Micro-organic Compounds in the Water Environment and Their Impact on the Quality of Potable Water Supplies*

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Abstract

The concern about micro-organic compounds in the water environment stemming from substantial proportions of return flows from wastewater treatment facilities, runoff from non-point sources and from atmospheric precipitation, has caused considerable alertness amongst scientists and environmentalists. Due to improved analytical techniques more and more organic compounds are identified at very low concentrations. This paper evaluates the reported literature on micro-organics in water and recommends a positive course of action which should be followed in South Africa to ensure the optimum exploitation of its limited water resources.

The paper deals with the specific micro-organic compounds, health aspects of micro-organics including the need for epidemiological studies, odour and taste in drinking water and with current capabilities of water purification technology ensuring health safety levels of micropollutants.

It is emphasized that prevention is better than cure, both socially and economically – natural waters should be kept clean and wastewater flows should be purified for reuse or return to the water environment in a degree of cleanliness compatible with optimum exploitation of available water resources and with the protection of public health.

The paper concludes that effective water renovation, reclamation and purification technologies and the elimination of pollutants at source for water quality protection, constitute a powerful double-acting tool for optimizing the utilization of water resources. It provides both preventive and curative technologies for the restoration of the cleanliness and amenities of the water environment and for relieving the pollution stresses which conventional water purification plants have to cope with, thus ensuring the health safety of public water supply systems.

Introduction

The natural drinking water sources in many parts of the world contain substantial proportions of return flows from municipal and industrial wastewater treatment facilities, runoff from non-point sources such as urban and agricultural areas and atmospheric precipitation. During dry periods, the aforementioned return flows may in many hydrographic regions be nearly 100 per cent of river flows. In this indirect recycle of polluted water, the self-purification powers and capacity of the natural water environment to degrade, dissipate and absorb the ever-increasing loads of waste products of socio-economic progress, have played a key role and will undoubtedly continue to do so as long as man will exist. This "first aid kit" has indeed been a valuable primary safety barrier in protecting the quality of the water environment and in ensuring urbanisation, technological advancement and agricultural development. However, during the past two decades scientific research has exposed notable limitations in the capacity of this "first aid tool" to ensure the preservation of the quality of our water resources, without which, life cannot continue to exist and socio-economic progress could grind to a standstill.

This "sword of Damocles" has manifested itself in many

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urbanised and industrialised hydrographic regions of the world through the growing imbalance between water demand and the supply of clean water. Urged by the implications of the situation and the active pressures of anti-pollution legislation, scientists generally, and chemists in particular, have been and still are responsible for remarkable achievements in the development of waste management technologies not only to prevent water pollution, but also to alleviate the pollution load on the self-purification processes of the water environment and to renovate water for reuse. In particular, one can mention the harnesssing of the self-purification process of the water environment in the advanced biological purification plants, especially the modified activated sludge processes incorporating denitrification and phosphate removal; combined biological and physical chemical purification of urban *cum* industrial wastewater to reclaim usable water for a multiplicity of purposes; modifications in chemical synthetic processes to produce bio-degradable materials for example the replacement of "hard" detergents with "soft" detergents; and industrial process management to recover chemicals and to prevent or minimise the pollution loads which leave the factory.

In spite of these laudable achievements, many questions remain unanswered. For example, whereas micro-concentrations of heavy metals and their bio-accumulation could be identified and quantified by available sensitive analytical tools, the micro-organic residues of natural and man-made origin remained for a long time an unanswered question with respect to their identity in the water environment and their fate during purification for human consumption. For several generations, the presence of colour, taste and odour in drinking water supplies have been regarded as indicators of organic contamination and therefore of the safety of water for human consumption. However, the dearth of accurate analytical tools to identify natural and man-made micro-organics in the water environment and the urgency of evaluating their possible impact on the quality of potable water supplies, have led to some major breakthroughs during the past decade in the development of highly sensitive analytical techniques capable of identifying and quantifying specific organic compounds at very low concentrations in the water environment.

As a consequence of this new development, more than one thousand organic compounds have been identified in the water environment, return wastewater flows and drinking water supplies (WHO, 1975). Although many of these compounds are known for their carcinogenic, toxic, mutagenic and teratogenic properties, they occur in micro-concentrations in the water environment. We must, however, accept that they have increased the complexity of water quality protection, domestic water supply and reuse of water by a further dimension. In view of public emotions and the tendency amongst professionals to excessively press the alarm button which centres around this issue, an attempt is made in this paper to objectively evaluate the facts which are reported in literature and to recommend a positive course of action which should be followed in the Republic of South Africa to ensure the optimum exploitation of its limited water resources.

Micro-organic Compounds in the Water Environment

Natural surface and underground waters contain organic contaminants from diverse sources and in concentrations often higher than in purified supplies for potable use. These organics are released continuously into the aquatic environment as a result of human, plant and animal activities and metabolic by-products of aquatic organisms.

According to Canale (1977) and data published in a wide range of records, Table 1 lists some of the sources of organic compounds in the aquatic environment.

TABLE 1
SOURCES OF ORGANICS IN NATURAL WATERS

1. *Decay of animal and plant life* Humic and fulvic acids; sesquiterpenes; alcohols; aldehydes and acids; pigments; and toxic compounds of vegetable origin
2. *Biological activities* Algal toxins; geosmin; 2-methylisoborneol; n-heptanal; 6-pentyl-α pyrone; dimethyl sulphide; and isopropyl mercaptan
3. *Industrial wastes* Over two million new compounds registered since 1965 — thus far over 1 000 identified in the water environment
4. *Domestic wastes* Proteins; carbohydrates; fatty acids; and compounds produced during biological and physical-chemical treatment
5. *Non-point sources* Agricultural insecticides and herbicides; atmospheric precipitation; urban runoff; waste dumps and landfills; polyaromatic hydrocarbons (PAH, PCB); and oils, solvents, fuels, and combustion products

Micro-organic contaminants in the water environment identified by workers engaged in water analysis in different locations in the world have been classified (Gomella, 1978), in Table 2.

TABLE 2
MICRO-ORGANIC CONTAMINANTS IDENTIFIED IN THE WATER ENVIRONMENT

Group	No. of Compounds
Polynuclear hydrocarbons	47
Amines and derivatives	60
Cyanide and azo compounds	12
Nitro and nitroso compounds	55
Organophosphorous compounds	12
Organochlorine compounds	231
Organometallic compounds	5
Mercaptans and sulphated products	36
Phenols and quinones	74
Heterocyclic compounds	39
Surfactants	8
Chemical brighteners	13
Ethers, aldehydes and ketones	71
Organic acids	79
Esters	40
Alcohols	40
Aryl alkanes	66
Alkals and alkenes	53
Amino acids and proteins	26
Glucides	16
Steroids	2
Pigments, enzymes, vitamins, etc.	16

With regard to specific classes of compounds detected in drinking water in the United States and Western Europe, the data listed in Table 3 (Tardiff, 1976 and Zoeteman, 1976) are noteworthy particularly with respect to the predominance of organo-halogens.

The frequency of detection of specific micro-organics in drinking water and their highest concentrations (Zoeteman, 1978) are recorded in Tables 4 and 5. The data for organo-halogens are again notable because of the emphasis which is attached to their presence in potable water supplies.

