Wood preservatives

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Chapter 7 Wood preservatives

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Chapter abstract:

This chapter presents the main wood preservatives with respect to their potential hazard due to the biocides release from treated wood products. The chapter first discusses the toxicological properties of the actives substances and the treated wood products chemistry in the exposure conditions. Then, after presenting the main physico-chemical mechanisms at the origin of biocide release, a paragraph is dedicated to methodologies applicable to toxicity assessment in service life scenarios. The main ecotoxic effects and examples of studies at laboratory or field scale are given, followed be several trends and alternative solutions.

Keywords:

wood preservatives, biocides, leaching, release mechanisms, treated wood toxicity

7.1. Introduction

Due to its abundance in nature and its versatility, the wood is one of the most important construction material mankind has ever come across. The taxonomy of woody plants is very complex. Nevertheless, it is common to classify wood in two main categories: the wood from conifers (e.g. pine, spruces, cedars, etc.) is called softwood, and the wood from dicotyledons (usually broad-leaved trees, e.g. oak, maple, birch, etc.) is called hardwood. Each one of these categories contains thousands of species. It should be mentioned that these categories are a bit misleading, as hardwoods are not necessarily hard (e.g. the balsa wood is actually softer than any commercial softwood) and softwoods are not necessarily soft (e.g. the yew wood are harder than many hardwoods).

Because of its organic nature, wood is sensitive to the biological attacks. If the wood-based product does not resist naturally to service conditions, in order to attend the performance level required by the user, an appropriate preservative treatment is carried out. The active substances used for the treatment are called biocides. The biocidal products are defined as '*active substances and preparations containing one or more active substances, put up in the form in which they are supplied to the user, intended to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means*' (EC, 1998). Thus, by definition, the biocide could be a threat to health or environment. Therefore, the retention of the biocide into the product is very important for the effectiveness of the treatment but also for the health and environmental impacts to due to its release into air, water and soil.

At the European level two main regulations concern the biocides and the construction materials with respect to the environmental and human health issues.

The Biocidal Products Directive (EC, 1998) – that will be replaced by the Biocidal Product Regulation (EC, 2011a) aims to harmonise the European market for biocidal products and their active substances including the wood preservatives which are classified as product-type 8 (PT8). At the same time it aims to provide a high level of protection for humans, animals and the environment. In order to meet this requirement, the Organisation for Economic Cooperation and Development (OECD) was charged to harmonize the methods for the assessment of the biocides. This work led to the leaching protocols presented in prCEN/TS 15119 (CEN, 2007; CEN, 2010).

The Construction Products Regulation (305/2011/EU - CPR) (EC, 2011b)– replacing the Construction Products Directive (89/106/EEC - CPD) (EC, 1989) is laying down harmonised conditions for the marketing of construction products. The CPR provides more clarification of the concepts and the use of CE marking. According to the CPR, the construction works must satisfy seven Basic Requirements (BR). Among them, the BR n° 3 Hygiene, Health and the Environment which 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 workers, occupants or neighbours, nor 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:(...) the emissions of dangerous substances,(...) into indoor or outdoor air; the release of dangerous substances into ground water, marine waters, surface waters or soil* (…)'. In order to comply with this requirement, the European Commission mandated CEN (TC 351 - Construction products - Assessment of emissions of regulated dangerous substances from construction products) to prepare horizontal (i.e. product independent) test methods with which construction products can be tested with respect to the potential release of dangerous substances to water, soil and indoor air.

This chapter presents the issues linked to the environmental impacts due to the biocides released form treated wood. The potential hazard for environment may arise in different stages of the product life cycle, i.e. manufacturing, distribution, construction, service life and end-of-life. During the service life and end-of-life (disposal or recycling) stages - which both usually spread over many decades - the release of substances due to contact with the water is the main potential hazard source, as a consequence of the leaching phenomenon.

Hereafter, the main preservatives used for wood treatment are presented together with their toxicological properties. Then, the wood chemistry is described in relation to the main biocide species interaction, resulting in biocide fixation/mobilisation. The exposure conditions of wood construction materials to environmental factors and especially the water contact scenarios are determining parameters for the biocide release. After presenting the main physico-chemical mechanisms at the origin of biocide release, a paragraph is dedicated to methodologies applicable to toxicity assessment in service life scenarios, together with the main experimental tools (leaching and toxicity tests) and current regulation. The main ecotoxic effects and examples of studies at field or laboratory scale are given, followed be several trends and alternative solutions.

7.2. Types of preservatives and their potential hazard

The hazardousness of treated wood is highly dependent on the nature and intrinsic toxicity of biocides (see § 7.2.1.) and also on the release potential of these molecules. The biocides release potential depends on:

- the wood chemistry with respect to interactions with the biocides (see § 7.2.2.),
- the exposure conditions of treated wood products (see § 7.2.3.).

7.2.1. The biocides types and their toxicological properties

Different classes of biocides were used in wood treatment according to the legislative constraints imposing increasingly strict conditions. Thus, in the Sixties, products as aldrin, pentachlorophenol and creosotes were usually employed. Because of the content in known carcinogenic chemicals, they were restricted or prohibited (JORF, 1992; EC, 2001). Then the alternatives were the products known under the name of 'CCA - chromated copper arsenate' which were extensively used. Nowadays, the CCA treatment is prohibited for residential constructions (with certain exceptions) (AWPA, 2001; JORF, 2004). The alternatives to these biocides are the so called 'new generation biocides' (chromium and arsenic free), such as Copper Boron Azoles (CBA), Ammoniacal Copper quaternary (ACQ), Copper HDO (CuHDO) etc. Recently, preservatives containing micro or nano-sized copper particles have been introduced to the market (usually with 'micronized' or 'micro' designations such as MCQ or MCA).

