

Supplementary Information for:

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

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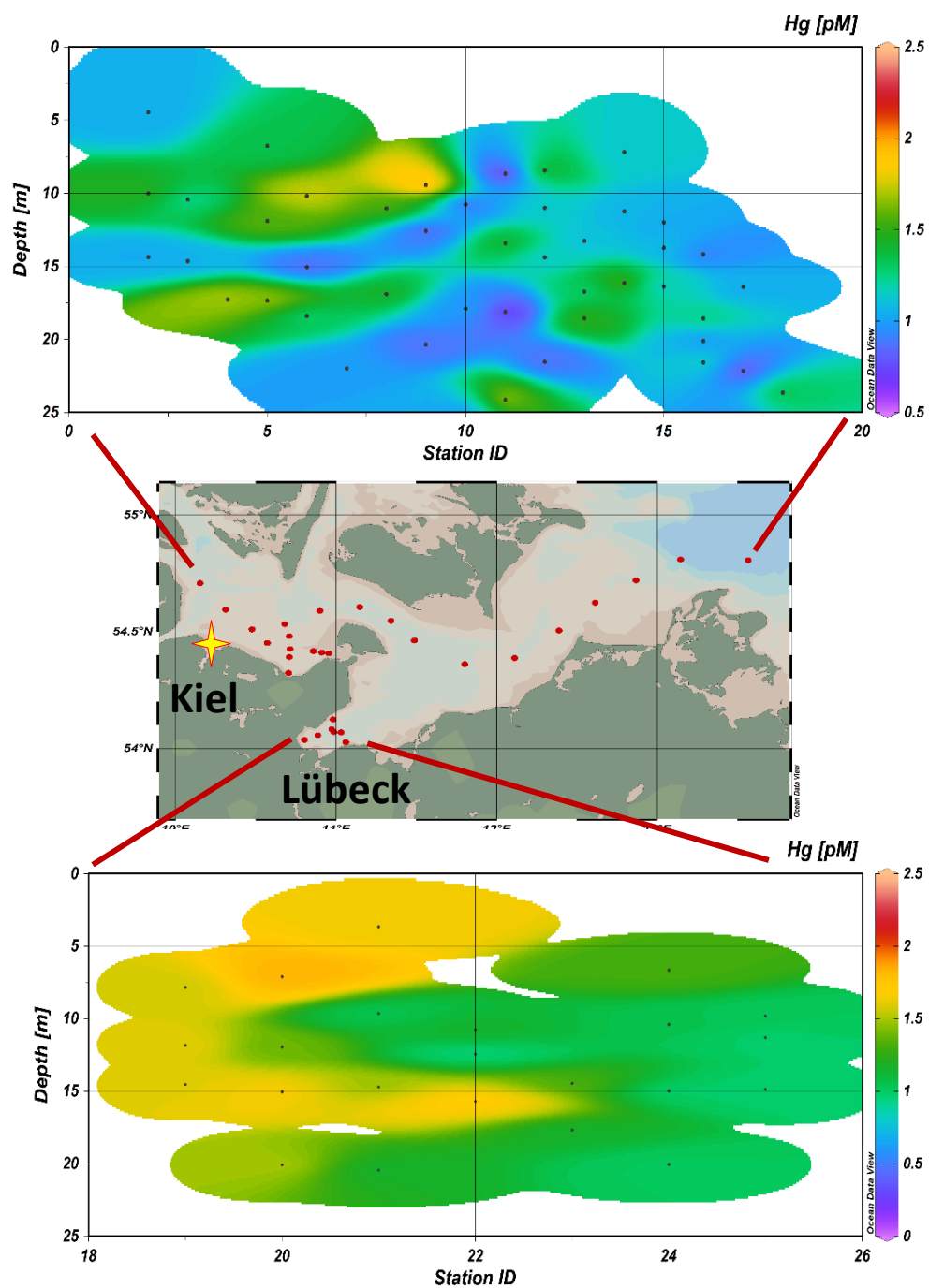


Figure S1. Total Hg (pM) results from a research cruise transect along the southern Baltic coast (top) and Lübeck (bottom). Mercury values reflect the low background levels consistent with coastal waters. The focused research area (KB, DN and CR) is noted by the star on the central map.

