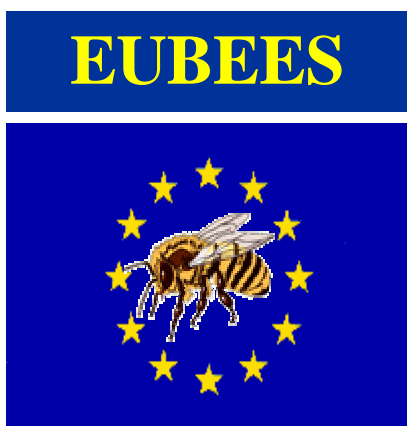


EMISSION SCENARIO DOCUMENT
on
DRINKING WATER DISINFECTANTS
(final version August 2003)

by
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This report has been developed in the context of the EU project "Development of environmental emission scenarios for active substances used in biocidal products" (EUBEES2). The content has been discussed and agreed by the EUBEES working group, consisting of representatives of some Member States, CEFIC and the Commission. The Commission's financial support of the project is gratefully acknowledged (Ref. ENV.C3/SER/2001/0058).

1 Preface

Environmental risk assessment of drinking water disinfectants commences at the mouth of the sewer sampling system. For the vast majority of sewer the receiving “compartment” will be a municipal sewage treatment plant (STP) ¹. The microorganisms of that STP are the first biota to getting exposed to disinfectant residues in the raw water and/or reaction products of those substances. For this reason the influent concentration of the STP is to be estimated and related to adverse effects on microorganisms for purposes of risk assessment.

This Emission Scenario Document was compiled for Product Type 5 of Annex V of Directive 98/8/EC of the European Parliament and the Council of 16 February 1998 concerning the placing of biocidal products on the market. It rests mainly on data from Germany and the situation may be somewhat different for other EU member states. However, it is assumed that the general principles of drinking water disinfection described in this scenario apply throughout all of the EU.

This interpretation draws from the fact that, unlike for other biocide product types, there is a frame legislation regime at EU level (98/83/EC) in place, setting minimum standards for certain ingredients in water for human consumption, including drinking water. Member states may prescribe additional, stricter requirements, where considered necessary – and some did so. Although aspects of human health protection drive the criteria, they also are suitable to prevent the environment from relevant risks. This holds true at least for the few currently used substances. Along with these limits, there exists (e.g. in the German Drinking Water Ordinance of 21st May 2001) a list of substances recommended by the Competent Authority that may be used by public water suppliers.

Elaborating an ESD for environmental exposure on drinking water disinfectants is very unusual and unique. It seems that all of the very reactive active ingredients will be used up during use or subsequently in the municipal canal sewer system. The data presented in this document should be regarded as illustrative and should be updated as more specific information becomes available within the review programme on existing biocidal substances.

All presently employed drinking water disinfectants are highly reactive chemicals. Although lacking final analytical evidence it is assumed that, on its way to the STP almost the entire residues of the active substances will be “consumed” by the abundant organic matter contained in the wastewater. On the other side quite a bunch of generally unidentified (transient?) reaction products can be expected. Hardly any general information can be given, neither on the identities of those artefacts nor on their concentrations. Specific information on the fate of each individual drinking water disinfectant must be given in the dossier. In addition, there are established monitoring systems, which ensure that drinking water meets the requirements of the respective national drinking water regulations. It is within the responsibility of the water distribution companies to verify that the quality of the drinking water obeys the quality standards laid down in the Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption (rf.[4])

¹ M.P. Vall, Abwasser in den europäischen Staaten – Von der Abwassersammlung und –behandlung zur Abwasserleitung. In: Statistik kurz gefasst – Umwelt und Energie, Thema 8 – 14/2001, EUROSTAT, ISSN 1562-3092, http://www.eu-datashop.de/download/EN/sta_kurz/thema8/nq_01_14.pdf: „77% of the EU population are connected to a public municipal sewage treatment plant.“

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1 Introduction

Water for human consumption is abstracted mainly from surface water (rivers, reservoirs) or from groundwater. The average abstraction in the EU15 countries is $659 \text{ m}^3 \cdot \text{capita}^{-1} \cdot \text{yr}^{-1}$ for all uses [1] though there are large variations between countries and usage pattern. On average about 14 % are consumed by urban water demand, the remaining part is demanded by other sectors; among those the most dominant are agriculture (30 %), industry (10 %) and energy (25 % hydropower and cooling water for power generation).

Table 1: Share of urban water abstraction in total abstraction in 1995 [1]

	Share of water for urban use in total abstraction			Share of water for urban use in total abstraction	
	$\times 10^6 \cdot \text{m}^3$	%		$\times 10^6 \cdot \text{m}^3$	%
Austria	786	33.3	Italy	7 980	14.2
Belgium	744	10.6	Luxembourg	35	58.9
Denmark	449	49	Netherlands	1 014	8.0
Finland	421	12.6	Portugal	576	7.9
France	5 946	14.6	Spain	4 667	13.2
Germany	3 826	6.5	Sweden	937	34.6
Greece	615	12.2	U.K.	6 337	52.3
Ireland	470	38.8	EU 15	34 803	14.1

There are considerable differences in drinking water consumption between EU Member States:

Table 2: Water consumption by households and small business in the EU [2]

	year	$10^6 \cdot \text{m}^3$	$\text{m}^3 \cdot \text{capita}^{-1} \cdot \text{yr}^{-1}$	% of public water consumption
Belgium	1998	381	41	68
Denmark	1994	301	58	61
Germany	1995	3 872	47	76
Greece	1997	670	64	
Spain	1995	2 849	73	94
France	1994	2 384	41	
Ireland				
Italy	1995	4 400	78	77
Luxembourg	1999	23	55	64
Netherlands	1996	733	47	59
Austria	1997	456	56	75
Portugal	1998	680	71	
Finland	1999	404	78	100
Sweden	1995	528	60	56
U.K.				

In countries with sufficient aquifers, over 75 % of the water for public water supply is abstracted from groundwater. Groundwater is generally of superior quality to surface water and requires less treatment. In the case of surface water, pre-treatment such as coagulation, sedimentation and filtration is generally used to prepare the water before its final disinfection. Hence, apt protective measures and management of raw water reservoirs are capable of minimising need for chemical disinfection of the drinking water.

One peculiarity of product type 5 of the biocidal products directive is the fact that specific quality standards are set up for water intended for human consumption. This means that only substances may get approval which have demonstrated that according to use instructions do not cause harm to human health.

For reasons of completeness some techniques of drinking water disinfection are included in this document which are actually not covered by the Biocidal Products Directive: these are all physical treatments but also in-situ generation of ozone.

2 General background information

2.1 Legislation

Ensuring the microbiological safety of the drinking water is of paramount importance. Hence it is subject to high standards ensuring the safety of drinking water through the elimination, or reduction to a minimum concentration, of constituents that are known to be hazardous to health, i.e. physical, microbiological and radiological contaminants [3]. According to EU legislation (Annex I to Directive 98/83/EC [4]) water intended for human consumption shall be free from microorganisms and parasites or other substances that may pose danger to human health. The Directive concerns the quality of water intended for drinking, cooking and food preparation whether from distribution systems, tanker, bottles or containers. Methods of treatment, encompassing disinfections, shall ensure that water conforms to the Directive. The requirements are laid down in Annex I to the Directive (parts A and B), together with parameters for monitoring (part C). Standards apply at the point where water emerges e.g. from the tap or at the point of use in food production. The Competent Authority regularly monitors the water in order to warrant that the quality standards are met. Member states may prescribe additional, stricter requirements, where considered necessary for human health protection. Indicator organisms like coliform bacteria and faecal streptococci are used as indicators to monitor routinely the water for harmful contamination prior to dumping it into the distribution system.

