



Metal Content of Ocean Sediment in Support of UXO Clearance – HMS Raleigh: Second Round

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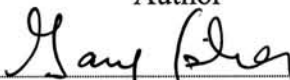
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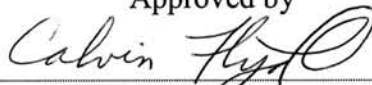
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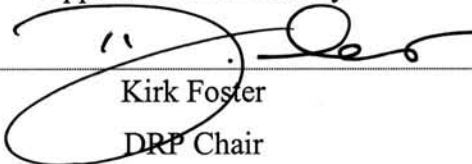
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Abstract

The wreck of the HMS RALEIGH in 1922 resulted in the dispersal of various unexploded ordnance (UXO) in shallow water 15 metres off the coast of Pointe Amour, Newfoundland. The risk posed by the UXO to nearby residents and recreational divers was considered unacceptable and therefore some remediation method was sought. Various studies indicated that the safest remediation method was on-site underwater detonation. However, it was recognized that on-site detonation could pose some environmental risks from release of energetic and metallic constituents into the ocean water and sediments. This report describes the results of a second round of UXO detonation and sediment sampling undertaken in support of UXO clearance operations for the HMS RALEIGH site. It was found that the concentration of copper, phosphorus and strontium in sediment did increase as a result of the UXO disposal activity. Conversely, the concentrations of molybdenum and tin in the ocean sediment were found to decrease.

Résumé

Le naufrage du HMS RALEIGH en 1922 a entraîné la dispersion de diverses munitions explosives non explosées (UXO) dans des eaux peu profondes à 15 mètres de la côte à Pointe Amour (Terre-Neuve). On a cherché à déterminer quelles mesures pourraient être mises en oeuvre pour remédier à la situation, car le risque que constituent ces UXO pour les personnes qui habitent à proximité et pour celles qui font de la plongée récréative a été jugé inacceptable. Selon les résultats de diverses études, la détonation de ces munitions directement sur place, c'est-à-dire dans leur milieu sous-marin, constituerait la méthode la plus sûre. Toutefois, on a reconnu que la détonation directement sur place pourrait comporter certains risques pour l'environnement, en raison du rejet de constituants énergétiques et métalliques dans les sédiments et les eaux océaniques. Dans ce rapport, on présente les résultats d'une seconde série de détonations de UXO et de prélèvements de sédiments, entreprise en appui aux opérations d'élimination des UXO au site du naufrage du HMS RALEIGH. Nous avons constaté que les concentrations de cuivre, de phosphore et de strontium dans les sédiments augmentaient à la suite de ces opérations d'élimination. Par contre, les concentrations de molybdène et d'étain dans les sédiments diminuaient.

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Executive summary

Background: In 1922 the British munitions ship, HMS RALEIGH, sank about 15 metres off Pointe Amour, Newfoundland. The wreck spread unexploded ordnance (UXO) over an area of about 200 x 50 m at water depths ranging from 5 to 9 m in Forteau Bay. Various remediation options were investigated and it was concluded that the best approach was on-site detonation of the UXO. It was recognized that on-site detonation could pose some environmental risks from release of energetic and metallic constituents into the ocean water and sediments. This report describes the results of a second round of UXO detonation and sediment sampling undertaken in support of UXO clearance operations for the HMS RALEIGH site.

Principal Results: The wreck site was divided into a 3x3 grid for sampling purposes. Sediment samples were collected from each point in the grid prior to and after detonation.

The analytical results further indicated that the concentrations of some metals in sediment at the wreck site increased as a result of the UXO detonation. The elements whose concentration increased were copper, phosphorus and strontium. Further, the concentration of molybdenum and tin was found to decrease in wreck site sediments.

The increase in copper concentration may be related to further degradation of metallic materials containing this element as a result of the detonation activity. The changes in concentrations of the other elements are more likely related to re-distribution of localized or stratified elemental concentrations in sediments near the wreck site.

Significance of Results: The on-site detonation of UXO from HMS RALEIGH did change the concentration of some metals in area sediments. While it is beyond the scope of this report to comment on the environmental implications, if any, of these findings, it would seem logical that the observed increase in copper concentration would be of the most concern due to its potential toxicity to marine life. However, given the danger posed by the UXO to residents on the shore of Forteau Bay, the release of a relatively small amount of copper into a large marine ecosystem seems a small price to pay.

