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Bioaccumulation of Halogenated Compounds by Limpets and Fucoid Seaweeds in the Vicinity of the Black Rock Sewage Outfall, Weston-Super-Mare.

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CONTENTS

1. ABSTRACT

Sewage effluent discharged from the Black Rock outfall at Weston-Super-Mare, is disinfected during the summer bathing season in order for local beaches to comply with E.C. permittable levels of faecal bacteria within bathing waters (76/160/EEC). The aim of this study was to investigate whether this disinfection process had resulted in the bioaccumulation of chlorinated and brominated compounds (principally trihalomethanes) by marine organisms living within and around Weston Bay.

Samples of limpets (*Patella spp.*) and fucoid seaweeds (*Fucus vesiculosus*) were collected from the mid-tidal reaches of the intertidal zone from four areas; Black Rock, Brean Down, Anchor Head and Sand Point.

Sampling was repeated on three occasions:

i) Outside the disinfection period - November 1991
ii) At the start of the disinfection period - June 1992
iii) At the end of the disinfection period - September 1992

Samples were analysed for chloroform, bromoform, trichloroethylene, tetrachloroethylene, dibromochloromethane and dichlorobromomethane.

Results varied according to the organism examined and the compound measured. Clear temporal and spatial patterns were not apparent from the limpet tissue data. Concentrations within these molluscs were also generally lower than those recorded in the seaweeds, suggesting that the limpets may be capable of regulating their uptake and or storage of chlorinated compounds.

Seaweed results revealed more informative data with high levels of chloroform occurring at Black Rock, elevated readings of bromoform at Anchor Head and high levels of dibromochloromethane occuring in samples collected from both Black Rock and Anchor Head. It is suggested that disinfection of the Black Rock outfall may be resulting in the bioaccumulation of trihalomethanes mainly at Black Rock and Anchor Head. This study is currently being repeated for November 1992 and the 1993 bathing season inorder to clarify the situation.

2. INTRODUCTION

2.1 Study Aims

The aim of this study was to determine whether the discharge of disinfected sewage effluent from the Black Rock outfall during the summer bathing season, was resulting in the bioaccumulation of chlorinated and brominated compounds in seaweeds (*Fucus vesiculosus*) and limpets (*Patella spp.*) collected from Weston and Sand Bay.

2.2 Disinfection Byproducts

Sewage effluent discharged from the Black Rock outfall at Weston-Super-Mare, is disinfected using sodium hypochlorite. The chemical behaviour of this compound in sewage is essentially the same as chlorine gas, but as a liquid is less dangerous to handle and transport. The chlorination of wastewater results in the formation of toxic chloramines and organic compounds such as trihalomethanes (D.O.E. PECD7/7/260). Other potentially dangerous organic compounds may be formed if industrial wastes are present. Various marine organisms are capable of accumulating halogenated hydrocarbons including winkles, mussels and seaweeds (Wharfe J. R. 1981).

2.3 Background Outfall Details

Black Rock Pumping Station currently receives sewage from up to 100,000 residents and visitors to Weston-Super-Mare, plus storm water from an area of over 10 square kilometres. The sewage is passed through fine (1.5mm) screens before being discharged from a short outfall at Black Rock into the channel of the River Axe. This discharge occurs on all states of the tide and during the summer bathing season is disinfected using sodium hypochlorite (Wessex Water WR91/23718). The summer bathing season is defined as beginning on the first Monday in May which falls a fortnight before the Spring Bank Holiday, and ending on the Sunday which falls in the second full weekend of September (D.O.E. COPA/1288).

Disinfection was first introduced in 1976 to ensure that local beaches (Uphill, Weston and Sand Bay) satisfied the requirements of the E.C. Bathing Water Directive (Council Directive 76/160/EEC). During the 1985 bathing season, levels of residual chlorine at the outfall were recorded as high as 31-34mg/l (Wessex Water 1985). Improvements at the pumping station in 1989 were introduced to provide better control of the hypochlorite dosing, and greater mixing and contact of the disinfectant with the effluent prior to discharge (Paynting T. 1989). The level of residual chlorine at the pumping station to achieve microbiological compliance during the 1991 bathing season was 35mg/l, actual dosing levels ranged between 33-34mg/l. Levels at the Black

Rock outfall probably ranged between 10-15mg/l, depending on residence time at the pumping station (Personal Communication - Keith Taylor).

