Assessing the cumulative effects of washwater discharges from ships' open-loop exhaust gas cleaning systems on a receiving ecosystem

Graeme E. Batley[a*], Luke Kidd[b], Brad M. Angel[a], Martin Budd[c] and Stuart L. Simpson[a]

[a]*CSIRO Land and Water, Lucas Heights NSW 2232, Australia*

[b]*Royal HaskoningDHV, Newcastle, NSW 2300, Australia*

[c]*Royal HaskoningDHV, North Sydney, NSW 2060, Australia*

*To whom correspondence may be addressed (Graeme.batley@csiro.au)

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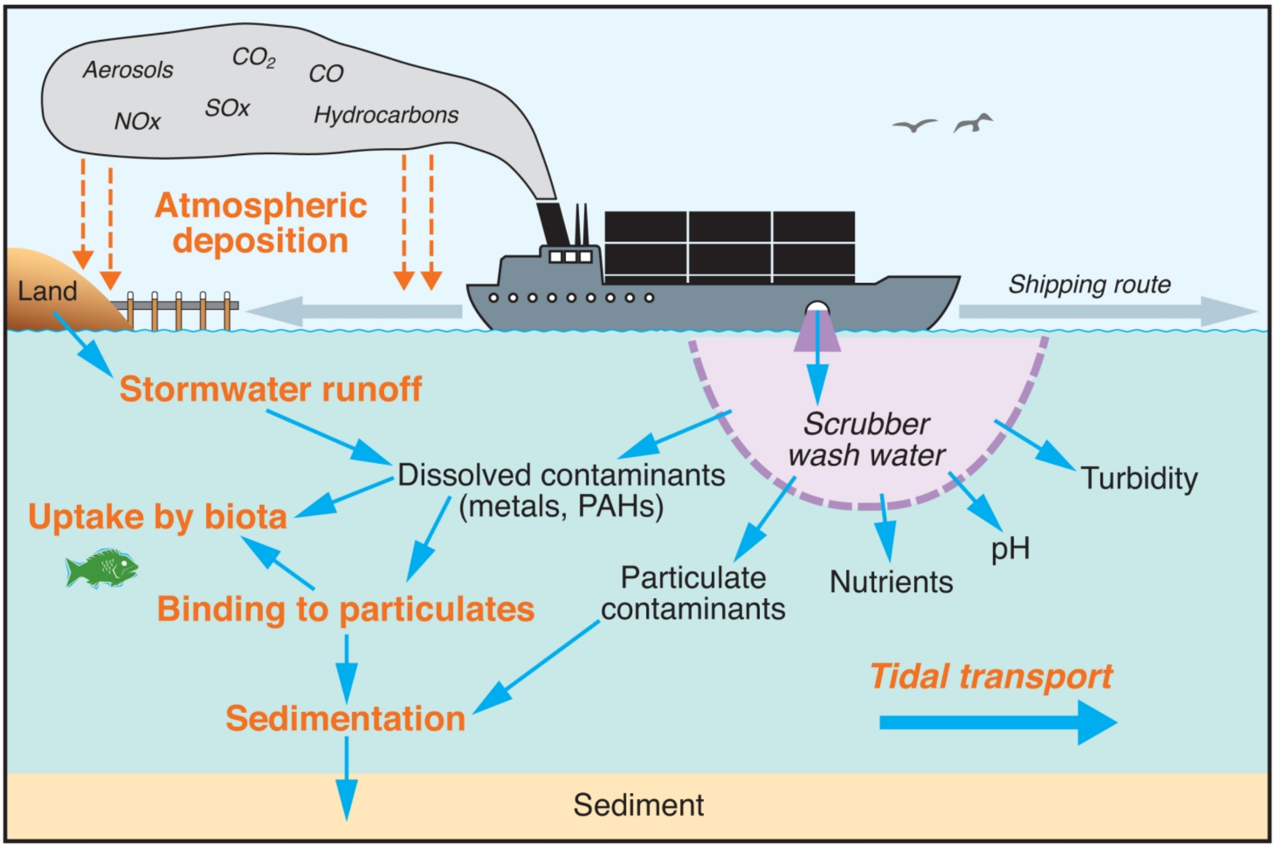
Highlights:

- Long-term ecosystem impacts of open-loop EGCS washwater discharges in a harbour port modelled and evaluated.
- Copper identified as a limiting contaminant.
- Safe dilutions of washwaters calculated from ratios of discharge data to guideline values.
- Shipping washwater contributions to Sydney harbour waters and sediments are negligible

Capsule Abstract

Modeling of long-term impacts of shipping washwater contaminants on harbour ecosystem health based on an Australian database of discharge concentrations indicated negligible impacts on harbour ecosystem health.

Graphical Abstract



ABSTRACT

The potential long-term impacts of washwater discharges from open-loop exhaust gas cleaning systems (EGCS) on ships in an urban harbour port have been examined. Measured washwater contaminant concentrations when compared against water quality guideline values (WQGVs) identified copper as the contaminant of greatest concern. A three-dimensional (3D) hydrodynamic and advection-dispersion model was used to evaluate the mixing and accumulation of effluent and contaminants from EGCS discharges over time from ships with engines running in port, taking into account the types of ships and volumes of traffic and tidal flushing. Using a conservative worst-case scenario, both near-field and far-field modelling for a representative harbour port, White Bay in Sydney Harbour, it was demonstrated that after 28 days, a combined near- and far-field dilution of between 1 in 1000 and 1 in 3600 would be achieved compared to a dilution of 1 in 52 required to comply with the WQGV for copper.

A 3D flushing box model of Sydney Harbour predicted that long-term (ten-year) EGCS washwater discharges would not result in tracer concentration accumulation, with flushing by tides and catchment rainfall ensuring that the washwater is readily mixed and diluted in the harbour. Predicted increases in harbour copper concentrations over 10 years due to washwater were 0.006 µg/L or <0.5% of the WQGV.

Our conservative estimates considered all contaminants to be in dissolved forms and ignored any partitioning to particulates and subsequent accumulation in bottom sediments. There was no evidence, however, of increases in contaminant concentrations in sediments, in particular of EGCS marker elements nickel and vanadium.

Overall, our results indicate that the EGCS washwater contaminant inputs will make a negligible contribution to any exceedance of WQGVs in White Bay and the greater Sydney Harbour.

1. Introduction

There is a worldwide concern for the potential long-term impacts of the use by ships of exhaust gas cleaning systems (EGCSs), to achieve compliance with the sulfur oxide (SOx) emission regulations of the International Convention for the Prevention of Pollution from Ships (MARPOL) Annex VI. To address this issue in relation to Australian ports, a detailed investigation was undertaken involving numerical modelling of the mixing of representative washwater discharges from multiple ships with engines running and open-loop EGCSs operational within a port, taking into account tidal flushing. The study focussed on White Bay in Sydney Harbour, Australia.

Cruise ships at berth in Sydney Harbour have been required, since the end of 2016, to use 0.10% low sulfur fuel ,or an equivalent method, such as EGCSs with higher sulfur fuels, to comply with a direction from the Australian Maritime Safety Authority (AMSA) (https://www.amsa.gov.au/marine-environment/air- pollution#collapseArea468), whereas all other ship types visiting Sydney Harbour have been permitted to use EGCSs since the global 0.50% sulfur limit took effect on January 1, 2020.

The specific objectives of the study were to:

(i) Determine representative EGCS washwater discharge volumes and associated effluent and contaminant concentrations for the types and operations of international ships in an Australian port.

(ii) Model (by application of a three dimensional (3D) hydrodynamic and advection-dispersion model) the mixing and accumulation of effluent and contaminants from EGCS discharges over time in the study area, taking into account the types of ships and volumes of traffic.

(iii) Assess whether modelled effluent and contaminant concentrations (represented as a conservative tracer) exceed identified or derived water and sediment quality guideline values (GVs) and are likely to result in long-term impacts on the aquatic environment.

Contaminants typically measured in washwaters are shown in Table 1. Based on these previous studies, metal contaminants were found to be of greatest concern with nickel, vanadium, copper and zinc being variously highlighted.

Table 1. International data for contaminant concentrations in EGCS washwaters

Study	Reference	Fuel oil sulfur content	Turbidity at outlet (NTU)	pH	PAH (phenanthrene) (µg/L)	Nitrate (mg/L)	Nitrite (mg/L)	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	V (µg/L)	Zn (µg/L)
Danish high load unfiltered	Kjoholt et al., 2012	2.2	-	3.7	0.96 TPAH	0.56 TN		<1	<0.2	-	260	43	21	180	450
		1.0	-	5.5	1.8 TPAH	0.36 TN		<1	<0.2	-	110	19	5.8	49	110
Danish low load unfiltered		2.2	-	5.2	1.1 TPAH	0.34 TN		1.8	<0.2	-	150	20	3.6	81	150
		1.0	-	5.8	1.6 TPAH	0.22 TN		<1	<0.2	-	150	9.1	3.8	25	98
Japan low load	MEPC, 2019		13.6	3.5	<0.005	-		0.03	0.03	-	3.0	18	1.4	39	17
Japan high load unfiltered					0.006	-		1.02	0.04	-	8.1	18	1.8	58	48
Netherlands[a]	Faber et al., 2019				2.0	-		6.4	1.9	18	250	120	0.2	140	320
Sweden filtered	MEPC, 2020					0.18			<0.5		14	32	0.63		82
	Magnusson et. al., 2018 (from Schmolke et al., 2020)			-	-	-			-		6-140	20-240	-		20-2000
Copenhagen Harbour unfiltered	Koski et al., 2017		-	-	-	-		1.4	-	1.9	21	41	0.61	162	6.7
Germany Unfiltered[b]	Schmolke et al., 2020			2.8-5.2	1.61	0.6	0.3	1-7	0.01-0.07	-	1-16	6-73	0.09-2.2	12-313	2-133

[a] Average total (net) concentrations post EGCS tower and before any post-treatment; [b] Dissolved concentrations only marginally lower

2. Methods

2.1 The site

White Bay is located within Port Jackson (Sydney Harbour), New South Wales, approximately 10 km from the entrance to Sydney Harbour (**Error! Reference source not found.**). It is the site of one of only two deep-water wharf locations in Sydney Harbour that are west of the Sydney Harbour Bridge. The deep-water wharves are used for a variety of port uses, including bulk vessel loading and vessel repairs and a cruise terminal. The area's use as a shipping port for container ships commenced around 1969; before this time, the area included a sawmill, a soap manufacturer and a coal-fired power station.

The White Bay port facility incorporates four operational berths and two berths used as lay-up berths. The port facilities are currently used as a cruise ship terminal, for unloading/loading of bulk vessels, as a marine refuelling facility, and for other *ad hoc* port and working harbour use. Operating since April 2013, the White Bay Cruise Terminal is situated at the northern end of White Bay (Sydney Ports Corporation and URS Australia, 2003).

Figure 1. White Bay in Sydney Harbour

2.2 Tidal hydrodynamics and coastal processes

Circulation within the Sydney Harbour estuary is tide-dominated with some influence from the dominant swell and wind waves that enter past the entrance headlands. Tidal velocities follow the semi-diurnal tidal pattern, with varying magnitude depending on the location within the estuary and the moment over a tidal period (Hedge et al., 2013).

Typical for a tide-dominated estuary, the harbour is well flushed near the opening but poorly flushed at the upper riverine reaches. Water residence time in the main harbour body varies from <20 days and up to 130 days towards the upper reaches. Due to its physical shape and sheltered position, White Bay is relatively protected from most wind and swell wave events.

2.3 Concentrations of contaminants in washwaters

A large dataset of contaminant concentrations in EGCS washwaters for ships using Australian ports was supplied by AMSA (Supplementary Information Table S1). This largely comprised data for bulk carriers (n=139) and cruise ships (n=65), with smaller entries for chemical and oil carriers, woodchip carriers, fully cellular container ships, multipurpose, heavy-lift, ore carriers, product carriers, tankers and Ro-Ro ships. A second large dataset (n=280) for cruise ships only was later supplied by Carnival Corporation.

2.4 Determining required washwater dilutions for compliance with guideline values

The measured contaminant concentrations in the EGCS washwaters were evaluated to determine which contaminant(s) required the greatest dilution in the receiving waters, in order for them to comply with water quality guideline values (WQGVs). In Australian and New Zealand, WQGVs for 95% species protection apply to slightly to moderately disturbed waters such as White Bay (ANZG, 2018) (these GVs are based on chronic toxicity data). The dilutions required for the limiting contaminant(s) were then compared with the predicted dilutions generated from the application of numerical models to determine whether washwater discharges posed a threat to ecosystem health.

2.5 Numerical modelling of washwater discharges

Numerical modelling involved two major components, near-field (ca. 10s of metres from vessels) and far-field (distances greater than near-field). Based on the review of available data and information, the following assumptions were adopted to schematise a worst-case EGCS washwater discharge scenario within the White Bay study area:

1. 100% of vessels are assumed to have EGCS installed and operational.
2. 'Ship-to-shore' power is not used. EGCSs are used 100% of the time when in port.
3. To account for higher engine operation during manoeuvring on arrival/departure, the washwater discharge rate for the hour preceding and following a vessel being berthed was

assumed to be 700 m^3/h. While at berth, the washwater discharge rate was assumed to be 300 m^3/h.

4. Five separate point source EGCS-discharge inputs were defined to coincide with the five berths at White Bay, namely:
    a. White Bay 3
    b. White Bay 4
    c. White Bay 5 (also known as White Bay Cruise Terminal)
    d. Glebe Island 7, and
    e. Glebe Island 8.
5. The occupancy of berths observed during January 2019 were used to provide the pattern of berthing occupancy.

2.5.1 Short-term (near-field) modelling

In the near field, the motion of the washwater is dominated by its initial momentum and buoyancy; the velocities and rates of dilution will be high near the washwater outlet. Near-field plume behaviour is generally dominated by the turbulence which results from buoyant jet mixing, or the vessel's hull and propeller when it is in motion, and usually occurs in short space and time scales (less than 1 to 100s of metres; several seconds to a few hours). For stationary vessels which were considered by this assessment, an estimate of the initial dilution in the near field is important. The JETLAG modelling program was used to estimate the dilution of EGCS washwater occurring at the sub-grid model scale (i.e., the initial dilution occurring over the first 10-20 m after discharge). Two sub-scenarios were simulated to investigate the influence of ambient conditions (stratification and current velocity) on the initial mixing of washwater. The initial dilution of EGCS washwater discharge was modelled for the following conditions:

1. Stratified water column and ambient current velocity of 0.005 m/s, and
2. Unstratified water column and ambient current velocity of 0.005 m/s.

Modelling inputs were defined to represent a single EGCS washwater discharge from a stationary vessel in White Bay. EGCS manufacturers expect initial dilutions of less than 1 in 10 under these stationary conditions (MEPC, 2021).

The following assumptions were adopted:

- Depth of water = 10 m (based on hydrographic survey data)
- Depth of washwater outlet = 2.5 m (assumed below the water surface)
- Outlet angled downward 30^{o} from the horizontal plane (assumed)
- Diameter of outlet = 200 mm (assumed; a smaller diameter will achieve greater dilution due to higher exit velocities)
- Ambient conditions (typical conditions based on application of the SHERM):
    - Salinity = 30 PSU (unstratified condition) and 5 PSU (stratified condition)
    - Water temperature = $20^{o}C$
    - Velocity = 0.005 m/s
- Washwater conditions:
    - Salinity = 30 PSU (unstratified condition) and 5 PSU (stratified condition)
    - Water temperature = $24^{o}C$ ($4^{o}C$ above ambient)
    - Discharge = 300 m^3/h = 0.0833 m^3/s

2.5.2 Medium-term (far-field) modelling (over a one-month duration)

Far-field hydrodynamic models simulate non-steady flows and can be applied to compute the far-field behaviour of the plume and recirculation effects. For this study, the far-field model best provides information about the mixing and fate of the washwater beyond the initial mixing zone, i.e., where it is transported to and how it behaves within the broader receiving environment.

Far-field processes were modelled using the Sydney Harbour Ecological Response Model (SHERM) (Freewater et al., 2014) to assess the advection and dispersion (mixing) and fate of EGCS washwater beyond the initial mixing zone released at White Bay for a worst-case discharge scenario.

Inputs to the modelling exercise relate particularly to the tidal characteristics of the White Bay area, the predicted washwater contaminant concentrations and the characteristics of port usage.

Based on a review of available data and information, the following additional assumptions were adopted to schematise a worst-case EGCS washwater discharge scenario within the White Bay study area:

1. Five separate point source EGCS-discharge inputs were defined to coincide with the five berths at White Bay, namely:
    a. White Bay 3
    b. White Bay 4
    c. White Bay 5 (also known as White Bay Cruise Terminal)
    d. Glebe Island 7, and
    e. Glebe Island 8.
2. During a single month:
    a. at least one vessel will be berthed in White Bay each day

b. up to 5 vessels will be berthed on any one day, and
c. the occupancy of berths observed during January 2019 will be used to provide the pattern of berthing occupancy.

2.5.3 Long-term (box) modelling (over a ten-year duration)

Additional modelling over a ten-year duration was completed for Sydney Harbour using an efficient 3D flushing box model of Sydney Harbour (SHBM), as described by Freewater et al. (2014, 2018). The SHBM was developed with hydrodynamic forcing from the same high-resolution model used for medium-term far-field modelling, but the hydrodynamic fluxes were aggregated into 33 compartments (Figure S2) which cover the extent of Sydney Harbour and reflect the varying hydraulic characteristics of different sections of the estuary.

The tide, wind and hydrological inputs into the SHBM are identical to the high-resolution far-field model. The SHBM was calibrated for transport-dispersion to replicate salinity gradients from the high-resolution model during recovery of the Sydney Harbour estuary after a wet weather event.

