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The Solent Strait: Water quality trends within a heavily trafficked marine environment, 2000 to 2020

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ABSTRACT

This study presents an important long-term historical analysis of water quality in an internationally crucial waterway (the Solent, Hampshire, UK), in the context of increasing adoption of open-loop Exhaust Gas Cleaning Systems by shipping. The pollutants studied were acidification (pH), zinc, and benzo [a] pyrene, alongside temperature. We compared baseline sites to locations likely to be impacted by pollution. The Solent's average water temperature is slightly increasing, with temperatures at wastewater sites significantly higher. Acidification suggests a complex story, with a highly significant small overall increase in pH during the study period but significantly different values at wastewater and port sites. Zn concentrations have significantly reduced but increased in enclosed waters such as marinas. BaP showed no long-term trend with values at marinas significantly and consistently higher. The findings provide valuable long-term background data and insights that can feed into the upcoming review of the European Union's Marine Strategy Framework Directive and ongoing discussions about the regulation of, and future monitoring and management strategies for coastal/marine waterways.

1. Introduction

There is considerable concern about our marine environment. At a global level, the International Convention for the Prevention of Pollution from Ships 1973 (modified by the Protocol of 1978), was developed by the International Maritime Organisation to minimize pollution of the oceans and seas. The current convention entered into force on 2 October 1983. As of January 2018, 156 states are parties to the convention. In Europe, the European Union (EU) adopted the Marine Strategy Framework Directive (MSFD) in 2008 to maintain healthy, productive and resilient marine ecosystems while securing a more sustainable use of marine resources. The MSFD set out a common EU approach and objectives for the prevention, protection and conservation of the marine environment while allowing for its sustainable use, by means of an ecosystem-based approach.

The MSFD builds on existing EU legislation to facilitate the creation of a network of marine protected areas. It is crucial since it covers specific elements of the marine environment not addressed in other policies, such as the water framework directive (Directive 2000/60/EC), the habitats directive (Directive 92/43/EEC), the birds directive (Directive 2009/147/EC) and, Regulation (EU) No 1380/2013 on the common fisheries policy. In 2020, the European Commission (EC) adopted a report on the first implementation cycle of the MSFD. It concludes that the MSFD needs enhancement to ensure that it can address issues such as overfishing and unsustainable fishing practices, plastic litter, excess nutrients, underwater noise and other pollution from shipping. In July 2021, the EC launched a public consultation to gather information and the views and ideas of parties involved in and affected by the MSFD. A review of the MSFD must take place by end 2023.

In this context, this long-term study provides important historical background for England's Solent region as part of the EMERGE project. The EMERGE project (https://emerge-h2020.eu/) is an innovative 4-year project funded by the European Commission under the Horizon 2020 programme. The project aims to quantify and evaluate the effects of potential emission reduction solutions for shipping in Europe and develop effective strategies and measures to reduce the environmental impacts of shipping.

With the largest export docks in the UK (ABP, 2016), the Royal Navy home port (Royal Navy, 2020), and multiple ferry services, including the only scheduled hovercraft service in the world (Hovertravel, 2020), the

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Solent Strait is heavily trafficked by commercial, naval, and public transport vessels. The impact these vessels has had on the marine environment has been acknowledged since the 1980s, when shipping inventories by Knap et al. (1982) and Houston et al. (1983) raised concerns regarding petroleum pollution effects on benthic communities. This research was developed in the early 1990's when Gough et al. (1994) studied antifouling paint particulates (APP) in the Solent, concluding that APP concentrations in coastal waters coincide with increased maritime activity, and Bray et al. (2012) showed local extinctions and – after regulation, some recovery. In 1998, Bianchi and Varney (1998) detailed volatile organic compound (VOC) pollution in the Solent and its ease of transmission via the air-sea interface. More recently, Xiong et al.'s (2023) long-term historical analysis of the impacts of recreational boating on marine surface water quality during a regatta (Cowes Week) in the Solent Strait showed that sewage discharge from recreational boats is the key contributor to localised faecal contamination of marine surface waters, putting bathers and shellfisheries at risk.

In 1997 the International Maritime Organisation (IMO) implemented Sulphur Emission Control Areas (SECAs), whereby airborne pollution from shipping was controlled within some waters via ultra-low sulphur diesel (ULSD) (Wankhede, 2019; IMO, 2020). The Solent waterway is part of the Baltic and North Sea SECA, consequently ships inside must be equipped with scrubber systems in exhausts or switch to ULSD fuel containing 0.1 % sulphur, thus reducing SOx and Particulate Matter (PM) emissions. Since 2020, outside of ECAs, only 0.5 % sulphur containing ULSD fuel is permitted, compared to 3.5 % previously (Sawchenko et al., 2020). Reduction in sulphur emissions and other exhaust gasses can be achieved through exhaust gas cleaning systems (EGCSs) (Sargun Sethi, 2020). These are favoured as acute one-off investments for large ships, versus chronic, ULSD budgeting (Abadie et al., 2017). Previous research suggests EGCS technology presents an effective mitigation method for heavily polluted bunker fuel exhaust gasses (Sargun Sethi, 2020).

Multiple EGCSs exist. Dry EGCSs force exhaust emissions through treatment chemicals and are not widely used. Wet EGCSs force exhaust emissions through recirculating fresh/seawater, with or without added treatment chemicals (Sawchenko et al., 2020). These wet EGCSs make up >70 % of current application (DNV GL, 2020a, 2020b) with the majority being open-loop; meaning seawater is used to filter exhaust emissions, and subsequently released with little treatment (Abadie et al., 2017).

These scrubbers are effective at removing significant SO_2 (Zhu et al., 2020) and black carbon (BC) particulates (Zhang et al., 2019) yet are ineffective at removing NOx (Yang et al., 2012). EGCSs have effectively reduced ship-borne atmospheric pollution of sulphur-containing compounds and black carbon particulates (Fridell and Salo, 2016), in line with international policy (Zhu et al., 2020).

Comer et al. (2020) and Winnes et al. (2020) have reviewed EGCSs. These studies reveal EGCSs only remove 32–43 % of particulate matter from heavy fuel oil (HFO) exhaust; and also suggests HFO with an EGCS does not present itself as an equivalent to low sulphur fuel oil (LSFO) usage. The study's methodology describes exhaust gas sampling compliant with International Standards Organisation (ISO) standards. However, the study notes HFO and LSFO measurements were conducted in differing seasons, meaning surface sea temperature (and thus pH) may have an influence on the emission values as illustrated in Ülpre and Eames (2014), due to the reliance on the natural alkalinity of seawater to reduce SOx emissions. Like other studies, Winnes et al. (2020) follows the convention of exhaust gas dilution before sampling, meaning the methodology is comparable to similar papers by Fridell and Salo (2016) and Kuittinen et al. (2020); all presenting similar findings.

Research by Ni et al. (2020) reinforces Winnes et al. (2020), in particular the implementation of injection systems alongside LSFs to achieve significant reductions in emissions at the combustion stage. Ni et al. (2020) compliments Comer et al. (2020) by giving technical diagrams of EGCSs and presenting alternative strategies for achieving similar emission reduction values. Within Comer et al. (2020), Teuchies et al. (2020), and Winnes et al. (2020), a link between open-loop EGCSs and increased ocean acidification has been identified.

The IMO sets limits for the permitted concentrations of specific contaminants present in EGCS washwater, including polycyclic aromatic hydrocarbons (PAHs) and nitrates, as well as limits on pH and turbidity (Lange and Markus, 2015). As part of a full scrubber mixture, PAHs may induce biological effects at low concentrations (Koski et al., 2017) Chen et al. (2022) demonstrated that PAHs in the sediments of commercial ports in Taiwan may have moderate to high potential ecological risks. PAHs are hydrophobic pollutants, and their emissions from scrubbers can be attributed to both the fuel content and the combustion process (Lunde Hermansson et al., 2021). The United States Environmental Protection Agency (USEPA) has identified sixteen PAHs as high priority pollutants due to their potential toxicity and increased prevalence in the environment (Hussar et al., 2012). This implies further implementation of open-loop EGCSs may have marked impacts on water quality around the world within coastal systems such as the heavily trafficked Solent Strait, in line with research by Dulière et al. (2020).