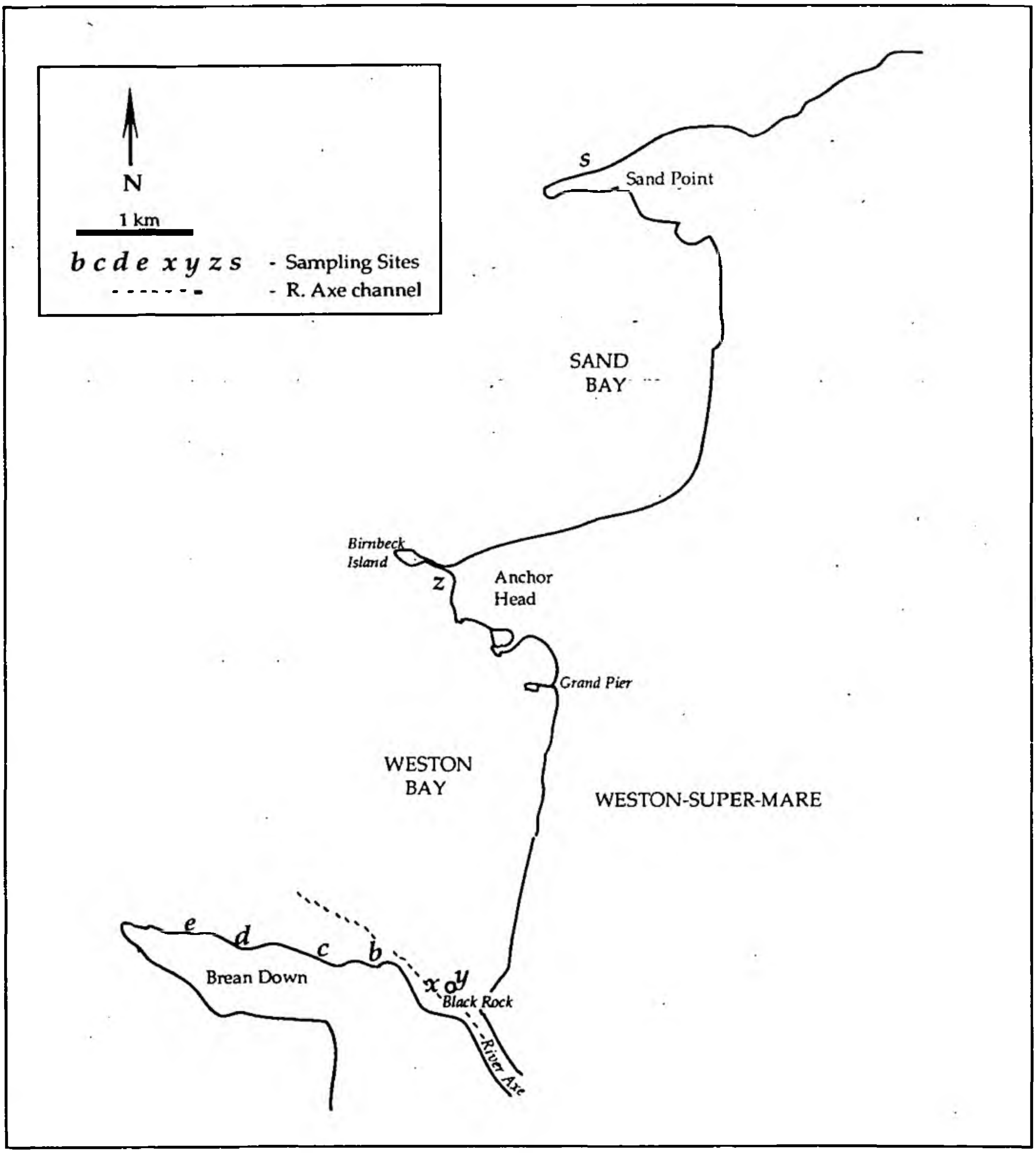
2.4 Sampling Programme

Samples of fucoid seaweeds and limpets were collected from 8 sites at Black Rock, Brean Down, Anchor Head and Sand Point (Figure 1). This was done on three separate occasions: the first outside the summer bathing season, the second at the start of the disinfection period and at the last at the end of this period. Samples were analysed for brominated and chlorinated compounds.

2.5 Improvements at Black Rock

Future improvements in the treatment of Weston-Super-Mare effluent have been proposed (Wessex Water WR91/23718) which would include the building of a new S.T.W. on the Bleadon Level (2km south of Weston-Super-Mare). This works would be served by the Black Rock P.S. and biologically treated effluent would be discharged into the R. Axe on the ebb tide. The Black Rock outfall would then only be used to discharge stormwater. However, the disinfection process would continue at both outfalls during the bathing season.

