SIDE EFFECTS OF CHLORINATION

Report from the Committee on the Side Effects of Chlorination

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TABLE OF CONTENTS

ACKNOWLEDGMENT

This report, which presents the state of the art on the effects of chlorination, was prepared by the Committee on Side Effects of Chlorination.
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- dr. J.C. Kruithof: chlorine use by the Netherlands Water Works;
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All contributions were discussed by the Committee on "Side Effects of Chlorination" and modified. Then, the chapters were adjusted with respect to one another by an editorial committee consisting of drs. L.A.C. Feij, dr. J.C. Kruithof, dr.ir. A.P. Meijers, drs. G. Oskam and ir. J. van Puffelen.

The final editing, introduction, evaluation and summary were the responsibility of dr. J.C. Kruithof.

SUMMARY

After investigators in the Netherlands and elsewhere in 1974 demonstrated that trihalomethanes (THM) can be formed during the chlorination of water, the Netherlands Water Works and KIWA performed many investigations in this area. A first inventory of available knowledge was made in 1978 by the KIWA ad hoc study group on "Chlorine". This inventory led to more detailed investigations, coordinated by the Committee on Side Effects of Chlorination. This report, prepared by the Committee, intends to provide a survey of the results obtained since 1978.
In most cases, the presentation of results obtained by the Netherlands Water Works and KIWA is taken as sufficient. When necessary, information is taken from the foreign literature. This pertains principally to the toxicologic aspects of disinfectants and the use of alternative disinfectants.

In section 2, an evaluation is given of the information available in the literature regarding the toxicologic aspects of the use of chlorine, chlorine dioxide and chloramine. It should be emphasized from the beginning that only a very limited fraction of the oxidized or chlorinated reaction products has been identified so that only a very incomplete picture of the toxicologic aspects can be given. No data are available in the literature indicating that chlorine, chlorine dioxide and chloramine at the customary dosages, as well as their byproducts, exert an acute or chronic toxic effect on the consumer.
The disinfectants themselves are neither carcinogenic nor mutagenic. In addition, no carcinogenic reaction products have been established, other than

chloroform.

However, it has been shown that the use of chlorine, chlorine dioxide and chloramine leads to the formation of mutagenic substances; chlorine seems to induce a higher mutagenicity than comparable doses of chlorine dioxide or chloramine. However, distinctly less attention has been paid to the side effects of chlorine dioxide and chloramine.

Epidemiologic investigations performed elsewhere did not reveal any causative relationship between products formed by chlorination and cancer. However, some investigators suggested a relationship between reaction products and tumors of the bladder, large intestine and colon. This suggestion and the increased mutagenic effect suggest a potential risk to public health. Therefore, a reduction of the level of reaction products must be attempted.

The significance of the effects found for human health in relation to the use of chlorine, however, is not yet sufficiently clear to permit us to draw conclusions on the basis of this.

Further investigation into the formation, presence and significance of genotoxic substances as well as epidemiologic investigation regarding the relationship between the substances present and certain forms of cancer is desirable. These results can lead to toxicologic recommendations by which a preference may be expressed for the use of chlorine, chlorine dioxide or chloramine.

Up to the present time, insufficient information is available to express a preference on a toxicologic basis. If a disinfectant is necessary, preference should be given to the agent whose disadvantages can be prevented or eliminated to the greatest extent.

It is considered worth recommending that chemical disinfection, especially post-disinfection, be eliminated if possible (see section 8).

In section 3 attention is paid to chlorine use in Netherlands Water Works. In 1977-1978, one of the recommendations for restricting the side effects of chlorination was that of reducing the chlorine consumption in the case of transport, breakpoint and process chlorination, while maintaining post-chlorination. Based on this recommendation, among others, the chlorine consumption was greatly reduced from 2100 tons per year in 1976 to 1250 tons per year in 1979, i.e., a 41 % reduction. The greatest reduction was brought about in the case of transport chlorination (23 %), followed by breakpoint chlorination (9 %) and iron(II)oxidation (5 %). In accordance with this recommendation during this time period, the reduction of chlorine use for post- chlorination was limited (1-2 %).
As a matter of course, these reductions are linked with the measures taken by the companies. The greatest reduction is due to the elimination of transport chlorination at low temperature and to using a lower chlorine dose in summer.
A good comparison of the side effects caused by chlorination in 1976 and 1979 is scarcely possible due to an insufficient number of measurements in 1976. A rough comparison can only be made for THM content. In 1976, THM contents of far above 100 µg/liter were recorded, while in 1979, the highest content was 53 µg/liter.
After 1979, as well, the chlorine use was further suppressed in some locations. Partially due to the new opinions, post-chlorination was stopped at some locations, while iron(II)oxidation was performed with oxygen according to the so-called Lurgi pro-

cess. In the immediate future, it can be expected that chlorine dioxide will be used in place of chlorine at some locations for transport or post-chlorination.

Section 4 discusses the contents of chlorination byproducts in Netherlands drinking water. In 1979-1980, the contents of chlorination byproducts were determined for all chlorine-using Water Works. The results obtained can be summarized as follows:

- the average THM content in drinking water upon leaving the pumping station varied from 1-38 μg/liter. After a residence time of 48 hr in the distribution network, this amounted to 3-45 μg/liter. The composition of the THM content appears to be related to the degree of pretreatment. Chlorination after carbon filtration leads to the formation of highly brominated THM; chlorination followed by infiltration or carbon filtration leads primarily to $CHCl_3$ in the water. A simple quantitative relationship cannot be found between chlorine dose and THM content. From the qualitative viewpoint transport chlorination seems scarcely to influence the THM content, while breakpoint chlorination influences it variably and post-chlorination greatly. The conceptual recommendation of VEWIN for the THM content of 0.55 μmol/liter was never exceeded;
- the THMFP of the drinking water was 0.4-2.9 μmol/liter. 1-50 % of this was converted to THM. For most groundwater and infiltration plants, this percentage is 1-4 % and for surface water plants 21-58 %. The THMFP is thus only partly converted to THM. In practice, the chlorine dose is of greater importance for the THM production than the THMFP;

- the average EOCl content was 0-5 µg/liter and the average AOCl content 10-80 µg/liter. On a molar basis, this is 0.8 times and respectively 30 times the THM content. It was thus revealed by the investigation that in addition to the THM content, the AOCl content, in particular, plays a very important role in the quantitative regard. It is not the THMFP but rather the chlorine dose which is of high determining significance for the THM content. This is all the more apparent in the post-chlorination of highly purified water, wherein a shift is seen toward the formation of highly brominated THM. As a result of this and the high AOCl contents, post-chlorination, in particular, is heavily under discussion.

In addition to the quantification of total effect of all chlorinations in drinking water treatment, a study was also performed regarding the effect per individual chlorination. This is discussed in section 5. This section pertains almost exclusively to the formation of THM; EOCl and AOCl data are practically lacking.

Is is apparent from model studies that a relationship exists between the breakpoint curve and the THM formation. Up to the peak in the breakpoint curve, THM is scarcely formed; immediately above it, marked THM formation takes place. The greater the degree of purification, the more THM formation takes place at low chlorine doses.

This observation is confirmed by results obtained in practice. In the case of transport chlorination with a Cl_2/NH_4^+ ratio of 2 to 3, low THM contents were found; at a Cl_2/NH_4^+ ratio of 20, the THM content is very high. This relationship was also found in the case of breakpoint chlorination. A Cl_2/NH_4^+

ratio of 15 leads to a THM content of 10-20 µg/liter, a ratio of 36 to a THM content of 80 µg/liter. Relatively much THM is formed in post-chlorination. Contents of 0.015-0.176 µmol/liter occur. The highest contents are encountered after extensive purification and in the case of the use of multiple chlorinations.

There are some indications that in certain cases, ozonation leads to the formation of halogenated products. However, the picture is by no means clear.

Under currently customary conditions, THM formation during transport chlorination has thus been substantially restricted. Relatively high THM contents occur after breakpoint chlorination and post-chlorination. In addition to the THM formation, the EOCl and particularly the AOCl may play a major role. However, only a very small amount of information is available in this regard, especially in terms of individual chlorination steps.

Section 6 discusses the removal of halogenated compounds. Despite the fact that in 1978 it was concluded that THM can only be removed to a moderate degree by adsorptive and oxidative processes, a relatively large amount of attention has been paid to this.

THM can scarcely be removed by means of intensive aeration at practical air-water ratios. Carbon filtration gives complete removal only for short carbon life, especially for chloroform. Carbon filtration is applicable when one is working with a criterion of, for example, 70 µg/liter. Encouraging results were obtained with alternative adsorbents. However, practical use does not appear economically justifiable. Oxidative processes appear to scarcely bring about a reduction of the THM content. Infiltration provides a high reduction of the THM content, especially concerning the more highly brominated components.

In this case as well, only a little information is available regarding the EOCl and AOCl contents. Carbon filtration provides for a reduction of both contents, wherein the filter runs are considerably longer than in the case of THM removal. Infiltration and reverse osmosis also give greater reductions of EOCl and AOCl contents.

Thus, THMs are difficult to remove from water. Only infiltration as well as carbon filtration during relatively short filter runs offer a favorable outlook overall. A reduction of the AOCl and EOCl contents can be brought about by carbon filtration, infiltration and reverse osmosis. More specific information is urgently needed in this regard.

As a supplement, some data pertaining to the removal of trichloroethylene are included. Aeration, carbon filtration and the use of alternative adsorbents offer excellent outlooks for good removal.

In 1978, the conversion or removal of THM precursors achieved very high priority. A great deal of investigation was therefore performed in this area; this is summarized in section 7. It appears that of all processes studied, specifically aeration, coagulation, carbon filtration, ion exchange, alternative adsorption, ozonization, infiltration and reverse osmosis, only reverse osmosis appears to give a very marked precursor removal. All other processes give a partial removal or give complete removal for only a short time.

It was apparent from the investigation performed that a partial THM precursor reduction does not

lead to a reduction of the THM content under practical conditions, since the precursor content is not of determining significance for this, but rather the chlorine dose. In addition, a shift takes place toward the formation of more highly brominated THM. This was found after coagulation, infiltration and especially in the case of granular activated carbon filtration after short filter runs. As a result of these observations, the removal of THM precursors was given a lower priority. Great attention is being directed toward THM under practical circumstances, expecially at the end of the process. For this, a consumer-directed determination (the THMFP consumer) was introduced, which describes this formation. Once again, in this case, attention is directed toward the limitation of post-chlorination.
In addition to THM precursors, there are also compounds which increase the EOCl and especially the AOCl content upon chlorination. However, once again, very little information is available on this subjects. There are indications that under conditions conventionally employed for post-chlorination, the organic matter content rather than the chlorine dosage is of determining significance for the AOCl content. However, this aspect should be investigated in greater detail.

In section 4 up to and including 7, extensive discussion is presented on the formation and removal of halogenated compounds and the removal of THM precursors. Section 8 discusses some possibilities for adjustment of process control in order to reduce the side effects of chlorination.
The chlorine use for transport chlorination can be further limited by replacing this chlorination by

transport purification. It is necessary to investigate whether this treatment is generally applicable.
The chlorine use for breakpoint chlorination can be greatly reduced by a selective water intake in combination with biological ammonium removal.
Much attention should be paid to the limitation or elimination of post-chlorination. If the bacteriologic or virologic composition of the water does not give any necessity for post-chlorination, this step should be eliminated. This can take place whenever several physical, mechanical and/or biological processes are present in the treatment system. Slow sand filtration as the final purification step appears to be of great significance here.

If chemical disinfection cannot be eliminated completely, the use of an alternative disinfectant can be considered. Attention is directed toward this in section 9.
Chlorine dioxide has a high disinfecting capacity which is independent of the pH; it has a slow decay and forms no THM. Chlorine dioxide thus appears to represent a good alternative for use in transport disinfection and post-disinfection.
As was already discussed in section 2, however, little is known to date regarding the formation of toxic organic substances and regarding the side effects of the inorganic byproducts, chlorite and chlorate.
Monochloramine has a weak disinfectant capacity and a low breakdown rate. It appears usable for transport disinfection, in which complete disinfection is not necessary. However, very little is known regarding the formation of byproducts.
The side effects of both disinfectants need to be

investigated in greater detail before use for transport disinfection and/or post-disinfection can be considered.

The major results are, once again, accentuated in an evaluation.

Emphasis is placed here on the following points:

- the toxicologic aspects of chlorine, chlorine dioxide and chloramine which should be investigated in greater detail;
- the formation of high molecular weight organohalogens, measured as the AOCl content, which, in addition to THM, play a very important role both quantitatively and qualitatively;
- the great importance of post-chlorination for both the quantity and the composition of the by-products formed;
- the decreased significance assigned to the THM precursor content. However, the reduction of the content of compounds which increase the AOCl content upon chlorination may be of importance;
- the elimination of transport chlorination and post-chlorination or replacement of chlorine in these processes by chloramine or chlorine dioxide.

The report concludes with some recommendations for more detailed investigations based on these considerations.

1 INTRODUCTION

1.1 Historical overview

In 1974, it was shown by various investigators in the Netherlands and elsewhere that trihalomethanes (THM) can be formed during the chlorination of water. The production of THM appears, among other things, to be linked with the concentration of the humic substances (precursors) present in the water. Certain investigations suggested the possibility that THMs are undesirable from the toxicologic viewpoint. Therefore, it was deemed necessary to investigate how these and other disadvantageous side effects can be avoided or limited. To summarize available knowledge on these problems, in 1977 KIWA established the ad hoc study group on "Chlorine".

In 1978, this study group wrote its final report and therein recommended that:

- for disinfection, chlorine may only be replaced by another disinfectant which is at least equally effective and has fewer harmful side effects;
- under process conditions customary in 1977, THM cannot be removed by aeration, adsorption and oxidation;
- reduction of the THM content may be achieved by restricting the chlorine consumption and by removal of precursors prior to chlorination.

Based on these recommendations, a great deal of investigation was performed by the Water Works in cooperation with KIWA.

This report describes the most important aspects of the investigation performed.

1.2 Composition of the report

In the report, attention is paid to the toxicologic aspects, the chlorine consumption, the concentration of byproducts in the drinking water and the formation of byproducts during a specific process. Then, the removal of halogenated products and THM precursors is discussed and finally attention is directed towards the alternatives for the use of chlorine.

Section 2 deals with the toxicologic aspects of chlorine, chlorine dioxide and chloramine. Extensive discussion is provided on the side effects of chlorine regarding the formation of chloroform.
Attention is also given to the formation of brominated THM.
The formation of other halogenated products is also discussed to a limited extent. Concerning the use of ClO_2, attention is almost exclusively devoted to the characteristics of ClO_2 itself and characteristics of the inorganic reaction products chlorite and chlorate. Due to a lack of information, little attention is paid to organic byproducts.
Finally, a brief discussion is given of the side effects of the use of chloramine.

Section 3 gives a survey of chlorine consumption among the Netherlands Water Works in 1976 en 1979. Subsequently, the chlorine use during both years is discussed with respect to the areas of transport chlorination, breakpoint chlorination and process chlorination, iron(II)oxidation and post-chlorination.
The total chlorine consumption is also reported. Then, the reduction of the chlorine consumption

which took place after 1979 is also discussed.

Section 4 provides quantification of the side effects of chlorination in Water Works which use chlorine in their treatment system. For all of the drinking water types, data are provided of the THM content upon leaving the pumping station and after a residence time of 48 hr in the distribution system, the THMFP (a measure for the content of THM precursors), the EOCl (extractable organic chlorine) and the AOCl (adsorbable organic chlorine) content for the period 1979/1980. Whenever possible, these contents are compared with the contents from 1975/1976. The data pertain to purified ground water with post-chlorination, purified dune filtrate with transport and/or post-chlorination, and purified reservoir water with transport and/or breakpoint and/or post-chlorination.

Section 5 deals with the formation of halogenated compounds. First, a model study is described for the chlorination of Biesbosch, Andelse Meuse and IJssel Lake water. From these data for a given instantaneous sample, it is possible to determine the THM content that can be anticipated during transport and breakpoint chlorination.
After this, a discussion is given of the concentrations found after application of transport, breakpoint and post-chlorination. Attention is also directed toward THM formation upon ozonation without further use of chlorine.

Section 6 discusses the removal of halogenated compounds; section 7 deals with the removal and conversion of THM precursors.
A description is given of the effects of aeration,

coagulation, granular activated carbon filtration, ion exchange, use of alternative adsorbents, ozonation, infiltration and reverse osmosis.

In chapters 8 en 9, some alternatives for the use of chlorine are given. This involves, among other things, the removal of ammonium by biological processes and the use of transport purification in place of transport chlorination. Furthermore, a great deal of attention is paid to the ideas which can lead to a reduction in chlorine dosage for post-chlorination.
Of the alternative disinfectants, attention is paid to ClO_2 and chloramine. Discussions are given of the disinfection capacity, the organic and inorganic byproducts, along with a brief toxicologic evaluation.
The report is closed with an evaluation of the results obtained and with recommendations for further investigation.

2 TOXICOLOGIC ASPECTS OF SOME DRINKING WATER DISINFECTANTS

2.1 Introduction

A variety of disinfectants can be used for the disinfection of drinking water. Chlorine is the most widely used disinfectant in the Netherlands. As a result of the discovery that haloforms and other halogenated compounds can be present in drinking water treated with chlorine (ref. 2.1, 2.2), a search is being made for alternative disinfectants which have fewer side effects from the toxicologic viewpoint. The two most important alternative disinfectants are chlorine dioxide and chloramine. In addition to their bactericidal effects, all chemical disinfectants react with organic compounds present in water. This reaction gives rise to the formation of chlorinated and oxidized compounds. This means that in addition to the presence of the disinfectant used these "byproducts" can also occur in the drinking water.

A number of byproducts have been identified with the aid of gas chromatography and mass spectrometry. Insofar as toxicity data for these substances are known, these will be evaluated.

In the case of the fraction of compounds whose identity is not known - and it may be anticipated that this includes a large fraction of the chlorinated and oxidized compounds - toxicologic evaluation is not possible. Therefore, it is obvious that only a limited picture of the toxicologic aspects of the three disinfectants mentioned can be given.

2.2 Chlorine and byproducts

In the Netherlands, under normal process conditions, the chlorine concentration in the tap water leaving the pumping station amounts to no more than 1.0 mg/liter. Before the tap water reaches the consumer, the chlorine concentration will usually have decreased to such an extent that chlorine can no longer be detected (detection limit about 0.01 mg/liter). Discussion of the toxicologic aspects of chlorine itself is thus no longer necessary.

The use of chlorine as a disinfectant for drinking water leads to the formation of halogenated and oxidized compounds. So little is known as yet regarding the occurrence and the identity of the oxidized compounds that a toxicologic evaluation is not possible, even though they can play an important role. They are thus left out of further consideration.

Much more is known regarding the halogenated compounds.

For practical and historical reasons, a distinction is made between:

a. trihalomethanes;

b. other halogenated organic compounds.

2.2.1 Trihalomethanes

Of the compounds which are formed under the influence of chlorination of water, the trihalomethanes form the most extensively investigated group, among other things, since they are readily analyzed and the concentrations of the four trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane and bromoform) are relatively

high.
Especially when chlorine is used during the initial phase of drinking water preparation (from surface water), chloroform occurs at the highest concentration. Concentrations of about 0.1 mg/liter chloroform were repeatedly demonstrated in the mid 1970's.
At the present, the chloroform concentration in the Netherlands in most cases is below 0.05 mg/liter.
The toxicologic aspects of chloroform will be discussed separately, since chloroform is known as a carcinogenic substance, and a great deal of information is available regarding the toxicologic aspects of chloroform. The other three trihalomethanes will be discussed together.

Chloroform

a. Acute toxicity

Chloroform is an agent which, when inhaled in large quantities, first leads to marked excitation, followed by dullness, loss of consciousness and deep narcosis.
Continued chloroform exposure can lead to respiratory paralysis and then death. The narcotic concentration of chloroform in man is 63 g/m^3 in air; 90 g/m^3 in air leads to collapse. In the case of prolonged anesthesia, the blood pressure decreases and myocardial damage occurs. Common side effects include heart and liver damage (jaundice, fatty degeneration, cell death) and renal damage. Because of the heart and liver damage, chloroform is no longer used as an anesthetic for humans.
The lethal dose for humans is between 15 and 30 ml (23-45 g) of chloroform.

Table 1 - Physiological reactions in humans to various concentrations of chloroform (ref. 2.3)

Chloroform conc. g/m^3 in air	Reactions
70-80	Max. concentration for anesthesia
20	Salivation, dizziness
7.2	Salivation and dizziness after a few minutes
5	Dizziness, impulse to vomit, pressure inside the head
5	Aftertreatment effects, fatigue, headache
1.9	No symptoms within 30 min.
1-1.5	Odor threshold

Finally, it can be stated that chloroform produces skin irritation which can be attributed to drying of the skin.

Investigation regarding the acute toxicity of chloroform in mice resulted in an oral LD50* of 1120 mg/kg body weight (ref. 2.4).

* Oral LD50: 1120 mg/kg means that oral administration of 1120 mg chloroform per kg body weight is lethal for 50 % of the test animals (in this case, mice) within 1 week.

Conclusion

In view of the values in table 1 and the LD50 value of chloroform for mice, it is clear that chloroform is not acutely toxic to humans at concentrations of < 0.05 mg/liter.

b. Chronic toxicity

Remarkably little information is available regarding the chronic toxicity of chloroform in air, and even less information is available regarding chronic oral toxicity.

Schwetz (ref. 2.5) stated that upon inhalation during pregnancy in the rat a concentration of as little as 147 mg/m^3 air chloroform was slightly toxic for the embryo and fetus, while higher concentrations were more highly embryotoxic and fetotoxic.

Orally administered chloroform during the pregnancy of rats at doses of 126 mg/kg/day led to a loss of appetite and weight losses. Doses of 316 mg/kg/day caused liver and renal damage.

The same differences were seen in rabbits at dosage levels of 63 and 100 mg/kg/day. No embryotoxic effects were found (ref. 2.6).

Munson et al (ref. 2.4) performed a subchronic 90 day test in mice in which chloroform was administered orally.

The lowest concentration of chloroform in which an effect was still seen amounted to 50 mg/kg body weight per day, while the highest concentration at which no effect was found was 12.5 mg/kg/day. Since the testing time was not long enough to determine chronic toxicity (the test duration in mice would have to be about two years in such a case), no maximum acceptable concentration for humans may be calculated from this.

Jorgenson et al (ref. 2.7) in a test on rats at chloroform concentrations of 900 and 1800 mg/liter (corresponding to about 85 en 135 mg/kg/day, respectively) in the drinking water after 18 months found deviations in the composition of the blood as well as in the activity of some serum enzymes. Effects on growth and mortality attributable to chloroform were not found. On the whole, no effects attributable to chloroform were found in mice up to a chloroform dosage of 1800 mg/liter. However, the investigation is not yet complete.

Conclusion

It may be concluded preliminarily from the results of various investigations that the chronic toxicity of chloroform is such that it should not be anticipated that concentrations such as those currently existing in drinking water (up to 0.05 mg/liter) will provoke toxic effects in humans.

c. Carcinogenicity

The earliest tests pertaining to the carcinogenicity of chloroform date from 1945.

Eschenbrenner and Miller (ref. 2.8) performed an experiment with five different strains of mice of both sexes. The mice received thirty oral doses of 0.1, 0.2, 0.4, 0.8 and 1.6 ml/kg chloroform, respectively. The chloroform was dissolved in olive oil and the doses were administered every four days. One month after the last treatment, the surviving animals were investigated for the presence of carcinomas.

All females at the highest dosage and all males at the highest three dosages died shortly after the beginning of the experiment. In all females of the 0.4 and 0.8 ml/kg group, nonmetastatic heptomas and liver cirrhosis were observed. The lower dosages and the control groups showed no hepatomas.

Roe et al performed a number of chronic toxicity studies on mice, rats and dogs (refs. 2.9-2.11). Chloroform was administered to male mice at 17 or 60 mg/kg/day six days a week for 80 weeks.

In male mice of three strains (C57 BL, CBA and CF/1), no effect of the treatment on any form of neoplasm was found. In male mice of a fourth strain (ICI) at the highest chloroform dose, a significant increase in the renal tumor frequency was seen. Administration of chloroform in peanut oil showed an even further increase in the renal tumor frequency only at the highest dosage. The $CHCl_3$ dosage of 17 mg/kg/day caused no increase in the renal tumor frequency with respect to the control group. In a study with SPF Sprague-Dawly rats in which chloroform was administered for 80 days at 60 mg/kg in toothpaste, no significantly elevated tumor frequency with respect to the control was detected. However, it should be noted that in this test, 35 % of the control animals (34 out of 98) displayed tumors, compared to 39 % (38 out of 98) in the group treated with $CHCl_3$.

In a third experiment, Beagle dogs were given chloroform at 30 mg/kg/day in gelatin capsules for seven years. An elevated frequency of fatty cysts was found upon histopathological examination. No increased tumor frequency was observed.

Powers et al (ref. 2.12) found, on the basis of a carcinogenicity study with chloroform in rats,

that renal tumors developed after 78 weeks of oral administration of chloroform in corn oil.
The groups of test animals which received daily chloroform doses of 180-200 mg/kg revealed renal tumors in 20 % of the male rats and in 2 % of the female rats. The group which received 90-120 mg of chloroform/kg showed distinctly fewer tumors.

A corresponding investigation in mice by Renne et al (ref. 2.13) revealed the following results. Chloroform was administered to two groups of male mice at 140 and 280 mg/kg/day and to female mice at 240 and 480 mg/kg/day.
Sixty-three percent of the male test animals and 87 % of the females showed hepatocellular carcinomas. The effects were distinctly dose-related; the groups of test animals to which the highest dose was administered appeared to have a higher frequency than the groups to which a lower dose was administered.
This phenomenon was found in all experiments in which tumors were able to be demonstrated as a consequence of chloroform exposure.
On the basis of the data available in 1979, the IARC found that chloroform must be regarded as a carcinogenic substance.

d. Risk evaluation
Two extrapolations were performed in evaluating the risks of the occurence of tumors in human populations, specifically:

1. the results from carcinogenicity tests in which small groups of animals (several dozen animals each) were exposed to high dosages were extrapolated to an acceptable low daily

dose which is believed to cause no tumors in a large group of animals (a population of 10^5-10^6 test animals);

2. the acceptable daily intake in test animals was extrapolated to human populations.

For such extrapolation, qualitatively and quantitatively highly reliable data are essential.

Both extrapolations are highly complex and difficult, especially since criticism has been directed toward the tests performed from several quarters. Indeed, at present, there is a lack of results from animal experiments in which chloroform was administered for a sufficiently long time in sufficiently low concentrations to various animal species.
An investigation of this type is just now being carried out with rats and mice (ref. 2.7). In this study, chloroform is added to drinking water in a concentration series of 0, 200, 400, 900 and 1800 mg/liter, corresponding to 0 and about 20, 35, 85 and 135 mg/kg/day. The results are not yet known.

There are several models which may be used to determine the maximum cancer risk as a consequence of the oral intake of chloroform via drinking water. These models are summarized in table 2 and will be discussed briefly (ref. 2.14).

Table 2* - Determination of the maximal risk due to chloroform intake** (ref. 14)

model	maximum risk (no. of cancer deaths)	maximum daily dose mg/kg body wt.
Margin of safety (10 x)	0 - negligible	0,03
Margin of safety (5.000 x)	0 - negligible	0,02
Probit-Log (slope = 1)	0,016 - 0,683/M/yr.	0,01
Probit-Log (actual slope)	1/B/lifetime	0,01
Linear	0,42 - 0,84 /M/yr.	0,01
Two step	0,267 - 0,283/M/yr.	0,01

* Adapted from Tardiff (ref. 2.14)

** Based on adults

M = million; B = billion

1. Margin of safety model

   This model presented by Weil (ref. 2.15) assumes that, at least for a number of potentially carcinogenic substances, it is possible to speak of a nonlinear dose-effect relationship and thus of a "no effect-level". Beginning from a properly conducted carcinogenicity study with test animals aimed at establishing the minimum concentration at which a carcinogenic effect is still found, he assumes a safety factor of 5.000 for the maximal quantity which a human may ingest.

   On the basis of the lowest concentration of chloroform which no longer induced tumors, namely 90 mg/kg/day and the safety factor of

5.000, a daily dose of 0,02 mg/kg should not induce tumors in humans.

The following models are statistical models which, at a specific maximum daily intake of chloroform, determine the maximum cancer risk as a consequence of this intake.

- "Probit log model (slope 1)" according to Mantel and Bryan (refs. 2.16, 2.17)*.

  For further details on the method of calculations, refer to the relevant publications.

  The result of the calculation shows that at a maximum daily chloroform dose of 0.01 mg/kg body weight, the cancer risk is between 0.016 and 0.683 per million per year.
- "Probit log model (actual slope)".

  This model proceeds from the actual slope of the dose/response curve of chloroform and the induction of tumors, while otherwise the same calculation method and test data are used as in the other probit log model. The cancer risk is now determined at less than 1 tumor in a population of 1 billion during the entire lifetime at a chloroform uptake of 0.01 mg/kg body weight.
- Linear model.

  This is the most conservative model and assumes a linear dose-effect relationship.

  This model gives a cancer risk of 0.42 to 0.84 tumors per year in a population of 1 million.

---

* In this model, a slope of one is assumed for the dose-response curve relating chloroform and the induction of tumors.

- "Two step model".
  This much praised model falls between the probit log model (slope one) and the linear model.
  This model yields a cancer risk of 0.267 and 0.283 tumors per year per 1 million population.
  The linear models begin from a genotoxic action mechanism, i.e., there is no dose which gives no risk.

At present, the cancer risk for humans is often expressed in terms of the quantity of a carcinogenic substance which produces a mortality risk of 1 in 100,000 or 1 in 10^6 during an entire lifetime (average 70 years). Table 3 gives a survey of the quantities of chloroform which, according to the various models and authors, give a mortality risk of 1 per 100,000 or 1 per 10^6 during the entire lifetime. In addition to four values recalculated from table 2, two more recent values are also presented. It is remarkable that the three linear models give values located close together. The linear model is also the most widely applied model in the Netherlands.

Table 3 - Quantities of $CHCl_3$ which produce a cancer mortality of 1 per 100,000 humans due to chloroform intake throughout the entire lifetime according to various models (expressed in µg chloroform per person per day)

model	µg chloroform pppd	remarks
probit-log (slope = 1)	6230-146	Recalculated from table 2, ref. 2.14
probit Log (actual slope)	7×10^6	Recalculated from table 2, ref. 2.14
two step	374-353	Recalculated from table 2, ref. 2.14
linear	238-119	Recalculated from table 2, ref. 2.14
linear multistage model	82	Crump and Guess, ref. 2.18
linear multistage model	60	WHO, 1981, ref. 2.19

In addition, it should be noted that appropriate reservation should be applied in evaluating the results of statistical models. Various models can give greatly differing results, since the

starting points and the factors involved in the calculations are different (see table 3).
Although the linear models are the most widely used, it should, nevertheless, be noted that they assume the most extreme conditions and present maximal calculated risks.

Conclusion
On the basis of a number of criteria and based on data from animal studies, chloroform is regarded as a carcinogenic substance. Beginning from these animal study data and a genotoxic action mechanism, it has been calculated that the risk of mortality due to tumors in humans as a result of an intake of 60 to 100 µg chloroform per day for 70 years amounts to one death per 100,000 individuals.

e. Mutagenicity
With two exceptions, chloroform was not genotoxic in short-term "in vitro" screening tests. The chloroform test program gave negative results with bacterial tests (Ames test and E. coli test systems, refs. 2.20, 2.23, 2.25) and with "in vitro" mammalian cell test systems in which point mutations, sister chromatid exchanges (SCE), unscheduled DNA synthesis (UDS) and cell transformation were investigated (refs. 2.21 and 2.23). In yeast cell tests, chloroform was not mutagenic in six studies. In one instance, a mutagenic effect was detected in yeast cells at a concentration at which 6 % of the cells survived treatment (ref. 2.22). A host mediated assay in which bacteria (Salmonella strain TA 1537) in the abdominal cavity of mice were exposed to orally administered chloroform

gave a mutagenic effect at dosages of 700 mg/kg or higher (Ref. 2.61).

In "in vitro" tests, chloroform, even at higher dosages, was negative in the micronucleus test in mice (Ref. 2.23). A similar negative result applied for the Drosophila test. In addition, neither chloroform nor metabolites formed "in vivo" were shown to have a significant interaction with DNA.

The similarity between all of the observed genotoxic effects is that they appear only at chloroform concentrations which cause marked toxic effects. On the basis of these data, various authors concluded that the carcinogenic effect of chloroform is not due to genotoxic effects of chloroform or its normal metabolites. Only toxic doses are believed to lead to tumor formation as a consequence of altered metabolism in the liver and kidneys (ref. 2.23).

Further development of this theory is desirable since mechanistic aspects of the tumorigenic process are of determining significance for the selected method of risk evaluation.

f. Epidemiology

Some epidemiologic investigations regarding the chronic toxic effects after oral intake of chloroform in humans have revealed that:

1. ingestion of an average of 30 mg chloroform/kg/day via a cough syrup for several years causes liver damage, and
2. intake of 0.3-0,96 mg chloroform/kg/day via toothpaste for 1 to 5 years causes no liver damage (ref. 2.24).

It may be assumed from this that the chronic toxicity of chloroform after oral intake in man is between 0.3 and 30 mg chloroform/kg/ day.

The epidemiologic aspects of chloroform intake via drinking water in relation to cancer cannot be separated from the consideration of the other trihalomethanes and high molecular weight halogenated compounds. These epidemologic aspects will be discussed in Section 2.2.3.

g. Conclusions with regard to chloroform

Chloroform is considered a carcinogenic substance. The most customary extrapolation of the carcinogenicity risk is based on a genotoxic action mechanism of chloroform. This has led to a proposal by the WHO to regard a daily intake of 60 µg chloroform per person per day as acceptable, corresponding to 30 µg/liter at a consumption of 2 liters of water per day. It is assumed that no other exposure to chloroform takes place. The risk evaluation is based on safety considerations assuming a genotoxic action mechanism.

Up to the present time, there is no indication that chloroform or its normal metabolites are genotoxic. Only at high concentrations is it believed possible for genotoxic manifestations to occur because of toxic effects. If this viewpoint is confirmed by further investigations, this would mean that somewhat higher acceptability levels would become possible for chloroform.

Other trihalomethanes

The toxicologic aspects of dibromochloromethane

($CHBr_2Cl$), bromodichloromethane ($CHBrCl_2$) and bromoform ($CHBr_3$) will be discussed together under this heading.

a. Acute toxicity

The volume of information available with regard to the acute toxicity of $CHBr_2Cl$, $CHBrCl_2$ and $CHBr_3$ is very low and is limited to the studies of Munson et al (ref. 2.4). He obtained the following results (the acute toxicity of chloroform is also given for comparison):

Table 4 - Acute oral toxicity of trihalomethanes for mice

THM	LD50, 7 days (mg/kg)
Chloroform	1120
Bromodichloromethane	450
Dibromochloromethane	1200
Bromoform	1500

It is remarkable that the acute toxicity of bromodichloromethane is about three times higher than that of the other three trihalomethanes, while these three trihalomethanes are equally toxic.

Comparison of the concentrations of trihalomethanes occurring in drinking water (order of magnitude several tens of micrograms per liter) with the values in table 3 shows that there is no reason to speak of acute toxicity of any of these trihalomethanes in drinking water.

b. Chronic toxicity

In this case also, as for chloroform, the results of wellconducted studies on chronic toxicity determination are lacking. Only a little information is available concerning the subchronic toxicity as determined by Munson et al (ref. 2.4). The subchronic toxicity of chloroform is also provided for comparison (see table 5).

Table 5 - Subchronic toxicity of trihalomethanes for mice (ref. 2.4)

Effect	THM	Dose (mg/kg)
LOAEL*	Chloroform	50
LOAEL*	Bromodichloromethane	50
LOAEL*	Dibromochloromethane	12.5
LOAEL*	Bromoform	50
NOAEL**	Chloroform	12.5
NOAEL**	Bromodichloromethane	12.5
NOAEL**	Dibromochloromethane	5
NOAEL**	Bromoform	12.5

* Lowest observed adverse effect level (lowest dose at which a harmful effect is found)

** No observed adverse effect level (highest dose at which no harmful effect is found)

The subchronic toxicity is determined during a 90 day test period. The LOAEL was primarily based on depression of humoral immunity.

In this test, however, no NOAEL was able to be established on the basis of which an acceptable intake for humans can be calculated.

Nevertheless, the subchronic toxicity found for THM is so low that in relation to the concentrations occurring in drinking water, it would not be expected that trihalomethanes can have chronic toxicity for the consumer.

c. Carcinogenicity

No carcinogenicity studies of dibromochloromethane, bromodichloromethane and bromoform were performed with mammals.
An evaluation of the carcinogenic aspects is then also not possible.

d. Mutagenicity

Dibromochloromethane, bromodichloromethane and bromoform are mutagenic in the Ames test with Strain TA 100 (ref. 2.25). This does not mean that these compounds are likewise mutagenic for mammals. The presence of brominated trihalomethanes in drinking water can involve a potential risk of the consumer.
Therefore, it is advisable to strive for the lowest possible concentration of these compounds in drinking water.

e. Epidemiology

See paragraph 2.2.3.

f. Conclusions

The concentration of the other trihalomethanes in drinking water is so low that no acute or chronic toxic effects are to be expected for the drinking water consumer. Although no carcinogenicity studies have been performed on the other trihalomethanes, the positive results with in vitro mutagenicity test indicate that the brominecontaining trihalomethanes are genotoxic. Thus, it is highly desirable to attempt to achieve the lowest possible concentrations of brominated trihalomethanes in drinking water.

2.2.2 Other halogenated organic compounds

The formation of trihalomethanes as byproducts of chlorination has gained a great deal of attention in recent years. However, in the meantime, it has become clear that in addition to trihalomethanes, other chlorination byproducts can also be found. The size of this group of compounds cannot yet be completely estimated since the isolation methods used do not capture all types of compounds.

Up to the present time, the largest number of toxicologic investigations on these nonvolatile byproducts have been carried out on the basis of sampling with the aid of XAD in combination with the Ames test. A variety of authors demonstrated mutagenic effects in lipophilic and moderately hydrophilic isolates and related them to the chlorination of water (refs. 2.40, 2.41, 2.59).

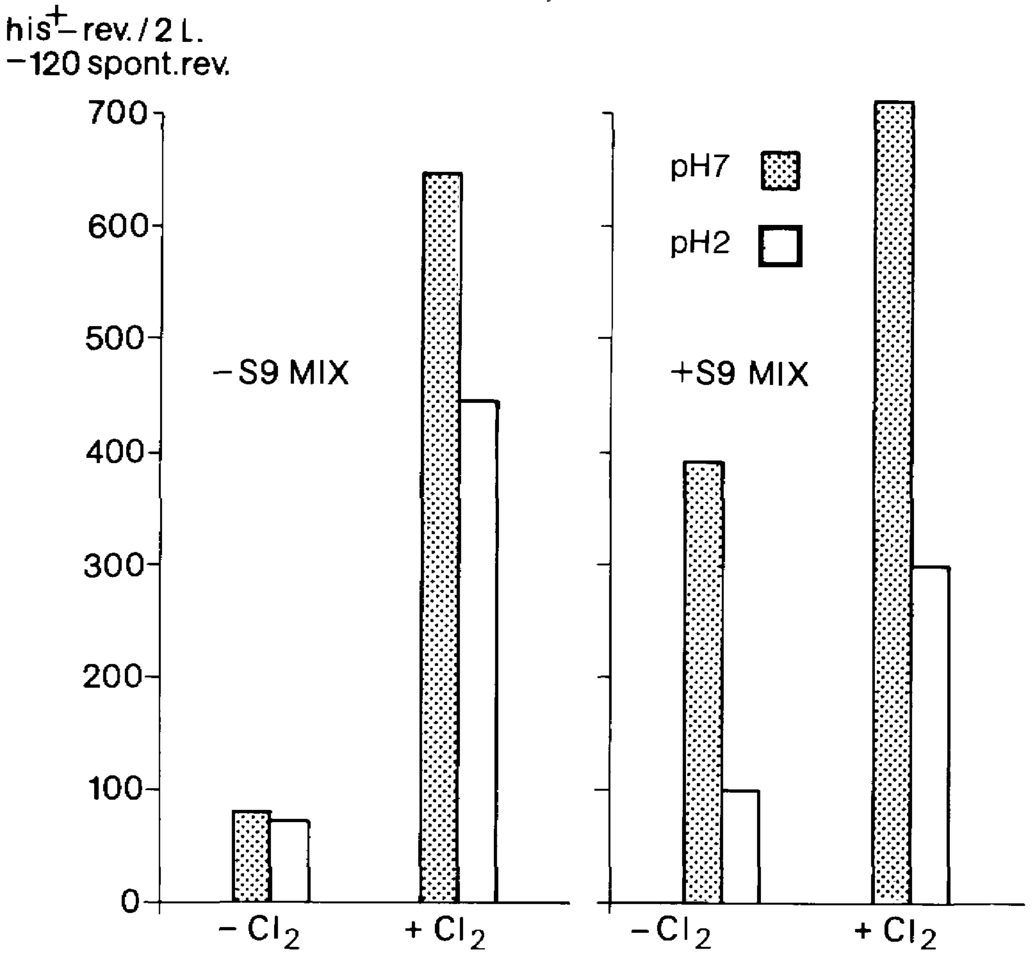
The mutagenic effect that develops under the influence of chlorination is principally seen with strain TA 100. In a number of situations, it was noted that the mutagenic effect formed was greater in the moderately hydrophilic fraction than in the lipophilic fraction (ref. 2.40). It is not known whether possible byproducts with a more highly hydrophilic character have escaped attention. The development of isolation methods for such compounds seems essential.

The halogenated compounds formed, which may be responsible for the mutagenic effects, have not yet

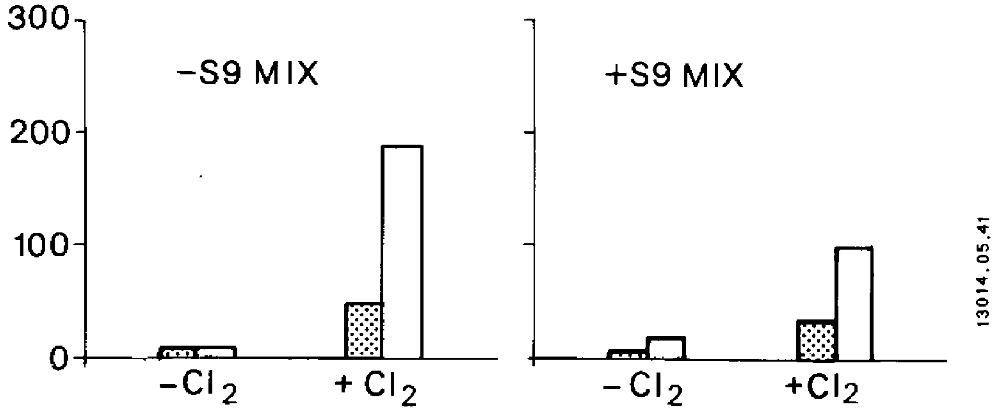
been identified up to the present. It was found from KIWA studies that in a specific type of water other than trihalomethanes, no halogenated compounds were formed by the safety chlorination which could be identified by GC-MS, while the AOCl content after stripping increased. This seems to represent an indication that the mutagenic substances formed have molecular weights of more than 350 (ref. 2.40).
A relationship also exists between the extent of the mutagenic effect developed by chlorination and the composition of the chlorinated water. In surface water after coagulation and rapid filtration, a much higher mutagenic effect develops under the influence of chlorination than after treatment with activated carbon (fig. 2.1, study at the KIWA pilot plant). It was also found in the same study that activated carbon filtration for some time (about 1,000 bed volumes) was able to remove from the water XAD adsorbable substances, which react with chlorine to form mutagenic materials. After 3,000 bed volumes, however, mutagenic effects were found in the XAD pH 2 fraction of the chlorinated effluent (ref. 2.59).

The influence of the chlorine dosage on the formation of mutagenic substance has hardly been investigated yet. In addition, it is not known whether the presence of bromide in the water influences the mutagenic effects produced by chlorination. More detailed investigation of these aspects is desirable.

The significance for the consumer of mutagenic effects of chlorination byproducts in the Ames test cannot be estimated at present. These effects



River water after coagulation/rapid filtration



Treated river water after granular activated carbon filtration

Fig. 2.1 - Effect of chlorination on the mutagenic action with TA 100 in various purification stages

should be confirmed in additional mutagenicity tests. One important aspect of this might be the fact that, at most, part of the mutagenic effect in the Ames test can be inactivated by liver enzymes (ref. 2.59).

Data on carcinogenicity studies wherein the byproducts of chlorination are specifically considered are limited and will not be discussed in further detail here.

