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Long term hazards of chemical weapon agents: Analysis of soil samples from Kurdistan years after exposure to sulphur mustard and nerve agents

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Abstract: Between 1987-1988 vast areas of Southern Kurdistan was subjected to repeated attacks of chemical weapons (CW). Very little is known about the long term fate of the CW agents in the environment and their residual hazard to man and plants. Ten soil samples were collected in farmed areas of Southern (Iraqi) Kurdistan between August and September, 1992 from sites of CW attacks reported in 1987-1988 and six control samples were collected from sites with no history of exposure to CW. The samples were analysed, at the Chemical and Biological Defence Establishment at Porton Down, U.K., for sulphur mustard, nerve agents and any other volatile components using full scanning gas chromatography-mass spectrometry, and for sulphur mustard and its hydrolysis product thiodiglycol using the more sensitive technique of selected ion monitoring. Extracts were also analysed for the hydrolysis products of the nerve agents GB, GD and GF using selected ion monitoring. Although six samples contained traces of the insecticide DDT and/or its decomposition product DDE, no traces of CW agents or their hydrolysis products were detected in the samples. It appears that the wet climatic periods during the winter and spring or other natural environmental conditions have completely hydrolysed the CW agents over the years and, therefore, no residual hazards remained in the soil from farmed areas.

Keywords: chemical weapon, mustard agents, nerve agents, Halabja

Introduction

During the period 1987-1988, Southern (Iraqi) Kurdistan was subjected to repeated attacks of chemical weapons, during Iraqi Government's military operations (Anfals) against the country's Kurdish population [1-3]. Vast areas of Kurdistan were exposed to different combinations of poisonous gases during this period. In March 1988, the famous town of Halabja was attacked with a mixture of both blistering sulphur mustard and organophosphorus nerve gases which killed and injured thousands of civilians. After the chemical weapon attacks until spring, 1991, Kurdish farmers and inhabitants of the countryside of Iraqi Kurdistan were prevented from cultivating their lands or re-inhabiting their villages. After the last Gulf War, most farmers returned to their previously poisoned farms and villages. Some 18 months later, some people complained from ill-growth of plants and a few more from headache and malaise since their return. The farmers and the officials within the Federal Government of Iraqi Kurdistan expressed uncertainty about the long term effects of the previously used poison gases on the well-being of the land, agricultural products and peoples health. Despite extensive use of sulphur mustard in Europe in World War I and other subsequent uses in this century, very

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little is known about the long term fate of chemical weapon agents in the environment.

This study was conducted to gain further information and to determine the safety of the soil in Kurdistan 4-5 years after exposure to multiple chemical weapon attacks and to obtain reassurance for Kurdish farmers to recommence cultivation and re-inhabiting of the attacked villages and towns. Soil samples were collected from five different locations in Iraqi Kurdistan where chemical attacks were documented and were analysed for traces of chemical weapon agents at the Chemical and Biological Defense Establishment (CEDE) at Porton Down, U.K.

Materials and methods

Sampling

Sampling was performed according to internationally recognised guidelines which were provided, along with sampling and safety equipments, by the CBDE. CBDE standards for handling SIBCA (Sampling and Identification of Biological and Chemical Agents) samples were followed, which required documentation, photographic records and maintenance of an audit trail.

Sixteen soil samples were collected during the period 24 August to 2 September 1992 from areas of Southern Kurdistan and delivered to CBDE on 23 September 1992. Control soil samples were collected on or near agricultural land in the village of Mureba of Aqra town (Kl and K2) and in the town of Zakho (K3-K6). These areas had no history of chemical weapon activity. Samples K7-K12 were collected on or near agricultural land where chemical weapon attacks had been reported in 1987 or 1988. These included the village of Ware of Balisan Valley (samples K7 and K8 collected from the edges of a bomb crater) and the villages of Ja'faran near west of Qaradagh town (samples K8-K12, collected 2-4 m from a bomb crater). Samples K13, K14, K21 and K22 were randomly collected in or near the town of Halabja, away from residential areas (no nearby crater or bomb site was located due to lack of eye-witnesses at the time of collection). Containers labeled K15-K20 contained no samples and returned empty. Details of the sites of collection and copies of the sample log sheets, with eye witness accounts of the associated chemical weapon attacks, were documented (Fig. 1 shows a typical example) and provided to CBDE. Sample wrapping for transportation and labeling upon arrival at CBDE are shown in figures 2 and 3.

