentially hazardous substances could be released by leaching, substances of which we are not aware. Moreover, innovative products should be also taken into consideration, for example construction products containing nanomaterials. Despite the high costs of production, companies use more and more nanotechnology to add special characteristics to product surfaces. Nanotechnology can enforce the mechanical characteristics of products, such as stain-resistance, colour durability, self-cleaning, improved hardness, scratch-resistance, corrosion, UV resistance and improved thermal performances. Nevertheless, hazardous aspects of exposure to nanoparticles should be taken into consideration. Leaching of nanoparticles is imminent. Leaching tests and analysis methods should be adapted for nanoparticles and the environmental and risk assessment should be taken into account.

The methodology presented in this study for the coupling of leaching data and LCA considers the cumulative emissions over the whole use stage of the product. Nevertheless, the dynamic character of the leaching phenomena is largely proved and should be included in the evaluation. But the temporal aspects are missing in conventional LCA which could be considered as ideal simplification of the real phenomena. The temporal aspects in LCA are very little studied so far, further researches and methodological developments will be necessary.

Once the leaching behaviour and impacts of individual construction products are assessed, the passage to building scale can raise several difficulties. The chemical-physical system is more complex. Eluates which contain released substances from a construction product become leachates for the next subsystem, e.g. eluates from the roof are leachates for the facade. Adapted experiments and models are needed in this case, cost and complexity rise. So far, no modelling attempt has been made in this direction.

Conclusion et discussion

Tous les produits de construction qui arrivent en contact avec l'eau météorique pendant la phase de vie en œuvre sont susceptibles de relarguer des substances dangereuses. Toutefois, ces émissions dans l'eau et le sol sont peu prises en compte dans les approches actuelles d'évaluation environnementale des produits de construction et des bâtiments.

La présente étude a deux objectifs principaux :

(I) L'évaluation du comportement à la lixiviation de différentes typologies des produits de construction ;

(II) Le développement d'une méthodologie pour l'intégration des données de lixiviation dans l'approche ACV - Analyse de Cycle de Vie des produits de construction et des bâtiments.

Afin de répondre au premier objectif, une méthodologie d'étude, basée sur des essais de lixiviation à l'échelle laboratoire et sur des modèles m écanistiques, a été proposée.

Les principaux produits de construction utilisés pour l'enveloppe des bâtiments (produits utilisés pour la toiture, la faade, les terrasses et dans les fondations) ont été identifiés et classés en fonction de leur structure et de la nature du matériau. Des essais de lixiviation préliminaires ont été menés en guise d'aide aux choix des produits pour la suite de l'étude (identification des produits qui relarguent des substances potentiellement dangereuses). En fonction de la représentativité sur le marché, la typologie de la matrice et du relargage des substances potentiellement dangereuses, trois produits de construction ont été sélectionnés pour la suite de l'étude : le bois traité CBA, la plaque fibrociment et la membrane bitumineuse.

Le travail expérimental a été basé essentiellement sur des essais de lixiviation à l'échelle laboratoire, représentatifs pour l'approche horizontale d'évaluation :

1. Les essais statiques de dépendance du pH (ANC) : ils contribuent à la caractérisation des mécanismes chimiques des phénomènes de lixiviation.
2. Les essais dynamiques pour produits monolithe (DSLT) : ils permettent d'obtenir des informations supplémentaires sur la dynamique de relargage, sur le mécanisme de diffusion dans les pores du produit et/ou sur le transfert de masse (convection) à la surface du monolithe.

Les travaux expérimentaux ont montré que ces essais sont adaptés pour les produits à matrice poreuse (bois traité et plaque fibrociment), mais peu adaptés pour la membrane bitumineuse –produit à matrice non poreuse et hydrophobe.

Ces essais ont permis d'acquérir les informations nécessaires à la compréhension du mécanisme de lixiviation et au développement des modèles numériques. Un modèle couplé chimie-transport a été développé pour le bois traité et pour la plaque fibrociment. La principale réalisation dans cette partie de l'étude consiste dans le développement des modèles mécanistiques décrivant les mécanismes de lixiviation pour le bois traité CBA et la plaque fibrociment, en considérant les composés inorganiques et organiques. Dans le cas du bois traité, la dynamique de relargage des biocides (cuivre, bore, tébuconazole) a été modélisée pour la première fois en se basant sur un modèle couplé chimie-transport décrivant les mécanismes physico-chimiques de lixiviation de composés minéraux et organiques. En ce qui concerne la plaque fibrociment, les expériences ont révélé la présence du biocide terbutryne dans les éluats. Ce biocide est probablement utilisé pour le traitement de fibres cellulosiques lors des étapes amont dans la fabrication du produit. Pour la membrane bitumineuse, les données d'entrée pour le développement du modèle mécanistique n'ont pas pu être obtenues à l'aide des essais horizontaux. Ces essais sont peu adaptés pour les produits à matrice équivalente à la membrane bitumineuse, i.e. matrice non poreuse à haute densité et hydrophobe. Aucune simulation numérique n'a été effectuée pour ce produit.

Le deuxième objectif de l'étude a été de développer une méthodologie pour l'intégration des données de lixiviation dans les outils ACV. La méthode proposée suit les étapes suivantes :

1. L'identification des scénarios d'émissions, i.e. dans quels compartiments sont émis les polluants lors de la phase de vie en œuvre du produit ;
2. Amélioration de l'inventaire de cycle de vie (ICV) avec des données de lixiviation, i.e. prendre en compte les données de lixiviation dans les flux d'inventaire correspondant aux émissions dans l'eau et dans le sol pendant la phase de vie en œuvre ;
3. Évaluation de l'impact en utilisant l'inventaire enrichi et des méthodes appropriées (LCIA) pour le calcul des indicateurs pollution de l'eau, écotoxicité et toxicité humaine.

La méthodologie a été appliquée pour l'évaluation de l'impact environnemental d'une maison individuelle simplifiée. Deux des produits sélectionnés ont été utilisés pour cette étude de cas, i.e. le bois traité CBA et la plaque fibrociment. Les données de lixiviation obtenues à partir de simulations du comportement à la lixiviation dans des conditions naturelles d'exposition sur un an ont été utilisées dans l'ICV et ensuite interprétées par le calcul de l'impact. Les données pour les autres étapes du cycle de vie des produits sont issues des Fiches de Déclaration Environnementale et Sanitaire (FDES) disponibles dans la base de données franaise de référence sur les caractéristiques environnementales et sanitaires des produits de construction (INIES). A l'échelle b âtiment, les évaluations ont été menées à l'aide du logiciel ELODIE. Le modèle USEtox™ a été utilisé pour le calcul des indicateurs écotoxicité et toxicité humaine (cancer et non-cancer). Pour le calcul de l'indicateur pollution de l'eau la méthode de la norme franaise NF P 01-010 (basée sur l'approche volume critique) a été utilisée.

La principale conclusion de cette partie est que l'impact des données de lixiviation peut représenter jusqu'à 90% de l'impact d aux émissions dans l'eau et le sol pendant toute la durée du cycle de vie du produit. Ceci a été observé pour les trois indicateurs calculés. Cependant, cette conclusion ne peut pas être généralisée ou extrapolée d'un produit à un autre, car le comportement à la lixiviation dépend fortement des propriétés physico-chimiques des matériaux. L'évaluation du comportement à la lixiviation à long terme nécessite des outils puissants tels que la modélisation mécanistique et la simulation numérique.

En ce qui concerne la faisabilité de l'intégration des impacts environnementaux dus à la lixiviation dans les FDES, plusieurs limites ont été identifiées :

- la considération ambigüe du compartiment d'émissions (eau, sol) pour toutes les étapes du cycle de vie d'un produit ;
- les classes génériques des substances (métaux, biocides, etc.), ce qui rend impossible une évaluation adéquate des impacts environnementaux à l'échelle locale ;
- l'absence des indicateurs écotoxicité et toxicité humaine ; ils devraient être considérés en complément ou à la place de l'indicateur pollution d'eau.

Les perspectives de cette étude concernent : (i) les tests de lixiviation, (ii) les produits de construction innovants, (iii) l'approche ACV dynamique et (iv) l'échelle bâtiment. Jusqu'à présent, les données de lixiviation ont été peu prises en compte dans l'évaluation environnementale des produits de construction. Une fois les méthodes d'essai horizontales proposées par le CEN TC 351 validées (validation prévue pour 2013), un intérêt plus élevé est attendu. Cette étude a montré que la modélisation du comportement à la lixiviation a une grande importance dans l'évaluation environnementale des produits de construction et des bâtiments. En ce sens, la compréhension des mécanismes de relargage est fondamentale. Les essais de lixiviation viennent en appui à cette démarche de compréhension. Cependant, pour certaines typologies de produits (e.g. la membrane bitumineuse), les essais actuellement disponibles (e.g. l'essai de dépendance de pH) ne permettent pas de répondre à cet objectif. L'idéal serait le développement d'essais adaptés à différentes typologies de matrices (non poreuse, hydrophobe, métallique, composites, etc.).

En plus des produits testés dans cette étude, de nombreux autres produits de construction doivent être considérés. Comme le relargage inattendu d'un biocide (i.e. terbutryne) par les plaques fibrociment, des substances potentiellement dangereuses pourraient être émises par d'autres produits de construction. En outre, des produits innovants devraient également être pris en considération, par exemple des produits de construction contenant des nanomatériaux. Malgré les coûts élevés de production, les entreprises utilisent de plus en plus la nanotechnologie par exemple pour ajouter des caractéristiques spéciales à la surface des produits (e.g. l'autonettoyage, la résistance aux rayures, à la corrosion, etc.). Néanmoins, la lixiviation des nanoparticules est imminente. Les méthodologies et les outils d'évaluation environnementale (les essais de lixiviation, les méthodes d'analyse) devraient être adaptés à cette typologie de produits.

La méthodologie présentée dans cette étude pour l'intégration des données de lixiviation dans les évaluations environnementales des produits et des bâtiments considère les émissions cumulées sur toute la phase d'utilisation du produit. Néanmoins, le caractère dynamique des phénomènes de lixiviation est largement prouvé et devrait être inclus dans l'évaluation. Les aspects temporels manquent dans les approches ACV utilisées couramment et du développement méthodologique est nécessaire à ce sujet.

Une fois le comportement à la lixiviation et les impacts des produits de constructions évalués, le passage à l'échelle bâtiment peut soulever quelques difficultés. Le système physico-chimique est plus complexe. Les éluats qui contiennent des substances émises par un produit de construction peuvent devenir des lixiviats pour le prochain sous-système, par exemple les éluats de la toiture peuvent devenir des lixiviats pour la façade. Des essais et des modèles adaptés sont nécessaires dans ce cas, le coût et la complexité augmentent. Jusqu'à présent, aucune tentative de modélisation n'a été faite en ce sens.

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Appendices

Appendix A

Analytical methods

A list of all substances (ionic species and organics) analysed within the screening tests performed in this study is given below. The analythical methods used, as well as the detection limits, along with the corresponding CAS number are listed.

Sandre	Paramétre	N° CAS	Méthode	Limite de quantification
Acide monochloroacétique (330)				
1465	Acide monochloroacétique		Chromatographie ionique	5 µg/l
Acide phosphoreux (2894)				
	Acide phosphoreux (H3PO3)		Methode interne selon ISO 10304-1	0.1 mg/l
Acrylamide (2645)				
1457	Acrylamide	79-06-1	HPLC MSMS EN DIRECT	0.1 µg/l
Agents de Surface-Détergent(Eau) (350)				
1444	Agents de surface (COFRAC)		NF EN 903	20 µg/l
Alcools (356)				
2595	1 Butanol	71-36-3	GC FID	10 µg/l
2570	2 Butanol	78-92-2	GC FID	10 µg/l
2577	2 Methyl 1 Butanol	137-32-6	GC FID	10 µg/l
2590	3 Methyl 1 Butanol	123-51-3	GC FID	10 µg/l
2582	2 Methyl 2 Butanol	75-85-4	GC FID	10 µg/l
1747	Ethanol	64-17-5	GC FID	50 µg/l
2574	2 Ethyl Hexanol	104-76-7	GC FID	10 µg/l
2052	Méthanol	67-56-1	GC FID	500 µg/l
2598	1 Pentanol	71-41-0	GC FID	100 µg/l
2584	2 Pentanol	032-29-7	GC FID	10 µg/l
2587	3 Pentanol	584-02-1	GC FID	10 µg/l
2617	1 Propanol	71-23-8	GC FID	10 µg/l
2585	2 Propanol	67-63-0	GC FID	10 µg/l
2579	2 Methyl 1 Propanol	78-83-1	GC FID	10 µg/l
2583	2 Methyl 2 Propanol	75-65-0	GC FID	10 µg/l
Alkylphénols (2628)				
1957	Nonylphénols	25154-52-3	GC MS	0.040 µg/l
1958	4-n-nonylphénol	104-40-5	GC MS	0.040 µg/l
1959	Octylphénol	1806-26-4	GC MS	0.040 µg/l
2971	Para-nonylphénol	25154-52-3	GC MS	0.040 µg/l
1959	Para-tert-octylphénol	140-66-9	GC MS	0.040 µg/l
2610	4-ter-butylphénol	98-54-4	GC MS	0.040 µg/l
Aluminium (ICP) (Al) (369)				
1370	Aluminium (Al) (COFRAC)		NF EN ISO 11885	5 µg/l
Amines (2577)				
2826	Diéthylamine	109-89-7	Chromatographie ionique	25 µg/l
2773	Diméthylamine	124-40-3	Chromatographie ionique	25 µg/l
Aminotriazole (2507)				
1105	Aminotriazole (COFRAC)	61-82-5	CMO_MT08	0.05 µg/l
Ammoniac non Ionisé (378)				
1351	Ammoniac non ionisé (NH3)		Calcul	0.005 mg/l
Ammonium (380)				
1335	Ammonium (NH4) (COFRAC)		NF T 90 015-2	0.05 mg/l
Anhydride Carbonique libre (408)				
1334	Anhydride carbonique libre		Infrarouge	5 mg/l
Anilines et dichloroanilines (409)				
1593	2-Chloroaniline	95-51-2	GC MS	0.02 µg/l
1592	3-Chloroaniline	108-42-9	GC MS	0.02 µg/l
1591	4-Chloroaniline	106-47-8	GC MS	0.02 µg/l
	Chloroanilines total (somme des 3 isomères)		GC MS	0.02 µg/l
1594	4-Chloro 2 nitroaniline	89-63-4	GC MS	0.02 µg/l
1590	2,3 Dichloroaniline	608-27-5	GC MS	0.02 µg/l
1589	2,4 Dichloroaniline	554-00-7	GC MS	0.02 µg/l
1588	2,5 Dichloroaniline	95-82-9	GC MS	0.02 µg/l
1587	2,6 Dichloroaniline	608-31-1	GC MS	0.02 µg/l
1586	3,4 Dichloroaniline	95-76-1	GC MS	0.02 µg/l
1585	3,5 Dichloroaniline	626-43-7	GC MS	0.02 µg/l

Sandre	*Paramétre*	*N° CAS*	*Méthode*	*Limite de quantification*
	Dichloroanilines total		GC MS	0.02 µg/l
2734	2,3,4 Trichloroaniline	634-67-3	GC MS	0.02 µg/l
2733	2,3,5 Trichloroaniline	634-91-3	GC MS	0.02 µg/l
2732	2,4,5 Trichloroaniline	636-30-6	GC MS	0.02 µg/l
1595	2,4,6 Trichloroaniline	634-93-5	GC MS	0.02 µg/l
Antimoine (ICP) (Sb) (423)				
1376	Antimoine (Sb) (COFRAC)	7440-36-0	NF EN ISO 11885	5 µg/l
Aox (424)				
1106	Aox (COFRAC)		NF EN ISO 9562	10 µg/l Cl
Argent (ICP) (Ag) (428)				
1368	Argent (Ag) (COFRAC)	7440-22-4	NF EN ISO 11885	5 µg/l
Arsenic (ICP) (As) (436)				
1369	Arsenic (As) (COFRAC)	7440-38-2	NF EN ISO 11885	5 µg/l
Azote ammoniacal (2551)				
	Azote ammoniacal (NH4) (COFRAC)		NF T 90 105-2	0.05 mg/l
Azote global (464)				
1551	Azote global		Calcul	mg (N)/l
Azote Kjeldahl (465)				
1319	Azote Kjeldahl (N) (COFRAC)		NF EN 25663	1 mg/l
Balance ionique calcul NE PAS ENREGISTRER EN TEST (478)				
	Balance ionique			
Baryum (ICP) (Ba) (481)				
1396	Baryum (Ba) (COFRAC)	7440-39-3	NF EN ISO 11885	5 µg/l
Beryllium (ICP) (Be) (506)				
1377	Beryllium (Be) (COFRAC)	7440-41-7	NF EN ISO 11885	5 µg/l
Bilan qualitatif anions cations (524)				
	Bilan qualitatif anions cations		Chromatographie ionique	
Bilan qualitatif HPLC (521)				
	Bilan qualitatif HPLC		HPLC DAD	
Bilan qualitatif métaux (527)				
	Bilan qualitatif métaux		NF EN ISO 11885	
Biphenyl, Oxyde de biphenyl (2692)				
1584	Biphényle (COFRAC)	92-52-4	CMO_MT02	0.1 µg/l
	Oxide de biphényle (Equivalent Biphényle) (COFRAC)	202-981-2	CMO_MT02	0.1 µg/l
	Equivalent Therminol		GC MS	0.2 µg/l
Bismuth (ICP) (Bi) (543)				
3315	Bismuth (Bi) (COFRAC)		NF EN ISO 11885	5 µg/l
Bore (ICP) (B) (546)				
1362	Bore (B) (COFRAC)	7440-42-8	NF EN ISO 11885	5 µg/l
Bromates (554)				
1751	Bromates (COFRAC)		NF EN ISO 10304-1	5 µg/l
Brome total (2893)				
	Brome total		NF T 90 037-2	
Bromures (562)				
1378	Bromures		NF EN ISO 10304-1	5 µg/l
Cadmium (ICP) (Cd) (595)				
1388	Cadmium (Cd) (COFRAC)	7440-43-9	NF EN ISO 11885	2 µg/l
Calcium (chromato ionique) (599)				
1374	Calcium total (COFRAC)		NF EN ISO 14911	1 mg/l
Carbamates (2602)				
1102	Aldicarbe (COFRAC)	116-06-3	CMO_MT19	0.02 µg/l
1807	Aldicarbe sulfone (COFRAC)	1646-88-4	CMO_MT19	0.02 µg/l
1806	Aldicarbe sulfoxyde (COFRAC)	1646-87-3	CMO_MT19	0.02 µg/l
1463	Carbaryl (COFRAC)	63-25-2	CMO_MT19	0.02 µg/l
1130	Carbofuran (COFRAC)	1563-66-2	CMO_MT19	0.02 µg/l

Sandre	Paramétre	N° CAS	Méthode	Limite de quantification
1805	Carbofuran-3-hydroxy (COFRAC)	16655-82-6	CMO_MT19	0.02 µg/l
1510	Mercaptodimétur (COFRAC)	2032-65-7	CMO_MT19	0.02 µg/l
1218	Méthomyl (COFRAC)	16752-77-5	CMO_MT19	0.02 µg/l
1535	Propoxur (COFRAC)	114-26-1	CMO_MT19	0.02 µg/l
1715	Thiofanox (COFRAC)	39196-18-4	CMO_MT19	0.05 µg/l
5476	Thiofanox-sulfone (COFRAC)		CMO_MT19	0.05 µg/l
5475	Thiofanox-sulfoxyde (COFRAC)		CMO_MT19	0.05 µg/l
Carbone inorganique total (TIC) (2728)				
	Carbone inorganique total (COFRAC)		NF EN 1484	1 mg/l C
Carbone organique dissous (Eau) COD (624)				
1318	Carbone organique dissous (COFRAC)		NF EN 1484	0.1 mg/l C
Carbone organique total (COT) (589)				
1841	Carbone organique total (COFRAC)		NF EN 1484	0.1 mg/l C
Cétones (880)				
1455	Acétone	67-64-1	GC FID	10 µg/l
1514	2 Butanone (Méthyl Ethyl Cétone)	78-93-3	GC FID	10 µg/l
2619	2 Heptanone (Méthyl Pentyl Cétone)	110-43-0	GC FID	10 µg/l
2635	3 Heptanone	106-35-4	GC FID	10 µg/l
2638	4 Heptanone	123-19-3	GC FID	10 µg/l
2627	2 Hexanone (Méthyl Butyl Cétone)	591-78-6	GC FID	10 µg/l
2630	2 Methyl CycloHexanone	583-60-8	GC FID	10 µg/l
2636	3 Methyl CycloHexanone	591-24-2	GC FID	10 µg/l
2639	4 Methyl CycloHexanone	589-92-4	GC FID	10 µg/l
1508	Méthyl Iso Butyl Cétone (MIBC)	105-30-06	GC FID	10 µg/l
2631	2 Nonanone	821-55-6	GC FID	10 µg/l
2640	5 Nonanone	502-56-7	GC FID	0.5 µg/l
2632	2 Octanone	111-13-7	GC FID	10 µg/l
2634	3 Octanone (Ethyl Pentyl Cétone)	106-68-3	GC FID	10 µg/l
2633	2 Pentanone (Méthyl Propyl Cétone)	107-87-9	GC FID	10 µg/l
2637	3 Pentanone (Ethyl Cétone)	96-22-0	GC FID	10 µg/l
Chlorates (635)				
1752	Chlorates		NF EN ISO 10304-1	5 µg/l
Chlore résiduel (labo) (647)				
	Chlore résiduel calculé (sur valeur laboratoire) (COFRAC)		Calcul	0.04 mg/l
Chlore total (labo) (648)				
1399	Chlore total (mesuré au laboratoire) (COFRAC)		NF EN ISO 7393-2	0.04 mg/l
Chlorites (654)				
1735	Chlorites (COFRAC)		NF EN ISO 10304-1	5 µg/l
Chloroalcanes (2740)				
1955	Chloroalcanes (C10-C13)		GC ECD	10 µg/l
Chlorobenzènes (2458)				
1467	Mono chlorobenzène (COFRAC)		NF ISO 11 423-1	0.2 µg/l
1165	Dichlorobenzène 1,2 (COFRAC)	541-73-1	NF EN ISO 10301	0.2 µg/l
1164	Dichlorobenzène 1,3 (COFRAC)	95-50-1	NF EN ISO 10301	0.2 µg/l
1166	Dichlorobenzène 1,4 (COFRAC)	106-46-7	NF EN ISO 10301	0.2 µg/l
2893	Dichlorobenzènes (somme des 3 isomères)		NF EN ISO 10301	0.5 µg/l
1630	Trichlorobenzène 123 (COFRAC)	87-61-6	CMO_MT02	0.010 µg/l
1283	Trichlorobenzène 124 (COFRAC)	120-82-1	CMO_MT02	0.010 µg/l
1629	Trichlorobenzène 135 (COFRAC)	108-70-3	CMO_MT02	0.010 µg/l
1774	Trichlorobenzène (total isomères)	12002-48-1	CMO_MT02	0.010 µg/l
1199	Hexachlorobenzene (COFRAC)	118-74-1	CMO_MT02	0.010 µg/l
1888	Pentachlorobenzène (COFRAC)	608-93-5	CMO_MT02	0.005 µg/l
2010	Tétrachlorobenzène 1,2,3,4 (COFRAC)	634-90-2	CMO_MT02	0.010 µg/l
1631	Tétrachlorobenzène 1,2,4,5 (COFRAC)	95-94-3	CMO_MT02	0.010 µg/l
Chloronitrobenzènes (2515)				
1469	1 Chloro 2 nitrobenzène	88-73-3	GC MS	0.02 µg/l
1468	1 Chloro 3 nitrobenzène	121-73-3	GC MS	0.02 µg/l
1470	1 Chloro 4 nitrobenzène	100-00-5	GC MS	0.02 µg/l
1612	1 Chloro 2.4 dinitrobenzène	97-00-7	GC MS	0.02 µg/l
1617	2.3 Dichloronitrobenzène	3209-22-1	GC MS	0.02 µg/l

