

Investigation of Long Term Hazards of Chemical Weapon Agents in the Environment of Sardasht Area, Iran

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Abstract

The present study aimed to investigate the persistence and existence of chemical warfare agents (CWAs) and related dissipation products in the environment. The study area is Sardasht district located in the western borderline of Iran and Iraq in which was subjected to attack with chemical weapons in July 1987 during the Iran-Iraq war. Three types of environmental samples including water, soil and native local plant materials were collected and analyzed. Gas chromatography-mass spectrometry in the electron impact ionization mode has been developed for the separation, screening, identification and qualification of chemicals after the sample preparation methods. In order to validate the applied extraction procedures, ethylene glycol was spiked to some of the samples including groundwater, surface soil, grape and alfalfa plants. All the recoveries were in the range of 83.6–107.4% with the relative standard deviations varying from 4.9–12.4% (n = 3) successfully. The initial results revealed that no trace of related compounds or CWAs was detected in the soil and water samples. However, trace amounts of some degradation products of blistering agents like Mustard gas (HD) and Lewisite were found in a tree wood from a house subjected to chemical attack as well as in barley samples (a mixture of leaves and root) collected from an agricultural field in the area indicating chronic low exposure to the environment and people.

1. Introduction

In several cases, the laws of war have been broken by both parties leading the war to be directed toward civilians, women, and children, or the use of mass destruction weapons against the military and civilians including chemical weapons, despite the use of which have been banned for decades under the Geneva Convention almost 100 years ago. After the war, the Chemical Convention has been established as a global convention with a control regime under the OPCW (Sydney 1972). Chemical war agents (CWAs) are strong chemicals that are used as mass destruction weapons. The chemical agents are used to kill, seriously injure, or disable people due to their physiological effects. The toxicity of these agents is because of their ability to interact with enzymes, proteins, and nucleic acids in living organs. The chemical agents are first cause stimulation in cells and then affect the cells as a cellular toxin in living tissues (Singha et al. 2016). Compounds such as sarin, soman, tabun, mustard gas, and lewisite are among the chemical warfare agents, which are also known as blistering, blood, nerve, asphyxiation, and riot control agents (Hellström and Ödalen 2013; Hanaoka 2005). Bis(2-chloroethyl) sulfide (sulfur mustard, mustard gas, also known as HD) is a blistering agent widely used during WWI, WWII, and also used during the Iran-Iraq conflict in the 1980s by the Iraqi army. Mustards can be divided into sulfur mustard and nitrogen mustard. As the injuries caused by mustard agents resemble those of burning and blisters, they are categorized as "blistering agents". Nonetheless, it is more suitable for those to be known as "blister and tissue destroying agents" as they cause severe eye, respiratory system injury, and internal organ failure. Also, because of the ability of mustard to covalently bind with a variety of biological molecules, the resultant biological damage could have considerably delayed consequences, and the first symptoms can occur between two to twenty-four hours after the exposure (Hellström et al. 2013). However, the mentioned issues are not the only destructive effects of sulfur mustard (Nilsson et al. 1992).

From the environmental point of view, most of the CWAs including mustard (HD) hydrolyze after solvation and produce degradable products such as thiodiglycol (TDG), 1,4-thioxane, 1,4-dithiane and 1,3-dithiolane. These compounds in aqueous media may act as a reliable proof of the original existence of HD. Moreover, some previous reports have been proven the persistence of these substances for up to 60 years (Tang and Keong Loke 2012). Therefore, these materials and their decomposition products are expected to exist in the environment and transferred from soil and water to plants and then to food chains, and finally to animals and humans. Thus, sensitive and precise determination methods for environmental and biomedical studies are required to verify the presence of sulfur mustard and its decomposition, oxidation and hydrolysis products (Tang and Keong Loke 2012; Deng and Evans 1997). However, despite the importance of this subject, the studies on the impact of chemical bombs onto the environment are very limited which can be due to the laboratory prohibition for working with CWAs or limited areas in the world in which these weapons have been used.

In this context, in 2005, Aldeen and Delaver studied the long term hazards of CWAs in the soil of Halabja in northern Iraq. Ten soil samples from contaminated areas and six samples from not contaminated areas were studied in this research. The presence of sulfur mustard or any other volatile agent in the samples was evaluated by Gas Chromatography-Mass Spectrometry (GC-MS) (Dlawer and Aldeen 2005).

In 2010, Toree et al. examined the environmental hazards of chemical weapons discharged into the South Adriatic Sea and demonstrated the effect of chemical gases on fish in the Mediterranean Sea (Torrea et al. 2010).

About the study area

The city of Sardasht with an area of 144.454 km² is located in northwestern of Iran and near the border of Iraq (Fig. 1). The altitude of this city is 1840 meters above sea level and it has a population of about 50,000 people. The city has about 96 km of border with Iraq and is located in the south and southwest of the small Zab River Basin. Sardasht city has a mountainous climate and a Mediterranean rainfall regime (Khezri 2010). During the years of the Iraq and Iran conflict, the city of Sardasht was considered as a point of contact between the two parties, culminating in the chemical bombing, which is still taking its toll on the people after so many years. In July 1987, Saddam Hussein's military had attacked the city of Sardasht with seven chemical bombs, four of which hit the city center and the other three land in a nearby valley inside Rashahrameh village.

It is the first city in which the weapons of mass destruction and chemical weapons have been used against its civilians after World War II. According to the letter of the Ministry of Foreign Affairs to the United Nations, at least 4600 peoples were killed or severely injured in that bombing. However, some resources were estimated this number to be about 7000 people (Ahmadi et al. 2010).

