

**TR397 SIZEWELL C HYDRAZINE ANALYSIS AND
DISCHARGE PLUME PREDICTIONS
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Executive summary

Hydrazine is an oxygen scavenger and is used in power plants to inhibit corrosion in steam generation circuits. It is used to condition the secondary circuit of Pressurised Water Reactor power stations and is also used in the primary circuit during start up. Most of the hydrazine injected on a daily basis into the Sizewell B (SZB) secondary circuit is consumed in the plant and only residual trace amounts are expected to be present in the SZB effluent upon discharge via the cooling water system. In order to confirm the levels that are discharged, samples were taken from the SZB waste treatment tanks before they were discharged into the cooling water system.

There is evidence that hydrazine is harmful to aquatic organisms at low concentrations with the lowest acute six-day EC_{50} of $0.4 \mu\text{g l}^{-1}$ (400 ng l^{-1}) for growth inhibition of a marine alga, *Dunaliella tertiolecta*. Hydrazine persistence in the marine environment is low to moderate (with more rapid apparent decay when the initial concentration is at the ng l^{-1} level compared to $\mu\text{g l}^{-1}$ or higher). In the absence of an established EQS for hydrazine, precautionary values for Predicted No-Effect Concentrations (PNECS) have previously been calculated; a chronic PNEC of 0.4 ng l^{-1} for long term discharges (calculated as the mean of the concentration values) and an acute PNEC of 4 ng l^{-1} for short term discharges (represented by the 95th percentile). More recently assessments used in support of Canadian Federal Water Quality Guidelines for hydrazine indicate concentrations below $0.2 \mu\text{g l}^{-1}$ (200 ng l^{-1}) have a low probability of adverse effects for marine life. Based on derivation of these more recent Canadian guidelines, the lower chronic and acute PNEC derivations (0.4 and 4 ng l^{-1}) are now only considered as precautionary triggers for further ecological investigation.

This study was intended to:

- i. Measure typical hydrazine concentrations in the two Sizewell B secondary liquid waste tanks prior to discharge via the cooling water system.
- ii. Use the measured concentrations to calculate a Sizewell B discharge source term that could be used for plume modelling if necessary using the validated GETM model developed for Sizewell C.

In the Edition 2 report the following changes were made:

- i. hydrazine concentration data obtained during the first measurement campaign were corrected to take account of the fact that hydrazine hydrate and not hydrazine alone was used to make up the primary stock solutions used for calibration.
- ii. Additional hydrazine concentration data from samples collected later in the year were included in order to assess potential variability of discharge concentrations.
- iii. In response to a query from Sizewell B staff, additional tests have been performed to compare the influence of the sample matrix upon hydrazine recovery and these data are included in Appendix A.1.

The two separate 100 m^3 secondary liquid waste tanks which hold Sizewell B wastewater effluent prior to discharge were sampled on 3 separate occasions (12 -16 January 2016) during a period of normal operation with six consecutive replicate samples taken from each tank. The samples were then returned directly to the Cefas Lowestoft laboratory for extraction and analysis.

To evaluate potential variability in hydrazine concentration a further set of measurements was taken later in the year from the secondary liquid waste tanks (4th July 2016).

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During the first measurement campaign, the mean hydrazine concentration in Tank sample 1 was $11.8 \mu\text{g l}^{-1} \pm 33\%$, Tank sample 2: $14.2 \mu\text{g l}^{-1} \pm 25\%$ and Tank sample 3: $14.3 \mu\text{g l}^{-1} \pm 25\%$. These samples were taken during a period of normal plant operation. The highest measured mean hydrazine concentration in the secondary liquid waste tanks for the first monitoring campaign was $14.3 \mu\text{g l}^{-1}$ with a standard deviation of $4.6 \mu\text{g l}^{-1}$. Each of the 2 secondary liquid waste tanks holds 100 m^3 and one tank per day is discharged into the cooling water system when it is typically 85% full i.e. when it contains approximately 1.2 g hydrazine (at $14.3 \mu\text{g l}^{-1}$). Each tank takes approximately 3 hours to empty into the cooling water flow of 51.5 cumecs producing a cooling water concentration of approximately 2.2 ng l^{-1} .

