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Determination of the Remnant Environmental Impacts Resulting from the Chemical Bombing of Halabja, Kurdistan- Iraq

Jean Simonis¹, Diary Ali Mohammed Al-Manmi^{2*}, Aram Dawood Abbas³, and Loffie Schoeman⁴

¹University of Zululand, Hydrology, South Africa

²Department of Geology, University of Sulaimani, Sulaymaniyah, Iraq

³Department of Geography, University of Sulaimani, Sulaymaniyah, Iraq

⁴NGO Global Relief, South Africa

Abstract

16 March of every year marked the anniversary of the chemical gas attack on the City of Halabja, Kurdistan, Iraq, and its nearby villages. In the process, 5000 people reportedly died from the attack. Many more were wounded and the event left nearly 60 000 people displaced. A perceived consequence of the chemical bombing of Halabja City was the environmental pollution of the soil and water. A recent questionnaire completed by the population of Halabja City indicated that 35% believed that water pollution was still an issue, and 55% thought that soil pollution posed a high risk.

In 2016, we were requested by the Halabja City governor to investigate the situation. And to lay to rest the perception and concerns of soil and water still being contaminated by the events that happened on that day in March 1988. A total of 8 soil and 18 water samples were collected, Soil samples were collected from the surface and as close as possible to bomb sites and craters, in contrast, water samples were collected from seven springs, ten water wells, and one surface streams downslope as close as possible to the bombed areas. The samples were analyzed for chemical warfare agents which are Arsenic, Cyanide, Fluoride, soluble orthophosphate, Nitrate, Phosphorous, Sulphate, and Sulphur. The results indicated no negative contamination remaining in both water and soil. The geology and hydrogeology in the area played an important role in helping the chemical warfare agents (CWA) to degrade during the past 28 years. Most of the CWA used are water- soluble and solubility increases when the agents are either hydrolyzed or oxidized. The hydrolysis products have equal toxicity to the parent chemicals, posing a similar threat to the environment. In contrast, the intact chemicals can be adsorbed onto sediment, where they can be stored for a longer time.

Keywords Aquifer, Chemical warfare agents (CWA), Halabja, Kurdistan, Soil and water contamination

*Email: diary.amin@univsul.edu.iq

تحديد الآثار البيئية الباقية الناتجة عن القصف الكيميائي في حلبجة ، كردستان - العراق

جين سيمونس¹، ديارى علي محمد امين المنمي*²، ارام داود عباس³ ، لوفى شويمان⁴

¹جامعة زولولاند ، الهيدرولوجيا ، جنوب أفريقيا

²قسم الجيولوجيا ، جامعة السليمانية، السليمانية، العراق

³قسم الجغرافيا ، جامعة السليمانية، السليمانية، العراق

⁴NGO Global Relief ، جنوب إفريقيا

الخلاصة

يصادف السادس عشر من شهر مارس من كل عام الذكرى السنوية للهجوم بالغاز الكيميائي على مدينة حلبجة، كردستان، العراق والقرى القريبة. في هذه العملية، قتل إن 5000 شخص قد ماتوا جراء الهجوم. أصيب الكثيرون بجروح وترك الحدث ما يقرب من 60 000 شخص مشردين. كانت النتيجة البيئية للقصف الكيميائي لمدينة حلبجة هي التلوث البيئي للتربة والمياه. أشار استبيان حديث أجرته سكان مدينة حلبجة إلى أن 35% يعتقدون أن تلوث المياه لا يزال يمثل مشكلة، وأن 55% اعتقدوا أن تلوث التربة يشكل خطراً كبيراً. يوجد فهم محدود من قبل الناس للعواقب البيئية للقصف. نتائج التحقيقات السابقة لم تكن قادرة على تهدئة مخاوف وتصورات الناس بشأن آثار التلوث البيئي.

في عام 2016، طلب محافظ مدينة حلبجة التحقيق في الموقف. ولوضع راحة تصورات ومخاوف التربة والمياه لا تزال ملوثة بالأحداث التي وقعت في ذلك اليوم في مارس 1988. تم جمع ما مجموعه 8 عينات من التربة و18 عينة من المياه، تم جمع عينات التربة من السطح وعلى مقربة قدر الإمكان من مواقع القصف والحفر، على النقيض من ذلك، تم جمع عينات من المياه من سبعة ينابيع وعشرة ابار ونهر واحد وأقرب ما يمكن من المناطق التي تم قصفها. تم تحليل العينات لمعرفة عوامل الحرب الكيميائية التي هي الزرنيخ والسايانيد والفلورايد وأورثوفوسفات الذوبان والنترات والفوسفور والكبريتات والكبريت، وقد أشارت النتائج إلى عدم وجود تلوث سلبي في المياه والتربة، وقد لعبت الجيولوجيا والهيدرولوجيا في المنطقة دوراً مهماً في مساعدة عوامل الحرب الكيميائية خلال الـ 28 عامًا الماضية، معظم أنواع عوامل الحرب الكيميائية المستخدمة قابلة للذوبان في الماء وتزداد قابلية الذوبان عندما تتحلل العوامل المؤكسدة أو تتأكسد للمواد الكيميائية الأصل، مما يشكل تهديداً ماثلاً للبيئة. في المقابل، يمكن امتصاص المواد الكيميائية السليمة على الرواسب، حيث يمكن تخزينها لفترة أطول.

