The Effect of Toxic Loads on Effluent Purification Systems*

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Abstract

Deterioration in the performance of biological wastewater treatment plants at Daspoort Sewage Works, Pretoria, during 1975, was attributed to toxic material in the sewage. Abnormally high concentrations of mercury, phenol, chromium and an organophosphorus compound were detected at the time. Any or all of these substances might have been responsible for the deterioration in performance. Inhibition of attached growth reactors, such as biological filters and rotating disc units, was more noticeable than in extended aeration activated sludge processes. Encystation by peritrichous ciliates caused high bacterial counts in biofilter effluents. Nitrification declined rapidly and recovery was delayed, while carbon oxidation (COD removal) was only affected to a limited extent. The LFB process, using lime flotation followed by biological treatment, was completely unaffected, suggesting protection of the biological part of the process by prior lime addition. The Stander Water Reclamation Plant produced the same high quality water throughout, even when the influent was little better than settled sewage.

Introduction

The importance of water reclamation in our modern society needs no amplification. In South Africa it is estimated that limited water resources will necessitate widespread re-use of effluents by the turn of the century. It is therefore essential that all the implications of reclamation should be studied well in advance, particularly in regard to obstacles confronting unrestricted re-use.

The fact that toxic materials may be discharged inadvertently or even wilfully in slug doses into communal sewers, is often quoted as one of the major objections to water reclamation. The National Institute for Water Research (NIWR) has, therefore, over the past number of years, devoted special attention to these aspects. A detailed study (Coombs and Van Vuuren, 1973) of the occurrence of heavy metals and cyanides in a municipal sewer showed that at the time of the survey there was no need for undue concern. It was also shown (Funke and Coombs, 1972) that the heavy metals normally occurring in sewage effluents were adequately taken care of in conventional sewage plants followed by the advanced purification processes used in the Stander Water Reclamation Plant in Pretoria.

Previously it has not, however, been possible to study the fate of organic toxicants such as pesticides etc., which do not normally occur in sewage effluents to any great extent. In fact, these toxicants are not even normally monitored by municipalities or sewage treatment authorities. It was therefore rather fortunate that the elaborate monitoring programme conducted at the Stander Water Reclamation Plant, provided for a more accurate assessment of the occurrence and effects of a toxic material at the Pretoria municipal sewage works during the latter part of 1975.

Although the presence of the toxicant which inhibited biological activity of the sewage purification plant was not realised immediately, it was nevertheless subsequently possible to review the analytical data recorded at various units operated by the NIWR in order to piece together the available evidence. The decline of biological activity, particularly in the biological filters at Daspoort, was also observed by the municipal staff during August, 1975, but it was impossible to identify the cause.

This report attempts to correlate all the data from the various biological plants and research units at Daspoort over the period of reduced efficiency and to evaluate the effects thereof on the quality of the water produced by the Stander Water Reclamation Plant.

The Occurrence of Toxic Material

The NIWR operates several pilot plant effluent purification units as well as a full-scale (4,5 Mℓ d^{-1}) reclamation plant, known as the Stander Water Reclamation Plant, at Daspoort, Pretoria. All these units derive their feed from the Pretoria municipal sewage works. They consist of two separate activated sludge units, one an Orbal plant and the other an extended aeration system with high rate recirculation to effect

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biological denitrification and phosphate removal (known as the Bardenpho plant), a Rotating Disc Unit and a physical-chemical-biological treatment plant, which all use settled sewage. The Stander plant utilises advanced techniques to produce potable water from humus tank effluent (HTE). Analyses of these feed waters provided a key to the incidence of toxic material in the Daspoort sewage.

During August, 1975, a reduction in efficiency of the sewage purification at Daspoort was noticed. This deterioration in effluent quality was arbitrarily ascribed to toxic waste and was also noticed in the influent to the Stander Water Reclamation Plant which takes HTE from the sewage purification plant. The inhibition of biological activity was primarily manifested in increased COD and ammonia concentrations in the HTE which necessitated the use of excessively large lime and chlorine dosages at the reclamation plant.

