SUPPORTING INFORMATION

In situ measurements of explosive compound dissolution fluxes from exposed munition material in the Baltic Sea

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number of tables: 0

Additional information on German-language references

Several references in our manuscript are only available in German language, but provide important information about our study site and the explosives present. To assist readers, we provide here additional information on the relevant portions of these references. Our translation suggestions are shown in brackets. Internet URLs to the original documents are provided for convenience (accessed 27 Nov 2018).

Frenz, U. *Autonome Unterwasserfahrzeuge mit SAS-Technologie. Lehre und Forsch.* 02-2014, 11–16 (2014). [“Autonomous underwater vehicles with SAS technology” SAS = Synthetic aperture sonar]

> Page 14. “*Abb. 5: Das HISAS-Sonarbild der WTD 71 zeigt ein Minenfeld mit ca. 70 Ankertauminen aus dem Zweiten Weltkrieg in der Kolberger Heide.”* [Fig. 5: The HISAS sonar image of the WTD71 (Defence Technical Service for Ships and Naval Weapons, Maritime Technology and Research) shows a pile of mines with approximately 70 anchor mines from the Second World War in Kolberger Heide.]

> Page 14. Section titled “*Suche nach Munitionsaltlasten in der Kolberger Heide (Ostsee)*” [Search for munition dumps in the Kolberger Heide (Baltic Sea)], fourth paragraph. “*Bei diesem Einsatz im Frühjahr 2012 wurde ein ca. 25 km^2 großes Gebiet abgesucht, in dem über 6600 munitionsartige Objekte gefunden warden konnten (Abb. 7).*” [During the mission in spring 2012, a 25 km^2 area was searched in which over 6600 ammunition-like objects were found (Fig. 7).]

Pfeiffer, F. *Bericht über die in-situ-Begleituntersuchungen zur Munitionssprengung in der Ostsee vom 18.2.2009 (Ausschreibungsnummer: 4123-2009-41F)*. (2009). at <https://www.schleswig-holstein.de/DE/Fachinhalte/M/meeresschutz/Downloads/Bericht_Begleituntersuchung_2009.pdf?__blob=publicationFile&v=1> [Report on in situ investigations during mine detonation in the Baltic Sea on 18.02.2009.]

> Page 6, number 2. “*Der Kampfmittelräumdienstes (KRD) des Landes Schleswig-Holstein konnte 5 Ankerminen mit je 250-300 kg* Schiesswolle 39 *sprengen. Zwei der Minen detonieren jedoch schwach und deren Ladung wurde nur unvollständig umgesetzt und statt dessen teilweise in Form schwebfähiger Partikel mobilisiert*.” [The explosive ordnance clearance service (KRD) of the state of Schleswig-Holstein detonated 5 anchor mines, each containing 250-300 kg of *Schiesswolle 39**. However two of the mines underwent low-order detonation and explosive material was partially mobilized in the form of suspended particles.] *Explosive mixture containing 45% TNT, 5% Hexyl, 20% Al-powder, and 30% ammonium nitrate (Haas and Thieme, 1996).

Pfeiffer, F. *Bericht über die in-situ-Begleituntersuchungen zur Munitionssprengung in der Ostsee vom 28.2. – 18.3.2012 (Ausschreibungsnummer: ZB-U0-12-0027000-4121.6*). (2012). at <https://www.schleswig-holstein.de/DE/Fachinhalte/M/meeresschutz/Downloads/Bericht_Heidkate.pdf?__blob=publicationFile&v=1> [Report on in situ investigations during mine detonation in the Baltic Sea during 28.02-18.03.2012.]

> Page 8, second sentence. “*Der Kampfmittelräumdienstes (KRD) des Landes Schleswig-Holstein konnte während der Einsatzzeit eine Anzahl Ankertauminen (mit je 250 – 300 kg) und Torpedominen/Boden*

(TMB) mit je 550 kg des Marinesprengstoffs Schießwolle 39 sprengen." [The explosive ordnance clearance service (KRD) of the state of Schleswig-Holstein detonated a number of anchor mines (250 - 300 kg each) and torpedo mines/ground mines (TMB) with 550 kg each of the naval explosive *Schiesswolle 39* during the operation period.]

