Cefas BEEMS Technical Report TR145
Sizewell Laboratory studies of the decay of Hydrazine measured in sea water samples.

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BEEMS Technical Report TR145 Sizewell: Laboratory studies of the decay of Hydrazine measured in seawater

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Sizewell: Laboratory studies of the decay of Hydrazine measured in seawater samples

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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 secondary circuit is consumed in the plant and only residual trace amounts are expected to be present in the effluent upon discharge via the cooling water system.

The studies described in this report provided an initial understanding of hydrazine decay in support of subsequent Sizewell C (SZC) cooling water discharge plume modelling assessments. These early studies used a blue book analytical method using UV-visible spectrophotometry with a level of detection (LOD) ca., 10 $\mu g\ l^{-1}$ that was the best that could be achieved at the time (2010). The studies indicated that hydrazine decay rate in seawater increased with reducing concentration, however the lowest hydrazine concentrations assessed in this decay study were limited by the LOD of the analytical methodology. The lowest concentration that was evaluated was ca., 54.7 $\mu g\ l^{-1}$ which is much greater than the predicted hydrazine concentration in the SZC operational cooling water discharge of 69ng l^{-1}.

The most comprehensive data set was produced for an initial hydrazine concentration of 291 $\mu g\ l^{-1}$ and therefore this was used to derive a conservative decay half-life value of ca., 34 hours. The estimated half-life at 54.7 $\mu g\ l^{-1}$ was lower at approximately 12 hours and there was, therefore, reason to consider that the use of the 34 hour half-life was precautionary for SZC cooling water discharge modelling purposes.

To improve the evidence on hydrazine half-life variability with initial concentration it was decided to develop a more sensitive analytical method. However, in the interim the 34 hour half-life was used to undertake the operational hydrazine discharge modelling that is presented in BEEMS Technical Report TR303. This work was considered precautionary as it was expected that hydrazine would decay faster at the expected SZC discharge concentrations resulting in a smaller plume size than that presented in TR303.

Subsequent development of a new analytical method for hydrazine analysis achieved an LOD of 1.5 ng l^{-1}. Further decay studies were therefore conducted and a more representative decay rate for the expected low nanogram to microgram discharge concentrations for SZC operation and commissioning (based on a half-life value of ca., 38 minutes) was derived and is described in BEEMS Technical report TR352. TR352 synthesised the available experimental data on hydrazine decay rates to produce an improved understanding of decay rate variability with initial hydrazine concentration. This data set was used for assessment of commissioning discharges at SZC (BEEMS Technical report TR494). However, it was not considered necessary to update the SZC operational discharge modelling reported in TR303 as the predicted operational plume sizes were not considered to create any significant environmental effects and the precautionary results were therefore reproduced in ES Appendix 21 E, BEEMS Technical Report TR306.

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1 Background

To reduce maintenance time and cost, corrosion inhibitors and oxygen scavengers are often added to control the pH of water in secondary and cooling systems for various industrial processes. 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). Nuclear power stations such as the Sizewell power station located on the East Suffolk coast of England require large amounts of water for cooling purposes and the discharged water may contain traces of some process chemicals such as total residual oxidants resulting from the use of biocides like chlorine as well as antioxidant chemicals such as hydrazine that are derived from boiler feed water effluent. Hydrazine (N_2H_4) is an ammonia-derived compound. It is generally considered that in all the aqueous solutions of hydrazine is present as hydrazine hydrate (Environment Canada, 2010).

There is significant 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 2015 if they are not designated as heavily modified in which case, they must achieve good ecological potential. Therefore, it is important to assess the potential for any components of cooling water discharges to harm the marine environment. This assessment considers the influence of sea water quality at Sizewell upon the degradation rate of hydrazine so that the potential area in the vicinity of the cooling water discharge plume that might be affected by hydrazine concentrations above levels of concern can be predicted.

2 Study Aim

This study aims to provide data for use in modelling hydrazine decay to predict likely concentrations in the vicinity of the Sizewell Nuclear power station.