The number of commercial preservatives products is very high but the number of active substances is relatively small. The main active substances are (FCBA, 2011):

- Inorganic :

- Copper as Copper Carbonate, Copper hydroxide, Copper oxychloride, Copper sulphate, Cuprous oxide, Copper Hydroxycarbonate or Copper organic compounds,
- Boron as Borax, Boric acid or Disodium Octoborate Tetrahydrate (DOT)
- Chromium as Chromium Trioxide, Sodium Dichromate,
- Arsenic as arsenate in CCA.

- Organic (by chemical class):
  - Azole : Azaconazole, Propiconazole, Tebuconazole, Cyproconazole, Thiabendazole,
  - Ammonium quaternary compounds : Chlorure de dimethyl alkyl benzylammoniun, Chlorure de dimethyl coco benzyl ammonium, Chlorure de dimethyl didecyl ammonium, Chlorure de trimethyl coco ammonium
  - Benzoylurea: Noviflumuron, Diflubenzuron, Flufenoxuron, Hexaflumuron,
  - Benzimidazole : Carbendazim,
  - Carbamates : Copper dimethyldithiocarbamate (CDDC), I.P.B.C.(3-iodo-2-propynyl-n-butyl carbamate), Fenoxycarb,
  - Diazenium-compounds: Bis-(N-cyclohexyldiazeniumdioxy)-copper (CuHDO),
  - Isothiazolone : DCOIT (4,5-dichloro-2-n-octyl-3(2H)-isothiazolone),
  - Morpholine : Fenpropimorph,
  - Neonicotinoids: Thiamethoxam,
  - Organophosphorus : Chlorpyrifos,
  - Pyrazole : Chlorfenapyr, Fipronil,
  - Pyrethroid: Cypermethrin, Permethrin, Bifenthrin, Cyfluthrin, Deltamethrin.

The class of toxicity of some biocides used for the wood preservation treatment is given in table 1. The classes of toxicity comply with the classification made by the World Health Organization (WHO, 2006).

Wood preservatives can be classified into four main categories:

- water-borne preservatives,
- oil-borne preservatives,
- light organic solvent preservatives (LOSPs),
- micro and nano sized particles preservatives.

The main water-borne preservatives are: the Copper Chromium Arsenic (CCA), the Copper Azoles, the Ammoniacal Copper Quaternary (ACQ), the Copper HDO (CuHDO) and the borates based formulation.

In the CCA treatment, the copper acts primarily to protect the wood against decay fungi and bacteria, while the arsenic is the main insecticidal component of CCA. The chromium acts as a chemical fixing agent, which also provides ultraviolet (UV) light resistance and has little or no preserving properties. Its role is to help the other chemicals to fix in the wood, binding them through chemical complexes to the wood's cellulose and lignin. It should be mentioned that even if CCA treatment is presently prohibited for residential uses, some CCA treated woods are still in service. Moreover, CCA products are still permitted for use in various industrial and public works, such as bridges, highway safety fencing, electric power transmission and telecommunications poles (FCBA, 2011). Thus, this kind of preservatives continues to be of concern to the environment.

The Copper Azole is a fungicide and an insecticide. There are two types of Copper Azole: type A (CBA-A), and type B (CA-B). Copper Boron Azole type A contains the following ingredients: copper (49%), boron as boric acid (49%), and azole as tebuconazole (2%). Copper Azole type B is composed of copper (96.1%) and azole as tebuconazole (3.9%) (EPA, 2011). Some of the commercial CBA contain also glycol (US –DOI, 2011). Despite research efforts, no effective means has yet been found to keep borate preservatives from leaching out of wet wood (US-DOI, 2011).

The Ammoniacal Copper Quaternary (ACQ) contains copper, as fungicide and a quaternary ammonium compound as insecticide. There are currently four AWPA standardized ACQ formulations (types A to D). All ACQ types contain the 2 active ingredients which may vary within the following limits: copper oxide (62%-71%) and a quaternary ammonium compound (29%-38%). The ACQ is considered as an alternative to CCA treatment. Nevertheless, because of its higher level of copper, ACQ-treated wood is more corrosive to common steel and the use of double-galvanized or stainless steel fasteners is necessary for this kind of treated wood processing (US-DOI, 2011).

The Cu-HDO is composed of copper and N-cyclohexyl-diazeniumdioxide (HDO). Cu-HDO affects sulfhydryl groups of essential amino acids of fungi and cause protein denaturation (EPA, 2011). It is classified as moderately hazardous (toxicity class II, with a LD_{50} of 380 mg/kg) (WHO, 2006).

Borate preservatives such as boric acid, oxides and salts (borates) are supplied under numerous brand names throughout the world. Borate treated wood is considered of low toxicity (toxicity class U – see Table 1). However, borate compounds do not become fixed in

the wood and can readily be leached out. They are efficient rather for use class 1 and 2 (see § 7.2.3), such as framing, sheathing, sill plates, furring strips, trusses and joists (EPA, 2011).

Oil-borne preservatives include creosote and some vegetal oils containing permethrin. Creosote is one of the oldest wood preservatives. Because of the content in known carcinogenic chemicals, it was restricted or prohibited (JORF, 1992; EC, 2001). However it is still used for railroad ties and utility poles. In recent years linseed oil has been incorporated in preservative formulations as a solvent and water repellent together with low water solubility preservatives, such as Permethrin. Permethrin is a broad spectrum non-systemic synthetic pyrethroid insecticide (Imgrund, 2003).

