The occurrence of organic micro-pollutants in the Vaal River between Grootdraai Dam and Parys*

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Abstract

The Vaal Dam – Vaal River Barrage system is a source of drinking water for approximately 40 per cent of the population of the Republic. This system also serves as a recipient of a multitude of organic compounds derived from numerous activities in the catchment area. Below the Vaal River Barrage a number of point source contamination sites were identified which could affect the water quality for users further down the river. The occurrence of organic compounds between the Grootdraai Dam and Parys was investigated. Twenty five organic compounds were identified by gas chromatography – mass spectrometry. Dibutyl phthalate and phenol were found at all the sampling points although their concentrations were considerably higher at sampling points below the Barrage.

Introduction

The Vaal River has its origin in the vicinity of Ermelo, approximately 200 km east of Johannesburg and joins the Orange River at Douglas in the northern Cape, measuring just over 1 000 km. The Pretoria-Witwatersrand-Vereeniging (PWV) area, which lies 800 km upstream from Douglas, receives most of its water from the largest impoundment on the Vaal River, namely the Vaal Dam. The PWV area presently accommodates 40 per cent of the total population of the RSA and 50 per cent of the Republic's industrial production (Rand Water Board 1984 Annual Report). The Rand Water Board draws nearly all of its water requirements from the Vaal Dam and Vaal River Barrage and it is essential that the quality of this supply should be safeguarded. Bruwer *et al.* (1985) reported that the discharge from the Vaal River Barrage could at times contain more than fifty per cent effluent (waste and/or treated waste water), which would imply that contamination of organic origin would be inevitable. Although there are at present no standards or criteria for organic compounds in South African waters, this survey could contribute to future participation in setting water quality guidelines for South Africa.

During 1977/78 the National Institute for Water Research carried out a national survey to determine the occurrence and extent of organic micro-pollutants in surface waters intended as ultimate drinking-water supplies (Van Rensburg, 1977). Although no specific organic compounds were positively identified at that stage, general organic profile concentrations determined by gas chromatography, indicated a deterioration in organic water quality from above to below the Vaal River Barrage (Figures 1 and 2). At that time it was recommended that the influence of this organic contamination on the water reaching Parys be investigated. Samples of raw intake water, taken at the purification works, were analysed after complaints had been received from the Parys Municipality (mid-1981) regarding objectionable taste and odour in the drinking water. The presence of micro-quantities of dibutyl phthalate, phenol, trichlorophenol, nitrophenol and a number of unidentified organic compounds was detected which could induce taste and odour problems when chlorinated. A subsequent survey was initiated during 1982 to determine the type of organic compounds, their origin and concentrations in the Vaal River.

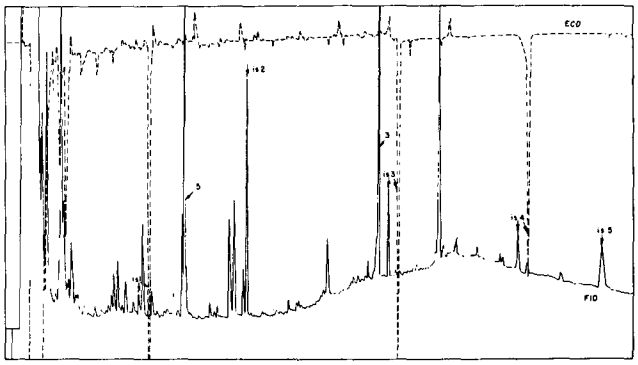

Figure 1
Gas chromatographic profile of outflow from the Vaal Dam (V4)

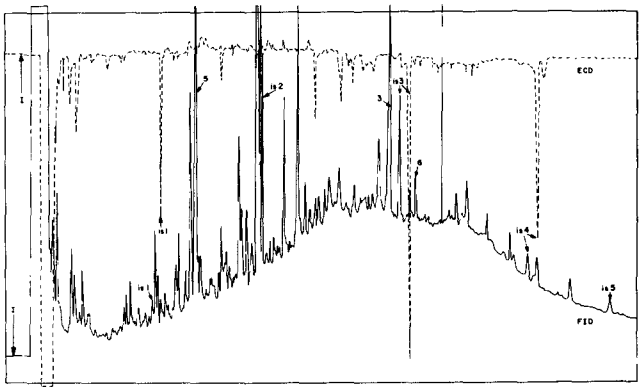

Figure 2
Gas chromatographic profile of the Vaal River below Barrage (V17)