The epidemiologic investigation discussed in section 2.2.1 is surely also applicable for this group of compounds, perhaps in an even stronger degree than for the trihalomethanes.

2.2.3 Epidemiology

Since the first publications regarding the possible association of cancer and chlorinated drinking water (ref. 2.26, 2.27), an intensive search was made for a correlation between certain forms of cancer and the presence in drinking water of:
- chloroform or
- trihalomethanes or
- organic compounds formed by chlorination.

In addition to the formation of chloroform and other THMs, chlorination of drinking water also leads to the formation of many other compounds. An attempt will be made to discuss the most important data pertaining to cancer and the presence of chlorinated compounds described in greater detail or not (including chloroform and the THMs) in drinking water. The following findings are reported in the literature and can be summarized as follows.

Page et al (ref. 2.27)

A positive correlation of bladder cancer and gastrointestinal tract cancer with the chlorine content of the drinking water.

Buncher (ref. 2.28)

A positive correlation of drinking water prepared from surface water with cancer of the bladder, liver and pancreas.

Kuzina (ref. 2.26)

A significant correlation between drinking water quality and the occurrence of intestinal and bladder cancer, as well as the overall cancer mortality.

Cantor (ref. 2.29)

A positive correlation between the THM content of drinking water and the occurrence of bladder cancer (highly positive), liver and brain cancer; a more positive correlation, the more bromine is present in the THM.

Hogan (ref. 2.30)

A significant positive correlation between the chloroform concentration of drinking water and bladder cancer.

McGabe (ref. 2.31)

A correlation between the chloroform content of drinking water and cancer mortality.

Carlo (ref. 2.32)

A significant positive correlation between the THM content in drinking water and pancreatic cancer; no correlation between THM and cancer of the esophagus, stomach, large intestine, rectum and bladder.

Kanarek (ref. 2.33)
A positive correlation between the chlorine dose in the drinking water and cancer of the large intestine; no correlation with cancer of other organs (gastrointestinal tract, urinary tract, brain, lungs, breast).

Amsel (ref. 2.34)
For an area with a relatively high frequency of large intestinal cancer among the inhabitants, it is anticipated that the contribution to this due to chlorination of the drinking water will be small, if it exists at all.

Isacson (ref. 2.35)
A positive correlation between cancer of the rectum and the THM concentration of drinking water. As more bromine is present in the THM, the correlation disappears. No correlation between chlorination of drinking water and cancer of the large intestine.

Gottlieb (ref. 2.36)
A highly significant correlation between chlorinated surface water and cancer of the rectum, a weak positive correlation with breast cancer and cancer of the brain, kidneys and prostate, and no correlation with cancer of the esophagus, stomach, large intestine and bladder.

No definite causative correlation between organic matter in water and human cancer was found from recently conducted so-called case control studies (refs. 2.37, 2.38). However, these studies contain many indications which suggest such a correlation.

As is apparent from this summary, most of the results are contradictory. Although tumors of the bladder, large intestine and rectum are associated with water quality parameters in many studies, a consistent picture is lacking. The reason for this may be sought, among other things, in the fact that:

- the investigations took place in various areas and/or cities;
- different computation methods were used;
- various experimental setups were used;
- the exposure of humans to chlorinated organic compounds cannot be readily quantitated;
- the exposure of humans can vary greatly over time and with regard to location and in relation to a latency time for the occurrence of cancer amounting from five to forty years;
- cancer is not caused solely by consumption of water.

Conclusions

Neither from the epidemiologic investigations nor from the animal studies it was found that a positive relationship exists between the presence of halogenated organic substances in drinking water and certain forms of cancer. However, it is noteworthy that a relatively large number of studies contain indications suggestive of a relationship between halogenated organic compounds in drinking water and cancer of the bladder, large intestine and/or rectum.

However, epidemiologists expect that more accurately defined, so-called "case control interview studies" would provide more clarity regarding a possible causative relationship (ref. 2.39). This is expected to be especially difficult, since the magnitude of the effects to be measured falls between the cracks of the measurement method used. For the present, it may be concluded that the contribution of the chlorination of drinking water to cancer is probably small, but the possibility of the existence of a causative relationship has not been excluded. Further study is then also desirable.

2.3 Chlorine dioxide and byproducts

2.3.1 Chlorine dioxide

One of the alternative disinfectants for chlorine is chlorine dioxide. Chlorine dioxide is added in quantities of 0.02 to 0.1 mg/liter, while in the Netherlands proportional addition of chlorine is also applied. A small amount of chlorine may also form during the preparation of chlorine dioxide.
It is known regarding chlorine dioxide that it does not give rise to the formation of trihalomethanes in water (ref. 2.42). Stevens confirms this, but states that chlorine dioxide may give rise to the formation of chlorinated and nonchlorinated compounds (ref. 2.43). At present, so little is known regarding the identity of these compounds that no toxicologic evaluation is possible.
Within the body, chlorine dioxide is broken down in a short time to chloride (Cl^-), chlorite (ClO_2^-) and chlorate (ClO_3^-).
Following prolonged administration of high chlorine dioxide concentrations to rats (100 and 1,000 mg/liter), elevated chloroform concentrations were found in the blood (ref. 2.42). For the toxicologic aspects of chloroform, reference is made to section 2.1.1.

The toxicologic aspects of chlorine dioxide and the two most important inorganic byproducts, chlorite and chlorate, will be discussed in greater detail. Chloride (Cl^-), also formed, is of such low toxicity at the existing concentration that the Cl^- ion as such is left out of the consideration.

a. Acute toxicity of chlorine dioxide

Acute toxicity data for chlorine dioxide pertain exclusively to pulmonary uptake. The threshold limit value (TLV) and the MAC value amount to 0.1 ppm or 0.3 mg/m^3. At PWN, experience has shown that this value is too high. Workers who work at this value develop a tendency to vomit after one hour (Schultink, personal communication).

b. Chronic toxicity of chlorine dioxide

The most important investigation regarding the long-term toxicity of chlorine dioxide was performed by Couri et al (ref. 2.44). Administration for one year of 1, 10, 100 or 1,000 mg/liter chlorine dioxide via the drinking water to rats in comparison to the control animals led to the following observations:

- at all dosages, a slight decrease in the body weight was found. This decrease was less than 15 % in all cases;
- between 2 and 9 months of exposure of the rats at all dosages, slight decreases are found in the number of red blood cells, the hematocrit value, the hemoglobin content and the average hemoglobin content per red blood cell;
- at all concentrations, changes in the morphology are found as well as a decrease in the "osmotic fragility" of the red blood cells. At

higher concentrations, a mild hemolytic anaemia occurred, which reduced lifetime of the red blood cells.

Bercz (ref. 2.45), upon exposure of monkeys (Cercopithecus aethiops) for 60 days to chlorine dioxide doses of 50, 100, 200 and 400 mg/ liter of drinking water, found little effect. With the exception of a temporary inhibition of the serum activity (at 100 and 400 mg/liter), no differences were found relative to the controls as concerned:

- numbers of various blood cells;
- hemoglobin contents;
- methemoglobin contents;
- osmotic fragility;
- contents of serum constituents (renal function);
- serum enzyme activities (renal and liver function).

The only remarkable finding from this investigation was the fact that upon direct introduction of chlorine dioxide into the stomachs of the monkeys, 95 % of the chlorine dioxide was already reduced to chloride after only 5 minutes.

It can be concluded from the data reported that the toxic effects of chlorine dioxide in rats and monkeys are contradictory. The possible toxic effects are probably caused by the decomposition products of chlorine dioxide, mainly chlorite and chlorate. Therefore, in considering the toxicologic significance of chlorine dioxide, it is necessary to keep in mind the slight effects found in test animals and the possible toxicity of chlorite and chorate.

c. Carcinogenicity and mutagenicity

There are no indications in the literature that chlorine dioxide itself is carcinogenic or mutagenic.

Chlorine dioxide treatment of 26 organic substances belonging to various classes of compounds did not lead to a mutagenic effect in the Ames test and in a mutagenicity test with yeast cells (ref. 2.46). It should be noted that for most compounds, only concentrations up to 150 µg per Petri dish were investigated. From these results, Simmon drew the conclusion that no potentially carcinogenic substances were formed as a consequence of chlorine dioxide treatment. However, in view of the test setup and the fairly small number of substances investigated, his conclusion is preliminary.

It was found from a study performed by Bull (ref. 2.47) that a chlorine dioxide-treated concentrate of organic substances from Ohio River water caused no increase in the number of skin tumors in mice. Although the induction of tumors in the skin of mice is a sensitive system, this is not a representative test for the oral uptake of substances via drinking water.

A preliminary investigation by Kool et al (ref. 2.41) revealed that at high additions of chlorine dioxide to Rhine River water, mutagenic compounds are formed; these were isolated with XAD at pH 7. Although, because of the dosages of 5 and 15 mg/liter, this investigation is not relevant for practical situations, it does indicate that chlorine dioxide can, in principle, give rise to the formation of mutagenic substances. In analogy to the findings with respect to chlorine, investigation regarding the formation of more hydrophilic compounds is desirable.

d. Epidemiology

Some studies were performed in which humans were directly exposed to chlorine dioxide-treated drinking water.

Miday et al (ref. 2.48) compared 198 individuals exposed for three months to chlorine dioxide-treated drinking water with a control group. As a consequence of disinfection with chlorine dioxide, the drinking water contained 5 mg/liter chlorite. An extensive and statistically confirmed study on the effects of a large number of blood parameters did not lead to the observation of significant differences between the two groups.

Bianchine et al (ref. 2.49) performed an extensive investigation with chlorine dioxide, chlorite, chlorate, chloramine and chlorine in drinking water. The drinking water was consumed by healthy individuals and by individuals who were extrasensitive to "oxidant stress" due to a deficiency of the enzyme, glucose-6-phosphate dehydrogenase (G-6-PD) in the red blood cells.

The various investigations indicate statistically significant trends in the measurement results in the case of all of the disinfectants and by-products mentioned. The problem in this investigation, however, was that the accuracy of the analytical methods of biochemical parameters fell in the order of magnitude of the normal fluctuations in biochemical processes, and the investigations lasted only three months. Although Bianchine cannot exclude the possibility that certain trends would continue and intensify upon more prolonged exposure, he notes that, in general, all of the substances investigated at an intake of 500 ml water per day containing 5 mg/liter of the substances for three months are relatively safe for healthy adults (including otherwise healthy individuals with G-6-PD deficiency).

Tuthill (ref. 2.50) investigated mortality ratios of newborns in two similar communities. In one community, high concentrations of chlorine dioxide were used for drinking water disinfection, while chlorination was performed in the other. He found a statistically significant positive correlation between exposure of the mother to chlorine dioxide-treated drinking water during pregnancy and premature birth, accompanied by a lower birth weight and higher weight loss immediately after birth. Because of the limited scope of the investigation, the results were considered more "suggestive" than "definitive".

e. Conclusions

Some authors found vague indications that chlorine dioxide at elevated concentrations may be harmful to humans and specifically to infants. The possible harmfulness of chlorine dioxide is probably due to its byproducts, chlorite and/or chlorate.

2.3.2 Byproducts

Although several organic compounds are formed under the influence of chlorine dioxide treatment (ref. 2.43), due to a lack of data, exclusive attention will be paid to the toxicologic aspects of chlorite and chlorate. At a chlorine dioxide dosage amounting to a maximum of 0.2 mg/liter, the chlorite content is below 0.1 mg/liter. The chlorate content is not measured in the Netherlands, but probably will not be higher than the chlorite content.

Chlorite

a. Acute toxicity

The acute toxicity of chlorite for the rat was investigated by Ammar (ref. 2.51). He established the following facts with reference to oral intake via drinking water:

- doses of 5 and of 20 g/liter chlorite for three weeks led to a decrease in body weight and a reduction of the water and feed intake by the rats. No mortality occurred;
- a chlorite dosage of 20 g/liter led to a highly abnormal morphology of the red blood cells;
- a dosage of 20 g/liter chlorite from day 8 to 15 of pregnancy in female rats leads to the delivery of fewer fetuses altogether and of more dead fetuses and results in more uterine resorption of fetuses. This concentration is thus clearly fetotoxic;
- doses of 1 and 5 g/liter chlorite do not reveal fetotoxic effects;
- up to a chlorite dosage of 20 g/liter, no histological abnormalities in the soft tissue nor skeletal abnormalities were found.

It may be concluded from these results that in the Netherlands, at the maximal chlorite content of 0.1 mg/liter occuring in the drinking water, there is no indication of acute toxic effects.

b. Chronic toxicity

The results of only two brief studies regarding subchronic toxicity of chlorite are available. Since chlorite is an oxidizing agent, in his investigation, Moore (ref. 2.52) made use of a special strain of mice which is hypersensitive to "oxidant stress" due to a deficiency of the enzyme glucose-6-phosphate dehydrogenase (G-6-PD) in the red blood cells.

He found that chlorite, at concentrations of 50 and 100 mg/liter in the drinking water after 30 days, leads to changes in the blood, namely:

- increase in the average volume;
- a higher osmotic fragility and a high activity of the enzyme G-6-PD in red blood cells;
- morphological alterations of these red blood cells.

The concentrations mentioned also have a disadvantageous effect on the growth of the fetus during the lactation period, and more mortalities of the fetuses occurred. However, Moore found no harmful effects on the kidneys and no increase in the blood pressure.

A similar investigation in sheep, which are known to be more sensitive to "oxidant stress", dit not lead to detectable disadvantageous effects.

Bercz (ref. 2.45), at dosages of 50-400 mg/liter chlorite in the drinking water of monkeys (Cercopithecus aethiops) after 60 days, found no lasting effect on blood parameters. He found only an initial reduction of the hemoglobin content and the number of red blood cells. Toward the end of the investigation, these effects has disappeared again, which is explained by stimulation of erythropoiesis (blood formation) under the influence of chlorite.

In view of the short testing time, no conclusions can be drawn from these investigations with respect to the chronic toxicity of chlorite. However, there are indications that newborns form a high risk group. It was found from epidemiologic investigations in humans by Bianchine (see section 2.3.1.d) that chlorite concentrations of 5 mg/liter in drinking water in the case of consumption for three months of 0.5 liters of water per day have no effect on healthy human adults. This investigation also featured a short testing time so that no firm conclusions can be drawn regarding the chronic toxicity of chlorite for humans and especially for babies. A well- planned investigation on chronic toxicity including prenatal exposure in some test animal species at relevant concentrations in drinking water is highly desirable.

c. Carcinogenicity/mutagenicity

No data are available regarding the general toxicity of chlorite.

d. Epidemiology

See section 2.3.1.d.

Chlorate

a. Acute toxicity

Little toxicologic information is also available for chlorate. The oral toxicity is in excess of

10 g/liter drinking water and is not relevant for drinking water practice.

b. Chronic toxicity

Only a little information is available with respect to chronic toxicity: Couri (ref. 2.44) found that rats which had been exposed for one year to a concentration of 10 g/liter chlorate in the drinking water showed a slight weight loss. In addition, between the second and ninth months of testing, he found a slight decrease in the number of red blood cells, the hemoglobin content, the hematocrit value and the average hemoglobin concentration in the red blood cells. Furthermore, abnormalities developed in the morphology of the red blood cells.

Bercz (ref. 2.45) found, up to a concentration of 400 mg/liter chlorate in the drinking water, no effect whatsoever on the blood parameters in monkeys (Cercopithecus aethiops) after 60 days. It may be concluded from the results that although no suitable investigations on chronic toxicity were conducted, in view of the high exposure concentrations in the tests and the low concentrations in drinking water, no chronic toxic effects of chlorate are to be anticipated. It is also apparent that chlorate is less toxic than chlorite.

c. Carcinogenicity/mutagenicity

No carcinogenicity data are available regarding chlorate.

Data were recently presented indicating that sodium chlorate is mutagenic in the Ames test (Strain TA 1535 + S9) as well as in the sex-linked recessive lethal test with Drosophila. The micronucleus test gave a negative result (ref. 2.53). The test concentrations and a description of the test procedure, however, were not provided. Nevertheless, the possibility that chlorate is a genotoxic substance must be kept in mind.

d. Epidemiology

For epidemiologic data, the reader is referred to section 2.3.1.d. From this section it may be concluded that chlorate concentrations of 5 mg/liter in drinking water in case of the consumption for three months of 0.5 liters of water per day, have no effects on healthy human adults.

2.4 Chloramine and byproducts

From the disinfectants discussed in this section chloramine has been investigated toxicologically least complete. Application of chloramine gives rise to the formation of some organic byproducts. The toxicologic properties of these byproducts will be reported seperately.

2.4.1 Chloramine

Only very little information is available regarding the toxicity of chloramine. The available data will be presented without distinguishing between acute and chronic toxicity.

a. Acute and chronic toxicity

- Eichelsdoerfer et al (ref. 2.54) established that a concentration of 4 mg/liter chloramine is more irritating to the mucous membranes of rabbit eyes than 20 mg/liter chlorine.

- Chloramine shortens the life of red blood cells in humans in vivo as well as in vitro by production of methemoglobin and by damaging the energy metabolism. 1 mg/liter chloramine gives in vitro the production of 8 % methemoglobin.

  Especially renal dialysis patients may be harmed by the presence of chloramine in the drinking water (ref. 2.55). Renal dialysis, in particular, is an area in which attention should be paid to this problem.

  Moore and Calabrese (ref. 2.56) are of the opinion that the chloramine concentration in the drinking water would have to be higher by several orders of magnitude than is currently practical in order to result in the presence of chloramine in the blood at a concentration of 1 mg/liter. Moore and Calabrese found that more toxicity data are necessary in order to achieve a good risk analysis.

  In particular, allowances must be made for high risk groups such as babies and individuals with G-6-PDH deficiencies.

- Bercz (ref. 2.45) found, after 60 days of exposure of monkeys (Cercopithecus aethiops) to concentrations of 400 mg/liter chloramine in the drinking water, that no effects were detectable on blood parameters.

- Bianchine (ref. 2.49) also found, after exposure of humans (volunteers) to 5 mg/liter chloramine in drinking water at a consumption of 500 ml water per day for 20 weeks, no effects that would make it necessary to conclude that chloramine is harmful to humans.

In summary, it can be concluded that the investigation results, despite their limitations, give no direct suggestion that chloramine, at normal levels in drinking water, would be harmful to humans.
The necessary certainty in this regard can only be achieved after performing well-planned investigations on chronic toxicity; exposure must already begin prenatally.

b. Carcinogenicity and mutagenicity

No data are available concerning the possible carcinogenicity of chloramine. The following is known with regard to mutagenicity:

- Shih and Lederberg (ref. 2.57) showed that chloramine is slightly mutagenic in Bacillus subtilis (Arp C/Arp + reversion). They suggested that chloramine has an influence on the DNA (deoxyribonucleic acid), since some "DNA repair mutants" were more sensitive to chloramine.

- Scully (ref. 2.58) found that under the influence of chloramine addition to drinking water, a number of byproducts are formed. In addition to the formation of several nonmutagenic substances, N-chloropiperidine was also occasionally detected. This compound is highly positive in the Ames test (Strains TA 100 and TA 1535) and causes chromosomal aberations in cell cultures from ovaries of Chinese hamsters.

In view of the mutagenic effects of chloramine treatment, it is necessary to perform systematic investigations on both the mutagenicity of chloramine itself and of the byproducts of chloramine in various mutagenicity tests.

2.4.2 Byproducts

The only information available on the formation of byproducts in the treatment of drinking water with chloramine originated from Scully (ref. 2.58). He frequently observed the formation of the following compounds: acetaldehyde, acetonitrile, isobutyraldehyde, methylbutanol, succinic acid and phenylacetic acid.
None of these compounds at the concentrations at which they can be formed under the influence of chloramine is believed to be toxicologically harmful.
In addition, in several instances, Scully demonstrated the formation of: N-chloroaniline, N-chloropiperidine (see section 2.4.1) and N-chlorodiethylamine.
The concentration of these substances were very low; however, the biological activity of N-chloropiperidine is very high (highly mutagenic).

In this instance, as well, a systematic investigation is necessary regarding the formation of byproducts and their biological activity.

2.5 Conclusions and recommendations

1. In view of the concentrations occurring under normal conditions in drinking water, no definite indications have been found in the literatu-

re that chlorine, chlorine dioxide and chloramine as well as their byproducts, can exert an acute or chronic toxic effect on the consumer.

2. No data have been reported in the literature suggesting that chlorine, chlorine dioxide or chloramine itself can be carcinogenic or mutagenic.

3. With the exception of chloroform, no investigation results are known which suggest that byproducts formed under the influence of chlorine, chlorine dioxide or chloramine addition to water should be interpreted as carcinogenic substances.

4. In the qualitative sense, mutagenicity studies with in vitro systems indicated that addition of chlorine, chlorine dioxide and chloramine to water can give rise to the formation of mutagenic byproducts.

5. From the quantitative viewpoint, it appears that a higher mutagenicity is induced under the influence of chlorine addition then a comparable doses of chlorine dioxide and chloramine. The byproducts of chlorine dioxide and chloramine treatment of drinking water, however, have been less intensively investigated than those of chlorine treatment.

6. For epidemiologic reasons, no causative relationship has yet been found between cancer and the presence of chlorinated and/or oxidized organic compounds formed under the influence of chlorination in drinking water.

7. A number of epidemiologic investigations have suggested that an association exists between the presence of organic chlorine compounds formed under the influence of chlorine and tumors of the bladder, large intestine and rectum.

8. The possible association between the presence of organic chlorine compounds formed under the influence of chlorine in drinking water and certain forms of cancer as well as the positive results of in vitro mutagenicity tests indicate a possible risk to the health of the drinking water consumer due to these byproducts.
   Thus, attempts should also be made to reduce the concentrations of the compounds mentioned in drinking water.

9. From the toxicologic viewpoint, at present, no preference can be expressed for any of the three disinfectants: chlorine, chlorine dioxide or chloramine. All three have advantages and disadvantages. It is only obvious that the disinfectant whose disadvantages (the presence of genotoxic byproducts) can be most readily eliminated in the future deserves preference for the disinfection of drinking water.

10. For toxicologic reasons, at present, there is no information that suggests that the disinfection of drinking water should be eliminated if this is indispensable for bacteriologic reasons.
    On one hand, disinfection of drinking water is an absolute necessity in order to keep pathogens and other organisms below unacceptable

numbers in drinking water and, on the other hand, the potential harmful effects as a consequence of disinfection are of such a nature and extent that there is no urgent necessity for very stringent measures.

11. Further investigations regarding the formation, presence and significance of genotoxic substances formed under the influence of drinking water disinfectants is highly desirable.
    Only if sufficient and clear results of these investigations are available will it be possible to make recommendations on the basis of toxicologic consideration.

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3 CHLORINE USE IN NETHERLANDS WATER WORKS

3.1 Introduction

In drinking water supply, chlorine is used at several locations for a variety of purposes. These include:

a. transport chlorination to prevent pressure losses due to growth of organisms in the distribution system;

b. breakpoint chlorination for oxidation of ammonium, oxidation of organic substances and disinfection;

c. process chlorination in order to obtain treatment without biological disturbances;

d. oxidation of iron(II)sulfate to the iron(III)-salt (iron(II)oxidation);

e. post-chlorination as "final disinfection" and/or to control growth of bacteria and higher organisms in the distribution network.

The ad hoc study group on "Chlorine" (ref. 3.1) developed an inventory of chlorine use by the Water Works on the basis of a questionnaire. This questionnaire was distributed in early 1977 with respect to the data for 1976.

In addition, the study group gathered and interpreted the technological information available at that time. Based on this interpretation recommendations were formulated for limiting the use of chlorine insofar as possible.

The following possibilities were given for this:

- replacement of transport chlorination by transport purification or by transport disinfection with chloramine or chlorine dioxide;
- replacement of breakpoint chlorination by biological processes;

- replacement of iron(II)oxidiation with chlorine by oxidation with oxygen.

However, for the present post-chlorination had to be maintained.

Based on these recommendations, especially in the time period from 1976 to 1979, a great reduction of chlorine consumption was brought about by the Water Works. For these reasons, the Committee on "Side Effects of Chlorination" decided to repeat the sending of the questionnaire on chlorine consumption.

The repetition of this inquiry was performed in mid-1980 for the 1979 data. Several questions were added to the questionnaire regarding the measures taken after 1976 to limit chlorine consumption, the consequences thereof, and the measures still being considered for the future.

The results of the two questionnaires are reproduced in this section. Modifications made in a later stage are added. However, the extent of these modifications has not been quantified using a questionnaire.

In addition, wherever possible, a discussion will be presented on the limitation of side effects of chlorination by the reduction of chlorine consumption accomplished. The side effects of chlorination will be extensively presented in section 4 for the contents of byproducts in drinking water and section 5 for the side effects relative to the type of chlorination.

3.2 Chlorine consumption for transport chlorination

Transport chlorination is used by the Rijn-Kennemerland Water Transport Company (WRK), the Water Supply Company Brabantse Biesbosch (WBB), The

Hague Dunes Water Works (DWL 's-Gravenhage) and the Water Works of South West Netherlands (WMZ). The chlorine consumption by these companies for transport chlorination in 1976 and 1979 is presented in table 3.1.

Table 3.1 - Chlorine consumption for transport disinfection

Company	1976		1979	
	Dose mg/l	Total use, tons/ yr.	Dose mg/l	Total use, tons/ yr.
WRK	2,4	300	winter 0 summer 2,5	160
WBB	winter 0 summer 4-7	400	winter 0 summer 1,4	100
DWL 's-Gravenhage				
Brakel - Bergambacht	1,5	55	1,5	55
Bergambacht-Scheveningen	winter 0 summer 2,2	66,5	winter 0 summer 0,55	14,7
WMZ Ouddorp	winter 0 summer 1	2	winter 0 summer 1	1,0
Haamstede	-	-	winter 0 summer 1	0,8
Total	-	823,5	-	331,5

The total chlorine consumption in 1976 of 823.5 tons per year declined to 331.5 tons per year in 1979. This comes down to a reduction of nearly 60 %. At WBB, the reduction actually amounted to 75 %.

This reduction is due to two factors. In 1976 in the winter, WBB, WMZ and DWL 's-Gravenhage in the Bergambacht-Scheveningen section eliminated chlorination completely. In 1979, WRK also eliminated chlorination in the winter.

In addition, the dosages in the summer were considerably reduced (e.g., WBB from 4-7 mg/liter to 1.4 mg/liter and DWL 's-Gravenhage from 2.2 mg/liter to 0.5 mg/liter).

3.3 Chlorine consumption for breakpoint chlorination

Breakpoint chlorination is used by the Dordrecht Municipal Energy Concern (GEB), the Provincial Water Works of North Holland (PWN) at Andijk, the Rotterdam Water Works (DWL-R) at the Berenplaat production plant and beginning in 1979 by the Water Works of North West Brabant (WNWB) at the Zevenbergen production plant.

The chlorine consumption by these companies for breakpoint chlorination is shown in table 3.2.

Table 3.2 - Chlorine consumption for breakpoint chlorination

Company	1976		1979	
	Dose mg/l	Total use, tons/year	Dose mg/l	Total use, tons/year
GEB	9	65	2,1	14,6
PWN	9	171	7,9	155
DWL-R	4,3	400	3,6	266
WNWB	-	-	1,7	5,5
Total	-	636	-	441,1

It is apparent from table 3.2 that a reduction in chlorine consumption from 636 tons per year to 441.1 tons per year occurred between 1976 and 1979. This is a 30.7 % reduction. At GEB, the reduction actually amounted to 77.5 %.

The total decrease in the chlorine consumption is thus appreciably smaller than in the case of transport chlorination. In addition, a large portion of the reduction was due to a decrease in production by the Berenplaat plant of the DWL Rotterdam. However, in view of the reason for the use of breakpoint chlorination (ammonium removal), no great reduction is to be expected.

3.4 Chlorine consumption for process chlorination

Process chlorination is used only by WMZ at the Braakman production plant. However, it should be noted that the breakpoint chlorination described in

paragraph 3.3 also serves the function of process chlorination in many instances.
The chlorine use at the Braakman production plant is shown in table 3.3.

Table 3.3 - Chlorine consumption for process chlorination

Company	1976		1979	
	Dose mg/l	Total consumption tons/year	Dose mg/l	Total consumption tons/year
WMZ Braakman	3	18	3	18
Total	-	18	-	18

Thus, 18 tons of chlorine were used in both years for this application.

3.5 Chlorine consumption for iron(II)oxidation

Iron(II)oxidation with chlorine was used by DWL Rotterdam at the Berenplaat production plant and by the WMZ at the Braakman production plant. The chlorine consumption of these plants for iron(II)oxidation is shown in table 3.4.

Table 3.4 - Chlorine use for iron(II)oxidation

Company	1976		1979	
	Dose mg/l	Total consumption tons/year	Dose mg/l	Total consumption tons/year
DWL-R Berenplaat	4,3	400	4,3	318
WMZ Braakman	10	30	10	3
Total	-	430	-	321

It is apparent from table 3.4 that in 1979, chlorine use for iron(II)oxidation was 25.3 % lower than in 1976. As in the case of the decrease in chlorine consumption for breakpoint chlorination, this reduction is largely caused by a decrease in water production by the Berenplaat production plant. In addition, ten times less drinking water was produced in 1979 than in 1976 at the Braakman plant, which primarily supplies process water.
For such uses as well, relative to the same quantity of water used, no marked reduction is to be anticipated, unless another oxidation process becomes utilized.

3.6 Chlorine consumption for post-chlorination

All of the companies participating in the inquiry, namely GEB Dordrecht, PWN, Amsterdam Municipal Water Works (GW), DWL Rotterdam, Groningen Municipal

Water Works (GWG), DWL 's-Gravenhage, WMZ, WNWB, Enschede Municipal Energy Concern (ONE), N.V. Leidsche Dune Water Works (LDM) and the Water Works of Overijssel (WMO) used post-disinfection in 1976 and 1979. However, it may be noted that DWL 's-Gravenhage and LDM performed chlorination only incidentally, while PWN uses no chlorine for post-disinfection, but adds a mixture of chlorine and chlorine dioxide.

The chlorine consumption of the companies using post-disinfection is presented in tables 3.5 and 3.6. Table 3.5 gives the chlorine consumption for the surface water treatment plants; table 3.6 gives the chlorine use for the plants which purify groundwater or infiltrated water.

For the production plants which use chlorine dioxide for post-disinfection, the ClO_2/Cl_2 mixture is reported as mg/liter chlorine. The quantity of sodium chlorite consumed is shown in table 3.7.

In the surface water treatment plants, the chlorine consumption for post-disinfection decreased from 118.5 tons/year to 93 tons/year. This is a 21.5 % reduction. In the groundwater and infiltration plants, the use decreased from 82 tons/year to 44.4 tons/year, a 46 % reduction.

Altogether, 200.5 tons of chlorine were used for post-disinfection in 1976, while in 1979, the figure was 137.4 tons. This is a 31.5 % decrease. The chlorite consumption decreased from 16.9 tons/year to 6.2 tons/year, which means a 63.3 % reduction.

Despite the recommendation of the ad hoc working group on "Chlorine" that post-chlorination should be maintained, a great decrease in chlorine consumption for this purpose was found. This decrease is due to:

Table 3.5 - Chlorine consumption for post-chlorination by companies treating surface water

Company	1976		1979	
	Dose mg/l	Total consumption tons/year	Dose mg/l	Total consumption tons/year
GEB	2	13	1,3	11,7
PWN Andijk	0,3*	6	0,03*	0,6
GW Driemond	0,5	10	0,4	8,4
DWL				
Berenplaat	0,5	45	0,45	33,3
Kralingen	0,8	30	0,6	20,2
GWG De Punt	0,25	2,5	0,4-0,5	5,2
WMZ Braakman	2	12	2	12
WNWB Zevenbergen	-	-	0,5	1,6
Total	-	118,5	-	93

* The indicated dosage pertains to a ClO_2/Cl_2 dosage

Table 3.6 - Chlorine consumption for post-chlorination by companies treating groundwater or infiltrated water

Company	1976		1979	
	Dose mg/l	Total consumption tons/year	Dose mg/l	Total consumption tons/year
ONE Weerseloseweg	0,5	7	0,5	4
PWN				
Bergen	0,3*	4	0,14*	1,9
Wijk aan Zee	0,3*	1,2	0,08*	0,6
Castricum	0,3*	4,5	0,18*	1,9
GW Leiduin	0,8	48	0,6	33,4
DWL 's-Gravenhage	0,8	15	normally 0, if necessary 0,7-1,0	-
LDM Katwijk	inc.	-	inc. 0,6-0,9	-
WMZ				
Ouddorp	0,15	0,3	0,2	0,4
Haamstede	-	-	0,2	0,2
WMO Diepenveen	0,6	2	0,6	2
Total	-	82	-	44,4

* The indicated dosage pertains to a ClO_2/Cl_2 addition

Table 3.7 - Sodium chlorite use required for post-disinfection with chlorine dioxide

Company	1976 Total consumption tons/year	1979 Total consumption tons/year
PWN		
Andijk	8	0,8
Bergen	4,9	2,3
Wijk aan Zee	-	0,7
Castricum	4	2,4
Total	16,9	6,2

- the selection of the chlorine dosage based on a sharper criterion;
- optimization of treatment, resulting in reduced chlorine demand of the water;
- introduction of additional purification steps, for example, granular activated carbon filtration.

In addition, DWL 's-Gravenhage did not perform any chlorination at all in 1979.

The only increase in chlorine consumption took place at GWG. This increase is due to a disturbance of the biological equilibrium in the slow sand filters after refilling and replacing the sand in these filters in the winter of 1976/1977. In combination with an increased drinking water production from surface water, this necessitated an increase in the chlorine dose from 0.25 mg/liter to 0.4 mg/liter. Incidentally, upon a change in the water intake from the Drentsche Aa, 0.5 mg/liter was added. Both in 1976 and in 1979, the residual chlorine content after 8 hr. was $\leqslant$ 0.01 mg/liter.

3.7 Total chlorine consumption

The total chlorine consumptions in 1976 and 1979 and the reduction in use are shown for all chlorine applications utilized in sections 3.2 up to and including 3.6. Table 3.8 shows the total consumption per chlorination, the reduction for each chlorination and the reduction relative to the total consumption.

The total chlorine consumption was thus reduced from 2108 tons/year in 1976 to 1249 tons/year in 1979. This is a total reduction of 40.7 %. By far, the largest quantities of this are supplied by the reduction of the transport chlorination (23.3 %), followed by breakpoint chlorination (9.2 %) and iron(II)-oxidation (5.2 %).

In the latter two processes, however, the decrease in water production plays an important role.

Table 3.8 - Total chlorine consumption

Chlorination type	1976 consumption tons/year	1979 consumption tons/year	Reduction %	Reduction with respect to total consumption %
Transport chlorination	823,5	331,5	59,7	23,3
Breakpoint chlorination	636	441,1	30,7	9,2
Process chlorination	18	18	0	0
Iron(II)oxidation	430	321	25,3	5,2
Post-disinfection				
Surface water	118,5	93	21,5	1,2
Groundwater + infiltrate	82	44,4	45,9	1,8
Total	2108	1249	40,7	40,7

3.8 Discussion

3.8.1 Adaptation of process control

As is apparent from paragraphs 3.2 up to and including 3.7, the chlorine consumption decreased greatly at several locations.

The following measures formed the basis for this reduction:

- at temperatures above 10 °C, WBB replaced the transport chlorination, performed as breakpoint chlorination, by chlorination with a far lower dose. At a temperature below 10 °C, chlorination is no longer performed at all;
- in 1976, WRK chlorinated year-round. In 1979, chlorination was stopped at temperatures below 11 °C;
- DWL 's-Gravenhage greatly reduced transport chlorination in the transport from Bergambacht to Scheveningen;
- GEB Dordrecht stopped transport chlorination for groundwater and greatly reduced chlorine consumption for breakpoint chlorination;
- ONE reduced chlorine consumption for post-chlorination by about 50 %. Other companies (GW) also used a somewhat sharper criterion;
- PWN greatly reduced the ClO_2 dose after introduction of activated carbon filtration;
- in addition, WBB and GWG performed a more selective water intake practice based on NH_4 and UV criteria.

Only GWG temporarily found it necessary to increase the chlorine dose caused by a disturbance of the biological equilibrium following refilling of the slow sand filters.

3.8.2 Further adaptations of the process sequence after 1979 and possible future adaptations

In addition to the adaptations in chlorine use reported for 1979 in paragraph 3.8.1, some companies also performed a number of measures after 1979 as well. This pertains to the following adaptations:

- following extensive bacteriologic, virologic and hydrologic investigations, WMZ stopped the post-chlorination at Haamstede.
  In the second half of 1982, GW, for test purposes, also started to decrease post-chlorination. Since March 1983, the water is distributed without further chlorination. These matters will be discussed in greater detail in section 8;
- at the Berenplaat production plant in early 1983, DWL Rotterdam replaced iron(II)oxidation with gaseous/liquid chlorine by oxidation with air oxygen (the so-called Lurgi process). This led to an additional 15 % reduction in the total chlorine use at the Berenplaat;
- at the end of 1982, GEB Dordrecht changed from Wantij water to Biesbosch water, and since the beginning of 1983, has also been using activated carbon filtration. The chlorine consumption was considerably reduced in this manner;
- in 1983, WRK reduced the temperature criterion for transport chlorination from 12 °C to 15 °C. In 1984 transport chlorination was omitted almost completely;
- beginning in 1982 on the Andel-Bergambacht section DWL 's-Gravenhage no longer used transport chlorination at a water temperature below 8 °C. Beginning in 1984, no more chlorination whatsoever is being performed in the Bergambacht-Scheveningen section.

As a result of all these measures, the total chlorine consumption at Netherlands Water Works has been further reduced. However, these reductions will not be further quantitated within the scope of the current report.

In the immediate future as well, some plants are still considering a number of measures. Some examples include:

- DWL 's-Gravenhage and WBB are investigating the extent to which it is possible to perform transport disinfection with the aid of chlorine dioxide;
- in 1984, ONE started using activated carbon filtration and hopes to be able to reduce the post-chlorination dosage in the near future;
- WMZ is thinking about stopping post-chlorination at Ouddorp like they did before at Haamstede;
- GWG has decided to eliminate chlorination under normal operating conditions after refurbishing the coagulation system for the purification of surface water (Drentsche Aa);
- in 1984, WNWB started an investigation with the goal of replacing post-chlorination by slow sand filtration or disinfection with UV radiation. In addition, an investigation is being conducted to determine whether breakpoint chlorination can also be eliminated.

3.8.3 Effect of measures taken on THM content

In 1976-1979, chlorine consumption in Netherlands water supply companies was greatly reduced. The question arises to what extent the side effects of chlorination have been restricted by the limitation of chlorine use. The problem arises that in 1976, the side effects of chlorination were not accurately measured. THM contents measured by the National Institute are known for some cities; EOCl and AOCl contents are not available at all.
Nevertheless, whenever possible, an attempt was made to compare the THM contents measured in 1976 with the average THM contents from the period 1979/1980. The results are reported in table 3.11.

Table 3.11 - THM contents in drinking water in 1976 and 1979/1980

Location	THM contents (in distribution system, incidental measurement)	Avg. THM content (pumping station)
Groningen	1	4
's-Gravenhage	< 1	< 1
Wijk aan Zee	> 4- 15	2
Enschede	14	3
Amsterdam	22- 36	8-24
Andijk	> 81-146	23
Rotterdam	61- 73	30
Dordrecht	82-147	38

The data on the period 1979/1980 are based on report 323 from KIWA (ref. 3.2) and will be discussed in detail in section 4.

It may be emphasized that the figures presented must be interpreted with extreme caution. Nevertheless, it is clear that over the entire line, the THM content has clearly decreased. This is especially true for the drinking water in which breakpoint chlorination is included in the treatment process. In addition, post-chlorination with a rather low chlorine dose appears to have a relatively marked influence on the THM content in drinking water.

In the following sections, all these topics will be discussed in detail.

3.9 Conclusions

Approximately 35 % of the Netherlands drinking water is treated with chlorine in one or more phases. In 1976, the total chlorine consumption amounted to 2108 tons/year; in 1979, it was reduced by 40.7 % to a quantity of 1249 tons/year.

This reduction was primarily brought about by a marked limitation of transport chlorination (23.3 %). The reduction of the chlorine consumption in breakpoint chlorination (9.2 %) and iron(II)oxidation (5.2 %) was principally due to a decrease in the quantity of water produced. The reduction of the chlorine consumption in post-chlorination (1.2 % for surface water, 1.8 % for groundwater and infiltrated water) remained rather limited. Incidentally, here also considerable reductions were achieved.

The reductions were linked to measures taken by the companies. The greatest reduction was achieved by eliminating transport chlorination below 8-11 °C and by reducing chlorination in the summer.

The measures taken have led to a considerable reduction in the THM content. Where contents of more than 100 μg/liter were present in 1976, in 1979/1980, the average contents were below 40 μg/liter. However, an accurate comparison is not possible, since little data are available for 1976. After the second inventory as well, some limitations in chlorine consumption were carried out. This includes the elimination of post-chlorination, iron(II)oxidation via the Lurgi process and increasing the temperature criterion for transport disinfection.

In the near future, the use of ClO_2 for transport and post-disinfection and, when possible, the elimination or restriction of post-chlorination have a high priority.

LITERATURE

3.1 Sybrandi, J.C., Meijers, A.P., Graveland, A., Poels, C.L.M., Rook, J.J., Piet, G.J.: Problems concerning haloforms. KIWA Communication no. 57, Rijswijk, May, 1978.

3.2 Kruithof, J.C., Paassen, J.A.M. van: Analytical investigation on the side effects of chlorination in water works using chlorine in their treatment. Report 323 from KIWA, 1981.

4 HALOGENATED COMPOUNDS FORMED BY CHLORINATION IN NETHERLANDS DRINKING WATER

4.1 Introduction

In the preparation of drinking water chlorine is used by a number of Water Works at various locations in the treatment system. During chlorination, a reaction can take place between free chlorine and precursors present in the water with formation of THM. The presence of these compounds is undesirable from the public health viewpoint.

For this reason, the ad hoc study group on "Chlorine" (ref. 4.1) recommended that the analytical chemical investigation regarding the occurrence of THM be intensified.

In addition, the ad hoc study group on "Chlorine" gave a high priority to the removal of THM precursors before these come into contact with chlorine.

After 1978, it became clear that during chlorination, in addition to THM, high molecular weight organohalogens are also formed. In mid-1979, there were already indications that this group of compounds could be very important both from the quantitative respect and in terms of toxicologic aspects.

For the above reasons, first of all, a coordinated analytical investigation was performed regarding the presence of THM in drinking water of all water treatment plants coming under consideration for this study. To evaluate the precursor content in drinking water, the THMFP precursor (trihalomethane formation potential) was determined. This THMFP is determined after a reaction time of 48 hr at a pH of 8 and a residual chlorine content after 48 hr of at least 5 mg/liter. In addition, the color, the UV extinction and the TOC content are determined in order to investigate whether a relationship exists between one of these parameters and the THMFP.

In order to gain an impression regarding the high molecular weight organohalogen content, the determination of the AOCl (adsorbable organochlorine) content was also added to the investigation. The EOCl (extractable organochlorine) content is also determined.

In addition, the chlorine consumption during the THMFP determination and the chlorine dose in the plant are established.

In the period from September, 1979, to July, 1980, in this connection 10 Water Works at 14 production locations carried out the following determinations:

a. the THM content in chlorinated drinking water after leaving the pumping station and after a residence time of about 48 hr in the distribution system;
b. the THMFP of the drinking water;
c. the TOC, UV extinction and color of the drinking water;
d. the AOCl and EOCl content in the chlorinated drinking water;
e. the chlorine consumption during the THMFP determination;
f. the chlorine dose applied by the Water Works.

The companies participating in the investigation with the relevant production plants and water types treated are reproduced in table 4.1. The plants are ranked according to water type. Plants 1 and 2 are groundwater processing plants, plants 3 up to and including 8 treat infiltrated water and plants 9-14 treat reservoir water. The geographical location of the participating production companies is shown in figure 4.1.

Table 4.1 - Water works participating in the analytical investigation to the side effects of chlorination together with production location and water type

nr.	Water Work	Production location	Abbr.	Water type
1	Water Works of Overijssel	Diepenveen	WMO	groundwater
2	Groningen Municipal Water Works	De Punt	GWG	groundwater
3	Dune Water Works of 's-Gravenhage	Scheveningen	DWL 's-Gravenhage	infiltrated Meuse water
4	Provincial Water Works of North Holland	Wijk aan Zee	PWN (W)	infiltrated Rhine water
5	Water Works of South West Netherlands	Ouddorp	WMZ (O)	infiltrated Haringvliet water
6	Enschede Municipal Energy Concern	Weerselose-weg	ONE	infiltrated Twente Canal water
7	Water Works of South West Netherlands	Haamstede	WMZ (H)	infiltrated Haringvliet water
8	Municipal Water Works of Amsterdam	Leiduin	GW (L)	infiltrated Rhine water
9	Municipal Water Works of Amsterdam	Driemond	GW (D)	Bethune polder water
10	Water Works of Rotterdam	Kralingen	DWL R (K)	Biesbosch water
11	Provincial Water Works of North Holland	Andijk	PWN (A)	IJssel Lake water
12	Water Works of North West Brabant	Zevenbergen	WNWB	Biesbosch water
13	Water Works of Rotterdam	Berenplaat	DWL R (B)	Biesbosch water
14	Dordrecht Municipal Energy Concerns	Baanhoek	GEBD	Wanty water

All of the study results are reported in report 323 from KIWA (ref. 4.2). An example of the manner in which the data in this report were processed will be given below for plant no. 12 (WNWB).

a. Process scheme

(R = reservoir; TrCl = transport chlorination; BrCl = breakpoint chlorination; RF = rapid filtration; GAC = granular activated carbon filtration; PCl = post-chlorination.)