TABLE 3
CLASSIFICATION OF ORGANIC COMPOUNDS IDENTIFIED IN DRINKING WATER IN THE U.S.A. AND WESTERN EUROPE

Class	% of total number of identified compounds in	
	U.S.A.	W.Europe
Alcohols	5,4	3,4
Aldehydes	4,8	2,7
Alkane hydrocarbons	7,1	10,6
Alkene hydrocarbons	0,7	2,2
Benzenoid hydrocarbons	7,1	20,5
Carboxylic acids	1,0	0,5
Esters	7,1	4,9
Ethers and Heterocyclic oxygen compounds	4,8	3,8
Halogenated aliphatic hydrocarbons	23,3	14,5
Halogenated aromatic hydrocarbons	13,3	11,7
Nitrogen compounds	10,3	6,5
Phenols and Naphthols	1,4	0,5
Phosphorous compounds	1,4	0,5
Polynuclear aromatic hydrocarbons	3,1	11,7
Sulfur compounds	3,1	2,2
Ketones	6,1	3,8
Total number of compounds	288	181

TABLE 4
ORGANIC COMPOUNDS DETECTED MOST FREQUENTLY IN 20 TYPES OF DRINKING WATER

Type of compounds	Name	Detection frequency[+]	Max. Conc. ($\mu g/\ell$)
Hydrocarbons	Toluene	20	0,3
	Xylenes	19	0,1
	C_3-benzenes	19	1,0
	Decanes	18	0,3
	Ethylbenzene	17	0,03
	Fluoranthene	16	0,05
	Nonanes	15	0,3
	Naphthalene	14	0,1
Oxygen compounds	Dibutyl phthalate	17	0,1
	1,1-Dimethoxyisobutane	13	0,3
	Methyl isobutyrate	13	1,0
Halogen compounds	Chloroform	16	60
	Tetrachloromethane	15	0,7

[+] Detection frequency: number of tapwaters, among the 20 types, in which the compound was detected

TABLE 5
ORGANIC SUBSTANCES DETECTED IN 20 TAPWATERS AT LEVELS OF 1$\mu g/\ell$ OR MORE

Compound	Highest detected concentration ($\mu g/\ell$)	Detection frequency
Chloroform	60	16
Bromodichloromethane	55	11
Dibromochloromethane	20	12
Bromoform	10	7
Trichloroethene	9	9
Trichloronitromethane	3	3
Bis(2-chloroisopropyl) ether	3	8
Octanol (isomers)	3	8
Dichloroiodomethane	1	4
1,1-Dichloroacetone	1	3
2-Cyclohexen-1-one	1	1
Methyl isobutyrate	1	13
Hexyl butyrate	1	1

Health Aspects of Micro-Organics in Drinking Water

The American Waterworks Association reported on some 60 compounds identified in drinking water (AWWA, 1974). These are listed in Table 6.

Tardiff and Deinzer (1973) reported on the toxicity ratings of these compounds and on the organs affected on body weight exposure. The data are recorded in Tables 7 and 8.

In the above toxicity classification (Tardiff and Deinzer, 1973) compounds with a LD_{50}[*] > 15 g/kg of body weight are regarded as "practically non-toxic"; for "slightly toxic" the LD_{50} lies in the range 5 – 15 g/kg; for "moderately toxic" LD_{50} = 500 mg – 5 g/kg; for "very toxic" LD_{50} = 50 – 500 mg/kg; for "extremely toxic" LD_{50} = 5 – 50 mg/kg, and for "super toxic" the LD_{50} is < 5 mg/kg.

It is obvious from Table 7 that no toxicity ratings are assigned to about half the compounds listed in Table 6 since their toxicity levels for body weight exposure to mammals are unknown. The organs listed in Table 8 are those likely to be affected by some of these compounds on exposure at the aforementioned toxic levels (Tardiff and Deinzer, 1973).

There is a need for perspective in the evaluation of these data. According to published data, the presence and concentrations of organic compounds in drinking water vary considerably at micro-level concentrations but are orders of magnitude

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[*] LD_{50} stands for "Lethal Dose 50", and represents the dose at which 50% of the test animals will be killed, under the experimental conditions (e.g. within a stated time, etc).

TABLE 6
ORGANIC COMPOUNDS IDENTIFIED IN FINISHED WATER

	Compound
1.	Acetone
2.	Acetophenone
3.	Acetylene dichloride
4.	Benzene
5.	Benzene thiazole
6.	Bromobenzene
7.	Bromochlorobenzene
8.	Bromodichloromethane
9.	Bromoform
10.	Bromophenyl phenyl ether
11.	Butylbenzene
12.	Camphanol
13.	Camphor
14.	Caprolactam
15.	Carbon tetrachloride
16.	Chloro-benzene
17.	Chlorodibromo methane
18.	Chloroethoxy ether
19.	Chloroethyl ether
20.	Chloroform
21.	Chlorohydroxy benzophenone
22.	Bis-chloroisopropyl ether
23.	Chloromethyl ether
24.	Chloronitro benzene
25.	Chloropyridine
26.	Chloromethyethyl ether
27.	Dibromobenzene
28.	Dichloroethane
29.	Dichloroethyl ether
30.	Dimethoxy benzene
31.	Dimethyl naphthalene
32.	Dimethyl sulfoxide
33.	Dinitrotoluene
34.	Ethylbenzene
35.	Ethylene dichloride
36.	Exo-2-camphanol
37.	Hexachlorobenzene
38.	Hexachloroethane
39.	Hydroxy adiponitrile
40.	Isoborneol
41.	Isocyanic acid
42.	Isopropanyl isopropyl benzene
43.	Isopropyl benzene
44.	p-Menth-1-en-8-pl
45.	o-Methoxy phenol
46.	2-Methoxy biphenyl
47.	Methylbenzothiazole
48.	Methylbiphenyl
49.	Methylchloride
50.	Nitroanisole
51.	Nitrobenzene
52.	Octane
53.	Pentane
54.	Propylbenzene
55.	Tetrachloroethylene
56.	Toluene
57.	Trichloroethane
58.	Triglycodichloride
59.	Thiomethylbenzothiazole
60.	Vinyl benzene

TABLE 7
TOXICITY CLASSIFICATION OF COMPOUNDS IDENTIFIED IN DRINKING WATER

Class	Number of Compounds
Practically nontoxic	1
Slightly toxic	0
Moderately toxic	14
Very toxic	16
Extremely toxic	2
Super toxic	0
Unknown	27
TOTAL	60

TABLE 8
ORGANS AFFECTED BY COMPOUNDS ON BODY WEIGHT EXPOSURE AT LD_{50} TOXICITY LEVELS

Effect	Number of Compounds
Depression of central nervous system	24
Stimulation of central nervous system	3
Liver pathology	15
Kidney pathology	10
Methaemoglobin production	4
Anaemia (decrease in red blood count)	1
Leucopenia (decrease in white blood count)	1
Hypersensitization	1
Skin irritation	3
Cardio-vascular changes	2
Synergism with Ethanol	2

below listed LD_{50} values. Two important sources of information in this regard can be quoted:

(1) Of the 350 compounds identified in drinking water in a number of countries (Europ-Cost, 1974) the concentrations of only 50 substances were above 1 μg/ℓ, five above 1 mg/ℓ while the rest were all at the nanogram per litre level.

(2) The Water Research Centre's computer base (Fielding and Packham, 1977) also gives a full listing of some 360 organic substances. It has entries for 27 classes of organics with concentrations generally less than one nanogram per litre. In the listed data a strong bias towards volatile substances are observed.

As specific illustration, take the incidence of chloroform in drinking water which has been a subject of considerable alarm and emotion in the United States (Stockinger, 1977). Measurable concentrations of $CHCl_3$ were found in the drinking water of two cities: 0,045 mg/ℓ in Cincinnatti and 0,311 mg/ℓ in Miami. The carcinogenic level of $CHCl_3$ for animals corresponds to a daily intake range of 17 000 to 34 000 mg/d. At 0,311 mg/ℓ $CHCl_3$ in drinking water, an individual has to drink between 57 000 and 114 000 ℓ/d — and would die from drowning before developing a type of tumour formation! It is indeed a fact that exposure to chloroform in drinking water constitutes a minute factor in relation to its content in patent medicines and products which are on the shelves of pharmacies and departmental stores.

