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IMPACT OF CHLORINATION ON THE FORMATION OF ODOUR COMPOUNDS AND THEIR PRECURSORS IN TREATMENT OF DRINKING WATER

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Title
IMPACT OF CHLORINATION ON THE
FORMATION OF ODOUR COMPOUNDS
AND THEIR PRECURSORS
IN TREATMENT OF DRINKING WATER

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Overview

The general purpose of this study is to optimise the removal of precursors of taste and odour compounds, especially 2,4,6-chlorophenol, at a water treatment plant.

Nowadays, there are frequently problems of taste and odour in drinking water due to the presence of various types of compounds. Some of these are already present in the resource but others are generated during the chlorination stage at the water treatment plant. Moreover, these compounds can be detected at very low detection limit by consumers, increasing the need to remove their precursors from the water. For instance, the odour threshold of 2,4,6,-trichloroanisol (TCA), which is generated by methylation of chlorophenol during treatment or in the distribution network can be detected at concentrations between 0.05 to 0.2 ng / L.

The present bibliographic study of the chlorination stage highlights the great number of by-products generated by reaction with organic matter, such as HAA, THM, chlorophenol… It also appears that the part of organic matter called precursors can be partially removed at different stages of a plant to lower the concentration of final organohalogeneted compounds. A variety of treatment processes are used:

- Coagulation / flocculation / decantation,
- Sand filtration,
- Adsorption onto activated carbon,
- Ozonation,
- Membrane filtration

The perspectives of this work are to conduct laboratory tests on the removal of precursors of tastes and odour compounds. This future study will be carried out with 2 targets, 2,4,6,-chlorophenols and 2,4,6,-chloroanisol which are emerging compounds, and lake water with taste and odour problems. In principle, chlorination will be done after each step of treatment in order to determine an index of reactivity with organic matter.

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1 Introduction

The majority of complaints received by water distributors concerns tastes and odours, which, although not dangerous, give the consumer the impression that the water is chemically non-conforming. In most of these cases, the complaints stem from chlorine or the presence of compounds with an "earthy" or "mouldy" taste. A better understanding of the origins and presence of these compounds in the resource or at the treatment plant would help manage these odour and taste problems.

It is commonly admitted that mouldy and earthy tastes in water can be traced to the presence of geosmin, methylisoborneol (MIB) and / or very low concentrations of haloanisols. For example, the olfactory detection threshold of 2,4,6-trichloroanisol is between 0.05 and 0.2 ng / l. Haloanisols are probably generated by methylation of chlorophenols during water treatment or in the distribution network. Similarly, chlorophenols, compounds that are precursors of haloanisols, are likely to be formed during the chlorination stage **by the action of chlorine on organic matter.**

The objective of this study is to follow the fate of the precursors of odorous compounds such as chlorophenols and especially 2,4,6 trichlorophenol during drinking water treatment, and to evaluate the efficacy of different treatment stages in eliminating them. The target treatment stages are:

- coagulation / flocculation / decantation
- adsorption onto activated carbon,
- ozonation
- nano-filtration

Experimentally, the basic idea is to evaluate the potential for chlorophenol formation by chlorination of inlet and outlet waters of each treatment. Evaluating this potential should allow us to better understand the development of these compounds and adapt or optimise existing processes.

The present bibliographic report examines the issues of taste and odour in the resource, formation during treatment, nuisances caused, and possible water treatment solutions.

The compounds responsible for taste and odour depend on the presence of precursors: phenolic compounds and organic matter (OM). The bibliographic research therefore addresses treatability of OM in water treatment, especially impact on the chlorination stage. This approach, which makes no claim to be exhaustive, is illustrated by different works and studies carried out on THM et AHA.

2 Chlorination

Several forms of chlorine are used to disinfect water:

- Gaseous chlorine Cl_2
- Hypochlorite, mostly sodium hypochlorite NaClO ("bleach")
- Chlorine dioxide ClO_2
- Chloramine NH_2Cl

2.1 Gaseous chlorine and sodium hypochlorite

Chlorine has been used in water treatment since the beginning of the 20th century. Like all disinfectants, chlorine is a bactericide but has the advantage of also being remanent, which allows the water to conserve good organoleptic (and especially bacteriological) qualities all along its distribution journey. [Gonzalez et al, 1989; Myers, 1990]. However, chlorine acts on mineral molecules–

Bromine		bromides
Iron (ferrous)	***Cl_2 (gaseous)***	ferric ions
Sulphide	$\longrightarrow$	sulphur or sulphuric acid
Mn		manganese dioxide
Cyanide		cyanates
Nitrites		nitrates

– as well as on a fraction of the organic matter to form chlorine derivatives:

Amino acids,		chloraldimines
Amines	***Cl_2 (g)***	chloramines
Aromatic compounds	$\longrightarrow$	chloro aromatic compounds
Phenols		chlorophenols

These mineral and organic molecules are precursors and the compounds formed in reaction with chlorine are called chlorination by-products. They may be harmful to health or give the water an unpleasant taste or smell. These precursors therefore must be eliminated to prevent these by-products from forming. Table 1 below presents a number of organic compounds after reaction with chlorine.

Trihalomethanes	**Halogen furanones**
chloroform	3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone
bromodichloromethane	oxobutanoic acid 2-chloro-3-(dichloromethyl)-4
dibromochloromethane	**Others**
bromoform	hydrate de chloral
dichloroiodomethane	chloropicrin
bromochloroiodomethane	5-chlorouracyle
dibromoiodomethane	5-chlorosalicylic acid
Haloacetic acids	4-chlororesorcinol
monochloroacetic acid	bromodichloronitromethane
dichloroacetic acid	bromochloronitromethane
trichloroacetic acid	formaldehyde
monobromoacetic acid	acetaldehyde
dibromoacetic acid	chlorhydroxybenzyl cyanide
Haloacetonitriles	tetrachloromethane
dichloroacetonitrile	pentachloropropene
trichloroacetonitrile	bromoethane
bromochloroacetonitrile	bromobutane
dibromoacetonitrile	bromochloromethane
Haloacetone s	bromochloropropane
1,1 dichloroacetone	bromopropane
1,1,1 trichloroacetone	bromopentane
Halogen phenols	bromotrichloroethylene
2 chlorophenol	chloroethane
4 chlorophenol	dibromomethane
2,4 dichlorophenol	dichloromethane
2,6 dichlorophenol	1,1 dichloroethane
2, 4,6 trichlorophenol	1,2 dichloroethane
pentachlorophenol	dichloropropene
bromodichlorophenol	hexachlorocyclopentadiene
chlorodibromophenol	
2,4 dibromophenol	
2,4,6 tribromophenol	

Table 1: Chlorination by-products

Gaseous chlorine needs to be dissolved in water (yielding chlorinated water or “Javel” water) before injection. Its use is thus relatively constraining but very common given its high remanent power and low cost. In water, free chlorine is dismutated and into three forms in state of equilibrium: hypochlorous acid (HOCl), hypochlorite ion (ClO^-) and et chloride ion (Cl^-). The term free chloride corresponds to types Cl_2, HClO et ClO^-, whereas total chlorine corresponds to types Cl_2, HClO, ClO^- and to chlorine bound to chloramines. Below are the reactions of chlorine dismutation in water and the release of hypochlorous acid.

$$Cl_2 + H_2O \rightleftharpoons HClO + Cl^- + H^+$$

$$HClO + H_2O \rightleftharpoons ClO^- + H_3O^+$$

The most representative types resulting from dissolution of molecular chlorine in natural water are hypochlorous acid and hypochlorite anion. Only the pH and the temperature of the medium determine the nature and proportion of these types.

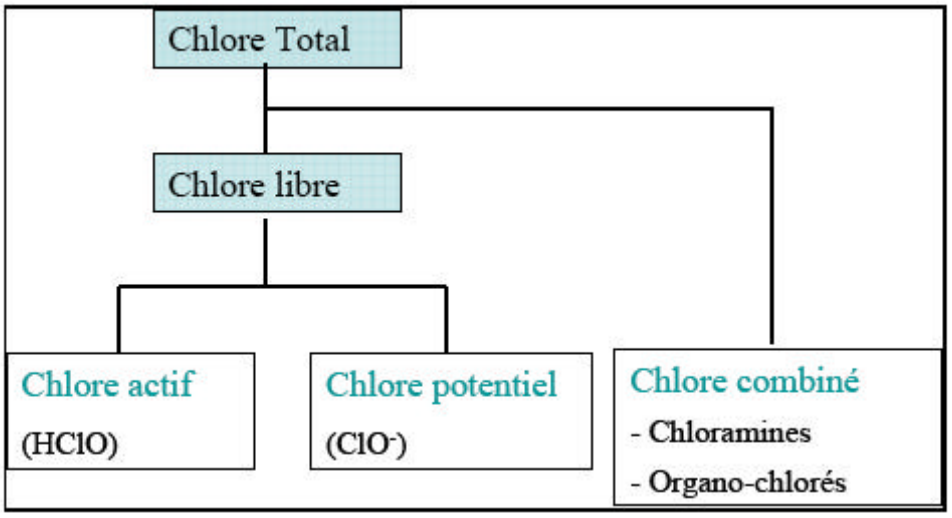


Figure 1: Different types of chlorine in water [Corbi, 2006]

Hypochlorous acid possesses the most effective biocidal action, which is why it is also known as "active chlorine". When increasing doses of chlorine are added to a water, residual chlorine at the end of a given elapsed time can be determined after different stages (see Figure 2 below).

- In stage 1, residual chlorine increases in proportion to the dose added. It is consumed primarily by organic matter (nitrogenous compounds, phenolics) resulting in combined chlorine (chlorine compounds such as chloramines, chlorophenols and trihalomethanes (THM)) with low germicide power.

- In stage 2, the dose of chlorine goes through an inflexion point and drops to a minimum called the "break point". Free chlorine is zero as long as residual chlorine has not reached this minimum. In this stage, the chlorine serves to destroy the compounds from the combined chlorine. The amount of chlorine needed to reach the break point in the presence of ammonia is, according to the authors, eight to ten times the amount of nitrogen present in the water to be treated.

- Finally, the added chlorine increases regularly. It possesses the desires disinfectant qualities and constitutes residual free chlorine (hypochlorous acid, hypochlorite).

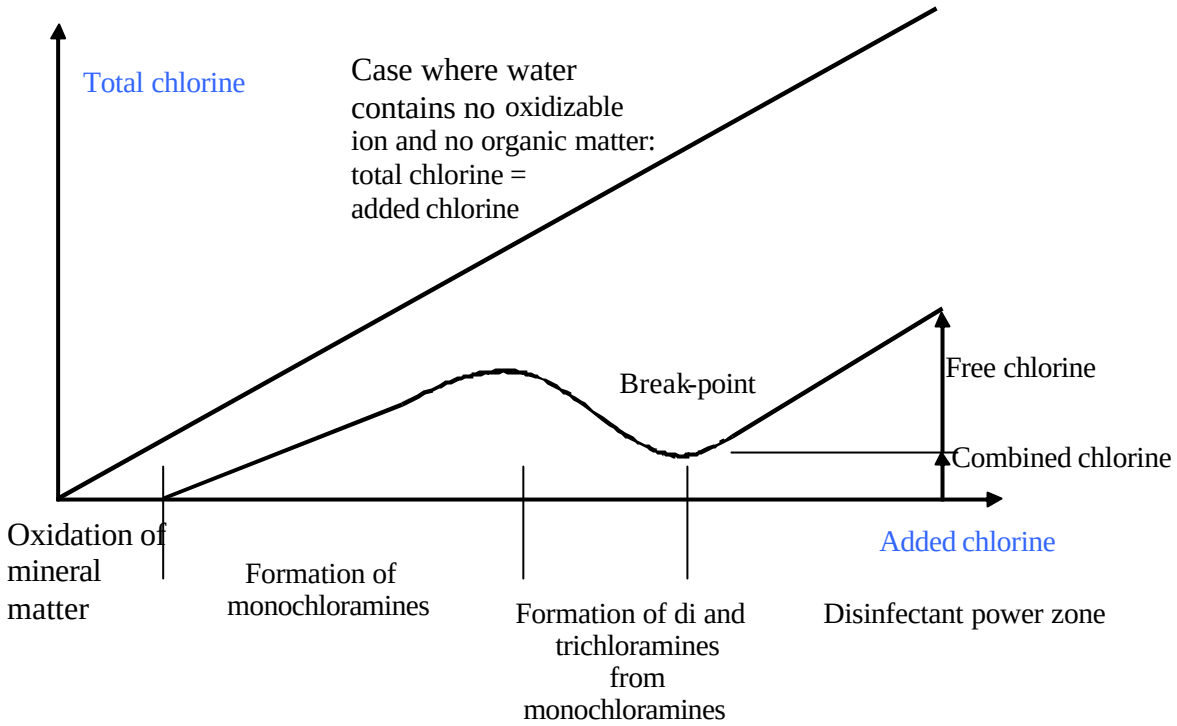


Figure 2: Free chlorine demand and break point

Chlorine may both eliminate and generate (directly or indirectly) certain odours or tastes in the water. If the resource water is low in organic matter and if the chlorination rate is high, the chlorine will give the water a bleachy taste with a detection threshold of around mg Cl/L.