Chlorinations:

- transport chlorination : winter 0 mg/liter; summer 1.8 mg/liter, contact time 48 hr.;
- breakpoint chlorination: 1.7 mg/liter, contact time 30-90 min.;
- post-chlorination : 0.5 mg/liter, contact time 4-15 hr..

b. Analytical data (also see figures 4.1 and 4.2)

- THM content on leaving the pumping station

	conc (µg/l)		
	min	max	average
$CHCl_3$	3,7	13,0	8,7
$CHBrCl_2$	2,3	12,0	6,8
$CHBr_2Cl$	2,3	9,6	5,9
$CHBr_3$	1,2	5,8	4,1
TTHM	11,0	39,2	25,5

- THM contents after 48 hr. in the distribution system

	conc (µg/l)		
	min	max	average
$CHCl_3$	7,1	16,0	10,9
$CHBrCl_2$	2,6	15,0	9,7
$CHBr_2Cl$	5,0	13,0	9,9
$CHBr_3$	4,2	10,0	7,0
TTHM	22,6	50,4	37,7

- THMFP prec.

	conc (µg/l)		
	min	max	average
$CHCl_3$	15,0	34,0	25,6
$CHBrCl_2$	12,0	30,0	22,6
$CHBr_2Cl$	12,0	19,0	17,0
$CHBr_3$	3,0	5,4	4,1
TTHM	42,9	89,3	69,2
THMFP (µmol/l)	0,269	0,580	0,450

	min	max	avg.
- EOCl content (µg/l)	0,8	4,5	1,7
- AOCl content (µg/l)	40	140	78
- TOC content (mg/C/l)	1,3	3,4	2,1
- UV extinction (m^{-1})	1,9	3,9	2,7
- color (mg Pt/l)	< 5	< 5	-

In the remainder of this section, only the total

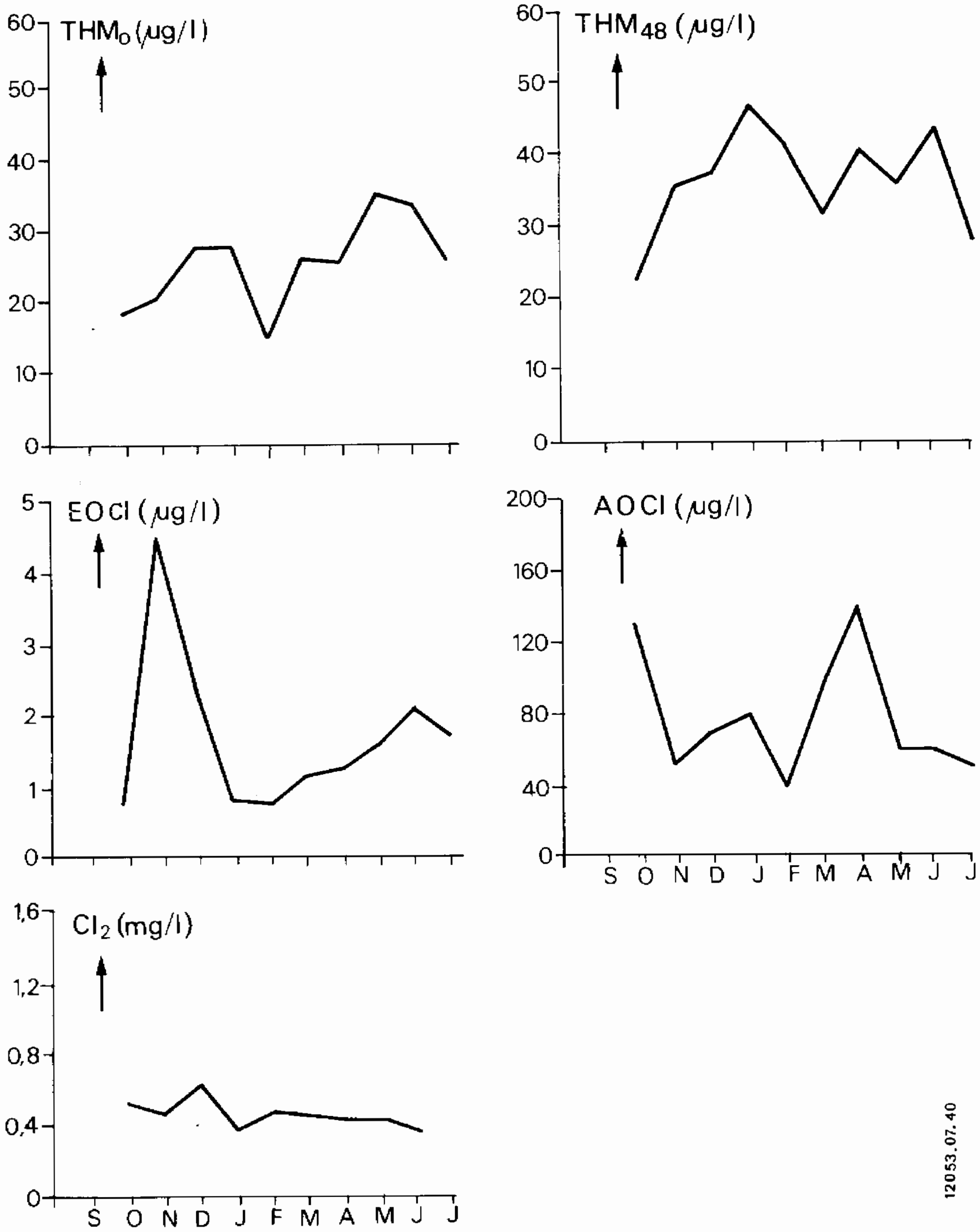

Figure 4.2 - Data on chlorination and side effects of chlorination, plant 12

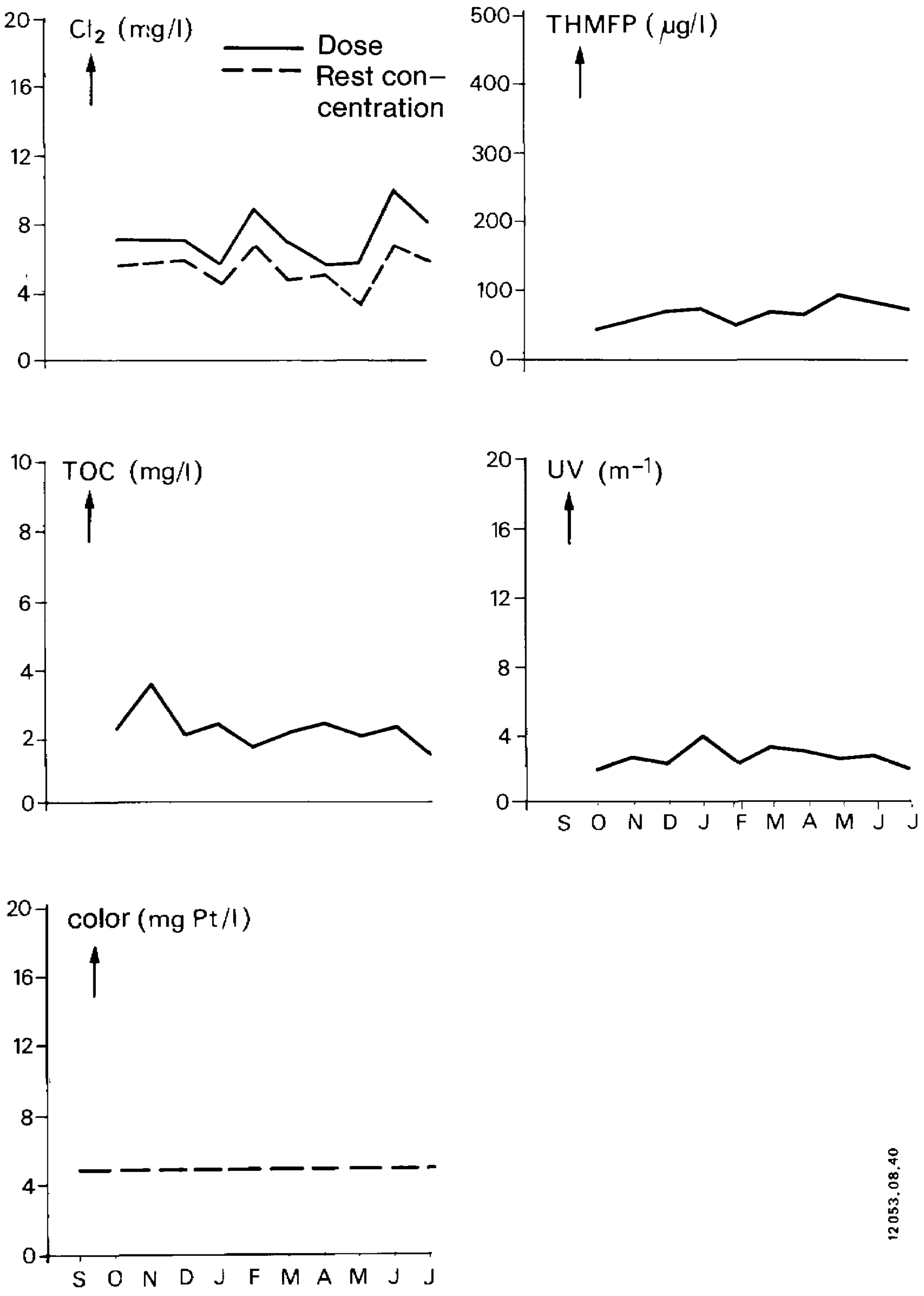

Figure 4.3 - Chlorine dose and chlorine consumption, THMFP determination and precursor data, plant 12

THM content is reported. For the composition thereof, refer to ref. 4.2.

In the following, the most important data in this connection will be reported. Subsequently, for drinking water prepared from groundwater, infiltrated water and reservoir water, the chlorine dosages and the minimal, maximal and average values will be given for the THM contents after 0 and 48 hr (THM_0 and THM_{48}), the THMFP, the EOCl and AOCl contents and likewise the TOC, UV extinction and color. The results obtained will be evaluated in a discussion.

4.2 Drinking water prepared from groundwater

WMO and GWG prepared drinking water (partially) from groundwater and used post-chlorination in the treatment. The results obtained from the study on the side effects of chlorination are shown in table 4.2.

Table 4.2 - Side effects of chlorination in drinking water prepared from groundwater

Parameter	WMO			GWG		
	min	max	avg.	min	max	avg.
THM_0 (µg/l)	0,8	4,8	2,6	1,1	13,2	4,3
THM_{48} (µg/l)	1,6	4,7	3,0	-	-	-
THMFP (µmol/l)	0,85	1,14	1,00	0,21	3,19	1,07
EOCl (µg/l)	0,1	0,6	0,4	0,1	0,5	0,3
AOCl (µg/l)	50	60	55	20	70	42
TOC (mg/l)	0,3	4,9	2,9	3,1	4,7	3,7
UV (m^{-1})	0	13,3	9,7	6,1	12,0	7,8
color (mg Pt/l)	12	15	13	5	7	6
Cl_2 total (mg/l)	0,6			0,4-0,5		
Cl_2 post-chlorination (mg/liter)	0,6			0,4-0,5		

4.3 Drinking water prepared from infiltrated water

DWL 's-Gravenhage, PWN at Wijk aan Zee, WMZ at Ouddorp, ONE, WMZ at Haamstede and GW at Leiduin prepare drinking water from infiltrated surface water and use chlorine at one or more points in the purification (see table 4.6). The most important results obtained from the study on the side effects of chlorination are reproduced in table 4.3. "Chlorine consumption" refers to the use of a chlorine dioxide/chlorine mixture.

Table 4.3 - Side effects of chlorination in drinking water prepared from infiltrated water

Parameter	DWL 's-Gravenhage			PWN (W)			WMZ (O)		
	min	max	avg.	min	max	avg.	min	max	avg.
THM_0 (µg/l)	0	5,0	0,8	0	5,1	2,0	0	4,4	2,6
THM_{48} (µg/l)	-	-	-	-	-	-	-	-	-
THMFP (µmol/l)	0,38	0,61	0,50	-	-	0,49	0,80	1,69	1,27
EOCl (µg/l)	< 0,1	0,4	<0,1	1,1	2,8	2,1	<0,1	1,1	0,4
AOCl (µg/l)	<10	50	13	10	40	25	10	80	36
TOC (mg/l)	2,5	4,2	3,4	2,2	5,3	3,4	1,5	8,1	4,3
UV (m^{-1})	5,5	8,6	6,3	3,8	6,0	5,0	-	-	-
color (mg Pt/l)	4	23	7	<1	10	4	8	13	10
Cl_2 total (mg/l)	1,5 t/m 2,05			2,0"0,08"			1,2		
Cl_2 post-chlorination (mg/liter)	0			"0,08"			0,2		

Tabel 4.3 - Continuation

Parameter	ONE			WMZ (H)			GW (L)		
	min	max	avg.	min	max	avg.	min	max	avg.
THM_0 (µg/l)	0	4,9	2,9	0	25,1	3,7	15,0	34,5	23,7
THM_{48} (µg/l)	0	9,4	5,8	-	-	-	9,9	30,8	21,2
THMFP (µmol/l)	2,29	3,33	2,87	0,32	0,74	0,50	0,68	1,09	0,92
EOCl (µg/l)	< 0,1	2,0	0,6	<0,1	1,8	0,5	1,7	11,0	5,1
AOCl (µg/l)	10	40	23	10	50	13	<10	40	20
TOC (mg/l)	5,6	6,5	6,0	0,7	3,1	1,6	2,5	3,4	3,0
UV (m^{-1})	14,5	19,5	16,1	-	-	-	5,0	6,1	5,6
color (mg Pt/l)	10	15	13	3	5	-	2,5	2,5	2,5
Cl_2 total (mg/l)	< 0,5			1,2			2,6-3,1		
Cl_2 post-chlorination (mg/liter)	< 0,5			0,2			0,6		

4.4 Drinking water prepared from reservoir water

GW at Driemond, DWLR at Kralingen, PWN at Andijk, WNWB, DWLR at Berenplaat and GEBD prepare drinking water from surface water and use chlorine at one or more points in the purification (see table 4.6). The results obtained from the study on the side effects of chlorination are summarized in table 4.4.

Table 4.4 - Side effects of chlorination in drinking water prepared from surface water

Parameter	GW (D)			DWL R (K)			PWN (A)		
	min	max	avg.	min	max	avg.	min	max	avg.
THM_0 (µg/l)	2,3	17,4	8,0	6,5	27,1	16,4	10,4	39,6	22,5
THM_{48} (µg/l)	5,1	14,9	8,2	13,5	35,3	22,3	7,7	40,6	21,4
THMFP (µmol/l)	0,93	3,55	2,37	0,30	0,68	0,46	-	-	0,34
EOCl (µg/l)	0,4	1,7	0,8	1,0	4,8	2,8	1,3	3,1	2,2
AOCl (µg/l)	-	-	30	<10	30	18	10	90	40
TOC (mg/l)	4,1	5,6	4,8	1,7	2,5	2,1	1,6	5,7	2,9
UV (m^{-1})	6,7	8,6	7,5	1,7	2,2	1,9	0,9	1,9	1,4
color (mg Pt/l)	<5	<5	-	<1	2	-	<1	5	-
Cl_2 total (mg/l)	0,4			0,6 t/m 2,4			7,9+"0,03"		
Cl_2 post-chlorination (mg/liter)	0,4			0,6			"0,03"		

Parameter	WNWB			DWL R (B)			GEB D		
	min	max	avg.	min	max	avg.	min	max	avg.
THM_0 (µg/l)	11,0	39,2	25,5	16,2	49,5	29,5	22,6	48,8	37,7
THM_{48} (µg/l)	22,6	50,4	37,7	27,5	50,6	38,4	21,9	53,3	44,7
THMFP (µmol/l)	0,27	0,58	0,45	0,54	1,38	0,87	0,69	1,14	0,93
EOCl (µg/l)	0,8	4,5	1,7	0,4	6,0	3,0	1,8	3,3	2,5
AOCl (µg/l)	40	140	78	20	90	59	40	120	79
TOC (mg/l)	1,3	3,4	2,1	2,6	3,5	3,1	2,5	3,0	2,8
UV (m^{-1})	1,9	3,9	2,7	4,3	5,3	5,0	4,0	5,0	4,7
color (mg Pt/l)	<5	<5	-	1,0	2,4	1,8	3,0	5,0	4,3
Cl_2 total (mg/l)	2,2 t/m 4,0			4,0 t/m 5,85			3,4		
Cl_2 post-chlorination (mg/liter)	0,4			0,6			1,3		

4.5 Discussion

4.5.1 THM contents in drinking water upon leaving the pumping station and after 48 hr in the distribution system

In paragraph 4.2 up to and including 4.4, the THM contents are presented for each plant. Upon leaving the pumping station, the following minimal, maximal and average THM values are encountered (see table 4.5).

Table 4.5 - Minimal, maximal and average THM contents in drinking water treated with chlorine upon leaving the pumping station

	All water types	Ground-water	Infiltrate*	Surface water*
THM_{min}	0 -22,6	0,8- 1,1	0- en 15,0	2,3 en 6,5-22,6
THM_{max}	4,4-49,5	4,8-13,2	4,4-25,1 en 34,5	17,4 en 27,1-49,5
$THM_{avg.}$	0,8-37,7	2,6- 4,3	0,8- 3,7 en 23,7	8,0 en 16,4-37,7

* In view of the distinctly deviating character, a separate site is reported for both infiltrate and surface water

The table shows that by far the lowest THM contents are present in drinking water prepared from groundwater and infiltrated water. Relatively high THM contents occur in drinking water prepared from surface water. Variations are seen in the THM content at GW (L) and GW (D) which are strikingly high for infiltrated water and strikingly low for surface water.

The data do not permit any quantitative correlation to be derived between the chlorine dose and the THM content. From the qualitative viewpoint transport chlorination before infiltration appears to have scarcely any effect on the THM content and transport chlorination in the case of surface water, to have a very limited effect on the THM content.

Especially in the absence of carbon filtration, breakpoint chlorination has a substantial influence. Post-chlorination with a relatively low chlorine dose coincides with a high THM content.

DWL 's-Gravenhage, which performs infiltration after two transport chlorinations and then performs no further chlorinations, has an average THM content of 0.8 µg/liter.

Following breakpoint chlorination PWN (A) uses carbon filtration, followed by ClO_2/Cl_2 dosage. The THM content (average 22.5 µg/liter) in this case is caused by breakthrough in carbon filters. GEB D with breakpoint and post-chlorination has the highest average THM content (37.7 µg/liter).

The THM composition differs greatly depending on the production location. This is illustrated in table 4.6 on the basis of the $CHBr_3$ contents in drinking water upon leaving the treatment plant.

Highly chlorinated THMs are found in the drinking water in the case of WMO, GWG, DWL 's-Gravenhage, PWN (W), WMZ (O) and PWN (A). Highly brominated THMs are found at the facilities of ONE, WMZ (H), GW (L), GW (D), DWL R (K), WNWB, DWL R (B) and GEB D. The average $CHBr_3$ content at these locations varies between 0 and 6.0 µg/liter.

DWL 's-Gravenhage and PWN (A) have low $CHBr_3$ con-

tents. It can be deduced from this that brominated THMs are removed better by infiltration and carbon filtration than chlorinated THMs.
It is remarkable that at DWL R (K) and WNWB, where post-chlorination is preceded by activated carbon filtration, by far the highest bromoform contents are encountered. This fact is also accompanied by the lowest TOC content. This phenomenon will be discussed in greater detail in section 7.
Here, too, the different nature of GW (L) is noted. In comparison to the other plants, a very high $CHBr_3$ content is found here.

Table 4.6 - Minimal, maximal and average $CHBr_3$ contents together with the adsorptive and oxidative process steps and the average TOC content

Plant	$CHBr_3$ (µg/l)			O_3, Cl_2 and activated carbon processes present	$TOC_{avg.}$ (mg/l)
	min	max	avg.		
WMO	0	0,1	0	PCl	2,9
GWG	0	0	0	PCl	3,7
DWL 's-Gravenhage	0	0	0	TrCl - TrCl - PAC	3,4
PWN (W)	0	0,9	0,1	TrCl - ClO_2	3,4
WMZ (O)	0	1,0	0,4	TrCl - O_3 - GAC - PCl	4,3
ONE	0	4,9	2,9	PCl	6,0
WMZ (H)	0	"14,5"	11,8	TrCl - O_3 - GAC - PCl	1,6
GW (L)	2,9	7,5	7,5	TrCl - PAC - PCl	3,0
GW (D)	0	4,0	0,9	O_3 - PCl	4,8
DWL R (K)	2,3	10,1	6,0	TrCl - O_3 - GAC - PCl	2,1
PWN (A)	0	0,7	0,2	BrCl - GAC - ClO_2	2,9
WNWB	1,2	5,8	4,1	TrCl - BrCl - GAC - PCl	2,1
DWL R (B)	0	2,8	1,2	TrCl - BrCl - PAC - PCl	3,1
GEB D	1,4	7,8	3,2	BrCl - O_3 - PCl	2,8

The 14.5 µg/liter $CHBr_3$ at WMZ (H) is a single observation. In addition, no value above 2.9 µg/liter is encountered.
Unfortunately, bromide contents are scarcely known for raw and treated water. The measurement of these parameters together with the TOC content make for a deepened insight into the THM composition after chlorination.

Nine plants have measured the THM content after a residence time of 48 hr in the distribution system. This is true of the WMO groundwater plant; the ONE and GW (L) infiltration plants and all surface water companies. The minimal, maximal and average THM contents encountered after 48 hr are presented in table 4.7.

Table 4.7 - Minimal, maximal and average THM contents in drinking water after 48 hr in the distribution system

	All water types	Groundwater	Infiltrate	Surface water
THMmin	0 -27,5	1,6	0 en 9,9	5,1-27,5
THMmax	4,7-53,3	4,7	9,4 en 30,8	14,9-53,3
THMavg.	3,0-44,7	3,0	5,8 en 21,2	8,2-44,7

Once again, it is apparent that relatively low THM contents occur in drinking water prepared from groundwater and infiltrated water and relatively high THM contents in drinking water prepared from surface water. Now also GW (L) and GW (D) have deviating values.

A significant formation of THM in the distribution-system occurs at ONE, DWL R (K), WNWB, DWL R (B) and GEB D plants. The average formed quantities of THM and $CHBr_3$ are presented along with the chlorine dose for post-chlorination and the purification system in table 4.8.

Table 4.8 - The average quantity of THM and $CHBr_3$ formed in the distribution system together with chlorine dose and purification system

Plant	Chlorine dose (mg/l)	Process	ΔTHM (μg/l)	$\Delta CHBr_3$ (μg/l)
ONE	< 0,5	PCl	2,9	0
DWL R (K)	0,6	TrCl-O_3-GAC-PCl	5,9	2,6
WNWB	0,5	TrCl-BrCl-GAC-PCl	12,2	2,9
DWL R (B)	0,45	TrCl-BrCl-PAC-PCl	8,9	0,6
GEB D	1,3	BrCl-O_3-PCl	7,0	0,3

No definite quantitative correlation exists between the chlorine dose and the formation of THM in the distribution system. A relationship between the residual chlorine contents after 1 hr and the THM formation in the distribution system also does not exist. After carbon filtration and post-chlorination, a relatively large amount of bromoform is formed in the distribution system.

4.5.2 The THMFP precursor of drinking water

In paragraph 4.2 up to and including 4.4, the THMFP precursors are given for all of the plants. In table 4.9, the average THMFP precursor is once again given, together with the average THM content upon leaving the pumping station. Both contents are expressed in μmol/liter. Also presented in this table is the percentage of the THMFP encountered as THM in practice.

Table 4.9 - Average THM contents upon leaving the pumping station, average THMFP and percentage conversion of THMFP in practice

Plant	THM_0 (μmol/l)	THMFP (μmol/l)	$\frac{THM_0}{THMFP} \times 100$
WMO	0,020	1,004	2,0
GWG	0,031	1,066	2,9
- - - - - - - - - -	- - - -	- - - -	- - - - -
DWL 's-Gravenhage	0,005	0,502	1,0
PWN (W)	0,013	0,486	2,7
WMZ (O)	0,015	1,272	1,2
ONE	0,023	2,869	0,8
WMZ (H)	0,018	0,504	3,6
GW (L)	0,131	0,915	14,3
- - - - - - - - - -	- - - -	- - - -	- - - - -
GW (D)	0,051	2,367	2,2
DWL R (K)	0,095	0,458	20,7
PWN (A)	0,173	0,343	50,4
WNWB	0,158	0,450	35,1
DWL R (B)	0,197	0,865	22,8
GEB D	0,232	0,929	25,0

It is apparent from the table that the average THMFP varies from 0.34 to 2.87 µmol/liter. The THMFP for treated groundwater at the two plants investigated is about 1 µmol/liter, for treated infiltrate 0.49-2.87 µmol/liter and treated surface water 0.34-2.37 µmol/liter.

It is very remarkable that only 0.8-3.6 % of the THMFP is converted in practice for most groundwater and infiltration plants. For most surface water companies, this figure is 20.7-50.4 %. A different behavior is, once again, shown by the infiltration plant GW (L) and the surface water plant GW (D) with 14.3 and 2.2 %, respectively. In all cases, however, under practical conditions, a large fraction of THMFP is not converted into THM. This shows that under normal process condition, it is not the THMFP but rather the chlorine dose which is of determining significance for the THM content in drinking water. The post- chlorination and, to a lesser extent, breakpoint chlorination are of importance in this regard. This will be discussed in further detail in section 7.

It can be deduced from these results that the precursor removal (THMFP reduction) demands a lower priority and that the chlorine dose during post-chlorination is specifically of great importance so that reduction of the chlorine consumption or an alternative disinfection step (ClO_2) should be considered.

4.5.3 The EOCl and AOCl contents in drinking water upon leaving the pumping station

In addition to THM, other halogenated compounds are also formed during chlorination. Some of these compounds can be characterized by the EOCl content

(lipophilic chlorinated compounds) and by the AOCl content (for example, chlorinated humic materials). The minimal, maximal and average EOCl and AOCl content per production plant are presented in paragraphs 4.2 up to and including 4.4.
Table 4.10 gives these contents, arranged according to water type.

Table 4.10 - Minimal, maximal and average EOCl and AOCl contents in drinking water upon leaving the pumping station

	All water types	Groundwater	Infiltrate	Surface water
EOClmin	<0,1- 1,8	0,1	<0,1- 1,7	0,4- 1,8
EOClmax	0,4- 11,0	0,5- 0,6	0,4-11,0	1,7- 6,0
EOClavg.	<0,1- 5,1	0,3- 0,4	<0,1- 5,1	0,8- 3,0
AOClmin	<10 - 50	20 -50	<10 -10	<10 - 40
AOClmax	30 -140	60 -70	40 -80	30 -140
AOClavg.	13 - 79	42 -55	13 -36	18 - 79

It is apparent from the table that the lowest EOCl and AOCl contents are found in drinking water prepared from groundwater and infiltrated water. Once again, the GW(L) plant forms an exception; it has a relatively very high EOCl content.
The EOCl content averages < 0.1-5.1 µg/liter. Contents of above 1 µg/liter occur quite regularly. The AOCl content averages 13-79 µg/liter, which is relatively high.
In order to gain an impression regarding the molar

ratio of the EOCl and AOCl contents formed to the THM formed and regarding the total quantity formed the average value together with the annual drinking water production throughout 1979 are presented in table 4.11.

Table 4.11 - Average THM, EOCl and AOCl contents on leaving the pumping station and the annual drinking water production in 1979

Plant	Annual produc. m^3/year	$\text{THM}_{\text{avg.}}$ µmol/l	$\text{EOCl}_{\text{avg.}}$ µmol/l	$\text{AOCl}_{\text{avg.}}$ µmol/l	$\frac{\text{EOCl}}{\text{THM}}$	$\frac{\text{AOCl}}{\text{THM}}$
WMO	2,9 x 10^6	0,020	0,011	1,55	0,55	77,5
GWG	12,6 x 10^6	0,031	0,009	1,18	0,29	32,8
DWL's G	45 x 10^6	0,005	< 0,003	0,37	< 0,60	74,0
PWN(N)	3,6 x 10^6	0,013	0,059	0,70	4,54	53,8
WMZ(O)	2,7 x 10^6	0,015	0,011	1,01	0,73	67,3
ONE	6,5 x 10^6	0,023	0,017	0,65	0,74	28,3
WMZ(H)	2,9 x 10^6	0,018	0,014	0,37	0,78	20,6
GW(L)	57,7 x 10^6	0,131	0,144	0,56	1,10	4,8
GW(D)	21,6 x 10^6	0,051	0,023	0,85	0,45	16,7
DWLR(K)	33,1 x 10^6	0,095	0,079	0,51	0,83	5,4
PWN(A)	21,6 x 10^6	0,173	0,062	1,13	0,36	6,5
WNWB	2,5 x 10^6	0,158	0,048	2,20	0,30	13,9
DWLR(B)	72,7 x 10^6	0,197	0,085	1,66	0,43	8,4
GEB/D	9 x 10^6	0,232	0,070	2,23	0,30	9,6

The average EOCl content thus varies from < 0,003 to 0,144 µmol/liter. From the molar viewpoint, this is an average of 0,8 times as high as the THM content. The AOCl content varies from 0,37 to

2,23 μmol/liter. On the average, on a molar basis, this is 30 x the THM content.

From this, it is also possible to deduce the ratios of the organohalogen contents in the various groups. Since each THM molecule contains three halogen atoms, the ratio between the content of halogens in EOCl and THM is about 0,3. For AOCl and THM, this ratio amounts to about 10.

In view of the types of compounds which make up the EOCl content and the undefined nature of the compounds which are determined with the AOCl content, further investigation regarding these two groups of compounds is urgently desired.

4.5.4 Total quantity of halogenated compounds in drinking water, 1979-1980

About $294,4 \times 10^6$ m^3 of drinking water treated in some way with chlorine was produced from September, 1979, to August, 1980.

The THM content in this water varied from 0,005 to 0,232 μmol/liter. In the total quantity of water produced this is 33,000 mol THM/year or about 4.000 kg THM per year. The EOCl content varied from < 0,003 to 0,144 μmol/liter. This means a total quantity of about 715 kg extractable organochlorine.

The AOCl content varied from 0,37-2,23 μmol/liter. This means a total quantity of 10,105 kg adsorbable organochlorine. Thus, about 15,000 kg organochlorine was distributed via purified water in the period in question.

The total THMFP in the distributed water was 268,090 mol THM/year. Thus, 33,000 mol of this was converted into THM. This means a conversion of 12,4 %.

4.5.5 Relationship between THMFP, UV extinction, TOC and color

Next, it was investigated whether the fairly complicated THMFP determination could be replaced by the determination of UV extinction, TOC content or color. The collected results of the 14 plants are presented in table 4.12.

It is apparent from the table that a simple relationship does not exists for any of the parameters. For certain plants or water types, the THMFP may be determined on the basis of, for example the TOC content. However, this is not possible for a national comparison.

Table 4.12 - Average values for THMFP, UV extinction, TOC content and color of the 14 plants

Plant	THMFP µmol/l	UV m^{-1}	TOC mg/l	Color mg Pt/l	$\frac{\text{THMFP}}{\text{UV}}$	$\frac{\text{THMFP}}{\text{TOC}}$	$\frac{\text{THMFP}}{\text{color}}$
WMO	1,004	9,7	2,9	13	0,10	0,35	0,08
GWG	1,066	7,8	3,7	6	0,14	0,29	0,18
DWL's G	0,502	6,3	3,4	7,2	0,08	0,15	0,07
PWN(W)	0,486	5,0	3,4	3,8	0,10	0,14	0,13
WMZ(O)	1,272	-	4,3	9,8	-	0,30	0,13
ONE	2,869	16,1	6,0	12,9	0,18	0,48	0,22
WMZ(H)	0,504	-	1,6	-	-	0,32	-
GW(L)	0,915	5,6	3,0	2,5	0,16	0,31	0,37
GW(D)	2,367	7,5	4,8	-	0,32	0,49	-
DWLR(K)	0,548	1,9	2,1	-	0,24	0,22	-
PWN(A)	0,343	1,4	2,9	-	0,25	0,12	-
WNWB	0,450	2,7	2,1	-	0,17	0,21	-
DWLR(B)	0,865	5,0	3,1	1,8	0,17	0,28	0,48
GEB D	0,929	4,7	2,8	4,3	0,20	0,33	0,22

4.6 Conclusions

The investigation described in the preceding paragraphs over the period of September, 1979, to July, 1980, can be summarized as follows.

1. The THM content in the pure water on leaving the pumping station amounted to an average of 0,8-37,7 µg/liter.
2. The THM content amounted to an average of 3,0-44,7 µg/liter after a residence time of 48 hour in the distribution system.
3. Principally chlorine-containing THM were formed at 6 plants; more highly brominated THM were also formed at 8 plants. The $CHBr_3$ content at these 8 plants averaged 0,9-6,0 µg/liter.
4. At 5 locations, a quantity of THM in excess of 1 µg/liter was formed in the distribution system. This THM content averaged 2,9-12,2 µg/liter, of which 0-2,9 µg/liter was $CHBr_3$.
5. The average THMFP of the pure water varied from 0,34-2,87 µmol/liter. Of this, 0,8-50,4 % was converted to THM. The conversion was 0,8-3,6 % for most groundwater and infiltration plants and 20,7-50,4 % for the surface water plants.
6. The EOCl content in the pure water averaged < 0,1-5,1 µg/liter.
7. The AOCl content in the pure water averaged 13-79 µg/liter.
8. In the period from September, 1979, to August, 1980, a total of 4.000 kg THM, 715 kg EOCl and 10,105 kg AOCl was formed.
9. Altogether in the period September, 1979, to August, 1980, 268,090 mol of THM precursors were distributed. 12,4 % (33,000 mol) was converted into THM.

10. No definite relationship exists between the THMFP on one hand and UV extinction, TOC and color on the other hand.

The investigation also led to the following general conclusions.

a. There is no generally applicable numerical relationship between the chlorine dose and the THM content. Transport chlorination appears to have scarcely any effect on the THM content, breakpoint chlorination a variable effect and post-chlorination a great effect.
b. The composition of the THM content appears to depend greatly on the purification. By far, the highest bromoform content is encountered in the case of chlorination after carbon filtration.
c. Predominantly chlorine-containing THMs are encountered in the water in the case of chlorination followed by infiltration or carbon filtration.
d. On a molar basis, EOCl content is 0,8 x the THM content and the AOCl content is 30 x the THM content.
e. The THM content is lowest in the case of drinking water prepared from groundwater and infiltrated water and highest in the case of drinking water prepared from surface water.
f. Especially in surface water plants, formation of THM in the distribution system occurs upon post-chlorination. In the case of this formation as well, more brominated THMs are found after carbon filtration and post-chlorination.
g. The concept recommendation of VEWIN for the standard for the THM content of 0,55 µmol/liter is not exceeded in any case. However, the guideline level for halogenated hydrocarbons (not

pesticides) of 1 µg/liter was exceeded.

h. Only part of the THMFP was converted to THM. In practice, the chlorine dose more frequently is of determining significance for the THM content than is the precursor content.

The investigation performed gives rise to the following recommendations.

1. Studies aimed at restricting or eliminating post-chlorination.
2. Studies regarding the effects and side effects of alternatives to chlorine.
3. Investigation regarding the influence of the bromide content on the composition of the THM content and on the composition of the contents of high molecular weight organohalides (AOX).
4. Study regarding the side effects of chemical disinfection with the aid of toxicity testing.

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5 FORMATION OF HALOGENATED COMPOUNDS DURING SINGLE CHLORINATION STEPS AND OZONATION

5.1 Introduction

The reduction of chlorine use in 1976-1979 is described in section 3. Whenever possible, in addition, the reduction of the THM content during this time period was discussed. In section 4, extensive attention was paid to the contents of byproducts of chlorination in Water Works using chlorine in their treatment. The THM, EOCl and AOCl contents found in the treated water are reported for the period of September, 1979, to July, 1980. In this section, we will discuss the formation of halogenated compounds in a specific chlorination step. THM formation will principally be discussed; scarcely any information is available regarding the EOCl and AOCl contents. First, a model study on the chlorination of Biesbosch, IJssellake, Andelse Meuse and Lek Canal water will be discussed. From this, an impression will be gained regarding the THM contents to be anticipated after transport-, breakpoint- and post-chlorination. Then, the side effects of transport chlorination will be discussed with reference to six plants, breakpoint chlorination at four plants and side effects of post-chlorination at eleven plants. Especially for post-chlorination, it will be difficult to differentiate between the side effects of post-chlorination and the prior treatment steps.

A discussion will be conducted regarding the formation of halogenated compounds by ozonation, with or without prior breakpoint chlorination.

5.2 Model study

5.2.1 Model study with non-purified Biesbosch, IJssellake and Andelse Meuse water

In 1979, single-time chlorination experiments were performed with non-purified Biesbosch, IJssellake and Andelse Meuse water (Refs. 5.1-5.3). For all water types, the THM formation was determined for a large number of chlorine dosages (0,25- 25,0 mg/ liter) and reaction times (0,25-96 hour). In addition, attention was directed toward the influence of the pH on THM formation in the pH range from 7,0-10,0 and toward the relationship between the breakpoint curve and THM formation. For this purpose, the breakpoint curve was determined for all water types.

Figure 5.1.a shows the THM content for reaction times up to 5 hours and figure 5.1.b gives the THM contents for reaction times up to 96 hours in the chlorination of Biesbosch water.

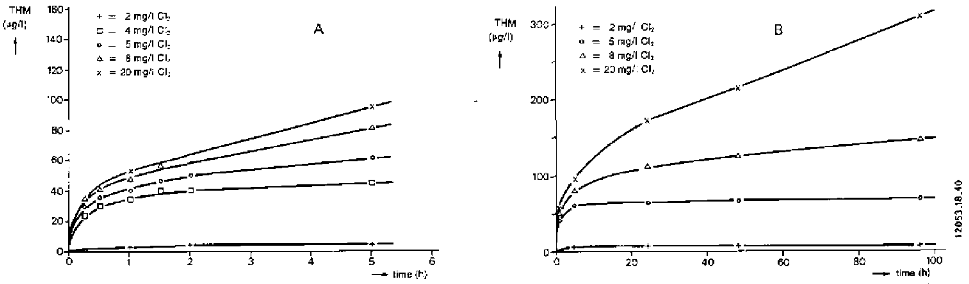


Figure 5.1 - THM content of Biesbosch water as a function of time at various chlorine dosages, date, July 5, 1979

It is apparent from the figure that for reaction times up to 5 hours, the THM contents amount to about 100 µg/liter at the highest chlorine dose. The highest THM content, 311 µg/liter, is encountered after 96 hours. In addition, for all water types, the THM formation was determined as a function of the chlorine dose along with the breakpoint curve.

Figure 5.2 presents these curves for the chlorination of IJssellake water for a reaction time of 4 hours.

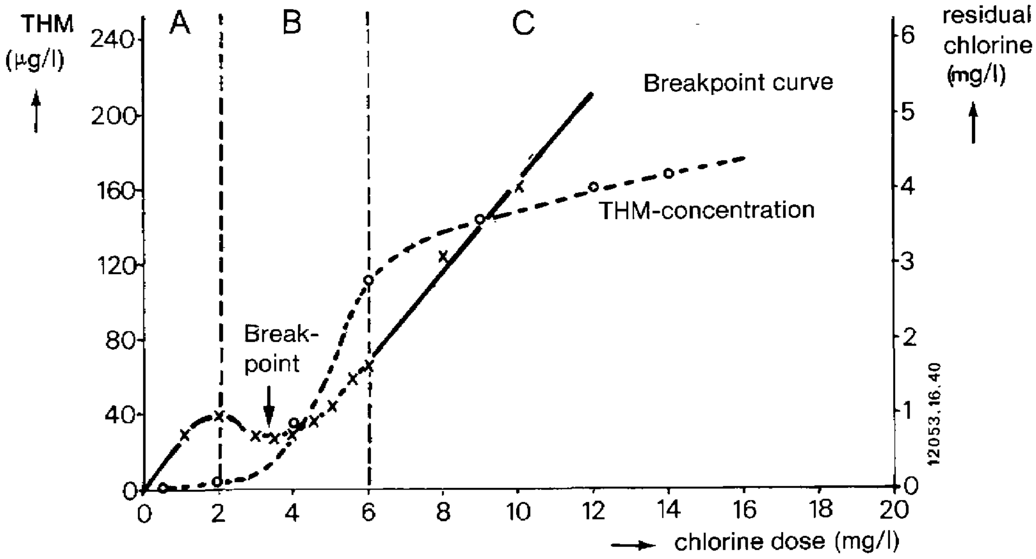


Figure 5.2 - THM concentration and residual chlorine content in the chlorination of IJssellake water

It is apparent from the figure that relatively little THM is formed up to the top of the breakpoint curve. The first free chlorine is detectable in the water at this point.

Immediately above this point, marked THM formation occurs; at higher dosages, the THM again increases only slightly. Thus, three regions can be differentiated at increasing chlorine dosages. Region A below the breakpoint where no free chlorine was detectable with scarcely any THM formation, region B somewhat below and immediately above the breakpoint with very marked THM formation and region C at high chlorine dosages with a limited extra THM formation. Regions A, B and C were determined for the three raw water types mentioned and for Lek Canal water. Table 5.1 gives the width of these regions expressed in mg/liter chlorine dosed as well as the THM formation per mg chlorine dosed.

Table 5.1 - THM formation for various water types

	A		B		C	
	Cl_2-dose mg/l	µgTHM mgCl_2	Cl_2-dose mg/l	µgTHM mgCl_2	Cl_2-dose mg/l	µgTHM mgCl_2
Lek Canal	0-2,8	2,5	2,8-4,3	14	4,3- 8	3
Biesbosch	0-2	2	2 -6	20	6 -20	1
Andelse Meuse	0-4	1	4 -9	12,5	9 -25	1-1,5
IJssellake	0-2	2	2 -6	35	6 -14	5

In region A where no free chlorine is detectable in the water, the chlorine added reacts with rapidly reacting substances. The width of this region is generally determined by the presence of ammonium compounds. In addition, a small amount of THM is formed by a competitive reaction of chlorine with rapidly reacting THM precursors. For each milligram of chlorine added in this region, only 1- 2,5 µg/liter THM is formed.

In region B the direct chlorine demand of the water is satisfied. In this region, free chlorine present for a long time reacts with organic materials including THM precursors. The width of this region is a measure of the quantity of organic substances reacting rather rapidly with chlorine. The number of µg THM per mg Cl_2 provides a preliminary characterization of the type of organic substances. For each milligram of added chlorine in this range, 12,5-35 µg/liter of THM are formed.

Chlorine and organic substances react with each other during very long reaction times, among other things, with formation of THM. This phenomenon is illustrated by region C.

It should be noted that the measurements presented in table 5.1 are based merely on an instantaneous portrait so that the numerical results may not be generally applicable. The relationship outlined between the breakpoint curve and THM formation with a breakdown into three regions of THM formation is believed always to occur from the qualitative viewpoint.

In 1976, the chlorine dose for transport chlorination often fell in region B. After this, the chlorine dose was greatly reduced and now almost always falls in region A. During transport chlorination in today's process control, only a limited THM formation will, therefore, probably take place.

For breakpoint chlorination in 1976, the chlorine dose fell in region B or possibly even in region C. For this application as well, the chlorine dose was greatly reduced, but still falls above the breakpoint, thus in region B. Breakpoint chlorination is thus always accompanied by an appreciable THM formation.

No conclusions regarding post-chlorination can be drawn from these experiments. This will be discussed in greater detail in the following paragraph.

A very definite pH dependence is apparent from the experiment (refs. 5.1 up to and including 5.3). For example, the THM content in the case of breakpoint chlorination can be greatly reduced by a pH reduction from 7,8 to 7,0. This can give a 25 % reduction in the THM content.

The fact that the ammonium content plays an important role has already become apparent from the course of the THM contents and the breakpoint curve. If chloramines are prepared seperately and then added, no THM formation whatsoever occurs. Upon addition of chlorine to ammonium-containing water, the THM formation is greatly limited. This indicates, once again, that low THM contents can be anticipated in the case of transport chlorination with low chlorine dosages.

