

World war munitions as a source of mercury in the southwest Baltic Sea

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5	World War Munitions as a source of Mercury in the Southwest Baltic Sea
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24	

25 Abstract

26

27 Mercury (Hg) fulminate was used as a primary fuse in World War (WW) munitions, and 28 may consequently be a Hg source for impacted environments. Mercury is a conspicuous and 29 persistent pollutant, with methylmercury (MeHg) acting as a notorious neurotoxin. Considerable 30 amounts of munitions were intentionally dumped in the North Sea and Baltic Sea following the 31 First and Second WWs. After more than 70 years on the seafloor many munitions have corroded 32 and likely release explosive compounds, including Hg fulminate. The Germany coastal city of 33 Kiel was a manufacturing centre for submarines, and accordingly a prominent target for bombing 34 and post-war disarmament. We collected water and sediment samples around Kiel Bay to assess 35 regional levels and quantify any Hg contamination. The munition dump site Kolberger Heide 36 (KH) and a former anti-aircraft training center Dänisch-Nienhof are situated in Kiel Bay, and 37 were targeted for sampling. Sediment Hg concentrations around KH were notably elevated. 38 Average Hg concentrations in KH sediments were 125 ± 76 ng/g, compared to 14 ± 18 ng/g at 39 background (control) sites. In contrast, dissolved Hg in the water column exhibited no site 40 variations, all ranging between 0.8 - 2.1 pM. Methylmercury in sediments and waters did not 41 have enhanced concentrations amongst sites (<30 pg/g and <50 fM, respectively). Sedimentwater exchange experiments showed elevated Hg and MeHg fluxes (i.e. >400 pmol $m^{-2} d^{-1}$ 42 43 MeHg) at one KH location, however remaining cores had low to no Hg and MeHg output (<0 to 27 pmol m⁻² d⁻¹ MeHg). Thus, sediments in Kiel Bay proximate to WW munitions could harbor 44 45 and form a source of Hg, however water column mixing and removal processes attenuate any 46 discharge from the seafloor to overlying waters.

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48 Keywords: Kolberger Heide, Mercury fulminate, Mercury speciation, methylmercury, UXO

50 1. Introduction

51

52 Mercury (Hg) is a naturally occurring element which is readily transferred between the 53 earth's geological reservoirs (Outridge et al., 2018; Edwards et al., 2021), yet also notoriously 54 toxic. Mercury is environmentally pervasive as a byproduct of coal and fossil fuel combustion, 55 paper processing (Boening, 2000; van Velzen et al., 2002), and furthermore still used during 56 illegal gold mining activities (Goncalves et al., 2017). Methylmercury (MeHg) is known for its 57 irreversible toxic effects on humans and wildlife. This highly bioavailable organic Hg form acts 58 as a neurotoxin, and damages DNA and RNA thereby causing permanent mobility damage 59 (Clarkson and Magos, 2006). Methylmercury species bioaccumulate in marine food chains, with 60 especially harmful levels in slow growing and predatory fish species (Lavoie et al., 2018). Hence 61 it is critical to assess levels of Hg and MeHg present in marine environments. 62 Mercury fulminate (HgFu) was originally formulated by alchemists in the seventeenth 63 century, making it one of the oldest known explosive compounds. The first and second World 64 Wars (WWI and WWII) stimulated extensive production and use of various types of munitions, 65 including mines, anti-aircraft grenades and submarine torpedoes. In addition to the primary 66 charge of e.g. trinitrotoluene (TNT), many WW anti-aircraft grenades contained HgFu as an 67 initial ignition compound. The WWI production of HgFu in Germany increased from 104 t up to 68 357 t between 1910 and 1917 (Matyáš and Pachman, 2013). Following a decline in 69 manufacturing during the 1920s through 1930s (primarily due to its toxicity), HgFu output again 70 increased in the 1940s with the inception of WWII (Horowitz et al., 2014). As much as 15% of 71 global Hg production was dedicated to the manufacturing of HgFu for munitions throughout 72 WWI and WWII (Horowitz et al., 2014).

73 The Germany coastal city of Kiel has been an active naval base and manufacturing centre 74 for submarines since 1864, and accordingly housed a notable reserve of munitions. Kiel was thus 75 a prime target for bombing and destruction during WWII. Numerous air strike campaigns 76 demolished Kiel between 1940 and 1944, destroying ~80% of its buildings. About 20-30% of the 77 munitions used during airstrikes and anti-aircraft defense activities did not explode (GICHD, 78 2016), resulting in unexploded ordnance (UXO) on land and in coastal waters. Following WWII, 79 the Allies hastily disposed the large quantities of remaining munitions directly in the North Sea and Baltic Sea (Carton and Jagusiewicz, 2009). It is estimated that approximately 1.6×10^6 t of 80 81 munitions were disposed in German waters following WWI and II (Böttcher et al., 2011). In 82 effect between 360,000 – 385,000 t of munitions were dumped in the Baltic Sea during the 83 demilitarization campaign after 1945 (Carton and Jagusiewicz, 2009). This could have 84 subsequently delivered an estimated 300 t of Hg just inside confined dump sites (Beldowski et 85 al., 2019).

86 Munition dumps in coastal waters pose substantial dangers due to explosion risks to ship 87 traffic, economic resource development and recreational as well as commercial fisheries (Carton 88 and Jagusiewicz, 2009; GICHD, 2016). There is furthermore a raised awareness of threats that 89 munition compounds and their degradation products that leach out of corroded ordnance pose to 90 the marine ecosystems (Carton and Jagusiewicz, 2009; Beck et al., 2018; Kampmeier et al., 91 2020). Kolberger Heide (KH) is a munition dumpsite located in Kiel Bay (KB) in the Baltic Sea, 92 and proximate to active ship routes and densely populated areas. Geophysical observations have 93 shown that KH contains over 1000 weapon objects, yielding an estimated 30,000 tons of 94 munitions (Kampmeier et al., 2020). The former anti-aircraft training site Dänisch-Nienhof (DN) 95 is also located on the northern coast outside of Kiel, and was heavily bombed during WWII. This 96 likely provided residual elemental Hg detonation fallout in addition to UXO remaining in coastal

97 sediments. Munitions possibly impacted an area of approximately 10.5 km² around DN
98 (HELCOM, 2015).