Halogenated hydrocarbons are regarded as very stable and of toxic significance. The data in Table 9 represent the maximum (Horvath, 1976) permissible or allowable concentrations of halogenated hydrocarbons in water. According to toxicological tests no activity was evident at these concentrations. These concentrations also represent the organoleptic threshold in drinking water.

TABLE 9
MAXIMUM PERMISSIBLE CONCENTRATIONS (MPC) IN WATER

Halogenated hydrocarbons	Formula	MPC (mg/l)
Methane, tetrachloro-	CCl_4	0,3
Methane, dichloro-	CH_2Cl_2	7,5
Ethane, hexachloro-	C_2Cl_6	0,01
Ethane, trichloro-	C_2HCl_3	0,5
Ethane, tetrachloro-	$C_2H_2Cl_4$	0,2
Propane, chlorotrifluoro-	$C_3H_4ClF_3$	0,1
Butene, dichloro-	$C_4H_6Cl_2$	0,05
Benzene, hexachloro-	C_6Cl_6	0,05
Benzene, 1,2,4,5-tetrachloro-	$C_6H_2Cl_4$	0,02
Benzene, trichloro-	$C_6H_3Cl_3$	0,03
Benzene, dichloro-	$C_6H_4Cl_2$	0,03
Benzene, o- and p-dichloro-	$C_6H_4Cl_2$	0,002
Benzene, chloro-	C_6H_5Cl	0,02
Cyclohexane, dichloro-	$C_6H_{10}Cl_2$	0,02
Cyclohexane, chloro-	$C_6H_{11}Cl$	0,05

Classes of chlorinated compounds (Tardiff *et al.*, 1978) under active investigation for their toxicologic activity are listed in Table 10. The chloroethers are chemical congeners of the human carcinogen bis-chloromethyl ether; the halobenzenes are known to occur in micro-concentrations in potable waters and the haloforms are synthetic by-products of conventional disinfection with chlorine.

TABLE 10
CLASSES OF CHLORINATED COMPOUNDS IN DRINKING WATER UNDER TOXICOLOGICAL INVESTIGATION

Chloroethers

1. Bis-(2-chloroethyl) ether
2. Bis-(2-chloroisopropyl) ether

Halobenzenes

1. Chlorobenzenes
2. Bromobenzenes
3. Chlorobromobenzenes

Haloforms

1. Chloroform
2. Bromodichloromethane
3. Chlorodibromomethane
4. Bromoform

The Council of the European Communities established guidelines (CEC, 1976) with respect to the discharge of substances into the water environment. It urged member countries to eliminate pollution of waters by compounds on the "Black List" and to reduce contamination by compounds on the "Grey List". The composition of these lists is presented in Tables 11 and 12. The list in Table 11 includes certain individual compounds of the following groups with exclusion of those which are biologically inoffensive or which are rapidly transformed into biologically inoffensive compounds. The list in Table 12 contains certain individual compounds of the following groups which have a local deleterious effect on the aquatic environment.

TABLE 11
LIST OF FAMILIES AND GROUPS OF "BLACK" COMPOUNDS

1. Organo halogens
2. Organic phosphorous compounds
3. Organotin compounds
4. Substances of which the carcinogenic effect is proven in or by means of the aquatic environment
5. Hg-compounds
6. Cd-compounds
7. Persistent mineral oils and hydrocarbons

TABLE 12
LIST OF FAMILIES AND GROUPS OF "GREY" COMPOUNDS

1. Metals and metalloids, including Zn, Cu, Ni, Cr, Pb, Se, As a.o.
2. Biocides, not included in the black list
3. Substances having a deleterious effect on taste and odour of products derived from the water for human consumption
4. Toxic and persistent organosilicon compounds
5. Inorganic phosphorous compounds and elementary phosphorous
6. Non-persistent mineral oils
7. Cyanides and fluorides
8. Certain substances which have an unfavourable effect on the oxygen balance such as ammonia and nitrite

A superficial look at the various data recorded in this paper could arouse alarm and emotions. However, an in-depth objective study of the facts will reveal that over-reaction has very little foundation for the so-called "scare" that drinking water supplies harbour the "ghost" of cancer for the user. A significant fact to take note of is that the demonstration of the presence of micro-organics, for example $CHCl_3$, is a relatively recent development. Many of the compounds recorded, both of natural and industrial origin have been known to exist and some have been in general use for generations, let alone decades. Obviously, some would find their way into the water environment and be present in drinking water derived from polluted water sources. The exposure of water users to many of these chemicals is therefore far from recent. The outcry against micro-organics identified in water supplies, stems from statements that as many as 90% of all cancers for example in the United States, may be caused by environmental factors, a substantial proportion of which are due to the exposure to industrial chemicals during production and general use in commerce. Because the water environment is a common contact factor, it comes under constant suspicion. Whereas it is obviously necessary not to overlook the incidence of micro-pollutants in water, it is all-important to note that, considering all factors in proper perspective, the body is continuously exposed to chemicals for example in the daily dietary intake of people and along the many other routes of contact with such chemicals. Currently, there is very limited evidence that micro-organics in drinking water are connected with health problems. The fact of the situation is that water constituents represent a very minor proportion of the dietary intake of the public. If there were any health effects attributable to organo-halogens, both short and long-term, the question is why has this not been identified since the introduction of water disinfection by chlorination. Be that as it may, the international meeting in 1975 organised by the World Health Organization (1975), listed ten specific micro-chemicals in drinking water derived from polluted sources which require toxicological study with respect to long-term health effects because of inadequate data. Justification for this work is that the water user has little choice to exercise in the drinking water available to him and it is incumbent on the authorities to evaluate the risks associated with the intake of these micro-chemicals through drinking water and technologies for their control.

Epidemiological studies on water-borne disease have led to remarkable achievements in water hygiene. It is, therefore, obviously essential that the incidence of micro-organics and the possible effect on human health should also come under the scrutiny of epidemiology as an important tool of constant vigilance. Without detracting in any way from the importance of the micro-organics in water hygiene, it is a fact that water abstracted from the world's most polluted rivers has been purified by conventional techniques for consumption by millions of people for scores of years. Furthermore, once waterborne infectious disease had been brought under control no other health hazard has been positively identified to be attributable to the presence of organic micro-pollutants in drinking water which had been adequately purified in spite of the formation of organo-halogens in the chlorination process. As a positive step to evaluate the efficiency of conventional water purification as a health safety barrier both in the short and long-term, or to demonstrate the necessity of additional processes in purification plants, it would be one of the most constructive lines of action to compare the health statistics for areas already utilizing polluted sources with those utilizing unpolluted sources. In fact, epidemiological studies and water quality monitoring by our South African scientists as part of the Windhoek water reclamation project up to the present demonstrate that advanced wastewater process units have the capability to yield a health safe water from wastewater which has undergone biological purification in sewage purification plants, in maturation ponds and in rivers. These studies also exposed the limitations of conventional water purification plants to purify polluted water sources.

Epidemiological studies must constitute the key tool (WHO, 1975) in the evaluation of the significance of micro-organics in water quality. Up to two or three years ago the emphasis in studies on health aspects of drinking water fell on epidemiology of areas subject to high degrees of indirect reuse, toxicology of single compounds, and improvement of analytical methods to be able to detect and identify compounds present in drinking water supplies at extremely low levels. Since then the emphasis has changed somewhat, partly as a result of the remarkable development in analytical methodology, whereby a competent analyst is today able to isolate and often identify very large numbers of compounds at extremely low levels of concentration. Furthermore, and partly as a result of this, it has become recognised that full toxicological evaluation of the host of synthetic chemicals entering the water environment year by year is a formidable if not impossible task.