FIGURE 1 MAP OF BIOACCUMULATION COLLECTION SITES



3. METHODS

3.1 Sampling Regime

Samples of limpets (*Patella spp.*) and fucoid seaweeds (*Fucus vesiculosus*) were collected on three occasions:

i) Outside the disinfection period - 25-26th November 1991
ii) At the start of the disinfection period - 1st-2nd June 1992
iii) At the end of the disinfection period - 17th & 22nd September

These samples were collected from sites within the mid-tidal zone at varying distances from the Black Rock outfall (Figure 1):

i)	Black Rock	- sites x and y
ii)	Brean Down	- sites b, c, d and e
iii)	Anchor Head	- site z
iv)	Sand Point	- site s

Mid-tide sites were selected in order to remove tidal height as an additional variable, ie: at each sampling station the period of submergence and thus potential exposure time to any chlorinated effluent were comparable.

Only limpets around 40mm in diameter were collected and approximately 25-30 were sampled at each site. The *Fucus vesiculosus* material was generally around 12" in length but due to the variability of the plants available this was not always possible, therefore a maximum size limit of 18" was set.

3.2 Sample Preparation

Once back at the laboratory the limpets were washed with distilled water to remove mud and surface debris, placed in labelled glass jars (previously cleaned with distilled water) and frozen prior to analysis.

Due to the time involved in preparation, seaweed samples were stored in the fridge for a maximum of 5 days. Each sample was washed in distilled water to remove surface debris and the excess water shaken prior to dissection. The aim of the dissection was to obtain samples of non-reproductive tissue which had grown in the preceding 12 months. This involved removing any fruiting bodies, bladders and seaweed tips which have the potential to form reproductive tissue. The amount of growth in any one year is not clear, but is thought to include two dichotomous divisions (Barrett, J & Yonge, C.M. 1958). Using this as a rule of thumb, light green (ie: newest growth) tissue was removed and chopped into thin strips using stainless steel scissors. The tissue was retained in clean glass jars and frozen prior to analysis.

Tissue was analysed for chloroform, bromoform, tetrachloroethylene, trichloroethylene, dibromochloromethane and dichlorobromomethane. This analysis could not be done in-house and was consequently sent to the Saltford laboratory run by Wessex Water Plc. All samples were coded to prevent site identification by the analysts.

4. RESULTS

Concentrations of chloroform, trichloroethylene, dichlorobromomethane, dibromochloromethane, tetrachloroethylene and bromoform within the limpet tissues are recorded in Table 1, and those of the fucoid seaweeds in Table 2. Overall, concentrations of compounds within seaweed tissues were up to 5 times greater than those recorded in corresponding limpets samples.

Of the parameters examined only chloroform, bromoform and dibromochloromethane provided a range of differing results between the sites, the remainder were generally below the laboratory's detection limit. All results are expressed as ng/g wet weight of tissue.

4.1 Limpet Tissues

i) Chloroform

Only 5 of the 23 limpet samples taken between November 1991 and September 1992 contained detectable levels of chloroform (Figure 2). Four of these were recorded in June (at the start of disinfection). No detectable levels were recorded in the September samples (at the end of the disinfection period).

The 1991 November result was recorded at site B which is the closest outfall station situated on Brean Down. The June results were recorded from sites at varying distances from the outfall, the highest being recorded from sites X (located on the west side of Black Rock) and S (situated at Sand Point). No temporal or spatial trends could be deduced.

ii) Bromoform

Traces of bromoform were recorded at sites throughout the sampling period (Figure 3). With the exception of Sand Point, levels were lowest during November, outside the bathing season. The highest bromoform concentrations were recorded along Brean Down at site C (June and September) and site B (June). Levels at Black Rock were highest in September and similar to those recorded at site D on Brean Down.

It is difficult to deduce any clear spatial patterns from this data, but it would appear that limpets on the eastern half of Brean Down may be susceptible to the bioaccumulation of bromoform during the bathing season.

iii) Trichloroethylene, Dichlorobromemethane, Dibromochoromethane and Tetrachloroethylene.

All results were below the laboratories detection limits.