99 Recent findings suggest that sediments close to munitions have elevated Hg content 100 (Gebka et al., 2016; Beldowski et al., 2019; Siedlewicz et al., 2020), however provide no 101 assessment for how surrounding waters could be affected. The primary aim of this study was to 102 evaluate if there is Hg contamination from legacy WW munitions in sediments around KH and 103 DN which is further prevalent in the ambient water column of Kiel Bay and greater southwest 104 Baltic Sea. Potential contributions were determined for dumped munitions and UXO in KH and 105 DN towards the burden of various Hg compounds in the water column and sediments. Moreover, 106 sediment water exchange fluxes were assessed for each site to evaluate if Hg and MeHg are 107 discharged from sediments to overlying water. These measurements and experiments provide 108 current regional background concentrations, as well as document if munition impacts represent a 109 Hg source and danger to the local marine environment. The human population in the surrounding 110 area of the Baltic Sea reaches nearly 90 million, therefore it is important to obtain a mechanistic 111 and quantitative understanding of any toxic residuals release from historic munition including Hg 112 and MeHg, and their distribution in the marine environment.

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115 **2. Methods**

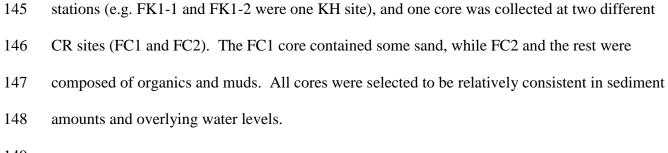
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117 2.1 Field Collection
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Seawater and sediment for Hg analysis were collected aboard the RV Littorina in KB, southwest Baltic Sea (Figure 1). Seasonal field sampling (December, May and July) occurred during 2019 and 2020 in the vicinity of DN, the munition dump site KH, and control sites within

121	KB (CR). The DN site was not sampled in December. No benthic biota were present within
122	sediments, therefore no Hg measurements are available for any organisms. Seawater samples for
123	coastal Hg concentrations were also collected on a cruise traverse in the south Baltic Sea between
124	Kiel and Lübeck in September 2018 on RV Alkor (SI; Figure S1). All seawater samples were
125	collected as depth profiles using a plastic-coated line with 8 L Go-Flo bottles (General Oceanics)
126	and according to trace metal-clean GEOTRACES sampling techniques (Cutter et al., 2017). Kiel
127	Bay and especially KH are relatively shallow (<20 m), and profiles were collected between ~1-2
128	m below the surface and ~1-2 m above the bottom to minimize potential contamination risk from
129	sediment disturbance or ship residue.
130	Water profiles were collected from between 3 to 7 stations at each site per season. Water
131	were filtered through 0.2 μ m filters (Nuclepore polycarbonate), then poured into acid-cleaned
132	borosilicate glass bottles for the separate Hg species, preserved acidified with hydrochloric acid
133	(0.2% v/v) upon returning to shore (<5 hours), then analyzed within ~5 months. Volumes of 500
134	mL were collected for MeHg measurements, and 250 mL for total Hg.
135	Surface sediment samples were obtained by box corer in areas corresponding to water
136	sampling. Sediment samples were selected to be visually uniform in their composition among
137	stations and sites, primarily of a muddy mix with limited sand. Some rocky and sandy sediments
138	areas in KB could not be obtained by box corer, so paired water and sediment samples were not
139	available. Nevertheless, sediments were obtained from a wide region around munition and
140	control sites (between 8-14 stations collected from each).
141	Intact sediment cores with their overlying water were additionally collected from each site
142	with a multicorer during the July 2020 Littorina cruise (SI; Figure S2). These cores were used
143	for sediment flux experiments to quantify sediment release and exchange of Hg species to the

144 overlying water column. Duplicate cores were collected from 2 different adjacent DN and KH



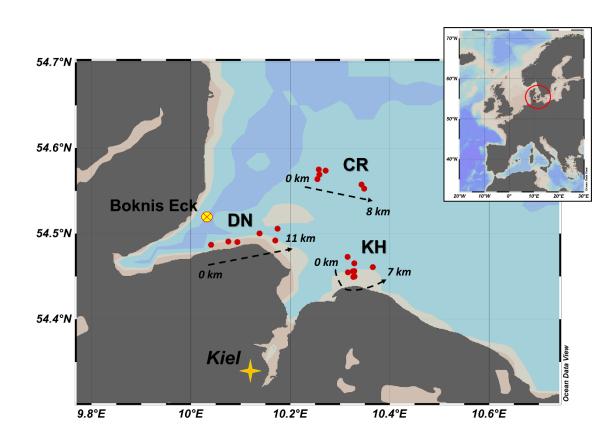


Figure 1. Map of stations for water and sediment sample collection in Kiel Bay in the southwest
Baltic Sea (north Germany). Sites are abbreviated as background control (CR), Dänisch Nienhof
(DN), and the munition dump site Kolberger Heide (KH). Section distances (km) for each site
are indicated. Water profiles (5 total) were collected at the Boknis Eck monitoring station
(yellow target) during 2020-2021 to provide additional water inventory.

159 2.2 Water Analysis

160 Dissolved Hg was analyzed at GEOMAR via gas chromatography and cold-vapor atomic 161 fluorescence spectrometry (CVAFS) following US EPA method 1631. Brominemonochloride 162 (0.2% v/v; BrCl; Brooks Rand) was added <5 hours after sampling to preserve and completely 163 extract complexed Hg. Hydroxylamine hydrochloride (0.1% v/v; Brooks Rand) was added to 164 samples ~0.5 h prior to analysis to quench excess anions. Sample aliquots (100 mL) were poured 165 into a sparging flask, and tin chloride reductant (20% w/v; 100 µL; Brooks Rand) was added 166 before closing. The sample was purged with N_2 (150 ml/min; trace metal grade) onto a gold-167 coated bead trap for 10 min. The gold trap was then removed and placed on a TDM-II (Brooks 168 Rand) instrument for desorption and CVAFS (Model-III; Brooks Rand). Triplicates were 169 measured on select samples yielding a relative standard deviation (RSD) of <4.5% (LoD = 0.02 170 pM). Quantification and detection were verified with ERM-CA400 reference seawater, and was 171 ~95% of accepted recovery.

172 Dissolved MeHg species were analyzed following a direct ethylation method (Munson et 173 al., 2014; US EPA method 1630). Briefly, acidified 50 mL sample aliquots were poured into the 174 sparging flask with ascorbic acid (2.5% w/v; 200 µL; Fischer), neutralized using 8 M potassium 175 hydroxide (KOH; 1.8 mL; Fischer), and adjusted to pH 4.9 with a 4 M ammonium acetate buffer 176 (~860 μ L). Sodium tetraethylborate (TEB; 100 μ L; 1% w/v; Strem chemicals 98%) was added to 177 each sparging flask, which was immediately closed tightly and allowed to react for 10 min. 178 Volatile ethyl derivates were then purged for 18 min onto a Tenax trap using N_2 (150 ml/min; 179 trace-metal grade), and dried offline under N_2 for 5 min (~50 ml/min). The Tenex trap was 180 removed and placed on the TDM-II for thermal desorption of ethylated Hg derivatives, then 181 separated by isothermal gas chromatography (GC) and detected by CVAFS on the Model-III. 182 Select samples were analyzed multiple times, yielding an RSD <9.2% (LoD = 3.4 fM).

