

**CEFAS REPORT TR217 EXPERIMENTAL STUDIES TO IDENTIFY KEY CHLORINATION
BYPRODUCTS (CBPS) IN COOLING WATER DISCHARGE FROM SIZEWELL C
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01	03/06/2014	Dave Sheahan	Principal Scientist	Paul Jespersen	Portfolio Lead	Paul Jespersen	Portfolio Lead

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**Experimental studies to identify key
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water discharge from Sizewell C**

Dave Sheahan, Tom McGowan

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Executive summary

Nuclear power stations such as that at Sizewell located on the East coast of England require large amounts of water for cooling purposes. The function of cooling water circuits can be compromised as a result of fouling with marine organisms.

To reduce fouling in cooling water systems the majority of coastal power plants use chlorine as a biocide. Although chlorine decay is rapid when added to seawater, various complex reactions occur resulting in the formation of chlorination by-products (CBP's). A large number of products are formed, the number and type being dependent on the composition and physical parameters of the seawater.

The formation of CBP's and their discharge into the environment can result in increased toxicity to marine organisms in the receiving water close to the cooling water outflow. For this reason, environmental assessment and monitoring is necessary.

This study provides a dataset from laboratory studies that can be used for modelling CBP production and decay to predict likely concentrations in the vicinity of Sizewell power station.

A representative dose of chlorine was added to seawater collected from Sizewell to provide the best indication of the type and maximum quantity of CBPs that may be produced at this location and these values will be used in subsequent modelling to predict the likely distribution and fate of CBPs in the marine environment at this site. CBPs are products of the reaction of chlorine in seawater; therefore similar methodology and experimental design was used as for previous studies looking at total residual oxidant (TRO) decay alone (BEEMS Technical Report TR142). The two study trials described here include the use of seawater samples with high and low suspended solids concentrations to compare the influence of this factor.

The addition of sodium hypochlorite to seawater collected from Sizewell produced a similar change in TRO concentration measured in seawater to that shown in previous studies: an initial rapid decrease in concentration (termed instantaneous demand) occurred in the first minute after addition and was followed by a slower decay phase. Also as shown in previous studies, a higher suspended sediment concentration reduced TRO degradation rate relative to samples with a lower suspended load.

The majority of CBPs formed are represented by a subset of compounds (BEEMS Science Advisory Report Series, 2010, No 009): bromoform; dibromochloromethane (DBCM); bromodichloromethane (BDCM); monobromoacetic acid; dibromoacetic acid (DBAA); dibromoacetonitrile (DBAN) and 2,4,6 tribromophenol. Of these CBPs only bromoform, DBCM, BDCM, DBAA and DBAN were analysed for in this study but BDCM (detection limit $<1 \mu\text{g l}^{-1}$), DBCM (detection limit $<1 \mu\text{g l}^{-1}$), DBAA (detection limit $<1 \mu\text{g l}^{-1}$) and DBAN (detection limit $<5 \mu\text{g l}^{-1}$) were not detected. Bromoform was detected in all replicate seawater samples at all three chlorine equivalent additions of hypochlorite of 0.25, 0.5 and $1.0 \text{ mg l}^{-1} \text{Cl}_2$.

Chlorine dose treatments of 0.25 and $0.5 \text{ mg Cl}_2 \text{ l}^{-1}$ reflect concentrations at either end of the likely range that might be applied at Sizewell C and at these maximum bromoform concentrations were achieved at 15 minutes to one hour after dosing. The range of maximum bromoform concentrations across both study trials was 4-14 and 9-29 $\mu\text{g l}^{-1}$ for a chlorine dose of 0.25 and $0.5 \text{ mg l}^{-1} \text{Cl}_2$ respectively. At a dose of $0.25 \text{ mg Cl}_2 \text{ l}^{-1}$ bromoform was $<1 \mu\text{g l}^{-1}$ after 24 hours but was still approximately 36-52% of maximum at a dose of $0.5 \text{ mg Cl}_2 \text{ l}^{-1}$.

Therefore in this study the mean value for the maximum range of bromoform that was measured at a dose of $0.5 \text{ mg l}^{-1} \text{Cl}_2$ between 15 and 30 minutes and for stirred and unstirred samples in this study ($20\text{-}29 \mu\text{g l}^{-1}$), provides a representative range from which to select an appropriate source term to use for subsequent modelling of bromoform produced in a chlorinated cooling water discharge from Sizewell C, with account being taken in the model for various environmental loss processes.

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1 Background

Nuclear power stations such as that at Sizewell located on the East Suffolk coast of England require large amounts of water for cooling purposes. Cooling water intake systems can become covered in slime and marine organisms (marine fouling), which can reduce the rate of thermal exchange, restrict water movement, clog or erode and perforate the walls of the condensers (Allonier *et al.*, 1999a). For example between 1957 and 1964, at Fawley oil-fired power station 4000 condenser tubes failed through a corrosion/erosion action associated with mussels (Coughlan and Whitehouse, 1977).

The majority of coastal power plants use chlorine, which is most frequently generated by an electro-chlorination process and added to the cooling water to protect culverts, condensers, heat exchangers and auxiliary tubular coolers against marine fouling. The cooling water is then discharged into the marine environment. The perceived benefit of chlorine use over other anti-foulants is its rapid decay (Davis and Coughlan, 1983).

Although chlorine decay is rapid when added to seawater, various complex reactions occur resulting in the formation of chlorination by-products (CBP's). A large number of products are formed, the number and type being dependent on the composition and physical parameters of the seawater. Firstly bromide is relatively abundant in seawater and, in the absence of ammonia, chlorine will react rapidly with bromide to form hypobromous acid (HOBr). Secondly chlorine will react with ammonia to form chloroamines. These reaction products then combine to form monobromamines (NH₂Br) and dibromamines (NHBr₂). Thirdly chlorine is very reactive towards natural organic matter, leading to the formation of several by-products. Trihalomethanes (THMs) are the major compounds formed e.g. the brominated methane compound bromoform but other by-products include haloaceto-nitriles (HANs), halophenols (HPHs) and haloacetic acids (HAAs) (Fisher *et al.* 1991).

CBPs are known to have toxic and carcinogenic properties (Allonier *et al.* 1999a, IARC, 1979, Jenner *et al.* 1997 and Rajamohan *et al.* 2007 and therefore their formation and discharge into the environment could result in increased toxicity to marine organisms in the receiving water close to the cooling water outflow. Some CBPs in outflow water are also more persistent in the environment than TRO compounds that change quickly through reactions of oxidation, addition and substitution with organic matters (e.g. Bean *et al.*, 1977). Due to concerns regarding both toxicity and persistence of some CBPs, environmental monitoring is important.