Nowadays, it is less used as it acts on organic matter and leads to formation of chlorinated organic compounds that can be unhealthy and sometimes give the water an unpleasant taste or odour [Corbi, 2006]. It may be replaced by chlorine dioxide.

Note: sodium hypochlorite causes the same type of phenomena as the types are identical in solution (NaClO is totally released in water in Na^+ *and* ClO^-*)*

Pros	Cons
Oxidation of iron and manganese. Improves water treatment and colour. May improve coagulation and consequently filtration. Effective Biocide. Chlorine is the easiest and cheapest solution regardless of system size. It is the most widely used method and therefore the best known. Chlorine is available in the form of calcium and sodium hypochlorite. Hypochlorites are easier and safer to use than gaseous chlorine. Less equipment is generally required. Chlorine has a remanent effect.	Formation of halogen by-products. After treatment, the water may have an unpleasant taste and smell depending on the amount used. Chlorine is a corrosive gas. Hypochlorites are more expensive than gaseous chlorine. Sodium hypochlorite degrades with time and exposure to light.. Sodium hypochlorite is a corrosive chemical product. Highly concentrated hypochlorite solutions are unstable and generate chlorate production. Less effective with high pH. Biodegradable oxygen by-products may be produced, contributing to bacteriological growth if the residual chlorine rate is not maintained.

Table 2: pros and cons of chlorine utilisation

2.2 Chlorine dioxide

Chlorine dioxide is currently more used in water treatment as its biocidal effect is similar to that of free chlorine and its efficacy increases with pH [Lykins, 1990]. Moreover, ClO2 is more stable than chlorine. Chlorine dioxide is a gaseous compound that is very soluble in water (70 g/L to 20°C and 1 atm). Given its instability, the chlorine dioxide is prepared onsite using:

- chlorite in presence of hydrochloric acid to maintain an acid medium:

The reaction implemented in this case is the following:

$$5\ NaClO_2 + 4\ HCl \longrightarrow 4\ ClO_2 + 2\ H_2O + 5\ NaCl$$

The yield of this reaction is good with a chlorite transformation rate close to 100%, in the presence of excess acid (pH below 4).

- chlorite and chlorine,

- chlorite, hydrochloric acid and sodium hypochlorite solution:

The chemical reaction is then the following:

$$NaClO + 2\ HCl + 2\ NaClO_2 \longrightarrow H_2O + 2\ ClO_2 + 3\ NaCl$$

Chlorine dioxide reacts faster than chlorine with iron and manganese. It oxidizes sulphurs, nitrites and cyanides. On the other hand, it can oxidize

neither bromides nor ammonia ions. Furthermore, it reacts rapidly with phenol derivatives by destroying them, with tertiary and secondary amines, as well as with organic sulphurous compounds, but is practically inert relative to unsaturated compounds other than phenolics, oxygenised products and primary amines (amino acids) [Duguet et al, 2006]. Chlorine dioxide chlorination thus does not necessarily lead to THM formation [Meyer, 1992] and diminishes formation of non-volatile organohalogen compounds. Nevertheless, it can be transformed during treatment into chlorites that will form chlorates and chlorides [Reynolds et al, 1989], which constitutes a problem since chlorite ions are regulated (<0.2 mg/L) and give water a bad taste.

Chlorine dioxide has an odour that is perceived by the consumer as from a concentration of 0.2 mg/L. Its remanent power is less than that of chlorine (although it does have some remanence).

Note: although chlorine dioxide chlorination does not form THM or other by-products, the latter may be present nonetheless. This is due to the "purity" of the chlorine dioxide; these compounds might have been introduced or formed during the preparation of the chlorine dioxide [Meyer, 1992].

Pros	Cons
Chlorine dioxide is more effective than chlorine and chloramines for the inactivation of viruses. Chlorine dioxide oxidizes iron, manganese and sulphurs. The taste and colour due to algae growth are effectively treated with chlorine dioxide . If the dosage is right, no halogened by-products, bromates or nitrates are formed. Chlorine dioxide is easily produced onsite. pH does not affect the biocidal capacities of chlorine dioxide . Chlorine dioxide has a remanent effect.	Utilization of chlorine dioxide implies formation of chlorite and chlorate. Adjustment of installations is difficult and over-dosage can lead to formation of halogen by-products. Chlorine dioxide decomposes in sunlight. Chlorine dioxide must be produced onsite.

Table 3: pros and cons of chlorine dioxide utilisation

2.3 Chloramines

Chloramines are little used in drinking water treatment since, because their disinfecting power is less than that of chlorine and chlorine dioxide, the amounts and/or contact time needed would (all things being equal) be much greater. Chloramines are obtained by a reaction of chlorine on ammonia as follows:

$$HOCl + NH3 \longrightarrow NH_2Cl + H_2O \quad \text{Monochloramine}$$

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O \quad \text{Dichloramine}$$

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O \quad \text{Trichloroamine}$$

The chloramines formed will depend on the pH as well as on the chlorine/ammonia ratio used. Conditions favourable for monochloramine are high pH and a ratio of 3:1.

Their bactericidal power is much less than that of chlorine, but they are more stable and so have a good remanent effect for large distribution networks [Meyer, 1992].

The molecule used to disinfect water is monochloramine for dichloroamine and trichloroamine give the treated water a nauseating smell. On the other hand, one of the big advantages of monochloramine is that it reacts little if at all with natural organic matter and therefore there is little or no formation of organohalogen compounds. [Myers, 1990; Reynolds, 1989]. However, Johnson (1986) notes that formation of halogen compounds remains possible by substitute reaction with organic matter. The hypothesis of a hydrolysis of NH_2Cl into HClO reacting with organic matter has also been formulated.

Pros	**Cons**
Utilisation of chloramines generates fewer disinfection by-products than free chlorine. Monochloramine residues are more stable and have a longer period of action than free chlorine or chlorine dioxide . This being said, excess ammonia can contribute to the formation of biofilm. Chloramine use is inexpensive. Chloramine production is simple.	Chloramines do not have as much disinfecting capacity as other processes, such as 'ozone, chlorine and chlorine dioxide. Chloramines do not oxidise iron and manganese. Excess ammonia can lead to nitrification problems. Monochloramines are less effective with high pH. Chloramines must be produced onsite

Table 4: pros and cons of monochloramine utilization

3 Taste and odours: presence and potential formation

Because of the presence of organic mater in the water, chlorination leads to the formation of various undesirable substances that may sometimes give the water a taste and/or odour. Given the position of chlorination in water treatment, particles in suspension, between a micron and a nanometre in size, such as humic substances or dissolved compounds such as organic micropollutants, are more likely to lead to the formation of chlorinated by-products. Moreover, the compounds that give water a certain flavour are not all formed during chlorination; it may in fact happen that odorous molecules are already present in the water. This may be the case, for example, of benzene from accidental pollution due to chemical industry waste or the presence of petrol. Organic matter may then be divided into two main classes: natural organic matter (NOM) and anthropogenic organic matter, ie micro-pollution.

3.1 Natural organic matter

Although the origin of NOM is not well-known, we can distinguish between two different origins of organic matter generated within the same aquatic medium:

- **autochthonous** (indigenous): resulting directly from biological activity (via photosynthesis and/or the metabolic activities of algae and micro-organisms) or of indirect origin, from the degradation of aquatic plants by organisms living in the medium (eg in sediments);
- **allochthonous** (non- indigenous) resulting from lixiviation or washing of floors and percolation of water containing vegetal debris as wells as products from the degradation of ground vegetal and animal biomass [Gruau, 2003].

The composition of NOM varies according to a number of parameters such as temperature, season, or geographic location [Freuze, 2004]. NOM is thus an extremely complex mixture of organic compounds found in sources of drinking water. NOM is mainly composed of humus substances and simple non-humus compounds such as lignin, carbohydrates, nitrogenous or amino compounds, lipids, terpenes (odorous vegetal compound), proteins, polysaccharides (as well as other classes of biopolymers) [Gruau, 2003]. There is no one universally accepted model for describing NOM, which, for the humus part, corresponds to a partially indefinite macromolecular structure. These humus substances present molecular masses varying from 500 to 5,000 daltons (Thurman, 1983).

For purposes of illustration, Figure 3 below shows the NOM model structure proposed by Weinberg (1999).

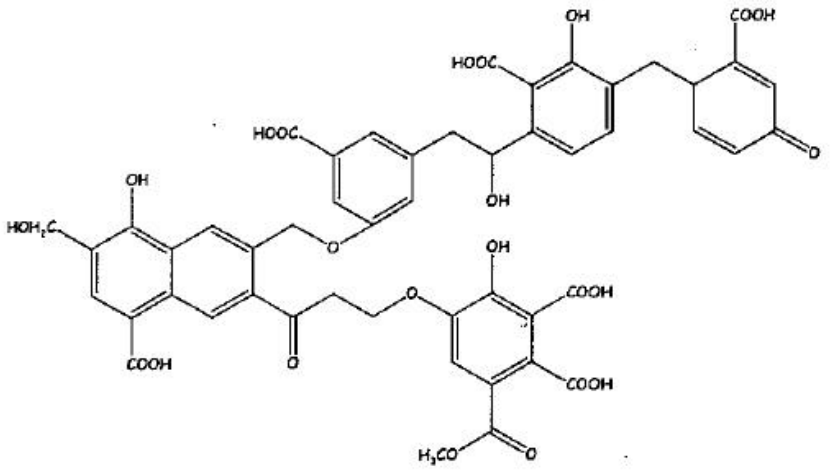


Figure 3: NOM model structure according to Weinberg (1999)

The indicator allowing proper detection of NOM is total organic carbon (TOC). A useful way to characterize NOM is to divide it into three fractions:

- dissolved organic matter (DOM) or dissolved organic carbon (DOC), which corresponds to the fraction passing through a filter with 0.45 µm porosity. Such organic matter often represents over 90% of TOC; it may come from diverse sources (allochthonous and/or autochthonous) and vary over time within the same body of water.

- Colloidal organic matter (COM), which is the set of organic molecules of which the molecular weight varies between 1,000 and 10,000 daltons (1 dalton = 1g/mol). COM is often associated with mineral colloids (iron hydroxide, clay).

- Particle organic matter (POM), which represents the fraction retained by this same filter; this consists most often of organisms such as algae or various vegetal debris (cellular tissues). This matter may be allochthonous (vegetal debris from the watershed) or autochthonous (algae) [Gruau, 2003].

NOM and more particularly its dissolved fraction DOC (POM represents only a fraction of total organic carbon and, moreover, tends to be relatively well removed during clarification stages) is at the origin of many reactions that affect water quality. In particular, it constitutes a precursor of most halogen and oxygenated disinfection by-products. Understanding these processes requires a finer characterization of NOM into different fractions. Only a small fraction of DOC is represented by simple compounds (sugars, amino acids, hydrocarbons), which may be analysed chromatographically. The other fraction of this DOC may be further divided into two parts a hydrophile (fulvic acid) on the one hand, and a hydrophobe (humus acid) on the other. These different parts may be extracted using specific ion-exchange resin. After analysis, it is possible to quantify the hydrophobe/hydrophile distribution of the dissolved organic carbon.

A study conducted on water of eight different origins showed that dam waters, richer in DOC and in aromatic compounds than river waters, also contain a higher proportion of hydrophobic structures [Croué et al, 1997].

The reactivity of humus substances with chlorine is manifested by oxidant demand, a decrease in colour and the formation of numerous chlorine compounds, despite a nearly insignificant increase in organic carbon. This chlorine demand is generally described by two successive kinetic steps [Croué, 1987; Reckow, 1984] of which the second may last several dozen hours. Furthermore, this chlorine demand will depend on OM and chlorine concentrations, on pH and on reaction temperature.

In general, NOM is a precursor of disinfection by-products that may be organohalogen but also non-chlorine components such as saturated and unsaturated aliphatic acids as well as aromatic compounds.

Organohalogens are described under the generic term TOX. Nonetheless, according to Reckow, [1984] the contribution of total organohalogenated compounds to chlorine consumption remains low (ie around 10% in mass). According to Norwood et al [1987], it should also be noted that most chlorination products come from the phenolic nucleus breakaway of lignin derivatives in humus substances.

Table 5 below shows type of by-product obtained according to the type of NOM fraction with which the disinfectant reacts:

compound	***sources***
trihalomethanes (THM)	humic substances
	proteins
haloacetic acids	humic substances
	carboxylic acids
Chlorophenols	humic substances
Acetaldehyde	humic substances
	proteins

Table 5: sources of precursors of different by-products [Croue et al*, 2000]*

3.2 Micropollutants

The main families of micropollutants are: hydrocarbons (bituminous products) and phenol and its derivatives (runoff water, industrial waste water, ash…), organohalogenated compounds (refrigerants, flame retardants…), pesticides (agriculture and private individuals), and polychlorinated biphenyls.

Few studies refer to the organoleptic properties of pesticides in water. [Montiel et al, 1987] list eighteen 18 pesticides having a "mouldy" taste. However, given that actual olfactory detection limits tend to be much greater than regulatory quality limits, these compounds are unlikely to affect water taste.

