

## Article



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# Identification of novel degradation products of sea-dumped chemical warfare agent-related phenylarsenic chemicals in marine sediment

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ABSTRACT: Previously unknown phenylarsenic chemicals originated from chemical warfare agents (CWAs) have been detected and identified in sediment samples collected from the vicinity of chemical munition dumpsites. Non-targeted screening by ultra-high performance liquid chromatography-high-resolution mass spectrometry (UHPLC-HRMS) was used for detection of 14 unknown CWA-related phenylarsenic chemicals. Methylated form of Clark I/II, Adamsite and phenyldichloroarsine were detected in all analysed sediment samples and their identification was based on synthesized chemicals. In addition, other previously unknown CWArelated phenylarsenic chemicals were detected and their structures were elucidated using MS/HRMS technique. Based on relative isotope ratios of protonated molecules and measures exact masses of formed fragment ions, it could be concluded that some of these unknown chemicals contained sulfur atom attached to arsenic atom. Addition to that, some of the samples contained chemicals which had formed via addition of OH-group to the aromatic ring. Yet it's not possible to say how these chemicals are formed, but the most plausible cause is activities of marine microbes in sediment. To our knowledge, these chemicals have not been detected from sediment samples previously. Sensitive analytical methods are needed for these novel chemicals to assess the total CWA burden in marine sediments and this information is essential for the risk assessment.

Recently, abandoned chemical weapons (CWs) containing toxic chemical warfare agents (CWAs) manufactured during World Wars (WWs) have raised concern not only for the environmental, but also for safety reasons. Until the 1970's, chemical munitions and containers filled with CWAs were disposed worldwide mainly by sea-dumping, and some countries were trying get rid of these toxic chemicals by burying them in the ground soil.<sup>1</sup> Huge dumping operations took place in the Baltic Sea area and Skagerrak Strait, where the load of dumped chemical weapons were approximately 50,000 and 170,000 tons, respectively.<sup>2</sup> These dumping operations were adopted all around Europe; Japanese, North-American coastal areas and Pacific Ocean were also loaded with chemical munitions. It has been estimated that the total amount of chemicals munitions dumped into seas and oceans is as high as 1 million tons including CWAs produced during WWs and post-war period.<sup>1</sup> In the Baltic Sea area dumped munitions contain mainly sulfur mustard and phenylarsenic CWAs, such as Clark I and II (DA and DC), and Adamsite (DM). Furthermore, technical Clark, so-called arsine oil, consisting of phenyldichloroarsine (Pfiffikus, PDCA), triphenylarsine (TPA), Clark I and arsenic trichloride (AsCl<sub>3</sub>), was dumped. Arsine oil is a tactical mixture and it was used as an additive in sulfur mustard to lower its freezing point. Structures of these CWA-related phenylarsenic chemicals are shown in Figure 1.





Several investigations dealing with identification, determination of exact location sites and corrosion stages of dumped warfare objects have been accomplished during the last two decades. Based on the information gained from several sediment monitoring campaigns the Baltic Sea area and Skagerrak it has been clearly demonstrated that corroded ammunitions are leaking into marine environment causing risk to marine ecosystem.<sup>1,3</sup> Moreover, it has been proven that these CWAs are uptaken by different marine biota species.<sup>4,5</sup>

All previous sediment monitoring campaigns in the Baltic Sea and Skagerrak areas have focused on analyzing intact CWAs and their known primary degradation products either by gas chromatography-electron impact (tandem) mass spectrometry (GC-EI/MS, GC-MS/MS) or liquid chromatography tandem mass spectrometry (LC-MS/MS).<sup>6–8</sup> The structures of known primary degradation products of sea-dumped phenylarsenic CWAs are presented in Figure 2. These degradation products are known to be formed via hydrolysis and subsequent oxidation reactions in the water environment.<sup>6,9</sup>



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Figure 2. Primary degradation products of sea-dumped CWAs: diphenylarsinine acid, DPA (1), phenarsazinic acid (2), phenylarsonic acid, PAA (3), and triphenylarsine oxide, TPAO (4)