2.2 Types of Drinking Water Disinfections

Three main types of disinfection processes may be distinguished:

- Primary disinfection: The main purpose is to kill the vast majority of microorganisms in order to prevent them to disturb further steps in the treatment process (clogging of filters/membranes); in many cases preceded by removal of organic matter and excess of inorganic ingredients (Fe, Mn)
- Residual disinfection: Routine application in order to maintain an anti-microbial potential in the distribution system
- Stand-by disinfection: High dosage-application to clean up a contaminated system or when taking a new system into use

The mode of action of most of the disinfectants applied is based on their strong oxidizing property. Prior to application of the disinfectant it is highly recommended to reduce any organic and inorganic compounds (e.g. phosphorous) as much as possible as these substances may serve not only as nutrient source for microorganisms but also consume considerable

portions of the disinfectant. Additionally, they may reduce access of the disinfectant to the target organisms, e.g. by enclosing the cells or spores.

For environmental risk assessment of drinking water disinfectants

- the active ingredients itself,
- the reduced degradation products and
- by-products potentially formed during reactions with organic compounds present in the drinking water

should be subject of consideration.

To this end it should be clearly stated that any reasonable effort should be taken to abstain from routine disinfection of drinking water by providing clean resource waters.

3 Active Substances applied

The most important chemical disinfection methods currently used comprise [5]

- chlorination with salts of hypochlorous acid
- chlorination with ClO₂
- ozone treatment (in-situ generation of ozone is not covered by BDP)
- treatment with hydrogen peroxide
- silver salts (small scale)
- potassium-/sodium-dichlor-isocyanurate (small scale)
- potassium permanganate: KMnO₄ (small scale)
- iodine (small scale).

The most important physical treatments, not covered by the Biocidal Products Directive, are :

- filtration
- UV radiation
- coagulation / flocculation.

Even if it is a small number of substances used for drinking water disinfectant purposes there is wide (temporal) variation in concentrations of substance(s) applied or combinations of chemical and physical treatments among the water suppliers. Beside economic grounds, easy-to-use considerations and reliability of the systems, the choice of an appropriate process depends mainly on the source water characteristics, e.g. concentration and seasonal variance of undesired ingredients, pH, etc.)

Table 3: The biocidal efficiency, the stability, and the effects of pH on the efficiency of some disinfectants [6].

Disinfectant	Biocidal Efficiency*	Stability*	Effect of the pH Efficiency (pH = 6-9)
Ozone	1	4	little influence
Chlorine Dioxide	2	2	efficiency slightly increases with the increase of pH
Chlorine	3	3	efficiency decreases considerably with the increase of pH
Chloramines	4	1	little influence

* The indicated characteristics decreases from 1 to 4 (1 is the maximum, 4 the minimum)

NOTE: Although data are provided in this document on the most commonly used disinfectants, this does not absolve applicants from providing a full dossier encompassing all endpoints, and the data provided in that dossier will be used for emission estimation and risk assessment.

3.1 Chlorine

3.1.1 Chemistry

Chlorine and chlorine compounds are strong oxidizing agents. Thus their reactivity can be easily dissipated in reactions with organic and inorganic materials in water before efficient disinfection can occur. Additionally they effectively oxidizes undesired flavour and odour compounds of source water. Accurate dosing of disinfectant is therefore of utmost importance to ensure efficacy throughout the water distribution system while at the same avoiding excessive over-dosing. A balance must be struck between reducing risks from microbial contamination of drinking water and the potential increase in risk from chemical contaminants that result from using any of the disinfectants.

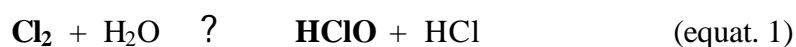
Chlorine is either directly fed to the drinking water or indirectly, i.e. as a solution in water. Addition of chlorine gas to pure water results in the formation of a mixture of hydrochloric acid (HCl) and hypochlorous acid (HOCl) according to law of mass action:

$$k = \frac{[HOCl] \times [H^+] \times [Cl^-]}{[Cl_2]}$$

Table 4: Equilibrium constant k for chlorine at equilibrium [7]

Temperature [°C]	Equilibrium constant k x 10 ⁴
0	1,46
15	2,81
25	3,94
35	5,10
45	6,05

The following reactions occur when chlorine is added to water (biocidal active species are in bold letters):



The disproportionation reaction of chlorine in the near-neutral pH region (equat. 1) runs in a nearly quantitative manner and is completed within seconds (cf. Table 4). Cl₂ is only prevailing at pH < 3 (rf. Figure 1).

The hypochlorous acid HClO in its non-dissociated form, predominant in the pH 5-7 region, is a more powerful oxidant than the hypochlorite anion (OCl⁻) and chlorine. The degree of dissociation is therefore important for disinfection efficacy. It strongly depends on the pH (rf. Figure 1) and much less on temperature. Dissociation is poor at pH levels below 6. From pH 6 to 8.5 a nearly complete dissociation of HClO occurs. Thus for disinfection with chlorine

control of pH is critical: As a consequence, an increasing pH of the potable water requires rising amounts of chlorine for the same disinfection efficacy. Equation (5) plays a minor role, although atomic oxygen is an also a very potent oxidizing (thus also disinfecting) agent.

3.1.2 Definitions of Chemical Terms

3.1.2.1 "Available Chlorine"

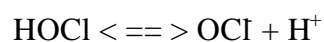
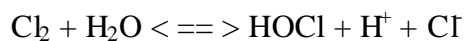
"Available chlorine" is a measurement of oxidizing capacity, expressed in terms of the equivalent amount of elemental chlorine. E.g. the concentration of hypochlorite may be expressed as available chlorine by determining the electrochemical equivalent amount of Cl_2 to that compound.

3.1.2.2 "Chlorine Demand"

In chlorination of the water a certain part of chlorine will be consumed by water impurities (Fe^{++} , Mn^{++} , NO_2^- , H_2S , organic matter) and by the piping system. The difference between the applied chlorine amount and the chlorine remaining in the water may be referred to as "chlorine demand".

3.1.2.3 "Free available Chlorine"

When elemental chlorine is dissolved in water, an equilibrium is established between chlorine, hypochlorous acid, and hypochlorite ion (Cl_2 , HOCl and OCl^- , respectively). The relative amount of each present depends primarily on the pH of the system.



The chlorine as HOCl and OCl^- is referred to as free available chlorine

3.1.2.4 "Combined Available Chlorine"

Nitrogen-containing compounds such as ammonia, amines and proteins are usually present in municipal wastewater. Free available chlorine reacts readily with these materials to form chloramines in which the chlorine is described as combined available chlorine.

3.1.2.5 "Total Residual (Available) Chlorine"

Collective term for free and combined available chlorine. Residual chlorine is found in many chemical forms in water systems. Residuals in clean water are often predominantly free chlorine while wastewater and chloraminated water can contain mixtures of free chlorine, combined chlorine and organochlorine species. Measurement of residual chlorine can be relatively difficult where a variety of chlorine forms exist and a measurement of "Total Residual Chlorine" is often required. This total chlorine measurement is normally done by reacting the chlorine in a water sample, buffered to pH 4, with potassium iodide. All of the various chlorine compounds react with the iodide to release an equivalent amount of iodine and the released iodine is measured.