Sandre	Paramétre	N° CAS	Méthode	Limite de quantification
1616	2.4 Dichloronitrobenzène	611-06-3	GC MS	0.02 µg/l
1615	2.5 Dichloronitrobenzène	89-61-2	GC MS	0.02 µg/l
1614	3.4 Dichloronitrobenzène	99-54-7	GC MS	0.02 µg/l
1613	3.5 Dichloronitrobenzene	618-62-2	GC MS	0.02 µg/l
Chlorophylle et phéopigments (674)				
1439	Chlorophylle A		XP T 90 117	1 µg/l
1438	Chlorophylle B		Méthode interne	1 µg/l
1437	Chlorophylle C		Méthode interne	1 µg/l
1436	Phéophytine		XP T 90 117	1 µg/l
Chlorure de vinyle (2576)				
1753	Chlorure de vinyle (COFRAC)	75-01-4	NF EN ISO 10301	0.5 µg/l
Chlorures (chromato ionique) (702)				
1337	Chlorures(Cl) (COFRAC)		NF EN ISO 10304-1	1 mg/l
Chrome Hexavalent (722)				
1371	Chrome Hexavalent		NF T 90 043	5 µg/l
Chrome Total (ICP) (Cr) (728)				
1389	Chrome total (Cr) (COFRAC)	7440-47-3	NF EN ISO 11885	2 µg/l
Cobalt (ICP) (Co) (744)				
1379	Cobalt (Co) (COFRAC)	7440-48-4	NF EN ISO 11885	5 µg/l
Coliformes Totaux (Eaux) sur membrane sur 100 ml (754)				
1447	Coliformes Totaux sur membrane		Rapid E coli 2 (BIORAD)	UFC/100ml
Conductivite (800)				
1303	Conductivité à 25°C (COFRAC)		NF EN 27888	1 µS/cm
	Conductivité à 20°C		Calcul	1 µS/cm
Conductivite sur place (2499)				
1303	Conductivité sur place (COFRAC)		NF EN 27888	1 µS/cm à 25°C
Créosote (828)				
1453	Acénaphthène		GC MS	0.05 µg/l
1622	Acénaphtylène		GC MS	0.05 µg/l
1584	Biphenyl (COFRAC)		GC MS	0.05 µg/l
1476	Chrysène		GC MS	0.05 µg/l
	Equivalent créosote (dibenzofuran)		GC MS	0.05 µg/l
	Dibenzofuran		GC MS	0.05 µg/l
Cryptosporidium (soustraitance) (2713)			nous consulter	
1065	Cryptosporidium oocyste		Soustraitance	
Cuivre (ICP) (Cu) (837)				
1392	Cuivre (Cu) (COFRAC)	7440-50-8	NF EN ISO 11885	2 µg/l
Cyanobactéries identification (soustraitance) (2676)				
	Cyanobactéries			n/ml
Cyanobactéries identification INRA (soustraitance) (2814)				
	Cyanobactéries identification			
Cyanures libres (Eau) (853)				
1084	Cyanures Libres		NF EN ISO 14403	5 µg/l
Cyanures Totaux (Eau) (849)				
1390	Cyanures Totaux (COFRAC)		NF EN ISO 14403	5 µg/l
DBOn (2447)				
1313	Demande biologique en oxygène (DBOn) (COFRAC)		NF EN 1899-2	0.5 mg O2/l
DBOn sans dilution (882)				
1313	Demande biologique en oxygène (DBOn) (COFRAC)			0.5 mg O2/l
DCO (890)				
1314	Demande chimique en oxygène (COFRAC)		NF T 90 101	15 mg O2/l
Désinfectant libre (labo) (1023)				
1395	Désinfectant libre (mesuré au laboratoire) (COFRAC)		NF T 90 037-2	0.04 mg/l
Désinfectant total (labo) (1027)				
1399	Désinfectant total (mesuré au laboratoire) (COFRAC)		NF T 90 037-2	0.04 mg/l

Sandre	*Paramétre*	*N° CAS*	*Méthode*	*Limite de quantification*
Diphényléthers bromés (2741)				
1815	Décabromodiphényléther	1163-19-5	CMO_MT02	0.010 µg/l
2609	Octabromodiphényléther	32536-52-0	CMO_MT02	0.010 µg/l
1921	Pentabromodiphényléther (COFRAC)	32534-81-9	CMO_MT02	0.010 µg/l
2601	Tetrabromodiphenyl ether 2,2',4,4' (COFRAC)		CMO_MT02	0.010 µg/l
2916	Pentabromodiphenyl ether 2,2',4,4',5 (COFRAC)		CMO_MT02	0.010 µg/l
2915	Pentabromodiphenyl ether 2,2',4,4',6 (COFRAC)		CMO_MT02	0.010 µg/l
2913	Hexabromodiphenyl ether 2,2',3,4,4',5' (COFRAC)		CMO_MT02	0.010 µg/l
2912	Hexabromodiphenyl ether 2,2',4,4',5,5' (COFRAC)		CMO_MT02	0.010 µg/l
2911	Hexabromodiphenyl ether 2,2',4,4',5,6' (COFRAC)		CMO_MT02	0.010 µg/l
Diquat Paraquat (2726)				
1699	Diquat (COFRAC)	2764-72-9	CMO_MT18	0.10 µg/l
1522	Paraquat (COFRAC)	4685-14-7	CMO_MT18	0.10 µg/l
Dithiocarbamates (CS2) (2574)				
2066	Dithiocarbamates (CS2)		GC- Espace de tête	1.0 µg/l
Dureté calculée (1010)				
	Dureté calculée (COFRAC)		CEA_M548	0.1 degré Fr
Dureté totale (TH) complexométrie (1011)				
1345	Dureté (COFRAC)		NF T 90 003	0.1 degré Fr
Epichlorhydrine (2578)				
1494	Epichlorhydrine	106-89-8	GC MS	1 µg/l
Escherichia coli (filtration) 100 ml (1063)				
1449	Escherichia coli (COFRAC)		NF EN ISO 9308-1	10 UFC/100ml
Escherichia coli sur microplaques (1064)				
	Escherichia coli sur microplaque (COFRAC)		NF EN ISO 9308-3	15 UFC/100ml
Etain (ICP) (Sn) (1076)				
1380	Etain (Sn) (COFRAC)	7440-31-5	NF EN ISO 11885	10 µg/l
Fenhexamid (2681)				
2743	Fenhexamid	126833-17-8	GC ECD	0.02 µg/l
Fer (ICP) (Fe) (1120)				
1393	Fer total (Fe) (COFRAC)		NF EN ISO 11885	5 µg/l
Fer dissous sur échantillon filtré (2718)				
	Fer dissous sur échantillon filtré (COFRAC)		NF EN ISO 11885	5 µg/l
Flazasulfuron E.Sup ISK (DTPP) (2657)				
1939	Flazasulfuron (COFRAC)	104040-78-0	ISK DTPP	0.1 µg/l
Fluorures (chromato ionique) (1190)				
1391	Fluorures (COFRAC)		NF EN ISO 10304-1	0.050 mg/l
Formaldéhyde (2822)				
1702	Formaldéhyde	50-00-0	Méthode interne	1 µg/l
Formiates (2920)				
	Formiates		NF EN ISO 10304-1	mg/l
Fosetyl-aluminium (2844)				
1975	Fosetyl-aluminium	39148-24-8	HPLC MS MS EN DIRECT	0.100 µg/l
Fosthiazate (2571)				
2744	Fosthiazate (COFRAC)	98886-44-3	CMO_MT02	0.02 µg/l
Geosmines (2816)				
150	Géosmine	19700-21-1	GC SPME	0.005 µg/l
	2-Methylisobornéol	2371-42-8	GC SPME	0.010 µg/l
Germes Totaux 48h à 36°C (2535)				
1041	Germes aérobies totaux à 36°C (COFRAC)		NF EN ISO 6222	1 n/ml
Germes Totaux 72h à 22°C (1239)				
1040	Germes aérobies totaux à 22°C (COFRAC)		NF EN ISO 6222	1 n/ml
Glycols et ethers de glycols (2641)				
2716	Diethylène glycol	111-46-6	GC FID	1.0 mg/l
2718	Ethylène glycol	107-21-1	GC FID	1.0 mg/l

Sandre	*Paramétre*	*N° CAS*	*Méthode*	*Limite de quantification*
2727	Propylène glycol	504-63-2	GC FID	1.0 mg/l
2641	Diethylène glycol butyl ether	112-34-5	GC FID	1.0 mg/l
2642	Diethylène glycol butyl ether acétate	124-17-4	GC FID	1.0 mg/l
2643	Diethylène glycol dimethyl ether	111-96-6	GC FID	1.0 mg/l
2644	Diethylène glycol ethyl ether	111-90-0	GC FID	1.0 mg/l
2645	Diethylène glycol ethyl ether acétate	112-15-2	GC FID	1.0 mg/l
2646	Diethylène glycol methyl ether	111-77-3	GC FID	1.0 mg/l
2647	Diethylène glycol n hexyl ether	112-59-4	GC FID	1.0 mg/l
2648	Diethylène glycol ter butyl ether methyl ether	52788-79-1	GC FID	1.0 mg/l
2649	Ethylène glycol Ethyl ether	110-80-5	GC FID	1.0 mg/l
2650	Ethylène glycol diethyl ether	629-14-1	GC FID	1.0 mg/l
2651	Ethylène glycol dimethyl ether	110-71-4	GC FID	1.0 mg/l
2653	Ethylène glycol ethyl ether acétate	111-15-9	GC FID	1.0 mg/l
2654	Ethylène glycol iso-propyl ether	109-59-1	GC FID	1.0 mg/l
2656	Ethylène glycol methyl ether acétate	110-49-6	GC FID	1.0 mg/l
2658	Ethylène glycol n butyl ether acétate	112-07-2	GC FID	1.0 mg/l
2657	Ethylène glycol n butyl ether	111-76-2	GC FID	1.0 mg/l
2659	Ethylène glycol n propyl ether	2807-30-9	GC FID	1.0 mg/l
2660	Ethylène glycol phényl ether	122-99-6	GC FID	1.0 mg/l
2655	Ethylène glycol methyl ether	109-86-4	GC FID	1.0 mg/l
2661	Triethylène glycol dimethyl ether	112-49-2	GC FID	1.0 mg/l
2662	Triethylène glycol ethyl ether	112-50-5	GC FID	1.0 mg/l
2663	Triethylène glycol methyl ether	112-35-6	GC FID	1.0 mg/l
Glyphosate , AMPA Glufosinate (2506)				
1506	Glyphosate (COFRAC)	1071-83-6	CMO_MT14	0.10 µg/l
1907	AcideAminoMéthylPhosphonique (AMPA) (COFRAC)	1066-51-9	CMO_MT14	0.10 µg/l
2731	Glufosinate d'ammonium (COFRAC)	77182-82-2	CMO_MT14	0.10 µg/l
Granulométrie (tamis- soustraitance) (2557)				
	Granulométrie (COFRAC)		Laser	
Herbicides forme ester (2668)				
2873	2,4 D-methyl-ester	1928-38-7	CMO_MT02	0.05 µg/l
	2,4 D- isopropyl-ester	94-11-1	CMO_MT02	0.05 µg/l
2871	Ioxynil methyl ester	3336-40-1	CMO_MT02	0.05 µg/l
1942	Ioxynil octanoate	3861-47-0	CMO_MT02	0.05 µg/l
2745	MCPA-1-butyl ester	1713-12-8	CMO_MT02	0.05 µg/l
2747	MCPA-butoxyethyl ester	19480-43-4	CMO_MT02	0.05 µg/l
2746	MCPA-2-ethylhexyl ester	26544-20-7	CMO_MT02	0.05 µg/l
2748	MCPA-ethyl-ester	2698-38-6	CMO_MT02	0.05 µg/l
2749	MCPA-methyl-ester	2436-73-9	CMO_MT02	0.05 µg/l
2870	Mecoprop-n iso-butyl ester		CMO_MT02	0.05 µg/l
	Mecoprop-2-butoxyethyl ester	23359-62-8	CMO_MT02	0.05 µg/l
2755	Mecoprop-methyl ester	2786-19-7	CMO_MT02	0.05 µg/l
	Mecoprop-1-octyl ester	161922-37-8	CMO_MT02	0.05 µg/l
2751	Mecoprop-2,4,4-trimethylpentyl ester	217487-13-3	CMO_MT02	0.05 µg/l
2753	Mecoprop-2-ethylhexyl ester	71526-69-7	CMO_MT02	0.05 µg/l
2754	Mecoprop-2-octyl ester	28473-03-2	CMO_MT02	0.05 µg/l
Hexachlorocyclopentadiène (2781)				
2612	Hexachlorocyclopendiène	77-47-4	CMO_MT02	0.05 µg/l
Hydrocarbures à chaînes longues (1323)				
1554	Dodecane ($C_{12}H_{26}$)	112-40-2	GC FID	1.0 µg/l
1555	Tridecane ($C_{13}H_{28}$)	629-50-5	GC FID	1.0 µg/l
1556	Tetradecane ($C_{14}H_{30}$)	629-59-4	GC FID	1.0 µg/l
1557	Pentadecane ($C_{15}H_{32}$)	629-62-9	GC FID	1.0 µg/l
1558	Hexadecane ($C_{16}H_{34}$)	544-76-3	GC FID	1.0 µg/l
1559	Heptadecane ($C_{17}H_{36}$)	629-78-7	GC FID	1.0 µg/l
1560	Octadecane ($C_{18}H_{38}$)	593-45-3	GC FID	1.0 µg/l
1561	Nonadecane ($C_{19}H_{40}$)	629-92-5	GC FID	1.0 µg/l
1562	Eicosane ($C_{20}H_{42}$)	112-95-8	GC FID	1.0 µg/l
1563	Heneicosane ($C_{21}H_{44}$)	629-94-7	GC FID	1.0 µg/l
1564	Docosane ($C_{22}H_{46}$)	929-97-0	GC FID	1.0 µg/l
1565	Tricosane ($C_{23}H_{48}$)	638-67-5	GC FID	1.0 µg/l
1566	Tetracosane ($C_{24}H_{50}$)	646-31-1	GC FID	1.0 µg/l
1567	Pentacosane ($C_{25}H_{52}$)	629-99-2	GC FID	1.0 µg/l

Sandre	*Paramétre*	*N° CAS*	*Méthode*	*Limite de quantification*
1568	Hexacosane ($C_{26}H_{54}$)	630-01-3	GC FID	1.0 µg/l
1569	Heptacosane ($C_{27}H_{56}$)	593-49-7	GC FID	1.0 µg/l
1570	Octacosane ($C_{28}H_{58}$)	630-02-4	GC FID	1.0 µg/l
1571	Nonacosane ($C_{29}H_{60}$)	630-03-5	GC FID	1.0 µg/l
1572	Triacontane ($C_{30}H_{62}$)	638-68-6	GC FID	1.0 µg/l
	Heneicosane11 decyl($C_{31}H_{64}$)	55320-06-4	GC FID	1.0 µg/l
1573	Dotriacontane ($C_{32}H_{66}$)	544-85-4	GC FID	1.0 µg/l
1574	Tritriacontane ($C_{33}H_{68}$)	630-05-7	GC FID	1.0 µg/l
1575	Tetratriacontane ($C_{34}H_{70}$)	114167-59-0	GC FID	1.0 µg/l
	Eicosane 10 heptyl 10 octyl $C_{35}H_{72}$)	55470-98-9	GC FID	1.0 µg/l
1576	Hexatriacontane ($C_{36}H_{74}$)	630-06-8	GC FID	1.0 µg/l
	Tetratetracontane $C_{44}H_{90}$	7098-22-8	GC FID	1.0 µg/l
Hydrocarbures legers BTEX NF ISO 11423 (2496)				
1581	Isooctane	540-84-1	NF ISO 11 423-1	5 µg/l
1114	Benzène (COFRAC)	71-43-2	NF ISO 11 423-1	0.2 µg/l
1632	Bromobenzène (COFRAC)	108-86-1	NF ISO 11 423-1	0.2 µg/l
1855	Butyl benzène n (COFRAC)	104-51-8	NF ISO 11 423-1	0.2 µg/l
1610	Butyl benzène sec (COFRAC)	135-98-8	NF ISO 11 423-1	0.2 µg/l
1611	Butyl benzène ter (COFRAC)	98-06-6	NF ISO 11 423-1	0.2 µg/l
1602	Chlorotoluène 2 (COFRAC)	95-49-8	NF ISO 11 423-1	0.2 µg/l
1601	Chlorotoluène3 (COFRAC)	108-41-8	NF ISO 11 423-1	0.2 µg/l
1600	Chlorotoluène 4 (COFRAC)	106-43-4	NF ISO 11 423-1	2 µg/l
1583	Cyclohexane	110-82-7	NF ISO 11 423-1	0.2 µg/l
2665	Decane (C10) (COFRAC)	124-18-5	NF ISO 11 423-1	1 µg/l
2666	Diméthylbutane 2,2	75-83-2	NF ISO 11 423-1	5 µg/l
2667	Diméthylbutane 2,3	79-29-8	NF ISO 11 423-1	5 µg/l
2668	Diméthylpentane 2,3	565-59-3	NF ISO 11 423-1	10 µg/l
1554	Dodecane (C12) (COFRAC)	112-40-3	NF ISO 11 423-1	1 µg/l
2673	EthylTertioButylEther	637-92-3	NF ISO 11 423-1	0.2 µg/l
1497	Ethylbenzène (COFRAC)	100-41-4	NF ISO 11 423-1	0.2 µg/l
2717	Ethyltoluene o	611-14-3	NF ISO 11 423-1	2 µg/l
	Ethyltoluenes p+m	622-96-8+620-14-4	NF ISO 11 423-1	2 µg/l
	Ethyltoluènes		NF ISO 11 423-1	2 µg/l
2674	Heptane (C7) (COFRAC)	142-82-5	NF ISO 11 423-1	1 µg/l
2675	Hexane (C6) (COFRAC)	110-54-3	NF ISO 11 423-1	1 µg/l
2676	Indane (COFRAC)	496-11-7	NF ISO 11 423-1	0.2 µg/l
2677	Indène (COFRAC)	95-13-6	NF ISO 11 423-1	0.2 µg/l
1836	Isobuthylbenzène (COFRAC)	538-93-2	NF ISO 11 423-1	0.4 µg/l
1633	Isopropylbenzène (cumène) (COFRAC)	98-82-8	NF ISO 11 423-1	0.2 µg/l
2680	Isopropyltoluène m (m cymène) (COFRAC)	535-77-3	NF ISO 11 423-1	2 µg/l
2681	Isopropyltoluène o (o cymène) (COFRAC)	527-84-4	NF ISO 11 423-1	0.2 µg/l
1856	Isopropyltoluène p (p cymène) (COFRAC)	99-87-6	NF ISO 11 423-1	0.2 µg/l
1512	Methyltertiobutylether (MTBE) (COFRAC)	1634-04-4	NF ISO 11 423-1	0.2 µg/l
	Méthyl cyclohexane	108-87-2	NF ISO 11 423-1	5 µg/l
2682	Méthylbutane 2	78-78-4	NF ISO 11 423-1	10 µg/l
2683	Méthylpentane 2	107-83-5	NF ISO 11 423-1	10 µg/l
1517	Naphtalène (COFRAC)	91-20-3	NF ISO 11 423-1	0.2 µg/l
2684	Nonane (C9) (COFRAC)	111-84-2	NF ISO 11 423-1	1 µg/l
2685	Octane (C8) (COFRAC)	111-65-9	NF ISO 11 423-1	1 µg/l
2686	Pentane (C5) (COFRAC)	109-66-0	NF ISO 11 423-1	1 µg/l
1837	Propylbenzène (COFRAC)	103-65-1	NF ISO 11 423-1	0.2 µg/l
1541	Styrène (COFRAC)	100-42-5	NF ISO 11 423-1	0.2 µg/l
1278	Toluène (COFRAC)	108-88-3	NF ISO 11 423-1	0.2 µg/l
1857	Trimethylbenzene 1,2,3 (COFRAC)	526-67-8	NF ISO 11 423-1	0.2 µg/l
1609	Trimethylbenzène 1,2,4 (COFRAC)	95-63-6	NF ISO 11 423-1	0.2 µg/l
1509	Trimethylbenzène 1,3,5 (COFRAC)	108-67-8	NF ISO 11 423-1	0.2 µg/l
2689	Tétraméthylbenzène 1235 (COFRAC)		NF ISO 11 423-1	0.2 µg/l
2688	Tétraméthylbenzène 1245 (COFRAC)	95-93-2	NF ISO 11 423-1	0.2 µg/l
2690	Undecane (C11) (COFRAC)	1120-21-4	NF ISO 11 423-1	1 µg/l
1292	Xylène ortho (COFRAC)	95-47-6	NF ISO 11 423-1	0.2 µg/l
1780	Xylènes (ortho, méta, para) (COFRAC)		NF ISO 11 423-1	0.2 µg/l
2925	Xyléne méta + para (COFRAC)	108-38-3+106-42-3	NF ISO 11 423-1	0.2 µg/l
2670	Equivalent essence		GC FID EQ ES	20 µg/l
2671	Equivalent pétrole		GC FID EQ PETROLE	20 µg/l
2672	Equivalent white spirit		GC FID EQ WP	20 µg/l

