Journal of Soils and Sediments

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--Manuscript Draft--

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Ref.: Ms. No. JSSS-D-18-00190R1

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Effects of Superdispersant-25 on the sorption dynamics of naphthalene and phenanthrene in marine sediments

Journal of Soils and Sediments

Dear Mr Perez Calderon,

We thank you for submitting your manuscript to the Journal of Soils and Sediments.

The editors of JSS have now had time to assess your manuscript and have made the following recommendations and comments.

They recommend a minor revision.

Please consider these comments carefully. If you feel that you are able to address these comments and suggestions sufficiently, then JSS would be happy to consider submission and assessment of a revised manuscript. Please be aware that we may ask the original and/or new referees to review the revised manuscript, although the final decision rests with the Editor-in-Chief.

For your guidance, the review reports are appended below. In addition, please address the following:

1) *Line 337 - change to "(Heath and Bailey 1994)"*

This has now been updated (line 337).

2) *For the bibliography - please only use a capital for the first letter of the first word of article titles.*

References have now been updated to include only the first letter of the first word in capital (except where there are names of places or rigs e.g. Faroe, *Deepwater Horizon*). An exception in the reference list is "ggplot2: elegant graphics for data analysis", in which the first letter of the title is lower case as this is the name of the software.

3) *For the bibliography - please give the full range of pages not just the first page.*

Page ranges have now been included for references where they were missing. Note some references are software or are articles with a single page. In these cases, no page number or a single page number is reported, respectively.

4) *Several references need more details (such as the publisher, report number, etc) - for example Dixon (2014), Fingas (2002), Florida State University (2013), Heath and Bailey (1994), USEPA (2008).*

These references, and others, have been edited to include the requested information (reference list).

5) *In the case of the Dixon reference, to me it looks like the report is from 2015 and "2014" should be added to the end of the title. Plus you should add the name of the publisher "Advisory Committee on Protection of the Sea, Cambridge, UK"*

This reference has now been updated (line 46 and reference list).

6) *There is still a problem with the reference on line 511-512 and the text on line 142-143, I suggest that you remove the text on line 511-512 and instead incorporate it on line 142-143 (perhaps in brackets).*

The reference has been included in brackets and removed from the Reference list at the end of the document (lines 141–143).

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> 7) *Line 341- please change to "(Figs 5,6)"*

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We thank you for considering JSS as an outlet for your work.

With kind regards,

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Journal of Soils and Sediments

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Thank you for your detained update on your article. In the future it would make evaluating your revisions easier if you state the line numbers in the revised document rather than just stating that it has been addressed in the discussion for example. I was able to find them with your track-changes, but page numbers would be appreciated by any editor in the future.

Apologies, thank you for the advice. Line comments have been included in this revision of the manuscript.

I feel that this paper is now acceptable for publication within JSS following a suggested 2 minor adjustments

> 1. *Please add one line justifying as to why 20 degrees was used. This can be similar to your response to Reviewer #2.*

This has been included in the Materials and methods section (lines 166–169).

> 2. *Please change your reference of Florida State University 2014. This reference is not easily obtainable by readers and should be replaced with a referenceable paper/document. There are many documents on Exopolymers with regard to flocculation, marine snow and interaction with contaminants.*

This reference has been updated by an easier-to-find one (line 410 and reference list):

Passow, U. (2016) 'Formation of rapidly-sinking, oil-associated marine snow', Deep Sea Research Part II: Topical Studies in Oceanography. Elsevier, 129, pp. 232–240. doi: 10.1016/j.dsr2.2014.10.001.

1   SEDIMENTS, SEC 2 • PHYSICAL AND BIOGEOCHEMICAL PROCESSES •

2   RESEARCH ARTICLE

3

4   **Effects of Superdispersant-25 on the sorption dynamics of naphthalene and**

5   **phenanthrene in marine sediments**

6

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19

Abstract

Purpose: The present study evaluated the effects of Superdispersant-25 (SD25), a commercial dispersant stockpiled in the United Kingdom for oil spill response, on the sorption dynamics of two polyaromatic hydrocarbons, naphthalene (NAP) and phenanthrene (PHE), in sediment-seawater systems using three sediments near hydrocarbon exploration areas in the Faroe-Shetland Channel and North Sea.

Materials and methods: Batch experiments were conducted to evaluate the effects of SD25 on the solubility (analysed by gas chromatography), distribution coefficients and desorption hysteresis of NAP and PHE separately as well as SD25 in the three sediments (analysed by UV-vis spectroscopy and surface tension measurements, respectively).

Results and discussion: The results revealed that SD25 readily adsorbed to all sediment types but did not desorb from silty loam. SD25 application increased the solubility in seawater of PHE but not of NAP. Adsorbed SD25 increased the distribution coefficients of both polyaromatic hydrocarbons in sand but not silty loam and the solubilising effect of SD25 appeared to drive increased adsorption of PHE rather than sediment-adsorbed SD25 concentration.

Conclusions: The findings highlight the influence of SD25 application on the sorption dynamics of NAP and PHE in marine sediments from areas near hydrocarbon exploration and production regions. An understanding of these interactions may aid responders in the decision-making process of dispersant application in the event of a spill as seabed characteristics affect oil-dispersant-sediment interactions.

Keywords Dispersant • Naphthalene • Oil spill • PAHs • Phenanthrene • Sediment • Solubility • Sorption

2

1 Introduction

Hydrocarbon exploration and extraction in the United Kingdom continental shelf has been on-going for approximately 40 years. In 2014 alone, a total of 30 oil spills (>2 t) have taken place in the United Kingdom Continental Shelf (Dixon 2015). More recently, the BP Clair spill resulted in the release of 95 t of crude oil into the North Sea in 2016 (Webster et al. 2016). Oil releases to the marine environment are ecologically undesirable due to the persistence of oil and the presence of toxic components in crude oil such as polyaromatic hydrocarbons (PAHs, hereafter) which are carcinogenic to humans, can bioaccumulate in marine organisms and persist in the environment for years (Mearns et al. 2010).

During the *Deepwater Horizon* (*DwH*, hereafter) oil spill (2010) 4.9 million barrels of oil were released to the Gulf of Mexico from the Macondo well MC252 (Beyer et al. 2016) and 4–14.4% of the oil settled on the deep seabed (Chanton et al. 2015). Contact of oil with sediment, particularly coastal sediments, is highly undesirable because it can cause negative environmental impacts if oil is stranded in sensitive areas such as salt marshes or on beaches for human use (Hayworth et al. 2015; Pietroski et al. 2015). Dissolved and dispersed oil in the marine environment can adsorb onto suspended particulate matter such as sediment particles, organic debris or actual organisms to form aggregates (Gong et al. 2014a). Particle size can influence the amount of oil adsorbed as a consequence of its relative surface area (Pignatello 1998). Fine sediments, with larger surface area per unit volume, can take up more oil than coarser ones, with lower surface area. Hydrophobic pollutants readily adsorb onto organic matter in sediments, organic carbon (OC) content has been shown to be the main driver of organic pollutant sorption to sediments (Xing et al. 1996). Therefore, OC-rich sediments are expected to uptake more organic pollutants than sediments low in OC. Other variables that affect sorption of organic compounds onto sediments include temperature, salinity and pressure (Piatt et al. 1996; Marini and Frapiccini 2013; Zhao et al. 2015). Oil-sediment aggregation can influence oil fate in the marine environment. Oil-sediment aggregates can be transported to the seabed by sedimentation or be mobilised horizontally by currents, waves and winds to locations far from the oil spill source (Bandara et al. 2011).

Oil spill models are tools used in prevention and response operations in the oil and gas industry to predict the trajectories and fates of spilled oil in the environment (Reed et al. 1999). A component of oil spill models is the interaction of oil with sediment particles and their subsequent fate. To our knowledge, the Oil Spill Contingency and Response (OSCAR) model

3

75 uses the algorithms from Bandara et al. (2011). This is an algorithm but considers oil droplets

76 as a single pollutant, and as such does not capture the distribution of single component

77 interactions. A useful property to implement in these models is the water-sediment distribution

78 coefficients (K_D; volume/mass). The coefficient represents the affinity of a pollutant for a

79 particular sediment and is defined as (Matthies 2011):

$$K_D = \frac{c_S}{c_W} \qquad \text{Eq. 1}$$

81 where C_S (mass/mass) and C_W (mass/volume) are the concentrations of a pollutant in sediment

82 and seawater, respectively. K_D coefficients are specific to each pollutant-sediment combination

83 since each sediment has different properties (e.g. particle size distribution, organic matter

84 content, etc.) (Matthies 2011). Further to this, it has been previously shown that K_D can vary

85 by orders of magnitude for a given compound under different environmental conditions (Baes

86 and Sharp 1983). Modelling K_D is difficult due to the large number of variables that influence

87 it and, as such, empirical determination is the most accurate method. Determination of K_D of

88 PAHs is relevant because of their toxicity, recalcitrance and importance in environmental

89 legislation (Yamada et al. 2003; Office of Solid Waste 2008; Mason et al. 2014).

90 Dispersants are employed during oil spills to lower the interfacial tension between water and

91 oil to facilitate the breaking up of oil slicks into smaller droplets that can then be more rapidly

92 degraded both physically and biologically (Fingas 2002). Following the *DwH* oil spill,

93 extensive work was undertaken to evaluate the effects of Corexit dispersants (those used during

94 the spill) on oil-suspended particulate matter aggregation (Gong et al. 2014b, a; Zhao et al.

95 2016). A recent study has shown that different dispersant formulations selectively solubilise

96 and affect the sorption of specific fractions of crude oil (Zhao et al. 2016). For example, Corexit

97 9500A preferentially dispersed C_{12}–C_{16} and C_{20}–C_{28} *n*-alkanes whereas Corexit 9527A

98 favoured C_{10}–C_{20} *n*-alkane dispersion. Consequently, the need arises to characterise the effects

99 of other ready-to-use and commercially available dispersants on oil-sediment interactions.

100 Zhao et al. (2015) reported that Corexit 9500A has contrasting effects on the extent to which

101 hydrocarbons adsorb onto sediments; (1) Corexit 9500A increased the solubility of

102 hydrocarbons in seawater and (2) surfactants in Corexit 9500A adsorb to sediment particles

103 and create additional adsorption sites for hydrocarbons.

104 Given that dispersant application is an important oil spill response strategy that directly affects

105 physicochemical properties of hydrocarbons in the marine environment (Fingas 2002), further

106 understanding of its effects on hydrocarbon-sediment interactions is important (Gong et al.

107 2014a). Over- or underestimation of sorption to sediments may lead to inappropriate choice of

108 resource allocation in the event of an oil spill whereby hydrocarbon uptake by different

109 sediment types may be erroneously estimated.

110 The aim of this work was to determine the effect of Superdispersant-25 (SD25, hereafter), a

111 dispersant stockpiled in the United Kingdom, on the sorption dynamics of naphthalene and

112 phenanthrene (NAP and PHE, hereafter, respectively) as well as its own sorption dynamics in

113 three sediment types from North Scotland. It was hypothesised that (1) SD25 and PAHs would

114 be taken up to a greater extent by fine than by coarse sediment, (2) an increase in SD25

115 concentration would favour the partitioning of PHE to the aqueous phase more than that of

116 NAP due to differences in water-solubility and (3) SD25 application would increase PAH

117 adsorption onto sediments by increasing PAH solubility and the creation of additional

118 adsorption sites on the sediment itself by adsorbing to it.

119

2   Materials and methods

2.1   Sediments and artificial seawater

122 Sediment samples were collected from the top 10 cm of sediment from the Faroe-Shetland

123 Channel (1000 m; FSC, hereafter) aboard *MRV Scotia* in May 2014 (61°35.02'N, 4°14.64'W),

124 Stonehaven Bay (14 m; SB, hereafter) aboard *MRV Temora* in June 2016 (56°58'18"N,

125 2°11'3"W) and the Ythan estuary (intertidal; YE, hereafter) in December 2016 (57°18'14"N,

126 1°59'25"W) (Fig. 1). Sampling methods were maxi-corer (OSIL, United Kingdom), Van Veen

127 grab and manual collection for FSC, SB and YE sediments, respectively. Sediments were

128 autoclaved at 121°C for 21 min at 100 kPa and oven dried at 60°C for three days to minimise

129 microbial activity prior to carrying out experiments. Artificial seawater was prepared by adding

130 pre-oven dried (at 130°C for 24 h) Seamix Artificial Sea Salt (Peacock Salt, United Kingdom)

131 at 3.4% (mass/volume) to ultra-pure (type 1) water and magnetically stirring for 8 h.

