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

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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). Sediment-
42 water exchange experiments showed elevated Hg and MeHg fluxes (i.e. >400 pmol m⁻² d⁻¹
43 MeHg) at one KH location, however remaining cores had low to no Hg and MeHg output (<0 to
44 27 pmol m⁻² d⁻¹ MeHg). Thus, sediments in Kiel Bay proximate to WW munitions could harbor
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

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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
80 and Baltic Sea (Carton and Jagusiewicz, 2009). It is estimated that approximately 1.6×10^6 t of
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 (Gębka 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***

118 Seawater and sediment for Hg analysis were collected aboard the RV Littorina in KB,
119 southwest Baltic Sea (Figure 1). Seasonal field sampling (December, May and July) occurred
120 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 µm 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.

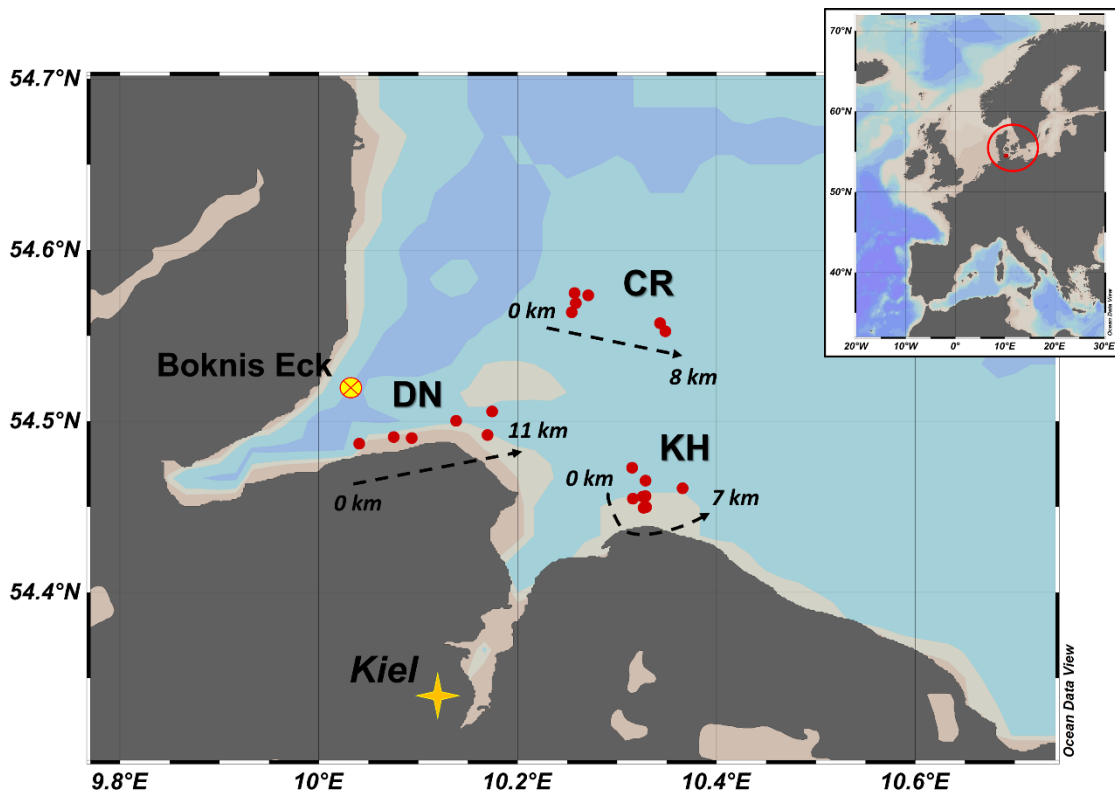
135 Surface sediment samples were obtained by box corer in areas corresponding to water
136 sampling. Sediment samples were selected to be visually uniform in their composition among
137 stations and sites, primarily of a muddy mix with limited sand. Some rocky and sandy sediments
138 areas in KB could 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

145 stations (e.g. FK1-1 and FK1-2 were one KH site), and one core was collected at two different
146 CR sites (FC1 and FC2). The FC1 core contained some sand, while FC2 and the rest were
147 composed of organics and muds. All cores were selected to be relatively consistent in sediment
148 amounts and overlying water levels.

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

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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 μ L; Brooks Rand) was added
166 before closing. The sample was purged with N₂ (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 μ L; 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 N₂ (150 ml/min;
179 trace-metal grade), and dried offline under N₂ for 5 min (~50 ml/min). The Tenax 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).

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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.