Any given marine waterbody will have a unique chemistry which will affect the various complex reactions that occur when dosed with hypochlorite. It is important therefore to assess what CBPs and in what concentrations may be produced in Sizewell seawater, under a representative chlorine dose.

This study aims to provide data for use in modelling CBP production and decay, to predict likely concentrations in the vicinity of the Sizewell site should chlorination be employed.

The methodology was based on previous modelling studies (Davis and Coughlan, 1983 and Lewis *et al.* 1994) used to predict the TRO decay in chlorinated seawater. CBPs are products of the reaction of chlorine in seawater and thus similar methodology and experimental design was used as for previous studies looking at TRO decay (BEEMS Technical Report TR142). These data will be used to provide an appropriate source term for modelling to predict the likely CBP concentrations in the vicinity of the potential discharge points for Sizewell C and B, to support an evaluation of compliance with current regulatory guidance on CBPs.

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2 Methods

An initial trial (trial 1) was conducted to investigate CBP formation following chlorine addition to seawater collected from Sizewell and included samples with low and high suspended solids concentrations. During sample preservation in trial 1 samples received additional mixing on a stirrer once preservative was added. Results from this trial indicated that additional stirring and preservation may reduce the concentration of some CBPs. Trial 2 therefore included a comparison of both preserved and unpreserved samples and an evaluation of the stirring of whole water samples to assess the influence of these factors on CBP concentration.

For trial 1 water was collected on 11/10/2011 in the vicinity of the future potential discharge points for Sizewell Power Station (52° 13.22'N, 001° 37.95'E World Geographical System 84). The water for trial 2 was collected inshore on 14/11/2011 (52°12.25'N', 001°23.77'E).

2.1 Treatment of water samples

In the laboratory seawater samples for trials 1 and 2 were maintained at 15°C prior to their use.

Table 1 shows the details of sampling locations and how individual seawater samples were handled during each of the experimental trials (1 and 2).

In trial 1 TRO decay and CBP production was compared in 'clear' and "turbid" samples. The water was allowed to settle for at least 7 days and water from the surface of sample vessels (e.g. with lower suspended solids) was drawn off to make up replicate samples at each of three chlorine treatment concentrations (initial concentration 1, 0.5 and 0.25 mg l⁻¹ Cl₂). The remaining water from the bottom of the containers (e.g. with the higher suspended sediment load) was also used to make up replicate 'turbid' samples at each of the chlorine treatment concentrations.

Table 1 Sample and treatment details in experimental trials 1 and 2

Trial	Sample site	Date sample collected	Chlorine addition levels (mg l ⁻¹)	Main methodology	Suspended solids
			Test volume (litres)		Mean (min-max) mg l ⁻¹
1	Offshore Sizewell	11/10/2011	1, 0.5, 0.25 (5 litres)	Sample in test vessel stirred 400 rpm sub sample for analysis not stirred during preservation	Clear: 100 (86-115) Turbid:137(90-165)
2	Inshore Sizewell	14/11/2011	1, 0.25 (4 litres)	Selected replicates stirred/unstirred in vessel 400 rpm sub-sample preserved/unpreserved no stirring, low sediment	96 (60-130)

In trial 2 chlorine was dosed at concentrations of 0.25 and 0.5 mg l⁻¹ Cl₂ as these values span the concentration range likely to be dosed by Sizewell C, seawater samples were mixed prior to sampling with

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some removal of coarse suspended material (e.g. $>425 \mu\text{m}$) to obtain a low suspended solids concentration similar to that of the 'clear' samples from trial 1.

2.2 Measuring Total Residual Oxidant (TRO) concentration

Prior to each experimental trial the Camlab colorimeter (model CW1000, which uses a LED and wavelength of 528 nm) was calibrated using chlorine reference standards purchased from Lovibond. A zero reading for absorbance was obtained using a sub-sample of the test solution. The measuring tolerance of this method is 0.02 mg l^{-1} .

A 10 ml sample of seawater was taken from each beaker with a mechanical pipette and added to a test tube containing Hach® DPD total chlorine reagent. After specific reaction time intervals the sample was filtered through a syringe fitted with a $0.2 \mu\text{m}$ filter into a 10 ml reading cell and analysed with the colorimeter. A total of three replicate solutions were sampled for each measurement.

2.3 Test conditions

Although TRO demand has been shown to decrease with cooler temperatures, the change in TRO demand as the cooling water is discharged and diluted is generally not incorporated into modelling (Taylor, 1992). In this study all experiments were conducted in a controlled temperature room at $15 \pm 2^\circ\text{C}$.

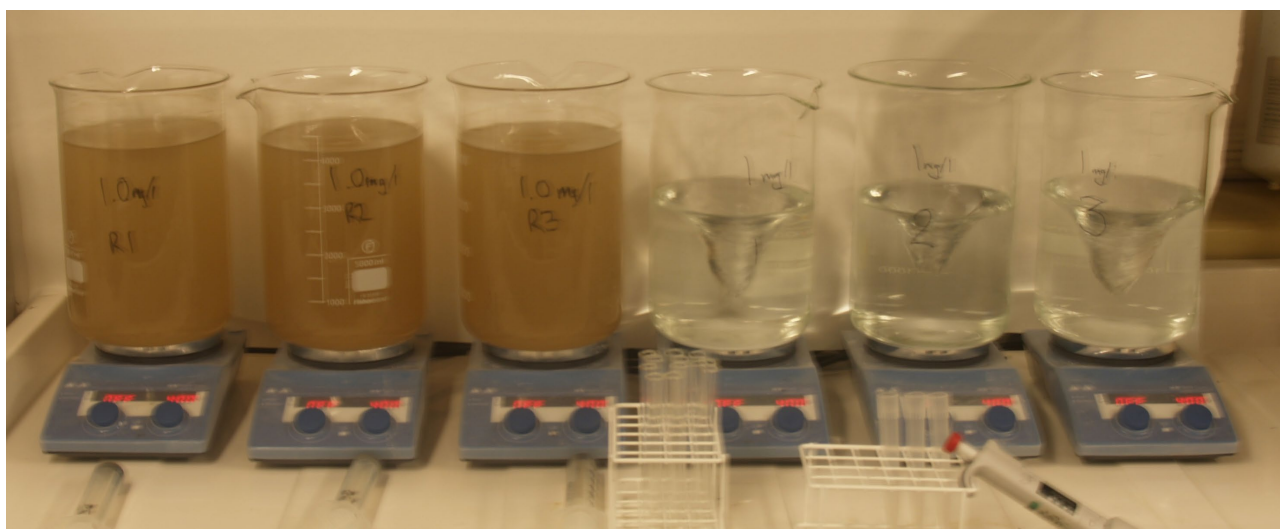


Figure 1 Samples of 'turbid' and 'clear' seawater from Sizewell on stirrer plates at 400 rpm