Sommaire

Introduction : En 1922, le navire britannique HMS RALEIGH, qui transportait des munitions, sombra à environ 15 mètres au large de Pointe Amour, à Terre-Neuve, en parsemant de munitions explosives non explosées (UXO) une zone d'environ 200 x 50 m à une profondeur allant de 5 à 9 m dans la baie Forteau. Plusieurs options ont été envisagées pour remédier à la situation, et il a été convenu que la détonation directement sur place des UXO constituait la meilleure méthode. On a reconnu que la détonation sur place pourrait comporter certains risques pour l'environnement, en raison du rejet de constituants énergétiques et métalliques dans les sédiments et les eaux océaniques. Dans ce rapport, on présente les résultats d'une seconde série de détonations de UXO et de prélèvements de sédiments, entreprise en appui aux opérations d'élimination des UXO au site du naufrage du HMS RALEIGH.

Résultats : En prévision des prélèvements, le site du naufrage a été quadrillé en une grille de 3x3. Des échantillons de sédiments ont été prélevés à chaque point de la grille, avant et après la détonation des munitions.

Les résultats d'analyse ont indiqué que les concentrations de certains métaux dans les sédiments au site du naufrage avaient augmenté à la suite de la détonation des UXO. Les concentrations de cuivre, de phosphore et de strontium avaient augmenté, tandis que les concentrations de molybdène et d'étain avaient diminué.

L'augmentation de la concentration de cuivre peut être reliée à la dégradation ultérieure de matériaux métalliques contenant cet élément, provoquée par les opérations d'élimination. Chez les autres éléments, les variations de concentration sont probablement davantage le résultat de la redistribution des concentrations locales ou stratifiées des éléments dans les sédiments à proximité du site du naufrage.

Portée : La concentration de certains métaux dans les sédiments de cette zone a changé en raison de la détonation directement sur place des UXO provenant du HMS RALEIGH. Tout commentaire portant sur les conséquences environnementales des constatations faites au cours de cette étude dépasserait le cadre de ce rapport; néanmoins, c'est la hausse de concentration de cuivre qui, logiquement, devrait susciter le plus d'inquiétude, en raison du risque de toxicité pour la flore et la faune marines qu'elle comporte. Toutefois, étant donné les risques que comportent les UXO pour les personnes qui habitent le long de la côte de la baie Forteau, le rejet d'une quantité relativement faible de cuivre dans un vaste écosystème marin ne représente qu'un faible tribut à payer.

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1. Introduction

In 1922 the British munitions ship, HMS RALEIGH, sank about 15 metres off Pointe Amour, Newfoundland. The wreck spread unexploded ordnance (UXO) over an area of about 200 x 50 m at water depths ranging from 5 to 9 m in Forteau Bay. Over time some of this UXO began to wash ashore, an obvious safety concern that needed to be addressed.

Removal of the UXO to an on-shore site for detonation and disposal was deemed too dangerous for Explosive Ordnance Disposal (EOD) personnel, as it was feared that pressure changes incurred by raising UXO to the surface would cause detonation. Therefore an alternate plan was developed whereby the UXO would be detonated underwater.

A UXO clearance operation was completed in Spring 2003. While the safety of EOD personnel necessitated on-site UXO clearance, it was recognized that the operation posed some environmental risk due to the release of energetic and metallic constituents into ocean sediments. Thus, a monitoring program was undertaken in which the elemental content of sediment at the site was compared before and after detonation rounds. The results of this program were reported at Reference 1 and indicated statistically significant increases of some elements. These increases were attributed to degradation of metallic materials deposited in the area as a result of the sinking of HMS RALEIGH and disturbance of the mineralogical content of surficial sediments.

This report details the results of a second UXO clearance operation completed in Forteau Bay in June 2004.

2. Procedures and Equipment

The HMS RALEIGH UXO detonation zone (wreck site) was divided into a 3x3 grid, as indicated below:

A	B	C
D	E	F
G	H	I

Sediment was sampled from each point in the grid before and after UXO detonation. It should be noted that the size of the grid was not known in advance and was, to some extent, irrelevant. The actual size was determined onsite and was dependent on UXO distribution. In effect, the purpose of the grid was to have a statistically significant number of samples (in this case 9) collected from the site before and after UXO detonation.