Introduction

The chemical bombing of the City of Halabja, Kurdistan, Iraq, and its nearby villages killed over 5000 people. Many more were wounded and the event left 60 000 people displaced. Many researches like [1-5] reported that at the end of the Iran-Iraq war on March 16, 1988, Halabja City and the surrounding areas were attacked with chemical bombs dropped from Iraqi planes and Iraqi artillery shelling. This was the culmination of an attempt by Saddam to eradicate the Iraqi Kurdish population. During the time of the bombing, Halabja City had a population of 60,000 people. The attack is believed to have included the following chemical warfare agents (CWA): cyanogen chloride, organophosphorus nerve gas, Tabun, Sarin, VX, Lewisite and mustard gas [6, 7].

The variety of chemicals together with prolonged bombing and shelling resulted in most of the deaths and long-term effects. According to [8-10] the poisonous gasses caused extreme pain, physiological damage, death, and long-term water and soil pollution. At least 5,000 people died as an immediate result of the chemical attack and it is estimated that about 7,000 people were injured or suffered long-term illness. Most of the victims of the attack on Halabja City were Kurdish civilians. After the bombing, the Iraqis moved in on the ground and completely destroyed the city leaving its nearly 60,000 occupants homeless [8- 10]. According to [11] more than 75% of the population left the area shortly after the bombing as the shelling destroyed most of the water and agriculture resources.

In spite of the time that has passed since the attack, as well as previous investigations proving that no after effects are still present, the local population is still reluctant to use the natural resources. A

recent survey (n = 100) conducted by [11] confirms this reluctance. The survey completed by 100 Halabja City citizens, for the period 1988 to 2014, indicated that 35% believed that water pollution was still an issue and 55% thought that soil pollution still posed a high risk. This lasting negative perception necessitated this study.

In 2016, researchers from the University of Zululand, University of Sulaimani and aid organization, Global Relief, were requested by the Halabja City governor to investigate the situation and lay to rest the perception and concerns of soil and water contamination from the events that occurred in March 1988.

Overview of Iraqi chemical warfare agents (CWA)

Attack by chemical bombing normally consists of a chemical dispersion of solids, liquids, vapors, and aerosols. People affected ingest/inhale/absorb the dispersions through their mouths, nose, eyes, and skin. It acts within seconds. CWA have different characteristics and classes with specific physicochemical, chemical and physiological properties [6, 12]. The physicochemical due to its volatility, solubility and persistency and chemical as organophosphorus, organosulfur and organofluorine compounds and arsenicals. The Physiological property according to its effect on humans categorized as: blood agents (cyanogenic agents), Choking agents (pulmonary agents), Nerve agents, Psychomimetic agents, Riot-control agents (tear gases), Toxins, and Vesicants (blistering agents).

Nerve agents and blood agents were mainly used by Iraq during the 1983–88 war [6]. Nerve agents are synthetic poisons, stable, solubilized into organic solvents which penetrate into water and soil causing extensive contamination. The spectrum of nerve agents varies due to differences in the toxicity and physical-chemical characteristics [6]. Based on their chemical structure, they can be classified as organophosphorus, organosulfur and organofluorine compounds and arsenicals. In contrast, blood agents are a cyanide group of chemicals that affect bodily functions by preventing the normal utilization of oxygen by body tissue. Hydrogen cyanide (HCN) and cyanogen chloride (CNCl) are the main CWA in this class.

According to [6] the Iraqi chemical arsenal of 3 800 t was accumulated with the help of foreign companies. Most of this stock was used in the war against Iran and the Kurds. An overview of the chemical warfare agents used is provided in the Table-1 [13].

Table 1- Overview of the possible CWA used in the war [13]

Agent class	Agent name	Abbreviation	Chemical name
Nerve	Tabun	GA	ethyl -dimethyl phosphoroamido cyanidat
	Sarin	GB	Isopropyl- methylphosphonofluoridate
	Soman	GD	(3,3-dimethylbutan-2-yl)- methylphosphonofluoridate
	Ethyl Sarin	GE	
	Cyclosarin	GF	Cyclohexyl- methylphosphonofluoridate
	VX agent	VX	S-[(2-diisopropylamino)ethyl]-O- ethyl-methylphosphonothiolate
	S-(Diethyl amino)ethyl O-ethyl ethylphosphonothioate	VE	
	Amiton or Tetram	VG	
Vesicants	Phosphonothioic acid, methyl-, S-(2-(diethyl amino)ethyl) O-ethyl ester	VM	
	Sulfur Mustard	H, HD	Bis(2-chloroethyl) sulfide
	Nitrogen Mustard	HN-3	Tris (2-chloroethyl) amine
	Lewisite	L	Dichlor(2-chlorovinyl) arsine
	Mustard-lewisite	HL	Dichlor (2-chloroethylsulfanyl) arsine
	Phenyldichloroarsine	PD	Phenyldichloroarsine
	Phosgene Oxime	CX	Carbonimidic dichloride, hydroxy-

			Dichloroformaldehyde oxime
	Phosphorus	OP	Organophosphorous
Blood	Hydrogen Cyanide	AC	Prussic acid Cyanwasserstoff
	Cyanogen Chloride	CK	Chlorocyanogen Chlorcyan
	Arsine	SA	Arsenwasserstoff AsH ₃
Choking	Chlorine	Cl	Chlorine
	Phosgene	CG	Carbonyl chloride
	Diphosgene	DP	Carbonyl chloride Phosgen
	Chloropicrin	PS	Nitrotrichloromethane
	Cyanide	CnCl	Cyanogen chloride
Note: Constituents in bold were used as indicators of CWA in this study			