TABLE 1 CONCENTRATIONS OF COMPOUNDS IN LIMPETS (ng/g)

DATE	SITE	chloroform	Trichloroethylene	Dichlorobromomethane	Dibromochloromethane	Tetrachloroethylene	Bromoform
26/11/91	X	<1.7	<1.7	<0.5	<0.6	<0.7	<0.8
26/11/91	Y	<1.7	<1.7	<0.5	<0.6	<0.7	<0.8
25/11/91	B	1.9	<1.7	<0.5	<0.6	<0.7	<0.8
25/11/91	C	<1.7	<1.7	<0.5	<0.6	<0.7	<0.8
25/11/91	D	<1.7	<1.7	<0.5	<0.6	<0.7	1.2
25/11/91	E	<1.7	<1.7	<0.5	<0.6	<0.7	0.9
26/11/91	Z	<1.7	<1.7	<0.5	<0.6	<0.7	<0.8
26/11/91	S	<1.7	<1.7	<0.5	<0.6	<0.7	1.2
2/6/92	X	2.4	<1.7	<0.5	<0.6	<0.7	0.8
2/6/92	Y	<1.7	<1.7	<0.5	<0.6	<0.7	<0.8
1/6/92	B	<1.7	<1.7	<0.5	<0.6	<0.7	1.6
1/6/92	C	<1.7	<1.7	<0.5	<0.6	<0.7	2
1/6/92	D	1.9	<1.7	<0.5	<0.6	<0.7	0.8
1/6/92	E	*no data*	*no data*	*no data*	*no data*	*no data*	*no data*
2/6/92	Z	<1.7	<1.7	<0.5	<0.6	<0.7	<0.8
2/6/92	S	2.4	<1.7	<0.5	<0.6	<0.7	<0.8
22/9/92	X	<1.7	<1.7	<0.5	<0.6	<0.7	1.2
22/9/92	Y	<1.7	<1.7	<0.5	<0.6	<0.7	<0.8
17/9/92	B	<1.7	<1.7	<0.5	<0.6	<0.7	<0.8
17/9/92	C	<1.7	<1.7	<0.5	<0.6	<0.7	1.6
17/9/92	D	<1.7	<1.7	<0.5	<0.6	<0.7	1.2
17/9/92	E	<1.7	<1.7	<0.5	<0.6	<0.7	<0.8
22/9/92	Z	<1.7	<1.7	<0.5	<0.6	<0.7	<0.8
22/9/92	S	<1.7	<1.7	<0.5	<0.6	<0.7	0.8

TABLE 2 CONCENTRATIONS OF COMPOUNDS IN SEAWEEDS (ng/g)

DATE	SITE	chloroform	Trichloroethylene	Dichlorobromomethane	DiBromochloromethane	Tetrachloroethylene	Bromoform
26/11/91	X	9.4	< 0.3	<0.1	0.3	0.1	4.2
26/11/91	Y	9.4	< 0.3	<0.1	0.3	0.1	4.9
25/11/91	B	3.1	< 0.3	<0.1	0.3	0.1	6.9
25/11/91	C	4.1	< 0.3	<0.1	0.2	0.1	3.6
25/11/91	D	3.9	< 0.3	<0.1	0.3	0.1	4.8
25/11/91	E	2.8	< 0.3	<0.1	0.3	0.1	4.4
26/11/91	Z	2.8	< 0.3	<0.1	0.2	0.1	3.3
26/11/91	S	1.2	< 0.3	<0.1	0.1	<0.1	2.9
2/6/92	X	3.1	< 0.3	<0.1	0.3	0.1	10.1
2/6/92	Y	5.1	< 0.3	<0.1	0.3	0.1	8.2
1/6/92	B	2.3	< 0.3	<0.1	0.2	0.1	4.9
1/6/92	C	1.6	< 0.3	<0.1	0.3	0.1	7.2
1/6/92	D	1.5	< 0.3	<0.1	0.2	<0.1	4.9
1/6/92	E	*no data*	*no data*	*no data*	*no data*	*no data*	*no data*
2/6/92	Z	1.7	< 0.3	<0.1	0.9	0.1	17.8
2/6/92	S	1.3	< 0.3	<0.1	0.4	0.1	8.2
22/9/92	X	2.1	< 0.3	<0.1	0.9	<0.1	9.5
22/9/92	Y	2.5	< 0.3	<0.1	0.4	<0.1	6
17/9/92	B	1.3	< 0.3	<0.1	0.3	0.1	5.8
17/9/92	C	1.2	< 0.3	<0.1	0.3	<0.1	6.4
17/9/92	D	1	< 0.3	<0.1	0.1	<0.1	3.1
17/9/92	E	2	< 0.3	<0.1	0.2	<0.1	5.9
22/9/92	Z	2.1	< 0.3	<0.1	0.6	0.3	20
22/9/92	S	1.2	< 0.3	<0.1	0.3	<0.1	8.8

Figure 2 Chloroform in Limpet Tissue.