Natural or synthetic amine compounds (eg medicines, plant protectants) may be present in the water to be treated. Among the main amino acids referenced in drinking water are alanine, glycine, valine and phenylaniline [Hureiki et al, 1994]. Their individual concentration may exceed 1µg / L.

Cyanobacteria or actinomycetes are also involved in generating different odorous compounds such as geosmin which has an "earthy" type taste, methyliosborneol (MIB), which has a mouldy taste, or ß-cyclocitral with a "tobacco" or "minty" taste. The odorous compounds secreted by the micro-organisms the most cited in the literature are shown in Table 6 below.

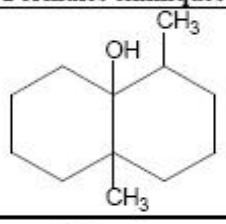
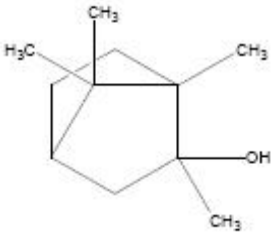
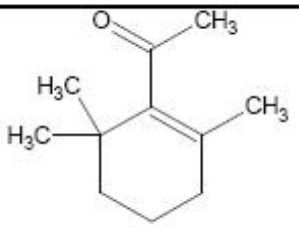
Composé	Nom systématique	Descripteurs	Formules chimiques
Géosmine	*trans*-1,10-diméthyl-*trans*-9-decalol	Terre, moisi	
2-méthylisobornéol (MIB)	1,2,7,7-tétraméthyl-exo-bicycloheptan-2-ol 2-exo-hydroxy-2-méthylborane 1,2,7,7-tétraméthyl-2-norbornanol	Moisi, camphre	
β-cyclocitral	2,6,6-triméthyl-1-cycohexène-1-carboxaldéhyde	Tabac, menthe, fruits verts	

Table 6: Examples of odorous compounds produced by Cyanobacteria [Corbi, 2006]

Phenol and its halogen derivatives are interesting to the study of water taste and odour, as these compounds, which may be of natural origin, generate by-products called haloanisols, for which perception levels are very low. Phenolic compounds may have several origins [Davi et al, 1999]:

- degradation of natural substances such as lignin resulting in the presence of alkylphenols, modification of aromatic oxygen compounds
- presence in colorants, plastics, tars, herbicides or during transformation of de detergents.

Chlorophenols are described in the literature as potential sources of taste in the water. [Krijgsheld et al, 1986] indicate that monochlorophenols and 2-4 dichlorophenols lead to pronounced "medicinal" taste. Concentrations of tastes detected are 100 to 1,000 times lower than concentrations with toxic effects on aquatic organisms. Moreover, the presence of chlorophenols may lead to formation of other types of compounds by biological methylation. Chloroanisols elicit mouldy organoleptic descriptors and have flavour thresholds lower than then phenolic precursors. [Malleret, 2001] mentions a significant olfactory gain of 8.10^5 for 2,4,6-trichloroanisol and 2.10^2 for 2,3,4,6-tétrachloroanisol compared to their respective phenolic precursors.

In sum, a number of compounds may be at the origin of tastes and odours in water due to their presence in the resource or their reactivity with chlorine, as in the case of natural organic matter and phenol nuclei. Perception thresholds depend on the type of compound as well as the sense concerned (taste or smell) [Young et al, 1996].

Table 7 below shows smell and taste detection thresholds for different compounds. It demonstrates the role that certain phenols and derivatives may play in taste and odour issues.

Compound	Odour Threshold ($\mu g\ l^{-1}$)	Taste Threshold ($\mu g\ l^{-1}$)
Pesticides		
Atrazine	9200	20
Bromoxynil	> 11,000	—
Carbaryl	37	44
Chlorfenvinphos	240	3.6
Chlormequat	> 8700	> 1400
Chlormequat dichloride	—	> 1400
Chlortoluron	> 9000	> 740
Dalapon	> 11000	—
Dichlobenil	40	—
Diazinon	40	> 55
Dichlorprop	> 9100	—
Diquat dibromide	> 8900	> 56
Isoproturon	> 8000	37
Linuron	> 9700	—
Maleic hydrazide	> 9900	9900
MCPA	460	4.1
MCPB	> 10,000	> 950
Mecoprop	> 8100	> 650
Paraquat dichloride	> 8600	> 28
Pirimicarb	> 1100	> 580
Propyzamide	700	—
Phenolic and anisole compounds		
4-Chloroanisole	> 2.0	6.2
4-Chloro-2-methylphenol	62	2.5
4-Chloro-3-methylphenol	2.5	2.5
4-Chloro-4-methylphenol	0.15	< 0.05
2-Chlorophenol	0.088	0.14
4-Chlorophenol	10	39
2,4-Dichloroanisole	0.21	0.08
2,4-Dichlorophenol	5.4	0.98
2,6-Dichlorophenol	5.9	0.0062
Pentachlorophenol	9.3	8
Phenol	9.5	< 2
2,4,6-Trichloroanisole	0.00008	0.025
2,4,5-Trichlorophenol	63	100
2,4,6-Trichlorophenol	380	> 12
Naturally occurring organic compounds		
Geosmin	0.0013	0.0075
2-Isobutyl-3-methoxypyrazine	< 0.00005	0.0004
2-Isopropyl-3-methoxypyrazine	< 0.00003	0.0099
2-Methyl-isoborneol	0.0063	0.0025
Other organic compounds		
Benzene	190	—
Chlorobenzene	190	190
Chloroform	7500	1200
2-Chlorotoluene	980	980
3-Chlorotoluene	150	390
4-Chlorotoluene	60	24
1,2-Dichlorobenzene	200	200
1,3-Dichlorobenzene	77	190
1,4-Dichlorobenzene	4.5	11
Ethylbenzene	150	390
HHCB	1.4	22
Isopropylbenzene	10	60
4-Isopropyltoluene	25	> 1000
Methyl tert-butyl ether	15	40
Naphthalene	2.5	25
Styrene	37	94
Toluene	960	960
1,1,1-Trichloroethane	3200	1500
Inorganic compounds		
Aluminium sulphate	—	4000[a] > 10,000[c]
Copper sulphate	—	> 990[a] 930[c]

Table 7: Types of compounds and detection threshold according to Young et al [1996]

4 Chlorination by-products

4.1 THM

Since Rook's first work in 1974, we know that the use of chlorinated products for disinfection of drinking water implies the formation of numerous chlorinated by-products potentially hazardous for health. Among these chlorinated by-products, THM, which has a highly carcinogenic potential, has certainly been one of the most widely studied compounds of the last twenty-five years. Classic THM's are chloroform ($CHCl_3$), dichlorobromoform ($CHCl_2Br$), dibromochloroform ($CHBr_2Cl$), and bromoform ($CHBr_3$). They are formed from reactions between NOM and hypochlorous acid (HOCl), in the presence or absence of bromides. The THM's formed are not just molecules with chlorine and brome. In fact, the presence in drinking water of dichloroiodomethane ($CHCl_2I$), bromochloroiodomethane (CHClBrI) and dibromoiodomethane ($CHBr_2I$) have been detected in several studies [Cancho et al 2000].

The chemical identity of the precursors of THM has not been well-defined. A study was conducted by Arguello et al [1979] to determine which organic compounds are likely to form THM's after chlorination. (See Table 9). In a study on ten different surface waters (seven artificial lakes and three rivers), Sorlini et al [2005] found that total THM (TTHM) increases according to the dose of chlorine applied during treatment, the organic matter present and the initial concentration of brome in the raw water. With a low bromide concentration brominated THM's represent approximately 40% of total THM, whereas with high bromide concentration they represent over 80%.

Studies by [Rhodes et al, 1978] on the influence of different parameters show that increasing pH and the amount of chlorine causes an increase in total THM. Furthermore, with THM speciation according to residual chlorine, it appears that the most brominated compounds are hampered when residual chlorine increases.

In a study of the kinetics of THM formation, [Gallard et al, 2002] found that the precursors of the NOM can be described in terms of THM formation potential corresponding to rapid-reaction precursors and that corresponding to slow-reaction precursors.

[Sorlini et al, 2005] also noted that use of chlorine dioxide and ozone reduces THM formation by roughly 97%, with equivalent chlorination rates but that during ozonation, bromates could be generated in water containing bromides.

As far as the taste and odour of THM is concerned, the thresholds of only a few THM's have been studied. Although the olfactory detection limit of chloroform is high [Young et al, 1996], that of iodoform is 300 ng/l [Suffet et al, 1999]. According to these authors, the presence of iodised haloforms with concentrations of 0.3 to 10 µg/L could give the water a medicinal taste and odour, increasing with the number of iodine atoms.

compound	odour threshold (µg/L)	taste threshold (µg/L)
chloroform	7500	1200
iodoform	0.3	5
bromoform	5	-

Table 8: taste and odour thresholds for different THM's

Composés ne produisant pas de THM (0,00)*	Composés donnant un faible rapport de production (0,01-0,09)*	Composés donnant un rapport de production intermédiaire (0,10-0,19)*
acide hexanoique acide picrique acide benzoique acide fulvique 1-pentanol alcool de benzyl 2-propanol 1,2-propanediol 1,2-éthanediol éthanol 1,3-propanediol 1,3-butanediol 2-nonanone 2-hexanone 1-naphthol 2-naphthol 2,3-dihydroxynaphtalène pyrogallol n-butylamine 1-naphthylamine toluène n-butylbenzène cumène sec-butylbenzène phtalate de diéthyl acétate d'éthyl méthoxybenzène éther de diéthyl tétrahydrofurane éthynylbenzène sucrose 1-hexène 1-octène styrène n-butyraldéhyde furfural 2-amino-2(hydroxyméthyl)-1,3propanediol	1-alanine 2-éthyl-1,3-hexanediol acétone diphénylcétone phénol 4-nitrophénol catéchol 2,4-diméthylaniline 2,5-diéthoxyaniline 2,3-dinitroaniline 3-nitroaniline 4-nitroaniline 3-pentène indole pyrrolidine benzènethiol 3-hydroxy-2-butanone	acide p-hydroxybenzoique 3,5-diméthylphénol 4-chlorophénol 2,4-dichlorophénol 4-aminophénol aniline n,n-diméthylaniline p-quinone aldol 2,4-pentanedione
		Composés donnant un rapport de production élevé (0,20-0,30)
		résorcinol 4-méthoxyphénol acide humique ◊ 2,6-diméthylphénol pentachlorophénol hydroquinone n,n-diéthylaniline

* les rapports de production (entre parenthèse) sont les rapports en moles de chloroforme formé par mole de composés
◊ acide humique produisant environ 25± 4µg de CHCl3 par mg d'acide humique

Table 9: THM production from pure compounds [Arguello et al,, 1979]

4.2 Haloacetic acids

Haloacetic acids (HAA) are made up of a multitude of compounds such as monochloroacetic acid ($CH_2ClCOOH$), dichloroacetic acid ($CHCl_2COOH$), trichloroacetic acid (CCl_3COOH) and trifluoroacetic acid (CF_3COOH). It is believed that certain AHA's form naturally in the environment, whereas others result from human activity. Haloacetic acids have been found in lakes, ground water tables, drinking water, ice age ice, precipitation, air and soil. In high concentrations, these acids are toxic for pants and it is suspected that some of them may be carcinogenic. The presence of bromide in water rapidly leads to the formation of brominated and acetic acids as well as mixed acetic acids (with different halogen atoms) that will predominate [Pourmoghaddas et al, 1993].

[Benanou et al, 1998] were the first to demonstrate the predominance of mixed haloacetic acids (chloro/bromo) after chlorination. In the waters of Brittany, levels as high as 120 µg/L have been detected with dichloroacetic acid the major component (62 µg/L).

A study of different waters in the United Kingdom [Malliarou et al, 2005] revealed the presence of acetic acids in several regions with concentrations sometimes as three to four times as high as that of THM.

The majority of analyses in a one-year investigation in Athens, Greece [Golfinopoulos et al, 2005] on chlorination by-products at four water treatment sites and in the network actually revealed monoacetic, dichloroacetic and trichloroacetic acid concentrations below standards in force.

PH plays a very important role in haloacetic acid concentration in water. For example, a study by Singer et al [2002] observed that, out of nine HAA's, most showed a decrease in concentration when pH was increased. This study also demonstrated that the type of NOM has a major impact on the formation of chlorination by-products. In fact, if the latter is composed mainly of hydrophobic organic carbon, it will lead to the formation of more HAA than THM.

Pourmaghaddas et al [1995] showed that water pH has a strong influence on the presence of HAA in waters and that at a pH below 5, there is a much higher concentration of HAA that total THM.

Wu et al [2001], in a study on the effect of temperature showed that THM's can be eliminated by heating the water but that temperature has practically no effect on AHA's.

Villanueva et al, [2003] showed that there is a correlation between total and specific THM's on the one hand, and total and specific AHA's on the other, and that AHA levels can be deduced from THM concentrations in consumption waters from different water production sources (different regions of Spain).