Accordingly, the emphasis in most scientists' thinking today falls on a series of tasks, such as the following, to be performed in the order stated:

(1) Epidemiological studies of community health in areas deriving drinking water from polluted sources, accompanied by bio-assay screening tests (e.g. Ames mutagenic test), to be applied to the water itself, concentrates thereof, industrial effluents in the catchment of the water supply, etc. This would enable comparatively cheap initial assessment of any significant hazards in the area.

(2) If the screening tests give any positive results, identification of the toxins in the water, concentrates, effluents, etc., should take place.

(3) (a) Full mammalian toxicology studies on the toxicants if information is not already available, or

(b) identification of the source of the toxicant and management or elimination of its use in the catchment in order to prevent its discharge to the environment and its appearance in the water supply.

The above represents the philosophy currently held by the Water Research Commission and the lines of action which it is felt should be followed not only at Windhoek, where part of the drinking water is reclaimed from secondary purified sewage effluent, but also in all other areas within the Republic where drinking water is derived from polluted sources.

Odour and Taste in Drinking Water

With a few exceptions, taste and odours in drinking water are caused by the presence of organic compounds in micro-concentrations, (μg-ng/ℓ range) particularly in surface waters and to some extent in groundwater sources. Some of these organic compounds can be introduced into rivers, lakes and dams by municipal and industrial effluent discharges, runoff water from residential and agricultural areas and can be produced by aquatic organisms and decaying vegetation.

Growth of aquatic organisms during open storage can produce micro-pollutants which may cause taste and odour in water (Zoeteman, 1978) especially when chlorinated. These are listed in Table 13.

Some of these organic compounds may be precursors to the formation of halogenated hydrocarbons. When such waters are chlorinated or breakpoint chlorinated in the water purification process, compounds can be produced which are of significance not only with respect to taste and odour, but also with respect to water hygiene. Chlorine disinfection produces substantially lower levels of haloform than breakpoint chlorination as is reflected in Table 14 (Zoeteman, 1978).

Volatile halogenated hydrocarbons (VHH) have been identified and quantified in various types of raw waters in Southern Africa (OO Hart, 1977) and are summarized in Table 15. From the data reported in this table, the increase in total VHH in the Vaal River between Suikerbosch and Vereeniging is due to a tributary which drains extensive urban and industrial areas and receives substantial volumes of secondary purified sewage effluent.

TABLE 13
ORGANIC COMPOUNDS POSSIBLY INTRODUCED INTO THE WATER DURING STORAGE IN OPEN RESERVOIRS

Compound	Max. conc. (µg/ℓ)	Compound	Max. conc. (µg/ℓ)
Octene-1	0,03	Hexanal	0,03
Nonene	0,01	Heptanal	0,1
Undecene	0,01	Octanal	0,03
4-Methyl-heptan-4-ol	1,0	Nonanal	0,1
2-Ethyl-1-hexanol	3,0	Decanal	0,1
2,6-Dimethyl-heptan-4-ol	0,03	Undecanal	0,03
trans-2-Hepten-1-ol	0,01	Heptan-3-one	0,1
trans-2-Nonen-1-ol	0,01	Dodec-2-ene-4-one	0,03
2-Methylisoborneol	0,03	2-Methylbutanenitrile	0,1
Geosmin	0,03		

TABLE 14
EFFECT OF CHLORINATION ON THE OCCURRENCE OF SOME HALOGENATED COMPOUNDS IN TAP WATER IN µg/ℓ

Parameters	Type of treatment with chlorine		
	None	Disinfection	Breakpoint chlorination
Number of supplies studied	13	4	3
Chloroform	<0,01–2,0	<0,1–10	25–60
Bromodichloromethane	<0,01–0,9	<0,01–10	15–55
Dibromochloromethane	<0,01–0,1	0,01–5	3–10
Dichloroiodomethane	<0,01	<0,01–0,3	0,01–10
Bromochloroiodomethane	<0,01	<0,01–0,03	<0,01–0,3
Bromoform	<0,01	<0,01–1,0	3,0–10
1,1-Dichloroacetone	<0,005	<0,005	0,1–1,0
Trichloronitromethane	<0,01	<0,01–3,0	<0,01–3,0

TABLE 15
OCCURRENCE OF VHH IN VARIOUS TYPES OF RAW WATER SUPPLY (µg/ℓ)

Origin	CCl_4	$CHCl_3$	C_2Cl_4	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	Total VHH
RIVER							
Vaal River at Zuikerbosch	0,01	0,11	0,15	0,03	0,00	0,00	0,30
Vaal River at Vereeniging	0,01	0,24	0,47	0,04	0,02	0,00	0,78
RESERVOIR							
Rietvlei Dam, Pretoria	0,01	0,09	0,13	0,03	0,00	0,45	0,71
Goreangab Dam, Windhoek	0,04	3,93	0,09	0,05	0,02	0,01	4,14
SPRING							
Rietvlei	0,27	0,00	0,00	0,00	0,00	0,00	0,27
Pretoria	0,03	0,68	0,04	0,18	0,16	0,04	1,13
SEWAGE WORKS							
Maturation pond effluent, Windhoek	0,01	0,61	0,04	0,00	0,00	0,00	0,66
Activated sludge effluent, Pretoria	0,07	2,17	0,18	0,13	0,06	0,00	2,61

In the case of the City of Windhoek, the Goreangab Dam is only a few kilometres from the maturation ponds which receive the purified sewage effluent and supply the raw water intake to the Windhoek 4 500 m^3/d water reclamation plant for direct domestic use. The substantially lower total VHH concentration in the raw water supply to the reclamation plant is considered to be due to their evaporation in the maturation ponds.

The chlorination of purified water from the sources reported in Table 15 will inevitably lead to an increase in VHH and therefore in taste and odour. Consequently, there is a necessity to include additional process units such as activated carbon filtration after chlorination.

Organic compounds are considered as potential causes of impaired taste and odour of drinking water (Zoeteman, 1978) when the ratio of the concentration of the compound i.e. C in $\mu g/\ell$ to its Odour Threshold Concentration (OTC) in $\mu g/\ell$ is 0,01 or higher. A survey of C/OTC ratios of taste impairing substances in water is reported in Table 16.

TABLE 16
ORGANIC COMPOUNDS PROBABLY INVOLVED IN TASTE IMPAIRMENT OF DRINKING WATER

Compound	Max. Conc. ($\mu g/\ell$)	OTC ($\mu g/\ell$)	C/OTC ratio
Octene-1	0,03	0,5	0,06
1,3,5-Trimethylbenzene	1,0	3	0,3
Naphthalene	0,1	5	0,02
Biphenyl	0,1	0,5	0,02
2-Ethyl-1-hexanol	3,0	300	0,01
2-Methylisoborneol	0,03	0,02	1,5
Geosmin	0,03	0,02	1,5
Heptana	0,1	3,0	0,03
Octanal	0,03	0,7	0,04
Nonanal	0,1	1,0	0,1
Decanal	0,1	0,1	1,0
Haptan-3-one	0,1	7,5	0,01
Chloroform	60	100	0,6
Bromoform	10	300	0,03
Hexachlorobutadiene	0,1	6	0,02
o-Dichlorobenzene	0,1	10	0,01
p-Dichlorobenzene	0,3	0,3	1,0
1,2,4-Trichlorobenzene	0,3	5	0,06
β-Hexachlorocyclohexane	0,1	0,3	0,03
Bis(2-chloroisopropyl) ether	3,0	300	0,01

Several compounds reported in the above table are most likely produced during impoundment of surface water e.g. 2-methylisoborneol and geosmin, 5-octene-1 and aldehydes, like decanal.

