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Environmental Monitoring of Munitions Constituents During a Demonstration of the Underwater Cut-and-Capture System Demilitarization Technology

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PURPOSE: The presence of underwater military munitions (UWMM) in aquatic environments may present explosive blast risks and potentially affect the environment because of the release of munitions constituents (MC). Therefore, in situ demilitarization of UWMM is highly desirable. This technical note presents the results of environmental monitoring measuring water and sediment contamination resulting from the demonstration of an in situ technology that uses high-pressure water jets to render UWMM safe.

BACKGROUND: Around the globe, many underwater sites contain underwater unexploded ordnance (UXO) and discarded military munitions (DMM), collectively referred to as *UWMM*, because of military training and combat or historic disposal events. Disposal of munitions at sea was extensively practiced as an acceptable option, with large quantities discarded into coastal waters following the World Wars (Davis 2009).

Release of MC, including 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazine (RDX), into aquatic environments has occurred because of UWMM corrosion and breaching of the munition's outer casing (Lewis et al. 2009; Rosen and Lotufo 2010; Wang et al. 2011; Voie and Mariussen 2017; Rosen et al. 2018; Beck et al. 2018; Rosen et al. 2022). In addition to safety concerns stemming from accidental or induced blasts, the release of MC may cause ecological and human health impacts (Cooper and Cooke 2018). Exposure to MC in water has been shown to cause toxicity to aquatic organisms belonging to various taxonomic groups (Nipper et al. 2009; Lotufo et al. 2013, 2017, 2021; Beck et al. 2018) and may accumulate in aquatic biota (Lotufo et al. 2009; Beck et al. 2022). As Lotufo et al. (2021) explain, "growing concern by public and regulatory communities has resulted in costly risk assessments and could lead to resource-intensive remediation efforts" involving removal (1; see also Detloff et al. 2012). The current mitigation tools available for UWMM include in situ approaches such as controlled blow-in-place (BIP) or intentional low-order detonations (Pedersen 2002), immobilization using geo-bags (Bunch et al. 2013), and ex situ approaches such as diver recovery or remotely operated vehicle, or ROV, recovery followed by at-sea demilitarization (Carton et al. 2012). While these tools show promise, none has been identified as the ideal solution (Lotufo et al. 2021, 47). For example, BIP can lead to local ecological consequences, even with the use of bubble curtains, because of blast overpressure (Koschinski 2011). Selection of a specific mitigation method or technique must be based primarily on the overall protection of human health and the environment, compliance with applicable laws and regulations, feasibility of implementation (for example, maturity of technology), cost, regulator acceptance, and community acceptance (Carton et al. 2019).

Technologies that use high-pressure water jets to render a munition safe in situ are expected to reduce the risk to response workers and the public and avoid potentially significant and costly environmental impacts (Schmit 2020).

CUT-AND-CAPTURE SYSTEM TECHNOLOGY FOR DEMILITARIZATION OF UNDERWATER MUNITIONS:

Over the past 10 years, Gradient Technology has been adapting widely used high-pressure abrasive water jet, or AWJ, technology for use underwater. As Schmit (2022) explains, "his adaptation has involved the integration of a variety of tools into a package that is deployed and operated from the surface to demilitarize munitions in shallow water" (less than 30 m) (2).* Collectively, this tool package and supporting utilities are called the Underwater Cut-and-Capture System, consisting of a three-axis underwater gantry and the cut-and-capture head (Figure 1). A full description of this system is provided in Schmit (2022).

Two demonstrations were conducted to validate the Underwater Cut-and-Capture System in shallow water (up to 30 m). US Navy underwater ranges in the Gulf of Mexico south of the Naval Support Activity–Panama City (NSA-PC) were selected for the first two of the demonstrations to fully test the integrated system by processing munitions such as the US Navy 5-inch/38-caliber and the US Army 105 mm M1 projectiles filled with inert material as surrogates of TNT. Two inert fills were used, microcrystalline cellulose and microcrystalline wax. After successful demonstrations with inert material (Schmit 2022), the Underwater Cut-and-Capture System was tested with TNT-filled projectiles. This demonstration was performed on a moon pool floating modular barge system (Poseidon Barge, Berne, Indiana) at the Naval Surface Warfare Center–Crane Division's Lake Glendora Test Facility (LGTF), near Sullivan, Indiana, in which 20 US Army 105 mm HE M1 projectiles filled with TNT were processed. The projectiles were numbered from 1 to 20 following the temporal sequence of processing. On the floating barge, trained explosives personnel secured the projectile in a cradle attached to the bottom of the tool package. The tool package and cradle were deployed into the moon pool, lowered into the water, and suspended in the water column at a depth of 7 m. Once lowered, the projectile was cut, and the TNT was captured. This cycle was repeated for each projectile until all 20 projectiles were processed over a three-day period (27–29 June 2022).