Considering that investigation onto the presence/absence or stability of these constituents in the environment and their possible threat to the health of residents thereby providing solutions for cleanup of

contaminated areas is of great importance, the aim of this work was to investigate screening of chemical weapon compounds and their decomposition by-products in soil, water, and plants in the Sardasht region of Iran (Sanderson et al. 2012). Gas chromatography-mass spectrometry (GC-MS) as one of the most popular and powerful instrumental methods was used for qualitative analysis of chemical warfare residuals through the comparison of obtained mass spectral data with authoritative known and analogous compounds available in the library (Hanaoka 2005; D'Agostino and Hancock 2003).

To the best of our knowledge, there has been no research onto the existence of chemical weapon residuals in the Sardasht area of Iran so far.

2. Experimental

2.1. Chemicals and materials

All the organic solvents used in this research including methanol (MeOH), ethanol, n-hexane, pyridine, ethyl acetate, and dichloromethane (DCM) were all GC grade (purity of 99/99%) and purchased from romil Co. (England). Trimethylchlorosilane (TMCS, 98%) as a derivatizing agent, potassium hydroxide (KOH), ethylene glycol (EG, 99%), sodium azide and anhydrous sodium sulphate (Na_2SO_4) were obtained from Merck (Darmstadt, Germany). All other reagents and materials were of analytical grade.

2.2. Sampling

In order to have a plenary investigation into the existence of chemical warfare agents and their related by-products, three types of environmental samples including two water and eight soil samples and eight local plant materials were selected and collected during a day from the study area. All samples were collected in July 2019 from eight sites (three sites inside the Sardasht city, four sites inside the Rashahrameh village and one site between city and village as a control sample) that were exposed directly to the chemical attack bombardment. Figure 2 (a and b) is Google Earth Images of the study area where has been subjected to chemical attack, and Fig. 3 shows map of sampling stations in Sardasht city and Rashahrameh village respectively. Two types of water including ground water in Sardasht City (W1) and surface water from Rashahrameh village (W2) were collected in 250 ml amber glass bottles from the point near to site of the attack. Care was taken to ensure that vials were filled full with no headspace and were quickly sealed with Teflon® lined screw caps.

Sodium azide solution (10 % W/V) was added in situ as a preservative to stop all enzymatic and degradation processes (Ahmadnezhad et al. 2021). Soil samples were collected with a grab or core sampler and then air-dried in the laboratory condition at room temperature for 48h before extraction (see Table 1). All the soil samples were homogenized with a manual pounder and sieved by a 2 mm sieve to remove any large particles (Rasoulifard et al. 2015). Plant samples including the mixture of leaves, roots and pedicles were selected from some endemic local plants located near or at the center point of subjected chemical attack sites. Then, they were air dried for seven days through consecutive aerations.

Table 1
Properties of selected soil specimens

Sample code	Matrix	Sampling Location	Sampling Amount
S1	Soil	A barley farmland in Rashaharameh village	80– 250 g
S2		A Wheat farmland in Rashaharameh village	
S3		A surface soil Subjected to chemical attack in Rashaharameh village	
S4		A house attacked to chemical bombardment in Sardasht City	
S5		A traditional cement from a house attacked to chemical bombardment in Sardasht City	
S7		A brick from a house attacked to chemical bombardment in Sardasht City	
S8		A brick from a district attacked to chemical bombardment in Sardasht City	
S9		A surface soil from a station between city and village	

To have homogenized fine plant powders leading to having effective extraction content, they were grinded completely with an electrical mortar and sieved through a 600 μ m sieve respectively. Some of the characteristics of selected plant samples are presented in Table 2. All the studied samples (water, soil and plant) were stored at 4°C and extracted within 14 days after collection.

Table 2
Characteristics of selected plant specimens

Sample code	Matrix	Sampling Location	Sampling Amount
P1	Plant	Mixture of tree skin and trunk of walnut from Rashaharameh village	80–250 g
P2		Mixture of leaves and pedicles of grape from a station after Rashaharameh village	
P3		A berry tree trunk in Sardasht city	
P5		Mixture of leaves and pedicles of grape from Rashaharameh village	
P6		Mixture of leaves, pedicles and fruit of sumac from Rashaharameh village	
P7		Alfalfa plant from Rashaharameh village	
P8		Mixture of leaves, root and seed of barley from Rashaharameh village	
P10		Wood from a house attacked in Sardasht City	

2.3. Extraction procedure

2.3.1. Water Samples

In this research liquid–liquid extraction (LLE) was recommended as a simple and cost-effective sample preparation technique for all the applied samples (Hanaoka 2005). For water specimens, the pH was checked and neutralized (pH ~ 7) with diluted hydrochloric acid and sodium hydroxide solutions before extraction. Then 10 ml of each sample was extracted with 2 ml dichloromethane as extraction solvent two times alternatively and shaken at 600 rpm for about 30 min. Then the solvent was collected and dried up to 0.5 ml under a stream of nitrogen. The necessary dehydration with anhydrous sodium sulfate was done at the end of extraction before injection.

2.3.2. Soil Samples

First of all, about 2 gr of each soil sample was weighted and coded according to the original sample boxes. Since the nitrogen/sulfur-containing compounds, phosphonothiolates, and corresponding alkylated or protonated salts so-called V agents are sometimes difficult to be efficiently extracted from soil specimens because of adsorbing to silicon hydroxide network (Hanaoka 2005), impregnation was done with 5 ml of 0.5 M potassium hydroxide/methanol for 3h as the first step of solvent extraction system. A sonication system with an ultrasonic disrupter of the horn type (300 watts power) was used to increase the transfer of the desired organic compounds to the solvent. After collecting the above solution (potassium hydroxide/methanol) in screw cap tubes, 5 ml of dichloromethane was added to the same

samples and sonicated for about 30 min. Further extraction was repeated 2 more times with dichloromethane to have good recoveries. The organic phase was then collected through centrifuging and added to the previous solution.