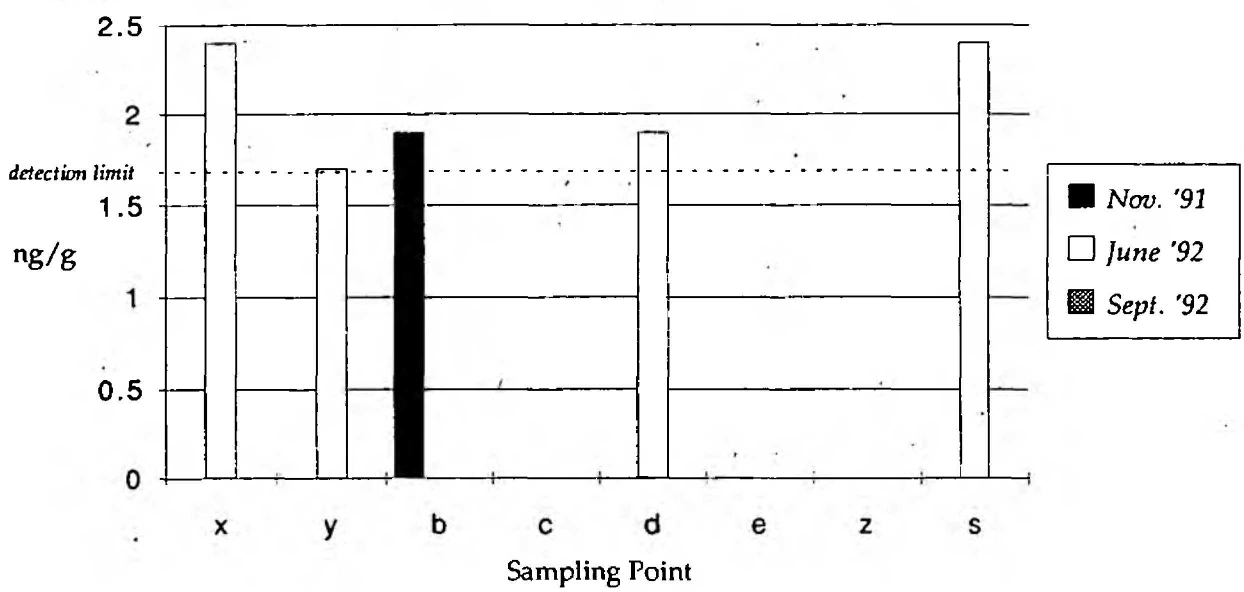
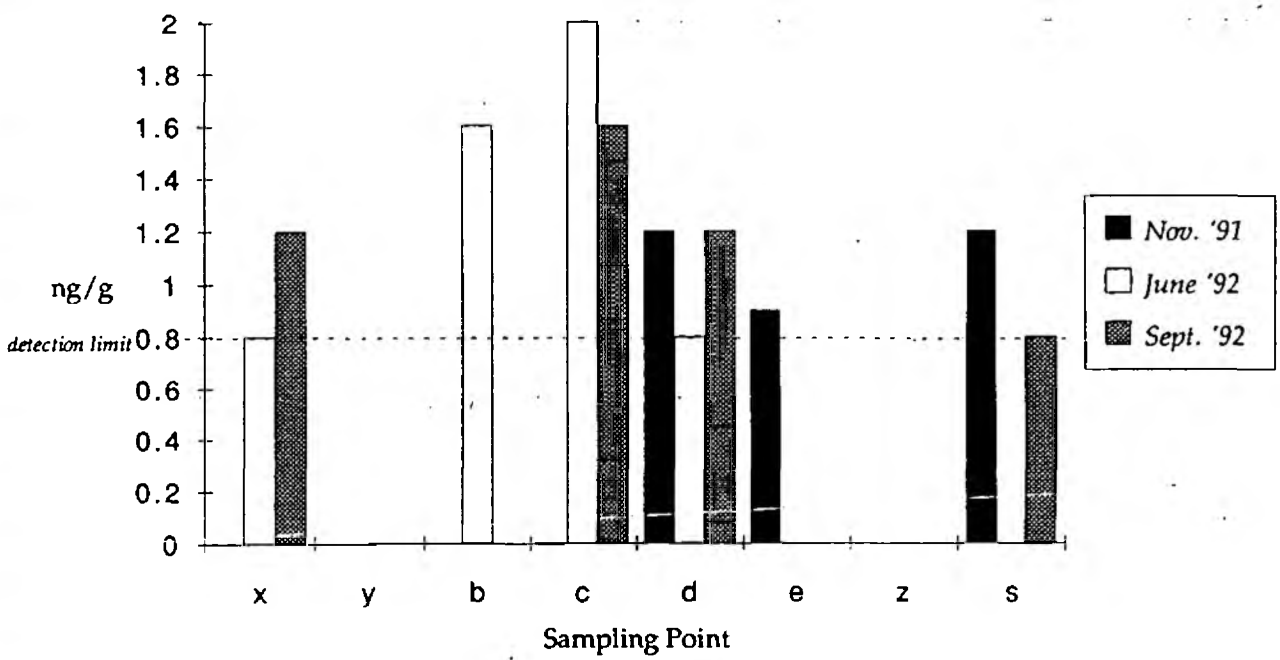


