Technical note

Hydrocarbon levels in the Swartkops estuary: a preliminary study

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Abstract

Above-background hydrocarbon levels were measured in five out of six stations on the Swartkops estuary. Post-rainfall hydrocarbon levels were higher than pre-rainfall levels, and were more likely of terrestrial origin than of sea-borne origin from Algoa Bay. Common oil products such as car and diesel sump oil, outboard engine oil and crude oil were not directly incriminated as the sources, but "runoff" containing coal dust may have been responsible in one sample.

Introduction

The Swartkops estuary in the eastern Cape experiences residential, recreational and industrial pollution to varying degrees due to its proximity to the towns of Port Elizabeth and Uitenhage. The area bordering the estuary is widely utilised for industrial purposes, which include the Swartkops power station, the Algorax carbon factory and the South African Transport Services yards. There is no discharge of sewage and industrial effluent directly into the estuary, but above the tidal limit there are four main input sources (Hill *et al.*, 1974a). These are two sewage outfalls and a wool washing factory near Uitenhage, and a tannery at Perseverance.

Past pollution studies have included heavy metal surveys (Watling and Watling, 1982), bacteriological aspects (Hill *et al.*, 1974b) and polychlorinated biphenyls and organochlorine levels (De Kock, 1985), but no information is available on hydrocarbon levels, which may help to assess the state of oil pollution in the estuary. The Swartkops estuary has been fortunate in not having been exposed to an acute crude oil spill as occurred, for instance, with the Sedgefield, Great Brak and Little Brak estuaries after the Venpet/Venoil collision (Moldan *et al.*, 1979). Oil pollution in the Swartkops is thus restricted to incidental pollution in the form of oil effluent from small powerboats, road runoff from bridges and industrial fallout from the surrounding areas.

Of importance to phytoplankton is the water-soluble fraction (WSF) of oil as this facilitates transport into the cells (Batterton *et al.*, 1978). Laboratory work on phytoplankton cultures has shown that the WSF of outboard motor exhaust emissions (Hilmer and Bate, 1983) and used lubricating oil (Bate and Crafford, 1985) are toxic to phytoplankton, inhibiting both carbon assimilation and oxygen evolution.

The aims of this preliminary study were to determine whether detectable amounts of hydrocarbon WSFs were present in the Swartkops estuary, and if so, to determine their origin.

Materials and methods

Sampling sites

Water samples were collected from six stations on the Swartkops estuary (Fig. 1) at Redhouse Village, from the water outlet of the power station (which derives its cooling water from the estuary), underneath the bridge at Swartkops Village, from the top end of Tippers Creek, underneath the National Road bridge near the mouth, and from the Blue Hole, a sidearm at the mouth which is used for rearing oysters. Samples were collected at low tide: the first set after a period of three weeks with no rainfall in the area, and the second set a day after the first rain subsequent to this period.

Sample collection

All glassware was carefully cleaned and rinsed twice with spectrophotometric grade carbon tetrachloride before use. Water samples of 250 ml each were collected in glass-stoppered flasks containing 10 ml of carbon tetrachloride, shaken vigorously, and transported back to the laboratory for analysis.

WSF of oil products and "road runoff"

A variety of methods are available for the determination of dissolved or finely dispersed petroleum residues in sea water. These include ultraviolet (Hennig, 1979) and infrared (Simard *et al.*, 1951) spectrophotometry, fluorescence spectrophotometry (Ehrhardt, 1983), gas chromatography and mass spectroscopy (Voudrias and Smith, 1986). As this was to be only a preliminary survey, the more elaborate methods were avoided and the infrared spectrophotometric method used. The infrared spectra obtained from field samples were compared with spectra of individual oil products for general identification.

Water soluble fractions were prepared from the following sources: used motor car sump oil, used LDV diesel sump oil, aged outboard motor oil (Castrol Super Outboard), aged Qatar Light crude oil, and "road runoff". The Swartkops Village bridge is situated close to the industrial areas of Port Elizabeth and as a consequence is heavily utilised by cars and trucks. It is visibly polluted with oil and coal dust and has drainage holes that empty directly into the estuary. Due to the unpredictable rainfall patterns of the eastern Cape, road runoff was simulated by flushing part of the bridge with 400 ℓ of freshwater. Sample 1 was collected from the first 10 ℓ passing through a drainage hole and sample 2 after approximately 150 ℓ had passed through it. Sample 3 was collected after scrubbing the road surface with nylon-bristle brooms and flushing with the remainder of the water.