202

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

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

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

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223 **3. Results & Discussion**

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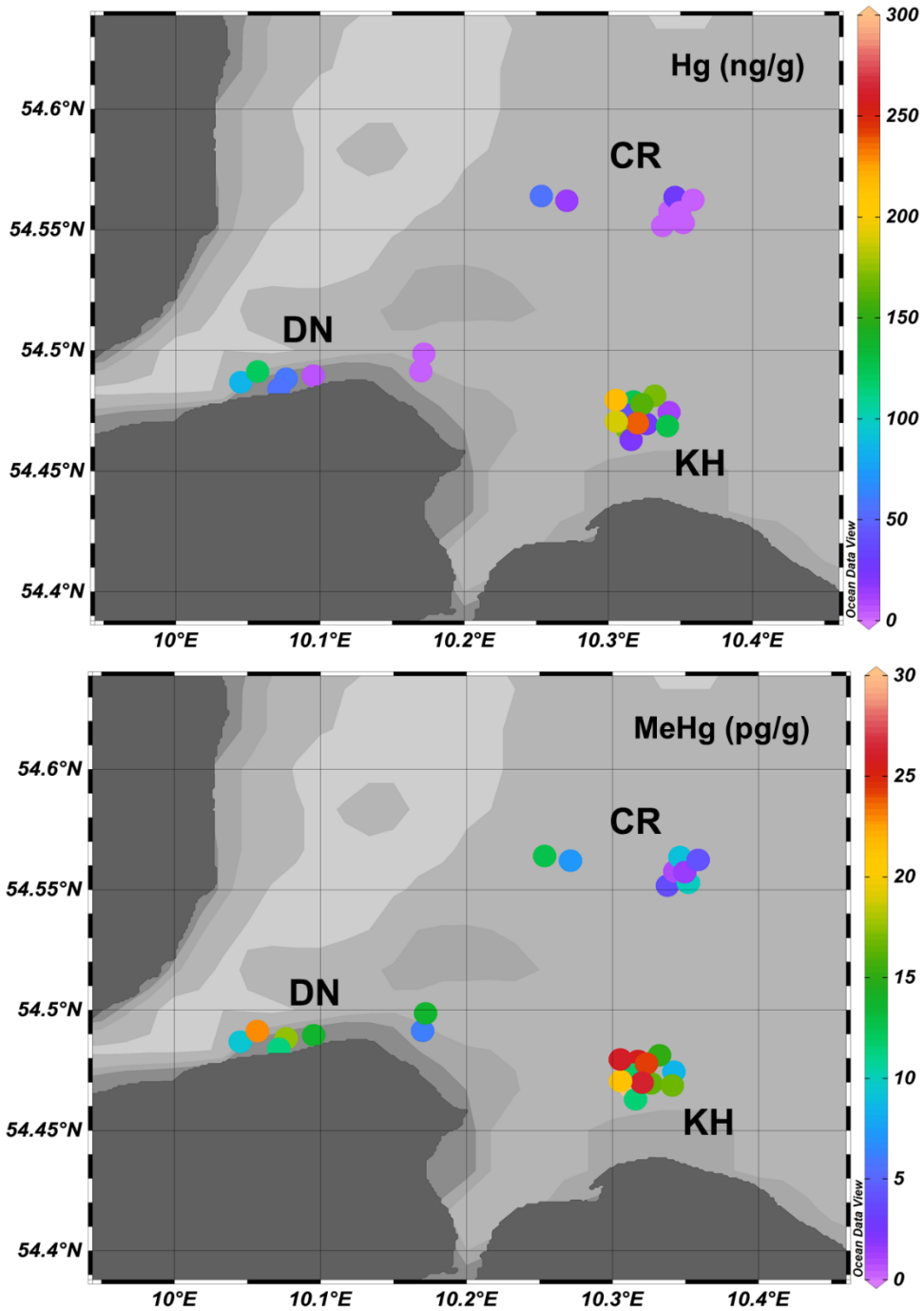
225 ***3.1 Sediment Hg Species***

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
228 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;

232 Table S1). Sediments from KH had the highest Hg concentrations, revealing a greater average of
233 124.5 ± 76 ng/g Hg, and larger range of ~12 to 237.8 ng/g Hg. Sediment MeHg concentrations
234 showed less variability between sites, with average values of 6.1 ± 4 pg/g for CR, 12 ± 5 pg/g for
235 DN, and 18.8 ± 7 pg/g for KH. The MeHg concentrations at KH were highest and ranged
236 between 9 to 30 pg/g (Figure 2; bottom). Notably, sediment %MeHg (MeHg/Hg) levels were all
237 <0.6% (SI; Table S1), with lowest %MeHg found at KH ($0.03 \pm 0.02\%$). All sites were
238 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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246 **Figure 2.** Mercury (Hg [ng/g] dry weight; top) and methylmercury (MeHg [pg/g] dry weight;
 247 bottom) concentrations in sediments collected within Dänisch Nienhof (DN), munition dump site
 248 Kolberger Heide (KH) and background control sites (CR).
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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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275 **Table 1.** Regression coefficients (r^2 , $n=29$) between Hg and MeHg and organic matter
 276 parameters (nitrogen content by weight: N %wt; total carbon: TC %wt; sulfur content: S %wt;
 277 organic carbon: C-org; and molar ratio: [C/N]). Associations are noted for the overall sediments,
 278 control sites (CR; $n=8$), Dänisch Nienhof (DN; $n=8$) and Kolberger Heide (KH; $n=13$).
 279

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

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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.

308 Excess Hg in some KH sediment can likely be attributed to the degradation and
309 dissolution of WW munitions containing HgFu. It has been reported that HgFu rapidly dissolves
310 into surrounding seawater upon contact (Gosnell et al., 2022). Mercury readily adheres to
311 sediment and resuspended particles and thus would deposit in nearby sediments (Bloom et al.,
312 1999; Ulrich et al., 2001). Thus, it is feasible that any release and deposition in sediments of Hg
313 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 ± 8 pg/g).