Samples collected in July of the same year had a higher average hydrazine concentration of $62.1 \mu\text{g l}^{-1}$ with a standard deviation of $25.1 \mu\text{g l}^{-1}$ (within a range from $25.9\text{-}102.7 \mu\text{g l}^{-1}$). This would produce a mean cooling water concentration of approximately 9.4 ng l^{-1} (maximum of 15.5 ng l^{-1}).

Therefore, during normal operation and following dilution in the cooling water flow, hydrazine concentrations would be at trace levels in low ng l^{-1} at the Sizewell B seal pit and then only for approximately 3 hours per day. In practice, as the SZB cooling water system is chlorinated the interaction of hydrazine and the residual chlorine would oxidize hydrazine to nontoxic nitrogen, sodium chloride and water with the hydrazine concentration considerably reduced. For example, in experiments described in BEEMS Technical Report TR363, an initial hydrazine concentration of 69 ng l^{-1} fell immediately to 8.4 ng l^{-1} in the presence of chlorinated seawater at an initial TRO concentration of 0.2 mg l^{-1} (SZB is permitted to a higher discharge level of 0.3 mg l^{-1}). Using the TR363 results, the residual hydrazine discharge from Sizewell B is expected to be reduced to a mean concentration of between 0.3 ng l^{-1} and 1.1 ng l^{-1} with a maximum of 1.9 ng l^{-1} .

A comparison of the recovery of Cefas method control samples, for which hydrazine was spiked into natural seawater as opposed to into a matrix derived from aged secondary liquid waste effluent showed 86 – 99% recovery for seawater and 99.3 – 117% for the secondary liquid waste effluent. Although the recoveries from both were very good and within acceptable limits the slightly higher recovery of hydrazine from the matrix was statistically significant. These results suggest that although seawater is a suitable method control matrix, where possible a relevant matrix blank i.e. secondary liquid waste should be used for e.g. for studies that consider hydrazine remediation in this waste source prior to discharge.

Estimated Sizewell B hydrazine discharge source term and the need for plume modelling

Based upon the measurements undertaken for this study, the predicted hydrazine concentrations in the Sizewell B seal pit for 3 hours per day are at trace levels in the range of 0.3 to 1.1 ng l^{-1} with a maximum of up to 1.9 ng l^{-1} .

Such levels are lower than the precautionary acute PNEC of 4 ng l^{-1} and well below the probable effects concentration of 200 ng l^{-1} based on the Canadian marine standard for hydrazine. Due to the thermal buoyancy of the cooling water effluent, the predicted trace SZB hydrazine plume is a very small, surface feature with negligible intersection with the seabed that would be unlikely to be detectable, even at the outfall, using the state of the art Cefas hydrazine analytical methodology. The SZB plume would have no environmental significance.

As the maximum predicted source term was below the precautionary acute PNEC level it was considered unnecessary to undertake modelling studies for the SZB hydrazine plume.

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1 Introduction

To reduce maintenance time and cost for various industrial processes, corrosion inhibitors and oxygen scavengers are often added to cooling water systems. Hydrazine is a strong reducing agent that is frequently used in the cooling water circuits of boilers in nuclear power stations because of its antioxidant properties (Audrieth and Ogg, 1951). Hydrazine ($N_2 H_4$) is an ammonia-derived compound, and it is generally considered that in all aqueous solutions of hydrazine it is present as hydrazine hydrate (Environment Canada, 2010). It is used to condition the secondary circuit of Pressurised Water Reactor power stations and is also used in the primary circuit during start up. Most of the hydrazine injected on a daily basis into the Sizewell B (SZB) secondary circuit is consumed in the plant and only residual trace amounts derived from boiler feed water effluent are expected to be present in the SZB effluent upon discharge via the cooling water system.

There is evidence that hydrazine is harmful to aquatic organisms at low concentrations and although its persistence is low to moderate this is dependent upon various water quality parameters (Environment Canada, 2010).