132

5

2.2 Sediment characterisation

Sediments were characterised in terms of particle size distribution and carbon content. YE and SB sediments were oven-dried at 105°C overnight and sieved through mesh sizes of 2000, 1000, 500, 250, 120 and 63 μm. Statistical analyses of particle size distribution were carried out using Gradistat v.8 (Blott and Pye 2001). FSC sediments were oven-dried at 105°C overnight and then wet sieved through a 63 μm mesh to separate coarse (>63 μm) from fine sediment (<63 μm). Coarse sediment was then analysed as described above and fine sediment was analysed using the hydrometer method (Ashworth et al. 2001) and statistical analysis of particle size distribution was performed using the Hydrometer Particle Size Calculator (Natural Resources Conservation Service - United States Department of Agriculture Hydrometer Particle Size Calculator - ASTM No. 1).

To determine carbon content, sediments were initially oven-dried at 60°C for three days. Thereafter, sediments were mechanically milled. Subsequently, total carbon content was determined using a NA2500 elemental analyser (Carlo Erba Instruments). Total OC content was determined by acidifying sediment with 10% HCl and oven-dried at 60°C for three days and subsequently analysed by elemental analysis. Total inorganic carbon content was determined by difference between total carbon and total OC.

2.3 Superdispersant-25 measurements and critical micelle concentration determination

Three independent stock solutions of SD25 in artificial seawater at 100 and 1000 mg l^{-1} were prepared and equilibrated. Dilutions were performed to obtain solutions at concentrations of 0, 0.25, 5, 10, 25, 50, 100, 200, 300, 400, 500 and 1000 mg l^{-1}. Thereafter, seawater surface tension measurements were performed using a tensiometer (White's instruments) fitted with a du Nouy ring to calibrate the response of surface tension to SD25 concentration. The apparent critical micelle concentration was calculated as the inflexion point in seawater surface tension as a function of SD25 concentration, as described elsewhere (Gong et al. 2014).

2.4 Effect of Superdispersant-25 on aqueous solubility of PAHs

Saturated solutions of PHE and NAP with increasing SD25 were prepared to assess the influence of initial SD25 concentration in seawater ($[SD25]_{SW,0}$, hereafter) on PAH solubility in seawater. Briefly, 200 mg of each PAH were added to separate 70 ml glass vials and stock solutions of seawater and SD25 were mixed to achieve concentrations in the range 0–1000 mg l^{-1} and added to the vials. The mixtures were then equilibrated by magnetic stirring at 20°C in complete darkness for three days to ensure dynamic equilibrium. 20°C was chosen as past sorption dynamics and sediment hydrocarbon biodegradation literature has been undertaken at this temperature. The experiments were performed in complete darkness to prevent photodegradation of PAHs. After equilibration, solutions were centrifuged in glass centrifuge tubes at 3000 rpm for 10 mins such that suspended PAH is removed from solution and only dissolved PAH remained. 25 and 50 ml of NAP and PHE solutions, respectively, were then sequentially liquid-liquid extracted three times with 10 ml dichloromethane using pristane as an internal extraction standard (100 µl at 20 µg ml^{-1}). PHE extracts were then evaporated to approximately 5 ml under nitrogen and analysed by gas chromatography with flame ionisation detection. NAP extracts were injected immediately after extraction. Further analysis details can be found elsewhere (Perez Calderon et al. 2018b).

2.5 Superdispersant-25 uptake by sediments

Sorption of SD25 by sediments was evaluated in two stages, (1) where SD25 solutions were equilibrated with sediment and (2) where supernatant solutions after equilibration were replaced with clean seawater. These were defined as adsorption and desorption stages, respectively. Pre-treated sediment (2.5 g) were added to 15 ml Pyrex centrifuge tubes with Teflon-lined caps. 12 ml of SD25 in artificial seawater solutions at concentrations of 0, 10, 20, 30, 100, 175, 250, 375 and 500, and 1000 mg l^{-1} were prepared and added to the centrifuge tubes. Thereafter, these were incubated in a horizontal shaker at 200 rpm for three days at 20°C in complete darkness. Vials were then centrifuged at 3000 rpm for 10 mins and 3 ml of supernatant was sampled to measure surface tension. The remaining supernatant was replaced with artificial seawater and incubated a further three days in complete darkness. Samples were centrifuged again at 3000 rpm for 10 mins and surface tension measurements taken. SD25 concentration was calculated from the calibration curves prepared for the critical micelle

7

191 concentration determination experiment. Measurements were conducted for each sediment
192 type in triplicate.

193

2.6   PAH sorption by sediments and effect of Superdispersant-25

195 The effect of SD25 concentration on PAH sorption by sediments was evaluated in two stages
196 as described in section 2.5. 12 ml solutions containing 0.40 mg PHE l^{-1} or 3.85 mg NAP l^{-1} and
197 SD25 at 0, 10, 20, 30, 100, 200, 300 mg l^{-1} in artificial seawater were prepared and added to
198 15 ml glass centrifuge tubes lined with Teflon-lined caps. Samples were incubated and
199 centrifuged as described in section 2.5. PAH concentration in seawater was determined by UV-
200 vis spectroscopy using a Lambda 25 UV/VIS Spectrometer (PerkinElmer). UV-vis spectra
201 were measured with a 10 mm path-length quartz cuvette over the range 200–400 nm. PHE and
202 NAP concentrations were calculated from absorbances at 251 and 275 nm, respectively. 5-
203 point calibration curves were prepared for each PAH and blanks with seawater only were ran
204 after every 5 samples. Absorbances of blanks and solutions of SD25 in seawater and sediment
205 were subtracted from measured values.

206

2.7   Chemicals

208 PHE (99%), NAP (99%), pristane (99%) and dichloromethane (HPLC grade) were acquired
209 from Sigma Aldrich (United Kingdom). Superdispersant-25 was acquired from Oil Technics
210 (United Kingdom).

211

2.8   Calculations and statistical modelling

213 K_D can be envisaged as being composed of two terms to evaluate the contributions of
214 surfactants to the sorption of PAHs to sediments (Lu and Zhu 2012):

$$K_D = \frac{C_{sed}}{C_{sw}} = K_{OC}f_{OC} + K_{sf}Q_{sf} \qquad \text{Eq. 2}$$

216 where C_{sed} is the PAH concentration in sediment (mg g^{-1}), C_{sw} is the PAH concentration in
217 seawater (mg l^{-1}), K_{oc} is the OC-normalised PAH distribution coefficient (ml g^{-1}), calculated as

8

218    $0.35K_{ow}$ (Octanol-water coefficient) (Seth et al. 1999), f_{oc} is the OC fraction of the sediment,

219   K_{sf} is the surfactant-normalised PAH distribution coefficient (ml g^{-1}), defined here as K_{SD25} (for

220   SD25) and Q_{sf} is the sediment-adsorbed surfactant concentration (mg g^{-1}), defined here as Q_{SD25}

221   and including all components of the SD25 formulation. Analyte concentrations in sediment

222   were calculated by subtracting the concentrations measured in in artificial seawater from initial

223   concentrations added. For calculating of K_D values when no analyte was detected in the

224   aqueous phase, a value of 0.001 mg l^{-1} was used as the concentration in seawater.

225   Response of sorption variables to SD25 concentration were modelled using locally weighed

226   regressions due to the non-linearity of the data, where sorption variables were the response

227   variable and SD25 concentration in either water or sediment was the explanatory variable,

228   subset by PAH, sediment type and experimental stage (adsorption: first inoculation; desorption:

229   replacement of supernatant with clean seawater). Briefly, the model fits a polynomial surface

230   determined by PAH solubility. Q_{SD25} values were estimated from locally weighed regressions

231   from experiments described in Section 2.5. All statistical analysis was undertaken using R (R

232   Development Core Team 2017) and the library *ggplot2* was used for locally weighted

233   regression analysis (Wickham and Chang 2009).

234

3   Results

3.1   Sediment characterisation and Superdispersant-25 critical micelle concentration

237   FSC, SB and YE sediments were classified as silty loam, medium and fine sands, respectively.

238   Details of particle size distribution and carbon content of the sediments analysed can be found

239   in Table 1. The critical micelle concentration of Superdispersant-25 in artificial seawater (T =

240   20°C, S = 34) was 5.8 mg l^{-1} (Fig. 2).

241

3.2   Effect of Superdispersant-25 concentration on PAH solubility in seawater

243   Solubility of PHE in artificial seawater linearly increased from 0.57 ± 0.20 to 4.44 ± 1.32 mg

244   l^{-1} from 0 to 250 mg SD25 l^{-1} and decreased to 2.07 ± 1.66 mg l^{-1} at 1000 mg SD25 l^{-1}. Solubility

9

245 of NAP in artificial seawater remained constant from 0 to 1000 mg SD25 l^{-1} (10.00 ± 1.89 and

246 11.18 ± 0.91 mg l^{-1}, respectively, Fig. 3).

247

3.3 Dispersant sorption onto sediments

249 SD25 uptake by sediments differed across sediment type and $[SD25]_{sw,0}$ range (Fig. 4). At

250 $[SD25]_{sw,0}<175$ mg l^{-1} all sediments took up all SD25 from solution and no evidence for

251 desorption back into solution was detected in the desorption stage. In FSC sediment, uptake of

252 all SD25 was observed across the range of $[SD25]_{sw,0}$ and no desorption was detected at any

253 $[SD25]_{sw,0}$. In SB sediment, as in FSC sediment, uptake of all SD25 was detected across the

254 $[SD25]_{sw,0}$ range tested. However, SD25 desorption was apparent at $[SD25]_{sw,0}>250$ mg SD

255 l^{-1}. At $[SD25]_{sw,0}>175$ mg SD25 l^{-1}, YE sediment uptake of SD25 plateaued at ~1.5 mg g^{-1},

256 and desorption could not be inferred also due to high variability of [PHE].

257

3.4 Effect of Superdispersant-25 on PAH uptake by sediments

259 K_D values of NAP and PHE as a function of Q_{SD25} to the sediments investigated varied with

260 sediment type and experimental stage (adsorption or desorption) (Fig. 5). During the adsorption

261 stage, SD25 application increased K_D values in YE and SB sediments but not in FSC sediment.

262 As Q_{SD25} increased, K_D values of both PAHs to SB and YE sediments increased. Desorption

263 stage K_D values of both PAHs decreased relative to the adsorption stage. Desorption stage K_D

264 values decreased with Q_{SD25} in FSC sediments and increased in other sediment types, except

265 for NAP in YE sediment, where no effect of Q_{SD25} was apparent. The adsorption of PAHs to

266 sediment-adsorbed SD25 was evaluated by comparing K_{SD25} to Q_{SD25} (Fig. 6). Overall, no clear

267 patterns emerged for K_{SD25} as a function of Q_{SD25} during either the adsorption or desorption

268 stages.

4 Discussion

4.1 Key findings

271 SD25 had contrasting effects on the water-solubility of PHE and NAP. PHE water-solubility

272 was increased from SD25 concentration as low as 10 mg l^{-1} but NAP water-solubility was not

10

273 affected by SD25, even at 1000 mg l^{-1}. Sorption of SD25 by sediments varied by sediment type.

274 FSC sediment took up all SD25 in solution across the [SD25]$_{SW,0}$ range tested and no

275 desorption of SD25 was detected. In contrast, in SB and YE sediments SD25 desorption was

276 apparent in experiments with [SD25]$_{sw0}$>250 mg l^{-1}. Sorption dynamics of PAHs varied by

277 PAH, sediment type and Q_{SD25}. Q_{SD25} increased K_D values of both PAHs in SB and YE

278 sediments but did not have a clear effect on the adsorption of either PAH in FSC sediments.

279 Desorption stage K_D values generally decreased with respect to the adsorption stage. There was

280 no clear trend of PAH sorption to sediment-adsorbed dispersant as a function of Q_{SD25}.

281

4.2   Effect of dispersant on PAH solubility in seawater

283 SD25 application increased the water-solubility of PHE but not of NAP. PHE water-solubility

284 could be increased up to seven-fold with dispersant application at 250 mg l^{-1} (Fig. 3). However,

285 at SD25 concentration above 250 mg l^{-1}, PHE solubility was reduced implying that SD25 may

286 have an optimal concentration to mobilise target pollutants. SD25 application, even at SD25

287 concentration <30 mg l^{-1}, resulted in increased PHE solubility indicating that PAHs such as

288 PHE can be readily dissolved and dispersed in the water column. Increasing the solubility of

289 PAHs in the water column by dispersant facilitates their dilution and dispersion in the marine

290 environment (Fingas 2002) which can aid in long-term removal. Hydrocarbons have been

291 shown to photodegrade more rapidly when chemically dispersed with Corexit 9500A than in

292 its absence (Zhao et al. 2016). Chemical dispersion may negatively impact or have no effect

293 on hydrocarbon biodegradation in the water column by modifying the microbial community

294 composition and selecting for potential dispersant-degrading bacteria *Colwellia* and not

295 *Marinobacter*, a natural hydrocarbon degrader (Kleindienst et al. 2015). The overall benefits

296 of dispersant to the marine environment remain debated although it can be beneficial given

297 specific circumstances (Prince 2015).