The SHBM model was set up to run for a continuous 10-year period, using a time series of daily EGCS discharges into White Bay. Modelling the transport-dispersion over a synthetic 10-year period was achieved by creating a sequence of different hydrological conditions, namely a wet year (85th-percentile annual rainfall used for 2 of the 10 annual periods), an average year (close to median annual rainfall used for 6 of the 10 annual periods) and a dry year (5th-percentile annual rainfall used for 2 of the 10 annual periods).

The SHBM was run for two EGCS discharge scenarios:

(i) the first (Base Case) had a constant annual discharge into White Bay, and

(ii) in the second scenario, the annual discharge volume gradually increased over the 10-year simulation until it was 20% higher than the Base Case in the final simulation year.

3. Results and Discussion

3.1 Washwater discharge composition

Table 2 summarises the total contaminant concentrations in washwater discharges supplied by AMSA (AMSA dataset) (the full dataset is in the Supplementary Information Table S1). Data included values for pH, turbidity, PAHs, nitrate and nitrite and a full suite of metals.

Table 2. Summary of analyses in the AMSA dataset for contaminant concentrations in EGCS washwaters

	Fuel oil sulfur content (%)	Turbidity at outlet (NTU)	pH	PAHs (µg/L) [a]	Nitrate (mg/L)	Nitrite (mg/L)	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	V (µg/L)	Zn (µg/L)
Bulk carriers (n = 139)														
Average (<3σ)	2.5	2.2	3.7	0.68	3.0	0.26	3.1	0.40	11	25	47	3.9	144	106
Minimum (<3σ)	1.5	0.19	2.5	0.019	0.02	0.005	0.1	0.1	1.0	0.1	1.0	0.1	2.0	0.1
Maximum (3σ)	3.4	11	6.8	2.1	15	1.2	10	1.0	95	207	240	20	555	750
95^{th} percentile (<3σ)	**-**	**7.3**	**6.5**	**1.7**	**14**	**-**	**10**	**-**	**77**	**151**	**185**	**18**	**418**	**370**
90^{th} percentile (<3σ)	3.4	4.9	5.9	1.5	13	1.2	7.4	1.0	27	64	118	14	350	307
Average (<3σ, plus screening)[b]	2.5	2.2	3.7	0.68	3.0	0.26	3.1	0.4	11	17	41	3.8	138	63
Minimum (<3σ, plus screening)	1.5	0.19	2.5	0.02	0.02	0.005	0.1	0.1	1.0	0.10	1.0	0.1	2.0	0.1
Maximum (<3σ, plus screening)	3.4	11	6.8	2.1	15	1.2	10	1.0	95	115	194	20	441	201
95^{th} percentile (<3σ, plus screening)	**-**	**7.3**	**6.5**	**1.7**	**14**	**-**	**10**	**-**	**77**	**67**	**137**	**18**	**416**	**186**
90^{th} percentile (<3σ, plus screening)	3.4	4.9	5.9	1.5	13	1.2	7.4	1.0	27	41	106	14	335	134
Cruise ships (n = 65)														
Average (<3σ)	2.1	-	5.7	1.0	0.23	0.11	2.3	0.1	2.9	5.9	14	3.3	36	16
Minimum (<3σ)	1.0	-	3.4	0.01	0.01	0.005	0.1	0.1	0.10	0.10	0.10	0.1	0.80	0.3
Maximum (<3σ)	3.2	-	7.1	3.6	1.4	1.1	5.2	0.1	15	35	100	18	298	52
95^{th} percentile (<3σ)	**3.2**	**-**	**6.8**	**3.1**	**1.2**	**0.30**	**5.2**	**0.1**	**10**	**19**	**73**	**10**	**79**	**50**
90^{th} percentile (<3σ)	3.2	-	6.4	2.1	0.50	0.30	5.2	0.1	10	10	30	10	66	41
ALL SHIPS														
Average (<3σ)	2.3	3.0	4.6	1.3	2.0	0.5	3	0.9	8	17	41	4	152	81
Minimum (<3σ)	1.0	0.19	2.5	0.005	0.05	0.01	0.10	0.1	0.10	0.10	0.10	0.1	0.80	0.10
Maximum (<3σ)	3.4	16	8.5	19.4	20.4	7.9	56	10	100	207	660	38	3470	1200

	Fuel oil sulfur content (%)	Turbidity at outlet (NTU)	pH	PAHs (μg/L) [a]	Nitrate (mg/L)	Nitrite (mg/L)	As (μg/L)	Cd (μg/L)	Cr (μg/L)	Cu (μg/L)	Ni (μg/L)	Pb (μg/L)	V (μg/L)	Zn (μg/L)
95th percentile (<3σ)	**3.3**	**11**	**6.7**	**5.9**	**13**	**2.4**	**9**	**2**	**36**	**92**	**178**	**17**	**441**	**354**
90th percentile (<3σ)	3.2	8.1	6.4	2.4	8.9	0.9	5	1	17	36	98	10	331	201

[a] PAHs were represented by phenanthrene equivalents (MEPC, 2015). [a] Screening involved removing high concentrations from the dataset before calculation of the average ±3σ criteria as they were expected to be due to contamination during sampling or from particulates in unfiltered samples; concentrations higher than 300 μg/L for Cu (n=2) and V (n=7) and 500 μg/L for Zn (n=2) were removed.

To be able to reliably use the AMSA data, there were several important screening considerations, including: (i) potential sample contamination during collection and handling, (ii) detection limits of the analytical methods and (iii) discrimination between dissolved and total metal concentrations.

A detailed review of both the AMSA and Cruise-line datasets showed that in many instances, a concentration could not be measured above the detection limit (DL) and the results were reported as <DL, however, in the case of copper, the DLs were variously reported as 100, 50, 10 and 1 µg/L. The usual procedure of using the DL or DL/2 in evaluating the data is not reliable where the DL is 100 or 50, so our approach was to ignore these values. In many cases, concentrations were at or below the laboratory reporting limits, however, these limits were highly variable, depending on the laboratory and analytical methods used. Results quoted as less than what we consider to be an overlying high reporting limit, e.g., <10 or <20 µg/L for metals, were not used, whereas metal concentrations of <1 µg/L and below were recorded as 1 µg/L.

There was a small number of samples where the reported metal concentrations were far higher than most of the other data. For example, from 200-700 µg Cu/L or 700-1300 µg Zn/L. This prompted questions of whether they represent a highly contaminated discharge, were they contaminated during collection, and should these outlier data be included in evaluating the dataset as an input to the modelling exercise? Following accepted practice, all values that were above 3 standard deviations (3σ) of the mean of the dataset were discarded. There were, however, a minority of instances where the ranges of total metal concentrations reported elsewhere were exceeded, e.g., the highest reported values were 260 µg Cu/L, 240 µg Ni/L, 860 µg V/L and 2000 µg Zn/L (the value for zinc seemed abnormally high and was possibly sampling contamination, zinc being a ubiquitous metal contaminant that requires special care in sample bottle preparation and sample collection). Concentrations higher than these values are rarely reported and are unexpected so a set of screening values (typically 300 µg/L) was used to further screen these apparent abnormalities, based on best professional judgement.

Using the AMSA data for bulk carriers and cruise ships, the 95th percentiles of the discharge concentrations were calculated in keeping with the recommendation for comparing measured concentrations to guideline values given by the Australian and New Zealand guidelines for fresh and marine water quality (ANZG, 2018). It is important to note that the use of the 95th percentile concentrations differs from what was done in other studies, e.g., Faber et al. (2019), where the average concentrations were used, which are much less conservative. In the case of bulk carriers, which gave rise to the greatest number of aberrant values, 90th percentile values were also considered. Concentrations often decreased rapidly as the percentile was decreased due to the relatively small number of high contaminant concentrations.

Focussing on copper (which as we will show later is the critical toxicant in dilution calculations), the 95th percentile concentration for bulk carriers after removing outliers was 151 µg Cu/L. The remaining bulk carrier data contained several values that could be considered excessive, and probably the result of contamination during sampling or the presence of particulate contamination. Given that we had no dissolved concentrations measured to confirm this, two options were used to remove these data: (i) use a lower percentile of the dataset or (ii) screen out values above a certain high concentration. Using the first option, the 95th percentile reduced from 151 to 64 µg/L for the 90th percentile. For the second option, a value of 300 µg/L was chosen above which two copper data were removed, after which the 95th percentile dropped to 67 µg/L (and the 90th percentile to 41 µg/L).

For cruise ships in the AMSA dataset, the 95th percentile value with statistical outliers (3σ) removed, was 19 µg/L. This can be compared with the analysis (Table 3) of the separate Cruise-line dataset, where a value of 37 µg/L was obtained for total copper and 25 µg/L for dissolved copper, where data >1000 µg/L were removed.

The chosen target concentration for copper, based on the above AMSA data was 67 µg/L as the highest corrected copper concentration.

A summary of the Cruise-line dataset for metal contaminants in washwaters is given in Table 3. Applying the same criteria as we did for the AMSA data, a much lower copper concentration of 25 µg/L dissolved and 37 µg/L total. The higher AMSA target concentration was therefore used in the assessment of risk.

Table 3. Analysis of the Cruise-line dataset (n=280) for metal contaminant concentrations in EGCS washwaters

	Total Cu	**Diss Cu**	**Total Ni**	**Diss Ni**	**Total V**	**Diss V**	**Total Zn**	**Diss Zn**
					µg/L			
Average (<3σ)	39	15	34	20	82	54	24	15
Minimum (<3σ)	0.02	0.00	1.0	0.90	1.0	1.0	0.10	0.48
Maximum (<3σ)	4360	1370	838	515	781	487	657	648
95th percentile (<3σ)	**50**	**39**	**131**	**78**	**262**	**179**	**114**	**69**
90th percentile (<3σ)	29	19	80	44	190	139	48	35
Average (<3σ, plus screening) [a]	10	5	25	16	72	49	13	10
Minimum (<3σ, plus screening) [a]	0.02	0.02	1.0	0.90	1.0	1.0	0.10	0.48
Maximum (<3σ, plus screening) [a]	261	81	185	143	386	234	247	176
95th percentile (<3σ, plus screening) [a]	**37**	**25**	**97**	**60**	**224**	**149**	**70**	**59**

[a] Screening involved removing high concentrations from the dataset before calculation of the average ± 3σ criteria as they were expected to be due to contamination during sampling or from particulates in unfiltered samples; concentrations higher than 300 µg/L for TCu (n=6), dCu (n=2), TNi (n=4), dNi (n=3), TZn (n=6), dZn (n=4) and 500 µg/L for TV (n=5) and dTV (n=1) were removed. Concentrations that were higher than 1000 µg/L were excluded from the dataset before calculation of the average ± 3σ criteria as they were expected to be due to contamination during sampling; excluded values included three for TCu, two for dCu, TNi, dNi, and one for TV, dV, TZn, and dZn.

Ideally, we wanted to use dissolved contaminant concentrations for the assessment of washwater contaminants as particulate-associated contaminants have low bioavailability to aquatic organisms and are not relevant for GV comparison. In the case of the AMSA data (Table 2) and many of the other published concentrations, the reported data represent total metal concentrations (dissolved plus suspended particulates) with no dissolved concentrations. Just why occasional samples should have excessively high particulate contents is unclear, especially where open-loop EGCSs are being used (particulate concentrations reach higher values in closed-loop EGCS systems (Schmolke et al., 2020)).

Schmolke et al. (2020) reported data for 5 ships operating near Hamburg, Germany, where ultratrace sampling and analysis protocols were used to measure dissolved and particulate concentrations . They found that average dissolved concentrations represented 91, 84, 88 and 99% of the average total Cu, Ni, V and Zn respectively (Supplementary Information Table S2). Measured discharge pH values were in the range 4.2 to 6.0. The apparently low particulate metal concentrations may be in part due to the lowered pH values. By comparison, for our much larger Cruise-line dataset which included both total and dissolved concentrations (Table 3), the respective dissolved concentrations were 68, 62, 67 and 84%.

Further details on the breakdown between dissolved and particulate metals in an open-loop EGCS washwater are provided in reports by MEPC (2018) and the Sub-committee on Pollution Prevention and Response (2019). In these samples, the majority of the metals were also in dissolved forms, largely as a consequence of the mildly acidic pH of the washwaters.

Data on inlet water quality were available for both the AMSA and Cruise-line data. They included instances where the inlet seawater contained very high concentrations (e.g., >100 and up to 500 µg total Cu/L), but the dissolved concentrations in the outlet water had the same values. These were outliers that exceeded reported background seawater concentrations (typically <10 µg Cu/L in ports and <1 µg Cu/L ocean water) and were approaching the solubility limit of copper in seawater (Angel et al., 2020) and these would distort the discharge water result. Schmolke et al.

(2020) noted that it is highly unlikely that EGCSs would be removing dissolved metals from inlet seawater, particularly since the pH would be lowered during scrubbing. It is more likely that this reflects contamination of the sample, a real issue for those not aware of the need for special handling techniques. For our study, we had background seawater metal concentrations for the White Bay site being modelled so this issue will not arise. In addition, data were also rejected where dissolved concentrations were ≥ total concentrations.

Although some reports have investigated the effects of ship power on discharge concentrations (Kjoholt et al., 2012; MEPC, 2019), these limited data showed an inconsistent increase in discharge concentrations with increasing power. Full details relating to engine type and power were not available for every entry in the AMSA dataset.

Metal concentrations in discharge waters will also depend on the fuel oil used by the ship. For example, the vanadium content of fuel oils was reported to vary from 150-400 mg/kg (MEPC, 2018).

Ships fitted with open-loop EGCSs may be fitted with a bleed-off treatment system that comprises washwater filtration and may involve pH adjustment. A comparison of analytical reports and the discharge data in the AMSA dataset, indicated that the data represented overboard discharge total concentrations, although the EGCSs may be fitted with the optional treatment module. By contrast, the Cruise-line data reported contaminant concentrations for inlet seawater and post-tower outlet, but not overboard discharge, although these data appeared in many of the original laboratory reports. Those include both total and dissolved data so can reveal additional useful information.

The AMSA data analysis presented in Table 2 revealed some interesting features:

(i) The pH values were quite variable (2.5 min to 7.1 max) with an average value of 4.5). This variation was greatest with bulk carriers with values as low as 2.6

(ii) The average turbidity for bulk carriers was 2.2 NTU, but this was not always recorded and could be as high as 11 NTU. Data on inlet water would be required to confirm that this was not the source of high turbidity in some waters.

(iii) Polycyclic aromatic hydrocarbon (PAH) concentrations were lowest with cruise ships and higher variability with bulk carriers from 0.021 µg/L up to 2.1 µg/L as phenanthrene equivalents.

(iv) Metal concentrations were also lowest with cruise ships. The average concentrations for all ship types were highest for vanadium, nickel, copper and zinc, consistent with findings from other international studies.

3.2 Evaluating measured washwater concentrations against water quality guideline values for key contaminants

3.2.1 Current guideline values

The benchmark concentrations of contaminants of concern in washwaters are defined in Australia by the Australian and New Zealand water and sediment quality GVs. These were fully documented in 2000 (ANZECC/ARMCANZ, 2000) but many have since been revised and updated (ANZG, 2018). These WQGVs are arguably the most advanced internationally, largely being derived from species sensitivity distributions (SSDs) of chronic aquatic toxicity data according to the protocols described by Warne et al. (2018).

The use of SSDs allows the calculation of WQGVs that are protective of a given percentage of species. Marine waters such as Sydney Harbour are considered to be slightly to moderately disturbed, and 95% species protection (PC95) values apply, whereas, in port areas that could be categorised as disturbed areas, it might be argued that 90% species protection values are appropriate, although the regulator would reason that the goal should be an improvement to the PC95 GVs. A listing of the current Australian and New Zealand default WQGVs is provided in Table 4.

Table 4. Australian and New Zealand default WQGVs for metal contaminants in marine waters

Guideline Value (GV)	As	Cd	Cr (III)	Cr(VI)	Cu	Ni	Pb	Hg	Tl	Se	V	Zn
						µg/L						
PC95 (2000)	-	5.5[b]	27.4	4.4	1.3	70	4.4	0.4[b]	17[c]	3[c]	100	15
PC90 (2000)	-	14	48.6	20	3	200	6.6	0.7	-	-	160	23
PC95 (2021)[a]	12					8.8	8.0				20	-
PC90 (2021)[a]	22					11	12				34	-

[a] Revised values using the latest data but not yet approved. All WQGVs are for dissolved (<0.45 µm filtered) concentrations.

[b]PC99 value recommended for Cd (0.7 µg/L) and Hg (0.1 µg/L)

[c] Low reliability (ANZECC/ARMCANZ, 2000)

Guideline values were available for all of the key contaminants. For the ANZG (2018) derivation, GVs were assigned as high, medium or low reliability. Values supplied for As(III) and As(V) were considered as low reliability and reported as environmental concern values, not default GVs, however, a more recent value has been derived (Golding et al., 2022). The GV for chromium(III) was considered of moderate reliability as it was derived using converted acute data. All other derivations were considered of high reliability. The criteria for deciding reliability have since been revised (Warne et al., 2018) and the vanadium GV derivation which had only six chronic LC50 values from a single study representing only three taxonomic groups, would now only be classified as low reliability.

The GV for vanadium is important as it is often the metal present at the highest concentration in the washwater. More recent toxicity data were available and these were used to derive revised GVs as listed in Table 4 (full derivation details given in the Supplementary Information Section S2).

Nickel is also a major washwater contaminant and a recent re-evaluation of the nickel marine WQGV (Gissi et al., 2020) has significantly lowered the values that were adopted in 2000 (Table 4).

There are no reliable Australian GVs for PAHs in marine waters. Although a moderate reliability value of 50 µg/L was available for naphthalene, the remaining PAH GVs were of low reliability, e.g., 0.6 µg/L for phenanthrene. There are no reliable marine GVs for PAHs available in Europe, Canada or the US.

Australian GVs are available for pH, turbidity and nitrate and nitrite concentrations in marine waters as shown in Table 5. There are no GVs for sulfate which is a natural constituent of marine waters.