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K9 + K10

SAMPLE LOGSHEET

Sample Number: K9 + K10 Date: 26.8.92
Time: 7.10 pm.

Taken By: D. ALA'ALDEEN Signature: D. Alaaldeen

Witness: David Hampson Signature:

Location: Village of Jifaran of Qaradgh area in Sulaymaniya province. A small farm behind KRO office, belonging to Mr Namiq Tawfiq Mohammad, 20m from the main road. The spot is opposit Siaw mountain

Description: The Crater was inside the small farm 1mx 1m in the middle of the farm. Last year, Mr Namiq had ploughed the farm and filled the crater with Soil from the surrounding area (upto 3m from the crater). This farm was cultivated last year and this year. The soil was soft and clearly watered few days befor. The samples (K9 + K10) were taken from ~~the~~ a spot some 6 m away from the crater. K9 is from the soft top and K10 was taken from 6 inches down.

Comments:
Mr. Namiq, 65 years, was living in the village, his house overlooks the farm and he witnessed the bombardment. The attack occured at midnight in April, 1988. He was injured with two of his sons ~~Asso~~ (Ramadan and Rizgar). Mr Asaad Mohamad Karim, 29 years, also witnessed the attack. It was a Rocket attack from a Multi-launcher which came from Tanjaro and Sangaw Military base. The smoke was not visible clearly, but the attack of the ~~next~~ following days (12 days) were the same and the colour of the smoke was Brown Yellow with unpleasant smell. 3 people died after 2 days and some 20 others injured. The soil in the area ~~stained~~ ~~Before~~ whitish. The injuries were mainly temporary blindness, watery eyes & later skin reactions, blisters and discoloured the skin permanently. They had chest problems Another witness is Mr Othman Latif Mohammed, 38 y.

Figure 1: Documenting sample collection. This form was completed in the presence of a witness for each sample, and all sample collections were filmed on tape and photographed beside a current daily newspaper.

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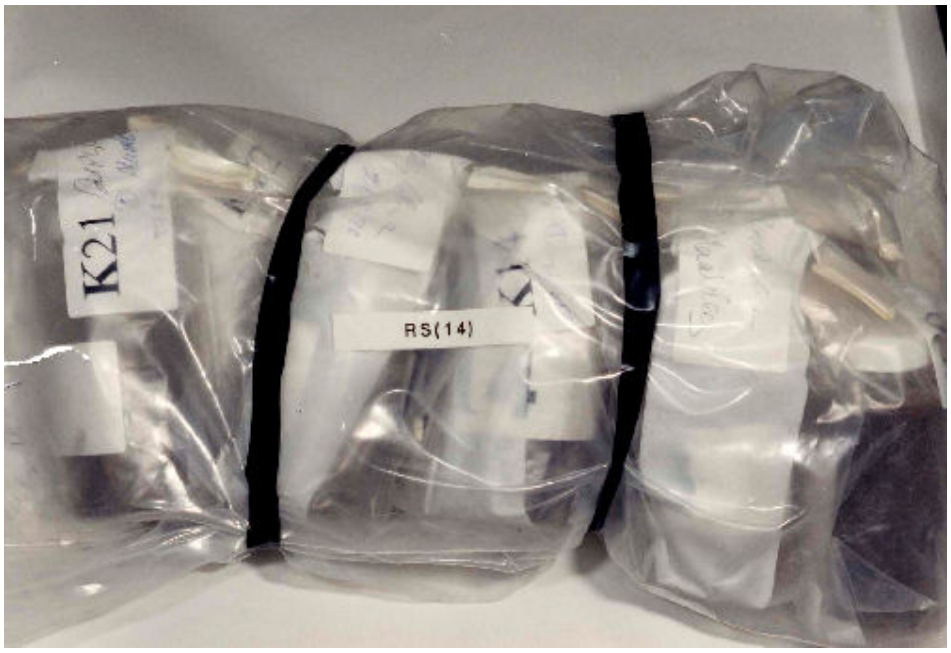

Figure 2: Soil samples were put in special containers, wrapped and remained unopened until arrived at CBDE, Porton Down. The chain of custody was not interrupted.

Figure 3: Soil samples were photographed on receipt at CBDE and split into two halves, one for analysis and another for reference.