The decay of hydrazine in the receiving water is estimated, based on laboratory studies of discrete water samples taken from a site offshore of the Sizewell nuclear power station. These data provide the basis for modelling to predict the likely hydrazine concentrations in the vicinity of the cooling water discharge. These modelling data can also support an evaluation of compliance with current regulatory guidance on discharges to estuarine and coastal waters.

3 Methods

For the main hydrazine decay studies water samples were collected at the water surface, 3 km offshore from the existing Sizewell B power station cooling water outfall (52.13.40º N, 001 40.68º E, World Geographical System 84) (Figure 1 station 11).

3.1 Method for collecting water samples

For this study surface water samples were collected in a stainless bucket and decanted into 20L plastic containers for return to the laboratory.

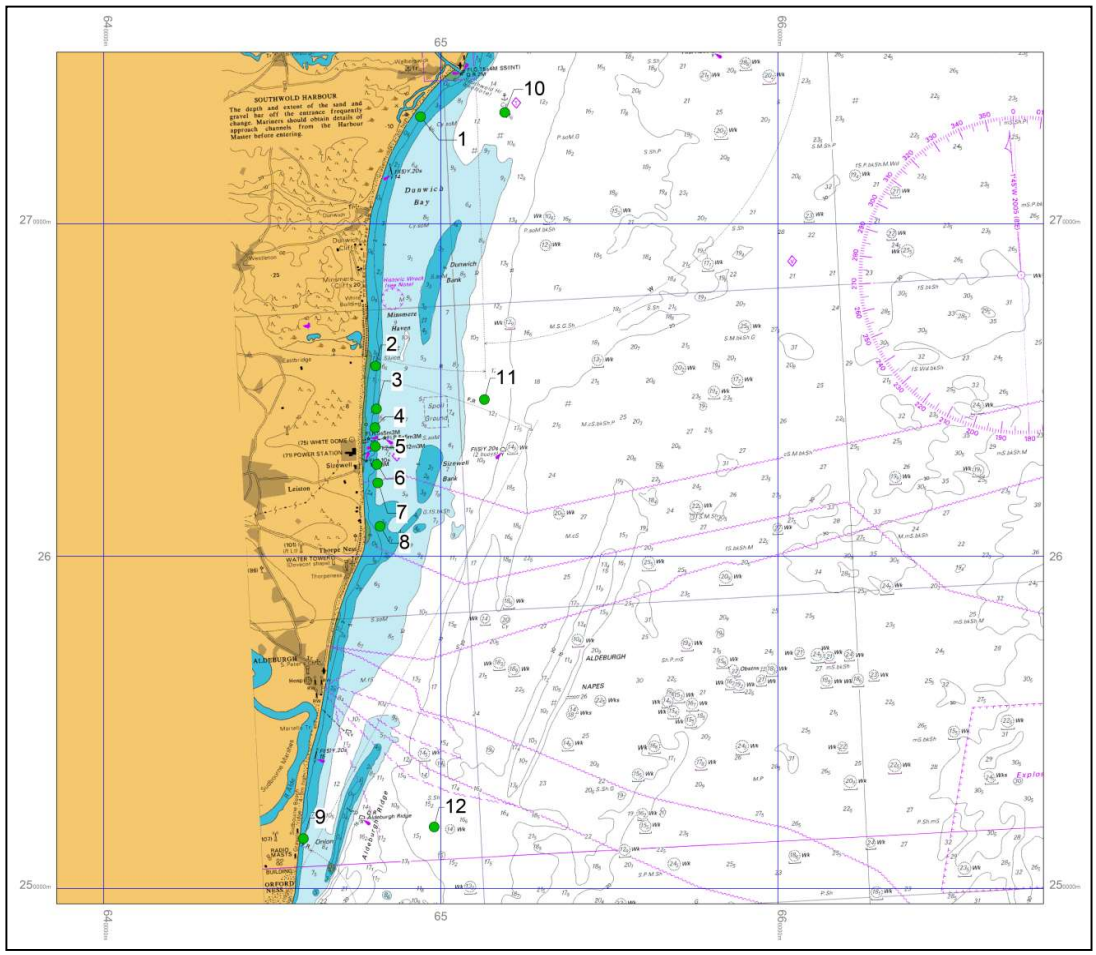

Figure 1. The location of the water sampling station 11 off Sizewell.