Light organic solvent preservatives (LOSP) are based on the use of white spirit, or light oils such as kerosene, as solvent carrier for biocides. Synthetic pyrethroids are typically used as an insecticide, such as permethrin, bifenthrin or deltamethrin. Other actives compounds are the Propiconazole and Tebuconazole as fungicides. These kinds of preservatives contain no heavy-metal compounds but they are still of concern for health and environmental impacts, due to the release of the volatile organic compounds (VOC) and of the organic biocides.

For few years now, preservatives containing micro or nano-sized copper particles are used for wood treatment. There are currently two particulate copper systems on the market. One system uses a quaternary biocide system (known as MCQ) and is based on ACQ. The other uses an azole biocide (known as MCA or μCA-C) and is based on Copper Azole. This kind of preservatives raised concerns regarding exposure to micron and nano-sized particles, in the context of the general debate about the nanotechnology hazard to humans and environment (Evans et al., 2008; Matsunaga et al., 2008; Matsunaga et al., 2010; ICTA, 2010).

7.2.2. The wood chemistry with respect to interactions with the biocides

The wood material is composed of mainly three biopolymers present in different proportions, namely cellulose (about 45% in weight), hemicellulose (about 30%) and lignin (20%) and a small fraction (about 5%) of low weight compounds extractible in water or other solvents, named extractives (Govin, 2004).

Cellulose is composed of linear chains of D-glucose linked by ß-1,4-glycosidic bonds with a degree of polymerization of about 10000. Cellulosed possesses hydroxyl groups and has the specific reactivity of primary and secondary alcohols (donor reactivity of hydroxyl groups).

Hemicelluloses are heteropolysacharides (containing glucose, galactose, xylose, arabinose, mannose, acides uroniques) with lower polymerization degree (50-300) and amorphous structure. The chemical structure of hemicellulose varies form soft to hard wood. It contains mainly hydroxyl groups but also carboxylic groups. The lignin is a complex network of polymers (molar mass that exceeds 10000) composed of phenolpropane units and containing characteristic methoxyl groups, phenolic hydroxyl groups and some terminal aldehyde groups. Lignin is associated with hemicellulose forming complexes that are resistant to hydrolysis. There is no evidence that lignin is associated with cellulose. Other minor polysaccharides present in wood are pectines, starch and proteins.

The low weight compounds are organics belonging to many chemical classes: fats, fatty acids, fatty alcohols, phenols, terpenes, polyphenols, tannins, lignans (combination of 2 phenylpropane units), steroids, resin acids, rosin, waxes, etc. Wood contains also inorganic species represented by silica, and several major elements Ca, Mg, K (up to 80% of the ash). These metals are probably bound to carboxyl groups in pectic materials, oxalates, carbonates, sulfates. Many other metals are present in lower quantity.

Wood is slightly acid material heaving pH values in contact with water in the range of 3 to 6, depending on wood species (e.g. pH 3 for the Western Red Cedar and pH 6 for the Ash tree). The acid/base properties and general reactivity of wood materials are determined by the functional groups linked to the polymeric structure. So, carboxyl groups are attached mainly to hemicelluloses and pectins and have acidity constants pK_a values between 3 and 5. Lignin contains phenolic groups (pK_a = 7.5–10.5) and small quantities of carboxyl as a result of oxidation processes. The acid/base properties of wood extractives in water is due mainly to carboxyl groups (pKa of 5.0–6.5) and their solubility rises with the temperature and alkali content (Balaban and Uçar, 2001; Ravat et al, 2000a; Duong et al, 2004).

Complexation and ion exchange are the two main interaction mechanisms of metal ions with wood components. The ion exchange mechanism is possible at the level of carboxyl functional groups present in hemicellulose, pectins or lignin. It manly concerns alkaline and alkaline-earth cations and is a non-specific electrostatic interaction. The heavy metals (like Cu, Cd, Ni, Zn, Pb) are mainly concerned by reactions of surface complexation with the functional groups phenol and carboxyl. The phenolic sites lying on lignin have significantly higher affinity for transition metals than the carboxylic sites. The conclusion of many studies is that cellulose has a lower sorption capacity for heavy metals compared to lignin. The extent of metal sorption depends on pH and aqueous ionic strength. Complexation constants for several heavy metals including Cu and Zn are reported in the literature (Ravat et al., 2000a; Merdy et al., 2002; Guo et al., 2008; Ravat et al., 2000b).

In the system wood/water, at low pH, the metals exist predominantly as free cations in solution. When the pH increases, the deprotonated carboxylic sites contribute significantly to their fixation by forming complexes. At higher pH, phenolic sites become deprotonated and

participate to metal binding. These complexes are in majority monodentate S1-O-M+, and in a lesser extent bidentate S1-O-M-O-S2 (here S1, S2 are organic functional groups, M is a bivalent metal). The proportion of the aqueous metal species and fixed complexes on biopolymers depends on pH and ionic strength, and can also be influenced by the presence of extractives.

The maximum metal quantity a wood material can fix by specific interactions is given by the number of binding sites. The site density depends on the wood species and biopolymer type. As for example, a lignin isolated from black liquor (a residue of paper industry) (Guo et al., 2008) contains about 0.08 mmol carboxyl and 0.28 mmol phenolic groups per g of dried wood. A hemicellulose extracted from cotton wood (DeGroot, 1985) contains about 0.08 mmol/g carboxyl groups.

The extractives are organic compounds able to undergo complexation reactions with free metals present in aqueous solution (by intermediary of carboxylic, phenolic groups, or other electron donor groups). Copper is particularly renowned for its capacity to complexate with dissolved organic matter, resulting in an increase of its global leachability.