184 2.3 Sediment Analysis

185 Sediment samples were freeze dried and homogenized via milling prior to analysis. Total 186 Hg in the sediments were analyzed using an Advanced Mercury Analyzer instrument (AMA254) 187 at the Mediterranean Institute of Oceanography (MIO). The AMA254 works by thermal 188 decomposition and atomic adsorption spectrometry. Quality assurance was validated with 189 analysis of blanks and certified reference materials (CRM; MESS-4, within >81% accepted 190 range) at the start and finish of each run, in addition to ~every 10 samples. Duplicates or 191 triplicates were analyzed for each sample and RSD was <9.6%. 192 Sediment MeHg analysis was completed using a MERX-M (Brooks Rand) at MIO. First, 193 a sample aliquot (between ~400-1200 mg) was carefully weighed into an acid cleaned glass tube. 194 Next, nitric acid (HNO₃; 5 mL) was added to the tube, which was then placed in an 80° C oven to 195 digest for 2 h. An aliquot of the digested sample was pipetted into fresh acid cleaned sample 196 flasks containing deionized water (MQ, Millipore), then adjusted to pH 4.9 using acetate buffer 197 (1.1 mL) and filled completely with MQ. The TEB (10 µL) was added to each sample and tightly 198 sealed prior to analysis. The CRM IAEA-456 was digested and analyzed concurrently with the 199 samples to verify MeHg recovery, and measured concentrations were within the accepted range 200 (Vassileva et al., 2018). Information about ancillary water and sediment methods (dissolved

201 organic carbon (DOC), nutrients and organic matter) are available in SI.

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203 2.4 Mercury Sediment-water Exchange Experiment

204 Cores for sediment water exchange (flux) experiments were sealed using fitted caps for 205 protection against contamination and to prevent gas exchange. Caps provided continuous 206 overlying water mixing, though were briefly opened during sampling. Cores were held to ~19-207 20°C and protected from most light during the experiment. Samples for DOC and total dissolved

Hg and MeHg were siphoned from overlying core water with an acid cleaned syringe, then
filtered, preserved and analyzed as noted above and in SI. Each core was sampled 5 times over a
period of 42 h. Oxygen saturation and temperature were measured and tracked at each sampling
point, and remained relatively constant. Surface sediment (0-2 cm) from each core was sectioned
off immediately after draining the core at the end of the experiment for Hg, MeHg and organic
characteristics, and analyzed as stated.

Following overlying water sampling at each time point, this amount (~350 mL) was replaced with water collected from depth at the corresponding site in KB in order to keep the volume consistent. Discharge of Hg and MeHg release were calculated from the averaged linear regression slope of the Hg species concentration change over time (see SI for equations), then averaged to obtain a general flux for each core. Any difference in Hg and MeHg concentrations for replacement water was considered for the calculations. Calculations were normalized to the approximate core water volume (3740 cm³).

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- 223 **3. Results & Discussion**
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225 3.1 Sediment Hg Species

226 Sediment Hg and MeHg concentrations displayed a wide spread among sites (Figure 2).

227 Control stations (CR) acting as background, had the lowest Hg concentrations, ranging from ~2.4

to 59.3 ng/g Hg (average 14 ± 18 ng/g), compared to DN which ranged between ~2.7 - 137.5

229 ng/g (average 47 ± 46 ng/g). At the DN location sediments were collected both inside and

- 230 outside the reported historic training area to allow comparisons with other nearshore
- 231 measurements, and showed a range consistent with overall sediment characteristics in KB (SI;

- Table S1). Sediments from KH had the highest Hg concentrations, revealing a greater average of
- 233 124.5 \pm 76 ng/g Hg, and larger range of ~12 to 237.8 ng/g Hg. Sediment MeHg concentrations
- showed less variability between sites, with average values of $6.1 \pm 4 \text{ pg/g}$ for CR, $12 \pm 5 \text{ pg/g}$ for
- 235 DN, and 18.8 ± 7 pg/g for KH. The MeHg concentrations at KH were highest and ranged
- between 9 to 30 pg/g (Figure 2; bottom). Notably, sediment %MeHg (MeHg/Hg) levels were all
- <0.6% (SI; Table S1), with lowest %MeHg found at KH (0.03 ± 0.02%). All sites were
- significantly different for Hg (p=<0.0001, n=61, ANOVA) and strongly different for MeHg
- 239 (p=0.0001, n=33, ANOVA). Overall KH sediments were predominantly higher in Hg and MeHg
- 240 (Figure 2), and sediments between sites displayed notable heterogeneity compared to the
- 241 consistency of water column observations (see section 3.3).
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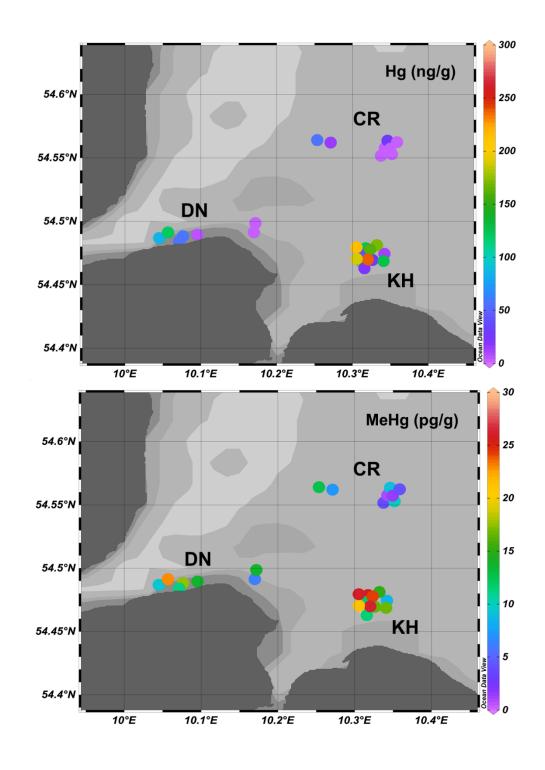


Figure 2. Mercury (Hg [ng/g] dry weight; top) and methylmercury (MeHg [pg/g] dry weight;
bottom) concentrations in sediments collected within Dänisch Nienhof (DN), munition dump site
Kolberger Heide (KH) and background control sites (CR).