Samples were returned to the laboratory within 5 hrs of collection. In the laboratory all seawater samples were maintained at 4±2° C prior to their use and all were used within 72 hours of collection.

3.2 Measurement of hydrazine concentration

The method used for measurement of hydrazine in sea water samples is based on the blue book method (SCA Blue Book, 1981) Briefly p-Dimethylaminobenzaldehyde is added to the acidified aqueous sample and reacts with hydrazine to form a yellow azine. The concentration of the azine is determined using UV-visible

spectrophotometry. A four-point calibration curve is prepared for each batch of samples and it is required to have a R^2 value of >0.990. Provided enough volume of sample is supplied, one duplicate sample is prepared per batch of samples and the duplicate must be within 20% of its corresponding sample. The stated detection limit for this method is 1 µg l^{-1}. Based on laboratory calibration studies in natural sea water samples with suspended sediments it is considered that a more conservative detection limit for hydrazine is 10 µg l^{-1} therefore only concentrations >10 µg l^{-1}but including the first concentration at and below 10 µg l^{-1}were used to derive degradation rates.

3.3 Test conditions

In this study all experiments were conducted in a controlled temperature room at 15 ± 2ºC as this is representative of the receiving water at Sizewell (it is between the mean and 98th percentile values for 2009 – 2013 (BEEMS Technical Report TR131).

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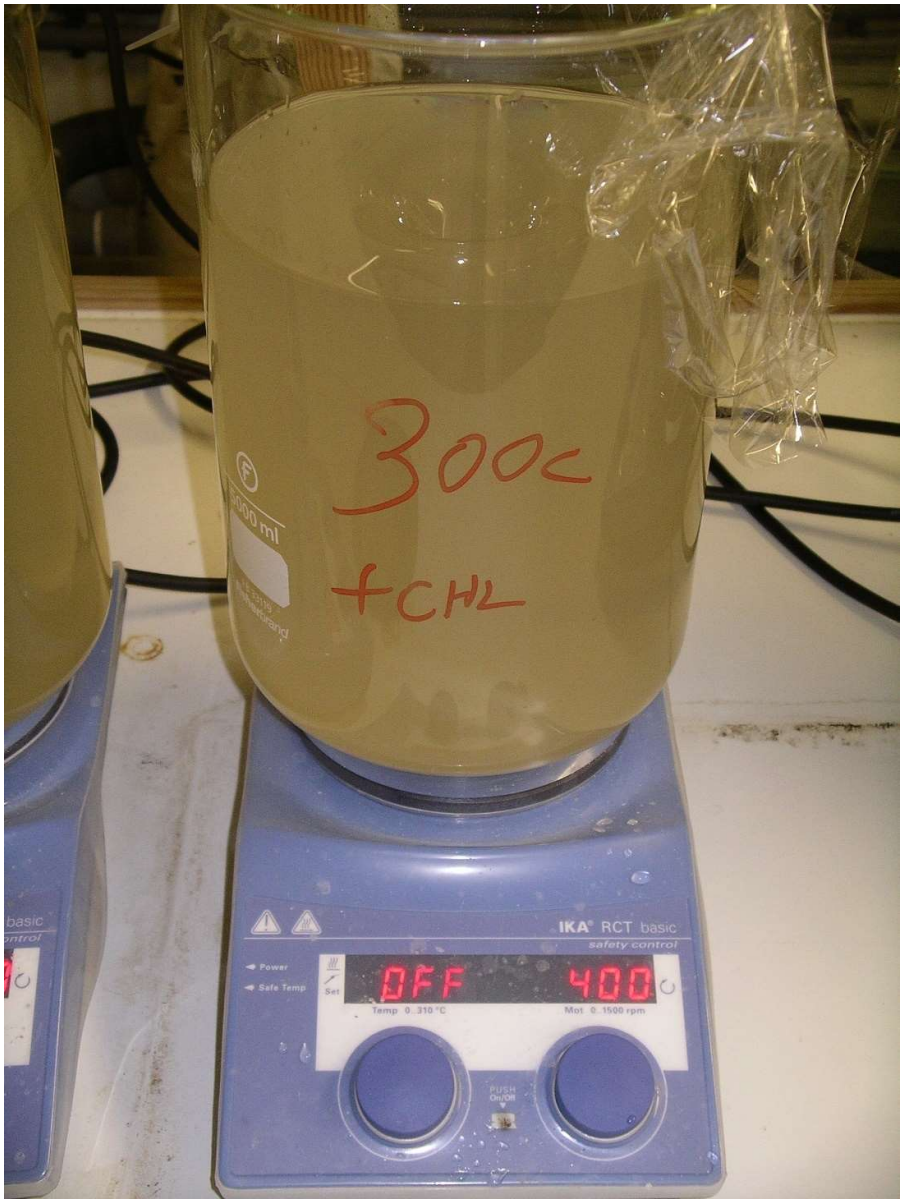