In aqueous phase chromium behaves as Cr(III) and Cr(VI).In contact with biomaterials like wood, Cr(VI) transforms into Cr(III) by an adsorption-coupled reduction mechanism involving adsorption steps of both species and reduction of Cr(VI) such that Cr(III) becomes dominant in the system (Dupont and Guillon, 2003; Park et al, 2007).

According to Bernardo et al. (2009), Cr(III) adsorption on biomaterials follows a reaction path involving phenolic or carboxylic groups leading to mono and polydentate complexes with free and hydroxylated Cr^{-3} ions. Despite the abundance of literature on the subject (Miretzky and Cirelli, 2010), no intrinsic complexation constants have been determined.

Boron leachability in treated wood is recognised to be high but its chemistry in wood is far from well understood. The most of authors consider that boron doesn't react with wood materials and is completely available for leaching. Other authors consider that B (as boric acid) can form organic complexes via O bridges with hydroxyl groups on polysaccharides (Obanda et al., 2008; Ramos et al., 2006). No complexation constants are available in the literature.

Generally, the wood preservatives are used as mixture of several chemical substances with complementary biocidal effects. The chemical behaviour of these substances is dependent also on the additives used. Research on products containing ammonia and Cu shown that ammonical copper is readily adsorbed to phenolic hydroxyls, such as found in lignin or extractives. Although, in absence of ammonia, precipitation may occur as copper carbonates, copper oxides, copper arsenate complexes. Also coarse deposits of almost pure copper were observed by spectroscopic investigations localized within the cell wall and on the microfibrils (Lebow 1996).

However, there is no unanimity concerning the formation of salt precipitates since they are reasonably soluble. Many investigations on CCA treated wood by XAFS (X ray absorption fine structure spectroscopy) indicated that Cu is not chemically associated with any heavy element (Bull, 2001). The results of leaching tests performed with different extractants (acetic acid, EDTA, oxalic acid, etc.) show that Cu is not dependent on Cr and As and exhibits a different release behaviour. The most plausible fixation mechanism for Cu remains the complexation on carboxyl and phenolic sites. Similar mechanisms are possible to occur in the case of Zn, although the binding forces are weaker.

Little information has been published on the fixation mechanism of organic biocides on the wooden materials (Woo et al., 2010). It was observed that these molecules are rather leach resistant suggesting possible interactions with the wood structure. It may be expected that the organic biocides interact with the different wood components at least by weak physical bonds (van der Waals, dipolar and charge transfer interactions) thus adsorbing on the biopolymers. Their partition between aqueous solution and wood's biopolymers depends on the biocide's hydrophobicity and its aqueous solubility. So, it is expected that hydrophobic molecules have more affinity for lignin than for cellulose. Stronger interactions can occur when biocides possess functional groups able to react with specific sites on wood like hydroxyls (hydrogen bonds).

Investigations (Kjellow et al., 2010) on tebuconazole, propiconazole and IPBC behaviour during wood impregnation allowed to observe their partition between the carrier solvent and wood samples and leaded to the conclusion that some (adsorption) interactions occur. The adsorption level decreases in order: tebuconazole > propiconazole > IPBC. It was suggested that tebuconazole forms stronger bonds with the hydrophilic biopolymers (hemicellulose for instance) due to the presence of a hydroxyl group.

7.2.3. The exposure conditions of treated wood products

The service life and end life are the longest steps during the life cycle of the treated wood products. Thus, during these two steps the environmental risk could be of more concern.

As function of exposure conditions, Europen Standard EN 335 (CEN, 2006) defines five use classes which represent different service situations to which wood-based products can be exposed. The classes described in the Europen Standard are based on an existing classification agreed on by the European Homologation Committee (EHC), after taking into account the

possibility of harmonisation with three moisture categories of Eurocode 5 and with other classes used outside Europe. It has, however, been judged that the following five classes are the most appropriate solution for European conditions:

- use class 1 : situation in which the wood-based product is under cover, not exposed to the weather and wetting (exposure to wetting: max 20%), e.g. indoor window frames/sills, doors, floors, etc.;
- use class 2 : situation in which the wood-based product is under cover and not exposed to the weather but where high environmental humidity can lead to occasional, but not persistent wetting (exposure to wetting : occasionally > 20%), e.g. some of the indoor window frames/sills, doors, flooring, etc;
- use class 3 : situation in which the wood-based product is not under cover and not in contact with the ground. It is either continually exposed to the weather or is protected from the weather but subject to wetting (exposure to wetting: occasionally or frequently > 20%), e.g. roofing, weatherboarding, facade cladding, outdoor window frames/sills and doors;
- use class 4 : situation in which the wood-based product is in contact with the ground or fresh water and thus is permanently exposed to wetting (exposure to wetting : predominantly or permanently > 20%), e.g. terraces, decks, play-ground equipment, garden furniture;
- use class 5 : situation in which the wood-based product is permanently exposed to salt water (exposure to wetting : permanently > 20%), e.g. decks, marine constructions, ship-decking.

Use class 1 and 2 are of concern mainly for the health impact via the indoor air emissions of eventual VOC contained in the treated wood, whereas the use class 3 to 5 are of concern for the environmental impact, especially via leaching phenomena.

During the service life, the biocide amount in wood products lessens following air emission, leaching and biodegradation processes. Nevertheless, the end of life management (incineration, recycling, landfilling) must take into account the presence of specific toxic substances.

The landfill disposal is allowed for wood wastes whose composition complies with the admission standards in different landfill categories. The biocide release in these systems will affect the landfill leachate composition and thus its management.

Biotransformation of organic compounds by using adapted leaving species (fungi, bacteria) could be envisaged before the entrance of wood residues back in the carbon cycle (Woo et al., 2010) by incineration.