The test temperature was chosen as representative of the receiving water at Sizewell as it is between the mean and 98% values for 2003–2008 (BEEMS Technical Report TR189). Samples for trials 1 and 2 with the exception of unstirred sample groups were continuously stirred throughout the experiment at approximately 400 rpm using a magnetic stirrer bar. Studies by other investigators (Davis and Coughlan, 1983 and Davis, 1992) indicate that test volumes of greater than 1 litre should be used to avoid 'edge' effects when investigating TRO decay and so at least 4 litres of seawater was used in each trial.

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2.4 Sodium hypochlorite solution

A laboratory grade solution of sodium hypochlorite (NaOCl) containing 5% chlorine was obtained from Acros Organics. The volume used varied from 7.5 to 200 µl depending on the intended initial TRO concentration.

2.5 CBP production

The primary objective of the trials was to measure the production of CBP's in parallel with the decay of TRO in the sample seawater at different initial concentrations of chlorine, and at different suspended sediment concentrations. In the first trial six specific CBPs were analysed for: bromoform; dibromochloromethane(DBCM); bromodichloromethane(BDCM) and dibromoacetonitrile(DBAN) were analysed by Headspace GCMS and dibromoacetic acid (DBAA);) and 2,4,6 tribromophenol by Liquid/liquid extraction followed by GCMS.

As BDCM (detection limit <1 µg l⁻¹), DBAA (detection limit <1 µg l⁻¹), DBAN (detection limit <5 µg l⁻¹) and 2,4,6 tribromophenol were not detected in trial 1 subsequent trials focussed on bromoform and DBCM.

2.5.1 Sodium thiosulphate solution

In trials 1 and 2 in order to stop the decay of TRO and production of CBP's before samples were sent for analysis, sodium thiosulphate solution was added to samples taken (Jenner *et al.*, 1997). This sodium thiosulphate solution was made daily at a concentration of 10 g/l. The solution was added at a ratio of 10 ml to every 1 litre of sample for preservation. In both trials preservative was added to sample containers after the sample had been taken but in trial 1 samples were then placed on a stirrer for one minute (Figure 2) before being sealed and put on ice ready for transport and analysis. In trial 2 as it was considered that stirring of samples may further influence bromoform loss a comparison of stirred and unstirred samples was made and none of the sub-samples for preservation were stirred after sodium thiosulphate addition. All samples regardless of preservation were filled to the top of sample containers before being sealed and directly placed in a cool box ready for transport for analysis.

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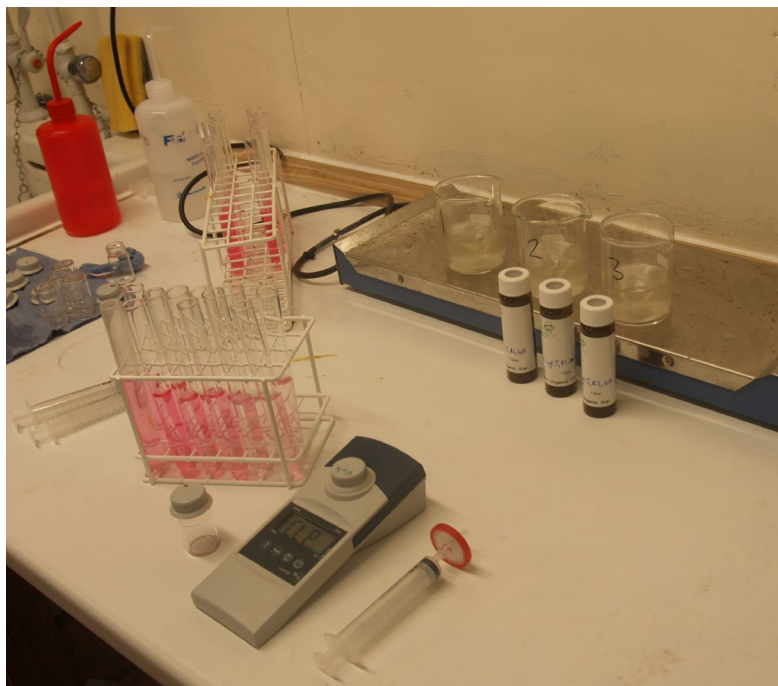


Figure 2 TRO analysis of Sizewell seawater sample and sample being prepared for VOC analysis in trial 1 being stirred following addition of sodium thiosulphate solution by magnetic stirrer prior to addition to the sample bottle.

2.5.2 Sample collection for CBP analysis

Samples for semi-volatile organic compounds (SVOC's) and for volatile organic compounds (VOC's) were collected as part of this study to quantify the production of CBPs within the samples. These samples were analysed on behalf of Cefas by Environmental Scientifics Group (ESG) using Headspace Gas Chromatography-Mass Spectrometry (GC-MS) for VOC's and liquid/liquid extraction as well as GC-MS for SVOC's. The substances measured that are relevant to this CBP assessment were bromoform, DBCM, BDCM and DBAA. The method for collecting SVOC and VOC samples in trials 1 and 2 was as follows;

1. At the appropriate time beakers containing the test solutions were removed from the stirrer plates and the required volume measured into a measuring cylinder. The beakers were then replaced on the stirrer plates.
2. The test solution was then added to a beaker containing sodium thiosulphate solution and in trial 1 was placed on a stirrer plate with magnetic stirrer bar and allowed to mix for approximately 2 minutes (Figure 2). This step was omitted for trial 2.
3. This preserved solution was then poured carefully into amber glass bottles provided by ESG (Figure 2). Bottles were filled to the top to allow no room for air at the top of the bottles and so minimise the likelihood of further reactions occurring or any volatile compounds escaping from solution.
4. Sample bottles were placed in a cool box containing freezer blocks while further sampling was taking place and were refrigerated ($4\pm 2^{\circ}\text{C}$) before being sent to ESG in cool boxes with freezer blocks.