Sandre	*Paramétre*	*N° CAS*	*Méthode*	*Limite de quantification*
	Indice C5 à C11		Projet IHV	20 µg/l
Hydrocarbures lourds (1304)				
F015	Equivalent Gas-oil (ou Fuel)		GC FID EQ GAS-OIL	20 µg/l
F016	Equivalent Huiles minérales		GC FID EQ HUILE	50 µg/l
	Equivalent hydrocarbures totaux		GC EQHYT	20 µg/l
1442	Indice hydrocarbure (9377-2) (COFRAC)		NF EN ISO 9377-2	50 µg/l
Hydrocarbures polyaromatiques (PAH) les 18 (1314)				
1458	Anthracène (COFRAC)	120-12-7	CMO_MT02	0.01 µg/l
1453	Acénaphthène (COFRAC)	83-32-9	CMO_MT02	0.01 µg/l
1622	Acénaphtylène (COFRAC)	208-96-8	CMO_MT02	0.03 µg/l
1115	Benzo (a) pyrène (COFRAC)	50-32-8	CMO_MT02	0.001 µg/l
1082	Benzo (a) anthracène (COFRAC)	569-55-3	CMO_MT02	0.03 µg/l
1116	Benzo (b) fluoranthène (COFRAC)	207-08-9	CMO_MT02	0.005 µg/l
1117	Benzo (k) fluoranthène (COFRAC)	205-99-2	CMO_MT02	0.005 µg/l
1118	Benzo (ghi) perylène (COFRAC)	191-24-2	CMO_MT02	0.005 µg/l
1476	Chrysène (COFRAC)	218-01-9	CMO_MT02	0.01 µg/l
1621	Dibenzo (a,h) anthracene (COFRAC)	53-70-3	CMO_MT02	0.01 µg/l
1191	Fluoranthène (COFRAC)	206-44-0	CMO_MT02	0.01 µg/l
1623	Fluorène (COFRAC)	869-73-7	CMO_MT02	0.01 µg/l
1204	Indéno (1,2,3-cd) pyrène (COFRAC)	193-39-5	CMO_MT02	0.01 µg/l
1619	Methyl 2 fluoranthène (COFRAC)	33453-31-6	CMO_MT02	0.05 µg/l
1618	Methyl 2 naphtalène (COFRAC)	91-57-6	CMO_MT02	0.05 µg/l
1517	Naphtalène (COFRAC)	91-20-3	CMO_MT02	0.02 µg/l
1524	Phénanthrène (COFRAC)	85-01-8	CMO_MT02	0.01 µg/l
1537	Pyrène (COFRAC)	129-00-0	CMO_MT02	0.01 µg/l
Hydrocarbures polyaromatiques (PAH) les 6 (1313)				
1115	Benzo (a) pyrène (COFRAC)	50-32-8	CMO_MT02	0.001 µg/l
1116	Benzo (b) fluoranthène (COFRAC)	205-99-2	CMO_MT02	0.005 µg/l
1117	Benzo (k) fluoranthène (COFRAC)	207-08-9	CMO_MT02	0.005 µg/l
1118	Benzo (ghi) perylène (COFRAC)	191-24-2	CMO_MT02	0.005 µg/l
1191	Fluoranthène (COFRAC)	206-44-0	CMO_MT02	0.01 µg/l
1204	Indéno (1,2,3-cd) pyrène (COFRAC)	193-39-5	CMO_MT02	0.03 µg/l
2034	Hydrocarb. Polycycl. Arom. (total 6 Substst.)		CMO_MT02	0.005 µg/l
Hydrogène Sulfure Quantitatif (Eau) (1332)				
1343	Hydrogène sulfuré: recherche quantitative		Potentiométrie	20 µg/l
Iode total (ICP) (I) (1365)				
1381	Iode total (I)		NF EN ISO 11885	20 µg/l
IPBC (2650)				
2741	3-Iodo-2-propynylbutybutylcarbamate	55406-53-6	GC MS	0.02 µg/l
Legionella pneumophila methode classique (1404)				
	Legionella (COFRAC)		NF T 90 431	UFC/l
	dont Légionella pneumophila (COFRAC)		NF T 90 431	UFC/l
Legionella pneumophila par PCR (2810)				
	Légionella pneumophila par PCR		NF T 90 431	
Lithium (ICP) (Li) (1442)				
1364	Lithium (Li) (COFRAC)		NF EN ISO 11885	5 µg/l
Magnésium (chromato ionique) (Mg) (2479)				
1372	Magnésium (Mg) (COFRAC)		NF EN ISO 14911 oct 98	1 mg/l
Manganèse (ICP) (Mn) (1484)				
1394	Manganèse (Mn) (COFRAC)		NF EN ISO 11885	5 µg/l
Manganèse dissous sur echantillon filtré (ICP) (Mn) (2791)				
1394	Manganèse dissous sur échantillon filtré (Mn)		NF EN ISO 11885	
Matières en Suspension totales (1488)				
1305	Matières en suspension totales (COFRAC)		NF EN 872	1 mg/l
Matières en Suspension Volatiles et minérales (1490)				
1434	Matières en suspension volatiles		NF EN 872	1
	Matières en suspension minérales		NF EN 872	1
Mercure (Hg) (1534)				
1387	Mercure (Hg) (COFRAC)	7439-97-6	NF EN 1483	0.1 µg/l

Sandre	Paramétre	N° CAS	Méthode	Limite de quantification
Metaldéhyde (2712)				
1796	Métaldéhyde	108-62-3	GC MS	0.05 µg/l
Métaux par ICP/MS (21) (2855)				
1376	Antimoine (Sb)	7440-36-0	NF EN ISO 17294-2	1 µg/l
1368	Argent (Ag)	7440-22-4	NF EN ISO 17294-2	1 µg/l
1369	Arsenic (As)		NF EN ISO 17294-2	1 µg/l
1396	Baryum (Ba)		NF EN ISO 17294-2	1 µg/l
1377	Beryllium (Be)		NF EN ISO 17294-2	1 µg/l
1362	Bore (B)		NF EN ISO 17294-2	2 µg/l
1388	Cadmium (Cd)		NF EN ISO 17294-2	0.5 µg/l
1389	Chrome Total (Cr)		NF EN ISO 17294-2	1 µg/l
1379	Cobalt (Co)		NF EN ISO 17294-2	1 µg/l
1392	Cuivre (Cu)		NF EN ISO 17294-2	1 µg/l
1380	Etain (Sn)		NF EN ISO 17294-2	1 µg/l
1395	Molybdène		NF EN ISO 17294-2	1 µg/l
1386	Nickel (Ni)		NF EN ISO 17294-2	1 µg/l
1382	Plomb (Pb)		NF EN ISO 17294-2	0.5 µg/l
1385	Sélénium (Se)		NF EN ISO 17294-2	2 µg/l
2559	Tellurium (Te)		NF EN ISO 17294-2	2 µg/l
2555	Thallium (Tl)		NF EN ISO 17294-2	0.5 µg/l
1373	Titane (Ti)		NF EN ISO 17294-2	1 µg/l
1361	Uranium (U)		NF EN ISO 17294-2	0.5 µg/l
1384	Vanadium (V)		NF EN ISO 17294-2	1 µg/l
1383	Zinc (Zn)		NF EN ISO 17294-2	1 µg/l
Microcystines (HPLCMS) (soustraitance) (2675)				
2058	Microcystines			
Microscystines (ELISA) (soustraitance) (2722)				
	Microcystine intra et extracellulaire		Technique ELISA	0.16 µg/l
	Microcystine extracellulaire		Technique ELISA	0.16 µg/l
	Microcystine intracellulaire		Technique ELISA	0.16 µg/l
Molybdène (ICP) (Mo) (1561)				
1395	Molybdène (Mo) (COFRAC)	7439-98-7	NF EN ISO 11885	5 µg/l
Nickel (ICP) (Ni) (1619)				
1386	Nickel (Ni) (COFRAC)	7440-02-0	NF EN ISO 11885	5 µg/l
Nitrates (1626)				
1340	Nitrates (COFRAC)		NF EN ISO 10304-1	1 mg (NO3) /l
Nitrites (1632)				
1339	Nitrites (COFRAC)		NF EN 26777	0.02 mg (NO2) /l
Nitrotoluènes (1636)				
1577	2,6 Dinitrotoluène		HPLC DAD	0.050 µg/l
Organohalogénés volatils OHV ISO 10301 (2014)				
2081	Dichloropropane 2,2		NF EN ISO 10301	0.2 µg/l
1121	Bromochlorométhane (COFRAC)	74-97-5	NF EN ISO 10301	0.2 µg/l
1122	Bromoforme (COFRAC)	75-25-2	NF EN ISO 10301	0.2 µg/l
1135	Chloroforme (COFRAC)	67-66-3	NF EN ISO 10301	0.2 µg/l
2695	Chloropropane 2	75-29-6	NF EN ISO 10301	2 µg/l
2611	2-Chloroprène (COFRAC)	126-99-8	NF EN ISO 10301	3 µg/l
2065	Chloroprène 3 (chlor.d'allyle) (COFRAC)	107-05-1	NF EN ISO 10301	0.3 µg/l
1158	Dibromomonochlorométhane (COFRAC)	124-48-1	NF EN ISO 10301	0.2 µg/l
1168	Dibromométhane (COFRAC)	74-95-3	NF EN ISO 10301	0.2 µg/l
1498	Dibromoéthane 1,2 (COFRAC)	106-93-4	NF EN ISO 10301	0.2 µg/l
1165	Dichlorobenzène 1,2 (COFRAC)	95-50-1	NF EN ISO 10301	0.2 µg/l
1164	Dichlorobenzène 1,3 (COFRAC)	541-73-1	NF EN ISO 10301	0.2 µg/l
1166	Dichlorobenzène 1,4 (COFRAC)	106-46-7	NF EN ISO 10301	0.2 µg/l
1158	Dichloromonobromométhane (COFRAC)	75-27-4	NF EN ISO 10301	0.2 µg/l
1168	Dichlorométhane (COFRAC)	75-09-2	NF EN ISO 10301	10.0 µg/l
2696	Dichloropropan-2-ol 1,3	96-23-1	NF EN ISO 10301	50 µg/l
1655	Dichloropropane 1,2 (COFRAC)	78-87-5	NF EN ISO 10301	0.2 µg/l
1654	Dichloropropane 1,3 (COFRAC)	142-28-9	NF EN ISO 10301	0.2 µg/l
2082	Dichloropropylène 1,1 (COFRAC)	563-5-8-6	NF EN ISO 10301	0.2 µg/l
1487	Dichloropropylène 1,3 (COFRAC)	542-75-6	NF EN ISO 10301	0.2 µg/l

Sandre	*Paramétre*	*N° CAS*	*Méthode*	*Limite de quantification*
1653	Dichloropropylène 2,3 (COFRAC)	78-88-6	NF EN ISO 10301	2 µg/l
1160	Dichloroéthane 1,1 (COFRAC)	75-34-3	NF EN ISO 10301	0.2 µg/l
1161	Dichloroéthane1,2 (COFRAC)	107-06-2	NF EN ISO 10301	0.2 µg/l
1162	Dichloroéthylène 1,1 (COFRAC)	75-35-4	NF EN ISO 10301	0.2 µg/l
1456	Dichloroéthylène cis 1,2 (COFRAC)	156-59-2	NF EN ISO 10301	0.2 µg/l
1727	Dichloroéthylène trans 1,2 (COFRAC)	156-60-5	NF EN ISO 10301	0.2 µg/l
1652	Hexachlorobutadiène (COFRAC)	87-68-3	NF EN ISO 10301	0.1 µg/l
1656	Hexachloroéthane (COFRAC)	67-72-1	NF EN ISO 10301	0.10 µg/l
1630	Trichlorobenzène 1,2,3 (COFRAC)	87-61-6	NF EN ISO 10301	0.2 µg/l
1283	Trichlorobenzène 1,2,4 (COFRAC)	120-82-1	NF EN ISO 10301	0.2 µg/l
1629	Trichlorobenzène 1,3,5, (COFRAC)	108-70-3	NF EN ISO 10301	0.2 µg/l
1195	Trichlorofluorométhane	75-69-4	NF EN ISO 10301	0.1 µg/l
1854	Trichloropropane 1,2,3 (COFRAC)	96-18-4	NF EN ISO 10301	0.2 µg/l
2072	Trichloropropène 1,1,3 (COFRAC)	2567-14-8	NF EN ISO 10301	0.1 µg/l
1196	Trichlorotrifluoroéthane (COFRAC)	76-13-1	NF EN ISO 10301	0.2 µg/l
1284	Trichloroéthane 1,1,1 (COFRAC)	71-55-6	NF EN ISO 10301	0.2 µg/l
1285	Trichloroéthane 1,1,2 (COFRAC)	79-00-5	NF EN ISO 10301	0.2 µg/l
1286	Trichloréthylène (COFRAC)	79-01-6	NF EN ISO 10301	0.2 µg/l
2704	Tétrachloropropane-1,1,1,2	812-03-3	NF EN ISO 10301	0.1 µg/l
2705	Tétrachloropropane-1,1,1,3	1070-78-6	NF EN ISO 10301	0.1 µg/l
1270	Tétrachloroéthane 1,1,1,2 (COFRAC)	630-20-6	NF EN ISO 10301	0.2 µg/l
1270	Tétrachloroéthane 1,1,2,2 (COFRAC)	79-34-5	NF EN ISO 10301	0.2 µg/l
1272	Tétrachloroéthylène (COFRAC)	127-18-4	NF EN ISO 10301	0.2 µg/l
1276	Tétrachlorure de carbone (COFRAC)	56-23-5	NF EN ISO 10301	0.2 µg/l
Organostanneux complet (2670)				
2542	Monobutylétain (COFRAC)		CMO_MT16	0.020 µg/l Sn
2890	Monooctylétain (COFRAC)		CMO_MT16	0.005 µg/l Sn
2889	Monophénylétain (COFRAC)		CMO_MT16	0.005 µg/l Sn
1771	Dibutylétain (COFRAC)	683-18-1	CMO_MT16	0.005 µg/l Sn
2888	Dioctylétain (COFRAC)		CMO_MT16	0.005 µg/l Sn
2887	Diphenylétain (COFRAC)		CMO_MT16	0.005 µg/l Sn
1936	Tétrabutylétain (COFRAC)		CMO_MT16	0.005 µg/l Sn
1820	Tributylétain (COFRAC)		CMO_MT16	0.005 µg/l Sn
2885	Tricyclohexylétain (COFRAC)		CMO_MT16	0.005 µg/l Sn
2886	Trioctylétain (COFRAC)		CMO_MT16	0.010 µg/l Sn
1779	Triphenylétain (COFRAC)		CMO_MT16	0.005 µg/l Sn
Orthophosphate (en P et PO4) (1665)				
	Orthophosphates (P) (COFRAC)		NF EN 1189	0.005 mg (P)/l
1433	Orthophosphates (PO4)		Calcul	0.02 mg (PO4)/l
Oxydabilité au permanganate en milieu acide (KMnO4) (1506)				
1315	Oxydabilité au permanganate en milieu acide (COFRAC)		NF EN ISO 8467	0.1 mg/l O2
Oxydabilité au permanganate en milieu alcalin (KMnO4) (1507)				
	Oxydabilité au permanganate en milieu alcalin (KMnO4)			0.1 mg/l O2
Oxygène Dissous (1680)				
1311	Oxygène Dissous (COFRAC)		NF EN 25814	0.2 mg O2/l
Oxygene dissous % de saturation (1679)				
	Oxygène dissous (% de saturation)		Calcul	%
Oxygène dissous mesure sur place (2519)				
1311	O2 Dissous mesure sur place (COFRAC)		NF EN 25814	mg O2/l
Palladium (Pd) (ICP) (1724)				
	Palladium (Pd)		ICP - AES	5 µg/l
PCB - Polychlorobiphenyls (2465)				
1239	PCB28 (COFRAC)	7012-37-5	CMO_MT02	0.005 µg/l
1240	PCB35	37680-69-6	CMO_MT02	0.005 µg/l
1628	PCB44 (COFRAC)	41464-39-5	CMO_MT02	0.005 µg/l
1241	PCB52 (COFRAC)	35693-99-3	CMO_MT02	0.005 µg/l
1091	PCB77	32598-13-3	CMO_MT02	0.005 µg/l
5432	PCB81	70362-50-4	CMO_MT02	0.005 µg/l
1242	PCB101 (COFRAC)	37680-73-2	CMO_MT02	0.005 µg/l
1627	PCB105 (COFRAC)	32598-14-4	CMO_MT02	0.005 µg/l
5433	PCB114	74472-37-0	CMO_MT02	0.005 µg/l

Sandre	*Paramétre*	*N° CAS*	*Méthode*	*Limite de quantification*
1243	PCB118 (COFRAC)	31508-00-6	CMO_MT02	0.005 µg/l
5434	PCB123	65510-44-3	CMO_MT02	0.005 µg/l
1089	PCB126	57465-28-8	CMO_MT02	0.005 µg/l
1244	PCB138 (COFRAC)	35065-28-2	CMO_MT02	0.005 µg/l
1245	PCB153 (COFRAC)	35065-27-1	CMO_MT02	0.005 µg/l
2032	PCB156	38380-08-4	CMO_MT02	0.005 µg/l
5435	PCB157	69782-90-7	CMO_MT02	0.005 µg/l
5436	PCB167	52663-72-6	CMO_MT02	0.005 µg/l
1090	PCB169	32774-16-6	CMO_MT02	0.005 µg/l
1626	PCB170 (COFRAC)	35065-30-6	CMO_MT02	0.005 µg/l
1246	PCB180 (COFRAC)	35065-29-3	CMO_MT02	0.005 µg/l
5437	PCB189	39635-31-9	CMO_MT02	0.005 µg/l
1625	PCB194 (COFRAC)	35694-08-7	CMO_MT02	0.005 µg/l
1624	PCB209 (COFRAC)	2051-24-3	CMO_MT02	0.005 µg/l
	PCB DIOXIN-LIKE		PCB DIOXINE LIKE	0.005 µg/l
	PCB INDICATEURS		PCB INDICATEURS	0.005 µg/l
1730	Equivalent Arochlor 1232	11141-16-5	CMO_MT02	0.050 µg/l
1249	Equivalent Arochlor 1242	53469-21-9	CMO_MT02	0.050 µg/l
1731	Equivalent Arochlor 1248	12672-29-6	CMO_MT02	0.050 µg/l
1250	Equivalent Arochlor 1254	11097-69-1	CMO_MT02	0.050 µg/l
1251	Equivalent Arochlor 1260	11096-82-5	CMO_MT02	0.050 µg/l
1032	PCB totaux		CMO_MT02	0.005 µg/l
PCT Polychlorotriphenyls (2419)				
2868	Arochlor 5060		CMO_MT02	0.05 µg/l
2769	Arochlor 5442		CMO_MT02	0.05 µg/l
2770	Arochlor 5460		CMO_MT02	0.05 µg/l
Pesticides (2420)				
1264	2,4,5-T (COFRAC)	93-76-5	CMO_MT02	0.020 µg/l
1141	2,4-D (COFRAC)	94-75-7	CMO_MT02	0.020 µg/l
	2,4 D- isopropyl-ester	94-11-1	CMO_MT02	0.050 µg/l
2873	2,4 D-methyl-ester	1928-38-7	CMO_MT02	0.050 µg/l
1142	2,4-DB	94-82-6	CMO_MT02	0.040 µg/l
1212	2,4-MCPA (COFRAC)	97-74-6	CMO_MT02	0.020 µg/l
2747	MCPA-butoxyethyl ester	19480-43-4	CMO_MT02	0.050 µg/l
2745	MCPA-1-butyl ester	1713-12-8	CMO_MT02	0.050 µg/l
2746	MCPA-2-ethylhexyl ester	26544-20-7	CMO_MT02	0.050 µg/l
2748	MCPA-ethyl-ester	2698-38-6	CMO_MT02	0.050 µg/l
2749	MCPA-methyl-ester	2436-73-9	CMO_MT02	0.050 µg/l
1213	2,4-MCPB (COFRAC)	94-81-5	CMO_MT02	0.040 µg/l
1903	Acetochlor (COFRAC)	34256-82-1	CMO_MT02	0.020 µg/l
1970	Acifluorfen	50594-66-6	CMO_MT02	0.040 µg/l
1688	Aclonifen (COFRAC)	74070-46-5	CMO_MT02	0.050 µg/l
1310	Acrinathrine	101007-06-1	CMO_MT02	0.020 µg/l
1101	Alachlore (COFRAC)	15972-60-8	CMO_MT02	0.040 µg/l
1102	Aldicarbe	116-06-3	CMO_MT02	0.050 µg/l
1103	Aldrine (COFRAC)	309-00-2	CMO_MT02	0.010 µg/l
1697	Allethrine	584-79-2	CMO_MT02	0.010 µg/l
1812	Alphaméthrine	67375-30-8	CMO_MT02	0.020 µg/l
1104	Amétryne (COFRAC)	834-12-8	CMO_MT02	0.020 µg/l
2012	Amidosulfuron	120923-37-7	CMO_MT02	0.100 µg/l
1308	Amitraze	33089-61-1	CMO_MT02	0.020 µg/l
2013	Anthraquinone (COFRAC)	84-65-1	CMO_MT02	0.020 µg/l
1965	Asulam	3337-71-1	CMO_MT02	0.100 µg/l
1107	Atrazine (COFRAC)	1912-24-9	CMO_MT02	0.020 µg/l
1108	Atrazine déséthyl (COFRAC)	6190-65-4	CMO_MT02	0.020 µg/l
1109	Atrazine déisopropyl (COFRAC)	1007-28-9	CMO_MT02	0.05 µg/l
2014	Azaconazol (COFRAC)	60207-31-0	CMO_MT02	0.040 µg/l
2015	Azamétiphos	35575-96-3	CMO_MT02	0.010 µg/l
1110	Azinphos éthyl (COFRAC)	2642-71-9	CMO_MT02	0.040 µg/l
1111	Azinphos méthyl (COFRAC)	86-50-0	CMO_MT02	0.040 µg/l
1951	Azoxystrobin (COFRAC)	131860-33-8	CMO_MT02	0.010 µg/l
1687	Bénalaxyl	71626-11-4	CMO_MT02	0.010 µg/l
1764	Benthiocarbe	28249-77-6	CMO_MT02	0.02 µg/l
1329	Bendiocarbe (COFRAC)	22781-23-3	CMO_MT02	0.020 µg/l
1112	Benfluraline	1861-40-1	CMO_MT02	0.020 µg/l

