J. Hrubec
Editor

Quality and Treatment of Drinking Water

The Handbook of Environmental Chemistry

5 · B

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The Handbook of Environmental Chemistry

Volume 5 Part B

Edited by O. Hutzinger

Water Pollution

Drinking Water and Drinking Water Treatment

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Preface

Environmental Chemistry is a relatively young science. Interest in this subject, however, is growing very rapidly and, although no agreement has been reached as yet about the exact content and limits of this interdisciplinary subject, there appears to be increasing interest in seeing environmental topics which are based on chemistry embodied in this subject. One of the first objectives of Environmental Chemistry must be the study of the environment and of natural chemical processes which occur in the environment. A major purpose of this series on Environmental Chemistry, therefore, is to present a reasonably uniform view of various aspects of the chemistry of the environment and chemical reactions occurring in the environment.

The industrial activities of man have given a new dimension to Environmental Chemistry. We have now synthesized and described over five million chemical compounds and chemical industry produces about one hundred and fifty million tons of synthetic chemicals annually. We ship billions of tons of oil per year and through mining operations and other geophysical modifications, large quantities of inorganic and organic materials are released from their natural deposits. Cities and metropolitan areas of up to 15 million inhabitants produce large quantities of waste in relatively small and confined areas. Much of the chemical products and waste products of modern society are released into the environment either during production, storage, transport, use or ultimate disposal. These released materials participate in natural cycles and reactions and frequently lead to interference and disturbance of natural systems.

Environmental Chemistry is concerned with *reactions in the environment*. It is about distribution and equilibria between environmental compartments. It is about reactions, pathways thermodynamics and kinetics. An important purpose of this Handbook is to aid understanding of the basic distribution and chemical reaction processes which occur in the environment.

Laws regulating toxic substances in various countries are designed to assess and control risk of chemicals to man and his environment. Science can contribute in two areas to this assessment: firstly in the area of toxicology and secondly in the area of chemical exposure. The available concentration ("environmental exposure concentration") depends on the fate of chemical compounds in the environment and thus their distribution and reaction behaviour in the environment. One very important contribution of Environmental Chemistry to the above mentioned toxic substances laws is to develop laboratory test methods, or mathematical correlations and models that predict the environmental fate of new chemical compounds. The third purpose of this Handbook is to help in the basic understanding and development of such test methods and models.

The last explicit purpose of the handbook is to present, in a concise form, the most important properties relating to environmental chemistry and hazard assessment for the most important series of chemical compounds.

At the moment three volumes of the Handbook are planned. Volume 1 deals with the natural environment and the biogeochemical cycles therein, including

some background information such as energetics and ecology, Volume 2 is concerned with reactions and processes in the environment and deals with physical factors such as transport and adsorption, and chemical, photochemical and biochemical reactions in the environment, as well as some aspects of pharmacokinetics and metabolism within organisms. Volume 3 deals with anthropogenic compounds, their chemical backgrounds, production methods and information about their use, their environmental behaviour, analytical methodology and some important aspects of their toxic effects. The material for volumes 1, 2, and 3 was more than could easily be fitted into a single volume, and for this reason, as well as for the purpose of rapid publication of available manuscripts, all three volumes are published as a volume series (e.g. Vol. 1; A, B, C). Publisher and editor hope to keep the material of the volumes 1 to 3 up to date and to extend coverage in the subject areas by publishing further parts in the future. Readers are encouraged to offer suggestions and advice as to future editions of "The Handbook of Experimental Chemistry".

Most chapters in the Handbook are written to a fairly advanced level and should be of interest to the graduate student and practising scientist. I also hope that the subject matter treated will be of interest to people outside chemistry and to scientists in industry as well as government and regulatory bodies. It would be very satisfying for me to see the books used as a basis for developing graduate courses on Environmental Chemistry.

Due to the breadth of the subject matter, it was not easy to edit this Handbook. Specialists had to be found in quite different areas of science who were willing to contribute a chapter within the prescribed schedule. It is with great satisfaction that I thank all authors for their understanding and for devoting their time to this effort. Special thanks are due to the Springer publishing house and finally I would like to thank my family, students and colleagues for being so patient with me during several critical phases of preparation for the Handbook, and also to some colleagues and the secretaries for their technical help.

I consider it a privilege to see my chosen subject grow. My interest in Environmental Chemistry dates back to my early college days in Vienna. I received significant impulses during my postdoctoral period at the University of California and my interest slowly developed during my time with the National Research Council of Canada, before I was able to devote my full time to Environmental Chemistry in Amsterdam. I hope this Handbook will help deepen the interest of other scientists in this subject

This preface was written in 1980. Since then publisher and editor have agreed to expand the Handbook by two new open-ended volume series: Air Pollution and Water Pollution. These broad topics could not be fitted easily into the headings of the first three volumes.

All five volume series will be integrated through the choice of topics covered and by a system of cross referencing.

The outline of the Handbook is thus as follows:

1. The Natural Environment and the Biogeochemical Cycles,
2. Reactions and Processes,

3. Anthropogenic Compounds,
4. Air Pollution,
5. Water Pollution.

Fifteen years have passed since the appearance of the first volumes of the Handbook and four years since the last preface. Our original concept of collecting solid scientific information in Environmental Chemistry has been well received, and with the help of many authors and volume-editors we have published a total of 24 books.

Although recent emphasis on chemical contaminants and industrial processes has broadened to include toxicological evaluation, risk assessment, life cycle analysis and similar approaches there is still a need for presentation of chemical and related facts pertaining to the environment. The publisher and editor therefore decided to continue our five volume series.

Bayreuth, January 1995 Otto Hutzinger

Contents

Introduction

In the last decades, contamination of drinking water and growing public concern about the health risks of contaminants have received much publicity and initiated many research efforts, as well as political and legal activities.

The majority of the recent problems related to drinking water contamination, associated with pollution of surface and ground water resources and with the formation of reaction by-products resulting from the use of disinfectants and oxidants in drinking water treatment, is closely connected with the rapid advances in analytical techniques. The modern analytical methods have resulted in the identification of a large number of chemical compounds and microbial pollutants since the early seventies. Continuing discoveries of new drinking water pollutants and related health hazards have had a shocking effect on the public. For the professional community they have created a multitude of unknown factors and uncertainties concerning toxicological, technological and regulatory aspects.

One of the major issues related to drinking water contamination is the assessment of the health hazards and associated risk comparisons, priority settings and risk management. The health hazard assessment plays an important role in the evaluation of the overall relevance of the problem and is one of the principal factors in the formulation of research needs. A specific feature of health hazards related to drinking water contamination constitutes a dilemma of "competing risk", leading to reduction of a "target risk" and simultaneously creating other kinds of risks. A well known example is the use of chemical disinfectants for elimination of microbial risk, resulting in an increase of health risks from the formation of reaction by-products and vice versa. As a result reduction of risk from formation of by-products by restrictive measures in the application of chemicals can result in an increase of microbial risk.

Health risk assessment has a decisive influence on the setting of national and international quality standards and directives. Due to the current limited state of scientific knowledge and the complexity of political and social reality the quality standards have only a temporary character and therefore constitute an unstable, but nevertheless the only available rational basis for the formulation of technological and technical goals and objectives.

As far as treatment of drinking water is concerned, since 1974, when the formation of trihalomethanes by chlorination was discovered, chlorination by-products are the major research topic. A large number of studies on identification of the reaction by-products of chlorination and on their toxicological effects has provided convincing reasons for avoiding the use of chlorine in drinking water treatment and for the use of alternative disinfection methods.

However, much less information is available on the consequences of the application of alternatives for chlorine, such as ozone and chlorine dioxide. Still, insufficient evidence exists that the reaction by-products of alternative disinfectants and oxidants are less hazardous than those of chlorine. An important

warning, which can be learned from the research on alternative disinfectants for drinking water treatment, is the fact, that the application of any "transformation" process in drinking water treatment introduces a high risk of formation of by-products, which are currently largely unidentifiable and have unknown health effects. Clearly a preference should be given to "real removal" processes, such as aeration, adsorption on activated carbon and membrane separation. Considerable progress has been made recently in the understanding and in the practical application of these processes.

The most serious threat for drinking water quality indeed is posed by the pollution of drinking water resources. As far as surface water is concerned it is caused by anthropogenic compounds, by pathogenic microorganisms and by pollutants related to eutrophication, such as odor and taste compounds and algae toxins.

Ground water, traditionally considered as the most safe drinking water source, has been threatened more and more by the waste dumping, by nitrate and pesticides, resulting from agricultural activities and from air pollution.

Finally still more attention is being given to the quality deterioration of drinking water during transportation and storage as a result of material corrosion and biological activity promoted by the presence of biodegradable compounds.

This volume does not attempt to be an exhaustive review of such a vast and complex subject as drinking water quality, but it is meant to give an overview of the developments in key areas related to chemical contamination, with special attention to organic micropollutants.

The two parts of the volume are organized as follows:

The first part principally addresses:

- The latest developments in quality regulation.
- The role of biological processes in degradation of organic micropollutants and in control of biological instability of drinking water.
- Significance of biological stability of drinking water.
- Control of organic micropollutants by adsorption on activated carbon.
- Origin and removal of tastes and odors.

The second part of the volume will focus mainly on identification of organic micropollutants, approaches to the evaluation of health hazards from chemical and microbiological pollution, the issue of algae toxins, the threat posed to groundwater quality by contamination from agricultural activities and quality changes due to application of ozone and chlorine dioxide.

From the important drinking water quality issues the volume does not address microbiological pollution, because of the scope of the Handbook. From the chemical issues, the principal topic of the reaction by-products of chlorination is not addressed, mainly because it is covered in great detail in a number of other publications. One of the basic aspects of the chlorination problem -health risks of chlorinated drinking water- has been already reviewed in the Handbook elsewhere (see Craun GF Vol. 5, Part A, p 1).

Statutory and Regulatory Basis for Control of Drinking Water Quality

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List of Symbols and Abbreviations

ADI	Acceptable Daily Intake (mostly used for food additives)
BAT	Best Available Technology
D-DBP	Disinfectant-Disinfection Byproduct
EC	European Community
EUREAU	Union of National Associations of Water Suppliers from countries within the European Community and the Economic Free Trade Association
GL	Guide Level
ICR	Information Collection Rule
MAC	Maximum Admissible Concentration
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
QSAR	Quantitative Structure Activity Relationship

SMCL	Secondary Maximum Contaminant Level
SWTR	Surface Water Treatment Rule
TDI	Tolerable Daily Intake (mostly used for contaminants which cannot be avoided)
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

Abstract

Drinking water standards and regulations have recently been developed and revised both at national and international level. The three main topics discussed in this article are the revision of the EC Drinking Water Directive (80/778/EEC), the revision of the 1984 WHO Guidelines for Drinking Water Quality and the standard setting procedure of the USEPA according to the 1986 amendments of the Safe Drinking Water Act. For future regulation of drinking water quality, the importance is stressed of:

a) integrated standards for human exposure to chemicals;
b) informing the public of health risks due to exposure to hazards via drinking water, food, air and skin.

The importance of effective monitoring and appropriate treatment techniques are also discussed.

Introduction

The first drinking water standards were issued probably more than 4000 years ago. Baker [1] quotes from a Sanskrit source: "... it is directed to heat foul water by boiling and exposing to sunlight and by dipping seven times into a piece of hot copper, then to filter and cool in an earthen vessel." During the development of water treatment processes as we know them today, in the last 150 years drinking water quality standards have evolved considerably.

Until 1980 the individual European countries had different regulations with standards covering about 24 parameters which were partly based on European [2] and International [3] standards for drinking water. In 1980, the EC Drinking Water Directive was issued with standards covering 62 parameters. This directive has been implemented in the national legislation of the Member States in subsequent years.

In the USA a standard covering coliforms was introduced in 1914 for protection of the traveling public, followed by standards covering other physical and chemical constituents in 1925. In 1943, 1946 and 1962 parameters were added and in 1974 the Public Law (Safe Drinking Water Act) passed Congress which allowed EPA to promulgate drinking water standards, which led to a list of 83 compounds in 1986 to be regulated or reevaluated.

WHO published its Guidelines for drinking water quality in 1984. For 40 physicochemical parameters and for microbiological parameters and radioactivity, guidelines were given [4].

In Russia, standards for drinking water have been set for 29 parameters but proposals for adding 40 new parameters are being discussed [5].

So looking back only a few decades it is clear that the number of standards and regulations has grown fast.

The ongoing progress in analytical chemistry, the growing awareness of the threats to our environment, the increase in industrial activities and the availability of toxicological data have recently resulted in (starting) a new revision of drinking water standards and regulations both on a national and international level. Three main topics in this area are:

1. the revision of the EC Drinking Water Directive (80/778/EEC);
2. the revision of the 1984 WHO Guidelines for Drinking Water Quality;
3. the ongoing standard setting procedure of the USEPA, according to the 1986 Amendments of the Safe Drinking Water Act.

These topics will also be important for the many new countries in Europe which will have to develop their own national drinking water standards in the near future.

Looking to the future, many questions may arise when setting and implementing standards, for instance:

- will standards and regulations provide a good quality drinking water under all circumstances?
- will we end up with regulations of hundreds of chemicals in drinking water?
- should we stimulate the public's knowledge of the basic ideas of standard setting and risk perception?

It will take some time before all the questions are answered and implemented in day to day practice. Nonetheless it seems worthwhile to stimulate discussion on these matters.

Revision of the EC Drinking Water Directive (80/778/EEC)

The present Directive was developed in the early seventies and was adapted in 1980. In subsequent years it has been implemented in the legislation of the European Member States. In the Drinking Water Directive (80/778/EEC) MACs (maximum admissible concentrations) have been set for 41 parameters. For 12 parameters, only guide levels (GL) have been set and for 16 parameters both a MAC and a GL (see Annex I). The values for the parameters to be fixed by the Member States should be less than or equal to the MAC value and the Member States should take the levels appearing in the "Guide level column" as a basis.

A summary of the way in which the directive is implemented in the different Member States is given by Premazzi et al. [6]. Apart from emergency situations

it is not possible to derogate from the MAC values for toxic or microbiological parameters. For the other parameters derogations from the Directive are only possible when:

- the nature and structure of the ground in the area from which the supply is taken into account;
- exceptional meteorological conditions arise.

There is no doubt that the Drinking Water Directive has made a valuable contribution to the recognition of the importance of drinking water quality and has been a trigger for improvements in water treatment. Recently, however, many Member States and other important parties have asked for a revision of the directive, based on the following:

1. in the past ten years progress has been made in technical and scientific understanding of water quality;
2. a number of points in the directive are not clear or should be modified;
3. several analytical methods given in the directive are not unambiguously defined;
4. the basis for the standards in the directive is not laid down. There are no health criteria documents available. This leads to confusion and a lot of questions when large investments are involved in order to comply with the standards (for example nitrate and pesticides).

In anticipation of the above, the Commission has opened a discussion on the general problems of the Member States associated with the implementation of the directive and for the exchange of ideas for possible modifications. Most delegations were in favour of updating the Directive, although there was still some controversy.

In 1991, EUREAU (The Union of National Associations of Watersuppliers from countries within the European Community and the Economic Free Trade Association) developed proposals for improvements and modifications of the directive [7]. These proposals have recently been updated [8]. A summary of the EUREAU proposals is given in Table 1.

At the third European conference of EUREAU (March, 1993), the Commission (via Garvey, Deputy Director General of DG XI), announced that a revision process of the directive would be initiated. In September 1993 a conference has been organized by the EC to make an inventory of the wishes of both the Member States and other interested parties (EUREAU, environmentalists, industrialists). The Commission has already made clear that [9]:

1. the revision process should include the results of the most recent scientific investigations;
2. the perception of the consumer regarding drinking water must be considered more extensively;
3. not only health aspects but also taste and other aesthetic/organoleptic aspects are important;
4. the consumer must be able to trust or regain trust in drinking water from the tap with regards to health and taste;

Table 1. Part of the EUREAU proposals for modification of the EC Drinking Water Directive

- The classification of the parameters in the present directive should be changed in such a way that it is easier to lay down criteria of exceedances and analytical obligations. Considering that the main objective is the protection of the health and comfort of the consumer EUREAU suggests dividing the parameters into health related (microbiological and chemical), aesthetic/organoleptic and operational.
- The revision should reassess the basis and use of Maximum Admissible Concentration. Limits should be based on the most recent scientific knowledge taking into account the work of international bodies such as WHO. In setting limits for health-related parameters account should be taken of the fact that WHO Guidelines are generally based on lifetime consumption and are not therefore equivalent to MACs.
- Operational parameters have no direct effect on the health of the consumers. They are operational indicators to achieve optimal drinking water conditions and are often highly valuable depending on local circumstances. Examples of these parameters are: temperature, pH, conductivity, chlorides, TOC and total bacteria counts in supplied water. Mandatory standards for these parameters should not be set by the EC, but on a national or regional level.
- The revision should evaluate all parameters in the current Directive. A number of parameters should be deleted from the directive because they are either not relevant to the drinking water quality (silica, potassium, Kjeldahl nitrogen) or covered by others (total hardness, dry residues, suspended solids).
- The addition of parameters should be subject to very careful consideration in view of the practical and financial implications.
- Guide levels should be removed, since they have no scientific basis and have often led to confusion on the part of the consumer.
- Procedures need to be developed to deal with exceedance of the limits. These procedures should take into account the nature of the parameters and the circumstances of the exceedance. For nonhealth-related parameters (for example colour) compliance rules and criteria for allowing for exceedances due to local natural conditions should be developed.
- Legislation for protecting water sources should be reviewed to provide a raw water that allows its use for drinking water without enhanced treatment. This will result in compliance with the Drinking Water Directive, thus lessening the reliance on water treatment. This will lead to more cost-effective consumer protection.

5. the EC will not tolerate a weakening of the directive;
6. an equilibrium must be found between a flexible application of the directive and the level of protection of the consumer;
7. financial implications should be taken into account when setting new standards.

Although the leeway for a revision of the directive is small in view of the above, the EC will have to ensure a sound basis for the standards due to the legal and financial implications involved.

WHO Guidelines for Drinking Water Quality

In 1984, the World Health Organisation (WHO) published its Guidelines for Drinking Water Quality [4]. These Guidelines are intended for use as a basis for the development of standards which, if properly implemented, will ensure

the safety of drinking water. It must be stressed that the WHO guidelines have to be interpreted in the correct way; the guideline values must be considered in the context of prevailing environmental, social, economic and cultural conditions.

Some important aspects of the nature of the WHO guideline values are:

1. a guideline value represents the level (a concentration or a number) of a constituent, that ensures an aesthetically pleasing water and does not result in any significant risk to the health of the consumer over a lifetime's consumption;
2. short-term deviations above the guideline values do not necessarily mean that the water is unsuitable for consumption. The amount by which and the period for which any guideline value can be exceeded without affecting public health depends on the specific substance involved;
3. when setting or developing national standards on the basis of the guidelines, it is necessary to take account of geographical, socio-economic, dietary and other conditions affecting potential exposure. This may lead to national standards which differ appreciably from the guideline values.

The information used for the 1984 Guidelines dates from 1980 or earlier. In 1988 it was decided that the Guidelines should be revised. Over a period of 4 years, 14 meetings were organized by WHO at which 127 chemical compounds as well as the microbiological parameters and radio-activity were evaluated.

The revision of the Guidelines was completed in September 1992 and Volume 1 of the revised Guidelines was published in November 1993 [10].

A few principles of the derivation of the guideline values are important:

1. the guideline values are based on toxicity data. For the majority of the substances for which guideline values are proposed the toxic effect in humans is predicted from studies with laboratory animals. In extrapolating such animal data to humans, safety factors or mathematical methods are used, depending on the toxicity of the compounds involved;
2. each country may choose its own risk level when mathematical models are used to derive a guideline value for a genotoxic carcinogen. As an example WHO has chosen a risk level of 10^{-5} at lifetime consumption;
3. WHO stresses that the guideline values of disinfectants and disinfectant byproducts may not influence the microbiological quality of the water. The microbiological quality of the water has a much higher priority;
4. some guideline values are still provisional. The term provisional guideline value is used for:
   - compounds for which there is some evidence of a potential hazard but where the available health effects information is limited; and/or where an uncertainty factor larger than 1000 is used in the derivation of the tolerable daily intake;
   - those substances for which the calculated guideline value based on toxicological information would be (a) below the practical quantification level or (b) below the level that can be achieved through practical

treatment methods or where disinfection is likely to result in the guideline value being exceeded;

5. in contrast with the guideline values of 1984, WHO has not given guideline values with regard to the aesthetic/organoleptic quality of the water. Numerical guidelines for acceptability aspects were found to be undesirable because of the danger of misinterpretation. When, for example, water sources are scarce, highly coloured drinking water may be refused although, from a health point of view, the drinking water can be consumed. In the revised Guidelines WHO only provides a table with values for aesthetic/organoleptic parameters, which may give rise to complaints from consumers. These values are given in Table 2 together with the nonenforceable USA federal guideline values, referred to as Secondary Maximum Contaminant Levels (SMCLs). The revised guideline values are given in Annex I.

In comparison with the WHO 1984 guidelines, 86 new parameters have been introduced. From these 86 guidelines values, 14 are still provisional.

Table 2. Substances and parameters in drinking water that may give rise to complaints from consumers [10] and SMCLs of the USEPA.

	WHO		USEPA
	Levels likely to give rise to consumer complaints[1]	Reasons for consumer complaints[2]	SMCL
A. Inorganics			
aluminium	0.2 mg/l	depositions, discoloration	0.05–0.2 mg/l
ammonia	1.5 mg/l	odour and taste	–
chloride	250 mg/l	taste, corrosion	250 mg/l
colour	15 TCU	appearance	15 TCU
copper	1 mg/l	staining of laundry and sanitary ware (health-based provisional GV 2 mg/l)	1 mg/l
hardness	–	high hardness: scale deposition, scum formation low hardness: possible corrosion	–
hydrogen sulfide	0.05 mg/l	odour and taste	–
iron	0.3 mg/l	staining of laundry and sanitary ware	0.3 mg/l
manganese	0.10 mg/l	staining of laundry and sanitary ware (health-based provisional GV 0.5 mg/l)	0.05 mg/l
dissolved oxygen	–	indirect effects	–
pH	–	low pH: corrosion high pH: taste, soapy feel preferably < 8.0 for effective disinfection with chlorine	6.5–8.5

Table 2. (*Contd.*)

	WHO		USEPA
	Levels likely to give rise to consumer complaints[1]	Reasons for consumer complaints[2]	SMCL
silver	–	–	0.1 mg/l
sodium	200 mg/l	taste	–
sulfate	250 mg/l	taste corrosion	250 mg/l
taste and odour	–	should be acceptable	3 threshold odour numbers
temperature	–	should be acceptable	
total dissolved solids	1000 mg/l	taste	500 mg/l
turbidity	5 NTU	appearance (for effective terminal disinfection median $\leqslant$ 1 NTU, single sample $\leqslant$ 5 NTU)	–
zinc	3 mg/l	appearance, taste	5 mg/l
B. Organics			
toluene	24–170 µg/l	odour, taste (health-based GV 700 µg/l)	
xylenes	20–180 µg/l	odour, taste (health-based GV 500 µg/l)	
ethylbenzene	2.4–200 µg/l	odour, taste (health-based GV 300 µg/l)	
styrene	4–2600 µg/l	odour, taste (health-based GV 20 µg/l)	
monochlorobenzene	10–120 µg/l	odour, taste (health-based GV 300 µg/l)	
1,2-dichlorobenzene	1–10 µg/l	odour, taste (health-based GV 1000 µg/l)	
1,4-dichlorobenzene	0.3–30 µg/l	odour, taste (health-based GV 300 µg/l)	
hexachlorocyclo-pentadiene[3]			8 µg/l
trichlorobenzenes (total)	5–50 µg/l	odour, taste (health-based GV 20 µg/l)	
synthetic detergents	–	foaming, taste, odour	0.5 mg/l
C. Disinfectants and disinfectant by-products			
Chlorine	600–1000 µg/l	taste and odour (health-based GV 5 mg/l)	
Chlorophenols			
2-chlorophenol	0.1–10 µg/l	taste, odour	
2,4-dichlorophenol	0.3–40 µg/l	taste, odour	
2,4,6-trichlorophenol	2–300 µg/l	taste, odour (health-based GV 200 µg/l)	

[1] These are not precise numbers. Problems may occur at lower or higher values according to local circumstances

[2] Range of taste and odour threshold concentrations given for organics

[3] Proposed

The guideline value for arsenic, cadmium, lead, cyanide and tetrachloromethane has been lowered, although the value for arsenic is still provisional. For 1,2,-dichloroethane, 1,1,1-trichloroethane, 1,1-dichloroethene, benzo(a)pyrene and chloroform, the 1984 guideline values are lower. The value of 1,1,1-trichloroethane is still provisional however.

Looking at the guideline values as such, some of them may present problems to the water suppliers depending on the location and kind of treatment used. A few examples are given below.

Inorganics

The guideline for lead (10 μg/l) has redrawn attention to the problems of concentrations of lead at the tap when lead pipes are present. Discussion on this subject is rather difficult due to the shared responsibility of water suppliers and house owners for the lead pipes in many countries.

Water suppliers have already made a lot of effort to reduce the lead content (pH adjustment, softening/hardening, phosphate dosing). The clear long term solution will be the removal of lead pipes both by the water suppliers and the house owners. This will take a lot of time and cost a lot of money. In the meantime a standard is needed.

For nickel a health based guideline of 20 μg/l is given. Nickel may originate from domestic fittings, but concentrations are also rising in drinking water sources. Due to environmental pollution nickel is mobilized from the soil, leading to increased concentrations in some groundwaters.

A provisional health based guideline of 2 mg/l for copper is given. This value may be exceeded at the tap after stagnation of the water. Due to the fact that problems with corrosion and staining may already occur at values of 1 mg/l, a standard should be based on aesthetic/organoleptic grounds.

The intake of the metals lead, copper and nickel depends on both concentration and the pattern of use. Therefore standard setting should focus on the translation of a health based guideline value into a limit for drinking water at the tap in combination with appropriate sampling procedures.

The WHO value for boron may cause difficulties for surface and ground water supplies. For surface water, control at the source may be necessary (domestic detergents). In groundwater, however, this is not always possible due to the natural occurrence of this element. The same applies to arsenic. Removal of these compounds will be especially difficult for smaller supplies which can have only a very limited treatment.

Organics and Disinfection/Oxidation Byproducts

A number of organic disinfection/oxidation byproducts may be present at the level of the WHO guideline values (e.g. trihalomethanes, chloralhydrate and trichloroacetonitrile). However, since the possible health effects of these products

are less immediate at low levels and of a lower magnitude than those from poor disinfection, WHO stresses that efforts to limit by-product formation should at no time compromise disinfection effectiveness. National authorities should keep this in mind when setting standards.

Inorganic disinfection byproducts like chlorite and bromate are also important health related parameters. Bromate is formed when ozone is used to treat bromide-containing waters. The WHO guideline value of 25 μg/l for bromate is still provisional due to analytical and treatment limitations.

Disinfection may not be compromised, however, and ozone may sometimes be necessary for the removal of other pollutants in the raw water. More research is needed on the prevention of bromate formation and the removal of this compound, which could involve major modifications in the way oxidants are used in treatment.

Chemicals which come into contact with drinking water during treatment and distribution, and for which the guideline values are relatively low, are: di-ethylhexylphthalate, acrylamide, epichlorohydrin and hexachlorobutadiene.

USEPA Drinking Water Regulations and Health Advisories

The Safe Drinking Water Act mandated the establishment of drinking water regulations to be applied to all public water systems in the USA. The federal government (USEPA) was authorized to set national drinking water regulations. State governments have the major responsibility (called primacy) for implementation and enforcement of these regulations.

In 1986 the congress amended the 1974 SDWA and added new sections. The amendments mandated the establishment of many new drinking water regulations according to very specific timetables.

Some water quality related regulations are:

- maximum contaminant level goals (MCLG) and MCLs (Maximum Contaminant Level) must be established for 83 specified contaminants;
- MCLGs and MCLs must be established every three years for 25 contaminants selected from a priority list. This priority list, to be prepared by USEPA, must be updated every 3 years. The first list (1988) contained 53 contaminants. Currently there are 77 contaminants on the list and an update has to be published in 1994;
- criteria must be established under which filtration is required for public systems using surface water sources;
- disinfection of all public water supplies is required (both surface and groundwater supplies).

In addition USEPA has to establish monitoring regulations for unregulated contaminants to develop occurrence data that can be used for evaluating health risks.

MCLGs are nonenforceable, health-based goals. They should be set at a level at which no known or anticipated adverse effect on human health occurs, without taking the cost into account.

MCLs are enforceable standards which are set as close to the MCLGs as feasible, with the use of the best available technology, treatment technique and other means available (referred to as BAT), taking cost into consideration.

Variances can be granted and exemptions made under certain conditions. Furthermore, for each substance there are analytical and compliance requirements and customers must be notified when standards are violated [11].

The USEPA may also require the use of a treatment technique in lieu of establishing an MCL if it is determined that monitoring for the contaminant is not economically or technically feasible. Examples are the Surface Water Treatment Rule (SWTR), Lead and Copper Rule and the Disinfectant-Disinfection-Byproduct Rule (D-DBP).

The SWTR establishes treatment technique requirements (disinfection and filtration) in lieu of MCLs for *Giardia lamblia,* viruses, colony counts (heterotrophic plate count bacteria), *Legionella* and turbidity. Removal efficiencies must be met, along with specified turbidity levels.

With the lead and copper rule the interim MCL for lead is replaced by a treatment technique requirement consisting of optimal corrosion control, source water treatment, public education and lead service line replacement. These steps are required when action levels of lead (0.015 mg/l) or copper (1.3 mg/l) are exceeded, measured in the ninetieth percentile at the customer's tap (first draw water after at least 6 hours stagnation). An action level is not an MCL but is a level at which additional action must be taken [13].

Development of a rule for D-DBPs is technically very complex and there are many uncertainties in various aspects of this rule. The USEPA chose to develop the proposed rule using the negotiated rule-making process referred to as regulatory negotiation or "reg neg" [12, 14].

The Information Collection Rule (ICR) is serving both the second stage of the D-DBP rule and the Enhanced Surface Water Treatment Rule (monitoring for *Cryptosporidium,* watershed protection provisions, enhanced coagulation requirements). This Rule was proposed in December 1993.

The time required to develop sound regulations was underestimated by congress and the regulatory agenda was adjusted several times. The most recent schedules of development for all current and anticipated regulations, with the lists of contaminants, are summarized by Pontius [14].

Current numerical standards for regulated contaminants are listed in Annex I. For 77 contaminants final values have been issued and for 7 contaminants values are proposed. Fluoride is again under study and the sulfate proposal is being reconsidered. Arsenic is still under review.

The USEPA also started a Program in 1978 to give health advisories for contaminants for which no national regulations exist (short and long term). Health Advisories are prepared for contaminants that have the potential for adverse health effects and which are known to occur or might occur in drinking water.

Regulation of Drinking Water Quality in the Future

Informing Consumers and Water Suppliers

Potable water should be free from organisms that are capable of causing disease and from minerals and organic compounds which may produce adverse physiological effects. Furthermore it should be organoleptically and aesthetically pleasant.

In Europe and other parts of the world, drinking water was until recently generally accepted as being safe. In recent years however, due to environmental pollution and advances in science, many questions are being raised about the safety of drinking water.

The task of the water suppliers to produce "reliable" drinking water is indeed becoming more difficult, due to the quality of the available ground and surface water. A lot of research is therefore directed to new or adjusted treatment techniques which enable the water suppliers to deliver good quality water.

It should be admitted however that sometimes there are compounds in drinking water which were not present before the industrial revolution. But at the same time we should consider that these compounds are also present in air and food. For future regulation it is therefore important to know more about the safety of drinking water and about the safety of other aspects of life.

The terms "safe" and "unsafe" are components of the risk concept and of the perception of risk.

The question "What is the risk of illness due to a contaminant in drinking water?" must not be separated from the question "What is the relative risk of illness due to a contaminant in drinking water compared to the risk of illness from exposure to other sources like food and air?" [16, 17].

Of course efforts should be directed primarily to obtaining a drinking water quality of the highest possible level. After all, the consumer is not free to choose to drink water or not! Water suppliers are obliged to optimize the treatment process and under certain circumstances may be able to use alternative ways of supply (infiltration, artificial recharge). However, investment to minimize an already minimal risk from drinking water, which lead to a higher price of drinking water for the consumer, can sometimes be better used in reducing risks from exposure to chemicals in air and food. In this way the harmful effects of pollution for the population will be reduced by a far greater percentage.

In the USA, for example, regulatory costs are rising at a very high speed. The cost during 1991 of mandates already in place has been estimated at $542 billion [18]. The fastest growing component of costs is that of environmental regulation, which is expected to grow to over $170 billion in the year 2000. There is however a growing questioning of all these regulations, because new and tighter regulations are draining funds at community level. For example, to achieve the USEPA-proposed levels of radon in drinking water, the Association of California Water Agencies found that the cost for meeting this standard in California alone would approach $3.7 billion. The reduction of public radon

exposure by this measure would however only be 1%. For this reason, people in the USA are asking for a ranking of environmental risks by independent experts and to use this information to protect society from the greatest risks with the resources available.

It is very important that both the consumer and the water suppliers become more familiar with the concepts of risk, risk perception and risk management. Information/knowledge on integrated standard setting will be helpful in this field.

Integrated Standard Setting

In some countries the formulation of integrated environmental standards is becoming government policy [19]. This means that standards for soil, water and air are coordinated to each other.

Such "integrated standard setting" should in fact also be applied in setting standards for human exposure to contaminants in drinking water, food and air (and by direct contact with soil or water). Which part of the exposure is allowed for which exposure route? Often an arbitrary 1, 10 or 20% of the total exposure is allocated to drinking water in standard setting procedures [20].

Drinking water (or a contaminant in drinking water) can enter the body via the lungs, the stomach and the skin.

Oral intake is obvious. Intake by the lungs can occur, for example, after spraying of the water. The skin can selectively absorb contaminants from drinking water (e.g. when taking a shower).

The relative exposure to inorganic substances through drinking water is usually low (< 1%), but for some compounds (lead, copper, nitrate, calcium and fluoride) it can be higher than 25%, depending on the local situation.

On the relative exposure to organic substances present in drinking water, much less is known due to inadequate data on the ingested amounts from food and air. For a few compounds a conservative estimate of the relative exposure by drinking water was made for the Dutch situation [21] using the average concentration in air and the concentration in different food products (Table 3).

Standards are set or being proposed for drinking water for the last three compounds in Table 3 on the basis of a 10% allocation and in assessing a

Table 3. Estimated exposure to organic micropollutants from drinking water as a percentage of the total exposure [21]

Parameter	Concentration in drinking water (μg/l)	Estimated exposure (as a percentage of the total exposure)
Acrylamide	0.05	50–80
Benzene	1	0.5
Ethylbenzene	1	8
Trichloroethene	1	1.5
Tetrachloromethane	1	5

Table 4. Maximum exposure to a substance from drinking water as a percentage of the TDI of the substance when assuming a consumption of drinking water of 2 l per day per person [21]

Parameter	Standard (μg/l) or proposed "precautionary standard"	Percentage of the TDI (%)
1,1-Dichloroethene	1	0.36
Monochlorobenzene	1	0.04
Toluene	1	0.012
Trichlororethene	1	0.14
Atrazine	0.1	0.48
Isoproturon	0.1	0.10
MCPA	0.1	0.66
Mecoprop	0.1	0.10
Metazachlor	0.1	0.02

standard for benzene for example, a general risk level of 10^{-6} is chosen for lifetime exposure via drinking water. The additional risks from other sources are not taken into account.

Another angle from which to look at the relative exposure via drinking water is to compare the maximal contribution of drinking water, if a certain standard is applied, with the tolerable daily intake (TDI). A few examples are given in Table 4.

For genotoxic carcinogens and endogenously produced compounds however, no TDIs can be given. Data on concentrations in air and 24-hour diet studies are needed in these cases to learn which exposure route is dominant and whether a reduction of exposure is possible through measures in the environmental area involved.

In general the exposure to organic contaminants in drinking water seems rather low, especially when "precautionary standards" are set. Exposure via drinking water may however be significant when the contaminants are volatile and could lead to an additional exposure by the use of drinking water for household or hygiene purposes. Examples are the exposure to trihalomethanes and formaldehyde. The total exposure via drinking water to these contaminants may sometimes be more than 50%.

Informing About the Risk Concept

When the toxicologists have determined a health related value for a compound in drinking water, food or air (risk assessment), the government will weigh the toxicological risks against economic, political, social and regulatory constraints and will ultimately determine a standard (risk management).

The public and the water supplier in general know little about the basic ideas behind standard setting, the uncertainty behind a value in a list and the

Table 5. Activities which decrease general life expectancy by 8 minutes or increase the risk of dying by 10^{-6} (data from [10, 22, 23, 24])

- living with someone who smokes for two months
- drinking half a glass of wine
- eating 40 spoons of peanut butter
- having an X-ray photograph taken in a good hospital
- two hours skiing
- drinking water containing 0.3 μg/l of bromate for 100 years
- drinking water containing 6 μg/l bromodichloromethane for 100 years

associated risks of contaminants in drinking water compared to the risks of daily life (Table 5).

The general public may react hysterically to a newspaper heading like "Cancer producing compound in our drinking water" or "Too much pesticide X in our drinking water: standard exceeded ten-fold". Although this is partly due to the way in which the media handles such matters, lack of information plays an important role [17, 24]. The causes of cancer are also often wrongly interpreted [25]. Popular true phrases like: "the risk of dying of a teaspoon of peanut butter a day is equal to the risk of consuming 2 l of drinking water a day with 100 μg/l benzene (10 or 100 times the standard)" should be clarified.

Informing the public on the above subjects will lead to:

- a better understanding of the exposure to contaminants from different sources and the risks involved for the consumer;
- a better insight into the effect of measures which are necessary in different areas (air, soil and water);
- the possibility for the consumer to determine which financial consequences he is willing to accept to reduce a certain risk.

For drinking water it is also very important that the risks of microbiological contamination of drinking water are presented in such a way that they can be compared with the risks of other drinking water contaminants like carcinogens.

In the USA the first attempts have been made to quantify the risk for the presence of Giardia in drinking water [26]. In this way it becomes possible to compare the advantages and disadvantages of chemical disinfection.

Other "public relation" problems are the so called "precautionary standards". The EC standard for pesticides is 0.1 μg/l for example. This standard is not health related or based on organoleptic or aesthetic considerations.

For other parameters these precautionary standards have been introduced in some countries to control the quality of the sources of drinking water. These standards are sometimes (as happened with the pesticide standard) a stimulus for an improvement in our environment (less use of fertilizer/manure and pesticides and the installation of waste treatment at disposal facilities on industrial sites).

It is very important, however, for the consumer to understand the basic thoughts behind these "precautionary" standards. Exceeding these standards will not automatically lead to "unsafe" drinking water.

In the future these kinds of standards for drinking water will possibly disappear. The sustaining and improvement of the quality of air, soil and surface water will then be regulated by standards.

Can Standards and Regulations Guarantee a Good Quality Drinking Water?

Although it is comforting to have a long list of parameters with appropriate standards that in principal can be met, this may not guarantee a good quality drinking water at all times. Strict protection of water sources is, of course, essential to ensure a good drinking water quality and will lessen the reliance on sophisticated drinking water production techniques. Monitoring and analysis of the water is another important subject.

Effective monitoring requires careful consideration of sampling frequency based on many factors, including the quality of the raw water, treatment and the quality of the distribution system [4].

A monitoring regime should therefore be developed at a local or regional level to cover both random and systematic variations in water quality. Aspects that should be taken into account are:

- the nature of the parameter;
- sampling location;
- sampling frequency;
- the way compliance with the quality requirement is to be judged.

The principle factors that determine the time and frequency of sampling are the concentration of the substance, its variation and the extent, if any, to which it is affected by treatment.

In the EC Drinking Water Directive a standard sampling and analysis programme is laid down, combining a certain number of parameters with the respective sampling frequency. There are four standard patterns of analysis, which are referring to the distributed water only. Annual minimum frequencies are related to the treatment system capacity/volume and to the population supplied (assuming a consumption of 200 l/day per person). A rigid application of these four standard monitoring schemes is however not advisable.

Each water category (untreated water, treated water at the plant, water in the distribution system and water at the household tap) should have its own monitoring schedule. The number of sampling points must be specified together with the frequency at which every point is sampled. Criteria for the location and monitoring of sampling points are especially important for microbiological parameters.

Monitoring schemes for the individual parameters vary greatly in different countries. For reasons of consistency and to be able to make "honest comparisons" (to afford a better protection to all consumers) it would be helpful to have a basic model which is flexible enough to allow the inclusion of specific needs, but which avoids routine monitoring of parameters who's values are consistently far below the standards.

In the USA, according to the Safe Drinking Water Act, monitoring programmes are specified for every parameter or group of parameters. Only for the microbiological parameters does the monitoring frequency depend on the population served. In contrast to the EEC requirements, procedures in case of non-compliance are indicated in detail and are different for every parameter and different depending on the raw water source. Compliance is also averaged over a certain time period of monitoring and procedures are given in detail.

The statistical aspects of compliance to standards are very important and in most cases not well understood. Full compliance can, in theory, never be met unless continuous monitoring is in place. For different compliance rules the protection afforded varies.

The chance of detecting a standard being exceeded can be calculated with the binomial sampling theory. With the aid of so-called "power curves" the relation between the true number of times a standard is exceeded and the chance of detecting these occurences can be illustrated.

As an example:

a) 12 samples in one year with 0 allowed transgressions (100% compliance);
b) 12 samples in one year with 1 allowed trangression (91.6% compliance);
c) 52 samples in one year with 0 allowed transgressions (100% compliance);
d) 52 samples in one year with 5 allowed transgressions (90.4% compliance).

At a 99% true compliance level the chance of detecting transgression is only 10% in case a) and 1% in case b). If the infringement rate is higher, for example 30% (70% true compliance), then a) has 98% chance of detection and b) 92%.

When increasing the number of samples to e.g. 52 in one year and approximately the same compliance percentage, the chance of detecting a transgression at a true compliance level of 99% is 30 and 10% respectively. A 100% chance of detection of a transgression is almost reached, however, even at a 90% true compliance level (case c) or at a 75% true compliance level (case d).

These data illustrate that the number of samples is all important to the protection. At commonly used frequencies the chance of detection (at high true compliance levels) is relatively low. Therefore extensive surveys are sometimes needed to establish the behaviour of parameters in a specific supply.

Although the compliance percentage can be the same, the number of samples determines the chance of detection of transgression at a certain true compliance level. It is important therefore when using a compliance percentage to define explicitly the maximum permitted number of transgressions for any given number of samples.

Number of Parameters to be Regulated

Until now, at any revision of drinking water standards or guidelines, the number of parameters has increased. It is clear, on practical and economic grounds, that this cannot go on forever (more than 70 000 compounds are present in the water phase).

It is possibly more helpful to regulate certain treatment techniques for different source waters than to increase the number of standards. The USEPA partly follows this line as for example with the Filtration Rule and the Lead and Copper Rule but, on the other hand, 25 new standards have to be issued every 3 years according to the Safe Drinking Water Act.

Some useful answers to this problem could be generated by using:

- available combined data on the quality of ground and surface waters and the drinking water prepared from these sources (when different treatment techniques are used);
- results of mathematical modelling of treatment techniques;
- QSARs (Quantitative Structure Activity Relationships).

Furthermore the introduction of more adequate standards for ground and surface water may also contribute to the stabilisation of the number of standards for drinking water. Even if the number of standards is stabilizing, however, they should be revised on a regular basis.

When parameters are health related, it should be remembered that continuous progress is being made in the field of toxicology. Much research is going on, especially on the mechanisms for tumour induction and the use of mathematical models for risk evaluation of genotoxic substances. This may result in more precise figures. Health related standards may therefore need revision on a continuous basis.

Returning to the introduction of this section, it is good to realise that the option to regulate drinking water quality by treatment techniques instead of issuing standards for hundreds of individual parameters was in fact already chosen some 4000 years ago.