Figure 3   Bromoform in Limpet Tissue



4.2 Seaweed Tissues

i) Chloroform

Chloroform levels were greatest at the Black Rock sites throughout the sampling period, the highest levels being recorded during November 1991 (Figure 4). From the data it would appear that seaweeds at Black Rock and thus nearest the outfall, were most susceptible to the bioaccumulation of this compound. A spatial pattern related to distance from the source of disinfected sewage would thus appear to exist.

A temporal pattern exhibiting a gradual increase in chloroform levels with increasing exposure time, was not apparent. In fact the opposite was observed with samples taken outside of the disinfection period containing higher levels than either at the start or end. The reason for this was not apparent.

ii) Bromoform

Bromoform levels in seaweed tissue followed a different pattern (Figure 5) to that observed with chloroform. Generally, levels at all sites were lowest during November, suggesting that bromoform is bioaccumulated during the bathing season. Levels recorded during June and September were similar, suggesting that the disinfection process has an immediate effect, and that no gradual increase was occurring over the bathing season.

The highest results were recorded from Anchor Head, here concentrations were over 1.5 times those recorded elsewhere. The next highest results in these months were at Black Rock (X and Y), although these were similar to those recorded at the 'control' site at Sand Point. It would therefore appear that despite the comparitively low levels recorded from sites close to Black Rock, the absence of any other chlorinated effluent in the immediate area, implied that disinfection of the Weston-Super-Mare effluent was resulting in the bioaccumulation of bromoform at Anchor Head. Bacteriological studies by Wessex Water Authority (Tarbox M. 1985) revealed that on a flood tide, a plume of disinfected sewage from Black Rock can extend northwards along the Bay, and thus potentially reach Anchor Head.

iii) Dibromochloromethane

Concentrations of this compound were relatively constant throughout the bay during November (Figure 6). The most significant concentrations were recorded at Anchor Head (June and September) and at site X on Black Rock (September).

From this information it would appear that seaweed at both Anchor Head and Black Rock, is susceptible to the bioaccumulation of dibromochloromethane during the summer bathing season. The source of