Pfeiffer, F. *Bericht über Zusammensetzung und Eigenschaften einer Schießwolleprobe (Vergabenummer: ZB-50-14-0292000-4121.7).* 1–26 (2014). at <https://www.schleswig-holstein.de/DE/Fachinhalte/M/meeresschutz/Downloads/Bericht_Heidkate.pdf?__blob=publicationFile&v=1> [Report on the composition and properties of a sample of *Schiesswolle 39*.]

Page 9, first paragraph. "*Der Massenanteil TNT lag bei ca. 49 Gewichtsprozenten, Hexyl bei ca. 6 Gewichtsprozenten.*" [The mass fraction TNT was approximately 49% by weight, and hexyl approximately 6% by weight.]

Page 10, last sentence: "*Die Resultate der Massenspektrometrie bestätigen die HPLC - Resultate dahingehend, dass in den untersuchten Proben keine Transformationsprodukte von STV, weder von TNT noch Hexyl, nachweisbar waren.*" [The results of mass spectrometry confirm the HPLC results to the extent that no transformation products of *STV* (*sprengstofftypischen Verbindungen* = munition compounds) from TNT or hexyl, were detectable in the examined samples.]

Page 11, last two sentences: "*Der Anteil an Ammoniumnitrat bei ca. 27 Gewichtsprozenten und der Aluminiumanteil bei ca. 18 Gewichtsprozenten der Ausgangssubstanz. Das Massenverhältnis deutet auf* Schießwolle 39 *hin.*" [The starting material contained approximately 27 wt% ammonium nitrate, and 18 wt% aluminum. This mass ratio identifies the material as *Schiesswolle 39*.]

Szala, M. 2nd DAIMON Meeting Goslar, Germany 17-19th October 2016. (2016). [Noted also in DAIMON project Newsletter #1, under heading "Analysis of Explosives", available at https://static-promote.weebly.com/share/244adc11-a0cb-4798-ba2b-eadcb867e011]

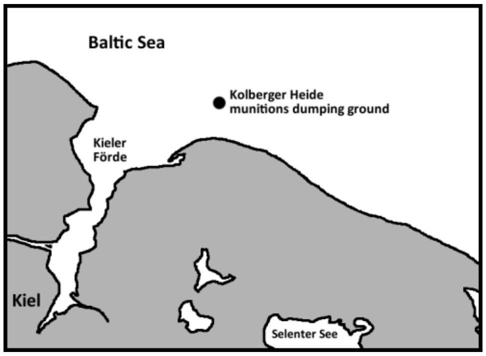

Figure S1. Study site: Kolberger Heide munitions dumping ground.