In Europe, the Water Framework Directive requires all waterbodies to achieve good status by agreed target dates unless they are designated as heavily modified in which case, they must achieve good ecological potential. A consideration of chemical quality is also required for any habitats designations likely to be influenced by a given discharge. Therefore, it is important that discharges to designated waterbodies are assessed for the potential for any components of e.g. cooling water to affect chemical quality of in this case the Suffolk coastal waterbody and the Outer Thames Estuary SPA and Southern North Sea SAC. For new developments such as the planned Sizewell C (SZC) it is necessary that in combination effects of a discharge are also considered.

1.1 Scope of work

This work was a supporting study for the SZC project and was intended to:

1. Measure typical hydrazine concentrations over several days in the two Sizewell B secondary liquid waste tanks prior to discharge via the cooling water system.
2. Use the measured concentrations to calculate a Sizewell B discharge source term that, if necessary, could be used for plume modelling using the validated GETM model developed for Sizewell C.

In the study water samples were collected from secondary liquid waste tanks at SZB prior to discharge to estimate the maximum likely residual concentration of hydrazine that could be discharged. The analytical methodology used for the hydrazine measurements were undertaken using Cefas' UKAS accredited analytical method with a Limit of Quantification of 1.5 ng l^{-1} .

There is no established EQS for hydrazine and so a chronic PNEC (Predicted No-Effect Concentration) of 0.4 ng l^{-1} has been calculated for long term discharges (calculated as the mean of the concentration values) and an acute PNEC of 4 ng l^{-1} for short term discharges (represented by the 95th percentile). Details of PNEC calculation are provided in BEEMS Technical Report TR193.

A meeting with Sizewell B chemists was held on 3rd November 2015 to discuss sampling arrangements and timing to quantify representative hydrazine concentrations present in discharges from SZB. It was agreed the safest and most convenient approach to enable the prediction of the final discharge concentration was to take subsamples from the secondary liquid waste tanks within

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the operational plant prior to any discharge and to consider further process dilution factors via modelling if required.

2 Methods

2.1 Water sample collection

Sample locations and dates are shown in Table 1. Samples were taken from the two Sizewell B secondary liquid waste tanks on 3 occasions (12 – 15/1/2016) during a period of normal operation.

A second set of samples was collected from the SZB secondary liquid waste tanks (04/07/2016). The tanks contained demineralised water and process chemicals with a potentially high concentration (25-100 µg l⁻¹) of hydrazine.

Table 1. Sampling locations and dates

Sample	SZB Location ref.	Date	SZB Discharge No.	Number of replicates
Tank 1	1HF-T01 -B	12/01/16	CRM-5013-16	6
Tank 2	1HF-T01 -A	13/01/16 and 14/01/16	CRM-5014-16	6
Tank 3	1HF-T01 -B	15/01/16	CRM-5015-16	6
Tank 3	1HF-T01 -A#1-#6	04/07/16	-	6

The concentration of hydrazine in samples collected from the waste tanks was expected to significantly exceed the working range of the Cefas analytical method for the determination of hydrazine at environmental levels, and this was mitigated by diluting the samples at two levels, and by adding a surrogate standard (isotopically labelled hydrazine) to each sample. Samples, along with internal standards, were analysed alongside appropriately designed calibration curves by gas chromatography tandem mass spectrometry (GC-MS/MS) following a derivatisation and extraction process.

Sample bottles containing preservative chemicals (0.025 g anhydrous sodium sulphite and 2.5 g of potassium hydrogen phosphate) were sent to the SZB, along with guidance on sample collection procedures. Each replicate bottle was filled to the 250 ml mark with sample water agitated carefully to mix and dissolve the pre added chemicals. Additional chemicals in labelled containers were required to be added to the samples according to the procedure at the point of sample collection: First addition of Vial A containing isotopically labelled hydrazine standard in approximately 5ml ethanol followed by Vial B containing approximately 3ml Acetone to derivatise hydrazine into a stable compound.

Replicates from each sample point were taken to provide enough samples to consider sample variability. Samples were collected from the locations and on the dates indicated in Table 1. Sampling details were provided on a sample log sheet and the securely packaged samples and log sheets were returned to Cefas Lowestoft laboratory for analysis.

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2.2.1 Sample extraction

Samples were extracted following Cefas Standard Operating Procedure (SOP 2153 Rv3) Determination of Hydrazine in sea water by GC/MS Triple Quadrupole.