331 Methylmercury in sediments was spatially variable, but within the range of reported
332 concentrations (Beldowski et al., 2019; Siedlewicz et al., 2020). However, Beldowski et al.
333 (2019) reported higher MeHg concentrations in some sediments near KH than were observed in
334 our study (e.g. <650 pg/g), yet did not directly link elevated MeHg to munitions. The
335 methylation of Hg within sediments depends on a range of factors, including sediment
336 composition (i.e. grain size), as well as ecological, physical and chemical properties, typically
337 governed by organic matter, oxygen and S concentrations (Bloom et al., 1999; Boening, 2000;

338 Bravo and Cosio, 2020). Beldowski et al (2014) noted that gradients in sediment properties
339 influenced discrepancies in MeHg in sediment for the Gulf of Gdansk, located off Poland in the
340 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
354 ($<0.5 \text{ nmol m}^{-2} \text{ d}^{-1}$). In contrast, both FK2 cores from KH had considerably higher overall Hg
355 fluxes ($>2 \text{ nmol m}^{-2} \text{ d}^{-1}$), matching enhanced concentrations of Hg found in sediment and
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 ($\pm\text{SD}$) 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.

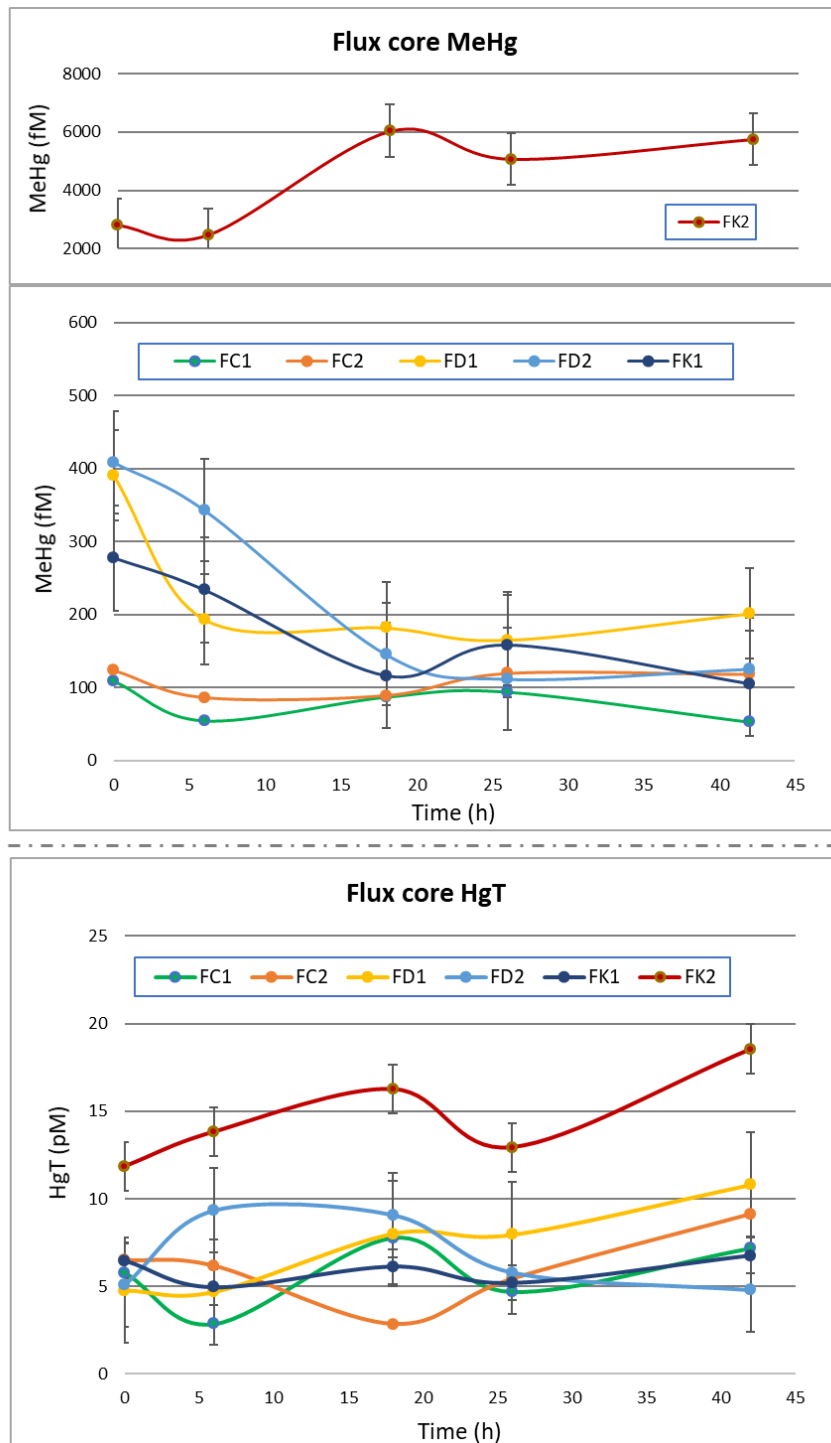
362 Results for MeHg fluxes derived from core incubations were different to those for Hg.
 363 The FK1 cores held high sediment MeHg concentrations, yet had a lower MeHg flux with greater
 364 spread than FK2 cores (Table 2). The FD1-2 core exhibited both high MeHg and Hg fluxes from
 365 sediment, although 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 ($>400 \text{ pmol m}^{-2} \text{ d}^{-1}$; 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 ($>2000 \text{ fM}$; Figure 3 top).
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373 **Table 2.** Observed sediment concentrations for Hg and MeHg, and %MeHg, total carbon (TC)
 374 and sulfur (S) in flux core samples for CR (FC1, FC2), and duplicate cores for KH (FK1, FK2)
 375 and DN (FD1, FD2) stations (see SI; Figure S2). Average calculated (flux) sediment-water
 376 exchange rates (\pm SD) for the experiment duration are reported for Hg and MeHg for each core.
 377