In trial 1 of the study samples were taken for SVOC's as well as VOC's at 15 minutes, 1, 6, 24 and 48 hours. In the second trial samples were taken for VOC's only, as SVOC's were not detected in the analysis of trial 1 samples. Samples for VOC's were taken at 15 and 30 minutes and at 1, 6, 24 and 48 hours.

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3 Results of Experimental studies

3.1 Physical readings of samples

During trial 1 the following mean physico-chemical parameters were maintained in the test water: temperature 14.48°C (St Dev 0.34); pH 8.07 (St Dev 0.04); salinity 33.9‰ (St Dev 1.3) and dissolved oxygen concentration 99.3% (St Dev 0.79). During trial 2 the following mean physico-chemical parameters were maintained in the test water: temperature 14.58°C (St Dev 0.09); pH 8.06 (St Dev 0.01); salinity 31.73‰ (St Dev 0.09) and dissolved oxygen concentration 100.92% (St Dev 0.87).

3.2 Evaluation of CBP production

Based on the methodology described in section 2.5.2 the CBP production was quantified in trial 1 at three initial chlorine additions (1, 0.5 and 0.25 mg l⁻¹) and in samples with low suspended solids (e.g. 86-115 mg l⁻¹) 'clear' and those with higher levels of suspended solids (e.g. 60-130 mg l⁻¹) 'turbid' (Figure 3). The only CBP found was bromoform. Following a chlorine addition of 0.25, 0.5 and 1 mg l⁻¹ the highest mean concentrations of bromoform measured in each concentration were 5, 15 and 21 µg l⁻¹ respectively in the 'clear' samples, and 4, 8 and 20 µg l⁻¹ respectively in the 'turbid' samples. The 1 mg l⁻¹ chlorine dose bromoform had peak concentrations of bromoform from 30 minutes to 1 hour in the sample with slightly higher values in the lower suspended solids concentration. Following an initial chlorine addition of 0.5 mg l⁻¹ the bromoform concentration was also higher in clear as compared to turbid samples, and concentrations remained at similar levels between 15 minutes and 1 hour after chlorine dosing and then decreased. The bromoform concentration in the 0.25mg l⁻¹ chlorine dose also remained at a similar concentration up to 1 hour after dosing and thereafter decreased.

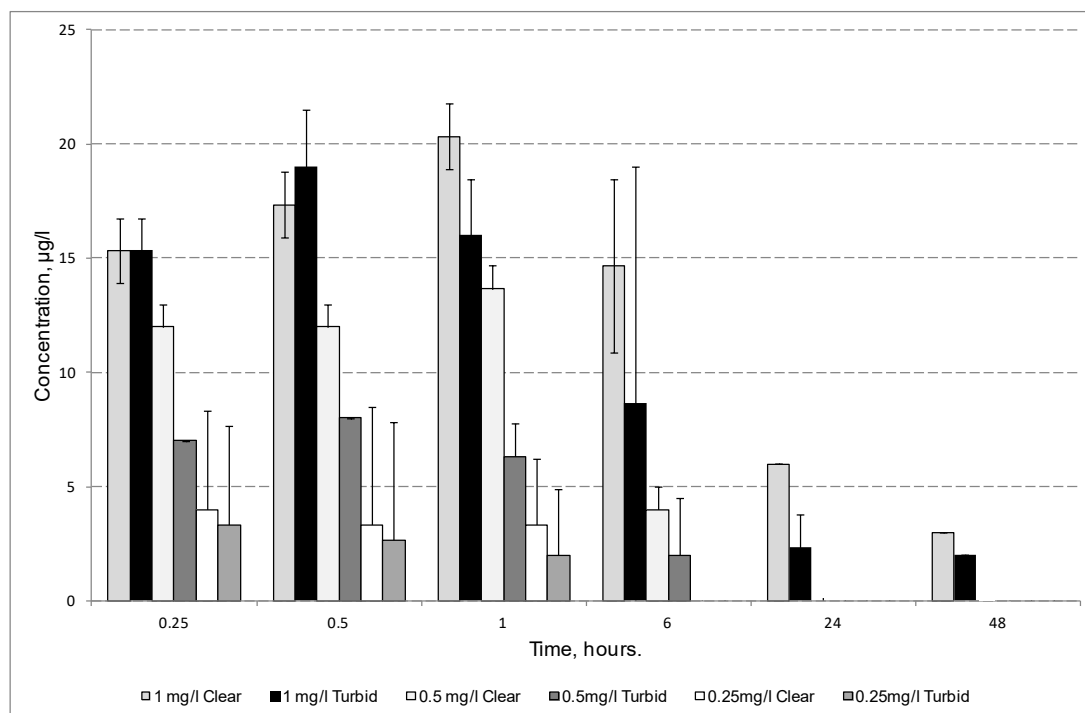


Figure 3 Mean (and 95% confidence limits n=3) CBP concentrations in trial 1 for 'clear' and 'turbid' Sizewell seawater over a 48 hour period following chlorine addition.

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For trial 2 for the same chlorine additions (0.25 and 0.5 mg l⁻¹) and in samples with low suspended solids the highest mean concentrations of bromoform measured were 9 and 29 µg l⁻¹ respectively in samples that were not stirred and were not preserved prior to analysis. As for trial 1 the bromoform concentration began to decrease after 1 hour although at a chlorine dose of 0.5 mg l⁻¹ in stirred and unstirred and unpreserved samples a decrease was apparent from 30 minutes onwards (Figure 5).