Metals found in washwater effluents from EGCSs come directly from the fuel type and the compositions of the tubing/units used metals (Faber et al., 2019). The origins and refinery of the fuels make up for the main heavy metal composition of washwater (Agrawal et al., 2009). In general, four metals consistently found in washwater effluents are vanadium, zinc, copper and nickel (Teuchies et al., 2020; Ytreberg et al., 2022), although the overwhelming majority of copper input from ships and leisure boats is often from antifouling paints (Ytreberg et al., 2022). Teuchies et al. (2020) also assessed more global ramifications of widespread EGCS implementation and targets (among other pollutants) benzo [a] pyrene (BaP), illustrating its dangers through the inclusion of BaP in the EU Water Framework Directive (WFD) 2013/39/EU (European Parliament, 2013). The report highlights many estuarine areas where ports are located are part of the Natura 2000 site network, presenting a distinct need for EGCS regulation. Much of the Solent Strait is part of this network (DEFRA, 2020) and also contains areas designated for shellfisheries. Teuchies et al. (2020) further highlights the issues of acidification of water through EGCS discharges, providing quantifiable release values for comparison purposes.

Furthering research by Dulière et al. (2020) and Teuchies et al. (2020), we studied pollutant concentrations throughout the Solent, focussing on shipping emission pollutants from 2000 to 2020 in the Solent Strait, UK. This was carried out to identify any trends within the 20-year time frame and to highlight any deviations from expected values using quantitative analysis of time-series data. The analysis has been undertaken by comparing United Kingdom Environment Agency (EA) Water Quality Information Monitoring System (WIMS) data at designated baseline locations throughout the Solent, to readings taken at likely pollution sites within the years 2000–2020 where possible. The pollutants studied were pH, zinc (Zn - Filtered (μg/l)), and BaP (μg/l), alongside temperature (°C) as an explanatory variable (The Maritime Executive, 2020; Sawchenko et al., 2020). Current reports on pollution in the area mainly focus on APPs, VOCs, nitrates, and petroleum pollution. Brief descriptions of sediment quality exist in the form of dredging reports and Maintenance Dredge Protocols by the Harbour Authority, Associated British Ports (ABP) in the Solent; these do not assess water quality directly and are targeted towards dredge locations and deposition sites (ABP, 2011; ABPmer, 2014). An overarching water quality report focussing on contaminants associated with ECGSs for the Solent does not yet exist in peer reviewed literature and is thus required to monitor changes in the state of water quality in one of the UK's busiest waterways (ABP, 2016) where open-loop scrubber effluent may influence pollutant levels in the future.

2. Methods

The baseline condition of the Solent strait of the English Channel, from the Needles (three rocks off the western extremity of the Isle of Wight) to the opening at Selsey Bill (a headland at the end of the Manhood Peninsula), from 2000 to 2020 has been assessed using a stratified sampling method (see Figs. 1 and 2). The start point for the study was dictated by data availability. This sample site selection allows a representative sample of Solent pollution corridors and the background levels of pollutants targeted in the study. Similar to research carried out by Green and Johnson (2020), this approach follows a similar procedure to that utilised in Herrera-Silveira et al. (2004). The systematic sampling method targets areas of likely pollutant release, alongside multiple baseline sample sites (US EPA, 2002a). Details on approach to sampling, selection and location of sampling points, measurements etc., can be found via the UK Environment Agency's Water Quality Archive (https://environment.data.gov.uk/water-quality/). For this study, data from selected wastewater treatment works (WTW), agricultural runoff sites, ports, marinas, and shipping lanes, were collated from the WIMS. Most sites selected were shellfish monitoring sites, as these records were the most complete for the twenty-year timeframe and sampled the greatest range of pollutants. To ensure the data collected remained representative of the areas selected, multiple sites have been used within each sample site category. Data was collected for the eight sites outlined in Fig. 1.

Three WTW sites were studied within the Solent: Budds Farm (SO-G0003473), Peel Common (SO-G0003520), and Millbrook (SO-G0003473). These sites were selected because of their relatively large size and to give broad geographical coverage across the Solent Strait. For agricultural sites, three locations were selected: Selsey (SO-F0001807), the Isle of Wight (I.O.W.) (SO-Y0017475) and the western Solent (SO-G0003696). The two large ports in the area, Portsmouth (SO-G0003626) and Southampton (SO-G0003661), were selected. Marina monitoring was made more difficult due to lack of shellfish monitoring sites. Consequently, the Itchen marina has two sample sites (SO-G0003781 and SO-G0017018) to consolidate a near-complete twenty-year dataset. No lock gates are necessary to access Itchen marinas. Simultaneously, data were collected from Cowes Marina (SO-Y0004385). Access to Cowes Marina is via lock gates. Finally, data from the entranceways and designated shipping lanes of the ports of Southampton (SO-G0003532) and Portsmouth (SO-G0003514), were collated. The selection of sites was conducted to establish a widespread distribution across the Solent that incorporated all large water bodies and major harbours. The selected sites are shown in Fig. 2.

Water temperature (°C) was studied alongside pollutants zinc (filtered, μg/l) (Zn), acidification (pH) and benzo [a]pyrene. These pollutants were assessed across the twenty-year dataset. Water temperature was assessed for two reasons. Firstly, the United States Environmental Protection Agency (US EPA), recommend temperature surveys are taken of EGCS effluent (US EPA, 2011), and furthermore, it provided a reference, and explanatory variable, for any large annual swings in data which were likely to be presented by pollutants influenced by temperature i.e. pH (Gieskes, 1969).

Targeted pH analysis was used to uncover any influence of acidic EGCS effluent on the baseline levels between 2000 and 2020 against a background global trend of ocean acidification (Ülpre and Eames, 2014). Unfortunately, after 2018 pH data is not recorded at any sample sites within this study and pH data across some sites is sporadic (but still present) after 2010. The EA was contacted for comment, and varying reasons exist for pH data being irregular, ranging from samples being taken as part of larger studies which have since ended, and changes in permit requirements between the years 2000–2020 (EA Support, 2020).

Zn was studied as a proxy for metal pollution from EGCS washwater, as research by Ytreberg et al. (2019) shows Zn forms a substantial proportion of metals present in EGCS discharge. Zn around marinas and boats/ships can be from sacrificial anodes and antifouling paint. Sampling Zn is not a requirement of final effluent sampling at WTW sites, and thus little Zn data exists for WTW sites.

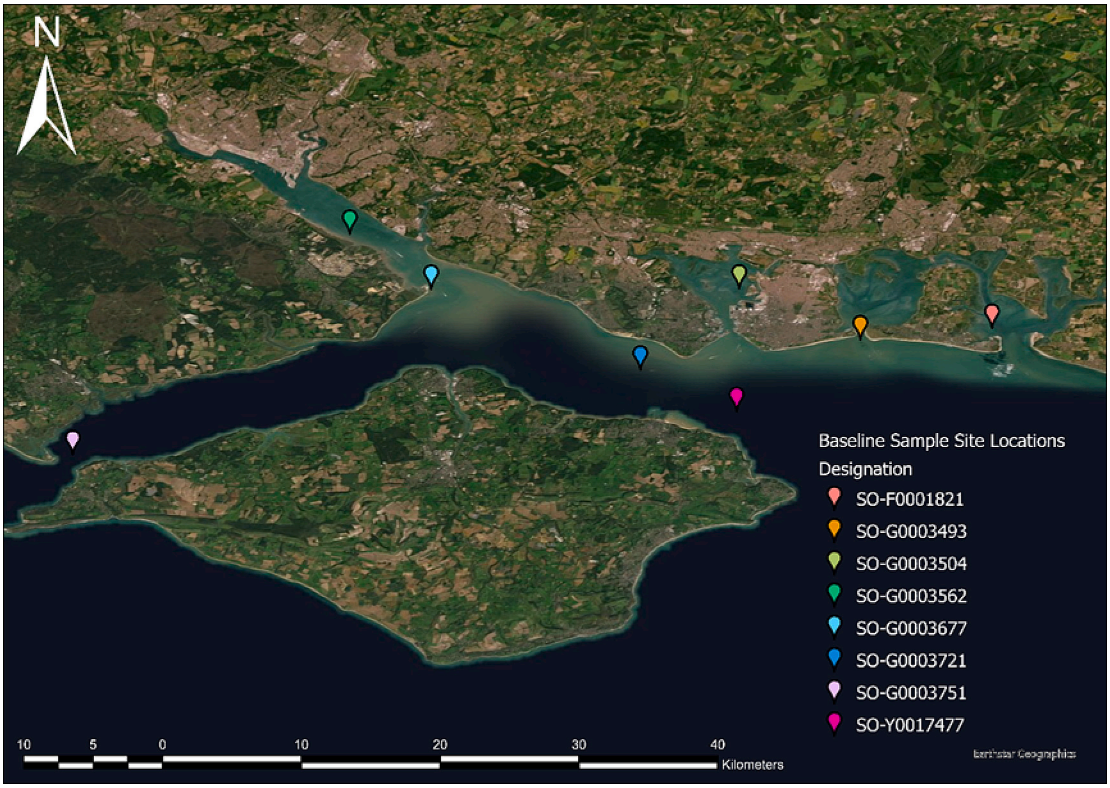

Fig. 1. Baseline sample sites selected for collation for pollutant values, with WIMS designation.