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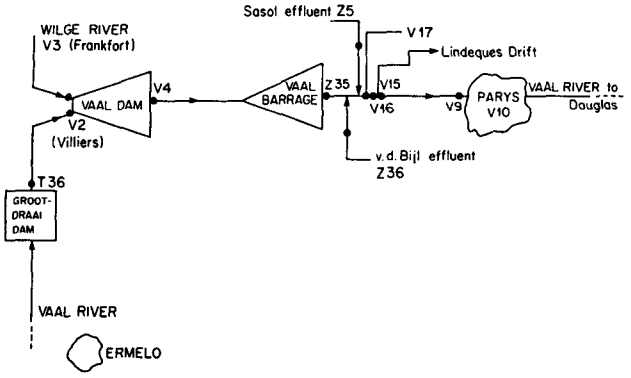

Figure 3
Sampling points on the Vaal River from Grootdraai Dam to Parys

This paper describes the occurrence of organic compounds in a very prominent sector of the Vaal River from the Grootdraai Dam to Parys (Figure 3).

Sampling procedures

To determine the influence of the PWV area on the quality of the Vaal River, samples were collected upstream as well as outside the PWV area namely the Grootdraai Dam and Wilge River. Stream striation and stratification at points V17/1 to V17/8 were also investigated (Figure 4). Samples were taken from the middle of the rivers. The identification of sampling sites is as follows:

T36: Grootdraai Dam
V2 : Vaal River at Villiers
V3 : Wilge River at Frankfort
V4 : Vaal Dam outlet
Z35: Barrage outlet
V17: 0,5 km below Barrage outlet
V16: 'Tahiti Rapids' 8 km below Barrage outlet
V15: Lindeque's Drift 15 km below Barrage outlet
V9 : Vaal River at Parys

Analytical procedures

Dissolved organic carbon (DOC) was determined according to the method described by Van Steenderen and Lin (1981). This entailed the stripping of inorganic carbon from a water sample prior to subjecting the sample to catalytic photo oxidation with ultraviolet irradiation and the detection of liberated carbon dioxide by means of infrared spectroscopy.

The total organohalogen potential value (TOHp) was determined in accordance with the method described by Van Steenderen (1980). A water sample was chlorinated to contain 60 mg/ℓ residual chlorine and left in a sealed glass container for 48 h. The organochlorine compounds which were formed during this period were extracted with petroleum ether and determined by microcoulometric titrations. Results are expressed as μg/ℓ chloroform.

General organic and organophenolic profile analysis was described by Theron and Hassett (1986). The analytical technique incorporates a liquid-liquid extraction procedure for the simultaneous recovery of a wide range of base/neutral organic compounds, e.g. chlorinated pesticides, polychlorinated biphenyls, polyaromatic hydrocarbons etc., and phenolic organic compounds. Detection was by means of gas chromatography/flame ionisation detection (FID).

Volatile halogenated hydrocarbon (VHH) compounds e.g. chloroform, were determined according to Van Rensburg and Hassett (1982). The method incorporated liquid-liquid extraction with an azeotrope consisting of hexane and isopropyl ether and final gas chromatography electron capture detection (ECD).

Gas chromatography – mass spectrometry (GC-MS) identification was accomplished with a HP5995 GC-MS and HP5993 data system. A DB5 J and W fused silica capillary column was used for the separation of the organic compounds prior to MS analysis.