All the tubes were centrifuged at 3500 rpm for about 5 min. Then, the total organic phase transferred to another ultra clean tube and filtered through a 0.45 µm Minisart SRP 15 polytetrafluoroethylene membrane dried into 0.5 ml under the nitrogen atmosphere and used for injection.

2.3.3. Plant Samples

Two grams of each dried and powdered sample were soaked with sort mixed of 10 ml ethanol and 10 ml distilled water and stored at room temperature for 48h. The extracts were then filtered through Whatman filter paper (No.41) to remove any sediments and fine particles. A simple liquid–liquid extraction (LLE) method was used to extract semi polar and polar by-product compounds (Gherman et al. 2000). The extraction procedure was as the following:

An aliquot of 5.0 ml extraction solvent (ethyl acetate: n-hexane: dichloromethane, 5:1:1, v:v:v) was mixed and agitated with the as-made hydro alcoholic plant extract for about 30 min. Since the two phases could be observed, the mixture was centrifuged at 4,000 rpm for 5 min. Finally, the organic phase including desired components was separated within a pipet pastor and dried under the nitrogen atmosphere into 1.0 ml and used for chemical derivatization for subsequent analysis with GC-MS. Figure 4 shows some of the sampling and clean up procedure schematic images.

2.4. Chemical Derivatization

Since CWAs are known as very reactive chemicals, which can react with the stationary phase of the chromatographic column in their underivatized forms, and also for having volatile compounds from non-volatile degradation products of HD, a derivatization step was carried out after the extraction procedures of all types of samples (water, soil and plant) and prior to GC–MS analysis (Matsuda et al. 1998). Herein, trimethylsilylation processing was applied as a most commonly used derivatization method that could sufficiently replace the active hydroxyl functional groups bonded to some degradation, remaining and reaction products of mustard gas. Briefly, the extraction procedure was carried out as follows: 200 µl of TMCS and 80 µl anhydrous pyridine added to the extracts and sonicated in 50°C for about 60 min. The above solution was dried under a stream of nitrogen, and finally the residual solution was dissolved in 100 µl dichloromethane before injection to GC chromatograph. With the simple mentioned method all the polar hydroxyl, carboxylic acid, thiol and amine functional groups could successfully replace with a TMS [$-\text{Si}(\text{CH}_3)_3$] group.

2.5. Gas chromatography-Mass spectrometry

All the chromatographic analyses were carried out using an Agilent 7890B GC/5977A MS (USA) instrument, equipped with an HP-5MS (5% phenyl methyl siloxane) capillary column (60 m × 0.25 mm Id × 0.25 µm film thickness). Helium (99.999%) was used as the carrier gas with a flow rate of 1.1 mL/min. The injector temperature was set at 290°C. The oven temperature program for all the target samples were

set as following: The initial temperature of 50°C was held for 2 min, then increased to 180°C with a ramp of 15°C/min (held 5 min) then increased to the final temperature of 295°C with ramp of 10°C/min and held 5 min. Samples were injected in the split mode with ratio of (1/10), and the total run time was 36 minutes. The GC-MS transfer line was held at 300°C, MS ion source temperature was set at 230 °C and MS single quadruple temperature was set at 150 °C. The ion source was operated in the electron ionization mode (EI; 70 eV). The mass spectrometer was tuned by Perfluorotributylamine (PFTBA) as a calibration substance once a week according to the instrumental manual. Full-scan mass spectra (45–600 m/z) were recorded for all types of species identifications.

2.6. Screening, Identification and processing of data

Data acquisition and interpretation on mass spectrum of GC-MS was conducted using the database of both National Institute Standard and Technology (NIST) and Wiley Registry of Mass Spectral Data, 6th Edition (Wiley Interscience, New York) with more than 140,000 patterns. One of the newest versions of Agilent commercial software package (Mass hunter) was used for efficient interpretation and acquisition data too. In addition to identify related by-product compounds in the studied environmental specimen, Retention Index (RI) values were used by comparing the obtained RI value with that of an authentic compound (Hanaoka 2005).

3. Results And Discussion

3.1. GC-MS Analysis

3.1.1. Water

Since the main purpose of this research is to detect and identification of any compound related to degradation by-products of Mustard gas (HD) and Lewisite as the authorized blistering agents, screening analysis was conducted for all the studied environmental samples including water, soil and plant. Figure 5(a) and 5(b), shows the chromatograms of ground water and surface water from the places subjected to the chemical attack, respectively. As can be seen no organic related compound was found fortunately in both water samples. This could be attributed to a phenomenon called self-purification and attenuation of water that progressively eliminates the additional organic contamination loaded due to any reason and leads the aquatic ecosystems to recover almost its original balance with the surrounding environment over the years (Vaezihir et al. 2020; Oliva González et al. 2014).

3.1.2. Soil

Soil samples were the second studied environmental sample evaluated for detection of probable contamination by chemical weapon by-products. Considering the important factors to have a systematic sampling plan such as exact specification of points, time and alternation of sampling and preservation of sample composition until the time of analysis, eight soil samples were prioritized according to Table 2. The screening data

from GC-MS analysis revealed that although some samples had trace amounts of organic compounds like insecticides and pesticides, no signs of chemical weapon agents were found in any of cases.