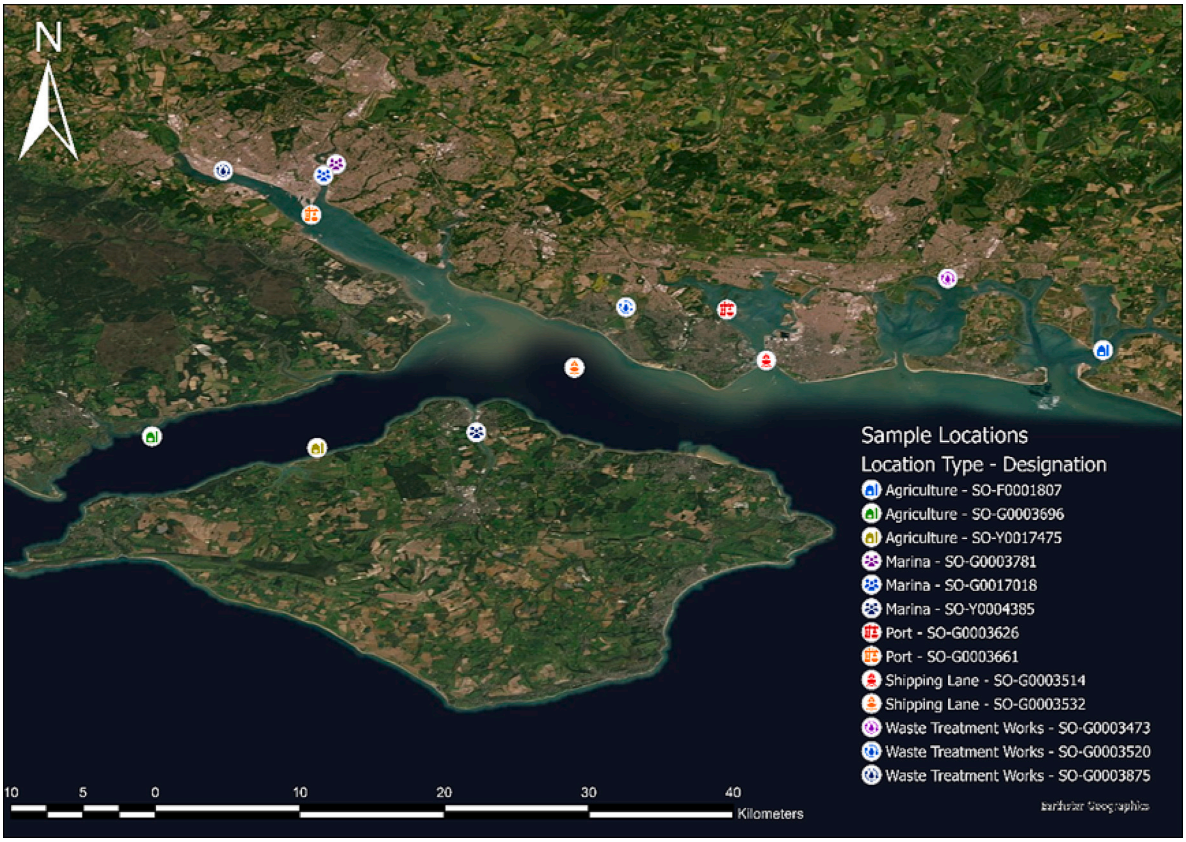

Fig. 2. Water quality monitoring sites selected for assessment near likely pollutant outflows.

Collation of benzo [a] pyrene (BaP) data was conducted to act as a proxy for fluctuations in polyaromatic hydrocarbon (PAH) pollution within the Solent (Fridell and Salo, 2016; Ushakov et al., 2020) The decision for this was based on BaP data forming the most complete set of any PAH pollutant measured at most sample sites, whilst the EA also utilise BaP as an indicator for PAHs (EA, 2019). As with Zn data, some BaP measurements are missing from WTW sites due to permit regulations not requiring a monitoring regime, this applies to all sites pre-2015 (EA Support, 2020). Thus, data only exists after 2015 for BaP levels in the Solent. However, the 2015 data itself has been removed from this analysis due to its anomalous nature: all baseline concentrations in 2015 were recorded as exactly 0.010 μg/l. Thus, in showing no deviation and being almost an order of magnitude greater than all other subsequent readings, 2015 BaP data was removed. The remaining BaP concentrations between 2016 and 2020 were taken to establish trends in the baseline.

The limitations in data availability outlined above are commonplace in pollution studies and imputation methods are often utilised (Ma et al., 2020) to create complete datasets. However, rectifying action has not been taken here to interpolate data from proxy variables (see Chen et al., 2016; Li et al., 2017), maintaining the integrity of the available data used within this study, and the reliability of its interpretation. It must be noted that data for 2020 may be updated in the future as new data are added to the SSD-2020 dataset. This study includes the latest available 2020 data, up to the acquisition date of 9th January 2021.

Long-term trends in the levels of each pollutant were assessed using general linear models, incorporating factors for site type, sample site and their interactions. It was necessary to disentangle trends in this way because the stop-start nature of sampling sometimes influenced apparent average pollutant levels. Following Richir et al. (2021), we also ran quantile regression models for the pollutant levels against time for comparison with the linear models. Quantile regression (Koenker and Bassett, 1978) is sometimes advantageous because of its robustness to outliers and invariance to monotonic transformations. We employed it here simply to assess how the median and mean pollutant level trends differed over time. For the linear models, the response variable was transformed using the automated features in R package bestNormalize where this improved the model residuals. Akaike's Information Criterion (AIC) was used to compare models incorporating the pollutant level alone with models adding factors for site type, sample site and their interactions. Owing to the cyclical nature of pollutant levels (e.g. annually), R-squared values on long-term trends tended to be low in some cases. In addition to examining long term linear trends, non-linear changes over time with 95 % confidence intervals were plotted using cubic splines for each site type through ggplot2 in R.

3. Results

3.1. Water temperature analysis

There was no significant long-term trend in temperature when other factors were taken into account (Table 1) and the median and mean regression lines were very close, suggesting minimal impact of outliers. However, temperatures at WTW sites were significantly higher ($p < 0.001$) by a minimum of 2^0C than those at other sites over the years (Fig. 3). Additionally, there was a non-significant suggestion that Marina temperatures are increasing.

Analysis of temperature across the twenty-year dataset yielded the expected seasonal variation driven by local climate. Fig. 4 shows the annual variation in water temperature at baseline sites and highlights a mean range of 10 °C (7 °C to 17 °C). During 2000 to 2009 there was a decreasing fluctuation in temperature which reduced to a mean range of ~6 °C, between 10 °C and 16 °C. This fluctuation then increased post 2009 where the annual range returned to its original 10 °C range until the year 2018 when an extreme reduction in range to ~3 °C occurred. This range increased to 5 °C in 2019 before the summer temperature of

Table 1

Significant predictors of pollutant levels in the linear models. NI = variable or factor level not included in the final model, either because it was not selected using AIC, or because the data were absent. Blanks indicate variable included but not significant at $p < 0.05$. Significant variables and factor levels are indicated with * p < 0.05, ** $p < 0.01$, *** $p < 0.001$.

	Temperature	pH	Benzo-a-pyrene	Zinc
Response transformation	None	None	Box-Cox	Standardized Yeo-Johnson
Date		***		***
Site type:				
Baseline				
Marina		NI	***	***
Port		**		***
Shipping Lane				**
Agriculture				
WTW	***	***	NI	NI
Sample site:	NI		NI	
SO-F0001821				
SO-G0003473		***		NI
SO-G0003493		***		NI
SO-G0003504				*
SO-G0003514		**		
SO-G0003520		***		NI
SO-G0003562				***
SO-G0003626		*		***
SO-G0003677				***
SO-G0003696				
SO-G0003721				
SO-G0003751				*
SO-G0017018		NI		***
SO-Y0017475				
Interactions	NI	NI	NI	NI
R-squared	6.8 %	78.4 %	24.4 %	31.5 %

Note: The significance levels in Table 1 are assessed simultaneously across the predictors used. This means, for example, that the trend in pH over time is significant even after the effects of site type and sample type have been considered.

2020 reached a value of 16 °C, returning to the expected temperature range by late 2020. Finally, a warming trend was observed in winter months over the 20 year period studied, with the only exceptions being 2009, 2010 and 2011.