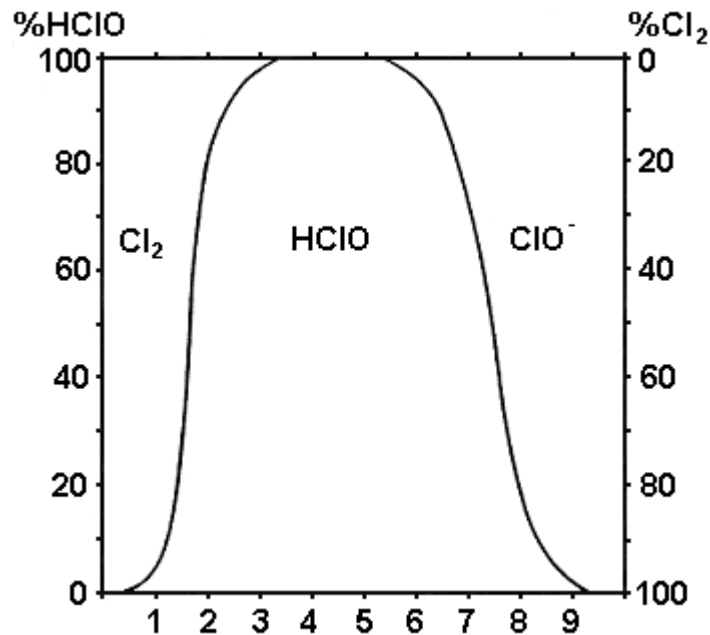


Figure 1: Dependence of non-dissociated hypochlorous acid on pH value (ordinate)

Disinfection efficacy is mainly determined by dose and time of contact, since the diffusion velocity through the membranes of bacteria or viruses controls it:

$$N = N_0 - 10^{-kt} \quad \text{or} \quad \lg \frac{N}{N_0} = -kt$$

with:

- N_0 initial number of microorganisms
- N final number of microorganisms
- t time for elimination
- k susceptibility constant.

3.1.3 Dosing

Chlorine is added to water either in its gaseous form or for ease of dosage after preparing a hypochlorite/hypochlorous acid solution by adding gaseous chlorine to an aqueous solution of NaOH.

The proper chlorine dosage depends upon a number of factors including:

- chlorine demand
- residual
- contact period
- temperature
- pH

There is no way to determine the required dosage directly without experimentation.

The amount of chlorine added to water depends on the specific content of oxidizable compounds, the amount needed to kill the microorganisms, plus a sufficient reserve to maintain a minimum concentration of “free available chlorine” at each point in the water pipe

(breakpoint). To keep up this requirement the range for chlorine dosage is about 0.1 mg.l⁻¹ for groundwater and up to 0.5 mg.l⁻¹ for surface water.

3.1.4 Pre-ammonisation

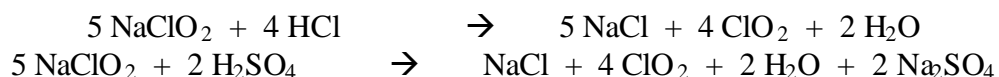
Hypochlorous acid is a very reactive compound. Therefore its concentration in the drinking water is continuously decreasing over time. In order to retain some of its disinfecting power in remote areas of extended distribution systems ammonia or ammonium salts may be added to the water to form N-chloro-compounds like monochloramine, dichloramine, trichloramine, etc. These compounds, also known as “combined available chlorine”, form a stable biocidal residual in the entire distribution system. Although, as compared to free available chlorine, combined available chlorine is much less efficient at a given level. It is useful to retain such a residual throughout the system to prevent re-infection.

Depending on the pH of the water different proportions of chlorinated amines are formed thereof, spanning a range for predominance of monochloro amine (NH₂Cl) at pH 8.5 and of trichloro amine (NCl₃) at pH 4. At pH 7 a mixture of monochloro amine and dichloro amine is prevailing.

Conversion of free available chlorine to combined available chlorine by means of adding ammonia prevents also from formation of chlorinated phenols (offensive odour and taste).

3.2 Chlorine Dioxide

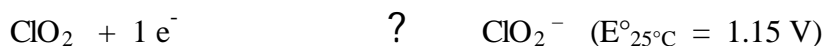
Chlorine dioxide (ClO₂) is most widely used in drinking water supplies as a very effective disinfectant as well as for oxidizing purposes (oxidation potential: 0.95 V). Unlike chlorine, chlorine dioxide remains a true gas dissolved in solution. Chlorine dioxide is clearly superior to chlorine in the destruction of spores, bacteria, viruses and other pathogen organisms on an equal residual base. Since gaseous chlorine dioxide is explosive (light, temperature) at concentrations > 300 g.m⁻³ (20 °C) and in aqueous solutions of > 30 g.l⁻¹ water, it is generated in aqueous solution on site (CIP)² mostly from reaction of chlorite (e.g. NaClO₂) and an oxidizing agent like mineral acids (HCl; H₂SO₄) according to



or like Cl₂ :



The oxidizing action of chlorine dioxide is based on strong electron affinity. Chlorite (ClO₂⁻) and chloride anions (Cl⁻) are the prevailing species arising from oxidation of organic matter by chlorine dioxide.



The lack of any significant reaction of chlorine dioxide with water is partly responsible for its retaining its biocidal effectiveness over a wide pH range [8] (cf. [Figure 2](#)).

² Clean In Place

INFLUENCE OF pH ON Cl₂ AND ClO₂ PERFORMANCE

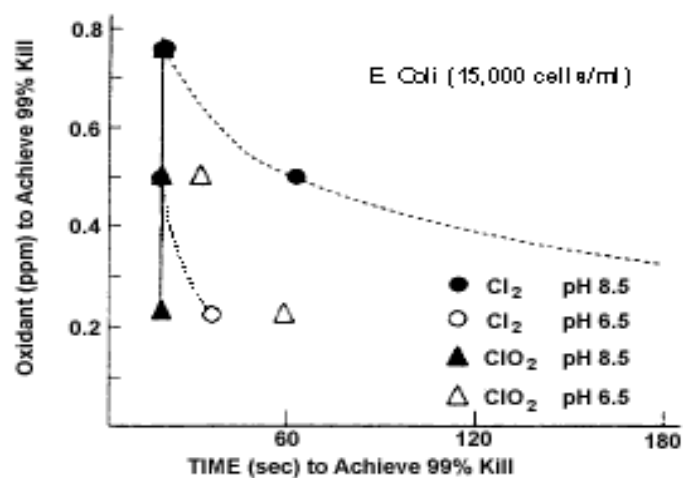


Figure 2: Disinfection Efficiencies of ClO₂ with Cl₂ at pH 6.5 and 8.5

On the other side, under specific circumstances chlorite may be formed from chlorine dioxide:



or chlorine dioxide disproportionates in basic solution forming chlorate anion [9].



This production of chlorate is the main disadvantage of chlorine dioxide as a water disinfection agent [10]. The amount of chlorate produced can be reduced by using hypochlorite solutions of less than 10% available chlorine in the disinfection step [11]. Even though being a highly active biocide (about 80-fold that of chlorine [12]) its main application is for decolourisation and organoleptic correction of the finished water by control of odour and taste problems. It also has a better performance in virucidal and sporicidal action.

Chlorine dioxide does not react as readily as chlorine with humic acids and other organic compounds; causing less problems of trihalomethanes formation during chlorine dioxide disinfection [13]. On the other hand potential adverse effects may result from the by-products chlorate and chlorite anion.

Typically, chlorine dioxide is used at concentration levels between 0.1 and 2.0 mg.l⁻¹ for water treatment [14]. In some cases the chlorine dioxide treatment is complemented by subsequent application of (small dose of) free chlorine.