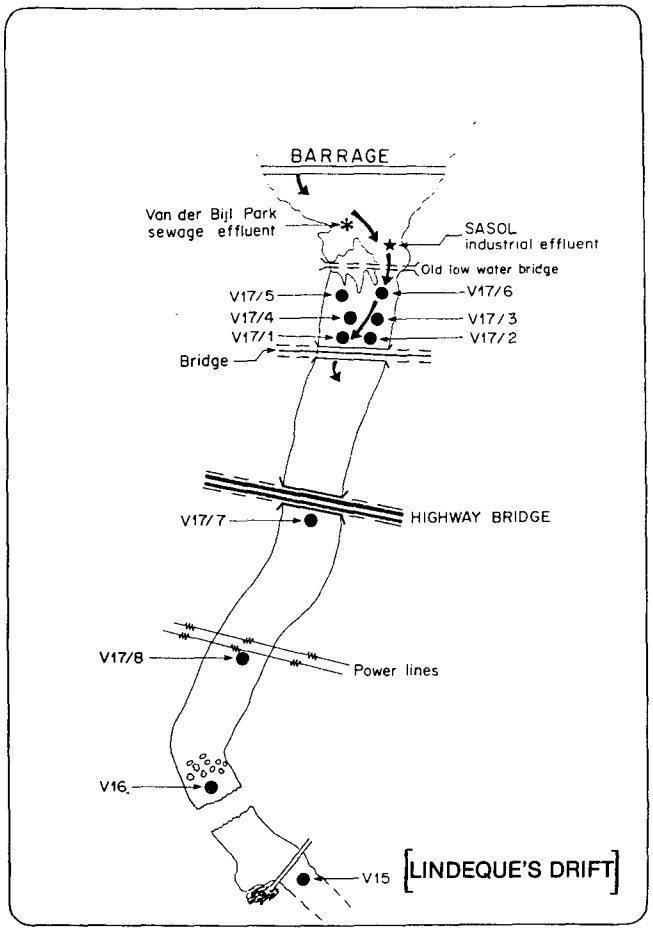

Figure 4
Sampling points of Vaal River between Barrage and Lindeque's Drift

Results and discussion

The Vaal Dam – Vaal River Barrage system is but one of many overburdened receive/supply systems in the country and contamination of these sources from runoff and/or point sources is unavoidable. Two point sources of considerable concern are for example the Sasol industrial effluent (Z5) and Vanderbijl sewage effluent (Z36). The effect on the organic water quality of the Vaal River below their points of discharge is illustrated by means of Figures 5, 6, 7 and 8. Where more than ten results were available for a sampling point, the distribution of data in these figures was divided into four equal parts by the two quartiles and the median. The dotted lines in Figures 5 to 8 refer to the average value of five or less results for that particular sampling point. The individual organic compounds tentatively identified by GC Reten-

TABLE 1
ACID EXTRACTABLE ORGANIC COMPOUNDS (BASE-NEUTRALS) IDENTIFIED BY RETENTION INDEX IN THE VAAL RIVER FROM GROOTDRAAI DAM (T36) TO PARYS (V9)

Compound	Sampling Point V2	V3	V4	Z35	V17	V16	V15	V9
Decane (C-10)/1,3 dichlorobenzene			✓		✓	✓	✓	
1,4-Dichlorobenzene				✓	✓			
1,2-Dichlorobenzene					✓			
N-Nitroso-Di-n-propylamine					✓			
Nitrobenzene					✓	✓	✓	
Hexachloroethane					✓			
Isophorone					✓		✓	
Bis(2-Chloroethoxy)Methane						✓	✓	
Naphthalene					✓	✓	✓	
Tridecane (C-13)					✓	✓	✓	
2,6-Dinitrotoluene	✓	✓	✓		✓			
Pentadecane (C-15)					✓	✓		
Diethyl Phthalate	✓	✓	✓		✓	✓	✓	
Hexadecane (C-16)					✓	✓		
gamma-BHC				✓				
Atrazine				✓				
Heptadecane (C-17)					✓	✓	✓	O
Phenanthrene					✓			O
Octadecane (C-18)					✓	✓		
Nonadecane (C-19)					✓	✓		
Dibutyl phthalate	✓	✓	✓	✓	✓	✓	✓	O
Benzidine	✓	✓			✓		✓	
Pyrene					✓		✓	
Heneicosane (C-21)					✓			
Docosane (C-22)					✓			O
Butyl-Benzyl Phthalate		✓						
Tricosane (C-23)					✓	✓	✓	
Tetracosane (C-24)					✓			O
Pentacosane (C-25)					✓			
Dioctyl Phthalate				✓				
Bis(2-Ethhex)Pht./Dioc-Pht.	✓	✓	✓		✓	✓	✓	
Hexacosane (C-26)					✓			
Coprostanol					✓	✓		
Hentriacontrane (C-31)				✓				
Cholesterol		✓	✓		✓	✓	✓	