The WSF was prepared by layering one volume of oil onto nine volumes of clean, autoclaved sea water in a sealed glass vessel and stirring for 24 h with a teflon coated magnetic stirrer bar. The stirring speed was adjusted so that the vortex extended one

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quarter into the water column without causing emulsification of the oil in the water. After stirring, 250 ml of the aqueous phase containing the WSF was removed and placed in a separating funnel. This was acidified with 1 ml of a 50% solution of HCl in distilled water (Rand *et al.*, 1976). The WSF was then extracted into 10 ml of carbon tetrachloride (Simard *et al.*, 1951) by shaking for 2 min and allowing the phases to separate for at least 5 min. The organic fraction was filtered through a solvent-moistened Whatman No. 1 phase separating filter and the extraction repeated twice more. A "clean" sea-water sample was also extracted to obtain a background concentration. The extracts were made up to 50 ml with carbon tetrachloride and read in a Beckman 4250 double beam infrared spectrophotometer. Percentage transmission spectra were obtained by scanning between wave numbers 3 200 cm^{-1} and 2 700 cm^{-1}.

Results and discussion

Field samples

The infrared spectra indicated hydrocarbons present in all but the Redhouse Village sample (Fig. 2). A hydrocarbon gradient existed in the estuary, ranging from background levels at Redhouse to the highest concentrations in the mouth region. The main absorption peaks were at 2 965 cm^{-1} and 2 925 cm^{-1}, with smaller peaks at 2 870 cm^{-1} and 2 850 cm^{-1}. The spectrum of the power station outlet sample showed modifications in that the peak at 2 965 cm^{-1} was slightly shifted, the minor peak at 2 870 cm^{-1} was absent in the post-rainfall sample, and there was a well-defined peak at 2 855 cm^{-1}. Post-rainfall hydrocarbon levels were higher in all but the Redhouse sample, with the main in-