Figure 4 Chloroform in Seaweed Tissue

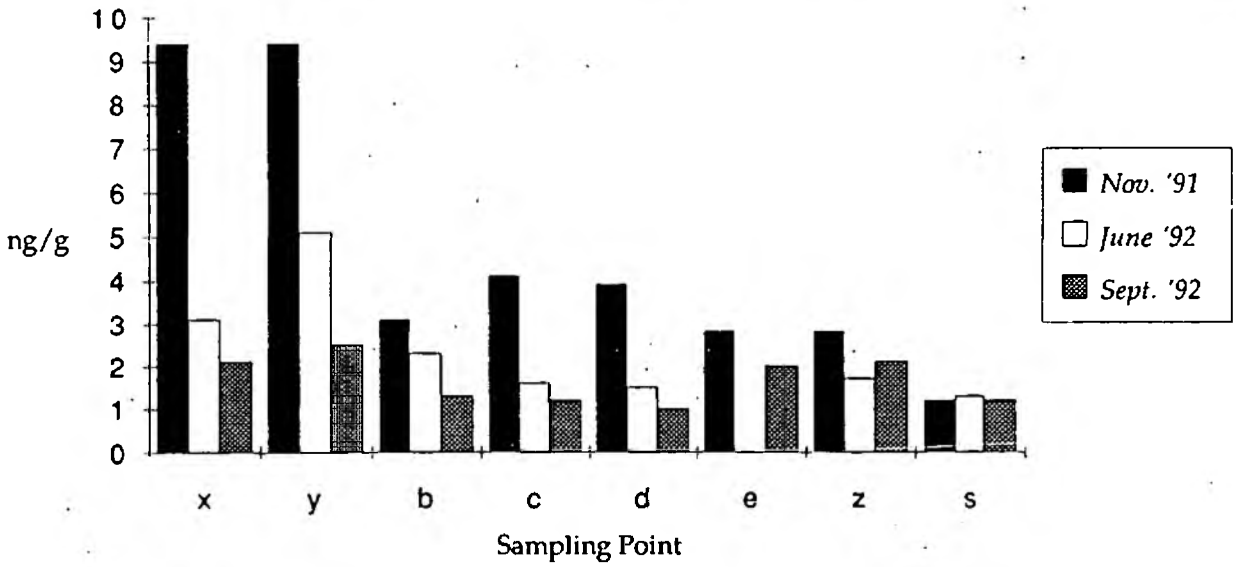


Figure 5 Bromoform in Seaweed Tissue

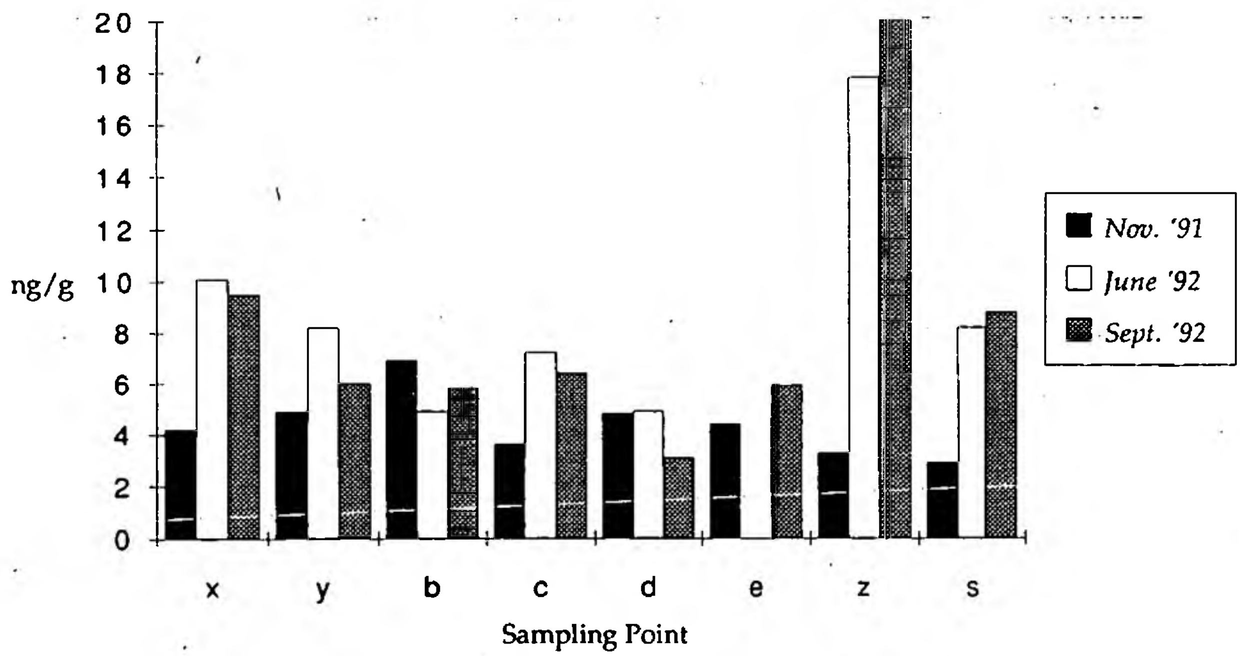
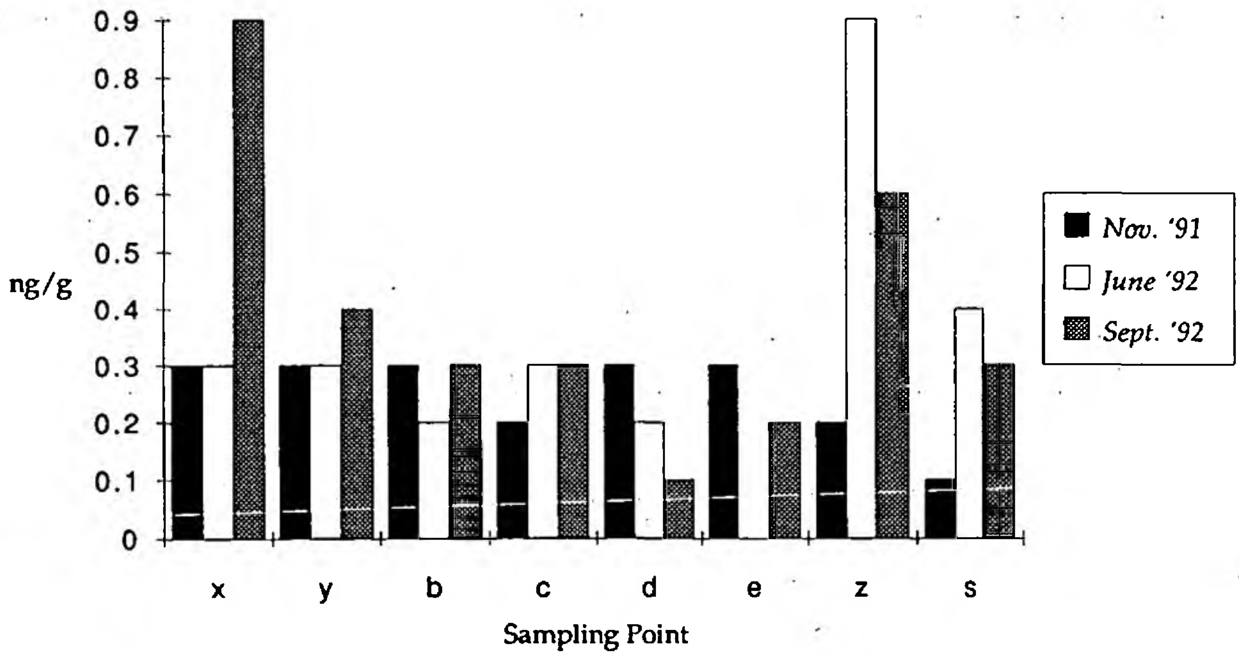