Sandre	*Paramétre*	*N° CAS*	*Méthode*	*Limite de quantification*
2924	Benfuracarbe	82560-54-1	CMO_MT02	0.1 µg/l
2074	Benoxacor	98730-04-2	CMO_MT02	0.02 µg/l
1407	Bénomyl	17804-35-2	CMO_MT02	0.080 µg/l
1113	Bentazone (COFRAC)	25057-89-0	CMO_MT02	0.020 µg/l
1119	Bifénox	42576-02-3	CMO_MT02	0.050 µg/l
1120	Bifentrine	82657-04-3	CMO_MT02	0.020 µg/l
1502	Bioresméthrine	28434-01-7	CMO_MT02	0.040 µg/l
1529	Bitertanol	70585-36-3	CMO_MT02	0.040 µg/l
1686	Bromacil (COFRAC)	314-40-9	CMO_MT02	0.050 µg/l
1859	Bromadiolone	28772-56-7	CMO_MT02	0.100 µg/l
1123	Bromophos éthyl (COFRAC)	4824-78-6	CMO_MT02	0.040 µg/l
1124	Bromophos méthyl (COFRAC)	2104-96-3	CMO_MT02	0.040 µg/l
1685	Bromopropylate	18181-80-1	CMO_MT02	0.020 µg/l
1125	Bromoxynil (COFRAC)	1689-84-5	CMO_MT02	0.040 µg/l
1941	Bromoxynil octanoate	1689-99-2	CMO_MT02	0.050 µg/l
1860	Bromuconazole	116255-48-2	CMO_MT02	0.020 µg/l
1861	Bupirimate	41483-43-6	CMO_MT02	0.020 µg/l
1862	Buprofézine	69327-76-0	CMO_MT02	0.050 µg/l
1126	Butraline	33629-47-9	CMO_MT02	0.040 µg/l
1531	Buturon (COFRAC)	3766-60-7	CMO_MT02	0.050 µg/l
1863	Cadusaphos	95465-99-9	CMO_MT02	0.020 µg/l
1127	Captafol	2425-06-1	CMO_MT02	0.020 µg/l
1128	Captane	133-06-2	CMO_MT02	0.040 µg/l
1463	Carbaryl	63-25-2	CMO_MT02	0.050 µg/l
1129	Carbendazime (COFRAC)	10605-21-7	CMO_MT02	0.100 µg/l
1333	Carbétamide	16118-49-3	CMO_MT02	0.040 µg/l
1130	Carbofuran (COFRAC)	1563-66-2	CMO_MT02	0.050 µg/l
1131	Carbophénothion (COFRAC)	786-19-6	CMO_MT02	0.04 µg/l
1864	Carbosulfan	55285-14-8	CMO_MT02	0.020 µg/l
1865	Chinométhionate	2439-01-2	CMO_MT02	0.020 µg/l
2016	Chlorbromuron	13360-45-7	CMO_MT02	0.010 µg/l
1336	Chlorbufame (COFRAC)	1967-16-4	CMO_MT02	0.040 µg/l
1132	Chlordane (COFRAC)	57-74-9	CMO_MT02	0.020 µg/l
1756	Chlordane alpha	5103-71-9	CMO_MT02	0.020 µg/l
1757	Chlordane Béta	5103-74-2	CMO_MT02	0.020 µg/l
1758	Chlordane gamma	5566-34-7	CMO_MT02	0.020 µg/l
1866	Chlordécone (COFRAC)	143-50-0	CMO_MT02	0.010 µg/l
1464	Chlorfenvinphos (COFRAC)	470-90-6	CMO_MT02	0.020 µg/l
2950	Chlorfluazuron	71422-67-8	CMO_MT02	0.05 µg/l
1133	Chloridazone	1698-60-8	CMO_MT02	0.050 µg/l
1134	Chlorméphos	24934-91-6	CMO_MT02	0.040 µg/l
1341	Chloroneb	2675-77-6	CMO_MT02	0.040 µg/l
1684	Chlorophacinone	3691-35-8	CMO_MT02	0.050 µg/l
1473	Chlorothalonil (COFRAC)	1897-45-6	CMO_MT02	0.040 µg/l
1683	Chloroxuron (COFRAC)	1982-47-4	CMO_MT02	0.050 µg/l
1474	Chlorpropham (COFRAC)	101-21-3	CMO_MT02	0.020 µg/l
1083	Chlorpyriphos éthyl (COFRAC)	2921-88-2	CMO_MT02	0.020 µg/l
1540	Chlorpyriphos méthyl (COFRAC)	5598-13-0	CMO_MT02	0.020 µg/l
1353	Chlorsulfuron	64902-72-3	CMO_MT02	0.040 µg/l
1867	Chlorthal	1861-32-1	CMO_MT02	0.040 µg/l
1813	Chlorthiamide	1918-13-4	CMO_MT02	0.010 µg/l
1136	Chlortoluron (COFRAC)	15545-48-9	CMO_MT02	0.050 µg/l
2017	Clomazone	81777-89-1	CMO_MT02	0.040 µg/l
2018	Cloquintocet méxyl	99607-70-2	CMO_MT02	0.100 µg/l
1682	Coumaphos	56-72-4	CMO_MT02	0.050 µg/l
2019	Coumatétralyl	5836-29-3	CMO_MT02	0.040 µg/l
1137	Cyanazine (COFRAC)	21725-46-2	CMO_MT02	0.040 µg/l
1696	Cycluron	2163-69-1	CMO_MT02	0.020 µg/l
1681	Cyfluthrine (COFRAC)	68359-37-5	CMO_MT02	0.020 µg/l
1139	Cymoxanil	57966-95-7	CMO_MT02	0.100 µg/l
1140	Cyperméthrine (COFRAC)	52315-07-8	CMO_MT02	0.020 µg/l
1680	Cyproconazol (COFRAC)	94361-06-5	CMO_MT02	0.050 µg/l
1359	Cyprodinil (COFRAC)	121552-61-2	CMO_MT02	0.040 µg/l
1143	DDD-2,4' (COFRAC)	53-19-0	CMO_MT02	0.010 µg/l
1144	DDD-4,4' (COFRAC)	72-54-8	CMO_MT02	0.010 µg/l
1145	DDE-2,4' (COFRAC)	3424-82-6	CMO_MT02	0.010 µg/l

Sandre	*Paramétre*	*N° CAS*	*Méthode*	*Limite de quantification*
1146	DDE-4,4' (COFRAC)	72-55-9	CMO_MT02	0.010 µg/l
1147	DDT-2,4' (COFRAC)	789-02-6	CMO_MT02	0.010 µg/l
1148	DDT-4,4' (COFRAC)	50-29-3	CMO_MT02	0.010 µg/l
1149	Deltaméthrine (COFRAC)	52918-63-5	CMO_MT02	0.020 µg/l
1550	Déméton (O+S)	8065-48-3	CMO_MT02	0.100 µg/l
1153	Déméton S methyl	919-86-8	CMO_MT02	0.100 µg/l
1154	Déméton S methyl sulfone	17040-19-6	CMO_MT02	0.100 µg/l
1155	Desmétryne	1014-69-3	CMO_MT02	0.020 µg/l
1156	Diallate	2303-16-4	CMO_MT02	0.050 µg/l
1157	Diazinon (COFRAC)	333-41-5	CMO_MT02	0.040 µg/l
1480	Dicamba	1918-00-9	CMO_MT02	0.040 µg/l
1679	Dichlobenil	1194-65-6	CMO_MT02	0.050 µg/l
1159	Dichlofenthion	97-17-6	CMO_MT02	0.020 µg/l
1360	Dichlofluanide	1085-98-9	CMO_MT02	0.040 µg/l
1171	Dichlofop méthyl (COFRAC)	51338-27-3	CMO_MT02	0.040 µg/l
2011	Dichloro benzamide 2,6	2008-58-4	CMO_MT02	0.020 µg/l
1169	Dichlorprop (COFRAC)	120-36-5	CMO_MT02	0.020 µg/l
1170	Dichlorvos (COFRAC)	62-73-7	CMO_MT02	0.040 µg/l
1172	Dicofol	115-32-2	CMO_MT02	0.020 µg/l
1173	Dieldrine (COFRAC)	60-57-1	CMO_MT02	0.010 µg/l
1402	Diéthofencarbe (COFRAC)	87130-20-9	CMO_MT02	0.040 µg/l
1905	Difénoconazole (COFRAC)	119446-68-3	CMO_MT02	0.050 µg/l
1488	Diflubenzuron	35367-38-5	CMO_MT02	0.050 µg/l
1814	Diflufénicanil (COFRAC)	83164-33-4	CMO_MT02	0.020 µg/l
1870	Diméfuron	34205-21-5	CMO_MT02	0.020 µg/l
2546	Dimétachlor	50563-36-5	CMO_MT02	0.05 µg/l
1678	Diméthénamide (COFRAC)	87674-68-8	CMO_MT02	0.040 µg/l
1175	Diméthoate (COFRAC)	60-51-5	CMO_MT02	0.050 µg/l
1403	Diméthomorphe (COFRAC)	110488-70-5	CMO_MT02	0.100 µg/l
1698	Dimetilan	644-64-4	CMO_MT02	0.040 µg/l
1871	Diniconazole (COFRAC)	83657-24-3	CMO_MT02	0.040 µg/l
1490	DiNitroOrthoCrésol (DNOC) (COFRAC)	534-52-1	CMO_MT02	0.050 µg/l
1677	Dinocap	39300-45-3	CMO_MT02	0.050 µg/l
1491	Dinosèbe (COFRAC)	88-85-7	CMO_MT02	0.050 µg/l
1176	Dinoterbe (COFRAC)	1420-07-1	CMO_MT02	0.050 µg/l
1492	Disulfoton	298-04-4	CMO_MT02	0.050 µg/l
1966	Dithianon	3347-22-6	CMO_MT02	0.050 µg/l
1177	Diuron (COFRAC)	330-54-1	CMO_MT02	0.020 µg/l
1929	1-(3,4-Dichlorophényl)-3-MéthylUrée (COFRAC)	3567-62-2	CMO_MT02	0.020 µg/l
1930	1-(3,4-DichloroPhényl) Urée (COFRAC)	2327-02-8	CMO_MT02	0.020 µg/l
1178	Endosulfan Aplha (COFRAC)	959-98-8	CMO_MT02	0.005 µg/l
1179	Endosulfan Béta (COFRAC)	33213-65-9	CMO_MT02	0.010 µg/l
1742	Endosulfan Sulfate (COFRAC)	1031-07-8	CMO_MT02	0.010 µg/l
1743	Endosulfan (somme)		CMO_MT02	0.010 µg/l
1181	Endrine (COFRAC)	72-20-8	CMO_MT02	0.005 µg/l
1744	Epoxyconazole (COFRAC)	106325-08-0	CMO_MT02	0.020 µg/l
1182	EPTC (COFRAC)	759-94-4	CMO_MT02	0.040 µg/l
2869	1-(4-IsopropylPhényl) Urée	56046-17-4	CMO_MT02	0.020 µg/l
1809	Esfenvalérate	66230-04-4	CMO_MT02	0.040 µg/l
1763	Ethidimuron	30043-49-3	CMO_MT02	0.050 µg/l
1183	Ethion (Diethion) (COFRAC)	563-12-2	CMO_MT02	0.020 µg/l
1874	Ethiophencarbe	29973-13-5	CMO_MT02	0.050 µg/l
1184	Ethofumésate	26225-79-6	CMO_MT02	0.040 µg/l
1495	Ethoprophos (COFRAC)	13194-48-4	CMO_MT02	0.040 µg/l
2020	Famoxadone	131807-57-3	CMO_MT02	0.020 µg/l
2057	Fénamidone	161326-34-7	CMO_MT02	0.050 µg/l
1185	Fénarimol	60168-88-9	CMO_MT02	0.040 µg/l
2742	Fénazaquin (COFRAC)	120928-09-8	CMO_MT02	0.020 µg/l
1906	Fenbuconazole (COFRAC)	114369-43-6	CMO_MT02	0.100 µg/l
1186	Fenchlorphos	299-84-3	CMO_MT02	0.050 µg/l
2743	Fenhéxamide	126833-17-8	CMO_MT02	0.050 µg/l
1187	Fénitrothion (COFRAC)	122-14-5	CMO_MT02	0.040 µg/l
1973	Fénoxaprop éthyl	82110-72-3	CMO_MT02	0.040 µg/l
1967	Fénoxycarbe	79127-80-3	CMO_MT02	0.040 µg/l
1188	Fenpropathrine	64257-84-7	CMO_MT02	0.020 µg/l
1700	Fenpropidine	67306-00-7	CMO_MT02	0.050 µg/l

Sandre	*Paramétre*	*N° CAS*	*Méthode*	*Limite de quantification*
1189	Fenpropimorphe (COFRAC)	67306-03-0	CMO_MT02	0.050 µg/l
1190	Fenthion	55-38-9	CMO_MT02	0.040 µg/l
1500	Fénuron	101-42-8	CMO_MT02	0.040 µg/l
2021	Ferbam	14484-64-1	CMO_MT02	0.080 µg/l
2009	Fipronil	1200068-37-3	CMO_MT02	0.010 µg/l
1939	Flazasulfuron	104040-78-0	CMO_MT02	0.100 µg/l
1404	Fluazifop-p-butyl	79241-46-6	CMO_MT02	0.050 µg/l
2022	Fludioxonil (COFRAC)	131341-86-1	CMO_MT02	0.040 µg/l
1676	Flufénoxuron (COFRAC)	101463-69-8	CMO_MT02	0.050 µg/l
2023	Flumioxazine	103361-09-7	CMO_MT02	0.020 µg/l
2565	Flupyrsulfuron méthyl	144740-54-5	CMO_MT02	0.100 µg/l
2056	Fluquinconazole (COFRAC)	114369-43-6	CMO_MT02	0.010 µg/l
1974	Fluridone	59756-60-4	CMO_MT02	0.050 µg/l
1675	Flurochloridone (COFRAC)	61213-25-0	CMO_MT02	0.040 µg/l
1765	Fluroxypyr (COFRAC)	69377-81-7	CMO_MT02	0.040 µg/l
2547	Fluroxypyr methyl heptyl ester	81406-37-3	CMO_MT02	0.050 µg/l
2024	Flurprimidol	56425-91-3	CMO_MT02	0.020 µg/l
2008	Flurtamone	96525-23-4	CMO_MT02	0.020 µg/l
1194	Flusilazole (COFRAC)	85509-19-9	CMO_MT02	0.050 µg/l
1503	Flutriafol (COFRAC)	76674-21-0	CMO_MT02	0.050 µg/l
1192	Folpel	133-07-3	CMO_MT02	0.020 µg/l
2075	Fomesafen	72178-02-0	CMO_MT02	0.050 µg/l
1674	Fonofos	944-22-9	CMO_MT02	0.020 µg/l
1504	Formothion	2540-82-1	CMO_MT02	0.040 µg/l
2744	Fosthiazate (COFRAC)	98886-44-3	CMO_MT02	0.020 µg/l
1908	Furalaxyl (COFRAC)	57646-30-7	CMO_MT02	0.050 µg/l
2567	Furathiocarbe	65907-30-4	CMO_MT02	0.020 µg/l
2047	Haloxyfop	69806-34-4	CMO_MT02	0.100 µg/l
2046	HCH epsilon (COFRAC)	6108-10-7	CMO_MT02	0.010 µg/l
1203	HCH Gamma (Lindane) (COFRAC)	58-89-9	CMO_MT02	0.010 µg/l
1200	HCH Alpha (COFRAC)	319-84-6	CMO_MT02	0.010 µg/l
1201	HCH Beta (COFRAC)	319-85-7	CMO_MT02	0.010 µg/l
1202	HCH Delta (COFRAC)	319-86-8	CMO_MT02	0.010 µg/l
1197	Heptachlore (COFRAC)	76-44-8	CMO_MT02	0.010 µg/l
1198	Heptachlore époxyde (COFRAC)	1024-57-3	CMO_MT02	0.010 µg/l
1910	Hepténophos	23560-59-0	CMO_MT02	0.020 µg/l
1199	Hexachlorobenzène (COFRAC)	118-74-1	CMO_MT02	0.010 µg/l
1405	Hexaconazole (COFRAC)	79983-71-4	CMO_MT02	0.100 µg/l
1875	Hexaflumuron (COFRAC)	86479-06-3	CMO_MT02	0.040 µg/l
1673	Hexazinone (COFRAC)	51235-04-2	CMO_MT02	0.050 µg/l
1876	Hexythiazox	78587-05-0	CMO_MT02	0.050 µg/l
1704	Imazalil	35554-44-0	CMO_MT02	0.020 µg/l
1911	Imazamétabenz-méthyl (COFRAC)	81405-85-8	CMO_MT02	0.050 µg/l
1877	Imidaclopride (COFRAC)	138261-41-3	CMO_MT02	0.050 µg/l
	Indoxacarbe	173584-44-6	CMO_MT02	0.020 µg/l
2025	Iodofenphos	18181-70-9	CMO_MT02	0.020 µg/l
2563	Iodosulfuron méthyl	144550-36-7	CMO_MT02	0.070 µg/l
2871	Ioxynil methyl ester	3336-40-1	CMO_MT02	0.050 µg/l
1942	Ioxynil octanoate	3861-47-0	CMO_MT02	0.050 µg/l
1205	Ioxynil (COFRAC)	1689-83-4	CMO_MT02	0.040 µg/l
1206	Iprodione (COFRAC)	36734-19-7	CMO_MT02	0.040 µg/l
2951	Iprovalicarbe	140923-17-7	CMO_MT02	0.100 µg/l
1976	Isazofos (COFRAC)	42509-80-8	CMO_MT02	0.040 µg/l
1207	Isodrine (COFRAC)	465-73-6	CMO_MT02	0.010 µg/l
1829	Isophenphos (COFRAC)	25311-71-1	CMO_MT02	0.040 µg/l
1208	Isoproturon (COFRAC)	34123-59-6	CMO_MT02	0.040 µg/l
1672	Isoxaben	82558-50-7	CMO_MT02	0.040 µg/l
1945	Isoxaflutole	14112-29-0	CMO_MT02	0.020 µg/l
1950	Kresoxim méthyl (COFRAC)	143390-89-0	CMO_MT02	0.010 µg/l
1094	Lambda cyhalothrine (COFRAC)	91465-08-6	CMO_MT02	0.020 µg/l
1406	Lénacile (COFRAC)	2164-08-1	CMO_MT02	0.100 µg/l
1209	Linuron (COFRAC)	330-55-2	CMO_MT02	0.020 µg/l
2026	Lufénuron	103055-07-8	CMO_MT02	0.020 µg/l
1210	Malathion (COFRAC)	121-75-5	CMO_MT02	0.040 µg/l
1214	Mecoprop (MCPP) (COFRAC)	7085-19-0	CMO_MT02	0.020 µg/l
2870	Mecoprop-n iso-butyl ester		CMO_MT02	0.050 µg/l