298 [SD25]$_{SW,0}$ up to 1000 mg l^{-1} did not enhance NAP solubility (~11 mg l^{-1}) although there have

299 been reports of higher water-solubility of NAP in seawater without surfactant addition (23.1

300 mg l^{-1} at 25°C (Adelman 1977) and 28 mg l^{-1} at 20°C (Zhao et al. 2015)). Previous work using

301 SD25 has shown that SD25 has limited effect on NAP mobility into sediments (Perez Calderon

302 et al. 2018b, c, a). In contrast, investigations into NAP water-solubility have shown that Corexit

303 9500A can linearly increase its solubility in seawater. Zhao et al. (2015) reported that 200 mg

304 Corexit 9500A l^{-1} increased NAP solubility in seawater from 28 to 36 mg l^{-1}. These apparent

305 contradictions illustrate that different commercial dispersants and seawater types may

306 solubilise specific hydrocarbons to different extents. Therefore, conclusions drawn from work

307 using one oil-dispersant-seawater system may not be transferable to another system with a

308 different dispersant or seawater. This is important given that a large body of literature has been

309 produced following the *DwH* oil spill using Corexit dispersants which may only be relevant in

310 the context of the Macondo oil-Corexit dispersant combination. Therefore, further research is

311 required into how different dispersants affect oil-water interactions.

312

4.3 Superdispersant-25 sorption by sediments

314 All SD25 across the concentration range tested was adsorbed onto FSC sediment and did not

315 desorb following water replacement (Fig. 4). This finding highlights the strong uptake capacity

316 of SD25 by fine deep-sea sediments. Subsea application of dispersant, as witnessed during the

317 *DwH* oil spill resulted in significant amounts of dispersant ending up on the seabed (White et

318 al. 2014). The proposed pathways of dispersant deposition on the Gulf of Mexico seabed are

319 thought to be surface sorption and settling of dispersant-suspended particle aggregates (Gong

320 et al. 2014b; White et al. 2014). Sorption of non-polar hydrophobic pollutants to sediments is

321 dependent on organic matter content and if it is above 0.01%, it may take up the majority of

322 the pollutant as opposed to the mineral component of the sediment (Pignatello 1998). In this

323 experiment, this was verified for SD25 as maximum uptake was observed by high OC-

324 containing sediments (FSC and SB) as opposed to low OC-containing sediment (YE).

325 Desorption of SD25 was detected in SB but not in FSC sediment potentially due to the

326 difference in percentage of fines between sediment types (Fig. 4). Dispersant has been found

327 to persist in deep-sea sediments and corals for over four years following the *DwH* oil spill and

328 that environmental conditions in deposition sites influenced its residence time (White et al.

329 2014). Results here suggest that responders should consider sediment characteristics as part of

330 the decision-making process for dispersant application in the marine environment due to the

331 capacity of dispersant to adsorb to marine sediments, particularly when sediments are fine or

332 OC-rich. For example, in a hypothetic offshore well blowout scenario, SD25 application near

333 fine sediments, such as FCS sediments, may enhance uptake of SD25, oil droplets and

334 dissolved hydrocarbons more readily than other sediments. This can yield more negative effects

335 for benthic ecosystems than application at surface waters where oil and dispersant are less

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likely to come into contact with the seabed. On the other hand, if the seabed is sandy, application of SD25 near the seabed is less likely to result in adsorption of hydrocarbons although it may enhance entrainment *via* advective pore-water transport (Perez Calderon et al. 2018c). This is particularly important if protected species such as sand eels are near the target site for SD25 application as they are sensitive to oil (Heath and Bailey 1994).

4.4 Effect of dispersant on PAH uptake by sediments

K_D values of NAP and PHE varied with sediment type, Q_{SD25} and experimental stage to varying extents (Figs 5,**Fig. 6**). In FSC sediments, Q_{SD25} did not affect K_D values of either PAH in the adsorption stage which is likely due to the high proportion of fines (70.8%) and OC (1.67%). In contrast, in sandy sediments with a lower proportion of fines such as SB and YE sediments, uptake increased with Q_{SD25} suggesting that surfactant sorption may create new adsorption sites in coarser sediments as previously reported for PHE in sandy loam and loamy sand using Corexit 9500A (Gong et al. 2014b). Corexit 9500A in solution (18 mg l^{-1}) has been shown to have limited effects on NAP sorption to sandy loam and loamy sand, increasing in NAP uptake by sediment of 2.9% and 3.3%, respectively (Zhao et al. 2015). Here, the highest uptake of NAP was measured in YE sediments at ~0.8 mg SD25 g^{-1} (Fig. 5) although no effect of SD25 on naphthalene solubility was apparent (Fig. 4). However, no NAP was detected in the aqueous phase in these samples and the default value of 0.001 mg l^{-1} was assigned which may have skewed the K_D values of NAP in these samples. Desorption-phase K_D values across sediments for both NAP and PHE decreased indicating that adsorption of both NAP and PHE in these sediments was partially reversible. Increasing Q_{SD25} reduced desorption stage K_D values of NAP in FSC sediments suggesting that SD25 uptake increased the partitioning of NAP to the aqueous phase. In contrast, desorption stage K_D values of NAP in SB or YE did not vary with Q_{SD25} suggesting that sediment-adsorbed SD25 does not retain NAP in sandy sediments with seawater exchange.

The effect of Q_{SD25} on the desorption of PHE was similar to that in the adsorption stage in SB and YE sediments suggesting that PHE remains more strongly adsorbed to marine sediments with increasing Q_{SD25} than NAP. Desorption stage K_D values of PHE in YE sediments were approximately one order of magnitude higher than those of NAP (Fig. 5) suggesting that, even in the absence of fines, PHE may remain strongly adsorbed onto sandy sediments. Strong

adsorption of PAHs to silty loams following continuous desorption experiments has been recently reported (Duan et al. 2018). The authors also reported that addition of Corexit 9500A and SPC 100 increased desorption of PAHs and to a lesser extent that of alkanes. Similarly, Gong et al. (2014) reported increased hysteresis of PHE in sandy loam and loamy sand at increasing Corexit 9500A, suggesting that SD25 may be less effective at desorbing NAP and PHE from marine sediments although it does increase their solubility in seawater. The contribution of Q_{SD25} to K_{SD25} values of either PAH in this experiment was unclear. Previous research showed increased adsorption of organic pollutants to sediment-bound dodecylpyridinium bromide, even in humic acid with ~50% OC where OC would be expected to adsorb the majority of the pollutant (Lu and Zhu 2012). This difference may arise from the use of a different dispersant formulation (SD25).

Disparity in response to SD25 application has been observed in hydrocarbon pore-water transport experiments where NAP and PHE were mixed with hydrocarbons from other fractions (BTEX, aliphatics and other PAHs) (Perez Calderon et al. 2018b, c, a). The effect of SD25 on NAP mobility in sediments in these experiments was limited, suggesting a similar "behaviour" to that observed here. In contrast, PHE mobility in sediments increased with SD25 application in these experiments. The solubilising effect of SD25 was masked by the high water-solubility of NAP but was apparent for PHE, even when in the same system. Other hydrocarbons were found to not be affected by SD25-application (e.g. BTEX) which are also highly water-soluble, suggesting this is the key property that governs the extent to which SD25 affects hydrocarbons in these systems.

The findings here show the effects of SD25 on PAH-sediment-seawater dynamics in three sediments from the North Sea and FSC. Adsorption of PAHs to sediments was facilitated by SD25 application. The driving mechanism appeared to be the solubilising effect of SD25 on PAHs as Q_{SD25} did not appear to drive PAH adsorption onto FSC sediments, suggesting that SD25 application in a subsea blowout in the FSC may not increase sorption of PAHs but may result in SD25 adsorption to sediment, where dispersants can persist for years (White et al. 2014) and affect microbial community composition (Ferguson et al. 2017; Perez Calderon et al. 2018b). In contrast, increased uptake of PAHs by SB and YE sediments with increasing Q_{SD25} suggest that less sorptive sediments (i.e. with lower OC and fines percentages) may increase their uptake of PAHs through sediment-adsorbed SD25. It is important to note that sediments here were sterilised and artificial seawater used and such bacterial activity in the sediments was reduced. Consequently, the role of biodegradation, biosurfactant production and

400 transparent exopolymeric particle production has not been considered here. These processes

401 may have a marked effect on sorption dynamics. For example, biodegradation reduces

402 surfactant concentration in media through microbial metabolism (Brakstad et al. 2018), which

403 may limit hydrocarbon uptake by sediments. Biosurfactant production increases PAH

404 bioavailability and can enhance biodegradation (Lu et al. 2011), which can decrease their

405 concentration in sediments. Finally, transparent exopolymeric particles (colloidal organic

406 carbon structures containing acidic polysaccharides) play a key role in adsorbing particulates

407 in the wider ocean (Rochelle-Newall et al. 2010). They can act as binding sites for dispersant

408 and remove surfactants and PAHs from solution as suggested in the MOSSFA hypothesis,

409 whereby marine snow acted as a pathway for deposition of hydrocarbons and dispersant on the

410 deep seabed after *DwH* (Passow 2016). The role of these biological processes cannot be ignored

411 in a real oil spill. However, the focus here was on the physical interactions between PAHs,

412 dispersants and sediments. Further research is required to evaluate the physicochemical

413 processes investigated here in conjunction with biological processes how the sorption

414 dynamics of other, larger PAHs are affected by dispersant application.

415

5   Conclusions

417 The present study evaluated the sorption dynamics of PHE and NAP in three marine sediments-

418 seawater systems and the effect of SD25 concentration on this process. The main findings of

419 the study were:

420   1. Dispersant increased the solubility of PHE in seawater up to seven-fold but had no

421   effect on the solubility of NAP. This contrasts with previous work, where NAP

422   solubility was enhanced with Corexit 9500A, suggesting that different dispersant

423   formulations can selectively solubilise specific PAHs in seawater. Dispersant choice

424   should be considered by responders to account for selective solubilisation of toxic

425   chemicals such as PAHs and the potential knock-on effects this choice may have on the

426   wider marine environment, e.g. the seabed as discussed here.

427   2. FSC and SB sediments adsorbed all SD25 across the concentration range tested (up to

428   ~5 mg g^{-1}) but no desorption could be measured in FSC sediments suggesting SD25

429   can remain strongly bound to fine sediments. In YE sediments, sorption of SD25 was

430   more limited (up to ~1.5 mg g^{-1}) and desorption of SD25 was highly variable.

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3. Sorption dynamics of both PAHs were affected by sediment type and Q_{SD25} to different extents. K_D values decreased in the desorption stage compared to the adsorption stage for both PAHs. Q_{SD25} increased adsorption of both PAHs in SB and YE but not FSC sediments. The finding suggests that SD25 increased sediment uptake of PAHs but did not retain them strongly adsorbed to the sediment following water replacement.

4. Q_{SD25} did not have a clear effect on K_{SD25} values of either PAH, suggesting that sediment-adsorbed SD25 increases the adsorption of these PAHs to sediment but not onto sediment-adsorbed SD25.

The results provide evidence of SD25 influence on the sorption dynamics of PAHs in marine sediments, which varies by sediment type and PAH. The results highlight the importance of considering the relationship between SD25 and sorption dynamics on the fate of PAHs in marine sediments following an oil spill. Further research into the sorption dynamics of PAHs across commercial dispersants, sediment types, within hydrocarbon mixtures and biotic interactions is required to evaluate the potential effects of dispersant on oil-sediment interactions.

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7 Tables

Table 1. Carbon content (total (TC), organic (TOC) and inorganic (TIC)) and particle size distribution of sediments used in sorption experiments. Average percentages are expressed in terms of mass and errors refer to standard deviation ($n = 3$).