* For a full list of the spelled-out forms of the units of measure used in this document, please refer to *US Government Publishing Office Style Manual*, 31st ed. (Washington, DC: US Government Publishing Office, 2016), 248–52, https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf.

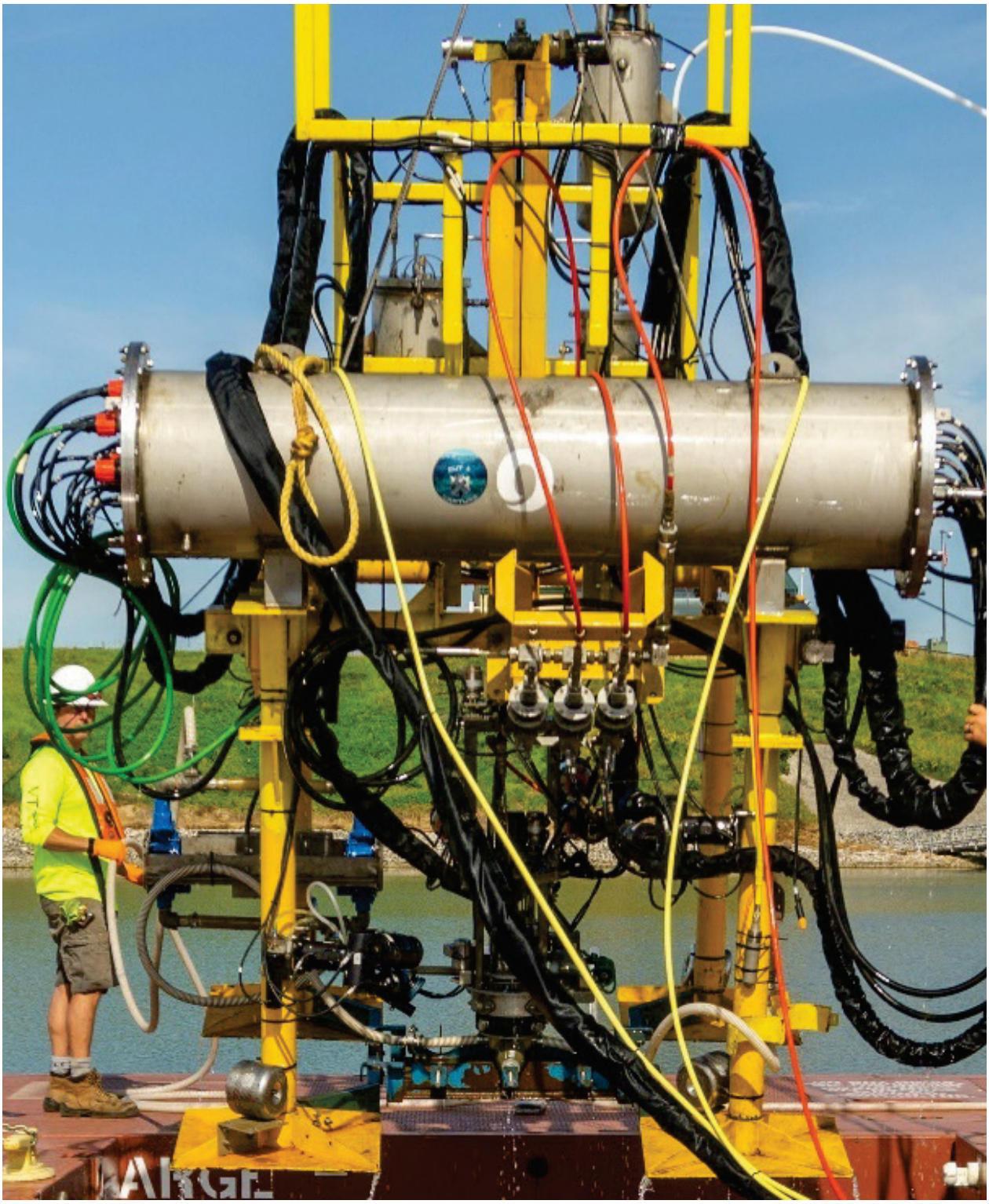

Figure 1. Underwater Cut-and-Capture System consisting of a three-axis underwater gantry and the cut-and-capture head is shown in this photograph taken during a demonstration at Lake Glendora Test Facility (LGTF) during 27–30 June 2022. (Photo credit: US Army Engineer Research and Development Center, public domain.)

METHODS:

Test site description. The Naval Surface Warfare Center's LGTF was an ideal site for live-munition demilitarization demonstrations: it is a purpose-built explosive test range that includes a 1.47 km^2 artificial lake for underwater and other acoustic testing. It has been operating since 1991, with explosive testing approved in 1996. A modular floating barge system made available by the LGTF was easily rearranged to accommodate the needs of the demonstration and to stage Gradient Underwater Cut-and-Capture System. Other LGTF support equipment made available included a crane and generator. Figure 2 shows a map of the LGTF and the arrangement of the modular floating barge system.