References

1. Baker MN (1981) The quest for pure water, vol 1, 2nd edn McGraw-Hill and AWWA, New York
2. World Health Organization (1970) European Standards for Drinking-Water, Geneva
3. World Health Organization (1971) International Standards for Drinking-Water, Geneva
4. World Health Organization (1984) Guidelines for drinking water quality, vol 1, Geneva
5. Doll R, Peto (1981) J Nat Cancer Inst 66: 1191
5. Rahmanin YA (1991) Sysin Research Institute of Human Ecology and Environmental Health, Academy of Medical Sciences, Moscow, Pers and communication.
6. Premazzi G, Chiaudani G, Ziglio G (1989) Scientific assessment of EC standards for Drinking Water Quality, Commission of the EC, EUR 12427 EN, Luxembourg, ISBN 92-826-0805-0
7. EUREAU, The Union of national associations of water suppliers from countries within the European Community and the Economic Free Trade Association (1991) Drinking Water Directive 80/778/EC: Proposals for Modification. Views of EUREAU, Brussels
8. EUREAU, The Union of national associations of water suppliers from countries within the European Community and the Economic Free Trade Association (1993) Updated comments by EUREAU on the revision of the drinking water directive 80/778/EEC, Brussels
9. Kreutz RHF (1993) H_2O 26: 8: 198 (in Dutch)
10. World Health Organization (1993) Guidelines for drinking water quality, Vol I, Geneva
11. Pontius FW (1990) J. Amer. Water Works Assn. 82:2: 32

12. Federal register (1992) 57:220; 52866.
13. Pontius FW (1992) J. Amer. Water Works Assn. 84:3: 36
14. Pontius FW (1993) J. Amer. Water Works Assn. 85:2: 42
16. Slovic P, Fischhoff B, Lichtenstein S (1986) Covello VT, Menkes J, Mumpower J, Risk Evaluation and Management (eds) pp 3 –25 Plenum Press, New York and London
17. Glicker JL (1992) Amer. Water Works Assn. 84: 2: 46
18. Abelson PH (1993) Science 259: 159
19. Langeweg F (1989) Concern for tomorrow (NMP), 3rd edn
20. EPA, Environmental Protection Agency (1990) Risk Assessment, Management and Communication of Drinking Water Contamination, EPA/625/4-89/024, Office of Drinking Water, Washington DC, USA
21. Dijk-Looijaard AM van (1993) H_2O 25: 8: 205
22. Kroes R (1986) Voeding in de praktijk VII-B5: 1 (in Dutch)
23. Ohnesorge FK (1983) Ernahrungs-Umschau 30: 103 (in German)
24. Kletz TA (1981) in: Griffiths RF, Manchester University Press, pp 36–54
26. Regli S, Rose JB, Hass CN. Gewrba CP (1991) J. Amer. Water Works Assn. 83: 76

Annex I – Standards and Guidelines for Drinking Water Quality (Abbreviations at the end of the table)

Parameters	Units	USEPA standard			EEC standard (80/778/EEC)		WHO Guideline Value 1984	WHO Guideline Value 1993
		Status	MCLG	MCL	GL	MAC		
ORGANICS								
Acrylamide	µg/l	F	0	TT				0.5 for 10^{-5} excess risk[a]
Alachlor	µg/l	F	0	2		0.1		20 for 10^{-5} excess risk[a]
Aldicarb	µg/l	D	7	7		0.1		10
Aldicarb sulfone	µg/l	D	7	7		0.1		
Aldicarb sulfoxide	µg/l	D	7	7		0.1		
Aldrin	µg/l					0.1	0.03	0.03
Atrazine	µg/l	F	3	3		0.1		2
Bentazon	µg/l					0.1		30
Benz(a)anthracene	µg/l	Pr	0	0.1		0.2[b]		
Benzene	µg/l	F	0	5			10 for 10^{-5} excess risk	10 for 10^{-5} excess risk[a]
Benzo(a)pyrene[c]	µg/l	F	0	0.2		0.2[b]	10 for 10^{-5} excess risk	0.7 for 10^{-5} excess risk[a]
Benzo(b)fluoranthene	µg/l	Pr	0	0.2		0.2[b]		
Benzo(k)fluoranthene	µg/l	Pr	0	0.2		0.2[b]		
Bromochloroacetonitrile					1[d]			NAD
Bromodichloromethane	µg/l	T	-	100 (as TTHM)				60 for 10^{-5} excess risk[a]
Bromoform	µg/l	T	-	100 (as TTHM)				100
Butyl benzyl phthalate	µg/l	Pr	0	100				
Carbofuran	µg/l	F	40	40		0.1		5
Carbon tetrachloride	µg/l	F	0	5	1[d]		3[e] at 10^{-5} excess risk	2
Chlordane	µg/l	F	0	2		0.1	0.3	0.2

Chlorodibromomethane	µg/l	T	–	100 (as TTHM)				
Chloroform	µg/l	T	–	100 (as TTHM)	1[d]		30[f] at 10^{-5} excess risk	200 for 10^{-5} excess risk[a]
2-Chlorophenol						0.5[g]		NAD
Chloropicrin								NAD
Chloropropanones					1[d]			NAD
Chlortoluron	µg/l					0.1		30
Chrysene	µg/l	Pr	0	0.2		0.1		
Cyanogen chloride (as CN^-)		L						70
2,4-D	µg/l	F	70	70		0.1	100	30
Dalapon	µg/l	F	200	200		0.1		
2,4-DB	µg/l					0.1		90
DDT	µg/l					0.1	1	2
Dialkyltins						0.1		NAD
Di[2-ethylhexyl]adipate	µg/l	F	400	400				
Dibenz(a, h)anthracene	µg/l	Pr	0	0.3		0.2[b]		
Dibromoacetonitrile	µg/l	L						100 (P)
1,2-Dibromo-3-chloropropane (DBCP)	µg/l	F	0	0.2				1 for 10^{-5} excess risk[a]
Dibromochloromethane		L		100 (as TTHM)				100
Dichloroacetic acid	µg/l	T	0		1[d]			50 (P)
Dichloroacetonitrile		L			1[d]			90 (P)
o-Dichlorobenzene	µg/l	F	600	600				1000 (ATO)
m-Dichlorobenzene	µg/l	F	60	600				NAD
p-Dichlorobenzene	µg/l	F	75	75				300 (ATO)
1,1-Dichloroethane	µg/l	L			1[d]			NAD
1,2-Dichloroethane	µg/l	F	0	5	1[d]		10 for 10^{-5} excess risk	30 for 10^{-5} excess risk[a]
1,1-Dichloroethene	µg/l	F	7	7	1[d]		0.3 for 10^{-5} excess risk	30
cis-1,2-Dichloroethene	µg/l	F	70	70	1[d]			50
trans-1,2-Dichloroethene	µg/l	F	100	100	1[d]			50
Dichloromethane	µg/l	F	0	5	1[d]			20
2,4-Dichlorophenol						0.5[g]		NAD

Annex I (*Contd.*)

Parameters	Units	USEPA standard			EEC standard (80/778/EEC)		WHO Guideline	WHO Guideline
		Status	MCLG	MCL	GL	MAC	Value 1984	Value 1993
1,2-Dichloropropane	µg/l	F	0	5	1[d]			20
1,3-Dichloropropane	µg/l	L			1[d]			NAD
1,3-Dichloropropene	µg/l	T	0		1[d]			20 for 10^{-5} excess risk[a]
Dichlorprop	µg/l					0.1		100
Dieldrin	µg/l					0.1	0.03	
Diethylhexyl phthalate	µg/l	F	0	6				8
Dinoseb	µg/l	F	7	7		0.1		
Diquat	µg/l	F	20	20		0.1		
EDTA								200 (P)
Endothall	µg/l	F	100	100		0.1		
Endrin	µg/l	F	2	2		0.1		
Epichlorohydrin	µg/l	F	0	TT				0.4 (P)
Ethylbenzene	µg/l	F	700	700				300 (ATO)
Ethylene dibromide (EDB)	µg/l	F	0	0.05		0.1		NAD
Formaldehyde								900
Glyphosate	µg/l	F	700	700		0.1		
Heptachlor	µg/l	F	0	0.4		0.1	0.1	0.03
Heptachlor epoxide	µg/l	F	0	0.2		0.1	0.1	0.03
Hexachlorobenzene	µg/l	F	0	1		0.1	0.01 for 10^{-5} excess risk	1 for 10^{-5} excess risk[a]
Hexachlorobutadiene	µg/l	T	1		1[d]			0.6
Hexachlorocyclopentadiene	µg/l	F	50	50		0.1		
Indeno(1,2,3-c,d)pyrene	µg/l	Pr	0	0.4		0.2[b]		
Isoproturon	µg/l					0.1		9
Lindane	µg/l	F	0.2	0.2		0.1	3	2
MCPA	µg/l					0.1		2
Metolachlor	µg/l					0.1		10
Molinate	µg/l					0.1		6
Mecoprop	µg/l					0.1		10
MCPB	µg/l					0.1		NAD
Methoxychlor	µg/l	F	40	40		0.1	30	20
Monochloroacetic acid		L			1[d]			NAD

Monochlorobenzene	µg/l	F	100	100	1[d]			300 (ATO)
MX								NAD
NTA								200
Oxamyl (Vydate)	µg/l	F	200	200		0.1		
Pendimethalin	µg/l					0.1		20
Pentachlorophenol	µg/l	F	0	1		0.1	10	9
Permethrin	µg/l					0.1		20
Picloram	µg/l	F	500	500		0.1		
Polychlorinated biphenyls	µg/l	F	0	0.5		0.1		
Propanil	µg/l					0.1		20
Pyridate	µg/l					0.1		100
Silvex	µg/l					0.1		9
Simazine	µg/l	F	4	4		0.1		2
Styrene	µg/l	F	100	100				20 ATO
2,4,5-T	µg/l	L				0.1		9
2,3,7,8-TCDD (Dioxin)	µg/l	F	0	3×10^{-5}				
Tetrachloroethene	µg/l	F	0	5	1[d]		10^{e} for 10^{-5} excess risk	40
Toluene	µg/l	F	1000	1000				700 (ATO)
Toxaphene	µg/l	F	0	3		0.1		
2,4,5-TP	µg/l	F	50	50		0.1		
Tributyltinoxide						0.1		2
Trichloroacetic acid	µg/l	T	100		1[d]			100 (P)
Trichloroacetaldehyde/chloral hydrate	µg/l	T	60		1[d]			10 (P)
Trichloroacetonitrile		L			1[d]			1 (P)
1,2,4-Trichlorobenzene	µg/l	F	70	70	1[d]			
Trichlorobenzenes (total)								20 (ATO)
1,1,1-Trichloroethane	µg/l	F	200	200	1[d]			2000 (P)
1,1,2-Trichloroethane	µg/l	F	3	5	1[d]			
Trichloroethene	µg/l	F	0	5	1[d]		30^{e} at 10^{-5} excess risk	70 (P)
2,4,6-Trichlorophenol		L				0.5[g]	10 at 10^{-5} excess risk	200 for 10^{-5} excess risk[a] (ATO)
Trifluralin	µg/l	L				0.1		20

Annex I (*Contd.*)

Parameters	Units	USEPA standard Status	MCLG	MCL	EEC standard (80/778/EEC) GL	MAC	WHO Guideline Value 1984	WHO Guideline Value 1993
Vinyl chloride	µg/l	F	0	2	1[d]			5 for 10^{-5} excess risk[a]
Xylenes	mg/l	F	10	10				0.5 (ATO)
INORGANICS								
Aluminium	µg/l	L			50	200	200	–
Antimony	µg/l	F	6	6		10		5 (P)
Arsenic	µg/l	(P)	–	50		50	50	10 for 6×10^{-4} excess skin cancer risk[a] (P)
Asbestos	fibres/l ¿ 10 µm	F	7 MFL	7 MFL				U
Barium	µg/l	F	2000	2000	100			700
Beryllium	µg/l	F	4	4				NAD
Boron	µg/l	L			1000			300
Bromate	µg/l							25 for 7×10^{-5} excess risk[a] (P)
Calcium					100		200 (as 500 mg/l $CaCO_3$)	
Cadmium	µg/l	F	5	5		5	5	3
Chloride					25[h]		250	–
Chlorine	µg/l	T	4000					5000 (ATO)[i]
Chlorine dioxide	µg/l	T	80					[j]
Chlorite		L						200 (P)
Chlorate		L						NAD
Chromium (total)	µg/l	F	100	100		50	50	50 (P)
Copper	µg/l	F	1300	TT[k]	100[l] 3000[m]		1000	2000 (P) (ATO)
Cyanide	µg/l	P	200	200		50	100	70
Di- and trichloramines	µg/l							NAD
Fluoride	µg/l	F	4000	4000		1500 700[n]	1500[o]	1500[o]
Iodine	µg/l							NAD
Iron	µg/l				50	200	300	–

Lead (at tap)	µg/l	F	0	TT[k]		50[p] in running water	50	10[q]
Magnesium					30	50		
Manganese	µg/l	L			20	50	100	500 (P) (ATO)
Mercury (inorganic)	µg/l	F	2	2		1	1	1
Molybdenum	µg/l	L						70
Monochloramine	µg/l							3000
Nickel	µg/l	F	100	100		50		20
Nitrate (as NO_3^-)	mg/l	F	44.3	44.3	25	50	44.3	50
Nitrite (as NO_2^-)	mg/l	F	4.4	4.4		0.1	–	3[r]
Nitrate + Nitrite (both as N)	mg/l	F	10	10				
Selenium	µg/l	F	50	50		10	10	10
Sodium					20	150[s]	200	
Sulfate	mg/l	Pr	deferred	deferred	25	250	400	
Thallium	µg/l	F	0.5	2				
Zinc	µg/l	L			100[l] 5000[m]		5000	–
OTHER PARAMETERS								
Colour	mg/l Pt/Co scale				1	20	15 TCU	–
Conductivity	µ S/cm (20 °C)				400			
Odour	dilution number					2 at 12 °C 3 at 25 °C	inoffensive to most consumers	–
pH					6.5 ⩽ pH ⩽ 8.5		6.5 < pH < 8.5	–
Silver	µg/l							U
Taste	dilution number					2 at 12 °C 3 at 25 °C	inoffensive to most consumers	
Temperature	°C				12	25		
Tin	µg/l							U
Turbidity	mg/l SiO_2			PS	1	10	5 NTU	
Total Dissolved Solids	mg/l				"none"		1000	–

Annex I (*Contd.*)

Parameters	Units	USEPA standard			EEC standard (80/778/EEC)		WHO Guideline	WHO Guideline
		Status	MCLG	MCL	GL	MAC	Value 1984	Value 1993
RADIONUCLIDES								
Beta particle and photon activity (formerly man-made radionuclides)	Bq/l	Pr	0	4 (mrem)			1[t]	1[t]
Gross alpha particle activity	Bq/l	Pr	0	0.56 (15 pCi/l)			0.1[t]	0.1[t]
Radium 226/228	Bq/l	Pr	0	0.74 (20 pCi/l)				
Radon	Bq/l	Pr	0	11.1 (300 pCi/l)				
Uranium	µg/l	Pr	0	20				NAD

[a] For substances that are considered to be carcinogenic, the guideline value is the concentration in drinking water associated with an excess lifetime cancer risk of 10^{-5} (one additional cancer per 100 000 of the population ingesting drinking water containing the substance at the GV for 70 years). Concentrations associated with estimated excess lifetime cancer risks of 10^{-4} and 10^{-6} can be calculated by multiplying and dividing, respectively, the GV by 10.

In cases in which the concentration associated with a 10^{-5} lifetime excess cancer risk is not feasible as a result of inadequate analytical or treatment technology, a provisional GV is recommended at a practicable level and the estimated associated cancer risk presented.

It should be emphasized that the guideline values for carcinogenic substances have been computed from hypothetical mathematical models that cannot be verified experimentally and that the values should be interpreted differently to TDI-based values because of the lack of precision of the models. At best, these values must be regarded as rough estimates of cancer risk. However, the models used are conservative and probably err on the side of caution. Because a linear relationship between dose and effect is assumed, the model overestimates cancer risks, which may be as low as zero. Moderate short-term exposure to levels exceeding the GV for carcinogens does not significantly affect the risk

[b] As the sum of polycyclic aromatic hydrocarbons

[c] Under review

[d] As parameter 32 "other organochlorine compounds not covered by parameter 55 (pesticides)"

[e] Tentative guideline value

[f] Disinfection efficiency must not be compromised when controlling chloroform content

[g] As parameter 29 (phenol index). Excluding natural phenols which do not react to chlorine

[h] Approximate concentration above which effects might occur: 200 mg/l

[i] For effective disinfection, there should be a free chlorine residue $\geqslant$ 0.5 mg/l after at least 30 min contact time at pH $<$ 8.0

[j] A guideline value has not been established because of chlorine dioxide's rapid breakdown and because the chlorite guideline value is adequately protective for potential toxicity from chlorine dioxide

[k] Copper – action level 1.3 mg/l
Lead – action level 0.015 mg/l

[l] At outlets of pumping and/or treatment works and their substations

[m] After the water has been standing 12 h in the piping and at the point where the water is made available to the consumer

[n] MAC varies according to average temperature in geographical area concerned

[o] Climatic conditions, volume of water consumed, and intake from other sources should be considered when setting national standards

[p] Where lead pipes are present, the lead content should not exceed 50 μg/l in a sample taken after flushing. If the sample is taken either directly or after flushing and the lead content either frequently or to an appreciable extent exceeds 100 μg/l, suitable measures must be taken to reduce the exposure to lead on the part of the consumer

[q] It is recognized that not all water will meet the guideline value immediately; meanwhile, all other recommended measures to reduce the total exposure to lead should be implemented

[r] The sum of the ratio of the concentration of each to their respective GV should not exceed 1

[s] As from 1987 and with a percentile of 80 (over a reference period of three years)

[t] If a screening value is exceeded, more detailed radionuclide analysis is necessary. Higher values do not necessarily imply that the water is unsuitable for human consumption

ATO Concentrations of the substance at or below the health-based GV may affect the appearance, taste, or odour of the water

D Draft

F Final

L Listed for regulation

MCL Maximu.n Contaminant Level

MCLG Maximum Contaminant Level Goal

NAD No adequate data to recommend a health-based GV

Pr Proposed

P Provisional guideline value. This term is used for constituents for which there is some evidence of a potential hazard but where the available information on health effects is limited; and/or where an uncertainty factor greater than 1000 is used in the derivation of the tolerable daily intake (TDI). Provisional guideline values are also recommended (I) for those substances for which the calculated guideline value would be (a) below the practical quantification level, or (b) below the level that can be achieved through practical treatment methods, or (ii) where disinfection is likely to result in the GV being exceeded

PS Performance Standard 0.5–1.0 NTU

SMCL Secondary Maximum Contaminant Level

U It is unnecessary to recommend a health-based GV for these compounds because they are not hazardous to human health at concentrations normally found in drinking water

Annex II – Microbiological Standards and Guidelines

	USEPA MCLG	MCL	EC GL	MAC	WHO Guidelines (1993)
Total coliforms	0	[1]		< 1 per 100 ml (MF = 0)[2]	< 1 per 100 ml[3]
Thermotolerant coliforms				< 1 per 100 ml (MF = 0)	
E. coli-or thermotolerant coliforms					< 1 per 100 ml
Faecal streptococci				< 1 per 100 ml (MF = 0)	
Spores of sulphite reducing *Clostridia*				< 1 per 20 ml	
Colony counts 22 °C	-	TT	< 100/ml		-
Colony counts 37 °C			< 10/ml		
Giardia lamblia	0	TT			
Legionella	0	TT			
Virusses	0	TT			

[1] No more than 5% of the samples per month may be positive. For systems collecting fewer than 40 samples per month, no more than 1 sample per month may be positive (Total Coliform Rule)

[2] 95% consistent results, provided a sufficient number of samples is examined

[3] Only for treated water in the distribution system; total coliform bacteria must not be detectable in any 100 ml sample. In case of large supplies, where sufficient samples are examined, they must not be present in 95% of samples taken througout any 12-month period

TT Treatment Technique required (under Surface Water Treatment Rule)

Transformation of Organic Micropollutants by Biological Processes

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List of Symbols and Abbreviations

a = specific surface area of biofilm, m^{-1}
C_2 = adsorbed density of the secondary substrate, gs gx^{-1}
D_2 = molecular diffusion coefficient for the secondary substrate in the bulk liquid, m^2 day^{-1}
D_{f2} = molecular diffusion coefficient for the secondary substrate in the biofilm, m^2 day^{-1}
$D_f^* = D_{f2}/D_2$
h = liquid holdup
H_2 = Henry's law constant for the secondary substrate, m^3 atm mol^{-1}

J_2 = secondary-substrate flux, $g_2\ m^{-2}\ day^{-1}$
J^* = dimensionless flux
k_m = mass-transport coefficient, $m^3\ day^{-1}$
K_2 = secondary-substrate concentration at which the utilization rate is one-half the maximum rate, $gs\ m^{-3}$
K_La_2 = overall mass-transfer rate coefficient for exchange of the secondary substrate between gas and water phases, day^{-1}
K_o = half-maximum-rate concentration for oxygen, $g_o\ m^{-3}$
K_p = linear partition coefficient, $m^3\ g_x^{-1}$
K'_p = adsorption coefficient for Eq. (24)
$L^* = L_2/\tau$
L_2 = thickness of an effective diffusion layer for the secondary substrate, m
L_f = biofilm thickness, m
$L_f^* = L_f/\tau$
MW_2 = molecular weight of the secondary substrate, $gs\ mol^{-1}$
M_x = rate at which biomass is removed from the reactor, $g_x\ day^{-1}$
n = adsorption exponent
O_f = the dissolved oxygen concentration at a position in the biofilm, $g_o\ m^{-3}$
P_2 = partial pressure of the secondary substrate, atm
Q = liquid flow rate, $m^3\ day^{-1}$
q_{m2} = maximum specific rate of secondary-substrate utilization, $gs\ gx^{-1}\ day^{-1}$
r_{ads} = rate of adsorption of the secondary substrate to biomass or other solids, $gs\ m^{-3}\ day^{-1}$
r_{diff2} = rate of secondary-substrate accumulation due to diffusion at a point in the biofilm, $gs\ m^{-3}\ day^{-1}$
r_{ut2} = rate of secondary-substrate utilization by suspended biomass, $gs\ m^{-3}\ day^{-1}$
r_{utf2} = rate of secondary-substrate utilization at a point in the biofilm, $gs\ m^{-3}\ day^{-1}$
r_{vol} = rate of volatilization of the secondary substrate, $gs\ m^{-3}\ day^{-1}$
S_2 = concentration of secondary substrate in the bulk liquid, $gs\ m^{-3}$
S_{f2} = secondary-substrate concentration at a point in the biofilm, $gs\ m^{-3}$
S_{min} = minimum substrate concentration to support a steady-state biofilm, $gs\ m^{-1}$
S_{s2} = secondary-substrate concentration at the outer surface of the biofilm, $gs\ m^{-3}$
S_2^0 = influent secondary-substrate concentration, $gs\ m^{-3}$
$S^* = S_2/K_2$ = dimensionless secondary-substrate concentration
$S_s^* = S_{s2}/K_2$
S'_s = checking value of S_s^*
$\bar{S}_2$ = the water-phase secondary-substrate concentration that is in equilibrium with the existing gas-phase concentration, $gs\ m^{-3}$
t = time, d

V = total volume of reactor or reactor segment, m^3
X_f = biomass density in the biofilm, gx m^{-3}
z = distance dimension normal to the biofilm surface, m
τ = standard biofilm depth dimension = $\sqrt{2K_2D_2/q_{mz}X_f}$, m
η = effectiveness factor
η' = checking value of η
$\phi = \sqrt{2}L_f^*/(1 + 2S_s^{*'})^{1/2}$

Abstract

Although the main goal of biological drinking-water treatment is production of a biologically stable drinking water, biological processes can also remove organic micropollutants that are of a health concern or that cause tastes and odors. Micropollutants are usually removed as secondary substrates, which means that their oxidation does not provide sufficient electrons or energy to support biomass growth and maintenance. This article develops the biochemical fundamentals and quantitative tools for describing the secondary utilization of micropollutants in biofilm processes. It connects the removals of the secondary substrates to the main goal of treatment, removal of biodegradable organic matter. The article critically reviews the biochemical potential for degrading micropollutants commonly found in drinking-water supplies: petroleum hydrocarbons, chlorinated hydrocarbons, and taste-and-odor compounds.

1 Introduction

Biological treatment is re-establishing itself as a critical component in the production of a drinking water that is microbiologically safe, has excellent taste and odor characteristics, contains low-risk levels of synthetic organic chemicals, and maintains its quality during distribution [1]. Whether the biological process is the classic slow sand filter or a modern, high-capacity fixed-film reactor [1–4], its most fundamental goal is to create a water that is biologically stable, or does not support significant growth of microorganisms during its distribution. Biological processing achieves that goal through biofilm accumulation of bacteria that oxidize organic and inorganic electron donors that support the bacteria's growth. The biofilm bacteria oxidize the biodegradable materials in the treatment process, thereby preventing their subsequent oxidation during distribution, which causes undesired microbial growth and leads to quality deterioration [1].

This report addresses the biodegradation of organic micropollutants that pose potential health risks or that reduce the water's aesthetic quality. While the biodegradation of organic micropollutants usually involves their oxidation, it often differs from the oxidation of the primary electron donor. The micropollutant's very low concentration and/or transient presence usually precludes its oxidation from growing and sustaining the bacteria that degrade it. For example, the micropollutant's S_{min} concentration [1] is substantially larger than

the actual concentration. Therefore, the micropollutant must be biodegraded as a *secondary substrate*, or a substrate whose utilization supports no or negligible biomas [1, 5, 6]. To be present to biodegrade a secondary substrate, the bacteria must utilize a more plentiful primary substrate, which is normally all or part of the general biodegradable organic material in the water [7].

2 Key Organic Micropollutants Found in Drinking Waters

The major organic micropollutants polluting drinking-water supplies fall into three general classes: petroleum hydrocarbons, halogenated hydrocarbons, and taste-and-odor compounds. The main constituents of each class and pertinent characteristics are reviewed in this section.

Petroleum hydrocarbons are among the most ubiquitous micropollutants [8, 9]. The most prevalent are the soluble aromatic components of gasoline: benzene, toluene, ethylbenzene, and xylenes (i.e., BTEX). These are found so frequently in water supplies – particularly, but certainly not exclusively in groundwaters – because of the widespread use of petroleum-based fuels and solvents and because of their relatively high water solubility (130–1780 mg/l at 20°C) [9]. Concentrations are frequently in the μg/l range, although mg/l levels are found in grossly polluted waters [8].

Also occurring frequently, but usually at very low concentrations, are more complex petroleum hydrocarbons, such as naphthalene, fluoroethene, isopropyl benzene, and phenanthrene. They have lower solubility than BTEX and are usually present as a small fraction of the petroleum product.

Oxygenated derivatives of petroleum hydrocarbons are widely used in industry as solvents, plasticizers, paints, varnishes, and paint removers. This wide use, when coupled with relatively high solubility, makes oxygenated derivatives common water pollutants [8, 9]. Prime examples included acetone, phenols, phthalates, ethers, methanol, and methyl ethyl ketone. Occasional contaminants are nitrosubstituted aromatics, such as nitrophenol and nitrobenzene.

The halogenated hydrocarbons are the most frequent pollutants of groundwaters [8] and are also found in surface waters [10]. The main source of halogenated hydrocarbons is inappropriate disposal of solvents, fumigants, and pesticides. Some are formed during drinking-water treatment.

Among the halogenated hydrocarbons, the most frequently occurring ones are the one- and two-carbon alkanes and alkenes [10]. Most of these are used as solvents and reach water supplies through improper disposal. Trichloroethene, trichloroethane, tetrachloroethene, tetrachloroethane, dichloromethane, carbon tetrachloride, and dichloroethane are prime examples of ubiquitous solvents. Most of the one-carbon compounds – particularly chloroform, bromodichloromethane, and dibromochloromethane – are formed by reaction of chlorine with natural organic matter during disinfection [11].

Pesticides are another important class of halogenated hydrocarbons [8, 12]. Chlorinated benzenes, dichloroethanes, hexachlorocyclohexane, and highly chlorinated phenols are good examples of simple halogenated molecules used as pesticides. More complex forms include the diphenyltrichloroethanes (e.g., DDT), chlorinated triazines (e.g., Triazine), chlorinated naphthalenes (e.g., Dieldrin and Aldrin), dichlorophenoxy acid, chlorinated methanoindenes (e.g., Heptachlor), nitrophenolthiophosphates (e.g., Parathion), and trichlorophenoxyaliphatic acids (e.g., 2,4,5-T and Silvex).

Besides being of health concern, many of the organic contaminants listed above create unpleasant tastes and odors when present at micropollutant concentrations. Some of the prime examples are benzene, chlorobenzene, dichlorobenzenes, trichlorobenzene, dichlorophenols, dichloroethene, ethylbenzene, naphthalene, and toluene. These compounds have odor threshold concentrations less than 100 μg/l [13–16].

Other taste and odor compounds are not of health concern, but have such a potent olfactory response that they render the water aesthetically objectionable, even though it is safe from a health perspective. These potent taste and odor compounds, which usually have odor threshold concentrations below 1 μg/l, are divided into classes according to the type of taste or odor they impart.

- Earthy-musty odors are most frequently attributed to geosmin and 2-methylisoborneol (MIB), which are an alicyclic alcohol and ketone, respectively [13, 14].
- Fishy odors are associated with aldehydes, amines, and dimethyl sulfide [13, 14, 17].
- Marshy-swampy-septic odors are caused by hydrogen sulfide and organic compounds containing reduced sulfur [13, 14].
- Medicinal-antiseptic odors are created when aromatic hydrocarbons are chlorinated [13, 14].

Most of these organic micropollutants are biodegradable under conditions that might be present in a biological process used for drinking-water treatment, and their biodegradabilities are reviewed in Sects. 4–6. Whether or not they are biodegraded within a biological treatment process depends upon their secondary-utilization kinetics by the biofilms present in the process. Section 3 systematically presents the modeling tools needed to assess micropollutant utilization kinetics.

3 Secondary-Utilization Kinetics

3.1 Mass Balance on a Secondary Substrate

The fate of a micropollutant entering a biological process is controlled by the rate at which it is biodegraded, its rates of input and output in the water, and rates for any other sources or sinks. All of these rates are linked quantitatively

through a mass balance on the micropollutant. Here, the micropollutant is treated as a secondary substrate, which means that its utilization does not support the growth and maintenance of the biomass that utilizes it. Instead, the biomass is sustained by utilizing a primary substrate, such as the aggregate biodegradable organic matter. Rittmann [1] described the kinetics for utilization of the primary substrate and how much biomass is accumulated. The development here is complementary to that in Rittmann [1].

The basic mass-balance equation for a secondary substrate in a completely mixed segment of a biofilm reactor is:

$$hV\frac{dS_2}{dt} = Q(S_2^0 - S_2) - r_{ut2}hV - J_2aV + r_{ads}V + r_{vol}V \tag{1}$$

where V = total volume of the reactor segment, m^3
h = liquid holdup, or ratio of bulk liquid volume to total volume
hV = volume of bulk liquid, m^3
a = specific surface area of biofilm, m^{-1}
aV = surface area of biofilm, m^2
Q = volumetric flow rate, $m^3\ day^{-1}$
S_2 = concentration of the secondary substrate in the bulk liquid, gs m^{-3}
S_2^0 = influent concentration of the secondary substrate, gs m^{-3}
r_{ut2} = rate of secondary-substrate utilization by suspended biomass, gs $m^{-3}\ day^{-1}$
J_2 = secondary-substrate flux into the biofilm, gs $m^{-2}\ day^{-1}$
r_{ads} = rate of adsorption of the secondary substrate to biomass or other solids, gs $m^{-3}\ day^{-1}$
r_{vol} = rate of volatilization of the secondary substrate, gs $m^{-3}\ day^{-1}$
t = time, days

For most situations, the reactor can be assumed to approach steady state, which means that the left side of Eq. (1) can be set to zero:

$$hV\frac{dS_2}{dt} = 0.$$

Furthermore, suspended biomass is usually such a small fraction of the total biomass that substrate utilization by suspended biomass can be neglected:

$$0 \approx r_{ut2}hV << J_2aV.$$

Implementing these simplifications converts Eq. (1) to

$$0 = Q(S_2^0 - S_2) - J_2aV + r_{ads}V + r_{vol}V. \tag{2}$$

The goal of the remainder of this section is to present relationships for J_2, r_{ads}, and r_{vol}. The development begins by considering simple secondary substrates, for which the tools are well established. The section then introduces the complications arising when a cosubstrate is needed to allow biodegradation of the secondary substrate. Finally, methods to estimate adsorption and volatilization rates are presented.

3.2 Simple Secondary Substrates

The model for biofilm utilization of a secondary substrate [5, 19] begins with the idealized biofilm described by Rittmann [1] and illustrated graphically in Fig. 1 of that document. As for primary substrates, internal and external mass-transport resistances, coupled with substrate utilization inside the biofilm, reduce the substrate concentration to values below S_2 in the bulk liquid. This concentration gradient drives the flux of substrate (J_2) from the bulk liquid and into the biofilm. Reductions of substrate concentration can be complete, creating a *deep* biofilm; partial for a *shallow* biofilm; or negligible for a *fully penetrated* biofilm.

3.2.1 Rate Expressions

At any position in the biofilm, the utilization rate for a simple secondary substrate is given by the Monod expression,

$$r_{utf2} = -q_{m2} X_f \frac{S_{f2}}{K_2 + S_{f2}} \tag{3}$$

where r_{utf2} = rate of secondary-substrate utilization at that position in the biofilm, gs m^{-3} day^{-1}
S_{f2} = secondary-substrate concentration at that position in the biofilm, gs m^{-3}
q_{m2} = maximum specific rate of secondary-substrate utilization, gs gx^{-1} day^{-1}
K_2 = secondary-substrate concentration at which the utilization rate is one-half its maximum rate, gs m^{-3}
X_f = biomass density of the biofilm, gx m^{-3}

The value for S_{f2} – and therefore r_{utf2} – can change with location inside the biofilm. Rates are usually highest near the outer surface of the biofilm and decline as S_{f2} decreases into the biofilm. (Fig. 1 of Rittmann [1] illustrates the decline in concentration.)

The substrate is transported inside the biofilm by molecular diffusion, represented by Fick's second law,

$$r_{diff2} = D_{f2} \frac{d^2 S_{f2}}{dz^2} \tag{4}$$

where r_{diff2} = rate of secondary-substrate accumulation due to diffusion, gs m^{-3} day^{-1}
D_{f2} = molecular diffusion coefficient for the secondary substrate inside the biofilm, m^2 day^{-1}
z = distance dimension normal to the biofilm surface, *m*

Utilization occurring simultaneously with molecular diffusion rapidly sets up a steady-state concentration profile that is described mathematically by combining Eqs. (3) and (4):

$$0 = D_{f2}\frac{d^2S_{f2}}{dz^2} - q_{m2}X_f\frac{S_{f2}}{K_2 + S_{f2}}. \tag{5}$$

Substrate must be transported from the bulk liquid to the outer surface of the biofilm, a process described by Fick's first law:

$$J_2 = \frac{D_2}{L_2}(S_2 - S_{s2}) \tag{6}$$

where D_2 = molecular diffusion coefficient for the secondary substrate in the bulk water, $m^2\ day^{-1}$
L_2 = thickness of an effective diffusion layer for the secondary substrate, m
S_{s2} = secondary-substrate concentration at $z = 0$, the outer surface of the biofilm, gs m^{-3}

A boundary condition must be specified for the attachment surface. The usual one is the no-flux condition:

$$\frac{dS_{f2}}{dz} = 0 \text{ for } z = L_f \tag{7}$$

where L_f = the thickness of the biofilm, m.

Because utilization of the secondary substrate does not support the biofilm, the accumulation of biofilm (X_fL_f, $g_x m^{-2}$) is not coupled to its utilization rate, as is the case for primary substrate [1, 20]. Instead, the biofilm accumulation must be supplied as an input. The input value for X_fL_f can be determined by first modeling the primary substrate [21–23] or by experimental measurements [24].

3.2.2 Model Solution

Equations (5), (6), and (7) constitute the mathematical model for the utilization of a secondary substrate in a biofilm of known accumulation (X_fL_f). While they can be solved numerically to predict the substrate flux, a simpler approach is to use the pseudo-analytical solution [20, 25] generated by fitting thousands of numerical results to a set of simple algebraic equations. The pseudo-analytical solution used for secondary substrates is termed the model for biofilms of any thickness. This terminology underlines that the biofilm is not at its steady-state thickness, where growth from substrate utilization just balances losses from decay and detachment [1], because the secondary substrate does not sustain the biofilm.

The pseudo-analytical solution expresses the flux in a modified Monod format:

$$J_2 = \eta q_{m2}X_fL_f\frac{S_{s2}}{K_2 + S_{s2}} \tag{8}$$

where S_{s2} = secondary-substrate concentration at the biofilm/water interface, gs m^{-3}
η = an effectiveness factor

S_{s2} normally is less than S_2, which reflects the effect of external mass-transport resistance. The effectiveness factor, which is less than or equal to one, accounts for the lowering of S_{f2} below S_{s2} due to internal mass-transport resistance. Fully penetrated biofilms have $\eta = 1$, while deep biofilms have the minimum value of η.

To use the pseudo-analytical solution, the eight concentration, utilization, and transport parameters are first combined into four dimensionless parameters:

$$S^* = S_2/K_2 \tag{9}$$

$$L^* = L_2/\tau \tag{10}$$

$$L_f^* = L_f/\tau \tag{11}$$

and

$$D_f^* = D_{f2}/D_2 \tag{12}$$

where

$$\tau = \sqrt{2K_2D_2/q_{m2}X_f}. \tag{13}$$

These four parameters are used to compute S_s and η, from which J_2 is computed via Eq. (8). The pseudo-analytical solution is iterative. The following steps are used [20, 25].

1. A starter value of η must be provided. A reasonable value can be computed from

$$\eta = \frac{\tanh(\sqrt{2}L_f^*)}{\sqrt{2}L_f^*} \tag{14}$$

where tanh is the hyperbolic tangent. The tanh operator is defined as

$$\tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}} \tag{15}$$

2. The η value is used to compute a trial S_s^* from S^*:

$$S_s^* = \frac{1}{2}[(S^* - 1 - 2L^*L_f^*D_f^*\eta) + \sqrt{(S^* - 1 - 2L^*L_f^*D_f^*\eta)^2 + 4S^*}] \tag{16}$$

where $S_s^* = S_2/K_2$.

3. A trial flux is computed from S_s^*:

$$J^* = 2D_f^*L_f^*\eta\frac{S_s^*}{1 + S_s^*} \tag{17}$$

4. A checking S_s^* (denoted $S_s^{*'}$) is computed from

$$S_s^{*'} = S^* - J^*L^* \tag{18}$$

5. An intermediate parameter, ϕ, is computed from

$$\Phi = \frac{\sqrt{2}L_f^*}{(1 + 2S_s^{*'})^{1/2}} \tag{19}$$

6. A checking value of η, called η', is computed from ϕ and the Atkinson equations for η [26], as adapted by Rittmann [20, 25]:

$$\eta' = 1 - \frac{\tanh(\sqrt{2}L_f^*)}{\sqrt{2}L_f^*}\left(\frac{\Phi}{\tanh\Phi} - 1\right) \quad \text{for } \Phi \leqslant 1 \tag{20a}$$

or

$$\eta' = \frac{1}{\Phi} - \frac{\tanh(\sqrt{2}L_f^*)}{\sqrt{2}L_f^*}\left(\frac{1}{\tanh\Phi} - 1\right) \quad \text{for } \Phi \geqslant 1 \tag{20b}$$

7. If η' is sufficiently close to η, the solution has converged, and you should go to step 8. On the other hand, if η and η' differ by more than the acceptable tolerance, you should use η' as a new estimator of η and return to step 2 above. Iterate from step 2 through step 7 until convergence is satisfied. [This usually occurs in fewer than 5 iterations.]

8. Compute J_2 from Eq. (8), $S_{s2} = S_s^{*'} K_2$, and $\eta = \eta'$.

The procedure for modeling simple secondary substrates has been demonstrated many times, e.g. [13, 22, 23] and is easy to implement on a computer. It requires input of biodegradation and transport parameters for the secondary substrate, as well as estimates for X_f and L_f.

One question that should be raised concerns the proper value of X_f. Probably not all active bacteria within a biofilm are capable of biodegrading a given micropollutant. In such instances, the X_f value used for the secondary substrate should be less than X_f computed or measured for the aggregate primary substrate. At this time we have no good means to differentiate what fraction of the total biomass is active in degrading a particular micropollutant. Empirical measurements of the degradative kinetics of the biofilm community can yield an estimate of $q_{m2}X_{f2}$, where X_{f2} is the concentration of biomass active in degrading the secondary substrate. If q_{m2} were known independently, then X_{f2} could be calculated. However, it is not always crucial to estimate X_{f2} separately from $q_{m2}X_{f2}$, because the model equations (in particular, Eqs. (8) and (13)) include the two parameters as a product and never independently. Hence, empirical measures of $q_{m2}X_{f2}$ should suffice, which means that the fraction of X_f active in degrading the secondary substrate can be expressed through changes in X_f, q_{m2}, or a combination.

Rittmann and McCarty [19] presented a family of curves showing how J_2 is controlled by S^* and L_f^*. When L_f^* is small enough (Suidan et al. [27] derived exact quantitative criteria), the biofilm is fully penetrated, $\eta = 1$, and the substrate flux follows the Monod function directly: i.e., first-order in S for low S and zero-order for high S. When L_f^* is very large (roughly greater than 3.0 [19, 27]) the biofilm is deep, $\eta < 1$, and the flux at very high concentrations does not follow the Monod function at high S: Instead of leveling off, J_2 increases with $\sqrt{S_{s2}}$.

3.3 Cosubstrate Effects

Successful biodegradation of the organic micropollutants sometimes requires that cosubstrates be present. Cosubstrates are reactants used directly by the enzymes carrying out transformation of the micropollutant. Cosubstrates are not the nutrients needed for general biomass synthesis or the primary substrates utilized for energy production. While those materials are necessary for supporting bacterial growth, they are not directly involved in the transformation reactions for the micropollutants. On the other hand, the kinetics of micropollutant degradation are directly controlled by concentrations of cosubstrates in some instances.

One key cosubstrate is molecular oxygen (O_2), which is a direct reactant in monooxygenase and dioxygenase reactions with aromatic hydrocarbons and selected chlorinated aliphatics; these reactions are described in Sects. 4 and 5. While catabolic reactions in aerobic systems can be affected by low concentrations of oxygen when it is used solely as the primary electron acceptor, the sensitivity to oxygen limitation appears to be substantially greater when O_2 is utilized directly as a cosubstrate [28]. Thus, monooxygenase and dioxygenase reactions can be slowed significantly by dissolved oxygen concentrations in the low mg/l range. Oxygen's effect can be incorporated into the kinetics by modifying Eq. (2) to

$$r_{utf2} = q_{m2} X_f \frac{S_{f2}}{K_2 + S_{f2}} \frac{O_f}{K_o + O_f} \tag{21}$$

where O_f = the dissolved oxygen concentration at a position within the biofilm, $g_o\ m^{-3}$

K_o = half-maximum rate concentration for dissolved oxygen acting as a cosubstrate, $g_o\ m^{-3}$.

Solutions for the effects of oxygen on substrate flux are much more complicated than for just the secondary substrate alone, because concentrations of both substrates must be represented by coupled equations similar to Eqs. (5)–(7). No pseudo-analytical solution exists, which means that numerical solutions are required.

A second type of cosubstrate is an intracellular carrier of electrons. The intracellular electron carriers usually are identified by acronyms:

NAD = nicotinamide adenine dinucleotide,
NADP = phosphorylated nicotinamide adenine dinucleotide,
FAD = flavin adenine dinucleotide.

Each carrier takes up two electrons, and two hydrogen ions are associated with the electrons. The reduced forms are indicated by NADH + H^+, NADPH + H^+, and $FADH_2$.

These carriers participate in reductive dehalogenation reactions and as a second cosubstrate in monooxygenations; again, the reactions are described in Sects. 4 and 5. Intracellular carriers are not present outside the cells, but their

internal concentrations are controlled indirectly by the external concentrations of electron donors and acceptors [29–31].

Although the best modeling approach to account for effects of intracellular electron carriers is not well established, success has been achieved by making the q_{ms} value a function of the concentrations of the primary substrates. The rate of reaction increases as more primary electron donor is available, while it decreases as the electron acceptor's availability increases [29–31].

3.4 Abiotic Removals

Many organic micropollutants are susceptible to the abiotic removal mechanisms of volatilization and adsorption. The halogenated aliphatics of one and two carbons and less complex petroleum hydrocarbons are volatile enough that significant air stripping is possible, especially when the biological process is aerated for oxygen supply. The larger and more complex hydrocarbons, including the pesticides, are usually hydrophobic and tend to adsorb onto or partition into organic solids, such as the biofilms in biological processes.

Volatilization occurs when the chemical activity of a dissolved compound is greater than the chemical activity of the same compound in the gas phase. This is expressed by the rate expression [13]:

$$r_{vol} = -K_L a_2 (S_2 - \bar{S}_2) \tag{22}$$

where $K_L a_2$ = the overall mass-transfer rate coefficient for exchange of the secondary substrate between water and gas phases, day^{-1}

$\bar{S}_2$ = the water-phase secondary-substrate concentration that is in equilibrium with the existing gas-phase concentration, gs m^{-3}.

$\bar{S}_2$ depends on the partial pressure of the secondary substrate, P_2 (atm), and the secondary substrate's Henry's law constant, H_2 (m^3 – atm mol^{-1}), according to

$$\bar{S}_2 = \frac{P_2 MW_2}{H_2} \tag{23}$$

where MW_2 = molecular weight of the secondary substrate, gs mol^{-1}.

The effect of volatilization is determined by substituting Eq. (22) for r_{vol} in Eqs. (1) or (2). Volatilization is important when H_2 is large, because $\bar{S}_2$ is always small, allowing r_{vol} to have a significant negative value, even when S_2 is not large. Volatilization is further enhanced when the gas flow rate is large enough to keep P_2 small. On the other hand, volatilization will be unimportant when H_2 is small or when another removal mechanism, such as biodegradation, drives S_2 to a very low level.

Adsorption of hydrophobic compounds to biomass can usually be described by equilibrium partitioning [21, 24, 32], which takes the form

$$C_2 = K'_p S_2^n \tag{24}$$

where C_2 = adsorbed density of the secondary substrate on the biomass solids, gs g_x^{-1}
n = adsorption exponent
K'_p = an adsorption coefficient whose units depend on n.

Although n is frequently somewhat larger than 1.0 [32], linear partitioning often gives a reasonable approximation and is assumed to simplify the mathematics:

$$C_2 = K_p S_2 \tag{26}$$

when K_p = linear partition coefficient for the secondary substrate, m^3 gx^{-1}.

When linear partitioning is used and the process has steady-state loading of the secondary substrate, the rate of adsorption is given by

$$r_{ads} V = -C_2 M_x \tag{27}$$

where M_x = the rate at which biomass is removed from the reactor, gx day^{-1}.

Equation (27) is substituted into Eq. (2). For most systems, $r_{ads}V$ is relatively small, unless K_p is extremely large. Therefore, steady-state removal by adsorption is minor, except for highly adsorbable compounds that are not biodegraded.

On the other hand, intermittent loading of an adsorbable micropollutant can result in significant short-term removal, because the accumulated biomass in the reactor can take up the micropollutant until equilibrium is reached. For nonsteady-state loadings, the rate turn for Eq. (1) is

$$r_{ads} V = -k_m (S - C_2/K_p) \tag{28}$$

where k_m = a mass-transport coefficient from the liquid to the solid surface, m^3 day^{-1}.

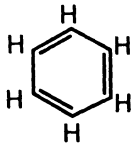
When a sudden load enters the reactor, C_2 is low (or zero), allowing $r_{ads}V$ to be a significant sink. With continued loading, C_2 approaches $K_p S_2$, and the rapid transfer of the micropollutant from the liquid to the biomass ceases. Removal of the micropollutant loading allows desorption of adsorbed micropollutant. Thus, rapid adsorption of a nonbiodegraded micropollutant sequesters and stores the micropollutant during its high loading, but gradually releases it during low loading. This phenomenon acts to "average out" micropollutant concentrations by preventing the pass through of high-concentration spikes. High values of K_p and biomass accumulation ($aX_f L_f V$) accentuate the sorption effects.

For a biodegradable micropollutant, adsorption and volatilization are competing mechanisms. Therefore, factors that increase volatilization (e.g., high H_2 and high gas-flow rates) or adsorption (e.g., high K_p and transient high loading) decrease S_2, which reduces the substrate flux for biodegradation. On the other hand, adsorbed micropollutants remain in the reactor for a longer time; this added contact time with the bacteria can result in increased net biodegradation over the long term [33].

4 Biodegradability of Petroleum Hydrocarbons

The term hydrocarbon comes from the fact that the simplest hydrocarbons are comprised of chains of carbon molecules to which hydrogen molecules are bonded. For example, the alkanes have carbon chains with only single bonds and have the general formula C_nH_{2n+2}, where n indicates the number of carbon molecules in the chain. Alkenes contain double bonds between two or more carbons and, therefore, have fewer than $2n+2$ hydrogen molecules per n carbon molecules. The aromatic hydrocarbons are based on the structure of benzene (C_6H_6), which has a 6-carbon ring in which the six carbons share 18 electron pairs through resonance bonding. The benzene ring is usually represented as

where each corner represents a carbon molecule and has one bonded H molecule,



Oxygenated derivatives of hydrocarbons contain one or more oxygen molecules bonded in the structure. Figure 1 presents several important types of oxygenated hydrocarbons. As oxygen is added, hydrogens are removed. Also removed from the carbon molecules during the oxygenation process are electrons, which means that the carbon molecules are oxidized.

Petroleum derivatives that contaminate water supplies come in oxygenated and unoxygenated forms. Important differences exist in the biodegradability characteristics of these two groups. Thus, biodegradability is discussed first for unoxygenated hydrocarbons and then for oxygenated derivatives.

4.1 Nonoxygenated Hydrocarbons

Considerable research has elucidated the biodegradability of straight-chain alkanes and many aromatics that are not oxygenated. The key to degradation of nonoxygenated alkanes is that one or more of the initial steps of biotransformation introduce oxygen into the molecule via oxygenase reactions. Thus, biodegradation of nonoxygenated hydrocarbons starts with their conversion to an oxygenated form, and molecular oxygen is required as a cosubstrate [9, 39]. Once converted to an appropriate oxygenated form, hydrocarbons can be completely oxidized by the pathways given in Sect. 4.2.

Although recent evidence [40–43] suggests that biodegradation of nonoxygenated hydrocarbons can occur without molecular oxygen in some cases, those

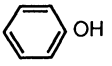
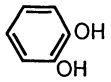
Group Name	Characteristic	Example
	ALIPHATICS	
ALCOHOLS	simple -OH anywhere	CH_3CH_2OH ethanol
ALDEHYDE	simple =O on a terminal C	CH_3CHO acetaldehyde
KETONE	simple =O on a nonterminal C	$CH_3COCH_2CH_3$ methyl ethyl ketone
ACID	 on a terminal C	CH_3COOH acetic acid
ESTER	 on a nonterminal C	CH_3COOCH_3 methyl acetate
	AROMATICS	
PHENOLICS	simple -OH on ring	 phenol
CATECHOLS	two -OH groups on ring	 catechol

Fig. 1. Examples of oxygenated derivatives of hydrocarbons

pathways are not discussed here, because the kinetics appear to be much slower than for aerobic degradation and because aerobic conditions are the norm for biological drinking-water treatment. Details on the biodegradation pathways for branched chains and cyclic alkanes are less well known than for the *n*-alkanes and aromatics. Even though biodegradation rates for these nonoxygenated hydrocarbons are slower than for the *n*-alkanes and aromatics [35, 36, 44, 45], they can be biodegraded, and their biodegradation pathways have the same type of reactions, including oxygenations.

Figure 2 presents the typical sequences of reactions needed to convert various types of aliphatic hydrocarbons to oxygenated compounds that follow the pathways given in Sect. 4.2. All of these initial pathways involve at least one monooxygenation, in which molecular oxygen and a reduced electron carrier are cosubstrates. One molecule of O_2 is incorporated into the aliphatic molecule, oxidizing the carbon by two electrons, while the other oxygen molecule reacts

Monooxygenation of a terminal C on an alkane

$$\underset{\text{alkane}}{CH_3CH_2CH_3} + 2H^+ + 2e^- + O_2 \xrightarrow{M} \underset{\text{alcohol}}{CH_3CH_2CH_2OH} + H_2O$$

Monooxygenations of a nonterminal C on an alkane

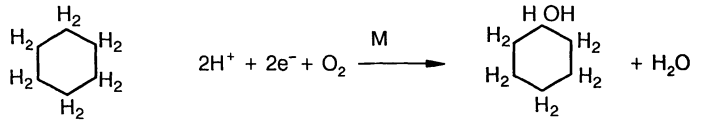
$$\underset{\text{alkane}}{CH_3CH_2CH_2CH_2CH_3} + 2H^+ + 2e^- + O_2 \xrightarrow{M} \underset{\text{alcohol}}{CH_3CH_2CHOHCH_2CH_3} + H_2O$$

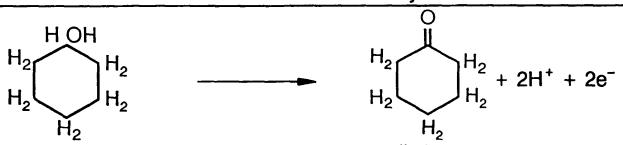
$$CH_3CH_2CHOHCH_2CH_3 \longrightarrow \underset{\text{ketone}}{CH_3CH_2COCH_2CH_3} + 2H^+ + 2e^-$$

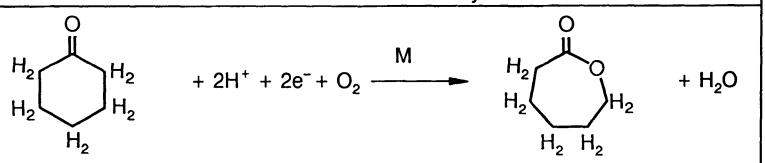
$$CH_3CH_2COCH_2CH_3 + 2H^+ + 2e^- + O_2 \xrightarrow{M} \underset{\text{ester}}{CH_3CH_2COOCH_2CH_3} + H_2O$$

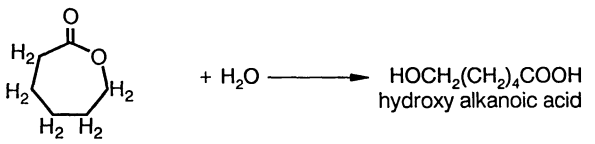
$$CH_3CH_2COOCH_2CH_3 + H_2O \longrightarrow \underset{\text{acid}}{CH_3CH_2COOH} + \underset{\text{alcohol}}{HOCH_2CH_3}$$

Monooxygenations of cyclic alkanes









M indicates a monooxygenase reaction. The electrons (e^-) and hydrogen ions (H^+) are carried to or from the reactions bound to reduced electron carriers, such as NADH, NADPH, and $FADH_2$

Fig. 2. Examples of initial oxygenation steps for aliphatic hydrocarbons

with the electrons and hydrogen ions from the carrier to form water. The initial reactions are complete when the products are simple alcohols or carboxylic acids.