251	Organic parameters (nitrogen content by percent weight: N % wt, sulfur content: S % wt,
252	organic carbon: C-org, molar ratio: [C/N], total carbon: TC %wt) facilitated us to resolve some
253	associations among sites. There were clear correlations between Hg concentrations for sites and
254	all analyzed organic matter parameters (Table 1). Organic content was highest and most variable
255	for KH, followed by intermediate levels at DN and lowest amounts found in CR sites (SI; Table
256	S1). The TC levels were 3.47 \pm 2.2% at KH and 2.49 \pm 1.7% for DN, with lowest TC of 0.71 \pm
257	0.9% in CR sites. Overall average sediment S content was $0.4 \pm 0.4\%$, with highest levels found
258	at KH (0.61 \pm 0.4%), compared to DN (0.34 \pm 0.2%) and CR (0.12 \pm 0.2%). Significant
259	relationships were observed between nearly all organic matter parameters and MeHg for KH
260	stations (Table 1). There were also significant relationships between MeHg and organic elements
261	for the overall dataset as well as the CR sites (excluding [C/N]). Conversely, no significant
262	relationships were present for DN stations between any organic matter parameters and Hg or
263	MeHg. But there were large deviations in organic matter levels, and ranges exhibited much
264	overlap for DN and KH (SI; Table S1).
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Table 1. Regression coefficients $(r^2, n=29)$ between Hg and MeHg and organic matter

parameters (nitrogen content by weight: N % wt; total carbon: TC % wt; sulfur content: S % wt;

- organic carbon: C-org; and molar ratio: [C/N]). Associations are noted for the overall sediments,
- control sites (CR; n=8), Dänisch Nienhof (DN; n=8) and Kolberger Heide (KH; n=13).
- 279

	Organic				
	parameter	overall	CR	DN	КН
Hg	N %wt	0.490	0.987	0.446	0.623
		p=<0.001	p=<0.001	p=0.101	p=0.001
Hg	TC %wt	0.502	0.988	0.529	0.648
		p=<0.001	p=<0.001	p=0.063	p=0.001
Hg	S %wt	0.538	0.983	0.374	0.689
		p=<0.001	p=<0.001	p=0.144	p=<0.001
Hg	C-org	0.504	0.988	0.429	0.647
		p=<0.001	p=<0.001	p=0.109	p=<0.001
Hg	[C/N]	0.383	0.779	0.023	0.361
		p=0.0001	p=0.003	p=0.743	p=0.029
MeHg	N %wt	0.489	0.566	0.266	0.426
		p=<0.001	p=0.059	p=0.067	p=0.001
MeHg	TC %wt	0.492	0.553	0.258	0.429
		p=<0.001	p=0.037	p=0.058	p=0.001
MeHg	S %wt	0.486	0.543	0.303	0.386
		p=<0.001	p=0.025	p=0.060	p=0.001
MeHg	C-org	0.487	0.561	0.243	0.410
		p=<0.001	p=0.028	p=0.064	p=0.001
MeHg	[C/N]	0.452	0.656	0.300	0.210
		p=0.038	p=0.153	p=0.120	p=0.624

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282 Sediments are a long-term repository for adsorbed contaminants, and may form a legacy 283 pollution source which can release Hg species once disturbed. Mercury and MeHg transfer from 284 sediment into the water column may occur through passive diffusion, advection and/or 285 resuspension (Bloom et al., 1999). Reported preindustrial Hg concentrations in Baltic Sea 286 surface sediments range between <20 to 40 ng/g (Leipe et al., 2013). Whereas modern sediment 287 Hg concentrations typically extend between <20 to 350 ng/g (Uscinowicz et al., 2011; Siedlewicz 288 et al., 2020; Kwasigroch et al., 2021), with higher levels associated to pollution sources, thereby 289 including munitions.

290 There is a large variety of anthropogenic Hg sources which contributes to watersheds and 291 coastal sediments, incorporating direct inputs from local industries including coal combustion 292 and waste incineration (van Velzen et al., 2002; Beldowska et al., 2014). Dating of Baltic Sea 293 sediments by Leipe et al. (2013) indicated that Hg values greatly increased around the mid-1970s. 294 A specific Hg point source derived from isotopic ratios analysis was not noticeable. However, 295 given that there was a coal fired power plant operating on the outskirts of Kiel (switched to 296 natural gas in 2020), it is expected that some Hg within the Bay results from energy production. 297 Yet it is unlikely that atmospheric Hg deposition from fossil fuel combustion would occur 298 specifically in sediments only around KH and less so at DN or CR sites. Both DN and KH are 299 located at the Kiel fjord outlet, and subjected to nearshore land runoff or other coastal 300 anthropogenic Hg sources. Visually the DN site exhibited a similar sediment consistency to KH. 301 The CR and DN sites have muddy as well as mixed sand sediments, while KH was muddy and 302 more organic with several samples containing sand in the mix. Hence, sediment basis and 303 organic matter content are important, but not the only explanation for differences in Hg and 304 MeHg concentration between KH and CR or DN. Orani et al (2020) documented sedimentary 305 Hg enrichments occurring during the period of 1917-1970 in KB. Notably, this time period also 306 corresponded with both WWI and WWII, during which munitions would have been 307 predominantly deployed, exploded and eventually corroded.

Excess Hg in some KH sediment can likely be attributed to the degradation and dissolution of WW munitions containing HgFu. It has been reported that HgFu rapidly dissolves into surrounding seawater upon contact (Gosnell et al., 2022). Mercury readily adheres to sediment and resuspended particles and thus would deposit in nearby sediments (Bloom et al., 1999; Ulrich et al., 2001). Thus, it is feasible that any release and deposition in sediments of Hg derived from HgFu would remain close to the munition source under typical conditions.

314 Beldowski et al (2019) proposed that dumped conventional munitions from WWII represent a 315 distinctive source of Hg for the Baltic Sea. In their study the highest Hg concentration observed 316 in the vicinity of ammunition was 322 ng/g, in agreement with the upper range of reported Baltic 317 observations of 300 ng/g (HELCOM, 2010). Comparatively, sediment Hg concentrations from 318 around the Bornholm Deep chemical munition dump site in the Baltic Sea ranged between 34 to 319 91.7 ng/g Hg (Beldowski et al., 2019), whereas 500 ng/g Hg has been reported for the Gotland 320 Deep munition dumpsite (Uscinowicz et al., 2011). Enhanced sediment Hg concentrations in this 321 study (>125 ng/g) were found only at the KH munition dump site.

322 Multibeam measurements in the area of our study allowed quantification and mapping of 323 munitions (Kampmeier et al., 2020). Geophysical observations continue to reveal anomalies 324 which are indicative of munitions (M. Kampmeier, personal communication). Unfortunately, due 325 to safety concerns, we were unable to sample directly below munitions or report coordinates 326 where anomalies reside in the KB area. Three sediment stations which were sampled close to a 327 geophysical abnormality had comparatively higher Hg concentrations: K6 (138 ng/g) and K7 328 (137 ng/g), whereas the third (K15) yielded 160 ng/g. Two of the 3 stations also had higher 329 MeHg concentrations: K15 (26.2 pg/g), and K6 (25.5 pg/g), though K7 was lower at 12.5 pg/g, 330 which was close to the KB average $(14.5 \pm 8 \text{ pg/g})$.