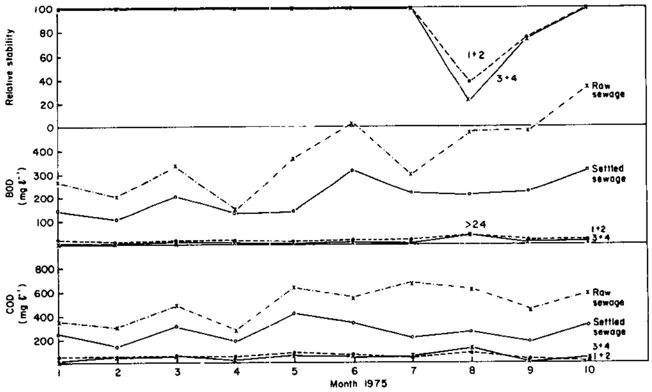

Figure 2
Carbon oxidation by municipal filters and relative stability of effluent

Observations at the Stander Water Reclamation Plant

Salient quality parameters of HTE are recorded in Figure 1. A significant decrease of nitrate with concomitant increases of total Kjeldahl nitrogen (TKN) and COD during the period 26th July to 6th September, 1975, was observed. The lime and chlorine demand of the plant further confirmed the inferior quality of the feed (HTE).

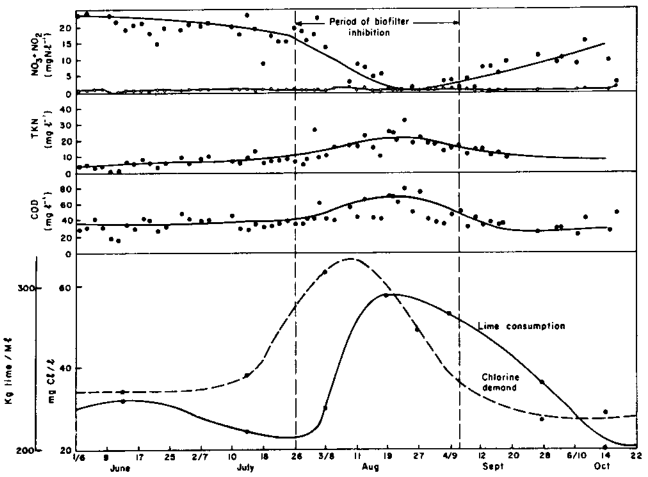

Figure 1
Salient parameters of HTE compared with lime and chlorine demand of reclamation plant

Observations by municipal personnel

Analytical data provided by the Pretoria municipal laboratory are recorded in Table 1 and are presented graphically in Figures 2, 3 and 4. These data are in agreement with the more frequent analytical record of the NIWR (Figure 1). It is clear that nitrification was impeded more severely than oxidation of carbonaceous matter but the major impact of toxicity was nevertheless observed during August for all quality parameters. Figure 4 shows that the bacterial population of settled sewage was reduced drastically during both June and July. This indicates that toxic ingredients may have been present in the sewage, even before its effects were manifested in deteriorating effluent quality.

Occurrence of trace toxicants

The phenomenon of declined biological activity was unfortunately not noticed until after the damage had been done. It was therefore not possible to ensure adequate monitoring before

TABLE 1

ANALYSES OF HTE FROM BIOLOGICAL FILTERS NOS. 1 TO 4 AT DASPOORT

	April	May	June	July	5 Aug.	20 Aug.	3 Sept.	18 Sept.	Oct.	Nov.	Dec.
Loading (g $m^{-3}d^{-1}$)	24,7	28,1	27,0	24,9	21,4	21,4	9,7	9,7	13,0	14,2	21,1
PV	7,6	7,5	7,4	7,2	17,0	11,5	9,4	6,0	6,0	6,5	6,4
BOD	10,0	9,5	14,0	10,8	>24	>24	20,2	7,5	13,5	14,0	11,5
COD	40	80	62	40	—	102	48	—	33	62	40
NH_3-N	6,4	6,4	6,5	6,7	24,0	17,7	12,6	8,0	7,8	7,0	8,0
NO_3-N	9,8	12,5	12,5	13,5	3,4	1,7	4,2	8,2	10,6	10,9	8,0
NO_2-N	0,30	0,26	0,30	0,22	0,65	0,73	0,26	0,16	0,30	0,28	0,28
MBAS	1,2	—	0,5	1,1	5,2	4,1	2,3	3,5	2,5	1,2	1,8
***E. coli*/100 mℓ**	16 000	45 000	52 000	56 000	85 000	1 400 000	395 000	47 000	214 000	124 000	140 000
Relative stability %	100	100	100	100	33	29	75	100	100	100	100

Note: All values in mg ℓ^{-1} where applicable.