2.2.2 Preparation of calibration solutions (Quality control and method blank samples)

The required amount of sample bottles was first prepared, one bottle was required per batch for a procedural blank and one was required for a quality control sample (SOP 2153 Rv3). As performing an extracted calibration per batch, enough bottles were prepared to extract all the calibration levels at 1.22 µg l⁻¹, 2.44 µg l⁻¹, 14.88 µg l⁻¹, 9.76 µg l⁻¹ and 18.3 µg l⁻¹ of equivalent hydrazine.

25 mg ± 0.03 mg of sodium sulphite and 2.5 g ± 0.025 g of potassium hydrogen phosphate were added to each bottle. 250 ml of clean filtered sea water was measured using a 250 ml measuring cylinder into the calibration, blank and quality control sample bottles, these were mixed well to ensure the reagents were fully dissolved before continuing.

The quality control sample bottle was spiked with 9.76 µg l⁻¹ of hydrazine standard control solution and all calibration, blanks and QC bottles were spiked with 7.62 µg l⁻¹ of hydrazine 15N2 surrogate standard solution and mixed well.

2.5 ml of acetone was added to each of the calibration, blank and QC sample bottles and mixed well to complete the derivatisation of all samples.

All the bottles were placed in a horizontal position on the mechanical shaker and secured using the securing bars, with padding to stop the bottles from moving against one another during shaking if necessary. The revolutions per minute (RPM) was set to 250 and shaking commenced for a minimum of 30 minutes to complete the derivatisation. Following derivatisation 20 g ± 0.2 g of sodium sulphate was added to every bottle and shaken immediately upon adding to dissolve.

Using an autopipette enough 4N Sodium Hydroxide solution was added to adjust the pH of every bottle to ~ pH 10. The pH was checked with a calibrated pH meter after each addition of reagent and more sodium hydroxide was added if necessary. 16 ml of dichloromethane was then added to each bottle and shaken briefly, and the pressure vented at least three times to help ensure no leaks occur from the bottle during shaking on the mechanical shaker. All bottles were placed in a horizontal position on the mechanical shaker as before and then the bottles shaken for a minimum of 6 minutes to complete the extraction.

The contents of each bottle were then poured into a 250 ml separating funnel and the phases allowed to separate for a minimum of 15 minutes. If separation did not occur due to the formation of an emulsion further aliquots of dichloromethane were added and further shaken to complete extraction until separate layers were visible. The lower dichloromethane layer was drained into a conical flask which contained approximately 12 g sodium sulphate (Figure 1).

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Figure 1. Solvent liquid separation of phases to clean and remove water from samples

The remaining aqueous layer was poured back into the correct bottle and extracted, described as before, a further two times combining the three dichloromethane extracts. The extracts were left in contact with the sodium sulphate to dry for a minimum of 30 minutes and then poured into a round bottomed flask and the residual sodium sulphate was rinsed with a small volume of dichloromethane three times and added to the sample in the round bottomed flask to ensure transfer of all analyte from the flask (Figure 2). The sample extracts were then evaporated using the rotary evaporation equipment to approximately 1 ml in volume.

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Figure 2. Sample transfer from sample flasks to auto sampler vials.

The samples were then transferred to an amber 2 ml glass autosampler vial and capped and stored at 2-8°C until GC/MS triple quadrupole analysis could commence (Figure 2).

2.2.3 Instrumental analysis and quantification

Aliquots of the extracts (2µl) were analysed on an Agilent GC; 7890A with autosampler coupled to an Agilent MS; 7000 triple quad using a Restek RXI 5Sil MS column 60m x 0.25 mm x 1µm with a 1 ml/min constant flow of helium carrier gas. The inlet temp was 150 °C with oven parameters at 35 °C held for 1 min ramped at 10 °C/min to 220 °C then held for 5 mins giving a total run time 24.5 min per sample.