5.2.2 Model study with untreated and partially treated Lek Canal water

In order to investigate the influence of treatment on THM formation during chlorination in 1979, KIWA performed chlorination experiments with untreated and treated Lek Canal water (ref. 5.4). The results for untreated water, rapid filtrate and carbon filtrate are summarized in table 5.2.

Table 5.2 - THM formation in raw Lek Canal water and in Lek Canal water after rapid filtration and activated carbon filtration

	A		B		C	
	Cl_2-dose mg/l	$\frac{\mu g\,THM}{mg\,Cl_2}$	Cl_2-dose mg/l	$\frac{\mu g\,THM}{mg\,Cl_2}$	Cl_2-dose mg/l	$\frac{\mu g\,THM}{mg\,Cl_2}$
Raw water	0-2,8	2,5	2,8-4,3	14	4,3-8	3
Fast filtrate	0-2,5	1,5	2,4-4,5	12	4,5-8	1
Carbon filtrate	0-0,8	3	0,8-1,5	12	1,5-5	1

It is apparent from the width of region B that in the raw water and the rapid filtrate practically the same THM formation takes place upon chlorination. The carbon filtrate is distinctly different in character. The THM formation as a function of the chlorine dose together with the breakpoint curve for carbon filtrate are shown in figure 5.3.

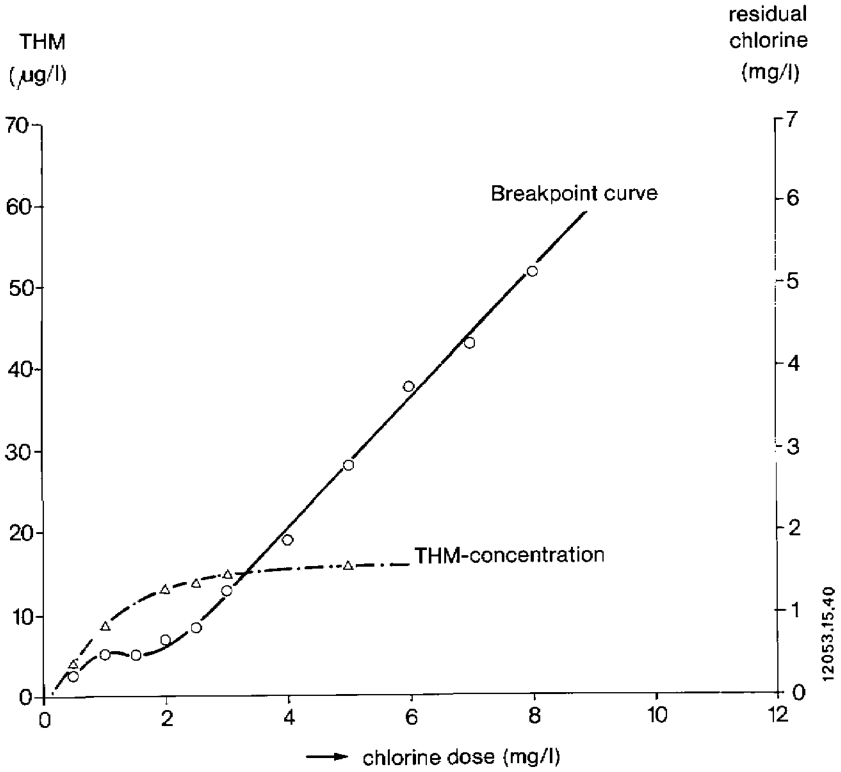


Figure 5.3 - THM content and residual chlorine content for carbon filtrate prepared from Lek Canal water

Free chlorine is detectable in the water even at very low chlorine dosages. It is apparent from the figure that even at very low chlorine doses relatively large amounts of THM are formed. The consequence of this is that in the post-chlorination of extensively purified water, relatively high THM contents can occur at low chlorine doses. This THM content can only be reduced by lowering the disinfection criterion. This criterion is established on the basis of the residual free chlorine content after a specific contact time (e.g., 0,2 mg/liter free chlorine after a 20 minute contact time). In view of the fact that the disinfection criteria in 1976 and 1979 were often the same, it can be anti cipated that THM formation during post-chlorination in both years will be practically unchanged.

5.2.3 Discussion

It was found from the model studies that a correlation can be drawn between THM formation as a function of the chlorine dose and the breakpoint curve. Below the breakpoint, as long as no free chlorine is detectable, THM formation scarcely occurs; immediately below and above the breakpoint, marked THM formation occurs; and at dosages far above the breakpoint, only a limited additional THM formation takes place. The consequence of this is that THM formation can be very limited during transport chlorination with low chlorine dosages. Breakpoint chlorination is always accompanied by relatively high THM contents.

As the water is further purified (and thus, for example, contains fewer ammonium ions), the breakpoint shifts toward lower chlorine dosages. As a result, free chlorine will be detectable in extensively purified water even at low chlorine dosages, and this wil cause a relatively marked THM formation.

The consequence of this is that during post-chlorination of pure water with low dosages, relatively high THM contents can, nevertheless, arise.

The question of whether these conclusions, based on model experiments, can be confirmed in practice will be considered in the following sections.

5.3 Formation of halogenated compounds during transport chlorination

5.3.1 Introduction

For the drinking water supply of the western Netherlands, extensive use is made of the surface water of the Rhine (Lek), Meuse and Haringvliet. Since the surface water source and the production plant are not close together, the water must be transported over considerable distances. Since the water is only partially pre-purified or is not pre-purified at all, in general, transport chlorination is used to prevent the growth on the pipe walls of, among other things, slime-forming bacteria and higher organisms such as mussels and sponges.

Sometimes chlorination and transport take place after storage in reservoirs (WBB) or prior to infiltration into the dunes (WRK, WMZ); sometimes a combination of both takes place (DWL Den Haag):

- The water supply company Brabantse Biesbosch (WBB) extracts raw water from the Meuse (Amer) at Kerksloot. Up to and including 1979, storage took place in two basins with a residence time of about 4 months; at present, storage takes place in three basins with an average residence time of 6 to 7 months. In the last basin (residence time 5 weeks), a hardness correction is carried out with the aid of sodium hydroxide addition. Prior to transport, the water is stabilized with sulfuric acid at a pH of 9.

  The water is transported to the production locations at Berenplaat and Kralingen on behalf of the Waterworks of Rotterdam, to the surface water treatment plant at Zevenbergen of the Waterworks of North-West-Brabant, and since the end of 1982,

to the Baanhoek production location of the Municipal Energy Concern of Dordrecht.
In 1974, chlorination was performed throughout the year with a chlorine dose of about 5 mg/liter. In 1979, the dose for transport chlorination was 1 mg/liter at temperatures above 6 °C (April-December). Beginning in 1980, this temperature criterion was increased to 10 °C (May-November).

- The Water Transport Company Rijn-Kennemerland (WRK) withdraws the raw water, which is Rhine water in origin, from the Lek Canal. The water is then coagulated and filtered after settling. The water is transported to the Leiduin treatment plant of GW and to Castricum on behalf of PWN. In the period from 1976-1979, the chlorine dosage remained practically constant (~ 2,5 mg/liter), but since 1978, chlorination was only performed at a water temperature above 10 °C. Beginning in 1983, chlorination is only performed at a water temperature above 15 °C. In 1984 transport chlorination is omitted almost completely.
- The Waterworks of Southwest Netherlands (WMZ) abstracts raw water from the Haringvliet. Up to 1976, the water was chlorinated with a chlorine dose of 2-3 mg/liter and transported to Ouddorp without further purification. Beginning in 1976, the chlorine dose was 1-1,5 mg/liter at a water temperature above 8 °C. In Ouddorp, part of the water was infiltrated; the rest was transported without further chlorination to Haamstede, being infiltrated there.
- The Dune Water Works of the Hague (DWL 's-G) abstracts water at the Meuse near Heusden. The water is treated with 9 mg/liter iron (II), then stored for about 2,5 months in the impounded Andelse Meuse. Following abstraction at Brakel,

the water is transported to Bergambacht, where, in 1979, transport chlorination with a chlorine dose of 1,5 mg/liter was used. Beginning in 1982, chlorination was only performed at a water temperature above 8 °C.

In Bergambacht, the water was rechlorinated after filtration and transported to Scheveningen, where infiltration takes place. Before 1978, the chlorine dose there was 2-3 mg/liter; after this time, the chlorine dose was reduced to 0,5 mg/liter at a water temperature above 8 °C (April-November). Beginning in 1984, no further transport chlorination at all was used in this sector.

5.3.2 Results

For the plants which use transport chlorination, the quality data for 1979 were gathered on the water prior to transport and chlorination using the data which could play a role in the formation of halogenated compounds. These involve the parameters TOC, $KMnO_4$-number, color, chlorophyll content, ammonium content, pH and temperature. The data are presented in table 5.3.

In addition, the data are gathered concerning the average transport time, chlorine dose, residual chlorine content after transport and the average THM and EOCl contents after transport. These data are presented in table 5.4.

It is apparent from the table that WRK during transport chlorination produces, by far, the highest average THM content and the highest EOC content (100 µg/liter and 3,1 µg/liter, respectively). All the other THM contents are significantly lower (4-13 µg/liter), while all other EOCl contents are indeed lower but fall in the same order of magnitude.

Table 5.3 - Average values of quality data for 1979 in water prior to transport and chlorination

Average quality 1979	WBB	WRK	WMZ Ouddorp and Haamstede	DWL 's-G	
				Brakel	Berg Ambacht
TOC (mg/l)	3,8	3,1	5,0	6,2	5,9
$KMnO_4$ (mg/l)	11	11	15	15	14,5
Color (mg Pt/l)	9	8	21	15	13,5
Chlorophyll (µg/l)	5	< 1	12	12	2
NH_4^+ (mg/l)	0,31	0,1	0,53	0,49	0,24
pH	9,0	7,8	7,9	7,85	7,7
Temperature (°C)	10,5	12,5	12	10,5	10,5

Table 5.4 - Chlorination conditions and side effects of transport chlorination in the year 1979

Company	Transport sector	Transport duration (h)	Chlorine dose (mg/l)	Residual chlorine content (mg/l)	THM (µg/l)	EOCl (µg/l)
WRK	Nieuwegein - Leiduin	24	2,5	0,1 -0,2	100	3,1
WMZ	Haringvliet - Ouddorp	2-4	1-1,5	< 0,1	2	2,6
	Haringvliet - Haamstede	15	1-1,5	< 0,1	< 1	1,5
DWL	Brakel - Bergambacht	11	1,5	0,2	4	-
's-G	Bergambacht - Scheveningen	12	0,5	0,1	9	-
WBB	Biesbosch - Berenplaat	8	1	0,35	6	1,4
	Biesbosch - Kralingen	13,5	1	0,35	6	1,1
	Biesbosch - Zevenbergen	48	1	0,03-0,08	13	1,0

5.3.3 Discussion

It can be deduced from the results reported in paragraph 5.3.2 that for the investigated water types, no definite correlation exists between the THM formation and the content of organic substances, expressed as TOC content, $KMnO_4$-number or color. At a comparable chlorine dose, DWL 's-G and WMZ produce less THM than WBB and WRK despite the fact that the organic matter contents for the first two plants are higher. The same is true for the chlorophyll content.

In addition, from the available data, no simple relationship can be derived between the pH and the THM formation. WBB maintains, by far, the highest pH during transport, but the THM content is not significantly higher than at the other plants.

In addition, for the chlorine dosages maintained, no definite relationship is detectable between either the chlorine dosage or the contact time and the THM content, although it appears that the highest THM contents occur at longer contact times.

In the model experiments described in section 5.2.1, a subdivision is made into three ranges of THM formation. The width of range A appeared to be principally determined by the presence of ammonium compounds. The presence of ammonium is then also of great determining significance for the phenomena observed. This also appears to be the case here.

For all plants, the ammonium content before transport, the chlorine dose, the ratio between these and the THM contents after transport are presented in table 5.5.

Table 5.5 - Ammonium content before transport, chlorine dose and THM content after transport

Plant	Transport	NH_4^+ (mg/l)	Cl_2-dose (mg/l)	$\frac{Cl_2}{NH_4^+}$	THM (µg/l)
WRK	Nieuwegein - Leiduin	0,10	2	20	$\leqslant$ 100
DWL 's-G	Bergambacht - Scheveningen	0,24	0,5	2,1	9
WBB	Biesbosch - Kralingen	0,31	1,0	3,2	6
DWL 's-G	Brakel - Bergambacht	0,49	1,5	3,1	4
WMZ	Haringvliet - Ouddorp	0,53	~ 1,25	2,3	2
	Haringvliet - Haamstede	0,53	~ 1,25	2,3	< 1

All the plants with a chlorine/ammonium weight ratio of 2-3 form less than 10 µg/liter THM. These plants principally form monochloramine, which does not yield THM. Only during chlorine addition is a limited amount of THM formed by free chlorine which is then still present.

At the WRK, however, the chlorine/ammonium ratio is 20. Thus, free chlorine is present here for a very long time; it reacts with THM precursors and leads to high THM contents.

It is apparent from these data that the chlorine/ammonium ratio is largely determining for the THM formation, a fact which was also suggested by the model experiments. This is supported by the course of the ammonium content and the THM formation in Biesbosch water during water transport to Berenplaat and Kralingen. The ammonium content and the THM content for 1979 are presented in figure 5.4. Beginning in mid-April, transport chlorination was begun with a dose of 1,0 mg/liter.

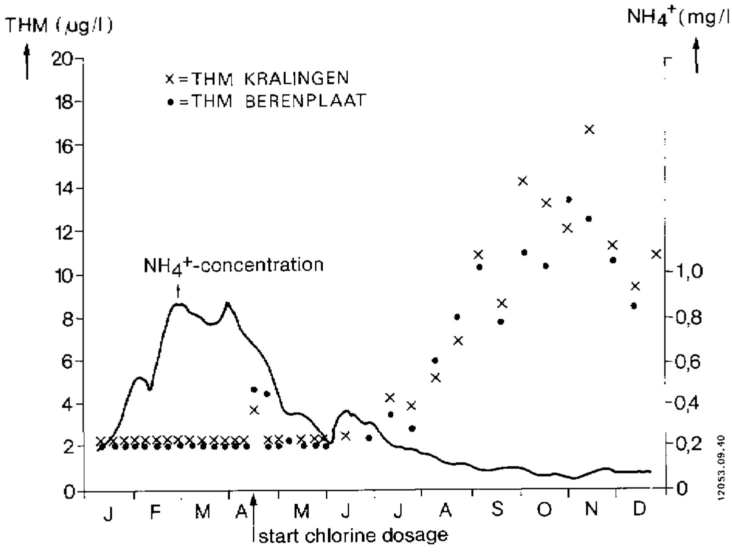


Figure 5.4 - Ammonium contents in Biesbosch water and the THM content after transport chlorination with 1,0 mg/liter chlorine

It is apparent from figure 5.4. that only when the ammonium content drops to 0,1 mg/liter or lower (chlorine/ammonium ratio > 10) does the THM formation display a distinct increase due to the presence of free chlorine. At ammonium contents in excess of 0,2 mg/liter (chlorine/ammonium ratio < 5), monochloramine formation takes place preferentially and thus only a very limited THM formation.

It seems apparent from the preceding that use should be made of the chloramine process for transport chlorination. A dosage of 1 mg/liter active chlorine goes together with an ammonium content of 0,25 mg/liter, which could be dosed partially. Such an ammonium content does not seem to give any problems for subsequent purification. However, it would be desirable to investigate the extent to which high molecular weight organohalogen compounds are formed by chloramine and whether the preservative effect of chloramine is adequate.

Relatively little information is available on the EOCl content. It appears that 1-2 µg/liter EOCl are formed even at low chlorine dosages, after which the content rises only slightly upon further chlorination. In general, no information is available regarding the AOCl content.

5.4 Formation of halogenated compounds during breakpoint chlorination (super-chlorination)

5.4.1 Introduction

Four water treatment plants use breakpoint chlorination in preparing drinking water from surface water. These four plants are:

1. the N.V. Waterworks of North-West-Brabant (WNWB) in the surface water plant at Zevenbergen;
2. the Rotterdam Waterworks (DWLR) in the Berenplaat production plant;
3. the Municipal Energy Concern of Dordrecht (GEB) in the Baanhoek production plant;
4. the Provincial Waterworks of North Holland (PWN) in the treatment plant at Andijk.

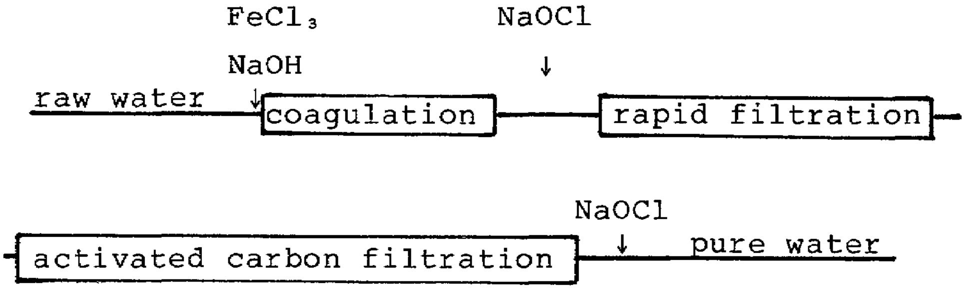
These four plants use breakpoint chlorination for the following reasons:

a. all plants use breakpoint chlorination to break down ammonium - GEB does this only at low temperatures;
b. all plants use chlorination for disinfection purposes;
c. GEB and PWN likewise use chlorination to control

the growth of the triangular mussel and to remove phyto- en zooplankton during treatment;

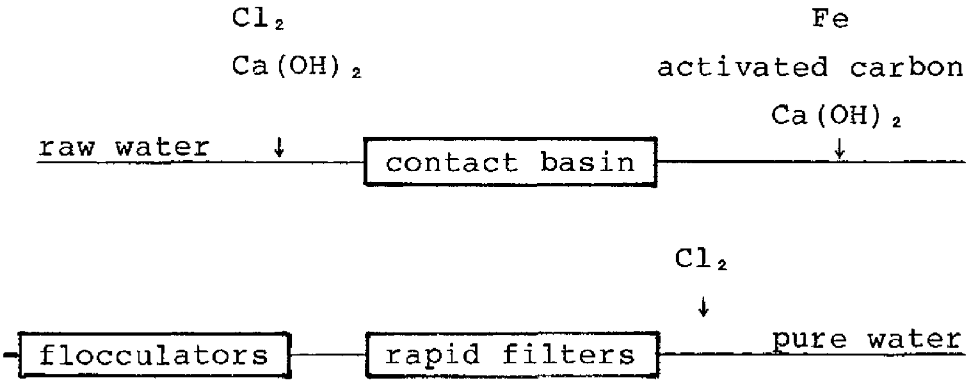
The raw water, the treatment scheme, the chlorine dose, the site of chlorination in the process and the residual chlorine contents after a certain contact time differ greatly from one plant to another:

- WNWB at Zevenbergen treats Biesbosch water with the aid of the following treatment process:



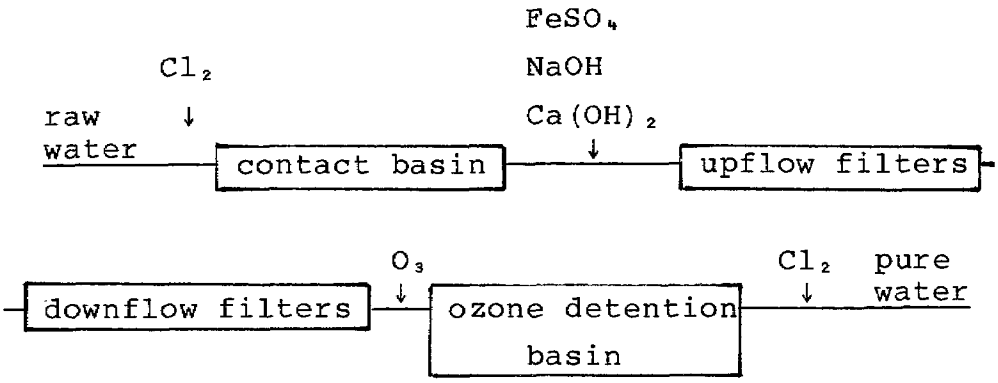
In 1980, the plant used a chlorine dose of 0,5-1,1 mg/liter for breakpoint chlorination, with an average chlorine dose of 0,8 mg/liter. The chlorine dose is determined on the basis of a residual free chlorine content of 0,2 mg/liter before the carbon filters. The contact time of the chlorine in this process is 30-90 minutes.

- At Berenplaat DWL R treats Biesbosch water using the following treatment process:



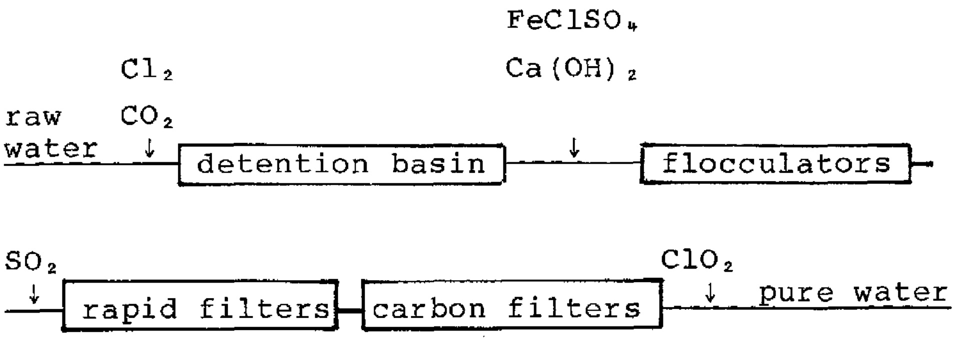
In 1978/1979, the plant used a chlorine dose of 1,4-8,2 mg/liter with an average dose of 3,3 mg/liter. The chlorine dose is determined on the basis of a residual chlorine content after the chlorine detention basin of 0,8-1,2 mg/liter. The contact time of the chlorine was 30 minutes.

- In 1979/1980 at Baanhoek GEB treated Wantij water using the following treatment process:



In 1978/1979 for breakpoint chlorination, this plant used a chlorine dose of 0,4-7,4 mg/liter with an average dose of 2,4 mg/liter. The chlorine dose is determined on the basis of a residual free chlorine content after the chlorine detention basin of 0,2-0,3 mg/liter. The contact time of the chlorine was 30-60 minutes.

- PWN at Andijk treats IJssellake water using the following treatment process:



In 1978/1979 for breakpoint chlorination, the plant used a chlorine dose of 4,2-10,5 mg/liter with an average dose of 7,5 mg/liter. The chlorine dose is determined on the basis of a residual total chlorine content after the chlorine contact basin of 1,5-2 mg/liter and a residual total chlorine before rapid filtration of 0,3-0,5 mg/liter. The contact time of the chlorine was 180 minutes.

Of the four plants, in 1978/1979, only WNWB at Zevenbergen used sodium hypochlorite; the other plants used chlorine gas. The average chlorine dose varies greatly (WNWB 0,8 mg/liter, PWN 7,5 mg/liter) and the minimal and maximal dosages used also differ greatly.
It is noteworthy that WNWB and GEB use a free chlorine residual as a guide, while DWL and PWN use a residual total chlorine as the parameter.

5.4.2 Results

For the plants which use breakpoint chlorination, for the raw water and the chlorinated water, the quality data were gathered over the period 1978/1979 insofar as these were believed to play a possible role in the formation of halogenated compounds. This concerns the parameters TOC, $KMnO_4$ demand, COD, UV extinction, ammonium content, bromide content, pH and temperature. For WNWB, the data for 1980 were taken. The data are presented in table 5.6.

Table 5.6 - Average values of quality data in 1978-1979 (for WNWB, 1980) before and after breakpoint chlorination

Parameter	WNWB			DWL			GEB			PWN		
	Before	After	Δ	Before	After	Δ	Before	After	Δ	Before	After	Δ
TOC (mg/l)	3,3	3,3	0	3,9	3,7	0,2	-	-	-	8,8	8,8	0
$KMnO_4$ (mg/l)	8,3	7,1	0,8	12	10	2	11,3	-	-	20	18	2
COD (mg/l)	6	6	0	12	-	-	-	-	-	24	23	1
UV (m^{-1})	-	5,4	-	9	7	2	8	-	-	16	13	3
NH_4^+ (mg/l)	< 0,05	< 0,05	0	0,22	< 0,03	> 0,19	0,19	-	(0,18)	0,21	< 0,03	> 0,18
Br^- (μg/l)	140	90	50	115	55	60	-	-	-	125	10	115
pH	8,2	8,2	0	8,9	8,4	0,5	-	-	-	8,7	8,3	0,4
T (°C)	8,0	8,0	-	10,7	10,7	-	-	-	-	10,5	10,5	-

- = not determined

In addition, the data are presented regarding the THM, POCl, EOCl and AOCl contents before and after breakpoint chlorination. These contents are presented in table 5.7 along with the chlorine dose and the residual chlorine content after 30 minutes.
It is apparent from the table that PWN has, by far, the highest contents of halogenated compounds, followed by DWL, WNWB and GEB. Unfortunately, only very few POCl and AOCl measurements are available. For the time being, it can be concluded from these analyses performed at PWN that the AOCl/THM ratio is lower than for chlorinated pure water (see chapter 4).

Table 5.7 - Chlorination conditions and side effects of breakpoint chlorination for 1978-1979 (for WNWB, 1980)

Parameter	WNWB			DWL			GEB			PWN		
	Before	After	Δ	Before	After	Δ	Before	After	Δ	Before	After	Δ
Cl_2 content (mg/l)	0,8	0	0,8	3,3	0,3	3,0	2,4	0,3	2,1	7,5	1,7	5,8
$CHCl_3$ (µg/l)	3,1	9,0	5,9	3,0	12,8	9,8	<0,1	2,6	2,6	< 0,1	30,5	30,5
$CHBrCl_2$ (µg/l)	1,4	7,3	5,9	0,7	7,3	6,6	<0,1	3,5	3,5	< 0,1	28	28
$CHbR_2Cl$ (µg/l)	0,6	4,4	3,8	<0,5	3,6	3,6	<0,1	2,8	2,8	< 0,1	17,5	17,5
$CHBr_3$ (µg/l)	<0,1	1,7	1,7	<0,5	0,7	0,7	<0,1	0,1	0,1	< 0,1	5	5
THM (µg/l)	5,1	22,4	17,3	3,7	24,4	20,7	<0,1	8,9	8,9	< 0,1	81	81
POCl (µg/l)	-	-	-	-	-	-	-	-	-	< 1	(85)	(85)
EOCl (µg/l)	0,5	1,5	1,0	1,5	4,0	2,5	-	-	-	1,0	10,5	9,5
AOCl (µg/l)	-	-	-	-	-	-	-	-	-	10	70	60

5.4.3 Discussion

It is apparent from the results presented in section 5.4.2 that a positive correlation exists between the magnitude of the chlorine dose and the THM content after chlorination. Figure 5.5 presents the chlorine doses and the THM contents at GEB for the periode 1978-1980.
It is apparent from the figure that on the whole, the THM content follows the chlorine dose. It may be expected that a limitation of the chlorine dosages would lead to a reduction of the THM content. It was found from model tests (see section 5.2.1) that the formation of THM is a function of time, wherein the production during the first 30 minutes is considerable. At PWN in practice, no difference is found in the THM contents after 30 and 60 minu-

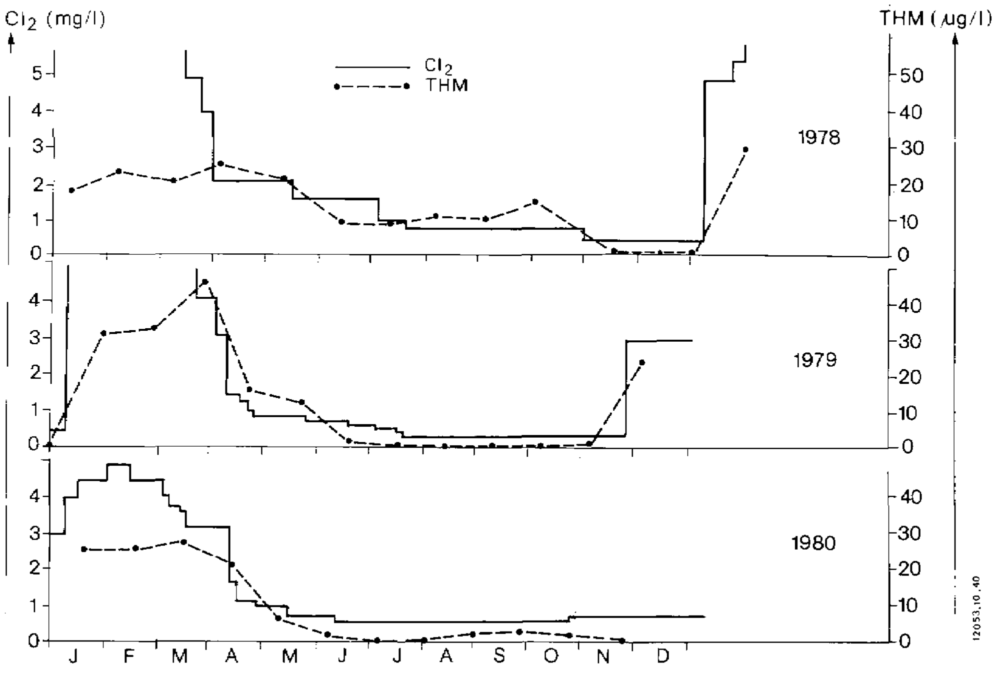


Figure 5.5 - Chlorine dose for breakpoint chlorination and THM content after chlorination at GEB in 1978-1980

tes. Unnecessary prolongation of the contact time, however, is not desirable. The chlorine dose is determined to a high degree by the ammonium content of the water. The ammonium content before breakpoint chlorination, the chlorine dose and the THM and EOCl contents after breakpoint chlorination are shown in table 5.8.

As in transport chlorination, a marked influence of the Cl_2/NH_4^+ ratio is seen. Plants with a Cl_2/NH_4^+ ratio of about 15 produce a THM content of 10-20 µg/liter and an EOCl content of 1-3 µg/liter.

Table 5.8 - Ammonium content before breakpoint chlorination, chlorine dose and THM and EOCl contents after breakpoint chlorination

Plant	NH_4^+ avg. mg/l	Cl_2 dose, avg. mg/l	$\frac{Cl_2\text{, avg.}}{NH_4^+\text{, avg.}}$	THM µg/l	EOCl µg/l
WNWB	< 0,05	0,8	> 16	17,3	1,0
DWL	0,22	3,3	15	20,7	2,5
GEB	0,19	2,4	13	8,9	-
PWN	0,21	7,5	36	81	9,5

PWN with a Cl_2/NH_4^+ ratio of 36 has far higher THM and EOCl contents (81 and 9,5 µg/liter, respectively). For breakpoint chlorination as well, sufficient information regarding the AOCl content is lacking.

In addition to the ammonium content, the pH can also play a role. Rook (ref. 5.5) showed that pH reduction leads to a reduction of chlorine consumption and thus to a decrease in the byproducts content. Upon comparing the operating data, it is seen that GEB, where the water to be treated has the lowest pH, has the lowest THM content relative to the chlorine dose and the chlorine : ammonium ratio.
It may be expected that a pH reduction from 8,6 to 7 can bring about a THM reduction of 15 to 30 %, while the chlorine also has a stronger disinfection capability.

No direct relationships were established between

the organic matter content and THM formation in plants using breakpoint chlorination. However, it may be anticipated that IJssellake water, with a TOC content of 8,8 mg/liter and marked algal bloom, would require a higher chlorine dose than the other water types with a TOC content of 3-4 mg/liter. This higher chlorine dosage then again leads to a higher THM content.
A lower chlorine consumption does not always lead to a lower THM content. Upon the transition from Meuse water to Biesbosch water, the chlorine use at DWL Rotterdam decreased considerably. However the THM content of the chlorinated water scarcely decreased. Increasing the pH from 7,8 to 9 and transport chlorination, however, may have played a role in this.

It is apparent from the preceding that relatively high THM and EOCl contents occur in breakpoint chlorination. In this case, as well, the chlorine/ammonium ratio is of great significance. High ratios lead to high THM and EOCl contents. In addition, the pH may play a role of some significance.
A significant reduction of the side effects can, therefore, be achieved by restricting chlorine use. DWL and PWN, therefore, reduced their demands for chlorine content after the detention basins, while GEB only adds chlorine in winter. A pH reduction has not yet been introduced for cost reasons. In view of the most important purpose of breakpoint chlorination, however, some free chlorine should always be present in the water. This will always be accompanied by a relatively great formation of by-products.

5.5 Formation of halogenated compounds during post-chlorination

5.5.1 Introduction

Eleven production plants used post-chlorination in the preparation of drinking water in 1979/1980. The plants are:

1. the Waterworks of Overijssel (WMO) at Diepenveen;
2. the Municipal Waterworks of Groningen (GWG) at De Punt;
3. the Waterworks of South-West-Netherlands (WMZO) at Ouddorp;
4. the Enschede Municipal Energy Concern (ONE) on the Weerseloseweg;
5. the Waterworks of South-West-Netherlands (WMZH) at Haamstede;
6. the Amsterdam Municipal Waterworks (GWL) at Leiduin;
7. the Amsterdam Municipal Waterworks (GWD) at Driemond;
8. the Rotterdam Waterworks (DWL R) at Kralingen;
9. the Waterworks of North-West-Brabant (WNWB) at Zevenbergen;
10. the Rotterdam Waterworks (DWL R) at the Berenplaat;
11. the Dordrecht Municipal Energy Concern (GEB) at the Baanhoek.

The first seven treatment plants use only post-chlorination or a combination of transport chlorination followed by infiltration and post-chlorination; no THMs occur after infiltration. Plants 8 through 11 inclusive use several chlorinations. Plant 1 treats groundwater, plants 2 and 11 treat mixed groundwater and surface water and the other plants treat surface water.

PWN (plants 12 and 13) uses post-disinfection with ClO_2 in its plants. This will be discussed in this section.

The plants use post-chlorination for the following reasons:

a. all plants use post-chlorination to control microorganisms;

b. eight plants (2, 3, 5, 6, 7, 8, 9 and 10) use post-chlorination to neutralize higher organisms;

c. four plants (7, 8, 10 and 11) use post-chlorination to maintain a chlorine residual in the distribution system;

d. four plants (2, 4, 8 and 10) see in post-chlorination a possibility for occasional disinfection of the distribution network.

5.5.2 Results

For the plants which use post-chlorination, data have been collected for the period of 1979-1980 with respect to the minimal, maximal and average chlorine dose, the residual chlorine content after 20 minutes and the criterion used for guiding the chlorine dosage. These data are presented in table 5.9.

The chlorine dose is given as the chlorine content determined immediately after addition so that the instantaneous dose may be somewhat higher. According to the table the average chlorine content immediately after addition appears to vary from 0,09 to 0,86 mg/liter; after 20 minutes, the residual chlorine content is < 0,02-0,49 mg/liter. In addition to the chlorine consumption of the water, these great differences are largely due to the criteria utilized for chlorination.

Table 5.9 - Chlorine dose, residual chlorine content after 20 minutes and the post-chlorination criterion in 1979-1980

plant	chlorine dose (mg/l)			residual chlorine content (mg/l)			criterion
	min.	max.	avg.	min.	max.	avg.	
1 WMO	0,75	1,20	0,86	-	-	<0,02	0,1 à 0,15 mg/l after 2 hr.
2 GWG	0,25	0,50	0,45	0,25	0,38	0,28	-
3 WMZ-O	0,05	0,25	0,18	0	0,05	0,03	0,05 mg/l after 2 min.
4 ONE	0,04	0,14	0,09	0	0,06	0,02	0,1 mg/l after 15 min.
5 WMZ-H	0,10	0,30	0,22	0	0,10	0,03	0,05 mg/l after 2 min.
6 GW-L	0,57	0,70	0,67	0,18	0,40	0,23	0,2 mg/l after 20 min.
7 GW-D	0,01	0,60	0,19	0,02	0,35	0,09	0,2 mg/l after 20 min.
8 DWL-K	-	-	0,46	-	-	0,33	0,05 mg/l after 48 hr.
9 WNWB	0,32	0,62	0,42	0,22	0,53	0,33	0,2 mg/l after 20 min.
10 DWL-B	-	-	0,46	-	-	0,23	0,05 mg/l after 48 hr.
11 GEB	0,46	1,20	0,80	0,25	0,90	0,49	0,2 mg/l after 18 hr.

Data on the THM content were also gathered. For plants 1-7 inclusive, where the water contains no THM prior to post-chlorination, only the contents after post-chlorination are reported. For plants 8-11 inclusive, the contents before and after post-chlorination, as well as the difference, are reported.

Table 5.10 shows that the THM content formed upon post-chlorination varies from 0.05-0.176 µmol/liter. By far, the highest contents occur at plants 6 and 11.

The EOCl and AOCl contents are reported for the pure chlorinated water in chapter 4. Since very little information is available regarding the non-chlorinated water, no attention will be devoted to those parameters in this section.

Table 5.10 - Chlorine dose, residual chlorine content and THM content before and after post-chlorination in 1979-1980

Plant	Average chlorine dose mg/l	Avg. resid. chlorine content after 20 min. mg/l	THM avg. µmol/l		
1	0,86	< 0,02	0,020		
2	0,45	0,28	0,031		
3	0,18	0,03	0,015		
4	0,09	0,02	0,023		
5	0,22	0,03	0,018		
6	0,67	0,23	0,131		
7	0,19	0,09	0,051		
			before	after	Δ
8	0,46	0,33	0,038	0,095	0,057
9	0,42	0,33	0,100	0,158	0,058
10	0,46	0,23	0,171	0,197	0,026
11	0,80	0,49	0,056	0,232	0,176

5.5.3 Discussion

It is apparent from the data reported in section 5.5.2 that the THM content varies from 0,015-0,176 µmol/liter. The lowest THM contents are found at plants which prepare drinking water from groundwater or water following soil passage and which can get by with a relatively low dosage for post-chlorination. Plant 7, which also treats infiltrated water, forms an exception in this regard.

The highest THM contents are found in the case of surface water-treatment plants which generally use several chlorinations. The curves for the THM contents at plants 10 and 11 are noteworthy here; both of these plants use breakpoint chlorination. Following breakpoint chlorination, plant 10 has a high THM content, and this content is only slightly further elevated during post-chorination. Plant 11, on the other hand, following breakpoint chlorination, has a relatively low THM content, but this content increases greatly upon post-chlorination.

Extensive discussion is presented regarding the composition of the THM in section 4. Without numerical illustrations, one must be content here with reporting the shift toward the formation of more highly brominated THM in the case of increasing purification. In this manner, highly brominated THMs are formed after carbon filtration especially at short filter runs (plants 8 and 9).

The results do not indicate any distinct relationship between the THM content and the chlorine dose or the residual chlorine content after 20 minutes. In addition, no distinct dependence upon the season is present. A few examples will be cited for illustration:

- at identical chlorine doses, plant 2 forms more THM in summer than in winter, while the opposite is true in plant 6;
- plant 10, at a variable chlorine dose and an equal residual chlorine content, forms a constant quantity of THM. Plants 8 and 11, at increasing chlorine doses and constant residual chlorine content, form more THM.

Thus, few definite conclusions can be drawn from the results, and few measurements have been made aside from the THM data.
A more extensive discussion of the reasons for use of post-chlorination, the dose limitation for this chlorination and alternatives to this chlorination will be presented in section 8.

5.6 Formation of halogenated compounds during ozonation

5.6.1 Introduction

Not only during chlorination, but also in some cases during ozonation, an increase in the content of halogenated compounds is found. This phenomenon will be illustrated in this section based on some data from Germany and the Netherlands.

5.6.2 Results

The formation of some low molecular weight halogenated compounds during ozonation was first noted by Stieglitz et al (ref. 5.6) in a study regarding the behaviour of chlorinated organic compounds during the treatment of Rhine water in some German Waterworks. Within the scope of this investigation, some specific halogen compounds were determined and some organochlorine determinations were performed following various treatment steps. Figure 5.6 shows the changes in the gas chromatographically determined organochlorine content.
According to figure 5.6 a distinct increase in aliphatically bound chlorine can be seen after ozonation. Of the specific compounds, the contents of chloroform, tetrachloromethane, trichloroethylene,

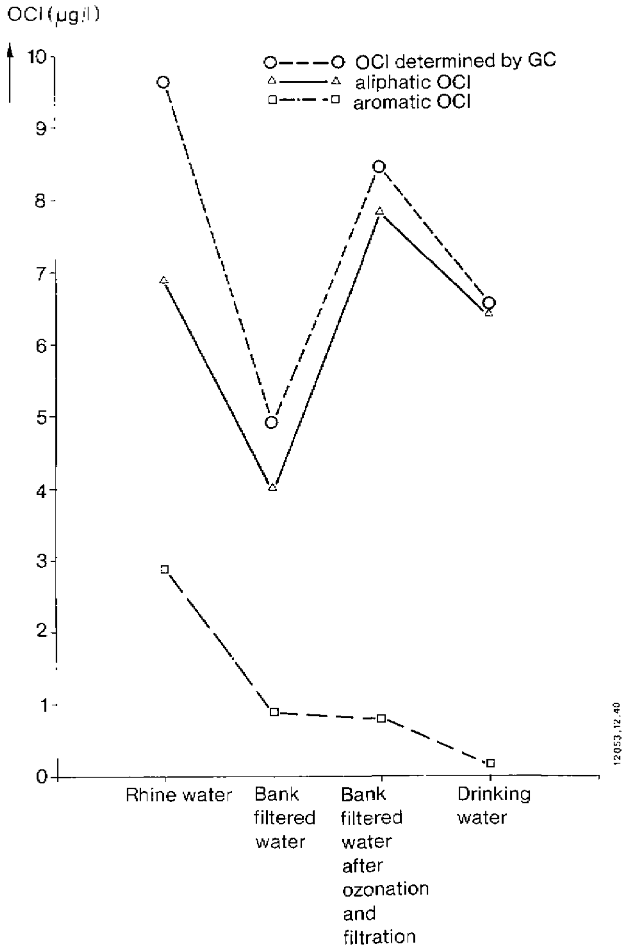


Figure 5.6 - Changes in total, aliphatic and aromatic organochlorine contents (determined by gas chromatography) during the purification of bank filtrate

tetrachloroethylene, tetrachlorobutadiene and hexachlorobutadiene increased. In the Netherlands, De Greef et al. (ref. 5.7) performed studies on the formation of organic microcontaminants during ozonation. Water was studied before and after ozonation at Zwijndrecht. In Zwijndrecht, ozonation is applied to bank filtrate which has undergone not submerged filtration. The content of some halogenated substances was measured both before and after ozonation.

The measurements indicate the occurence of a slight increase in the THM content and in the tri- and tetrachloroethylene contents.

In the case of GEB at Dordrecht, water is chlorinated, coagulated and filtered prior to ozonation. The increase in the contents of some bromine- and iodine-containing compounds is remarkable. This increase in the content of brominated THM was also found during the ozonation of ground water from Dordrecht. In this process, the $CHBr_2Cl$ contents increased from 0 to 1,5-1,7 µg/liter.

5.6.3 Discussion

It is apparent from the results, that in some cases, a slight increase in the content of halogenated compounds is observed. This generally involves an increase in bromine(iodine)-containing THM. The reason for this may be oxidation of bromide, as is indicated in the case of chlorination (refs. 5.5, 5.8); however, it should be noted that direct oxidation of bromide by ozone does not take place under practical conditions. A concentration increase after ozonation is not always found. In ozonation experiments at Leiduin and Helvoirt (not discussed here), no increase was found.

The formation of chlorinated compounds during ozonation is even more difficult to explain. The breakdown of high molecular weight chlorinated compounds during isolation may play a role here, and the phenomenon may be based on an artifact.

In summary, it can be stated that an increase in the content of halogenated compounds is found in some cases after ozonation. This involves the formation of, at most, a few µg/liter of compounds, frequently bromine-containing.

The explanations for the formation of these compounds are somewhat speculative.

5.7 Discussion

In this section, attention was devoted to the formation of halogenated substances during transport-, breakpoint- and post-chlorination and during ozonation. Many analyses of the THM contents are available for all of the processes; other measurements (POCl, EOCl and AOCl contents) were performed far less extensively and mostly for treated water prior to post-chlorination. An urgent need exists for such data, supplemented by toxicity tests.