According to the latest published study, 31% of the sediment samples collected near the CW dumping areas, contained at least one of the target CWA compounds.<sup>7</sup> For example concentrations such as 210, 1300, and 41 µg/kg dried sediment were detected by LC-MS/MS for phenarsazinic acid, diphenylarsinic acid (DPA), and phenylarsonic acid (PAA), respectively. Results obtained during EU BSR Project DAIMON (www.daimonproject.com) in 2019, showed that the CWA pollution level in some sampling sites in Bornholm deep was as high as 55, 2000, and 5700 µg/kg dried sediment analysed by LC-MS/MS for phenarsazinic acid, DPA, and PAA, respectively.<sup>10</sup> Similar results have been obtained from Skagerrak area: 1100 mg/kg from dried sediment for propanethiol derivatives of Clark I and PDCA analysed by GC-EI/MS.<sup>8</sup>

Kizaki area in Japan is one of those areas where CWs containing phenylarsenic chemicals were buried in the ground soil. In 2002 people started to get serious central nervous system symptoms after drinking contaminated well-water.<sup>11</sup> Graphite furnace atomic absorption spectrometry (AAS) analysis revealed that arsenic level in well-water was 450-times higher than recommendations of World Health Organization (WHO).12 Further investigations based on GC-MS and inductively coupled plasma mass spectrometry (ICP/MS) demonstrated that the source of elevated arsenic concentrations was degradation products of arsenic-containing CWAs such as DPA, PAA (See Figure 2) and bis(diphenyl)arsine oxide (BDPAO) originated from CWs buried in the soil.<sup>12</sup> BDPAO is a dimerized degradation product of Clark I/II.9 Soil samples taken in Kizaki area showed contamination with these chemicals and furthermore, methylphenylarsinic acid (MPAA), oxide (DMPAO) dimethylphenylarsine and methyldiphenylarsine oxide (MDPAO) were detected.13 Structures of these methylated degradation products of CWAs are presented in Figure 3.



Figure 3. Methylated degradation products of CWAs: methylphenylarsinic acid, MPAA (1), dimethylphenylarsine oxide, DMPAO (2), and methyldiphenylarsine oxide, MDPAO (3)

It has been suggested that these methylated phenylarsenicals are formed by bacteria under anaerobic conditions.<sup>14,15</sup> Unlike in the water environment, the behaviour of these chemicals in terrestrial environment have been studied to some extent. Transformation of DPA was investigated in the soil cultures under sulfate-reducing conditions.<sup>16</sup> After 5-week incubation samples were analysed by LC-ICP/MS showing that DPA was decomposed into arsenate, PAA, MPAA, and MDPAO. Moreover, three unknown metabolites were detected but not identified. These unknowns were eluted after DPA when C18 column was used suggesting that metabolites have more hydrophobic nature compared to DPA. A paper published a year later demonstrated the identification of the major metabolite formed in soil cultures spiked with DPA.<sup>17</sup> Time-of-flight highresolution mass spectrometry (TOF-HRMS) was utilized for obtaining the exact mass and proposed elemental composition for detected degradation product. In HRMS spectrum, a peaks at m/z 260.97179 with the elemental composition of  $C_{12}H_{12}AsSO$  was detected. This suggested that ion at m/z 279 is a protonated molecule ion of diphenylthioarsinic acid, but further structure elucidation of detected metabolite wasn't enable by TOF-MS.

In this paper, we describe identification of previously unknown degradation products originated from sea-dumped CWAs based on synthesized chemicals and Orbitrap high-resolution mass spectrometry (OT-HRMS) measurements. Selected marine sediment samples were analysed using non-targeted screening method in order to investigate whether unknown phenylarsenic chemicals originated from CWAs are existing in sediments. These samples were previously analyzed quantitatively for known primary degradation products of CWA-related phenylarsenic chemicals containing high concentrations of target chemicals (see Figure 2). OT-HRMS was utilized for detection and identification of unknowns. High-resolving power and high mass accuracy provided by OT-HRMS enables screening and identification of unknown chemicals without reference standard from complex matrix, such as marine sediment.

By this far, the investigations has focused only intact seadumped chemicals and their known primary degradation products. To estimate the total CWA burden in the sea bed, information provided in this study is crucial. To our knowledge, there are no previous published studies on methylated, sulfurcontaining, and hydroxylated degradation products of phenylarsenic CWAs in marine sediment. In addition, this is first time that these chemicals have been detected and identified in any sediment samples.