Quantitative analysis of samples was carried out using the Quantitative Analysis Mass Hunter software programme. Hydrazine present in the samples was derivatised to acetone azine and the labelled 15N₂ hydrazine surrogate solution is derivatised to 15N₂ acetone azine. These derivatives elute from the column unresolved from one another as a single peak at approximately 12.2 minutes. 15N₂ acetone azine was quantified using the peak with product ion of m/z 99. Acetone azine was quantified using the peak with product ion of m/z 97. For each sample, the response ratio was calculated by; Peak area of m/z ion 97 / Peak area of m/z ion 99 = response ratio.

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2.3 Water quality thresholds for hydrazine

Based on work conducted in 2006 and reported in BEEMS TR193 (Appendix B) acute and chronic Predicted No Effect Concentration (PNEC) values were derived for hydrazine. Toxicity data for growth inhibition of a marine alga, *Dunaliella tertiolecta* produced the lowest acute six-day EC₅₀ of 0.4 µg l⁻¹ for the dataset reviewed and forms the basis of PNEC derivation. There is no established EQS for hydrazine and so a chronic PNEC (Predicted No-Effect Concentration) of 0.4 ng l⁻¹ was derived for long term discharges (calculated as the mean of the concentration values) and an acute PNEC of 4 ng l⁻¹ for short term discharges (represented by the 95th percentile).

More recent assessments used in support of Canadian Federal Water Quality Guidelines for hydrazine indicate concentrations below 0.2µg l⁻¹ have a low probability of adverse effects for marine life, whilst a freshwater threshold of 2.6µg l⁻¹ is applied based on a greater availability of data in the freshwater environment (Environment Canada, 2013). Therefore, based on derivation of the more recent Canadian guidelines the lower chronic and acute PNEC derivations (0.4 and 4ng l⁻¹) are considered as precautionary triggers for further ecological investigation.

3 Results

3.1 Concentrations of hydrazine detected in Sizewell B secondary liquid waste tank

Samples were extracted following Cefas Standard Operating Procedure (SOP 2153 Rv3): Determination of Hydrazine in sea water by GC/MS Triple Quadrupole.

3.1.1 Quality control: Spiked seawater recovery data

Clean filtered seawater spiked with 9.76 µg l⁻¹ hydrazine dihydrochloride was used as a representative quality control sample falling within the calibration range for these analyses (Table 2). Each batch analysed contained within it a QC and Blank sample. Data for the in-house quality control were compared to our method validation criteria and all sample concentrations were blank corrected to allow for any matrix determinations. Standard validation criteria states recoveries for concentration ranges 0.01 – 0.1 mg kg⁻¹ (ppm) should be found to be between 70-120 %.

Table 2. Quality control: Spike recovery data

Sample Details	Sample concentration (µg l ⁻¹)	Blank concentration (µg l ⁻¹)	Blank corrected Sample concentration (µg l ⁻¹)	Recovery of target concentration (%)
9.76 µg l ⁻¹ spiked seawater	10.44	0.1457	10.29	105
9.76 µg l ⁻¹ spiked seawater	10.11	0	10.11	104
9.76 µg l ⁻¹ spiked seawater	10.41	0.0546	10.36	106

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It was noted that samples of the processed water contained flocculated material, others were slightly frothy, and a slight sulphide smell was associated with some samples. Some bottles were clear, and others slightly discoloured indicating that samples from the secondary liquid waste tanks were potentially representative of different batches and residence times of process water.

All sample concentrations were blank corrected to allow for any matrix effects. There was found to be good overall reproducibility within Tank 1 having five samples with concentrations found at $10.25 \mu\text{g l}^{-1}$ average $\pm 9\%$ except for the inclusion of one sample at $19.7 \mu\text{g l}^{-1}$ which consequently gave an overall average concentration of $11.8 \mu\text{g l}^{-1} \pm 33\%$ (Table 3).

Tank 2 was found to be more variable with a minimum concentration found to be at $9.91 \mu\text{g l}^{-1}$ and a maximum found to be at $19.5 \mu\text{g l}^{-1}$ giving an average concentration of Tank 2 of $14.2 \mu\text{g l}^{-1} \pm 25\%$ (Table 4).

Tank 3 was also found to be more variable with a minimum concentration found to be at $8.7 \mu\text{g l}^{-1}$ and a maximum found to be at $21.9 \mu\text{g l}^{-1}$ giving an average concentration of Tank 3 of $14.3 \mu\text{g l}^{-1} \pm 32\%$ (Table 5).