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 \pm 2.9	4.523 \pm 19.9
FC2	36.99	15.17	0.04	1.85	0.35	0.393 \pm 2	14.369 \pm 17.7
FD1-1	38.91	23.19	0.06	2.07	0.31	-0.013 \pm 1.5	-14.597 \pm 34.7
FD1-2	37.91	13.55	0.04	1.76	0.22	1.962 \pm 1.5	26.942 \pm 22.4
FD2-1	83.32	14.94	0.02	4.46	0.89	1.209 \pm 4.2	-5.618 \pm 17.6
FD2-2	81.49	8.28	0.01	4.46	0.87	-0.095 \pm 3.5	-7.675 \pm 29.1
FK1-1	105.09	46.77	0.04	4.26	0.79	0.131 \pm 2.4	6.604 \pm 76.6
FK1-2	179.27	66.61	0.04	2.53	0.46	0.154 \pm 0.6	16.633 \pm 35.4
FK2-1	212.57	42.97	0.02	5.90	1.11	2.979 \pm 1.5	934.18 \pm 580.4
FK2-2	253.54	28.73	0.01	5.79	1.05	2.828 \pm 0.4	440.71 \pm 669.1

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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 (\pm SD) concentration. The FK2 MeHg concentrations are plotted separate (fM: top) as they were quite excessive.

390
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.

433 Dissolved organic matter (DOM) and DOC can influence Hg speciation, methylation and
434 photoreduction within marine and fresh waters and sediments (Ullrich et al., 2001; Mason et al.,
435 2006; Bravo et al., 2018; Lou et al., 2020). The DOC concentrations were higher in covering
436 waters from core experiments compared to those measured in the water column. The FK2 core
437 waters contained the highest DOC at $\sim 933 \mu\text{M}$, whereas FD1 had $809 \mu\text{M}$ and FD2 had $883 \mu\text{M}$.

438 DOC concentrations for control site (FC1 and FC2) and FK1 cores were $\sim 698 \mu\text{M}$ (± 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 dominant 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 $\sim 10\%$ 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 ensures
451 that most MeHg would quickly demethylate and the Hg will redeposit back into sediments.

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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

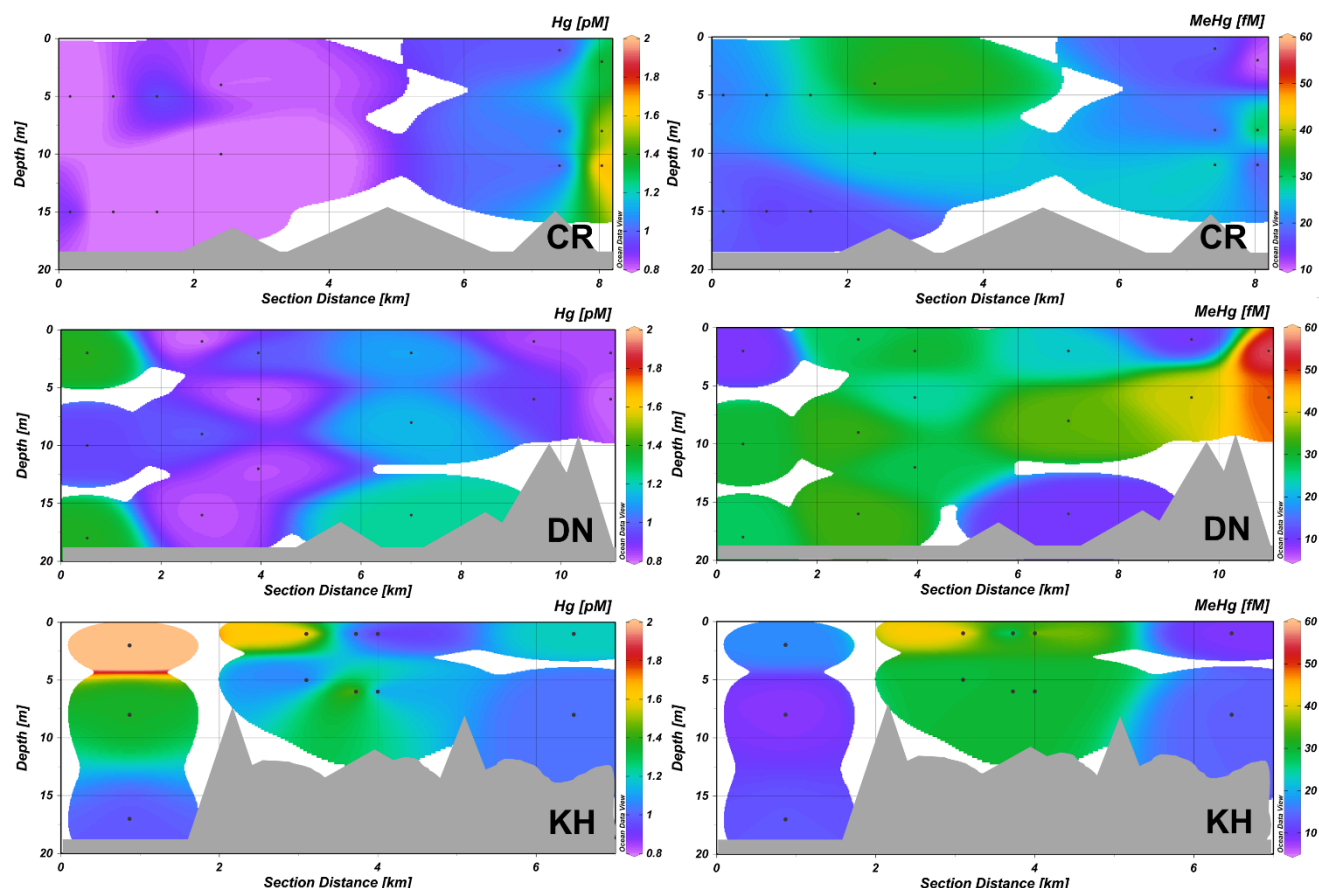
462 within the reported range of the waters collected directly in Kiel Fjord as well as our
463 measurements further offshore along the German Baltic coast (0.8 - 2.1 pM; SI, Figure S1 &
464 Table S2), and those reported for nearby coastal and Baltic waters (Soerensen et al., 2016; Kuss
465 et al., 2017).