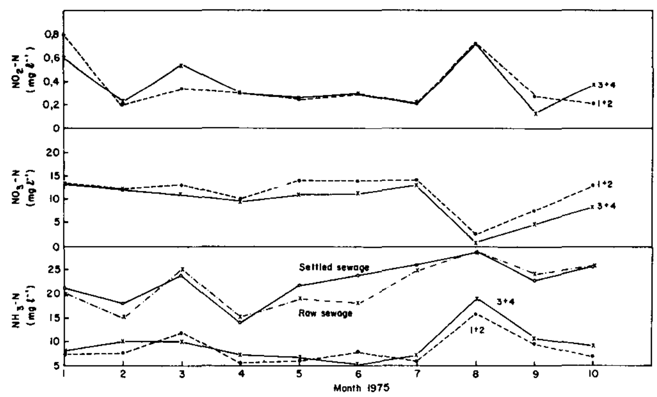

Figure 3
Nitrification by municipal filters

and during the occurrence. However, the available information indicates that several substances, e.g. chromium, phenol, mercury and an unidentified phosphorous organic insecticide, may have been the cause of the trouble.

Chromium concentration in the humus tank effluent is normally below 25 $\mu g\ \ell^{-1}$, phenol less than 50 $\mu g\ \ell^{-1}$ and mercury under 1 $\mu g\ \ell^{-1}$. In the week between 24th and 31st July, however, abnormally high concentrations of each of these substances were detected. For example, on 24th July the phenol concentration in the influent to the reclamation plant rose to 1040 $\mu g\ \ell^{-1}$. This was followed a week later by a further peak of 630 $\mu g\ \ell^{-1}$. Yet another phenol peak occurred on 5th September. Since it had already been found that the former heavy metals need not cause undue concern (Funke & Coombs, 1972), primary attention was devoted to the occurrence of phenol which may well have been responsible for the low bacterial counts recorded in both biofilter effluent and HTE (Figure 4).

Effect on Individual Plants

The available data indicate that the biological filtration plant and an experimental rotating disc unit (RDU) were very much more susceptible to the toxicants than two separate extended aeration activated sludge plants which were operated on the same sewage. Both the latter plants showed very little adverse effect. It was simultaneously observed that physical-chemical treatment completely eliminated any detectable toxicants and the product water from the latter plant maintained its usual high standard throughout.

The phenomena are dealt with in more detail below.

Deterioration of municipal biofilters

The first significant signs of deteriorating quality of HTE were noticed towards the end of July, when peaks occurred in TKN and COD concentrations. This was followed by a rapid decline in nitrifying activity (Figure 1). Concurrently with this decline, phosphorus concentration showed a gradual increase, to reach a maximum of 21 mg ℓ^{-1} towards the middle of August.

COD removal was adversely affected over the period of maximum inhibition of nitrification, at times reaching 80 mg ℓ^{-1}; or double the normal concentration. Relative stability in the same month declined from 100% to between 20 and 40% (Figure 2). Nitrification was markedly affected, ammonia increasing from 7 to 17 mg ℓ^{-1} as N while nitrate fell from 13 to 2 mg ℓ^{-1} as N (Figure 3). This was accompanied by a significant increase in nitrite concentration, from 0,2 to 0,7 mg ℓ^{-1}, indicating greater inhibition of *Nitrobacter* than *Nitrosomonas*. Nitrification did not recommence until early in September and had not reached its former efficiency when this investigation was terminated (18th October).