✓ Tentatively identified by GC
Detection limit 0,01 $\mu g/\ell$
O Identifications obtained from Bruwer *et al.*, 1985.

TABLE 2
ORGANO PHENOLIC COMPOUNDS IDENTIFIED BY RETENTION INDEX IN THE VAAL RIVER FROM GROOTDRAAI (T36) TO PARYS (V9)

Compound	Sampling Point V2	V3	V4	Z35	V17	V16	V15	V9
Phenol	✓	✓	✓	✓	✓	✓	✓	n
2- Chlorophenol					✓		✓	n
2,4-Dichlorophenol				✓	✓	✓		n
4-Chloro-3-methylphenol					✓			n
2-Nitrophenol					✓	✓		n
2,4,6-Trichlorophenol					✓	✓		n
4-Nitrophenol					✓			n
Pentachlorophenol					✓	✓	✓	n

✓ Tentatively identified by GC
n No identifications done.
Detection limit 0,05 $\mu g/\ell$

tion Indices are tabulated in Tables (1) and (2). Twenty seven of the compounds listed in Tables (1) and (2) are amongst the organic compounds tabled by the Environmental Protection Agency as priority pollutants (Federal Register, 1979). Table 3 indicates the organic compounds confirmed by GC-MS identification.

Dibutyl phthalate and phenol were identified at all the sampling points while some of the other phenolic compounds such as 2,4-dichlorophenol and pentachlorophenol occurred frequently (Table 2). The average concentration of phenolic compounds determined in Parys raw water was 10 $\mu g/\ell$ (Figure 7).

The organoleptic properties of phenolics in water, especially upon chlorination are a major aesthetic problem. Threshold concentrations for taste and odour of phenol alone, have been reported from 0,01 to 60 mg/ℓ while in chlorinated waters this threshold is considerably lower, namely 0,01 to 20 $\mu g/\ell$ (McKee and Wolf, 1963).

Although the Vaal River below the Barrage is only a few meters deep, sampling at various depths indicated stratification in respect of the organic compounds measured (Table 4). This stratification was not observed for either the inorganic determinands or trace metal contents (not discussed here).

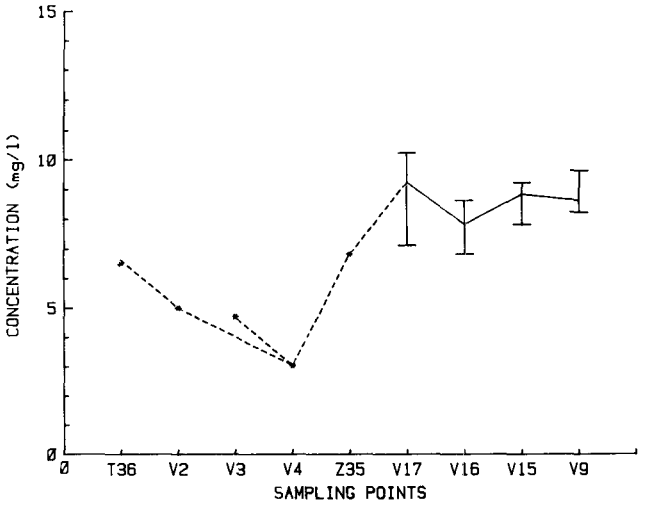

Figure 5
Dissolved organic carbon concentrations between Grootdraai Dam and Parys