According to [14, 6, 8, 15], CWA can furthermore be classified based on their volatility in the environment (either as persistent or as non-persistent). The more volatile an agent, the quicker it evaporates and disperses. The more volatile agents like chlorine, phosgene and hydrogen cyanide are non-persistent agents whereas the less volatile agents like Sulphur/nitrogen mustard and VX are persistent agents. The persistence of the agents with metals allows for its evaluation and attribution back to the parent substance [16]. According to [15] Sulphur mustard is persistent in the environment. They use the term "environmental persistence" for the presence of these products in soil and water, Figure -1. [17, 18, 14] found most of the CWA to be water soluble and their solubility in the water increased when they were hydrolyzed and/or oxidized. In water, sulfur mustard degrades into thiodiglycol (TDG) which oxidizes into thiodiglycol sulfoxide. In contrast, Lewisite oxide is relatively insoluble in water and once dry will not dissolve in water. Eventually, however, it will degrade to arsenical compounds. Tabun degrades through some intermediates into phosphoric acid [15]. The half-life Tabun in water is 4.5 h at 20 °C. The solubility of all these chemicals is increased at higher temperatures.

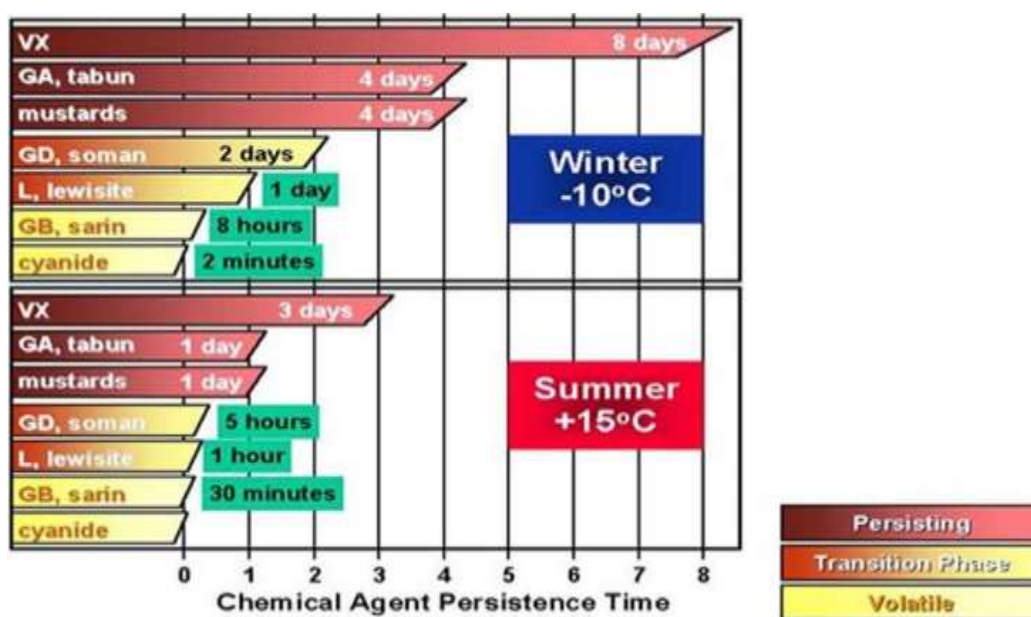


Figure 1- Persistency of CWA in the environment [14]

[18, 14, 19] state that CWA varies greatly in their physical-chemical impacts on the environment. Each substance or class of substance, therefore, has its own chemical character determining its partitioning and degradability in the environment. The intact chemicals can easily be adsorbed onto sediment, where they can be stored for a longer time. They also found it common for both mustard and arsenic-containing chemicals to oxidize in the environment. Many arsenic-containing chemicals may form the same hydrolysis and oxidation product. The hydrolysis products have equal toxicity as the parent chemicals, posing a long-lasting threat to the environment. Similarly, all other CWA left in the environment will weather (decay).

Most of the chemicals used in CWA therefore probably lie in the intermediate range with degradation half-lives in the range of a few days to a year. For highly contaminated soils such processes can take years to reach normal levels [20]. The following important degradation reactions can take place which also impacts on the sampling procedure [15]: hydrolysis (water in the environment), oxidation (atmospheric oxygen), photochemical (sunlight), thermochemical, and biological (coverings, vegetation, and surfaces).

The study area

Halabja City is located in the northeastern part of Iraq approximately 13 km east of Derbendikhan Lake. Halabja City is approximately 76 km away from the governorate capital, Sulaymaniyah. Geographically, the area is located between the latitudes ($35^{\circ} 07' 22''$ and $35^{\circ} 14' 49''$) north and longitudes ($45^{\circ} 51' 50''$ and $46^{\circ} 06' 50''$) east (Figure-2). Halabja City covers an area about 78.1 km^2 and is expanding fast and is highly populated with 190,727 people generating large amounts of both solid and liquid waste in the built-up areas. The topographical elevation ranges from 443 to 2053 m above mean sea level. Halabja Municipal city center comprises three other subdistricts: Khormal, Byara, and Sirwan. Halabja district shares a border with Iran to the east and about 12 km from the Iranian border.

The area experiences a Mediterranean type climate with hot summers and cold winters. Winters are very cold with temperatures ranging between -2 and -10°C . Spring and fall are moderate with temperatures between 10 and 30°C , while summers are hot (30 to 45°C). The average annual rainfall in the area ranges between 500 to 700 mm causing high percolation and groundwater recharge of the thick alluvium soils.