The biomass on the filter bed appeared to be dead during this period. Samples of biomass were analysed and are reported under Identification of Purported Toxin below. During August the monthly bacteriological examination of the biofilter effluents revealed a significant increase in the number of bacteria remaining after treatment (Figure 4), indicating that the biofilters were unable to effect their usual bacterial purification. A similar peak which occurred in April is ascribed to a general increase in bacterial count of the settled sewage. Coliforms and faecal coliforms were similarly unaffected during this period.

Daily examination of HTE at the reclamation plant showed a dramatic increase in the total number of bacteria on 4th and 5th August (Figure 5). From 3000 bacteria mℓ^{-1} on 3rd August, the numbers had become uncountable on 5th August and remained so until the 9th. Bacterial counts remained abnormally high throughout the period of investigation, but declined to below 10^6 mℓ^{-1} from 10th September onwards.

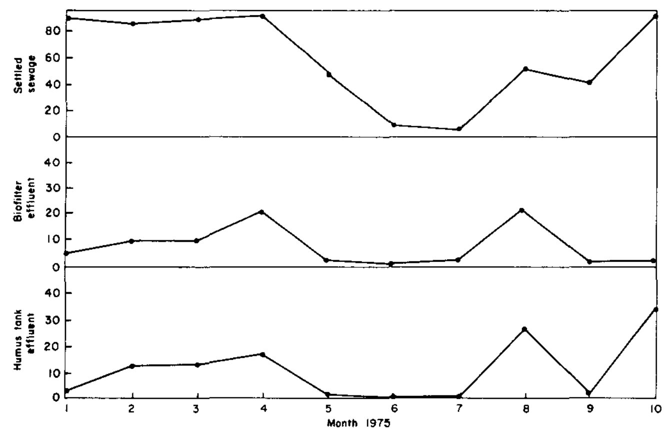

Figure 4
Total plate count of bacteria x 10^5 mℓ^{-1}

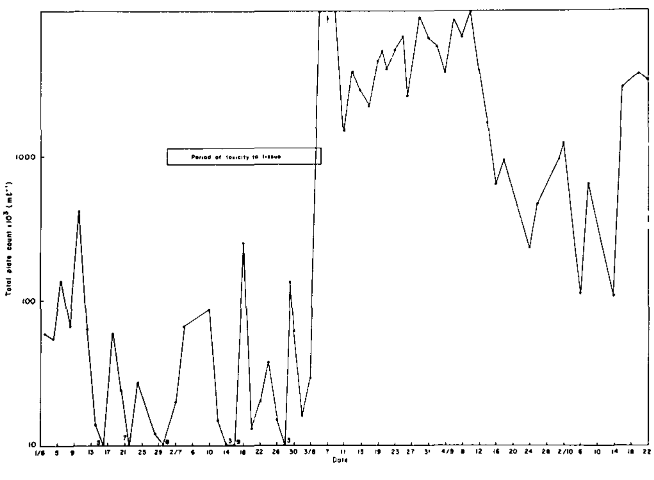

Figure 5
Total plate count of bacteria in reclamation plant influent

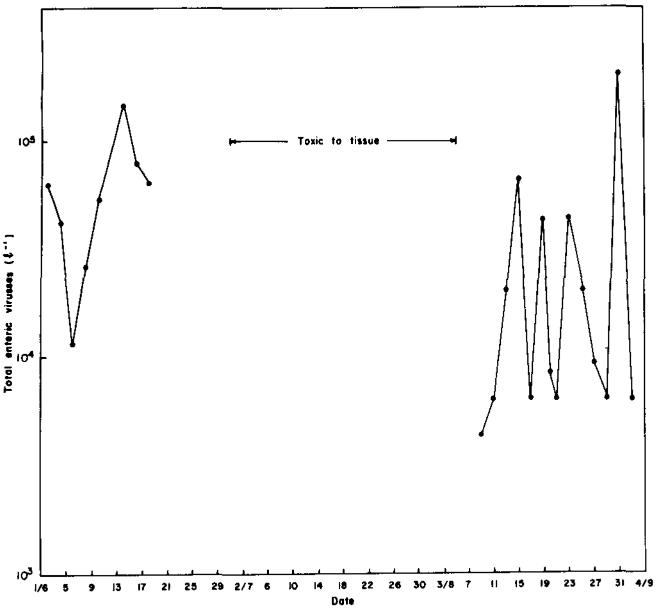

Figure 6
Total enteric viruses in reclamation plant influent

Enteric viruses in HTE at the reclamation plant did not show any marked increase over the period in question (Figure 6). The pattern is obscured, however, by the fact that viable tissue could not be maintained between 30th June and 5th August. This was apparently due to some substance present in the samples tested. This observation is substantiated by the data recorded in Figure 4, viz. that a substance which was toxic to bacteria occurred during June and July.