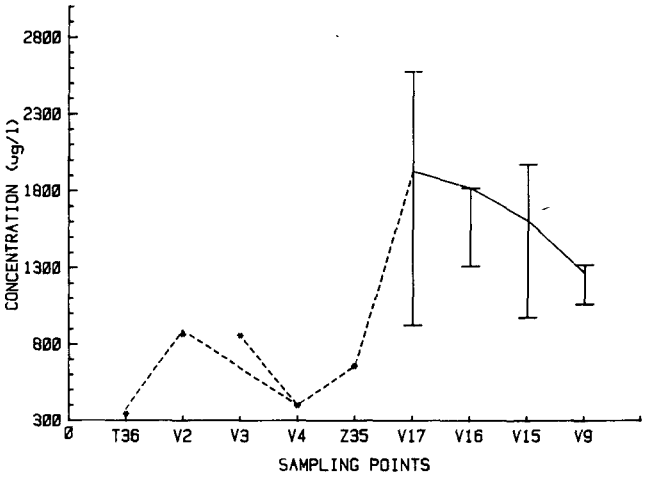

Figure 6
Total organohalogen potential values between Grootdraai Dam and Parys

TABLE 3
ORGANIC COMPOUNDS CONFIRMED BY GC/MS IN THE VAAL RIVER FROM THE BARRAGE TO LINDEQUE'S DRIFT

Dibutyl phthalate
Diethyl phthalate
Bis (2-ethylhexyl) phthalate
Tetradecanoic acid
Oleic acid
Saturated hydrocarbons:
C-15, C-16, C-17, C-19, C-21, C-22, C-23, C-24, C-25
2,6,11-trimethyl-dodecane
Phenol
Cresol (methyl phenol) and isomers
Xylenol (Dimethyl phenol) and isomers
4-Chloro-2-methyl phenol
Isophorone
Atrazine
2-Methyl-thiobenzothiazole
Cholesterol
Coprostanol
Caffeine

Detection limit 0,1 $\mu g/\ell$.

TABLE 4
STRATIFICATION OF ORGANIC COMPOUNDS AT SAMPLING POINT (V17). DEPTH AT THIS POINT WAS 2 m.

Depth sampled	DOC mg/ℓ	COD mg/ℓ	Phenol $\mu g/\ell$	Electrical conductivity mS/m
Surface	7,2	23	<10	77
1,0 meter	8,4	29	83	77
1,5 meter	13,0	135	<10	77

Various environmental conditions will increase the toxicity of phenol in water (Train, 1979) e.g. low dissolved oxygen concentrations, increased salinity and increased temperatures. Three samples taken of the sediment at site V17 revealed anaerobic conditions and the presence of considerable concentrations of phenolic compounds. The possibility of organic compounds being adsorbed and desorbed from the bottom sediments must therefore not be ruled out and could form the basis of further studies.

In addition, phenolic compounds are known to be organohalogen precursors. Upon chlorination phenols take part in the haloform reactions to form a group of compounds known as the trihalomethanes (THM) of which chloroform is usually predominant. The presence of phenols could explain the high organohalogen potential values (TOHp) as illustrated in Figure 6. A correlation was observed between the four organic groups (Figure 9), especially between the general organic, organic phenol and dissolved organic carbon profiles. This correlation could hold advantages in that DOC, which requires 4 min per determina-