Sandre	*Paramétre*	*N° CAS*	*Méthode*	*Limite de quantification*
	Mecoprop-2-butoxyethyl ester	23359-62-8	CMO_MT02	0.050 µg/l
2755	Mecoprop-methyl ester	2786-19-7	CMO_MT02	0.050 µg/l
	Mecoprop-1-octyl ester	161922-37-8	CMO_MT02	0.050 µg/l
2751	Mecoprop-2,4,4-trimethylpentyl ester	217487-13-3	CMO_MT02	0.050 µg/l
2753	Mecoprop-2-ethylhexyl ester	71526-69-7	CMO_MT02	0.050 µg/l
2754	Mecoprop-2-octyl ester	28473-03-2	CMO_MT02	0.050 µg/l
1968	Mefénacet	73250-68-7	CMO_MT02	0.040 µg/l
2930	Mefenpyr-diéthyl	135590-91-9	CMO_MT02	0.020 µg/l
2568	Mefluidide	53780-34-0	CMO_MT02	0.070 µg/l
1878	Mépronil	55814-41-0	CMO_MT02	0.040 µg/l
2578	Mésosulfuron Méthyl	208465-21-8	CMO_MT02	0.100 µg/l
1510	Mercaptodiméthur	2032-65-7	CMO_MT02	0.050 µg/l
1706	Métalaxyle (COFRAC)	57837-19-1	CMO_MT02	0.020 µg/l
1215	Métamitron (COFRAC)	41394-05-02	CMO_MT02	0.050 µg/l
1670	Métazachlore (COFRAC)	67129-08-2	CMO_MT02	0.050 µg/l
1216	Méthabenzthiazuron (COFRAC)	18691-97-9	CMO_MT02	0.040 µg/l
1217	Méthidathion (COFRAC)	950-37-8	CMO_MT02	0.040 µg/l
1218	Méthomyl	16752-77-5	CMO_MT02	0.100 µg/l
1511	Méthoxychlore (COFRAC)	72-43-5	CMO_MT02	0.020 µg/l
1515	Métobromuron (COFRAC)	3060-89-7	CMO_MT02	0.020 µg/l
1221	Métolachlore (COFRAC)	51218-45-2	CMO_MT02	0.020 µg/l
1912	Métosulam	139525-85-1	CMO_MT02	0.100 µg/l
1222	Métoxuron (COFRAC)	19937-59-8	CMO_MT02	0.040 µg/l
1225	Métribuzine	21087-64-9	CMO_MT02	0.050 µg/l
1797	Metsulfuron méthyl	74223-64-6	CMO_MT02	0.100 µg/l
1226	Mévinphos (COFRAC)	7786-34-7	CMO_MT02	0.040 µg/l
5438	Mirex (COFRAC)	2385-85-5	CMO_MT02	0.020 µg/l
1707	Molinate	2212-67-1	CMO_MT02	0.020 µg/l
1227	Monolinuron (COFRAC)	1746-81-2	CMO_MT02	0.020 µg/l
1228	Monuron (COFRAC)	150-68-5	CMO_MT02	0.020 µg/l
1881	Myclobutanyl (COFRAC)	88671-89-0	CMO_MT02	0.050 µg/l
1516	Naled	300-76-5	CMO_MT02	0.040 µg/l
1519	Napropamide (COFRAC)	15299-99-7	CMO_MT02	0.020 µg/l
1937	Naptalam	132-66-1	CMO_MT02	0.020 µg/l
1520	Néburon (COFRAC)	555-37-3	CMO_MT02	0.040 µg/l
1669	Norflurazon (COFRAC)	27314-13-2	CMO_MT02	0.050 µg/l
2737	Nor flurazon desméthyl (COFRAC)		CMO_MT02	0.050 µg/l
1883	Nuarimol	63284-71-9	CMO_MT02	0.040 µg/l
2027	Ofurace	58810-48-3	CMO_MT02	0.010 µg/l
1668	Oryzalin	19044-88-3	CMO_MT02	0.050 µg/l
2068	Oxadiargyl	39807-15-3	CMO_MT02	0.100 µg/l
1667	Oxadiazon (COFRAC)	19666-30-9	CMO_MT02	0.020 µg/l
1666	Oxadixyl (COFRAC)	77732-09-3	CMO_MT02	0.020 µg/l
1850	Oxamyl	23135-22-0	CMO_MT02	0.100 µg/l
1231	Oxydéméton méthyl	301-12-2	CMO_MT02	0.100 µg/l
1952	Oxyfluorfène	42874-03-3	CMO_MT02	0.100 µg/l
2545	Paclobutrazole	76738-62-0	CMO_MT02	0.060 µg/l
1232	Parathion éthyl (COFRAC)	56-38-2	CMO_MT02	0.040 µg/l
1233	Parathion méthyl (COFRAC)	298-00-0	CMO_MT02	0.040 µg/l
1762	Penconazole (COFRAC)	66246-88-6	CMO_MT02	0.050 µg/l
1887	Pencycuron	66063-05-6	CMO_MT02	0.050 µg/l
1234	Pendiméthaline (COFRAC)	40487-42-1	CMO_MT02	0.020 µg/l
1235	Pentachlorophénol (COFRAC)	87-86-5	CMO_MT02	0.020 µg/l
1888	Pentachlorobenzène (COFRAC)	608-93-5	CMO_MT02	0.010 µg/l
1523	Perméthrine (COFRAC)	52645-53-1	CMO_MT02	0.020 µg/l
1236	Phenmédiphame	13684-63-4	CMO_MT02	0.100 µg/l
1525	Phorate	298-02-2	CMO_MT02	0.040 µg/l
1237	Phosalone (COFRAC)	2310-17-0	CMO_MT02	0.040 µg/l
1971	Phosmet (COFRAC)	732-11-6	CMO_MT02	0.020 µg/l
1238	Phosphamidon (COFRAC)	13171-21-6	CMO_MT02	0.050 µg/l
1665	Phoxime	14816-18-3	CMO_MT02	0.100 µg/l
2669	Picoxystrobine	117428-22-5	CMO_MT02	0.020 µg/l
1709	Piperonyl butoxide (COFRAC)	51-03-6	CMO_MT02	0.040 µg/l
1528	Pirimicarbe	23103-98-2	CMO_MT02	0.02 µg/l
1253	Prochloraze	67747-09-5	CMO_MT02	0.050 µg/l
1664	Procymidone (COFRAC)	32809-16-8	CMO_MT02	0.040 µg/l

Sandre	*Paramétre*	*N° CAS*	*Méthode*	*Limite de quantification*
1710	Promecarbe	28916-00-9	CMO_MT02	0.050 µg/l
1711	Prométon	1610-18-0	CMO_MT02	0.040 µg/l
1254	Prométhryne (COFRAC)	7287-19-6	CMO_MT02	0.050 µg/l
1712	Propachlor (COFRAC)	1918-16-7	CMO_MT02	0.040 µg/l
1532	Propanil (COFRAC)	709-98-8	CMO_MT02	0.040 µg/l
1972	Propaquizafop	111479-05-1	CMO_MT02	0.040 µg/l
1255	Propargite	2312-35-8	CMO_MT02	0.050 µg/l
1256	Propazine (COFRAC)	139-40-2	CMO_MT02	0.020 µg/l
1533	Propétamphos (COFRAC)	31218-83-4	CMO_MT02	0.040 µg/l
1889	Prophénophos	41138-08-7	CMO_MT02	0.040 µg/l
1257	Propiconazole (COFRAC)	60207-90-1	CMO_MT02	0.100 µg/l
1535	Propoxur (COFRAC)	114-26-1	CMO_MT02	0.040 µg/l
1414	Propyzamide (COFRAC)	23950-58-5	CMO_MT02	0.040 µg/l
1092	Prosulfocarbe	52888-80-9	CMO_MT02	0.040 µg/l
1949	Prétilachlore	51218-49-6	CMO_MT02	0.02 µg/l
2576	Pyraclostrobine	175013-18-0	CMO_MT02	0.05 µg/l
1258	Pyrazophos	13457-18-6	CMO_MT02	0.020 µg/l
1890	Pyridabène	96489-71-3	CMO_MT02	0.040 µg/l
1259	Pyridate	55512-33-9	CMO_MT02	0.050 µg/l
1663	Pyrifénox	88283-41-4	CMO_MT02	0.020 µg/l
1432	Pyriméthanil (COFRAC)	53112-28-0	CMO_MT02	0.040 µg/l
1260	Pyrimiphos éthyl (COFRAC)	23505-41-1	CMO_MT02	0.040 µg/l
1261	Pyrimiphos méthyl (COFRAC)	29232-93-7	CMO_MT02	0.040 µg/l
	Pyriproxyfen	95737-68-1	CMO_MT02	0.020 µg/l
1891	Quinalphos (COFRAC)	13593-03-8	CMO_MT02	0.040 µg/l
2028	Quinoxyfen	124495-18-7	CMO_MT02	0.010 µg/l
1538	Quintozène (COFRAC)	82-68-8	CMO_MT02	0.010 µg/l
2069	Quizalofop	76578-12-6	CMO_MT02	0.05 µg/l
2070	Quizalofop éthyl	76578-14-8	CMO_MT02	0.02 µg/l
2029	Rotenone	83-79-4	CMO_MT02	0.040 µg/l
2974	S-Métolachlore	87392-12-9	CMO_MT02	0.05 µg/l
1923	Sébuthylazine (COFRAC)	7286-69-3	CMO_MT02	0.020 µg/l
1262	Secbuméton (COFRAC)	26259-45-0	CMO_MT02	0.040 µg/l
1263	Simazine (COFRAC)	122-34-9	CMO_MT02	0.020 µg/l
2664	Spiroxamine	118134-30-8	CMO_MT02	0.100 µg/l
1662	Sulcotrione	99105-77-8	CMO_MT02	0.040 µg/l
1894	Sulfotep	3689-24-5	CMO_MT02	0.050 µg/l
1193	Tau-fluvalinate (COFRAC)	102851-06-9	CMO_MT02	0.040 µg/l
1694	Tébuconazole (COFRAC)	107534-96-3	CMO_MT02	0.060 µg/l
1895	Tébufénozide	112410-23-8	CMO_MT02	0.040 µg/l
1896	Tébufenpyrad (COFRAC)	119168-77-3	CMO_MT02	0.040 µg/l
1661	Tébutame (COFRAC)	35256-85-0	CMO_MT02	0.020 µg/l
1897	Téflubenzuron (COFRAC)	83121-18-0	CMO_MT02	0.050 µg/l
1898	Teméphos	3383-96-8	CMO_MT02	0.100 µg/l
1659	Terbacile	5902-51-2	CMO_MT02	0.040 µg/l
1267	Terbuphos	13071-79-9	CMO_MT02	0.020 µg/l
1269	Terbutryne (COFRAC)	886-50-0	CMO_MT02	0.040 µg/l
1266	Terbuméton (COFRAC)	33693-04-8	CMO_MT02	0.020 µg/l
2051	Terbuméton-Déséthyl	30125-64-5	CMO_MT02	0.020 µg/l
1268	Terbutylazine (COFRAC)	5915-41-3	CMO_MT02	0.020 µg/l
2045	Terbutylazine deséthyl (COFRAC)	30125-63-4	CMO_MT02	0.020 µg/l
2010	Tétrachlorobenzène (COFRAC)	634-66-2	CMO_MT02	0.050 µg/l
1277	Tétrachlorvinphos	961-11-5	CMO_MT02	0.040 µg/l
1660	Tétraconazole (COFRAC)	112281-77-3	CMO_MT02	0.100 µg/l
1900	Tétradifon	116-29-0	CMO_MT02	0.100 µg/l
1713	Thiabendazole	148-79-8	CMO_MT02	0.020 µg/l
1940	Thiafluamide (flufenacet)	142459-58-3	CMO_MT02	0.020 µg/l
1714	Thiazasulfuron (COFRAC)	25366-23-8	CMO_MT02	0.080 µg/l
1913	Thifensulfuron méthyl	79277-27-3	CMO_MT02	0.100 µg/l
1093	Thiodicarbe	59669-26-0	CMO_MT02	0.060 µg/l
2071	Thiométon	640-15-3	CMO_MT02	0.100 µg/l
1719	Tolylfluanide (COFRAC)	731-27-1	CMO_MT02	0.040 µg/l
1658	Tralomethrine	66841-25-6	CMO_MT02	0.020 µg/l
1544	Triadimefon (COFRAC)	43121-43-3	CMO_MT02	0.050 µg/l
1280	Triadimenol	55219-65-3	CMO_MT02	0.100 µg/l
1281	Triallate (COFRAC)	2303-17-5	CMO_MT02	0.040 µg/l

Sandre	Paramétre	N° CAS	Méthode	Limite de quantification
1914	Triasulfuron	82097-50-5	CMO_MT02	0.100 µg/l
1901	Triazamate	112143-82-5	CMO_MT02	0.100 µg/l
1657	Triazophos (COFRAC)	24017-47-8	CMO_MT02	0.100 µg/l
1288	Triclopyr (COFRAC)	55335-06-3	CMO_MT02	0.020 µg/l
2678	Trifloxystrobine	141517-21-7	CMO_MT02	0.05 µg/l
1902	Triflumuron (COFRAC)	64628-44-0	CMO_MT02	0.100 µg/l
1289	Trifluraline (COFRAC)	1582-09-8	CMO_MT02	0.020 µg/l
2096	Trinexapac éthyl	95266-40-3	CMO_MT02	0.020 µg/l
1291	Vinchlozoline (COFRAC)	50471-44-8	CMO_MT02	0.020 µg/l
2858	Zoxamide	156052-68-5	CMO_MT02	0.030 µg/l
Pesticides - liquide/solide (2753)				
1810	Clopyralide	1702-17-6	HPLC MS MS ON LINE	0.100 µg/l
1832	Hydroxyatrazine	2163-68-0	HPLC MS MS ON LINE	0.100 µg/l
1954	Hydroxyterbuthylazine		HPLC MS MS ON LINE	0.100 µg/l
1671	Methamidophos	10265-92-6	HPLC MS MS ON LINE	0.100 µg/l
1882	Nicosulfuron (COFRAC)	111991-09-4	HPLC MS MS ON LINE	0.05 µg/l
1230	Ométhoate	1113-02-6	HPLC MS MS ON LINE	0.10 µg/l
1892	Rimsulfuron (COFRAC)	122931-48-0	HPLC MS MS ON LINE	0.02 µg/l
1831	Simazine 2 hydroxy		HPLC MS MS ON LINE	0.100 µg/l
1287	Trichlorfon	52-68-6	HPLC MS MS ON LINE	0.10 µg/l
Pesticides Dinoterbe Dinosèbe (1764)				
1491	Dinosèbe (COFRAC)	88-85-7	CMO_MT02	0.04 µg/l
1176	Dinoterbe (COFRAC)	1420-07-1	CMO_MT02	0.04 µg/l
Pesticides Dinoterbe Dinosèbe Traceurs (1765)				
1578	2,4 Dinitrotoluène	121-14-2	CMO_MT02	0.05 µg/l
1577	2,6 Dinitrotoluène	606-20-2	CMO_MT02	0.05 µg/l
1491	Dinosèbe (COFRAC)	88-85-7	CMO_MT02	0.04 µg/l
1176	Dinoterbe (COFRAC)	1420-07-1	CMO_MT02	0.04 µg/l
2736	Trinitrotoluène	118-96-7	CMO_MT02	0.10 µg/l
Pesticides HPLC MS MS Direct (2841)				
1107	Atrazine (COFRAC)	1912-24-9	CMO_MT22	0.020 µg/l
1108	Atrazine déséthyl (COFRAC)	6190-65-4	CMO_MT22	0.030 µg/l
1109	Atrazine déisopropyl (COFRAC)	1007-28-9	CMO_MT22	0.050 µg/l
2014	Azaconazol (COFRAC)	60207-31-0	CMO_MT22	0.020 µg/l
1113	Bentazone (COFRAC)	25057-89-0	CMO_MT22	0.020 µg/l
1531	Buturon (COFRAC)	3766-60-7	CMO_MT22	0.020 µg/l
1129	Carbendazime (COFRAC)	10605-21-7	CMO_MT22	0.020 µg/l
1130	Carbofuran (COFRAC)	1563-66-2	CMO_MT22	0.020 µg/l
2097	Chlorméquat	999-81-5	CMO_MT22	0.020 µg/l
1683	Chloroxuron (COFRAC)	1982-47-4	CMO_MT22	0.020 µg/l
1136	Chlortoluron (COFRAC)	15545-48-9	CMO_MT22	0.020 µg/l
1137	Cyanazine (COFRAC)	21725-46-2	CMO_MT22	0.020 µg/l
1680	Cyproconazol (COFRAC)	94361-06-5	CMO_MT22	0.020 µg/l
1830	Desethyldeisopropylatrazine	3397-62-4	CMO_MT22	0.100 µg/l
1905	Difénoconazole (COFRAC)	119446-68-3	CMO_MT22	0.020 µg/l
1678	Diméthénamide (COFRAC)	87674-68-8	CMO_MT22	0.020 µg/l
1403	Diméthomorphe (COFRAC)	110488-70-5	CMO_MT22	0.020 µg/l
1177	Diuron (COFRAC)	330-54-1	CMO_MT22	0.020 µg/l
1929	1-(3,4-Dichlorophényl)-3-MéthylUrée (COFRAC)	3567-62-2	CMO_MT22	0.050 µg/l
1930	1-(3,4-DichloroPhényl) Urée (COFRAC)	2327-02-8	CMO_MT22	0.020 µg/l
1763	Ethidimuron (COFRAC)	30043-49-3	CMO_MT22	0.020 µg/l
1185	Fénarimol (COFRAC)	60168-88-9	CMO_MT22	0.020 µg/l
1673	Hexazinone (COFRAC)	51235-04-2	CMO_MT22	0.020 µg/l
1208	Isoproturon (COFRAC)	34123-59-6	CMO_MT22	0.020 µg/l
1209	Linuron (COFRAC)	330-55-2	CMO_MT22	0.020 µg/l
2089	Mépiquat	24307-26-4	CMO_MT22	0.020 µg/l
1706	Métalaxyle (COFRAC)	57837-19-1	CMO_MT22	0.020 µg/l
1670	Métazachlore (COFRAC)	67129-08-2	CMO_MT22	0.020 µg/l
1515	Métobromuron (COFRAC)	3060-89-7	CMO_MT22	0.020 µg/l
1221	Métolachlore (COFRAC)	51218-45-2	CMO_MT22	0.020 µg/l
1222	Métoxuron (COFRAC)	19937-59-8	CMO_MT22	0.020 µg/l
1227	Monolinuron (COFRAC)	1746-81-2	CMO_MT22	0.020 µg/l
1228	Monuron (COFRAC)	150-68-5	CMO_MT22	0.020 µg/l
1881	Myclobutanyl (COFRAC)	88671-89-0	CMO_MT22	0.020 µg/l