Hydrologically, the district is situated in the Diyala (Sirwan) River catchment area, with streams flowing to the west, discharging into Derbendikhan Lake, according to [21] the basin can be divided into Halabja and Said Sadeq sub-basins. The basin boundary at the north, northeast, and southeast coincides with the summits of Avroman, Shinrwe, and Balambo mountains, respectively. Sources of potable water in the Halabja District include Derbendikhan Lake, artesian wells, springs, and streams. It is reported that potable water in Halabja is available for about 75 percent of the population [22].

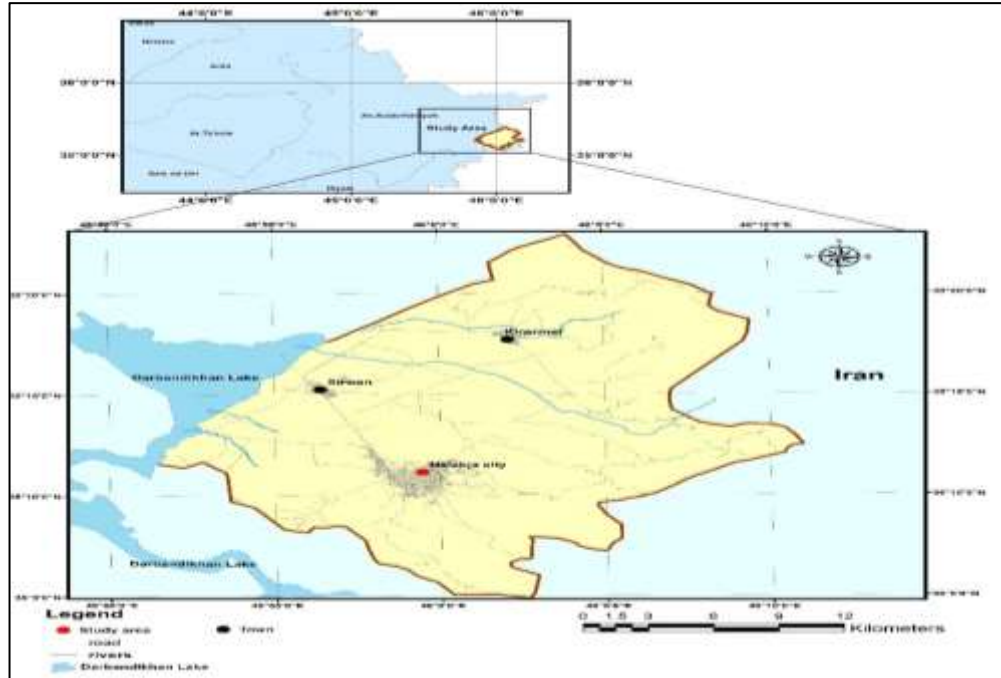


Figure 2- Location map of the study area

Geological and hydrogeological setting

The study area is located within the western Zagros fold-thrust belt. Structurally, it is located within the high folded zone, Imbricated, and Thrust Zones [23, 24]. The age of the geological formation ranges from Jurassic to recent, Figure-3.

Early Jurassic includes Sarki Formation (thin bedded fine grained cherty and dolomitic limestone) and Sehkaniyan Formation (comprises dark saccharide dolomites and dolomitic limestone with some solution breccias), [25]. Lower and middle Jurassic rocks included Barsarin (limestone and dolomitic limestone), Naokelekan (bituminous limestone) and Sargelu Formations, the last one consists of well-bedded and well-crystallized, black bituminous limestone and dolomitic limestone, [26]. The Qulqula Group consists of two formations, the Qulqula Radiolarian, and the Qulqula Conglomerate. The Upper Cretaceous Kometan (Turonian) and Lower Cretaceous Balambo (Valanginian-Cenomanian) Formations are lithologically very similar and composed.

The affected area consists mostly of thick (up to 300m thickness) Quaternary (alluvial) sediments aquifers resulting from the sediments are extensively developed for water supply. These alluvial deposits can be easily polluted but at the same time can be easily diluted from precipitation, the formation, therefore, needs intensive protection against pollution.

Hydrgeologically the study area is characterized by at least three aquifer types: intergranular (lower lying areas), fissured (mountainous areas) and fissured-karstic types [27, 21]. Data from Groundwater Directorate, Sulaymaniyah show that the surrounding mountainous areas are characterized by deep groundwater levels. Whereas the central and southeastern part (Halabja) the groundwater levels occur at shallower depths: groundwater can be expected to flow from the surrounding higher elevation surrounding the area and generally toward the lower parts of the basin where the Derbendikhan Dam is located. Also, there are several springs inside the basin. These springs are classified into three classes, less than 10 L/sec such as Anab, Baharany Ababaile, Hana Swra and 10-100 L/sec such as Kany Maran Hamoghan springs and more than 100 L/sec such as Chawg spring. Springs occur within the basin and are used as water supply [28].

Intergranular Aquifer (AIA) Intergranular aquifer is a very rich aquifer that covers a surface of more than 166 square kilometers in the area of interest. Based on the data of previous investigations, including deep-well drilling, the total thickness at the area is assumed to be more than 300 m.

Karstic aquifers unit or formations in the area of interest are - JKA (Jurassic Karstic Aquifer). Jurassic age formations, developed mainly in carbonate facies (limestones and dolomites and their varieties). This type of aquifer is characterized by its high permeability and transmissivity values. Also, the drawdown values in the wells that are drilled in such aquifers are relatively small [26].

Karstic- Fissured Aquifers (CKFA) This type of aquifer is developed in a different type of rocks such as the limestone, dolomitic limestone, marly limestone, and dolomite. The karstic-fissured aquifers are characterized by high permeability and transmissivity values but to a lesser extent than those in karstic aquifer [28].