4.3 Chlorophenols and chloroanisols

Chlorophenols are widely described in the literature as a potential source of tastes in water. Obtained by direct chlorination of phenol, these compounds come from various industrial sectors. They are good agents for preserving wood, paint, vegetal fibres and leather (especially pentachlorophenol and tetrachlorophenol). They are also used as herbicides, fungicides and insecticides, and even have pharmaceutical applications (eg disinfectants, antiseptics, synthesis of medicines).

Nowadays, utilisation of chlorophenols is regulated. In France, the maximum concentration allowed in surface waters is 0.1 mg/L. Monochlorophenols and 2,4-dichlorophenol lead to pronounced medical tastes in water. When bromides are present in the water bromophenol may form. Table 10 presents the different phenol derivative detection thresholds reported in the literature.

Chlorophenols have a mixed origin: they may be initially present in the water as micropollutants, but they may also be formed during chlorination via the action of the disinfectant on the phenols. Their major drawback is the development of very unpleasant (medicinal) odour and taste, even in low concentration. Type of smell may vary according to concentration. Formation of chlorophenol (and more generally of phenolic compounds) depends on the ratio of chlorine to phenol during the chlorination process, as well as on pH. Practically no odour is detected for pH's below 7, as the optimum pH for appearance of chlorophenols tends to be between 8 and 9.

In addition, chlorinated phenols produced during water treatment may be transformed into chlorinated anisols by biomethylation in the distribution system. In fact, formation of trichloroanisol during distribution is probably caused by microbial methylation of trichlorophenol by certain micro-organisms [Nyström et al, 1992].

Investigations are continuously carried out on new compounds that might influence water taste or odour. In addition to geosmin and 2-methyliosborneol, 2,3,6- and 2,4,6-trichloroanisols and other haloanisols may lead to earthy or mouldy water tastes, even in very low concentrations. It is thus supposed that the presence of mixed chlorinated and brominated haloanisols could act on the odour of consumption water particularly rich in brome. Synthesis of 2,3,6- and 2,4,6-chlorobromoanisols has permitted an initial evaluation of organoleptic characteristics and detection limit thresholds of these compounds. The results obtained show that the thresholds of these compounds are between 2 and 14 ng/L and the common descriptors of these compounds tend to be "rubbery", "earthy" and "mouldy" [Corbi, 2006]. Some of these compounds are present in Table 10 below.

Composés	Seuils de détection organoleptiques (µg/L)		Descripteurs	Références
	Saveur*	Odeur*		
Phénol	-	31 (40°C)	Papier humide Journal humide	[Young *et al.*, 1996]
Monochlorophénols : 2-chlorophénol	0,97 (25°C) 0,1	0,36 (40°C) 0,1 10	-	[Young *et al.*, 1996] ; [HealthCanada, 1987]; [WHO, 1996]
4-chlorophénol	62 (25°C)	20 (40°C) 0,1	-	[Young *et al.*, 1996] ; [HealthCanada, 1987]
Dichlorophénols : 2,4-dichlorophénol	2,5 (25°C) 0,3	29 (40°C) 0,3 40	Moisi Antiseptique Médicinal	[Young *et al.*, 1996] ; [HealthCanada, 1987] ; [WHO, 1996]
2,6-dichlorophénol	0,02 (25°C)	22 (40°C) 0,2	Moisi Antiseptique Médicinal	[Young *et al.*, 1996] ; [HealthCanada, 1987]
Trichlorophénols : 2,4,5-trichlorophénol	-	350 (40°C) 1	Fruité Médicinal	[Young *et al.*, 1996] ; [HealthCanada, 1987]
2,3,6-trichlorophénol	-	3	-	[Schlett, 1992]
2,4,6-trichlorophénol	2 12 (25°C)	380 (40°C) 25 2 300 >1000	-	[Young *et al.*, 1996] ; [Schlett, 1992] ; [HealthCanada, 1987] ; [WHO, 1996] [Tomboulian *et al.*, 2004]
2,3,4,6-tétrachlorophénol	-	1	-	[Montiel *et al.*, 1987] ;
pentachlorophénol	30 (25°C)	23 (40°C) 30 1600 860	-	[Young *et al.*, 1996] ; [HealthCanada, 1987] ; [WHO, 1996]
Bromophénols : 2-bromophénol 4-bromophénol 2,4-dibromophénol 2,6-dibromophénol 2,4,6-tribromophénol	-	0,03 23 4 0,0005 0,6	Phénolique, iodé Phénolique Phénolique Iodoforme Iodoforme	[Whitfield *et al.*, 1988]

* Pour certaines limites, la littérature ne précise pas les températures auxquelles ont été effectuées les dégustations

Table 10: detection limit thresholds for chlorophenols and bromophenols [Corbi, 2006]

In a Canadian study, chlorophenol concentrations in surface water rarely exceeded 2 µg/L. Chlorophenol level in raw water arriving at forty drinking water treatment plants across Canada were measured. Pentachlorophenol was found in more than 20% of raw water samples taken in Autumn and Winter, in concentrations reaching 53 ng/L. Mean concentrations were 1.9 ng/L in Autumn and 2.8 ng/L in Winter. The chlorophenols the most frequently identified in the treated water samples were 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol. The first two of these had mean concentrations below 10 ng/L, regardless of season. The mean concentrations of 2,4,6-trichlorophenol were 40 ng/L.

The treated water of twenty-nine public drinking water distribution networks in the province of Alberta was sampled for five chlorophenols (2-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol) for two to four years. 2,4,6-trichlorophenol was detected in twelve out of the twenty-nine drinking water networks, in concentrations ranging from mere traces up to 3 µg/L. Penta-chlorophenol was also detected in two out of the twenty-nine networks, in a concentration equal to the detection threshold of 1 µg/L) [HealthCanada, *les chlorophenols*, 1987].

The study of a taste incident at the St Maur treatment plant (northeast of Paris) revealed that the raw water from the Marne river contained phenols that were not eliminated by the water treatment process (at that time consisting in two sand filtration stages– one fast and one slow – followed by a chlorination stage). During chlorination, chlorophenols were formed then methylated by the biofilm present in the distribution system, yielding chloroanisols [Montiel et al, 1999].

[Acero et al, 2005] showed that oxidation of bromides by chlorine occurs more rapidly than that of phenols and that during phenol chlorination, in the presence of bromides, bromation of phenols predominates until there is no more bromide or hypobromus acid (HBrO). Furthermore, the presence of excess bromide relative to phenol facilitates bromation of the odorous compounds 2-bromophenol and 2,6-dibromophenol, yielding even more heavily bromated compounds..

Various studies show that 2,4,6-trichloroanisol and other chloroanisols have caused serious odour problems. 2,4,6-trichlorophenol, which is the precursor of 2,4,6-trichloroanisol, is a well-identified chlorine disinfection by-product. In a study by Nyström et al [1992] on three different Swedish waters, it is seen that trichlorophenol is formed in weak concentrations of around 1ng/L, even if ClO_2 or monochloramine is used. It is also indicated that trichlorophenol is already naturally present in many Swedish surface waters. The presence of trichlorophenol in natural water can be explained by enzymatic chlorination (ie by an enzyme called chloroperoxydase of the natural organic matter of the soil) [Hodin et al, 1991].

Olfactory detection thresholds of different chloroanisols are recapped in Table 11 below.

Compound	*Odour threshold (ng/L)*	*Descriptor*
Haloanisols:		
2,4,6-trichloroanisol	0.03-5	Fruity, mouldy, earthy
2,3,6-trichloroanisol	0.0007 - 5	-
2,3,4,6-tétrachloroanisol	4	-
4-chloroanisol	20000	Mouldy, medicinal, musky
2,4 dichloroanisol	500	Mouldy, chemical, rose, stagnant
2,4-dichloro-6-bromoanisol	-	-
2,6-dichloro-4-bromoanisol	4	Mouldy
2,4-dibromo-6-chloroanisol	-	-
2,6-dibromo-4-chloroanisol	2	Mouldy
2,3-dibromo-6-chloroanisol	14	Rubbery, fruity
2,3-dichloro-6-bromoanisol	5	Rubbery, fruity
2,5-dibromo-6-chloroanisol	6	Rubbery, mouldy
2,5-dichloro-6-bromoanisol	2	Rubbery, plastic
2,6-dichloro-3-bromoanisol	3	Rubbery, carton
2,6-dibromo-3-chloroanisol	2	Rubbery, mouldy
2,4,6-tribromoanisol	12	Rubbery, earthy
2,3,6 tribromoanisol	0.03-10	Rubbery, sweetish

Table 11: detection limit thresholds for chloroanisols et bromoanisols [Corbi, 2006]

5 Main water treatment techniques for human consumption

As disinfection is a crucial aim of water treatment, the entire process is defined so as to ensure optimal effectiveness at this stage.

Natural waters contain several compounds that may be divided into four groups as follows:

- Suspended solids: may be mineral or organic (sand; silt; clay…)
- Colloidal matter: mineral or organic particles with a diameter of less than one micron particles, which settle excessively slowly
- Dissolved matter: solids less than a few nanometres; generally cations and anions, des fulvic acids, dissolved gases…
- Micro-organisms (algae, bacteria…).

The compounds in each of these groups will be treated according to their size, either by clarification, or by refining if they are in dissolved state.

5.1 Clarification

Clarification refers to a set of treatment processes: coagulation, flocculation, decantation or flotation, and filtration, which eliminate suspended solids and colloids present in the raw water.

5.1.1 Coagulation

The role of coagulation is to eliminate colloids. Les colloidal particles all have a negative surface charge and a light molecular weight, which mean that electrostatic forces become preponderant compared to the force of gravity. They naturally settle very slowly. To assist settling, a chemical substance is added: a coagulant, which is generally a metallic salt (eg aluminium sulphate, aluminium polychloride, aluminium chlorosulphate , ferric chloride, ferric sulphate, ferric chlorosulphate…).

Several theories have been developed. That given below, the so-called “double-layer” theory, is the one most often cited in the literature. In order to neutralize the charge, the positive ions present in the raw water come “stick” to negatively charged ions (fixed layers) and beyond form a broth around these particles (diffused layer) as shown in figure 4 below:

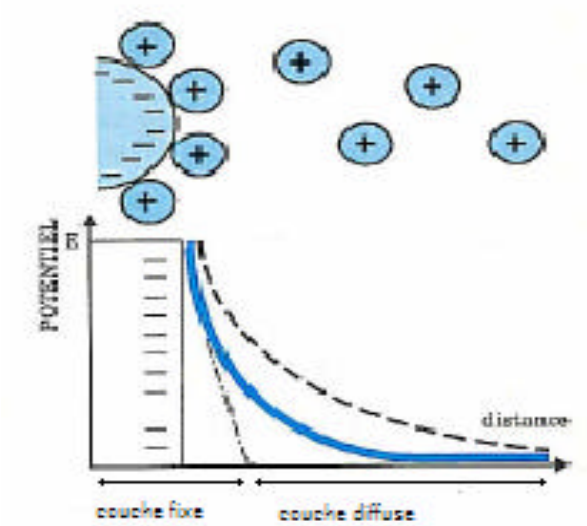


Figure 4: double layer theory [Degrémont, 1989]

The colloids are subjected to several types of force, including electrostatic repulsion due to the surface charges of the particles. Coagulation can reduce or even cancel these repulsive forces in order to enable contact between the particles and their agglomeration. The role of the coagulant will therefore be to destabilize these particles, form ligands binding the particles together, and form hydroxide precipitate that will collect aggregate called *floc* and adsorb certain dissolved molecules. This step is performed under intense agitation in order to assist particle agglomeration. In practice, the mean coagulant dose used is 50mg per litre of water to be treated (variable from 25 to 80 mg/L, depending on the turbidity and organic matter content of the water to treat).

5.1.2 Flocculation

This stage consists in slow agitation to agglomerate the various flocs that have formed. To improve this stage, it may be necessary to use an additional reactant called *flocculation additive* or simply *flocculant* (eg activated silica, colloidal clay, starch, alginates, polymers…). The most important parameter in this stage is speed. If the speed gradient increases too sharply, flocs are destroyed; if it is too low, the probability of contact between two particles is lessoned. It is important that the coagulation and flocculation steps be implemented properly. In fact, formation of too fine or too light a floc leads to poor settling and produces loaded decanted water that rapidly fouls filters and requires frequent washing.

5.1.3 Decantation or flotation

During this stage, the flocs settle under the force of gravity (decantation). The accumulation of these flocs at the bottom of the decanter is called *sludge*. Another process is to make the flocs surface by injecting air bubbles (flotation) so that the flocs may then be removed with a skimmer. A number of processes have been created in order to optimise this step: vertical flow decanters, horizontal, lamellar etc.)

5.1.4 Filtration

Generally placed after coagulation, flocculation and decantation stages, the purpose of filtration is to clarify a liquid that contains few suspended solids by running it through a granular or porous medium (eg sand or granulated activated carbon). This eliminates residual particles and may sometimes play a biological role. This step eliminates suspended particles, a large portion of colloids, and dissolved matter that is adsorbed. The water runs through a filtering bed made up of granular matter. The height of the layer is important and depends on the type of filter. Suspended solids are retained in the inter-granular spaces on the largest part of the top of the layer. The porous medium may be made of different substances:

- quartzy sand (most commonly used)
- anthracite or marble may be used instead if quartzy sand if necessary to avoid any trace of silica (eg for treatment of industrial water)
- granular activated carbon (see §5.2.2.2 below).