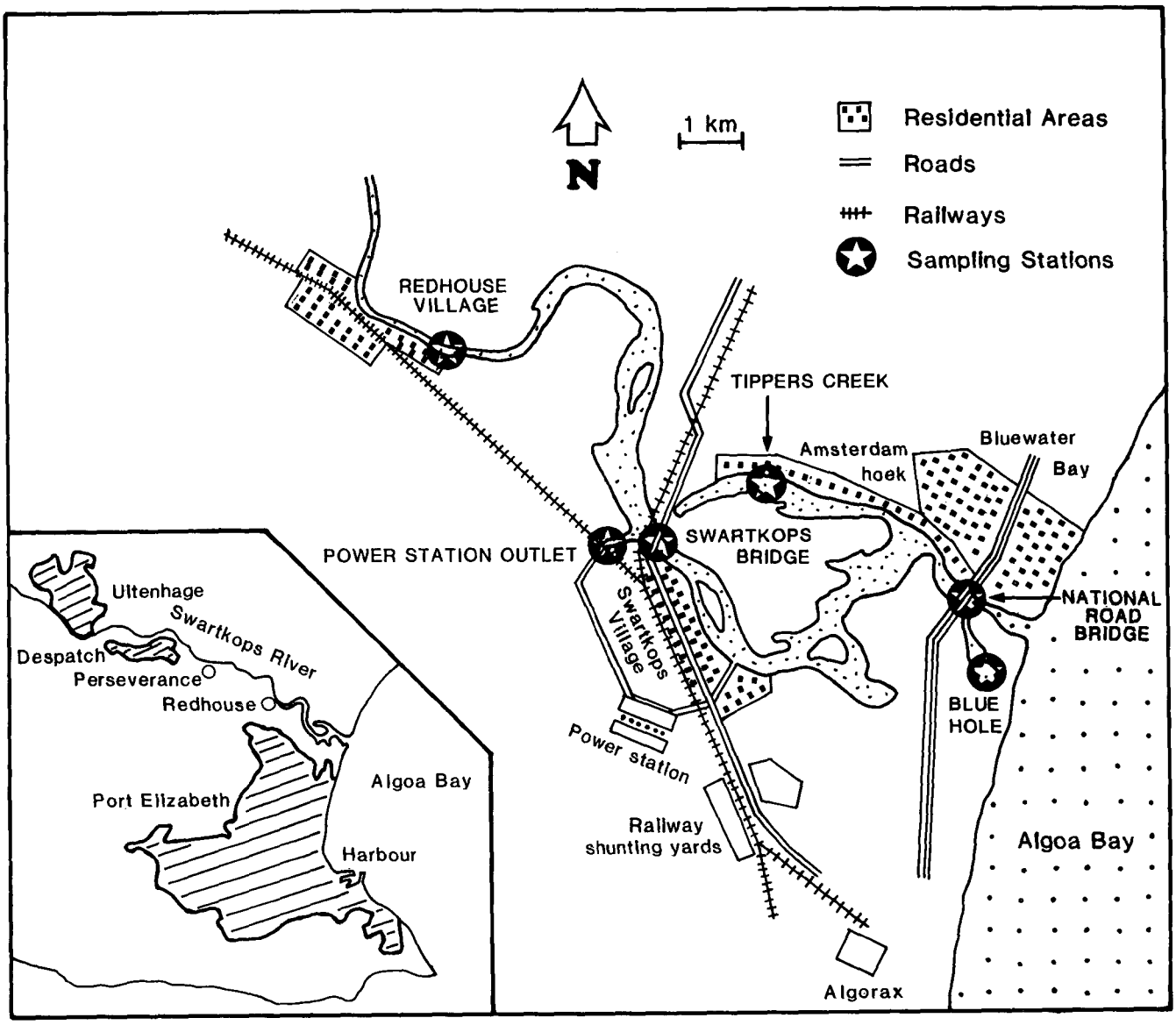

Figure 1
Map of the Swartkops estuary showing the sampling sites.

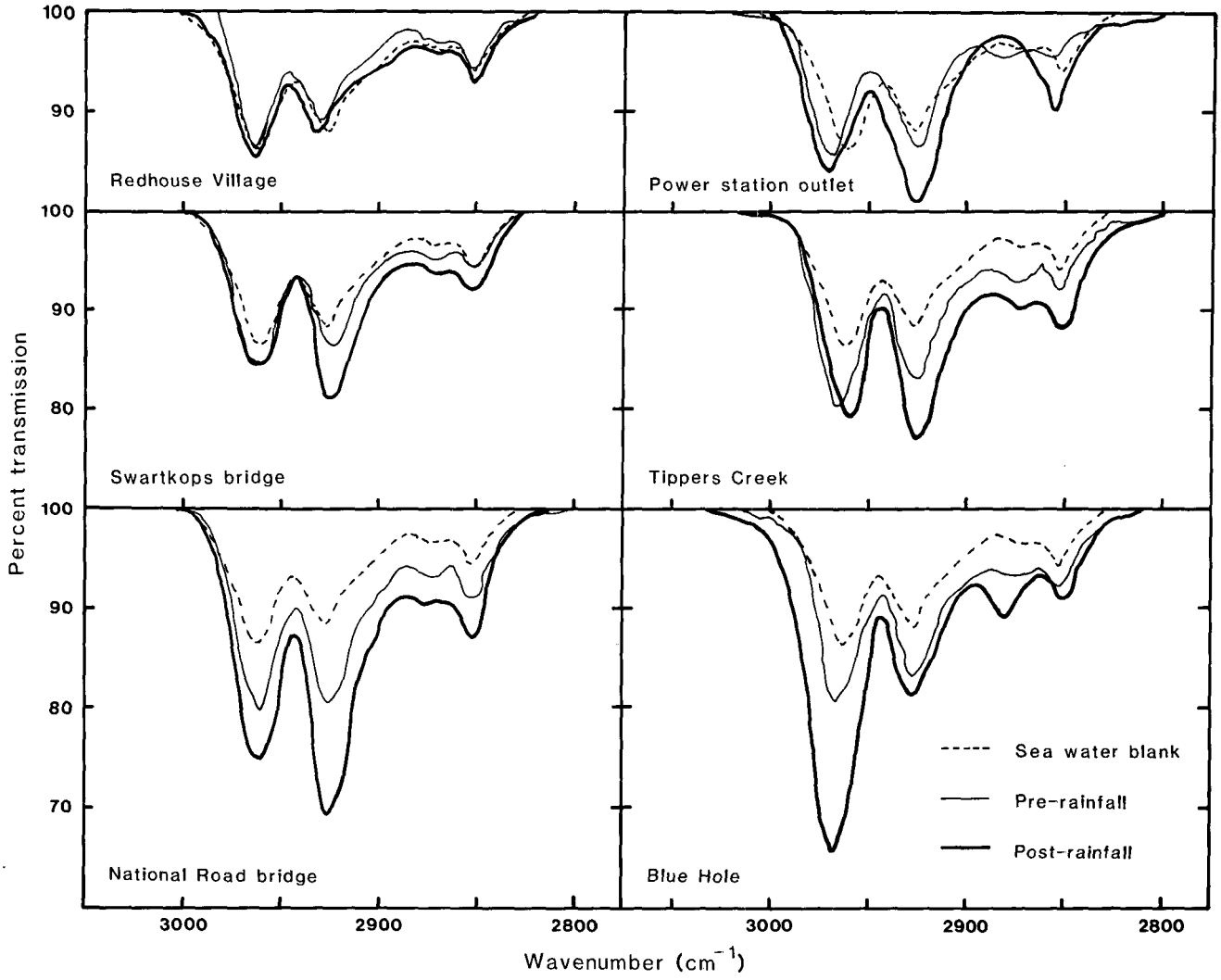

Figure 2
Infrared spectra of the WSF of field samples.

crease in absorption at 2 925 cm^{-1}. An exception was the Blue Hole sample where a major increase in absorption occurred at 2 970 cm^{-1} and a smaller one at 2 880 cm^{-1}. The post-rainfall increase in hydrocarbons suggests a terrestrial origin rather than import into the estuary from Algoa Bay, as sources of industrial hydrocarbons entering the bay are restricted to the harbour and immediate vicinity of Port Elizabeth. The distance involved precludes any substantial amounts of hydrocarbons entering the estuary from this source.