Methylmercury in sediments was spatially variable, but within the range of reported concentrations (Beldowski et al., 2019; Siedlewicz et al., 2020). However, Beldowski et al. (2019) reported higher MeHg concentrations in some sediments near KH than were observed in our study (e.g. <650 pg/g), yet did not directly link elevated MeHg to munitions. The methylation of Hg within sediments depends on a range of factors, including sediment composition (i.e. grain size), as well as ecological, physical and chemical properties, typically governed by organic matter, oxygen and S concentrations (Bloom et al., 1999; Boening, 2000;

Bravo and Cosio, 2020). Beldowski et al (2014) noted that gradients in sediment properties
influenced discrepancies in MeHg in sediment for the Gulf of Gdansk, located off Poland in the
southern Baltic.

341 It appears that some of the significantly elevated concentrations of Hg observed in KH 342 sediment are resulting from the release of WW munition derived HgFu. Enhanced organic 343 material concentrations are favorable to consolidating Hg within sediments and facilitate to keep 344 Hg proximate to where it was released, likely resulting in overall higher Hg around KH. It is 345 possible that sediments around DN harbors some WW residues considering the higher Hg 346 compared to CR sites. However, organic matter concentrations in DN sediments were lower and 347 less favorable to storage of Hg compared to KH. Furthermore, degrading munitions at the KH 348 dumpsite continues to supply Hg, whereas DN levels are more related to historic fallout, 349 background or alternative sources.

350

351 **3.2 Mercury Fluxes from Sediments**

352 There were overall no pronounced differences between sediment to water exchange fluxes 353 of Hg for the CR and DN sites (Figure 3; Table 2). Most cores show a low Hg release over time (<0.5 nmol m⁻² d⁻¹). In contrast, both FK2 cores from KH had considerably higher overall Hg 354 fluxes (>2 nmol m⁻² d⁻¹), matching enhanced concentrations of Hg found in sediment and 355 356 overlying waters (Table 2). Both FD1 cores from DH also showed a positive Hg flux, and 357 overlying water concentrations were higher at the incubation experiments end, however sediment 358 Hg concentrations were not markedly higher, and their variability $(\pm SD)$ likely negated any 359 positive output. The FK1 cores displayed high sediment concentrations yet did not have 360 remarkably high Hg fluxes. Several cores exhibited negative flux rates, indicating Hg incursion 361 instead of release from sediment.

362	Results for MeHg fluxes derived from core incubations were different to those for Hg.
363	The FK1 cores held high sediment MeHg concentrations, yet had a lower MeHg flux with greater
364	spread than FK2 cores (Table 2). The FD1-2 core exhibited both high MeHg and Hg fluxes from
365	sediment, although the associated FD1-1 core had a negative MeHg flux (and higher \pm SD). Yet
366	the large standard deviations for both FD1 cores encompass both outputs. The FK2 cores
367	provided substantial MeHg release into the overlying waters. Both FK2 cores yielded MeHg flux
368	rates that were strikingly higher than for all other cores and sites (>400 pmol m ⁻² d ⁻¹ ; Table 2),
369	even considering the high variation. There were also quite enhanced MeHg concentrations found
370	in overlying core waters, with levels up to 1000-fold higher than others (>2000 fM; Figure 3 top).
371	

Table 2. Observed sediment concentrations for Hg and MeHg, and %MeHg, total carbon (TC)
and sulfur (S) in flux core samples for CR (FC1, FC2), and duplicate cores for KH (FK1, FK2)
and DN (FD1, FD2) stations (see SI; Figure S2). Average calculated (flux) sediment-water
exchange rates (± SD) for the experiment duration are reported for Hg and MeHg for each core.

Site core ID	Hg [ng/g]	MeHg [pg/g]	%MeHg	TC [% wt.]	S [% wt.]	Hg flux [nmol m ⁻² d ⁻¹]	MeHg flux [pmol m ⁻² d ⁻¹]
FC1	2.45	1.72	0.08	0.13	0.02	-0.428 ± 2.9	4.523 ± 19.9
FC2	36.99	15.17	0.04	1.85	0.35	0.393 ± 2	14.369 ± 17.7
FD1-1	38.91	23.19	0.06	2.07	0.31	-0.013 ± 1.5	-14.597 ± 34.7
FD1-2	37.91	13.55	0.04	1.76	0.22	1.962 ± 1.5	26.942 ± 22.4
FD2-1	83.32	14.94	0.02	4.46	0.89	1.209 ± 4.2	-5.618 ± 17.6
FD2-2	81.49	8.28	0.01	4.46	0.87	-0.095 ± 3.5	-7.675 ± 29.1
FK1-1	105.09	46.77	0.04	4.26	0.79	0.131 ± 2.4	6.604 ± 76.6
FK1-2	179.27	66.61	0.04	2.53	0.46	0.154 ± 0.6	16.633 ± 35.4
FK2-1	212.57	42.97	0.02	5.90	1.11	2.979 ± 1.5	934.18 ± 580.4
FK2-2	253.54	28.73	0.01	5.79	1.05	2.828 ± 0.4	440.71 ± 669.1

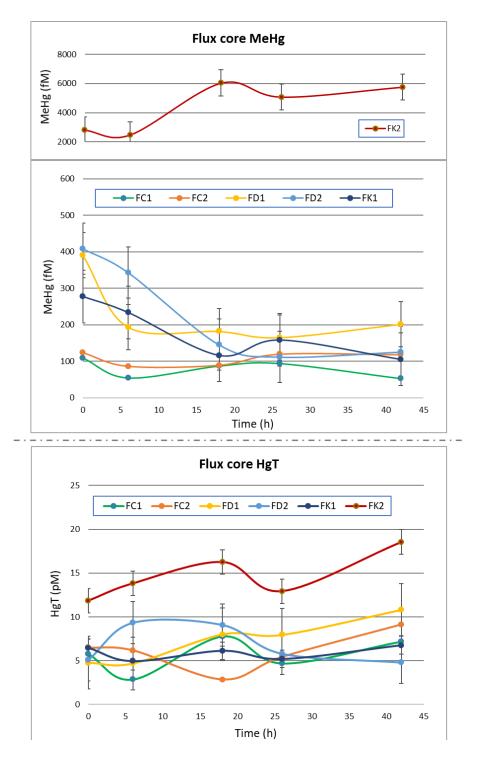


Figure 3. Observed concentration variations over time of Hg (pM; bottom) and MeHg (fM;
middle) in overlying core waters for CR (FC1, FC2), DN (FD1, FD2) and KH (FK1, FK2) core
stations (SI; Figure S1). Duplicates were collected at KH and DN sites, and are presented as
average (±SD) concentration. The FK2 MeHg concentrations are plotted separate (fM: top) as
they were quite excessive.