This could be attributed to environmental soil bioremediation by heterotrophic microorganisms such as aerobic and anaerobic bacteria via biological processes. Therefore, decomposition and biodegradation of the impacted media could be occurred successfully (Certini et al. 2013).

Since in this study soil samples were collected from topsoil (0–30 cm), leaching the organic contaminants by passing over the years deeper into the soil might be another reason to found no chemical warfare agents in the soil. Figure 6(a) and 6(b) shows chromatograms of samples S9 and S5 as the representatives of soil samples, respectively.

3.1.3. Plants

Since most of the chemical warfare residuals are classified into polar and semi polar decomposition products, a mixture of polar and nonpolar extraction solvents were used as described in Sect. 2.3. According to the GC-MS profiles of plant extracts

(P1 to P10) a widely interesting organic compounds were found in all the samples. Fatty acids as methylsilylated derivatized form, phenolic compounds, some of the antibacterial constituents, a group of antioxidants and also some metabolites were a series of compounds identified in plant samples. In Fig. 7(a) and 7(b), we can see GC-MS chromatograms of samples P5 (grape) and P1 (walnut) as the representative plant samples. As can be seen some of characteristics of the identified compounds in Table 3, Arsine oxophenyl (C_6H_5AsO) in retention time (RT) of 15.60 min and with a content of 0.55% was detected in sample P8, as a stable component. Some of the most frequent m/z ions were found as following: 133, 119, 96 and 116. It could be originated from hydrolysis of phenylarsonic acid ($C_6H_5AsO(OH)_2$) which again can originate from Lewisite as one of the utilized organoarsenic chemical warfare agents (Hatlelid et al. 2010; Sanderson 2011) (See Fig. 7c and d).

Table 3
Some of the properties of identified compounds

Compound name	Tr ^a (min)	MW	Quantitation ion (m/z)	RI ^b (Retention Index)	Identification Method ^c
Arsine oxophenyl	15.60	168	133	-	2
Diglycolic acid, isobutyl octadecyl ester	18.11	442	191	3685	1,2
a Retention time					
b Retention index HP-5MS: 5% phenylmethylpolysiloxane (SE-54, DB-5ms, CPSi18, etc.).					
c 1-Retention indices; 2-NIST & Wiley libraries					

The presence of nonbonded pairing electrons onto the Arsenic and Oxygen atoms along with unstable phenylic Π electron pairs could lead to a high affinity between this volunteer composition and most of biochemical metabolites via electrostatic and covalent bonding. Since Mustard gas (HD) was one of the major chemical weapons used in the study area, most emphasis was placed on its primary or multi stage degradation products like thiodiglycol (TDG), 1-oxa-4,5-dithiepane and 1,2,5- trithiepane (Chmielińska et al. 2019). Herein, diglycolic acid, isobutyl octadecyl ester as its derivitized form in retention time of 18.11 min with content of 0.65% was found in sample P10 (See Fig. 7e and f). Some of the important m/z ions with the most abundance were found as following: 191, 71.1, 57.1, and 85.1. It could be one of the probable toxic oxidized degradation metabolites of mustard agents (HD) like thioglycol acid methyl ester (TGM), ethylene glycol monomethyl ester via releasing of thiol molecules.

These two plant samples were of different sampling stations but from the heart of center of chemical attack. So of special importance is the matrix of the environmental case studies. Bioavailability and the ability of residual organic/inorganic compounds to be absorbed and uptake from contaminated soil into plant tissues so-called bioaccumulation especially by crop plants such as barley and wheat, could lead to confirm the results founded in P8 and P10 samples. This phenomenon depends on many environmental factors in terms of the effects of organic target on plant growth, shoot biomass, root development, or other physiological functions thereby help environmental monitoring and risk assessment of organic residuals in contaminated study area respectively (Ait et al. 2004).

Since plant-soil system, has a unique ecotoxicological environment, the clear distinguish of whether soil or plant contamination is still ambiguous and needs more information or database too.

3.2. Validation Test

In order to evaluate the validation of the sample preparation methods described above (See Sect. 2.3), a recovery test was carried out onto different random studied samples (W1, S3, P7, P2). Ethylene glycol (EG) was utilized for this purpose owing to its similarity to thiodiglycol (TDG) and corresponding related hydrolysis products of mustard gas. So it was spiked at two concentration levels of 1.0 mgL^{-1} and 0.5 mgL^{-1} to each selected samples before the main extraction procedure and performed in triplicate. The average recoveries ranged between 83.6 and 107.4% depending on the matrices of the spices with the admissible RSD% (relative standard deviation) varied from 4.9–12.40% ($n = 3$). The obtained results confirmed the suitability of the applied sample preparation methods to various environmental samples with having a good accuracy and precision (see Table 4).

Table 4
Results of the accuracy and precision in some environmental samples

Sample code	Matrix	Spiked level of EG (mg L ⁻¹)	Founded level of EG (mg L ⁻¹)	Recovery (%)	RSD (%) (n = 3)
W1	Ground water	0.5	0.48	96.0	8.6
		1.0	0.98	98.0	4.9
S3	Surface soil	0.5	0.455	0.91	9.5
		1.00	0.836	83.6	8.4
P2	Grape plant	0.5	0.44	88.0	11.6
		1.00	1.074	107.4	10.2
P7	Alfalfa plant	0.5	0.47	0.94	10.4
		1.00	1.053	105.3	12.3