It is worth considering whether water, which is free of taste and odour, is safe to drink and whether water with an impaired flavour, can be regarded as a potential danger to health. For this purpose, Zoeteman (1978) made a comparison of OTC values of 12 pesticides found in water with the Acceptable Daily Intakes (ADI) of these chemicals. The ADI (mg/kg body weight per day) of a compound is the permissible total daily intake of a chemical during the entire lifetime without appreciable risk on the basis of all known facts at the time (WHO, 1976). In the OTC/ADI ratio the OTC of the compound is calculated in g/m^3 for an adult of 70 kg consuming 2 ℓ of water per 24 h while exposed to the ADI. These data are recorded in Table 17.

TABLE 17
OTC AND MAXIMUM ACCEPTABLE DAILY INTAKE (ADI) VALUES FOR SOME PESTICIDES

Compound name	OTC (g/m^3)	ADI (mg/kg body weight per day)	OTC/ADI ratio
Aldrin	0,017	0,000 1	170
sec-Butylamine	5*	0,2	25
Chlordane	0,000 5	0,001	0,5
2,4-D	3,1	0,3	10
DDT	0,35	0,005	70
Dieldrin	0,041	0,000 1	410
Endrin	0,018	0,000 2	90
α-HCH	12	0,01	1 200
Heptachlor	0,02	0,000 5	40
Malathion	1,0	0,02	50
Methoxychlor	4,7	0,1	47
Parathion	0,04	0,005	8

*estimate on basis of related amines

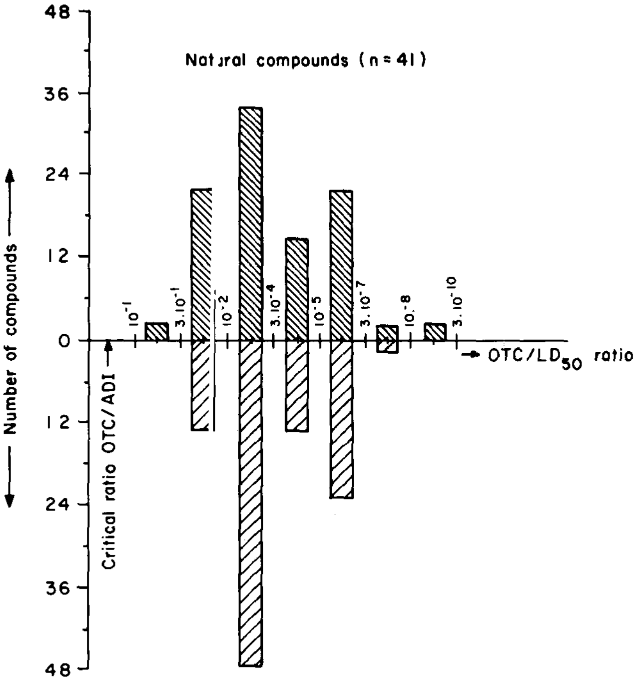

Figure 1
Frequency distribution of OTC/LD_{50} ratios for 41 natural and 52 industrial compounds

The critical OTC/ADI ratio is considered to be conservatively of the order 35 ($g \cdot m^{-3} \cdot mg^{-1} \cdot kg$) (Zoeteman, 1978) since the OTC applies to 50% of individuals in the population under test, whereas the ADI applies to 95–99% of the individuals. According to the data recorded in Table 17, 4 of the 12 pesticides when present as single compounds would not warn the water consumer against the presence of toxic substances which exceed the critical OTC/ADI value. The consumer may, however, be warned by the presence of accompanying odour intensive compounds as is evident from the comparison of chemoreception for natural and industrial compounds as shown in Figure 1. The motivation for this comparison by Zoeteman (1978) stems from the hypothesis of certain workers on micropollutants in water, that chemo-reception more effectively detects critical levels of naturally occurring compounds than those of compounds originating from industrial origin. For this comparison he compiled OTC/LD_{50} ratios for known natural and industrial organics as presented in Figure 1.

In this comparison, compounds of biological origin distributed in the environment by industrial activity e.g. oil compounds, were considered to be of industrial origin. Organics such as aliphatic alcohols, aldehydes and acids also produced industrially were considered of natural origin because of their omnipresence in plant life, body fluid etc.

It is obvious that the sensitivity of chemo-reception of industrial organics does not differ substantially from that of natural compounds, consequently taste and odours in drinking water may not only be effective indicators of compounds of toxicological significance but also act as a signal of concentrations of organics considerably lower than levels for lethal effects.

With a view to evaluate whether odour and taste in drinking water could indirectly detect contamination by carcinogens, bacterial mutagens or teratogens, Zoeteman (1978) compiled Table 18.

The results show that for several compounds like tetrachloromethane, the haloforms and bis(2-chloroethyl) ether, increased concentrations correspond to increased taste impairment. Furthermore, a possible relationship exists between taste assessment and the presence of suspected carcinogenic, mutagenic or teratogenic compounds when associated with a wide range of compounds in heavily contaminated surface water which is used as raw water intake to a purification plant. There are of course carcinogens which do not cause a taste and odour in water when present as a single contaminant, consequently taste and odour will not be a reliable warning against the toxicity of single compounds. Therefore, *the absence* of taste and odour in water will not guarantee its safety, but on the other hand, impaired odour and taste may largely indicate the presence of components exerting carcinogenic or other chronic toxic effects.

Since generally, most organic compounds in drinking water are not present in concentrations above 1 $\mu g/\ell$, and because odour and taste perception occur at concentrations below this level, we have here a significant parameter in the evaluation of the potability and the hygienic quality of a water supply. Taste and odour of drinking water could provide an excellent "first aid" warning tool in measuring the health safety of public water supply.

Current Capability of Water Purification Technology to Ensure Health Safety Levels of Micropollutants

There is general consensus that conventional water purification processes can effectively ensure that concentrations of micropollutants in the finished water are maintained at health safety levels. This largely depends on the selection of each unit process

TABLE 18
PRESENCE OF SOME KNOWN OR SUSPECTED CARCINOGENS, BACTERIAL MUTAGENS AND TERATOGENS IN DRINKING WATER, BELONGING TO DIFFERENT TASTE CATEGORIES

Compound and Toxicity Category	Concentrations detected in drinking water of a certain taste category in $\mu g/\ell$		
	1,10—1,45	1,45—1,80	1,80—2,15
Suspected human carcinogens			
– Benzene	<0,01–0,03	<0,01–0,1	<0,01–0,1
– 3,4-Benzopyrene	<0,005–0,01	<0,005–0,1	<0,005–0,005
Animal carcinogens			
– Lindane	<0,01–0,01	<0,01–0,1	<0,01–0,02
– Chloroform	<0,01–2,0	<0,01–25	0,2–60
– Tetrachloromethane	<0,01–0,1	<0,01–0,1	<0,01–0,7
– Trichloroethene	<0,01–9,0	<0,01–3,0	<0,01–0,5
Suspected animal carcinogens			
– Bis(2-chloroethyl) ether	<0,005	<0,005	<0,005–0,03
Bacterial mutagens			
– Dibromochloromethane	<0,01–0,3	<0,01–5,0	<0,01–20
– Bromoform	<0,01–0,3	<0,01–3,0	<0,01–10
Teratogens			
– Nicotine	<0,005	<0,005–0,005	<0,005–0,03
– Diethyl phthalate	<0,005–0,03	<0,005–0,1	<0,005–0,03
– Dibutyl phthalate	<0,005–0,1	0,01–0,3	0,005–0,1

in the treatment system which should be capable of reducing the concentration of pollutants and act as a buffer against pollution by inadequately purified industrial and urban wastes. However, there is a limit to the capability of conventional water purification systems which have polluted rivers and impoundments as raw water intakes. Improperly purified or pretreated wastewater discharged into the water environment can escape dilution and self-purification and thus pass directly into a conventional water purification system. Any undesirable pollutant for which no effective unit process is incorporated in the purification plant for its removal, can be expected to be present periodically or continuously in the finished water — admittedly at safe or sub-lethal concentrations, but the fact remains it can be present in the public water supply. It can be stated unequivocally that situations reported in this paper on the incidence of micro-organics in drinking water, are largely due to an over-assessment of, firstly, the capacity of self-purification processes and of the role of dilution of the water environment in degrading and dissipating these compounds and, secondly, the adequacy of the physical chemical unit processes of conventional water purification systems to remove compounds which are present in the raw water intake at micro-concentration levels.