Figure 2 Sizewell sea water samples (4L) spiked with hydrazine and maintained on magnetic stirrer during hydrazine degradation study.

All samples were continuously stirred throughout the experiment using a magnetic stirrer bar. The beakers were lightly covered during the experiment (see **Figure 2**) to reduce evaporation. A test volume of 4 L in a 5 L beaker was used as it provided the most practical maximum volume to allow sufficient subsamples to be collected and to allow the seawater to be continuously mixed.

Three replicate beakers were used at each of three initial nominal hydrazine addition concentrations, 10, 50, and 300 µg l^{-1}. Temperature, salinity, and pH were measured in a representative sample of the seawater at the start of the study. An additional series of replicates that contained sea water that had been filtered through a GF/F grade filter was also dosed with 300 µg l^{-1} to evaluate the influence upon degradation rate.

3.4 Hydrazine spiking procedure

A laboratory grade solution of hydrazine hydrate ($NH_2NH_2.H_2O$) Sigma-Aldrich (CAS number: 10217-52-4) was used for the spiking studies. A hydrazine stock solution was made up using 0.2 µm filtered sea water and this was used to spike the test beakers to achieve the required initial target concentrations: 300, 50 and 10 µg l^{-1}. One additional treatment group was introduced into the experimental design this was sea water filtered through a GF/F filter and spiked at a nominal concentration of 300 µg l-1. Hydrazine was spiked into the vortex of the stirring sea water to facilitate more rapid mixing.

3.5 Sampling and preservation of sea water

Following the spiking of the hydrazine 200 ml samples of sea water were taken from each replicate beaker at intervals of 15 minutes, 3 hours, 8 hours, 24 hours, 32 hours, 48 hours, 54 hours, 72 hours, 96 hours and placed in amber glass bottles and acidified with 2 mls of concentrated HCl - 37%. Samples were stored refrigerated at 4 °C prior to being transported for analysis.

4 Results

4.1 Physical readings

The Sizewell seawater used for studies during this period in 2010 had the following characteristics the salinity was 32 psu, pH was 8 and samples were held in a constant temperature room maintained at 15 ± 2ºC.

4.2 Evaluation of hydrazine decay

Hydrazine decay following a calculated addition of 291 µg l^{-1} is shown in Figure 3. During the first 15 minutes hydrazine concentration decreased by less than 10% and reached a 56% reduction after 48 hours. For an initial hydrazine concentration spike of 54.7 µg l^{-1} decay was more rapid following this lower concentration spike and was reduced to 57% of the initial concentration within 8 hours (Figure 4). A nominal spiked concentration of 10 µg l^{-1} did not produce a clear pattern of decay and it suggests that the method detection limit for natural sea water samples is close to 10 µg l^{-1}.