4. Conclusion

In this work, the persistence of chemical weapon by-products in the environment of Sardasht, Iran was investigated successfully. Water, soil and plants were the target studied samples. Gas chromatography-mass spectrometry was used as a highly regarded instrumental analysis method due to its good resolution, sensitivity and selectivity. Comparison of the mass spectral data obtained from specimens with those of the authentic compounds could give us an accurate impression to identify and qualify the chemical warfare agents. The results indicated that no trace of related chemical warfare compounds was found in the soil and water samples. However, a trace amount of arsine oxophenyl (0.55%), as one of the oxidation products of organoarsenic chemical weapon agents was found in one plant sample (mixture of the barley organ from Rashaharameh village). Also diglycolic acid, isobutyl octadecyl ester (0.65%) as one of the toxic degradation products of chemical warfare agents was identified in another plant sample (Wood from a house attacked in Sardasht City). Additionally, a validation test was carried out by spiking a constant concentration of Ethylene glycol to some of the samples which approved the accuracy and precision of the method respectively. Hence this contribution could give us a long window of opportunity to study the other environmental contaminated areas. The objective of the next stage of the work is to address potential public health risks from potential exposure to chronic low exposures to chemical warfare related compounds via the environment.

Abbreviations

CWAs Chemical Warfare Agents

EM Electron Impact

EG Ethylene Glycol

GC-MS Gas Chromatography-Mass Spectrometry

HD Mustard Gas

LLE Liquid-Liquid Extraction

OPCW [Organization for the Prohibition of Chemical Weapons](#)

TDG Thiodiglycol

TGM Thioglycol Acid Methyl Ester

TMCS Trimethyl Chlorosilane

WWI World War I

WWII World War II

Declarations

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Ethical Approval and consent to participate

All authors approve the ethics and consent to participate in this research.

Consent for publication

All authors have consent to publish this paper.

This manuscript doesn't contain data from any individual person: "Not applicable".

Availability of data and materials

The datasets generated and/or analysed during the current study are not publicly available due [because this data is the results of author's efforts and studies] but are available from the corresponding author on reasonable request.

Competing interests

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Authors' contributions

Abdorrezza Vaezihir: Project administration and Supervision, Conceiving the original idea, Methodology, Review & editing of the manuscript

Asra Pirkhezranian: Data curation, Field works, Investigation, Conceptualization

Negar Sehati: Lab analysis and interpretation of data, Writing original draft, Validation, Methodology

Mohammad Reza Hosseinzadeh: Administration and Supervision, Investigation

Seyed Yahya Salehi-Lisar: Conceiving the original idea, Field works, Review & editing of the manuscript

Hans Sanderson: Conceiving the original idea, Methodology, Review & editing of the manuscript.

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Figures



Figure 1

Location of Sardasht region along with neighboring countries Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

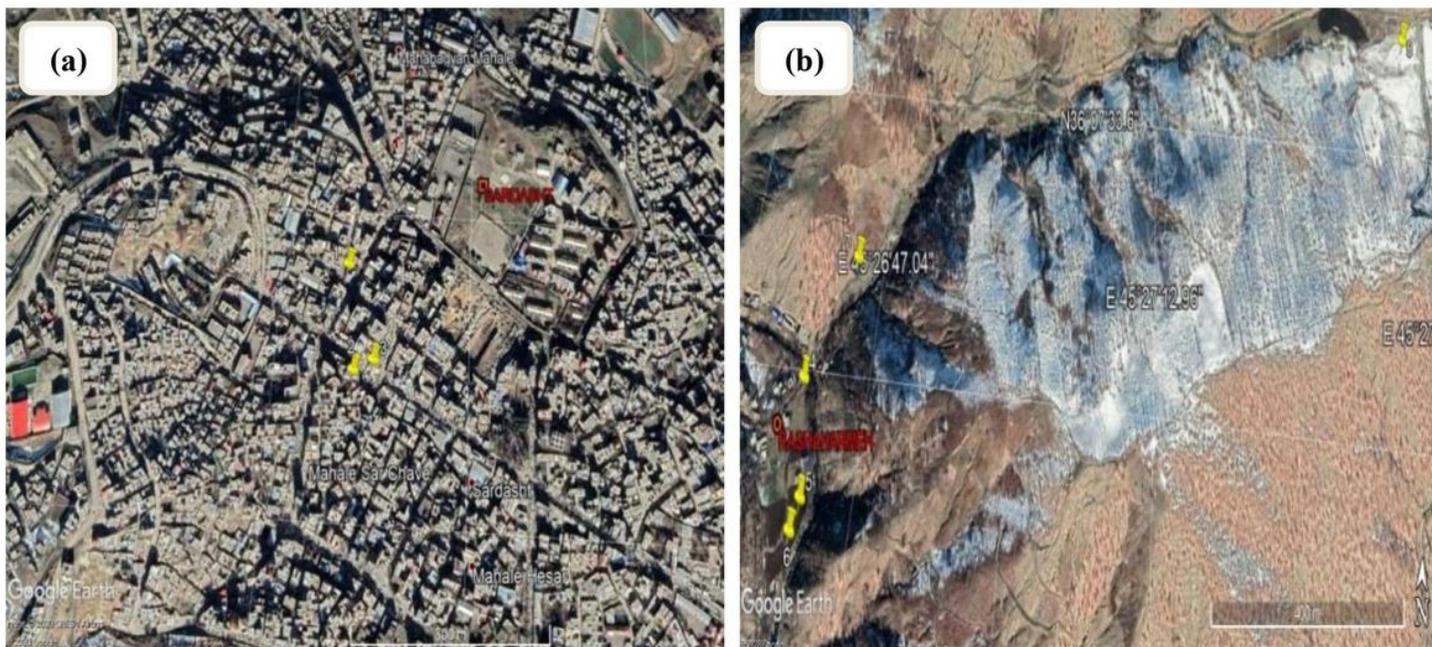


Figure 2

Google Earth Images of study points subjected to chemical attack (a) Sardasht city and (b) Rashaharameh village Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