3.3 Iodine

Iodine is an excellent prompt effective microbiocide with a broad range of action. The combination of unfavourable economies (costs about 20 times than chlorine) and possibly deleterious effects health effects on individuals with thyroid problems makes continuous use unwarranted for large public water suppliers. However, iodine disinfection has been studied intensively as an emergency drinking water disinfectant or as a disinfectant for small

individual supplies, transient emergency situations, and preliminary military or as "pocket purifier" for travellers. [15]. Iodine is used similarly as chlorine:



Like for chlorine the equilibrium strongly depends on the pH. At pH 5 about 99 % is present as molecular iodine while 88 % are present as hypoiodous acid at pH 8. Effective concentrations for iodine/hypoiodous acid are in a range of 0.25 – 2.5 mg.l⁻¹ [16]

3.4 Ozone

Note: In-situ generation of ozone (O₃) is not covered by the BPD. Nevertheless for reasons of completeness it is included here.

Ozone is a very powerful oxidizing agent (at a potential of + 2.07 V stronger than chlorine, chlorine dioxide or hypochlorous acid). For safe disinfections a concentration of 0.3 – 0.4 mg.l⁻¹ at a contact time of 4 minutes is recommended.

Ozone is generated on site by electronic corona discharge in pure oxygen or in air.

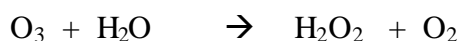
Accomplished concentrations in this endothermic process are around 50 g.m⁻³ from air and 100 g.m⁻³ from oxygen. The gas is dissolved in water in proportion to its partial pressure in the overlaying gas phase:

Table 5: Solubility of ozone in water (at 10 g.m⁻³ in the head space) [17]

Temperature [°C]	Water solubility [mg.l ⁻¹]
5	4.4
10	3.8
20	2.9

In acidic solution the ozone molecule is the active ingredient; at increasing pH OH⁻ radicals are formed from ozone that cause the oxidizing effects. For oxidation of organic traces in the water 0.5 – 3.0 mg.l⁻¹ ozone are normally required, corresponding to 0.5 – 1,5 g ozone. g⁻¹ DOC. Due to its toxicity the residues of ozone must not exceed 0.05 mg.l⁻¹. In order to comply with this limit residues have to be reduced either by adding reducing agents (sulfites or sodium thiosulfate) or combined with subsequent sand filtration passage and/or an adsorption step (activated carbon).

Surpluses of ozone may be transformed to hydrogen peroxide according to:



H₂O₂ is also a very potent oxidizing agent and thus of strong germicidal power. The high reactivity prevents a lasting concentration in extended water pipe systems from the feeding point until the final tap; a collateral chlorination is often required.

Ozone decomposes relatively fast in water, making it a less suitable agent for extended distribution systems. For this reason ozone is often used for instant disinfection, demanding (substantially reduced) addition of chlorine, to retain a necessary residual.

3.5 Potassium Permanganate

KMnO₄ is normally employed as an oxidizing agent, but not for disinfectant purposes in the final step of drinking water treatment. For concrete-lined distribution pipes, which are to be put on stream for the first time 50 mg.m⁻³ for 12–24 hours, are recommended to clean up the system.

Beside its bactericidal efficacy, KMnO₄ is also effective against filamentous algae. 0.5–2.0 g.m⁻³ are therefore used to control those species in infiltration and reaction basins. Its impact is thereby based on a combination of toxicity, light attenuation, combined flocculation of algae and Mn(IV)oxyhydrate [18].

3.6 Silver

Metal ions adsorb to membranes of bacteria, causing lethal effects. Silver salts are commonly employed for this purpose. This oligodynamic effect requires higher contact time (several hours) and causes significantly higher costs than other disinfection methods. As a result they are normally restricted to special smaller case applications or mobile set-ups, like conservation of water tanks on ships (also for preservation), spare time activities, emergency measures, etc. In some cases Ag⁺ is applied as catalytic component in special “systems” containing H₂O₂. Concentrations of silver in the water should not exceed 80 µg.l⁻¹.

3.7 Isocyanuric Acid Compounds

These products (sodium dichloroisocyanurate dihydrate / anhydrous, trichloroisocyanurate) are employed only in rare cases: Either in case of emergency (flood, earthquake etc.) or for disinfection and cleaning of waterworks apparatus and distribution systems.

The final concentrations in the water used to wash installations do not exceed 1000 mg.l⁻¹ of free chlorine. After cleaning and disinfection, the installation is flushed to ensure that the residual concentration is acceptable to consumers. Permission or consent for disposal of wastewater generated to the sewer must be obtained from the local water authorities.

For emergency use and grossly contaminated water sources sodium dichloroisocyanurate and potassium dichloroisocyanurate are recommended at 20 – 40 mg.l⁻¹ as a minimum for safe antimicrobial effect, if the water sources are grossly contaminated. They are formulated as easy-to-use tablets for dosing e.g. 1 litre. It is recommended that consumers should be exposed to this treated water for only as long as is required to restore conventional treatment.

3.8 Physical Disinfection Methods

Although not involving biocides these methods are mentioned also. UV irradiation and membrane processes are increasingly used to replace, or at least greatly reduce, the use of chemical disinfection.

For some biocides incubation periods of about 48 hours are necessary to prove microbial infection of drinking water systems, while physical treatments are of immediate action.

Unlike chlorination the continuously operating physical disinfection techniques also prevent from unperceived microbial contamination. Furthermore, no undesired by-products are formed from disinfectants (e.g. trihalomethanes). Before operating without residual disinfectant, considerable renovation and cleaning may be required to prevent from serious post-treatment contamination. In some cases a low dose of chemical disinfectant is still added to provide a residual in distribution.

3.8.1 UV radiation

The short-wave radiation spectrum of mercury lamps (e.g. λ = 254 nm) is employed to cause lethal damage to the DNA of microbes. The raw water should (normally) be pre-treated (coagulation/flocculation) in order to minimise light attenuation from suspended matter or

iron content. The necessary dose is a function of radiation intensity (about 40 mJ.cm^{-2}) and duration of impact (few seconds).

3.8.2 Micro-filtration

A range of pressure-driven membrane processes – micro-filtration, ultra-filtration, nano-filtration, reverse osmosis - in order of decreasing pore size- are also capable of disinfection as well as retention of chemical contamination, depending on pore size. In particular at multi-stage facilities and combined with UV radiation or ozonisation they are capable of producing drinking water quality from polluted reservoirs and/or salty source water.

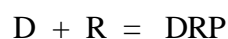
4 Exposure Estimation For Sewage Treatment Plants (STP)

4.1 Disinfection

Decay of residual disinfectants starts after leaving the tap during domestic application, in the sewer, in the sewage treatment plant and in the river receiving the discharge of the STP. Yet the microorganisms of the STP are the primary non-target organisms to be protected. In a first simplified approach on estimating the exposure of STP microorganisms it can be assumed that:

- the recommended maximum concentration of disinfectant residual is assumed to leave the tap,
- the STP is exclusively fed by water originating from the water supply (no dilution from precipitation),
- during use (washing, cooking, toilet flushing, etc.) and in the municipal canal sewer system it can be expected that the disinfectant be in contact with an excessive surplus of dissolved and suspended organic matter³,
- decomposition during residence time in the municipal canal sewer system is taken into account,
- the residence time (time for biotic/abiotic degradation) in the municipal canal sewer system from the tap (in the household) to the STP is assumed to be one hour. This assumption is based upon the average distance of 4.5 km from the household to the STP and an estimated flow rate of 1.5 km in 20 minutes in the municipal canal sewer system. The temperature of the wastewater being $12 \text{ }^\circ\text{C}$ on average.