It is remarkable that the period of toxicity to tissue ended on the very day bacterial counts soared, but the reasons for this and the toxicity itself have not been established in the present survey.

During the entire period of biological filter inhibition, the municipal anaerobic digesters showed no ill effects, indicating that the purported toxin probably remained in solution.

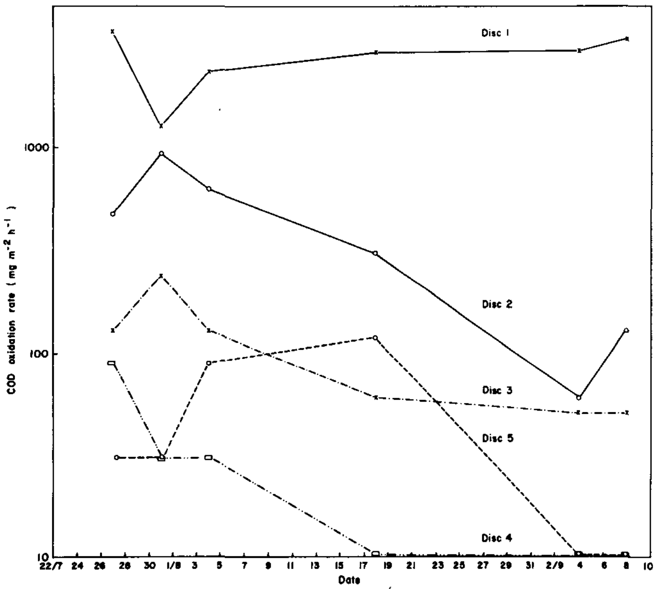

Figure 7
Rates of COD oxidation throughout the RDU series

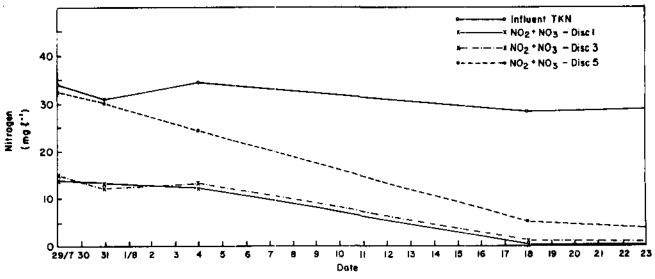

Figure 8
Nitrification by the RDU

Effect on the rotating disc unit (RDU)

The RDU showed several signs of inhibition after the toxic sewage had passed through the system. Nitrification was once again affected most severely, but COD removal also declined.

The rate of COD oxidation on the first set of discs declined from 3800 mg m^{-2} h^{-1} between 27th and 31st July, but subsequent discs in the series showed increased rates of oxidation due to the heavier COD load imposed on them (Figure 7). This compensation resulted in the final effluent COD concentrations remaining unchanged at about 100 mg ℓ^{-1}. This high figure is due to the fact that the discs had not reached steady state during the period in question.

Nitrification declined steadily from between 29th and 31st July (Figure 8). This could have been due to the onset of colder weather or to a toxic effect. Such a severe inhibition, however, is unlikely to be a temperature effect and in view of the Q_{10} of 1,23 determined for nitrification with the RDU (Pretorius, 1974) the severe reduction in nitrifying activity can be mainly attributed to toxic compounds in the feed.

Effect on activated sludge processes

The Bardenpho pilot plant showed little response to the toxic sewage. Neither nitrification nor COD removal was noticeably inhibited during this period (Figure 9). The peaks in TKN coincided with the installation of aeration equipment and were probably due to inadequate aeration control coupled with the low temperatures experienced at the time (15 to 16°C) as well as the short sludge age used (14 days).