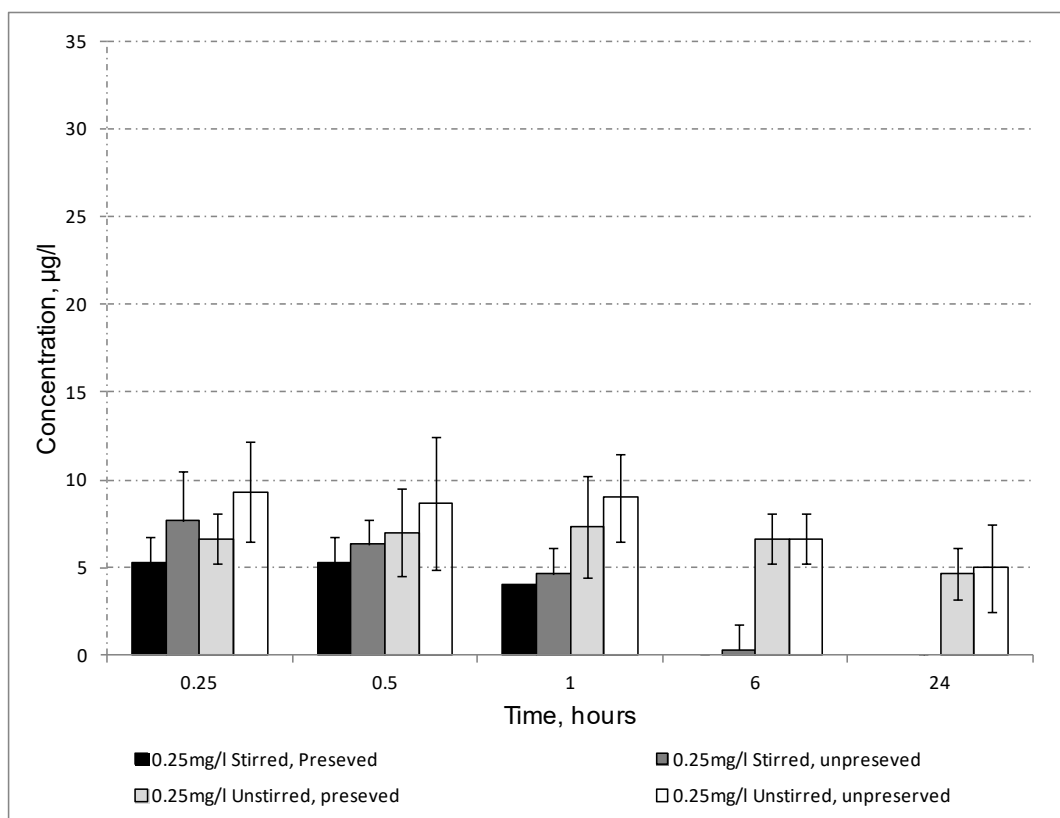


Figure 4 Mean ($\pm 95\%$ CL, $n=3$) bromoform concentrations for Sizewell seawater over a 48 hour period following an initial chlorine addition of 0.25 mg l⁻¹ in samples with or without stirring and preservation, trial 2.

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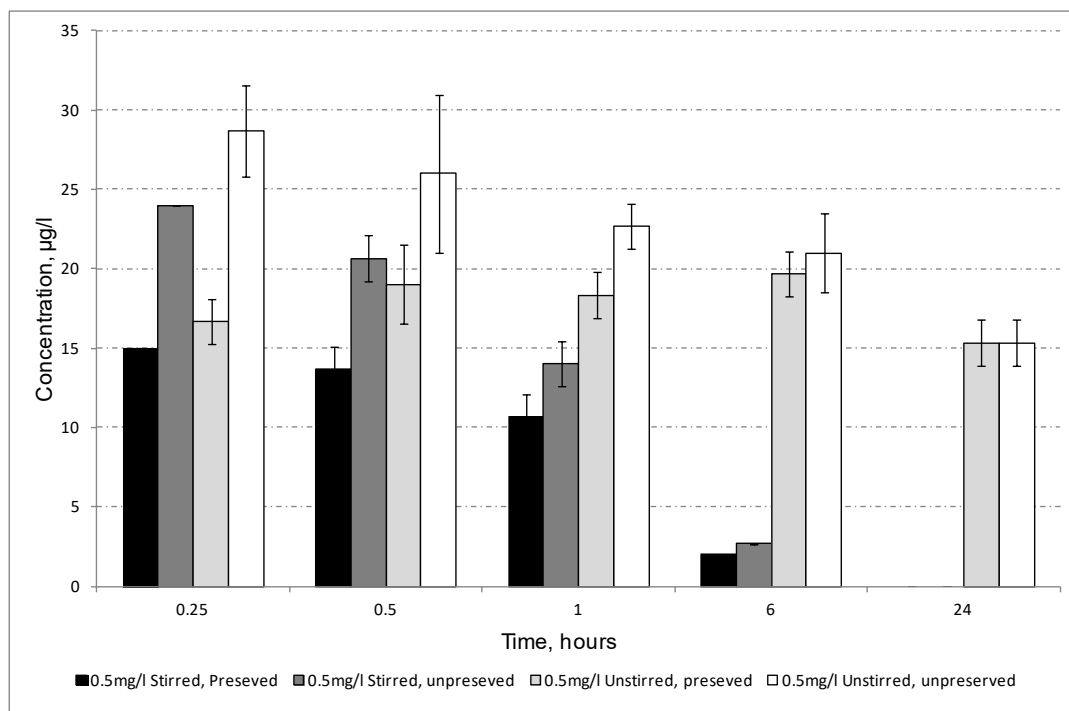


Figure 5 Mean ($\pm 95\%$ CL, $n=3$) bromoform concentrations for Sizewell seawater over a 24 hour period following an initial chlorine addition of 0.5 mg l^{-1} , in samples with or without stirring and preservation, trial 2.

4 Discussion

The behaviour of TRO degradation in the first part of the study (Appendix A, Figure A1 and A2) was largely as expected based on previous studies in that it showed evidence of an instantaneous chlorine demand followed by slower degradation (BEEMS Technical Report TR142). The effect of suspended load on TRO was also consistent with that documented in previous studies carried out by Cefas with TRO decay apparently reduced in the presence of higher suspended solids concentrations. However it should be noted during some states of the tide at Sizewell that suspended solids concentration may be considerably higher (e.g. $400\text{--}700 \text{ mg l}^{-1}$, BEEMS Technical Report TR189) and therefore TRO values may show greater reduction than was apparent in 'turbid' conditions in these studies e.g. Figure 3.

Bromoform was the only CBP detected and was present in all samples of Sizewell seawater immediately following addition of chlorine and in both 'clear' and 'turbid' samples.

Bromoform has commonly been reported as the main CBP in previous investigations into chlorinated seawater in the laboratory (Allonier *et al.*, 1999a) and from samples taken from active power station discharge cooling waters (Allonier *et al.*, 1999b and Khalanski, 2002) and represents 93-97% of the total THMs (Khalanski, 2002).

DBCM has also been reported as one of the more common THMs produced as part of the CBPs in power station discharge water (Jenner *et al.*, 1997 and Khalanski, 2002). In this study DBCM was not detected.