Table 5. Australian and New Zealand guideline values and IMO EGCS limits for other contaminants

Nitrate and nitrite (µg/L)	Turbidity (NTU)	pH	Reference
5	0.5-10	8.0-8.4 (7.0-8.5 estuary)	ANZG (2018)
60 mg/L	<25	>6.5	MEPC (2015, 2018)

The 2015 Guidelines for Exhaust Gas Cleaning Systems (MEPC, 2015) stipulate the following discharge criteria for washwater from EGCS (reviewed in MEPC, 2018), but these are not necessarily as those derived in this study:

pH – The discharge washwater should have a pH of no less than 6.5 measured at the ship's overboard discharge with the exception that during manoeuvring and transit, the maximum difference between inlet and outlet of 2 pH units is allowed measured at the ship's inlet and overboard discharge. The pH discharge limit, at the overboard monitoring position, is the value that will achieve as a minimum pH 6.5 at 4 m from the overboard discharge point with the ship stationary.

Turbidity – To be <25 NTU (Nephelometric Turbidity Unit) above the inlet concentration without any dilution for pH control.

Nitrate – The washwater treatment system should prevent the discharge of nitrates beyond that associated with a 12% removal of NO_X from the exhaust or beyond 60 mg/L normalised for washwater discharge rate of 45 tonnes (t)/MWh whichever is greater.

PAHs – The maximum continuous PAH concentration is to be <50 µg/L phenanthrene equivalents (PAHphe) for a flow of 45 t/MWh above inlet concentration without dilution for pH. This is an unusual measure of PAH concentration as this is but one of a suite of PAH compounds. The document indicates that this is equivalent to a total PAH concentration of 310 µg/L. For 15 minutes in any 12 hours, the continuous PAHphe concentration limit may exceed the limit described above by up to 100%. This would allow for an abnormal start-up of the EGCS unit.

Australian and New Zealand sediment quality GVs (SQGVs) for key contaminants are shown in Table 6. Two values are shown, derived from an effects database as explained by Simpson et al. (2013). The lower value is used in regulation requiring further investigation if exceeded, while the upper value (SQG-High) represents a concentration above which there is a high probability of biological impacts (ANZG, 2018).

Table 6. Australian and New Zealand default SQGVs for metal and PAH contaminants in marine sediments

Sediment quality guideline value	**As**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Hg**	**Tl**	**Se**	**V**	**Zn**	**Total PAHs**
						mg/kg						
SQGV	20	1.5	80	65	21	50	0.15	-	-	-	200	10

Sediment quality guideline value	As	Cd	Cr	Cu	Ni	Pb	Hg	Tl	Se	V	Zn	Total PAHs
	mg/kg											
SQGV-High	70	10	370	270	52	220	1.0	-	-	50[a]	410	50

[a] Not an Australian and New Zealand value but the value of unknown reliability listed by Buchman et al. (2008)

3.2.2 Assessment of washwater contaminant concentrations against guideline values

To determine the dilutions required to reduce the discharged concentrations to a value that would be protective of organisms in the receiving ecosystem, the values from Tables 1 and 2 were compared to the Australian and New Zealand WQGVs for 95% species protection that applies to slightly to moderately disturbed waters (ANZG, 2018). The comparisons are given in Table 7. A review of the data shows that measured concentrations agree with previous studies that the contaminants of greatest concern are copper, nickel, vanadium and zinc, in that order. Discharge concentrations for arsenic and cadmium were below GVs, while lead and chromium were respectively 2 and 1.3 (Cr VI) or 8 (CrIII) times GVs. The PAHs as phenanthrene equivalent concentrations were all below acceptable IMO limits. There are no reliable Australian and New Zealand guideline values for PAHs, including phenanthrene. The turbidity at 11 NTU was well within the 25 NTU IMO limit. Nitrate discharge concentrations were frequently not detected but overall the 95th percentile concentrations at 13 mg/L were well below the IMO limit of 60 mg/L but above the low-reliability ANZECC/ARMCANZ (2000) value of 700 µg/L for marine waters. Nitrite concentrations were far lower.

Table 7. Required dilutions of washwaters for 95% species protection based on ratios of limiting concentrations to WQGVs

	Discharge concentrations (from the data sets) and required dilutions in parentheses calculated as the ratio of the discharge concentration to the WQGV)							
	Total Cu	Diss Cu	Total Ni	Diss Ni	Total V	Diss V	Total Zn	Diss Zn
AMSA Bulk carriers, µg/L [a]	151 (116)		185 (21)		418 (23)		370 (25)	
AMSA Bulk carriers, µg/L [b]	67 (52)		118 (13)		350 (19)		307 (20)	

	Discharge concentrations (from the data sets) and required dilutions in parentheses calculated as the ratio of the discharge concentration to the WQGV)							
	Total Cu	**Diss Cu**	**Total Ni**	**Diss Ni**	**Total V**	**Diss V**	**Total Zn**	**Diss Zn**
AMSA Cruise [a] ships, µg/L	19 (15)		73 (8.3)		79 (4.4)		50 (3.3)	
AMSA All ships, µg/L [a]	92 (71)		178 (20)		441 (25)		354 (24)	
AMSA All ships, µg/L [b]	36 (28)		98 (11)		331 (18)		201 (13)	
Cruise-line ships, µg/L [c]	37 (28)	25 (19)	97 (11)	60 (6.8)	224 (12)	149 (8.3)	70 (4.7)	59 (3.9)
WQGV, µg/L	1.3	1.3	8.8	8.8	18	18	15	15

[a] 95th percentile; [b] 90th percentile; [c] 95th percentile with values >1000 µg/L screened out

Overall, the recommended required dilution to have no contaminant concentrations exceeding GVs was calculated as 1 in 28 based on total copper concentrations, except for bulk carriers where a dilution of 1 in 52 was determined. This dilution factor for bulk carriers is a liberal estimate based on the fact that it is biased by the presence of particulate metals. The required dilution becomes 1 in 19 if based on dissolved copper concentrations. Note that while the AMSA data were provided by ships visiting Australian ports, the washwater samples were not necessarily taken (most likely not taken) while in Australian ports or waters. If we rely only on the AMSA dataset, the dilution limit is 1 in 15 for cruise ships.

It is important to consider dissolved and not particulate-associated contaminants as the dissolved forms are the most bioavailable (ANZG, 2018). Transport of dissolved contaminants will be different from that of particulate forms which will be lost from the water column to sediments over a shorter distance due to the binding to and settling of suspended sediments and other particulate matter.

3.3 Other shipping-related inputs

3.3.1 Antifouling systems

Antifouling paints are used on ship's hulls to prevent biofouling. Most paints in use today contain copper as the primary biocide, in some cases supplemented by organic biocides. Copper is designed to be released from the painted surface at a controlled release rate of ca 5-10 µg/cm^2/day (Lagerstrom et al., 2020). Srinivasan and Swain (2007) examined the release of copper from cruise ships at Port Canaveral in Florida, USA. The wetted hull areas ranged from 6 900 to 11 900 m^2 in the largest vessels. Based on a consideration of days in port, hull area and leach rate, they calculated that released copper could range from 69 to 572 kg/year (assuming a high leach rate of 17 µg/cm^2/day).

Turner et al. (2017) estimated that EGCS washwater discharges of copper were some 2.5 times greater than that from antifouled ships. Their calculations were based on a Ro-Ro vessel with a wetted hull area of 3,817 m^2 releasing 310 g Cu/day. The situation would be different, however, for a cruise ship with a hull area as high as 11 900 m^2. Considering an area of 1 m width around the hull, a concentration of dissolved copper was calculated to be 21 µg/L after 1 h. By contrast, a washwater discharge for cruise ships had a mean copper concentration of 7 µg Cu/L (Table 1). Clearly, the much larger hull size of a cruise ship is a factor. Assuming a standard antifouling paint leach rate of 5 µg/cm^2/day, a cruise ship is likely to contribute 600 g Cu/day compared to a washwater load of near 260 g Cu/day based on the concentration of 19 µg Cu/L from the AMSA data in Table 7, or 500 g Cu/day based on the Cruise- line data. This means that the antifouling paint contribution of copper from a cruise ship could be as much as twice that of the washwater copper contribution, the only difference being that it is already dispersed and diluted compared to the point source washwater discharge.

Marine growth protection systems are also used to prevent biofouling via seawater used in sea chests and internal pipework. Biocides typically include oxidants such as chlorine or hypochlorite (Growcott et al., 2016), although such chemicals have a relatively short half-life and the potential for impact of discharges on marine biota is likely to be localised and low (Batley and Simpson, 2020).

3.3.2 Treated sewage

Ships can discharge as much as 0.7 ML of treated sewage per day. The ability to discharge in port is governed by appropriate regulations. Under MARPOL, the discharge of sewage from ships is permitted 'if the ship has in operation an approved sewage treatment plant certified by the administration to meet the operational requirements referred to in regulation 9.2.1 of MARPOL Annex IV', however, local laws may prohibit discharge in ports or regulate to occur in designated port zones. With an approved treatment system, concentrations of nutrients and ammonia as major contaminants are acceptably reduced in any discharges (Hanninen and Sassi, 2009). The White Bay port complies with the MARPOL requirements.

3.4 Non-shipping-related inputs

In working harbours, there is a range of non-shipping contaminants, e.g., stormwater inputs, discharges from industrial and commercial facilities, petrochemical spills, nearby fuel storage depots, firefighting or firefighting training, non-point sources such as roads, parking lots, and storm drains, sewage treatment plant discharges and overflows, and both licensed and unlicensed discharges. These are largely localised contaminant impacts that are receiving increasing management attention and are more of a concern than EGCS discharges. Stormwater, in particular, is the major source of metal contaminants and PAHs to urban waterways such as Sydney Harbour, largely from road runoff.

3.4.1 Stormwater

There have been many studies of stormwater inputs to waterways (e.g., Ewart et al., 2018). As the main inputs frequently occur as rainfall driven events for short periods, their characteristics include the presence of a first-flush, peak concentration that contains dissolved contaminants such as zinc, copper and lead, associated with road runoff and derived from motor vehicles (brake linings and tyres). In addition, hydrocarbons, including PAHs derived from fuels, can be delivered via stormwater runoff from roads and other hardstand areas. The peak of particulate-associated contaminants appears slightly later in the event period and with a continuing rain event the concentrations then continually decrease. Depending on the size of the catchment and the drainage system, these contaminants can be funnelled into port areas to add to shipping-related contaminant concentrations.

There have been several studies of stormwater inputs to Sydney Harbour (Rochford, 2008; Birch and Rochford, 2010; Beck and Birch, 2011), although none have specifically addressed White Bay. Data from equivalent waterways provide some indication of the typical metal concentrations that might be found and the loads that might be expected from low- and high-flow storm events (Table 8). Notably, these did not include vanadium, an unlikely stormwater contaminant.

Measurements of PAH concentrations were undertaken earlier by Brockbank et al. (1999). Despite having two highly trafficked road sites in Sydney (Mascot and Gymea) average stormwater event concentrations for total PAHs associated with suspended sediment particulates ranged from 2.2 to 12.3 mg/kg (3.9 to 9.4 µg/L). These values were close to the SQGVs and did not represent a threat to aquatic biota.

Beck and Birch (2011) noted that in three Sydney estuary sub-catchments that they studied, the majority (>90%) of TSS, Cu, Pb and Zn was discharged during high-flow events, with much being transported seawards in freshwater plumes at the surface.

Table 13. Indicative contaminant concentrations in stormwater runoff entering Sydney Harbour

Site	Average dissolved metals, μg/L[a]					Reference
	Cd	Cu	Ni	Pb	Zn	
Hawthorn Canal (low flow)	0.5	6.6	3.0	0.8	3.0	Birch and Rochford, 2010
Hawthorn Canal (high flow)	2.3	3.8	3.0	0.3	43	Birch and Rochford, 2010
Dobroyd Canal (low flow)	0.5	6.6	3.0	0.7	22	Birch and Rochford, 2010
Dobroyd Canal (high flow)	2.2	6.5	3.0	2.0	49	Birch and Rochford, 2010
Garden Island (site G2)[b]	0.4	34	11	12	62	Kjoerstad, 2008
Garden Island (site G5)[b]	0.6	26	5	9	35	Kjoerstad, 2008

[a] Particulate concentrations were on average 30-60% of total except for Pb which was >90%

[b] Results are total metals (dissolved + particulate)

While loads of contaminants from a storm event can be high, the average concentrations of metal and PAH contaminants observed in many road runoff studies demonstrate short-term first flush concentrations with average event concentrations only marginally above GVs. These will cause short-term (hours-days) increases in turbidity and reductions in salinity throughout the harbour system. Overall, the added stormwater contaminant concentrations are likely to be below those in the EGCS discharges.

3.4.2 Licenced discharges

State regulatory agencies licence discharges from an industry that could impact port waterways. These are usually carefully controlled by an imposed receiving area monitoring program, such that the impacts of associated contaminants are minimised.

3.4. Atmospheric deposition

Atmospheric deposition is a contributor of metals (mainly copper, zinc and lead) together with nitrate and sulfate and acidity. The concentrations of these will be site-specific, related to emissions from multiple sources, including the transport of particulates associated with roads and soils, as well as with shipping and other exhaust emissions. Both wet and dry deposition sources contribute. Davis and Birch (2012) reported a comprehensive survey of the deposition of copper, lead and zinc in metropolitan Sydney. Daily deposition rates were calculated as 28-342 µg Cu/m^2, 238-1780 µg Zn/m^2, 22-144 µg Pb/m^2 and 58-387 µg total $particulates/m^2$, with concentrations ranging from low to very high correlated both the population and traffic density. Many of the deposited metals will be in insoluble, non-bioavailable forms. Using the upper value for copper deposition and the area of White Bay, resulted in an estimated copper concentration in surface waters of White Bay from atmospheric deposition of 34 µg/L, more significant than washwater concentrations.

3.5 Modelling of washwater discharges

3.5.1 Near-field modelling

Near-field plume behaviour is generally dominated by turbulent jet mixing and usually occurs in short space and time scales (less than 1 to 100s of meters; several seconds to a few hours). Generally, the plume behaviour in the near field is controlled by the source properties (close to the discharge) and can be influenced by discharge design and configuration.

The near-field model (JETLAG) calculates how a discharge mixes in the receiving water. The near-field model estimates a 1 in 18 dilution within 10 metres of the discharge location. Beyond the near-field mixing zone, the washwater would be subject to far-field mixing processes and transport in the broader receiving environment.

3.5.2 Far-field modelling

Two far-field scenarios were examined: (i) a dry weather period, (ii) a wet weather period.

Dry weather discharge scenario

The following provides a summary of draft modelling results for the dry weather discharge scenario. Spatial (surface maps) and temporal (time series) results are reported at selected reporting locations (A to J) as shown below in Figure 2.

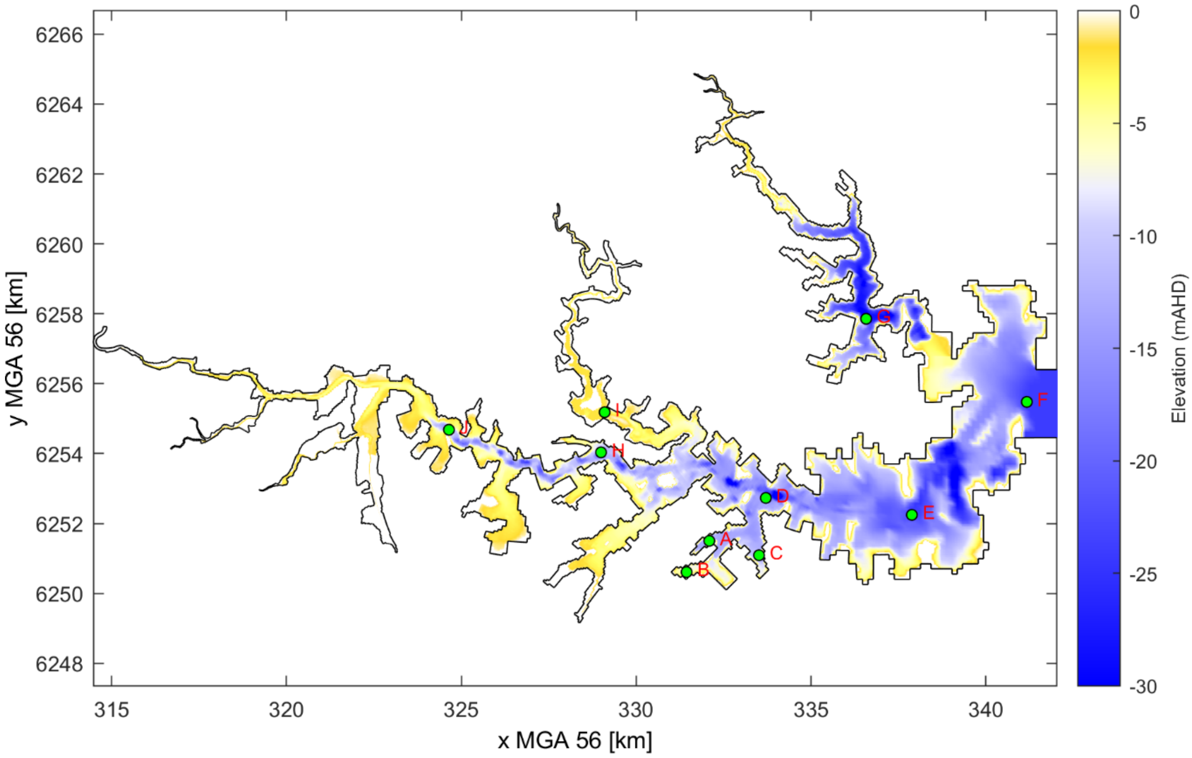


Figure 2. White Bay model domain, reporting locations and bathymetry elevation (Z)

A map showing the dry weather extent and concentration of the tracer (to represent the mixing and dilution of washwater contaminants) released at White Bay is presented in Figure 3. Time series results are also provided below to show the concentration of the EGCS tracer near the surface, mid-depth and near bed at selected locations in Port Jackson.