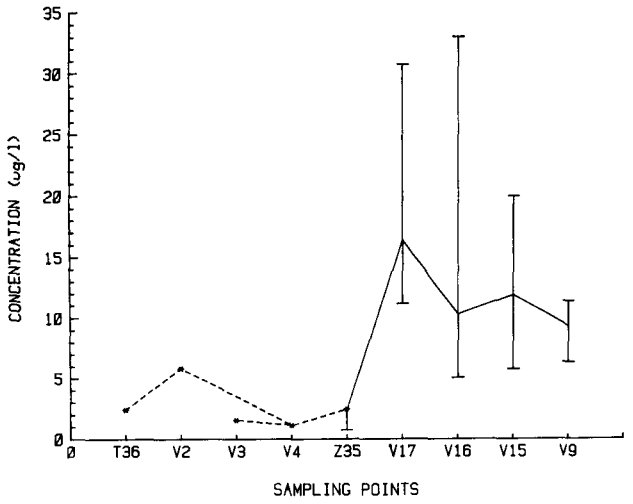

Figure 7
Phenolic organic compound concentrations from Grootdraai Dam to Parys

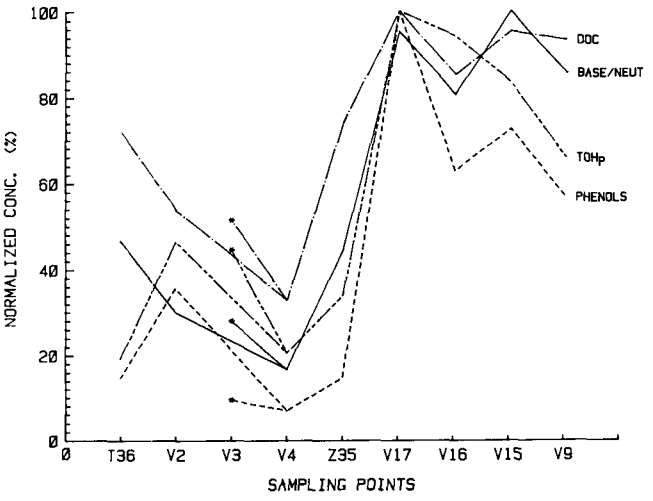

Figure 9
Comparison of DOC, TOHp, Phenols and Base/Neutral profiles

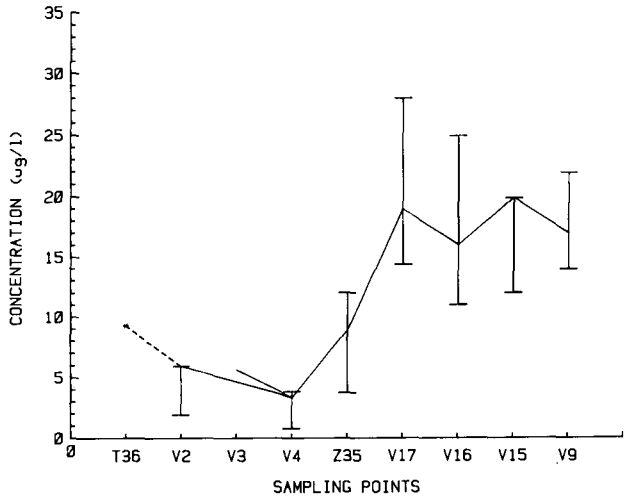

Figure 8
Organic compound (Base/Neutral) concentrations from Grootdraai Dam to Parys

tion, could be used to predict the concentration of the other three group determinands which require from 2 to 4 d per determination.

The effect of the high TOHp values in the Vaal River was reflected in the final water of Parys. VHH analysis of the final Parys water showed fluctuating values between 102 and 765 $\mu g/\ell$ (predominantly chloroform) with an average value of 169 $\mu g/\ell$. This value exceeds the maximum limit of 100 $\mu g/\ell$ total trihalomethanes promulgated by the USEPA for drinking water.

Conclusions

Relative to the Vaal Dam water quality, contamination by organic micro-pollutants escalates and reaches a peak at a point approximately 0,5 km below the Vaal River Barrage. High concentrations of phenol and phenolic type compounds were detected. The TOHp results closely follow the trend of the organic phenol concentrations, suggesting that a large percentage of the organohalogen precursors responsible for the formation of VHH's after chlorination are phenolic in nature. In this study forty three organic compounds were tentatively identified by GC and twenty five confirmed by GC/MS. Twenty seven of these compounds appear in the Federal Register (1980) of proposed USEPA priority pollutants.

Studies such as this are necessary in order to ultimately formulate organic water quality guidelines for South African waters.

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