The Orbal system similarly appeared to be unaffected by the toxic sewage (Figure 10). Neither COD removal nor nitrification was seriously impaired, the system functioning normally

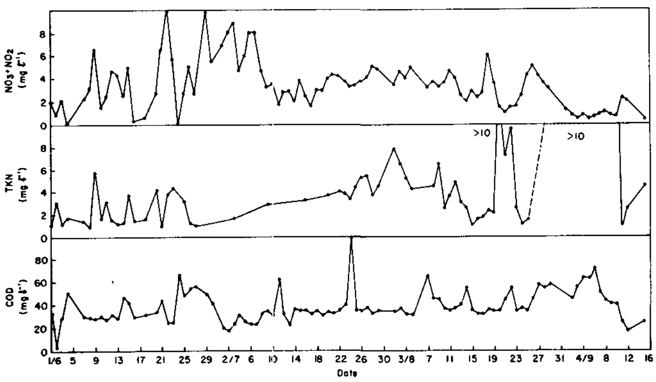

Figure 9
Nutrient concentrations in Bardenpho effluent

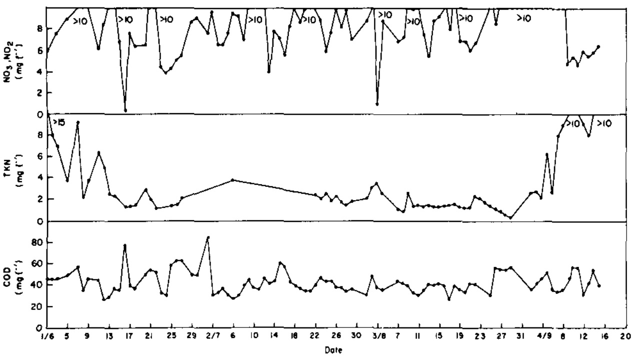

Figure 10
Nutrient concentration in Orbal effluent

except for high phosphate concentrations detected in mid-August, a phenomenon apparently unrelated to other recorded events. The high nitrates present from August 25th onwards were apparently due to a short sludge age reducing the mixed liquor suspended solids and subsequent over-aeration. The reduction in nitrate concentrations on 9th September coincided with a decrease in nitrifying activity rather than an improvement in denitrification rates.

It should be stressed that both types of activated sludge processes were operated on the extended aeration principle. Consequently a large percentage of bacteria would have to cease functioning before the effects of inhibition became noticeable by deterioration in the effluent quality.

By contrast, the biofilters and rotating discs were operating under maximum load and any inhibition would immediately affect the efficiency of purification.

Physical-chemical treatment followed by biological oxidation

A pilot plant (110 kℓ d^{-1}) utilising lime flotation of settled sewage followed by biological oxidation with activated sludge (LFB process) was operated and monitored by the NIWR during this period.

Research into the optimization of this process meant that it was operated in several different modes over the period under investigation. The pattern is further obscured by the fact that no samples were taken from the LFB plant between 18th July and 11th August, the period during which toxic compounds were detected in the influent sewage and most biological response was measured.

Nitrate concentration remained high and ammonia concentration low in the activated sludge unit throughout the period in question, indicating no measured inhibition of nitrification at any stage in this type of plant (Figure 11).

Effect on Stander Water Reclamation Plant

The operation and careful monitoring of the reclamation plant, during the period under review, provided an excellent opportunity to examine the extent to which physical-chemical processes could be relied upon to remove biological toxins. As indicated in Figure 1, severe deterioration of quality of influent to the plant occurred during August and the beginning of September. This could, however, be combated by increased lime and chlorine dosages.

It must, of course be stressed that the high COD imposed an unusually high load upon the carbon filters, which consisted of single-stage contact units during this period. Although the carbon filters were already approaching exhaustion, they performed reasonably well in producing reclaimed water with a COD concentration of circa 25 mg ℓ^{-1} (Figure 12). The replacement of exhausted carbon with virgin carbon resulted in a substantial decrease in COD concentration of the product water to about 10 mg ℓ^{-1}.