391

392	Methylating bacteria typically increase their activity and MeHg release during warmer
393	summer months (Ullrich et al., 2001; Gosnell et al., 2016; Bravo and Cosio, 2020), and flux cores
394	were collected in July when Hg methylation theoretically is higher. It is feasible that the first
395	time point is not accurate, as waters measured then had been sitting in the dark cores during
396	transport and setup in the lab (>14 h), and thus likely contained an unrealistic baseline for MeHg.
397	Subsequently, MeHg is unstable, and will rapidly demethylate naturally and via photoreduction
398	processes (Costa and Liss, 2000; Ullrich et al., 2001; Luo et al., 2020). This would explain the
399	comparably steep drop in MeHg levels after the first time point in the flux core experiment.
400	Accordingly, MeHg sediment water exchange flux rates are only reported for the times after 6 h
401	(Table 2), as exchange had stabilized. Sediment methylation rates are usually calculated for 2 h
402	as demethylation typically overrides methylation over longer periods (Hintermann et al., 2000).
403	Hence MeHg demethylation in ambient overlying core water was greater or consistent with what
404	could be resupplied via sediment efflux. This is evident by the relatively consistent MeHg
405	concentrations (considering SD) measured in core waters over the experiment duration (Figure
406	3). Several cores had negative fluxes, indicating MeHg demethylation or particle adsorption and
407	deposition (i.e. onto sediments). Yet enhanced MeHg production and higher Hg species fluxes
408	were observed at site FK2. Given the variability in sediment water exchange rates for most of the
409	cores it is evident that only select KH sediments transferred Hg and MeHg into overlying waters.
410	The methylation process can be influenced by organic matter elemental composition, and
411	increased microbial activity might likewise be driven by organic matter abundance and lability
412	(Bravo and Cosio, 2020; Capo et al., 2022). A minor association with C-org was observed for the
413	MeHg flux rates (r^2 =0.449, p=0.033, n=10), however not for Hg flux rates (r^2 =0.311, p=0.093,

414 n=10) for the sediment cores. The Hg flux rate was furthermore not related to S content 415 $(r^2=0.255, p=0.136, n=10)$. But there was some significance between S content and MeHg flux 416 rate $(r^2=0.406, p=0.047, n=10)$. This suggests that the degree of MeHg formation and output for 417 flux cores could have been in part controlled by organic matter and S content of sediment, while 418 Hg release was independent of those factors. Thus, if there is a sufficient pool of Hg, then it is 419 possible for local sulfur reducing bacteria (SRB) and other sediment microbes to transform and 420 then facilitate transfer of MeHg into overlying waters.

421 Methylmercury in flux core sediments was spatially variable, though within the range of 422 site values as well as other reported concentrations (Beldowski et al., 2019; Siedlewicz et al., 423 2020). It was surprising that excessive MeHg sediment concentrations were not measured in FK2 424 cores considering the higher MeHg and Hg fluxes. Moreover, the MeHg as well as %MeHg was 425 higher in FK1 core sediments. Accordingly, the high MeHg discharge recorded in FK2 cores 426 could explain the low levels of sediment MeHg and %MeHg observed. Specifically, if MeHg is 427 produced and released at high rates, then the MeHg would be low in sediment due to its transfer 428 instead to overlying waters. There is evidence of this occurring in estuarine systems (Gosnell et 429 al., 2016). Once released into the shallow water column and subjected to UV light MeHg can be 430 rapidly demethylated back to Hg (Costa and Liss, 2000; Luo et al., 2020). Likewise, even if 431 MeHg is supplied into the water column via sediment release, then it would not necessarily be 432 measurable at high levels for long.

Dissolved organic matter (DOM) and DOC can influence Hg speciation, methylation and
photoreduction within marine and fresh waters and sediments (Ullrich et al., 2001; Mason et al.,
2006; Bravo et al., 2018; Lou et al., 2020). The DOC concentrations were higher in covering
waters from core experiments compared to those measured in the water column. The FK2 core
waters contained the highest DOC at ~933 µM, whereas FD1 had 809 µM and FD2 had 883 µM.

438 DOC concentrations for control site (FC1 and FC2) and FK1 cores were ~698 μ M (± 186). Thus, 439 higher Hg and MeHg levels for the FK2 core waters were associated with higher DOC in 440 covering waters. However, DOC concentrations were not disproportionate relative to other cores 441 as to form a dominat factor towards enhanced Hg species levels in overlying waters of the FK2 442 core. Furthermore, DOC concentrations did not selectively change during the experiment. 443 Under low oxygen conditions in sediments Hg can be transformed into MeHg by SRB, 444 and can furthermore bind to sulfide which is produced from sulfate (King et al., 2000; Ma et al., 445 2019; Bravo and Cosio, 2020; Capo et al., 2022). Oxygen saturation had decreased by ~10% in 446 all overlying core waters by the end of the experiment, yet did not reach hypoxic or anoxic levels. 447 Therefore, it is not likely that Hg speciation within individual core waters was influenced by 448 oxygen state during experiments, especially as the experiment was not under completely closed 449 conditions. Yet even if dissolved Hg or MeHg is released by sediments, the natural oxidative 450 state within the shallow and well mixed water column and reactivity of ambient particles ensues 451 that most MeHg would quickly demethylate and the Hg will redeposit back into sediments.

452

453 3.3 Mercury in the Water Column

454 Stations in Kiel Bay feature shallow and well mixed waters, resulting in no pronounced 455 temperature and salinity variations in depth profiles. There was a slight increase for salinity and 456 decrease in temperature and oxygen saturation with depth for CR stations in May, as is consistent 457 with offshore observations (SI; Figure S3). Overall vertical nutrient profiles did not show major 458 deviations with depth or amongst sites for a given month or season. (See SI for more detail on 459 measured nutrients.)

460 The Hg concentrations were not significantly higher at KH and DN compared to the outer 461 CR sites, with most observations below 2 pM (Figure 4; SI, Figure S4). These values also reside within the reported range of the waters collected directly in Kiel Fjord as well as our
measurements further offshore along the German Baltic coast (0.8 - 2.1 pM; SI, Figure S1 &
Table S2), and those reported for nearby coastal and Baltic waters (Soerensen et al., 2016; Kuss
et al., 2017).