The material used may be characterized in various ways: granulometry (grain size), grain shape (round or angular), or brittleness (capacity to produce smaller particles during shocks such as during washing) These parameters are chosen according to filtering layer thickness, filtration speed, and type of water to treated. In general, the direction of the filtration is descending. All of these steps lead to the formation of water that is clarified but in most cases still unfit for human consumption. Clarification may be optimised by playing on certain parameters such as:

- coagulant or flocculant dosage
- pH of water treated
- decantation speed
- filtration speed
- filter granulometry

This stage is key, for it determines the effectiveness of the stages downstream. Moreover, turbidity is one of the most pertinent indicators of treated water quality and is a crucial sign of proper disinfection.

5.2 Refining

After clarification, the water may go through several additional treatment steps, mainly to eliminate dissolved micro-pollution. These may include:

- Ozonation
- Adsorption onto activated carbon.
- Membrane filtration

Chlorination and UV radiation are not steps for treating dissolved organic micro-pollution. The objective of these steps is to disinfect the water. Remanence in the networks is provided by the chlorine.

5.2.1 Ozonation

Ozone is a gas formed during electrical discharges produced in a reactor called an *ozoner* into which dioxygen (or air) is injected. Ozone is produced according to the total reaction expressed as:

$$3O_2 \rightleftharpoons 2O_3$$

Ozone is the most powerful oxidizer that can be used at many points of the water treatment process. It reacts with a number of mineral compounds (eg Fe, Mn, sulphur, cyanide, ammonia nitrogen, chlorine dioxide, chlorine, brome) and organic compounds (eg pesticides, chlorinated solvents, PAH, pharmaceutical compounds). It also can eliminate every trace of virus and bacteria with its disinfection action, but does not have any remanent power and therefore can not be used to preserve good bacteriological quality in drinking water networks.

Applied at the head of treatment, the objectives are :

- optimise the clarification stage (called *pre-oxidation*)
- oxidize mineral compounds
- inhibit algae growth
- eliminate tastes and odours

The small amounts used (at the mg level) are insufficient to tackle dissolved organic micro-pollution.

After a clarification stage:

Disinfection is the main goal defined with the C*T criteria (time, concentration) for elimination of bacteria and viruses. Ozone increases also biodegradability of organic matter before filtration on granulated activated carbon and oxidation of dissolved organic micro-pollution (notably pesticides). The doses used may reach 4mg/l. During this treatment stage, the ozone may be combined with hydrogen peroxide to obtained a very high level of oxidation (unauthorized in France).

Given its structure, aqueous phase oxidation may result in two different types of action that are sometimes complementary [Doré, 1989]:

- **direct** action of the molecular ozone– a very selective means of oxidising electrophile sites, stimulated by an acid pH
- **indirect** action of oxidising radical OH entities very reactive and not very selective hydroxyl radicals) formed by the breakdown of ozone in the water and preponderant in base mediums. This transformation takes place under the influence of OH- hydroxyl ions or other oxidants such as hydrogen peroxide and UV radiation.

These radicals may be involved in chain reactions and lead to total mineralisation of the dissolved organic matter. The reactivity of ozone depends on the conditions encountered in the medium: pH, type of substratum, dissolved salts… and on the pH of the natural waters to be made fit for consumption.

Direct ozone reaction is preponderant. Nevertheless, with constant direct oxidation rarely exceeding 10^3 l/mol.s, this reaction is slow and incomplete; on the other hand, with constant kinetics over 10^6 l/mol.s, radical indirect action is significantly more suitable for elimination of dissolved organic products [Paillard 1991].

5.2.2 Adsorption onto activated carbon

Adsorption defines the property of certain materials to attach molecules to their surface their surface (gas, metallic ions, organic molecules etc), more or less reversibly. This is an operation where matter is transferred from a liquid or gaseous phase to a solid one. In water treatment, adsorption onto activated carbon is a very process for eliminating a wide range of organic compounds, notably many of those responsible for unwanted tastes and odours.

One of the principal properties of activated carbon it its capacity to absorb more or less effectively any type of molecule (wide spectrum). This solid absorption capacity depends on the specific surface of the material (surface accessible to molecules), the type of adsorbate-adsorbant bond and the contact time between the solid and the solutes.

Activated carbon is a general term that describes a wide range of substances with a high amount of porosity and significant surface development (500-1500 $m^2.g^{-1}$). Depending on carbonisation, activation (temperature, concentration, type of chemical reactants) and the origin of the raw material, the finished product may exhibit different characteristics, notably in terms of structure, texture (porosity, specific area) and superficial properties (chemical functions). All of these parameters have a significant impact on the adsorbent properties of an activated carbon. In particular, the structural characteristics (porosity, specific area) effect capacity and adsorption kinetics. Pores are generally classified in three categories according to size: macro-pores (play no adsorption capacity role as they have weak specific surfaces, 50 to 100nm ranging up to 2,000), meso-pores (intermediate size) and micro-pores (1.8-2 nm) [De Laat, 1988].

5.2.2.1 Adsorbant-adsorbate and medium

Carbon performance depends on the special relation between adsorbate - adsorbant and medium. The solubility of the adsorbate plays an important role: the higher the solubility, the stronger the forces bonding the solute to the solvent, and, in general, the weaker the adsorption. Matsui et al [1994] note the adsorption capacity of a large number of pesticides is inversely proportional to their solubility.

The presence of polar functional groups (eg carbonyl, carboxyl) also modifies adsorption balance. Increasing the polarity of the solute generally results in less effective adsorption. In the case of phenolic and carboxylic compounds, the molecular forms are better adsorbed than the ionised forms, which are more soluble in water.

The effect of different compounds competing for adsorption sites influences the adsorption capacity of a carbon relative to a target molecule. IN the filed of water treatment, dissolved organic matter (OM) plays a considerable role and may alter carbon performance in significant proportions, both in terms of capacity and adsorption kinetics [Bernazeau, Knappe 1999].

As adsorption is a balance phenomenon, adsorption capacity will also depend on the initial adsorbate concentration, especially when there is a phenomenon of competition for the adsorption sites. The adsorption balance of a solute on activated carbon is also influenced by the pH and ionic force of the solution. In particular, these parameters affect solubility and the degree of dissociation of the polar compounds.

5.2.2.2 Implementation and optimisation

Powdered activated carbon (PAC) is used either during the clarification stage where it will be injected at the same time as the coagulation-flocculation reactants and end up in the decanter sludge; or in a refining stage, in combination with membranes or a lamellar decanter. Typically, PAC is used when there is a surge in pesticide pollution or very high algae level that can result in undesired water taste. In general, the dose of PAC added to water is from 10 to 30 mg per lire of water to treat.

Granulated activated carbon (GAC) is used in the form of a filtering bed through which the treatment water is run. It is used at different stages (eg refining of groundwaters instead of a sand filter; after ozonation…). The GAC resembles a classic filter with material 1 to 2.5m in height. Like sand, it can serve a biological role (bacterial medium).

Optimisation of this treatment has led over the last few years to a large amount of research aiming to fundamentally understand the mechanisms and factors that determine adsorption onto activated carbon. In this context, several mathematical models (Carter et al, 1994, Knappe e al., 1999) have been developed in order to predict carbon performance given the matrix effect and target molecule concentration. These mathematical models help evaluate performance in terms of:

- capacity (production of Langmuir or Freundlich adsorption isotherms
- kinetics (determination of transfer and diffusion coefficients)

These models facilitate design of reliable industrial filtration units allowing different dose/contact-time combinations for PAC, and lifespan or breakthrough curves for GAC.

5.3 Membrane filtration

Membrane processes are among the new technologies that may in the future play an important role in drinking water production. Membrane processes open up new possibilities in water sources including sea water, which was not feasible to use in the past for technical or economic reasons.

A membrane is a semi-permeable barrier that selectively separates compounds present in the water under the effect of a pressure gradient (see Figure 5) that can, depending on the technique used, work either frontally or tangentially (Figure 6).

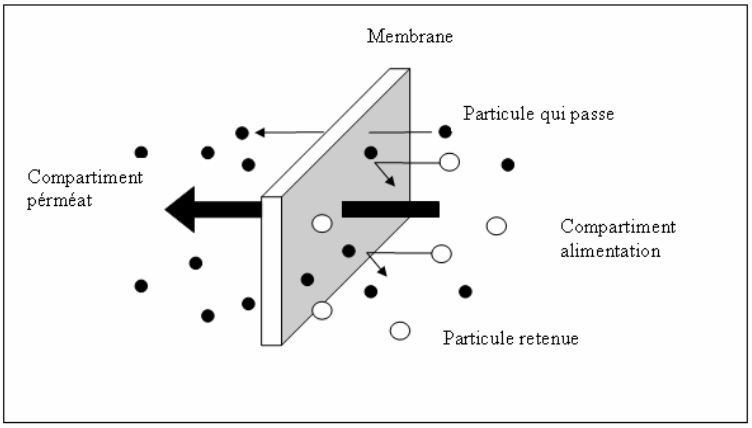
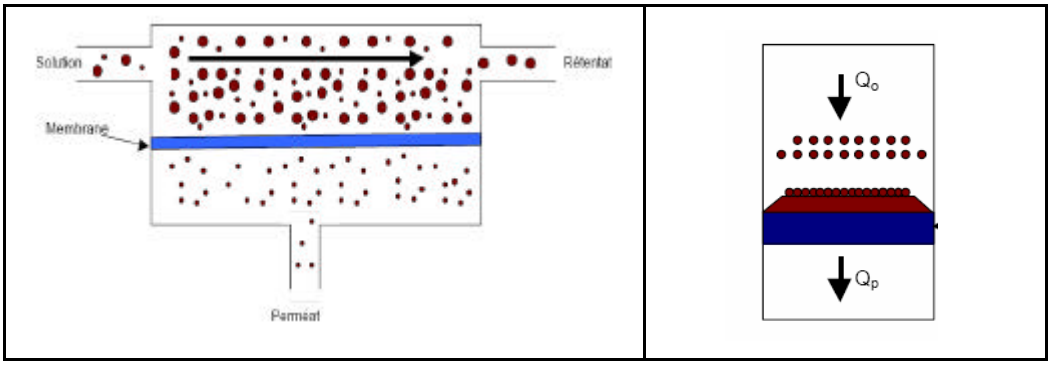


Figure 5: Principe of membrane filtration



Tangential ***Frontal***

Figure 6: tangential vs frontal membrane filtration

The different membrane separation processes are classified according to the theoretical diameter of the pores:

- Micro-filtration is a solid-liquid separation process using membranes with pore diameter between 0.1 and 10 µm. It allows retention of particles in suspension, bacteria, and (indirectly) colloids and certain ions after fixation of the latter to the largest particles obtained through complexation, precipitation or flocculation. Theoretically, there is a distinct difference between micro-filtration and ultra-filtration.

- ultra-filtration is used in liquid phase whereas micro-filtration is used to separate solid from liquid
  - operating pressure is generally lower with micro-filtration (trans-membrane pressure < 3 bars);
  - filtration flows are often higher with micro-filtration.

However, from a technological point of view, the two techniques may be considered relatively similar. Thus, to minimize clogging and avoid solid particles entering membrane pores, it is sometimes advisable to use an ultra-filtration membrane for a micro-filtration operation. Inversely, a micro-filtration membrane may become an ultra-filtration membrane (1 to 100nm) or even an reverse osmosis membrane (< 1 nm) following formation during use of a very fine-porosity gel layer (dynamic membrane).

- Ultra-filtration uses micro-porous membranes with pore diameter between 1 and 100 nm. Such membranes let through small molecules (water, salts) and stop molecules with high molecular mass (polymers, proteins, colloids). Given pore size, certain UF membranes (in the field closest to NF) are capable of also removing viruses and possibly a part of trihalomethanes (THM) precursors and part of the colour [Bouchard et al, 2003C].

- Nano-filtration is situated between reverse osmosis and ultra-filtration. It separates out nanometre-sized (around 10A) particles, hence its name. Monovalent ionised salts and non-ionised organic compounds with molecular mass under around 200 - 250 g / mol are not retained by this type of membrane. On the other hand, multivalent ionised salts (calcium, magnesium, aluminium, sulphates…) and non-ionised organic compounds with molecular mass over roughly 250 g / mol are highly retained. The NF allows high removal of *NOM, thus sharply reducing the total organic carbon (TOC) concentration.).* Colour, in relation with Fe and the NOM are removed very well by this process, which makes it an attractive solution for surface waters.

  Transfer mechanisms are intermediaries between those of reverse osmosis and those of ultra-filtration. This technique is often used for water softening.

- Reverse osmosis uses dense membranes that let through water but stomp all salts. This technique is used for desalination of seawaters brackish water. This technique is not used to produce drinking water from surface or underground waters

Figure seven below shows different types of membranes and their theoretical cut-off thresholds.