Analysis of variance (ANOVAs) carried out on temperature readings highlighted multiple significant differences in mean values between WTW outflows and all other sample site designations. The results summarised in Table 2 suggest WTW temperature means are significantly different from any other sample site's mean temperature. Spearman's Rank analysis yielded significant correlations between baseline temperatures and marina, shipping lane and WTW sites. Firstly, a correlation coefficient of −0.089 was observed to be significant between baseline ($N = 1595$) and marina ($N = 500$) temperatures $P = 0.046$. A more significant negative correlation coefficient of −0.157 was observed between baseline and shipping lane ($N = 514$) temperatures to a significance of $P < 0.000$. Lastly, a small positive correlation was detected between baseline and WTW ($N = 996$) temperatures. The positive correlation coefficient of 0.070 was found to be significant to $P = 0.028$.

3.2. pH analysis

The pH readings were similarly subject to annual fluctuations across the studied time period. However, linear modelling showed there was a highly significant (although numerically small) overall increase in pH during the 15 year period when data were available (Table 1; Fig. 5). The pH values at WTW sites were significantly lower ($p < 0.001$) than those elsewhere and showed a curvilinear relationship downwards against time (dates) that differed among individual WTW sites. These anomalous trends at the WTW sites pulled the linear regression line lower than the median regression line, but the slopes were unaffected.

Although it is difficult to discern in Fig. 5, port sites were also significantly different ($p < 0.01$) from the others. Analysis of pH in the ports of Southampton and Portsmouth revealed wildly fluctuating ranges between the years of 2000 and 2007. This occurred until a more stable fluctuating trend occurred at about pH 8.1 from 2007 until 2015. Within the port of Portsmouth (SO-F0003626), pH values increased between the years of 2000 to 2004, from ~pH 8.05 to ~pH 8.15 before

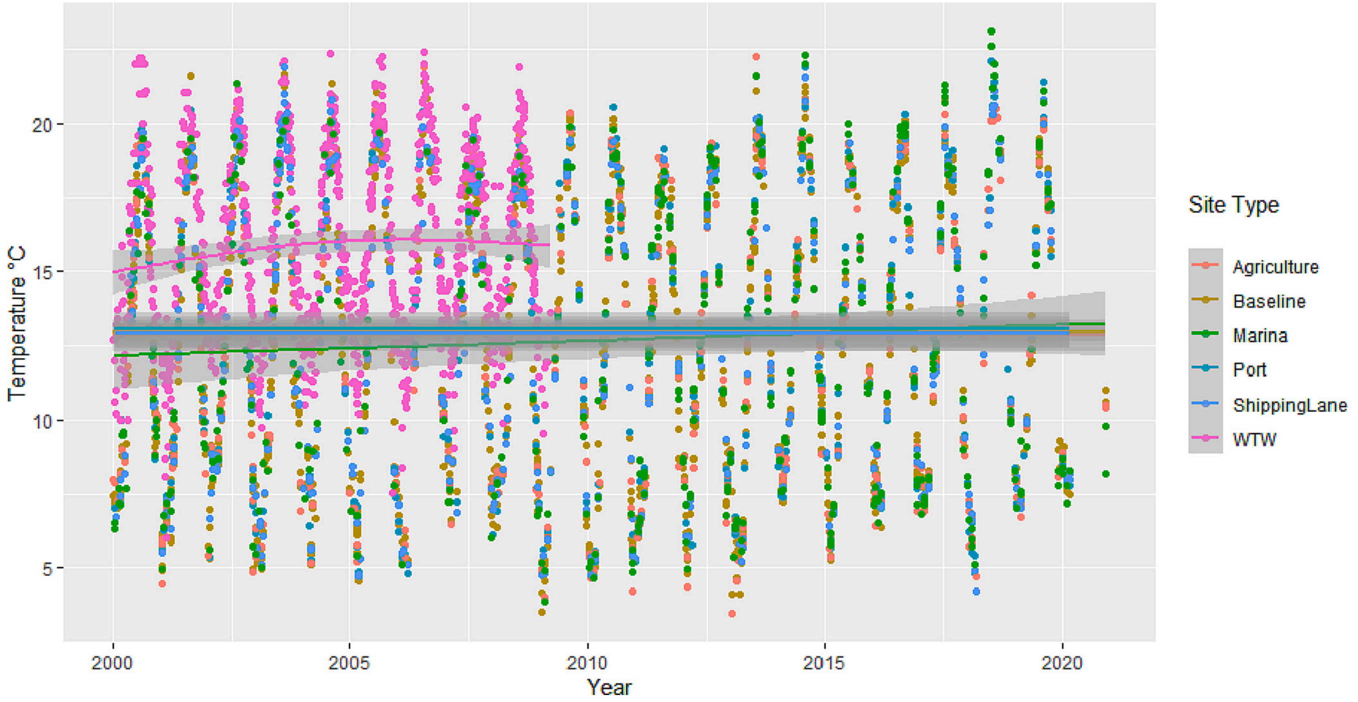

Fig. 3. Long-term (2000−2020) trends in water temperature at selected sites in the Solent, classified by site type.

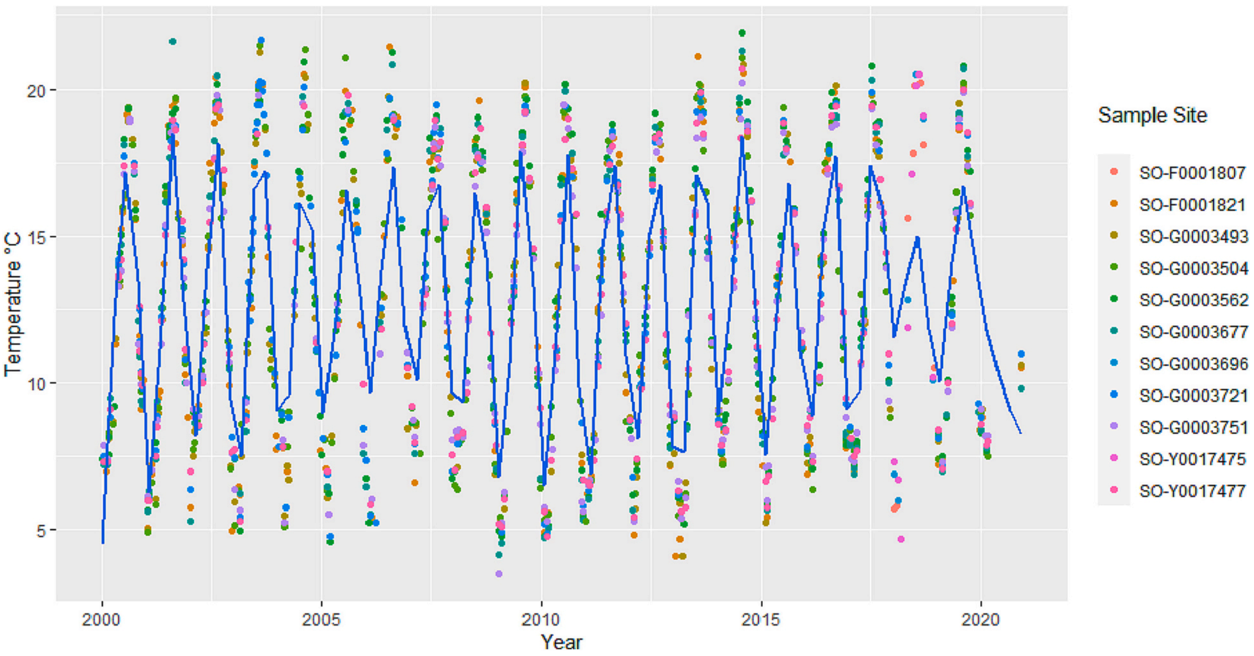

Fig. 4. Annual variations in water temperature at baseline sites in the Solent. Trend line fitted using loess with span = 0.06 to emphasise the annual fluctuations.

Table 2
Collated significant analysis of variance (ANOVA) statistical outputs for differences between mean values observed at all sample sites. Standard Deviation (S.D.).