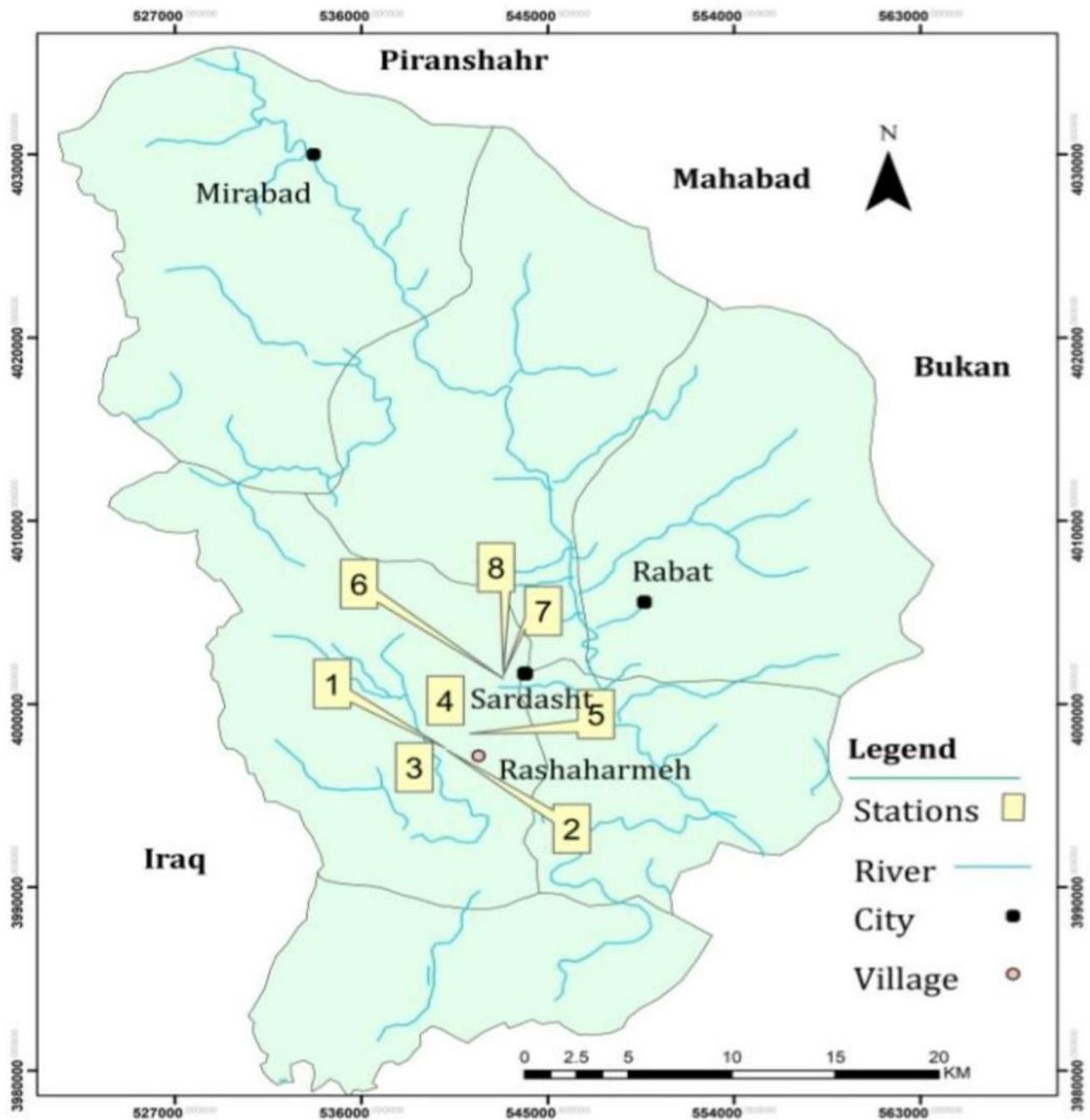


Figure 3

Map of sampling stations in Sardasht city and Rashaharmeh village Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.



Figure 4

Schematic images from Steps of sample preparation procedure of water, soil and plant species.