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Table 3. Concentrations of hydrazine measured in Sizewell B Secondary liquid waste Tank 1 (12/01/2016)

Cefas Laboratory Sample Number (LSN)	Sample Details	Sample concentration ($\mu\text{g l}^{-1}$)	Blank concentration ($\mu\text{g l}^{-1}$)	Blank corrected Sample concentration ($\mu\text{g l}^{-1}$)	Average /Tank ($\mu\text{g l}^{-1}$)	Std Dev/Tank ($\mu\text{g l}^{-1}$)
27327	Tank 1 Replicate 1	9.9142	0.1457	9.8	11.8	3.9
27328	Tank 1 Replicate 2	9.9133	0.1457	9.8		
27329	Tank 1 Replicate 3	10.874	0.1457	10.7		
27330	Tank 1 Replicate 4	19.873	0.1457	19.7		
27331	Tank 1 Replicate 5	9.557	0.1457	9.4		
27332	Tank 1 Replicate 6	11.772	0.1457	11.6		

Table 4. Concentrations of hydrazine found in Sizewell B Secondary liquid waste Tank 2 (13 and 14/01/2016)

Cefas Laboratory Sample Number (LSN)	Sample Details	Sample concentration ($\mu\text{g l}^{-1}$)	Blank concentration ($\mu\text{g l}^{-1}$)	Blank corrected Sample concentration ($\mu\text{g l}^{-1}$)	Average /Tank ($\mu\text{g l}^{-1}$)	Std Dev/Tank ($\mu\text{g l}^{-1}$)
27335	Tank 2 Replicate 1	9.91	0	9.91	14.2	3.6
27336	Tank 2 Replicate 2	12.57	0	12.57		
27337	Tank 2 Replicate 3	17.26	0	17.26		
27338	Tank 2 Replicate 4	14.78	0	14.78		
27339	Tank 2 Replicate 5	19.45	0	19.45		
27340	Tank 2 Replicate 6	11.38	0	11.38		

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Table 5. Concentrations of hydrazine found in Sizewell B Secondary liquid waste Tank 3 (15/01/2016)

Cefas Laboratory Sample Number (LSN)	Sample Details	Sample concentration ($\mu\text{g l}^{-1}$)	Blank concentration ($\mu\text{g l}^{-1}$)	Blank corrected Sample concentration ($\mu\text{g l}^{-1}$)	Average /Tank ($\mu\text{g l}^{-1}$)	Std Dev/Tank ($\mu\text{g l}^{-1}$)
27343	Tank 3 Replicate 1	16.22	0.0546	16.16	14.3	4.6
27344	Tank 3 Replicate 2	11.88	0.0546	11.82		
27345	Tank 3 Replicate 3	8.79	0.0546	8.73		
27346	Tank 3 Replicate 4	21.91	0.0546	21.85		
27347	Tank 3 Replicate 5	11.87	0.0546	11.82		
27348	Tank 3 Replicate 6	15.53	0.0546	15.48		

Table 6. Concentrations of hydrazine found in Sizewell B Secondary liquid waste Tank 3 during second sampling campaign on 04/07/2016.

Cefas Laboratory Sample Number (LSN)	Sample Details	Sample concentration ($\mu\text{g l}^{-1}$)	Blank concentration ($\mu\text{g l}^{-1}$)	Blank corrected Sample concentration ($\mu\text{g l}^{-1}$)	Average /Tank ($\mu\text{g l}^{-1}$)	Std Dev/Tank ($\mu\text{g l}^{-1}$) (%Std)
28487	Tank 3 Replicate 1	25.96	0.0489	25.9	62.1	25.1 (40)
28488	Tank 3 Replicate 2	42.574	0.0489	42.5		
28489	Tank 3 Replicate 3	61.567	0.0489	61.5		
28490	Tank 3 Replicate 4	39.131	0.0489	39.1		
28491	Tank 3 Replicate 5	71.385	0.0489	71.3		
28492	Tank 3 Replicate 6	76.827	0.0489	76.8		
24893	Tank 3 Replicate 7	76.993	0.0489	76.9		
24894	Tank 3 Replicate 8	102.7	0.0489	102.7		