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Analytical methods

Separate aliquots of each soil sample were extracted with dichloromethane and ethyl acetate respectively. The dichloromethane extracts were analysed by full scanning GC-MS for volatile chemical weapon agents and any other identifiable volatile contaminants. This screen should detect quantities around 1 ug/g of soil extracted. The dichloromehtane extracts were further analysed for sulphur mustard by the more sensitive technique of GC-MS with selected ion monitoring. The ethyl acetate extracts were also analysed by full scanning GC-MS, and, after derivatisation, for thiodiglycol using selected ion monitoring. The derivatised extracts were additionally analysed for methylphosphonic acid, isopropyi mehylphosphonic acid, cyclohexyle metholphosphonic acid and pinacolyl methylphosphonic acid, the hydrolysis products of GB, GD and GF, using selected ion monitoring.

An aliquot of each sample (ca 4 g) was extracted with dichloromethane (5 ml) using ultrasonication for 30 min and stood overnight. The extracts were analysed directly by full scanning GC-MS. The gas chromatograph was fitted with an HP Ultra 2 column, 25 m x 0.2 mm, film thickness 0.33 um; the oven temperature was held at 35 °C for 5 min, programmed from 35 °C to 280 °C at 10 C/min, and held at 280 C for 10 min; splitless injection (1 ul) was used, injector temperature 250 °C; helium was used as carrier gas. A VG Autospec mass spectrometer was employed using electron impact ionisation and scanning the mass range 40-650 amu at 1 scan/s. Selected ion monitoring for sulphur mustard was performed using the same equipment but using a modified temperature programme. Ions monitored were m/z 109, 111, 158, 160 and 162. The method would detect levels of sulphur mustard down to 25 ng present in the total extract.

A second aliquot of each sample (ca 4 g) was extracted with ethyl acetate (5 ml) by tumbling for 30 min in a screw-capped vial. The extracts were analysed directly for volatile components by full scanning capillary GC-MS using a Finnigan 4600 quadrupole mass spectrometer. The GC was fitted with a BPX5 column, 25 m x 0.22 mm, 0.25 um film thickness. The oven temperature was held at 65 °C for 1 min, programmed from 65 °C to 300 °C at 15 °C/min, and held at 300 °C for 2 min. Splitless injection (1 ul) was used, injector temperature 260 °C; helium was used as carrier gas at 15 psi. The mass spectrometer was scanned from 40-500 amu at 1 scan/sec using electron impact ionisation PX5 column, 25 m x 0.22 mm, 0.25 um film thickness. The oven temperature was held at 65 °C for 1 min, programmed from 65 °C to 300 '°C at 15 "C/min, and held at 300 °C for 2 min. Splitless injection (1 ul) was used, injector temperature 260 °C; helium was used as carrier gas at 15 psi. The mass spectrometer was scanned from 40-500 amu at 1 scan/sec using electron impact ionisation.

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For the detection of thiodiglycol and the phosphomc acids, a 1 ml aliquot of the extract was concentrated to dryness, dissolved in acetonitrile (80 ul) and derivatised by heating with 20 ul MTBSFA/1% TBDMCS at 60 °C for 1 h. Aliquots (1 ul) were analysed by GC-MS-selected ion monitoring for the t- butyldimethylsilyl derivatives of thiodiglycol, isopropyi methylphosphonic acid, cyclohexyl meholphosphonic acid, pinacolyl methylphosphonic acid and methylphosphonic acid. Chromatographic conditions were as above; ions monitored were m/z 153 (alkyi methylphosphonic acids), 267 (methyl phosphomc acid) and 293 (thiodiglycol).

Results and discussion

Full scanning GC-MS analysis of the dichloromethane and ethyl acetate extracts revealed no traces of sulphur mustard or its hydrolysis product thiodiglycol. No traces of the volatile organophosphorus chemical weapon nerve agents GB, GD, GF, their corresponding hydrolysis products or any other volatile chemical weapon agents were detected in the samples. Extracts from samples K7&, K8, Kl 1 and K12 were devoid of significant volatile contaminants which were not present in the glassware blanks or extracts of control samples. Dicholoromethane extracts from samples K9, K10, K13, K14, K21 and K22 contained traces of a volatile component identified as DDE, [2,2-bis(4-chlorophenyl)-l,l-dichloroethene], a decomposition product of the insecticide DDT [2,2-bis(4-chlorophenyl)-l,l,l-tricholorethane]. DDE was similarly detected in the ethyl acetate extracts from samples K13, K14, K21 and K22. The parent compound DDT, and its ortho, para isomer, were detected at very low levels in dichlbromethane extracts of samples K13 and kl4. Identification was confirmed by comparison with an authentic standard of DDT containing the ortho, para isomer and DDE as impurities. A mass chromoatogram of the ion m/z 235 revealed traces of DDT in the ethyl acetate extracts of samples K14, K21 and K22. No traces of sulphur mustard, thiodiglycol or the nerve agent hydrolysis products were detected in the extracts using selected ion monitoring (Figures 4-8 show typical findings).