Environmental sampling.

Water sampling via pumping. To sample water near the projectile, two stainless-steel electric submersible pumps (Fultz Pumps, Lewistown, Pennsylvania) were used, each fastened to a separate gantry leg (approximately 1 m from the projectile) and each connected to the surface with 46 m of Teflon-lined polyethylene hose with integrated power wire (Figures 3 and 4). On the surface, the hose was laid out on the deck of the barge system and terminated at a table where water was collected. At the table, the hose's integrated power wire for each pump was connected to a portable power supply control case that featured a variable speed control dial to accurately and consistently produce low flow rates (for example, less than 1 L per minute). Power (110 volts AC power, or VAC) to each control case was sourced from the on-site generator (Figure 4). Water was sampled for projectiles 1 to 15. In a typical cycle, the pumps sampled water as the water jet cut the access hole, then the pumps were paused while the coupon (that is, metal plug cut out with the water jet) was removed, then the pumps were restarted when the water jet washed out munition constituents. Finally, the pumps were turned off when washout was completed. In several cycles, the coupon could not be removed while underwater; therefore, the entire system was hoisted back to the surface for inspection and then lowered back into the water to complete the cycle. The mean (± standard deviation) time the pumps were used to collect water samples for each projectile was 13 (± 3.5) minutes (range 8 to 18 minutes; total pump time for the 15 projectiles was 195 minutes; Table 1). For each projectile cycle, approximately 22 L of water was pumped into an HDPE carboy and homogenized. From the carboy, 2 L subsamples were collected and distributed into two 1 L jars and maintained on ice or under refrigeration (4°C) until analysis. Background MC contamination of the water column was evaluated by collecting water from the moon pool prior to the deployment of the Underwater Cut-and-Capture System. After each munition cycle was complete, the entire system was hoisted out of the water. Water in the hoses drained out through the pump prior to the next cycle.

Passive sampling. In situ passive sampling using polar organic chemical integrative samplers (POCIS) (Alvarez et al. 2010) was used for the detection and quantification of MC in water. Oasis HLB Disk (Hydrophilic-Lipophilic-Balanced; Waters Corporation, Milford, Massachusetts) sorbent, sandwiched in a housing between two polyethersulfone (PES) membranes, hereafter termed POCIS, and mounted in POCIS canisters designed for holding three samplers, were purchased from Environmental Sampling Technologies (St. Joseph, Missouri) (see also Rosen et al. 2022 for an example of this setup deployed in Vieques, Puerto Rico). One canister containing three samplers was fastened to each of the gantry legs of the Underwater Cut-and-Capture System (Figure 5). The canisters remained attached to the Underwater Cut-and-Capture System during the

period corresponding to the processing of the first 15 projectiles, the same that were monitored using direct water sampling via pumping. The POCIS were exposed to air every time the Underwater Cut-and-Capture System was brought to the surface during the period projectiles were being processed. The time the POCIS were passively sampling water during cut and capture of 15 projectiles was estimated to be 12 h. The POCIS were kept submerged in water at the designated reference location during the overnight period after processing had ended for the day (approximately 1700) and the following morning when processing started around 0900. The designated reference area was located at the edge of the floating pier most distal from the moon pool (Figure 2) One canister was placed at the reference location. To characterize background conditions, one canister containing three POCIS remained in the water uninterruptedly for approximately 30 h at the designated reference area.

Table 1. Start and end times for pumps used to collect water samples near 2,4,6-trinitrotoluene (TNT)–filled projectiles 1 to 15 during the demonstration of the Underwater Cut-and-Capture System at the LGTF, 27–29 June 2022. Approximately 22 L of water was collected near each projectile, from which 2 L was subsampled for testing.

Date	Munition Projectile	Start	Pause or End[a]	Restart	Pause or End	Restart	End	Total Pump Time (min)
27 June	1	1307	1320	—	—	—	—	13
28 June	2	0838	0845	0850	0900	—	—	17
28 June	3	0937	0954	—	—	—	—	17
28 June	4	1131	1134	1136	1140	1151	1200	16
28 June	5	1315	1319	1327	1336	—	—	13
28 June	6	1422	1424	1432	1441	—	—	11
28 June	7	1619	1621	1717	1730	—	—	15
29 June	8	1033	1039	1056	1103	—	—	13
29 June	9	1230	1234	1235	1249	—	—	18
29 June	10	1306	1315	—	—	—	—	9
29 June	10(2)[b]	1350	1356	—	—	—	—	6
29 June	11	1407	1409	1412	1420	—	—	10
29 June	12	1436	1439	1440	1448	—	—	11
29 June	13	1513	1515	1518	1525	—	—	9
29 June	14	1553	1601	—	—	—	—	8
29 June	15	1611	1613	1629	1636	—	—	9

[a] Paused while coupon was removed or gantry system was brought to surface for inspection or downtime.
[b] Rewash of projectile 10 to remove remaining TNT.