All samples were collected by FDU(A) divers into new, unused wide-mouth borosilicate 250 mL jars. The samples were collected by scooping sediment into the jar from the vicinity of the appropriate grid location. GPS coordinates were taken for each sample location.

Each sample was labelled using the following scheme: **X-Y**, where:

X - indicates the timing of the sample (**B** = before detonation and **C** = after detonation); and,

Y – indicates location within the 3x3 grid.

As soon as possible after collection, each sample was prepared and stored for analysis in accordance with ASTM D3976. [2]

Due to the presence of a rocky bottom at the wreck site, all samples consisted primarily of water with relatively little sediment. Therefore each sample was filtered through weighed Whatman 41 filter paper and dried for 24 hours at 110°C. The filter paper and sediment were then digested in a hot nitric-hydrochloric acid mixture for several hours, in accordance with ASTM D3974 Digestion Practice A. [3] A test blank, consisting of a Whatman 41 filter paper through which 100 mL of distilled water had been filtered, was also treated in the same manner and carried through all subsequent analyses. Note that insufficient sediment was present in sample BG to permit analysis.

After digestion, each sample was transferred to a 50 mL volumetric flask and diluted to the mark with distilled water. Each sample was then analyzed for metal content using

a Liberty Series II (Varian Ltd.) inductively coupled plasma – atomic emission spectrometer (ICP-AES). Instrument parameters are detailed in Table 1.

Emission lines for each analyzed element were selected on the basis of sensitivity and lack of interfering lines from other elements. Analysis parameters for each line were selected to minimize detection limits (maximize signal-to-background ratio) and are detailed in Table 2.

Table 1. ICP-AES instrument parameters

PARAMETER	VALUE
Plasma gas rate	15 L/min
Auxiliary gas rate	1.5 L/min
PMT Voltage	650 V
Sample pump rate	15 rpm
Sample uptake delay	30 sec
Sample rinse time	10 sec

Table 2. *Element line parameters*

ELEMENT	WAVELENGTH (nm)	RF POWER (KW)	VIEWING HEIGHT (mm)
Aluminum	396.152	1.00	10
Antimony	217.581	1.50	16
Arsenic	228.812	1.50	11
Barium	493.409	1.00	23
Beryllium	234.861	1.50	15
Bismuth	190.178	1.50	15
Boron	208.959	1.50	10
Cadmium	228.802	1.50	8
Chromium	267.716	1.50	10
Cobalt	228.616	1.50	10
Copper	324.754	1.00	10
Iron	258.588	1.50	10
Lead	220.353	1.50	10
Manganese	257.610	1.50	10
Mercury	194.163	1.50	12
Molybdenum	202.030	1.50	10
Nickel	231.604	1.50	10
Phosphorus	213.618	1.50	10
Silicon	251.611	1.00	10
Silver	328.068	1.00	14
Strontium	421.552	1.00	17
Tin	189.926	1.50	10
Titanium	368.520	1.00	9
Uranium	385.958	1.00	16
Vanadium	290.882	1.50	14
Zinc	213.856	1.50	10

3. Results and Discussion

The results of all sediment analyses are detailed in Annex A. Note that values are not shown for the test blank run along with the samples. This is because the determined values for all analyzed elements in the test blank were either below the detection limit or were less than 0.1% of the observed sediment values.

3.1 Effect of UXO Detonation

Comparison of metal concentrations on a point-by-point basis within the detonation zone grid is difficult to interpret due to the high variability of the results. To simplify matters, mean values of element concentration in the entire detonation zone grid were utilized. (To calculate these means, responses of “not detected” were interpreted as zero.) The mean concentrations are shown in Table 3.

Direct comparison of the mean concentrations before and after detonation appears to indicate that some elements increased in concentration while others decreased or remained constant. However, the previously noted high variability of the concentration results suggests that these apparent changes may not be statistically valid. Thus, to clarify matters, a two-sided t-test was used to determine whether there was a statistically significant difference between the “before” and “after” means for each element.

The elements for which a statistically significant difference in mean concentrations at a 95% confidence level was found were copper, molybdenum, phosphorus, strontium and tin. The mean concentration of three of these elements (Cu, P and Sr) were found to increase in the samples taken after detonation whereas the Mo and Sn concentrations decreased.