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).

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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.

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Water profiles exhibited no or minimal distinctive features indicating well-mixed water column at the various stations. There was no significant difference between KH and DN compared to CR sites for Hg in May ($p=0.11$, $n=35$, ANOVA). On the other hand, there were significant differences in Hg concentrations between seasons (December, May and July) for KH ($p=0.001$, $n=32$, ANOVA) and CR sites ($p=0.05$, $n=27$, ANOVA). There were also no differences in MeHg concentrations in water samples between sites in May ($p=0.223$, $n=53$,

498 ANOVA), but strong seasonal differences were observed for both CR ($p=0.001$, $n=27$, ANOVA)
499 as well as KH sites ($p=0.024$, $n=30$, ANOVA). Considering seasonal differences, concentrations
500 were highest in July (Hg) or May (MeHg) for all sites. However average %MeHg values for all
501 sites were lowest in July ($<1\%$; SI, Table S2). Thus, extensive sunlight radiation likely facilitated
502 photoreduction of MeHg in shallow waters during summertime (Costa and Liss, 2000; Luo et al.,
503 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).

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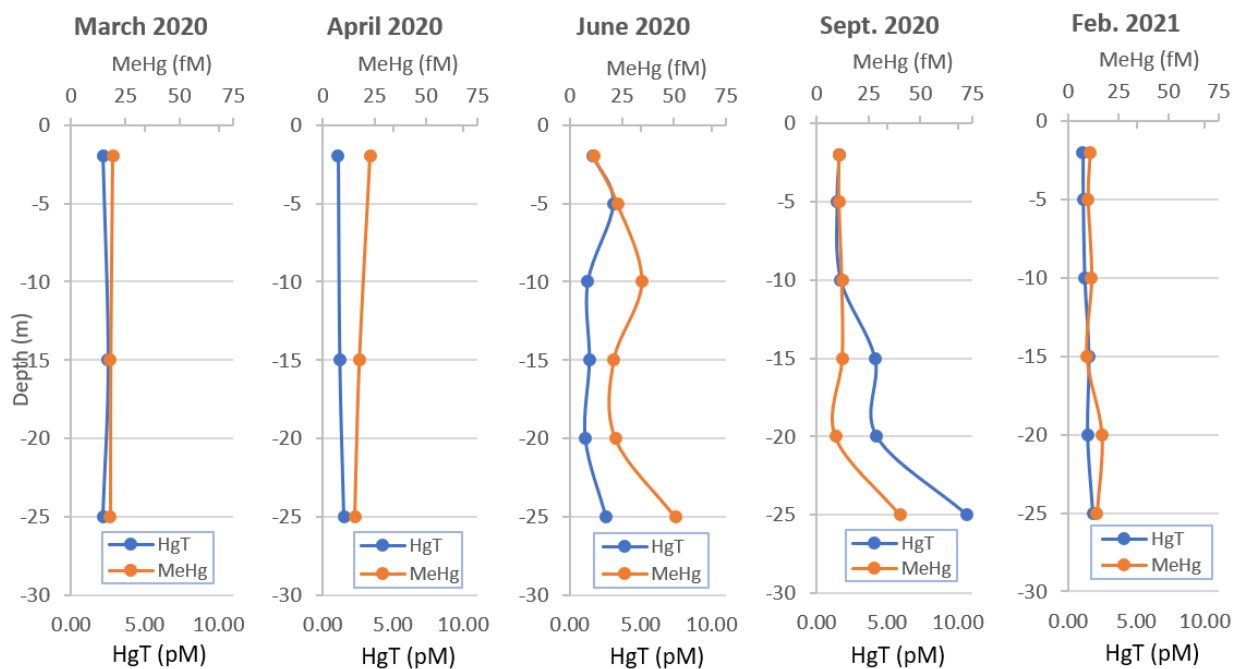
518 ***3.4 Water Development in the southwest Baltic Sea***