Station	TC (%)	TIC (%)	TOC (%)	Sand (%)	Silt (%)	Clay (%)
FSC	2.164 ± 0.028	0.490 ± 0.009	1.674 ± 0.019	29.3 ± 4.2	65.5 ± 4.4	5.3 ± 2.4
SB	1.014 ± 0.027	0.040 ± 0.080	0.977 ± 0.103	95.6 ± 1.2	3.7 ± 1.0	0.7 ± 0.2

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| YE | 0.102 ± 0.014 | 0.076 ± 0.008 | 0.026 ± 0.007 | 100.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |

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8   Figure captions

Fig. 1. Sampling locations of sediments used in sorption experiments from the Faroe-Shetland Channel (FSC, yellow pin), Ythan estuary (YE, red pin) and Stonehaven Bay (SB, green pin).
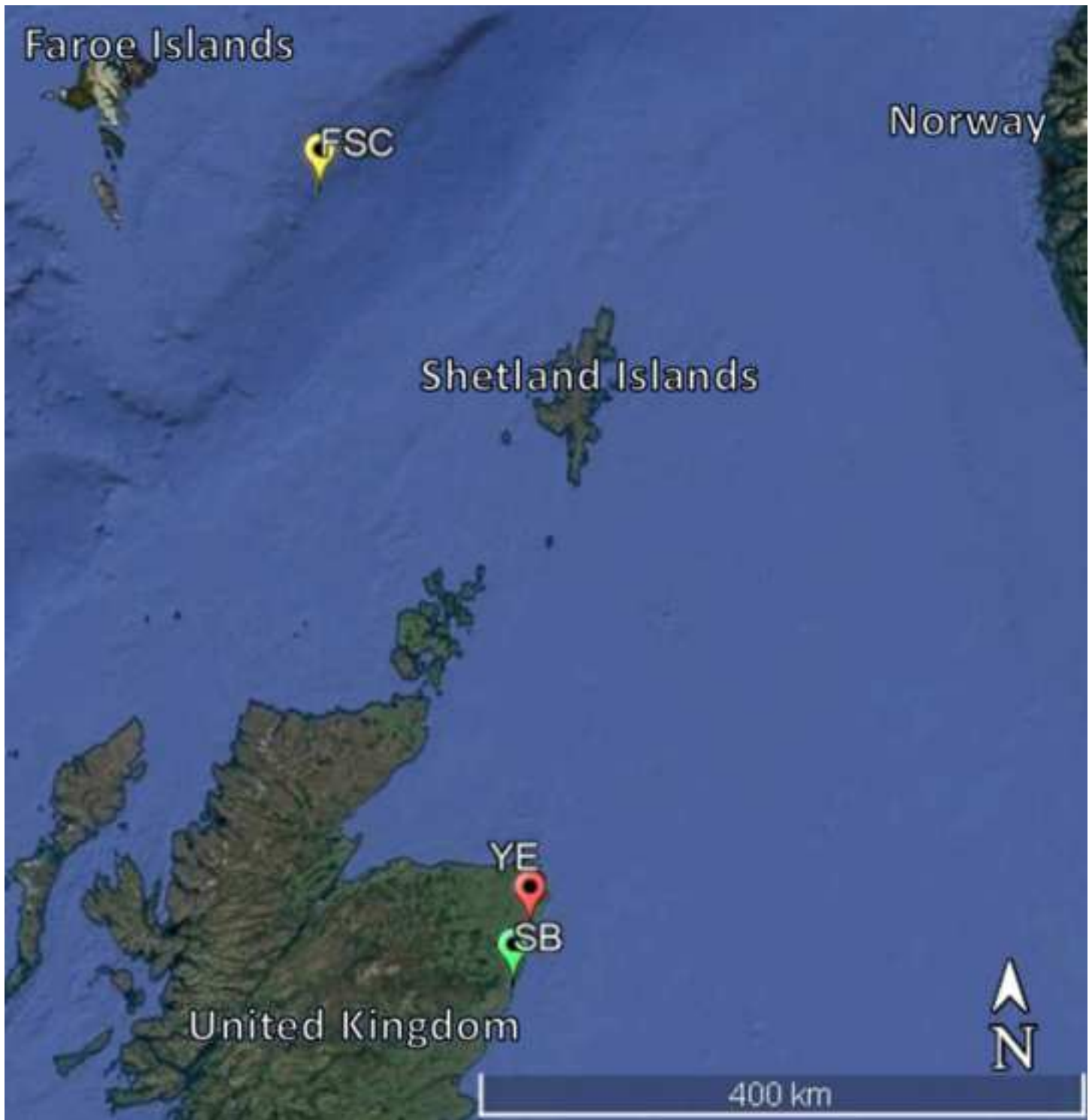
Fig. 2. Effect of Superdispersant-25 on artificial seawater surface tension. Circles and crosses represent values below and above the change in slope. The solid and dashed lines represent models before and after slope change. The solution for the intersection of the two equations is the CMC the critical micelle concentration of Superdispersant-25 (4.63 mg l^{-1}). Grey bands represent standard error of linear models. Note SD25 concentration has been log(x+1) transformed.
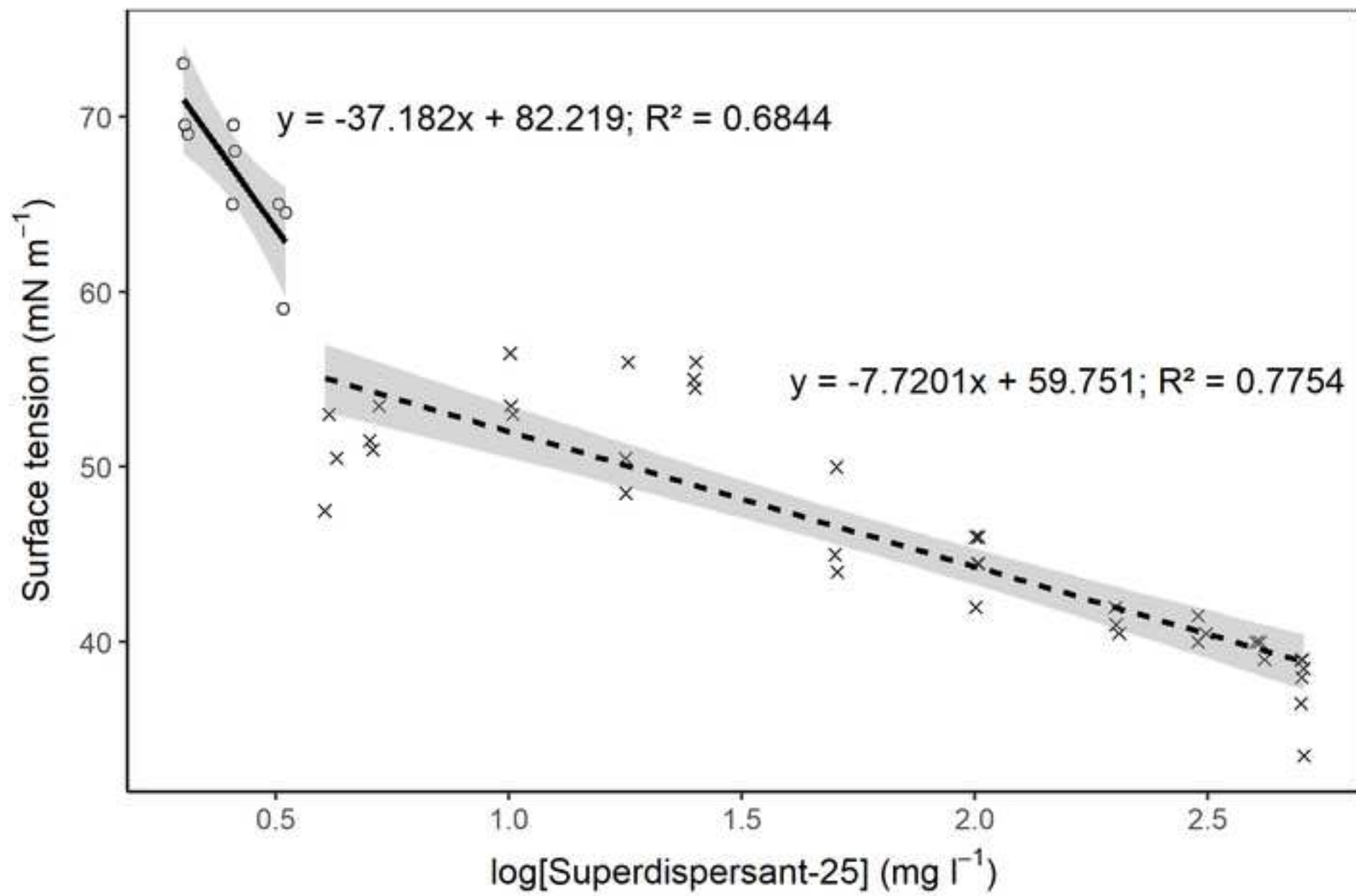
Fig. 3. Effect of initial Superdispersant-25 concentration in seawater ([SD25]$_{SW,0}$) on PAH solubility in artificial seawater (S = 34). Circles and crosses represent concentrations of naphthalene and phenanthrene, respectively. Solid and dashed lines, and grey bands represent locally weighted smooth regression predicted values and standard errors for naphthalene and phenanthrene, respectively.
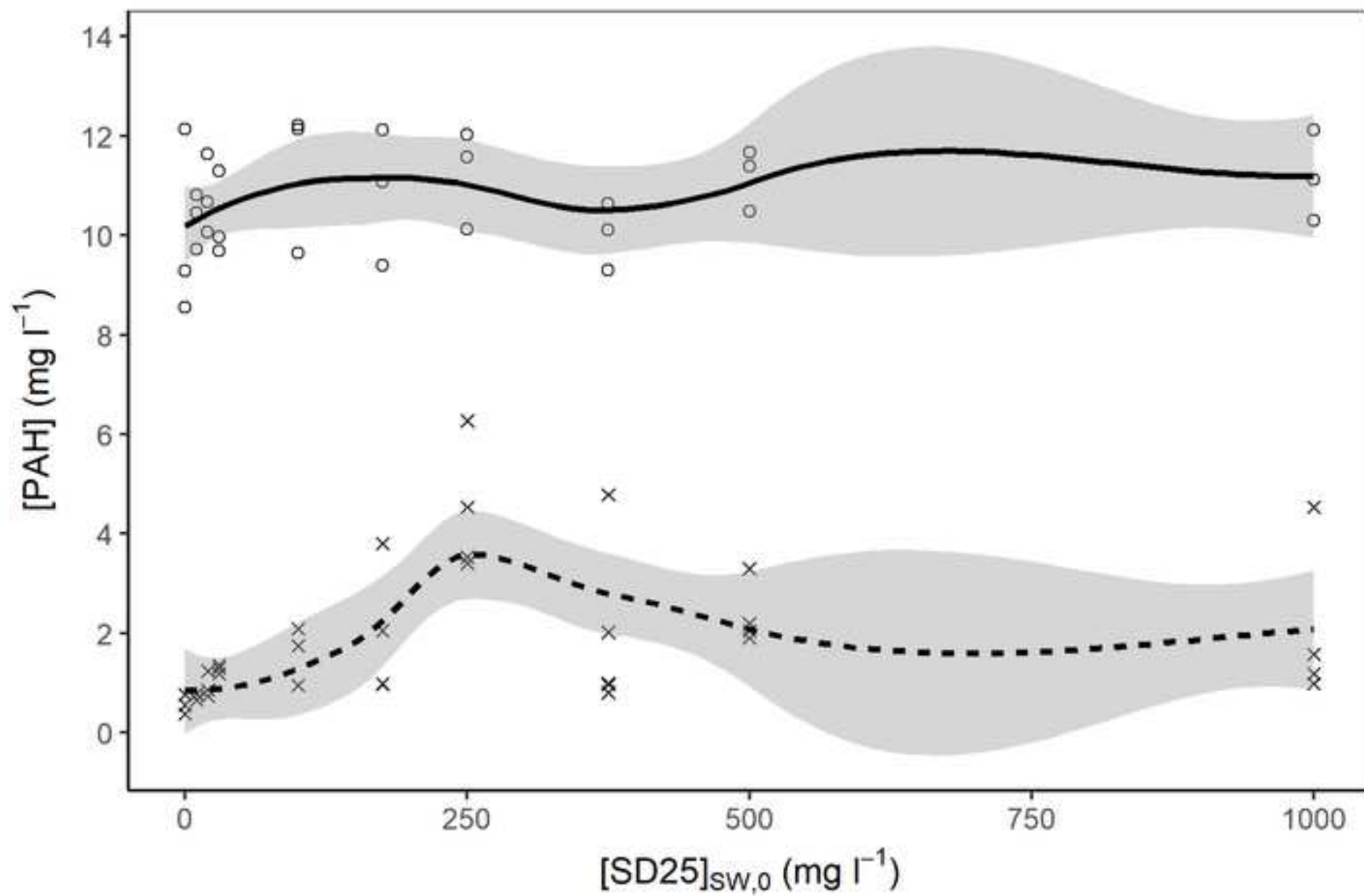
Fig. 4. Superdispersant-25 uptake (Q_{SD25}) onto sediments from the Faroe-Shetland Channel (70.8% fines), Stonehaven Bay (4.4% fines) and Ythan Estuary (0% fines) as a function of initial Superdispersant-25 concentration in seawater ([SD25]$_{SW,0}$). Circles and crosses represent adsorption and desorption steps, respectively. Solid and dashed lines, and grey bands represent locally weighted smooth regression predicted values and standard errors for adsorption and desorption isotherms, respectively.