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Decay data for the GF/F filtered samples spiked with a calculated concentration of 291 µg l^{-1} is shown in Figure 5. The dataset is more variable, but the hydrazine decay rate indicated is much lower than that in the unfiltered samples with a reduction of 50 -53% achieved between 54 and 96 hours.

Figure 6 shows the rate of hydrazine degradation with the calculation of rate(slope) factors that are used to derive degradation half-life for each starting concentration.

The calculated half-life values are shown in Table 1. Half-life decreases with reduction in the starting concentration so that the calculated half-life for a starting concentration of 291 ug l^{-1} is 34.2 hours as compared to a value of ca.,12 hours for a starting concentration of 54.7 ug l^{-1}. The use of GF/F filtered sea water considerably reduced the degradation of hydrazine added at a concentration of 291 ug l^{-1}, with a calculated half-life of 86.6 hours.

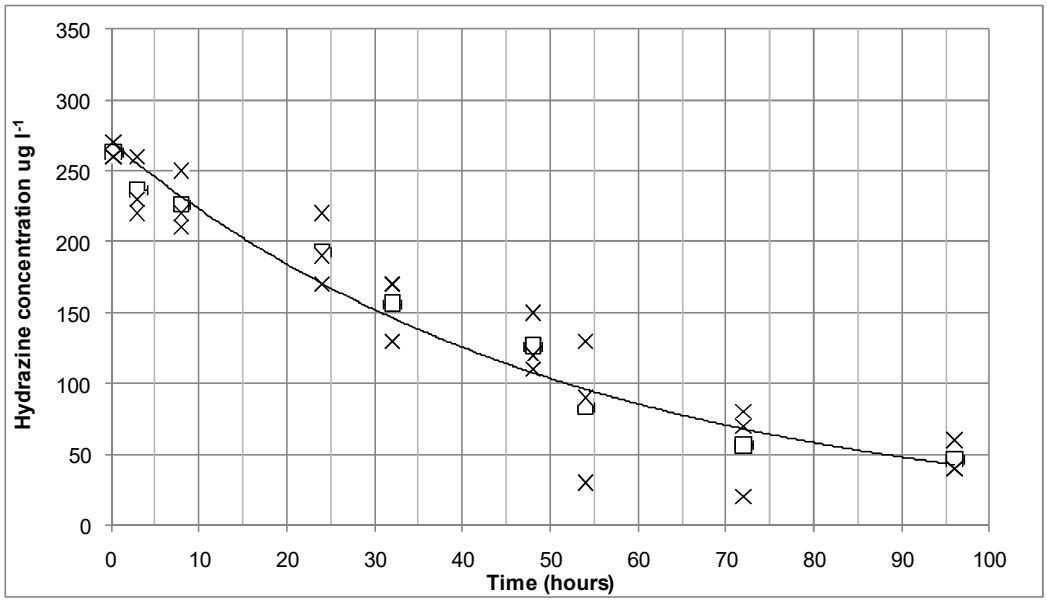

Figure 3 Mean hydrazine degradation (squares) and data points (crosses) after the addition of 291 µg l^{-1} fitted with an exponential decay curve