3.2 Calculation of the SZB hydrazine operational daily discharges

The highest measured mean hydrazine concentration in the SZB secondary liquid waste tanks during the first measuring campaign was $14.3 \mu\text{g l}^{-1}$ with a standard deviation of $4.6 \mu\text{g l}^{-1}$. The

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tanks hold 100 m³ and are typically discharged into the cooling water system when they are 85% full i.e. when they contain approximately 1.2 g hydrazine (at 14.3 µg l⁻¹). The tank takes approximately 3 hours to empty into the cooling water flow of 51.5 cumecs producing a mean cooling water concentration of approximately 2.2 ng l⁻¹.

The second set of samples taken in July 2016 had a higher average hydrazine concentration of 62.1 µg l⁻¹ with a standard deviation of 25.1 µg l⁻¹ (Table 6). This would produce a mean cooling water concentration of approximately 9.4 ng l⁻¹ and a maximum of 15.5 ng l⁻¹.

3.3 Effect of the presence of TROs in the SZB cooling water system

During normal operation and following dilution in the cooling water flow, hydrazine concentrations would be at trace levels in low ng l⁻¹ levels at the Sizewell B seal pit and then only for approximately 3 hours per day. In practice, as the SZB cooling water system is chlorinated the interaction of hydrazine and the residual chlorine would oxidize hydrazine to nontoxic nitrogen, sodium chloride and water with the hydrazine concentration considerably reduced. For example, in experiments described in BEEMS Technical Report TR363, an initial hydrazine concentration of 69 ng l⁻¹ fell immediately to 8.4 ng l⁻¹ in the presence of chlorinated seawater at an initial TRO concentration of 0.2 mg l⁻¹ (SZB is permitted to a higher discharge level of 0.3 mg l⁻¹). Using the TR363 results, the residual hydrazine discharge from Sizewell B is expected to be reduced to a mean concentration of between 0.3 ng l⁻¹ and 1.1 ng l⁻¹ with a maximum of 1.9 ng l⁻¹. These concentrations fall within the range of the precautionary acute and chronic PNECs of 4 – 0.4 ng l⁻¹. Even without the effects of TROs, the expected discharges are well below the Canadian standard of 200 ng l⁻¹ and would therefore be expected to have no significant environmental effects.

4 Conclusions

4.1 Hydrazine analysis method validation

This method has previously been validated and follows Cefas Standard protocols. Compared to standard validation criteria recoveries for concentration ranges 0.01 – 0.1 mg kg⁻¹ (ppm) should be found to be between 70-120%. Expected values of 9.76 ppb for the in-house quality control samples were within these criteria indicating good analytical control of this method.

A comparison of the recovery of Cefas method control samples, for which hydrazine is spiked into natural seawater as opposed to matrix derived from aged secondary liquid waste effluent showed 86 – 99% recovery for seawater and 99.3 – 117% for the secondary liquid waste effluent. Although the recoveries from both were very good and within acceptable limits the slightly higher recovery of hydrazine from the matrix was statistically significant. These results suggest that although seawater is a suitable method control matrix, where possible a relevant matrix blank i.e. secondary liquid waste should be used for e.g. studies that consider hydrazine remediation in this waste source prior to discharge.

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The measured mean hydrazine concentrations in the 3 tank samples obtained during the first measurement campaign were similar but there was some scatter in the replicates from each tank. It is considered likely that the concentration variations were due to a combination of incomplete mixing within each tank and how quickly/often tanks are replenished/emptied with the process water. From discussions with the Sizewell B chemists, it was considered that hydrazine is largely consumed during plant operations and that the maximum expected concentrations would be of the order of $50 \mu\text{g l}^{-1}$ (ppb) in the secondary liquid waste tanks. From the replicate analysis of subsamples during measurement campaign 1, the mean hydrazine concentration in Tank 1 was $11.8 \mu\text{g l}^{-1} \pm 33\%$, Tank 2 was of $14.2 \mu\text{g l}^{-1} \pm 25\%$ and Tank 3 was of $14.3 \mu\text{g l}^{-1} \pm 25\%$.