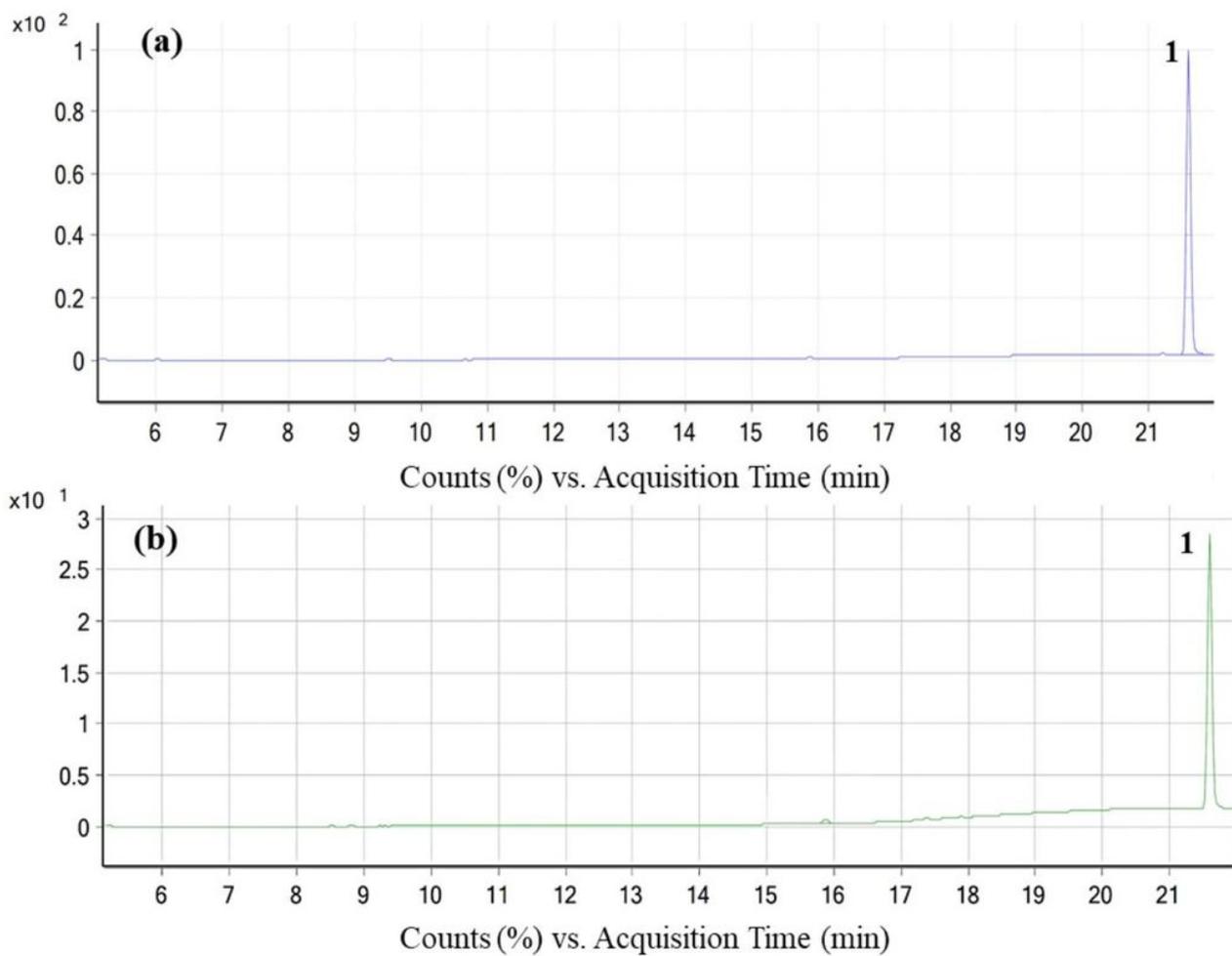


Figure 5

Total ion chromatogram of (a) Ground water and (b) Surface water, peak (1) di-ethyl phthalate