The following “reaction” (disappearance of the disinfectant) is assumed:



where is:

D = disinfectant

R = any reactants in municipal canal sewer system

DRP = disinfectant reaction product entering the STP.

The kinetic equation for the influent concentration into the STP is:

³ The chemical oxygen demand of drinking water, expressed in $\text{mg.l}^{-1} \text{O}_2$ [measured by consumption rate of potassium permanganate] should not exceed 5 mg.l^{-1} .

$$\frac{dC_{\text{influent}}}{dt} = -kC_{\text{drinkingwater}}$$

$$C_{\text{influent}} = C_{\text{drinkingwater}} * e^{-kt}$$

with:

Variable	Symbol	unit	default	S/D/O/P
INPUT				
Maximum concentration of disinfectant in drinking water at the tap	$C_{\text{drinking water}}$	mg.l ⁻¹	P	P
Reaction rate constant in sewer system	k	d ⁻¹		S *
Residence time in municipal sewer system	T	hr	1	D
OUTPUT				
Influent concentration of disinfectant in STP	C_{influent}	mg.l ⁻¹		O

S = data set from applicant, D = default, O = output, P = pick list (e.g. Table 6).

* **Note:** Due to the heterogenous and varying composition of raw waters such rate constant can normally be just estimated, e.g. by measuring rates with “reference” components, or drawing from efficacy data.

In a more in-depth approach kinetic models may be applied to estimate decay of the disinfectant and its reaction products. Yet this requires consideration of various related reaction steps and includes apt data for rate constants. As an example it is referred to the risk assessment for sodium hypochlorite within the EU risk assessment for existing chemicals (Annex II to this document). The authors of that model estimated a quick elimination of NaOCl/CLO⁻ ("free available chlorine" or FAC) during transport in the sewer. From the abundance of reduced reaction partners in the waste water and high rate constants they estimated that FAC would drop to 10⁻³² µg.l⁻¹ at the end of the sewer. Among other reacting products chloramines are formed which itself is very reactive and acts as an oxidiser of reduced (in)organics thus being used up in the sewer and in the activated sludge. For assessing risk to STP microorganisms the standardised STP parameters from the Technical Guidance Document 2003 [19] shall apply, respectively. As already mentioned, there is a wide span for type and concentration as well as combination of chemical disinfectants applied by public water suppliers over Europe, including temporal variations within the same work. In Table 4.1 a range is given for most common concentrations that can be expected as reasonable worst-case concentrations (= $C_{\text{drinkingwater}}$) for exposure assessment.

Table 6: Default values for disinfectant residuals in tap water

"free available chlorine"	0.3 – (0.6) mg.l ⁻¹
chlorine dioxide	0.1 – 2.0 mg.l ⁻¹
Ozone	0.05 mg.l ⁻¹

For the existing drinking water disinfectant actives it is expected that the reaction rate constant k is as high as to avert any relevant residual of the active ingredient in the wastewater

on entering the STP tanks. At normal operating conditions potential minor remainings are then – at the latest - either “consumed up” by the organic matter in the primary settler or released to the atmosphere. So, there is a sort of staggered system of barriers, which minimises disinfectant residues from entering the aquatic environment. This expectation gets true evidence from day-to-day practice in running municipal STPs all over the EU.

Note: The Technical Guidance Document for Risk Assessment foresees that on a local scale all waste water is collected in a sewer system and subsequently undergoes treatment. In some cases it may be appropriate to assume that no connection to a public sewerage system be in place, thus public waste water is directly discharged to surface water. The residual concentrations (efficacy data provided by applicator) should be used as starting concentration for further risk consideration.

4.2 Disinfestation / Disinfection of Distribution System

As a worst-case it can be assumed that microbial contamination has been observed, or a pipe burst has occurred which requires immediate remedial measure to restore quality standards. A tenfold concentration of disinfectant concentration is assumed to be applied for this purpose ("super chlorination"). Unlike for routine dosage, this application is an irregular one and can be classified as intermittent release type (duration less than 24 hours, less than once per month).

Such (smaller scale) operations are undertaken only in selected sectors of the distribution system since the concentration of the disinfectant in the water exceeds the limits set in national drinking water legislation. Hence, the water is collected separately after required contact time and either pre-treated or diluted prior to release to the drain. In addition shock treatments require to clean equipment are followed by extended rinsing steps. Permission or consent for disposal of any wastewater generated to a sewer or watercourse must be obtained from the relevant water Service Company or environmental authority, as appropriate.

5 Disinfection By-Products

Dosing highly reactive species like hypochlorous acid, ozone or chlorine to water does not mean selective reaction with target organisms but also causes reaction with other organic and inorganic constituents of the water (mainly fulvic and humic acids) ([20], [21], [22]) forming low-molecular weight compounds from cracking of larger organic molecules [23] and/or chlorination reactions. This may render previously “harmless” substances to potentially "harmful". There are numerous by-products of water disinfections [23] that are still not fully understood and can be potentially harmful [24]. Some of these substances, e.g. trihalomethanes, generated during chlorination or bromate (BrO_3^-), formed from bromide during ozone treatment are proven or suspected to be potent carcinogens. Though present in the water generally in very low concentrations, daily ingestion by humans or continuous exposure of the environment may cause a risk on the long run.

Concentration of such by-products formed during disinfection treatment can be controlled by minimizing DOC^4 content. Hence, not only for saving disinfectant costs any reasonable attempt should be undertaken to remove precursor compounds prior to adding the disinfectant. Disinfections should not compensate for poor water treatment quality.

According to Directive 98/83/EC on quality of water for human consumption the following concentration limits for volatile chlorinated hydrocarbons should not be exceeded:

⁴ Dissolved Organic Carbon

Table 7: Standards for maximum concentration limits of trihalomethanes, set out in Directive 98/83/EC

<u>S TRIHALOMETHANES</u> - trichloromethane (chloroform) - dichlorobromomethane - chlorodibromomethane - tribromomethane (bromoform)	100 µg.Γ ⁻⁵⁾
tetrachloroethene + trichloroethene	10 µg.Γ ⁻¹
1,2 dichloroethane	3 µg.Γ ⁻¹

The kinetics of reaction products formed in the reaction of the disinfectant with water constituents should be provided in the dossier qualitatively, preferably quantitatively and, according to the BPD, the applicant should assess the risks of by-products formed. In principle two types of reaction pattern can be distinguished:

- the reaction by-product (S) is environmentally stable and does not degrade further, or
- the reaction by-product (S) is environmentally instable and does degrade further (Figure 3).

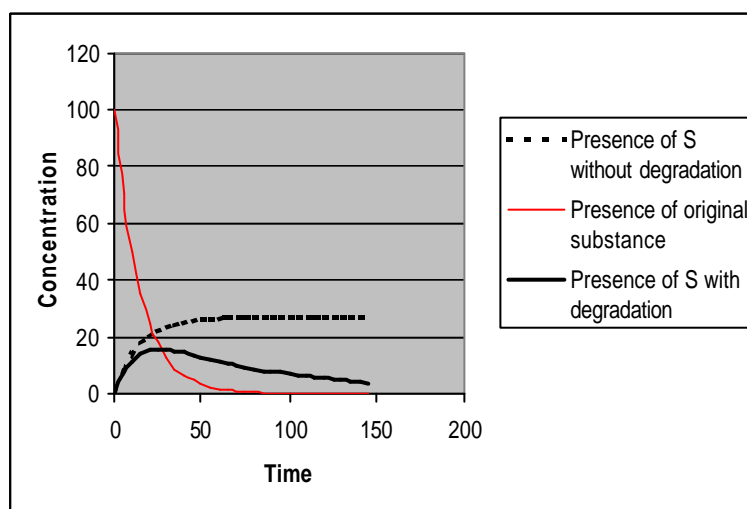


Figure 3: Decay of original substance (disinfectant) and occurrence of degradable or non-degradable by-product (S)

⁵ "must not" from 24 November 2008 (during 24 November 2003 : 150 µg.Γ⁻¹)

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Annex I

Human-health based limits for drinking water quality (WHO 1996 [22]); some of the values are of provisional value, no figure given means that no adequate data to permit recommendation are available.

