

Acute and Chronic Toxicity of Produced Water from a North Sea Oil Production Platform to the Calanoid Copepod Acartia tonsa

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The routine operation of offshore oil production platforms results in the discharge to the sea of 'produced water' after it has been separated from oil drawn from the reservoir. Discharge of produced water in the UK sector of the North Sea is given an exemption from the provisions of the 1971 Prevention of Oil Pollution Act providing the monthly average oil-in-water content measured twice per day does not exceed 40 mg kg $^{-1}$.

To assess the toxic hazard to marine organisms of produced water discharged to the North Sea, within this exemption, Shell UK Exploration and Production has implemented a research program. The study reported here formed only a part of this program. Other elements of the program have been reported elsewhere (Somerville et al. 1987).

Methods for determining the acute and chronic toxicity of produced water to the marine calanoid copepod <u>Acartia tonsa</u> have been established and applied at Shell's Sittingbourne Research Centre to samples from the Shell/Esso Dunlin 'A' platform. <u>A. tonsa</u> was selected as the test species in view of: the general susceptibility of calanoid copepods to the effects of oil and in particular hydrocarbons (Davies et al. 1980; Berman and Heinle 1980); the role of copepods as important links in the marine food web (Ward et al. 1988); the presence of <u>A. tonsa</u> in the fauna of the North Sea (Conover 1956); its ease of culture in the laboratory and the availability of documented test methods (EPA 1976).

This paper describes the methods used to assess acute and chronic toxicity and the results of tests performed on a sample of produced water collected in February 1986. Tests were performed on subsamples of the bulk sample which: (a) were untreated (other than receiving initial acidification followed by pH readjustment prior to testing) (b) had been filtered and (c) biodegraded (i.e., organic substances present in the produced water were degraded by micro-organisms) and then filtered. The results of the tests are discussed in relation to the likely patterns of dilution offshore in the North Sea.

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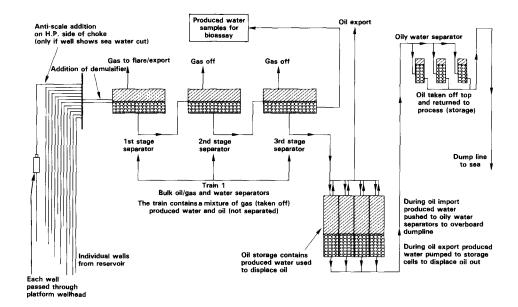


Figure 1 — Origin of produced water samples on the platform

MATERIALS AND METHODS

Produced water was collected from the oil/water phase in the train 1, 3rd stage bulk oil/gas and water separator on the Shell/Esso Dunlin 'A' platform (Figure 1). To inhibit the development of microbial populations the pH of the sample was adjusted to 4.0 on collection by the addition of concentrated hydrochloric acid. The sample was then sent directly to the laboratory in 11-L steel International Air Transport Association cans internally coated with an inert resin. In the laboratory the sample was transferred to a glass aspirator and further acidified to pH 1.5 with hydrochloric acid.

The sample was subsequently divided into three subsamples, one of which was not treated further. One of the two remaining subsamples was filtered through a 0.45- μ m Millipore filter (Millipore SA, Molsheim, France). Prior to filtration (0.45- μ m Millipore), organic substances present in the other subsample were biodegraded using a mixed species bacteria inoculum.

The inoculum used to biodegrade the organic substances in the produced water was obtained from an oily water separator (Figure 1) of a platform in the Brent field and was grown in artificial seawater enriched with 0.02 g L $^{-1}$ KH₂PO₄, 0.18 g L $^{-1}$ (NH₄)₂SO₄ and 1.17 g L $^{-1}$ sodium acetate whilst being incubated on a shaker at 200 rpm and 20°C.