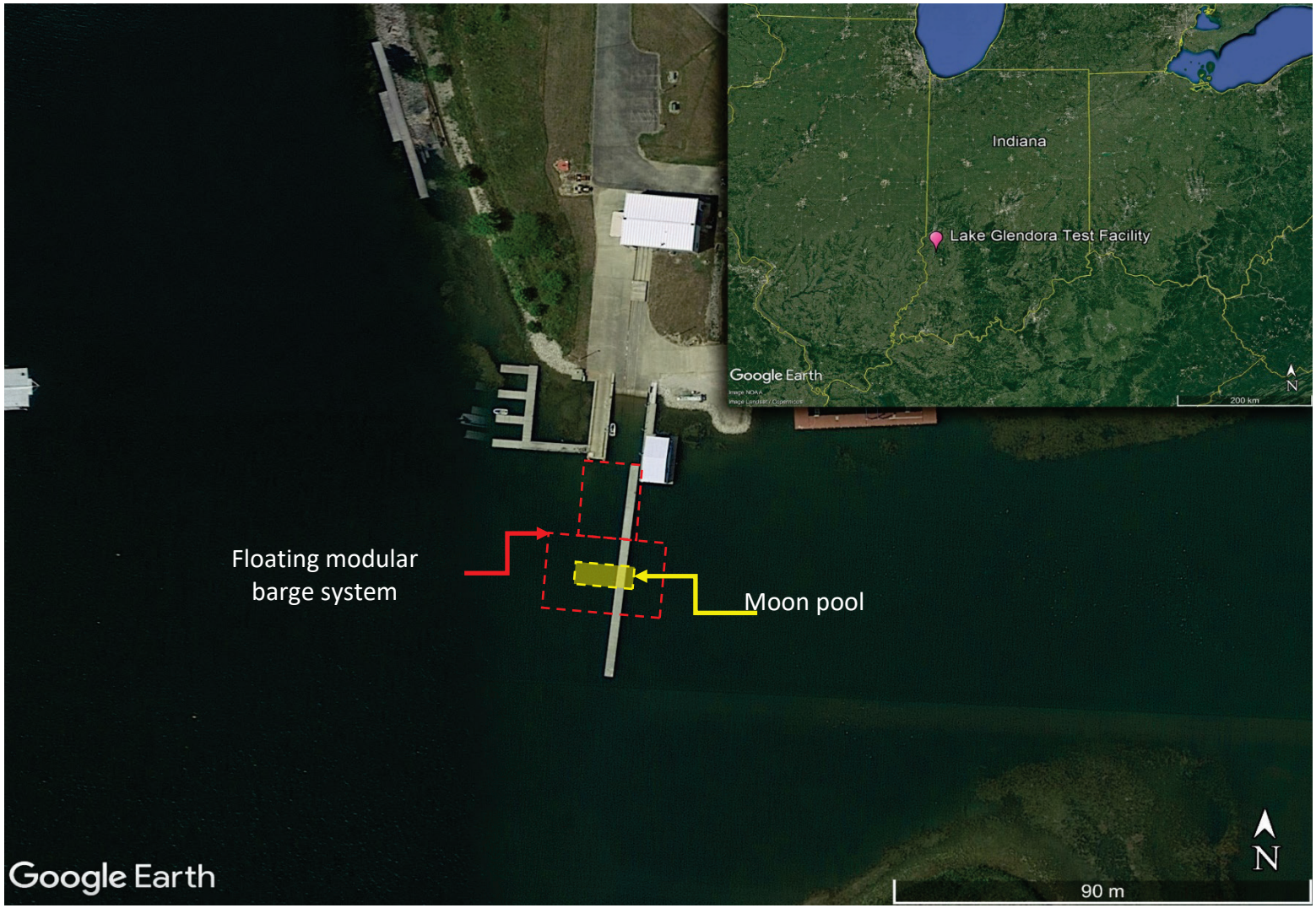

Figure 2. Demonstration of the Underwater Cut-and-Capture System took place on a floating modular barge system (relative location of barges shown by *red dashed lines*) containing a moon pool, an open-water area within the barge system (indicated by the *yellow shaded area*), for deploying and retrieving the system at the LGTF near Sullivan, Indiana (Satellite images credit: Google Earth, NOAA, and Landsat/Copernicus).