Figure 3 summarizes the main types of initial reactions for aromatic hydrocarbons. Similar to the reactions in Fig. 2, one or more reactions involving molecular oxygen are required.

In the first case, a typical monooxygenation reaction on the fully nonoxygenated ring leads to an epoxide, which is unstable and rapidly converted to catechol by addition of water. For a partly oxygenated ring, such as phenol, the monooxygenation leads directly to catechol. The unoxygenated ring can also be

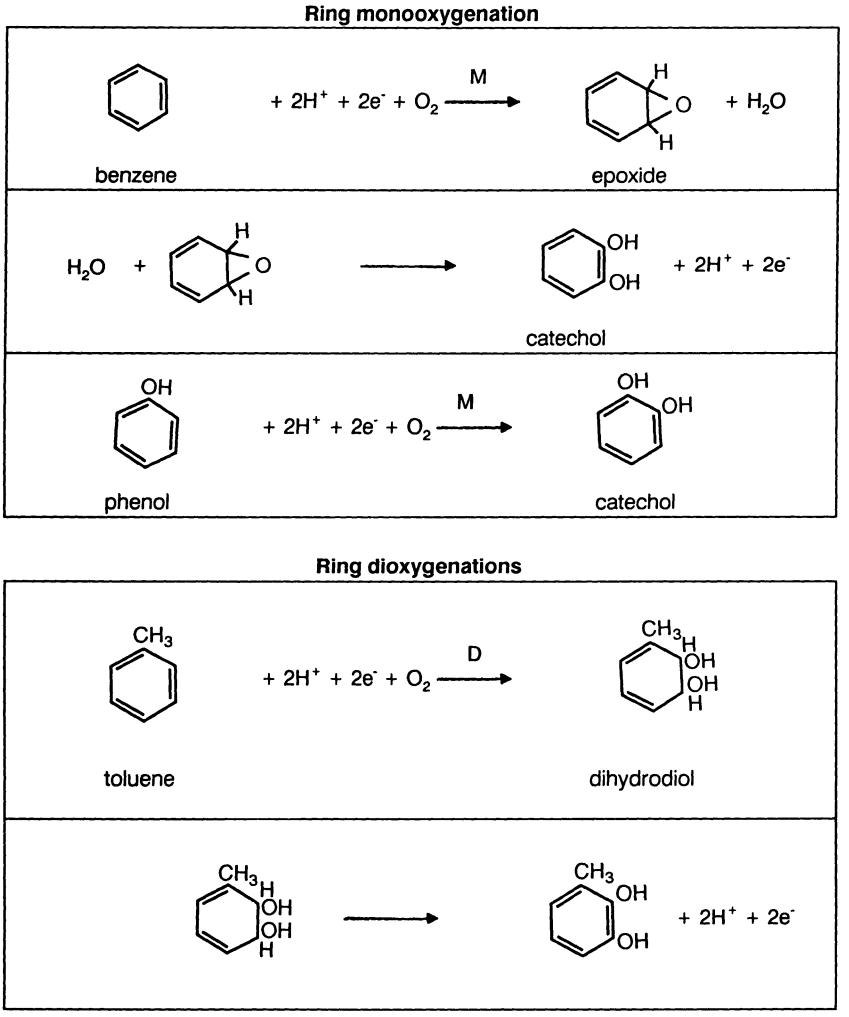
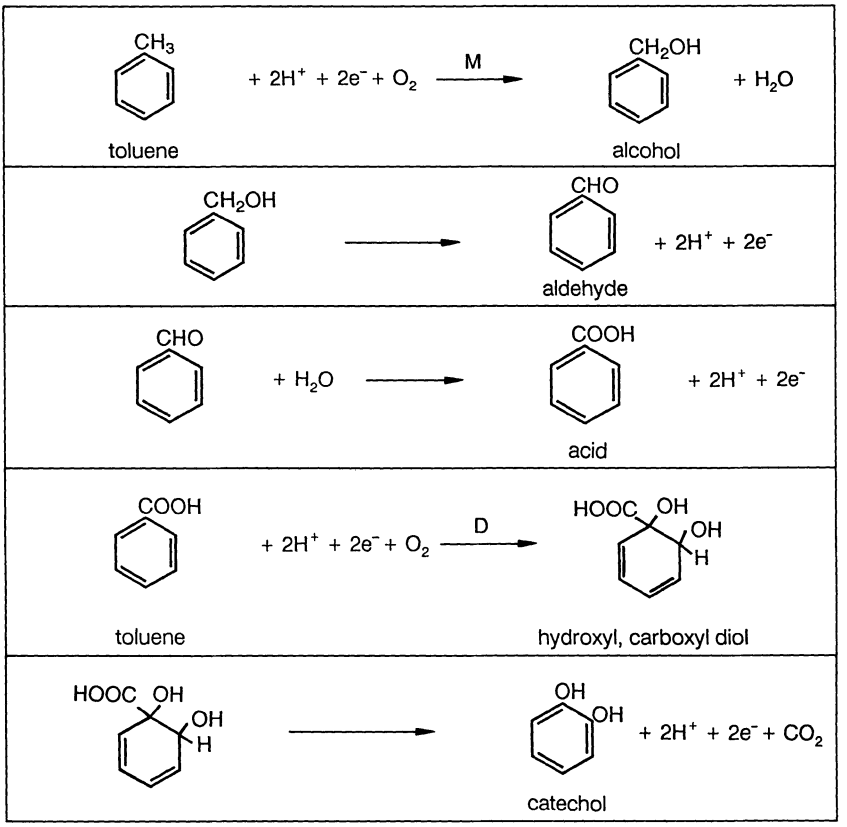


Fig. 3. Examples of initial oxygenation steps for aromatic hydrocarbons

Substituent monooxygenation with ring dioxygenation and decarboxylation



Cleavage of catechols

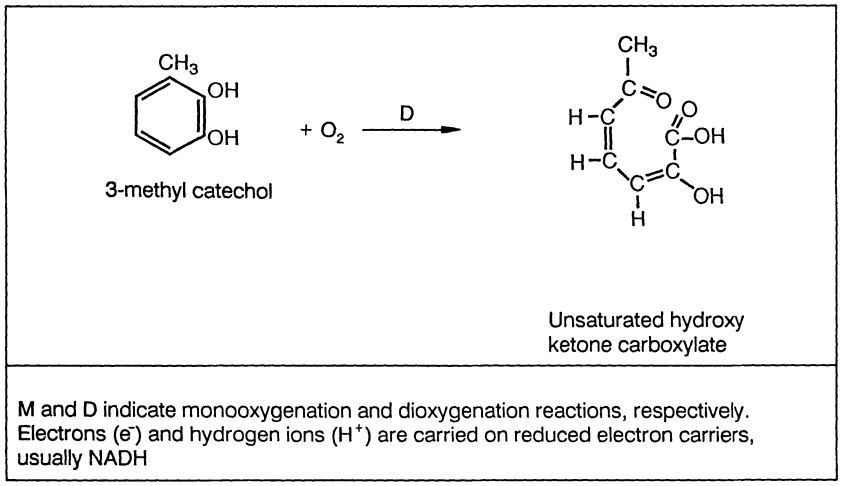


Fig. 3. (*Contd.*)

initially attacked by a dioxygenation, in which both O molecules are added to the ring. However, ring dioxygenation behaves much like a monooxygenation in that a reduced electron carrier is needed as another cosubstrate. Subsequent dehydrogenation regenerates the electron carrier and produces an alkyl catechol.

For substituted aromatics, such as toluene, the alkyl substituent can be oxidized first. The third example in Fig. 3 shows an initial monooxygenation of toluene's methyl group. After a dehydrogenation and hydroxylation of the methyl group to form the carboxylate, a dioxygenase reaction leads to a hydroxylcarboxyldiol that can be oxidatively decarboylated to catechol.

The last reaction in Fig. 3 illustrates the final step for the initial reactions of aromatic hydrocarbons. The catechol is cleaved to an unsaturated hydroxy ketone carboxylic acid. The example is for 3-methyl catechol. Reactions are similar for unsubstituted catechol, although cleavage can also lead to a dicarboxylic acid. Catechol cleavage is catalyzed by a dioxygenase enzyme, which inserts both O molecules into the organic structure. Unlike the dioxygenases used for adding oxygen to the ring, the ring-cleavage dioxygenase does not require an electron-carrier cosubstrate.

4.2 Fully Oxygenated Hydrocarbons

Once hydrocarbons are oxygenated to the final products in Fig. 2 and 3 (i.e., alcohols, acids, ketones, and aldehydes (not shown)), they can almost always be fully mineralized to CO_2 and H_2O by a series of oxidation reactions that do not involve molecular oxygen. The oxidation steps fall into two categories: those leading to acetyl CoA and those oxidizing acetyl CoA to CO_2 and H_2O.

Figure 4 presents a pathway that illustrates all of the reaction types needed to produce the key intermediate, acetyl CoA. The first two steps are two-electron oxidations leading to a carboxylic acid. If the compound already is an acid, the first oxidation step is not needed. The carboxylic acid is then "activated" by being bound to coenzyme A (denoted CoASH, because its active group is the sulfhydryl). The binding of coenzyme A produces H_2O from the acid's OH group and the H from the coenzyme's sulfhydryl. Activation is an energy-demanding process, and the energy is provided by breaking two high-energy phosphodiester bonds in adenosine triphosphate (ATP).

Once activated to carboxyl CoA, the substrate undergoes three steps of two-electron oxidation (called β oxidation) before an acetyl CoA is cleaved to leave a carboxyl CoA with two fewer carbons. The example in Fig. 4 shows formation of two acetyl CoAs, because the original carboxylic acid had four carbons. For carboxyl CoAs longer than two carbons, the process of β oxidation is repeated until all carboxyl CoAs have one or two carbons.

The acetyl CoA is then stepwise oxidized by means of the tricarboxylic acid (TCA) cycle. The details of the TCA cycle are not repeated here, as they can be found in a biochemistry or microbiology text [e.g., 46, 47]. In brief, CoASH is released when acetate is bonded to a four-carbon compound, oxaloacetate, to

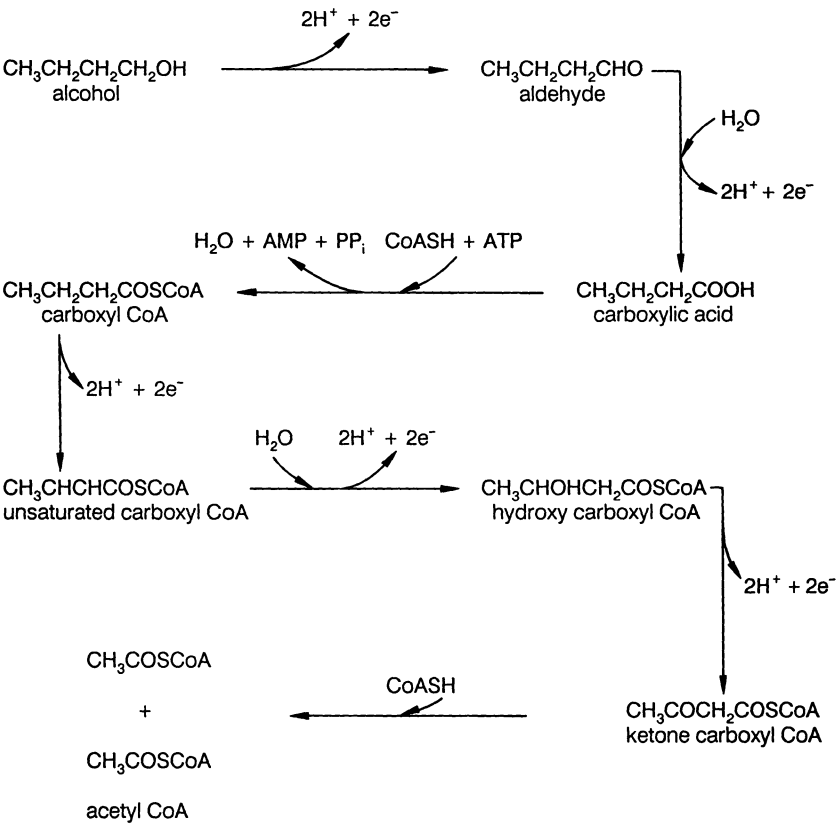


Fig. 4. Pathway for oxidation of an oxygenated hydrocarbon showing the key types of reactions to produce acetyl CoA. Electrons (e^-) and hydrogen ions (H^+) are associated with reduced electron carriers

form citrate, a six-carbon, tricarboxylic acid. Citrate is stepwise oxidized and decarboxylated, yielding two CO_2 molecules, four reduced electron carriers (each with electrons), and one ATP equivalent.

Because the oxidation steps for fully oxygenated hydrocarbons do not require O_2, the electrons are transferred to electron carriers. These electron carriers can be regenerated by transfer of the electrons to any of the common terminal electron acceptors used in respiration: O_2, NO_3^-, NO_2^-, SO_4^{2-}, CO_2, and Fe^{3+} are the main acceptors. This regeneration by terminal electron acceptors is very significant in two ways. First, the degradation of fully oxygenated hydrocarbons is not necessarily aerobic. Second, and probably more important for the drinking water application, the sensitivity to low oxygen concentration seems to be much less for respiratory use of oxygen than it is for

use as a cosubstrate [28]. Thus, situations of low dissolved oxygen concentration might impede degradation of nonoxygenated hydrocarbons much more than for fully oxygenated derivatives.

5 Biodegradability of Halogenated Hydrocarbons

Although halogenated hydrocarbons are noted and used for their nonreactivity, they often can be biodegraded if the environmental conditions are properly manipulated. In many cases, the key steps for biodegradation are dehalogenations. Once dehalogenated, the compounds follow the degradation sequences outlined in Sect. 4.

This section focuses on dechlorination reactions, which are the dehalogenations for chlorinated compounds, by far the most prevalent of the halogenated micropollutants. Dechlorination reactions occur by hydrolytic, oxidative, and reductive mechanisms [9] for aliphatic and aromatic compounds. Therefore this section is organized according to those three reactions and compounds susceptible to them.

5.1 Hydrolytic Dechlorination

Hydrolysis is a common example of nucleophilic substitution. An electron-rich nucleophile, H_2O or OH^- in this case, replaces an electron-withdrawing substituent, Cl^- in the case of dechlorination, present on an electron-deficient carbon atom [9, 48, 49]. In general, strong electron-withdrawing groups attached to a carbon atom or an adjacent carbon atom tend to make the carbon atom more electron deficient and a better candidate for nucleophilic attack. Strong electron-withdrawing substituents include all halogens, undissociated carboxylate groups, aromatic rings, and nitro groups. This trend is broken when the substituents are large and block access of the attacking nucleophile.

Figure 5 presents typical hydrolytic dechlorination pathways for chlorinated aliphatic and aromatic hydrocarbons. Both reactions demonstrate an important common feature: hydrolysis yields an organic molecule having the same number of electron equivalents. The dichloromethane reaction, which is common and seems to be rapid [50–53], illustrates that enzyme-catalyzed hydrolysis of carbon-chlorine bonds frequently requires an intracellular, nucleophilic cosubstrate, such as glutathione, which has the nucleophilic -SH group. After hydrolytic attack by H_2O, the glutathione is released, yielding formaldehyde, a common metabolic intermediate.

For the aromatic example, a chlorohydroxy intermediate is formed. The resonance structures illustrate that a negative charge is distributed at the *ortho* and *para* positions relative to the chlorine. Having a strong electron withdrawing substituent at those positions (like the carboxyl group in the *ortho* position

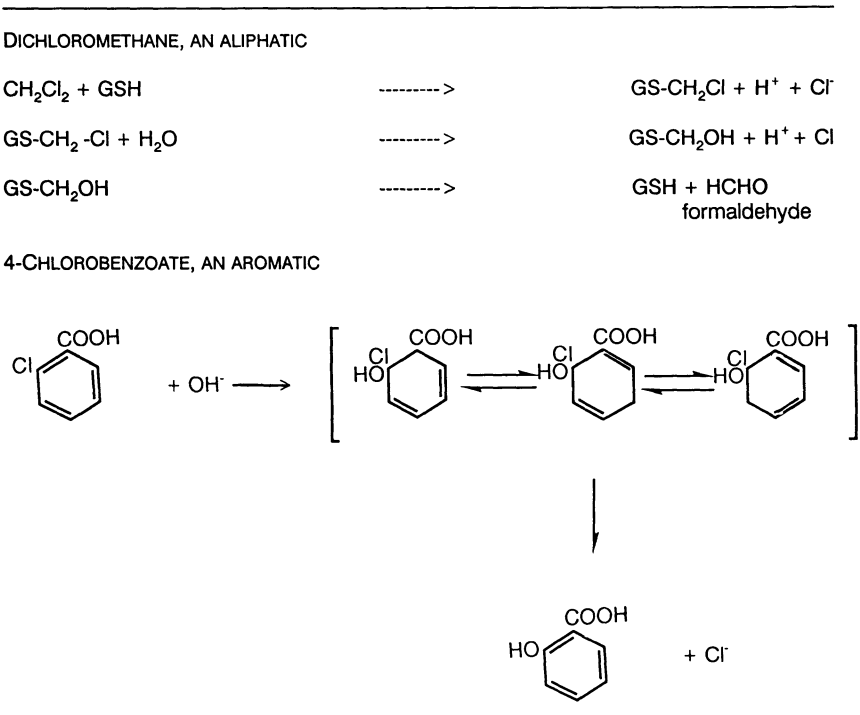


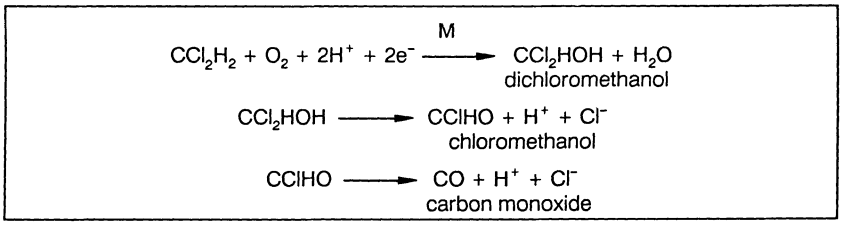
Fig. 5. Examples of hydrolytic dechlorination of an aliphatic and an aromatic hydrocarbon. GSH represents glutathione. The bracket represents resonance structures for the chlorohydroxybenzoic acid intermediate

here) helps stabilize the intermediate and allow hydrolysis. The final product, a hydroxybenzoic acid, is susceptible to the reactions reviewed in Sect. 4.

5.2 Oxidative Dehalogenation

Aerobic metabolism of halogenated 1- and 2-carbon aliphatics, once considered unlikely or even impossible [6], has now been reported for several microorganisms known to have oxygenase enzymes: methane monooxygenase in methanotrophs [54–56], toluene dioxygenase [57, 58], and ammonium monooxygenase [60]. Although details of the mechanisms differ among the oxygenase enzymes, all are similar in that part of the enzyme first accepts electrons from the reduced electron carrier (e.g., NADH) and then inserts oxygen from O_2 into the compound while eliminating Cl^- [9]. Figure 6 illustrates the reactions for dichloromethane and trichloroethene (TCE). In both cases, the first step is the oxygenation, which creates carbon atoms having bonds to O and Cl. These bonding arrangements are unstable, resulting in dechlorination and formation

Dichloromethane



Trichloroethene

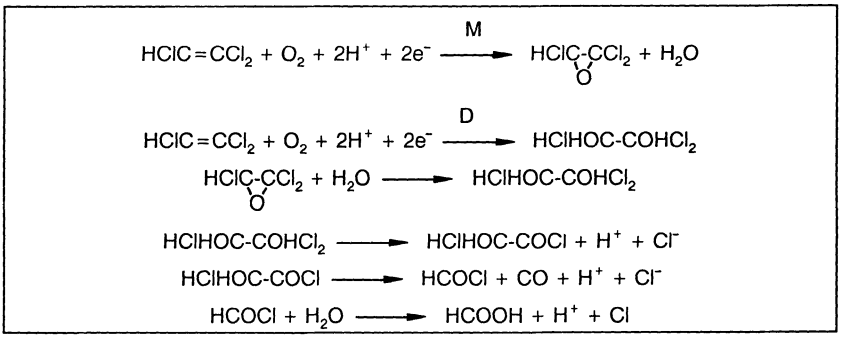


Fig. 6. Examples of oxidation dechlorination reactions initiated by the methane monooxygenase reaction (M) and by the toluene dioxygenase reaction (D) for chlorinated 1- and 2-carbon aliphatics. Electrons (e^-) are associated with electron carriers

of oxidized products (e.g., CO and HCOOH) that are further metabolized by common pathways.

Besides dichloromethane and TCE, the methane monooxygenase in methanotrophs is capable of oxidative dechlorination of several other halomethanes [54, 55, 60]. *Pseudomonas putido* Fl degrades TCE and all of the dichloroethenes [57, 58] when induced to produce the toluene dioxygenase. Vannelli et al. [61] report that the ammonium monooxygenase of *Nitrosomonas europaea* attacks a range of halomethanes, haloethanes, and haloethenes.

Oxidative dehalogenation of aromatics can follow the two strategies exemplified in Fig. 7. The first strategy, illustrated by 2-fluorobenzoate, is initial oxidative dehalogenation on the ring [61, 62] by a dioxygenase. Unfortunately, the dioxygenase enzyme also produces small amounts of 3-fluorocatechol (not shown in Fig. 7) through oxidative decarboxylation. The fluorocatechol is inhibitory and can thwart overall degradation by initial ring dehalogenation.

The more promising strategy employs initial ring cleavage, which is followed by dehalogenation. This is illustrated for the pesticide 2,4-dichlorophenoxyacetic acid, known as 2,4-D. The reaction is initiated by monooxygenation reactions that produce halogenated catechols [61, 63], which are subsequently *ortho* cleaved by a dioxygenase. Halogen ions are reduced from the unsaturated aliphatic by a series of reactions that differ from the reactions used for nonhalogenated analogs. The enzymes are induced by the halogenated substrates [61].

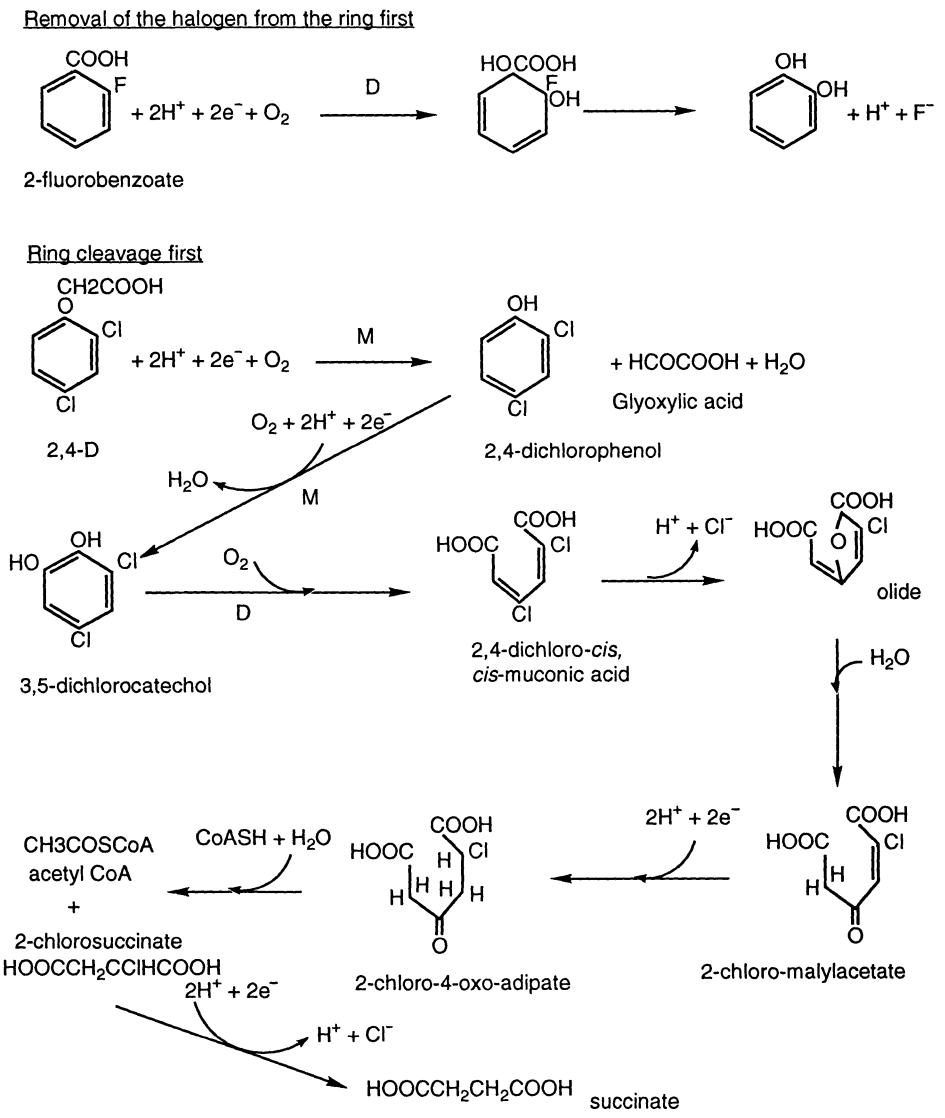


Fig. 7. Examples of oxidation dechlorination reactions for chlorinated aromatics. M and D indicate monooxygenase and dioxygenase reactions, respectively, Electrons (e^-) are associated with carriers

Among the aromatic compounds susceptible to oxidative dehalogenation are the polychlorinated biphenyls (PCBs) having relatively few Cl substituents [9, 64, 65]. PCB degradation begins with deoxygenation and ring cleavage of the PCB ring containing fewer Cl substituents. Unfortunately, the more chlorinated ring often remains undegraded, leading to a buildup of chlorinated benzoic acids.

5.3 Reductive Dechlorination

Reductive dechlorination is probably the most broadly acting means of dechlorinating aliphatic and aromatic compounds. However, its importance in drinking water treatment must be considered speculative, because reductive dechlorination is associated with anaerobic environments, where strongly reducing conditions are more likely than the aerobic conditions of most drinking-water processes.

Figure 8 illustrates the paths of reductive dechlorination [9, 66]. Dihaloelimination is possible when Cl is a substituent on adjacent carbon molecules connected via a single bond, as for 1, 2 dichloroethane (DCA). The alkane bond

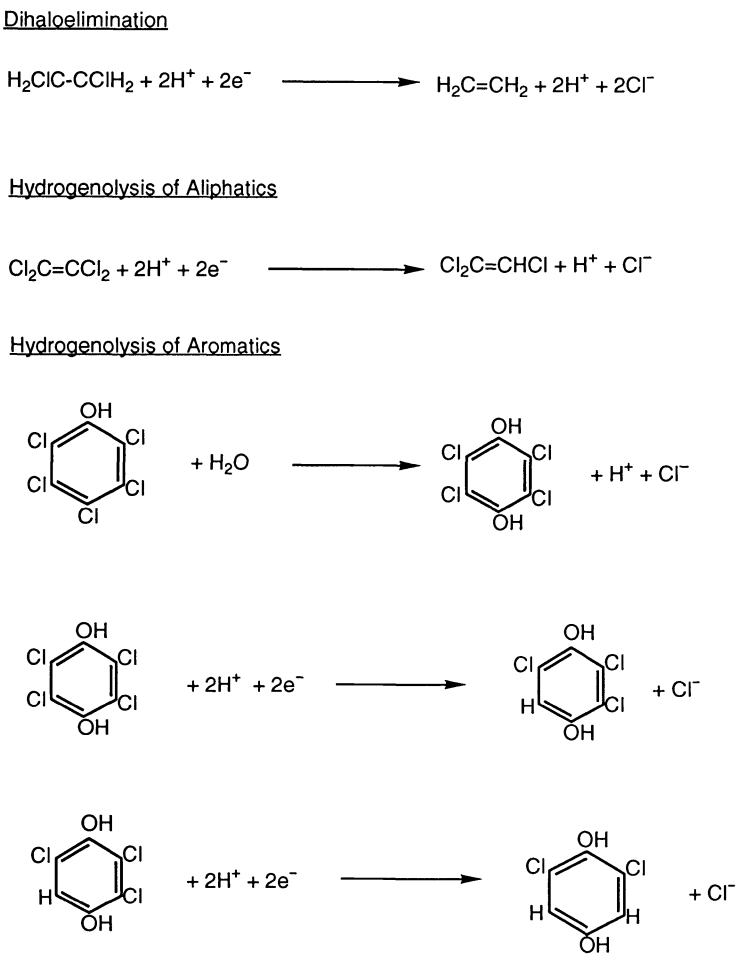


Fig. 8. Examples of reductive dechlorination reactions. Electrons (e^-) are associated with carriers

is converted to an alkene bond, while one Cl^- is released from each carbon. Two electrons are added from a reduced carrier.

Hydrogenolysis can occur for aliphatics and aromatics. As shown for tetrachloroethene (PCE) and pentachlorophenol (PCP), one Cl^- is released as that carbon is reduced by two electrons. The hydrogenolysis reactions can continue to remove Cl^- one-by-one, yielding a nonchlorinated species. However, the reductive reactions tend to slow as the number of Cl constituents declines [66]; hence, slightly chlorinated intermediates such as vinyl chloride (H_2CCHCl) and dichlorohydroquinone sometimes accumulate.

Reductive dechlorination is well established for the chlorinated methanes [67, 68], 2-carbon alkanes and alkenes [30, 68, 70, 74], pentachlorophenol [63, 75], chlorinated benzoates [77], PCBs [77], and other aromatics [78, 79]. Three recent research trends are potentially important. First, H_2 seems to be an excellent electron donor for microorganisms that carry out reductive dechlorinations [30, 74, 75]. Second, reductive dehalogenations have been observed in sulfate-, nitrate-, and oxygen-respiring systems [67, 30, 80], as well as in methanogenic systems. Third, manipulation of primary acceptor and donor concentrations allows the buildup of intracellular electron carriers and acceleration of reductive reactions [29, 30, 68]. These trends, when combined, suggest that reductive first steps are possible in the aerobic and denitrifying systems used in drinking water treatment, especially if concentrations of H_2 or other electron donors can be augmented.

5.4 Applicability

While most chlorinated organic compounds can be biodegraded under the proper conditions, the critical issue is whether or not these reactions actually occur with the microorganisms and conditions that are actually present during drinking-water treatment. In drinking-water treatment, the primary electron-donor substrate is usually a relatively low concentration of the natural humic material in water. Furthermore, micropollutant concentrations are usually low, while dissolved oxygen is high. These factors call into question the inducement of enzymes needed for biodegradation of the micropollutants and the feasibility of having reductive dechlorination steps.

Although little information is available to evaluate these issues, Manem and Rittmann [81] and Bae and Rittmann [68] studied key aspects. Manem and Rittmann [81] simulated biofilm processes used in drinking water treatment and demonstrated that μg/l levels of mono- and dichlorophenols and mono- and dichlorobenzenes were efficiently removed immediately or after a short induction period. Bae and Rittmann [68] demonstrated that carbon tetrachloride was removed reductively in aerobic and denitrifying biofilm reactors and that its removal could be accelerated by supplementation of a simple electron donor substrate (acetate in this case). These results, while limited, illustrate that the

biodegradative potentials can be made manifest in biofilm processes operated under drinking-water conditions.

6 Biodegradability of Taste-and-Odor Compounds

Although biodegradabilities in a number of the organic compounds causing tastes and odors were covered in Sects. 4 and 5, most of the important taste-and-odor compounds are sufficiently unique that special attention is warranted. Since Rittmann et al. [13] provide a detailed review of the biodegradability of taste-and-odor compounds, this section provides a succinct summary for those compounds not addressed directly in Sects. 4 and 5.

Geosmin and methylisobormeol (MIB), the two compounds most associated with earthy-musty odors, are an alicyclic alcohol and an alicyclic ketone, respectively. Degradation of alicyclic compounds is typically initiated by a monooxygenation to a lactone, which is unstable and is cleaved to a diacid. Although containing oxygen originally, geosmin and MIB require further oxygenation to insert O from molecular oxygen. Hence, their degradation should be similar to that of aromatics and monoxygenated aliphatics.

Biodegradation of geosmin and MIB is now well established [84, 89]. Most significantly, several of these studies [84, 87, 88] used biofilm reactors operated under conditions relevant to drinking-water treatment and found significant (up to 95%) removals of geosmin and MIB. Thus the biodegradation of these sources for earthy-musty odors should be expected in biological processes used to treat drinking water.

One special case is the chloroanisoles (i.e., chlorinated methyl phenol ethers). While ethers often are resistant to biodegradation, anisole is biodegradable [92]. Furthermore, Lundgren et al. [88] showed removal of 2,4,6-trichloroanisole in a sand filter.

The main causes of fishy odors – primary amines and aliphatic aldehydes – are easily biodegraded. The aliphatic aldehydes were discussed in Sect. 4. Primary amines are usually biodegraded by an initial oxidative deamination, which creates an aliphatic that fits into the pathway in Sect. 4.

Marshy-swampy-septic odors are associated with hydrogen sulfide and organic sulfur. All of these compounds are biodegradable in aerobic processes. The hydrogen sulfide serves as an electron donor by many sulfur-oxidizing bacteria [90, 91], while the organic sulfur compounds are converted to H_2S and aliphatic alcohols. Lundgren et al. [88] observed removal of dimethyltrisulfide in a sand filter.

Medicinal-antiseptic odors, which are usually caused by chlorination of phenolics, and odors associated with anthropogenic sources (e.g., chlorinated solvents, chlorinated benzenes, and BTEX) and disinfectant byproducts (e.g., chloroform and aldehydes) are caused by the compounds discussed in Sects. 4

and 5. With the possible exception of chloroform, these compounds appear to be biodegraded during biological treatment.

7 Summary

While biofilm processes are mainly used to remove organic and inorganic electron donors that cause the water to be biologically unstable, they also are able to biodegrade a range of organic micropollutants of health and aesthetic concern. In most cases the organic micropollutants are biodegraded as secondary substrates, because these concentrations are too low and/or they are present too fleetingly to allow their biodegradation to support a steady-state biofilm. Therefore the appropriate tool for modeling the degradation kinetics of these secondary substrates is the nonsteady-state-biofilm model described in Sect. 3.

Although almost all of the micropollutants are biodegradable, Sects. 4–6 illustrate that many of them require initial oxygenation steps that insert molecular oxygen into the substrate. Once fully oxygenated, these substrates are normally biodegraded by pathways common to many bacteria. For highly chlorinated micropollutants, initial biodegradation steps may be reductive dechlorinations.

We are still at the early stages of defining what biodegradations are possible and practical in biological drinking-water treatment. Significant questions remain about the kinetics of initial oxygenation and dechlorination reactions under realistic treatment conditions. Nevertheless, initially positive results [23, 68, 81, 84, 87, 88] with some of the most difficult chlorinated and taste-and-odor compounds, as well as important advances with methanotrophic bacteria and accelerating reductive reactions, give reason for optimism that micropollutant biodegradation will become a reliable facet of biological drinking-water treatment.

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8 References

1. Rittmann BE (1993) Fundamentals and applications of biofilm processes in drinking-water treatment Handbook Environ Chem, this volume
2. Rittmann BE, Huck PM (1989) CRC Crit Rev Environ Control 19: 2:119
3. Bouwer EJ, Crowe PB (1988) J Amer Water Works Assn 80: 9:82

4. Rittmann BE, Snoeyink VL (1984) J Amer Water Works Assn 76: 10:106
5. Stratton R, Namkung E, Rittmann BE (1983) J Amer Water Works Assn 75:463
6. Kobayashi H, Rittmann BE (1982) Environ Sci Technol 16:170A
7. Rittmann BE (1985) Sci Total Environ 47:99
8. Office of Technology Assessment (1984) Protecting the Nation's Groundwater from Contamination, Vol. 1. OTA-0-233, Washington, DC, p. 18
9. Rittmann BE, Seagren E, Wrenn B, Valocchi AJ, Ray C, Raskin L (1994) In Situ Bioremediation, second ed., Noyes Publ., Inc., Park Ridge, New Jersey.
10. Hubbs SA (1983) Occurrence of volatile organic chemicals, in Occurrence and Removal of Volatile Organic Chemicals in Drinking Water, Amer Water Works Assn Res Foundation, Denver, Colorado, p. 31
11. Fleischacker SJ, Randtke SJ (1983), J Amer Water Works Assn 75:132
12. Hubbs SA, Wise C, Vaughn WC (1981) Trace organic monitoring in the Ohio River. Proc Natl Conf Environ Engr, Am Soc Civil Engrs (Atlanta, Georgia), p. 189
13. Rittmann BE, Gantzer CJ, Montiel A (1994) in: Suffett M, Mallevialle J (eds) Control of Tastes and Odors in Drinking Water, Amer Water Works Assn, Denver, Colorado, p 203
14. Mallevialle J, Suffett IH (1987) Identification and Treatment of Tastes and Odors in Drinking Water. Amer Water Works Assn Res Foundation, Denver, Colorado
15. Alexander HC et al (1982) J Amer Water Works Assn 74: 11:595
16. Verschueren K (1983) Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York
17. Amoore JE (1986) J Amer Water Works Assn 78: 3:70
18. Palmer CM (1962) Algae in water supplies, U.S. Public Health Service Pub No 657, Washington, DC
19. Rittmann BE, McCarty PL (1981) J Environ Engr 107:831
20. Rittmann BE, McCarty PL (1980) Biotechnol Bioengr 22:2343
21. Rittmann BE, Jackson D, Storck SL (1988) in: Wise DL (ed), Biotreatment Systems, Vol 3, CRC Press, Boca Raton, Florida, p. 15
22. Namkung E, Stratton RG, Rittmann BE (1983) J Water Poll Control Fedn 55:1366
23. Bae W, Odencrantz JE, Rittmann BE, Valocchi AJ (1990) J Contam Hydrol 6:53
24. Namkung E, Rittmann BE (1987) J Water Poll Control Fedn 59:670
25. Rittmann BE (1982) Biotechnol Bioengr 24:1341
26. Atkinson B, Daoud IS (1968) Trans Inst Chem Engrs 46:19
27. Suidan MT, Rittmann BE, Traegner U (1987) Water Res 21:491
28. Malmstead MJ (1992) Modeling oxygen-dependent biodegradation of quinoline in batch and column studies. MS thesis, Dept. of Civil Engineering, University of Illinois, Urbana, Illinois
29. Bae W (1992) Modeling dual-limitation kinetics incorporating intracellular cofactor responses. PhD dissertation, Dept. of Civil Engineering, University of Illinois, Urbana, Illinois
30. Wrenn BA (1991) Substrate interactions during the anaerobic biodegradation of 111-trichloroethane, PhD dissertation, Dept. Civil Engineering, University of Illinois, Urbana, Illinois
31. Sáez PB, Rittmann BE (1993) Biodegradation kinetics of a mixture containing a primary substrate (phenol) and an inhibitory co-metabolite (4-chlorophenol). Biodegradation, 4:3
32. Smets BF, Rittmann BE (1990) Water Res 24:355
33. Rittmann BE, Henry B, Odencrantz JE, Sutfin JA (1992). Biodegradation 2:171
34. Gottschalk G (1986) Bacterial Metabolism, 2nd ed., Springer-Verlag Inc., New York
35. Higgins IJ, Gilbert PD (1978) in: Chater KWA, Somerville, HS, (eds) The Oil Industry and Microbial Ecosystems, Heydon and Sons Ltd., London, p. 80
36. Singer DR, Finnerty WR (1984) in: Atlas RM (ed) Petroleum Microbiology, Macmillan Publ. Co., New York, p 1
37. Shelton RA, Kochi JK (1981) Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York, p 231
38. Ribbons DW, Eaton RW (1982) in: Chakrabartg AM (ed) Biodegradation and Detoxification of Environmental Pollutants, CRC Press Inc., Boca Raton, Florida, p 59
39. Gibson DT, Subramanian V (1984) in: Gibson DT (ed) Microbial Degradation of Organic Compounds, Marcel Dekker Inc., New York, p 181
40. Traxler RW, Bernard JM (1969) Intl Biodeterioration Bull 5:21
41. Parekh VR, Traxler RW, Sobek JM (1977) Appl Environ Microb 33:881
42. Grbic-Galic D, Vogel TM (1987) Appl Environ Microb 53:254
43. Zeyer J, Kuhn EP, Schwarzenbach RP (1986) Appl Environ Microb 52:944
44. Pirnik MP (1977) CRC Crit Rev Microb 5:413

45. Perry JJ (1984) in: Atlas RM (ed) Petroleum Microb, Macmillan Publ. Co., New York, p 61
46. Lehninger AL (1975) Biochemistry, 2nd ed., Worth Publishers Inc., New York
47. Brock TD, Madigan MT (1991) Biology of Microorganisms, 6th ed., Prentice-Hall Inc., Engelwood Cliffs, New Jersey
48. Morrison RT, Boyd RN (1973) Organic Chemistry, Allyn and Bacon, Boston, Mass.
49. Goldman P (1972) in: The Degradation of Synthetic Organic Molecules in the Biosphere, Nat. Acad. Sci. Press, Washington, D.C., p 147
50. Rittmann BE, McCarty PL (1980) Appl Environ Microb 39:1225
51. Brunner W, Staub D, Leisinger T (1980) Appl Environ Microb 40:950
52. LaPat-Polasko LT, McCarty PL, Zehnder AJB (1984) Appl Environ Microb 47:825
53. Kohler-Staub D, Leisinger T, J Bacteriology 162:676
54. Colby J, Stirling DI, Dalton H (1977) Biochem J 165:395
55. Patel RN, Hou CT, Laskin AI, Felix A (1982) Appl Environ Microb 44:1130
56. Tsien HC, Brusseau GA, Hanson RS, Wackett LP (1989) Appl Environ Microb 55:3155
57. Nelson MJK, Montgomery SO, Pritchard PH (1988) Appl Environ Microb 54:604
58. Wackett LP, Gibson DT (1988) Appl Environ Microb 54:1703
59. Vannelli T, Logan M, Arciero DM, Hooper AB (1990) Appl Environ Microb 56:1169
60. Dalton H, Stirling DI (1982) Phil Trans Royal Soc. London, B. Biol. Sci. 297:481
61. Reineke W (1984) in: Gibson DT (ed) Microbial Degradation of Organic Compounds, Marcel Dekker Inc., New York, p 319
62. Reineke W, Knackmuss HJ (1988) Ann Rev Microb 42:263
63. Steiert JG, Crawford RL (1985) Trends in Biotechnology 3:300
64. Furukawa K (1982) in: Chakrabarty AM (ed) Biodegradation and Detoxification of Environmental Pollutants, CRC Press, Boca Raton, Florida, p 33
65. Safe SH (1984) in: Gibson DT (ed) Microbial Degradation of Organic Compounds, Marcel Dekker Inc., New York, p 361
66. Vogel TM, Criddle CS, McCarty PL (1987) Environ Sci Technol 21:722
67. Bouwer EJ, McCarty PL (1983) Appl Environ Microb 45:1295
68. Bae W, Rittmann BE (1990) Effects of electron acceptor and electron donor on biodegradation of CCl_4 by biofilms. Proc 1990 Spec Conf Environ Engr, Amer. Soc. Civil Engrs., Arlington, Virginia (July 1990), p 390
69. Galli R, McCarty PL (1989) Appl Environ Microb 55:837
70. Parsons F, Lage GB (1985) J Amer Water Works Assn 77:52
71. Fathepure BZ, Nengu JP, Boyd SA (1987) Appl Environ Microb 52:2671
72. Freedman DL, Gossett JM (1989) Appl Environ Microb 55:2144
73. Belay N, Daniels L (1987) Appl Environ Microb 53:1604
74. Elgi C, Scholtz R, Cook AM, Leisinger T (1987) FEMS Microbiology Letters 43:257
75. Apajalhti JHA, Salkinoja-Salonen MS (1987) J Bacteriology 169:5125
76. Shelton DR, Tiedje JM (1984) Appl Environ Microb 48:840
77. Nies L, Vogel TM (1990) Appl Environ Microb 56:2612
78. Suflita JM, Robinson JA, Tiedje JM (1983) Appl Environ Microb, 45:1466
79. Gibson SA, Suflita JM (1990) Appl Environ Microb 56:1825
80. Stevens TO, Linkfield TG, Tiedje JM (1988) Appl Environ Microb 54:2938
81. Manem JA, Rittmann BE (1992) J. Amer. Water Works Assn. 84:152
82. Trudgill PW (1984) in: Gibson DT (ed) Microbial Degradation of Organic Compounds, Marcel Dekker Inc., New York
83. Trudgill PW (1990) Biodegradation 1:93
84. Namkung E, Rittmann BE (1987) J Amer Water Works Assn 79: 7:107
85. Izaguirre G, Wolfe RL, Means EG (1988) Appl Environ Microb 54:2424
86. Izaguirre G, Wolfe RL, Means EG, Water Sci Technol 20: 8/9:205
87. Hattori K (1988) Water Sci Technol 20: 8/9:237
88. Lundgren BV, Grimvall A, Sävenhed R (1988) Water Sci Technol 20: 8/9:245
89. Narayan LV, Nunez WJ (1974) J Amer Water Works Assn 66: 9:532
90. Grady CPL, Lim HC (1980) Biological Wastewater Treatment, Marcel Dekker Inc., New York
91. Ludzack FJ, Ettinger MB (1960) J Water Pollution Control Fedn 32:1173

Fundamentals and Application of Biofilm Processes in Drinking-Water Treatment

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List of Symbols and Abbreviations

a = specific surface area of biofilm, m^{-1}
b = biomass endogenous-decay coefficient, day^{-1}
b' = $b + b_{det}$ = overall biofilm loss-rate coefficient, day^{-1}
b_{det} = first-order rate coefficient for biofilm detachment, day^{-1}
d_p = medium-particle diameter, m
D = molecular diffusion coefficient for the substrate in the bulk liquid, m^2 day^{-1}
D_f = molecular diffusion coefficient for the substrate in the biofilm, m^2 day^{-1}
D_f^* = D_f/D
f = ratio of actual steady-state flux to the deep flux
g = gravitational constant, 9.8 ms^{-2}
h = liquid holdup
J = substrate flux, gs m^{-2} day^{-1}

J_R = reference flux = minimum flux giving a deep, steady-state biofilm, gs m^{-2} day^{-1}
J^* = dimensionless flux = $J[Kq_mX_fD_f]^{1/2}$
J^*_{deep} = dimensionless substrate flux into a deep biofilm
J^*_R = dimensionless value of J_R
k_m = mass-transport coefficient, m day^{-1}
K = substrate concentration at which the utilization rate is one-half the maximum rate, gs m^{-3}
K^* = dimensionless mass transfer coefficient = $D/L[K/q_mX_fD_f]^{1/2}$
L = thickness of an effective diffusion layer, m
L_f = biofilm thickness, m
L^* = L/τ
q_m = maximum specific rate of substrate utilization, gs gx^{-1} day^{-1}
Q = liquid flow rate, m^3 day^{-1}
r_{dep} = rate of deposition of suspended biomass, gx day^{-1}
r_{det} = rate of biofilm detachment, gx day^{-1}
r_{diff} = rate of substrate accumulation due to diffusion at a point in the biofilm, gs m^{-3} day^{-1}
r_{ut} = rate of substrate utilization by suspended biomass, gs m^{-3} day^{-1}
r_{utf} = rate of substrate utilization at a point in the biofilm, gs m^{-3} day^{-1}
S = concentration of rate-limiting substrate in the bulk liquid, gs m^{-3}
S_f = substrate concentration at a point in the biofilm, gs m^{-3}
S_{min} = minimum substrate concentration to support a steady-state biofilm = $K(b'/Yq_m - b')$, gs m^{-3}
S_s = substrate concentration at the outer surface of the biofilm, gs m^{-3}
S^0 = influent substrate concentration, gs m^{-3}
S^* = S/K = dimensionless substrate concentration
S^*_{min} = growth potential = $b'/Yq_m - b'$
t = time, days
u = superficial flow velocity m day^{-1}
V = total volume of reactor or reactor segment, m^3
X_a = concentration of active biomass in the bulk liquid, gx m^{-3}
X_f = biomass density in the biofilm, gx m^{-3}
X^0_a = influent active-biomass concentration, gx m^{-3}
Y = true yield, gx gs^{-1}
z = distance dimension normal to the biofilm surface, m
α = constant used to compute f
β = constant used to compute f
ε = porosity of the bed
μ = absolute viscosity of the liquid, g m^{-1} day^{-1}
μ_m = maximum specific growth rate, day^{-1}
ρ_p = density of the medium particles, g m^{-3}
ρ_w = density of the liquid, g m^{-3}
σ = liquid shear stress, dyne cm^{-2}
τ = standard biofilm depth dimension [21], m

Abstract

Biofilm processes are used primarily to produce a biologically stable drinking water, which does not foster growth of microorganisms during its distribution. This article describes the characteristics of biofilms and biofilm processes. It emphasizes quantitative modeling of the phenomenon controlling the accumulation of biofilm and the removal of organic and inorganic materials comprising biological instability. The article describes a practical means, the normalized surface loading, for applying biofilm modeling to the design and analysis of biofilm processes. Special attention is given to the most common applications in drinking-water treatment: aerobic oxidation of low concentrations of biodegradable organic material, nitrification of ammonium nitrogen, and denitrification of nitrate nitrogen.