466 The MeHg concentrations were relatively uniform with depth for stations throughout KB 467 (SI; Figure S4 & Table S2), although some shallow stations at DN had slightly higher 468 concentrations (Figure 4). There was not strong evidence of elevated MeHg concentrations in the 469 water column (<6 m) following release from shallow sediments, as MeHg concentrations in 470 overlying waters of flux core experiments were much higher than measured at all sites (Figure 3). 471 Average water column MeHg concentrations in May were 24 ± 9 fM (CR), 28.7 ± 13 fM (DN) 472 and 24.5 ± 12 fM (KH), hence low and typical for Baltic and coastal waters. Soerensen et al 473 (2016) reported MeHg concentrations of 1500 fM for deep waters in Gotland basin off eastern 474 Sweden, however noted the rest of the south Baltic did not exceed ~100 fM. Overall, MeHg was 475 not enhanced at KH or DN or overall in waters of KB compared to other coastal regions, and was 476 consistent with MeHg measurements in the south Baltic (Soerensen et al., 2016; Kuss et al., 477 2017). Dissolved %MeHg did not exceed 6% at any station, and overall KB levels were 2.7 \pm 478 0.6% (December), $2.5 \pm 1.5\%$ (May) and $0.8 \pm 0.4\%$ (July). 479

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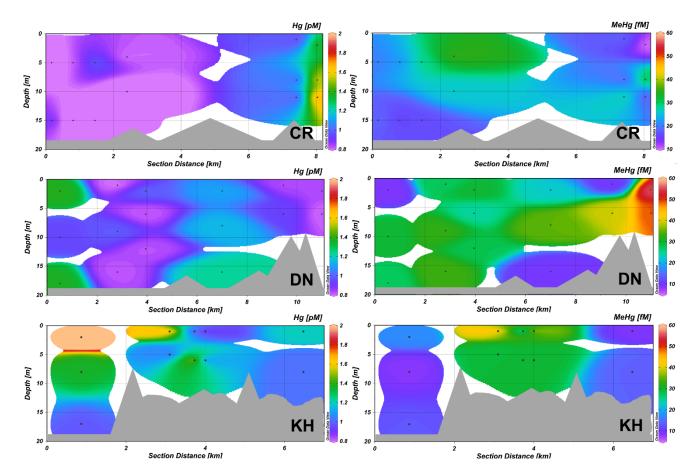
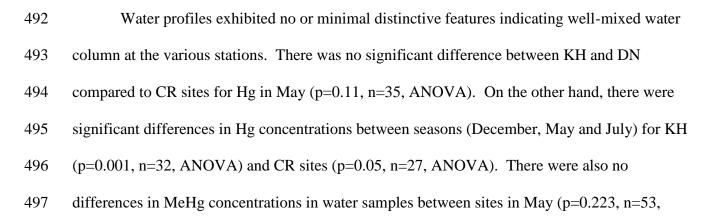




Figure 4. Water concentrations of total mercury (Hg; pM) and methylmercury (MeHg; fM) for the three sites in Kiel Bay for May. Total Hg profiles are on the left while MeHg is on the right. Sites displayed are grouped outskirts of Kiel Bay (CR; top), Dänisch Nienhof (DN; middle) is a coastal transect, and circling the munition dump site Kolberger Heide (KH; bottom). The direction for each section distance is specified on the map (Figure 1). The deepest sample for each station was collected ~1-2 m above the bottom, thus topography is approximate.



ANOVA), but strong seasonal differences were observed for both CR (p=0.001, n=27, ANOVA)
as well as KH sites (p=0.024, n=30, ANOVA). Considering seasonal differences, concentrations
were highest in July (Hg) or May (MeHg) for all sites. However average %MeHg values for all
sites were lowest in July (<1%; SI, Table S2). Thus, extensive sunlight radiation likely facilitated
photoreduction of MeHg in shallow waters during summertime (Costa and Liss, 2000; Luo et al.,
2020).

504 Some Baltic Sea regions exhibit enhanced concentrations of Hg (i.e. >4 pM) and MeHg 505 within its brackish waters (Pempkowiak et al., 1998; Elmgren, 2001; Beldowski et al., 2014; 506 Gubelit et al., 2016; Soerensen et al., 2016; Kuss et al., 2017), but concentrations within KB were 507 not higher compared to other coastal waters. Kiel Bay supports an active industrial shipyard and 508 much merchant and military traffic, and thus has several prospective sources of anthropogenic Hg 509 (Kwasigroch et al., 2021). However, there were no observations of waters reaching what would 510 be considered contaminated levels for dissolved Hg and MeHg. Even the highest concentrations 511 at DN and KH did not exceed 55 fM MeHg or 2 pM Hg (Figure 4). Furthermore, data from KB 512 indicates a decreasing trend in Hg within biological tissues over the last 20 years (HELCOM, 513 2015). Consistent water column concentrations indicate no site-specific contamination of Hg and 514 MeHg emitting from WWII munitions, in contrast to the sediments. Likewise, higher or point 515 source specific fish contamination has not been associated with the WWII munition dump sites in 516 KB (Kammann et al., 2021).

517

518 3.4 Water Development in the southwest Baltic Sea

519 The Baltic Sea is a unique and important ecosystem incorporating an overall shallow 520 basin with a mean depth of 55 m and no permanent current structure. Water renewal from the 521 North Sea is relatively poor for the Baltic, as it enters only via scattered inlets flowing through

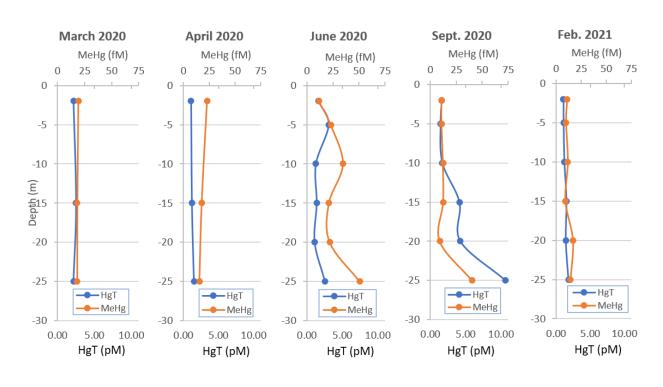
522 the southwest corner, yielding an overall low and fluctuating salinity. Marine waters moving into 523 KB originate from the northern Kattegat and North Sea (Stedmon et al., 2010), delivering one of 524 the smallest measured semi-diurnal tidal ranges (typically ~5-10 cm). Atmospheric and riverine 525 sources dominate aquatic Hg inputs to the Baltic Sea. Recent estimates indicate that rivers 526 introduce approximately 70% of Hg to the Baltic (Lilja et al., 2009; Beldowska et al., 2014; 527 HELCOM 2015), whereas the remaining 30% enters via erosion and atmospheric deposition 528 (HELCOM 2010; Leipe et al., 2013; Beldowski et al., 2014). Inputs are typically high 529 considering the historical and extensive use of coal as an energy source throughout Germany and 530 surrounding countries, which considerably contribute to atmospheric and depositional Hg levels. 531 River catchments with farmlands can also deliver high Hg inputs owing to a historical use of 532 fungicides associated with Hg (Beldowska et al., 2014). Accordingly, it is clear that the 533 dominant atmospheric and riverine Hg sources provide a homogeneous effect for Baltic Sea 534 waters. This would in turn conceal lesser point sources of Hg such as directly seeping out of 535 munitions at KH.