The 5-L subsample of produced water was biodegraded after initially adjusting its pH to 8.2 with concentrated NaOH. The produced water was supplemented with excess phosphate (0.04 g $\rm L^{-1}$ KH₂PO₄) and dosed with 100-mL of the inoculum (in the logarithmic growth phase). The produced water was then incubated at 20°C with continuous stirring to provide aeration (Note: under these conditions potentially toxic components of the produced water may also have been lost by other forms of degradation and/or volatilization).

Biodegradation was monitored by total organic carbon analysis and after 10 days adjudged complete. Suspended bacteria and oil droplets were then removed by passage of the produced water through the 0.45- μm Millipore filter.

After treatment all three subsamples were stored in the dark at $4^{\mbox{\scriptsize OC}}$ prior to use.

Stock cultures of <u>A. tonsa</u> were maintained in 10-L glass aspirators containing full strength synthetic sea water, 34% Tropic Marin (Aquatechnik, Wartenberg, West Germany) in distilled water, at a temperature of 20° C. The sea water culture medium was continuously replaced using a flow-through system with a replacement time of 36-hr. Cool, white fluorescent lights provided 1800-2100 lux illumination incident on the culture vessel with a 14-hr light, 10-hr dark, cycle. The <u>A. tonsa</u> cultures were fed an algal diet comprising four species in the proportions described in Table 1. The algae were added to the culture medium before it entered the culture vessel.

Table 1 - Composition of algal diet and feeding rates during chronic toxicity tests with <u>Acartia tonsa</u> (Modified from EPA 1976)

Algal species	Feeding rates (cells/L)		
Skeletonema costatum	5.0 x 10 ⁶		
Thallasiosira pseudonoma	7.0×10^{6}		
Isochrysis galbana	5.0×10^{6}		
Tetraselmis suecica*	3.0×10^6		
Total	2.0 x 10 ⁷		

^{* &}lt;u>T. suecica</u> replaces <u>Rhodomonas baltica</u> in the EPA (1976) recommended diet.

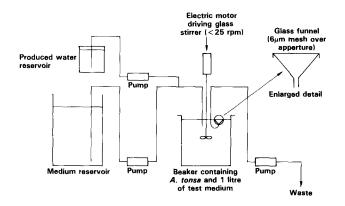


Figure 2 — Chronic toxicity test system

A. tonsa for use in the toxicity tests were taken from agestandardized, stock cultures. These were produced by isolating eggs born on the same day and culturing the resulting young under the conditions described above. Only individuals born on the same day and aged between 17 and 21 days were used in any one test.

All acute toxicity tests were conducted in 150-mL pyrex glass crystallising dishes. The toxicities of the three subsamples were determined by exposing triplicate groups of 10 animals to 100-mL of each of a logarithmic series of concentrations of produced water in synthetic seawater (Tropic Marin -34%) for 48-hr. The animals were not fed during the exposure period. A set of controls, similarly treated but containing no produced water, was also prepared. After 24- and 48-hr exposure the contents of each dish were gently stirred, the animals were observed for signs of activity and the number immobilized were recorded. EC50 values the concentration resulting in 50% of the exposed organisms being immobilized - were calculated by probit analysis (Finney, 1971).

In view of the similar acute toxicity of the untreated and filtered subsamples, chronic toxicity studies were carried out only with the filtered produced water and the produced water which had been biodegraded and then subsequently filtered.

Chronic toxicity was assessed on the basis of a reproduction study. Twenty-five, 17-21 days old adult <u>A. tonsa</u> (see above) were added to each of a series of 1-L beakers. Each beaker was supplied with fresh medium and algal diet via a flow-through system (Figure 2). Produced water from a reservoir was pumped into the pipe delivering the culture medium to ensure thorough mixing before entry into the test beaker.