Fig. 5. Effect of sediment Superdispersant-25 concentration (Q_{SD25}) on the distribution coefficient (K_D) of naphthalene and phenanthrene in sediments from the Faroe-Shetland Channel (70.8% fines), Stonehaven Bay (4.4% fines) and Ythan Estuary (0% fines). Circles and crosses represent adsorption and desorption steps, respectively. Solid and dashed lines, and grey bands represent locally weighted smooth regression predicted values and standard errors for adsorption and desorption isotherms, respectively. Note the log-scale in the y-axis.

Fig. 6. Effect of sediment uptake of Superdispersant-25 (Q_{SD25}) on the distribution coefficient (K_{SD25}) of naphthalene and phenanthrene to sediment-adsorbed Superdispersant-25 surfactants in sediments from the Faroe-Shetland Channel (70.8% fines), Stonehaven Bay (4.4% fines) and Ythan Estuary (0% fines). Circles and crosses represent adsorption and desorption steps, respectively. Solid and dashed lines, and grey bands represent locally weighted smooth regression predicted values and standard errors for adsorption and desorption isotherms, respectively. Y-axis scaling is log-modulus transformed to facilitate visualisation (John and Draper 1980).

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Figure 1

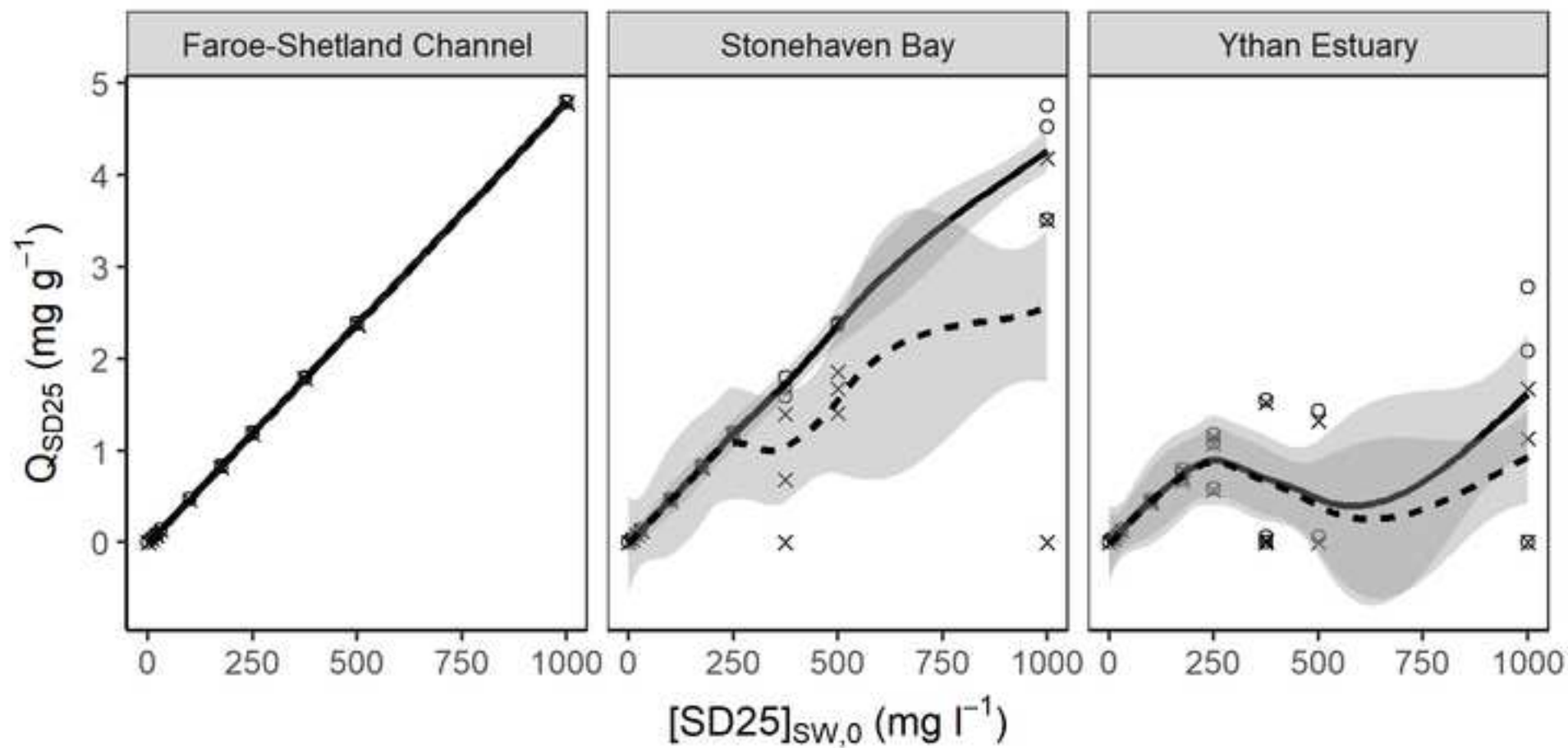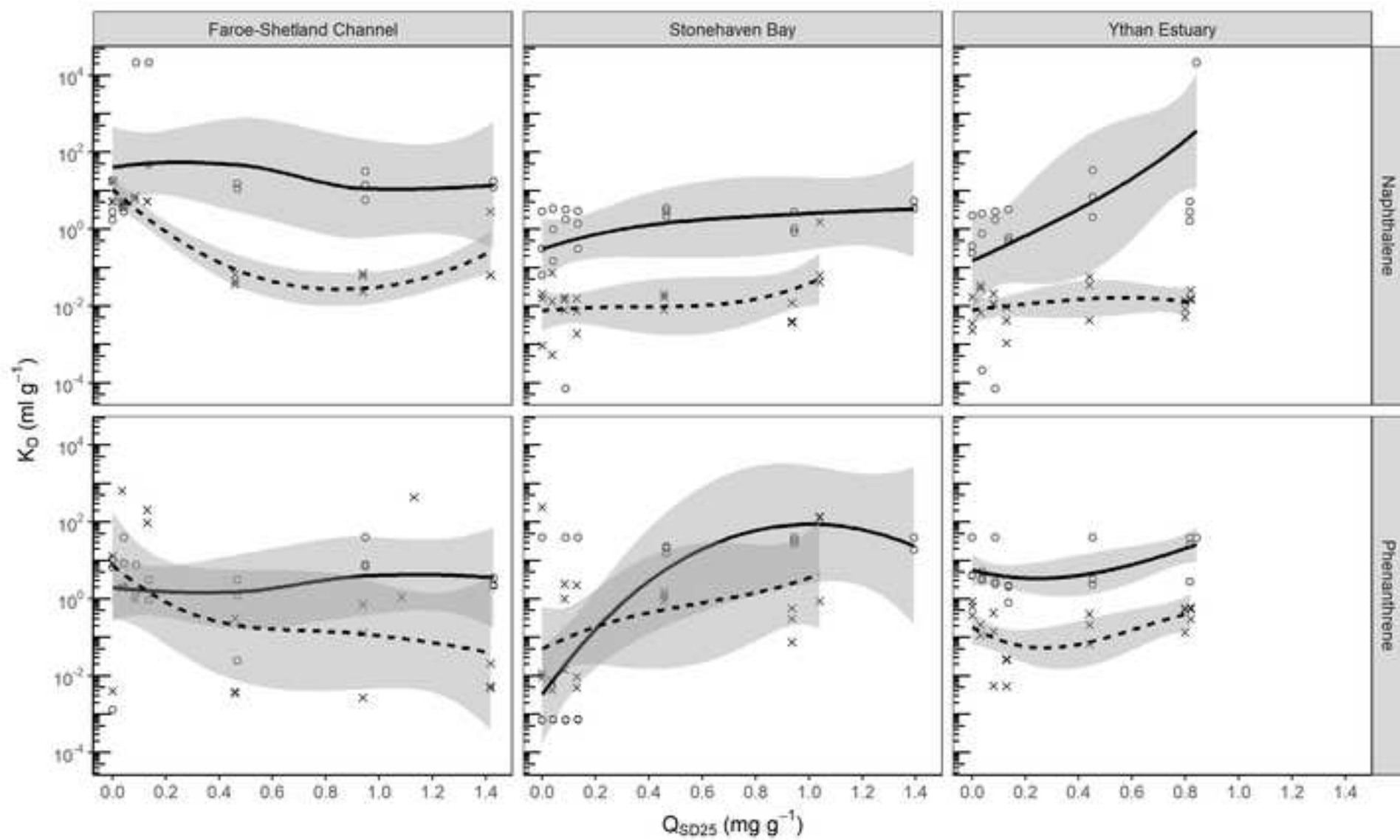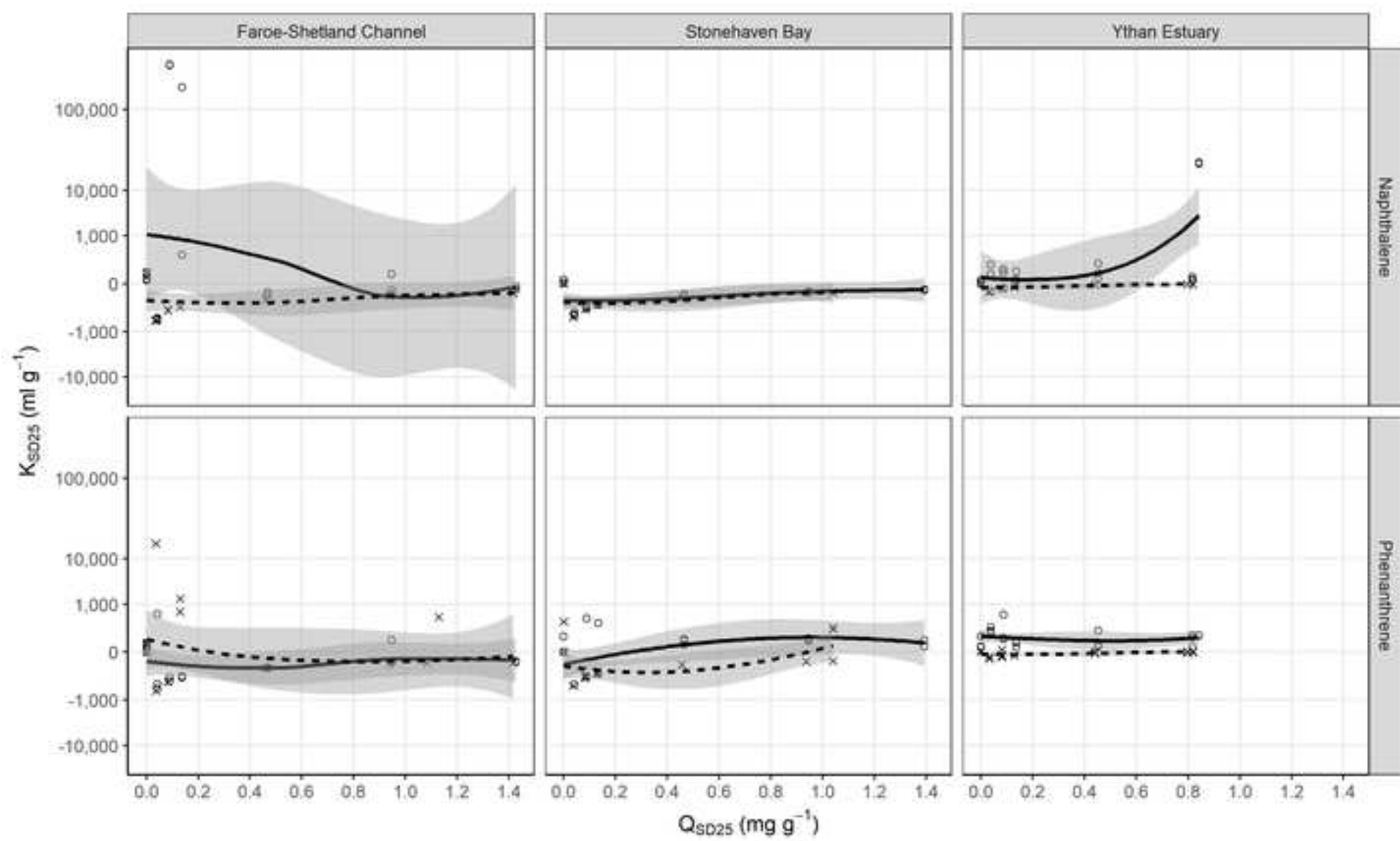The chart shows two regression relationships:

$$y = -37.182x + 82.219; R^2 = 0.6844$$

$$y = -7.7201x + 59.751; R^2 = 0.7754$$

Axis labels: Surface tension (mN m^{-1}) versus log[Superdispersant-25] (mg l^{-1})

Figure 3

Figure 4

Figure 4

Figure 5

Figure 6

1   SEDIMENTS, SEC 2 • PHYSICAL AND BIOGEOCHEMICAL PROCESSES •

2   RESEARCH ARTICLE

3

4   Effects of Superdispersant-25 on the sorption dynamics of naphthalene and

5   phenanthrene in marine sediments

6

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19

Abstract

Purpose: The present study evaluated the effects of Superdispersant-25 (SD25), a commercial dispersant stockpiled in the United Kingdom for oil spill response, on the sorption dynamics of two polyaromatic hydrocarbons, naphthalene (NAP) and phenanthrene (PHE), in sediment-seawater systems using three sediments near hydrocarbon exploration areas in the Faroe-Shetland Channel and North Sea.