Disinfectants	Guideline value (mg.l⁻¹)
monochloro amine	3
di- and trichloro amines	
Chlorine	For effective disinfection there should be a residual concentration of free chlorine of = 0.5 mg.l ⁻¹ after at least 30 minutes contact time at pH <8.
chlorine dioxide	A guideline value has not been established because of the rapid breakdown of chlorine dioxide and because the chlorite guideline value is adequately protective for potential toxicity from chlorine dioxide
Iodine	
Disinfectant by-products	Guideline value µg.l⁻¹)
bromate	25
chlorate	
chlorite	200
Chlorophenols	
2-chlorophenol	
2,4-dichlorophenol	
2,4,6-trichlorophenol	200
formaldehyde	900
trihalomethanes	The sum of the ratio of the concentration of each to its respective guideline value should not exceed 1
bromoform	100

Disinfectants	Guideline value (mg.l⁻¹)
dibromochloromethane	100
bromodichloromethane	60
chloroform	200
Chlorinated acetic acids	
monochloroacetic acid	
dichloroacetic acid	50
trichloroacetic acid	100
chloral hydrate (trichloroacetaldehyde)	10
chloroacetone	
Halogenated acetonitriles	
dichloroacetonitrile	90
dibromoacetonitrile	100
bromochloroacetonitrile	
trichloroacetonitrile	1
cyanogen chloride (as CN)	70
chloropicrin	

WHO recommendation for microbiological quality of drinking water (1996):

Organisms	Guideline value
All water intended for drinking	
<i>E. coli</i> or thermotolerant coliform bacteria	Must not be detectable in any 100- mL sample
Treated water entering the distribution system	
<i>E. coli</i> or thermotolerant coliform	Must not be detectable in any 100- mL

bacteria	sample
Total coliform bacteria	Must not be detectable in any 100- mL sample
Treated water in the distribution system	
<i>E. coli</i> or thermotolerant coliform bacteria	Must not be detectable in any 100- mL sample
Total coliform bacteria	Must not be detectable in any 100- mL sample. In the case of large supplies, where sufficient samples are examined, must not be present in 95% of samples taken throughout any 12- month period

Annex II

Kinetic Model on the Long Term Hypochlorite Decay in the Environment

A Specific Model for Use in the HOCl Risk Assessment

Vincent Vandepitte and Diederik Schowanek

Poster presentation at the IAWQ 19th Biennial International Conference, Vancouver, Canada (1998)

INTRODUCTION

Questions about the environmental effects of residual oxidants resulting from domestic or industrial use of hypochlorite has prompted efforts to model the decay of hypochlorite in the environment. There have been several efforts to model the kinetics of chlorine decay in estuarine and sea water near power plants (Lietzke 1975; Abarnou and Miossec, 1991;). However, the availability of reports dealing with the decay of HOCl (Free Available Chlorine (FAC)) and NH_2Cl (Combined Available Chlorine (CAC)) in river water is much less (Heinemann et al., 1975). There is hardly any data available on the disappearance of HOCl in sewage and activated sludge (Haas and Karra, 1984). In general, described models to simulate TRO (total residual oxidant (= CAC+FAC)) in the environment are empirical i.e. they are mathematical descriptions which are not related to the mechanisms driving the TRO decay (Heinemann et al., 1975; Qualls and Johnson, 1983; Haas and Karra, 1984; Yamamoto et al., 1988). The here proposed model is at the contrary chemical reactions based and tries to model the real chemical processes involved in the environmental decay of TRO. The advantage of models based on chemical reactions is that these apply at any concentration.

OBJECTIVE

The general objective of this study was to develop 1) a simple but relatively accurate kinetic model that could predict the consumption of HOCl in the sewer, the activated sludge unit and the river and 2) to predict the concentration TRO below analytical detection limits (i.e. $\pm 10 \mu\text{g.l}^{-1}$ in environmental samples).

Material and methods

Model setup

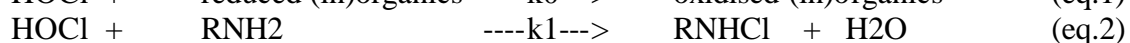
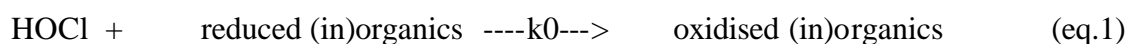
HOCl decay in the environment occurs in 4 "environmental compartments": 1) during use, 2) during sewer transport, 3) during sewage treatment, and 4) in surface water (characterised by a dilution phase). Every environmental compartment is characterised by the presence of specific reaction partners and a specific reaction time. Overall, HOCl decay can be described by the following chemical reactions (eq 1-5). This is a purely chemical process, no biodegradation occurs.

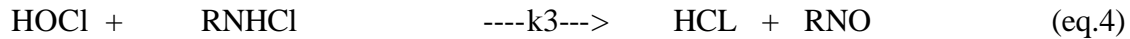
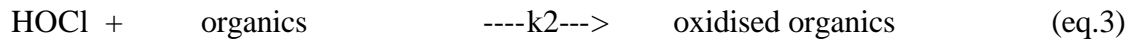
Simplification

For simplification and especially to avoid over-parameterisation of the model it was assumed that 1) the pH was 7 and that 2) The reaction products of HOCl with NH_3 were limited to NH_2Cl or its organic form as these will be the predominant species in the environment.

Conservatism

Some other additional simplification assumptions were chosen in the interest of the conservatism of the model. They are 1) No decay of HOCl during the use phase; 2) No volatilisation of FAC/CAC and 3) No decay of FAC/CAC due to light. The results of the model is therefore only a conservative approximation and will generally give an overestimation of the TRO in the environment.





These chemical equations can be translated to the following mass balance kinetic equations (eq.6-10) (equations are summarised and simplified from: Lawler, 1984; Birch and Fletcher, 1980; Hostgaard-Jensen et al., 1977; Lietzke, 1975 and Schowanek et al., 1996).

$$\frac{d[\text{HOCl}]}{dt} = -k_0 \cdot [\text{HOCl}] \cdot [\text{red.inorganic}] - k_1 \cdot [\text{HOCl}] \cdot [\text{RNH}_2] - k_3 \cdot [\text{HOCl}] \cdot [\text{RNHCl}] - k_2 \cdot [\text{HOCl}] \cdot [\text{organics}] \quad (\text{eq.6})$$

$$\frac{d[\text{RNHCl}]}{dt} = k_1 \cdot [\text{HOCl}] \cdot [\text{RNH}_2] - k_3 \cdot [\text{HOCl}] \cdot [\text{RNHCl}] - k_4 \cdot [\text{RNHCl}] \cdot [\text{organics}] \quad (\text{eq.7})$$

$$\frac{d[\text{RNH}_2]}{dt} = k_1 \cdot [\text{HOCl}] \cdot [\text{RNH}_2] \quad (\text{eq.8})$$

$$\frac{d[\text{organic}]}{dt} = -k_4 \cdot [\text{RNHCl}] \cdot [\text{organic}] - k_2 \cdot [\text{HOCl}] \cdot [\text{organic}] \quad (\text{eq.9})$$

$$\frac{d[\text{red.inorganic}]}{dt} = -k_0 \cdot [\text{HOCl}] \cdot [\text{red.inorganic}] \quad (\text{eq.10})$$

An analytical solution for this type of multiple order competition reactions is not existing. Therefore, the differential equations 6-10 were numerically solved by a variable-step 5th order Runge-Kutta routine. The mathematical problem was programmed in the ISIM (interactive simulator) program.