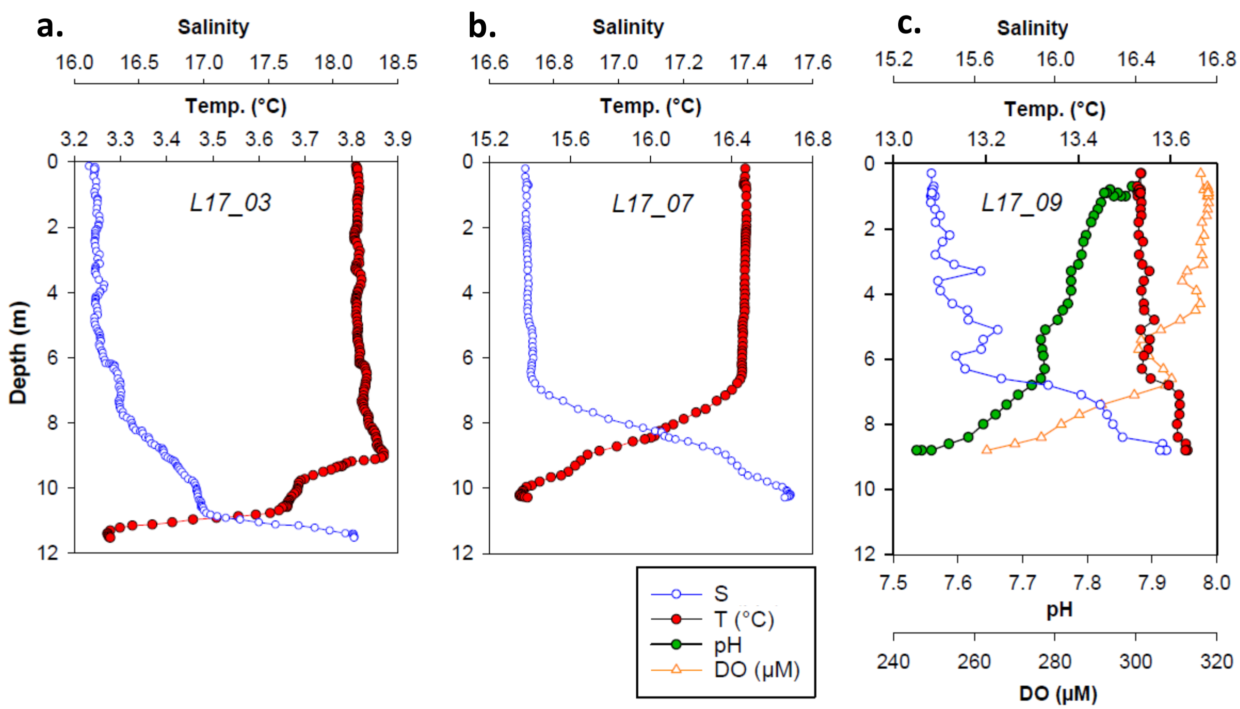

Figure S2. Water column profiles. a) L17_03: March 2017, b) L17_07: June 2017, c) L17_09: October 2017. pH and dissolved oxygen data were only collected during the October cruise. The water depth ranges between 12 and 14 m.

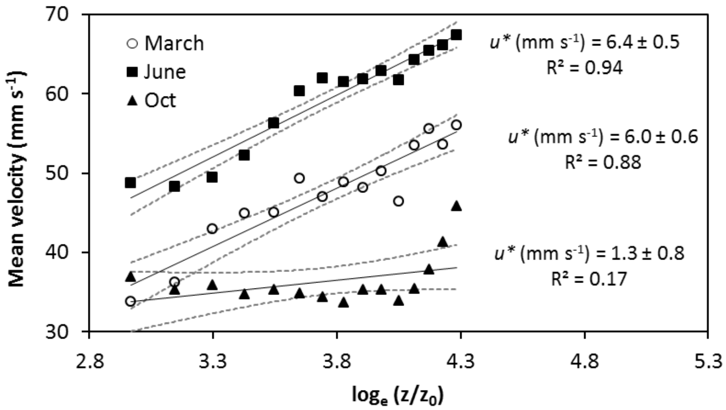

Figure S3. ADCP velocity profiles. Mean velocity of 66 (March), 208 (June) and 128 (October) individual profiles as a function of the natural log-transformed quantity (z/z_0), from 1.3 to 4.8 m above the seabed (15 bins = 15 data points per profile). Circles indicate March 2017, squares indicate June, and triangles indicate October. Solid lines represent linear regression of each monthly dataset, and dashed lines represent 95% confidence intervals. Correlation coefficients of the regression lines are indicated, as are resultant friction velocities, u_*, and their error.

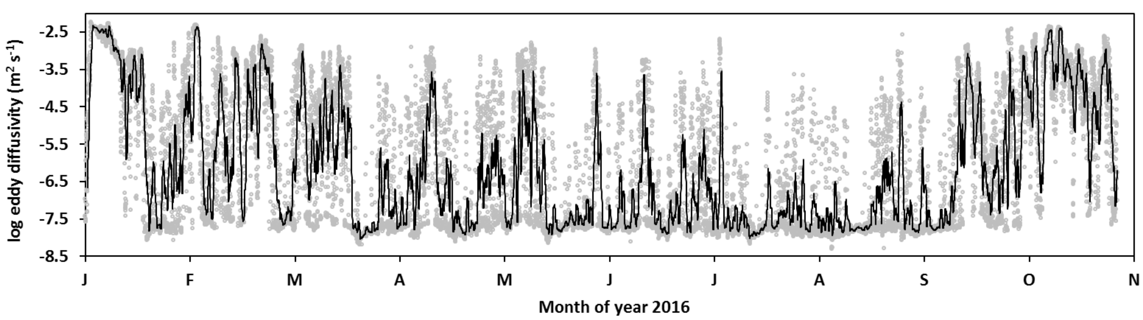

Figure S4. Eddy diffusion coefficients calculated using the GETM model. Individual data points represent 30 minute intervals, and the solid line is a 24 hour running mean to help guide the eye.