Stirring of samples appears to reduce bromoform concentration and this was also shown to be the case in previous trials (BEEMS Technical Report TR-S 205). There is some evidence from this trial too that

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preservation of samples also reduced the bromoform concentration as preserved unstirred replicate samples following addition of $0.5 \text{ mg l}^{-1} \text{ Cl}_2$ had $19 \text{ } \mu\text{g l}^{-1}$ of bromoform compared to the much higher value of $29 \text{ } \mu\text{g l}^{-1}$ that was reported for unstirred and unpreserved replicate samples.

In the environment the main route for loss of bromoform is volatilisation; other processes (adsorption and bioconcentration, abiotic degradation and aerobic biodegradation) are thought to be limited for bromoform and DBCM (De Potter *et al.*, 1997). Laboratory studies using 150 litre closed glass containers reported a half-life of 26 hours for bromoform (Taylor, 2006) and this is comparable to the results for the unstirred samples in this study. Volatilisation of bromoform and DBCM is an important fate process in the environment and the comparison of stirred and unstirred samples in this study indicates that losses due to volatilisation probably occurred as a result of sample stirring. The ratio of bromoform concentrations measured in stirred versus unstirred samples indicates that stirring reduced the bromoform concentration by between 40–50% after one hour increasing to greater than 90% after 6 hours. Bromoform concentration appeared to be close to maximum fifteen minutes after chlorine dosing and may therefore not show much change during passage through the cooling water circuit even though some previous studies have reported that an increase in bromoform may occur after the point of discharge (BEEMS Science Advisory Report 009, 2010). But it is important to emphasise that as with investigations of TRO decay, the influence of dilution upon the chemical interactions must also be taken into account when modelling the likely concentration and fate of bromoform in the cooling water discharge.

Chlorine dose treatments of 0.25 and $0.5 \text{ mg Cl}_2 \text{ l}^{-1}$ reflect concentrations covering the likely range that might be applied at Sizewell C and at these concentrations maximum bromoform concentrations were achieved at 15 minutes to one hour after dosing. The range of maximum bromoform concentrations across both study trials was 4-14 and 9-29 $\mu\text{g l}^{-1}$ for a chlorine dose of 0.25 and $0.5 \text{ mg l}^{-1} \text{ Cl}_2$ respectively. At a dose of $0.25 \text{ mg Cl}_2 \text{ l}^{-1}$ bromoform was $<1 \text{ } \mu\text{g l}^{-1}$ after 24 hours but was still approximately 36-52% of maximum at a dose of $0.5 \text{ mg Cl}_2 \text{ l}^{-1}$.

Previous studies have reported mean Bromoform production rates of $26.75 \pm 5.88 \text{ } \mu\text{g l}^{-1}$ in chlorinated effluents from active power stations (Allonier *et al.*, 1999b) and at an average level of $16.32 \pm 2.10 \text{ } \mu\text{g l}^{-1}$ with chlorine dose of 1 mg l^{-1} (BEEMS Science Advisory Report 009 and Jenner *et al.*, 1997), these results are comparable to the range of the levels found in this study (Figure 3 - 5). For UK power stations the bromoform range was just over 3 to $29 \text{ } \mu\text{g l}^{-1}$ but these values were associated with a chlorine dosage range of 0.3 - 1.0 mg l^{-1} and there was no information on the dosing regime.

In the context of the bromoform concentration range reported for other UK sites the maximum concentration range for bromoform at a dose $0.5 \text{ mg l}^{-1} \text{ Cl}_2$ between 15 and 30 minutes and for stirred and unstirred samples in this study (20 - $29 \text{ } \mu\text{g l}^{-1}$) provided a representative range from which to select an appropriate source term to use for subsequent modelling for Sizewell C.

In terms of the likely effects of bromoform and other THMs toxicity data from the literature for marine organisms shows the lowest reported lethal concentration (LC_{50}) for bromoform as 1 mg l^{-1} for Oyster larvae (*Crassostrea virginica*) and the lowest non observable effect concentration (NOEC) as $500 \text{ } \mu\text{g l}^{-1}$ for Clam gill tissue (Allonier, 2000). DBCM has a NOEC of $2,500 \text{ } \mu\text{g l}^{-1}$ to Urchins (His *et al.*, 1999). The highest level of bromoform measured in this study is seventeen times lower than the NOEC described above.

THMs also occur naturally in the environment and therefore any natural background level must be taken account when assessing any potential impact from discharge of cooling water effluents. Benthic and planktonic algae produce bromoform and other THMs naturally as a means of defence, and bromoform is found naturally at $10.1 \pm 5.9 \text{ ng l}^{-1}$ in the English Channel and $8.4 \pm 7.7 \text{ ng l}^{-1}$ in the North Sea (Fogelqvist and Krysell, 1991). Although mean naturally occurring levels of bromoform may be lower than those in cooling water effluents, total cumulative natural bromoform is likely to be much higher than that produced by a single power station (BEEMS Science Advisory Report 009, 2010). Concentrations of naturally occurring bromoform may also be much higher at points of source e.g. beds of benthic algae, than the mean values described above.

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For the chlorinated byproducts the evidence suggests that these do not represent a long term threat based in particular on the long term studies on sea bass in which little of the bromoform that was accumulated was ultimately retained in the tissues (BEEMS Technical Report TR186). These data will be further evaluated under different modelled scenarios to confirm whether the area of sea bed and surface that are likely to be affected by concentrations of bromoform that exceed the 95 percentile maximum allowable concentration can be considered of low concern.

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Appendix A TRO demand and decay in Sizewell seawater

A.1 Measurement of TRO demand and decay

The procedure for measurement of TRO demand and decay was as follows:

1. Five litres of seawater were added to a glass beaker.
2. A sample of sodium hypochlorite was added to the seawater using a pipettor to the middle of the container (next to the vortex), whilst stirring at 400 rpm. As soon as the addition occurred a timer was initiated. This was done to provide the required test concentrations, by adding 100µl to provide equivalent of 1 mg l⁻¹, 50 µl to give 0.5 mg l⁻¹ and 25 µl to give 0.25 mg l⁻¹. All concentrations were tested in triplicate.
 - a. The TRO concentration was measured at 1, 3, 6, 10, 15, 30, 45, 60, minutes and at 24 and 48 hours for all concentrations and also at two, three, four, five and six hours for 1 mg l⁻¹ and 0.5 mg l⁻¹ samples.
 - b. The above methodology was also replicated for control, Sizewell water with no addition of sodium hypochlorite. TRO was measured in the control at 1, 24 and 48 hours.