The results reported in this section can be summarized as follows:

- the model studies indicate a relationship between the breakpoint curve and THM formation. Scarcely any THMs are formed up to the top of the breakpoint curve; marked THM formation takes place immediately below and above the breakpoint. At higher chlorine dosages, the THM content shows only a slight further increase. With increasing purification and lower chlorine dosages, a relatively extensive THM formation occurs so that it can be anticipated that the post-chlorination of treated water coincides with relatively high THM contents. The THM formation is pH dependent; less THMs are formed at low pH;
- a marked influence of the ammonium content is apparent from the data on transport chlorination. At Cl_2/NH_4 ratios of 2-3, the THM content is low; a Cl_2/NH_4 ratio of 20 leads to high contents (up to 100 µg/liter). All other parameters investigated appear to have no definite effect;
- in the case of breakpoint chlorination as well, the Cl_2/NH_4 ratio is greatly determining for the side effects. At a Cl_2/NH_4 ratio of 15, the THM content is 10-20 µg/liter; at a ratio of 36, the

THM content increases to 80 µg/liter. In addition, the pH appears to have some effect on the THM content;

- relatively large quantities of THM are formed during the post-chlorination of treated water. The content is between 0,015 and 0,176 µmol/liter. The highest contents occur during the post-chlorination of treated water in which several chlorinations are generally used.

  No definite quantitive correlation exists between the THM content, on one hand, and the chlorine dose, the residual chlorine content after 20 minutes, the raw material or the season on the other hand;
- during ozonation, some halogenated compounds are occasionally formed at low concentrations. No definite concepts exist concerning the path of formation.

In summary, it can be stated that the THM formation during transport chlorination can be greatly limited by reducing the Cl_2/NH_4^+ ratio. Relatively high THM contents may develop in the case of breakpoint chlorination and post-chlorination. Little data are available on POCl, EOCl and AOCl with reference to individual chlorinations. However, data are available for the treated water in 1979-1980 (see section 4). For the sake of illustration, the average THM, EOCl and AOCl contents and the spread over the year are shown in figure 5.7.

It is apparent from this that the largest number of side effects occur in the surface water treatment plants (plants 8-11, inclusive), which use breakpoint and post-chlorination.

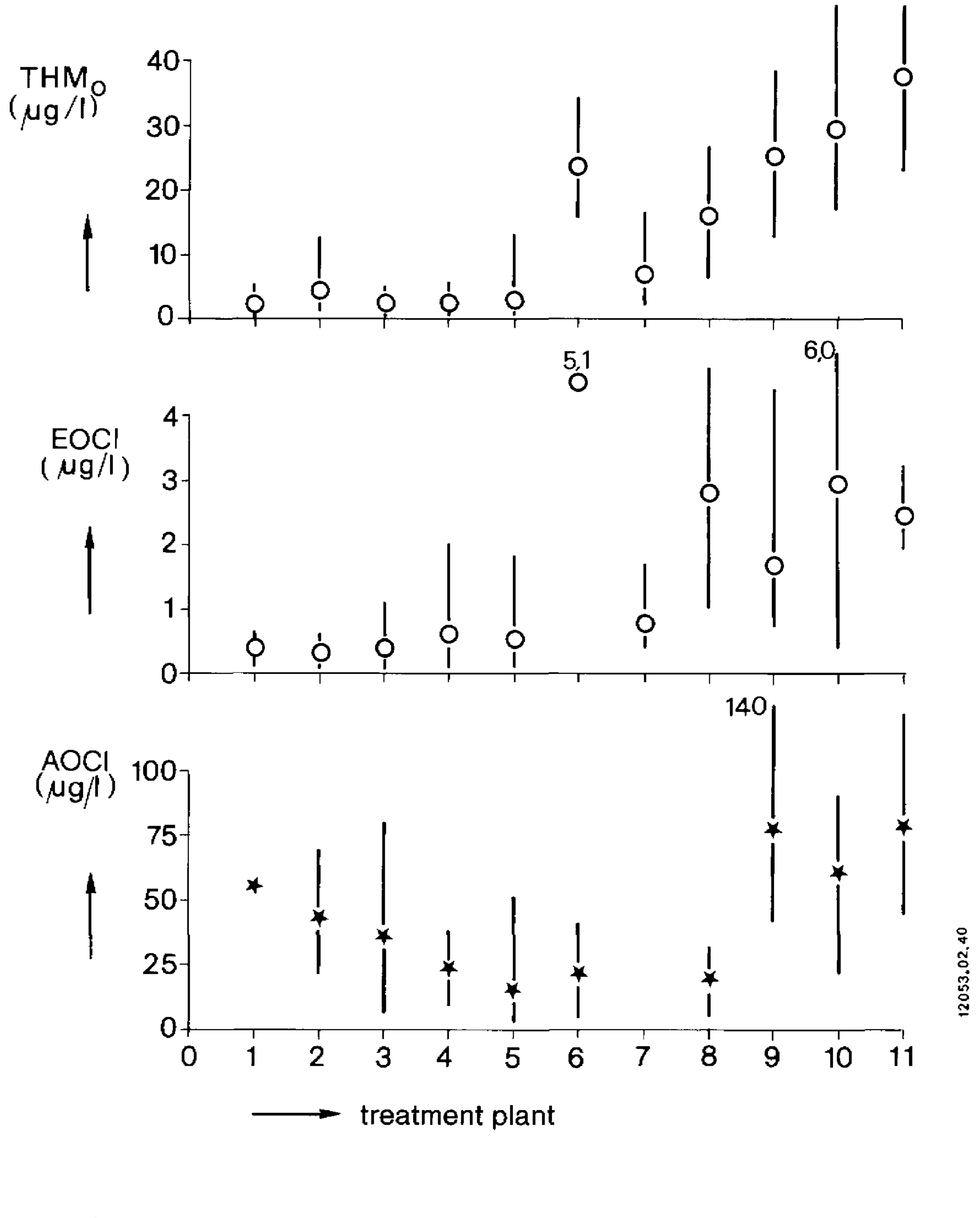


Figure 5.7 - THM, EOCl and AOCl content in Netherlands water treatment plants. Period: September, 1979-July, 1980

5.8 Recommendations

The results described in this section have suggested the following points for investigation:

- investigation regarding the possibilities for restricting chlorine use for transport disinfection. The following possibilities arise thereby:
  - a. use of transport purification;
  - b. use of intermittent chlorination;
  - c. transport disinfection with chloramine or chlorine dioxide;
- investigation regarding the possibilities for limiting post-chlorination, replacing it by chlorine dioxide treatment, or eliminating it;
- investigation regarding the formation of halogenated compounds during ozonation.

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6 REMOVAL OF HALOGENATED COMPOUNDS

6.1 Introduction

Despite the fact that the ad hoc study group on chlorine came to the conclusion that under the process conditions customarily employed in 1977, THM can not be removed or destroyed by processes such as aeration, adsorption and oxidation, nevertheless, a great deal of study was performed in order to pursue such possibilities.

This section describes the removal of halogenated compounds during aeration, activated carbon filtration, adsorption on alternative adsorbents, ozonation, infiltration and reverse osmosis.

Practically the entire section deals with the removal or conversion of THM. Scarcely any information is available regarding other byproducts formed during chlorination (individual products or groups of products expressed as the EOCl and AOCl content). However, some data are included regarding the removal of TCE (trichloroethylene) and tetrachloroethylene, in view of the related nature of these compounds.

The effect of the processes investigated will be considered in greater detail and recommendations will be made for further study.

6.2 Removal of halogenated compounds by aeration

6.2.1 Introduction

Aeration is a process widely used in the chemical industry and in water treatment for the removal of ammonia, carbon dioxide and hydrogen sulfide. The possibilities have extended to the removal of spe-

cific organic microcontaminants from drinking water. Up to 1976, primarily general literature appeared wherein an idea was gained regarding the effectiveness of aeration based on Henry's constant (H). Dilling (ref. 6.1) finds here that the half-life for aeration in the case of $H > 1$ is equal to the square root of the molecular weight and is independent of H.
Beginning in 1976, increasing amounts of literature appeared which pertained to the removal of THM and other halogenated hydrocarbons such as tri- and tetrachloroethylene.

6.2.2 Removal of THM

Rook (ref. 6.2) describes the removal of chloroform in a cascade aerator, 4 m in height. He finds 89 % removal at an air/water ratio of 11 : 1 and a 50 % at a ratio of 3,2 : 1. Love et al. (ref. 6.3) describe experiments in a countercurrent aerator with a diameter of 37 mm. They find reductions in the chloroform content ranging from 53 % at an air/water ratio of 8 : 1 to 83 % at a 20 : 1 ratio. These data were confirmed by Symons et al. (ref. 6.4) who find an 80 % chloroform reduction at an air/water ratio of 20 : 1. They, likewise, conclude for 8 halogenated hydrocarbons that there is a correlation between the solubility and the aeration efficiency. McCarty et al. (ref. 6.5) also find reductions in the chloroform content to about 80 %.
Houel et al. (ref. 6.6) remove chloroform to the extent of 97,5 %. For this purpose, however, they require an air/water ratio of 1750 : 1. Singley et al. (ref. 6.7) describe the removal of 9 volatile substances, including $CHCl_3$, $CHBrCl_2$ and $CHBr_2Cl$ by aeration. They state that aeration is possible in

the case of Henry's constant H > 0,05. For the three THM mentioned in a packed countercurrent aerator, they find the following efficiencies (see table 6.1).

Table 6.1 - Aeration efficiencies for THM

Component	Bed height m	Avg. concen. µg/l	air/water ratio	removal %
$CHCl_3$	1,3	33	0,7-6,5	44-69
	1,8	45	0,7-5,3	61-85
	2,8	32	0,8-6,4	56-87
$CHBrCl_2$	1,3	8	0,7-6,5	42-83
	1,8	11	0,7-5,3	47-91
	2,8	9	0,8-6,4	55-98
$CHBr_2Cl$	1,3	3	0,8-5,2	32-79
	1,8	3	2,7-5,3	74-88
	2,8	2	1,1-6,4	62-96

Trihalomethanes can thus be removed to the extent of about 80 % by aeration, with air/water ratios amounting to 20 : 1. An extremely high air/water ratio is necessary in order to remove 97,5 % of the $CHCl_3$.

6.2.3 Removal of trichloroethylene and tetrachloroethylene

After such compounds as tri- and tetrachloroethylene were encountered in groundwater in 1976, the removal of these substances by aeration was also investigated. Van der Laan (ref. 6.8) finds a TCE removal of 74-99 % at air/water ratios of 22 : 1 to 80 : 1 in a plate aerator. Doets (ref. 6.9) also finds very high removal efficiencies for TCE. In the case of a double aeration in a cooling tower aerator, he finds up to 96 % reduction. In the case of a perforated vacuum plate aerator, he even finds yields in excess of 99 %. These yields are even higher for tetrachloroethylene.

Symons et al. (ref. 6.4) also find very high removal percentages for tri- and tetrachloroethylene. Figure 6.1 gives the removal as a function of the air/water ratio (A/W) for a contact time of 10 minutes for the substances C_2CL_4, C_2HCl_3, CCl_4 and $CHCl_3$.

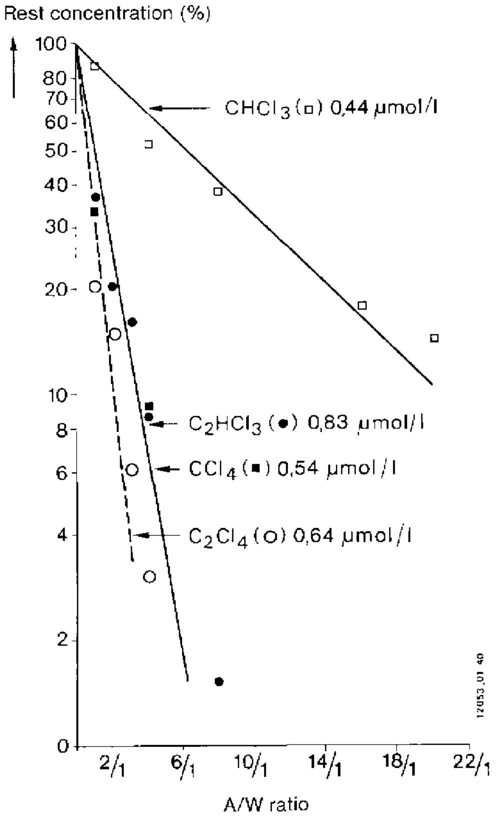

Figure 6.1 - Removal of C_2Cl_4, C_2HCl_3 CCl_4 and $CHCl_3$ as a function of the air/water ratio A/W

Thus aeration offers very good possibilities for removing such compounds as C_2Cl_4 and C_2HCl_3 from water. Efficiencies of 99 % at air/water ratios that are not excessive are possible.

6.3 Removal of halogenated compounds by activated carbon filtration

6.3.1 Introduction

Nine carbon filter installations were used in the Netherlands in mid -1983 (ref. 6.10). Three of them were supplied with chlorinated water, namely, the installation at the Waterworks of Rotterdam at Kralingen (summer only), the installation at Waterworks of Northwest Brabant at Zevenbergen, and the filters of the Provincial Waterworks of North Holland at Andijk. The removal of THM in these carbon filter installations was extensively investigated; much less is known regarding the removal of high molecular weight halogenated compounds. First, the THM removal for the three installations mentioned will be discussed. Then, a brief discussion will be given regarding the removal of TCE and high molecular weight compounds, determined as the reduction of the AOCl content.

6.3.2 Removal of THM

At the Waterworks of Rotterdam at Kralingen carbon filtration is performed in cylindrical steel pressure tanks with a diameter of 6 m and height of 9 m (ref. 6.11). The height of the carbon bed is 4 m. The filters were put into operation in 1977; the water has an empty bed contact time of 13 minutes. The carbon filtration is applied to purify Biesbosch water which has successively passed through the following purification steps: transport chlorination (with 5,5 mg/liter in 1977, later with about 1 mg/liter), coagulation, floc separation, ozonation and dual media filtration.
Table 6.2 gives the THM breakthrough of the filters in 1977 for a number of carbon lifes and bed volumes passed trough.

Table 6.2 - THM breakthrough by activated carbon at the treatment plant at Kralingen in 1977

Carbon life	No. of bed volumes	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
18	2000	1,2	1,0	0	0
47	5200	8,9	2,5	0,3	0
74	8000	24,1	8,4	2,2	0
109	11500	32,6	12,0	3,8	0,1
140	14500	33,2	14,6	4,7	0,4
Avg. incoming concentration		35±5	24±3	11,5±1	1,8±0,8

After only 10 weeks (8000 bed volumes), an appreciable breakthrough is already occuring for $CHCl_3$, $CHBrCl_2$ and $CHBr_2Cl$. The breakthrough is highest for $CHCl_3$ (70 %), followed by $CHBrCl_2$ (35 %) and $CHBr_2Cl$ (20 %). The first $CHBr_3$ breakthrough takes place after nearly 14 weeks (11,500 bed volumes). $CHCl_3$ and $CHBrCl_2$, in particular, are only moderately adsorbed. One consequence of this is the occurrence of elution phenomena when the influent concentration declines. One example of this is given by the adsorption of chloroform in the winter of 1977/1978. After about 17,000 bed volumes had passed through the filter transport chlorination was stopped. After this, the THM content in the influent declined to 0 µg/liter. However, the effluent still contained $CHCl_3$ (see figure 6.2).

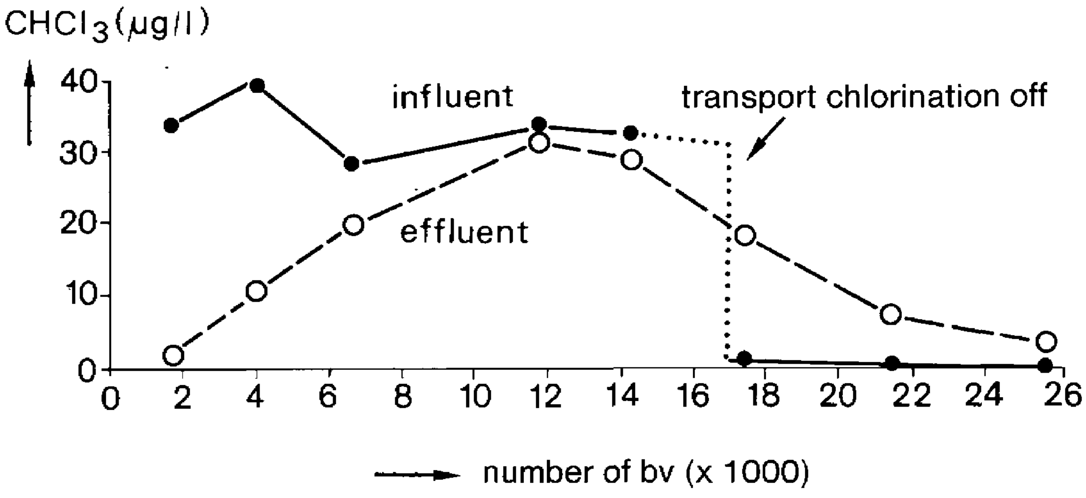

Figure 6.2 - The $CHCl_3$ content before and after carbon filtration at DWL at Kralingen (for 1977/1978)

The $CHCl_3$-free water elutes the weakly bound $CHCl_3$ from the carbon filter. This phenomenon also occurs though to a lesser extent, in the case of the three brominated THM compounds.

At the Waterworks of North-West-Brabant at Zevenbergen carbon filtration is performed in concrete basins with a surface area of 27,8 m^2 (ref. 6.12). The depth of the carbon bed is 2,12 m. The filters were put into use in 1979; the empty bed contact time of the water was about 25 minutes.

Carbon filtration was applied to treated Biesbosch water which subsequently passed through the following treatment steps: transport chlorination with 1 mg/liter chlorine, coagulation, flotation, breakpoint chlorination and dual media filtration. In 1979, the average THM content in the dual media filtrate was 44 µg/liter; in 1980, this content was about 25 µg/liter.

The course of the cumulative THM content as a function of the time and the number of bed volumes is presented in figure 6.3.

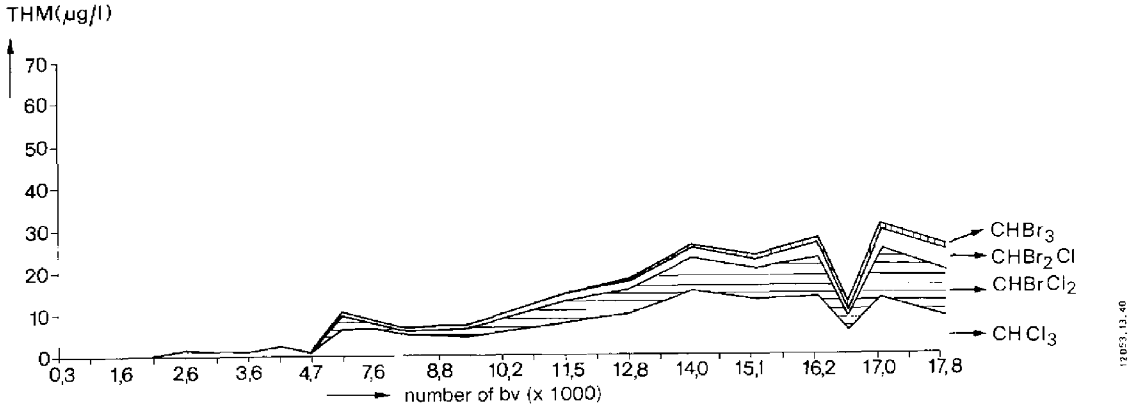

Figure 6.3 - The cumulative THM content as a function of time and number of bed volumes in the carbon filtrate of the WNWB at Zevenbergen (1980)

It is apparent from figure 6.3 that no breakthrough occurred within 6 weeks (2100 bv). Only then does breakthrough of $CHCl_3$ begin, followed after 16 weeks (4700 bv) by $CHBrCl_2$ and $CHBr_2Cl$. The breakthrough of $CHBr_3$ is very limited for the entire time (< 1 µg/liter). In this case also after more prolonged lifetimes (40 weeks, 14.000 bv) elution takes place principally of $CHCl_3$ and $CHBrCl_2$. This elution is caused by the reduction of the dose for breakpoint chlorination, which has led to a reduction of the THM content in the influent from 44 to 25 µg/liter.

At the Provincial Waterworks of North Holland at Andijk, carbon filtration is performed in concrete basins with a surface area of 27 m^2. The carbon bed length is 3 m. Filters are set up in series in two groups of 12 and have a contact time with the water of 20-30 minutes. The throughput over the filters is constant and is equal to 3000 m^3/hour. At a production of 2250 m^3/hour, 750 m^3/hour of carbon filtrate is recirculated.

The carbon filters were first set up as second stage filters for 5 or 6 months. Then, they were used as first stage filters, while a fresh/regenerated filter was connected thereafter as a second step filter.

Carbon filtration was applied to treated IJssellake water which had passed through the following treatment steps in succession: breakpoint chlorination, coagulation, floc removal and filtration.

The operating data for 1980 are shown in figure 6.4. Subsequently for $CHCl_3$, $CHBr_2Cl$ and $CHBr_3$, the contents are given in the rapid filtrate, the inlet of the first step carbon filter, the inlet of the second stage carbon filter and the effluent. It is apparent from figure 6.4 that for the first stage carbon filters elution of $CHCl_3$ and $CHBrCl_2$ occurs over the entire test period; an appreciable further reduction takes place in the $CHBr_2Cl$ and $CHBr_3$ contents. In the second stage filter, THM removal takes place over the entire period. On the average, the THM removal after the second stage carbon filtration amounts to 70 % (on a weight basis) for 1980. On the average, the $CHCl_3$ content is reduced from 26,5 to 15 µg/liter, $CHBrCl_2$ from 28,5 to 7 µg/liter, $CHBr_2Cl$ from 23 µg/liter to 1 µg/liter and $CHBr_3$ from 4 to 0 µg/liter.

Thus, trihalomethanes can only be removed by carbon filtration to a limited degree. Even after relatively short filter runs, breakthrough of $CHCl_3$ and $CHBrCl_2$ takes place. $CHBr_2Cl$ and $CHBr_3$ are adsorbed significantly better.

In addition, elution takes place for $CHCl_3$ and $CHBrCl_2$. This takes place in time periods when no transport chlorination is used (so that the influent content is 0 µg/liter), or when due to reduction of the chlorine dose (for example, for breakpoint chlorination) the influent content has declined over time. Elution can also take place in the first stage of two-stage carbon filtration. Carbon filtration is thus not a highly suitable treatment technique for completely removing all THM over long periods of time. However, the utilization possibilities are good when partial removal is sufficient and when a criterion of several tens of µg/liter is aimed for. In that case, filter runs will be longer when THM are more brominated. It should be emphasized that in the case of post-chlorination after carbon filtration even at short filter runs, marked THM formation takes place, wherein principally brominated THMs are formed. This THM formation during post-chlorination is discussed in section 5.5.2.

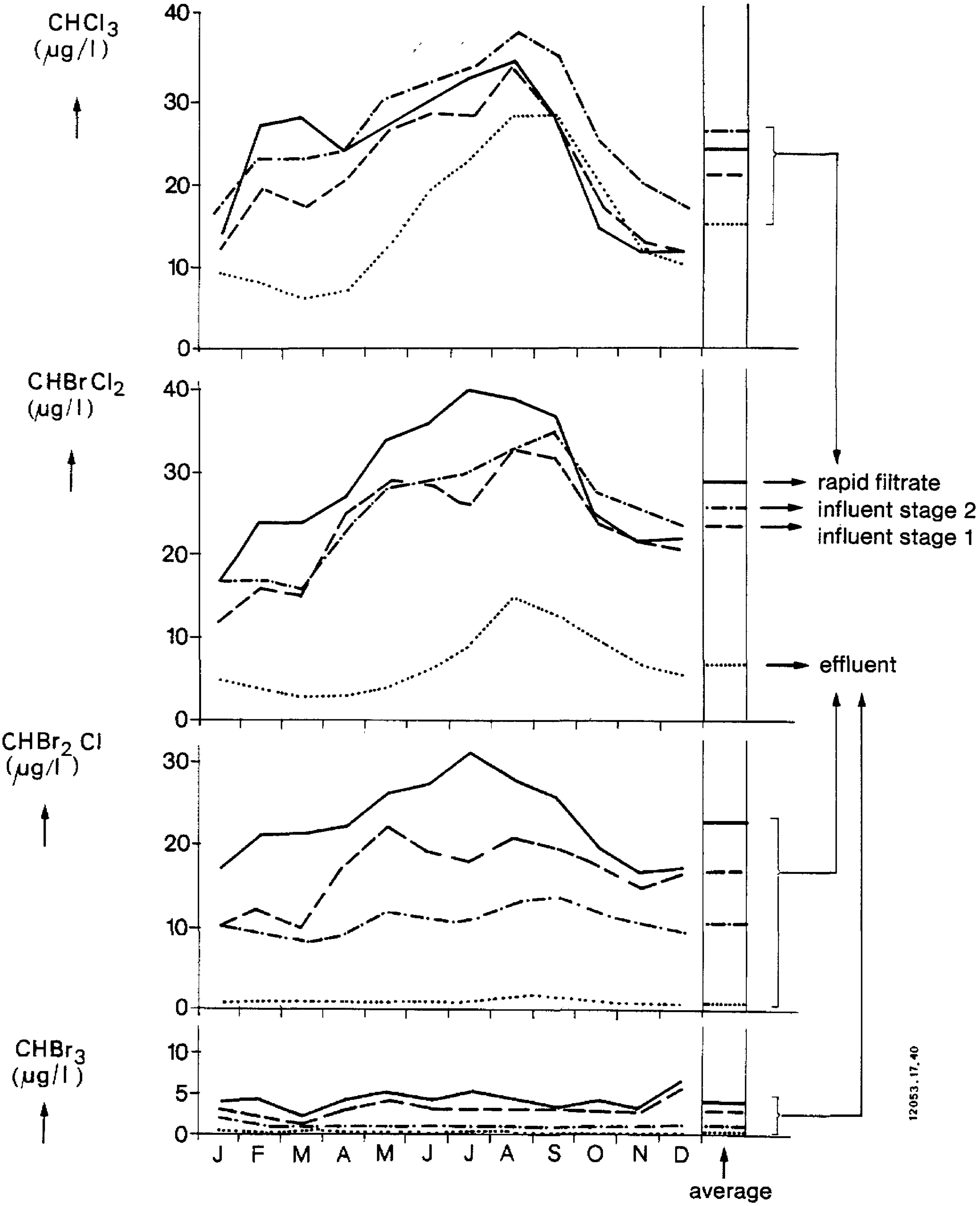

Figure 6.4 - Contents of $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$ as a function in the rapid filtrate, inlet to first and second stages and effluent from the carbon filters at the PWN at Andijk (1980)

6.3.3 Removal of TCE

At the Waterworks of the Mid Netherlands (WMN) at Zeist, carbon filtration is performed in cylindrical steel pressure tanks with a diameter of 3,2 m and a height of 4 m (refs. 6.8, 6.11). The height of the carbon bed is 1,5 m. The filters were put into use in 1978; the empty bed contact time is two x 6 minutes (pseudo moving bed principle).
The carbon filtration is applied to treated groundwater which has successively passed through the following treatment steps: intensive aeration, iron removal/manganese removal and subsequent deacidification.
The use of carbon filtration was preceded by a pilot plant study with an empty bed contact time of 8 minutes. The bed was backwashed in fixed form in this process. The results of this investigation are shown in figure 6.5.

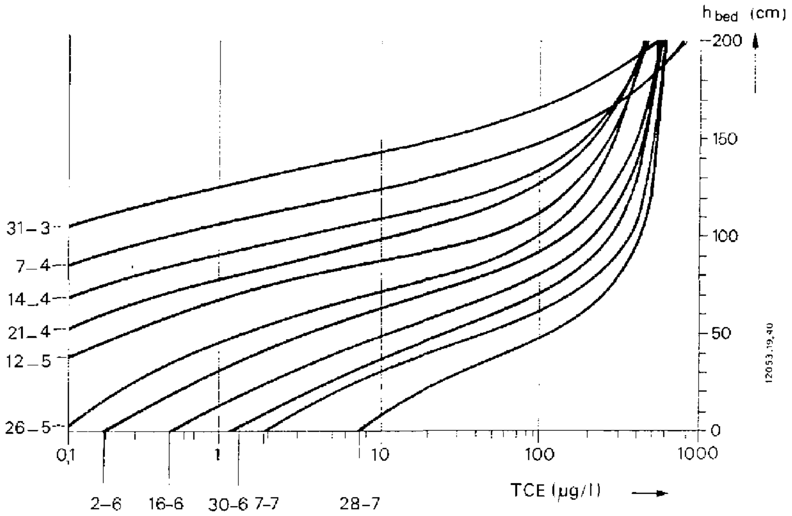

Figure 6.5 - Breakthrough curves of TCE for carbon filtration at WMN, Zeist

It is apparent from figure 6.5 that in the case of the in those days applied operating criterion for breakthrough of 6 µg/liter, a lifetime of about 4 months is achieved (20,000 bv). The equilibrium carbon load was 50 g TCE/kg carbon at a TCE influent concentration of 550 µg/liter.

The Amsterdam Municipal Waterworks at Hilversum also use carbon filtration in cylindrical tanks with a diameter of 3,0 m and a height of 4,0 m. The height of the carbon bed is 2,5 m. The empty bed contact time is 17 minutes.
In pilot plant studies with an influent TCE concentration of 30 µg/liter, the lifetime was 216 days (17,500 bv) when 1 µg/liter was set as the standard for the maximum breakthrough. In the case of current process control with an influent TCE content of 1,8-8,9 µg/liter, the average carbon life is 12 months, likewise, with a criterion of 1 µg/liter.

Thus, TCE can be removed well by activated carbon filtration. At influent TCE contents of 550 µg/liter, filter runs of 3-4 months are possible. At an influent content of 10-30 µg/liter, the carbon life can exceed 12 months if a standard of 1 µg/liter for the maximal breakthrough is maintained.
Thus, activated carbon is highly suitable for the removal of TCE. It should be noted, however, that WMN has found a decrease in the adsorption capacity upon regeneration of the carbon.

6.3.4 Removal of high molecular weight halogenated compounds

Recently increasing attention has been paid to the presence of high molecular weight organohalogens in water. These groups of organic substances are fre-

quently characterized by surrogate parameters such as the extractable and adsorbable organic chlorine contents (EOCl and AOCl, respectively).
For the sake of illustration in the case of the carbon filter installation of WNWB at Zevenbergen, the EOCl and AOCl contents are given as a function of the lifetime of the carbon filter (ref. 6.13). For the conditions, see section 6.3.2.
It is apparent from figure 6.6 that both the EOCl and AOCl contents are completely removed during relatively long filter runs. The first breakthrough of the EOCl content takes place after 12 weeks (3300 bv). The first breakthrough of the AOCl content takes place after 18 weeks (4600 bv).

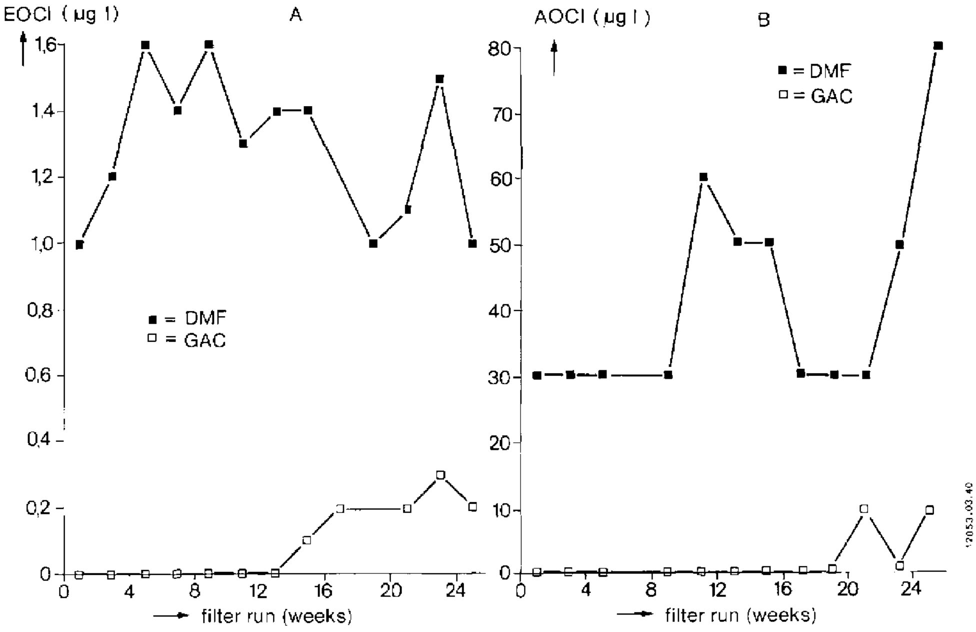

Figure 6.6 - EOCl (A) and AOCl (B) contents before and after carbon filtration at Zevenbergen (period 1980/1981)

It can be deduced from the results presented that the EOCl and AOCl contents are greatly reduced by

activated carbon filtration. However, it should be emphasized that up to the present time, only a limited amount of information is available so that conclusions should be drawn with great caution.
It should also be noted that in the case of chlorination following carbon filtration, both the EOCl and AOCl contents increase greatly even at brief filter runs (4 weeks, 1200 bv).

6.4 Removal of halogenated compounds by alternative adsorbents

6.4.1 Introduction

In 1976, a number of adsorbents were introduced which, in terms of their composition, occupy the middle ground between activated carbon and polymeric adsorbents (ref. 6.14). One of these agents, Ambersorb XE-340, was recommended for the removal of chloroform, pesticides, chloroethyl ether and carbon tetrachloride. Regeneration can be performed by steam treatment, methanol treatment must be performed after 5 regenerations. Several American investigators used Ambersorb XE-340 for removing THM and other halogenated hydrocarbons from water.

6.4.2 Removal of THM

Symons et al. (ref.6.4) describe the removal of $CHCl_3$ and $CHBrCl_2$ from water by adsorption on XE-340. The results are summarized in table 6.3.
Thus, good removal of both THMs takes place, strongly dependent upon the empty bed contact time and the TOC content of the water. Desorption takes place when the influent concentration is reduced. Regeneration with steam restores the ability to

adsorb $CHCl_3$, although the filter runs become shorter.

Table 6.3 - Removal of $CHCl_3$ and $CHBrCl_2$ by XE-340

Substance	Conc. (µg/l)	Contact time (min)	no. of bed volumes	filter run up to 10 % breakthrough (days)	TOC (mg/l)
$CHCl_3$	55	6,2	5342	23	6
	40	10,0	11088	77	1-2
	65	5,0	6048	21	1-2
$CHBrCl_2$	28	6,2	11615	50	6
	14	10,0	14688	102	1-2
	26-39	5,0	12097	42	1-2

Snoeyink (ref. 6.15), O'Connor et al. (ref. 6.16) and Oulmans (ref. 6.17) also studied the use of XE-340 for the removal of THM in a series of 15 adsorbents. Based on the batch experiments of Snoeyink and the pilot scale studies of O'Connor, Oulmans concludes that XE-340 adsorbs THM the best. O'Connor found that the capacity of XE-340 decreased after regeneration with steam. However, the results were obscured by the fact that a shorter contact time was used after regeneration.

THM can thus be removed to the extent of more than 90 % by using XE-340 over long filter runs. Varying influent concentrations, however, can produce elution. Regeneration with steam is another point for further investigation.

6.4.3 Removal of TCE and other halogenated hydrocarbons

Symons et al. (ref. 6.4), in addition to the removal of THM, also investigated the adsorption of 8 other halogenated compounds. The most important data from this study are presented in table 6.4.

Table 6.4 - Removal of TCE, C_2Cl_4, $CCl_2{=}CH_2$ and $CCL_3{-}CH_3$ by XE-340, TOC < 1 mg/liter

Substance	Conc. (µg/l)	Contact time (min)	Lifetime up to 10 % breakthrough (days)
TCE	120-276	9	> 126
C_2Cl_4	60-205	5	> 146
$CCl_2{=}CH_2$	41- 74	5	> 146
$CCl_3{-}CH_3$	172-286	5	> 146

Thus, at low TOC contents, excellent removal takes place over very long filter runs. At higher TOC contents, however, the effect decreases somewhat. In this case as well, elution takes place at varying influent concentrations.
XE-340 thus appears to be a very suitable adsorbent for removing TCE from groundwater with a low TOC content.

6.4.4 Use of other adsorbents

In recent years, a variety of porous polymers were introduced for which good removal of halogenated compounds is claimed. Some examples are Syn 46 and Syn 72, Polysorb and Lyposorb. However, no detailed information is available as yet regarding the efficiency of these agents.

In addition, some experiments were performed with Compalox (aluminium oxide). However, no direct use can be anticipated for this agent in the removal of halogenated compounds.

6.5 Removal of halogenated compounds by oxidation

Little attention has been paid to the removal of halogenated compounds by oxidation, since the conversion to be expected is generally small.

Symons (ref. 6.18) and Symons and Stevens (ref. 6.19) describe the effects of ozone and chlorine dioxide on the THM contents. They found that these oxidizing agents do not influence the THM contents. Love et al. (ref. 6.3) even found an increase in the THM content when ozonation is preceded by chlorination. This phenomenon was already discussed in section 5.6.

Kruithof and Van Paassen (ref. 6.20) found that treatment of water with chloramines does not lead to a change in the THM content. By using oxidation agents such as chlorine dioxide and chloramines, no change in the THM content is expected to be achieved. At most, a slight increase will occur when impure agents (contaminated with chlorine) are used. For ozonation as well, aside from an aeration effect, no reduction of the THM content is to be anticipated. However in some cases, an increase in the THM contents can be expected.

6.6 Reduction of the content of halogenated compounds during infiltration

6.6.1 Introduction

Only a little information is available on the reduction of the content of halogenated compounds during infiltration. Some information is available from the Amsterdam Municipal Waterworks, the Dune Waterworks of the Hague and the Provincial Waterworks of North Holland. All three of these companies provide information on the decline of the THM and the EOCl contents. The Municipal Waterworks and the DWL-The Hague likewise provide some information concerning AOCl and AOBr decline. No distinction is made between removal by aeration in the infiltration canals and removal by infiltration. Especially for the removal of THM, however, aeration can play a major role. 90 % reductions are even possible here.

6.6.2 Behavior of THM

It is apparent from studies performed at the Municipal Waterworks that a marked decrease in the THM content takes place upon infiltration. It appears that the more highly brominated THM are better removed than $CHCl_3$ in this case. After an average soil residence time of 60 days, only traces of $CHCl_3$ appear to be present (< 1 µg/ liter); other THMs are not detected.
A considerable reduction of THM also takes place at the Dune Waterworks of The Hague. Following aeration and infiltration, however, the THM content has not already declined to beneath the detection limit. Sometimes THM contents of 5 µg/liter occur

after infiltration. Here, only $CHCl_3$ and $CHBrCl_2$ were demonstrated; more highly brominated THMs were not present.

The concentration change of THM by infiltration is also determined by the PWN. Figure 6.7 shows the course of the $CHCl_3$ concentration after a residence time of 1 week in the infiltration area.

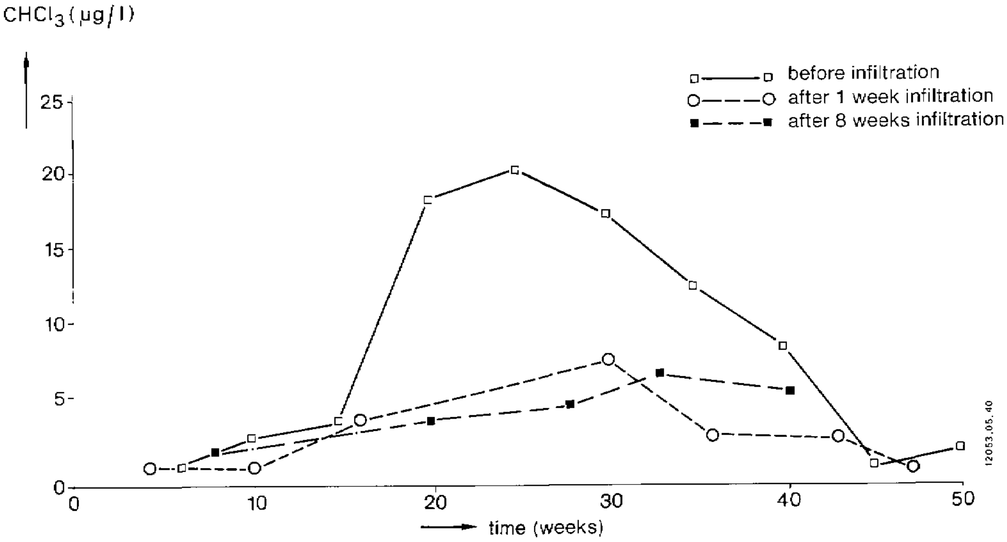

Figure 6.7 - Removal of $CHCl_3$ by infiltration at the PWN (corrected for the residence time)

Here, as well, a considerable $CHCl_3$ reduction takes place; once again, no distinction can be made between aeration and infiltration. After 8 weeks residence time, some breakthrough always occurs, wherein the breakthrough curve follows the pattern of the introduction curve, taking the residence time of 8 weeks into account.

The removal of $CHBrCl_2$ follows more or less the same pattern. The removal of $CHBr_2Cl$ is shown in figure 6.8.

It is apparent that between 1 and 8 weeks of residence time for $CHCl_3$, 100-200 % desorption occurs, while for $CHBr_2Cl$, a removal of about 60 % still takes place. For $CHBrCl_2$, the removal still amounts to about 25 %. Thus, here, as well, there are indications for a greater concentration reduction of more highly brominated THM. No further THM can be detected in the abstracted water.

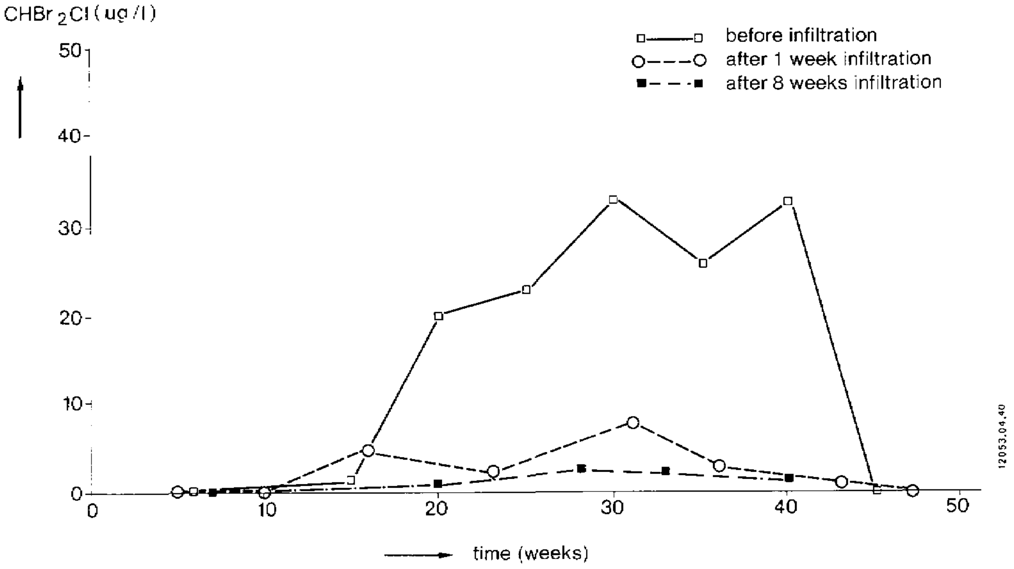

Figure 6.8 - Removal of $CHBr_2Cl$ by infiltration at PWN (corrected for the residence time)

Thus, THM are largely removed by infiltration. The aeration which precedes the infiltration plays an important role in this. In two instances, the water contains no THM after infiltration. In one case, incidentally 10-25 % breakthrough of the more highly chlorinated THM occurred.

6.6.3 Lowering of the EOCl, AOCl and AOBr content

At the Municipal Waterworks, a considerable reduction of the EOCl content appears to occur. After only 50 cm soil passage, the reduction appears to amount to 75 %; after complete infiltration, the decrease is 100 %.

This good removal is undoubtedly related to the lipophilic character of the compounds occurring in this group.

In the case of the Dune Waterworks as well, a reduction of the EOCl occurs (see figure 6.9).

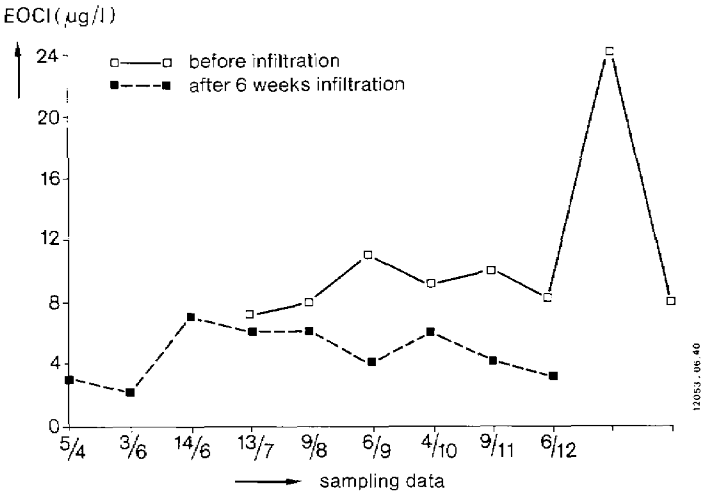

Figure 6.9 - The EOCl content before and after infiltration at DWL-The Hague (corrected for the residence time)

However, the residual content is considerable here and amounts to about 45 % of the influent value.