A second-stage carbon contact unit will, by virtue of the inherent characteristics of a two-stage adsorption system design,

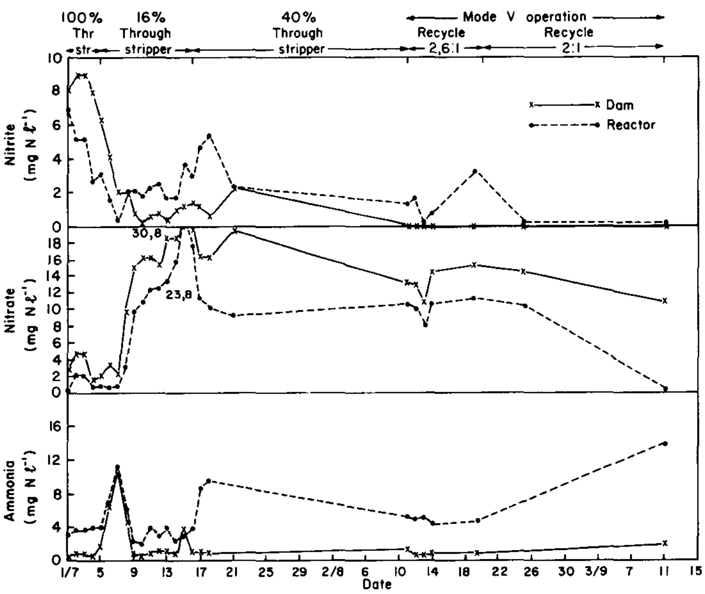

Figure 11
Biological nitrification in the LFB plant

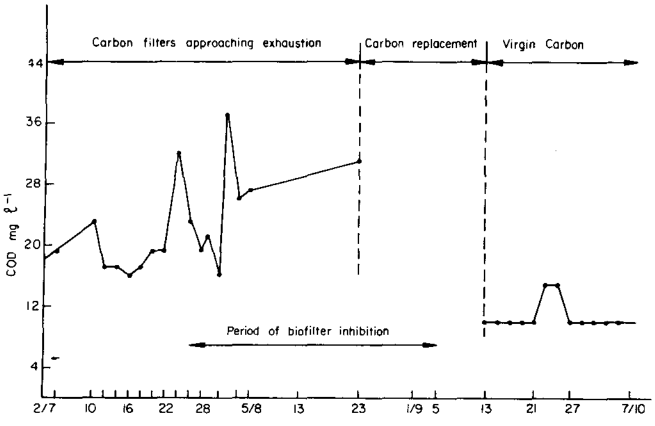

Figure 12
COD concentration of reclaimed water

always contain active carbon with a near virgin adsorption capacity. Consequently, a two-stage carbon contact system, such as has been installed at the Stander Water Reclamation Plant in January 1976, will ensure a low COD concentration in the product water at all times.

Bacterial counts of the product water showed accidental occurrences (up to 100 $m\ell^{-1}$). These occurrences coincided with the excessively high counts in the HTE feed already described (Figure 5), and were probably due to momentary inadequate chlorination. This resulted from excessively high chlorine demands caused by erratic increases in ammonia concentration. Coliforms and faecal coli were absent throughout. This experience, however, stressed the importance of adequate chlorination and a reliable bypass and alarm system has now been installed on the reclamation plant.

No toxins were detected in the product water throughout, although certain organophosphorus pesticides were detected in the influent. This phenomenon is further described below.

Identification of Purported Toxin

In an attempt to identify the cause of biological inhibition, samples of both biomass and effluent from the Daspoort biological filters were investigated. The first samples were received on 7th August and thereafter again on 18th September.

Extracts of these samples were prepared and the extracts analysed for chlorinated hydrocarbons and organophosphate compounds by means of gas chromatography. No increase of chlorinated hydrocarbons was observed but there was an increase in the organophosphate concentration of both the biomass and effluent extracts. This increase was detected by a change in the chromatographic profile as compared with that obtained from HTE samples which had been analysed previously. Three peaks in the profile which had not previously appeared were observed with both the phosphorus and the sulphur detectors. It can thus be assumed that these compounds contain both phosphorus and sulphur linkages.