A logarithmically-spaced series of concentrations of produced water, diluted with the synthetic seawater medium, was achieved by adjusting the rate of addition of produced water to each beaker whilst maintaining a constant rate of medium addition. A beaker which received no produced water served as a control. The development of <u>A. tonsa</u> populations was subsequently monitored by counting the numbers of adults present in each beaker at seven day intervals for a period of three weeks. Chronic effects were assessed by subjectively evaluting trends in the data. Effects were considered significant if, over the exposure period, adult populations declined to below starting densities.

The pH values of all test media were adjusted to 8.0 prior to introducing the <u>A. tonsa</u> by the addition of concentrated hydrochloric acid or sodium hydroxide solution. All tests were conducted in a temperature controlled room $(20^{\circ}\text{C nominal} \pm 2^{\circ}\text{C})$ with a 16/8 hr light/dark regime.

RESULTS AND DISCUSSION

Results of the acute toxicity tests with <u>A. tonsa</u> on the three subsamples of produced water are summarized in Table 2. The 24-and 48-hr EC_{50} values for the untreated and filtered subsamples were similar with 24-hr mean EC_{50} values for three tests of 6.5 and 7.4% (equivalent to 15 and 14-fold dilution in the receiving environment) and 48-hr EC_{50} mean values for three tests of 3.6 and 2.7% (equivalent to 28 and 37-fold dilution). The biodegraded subsample was less toxic with 24- and 48-hr EC_{50} mean values for three tests of 31 and 18% (equivalent to 3.2 and 5.6-fold dilution).

Table 2 - Results of the acute toxicity tests on the three subsamples of Dunlin A produced water with <u>Acartia tonsa</u>

Subsample	Exposure period (hr)	Mean* EC ₅₀ (% Produced water in test medium)	Range (%)	Equivalent Dilution Factor in Receiving Environment
Untreated	24	6.5	5.3 - 7.7	15
	48	3.6	2.6 - 4.5	28
Filtered	24	7.4	5.4 - 9.3	14
	48	2.7	2.3 - 3.2	37
Filtered	24	31	25 - 40	3.2
Biodegraded	48	18	15 - 20	5.6

^{*} Based on three tests.

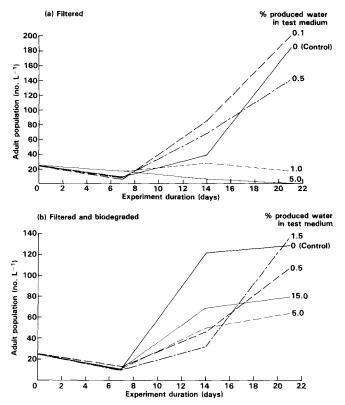


Figure 3 — Population development of adult *A. tonsa* in (a) filtered produced water and (b) filtered and biodegraded produced water monitored at 7 day intervals

Results of the chronic toxicity tests with <u>A. tonsa</u> on the filtered and filtered, biodegraded subsamples of produced water are shown in Figure 3. Exposure to concentrations of 1 and 5% of filtered produced water resulted in adult populations declining to below starting densities after 21 days. In contrast, adult populations increased in all of the 0.5 to 15% concentrations of filtered, biodegraded produced water over the same period.

Dispersion of an effluent of similar density to sea water discharged under North Sea conditions has been modelled mathematically using standard diffusion equations (Read and Blackman 1980) and in laboratory flume experiments (Somerville et al. 1987). Resulting estimates of dilution rates around platform discharge points range from 800-fold within 320-m (mathematical model) to 1000-fold within 50-m (flume model).

The results of our laboratory experiments presented here show that produced water from the Shell/Esso Dunlin 'A' platform has no acute (48-hr) or chronic (21 day) toxicity to $\underline{A.\text{ tonsa}}$ at dilutions in the receiving environment greater than approximately 40 and 200-fold, respectively. These results allow us to draw a similar conclusion to that derived by others (Gamble et al. 1987) from the

results of mesocosm experiments, that, in view of the predicted dilution rates in the region of North Sea platforms, toxic effects of produced water discharges on planktonic copepods will be limited to the immediate vicinity of the point of discharge.

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