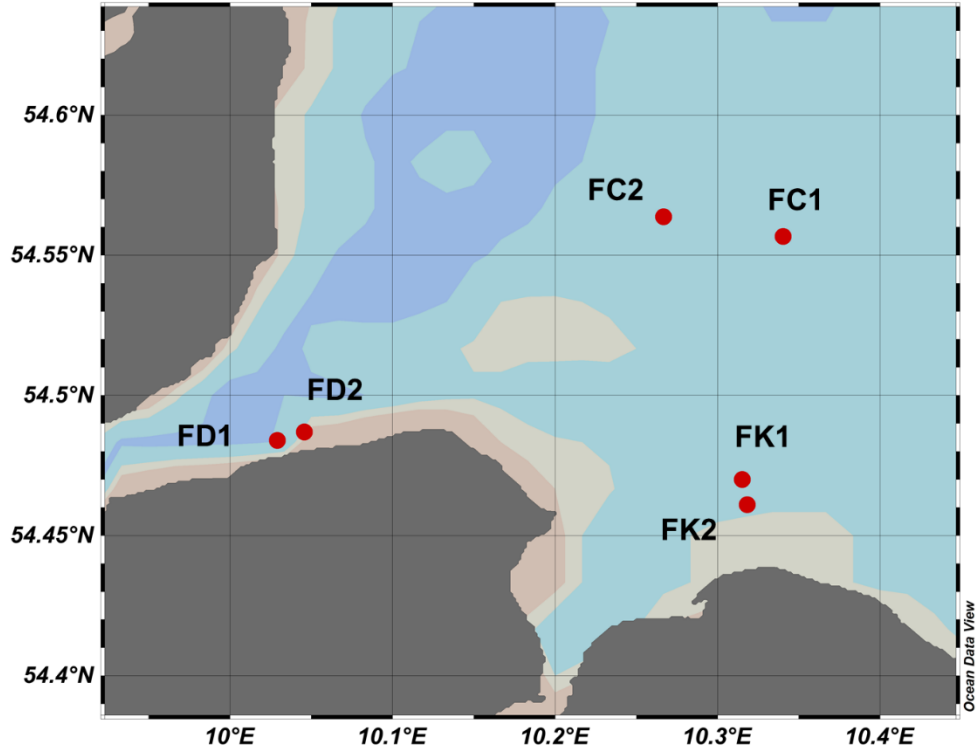


Figure S2. Map displaying flux cores locations from each site. Duplicate cores were collected from 2 proximate locations at Dänisch Nienhof (FD1 and FD2) and Kolberger Heide (FK1 and FK2), while only 1 core was collected at FC1 and FC2 (for CR representation).