Based on the methodology described in section 2.2 TRO demand and decay was assessed following the addition of sodium hypochlorite at three dose levels to Sizewell seawater for trial 1 (Figures A.1 and A.2). There was an initial rapid and substantial decrease in measured TRO within the first minute at all concentrations, this has been noted in previous studies [BEEMS TR091] and has been termed the instantaneous chlorine demand [Coughlan and Whitehouse, 1997]. In all concentrations after the instantaneous chlorine demand and the following 10 to 15 minute period the rate of decay slows, and is minimal over the next 24 to 48 hours.

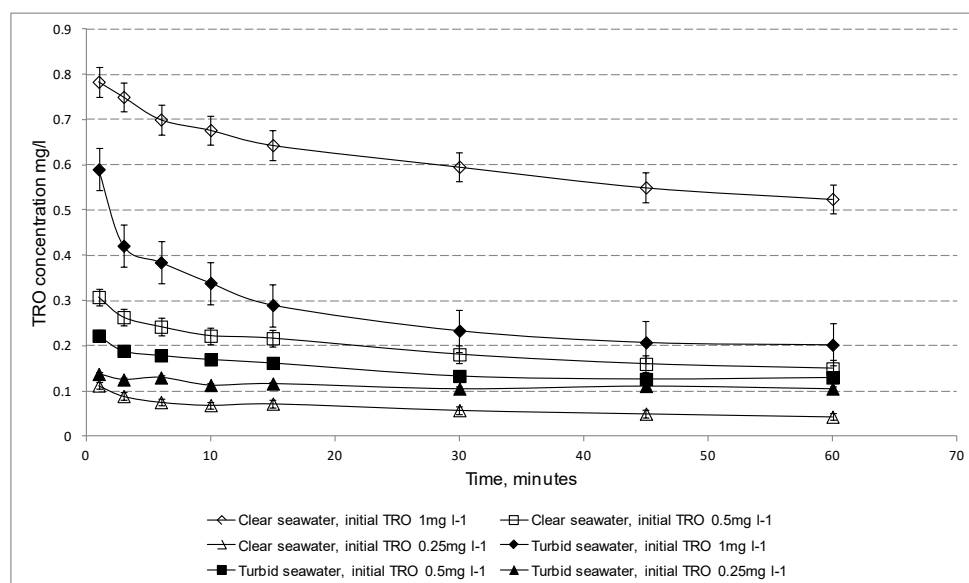


Figure A.1 Total Residual Oxidant decay for Sizewell seawater in Trial 1 during the first hour following chlorine addition. Values shown are mean and 95% confidence limits (n=3) TRO concentration.

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TRO concentration remains around similar levels from 24 to 48 hours between concentrations of 0.25 and 1 mg l⁻¹ initial chlorine dose in all samples (Figure A.2).

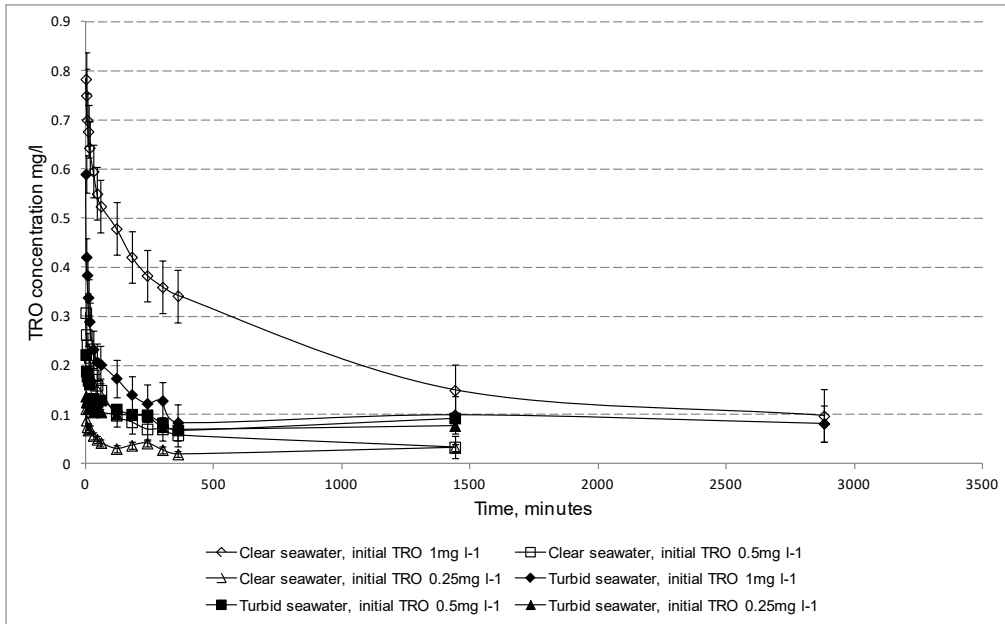


Figure A.2 Total Residual Oxidant decay for Sizewell seawater in trial 1 during the 48 hour period following chlorine addition. Values shown are mean and 95% confidence limits (n=3) TRO concentration.

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Appendix B: Bromoform concentrations measured in trials 1 and 2

Table B1 Trial 1 Bromoform concentration measured and sampling time following the addition of chlorine at three concentrations (in the form of sodium hypochlorite) to seawater with low suspended solids ('clear' – mean 100 mg l⁻¹) sampled from Sizewell. All test water replicates were continuously stirred at 400 rpm following addition of chlorine and subsamples were preserved using sodium thiosulphate prior to analysis.

Chlorine concentration added	replicate	15 minutes CHBr ₃ µg l ⁻¹	30 minutes CHBr ₃ µg l ⁻¹	1 hour CHBr ₃ µg l ⁻¹	6 hours CHBr ₃ µg l ⁻¹	24 hours CHBr ₃ µg l ⁻¹	48 hours CHBr ₃ µg l ⁻¹
0.25 mg l ⁻¹ chlorine	1	5	4	4	<1	<1	
0.25 mg l ⁻¹ chlorine	2	2	1	2	<1	<1	
0.25 mg l ⁻¹ chlorine	3	5	5	4	<1	<1	
0.5 mg l ⁻¹ chlorine	1	12	12	14	4	<1	
0.5 mg l ⁻¹ chlorine	2	12	12	12	3	<1	
0.5 mg l ⁻¹ chlorine	3	12	12	15	5	<1	
1 mg l ⁻¹ chlorine	1	16	17	20	13	6	3
1 mg l ⁻¹ chlorine	2	15	17	21	15	6	3
1 mg l ⁻¹ chlorine	3	15	18	20	16	6	3

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Table B2 Trial 1 Bromoform concentration measured and sampling time following the addition of chlorine at three concentrations (in the form of sodium hypochlorite) to seawater with high suspended solids ('turbid' – mean 137 mg l⁻¹) sampled from Sizewell. All test water replicates were continuously stirred at 400 rpm following addition of chlorine and subsamples were preserved using sodium thiosulphate prior to analysis.