Figure 6 Dibromochloromethane in Seaweed Tissue



this compound would appear to be the disinfected effluent discharged from Black Rock.

vi) Tetrachloroethylene

The results for this compound were generally either 0.1 or <0.1 during this study. Only Anchor Head had levels different to these (0.3ng/g) recorded during September.

v) Dichlorobromomethane, and Trichloroethylene

Results for these compounds were all below the laboratories detection limits.

5. DISCUSSION

From the results it can be seen that the information provided by the limpet tissue data was unclear, with temporal and spatial bioaccumulation patterns being hard to ascertain. A similar study examining the effects of chlorinated effluent from Pwll sewage treatment works in South Wales (Wharfe et al 1981), revealed a gradual increase in halogenated compounds within the organisms collected during the bathing season and the levels recorded decreased with increasing distance from the outfall. Such clear patterns were not observed with the limpet tissues collected in this study. Work undertaken at Weston-Super-Mare by the Wessex Water Authority during the disinfection period (Tarbox & Tuckwell 1989), revealed higher concentrations of chloroform in limpets adjacent the outfall at Black Rock than at Anchor Head. The levels recorded were substantially higher than those recorded in this study (25ng/g compared to 2.4ng/g).

The data reveals that, of the chlorinated compounds examined, only chloroform and bromoform were recorded at detectable levels during the study period, and that in both cases the highest readings were taken during June, just after the start of disinfection. It is difficult to form any conclusions based on a single season of sampling, a repeat of this survey in 1993 will provide further information and will hopefully enable better and more reliable interpretation of the results.

Seaweed tissues provided more informative data. Samples of *Fucus vesiculosus* collected from Black Rock and Anchor Head tended to contain the highest levels of trihalomethanes within the area surveyed. However the pattern of distribution varied according to the compound in question. For dibromochloromethane, both sites exhibited similar levels at some point during the study. Chloroform seemed to be concentrated mainly close to the point of discharge at Black Rock, while bromoform accumulated on the opposite side of the Bay at Anchor Head. As the Black Rock outfall is apparently the only source of halogenated compounds within the area surveyed, it would appear that the results observed at both sites are from this source.

A study of faecal bacteria from beach and offshore samples by the Wessex Water Authority (Tarbox 1985) revealed that on the flood tide a narrowing plume of sewage and R. Axe water is pushed northwards along the shoreline. It would thus appear to be possible for halogenated compounds to reach Anchor Head under such conditions. However from this study not all compounds appear to behave in the same way; bromoform (and perhaps other brominated compounds) being more likely to be bioaccumulated at Anchor Head than chloroform.

The previously mentioned Wessex Water Authority work (Tarbox & Tuckwell 1989) also examined chloroform levels in seaweeds. Although different material was used (*Ascophyllum nodosum*) a similar pattern of distribution to the present study was observed. The concentrations at Black Rock were again substantially higher than in this study (15ng/g compared with 9.4ng/g).

To conclude, the levels of trihalomethanes recorded in this study were mainly accumulated within seaweed tissue collected from Black Rock and Anchor Head. The concentrations recorded however were less than in an earlier survey carried out by Wessex Water. This study is currently being repeated for November 1992 and the 1993 bathing season. This will provide additional data which will help ascertain any true spatial and temporal bioaccumulation which may not be detected by a single season of sampling.

7. REFERENCES

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