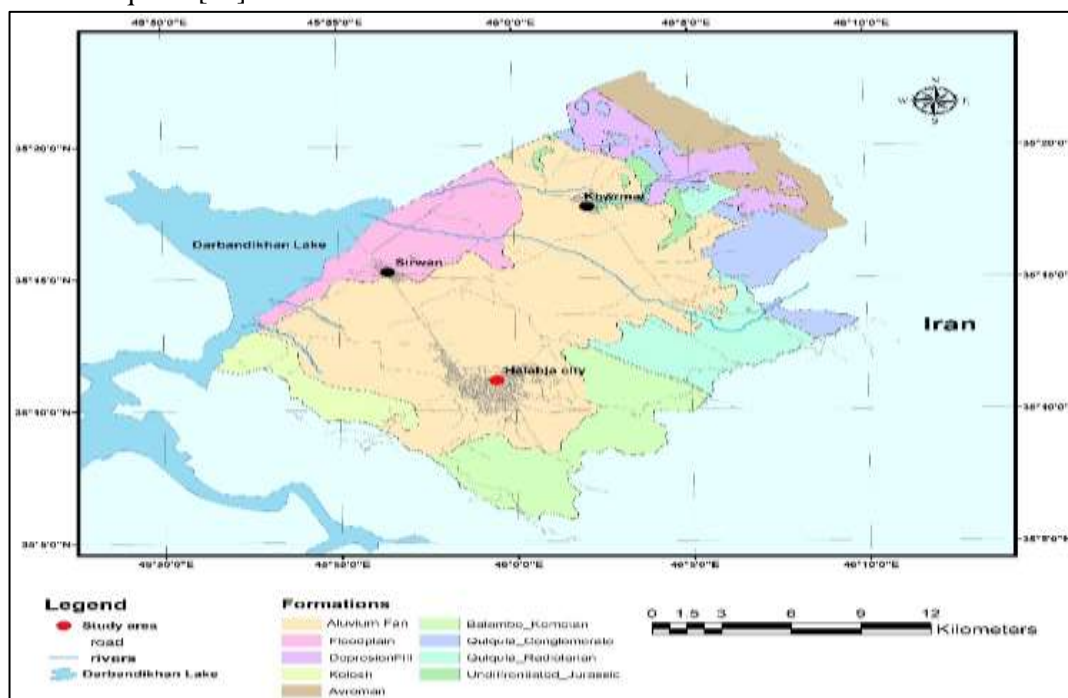


Figure 3- Geological setting of the study area

Previous investigations in Halabja related to soil and water quality

The following soil and water investigations, unrelated to CWA in the area, were conducted: [26] tested the groundwater for (Zn^{2+} , Pb^{2+} , Cu^{2+} , Cr^{2+} , Cd^{2+} , Cd^{2+} , and Fe^{total}) constituents and the results showed that all the sampled springs and wells water contain very low concentrations that are beyond the WHO and IQS standards and in many cases even below the detection limits. [29] Also conducted a water pollution study in the Halabja. Water samples were collected from five different locations radially around and within Halabja town. The samples were tested for phosphorus, nitrate, nitrite, and chloride. The results were evaluated against WHO guidelines and were mostly of good-quality. [30] Investigated the impact of a solid waste disposal site in Halabja on water and soil physicochemical characteristics. Soil and water samples were analyzed for physicochemical characteristics, Sulphur, nitrogen and trace metal concentrations. The investigator found little sign of trace metal contamination in the area, [21] Used nitrate as a primary control parameter when modifying the DRASTIC groundwater vulnerability index to the Halabja area. Nitrate, in contaminated areas, infiltrates from the surface toward the groundwater, acting as a good indicator of contamination. Their study showed that Halabja area to have a low vulnerability risk. [28] collected water samples from water wells and springs, samples were tested chemically and physically for several variables: electrical conductivity (EC), Ca^{2+} , Mg^{2+} , Cl^{-} , Na^{+} , and HCO_3^{-} . Considerable variations were noted between constituents from dry to wet seasons but in general, the quality was acceptable.

The only study related to the CWA bombing was reported by [4]. This study was conducted to determine the safety of the soil in Halabja five years after the CWA attacks. Soil samples were collected from 5 sites where chemical attacks were documented. A total of 16 samples were collected during 24 August to 2 September 1992. Control soil samples were also collected from areas with no history of chemical weapon activity. Separate aliquots of each soil sample were extracted using dichloromethane and ethyl acetate. The extracts were analyzed by full scanning GC- MS for volatile chemical weapon agents and any other identifiable volatile contaminants by the Chemical and Biological Defense Establishment (CEDE) at Porton Down, U.K. The results of the analysis of these soil samples showed no evidence of any residual hazard in the soil.

Investigations in Halabja related to the medical effects by CW agents

[8], director of the Halabja Hospital at the time of the bombing, reported that mustard gas and nerve gas used in the bombing of Halabja on their own could have caused severe physiological damage and death within minutes of exposure. However, it was the combination of CWA together with prolonged bombing exposure that resulted in disastrous effects on victims exposed physically, mentally and emotionally. According to [8] one of the effects of the chemicals is the higher incidence of cancer in the region. Results from surveys conducted by the director of the Halabja Centre, Dr. Fouad Baban, showed that Halabja when compared with the neighboring Chamchamal, had evidence of lasting effects from the chemical bombing. Miscarriages were as much as 14 times higher and colon cancer found to be 10 times higher in Halabja when compared with neighboring towns, [11] Agreed that Halabja's exposure to chemical weapons resulted in many deaths. Additionally, he also stated that survivors are still suffering after 28 years. They conducted a survey and distributed 100 questionnaires in four areas of the City. The study showed diseases such as ocular diseases, hard breathing, and body and skin malformation are still affecting the survivors. In contrast [31] reported that little pre -1991 Gulf War data on the prevalence of birth defects in Iraq are available. Furthermore, according to them, the birth defects ranges reported in reviewed studies for Iraq do not clearly indicate signs of environmental exposure to CWA.