The concentration of the organophosphorus compounds was calculated relative to the response produced by methyl trithion. The concentration in the effluent was relatively high (> 1 $\mu g\ \ell^{-1}$) compared with normal sewage (Table 2). The concentration of this compound in the biomass was at least 3 orders of magnitude greater than in the effluent (Table 3). This indicates that the compound was adsorbed on the biomass and was only released gradually – hence the residual concentration recorded on 18th September.

TABLE 2

GAS CHROMATOGRAPHIC ANALYSIS OF BIOFILTER EFFLUENT SAMPLED 7TH AUGUST, 1975

Retention time in G.C. (min)	Organophosphorus concentration ($\mu g\ \ell^{-1}$)			
	Bio-filters 1-4	Bio-filters 5-8	Bio-filters 9-12	Bio-filters 13-16
15,80	0,340	0,338	0,390	0,298
16,80	0,572	0,516	0,616	0,398
18,32	1,561	1,397	1,725	1,032

The peak concentration recorded for HTE reduced more rapidly. After one week, it was still detected but at a much lower concentration, and on 18th September only between 10 and 50 ng ℓ^{-1} were present. It is likely that this low concentration was being eluted from the biomass.

Although these organophosphorus compounds were detected repeatedly in the HTE feed to the Stander Water Reclamation Plant, they were completely removed by the advanced purification processes.

Analyses of the biomass for heavy metals, conducted by the Pretoria municipal staff, did not reveal any abnormal situation.

Conclusions

The occurrence of unidentified organophosphorus compounds in Pretoria raw sewage provided an excellent opportunity to trace its effect on a conventional biological filter plant as well as

TABLE 3

GAS CHROMATOGRAPHIC ANALYSIS OF BIOMASS ON FILTER STONES

Retention time in G.C. (min)	Organophosphorus concentration ($\mu g\ kg^{-1}$)	
	7th August	18th September
15,80	700	130
16,80	1 100	200
18,32	3 200	560

Note: All concentrations calculated relative to methyl trithion, as standard.

through various experimental units operated by the NIWR. Unfortunately most of the biological systems studied were pilot plants on which experiments were being performed. The operating conditions were therefore frequently changed, obscuring data which might indicate a toxic effect. It was nevertheless possible to derive the following significant conclusions from the available evidence:

1. It has been generally accepted that biological filtration is less susceptible to shock doses than activated sludge units. Experience in this survey, however, has indicated the contrary. There is some evidence that toxicants were adsorbed onto the fixed biomass of both biofilters and the RDU, but the significance of differences in organic loading of the various processes should not be overlooked. The apparent lower sensitivity of activated sludge units during the present survey may also have been due to volatilisation of the toxin.
2. The prolonged abnormally high counts of bacteria present in the biofilter effluents indicates that the grazing microfauna was even more susceptible to the toxins than the autotrophic bacteria. This is in agreement with the microscopic observations of sludge over this period, which indicated that the micro-invertebrates were most sensitive indicators of a toxic condition existing in a biological system (Knoetze and Davies, 1976).
3. The deterioration of biological purification processes was primarily exemplified in reduced nitrification and an increase in ammonia or TKN concentration. Carbon oxidation (COD removal) was affected to a lesser extent. Heterotrophic bacteria thus apparently recovered faster than the autotrophic nitrifiers, which are known to require a relatively long regeneration time.
4. The decline in biological activity was probably caused by mixed concentrated toxic industrial discharges into the Pretoria municipal sewer during June and particularly at the end of July 1975. During the latter period, relatively high concentrations of mercury, phenol, chromium and an organophosphorus compound were detected in the sewage.
5. The LFB process utilizing lime flotation followed by biological treatment, was completely unaffected, suggesting protection of the biological part of the process by prior physical-chemical treatment.
6. The Stander Water Reclamation Plant amply proved its ability to cope with unexpected loads and toxic conditions. Although the influent to the plant was little better than settled sewage and in addition contained toxic materials, the advanced purification processes could nevertheless be relied upon to produce the same high quality water throughout.

Acknowledgement

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