The elemental content of ocean sediment in the vicinity of a wreck site can be attributed to two main factors: the composition of the surficial sediment in the area and contributions from degradation/corrosion of materials (primarily metallic) strewn about the vicinity during the wreck. UXO clearance operations involving on-site detonation could reasonably be expected to alter sediment composition in three ways. Firstly, the force released during the detonation could be expected to cause further degradation of nearby metallic materials. This would have the effect of increasing the concentration of these metals in the sediment. Secondly, the energy released during detonation would re-distribute elemental components throughout the affected area. If sediment composition was stratified or localized, average concentrations could be raised for some elements and lowered for others. For example, if the surficial sediment contained an elevated concentration of a particular metallic element (perhaps, due to degradation of materials from the wreck), the re-distribution of the sediment during detonation may cause that elemental concentration to lower due to mixing of the surficial sediments with underlying materials. Conversely, other elemental concentrations may increase as a result of the same mixing effect or by destruction of

natural features, such as small rocks and pebbles. Lastly, the detonation process itself may introduce new or elevated concentrations of some materials into the environment. This last factor is not expected to play a significant factor for inorganic elements due to the use of plastic explosives in this operation.

The observed increase in Cu concentration seems likely to have been caused by degradation of copper materials from the wreck. As copper is routinely used in engineering materials (particularly in items such as shell casings), this result is not unexpected and was, in fact, also found to occur in the first round. [1] A similar argument could be made for the observed increase in P concentration, although the possibility that sediment mixing played a role can not be discounted.

The observed changes in Mo, Sn and Sr concentrations are likely attributable to sediment mixing. For example, examination of the full results detailed in Annex A indicate that prior to the detonation cycle Mo was below detection limit in 3 of the 8 samples. While the detection limit varies in proportion to the amount of sediment sampled, it can safely be assumed to be 1 ppm for molybdenum. The 5 samples in which Mo was detected prior to detonation generally contained a concentration an order of magnitude higher than this lower limit. This strongly suggests localized elevated levels of molybdenum were present in the sediment prior to detonation. None of the 9 samples taken after detonation contained a detectable level of molybdenum, suggesting that the localized concentrations had become more evenly distributed. Similar arguments can be made to explain the changes observed in the Sn and Sr concentrations.

Table 3. Mean metal concentration over detonation zone grid.

ELEMENT	CONCENTRATION (PPM)	
	BEFORE	AFTER
Aluminum	3950	3620
Antimony	100	300
Arsenic	130	230
Barium	151	86
Beryllium	3.0	6
Bismuth	20	150
Boron	65	59
Cadmium	0.4	1.0
Chromium	50	70
Cobalt	10	17
Copper	270	560
Iron	175,000	215,000
Lead	760	1500
Manganese	740	880
Mercury	0	0
Molybdenum	10	0
Nickel	80	160
Phosphorus	900	1600
Silicon	3230	2810
Silver	0	0
Strontium	60	140
Tin	2800	310
Titanium	110	80
Uranium	0	0
Vanadium	50	60
Zinc	210	360

4. Conclusions

The detonation of UXO from the HMS RALEIGH wreck caused a statistically significant increase in the concentration of copper, phosphorus and strontium in nearby sediments. Conversely, the concentration of molybdenum and tin was found to decrease after UXO detonation.

While it is beyond the scope of this report to comment on the environmental implications, if any, of these findings, it would seem logical that the observed increase in copper concentration would be of the most concern due to its potential toxicity to marine life. However, given the danger posed by the UXO to residents on the shore of Forteau Bay, the release of a relatively small amount of copper into a large marine ecosystem seems a small price to pay.

5. References

1. Fisher, G., "Metal Content of Ocean Sediment in Support of UXO Clearance – HMS Raleigh", DRDC Atlantic Technical Memorandum 2003-154, December 2003.
2. ASTM D3976-92, Standard Practice for Preparation of Sediment Samples for Chemical Analysis, ASTM, West Conshocken, Pa., 2000.
3. ASTM D3974-81, Standard Practices for Extraction of Trace Elements from Sediments, ASTM, West Conshocken, Pa., 2000.