The identification of an increasing number of micro-organics in drinking water demonstrates the aforementioned fact most convincingly, and hence the need of introducing the system of multiple safety barriers into water purification plants i.e. a number of lines of defence against the breakthrough of pollutants. Therefore, depending on the degree of pollution control and quality of the water intake "each pollutant should be reduced in concentration by at least two processes and preferably by three or more" (WHO, 1975). Furthermore, it is a prerequisite to control industrial waste discharges into the sewerage system or the raw water source to the maximum degree to remove or eliminate at source as many potentially toxic or potentially harmful chemicals as possible. It is obvious from Figure 2 (Stander, 1972) that the selection and combination of process units for a multiple safety barrier water purification system will depend on the predominance of specific pollutants in the raw water intake and on the degree of renovation of wastewaters prior to discharge into the water environment.

The design and construction of an advanced water purification system to remove hundreds of micro-organics present in tap waters derived from polluted sources to zero concentration (in order to comply with the belief of toxicologists that there is no threshold for long-term effects of toxic agents below which the substances are harmless), would involve the combination of unit processes completely beyond the financial resources of the community, and would in any case be a ridiculous venture and

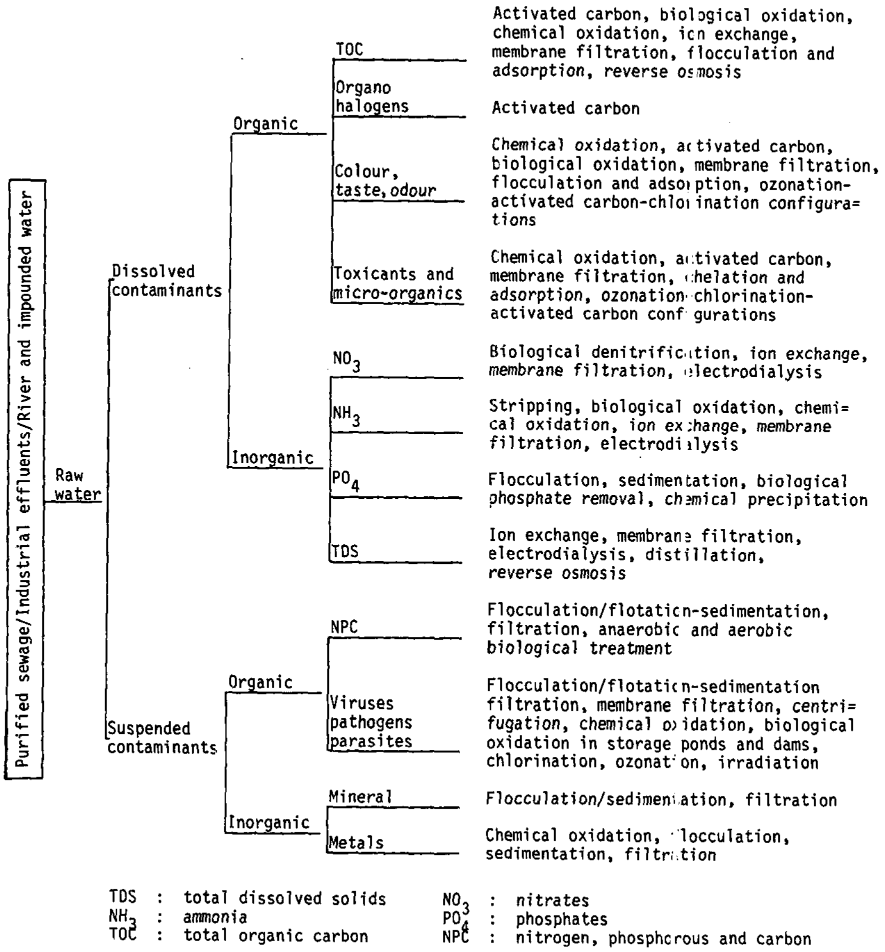

Figure 2
Classification of water contaminants and selection of process units for their removal

way of tackling the problem. The problem of potentially toxic organics should effectively be tackled and solved at source as a first line of action and the first options should be for their elimination instead of investing large sums of money in removing micro-organics from a polluted water environment for which the causes are obvious.

It is a *sine qua non* that if we expect advanced water purification technology to produce health-safe drinking water, the water environment itself requires health-effective management. Prevention is better than cure, both socially and economically. Natural waters should be kept clean and wastewater flows should be purified for reuse or return to the water environment in a degree of cleanliness compatible with optimum exploitation of available water resources and with the protection of public health. This indeed is the approach in the Republic of South Africa where studies have been specifically directed at the reclamation of sewage effluents for potable and other uses. In the case of the 4 500 m^3/d Stander Water Reclamation Plant (Figure 3) the intake water is effectively purified domestic sewage containing some industrial discharges. (Manual for water renovation and reclamation, 1978.)

In this plant the multiple safety barrier system incorporates four contaminant barriers for pathogenic micro-organisms, two for heavy metals and three for organic contaminants. The effectiveness of these contaminant barriers is demonstrated by the fate of selected organic compounds during reclamation as reported in Table 19. In the feed to the plant, a total of ten dif-

TABLE 19
POLYNUCLEAR AROMATIC HYDROCARBONS DETECTED IN THE INFLUENT TO AND THE FINAL WATER FROM THE STANDER PLANT

Compound	Toxicity level ∅	Influent	Final water
Dibenz(a,c) anthracene		—	—
Dibenz(a,h) anthracene	∅∅∅	+	—
Benz(a) anthracene	∅	+	—
Perylene		—	—
Benzo(ghi) perylene		+	—
Pyrene		+	+
Indeno(1,2,3,cd) pyrene	∅	+	—
3-Methylpyrene		—	—
Benzo(a) pyrene	∅∅∅	—	—
Fluoranthene		+	+
Benzo(b) fluoranthene	∅∅	+	—
Benzo(j) fluoranthene	∅∅	+	—
Benzo(k) fluoranthene		+	—
Coronene		—	—
22-Methyl chloranthrene		—	—
9,10-Benzophenathrene		+	—

+ Present
— Absent
∅ Andelman and Suess (1970)