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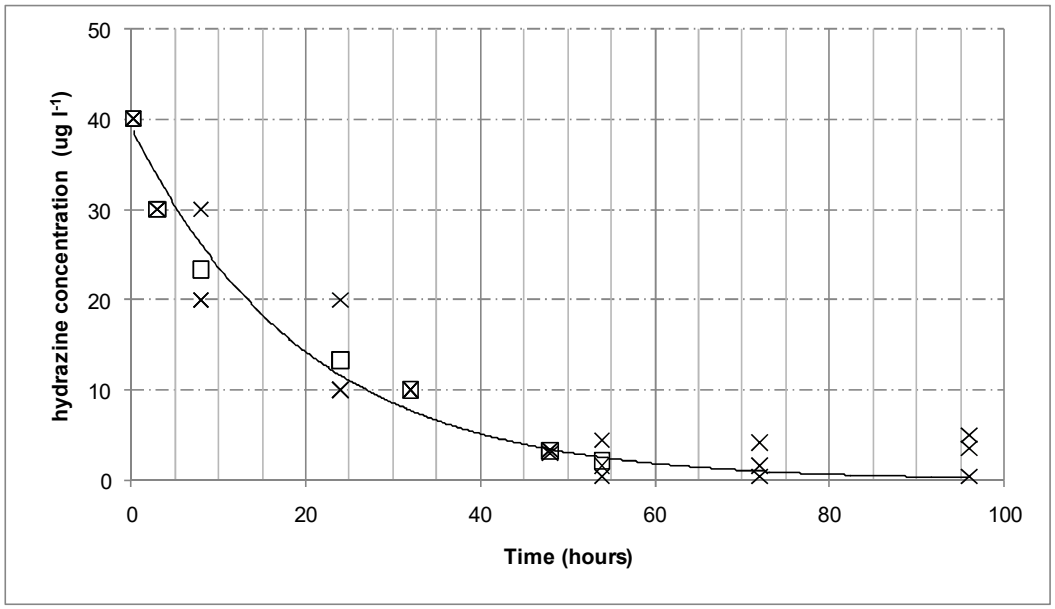

Figure 4 Mean hydrazine degradation (squares) and data points (crosses) after the addition of 54.7 µg l^{-1} fitted with an exponential decay curve

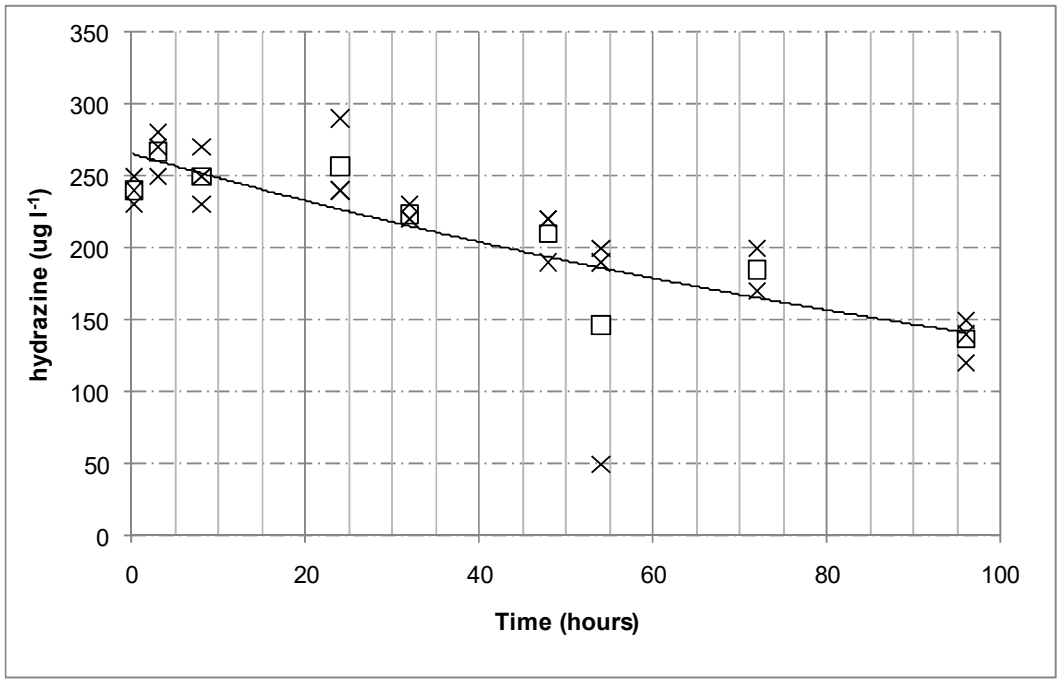

Figure 5 Mean hydrazine degradation (squares) and data points (crosses) in GF/F filtered sea water after the addition of 291 µg l^{-1} fitted with an exponential decay curve