Materials and methods: Batch experiments were conducted to evaluate the effects of SD25 on the solubility (analysed by gas chromatography), distribution coefficients and desorption hysteresis of NAP and PHE separately as well as SD25 in the three sediments (analysed by UV-vis spectroscopy and surface tension measurements, respectively).

Results and discussion: The results revealed that SD25 readily adsorbed to all sediment types but did not desorb from silty loam. SD25 application increased the solubility in seawater of PHE but not of NAP. Adsorbed SD25 increased the distribution coefficients of both polyaromatic hydrocarbons in sand but not silty loam and the solubilising effect of SD25 appeared to drive increased adsorption of PHE rather than sediment-adsorbed SD25 concentration.

Conclusions: The findings highlight the influence of SD25 application on the sorption dynamics of NAP and PHE in marine sediments from areas near hydrocarbon exploration and production regions. An understanding of these interactions may aid responders in the decision-making process of dispersant application in the event of a spill as seabed characteristics affect oil-dispersant-sediment interactions.

Keywords Dispersant • Naphthalene • Oil spill • PAHs • Phenanthrene • Sediment • Solubility • Sorption

1 Introduction

Hydrocarbon exploration and extraction in the United Kingdom continental shelf has been on-going for approximately 40 years. In 2014 alone, a total of 30 oil spills (>2 t) have taken place in the United Kingdom Continental Shelf (Dixon 2015). More recently, the BP Clair spill resulted in the release of 95 t of crude oil into the North Sea in 2016 (Webster et al. 2016). Oil releases to the marine environment are ecologically undesirable due to the persistence of oil and the presence of toxic components in crude oil such as polyaromatic hydrocarbons (PAHs, hereafter) which are carcinogenic to humans, can bioaccumulate in marine organisms and persist in the environment for years (Mearns et al. 2010).

During the *Deepwater Horizon* (*DwH*, hereafter) oil spill (2010) 4.9 million barrels of oil were released to the Gulf of Mexico from the Macondo well MC252 (Beyer et al. 2016) and 4–14.4% of the oil settled on the deep seabed (Chanton et al. 2015). Contact of oil with sediment, particularly coastal sediments, is highly undesirable because it can cause negative environmental impacts if oil is stranded in sensitive areas such as salt marshes or on beaches for human use (Hayworth et al. 2015; Pietroski et al. 2015). Dissolved and dispersed oil in the marine environment can adsorb onto suspended particulate matter such as sediment particles, organic debris or actual organisms to form aggregates (Gong et al. 2014a). Particle size can influence the amount of oil adsorbed as a consequence of its relative surface area (Pignatello 1998). Fine sediments, with larger surface area per unit volume, can take up more oil than coarser ones, with lower surface area. Hydrophobic pollutants readily adsorb onto organic matter in sediments, organic carbon (OC) content has been shown to be the main driver of organic pollutant sorption to sediments (Xing et al. 1996). Therefore, OC-rich sediments are expected to uptake more organic pollutants than sediments low in OC. Other variables that affect sorption of organic compounds onto sediments include temperature, salinity and pressure (Piatt et al. 1996; Marini and Frapiccini 2013; Zhao et al. 2015). Oil-sediment aggregation can influence oil fate in the marine environment. Oil-sediment aggregates can be transported to the seabed by sedimentation or be mobilised horizontally by currents, waves and winds to locations far from the oil spill source (Bandara et al. 2011).

Oil spill models are tools used in prevention and response operations in the oil and gas industry to predict the trajectories and fates of spilled oil in the environment (Reed et al. 1999). A component of oil spill models is the interaction of oil with sediment particles and their subsequent fate. To our knowledge, the Oil Spill Contingency and Response (OSCAR) model

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75   uses the algorithms from Bandara et al. (2011). This is an algorithm but considers oil droplets

76   as a single pollutant, and as such does not capture the distribution of single component

77   interactions. A useful property to implement in these models is the water-sediment distribution

78   coefficients (K_D; volume/mass). The coefficient represents the affinity of a pollutant for a

79   particular sediment and is defined as (Matthies 2011):

80
$$K_D = \frac{c_S}{c_W} \qquad \text{Eq. 1}$$

81   where C_S (mass/mass) and C_W (mass/volume) are the concentrations of a pollutant in sediment

82   and seawater, respectively. K_D coefficients are specific to each pollutant-sediment combination

83   since each sediment has different properties (e.g. particle size distribution, organic matter

84   content, etc.) (Matthies 2011). Further to this, it has been previously shown that K_D can vary

85   by orders of magnitude for a given compound under different environmental conditions (Baes

86   and Sharp 1983). Modelling K_D is difficult due to the large number of variables that influence

87   it and, as such, empirical determination is the most accurate method. Determination of K_D of

88   PAHs is relevant because of their toxicity, recalcitrance and importance in environmental

89   legislation (Yamada et al. 2003; Office of Solid Waste 2008; Mason et al. 2014).

90   Dispersants are employed during oil spills to lower the interfacial tension between water and

91   oil to facilitate the breaking up of oil slicks into smaller droplets that can then be more rapidly

92   degraded both physically and biologically (Fingas 2002). Following the *DwH* oil spill,

93   extensive work was undertaken to evaluate the effects of Corexit dispersants (those used during

94   the spill) on oil-suspended particulate matter aggregation (Gong et al. 2014b, a; Zhao et al.

95   2016). A recent study has shown that different dispersant formulations selectively solubilise

96   and affect the sorption of specific fractions of crude oil (Zhao et al. 2016). For example, Corexit

97   9500A preferentially dispersed C_{12}–C_{16} and C_{20}–C_{28} *n*-alkanes whereas Corexit 9527A

98   favoured C_{10}–C_{20} *n*-alkane dispersion. Consequently, the need arises to characterise the effects

99   of other ready-to-use and commercially available dispersants on oil-sediment interactions.

100   Zhao et al. (2015) reported that Corexit 9500A has contrasting effects on the extent to which

101   hydrocarbons adsorb onto sediments; (1) Corexit 9500A increased the solubility of

102   hydrocarbons in seawater and (2) surfactants in Corexit 9500A adsorb to sediment particles

103   and create additional adsorption sites for hydrocarbons.

104   Given that dispersant application is an important oil spill response strategy that directly affects

105   physicochemical properties of hydrocarbons in the marine environment (Fingas 2002), further

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106 understanding of its effects on hydrocarbon-sediment interactions is important (Gong et al.
107 2014a). Over- or underestimation of sorption to sediments may lead to inappropriate choice of
108 resource allocation in the event of an oil spill whereby hydrocarbon uptake by different
109 sediment types may be erroneously estimated.

110 The aim of this work was to determine the effect of Superdispersant-25 (SD25, hereafter), a
111 dispersant stockpiled in the United Kingdom, on the sorption dynamics of naphthalene and
112 phenanthrene (NAP and PHE, hereafter, respectively) as well as its own sorption dynamics in
113 three sediment types from North Scotland. It was hypothesised that (1) SD25 and PAHs would
114 be taken up to a greater extent by fine than by coarse sediment, (2) an increase in SD25
115 concentration would favour the partitioning of PHE to the aqueous phase more than that of
116 NAP due to differences in water-solubility and (3) SD25 application would increase PAH
117 adsorption onto sediments by increasing PAH solubility and the creation of additional
118 adsorption sites on the sediment itself by adsorbing to it.

119

2   Materials and methods

2.1   Sediments and artificial seawater

122 Sediment samples were collected from the top 10 cm of sediment from the Faroe-Shetland
123 Channel (1000 m; FSC, hereafter) aboard *MRV Scotia* in May 2014 (61°35.02'N, 4°14.64'W),
124 Stonehaven Bay (14 m; SB, hereafter) aboard *MRV Temora* in June 2016 (56°58'18"N,
125 2°11'3"W) and the Ythan estuary (intertidal; YE, hereafter) in December 2016 (57°18'14"N,
126 1°59'25"W) (Fig. 1). Sampling methods were maxi-corer (OSIL, United Kingdom), Van Veen
127 grab and manual collection for FSC, SB and YE sediments, respectively. Sediments were
128 autoclaved at 121°C for 21 min at 100 kPa and oven dried at 60°C for three days to minimise
129 microbial activity prior to carrying out experiments. Artificial seawater was prepared by adding
130 pre-oven dried (at 130°C for 24 h) Seamix Artificial Sea Salt (Peacock Salt, United Kingdom)
131 at 3.4% (mass/volume) to ultra-pure (type 1) water and magnetically stirring for 8 h.

132

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2.2 Sediment characterisation

Sediments were characterised in terms of particle size distribution and carbon content. YE and SB sediments were oven-dried at 105°C overnight and sieved through mesh sizes of 2000, 1000, 500, 250, 120 and 63 μm. Statistical analyses of particle size distribution were carried out using Gradistat v.8 (Blott and Pye 2001). FSC sediments were oven-dried at 105°C overnight and then wet sieved through a 63 μm mesh to separate coarse (>63 μm) from fine sediment (<63 μm). Coarse sediment was then analysed as described above and fine sediment was analysed using the hydrometer method (Ashworth et al. 2001) and statistical analysis of particle size distribution was performed using the Hydrometer Particle Size Calculator (Natural Resources Conservation Service - United States Department of Agriculture Hydrometer Particle Size Calculator - ASTM No. 1).

To determine carbon content, sediments were initially oven-dried at 60°C for three days. Thereafter, sediments were mechanically milled. Subsequently, total carbon content was determined using a NA2500 elemental analyser (Carlo Erba Instruments). Total OC content was determined by acidifying sediment with 10% HCl and oven-dried at 60°C for three days and subsequently analysed by elemental analysis. Total inorganic carbon content was determined by difference between total carbon and total OC.

2.3 Superdispersant-25 measurements and critical micelle concentration determination

Three independent stock solutions of SD25 in artificial seawater at 100 and 1000 mg l^{-1} were prepared and equilibrated. Dilutions were performed to obtain solutions at concentrations of 0, 0.25, 5, 10, 25, 50, 100, 200, 300, 400, 500 and 1000 mg l^{-1}. Thereafter, seawater surface tension measurements were performed using a tensiometer (White's instruments) fitted with a du Nouy ring to calibrate the response of surface tension to SD25 concentration. The apparent critical micelle concentration was calculated as the inflexion point in seawater surface tension as a function of SD25 concentration, as described elsewhere (Gong et al. 2014).

2.4   Effect of Superdispersant-25 on aqueous solubility of PAHs

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161 Saturated solutions of PHE and NAP with increasing SD25 were prepared to assess the
162 influence of initial SD25 concentration in seawater ($[SD25]_{sw,0}$, hereafter) on PAH solubility
163 in seawater. Briefly, 200 mg of each PAH were added to separate 70 ml glass vials and stock
164 solutions of seawater and SD25 were mixed to achieve concentrations in the range 0–1000 mg
165 l^{-1} and added to the vials. The mixtures were then equilibrated by magnetic stirring at 20°C in
166 complete darkness for three days to ensure dynamic equilibrium. 20°C was chosen as past
167 sorption dynamics and sediment hydrocarbon biodegradation literature has been undertaken at
168 this temperature. The experiments were performed in complete darkness to prevent
169 photodegradation of PAHs. After equilibration, solutions were centrifuged in glass centrifuge
170 tubes at 3000 rpm for 10 mins such that suspended PAH is removed from solution and only
171 dissolved PAH remained. 25 and 50 ml of NAP and PHE solutions, respectively, were then
172 sequentially liquid-liquid extracted three times with 10 ml dichloromethane using pristane as
173 an internal extraction standard (100 µl at 20 µg ml^{-1}). PHE extracts were then evaporated to
174 approximately 5 ml under nitrogen and analysed by gas chromatography with flame ionisation
175 detection. NAP extracts were injected immediately after extraction. Further analysis details can
176 be found elsewhere (Perez Calderon et al. 2018b).