At PWN, a considerable decrease in the EOCl takes place. This reduction is greater than at The Hague and amounts to an average of about 80 %.

Thus, like the THM content, the EOCl content is also clearly reduced by infiltration. The relatively small reduction at DWL-The Hague (55 %) is noteworthy, compared to the 80 % at PWN and the 100 % at GW.

In addition, GW measured the decrease in AOCl and AOBr content during infiltration. For the results, see figure 6.10.

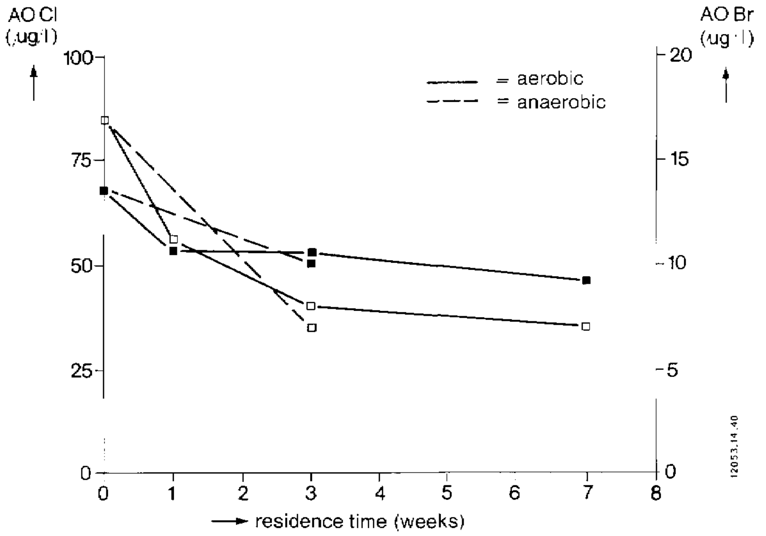

Figure 6.10 - The behavior of the AOCl (■) and the AOBr (□) contents during infiltration in the Dunes (GW, ref. 6.23)

It is apparent from the figure that the reduction of the AOCl content up to 7 weeks' residence time amounts to about 35 %; for the AOBr content, this figure is 60 %. Up to a residence time of about 3 weeks, there is no difference between aerobic and anaerobic conditions.

For the infiltration at The Hague, some data are also known regarding the behavior of AOCl and AOBr during infiltration. It is apparent from this that the average reduction of AOCl is nil after about 7 weeks' residence time (3 observations in 1981). A 60 % reduction was found for AOBr (1 observation in 1981).

Thus, for AOCl and AOBr as well, a more marked decrease in the content of brominated products appeared to occur. The number of available measurements, however, is highly limited.

6.7 Removal of halogenated products by reverse osmosis

6.7.1 Introduction

Reverse osmosis is capable of reducing organic material parameters such as permanganate number and the TOC content to a level which is at or below the level of detection. However, it cannot yet be concluded from this that all compounds are also removed completely. In this section, we will discuss the removal of THM and other low molecular weight compounds and the reduction of the AOCl content.

6.7.2 Removal of THM and other halogenated compounds

Schippers et al. (ref. 6.21) chlorinated Rhinewater with a chlorine dose of 5 mg/liter. Immediately after chlorination, the water was subjected to reverse osmosis with cellulose acetate membranes. After 24 hour, the excess chlorine in the feed and the product were eliminated using $Na_2S_2O_3$. The concentrations of halogenated compounds in the water were determined.

The THM concentration was reduced, but this was principally due to the removal of high molecular weight THM precursors rather than to removal of THM itself.

The removal of THM is illustrated on the basis of table 6.6. This shows the removal of THM by reverse osmosis with cellulose acetate and with polyamide membranes (ref. 6.22).

Thus, reverse osmosis with cellulose acetate membranes achieves no removal whatsoever; the removal with polyamide membranes is clearly better (greater than 80 %).

Table 6.6 - Removal of THM by reverse osmosis

	Cellulose acetate		Polyamide	
	concentration (µg/l)		concentration (µg/l)	
compound	feed	product	feed	product
CCl_4	0,1	< 0,1	0,3	< 0,1
$CHCl_3$	24	24	23	4
$CHBrCl_2$	37	36	34	6
$CHBr_2Cl$	23	23	22	3
$CHBr_3$	3,7	3,7	3	0,5
TTHM	87,8	86,7	82,3	13,5

6.7.3 Reduction of the AOCl content

Subsequently, in some instances, the reduction of the AOCl content was determined both for cellulose acetate and for polyamide membranes. It appears that both membrane types bring the AOCl content of 70 µg/liter back to the level of the detection limit (< 10 µg/liter).
Reverse osmosis is thus well suited for the removal for high molecular weight halogenated compounds.

6.8 Discussion

In this section, attention was paid to the removal of halogenated compounds during aeration, activated carbon filtration, adsorption on alternative adsorbents, oxidation, infiltration and reverse osmosis. In general, it should be noted that a great deal of information is available on THM removal for all treatment steps. For certain techniques, the removal of TCE has also been investigated extensively. Far less information is available concerning the removal of high molecular weight compounds. In view of the recently noted characteristics of these compounds, this material deserves great attention.

The following may be noted concerning the individual processes.

- Aeration

  Using aeration, THM may be removed to the extent of about 80 % with air/water ratios of 20 : 1. TCE can be fairly easily removed to the extent of 99 %.
- Activated carbon adsorption

  Carbon filtration gives a moderate removal of THM. $CHCl_3$ breaks through rapidly, followed by the other THM. The adsorption is better, the more highly brominated is the THM. Elution of THM may take place through reduction of the THM content in the influent, for example, by stopping transport chlorination or by reducing the chlorine dose in breakpoint chlorination. This is principally the case with the more highly chlorinated THM: $CHCl_3$ and $CHBrCl_2$.

  Thus, marked THM reduction cannot be brought about over long filter runs using carbon filtration. Nevertheless, carbon filtration is readily usable when it is based on a specific criterion (for example, of 70 µg/liter, as is the case with PWN at Andijk).

  TCE is removed well by carbon filtration. During long filter runs (for example, 1 year), it is possible to keep the effluent content below 1 µg/liter.

  Relatively little is known regarding the reduction of the EOCl and AOCl contents. Occasional measurements have shown that the removal of these is better than THM removal.

- Adsorption on alternative adsorbents
  Among the alternative adsorbents, attention has principally been paid to the carbon-containing polymer XE-340. Both $CHCl_3$ and TCE appear to be removed very well, especially at a low TOC content. However, it should be noted that the production costs are about 10 times as high as for activated carbon and that it is unlikely that the manufacturer will place this agent on the market in the near future.
- Oxidation
  Little is known regarding the removal of THM using ozone, chlorine dioxide and chloramine. However, the available results suggest that scarcely any removal effect is to be anticipated.
- Infiltration
  Infiltration brings about a marked decrease in the THM, EOCl and AOCl contents. In the case of breakthrough, first of all, the volatile chlorinated compounds appear. Up to the present time, however, little information has become available, and the contribution of the aeration preceding infiltration to the removal process is also not clear.
- Reverse osmosis
  THM are not removed by reverse osmosis with cellulose acetate membranes; the use of polyamide membranes gives far better results. The AOCl content is greatly reduced.

In summary, it can be stated that the THM content decreases greatly during infiltration, while the use of carbon filtration provides for a certain removal. Alternative adsorbents may provide more possibilities, possibly in combination with a prior aeration.

TCE can be removed very well by aeration and carbon filtration. The use of alternative adsorbents can also offer interesting possibilities.

Little is known regarding the reduction of the AOCl contents. Reverse osmosis gives good results, while infiltration and activated carbon filtration also appear to have good utilization possibilities.

In addition, attention should be drawn to the effect of post-chlorination. Relatively high contents of halogenated products can always be formed here.

6.9 Recommendations

The results described in this section give rise to the following points of investigation:

- investigation regarding the removal of high molecular weight halogenated compounds, for example, by adsorption techniques and by infiltration;
- use of alternative adsorbents such as XE-340 for the removal of TCE. The regeneration aspects appear to be of particular importance here;
- in general, more information is desired regarding infiltration, for example, regarding the effect of aeration preceding infiltration and the nature of the processes taking place in the soil layer;
- furthermore, combination of processes is worthy of attention, for example, the combination of aeration and carbon filtration for the removal of THM or TCE;
- Studies on the effect of post-chlorination following removal of halogenated compounds.

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7 REMOVAL AND CONVERSION OF THM PRECURSORS

7.1 Introduction

One of the very high priority recommendations of the ad hoc study group on chlorine was the removal of THM precursors using, for example, coagulation, ozonation, anion exchange, granular activated carbon filtration and membrane filtration before they come into contact with chlorine. Beginning in 1978, a great deal of attention was paid to these removal possibilities.

This section successively discusses precursors removal by aeration, coagulation, carbon filtration, ion exchange and alternative adsorbents. Then, consideration is given to the conversion of precursors by ozonation, the behavior of precursors during infiltration and precursor removal by reverse osmosis.

In describing the removal and conversion of precursors, the problem arises regarding the manner in which the precursor content should be determined. It is generally assumed that precursors are natural substances, for example, humic materials. The content of these substances has long been established by determining parameters such as the TOC content, the $KMnO_4$ number, the UV extinction or the color. However, it is not certain that these organic substance contents precisely parallel the precursor content. This will often be true for removal processes, but not for conversion processes.

For these reasons, a specific test was developed to determine the precursor content, the so-called THMFP (trihalomethane formation potential) determination. However, this test was not always performed uniformly over time. Great differences were noted in temperature, pH, reaction time and chlorine dose. The results of all THMFP determination used will necessarily be included and, if neccessary, organic parameters will also be reported.

In the course of the investigation, it was found that the precursor content and thus the THMFP-precursor was not of determining significance for the THM content supplied to the consumer. This led to the development of the determination of the THMFP-consumer, a determination which begins with the pH, reaction time and chlorine dose as employed in practice. This THMFP-consumer will also be discussed in this section.

At the end of this section, the processes investigated will be considered in further detail, and recommendations will be made for closer examination.

7.2 Precursor removal by aeration

In the time period in which it was assumed that, in addition to humic materials, certain volatile substances (for example, acetone) could also contribute to the THMFP-precursor, some investigations were conducted to determine whether the precursor content could be reduced by aeration. Both Symons et al. (ref. 7.1) and Singley et al. (ref. 7.2), however, found no significant removals at air/water ratios amounting to as much as 50 : 1.

It is apparent from this that volatile substances thus make no major contribution to the THMFP-precursor and that precursors cannot be removed by aeration.

7.3 Removal of precursors by coagulation

The coagulation process is used in almost every surface water treatment system for drinking water supply. In addition to the removal of turbidity, its principal goal is based on the general observation that removal of organic substances is also accomplished. This removal is frequently established on the basis of a reduction of the TOC content, the $KMnO_4$ number, the UV extinction or the color. The degree of removal depends greatly on the coagulant dose and the pH, while the nature of the organic materials in the water to be treated is also of essential significance. The removal percentages, determined as the reduction of the TOC content, are often at the level of several tens percent. However, it is questionable whether this organic matter removal is also applicable to precursor removal expressed as the THMFP-precursor.
Love et al. (ref. 7.3) found a partial precursor removal by coagulation. Iron(III)chloride appears to give a better result than aluminium sulfate. The shift toward more highly brominated THM which they observed is caused by the reaction conditions during the THMFP determination. These results are included in the final report of the ad hoc study group on chlorine (ref. 7.4). Since that time, investigations at KIWA and at the Dutch treatment plants gave somewhat more information, but the interpretation of this is greatly impeded by the nonuniform performance of the THMFP determination.
Rook (ref. 7.5) found a marked decline in the precursor content, measured as the chloroform content, after 24 hour with a chlorine dose of 5 mg/liter. In a pilot plant with lamella sedimentation, the chloroform content decreased by about 50 % at an

iron addition of 5-10 mg/liter and a pH of 7,8. The TOC content decreased by 20 % and the $KMnO_4$ value by 50 %. Higher iron doses did not lead to a further reduction of the chloroform content (here, a measure of the precursor content) and the permanganate number, while TOC content, UV extinction and color showed something of a further decrease. This decrease in the precursor content was also observed in many other investigations. However, a removal percentage of 50 % was practically never achieved, which may be explained to some degree by the THMFP determination method used by Rook. Kruithof and Van Paassen (ref. 7.6) specifically found in the treatment process at Kralingen a far smaller reduction of the precursor content. The THMFP-precursor, determined after a reaction time of 48 hour and with a residual chlorine content after 48 hour or 5 mg/liter, decreased from 214 µg/liter for the raw water to 188 µg/liter after coagulation. This is a 12 % reduction. It should be noted that the water was not passed over rapid filter after coagulation, but was sampled immediately after lamella sedimentation.

In addition, in this investigation, a THMFP-consumer determination was carried out with a shorter reaction time and a lower chlorine dose. This THMFP-consumer, which is not a measure of the precursor content, but rather of the quantity of THM which may occur in the drinking water as a consequence of the post-chlorination, did not appear to decreaese during coagulation. It is apparent from this that sufficient fast reacting precursors are still present after coagulation to form just as much THM under practical conditions as before coagulation. This experience was also confirmed with Biesbosch water in the treatment process at

Zevenbergen (ref. 7.7) and with Lekcanal water at Nieuwegein.
KIWA investigated the precursor removal from Lekcanal water by coagulation using a standard jar test equipment (ref. 7.24) with the pH and metal salt addition as variables. The results are reported in table 7.1.
It is apparent from the table that the pH in the range from 6.2 to 8.5 has only a slight influence on the THMPF-precursor at an iron dose of 4 mg/liter and an aluminium dose of 2 mg/liter. At an iron dose of 4 mg/liter and a pH of 7 to 8, the THMFP reduction is about 20 %, and at an aluminium dose of 2 mg/liter and a pH of 6,5-7,0, it is about 30 %. Increasing the aluminium dose from 2 to 5 mg/liter does not result in any THMFP reduction, whereas the organic material parameters do decrease somewhat more. Increasing the iron dose from 4 to 8 mg/liter does lead to an additional 10 % THMFP reduction. Since the measurements were only performed one time, the findings are very preliminary in nature.

GEB Dordrecht performed some experiments with Rhine water after storage in a reservoir in terms of the removal of precursors by coagulation. At an iron dose of 10 mg/liter and a pH of 7,5, the THMFP decreases by about 50 %, from 1,2 µmol/liter to 0,65 µmol/liter.

Although the quantity of data is still quite limited and the determination for the THMFP-precursor was not performed in a standardized manner, nevertheless, some preliminary conclusions can be drawn. The coagulation process is able to reduce the THMFP-precursor. The removal percentages generally

Table 7.1 - Coagulation of Lekcanal water performed in the standard jar test apparatus

Fe mg/l	Al mg/l	pH	Color mg Pt/l	UV m^{-1}	TOC mg C/l	THMFP µg/l
0	0	7,6	16,2	9,0	4,4	229
4	0	6,2	12,7	7,1	3,7	179
4	0	6,8	13,1	7,6	-	179
4	0	7,2	12,3	7,5	3,8	184
4	0	7,7	13,9	8,0	4,2	184
4	0	8,1	13,9	8,3	4,2	192
4	0	8,5	13,9	8,2	4,7	192
0	2	6,4	9,2	6,5	2,4	158
0	2	6,8	9,6	6,3	2,4	158
0	2	7,2	11,2	7,0	2,8	156
0	2	7,6	13,1	7,8	3,0	170
0	2	7,9	12,7	7,6	3,0	173
0	2	8,3	13,5	7,8	3,1	171
0	0	-	13,5	8,6	4,4	252
2	0	7,7	13,1	8,1	3,5	221
3	0	7,9	11,2	7,5	3,4	208
4	0	7,8	11,2	7,5	-	208
5	0	7,8	10,0	6,9	3,2	195
6	0	7,8	9,6	6,7	3,2	195
8	0	7,9	10,4	6,6	3,0	182
0	1	7,2	10,8	7,2	3,7	218
0	1,5	7,1	9,6	6,5	3,8	211
0	2	7,1	9,2	6,2	-	203
0	2,5	7,0	8,5	6,0	-	205
0	3	7,0	8,5	5,9	-	196
0	5	7,0	7,8	5,4	-	215

correspond to those for organic material parameters such as the $KMnO_4$ number, TOC content, UV extinction and color. However, definite quantitative correlations are nor detectable in view of the limited number of measurements.
The degree of precursor removal depends on the magnitude of the iron dose and, to a slight degree, on the pH. However, it seems that precursor removal (thus reduction of the THMFP-precursor) by coagulation does not lead to lower THM contents upon chlorination in practice (thus, reduction of the THMFP-consumer), wherein relatively low chlorine dosages and short reaction times are used. More detailed investigation in this area appears desirable.

7.4 Precursor removal by activated carbon filtration and ion exchange

7.4.1 Introduction

In recent years, a great deal has been published regarding the removal of organic matter by granular activated carbon filtration, measured as, for example, the TOC reduction or the reduction of the UV extinction. For example, reference may be made to Meyers et al. (ref. 7.8) who present operating data from the DWL Rotterdam at Kralingen, the PWN at Andijk and pilot installation data from GW at Leiduin. In this section, we will limit our consideration to the removal of precursors, measured as a reduction of the THMFP-precursor. Some data from pilot plant studies at Dordrecht and full scale studies at Zevenbergen will be presented. Then, a discussion will be presented regarding the course of the THMFP-consumer levels before and after carbon filtration, as meaured in pilot plant studies at Leiduin and full scale studies at Zevenbergen. Finally, considerations will be presented on the reduction of the THMFP-precursor by ion exchange; the effect of an ion exchanger will be compared with activated carbon adsorption.

7.4.2 Reduction of the THMFP-precursor by activated carbon filtration

In 1979 at GEB Dordrecht, a pilot investigation was performed with reference to the removal of THM precursors from treated surface water and groundwater by activated carbon filtration. The empty bed contact time in the carbon filters was 20 minutes; the apparent linear velocity was 3 m/hour. The reduction of the THMFP-precursor is presented in figure 7.1 for treated surface water.

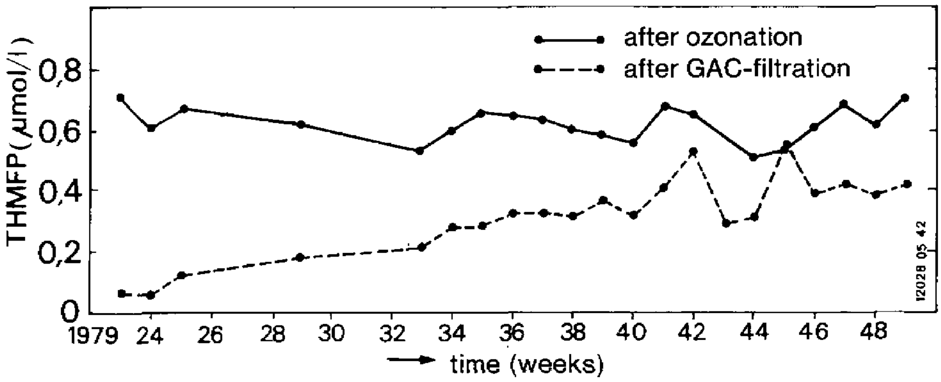

Figure 7.1 - Removal of THM precursors by carbon filtration at Dordrecht. Pretreatment: coagulation, rapid filtration, ozonation (1979)

In the treated surface water, the THMFP-precursor is 0,64 μmol/liter. As a result of carbon filtration in the first 10-12 weeks (5500 bv), a minimum

60 % reduction is achieved by carbon filtration. After this, the reduction decreases and stabilizes at about 35-40 % until the end of the 6-month run (13,000 bv).

The THMFP-precursor in the treated groundwater amounts to 1,08 µmol/liter. Carbon filtration results in an initial 90 % reduction. This percentage gradually declines until, after 11 weeks (5500 bv), a 45 % reduction has been attained.

At the Waterworks of North-West-Brabant at Zevenbergen, carbon filtration was applied to treated Biesbosch water (ref. 7.9). The THMFP-precursor of this water was determined at a pH of 8 by chlorine addition of 35 mg/liter. The THM content was determined after a reaction time of 48 hour. The THMFP-precursor appeared to vary from 150-240 µg/liter and to consist principally of $CHCl_3$. All variations were also found as variations in the $CHCl_3$ content. This is explainable by the reaction conditions selected for the THMFP-precursor determination.

The THMFP-precursor in the carbon filtration was determined as a function of the running time of the filter. The results are presented in figure 7.2.

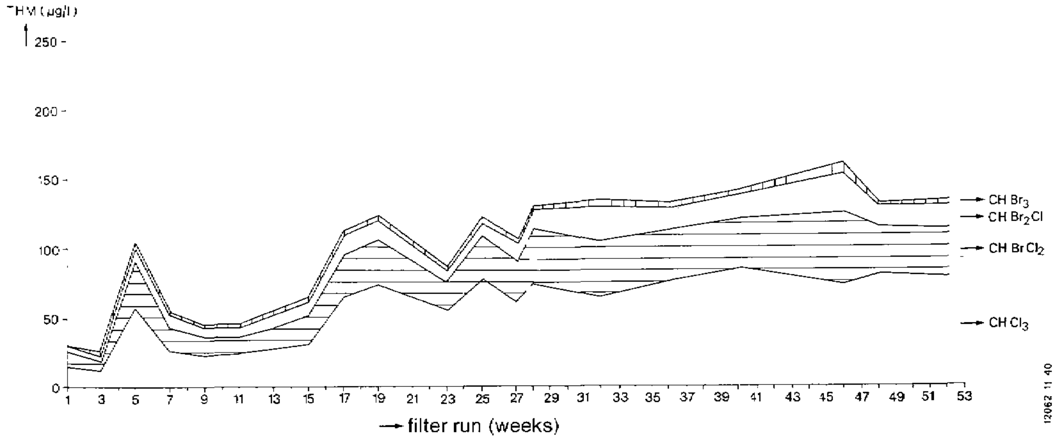

Figure 7.2 - The cumulative THMFP-precursor as a function of the carbon filter runs at WNWB-Zevenbergen (1980). Preliminary treatment: transport chlorination, coagulation, flotation, breakpoint chlorination and dual media filtration

It can be deduced from figure 7.2 that the THMFP increases with increasing carbon life, from 20 to 160 µg/liter. Marked THMFP reduction only occurs during very short filter runs (3 weeks, 900 bv). The precursor removal rapidly decreases, and after 28 weeks (10,000 bv), amounts to about 20 %, then becoming fairly constant.

Thus, carbon filtration appears to accomplish a considerable precursor reduction only during short filter runs.

In addition, precursor removal is meaningful only if it also results in a decrease in the THM content under practical conditions. In other words: reduction of the THMFP-precursor is only meaningful if it also leads to a reduction of the THMFP-consumer.

7.4.3 Reduction of the THMFP-consumer by activated carbon filtration

As was previously noted, reduction of the THMFP-precursor is only worthwhile if it also leads to a reduction of the THMFP-consumer, wherein a lower chlorine dose and a shorter contact time are maintained. The fact that the chlorine dose is extremely important is apparent from figure 7.3, where the THM content is given as a function of the chlorine dose for a carbon filtrate at Leiduin.

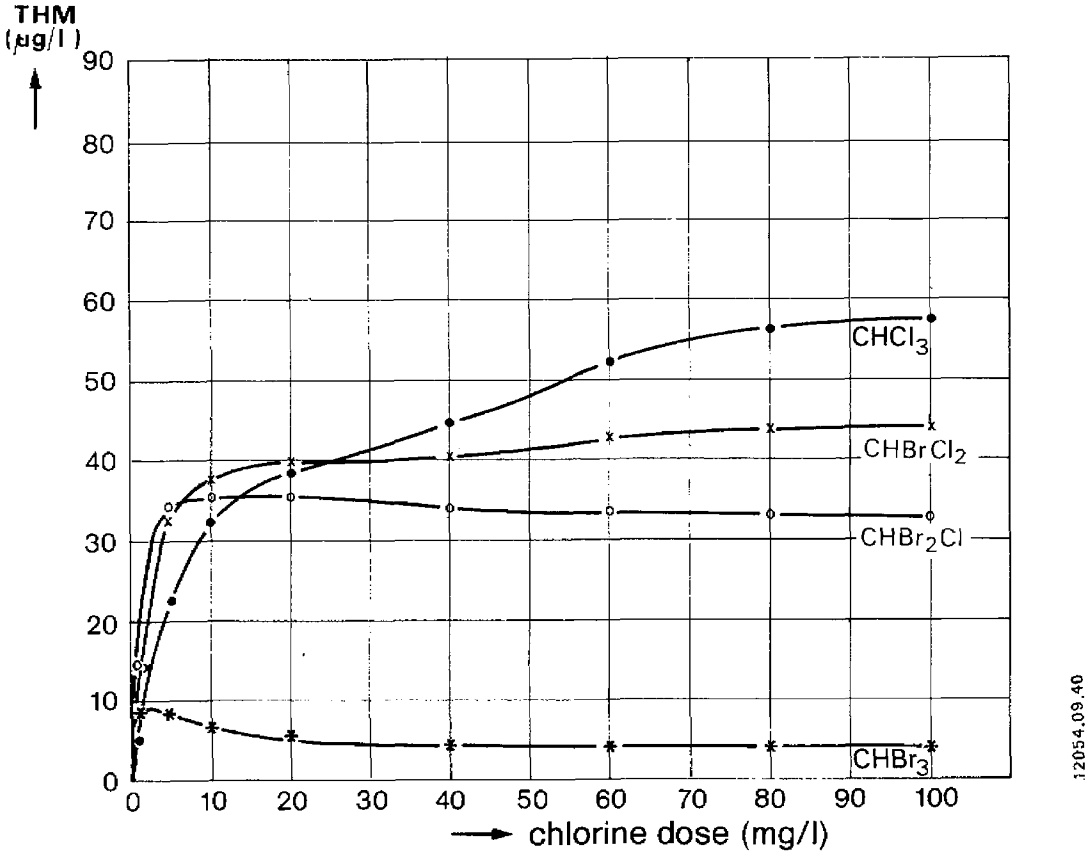

Figure 7.3 - THM content as a function of chlorine dose in a carbon filtrate at Leiduin

It is apparent that the $CHBr_3$ content shows a maximum for a chlorine dose of 0,5 mg/liter, the $CHBr_2Cl$ content at a chlorine dose of 10 mg/liter, while the $CHBrCl_2$ and $CHCl_3$ contents also continue to increase at very high chlorine dosages. The chlorine dose thus not only influences the total THM content, but also the ratio between the contents of the individual THMs. Especially under practical circumstances, the chlorine dose is of great importance for this ratio.

This phenomenon has led, among other things, to the introduction of a THMFP-consumer determination. However, in the case of this determination as well, the procedure employed is not uniform universally. The Municipal Waterworks add 0,3 to 0,6 mg/liter chlorine and use as a guideline a residual chlorine content of 0,2 mg/liter chlorine after a contact time of 20 minutes. KIWA and WNWB perform the determination with a fixed chlorine dose (e.g., 0,5 mg/liter). Both determinations, however, give a good indication of the THM content that can be expected by the consumer.

The results of the pilot plan study at Leiduin are presented in figure 7.4. In all cases, the THMFP-consumer is shown as a function of time (ref. 7.10).

The following abbreviations are used in figure 7.4:

CF = carbon filtration
SSF = slow sand filtration
HR = hardness reduction
O_3 = ozonation.

It is apparent from the figure that the systems 1-4 with carbon filtration, which have the lowest TOC contents (1,7-2,1 mg/liter) and the lowest THMFP-precursor (40-80 µg/liter), in all cases have given the lowest $CHCl_3$ and the highest $CHBr_3$, while the total THMFP-consumer is also quite high. Systems 5-

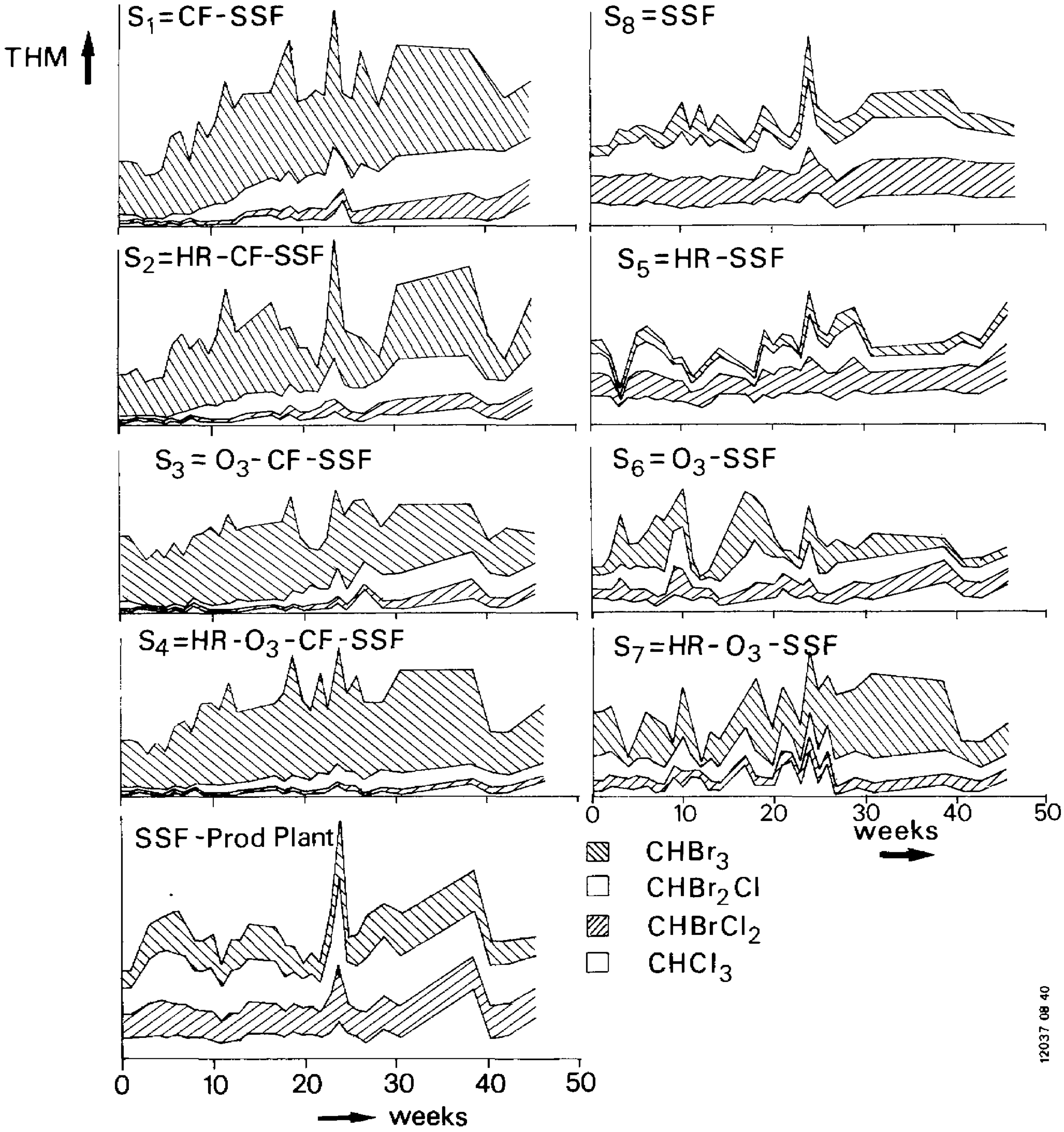

Figure 7.4 - THMFP-consumer in water after SSF (slow sand filtration) with carbon filtration (S1-S4) and without carbon filtration (S5-S8) in the pilot plant at Leiduin

8 without carbon filtration, with higher TOC contents (2,4-2,9 mg/liter) and higher THMFP-precursor (75-150 µg/liter), on the other hand, give much lower $CHBr_3$ contents, while the THMFP-consumer is also lower. Carbon filtration thus gives the lowest THMFP-precursor. However, this coincides with high $CHBr_3$ contents and a relatively high THMFP-consumer.

A similar study was performed by WNWB and KIWA in the production plant at Zevenbergen (refs. 7.9, 7.10). First, the THM formation was determined as a function of the chlorine dose in the dual media filtrate and the carbon filtrate. The results are presented in figure 7.5.

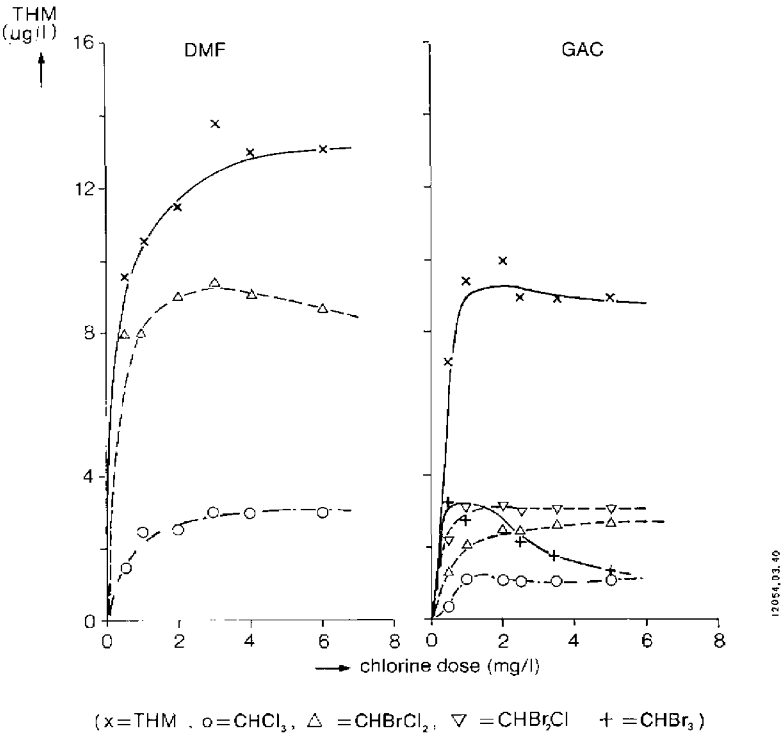

Figure 7.5 - Formation of THM as a function of chlorine dose in the dual media filtrate and the carbon filtrate at Zevenbergen

It is apparent from figure 7.5 that in already chlorinated dual media filtrate upon further chlorination, only $CHCl_3$ and $CHBrCl_2$ are formed. All THM are formed in the carbon filtrate, with $CHCl_3$ at the lowest concentrations. The $CHBr_3$ content passes over a maximum at a chlorine dose of 0,5-1,0 mg/liter. For a low chlorine dose (0,5 mg/liter), the THM content in the carbon filtrate is somewhat higher than in the dual media filtrate.
In addition, the THMFP-consumer was determined for both the dual media filtrate and the carbon filtrate. The THMFP-consumer of the dual media filtrate amounted to 13-25 µg/liter with $CHCl_3$ in the highest concentrations, followed by $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$. The THMFP-consumer of the carbon filtrate is given in figure 7.6.

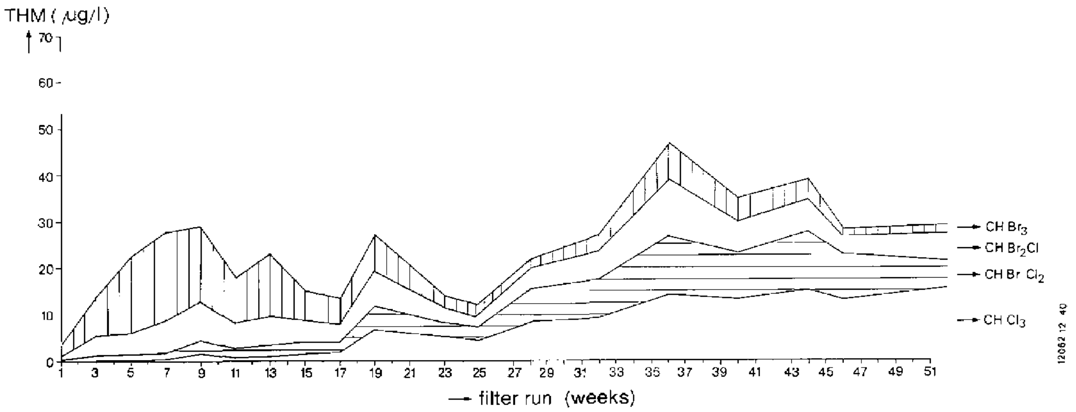

Figure 7.6 - Cumulative THMFP-consumer as a function of the running time of the carbon filter at Zevenbergen

The THMFP-consumer increases from 5 to 30 µg/liter. By far, the highest contents were encountered for $CHBr_3$ (to a maximum of 20 µg/liter), followed by $CHBr_2Cl$, $CHBrCl_2$ and $CHCl_3$.

Thus, in comparison with the dual media filtrate, a marked shift is seen toward the formation of more highly brominated THM. This shift is greatest for relatively short filter runs (3-11 weeks, 900-3100 bv).

Thus, as was previously reported in section 7.4.2, carbon filtration leads to a certain THMFP-precursor reduction. This reduction, however, is not accompanied by a THMFP-consumer reduction and leads to a shift toward the formation of more highly brominated THM. This shift is the greatest in the case of relatively short filter runs.

The entire phenomenon is once again illustrated on the basis of figure 7.7 (ref. 7.11).

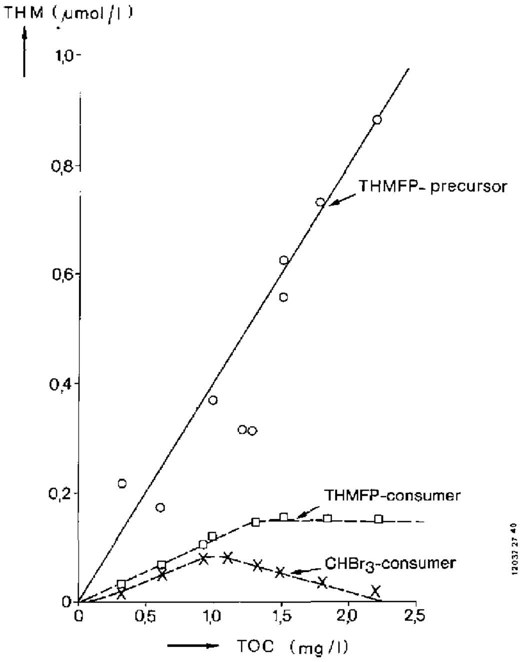

Figure 7.7 - THMFP-precursor, THMFP-consumer and $CHBr_3$-consumer as a function of the TOC content in carbon filtrate at Zevenbergen

The THMFP-precursor increases as a function of the

TOC content. The THMFP-consumer (at a fixed chlorine dose) rises to a certain TOC value, then remains constant. The $CHBr_3$-consumer rises to a somewhat lower TOC value, then decreases.
Only precursor removal to a THMFP-precursor lower than about 0,5 µmol/liter (60 µg/l for $CHCl_3$) leads to a reduction of the THMFP-consumer. This coincides with a TOC reduction to 1,2 mg C/liter. At this TOC content, maximal formation of $CHBr_3$ takes place in the presence of about 70 µg/liter bromide.

The above-mentioned example is not generalizable numerically. The trends, however, are generalizable. Only a marked THMFP-precursor reduction leads to a reduction of the THMFP-consumer. In addition, in the presence of bromide ions upon a decrease in the THMFP-precursor, a shift takes place toward the more highly brominated THM in the THMFP-consumer.
A limited precursor removal thus does not give the desired results. Therefore, precursor removal and establishment of a uniform prerequisite for the THMFP-precursor determination has not received a very high priority.

7.4.4 Precursor removal by ion exchange in comparison with activated carbon

At many locations in the literature, the removal of humic substances by ion exchange is described. In many instances, the decrease in the humic acid concentration is shown by the decrease in color, UV extinction or TOC content, while the THMFP has also been determined in some more recent articles. Some of the most important literature references will be described next.

- Gauntlett (ref. 7.12) compares the activity of ion exchangers with that of activated carbon on the basis of UV and TOC reduction. He expresses a definite preference for the use of activated carbon.
- Anderson and Maier (refs. 7.13 and 7.14) found strongly basic ion exchangers can reduce the TOC content to below the detection limit as long as the exchanger is in the chloride or hydrogen carbonate form. In the case of conversion to the sulfate form, TOC breakthrough begins to take place. They give a cost-price calculation, wherein ion exchange comes out favorably relative to carbon filtration.
- Kölle (ref. 7.15) also performed a great deal of investigation on the use of strongly basic ion exchangers. Beginning in 1978, Kolle (ref. 7.16) applied these in practice and found a reduction in the TOC content of 50 %.
- Rook and Evans (ref. 7.17) studied the action of weakly basic ion exchangers. At runs of 1000-1800 bv per cycle, they found a THMFP reduction of 60 %.

Kruithof and Van Paassen (ref. 7.18) performed batch and continuous experiments on a laboratory scale regarding the precursor removal by 11 ion exchangers and 3 carbon types. This was followed by a pilot scale study with the best ion exchanger and the best carbon type. The results of this investigation are presented in figure 7.8.

For both adsorbents, the reduction is determined by the UV extinction, fluorescence emission, color, TOC and THMFP. There is no definite difference in color removal for the two agents. For all other parameters, activated carbon gives the best removal.

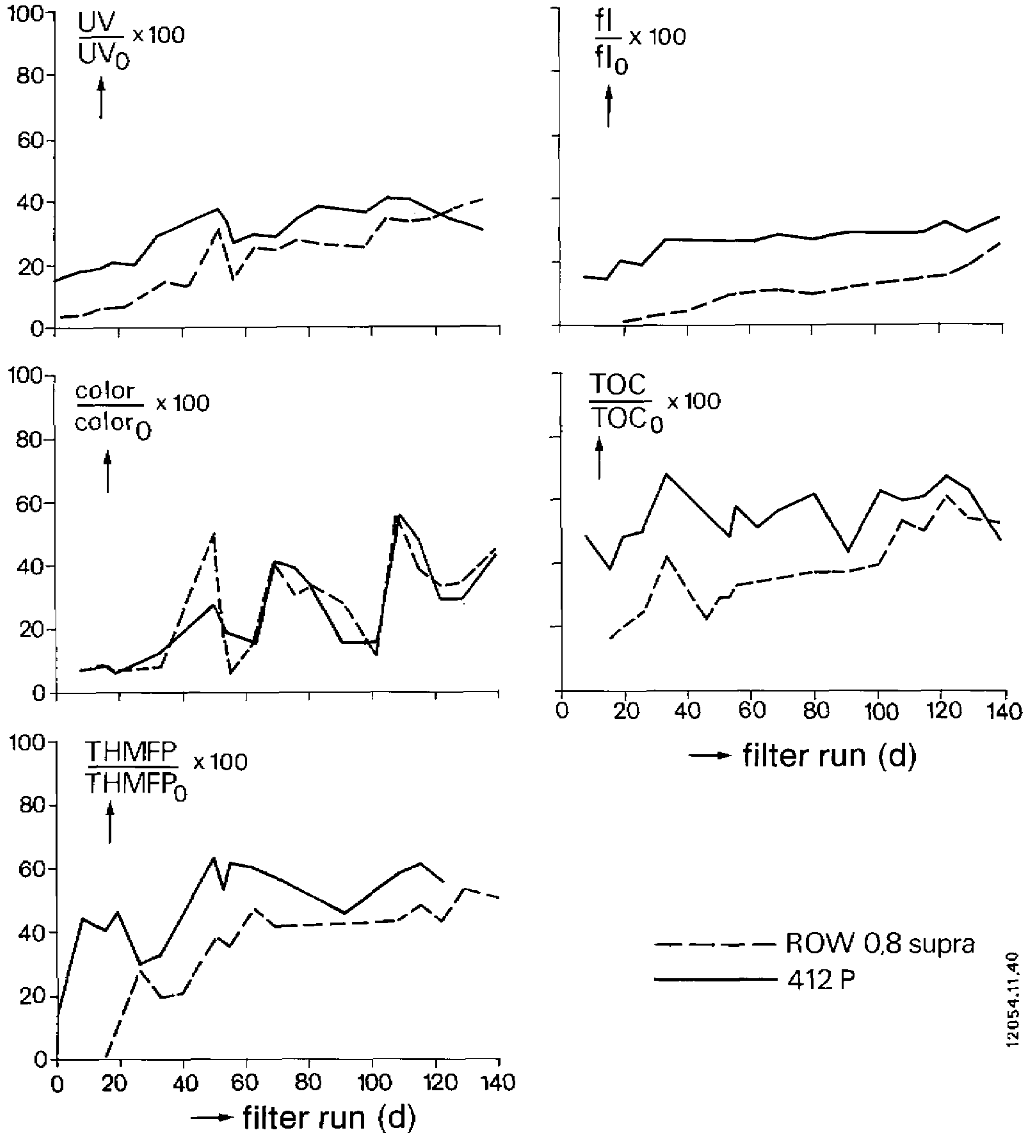

Figure 7.8 - Percentage breakthrough of UV extinction (a), fluorescence emission (b), color (c), TOC (d) and THMFP (e) as a function of the life time for the exchanger 412 P and the carbon type ROW 0.8 s

However, no individual parameter is removed in very high percentage throughout prolonged filter runs. The ion exchanger was regenerated after runs of 20, 40 and 80 days (2750, 5500 and 11,000 bv). Following regeneration, the effect of the ion exchanger did not increase greatly for any of the parameters. Thus, both ion exchange and carbon filtration are able to bring about only a limited precursor removal. This reduction also is not expected to lead to a reduction of the THMFP-consumer.