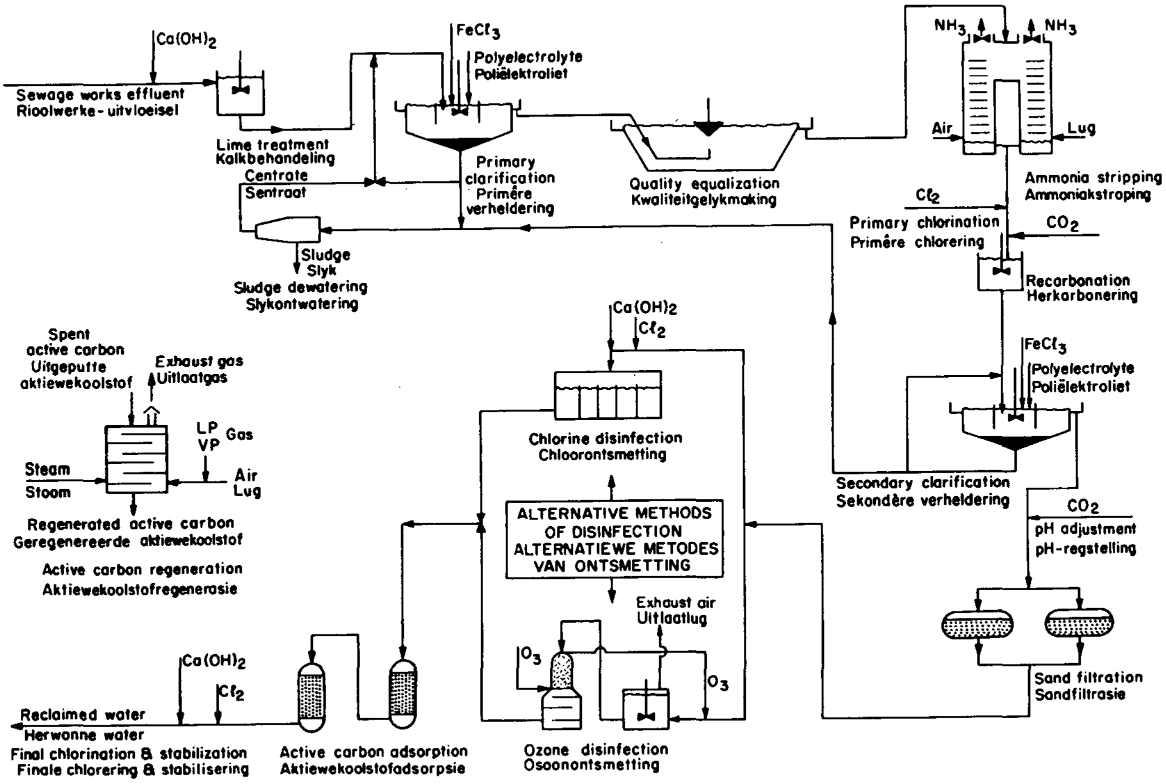

Figure 3
Flow diagram of the 4 500 m^3/d Stander Water Reclamation Plant

ferent polynuclear aromatic hydrocarbons were detected in the nanogram per litre range, whilst in the final water only two compounds (pyrene and fluoranthene), both of no toxicological importance could be detected.

The gas chromatographic profiles reported (Hart, 1978a) in Figures 4(a) and 4(b) indicate that the Stander Reclamation Plant not only reduces the concentration of organics but also substantially decreases the number of compounds as illustrated by the height and number of peaks.

It will also be observed from Figures 4(b), 5(a), 5(b) and 5(c) that the reclaimed water contains less organic substances and at lower concentrations than water purified by conventional treatment of raw surface waters receiving pollutants from non-point sources and from discharges of purified sewage and industrial effluents. In this connection it should be stated that the conventional water purification facilities reported on in these

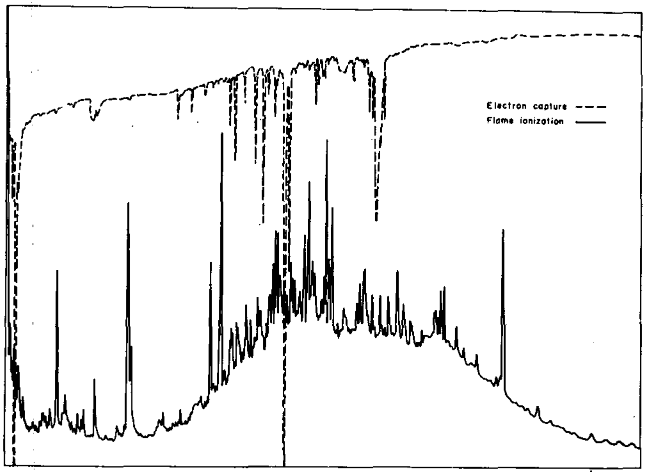

Figure 4(a)
G.C. profile — secondary sewage effluent intake to the Stander Reclamation Plant

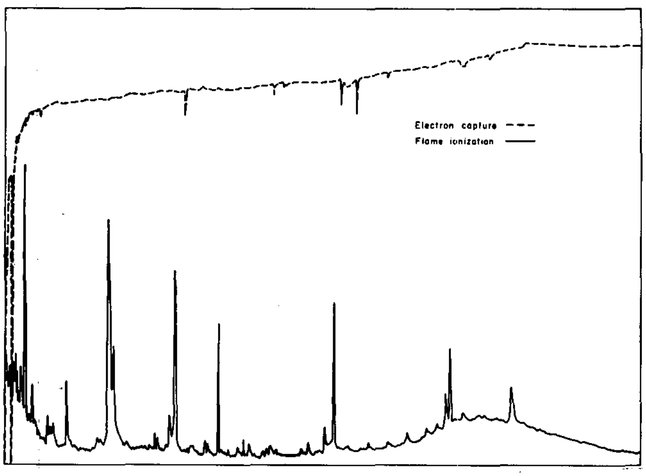

Figure 4(b)
G.C. profile — Stander Reclamation Plant effluent

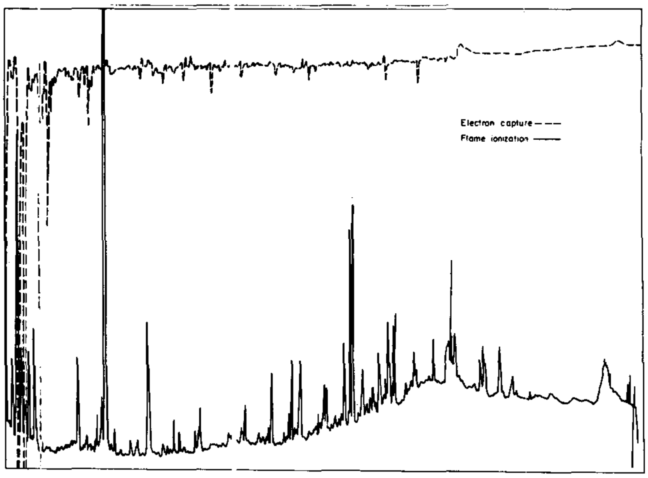

Figure 5(a)
G.C. profile — Rand Water Board drinking water supply (Klapperkop, Pretoria)

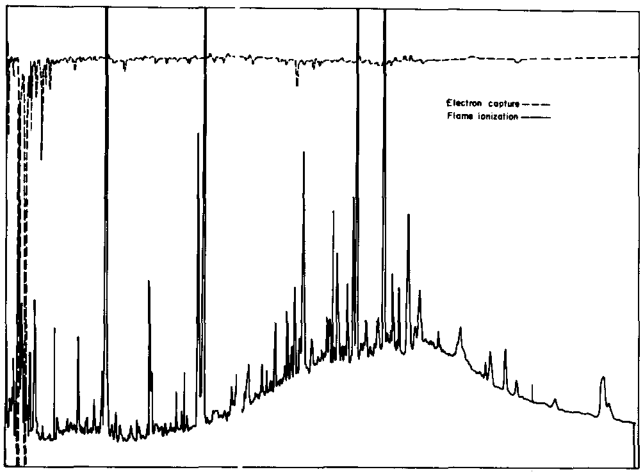

Figure 5(b)
G.C. profile — drinking water supply for Pretoria derived from Rietvlei Dam

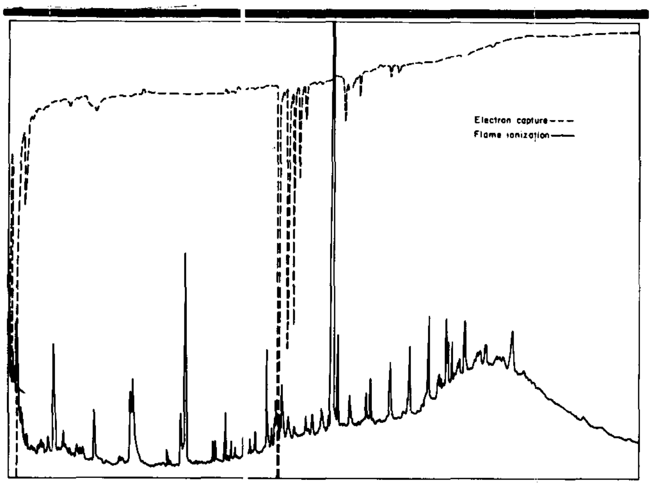

Figure 5(c)
G.C. profile — drinking water supply for Brits derived from Hartbeespoort Dam

gaschromatographs do not include activated carbon filtration. It, therefore, does seem essential that the inclusion of activated carbon filtration into conventional water purification treatment plants has become a necessary preventive tool to control micropollutants. Activated carbon has in fact been used as a utility tool for generations to control taste and odour in drinking water and consequently unintentionally ensured the health safety of the public water supply.