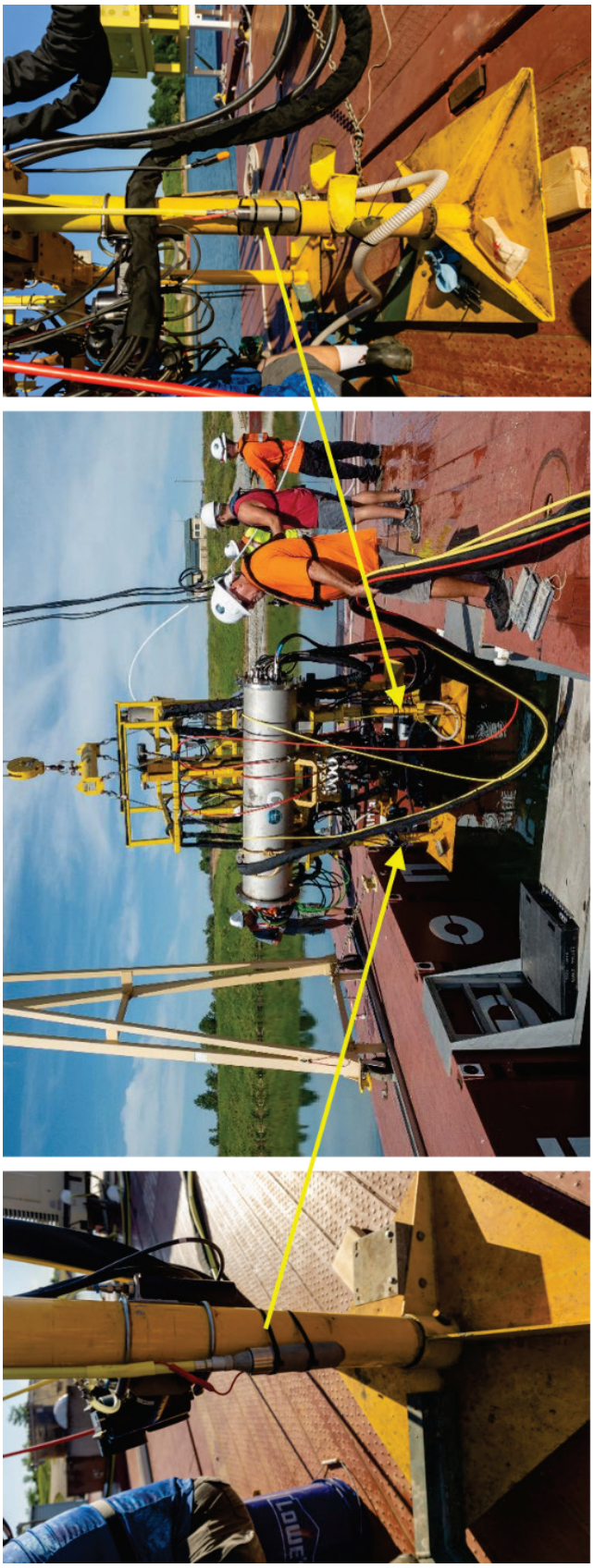

Figure 3. Photo of the Underwater Cut-and-Capture System (*middle*) and the submersible electric pumps (*left* and *right*) attached to each gantry leg. The pumps were used to collect water samples near the workup of projectiles 1 to 15. (Photos credit: ERDC. Public domain.)

Figure 4. Moon pool (*a*) where the Underwater Cut-and-Capture System was lowered to work up projectiles. Yellow Teflon-lined polyethylene hose (*b*) connected to pumps on gantry legs and terminated at the table. Portable control cases (*c*) with variable speed dials to control water flow and carboy where water was composited prior to subsample collection. A 1 L sample jar (*d*) used to subsample water from carboy. (Photos credit: ERDC. Public domain.)

Figure 5. Canister containing three polar organic chemical integrative samplers (POCIS) fastened to one of the gantry legs of the Underwater Cut-and-Capture System. (Photo credit: ERDC. Public domain.)

The membranes were cut to keep only the inner part which had been exposed at the center of the POCIS. The inner pieces were further rinsed with water purified using a Millipore Milli-Q (MilliporeSigma, Burlington, Massachusetts) laboratory water system water to remove any remaining grain of sorbent and left to dry under the fume hood for several hours. Once dry, they were put into individual 60 mL amber glass vials. 1,2-DNB was added as a laboratory surrogate spike by pipetting it directly onto the membranes. 1 mL increments of acetonitrile were added until the membranes were covered in solvent. The samples were then placed in an ultrasonic bath for 18 hours. Afterwards, the samples were transferred to clean vials. The samples were kept in the refrigerator (less than or equal to 4°C) until analysis.

Sediment samples (2 g) were placed in 12 mL amber glass vials and spiked with 1,2-DNB surrogate. 10 mL of acetonitrile were added to each sample. Afterwards, the samples were placed on an ultrasonic bath for 18 h. The samples were then transferred to 12 mL amber vials and stored in the refrigerator (≤4°C) until analysis.