Annex A

SAMPLE	CONCENTRATION (PPM)																									
	BEFORE DETONATION																									
	Ag	Al	As	B	Ba	Be	Bi	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Ni	P	Pb	Sb	Si	Sn	Sr	Ti	U	V	Zn
BA	ND	3330	220	36	117	8	ND	ND	5	33	430	179k	ND	918	ND	71	1700	1100	ND	4310	400	69	130	ND	67	364
BB	ND	3260	120	61	93	4	ND	ND	2	32	157	159k	ND	767	ND	84	1300	620	220	1970	330	16	93	ND	51	141
BC	ND	11,100	430	79	120	12	ND	0.04	39	203	449	343k	ND	1110	ND	253	1300	260	540	2320	1300	14	32	ND	100	59
BD	ND	4140	39	71	195	ND	ND	0.2	6	22	118	92k	ND	677	13	20	630	450	3	6760	1400	82	188	ND	33	137
BE	ND	2930	71	93	485	ND	57	2.1	11	54	188	197k	ND	718	22	80	620	2100	34	4080	3100	80	115	ND	43	563
BF	ND	2150	33	41	63	ND	17	1.1	4	13	231	94k	ND	516	8	21	520	360	9	1930	4700	73	106	ND	27	81
BH	0.2	2550	56	75	89	ND	26	0.09	7	20	421	194k	ND	585	20	41	620	850	10	2460	9000	53	95	ND	42	172
BI	0.4	2100	45	61	50	ND	46	0.02	7	22	176	144k	ND	636	13	44	560	300	16	2010	2100	56	97	ND	31	125

ND = not detected; k = thousand

Annex A (cont.)

SAMPLE	CONCENTRATION (PPM)																										
	AFTER DETONATION																										
	Ag	Al	As	B	Ba	Be	Bi	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Ni	P	Pb	Sb	Si	Sn	Sr	Ti	U	V	Zn	
CA	ND	2010	120	83	201	4	ND	2	17	71	717	261k	ND	989	ND	120	1500	3900	220	2550	89	206	65	ND	59	991	
CB	ND	3830	590	62	5	15	560	ND	18	71	362	188k	ND	630	ND	320	2800	330	700	3980	74	285	59	ND	55	120	
CC	ND	2620	13	35	53	ND	110	ND	4	22	165	87k	ND	638	ND	25	1200	510	99	1630	97	132	114	ND	30	142	
CD	ND	2840	120	69	160	4	ND	2	18	88	747	224k	ND	945	ND	110	1500	2000	ND	3120	110	119	94	ND	83	574	
CE	ND	2910	280	84	41	ND	200	3	29	105	695	293k	ND	1140	ND	210	1400	1500	300	3160	3	201	89	ND	68	536	
CF	ND	2360	290	66	36	10	330	ND	25	94	755	249k	ND	910	ND	190	1400	710	370	3680	110	195	53	ND	56	221	
CG	ND	4920	280	ND	96	15	120	ND	2	65	271	178k	ND	619	ND	190	1100	960	670	2470	ND	53	58	ND	90	159	
CH	ND	9010	230	84	80	ND	3	ND	34	90	1120	292k	ND	1180	ND	280	1800	2600	140	2360	2300	85	83	ND	90	254	
CI	ND	2150	130	50	105	3	ND	1	7	28	180	159k	ND	902	ND	48	1500	890	140	2360	ND	10	91	ND	48	212	

ND = not detected; k = thousand

List of symbols/abbreviations/acronyms/initialisms

ASTM	American Society for the Testing of Materials
DND	Department of National Defence
EOD	Explosive Ordnance Disposal
FDU(A)	Fleet Diving Unit (Atlantic)
gm	Gram
ICP-AES	Inductively coupled plasma – atomic emission spectroscopy
KW	Kilowatt
L/min	Litres per minute
mm	Millimetre
nm	Nanometre
ppm	Parts per million
rpm	Revolutions per minute
Sec	Second
UXO	Unexploded ordnance
V	volt

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The wreck of the HMS RALEIGH in 1922 resulted in the dispersal of various unexploded ordnance (UXO) in shallow water 15 metres off the coast of Pointe Amour, Newfoundland. The risk posed by the UXO to nearby residents and recreational divers was considered unacceptable and therefore some remediation method was sought. Various studies indicated that the safest remediation method was on-site underwater detonation. However, it was recognized that on-site detonation could pose some environmental risks from release of energetic and metallic constituents into the ocean water and sediments. This report describes the results of a second round of UXO detonation and sediment sampling undertaken in support of UXO clearance operations for the HMS RALEIGH site. It was found that the concentration of copper, phosphorus and strontium in sediment did increase as a result of the UXO disposal activity. Conversely, the concentrations of molybdenum and tin in the ocean sediment were found to decrease. (U)

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UXO, unexploded ordnance, HMS RALEIGH, clearance

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