1 Biological Drinking Water Treatment

Although drinking-water treatment is normally equated with physical/chemical processes, biological treatment is playing an increasingly important role. In fact, biological treatment is becoming an indispensable part of a state-of-the-art treatment facility that produces a drinking water that is simultaneously microbiologically safe, has excellent taste and odor characteristics, contains low-risk levels of synthetic organic chemicals, and maintains its high quality through distribution. Biological treatment is gaining acceptance worldwide, because it is the most effective means to expand the capabilities of more traditional physical/chemical processes to handle a suite of new water-quality challenges, such as disinfection byproducts, bacterial regrowth, and high nitrogen concentrations.

1.1 Treatment Goals

The most fundamental goal of biological treatment is to produce a water that is biologically stable, which means that it does not support significant growth of microorganisms during its distribution [1]. That goal is accomplished in the treatment process by bacterially catalyzed removal of reduced compounds whose oxidation yields energy that can be used for microbial growth. Because oxidation, energy yield, and growth occur within the treatment process, the finished water is free of growth-supporting materials and is biologically stable. A water that is biologically unstable can lead to serious water-quality problems, such as tastes, odors, excessive bacterial counts, turbidity, and accelerated corrosion [1].

The term that encompasses all materials causing biological instability is *primary electron-donor substrate*. The word *substrate* indicates that the compound is biochemically utilized by the bacteria. The term *electron donor* means that the substrate is reduced and can release electrons through a series of oxidation reactions; these electron-transfer reactions are responsible for energy production by the bacteria. The word *primary* indicates that the electrons and energy

generated from this substrate are used to grow and maintain the bacteria [2, 3]. Therefore the fundamental goal of a biological treatment of drinking water is to reduce the concentrations of primary electron-donor substrates.

Biological treatment can achieve additional goals, which can be placed into three broad categories: indirect quality improvements, secondary removals, and removals of primary electron-acceptor substrates.

When biological stability is achieved, the water quality can be improved in the following indirect ways [1, 4]:

- Disinfectant byproducts are reduced, because high chlorine residuals are not needed to arrest bacterial growth during distribution
- Corrosion, tastes, and odors caused by disinfectants are reduced
- Tastes, odors, and turbidity caused by bacteria in the distribution system are minimized.

When a substantial amount of active biomass is accumulated in a biological process due to primary substrate utilization, secondary utilization [2, 3] of biodegradable materials that do not act as primary substrates is possible. Secondary removals occur for compounds causing tastes and odors [5, 6] and for a range of synthetic organic chemicals of health concern [5, 7].

Finally, biological processes are sometimes employed to remove primary electron-acceptor substrates that are of water-quality concern. The notable example is NO_3^- present at concentrations greater than about 10 mg N/l [8], which places infants at risk of methemoglobinemia. While the normal goal of biological treatment is to remove the primary electron donor substrate, the special case of NO_3^- requires removal of the substrate to which the electrons are transferred. Ironically, extra electron donor must often be added to assure adequate removal of NO_3^-.

1.2 Biofilms

A biofilm is an aggregate of bacteria and extracellular polymers that is attached to a solid surface. The key words in the definition are *aggregate* and *attached*. *Aggregation* distinguishes biofilms from dispersed bacteria by the significant role that mass-transport processes play in controlling the rate of substrate utilization, especially by bacteria deep inside the aggregate [9, 10]. *Attachment* to a solid surface means that the bacteria do not move with the flowing water, but are selectively retained.

Aggregation and attachment present potential benefits and disadvantages to bacteria. The main disadvantage is that mass-transport resistances expose the bacteria in the biofilm to substrate concentrations lower than occur in the bulk liquid; because bacterial growth rates are usually proportional to substrate concentration, being in a biofilm is a competitive disadvantage compared to dispersed growth. On the other hand, good retention by attachment keeps bacteria in the system, where they can be continually exposed to a fresh supply of substrate. Furthermore, bacteria deep inside the biofilm are the most protected

from loss [10, 11]. The fact the biofilms are ubiquitous in aqueous environments suggests that the benefits the bacteria receive from biofilm growth frequently outweigh the disadvantages.

The drinking-water application accentuates the advantages of biofilm growth for the users of biological treatment, and virtually all biological processes used in drinking-water treatment are of the biofilm type. The advantages stem from the need to provide reliable and economical treatment for large volumes of water containing low concentrations of biodegradable materials. Economy and large volumes dictate that the processes have short liquid detention times, but reliability requires a large and stable accumulation of bacteria. Thus, the excellent biomass retention of biofilms, even when the liquid detention is very short, is the paramount advantage for achieving economical and reliable treatment.

1.3 Biofilm Reactors Used in Drinking-Water Treatment

Biofilm treatment of drinking water takes many forms [4, 12]. It can be a stand-alone process designed solely for biological treatment, or it can be integrated into the function of physical/chemical processes that utilize solid media. The following summary describes the three main configurations that biofilm processes take: small-granule filters, large-granule fixed beds, and fluidized beds.

Slow sand filters, rapid sand filters, mixed-media rapid filters, floc-blanket reactors, and granular activated carbon (GAC) absorbers [4, 12, 13] are the examples of small-granule filters that have biofilm activity. Small granules (i.e., less than 1 mm in diameter) are used to accentuate the physical/chemical phenomena of particle filtration (for the first four processes) or organic-solute absorption (for the GAC).

Biofilm accumulation is a naturally occurring event in these processes, but it can be enhanced by pre-ozonation of the water, which is well known to make the natural organic material more biodegradable. However, enhanced biofilm accumulation can be deleterious in small-granule processes when the concentration of biodegradable material is too large, creating problems of oxygen depletion, which can result in tastes and odors; poor removal of biodegradable material; and excessive head loss caused by too much biomass clogging the pores [4, 5].

When small-granule processes are not feasible, their problems can be overcome by employing large-granule media such as expanded clay, gravel, pozzolona, or plastic [4, 5]. The larger pore size, typically 4–10 mm, allows bed aeration for oxygen supply and nearly eliminates pore clogging. Use of large granules normally means that the process is dedicated to biological treatment, and filtration or absorption must be carried out in subsequent small-granule filters.

The fluidized-bed biofilm process combines advantages of small- and large-granule processes. Here, small granules of sand or carbon are fluidized by the upward flow of water. Fluidization expands the medium particles, thereby giving

large pores with small media. The large pores prevent clogging and allow bed aeration, if necessary. The small particles give a very high surface area, which maintains the potential for very high biofilm accumulation. In general, fluidized beds are not good particle filters [14], although they can be effective in solute absorption [15].

2 Fundamentals of Biofilm Kinetics

Although biofilm processes come in many different configurations and remove a wide range of materials, the basic phenomena that control performance are the same: substrate utilization and diffusion inside the biofilm, mass transport between the bulk liquid and the biofilm, and biofilm growth and loss. Furthermore, these phenomena occur in reactors that are essentially governed by the same mass balances on substrates and biomass. Therefore, this section on fundamentals of biofilm kinetics starts with the required mass balances that govern all biofilm processes. Then it develops the most important rate expressions needed to quantify the mass balances. Finally, it presents a practical means, the normalized surface loading, to solve the mass balances in such a manner that design and analysis are straightforward and intuitive.

The development addresses the removal of the primary electron-donor substrate and its relationship to the accumulation of biomass. Hence, this article pertains directly to the removal of biological instability, the most fundamental goal of biological drinking-water treatment. It does not explicitly address indirect quality improvements and secondary removals, which are discussed elsewhere [16]. However, the article's scope is expanded to include the removal of NO_3^-, a primary electron acceptor, in the section on applications.

2.1 Mass Balances for a Biofilm Reactor

The minimum requirement to model a microbiological process is to have mass balances on active biomass and the primary substrate that limits the rate of biomass growth. In most cases, the rate-limiting primary substrate is the electron donor, and this development makes that assumption.

Three mass balances are needed for a biofilm process: substrate in the bulk liquid, biomass suspended in the bulk liquid, and biomass attached as biofilm. (Substrate in the biofilm can normally be neglected, because the biofilm's liquid volume is insignificant.) For a completely mixed reactor or segment of a reactor, the three mass balances are:

Substrate

$$hV\frac{dS}{dt} = Q(S^\circ - S) - r_{ut}hV - JaV \tag{1}$$

Suspended Biomass

$$hV\frac{dX_a}{dt} = Q(X_a^\circ - X_a) + (Yr_{ut} - bX_a)hV + r_{det} - r_{dep} \quad (2)$$

Biofilm Biomass

$$aV\frac{dX_fL_f}{dt} = (JY - bX_fL_f)aV - r_{det} + r_{dep} \quad (3)$$

where V = total volume of the reactor or reactor segment, m^3
h = liquid holdup, or ratio of bulk liquid volume to total volume
hV = volume of bulk liquid, m^3
a = specific surface area of biofilm, m^{-1}
aV = surface area of biofilm, m^2
S = concentration of rate-limiting substrate in the bulk liquid, gs m^{-3}
X_a = concentration of active biomass in the bulk liquid, gx m^{-3}
X_ahV = biomass in the bulk liquid, gx
X_f = biomass density of the biofilm, gx m^{-3}
L_f = biofilm thickness, m
X_fL_f = biofilm accumulation per unit surface area, gx m^{-2}
X_fL_faV = biofilm mass, gx
t = time, days
Q = liquid flow rate, m^3 day^{-1}
S° = influent substrate concentration, gs m^{-3}
X_a° = influent concentration of suspended biomass, gx m^{-3}
r_{ut} = rate of substrate utilization by the suspended biomass, gs m^{-3} day^{-1}
J = substrate flux into the biofilm, gs m^{-2} day^{-1}
Y = true yield of biomass grown per unit of substrate consumed, gx gs^{-1}
b = biomass endogenous decay rate, $days^{-1}$
r_{det} = rate of detachment of biofilm, gx day^{-1}
r_{dep} = rate of deposition of suspended biomass, gx day^{-1}

For most treatment reactors, a set of simplifications can be made to reduce the complexity of Eqs. (1)–(3).

- Operating conditions usually change slowly enough that steady state can be assumed. Hence, the left side of each equation is set to zero: $hV(dS/dt) = hV(dX_a/dt) = aV(dX_fL_f/dt) = 0$.
- Because the suspended biomass (hVX_a) is usually only a very small fraction of the biofilm biomass (aVX_fL_f) in biofilm reactors [5, 17], the suspended removal of substrate can be neglected in Eq. (1), i.e., $0 \simeq r_{ut}hV \ll JaV$.
- When biofilm biomass greatly exceeds suspended biomass, the rate of biofilm detachment greatly exceeds the other nonadvective sources and sinks suspended biomass in Eq. (2), i.e., $0 \simeq QX_a^\circ + (Yr_{ut} - bX_a)hV - r_{dep} \prec\prec r_{det}$.

- Similarly, r_{dep} can be neglected in Eq. (3).

These simplifications reduce Eqs. (1)–(3) to Eqs. (4)–(6):

$$0 = Q(S^\circ - S) - JaV \tag{4}$$

$$0 = -QX_a + r_{det} \tag{5}$$

$$0 = (JY - bX_fL_f)aV - r_{det}. \tag{6}$$

In simple terms, these equations state that substrate removal ($S^\circ - S$) is proportional to the substrate flux (J), effluent biomass (X_a) is proportional to the detachment rate, and the net biofilm growth rate ($YJ - bX_fL_f$) is proportional to the detachment rate.

The goal of biofilm kinetic modeling, which is presented in the next two sections, is to provide relationships for the biofilm-specific terms in Eqs. (4)–(6). In particular, expressions are needed for J and r_{det}.

The simplifications used to convert Eqs. (1)–(3) to Eqs. (4)–(6) are normally valid for biofilm processes used in drinking-water treatment, because the liquid detention times are very short and substrate concentrations are very low [1, 4]. These conditions prevent buildup of suspended biomass. However, the simplifications may not be correct for all cases in which biofilm is important. When liquid detention times are long and/or substrate concentrations are large, suspended biomass and deposition cannot be neglected. Examples include certain situations of groundwater flow and the anaerobic treatment of high-strength wastewaters. In such cases, the validity of each simplification must be examined.

2.2 Rate Expressions for the Biofilm

This section builds the foundation for the relationship for J. It starts with the description of an idealized biofilm and then derives the differential and algebraic equations describing substrate utilization and biomass accumulations in the biofilm. A relationship for b_{det} is presented as part of the development.

Figure 1 is a sketch of the idealized biofilm used for kinetic modeling. The idealized biofilm conforms to the definition of a base biofilm [9, 19], which is impermeable to water flow, has a relatively smooth surface, has a uniform biomass density of X_f, and has a locally uniform thickness of L_f. Figure 1 illustrates how internal and external mass-transport resistances reduce the substrate concentrations that the bacteria "see", i.e., S_f, to values below S in the bulk liquid. In some cases the reduction in concentration is complete, giving the so-called *deep* biofilm, in which the substrate concentration reaches zero. When the reduction does not take the concentrations to zero, the biofilm is called *shallow*. In some cases the concentration reduction is minimal, yielding the *fully penetrated* biofilm having $S_f = S$.

At any position inside the biofilm, substrate is utilized in the same manner as it is for suspended bacteria. The most common expression for the utilization rate is the Monod expression:

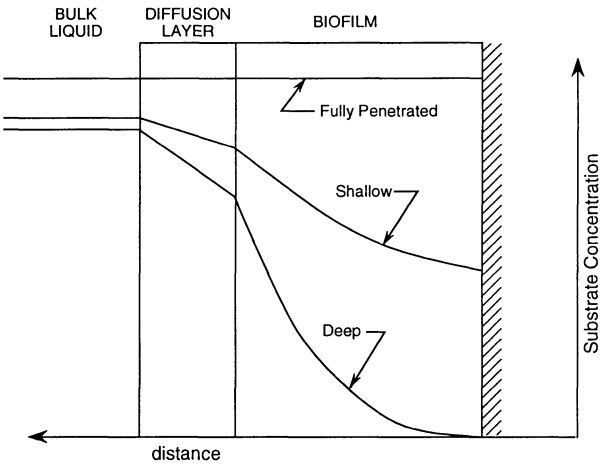

Fig. 1. Sketch of the idealized biofilm and characteristic deep, shallow, and fully penetrated profiles of substrate concentration

$$r_{utf} = \frac{q_m X_f S_f}{K + S_f} \tag{7}$$

in which r_{utf} = rate of substrate utilization at a position in the biofilm, gs m^{-3} day^{-1}
S_f = substrate concentration at that point in the biofilm, gs m^{-3}
q_m = maximum specific rate of substrate utilization, gs gx^{-1} day^{-1}
K = substrate concentrations at which the utilization rate is one-half its maximum rate, gs m^{-3}

The key features of Eq. (7) are that S_f is the substrate concentration at a position inside the biofilm and can change with position.

The substrate is transported to the bacteria inside the biofilm by molecular diffusion, given by Fick's second law:

$$r_{diff} = D_f \frac{d^2 S_f}{dz^2} \tag{8}$$

in which r_{diff} = rate of substrate accumulation due to diffusion, gs m^{-3} day^{-1}
D_f = molecular diffusion coefficient for the substrate inside the biofilm, m^2 day^{-1}
z = distance dimension normal to the biofilm surface, m.

Because utilization and diffusion occur simultaneously, the rates in Eqs. (7) and (8) must equal each other when the substrate concentration reaches steady-state, which occurs rapidly [20]. Then the governing equation for substrate inside the biofilm is

$$0 = D_f \frac{d^2 S_f}{dz^2} - \frac{q_m X_f S_f}{K + S_f}. \tag{9}$$

Substrate must be transported from the bulk liquid to the outer surface of the biofilm. This is described with Fick's first law:

$$J = \frac{D}{L}(S - S_s) \tag{10}$$

in which D = molecular diffusion coefficient for the substrate in the bulk water, $m^2\ day^{-1}$
L = thickness of an effective diffusion layer, m; L is frequently computed from a mass transport coefficient (k_m, $m\ day^{-1}$) by $L = D/k_m$.
S_s = substrate concentration at $z = 0$, which is the outer surface of the biofilm, $gs\ m^{-1}$.

Equation (10) is often used as a boundary condition for Eq. (9). The second boundary condition is no substrate flux into the attachment surface,

$$\frac{dS_f}{dz} = 0 \qquad \text{for } z = L_f \tag{11}$$

If L_f is known, solution of Eq. (9), subject to the boundary conditions of Eqs. (10) and (11), yields the substrate flux and the substrate-concentration profile [21]. Since the model is for the rate-limiting primary substrate, its utilization determines the amount of biofilm accumulation. Thus, L_f cannot be known *a priori*; instead, it must be predicted by linking substrate utilization (Eq. (9)) to the biofilm mass balance, Eq. (6), which is repeated here for convenience, $0 = (JY - bX_fL_f)aV - r_{det}$.

In Eq. (6), Y, b, X_f, a, and V are constants. J and L_f are the dependent variables for which a solution is desired. However, r_{det} is a rate term that requires a mathematical expression.

Detachment of biofilm is a complicated phenomenon that can involve erosion due to liquid shear stress, attrition due to particle-to-particle abrasion, loss due to turbulence-induced pressure fluctuations, and massive sloughing due to chemically induced "faults" inside the biofilm [19, 22, 23].

Except when sloughing occurs, the rate of detachment can be written in the general form [22, 24]:

$$r_{det} = b_{det}X_fL_faV \tag{12}$$

in which b_{det} = first-order rate coefficient for biofilm detachment, day^{-1}.

Substitution of Eq. (12) into Eq. (6) gives

$$0 = (JY - bX_fL_f)aV - b_{det}X_fL_faV \tag{13}$$

which simplifies to

$$0 = JY - (b + b_{det})X_fL_f = JY - b'aX_fL_f. \tag{14}$$

The total biofilm loss coefficient is b' (day^{-1}) and is the sum of loss from endogenous decay (b) and detachment (b_{det}).

Depending on experimental conditions, a range of factors affect b_{det}. These factors include the liquid shear stress [22, 24, 25, 26], the biofilm density [25, 26], the biofilm thickness [24, 25, 26, 27], abrasion [26, 27], turbulence [26, 27], surface irregularity [28], and growth rate [29]. No consensus has emerged, largely because very different systems have been studied. Therefore estimation of values for b_{det} must be done with caution.

The following equation provides a first approximation for media that are not highly irregular and not aerated. It was derived by Rittmann [24] and shown to be a good predictor for relatively smooth, regular media by Chang and Rittmann [28].

$$b_{det} = 8.42 \times 10^{-2}\sigma^{0.58} \tag{15}$$

in which σ = liquid shear stress, dynes cm^{-2}. (Note that one dyne = 1 g cm^{-1} s^{-2}.) The shear stress can be computed for fixed beds of porous media from

$$\sigma = \frac{200\mu u(1-\varepsilon)^2}{d_p^2\varepsilon^3 a(7.46 \times 10^{11}\ \text{cm s}^2\ \text{m}^{-1}\ \text{day}^{-2})} \tag{16}$$

and for fluidized beds from

$$\sigma = \frac{(\rho_p - \rho_w)(1-\varepsilon)g}{a(100\ \text{cm m}^{-1})} \tag{17}$$

in which μ = absolute viscosity of the liquid, g m^{-1} day^{-1}
u = superficial flow velocity, m day^{-1}
ε = porosity of the bed
d_p = medium-particle diameter, m
ρ_p = density of the medium particles, g m^{-3}
ρ_w = density of water, g m^{-3}
g = gravitational constant, 9.8 m s^{-2}

A final step is to rewrite Eq. (14) in a more convenient form:

$$X_f L_f = \frac{JY}{b'} \tag{18}$$

2.3 The Steady-State-Biofilm Solution

Equations (9), (10), (11), and (18) comprise the steady-state-biofilm model. The key features of this model are as follows [30].

- The biofilm accumulation ($X_f L_f$) is at steady state, which means that growing sections of the biofilm are expanding to replace sections being lost through detachment or decay.
- The biofilm accumulation and substrate flux are intimately linked, as both appear in Eqs. (9) and (18).

The first solution to the steady-state-biofilm model was provided by Rittmann and McCarty [30], who solved the four equations numerically and

fitted the numerical results to algebraic equations. This approach provides a *pseudo-analytical solution*, because the algebraic equations can be used like a true analytical solution for J, but they are obtained from numerical solutions. Although the original solution defined the general approach for the pseudo-analytical solution, two improved versions were published [31, 32]. The most accurate solution [32] is summarized here.

First, the parameters are put into a nondimensional format (denoted by an asterisk) that minimizes the number of independent variables.

$$S^* = S/K \tag{19}$$

$$K^* = \frac{D}{L}\left[\frac{K}{q_m X_f D_f}\right]^{1/2} \tag{20}$$

$$J^* = J[K q_m X_f D_f]^{-1/2} \tag{21}$$

$$S^*_{min} = \frac{b'}{Y q_m - b'} \tag{22}$$

The fourth dimensionless parameter, S^*_{min}, is particularly important, because it is the ratio of the loss rate (b') to the maximum possible growth rate ($Y q_m - b'$). Values of S^*_{min} much less than 1.0 indicate microorganisms having a high growth potential, while values near to or greater than 1.0 mean that the cells' growth potential is small [33, 34]. S^*_{min} is related to its dimensional analogue,

$$S_{min} = K\frac{b'}{Y q_m - b'} \tag{23}$$

which is the minimum substrate concentration able to sustain steady-state biomass [30, 35].

Second, the actual dimensionless flux, J^*, is related to the dimensionless flux (J^*_{dep}) that would occur if the biofilm were infinitely thick, ensuring a *deep* biofilm [31]:

$$J^* = f J^*_{deep} \tag{24}$$

$$J^*_{deep} = \sqrt{2[S^*_s - \ln(1 + S^*_s)]} \tag{25}$$

$$S^*_s = \frac{S_s}{K} \tag{26}$$

$$f = \tanh\left[\alpha\left(\frac{S^*_s}{S^*_{min}} - 1\right)^{\beta}\right] \tag{27}$$

in which $\tanh(x)$ = hyperbolic tangent operator = $(e^x - e^{-x})/(e^x + e^{-x})$

α, β = coefficients that depend on S^*_{min}.

Third, the α and β coefficients were determined by Sáez and Rittmann [32] to be

$$\alpha = 1.5557 - 0.4117\tanh[\log S^*_{min}] \tag{28}$$

$$\beta = 0.5035 - 0.0257\tanh[\log S^*_{min}] \tag{29}$$

in which log is in base 10.

Finally, the relationship between S_s^* and S^* is

$$S_s^* = S^* - \frac{f J_{deep}^*}{K^*}. \tag{30}$$

Use of the steady-state-biofilm solution proceeds with the following 6 steps.

1. Compute S^*, K^*, and S_{min}^* from Eqs. (19), (20), and (22).
2. Compute α and β from S_{min}^* and Eqs. (28) and (29).
3. Using α, β, K^*, and S^*, compute S_s^* interactively from Eq. (30), which also requires Eq. (25) for J_{deep}^* and Eq. (27) for f. Since S_s^* appears on both sides, iterate on S_s^* until the S_s^* value on the left side equals the S_s^* value used to compute f and J_{deep}^* on the right side.
4. Compute J^* from S_s^* using
$$J^* = K^*(S^* - S_s^*). \tag{31}$$
5. Convert to the dimensional domain by rearranging Eq. (21) to solve for J:
$$J = J^*[K q_m X_f D_f]^{1/2}. \tag{32}$$
6. Compute the steady-state biofilm accumulation from Eq. (18).

Although the solution requires several steps, none is particularly difficult, and the procedure can be coded into a computer subroutine or spreadsheet computation.

Figure 2 presents a typical output of the steady-state model. Key features of the model solution are as follows.

- $J = 0$ for all $S \leqslant S_{min}$, but J has a unique value for all $S > S_{min}$.
- $X_f L_f$ (or L_f) is an output of the model; each $S > S_{min}$ has a unique value for $X_f L_f$ (or L_f).
- The flux and biofilm accumulation rapidly approach zero as S approaches S_{min}, which occurs because f is rapidly declining toward zero. This is the region in which the biofilm is *shallow*, and it approaches the *fully penetrated* case more closely as S becomes closer to S_{min}.
- When S is significantly greater than S_{min}, f equals 1.0, and the biofilm is *deep*.

The solution to the steady-state biofilm model can be used to compute J and $X_f L_f$ for an overall mass balance model, such as given by Eqs. (4)–(6) for a completely mixed reactor or reactor segment. The approach was illustrated in detail by Rittmann [35], who showed how to apply the steady-state-biofilm solution to fixed bed and fluidized-bed reactors having more complicated hydrodynamics.

2.4 Normalized Surface Loading

Although direct application of the steady-state-biofilm model is not especially difficult when the pseudo-analytical solution is used, it is not as straightforward as the typical design procedures used for suspended-growth processes [36].

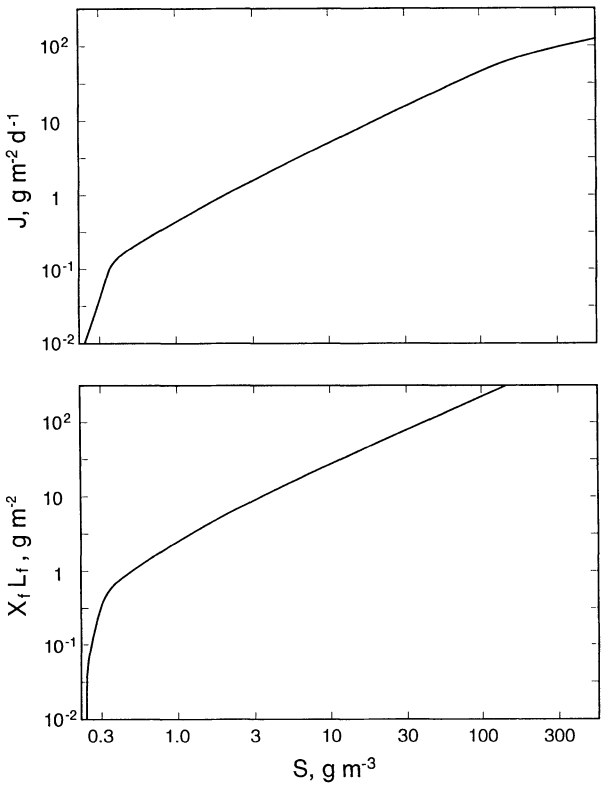

Fig. 2. Typical output of the steady-state-biofilm model. Kinetic parameters are: $q_m = 8$ gs gx^{-1} day^{-1}, $K = 10$ gs m^{-3}, $D = 8 \times 10^{-5}$ m^2 day^{-1}, $D_f = 6.4 \times 10^{-5}$ m^2 day^{-1}, $L = 10^{-4}$ m, $b' = 0.1$ day^{-1}, $S_{min} = 0.2564$ gs m^{-3}, $S^*_{min} = 0.02564$

A desirable goal is to make analysis and design of biofilm processes approximately as straightforward as design of suspended-growth processes. That goal is achieved through the concept of the normalized surface loading [12, 33, 34, 37].

The concept of normalized surface loading is based on solving the substrate mass balance, Eq. 4, when the pseudo-analytical solution is used to compute J, which is the substrate surface loading (gs m^{-2} day^{-1}). The solution is generalized by proper normalization of the independent parameters, S and J. The substrate concentration is normalized as S/S_{min}; this normalized substrate concentration has a lower limit of 1.0 for steady-state biofilms (see Fig. 2). The surface loading is normalized as J/J_R, where J_R is the minimum surface loading able to support a deep, steady-state biofilm. (Means to compute J_R are given below.) Then, generalized solutions can be presented as a series of normalized loading curves that have common characteristics.

Figure 3 presents a set of normalized loading curves that illustrate how the normalized surface loading controls the normalized substrate concentration.

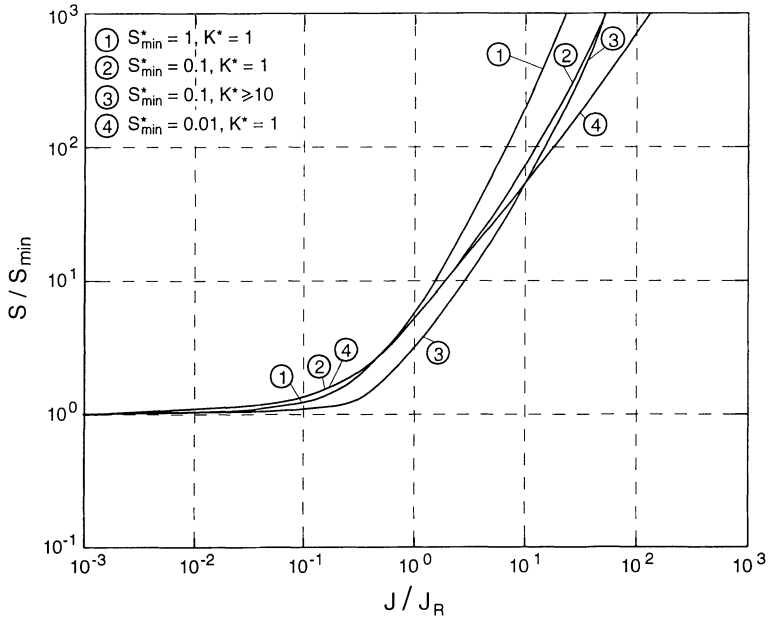

Fig. 3. Selected normalized loading curves illustrate how J/J_R is related to S/S_{min} and how S^*_{min} and K^* affect the relationship

More curves can be found in [37]. Inspection of any individual curve shows four common and critical features.

- For low normalized surface loads (i.e., $J/J_R \ll 1$), S/S_{min} approaches 1.0 (or log S/S_{min} approaches 0). When the normalized surface loading is low, S goes to its delimiting value of S_{min}, the biofilm approaches fully penetrated, and the process is controlled by the ability to accumulate biomass.
- In the low-load region, the slope of the curve is very small. Thus, S/S_{min} is not sensitive to changes in J/J_R for steady state.
- For high normalized surface loads, S/S_{min} is much greater than 1. High load process cannot achieve S near S_{min}, and the process is controlled by the kinetics of substrate utilization and mass transport, because biofilm accumulation is relatively large.
- In the high-load region, S/S_{min} is very sensitive to changes in J/J_R. Relatively small changes to surface loading can have profound effects on the steady-state substrate concentration.

Figure 3 also shows that growth potential and mass transport resistance control details of the relationship between S/S_{min} and J/J_R. Increased growth potential, represented by a reduced value of S^*_{min}, shifts the curves downward in the high-load region. Increased external mass-transport resistance, represented by a decrease in K^*, shifts the curve upward in the high-load region.

Although S^*_{min} and K^* shift the normalized loading curves somewhat, the four common features always hold. For example, to have S/S_{min} approaching 1.0 and low sensitivity to loading changes, J/J_R must be in the low-load region. Examples of the use of normalized loading curves are illustrated for process design [33] and for analysis of the performance of existing reactors [12, 34].

To use the normalized surface loading, J_R must be computed. J_R is normally computed from its dimensionless analogue, J^*_R, using the relation in Eq. (32), which is rewritten here specifically for J_R:

$$J_R = J^*_R[Kq_m X_f D_S]^{1/2}. \tag{33}$$

Cannon [38] presented a simple graphical means to estimate J^*_R from S^*_{min}. For $S^*_{min} < 0.1$, J^*_R is a constant equal to $2.8S^*_{min}$. In addition, J^*_R can be computed analytically by letting $f = 0.99$ in Eq. (27) and solving for S^*_s, which is then substituted into Eq. (25) to obtain J^*_R.

3 Applications

This section applies the concepts and tools of biofilm kinetics to the three most common uses of biological treatment in drinking-water treatment: aerobic oxidation of low concentrations of biodegradable organic material, nitrification of ammonia nitrogen, and denitrification of nitrate nitrogen. The first two are direct examples of removing sources of biological instability, while denitrification is used to remove an electron acceptor. Removal of less commonly encountered sources of biological instability – such as reduced iron, manganese, and sulfur – is not presented. Information on their removal can be found in [1] and [4].

3.1 Aerobic Oxidation of Low Concentrations of Biodegradable Organic Material

All water supplies contain biodegradable organic material of natural origin. Much of this material is of a humic nature, which means that it is of moderate to high molecular weight (e.g., greater than 1000 daltons) and has relatively slow biodegradation kinetics. Despite the slow kinetics, at least some of the humic-like material is biodegraded fast enough to support biofilm accumulation in biofilm processes [39]. Whereas some polluted supplies may also contain low-molecular-weight solutes from sewage or industrial wastewater, all supplies contain the naturally occurring, humic-like material. Therefore the analyses in this section focus on the natural organic material, which serves as the primary electron donor. Since biological processes used in drinking water are aerobic [4], oxygen is the primary electron acceptor.

The concentrations of biodegradable organic material (BOM) causing problems during distribution can be as low as 0.02 gC m^{-3} (= 20 μ gC l^{-1}), and a particularly poor water supply has BOM in excess of about 5 gC m^{-3}. A typical ratio of 3 g chemical oxygen demand (COD) $(gC)^{-1}$ converts these markers to < 0.06 g COD m^{-3} and > 15 g COD m^{-3}, respectively. Some caution must be used for interpreting concentrations of BOM, because the wide range of measurement techniques give quite different values for the same sample. The techniques and results are compared by Huck [40], Block et al. [41], Rittmann and Huck [12], and van der Kooij [42]. Results based on growth of specific bacterial strains tend to give very low values, while methods using mixed inocula and loss of organic carbon give higher values. For the purposes of reactor analysis and design, the higher values seem to be more relevant. Therefore the development presented here is based on measurements of biodegradable dissolved organic carbon (BDOC).

Although BOM concentrations vary significantly, all can be characterized as low compared to those encountered in wastewater treatment. The highest concentrations found in raw waters are roughly similar to concentrations found in wastewater effluents, and desired concentrations in the finished water must be at least 100-fold lower, say < 0.1 g COD m^{-3}. This need to achieve very low BOM concentrations by treatment of a water already containing relatively low concentrations defines the characteristics of a successful biological process.

Rittmann [12] utilized the normalized surface loading to analyze and compare the designs of different types of biofilm systems. Table 1 summarizes the kinetic parameters used to evaluate the kinetics of humic-like BOM. The values in Table 1 show that aerobic degradation of BOM gives a microbiological system with a high growth potential ($S^*_{min} \ll 1$), an S_{min} in the range of desired effluent quality (0.032 g COD m^{-3} = 32 μ gC l^{-1}), and a moderate control by external mass-transport resistance ($K^* = 0.2$). These characteristics are very useful for providing a "generic" evaluation of biofilm processes and for outlining the most important trends. However, a generic analysis is not a substitute for the site-specific evaluation needed for a final design.

Table 2 compares J_R to observed values of surface loading for a range of processes used in drinking-water treatment, as well as to trickling filters used in wastewater treatment. Four trends are clear.

- The surface loads are much lower for all drinking-water processes than for the typical wastewater processes. This trend is a direct result of the need to drive the effluent BOM to a concentration near S_{min} to meet the low-concentration criterion of a biologically stable drinking water.
- Except for rapid sand filters, J/J_R is less than 1, which reinforces the conclusion that drinking-water processing cannot operate successfully in the high-load region.
- The rapid filters have somewhat higher surface loads, which reflect the fact that rapid filters are not designed as biofilm reactors. Biodegradation is an incidental benefit that occurs if biological activity is not suppressed.

Table 1. Summary of kinetic parameters for aerobic oxidation of biodegradable organic material

Parameter	Value
Y	0.45 (g cells) (g COD)$^{-1}$
q_m	15.6 (g COD) (g cells)$^{-1}$ day^{-1}
K	1.0 (g COD) m^{-3}
b'	0.22 day^{-1}
D	5.3×10^{-6} m^2 day^{-1}
D_f	4.2×10^{-6} m^2 day^{-1}
L	1.6×10^{-5} m
X_f	4×10^4 (g cells) m^{-3}
S_{min}	0.032 g COD m^{-3}
S^*_{min}	0.032
K^*	0.2
J_R	0.15 g COD m^2 day^{-1}

Values for the basic kinetic parameters are taken from Rittmann [12]. Note that K^* was not used in the original paper and replaces τ, L^*, and $L^*D_f^*$, which are no longer needed. Also note that these parameters are for molecules with a molecular weight of 10^4 daltons; the column headings were reversed in Table 1 of Rittmann [12]

Table 2. Comparison of observed surface loadings to the reference flux ($J_R = 0.15$ g COD m^{-2} day) for aerobic oxidation of biodegradable organic material

Process Type	J, g COD m^{-2} d	J/J_R
Large-Granule Aerated		
Pozzolana Bed	0.14	0.93
Fluidized Sand Bed	0.013	0.087
Rapid Filters	0.14–0.32	0.93–2.1
GAC Adsorbers	0.01–0.028	0.067–0.19
Slow Sand Filters	0.0005–0.0038	0.0033–0.025
Trickling Filters	7–20	10–30

These observed loads were tabulated by Rittmann [12]

- Slow sand filters and GAC filters, which are often used explicitly for biodegradation, have very low loads that are limited by pore clogging. These low loads emphasize the limitations of small-granule fixed beds when significant concentrations of BOM must be removed.

Another key aspect for aerobic oxidation of BOM is oxygen supply. As a first approximation, the oxygen demand is about 70% of the COD removed by biodegradation. Thus, 8 g m^{-3} of oxygen can support removal of approximately 11 g COD m^{-3} of BOM. This simple computation indicates that aeration is seldom required for BOM oxidation, as long as the water entering the biological processes is near oxygen saturation, the temperature is not so high that the

saturation concentration is low, the BOM is not exceedingly high, and no other significant oxygen sinks exist. The last condition is often the most critical, because waters high in BOM often contain significant amounts of NH_4^+–N and can contain other reduced species.

Thus, the need for oxygen supply, which often precludes use of small-granule processes, depends on the sum of oxygen demand of all sources of biological instability.

3.2 Nitrification of Ammonium Nitrogen

Ammonium nitrogen is the second major cause of biological instability. Nitrogen pollution from heavy fertilizer use is a growing cause of high ammonium concentrations in waters affected by agriculture. Additionally, ammonium is almost always significant when natural organic matter is present in high concentrations, because nitrogen and humic-like organic materials originate from the breakdown of vegetation and microbial biomass, both of which contain nitrogen as a major constituent.

Besides creating the normal problems associated with biological instability, ammonium nitrogen creates its own set of water-quality problems:

- NH_4^+–N reacts rapidly with free chlorine to create chloramines. While chloramines have the advantages of being more stable than free chlorine in certain circumstances [43] and of producing fewer disinfection by-products [44], they are generally substantially weaker disinfectants than is free chlorine. Having substantial NH_4^+–N reduces the disinfection options. Furthermore, dissipation of chloramines during distribution regenerates the NH_4^+–N.
- Biological oxidation of NH_4^+–N (described below) consumes up to 4.57 g O_2 $(gN)^{-1}$ and 7.1 g alkalinity as $CaCO_3$ $(gN)^{-1}$. These large stoichiometric ratios mean that oxidation of even small concentrations of NH_4^+–N can deplete dissolved oxygen and acidify low-alkalinity waters.
- Uncontrolled oxidation of NH_4^+–N can lead to formation of NO_2^-–N, which is acutely hazardous to infants [12, 45] and is also implicated in the destruction of chloramine residuals [46].

The goal of a nitrification process is to bring about complete oxidation of NH_4^+–N to NO_3^-–N under controlled conditions. The overall reaction for NH_4^+–N oxidation is

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_20.$$

This reaction illustrates three key features of nitrification.

- NH_4^+–N is the primary electron acceptor, while O_2 is the primary electron donor. The mole ratio of 2 moles O_2 per mole NH_4^+–N converts to a maximum ratio for oxygen consumption of 4.57 g O_2 $(gN)^{-1}$.
- Since neither primary substrate contains *C*, the nitrifying bacteria reduce inorganic carbon (commonly represented by CO_2) to create an organic-C

supply. Reducing inorganic C, called autotrophy, consumes a large amount of electrons and energy from the primary-substrate reaction, thereby making the bacterial yield small when expressed as g cell mass per electron equivalent of electron donor consumed. The yield for aerobic heterotrophs is roughly five times greater than for the autotrophic nitrifiers.

- Each mole of NH_4^+–N oxidized produces two moles of strong acid, shown in the reaction as H^+. This molar stoichiometry converts to a maximum ratio of alkalinity consumption of 7.14 g as $CaCO_3$ $(gN)^{-1}$.

Nitrification occurs in two steps mediated by genetically distinct, although physiologically similar bacteria. In the first step, NH_4^+–N is the electron donor and is oxidized stepwise to NO_2^-–N according to the following primary-substrate reaction:

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O.$$

The most common genus of bacteria that carry out this reaction is *Nitrosomonas*, although *Nitrosolobus, Nitrosospira*, and *Nitrosococcus* also are able to oxidize NH_4^+–N to NO_2^-–N [1, 46].

The second step of nitrification is oxidation of NO_2^-–N to NO_3^-–N according to the following primary-substrate reaction:

$$NO_2^- + 0.5O_2 \rightarrow NO_3^-.$$

Although *Nitrospira, Nitrococcus*, and *Nitrocystis* are known to sustain themselves from the second reaction, *Nitrobacter* is the most common genus of NO_2^-–N oxidizers.

Both groups of nitrifiers share important physiological traits:

- Both are autotrophs, must reduce inorganic carbon, and have similarly low yields of biomass per unit of electron donor oxidized.
- Because of the low yields, both have relatively low maximum specific growth rates (μ_m, which equals Yq_m and has unit of day^{-1}); a typical μ_m for nitrifiers, 0.56 day^{-1} [12], is roughly ten times smaller than for aerobic heterotrophs.
- The low maximum specific growth rates accentuate the need to provide excellent biomass retention.
- Both types of nitrifiers use O_2 as the terminal electron acceptor. In fact, nitrifying bacteria tend to be more sensitive to oxygen limitation than are most heterotrophic bacteria [1].

On the other hand, three differences occur. First, only the *Nitrosomonas* strains generate strong acid; hence, the alkalinity consumption is related only to the step of NH_4^+–N oxidation. Second, the first step consumes three times more O_2 per mole of N than does the second step; again, the first step is primarily responsible for the oxygen demand of nitrification. Third, the second step occurs only after the first step has generated NO_2^-.

This situation can cause the buildup of NO_2^-, particularly when substrate loading or other environmental conditions (such as pH or temperature) change rapidly [45]. The sudden increased production of NO_2^- can overwhelm the

metabolic capability of the NO_2^- oxidizers, at least until they are able to grow in response to increased NO_2^-. Although the transient appearance of NO_2^- can serve as a sensitive warning about changes in the status of nitrification, it is also a serious problem in drinking-water treatment, because NO_2^- has severe health effects and has the ability to destroy chloramines [44]. Therefore stability for both steps of nitrification must be a treatment objective.

Rittmann [12] analyzed nitrification processes with the tool of normalized surface loading. This approach, which is summarized below, gives a good generic evaluation of key trends for biofilm processes operating at or near steady-state. As was true for analyzing the processes for BOM removal, the generic analysis is not a substitute for a detailed evaluation for site-specific conditions. Furthermore, this generic analysis does not consider interactions between the two types of nitrifiers or between nitrifiers and heterotrophs. These factors are discussed after the generic analysis.

Table 3 summarizes the kinetic parameters for nitrification. Since the two types of nitrifiers are physiologically similar in terms of growth rate, the analysis assumes that the step of NH_4^+ oxidation is rate limiting overall. The values in Table 3 indicate that nitrification has only a moderate growth potential ($S^*_{min} = 0.17$), an S_{min} in the range of desired effluent quality (0.1 gN m^{-3} = 0.1 mgN l^{-1}), and only modest control by external mass-transport resistance ($K^* = 1.2$).

Table 4 compares J_R to observed values of surface loading for the range of biofilm processes used in drinking-water treatment, as well as for several biofilm processes used in wastewater nitrification. Four trends are evident.

- Some of the surface loads used in drinking-water treatment are similar to those used in wastewater treatment. This situation occurs because the

Table 3. Summary of kinetic parameters for the first step of nitrification

Parameter	Value
Y	0.33 (g cells) (g N)$^{-1}$
q_m	1.7 (g N) (g cells)$^{-1}$ day^{-1}
K	0.57 g N m^{-3}
b'	0.082 day^{-1}
D	1.3×10^{-4} m^2 day^{-1}
D_f	1.04×10^{-4} m^2 day^{-1}
L	4×10^{-5} m
X_f	4×10^4 (g cells) m^{-3}
S_{min}	0.1 g N m^{-3}
S^*_{min}	0.17
K^*	1.2
J_R	1.0 g N m^{-2} day^{-1}

Values for the basic kinetic parameters are taken from Rittmann [12]. Note that K^* was not used in the original paper and replaces τ, L^*, and $L^* D_f^*$, which are no longer needed

Table 4. Comparison of observed surface loadings to the reference flux ($J_R = 1$ g N m^{-2} day^{-1}) for nitrification

Process Type	J (g N m^{-2} day^{-1}) and J/J$_R$
Aerated Large-Granule Beds	0.17–0.38
Fluidized Sand Beds	0.013–0.032
Rapid Filters	0.021–0.6
GAC Adsorbers	0 to 0.53
Slow Sand Filters	0.003
Wastewater Biofilm Processes	0.3–1.0

These observed loads were tabulated by Rittmann [12]

treatment goals for effluent NH_4^+–N are not nearly as different for NH_4^+–N as they are for BOM.

- All surface loads, including for wastewater treatment, are in the medium- and low-load regions. Rittmann [12] suggests that the relatively poor growth potential (i.e., high S^*_{min}) forces operation to be in or near the low-load region if nitrification is to be stable. Furthermore, high surface loads can lead to thick biofilms that create oxygen limitation inside the biofilm [10].
- Surface loads for fluidized beds and slow sand filters are much lower than for the other processes. These low surface loads probably reflect clogging potential for the small grains and oxygen-supply limitation.
- The surface loads for rapid filters and GAC absorbers vary widely. This occurs because nitrification is not a design objective, but occurs coincidentally.

One important aspect of nitrification cannot be captured simply by analyzing just the surface loading of NH_4^+–N: interactions among the two nitrifying strains and the heterotrophs. Multispecies modeling [10, 11, 26, 27] and limited experimental measurements [11, 45] indicate that the nitrifying bacteria usually reside inside the biofilm, while the heterotrophs predominate at the outer surface. This situation can help or hinder stable nitrification. It helps nitrification by protecting the nitrifiers from detachment, which lowers b', S_{min}, and S^*_{min} for the nitrifiers [10, 11]. In fact, the advantage of protection is accentuated when the BOM load is high enough to effectively exclude nitrifiers from the outer surface [11]. On the other hand, having the nitrifiers inside the biofilm increases the mass-transfer resistance for NH_4^+ and O_2. While the impact is relatively minor for NH_4^+ [11], increased mass-transfer resistance for O_2, coupled with O_2 consumption by heterotrophs along the diffusion path, can make nitrification unstable when BOM and/or NH_4^+–N loads are high or when the dissolved oxygen supply is limited [10].

Changes in substrate loading – NH_4^+, O_2, or BOM – can upset stable nitrification. For example, Manem and Rittmann [45] showed that a sudden increase in BOM loading, which caused a sudden increase in the growth of heterotrophs, diluted the nitrifiers out of the biofilm and caused a transient loss of nitrification. Although steady-state nitrification was reestablished in every case (as long as

sufficient oxygen was supplied), NO_2^- oxidation required a much longer time to become established. This lag period for NO_2^- oxidation, which also occurs with an increase in NH_4^+ loading, is a natural result of the facts that both types of nitrifiers grow slowly, but NO_2^- oxidizers can increase in biomass only after NO_2^- has built up to concentrations well above the trace levels required for successful treatment.

While clear experimental verification is not yet available, modeling and experiments suggest that stable nitrification, especially including continuously maintaining very low NO_2^- concentrations, is aided by keeping BOM surface loadings above the low-load region and by ensuring high dissolved oxygen concentrations. The moderate BOM loading allows enough biomass accumulation so that nitrifiers are protected from detachment and changes in heterotroph growth. High dissolved oxygen concentration is required to preclude oxygen limitation, especially when the nitrifiers are deep inside the biofilm.

3.3 Denitrification of Nitrate Nitrogen

Denitrification is the microbiological process in which NO_3^- (or NO_2^-) serves as the primary electron-acceptor substrate and is reduced to (mainly) N_2 gas. The primary electron donor can be BOM, H_2, and several reduced-sulfur species. In the first case, the denitrifying bacteria are the same kind of heterotrophic bacteria as occur during the aerobic oxidation of BOM. In fact many common strains of aerobic heterotrophs can shift to nitrate respiration when dissolved oxygen is less than about 0.1–0.2 g m^{-3} [47]. When H_2 or reduced sulfur serve as the electron donor, the bacteria are autotrophic.