Sandre	*Paramétre*	*N° CAS*	*Méthode*	*Limite de quantification*
1520	Néburon (COFRAC)	555-37-3	CMO_MT22	0.020 µg/l
1666	Oxadixyl (COFRAC)	77732-09-3	CMO_MT22	0.020 µg/l
1238	Phosphamidon (COFRAC)	13171-21-6	CMO_MT22	0.020 µg/l
1528	Pirimicarbe (COFRAC)	23103-98-2	CMO_MT22	0.020 µg/l
1256	Propazine (COFRAC)	139-40-2	CMO_MT22	0.020 µg/l
1535	Propoxur (COFRAC)	114-26-1	CMO_MT22	0.020 µg/l
1663	Pyrifénox (COFRAC)	88283-41-4	CMO_MT22	0.020 µg/l
1923	Sébuthylazine (COFRAC)	7286-69-3	CMO_MT22	0.020 µg/l
1263	Simazine (COFRAC)	122-34-9	CMO_MT22	0.020 µg/l
1694	Tébuconazole (COFRAC)	107534-96-3	CMO_MT22	0.020 µg/l
1266	Terbuméton (COFRAC)	33693-04-8	CMO_MT22	0.020 µg/l
1268	Terbutylazine (COFRAC)	5915-41-3	CMO_MT22	0.020 µg/l
2045	Terbutylazine deséthyl (COFRAC)	30125-63-4	CMO_MT22	0.020 µg/l
Pesticides on line (carbamates,urées,triazines) (2853)				
1102	Aldicarbe (COFRAC)	116-06-3	CMO_MT19	0.020 µg/l
1807	Aldicarbe sulfone (COFRAC)	1646-88-4	CMO_MT19	0.020 µg/l
1806	Aldicarbe sulfoxyde (COFRAC)	1646-87-3	CMO_MT19	0.020 µg/l
1107	Atrazine (COFRAC)	1912-24-9	CMO_MT19	0.020 µg/l
1108	Atrazine déséthyl (COFRAC)	6190-65-4	CMO_MT19	0.020 µg/l
1109	Atrazine déisopropyl (COFRAC)	1007-28-9	CMO_MT19	0.020 µg/l
1832	Hydroxyatrazine (COFRAC)	2163-68-0	CMO_MT19	0.040 µg/l
1463	Carbaryl (COFRAC)	63-25-2	CMO_MT19	0.020 µg/l
1129	Carbendazime (COFRAC)	10605-21-7	CMO_MT19	0.020 µg/l
1130	Carbofuran (COFRAC)	1563-66-2	CMO_MT19	0.020 µg/l
1805	Carbofuran-3-hydroxy (COFRAC)	16655-82-6	CMO_MT19	0.025 µg/l
1136	Chlortoluron (COFRAC)	15545-48-9	CMO_MT19	0.020 µg/l
1137	Cyanazine (COFRAC)	21725-46-2	CMO_MT19	0.020 µg/l
1177	Diuron (COFRAC)	330-54-1	CMO_MT19	0.020 µg/l
1208	Isoproturon (COFRAC)	34123-59-6	CMO_MT19	0.020 µg/l
2869	1-(4-IsopropylPhényl) Urée (COFRAC)	56046-17-4	CMO_MT19	0.020 µg/l
	3,4 (Isopropylphenyl)-1-methylurée (IPPMU) (COFRAC)	34123-57-4	CMO_MT19	0.020 µg/l
1209	Linuron (COFRAC)	330-55-2	CMO_MT19	0.020 µg/l
1510	Mercaptodimétur (COFRAC)	2032-65-7	CMO_MT19	0.020 µg/l
1216	Méthabenzthiazuron (COFRAC)	18691-97-9	CMO_MT19	0.020 µg/l
1218	Méthomyl (COFRAC)	16752-77-5	CMO_MT19	0.020 µg/l
1515	Métobromuron (COFRAC)	3060-89-7	CMO_MT19	0.020 µg/l
1222	Métoxuron (COFRAC)	19937-59-8	CMO_MT19	0.020 µg/l
1227	Monolinuron (COFRAC)	1746-81-2	CMO_MT19	0.020 µg/l
1520	Néburon (COFRAC)	555-37-3	CMO_MT19	0.020 µg/l
1882	Nicosulfuron (COFRAC)	111991-09-4	CMO_MT19	0.020 µg/l
1535	Propoxur (COFRAC)	114-26-1	CMO_MT19	0.020 µg/l
1892	Rimsulfuron (COFRAC)	122931-48-0	CMO_MT19	0.020 µg/l
1263	Simazine (COFRAC)	122-34-9	CMO_MT19	0.020 µg/l
1831	Simazine 2 hydroxy (COFRAC)		CMO_MT19	0.020 µg/l
1542	Tébuthiuron (COFRAC)	34014-18-1	CMO_MT19	0.020 µg/l
1268	Terbutylazine (COFRAC)	5915-41-3	CMO_MT19	0.020 µg/l
1954	Hydroxyterbuthylazine (COFRAC)		CMO_MT19	0.020 µg/l
1715	Thiofanox (COFRAC)	39196-18-4	CMO_MT19	0.050 µg/l
5476	Thiofanox-sulfone (COFRAC)		CMO_MT19	0.050 µg/l
5475	Thiofanox-sulfoxyde (COFRAC)		CMO_MT19	0.050 µg/l
PH (mesure au laboratoire) (1711)				
1302	PH (mesure au laboratoire) (COFRAC)		NF T 90 008	unité pH
	Température à la mesure du pH			°C
PH (mesure sur place) (1712)				
	PH (mesure sur place) (COFRAC)		NF T 90 008	unité pH
Phénol par chromatographie (1846)				
	Phénol par chromatographie	108-95-2	GC SPME	0.5 µg/l
Phénols et chlorophénols (2516)				
2537	2 Amino 4 chlorophénol	95-85-2	GC MS	2 µg/l
1471	2 Chlorophénol	95-57-8	GC MS	0.05 µg/l
1651	3 Chlorophénol	108-43-0	GC MS	0.05 µg/l
1650	4 Chlorophénol	106-48-9	GC MS	0.05 µg/l
	Chlorophénols total (somme des 3 isomères)	25167.80.0	GC MS	0.05 µg/l

		N° CAS	*Méthode*	*Limite de quantification*
1635	2 Chloro 5 méthyl phénol	615-74-7	GC MS	0.05 µg/l
2759	2 Chloro 6 méthyl phénol	87-64-9	GC MS	0.05 µg/l
1636	4 Chloro 3 méthy phénol	59-50-7	GC MS	0.05 µg/l
1645	Dichlorophénol 2,3	576-24-9	GC MS	0.05 µg/l
1486	Dichlorophénol 2,4	120-83-2	GC MS	0.05 µg/l
1649	Dichlorophénol 2,5	583-78-8	GC MS	0.05 µg/l
1648	Dichlorophénol 2,6	87-65-0	GC MS	0.05 µg/l
1647	Dichlorophénol 3,4	95-77-2	GC MS	0.05 µg/l
1641	Diméthyl phénol 2,4	105-67-9	GC MS	0.05 µg/l
	Dichlorophénols total (somme des isomères)		GC MS	0.05 µg/l
1640	Méthyl phénol 2	95-48-7	GC MS	0.05 µg/l
1639	Méthyl phénol 3	108-39-4	GC MS	0.05 µg/l
1638	Méthyl phénol 4	106-44-5	GC MS	0.05 µg/l
1637	Nitrophénol 2	88-75-5	GC MS	0.05 µg/l
1235	Pentachlorophénol	87-86-5	GC MS	0.02 µg/l
1644	Trichlorophénol 2,3,4	15950-66-0	GC MS	0.05 µg/l
1643	Trichlorophénol 2,3,5	933-78-8	GC MS	0.05 µg/l
1642	Trichlorophénol 2,3,6	933-75-5	GC MS	0.05 µg/l
1548	Trichlorophénol 2,4,5	95-95-4	GC MS	0.05 µg/l
1549	Trichlorophénol 2,4,6	88-06-2	GC MS	0.05 µg/l
	Trichlorophénols (somme des isomères)	25167-82-2	GC MS	0.05 µg/l
1273	Tétrachlorophénol 2,3,4,5	4901-51-3	GC MS	0.05 µg/l
1274	Tétrachlorophénol 2,3,4,6	58-90-2	GC MS	0.05 µg/l
1275	Tétrachlorophénol 2,3,5,6	935-95-5	GC MS	0.05 µg/l
Phénols indice (eaux-effluents) (1346)				
1440	Indice Phénols (COFRAC)		NF EN ISO 14402	10 µg/l
Phosphore total (Eau - E.Sup - E. Inter.) (ICP) (P) (1830)				
1350	Phosphore Total (en P) (COFRAC)		NF EN ISO 11885	5 µg (P)/l
	Phosphore total (en P2O5) (COFRAC)		Calcul	0.005 mg (P2O5)/
Phtalates (2734)				
1924	Benzyl Butyl Phtalate	85-68-7	GC FID	0.5 µg/l
1462	Di butyl phtalate	84-74-2	GC FID	0.5 µg/l
1527	Di ethyl phtalate	84-66-2	GC FID	1 µg/l
1489	Di methyl phtalate	131-11-3	GC FID	0.5 µg/l
	Di octyl phtalate	117-84-0	GC FID	5 µg/l
1461	Bis 2 ethylhexylphtalate	117-81-7	GC FID	1 µg/l
Phtalates - Plastifiants (2597)				
1924	Benzyl Butyl Phtalate	85-68-7	GC FID	0.5 µg/l
	Di OctylPhtalate	117-81-7	GC FID	5 µg/l
	OctylButylPhtalate	84-78-6	GC FID	0.5 µg/l
	Di Iso Heptyl Phtalate	3648-21-3	GC FID	5 µg/l
	D100		GC FID	5 µg/l
	Petrelab		GC FID	5 µg/l
	Isobutyrate de Texanol	6846-50-0	GC FID	0.5 µg/l
	Dodécyl Benzène	123-01-3	GC FID	5 µg/l
	Di Octyl Adipate	103-23-1	GC FID	1 µg/l
Platine (Pt) (1859)				
	Platine (Pt)		ICP - AES	10 µg/l
Plomb (ICP) (Pb) (1866)				
1382	Plomb (Pb) (COFRAC)	7439-92-1	NF EN ISO 11885	5 µg/l
Potassium chromato ionique (K) (1875)				
1367	Potassium (K) (COFRAC)		NF EN ISO 14911	1 mg/l
Pyraclostrobine (2716)				
2576	Pyraclostrobine	175013-18-0	GC ECD	0.1 µg/l
Radioactivité alpha total (517)				
1034	Activité alpha globale		Compteur alpha	5 Bq/l
Radioactivité Beta total (sous traitance) (2601)				
1035	Activité béta globale		Compteur Béta	5 Bq/l
Radioactivité bilan spectrométrie gamma (2485)				
2555	Césium 134		Spectrométrie Gamma (Germanium)	5 Bq/l

Sandre	Paramétre	N° CAS	Méthode	Limite de quantification
1031	Césium 137		Spectrométrie Gamma (Germanium)	5 Bq/l
2554	Cobalt 60		Spectrométrie Gamma (Germanium)	5 Bq/l
2553	Iode 131		Spectrométrie Gamma (Germanium)	5 Bq/l
Radioactivité Césium (soustraitance) (2634)				
2555	Césium 134		Spectrométrie Gamma (Germanium)	5 Bq/l
1031	Césium 137		Spectrométrie Gamma (Germanium)	5 Bq/l
Résidus Secs à 180°C (1957)				
1750	Résidu sec à 180°C (COFRAC)		NF T 90 029	5 mg/l
Rhodium (ICP) (Rh) (2735)				
	Rhodium (Rh)		NF EN ISO 11885	10 µg/l
Selénium (ICP) (Se) (1990)				
1385	Sélénium (Se) (COFRAC)	7782-49-2	NF EN ISO 11885	10 µg/l
Semi volatils organiques divers (2764)				
2743	Fenhexamid	126833-17-8	GC ECD	0.02 µg/l
1652	Hexachlachlorobutadiène	118-74-1	CMO_MT02	0.02 µg/l
2612	Hexachlorocyclopendiène	77-47-4	CMO_MT02	0.05 µg/l
2076	Mésotrione	104206-82-8	CMO_MT02	0.02 µg/l
	Metconazole	125116-23-6	CMO_MT02	0.02 µg/l
	Pyriproxyfen	95737-68-1	HPLC MS MS EN DIRECT	0.05 µg/l
1607	Benzidine	92-87-5	GC MS	10 µg/l
1584	Biphényle	92-52-4	GC MS	0.01 µg/l
1603	1-Chloronaphtalène	90-13-1	GC MS	0.1 µg/l
1604	2-Chloronaphtalène	91-58-7	GC MS	1 µg/l
1539	245-TP	93-72-1	GC MS	0.05 µg/l
	Chloronaphtalènes autres		GC MS	0.05 µg/l
2814	2-Chloro-3-nitrotoluène	3970-40-9	GC MS	0.05 µg/l
	2-Chloro-4-nitrotoluène	121-86-8	GC MS	0.05 µg/l
	2-Chloro-6-nitrotoluène	83-42-1	GC MS	0.05 µg/l
1605	4-Chloro-2-nitrotoluène	89-59-8	GC MS	0.1 µg/l
1539	Chloronitrotoluènes		GC MS	0.05 µg/l
1606	2-Chloro-p-toluidine		GC MS	0.1 µg/l
	Chlorotoluidines (autres)		GC MS	5 µg/l
2767	Chlorure de cyanuryle	108-77-0	GC MS	0.5 µg/l
1461	Di(2-éthylhexyl)phtalate (DEHP)	117-81-7	GC MS	1.0 µg/l
1484	Dichlorobenzidines		GC MS	0.1 µg/l
2984	Fluazinam	79622-59-6	GC MS	0.05 µg/l
	2,4 Dinitrophénol	51-28-5	GC MS	0.05 µg/l
1230	Omethoate	1113-02-6	GC MS	0.05 µg/l
	Paclobutrazole	76738-62-0	CMO_MT02	0.02 µg/l
1847	Tributylphosphate	126-73-8	GC MS	0.05 µg/l
Silicates (2878)				
1348	Silicium (COFRAC)		NF EN ISO 11885	0.1 mg/l
	Silicates (SiO4) (COFRAC)		Calcul	0.3 mg/l
Silice (1995)				
1348	Silicium (COFRAC)		NF EN ISO 11885	0.1 mg/l
1348	Silice totale (SiO2) (COFRAC)		Calcul	0.2 mg/l
Silice dissoute (echantillon filtré) (2607)				
1348	Silicium dissout (échantillon filtré) (COFRAC)		NF EN ISO 11885	0.1 mg/l
1348	Silice dissoute (echantillon filtré) (COFRAC)		Calcul	0.1 mg/l
Sodium (Chromato ionique) (Na) (2007)				
1375	Sodium(Na) (COFRAC)		NF EN ISO 14911	1 mg/l
Solvants industriels COV (2503)				
1454	Acétaldéhyde	75-07-0	GC MS	1.0 µg/l
1457	Acrylamide	91-57-6	GC FID	0.25 mg/l
2707	Acrylate méthyl	96-33-3	GC FID	50 µg/l
2708	Acrylate éthyl	140-88-5	GC FID	50 µg/l
2709	Acrylonitrile	107-13-1	GC FID	600 µg/l
2710	Acétate d'Isopropyl	108-21-4	GC FID	0.5 mg/l
1496	Acétate d'éthyle	141-78-6	GC FID	0.5 mg/l
2711	Acétate de n butyl	123-86-4	GC FID	0.5 mg/l
5316	Acétonitrile	75-05-8	GC FID	0.5 mg/l

Sandre	Paramétre	N° CAS	Méthode	Limite de quantification
2694	Bromofluorobenzène 4	460-00-4	NF EN ISO 10301	5 µg/l
2712	Butyl Acrylate	141-32-2	GC FID	800 µg/l
2824	Chloroéthanol 2	107-07-3	NF EN ISO 10301	100 µg/l
1603	Chloronaphtalène 1	90-13-1	NF ISO 11 423-1	10 µg/l
1604	Chloronaphtalène 2	91-58-7	GC FID	10 µg/l
2714	Chlorure de benzyle	100-44-7	NF EN ISO 10301	10 µg/l
2715	Chlorure de benzylidène	98-87-3	NF EN ISO 10301	10 µg/l
2699	Difluorobenzène 1,4	540-36-3	GC FID	10 µg/l
5314	Diméthylformamide N,N	68-12-2	GC FID	1 µg/l
1580	Dioxane-1,4	123-91-1	GC FID	0.5 mg/l
2719	Fluoronaphtalène 1	321-38-0	NF ISO 11 423-1	10 µg/l
1702	Formaldéhyde	50-00-0	GC MS	1 µg/l
2720	Furfural	98-01-1	GC FID	5 µg/l
2721	Methoxy 3 butanol 1	2517-43-3	GC- Espace de tête	1.0 mg/l
	1 Methoxypropane 2 ol	107-98-2	GC FID	2 µg/l
2722	Méhylisothiocyanate	556-61-6	GC FID	50 µg/l
2723	Méthacrylate méthyl	80-62-6	GC FID	10 µg/l
	Méthyl de méthacrylate	80-62-6	GC- Espace de tête	1.0 mg/l
2725	Méthylnaphtalène 1	90-12-0	NF ISO 11 423-1	10 µg/l
2726	Méthylnaphtalène 2	91-57-6	GC FID	10 µg/l
2614	Nitrobenzène	98-95-3	NF ISO 11 423-1	0.5 µg/l
2613	2 Nitrotoluène	88-72-2	NF ISO 11 423-1	4 µg/l
2728	Pyridine	110-86-1	GC FID	1 mg/l
1582	Tetrahydrofurane	109-99-9	NF ISO 11 423-1	0.5 µg/l
Soufre combiné (eq SO4) (2026)				
	Soufre combiné (equivalent SO4)		Calcul	1.0 mg/l
Soufre total (eq SO4) (2027)				
	Soufre total		Calcul	1.0 mg/l
Soufre total (ICP) (S) (2484)				
1819	Soufre total (S)		NF EN ISO 11885	0.5 mg/l
Streptocoques Fécaux (membrane) (2045)				
1450	Enterocoques intestinaux (COFRAC)		NF EN ISO 7899-2	UFC/100ml
Streptocoques Fécaux-Entérocoques en microplaques (2047)				
1450	Entérocoques sur microplaque (COFRAC)		NF EN ISO 7899-1	15 UFC/100ml
Substance extractible au dichlorométhane (2070)				
1435	Substances extractibles au dichlorométhane		Extraction - Pesée	1 mg/l
Sulfates (SO4) (2085)				
1338	Sulfates (SO4) (COFRAC)		NF EN ISO 10304-1	1 mg/l
Sulfures (S--) quantitatif (2093)				
1355	Sulfures (S--)		Potentiométrie	0.1 mg/l
Sulfures dissous quantitatif (2608)				
1355	Sulfures sur échantillon filtré		Potentiométrie	0.1 mg/l
T.A (2097)				
1346	Titre alcalimétrique (COFRAC)		NF EN ISO 9963-1	0.5 degré Fr
T.A.C (2099)				
1347	T.A.C. (COFRAC)		NF EN ISO 9963-1	0.5 dégré Fr
Tantale (Ta) (ICP) (2106)				
	Tantale (Ta)		NF EN ISO 11885	5 µg/l
Tellurium (Te) (ICP) (2114)				
2559	Tellurium (Te) (COFRAC)	13494-80-9	NF EN ISO 11885	5 µg/l
Température (2117)				
1301	Température		Sonde de température	°C
Température de l eau (sur place) (2498)				
1301	Température de l eau sur place (COFRAC)		PEA_001	°C
TH direct (2103)				
1345	Titre Hydrotimétrique (COFRAC)		NF T 90 003	0.1 degré Fr
Thallium (Tl) (ICP) (2134)				
2555	Thallium (Tl) (COFRAC)	7440-28-0	NF EN ISO 11885	5 µg/l

Sandre	Paramétre	N° CAS	Méthode	Limite de quantification
Titane (ICP) (Ti) (2145)				
1373	Titane (Ti) (COFRAC)	7440-32-6	NF EN ISO 11885	5 µg/l
Tributylphosphate (2570)				
1847	Tributylphosphate	126-73-8	GC ECD	0.02 µg/l
Trichlorophénols (2455)				
1235	Pentachlorophénol	87-86-5	GC MS	0.05 µg/l
1644	2,3,4 Trichlorophénol	15950-66-0	GC MS	0.05 µg/l
1643	2,3,5 Trichlorophénol	933-78-8	GC MS	0.05 µg/l
1642	2,3,6 Trichlorophénol	933-75-5	GC MS	0.05 µg/l
1548	2,4,5 trichlorophénol	95-95-4	GC MS	0.05 µg/l
1549	2,4,6 Trichlorophénol	88-06-2	GC MS	0.05 µg/l
1274	2,3,4,6 tétrachlorophénol	58-90-2	GC MS	0.05 µg/l
Tritium (soustraitance) (2543)				
2098	Tritium			2 Bq/l
Tungstene (ICP) (W) (2210)				
2797	Tungstène (W) (COFRAC)		NF EN ISO 11885	5 µg/l
Turbidité (NTU) (2213)				
1295	Turbidité (NTU) (COFRAC)		NF EN ISO 7027	0.1 NTU
Turbidité (NTU) sur place (2788)				
1295	Turbidité (NTU) sur place		NF EN ISO 7027	0.1 NTU
Uranium (ICP) (U) (2227)				
1361	Uranium (U) (COFRAC)	7440-61-1	NF EN ISO 11885	5 µg/l
Vanadium (ICP) (V) (2237)				
1384	Vanadium (V) (COFRAC)	7440-62-2	NF EN ISO 11885	5 µg/l
Zinc (ICP) (Zn) (2274)				
1383	Zinc (Zn) (COFRAC)	7440-66-6	NF EN ISO 11885	2 µg/l
Zirconium (Zr) (ICP) (2277)				
1800	Zirconium (Zr) (COFRAC)		NF EN ISO 11885	5 µg/l

Appendix B

Biocide leaching from CBA-amine treated wood

1 Theoretical background copper fixation in wood

In solution monoethanolamine (Mea) coordinates with copper to form monovalent, divalent and neutral Cu−Mea complexes with different metal-ligand stoichiometry, such as $[CuMea]^{2+}$, $[CuMea_2]^{2+}$, $[CuMea_3]^{2+}$, $[CuMea_4]^{2+}$, $[CuMea_{2\text{-}H}]^{+}$ and $[CuMea_{2\text{-}2H}]^{0}$ (Jiang, 2000; Zhang and Kamdem, 2000; Lee and Cooper, 2010; Mettlemary, 2011). The stability of these complexes depends on ionic strength and temperature. Neutral complexes dominate under basic conditions (pH above 10) and are relatively stable (log of the stability constant K, i.e. ratio between complex and dissociated form, is around 20) whereas monovalent complexes are less stable (log K for $[Cu{-}Mea_{2\text{-}H}])^{+}$: about 1.5) and therefore its reactivity is higher (Mettlemary, 2011). Divalent complexes can be formed while the pH of the solution decreases during penetration into wood.