177

2.5   Superdispersant-25 uptake by sediments

178

179 Sorption of SD25 by sediments was evaluated in two stages, (1) where SD25 solutions were
180 equilibrated with sediment and (2) where supernatant solutions after equilibration were
181 replaced with clean seawater. These were defined as adsorption and desorption stages,
182 respectively. Pre-treated sediment (2.5 g) were added to 15 ml Pyrex centrifuge tubes with
183 Teflon-lined caps. 12 ml of SD25 in artificial seawater solutions at concentrations of 0, 10, 20,
184 30, 100, 175, 250, 375 and 500, and 1000 mg l^{-1} were prepared and added to the centrifuge
185 tubes. Thereafter, these were incubated in a horizontal shaker at 200 rpm for three days at 20°C
186 in complete darkness. Vials were then centrifuged at 3000 rpm for 10 mins and 3 ml of
187 supernatant was sampled to measure surface tension. The remaining supernatant was replaced
188 with artificial seawater and incubated a further three days in complete darkness. Samples were
189 centrifuged again at 3000 rpm for 10 mins and surface tension measurements taken. SD25
190 concentration was calculated from the calibration curves prepared for the critical micelle

191 concentration determination experiment. Measurements were conducted for each sediment
192 type in triplicate.

193

2.6   PAH sorption by sediments and effect of Superdispersant-25

195 The effect of SD25 concentration on PAH sorption by sediments was evaluated in two stages
196 as described in section 2.5. 12 ml solutions containing 0.40 mg PHE l^{-1} or 3.85 mg NAP l^{-1} and
197 SD25 at 0, 10, 20, 30, 100, 200, 300 mg l^{-1} in artificial seawater were prepared and added to
198 15 ml glass centrifuge tubes lined with Teflon-lined caps. Samples were incubated and
199 centrifuged as described in section 2.5. PAH concentration in seawater was determined by UV-
200 vis spectroscopy using a Lambda 25 UV/VIS Spectrometer (PerkinElmer). UV-vis spectra
201 were measured with a 10 mm path-length quartz cuvette over the range 200–400 nm. PHE and
202 NAP concentrations were calculated from absorbances at 251 and 275 nm, respectively. 5-
203 point calibration curves were prepared for each PAH and blanks with seawater only were ran
204 after every 5 samples. Absorbances of blanks and solutions of SD25 in seawater and sediment
205 were subtracted from measured values.

206

2.7   Chemicals

208 PHE (99%), NAP (99%), pristane (99%) and dichloromethane (HPLC grade) were acquired
209 from Sigma Aldrich (United Kingdom). Superdispersant-25 was acquired from Oil Technics
210 (United Kingdom).

211

2.8   Calculations and statistical modelling

213 K_D can be envisaged as being composed of two terms to evaluate the contributions of
214 surfactants to the sorption of PAHs to sediments (Lu and Zhu 2012):

215
$$K_D = \frac{C_{sed}}{C_{sw}} = K_{OC}f_{OC} + K_{sf}Q_{sf} \qquad \text{Eq. 2}$$

216 where C_{sed} is the PAH concentration in sediment (mg g^{-1}), C_{sw} is the PAH concentration in
217 seawater (mg l^{-1}), K_{oc} is the OC-normalised PAH distribution coefficient (ml g^{-1}), calculated as

218   $0.35K_{ow}$ (Octanol-water coefficient) (Seth et al. 1999), f_{oc} is the OC fraction of the sediment,

219   K_{sf} is the surfactant-normalised PAH distribution coefficient (ml g^{-1}), defined here as K_{SD25} (for

220   SD25) and Q_{sf} is the sediment-adsorbed surfactant concentration (mg g^{-1}), defined here as Q_{SD25}

221   and including all components of the SD25 formulation. Analyte concentrations in sediment

222   were calculated by subtracting the concentrations measured in in artificial seawater from initial

223   concentrations added. For calculating of K_D values when no analyte was detected in the

224   aqueous phase, a value of 0.001 mg l^{-1} was used as the concentration in seawater.

225   Response of sorption variables to SD25 concentration were modelled using locally weighed

226   regressions due to the non-linearity of the data, where sorption variables were the response

227   variable and SD25 concentration in either water or sediment was the explanatory variable,

228   subset by PAH, sediment type and experimental stage (adsorption: first inoculation; desorption:

229   replacement of supernatant with clean seawater). Briefly, the model fits a polynomial surface

230   determined by PAH solubility. Q_{SD25} values were estimated from locally weighed regressions

231   from experiments described in Section 2.5. All statistical analysis was undertaken using R (R

232   Development Core Team 2017) and the library *ggplot2* was used for locally weighted

233   regression analysis (Wickham and Chang 2009).

234

3   Results

3.1   Sediment characterisation and Superdispersant-25 critical micelle concentration

237   FSC, SB and YE sediments were classified as silty loam, medium and fine sands, respectively.

238   Details of particle size distribution and carbon content of the sediments analysed can be found

239   in Table 1. The critical micelle concentration of Superdispersant-25 in artificial seawater (T =

240   20°C, S = 34) was 5.8 mg l^{-1} (Fig. 2).

241

3.2   Effect of Superdispersant-25 concentration on PAH solubility in seawater

243   Solubility of PHE in artificial seawater linearly increased from 0.57 ± 0.20 to 4.44 ± 1.32 mg

244   l^{-1} from 0 to 250 mg SD25 l^{-1} and decreased to 2.07 ± 1.66 mg l^{-1} at 1000 mg SD25 l^{-1}. Solubility

245 of NAP in artificial seawater remained constant from 0 to 1000 mg SD25 l^{-1} (10.00 ± 1.89 and

246 11.18 ± 0.91 mg l^{-1}, respectively, Fig. 3).

247

3.3 Dispersant sorption onto sediments

249 SD25 uptake by sediments differed across sediment type and $[SD25]_{sw,0}$ range (Fig. 4). At

250 $[SD25]_{sw,0}<175$ mg l^{-1} all sediments took up all SD25 from solution and no evidence for

251 desorption back into solution was detected in the desorption stage. In FSC sediment, uptake of

252 all SD25 was observed across the range of $[SD25]_{sw,0}$ and no desorption was detected at any

253 $[SD25]_{sw,0}$. In SB sediment, as in FSC sediment, uptake of all SD25 was detected across the

254 $[SD25]_{sw,0}$ range tested. However, SD25 desorption was apparent at $[SD25]_{sw,0}>250$ mg SD

255 l^{-1}. At $[SD25]_{sw,0}>175$ mg SD25 l^{-1}, YE sediment uptake of SD25 plateaued at ~1.5 mg g^{-1},

256 and desorption could not be inferred also due to high variability of [PHE].

257

3.4 Effect of Superdispersant-25 on PAH uptake by sediments

259 K_D values of NAP and PHE as a function of Q_{SD25} to the sediments investigated varied with

260 sediment type and experimental stage (adsorption or desorption) (Fig. 5). During the adsorption

261 stage, SD25 application increased K_D values in YE and SB sediments but not in FSC sediment.

262 As Q_{SD25} increased, K_D values of both PAHs to SB and YE sediments increased. Desorption

263 stage K_D values of both PAHs decreased relative to the adsorption stage. Desorption stage K_D

264 values decreased with Q_{SD25} in FSC sediments and increased in other sediment types, except

265 for NAP in YE sediment, where no effect of Q_{SD25} was apparent. The adsorption of PAHs to

266 sediment-adsorbed SD25 was evaluated by comparing K_{SD25} to Q_{SD25} (Fig. 6). Overall, no clear

267 patterns emerged for K_{SD25} as a function of Q_{SD25} during either the adsorption or desorption

268 stages.

4   Discussion

4.1 Key findings

271 SD25 had contrasting effects on the water-solubility of PHE and NAP. PHE water-solubility

272 was increased from SD25 concentration as low as 10 mg l^{-1} but NAP water-solubility was not

10

273 affected by SD25, even at 1000 mg l^{-1}. Sorption of SD25 by sediments varied by sediment type.

274 FSC sediment took up all SD25 in solution across the [SD25]$_{SW,0}$ range tested and no

275 desorption of SD25 was detected. In contrast, in SB and YE sediments SD25 desorption was

276 apparent in experiments with [SD25]$_{SW0}$>250 mg l^{-1}. Sorption dynamics of PAHs varied by

277 PAH, sediment type and Q_{SD25}. Q_{SD25} increased K_D values of both PAHs in SB and YE

278 sediments but did not have a clear effect on the adsorption of either PAH in FSC sediments.

279 Desorption stage K_D values generally decreased with respect to the adsorption stage. There was

280 no clear trend of PAH sorption to sediment-adsorbed dispersant as a function of Q_{SD25}.

281

4.2   Effect of dispersant on PAH solubility in seawater

283 SD25 application increased the water-solubility of PHE but not of NAP. PHE water-solubility

284 could be increased up to seven-fold with dispersant application at 250 mg l^{-1} (Fig. 3). However,

285 at SD25 concentration above 250 mg l^{-1}, PHE solubility was reduced implying that SD25 may

286 have an optimal concentration to mobilise target pollutants. SD25 application, even at SD25

287 concentration <30 mg l^{-1}, resulted in increased PHE solubility indicating that PAHs such as

288 PHE can be readily dissolved and dispersed in the water column. Increasing the solubility of

289 PAHs in the water column by dispersant facilitates their dilution and dispersion in the marine

290 environment (Fingas 2002) which can aid in long-term removal. Hydrocarbons have been

291 shown to photodegrade more rapidly when chemically dispersed with Corexit 9500A than in

292 its absence (Zhao et al. 2016). Chemical dispersion may negatively impact or have no effect

293 on hydrocarbon biodegradation in the water column by modifying the microbial community

294 composition and selecting for potential dispersant-degrading bacteria *Colwellia* and not

295 *Marinobacter*, a natural hydrocarbon degrader (Kleindienst et al. 2015). The overall benefits

296 of dispersant to the marine environment remain debated although it can be beneficial given

297 specific circumstances (Prince 2015).

298 [SD25]$_{SW,0}$ up to 1000 mg l^{-1} did not enhance NAP solubility (~11 mg l^{-1}) although there have

299 been reports of higher water-solubility of NAP in seawater without surfactant addition (23.1

300 mg l^{-1} at 25°C (Adelman 1977) and 28 mg l^{-1} at 20°C (Zhao et al. 2015)). Previous work using

301 SD25 has shown that SD25 has limited effect on NAP mobility into sediments (Perez Calderon

302 et al. 2018b, c, a). In contrast, investigations into NAP water-solubility have shown that Corexit

303 9500A can linearly increase its solubility in seawater. Zhao et al. (2015) reported that 200 mg

304 Corexit 9500A l^{-1} increased NAP solubility in seawater from 28 to 36 mg l^{-1}. These apparent

305 contradictions illustrate that different commercial dispersants and seawater types may

306 solubilise specific hydrocarbons to different extents. Therefore, conclusions drawn from work

307 using one oil-dispersant-seawater system may not be transferable to another system with a

308 different dispersant or seawater. This is important given that a large body of literature has been

309 produced following the *DwH* oil spill using Corexit dispersants which may only be relevant in

310 the context of the Macondo oil-Corexit dispersant combination. Therefore, further research is

311 required into how different dispersants affect oil-water interactions.

312

4.3 Superdispersant-25 sorption by sediments

314 All SD25 across the concentration range tested was adsorbed onto FSC sediment and did not

315 desorb following water replacement (Fig. 4). This finding highlights the strong uptake capacity

316 of SD25 by fine deep-sea sediments. Subsea application of dispersant, as witnessed during the

317 *DwH* oil spill resulted in significant amounts of dispersant ending up on the seabed (White et

318 al. 2014). The proposed pathways of dispersant deposition on the Gulf of Mexico seabed are

319 thought to be surface sorption and settling of dispersant-suspended particle aggregates (Gong

320 et al. 2014b; White et al. 2014). Sorption of non-polar hydrophobic pollutants to sediments is

321 dependent on organic matter content and if it is above 0.01%, it may take up the majority of

322 the pollutant as opposed to the mineral component of the sediment (Pignatello 1998). In this

323 experiment, this was verified for SD25 as maximum uptake was observed by high OC-

324 containing sediments (FSC and SB) as opposed to low OC-containing sediment (YE).

325 Desorption of SD25 was detected in SB but not in FSC sediment potentially due to the

326 difference in percentage of fines between sediment types (Fig. 4). Dispersant has been found

327 to persist in deep-sea sediments and corals for over four years following the *DwH* oil spill and

328 that environmental conditions in deposition sites influenced its residence time (White et al.