The following are typical primary-substrate reactions for denitrification:
Heterotrophic with acetic acid as electron donor

$$0.625CH_3COOH + NO_3^- + H^+ \rightarrow 0.5N_2 + 1.25HCO_3^- + 0.5H_2O$$

Autotrophic with H_2 as electron donor

$$2.5H_2 + NO_3^- + H^+ \rightarrow 0.5N_2 + 3H_2O$$

Autotrophic with $S(s)$ as electron donor

$$0.833S + NO_3^- + 0.333H_2O \rightarrow 0.5N_2 + 0.833SO_4^{2-} + 0.666H^+$$

Each represents reduction of one mole of NO_3^-–N to N_2 and the consumption of 2.86 g electron-donor COD per g NO_3^-–N. The first two reactions show the net consumption of strong acid (H^+), a characteristic often attributed to denitrification. However, the oxidation of elemental sulfur produces strong acid. These acid/base features are key factors for poorly buffered waters, and the opposite trend when sulfur is oxidized must not be overlooked. For example, denitrification of 10g NO_3^-–N m^{-3} creates alkalinity of approximately 35 g as $CaCO_3$ m^{-3} when BOM or H_2 are oxidized, but it destroys about 24 g as $CaCO_3$ m^{-3} if S is oxidized.

Denitrification is seldom necessary unless the NO_3^- concentration exceeds 10 g N m^{-3}, a typical health-based standard. Then treatment normally only needs to reduce the NO_3^- level to below the standard. Thus full denitrification need not always be practiced. However, partial denitrification can result in production of NO_2^- as an intermediate. More research is needed on the formation of NO_2^- during partial denitrification.

Even when denitrification is only partial, the amount of electron-donor substrate available in a drinking-water supply is almost always too low to support enough denitrification. For example, removal of 5 g NO_3^-–N m^{-3} by heterotrophic denitrification consumes roughly 20 g COD m^{-3} of BOM for electron and carbon supplies [47]. Not even the poorest drinking-water supplies contain 20 g COD m^{-3} of BOM. This shortfall of BOM means that an exogenous electron donor must be added. The most common exogenous electron donors are simple organic compounds such as acetate or glucose, H_2 gas, or S that dissolves from a solid medium [4].

The addition of exogenous electron donor must be carefully controlled to prevent overdosing, which leaves the finished water biologically unstable. Stoichiometric principles [48, 49, 50] can be used to compute doses. For a situation in which addition of an electron donor at a rate less than that needed to remove all the NO_3^- (as well as NO_2^- and O_2) is not possible due to NO_2^- buildup, a full-denitrification process can be followed by an aerobic process to remove excess electron donor.

Denitrification has been studied extensively for tertiary wastewater treatment. Because early studies [50] showed that methanol had technical and economic advantages as an exogenous electron donor, a large body of information has been compiled with methanol. This pool of knowledge has convinced some workers that methanol can be used as the exogenous electron donor in drinking-water treatment. While use of methanol is technically possible in principle, its use must be advocated with the greatest caution, because methanol is acutely toxic to humans, causing blindness and death at high doses. Furthermore, methanol, as well as the much less toxic ethanol, is an alcohol whose possible presence in a drinking water could create serious political problems from those who do not wish to consume alcohol for medical or religious reasons. While dosing of alcoholic electron donors ought to be controllable to prevent any leakage, no system is fail-safe. Therefore, use of methanol (and ethanol) should not be encouraged.

Similar to the prior analysis, denitrification is evaluated through the tool of the normalized surface loading. Table 5 summarizes generic kinetic parameters appropriate to denitrification when a simple organic compound, H_2, and S serve as the electron donor. Implicit in Table 5 is that the electron donor is the rate-limiting substrate; the significance of the assumption is discussed below. As before, these parameters are typical ones used to illustrate major trends. More detailed analyses are needed for a site-specific design.

Table 5. Summary of generic kinetic parameters for analyzing denitrification processes

Parameter Substrate	Electron-Donor Substrate		
	Organic Acetate as COD	Hydrogen H_2	Sulfur S
Y, g cell g^{-1}	0.27	0.85	0.14
q_m, g (g cells)$^{-1}$ day^{-1}	11.8	1.6	8.1
K, g m^{-3}	1.0	0.125	0.67
b', day^{-1}	0.1	0.1	0.1
D, m^2 day^{-1}	1.0×10^{-4}	3.9×10^{-4}	9.8×10^{-5}
D_f, m^2 day^{-1}	8.0×10^{-5}	3.1×10^{-4}	7.8×10^{-5}
L, m	4×10^{-5}	5×10^{-5}	4×10^{-5}
X_f, g cells m^{-3}	4×10^4	4×10^4	4×10^4
S_{min}, g m^{-3}	0.032	0.010	0.067
S^*_{min}	0.032	0.078	0.1
K^*	0.4	0.61	0.4
J_R, g m^{-2} day^{-1}	0.55	0.35	3.6
g COD m^{-2} day^{-1}	0.55	2.8	5.5

Table 5 presents three general trends.

- All three situations give low values of S_{min}. Thus, achieving a water with low residual electron donor is feasible.
- The autotrophic process has S^*_{min} values larger than the heterotrophic process. This reflects the high energy cost to reduce inorganic carbon for cell synthesis. However, none of the processes has a very poor growth potential.
- External mass-transport resistance has moderate control over the kinetics.

The J_R values indicate loadings needed to drive the concentration of electron donor near S_{min}. The low-load region has actual surface loadings substantially less than 0.55 g COD m^{-2} day^{-1}, 0.35 g H_2 m^{-2} day^{-1}, or 3.6 g S m^{-2} day^{-1}. Feeding rates to achieve the desired surface loading are simple to compute for organic compounds and H_2. Since S normally is supplied via dissolution of a solid, controlling S loading is less obvious and a good subject for further research.

Even though the goal of denitrification is to remove N, the process kinetics are usually controlled by the electron donor. This concept is true because K values for primary electron acceptors (like NO_3^- and O_2) are usually much less than 1 g m^{-3}. The electron acceptor becomes limiting only when a substantial excess of donor allows the acceptor concentration to be driven to very low levels. Because drinking-water treatment strives to prevent leakage of electron donors and because partial denitrification is acceptable, a large excess of electron donor is unlikely in drinking-water treatment. Therefore, the assumption that the electron donor is rate limiting is justified.

The J values expected to be appropriate for drinking water treatment should be substantially lower than for wastewater treatment, for which N removal

is paramount, while having some residual electron donor is not a serious problem. Surface loads for wastewater denitrification are usually greater than 10 g COD m^{-2} day^{-1}, values indicative of the high surface loads of the electron donor needed to force the electron acceptor to low concentrations. If moderate to high surface loads were to be used for denitrification of drinking water, a subsequent aerobic process would be needed to make the water biologically stable.

4 Summary

Biofilm processes are becoming more widely used to produce a biologically stable drinking water by removing electron donors and to reduce excessively high NO_3^- concentrations, a common electron acceptor. While many process configurations are possible, the same fundamentals of biofilm kinetics apply in each case. The foundation for properly designing biofilm processes is the steady-state biofilm, which integrates the mechanisms of substrate utilization, mass transport, and biofilm growth and loss. Normalized surface loadings can be used to combine the kinetics of steady-state biofilms with reactor mass balances, thereby achieving a simple and intuitive design/analysis tool.

Because electron-donor concentrations must be as low as possible in order to have a biologically stable water, surface loadings successful for drinking-water treatment are moderate to low. In other words, the normalized surface loading, J/J_R, is less than one. Except for nitrification, normalized surface loads must be substantially less than those typically used in wastewater-treatment processes carrying out the same reactions.

5 References

1. Rittmann BE, Snoeyink VL (1984) J Amer Water Works Assn 76 10:106
2. Kobayashi H, Ritmann BE (1982) Environ Sci Technol 16:170A
3. Stratton RE, Namkung E, Ritmann BE (1983) J Amer Water Works Assn 75:463
4. Rittmann BE, Huck PM (1989) CRC Crit Rev Environ Control 19 2:119
5. Rittmann BE, Gantzer CJ, Montiel A (1994) In: Suffett M, Mallevialle J (eds) Control of tastes and odors in drinking water. American Water Works Assn., Denver, p 203
6. Namkung E, Rittmann BE (1987) J Amer Water Works Assn 79:7:107
7. Manem JA, Rittmann BE (1992) J Amer Water Works Assn 84:4:152
8. JM Montgomery Consulting Engineers, Inc. (1985) Water treatment principles and practices, John Wiley & Sons, Inc., New York
9. Characklis WG, Marshall KC (eds) (1990), Biofilms, Wiley-Interscience, New York
10. Furumai H, Rittmann BE (1994) Evaluation of multispecies biofilm and floc processes using a simplified aggregate model, Water Sci Technol, in press
11. Rittmann BE, Manem JA (1992) Biotechnol Bioengr 39:914
12. Rittmann BE (1990) J Amer Water Works Assn 82:1:62
13. Davis ML, Cornwell DA (1991) Introduction to environmental engineering, 2nd edn., McGraw-Hill Book Co., New York

14. Sprouse GB, Rittmann BE (1990) J Environ Engr 116:314
15. Najm IN, Snoeyink VL, Suidan MT, Lee CH, Richard Y (1990) J Amer Water Works Assn 82:1:65
16. Rittmann BE (1993) Transformation of organic micropollutants in biological processes, this volume
17. Harvey RW, Smith RL, George L (1984) Appl Environ Microb 48:1197
18. Rittmann BE (1993) The significance of biofilms in porous media. Water Resources F esearch 29:2195.
19. Gantzer CJ, Cunningham AB, Gujer W, Gutekunst B, Heijnen JJ, Lightfoot EN, Odham G, Rittmann BE, Rosenberg E, Stolzenbach KD, Zehnder AJB (1989) in: Characklis WG, Wilderer PA (eds) Structure and function of biofilms, John Wiley & Sons, Inc., Chichester, England, pp 73-90
20. Kissel JC, McCarty PL, Street RL (1984) J Environ Engr 110:393
21. Rittmann BE, McCarty PL (1981) J Environ Engr 104:889
22. Rittmann BE (1989) in: Characklis WG, Wilderer PA (eds) Structure and function of biofilms, John Wiley & Sons, Inc., Chichester, England, pp 49-58
23. Characklis WG, Turakhia MH, Zelver N (1990) in: Characklis WG, Marshall KC (eds) Biofilms, Wiley-Interscience, New York, pp 265-340
24. Rittmann BE (1982) Biotechnol Bioengr 24:501
25. Chang HT, Rittmann BE, Amar D, Ehlinger O, Lesty Y (1991) Biotechnol Bioengr 38:499
26. Trinet F, Heim R, Amar D, Chang HT, Rittmann BE (1991) Water Sci Technol 23:1347
27. Wanner O, Gujer W (1986) Biotechnol Bioengr 28:314
28. Chang HT, Rittmann BE (1988) J Water Pollution Control Fedn 60:362
29. Speitel JR, DiGiano FA (1986) J Environ Engr 113:464
30. Rittmann BE, McCarty PL (1980) Biotechnol Bioengr 22:2343
31. Sáez PB, Rittmann BE (1988) Biotechnol Bioengr 32:379
32. Sáez PB, Rittmann BE (1992) Biotechnol Bioengr 39:790
33. Heath MS, Wirtel SA, Rittmann BE (1990) Res J Water Pollution Control Fedn 62:185
34. Wirtel SA, Noguera DR, Kampreier DT, Heath MS, Rittmann BE (1992) Water Environ Res 64:706
35. Rittmann BE (1982) Biotechnol Bioengr 24:1341
36. Metcalf & Eddy, Inc. (1991) Wastewater engineering: treatment, disposal, and reuse, McGraw-Hill Book Co., New York
37. Heath MS, Wirtel SA, Rittmann BE, Noguera DR (1991) Res J Water Pollution Control Fedn 63:91
38. Cannon FS (1991) Res J Water Pollution Control Fedn 63:90
39. Namkung E, Rittmann BE (1987) J Amer Water Works Assn 79:7:107
40. Huck PM (1990) J Amer Water Works Assn 82:7:78
41. Block JC, Mathieu L, Servais P, Fontvieille D, Werner P (1992) Water Res 26:481
42. van der Kooij D (1993) this volume
43. LeChevallier M, Cawthon CD, Lee RG (1990) J Amer Water Works Assn 82:7:87
44. Johnson JD, Jensen JN (1986) J Amer Water Works Assn 78:4:156
45. Manem JA, Rittmann BE (1992) J Amer Water Works Assn 84:4:147
46. Valentine RL (1985) in: Jolley RL (ed) Water chlorination: environmental impact and health effects, vol. 5, Lewis Publ., Chelsea, Mich
47. Rittmann BE, Langeland WE (1985) J. Water Pollution Control Fedn. 57:300
48. McCarty PL (1972) Stoichiometry of biological reactions, Proc intl conf towards a unified concept of biological waste treatment design, Atlanta, Georgia (Oct. 1972)
49. Christensen DR, McCarty PL (1975) J Water Pollution Contol Fedn 47:2653
50. McCarty PL, Beck L, St. Amant P (1969) Proc 24th Purdue industrial waste conference, West Lafayette, Ind., p 1271

Significance and Assessment of the Biological Stability of Drinking Water

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List of Abbreviations and Symbols

ATP	adenosinetriphosphate (ng/l)
AOC	assimilable organic carbon (μg acetate-C equivalents/l)
b	die-off rate (h^{-1})
BDOC	biodegradable dissolved organic carbon (mg/l)
C	organic carbon
CFU	colony forming units
D	pipe diameter (internal) (m)
DBA	diluted broth agar
DOC	dissolved organic carbon (mg/l)
GAC	granular activated carbon
K_s	substrate saturation constant (μg C/l)
N_{max}	maximum colony count (CFU/ml)
Re	Reynolds number (dimensionless)
S	substrate concentration (μg C/l)
S_{min}	substrate concentration at which net growth rate equals zero (threshold substrate concentration) (μg C/l)
V	growth rate (h^{-1})

V_{max} maximum growth rate (h^{-1})
v flow rate (m/s)
v' kinematic viscosity of water (m^2/s)
Y bacterial growth yield (CFU/μg C)

Abstract

Biologically-stable drinking water does not support the multiplication of micro-organisms in drinking water distribution systems. Such multiplication (regrowth) adversely affects water quality, e.g. by the presence of opportunistic pathogens, coliforms, increased heterotrophic colony counts, development of invertebrates. Disinfection is not effective against biofilms and sediments, which play a key role in regrowth, and cleaning methods are labor intensive. Regrowth therefore should be prevented by strictly limiting the concentration of compounds serving as energy sources for microorganisms. Growth measurements with selected pure bacterial cultures are used for assessing the concentration of easily assimilable organic carbon (AOC) in drinking water. Regrowth of heterotrophic bacteria is very limited in water supplies in the Netherlands at AOC concentrations below 10 μg of acetate-C equivalents per liter. The concentration of biodegradable organic carbon (BDOC), which is assessed as the reduction in DOC concentration in samples incubated with an assemblage of bacteria, did not decrease below the level of 0.2 mg/l in drinking water during distribution in Paris. Biological filtration processes are needed to remove the concentration of growth promoting compounds for obtaining biostable drinking water.

Introduction

Biological Stability: a New Microbiological Water Quality Objective

Water intended for human consumption should not contain pathogenic micro-organisms. This is one of the most important criteria for drinking water quality. The 'classical' waterborne diseases transmitted via drinking water are caused by micro-organisms originating from the faeces of man and warm-blooded animals, e.g. species of the bacteria *Salmonella, Vibrio* and *Shigella.* These and other pathogens of faecal origin are difficult to detect in water and therefore, methods for assessing the presence/absence of bacteria of faecal origin, particularly *Escherichia coli*, are used for monitoring the efficacy of water treatment and the integrity of the distribution system.

Practical experience in the past decade has revealed that certain types of bacteria with pathogenic properties, including *Pseudomonas* spp., *Aeromonas* spp., *Legionella* spp. and *Mycobacterium* spp., which are not of enteric origin, can multiply in drinking water distribution systems and/or in drinking water installations [1–5]. Also, numbers of non-pathogenic heterotrophic bacteria such as coliforms may exceed legislative standards as a result of multiplication in drinking water distribution systems [6]. Growth of micro-organisms may also cause

esthetical problems, e.g. complaints about taste, odour, colour, or induce the presence of invertebrates. Moreover, microbiological activity can cause certain technical problems, e.g. enhanced attack of construction materials [7, 8].

Multiplication of bacteria in drinking water during distribution, is usually referred to as regrowth of aftergrowth. Such growth mainly takes place on the inner surface of the pipes and reservoirs in contact with drinking water, followed by the release of bacteria from these surfaces into the water. A large number of studies, using both microscopic techniques and cultivation methods have clearly demonstrated the presence of microorganisms on surfaces in contact with drinking water, even in the presence of a disinfectant residual [9–13]. Nutrients present in the water serve as food sources for the microorganisms on the water-exposed surfaces. Certain synthetic materials release biodegradable components [14, 15].

Regrowth has become a matter of increasing concern for those responsible for the quality of drinking water. The detection of organohalogens as byproducts of chlorination [16] made post chlorination less attractive for controlling regrowth. Furthermore, it was demonstrated that low concentrations of chlorine are not effective in biofilms [17, 18]. Curative measures in the distribution system, such as flushing and swabbing, which usually are labour intensive and therefore expensive, apparently are insufficiently effective for controlling regrowth phenomena in a number of situations. As a result of these developments, interest in producing drinking water in which multiplication is strictly limited by a far-reaching removal of growth-promoting compounds is gaining much interest. This type of drinking water has been characterized as 'biologically-stable' drinking water [19]. In the Netherlands, most water supplies distribute drinking water without a disinfectant residual [20]. The integrity of the distribution systems is ensured by a series of technical measures and procedures, aiming at protecting drinking water against contamination. This approach requires drinking water to have a high degree of biological stability. The regrowth problems have stimulated the development of methods for determining the biological stability of drinking water. Such methods are needed to direct adaptations of water treatment to increase the biostability of drinking water.

Multiplication of Bacteria at Low Substrate Concentrations

As in other environments, the rate and extend of multiplication of microorganisms in drinking water distribution systems water is affected by a series of conditions, which include: (1), the concentration of compounds serving as source of energy and/or carbon; (2), the nature of these compounds; (3), temperature; (4), presence of growth-inhibiting compounds. In addition, the residence time of water also effects the extend of multiplication. Certain parameters, in particular water temperature and residence time are difficult to influence. Moreover, the use of growth-inhibiting compounds (disinfectants) has undesirable side affects. Consequently, the rate and extend of growth should be limited

by a farreaching nutrient removal in water treatment. The relative amounts of the major nutrients needed for the growth of heterotrophic microorganisms can be derived from the gross composition of microbial biomass, $C_5H_7NO_2P_{1/30}$, and the proportion (50%) of organic carbon used for dissimilation. Organic compounds serving as energy and carbon source are needed in a much larger amount than the inorganic nutrients N and P.

The relationship between growth rate and concentration of the growth-limiting substrate is given by the Monod equation:

$$V = V_{max} \times \frac{S}{(K_s + S)} \tag{1}$$

where: V = growth rate (doublings/hour) at substrate concentration S;
V_{max} = maximum growth rate (h^{-1});
K_s = the substrate saturation constant, is the concentration of S at which $V = 1/2V_{max}$.

When: $S \ll K_s$ then:

$$V = V_{max}/K_s \times S \tag{2}$$

and the growth rate is linearly related with the substrate concentration S and also depending on the values for V_{max} en K_s, which are constants for specific combinations of organism and substrate.

Bacteria representing the indigenous bacterial flora of drinking water have K_s values for easily degradable low molecular weight compounds as low as a few micrograms of C/liter (Table 1). Even for starch, which includes the large molecular weight compounds amylopectin and amylose, K_s values below 10 μg C/l have been reported. These observations indicate that bacteria with very low K_s values for compounds, such as amino acids, peptides, carbohydrates and carboxylic acids, commonly occur in drinking water and in other aquatic environments. The coliforms have clearly higher K_s values, even for their favourite substrate glucose [21], than the indigenous bacteria (Table 1). *Escherichia coli*, coliforms, and also *Pseudomonas aeruginosa*, do not belong to the indigenous bacterial population of drinking water. In addition to having higher K_s values than the indigenous bacteria, *E. coli* and *P. aeruginosa* grow relatively slowly at low temperatures.

Bacteria multiply relatively fast at concentrations at the level of the K_s-value. Easily assimilable organic carbon compounds therefore can be utilized at concentrations below 1 μg C/l. However, complete removal of a single biodegradable compound is not possible, even when exposure time is very long. Micro-organisms use a part of the available compounds for maintaining the integrity of the cell. At very low substrate concentrations, the rate of uptake becomes very slow and approaches the amount required for maintenance. Under these conditions, multiplication does not occur and the bacteria die from starvation at lower concentrations. The concentration at which growth is not possible is the threshold concentration (S_{min}). The S_{min} value can be calculated for a

Table 1. Growth kinetics of bacteria, isolated from drinking water, for glucose and a few other substrates[1]

Compound	Organism	K_s (μg C/L)	V_{max} (h^{-1})	Reference
Glucose	*Flavobacterium* sp.	3.3	0.21	41
Glucose	*A. hydrophila*	16	0.28	23
Glucose	*P. fluorescens*	57	0.22	42
Glucose	*Enterobacter* sp.	60	0.21	21
Glucose	*Flavobacterium* sp.	109	0.15	56
Acetate	*P. fluorescens*	4	0.18	42
Acetate	*P. aeruginosa*	28	0.09	57
Oleate	*A. hydrophila*	2.1	0.23	23
Starch	*Flavobacterium* sp.	8.4	0.41	56

[1]growth measurements were conducted in slow sand filtrate at 15 °C.

certain organism–substrate combination using an adaptation of Eq (1):

$$V = V_{max} \cdot \frac{S}{(K_s + S)} - b \tag{3}$$

In this equation, b is the rate at which the bacterial population decreases as a result of endogenous respiration. Under certain conditions, this decay rate also includes the wash out of cells, or the consumption of cells by predators.
S_{min} equals the substrate concentration at which the net growth rate = 0. Hence:

$$S_{min} = b \times \frac{K_s}{(V_{max} - b)} \tag{4}$$

For aerobic bacteria utilizing organic compounds typical values for the die-off rate b range from 0.005 to 0.02 h^{-1} [22], i.e. 5 to 10% of the maximal growth rate V_{max}. Consequently:

$$S_{min} = b \times \frac{K_s}{V_{max}} \tag{5}$$

Assuming $b = 0.01$ h^{-1} gives S_{min} values as low as 0.1 to 0.2 μg of C/l for certain combinations of substrate and organism, particularly bacteria belonging to the indigenous flora of drinking water. Figure 1 shows the relationship between glucose concentration and growth rate, including the effect of endogenous respiration, for a number of organisms.

At low substrate concentrations, bacteria are able to utilize a number of substrates simultaneously. In the presence of a mixture of easily biodegradable compounds, S_{min} for individual compounds therefore depends on the total concentration of compounds available for the organism. This results in individual compound concentrations which are far below 0.1 μg C/l. For *A. hydrophila*, an S_{min} value of 0.23 μg C/l was calculated from the data of the growth of this organism on a mixture of 21 amino acids and also for growth on a mixture of 10 long-chain fatty acids. Consequently, the average S_{min} value for each

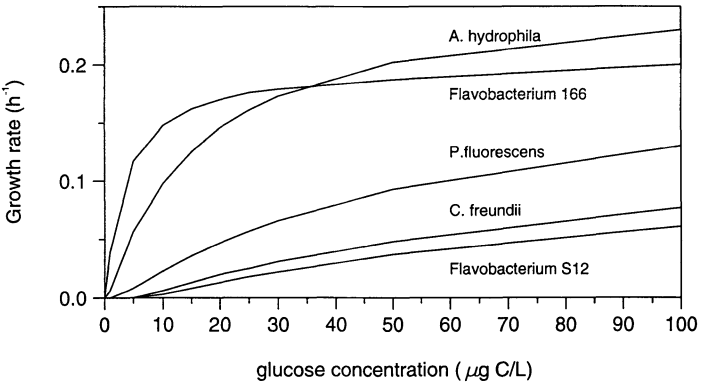

Fig. 1. The relationship between growth rate and substrate concentration for a number of bacteria isolated from drinking water, based on growth kinetics (cf. Table 1), assuming a die-off rate of 0.01 h^{-1} and using the relationship $V = V_{max} \cdot S/(Ks + S) - b$

individual amino acid and for each fatty acid in these mixtures may be as low as 0.01 μg C/l or 0.02 μg C/l, respectively [23].

The total concentration of dissolved organic carbon (DOC) in drinking water usually ranges from less than 0.5 to 5 mg/l, and includes a large number of different substances. Most of these compounds originate from natural organic material, i.e. humic and fulvic acids, breakdown products of biomass degradation, etc. Growth measurements with pure bacterial cultures such as fluorescent pseudomonads, which are able to ultilize a wide range of organic compounds, demonstrate that only a minor part (usually $< 1\%$) of the DOC concentration is easily biodegradable. Slowly biodegradable compounds thus are present in higher concentrations. The nature of such compounds is still insufficiently known.

Biofilm Development

The major fraction of microbial biomass in drinking water distribution systems is present as a biofilm on the walls of the pipes and the reservoirs and in sediments. Consequently, the available substrates must be transported to these surfaces. Transport of substrates to the pipe wall is influenced by the flow pattern in the pipe, i.e. laminar flow or turbulent flow. In the latter case, whirling causes a continuing replacement of the water in contact with the biofilm on the pipe wall. The flow pattern, which depends on the flow rate, the pipe diameter and the viscosity of the water, is characterized by the dimensionless Reynolds number (Re):

$$\mathrm{Re} = \frac{v \times D}{v'} \tag{6}$$

in which v = flow rate (m/s);
D = internal pipe diameter;
and v' = kinematic viscosity (m^2/s).

For water at 20 °C, $v' = 10^{-6}\ m^2/s$. The flow pattern usually is turbulent when Re > 2300. This value is clearly exceeded at a typical flow rate of 0.1 m/s and a pipe diameter of 100 mm (Re = 10^4). Substrates present in the bulk water are transported to the biofilm, but must diffuse through the thin layer of stagnant water containing the biofilm. Transport of substrates by diffusion is described by Fick's first law. Diffusion constants are largest for the smallest molecules, and consequently, at equal concentrations, low molecular weight compounds will be more easily transported to the biofilm than large molecular weight compounds. The theoretical aspects of substrate diffusion, substrate uptake and growth in biofilms have been described in detail in Chapter 2 and will not be further described here.

As a consequence of biofilm development and the turbulent flow bacteria detach from the biofilm and are transported in the water phase. In situations with a strong biofilm development, such processes may lead to the formation of sediments. At certain locations in the distribution, biomass accumulated in sediments may induce conditions favouring the multiplication of undesirable bacteria, including coliforms [24, 25], and invertebrates [26].

The concentration of available substrates directly determines the rate of bacterial growth in the biofilm and the biostability of drinking water increases with decreasing concentration of compounds contribution to biofilm development. Several methods have become available in the past decade to assess the concentration of growth-promoting compounds in drinking water.

Assessing the Biological Stability of Drinking Water

General Aspects

Compounds which promote the growth of micro-organisms in drinking water distribution systems may be present as the result of:

- insufficient removal from the raw water;
- formation in water treatment, e.g. by ozonation [27, 28], the use of certain organic coagulant aids, or the addition of compounds to achieve denitrification [29];
- release from materials in contact with drinking water [14, 15];
- release from sediments in pipes and reservoirs.

The presence in drinking water of a few specific biodegradable compounds, including ammonia, nitrite, methane, can be determined with chemical techniques. However, it is difficult to use chemical analysis for determining the concentration of all growth-promoting organic compounds in drinking water, because:

- concentrations of biodegradable compounds must be determined at very low concentrations;
- a wide variety of compounds ranging from low molecular weight compounds, such as carboxylic acids, amino acids, to larger and more complex molecules, including humic and fulvic acids containing biodegradable fractions, must be included in the analysis;
- for many compounds, no data will be available about their significance as a source of energy and/or carbon;
- the importance of a number of compounds may depend on the nature of other compounds present (synergistic effects).

The limited possibilities of chemical analysis have led to the conclusion that biological methods (bioassays) are needed to assess the growth-promoting properties (growth potential) of drinking water. Subsequently, a criterion for biological stability should be based on relationships between such parameters and regrowth phenomena. In the recent past, a variety of methods has been developed to assess biological stability of drinking water. One group of methods include the determination of the rate and extend of bacterial multiplication in samples of the water to be investigated, either by using colony counts [30], turbidity measurements [31], ATP analysis [32] or microscopic techniques [33]. Other methods aim at assessing the degree of removal of dissolved organic carbon (DOC), the disappearing fraction is called biodegradable dissolved organic carbon (BDOC) [34–37]. Most of these methods have recently been reviewed [38]. This chapter will deal with:

- assessment of the concentration of easily assimilable organic carbon (AOC);
- assessment of the concentration of biodegradable dissolved organic carbon (BDOC);

In addition to methods for assessing the presence of growth promoting compounds in drinking water, which are important for determining the effects of water treatment, methods are available which enable the assessment of the growth-promoting properties of materials in contact with drinking water [39, 40]. This subject will not be dealt with in this Chapter.

Assimilable Organic Carbon (AOC)

Investigations concerning the multiplication of either the autochthonous heterotrophic bacterial population or pure cultures in drinking water, have shown that such growth usually is very limited with respect of the DOC concentration. Contrastingly, such growth is strongly promoted by adding very low amounts of easily biodegradable compounds [41, 42]. Such observations demonstrate the importance of trace amounts of easily biodegradable compounds for bacterial growth in drinking water. Hence, a bioassay procedure was developed to assess low concentrations of the easily assimilable organic carbon (AOC) compounds in drinking water and in water in various stages of water treatment. The AOC

determination is based on measuring the maximum growth level (colony counts) of a selected pure culture or cultures of bacteria, inoculated into heat-treated samples of drinking water [30, 43]. Pure cultures were used instead of the indigenous population, to standardize the test and to enable quantification of the growth with the colony count technique. The two organisms, *Pseudomonas fluorescens* strain P17 and *Spirillum* species strain NOX, selected for the AOC-determination, are both able to multiply at low substrate concentrations and preferentially utilize different groups of compounds (Table 2). These organisms grow with simple N-sources ammonia and nitrate, do not require vitamins and produce clearly visible colonies on non-selective cultivation media. Presently, the two pure cultures are inoculated as a mixture in samples of the water to be tested [44, 45]. The AOC concentration is calculated from the maximum colony counts (N_{max}, CFU/ml) of the used organisms (Fig. 2) and their growth

Table 2. Properties of bacteria selected for the AOC determination [42, 53]

Organism	Classes of potential substrates	Yield on acetate (CFU/μg C)
Pseudomonas fluorescens P17	Amino acids, carboxylic acids[1] carbohydrates, aromatic acids	4.1×10^6
Spirillum sp. NOX	carboxylic acids	1.2×10^7

[1]strain P17 does not utilize formic and oxalic acids.

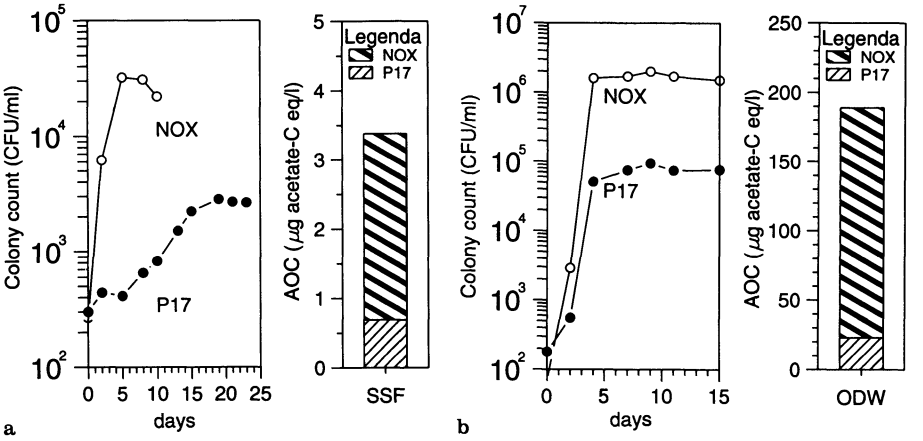

Fig. 2. Assessment of AOC concentrations from growth curves of *Pseudomonas fluorescens* P17 and *Spirillum* sp. NOX grown simultaneously in heat-treated samples of (a) slow sand filtrate (SSF; DOC = 1.8 mg/l) and (b) ozonated dune water (ODW; DOC = 4.4 mg/l). AOC concentration and composition is presented by the *bars*

yield for acetate (Table 2). Consequently, the AOC concentration is expressed as acetate-carbon equivalents (ac-C eq)/l.

Growth measurements with the pure cultures in (drinking) water give information about: (1), the concentration level of easily assimilable organic compounds and (2), the concentration of specific classes of compounds. Figure 2 shows that the concentration of compounds available for strain NOX dominates AOC in slow sand filtrate and in ozonated dune water. In these water types, less than 10% of the growth promoting compounds is available for strain P17. These observations indicate that the concentration of carboxylic acids predominates AOC in slow sand filtrate and in water after ozonation.

Growth measurements can also be conducted with pure cultures of certain undesirable bacteria, e.g. aeromonads [23] or coliforms [46, 47].

AOC concentrations (mixed inoculum of strain P17 and strain NOX) have been determined along with data about the presence of bacteria in a series of 20 drinking water supplies in the Netherlands to investigate the relationship between AOC concentration and regrowth of heterotrophic bacteria [45]. Apart from a few locations close to some of the treatment works, no disinfectant residual was present in drinking water during distribution. This investigation, revealed that AOC concentrations ranged from about 2 μg C/l (in a groundwater supply) to 60 μg C/l (in a surface-water supply). The major part (⩾90%) of the AOC concentration was available for strain NOX and AOC concentrations greater than 10 μg C/l decreased during distribution (Fig. 3).

Heterotrophic colony counts as determined on Diluted Broth Agar (DBA) medium (streak plate, incubation at 25 °C for 10 days) did not increase significantly at AOC values below 10 μg C/l. Furthermore, a statistically highly significant correlation was found between the AOC concentration and the geometric mean value of the heterotrophic colony count in drinking water during distribution.

Based on the results of the investigations described above, it has been concluded that drinking water has a limited growth potential for heterotrophic bacteria at AOC concentrations below 10 μg of C/l. It was also observed that the AOC-P17/NOX concentration was linearly related with the DOC concentration

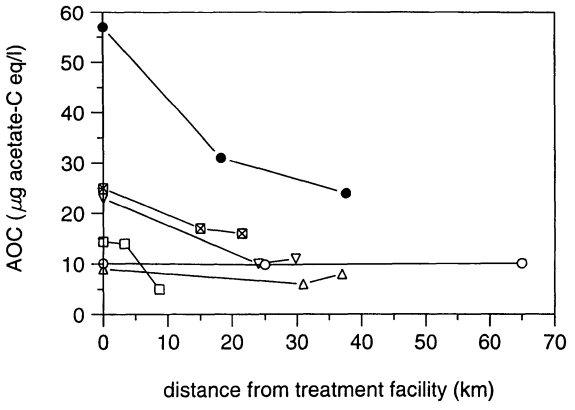

Fig. 3. The effect of distance from the water treatment facility on the AOC concentration of drinking water during distribution in a number of water supplies in the Netherlands [45] (published in the Journal of the American Water Works Association)

in groundwater-derived drinking water and in river water treated with dune filtration and slow sand filtration. Regrowth of heterotrophic bacteria was very limited in these types of drinking water. Hence, the observed AOC/DOC ratio of 1.4 μg C/mg DOC is indicative for biologically-stable organic carbon.

Studies in the United States revealed that coliform growth in drinking water during distribution correlated with the AOC concentration and it was concluded that the AOC level should be reduced to < 50 μg C/l to prevent coliform regrowth [48].

Biodegradable Dissolved Organic Carbon (BDOC)

A method for determining the concentration of biodegradable organic carbon in drinking water was first published in 1986 [34]. This method is based on exposing a sample of the water to be tested to washed sand obtained from a biologically active filter. The DOC concentration in the water decreases upon incubation of the sample and the BDOC concentration is defined as the difference between the initial concentration and the minimum concentration which usually is reached after 5 days [34, 36, 49]. Servais and Billen [33] developed another approach for assessing the BDOC concentration. A sample of water was membrane-filtered (0.2 μm), reinoculated with a natural assemblage of bacteria, and incubated at 20 °C. BDOC concentrations were calculated from the amount of bacterial biomass present in the water samples in periods up to 30 days, using known yield values. More recently, the assay has been adapted, and DOC concentrations are assessed in the samples [36].

BDOC values constitute a significant proportion (19 to 54%) of the DOC concentration (3.5–13.3 mg/l) of river water. The accuracy of the method depends on the reproducibility of the measurements of the DOC concentration and enables assessment of BDOC values greater than 0.2–0.3 mg/l. In drinking water from 79 utilities in the U.S., BDOC concentrations, which were assessed as the difference between the initial DOC concentration and the DOC concentration after 28 days of incubation at room temperature, ranged from 1 to 1521 μg C/l with a median value of 242 μg C/l [50]. These BDOC concentrations correlated with the DOC concentration, on average constituting 10.5% of the DOC concentration.

The effect of distribution on the BDOC concentration of drinking water has been studied in several investigations. A study on drinking water in Paris showed that the BDOC concentration did not decrease at values ⩽ 0.2 mg/l [51]. BDOC values were below the detection limit in drinking water of Nice, and no regrowth was observed in this system [52].

Comparison of AOC and BDOC

In the study on AOC concentrations in drinking water in the Netherlands, as referred to above, DOC concentrations of water sampled from the distribution

system were also measured. DOC concentrations usually did not decrease during distribution thus suggesting that in these water types the concentration of organic compounds available for microorganisms during distribution was below than 0.2 mg/l. A significant correlation has been observed between values for BDOC (using bacteria attached onto sand) and the maximum colony counts of strain P17 in a number of water types [49]. These observations indicate that the AOC values, as calculated from the maximum colony count were about 15% of the BDOC concentration. The AOC concentration in 76 types of drinking water in the U.S. as assessed with a modified method using 40-ml vials for sample incubation, ranged from 18 to 322 μg C/l, with a median value of 114 μg C/l. AOC and BDOC concentrations in these water types strongly correlated, with AOC levels constituting 22.4% of the BDOC concentration [50].

These observations suggest that AOC values may represent 15 to 22% of the BDOC concentration. There is little doubt that using two bacterial cultures is limiting the number of different compounds that is consumed in a biodegradation test. However, other factors also influence the difference between AOC and BDOC concentrations. First, the AOC concentration is calculated on the basis of the growth yield (Y) of the used strains for acetate. For certain biodegradable compounds, the growth yield is significantly lower than for acetate, e.g. $Y_{\text{acetate-C}} = 2.9 \times Y_{\text{oxalate-C}}$ [53]. Thus, using the yield value for oxalate, would give much higher AOC values than using those for acetate. Consequently, BDOC values do not clearly indicate the growth potential of a water type, because biomass production is not taken into account. Another difference is the fact that the maximum level of growth in the AOC test usually is reached within one week, whereas for the BDOC test samples are incubated for a period up to 4 weeks. In the rapid BDOC test, using sand from a biologically active filter as inoculum, the water is exposed to a large amount of biomass. It is unclear yet as to what extend the concentration of biodegradable organic carbon obtained under these conditions predicts multiplication in drinking water during distribution. Finally, there is a large difference in sensitivity of the two methods. The AOC determination allows assessment of concentrations down to a few μg/l. The detection limit of the BDOC determination depends on the precision of the DOC analysis and generally is about 0.2 mg/l. With highly accurate DOC measurements, lower detection limits may be achieved [50].

Effects of Water Treatment on Biostability

The effects of water treatment on the concentration of AOC and/or BDOC have been studied in a large number of investigations. It is beyond the scope of this paper to evaluate the obtained results in detail. Therefore only a few summarizing remarks will be made here. Most of the studies focussed on the effects of ozonation and biological filtration on AOC and BDOC concentrations. Ozonation causes a clear increase of the concentration of growth-promoting compounds as the result of partial oxidation of the large molecules of humic

and fulvic acids. The amount of biodegradable compounds produced depends on the ozone dosage [44, 55]. AOC concentrations in ozonated water usually range from 100 to 300 μg C/l (as acetate-C equivalents). Biological filtration reduces the concentration of biodegradable compounds to levels below 50 μg of C/l, with GAC filtration being more effective than filtration using sand or anthracite beds [43, 56]. The removal efficiency for AOC can be as large as 80% for water after ozonation, but decreases at decreasing AOC concentration [43]. Observations in the Netherlands revealed that two filtration stages, e.g. anthracite or anthracite/sand filtration followed by GAC filtration, are needed to sufficiently reduce the AOC concentration. The effects of nature and age of the filter media, contact time, frequency of backwashing, need further study to design of water treatment resulting in biologically stable drinking water. The final design of water treatment processes is also affected by the required disinfection, and the removal of pollutants such as solvents and pesticides. An integral approach is therefore needed to optimize water treatment.

Summary and Conclusions

Achieving and distributing biologically-stable drinking water is becoming an important objective in water supply. A number of techniques are available to assess the concentration of compounds which can be utilized by micro-organisms. Studies using tests for determing the concentration of AOC or BDOC in drinking water during distribution in relation with regrowth phenomena have resulted in criteria for drinking water with a limited growth potential for heterotrophic bacteria. A large number of data obtained in surveys and pilot plant studies clearly demonstrate the effects of ozonation and biological filtration on the biostability of drinking water. However, further investigations are needed to define conditions for filtration processes which enable to achieve biologically stable drinking water after ozonation and biological nitrate removal. Furthermore, controlling biofilm formation on the walls of the pipes in distribution systems requires further research.

References

1. Engel HWB, Berwald LG and Havelaar AH (1980) Tubercle 61:21
2. Schoenen D, Striegler B, Titulaer P (1985). Off Gesundh Wes 47:32
3. Tobin JOH, Beare J, Dunnil MS (1980). Lancet :118
4. Schulze-Robbecke R and Fischeder R (1989) Zbl Hyg 188:385
5. Burke V, Robinson J, Gracey M, Petersen D and Partridge K (1984) Appl. Environ Microbiol 48:361
6. LeChevallier MW (1990). J. Am. Wat. Works Assoc. 82:74
7. O'Connor JT, Nash L and Edwards AB (1975) J. Am. Water Works Assoc. 67:113

8. Lee SH, O'Connor JT and Banerji SK (1980) J. Am. Water Works Assoc. 72:636
9. Allen MJ, Taylor RH and Geldreich EE (1980) J. Am. Water Works Assoc. 72:614
10. Ridgway HE and Olson BH (1981) Appl. Environ. Microbiol. 41:274
11. Nagy LA and Olson BH (1985) Proc. Am Water Works Water Quality Technology Conference, Houston, Tex. American Water Works Association. Denver.
12. LeChevallier MW, Babcock TM and Lee RG (1987) Appl. Environ. Microbiol. 53:2714
13. Donlan RM and Pipes WO (1988). J. Am. Water Works Assoc. 80:70
14. Colbourne JS and Brown DA (1979) J. Appl. Bacteriol. 47:223
15. Schoenen D and Schöler HF (1985) DVGW Schriftenreihe Wasser nr. 37. Deutscher Verein des Gas- und Wasserfaches, Frankfurt, Germany.
16. Rook J (1974) J. Soc. Water Treatment Exam. 23:234
17. Herson DS McGonigle B, Payer MA and Baker KH (1987) Appl. Environ. Microbiol. 53:1178
18. LeChevallier MW, Cawthon CD and Lee RG (1988) Appl. Environ. Microbiol. 54:649
19. Rittmann BE and Snoeyink VL (1984) J. Am. Water Works Assoc. 76:106
20. Schellart JA (1986) Water Supply 4:217
21. Van der Kooij D and Hijnen WAM (1985) J. Francais d'Hydrology 16:201
22. Servais P, Billen G and Rego JV (1985) Appl. Environ. Micrbiol 49:1448
23. Van der Kooij D and Hijnen WAM (1988) Appl. Environ. Microbiol. 54:2842
24. Baylis, JR, Chase, ES Cox CR Ellms JW Emerson CA Knouse HV and Streeter HW (1930) Am. J. Publ. Hlth 20:485
25. Martin RS et al (1982) J. Am. Water Works Assoc. 74:34
26. Smalls LC and Greaves GF (1968) J. Soc. Water Treatment Exam 17:445
27. Schalekamp M (1969) Gas, Wasser, Abwasser 49:253
28. Dietlicher K (1970) Schrftr. Ver. Wasser- Boden- Lufthyg. 31:1
29. Hijnen WAM, Koning D, Kruithof JC and Van der Kooij D (1988) Water Supply 6:265
30. Van der Kooij D, Visser A and Hijnen WAM (1982) J. Am. Water Works Assoc. 74:540
31. Werner P (1985) Vom Wasser 65:257
32. Stanfield G and Jago PH (1987) Report PRU 1628-M, Water Research Centre, Medmenham. U.K.
33. Servais P, Billen G, Hascoet MC (1987) Water Res. 21:445
34. Joret JC and Levy Y (1986) Trib. Cebedeau. 39:3
35. Ribas F, Frias J and Lucena F (1991) J. Appl. Bacteriol. 71:371
36. Servais P, Anzil A, Ventresque C (1989) Appl. Environ. Microbiol. 55:2723
37. Block JC, Mathieu J, Servais P, Fontvielle D, Werner P (1992) Wat. Res. 26:481
38. Huck PM (1990) J Am Water Works Assoc 82:78
39. BSI, 1988. British Standard 6920. British Standards Institution, United Kingdom.
40. DVGW, 1990. Technische Regeln Arbeitsblatt W270. DVGW Eschborn. Germany.
41. Van der Kooij D, Hijnen WAM (1981) Appl. Environ. Microbiol. 41:216
42. Van der Kooij D, Visser A, Oranje JP (1982) Antonie van Leeuwenhoek 48:229
43. Van der Kooij (1990) In: McFeters GA (ed) Drinking water microbiology; progress and developments, Brock/Springer Series in Contemporary Bioscience, Springer, Berlin Heidelberg New York, p 57
44. Van der Kooij D, Hijnen WAM and Kruithof JC (1989) Ozone Sci. Eng. 11:297
45. Van der Kooij D (1992) J. Am. Water Works Assoc. 84:57
46. Van der Kooij D and Hijnen WAM 1989 Wat. Sci. Technol. 20:117
47. Rice EW, Scarpino PV, Reasoner DJ, Logsdon GS and Wild DK (1991) J. Am. Water Works Assoc. 88:98
48. LeChevallier MW, Schulz, W and Lee RG (1991) Appl. Environ. Microbiol 57:857
49. Joret JC, Levy Y and Volk C (1991). Wat. Sci. Technol 24:95
50. Kaplan LA, Reasoner DJ, Rice EW and Bott Tl (1992) Rev Sci de L'eau 5:225
51. Servais P, Billen G, Laurent P, Levy Y, Randon G (1992). Rev, Sci. L'eau 5:69
52. Levy Y, Randon G. Denojean C, Pagliardini A, Vajente G. Champsaur H (1992). Rev. Sci L'eau 5:225
53. Van der Kooij D, Hijnen WAM (1984) Appl. Environ. Microbiol. 47:551
54. Miltner RJ, Shukairy HM and Summers RS (1992) J. Am. Water Works Assoc. 84:53
55. Lechevallier et MW, Becker WC, Schorr P and Lee RG (1992) J. Am. Water Works Assoc. 84:136
56. Van der Kooij D and Hijnen WAM (1985) Appl. Environ. Microbiol. 49:765
57. Van der Kooij D, Oranje JP and Hijnen WAM (1982) Appl. Environ. Microbiol. 44:1086

Removal of Organic Micropollutants by Activated Carbon

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List of Symbols and Abbreviations

AC	Activated Carbon
DOC	Dissolved Organic Carbon
EDTA	Ethylenediaminetetraacetate
GAC	Granular Activated Carbon
PAC	Powdered Activated Carbon
PCB	Polychlorinated Biphenyls
TCP	Trichlorophenol
c	liquid-phase concentration
c_0	initial concentration
h	filterbed depth
K	Freundlich constant
l	filterbed depth
n	Freundlich exponent
q	solid-phase concentration

T temperature
v_F filter velocity

Abstract

Activated carbon adsorption is the most important treatment step for micropollutant removal from surface- and groundwaters. Due to the competitive adsorption between the natural organic substances present in the raw water and the trace organic compounds, the carbon capacity for the micropollutant is reduced compared to the single solute system. Therefore the efficiency of the activated carbon for the micropollutant elimination depends on the kind and the adsorbability of the organic background on one side and the adsorbability and the concentration of the trace organic compound itself. In addition, optimal operation conditions will lead to greater efficiency of the activated carbon. However different trace organic compounds behave differently during adsorption from natural waters as has been shown in pilot studies.