Possible complexation reactions between the monovalent Cu−Mea complex and

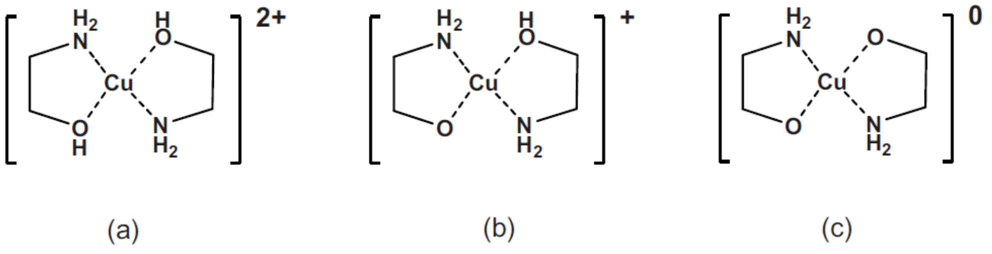


Figure B.1: (a) Divalent ($[CuMea_2]^{2+}$), (b) monovalent ($[CuMea_{2\text{-}H}]^{+}$), and (c) neutral CuMea complexes ($[CuMea_{2\text{-}2H}]^{0}$) (Zhang and Kamdem, 2000)

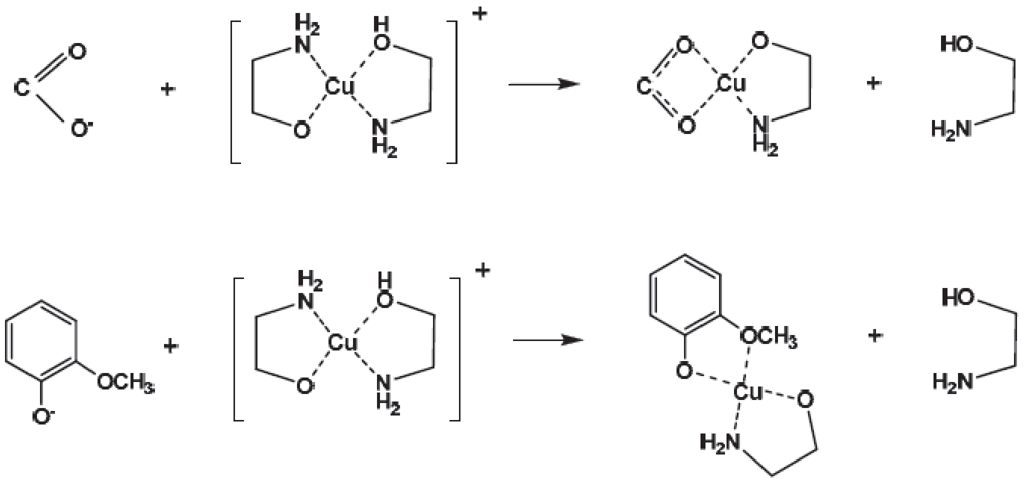
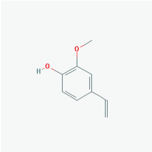


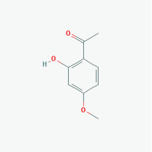
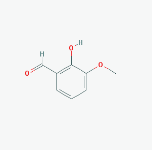
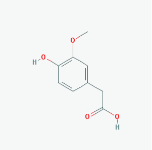
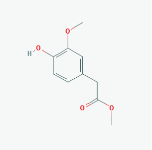
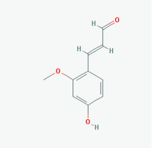
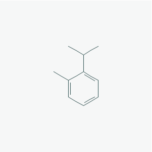
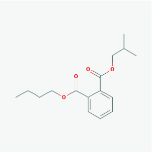
Figure B.2: Interaction of monovalent CuMea complexes with carboxyl and phenyl groups of wood (Lee, 2011)

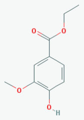
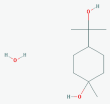
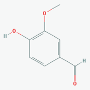
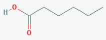
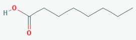
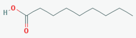
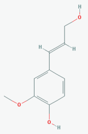
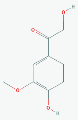
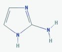
the active sites from wood are shown in Figure S2. One Mea−ligand is exchanged, and one molecule of Mea is eliminated (Klemm et al., 1998; Lee, 2011). Stable complexes are formed by interaction of [CuMea$_{\text{-H}}$]$^+$ with acidic groups (carboxyl and phenyl). Two coordination sites of the copper atom are occupied by the deprotonated O atoms of an acidic group of wood components, and the other two coordination sites bind one Mea molecule.

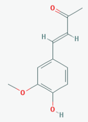
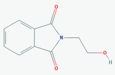
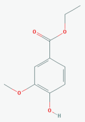
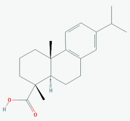
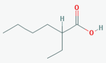
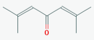
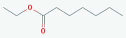
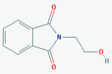
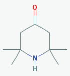
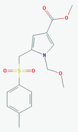
2 Analytical methods

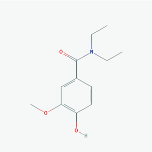
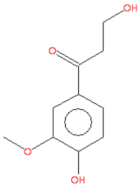
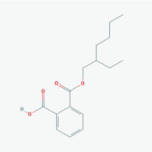
Table B.2: Substances identified by GC−MS analysis of lyophilised samples from untreated and treated wood. The substances were identified by library search with the NIST 02 library. The Table includes only substances that were identified with compliance value higher than 80%.

		Treated wood pH of elute		Untreated wood pH of eluate		
Chemical substance CAS Number	Structure	native 4.37	basic 7.4–8.3	acid 4.2–6.5	native 7.5	basic 8.7–9.5
2-Methoxy-4-vinylphenol 7786-61-0		×				

		pH of elute		pH of eluate		
Chemical substance CAS Number	Structure	native 4.37	basic 7.4–8.3	acid 4.2–6.5	native 7.5	basic 8.7–9.5
1-(2-Hydroxy-4-methoxyphenyl)- ethanone 552-41-0		×				
alpha,alpha,4-Trimethyl-benzenem ethanol 001197-01-9		×				
2-Hydroxy-3-methoxy-vanillin ben zaldehyde 148-53-8		×				
4-Hydroxy-3-methoxy-benzeneacetic acid 306-08-1		×				
4-Hydroxy-3-methoxy-, benzeneacetic acid methylester 15964-80-4		×				
4-Hydroxy-2-methoxycinnamaldehyde 127321-19-1		×				
2,3-Dihydro-2,2-dimethyl-3,7-benzofurandiol 017781-15-6		×				
2,4′-Dihydroxy-3′-methoxyacetophenone 018256-48-9		×	×			
1-Methyl-2-(1-methylethyl)- benzene 527-84-4			×			
2-Methoxy-4-vinylphenol 7786-61-0			×			
s-(+)-5-(1-Hydroxy-1-methylethyl)-2-methyl-2-cyclohexen-1-one 060593-11-5			×			

		pH of elute		pH of eluate		
Chemical substance CAS Number	Structure	native 4.37	basic 7.4–8.3	acid 4.2–6.5	native 7.5	basic 8.7–9.5
1,2-Benzenedicarboxylic acid but yl 2-methylpropylester 17851-53-5			×			
4-Hydroxy-3-methoxy benzoic acid ethyl ester 617-05-0		×			×	
Terpin hydrate 2451-01-6		×	×	×	×	×
Vanillin 121-33-5						
Hexanoic acid 142-62-1		×	×		×	×
Octanoic Acid 124-07-2		×	×		×	×
Nonanoic acid 112-05-0		×	×	×		×
4-((1E)-3-Hydroxy-1-propenyl)-2- methoxyphenol Coniferyl alcohol 458-35-5			×		×	×
2,4′-Dihydroxy-3′-methoxyacetoph enone 18256-48-9			×			×
1H-Imidazol-2-amine 7720-39-0					×	

		pH of elute		pH of eluate		
Chemical substance CAS Number	Structure	native 4.37	basic 7.4–8.3	acid 4.2–6.5	native 7.5	basic 8.7–9.5
2,5-Dimethyl-1-(1,1-dimethylethy l)-piperidin-4-ol 29849-46-5					×	
4-(4-Hydroxy-3-methoxyphenyl)-3-buten-2-one 1080-12-2					×	
2-(2-Hydroxyethyl)-1H-isoindole- 1,3(2H)-dione 3891-07-4				×	×	×
4-Hydroxy-3-methoxy benzoic acid ethyl ester 617-05-0				×	×	×
1,2,3,4,4a,9,10,10a-Octahydro-1, 4a-dimethyl-7-(1-methylethyl)-, [1R-(1,4a,10a)]-1-phenanthrenecarboxylic acid 1740-19-8				×	×	×
2-Ethyl hexanoic acid 149-57-5				×	×	×
2,6-Dimethyl- 2,5-heptadien-4-on e 504-20-1				×		
Heptanoic acid ethyl ester 106-30-9				×		
2-(2-Hydroxyethyl)-1H-isoindole- 1,3(2H)-dione 3891-07-4					×	×
2,2,6,6-Tetramethyl-4-piperidino ne 826-36-8					×	×

		pH of elute		pH of eluate		
Chemical substance CAS Number	Structure	native 4.37	basic 7.4–8.3	acid 4.2–6.5	native 7.5	basic 8.7–9.5
1-(Methoxymethyl)-5-[[4-(methylphenyl)sulfonyl]methyl]-(1H)pyrrole-3-carboxylic acid methyl ester 155345-18-9						×
Ethamivan N,N-diethyl-4-hydroxy-3-methoxybenzamide 304-84-7						×
alpha-Amino-3′-hydroxy-4′-methox yacetophenone 90765-44-9						×
3-Hydroxy-1-(4-hydroxy-3-methoxy phenyl)-1-propanone 2196-18-1						×
1,2-Benzenedicarboxylic acid mon o(2-ethylhexyl) ester 4376-20-9						×

The quantification limits and uncertainty of measurement for all analytical methods used to quantify the concerned compounds in eluates from treated and untreated wood samples are presented in Table B.1.

Table S3 presents the results of GC-MS compound identification, carried out on the lyophilised eluates. The full name, the CAS number and the corresponding eluates are shown. The last column contains remarks concerning the structure and the active sites representative for each identified species. Information obtained by GC-MS analysis of acetone extracts of lyophilised eluates is restricted to substances that are eluted during the ANC test, resist the lyophilisation procedure and can be extracted by acetone. In addition, the substances have to be volatile, ionisable in the mass spectrometer and split into ionic fragments that can be detected by the mass spectrometer. The identification of substances from the fragment patterns depends on the substances and mass spectra that are included in the used library. Plausibility of the structures proposed by library research was controlled, but the identity was not verified by analysis of corresponding standards.

Table B.1: Limit of quantification and uncertainty of measurement for the analytical methods used.

Substance	Analytical method	Unit	Limit of quantification	Uncertainty of measurement
TO	TOC analysis	mg/L	0.05	$\pm 1 - 5\%$
Cl^-	IC	mg/L	0.4	
NO_2^-		mg/L	0.4	
Br^-		mg/L	0.3	
NO_3^-		mg/L	1	
PO_4^{3-}		mg/L	1	
SO_4^{2-}		mg/L	2	
B	ICP-OES	mg/L	0.001	
Ca		mg/L	0.4	
Cu		mg/L	0.008	
K		mg/L	0.6	
Zn		mg/L	0.3	
Formic acid	UHPLC	mg/L	1.0	
Acetic acid		mg/L	1.0	
Tebuconazole		mg/L	0.1	
Tebuconazole	GC-MS	mg/L	1.0	
C	Macro-elementary analysis	µg	42	
N		µg	10	

Table B.3: Characteristic position of absorption bands of selected bonds in infrared spectra according to Gottwald and Wachter (1999).

FTIR – bands position (cm^{-1})	Corresponding functional groups and bonds
$3400 - 3000$	OH stretching
$2935 - 2840$	C−H stretching in CH_2, CH_3
$1730 - 1680$	C=0
$1600 - 1560$	−COO (carboxylate)
1516	O−H (polysaccharides)
1460	$R-NH_2$, $R-NH-R$ (amines)
1360	tertiary aromatic amines
$1350 - 1250$	secundary aromatic amines
1070	$R-NH_2$, $R-NH-R$ (amines)
1030	O−H (polysaccharides)

3 TOC release by untreated and treated samples

The concentrations of TOC in eluates obtained from both “fresh” and “conditioned” samples were compared. The total amount of carbon added to wood with the treatment solution was calculated (first column in Table B.4). TOC concentrations from ANC tests (at native pH) on treated samples have been selected and compared to theoretical amounts obtained by summing up TOC concentration from untreated samples with carbon concentration in treatment solution. TOC is released in almost 2 times higher concentrations from treated wood during ANC tests, than expected. This shows that the presence of preservatives in wood forces emissions from the wood structure.

Table B.4: Carbon emissions during leaching

	TOC			
C in CBA solution	UA*	UF*	BA*	BF*
mg/L 740.2**	mg/L 558.6	mg/L 676.5	mg/L 2338.0	mg/L 1671.0
Theoretical leached C from treated samples			1298.8	1416.7

* At native pH.

** Expected concentration if all carbon containing preservatives leached during the ANC test.

Appendix C

Numerical model – leaching from CBA-amine treated wood

1 Experimental platform

Figure C.1 presents an overview of the analytical methods performed on eluates from ANC and DSLT tests. ANC eluates were divided into two parts: (i) eluates analysed in liquid state and (ii) eluates lyophilised and then used for the identification and quantification of several organic compounds. DSLT eluates were analysed only in liquid state, being too diluted for lyophilisation.

Analysis of liquid eluates. Eluate samples were directly used to determine TOC (total organic carbon), formic, acetic and maleic acid by UHPLC (Ultra High Performance Liquid Chromatography), inorganic species: anions (Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) by IC (Ion Chromatography) and cations (Cu, K, Ca, B) by ICP-OES (Optical Emission Spectrometry). Total concentration of carboxyl groups was estimated by titration with a 0.1 M NaOH solution in presence of phenolphthalein. Since concentrations of inorganic acids were neglectable compared to the total amount of acid groups, the acid groups determined with this test were considered as carboxyl groups. A photometric method was used to quantify the total content of phenols, namely the modified Prussian Blue Assay for Total Phenols (Hagerman, 2002).

Analyse of lyophilised eluates. After filtration, ANC eluates with alkaline pH were first neutralised with a 0.1 M HCl solution. Then the acid, neutral and neutralised (former alkaline) samples were lyophilised to remove water in order to be able to identify functional organic groups ($-$COOH, $-$OH, R$-$N, $-$NO, etc.) in the solid samples by FTIR (Fourier Transformed InfraRed spectroscopy). Parts of the lyophilised samples were extracted by acetone and analysed by GC-MS (Gas

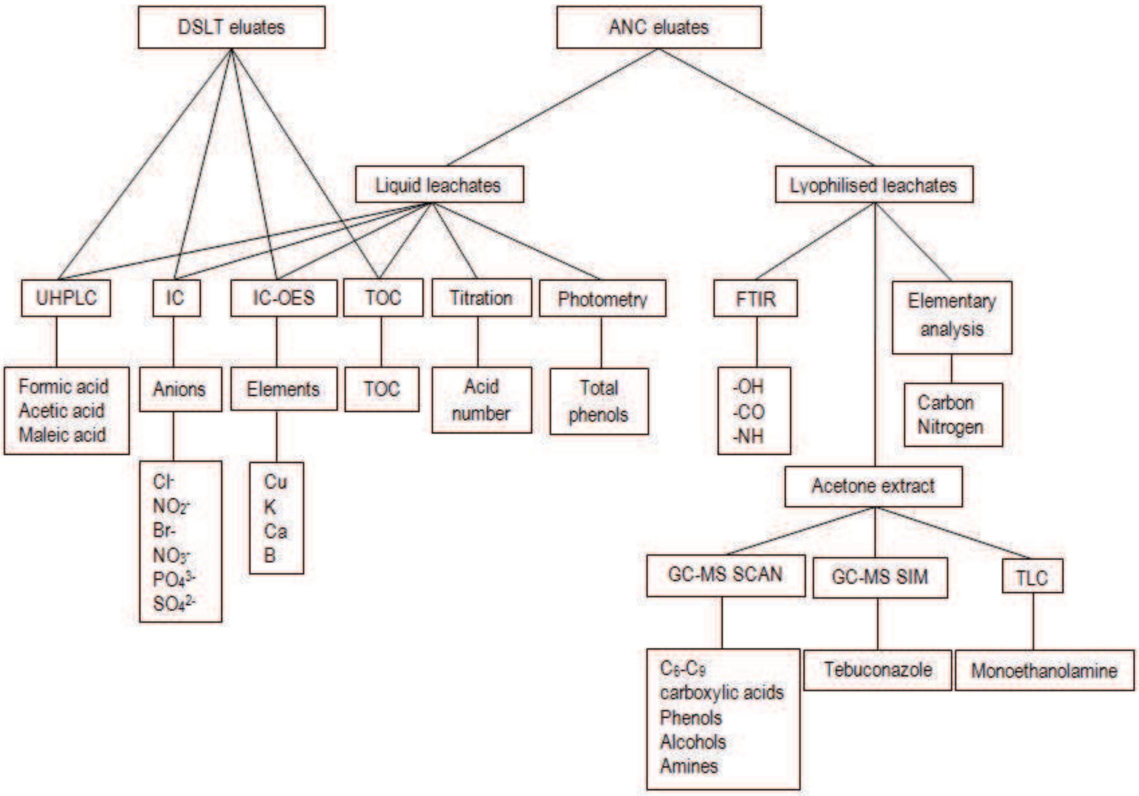


Figure C.1: Analysis of eluates from ANC and DSLT tests and target parameters.

Chromatography coupled with Mass Spectrometry) and TLC (Thin Layer Chromatography). An elemental analysis for carbon and nitrogen was also performed using a Macro-Elementary Analyser.

2 Experimental results

ANC test delivered two types of results, as presented in reference (Lupsea et al., 2013a) (i) pH of the system in function of H^+ moles added per L solution, and (ii) variation with pH of the concentration of target substances in eluates. The native pH of CBA treated wood in contact with demineralised water was 7.46 (Figure 3.6).

Cu concentrations varied up to one order of magnitude over the pH range, with a minimum at native pH. B exhibited a pH independent behaviour while tebuconazole concentrations in eluates increased with pH. Up to 30% of the initial content of Cu (maximum at pH 5.6) and B, and up to 17% (maximum at pH 9.5) of the initial content of tebuconazole were eluted under the ANC test conditions, proving that their binding on wood structure is relatively important. Other inorganic species found in eluates are K and Ca, very probably as endogenous species in wood. K concentration was almost constant with pH, while Ca was present in part of eluates. Cl^-, SO_4^{2-} and PO_4^{3-} were also present in low and dispersed concentrations (not shown here).

The concentration of carboxylic acids, phenols and TOC increased with pH. The release of acetic acid increased with pH while the concentrations of formic acid in eluates were only slightly higher under alkaline conditions.

3 Model sensitivity analysis

The final form of the chemical model was defined after the sensitivity analysis of different possible reactions and their equilibrium constants. The final form of the model contains literature confirmed reactions and constants. For several reactions considered by literature as important or major mechanisms, but for which no constants exist, an adjustment was performed based on the experimental data concentration-vs-pH, for the target species.

3.1 Flavonoids – copper complexes

Supplementary reactions were tested for representing copper – extractives possible interactions. Flavonoids are a class of plant secondary metabolites.

Interactions of Cu with several polyflavonoids (containing phenol groups) were described by (Thomason and Pasek, 1997; Teixeira et al., 2005). Studying the reactions of taxifolin and chrysin with the Cu−MeaH complex, (Jiang, 2000) found in both cases a green extensive precipitation. FTIR, XPS (X-ray Photoelectron Spectroscopy) and ESR (Electron Spin Resonance) suggested that phenol and ketone groups of the extractives are the major sites for Cu chelation – one mole of Cu is coordinated to two moles of amine in the Cu−MeaH−taxifolin or Cu−MeaH−chrysin complexes. Under severe alkaline conditions the phenol groups are deprotonated and the Cu−MeaH monovalent complex is easily chelated to phenol groups and the adjacent ketone groups. Due to lack of information (exact structure of compounds, formation/stability constants), we considered all polyflavonoids as one component, which we called “Flavonoids” and thus two reactions corresponding to the complexation of Cu, respectively Cu−MeaH with polyflavonoids. These compounds are in solid state, hence in the model they were considered as surface complexes bound to an organic solid matrix named “Flavonoids_”.

Table C.1: Reactions and parameters for Cu−flavonoids interactions

Reaction	$\log K$	Reference
Flavonoids_phO$^-$ + H$^+$ = Flavonoids_phOH	6.68	(Teixeira et al., 2005)
Cu^{2+} + Flavonoids_phO$^-$ = Flavonoids_phOCu$^+$	5	deduced from (Teixeira et al., 2005)
(CuMeaH(Mea))$^+$ + Flavonoids_phO$^-$ = Flavonoids_phO(CuMeaH(Mea))	5	this study
Surface parameters		
Site density phenol (flavonoids) 0.001 mol/kg wood		this study

The flavonoid's acidity constants and stability constant of the Cu−Flavonoids complex were deduced from those of chrysin (Teixeira et al., 2005). The reaction of Cu with polyflavonoids involving MeaH has not been studied before, so its constant has been set to the same value as for Cu−Flavonoids reaction.

The specialised literature in the field of treated wood doesn't mention this kind of mechanism as crucial for copper binding, probably because of the small quantity of free flavonoids in wood when compared to lignin and hemicellulose. For example, (Nuopponen et al., 2004) reported that flavonoids extracted from a *Pinus sylvestris* account for about 0.01% of wood mass. Using this order of magnitude in the model, it was found that flavonoids represent no more than 1% of the total binding sites density (estimated at 0.11 mol/kg wood).

Simulations performed by including these reactions into the chemical model shown that the discussed mechanism is not influent and can be neglected at least for the operation conditions of the laboratory leaching assays.