The sample extracts were then analyzed on an Agilent 1200 HPLC (Agilent, Santa Clara, California) equipped with a quaternary pump. The HPLC was fitted with both a Phenomonex Synergi 4u Hydro-RP 80A (Phenomonex, Torrance, California) column for primary analysis and a Restek Pinnacle II Biphenyl 5 µm column (Restek, Bellefonte, Pennsylvania) for secondary analysis. HPLC-grade acetonitrile, methanol, and water made up the mobile phase. The analytes of interest were detected at a wavelength of 254 nm. Calibration was achieved using commercially available Restek standards. The calibration curve consisted of a blank and eight concentration points, ranging from 20 mg/L to 0.01 mg/L. The curve was validated immediately after calibration with analysis of an independent standard, with analyte recoveries falling within 10% of their nominal concentration. During sample analysis, continuing calibration verification standards were analyzed at 10 sampling intervals within 10% of their nominal concentration.

RESULTS:

Contamination in water samples collected by the pumps. TNT and TNT transformation products (2-ADNT, 4-ADNT, or both) were present in quantifiable concentrations in water sampled by the pumps positioned near the processing of projectiles 1 to 15 (Table 2). The nitroaromatic compounds 2,4- and 2,6-DNT, which are manufacturing impurities of TNT, were not detected in any sample. Jenkins et al. (2001) reported that 2,4-DNT accounted for 0.08% of military-grade TNT. No MC were detected in the sample taken prior to processing on munitions to assess background contamination. The detection limit for all analytes was 0.01 µg/L. The concentration of TNT ranged widely, from 0.5 to 93 µg/L across samples, while the concentration of 4-ADNT and the concentration of 2-ADNT ranged narrowly, from 0.2 to 3 µg/L (Table 2). The concentration of the sum of TNT, 2-ADNT, and 4-ADNT (SumTNT) ranged from 0.7 to 98 µg/L (Figure 6), and the contribution of TNT to the SumTNT ranged from 50% to 96% and was highest for the highest SumTNT concentrations (Table 3, Figure 6). When the concentrations of SumTNT ranged from 0.7 to 3.9 µg/L, the contribution of TNT ranged from 50% to 77%, but when the concentrations of SumTNT ranged from 8.7 to 98 µg/L (highest measured concentrations), the contribution of TNT ranged from 80% to 96% (Figure 6).

Contamination as detected by passive samplers. The MC TNT, 2-ADNTand 4-ADNT were present in quantifiable amounts in the sorbent phase and PES membranes of the 12 composited POCIS deployed during processing of projectiles 1 to 15 in (Table 4). The MC 2,4- and 2,6-DNT were not detected. No MC were detected in the three composited POCIS deployed at the reference location. The reporting limit for all MC was 0.05 µg. The contribution of TNT to the SumTNT was 98.7% for the sorbent and 96.6% for the membranes (Table 4).

Sediment contamination. No MC were detected in sediment samples collected from the three sampling locations. The detection limit was 46 µg/kg.

Table 2. Concentrations of TNT and 2- and 4-aminodinitrotoluene (2- and 4-ADNT) and the sum of TNT, 2-ADNT, and 4-ADNT (SumTNT) in water samples taken during processing of TNT-filled projectiles.

	Concentration (µg/L)			
Projectile	2,4,6-TNT	2-ADNT	4-ADNT	SumTNT
1	0.5	ND	0.2	0.7
2	0.6	0.3	0.3	1.2
3	1	0.3	0.3	1.6
4	0.8	0.3	0.2	1.3
5	1	0.3	0.4	1.7
6	31	1	3	35
7	0.6	0.3	0.3	1.2
8	1	0.3	0.4	1.7
9	2	0.4	0.7	3.1
10	3	0.4	0.5	3.9
10(2)[a]	69	0.8	2	72
11	93	2	3	98
12	7	0.7	1	8.7
13	2	0.3	0.4	2.7
14	2	0.3	0.6	2.9
15	1	0.3	0.6	1.9

Note: ND—nondetect.
[a] Rewash of projectile 10 to remove remaining TNT.

Table 3. Percentage of the SumTNT concentration corresponding to TNT and 2- and 4-ADNT in water samples taken during processing of TNT-filled projectiles.

	SumTNT Concentration (%)		
Projectile	2,4,6-TNT	2-ADNT	4-ADNT
1	71.4	0.0	28.6
2	50.0	25.0	25.0
3	62.5	18.8	18.8
4	61.5	23.1	15.4
5	58.8	17.6	23.5
6	88.6	2.9	8.6
7	50.0	25.0	25.0
8	58.8	17.6	23.5
9	64.5	12.9	22.6
10	76.9	10.3	12.8
10(2)[a]	96.1	1.1	2.8
11	94.9	2.0	3.1
12	80.5	8.0	11.5
13	74.1	11.1	14.8
14	69.0	10.3	20.7
15	52.6	15.8	31.6

[a] Rewash of projectile 10 to remove remaining TNT.