The tracer concentration is presented as the percentage of the initial concentration (100 000 mg/L) applied at the EGCS discharge boundary condition. By way of example, the tracer concentration at reporting Site B was approximately 1% which means the concentration of an EGCS contaminant was estimated to be 0.01 times the concentration at the discharge site (or there would be a 100-fold dilution of the concentration after near-field dilution has occurred). Similarly, at reporting Site D, the tracer concentration was approximately 0.1% which means there had been a 1 000-fold dilution of the initial discharge concentration at this location. Examples of a time series of tracer concentrations at different sites are shown in Figure 4. It can be seen that, apart from occasional differences, the far-field dilution modelling indicated negligible differences in the dilution of the EGCS in the near-surface, middle and near-bottom depths.

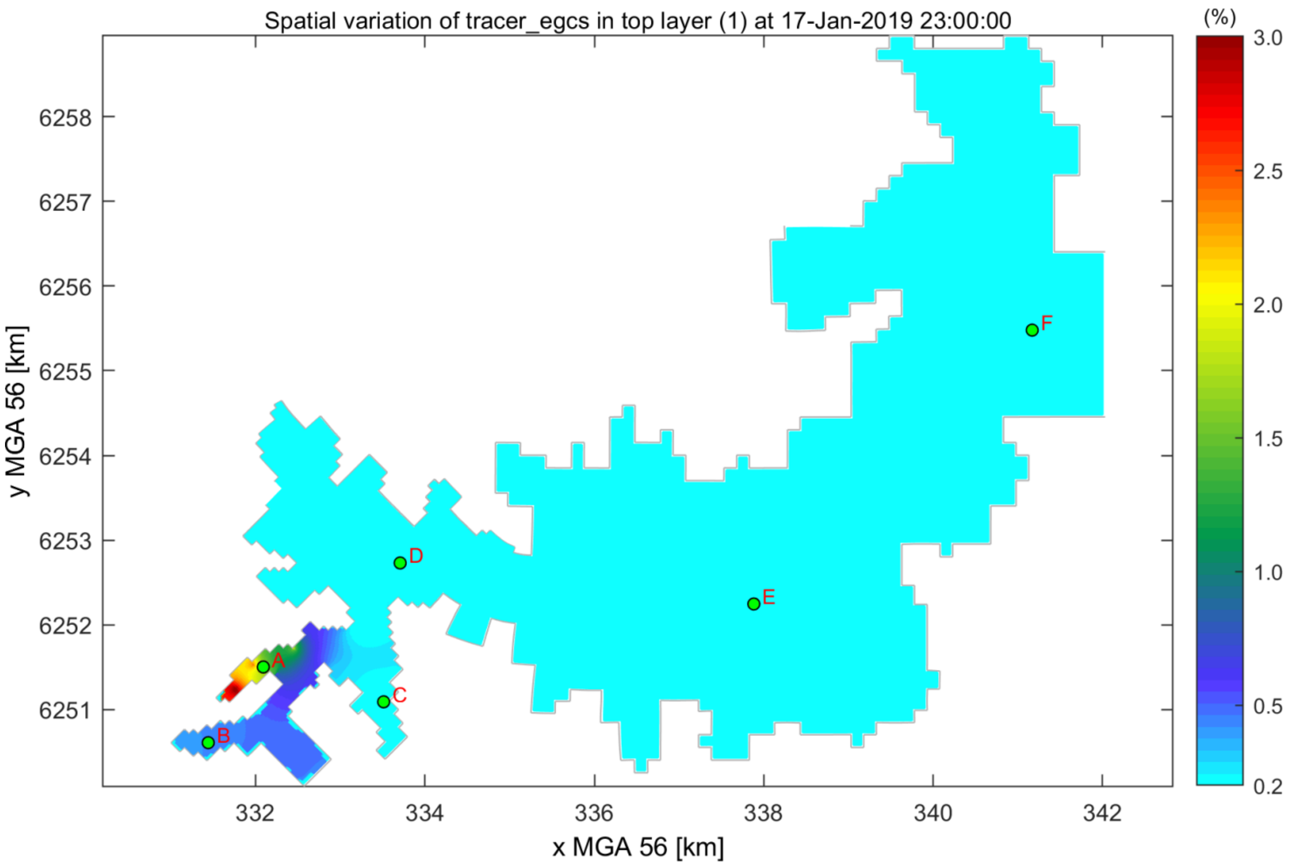
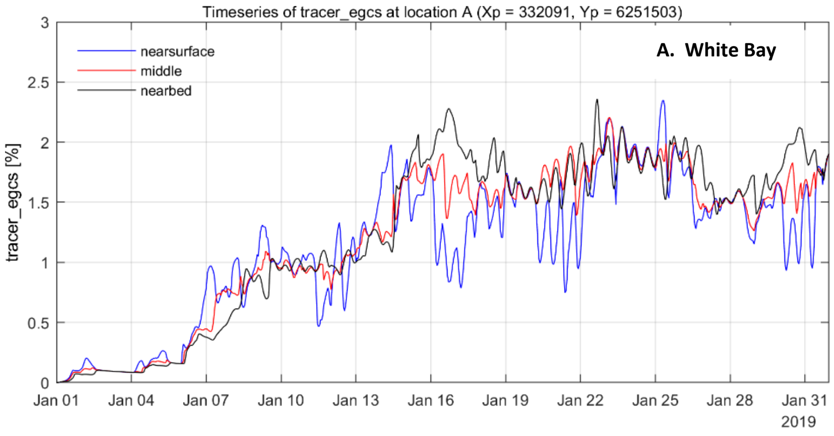
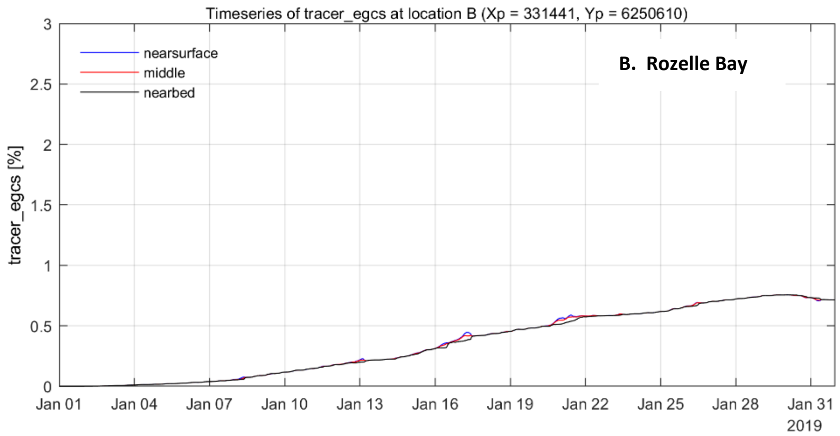


Figure 3. Spatial variation of EGCS tracer (% of initial concentration) in Port Jackson near the surface after 17 days under a dry weather scenario. To express as a total dilution this needs to be multiplied by the near-field dilution of 1 in 18.

The far-field tracer modelling results showed that over a month, washwater discharges into White Bay may accumulate in the shallow embayments surrounding White Bay, including Rozelle Bay, Blackwattle Bay and Cockle Bay. Higher tracer concentrations were modelled to occur within Darling Harbour. A 200-fold dilution (excluding any initial dilution near the vessel) or greater may be achieved within this region. Beyond Darling Harbour, the tracer concentration diminished rapidly. Near Goat Island (Location D), above background concentrations would be negligible due to the high flushing potential of Port Jackson, effective tidal mixing and deep waters. At Location D, 1 000-fold dilution or greater may be expected. Further downstream in Port Jackson (Location E), the tracer concentration above the background is negligible with a modelled dilution of 10 000 or greater.


Timeseries of tracer_egcs at location A (Xp = 332091, Yp = 6251503)
A. White Bay
nearsurface
middle
nearbed
tracer_egcs [%]
3
2.5
2
1.5
1
0.5
0
Jan 01
Jan 04
Jan 07
Jan 10
Jan 13
Jan 16
Jan 19
Jan 22
Jan 25
Jan 28
Jan 31
2019


Timeseries of tracer_egcs at location B (Xp = 331441, Yp = 6250610)
B. Rozelle Bay
nearsurface
middle
nearbed
tracer_egcs [%]
3
2.5
2
1.5
1
0.5
0
Jan 01
Jan 04
Jan 07
Jan 10
Jan 13
Jan 16
Jan 19
Jan 22
Jan 25
Jan 28
Jan 31
2019

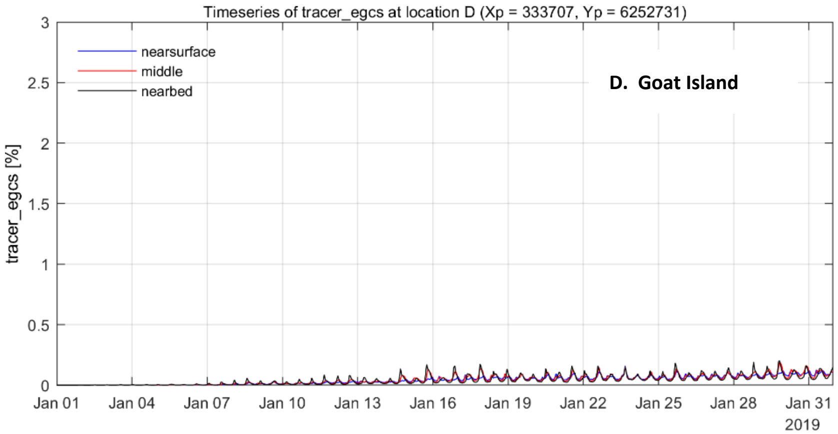

Timeseries of tracer_egcs at location D (Xp = 333707, Yp = 6252731)
D. Goat Island
nearsurface
middle
nearbed
tracer_egcs [%]
3
2.5
2
1.5
1
0.5
0
Jan 01
Jan 04
Jan 07
Jan 10
Jan 13
Jan 16
Jan 19
Jan 22
Jan 25
Jan 28
Jan 31
2019

Figure 4. Time series of the far-field dilution of the EGCS tracer (% of initial concentration) at reporting locations in Sydney Harbour under a dry weather scenario. To express as a total dilution this needs to be multiplied by the near-field dilution of 1 in 18. The near-surface and middle series are not discernible from the near-bed series when they overlap, i.e., negligible differences.

A review of the far-field modelling results (excluding any initial dilution in the near-field mixing zone) for the dry weather EGCS discharge scenario highlighted the following:

- The concentration of the EGCS tracer was greatest inside White Bay near the berths, as expected.
- The discharge results in a 50 to a 100-fold dilution of the tracer within metres of the point of discharge with slightly higher concentrations occurring near the bed. Within about 3 weeks, the EGCS washwater discharges were moved by tides into nearby embayments including Rozelle Bay, Blackwattle Bay, and Cockle Bay at reporting Location B and Location C. After 3 weeks, the tracer concentrations at reporting Locations A, B and C were approximately 1.5%, 0.5% and 0.25% respectively.
- Outside of White Bay, the highest EGCS tracer concentrations occurred in Rozelle Bay and Blackwattle Bay (Location B), and Cockle Bay (Location C). The results suggest that there is a tendency for washwater to accumulate in these nearby shallow embayments during dry weather periods. After 3 to 4 weeks the tracer concentrations approached an equilibrium (steady-state) with the local tidal flushing condition.
- Downstream of White Bay near Goat Island, for example (Location D), the EGCS tracer concentration was lower as a result of greater tidal mixing and deeper waters in this area. The concentration of the tracer at Locations E and F were smaller than Location D (< 0.05%) due to deep water and frequent flushing of the main waterway by tides.
- During dry weather (tides only), the results show that EGCS washwater may be transported upstream of White Bay to Lane Cove and the Paramatta River (Locations H, I and J) albeit at low concentrations in the range of 0.05% or less.

Overall, the dry weather discharge scenario results showed that there is potential for washwater to accumulate in nearby embayments (e.g., Rozelle Bay) but the initial dilution occurring at White Bay and further mixing by tides, results in tracer concentrations that are approximately 1-1.5% of the discharge concentration. The results showed a gradual increase in tracer concentration within White Bay over the first 3 weeks. After the first 3 weeks, the tracer approached an equilibrium concentration. At Rozelle Bay, (Location B), tracer concentrations also approached an equilibrium with tidal flushing that was lower than concentrations at White Bay, after 4 weeks. Similarly, washwater may be transported upstream by tides but the concentration of the tracer was substantially lower than White Bay and nearby embayments.

Wet weather discharge scenario

Time series results were also obtained for the wet weather discharge scenario which showed the concentration of the EGCS tracer near the surface, mid-depth, and near bed at selected locations in Port Jackson. Results at Locations A, B and D are provided in the Supplementary information Figure S3). As for the dry weather scenario, there were negligible differences in the dilution of the EGCS in the near-surface, middle and near-bottom depths apart from at White Bay where the near-bottom depth frequently had a marginally lower dilution.

The review of the far-field modelling results for the wet weather EGCS discharge scenario highlighted the following:

- The concentration of the EGCS tracer was greatest within White Bay near the berths as expected. The discharge results in a 20- to 40-fold dilution of the tracer within metres of the point of discharge with slightly higher concentrations near the surface and mid-depth than near the bed.
- Within about three weeks, the EGCS washwater discharges were transported into nearby embayments including Rozelle Bay, Blackwattle Bay, and Cockle Bay (reporting Locations B and C). After three weeks, results at reporting Locations A, B and D showed tracer concentrations of approximately 3%, 1.3% and 0.1% respectively.
- Outside of White Bay, the highest EGCS tracer concentrations occurred at Rozelle Bay and Blackwattle Bay (Location B), followed by Cockle Bay (Location C). As noted above, the wet scenario results showed accumulation of washwater (albeit at very low concentrations) in these nearby shallow embayments during wet weather periods as well.
- Tracer concentrations within White Bay and surrounding shallow embayments (Locations A, B and C) were higher at the end of the simulation than in the dry weather scenario. However, in the main channel of Port Jackson near Goat Island (Location D), peak tracer concentrations associated with tidal movements in the dry scenario (Figure 4), were reduced during the wet weather conditions (Figure S3). Consequently, tracer concentrations were marginally lower at Location D during the wet weather scenario, which may be a result of higher flows and stronger currents associated with catchment inputs upstream that reduce the tidal flushing of the shallow embayments around White Bay.

- Downstream of White Bay near Goat Island, for example (Location D), the EGCS tracer concentration was much lower as a result of greater tidal mixing and deeper waters in this area. The concentrations of the tracer at Locations E and F were even smaller (< 0.05%) due to deep water and frequent flushing of the region by tides.
- During the wet weather scenario, the results showed that EGCS washwater may be transported upstream of White Bay to Lane Cove and the Paramatta River (Locations H, I and J) albeit at low concentrations in the range of 0.05% or less.

Overall, the wet weather discharge scenario results showed that there is potential for washwater to accumulate in White Bay and nearby embayments. The results showed a gradual increase in tracer concentration at White Bay over the first 3 weeks but to very low concentrations. After these first 3 weeks, tracer concentrations modelled at Location A (White Bay) approached an equilibrium concentration of between 2.5% and 3.5%. A similar response was modelled at Rozelle Bay (Location B) with tracer concentrations of approximately 1.5% or less.

3.5.3 Total near-field plus far-field dilutions

For a conservative estimate of the total or combined dilution (near-field and far-field dilution), the modelled far-field dilution can be multiplied by 18 to account for the initial mixing that occurs in the first 10 metres from the vessel. For example, a far-field dilution of 200 at White Bay would correspond to a total dilution of 200 times 18 or 1 in 3 600. Even adopting a conservative estimate of initial dilution of 1 in 100, a total dilution at White Bay of 1 in 1 800 could be expected. Much higher dilutions of 1 in 2 500 (excluding any initial dilution near the vessel) or more are estimated for areas downstream of Goat Island. Taking into account initial mixing near the vessel(s), the total dilution downstream of Goat Island was approximately 1 in 40 000.

The modelling considered both wet weather season and dry weather season scenarios. For White Bay, the modelled dilution was surprisingly less under the wet-weather scenario. More detailed modelling to consider both dissolved and particulate metals is not necessary as no effects are predicted based on total concentrations, however, field-sampling of discharges using expert techniques that minimise contamination would be useful to try and better account for any uncertainties in the washwater data that might have been due to poor sampling techniques

The far-field dilution modelling indicated negligible differences in the dilution of the EGCS in the near-surface, middle and near-bottom depths in Sydney Harbour. An estimate of near-field dilution was based on a representative ambient current speed of 0.005 m/s near a berth White Bay. These currents would be exceeded approximately 90% of the time. The 'lower estimate' of near-field dilution is based on EGCS manufacturer estimation. The 'best estimate' in this figure is representative of the main impact areas where dilution is lowest in the far-field modelling. In the case of White Bay, a total of 1 000 to 3 600-fold dilution was estimated for Darling Harbour.

The near- and far-field and total washwater dilutions for White Bay are summarised in Figure 5.

Taking into account both near-field and far-field mixing processes, the total dilution of washwater inside White Bay (the area that will receive the greatest load of washwater) was estimated to be 1 in 1 800.