Site A	Mean	S.D.	Site B	Mean	S.D.	Mean Difference	Standard Error	*P*
Temperature (°C)								
WWTW			Agriculture	12.84	± 4.87	+2.97	±0.24	<0.000
			Baseline	12.95	± 4.70	+2.86	±0.18	<0.000
			Marina	12.74	± 4.81	+3.07	±0.24	<0.000
			Port	13.04	±4.80	+2.77	±0.25	<0.000
			Shipping Lane	12.92	± 4.68	+2.89	±0.24	<0.000
	15.81	±3.17						
pH								
Agriculture	8.80	±0.12	Shipping Lane	8.05	±0.15	+0.05	±0.02	0.017
WTW			Agriculture	8.80	±0.12	−0.71	±0.12	<0.000
			Baseline	8.07	±0.14	−0.68	±0.01	<0.000
			Port	8.08	±0.12	−0.68	±0.01	<0.000
	7.40	±0.27	Shipping Lane	8.05	±0.15	−0.65	±0.01	<0.000
Marina			Agriculture	8.80	±0.12	−0.11	±0.02	<0.000
			Baseline	8.07	±0.14	−0.08	±0.02	<0.000
			Port	8.08	±0.12	−0.09	±0.02	<0.000
			Shipping Lane	8.05	±0.15	−0.06	±0.02	0.032
	7.99	±0.20	WTW	7.40	±0.27	+0.60	±0.02	<0.000
Zn (ug/l)								
Marina			Agriculture	2.04	±1.92	+1.85	±0.29	<0.000
			Baseline	2.43	±1.66	+1.47	±0.26	<0.000
	3.90	±1.67	Shipping Lane	2.27	±1.71	−1.62	±0.31	<0.000
Port			Agriculture	2.04	±1.92	+1.21	±0.23	<0.000
			Baseline	2.43	±1.66	+0.82	±0.20	<0.000
	3.25	±2.14	Shipping Lane	2.27	±1.71	+1.00	±0.26	<0.000
BaP (x10^{-4} μg/l)								
Marina			Agriculture	1.725	±1.0704	+5.9212	±1.2729	<0.000
			Baseline	2.145	±2.7386	+5.5011	±0.8789	<0.000
			Port	2.598	±2.4060	+5.0487	±0.9188	<0.000
	7.646	±6.9162	Shipping Lane	2.632	±2.8082	+5.0140	±0.9934	<0.000

descending back to pH 8.1 in 2009. Post 2009 values gradually increased again to ~pH 8.15 in 2014 where the data stops. The port of Southampton (SO-G0003661) followed a similar pattern to Portsmouth and an inverse one to baseline sites. Southampton's pH values increased steadily from ~pH 7.95 to a peak in 2010 around ~pH 8.1 at the same time as a trough in Portsmouth's pH values.

ANOVA tests revealed multiple significant variations in means across some locational designations, as outlined in Table 2. One significant correlation was detected, occurring between baseline pH ($N = 790$) and shipping lane pH ($N = 239$). Here, a negative correlation of (−)0.290

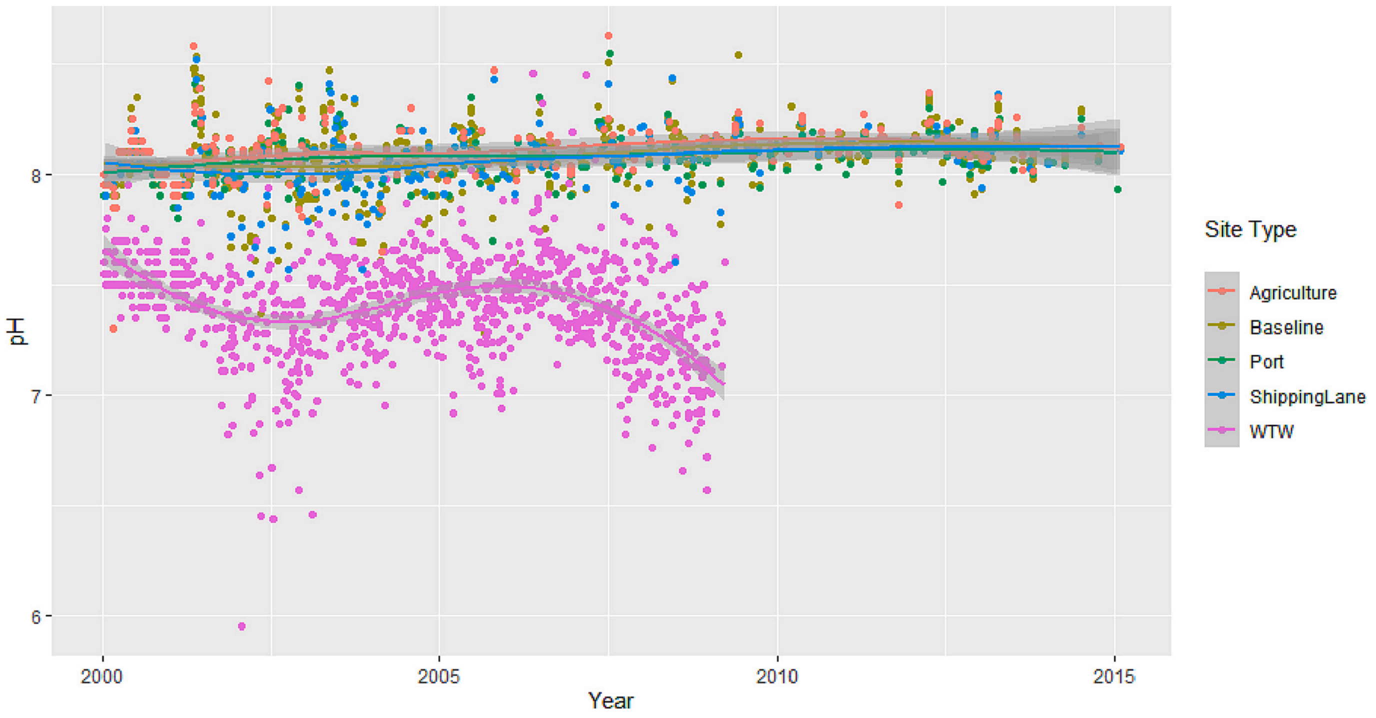

Fig. 5. Long-term (2000–2015) trends in water pH at selected sites in the Solent, classified by site type.

was observed to a significance of $P < 0.000$.

3.3. Zinc analysis

Time-series analysis of Zn concentrations (Fig. 6) showed an overall linear trend over time that was significantly downwards ($p < 0.001$; Table 1). Neither the slope nor the position of the regression line was affected by the extreme values in Fig. 6 as the linear regression and quantile regression lines were virtually identical. However, some caution is needed in drawing conclusions due to the change in data availability among sites. Significant site type effects were observed for Marina and Port ($p < 0.001$) and Shipping Lane ($p < 0.01$). While Port and Shipping Lane showed downward trends, values at Marina sites apparently rose over the years. Note, two different Marina sites contributed the data with only a small overlap in 2012/13, although the data still showed that Marina sites have the potential to carry higher levels of zinc than other sites. The baseline linear trend of Zn concentration is a decreasing one, from a mean concentration of 3 μg/l to 1.6 μg/l between 2000 and 2020. All other sites show a similar reduction in Zn concentrations, except for Marinas, which increased from around 3

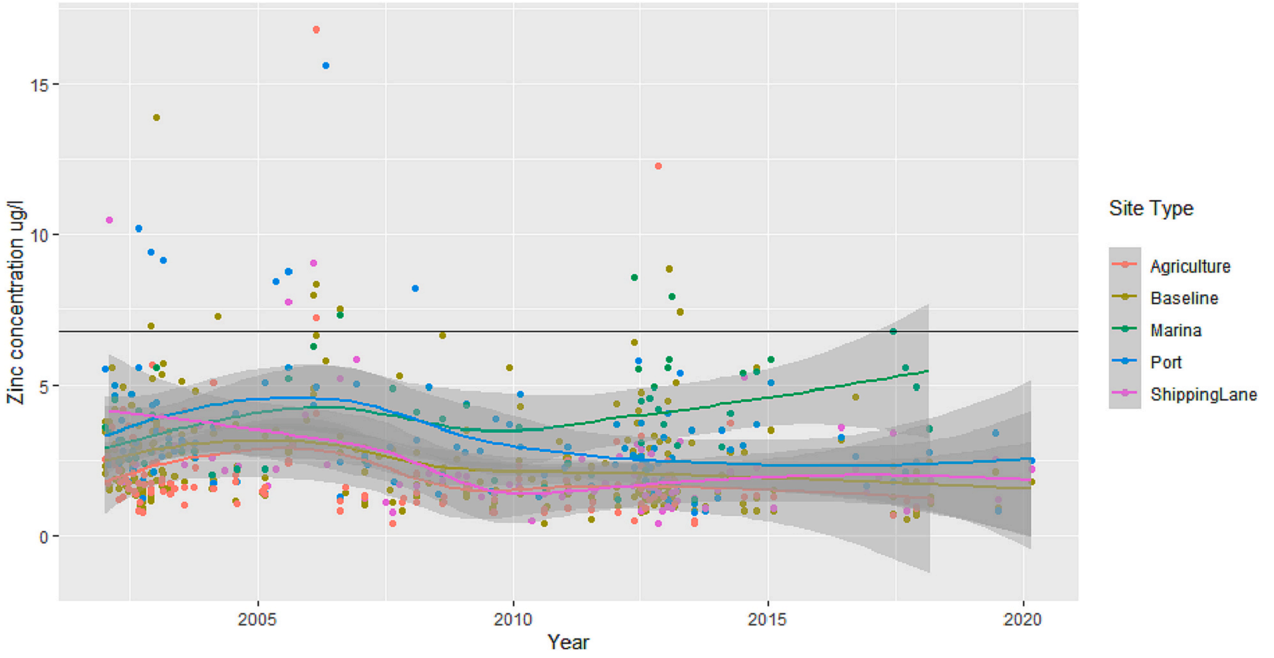

Fig. 6. Long-term (2000–2020) trends in zinc concentrations in water at selected sites in the Solent, classified by site type. The horizontal line shows the 6.8 μg/l limit for saline environments (HM Government, 2015).