From the study by [32], war and human rights abuses do contribute to increased prevalence of posttraumatic stress (PTS) disorder and low social functioning among the affected communities. There is relatively little evidence, however about the long-term mental health impact of war on general populations. They examined the prevalence of PTS symptoms and poor social functioning in Halabja 18 years after the chemical attack. They systematically sampled 291 persons, representative of the population of Halabja, from the city emergency department and 4 outpatient clinical sites. PTS symptoms and poor social functioning were common. After adjustment for covariates, female gender, older age, and cumulative exposure to multiple traumas, all were associated with higher PTS scores

and worse social functioning. Their conclusion was that exposure to CWA seems to continue the risks of psychiatric and social dysfunction even decades after the incident. [33] Studied Iranian soldiers and people affected by the Iran- Iraq war. Their studies also showed frequencies of PTSD, sleep disorders, emotional problems, behavioral disorders, personality disorders, paranoia symptoms, obsessive-compulsive disorders, depression, and mood disorders. They found that amongst people exposed to CWA the frequency of ailments was higher when compared with unexposed populations.

Background to our investigation

People in Halabja still believe that water and soil pollution resulting from CWA poses a high risk. This belief was confirmed by the [31] survey. This resulted in the researchers receiving a request from the Halabja governor to investigate and put to rest the perception and concerns resulting from the events that occurred on that day in March 1988. Due to their previous hydrological investigations in the area, a scientist from Departments of Geology and Geography, University of Sulaimani, participated in the investigation.

Current security issues and insecurity in the area necessitated having security protection and moving into and out of the area as quickly as possible. It was, however, important to use techniques identified from other CWA researchers and investigators. Sampling adhered to internationally recognized guidelines (documentation, photographic records, and maintenance of an audit trail). A control soil sample was also collected from a site with no history of CWA. As sedimentation in the affected areas has changed little in the last number of years we followed the same sampling techniques as advised by researchers investigating bombed areas as well as CWA dumpsites: a) soil sampling from the top 5 cm of the surface (limited sedimentation occurring and b) water sampling within a radius of between 0.5 m and 1.5 m or downslope of the bombed areas (from eye witness testimony) or where available, downslope of the bombed area. Previous studies showed that the Halabja bombed areas had homogenous alluvium, therefore requiring lower sampling density and therefore reducing the chances of sampling error.

As a result of degrading (28 years) and limited persistence, alternative investigation techniques had to be identified. The analysis techniques used are standard water analysis techniques available anywhere in the world. These techniques should be sufficient to provide conclusive evidence of the presence or absence of CWA contaminants. From the literature study, it is clear that analysis of CWA serves as a screening tool for water and soil monitoring indicating the presence or absence of contaminants. Elemental formulations can be used for identifying explosives and selective detectors can also provide information on the presence or absence of certain elements. Metals can also exist in the following forms: elemental, free cationic forms as well as various charged organic and inorganic complexes.

Factors impacting the remnant pollution in the area include rainfall, temperature and time. Additionally, environmental factors such as soil characteristics, geology, and geohydrology, from the CW sites, should also play an important role.

Methodology

Soil Sampling

Both the soil and water samples collected were analyzed for arsenic, cyanide, fluoride, nitrate, sulphate, and phosphates as possible indicators of the bombing. A similar sample was also taken from an area not affected by bombing for use as a baseline value. Due to the solubility and long-term degradability of the CWA in the Halabja City bombing, the Chemical Warfare Convention (CWC) and its accreditation authority were not used for the analyses. Due to cost and time constraints, it was decided to use more conventional water and soil analytical techniques to identify such degraded products. The analysis techniques used were standard, water and soil analyses techniques such as inductively coupled plasma-mass spectrometry (ICPMS), ion selective electrode, ion chromatography, and coulometer.

As mentioned earlier, [17] found that most CWA degraded in the presence of water (hydrolysis) while investigating the location and distribution of dumped chemical weapons. Their sampling protocol was limited to removing the top 5 cm of cores (augured). They recommended sampling within a radius of between 0.5 m (after 10 years) and 1.5 m (after 100 years) for CWA containing an estimated 44 g of arsenic. They expected the contaminated area to increase for larger quantities of CWA.

A total of 8 soil samples were collected from the area of interest in March 2016 from the surface

and as close as possible to bomb sites and craters (mostly downslope where possible) as recommended by [17], Figure-4 and Table-2. Samples were collected using a scraper after first carefully removing surface vegetation and loose material. Samples were collected from a maximum depth of 0-10 cm below the surface and within 0 to 1.0 m from crater sites pointed out by survivors/witnesses.

In this study, the environmental impacts of CWA contamination on soil and water resulting from the bombing in the area were investigated. The Toxicity Characteristic Leaching Procedure [34, 35, 36] was used for investigating the soil samples. With this procedure, the inorganic analytes were determined which were present in the impacted soil samples [37]. The method allows for the leaching of the mobile phase (remnant effects from bombing) present in the contaminated soil. The resulting extract was analyzed to determine if a given soil sample is hazardous.

Due to the solubility and degradability of the CWA it is possible to use more common analytical techniques to identify such degraded products. This, therefore, allows for the identification of the parent (CWA) substances. The analysis techniques used for the water quality analysis are standard, water analyses techniques such as ICPMS, Ion selective electrode, ion chromatography, and coulometer.