1 Introduction

The most common process for the removal of organic micropollutants in drinking water treatment is activated carbon adsorption, whereas in Europe, in most cases, granular activated carbon in fixed-bed adsorbers is preferred. In the past few years a lot of experience for the adsorption of micropollutants in a concentration range of several mg m^{-3} has been obtained. A new problem has arisen, hence the European Community directive-as well as the German drinking water regulations-demand a maximum concentration for pesticides in drinking water which is 0.1 mg m^{-3} for every individual pesticide and 0.5 mg m^{-3} for the total of pesticides including the toxic main metabolites. Some groundwaters and surface waters contain pesticides in concentrations below 1 mg m^{-3} and this is 3 to 4 orders of magnitude lower than the concentration of the natural organic substances in the raw water. Therefore a strong competitive adsorption between the natural organic substances and the pesticides must be expected, resulting in a decreasing adsorption capacity for micropollutants compared to the single solute system.

The following illustrates the general tendencies which are observed in micropollutant removal by activated carbon under practical conditions. The experience of the Engler-Bunte-Institute is mainly presented, extended by a few results from the literature. Some of the discussed effects are already published in the monographs from Sontheimer et al. [1, 2].

2 Adsorption Isotherms of Micropollutants

2.1 Background Information

The basic information for the adsorbability of a single compound gives the adsorption isotherm, which is the result of an adsorption equilibrium study conducted at a constant temperature. The single solute adsorption isotherm can be described by the function

$$q = f(c) \qquad T = \text{constant} \tag{1}$$

in which q is the solid-phase concentration (usually given in g kg^{-1} or mg g^{-1}) and c the liquid-phase concentration (usually given in mg l^{-1} or mg m^{-3}).

Adsorption equilibrium studies are usually conducted using the bottlepoint isotherm technique as described by Sontheimer et al. [1, 2]. Different quantities of powdered activated carbon are added to several bottles containing defined quantities of solution with the same initial concentration of the sorbate. The samples are tumbled until steady state is reached. Then the carbon particles are separated from the liquid phase by filtration using 0.45 μm membranes. The sorbate concentration in the liquid phase is analysed before and after adsorption. The sorbate solid phase concentration can be calculated from a mass balance.

In order to apply calculations to the design of treatment plants, the isotherm data are usually described using a mathematical model. Several different isotherm models exist which are described elsewhere [1–3]. For the adsorption of a defined compound out of an aqueous solution the empirical equation of Freundlich [4] is often used.

$$\text{Freundlich isotherm: } q = Kc^n \tag{2}$$

In this equation, K is the Freundlich constant and n the Freundlich exponent. Both parameters can be determined by a linear regression of $\log q = f(\log c)$, where K is the solid-phase concentration at $c = 1$ and n is the slope of the straight line.

The Freundlich isotherm can only be used in a limited concentration range and, furthermore, this isotherm does not change into the Henry equation for very low concentrations.

2.2 Single Solute Isotherms for Different Synthetic Organic Compounds

The isotherms of several synthetic organic micropollutants with different adsorbabilities are shown in Fig. 1. The isotherms are evaluated by the Freundlich equation and the Freundlich parameters are also given in this figure.

According to Fig. 1, most of the common pesticides are strongly adsorbable and therefore activated carbon adsorption should be an effective method for

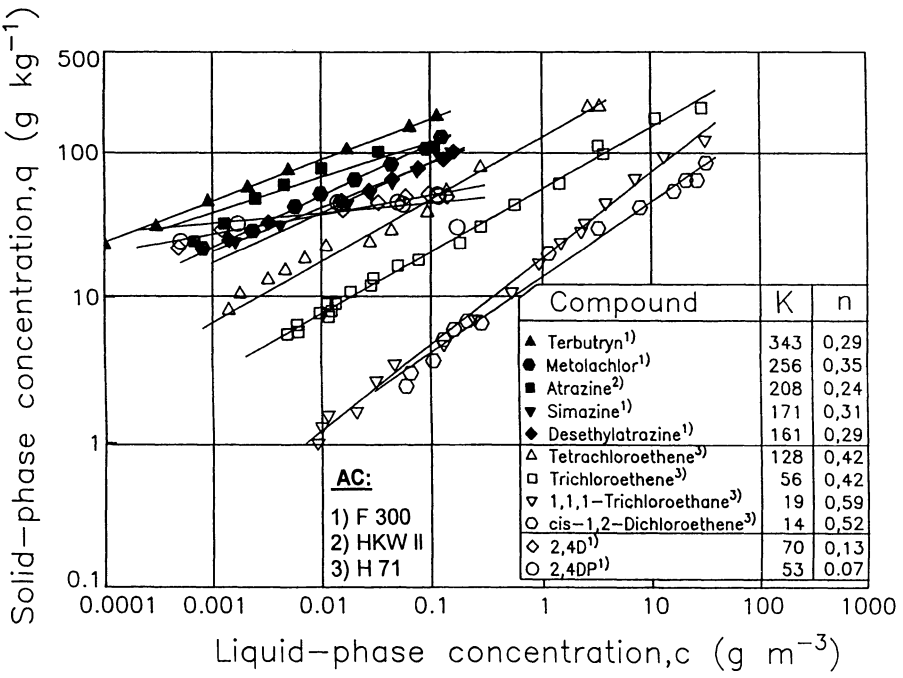

Fig. 1. Adsorption isotherms of different synthetic organic compounds [5]

their elimination in water purification processes. The chlorinated hydrocarbons tetrachloroethene and trichloroethene are also strongly adsorbable. 1,1,1-Trichloroethane, *cis*-1,2-Dichloroethene, Chloroform and Trichloroacetic acid are weakly adsorbable [6] like most of the polar aliphatic compounds [5]. A low adsorption capacity is also observed for the pesticides Diquat and Paraquat [7]. The adsorption characteristics of other compounds can be seen from the Freundlich parameters which are summarized in the literature for different types of activated carbon [1, 2].

From the single solute isotherm data the efficiency of the activated carbon adsorption for the micropollutant removal cannot be predicted. More information is necessary for the design of treatment plants with activated carbon due to the competitive adsorption of the micropollutants and the natural organic substances as shown in the following chapter.

2.3 Coadsorption Isotherms of Micropollutants

In most raw waters which have to be treated, the natural organic substances are present in much higher concentrations than an individual organic micropollutant and the micropollutant adsorption is affected by these compounds as, for example, is shown in Fig. 2. The presence of 0.6 g m^{-3} of DOC (dissolved organic carbon) in the groundwater causes a capacity reduction for trichloroethene of

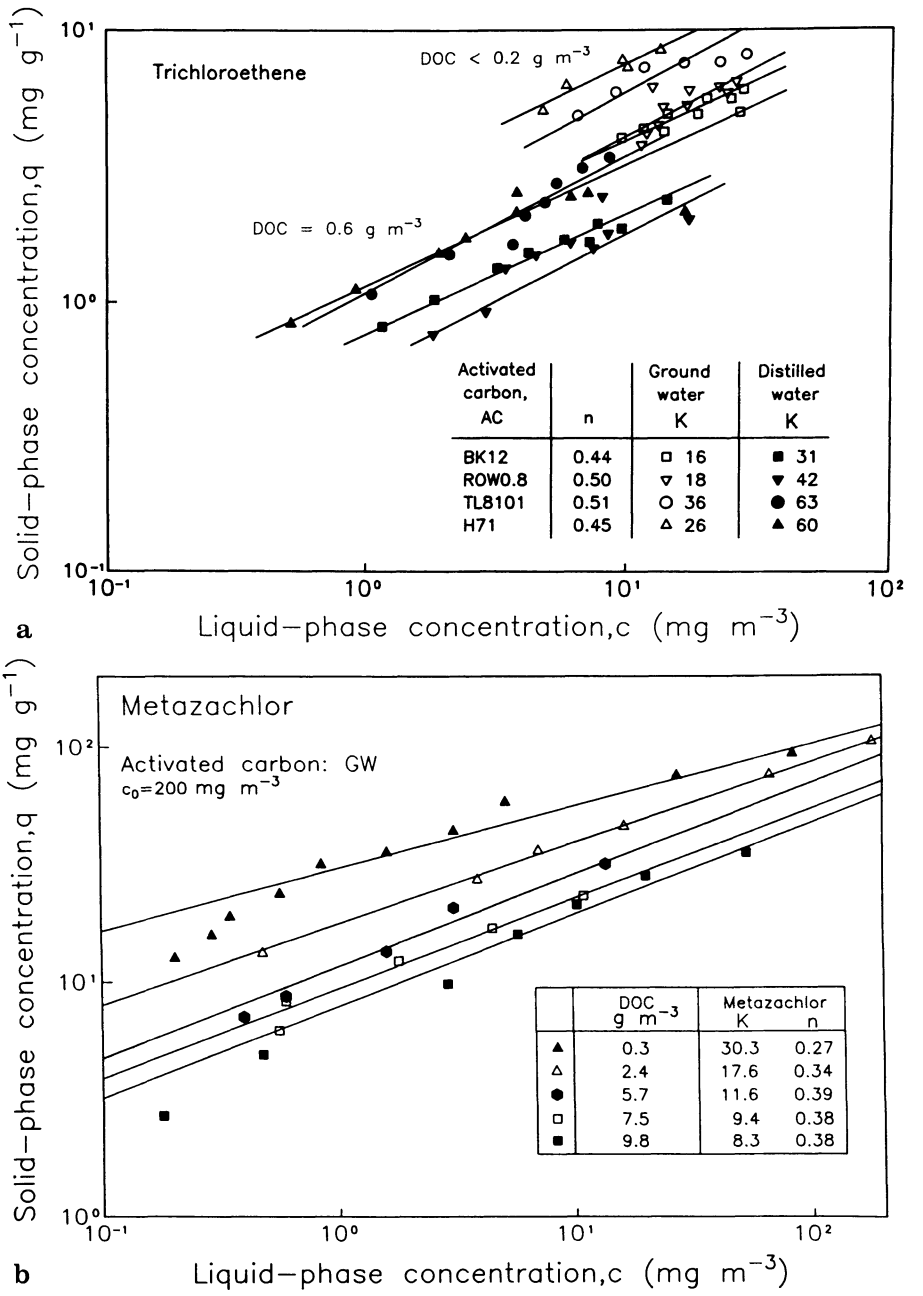

Fig. 2a, b. Single solute and coadsorption isotherms for trichloroethene and Metazachlor [2, 9]

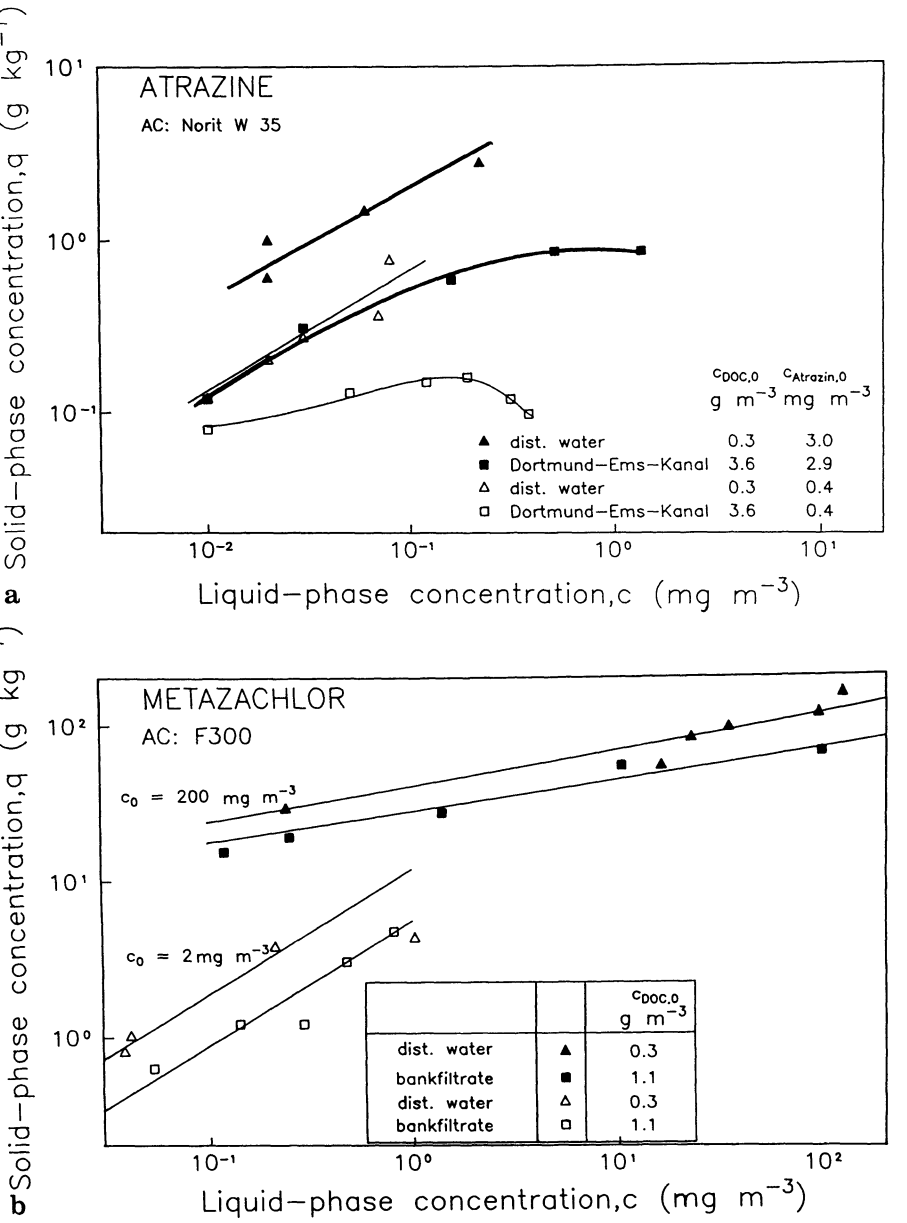

Fig. 3a, b. Adsorption isotherms of Metazachlor and Atrazine with different initial concentrations from different raw waters [19, 31]

more than 50% for all the carbons used in this study [8]. Figure 2b shows the results from batch studies in which humic substances from the Hohloh Lake water, a muddy lake in the Black Forest, have been added to the solutions. It can be seen that, with increasing concentration of dissolved organic carbon, the solid-phase concentration for Metazachlor decreases [9].

However, micropollutants can behave differently in the presence of natural organic substances. For the adsorption of chlorinated hydrocarbons from groundwaters, several authors have found similar effects to those shown in Fig. 2a [10–14]. In contrast, some investigations have shown no or only a very small impact of the natural organic background on the adsorption isotherms of aliphatic chlorinated hydrocarbons and chlorinated benzenes [15–19].

Corresponding results are found for the adsorption of pesticides and odor compounds like 2-Methylisoborneol and Geosmin, chlorinated phenols and polychlorinated biphenyls (PCB) in the presence of humic substances [6, 9, 20–29]. The investigators report a significant capacity reduction of the carbon for the micropollutant carbon compared to the single solute isotherms.

Sontheimer et al. [1, 2] and Najm et al. [30] have summarized the different observations and have concluded that the impact of humic substances on micropollutant adsorption depends on the kind and the source of the raw water, the sorbate and the trace organic compound. Usually the single compound and the natural organic substances have different molecular sizes and therefore different effects in the competitive adsorption are observed.

Another important effect which has been found for many pesticide- [6, 19], PCB- [29] and trichlorophenol (TCP) [30] -isotherms is the dependency of the solid-phase concentration on the initial concentration as shown in Fig. 3a, b for the adsorption of the pesticides Atrazine and Metazachlor [19, 31].

For the adsorption of pesticides from surface water, the solid-phase concentrations are lower with lower initial concentrations of the micropollutants. On decreasing the initial concentration of Metazachlor from 200 mg m^{-3} to 2 mg m^{-3} the solid-phase concentration is reduced by more than one order of magnitude. Even a reduction of the initial concentration in the surface water from 3.1 mg m^{-3} to 0.43 mg m^{-3} diminishes the solid-phase concentration by about 70% under the given conditions in the batch test. So the activated carbon efficiency decreases with decreasing concentration of the micropollutant in the raw water. From Fig. 3a, it can also be seen that coadsorption isotherms do not have to be straight lines in a log-log scale, depending on the adsorbabilities of the micropollutant itself and the other adsorbable compounds in the raw water.

This dependency of the coadsorption isotherms on the initial concentrations is characteristic for the adsorption of a defined compound from mixtures and such behavior is expected due to competitive adsorption. However, a similar effect has not been found in all cases for the adsorption of aliphatic chlorinated hydrocarbons [18, 19]. From Fig. 4 it can be seen that the adsorption isotherms of 1,1,1-trichloroethane and trichloroethene are independent of the initial concentration of the chlorinated hydrocarbons. Furthermore the isotherms are not affected by the natural organic background [19].

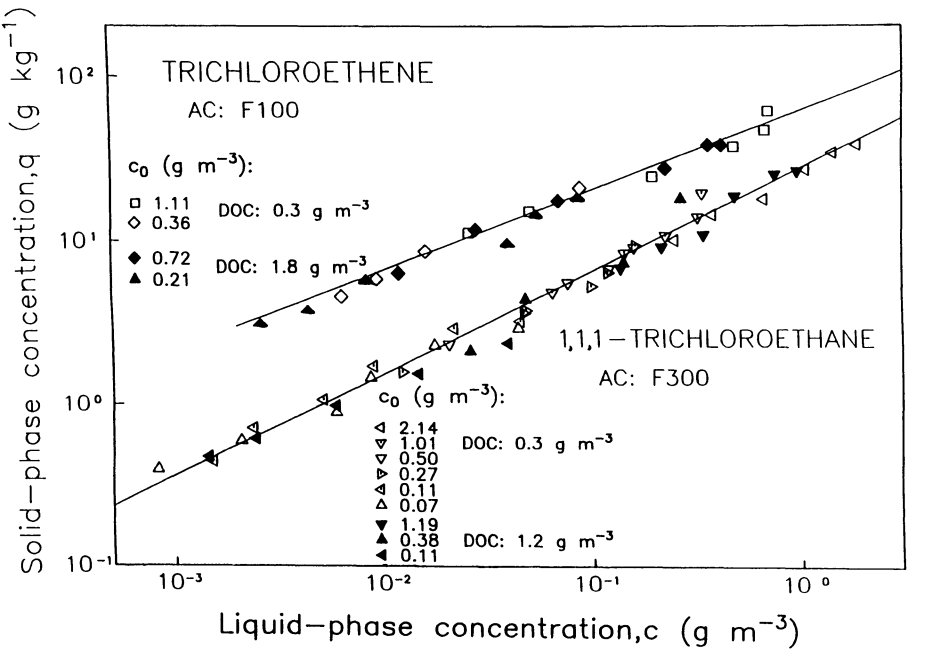

Fig. 4. Single-solute and coadsorption isotherms of 1,1,1-trichloroethane and trichloroethene with different initial concentrations and raw waters [19]

These basic investigations show that important information on the effectiveness of the activated carbon application can already be obtained from laboratory studies. For the elimination of micropollutants the raw water quality and the initial concentration of the trace organic compound have to be taken into account. Some methods exist for the prediction of coadsorption isotherms.

3 The Application of Powdered Activated Carbon (PAC)

3.1 The PAC Process

The use of PAC in drinking water treatment is, in most cases, for the removal of compounds causing taste and odor problems and for the treatment of some surface waters with seasonal changes in raw water quality. Furthermore, some waterworks treating surface water use the PAC process as a security measure in case of chemical spills. In Germany the application of PAC for the elimination of trace organic compounds has become more important in the past few years, especially for the removal of pesticides.

One special advantage of the PAC process, compared to the use of granular activated carbon (GAC) in fixed-bed adsorbers, is the ability to change the

carbon dose in order to achieve the required water quality with changing raw water quality. This requires frequent monitoring of the raw water quality.

In general 90% of the PAC particles are smaller than 0.05 mm. The PAC is added to the water as a suspension and carbon doses between 10 to 50 g m^{-3} are often used [1, 2]. After a contact time of 5 to 45 min the PAC is separated from the raw water by flocculation and/ or filtration.

In a convential treatment plant with a flocculation step, the PAC is usually added to the raw water within the rapid mix tank. Variations to this process include adding the PAC before or after the flocculant dosing. Adding the PAC before the flocculant dosing improves the adsorption kinetics because the PAC particles are not immediately incorporated within the flocs. A disadvantage of this procedure can be seen in the increased adsorption competition from the compounds which can be removed by flocculation. In contrast, the competition is diminished by dosing the PAC behind the rapid mix tank because the natural organic substances can be partly removed by flocculation [1, 2].

PAC can be separated from the raw water by sedimentation or filtration. Using filtration the PAC is retained in a sand or anthracite filter and the PAC efficiency for the micropollutant removal is usually higher compared to the procedure where the PAC is removed by sedimentation. Dosing of the PAC into the filter influent can lead to an increased headloss in the filter which may be further increased by the additional dosing of flocculant or flocculation aid. The operation time of the filter is determined by the headloss and/or the turbidity in the filter effluent. Then the filter has to be backwashed. A breakthrough of PAC particles must be avoided as this may cause corrosion problems in the distribution system.

Good results can be achieved by adding the PAC before a slow sandfilter because the adsorption step and the biodegredation are combined.

Other possibilities in the use of PAC in filters are putting the carbon on a filter media like sand or anthracite, operating the filter like a fixed-bed adsorber with granular activated carbon and coating polystyrene spheres with PAC in a filter layer [32].

In drinking water treatment plants PAC can be applied in a single- or multi-stage concurrent flow processes. The design and the basic mathematical relations for these processes are given by Sontheimer et al. [1, 2].

Some experience has been gained in the removal of compounds causing taste and odor problems in low concentrations. Only few results from the application of PAC to micropollutant removal from drinking water under practical conditions are published.

3.2 The Application of PAC

The PAC demand for micropollutant removal depends on the kind and the concentration of the organic background, the adsorbability of the micropollutants and their concentration as shown in Sect. 2.2. For the elimination of pesticides in full-scale treatment plants, a PAC demand between 5

and 20 g m^{-3} is required to reduce the pesticide concentration from a maximum 1.0 mg m^{-3} to 0.1 mg m^{-3}. The theoretical carbon dose for achieving the standard can be determined by measuring isotherm data under practical conditions (see Sect. 2).

An important factor for a good design and operation of PAC treatment plants will be the contact time. Due to the small particle size and the great specific surface, steady state should be quickly achieved by intensive mixing. However, for the elimination of pesticides from distilled water, it is reported that only 56 to 90% of the equilibrium concentration can be achieved after 2 h of contact time [33].

The contact time for reaching equilibrium depends on the PAC particle size and the molecule size of the micropollutant [34]. With decreasing PAC particle size the contact time for reaching equilibrium decreases. As the molecule size increases the diffusion into the pores is delayed and therefore the contact time increases [35].

For the adsorption of Isoproturon from surface water in a full-scale single-stage reactor the influence of the contact time is shown in Fig. 5. Under the given conditions and a carbon dose of 5 g m^{-3} and 0.2 h contact time, less than 50% of the equilibrium solid-phase concentration (24 h contact time) has been achieved. With increasing carbon dose the contact time for reaching equilibrium decreases as the carbon loading will be lower [5].

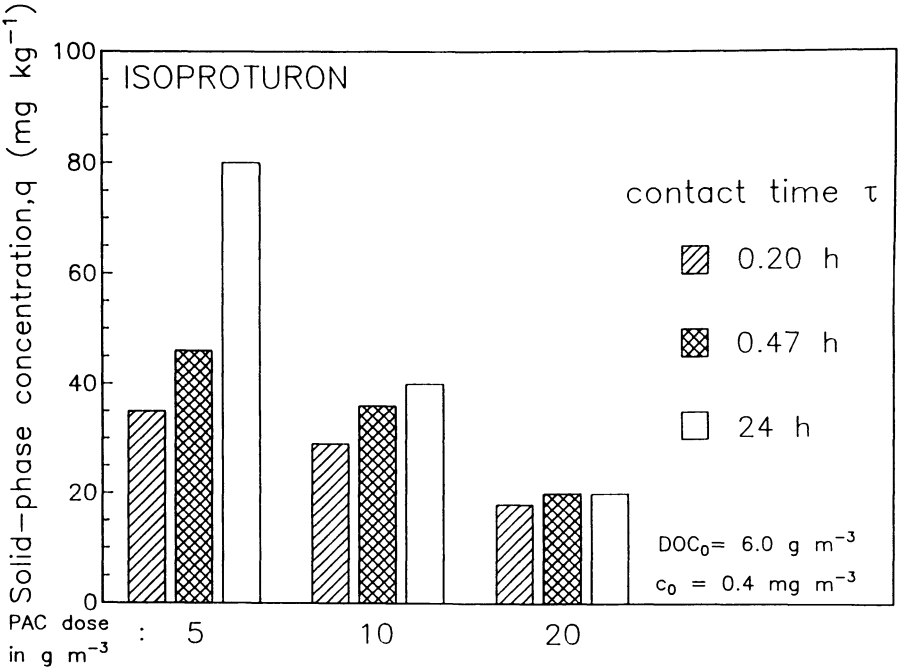

Fig. 5. Influence of the contact time on the PAC solid-phase concentration for Isoproturon [5]

In the treatment plant where the data shown in Fig. 5 were measured, $FeClSO_4$ is added behind the PAC reactor and the PAC is separated from the water by sand filtration. The concentration of the pesticides can be reduced to a larger extent during PAC filtration as shown in Table 1 for Atrazine and Chlortoluron.

A further reduction in concentration of the pesticide DDT has been found by adding the PAC after the flocculant compared to the simultaneous dosing of the PAC and the flocculant [36].

In a laboratory study the impact of the raw water quality on the PAC demand has been investigated for the removal of Atrazine within a contact time of 24 h. The organic content of the surface water (DOC: 3.6 g m^{-3}) has increased the

Table 1. Pesticide concentration after the PAC reactor and after sandfiltration (carbon dosage: 5 g m^{-3})

	influent concentration (mg m^{-3})	effluent concentration (PAC) reactor (mg m^{-3})		effluent concentration sandfilter (mg m^{-3})
		contact time 31 min	45 min	
Atrazine	2.9	2.5	2.1	0.41
Chlortoluron	2.3	1.4	1.2	0.09

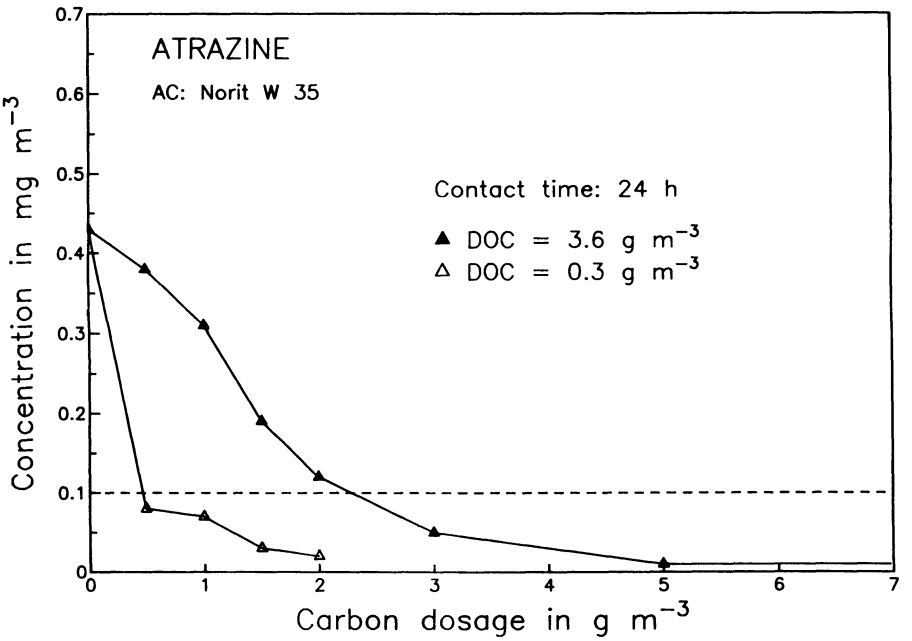

Fig. 6. PAC demand for the removal of Atrazine in a laboratory study for two different waters

carbon dose for achieving 0.1 mg m^{-3} by more than 400% compared to the results in distilled water, as can be seen from Fig. 6.

The examples given in Sect. 2 show that the usable capacity of the PAC for some micropollutants decreases with increasing DOC concentration of the water to be treated. Besides this, the initial concentration of the micropollutant in the raw water can affect the isotherm and therefore the capacity as well. These observations show that, due to the very low concentration of the pesticides, only a few percent of the adsorption sites on the carbon surface will be occupied by the micropollutant and many more are blocked by the humic substances. Nevertheless the PAC process can be an economic procedure for the removal of some pesticides. This has been shown in full scale treatment plants.

4 The Application of Granular Activated Carbon (GAC)

On a worldwide basis, powdered activated carbon (PAC) is used much more than granular activated carbon (GAC) in drinking water treatment. However, in Europe, many waterworks prefer GAC for the removal of micropollutants. In the case of the elimination of chlorinated hydrocarbons, much experience has been gained with GAC during the last decade.

4.1 Removal of Micropollutants in GAC Fixed-Bed Adsorbers

During GAC filtration the micropollutant adsorption is, as in PAC processes, affected by the natural organic substances. Due to the simultaneous removal of natural organic substances and pollutants in fixed-bed adsorbers the filter capacity for the micropollutants will be significantly reduced.

As an example, Fig. 7 shows breakthrough curves for trichloroethene [8]. In the first study a groundwater (DOC: 2.4 g m^{-3}) has been used, and for the second study the groundwater has been prefiltered over activated carbon and then the water (DOC < 0.2 g m^{-3}) has been spiked with trichloroethene again for the experiment. For the adsorption of trichloroethene from the groundwater the carbon capacity at complete breakthrough of the micropollutant has been reduced by about 60% compared to the adsorption from the prefiltered water. The carbon capacity for trichloroethene in the column test with prefiltered water corresponds to the single solute isotherm data [8].

Under the conditions prevailing in waterworks, only 20–40% of the single-solute capacity for trichloroethene has been achieved in a GAC fixed-bed adsorber at a complete breakthrough of the trace organic compound [8]. Furthermore, a capacity reduction of 90% for tetrachloroethene and about 40% for 1,1,1-trichloroethane has been reported in a GAC filter column at complete breakthrough compared to the single solute isotherm. As the data show, the carbon

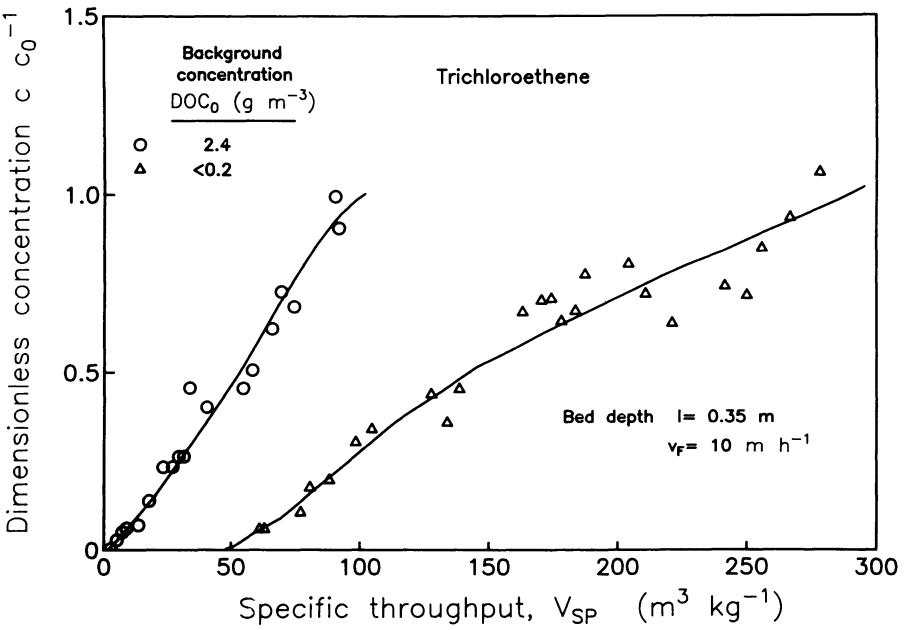

Fig. 7. Impact on the natural organic matter on the breakthrough curve of trichloroethene

capacity in a GAC adsorber at complete breakthrough is reduced much more for strong adsorbing compounds like tetrachloroethene than for weak adsorbing micropollutants. This can be explained by the fact that the adsorption fronts of the stronger adsorbing micropollutants pass through the fixed bed with a lower velocity and therefore the micropollutant competes with most compounds of the raw water throughout the fixed bed which results in a high capacity reduction. Conversely, weak adsorbing micropollutants pass through the carbon bed comparatively quickly and compete with only a few substances in the deeper filter bed. After the complete breakthrough of these weak adsorbable compounds they are displaced by more highly adsorbable compounds to a great extent. Then the filter effluent concentration is higher than the influent concentration. However a fixed bed adsorber will never be operated to these operation times.

Similar significant capacity reductions of the GAC as shown in Fig. 7 have been found for other chlorinated hydrocarbons in the presence of natural organic substances of ground and surface waters [8, 14, 19].

As reported in Sect. 2, in some isotherm studies the solid-phase concentration of activated carbon for chlorinated hydrocarbons is not reduced in the presence of humic substances in all cases. However, for the removal of micropollutants from natural waters in GAC fixed-bed adsorbers, lower carbon capacities for trace organic compounds have been found in all cases compared to the equilibria studies. The discrepancy between batch studies and the practical results can be explained by the preadsorption of the natural organic substances in fixed-bed adsorbers [18]. The high initial concentration of humic substances

and their low adsorption kinetics lead to a fast breakthrough of humic substances. Therefore the micropollutants adsorb onto preloaded carbon with a lower adsorption capacity for the pollutants than onto the virgin carbon. This effect is called carbon-fouling [18].

In order to investigate this reduction in the adsorption capacity resulting from the background substances, GAC samples can be taken from a fixed-bed adsorber after various operation times and from different filter depths. After drying and grinding the carbon, adsorption isotherms have been conducted. Figure 8 shows that, with increased preloading time for the carbon, the capacity for 1,1,1-trichloroethane decreases. Within the first 16 weeks during the operation of this filter, which has been used for the removal of natural organic substances in the water treatment facility, the capacity of the GAC for 1,1,1-trichloroethane at a filter depth of 0.58 m decreases by more than 70% under the given conditions [19].

Due to the parallel shift of micropollutant isotherms on preloaded carbon, the capacity reduction can be given by the quotient of the Freundlich K-values of the preloading and the single-solute isotherm [18, 19]. These relative Freundlich parameters are given in Fig. 9 for different preloading times and different bed depths of the fixed-bed adsorber. For a given preloading time the relative Freundlich parameter which is equal to the relative carbon capacity is lowest at the top of the filter column and highest at the bottom. This corresponds to a smaller amount of preadsorbed humic material [19]. The capacity reduction of

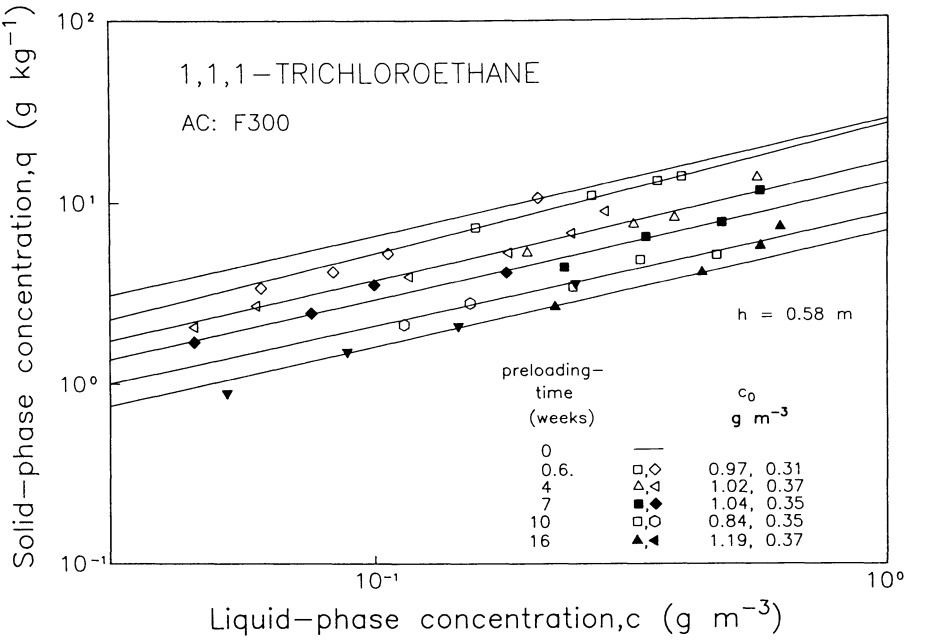

Fig. 8. Isotherms of 1,1,1-trichloroethane on preloaded carbon [19]

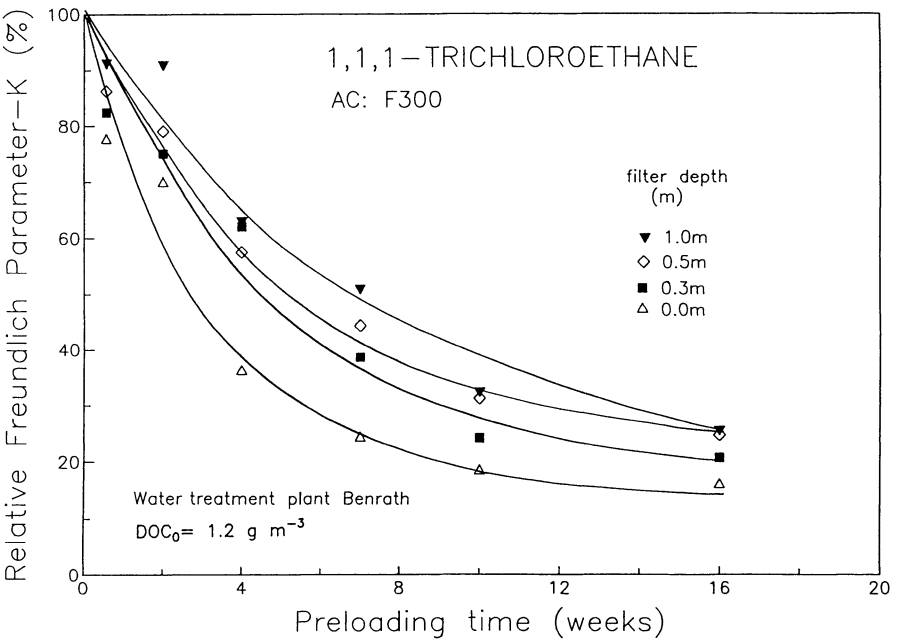

Fig. 9. Dependency of the GAC capacity reduction for 1, 1, 1-trichloroethane and preloading time in different bed depths [19]

the GAC for micropollutants is a function of the DOC solid-phase concentration as shown in Fig. 10 [19, 37].

The fouling effect has also been found for the removal of pesticides [19, 31] in GAC fixed-bed adsorbers. Table 2 shows the specific throughputs to the filter effluent concentration of 0.1 mg m^{-3} for different pesticides, which result from pilot studies with preloaded and reactivated carbon. The reactivated carbon is equivalent to virgin carbon. Due to carbon fouling, shorter specific throughputs

Table 2. Comparison of the efficiency of reactivated and preloaded carbon F300 for the removal of pesticides from Rhine bankfiltrate in GAC filters

Compound	initial concentration (mg m^{-3})	specific throughput (m^3kg^{-1})[a]	
		Reactivated carbon	Preloaded carbon[b]
Simazine	0.53	110	98
Isoproturon	1.56	76	56
Terbutylazine	1.13	63	36
Atrazine	1.76	54	18
Metolachlor	1.96	48	12
Metazachlor	2.09	39	8

[a]Specific throughput to the effluent concentration of 0.1 mg m^{-3} [b]Carbon was preloaded with 16 m^3 river Rhine bankfiltrate (DOC: 1.3 g m^{-3}) per kg activated carbon

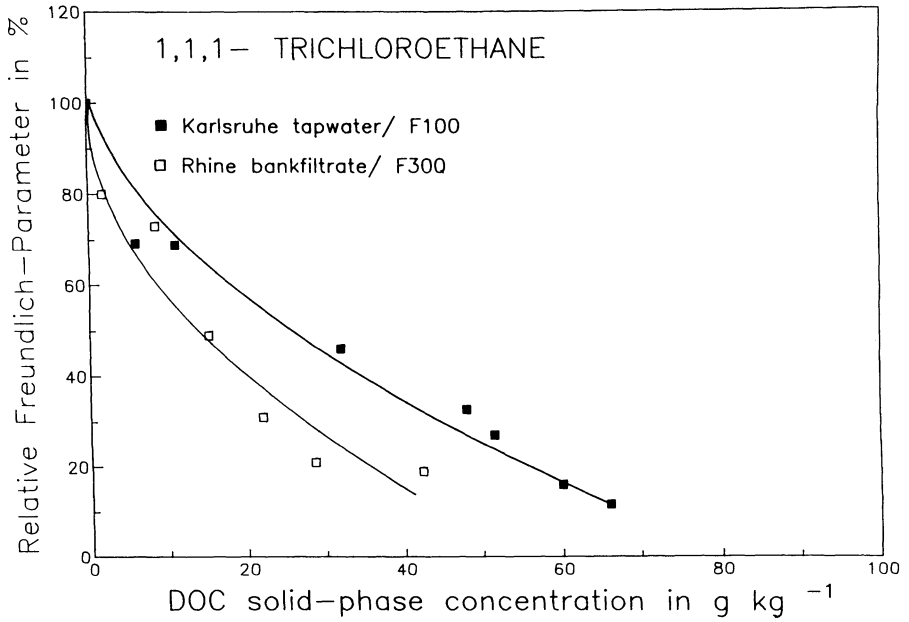

Fig. 10. Dependency of the GAC capacity for trichloroethene and the DOC loading [19]

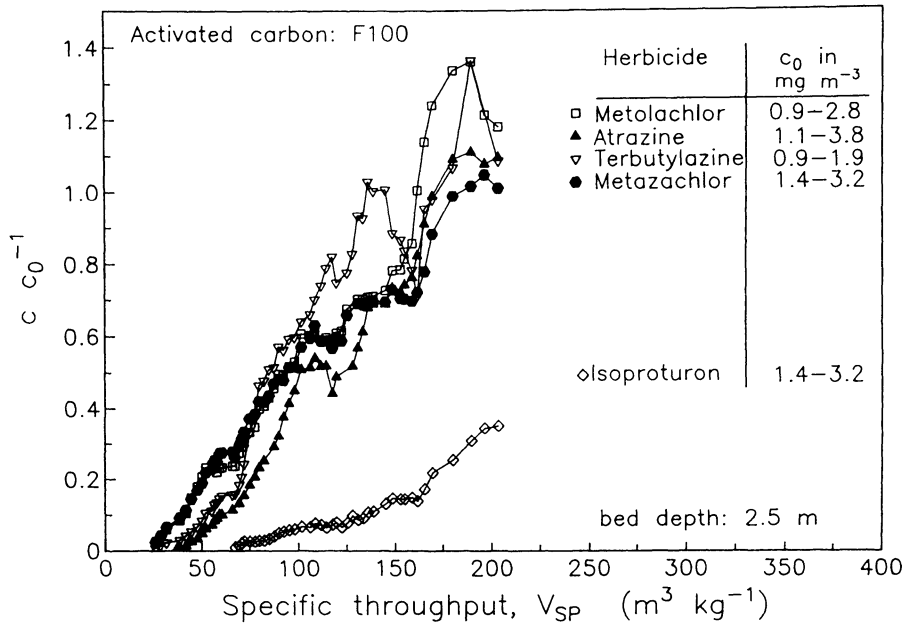

Fig. 11. Breakthrough curves of different pesticides [39]

have been achieved using preloaded carbon. The specific throughputs for Isoproturon and Simazine show a lower capacity reduction compared to Metazachlor and Metolachlor with a very low specific throughput using preloaded carbon.

For the application of GAC as a security step, it has to be remembered that the efficiency of the GAC in case of a chemical spill depends on the amount of preloaded material and therefore on the operation time of an adsorber. For continuous removal of micropollutants in GAC fixed-bed adsorbers a higher micropollutant loading of the GAC can be achieved by alternately operating two adsorbers in series [38].

Figure 11 shows breakthrough curves for pesticides with different adsorbabilities from groundwater [39]. The initial concentrations of the pesticides were between 0.9 and 3.8 mg m^{-3} per single substance, the filter velocity being 10 m h^{-1}. Under the given conditions the specific throughput at an effluent concentration of 0.1 mg m^{-3} for each single pesticide is about 30 m^3 per kg activated carbon for Metazachlor and Metolachlor. The highly adsorbable Isoproturon can be completely removed from the raw water at a specific throughput of 70 m^3 kg^{-1}. In this study the carbon capacity for Atrazine, at the relative effluent concentration of 1.0, has been 0.22 g kg^{-1} and is less than 1% of the solid-phase concentration of the single-solute isotherm, conducted at an initial concentration of 200 mg m^{-3}.

Due to the very low initial concentration of the pesticides in the raw waters, below 1 mg m^{-3} in most cases, the shape of the breakthrough curve of pesticides is rather flat (Fig. 12).

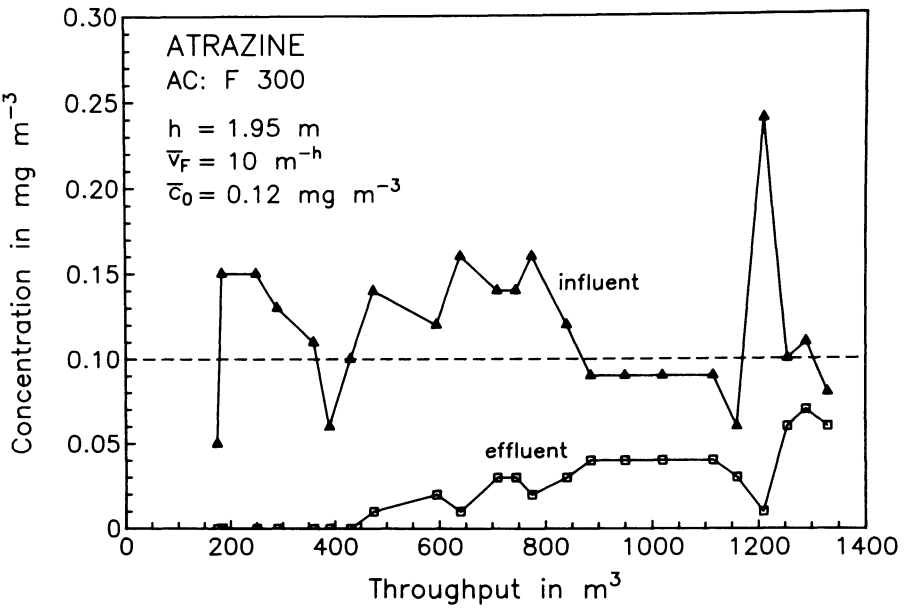

Fig. 12. Breakthrough curve of Atrazine in a pilot plant

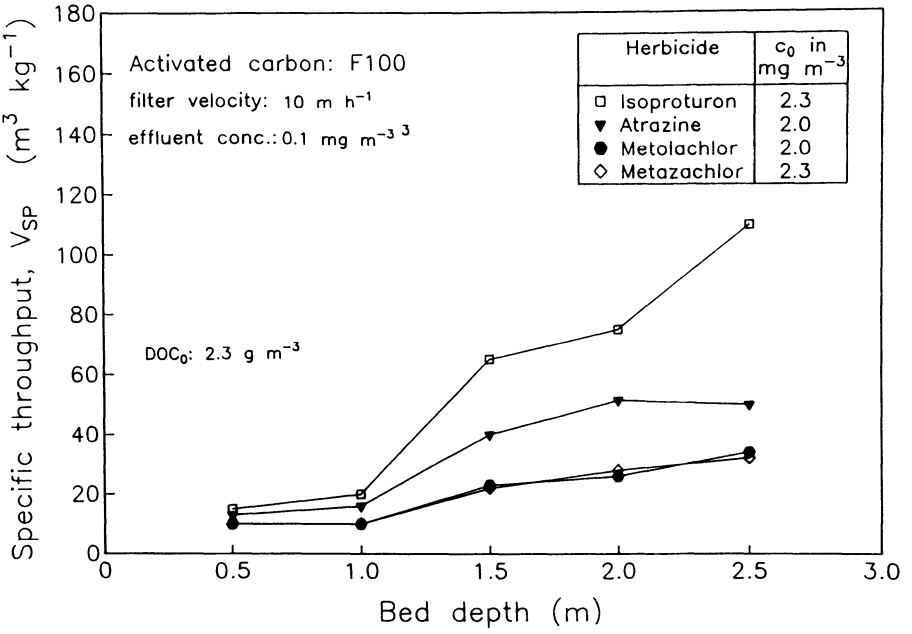

Fig. 13. Relationship of the specific throughput and the carbon bed depth for the removal of pesticides [31]

The operation time of a fixed-bed adsorber working at the required effluent concentration of 0.1 mg m^{-3} for pesticides also depends on the length of the filter bed, as can be seen in Fig. 13 [31]. The specific throughput increases with increasing bed depth. This dependency has also been found for the removal of pesticides from surface water [31]. According to Fig. 13, a fixed-bed adsorber for the removal of pesticides should have a bed length of at least 1.5 to 2.0 m for adequate efficiency of the activated carbon under the given conditions. The comparatively low specific throughput in short bed depths is probably due to the long mass transfer zone which can be observed for pesticides in all fixed-bed adsorbers under practical conditions with filter effluent concentrations of about 0.1 mg m^{-3} (see Fig. 12).