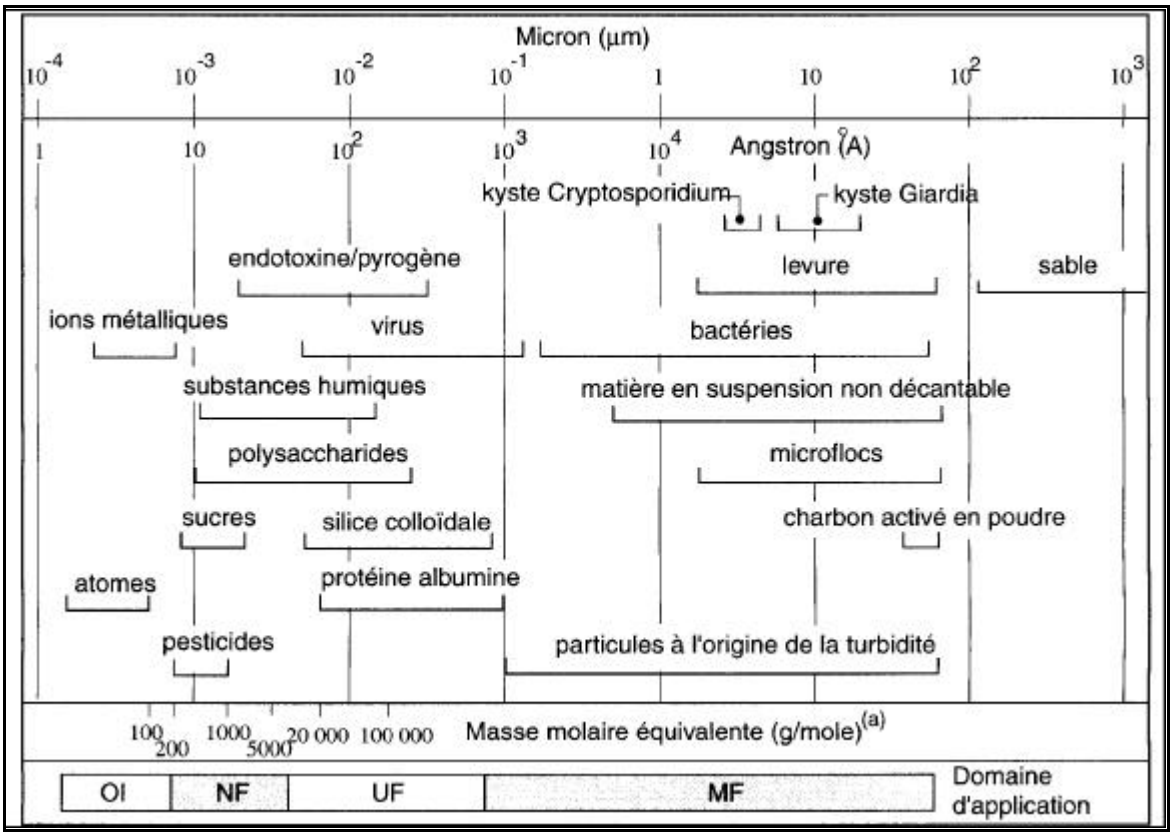


Figure 7: cut-off thresholds for different types of membrane
http://www.fndae.fr/documentation/PDF/fndae14.pdf]

6 Treatability of organic matter

In the field of water treatment, dissolved organic carbon (DOC) is a key parameter since its value and composition will determine reactant dosage (coagulant, oxidizer and adsorbent), refining yield, and oxidation by-product level. Its elimination thus constitutes a prime objective of treatment.

Ozone oxidation does eliminate by simply transforms TOC. On the other hand, ozone facilitates later elimination by coagulation or biological filtration by boosting the biodegradability of the organic matter. Membrane filtration, particularly nano-filtration, is also a highly effective process but which nonetheless requires pre-treatment to avoid clogging. TOC must therefore be lowered for the most part during clarification stages, which must be optimised by adjusting the pH, adsorption and reactant dosage.

- Clarification

The type of organic matter depends on multiple parameters such as the geographic area or the type of source. During the different clarification stages, various characteristics of the dissolved OM such as molecular weight distribution, carboxylic acidity and humic substance compounds affect elimination effectiveness [Collins et al, 1986].

The effectiveness of the coagulation stage depends on the type of NOM present in the raw water but also on the coagulant dose and of the pH of the water. Generally, elimination of NOM increases as the dose of coagulant increases, unless there is overdosage. Other parameters affecting elimination are the concentration of anions et inorganic cations present in the water, and alkalinity [Randtke, 1988].

A significant decrease in dissolved biodegradable organic matter (OM) represented by *biodegradable dissolved organic carbon* (BDOC) can be observed after coagulation-flocculation-decantation (40% to 80% reduction) as shown in Table 12 below.

Overall, coagulation causes a drop in the fraction of humic substances, leading to an increase in the proportion of hydrophile compounds [Croué et al, 1997; Owen et al, 1995].

water source	coagulant	dose (mg Me/mg de C)	pH	DOC (mg/L)	DOC reduction(%)	BDOC (mg/L)	BDOC reduction (%)
Reservoir Inlet	aluminium sulphate	1.5	6.5	7.1	38	1.7	41
Reservoir Outlet				4.4		1	
Reservoir Inlet	aluminium polychloride	0.8	5.8	7.2	54	ne	
Reservoir Outlet				3.3		ne	
River Inlet	Ferric chloride	1.2 to 1.4	5.5-6.0	8	45	1.8	83.5
River Outlet				4.4		0.3	
River Inlet	aluminium sulphate	1.1	8.2	2.8	25	ne	
River Outlet				2.1		ne	
Me=metal expressed in Al2O3 for aluminium salts and in Fe for ferric salts						ne=not evaluated	

Table 12: impact of clarification on DOC and its biodegradable fraction

Optimising coagulation by adjusting pH, which is a preponderant factor and choosing the right coagulant enhance NOM reduction. According to [Crozes et al, 1995], the most appropriate coagulant appears to be FeCl3 for six waters with TOC varying from 2 to 11 mg/L. In fact, series of TOC measurements after coagulation with different types of coagulant in equivalent doses (0 to 120 mg/L depending on the experiment) show that $FeCl_3$ is the most effective coagulant for eliminating TOC from these waters. Typically, for this coagulant, a pH of around 6 enables elimination of roughly 65 % of NOM with 60% less reactant dose.

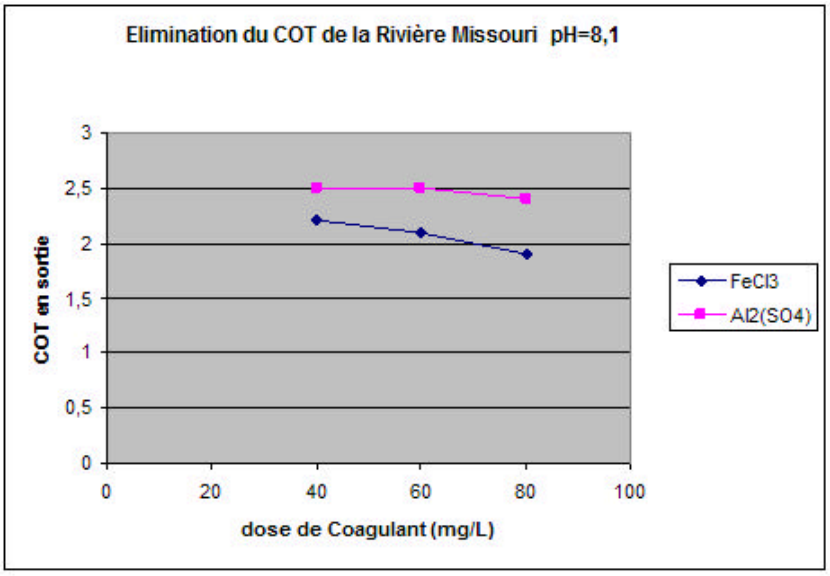


Figure 8: impact of clarification on TOC [Crozes et al, *1995]*

Utilisation of $FeCl_3$ on two samples S1 and S2 [Rizzo et al, 2005] also show it to be the best coagulant for eliminating NOM, reducing UV_{254} by over 50% with a dose of 60 mg/L of $FeCl_3$.

	S1	S2
pH	8.1	7.8
Turbidity (NTU)	15.2	5.4
UV_{254} (l/cm)	0.116	0.103
TOC (mg/L)	3.4	2.3
DOC (mg/L)	3.1	2.1

Table 13: characteristics of samples studied [Rizzo et al*, 2005]*

On the other hand, turbidity reduction is improved by using PACl. For S1, 84% elimination is observed with a dose of 20 mg/L de PACl whereas, with the same dosage, $FeCl_3$ and aluminium sulphate respectively produce only 14% and 31% elimination [Rizzo et al, 2005].

Slow filtration on sand can eliminate a large part of the BDOC (50 to 60%) and cut DOC 27 to 35%, according to Welté et al [1992]. Nevertheless, since biological life inside the filters is very intense, by-products may be released, and therefore it may be necessary following slow filtration to use activated carbon filtration to assist the adsorption process.

- Ozonation

Ozone does not reduce dissolved OM content but dies alter its composition, generating hydrophile compounds and increasing BDOC. The humic part is converted into non-humic products [Croué et al, 1997; Owen et al1995].

Ozonation of dissolved organic matter makes it more polar, more hydrophile, richer in oxygen, and more acid (through introduction of COOH groups). It reduces the molecular weight of OM and increases its biodegradability. Optimal ozone doses are between 0.5 and 1 mg O3/mg TOC. When ozonation takes place at the head of treatment (pre-ozonation), it facilitates the coagulation/flocculation stage, since transformed OM is easier to flocculate) [Philipot *et al*,. 1991].

Ozonation of humic substances causes formation of carboxylic acids and aldehydes likely to give the water undesired taste and odour. Presence of short-chain alkylbenzoic acid has also been observed. This can be explained by the fact that humic substances are capable of trapping relatively small molecules in their structures. (This phenomenon is relatively wide-scale and is the basis of micro-pollutant transport.) It has also been observed that the effectiveness of the treatment increases when ozonation is performed intermittently rather than in a single strong dose [Killops, 1986]. Ozonation of humic substances leads to significant decolouration of humus material solutions, lessoned UV absorbance and sometimes a slight reduction in TOC as well as an increase in carboxylic acids. It has been observed that the presence of bicarbonate ions results in lower production of organo-chloride compounds formed during chlorination.

- Adsorption

GAC filters are very good media for bacteria. During GAC water filtration, bacteria fixed to the carbon continuously degrade the organic content in the water, eliminating 60 to 80% of the BDOC [Bouillot et al, 1992].

PH plays an important role in the distribution of the humus and fulvic acids of the organic matter. The parts of these acids with low molecular weight are those that adbsorb the best onto the carbon. Moreover, the least soluble part of the humic acids adsorbs better than the fulvic acid part [McCreary et al, 1979].

Ozonation of the OM before running it over a carbon bed alters its structure. Although the OM is not changed quantitatively, there is a qualitative change resulting in generation of biodegradable by-products. This biogeneration significantly boosts elimination of the organic mater.

- Membrane filtration

Use of ultra-filtration and nano-filtration membranes is suitable for eliminating NOM from raw water sources. In fact, nano-filtration eliminates most OM whereas ultra-filtration eliminates mainly molecules with high molecular weight. Furthermore, a study of membrane condition after filtration of several litres/m² (16.5 and 37 L/m²/h) has shown that the effectiveness of an ultra-filtration membrane with clogged pores is close to that of a nano-filtration membrane [Frimmel et al, 2004].

A 120-day study of nano- and reverse-osmosis membrane filtration was performed in order to determine how clogging occurs. For this purpose, raw water was first filtered by ultra-filtration and then the filtered water was run through different types de membranes. Next, the filters were examined to observe clogging after treatment. It was shown that the system can eliminate between 76.3% and 95.3% of dissolved inorganic compounds, as well as between 80.0% and 83.8% of dissolved organic compounds. In addition, traces of iron were observed in the treatment water. Iron remains in the membrane even after chemical treatment [Gwon et al, 2003].

7 Impact of eliminating OM on the formation of chlorination by-products

Since chlorination is the ultimate treatment stage, it must generate an absolute minimum of by-products before distribution. It would then appear that haloform precursors and other chloride compounds must be eliminated upstream by setting up multi-barrier treatment when possible. Multi-barrier treatment can also partially or fully eliminate these compounds when they are present in the resource.

7.1 Treatability of THM

- Clarification:

Rizzo et al [2005] studied the effectiveness of coagulation measuring TOC, UV_{254} and potential TTHM formation during a series of jar tests (adding coagulants $Al_2(SO_4)_2 .18H_2O$, $FeCl_3$, and aluminium polychloride (PACl) in a range of 0 to 80 mg/L. They observed that PACl does in fact diminish turbidity but is less effective in eliminating THM precursors than $Al_2(SO_4)_2$ and $FeCl_3$. Two water samples (S1 et S2) with different characteristic (Table 14) were used for this study.

	S1	**S2**
pH	8.08	7.8
Turbidity (NTU)	15.2	5.4
TOC (mg/L)	3.4	2.3
DOC (mg/L)	3.1	2.1
TTHMFP (µg/L)	200	135

Table 14: characteristics of the samples studied [Rizzo et al, 2005]

TTHMFP elimination results (total THM formation potential) are summarized in Figures 9 and 10 below.