Results and DISCUSSION

A) Model evaluation/validation:

The appropriateness of the model for estimating the decay of HOCl was evaluated by simulating the available experimental HOCl decay data of Birch and Fletcher (1980) for activated sludge and of Yamamoto et al., 1985 for river water. Results are shown in Figure 1A and 1B respectively. The given initial environmental parameters are shown in Table 1.

Table 1: Given initial environmental parameters

parameter	ACTIVATED SLUDGE (AS)	RIVER
NaOCl conc. mg.l^{-1}	6	11
Ammonium conc. (mg.l^{-1})	1	0.1
Chloramine (mg.l^{-1})	calculated (model)	calculated (model)
Reduced compounds ($\text{mg.l}^{-1}\text{S}^{2-}$)	0	0
Organic material (mg.l^{-1}) (suspended solids)	3000	19

The kinetic parameters (Table 2) were estimated by visual fitting of the simulation curves to the experimental datapoints:

Table 2: Estimated kinetic parameters (units: l.mol.s^{-1})

parameter	ACTIVATED SLUDGE (AS)	RIVER
k0	not involved (no reduced compounds present)	not involved (no reduced compounds present)
k1	100	12
k2	10	1
k3	1.5	0.025
k4	0.07	0.01

For comparison, literature data with respect to the general reaction kinetics of the considered data are: $k_0 = 25$, $k_1 = 12$, $k_2 = 1$, $k_3 = 2$, $k_4 = 0.1$ (units: l.mol.s^{-1}) (These reaction constants are the slowest values summarised from: Lawler, 1984; Birch and Fletcher, 1980; Hostgaard-Jensen et al., 1977; Lietzke, 1975 and Schowanek et al., 1996). These parameters are in the same order of magnitude as the estimated ones.

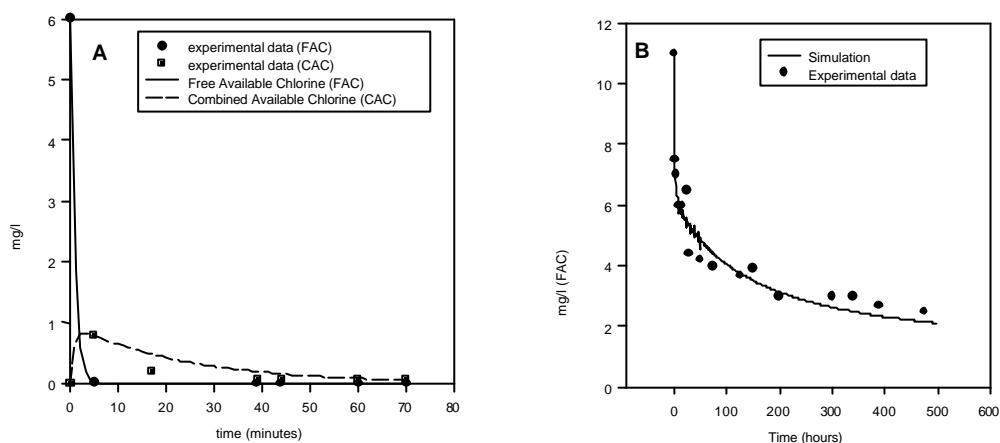


Figure 1: Experimental and simulated decay of FAC and CAC in activated sludge (A) and in fresh river water (B)

It becomes clear from Figure 1 that the model predicts quite well the decay of HOCl (FAC) and RH_2Cl (CAC) in river water and sludge. An even better fit is expected by mathematically fitting the differential equations to the data by minimizing the sum of squares of errors. A more precise parameter estimation requires additional software and was out of the scope of this work since it would be more of theoretical interest.

B) Simulation of the FAC/CAC decay in the "environmental compartments" for purpose of risk assessment

The model was used to estimate the level of FAC and CAC after transport in the environment incl. sewer, activated sludge processing and river water transport. A worst case scenario was adopted, and all HOCl was considered to arrive in the sewer, i.e. assuming no decay during application. As all estimated reaction constants appeared to be similar within an order of magnitude (cfr. supra) we assumed the following reaction constants $k_0 = 25$, $k_1 = 12$, $k_2 = 1$, $k_3 = 2$, $k_4 = 0.1$ (units: l.mol.s^{-1}) throughout the three exposure scenarios; sewer, activated

sludge and river water. The decay through the 3 environmental compartments sewer, activated sludge and river, was simulated using the following initial parameters (Table 3):

Table 3: Assumed initial environmental parameters

	SEWER	ACTIVATED SLUDGE (AS)	RIVER
Ammonium conc. (mg.l^{-1})	36	1	0.1
FAC mg.l^{-1}	7.5 (<u>max. value</u> as estimated from HOCl consumption data)	calculated (model)	calculated (model)
Chloramine (mg.l^{-1})	0	calculated (model)	calculated (model)
Reduced compounds ($\text{mg.l}^{-1}\text{S}^{2-}$)	0.00015	0	0
Organic material (mg.l^{-1})	300	3000	50
Dilution factor in the river			10
Residence time	1 h (3600 sec)	8 h (28800 sec)	10 min (600 sec)

Simulations show a quick elimination of $\text{NaOCl}/\text{ClO}^-$ (expressed as FAC) (Fig. 2 a) during transport in the sewer. The abundance of reduced reaction partners allows a fast initial FAC elimination reaction. The FAC concentration estimated at the end of the sewer drops below $1.10^{-32} \mu\text{g.l}^{-1}$. The drop in FAC is in parallel with a sharp increase of the chloramine concentration, which can be explained by the high availability of ammonia in the sewer and the rapid reaction of NaOCl with NH_3 (within minutes). Chloramine further reacts as an oxidant during further transport in the sewer (Fig. 2 a), the activated sludge unit (Fig. 2. b) and in the river (Fig. 2 c). The extensive degradation of chloramine in the activated sludge unit can be explained by the presence of organic material acting as reductant. Chloramine is estimated to fall below $5.10^{-10} \mu\text{g.l}^{-1}$ in the river.