Table 4. Amounts of of TNT and 2- and 4-ADNT extracted from the sorbent or membranes of POCIS deployed during processing of TNT-filled projectiles 1 to 15 over a period of three days.

Mass of MC in Sorbent (µg per POCIS)			Mass of MC in Membranes (µg per POCIS)		
2,4,6-TNT	2-ADNT	4-ADNT	2,4,6-TNT	2-ADNT	4-ADNT
18.4	0.17	0.08	9.6	0.17	0.17
Fraction of SumTNT Concentration (%)			Fraction of SumTNT concentration (%)		
98.7	0.8	0.4	96.6	1.7	1.7

Note: MC—munitions constituents.

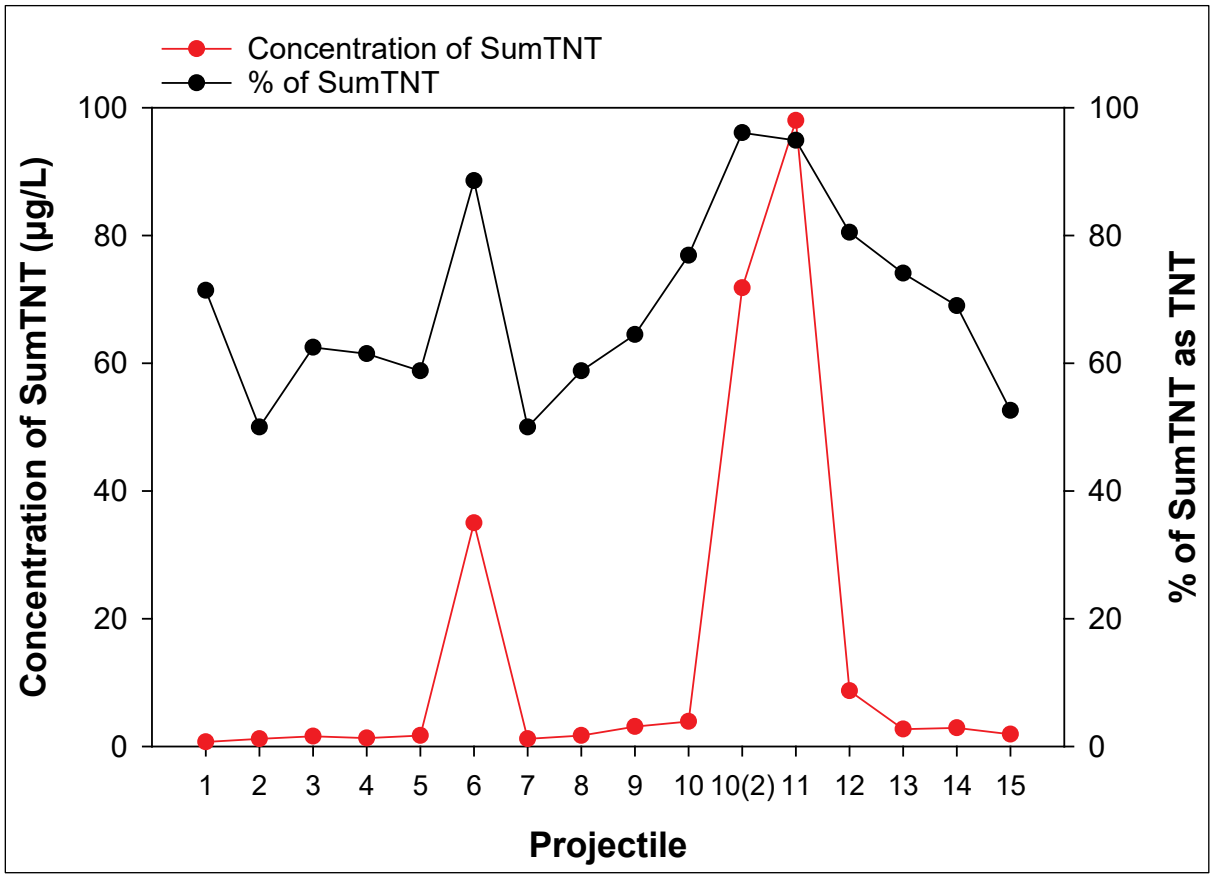

Figure 6. Concentrations of SumTNT and the percentage of the SumTNT concentration corresponding to TNT in water samples taken during processing of TNT field projectiles.

DISCUSSION: The SumTNT concentration plotted against time is shown in Figure 7. The observed increase in concentration for projectile 6 was caused by a brief (less than 10 s) leak of washout effluent when the capture-pump check valves failed during washout. When a check valve fails, the pump loses its ability to move fluid through it. As a result, the high-pressure water used during washout accumulates inside the boot, raising its pressure. The washout process and capture

pump were immediately stopped when the leakage was noticed. The capture-pump check valves failed again during the washout of projectile 10. The Underwater Cut-and-Capture System was retrieved, and the check valves were replaced. The concentration spike observed for the rewash of projectile 10 may have been due to external contamination of the capture pump that occurred during check-valve replacement; the pump was heavily contaminated internally with TNT and could have been transferred to the exterior of the pump and associated plumbing. It is also likely this contamination could have carried over to the processing of the next projectile since no leaks were observed during the processing of projectile 11.