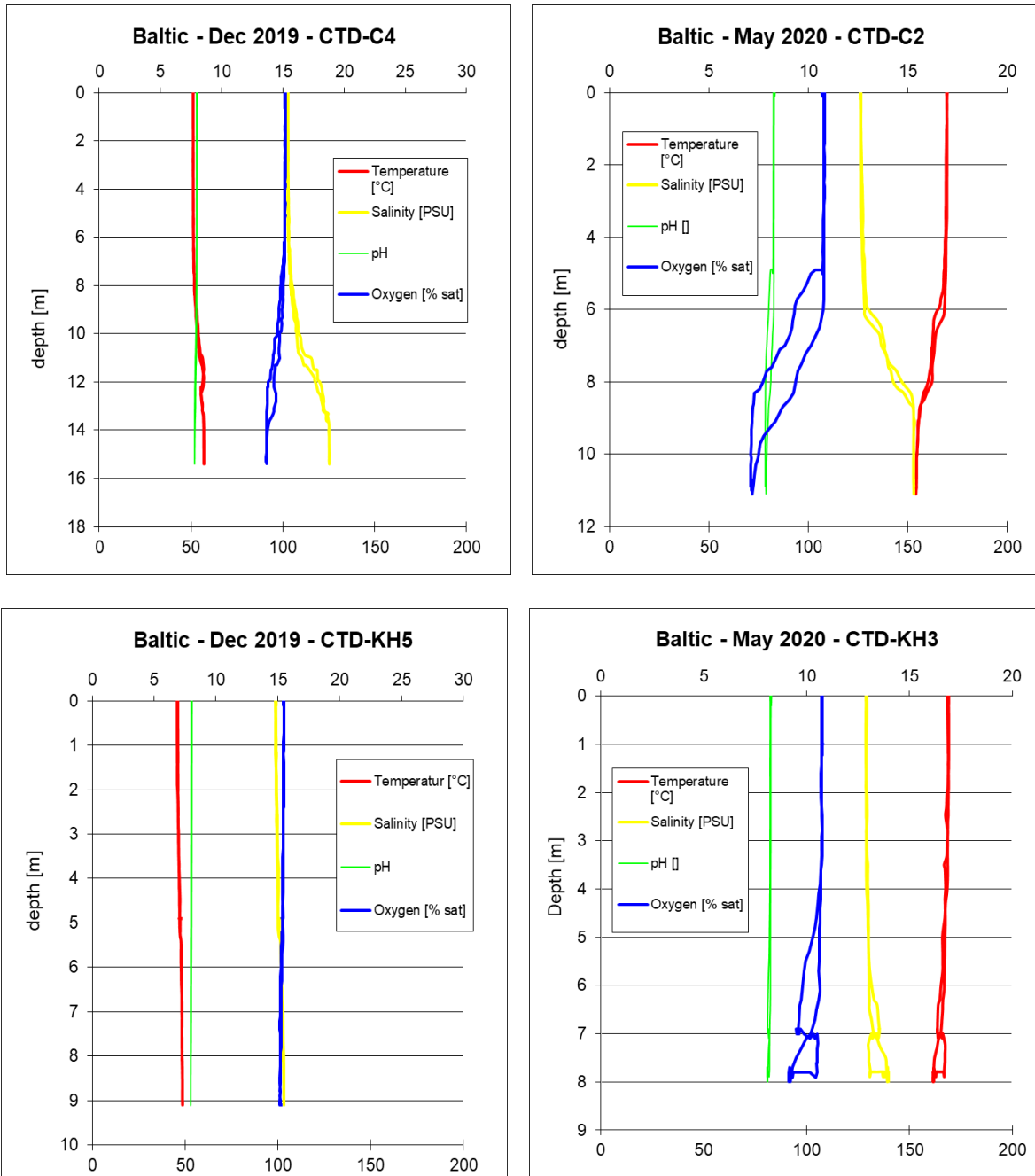


Figure S3. Typical CTD profiles of Kiel Bay displaying the temperature ($^{\circ}\text{C}$), salinity (psu), pH and oxygen (% sat) with depth (m). Demonstrative profiles are displayed for control station (CR; top) and Kolberger Heide (KH; bottom). Both left profiles were collected during the December cruise, while right profiles are from May. Top axis range is for temperature, salinity and pH, while the bottom axis range is for oxygen. Depth profiles were relatively consistent indicating an unremarkable or well-mixed water column among stations. However, CR sites did show a slight salinity increase as well as a temperature and oxygen saturation decrease with depth, as is consistent with seasonality, and this effect was more pronounced in May. Overall temperatures were higher, and oxygen saturation and salinity were lower in May and July than December at all sites. July CTD observations were consistent with May, and physical characteristics of Dänisch Nienhof waters overlapped with KH.