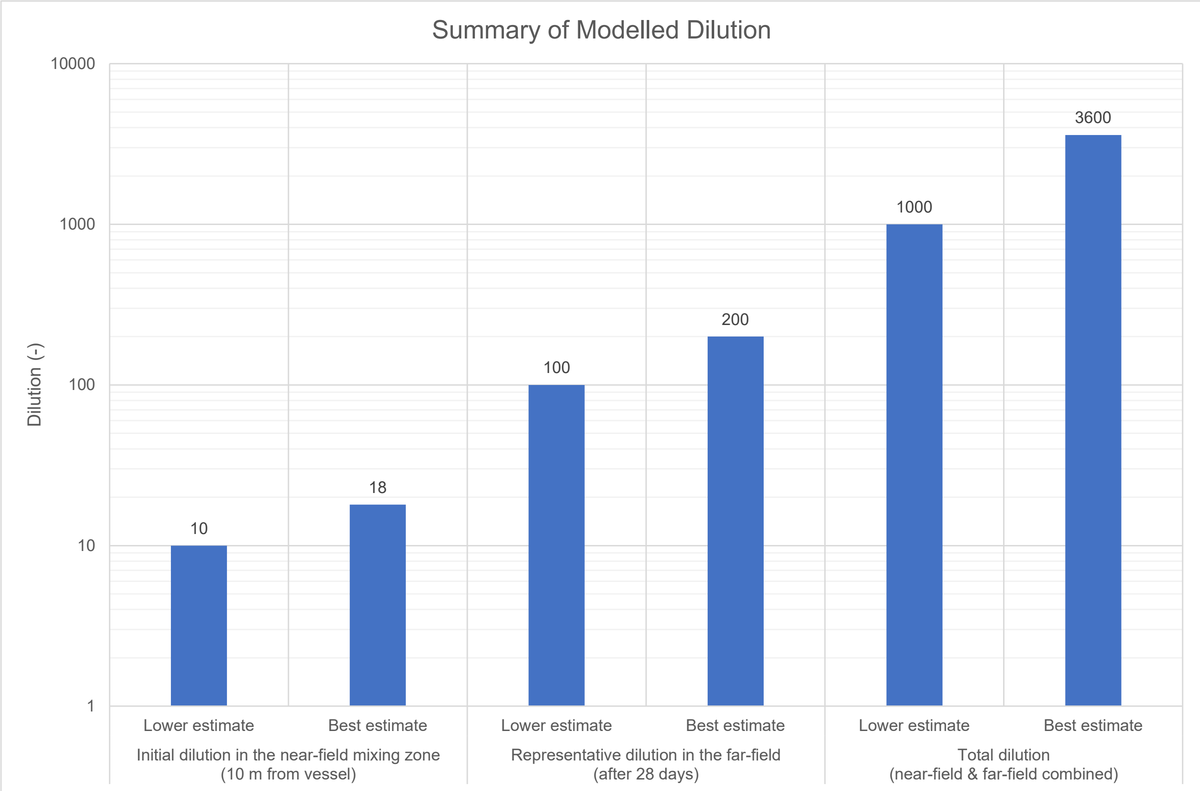


Figure 5. Estimated dilutions of EGCS washwater discharges for White Bay

3.5.4 Long-term modelling

Time series of modelled EGCS discharge concentrations at White Bay and Middle Harbour are shown in Figures 6 and 7. Discharge concentrations are presented as relative (percentage) concentrations to the initial discharge source in White Bay.

The model results indicate that, for Sydney Harbour, the long-term EGCS concentrations throughout the Harbour will be strongly correlated with the annual discharge volume into White Bay. The concentration of EGCS washwater in White Bay is lower in the wet and dry years, whereas in the Parramatta River, the Lane Cove River and Middle Harbour, concentrations of EGCS discharge are higher in average or wet-year conditions.

At all locations, the EGCS discharge concentration reached a dynamic equilibrium (a state of balance between continuous processes including catchment rainfall/runoff, tides and metocean variables) for the Base Case, and the EGCS discharge concentration for the 20% increase in discharge over the 10-year simulation, was reflected in proportional increases in concentration during each annual period.

The long-term modelling indicates that the EGCS washwater tracer concentration does not accumulate, i.e., flushing by tides and catchment rainfall ensure that the washwater is readily mixed and diluted in the harbour.

At White Bay, the maximum tracer concentration as a percentage of the discharge source is less than 1%. Further away from White Bay, including Middle Harbour and the Parramatta River, the tracer concentration is less than 0.1%. Overall, the long-term modelling indicates that washwater would be substantially diluted and that contaminants in EGCS washwater would not be at problematic concentrations even with an allowance of an additional 20% increase above the worst-case discharge scenario.

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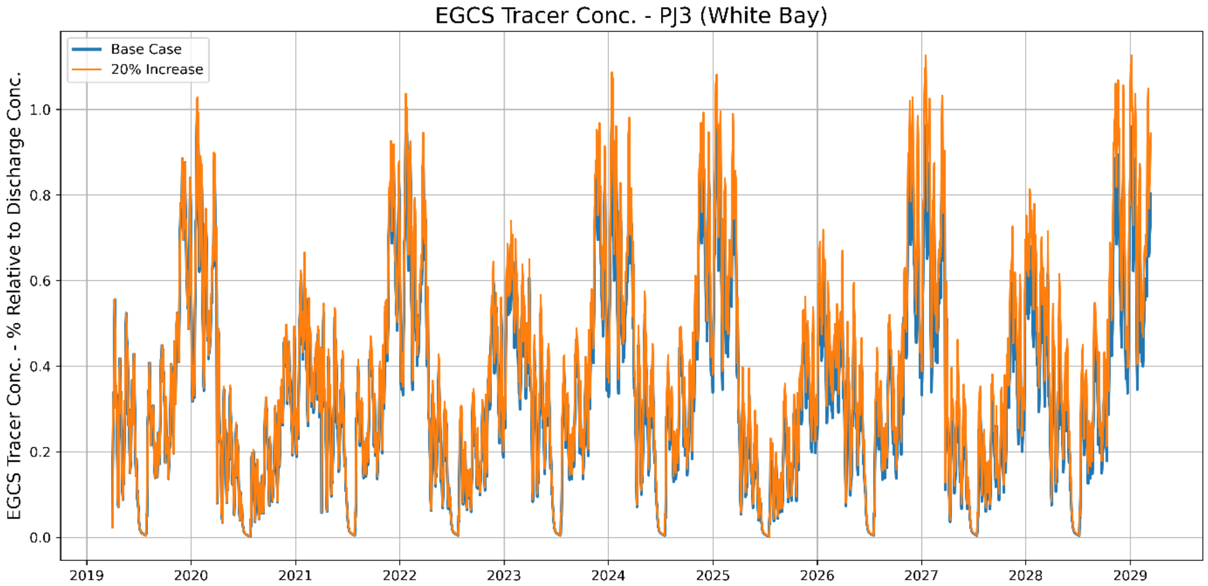

711 **Figure 6. Time series of EGCS concentration (depth-average) over 10 years: Location PJ3 covering White Bay discharge site**

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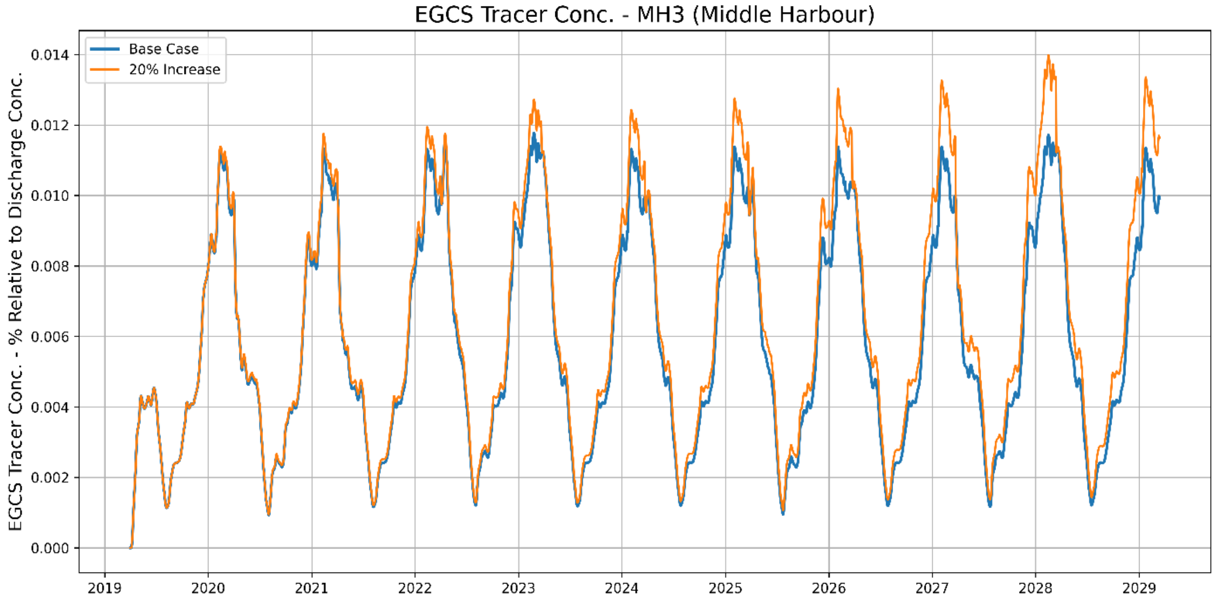

Figure 7. Time series of EGCS concentration (depth-average) over 10 years: Location MH3 in Middle Harbour

3.5.5 Limitations and other considerations

Importantly, the results presented here correspond to a suite of worst-case conditions for EGCS discharges. The following additional points should be considered:

- The EGCS tracer assumes that a contaminant would be in a dissolved (soluble) form and could therefore be readily transported from White Bay into surrounding waters. In reality, there are likely to be other transport pathways for contaminants from washwater such as attachment (adsorption) to fine sediments that remove contaminants from the more toxic dissolved phase, thereby decreasing their bioavailability.

These particulates may settle in the deep waters of White Bay or be transported throughout and out of the harbour. There is also the potential for partitioning of contaminants between surface waters and bed sediments that would limit the potential for washwater contaminants to be transported away from White Bay. However, based on the modelling presented, even under a worst-case scenario, this transport is largely limited to areas within 2 km of White Bay.

- Tides would aid with mixing and dispersion of the washwater released at White Bay, but the modelling shows an increase in the tracer concentration at some of the upstream embayments. The model suggests that tides alone could establish an equilibrium concentration over one to two months. During wet weather, these local shallow embayments would be flushed by catchment rainfall and stormwater runoff from the local contributing catchments. This additional freshwater input would help to mix and disperse washwater that may accumulate in these areas and ultimately reduce the concentration in the embayments and transport the EGCS washwater downstream into deeper harbour waters where further dilution may occur.

3.6 Appraisal of EGCS washwater discharge impact for White Bay

Our study has highlighted that cruise ships represent the majority of vessels operating at White Bay while bulk carriers account for a small number of vessels each year. Even those bulk carriers that do operate in White Bay are smaller than the likely vessel size represented by the bulk carrier washwater dataset. It is also likely that the smaller carriers would not be using EGCSs. On this basis, target dilutions calculated from datasets representative of cruise ships are deemed most relevant to the White Bay study area.

Nevertheless, applying the most conservative required dilution of 1 in 52 (albeit based on bulk carriers), as shown in Table 7, it is clear that this dilution is easily achieved, with total dilutions of 1 800-fold in White Bay increasing to 3 200- fold or more in the Darling Harbour area, based on far-field dilutions of 1 in 100 and 1 in 200 respectively for White Bay and Darling Harbour.

As already noted, open-loop EGCS discharge data for ships using Australian ports indicated that the major contaminants in order of concern were copper, nickel, vanadium and zinc. This is consistent with findings from international research.

These data were for total rather than dissolved metal concentrations, which over-estimates the environmental concern as it is only the dissolved fraction that is bioavailable and potentially toxic to biota. Cruise-line data indicated the dissolved fraction for copper, the metal of greatest concern, was typically 67% of the total concentrations. Bulk carriers had higher discharge metal concentrations than cruise ships, while there were insufficient data for other ship types.

Given that a significant proportion of the discharged contaminants is likely to be in a particulate form, it would be expected that these would ultimately deposit in bottom sediment further reducing the dissolved contaminant concentrations. If we were to consider the dissolved component only and assume that the dissolved fraction is 68% of the total as seen in the Cruise-line data, the dilutions would be further reduced by that factor.

We have noted the significant particulate concentrations that we predict will deposit in the sediments both in White Bay and nearby. As already discussed, it was probably too early to see evidence of elevated vanadium and nickel, which would be expected to be good indicators of washwater particulates, in any of the sediments sampled in the region. We know that dissolved contaminants will partition to suspended particulate matter and interact with dissolved organic carbon in the water column, both of which minimise the worst-case water column transport predictions of the modelling.

Other inputs likely to the White Bay area, in particular copper in antifouling paints is likely to add to the dissolved copper contaminant load to the region. As already discussed, this may contribute more than three times the copper concentration from EGCSs. This should not be sufficient to raise the near-field copper concentrations to above the GV. Stormwater discharges will involve initial first flush concentrations of dissolved and particulate metals, accompanied by high and diluting water inputs.

Even when modelling worst-case scenarios, the modelling suggests that WQGVs would not be exceeded in White Bay as a consequence of EGCS discharge. This applies not only to copper but also to Ni, V, Zn Cd, Cr, Hg, Tl, Se and As which have lower discharge concentration to GV ratios. Concentrations of PAHs, nitrate, nitrite and nutrients were below accepted guideline values (where they exist) and within the IMO limits so are not expected to be an issue.

While the discharges occasionally had low pH values (2.8 to 5.8), these were effectively neutralised upon mixing with seawater. No significant lowering of pH was predicted beyond the near-field mixing zone. It is noteworthy that the lower pH values favour metal solubilisation, but this increased bioavailability will be reduced on reaching the natural pH of seawater (8.1).

Separate studies have examined the effects of sulfate and nitrate in discharge waters. Hufnagl et al. (2005) noted that since EGCSs removed sulfur oxides as sulfate ions, the inlet seawater sulfate concentration was increased by 14-18% in the discharge, however, the effects on the receiving seawater sulfate from the discharge from channel ferry, Pride of Kent, were insignificant. Nitrate concentrations increased in the washwater by a factor of 2 over inlet seawater concentrations, but the effects on primary productivity were not abnormal.

Similarly, no impact is expected from temperature changes from that of the discharge to the receiving water. The differences in temperature between washwater inlet and outlet samples are easily modelled. A study of the cruise ship *MV Zaandam* found that the increase in washwater temperature was less than 3.5°C (HA and HK, 2010; USEPA. 2011).

The far-field modelling indicates that in White Bay, under dry weather conditions, an equilibrium dilution concentration is achieved after as little as 16 days. The typical flushing time for Sydney Harbour is about 60 days, i.e., it takes about two months for saline recovery to occur after a large freshwater/catchment rainfall event. There is a tendency towards an equilibrium concentration after 2 to 4 weeks and this is consistent with White Bay being located closer to the harbour entrance. Box modelling confirmed that the dynamic equilibrium observed in the medium-term model simulations will persist in the longer term (over 10 years).

White Bay is less well-flushed than open coastal waters and the far-field modelling indicated that nearby areas including Rozelle Bay and Blackwattle Bay would receive diluted washwaters albeit at very low concentrations. Meanwhile, in the more open location near Goat Island, far-field dilution was more than adequate with dilutions of up to 5 000-fold.

Studies of washwater impacts were also undertaken of Gladstone Harbour, Queensland and Port Hedland, Western Australia, both of which are better flushed than White Bay and hence greater dilutions were achieved, making any impacts from washwaters even less likely at these sites.

3.6.1 Long-term impacts of EGCS discharges

A specific objective of this study was to comment on the cumulative long-term impacts of washwater discharges. In contaminant ecotoxicology, 'long-term' refers to chronic impacts on biota that occur over a substantial span of an organism's lifetime, which is typically in the range 3-14 days, as distinct from short-term (acute) impacts that occur over ≤3 days. Our modelling studies have shown that there are no long-term impacts of this type.

We have shown that in the absence of increased ship numbers, equilibrium dilutions are achieved after as little as 16-28 days in the mid-field with negligible far-field impacts. This, however, is based on a worst-case scenario, that considers all contaminants to be in dissolved forms, and ignores any partitioning to particulates and subsequent accumulation in bottom sediments. While it is conceivable that dissolved contaminants might not increase over time, there is a distinct possibility that sedimentation could lead to detectable washwater-related contaminants in harbour sediments loads after 10 years. Over this period, there is likely to be changing harbour usage and variable weather conditions that could confound predictions. Sediment metal and PAH concentrations may well increase, but with particulate inputs from other sources, e.g., stormwater, concentrations are unlikely to significantly exceed sediment quality guideline values, which were derived conservatively. Sydney Harbour is more likely to show this as the sediments are silty. Confirmation of washwater impacts would require identification in surface sediments (0-2 cm) of marker metals nickel and vanadium.

A comprehensive study of the fate of washwater contaminants was very recently published by Faber et al. (2021) looking at contaminant behaviour out to 20 years in a commercial harbour (Port of Rotterdam), in shipping lanes, and the open ocean. This followed an earlier study (Faber et al., 2019) looking at a 5-year scenario. They modelled concentrations of metals and PAHs in the receiving waters using the Marine Antifoulant Model to

Predict Environmental Concentrations (MAMPEC), a more coarse 2D hydrodynamic and chemical fate model than our high-resolution 3D model. This model calculates steady-state concentrations for water (total and freely dissolved), suspended matter and sediment. For sediments, concentrations after 20 years of EGCS emissions were selected to represent a worst-case situation after long-term emissions of persistent compounds.