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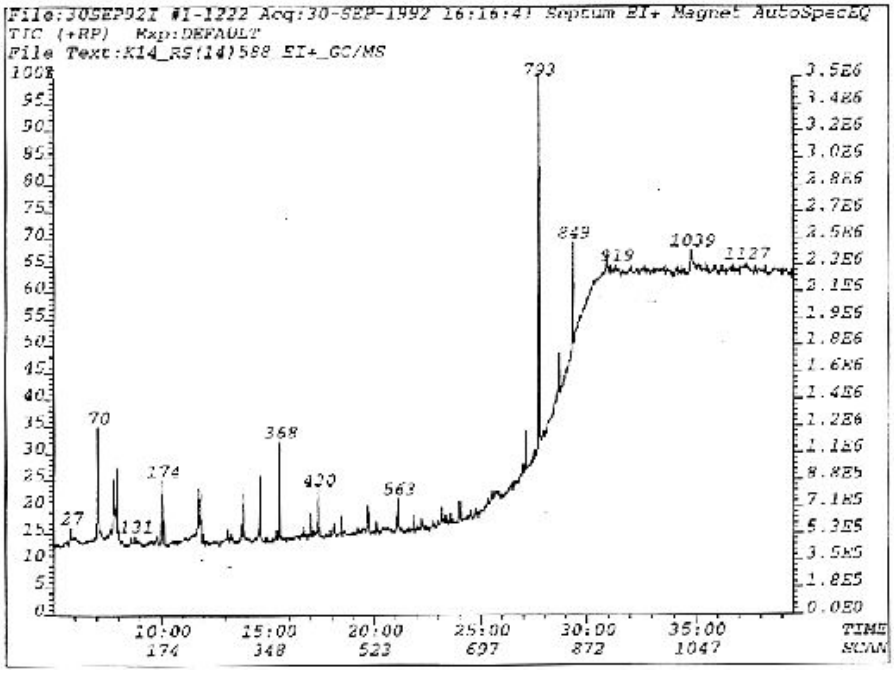

Figure 4: Total ion current chromatogram fro the dichloromethane extract of sample k14; peaks a, b and c were identified as dde, 0,p-ddt and ddt respectively

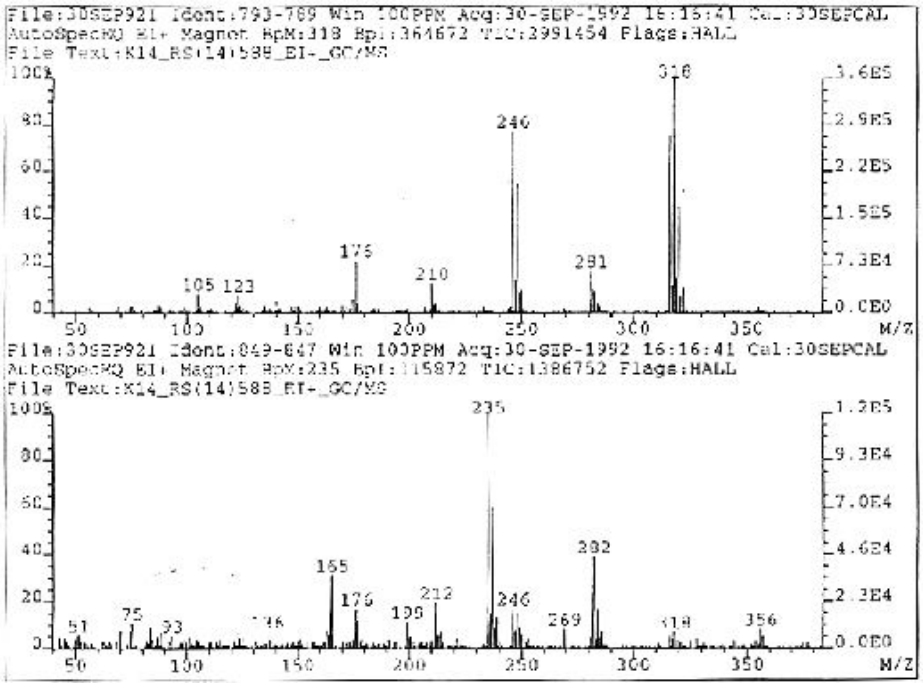

Figure 5: Mass Spectra of DDE (upper) and DDT (lower) in the dichlormethane extract of sample K14.