#### EXPERIMENTAL SECTION

**Chemicals and reagents** PDCA, DM and DA were synthesized at Finnish Institute for Verification of the Chemical Weapons Convention. Methanol (MeOH) (LC-MS grade) and acetonitrile (ACN) (HPLC grade) used in sample pre-treatment and tetrahydrofuran (THF9 (HPLC grade) were obtained from VWR International (Belgium) and Merck Group (Germany), respectively. ACN and formic acid (FA) (both LC-MS grade) was purchased from Merck and hydrogen peroxide (33 %) was obtained from VWR International. Methyl lithium (MeLi) (99 %) was obtained from Sigma Aldrich. Water was purified using a Direct-Q3 UV system (Millipore, Germany).

**Sediment samples** Samples containing high concentrations of phenylarsenic CWAs collected during the previous international projects dealing with marine munitions (CHEMSEA, MODUM and DAIMON projects) were selected for non-targeted screening by UHPLC-HRMS. The list of the current target phenylarsenic CWA chemicals<sup>18</sup> is presented in Supporting information (Table S-1) and the concentrations of

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target chemicals in these sediment samples are given in Supporting information (Table S-2). Sediment samples collected from area were no CWA contamination has occurred were also analysed as matrix blanks. The samples were shipped frozen on dry ice and stored at -20 °C prior to reanalysis.

Sample preparation Sediment samples were prepared according to "Recommended Procedures for Sampling and Analysis in Verification of Chemical Disarmament" (ROP).<sup>18</sup> In generally, sample preparation consisted of removal of pore water, extraction with ACN, filtration, and solvent exchange (H2O/MeOH, 50:50, v/v) steps. The sample pre-treatment 10 controls were done by spiking DA, DM, and TPA in blank 11 sediment.

UHPLC-HRMS analysis The UHPLC-HRMS analysis were 13 performed on Thermo Scientific Orbitrap Fusion mass 14 spectrometer (San Jose, USA) connected to Thermo Scientific 15 Dionex Ultimate 3000 ultra-high performance liquid 16 chromatograph (Germering, Germany).

17 UHPLC separation was done using Waters XBridge BEH C18 18 column (2.1 x 50 mm, 1.7 µm) at 40 °C using a linear gradient 19 of two mobile phases: 0.1 % FA in water (A) and 0.1 % FA in 20 ACN (B). The gradient was run from 5 % B at 0 min to 100 % 21 B at 2 min. After this the B eluent was kept 100% for 1 min and 22 at 5% for 2 min. The flow rate was 0.5 ml/min and the injection 23 volume was 5 µl.

The ionization was done using a heated electrospray (HESI) probe in the positive ion mode. The instrumental parameters were set as follows: spray voltage 3000 V, source temperature 300 °C, ion transfer tube temperature 350 °C, sheath gas 30, auxiliary gas 10 and sweep gas 0. Mass measurement in full scan mode was done with mass range m/z 60–600 using RF lens at 60% and quadrupole isolation (m/z 60–600) at resolution of 120,000. Mass accuracy of the instrument using external calibration was specified to be ≤ 3ppm. For MS/HRMS measurements higher-energy collisional dissociation (HCD) was used for induce the fragmentation of selected protonated molecule ions.

#### RESULT AND DISCUSSION

Analysis of sediment samples. All samples were analysed in full scan mode using non-targeted analysis. An example of total ion chromatogram (TIC) of a sediment sample is given in Supporting information (Figure S-1). Matrix blank samples (sediment extracts and solvent) were analysed before and after sediment samples analysis. No cross-contamination arose from sample pretreatment and no carry over occurred during instrumental analysis. Novel chemicals discussed in this paper were not detected in matrix blank sediment samples nor sample pre-treatment controls.

Identification of methylated phenylarsenic chemicals In full scan mode, unknown peaks were detected in sediment samples at *m/z* 199.01034, 274.02084 and 261.02562 with the elemental composition of C<sub>8</sub>H<sub>12</sub>OAs, C<sub>13</sub>H<sub>13</sub>ONAs and C<sub>13</sub>H<sub>14</sub>OAs, respectively. This strongly suggests that sediment samples contained DMPAO, 10-5H-PAO and MDPAO, respectively.

For reliable qualitative identification, methylated phenylarsenic chemicals were prepared using MeLi as a methyl group donor. Detailed synthesis procedure are described below for synthesized chemicals. Synthesis of MDPAO is presented in Scheme 1.



Scheme 1. Synthesis scheme for MDPAO

Methyldiphenylarsine oxide (MDPAO) 12.3 mg of Clark I (0.047 mmol) was dissolved in dry THF (0.5 mL) under argon atmosphere. 35 µL of MeLi was added through the septum and the reaction mixture was strirred for one hour at the room temperature. Reaction was stopped by adding 0.5 ml of water.