Preliminary evaluations included soil particle size reduction required and the particles should not pass through 9.5mm screen. The pH of the sample suspension is determined and the selection of the extraction fluid type was based on the pH. The appropriate extraction fluid is determined as follow:

A sample size of 100 g was used and transferred into a borosilicate glass bottle. The amount of extraction fluid added to the glass bottle was calculated as follows: $20 \times \% \text{ solids} \times \text{mass of waste filtered} / 100 \text{ ml}$. The extraction fluid was carefully added to the glass bottle. The bottle lid was closed tightly and Teflon tape was also added for an improved seal. The bottle was secured in a rotating incubator and shaken at 30 RPM for 18 h. The incubator temperature was kept at 23 ° C during the extraction. After extraction, the extract was filtered through the prepared glass fiber filter and the pH recorded. The extract was immediately aliquoted and stored under refrigeration (4° C) for analysis if the concentration of metallic analyte exceeds TCLP limits, then the soil sampled would be hazardous and further rehabilitation of the area might be required. The samples were returned to the Mhlathuze Water Laboratory in Richards Bay, South Africa for analysis.

Water Sampling

Water samples were collected from seven springs, ten water well, and one surface water downslope and as close as possible to the bombed areas. Surface and spring samples were collected after first flushing the plastic bottle 3 times. Borehole samples were pumped until constant electrical conductivity (EC) was reached. Pump depth was requested from owners and recorded where available. From previous studies, it was known that groundwater level in the area is shallow. The Water samples were collected in polyethylene bottles 250 ml bottles for analyzing the compounds acting as indicators for the effects of the bombing are listed in Table-3.

Physical parameters such as pH, temperature, and EC were determined on site using the multi-parameter device (Fisher AP85 and AP75). The sample bottles were placed in a cool box and refrigerated until transported to South Africa. The water samples were analyzed at an accredited (water quality testing) Mhlathuze Water Laboratory in Richards Bay, South Africa following the techniques as shown in the Table -3.

When looking at CWA dumpsites, determined that when sampling in locations with soil heterogeneity, sampling error can supersede analytical error. Concentration in the soil samples can vary between undetectable to extreme concentrations within 1m of each other and is therefore dependent on the geology, hydrogeology, and climate [38].



Figure 4-Soil and water sampling sites in the study area

Table 2- Names of selected soil, wells, springs, and samples for CWA indicators analysis.

Sample No.		Site name	Elevation (m)	Physiochemical testing for water sample	
Water	Soil			pH	EC ($\mu\text{s}/\text{cm}$)
Hal 1(S)	SS1	Blaquwe	693	7.98	387
Hal 2(B)	SS2	Mosque	744	7.55	651
Hal 3 (S)	SS3	Mosque spring	728	7.63	396
Hal 4 (S)		Rock cliff	740	7.58	460
	SS4	Rock cliff	746		
Hal 6 (S)		Mosque Anab	738	7.89	400
Hal 7 (S)		Kalich spring	752	7.66	358
	SS8	Cemetery and monument	765		
Hal 9 (B)	SS9	Merzaboto street	710	7.16	723
	SS10	Dead children arm			
Hal 11 (B)		Omer Khawer house	715	7.05	1243
Hal 12 (B)		Aras Said Abbas house	738	7.68	510
Hal 13 (B)	SS13		723	7.5	581
Hal 14 (B)			745	7.3	685
Hal 15A (S)		Bamok village	780	7.13	569
Hal 15B (B)		Bamok village	780	7.7	349
Hal 16 (B)		Zamake farm	624	6.91	740
Hal 17 (B)		Zamake farm	624	7.27	571
Hal 18 (R)		Prees	740	8.4	348
Hal 19 (S)		Chawg spring	848	7.4	384
Hal 20 (B)		Mamuzen		8.06	372

Note: B borehole (water well), R-River S-Spring

Table 3- Analyses techniques used to identify CWA indicator

Analysis	Units	Method Nr	Technique	Detection limit
Arsenic as As	µg/l	MWIM 355	ICPMS	0.21
Cyanide free as CN	mg/l	MWIM 210	Ion selective electrode (ISE)	0.07
Fluoride as F	mg/l	MWIM 071	Ion chromatograph (IC)	0.05
Nitrate as N	mg/l	MWIM 071	Ion chromatograph (IC)	0.08
Soluble orthophosphate as PO ₄	mg/l	MWIM 400	Coulometry	0.03
Phosphorous	mg/l		Calculated	-
Sulphate as SO ₄	mg/l	MWIM 071	Ion chromatograph	0.5
Sulphur	mg/l		Calculated	-

Results and discussion

Soil samples results

The results of the chemical analysis of soil samples for all selected sites are presented in Table-4. The concentration of Arsenic ranges from 2.5 to 17.5 µg/l with an average 7 µg/l, and for Cyanide below the detection limit. The concentration of Fluoride, soluble orthophosphate, Nitrate, and Phosphorous was 24 to 203 mg/l with average 157 mg/l, 0.04 to 14.4 mg/l with average 3.06 mg/l, 0.12 to 31.1 mg/l with average 1.0mg/l respectively. While for Sulphate and Sulphur was 49 to 803 mg/l with average 186 mg/l, 32.6 to 536 mg/l with average 124.3 mg/l respectively.

Water samples results

The results of the physical test and chemical analysis of water samples for all selected springs, wells, and surface water are presented in the Tables-(2, 5).