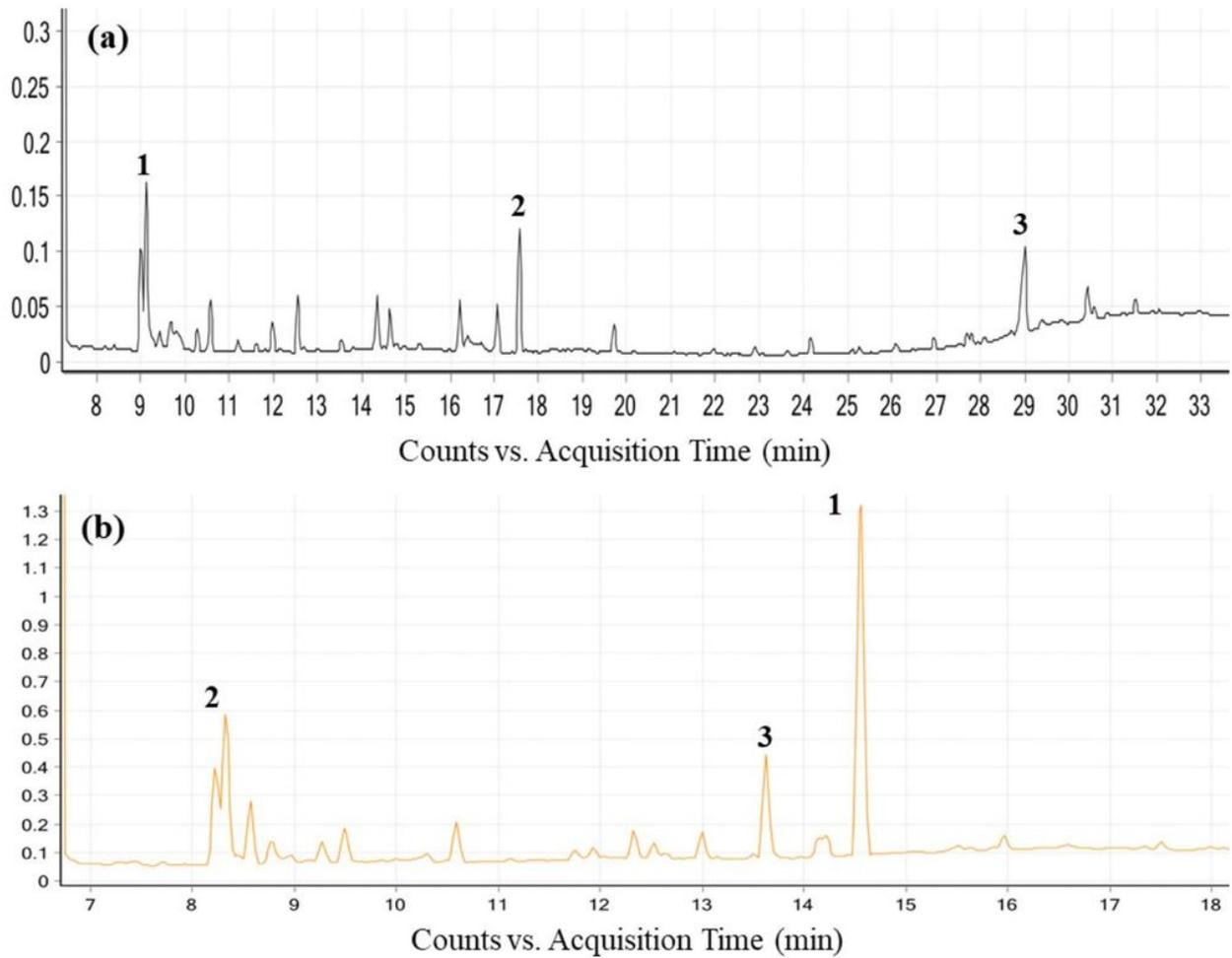


Figure 6

GC-MS chromatograms of (a) S9 peaks (1) chlorotrimethyl Silane (2) thiophene (3) hexadecanoic acid (b) S5 peaks (1) eicosanoic acid (2) chlorotrimethyl Silane and dichlorodimethyl Silane (3) oxalic acid, 6-ethyloct-3-yl isobutyl ester

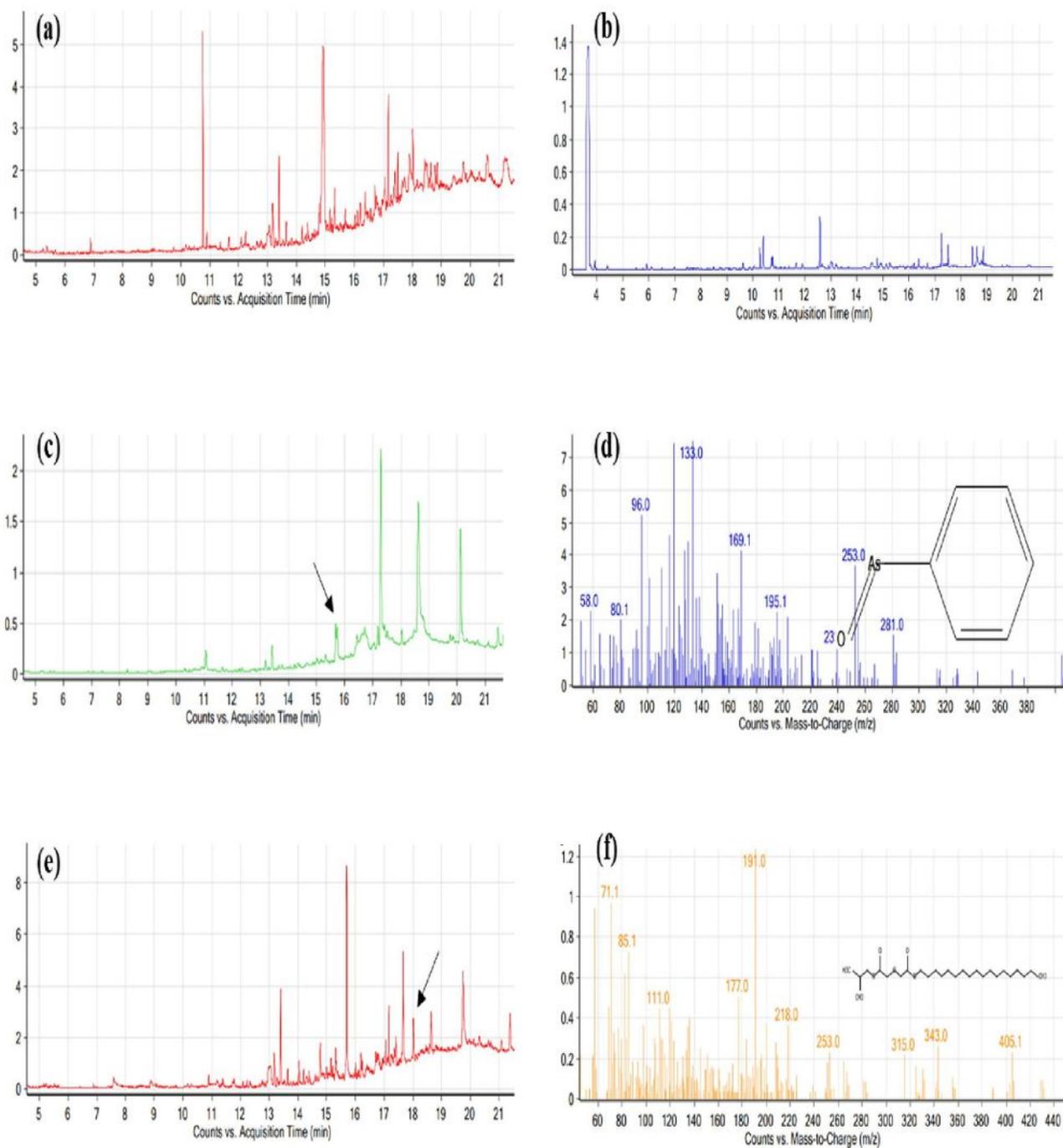


Figure 7

Total ion chromatogram (TIC) from GC-MS analysis for (a) P5, (b) P1, (c) P8, (e) P10, (d) and (f) mass spectra of Arsinic acid, 15.60 min and Diglycolic acid, isobutyl octadecyl ester, 18.11 min.

Supplementary Files

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