Oil products and "road runoff"

The infrared spectra obtained from the WSFs of the oil products and road runoff are shown in Fig. 3. Aged Qatar Light crude oil and used sump oils absorbed strongly at 2 960 cm^{-1} and 2 930 cm^{-1}, with a smaller peak at 2 870 cm^{-1} and a "shoulder" at 2 855 cm^{-1}. The outboard oil absorbed at similar positions but had additional peaks at 3 030 cm^{-1}, 3 070 cm^{-1} and 3 090 cm^{-1}. Road runoff displayed only two main absorption peaks, at 2 970 cm^{-1} and 2 880 cm^{-1}. Scrubbing of the road surface (sample 3) had little effect and resulted in the same amount of hydrocarbons recovered as in the initial sample collected (sample 1). The sample collected after approximately 150 ℓ of water had passed over the bridge section displayed only a small decrease in the amount of hydrocarbons recovered (sample 2).

Comparisons

Although the absorption peaks were often similar, none of the infrared spectra of the oil products were directly comparable to those of the field samples. This showed that no one particular oil product could be directly incriminated as the main source of hydrocarbons in the estuary. Conversely, this does not necessarily exclude any of them either as the field samples are bound to reflect a mixture of hydrocarbons of varied origins. The only sample which may give some indication of its hydrocarbon origin was that collected from the Blue Hole. It was the only sample which displayed major post-rainfall increases in absorption at 2 970 cm^{-1} and 2 880 cm^{-1}, corresponding to the peaks obtained from the road runoff samples. Visible inspection of the road runoff showed it to consist mainly of coal dust and some vehicle-derived sump oil or similar exhaust products. The power station and coal-fired steam railway engines are the major contributors to atmospheric pollution in the lower part of the estuary (Hill *et al.*,

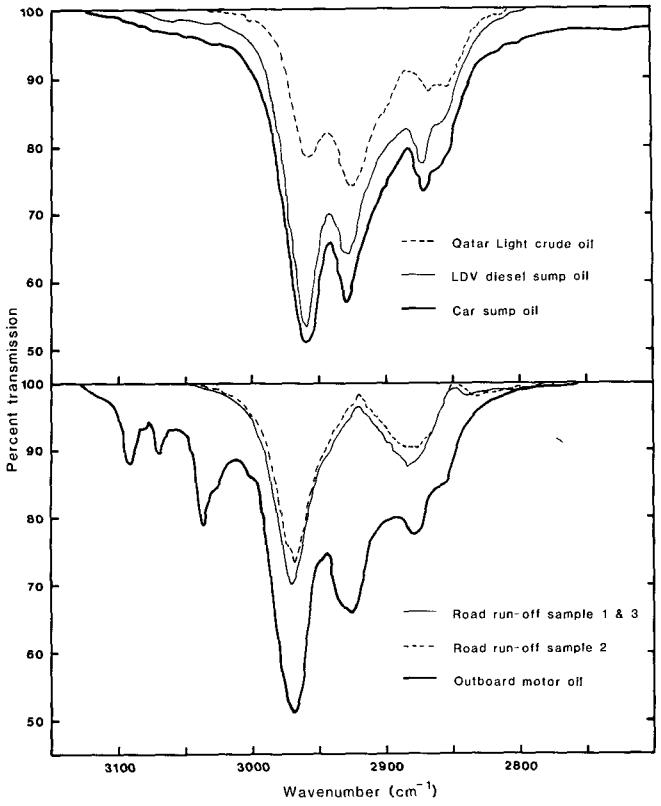

Figure 3
Infrared spectra of the WSF of oil products.

1974c), causing about 15 t.km^{-2}.month^{-1} of fallout pollution at Swartkops Village. Of this, approximately one quarter is in the form of unburnt volatiles present in coal dust and cinders. Road runoff *per se* may thus not be important in the overall input of coal dust-related hydrocarbons into the estuary, but bridges and roads may be important in concentrating this form of pollution, resulting in short input peaks of high concentration after rains.

The presence of detectable amounts of hydrocarbon WSFs in the Swartkops estuary highlights the need for more information on actual field concentrations of hydrocarbons in our marine environment. Only the WSF in the water column was investigated in this study. Any further studies would have to:

- include detailed chemical analyses of sediments and organisms in order to identify and quantify the accumulation and retention time of hydrocarbons; and
- investigate the sources and entry mechanisms of hydrocarbons into the marine environment.

Acknowledgements

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