Recent research (Tame et al., 2007) found that the presence of Cu-based biocides favours dioxin formation during the combustion of treated wood. The explanation resides mainly in the catalytic activity of Cu for dioxin formation, the smouldering of wood char by the metals providing a favourable temperature environment and the presence of chlorinated organic biocides as precursors for dioxin formation.

7.3. Potential toxic effect and ways it can be assessed

As water exposure of treated wood represents the main route for toxic biocides emission in environment, this chapter is dedicated to the mechanisms and methodologies for assessing the toxic effect via leaching processes. The extent of biocide release from treated wood in contact

with water is a crucial parameter determining the hazardous effect on human health and on other leaving organisms.

7.3.1. Release mechanisms and parameters of influence

The biocide release from treated wood products is the result of coupled chemical reactions, transport processes and biological activity.

In contact with water, wood material undergoes chemical and structural changes, soluble compounds as natural mineral salts and extractives are released. Fixed biocides are partially desorbed following the thermodynamic equilibrium. All these chemical reactions are influenced by the pH. The natural pH of wood is often acidic so, the contact with neutral water could cause chemical and structural modifications of the wooden material (hydrolysis, deprotonation of acidic functions, dissolution/precipitation of extractives, etc.). pH strongly influences the mineral biocides (Cu, Cr, As, B) binding by complexation reactions on carboxyl and phenol groups, but also the interaction between hydrophilic organic compounds. The presence of oxygen is a factor of wood ageing by oxidation of, for examples, phenol groups and depolymerisation of lignin.

Besides chemical processes, the organic natural compounds and biocides can be transformed by biological activity of bacteria or fungi. The decay period of organic biocides is variable as well as the secondary compounds formed, following the surrounding conditions.

Wood is a porous, hygroscopic material, all the processes mentioned above take place in the porous structure. There are gradients of composition between the core and the product surface following water contact conditions the product undergoes. The dynamics of the biocide release from a given wood piece is then determined by the diffusion processes in the porous

structure. Wood is an anisotropic material; the diffusion rate varies following the orientation: it is maximal along the fibres, minimal in tangential and intermediary in radial direction.

Once the biocides reach the external surface of the wood piece, their dispersion in the environment is ensured by the water circulation in soils, surface and ground waters, potentially affecting the quality of environmental compartments (including water resources for human consumption) and the integrity of living targets. In some cases attenuation could occur through soil infiltration by chemical (retention, decay) and biological (degradation) mechanisms. Dispersion of the released pollutants into surrounding water and soils plays a diluting role of the initial leachate.

Numerous leaching studies have been realized at laboratory or field scales for determining the biocide release from wood products (Cooper, 1991; Lebow et al., 1996 ; Brooks, 1997; Hingston et al., 2001; Solo-Gabriele, 2003; etc.) and highlighted the role of different influence parameters, described here below.

1) *The nature of preservation product and treatment process used*. The chemical nature of biocide compounds and accompanying additives are determinant, as discussed in paragraph 7.2. The method used for incorporating biocides in wood could modify the porous structure (effect of pressure or chemical reactions) and the speciation of metals at the beginning of the service life. Precipitations after wood drying can occur followed by subsequent redistribution of metals between the wood polymers, pore solution and mineral salts. A long period between treatment and immersion in water allows a more effective biocide fixation and lessen the release magnitude.

2) *The geometry of wood products and type of water contact*. A great specific external surface (low size pieces) enhances the mass transfer process and then the leaching rates. Water contact is an important factor: intermittent or continuous, stagnant or flowing – the total

extracted amount depends on the cumulated liquid/solid ratio and the water residence time. The aqueous leachant can have various compositions following the exposure scenario: fresh, rain, sea waters or soil water, containing salts, natural organic matter, dissolved gases, in different proportions and affecting the wood's and biocides' chemistry at different extents (for example, Cu leaching is favoured by the presence of dissolved organic matter). The exposure time results in a more or less released quantity; the leaching is more intensive at the beginning of the exposure scenario and slows with the product ageing.

3) *The exposure climate conditions*. Rain events determine the water contact type and parameters (discussed here above). A temperature increase can accelerate chemical reactions and biologic activity. UV radiation and oxygen contribute to degradation by breaking and oxidation of wood polymers and thus enhance the release (Schiopu, 2007).

7.3.2. Methodologies of toxic effect assessment

Biocides are intrinsically toxic substances and the harmful effect will strongly depend on their release behaviour.

The extrapolation of partial field observations or laboratory assays to conditions encountered in real scenarios of service life is not obvious. The assessment of toxic effects needs comprehensive methodologies and adapted experimental and modelling tools, these requirements being the reason for the European authorities endeavour to develop standard assessment methods.

The assessment of the potential harmful effects of biocides released in a given scenario of wood product utilization can be realized following classical methodologies of risk assessment on ecosystems and human health. These methodologies consist on the evaluation of three components of the cause-effect chain: the source of pollution (the wood product for instance),

the pollutant transport through environmental compartments (soils, waters) and the effects on living targets. A sound evaluation of the physico-chemical and biological processes at the level of these three terms is necessary and possible by using appropriate experiments, models and data bases. A more detailed description is given in chapter 15 of this book.

The hazardous effect of biocides as toxic molecules present in different environmental compartments is evaluated by bioassays (toxicity tests) on selected species, then the risk is evaluated by comparing the test results with toxicological parameters (lethal or effect doses and concentration).

The key point in the assessment process is the evaluation of the exposure of living targets to a biocide, i.e. the knowledge of the biocide concentration and its time evolution, the released flux from the wood product. So, the knowledge of the wood product behaviour in its utilization scenario (the source term of pollution) is fundamental for the evaluation of the exposure conditions. The most common experimental tools for studying the leaching phenomenon are the leaching tests. Some of these tests (i.e. static leaching tests) give information about different intrinsic properties of the material (e.g. acid/base neutralisation capacity, pH influence on pollutant release) and others (i.e. dynamic leaching tests) provide knowledge about the release dynamics – see also chapter 15 of this book.