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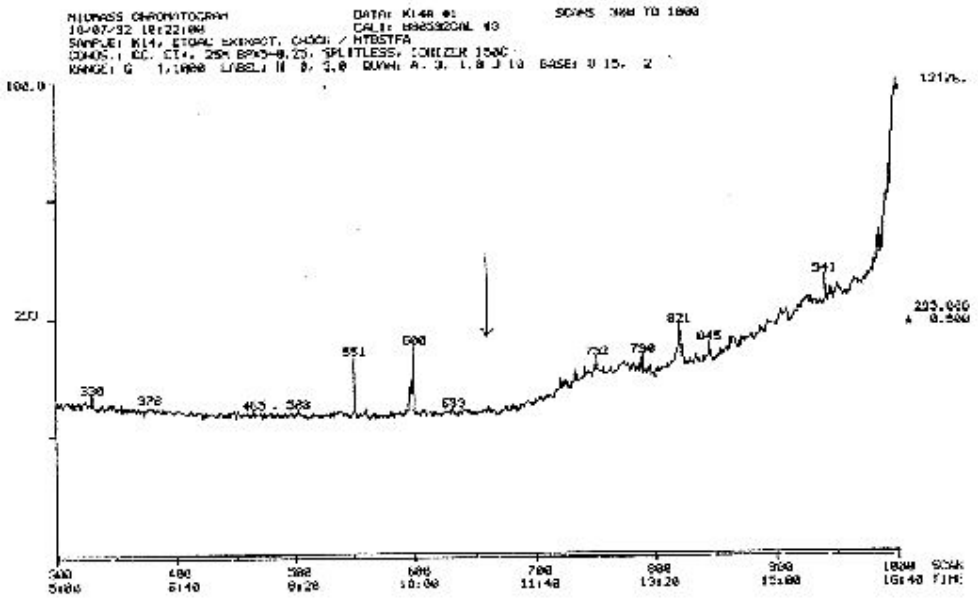

Figure 6: Selected ion current chromatogram showing the absence of thiodiglycol in the ethyl acetate extract from sample K14.

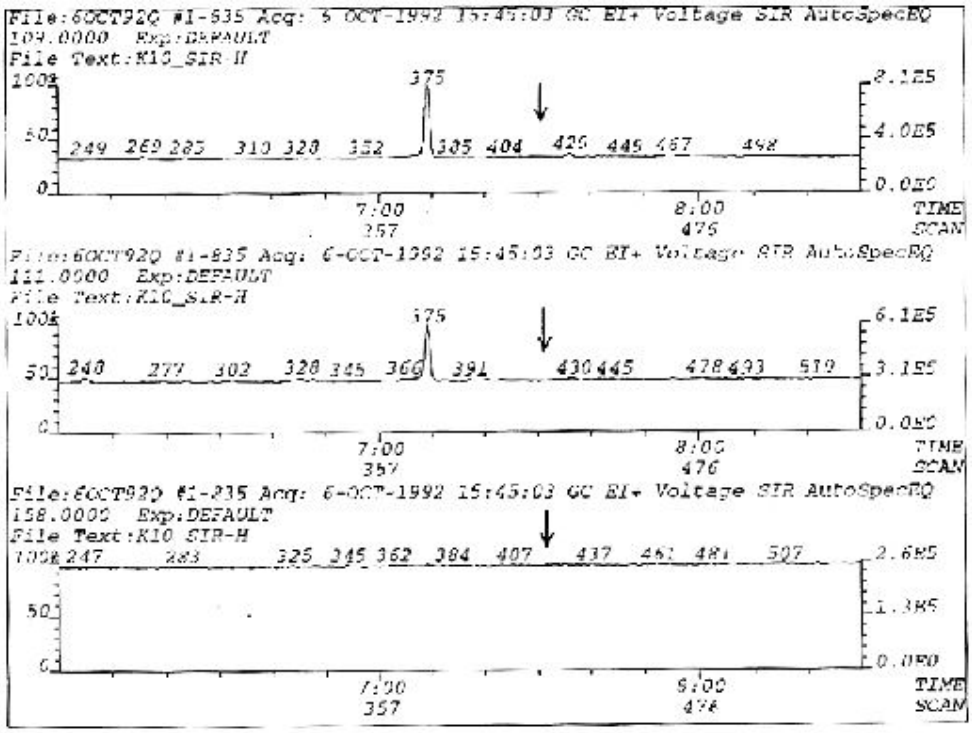

Figure 7: Selected ioin current chromatograms showing the absence of sulphur mustard in the dichloromethane extract from sample K10.