The impact of the organic background on the pesticide adsorption in fixed-bed adsorbers also depends on the source and the concentration of the natural organic substances as seen in Fig. 14 [31]. In both studies the filter parameters, the activated carbon quality and the initial concentration of Terbutylazine have been equal. The different sources of the DOC cause a different adsorption behavior of the pesticides and determine the operation time of the activated carbon filters. For the adsorption of terbutylazine from groundwater with a DOC concentration of 2.3 g m^{-3}, the operation time is significantly lower than for the adsorption from groundwater with a DOC concentration of 0.7 g m^{-3}.

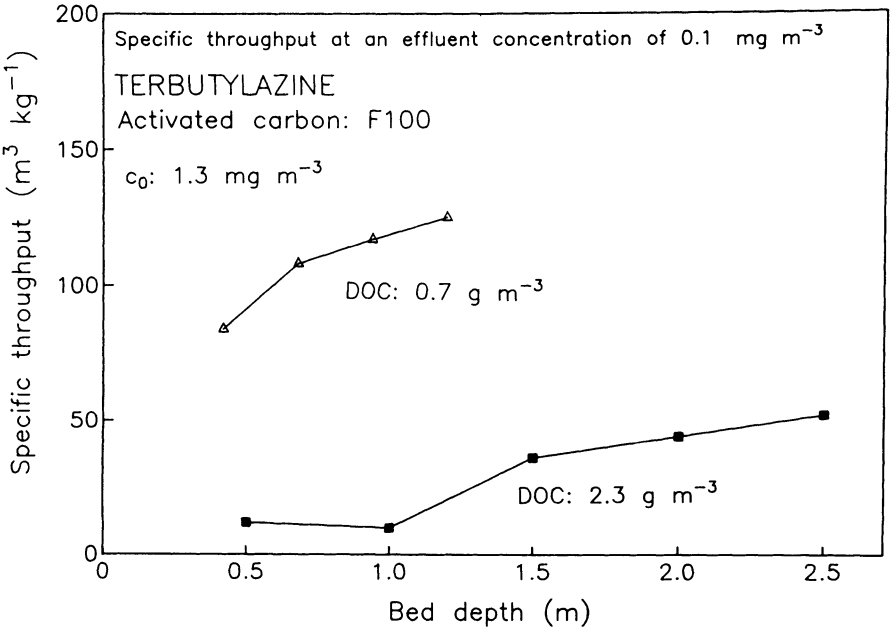

Fig. 14. Impact of the raw water quality on the specific throughput for the adsorption of terbutylazine [31]

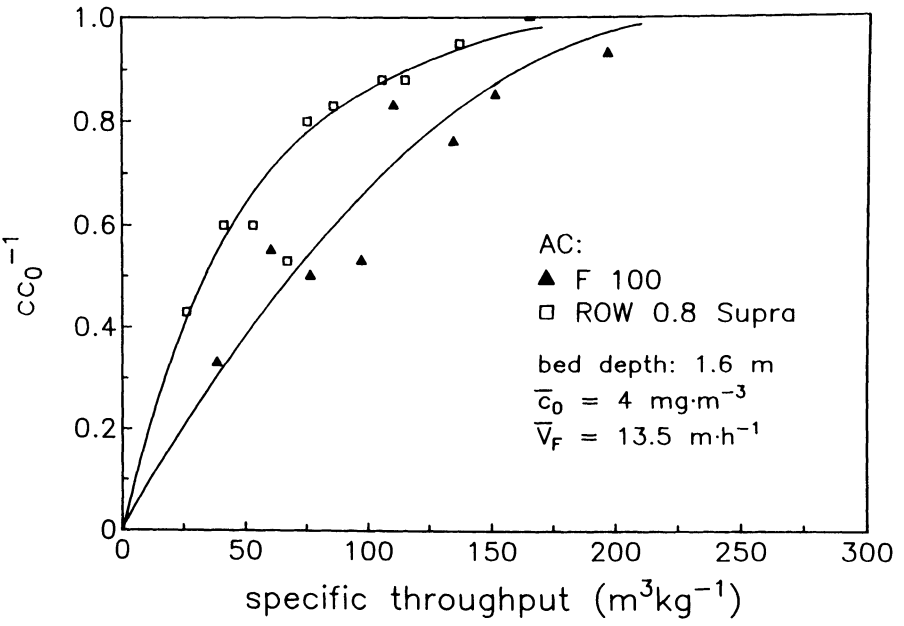

Fig. 15. Breakthrough curves of EDTA for two different activated carbons

Baldauf and Zimmer [41] have found that the filter capacities of GAC adsorbers for chlorinated hydrocarbons are almost independent of the carbon type in the various commercial carbons. These results cannot be generalized for all pollutants and all activated carbon qualities. In Fig. 15 differences in adsorption capacities for two activated carbon types can be seen for the removal of ethylenediaminetetraacetate (EDTA) from groundwater.

4.2 Biological Activity in GAC Fixed-Bed Adsorbers

During the operation of activated carbon adsorbers, microorganisms settle on the carbon surface and, after a starting period of 5 to 20 days, biological processes can occur in addition to adsorption processes [2]. This biological activity can lead to a concentration reduction for biodegradable pollutants or to an increase in carbon capacity resulting from the biodegradation of adsorbed substances. In addition, in some cases metabolites can be found in the effluent of activated carbon filters.

An example in the form of the reduction of the trichlorobenzene concentration in fixed-bed adsorbers under aerobic conditions is given in the literature [14, 40]. The breakthrough behavior has been characterized by an

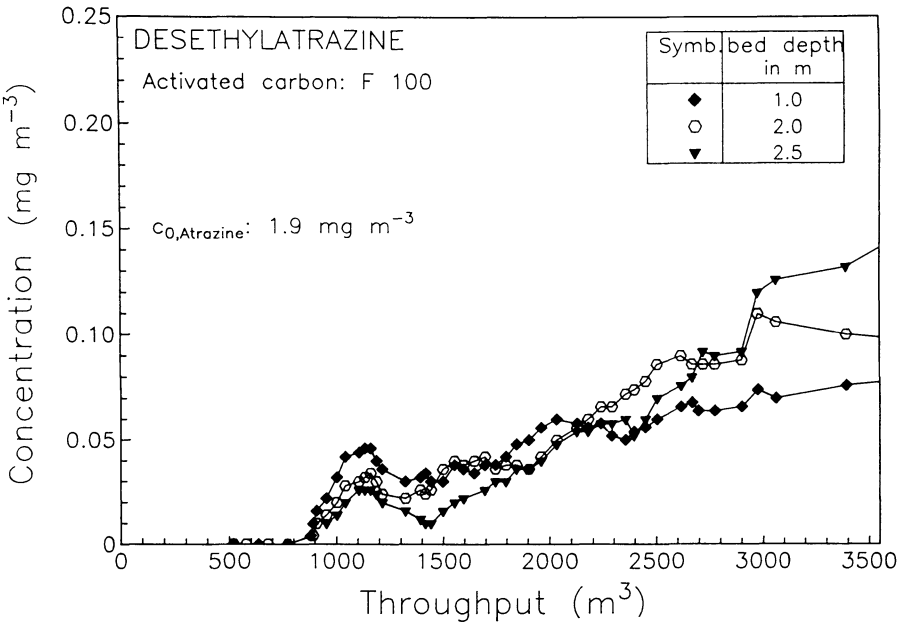

Fig. 16. Formation of Desethylatrazine in a granular activated carbon filter

initial breakthrough of trichlorobenzene followed by a constant concentration level in the filter effluent. Then after about 40 days the effluent concentration has decreased below the detection limit.

Another study [31] reports that atrazine is partly biodegraded to desethylatrazine in fixed-bed adsorbers. Figure 16 shows the filter effluent concentration of desethylatrazine formed during the operation of the filter because it could not be identified in the raw water. The mean influent concentration of atrazine in this study has been 1.9 mg m^{-3}. The occurrence of desethylatrazine in the effluent began after a throughput of about 900 m^3, which corresponds to an operation time of 210 days. Before then there might have been a formation of desethylatrazine but it would have been adsorbed on the carbon surface. From Fig. 16 it can be seen that, after the first occurence of desethylatrazine in the filter effluent, the concentration of this compound was higher the deeper the filter bed.

4.3 Practical Aspects for the Design of Fixed-Bed Adsorbers

In some cases it might be an advantage, due to carbon-fouling to operate fixed-bed adsorbers alternately in series, e.g., for chlorinated hydrocarbons [18]. For the removal of pesticides or other micropollutants which show a long and flat adsorption front, fixed-bed adsorbers with long carbon beds or several fixed-bed adsorbers in series can improve the effectiveness of the micropollutant removal.

Baldauf and Zimmer [41] have demonstrated a correlation between the filter capacity for chlorinated hydrocarbons and their initial concentration. Results from full scale plants give a functional correlation of the filter capacity and the filter influent concentration for trichloroethene despite different raw waters and different carbon qualities as shown in Fig. 17. The filter capacities have been determined by integrating the breakthrough curves to the complete breakthrough of the micropollutant. Filter correlations have also been found for tetrachloroethene and 1,1,1-trichloroethene.

Figure 18 shows the specific throughput in m^3 treated water per kg activated carbon at the effluent concentration of the German drinking water regulation of 10 mg m^{-3} for trichloroethene, tetrachloroethene, 1,1,1-trichloroethane and dichloromethane depending on the initial concentration of the chlorinated hydrocarbon in the raw water. For a given initial concentration the longest operation times can be achieved for the strongly adsorbable tetrachloroethene. In contrast, 1,1,1-trichloroethane has shown a fast breakthrough.

In practice GAC adsorbers can be operated economically at a specific throughput higher than 30–50 m^3 kg^{-1}. This corresponds to an activated carbon demand of 20–30 g m^{-3} drinking water. Weakly adsorbable compounds like 1,1,1-trichloroethane, chloroform or *cis*-1,2-dichloroethene can only be removed in a fixed-bed adsorber for a short time. The activated carbon has to be reactivated after comparatively short intervals.

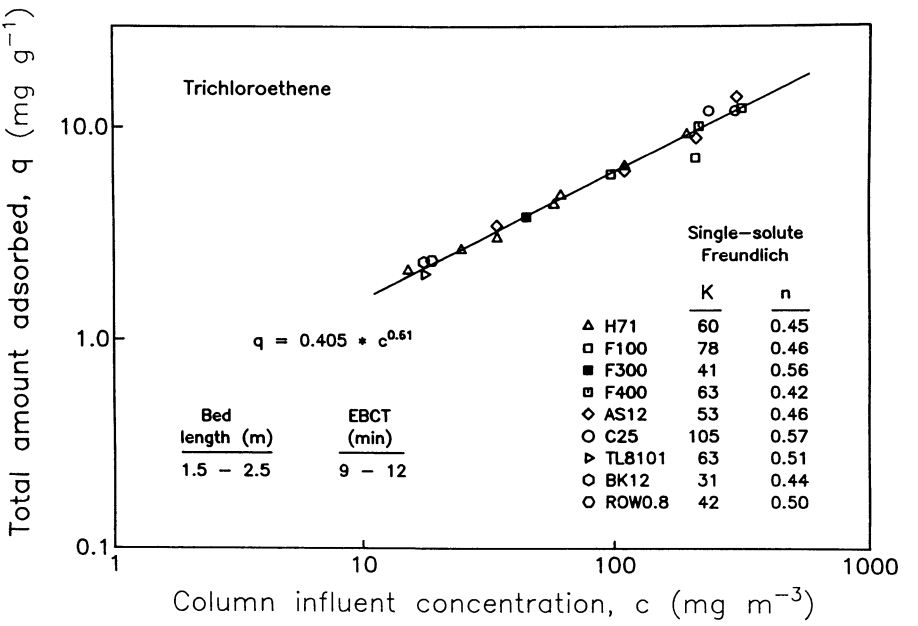

Fig. 17. Correlation of the filter capacity and the influent concentration for trichloroethene [41]

5 Aspects for the Operation of Activated Carbon Treatment Plants

In most cases PAC has primarily been applied to both drinking water and wastewater treatment. In the last few years GAC has become more widely used. An important advantage of GAC used in fixed-bed adsorbers is that it can be operated to higher solid-phase concentrations than PAC because the carbon loading in the upper part of the filter bed is in equilibrium with the influent concentration. On the other hand there are much higher investment costs for GAC columns. GAC is easier to handle and can be reactivated several times. In principle PAC can be regenerated as well but problems occur when the PAC is incorporated with flocs and has to be separated from the floc sludge [6]. Therefore PAC applied to drinking water treatment is not regenerated at present.

The operational costs for the removal of micropollutants by activated carbon depend on their initial concentrations, their adsorbabilities and/or the source and the concentration of the organic background. Therefore no overall conclusions will be possible. As mentioned in Sect. 4, a fixed-bed adsorber can be operated economically achieving a specific throughput of 30–50 m^3 kg^{-1}. This means costs for the activated carbon of 6–9 DPf m^{-3} drinking water supposing 3 DM per kg GAC.

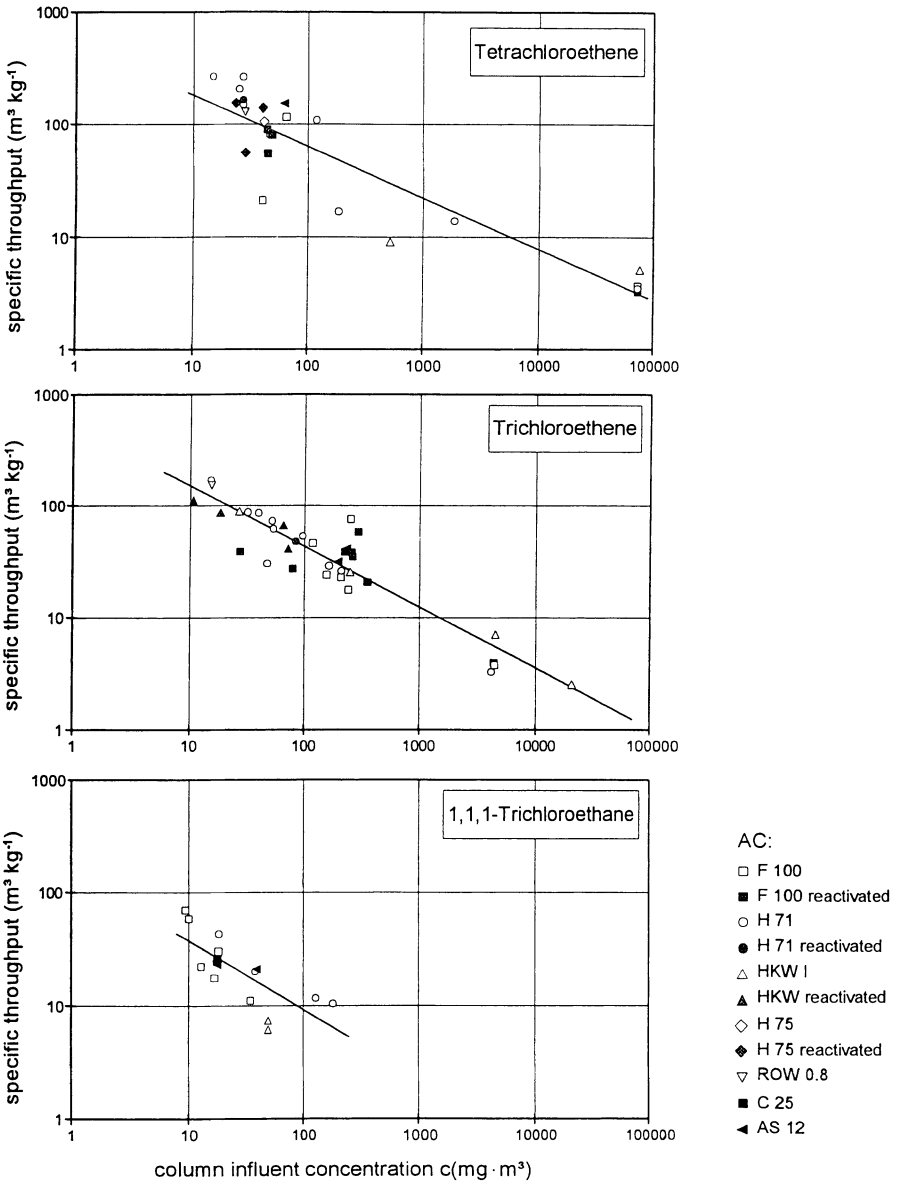

Fig. 18. Correlation of the specific throughput to the effluent concentration of 10 mg m^{-3} and the initial concentration [6]

Table 3. Operational costs for the use of activated carbon

GAC	F 300		F 100		F 100		ROW 0.8 S	
DOC g m^{-3}	1.3		2.3		0.7		1.0	
bedlength m	1.0		2.5		1.5		2.0	
	c_0^a	costs[b]	c_0^a	costs[b]	c_0^a	costs[b]	c_0^a	costs[b]
Atrazine	1.7	0.06	2.2	0.06				
Simazine	0.5	0.03	0.3	0.03	1.3	0.01		
Isoproturon	1.6	0.04	2.3	0.03				
Metazachlor	2.1	0.08	2.3	0.09				
Metolachlor	2.0	0.17	2.0	0.10				
Terbutylazine	1.1	0.05	1.0	0.06	1.2	0.02		
Hexazinone					1.0	0.04		
Bromacil							0.22	0.02

PAC	Norit W 35	
DOC g m^{-3}	3.1	
	c_0^a	costs[b]
Bromacil	0.9	0.05
Chlortoluron	1.7	0.03
Methabenzthiazuron	0.7	0.03

[a]Concentration in the raw water in mg m^{-3}
[b]Activated carbon costs per m^{-3} drinking water for reaching the demanded standard for pesticides (0.1 mg m^{-3}) in DM m^{-3}
Assumption: GAC: DM 3.00 per kg
PAC: DM 2.50 per kg

From Fig. 18 it can be concluded that, for the removal of chlorinated hydrocarbons with an initial concentration of 30 mg m^{-3} and an effluent concentration of 10 mg m^{-3}, the costs for the activated carbon per m^3 drinking water are about 3 DPf for tetrachloroethene, 4 DPf for trichloroethene and 9 DPF for the weakly adsorbable 1,1,1-trichloroethane. Referring to Fig. 18, higher costs result from higher filter influent concentrations.

Table 3 shows the specific operation costs per m^3 treated water which are necessary to achieve 0.1 mg m^{-3} for every individual pesticide using activated carbon in different treatment plants. Depending on the raw water quality, the carbon type, the adsorbability and the initial concentration of the pesticide, the costs for the activated carbon range between 0.01 and 0.17 DM per m^3 for the use of GAC and between 0.03 and 0.05 DM per m^3 for the use of PAC. The installation costs are not included in this calculation.

6 References

1. Sontheimer H, Frick B, Fettig J, Hörner G, Hubele C, Zimmer G (1985) Adsorptionsverfahren zur Wasserreinigung. DVGW-Forschungsstelle, Karlsruhe
2. Sontheimer H, Crittenden J C, Summers R S (1988) Activated carbon for water treatment. 2nd edn in English of Sontheimer H, Frick B, Fettig J, Hörner G, Hubele C, Zimmer G (1985) Adsorptionsverfahren zur Wasserreinigung. DVGW-Forschungsstelle, Karlsruhe
3. Kümmel R, Worch E (1990) Adsorption aus wäßrigen Lösungen. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig
4. Freundlich H (1906) Z Phys Chem 57: 385
5. Baldauf G (1989). In: DVGW-Schriftenreihe Wasser, ZfGW-Verlag, Frankfurt 65: 109–142
6. Baldauf G, Henkel M (1992) in: Proceeding Acque potabili-Acque reflue. Conference Padua
7. Akhavein A A, Linscott D L (1968) Residue Reviews, 23, 97
8. Baldauf G (1986) in: Vom Wasser. Verlag Chemie, Weinheim New York (vol. 67, pp 11–21)
9. Haist-Gulde B, Johannsen K, Stauder S, Baldauf G, Sontheimer H (1991) gwf Wasser-Abwasser 1: 8
10. Hörner G (1985) Adsorption von Chlorkohlenwasserstoffen an Aktivkohlen und deren Regeneration durch thermische Desorption. Thesis, University of Karlsruhe
11. Crittenden J C, Luft P, Hand D W (1985) Wat Res 19, 12: 1537
12. Narbaitz R M, Benedek A (1986) in: Proceeding J Amer Water Works Assoc confrence, Denver
13. Amy G L, Narbaitz R M, Coopeer W J (1987) J Amer Water Works Assoc 79, 8: 49
14. Summers R S, Haist B, Köhler, J, Ritz J, Zimmer G, Sontheimer H (1989) J Amer Water Works Assoc 81, 5: 66
15. Weber W J, Pirbazari M (1982) J Amer Water Works Assoc 74: 203
16. Pirbazari M, Weber W J (1984) J Amer Water Works Assoc 84, 2: 82
17. Pirbazari M, Moore L A, Weber W J, Stevens A A (1984) in: (ed) Meyers A L, Belfort G: Fundamentals of adsorption Proc of the Eng Found Conf at Schloß Elmar Ed Meyers A L, Belfort G: et al
18. Zimmer G (1988) Untersuchungen zur Adsorption organischer Wasserinhaltsstoffe aus natürlichen Wässern. Thesis, University of Karlsruhe
19. Haist-Gulde B (1991) Zur Adsorption von Spurenverunreinigungen aus Oberflächenwässern Thesis, University of Karlsruhe
20. Robeck G G, Dostal K A, Cohen M C, Kreissl J F (11965) J Amer Water Works Assoc 84, 2: 82
21. Pirbazari M, Weber W J (1984) J Environ Eng: 656
22. Miltner R J, Baker D B, Speth T F, Fronk C A (1989) J Amer Water Works Assoc 1: 43
23. Speth T F, Miltner R J (1990) J Amer Water Works Assoc 2: 72
24. Speth T F (1990) in: Proceeding J Amer Water Works Assoc conference, Cincinnati
25. Herzing D R, Snoeyink V L, Wood N F (1977) J Amer Water Works Assoc 1: 43
26. Murin C J, Snoeyink V L (1979) Environ Sci & Techn 13, 3: 305
27. Najm I N, Snoeyink V L, Suidan M T, Lee C H, Richard Y (1990) J Amer Water Works Assoc 1: 65
28. Symons J M (1978) Interim Treatment Guide for Controlling Organic Contaminants in Drinking Water Using Granular Activated Carbon. USEPA Report Fed Reg 43, No 28: pp 5756
29. Pirbazari M, Badri N B, Sung-Hyun K, Miltner R J (1992) J Amer Water Works Assoc 2: 83
30. Najm I N, Snoeyink V L, Richard Y (1990) in: Proceeding J Amer Water Works Assoc conference, Cincinnati
31. Haist-Gulde B, Baldauf, G, Brauch H-J (1992) Water Supply, 11: 159
32. Haberer K, Normann S (1977) in: Vom Wasser Verlag Chemie, Weinheim New York (vol. 49, pp 334)
33. Schwartz H G (1967) Env Sci and Technol 4: 33
34. Najm I N, Snoeyink V L, Lynkins B W (1991) J Amer Water Works Assoc 1: 65
35. Randtke S J, Snoeyink V L (1983) J Amer Water Works Assoc 75, 8: 406

36. Carollo J A (1945) J Amer Water Works Assoc 37: 1310
37. Benz M (1989) Untersuchungen zum Adsorptionsverhalten von Vielstoffgemischen unbekannter Zusammensetzung. Thesis, University of Karlsruhe
38. Baldauf G (1990) in: Berichte aus Wassergütewirtschaft und Gesundheitsingenieurwesen, Technische universität München, vol. 95
39. Baldauf G (1992) gwf Wasser-Abwasser 133, 4: 187
40. Bouwer E, McCarty P L (1982) Envir Sci Technol 1: 40
41. Baldauf G, Zimmer G (1986) in: Vom Wasser. Verlag Chemie, Weinheim New York (vol. 66, pp 61)

Models and Predictability of the Micropollutant Removal by Adsorption on Activated Carbon

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List of Symbols and Abbreviations

AC	Activated Carbon
DOC	Dissolved Organic Carbon
EBC	Equivalent Background Compound
EBCT	Empty Bed Contact Time
GAC	Granular Activated Carbon
IAS- Theory/IAST	Ideal Adsorbed Solution Theory
PAC	Powdered Activated Carbon
PFHSD-Model	Plug-Flow Homogeneous Surface Diffusion Model
PFPD-Model	Plug-Flow Pore Diffusion Model
SCA-Model/SCAM	Simplified Competitive Adsorption Model
c	liquid-phase concentration
c_0	initial concentration
h	filterbed depth
K	Freundlich constant
n	Freundlich exponent
q	solid-phase concentration
v_F	filter velocity
D_S	surface diffusion coefficient
β_L	film diffusion coefficient

Abstract

The micropollutant adsorption out of ground and surface waters is difficult to describe theoretically due to the partly non-ideal adsorption behavior of natural organic substances as, e.g., irreversible adsorption. Based on practical results over the past few years, simplified methods have been developed to describe the micropollutant adsorption in powdered and granular activated carbon treatment plants. These methods have led to the design of activated carbon treatment plants and predictions for the carbon efficiency in the event of changing raw water quality.

1 Introduction

In most cases the design of activated carbon treatment plants is based on experience or on pilot-plant studies, which are time-consuming and expensive. The description of the adsorption process in a multicomponent system as the micropollutant adsorption out of natural waters is very complex. Often the adsorption of a micropollutant out of a ground or surface water cannot be described exactly by one of the known models for competitive adsorption. Sometimes, especially during surface water treatment after a chemical spill, fast predictions are required regarding the efficiency of the activated carbon treatment step. In this case methods for the estimation of the carbon dose in a PAC (powdered activated carbon) reactor or the breakthrough behavior in a GAC (granular activated carbon) fixed bed adsorber are sufficient. Thus simplified methods have been developed in the last few years to estimate the data for the adsorption behavior of micropollutants in natural waters.

2 Models to Describe Adsorption Equilibria in Multicomponent Systems

For the description of the adsorption equilibria of a single compound out of an organic free water, various models exist which are described in the literature [1–11]. In most cases the equation of Freundlich [11] is used. The adsorption equilibria of multicomponent systems with known composition cannot be described and predicted in every case. Models for describing the competitive adsorption of two or more compounds like the IAS-Theory (Ideal adsorbed solution theory) [12–15] or SCA-Model (Simplified competitive adsorption model) [17] can be applied successfully if the adsorption compounds show a similar adsorption behavior [17–20]. Some multicomponent systems with different adsorbabilities of the solutes cannot be described exactly, e.g., the competitive adsorption of 4-nitrophenol and chloroform [17] or trichloroethene and tetrachloroethene [21]. In other systems the surface of the sorbate is not accessible in the same way for all compounds especially when the compounds differ in their molecular sizes. In this case the assumptions of the IAS-Theory are not

fullfilled and therefore model calculations do not correspond to the experiments [17, 18, 22]. Differences between measured and predicted isotherms also occur in case of very different initial concentrations of solutes in binary or multicomponent mixtures [17–19] or if the compounds have different physical chernical properties [17].

In drinking water treatment with activated carbon the problems are still more complex with respect to the description of the adsorption processes as the raw water contains natural organic substances. These humic substances and the trace organic compound of interest compete for the adsorption sites on the carbon surface.

It has already been shown that different micropollutants show a different adsorption behavior during adsorption out of a natural water. In most cases the adsorption equilibria of chlorinated aliphatic compounds are not affected by the humic substances [23–27]. On the other hand the impact of natural organic substances on pesticide adsorption results in a significant capacity reduction of the activated carbon for those compounds especially in the very low concentration range at which pesticides usually occur [27–33]. So far no explanation is found for such a different adsorption behavior of the synthetic organic compounds.

Only a mathematical description of the adsorption process admits the prediction of the adsorption behavior under different conditions, e.g., a changing raw water quality. Because of the different adsorption behavior of micropollutants, exact operation parameters can only be obtained from experiments under practical conditions. This means that the raw water quality and the initial concentration in the experiment have to equal the influent of the activated carbon treatment plant. Then the demand of the powdered activated carbon for achieving the treatment objective can be taken from the measured isotherm. For the mathematical description of adsorption equilibria in multicomponent systems no overal method for all compounds exists so far.

Models to describe the adsorption equilibria of a micropollutant out of raw water are developed by Najm et al. [34] and Haist-Gulde et al. [28]. Najm et al propose to consider the adsorption system as a binary mixture. The natural organic background is one competing compound called the equivalent background compound (EBC). For this method the Freundlich parameters of the micropollutant are determined by conducting a single-solute isotherm. The Freundlich parameters of the EBC are unknown and have to be determined by measuring a coadsorption isotherm, which is the micropollutant isotherm for the adsorption out of the raw water at any initial concentration of the micropollutant. In the model the IAS-Theory is used for describing the competitive adsorption between the micropollutant and the EBC. The Freundlich parameters of the EBC are determined by variation of these parameters in the IAST-equations until the calculated coadsorption isotherm data fit the measured. With the knowledge of the Freundlich parameters of the micropollutant and the EBC, coadsorption isotherms of the micropollutant can be predicted for every given initial concentration. The model has been applied sucessfully to the adsorption of 2,4,6-trichlorophenol, Alachlor and Metazachlor in natural waters.

Extending the work of Frick [35], Haist-Gulde et al. [28] propose to characterize the adsorption behavior of a raw water by adsorption analysis. This method for the description of adsorption equilibria of mixtures with unknown composition [22, 35–38] requires a measured DOC (dissolved organic carbon) isotherm for the raw water. For the mathematical description of this isotherm it is assumed that the raw water consists of different groups of substances with different adsorbabilities what means different Freundlich parameters. These different fractions of the raw water, which are called the fictive components, compete for the adsorption sites on the carbon surface as can predicted by the IAS-Theory or the SCA-Model. Usually three to five fictive components are used for adsorption analysis. Examples for measured and predicted DOC isotherms for two surface waters are shown in Fig. 1.

Modelling coadsorption isotherms, the adsorption competition of the micropollutant and the natural organic substances are described by IAS-Theory or SCA-Model, whereas the competing compounds are the fictive components and the micropollutant of interest. For these calculations the Freundlich parameters of the micropollutant have to be determined from the single-solute isotherm whereas the concentration DOC is used for the liquid- and the solid-phase concentration.

For compounds of which the adsorption behavior is affected by the natural organic matter, e.g. Metazachlor, the coadsorption isotherms for any initial concentration can be calculated by this method as shown in Fig. 2.

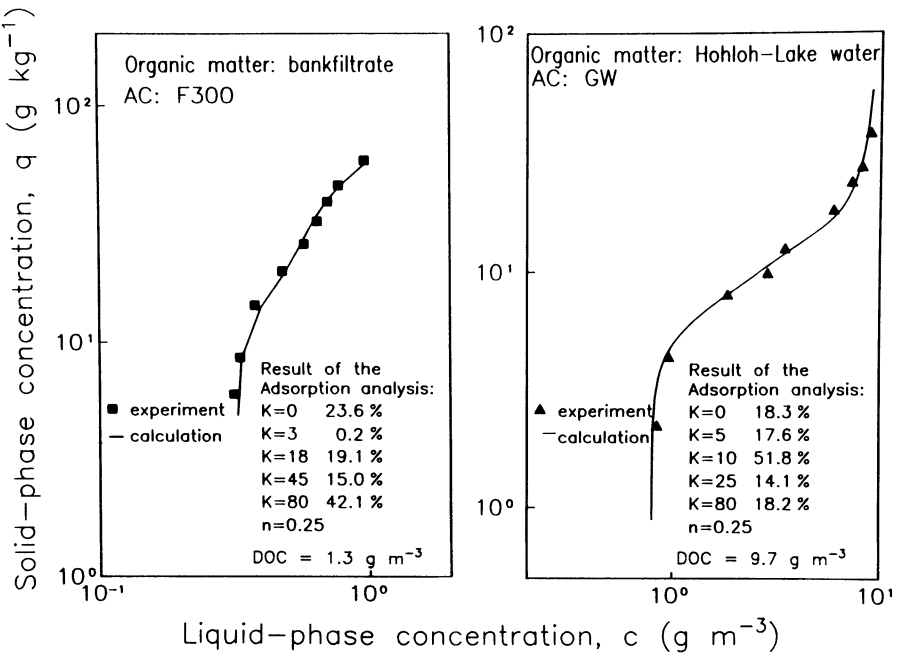

Fig. 1. Measured and calculated DOC isotherms of natural waters [27]

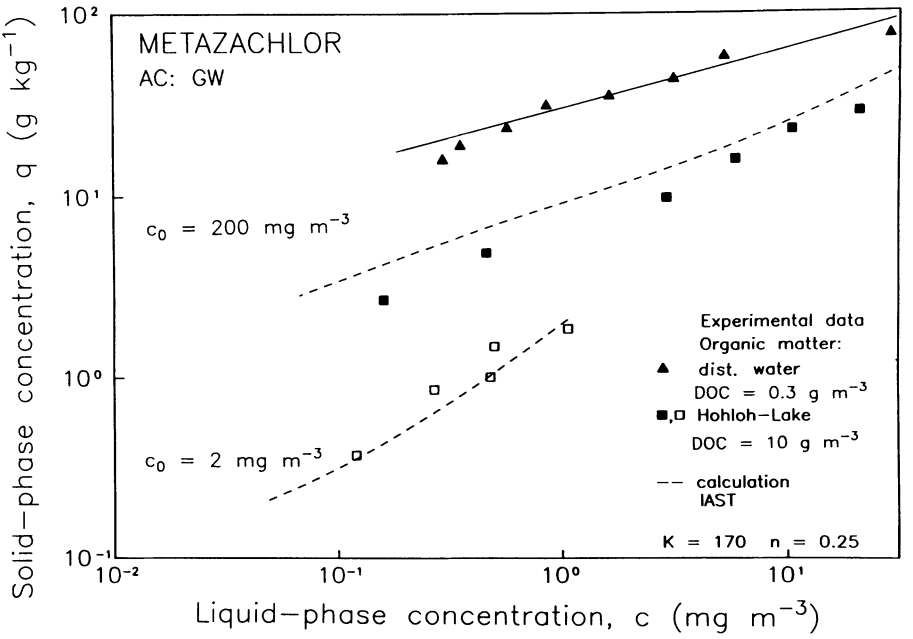

Fig. 2. Measured and calculated coadsorption isotherms of Metazachlor [28]

Comparing practical results and model calculations, the competitive adsorption between aliphatic chlorinated compounds and the natural organic matter is less than is predicted by IAS-Theory or SCA-Model. Therefore, in practice, higher solid-phase concentrations are achieved than calculated by this method [27].

3 Modeling of Micropollutant Breakthrough Curves

Breakthrough behavior of micropollutants in fixed bed adsorbers is often described by the models PFHSD-Model (plug-flow homogeneous surface diffusion model) or PFPD-Model (plug-flow pore diffusion model). Detailed information about these models is given by Sontheimer et al. [14, 15]. These filter models require adsorption equilibrium data (e.g., Freundlich parameters) and kinetic parameters (e.g., film- surface-, pore diffusion coefficients) of all adsorbing compounds. Using the fictive components of the raw water (see Sect. 2) and the micropollutant as competing compounds, calculations have to be done with a multicomponent model. However the breakthrough behavior of the fictive components in a fixed bed adsorber cannot be predicted correctly which is probably due to irreversible adsorption of humic substances [39]. On the other hand, using a model for a single component, competition

between the micropollutant and the natural organic background is not taken into account. Based on these facts, simplified methods for describing the competition of micropollutants and humic substances in fixed-bed absorbers have been developed.

The breakthrough behavior of micropollutants in fixed-bed adsorbers is affected by the natural organic background. Taking into account the capacity reduction for the micropollutant in fixed-bed adsorbers due to the preadsorption of humic substances (carbon fouling), it has been proposed to measure adsorption isotherms of the pollutant on preloaded activated carbon (preloadingisotherms), whereas the carbon is preloaded with the natural organic background of the raw water for different time intervals [26]. The investigations have shown that the capacity reduction of the carbon for the micropollutant with increasing preloading time can be described by a time variable Freundlich K-value K(t) [26].

Extending the PFHSD-Model or the PFPD-Model by this time dependent K-value, breakthrough curves for micropollutants can be predicted [26]. The film diffusion coefficient could be calculated by Gnielinski [40] or determined by fitting calculated breakthrough data with measured ones. The surface diffusion coefficient decreases with increasing preloading of the carbon [26]. Modifying the filter model as well by time dependent kinetic data, a good agreement between measured and calculated breakthrough curves has been found for trichloroethene and tetrachloroethene [26].

It is assumed that the determined function for the K-value is valid for all types of groundwaters. However for the adsorption of micropollutants out of surface waters, preloading isotherms have to be determined in every case because the K (t)-functions differ from groundwater results [27]. A comparison between measured and calculated breakthrough curves for chlorinated hydrocarbons for the adsorption out of groundwaters is shown in Fig. 3 [26].

For raw waters which contain two or more micropollutants, the K(t)-functions for each single compound must be known and these can be used in a multicomponent calculation using IAST or SCAM.

The model described takes into account the impact of the natural organic substances on the micropollutant adsorption by a time variable capacity of the carbon for the trace organic compound. This model requires extensive experiments for the determination of the K (t)-function which have to be conducted for each micropollutant and for each surface water of interest. In addition for compounds such as Atrazine and Metazachlor, of which the adsorption equilibria also depend on the initial concentration of the micropollutant itself, preloading isotherms have to be conducted for every initial concentration.

Haist-Gulde et al. [28] have extended this model by precalculating the preloading isotherms. For these calculations it is assumed that the micropollutant and the preadsorbed humic substances compete for the adsorption sites as can be predicted by IAS-Theory. The partly irreversible adsorption of humic substances is not taken into account. Nevertheless an approximate agreement between measured and predicted preloading isotherms is obtained.

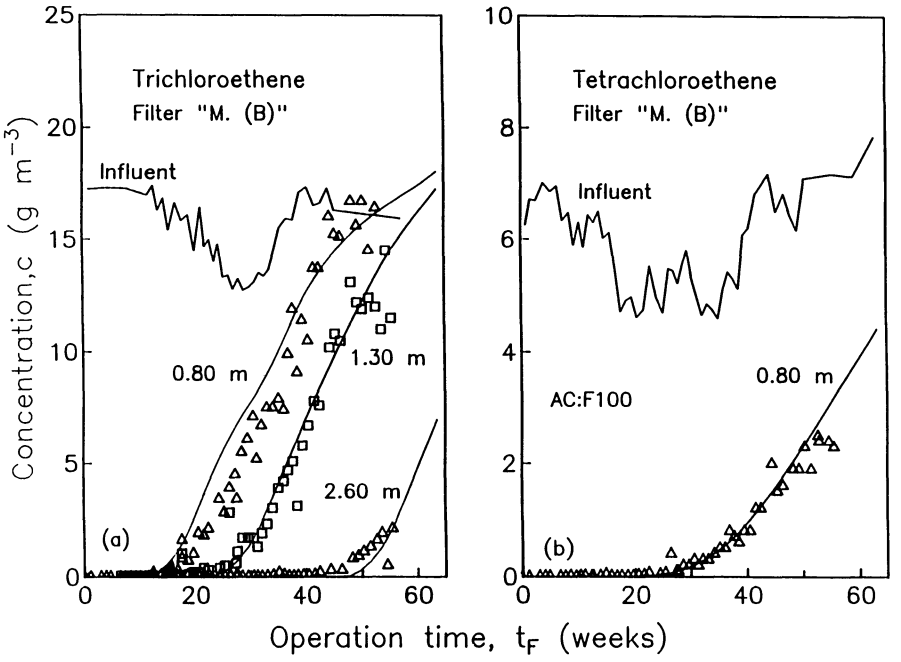

Fig. 3. Measured and calculated breakthrough curves for chlorinated hydrocarbons in groundwates [26]

For calculating preloading isotherms, the DOC isotherm of the raw water in combination with the adsorption analysis have to be known. The amount preadsorbed on the carbon surface in different bed depths can be determined by a calculated DOC-breakthrough curve for each fictive component. For the calculation of preloading isotherms it is assumed that the preadsorbed natural organic substances and the micropollutant compete for the adsorption sites as during a simultaneous adsorption of all compounds out of the solution. Using the Freundlich parameters of the preloading isotherms in a filter model for a single compound, the micropollutant breakthrough curves can be determined for the given preloading times corresponding to a throughput in bed volumes (BV) as it is shown in Fig. 4 from the interrupted lines [27]. Each breakthrough curve is only accurate at the operation time the preloading isotherm data are determined. Connecting those points of the calculated breakthrough curves, an approximative breakthrough curve for the micropollutant is obtained.

In contrast to chlorinated hydrocarbon adsorption, good agreement between measured and calculated breakthrough curves for compounds like Atrazine and Metazachlor has been obtained by calculating the coadsorption isotherm for the system of interest by taking into account the competitive adsorption of the fictive components of the raw water and not only that of the preadsorbed fraction as mentioned above [27] (see Sect. 2). For those compounds it is assumed that

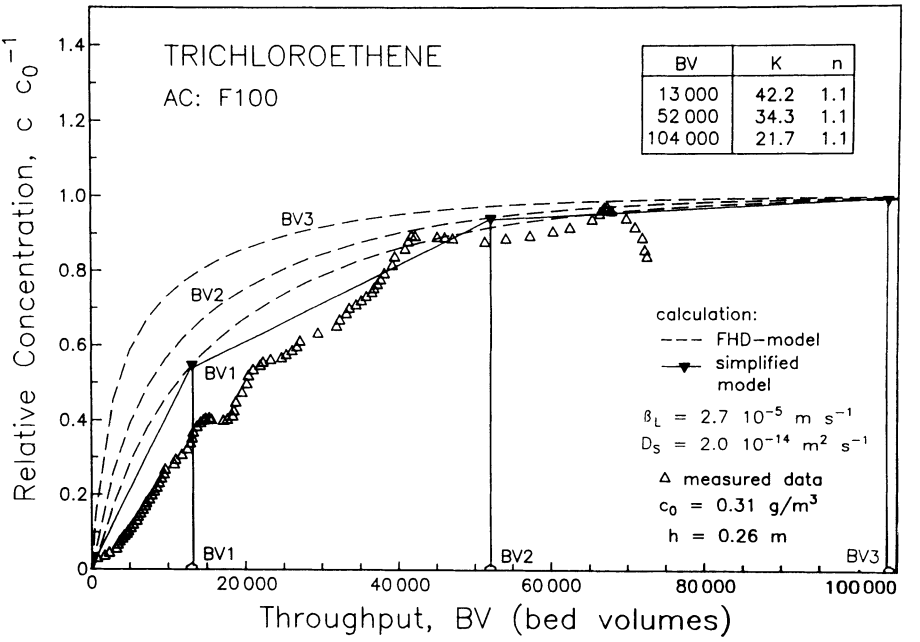

Fig. 4. Simplified method with preloading isotherm data [27]

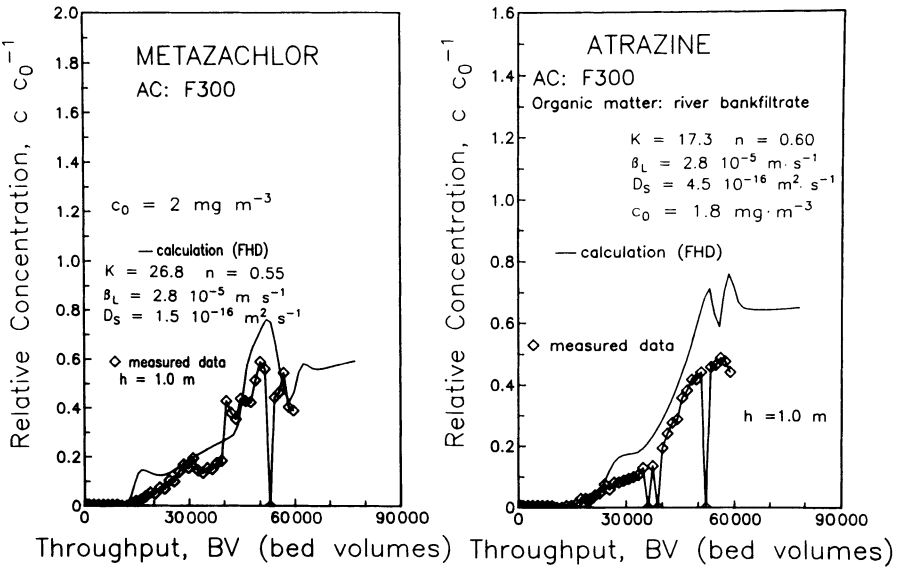

Fig. 5. Measured and calculated breakthrough curves for pesticides [27]

the micropollutant competes for the adsorption sites with all the compounds in the raw water in every filter bed depth due to the low initial concentration. So the capacity of the activated carbon in the fixed-bed adsorber is equal to the coadsorption isotherm data. Therefore the Freundlich data of the coadsorption isotherm are used in a filter model for calculating the micropollutant breakthrough curve. Such breakthrough curves are shown in Fig. 5.

This is a simplified method for the calculation of micropollutant breakthrough curves and can be conducted using a filter model for single-solutes. For a first approximation, the kinetic data can be taken from the literature for any micropollutant for the adsorption out of a natural water at about the same initial concentration. Kinetic data can also be determined in a small column run [14, 15, 22] or by fitting measured and calculated breakthrough data.

4 The RSSCT (Rapid Small Scale Column Test)

Another procedure to estimate the filter capacity and the kinetic data for the micropollutant that are required in mathematical models to predict breakthrough curves in full scale adsorbers is the RSSCT (rapid small scale column test) [15, 41]. The RSSCT is a method for obtaining filter data for large columns on the basis of small filter studies. The advantage of RSSCT is that it can be conducted in a fraction of time compared to pilot studies.

The principle of this method is that, for the design of the small column, the dimensionless groups that describe the adsorption process (e.g., Reynolds number) remain constant as the full-scale adsorber is scaled down to the RSSCT. Similarity between the small-and the full-scale column assumes proper selection of the particle size, the hydraulic loading and the empty bed contact time (EBCT) of the small adsorber. Changes in the adsorption capacity or kinetics of GAC resulting from changing particle size must be taken into account. The development of scaling equations is given by Sontheimer et al. [15].

He have summarized the results mentioned in the literature and it is reported that good corresponding results in pilot studies and RSSCTs are obtained for the removal of micropollutants like chloroform, 1,2-dibromoethane, and 1,2-dichloropropane out of groundwaters with low concentrations of DOC. Good results from applying RSSCT for the micropollutant adsorption out of surface waters can only be observed if the DOC of the surface waters is primarily of natural origin.