As mentioned above, the leaching of biocides from construction materials is a research subject receiving attention from the European regulation authorities. The main standards concerning the leaching behaviour, presently under development are : CEN/TC 351/WG 1 N 178 - 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 ; CEN/TC 351/WG 1 N 177- Guidance standard for CEN Product TCs for selection of leaching tests appropriate for their product(s) - General principles and CEN/TC 351/WG 1

N 162 - Generic horizontal up-flow percolation test for determination of the release of substances from granular construction products (CEN, 2011). Up to these protocols, at the European level two standards referred to the leaching of wood preservatives: the XP ENV 1250-2 (CEN, 1994) and the EN 84 (CEN, 1997). The XP ENV 1250-2 specifies that '*the results cannot be connected to the conditions of exposure in the service life of wood based products, as part of the building*'. The EN 84 aims the accelerated ageing of treated wood prior to biological testing. These two standards are rather tests that aim to evaluate the effectiveness of the wood preservation treatment and not the environmental impact due to the biocides leaching.

A lot of works have been performed aiming at the leaching process characterisation, at different scales and following different experimental protocols. As mentioned above, we distinguish between two types of leaching assays: 1) equilibrium tests - the wood material (generally of very small size, crushed) is put in contact with a leachant for a given duration, allowing chemical equilibriums to occur (e.g. batch assays); 2) dynamic tests – processes like diffusion or leachant flow determine the time evolution of the released quantities (e.g. block diffusion, runoff). The results are weakly comparable and generalisation is not possible, especially when transport phenomena play a major role in the release process. For these reasons only few examples are given here; the interested reader may consult the multiple other journal articles.

The biocide solubilisation under different pH conditions was investigated (Esser et al., 2001; Schiopu, 2007; Schiopu et al, 2011) showing similar leaching patterns for the inorganic biocides (Cu, Cr , As, B, Zn). In the case of wood samples treated with CCA and Cu-quat (copper oxide, didecyldimethylammonniumchloride or DDAC) preservatives (Esser et al., 2001), it was showed that Cu, Cr and As have a maximum fixation at pH 7-8 and the

solubilisation augments for many orders of magnitude at acid or alkaline pH. So, for natural pH values of the most wood species (i.e. acid), the element fixation is not optimal (see figure 1 (Tiruta-Barna and Schiopu, 2011)). The most important variation was observed for Cu, while As behaviour is slightly different following the type of preservative. Complementary, the behaviour of extractives was observed, their global concentration (determined as dissolved organic carbon) augments with the solution alkalinity.

Dynamic tests were performed at lab and field scales (Esser et al, 2001; Schiopu, 2007; Hingston et al., 2002, Hasan et al., 2010) and made subject of inter-laboratory studies for the development of leaching assessment methods and leaching tests (Schoknecht et al., 2005).

A comparison was made (see figure 2) between the dynamic release in laboratory leaching tests (MBT sequential renewal of leachate, CMLT continuous renewal) and field assays on a commercial wood product treated with Copper – Boron - Azole based preservatives (Schiopu, 2007; Schiopu et al, 2007). The field pilot simulates two scenarios of intermittent rainwater contact: immersion in rain water (stagnation) and run off rain water, during one year (leachates' concentrations and rainfall events were monitored). It was observed that the cumulated release increases for many orders of magnitude with the effective leaching time (the duration of dry periods was not accounted for). More or less significant differences have been observed between the tests, following the target element (Cu: similar releases; Zn: different shapes). During one year of rain exposure, the stagnant scenario accounts for more effective contact time (about 300 days) than the runoff scenario (30 days). The releases' increase in stagnation scenario after 30 days could be explained by a weathered process of the wood samples. Therefore, the release level in this scenario tends to those of an aged wood sample after about 100 days.

Despite the literature abundance on studies dedicated to the biocide leaching and wood retention mechanisms, there are few studies which structure the information and knowledge on mechanistic models. The interest of modelling of physic-chemical processes resides in the possibility to confirm hypotheses based on experimental observations, to identify and calculate related parameters, and to foresee the system behaviour for different exposure conditions. Modelling could make interpretation bridges between different observed systems, different scales and resolve unexplained experimental results.

Diffusion transport in the wood porosity is one of the earlier modelling tentative (other than empirical regression equations). Recently, the leaching from wood was modelled (Waldron and Cooper, 2010) by soluble species (no chemical reactions) and their tridimensional diffusion following the wood anisotropy (along fibres, radial and tangential directions). Diffusion coefficients of 10^{-10} – 10^{-9} m^2/s have been calculated for the longitudinal direction.

The transport mechanisms are not sufficient for representing the leaching behaviour. The chemistry of wood/biocide system, although very complex, must be formalised and integrated on coupled chemical-transport models. Chemical models are very few in the literature. A realistic chemical model was established (Tiruta-Barna and Schiopu, 2011) for explaining the leaching behaviour of a wood product made on Copper Boron Azole (CBA) treated Pinus Sylvestris. The model considers the main fixation mechanisms for Cu, B and other trace species present in wood (Cr, Zn, Ca, SO_4^{-2}). The influence of dissolved organic matter on Cu release was modelled by pH dependent complexation reactions. The model can explain the leaching behaviour in closed system (at equilibrium) for a pH range from 3 to 11 (cf. prCEN/TS 14429 (CEN, 2002)) (figure 1). This kind of models represents steps forward but more efforts are needed to integrate transport and reliable chemical models into useful predictive tools for the leaching behaviour assessment.