Table 8. Modelled long-term increase in water and sediment contaminant concentrations as a result of EGCS washwater discharges in the Port of Rotterdam (from Faber et al., 2021)

Contaminant	Increase in Port water concentration, µg/L	Increase as % of WQGV	Increase in surrounding harbour water concentration, µg/L	20-y increase in Port sediment concentration, mg/kg	Increase as % of SQGV	20-y increase in surrounding harbour sediment concentration, mg/kg
Cu	0.008	0.60	0.0013	0.27	0.42	0.05
Ni	0.005	0.06	0.001	0.10	0.48	0.02
V	0.010	0.06	0.0018	0.04	-	0.005
Zn	0.006	0.04	0.001	0.42	0.21	0.08
Naphthalene	0.00026	-	$5x10^{-5}$	$0.5x10^{-5}$	-	-
Phenanthrene	0.00016	-	$3x10^{-5}$	5.6×10^{-5}	-	-

The findings of their modelling are shown in Table 8. The highest accumulated metal concentrations after 20 years, were in the order zinc > copper > nickel > vanadium, but these amounted to less than an additional 0.5% of the Australian and New Zealand sediment quality GVs (Table 6) (ANZG, 2018). The increases in concentrations of PAHs were extremely small, with the highest individual PAH concentrations being many orders of magnitude below the total PAH sediment quality GV of 10 mg/kg.

Accumulation in waters was not seen as a major issue. For Sydney Harbour (White Bay), long-term modelling for a continuous 10-year period revealed that the EGCS discharge concentration reached a dynamic equilibrium (at all locations across the harbour) within the first year of the simulation. The flushing by tides and catchment rainfall was sufficient to readily mix and dilute EGCS washwaters and the accumulation of washwater in local embayments was not evident in the model results. The maximum tracer concentration as a percentage of the discharge source was less than 1%. Further away from White Bay, including Middle Harbour and the Parramatta River, the modelled tracer concentration was less than 0.1%. The long-term modelling indicated that contaminants in EGCS washwater would not be at problematic concentrations even with an allowance of an additional 20% increase above the worst-case discharge scenario.

Our predictions of increases in the concentration of the contaminants of greatest concern, Cu, Ni and Zn, relative to existing concentrations in the harbours and guideline values are shown in Table 9. The dissolved concentrations are predicted to increase by less than 0.10 µg/L. The predicted increases were compared to concentrations previously measured in the harbour to determine the likely contribution from washwaters. Concentrations of dissolved copper, the contaminant of greatest concern due to the WQGV being most exceeded in washwater discharges, are predicted to increase by <1%. Any greater increases if seen would be due to other anthropogenic sources. The predicted increases in nickel and zinc are generally higher than for copper due to the higher predicted concentrations in the EGCS washwaters. However, the nickel and zinc guideline values are much higher than that of copper, and the predicted increase relative to the WQGVs are all <0.5%. Together these results indicate that the EGCS washwater contaminant inputs will make a negligible contribution to any exceedance of WQGVs.

Table 9. Predicted increases in the dissolved Cu, Ni and Zn due to EGCS washwaters released to Sydney Harbour after 10 years

Port	Contaminant	Increase in surrounding harbour water concentration, µg/L	% increase in surrounding harbour water concentration	Increase as % of WQGV
	Cu	0.006	0.63	0.49
White Bay	Ni	0.026	3.0	0.037
	Zn	0.053	0.82	0.35

Internationally, despite no evidence in terms of impacts on sediments or surrounding waters, there are only a few ports and nations that have prohibited the use of open-loop scrubbers in their territorial waters. For instance, Germany prohibited open-loop EGCSs in Hamburg but permits ships to use open-loop scrubbing in the Kiel Canal (Schmolke et al., 2020). Our modelling of a worst-case scenario supports international findings that open-loop EGCS discharges currently pose no long-term threat to the environment and offer a preferred option to atmospheric emissions from the use of 0.50% sulfur fuels which while not necessarily impacting on ecosystem health of the local port environment, have undesirable impacts on the health of the nearby population, especially in harbour cities.

4. Acknowledgments

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Supplementary Information

Assessing the cumulative effects of washwater discharges from ships' open-loop exhaust gas cleaning systems on a receiving ecosystem

Graeme E. Batley[a*], Luke Kidd[b], Brad M. Angel[a], Martin Budd[c] and Stuart L. Simpson[a]

[a]*CSIRO Land and Water, Lucas Heights NSW 2232, Australia*

[b]*Royal HaskoningDHV, Newcastle, NSW 2300, Australia*

[c]*Royal HaskoningDHV, North Sydney, NSW 2060, Australia*

*To whom correspondence may be addressed (Graeme.batley@csiro.au)

SI. WASHWATER DATA

Table S1. Contaminants measured in EGCS washwaters from a dataset provided by AMSA[a]

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenanthrene) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	As (µg/L)	Cr (µg/L)	V (µg/L)
Asphalt and bitumen carrier	×	×	×	×	0.016	×	×	×	×	×	×	×	×	×
Asphalt and bitumen carrier	2.8	0.39	4.95	6.62	×	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	ND	ND(<5.00)	ND(<5.00)	ND(<1)	ND(<10)	15	ND(<10)	56	ND(<50)	ND(<10)	60
Bulk carrier	×	×	2.9	0.5	0.029	<.005	<1	42	19	<.001	90	2	6	55
Bulk carrier	×	×	×	0.4	3.2	<0.2	<2	25	30	<20	750	<20	<20	120
Bulk carrier	×	ND	2.6	0.8	0.12	ND(<.50)	ND	8	44	2	39	ND	4	226
Bulk carrier	×	1.3	3.8	0.2	<.5	<.005	<.1	2	21	<1	13	2	5	70
Bulk carrier	×	×	×	×	<5	×	×	×	×	×	×	×	×	×
Bulk carrier	1.54		5.76	0.06	<0.9	<0.9	ND	20.3	22.8	ND	4.3	1.9	3.8	35.9
Bulk carrier	1.54		5.66	0.55	<0.9	<0.9	2	7.8	16	0.1	1.5	1.9	1.1	38.8
Bulk carrier	1.54		5.34	1.24	<0.9	<0.9	0.2	9.4	16.6	0.2	15.1	2.1	2	44.6
Bulk carrier	×	×	6.3	×	×	×	×	×	×	×	×	×	×	×
Bulk carrier	×	2	3	ND	ND(<5.0)	ND(<5.0)	ND	5	61	4	39	ND	8	555
Bulk carrier	2.21	×	×	×	0.299	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	×	27	×	×	×	×	×	×	×	×	×
Bulk carrier	×	2.4	2.8	ND(<0.1)	1.4	0.8	ND(<100)	ND(<100)	<100	ND(<100)	ND<100	<10	ND<100	<100
Bulk carrier	2.67	×	×	×	0.184	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	×	2.2	×	×	×	×	×	×	×	×	×
Bulk carrier	3.37	×	×	×	0.158	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	ND	<.05	0.01	ND	ND	<20	ND	22	<2	ND	39
Bulk carrier	×	3.5	2.6	ND(<0.1)	2.1	ND(<0.1)	ND(<100)	ND(<100)	<100	ND(<100)	<100	<100	ND(100)	100

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenanthrene) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	As (µg/L)	Cr (µg/L)	V (µg/L)
Bulk carrier	×	×	×	×	0.2	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	<5	1.1	0.02	<.4	<10	<10	<5	79	2	21	82
Bulk carrier	×	ND	2.6	0.7	9.98	×	×	×	×	×	×	×	×	×
Bulk carrier	2.96	×	×	×	0.176	×	×	×	×	×	×	×	×	×
Bulk carrier	×	1.13	3.16	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bulk carrier	×	2		×	<.01	0.12	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	×	1.79	×	×	×	×	×	×	×	×	×
Bulk carrier	×	0.4	3.9	ND(<.01)	2.2	ND(<.01)	ND(<100)	<100	ND(<100)	ND(<100)	<100	<100	ND(<100)	<100
Bulk carrier	×	×	3.04	0.458	ND(<.5)	ND(<.5)	ND(<10)	ND(<14)	ND(<14)	ND(<6)	ND(<80)	ND(<6)	ND(<12)	14
Bulk carrier	×	1	2.8	0.3	ND(<5.00)	ND(<5.00)	ND(<1)	ND(<10)	12	ND(<10)	ND(<50)	ND(<50)	ND(<10)	51
Bulk carrier	×	ND	2.5	×	11.2	ND(<5.00)	ND(<1)	22	56	ND(<10)	197	ND(<50)	ND(<10)	335
Bulk carrier	3.25	×	×	×	0.0941	×	×	×	×	×	×	×	×	×
Bulk carrier	×	6	2.8	0.4	12.8	ND(<5.00)	0.5	115	32	16	370	10	4	147
Bulk carrier	×	×	×	×	ND(<5.00)	×	×	×	×	×	×	×	×	×
Bulk carrier	×	ND	2.9	0.5	ND(<5.0)	ND(<5.0)	ND(<1)	ND(<10)	17	ND(<10)	85	ND(<50)	13	84
Bulk carrier	×	×	×	ND	ND(<2.5)	ND(<2.5)	ND(<1)	157	194	ND(<10)	97	ND(<50)	ND(<10)	404
Bulk carrier	×	0.95	3.2	ND	0.033	ND	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	ND	ND(<5.0)	ND(<5.0)	ND(<1)	ND(<10)	111	ND(<10)	ND(<50)	ND(<50)	27	203
Bulk carrier	×	×	×	ND	12.7	ND(<5.0)	ND(<1)	ND(<10)	22	ND(<10)	ND(<50)	ND(<50)	ND(<10)	108
Bulk carrier	×	×	×	ND	ND(<5.0)	ND(<5.0)	ND	14	1	1	56	ND	4	2

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenanthrene) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	As (µg/L)	Cr (µg/L)	V (µg/L)
Bulk carrier	×	×	×	ND	ND(<5.0)	ND(<5.0)	ND(<1.0)	ND(<10)	73	ND(<10)	ND(<50)	ND(<50)	ND(<10)	326
Bulk carrier	×	×	×	ND	ND(<5.0)	ND(<5.0)	ND(<1)	ND(<10)	39	ND(<10)	ND(<50)	ND(<50)	11	82
Bulk carrier	×	5.44	3.21	9.33	×	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	1.1	ND(<5.0)	ND(<5.0)	ND(<1)	ND(<10)	15	ND(<10)	ND(<50)	ND(<50)	ND(<10)	64
Bulk carrier	×	2	3.7	ND(<0.1)	ND(<0.1)	ND(<0.1)	ND(<100)	ND(<100)	210	<0.100	<0.100	ND(<100)	ND(<100)	440
Bulk carrier	×	×	×	×	ND	ND	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	×	ND	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	×	ND	×	×	×	×	×	×	×	×	×
Bulk carrier	×	3	2.8	×	14.3	ND(<5.00)	ND	5	21	4	26	ND	1	105
Bulk carrier	×	×	6.8	<.05	<0.1	<0.1	<10	<10	10	<50	100	<50	<50	50
Bulk carrier	×	×	×	×	0.13	<.01	×	×	×	×	×	×	×	×
Bulk carrier	×	×	6	ND	ND	7.9	ND	9	32	2	51	ND	5	75
Bulk carrier	×	×	2.86	ND	ND	ND	ND	ND	240	ND	ND	ND	160	250
Bulk carrier	×	×	3.04	0.675	<.5	<.5	<10	<14	<14	<6	<80	<6	<12	38
Bulk carrier	×	1.6	×	×	0.3	<0.1	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	0.2	ND(<5.00)	ND(<5.00)	ND(<1)	ND(<10)	15	ND(<10)	ND(<50)	ND(<50)	ND(<10)	63
Bulk carrier	×	×	2.7	0.9	ND(<5.00)	ND(<5.00)	ND(<10)	ND(<100)	ND(<100)	ND(<100)	ND(<500)	ND(<500)	ND(<100)	102
Bulk carrier	×	×	×	×	0.5	×	×	×	×	×	×	×	×	×
Bulk carrier	×	4.6	5.4	ND	×	×	ND	ND	<20	ND	43	<2	<10	27
Bulk carrier	×	1.17	3.22	ND	0.24	ND	ND	ND	30	ND	80	ND	ND	100
Bulk carrier	×	0.33	2.9	0.69	<0.5	<0.5	<1	<1	26	<1	<5	1	2	101
Bulk carrier	×	×	×	×	ND(<5.00)	ND(<5.00)	×	×	×	×	×	×	×	×

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenanthrene) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	As (µg/L)	Cr (µg/L)	V (µg/L)
Bulk carrier	×	×	2.7	0.85	<0.5	<0.5	<1	449	33	136	2162	1	2	96
Bulk carrier	×	4	3	0.8	ND(<5.00)	ND(<5.00)	ND(<1.0)	207	62	ND(<10)	85	ND(<50)	ND(<10)	259
Bulk carrier	×	×	×	×	0.2	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	<1	0.35	<.066	<.5	24	40	13	280	3.7	6.5	170
Bulk carrier	×	11	×	ND	12.8	ND(<5.00)	0.2	7	13	ND	53	6	3	75
Bulk carrier	×	ND	3.2	0.3	ND(<5.00)	ND(<5.00)	ND(<1)	13	24	ND(<10)	98	ND(<50)	ND(<10)	53
Bulk carrier	×	×	3.4	0.79	0.3	<.066	<4	<5	15	<50	<4	<75	<10	<10
Bulk carrier	×	4	2.8	ND	1.1	ND	0.3	[4.89x103]	117	5	33	9	16	441
Bulk carrier	×	×	4.58	<1	1.03	<.05	<.1	<.1	340	<.1	<.1	<.1	130	1148
Bulk carrier	×	×	×	×	ND(<5.0)	ND(<5.0)	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	×	0.058	<.005	×	×	×	×	×	×	×	×
Bulk carrier	3.43	2.9	2.86	ND	ND	ND	ND	55	26.7	0.3	90	3.3	6.2	100
Bulk carrier	×	×	×	×	0.3	<.2	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	1.68	<.5	<.5	<.5	5	39	<1	89	3	8	163
Bulk carrier	×	2	3.1	0.8	ND(<5.00)	ND(<5.00)	ND(<1)	ND(<10)	70	ND(<10)	ND(<50)	ND(<50)	ND(<10)	265
Bulk carrier	×	ND	3	0.2	<5.00	<5.00	ND(<1)	ND(<10)	18	ND(<10)	ND(<50)	ND(<50)	ND(<10)	70
Bulk carrier	×	×	×	1.57	1	<.5	<.5	9	34	<1	106	2	5	114
Bulk carrier	×	3	×	0.87	<0.1	<0.1	<10	<10	30	<50	20	<50	<50	<50
Bulk carrier	×	1.2	3	0.07	<0.5	<.01	0.8	631	167	20	3388	2	77	178
Bulk carrier	×	0.6	4.6	ND(<0.1)	ND(<0.1)	1.2	ND(<100)	ND(<100)	ND(<100)	ND(<100)	ND(<100)	<100	ND(<100)	ND(<100)
Bulk carrier	×	0.6	4.3	ND(<0.1)	1.6	1.2	ND(<100)	ND(<100)	ND(<100)	ND(<100)	ND(<100)	<100	ND(<100)	ND(<100)
Bulk carrier	×	2	2.7	0.3	<5.0	<5.0	ND(<1.0)	11	27	10	ND<50)	ND(<50)	ND(<10)	187

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenanthrene) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (μg/L)	Cu (μg/L)	Ni (μg/L)	Pb (μg/L)	Zn (μg/L)	As (μg/L)	Cr (μg/L)	V (μg/L)
Bulk carrier	×	×	×	×	14.9	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	ND	ND(<5.00)	ND(<5.00)	ND(<1.0)	ND(<10)	96	ND(<10)	100	ND(<50)	ND(<10)	241
Bulk carrier	×	×	×	×	4.76	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	ND	ND(<5.00)	ND(<5.00)	ND(<1.0)	29	366	ND(<10)	371	ND(<50)	26	406
Bulk carrier	×	×	×	<0.2	20.4	<5.00	<0.1	6	143	<1	161	<5	4	265
Bulk carrier	×	×	×	0.72	<0.5	<0.5	<0.5	17	100	<1	15	2	95	293
Bulk carrier	×	×	×	1	<5	<5	ND	25	25	ND	66	7	3	72
Bulk carrier	×	×	×	<0.2	×	×	<0.1	6	33	1	201	<5	5	159
Bulk carrier	×	×	×	1	×	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	×	0.23	<.01	×	×	×	×	×	×	×	×
Bulk carrier	2.43	1	3.3	<2.0	0.18	<.01	<0.2	32	119	<1.0	46	6	1	336
Bulk carrier	×	0.66	6.47	ND	ND	ND	ND	ND	ND	ND	340	ND	ND	ND
Bulk carrier	×	2.6	×	×	0.6	<0.1	×	×	×	×	×	×	×	×
Bulk carrier	×	1.8	×	×	0.6	<0.1	×	×	×	×	×	×	×	×
Bulk carrier	×	ND	2.8	ND	ND(<5.00)	×	×	×	×	×	×	×	×	×
Bulk carrier	×	1	3.2	ND	4.39	×	×	×	×	×	×	×	×	×
Bulk carrier	×	2	2.8	0.4	ND(<5.00)	×	×	×	×	×	×	×	×	×
Bulk carrier	×	ND	2.9	0.8	ND(<5.00)	×	×	×	×	×	×	×	×	×
Bulk carrier	×	0.71	5.65	×	×	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	×	0.7	<0.1	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	×	0.3	×	×	×	×	×	×	×	x	x
Bulk carrier	×	ND	3	1.5	ND(<5.0)	ND(<5.0)	ND(<1)	ND(<10)	68	ND(<10)	ND(<50)	ND(<50)	ND(<10)	416
Bulk carrier	×	0.71	×	<.05	0.54	×	×	×	×	×	×	×	×	×