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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 559 **Figure 5.** Dissolved Hg (pM) and MeHg (fM) concentrations in several monthly profiles
 560 collected at the monitoring station Boknis Eke during 2020-2021.
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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 μM) for May and July. These values agree with the seasonal changes in DOC between $\sim 200 -$
568 $380 \mu\text{M}$ 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
575 extent as demonstrated at Boknis Eck, where MeHg concentrations increased in waters
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 $>4000 \text{ fM}$ 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.

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588 **4. Conclusion**

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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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637 **References**

638

639 Beck, A., Gledhill, M., Schlosser, C., Stamer, B., Böttcher, C., Sternhelm, J., Greinert, J.,
640 Achterberg, E.P. (2018). Spread, behavior and ecosystem consequences of conventional
641 munitions compounds in coastal marine waters. *Front. Mar. Sci.*, 5, 141.

642

643 Beldowska, M., Saniewska, D., Falkowska, L. (2014). Factors influencing variability of mercury
644 input to the southern Baltic Sea. *Marine Pollution Bulletin*, 86, pp. 283-290.

645

646 Beldowski, J., Miotk, M., Beldowska, M., Pempkowiak, J. (2014). Total, methyl and organic
647 mercury in sediments of the Southern Baltic Sea. *Marine Pollution Bulletin*, 87, pp. 388-395.

648

649 Beldowski, J., Szubska, M., Siedlewicz, G., Korejwo, E., Grabowski, M., Beldowska, M.,
650 Kwasigroch, U., Fabisiak, J., Lonska, E., Szala, M., Pempkowiak, J. (2019). Sea-dumped
651 ammunition as a possible source of mercury to the Baltic Sea Sediments. *Science of the Total*
652 *Environment*, 674, pp. 363-373.

653

654 Bloom, N., Gill, G., Cappellino, S., Dobbs, C., McShea, L., Driscoll, C., Mason, R., Rudd, J.
655 (1999). Speciation and Cycling of Mercury in Lavaca Bay, Texas, Sediments. *Environ Sci Tech*,
656 33, 1, pp. 7-13.

657

658 Boening, D.W. (2000). Ecological effects, transport and fate of mercury: a general review.
659 *Chemosphere*, 40, 1335-1351.

660

661 Bravo, A.G. *et al.*, (2018). The interplay between total mercury, methylmercury and dissolved
662 organic matter in fluvial systems: A latitudinal study across Europe, *Water Research*, 144, pp.
663 172-182.

664

665 Bravo, A. and Cosio, C. (2020). Biotic formation of methylmercury: A bio-physio-chemical
666 conundrum. *Limnology and Oceanography*, 65, pp. 1010-1027.

667

668 Böttcher, C., Knobloch, T., Rühl, N., Sternheim, J., Weinberg, I., Wichert, U., Wöhler, J. (2011).
669 Munitionsbelastung der deutschen Meersgewässer – Bestandsaufnahme und Empfehlungen
670 (stand 2011). Meersmuwelt Aktuell Nord- und Ostsee 2011-3. Rostock Bundesand für
671 Seeschiffahrt und Hydrographie (BSH), Hamburg.

672

673 Capo, E., Broman, E., Bonaglia, S., Bravo, A., Bertilsson, S., Soerensen, A., Pinhassi, J., Lundin,
674 D., Buck, M., Hall, P., Nascimento, F., Bjorn, E. (2022). Oxygen-deficient water zones in the
675 Baltic Sea promote uncharacterized Hg methylating microorganisms in underlying sediments.
676 *Limnology and Oceanography*, 67, pp. 135-146.

677

678 Carstensen, J., Andersen, J. H., Gustafsson, B. G., Conley, D. J. (2014). Deoxygenation of the
679 Baltic Sea During the Last Century. *PNAS*, 111, 15, 5628–5633.

680

681 Clarkson, T., Magos, L. (2006). The Toxicology of Mercury and its Chemical compounds.
682 *Critical Rev in Toxicol*, 36, pp. 609-662
683

684 Carton, G. and Jagusiewicz, A. (2009). Historic Disposal of Munitions in U.S. and European
685 Coastal Waters, How Historic Information Can be Used in Characterizing and Managing Risk.
686 *Marine Technology Society Journal*, 43, 4, pp. 16-32.
687

688 Costa, M. and Liss, P. (2000). Photoreduction and evolution of mercury from seawater. *Science*
689 *of the Total Environment*, 16, pp. 125-135.
690

691 Cutter, G.A., Casciotti, K., Croot, P., Geibert, W., Heimbürger, L.E., Lohan, M.C., Planquette, H.
692 and van de Flierdt, T. (2017). Sampling and sample-handling protocols for GEOTRACES
693 Cruises, Version 3.0.
694