7.3.3. Toxicity studies - case examples

Despite the fact that the biocide release issue gains more and more interest, there are few available studies in the literature evaluating the harmful effect or risk for real service life scenarios of commercial products by using standard methodologies and tools. Ecotoxicological studies were carried out mainly on conventional preservatives using different methods, experimental assays and conditions, and expressing the results in different, often incomparable manners.

The compilation of field observations of biocide release from wood products in their service life (Lebow et al.,1996; Hingston et al., 2001) highlighted that the methods and experiments used since many dozens of years vary from a study to another and a coherent analysis of the leaching process and involved mechanisms is very difficult, due to lack of complete information. The most monitored preservatives as far are Cu-based with different compositions: CCA (the most studied), ACA, ACZA, ACQ, DDAC, CC, CuAz. For all study cases the behaviours of Cu, As and Cr were observed in terms of wood residual composition and soil or water concentration.

One of the most studied scenarios is of type ‘underground contact’ (poles, posts, plywood, stakes) considered as the worst case of biocide emission. The biocide emission and pollution is demonstrated by a higher soil concentration than in the natural background. In these different studies, higher concentrations of about several to 1000 times were measured on the soil volume around the wood product within a radius of about 1 m. The biocide loss by the wood products was of about 10 to 30 % in several years, with various levels for Cu, Cr and As.

In marine environments, the immersed wood products release important quantities of inorganic biocides, as was observed in the majority of reported studies. Biocide concentration depletion of the surface layer of wood samples of 40% to 85% was observed after several years of service life. It was noted that the major part of biocide losses occur in the first weeks of sea water contact. The contamination of the living marine species was demonstrated by measuring the level of Cu, Cr and As in green algae, oysters and crabs collected from the wood sites (including sediments), which has been found to be higher than the natural concentration.

The immersion scenario in fresh water was less studied. Slightly higher concentrations in CCA components were found downstream and depleted biocide concentration was measured in the wood surface layer.

The 'above-ground' contact is considered less harmful because the contact with water is rather intermittent, depending strongly on the surface area exposed to rain.

All the above mentioned studies (based on field measurements of pollutant concentrations) concluded at a non-impact or insignificant effect given the low concentration and the limited dispersion of the target biocides in soils and waters (effects of dilution and natural attenuation), although the toxic effect was not properly assessed.

On the opposite, studies performed on controlled conditions, using leachates from treated wood, with or without dilution, and using various toxicity tests on living organisms have concluded on the possible or effective harmful impact on aquatic compartments and, in a less extent on top-soil organisms. Several case studies and their main findings are presented here.

The toxicity of commercial preservatives (propiconazole, tebuconazole, IPBC, cypermethrin) for aquatic organisms was studied (Adam et al., 2009) using bioassays (freshwater amphipods *Gammarus pulex* (L.)) and the results obtained for individual biocides shown the toxicity

increases from propiconazole to cypermethrin, and that there are synergic effects enhancing the harmful effect of the commercial mixture.

The top-soil ecotoxicity from a contaminated site with wood preservatives Cu-sulphate and CCA was studied (Mench and Bes, 2009) using target organisms (radish, lettuce, slug Arion rufus L., and earthworm Dendrobaena octaedra). The levels of contamination (variables on the site) were of 65 to 2600 mg Cu kg^{-1}, 0-52 mg As kg^{-1} and 0-87 mg Cr kg^{-1} . The results showed a high Cu content in plants and negative effect on plants growth for the most contaminated site.

Dubey et al (2007) studied the aquatic toxicity of leachates obtained from blocks of wood treated with Cu based preservatives (CCA, ACQ, CBA). A specific heavy metal toxicity assay was used, based on inhibition of ß-galactosidase activity in an *E. coli* strain. Natural water compartments were considered (rivers, lakes, wetlands, and seawater) along with synthetic moderate hard water and deionized water. In their study, Cu was released from ACQ- and CBA-treated wood about 10 to 20 times more than from CCA-wood. The toxicity of aquatic compartements was found to correlate with the labile (non complexated) Cu concentration in waters. The bioavailability (and hence the toxic effect) is reduced in the presence of organic and mineral complexes in natural waters.

The new generation preservatives replaced CCA for residential constructions; however, not enough hazard assessment has been performed as far. Furfurylated wood as alternative to CCA-wood, was tested for its aquatic toxicity (Pilgard et al., 2010). Aquatic organisms were used in Microtox and Daphtox, applied to leachates obtained from different treated woods, in two leaching tests. The most relevant results concern the influence of the treatment procedure on the potential toxicity: those processes which favour the curing/polymerisation led to less impacting products. Hemlock stakes treated with different preservatives (e.g. CCA, creosote, ACQ, zinc naphthenate, copper naphthenate) was tested (Lalonde et al., 2011) for the aqueous

toxicity, acute lethality tests being performed with Daphnia magna, Vibrio fischeri, rainbow trout and threespine stickleback. For the samples tested, the toxicity varied in the order: ACQ > creosote > zinc naphthenate > copper naphthenate > CCA.

7.4. Remedial action

Different remedial actions were imagined in order to replace the biocides use for the wood preservation. The most evident was to use naturally durable species such as red pine (Pinus resinosa), teak (Tectona grandis), merbau (Intsia bijuga), ironbark (Eucalyptus spp.), instead of treated wood. Natural durability consists on the capability of wood to develop self-resistance by the presence of fungitoxic components (mainly the polyphenols) formed by chemical reactions during the transition from living sapwood to dead heartwood. However, there is no evidence of such performance for all the services conditions required by the construction field. Moreover, economical issue (many of these species are prohibitively expensive for general construction applications) and global environmental impacts may restrain this alternative of using treated wood (sometimes they are logged in an unsustainable manner and many of these species grow only in specific area, therefore the environmental impact due to the worldwide transportation is high).