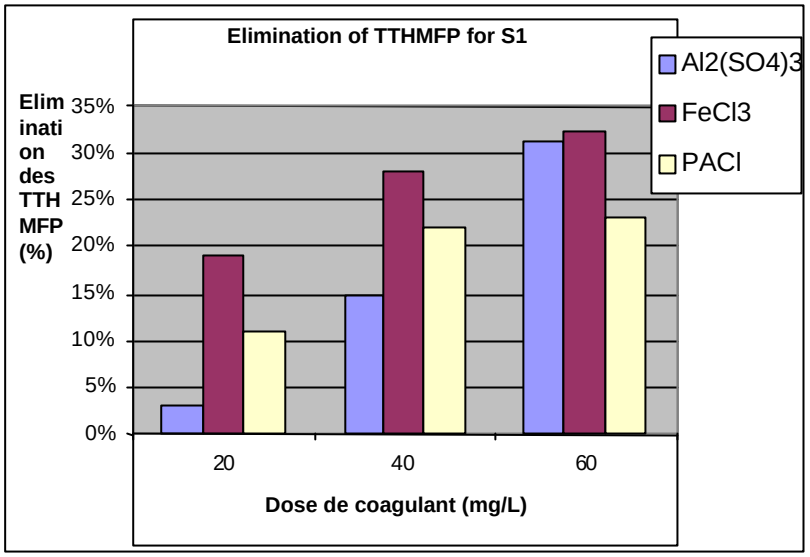


Figure 9: elimination of THM by coagulation [Rizzo et al, *2005]*

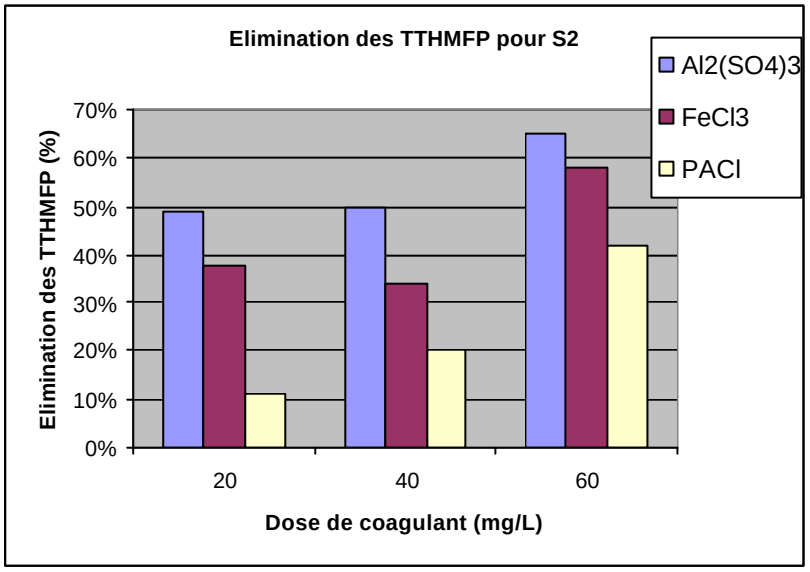


Figure 10: elimination of THM by coagulation [Rizzo et al, *2005]*

According to this data, 80 mg/L of $FeCl_3$, we obtain a final TTHMPF level of 128 µg/L for S1 and 57,6 µg/L for S2.

Optimised elimination of THM precursors in lake water by coagulation at different times of the year with DOC ranging from 6.8 to 8.8 mg/L gives an $FeCl_3$ coagulant dose of 150 mg/L for an optimum pH of 5 to eliminate as many precursors as possible. This study also showed that dissolved air floatation can reduce THM precursor content [Gehr et al, 1993].

Moreover, different studies have shown that increasing the coagulant treatment rate can improve THM precursor reduction. Aluminium sulphate is the coagulant that best eliminates humic acids, the main precursors of THM, notably chloroform.

En 1999, Ivancev-Tumbas et al modelled the occurrence of chloroform ($CHCl_3$) in water for two hours with a chlorine concentration of 100 mg/L. This value was deliberately high in order to emulate the contact time in studies on the same subject that were conducted not for two hours but for three to seven days with Cl_2 doses of 10 to 20 mg/L. It was observed that the chloroform formation rate for ten minutes diminished 2.6 to 6.4 times after coagulation and 13.2 to 15.5 times after GAC filtration.

Parameter	Mean value
TOC (mg/L)	5.6
pH	8.1
THM (µg/L)	<1
ChFP (µg/L)	328

Table 15: characteristics of the water studied

After studying the fraction and coagulation of the NOM of eight waters, two Australians and six Americans [Bolto et al, *2002*] found that the fraction of NOM corresponding to THM formation potential is 11 to 24 µg/mg of DOC. They also showed that the most hydrophobic acetic acids have the highest THM formation potential.

- Ozonation

Ozone is reactive to aromatic structures which are THM precursor sites. The ozone reaction opens these cycles thereby reducing the potential for forming THM. It can happen that when ozone dose is too low, new precursors are formed, in which case the reverse effect is observed). The type of water to treat, in particular its alkalinity, will also influence the reduction in THM formation potential. Ozonation transforms precursors with high molecular weights into by-products with low molecular weights that are less reactive to chlorine. Ozonation also oxidises bromides into hypobromous acid (HBrO), thereby increasing the relative abundance of brominated THM. This is based on a study by Amy et al [1991] conducted with treatment rates of 0 to 1.5 mg of ozone per mg of DOC. Galapate et al [2001] also observed this reactivity of DOC after ozonation at the same treatment rates.

Similarly, Guay et al [2005] studied water treatment of this type:

Raw water → slow filtration on sand → disinfection (Cl_2) → Storage

	Raw water	Treated water (without ozonation)	Treated water (with ozonation)
pH	7.15	7.4	7.2
TOC (mg/L)	3.9	3.7	3.3
Turbidity (NTU)	0.54	0.2	0.2

Table 16: characteristics of samples studied [Guay et al, *2005]*

The study revealed that when ozonation is performed before slow filtration on sand, THM production is significantly less compared to slow filtration on sand without upstream ozonation. Total THM concentration output without ozonation is 110 µg/L, where with ozonation it drops to 60 µg/L. [Plummer et al, 1998] studied pre-ozonation of raw water loaded with algae and noted a increase in DOC over 400% after ozonation, and hence a significant increase in THM precursors.

- Adsorption

Adsorption on PAC highly limits THM occurrence but does not adsorb Br ions, resulting in a percentage of brominated THM higher in the treated water (PAC treatment: 50 and 100 mg/L) for THM formation potential rates of 30 to 200 µg/L according to the fraction of NOM analysed [Amy et al, 1991]. Adding PAC prior to the coagulation stage has been shown to reduce THM precursors by over 70%.

GAC has proven to be a very effective tool for eliminating NOM from treatment water to supply the city of Ankara. The THM present is highly adsorbed by the activated carbon. Even after 8,000 volumes of water bed, total THM is only 0.2 µg/L leaving treatment whereas its initial concentration was 10 to 30 µg/L [Çapar et al, 2002].

In a study of different NOM elimination treatments, GAC trials showed elimination of 60% of THM precursors after six months of operation with an initial concentration. [Jacangelo et al, 1995].

- Membrane filtration

Nano-filtration membranes can control THM formation potential, but require that input water already have low turbidity to avoid shortening membrane life. [Taylor et al, 1987]. Turbidity can be lowered with conventional treatments such as coagulation-flocculation and/or use of ultra-filtration or micro-filtration membranes. According to [Siddiqui et al, 2000] elimination of THM from surface water with low turbidity is over 80% by nano-filtration and only 50% by ultra-filtration. Results after filtration with different nano-filtration membranes are given in Table 17.

Water	DOC (mg/L)	DOC (mg/L) after filtration	THMFP (µg/L)	THMFP (µg/L) after filtration	mean reduction (%)
1	3.82	0.21 to 0.38	240	3 to 4.5	97%
2	2.21	0.21 to 0.32	75	2.4 to 4.2	
3	3.21	0.21 to 0.33	45	de 1 to 2.5	
4	1.55	0.18 to 0.22	15	de 1.2 to 3.1	
THMFP = THM formation potential					

Table 17: results after filtration with different nano-filtration membranes

The study of three types of waters spiked with a certain concentration of CHCl3 and filtered through a reverse-osmosis membrane showed that the effectiveness THM elimination by reverse osmosis depends on the type of membrane as well as on the pressure exerted. (Elimination is actually less if the pressure is too high) [Karakulshi et al, 2001].

Several studies on ultra-filtration contradict each other on the effectiveness of this process, as in certain cases ultra-filtration eliminates virtually all THM precursors, whereas in others ultra-filtration appears to be totally ineffective. [Mallevialle et al; Lin et al, 2000]. These contradictory results would seem to stem from the intrinsic characteristics of the membranes, which may be very different.

A study conducted by Jacangelo et al [1995] on different NOM elimination treatments shows that nano-filtration membrane treatment is very effective for eliminating THM. $CHCl_3$ drops from 49 µg/L to just 5 µg/L whereas 90% of THM precursors are eliminated. Nevertheless, one problem was observed: occurrence of brominated by-products. This may be explained by the fact that bromides are not eliminated and so may react with remaining OM.

The results of the study presented in Table 18 on nano-filtration membranes show that THM formation potential drops from 544 µg/L in raw water to 31 µg/L in the filtrate:

Quality of input water / Quality of filtrate				
	Turbidity (NTU)	UV254 Absorbance	TOC (mg/l)	TTHM (µg/l)
Mean	3.4 / 0.056	0.52 / 0.012	15 / 0.7	544 / 31
Minimum	2.8 / 0.039	0.41 / 0	9.3 / 0.4	400 / 21
Maximum	4.5 / 0.165	1.53 / 0.032	16 / 1.2	605 / 46

Table 18: effectiveness of nano-filtration on THM

www.uas.alaska.edu/attac/ETV_FyneFinal.pdf

Conclusion

THM control is primordial for the distribution of consumption water since these components are taken into account in drinking water standards. The bibliographic background gathered shows that eliminating haloform precursors is effective at each stage of the treatment process. Elimination nevertheless depends on operating conditions (eg reactants, contact time, membrane pore size). Nano-filtration proves to be highly effective but requires prior treatment in order to avoid clogging and fouling. Granulated activated carbon filtering also effectively reduces THM formation. The amount of reduction depends on the type and adsorbability of the organic matter in the water, as well as the sizing parameters of the process [HealthCanada *Les trihalomethanes,* 2006].
Stages of adsorption on carbon and nano-filtration also appear very effective for eliminating THM present at entry into the treatment plant.

7.2 Treatability of AHA precursors

- Clarification

The works of [Gang et al, 2005] show that coagulation using aluminium sulphate can eliminate a part of the monohaloacetic acid and trihaloacetic acid precursors but is much less effective with dihaloacetic precursors. Reckhow et al [1990] made the same observation.

The precursors of the nine main haloacetic acids are better eliminated by coagulation than those of the four main THM [Singer et al, 2004].

It was observed in waters with high UV absorbance (254 nm), AHA precursors were better eliminated than those of THM during coagulation, which is coherent with the fact that AHA precursors belong to the hydrophobic fraction of the NOM [Singer et al, 2002].

Conventional water treatment techniques (coagulation, sedimentation, dissolved air floatation, and filtration) can reduce the quantities of AHA precursors but cannot eliminate the latter once they have been formed. [HealthCanada, H*aloacetic acids in drinking water*, 2006].

- Ozonation

A study by Guay et al [2005] on a water treatment process of this type–

Raw water → slow filtration on sand → disinfection (Cl2) → storage

	Raw water	Treated water (without ozonation)	Treated water (with ozonation)
pH	7.15	7.4	7.2
TOC (mg/L)	3.9	3.7	3.3
Turbidity (NTU)	0.54	0.2	0.2

Table 19: Characteristics of raw water [Guay et al*, 2005].*

–showed that when ozonation is performed before slow filtration on sand, AHA production is significantly reduced compared to slow filtration on sand without ozonation upstream. Total AHA concentration is 125 µg/L leaving the treatment process without ozonation, whereas with ozonation, the concentration drops to 80 µg/L. [Karnik et al, 2005] made a similar observation with a reduction in AHA of over 65%. On the other hand, ozonation of water loaded with algae actually increased AHA [Plummer et al, 1998].

Ozonation rapidly reduces formation potential of three AHA (over 50% after nearly five minutes of treatment) with no effect on the percentage of elimination by increasing the contact time [Chin et al, 2005].

Ozone dose, pH, alkalinity and type of organic matter present in the water constitute the main variables which seem to determine the effect of ozone. It has been shown that ozone effectively reduces AHA precursors when pH is low. However, with pH above 7.5, it can actually increase by-product precursor production [HealthCanada, *haloacetic acids in drinking water*, 2006]. Ozonation treatment results form several treatment plants in the city of Montreal have shown that ozonation reduces chlorine dosage and thus short- and long-term AHA formation [Gagné et al, 1996].