Chlorine concentration added	replicate	15 minutes CHBr ₃ µg l ⁻¹	30 minutes CHBr ₃ µg l ⁻¹	1 hour CHBr ₃ µg l ⁻¹	6 hours CHBr ₃ µg l ⁻¹	24 hours CHBr ₃ µg l ⁻¹	48 hours CHBr ₃ µg l ⁻¹
0.25 mg l ⁻¹ chlorine	1	4	2	2	<1	<1	
0.25 mg l ⁻¹ chlorine	2	3	3	2	<1	<1	
0.25 mg l ⁻¹ chlorine	3	3	3	2	<1	<1	
0.5 mg l ⁻¹ chlorine	1	7	8	6	1	<1	
0.5 mg l ⁻¹ chlorine	2	7	8	7	3	<1	
0.5 mg l ⁻¹ chlorine	3	7	8	6	2	<1	
1 mg l ⁻¹ chlorine	1	15	18	15	4	2	2
1 mg l ⁻¹ chlorine	2	16	19	16	10	2	2
1 mg l ⁻¹ chlorine	3	15	20	17	12	3	2

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Table B3 Trial 2 Concentration measured and sampling time for bromoform following the addition to seawater sampled from Hinkley Point of chlorine at a concentration of 0.25 mg l⁻¹(in the form of sodium hypochlorite). All test water replicates were continuously stirred at 400 rpm following addition of chlorine with one batch of subsamples preserved using sodium thiosulphate and some not having this added prior to analysis.

Concentration Added <u>stirred</u> samples	replicate	15 minutes CHBr₃ µg l⁻¹	30 minutes CHBr₃ µg l⁻¹	1 hour CHBr₃ µg l⁻¹	6 hours CHBr₃ µg l⁻¹	24hours CHBr₃ µg l⁻¹
0.25 mg l ⁻¹ preserved	1	5	5	4	<1	<1
0.25 mg l ⁻¹ preserved	2	5	5	4	<1	<1
0.25 mg l ⁻¹ preserved	3	6	6	4	<1	<1
0.25 mg l ⁻¹ unpreserved	1	7	6	4	<1	<1
0.25 mg l ⁻¹ unpreserved	2	7	6	5	<1	<1
0.25 mg l ⁻¹ unpreserved	3	9	7	5	1	<1

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Table B4 Trial 2 Concentration measured and sampling time for bromoform following the addition to seawater sampled from Sizwell of chlorine at a concentration of 0.25 mg l⁻¹ (in the form of sodium hypochlorite). All test water replicates were initially mixed following addition of chlorine but remained static thereafter. One batch of subsamples were preserved using sodium thiosulphate and one remained unpreserved prior to analysis.

Concentration Added un-stirred samples	replicate	15 minutes CHBr₃ µg l⁻¹	30 minutes CHBr₃ µg l⁻¹	1 hour CHBr₃ µg l⁻¹	6 hours CHBr₃ µg l⁻¹	24 hours CHBr₃ µg l⁻¹
0.25 mg l ⁻¹ preserved	1	6	6	6	6	4
0.25 mg l ⁻¹ preserved	2	7	7	8	7	5
0.25 mg l ⁻¹ preserved	3	7	8	8	7	5
0.25 mg l ⁻¹ unpreserved	1	8	7	8	6	4
0.25 mg l ⁻¹ unpreserved	2	10	9	10	7	5
0.25 mg l ⁻¹ unpreserved	3	10	10	9	7	6

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Table B5 Trial 2 Concentration measured and sampling time for bromoform following the addition to seawater sampled from Hinkley Point of chlorine at a concentration of 0.5 mg l⁻¹ (in the form of sodium hypochlorite). All test water replicates were continuously stirred at 400 rpm following addition of chlorine with one batch of subsamples preserved using sodium thiosulphate and some not having this added prior to analysis.

Concentration Added <u>stirred</u> samples	replicate	15 minutes CHBr₃ µg l⁻¹	30 minutes CHBr₃ µg l⁻¹	1 hour CHBr₃ µg l⁻¹	6 hours CHBr₃ µg l⁻¹	24 hours CHBr₃ µg l⁻¹
0.5 mg l ⁻¹ preserved	1	15	14	10	2	<1
0.5 mg l ⁻¹ preserved	2	15	14	11	2	<1
0.5 mg l ⁻¹ preserved	3	15	13	11	2	<1
0.5 mg l ⁻¹ unpreserved	1	24	20	14	3	<1
0.5 mg l ⁻¹ unpreserved	2	23	22	14	2	<1
0.5 mg l ⁻¹ unpreserved	3	25	20	14	3	<1

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Table B6 Trial 2 Concentration measured and sampling time for bromoform following the addition to seawater sampled from Hinkley Point of chlorine at a concentration of 0.5 mg l⁻¹ (in the form of sodium hypochlorite). All test water replicates were initially mixed following addition of chlorine but remained static thereafter. One batch of subsamples were preserved using sodium thiosulphate and one remained unpreserved prior to analysis.

Concentration Added <u>stirred</u> samples	replicate	15 minutes CHBr₃ µg l⁻¹	30 minutes CHBr₃ µg l⁻¹	1 hour CHBr₃ µg l⁻¹	6 hours CHBr₃ µg l⁻¹	24 hours CHBr₃ µg l⁻¹
0.5 mg l ⁻¹ preserved	1	17	19	19	20	15
0.5 mg l ⁻¹ preserved	2	16	18	18	19	15
0.5 mg l ⁻¹ preserved	3	17	20	18	20	16
0.5 mg l ⁻¹ unpreserved	1	28	28	23	22	16
0.5 mg l ⁻¹ unpreserved	2	30	24	22	20	15
0.5 mg l ⁻¹ unpreserved	3	28	26	23	21	15