From Figure 7 it is apparent that successful processing of TNT-filled HE M1 projectiles resulted in SumTNT concentrations in the surrounding water ranging from approximately 1 to 10 µg/L, and concentrations up to approximately 100 µg/L were measured when system failures temporarily increased the release of the washout.

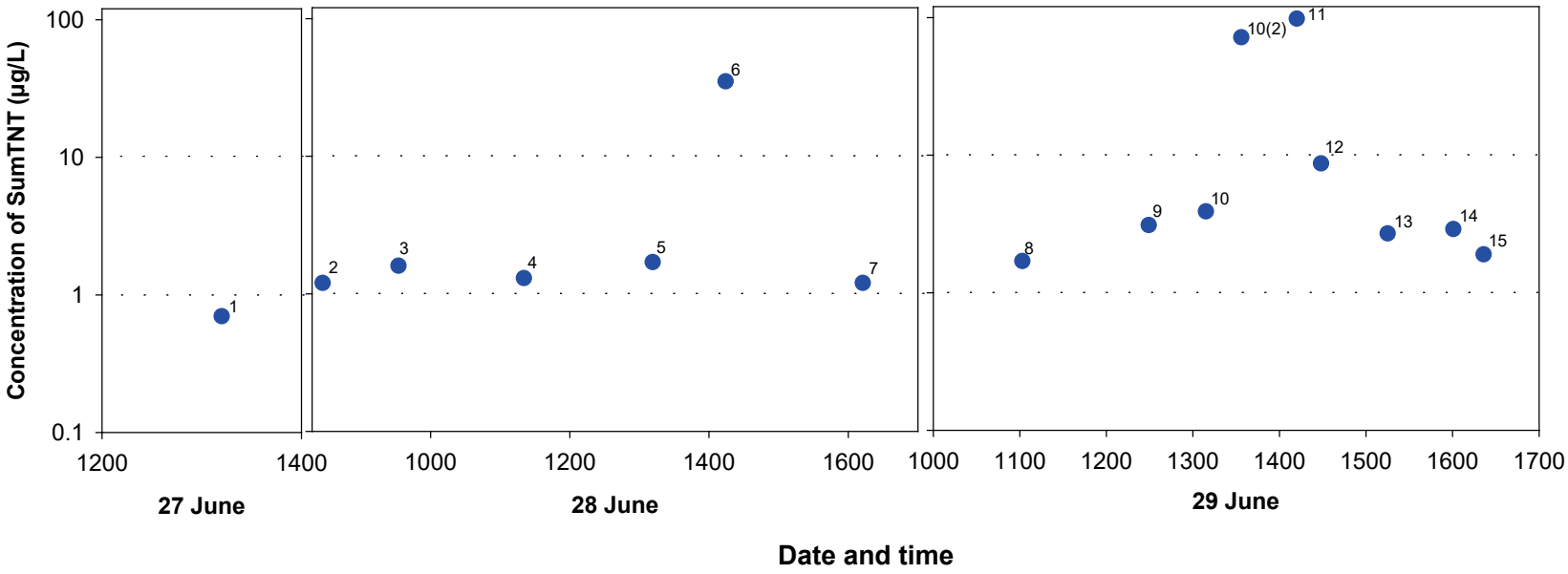

Figure 7. Concentration of SumTNT in water samples taken during processing of TNT-filled projectiles along time. Each data point represents the sampling event of a projectile. The project time number is shown next to each data point. The data point 10(2) indicates the rewash of projectile 10 to remove remaining TNT. No munitions constituents (MC) were detected in the sample taken prior to processing on munitions to assess background contamination.

CONCLUSION: The sampling methodology for using pumps has been proved as effective in monitoring contamination associated with in situ demilitarization of UWMM using high-pressure-water-jet technology. The sampling methodology is adaptable and effective for monitoring modified versions of the high-pressure water-jet technology. The concentration of MC in the water during demilitarization of munitions in this demonstration was overall low (for example, 1 to 10 µg/L), but orders-of-magnitude increases were reported when system failures temporarily increased the release of the washout.

ADDITIONAL INFORMATION: This technical note was developed under the Environmental Quality and Technology (VEQT) program. The program manager is Mr. John Ballard, and the technical director is Dr. Elizabeth Ferguson. For additional information on this technical note, contact Dr. Guilherme Lotufo, guilherme.lotufo@usace.army.mil, (601) 634-4103 or the authors as listed below:

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