10-methyl-5H-phenarsazinine 10-oxide (10-M-5H-PAO) 14.5 mg of Adamsite (0.052 mmol) was dissolved in dry THF (0.5 mL) under argon atmosphere. 35 µL of MeLi was added through the septum and the reaction mixture was stirred for one hour at the room temperature. Reaction was stopped by adding 0.5 ml of water.

Dimethyl(phenyl)arsine oxide (DMPAO) 15.3 mg of PDCA (0.069 mmol) was dissolved in dry THF (0.5 mL) under argon atmosphere. 50 µL of MeLi was added through the septum and the reaction mixture was stirred for one hour at the room temperature. Reaction was stopped by adding 0.5 ml of water.

The synthesis products were used as an analytical standards after dilution.

The qualitative identification of the these methylated phenylarsenic compounds were based on criteria of the Organisation for the Prohibition of Chemical Weapons (OPCW).<sup>19</sup> In LC analysis, retention time of the identified compound shall not differ more than  $\pm 0.2$  min from reference standard sample (see Figure 4). For HRMS techniques, the elemental composition has to be obtained and the mass accuracy with a mass error must be below 2.5 parts per million (ppm).



Figure 4: UHPLC-HESI/HRMS total ion chromatograms for DMPAO, 10-M-5H-PAO and MDPAO in analytical standard (A) and sediment sample (B)

For further structure elucidation, HCD was used for generating fragments from protonated molecule ions of different methylated phenylarsenicals. Spectrometric parameters for different methylated phenyl arsenic chemicals are presented in Table 1.

Table 1. Mass spectrometric parameters used for the detection and characterization of methylated phenylarsenic chemicals

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Compound	Parent ion	HCD	scan range		
	[m/z]	[%]	[m/z]		
DMPAO	199	50	70-210		
10-M-5 <i>H</i> -PAO	274	40	70-300		
MDPAO	261	50	70-280		

MS/HRMS spectra for different methylated phenylarsenic chemicals detected in analytical standards and sediment sample are presented in Figure 5. MS/HRMS spectra A, C and E are presenting synthesized chemicals and spectra B, D and F are from original the sediment sample. The elemental composition of protonated molecules and formed fragments were found to match with the elemental compositions of protonated molecules and formed fragments of synthesized chemicals.

As seen in Figure 5, fragmentation of DMPAO (A and B), generates signals at m/z 168.96291 and 152.96805, fragmentation of 10-M-5H-PAO (C and D) generates signals at m/z 241.99458 and 167.07298, and fragmentation of MDPAO (E and F) generates signals at m/z 226.98369, 168.96283 and 154.07776. These fragments are generally known to be specific for PAA, phenarsazinic acid and DPA (see Figure 2), respectively. This indicates undisputable that these detected chemicals are originated from phenylarsenic CWAs. Determination of purity and concentrations of synthesized chemicals wasn't enabled in the framework of this study, therefore the quantitative analysis of methylated phenylarsenic chemicals in sediment samples wasn't possible. However, peak areas of these chemicals was compared to peak areas of primary degradation products found in same sediment sample. Even though the ionization efficiency of analytes with different chemical properties varies, the peak areas of methylated chemicals in some sediment samples are even higher than peak areas of current target chemicals. Data is shown in Supporting information (Figure S-2). 



Figure 5. MS/HRMS spectra for DMPAO in analytical standard (A) and sediment sample (B), 10-M-5*H*-PAO in analytical standard ((C) and sediment sample (D) and MDPAO in analytical standard ((E) and sediment sample (F)

Identification of sulfur containing phenylarsenic chemicals All analysed sediment samples contained unknown chemicals which didn't appear in TICs of blank sediment samples. Proposed structures for protonated molecule ions, their elemental compositions, measured masses, mass differences compared to theoretical masses, retention times, and relative abundance of isotope <sup>34</sup>S are presented in Table 2. The presence of distinct [M+H]<sup>++2</sup> peak for detected chemicals indicates that the structures of these chemicals contain one sulfur atom. In generally, the relative abundance of [M+H]<sup>++2</sup> peak of detected compounds varied from 3.79 to 4.4 %. Ratios of [M+H]<sup>+</sup> and [M+H]<sup>++2</sup> peaks strongly suggests that each compounds contained <sup>32</sup>S and <sup>34</sup>S isotopes, which is crucial for elemental composition elucidation.