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenanthrene) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	As (µg/L)	Cr (µg/L)	V (µg/L)
Bulk carrier	×	×	×	ND	ND(5.00)	ND(<5.00)	ND	11	48	ND	ND	ND	9	203
Bulk carrier	×	×	×	1.1	ND(5.00)	ND(<5.00)	ND	6	26	ND	11	ND	3	90
Bulk carrier	×	ND	3	1.5	ND(<5.0)	ND(<5.0)	ND(<1.0)	ND(<10)	68	ND(<10)	ND(<50)	ND(<50)	ND(<10)	416
Bulk carrier	×	1.2	3.1	0.019	<0.20	<0.20	<0.5	9	29	<1	148	3	3	176
Bulk carrier	×	×	×	ND	<.30	<.30	<2	<40	<40	<2	<50	<2	<2	<50
Bulk carrier	×	1.67	3.92	6.42	1.05	<0.02	ND	ND	20	ND	30	2	ND	76
Bulk carrier	×	×	6.5	2.1	0.022	0.072	<1	7	13	1	10	2	1	31
Bulk carrier	×	8	2.8	1.4	14.4	ND(<5.0)	0.1	6	27	2	54	ND	1	164
Bulk carrier	×	0.71	3.01	ND	ND	ND	ND	ND	ND	ND	310	ND	ND	80
Bulk carrier	×	ND	2.7	0.5	ND(<5.0)	ND(<5.0)	ND(<1.0)	11	12	ND(<10)	ND(<50)	ND(<50)	ND(<10)	55
Bulk carrier	×	×	5.2	0.019	ND(<1.60)	ND(<1.60)	0.91	6.42	10	1.19	8.51	1.89	2.05	61.3
Bulk carrier	×	×	3.1	1.2	<5.0	<5.0	<0.1	4	17	2	40	<5	3	46
Bulk carrier	×	×	3.53	×	<.50	<.50	<10	67.4	<14	<6	<80	<6	<12	24.2
Bulk carrier	×	×	×	×	ND(<5.00)	ND(<5.00)	ND(<1.0)	ND(<10)	ND(<10)	ND(<10)	ND(<50)	ND(<50)	ND(<10)	ND(<10)
Bulk carrier	×	×	×	<0.2	0.76	0.59	<10	16	<10	<10	<200	<10	<10	<10
Bulk carrier	×	ND	2.8	1.8	ND(<5.0)	ND(<5.0)	ND(<1)	ND(<10)	ND(<10)	ND(<10)	124	ND(<50)	ND(<10)	ND(<10)
Bulk carrier	×	ND	[3]	[1.6]	ND(<5.00)	ND(<5.00)	[197]	[171]	[173]	[189]	[269]	[178]	[197]	[216]
Bulk carrier	×	ND	3.1	1.7	ND(<5.0)	ND(<5.0)	ND(<1.0)	ND(<10)	23	ND(<10)	85	ND(<50)	ND(<10)	67
Bulk carrier	×	×	×	×	10.7	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	ND	ND(<5.0)	ND(<5.0)	ND(<1)	ND(<10)	30	ND(<10)	ND(<50)	ND(<50)	ND(<10)	132
Bulk carrier	×	×	3	ND	×	ND	ND	ND	20	ND	ND	ND	ND	60

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenan threne) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	As (µg/L)	Cr (µg/L)	V (µg/L)
Bulk carrier	×	×	×	×	10.9	×	×	×	×	×	×	×	×	×
Bulk carrier	×	×	2.93	ND	ND	ND	ND	ND	ND	ND	340	ND	ND	ND
Bulk carrier	×	×	6.43	ND	0.3	ND	ND	ND	ND	ND	73	ND	ND	ND
Bulk carrier	×	0.33	6.79	0.3	<0.5	<0.5	<0.5	3	22	<1	<5	2	5	42
Bulk carrier	×	0.4	4.2	0.96	<.066	<.066	<4	17	<15	<50	<4	<75	<10	<10
Bulk carrier	×	×	3.8	ND	0.08	0.01	ND	ND	<20	ND	<20	<2	<20	38
Bulk carrier	×	0.7	5.8	0.3	0.11	0.15	<10	<50	<50	<50	<50	<200	<50	<50
Bulk carrier	×	1.43	4.1	0.4	ND	ND	ND	4.7	44.4	ND	49.4	2.3	37.2	99.4
Bulk carrier	×	16.6	3.84	×	×	×	×	×	×	×	×	×	×	×
Bulk carrier	×	<0.5	6.1	0.4	3.2	<0.2	<20	<20	<20	<20	<100	<20	<20	49
Bulk carrier	×	0.19	3.62	0.59	<0.5	<0.5	<0.5	6	7	<1	<5	2	<1	22
Bulk carrier	×	×	×	×	ND(<5.0 0)	×	×	×	×	×	×	×	×	×
Bulk carrier	×	2.1	×	×	0.4	<0.1	×	×	×	×	×	×	×	×
Bulk carrier	×	×	×	×	0.2	×	×	×	×	×	×	×	×	×
Bulk carrier	×	2.68	5.04	6.45	×	×	×	×	×	×	×	×	×	×
Bulk carrier	×	ND	2.6	0.3	13.3	ND(<5.0)	ND(<1. 0)	ND(<10)	27	13	ND(<5 0)	ND(<5 0)	ND(<10)	121
Bulk carrier	×	×	4.2	ND	0.06	0.12	ND	ND	<20	ND	<10	<2	ND	26
Chemical and Oil carrier	×	×	5.7	1	0.05	×	×	×	×	×	×	×	×	×
Chemical and Oil carrier	×	×	2.7	×	×	×	×	×	×	×	×	×	×	×
Chemical and Oil carrier	×	1.68	3.1	0.44	0.022	ND	ND	ND	ND	ND	4.3	ND	1.2	ND
Chemical and Oil carrier	×	×	3.41	ND	ND	ND	ND	ND	30	ND	ND	ND	ND	ND
Chemical and Oil carrier	×	×	5.5	0.3	<0.5	0.056	<0.1	11	52	<1	23	2	18	23

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenan threne) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	As (µg/L)	Cr (µg/L)	V (µg/L)
Chemical and Oil carrier	×	×	6.57	×	ND(<5.0)	ND(<5.0)	×	×	×	×	×	×	×	×
Chemical and Oil carrier	×	1.4	3.67	0.05	ND	×	×	×	×	×	×	×	×	×
Chip carrier	×	×	2.81	0.519	<.5	<.5	<10	<14	<14	<6	<80	<6	<12	86.2
Chip carrier	×	×	×	0.5	22.7	ND(<5.0)	ND(<1)	ND(<10)	51	ND(<10)	ND(<50)	ND(<50)	ND(<10)	351
Chip carrier	×	×	3.1	0.012	0.04	<.003	<10	<10	20	10	10	10	10	3100
Cruise ship	1.82	×	6.11	0.34	ND	ND	ND	31.2	6.8	0.4	14.1	1.7	1.5	18.5
Cruise ship	1.82	×	5.89	0.5	ND	ND	ND	34.9	7	0.4	11.5	2.2	1.7	21.3
Cruise ship	1.82	×	6.18	0.26	ND	ND	ND	0.6	7.6	0.7	1.2	1.9	0.8	13.9
Cruise ship	×	1.3	3.9	ND(<0.1)	1.4	1.1	ND(<100)	ND(<100)	<100	ND(<100)	ND(<100)	<100	ND(<100)	ND(<100)
Cruise ship	1.42	×	6.2	0.53	<0.31	<0.31	<1	5	<1	18	11	2	3	43
Cruise ship	1.42	×	6.3	0.5	<0.34	<0.34	<1	6	<1	38	<10	3	15	79
Cruise ship	1.42	×	6	0.49	<.3	<.3	<1	4	<1	6	<10	3	1	23
Cruise ship	2.44	×	6.1	0.3	0.023	0.049	<1	6	13	1	<5	2	6	29
Cruise ship	2.44	×	6.2	0.3	0.012	0.04	<1	7	17	8	<8	2	7	32
Cruise ship	2.44	×	6.2	<.01	0.023	0.08	<1	6	100	1	<5	2	3	32
Cruise ship	2.1	×	5.7	4.3	<0.5	<.02	<2	<10	20	<10	50	<10	<10	60
Cruise ship	2.1	×	5.7	1.9	<.05	<.02	<2	<10	20	<10	50	<10	<10	60
Cruise ship	1.77	×	5.8	1.2	<0.5	0.17	<2	<10	30	<10	<20	<10	<10	30
Cruise ship	×	×	×	0.99	1.1	<.02	<2	<10	10	<10	<20	<10	<10	60

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenanthrene) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	As (µg/L)	Cr (µg/L)	V (µg/L)
Cruise ship	×	×	×	0.83	<0.5	<.02	<2	<10	20	<10	<20	<10	<5	70
Cruise ship	×	×	×	1.5	<0.5	<.02	<2	<10	<10	<10	<20	<10	<10	20
Cruise ship	×	×	×	0.78	<.05	<.02	<2	<10	<10	<10	<20	<10	<10	40
Cruise ship	×	×	6.23	2.9	0.074	0.074	ND	ND	14	ND	38.9	ND	ND	49.7
Cruise ship	×	×	6.08	3.1	0.071	0.071	ND	ND	16.3	ND	41.1	ND	ND	57.1
Cruise ship	1.92 + 1.47	×	6	0.65	<0.1	<0.1	<0.1	0.2	0.6	<0.1	<12	<0.1	<0.1	0.8
Cruise ship	1.92 + 1.47	×	7	1.16	<0.1	<0.1	<0.1	2.1	1.7	0.2	<12	0.2	0.4	4.2
Cruise ship	3.19	×	5.44	1.02	ND	ND	ND	6.2	13	ND	ND	1.5	0.9	41
Cruise ship	3.19	×	5.62	0.41	ND	ND	ND	5.1	9.7	ND	ND	1.5	0.9	34
Cruise ship	1.97	×	5.8	0.18	ND	ND	ND	7.8	14	ND	ND	1.5	2	55
Cruise ship	1.97	×	5.9	0.13	ND	ND	ND	6.1	22	ND	ND	1.3	2.2	71
Cruise ship	0.98	×	5.9	2.54	<0.1	<0.1	<0.1	3.6	<0.1	1	42	1.4	3.8	16
Cruise ship	0.98	×	5.93	3.37	<0.1	<0.1	<0.1	3.2	<0.1	6.3	120	1.5	1.7	21
Cruise ship	2.34	×	6.39	0.78	<0.1	<0.1	<0.1	3.6	14	0.2	<12	2.2	0.5	51
Cruise ship	2.34	×	6.37	0.46	<.01	<0.1	<0.1	0.3	30	0.1	<12	2.7	2.7	110
Cruise ship	×	×	5	1.6	22.15	16.5	<.6	10.4	22.1	<1.36	<26	3.08	6.46	59.6
Cruise ship	×	×	7.1	[159]	ND	[50]	ND	[247]	[6810]	[15.4]	[593]	[56.2]	[220]	[18800]
Cruise ship	×	×	4.2	1.1	<.5	<.005	<.1	1	13	<1	7	2	3	38
Cruise ship	×	×	4.5	1.1	<.5	<.005	<.1	3	13	<1	<5	2	2	38
Cruise ship	×	×	3.5	1.4	<.5	<.005	<.1	5	25	<1	8	2	4	64
Cruise ship	×	×	3.4	1.5	<.5	<.005	<.1	3	25	<1	9	2	4	63
Cruise ship	1.56	×	5.93	0.3	ND	ND	ND	4.2	14.9	0.3	7.3	5.2	0.9	66.4
Cruise ship	1.56	×	6.41	0.32	ND	ND	0.1	3	4.8	ND	4.4	4.7	0.7	36.5

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenanthrene) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (μg/L)	Cu (μg/L)	Ni (μg/L)	Pb (μg/L)	Zn (μg/L)	As (μg/L)	Cr (μg/L)	V (μg/L)
Cruise ship	2.1	×	5.2	0.63	<0.5	0.039	<1	11	<1	7	<10	2	2	25
Cruise ship	2.1	×	5.5	0.88	<0.55	0.046	<1	3	<1	7	<10	2	1	21
Cruise ship	1.58	×	5.95	0.28	<0.9	<0.9	ND	0.2	0.9	ND	1.1	ND	0.2	2.8
Cruise ship	1.58	×	5.79	0.27	<0.9	<0.9	ND	0.1	0.8	ND	0.9	ND	0.1	2.3
Cruise ship	1.58	×	5.57	0.22	<0.9	<0.9	ND	0.1	0.9	ND	0.3	ND	0.1	2.7
Cruise ship	2.38	×	6.2	1.95	<0.1	<0.1	<0.1	<0.1	3.9	<0.1	<12	<0.1	<0.1	1.2
Cruise ship	2.38	×	6.2	2.22	<0.1	<0.1	<0.1	<0.1	3.2	<0.1	<12	<0.1	<0.1	0.8
Cruise ship	×	×	5.6	0.79	<0.1	<0.1	<0.1	<0.1	1.4	<0.1	<12	<0.1	<0.1	4.4
Cruise ship	×	×	5.3	1.16	<0.1	<0.1	<0.1	<0.1	0.9	<0.1	<12	<0.1	<0.1	2.8
Cruise ship	3.245	×	×	0.69	<0.9	<0.9	ND	ND	1.8	ND	4	1.8	1	9.5
Cruise ship	3.245	×	×	0.52	<0.9	<0.9	0.1	ND	3.2	ND	2.6	2.2	0.5	7.6
Cruise ship	3.245	×	×	0.58	<0.9	<0.9	ND	5.6	2.9	ND	7.8	2.1	1.4	11.5
Cruise ship	3.245	×	×	0.76	<0.9	<0.9	ND	6.8	4.5	ND	2.2	1.9	0.7	20.9
Cruise ship	3.245	×	×	0.9	<0.9	<0.9	0.1	8.8	5.9	ND	7.5	1.9	1.7	20
Cruise ship	2.3	×	5.6	0.31	<0.1	<0.1	<0.1	1.7	3.3	<0.1	<12	1.4	1	10
Cruise ship	2.3	×	5.6	0.66	<0.1	<0.1	<0.1	2.8	3.3	<0.1	<12	1.5	0.3	14
Cruise ship	2.3	×	5.6	0.42	<0.1	<0.1	<0.1	3.1	3.8	<0.1	<12	1.4	1	12
Cruise ship	2.7	×	5.5	0.38	<0.25	0.051	<1	18	16	<1	<10	2	3	42
Cruise ship	2.42	×	5.12	0.94	ND	ND	ND	82.8	205	1	52	3.3	35.5	529
Cruise ship	2.42	×	5.54	1.11	<0.9	<0.9	ND	6.9	45.8	0.9	16.3	2.3	2.5	298
Cruise ship	2.42	×	4.19	1.58	<0.9	<0.9	ND	8.4	74.6	0.3	16.4	2.1	2	576
Cruise ship	2.42	×	4.04	1.72	<0.9	<0.9	ND	15.4	93.9	0.6	25.2	2.4	6.9	556
Cruise ship	×	×	5.7	1.2	ND	ND	ND	1	8.2	0.4	7.9	3	1.5	26.9

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenanthrene) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	As (µg/L)	Cr (µg/L)	V (µg/L)
Cruise ship	×	×	5.9	1.43	ND	ND	ND	2	9.4	0.2	1.1	1.9	3.1	29
Cruise ship	1.37	×	5.7	0.46	ND	ND	0.1	1	6	0.2	30.4	2	1.8	26.5
Cruise ship	1.37	×	5.6	0.34	ND	ND	0.1	1.2	4.7	0.1	26	2.2	1.5	26.7
Cruise ship	1.08	×	5.96	3.56	0.099	0.099	<0.5	2	10	<1	24	3	<1	28
Cruise ship	1.08	×	6.39	0.77	0.082	0.082	<0.5	2	4	<1	25	2	<1	14
Cruise ship	×	×	6.74	<1	[65]	0.085	<1	[64]	[660]	<2	[116000]	<2.5	<1	[3470]
Fully cellular container	×	×	3.3	×	0.181	ND	ND	334	49	21	1715	ND	49	ND
Fully cellular container	×	×	×	×	ND(<5.0)	×	×	×	×	×	×	×	×	×
Fully cellular container	×	×	×	×	18.7	ND(<5.0)	×	×	×	×	×	×	×	×
Fully cellular container	2.88	8.32	4.85	4.4	×	×	×	×	×	×	×	×	×	×
Fully cellular container	×	5.41	3.42	4.47	0.36	0.18	×	×	×	×	×	×	×	×
Fully cellular container	×	×	×	×	[11.3]	[22.5]	×	×	×	×	×	×	×	×
Fully cellular container	2.39	7.49	4.67	7.16	×	×	×	×	×	×	×	×	×	×
Fully cellular container	2.39	[7.01]	[7.83]	[9.24]	×	×	×	×	×	×	×	×	×	×
Fully cellular container	×	10.28	5.7	19.35	×	×	×	×	×	×	×	×	×	×
Fully cellular container	×	[8.64]	[8.53]	[15.56]	×	×	×	×	×	×	×	×	×	×
Fully cellular container	3.06	16	6.1	1.28	0.01	0.001	<5	6	<5	<5	<5	40	<5	22
Fully cellular container	3.22	4	3.8	×	×	×	×	×	×	×	×	×	×	×
Fully cellular container	3.22	×	×	×	×	×	×	×	×	×	×	×	×	×