695 Edwards, B.A., Kushner, D.S., Outridge, P.M., Wang, F. (2021). Fifty years of volcanic mercury
696 emission research: Knowledge gaps and future directions. *Science of the Total Environment*,
697 757, 143800
698

699 Elmgren, R. (2001). Understanding Human Impact on the Baltic Ecosystem: Changing Views in
700 Recent Decades. *AMBIO: J. of the Human Environment*, 30(4), pp. 222-231.
701

702 GICHD (2016). A Guide to Survey and Clearance of Underwater Explosive Ordnance. Geneva:
703 Geneva International Centre for Humanitarian Demining.
704

705 Gębka K., Beldowski J., Beldowska M. (2016). The impact of military activities on the
706 concentration of mercury in soils of military training grounds and marine sediments.
707 *Environmental Science and Pollution Research*, DOI: 10.1007/s11356-016-7436-0.
708

709 Goncalves, A., Marshall, B., Kaplan, R., Moreno-Chavez, J., Viega, M. (2017). Evidence of
710 reduced mercury loss and increased use of cyanidation at gold processing centers in southern
711 Ecuador. *Journal of Cleaner Production*, 165, pp. 836-845.
712

713 Gosnell, K., Balcom, P., Ortiz, V., DiMento, B., Schartup, A., Greene, R., Mason, R. (2016).
714 Seasonal Cycling and Transport of Mercury and Methylmercury in the Turbidity Maximum of
715 the Delaware Estuary. *Aquatic Geochemistry*, doi:10.1007/s10498-015-9283-x.
716

717 Gosnell, K.J., Beck, A.J., Müller, P., Keßler, A. and Achterberg, E.P. (2022). Effects of salinity
718 and temperature on seawater dissolution rate of initial detonation agent mercury fulminate.
719 *Marine Pollution Bulletin*, 185, p.114311.
720

721 Gubelit, Y., Polyak, Y., Dembska, G., Pazikowska-Sapota, G., Zegarowski, L., Kochura, D.,
722 Krivorotov, D., Podgornaya, E., Burova, O., Maazouzi, C. (2016). Nutrient and metal pollution
723 of the eastern Gulf of Finland coastline: Sediments, macroalgae, microbiota. *Science of the Total*
724 *Environment*, 550, pp. 806-819.
725

726 HELCOM (2010). Towards a tool for quantifying anthropogenic pressures and potential impacts
727 on the Baltic Sea marine environment: A background document on the method, data and testing
728 of the Baltic Sea Pressure and Impact Indices. *Baltic Sea Environ. Proc.* No 125.
729

730 HELCOM (2015). Updated Fifth Baltic Sea pollution load compilation (PLC-5.5). *Baltic Sea*
731 *Environ. Proc.* No 145.
732

733 Hintelmann, H., Keppel-Jones, K., Evans, D. (2000). Constants of Mercury Methylation and
734 Demethylation rates in sediments and comparison of tracer and ambient mercury availability.
735 *Environmental Toxicology and Chemistry*, 19, 9, pp. 2204-2211.
736

737 Horowitz, H.M., Jacob, D.J., Amos, H.M., Streets, D.G., Sunderland, E.M. (2014). Historical
738 mercury releases from commercial products: Global environmental implications. *Environ Sci*
739 *Tech*, 48, pp. 10242–10250. doi:10.1021/es501337j
740

741 Kammann, U., Aust, M., Siegmund, M., Schmidt, N., Straumer, K., Lang, T. (2021). Deep
742 impact? Is mercury in dab (*Limanda limanda*) a marker for dumped munitions? Results from
743 munition dump site Kolberger Heide (Baltic Sea). *Environmental Monitoring and Assessment*,
744 193, 788.
745

746 Kampmeier, M., van der Lee, E., Wichert, U., Greinert, J. (2020). Exploration of the munition
747 dumpsite Kolberger Heide in Kiel Bay, Germany: Example for a standardized hydroacoustic and
748 optic monitoring approach. *Continental Shelf Research*, 198, 104108.
749

750 King, J., Kostka, J., Frischer, M., Saunders, M. (2000). Sulfate-Reducing Bacteria Methylate
751 Mercury at Variable Rates in Pure Culture and in Marine Sediments. *Applied and Environmental*
752 *Microbiology*, 66, pp. 2430-2437.
753

754 Kuss, J., Cordes, F., Mohrholz, V., Nausch, G., Naumann, M., Krüger, S., Schulz-Bull, D.
755 (2017). The impact of the Major Baltic Inflow of December 2014 on the Mercury Species
756 Distribution in the Baltic Sea. *Environ Sci Tech*, 51, pp. 11692-11700.
757

758 Kwasigroch, U., Beldowska, M., Jędruch, A., Lukawska-Matusyewska, K. (2021). Distribution
759 and bioavailability of mercury in the surface sediments of the Baltic Sea. *Environ Sci Pollut*
760 *Res*, 28, 35690–35708.
761

762 Lavoie, R., Bouffard, A., Maranger, R., Amyot, M. (2018). Mercury transport and human
763 exposure from global marine fisheries. *Science Reports*, 8, 6705.
764