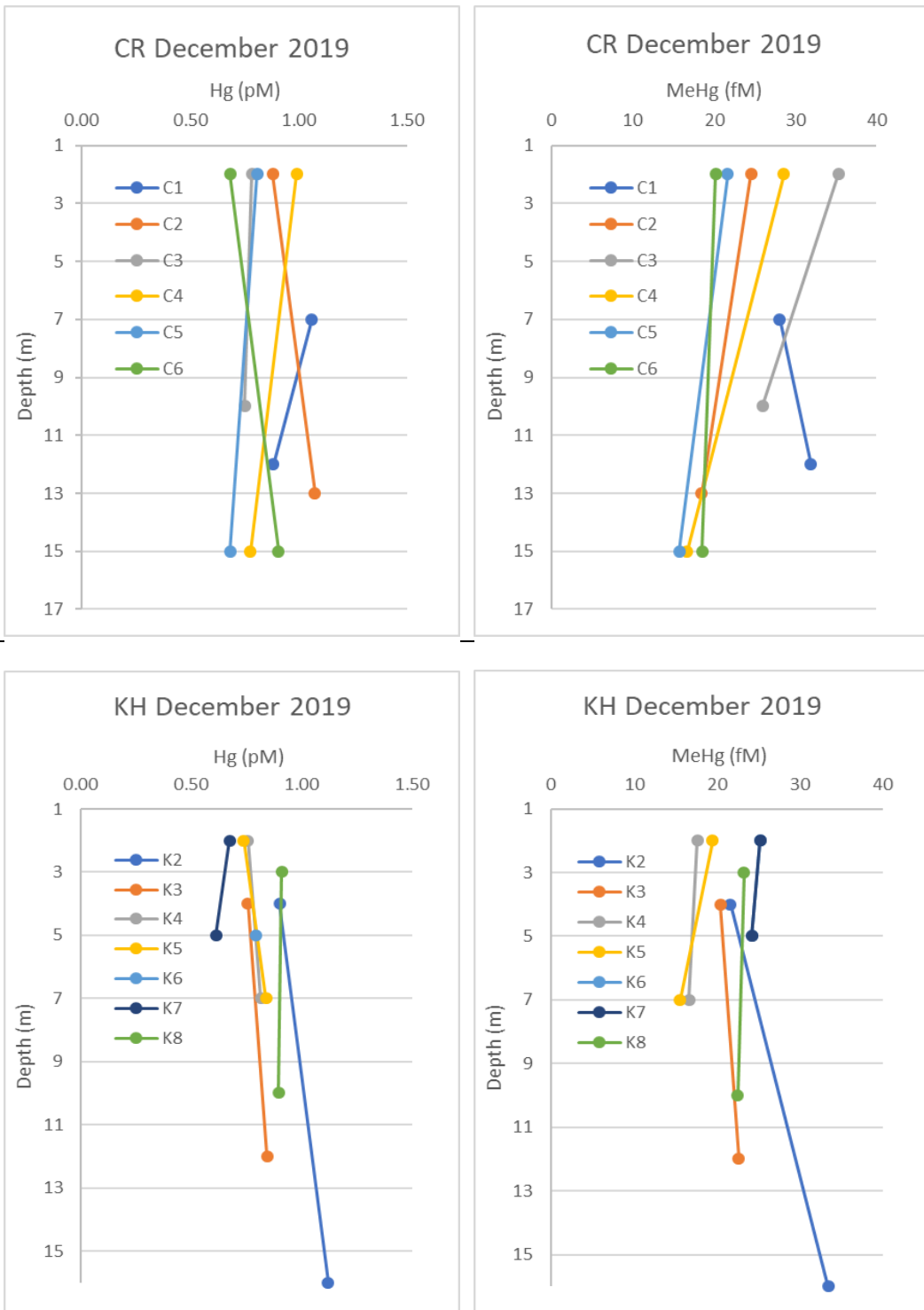


Figure S4. Depth profiles collected in December for background/control station (CR; top) and Kolberger Heide (KH; bottom) for Hg (pM; left) and MeHg (fM; right).

Table S1. Average (\pm SD) sediment organic characteristics for overall as well as from each site: control stations (CR, n=8), Dänisch Nienhof (DN, n=8), and Kolberger Heide (KH, n=13). Results for sediment %MeHg (MeHg/Hg) are noted. Reported characteristics are: Nitrogen content (percentage of weight (% wt.); N % wt); total carbon (TC % wt); sulfur content (S % wt); organic carbon (C-org), Carbon (C [mol]), Nitrogen (N [mol]), and molar ratio ([C/N]).

	%MeHg (MeHg/Hg) %	N (% wt.)	TC (% wt.)	S (% wt.)	Corg (% wt.)	C [mol]	N [mol]	C/N (mol:mol)
CR	0.12 \pm 0.1	0.11 \pm 0.1	0.71 \pm 0.9	0.12 \pm 0.2	0.65 \pm 0.9	0.05 \pm 0.1	0.01 \pm 0.01	5.86 \pm 1.6
DN	0.16 \pm 0.2	0.30 \pm 0.2	2.49 \pm 1.7	0.34 \pm 0.2	2.06 \pm 1.3	0.17 \pm 0.1	0.02 \pm 0.01	8.15 \pm 0.4
KH	0.03 \pm 0.02	0.43 \pm 0.3	3.47 \pm 2.2	0.61 \pm 0.4	3.21 \pm 2.2	0.27 \pm 0.2	0.03 \pm 0.02	8.34 \pm 1.0
Overall	0.1 \pm 0.1	0.31 \pm 0.3	2.43 \pm 2.1	0.40 \pm 0.4	2.19 \pm 1.9	0.18 \pm 0.2	0.02 \pm 0.02	7.59 \pm 1.5

Table S2. Average water column values (\pm SD) for each cruise (December, May and July) collected from control stations (CR), Dänisch Nienhof (DN), and Kolberger Heide (KH). Results for Hg (pM), MeHg (fM) and the %MeHg (MeHg/Hg) are given. The DN site was not sampled in December. For December and May, 5 - 7 stations were sampled, while 3 stations were sampled in July, at each site. Overall average Hg (pM) values for KB were: 0.85 \pm 0.1 (December), 1.16 \pm 0.35 (May), and 1.5 \pm 0.6 (July). While overall MeHg (fM) averages were: 22.9 \pm 5.7 (December), 26.5 \pm 11.7 (May), and 10.8 \pm 2.9 (July).