μg/l to 5 μg/l.

ANOVA analysis of Zn concentrations revealed statistical differences highlighted in Table 2. Further statistical analysis of Zn concentrations via Spearman's Rank analysis, yielded no significant results.

3.4. Benzo[a]pyrene analysis

Analysis of the BaP data demonstrated the pitfalls of combining incomplete datasets. Ignoring sample site identity, there was a sharp downward trend in BaP concentrations over time that was even stronger when using quantile regression instead of a linear model. However, this was entirely due to differing values at Marina sites that were only sampled early on in the time series (Fig. 7). BaP showed no long-term time trend when looked at simultaneously with other factors, with values fluctuating over the years. Levels at Marina sites were consistently higher throughout the years they were sampled ($p < 0.001$; Table 1). Indeed, rather than decreasing, concentrations of BaP at baseline sample sites increased from ~0.00020 μg/l in 2016 to 0.00025 μg/l in 2020 (Fig. 7).

BaP concentration analysis, in the form of ANOVA tests, generated significant differences between the mean concentrations of BaP in marina sites and agriculture, baseline, port, and shipping lane sample sites. These are outlined in Table 2. Further statistical analysis comparing the correlation in BaP concentration between baseline sites and other locations studied yielded no significant results. However, there was an almost significant correlation between baseline and shipping lane BaP concentrations with $P = 0.073$ and a correlation coefficient of 0.344; suggesting there was some, albeit limited, correlation between baseline sample sites ($N = 51$) and shipping lanes ($N = 28$). A second less significant result was found when comparing baseline BaP concentrations to marina ($N = 26$) concentrations. The correlation coefficient here was the same as baseline and shipping lane BaP concentrations (0.344) yet a less significant $P = 0.085$ was returned.

4. Discussion

Before individual pollutant analysis is considered, overarching factors influencing on pollutant concentrations within the Solent must be examined. The trends in pH were similar to those of temperature. Other meteorological impacts likely to influence all pollutant levels in the Solent include coastal winds, rainfall, and in particular, storm events. Wind patterns have been shown to influence surface pollutant distribution alongside resuspension of sediment locked pollutants in shallow water (Seiler et al., 2020) and in-situ mixing of pollutants in the water column through Ekman transport (Onink et al., 2019), and coastal upwelling patterns (Choy et al., 2019). Freshwater influxes to marine environments are likely to influence these upwelling patterns due to density changes in saline environments (Kennish, 2002), and thus additional freshwater input may influence pollutant levels in the Solent via dilution and changes to water stratification (Gratiot et al., 2017). More broadly, the Solent watercourse is a unique location with exclusive tidal patterns. These involve a double high tide framework around which a rapid ebb flow is created. However, it is widely acknowledged pollutant removal occurs during ebb flow (Cook, 1984), and thus residence times of pollutants in the Solent are probably comparatively high, with the ebb flow only taking up only 3.5 of the 12.5 h tidal cycle (ABP, 2021). Thus, low solubility pollutants are likely settled on the seabed of the Solent during this 9-h comparative calm, with subsequent resuspension during maintenance dredging activities (ABPmer, 2014).

4.1. Temperature variations

The temperature variations in the Solent area are similar to globally accepted research on rising ocean temperatures. The Solent's baseline average temperature across all baseline sites is slightly increasing in line with research by the IPCC (Hoegh-Guldberg et al., 2014). The Solent Strait has unique characteristics when compared to global oceans. The more localised temperature changes that emerged during this study help explain some of the pH changes observed, such as annual fluctuations within the Solent (Gieskes, 1969). There is some indication that enclosed shallow environments in the Solent, such as marinas, have an increased rate of temperature increase. In such environments, increasing water temperatures can be driven by climate change, localised urbanization, runoff from impervious surfaces, discharges from recreational boats and industrial processes, and limited water exchange with open waters.

4.2. pH variations

Analysis of pH across the Solent sample sites revealed inverse trends analogous to those found with temperature, in line with research by Gieskes (1969). The increase from pH 8 to pH 8.15 is in opposition to acknowledged ocean acidification (Hoegh-Guldberg et al., 2014),

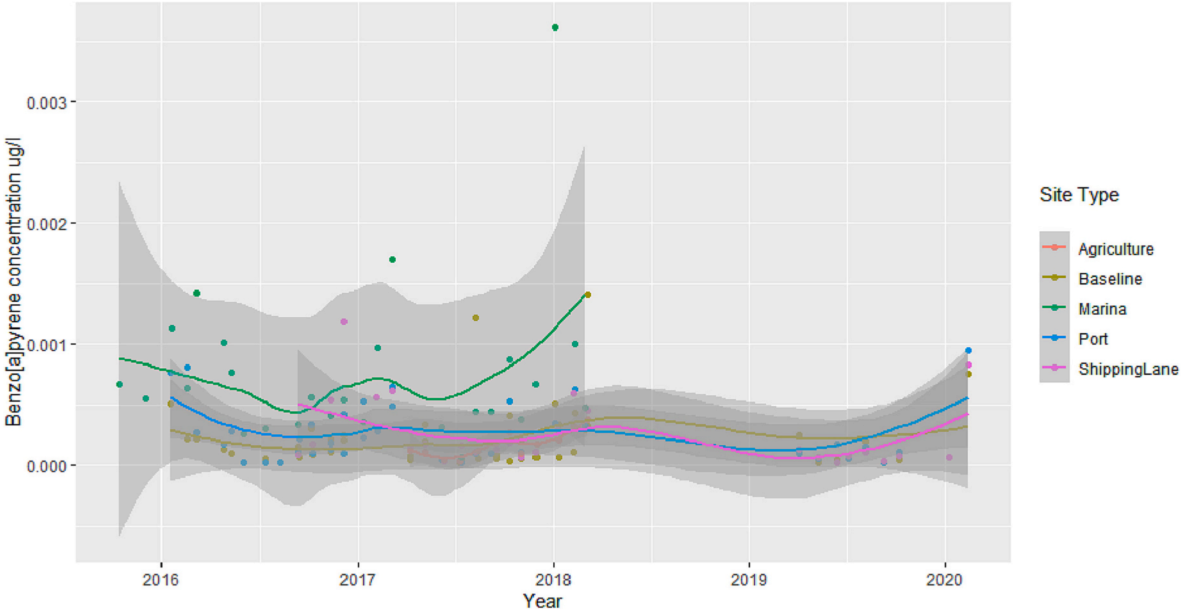

Fig. 7. Long-term (2000–2020) trends in benzo-a-pyrene concentrations in water at selected sites in the Solent, classified by site type.

caused by the dissolution of anthropogenically generated CO_2 into seawater and eutrophication via the addition of inorganic nutrients. Therefore, other drivers must be acting upon pH levels in the Solent driving it against the trends shown elsewhere (Hoegh-Guldberg et al., 2014). Several factors are known to influence pH levels in coastal waterways. Anthropogenically driven drivers include fertiliser runoff and its associated eutrophication. This should lead to reductions in pH through the breakdown of ammonia into nitrite via reactions with bicarbonate (US EPA, 2002b). This is especially noteworthy in the Solent due to increasing nitrification concerns (CIEEM, 2020).

Furthermore, there is some evidence that heavily trafficked port environments show small modelled decreases in pH stemming from acidic EGCS effluent (Teuchies et al., 2020). The Solent is heavily trafficked by such large cargo vessels (ABP, 2016) but research by Stips et al. (2016) and Kjølholt et al. (2012) suggest only "negligible" change will be observed due to the buffering capacity of the ocean in such strait environments. However, the recent growth in EGCS implementation is reason for concern (DNV GL, 2020a) due to research conducted by Koski et al. (2017) stating EGC effluent can reach as low as pH 3, but mostly falls between pH 5–6 (Faber et al., 2019). In this case, greater volumes of reactant water are required to bring pH to 6.5 units during stationary running, or to return the outfall value to less than a deviation of 2 pH units from inlet pH; as required under the IMO EGCS guidelines (IMO, 2015). Thus, the increasing adoption of both total and total proportion of open-loop EGCS (EGCSA, 2018; DNV GL, 2020a, 2020b) may have an acidifying effect on the Solent waterway in the future, deviating from its previous baseline of pH ~8.0 found in this study. A weak yet significant negative correlation ($\text{rho} = -0.29$) between baseline and shipping lane samples shows there is an inverse monotonic relationship across the Solent, suggesting the two location types are diverting from their expected values. In context this could mean as baseline values increase in pH, the shipping lane sites are decreasing in pH, in line with the acidic EGCS washwater hypothesis. This is reinforced by Dulière et al. (2020), who propose a 30 % adoption of open-loop scrubbers by English Channel and North Sea shipping fleets would lead to acidification at a rate of 0.008 to 0.010 pH annually in heavily trafficked areas, and at 10–50 times the rate of expected climate change driven ocean acidification. Analysis by Kroeker et al. (2013) and Birchenough et al. (2017) reveals varying impacts on marine organisms depending on pH change severity, taxonomic group and habitat preference. For example, with a 0.2 pH reduction, over 8 days, *Ophiothrix fragilis* larvae experienced 100 % mortality in the keystone species of sea star, in low pH concentrations, surviving larvae showed skeletal malformations (Dupont et al., 2008). However marine vegetation appears to show positive change with reduced ocean pH due to increased availability of dissolved CO_2 for photosynthesis in autotrophic species (Koch et al., 2013).