536 Consequently, it is likely that Hg species in the KB water column are more influenced by 537 seasonal factors (i.e. temperature or hypoxia) than proximity to underlying relic WW munitions. 538 To further investigate seasonal variations, water samples were collected from the nearby station 539 Boknis Eck, located outside Eckernförde Bay within the study area (Figure 1). Boknis Eck is one 540 of the oldest continuous monitoring stations for marine parameters worldwide, with approximate 541 monthly sampling since April 1957 (Lennartz, et al., 2014). Boknis Eck consistently experiences 542 seasonal anoxia during late summer/early fall, partially due to decreasing oxygen solubility with 543 increasing temperature, and enhanced respiration rates from reduced atmospheric oxygen supply 544 by ventilation due to water column stratification (Lennartz et al., 2014). Dissolved Hg and MeHg 545 samples were collected periodically at Boknis Eck during 2020-2021 in order to characterize any

546 seasonal impacts on Hg species and concentrations (Figure 5). Through spring the waters were 547 well mixed with no distinct profile features noted, and exhibited low Hg and MeHg as observed 548 for KB waters. However, Hg and MeHg concentrations increased in summer and autumn. The 549 MeHg was highest in June and Hg peaked in September at depth and coincided with recorded 550 anoxia and organic matter remineralization. The %MeHg at Boknis Eck was between 1-2% for 551 April and June, but <1% for other months. In winter, the Hg and MeHg decreased to low values 552 and the observed profile features dispersed. Hence, it is likely that waters in summer through to 553 September featured characteristics that facilitated methylation, such as eutrophication and 554 hypoxia, compared to spring or winter when enhanced mixing and oxygen renewal occur.

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557 558

Figure 5. Dissolved Hg (pM) and MeHg (fM) concentrations in several monthly profiles
collected at the monitoring station Boknis Eke during 2020-2021.

564	Baltic waters typically exhibit enhanced primary production and high concentrations of
565	freshwater derived marine and terrestrial DOM (Lennartz et al., 2014; Seidel et al., 2017). The
566	DOC concentrations did not differ between KH and CR or DN, measuring around 330 μM (± 77
567	μ M) for May and July. These values agree with the seasonal changes in DOC between ~200 –
568	380 μ M reported by Lodeiro et al (2021) for Boknis Eck. Thus, DOC concentrations are not a
569	prominent factor for different Hg levels for Boknis Eck, and overall relatively consistent within
570	KB.
571	Approximately 10% of the Baltic Sea has anoxic or hypoxic waters (Cartensen et al.,
572	2014), which can potentially lead to elevated MeHg concentrations. Soerensen et al (2016)
573	proposed that eutrophication and the ensuing anoxic bottom waters resulted in an up to 80-fold
574	increase in MeHg concentrations for Gotland Basin. This likely occurred at KB to a smaller

576 coinciding with the seasonal anoxia of late summer and autumn. As noted, SRB that methylate 577 Hg are more active, and hence methylate more Hg with warmer temperatures (King et al., 2000; 578 Gosnell et al., 2016; Ma et al., 2019; Bravo and Cosio, 2020; Capo et al., 2022). The KB water 579 column was not anoxic, but it is likely that the anoxic horizon in its sediments was shallower and 580 caused an elevated flux of MeHg to overlying waters. This was evident at the munition dump 581 KH considering the active FK2 flux cores had >4000 fM MeHg within the overlying water. 582 However overall the well-mixed and oxygenated water column dissipates and removes most 583 effluxes. Hence, though sediments harbor Hg from munition dumps and other anthropogenic 584 sources, it currently does not transmit enhanced fluxes into overlaying waters or provide a 585 distinctive higher water column concentration of Hg for KB residents.

588 4. Conclusion

589

590 This study observed high Hg concentrations in sediments of Kiel Bay (KB) and most 591 prominently around the munition dump site Kolberger Heide (KH). There were some elevated 592 Hg concentrations in sediments near Dänisch-Nienhof (DN), where munition deployment may 593 have delivered Hg during combat operations and training. But Hg levels in DN sediments are not 594 as high as those at KH, possibly reflecting background, or a historical burden by artillery sources 595 containing Hg rather than any new HgFu supplied from recent munition corrosion. Munitions are 596 only a notable source of Hg contamination when in direct vicinity of WWII ordnance. Enhanced 597 organic matter concentrations furthermore facilitated better storage of Hg species in KH 598 sediments compared to DN and CR. All the same, there was no clear evidence of sediment 599 MeHg which could be associated with munitions, and overall sediment MeHg and % MeHg were 600 low.

601 Sediment-water exchange core experiments suggest that sediment around KH could 602 provide elevated Hg and MeHg fluxes into overlying waters. However, the variations in Hg and 603 MeHg concentration concentrations over time and between cores indicated that higher levels 604 were not established in the open and well mixed oxygenated water column of KB. The 605 mechanism of release for possible munition derived Hg species from sediment was not assessed 606 in this study, thus this requires further exploration. But it is likely that sediments containing a 607 higher content of organic matter, such as those surrounding KH, could accumulate and release 608 more Hg and MeHg than sediments which are sandy or barren.

609 Our results indicate that munitions are not a noticeable source of Hg contamination to 610 waters of KB. These findings align with other observations indicting that fish found in KB were

611 not impacted by Hg sourced from the munition dump KH. Overall water column Hg and MeHg 612 values were relatively uniform throughout the region, and not higher within waters in the vicinity 613 of the munition dump site KH. Thus, whilst enhanced fluxes into overlying waters were 614 observed from FK2 cores, general removal and mixing processes in the water column resulted in 615 an absence of clear sediment source signatures at KH or in KB. There were minor seasonal 616 concentration variations for Hg and MeHg values, such as increased levels during the summer 617 season, and hence possible subsidiary changes associated with environmental parameters (e.g. 618 sunlight, oxygen or DOC). For example, water column %MeHg was highest in December and 619 lowest in July, which may be associated with longer days and enhanced sunlight duration, and 620 thus stronger MeHg photodegradation during summertime. However, above all for Kiel and 621 Baltic citizens, Hg and MeHg do not presently reach concerning or endangering concentrations in 622 waters overlying the resting grounds of historic WWs munitions.

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- 624

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