	CR			DN			KH		
	Hg (pM)	MeHg (fM)	%MeHg	Hg (pM)	MeHg (fM)	%MeHg	Hg (pM)	MeHg (fM)	%MeHg
December	0.9 \pm 0.2	23.8 \pm 6.2	2.7 \pm 0.8	-	-	-	0.8 \pm 0.1	22.1 \pm 5.2	2.6 \pm 0.5
May	1.3 \pm 0.3	24 \pm 8.5	2 \pm 0.7	1 \pm 0.2	28.7 \pm 12.8	3.1 \pm 1.6	1.3 \pm 0.5	24.5 \pm 12.3	2 \pm 1.3
July	1.5 \pm 0.6	9 \pm 0.9	0.7 \pm 0.3	2.7 \pm 2.4	11 \pm 2.9	0.8 \pm 0.6	1.5 \pm 0.4	11.7 \pm 3.6	0.8 \pm 0.2

SI: Methods

Dissolved organic carbon (DOC) samples were collected in pre-combusted 25 mL borosilicate glass vials for the 2020 cruises as well as at each time point during flux core measurements. The DOC analysis was completed using a Shimadzu TOC-L analyzer equipped with an ASI autosampler. Nutrient analysis (nitrate, nitrite, phosphate, silicic acid) for all water stations was completed with a QUAATRO (Seal Analytical) auto-analyzer following the method of Grasshoff et al (2007).

Sediment samples were measured for several organic parameters (nitrogen content: N % wt; sulfur content: S % wt; organic carbon: C-org; molar ratio: [C/N]; total carbon: TC % wt) with an EA3000 Elemental Analyzer to assess and constrain elemental factors that control Hg and MeHg concentrations and mobility.

Equations for flux calculations:

Reported rate calculations in Table 2 are calculated for each time point, then averaged (\pm SD) for the overall experiment duration. However average reported rates for MeHg fluxes exclude the first time point, as it was deemed unrealistic.

Concentration correction for replacement water addition:

$$[(C1 \times V1) + (C2 \times V2)] / (V_{\text{total}}) = C_{\text{new}}$$

C1 = concentration measured in overlying waters in core

C2 = bulk refill water concentration

V1 = volume of overlying water

V2 = volume of replacement deep water added

Rate calculation: $[h_{\text{core}} \times (C_{\text{time } n-1} - C_{\text{new}})] / (\Delta t)$

h_{core} = core height (in dm)

Δt = change in time (in days)

SI: Results and Discussion

SI 3.2 Mercury fluxes from sediments

Organic matter contents for sediment around KH were higher than those around DN and CR sites, therefore some of the higher Hg and MeHg at KH could be associated with organic content. There was a correlation between sediment Hg and C-org content ($r^2=0.619$, $p=0.007$, $n=10$), as well as S concentrations for the cores ($r^2=0.579$, $p=0.010$, $n=10$). However, it is more difficult to relate MeHg concentrations to nutrients, as environmental measurements also yield substantial variance (Beldoswki et al., 2019). Results from this study suggest no influence of S ($r^2=0.105$, $p=0.360$, $n=10$) and C-org content ($r^2=0.101$, $p=0.325$, $n=10$) on MeHg sediment concentrations for flux cores (Table 2).

SI 3.3 Mercury in the water column

For May, nitrate concentrations averaged 0.05 μM for all stations, with nitrite at 0.012 μM , and phosphate around 0.076 μM . Silicic acid profiles did show some increases with depth. For example, silicic acid concentrations at typical KH stations at a greater depth (~15 m) were 35.6 μM (Dec), 27.9 μM (May), and 41.6 μM (July), with DN also displaying elevated values at depth in July (e.g. 56.7 μM). Silicic acid concentrations at surface and intermediate depths for all stations averaged ~9.8 μM . Most nutrient profiles did exhibit seasonal variations. For example, at KH the average concentrations in December were 1.39 μM (nitrate), 0.209 μM (nitrite), 0.537 μM (phosphate) and 11.9 μM (silicic acid), compared to July when nitrate was 0.016 μM , nitrite below detection, phosphate was 0.203 μM , and silicic acid was 13.5 μM .

SI: References

Grasshoff, K., Kremling, K., Ehrhardt, M. (2007). *Methods of Seawater Analysis*. John Wiley and Sons.