329 2014). Results here suggest that responders should consider sediment characteristics as part of

330 the decision-making process for dispersant application in the marine environment due to the

331 capacity of dispersant to adsorb to marine sediments, particularly when sediments are fine or

332 OC-rich. For example, in a hypothetic offshore well blowout scenario, SD25 application near

333 fine sediments, such as FCS sediments, may enhance uptake of SD25, oil droplets and

334 dissolved hydrocarbons more readily than other sediments. This can yield more negative effects

335 for benthic ecosystems than application at surface waters where oil and dispersant are less

12

336 likely to come into contact with the seabed. On the other hand, if the seabed is sandy,
337 application of SD25 near the seabed is less likely to result in adsorption of hydrocarbons
338 although it may enhance entrainment *via* advective pore-water transport (Perez Calderon et al.
339 2018c). This is particularly important if protected species such as sand eels are near the target
340 site for SD25 application as they are sensitive to oil (Heath and Bailey 1994).

341

4.4 Effect of dispersant on PAH uptake by sediments

343 K_D values of NAP and PHE varied with sediment type, Q_{SD25} and experimental stage to varying
344 extents (Figs 5, **Fig. 6**). In FSC sediments, Q_{SD25} did not affect K_D values of either PAH in the
345 adsorption stage which is likely due to the high proportion of fines (70.8%) and OC (1.67%).
346 In contrast, in sandy sediments with a lower proportion of fines such as SB and YE sediments,
347 uptake increased with Q_{SD25} suggesting that surfactant sorption may create new adsorption sites
348 in coarser sediments as previously reported for PHE in sandy loam and loamy sand using
349 Corexit 9500A (Gong et al. 2014b). Corexit 9500A in solution (18 mg l^{-1}) has been shown to
350 have limited effects on NAP sorption to sandy loam and loamy sand, increasing in NAP uptake
351 by sediment of 2.9% and 3.3%, respectively (Zhao et al. 2015). Here, the highest uptake of
352 NAP was measured in YE sediments at ~0.8 mg SD25 g^{-1} (Fig. 5) although no effect of SD25
353 on naphthalene solubility was apparent (Fig. 4). However, no NAP was detected in the aqueous
354 phase in these samples and the default value of 0.001 mg l^{-1} was assigned which may have
355 skewed the K_D values of NAP in these samples. Desorption-phase K_D values across sediments
356 for both NAP and PHE decreased indicating that adsorption of both NAP and PHE in these
357 sediments was partially reversible. Increasing Q_{SD25} reduced desorption stage K_D values of
358 NAP in FSC sediments suggesting that SD25 uptake increased the partitioning of NAP to the
359 aqueous phase. In contrast, desorption stage K_D values of NAP in SB or YE did not vary with
360 Q_{SD25} suggesting that sediment-adsorbed SD25 does not retain NAP in sandy sediments with
361 seawater exchange.

362 The effect of Q_{SD25} on the desorption of PHE was similar to that in the adsorption stage in SB
363 and YE sediments suggesting that PHE remains more strongly adsorbed to marine sediments
364 with increasing Q_{SD25} than NAP. Desorption stage K_D values of PHE in YE sediments were
365 approximately one order of magnitude higher than those of NAP (Fig. 5) suggesting that, even
366 in the absence of fines, PHE may remain strongly adsorbed onto sandy sediments. Strong

13

adsorption of PAHs to silty loams following continuous desorption experiments has been recently reported (Duan et al. 2018). The authors also reported that addition of Corexit 9500A and SPC 100 increased desorption of PAHs and to a lesser extent that of alkanes. Similarly, Gong et al. (2014) reported increased hysteresis of PHE in sandy loam and loamy sand at increasing Corexit 9500A, suggesting that SD25 may be less effective at desorbing NAP and PHE from marine sediments although it does increase their solubility in seawater. The contribution of Q_{SD25} to K_{SD25} values of either PAH in this experiment was unclear. Previous research showed increased adsorption of organic pollutants to sediment-bound dodecylpyridinium bromide, even in humic acid with ~50% OC where OC would be expected to adsorb the majority of the pollutant (Lu and Zhu 2012). This difference may arise from the use of a different dispersant formulation (SD25).

Disparity in response to SD25 application has been observed in hydrocarbon pore-water transport experiments where NAP and PHE were mixed with hydrocarbons from other fractions (BTEX, aliphatics and other PAHs) (Perez Calderon et al. 2018b, c, a). The effect of SD25 on NAP mobility in sediments in these experiments was limited, suggesting a similar "behaviour" to that observed here. In contrast, PHE mobility in sediments increased with SD25 application in these experiments. The solubilising effect of SD25 was masked by the high water-solubility of NAP but was apparent for PHE, even when in the same system. Other hydrocarbons were found to not be affected by SD25-application (e.g. BTEX) which are also highly water-soluble, suggesting this is the key property that governs the extent to which SD25 affects hydrocarbons in these systems.

The findings here show the effects of SD25 on PAH-sediment-seawater dynamics in three sediments from the North Sea and FSC. Adsorption of PAHs to sediments was facilitated by SD25 application. The driving mechanism appeared to be the solubilising effect of SD25 on PAHs as Q_{SD25} did not appear to drive PAH adsorption onto FSC sediments, suggesting that SD25 application in a subsea blowout in the FSC may not increase sorption of PAHs but may result in SD25 adsorption to sediment, where dispersants can persist for years (White et al. 2014) and affect microbial community composition (Ferguson et al. 2017; Perez Calderon et al. 2018b). In contrast, increased uptake of PAHs by SB and YE sediments with increasing Q_{SD25} suggest that less sorptive sediments (i.e. with lower OC and fines percentages) may increase their uptake of PAHs through sediment-adsorbed SD25. It is important to note that sediments here were sterilised and artificial seawater used and such bacterial activity in the sediments was reduced. Consequently, the role of biodegradation, biosurfactant production and

400 transparent exopolymeric particle production has not been considered here. These processes
401 may have a marked effect on sorption dynamics. For example, biodegradation reduces
402 surfactant concentration in media through microbial metabolism (Brakstad et al. 2018), which
403 may limit hydrocarbon uptake by sediments. Biosurfactant production increases PAH
404 bioavailability and can enhance biodegradation (Lu et al. 2011), which can decrease their
405 concentration in sediments. Finally, transparent exopolymeric particles (colloidal organic
406 carbon structures containing acidic polysaccharides) play a key role in adsorbing particulates
407 in the wider ocean (Rochelle-Newall et al. 2010). They can act as binding sites for dispersant
408 and remove surfactants and PAHs from solution as suggested in the MOSSFA hypothesis,
409 whereby marine snow acted as a pathway for deposition of hydrocarbons and dispersant on the
410 deep seabed after *DwH* (Passow 2016). The role of these biological processes cannot be ignored
411 in a real oil spill. However, the focus here was on the physical interactions between PAHs,
412 dispersants and sediments. Further research is required to evaluate the physicochemical
413 processes investigated here in conjunction with biological processes how the sorption
414 dynamics of other, larger PAHs are affected by dispersant application.

415

5   Conclusions

417 The present study evaluated the sorption dynamics of PHE and NAP in three marine sediments-
418 seawater systems and the effect of SD25 concentration on this process. The main findings of
419 the study were:

420   1. Dispersant increased the solubility of PHE in seawater up to seven-fold but had no
421   effect on the solubility of NAP. This contrasts with previous work, where NAP
422   solubility was enhanced with Corexit 9500A, suggesting that different dispersant
423   formulations can selectively solubilise specific PAHs in seawater. Dispersant choice
424   should be considered by responders to account for selective solubilisation of toxic
425   chemicals such as PAHs and the potential knock-on effects this choice may have on the
426   wider marine environment, e.g. the seabed as discussed here.
427   2. FSC and SB sediments adsorbed all SD25 across the concentration range tested (up to
428   ~5 mg g^{-1}) but no desorption could be measured in FSC sediments suggesting SD25
429   can remain strongly bound to fine sediments. In YE sediments, sorption of SD25 was
430   more limited (up to ~1.5 mg g^{-1}) and desorption of SD25 was highly variable.

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3. Sorption dynamics of both PAHs were affected by sediment type and Q_{SD25} to different extents. K_D values decreased in the desorption stage compared to the adsorption stage for both PAHs. Q_{SD25} increased adsorption of both PAHs in SB and YE but not FSC sediments. The finding suggests that SD25 increased sediment uptake of PAHs but did not retain them strongly adsorbed to the sediment following water replacement.

4. Q_{SD25} did not have a clear effect on K_{SD25} values of either PAH, suggesting that sediment-adsorbed SD25 increases the adsorption of these PAHs to sediment but not onto sediment-adsorbed SD25.

The results provide evidence of SD25 influence on the sorption dynamics of PAHs in marine sediments, which varies by sediment type and PAH. The results highlight the importance of considering the relationship between SD25 and sorption dynamics on the fate of PAHs in marine sediments following an oil spill. Further research into the sorption dynamics of PAHs across commercial dispersants, sediment types, within hydrocarbon mixtures and biotic interactions is required to evaluate the potential effects of dispersant on oil-sediment interactions.

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565 **7 Tables**

566 **Table 1**. Carbon content (total (TC), organic (TOC) and inorganic (TIC)) and particle size distribution
567 of sediments used in sorption experiments. Average percentages are expressed in terms of mass and
568 errors refer to standard deviation ($n = 3$).

Station	TC (%)	TIC (%)	TOC (%)	Sand (%)	Silt (%)	Clay (%)
FSC	2.164 ± 0.028	0.490 ± 0.009	1.674 ± 0.019	29.3 ± 4.2	65.5 ± 4.4	5.3 ± 2.4
SB	1.014 ± 0.027	0.040 ± 0.080	0.977 ± 0.103	95.6 ± 1.2	3.7 ± 1.0	0.7 ± 0.2

YE	0.102 ± 0.014	0.076 ± 0.008	0.026 ± 0.007	100.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0

8   Figure captions

Fig. 1. Sampling locations of sediments used in sorption experiments from the Faroe-Shetland Channel (FSC, yellow pin), Ythan estuary (YE, red pin) and Stonehaven Bay (SB, green pin).

Fig. 2. Effect of Superdispersant-25 on artificial seawater surface tension. Circles and crosses represent values below and above the change in slope. The solid and dashed lines represent models before and after slope change. The solution for the intersection of the two equations is the CMC the critical micelle concentration of Superdispersant-25 (4.63 mg l^{-1}). Grey bands represent standard error of linear models. Note SD25 concentration has been log(x+1) transformed.

Fig. 3. Effect of initial Superdispersant-25 concentration in seawater ($[SD25]_{SW,0}$) on PAH solubility in artificial seawater ($S = 34$). Circles and crosses represent concentrations of naphthalene and phenanthrene, respectively. Solid and dashed lines, and grey bands represent locally weighted smooth regression predicted values and standard errors for naphthalene and phenanthrene, respectively.

Fig. 4. Superdispersant-25 uptake (Q_{SD25}) onto sediments from the Faroe-Shetland Channel (70.8% fines), Stonehaven Bay (4.4% fines) and Ythan Estuary (0% fines) as a function of initial Superdispersant-25 concentration in seawater ($[SD25]_{SW,0}$). Circles and crosses represent adsorption and desorption steps, respectively. Solid and dashed lines, and grey bands represent locally weighted smooth regression predicted values and standard errors for adsorption and desorption isotherms, respectively.

Fig. 5. Effect of sediment Superdispersant-25 concentration (Q_{SD25}) on the distribution coefficient (K_D) of naphthalene and phenanthrene in sediments from the Faroe-Shetland Channel (70.8% fines), Stonehaven Bay (4.4% fines) and Ythan Estuary (0% fines). Circles and crosses represent adsorption and desorption steps, respectively. Solid and dashed lines, and grey bands represent locally weighted smooth regression predicted values and standard errors for adsorption and desorption isotherms, respectively. Note the log-scale in the y-axis.

Fig. 6. Effect of sediment uptake of Superdispersant-25 (Q_{SD25}) on the distribution coefficient (K_{SD25}) of naphthalene and phenanthrene to sediment-adsorbed Superdispersant-25 surfactants in sediments from the Faroe-Shetland Channel (70.8% fines), Stonehaven Bay (4.4% fines) and Ythan Estuary (0% fines). Circles and crosses represent adsorption and desorption steps, respectively. Solid and dashed lines, and grey bands represent locally weighted smooth regression predicted values and standard errors for adsorption and desorption isotherms, respectively. Y-axis scaling is log-modulus transformed to facilitate visualisation (John and Draper 1980).

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