In addition, since ion exchange gives a somewhat lower removal than carbon filtration and, furthermore, problems can arise with the disposal of the regenerant, further studies on precursor removal by ion exchange deserve a low priority.

7.5 Precursor removal using alternative adsorbents

In addition to the removal of halogenated compounds, Ambersorb XE-340 was also tested for the removal of precursors. Symons et al. (ref. 7.1) found that adsorption on XE-340 and coagulation give the same precursor removal from raw water. XE-340 gives no further precursor removal from coagulated water.

O'Connor et al. (ref. 7.19) also investigated the precursor removal by XE-340. They also found no reduction of the precursor content, measured as a TOC decrease.

Ambersorb XE-340 is thus not a suitable agent for precursor removal.

7.6 Conversion of precursors by ozonation

Ozonation can be used for various purposes in drinking water treatment. Specifically, ozone has a high bactericidal and virucidal action. In addition, it is also highly suitable for degrading materials which impart odor and taste of for the partial breakdown of colored humic materials. Based on this latter use, it seems quite likely that ozonation leads to a breakdown of precursors.

Two possibilities arise in this connection:

- ozone reacts at the sites of the humic acid molecule which cause THM formation during chlorination and converts these into nonreactive sites;
- ozone converts precursors into modified humic compounds which are more readily removed in a subsequent treatment step, for example coagulation.

Only the first point will be discussed in this section. The determination of the precursor content was achieved by means of a THMFP determination. The difference in determination conditions occurring thereby have already been discussed at several points. For these reasons, data concerning the reductions of color, UV extinction, TOC and $KMnO_4$ consumption were also added.

Love (ref. 7.3) and Symons and Stevens (ref. 7.20) determined the THMFP before and after ozonation. The THMFP was determined at a chlorine dose of 8 mg/liter and a contact time of 6 days. The principal results are summarized in table 7.2.

Table 7.2 - Effect of ozonation on the THMFP-precursor (ref. 7.20)

Water type	ozone dose mg/l	$CHCl_3$ µg/l	$CHBrC_2$ µg/l	$CHBr_2Cl$ µg/l	THMFP µg/l
Dual media filtrate	0	6	14	4	24
	0,7	15	8	3	26
Dual media filtrate	0	12	9	2	23
	8	14	8	8	30
Dual media filtrate	0	91	26	6	123
	227	62	7	1	70
Carbon filtrate	0	2	3	1	5
	0,7	3	3	2	8
Carbon filtrate	0	4	4	2	10
	20,9	5	4	2	11

It is apparent from the table that for all ozone doses up to 20 mg/liter at a contact time of 5-6 minutes, the THMFP shows a slight increase. Only at an ozone dose of more than 200 mg/liter did a THMFP reduction of about 40 % take place.

The THMFP-precursor decreased as a function of the contact time. At a very high ozone dose of 43 mg/liter, the THMFP decreased from 0,5 µmol/liter after a contact time of 30 minutes to less than 0,1 µmol/liter after a contact time of 6 hour. In addition, Love (ref. 7.3) and Symons and Stevens (ref. 7.20) studied the combined action of ozone and UV radiation on precursor removal.

The results are reported in figure 7.9.

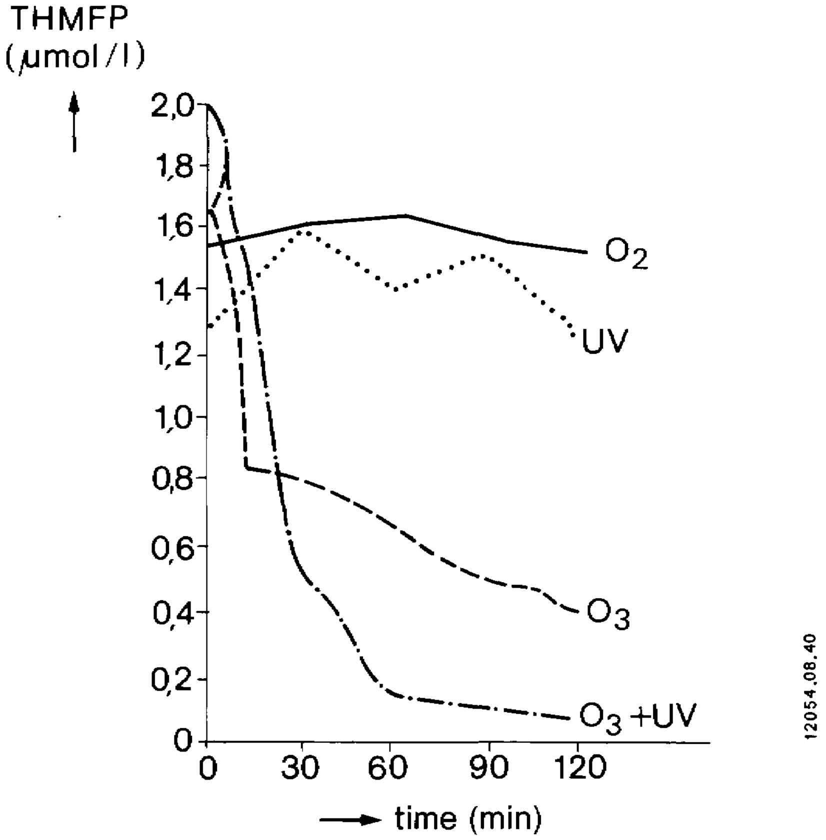

Figure 7.9 - Effect of ozone and UV radiation on the THMFP

It is apparent from the figure that good results can principally be achieved with combined use of ozone and UV radiation. After a contact time of 2 hours, the precursor conversion amounts to about 95 %. Rook (ref. 7.5) found results that did not correspond to the American investigations. Both for an ozone dose of 2,5 mg/liter and for 20,0 mg/liter, he finds a positive correlation between the THM formation and the contact time. Here, he determines the THMFP with a chlorine dose of 6 mg/liter and a contact time of 6 hour.

Contradictions in results were also found by Trussell (ref. 7.21). Both THMFP increases of 30 % and decreases of 90 % were found. For an ozon dose

Table 7.3 - Conversion of precursors by ozonation in the Netherlands

Parameter	GEB D				LDM		DWL		GW						WMZ			
	Plant				Plant		Plant		Plant		Pilot plant				Plant			
	Oranjelaan		Baanhoek		-		Kralingen		Weesp		Weesp		Leiduin		Haamstede		Ouddorp	
TOC mg/l							3,1	3,0	7,2	6,8	6,3	6,0	3,1	2,6	2,8	1,9	5,4	5,2
Color mg Pt/l	15	11	7	4	32	23	8	1	17	5	19	8			8	5	22	13
$KMnO_4$ mg/l	12	11	7	6	28	25	8	7	16	13	19	16	9	7	8	6	18	15
UV m^{-1}	13	8	5	4	29	25	6	5	17	11	17	11	7	3				
AOCl mg/m^3													30	10				
THMFP mmol/m^3	0,9	0,6	0,9	1,0			2	1,1	2,3	1,9	3,1	2,7	1,0	0,7	0,5	0,7	1,1	1,1
- No. of determin.	1	1	4	4			1	1	5	5	15	15	40	40	2	2	2	2
- Reduction, %	33 %		-10 %				45 %		18 %		13 %		30 %		-40 %		-	
O_3 dose mg/l	1,5		1,5		2		3,2		2,2		4		4		1		3	
Contact time, min					2				20		30		20		20		20	
Residual ozone mg/l	0		0		0		0,4		0,05		0,1-0,2		0,4		0		0	

of 2 mg/liter, both a 13 % THMFP increase and a 22 % decrease were found. The test conditions and the nature of the organic matter will undoubtedly play an important role here.

In the Netherlands, five waterworks use both ozone and chlorine in drinking water treatment. Data from these plants which play a role in possible precursor removal are presented in table 7.3.
When two numbers are given in one column, the first number pertains to the situation before ozonation, and the second applies to the situation after ozonation.
It is apparent from the table that practically no organic material (TOC) is removed, but that the organic material is highly modified (color, UV).
According to the sparsely available THMFP data, the precursor removal appears to vary somewhat from plant to plant. Amounts varying from 40 % increase to 45 % reduction were found. A correlation between precursor removal on one hand and ozone dose, contact time or water quality on the other hand cannot be drawn on the basis of the available data.
Thus, little definite information is available regarding precursor conversion by ozonation. Under conditions customary for drinking water preparation, only a slight removal or even an increase is found. Only at very high doses, unusually long contact times or additional use of UV radiation does extensive precursor conversion appear possible.

7.7 Precursor behavior during infiltration

The precursor behavior during infiltration was studied by the Municipal Waterworks (GW), the Dunes Waterworks of the Hague (DWL Den Haag), the

Municipal Energy Concern of Enschede (ONE) and the Waterworks of South West Netherlands (WMZ). Each of these companies determines THMFP in a different way. GW buffers the water to a pH of 8 and adds chlorine to a residual chlorine content of 0,5 mg/liter after 24 hour. The sample is stored for 24 hour at 25 °C.
DWL Den Haag adds 5,3 mg/liter of chlorine to an unbuffered solution, after which the solution is stored for 18 hour at 25 °C.
ONE and WMZ add to a nonbuffered solution sufficient chlorine so that the residual content after 48 hour is 5 mg/liter. The sample is stored for 48 hour at 25 °C. Later, the samples are buffered to a pH of 8.
It is necessary to take these differences into consideration in the interpretation of the data. A shift toward the formation of more highly brominated THM is indicative, among other things, of the maintenance of an inadequate chlorine dose for proper THMFP-precursor determination.

GW performed only a limited number of measurements at a soil residence time of 2 months. The quality parameters before and after infiltration are shown in table 7.4. The data after infiltration are the average values over ten discharge basins.

Table 7.4 - Quality parameters before and after infiltration at Leiduin

Parameter		before infiltration	after infiltration
TOC	mg/l	3,5	2,7
$KMnO_4$	mg/l	9	11
AOH*	mg/l	0,02	0,03
Chlorine dose	mg/l	4,2	4,0
$CHCl_3$	µg/l	110,0	63,8
$CHBrCl_2$	µg/l	2,0	21,2
$CHBr_2Cl$	µg/l	14,7	22,3
$CHBr_3$	µg/l	2,0	6,0
"THMFP"	µmol/l	1,13	0,82
AOHFP	µmol/l	0,18	0,15

* In the table, AOH stands for adsorbable organohalogen and AOHFP is adsorbable halogens in water treated in accordance with the THMFP prescription

The table indicates a shift toward the formation of more highly brominated THM which coincides with a precursor (TOC) reduction and a relatively low chlorine dose. The THMFP reduction appears to amount to 27 %; the AOHFP, a measure for the high molecular weight organohalogens that may be formed, appears to decrease by 17 %.

The Hague has also performed only a limited number of measurements. Here, after infiltration, a shift likewise takes place toward the formation of more highly brominated THM. The THMFP does not show a definite course. After infiltration, both increases and decreases have been observed. It is possible that the low chlorine dose plays a role here. As a result of the low chlorine dose here, the THM formation is no longer independent thereof so that random errors can play a major role. As a result, any possible small effects are not observed.

In addition, some data are available from six measurements performed by ONE for a residence time in the soil of about 3 weeks. The data are reported in table 7.5.

Table 7.5 - THMFP before and after infiltration at Enschede

Parameter	before infiltration			after infiltration		
$CHCl_3$ µg/l	320	390	420	180	210	210
$CHBrCl_2$ µg/l	64	80	75	56	65	66
$CHBr_2Cl$ µg/l	5,8	7	5,1	5,8	4,9	6,2
$CHBr_3$ µg/l	0,1	0,1	0,1	0,1	0,1	0,2
THMFP µmol/l	3,1	3,8	4,0	1,9	2,2	2,2
$CHCl_3$ µg/l	460	500	510	280	260	200
$CHBrCl_2$ µg/l	100	79	69	73	4,3	52
$CHBr_2Cl$ µg/l	9,2	5,1	10	6,0	7,5	4,5
$CHBr_3$ µg/l	0,2	1,2	0,1	0,2	0,1	5,9
THMFP µmol/l	4,5	4,7	4,7	2,8	2,5	2,0

The first three measurements pertain to unbuffered THMFP determinations; the reduction upon infiltration was about 45 %. In the second series, the THMFP determinations were performed with buffering. In this case, the reduction was 53 %.

In addition, WMZ has some information regarding the decrease in the THMFP after infiltration at Haamstede. A reduction of about 33 % appears to occur here.

It is apparent from the summarized data that a limited THMFP reduction is brought about by infiltration. The same is true at GW for the formation potential of adsorbable organohalogens. However, more data are desired.
The shift toward the formation of more highly brominated THM during chlorination coincides with the reduction of the THMFP-precursor as well as the low chlorine dose. The shift is also perceived in the case of the THMFP-consumer (sometimes determined).

7.8 Precursor removal by reverse osmosis

It was found from a large number of experiments that reverse osmosis membranes are able to retain high molecular weight organic substances. The organic matter content is usually measured in the form of TOC, $KMnO_4$ value or UV extinction. Schippers et al. (ref. 7.22) measured these parameters in Rhine water, pretreated Rhine water and water after membrane passage. The results are reported in table 7.6.

Table 7.6 - Removal of organic substances by reverse osmosis

Parameter	Rhine water	pretreated Rhine water	water after reverse osmosis
TOC (mg/l)	4,7	3,9	0,5
$KMnO_4$ (mg/l)	19	11	3
UV (m^{-1})	14,6	6,8	0

Reductions in TOC and UV extinction of 90 % are thus achievable. It is to be anticipated that this will also be true for precursors. Figure 7.10 shows the THM formation in rapid filtrate produced by the WRK (pretreated Rhine water) and in water after reverse osmosis under the influence of a chlorine dose of 7 mg/liter (ref. 7.23).

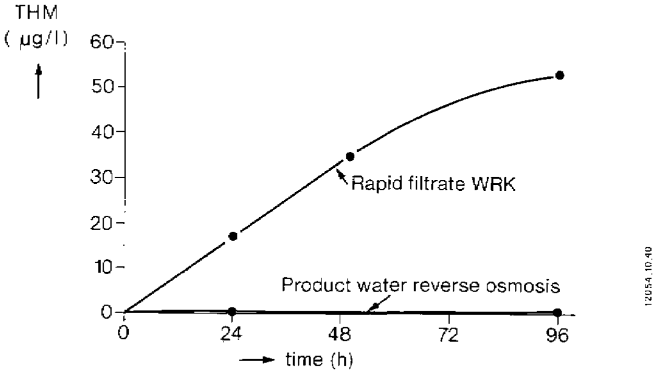

Figure 7.10 - Formation of trihalomethanes in rapid filtrate from the WRK and in water treated by reverse osmosis

It is apparent from the figure that precursors are excellently retained by reverse osmosis. The removal amounts to nearly 100 %.
Reverse osmosis is thus the only process which removes a high percentage of THM precursors over a long time. Whether reverse osmosis is used for this purpose comes down to an economic consideration.

7.9 Discussion

In this section, attention was paid to the removal of THM precursors by aeration, coagulation, carbon filtration, ion exchange, adsorption on alternative agents and reverse osmosis, as well as the conversion of precursors by ozonation and behavior during infiltration.

The precursor content is established with the aid of a THMFP-precursor determination. The performance of this determination was not standardized so that great differences were noted in the chlorine dose, contact time and pH.

Nevertheless, the following can be concluded regarding precursor removal by the individual treatment stages:

- Aeration

  On the whole, precursors are not removed by intensive aeration.
- Coagulation

  The coagulation process reduces the precursor content by 20-50 %. The degree of removal depends on the magnitude of the coagulant dose and the pH. The precursor reduction appears to parallel the reduction of organic material parameters such as color and TOC.
- Activated carbon filtration and ion exchange

  Carbon filtration accomplishes a considerable precursor reduction (about 90 %) only within relatively brief filter runs. This removal rapidly decreases and amounts to 20-40 % after 6 months.

  From the qualitative viewpoint, the same is true for precursor removal by ion exchange. In this case, as well, marked THMFP reductions take place only over short filter runs. However, this reduction decreases even more slowly than in the case of carbon filtration, wherein regeneration restores the adsorption capability only to a very limited degree.

- Adsorption on alternative adsorbents

  The Ambersorb XE-340 investigated gives only a very limited reduction of the precursor content. No further removal takes place from coagulated water.
- Ozonation

  Under conditions customary for drinking water treatment, only a slight precursor reduction takes place and sometimes a THMFP increase is even found. Only ozone doses of more than 100 mg/liter and combination with UV radiation give a considerable reduction.
- Infiltration

  Infiltration gives a limited THMFP-precursor reduction. The maximal removal is about 50 %.
- Reverse osmosis

  Reverse osmosis appears to remove precursors very well (90-100 %).

Thus, of the processes studied only reverse osmosis appears to accomplish a high degree of precursor removal. All other processes give only a partial removal or give good removal only during a very short time.

In addition, the question arises regarding the extent to which a partial precursor removal is of importance for chlorination under practical conditions. Very frequently, during the investigation, it was seen that partial THMFP-precursor reduction under chlorination conditions customary in the Netherlands did not lead to a decrease in the THM content and in addition, a shift took place toward the formation of more highly brominated THM. This was found in the case of chlorination following processes such as coagulation, infiltration and especially activated carbon filtration.

This development led to the introduction of a THMFP-consumer determination which gives a measure for the THM content under practical conditions. Unfortunately, however, no uniform determination was used here either. Studies were conducted both with a fixed chlorine dose and with a fixed residual chlorine content after 20 minutes. Nevertheless, the investigation led to a number of very definite conclusions:

- only high reductions of the THMFP-precursor led to a decrease in the THMFP-consumer;
- a reduction of the THMFP-precursor leads to a shift toward the formation of more highly brominated THM in the THMFP-consumer in the presence of bromide ions.

As a result of this development, the removal of precursors was given a lower priority and, therefore, a specification for a uniform THMFP-precursor determination is also of little more than academic significance.

Much attention should be paid to the formation of halogenated products under practical conditions, not only in the first stages of the process, but specifically at the end of the process. A good determination for the THMFP-consumer is of great significance here.

In contrast to the recommendations from 1978, restriction of the postchlorination is thus of central importance here. We will return to this in section 8.

7.10 Recommendations

The results described in this section give rise to the following investigation points:

- establishment of a uniform specification for the

THMFP-consumer determination;
- investigation on the formation of halogenated compounds in chlorination following precursor removal. It is possible to think here of infiltration or carbon filtration followed by chlorination.

This entire section has been devoted to the removal of THM-precursors. In addition, relatively high AOH contents have been encountered after chlorination; these may be of even greater importance from the toxicologic viewpoint. This group of compounds is to be determined with the aid of the AOH (adsorbable organohalogen) determination. The precursors for these compounds are to be determined with an AOHFP. It appears highly desirable to investigate whether the AOHFP follows the same trends as the THMFP. This leads to the following recommendation:
- investigation regarding the removal of AOHFP and the consequences thereof for chlorination following this removal.

In this process, it may be desirable to distinguish between an AOCl and an AOBr.

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8 POSSIBILITIES FOR ADAPTION OF PROCESS CONTROL

8.1 Introduction

In the preceding sections, among other things, extensive attention was devoted to the formation of halogenated compounds during chlorination, the removal of halogenated compounds and the removal of THM precursors.

In the current section, we will, once again, discuss the formation of halogenated compounds; however, in this instance, emphasis will be placed on restricting the formation of these by modifying the process control.

First, we will discuss the presence of THM as found, and some general guidelines will be given regarding the manner in which these side effects can be limited. In subsequent paragraphs, some of these suggestions will be worked out for restricting or eliminating transport and breakpoint chlorination. After that, a detailed discussion will be given of the possibilities for reducing the dosage for postchlorination or even eliminating it. These problems will be illustrated on the basis of the postchlorination philosophy developed at the Municipal Waterworks of Amsterdam. The chapter will end with some conclusions and recommendations.

The use of alternative disinfectants will not be discussed in this section. This will be dealt with in section 9.

8.2 Possibilities for reducing chlorine use in relation to process control

8.2.1 State of the art

The THM content in drinking water is given for various types of water in section 4, and the THM formation for the individual types of chlorination in section 5. Here, a classification will be made relative to the number of chlorinations, with subdivision into the postchlorination dose. This leads to the following classification:

Group a: plants with only transport chlorination prior to infiltration;

Group b: plants with transport chlorination prior to infiltration and postchlorination with a dose of < 0,2 mg/liter Cl_2 or ClO_2;

Group c: plants with only postchlorination with a chlorine dose of about 0,5 mg/liter Cl_2;

Group d: plants with transport chlorination and postchlorination with a dosage of 0,6-1,0 mg/liter;

Group e: plants with breakpoint chlorination and postchlorination. Here, postchlorination doses of < 0,2 mg/liter ClO_2, about 0,5 mg/liter Cl_2 and > 1 mg/liter Cl_2 occur.

The THM, EOCl and AOCl contents in the water supplied are shown in table 8.1. This table shows only the chlorinations. Other process steps such as carbon filtration and infiltration which greatly influence the THM content will not be discussed in this connection.

Table 8.1 - THM contents in the water supplied from 17 production locations arranged according to the type of chlorination.
Period: '79-'80

Group	Production plants	Chlorine dose in mg/liter for			$THM_{avg.}$ (µg/l)	$EOCl_{avg.}$ (µg/l)	$AOCl_{avg.}$ (µg/l)
		Transport chlorin.	Breakpoint chlorin.	Post-chlorin.			
a	Scheveningen	1,5-2,0			0,8	< 0,1	13
b	Bergen	0 -1,5		"0,14"	2,0	-	-
	Ouddorp	1,0		0,2	2,6	0,4	36
	W Mensink	0 -1,5		"0,08"	2,0	2,1	25
	Haamstede	1,0		0,2	3,7	0,5	13
	Castricum	0 -1,5		"0,18"	5,0	-	-
c	Diepenveen			0,6	2,6	0,4	55
	Weerseloseweg			0,5	2,9	0,6	23
	De Punt			0,4-0,5	4,3	0,3	42
	Weesperkarspel			0,4	8,0	0,8	30
	Kralingen winter			0,6	12,6	~ 2,8	~ 18
d	Scheveningen (incidental)	1,5-2,0		0,8-1,0	11,3	-	-
	Kralingen summer	1,0-1,8		0,6	19,7	~ 2,8	~ 18
	Leiduin	0 -1,5		0,6	23,7	5,1	20
e	Andijk		7,9	"0,03"	22,5	2,2	40
	Zevenbergen	0 -1,8	1,7	0,5	25,5	1,7	78
	Berenplaat	0 -1,8	3,6	0,45	29,5	3,0	59
	Baanhoek		3,1	1,3	37,7	2,5	79

A dosage given in quotation marks refers to a ClO_2/Cl_2 addition (1 : 1).

It is apparent from the table that there is a general relationship between the THM contents in the drinking water on the one hand and the number of chlorinations and the magnitude of the chlorine dose for postchlorination on the other hand. The relationship between the EOCl and the AOCl contents on one hand and the number of chlorinations and/or chlorine dose for postchlorination is less clear (see table 8.2).

Table 8.2 - General relationship between THM, EOCl and AOCl contents in drinking water and the use of chlorine with a distribution into doses for postchlorination

Group	Chlorine use and dose (mg/l)	$THM_{avg.}$ (µg/l)	$EOCl_{avg.}$ (µg/l)	$AOCl_{avg.}$ (µg/l)
a,b	Transport chlorination Transport chlorin. + postchlorination (< 0,2 mg/l)	0- 5	0-2	15-35
c	Postchlorination (0,4 -0,6 mg/l)	3-13	0-3	20-55
d	Transport chlorin. + postchlorination (0,6 -1,0 mg/l)	11-24	3-5	20
e	Transport chlorin. + breakpoint chlorin. + postchlorination (0,03-1,3 mg/l)	23-28	2-3	40-80

The THM content is thus clearly determined by the number of chlorinations and the size of the postchlorination dose. This is less true for the EOCl and AOCl contents, but here also in most cases, an increase occurs with increasing number of chlorinations and increasing chlorine dose. Transport chlorination is frequently used prior to infiltration and then plays no major role for the THM content in drinking water. However, transport chlorination can play a limited role in the case of use after storage in reservoirs. Breakpoint chlorination and postchlorination play a definite role in THM formation. When only postchlorination is used, a clear dependence on the dose is recognizable. Whenever breakpoint chlorination and postchlorination are used, this dependence is less clear. In that case, the chlorine dose for breakpoint chlorination and the treatment following the breakpoint chlorination also play important roles.

In summary, it can be stated that concerning the chlorine dose, the side effects can principally be limited by:

a. reduction of the postchlorination dose;
b. reduction of the dose for breakpoint chlorination and further purification following breakpoint chlorination.

In addition, transport chlorination plays a limited role for drinking water transport chlorination if infiltration is not used. Organohalogens are possibly adsorbed or degraded in the infiltrating aquifer during infiltration.

8.2.2 Possibilities for process adaptation

The most obvious and already partially performed adaptation in process control to restrict the side effects of chlorination is the reduction of the chlorine dose. The possibilities for this should be considered for each chlorination.

a. Transport chlorination

In some instances, transport chlorination is used prior to infiltration. In such cases, the THMs reach the drinking water produced scarcely or not at all, but they are partially adsorbed and degraded in the infiltrating aquifer. Most of the THM, however, disappears during an aeration step prior to infiltration.

In the case of transport chlorination after storage, the THM compounds are partially found in the drinking water. The side effects can be greatly limited by reducing the chlorine dose to below the breakpoint. In such a case, it appears that scarcely any THM is formed, while the chloramine formed has a sufficiently strong preservative effect. This reduction of the chlorine dose has already taken place in many instances (see section 3 and 5).

In addition, the possibility may be considered of replacing transport chlorination by a transport purification such as coagulation followed by filtration. The costs of this are high.

b. Breakpoint chlorination

In breakpoint chlorination, the chlorine dose is greatly determined by the ammonium content of the water. The chlorine dose used is above the breakpoint. To restrict the side effects, the quantity of chlorine added above the breakpoint should be as low as possible. Reduction of the pH should lead to a reduction of the THM content. A pH reduction from 8.6 to 7.0 can lead to a decrease in the THM content of 15-30 %. In addition, the possibility of eliminating breakpoint chlorination and replacing it by biological ammonium degradation during storage and filtration may be considered. The chlorine dose for breakpoint chlorination can be greatly influenced by a selective water guideline, for example, based on an ammonium criterion. However, this decrease in the chlorine dose needs not always to coincide with a limitation of the side effects.

c. Postchlorination

In the preparation of drinking water from surface water in almost all cases, disinfection (postdisinfection) is used as the last treatment step. Until very recently, the only exception was DWL Den Haag, which does not perform chlorination after slow sand filtration under normal conditions. In other Water Works as well, developments have proceeded in order to reduce or even completely eliminate postchlorination after infiltration and slow sand filtration. Extensive discussions of these matters will be presented in the current section.

In addition, the possibility exists for removing the THM formed during transport and breakpoint chlorinations, for example, by aeration and carbon filtration. Extensive discussions of these possibilities were presented in section 6.

THM precursor removal results in a restriction of the side effects only in the case of a high removal percentage. This was extensively discussed in section 7.

The side effects of chlorination can also be limited by using alternative disinfectants. The following aspects, in particular, deserve attention:

- use of ClO_2 and chloramine for transport chlorination;
- use of ClO_2 for postdisinfection if it cannot be completely eliminated.

In section 9, the characteristics of ClO_2 and chloramine will be discussed. Ozone and UV radiation may also be used. No discussion will be devoted to these topics.

8.3 Use of transport treatment in place of transport chlorination

Filtration, possibly combined with coagulation and settling, may be used as a transport treatment.
Coagulation, settling and rapid filtration are used by GW for water transport from the Loenderveen lake to the treatment plant at Weesperkarspel over a distance of 16 km. Experience was gained with this system beginning in 1978; no growth problems were found in the transport line.
WRK also uses coagulation, settling and rapid filtration for the transport treatment of Lek canal water. At this location, however, one is not completely convinced that this treatment is sufficient to completely eliminate the use of chlorine at times with higher temperatures (> 15 °C), although in 1984 chlorine was applied only incidentally.
Up to and including 1982, the same considerations applied to the transport of water from the Andelse Meuse basin to the Hague dunes. The water from the Andelse Meuse basin was filtered at Bergambacht (always with chlorination). Then, in time periods with higher temperatures, a small quantity of chlorine was again added prior to transport to the dunes. Beginning in 1982, chlorination was no longer performed in the Andel-Bergambacht section at a water temperature below 8 °C. Beginning 1984, transport chlorination between Bergambacht and Scheveningen was completely eliminated.

The extent to which transport disinfection can be replaced by transport treatment appears to depend greatly on the quality of the water to be transported. It is necessary to investigate whether a sufficiently good quality can be achieved in all cases by using coagulation and rapid filtration prior to transport.

A theoretical possibility for eliminating transport disinfection is to transport the water anaerobically. However, nothing is known as yet regarding the adaptation possibilities of this process.

8.4 Techniques for ammonium removal as an alternative for breakpoint chlorination

8.4.1 Biological degradation

In the 1960's, the ammonium content of the Rhine and the Meuse in winter often exceeded 5 mg/liter. These contents could not be completely removed by biological processes at temperatures 4 °C. In direct surface water recovery, it was then also customary to remove the ammonium via a breakpoint chlorination.
Since that time, the ammonium contents of the Rhine and the Meuse decreased to 1-2 mg/liter in winter. In addition, in the storage phase, an appreciable reduction of the ammonium content takes place. As a result, it has become possible in principle to eliminate breakpoint chlorination and to remove ammonium by a biological process.

The biological oxidation of ammonium is called nitrification and takes place in two steps by nitrifying bacteria:

a. $NH_4^+ + 1\frac{1}{2}O_2 \rightarrow NO_2^- + H_2O + 2H^+$

This is the oxidation to nitrite by Nitrosomonas (nitrite bacteria)

b. $NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^-$

This is the oxidation of nitrite to nitrate by Nitrobacter (nitrate bacteria). The overall reaction for nitrification is:

$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$

Of the two types of nitrifying bacteria, Nitrobacter is the most temperature sensitive. This means that at lower temperatures, reaction a. still takes place, but reaction b. no longer takes place completely. This results in an increase in the nitrite content in the water.
If such a situation arises in drinking water treatment, chlorine use for nitrite and ammonium oxidation is practically indispensable. During the past ten years, some methods were developed, directed toward the removal of ammonium by biological means. These will be discussed later.

8.4.2 Selective intake guidelines during storage in reservoirs using the ammonium content as a criterion

Since the third Biesbosch storage basin at De Gijster was put into operation the WBB took as its goal that of supplying water with a quality such that chlorination to achieve ammonium removal will no longer be necessary. This led to the establishment of a desirable value of the ammonium content in the water supplied amounting to 0,2 mg/liter. This content is in agreement with the strictest standard for surface water imposed by the IAWR

(International Working Group of Waterworks in the Rhine Catchment).

The flow diagram of the Biesbosch basins since 1979 is shown in figure 8.1. The basins are passed through in series. By letting the water in "high" and abstracting it "low", the short circuit in De Gijster was limited to 5-10 %.

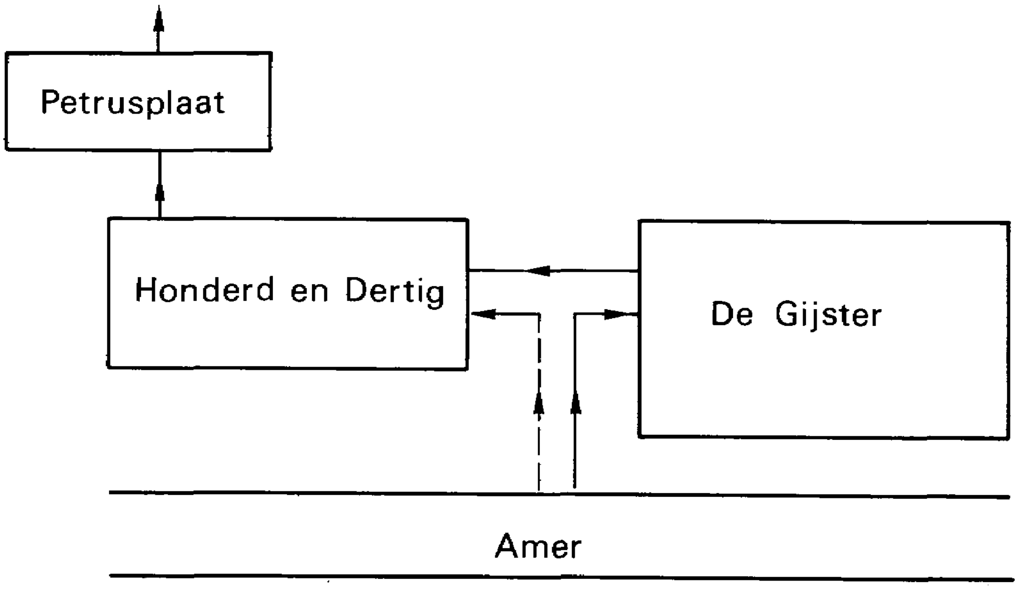

Figure 8.1 - Biesbosch basins flow scheme

With the aid of the data on the period from 1977-1979 at the basins Honderd en Dertig and Petrusplaat, it has become possible to provide a model description of the behavior of ammonium in the basins, on one hand, based on nitrification and, on the other hand, on equalization as the processes of determining significance.

One example of a model calculation is presented in figure 8.2. The starting points for this are:

- half of the supply in De Gijster is used up after a dry summer;

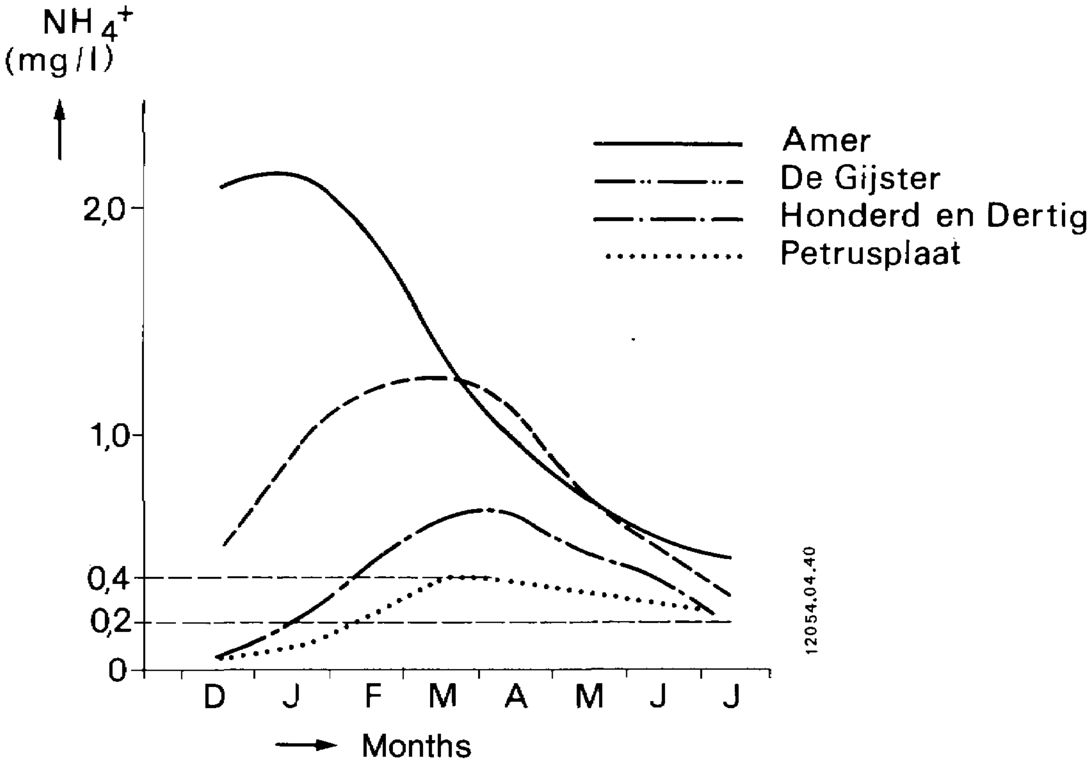

Figure 8.2 - Calculated winter levels of the ammonium content in the basins after a dry summer

- the schematic ammonium course in the river pertains to a cold winter;
- river water is taken in continuously.

It is apparent from the calculated course in the basins that under these conditions, the ammonium concentration in the Petrusplaat exceeds the desired level of 0,2 mg/liter for a long time. It can be concluded from this that storage in De Gijster, which is intended for getting by in dry periods in the summer can (should) be used in the winter for regulating the ammonium content. A selective intake program with ammonium as the intake criterion is necessary for this purpose.

With the same marginal values as above, it can be

anticipated that at a maximum ammonium content of 0,2 mg/liter in the Petrusplaat, the content in the Honderd and Dertig and De Gijster should not be higher than 0,4 and 0,8 mg/liter, respectively. From week to week, the critical ammonium concentration of the river water can be calculated at which water intake is still acceptable.
This selective intake guideline for ammonium was successfully employed in the winters after 1980. The ammonium content of the water supplied in all cases was not higher than 0,19 mg/liter.

8.4.3 Biological purification by filtration

The elimination of prechlorination (process chlorination, breakpoint chlorination) means that biological activity is possible throughout the course of treatment. Especially during filtration steps, a considerable nitrification will be able to take place. This is true for rapid filtration and slow sand filtration as well as activated carbon filtration. In the treatment systems for surface water, two filtration phases are almost always involved (for example, rapid filtration and activated carbon filtration or rapid filtration and slow sand filtration), so that nitrification will almost always proceed completely.
According to French and German experiences, a modest preozonization will promote the growth of not only heterotrophic but also nitrifying bacteria. Thus, the treatment plant at Mulheim, which treats Ruhr water, appeared to nitrify 1 to 2 mg/liter ammonium in this manner at water temperatures of 0-1 °C. One prerequisite for this is apparently that the filters have a nitrifying flora when the temperature drops or that the raw water continues to

contain an active nitrifying flora.
These prerequisites are generally not applicable for reservoir water in the situation in the Netherlands, since the ammonium content in the reservoir water is especially low in summer and fall. This means that the ammonium only increases when the temperature is already very close to the winter level. The experiences in Kralingen in the winter of 1978/1979 showed that then the problem of incomplete nitrification (nitrite formation) can arise at ammonium contents of about 0,5 mg/liter.

8.4.4 New methods

If the biological activity of the treatment system appears inadequate to remove ammonium completely, special treatment steps intended for nitrification may be added, which also remain effective at lower temperatures.
In England, biological sedimentation is used to remove ammonium. This process is based on "upflow sludge blanket filtration", and is carried out in an inverted conical tank.
The WRC (Water Research Center) investigated this process and concluded that the temperature sensitivity is low. However, in the winter, an extra high "sludge concentration" is required to create sufficient surface area for the nitrifying bacteria. This is achieved by adding very fine sand (0,1 mm). The process is being applied on a practical scale at various plants.

8.5 Philosophy concerning the restriction/elimination of postchlorination

8.5.1 Importance of postchlorination

In large parts of the world, chlorine is used for disinfection purposes. The Netherlands water supply law prescribes that upon leaving the pumping station, not a single bacteria of the coli group or fecal streptococcus may be present in 300 ml of water. Viruses also are not allowed to be present in the water. According to the WHO recommendation, no viruses may be detectable in 500 or 1.000 liter water samples. In addition, the VEWIN recommendation regarding the water supply law gives a limiting value for the colony count of 100/ml measured after three days at temperatures of 22 °C.

Chemical disinfection is of great importance in the case of less well functioning and unreliable treatment systems (for example, open post-filters). At present, process control in the Netherlands is highly reliable, and good, rapid microbiological analysis techniques are available. Furthermore, in recent years, more knowledge had been gained in both the biological and toxicological areas. As a result, postchlorination has come to stand in a different light in the Netherlands. This material will be further illustrated here on the basis of the Amsterdam production plants at Leiduin and Weesperkarspel, after which some general possibilities will be outlined.

8.5.2 State of the art in Municipal Waterworks treatment plants

The production plant at Leiduin treats Lekcanal water, which is infiltrated into the dunes after coagulation and rapid filtration. After infiltration, the water is aerated, treated with powdered activated carbon and subjected to rapid filtration and slow sand filtration. In addition, postchlorination is present in the process (situation in mid-1982).

In the production plant at Driemond water from the Lakes at Loenderveen is treated; it is transported to Driemond after coagulation and rapid filtration. There ozonation, coagulation, rapid filtration and slow sand filtration are performed in succession. In addition, postchlorination is included in the process here as well (situation in mid-1982).

Both plants use as their last treatment step a covered slow sand filtration, followed by a continuous postchlorination. The need for this postchlorination has come under increasing doubt over the course of the years. For illustration, the following data are presented for 1979/1981:

- Total content of bacteria of the coli group:
  At Leiduin, the average value of the number of bacteria from the coli group in the slow sand filtrate is less than 1 per 300 to 500 ml. In very severe winters, these bacteria are sometimes found caused by the presence of an open abstraction. Thermotolerant bacteria of the coli group (E. coli) have never been detected in 300-500 ml of post-filtrate.

- Colony count 37 °C:
  At Leiduin, the colony count in rapid filtrate is 0-10 per ml. The slow sand filtrate is not routinely investigated.
  In Driemond, the colony count in the slow sand

filtrate is an average of 1 per ml; the slow sand filtrate gave a decrease with a factor of 10.

- Colony count 22 °C:
  In most cases at both production locations, the colony counts were between 5 and 50 per ml; the colony counts for Leiduin are lower than for Driemond.

Thus, during a large part of the year, both plants meet the legal requirements without the use of postchlorination. Quality deviations in excess of the norm may be controlled by using occasional chlorination.

Recently, some virologic investigation has also been performed. Up to the present time, no human enteroviruses have been demonstrated in 500 liters post-filtrate. In addition, it is necessary to keep in mind that the level of postchlorination (dose for Leiduin 0,2-0,6 mg/liter, dose for Driemond 0,4-0,6 mg/liter, criterion 0,15 mg/liter free chlorine after 20 minutes) will have little or no effect in terms of virus removal.

The comparison of the Amsterdam plants with Dune Water Company of The Hague seems important. There also, the last step is a slow sand filtration. However, postchlorination is used there only if bacteria of the coli group are encountered in the post-filtrate. Intensive microbiological monitoring is performed at The Hague.

After postchlorination has been eliminated, GW also intends to initiate such control. Thus, in the microbiologic respect at GW, there appears to be no reason to maintain a continuous postchlorination.

8.5.3 Aspects which play a role in the restriction/ elimination of postchlorination

In addition to the microbiological matter already discussed, the following aspects also play a role at GW.

- Toxicologic aspects:
  This pertains to the formation of both low- and high-molecular-weight organohalogen compounds during postchlorination. It has been found that postchlorination causes an appreciable increase in the mutagenicity determined in the Ames test using strain TA 100. In view of the experimental structure of the Ames test, this effect may be attributed to nonvolatile organohalogen compounds.
  In addition, in 1979/1980 in studies with trout eggs at Leiduin, the percentage of nonviable eggs was increased by postchlorination.

- Biological aspects:
  In addition to substitution and addition reactions, chlorine also causes oxidation reactions. This can lead to an increase in the assimilable organic carbon (AOC) content, which, in turn, can lead to increased after-growth in the distribution network when all the chlorine has reacted. Both at Leiduin and at Driemond, postchlorination causes a doubling of the AOC content. However, no distinct general increase in after-growth in the network has been found. This can be caused, among other things, by the presence of higher organisms (e.g., Rotifera) at relatively high levels in the distribution network.

- Esthetic aspects:
  Postchlorination has a definite effect on the taste of the water. Elimination of postchlorination may lead to a change in the taste. Test pipeline experiments at Leiduin have shown that chlorinated post-filtrate after two days in a test pipeline is given a poorer rating by a taste panel than in non-chlorinated filtrate.

- General aspects:
  In general, it is desirable to add the minimum possible quantities of chemicals in drinking water treatment. This is especially true for chemicals which lead to the formation of non-biodegradable or poorly biodegradable and toxicologically suspicious compounds, since these enter the environment via waste water.

- Cost aspects:
  In addition, costs play an important role in a plant. Chlorine addition at Leiduin and Driemond costs about 150.000 Dutch guilders per year for chemicals.