The localised basification of Portsmouth Harbour can likely be explained by Duarte et al. (2013) who highlighted multiple drivers of coastal basification, for example agricultural run-off and metabolic fluxes of the biosphere. Noting the high localised nitrate pollutant levels in the "Nitrate vulnerable zone (NVZ) [of] Portsmouth Harbour, Langstone Harbour and Chichester Harbour" (Environment Agency, 2016), it may be hypothesised the Portsmouth Harbour Special Protection Area (SPA) has been uniquely affected by eutrophication due to its "[nitrate] polluted water" designation (US EPA, 2002b; Jha, 2009; Environment Agency, 2016). The impacts of coastal basification is an emerging field, but initial research by Stein and Harzsch (2021), suggests similar challenges are presented to marine organisms as is presented by ocean acidification, including the limited physiological capacity of decapod crustaceans to adjust their buffering capacity when exposed to such environmental changes. Eutrophication amplifies the phytoplankton biomass that can be supported during an algal bloom. The ensuing uptake of dissolved inorganic carbon during photosynthesis increases water-column pH (known as "bloom-induced basification"). The removal of CO_2 by primary production leads to localised seawater basification (i.e. increase in pH), and this tendency is boosted by increased nutrient availability (Flynn et al., 2015). Thus in enclosed environments such as Portsmouth Harbour, which has often been subjected to eutrophication via addition of inorganic nutrients that support large algal blooms, the increase in pH can be significant and can override any signal from global ocean acidification (Borges and Gypens, 2010).

It may be hypothesised that inverse reactions occur with marine vegetation as dissolved CO_2 is removed from the aquatic environment during eutrophication (US EPA, 2002b), thus limiting the growth of species such as *Pelvetia canaliculata* (Koch et al., 2013). With regards to Solent protected areas, the MCZ's around the Isle of Wight and Selsey, alongside the extensive network of Special Areas of Conservation (SACs) and SPAs within the wider Solent area, present a range of habitat types (JNCC, 2021). Taken together, this research suggests Solent habitats, namely "*Crepidula fornicata* and *Mediomastus fragilis* in variable salinity infralittoral mixed sediment" housing *Ophiothrix fragilis,* and "*Laminaria digitata* on moderately exposed sublittoral fringe bedrock", containing a range of kelp species' (JNCC, 2021) may undergo complex changes in response to alterations in local pH. Therefore, ongoing monitoring of the Solent Strait pH levels, is required to prevent changes in the protected areas of the Solent in line with the EU Habitats Directive 92/43/EEC (European Parliament, 1992).

Recommending changes to policy requires further study of specific pollutant sources. Yet, in line with research by Dulière et al. (2020), this research suggests a tightening of open-loop EGCS effluent release laws within the Solent. The aim would be to reduce acidic EGCS effluent release, specifically in areas such as Southampton Water where this paper has suggested acidification is already occurring, as illustrated in Fig. 6. Conversely, current measures in place to limit localised basification in Portsmouth Harbour include redirection of sewage outfalls to open water and nutrient stripping at WTW sites (Environment Agency, 2016) and Defra's relatively new (2020) nitrate offset scheme (CIEEM, 2020). This suggests, the nitrate, and thus basification of the Solent, is being addressed, but continual monitoring is required to confirm nitrification and subsequent eutrophication, is the underlying driver of Portsmouth Harbour basification.

A significant difference observed between agricultural and shipping lane sites (±pH 0.052) exemplifies two contrasting pH inputs into the Solent: more alkaline inland runoff, and more acidic open water. The significantly different pH values obtained at marina sites within this study help lend weight to any runoff and subsequent basification hypotheses, whilst supporting the isolation of marine-trafficked sites and their possible acidification by large quantities of EGCS effluent.

4.3. Zinc variations

Findings from Zn analysis suggested a decrease in Zn concentrations over time throughout the Solent. In contrast, a trend of increasing Zn concentration was observed in enclosed water scenarios, such as marinas. This reinforces similar findings by Tzempelikou et al. (2021). Rees et al. (2020) suggest one source of Zn in recreational waters could be sacrificial anodes. These disposable Zn slabs have a suggested dissolution rate in saline water of 477 g/yr/kg (Rees et al., 2020). When combined with the low-level chronic pollution pressure of Zn from motor oil (EPA, 2001) it is conceivable the high concentrations of recreational marine vessels in both the Itchen and Cowes marinas (Marine Traffic, 2021), have led to elevated levels of Zn in these waterways. However, Zn pollution of coastal waterways has also been attributed to urban runoff from sources such as vehicle brake dust (Froger et al., 2020). Lunde Hermansson et al. (2023a, 2023b) discuss the environmental risk assessment of a range of metals, including Zn, from ship activities at European ports. Given the high urbanization surrounding the coastal waterways of the Solent Strait, a terrestrial explanation for elevated Zn levels in the Itchen and Cowes marinas is entirely possible and warrants further study.

The elevated levels of Zn detected in this study's marina sites at around 5 μg/l, are well in excess of global average concentrations which are an order of magnitude less (Neff, 2002). However the 5 μg/l identified at marina sites is unlikely to have significant effects on marine invertebrates. Sediment dwelling amphipod organisms such as *Corophium volutator* until concentrations of 200 μg/l are reached (Fabrega et al., 2011). Furthermore, bivalves such as the common mussel *Mytilus edulis* show strong resistance to Zn concentrations below 1.35 mg/l, with mortality occurring at 20.8 mg/l (Hietanen et al., 1988). The crustacean species *Carcinus maenas* also shows resistance to Zn pollution up to 3.162 mg/l via low uptake rate as opposed to rapid turnover rate (Chan and Rainbow, 1993), with Zn having no effect on the uptake of calcium used for exoskeleton development (Rainbow and Black, 2005).

It can be tentatively concluded that the Solent Strait JNCC designated habitats of "Mussel and/or barnacle" inhabited by *Mytilus edulis,* alongside "*Fucus ceranoides* on reduced salinity eulittoral rock", the domain of *Carcinus mamas* (JNCC, 2021)*,* have organisms highly resistant to the observed Zn concentrations, and thus will see little to no ill-effects of an increase in dissolved Zn concentrations from EGCS effluent or otherwise. Furthermore negligible negative effects of chronic Zn exposure on polychaete worms has been studied by Watson et al. (2018) and King et al. (2004). Both papers suggest polychaetes tolerate elevated Zn concentrations through homeostatic regulation. Consequently, the JNCC designated "Polychaete/bivalve-dominated mid estuarine mud shores" habitats will also present little impact from elevated Zn concentrations. Consolidating the research, many of the Solent Strait ecosystems show resilience to increases in Zn concentration. Therefore, the internationally designated sites in the Solent Strait are unlikely to undergo negative changes until concentrations of around 200 μg/l Zn are reached. Furthermore, research by Chishty et al. (2012) outlines the low toxicity of Zn to zooplankton. Therefore, further research into the more toxic EGCS effluent trace metals, is desirable. It is therefore suggested that mediating measures for Zn pollution be implemented carefully, as current trends within the Solent Strait (excluding marinas) indicate values half that of the WFD standards of 6.8 μg/l in saline environments (HM Government, 2015). If the current trend is maintained, the concentration of Zn in marinas around the Solent could reach 6.8–7.0 μg/l between 2025 and 2030. Remedial action of Zn pollution in marina sites, should be implemented cautiously as alternative metals are still proven to accumulate in bivalve organisms (Mao et al., 2011). However, use of active anti-corrosion systems such as electronic cathodic protection (Harvey, 2020) like those used aboard some Royal Navy vessels present in Solent waters (Royal Navy, 2019; Pape et al., 2020), may prove to limit further trace metal deposition from recreational vessels.