- Adsorption

Even if one considers that eliminating precursors is the most effective way to reduce AHA concentration, it is also possible to eliminate AHA per se. Adsorption on activated carbon is generally used to eliminate organic compounds such as AHA from. GAC colonised by bacteria (biologically active carbon) constitutes an effective means of eliminating AHA [HealthCanada, *haloacetic acids in drinking water*, 2006]. It has been shown that AHA can be eliminated by GAC filtration, probably by biodegradation processes when the AHA runs over the carbon bed. In addition, elimination effectiveness depends on water temperature (the hotter the water, the better the elimination). Dihaloacetic acids are better degraded than trihaloacetics [Singer et al, 2002].

Adsorption isotherms produced with monohaloacetic and dihaloacetic acids show low adsorption capacities. On the other hand, trihaloacetics have slightly higher adsorption capacity than chloroform ($CHCl_3$). Given these pour AHA adsorption capacities, GAC adsorption plays a minor role in AHA elimination at the start of filter life, and AHA elimination in aged GAC filters may be attributed to biodegradation [Tung et al, 2006]. In a study on different NOM elimination treatments, GAC trials showed elimination of over 80% of the precursors of the five main AHA after six months of operation [Jacangelo et al, 1995].

- Membrane filtration

In a study on nano-filtration membranes, it was found that between 98ù and 100% of AHA are eliminated by this membrane treatment, but that dibromoacetic acid was practically not eliminated (it represented 2% of AHA present in input water against 80% to 100% by the end of treatment.) In fact, during trials, total AHA concentration in incoming water (five different AHA) was 405 µg/L vs 6.7 µg/L in outgoing water.

Input water quality / Filtrate water quality				
	Turbidity (NTU)	UV254 Absorbance	TOC (mg/l)	AHA5*(µg/l)
Mean	3.4 / 0.056	0.52 / 0.012	15 / 0.7	405 / 6.7
Minimum	2.8 / 0.039	0.41 / 0	9.3 / 0.4	306 / 4
Maximum	4.5 / 0.165	1.53 / 0.032	16 / 1.2	480 / 11

*sum of concentrations of five different AHA

Table 20:main parameters characterising treatment water

www.uas.alaska.edu/attac/ETV_FyneFinal.pdf

[Siddiqui et al, 2000] report that micro-filtration reduces AHA formation at least 1%, ultra-filtration eliminates 32%, and nano-filtration more than 80%. However, these authors emphasise that nano-filtration use requires water with low turbidity and that pre-treatment is therefore necessary to eliminate particles and colloids. Results obtained after filtration with different nano-filtration membranes are shown in Table 21 below:

Waters	DOC (mg/L)	DOC (mg/L) after filtration	HAAFP (µg/L)	HAAFP (µg/L) after filtration	Mean reduction (%)
1	3.82	0.21 to 0.38	245	de 4.8 to 6.5	94%
2	2.21	0.21 to 0.32	80	3 to 7.5	
3	3.21	0.21 to 0.33	92	2.8 to 8.2	
4	1.55	0.18 to 0.22	40	3 to 8.5	
HAAFP = AHA formation potential					

Table 21: results obtained after filtration with different nano-filtration membranes
[Siddiqui et al, 2000]

By testing different types of ultra-filtration membranes, Lee et al [2004] showed that the latter are capable of eliminating 55 to 80% of AHA precursors, even with low reduction of dissolved organic carbon.

In a study on different NOM elimination treatments, nano-filtration trials showed over 95% elimination of AHA precursors [Jacangelo et al, *1995*].

Conclusion:

Haloacetic acids are essentially formed during chlorination. Various studies show that their precursors can be partially eliminated by different treatments conventionally used at water treatment plants as well as by membrane filtration. The effectiveness of membrane filtration nonetheless depends on the characteristics of the membrane. Furthermore, it would seem that these compounds, when present at the start of treatment, can be eliminated with GAC operating in biological mode and almost entirely by nano-filtration.

7.3 Treatability of chlorophenols and chloroanisols

In general, clarification techniques have no effect on water tastes and odour. [Sävenhed et al, 1987] studied aluminium sulphate coagulation followed by sand filtration to determine if this treatment is effective in eliminating bad odour and taste in water. They in fact showed that this treatment is ineffective for it cannot remove compounds such as geosmin, 2-MIB, 2,4,6-trichloroanisol which are responsible for bad taste and odour.

In order to optimise this coagulation stage, powdered activated carbon may be added. Tomaszewska et al [2004] showed that "simple" coagulation (without adding PAC) cannot effectively eliminate phenol, (0% elimination yield) regardless of the coagulant dose added (the coagulant was aluminium sulphate) whereas PAC adsorption followed by coagulation eliminated practically 100% of the phenol, as well at pH 6 as at pH 7. It should also be noted that at pH 7, the optimal coagulant dose (3.1 mg Al/L) is lower than at pH 6 (4.6 mg Al/L).

- Ozonation

Ozonation of phenol and its derivatives occurs with degradation of the molecule and more precisely by opening the aromatic cycle for a O3/phenol mole ratio of 5. It may happen that quinine is formed during treatment, in which case the dose must be increased [Doré et al, 1978].

Manojlovic et al [2007] showed that phenol dissolved in bi-distilled water was 98.5% eliminated by ozonation. The same experiment conducted with 4-chlorophenol and 2,4-dichlorophenol resulted in 99.8% and 98.9% elimination respectively. Two identical experiments conducted with Danube water resulted in 80.0% and 83.3% phenol elimination. Each experiment was conducted with compound concentration of 6 mg/L and ozonation rates of 2.6 mg of O3/mg of C for phenol and 2,4-dichlorophenol and 2.0 mg of O3/mg of C for 4-chlorophenol.

A study on oxidation of chlorophenols showed that temperature did not play a role in the degradation of the chlorophenols studied (ie 2-chlorophenol and 4-chlorophenol). According to a study of reactional mechanisms, a radical mechanism occurs. A chlorine atom is lost due to hydroxyl radical action. However, the preponderant mechanism is in fact that of direct oxidation by the ozone of the chlorophenols. PH influences the reactivity of the molecules. When pH goes up, the chlorophenols are in anion phenolate form, which is more reactive to ozone than their corresponding phenol [Boncz et al, 1997].

PH is this a predominant factor in the elimination of phenolic compounds. The higher the pH, the better the elimination of this sort of compounds. This would lead one to think that at high pH, hydroxyl radicals are the predominant oxidising types of phenolic compounds [Gurol et al, 1987].

- Adsorption

A study carried by Radhika et al [2006] with two different activated carbons (one commercial and one prepared with different chemical agents) showed that the effectiveness of activated carbon relative to parachlorophenol and 2,4,6 trichlorophenol was 95% superior for a phenolic compound concentration of 50 mg/L. A study on adsorption of different compounds using bi-distilled de-ionised mother water solutions doped with 500 ppm of each compound, 100 mg of PAC and 200 mL of diluted solution with the de sired concentration were introduced into 250ml beakers and then agitated for 24 hours at 30°C.

The results of this adsorption isotherm presented in Table 22 below show the strong affinity of phenol and chlorophenols for the carbon [Khan et al, 1997].

Compound	Freundlich coefficients ($q_e=kC_e^{1/n}$)	
	k	n
Phenol	1.41	5.30
o-chlorophenol	2.00	4.84
m-chlorophenol	2.07	5.42
p-chlorophenol	2.00	4.89

Table 22: Adsorption of chlorophenols o powdered activated carbon [Khan et al*, 1997]*

A study of the adsorption capacities of the adsorption capacities of different carbons with different initial pollutant concentrations revealed that adsorption isotherms for the 2,4,6 trichlorophenol (TCP) were nonetheless highly dependent on initial concentrations. This phenomenon must be taken into account in determining treatment dosage for it leads to underestimate the dose of carbon to apply to reduce the concentration of this pollutant. For example, an adsorption isotherm produced from an initial concentration of 500 µg/L in TCP led to a dose of 1 mg PAC/L, to reduce a concentration of 10 µg/L to 0.5 µg/L, whereas with a isotherm produced with an initial concentration of 10µg/L the treatment rate is 6.5 mg PAC/L for the same reduction in concentration [Najm et al, 1991].

Adsorption of different components including phenol, 2-chlorophenol and 2,4-dichlorophenol on activated carbon based on apricot pits revealed that phenolic compounds were adsorbed in identical or greater quantities than those obtained using classic activated carbon. This adsorption was related to the dimensions of the molecules adsorbed (molecular weight, molecular volume, surface and diameter). It is also inversely proportional to the solubility and pKa of the phenols [Daifullah et al, 1998].

When pre-chlorination was still used, a study conducted to determine the role of GAC filters in chlorinated by-product formation showed out that phenolic compounds adsorbed on the carbon reacted with the chlorine, producing by-products such as chlorophenols. It was concluded that the GAC played a role of “catalyser” for the formation of these compounds [Voudrlas et al, 1985].

The presence of oxygen during GAC adsorption of phenolic compounds shows an improvement in the adsorption capacity of the carbon compared to anoxic conditions (ie absence of O_2). Vidic et al [1992] also note that the presence of these compounds on GAC makes regeneration difficult.

Works by Chiang et al [1997] on adsorption of different phenolic compounds showed that their adsorption increases with their molecular weight. As for regeneration, its effectiveness by chemical means decreases as the molecular weight of the phenolic compounds increases.

- Membrane filtration

Studies on membrane nano- and reverse-osmosis filtration [Bruchet et al, 2004] have shown that the latter can reduce filtrate 2,4,6-trichlorophenol and 2,4,6-trichloroanisol concentrations to trichloroanisole levels below 0.1ng/L and trichlorophenol levels below 10 ng/L, which are below detection and perception thresholds.

Note: Little has been published on the traceability of this type of compound.

7.4 Conclusion

All of the bibliographical information gathered show that the precursors of THM and haloacetic acids can be reduced on water treatment plants using conventional processes or membrane filtration. As these precursors are not necessarily the same, it is also interesting to note that treatments effective for THM precursors may also be effective for haloacetic acids.

The little information in the literature regarding elimination of chlorophenol precursors does not allow us to conclude that current water treatment is effective, although data on THM and AHA do allow us to think that treatment of these precursors could be effective depending on operating conditions. On the other hand, chlorophenols present at the head of the treatment process could be eliminated by adsorption, ozonation and nano-filtration, thereby minimising the total quantity present in output water.

8 Overall conclusions:

The general purpose of task 5.3.3 of the Techneau project is to study the impact of chlorination on the formation of chlorophenols such as 2,4,6-chlorophenol and haloanisols such as 2,4,6-trichloroanisol generated by methylation at water treatment plants or in water distribution networks.

In fact, the organoleptic qualities of water are dependent on multiple physico-chemical and biological parameters, but the main characteristics to which water consumers are sensitive are colour, taste and odour. As the majority of complaints received concern odorous compounds, analytic techniques have been developed over the last few years to identify them. Research has revealed that chlorophenols and chloroanisoles are important to this problem but the traceability of their precursors in drinking water treatment is still not well known. This will be the subject of our experimental work.

Little information on the elimination of these precursors can be found in the data. Nevertheless, information on treatability collected during the present work show that both THM and haloacetic acid precursors can be partially eliminated by water treatment plants. Treatability of chlorophenol precursors would thus seem to be of interest.

The present bibliographical work has aimed to present the issue of chlorination by-products leading to bad taste and odours. The following main points were made:

- Chlorination is an effective way of eliminating micro-organisms in water distribution networks as its action is remanent. However the drawbacks of this type of disinfection are the generation of unwanted water taste and/or odour as well as the formation of sapid chlorinated by-products by reaction of the chlorine with organic matter.

- As chlorination is the last treatment stage before distribution, by-product precursors must be eliminated upstream in the water treatment process. However, here are a number of inherent difficulties in doing so including: the low olfactory detection threshold of certain compounds as well as the great variability of the organic matter and the multiplicity of possible reactions (detection). In addition, different reactants– chlorine, chlorine dioxide and chloramine may be used and they use may generate more or fewer by-products. Finally, if certain chlorinated compounds occurred in the resource, they would also be treated by the water plant.

- THM and AHA present in the resource may be eliminated by GAC filtration in adsorption mode for THM or biological mode for AHA or by nano-filtration.

  Chlorophenols are not eliminated by this clarification stage. However, adsorption on powdered or granulated activated carbon, ozonation and nano-filtration are effective steps in treating these compounds. This point is important because these compounds eliminated will not add to the compounds generated during chlorination. As no given drinking water

treatment process absolutely eliminates these chlorinated compounds and their precursors, a multi-barrier approach is called for.

- In terms of perspectives, it would seem appropriate to conduct laboratory tests on the possibilities of eliminating precursors of 2,4,6-chlorophenol and 2,4,6-trichloroanisol, which are emerging compounds. This would involve implementing different reactants – sodium hypochlorite, chlorine dioxide and / or monochloramine with lake water exhibiting the referenced taste and odour problems. In principle, this water would be treated by clarification, ozonation, adsorption and nano-filtration. Chlorination before and after treatment should allow us to evaluate the chlorophenol formation potential of this water, which is essential to optimisation of treatment.

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