However, samples collected in July 2016 had a higher average hydrazine concentration of $62.1 \mu\text{g l}^{-1}$ with a range from 25.9 - $102.7 \mu\text{g l}^{-1}$.

4.3 Predicted Sizewell B hydrazine source term

From measurements made in the SZB waste treatment tanks, the predicted mean SZB hydrazine source term at the seal pit (i.e. before discharge through the outfall tunnel) is in the range 2.2 to 9.4 ng l^{-1} for approximately 3 hours per day with a maximum concentration of 15.5 ng l^{-1} . However, as the SZB cooling water system is chlorinated, the effect of TROs would be expected to reduce the mean hydrazine concentration to 0.3 to 1.1 ng l^{-1} with a maximum of 1.9 ng l^{-1} .

Such levels are within the concentration range of the precautionary acute and chronic PNECs of 4 and 0.4 ng l^{-1} and well below the probable effects concentration of 200 ng l^{-1} based on the Canadian marine standard for hydrazine. Due to the thermal buoyancy of the cooling water effluent, the predicted trace SZB hydrazine plume is a very small, surface feature with negligible intersection with the seabed that would be unlikely to be detectable, even at the outfall, using the state of the art Cefas hydrazine analytical methodology. The SZB plume would have no environmental significance.

As the maximum predicted source term was below the precautionary acute PNEC level it was considered unnecessary to undertake modelling studies for the SZB hydrazine plume.

Based upon the results of SZC hydrazine modelling (BEEMS Technical Report TR303), there would be no predicted overlap or interaction between the trace residual hydrazine plume from SZB and that from SZC. The SZC plume would not intersect the Suffolk coastal water body.

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5 References

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Appendix A Supplementary analysis

A.1 Quality control: Spike recovery data comparison between spiked seawater and spiked aged secondary liquid waste water matrix

Table 7. Quality control: Spike recovery data for Lowestoft seawater and for aged secondary liquid waste water matrix for which the background hydrazine concentration was below the limit of quantification (1.5 ng l^{-1})¹⁾

Sample Type	Concentration of hydrazine added as QC sample	Concentration of Hydrazine extracted in QC sample	% recovery of expected value
Method blank	-	$0.269 \text{ } \mu\text{g l}^{-1}$	-
Method control	-	$50.65 \text{ } \mu\text{g l}^{-1}$	-
Seawater	$50 \text{ } \mu\text{g l}^{-1}$	$43.32 \text{ } \mu\text{g l}^{-1}$	86%
Seawater	$50 \text{ } \mu\text{g l}^{-1}$	$45.14 \text{ } \mu\text{g l}^{-1}$	90%
Seawater	$50 \text{ } \mu\text{g l}^{-1}$	$44.34 \text{ } \mu\text{g l}^{-1}$	87%
Seawater	$50 \text{ } \mu\text{g l}^{-1}$	$49.61 \text{ } \mu\text{g l}^{-1}$	99%
Seawater	$50 \text{ } \mu\text{g l}^{-1}$	$47.96 \text{ } \mu\text{g l}^{-1}$	96%
Method blank	-	$0.142 \text{ } \mu\text{g l}^{-1}$	-
Method control	-	$49.17 \text{ } \mu\text{g l}^{-1}$	-
SZB matrix	$50 \text{ } \mu\text{g l}^{-1}$	$58.89 \text{ } \mu\text{g l}^{-1}$	117%
SZB matrix	$50 \text{ } \mu\text{g l}^{-1}$	$54.63 \text{ } \mu\text{g l}^{-1}$	109%
SZB matrix	$50 \text{ } \mu\text{g l}^{-1}$	$48.54 \text{ } \mu\text{g l}^{-1}$	97%
SZB matrix	$50 \text{ } \mu\text{g l}^{-1}$	$55.43 \text{ } \mu\text{g l}^{-1}$	111%
SZB matrix	$50 \text{ } \mu\text{g l}^{-1}$	$49.65 \text{ } \mu\text{g l}^{-1}$	99.3%
SZB matrix	$50 \text{ } \mu\text{g l}^{-1}$	$49.91 \text{ } \mu\text{g l}^{-1}$	99.8%