5 References

1. Toth J (1962) Acta Chimica Hungaria 39/31
2. Radke C J, Prausnitz J M (1972) Ind Engng Fundam 11:445
3. Redlich O, Petersen D L (1959) J Phys Chem 163:1024

4. Jossens L, Prausnitz J M, Schlünder E U, Myers A L (1978) Chem Eng Sci 33: 1097
5. Polanyi M (1916) Ber Deutsche Phys Gesellschaft 18:55
6. Manes M, Hofer L J (1969) J Phys Chem 73:440
7. Greenbank M, Manes M (1982) J Phys Chem 85:3050
8. Greenbank M, Manes M (1982) J Phys Chem 86:4216
9. Greenbank M, Manes M (1982) Amer Inst Chem Eng J.:403
10. Langmuir I (1918) J Amer Chem Soc 40:1361
11. Freundlich H (1906) Z Phys Chem 57:385
12. Myers A L, Prausnitz J M (1965) Amer Inst Chem Eng J. 11:121
13. Radke C J, Prausnitz J M (1972) Amer Inst Chem Eng J. 18:761
14. Sontheimer H, Frick B, Fettig J, Hörner G. Hubele C., Zimmer G. (1985) Adsorptionsverfahren zur Wasserreinigung. DVGW-Forschungsstelle, Karlsruhe
15. Sontheimer H, Crittenden J C, Summers R S (1988) Activated Carbon for Water Treatment. 2nd edition in English of Sontheimer H, Frick B, Fettig J, Hörner G, Hubele C, Zimmer G. (1985) Adsorptionsverfahren zur Wasserreinigung. DVGW-Forschungsstelle, Karlsruhe
16. Baldauf G, Frick B, Sontheimer H (1977) in: Vom Wasser, Verlag Chemie. Weinheim New York (vol 49, pp 315)
17. Baldauf G (1978) Untersuchungen über die konkurrierende Adsorption von Zweistoffgemischen an Aktivkohle. Thesis, University of Karlsruhe
18. Fritz W (1978) Konkurrierende Adsorption von zwei organischen Wasserinhaltsstoffen an Aktivkohlekörnern. Thesis, University of Karlsruhe
19. Merk W (1978) Konkurrierende Adsorption verschiedener organischer Wasserinhaltsstoffe in Aktivkohlefiltern. Thesis, University of Karlsruhe
20. Crittenden J C, Luft P, Hand D W, Orawitz J L, Looper S W, Ari M (1985)) Enviiiron Sci & Techn 19:1037
21. Baldauf G, Zimmer G (1986) in: Vom Wasser, Verlag Chemie. Weinheim New York (vol 66, pp 21)
22. Fettig J (1985) Zur Kinetik der Adsorption organischer Substanzgemische aus wässrigen Lösungen. Thesis, University of Karlsruhe
23. Weber W J, Pirbazari M (1982) J Amer Water Works Assoc 74:203
24. Pirbazari M, Weber W J (1984) J Amer Water Works Assoc 84, 2:82
25. Pirbazari M, Moore L A, Weber W J, Stevens A A (1984) in: (ed) Meyers A L, Belfort G: Fundamentals of adsorption. Proc of the Eng Found Conf at Schloß Elmar Ed Meyers A L, Belfort G: et al
26. Zimmer G (1988) Untersuchungen zur Adsorption organischer Wasserinhaltsstoffe aus natürlichen Wässern. Thesis, University of Karlsruhe
27. Haist-Gulde B (1991) Zur Adsorption von Spurenverunreinigungen aus Oberflächenwässern Thesis, University of Karlsruhe
28. Haist-Gulde B, Johannsen K, Stauder S, Baldauf G, Sontheimer H (1991) gwf Wasser- Abwasser 1:8
29. Robeck G G, Dostal K A, Cohen M C, Kreissl J F (11965) J Amer Water Works Assoc 84, 2:82
30. Pirbazari M, Weber W J (1984) J Environ Eng.: 656
31. Miltner R J, Baker D B, Speth T F, Fronk C A (1989) J Amer Water Works Assoc 1:43
32. Speth T F, Miltner R J (1990) J Amer Water Works Assoc 2:72
33. Speth T F (1990) in: Proceeding J Amer Water Works Assoc conference, Cincinnati
34. Najm I N, Snoeyink V L, Richard Y (1990) in: Proceeding J Amer Water Works Assoc conference Cincinnati
35. Frick B (1980) Adsorptionsgleichgewichte zwischen Aktivkohle und organischen Wasserinhaltsstoffen in Mehrstoffgemischen bekannter und unbekannter Zusammensetzung. Thesis, University of Karlsruhe
36. Hubele C (1985) Adsorption und biologischer Abbau von Huminstoffen in Aktivkohlefiltern Thesis, University of Karlsruhe
37. Völker E (1989) Charakterisierung von Abwässern aus der Sicht der Trinkwasserversorgung. Thesis, University of Karlsruhe
38. Benz M (1989) Untersuchungen zum Adsorptionsverhalten von Vielstoffgemischen unbekannter Zusammensetzung. Thesis, University of Karlsruhe
39. Schwickert S (1984) Untersuchungen zum Einflußdes Konkurrenzverhaltens eines Vielstoffgemisches bei der Adsorptiom im Aktivkohlefilter. Thesis, University of Karlsruhe
40. Gnielinski V (1978) Verf Techn 12:363
41. Berrigan J K, Hand D W (1986) J Water Pollution Control Fed.: 312

Origin and Elimination of Tastes and Odors in Water Treatment Systems

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Abstract

This chapter discusses the remedial actions which can be taken at the three different levels involved in the generation of taste and odor problems, the resource, the water treatment plant and the distribution system. A general approach methodology to cope efficiently with taste and odor problems is described. The section dealing with treatment at the resource level primarily discusses reservoir management practices necessary for controling problems arising from algal and microbial metabolites. The next section deals extensively with the beneficial and detrimental effects associated with each drinking water treatment step including clarification, aeration, oxidation with potassium permanganate and ozone, disinfection with chlorine and chlorine dioxide, activated carbon adsorption and biological treatments. The effects of these processes on the elimination of algal toxins occasionally associated with taste and odor problems generated by blue-green algae, are also discussed. A case study describing the behavior of taste and odor descriptors determined by flavor profile analysis and specific volatile organics during the treatment of an artificially recharged ground water, illustrates the global methodology required to understand tastes and odors originating from complex mixtures of trace organics.

Introduction

The resolution of taste and odor (T&O) problems that occur in the field of potable water production has evolved in recent years toward more and more sophisticated techniques. In the past, plant managers tried to modify treatment operations empirically. Today, in some of the newest plants, processes or process combinations have been implemented as preventative measures. These are intended to significantly decrease the probability of organoleptic problems in the water supply.

In an ideal system, a water supplier must be able to identify the compounds responsible for T&O in real time and implement an appropriate treatment before the compound(s) reach the consumer's faucets. In reality, T&O elimination remains a combination of know-how and scientific approaches and is indeed a very complex water quality problem to understand and control. This complexity is due to several factors: possible appearance of many types of T&O problems (e.g. hydrocarbon, medicinal ...), potential presence of numerous trace organic compounds (at nanogram to several micrograms per liter) which can lead to synergetic and antagonistic effects, which in turn result in transient incidents. In all probability, the Expert Systems technique represents one of the methods of the future to fully exploit this combination of know-how and scientific approaches [1].

T&O can be generated at three different levels: the resource, the water treatment plant (notably by the formation of oxidation by-products) and finally, the distribution network. Solutions obviously depend on what chemical(s) are causing the problem and at what concentration levels the chemical(s) are present. Many of the treatment solutions implemented to solve T&O problems are also appropriate for simultaneously removing a wide range of organic contaminants. This property may be particularly useful when dealing with tastes and odors induced by blue-green algae which sometimes release highly potent toxins in addition to odorous metabolites.

Global Approach Methodology

T&O problems can, in certain cases, be relatively simple to solve if they are approached sytematically. The first thing to do is try to determine the origin of the problem as rapidly as possible by taking taste-and-odor sensory panel measurements at the resource, after each treatment step and at different points on the distribution network. Then, several solutions can be considered:

-When the resource quality is the cause, it is advisable to determine if the problem is due to one or many compounds which are present in concentrations above their taste or smell detection threshold. If this is the case, it should be possible to treat the problem at the resource level (e.g., take action on the natural environment for the control of microbial or algal metabolites), search and

shutdown pollution sources of anthropogenic origin or adopt a specific treatment at the potable water treatment plant. When an algal bloom is the likely cause, it is also necessary to determine accurately the species involved. In the case when the dominant species are known to produce neurotoxins or hepatotoxins, steps have to be taken to ensure that these toxins do not enter the distribution system.

In numerous cases, however, tastes and odors are produced by a complex mixture of organic compounds which are present in concentrations less than their sensory detection threshold. It is extremely difficult to develop curative action at the source level and at the treatment plant level. One can only consider empirical solutions such as increasing the reagent dose at the treatment level. If the T&O problems re-occur frequently, it would be useful to generate a data base relating flavor profile analysis (FPA) (list of descriptors such as chlorine, hydrocarbons, etc.) to gas chromatographic profiles (lists of compounds identified by mass spectrometry) determined under very controlled laboratory conditions [2, 3]. This is the only approach that makes it possible to optimize the operation of a treatment line with the least empirical data. It also enables the operator to consider the temporary use of an alternative resource or a dilution with a water of different origin as described by McGuire et al. [4, 5] and Means and McGuire [6].

–When T&O are generated during potable water production, as a general rule it is easy to pinpoint the treatment phase(s) where the problem is occurring, but much more difficult to identify the responsible compounds with certainty and precision. Once again, the solution rests with a combination of know-how and the scientific approach as will be shown by examples given below.

–In the case when the distribution network is responsible, the phenomena can be described by many factors:

–Bacteria regrowth problems: the solution is inevitably the optimization of the treatment line in order to lower the concentration of assimilable organic carbon as much as possible and increase the level of residual chlorine or implement rechlorination in the network.

–By-product formation due to slow kinetic reactions between residual disinfectant and organic compounds in the water: the determination of which compounds are responsible is usually difficult because one is often faced with synergetic effects. The solutions are treatment line optimization for more efficient dissolved organic carbon elimination, low dose chlorination at various points on the network or the use of another disinfectant.

–Interaction with pipes or reservoir coating if the identification methodology has been relatively well conducted for different types of material: curing the problem is expensive because it may be necessary to change the incriminated material. It is thus preferable to take preventative measures by testing the materials before their implementation and by scrupulously respecting installation protocol [7, 8, 9].

–Pollutant diffusion: generally diffusion of solvents or hydrocarbons occuring in the soil where polyethelene or PVC pipes are installed. Even if the problem is easily discovered the remedy is likely to be costly (pipe replacement, soil purification, etc.) [10, 11].

Treatment at the Resource Level

In this section, only actions undertaken to resolve the problem of algal and microbial metabolites generated by various organisms living in raw water reservoirs will be developed [2]. A bibliographic review has recently been published by the Research Foundation of the American Water Works Association [12]. The following check-list includes the principal actions to take in order to ensure an efficient control of this type of resource.

-Catchment basin protection. It is advisable to set local legal regulations in order to allow the purchase of neighboring property, to restrict industrial or agricultural activity and to control the discharge of nutrients such as nitrogen and phosphorus.

-Monitoring system. It is recommended that a sampling program be established to analyze plankton and benthic fauna as well as different physical-chemical parameters. It is particularly necessary to have access to reliable analytical techniques for sensory analysis and identification of characteristic metabolites. Monitoring programs allowing the early detection of algal blooms would also be of interest, especially when dealing with toxic blooms.

-Position of the water intake. It is important to be able to position the water intake at different heights on both sides of the thermocline in order to pump high quality water. However, this technique is not valid during reservoir overturn periods.

-Reservoir water level. It is possible to lower the water level to expose algae attached to sediments and rocks in shallow areas and to let them dry out. This technique, nevertheless, has two inconveniences, a rapid lowering of the water level can affect recreational activities on the basin (swimming, boating, etc.) and it leads to a reduction of storage capacity which can be important.

-Aeration. The hypolimnic zone can be destratified and oxygenated by aeration. This technique, which has been shown to be very effective in certain cases, cannot be considered to be a universal "miracle" remedy.

-Copper sulfate addition. This facilitates planktonic algae control using copper sulfate application in liquid or small crystal form and blue algae of the *Oscillatoria curviceps* type by using large sized pieces. This treatment, can be carried out from boats or helicopters, but may lead to conflicts with people in charge of recreational activities (!).

-Biological activity control. This involves removing problems caused by algae, allowing natural microorganisms to degrade microbial metabolites and monitoring the mineral composition of the water, such as alkalinity, in order to avoid algal growth.

One or the other of these techniques are used in numerous countries. It should be noted that certain water distribution services have organized themselves so as to make use of all of them [5, 6, 13].

Drinking Water Treatment Processes

Practically all the different treatment processes used to produce potable water have an effect on T&O and algae toxins: in a positive way by eliminating microbial compounds or their precursors or, in a negative way by leading to microbial by-product formation or release of intracellular toxins. It is thus necessary to consider the whole treatment line in order to understand T&O treatment.

Coagulation/Settling/Filtration

The main objective of the processes is to remove suspended particles and colloidal substances which, for the most part, are not linked to removal of the organoleptic chemicals in the water. However, the following points should be noted:

-Clarification processes with settling or flotation remove planktonic algae which could lyse and leak T&O compounds such as geosmin and methylisoborneol (MIB) [14]. These algae cause a certain number of practical problems that are not always easily resolved, such as floc flotation in settling tanks. Covering the process is thus recommended. Intracellular toxins are hence eliminated during the physical removal of the algae cells. Dissolved toxins previously released during cell breakage in the raw water are, however, not removed by conventional coagulation.

-Sludge collection and disposal systems must be designed in such a way so as to avoid fermentations which can generate septic type T&O.

-Coagulant doses must be optimized for maximum removal of the organic matrix from water which, under the subsequent action of an oxidant or disinfectant, leads to the formation of aldehyde type by-products or chlorinated phenolic type odors [15].

-Powdered activated carbon (PAC) addition at the clarification treatment step allows the removal of a certain number of microbial compounds such as hydrocarbons and certain solvents. The PAC dose necessary to obtain efficient pollutant removal can be calculated by Freundlich's coefficients which can be found in the literature [16]. It has been shown that PAC addition slightly improves the elimination of hepatotoxins from Microcystis and Oscillatoria and neurotoxins from *Anabaena flos-aquae* [17].

-When an oxidant like chlorine is used to maintain cleanliness of clarification equipment, it can generate intense taste problems (see "oxidation" paragraph), some of which are excellent examples of the effects of synergism. Many authors [18, 19] have observed that the occurrence of earthy and musty odors often increase after prechlorination. This phenomenon can be explained either by synergism between the residual free chlorine and certain products with a earthy/musty odor in the water or by chlorinated by-product formation with an earthy/musty odor such as the formation of chloroanisols. Chlorination of

the algae may also result in an artificial release of their intracellular odorous metabolites into the surrounding water [20].

Aeration

In the case where the compounds responsible for odors or aromas have a relatively high vapor pressure, any treatment involving aeration such as a waterfall or bubbling will lead to a total or partial removal. For such a treatment to be efficient, the compounds must have a Henry's constant greater than 10^{-3} m^3 atm/mol. Compounds such as H_2S, chlorinated solvents or hydrocarbons can be removed. With Henry's constants around 10^{-5} m^3 atm/mol, geosmin and methylisoborneol are hardly removed [21]. This air stripping effect can be found in processes for iron removal or in biological nitrification.

Oxidation

Oxidants or disinfectants (ozone, halogens, chloramines, chlorine dioxide) react with all or part of the organic compounds occurring in water. The degradation level, in other words the nature of the by-products, depends on several factors such as:

- oxidant strength;
- the type of reaction (additive/substitution) leading to the elimination of chemical bonds in the compound;
- the structure of the compound;
- environmental factors such as pH, temperature, the presence of compounds likely to interfere with the oxidant, etc. are important.

The efficiency of each oxidant for T&O removal will thus depend on the balance between positive and negative effects.

Ozonation

A review of different mechanisms of ozone action on aqueous organic pollutants by Doré [22], based on work completed by Hoigné and Bader [23, 24, 25, 26, 27, 28] shows that ozone can react directly with aqueous organic matter to form carboxylic acids/carbonyls by acting as:

- A dipole on C=C double bonds;
- An electrophilic agent on aromatics by ring hydroxylation;
- A nucleophilic agent on C=N double bonds.

Ozone is one of the most efficient agents for T&O removal, but intermediate reaction products are formed during water treatment. The type and quantity of these disinfectant by-products depends upon ozone dosage, reaction time,

radical inhibiting agents/scavengers and pH. Aliphatic and aromatic aldehyde formation (>C-6), is frequently reported in the literature [15, 29] to develop fruity, fragrant and orange-like odors [30].

Figure 1 (top) shows an example of the production of a fruity-oxidant odor through the ozonation line at the Le Pecq-Minor plant in the Parisian region. These fruity-oxidant odors are caused by the formation of several hundred nanograms per liter of aliphatic aldehydes (bottom of Fig. 1). These fruity odors are generally easily removed by granulated activated carbon (GAC) filtration after ozonation treatment [19].

In all illustrated cases where the compounds responsible for T&O are identified, it is possible to evaluate their ozone removal potential. For this purpose, it is sufficient to refer to the different publications which list the kinetic reaction constants (e.g. 22, 28, 3). However, when there is time, it would be preferable to re-determine the kinetics constants on the specific water, as is shown in a series of publications dealing with geosmin and methylisoborneol removal. In 1986, Lalezary et al. [31] showed that these two compounds were not attacked by ozone in distilled water. In 1987 and 1988, respectively Glaze et al. and Terashima [32, 33] showed that the same compounds were largely removed when they were ozonated in surface water. The explanation currently given comes from the fact that the natural organic matrix can play the role of "promoter" in the generation of hydroxyl radicals (OH·) that are capable of degrading these two compounds. This hypothesis is confirmed by results obtained by Glaze [34] and Duguet et al., [35] who have demonstrated that the H_2O_2/ozone combination (0.4 to 1 ratio) was very efficient at removing geosmin and methylisoborneol. As it can be expected from their peptidic nature laboratory scale and pilot experiments have also shown that ozone is rather efficient at removing of Microcystis hepatotoxins [17].

In the years to come, the ozone/H_2O_2 combination will most likely be used as one of the major tools in the fight against chronic tastes and odors or even accidental pollution. It is best to consider ozonated water as a reagent that can be put into use quickly in crisis situations [35].

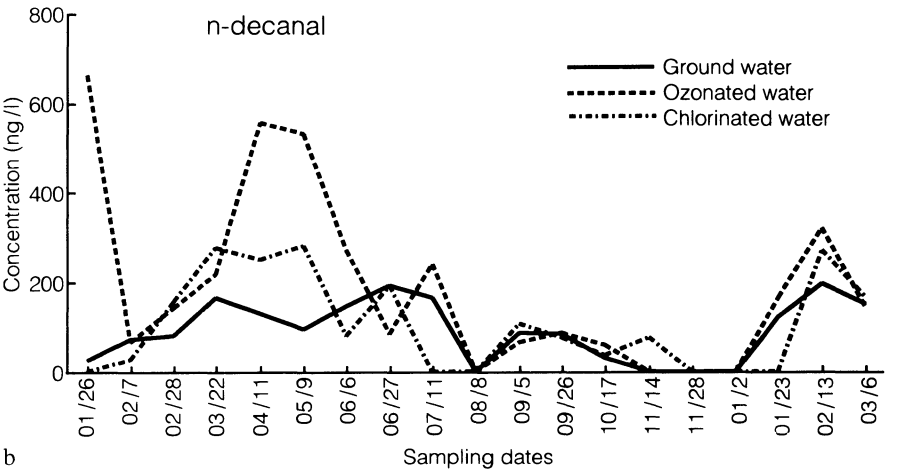
Chlorination (Chlorine and Chloramines)

The free halogens (e.g. chlorine) and chloramines that are used as water disinfectants can leave undesirable tastes and odors in the water. Bryan et al. [36] evaluated the effect of chlorine, bromine and iodine on the taste of water at different pH values [5, 7 and 9]. Free chlorine has a taste threshold that is variable according to pH (0.075 mg/L at pH = 5, 0.156 mg/L at pH = 7 and 0.450 mg/L at pH = 9) whereas bromine and iodine have taste thresholds that are more consistent. The threshold scale according to pH for bromine goes from 0.168 to 0.226 mg/L and for iodine from 0.147 to 0.204 mg/L.

Krasner and Barrett [37] determined the sensory threshold values for various chlorine based disinfectants (Table 1). Hypochlorous acid and hypochlorite ions

Descriptor		Recharge		Ground		Nitrified		Ozonated		GAC		Treated	
		Fr.	Int	Fr	Int	Fr	Int	Fr	Int	Fr	Int	Fr	Int
Earthy	O.	60	8.0	43	5.2	29	4.0	17	3.3	41	3.1	12	2.5
	T.	60	6.2	43	4.8	52	3.3	29	2.0	35	2.7	18	3.3
Musty	O.	40	9.0	75	4.8	58	4.4	35	2.6	70	2.6	25	2.5
	T.	33	6.0	75	4.3	82	3.1	52	2.4	52	2.3	37	2.5
Muddy	O.	93	8.4	37	5.3	52	4.4	-	-	17	4.6	6.2	6.0
	T.	73	6.7	25	4.0	41	3.1	6	2.0	6	4.0	18	3.0
Septic	O.	40	8.3	-	-	-	-	-	-	-	-	-	-
	T.	33	5.2	6	4.0	-	-	-	-	-	-	-	-
Plastic	O.	-	-	12	7.0	6	4.0	23	2.0	-	-	6	4.0
	T.	40	7.0	68	5.0	11	3.0	29	2.4	29	6.0	31	3.2
Chlorin.	O.	-	-	-	-	-	-	11	2.0	-	-	37	3.0
	T.	-	-	-	-	-	-	6	4.0	-	-	43	3.9
Oxidant	O.	-	-	-	-	-	-	23	4.0	-	-	-	-
	T.	-	-	-	-	-	-	29	3.0	-	-	-	-
Fruity	O.	-	-	-	-	6	4.0	17	2.5	6	4.0	-	-
	T.	-	-	-	-	-	-	-	-	-	-	-	-
Unkno.	O.	6	6.0	18	5.3	11	5.0	23	2.5	29	3.2	62	2.3
	T.	13	5.0	-	-	23	2.5	11	1.5	23	2.2	25	2.0
Fishy	O.	-	-	5	10.0	6	6.0	-	-	-	-	-	-
	T.	-	-	-	-	-	-	-	-	-	-	-	-

a



b

Fig. 1. **a** Frequency of Occurrence (Fr%) and Average Intensity (Int) of Taste and Odor Descriptors During the Recharge and Treatment Process at the Le Pecq-Minor Plant, **b** Formation of n-Decanal in Relationship with Fruity-Oxidant Odors During Ozonation

Table 1. Sensory thresholds of different chlorine compounds

Thresholds (in mg/L as Cl_2		
Compounds	Odor mg/L as Cl2	Taste
Hypochlorous acid	0.28	0.24
Hypochlorite ion	0.36	0.30
Monochloramine	0.65	0.48
Dichloramine	0.15	0.13

both have similar chlorinous taste and odor. Monochloramine solutions give a chlorine-like odor and taste, while the flavor profile panel tended to describe the dichloramine odor and taste as swimming pool-like, chlorine-like or bleachy, particularly at high concentrations. Because of the presence of ammonia in raw waters or the addition of ammonia through use of chloramines as a disinfectant, it is interesting to compare the evolution of chloramines, the free-chlorine residual and the flavor profile intensities for a given NH_3/Cl ratio, as shown in Fig. 2 [37]. Based on those curves, one would not expect monochloramine to cause a taste problem by itself if the treated water has a residual of less than 1.5 mg/L.

T&O problems that develop in water utilities that use chlorinous disinfection are frequently an indirect consequence of chlorination. Chlorine can react with naturally occuring organics in two basically different ways. First, chlorine can oxidize organics by accepting electrons from the organic substrate. Second, chlorine can substitute into the organic matrix or, by addition lead to the formation of chlorinated organic products. Only a small percentage of the free chlorine that is consumed as the chlorine demand of natural waters actually substitutes onto organic compounds; the majority is simply reduced to chloride [38]. Substitution reactions on carbon atoms in benzene rings is generally slow but the mechanism can be accelerated if the carbon atom is activated. This activation occurs if neighboring carbon atoms are bonded to electron-donating groups, such as oxygen, for example, in phenols.

The odor threshold values of these chlorinated by-products are generally significantly lower than the original products as shown in Table 2 [2, 39]. Their influence on the organoleptic quality of waters would thus be considerable as shown in the examples in the table.

Substitution on nitrogen atoms also occurs (e.g. formation of organic chloramines). Many nitrogen-containing organic compounds react in a breakpoint-type reaction in which nitrogen to carbon bonds are oxidized off from the organic carbon. For example, some amino acids form stable monochloramines as intermediates when chlorinated. The reaction then proceeds to yield nitriles and aldehydes which may, in turn, induce taste and odor problems [40].

- A great deal of attention has recently been focused on the problem of trihalomethane (THM) formation in chlorination of natural waters [41]. The

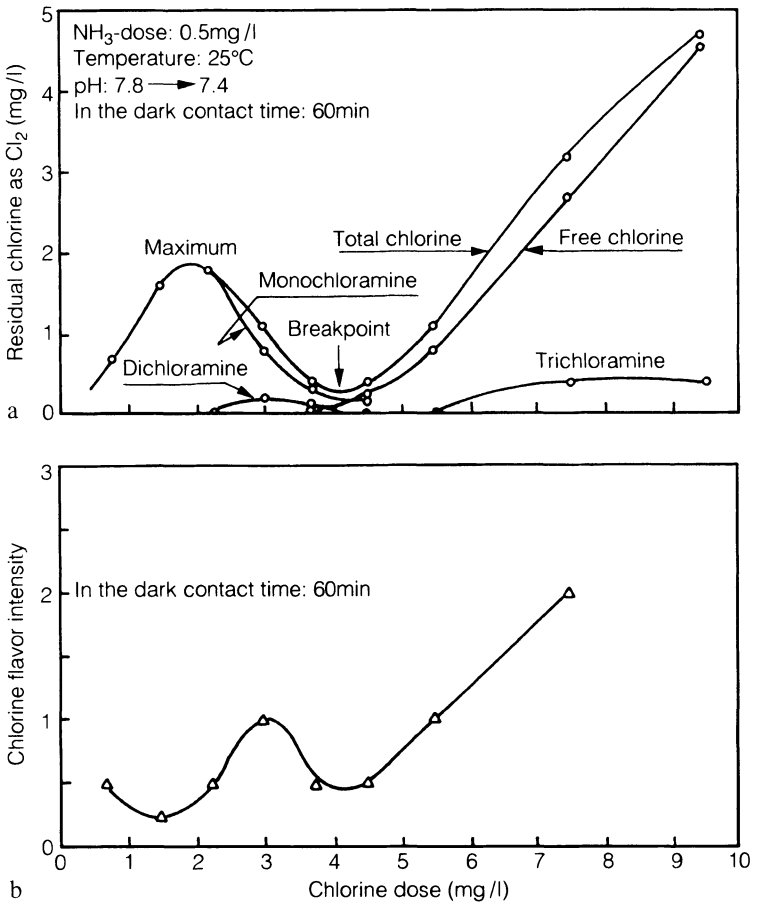


Fig. 2. **a** Chlorme residual as a function of chlorine dose, **b** effect of chlorine dose on flavor intensity

THM concentrations measured in chlorinated waters are generally between 0.001 and 0.2 mg/L, while the odor threshold value is 0.1 mg/L for chloroform and 0.3 mg/L for bromoform [42].

- However, THMs are only the tip of the total organic halogen (TOX) iceberg [38]. Some of the compounds that constitute TOX have been identified, such as di- and trichloroacetone [18] and di- and trichloroacetic acid [43]. More research should be undertaken to correlate T&O problems with the major chlorinated products, most notably those produced by reactions of chlorine with natural substances in waters. For example, the detection odor threshold of dichloroacetic acid is 0.2 mg/m^3 air [42].

Table 2. Comparison between the detection of odor threshold values of chlorinated and nonchlorinated phenols (source: [42, 39])

Compound	Threshold value μg/L
Phenol (1)	1.0–5.9
4-Chlorophenol (1)	0.0005–1.2
2,4-Dichlorophenol (1)	0.002–0.21
Anisole (1)	0.05
2,3,6-Trichloranisole (1)	3×10^{-10}
2,4,6-Trichloranisole (1)	3×10^{-8}
2-Chlorophenol (2)	0.25
3-Chlorophenol	10
2,3-Dichlorophenol	2
2,5-Dichlorrophenol	0.5
2,6-Dichlorophenol	0.1
3,4-Dichlorophenol	5
3,5-Dichlorophenol	60
2,3,4-Trichlorophenol	15
2,3,5-Trichlorophenol	3
2,3,6-Trichlorophenol	3
2,4,5-Trichlorophenol	12
2,4,6-Trichlorophenol	25
3-methyl-4-chlorophenol	40

- In many cases of underground waters containing traces of bromide and iodide at concentration levels around 0.1 mg/L, disinfection with chlorine leads to oxidation of the bromide and iodide ions into bromine and iodine, which react with the organic matrix to form brominated and iodinated THMs that are responsible for intense pharmaceutical tastes and odors [44]. The presence of iodinated THMs at concentrations between 0.001 and 0.01 mg/L seems to be the predominant factor in the degradation of organoleptic properties of waters. The detection odor threshold of iodoform is, for example, 1 μg/L.

To summarize, treatment by chlorination (chlorine or chloramines) seems to create more problems than it resolves. However, it should be noted that certain "fishy" or "muddy" odors due to anaerobic conditions can be eliminated by the presence of free chlorine [45, 46]. The above mentionned taste and odor problems associated with the use of high chlorine dose seem to preclude the use of this oxidant to control algal toxins under normal operating conditions.

Oxidation/Disinfection by Chlorine Dioxide

The main advantage of chlorine dioxide is that it produces considerably fewer chlorinated by-products, both volatile and nonvolatile, than chlorine does. The small amounts of chlorinated organic compounds formed during chlorine dioxide disinfection can probably be attributed to secondary reactions taking place

between organic products and free chlorine released during ClO_2 decomposition. As for the mechanics of this process, most studies indicate that chlorine dioxide reacts primarily as a one-electron acceptor. Consequently, the reactions of ClO_2 are much more specific than those of chlorine and do not lead to the development of as many chlorinous T&O.

In a few cases [2] ClO_2 disinfection of potable water has been observed to produce strong fishy odors. This phenomenon is particularly noticable, for example, in the shower.

In a comparative study of the efficiency of different oxidants (chlorine, chlorine dioxide, ozone and permanganate) to remove geosmin, 2,3,6-trichloranisole (TCA), isopropyl-3-methoxypyrazine (IMP), 2-isobutyl-3-methoxypyrazine (IBMP) and methylisoborneol, Lalezary et al. [31] showed that chlorine dioxide was the most efficient. Nevertheless, it should be noted that these experiments were done with distilled water solutions.

In summary, chlorine dioxide constitutes an excellent alternative to chlorination treatment in all cases where chlorine generates T&O [47]. However, questions do remain about the health effects produced by chlorite and chlorate that are produced during the use of chlorine dioxide.

Oxidation Using Potassium Permanganate

Many water purveyors have described the efficiency of this oxidation method. In the study mentioned above, Lalezary et al. [31] have shown that with a contact time of two hours, only the IMP, IBMP and TCA are somewhat removed. The removal was apparently due to an adsorption on the manganese dioxide which is formed by permanganate reduction at neutral pH. Most studies with permanganate are not clear-cut as it is used in combination with other operations.

Activated Carbon Adsorption

Activated carbon, either in powdered form (PAC) or granular form (GAC), has been successfully used to treat tastes and odors in many water treatment facilities [48, 49, 50, 51, 52]. Many studies indicate that PAC is not as effective as GAC, but the cost is lower. In fact, as shown by Fiessinger and Richard [50], when the required dose of PAC is greater than 20 mg/L, it is generally preferable to rely on GAC filtration with contact times ranging from 5 to 30 minutes.

Several examples can be quoted from the literature. In pilot studies involving PAC, Lalezary et al. [53] observed geosmin and methylisoborneol removal from 66 ng/L to a few ng/L by additions of PAC doses ranging from 5 to 23 mg/L. This result is confirmed by Yagi et al. [49] who found, however, that more than 100 mg/L were necessary to remove 100 ng/L of geosmin. Montiel [54]

Table 3. Efficiency of chlorine, ozone and PAC for treating mircocystin LR [55]

Microcystin LR solution	Treatment efficiency		
	Chlorine	Ozone	Powder activated carbon
In organic free water	>80% chlorine dose: 1 mg/l 2 hours	>99% ozone dose: 0.2 mg/l 10 min.	>99% 40 mg/l of PAC
500 μg/l In filtered Seine river water	not determined	50% ozone dose: 0; 5 mg/l 10 min.	Not determined
In organic free water	not determined	>99% ozone dose: 0.2 mg/l 10 min.	>99% 1.5 mg/l of PAC
50 μg/l In filtered Seine river water	not determined	not determined	>95% 12 mg/l of PAC

indicates that PAC is very efficient at removing T&O, but doses greater than 200 mg/L are necessary to lower the taste threshold in some instances.

In fact, here again if one wants to assess scientifically the efficiency of activated carbon, it is necessary to identify the T&O compounds and check isotherm data. Only on-site experiments can account for parameters such as competition effects, carbon saturation, biological degradation, slow adsorption, etc. [16]. At present, activated carbon constitutes the best tool for tacking T&O problems either as a crisis reactant (PAC) or as a preventive measure (GAC). In combination with ozone, treatment with activated carbon is also the method of choice for removing algae toxins, as illustrated in Table 3 which compares the efficiency of chlorine, ozone and activated carbon with respect to microcystin LR removal [55].

Biological Treatments

In some cases, water treatment lines involve processes in which biological activity occurs (slow sand filtration, GAC, denitrification ...) that may have a significant influence on tastes and odors. The biological degradation of organic products leads to the formation of by-products that are not yet well known. Some of these by-products, such as phenols, aldehydes or carboxylic acids, produced by the biodegradation of aromatic compounds such as the ever present alkylbenzenes, could play an important role in T&O generation within the treatment line.

An example of chloroanisole formation during a slow sand filtration operation of clarified Seine river water is given by Montiel and Ourvrard [56]. According to several authors [57, 58] some organisms could make methyl-substituted chlorophenols into chloroanisoles which are responsible for musty odors with odor thresholds less than 0.1 ng/L.

Namkung and Ritman [59] recently published a survey of biological processes for the removal of T&O especially due to geosmin, MIB, phenol and

naphthalenes. Bank filtration [60] and dune filtration [61] have been shown to be efficient at removing some T&O organic micropollutants.

If one takes into account the fact that ozonation increases the biological activity that develops within a carbon filter, many authors found that ozone/GAC combination was very efficient at removing earthy and musty T&O [19, 62, 33, 63]. However, Yagi et al. [49, 64] and Ashitani et al. [14] also showed that geosmin and MIB could be degraded by microorganisms fixed onto activated carbon beds.

A Case Study

At a great number of sites, T&O are actually generated by a complex mixture of trace organics of natural or anthropogenic origin occurring at concentrations lower than their sensory detection limit. Moreover, the method of flavor profile analysis showed that for a given water, an aroma or an odor could be decomposed into several descriptors of different intensities [2]. How to understand and solve such complex problems?

A case study was completed on one of the treatment lines (1 500 m^3/h) of the potable water production plant located at Le Pecq and Croissy facilities, west of Paris, which supply drinking water to a population of 500 000 people at a rate of 150 000 m3/day. Because the demand exceeds the volume of water that can be resupplied by natural means, the Croissy limestone aquifer is artificially recharged with Seine river water treated at the Croissy plant, as follows: the treatment process includes prechlorination below the breakpoint (applied dose $\cong$ 0.8 ppm), coagulation with aluminum polychloride, flocculation settling in a pulsating sludge-blanket-type clarifier with the addition of PAC and quick filtration through sand filters. Following step aeration, the water then percolates through 10 sand-gravel basins with a total surface of 13 ha. Depending on the number of basins in operation, the percolation speed varies between 0.7 and 1.4 m/d. The aquifer water is then pumped through 27 boreholes ranging in depth from 25 to 30 m, and is treated at the Le Pecq Medium, Minor and Major plants.

The Le Pecq-Minor plant studied carries out aeration, biological nitrification, ozonation in a deep U tube contactor (applied dose between 0.5 and 0.7 mg/l, residual $\cong$ 0.2 mg/l), pH correction to avoid clogging of the carbon filters, GAC filtration (4–6 min EBCT) and final disinfection with chlorine (applied dose between 0.1 and 0.15 mg/l, residual $\cong$ 0.06 mg/l).

Samples were collected weekly after each treatment step at intervals of 3 weeks during 1 year. Two types of analyses were performed: a sensory technique (flavor profile analysis) and an identification technique for trace volatile organics (closed – loop stripping extraction and GC-MS) [65, 2]. Without presenting details, it can be said that about 20 T and O descriptors were detected. Amongst the most frequent were earthy, musty, muddy, plastic, chlorine, fishy, oxidant and fruity. During the study, about 400 volatile organic compounds were detected and 150 could be identified by GC-MS (aliphatic and aromatic hydrocarbons, various solvents, aldehydes, esters, alcohols, plasticizers and plastic

additives ...) but always at such low concentrations that it was impossible to determine the molecules responsible. Thus the authors have treated the totality of the data statistically in order to develop correlations between T&O descriptors and specific volatile organics. The statistical links established during this study at the Le Pecq and Croissy plants, together with the links found during a similar study at a nearby site (Aubergenville) are summarized in Table 4. The earthy-musty-muddy descriptors were correlated with C2 to C4 alkylbenzenes and various terpenic compounds, the petroleum descriptor was correlated with low molecular weight alkanes, cycloalkanes and alkylbenzenes while the chlorinous descriptor was associated with chlorinated, brominated and iodinated trihalomethanes. These statistical links add up to previous correlations established at another site [2] such as: higher than C-6 aldehydes and fruity, pyrazines and fishy, iodized haloforms and pharmaceutic, alkylphenols and plastic ... Besides helping to designate the responsible molecules, this correlation approach has made it possible to begin to understand and optimize the influence of different treatment processes.

From the results in Fig. 1 which summarize the behaviour of all the descriptors during the one year study of the recharge and treatment process at the Croissy and Le Pecq-Minor facilities, one can conclude that the artificial recharge is particularly efficient in removing septic aromas while the ozonation step decreases the frequency of occurrence and average intensity of the earthy-musty-muddy aromas. On the other hand, the GAC filter which was saturated at the time of the study did not exert any significant influence on the low intensity descriptors that went through the ozonation step. Although saturated, this GAC filter remained efficient at removing the oxidant odors generated during ozonation.

Table 4. Relationships between taste and odor descriptors and specific organics based on statistical analysis (Croissy and Aubergenville)

Descriptor	Compounds
Earthy/musty/muddy	*C2 ⟹ C4 alkylbenzenes* *o,m,p*-xylene *m,p*-ethyltoluene 1,3,5-trimethylbenzene Tetramethylbenzene *Terpenes* Beta-pinene Phelandrene Eucalyptol Unknown terpenes
Petroleum	*Low molecular weight:* Alkanes Cycloalkanes Alkylbenzenes
Chlorinous	*Trihalomethanes* (chlorinated, brominated, iodinated)

In conclusion, such an approach can help decide when to regenerate the GAC filter to optimize the efficiency of the treatment process for resolving T&O problems due to complex mixtures of trace substances.

Conclusions

Beyond any doubt, one of the most difficult problems faced by water distributors is to guarantee the organoleptic properties and the non toxicity of the product provided to the consumer. Indeed, how is it possible to control a phenomenon that is not well understood? Today, the solution is still a combination of know-how and developing scientific approaches.

It is rare to have a simple T&O problem to resolve; thus, it is best to have a systematic approach to the problem. The first step necessarily involves the command of a certain number of scientific tools, notably analytical (sensory techniques, trace organics identification). This will make it possible to have a knowledge of the water quality as thorough as possible in the water resource as well as in the treatment line and in the distribution network. These results then constitute a data base that will help the interpretation of the observed changes when T&O are detected. Once the T&O causes are known adequate solutions can be proposed quickly.

As far as the water resource is concerned, the solutions are easy to list but much more difficult to implement, as the solutions often depend on other factors outside the water distributor's responsibility. On the other hand, as far as the water treatment plant is concerned, the examples described in this chapter show that each of the processes that can be used have positive effects and negative effects that have to be taken into account for the whole treatment line. The oxidation/adsorption coupling (ozone only or in combination with hydrogen peroxide – activated carbon) is, as of today, the most efficient process for lowering the probability of the occurence of T&O problems. As far as the distribution network is concerned, the understanding and the solution to the problems will be greatly facilitated by the help of consumer sensory panels, who constitute an excellent detection network. It has also been demonstrated that the best treatment processes for T&O removal are also the most efficient in cases where an algal toxin problem was experienced.

References

1. Anselme C, Davagnier M, Mallevialle J, Bordet JP (1989) Système expert d'aide au diagnostic pour la résolution de problèmes de goûts et odeurs indésirables dans l'eau potable. Conférence spécialisée IWSA-AIDE "OrganicMicropollutants", Sept 1989, Barcelona, Spain
2. Mallevialle J Suffet IH (eds) (1987). Identification and treatment of tastes and odors in drinking water. AWWA Research foundation, Denver, CO, USA

3. Bartels JHM, Brady BM, Suffet IH, (1989). Taste and odor in drinking water supplies. Phase I and II. AWWA Research Foundation Report, Denver, Colorado, USA
4. Mcguire MJ, Krasner SW, Hwang CJ, Izaguirre G, (1981) Jour AWWA 73:530
5. Mcguire MJ, Krasner SW, Hwang CJ, IzaguIrre G (1983) Wat Sci Tech 15:267
6. Means EG, McGuire MJ, (1986) Jour. AWWA, 78:77
7. Anselme C, Bruchet A, N'Guyen K, Mallevialle J, (1987). Caractérisation des produits de relargage de canalisations en polyéthylène défectueuses. L'Eau, l'Industrie, les Nuisances, 108:75
8. Bruchet A, Leroy P, Mallevialle J (1988). Controlling drinking water coating materials: implementation of a test Protocol and examples of application. Water quality Technology conference (AWWA), St Louis, MI, USA, November
9. Krasner SW, Means EG III (1986). Jour AWWA 78:94
10. Marshall J, Hope PS, Ward H (1982). Sorption and diffusion of solvents in highly oriented polyethylene. Polymer Repts, vol. 23
11. Vonk MW (1984). The diffusion of water and solvents into high density polyethylene. IWSA conf. Monastir, Tunisie
12. Casitas Municipal Water District (1987). Current methodology for the control of algae in surface reservoirs. AWWA Research Foundation, Denver, CO, USA
13. Means EG, Preston AE, McGuire MJ (1984). Scubadiving as a cost-effective tool for managing water quality problems. Jour. AWWA, 76, 10, 86–92
14. Ashitani K, Hishida Y, Funwara K (1988). Behavior of musty odorous compounds during the process of water treatment. Wat. Sci. Tech., 20, 8/9, 261–267
15. Anselme C, Suffet IH, Mallevialle J (1988). Effects of ozonation on tastes and odors, Jour. AWWA, 10, vol. 80, October
16. Sontheimer H, Crittenden J, Summers S (1988). Activated carbon for water treatment. Appendix A, DVGW, Forschungstelle, Engler Bunte Institute, Karlsruhe, FRG
17. Lathi K, Hiisvirta L (1989). Removal of cyanobacterial toxins in water treatment processes: review of studies conducted in Finland. Water Supply, Vol. 7, Barcelona, pp. 149–154
18. Baker RJ, Suffet IH (1986). Evaluation of water treatment methods for removal of taste and odor causing compounds from drinking water. Water Quality Technology Conference (AWWA), Portland, Oregon, November
19. Anselme C, N'guyen K, Mallevialle J (1985). Influence des traitements de désinfection et d'oxydation sur les qualités organoleptiques de l'eau: cas de l'usine de Morsang/Seine. Proc. 38émes journées int. du Cebedeau, Bruselles, Belgium
20. Ando A et al. (1992). Removal of musty-odorous compounds in water and retained in algal cells through water purification processes, Wat. Sci. Tech. Vol. 25, pp. 299–306
21. Lalezary S, Pirbazari M, Mcguire MJ, Krasner SW (1984) Jour AWWA 76:83
22. Doré M (1985). The different mechanisms of the action of ozone on aqueous organic pollutants. Proc. Intl. Conf. The role of ozone in water and wastewater treatment. Edited by R. Perry and McIntyre, AE, Sp Press, London, England
23. Hoigné J, Bader H (1976). The Role of Hydroxyl Radical Reactions in Ozonation Processes in Aqueous Solutions. Wtr. Res., 10:377
24. Hoigné J (1977). Ozonation of Water: Selectivity and Rate of Oxidation of Solutes. 3rd Congress of I.O.A. Paris
25. Hoigné J (1977). Rate Constants for Reactions of Ozone With Organic Pollutants. I.O.A. Symp. Adv. Ozone Technol., Toronto, Canada
26. Hoigné J (1977) Vom Wasser 48:283
27. Hoigne J (1978). Ozonation of Water; Kinetics of the Oxidation of Ammonia by Ozone and Hydroxyl Radicals. Prog. Wtr. Technol., 12:79
28. Hoigné J (1984) In: RG Rice and A Netzer (eds) Ozone and its Practical Application. Ann Arbor Science Publishers, Ann Arbor, MI, USA
29. Schalekamp M (1983). All about Ozone. Its Advantages and Disadvantages in Treating Water. Aqua, 3:89.
30. Suffet IH, Anselme C, Mallevialle J, (1986). Removal of tastes and odors by ozone. Sem. Ozonation and water Treatment. Proc. AWWA, Ann. Conf, Denver, CO, USA
31. Lalezary S, Pirbazari M, McGuire MJ (1986). Oxidation of five earthy. Musty taste and odor compounds. Jour AWWA, 78:3:62
32. Glaze WH, Schep R, Ruth R, Madjoob S, Chauncey W, (1987). Removal of taste and odor compounds by oxidation processes: summary report, phase I. Submitted to Metropolitan Water District of Southern California, July 15

33. Terashima (1988). Reduction of musty odor substances in drinking water: A pilot plant study. Presented at the Second Intemational Symposium on Off-flavours in the Aquatic Environment, Kagoshima, Japan, Wat. Sci. Tech., 20:275
34. Glaze WH (1987). Drinking water treatment with ozone. Env. Sci. Tech. 21, 3, 224-230
35. Duguet JP, Bruchet A, Mallevialle J, (1989). New advances in oxidation processes: the use of the ozone/hydrogen peroxide combination for the micropollutants removal in drinking water. Proc. Conférence spécialisée IWSA-AIDE "Organic Micropollutants", Barcelona, September 1989
36. Bryan PE et al. (1973). Taste Thresholds of Halogens in Water. Jour. AWWA 65, 5, 363
37. Krasner SW, Barrett SE, (1984). Aroma and flavor characteristics of free chlorine and chloramines. Proc. AWWA WQTC, Denver, CO, USA
38. Johnson JD, Jensen JN, 1986. T.H.M. and TOX formation: routes, rates and precursors. Jour. AWWA, 78, 4, 156
39. Schlett C (1992). Phenols as odour components of drinking and surface water. Water Supply, Vol. 10, Jönköping, p 29
40. Bruchet A et al. (1992). Influence of the chlorination of natural nitrogenous organic compounds on tastes and odors in finished drinking waters. Wat. Sci. Tech. Vol. 25, N° 2, p 323
41. Rook JJ (1980). Possible pathways for the formation of chlorinated degradation products during chlorination of humic acids and resorcinol. In: Jolley RL, Brungs WA, Cummings RB. (eds) Water Chlorination: Environmental Impact and health Effects, Ann Arbor Science Publishers, Ann Arbor, MI., USA
42. Van Gemert LJ et Nettenbrelier AH (1977). Compilation of Odour Threshold Values in Air and Water. TNO, Zeist, Netherlands
43. Christman RF et al. (1983). Identity and yields of major halogenated products of aquatic fulvic acid chlorination. Env. Sci. Tech., 17, 10, 625
44. Bruchet A, N'guyen K, Anselme C, Mallevialle J (1989). Identification and Behaviour of Iodinate Haloform Medicinal Odor. Proc. Sunday Seminar on Taste and Odor, AWWA Conf., Los Angeles, Ca., June 1989
45. Wajon JE, Alexander R, Kagi RI, Kavanaugh B (1985). Dimethyltrisulphide and objectionnable odours in potable water. Chemosphere, 14, 1, 85-89
46. Krasner SW, Barrett SE, Dale MS, Hwang CJ (1986). Free chlorine versus monochloramine in controlling off-tastes and odors in drinking water. Proc. AWWA Ann. Conf., Denver, Colorado, USA
47. Walker GS, Lee FP, Aieta EM (1986). Chlorine dioxide for taste and odor control. Jour. AWWA, 78, 3, 84
48. Gammie L, Giesbrecht G (1986). Full-scale operation of granular activated carbon contactors at Regina/Moose JAW. Proc. AWWA, Ann. Conf., Denver, Colorado, USA
49. Yagi M, Kajino M, Matsuo V, Ashitani K, Kita T, Nakamura T (1983). Odor Problems in Lake Biwa. Wat. Sci. Tech., 15, 6/7, 311
50. Fiessinger F, Richard Y (1975a). La technologie du traitement des eaux potables par le charbon actif granulé: I Le choix du charbon. T.S.M. L'eau, 7, 271
51. Fiessinger F, Richard Y (1975b). Même titre III. La régénération du charbon. T.S.M., 10, 415
52. Graese SL, Snoeyink VL, Lee RG (1987). Granular activated carbon filter-adsorber systems. Jour. AWWA, 79, 12, 64-74
53. Lalezary S et al. (1985). Pilot plant studies for the removal of geosmin and 2-MIB by powdered activated carbon. Proc. AWWA, Ann. Conf., Washington, D.C., USA
54. Montiel A (1983). Municipal drinking water treatment procedures for taste and odour abatement: a review. Wat. Sci. Tach., 15, 6/7, 279
55. Bernazeau F (1994). Can microcystins enter drinking water distribution systems? Bluegreen algal toxins workshop, Adelaide, Australia, March 22-26.
56. Montiel A, Ouvrard J (1986). Origine et identification de certains goûts de moisi dont l'intensité augmente dans le réseau de distribution. Conf. 66e Congrés AGHTM, Barcelone
57. Bemelmans MH, Ten Never de Brauw MC (1974). Chloroanisoles as Off-Flavor Components in Eggs and Broilers. Jour. Agric. Food Chem., 22:1137
58. Rigaud J et al. (1984). Incidence des composés volatils issus du liége sur le "goût de bouchon" des vins. Science des Aliments, 4:81
59. Namkung E, Rittmann BE (1987). Removal of taste and odor causing compounds by biofilms grown on humic substances. Jour. AWWA, 79, 7, 197-112
60. Sontheimer H, (1980). Experiences with riverbank filtration along the Rhine river. Jour. AWWA, 72, 7, 386

61. Hrubeck J, de Kruijf HAM (1983). Treatment methods for the removal of off-flavours from heavily polluted river water in the Netherlands: a review. Wat. Sci. Tech., 15, 6/7, 301
62. Sasaki T, Kobayashi K, Ueda S (1987). Application of odor removal process to an existing water treatment system. Pres. Second Int. Symp. on Off-flavours in the Aquatic Environment, Kagoshima, Japan, October 12–16.
63. Vik EA, Storhaug R, Naes H, Utkilen HC (1988). Pilot scale studies on geosmin and MIB removal. Wat. Sci. Tech., 20, 8/9, 229–236
64. Yagi M, Nakashima S, Muramotos S (1988). Biological degradation of musty odor compounds, 2-MIB and geosmin, in a bio-activated carbon filter. Wat. Sci. Tech., 20, 8/9, 255–260
65. Anselme C (1987). Etude et caractérisation des problémes de mauvais goûts de l'eau potable. Thése de doctorat présentée à l'Université de Paris VII le 16 Octobre 1987

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