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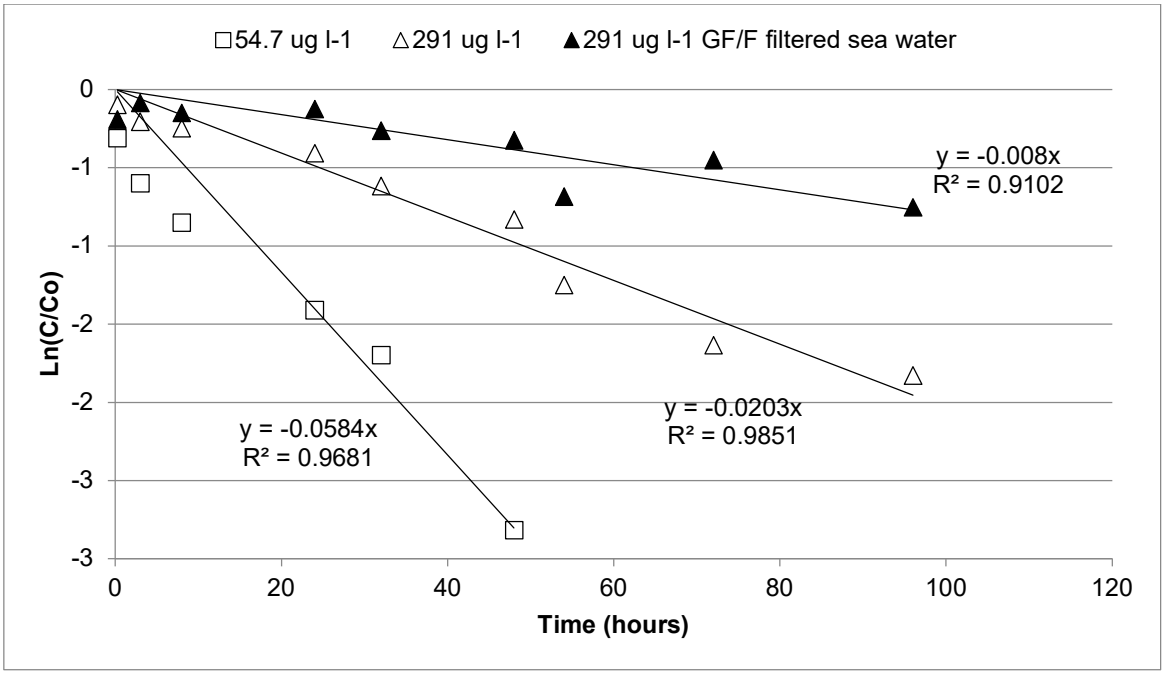

Figure 6 Kinetics of hydrazine degradation for starting concentrations of 54.7 and 291 ug l^{-1} as well as a GF/F filtered sea water sample spiked with 291 ug l^{-1} for volume: 4 L, pH: 8, suspended matter: 46 mg l^{-1}, temperature: 15±2ºC, continuously stirred.

Table 1. Half-Life (hours) of hydrazine added to sea water sampled from offshore at Sizewell

Theoretical initial concentration	291 ug l^{-1}	54.7 ug l^{-1}	291 ug l^{-1} in seawater following filtration through GF/F filter
Measured hydrazine concentration 15 minutes after spiking	263	40	240
Half –Life (hours)	34.15	11.87	86.64
Degradation rate h^{-1}	0.0203	0.0584	0.008

5 Discussion

The objective of this study was to establish hydrazine decay rate in Sizewell sea water so that these data could be used to model the behaviour of hydrazine in the cooling water discharge plume. During the first 3 hours following hydrazine addition at the lowest concentration of 54.7 µg l^{-1} there is a rapid decrease in concentration to 45% of the original concentration applied (**Figure 4**). The lower rate of degradation in GF/F filtered (0.7µm) sea water has also been demonstrated previously but for sea water filtered through 0.22 µm in which degradation was reduced to one tenth of that of unfiltered samples (Environment Canada, 2010). Bacterial abundance has been demonstrated to be an important determinant of degradation in water (Ou and Street, 1987) as have colloidal matter and humic and fulvic acids and complexed metal ions such as copper which may also enhance the degradation rate and would be reduced by filtration. Copper concentrations in sea water in the vicinity of Sizewell are in fact close to those that have been shown to enhance hydrazine degradation rate and so may have had some influence (Moliner and Street, 1989, BEEMS Technical Report TR131).