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenanthrene) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	As (µg/L)	Cr (µg/L)	V (µg/L)
Fully cellular container	×	×	×	0.7	ND(<5.0)	ND(<5.0)	ND(<1.0)	ND(<10)	48	ND(<10)	ND(<50)	ND(<50)	ND(<10)	199
Heavy lift cargo	×	×	5.9	×	×	×	×	×	×	×	×	×	×	×
Multipurpose	2.5	×	6.8	<0.1	<.05	0.038	<1	<5	<5	<5	<20	<4	<5	8.5
Multipurpose	×	×	×	×	<1	×	×	×	×	×	×	×	×	×
Multipurpose	2.23	×	6.2	0.3	<.05	0.036	<1	<5	26	<5	<20	<4	<5	43
Multipurpose heavy lift cargo	2.55	×	6.7	<0.1	0.074	0.041	<1	<5	<5	<5	<20	<4	<5	14
Ore carrier	×	0.5		×	0.4	<0.1	×	×	×	×	×	×	×	×
Ore carrier	×	×	×	×	0.54	<.01	×	×	×	×	×	×	×	×
Ore carrier	2.71	×	×	×	0.555	×	×	×	×	×	×	×	×	×
Ore carrier	3.28	×	×	×	0.0639	×	×	×	×	×	×	×	×	×
Ore carrier	2.91	×	×	×	0.012	×	×	×	×	×	×	×	×	×
Ore carrier	2.23	5.3	3.4	×	0.153	×	×	×	×	×	×	×	×	×
Ore carrier	×	ND	2.8	0.3	ND(<5.0)	×	×	×	×	×	×	×	×	×
Ore carrier	×	×	2.5	1.2	0.8	<.01	<.5	7	15	<1	15	2	<1	43
Ore carrier	×	ND	3	ND	ND(<5.00)	×	×	×	×	×	×	×	×	×
Ore carrier	×	ND	2.8	0.3	ND(<5.00)	×	×	×	×	×	×	×	×	×
Ore carrier	×	1	2.7	0.4	ND(<5.00)	×	×	×	×	×	×	×	×	×
Ore carrier	x	x	x	x	0.74	<.01	x	x	x	x	x	x	x	x
Ore carrier	x	x	x	x	8.47	x	x	x	x	x	x	x	x	x
Ore carrier	×	×	×	ND	ND(<5.0)	ND(<5.0)	ND(<1)	ND(<10)	75	ND(<10)	87	ND(<50)	ND(<10)	317
Ore carrier	×	ND	2.8	0.8	ND(<5.0)	×	×	×	×	×	×	×	×	×

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenanthrene) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	As (µg/L)	Cr (µg/L)	V (µg/L)
Ore carrier	×	×	×	<.005	<.005	<.001	<1	<50	<10	<10	<50	<.5	<5	×
Ore carrier	×	×	×	0.3	0.89	0.45	<5	<5	21	<5	<100	<5	19	89
Product carrier	×	0.7	3.9	ND(<0.1)	2.6	ND(<0.1)	ND(<100)	100	<100	ND(<100)	1200	<100	ND(<100)	200
Product carrier	×	×	×	×	ND(<5.0)	ND(<5.0)	×	×	×	×	×	×	×	×
Product carrier	×	×	4.1	0.6	ND	ND	ND	3	16	ND	ND	2	1	120
Ro-Ro	3.44	20.93	6.5	1.8	10.6	<.02	<2	10	30	<10	<20	<10	<10	70
Ro-Ro	2.79	15	3.5	×	×	×	×	×	×	×	×	×	×	×
Ro-Ro	2.79	×	×	×	×	×	×	×	×	×	×	×	×	×
Tanker	×	×	×	ND	18.3	<5.00	ND	2	19	ND	66	ND	3	95
Tanker	×	×	×	×	ND	ND	×	×	×	×	×	×	×	×
Tanker	×	×	×	×	ND(<5.0)	ND(<5.0)	×	×	×	×	×	×	×	×
Tanker	×	×	6.4	ND	ND	ND	ND	ND	30	ND	ND	ND	ND	70
Tanker	2.83	×	×	×	×	×	×	×	×	×	×	×	×	×
Tanker	×	×	6.27	ND	0.26	ND	ND	ND	ND	ND	80	ND	ND	ND
Tanker	×	×	3.97	ND	×	×	ND	ND	30	ND	60	ND	ND	50
Tanker	×	0.58	×	<1.0	0.26	×	×	×	×	×	×	×	×	×
Tanker	×	×	×	ND	ND(<5.0)	ND(<5.0)	ND(<1.0)	ND(<10)	30	ND(<10)	56	ND(<50)	ND(<10)	106
Tanker or Bulk carrier	×	×	3	ND	<.30	<.30	<2	<40	<40	<2	<50	2.8	<2	<50
Number of samples reported as "ND"	0	19	0	41	31	34	55	22	7	41	11	28	16	8
Number of samples reported as "ND(<*)"	0	0	0	8	48	51	40	31	7	37	22	33	34	5

Ship type	Fuel oil sulfur content	Turbidity at outlet	pH	PAH (phenanthrene) (ug/L)	Nitrate (mg/L)	Nitrite (mg/L)	Cd (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	As (µg/L)	Cr (µg/L)	V (µg/L)
Number of samples reported as "ND"	0	19	0	41	31	34	55	22	7	41	11	28	16	8
Number of samples where result of analysis is specified	**74**	**64**	**170**	**139**	**96**	**33**	**13**	**100**	**139**	**47**	**97**	**78**	**95**	**161**
Average of samples where result of analysis is specified	**2.33**	**3.39**	**4.52**	**1.28**	**3.52**	**0.95**	**0.42**	**29.7**	**39.0**	**7.75**	**157**	**3.09**	**10.3**	**131**
Maximum	**3.44**	**20.9**	**7.1**	**19.4**	**27**	**16.5**	**2**	**631**	**366**	**136**	**3390**	**40**	**160**	**3100**

928 [a] Excludes information on engine type and power, EGCS discharge rate, laboratory and date of report

Table S2. Particulate vs dissolved metal measurements in washwaters (Schmolke et al., 2020)

Metal	Dissolved metal, µg/L			Particulate metal, µg/L		
	minimum	maximum	average	minimum	maximum	average
Copper	1.6	15.7	7.3	0.1	4.0	0.7
Nickel	4.1	67.4	20.0	1.4	7.3	3.8
Vanadium	10.6	290	78.4	1.6	238	10.6
Zinc	2.1	133	22.8	0.1	0.8	0.3

S2. TOXICITY DATA FOR VANADIUM IN MARINE WATERS

A search of more recent data for vanadium toxicity marine biota enabled updating of the GV derived in 2000 (ANZECC/ARMCANZ, 2000), which as we have already discussed would be considered as being of low reliability. The updated dataset is shown in Table S3, representing 10 species from eight different taxonomic groups. A species sensitivity distribution of these data is shown in Figure S1, resulting in a GV now classified according to Warne et al. (2018) as moderate reliability. The revised PC99, 95 and 90 values are respectively 8.9, 20 and 34 µg/L.

Table S3. Updated toxicity data for vanadium in marine waters for use in GV derivation

Taxonomic Group	Species	Life stage	Exposure duration (d)	Effect	Toxicity measure	Salinity (‰)	Temp (°C)	Concentration (µg/L)	Reference
Diatom	*Nitzschia closterium*	Exponential phase	3	Growth rate	IC10	35	32	9100	Harford et al. 2011
								9100	**Value used in SSD**
Diatom	*Asterionella japonica*	Exponential phase	15	Mortality	LC50	38	14	2000	Miramand and Unsal 1978
								400	**Value used in SSD**
Green alga	*Dunaliella salina*	Exponential phase	15	Mortality	LC50	38	14	500	Miramand and Unsal 1978
								100	**Value used in SSD**
Dioflagellate	*Prorocentrum micans*	Exponential phase	15	Mortality	LC50	38	14	3000	Miramand and Unsal 1978
								600	**Value used in SSD**
Bivalve mollusc	*Crassostrea gigas*	Larvae	2	Abnormalities	LOEC	34	24	50	Fichet and Miramand 1998
								20	**Value used in SSD**
Crustacean	*Artemia salina*	Larvae	2	Abnormalities	LOEC	34	24	100	Fichet and Miramand 1998
								40	**Value used in SSD**
Echinoderm	*Paracentrotus lividus*	Larvae	2	Abnormalities	LOEC	34	24	100	Fichet and Miramand 1998
								40	**Value used in SSD**
Bivalve mollusc	*Mytilus galloprovincialis*	Adults	9	Mortality	LC50	38	14	65000	Miramand and Unsal 1978
								13000	**Value used in SSD**
Arthropod	*Carcinus maenas*	Adults	9	Mortality	LC50	38	14	35000	Miramand and Unsal 1978
								7000	**Value used in SSD**
Polychaete	*Nereis diversicolor*	Adults	9	Mortality	LC50	38	14	10000	Miramand and Unsal 1978
								2000	**Value used in SSD**
Coral	*Acropora tenuis*	Larvae	18 h	Metamorphosis	IC10	35	27	463	Negri et al., 2011
								463	**Value used in SSD**

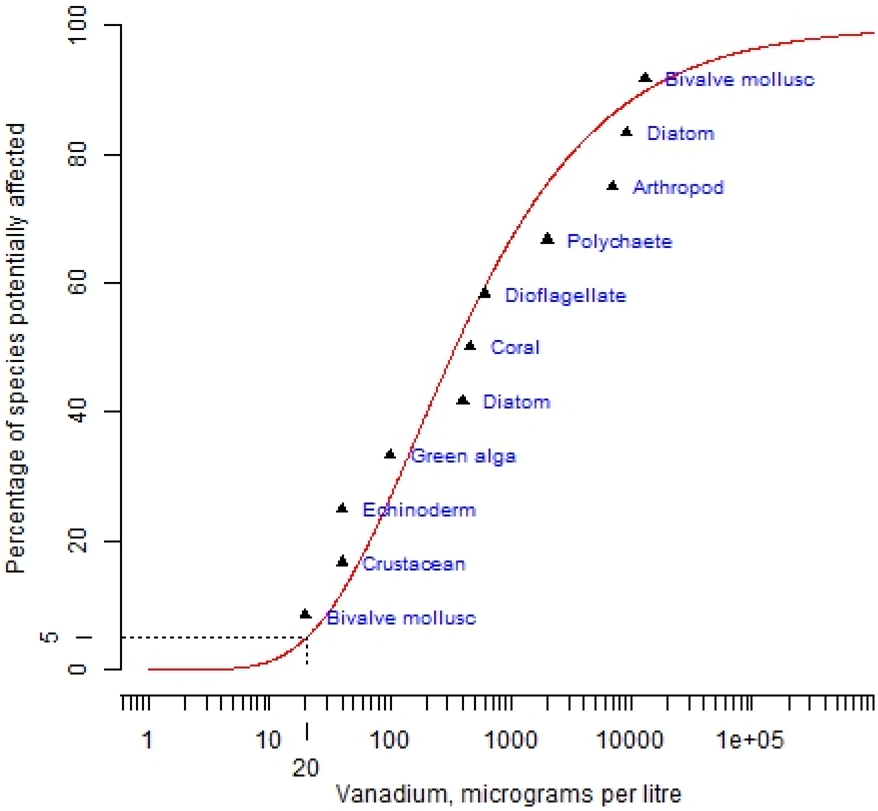

Figure S1. Species sensitivity distribution of vanadium toxicity data for marine waters

S3. ADDITIONAL MODELLING RESULTS

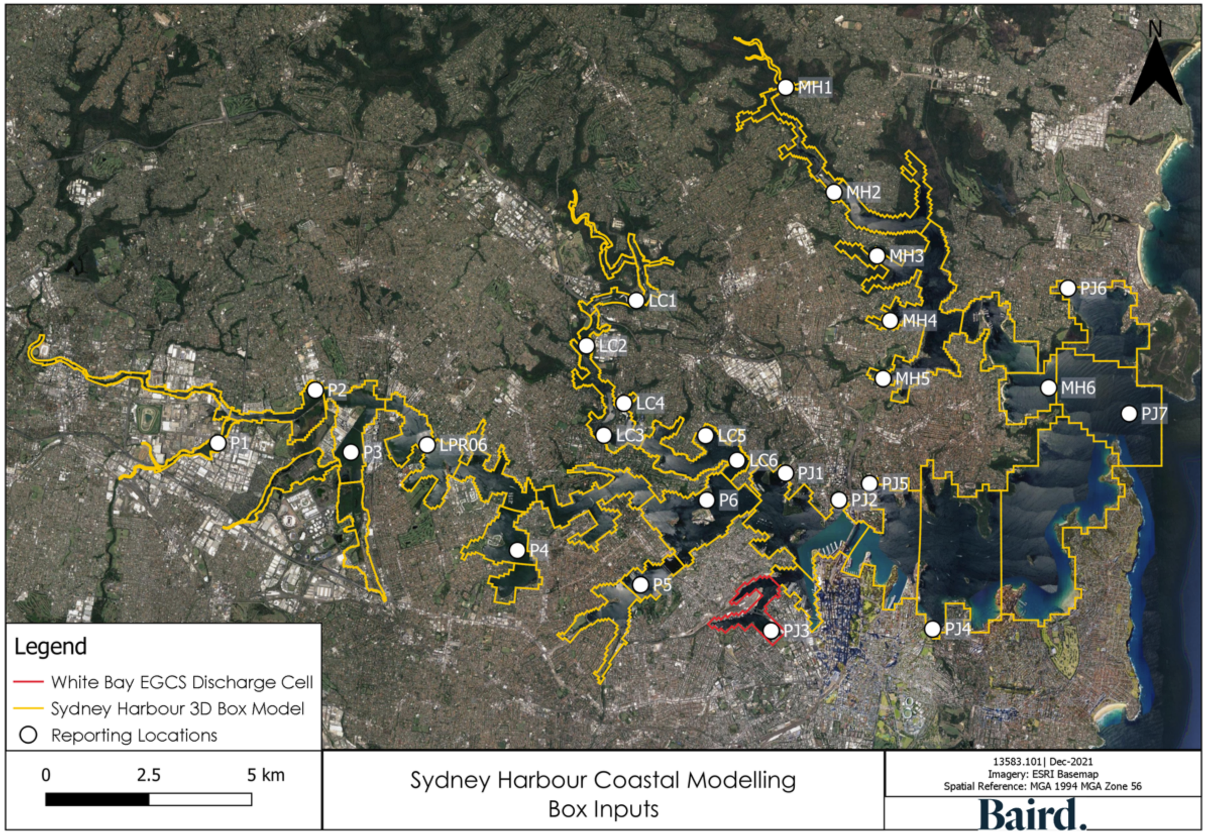

Figure S2. Spatial outline of SHBM with an outline of individual computational cells. Model output locations and the location of White Bay EGCS discharge also shown.

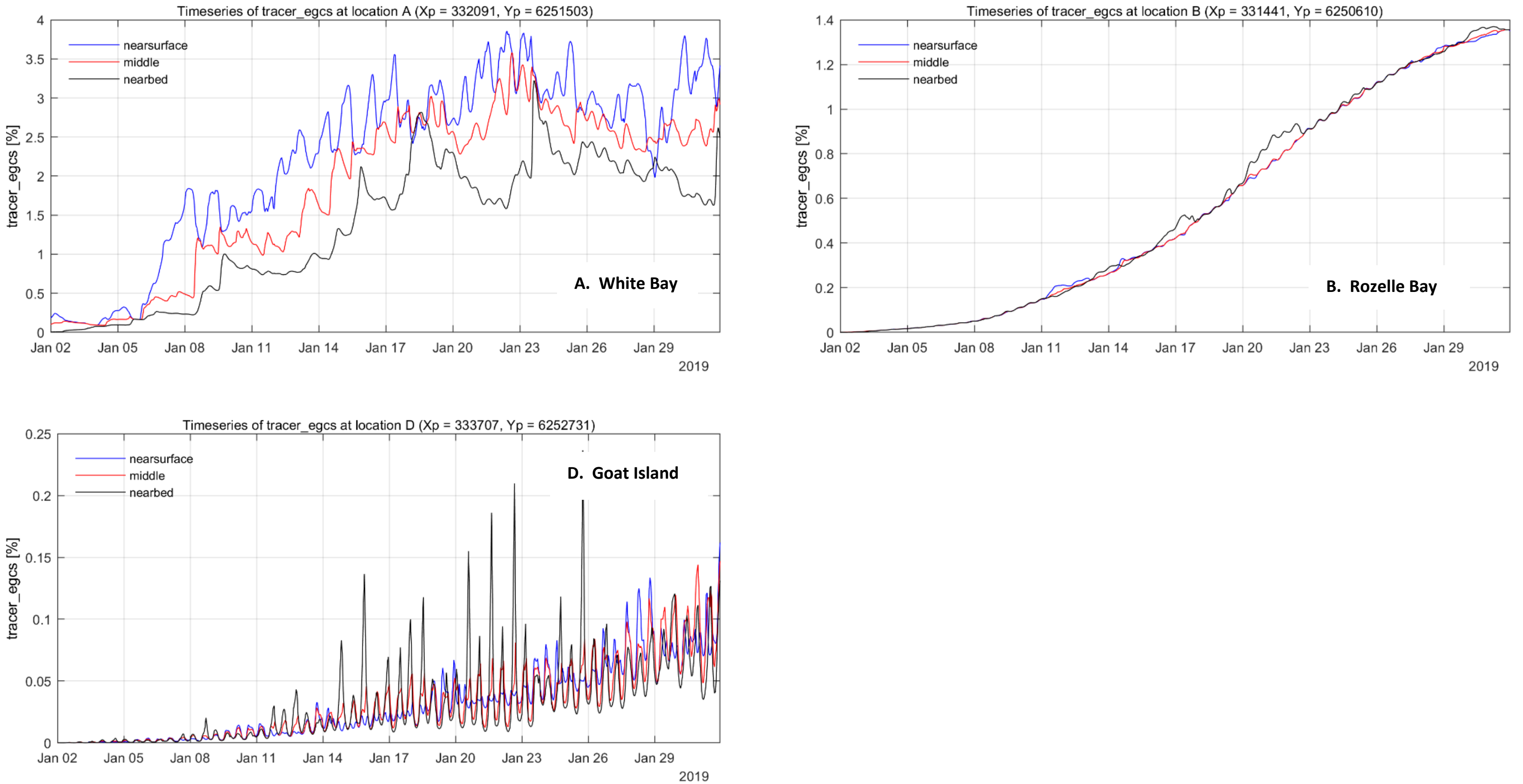

Figure S3. Time series of EGCS tracer (% of initial concentration) during wet weather scenario at reporting locations in Sydney Harbour. To express as a total dilution this needs to be multiplied by the near-field dilution of 1 in 18. The near-surface and middle series are not discernible from the near-bed series when they overlap, i.e., negligible differences.

S4. REFERENCES

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