The results of this study suggest Solent port mean Zn concentrations are still significantly greater than baseline, agriculture, and shipping lane sites, yet this may be explained by significant recreational craft usage around both Southampton and Portsmouth commercial ports. When considering the decreasing concentrations in open water, the double high tide and rapid ebb flow could be increasing the flushing rate of Zn at open water sites, whilst stagnating Zn in marinas (ABP, 2021). Consequently, no changes in local policy are currently suggested due to the decreasing nature of Zn concentrations at most Solent Strait sample sites. However, where elevated Zn concentrations are observed in marina environments, monitoring of runoff sites such as storm drains to identify possible influx areas alongside educational reform on the use of Zn based sacrificial anodes and the use of alternatives.

Reinforcing remedial action, studies have begun to show a link between ocean pH and Zn toxicity, especially in high trophic level organisms (Li et al., 2019). This signifies that the combination of acidic EGCS discharge and Zn could have a negative synergistic effect on marine life in future scenarios, but further research is vital to identify the implications for keystone species.

4.4. Benzo[a]pyrene variations

No long-term linear trend for concentrations of BaP across the Solent was evident, although data has only been available since 2015. It is possible that Marina sites (where concentrations are elevated) are a source of BaP and thus remedial action could be targeted at such locations. However, the sporadic, short-term nature of samples taken by the EA WIMS means that no firm conclusions can be drawn. The BaP concentrations in the Solent range provide a mean value of 0.0005921 μg/l of BaP, between the values at Marina (0.0007646 μg/l) and Agriculture (0.0001725 μg/l) sites.

All observed concentrations indicate BaP is below the 0.027 μg/l maximum allowed concentration in the Hazardous Substances Directive 2013/39/EU (European Parliament, 2013). Possible sources of the BaP found within the Solent, aside from EGCS effluent, include the assimilation of airborne BaP into the marine environment. Sourced from combustion, anthropogenic or otherwise (Liu et al., 2014), airborne BaP is assimilated at the air-sea interface via surface turbulence, rainfall or partial pressure differentials (Garbe et al., 2014). However, the significant differences in means observed between marina sites and agriculture, baseline, port, and shipping lane sites, indicates a scenario in Solent marinas that is unlikely to be caused by universal air-sea interface transfers of BaP (Liu et al., 2014). Lunde Hermansson et al. (2023a, 2023b) discuss the environmental risk assessment of a range of PAHs, including BaP, from ship activities at European ports.

The concentrations reported in the Solent are unlikely to impact organisms at observed concentrations. However, when studying the effects of BaP pollution on *Mytilus edulis*, a keystone species of "Mussel and/or barnacle" habitats present in the Solent (JNCC, 2021), interesting conclusions were drawn with relation to its bioaccumulation within algal colonies subsequently consumed by *M. edulis.* Research by Okay et al. (2000) revealed elevated concentrations of BaP in *M. edulis* when exposed to BaP-dosed algae, suggesting the combination of nitrification, and BaP pollution in Solent estuaries may be having as yet unstudied negative impacts on *M.edulis* dominated "Mussel and/or barnacle" (JNCC, 2021) communities (Perugini et al., 2007). Additionally research has begun to show the synergistic effects of BaP on fish embryos and early life stages when combined with microplastics (Le Bihanic et al., 2020). Other high-trophic level organisms such as *Nephrops norvegicus*, a species harvested elsewhere for human consumption, and occurring in the "Sublittoral cohesive mud and sandy mud communities" habitats of the Solent (JNCC, 2021), show elevated BaP concentrations when exposed to BaP contaminated water, yet no impacts on the organisms' vitality were observed, suggesting bioaccumulation of BaP is a significant risk, but bioconcentration factors for predominant Solent Strait organisms are currently unknown. Biological cycling of BaP in the aquatic environment via algal colonies is a significant process for BaP removal (Kahla et al., 2021). Within the nitrate-polluted Solent, it is conceivable the elevated concentrations of algal populations (Environment Agency, 2016) are removing BaP from the Solent watercourse. This supports findings made at locations outside of marina designated sites in this study, where BaP levels have been found to be decreasing.

Although BaP concentrations have been identified as below both legislative and impactful concentrations, remedial action of BaP via sustainable urban drainage systems (EA, 2019) is still recommended to maintain low BaP concentrations in the Solent, particularly as BaP is listed as one of the most "potent" PAHs (Nisbet and LaGoy, 1992). In the context of EGCSs, current BaP trends suggest concentrations in the Solent are not yet a cause for concern at current EGCS implementation levels. However, as BaP has low solubility, in the context of globally increased EGCS implementation, excess BaP may be deposited in Solent sediments. This presents an issue of accountability, and the polluter pays principle, as future dredging within the Strait, may lead to a breach of PAH Action Levels (ALs) (CEFAS, n.d.; Marine Management Organisation (MMO), 2015). Finally, other factors may lead to BaP's future increase, such as a reduction in biological cycling as nitrate is removed from the Solent, through EA initiatives (Environment Agency, 2016). Lunde Hermansson et al. (2023a, 2023b) highlight the need to account for a range of PAH sources when evaluating the marine environmental risks of shipping and question the fitness of the proposed new international guidelines on how to assess risk of scrubber water discharge.

5. Conclusions

Using carefully selected indicators of pollution, an important long-term historical analysis of water quality in an internationally crucial waterway, the Solent Strait (Hampshire, UK), has been successfully delivered. Whilst the study has shown that key selected pollutant concentrations in the Solent are below legislative limits, it also flags important issues relating to temperature, pH and the potential for WTW and EGCS discharges to impact on water quality, organisms and ecosystems.

The Solent's baseline average water temperature is slightly increasing (in line with research by the IPCC) BUT a significant long-term trend in temperature is not yet evident. However, temperatures at WTW sites were significantly higher and there is a non-significant suggestion that temperatures in marinas are also increasing, which requires further monitoring. These observations are important because water temperature is a crucial factor in understanding the functioning of aquatic ecosystems. Small changes in water temperature signals spawning time for fish and shellfish; warmer water holds less DO than colder water, thereby potentially making marina ecosystems experience eutrophication or algal blooms.

A complex story is emerging about pH values in the Solent. In contrast to expectations, there was a highly significant small overall increase in pH during the 15-year period when data were available. However, pH values at WTW sites were significantly lower than those elsewhere and showed a curvilinear relationship downwards with dates that differed among individual WTW sites. pH values at port sites were significantly different from the others; in enclosed environments such as Solent's Portsmouth Harbour, localised bloom-induced basification can outweigh the effects from global ocean acidification. Thus although globally marine water is acidifying, and it might be expected that EGCS discharges from shipping will enhance this trend, in the Solent, local inputs from agriculture, WTWs and urban runoff must be generally acting upon pH driving it against the trends shown elsewhere.

We can cautiously report that zinc concentrations in the Solent's water have significantly reduced over time, although at specific periods they exceed the quality standard. Significant site effects were observed for marina, port and shipping lane sites, with potential sources of Zn in each environment identified. Notwithstanding the pH trends already mentioned, we note that the combination of acidic EGCS discharge and increasing Zn could have a negative synergistic effect on marine life in future scenarios, and that further research is vital to identify the implications for keystone species.

BaP showed no long-term linear trend in Solent water, but values at marina sites were significantly and consistently higher throughout the years. Whilst concentrations reported in the Solent seem unlikely to impact organisms at observed values, bioconcentration factors for predominant Solent Strait organisms are currently unknown and ongoing monitoring is strongly recommended.

The study's findings provide valuable long-term background data and insights that can feed into the upcoming review of the European Union's Marine Strategy Framework Directive and ongoing discussions about the proposed new international guidelines on how to assess risk of scrubber water discharge. This has important implications for the regulation of, and future management strategies for, waterways such as the Solent Strait and current/future models of water quality. The Solent is a complex system of multiple confounding factors, making isolation of sole pollutant sources difficult. Consequently, monitoring of pollutants at point sources is recommended as preventative action for ecological damage within a waterway of international importance. In the context of changing IMO sulphur emission legislation, this study has addressed the need for more stringent monitoring of open-loop EGCS use within heavily trafficked strait environments such as the Solent.

CRediT authorship contribution statement

Connor May: Data curation; Formal analysis; Investigation; Methodology; Validation; Visualization; Roles/Writing - original draft.

Ian D. Williams: Conceptualization; Formal analysis; Investigation; Methodology; Project administration; Resources; Supervision; Validation; Visualization; Roles/Writing - review & editing.

Malcolm D. Hudson: Formal analysis; Validation; Visualization; Roles/Writing - review & editing.

Patrick E. Osborne: Data curation; Formal analysis; Methodology; Validation; Visualization; Roles/Writing - review & editing.

Lina M. Zapata-Restrepo: Validation; Visualization; Roles/Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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