The use of composite materials made of wood fibers and recycled plastics was also proposed as alternative to treated wood. The main advantages are considered the fact that it doesn't warp, split, chip or rot, it requires little maintenance, being resistant to moisture and presents a variety of colours to choose from. Nevertheless, it has some disadvantages: it is not rated for structural use, it is susceptible to mildew, mold and stains and it is also more expensive compared to treated wood (EPA, 2011).

Other alternatives are based on the well known concept that the physical properties of any material are determined by its chemical structure. The degradation of wood is considered to be initiated by enzymes attack at the free hydroxyl sites contained in the wood (Roger et al, 2008). Therefore, in order to make the wood resistant to biologic attacks, the main alternative techniques are based on the sealing or transformation methods of these free hydroxyls.

One of these techniques is the autoclave impregnation with linseed, sunflower or rapeseed oil (without synthetic preservative). The tung oil has been also used for hundreds of years in some countries (without any pressure treatment). The function of these oils as preservatives is related to their action as water repellents and drying agents rather than a direct biocidal activity. Nevertheless, their effectiveness is restricted to some specific applications.

Other method is based on glass encapsulation of the wood fibres. The so called ‘glass fortified wood’ or ‘glass wood’ is obtained through a process that intermixes a sodium silicate based formula throughout the wood fibres (Flynn, 2006). The glass wood can be used for in ground contact applications and in water applications.

The modification of wood chemical structure was proposed by acetylation or heat treatments. The acetylation methods are based on wood reaction with some anhydrides, such as acetic anhydride. Acetylation process changes the free hydroxyls within wood into acetyl groups. The acetylation of wood was first done in 1928 but the large-scale production of acetylated wood began only in 2007 (Rowell et al., 2008).

The heat treatments were recently developed. These processes (e.g. Retification®, Thermowood ®, Plato®, etc.) autoclave the wood subjecting it to pressure and heat (180 to

230 °C), along with nitrogen or water vapour for 24 to 48 hours (Yan-jun et al, 2002). These processes increase the durability, dimensional stability and hardness of the treated wood. However, there are changes in aesthetic and certain mechanical characteristics. Wood treated with this process is often used for cladding or siding, flooring, furniture and windows.

Other « compromise » techniques are based on a combined treatment by biocidal products and natural compounds playing the role of water repellents. In addition, these compounds can have a biocidal effect. This method seems to be promising for the leachability reduction of boron based preservatives, as reported by different studies. Temiz et al. (2008) propose the impregnation of boron-treated wood by tall oils in order to avoid the water penetration in wood porous structure. Tall oils are exctractives obtained as by-products of pulp processing of softwood (sulphate method). Their water repellency property is due to the chemical composition (variable following the wood species): 40-55% resin acids, 40-60% fatty acids, 5-10% neutral compounds. Tall oil can protect the boron compounds against leaching allowing the preservation of the wood resistance for more long periods and at the same time, avoiding the release of toxic leachates. Similar effect was reported by Baysal et al.(2006). In this study, a treatment with polyethylene glycol-400 helped to decrease the water adsorption in wood and an additional water repellent (styrene, methyl methacrylate and isocyanate) treatment diminished the boron leaching. Leaching tests realized in continuous and discontinuous modes on treated wood impregnated with montan wax emulsion clearly showed the reduction of boron leaching for 20% up to 50% (Lesar et al., 2009). In another study (Sen et al., 2009) extractives from different plants were tested for their efficiency for wood preservation (by their high tannin content) and for avoiding the preservatives (salts containing B, Cu) leaching from different species of treated wood. The highest effects were seen in wood treated with sumac leaf extract and oak valonia extract, in presence of 1 to 3% of salts.

7.5. Conclusion and future trends

The treatment of wood has been practised for almost as long as the use of wood itself. Different types of preservatives were used, according to the consumers and legislative constraints, imposing increasingly strict conditions concerning both the effectiveness and the innocuousness of the wood treatment.

Concerning the potential hazard of treated wood, the service life and end life are the longest steps during the life cycle of the treated wood products. Thus, during these two steps the environmental risk could be of more concern, via the leaching phenomena of biocides used for the treatment. One could conclude that different experimental protocols co-exist meaning to assess the leaching behaviour of biocides form treated wood. The objectives of these protocols are different. Moreover, the application of an experimental method alone is not sufficient for a pertinent and scientifically sound assessment. A mechanistic modelling approach is necessary. Indeed, the release of wood preservatives and risk assessment for ecosystems is closely linked to the physico-chemical mechanisms induced by wood/water contact. Despite the literature abundance on studies dedicated to the biocide leaching and wood retention mechanisms, there are few studies which structure the information and knowledge on mechanistic models. The interest of modelling of physic-chemical processes resides in the possibility to confirm hypotheses based on experimental observations, to identify and calculate related parameters, and to foresee the system behaviour for different exposure conditions. Modelling could make interpretation bridges between different observed systems, different scales and resolve unexplained experimental results. Also, different remedial actions were imagined in order to replace the biocides use for the wood preservation, such as the use of naturally durable species or the use of the composite materials made of wood fibers and recycled plastics. In order to make the wood resistant to biologic attacks,

other alternatives to treated wood are based on the sealing of active sites (free hydroxyls) or the wood chemical structure transformation.

The main issue for the future is to develop more knowledge on the wood chemistry and different treatment mechanisms, in order to help the decision makers to reach equilibrium between the treatment effectiveness, the global environmental and health impacts and the economical costs of the process, on the basis of the global thinking concept.

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