Very likely polar properties of these phenylarsenic chemicals are decreasing when sulfur is attached to arsenic atom compared to their corresponding oxygen analogues (structures presented in Fig 2). This is seen in retention times: their elution out of C18 column is delayed 1.25-1.79 minutes compared to their oxygen containing analogues. The structure elucidation of these sulfurcontaining chemicals were done by MS/HRMS using different HCD energies. MS/HRMS spectra were recorded and the structures of formed fragments were elucidated based on measured mass. Proposed fragmentation pathways for methyldiphenylarsine sulfide, 10-methyl-5H-phenarsazinine sulfide, dimethylphenylarsine sulfide, and triphenylarsine sulfide are shown in Figure 6. Masses of the fragments presented in Figure 6 are theoretical and they all are present in spectra of corresponding novel compounds within mass accuracy of 1 ppm. TICs and MS/HRMS spectra for six detected sulfur-containing chemicals (see proposed structures in Table 2) are presented in Supporting Information (Figures S3-S7) and relative ion intensities for detected fragments are presented in Supporting Information (Table S3).

As seen in Figure 6, compounds that have analogous structures, form same fragments. This indicates very clearly, that structures of these chemicals are similar to each other. For example fragment with mass at m/z 151.96017 are generated from protonated molecules of dimethylphenylarsine sulfide and triphenylarsine sulfide (See Figure 6 C and D), which have analogous structures. Same fragment is generated from DPA, a primary degradation product of DA.

This further supports the assumption, that these sulfur-

containing chemicals are originated from CWAs. As in case of

methylated phenylarsenic chemicals, peak areas of sulfur-containing

chemicals were compared to peak areas of target chemicals found in same sediment sample. Data is shown in Supporting information (Figure S8-S9).

Table 2. Proposed structures of novel sulfur-containing phenylarsenic chemicals in sediment, corresponding elemental composition, measures masses, mass differences compared to theoretical values, retention times, and relative abundance of [M+H]<sup>+</sup>+2 ion

Proposed structure and elemental composition		Measured mass	Mass difference [ppm]	R <sub>t</sub> [min]	Relative abundance of [M+H] <sup>+</sup> +2 peak ( <sup>34</sup> S )*	
		PDCA-related	chemical			
$\overset{HS^{+}_{AS^{+}CH_{3}}}{\underset{CH_{3}}{\bigcup}}$ Dimetylpenylarsi ne sulfide	$C_8H_{12}AsS^+$	214.98701	0.02052	1.96	3.97 %	
	Α	damsite-relate	d chemicals			
HS, OH N 10-hydroxy-5 <i>H</i> - phenarsazinine- 10-acid	C <sub>12</sub> H <sub>11</sub> AsNOS <sup>+</sup>	291.97723	0.05111	2.57	4.44 %	
10-methyl-5 <i>H</i> - phenarsazinine- 10-sulfide	$C_{13}H_{13}AsNS^+$	289.99792	0.02315	2.92	4.16 %	
Clark-related chemicals						
Diphenylthiorsini c acid	$C_{12}H_{12}AsOS^+$	278.98196	0.10915	3.30	3.82 %	
Methyldiphenyla rsine sulfide	$C_{13}H_{14}AsS^{+}$	277.00275	0.07746	3.41	3.93 %	
Triphenylarsine-related chemical						
HS, <sup>AS</sup> Triphenylarsine sulfide	$C_{18}H_{16}AsS^+$	339.01842	0.30191	4.53	4.24 %	

\*Observed interval of  $^{34}\!\mathrm{S}$  isotope-abundance in natural material is 3.96-4.77  $\%^{20}$ 

Analytical Chemistry



Figure 6. Proposed structures for fragment ions in the MS/HRMS spectra of methyldiphenylarsine sulfide (A), 10-methyl-5*H*-phenarsazine-10-sulfide (B), dimethylphenylarsine sulfide (C), and triphenylarsine sulfide (D)

Identification of hydroxylated phenylarsenic chemicals. Addition to chemicals discussed previously, five unknown degradation products were detected. Based on measured masses of protonated molecules and retention times of detected chemicals, it was assumable that hydroxylation reactions have occurred on aromatic ring. Proposed structures for hydroxylated phenylarsenic chemicals, corresponding elemental compositions, measures masses, mass differences compared to theoretical values, and retention times are presented in Table 3.