Water reclamation and the concomitant utilization of advanced water treatment processes not only drew attention to the shortcomings of conventional water purification systems with respect to micro-pollutant removal, but focused attention on the versatility with which these unit processes could be used to achieve specific goals. The present concern over VHH and other micro-organics and methods to reduce their concentration in public water supplies serves as a good example. The basic approaches to reduce VHH concentrations in finished water are to reduce the precursor compounds (i.e. micro-organics), to remove the VHH after formation and to change the disinfectant. By manipulating the process sequences of activated carbon, chlorination and ozonation at the Stander Plant, all three the above approaches are under investigation (Hart, 1978b) with most encouraging results. The development of VHH in the distribution system after final chlorination at the pH7 range is shown in Figure 6 for four different process configurations (Hart, 1978b).

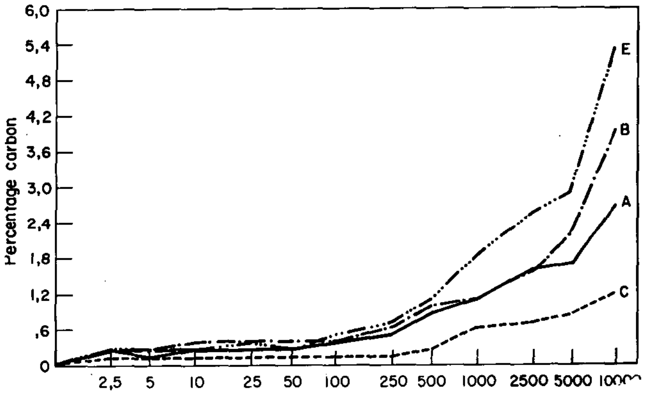

Figure 6
Carbon yield in total VHH for configurations A7, B7, C7 and E7

In configurations A and C breakpoint chlorination was used in the disinfection stage ahead of or in between the two activated carbon adsorption stages. In configuration B and E ozone replaced chlorine in the same sequence. The graphs show the percentage yield of carbon in the VHH per Total Organic Carbon (TOC) in the water after final chlorination. It was inferred from this study that when ozone is used as disinfectant, more VHH will develop in the distribution system on subsequent chlorination. It would also be advantageous to have the disinfection stage ahead of active carbon adsorption with post-chlorination after adsorption.

Conclusion — The Practicalities of the Situation

We have a most interesting situation of an interplay between "old news" and "good news" which demonstrates most effectively the resourcefulness, imagination and creative ability of the chemist.

Disinfection of water by chlorine to control waterborne disease and eventually to eliminate it effectively from drinking water supplies, had its beginning at the turn of the nineteenth century (Johnson, 1975) though British patents were registered (Skeat, 1961) for sterilisation of water by chlorination in the middle of the nineteenth century. However, the first permanent (Skeat, 1961) introduction of chlorination was directed by Sir Alexander Houston. It was not long after the virtually universal application of chlorination that chlorinous and chlorophenol tastes and odours in drinking water became prevalent and activated carbon was used as a utility tool to control it. Obviously, organo-halogens, and may it be said unequivocally $CHCl_3$, must have been present in the drinking water then already though analytical tools to identify it were non-existent. No wonder that Thresh, Beale and Suckling (1958) warned — "When used as a final process, chlorination should be regarded as an additional safeguard to public water supplies, and not as the treatment on which the bacterial purity of water solely depends. It should, therefore, be applied to waters which, naturally or as a result of treatment are clear and bright and of good quality. In normal practice, chlorination may permit modification of waterworks' design, but it does not permit the omission of filters or the inefficient purification of impure waters containing suspended matter or appreciable organic matter."

Now for the good news. This is indeed clearly and specifically reported in the substance of this paper which gives great credit to the creative ability of the chemist to probe the changes in our water environment and its impact on human health. With a considerable degree of concern the measurement of the hygienic quality of water by means of taste and odour techniques, seemed to have paled into insignificance in the path of development of powerful analytical tools by chemists. However, the pioneering research of Zoeteman (1978) promises a resuscitation of research into the natural self-defence mechanisms of man, namely the establishment of "a sensitive and odour selective instrumental equivalent of the nose and mouth such as the photocell for our eyes and the microphone for our ears" (Zoeteman and Piet, 1972/73). We must never lose sight of the fact that for many decades taste- and odourgrams have been, and in many water supply laboratories still are, effective "first aid" tools to judge the safety of drinking water for the public.

For the Republic of South Africa, the substance of this paper provides a considerable degree of good news, but also carries with it serious warnings most pertinently if we are desirous of keeping our clean waters clean and to get the maximum number of "kilometres" of water usage out of each "kilolitre" of water.

It is almost axiomatic in public health control that prevention is better than cure. If one examines critically the data reported in this paper and that reported in some two hundred publications consulted by the author and attempts to reconstruct the circumstances which led to the current situations in many countries of the world, one cannot escape the conclusion that the application of the aforementioned public health principle played a secondary role in the total planning and exploitation of the water resources of the countries concerned and only came into consideration as the final safety barriers of a water purification plant. Had this been otherwise, and progressive attention been given to the micro-impacts of socio-economic developments on the total water environment, (however insignificant it may be yet with respect to the health safety of water supplies in these countries) public water supply authorities, and for that matter governments would not have found themselves under the pressures of emotionalists and "alarm button pressers". It is within this sensitive and confused climate that decision makers "with almost the elements of heaven pouring on their heads" have to carve out a critical path of action, the implementation of which will involve the risks of irreversible decisions and of the expenditure of funds running in the multimilliard ranges. The question is where has the decision maker to invest funds to really solve the problem? In a monstrous water renovation plant or shall we say water factory to remove the micro-organics thereby curing the problem or investment in cooperative programmes to mobilise the resources of industry, agriculture, urban authorities and of the exploiters of the water environment, thereby preventing at practical level the problem from arising?

For South Africa the roads we have to follow are very clear. No doubt current purification technologies can be exploited effectively (refer Figure 2) to produce potable water from very polluted sources and new research frontiers show promises of breakthroughs which make them versatile tools in the removal of pollutants. However, the harnessing of advanced treatment systems as essentially end-of-the-line quality control tools, i.e. only as curative technologies built into public water supply facilities would indeed be a sad situation. It will leave the backdoor open to increased pollution with consequent progressive escalation of unit production costs and of the complexity of purification facilities.

Effective water renovation, reclamation and purification technologies and the elimination of pollutants at source for water quality protection constitute a powerful double-acting tool for optimizing the utilization of water resources — it provides both preventive and curative technologies for the restoration of the cleanliness and amenities of the water environment and for relieving the pollution stresses which conventional water purification plants have to cope with, thus ensuring the health safety of public water supply systems.

Acknowledgement

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