6 Conclusions

The fate of hydrazine in the aquatic environment is dependent on dilution/dispersion and chemical and biological degradation as well as processes such as volatilisation and sedimentation (Kuch, 1996).

Based on the most conservative decay rate in un-filtered natural seawater derived in this study (i.e. 291 µg l^{-1}, half-life ca., 34 hours) a decay rate of 6 x 10^{-6} s^{-1} was taken forward for operational hydrazine discharge plume modelling.

7 References

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8 Appendix Raw data

Hydrazine degradation data used for calculation of half-life values:

Table (i) degradation of hydrazine in seawater after spiking nominal 300 ug l^{-1} triplicates (3 different beakers) : a, b, c

time (hours)	time (minutes)	replicate (a)	b	c
0.25	15	270	260	260
3	180	260	230	220
8	480	220	250	210
24	1440	170	190	220
32	1920	170	130	170
48	2880	120	110	150
54	3240	130	90	30
72	4320	80	70	20
96	5760	60	40	40

Table (ii) degradation of hydrazine in seawater after spiking nominal 50 ug l^{-1} triplicates (3 different beakers) : a, b, c

time (hours)	time (minutes)	replicate (a)	b	c
0.25	15	40	40	40
3	180	30	30	30
8	480	20	20	30
24	1440	10	10	20
32	1920	10	10	10
48	2880	3.4	3	3.4
54	3240	1.6	4.5	0.5
72	4320	4.2	1.6	0.5
96	5760	3.5	0.5	5

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Table (iii) degradation of hydrazine in seawater after spiking nominal 300 ug/l into GF/F filtered sea water triplicates (3 different beakers) : a, b, c

time (hours)	time (minutes)	replicate (a)	b	c
0.25	15	240	250	230
3	180	270	280	250
8	480	250	270	230
24	1440	240	240	290
32	1920	220	230	220
48	2880	190	220	220
54	3240	190	200	50
72	4320	170		200
96	5760	120	140	150

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Table (iv) Mean concentration, standard deviation and 95 % confidence limits of hydrazine in seawater after spiking nominal 300, 50 ug/l in Sizewell sea water and 300 ug/l into GF/F filtered sea water triplicates (3 different beakers) : a, b, c

		mean	mean	mean	sdve	sdve	sdve	95% CI	95% CI	95% CI
Time (hours)	Time (minutes)	300 ug/l	50ug/l	300ug/l (GF/F)	300ug/l	50ug/l	300ug/l (GF/F)	300ug/l	50ug/l	300ug/l (GF/F)
0	0	291	54.7							
0.25	15	263.3	40.0	240.0	5.8	0.0	10.0	24.84	0.00	43.03
3	180	236.7	30.0	266.7	20.8	0.0	15.3	89.57	0.00	65.73
8	480	226.7	23.3	250.0	20.8	5.8	20.0	89.57	24.84	86.06
24	1440	193.3	13.3	256.7	25.2	5.8	28.9	108.29	24.84	124.22
32	1920	156.7	10.0	223.3	23.1	0.0	5.8	99.37	0.00	24.84
48	2880	126.7	3.3	210.0	20.8	0.2	17.3	89.57	0.99	74.53
54	3240	83.3	2.2	146.7	50.3	2.1	83.9	216.58	8.89	360.87
72	4320	56.7	2.1	185.0	32.1	1.9	21.2	138.32	8.18	91.28
96	5760	46.7	3.0	136.7	11.5	2.3	15.3	49.69	9.86	65.73