765 Leipe, T., M. Moros, A. Kotilainen, H. Vallius, K. Kabel, M. Endler, and N. Kowalski (2013).
766 Mercury in Baltic Sea Sediments-Natural background and anthropogenic impact, Earth's
767 chemistry. *Geochemistry*, 73 (3), 249-259.
768

769 Lennartz, S., Lehnamn, A., Herrford, J., Malien, F., Hansen, H.-P., Biester, H., Bange, H.
770 (2014). Long-term trends at the Boknis Eck time series station (Baltic Sea), 1957-2013: does
771 climate change counteract the decline in eutrophication? *Biogeosciences*, 11, pp. 6323-6339.
772

773 Lilja, K., Norström, K., Remberger, M., Kaj, L., Egelrud, L., Junedahl, E., Brorström-Lunden, E.,
774 Schlabach, M. Ghebremeskel, M. (2009). Screening study on occurrence of hazardous substances
775 in the eastern Baltic Sea.
776

777 Lodeiro, P., Rey-Castro, C., David, C., Puy, J., Achterberg, E.P. and Gledhill, M. (2021).
778 Seasonal variations in proton binding characteristics of dissolved organic matter isolated from the
779 Southwest Baltic Sea. *Environmental Science and Technology*, 55, pp.16215-16223.
780

781 Luo, H., Cheng, Q., Pah, X. (2020). Photochemical behaviors of mercury (Hg) species in aquatic
782 systems: A systematic review on reaction processes, mechanisms, and influencing factor.
783 *Science of the Total Environment*, 720, 10, 137540.
784

785 Ma, M., Du, H., Wang, D. (2019). Mercury methylation by anaerobic microorganisms: A
786 review. *Critical Reviews in Environmental Science and Technology*, 49, pp. 1893-1936.
787

788 Mason, R., Kim, E., Cornwell, J. and Heyes, D. (2006). An examination of the factors
789 influencing the flux of mercury, methylmercury and other constituents from estuarine sediment.
790 *Marine Chemistry*, 102, pp.96-110.
791

792 Matyáš, R., and Pachman, J. (2013). *Primary explosives*. Heidelberg: Springer
793

794 Munson, K., Babi, D. Lamborg, C. (2014). Determination of monomethylmercury from seawater
795 with ascorbic acid-assisted direct ethylation. *Limnology and Oceanography:Methods*, 12, pp.1-9.
796

797 Orani, A., Vassileva, E., Schmidt, S., Berail, S., Barre J. (2020) Temporal variation of trace
798 elements, rare earth elements and Pb isotope ratios in sediment core from Kiel Bay, western
799 Baltic Sea. *Environmental Chemistry* 17, 579-593.
800

801 Outridge, P.M., Mason, R.P., Wang, F., Guerrero, S., Heimburger-Boavida, L.E. (2018). Updated
802 global and oceanic mercury budgets for the United Nations Global Mercury Assessment 2018.
803 *Environ. Sci. Technol.* 52, 11466-11477.
804

805 Pempkowiak, J., Cossa, D., Sikora, A., Sanjuan, J. (1998). Mercury in water and sediments of
806 the southern Baltic Sea. *Science of the Total Environment*, 213, pp. 185-192.
807

808 Seidel, M., Manecki, M., Herlemann, D., Deutsch, B., Schulz-Bull, D., Jürgens, K., Dittmar, T.
809 (2017). Composition and Transformation of Dissolved Organic Matter in the Baltic Sea. *Front.*
810 *Earth Sci.*, 5, 31.
811

812 Siedlewicz, G., Korejwo, E., Szubska, M., Grabowski, M., Kwasigroch, U., Beldowski, J. (2020).
813 Presence of mercury and methylmercury in Baltic Sea sediments, collected in ammunition
814 dumpsites. *Marine Environmental Research*, 162, 105158.
815

816 Soerensen, A., Schartup, A., Gustafsson, E., Gustafsson, B., Undeman, E., Björn, E. (2016).
817 Eutrophication increases phytoplankton methylmercury concentrations in a coastal sea – A Baltic
818 Sea case study. *Environ Sci Tech*, 50, pp. 11787-11796.
819

820 Stedmon, C., Osburn, C., Kragh, T. (2010). Tracing water mass mixing in the Baltic-North Sea
821 transition zone using the optical properties of colored dissolved organic matter. *Estuarine,*
822 *Coastal and Shelf Science*, 87, pp. 156-162.
823

824 Ullrich, S.M., Tanton, T.W., Abdrashitova, S.A. (2001). Mercury in the aquatic environment: a
825 review of factors affecting methylation. *Critical Rev. Environ. Sci. Technol.*, 31, pp. 241-293.
826

827 Uścińowicz, S., Szefer, P., Sokołowski, K. (2011). Trace metals in the Baltic Sea sediments. In:
828 Uścińowicz, S. (Ed.), *Geochemistry of the Baltic Sea Surface Sediments 2011*, p. 356
829 (Warszawa).
830

831 van Velzen, D., Langenkamp, H., Herb, G. (2002). Mercury in waste incineration. *Waste*
832 *Management & Research*, 20, 6, 556-568.
833

834 Vassileva, E., Azemard, S. & Mandjukov, P. (2018). Certification for trace elements and methyl
835 mercury mass fractions in IAEA-456 marine sediment sample. *Accred Qual Assur*, 23, 29-37.
836
837
838