Table 3. Proposed structures for hydroxylated phenylarsenic chemicals, corresponding elemental composition, measures masses, mass differences compared to theoretical values, and retention times

Proposed novel structure and elemental composition		Measured mass	Mass differen ce [ppm]	Rt [min]
но, он As H DM-OH	$C_{12}H_{13}AsNO_2^+$	291.99521	0.93012	1.17
но СН <sub>3</sub> М СН <sub>3</sub> ОН 10-М-5Н- РАО-ОН	$C_{13}H_{13}AsNO_2^+$	290.01562	0.18097	1.32
DPA-OH	$C_{12}H_{12}AsO_{3}^{+}$	278.99968	0.03547	1.57; 1.73
но <sup>+</sup> СН <sub>3</sub> МDPAO-OH	$C_{13}H_{14}AsO^+$	277.02040	0.09030	1.50; 1.64
	$C_{18}H_{16}AsO_2^+$	339.03594	0.40047	2.39; 2.52

For example, DPA, an abiotic degradation of Clark I/II and MDPAO identified in this study (see Figure 6) are seen in mass spectra at m/z 263.00046 and 261.02562, respectively. Two

Clark-type chemicals were detected with mass difference of 16 amu compared to protonated molecules of DPA and MDPAO, suggesting that addition of hydroxyl group have been occurred to aromatic ring. These protonated chemicals were detected at m/z 278.99968 and 277.02040. Retention times of these chemicals are decreased compared to DPA and MDPAO suggesting that these unknows are more hydrophilic. Based on measured masses, obtained elemental compositions and retention times, these chemicals are hydroxydiphenylarsinic acid (DPA-OH) and hydroxymethyldiphenylarsine oxide (MDPAO-OH). Extracted ion chromatograms (EICs) for DPA, DPA-OH, MDPAO, MDPAO-OH and HMRS spectra of DPA-OH and MDPAO-OH are presented in Figure 7. It is also noticed that both chemicals formed two isomers where hydroxylation have occurred on different position on the aromatic rings. This is seen in EICs (Figure 7) where two peaks are detected at 1.57 and 1.73 min for m/z 278,99968 and 1.50 and 1.64 min for m/z 277.02040, respectively. Same phenomenon was observed with hydroxytriphenylarsine oxide (TPAO-OH), but hydroxylated forms of Adamsite-related chemicals formed only one isomer.

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The more detailed structure elucidation was done by MS/HRMS for hydroxylated products of Clark- and TPA-related chemicals. HRMS spectra with identified fragment are presented in Supporting Information (Figures S11-S13).

100 A) DPA 100 HO OF 1.57 DPA-OH OF 100 HO ,CH₃ **MDPAO** 0-HO CH. MDPAO-OH 49 0.0 3.0 4.0 Time (min) 1.0 2.0 6.0 5.0 278.99972 C12H12O3As 100 B) 80 Abundance 60 Ne 40 Relati 20 300 m/z 100 200 400 500 600 277.02040 C13H14O2As 100 C) 259.04632 80 Relative Abundance 100 200 300 400 500 600 m/z

Figure 7. UHPLC–HESI/HRMS EICs for hydroxylated degradation products of Clark (A) and HRMS spectra for DPA-OH (B) and MDPAO-OH (C) in sediment sample

#### CONCLUSIONS

High mass accuracy provided by OT-HRMS decreases matrix background effects allowing reliable identification and exact molecular formula assignment for unknowns. When comparing to TOF-HRMS utilized in previously published study on identification of degradation products of CWA-related chemicals in soil samples, OT-HRMS enables more exact structure elucidation by fragmentation of protonated molecules using HCD providing detection of fragment ions at high resolution and mass accuracy.

Detected novel phenylarsenic chemicals discussed in this paper are originated from PDCA, DA, DM, and TPA, which are widely dumped at the sea bed in the Baltic Sea and Skagerrak areas. In the framework of this study, we weren't able to determine exact concentration of these identified CWA-related chemicals discussed in this paper. Comparing peak areas of identified phenylarsenic chemicals to peak area of target chemicals in the same sediment sample, we can assume that the concentration levels of methylated and sulfur-containing chemicals are at the same level or even higher. Due to lack of information, it's not possible to say for sure how these novel chemicals are formed. Methylated degradation products identified in this study are the same as have been previously detected from CWA contaminated soil which strongly indicates that formation is due to microbiological activities. To prove bacterial transformations of these phenylarsenic CWAs into detected chemicals identified in this study, elaborate research needs to carry out. If these transformations are resulting from bacterial activities in the sediment, some, or maybe even most of the intact phenylarsenic CWAs in the marine sediment will be transformed into methylated and sulfur-containing phenylarsenic chemicals over time and they can be further degrade in some yet unknown species.