The water samples are neutral to slightly alkaline with pH ranging from 6.9 to 8.4. The EC value for the whole water samples ranges from 348 to 1243 µs/cm with an average 540 µs/cm. The concentration of Arsenic ranges from below detection limit to 1.16 µg/l with average 0.55 µg/l, and for Cyanide, soluble orthophosphate, and Phosphorous was below detection limit except for samples (13, 14, and 20). The concentration for fluoride, nitrate, Sulphate, and Sulphur ranges from 0.07 to 0.58 mg/l, 0.61 to 15.9 mg/l, 5.8 to 225 mg/l, and 3.9 to 150 mg/l respectively with average 0.14, 5.3, 32, and 21.3 mg/l. All water samples are safe and the chemical contaminants do not exceed the permissible limit according to [39].

Table 4- Soil sample analysis results

Sample	Arsenic as AS/MWIM 355 µg/l	Cyanide free as CN/ MWIM 210 mg/l	Fluoride as F/ MWIM 071 mg/l	Soluble orthophosphate as PO ₄ / MWIM 400* mg/l	Nitrate as N/ MWIM 071 mg/l	Phosphorous as P mg/l	Sulphate as SO ₄ / MWIM 071 mg/l	Sulphur as S mg/l
SS-1	2.52	<0.07	202.8	0.04	2.34	0.01	135	90
SS-2	6.82	<0.07	196.06	0.66	0.3	0.21	55.8	37.3
SS-3	6.42	<0.07	195.19	2.66	0.81	0.87	52.6	35.1
SS-5	6.11	<0.07	189.37	14.40	2.96	4.67	88.7	59.2
SS-8	3.49	<0.07	198.19	0.06	0.12	0.02	48.9	32.6
SS-9	17.45	<0.07	162.21	1.51	31.1	0.49	803	536
SS-10	12.06	<0.07	41.04	7.54	0.26	2.46	94	62.8
SS-13	4.48	<0.07	202.68	0.35	4.89	0.11	145.6	97.2
SS-16	3.87	<0.07	24.19	0.24	2.51	0.08	253	168.9
USEPA method 1311(soil extraction) mg/l	5	10	15-18					

Table 5- Water sample results

Sample	Arsenic as AS/MWIM 355 µg/l	Cyanide free as CN/ MWIM 210 mg/l	Fluoride as F/ MWIM 071 mg/l	Soluble orthophosphate as PO ₄ / MWIM 400* mg/l	Nitrate as N/ MWIM 071 mg/l	Phosphorous mg/l	Sulphate as SO ₄ / MWIM 071 mg/l	Sulphur as S mg/l
MUN1	<0.21	<0.07	0.07	<0.03	0.61	0.0	6.3	4.2
HAL 1	0.75	<0.07	0.58	<0.03	2.54	0.0	6.3	4.2
HAL 2	0.69	<0.07	0.12	<0.03	0.84	0.0	9.7	6.5
HAL 3	0.69	<0.07	0.12	<0.03	2.54	0.0	5.8	3.9
HAL 4	0.66	<0.07	0.13	<0.03	3.01	0.0	6	4
HAL 7	0.54	<0.07	0.13	<0.03	3.68	0.0	8.2	5.5
HAL 9	<0.21	<0.07	0.1	<0.03	9.55	0.0	83.6	55.8
HAL 11	0.94	<0.07	0.08	<0.03	15.4	0.0	225	150
HAL 12	0.27	<0.07	0.11	0.14	8.93	0.05	27.6	18.4
HAL 13	0.21	<0.07	0.12	0.03	7.96	0.01	14.5	9.7
HAL 14	0.31	<0.07	0.08	<0.03	15.9	0.0	24.9	16.6
HAL 15A	0.38	<0.07	0.12	<0.03	3.96	0.0	27.4	18.3
HAL 15B	<0.21	<0.07	0.07	<0.03	3.14	0.0	20.4	13.6
HAL 16A	0.3	<0.07	0.18	<0.03	7.6	0.0	25.1	16.8
HAL 16B	0.51	<0.07	0.17	<0.03	2.69	0.0	44.4	29.6
HAL 18	1.16	<0.07	0.12	<0.03	2.42	0.0	9	6
HAL 19	0.25	<0.07	0.12	<0.03	2.28	0.0	6.8	4.5
HAL 20	<0.21	<0.07	0.1	0.04	2.36	0.01	23.4	15.6
WHO(2011) in drinking water (mg/l)	0.01	0.07	1.5	0.4	50		500	

Conclusion

From the results obtained for the determination of the environmental impacts of chemical bombing on the availability of indicator metals in the water and soil it concluded that the absence of detectable levels of mustard, nerve agents and their hydrolysis products suggest that Southern Kurdistan's wet climatic periods during the winter and spring would most probably have resulted in the hydrolysis of any agent originally present and the hydrolysis products are likely to have been leached out of the soil by runoff water or microbial decomposition in the intervening period.

From the initial investigation using the indicators (As, Cn, P, TN & F) both soil and water analyses show no sign of remnant pollution in the area. Most of the bombing constituents were organic in nature which could have been chemically weathered as a result of the high permeability and porosity of the overlying soils and underlying aquifers. The potential dilution flushing of the porous sediment by annual rainfall also assisted over the 28 years since the attack. Soil pH indicated slightly acidic pH which also determined the extraction liquid. This probably allowed for the release of geologically bound fluorides from the soil. No indication of fluorides was found in groundwater and spring samples from the area. It can be assumed that due to the lack of concentration levels above allowable limits for the indicators tested from the sampled sites no remnant impact from the bombing remained.

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