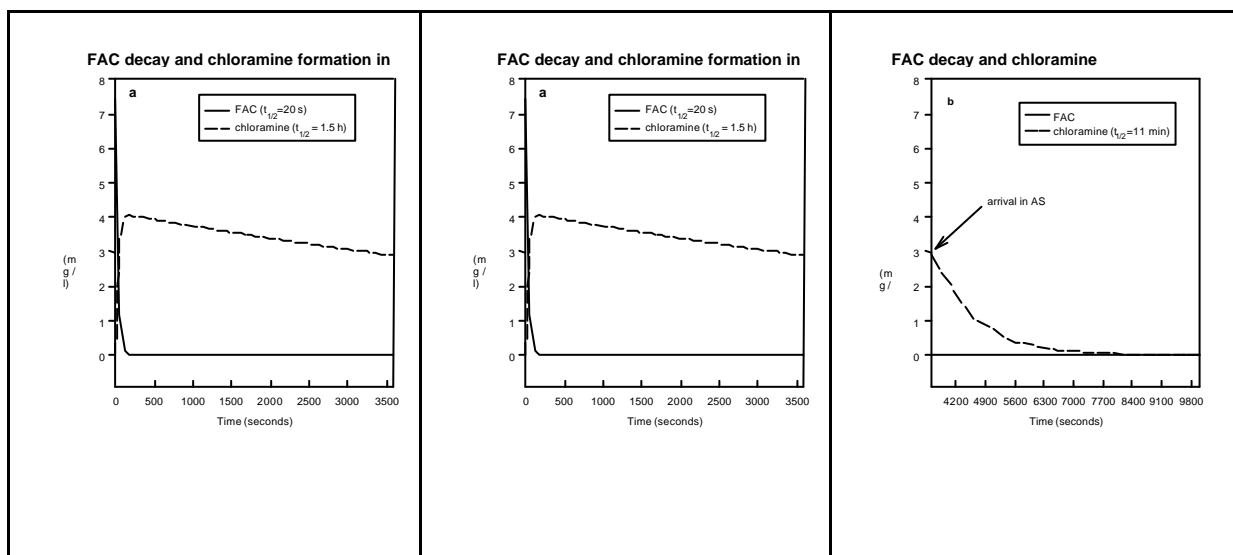


Figure 2: Simulation of the decay of FAC and formation/decay of chloramine during transport in the environment.

It has to be clear that due to the assumptions made during the setup of the model (i.e. 1: No decay of HOCl during the use phase; 2) No volatilisation of FAC/CAC and 3) No decay of

FAC/CAC due to light). The model is expected to predict an overestimated environmental HOCl concentration i.e actual data may be lower.

C) Sensitivity analysis of the model

Variation of the HOCl influent concentration:

The above specified parameters were used to simulate the effect of the initial NaOCl concentration on the estimated environmental concentration. In a first set of simulations the NaOCl in the influent was varied between 7.5 mg NaOCl.l⁻¹ to 75 mg mg NaOCl.l⁻¹. Results on the NaOCl decay during the first 300 sec i.e. in the sewer are represented in Figure 3a. The decay of the NaOCl is dependent on the concentration with a faster decay rate at higher NaOCl concentrations. In all cases the NaOCl concentration dropped below 4.10⁻²⁷ (virtually nil) μg mg NaOCl.l⁻¹ when extrapolating the data to the river and taking into account the above specified assumptions. The evolution of chloramines at different NaOCl concentrations is represented in Figure 3b. The decay is most important in the activated sludge unit and drops to 1.10⁻¹⁰ μg.l⁻¹ in the river even at a NaOCl dosage in the sewer of 75 mg.l⁻¹.

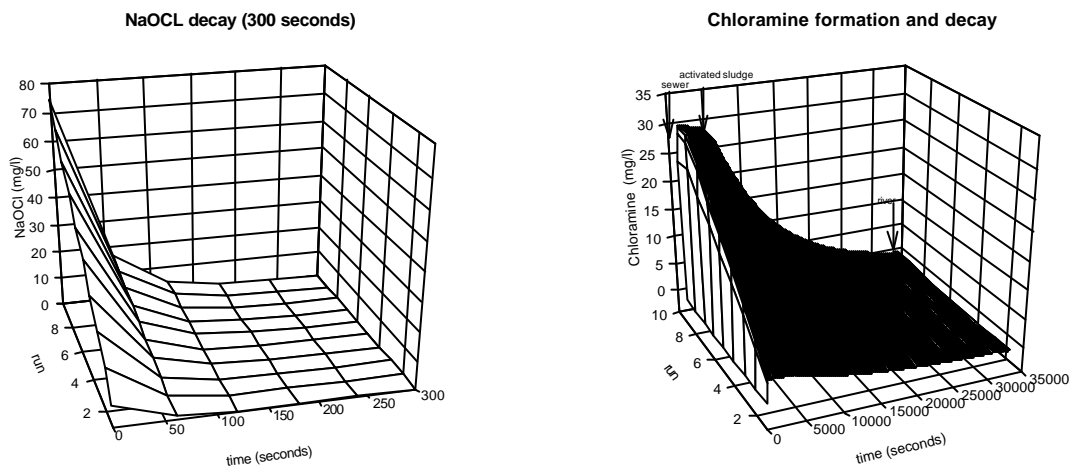


Figure 3: NaOCl and chloramine decay in function of the initial NaOCl concentration (7.5, 15, 22.5, 30, 37.5, 45, 52.5, 60, 67.5 and 75 mg.l⁻¹; run 1 to run 10).

Variation of the reaction kinetics:

The effect of decreasing the reaction kinetics by a factor 10 was assessed to evaluate sensitivity of the model for changes in reaction rate. The dosed NaOCl concentration was set at 7.5 mg.l⁻¹. In all cases the NaOCl concentration in the river drops below 4.10⁻²⁷ μg.l⁻¹ when extrapolating the data to the river. The chloramine evolution for different reaction constants is given in Figure 4. According to the simulation, the chloramine concentration in the river varies from < 1.10⁻¹⁰ μg.l⁻¹ (run 1) to 15 μg.l⁻¹ (run 10) in an unrealistic worst case scenario i.e. all reaction constants 10 times slower (Figure 4).

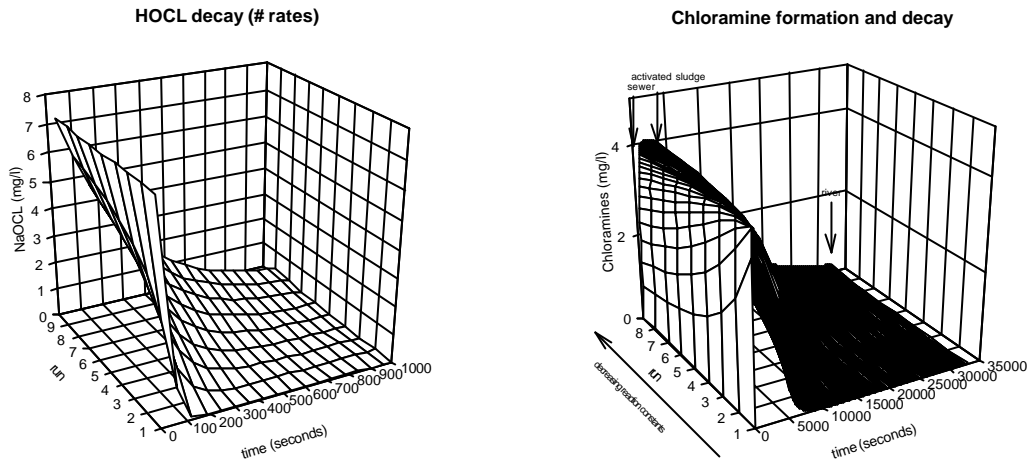


Figure 4: NaOCl decay (initial 7.5 mg.l^{-1}) in function of decreasing reaction constants (run 10 is 10 times slower compared to run 1)

CONCLUSIONS

It was shown that the presented model describes quite well the decay of FAC and CAC in the different "environmental compartments" activated sludge and river water. By using the same reaction mechanisms and kinetics, an attempt was made to estimate the FAC/CAC decay in sewage. In a reasonable case for the environment, the FAC concentration estimated at the end of the sewer drops to $0 \text{ } \mu\text{g.l}^{-1}$. Chloramine is estimated to fall below 5.10^{-10} (virtually nil) $\mu\text{g.l}^{-1}$ in the river. These data have to be compared with the PNEC values in the risk assessment.

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