Monitoring the sea floor quality is crucial for environmental risk assessment and furthermore maritime spatial planning. Increasing pressure for building wind power stations, underwater pipelines and cables require a survey of the condition of the seabed. These previously unknown chemicals identified in this study have significant role in the future when analysing concentrations of CWA-related phenylarsenic chemicals in the marine sediment. Targeted analytical methods for these novel chemicals are needed to assess the total CWA burden in marine sediments. Especially methylated and sulfur containing degradation products of phenylarsenic CWAs should be taken into account when measuring CWA contamination levels in marine sediments

These novel chemicals discussed in this paper, might also have a hazardous impact to ecosystem. There are no toxicity data available for these methylated and sulfur-containing phenylarsenic chemicals and non-existent knowledge on how they behave in aqueous environment. It has already proven that abiotic degradation product of Clark I and/or II is accumulating in fish tissues. These novel chemicals identified in this study are most like more lipophilic than known abiotic degradation products suggesting that these chemicals are more prone to accumulate in fish tissues.

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#### ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

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12 Figure S-4 Total ion chromatogram and spectrum for 13 methyldiphenylarsine sulfide. Figure S-5 Total ion chromatogram 14 and spectrum for 10-methyl-5H-phenarsazinine-10-sulfide. Figure S-6 Total ion chromatogram and spectrum for 15 dimethylphenylarsine sulfide. Figure S-7 Total ion chromatogram 16 and spectrum for triphenylarsine sulfide. Table S-3 Detected 17 fragments and their relative abundance for all detected sulfur 18 containing chemicals. Figure S-8 Extracted ion chromatogram for 19 sediment sample #8 containing sulfur-containing phenylarsenic 20 chemicals and target chemicals. 21

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Notes

The authors declare no competing financial interest.

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Analytical Chemistry





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Proposed structure composi	and elemental tion	Measured mass	Mass difference [ppm]	R <sub>t</sub> [min]	Relative abundance of [M+H] <sup>+</sup> +2 peak ( <sup>34</sup> S )*	
	PE	CA-related ch	emical			
HS <sup>+</sup> CH <sub>3</sub> CH <sub>3</sub> dimetylpenylarsine sulfide	$C_8H_{12}AsS^+$	214.98701	0.02052	1.96	3.97	
	Ada	msite-related c	hemicals			
HS <sup>+</sup> OH As 10-hydroxy-5H- phenarsazinine-10- acid HS <sup>-</sup> OH	C <sub>12</sub> H <sub>11</sub> AsNOS <sup>+</sup>	291.97723	0.05111	2.57	4.44	
10-methyl-5H- phenarsazinine-10- sulfide	$C_{13}H_{13}AsNS^+$	289.99792	0.02315	2.92	4.16	
Clark-related chemicals						
diphenylthiorsinic acid	$C_{12}H_{12}AsOS^+ \\$	278.98196	0.10915	3.30	3.82	
HS <sup>+</sup> CH <sub>3</sub> As methyldiphenylarsine sulfide	$C_{13}H_{14}AsS^+$	277.00275	0.07746	3.41	3.93	
Triphenylarsine-related chemical						
HS <sup>*</sup> As triphenylarsine sulfide	$C_{18}H_{16}AsS^+$	339.01842	0.30191	4.53	4.24	

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Proposed novel structure and elemental composition		Measured mass	Mass differen ce [ppm]	Rt [min]
HO <sup>↑</sup> OH As H DM-OH	$C_{12}H_{13}AsNO_2^+$	291.99521	0.93012	1.17
нот сна 10-M-5H- РАО-ОН	$C_{13}H_{13}AsNO_2^+$	290.01562	0.18097	1.32
но, он Даз Он DPA-OH	$C_{12}H_{12}AsO_{3}^{+}$	278.99968	0.03547	1.57; 1.73
но, сна МDPAO-OH	$C_{13}H_{14}AsO^+$	277.02040	0.09030	1.50; 1.64
HO - COH	$C_{18}H_{16}AsO_{2}^{+}$	339.03594	0.40047	2.39; 2.52