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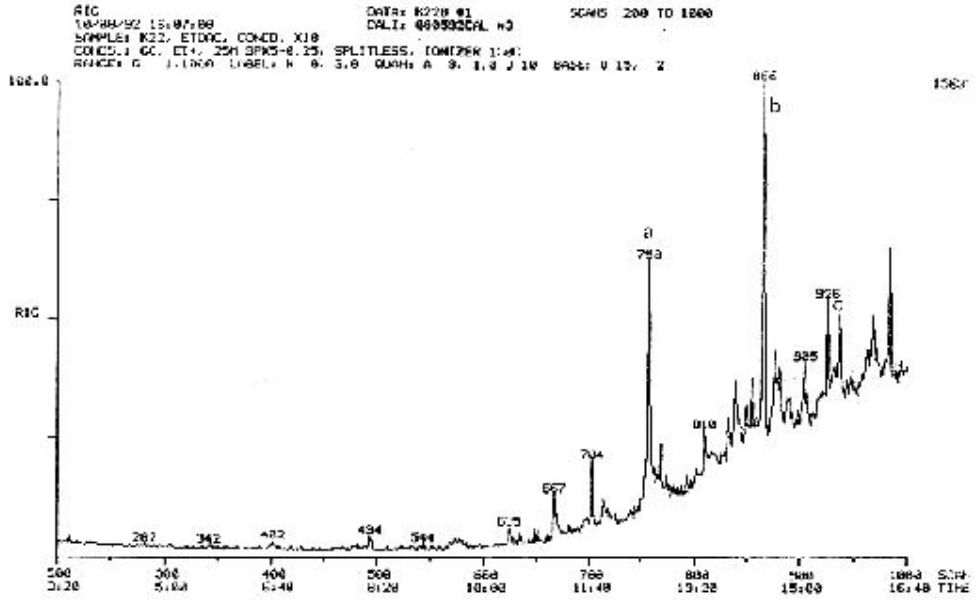

Figure 8: Total on current chromatogram from the ethyl acetate extract of sample K22; peaks B and C were identified as DDE and DDT, and peak A as hexadecanoic acid.

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 almost certainly have resulted in the hydrolysis of any agent originally present and the hydrolysis products are likely to have been leached out of the soil or microbially decomposed in the intervening period. It is possible that the collected samples may have not been representative, however, this is appears unlikely considering the careful selection methods followed. Samples K7-K12 were collected in or within 2-4 m around craters of chemical bombs. Almost all the samples were collected in the presence of a number of eye witnesses many of whom bore scars of injuries inflicted the described occasions. Lipophilic and less reactive organochlorine based pesticides, such as DDT, are much more persistent in the environment; one reason why the organophosphorus pesticides superceded organochlorine pesticides such as DDT was because their residues remained in the soil for much shorter periods.

The results of the analysis of these soil samples show no evidence of any residual hazard in the soil, indicating that four to five years of temperate climatic conditions of Southern Kurdistan and/or other natural environmental protective mechanisms have sufficient hydrolysing effects to rid itself of hazardous poisons. It is known that trees and plants are severely affected by direct exposure to chemical agents and large trees may recover slowly over time. However, continued ill-growth of the small plants or vegetables in some areas of the Kurdish countryside can not be

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attributed to on-going exposure to trace residual chemical weapons agents or any of their breakdown products. Similarly, the headache and malaise experienced by some farmers may not be related to their exposure to any contaminated soil. This does not rule out the possibility of on-going exposure to residual chemical weapons (particularly sulphur mustard) or its breakdown products that are known to remain active on house paints, metals and other hard objects which are not affected by changing weather [3]. This study was the first to be carried out on farmland soil years after exposure to chemical weapons.

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I would like to thank Dr Graham Pearson, the Director General of the Chemical and Biological Defense Establishment (CBDE), Porton Down, Salisbury, U.K., Dr Mary French, superintendent of the Chemistry and Documentation Division at CBDE, and Dr Robin Black, a scientist at the latter division, for their kind cooperation and carrying out the full analysis of the soil samples in the CBDE laboratories.

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