3.2 Copper-monoethanolamine-wood complexes

Direct complexation of Cu with phenolic and carboxylic sites of wood was studied so far and complexation constants exist in the literature. Amine-CBA treatment introduces in wood monoethanolamine (MeaH). Literature mentions the possibility of Cu to be linked in mixed complexes like wood−Cu−MeaH, but no reaction constants are known. The developed model contains both mechanisms and allows identifying the most probable. A sensitivity study realised by removing from the model the direct wood−Cu mechanism shows that Cu amount fixed via MeaH (wood−Cu−MeaH) strongly rises with pH and aqueous Cu diminishes correspondingly (Figure C.2). The shape of copper concentration-vs-pH didn't

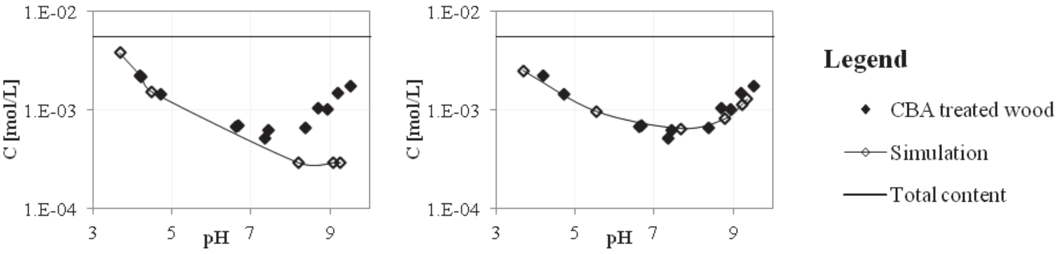


Figure C.2: Cu release in ANC simulation: (left) only wood−Cu−MeaH complexation modelled; (right) only wood−Cu mechanisms modelled.

fit the experimental data for any values assigned to the respective equilibrium constants. Contrarily, simulation considering only the direct complexation of Cu on active sites of wood (wood−Cu) showed a very good fit to the experimental data. It can be concluded that, if it exists, the mixed complex must be less stable than the simple wood−Cu complex which dominates at least in the used experimental leaching conditions.

3.3 Influence of the wood samples' homogeneity on the modelling results

Information about the biocides distribution in wood blocks having undergone a vacuum pressure treatment is very scarce. (Schoknecht et al., 2005) presented a set of data obtained on similar samples (following EN 113 treatment standard) as those used in our study. In this reference, Cu concentration varies slightly from the surface to the material core, while tebuconazole variation seems more pronounced. More important, this variation occurs on the first millimetre of the specimen surface and seems to stabilize in the deeper wood layers.

The leaching process affects not only the specimen surface but also its core. The effect of the surface accumulation of biocides on their release can be visible mainly at the beginning of the leaching test (the first leachate). The treatment by vacuum pressure impregnation (treatment solution with all its constituents is forced to penetrate) and long-time conditioning of small wood pieces of $15\,\mathrm{mm} \times 25\,\mathrm{mm} \times 50\,\mathrm{mm}$ (internal diffusion reduces the concentration gradients) leads to the hypothesis that the preservatives are homogenously distributed in the samples (hypothesis discussed further). However, we realised a sensitivity study on the homogeneity of biocide initial distribution in wood blocks.

Results from simulations performed with a nonhomogeneous distribution of biocides in wood samples are presented in Figure C.3. A similar distribution was

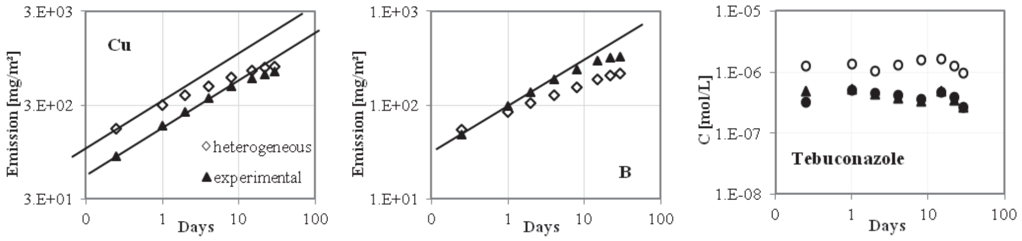


Figure C.3: Simulation of biocide release in DSLT test with the hypothesis of non-homogeneous initial distribution of biocides in wood specimens.

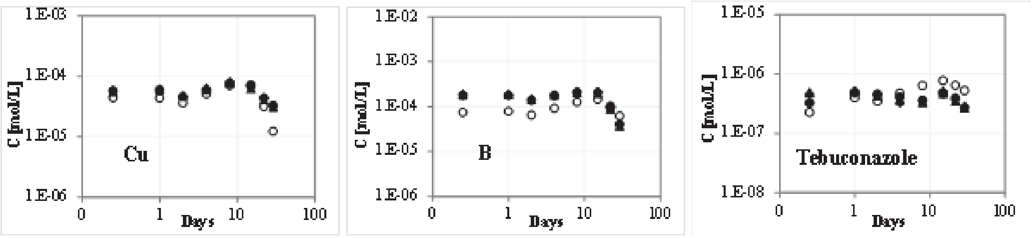


Figure C.4: Simulation of biocide release in DSLT test with a water content of 30% (volume of absorbed water/volume of wood specimen).

considered as in (Schoknecht et al., 2005) for fixed Cu and tebuconazole. In this reference, in the superficial 1 mm layer of treated sample, Cu concentration is 20% higher and tebuconazole is four times higher than their respective concentrations in the core of wood sample. In simulations, B was additionally included with similar inhomogeneous distribution as tebuconazole.

One observes that the diffusional regime of Cu and B (experimental data for the first 10 days) is perturbed by the surface heterogeneity (the 0.5 slope is no longer valid). Tebuconazole release simulated in case of the initial heterogeneous distribution is far from the observed experimental release (and worse than the original modelled release). These observations have led to the hypothesis that wood treated samples used in DSLT leaching test were rather homogenous.

3.4 Influence of the water content in wood samples

During DSLT experiments, the wood samples have been weighted after each leachant renewal in order to evaluate the water quantity absorbed by wood. It was observed that the water quantity increased in time from 20% to 40% expressed in volume of water absorbed/volume of wood specimen.

The simulations presented in the main paper document have been realised considering the final water content in wood specimens. In order to evaluate the influence of water content, simulations have been performed also for lower water content. The modelling hypothesis was that the pores are partially filled with water, and then the initial concentration of different existent species in porewater was recalculated accordingly. The simulation results are presented in Figure C.4. When compared to Figure 3.7, only small differences are observed for biocides behaviour. Water content is not a determinant parameter in the tested % interval.

Appendix D

FDES fibre-cement sheets

The inventory data found in the EPD file for fibre-cement sheets is presented below, along with the contributions to the environmental impact associated to all considered indicators – data taken from (Eternit, 2003).

2.2.4 Emissions dans l'eau liées aux étapes de mise en œuvre et de vie en œuvre (données utiles à la maîtrise des risques sanitaires) (XP P 01 010-1 § 5.3.4)

Flux	Unités	Mise en œuvre	Vie en œuvre	Observations et commentaires
DCO (Demande Chimique en Oxygène)	g	0,63	0	Les émissions décrites ci-dessus ne participent pas aux risques sanitaires des opérateurs. Elles sont dues à la fabrication des fixations décrites en 1.2 indispensables à la pose du produit et de l'énergie nécessaire au perçage des plaques ondulées et des pannes.
DBO5 (Demande Biochimique en Oxygène)	g	0,0029	0	
Matière en Suspension (MES)	g	0,11	0	
Sulfate (SO^4--)	g	0,14	0	
Cyanure (CN-)	g	0,00022	0	
AOX (Halogènes des composés organiques adsorbables)	g	0	0	
Hydrocarbures (non spécifiés)	g	0,0048	0	
Composés azotés (en N)	g	0,027	0	
Composés phosphorés (en P)	g	0	0	
Composés fluorés organiques (en F)	g	0,0035	0	
Composés fluorés inorganiques (en F)	g	0	0	
Composés fluorés non spécifiés (en F)	g	0	0	
Composés chlorés organiques (en Cl)	g	0	0	
Composés chlorés inorganiques (en Cl)	g	0,63	0	
Composés chlorés non spécifiés (en Cl)	g	0	0	
HAP (non spécifiés)	g	0	0	
Métaux (non spécifiés)	g	0,00020	0	
Aluminium et ses composés (en Al)	g	0,00014	0	
Arsenic et ses composés (en As)	g	0	0	
Cadmium et ses composés (en Cd)	g	0	0	
Chrome et ses composés (en Cr)	g	0,00050	0	
Cuivre et ses composés (en Cu)	g	0	0	
Etain et ses composés (en Sn)	g	0	0	
Fer et ses composés (en Fe)	g	0,0050	0	
Mercure et ses composés (en Hg)	g	0	0	
Nickel et ses composés (en Ni)	g	0,00058	0	
Plomb et ses composés	g	0,00047	0	
Zinc et ses composés (en Zn)	g	0,0012	0	
Eau rejetée	Litre	2,1	0	
Composés organiques dissous non spécifiés	g	0,00017	0	
Composés inorganiques non spécifiés	g	0,0019	0	
Métaux alcalins (Na+, K+)	g	0,41	0	

2.2.5 Emissions dans le sol hors étape mise en œuvre et vie en œuvre (XP P 01 010-1 § 5.3.5)

Flux	Unités	Production	Transport	Mise en œuvre	Vie en œuvre	Fin de vie	Total cycle de vie	
							Par annuité	Pour toute la DVT
Arsenic et ses composés (en As)	g	0	0	0	0	0	0	0
Biocides[a]	g	0	0	0	0	0	0	0
Cadmium et ses composés (en Cd)	g	0	0	0	0	0	0	0
Chrome et ses composés (en Cr)	g	0	0	0	0	0	0	0,00090
Cuivre et ses composés(en Cu)	g	0	0	0	0	0	0	0
Etain et ses composés (en Sn)	g	0	0	0	0	0	0	0
Fer et ses composés (en Fe)	g	0,0071	0	0	0	0	0,0072	0,36
Plomb et ses composés (en Pb)	g	0	0	0	0	0	0	0
Mercure et ses composés (en Hg)	g	0	0	0	0	0	0	0
Nickel et ses composés (en Ni)	g	0	0	0	0	0	0	0
Zinc et ses composés (en Zn)	g	0	0	0	0	0	0	0,0027
Métaux lourds (non spécifiés)	g	0	0	0	0	0	0	0

[a] Biocides : par exemple, pesticides, herbicides, fongicides, insecticides, bactéricides, etc..

Commentaires sur les émissions dans le sol hors étapes de mise en œuvre et de vie en œuvre

Les émissions dans le sol mentionnées ci-dessus ne sont pas directement imputables au cycle de vie du produit. Elles sont dues à des étapes amonts telles que la production d'énergie.

2.2.6 Emissions dans le sol liées aux étapes de mise en œuvre et vie en œuvre (données utiles à la maîtrise des risques sanitaires) (XP P 01 010-1 § 5.3.6)

Flux	Unités	Mise en œuvre	Vie en œuvre	Observations et commentaires
Arsenic et ses composés (en As)	g	0	0	Les étapes de mises en œuvre et de vie en œuvre n'engendrent pas d'émission dans le sol.
Biocides[a]	g	0	0	
Cadmium et ses composés (en Cd)	g	0	0	
Chrome et ses composés (en Cr)	g	0	0	
Cuivre et ses composés(en Cu)	g	0	0	
Etain et ses composés (en Sn)	g	0	0	
Fer et ses composés (en Fe)	g	0	0	
Plomb et ses composés (en Pb)	g	0	0	
Mercure et ses composés (en Hg)	g	0	0	
Nickel et ses composés (en Ni)	g	0	0	
Zinc et ses composés (en Zn)	g	0	0	
Métaux lourds (non spécifiés)	g	0	0	

[a] Biocides : par exemples, pesticides, herbicides, fongicides, insecticides, bactéricides, etc..

3/Contribution du produit aux impacts environnementaux selon XP P01 010 - 2 § 4.1 et 4.2

Tous ces impacts sont renseignés ou calculés conformément aux indications des paragraphes 4.1 et 4.2 de la norme XP P01 010-2, à partir des données du chapitre 2 de la présente fiche.

Impact environnemental	Valeur - Unité
Consommation de ressources énergétiques	
Energie primaire totale	311 MJ/UF
Energie renouvelable	38 MJ/UF
Energie non renouvelable	273 MJ/UF
Consommation de ressources non énergétiques	36 kg/UF
Consommation de l'eau	80 l/UF
Déchets solides	
Valorisés	0,30 kg/UF
Eliminés	
Déchets dangereux	0,030 kg/UF
Déchets non dangereux	0,16 kg/UF
Déchets inertes	37 kg/UF
Déchets radioactifs	0,0025 kg/UF
Changement climatique	25 kg équivalent CO^2/UF
Acidification atmosphérique	0,108 kg équivalent SO^2/UF
Pollution de l'air	1 358 m^3/UF
Pollution de l'eau	1 264 m^3/UF
Pollution des sols	Il n'y a pas d'émissions dans le sol.
Destruction de la couche d'ozone stratosphérique	0 kg équivalent CFC 11 / UF(2)
Formation d'ozone photochimique	10,6 g équivalent éthylène/UF
Modification de la biodiversité	Les carrières utilisées pour la production de ciment sont réaménagées de façon à limiter les impacts sur la biodiversité.

(2) Aucune émission de CFC ou HCFC ne ressort de l'analyse du cycle de vie.

Appendix E

FDES treated wood

The inventory data found in the EPD file for a CBA treated wood product is presented below, along with the contributions to the environmental impact associated to all considered indicators – data taken from (FCBA, 2011).

2.2.2 Emissions dans l'eau (*NF P 01-010 § 5.2.2*)

Un guide de lecture des tableaux est disponible page 4.

	Unités	**Production**	**Transport**	**Mise en œuvre**	**Vie en œuvre**	**Fin de vie**	**Total cycle de vie**	
Flux							**Par annuité**	**Pour toute la DVT**
DCO (Demande Chimique en Oxygène)	g	0,256	0,000641	0	0	0,0163	0,273	13,6
DBO5 (Demande Biochimique en Oxygène à 5 jours)	g	0,141	1,94 E-05	0	0	0,00296	0,144	7,21
Matière en Suspension (MES)	g	0,0558	0,000111	0	0	0,00139	0,0573	2,87
Cyanure (CN-)	g	0,000133	9,42 E-07	0	0	4,02 E-07	0,000134	0,00670
AOX (Halogènes des composés organiques adsorbables)	g	3,43 E-06	9,06 E-07	0	0	2,62 E-07	4,60 E-06	0,000230
Hydrocarbures (non spécifiés)	g	0,0212	0,00329	0	0	0,00121	0,0257	1,29
Composés azotés (en N)	g	0,0106	0,000534	0	0	0,00564	0,0168	0,839
Composés phosphorés (en P)	g	0,00465	1,79 E-06	0	0	8,27 E-05	0,00473	0,236
Composés fluorés organiques (en F)	g	0	0	0	0	0	0	0
Composés fluorés inorganiques (en F)	g	0,00136	4,55 E-06	0	0	1,65 E-06	0,00137	0,0683
Composés fluorés non spécifiés (en F)	g	0	0	0	0	0	0	0
Composés chlorés organiques (en Cl)	g	3,54 E-06	1,06 E-08	0	0	1,28 E-06	4,83 E-06	0,000242
Composés chlorés inorganiques (en Cl)	g	0,962	0,221	0	0	0,120	1,30	65,1
Composés chlorés non spécifiés (en Cl)	g	0,000201	4,06 E-06	0	0	2,68 E-06	0,000207	0,0104
HAP (non spécifiés)	g	1,50 E-05	5,55 E-06	0	0	1,51 E-06	2,20 E-05	0,00110
Métaux (non spécifiés)	g	0,0212	0,00369	0	0	0,00107	0,0260	1,30
Aluminium et ses composés (en Al)	g	0,0303	2,15 E-06	0	0	6,36 E-05	0,0304	1,52
Arsenic et ses composés (en As)	g	4,42 E-05	1,80 E-07	0	0	5,84 E-07	4,49 E-05	0,00225
Cadmium et ses composés (en Cd)	g	5,60 E-06	3,00 E-07	0	0	2,52 E-07	6,15 E-06	0,000308
Chrome et ses composés (en Cr)	g	0,00125	1,05 E-06	0	0	3,65 E-06	0,00126	0,0630
Cuivre et ses composés (en Cu)	g	0,00436	6,08 E-07	0	0,0809	4,54 E-07	0,0853	4,26
Etain et ses composés (en Sn)	g	8,05 E-06	6,74 E-12	0	0	1,28 E-10	8,05 E-06	0,000402
Fer et ses composés (en Fe)	g	0,0709	5,30 E-05	0	0	0,000232	0,0711	3,56
Mercure et ses composés (en Hg)	g	1,93 E-06	1,79 E-09	0	0	1,51 E-08	1,95 E-06	9,74 E-05
Nickel et ses composés (en Ni)	g	0,0189	1,04 E-06	0	0	5,86 E-07	0,0189	0,944
Plomb et ses composés (en Pb)	g	6,71 E-05	2,08 E-07	0	0	2,08 E-06	6,94 E-05	0,00347
Zinc et ses composés (en Zn)	g	0,000261	1,81 E-06	0	0	1,28 E-05	0,000275	0,0138
Eau rejetée	Litre	0,0261	0,000764	0	0	0,0473	0,0742	3,71

Commentaires sur les émissions dans l’eau :

Les émissions decuivre liées au délavage du bois sont comptabilisées dans les émissions dans l’eau. Etant donné qu’il n’existe pas de rubrique pour les émissions dans l’eau liées aux autres biocide dans le format NF P01-010, ces émissions ont été comptabilisées dans les émissions dans le sol.

2.2.3 Emissions dans le sol (*NF P 01-010 § 5.2.3*)

Un guide de lecture des tableaux est disponible page 4.

	Unités	Production	Transport	Mise en œuvre	Vie en œuvre	Fin de vie	Total cycle de vie	
Flux							**Par annuité**	**Pour toute la DVT**
Arsenic et ses composés (en As)	g	7,90 E-08	7,20 E-10	0	0	4,74 E-10	8,02 E-08	4,01 E-06
Biocides[a]	g	0,000562	6,96 E-06	0	0,0237	2,57 E-06	0,0242	1,21
Cadmium et ses composés (en Cd)	g	1,26 E-08	3,26 E-13	0	0	2,14 E-13	1,26 E-08	6,31 E-07
Chrome et ses composés (en Cr)	g	3,71 E-06	9,02 E-09	0	0	5,94 E-09	3,72 E-06	0,000186
Cuivre et ses composés(en Cu)	g	9,78 E-07	1,66 E-12	0	0	1,09 E-12	9,78 E-07	4,89 E-05
Etain et ses composés (en Sn)	g	2,25 E-09	0	0	0	0	2,25 E-09	1,13 E-07
Fer et ses composés (en Fe)	g	0,00127	3,60 E-06	0	0	2,37 E-06	0,00128	0,0638
Plomb et ses composés (en Pb)	g	1,14 E-07	7,56 E-12	0	0	4,98 E-12	1,14 E-07	5,69 E-06
Mercure et ses composés (en Hg)	g	2,79 E-10	6,00 E-14	0	0	3,96 E-14	2,79 E-10	1,39 E-08
Nickel et ses composés (en Ni)	g	9,60 E-08	2,48 E-12	0	0	1,64 E-12	9,60 E-08	4,80 E-06
Zinc et ses composés (en Zn)	g	5,86 E-06	2,70 E-08	0	0	1,78 E-08	5,90 E-06	0,000295
Métaux lourds (non spécifiés)	g	6,86 E-05	7,20 E-08	0	0	5,32 E-05	0,000122	0,00610
Etc.	g							

[a] Biocides : par exemple, pesticides, herbicides, fongicides, insecticides, bactéricides, etc.

Commentaires sur les émissions dans le sol :

3 Impacts environnementaux représentatifs des produits de construction selon NF P 01-010 § 6

Tous ces impacts sont renseignés ou calculés conformément aux indications du § 6.1 de la norme NF P01-010, à partir des données du § 2 et pour l'unité fonctionnelle de référence par annuité définie au § 1.1 et 1.2 de la présente déclaration, ainsi que pour l'unité fonctionnelle rapportée à toute la DVT (Durée de Vie Typique).

N°	Impact environnemental	Valeur de l'indicateur pour l'unité fonctionnelle		Valeur de l'indicateur pour toute la DVT	
1	Consommation de ressources énergétiques				
	Energie primaire totale*	10,9	MJ/UF	544	MJ
	Energie renouvelable**	8,05	MJ/UF	403	MJ
	Energie non renouvelable	2,83	MJ/UF	142	MJ
2	Epuisement de ressources (ADP)	0,000885	kg éq. antimoine (Sb)/UF	0,0442	kg équivalent antimoine (Sb)
3	Consommation d'eau totale	1,07	litre/UF	53,3	litre
4	Déchets solides				
	Déchets valorisés (total)	0,996	kg/UF	49,8	kg
	Déchets éliminés				
	Déchets dangereux	0,000494	kg/UF	0,0247	kg
	Déchets non dangereux	0,434	kg/UF	21,7	kg
	Déchets inertes	0,00907	kg/UF	0,454	kg
	Déchets radioactifs	2,55 E-05	kg/UF	0,00128	kg
5	Changement climatique	-0,375	kg éq. CO_2/UF	-18,8	kg équivalent CO_2
6	Acidification atmosphérique	0,00102	kg éq. SO_2/UF	0,0509	kg équivalent SO_2
7	Pollution de l'air	26,7	m^3/UF	1 336	m^3
8	Pollution de l'eau	0,770	m^3/UF	38,5	m^3
9	Destruction de la couche d'ozone stratosphérique	3,47 E-11	kg CFC éq. R11/UF	1,73 E-09	kg CFC équivalent R11
10	Formation d'ozone photochimique	0,000139	kg éq. éthylène/UF	0,00695	kg équivalent éthylène

* Cet indicateur énergétique doit être utilisé avec précaution car il additionne des énergies d'origine différente qui n'ont pas les mêmes impacts environnementaux (voir commentaire du chapitre 2.1.1)

**dont 88% correspondent au contenu énergétique du platelage et des lambourdes et 12% pour l'énergie contenue dans les déchets de bois valorisés en interne de façon énergétique

Epuisement des ressources :

Il faut noter que cet indicateur concerne uniquement les ressources abiotiques et donc n'évalue pas l'épuisement des ressources biotiques telles que le bois.

En ce qui concerne la ressource bois, les bois utilisés ici proviennent de France où la forêt est renouvelée et en croissance[2].