Loss of analyte by sorption to sampling materials

1. Analyte loss during sample storage in sampling materials was compared between 1L glass and high-density polypropylene bottles. Ultrapure water (18 MΩ-cm) was spiked to 800 µg/L with 2,4,6-TNT, 1,3-DNB, and RDX (AccuStandard, Inc.). Solutions were stored at room temperature for different periods of time, and extracted and processed as for samples. In general, RDX and TNT show limited or negligible loss over the incubation period, and no difference between glass and plastic (Fig. S5). In contrast, there was a clear difference between glass and plastic for DNB, and removal was apparent. However, DNB tends to be more difficult to analyze, with greater variability in sensitivity over time and less precision on individual measurements. Therefore, the experiment was repeated again using isotope-labeled compounds as detailed by Gledhill et al. (2019).

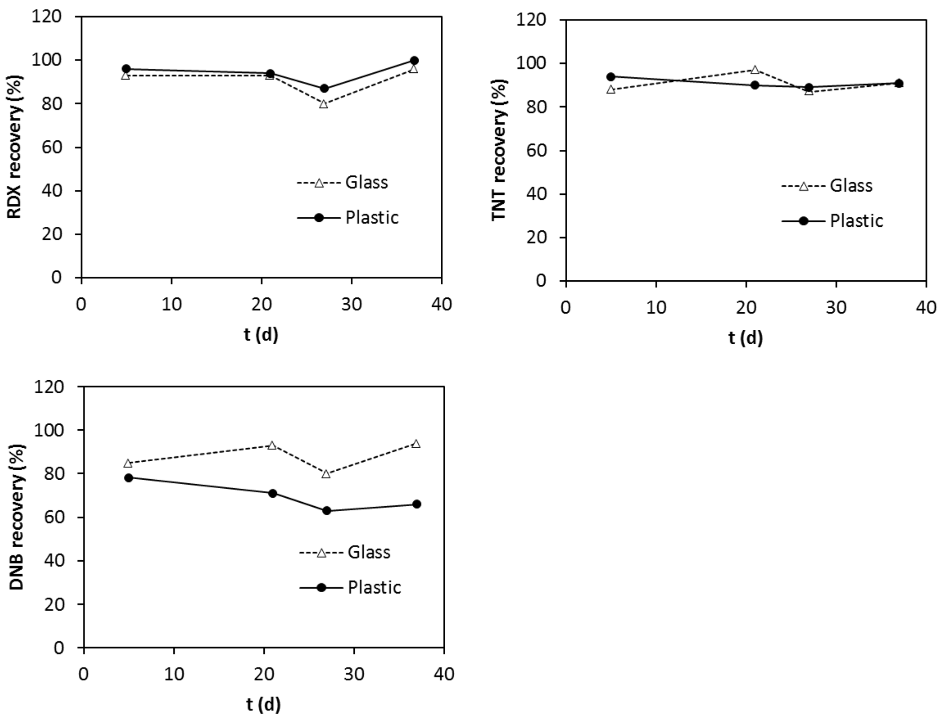

Figure S5. Recovery of MC analytes during storage.

2. To improve precision and accuracy of the analyses, the experiment was repeated using stable isotope-labeled 2,4,6-TNT ($^{13}C_7$, $^{15}N_3$) and 1,3-DNB ($^{13}C_6$) (Cambridge Isotope Laboratories, Inc., as described in Gledhill et al., 2019; no isotope-enriched version was available for RDX). Analytes were spiked into sterile artificial seawater (S = 18 psu, 1 µg/L TNT and DNB), and stored at 4°C in triplicate polypropylene centrifuge tubes. At various intervals, test solutions were extracted as described for samples and analyzed. No substantial loss was evident over the 4-week test period (Fig. S6). Replicates (n=3) indicated reproducibility between 1 and 4% for TNT and between 1 and 10% for DNB. These results confirm negligible loss of analytes under the conditions used for samples (samples kept cool and processed within 24h).

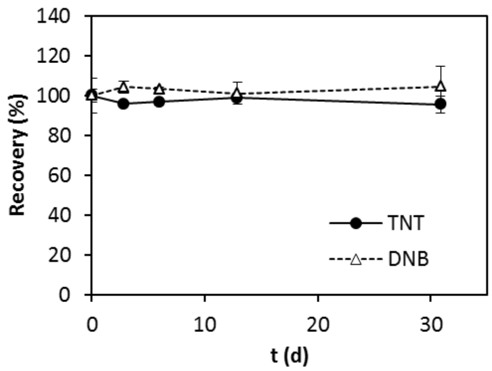

Figure S6. Recovery of stable isotope-labeled TNT and DNB. Error bars represent standard deviation of the mean of triplicate incubations.