All these points illustrate the desirability of eliminating postchlorination, as long as the microbiological aspects make this possible.

8.5.4 Status determination of follow-up at GW

Consideration of the points mentioned has resulted in the fact that GW has decided to reduce postchlorination as a full scale experiment. Beginning in mid-1982, the dose for postchlorination was reduced by 0,1 mg/liter per month. It was intended to continue this reduction down to a chlorine dose of

0,2 mg/liter, which would be maintained for one year. After one year of using a chlorine dose of 0,2 mg/liter, a decision would be made regarding whether or not the dose will be brought all the way down to zero. In practice, the chlorine dose was already brought down to zero in March 1983, still in the manner of a trial. In 1986, a definite decision will be made regarding the continuation of the current situation. A hypochlorite installation is available at both plants for emergencies.
The reduction of the chlorine dose is being intensively investigated with the aid of microbiological, analytical and toxicologic investigations for both the post-filtrate and the water in the distribution system.

8.5.5 Possibilities for eliminating postchlorination

In general, it appears desirable for plants which use slow sand filtration to subject the post-filtrate from their plants to very extensive microbiological and virological testing. Based on this, it may be decided to omit postchlorination in view of the side effects observed. A hypochlorite installation should then be available on a standby basis for emergencies in the plant or in the distribution network.
In addition, a limitation or elimination of postchlorination should not merely be reserved for infiltrating plants which likewise use slow sand filtration. One example may be WMZ, which at Haamstede and Ouddorp, treats infiltrated Haringvliet water using a combined carbon filtration/ rapid filtration as the last step. Following extensive bacteriologic, virologic and hydrologic investigations at Haamstede, postchlorination was

eliminated, and consideration is being given to doing this in Ouddorp as well.
A number of water types in which no bacteria of the coli group or viruses are found do not fulfill the VEWIN recommendation for colony count, which should be lower than 100/ml, without postchlorination. Consideration may be given to replacing postchlorination by chlorine dioxide addition. A small chlorine dioxide dosage is already being used by PWN in order to limit after growth following carbon filtration.
In addition to the use of ClO_2, UV radiation should also be able to be used to control high colony counts. This method, which is beginning to find increasing use, is also worthy of further investigation.
When the water is contaminated with bacteria of the coli group or viruses, for the present, the use of chlorine as a disinfectant should be maintained. More information needs to be provided regarding the disinfecting action of chlorine relative to viruses. Chlorine dioxide may also be able to be used. For this purpose, however, more information should be supplied regarding the disinfecting action of ClO_2, linked with the previously mentioned side effects.

8.6 Discussion

In this section, attention was paid to the possibilities for the adaptation of process control. First, a picture was outlined of the THM formation, subdivided according to the number of chlorinations, with a further subdivision according to the dose for postchlorination. A global relationship appears to exist between the THM content and the number of chlorinations and between the THM content and the magnitude of the chlorine dose for postchlorination. According to the possibilities already discussed, the side effects of chlorination can thus be greatly reduced by reducing the chlorine dose. This limitation of the side effects should be the greatest in the case of reducing the chlorine dose for postchlorination, followed by a reduction of the dose for breakpoint chlorination. Especially after infiltration, transport chlorination plays only a limited role in the case of the THM content in drinking water. Poorly biodegradable substances may be adsorbed and degraded in the infiltration aquifer.

Chlorine use for transport chlorination can be restricted by using transport treatment in the place of transport chlorination. The possibility for this will depend greatly on the quality of the water to be transported after treatment. It will be necessary to investigate whether coagulation, followed by rapid filtration, in all cases gives a sufficiently good quality in order to eliminate transport chlorination.

The use of chlorine for breakpoint chlorination can be greatly limited, among other things, by means of a selective intake guideline in the case of storage in reservoirs. The intake guideline of the WBB is directed toward a maximum ammonium content in the water supplied of 0,2 mg/liter. In this manner, it is possible, in principle, to eliminate breakpoint chlorination and to replace it by a biological treatment process. However, this process is temperature sensitive, so that incomplete nitrification can occur. The nitrification can be activated by ozonation. In addition, some treatment steps specially directed toward nitrification are under de-

velopment, for example, biological sedimentation.
The restriction or even elimination of postchlorination deserves a great deal of attention. If there are no bacteriologic problems, continuous postchlorination can be eliminated. In the case of emergencies in the treatment plant or in the distribution system, a hypochlorite installation should be available on a standby basis. This situation exists in the case of plants which use infiltration and have a covered slow sand filtration as the final treatment step.
In the case of other treatment systems as well, postchlorination for disinfection purposes may often be eliminated. In some cases, however, high colony counts are found in the water. In these cases, consideration should be given to replacing postchlorination by chlorine dioxide addition, while the use of UV radiation may also offer an alternative.
However, the side effects of the alternatives mentioned should be investigated and evaluated.

8.7 Recommendations

The results described in this section give rise to the following points for investigation:

- investigations regarding the extent to which transport chlorination can be eliminated in all cases by the use of coagulation and rapid filtration;
- investigation of ammonium removal by biological processes;
- investigation regarding the possibilities of eliminating or replacing postchlorination using ClO_2 or UV radiation;
- investigation regarding the effectiveness of the

existing disinfection steps with chlorine in the case of viruses;
- investigation with respect to the occurence of viruses.

9 USE OF ALTERNATIVE DISINFECTANTS

9.1 Introduction

The side effects which may be caused by the use of chlorine were discussed in detail in the preceding sections. In section 8, attention was paid to some possibilities for limiting the side effects. In the present section, the use of alternative disinfectants will be discussed.

In view of the significance of disinfection in the preparation of hygienically reliable drinking water, the replacement of chlorine by an alternative agent should be considered very cautiously.

The following plays a role in this consideration:

- the disinfecting power of the disinfectant;
- the toxicity of the disinfectant;
- the formation of inorganic and organic reaction products;
- the toxicity of these reaction products.

In KIWA communication no. 58 "Problems concerning haloforms" (ref. 9.1), a summary was presented of some disinfectants which might be considered for replacing chlorine. These include the agents bromine, iodine, ferrate, chlorine dioxide, chloramine, ozone and UV radiation.

Recent developments have made it clear that in view of considerations of treatment technology, economy and health, only chlorine dioxide, chloramine, ozone and UV radiation come into consideration for use on a full scale. These four agents can also generally fulfill the requirements imposed on disinfectants by Symons et al. (ref. 9.2):

- the disinfectant must be an effective bactericide;
- the residual levels of disinfectant must be easi-

ly measured;
- the disinfectant must be easily manufactured and/or it must be able to be transported and stored conveniently and safely;
- the agent must be able to be used in an economically justifiable manner;
- the disinfectant must be unlikely or less likely than chlorine to give rise to the formation of harmful reaction products.

In this section as well as in section 2, only the persistent disinfectants, chlorine dioxide and chloramine, will be discussed.

9.2 Use of chlorine dioxide

9.2.1 Characteristics and preparation

Chlorine dioxide (ClO_2) is a yellow gas with a boiling point of 10 °C at 100 kPa. The gas is explosive at a concentration of more than 10 vol. % in air. As a result, transport is scarcely possible, and ClO_2 must be prepared in situ.

ClO_2 is fairly stable in water. Preparation in water can be accomplished from sodium chlorite in various ways by reaction, for example, with hydrochloric acid or chlorine:

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

or

$$2NaClO_2 + HCl + HOCl \rightarrow 2ClO_2 + 2NaCl + H_2O$$

The second process was initially the most widely used in drinking water treatment (ref. 9.3). Sodium chlorite and chlorine were combined in a reaction

tower at a 1 : 1 ratio and a pH of 2 to 4. This means that an excess of chlorine was added to prevent an undesirable chlorite residue.
However, since this method entails some difficulties (use of excess chlorine, chlorine storage) preparation from chlorite and hydrochloric acid is becoming increasingly common.
For an extensive discussion on the chemical aspects of ClO_2, the reader is referred to Masschelein et al. (ref. 9.4). Here, a more detailed discussion will be given regarding the use of ClO_2 in drinking water treatment, the disinfection capacity and the inorganic and organic reaction products. The toxicologic characteristics were already extensively treated in section 2.

9.2.2 Use of chlorine dioxide in drinking water preparation

Chlorine dioxide is principally used in drinking water preparation for:

a. improving the odor and taste of the water, primarily in the case of problems produced by phenols and algae;
b. oxidation of divalent iron and manganese, specifically when these are present in organic complexes;
c. disinfection of water, especially if disinfection is to be performed with a persistent disinfectant.

In 1977, Fuchs (ref. 9.5) performed a survey regarding the use of ClO_2 in water supply companies in some European countries. The results are presented in table 9.1.

Table 9.1 - Purposes of the use of ClO_2 in some European countries

Purpose	No. of plants				
	Germany	Great Britain	France	Switzerland	Austria
Bactericidal effect	33	5	22	12	2
Safety disinfection	22	4	1	3	2
Taste improvement	9	4	12		
Iron removal	2		5		
Removal of organic matter			10		
Odor removal		3	10		
Color improvement			10		
Virucidal activity			6		
Manganese removal	2		2		
Turbidity removal			1		

9.2.3 The disinfecting capacity of ClO_2

ClO_2 is known to be a strong disinfectant. As early as the 1940's, the bactericidal capacity of ClO_2 was investigated by Ridenour et al. (refs. 9.6, 9.7 and 9.8). The following conclusions can be drawn from these investigations:

- with the aid of ClO_2, it is possible to inactivate E. coli just as efficiently as with chlorine. The effect of ClO_2, in contrast to that of chlorine, is independent of the pH in the pH range from 6 to 10;
- ClO_2 is more effective than free chlorine for the removal of B. subtilis, B. mesentericus and B. megatherium;

- ClO_2 is as effective as free chlorine against the polio virus.

In later years, these conclusions were generally confirmed by Berndt (refs. 9.9 and 9.10), Bedulevich et al. (ref. 9.11), Cronier et al. (ref. 9.12) and Benarde et al. (refs. 9.13 and 9.14). However, stronger virucidal characteristics are attributed to ClO_2 than to chlorine.

Morris (ref. 9.15) summarized the resuls of the above mentioned investigations as well as the results of Warriner (ref. 9.16) and Fair et al. (ref. 9.17). He reports the ClO_2 concentration which is necessary to achieve a 99 % kill in 10 minutes. The data are presented in table 9.2.

Table 9.2 - Bactericidal effect of ClO_2

Microorganism	temp. °C	pH -	Ct_{99} 10 min. mg/l	ref.
Escherichia coli	5	6,5	0,4	9.13
	5	7	0,5	9.12
	10	6,5	0,25	9.14
	15	7	0,38	9.12
	20	6,5	0,18	9.14
	25	7	0,28	9.12
	25	8,5	0,06	9.14
	32	6,5	0,10	9.14
Poliovirus 3	20	5,6	5	9.16
	20	7,1	2	9.16
	20	8	0,3	9.16
Poliovirus 1	5	7	5,5	9.12
	15	7	5,5	9.12
	21	4,5	2,5	9.12
	21	7	1,5	9.12
	21	9	0,4	9.12
	25	7	1,1	9.12
Coxsackie Virus A9	15	7	0,3	9.12
Enystolytica cysts	23	7	53	9.17
Bacillus spores	23	7	30	9.17

For both toxicologic and organoleptic reasons, the maximum permissible dose for drinkig water preparation should be about 0,2 mg/liter. For this reason, table 9.2 gives only very limited information regarding characteristics of ClO_2 under conditions corresponding to those of drinking water preparation.

9.2.4 Inorganic reaction products of ClO_2

Chlorite and chlorate can be formed during reactions of chlorine dioxide in water. Chlorite is formed principally as a consequence of the oxidation reactions of chlorine dioxide with impurities in accordance with the reaction:

$$ClO_2 + e \rightarrow ClO_2^-$$

Only at very low pH is ClO_2 completely reduced to chloride. In drinking water preparation, however, this is not the case. At high pH (pH > 10), the following disproportionation takes place:

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

In addition, under the influence of light, as a consequence of photo chemical reactions, chlorite, chlorate, chloride and hydrogen peroxide can be formed (ref. 9.18).

Miltner (ref. 9.19) determined the contents of Cl^-, ClO_2^- and ClO_3^- at various pH values after treating coagulated river water with ClO_2. The results are presented in figure 9.1. At a pH of 5, more than 100 % reaction products are recovered in an unexplained manner.

In addition, ClO_3^- and ClO_2^- may also be introduced even during the addition of ClO_2 to the water. The

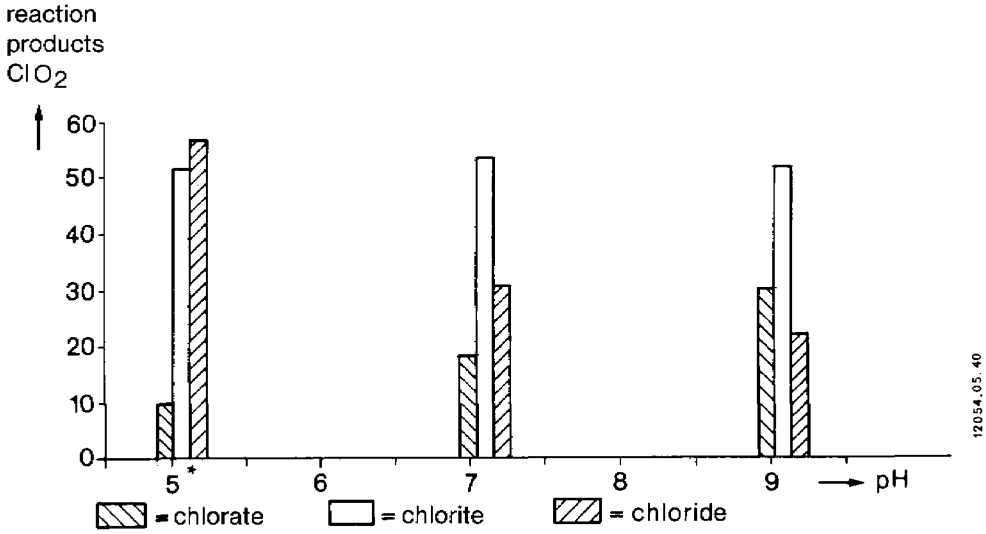

Figure 9.1 - Contents of chlorate, chlorite and chloride as a function of the pH in coagulated river water with ClO_2 (according to Miltner, ref. 9.19)

quantity of chlorite depends greatly on the yield of the ClO_2 preparation method. Specifically, a low yield in the case of the acid preparation can bring about an unpredictable increase in the chlorite concentration in water. The introduction of chlorate is generally due to the use of contaminated chlorite.

The concentrations of ClO_2 and the inorganic reaction products in drinking water are greatly influenced by the stage in the treatment process of the ClO_2 addition. When ClO_2 is used as a post-disinfectant, a fairly low dosage can probably be tolerated (several tenths of milligrams per liter). As a result, chlorite and chlorate are also encountered at this concentration level. A great need exists for methods of determining ClO_2, chlorite and chlorate in this concentration range. Up to the present time, no good analytical method has yet become available. Polarography or ion chromatography may present possibilities.

Especially because of the lack of a good analytical technique, little is known regarding the behavior of ClO_2, ClO_2^- and ClO_3^- during various treatment processes, such as oxidation and adsorption. Preliminary investigation (ref. 9.20) has shown that chlorite is converted to chloride during carbon filtration. DWL Rotterdam has shown that chlorite is converted to chlorate during ozonation.

9.2.5 Organic reaction products of ClO_2

A great deal of attention has been devoted to the reaction between ClO_2 and various organic materials (refs. 9.2, 9.4, 9.15, 9.21 and 9.22). However, most experiments have been performed under conditions which are not representative for drinking water preparation in terms of concentration, pH and temperature. A division of opinion exists concerning the oxidation reactions of ClO_2.

Miller (ref. 9.21) assumed an electrophilic reaction mechanism, wherein reaction products similar to those in ozonation are formed. In addition, the opinion exists that oxidation with chlorine dioxide proceeds by a free radical reaction.

From the public health viewpoint, the formation of halogenated organic substances during the use of ClO_2 is of great significance. There are substantial indications that under conditions customary in drinking water treatment, the use of ClO_2 has little or no likelihood of leading to the formation of THM (refs. 9.15, 9.21, 9.23 and 9.24). This is also apparent from studies on the use of Cl_2 and ClO_2 for the treatment of surface waters (De Greef et al., ref. 9.25).

However, Miller (9.21) and Masschelein (9.4) did demonstrate the formation of chlorinated compounds in reaction with ClO_2. Lindgren (ref. 9.26) cites as the reason for the formation of chlorinated compounds during the use of ClO_2 the production of HOCl during the reaction of chlorite with organic materials. Morris (ref. 9.15) attributes a nucleophilic character to the bond between organic materials and chlorite so that a chlorinated product can form via substitution of a chlorine atom.

Noack and Doerr (ref. 9.27) provide a detailed description of the reaction of ClO_2 with phenols. As the end products, quinones and organic acids are formed; however, chlorophenols can form as the intermediate products (refs. 9.15, 9.22). These chlorinated phenols can be formed as end products if the ClO_2/phenol ratio is very low. Other substances besides chlorophenols which may have consequences for public health include some quinones and 1,2-epoxy compounds (refs. 9.14, 9.15, 9.22 and 9.27).

In addition to the reaction with phenol, the reactions between ClO_2 and amines, alcohols, ketones, aldehydes and organic acids have also been studied. In the group of organic amines, the tertiary amines are the most highly reactive; aldehydes and secondary amines are formed. Secondary amines react far more slowly and primary amines generally do not react with ClO_2 (refs. 9.18, 9.22). Aldehydes are oxidized to organic acids. ClO_2 appears not to react with amino acids, alcohols, ketones, organic acids and aliphatic compounds (unsaturated as well as saturated) in dilute aqueous solution (ref. 9.13).

9.2.6 Discussion

In the preceding sections, attention was paid to some aspects of the use of ClO_2. In view of the characteristics of ClO_2, this agent should always be prepared for use in situ. It is necessary to recall that ClO_2 is explosive in the gas phase at a concentration above 10 vol. %. Depending on the preparation method, ClO_2 may be contaminated with chlorine, chlorite and (a little) chlorate. ClO_2 has been used several years in a number of western European countries. The most common use is based on the excellent bactericidal activity of ClO_2, but the agent is also used for the treatment of organic substances, wherein odor, taste and coloring materials are broken down.

In many instances, ClO_2 is equally effective to chlorine in terms of bacteriologic activity, and in some instances, it is even more effective. An additional advantage is that under practical conditions, ClO_2 is far less sensitive to pH than is chlorine.

ClO_2 forms both inorganic and organic byproducts. The inorganic byproducts are principally chlorite and chlorate, which are formed, among other things, by the disproportionation of ClO_2 at high pH. However, this is not of importance in practice. ClO_2 forms far fewer organohalogens than does chlorine. No THM are formed, and the EOCl and AOCl contents are also distinctly lower than in the use of chlorine. Chlorophenols can be formed in certain cases. Quinones and 1,2-epoxy compounds are other reaction products which may exist.

Toxicologic aspects of ClO_2 and its inorganic and organic byproducts have already been discussed in some detail in section 2.

The information regarding these substances appears to be quite incomplete as yet. This has given rise to rather stringent limitations on the use of ClO_2 for the disinfection of drinking water in many countries. A maximum addition rate of 0,1 mg/liter ClO_2 is recommended in Germany and in Belgium a maximum dose of 0,25 mg/liter (ref. 9.4). In Norway, the use of ClO_2 for drinking water disinfection is actually prohibited (ref. 9.28).
Much study has been performed in the United States on the toxicologic aspects of the use of ClO_2 (refs. 9.29-9.31). On the basis of this, first of all, a maximum dosage for drinking water disinfection of 1 mg/liter ClO_2 has been suggested. Later, the National Academy of Science recommended that the standard be based on the maximum permissible residual contents of ClO_2 and ClO_2^-. Considering a safety factor of 100, this leads to residual contents of 0,3 mg/liter ClO_2 and 0,21 mg/liter ClO_2^- (ref. 9.32). While awaiting the results of further studies, the EPA has taken the above suggestion under consideration.
Especially in terms of toxicology, further study on the side effects of ClO_2 is thus urgently desirable. The results of these investigations will be of great determining significance for the large-scale use of ClO_2.

9.3 Use of monochloramine

9.3.1 Preparation

In practice, chloramines are prepared by adding both ammonia and chlorine to water. In treatment, the formation of monochloramine is pursued. Production takes place via the following reaction equation

$$NH_3 + HOCl \rightleftarrows NH_2Cl + H_2O$$

Monochloramine is formed at a chlorine/ammonium weight ratio of 3 : 1 to 4 : 1. The optimal reaction pH is 7 to 8.

At greater chlorine/ammonium ratios and lower pH, dichloramine and possibly the undesirable compound, trichloramine is formed. Immediately above the weight ratio of 3 : 1 to 4 : 1, the total chlorine content likewise declines. The course of the chlorine content as a function of the chlorine dose is reproduced by the breakpoint curve. A detailed consideration of this is given in section 5.

The reaction rate for the formation of monochloramine is fairly high. At pH 7-8, the reaction is 90 % complete within one minute (ref. 9.33). The rate of dichloramine formation is considerably lower at pH 7-8.

9.3.2 Use of monochloramine in drinking water

Monochloramine was first used during the First World War in Denver (Colorado) to prevent aftergrowth within the distribution system (ref. 9.2).

In the 1930's, the use of chloramine became fairly popular in the United States since the water developed a "chlorophenol" odor or taste due to reaction with phenols when chlorine was used. During the Second World War, the use of the chloramine process decreased greatly as a consequence of the ammonia shortage. After this, the process never regained the extent of use in the 1930's.

The chloramine process is rarely used in drinking water treatment in Europe. However, during the transport chlorination of ammonium-containing river water, the actual disinfectant action takes place as a result of the monochloramine formed.

9.3.3 The disinfecting capability of monochloramine

Monochloramine is a weak disinfectant. The limited bactericidal activity was already demonstrated in the 1940's by Butterfield and Wattie (ref. 9.34). It was found from their study that when equal dosages were used, the use of chloramine required a 100 times longer contact time than the use of chlorine to achieve the same deactivation of coliforms. These results were confirmed by Siders et al. (ref. 9.35). The limited disinfectant capability of chloramine with respect to viruses and Entamoeba histolytica was demonstrated by Fair (ref. 9.17).
Kelly and Sanderson (ref. 9.36) found that at a content of 1 mg/liter chloramine at pH 10, a contact time of 6-8 hour is required, and at pH 7, a contact time of 4 hour is required to bring about 99,7 % removal of poliovirus. Siders et al. (ref. 9.35) showed that for a 99 % reduction of the number of enteroviruses within 20 minutes, a chloramine content of 60 mg/liter is necessary.
Because of the limited disinfection capability of chloramine, the EPA recommended in "the National Interim Primary Water Regulations: Control of THM in Drinking Water" (ref. 9.32) that chloramine not be used as a primary disinfectant. Chloramine is usable as a preservative to control after-growth during drinking water transport when the water fulfills all bacteriologic standards.

9.3.4 Organic reaction products of chloramine

The problems of THM formation during disinfection with chloramine were studied by Stevens et al. (ref. 9.36). The tests were performed with untreated water from the Ohio using chlorine and monochloramine as disinfectants. After a contact time of 72 hour, 160 µg/liter THM were found in the chlorine-treated water. The water treated with chloramine contained 16 µg/liter THM. In 1975, within the scope of the "National Organics Reconnaissance Survey" (ref. 9.37) in the USA, the drinking water from 80 water supply companies was investigated. Ten of these companies used chloramine. In these companies, the THM content varied from 1-81 µg/liter (average 19 µg/liter). In the case of the companies which used breakpoint chlorination, THM contents up to 472 µg/liter occured (average 72 µg/liter). The reason for the relatively high THM contents in the water of some chloramine-using plants is the fact that first chlorine is added in this process and only thereafter, ammonium.

More detailed study has hardly been performed regarding the formation of other organic reaction products during the use of chloramine. Burttschell (ref. 9.38) found formation of chlorophenols by the reaction of chloramine with phenol.

Mergerum and Gray (ref. 9.39) found formation of N-chloroglycine by reaction of monochloramine with glycine under conditions customarily employed for drinking water. They theorized that the reaction takes place via hydrolysis of monochloramine with formation of ammonium and HOCl. However, the equilibrium constant of this hydrolysis reaction is very low ($6,7.10^{-12}$).

9.3.5 Discussion

In the preceding sections, some aspects of the use of monochloramine were considered. Chloramine was prepared by successively adding ammonium and chlorine or chlorine and ammonium to the water. The first method is prefered because of the THM problems. Especially in the USA during the 1930's, the chloramine process was used extensively. The use decreased distinctly after 1940. In Europe, the chloramine process is used only occasionally. The use is mostly based on a low chlorine addition to ammonium-containing water. The disinfection capability of chloramine is low. Therefore, it is principally suitable as a preservative during transport and less suitable as a primary disinfectant.

Little study has been directed toward the formation of organic reaction products by the use of chloramine. Low THM contents occur. The toxicologic aspects of chloramine were already discussed in section 2. The available data are greatly limited and sometimes contradictory. More detailed study in this connection study is desirable.

As for ClO_2, there is thus a large gap in knowlegde in the toxicology area. The more extensive use of chloramine, wherein transport disinfection is principally considered, will depend greatly upon this.

9.4 Conclusions

Chlorine dioxide appears to be one of the most hopeful alternatives to chlorine for transport, primary and post-disinfection when a persistent disinfectant is to be used. The principal reasons for this are its great disinfecting capacity, which

is practically independent of the pH, its low degradation rate and the lack of formation of THM.
However, some important questions exist in connection with the use of ClO_2. These include the formation of potentially harmful substances during the reaction with organic matter and the problems of the toxicologic effects of ClO_2, chlorite and chlorate in drinking water.
Monochloramine can be characterized as a weak disinfectant with a low degradation rate. As a result, it will principally be used for transport disinfection, wherein complete disinfection is not necessary.
Before a changeover can be made to the use of the chloramine process, the problems of the toxicity of chloramine and possible reaction products in the drinking water should be clarified.

9.5 Recommendations

The information described in this section regarding the characteristics of chlorine dioxide and chloramine gives rise to the following recommendations for further investigation:

- investigation regarding the disinfectant capability of ClO_2 at practical dosages;
- investigation with respect to the formation of potentially harmful organic substances in the use of ClO_2;
- investigation on the toxicologic effects of ClO_2, chlorite, chlorate and the organic reaction products;
- investigation on the toxicity of chloramine;
- investigation on the formation of organic reaction products during the use of chloramine.

In general, it seems advisable to investigate further the use of ClO_2 and chloramine in transport chlorination, while the use of ClO_2 for post-disinfection should, likewise, be considered in greater detail.

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10 EVALUATION

10.1 Introduction

In 1974, investigations in the Netherlands and elsewhere showed that THM are formed during chlorination. Investigations raised the suspicions that THMs are undesirable from the toxicologic viewpoint. Therefore, an investigation was conducted on the manner in which the formation of these byproducts can be restricted.

In 1977, the KIWA ad hoc study group on "Chlorine" took an inventory of the situation at that time. In its final report, published in 1978, the working group concluded that:

- chlorine for disinfection may only be replaced by another disinfectant which is at least equally effective and has fewer adverse effects;
- THM cannot be economically removed by aeration, adsorption and oxidation;
- reduction of the THM content may be accomplished by precursor removal prior to chlorination and by limiting the chlorine use while maintaining post-chlorination.

Based on its inventory, the working group made the following recommendations with a high priority:

- preparing an inventory of the toxicologic aspects of disinfection;
- preparing an inventory of chlorine consumption in Netherlands water treatment plants;
- establishing the THM content in drinking water in the Netherlands;
- investigation on the possibilities of reducing the chlorine dose for transport and breakpoint chlorinations;
- investigation on the removal of THM precursors.

Since 1978, a great deal of attention has been devoted to all of these points. THM removal and the use of alternative disinfectants have also been considered.

In addition to the formation of THM over the years, the formation of nonvolatile organohalogens has come to occupy the focal point of attention since specifically, this group of compounds appears to be toxicologically suspect. These compounds are determined on the basis of the surrogate parameters, adsorbable and extractable organochlorine (AOCl and EOCl). These parameters have already been determined during the analytic investigation on the side effects of chlorination in drinking water, 1979/1980. Attention was also devoted to them in more recent investigations on treatment processes. However, more information in this area along the performance of mutagenicity tests is urgently desired. The inventories and studies performed have led to the following findings.

10.2 Toxicologic findings

The literature contains only a limited amount of information regarding the toxicologic effects of chlorine, chlorine dioxide, chloramine and their reaction products. It can be concluded from the available information that at the customary concentration level of disinfectant, no acute or chronic effects are to be anticipated. The disinfectants themselves are also not carcinogenic. The only carcinogenic substance that is found as a reaction product is chloroform.

The use of disinfectants does lead to the formation of mutagenic substances; chlorine introduces more mutagenicity than chlorine dioxide or chloramine.

Epidemiologic investigation up to the present time has only given suggestions of a relationship between reaction products of chlorination and tumors of the bladder, large intestine and rectum. However, causative relationships have not yet been found.

The increase in the mutagenic effects and the possible relationship between formation of reaction products of chlorination and tumorigenesis of the bladder, large intestine and rectum indicated a potential risk for public health so that a reduction of the content of reaction products appears desirable.

However, there is no reason at the present time to eliminate chemical disinfection for toxicologic reasons if it is necessary for bacteriologic reasons. Also at this time, no preference can be expressed on a toxicologic basis for chlorine, chlorine dioxide or chloramine. Further investigation regarding the formation, presence and significance of toxicologically important substances is urgently desired. The results of this investigation together with epidemiologic data may lead to a recommendation on the basis of toxicologic considerations in the future.

10.3 Inventory

In 1979, the chlorine consumption appears to have been reduced to 1249 tons per year, while in 1976, 2108 tons per year was still used. This 41 % reduction is principally due to a marked decrease in the chlorine consumption for transport chlorination. The dose for postchlorination has remained practically constant.

This reduction of chlorine consumption has, among other things, affected the magnitude of the THM content. In 1976, contents in excess of 100 µg/liter were found. In 1979/1980, the highest measured content was 53 µg/liter. In the period 1979-1980, the side effects of chlorination were quantitated in all chlorine-using water treatment plants in the Netherlands. The THM content in drinking water amounted to a maximum of 53 µg/liter. The THM composition appeared to depend greatly on the degree of treatment prior to chlorination. In the case of more highly treated water, larger amounts of more brominated THM were found. A definite quantitative correlation between THM content and chlorine dose did not appear to exist; however, postchlorination, in particular, had a marked effect on the THM contents.

EOCl contents up to a maximum of 11 µg/liter and AOCl contents up to a maximum of 140 µg/liter occured in the drinking water. Especially the AOCl content was high with respect to the THM content. Preliminary toxicologic investigations showed that the fraction of non-volatile halogenated compounds, which is reflected by the AOCl content, causes an increase in the mutagenic effect in the Ames test. Therefore, this group of compounds, in particular, is worthy of further investigation.

The THM precursor content was also determined, measured as the THMFP ("trihalomethane formation potential"). The THMFP averaged 0,3-2,9 µmol/liter. From this, 1-50 % was converted into THM, specifically 1-4 % in the groundwater treatment plants and 21-50 % in the surface water treatment plants. Thus, a large fraction of the THMFP was not converted to THM so that it was not the precursor content but rather the chlorine dose which was of determining significance for the THM content in drinking water.

It can be deduced from the inventory prepared that the concept recommendation of VEWIN for the THM content of 0,55 µmol/liter is never exceeded. However, continued efforts must be made to reduce the THM content insofar as possible. From the toxicologic viewpoint, the AOCl is probably even more important than the THM content. Therefore, this parameter should also be determined frequently.

Finally, in most cases, precursor removal did not appear to lead to a reduction of the THM content under practical conditions. Instead, the chlorine dose seemed to be of determining significance for the THM content.

10.4 Measures

Beginning in 1977, a great deal of investigation was directed toward the measures which may be taken to limit the side effects of chlorination. THM formation, THM removal and precursor removal were principally investigated. Far less attention was paid to the formation and removal of other halogenated compounds. More detailed investigation in this area is urgently desired in view of the nature of the substances. It was found from model studies that a relationship exists between THM formation and the breakpoint curve. Scarcely any THM is formed up to the top in the breakpoint curve; the greatest THM formation takes place immediately above this. In highly treated water relatively marked THM formation already occurs at low chlorine doses.

This picture is confirmed by results obtained in practice. During transport chlorination with Cl_2/NH_4^+ ratios of 2 to 3 scarcely any THM is formed. Transport and breakpoint chlorination with Cl_2/NH_4^+ ratios of 15 to 40 lead to high THM contents. The THM formation during transport chlorination can thus be limited considerably. Breakpoint chlorination is always accompanied by a high THM content. Postchlorination of the treated water, even with a low chlorine dose, is always accompanied by a relatively marked THM formation.

THMs, once formed, are difficult to remove in high percentage over long periods. Oxidation gives scarcely any removal; aeration and reverse osmosis moderate results. Adsorption on activated carbon and alternative adsorbents give good removal only during relatively short filter runs. In this process, better THM removal is achieved, the more highly brominated they are. A very marked reduction of the THM content takes place during infiltration. A large portion of the removal is due to the aeration which is also performed. During the infiltration itself, the removal of more highly brominated THM is most effective.

THM precursors are readily removed by reverse osmosis. All other processes investigated, i.e., aeration, coagulation, adsorption, ion exchange, ozonation and infiltration, give a limited or only briefly a good removal. Partial precursor removal does not result in a reduction of the THM contents under practical conditions, since, in practice, the chlorine dose rather than the precursor content, is of determining significance for THM formation. In addition, more highly brominated THM are formed in the case of a marked reduction of the precursor content, which is undesirable in view of health considerations.

As a result of these findings, less attention was paid to precursor removal, and the possibilities for reducing the postchlorination dose were mostly considered worthy of additional investigation. The determination of the precursor content here is also of lesser significance. As a result, determination of the THM content occuring in the water under practical conditions is of great significance.

The removal of non-volatile organohalogens, measured as the AOCl content, is of great significance. Carbon filtration reduces the AOCl content over longer filter runs than the THM content. Infiltration and reverse osmosis also bring about a reduction of the AOCl content. However, only a very limited number of measurements is available.

10.5 Alternatives

In addition to the measures already discussed, a few other possibilities are also available. One of the possibilities is the use of alternative disinfectants such as chlorine dioxide and chloramine. Chlorine dioxide is said to be suitable to be used for transport- and postdisinfection and chloramine for transport disinfection. Before its use can be considered, the toxicologic side effects should be investigated more thoroughly. Ozone and UV radiation may also be used for primary disinfection and postdisinfection, respectively. However, no attention was devoted to these processes within the scope of the present report.

Depending on the local situation, certain chlorination steps can be eliminated or replaced by treatment processes. Examples that may be mentioned include the replacement of transport chlorination by transport purification and the replacement of breakpoint chlorination by biological processes, linked with a selective water intake criterion. The general applicability of these processes should be more closely investigated.

The elimination of postchlorination deserves much attention. If the bacteriologic and virologic quality is protected by the presence of adequate physical, mechanical and biological barriers, this possibility may be considered. One can principally think about plants with slow sand filtration as the final treatment step. This process sequence has already been used for many years at the Dune Waterworks of The Hague, and has also been introduced at the Municipal Waterworks of Amsterdam and the Waterworks of South-West-Nederland.

10.6 Current state of the art

The work performed since 1977 greatly extended our understanding of the problems. If chlorine is necessary as a disinfectant, the side effects do not demand its elimination. However, an increase in the mutagenic effect and possible epidemiologic relationships suggest a potential risk to public health so that the byproduct contents need to be kept as low as possible. More study on the side effects and side reactions of chlorine, chlorine dioxide and chloramine as well as ozone and UV radiation is desirable.

The chlorine consumption decreased greatly in 1976-1979, especially in the case of transport chlorination. In 1979/1980, it appeared that the THM content never exceeded the concept recommendation of VEWIN. However, relatively high AOCl contents occured.

The reduction of the chlorine use led to a reduction of the THM content. Especialy during postchlorination, however, a good deal of THM is still formed, and this is more highly brominated, the more complete is the purification.

THM, once formed, can only be removed poorly. Only infiltration and carbon filtration for short filter runs give good results.

THM precursors are also difficult to remove. Partial precursor removal does not lead to THM reduction in practice and leads to the formation of more highly brominated THM during postchlorination.

The formation of non-volatile organohalogens is of great importance. This is due to both the nature and the quantity of the products formed. However, little information is available on this material. This group of compounds demands great attention (AOCl determination, mutagenicity study).

As additional possibilities, alternative disinfectants can be used if the side effects of these agents permit this. Limitation or even elimination of chlorination should be considered. In particular, this is true for the elimination of postchlorination if the total treatment process allows this.

10.7 Future developments

Based on the current situation, some important study areas can be indicated. These include:

- toxicologic study on the side effects of chlorine, chlorine dioxide, chloramine, ozone and UV radiation;
- investigation on the formation and the characteristics of high molecular weight organohalogens;
- investigation on the removal of high molecular weight organohalogens;
- elimination of postchlorination if sufficient barriers are present;

- use of alternative disinfectants.

These investigation areas will be further discussed in section 11.

11 RECOMMENDATIONS

In the preceding sections, recommendations for further investigation have been formulated since current knowledge should be expanded. These recommendations are detailed in section 11.1 for all objects. In addition, an attempt is made at establishing priorities in section 11.2.

11.1 Recommendations for further investigation

- Toxicologic aspects of some disinfectants for drinking water.
  1. Investigation on the formation, occurence and significance of genotoxic substances formed under the influence of drinking water disinfection.
  2. Epidemiologic investigation on the possible relationship between the presence of organohalogens formed under the influence of disinfectants in drinking water and certain forms of cancer.

- Halogenated compounds formed in Netherlands drinking water by chlorination.
  1. Investigation on the restriction or elimination of postchlorination.
  2. Investigation on the influence of the bromide content on the composition of the THM content and the composition of the content of non-volatile organohalogens.
  3. Investigation on the formation and removal of (non-volatile) organohalogens by treatment as a whole.
  4. Investigation on the effects and side effects of alternatives to chlorine.

5. Investigation on the side effects of chemical disinfection with the aid of toxicity tests.

- Formation of halogenated compounds during individual chlorinations and ozonation.
  1. Investigation of the possibilities for restricting the use of chlorine in transport disinfection. The following possibilities arise:
     a. use of transport purification;
     b. use of intermittent chlorination;
     c. use of chlorine dioxide or chloramine.
  2. Investigation on the side effects of postchlorination by performing organohalogen determinations and toxicity tests.
  3. Investigation on the possibilities for restricting postchlorination, replacing it by chlorine dioxide treatment or eliminating it.
  4. Investigation on the formation of halogenated compounds during ozonation.

- Removal of halogenated compounds.
  1. Investigation on the removal of non-volatile organohalogens by infiltration and adsorption techniques.
  2. Use of alternative adsorbents for removing volatile organohalogens.
  3. Study on the effect of postchlorination following the removal of organohalogens formed in a previous chlorination.
  4. Investigation on the use of combination of processes (e.g., removal of trichloroethylene by a combination of aeration and carbon filtration).
  5. Obtainment of more information on infiltration, e.g., concerning the effect of aeration prior to infiltration.

- Removal and conversion of THM precursors.
  1. Setting up a uniform prescription for a consumer-based THMFP determination.
  2. Study on the formation of organohalogens with chlorination following different measures of organic substance removal.
  3. Study on the removal of substances that form non-volatile organohalogens during chlorination.
  4. Investigation on the separate determination of organochlorine and organobromine.

- Possibilities for use of process control.
  1. Investigation of the extent to which the use of coagulation and rapid filtration can permit elimination of transport chlorination in all cases.
  2. Investigation on optimization of ammonium removal by biological processes.
  3. Investigation on the possibilities of elimination postchlorination or replacing it by the use of ClO_2 or UV radiation. Virologic aspects are also of importance here.

- Use of alternative disinfectants.
  1. Investigation on the formation of potentially harmful substances (chlorite, chlorate, organic reaction products) during the use of chlorine dioxide.
  2. Investigation on the formation of potentially harmful substances upon the use of chloramine.
  3. Investigation on the toxicity of chlorine dioxide and chloramine.
  4. Study on the use of chlorine dioxide for transport- and post-disinfection.
  5. Study on the use of chloramine for transport

disinfection.

11.2 Establishment of priorities

The recommendations for further investigation are ranked by subject in section 11.1. Permeating all of the previous sections, three investigation fields are strongly predominant. These are:

a. investigation on the formation and removal of non-volatile organohalogens;

b. investigation on postchlorination. This pertains to both more detailed quantitation of the side effects of postchlorination and investigation on the possibility of eliminating postchlorination or replacing it by using ClO_2 or UV radiation. In this process, the water quality should be evaluated bacteriologically and virologically;

c. investigation on transport chlorination. This pertains to replacement by transport treatment or replacement by addition of chlorine dioxide or chloramine.

In all these studies, the quantitation of side effects plays a large role. Far more than before, mutagenicity tests such as the Ames test must be used for evaluating the quality of the treated water.

Concerning the chemical parameters, in addition to the THM content, parameters for determining non-volatile organohalogens play a very important role. For this purpose, organohalogens can be determined after adsorption on activated carbon (AOCl) or after isolation on XAD (XOCl). It is likewise highly desirable to be able to make a distinction between organochlorine and organobromine.

There is also a need for quantitation of the inorganic byproducts of ClO_2, chlorite and chlorate. An analytical method needs to be developed for the concentration range of 0,01-0,1 mg/liter.

APPENDIX 1

- **Chromosome aberration:** microscopically detectable changes in the structure and/or number of chromosomes.
- **Chronic toxicity:** a substance is said to have chronic toxicity if, after repeated (usually daily) administration of small doses of a substance during at least 90 % of the average lifetime of a specific test animal species, harmful (slight to serious) adverse effects arise.
- **Cyst:** a cavity filled with fluid.
- **Embryotoxic:** toxic (harmful) to the unborn offspring (in a relatively early stage of development).
- **Fetotoxic:** toxic (harmful) for the unborn offspring (in a relatively late stage of development).
- **Genotoxic:** causing damage to the hereditary material.
- **Hematocrit value:** the volume-percentage of red blood cells in whole blood.
- **Hemoglobin:** red blood pigment (has capability to bind and release oxygen).
- **Hemolysis:** the destruction of red blood cells.
- **Hepatoma:** liver tumor.
- **Cancer:** general term for all forms of malignant tumor growth. A tumor is called malignant if it is characterized by invasive growth, wherein the tumor tissue spreads to beyond the tissue or the organ in which it iriginated, infiltrates into adjacent tissue and penetrates into body cavities or into lymphatic and blood vessels. In the last case, the tumor cells can also nest in other organs and produce additional tumors.

- **Metastasis:** the sowing of tumor cells.
- **Mutation:** a change in the content or organization of the genetic information which is transferred to daughter cells and leads to distinct changes in the cell or organism involved. Mutations can arise spontaneously or be induced under the influence of mutagenic agents such as radiation of chemicals. Such chemicals are called mutagens.
- **Neoplasm:** see tumor.
- **Osmotic fragility:** breakability of the wall of red blood cells under the influence of volume changes as a consequence of changes in the osmotic value of the blood.
- **Teratogenic:** damaging to the offspring.

APPENDIX 2: ABBREVIATIONS

Water works

DWL 's G : Dune Water Works of The Hague
DWL R : Water Works of Rotterdam
GEB D : Municipal Energy Concern of Dordrecht
GW : Municipal Water Works of Amsterdam
GWG : Municipal Water Works of Groningen
LDM : Dune Water Works of Leiden
ONE : Municipal Energy Concern of Enschede
PWN : Provincial Water Works of North Holland
WBB : Water Supply Company Brabantsche Biesbosch
WMO : Water Works of Overijssel
WMZ : Water Works of South West Netherlands
WNWB : Water Works of North West Brabant
WRK : Water Transport Company Rijn-Kennemerland

The abbreviations stand for the Dutch namegiving of the Water Works.

Purification processes

AC : application of activated carbon (powdered or granular)
BrCl : breakpoint chlorination
CF : carbon filtration
Cl : chlorination
Coag : coagulation
DMF : dual media filtration
GAC : granular activated carbon
HR : hardness reduction
NSF : not submerged filtration
O_3 : ozonation

PCl : post chlorination
RF : rapid filtration
SSF : slow sand filtration
TrCl : transport chlorination

Analytical parameters

AOBr : adsorbable organo bromine
AOCl : adsorbable organo chlorine
AOH : adsorbable organo halogen
AOHFP : adsorbable organo halogen, determined according to the THMFP prescription
COD : chemical oxygen demand
EOCl : extractable organo chlorine
POCl : purgeable organo chlorine
THM : trihalomethane
THMFP : trihalomethane formation potential
TOC : total organic carbon
UV : ultra violet-extinction