Hair and Natural Textiles as Detectors for Chlorine Gas Exposure

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INTRODUCTION

This research investigated new methods for assessing whether people and their clothing were exposed to chlorine gas, a resurgent chemical warfare (CW) agent which has the potential to cause hundreds to thousands of civilian and military causalities and deaths. This research examined changes to the micro-structure of human hair and natural textile fibers that may occur due to Cl_2 dosage (exposure time and concentration of Cl_2). A suite of micro-analytical methods were used to examine and characterize hair and fibers that were exposed to Cl_2 gas.

BACKGROUND

At standard temperature and pressure (STP), chlorine is a diatomic greenish-yellow pungent smelling poisonous gas that is approximately 2.49 times denser than air. The toxicity of Cl_2 gas stems from the formation of two acids (hydrochloric [HCl] and hypochlorous [HOCl] acid) when it is exposed to water:

$$Cl_2 + H_2O \leftrightarrow HCl + HOCl \leftrightarrow 2HCl + O^{-}$$

The two acids and the oxygen free radicals damage cell walls and interact with sulfhydryl groups in amino acids and enzyme systems (1). At a concentration of ~1,000 ppm, Cl_2 gas kills most animals in a short time (2-4). Cl_2 concentrations of 40-60 ppm are considered dangerous if exposure is 30-60 mins (2-4). The maximum concentration for an exposure of 60 mins without serious injury is only 4 ppm.

Origin of Cl_2 as a CW Agent

CW agents were pioneered by the German chemist Fritz Haber during World War 1 (WW1). It is estimated that Cl_2 gas attacks resulted in approximately 90,000 deaths and 1.2 million casualties during WW1 (5). Public outcry from the use of CW agents during the Great War resulted in the 1925 Geneva Protocol, which prohibited the use of chemical weapons in warfare (6). Cl_2 gas had a significant resurgence during Operation Iraqi Freedom. A review of open-source literature shows that at least 15 separate times Cl_2 gas was used as a weapon of mass destruction against coalition forces and civilian populations (7-12). Chlorine gas was an attractive agent to use in these attacks because it was readily available in large quantities. Chlorine gas is legitimately used in municipal water treatment facilities to treat waste water and to provide clean drinking water. Chlorine is imported by tanker truck (Figure 1) into Iraq from surrounding countries. These tankers were hijacked by insurgents enroute to their destinations and subsequently detonated to disperse the poisonous gas.

One of the most widely known uses of CW agents (which includes Cl_2) was during the Syrian Civil War (13). Here, the Syrian government along with the Islamic State (ISIL) deployed CW agents on the Syrian people that opposed the Assad regime. The Organisation for the Prohibition of Chemical Weapons (OPCW) released reports concluding the Syrian army dropped Cl_2 bombs from helicopters onto civilian groups of the Syrian population (13-15).

Figure 1. (A.) Large tanker truck used to transport Cl_2 gas for legitimate municipal activities. (B.) These tank trucks can be hijacked and detonated with large-scale improvised explosive devices.

METHODS

To investigate the effects of Cl_2 gas on relevant materials that could be exposed during a CW event, we examined human head hair as well as two common natural textile fabrics. Cotton (which also served as a proxy for other cellulosic fibers such as linen or flax) and silk are common textile fibers worldwide. During an initial pilot study, the authors first investigated the affects of Cl_2 exposure on the micro-structure of human hair using an in-house chemical reaction vessel (Figure 2A). A second phase of this research involved acquiring cylinders of Cl_2 gas at known concentrations. Hair and textile fibers were exposed for varying time intervals to determine whether observable physiochemical changes occurred.

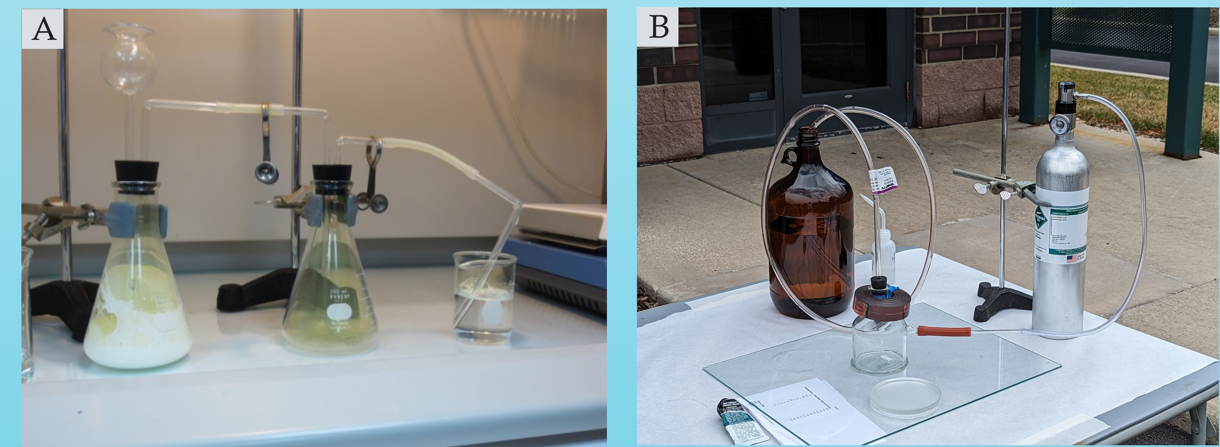

Figure 2. (A.) In-house Cl_2 gas generation and delivery system. Note the Cl_2 concentration was not known during exposures, thus the true dose was not known for this set of experiments. (B.) In-house Cl_2 gas delivery system. Note the Cl_2 concentration was known (1,200 ppm in air), thus the dosage (concentration x time) could be adjusted according to the required experimental conditions.

The hairs and textile fibers were examined by polarized light microscopy (PLM). A subset of the hairs and fibers were stained with either methylene blue or Neocarmine (red). Normally, hairs and textile fibers would not be stained with either of these stains. However, if their outer surface (e.g., cuticle layer of hair) is disrupted by Cl_2 gas exposure, the hairs and fibers may have the potential to take up the stains. A subset of the hairs were also examined at high magnification using a scanning electron microscope (SEM).

RESULTS

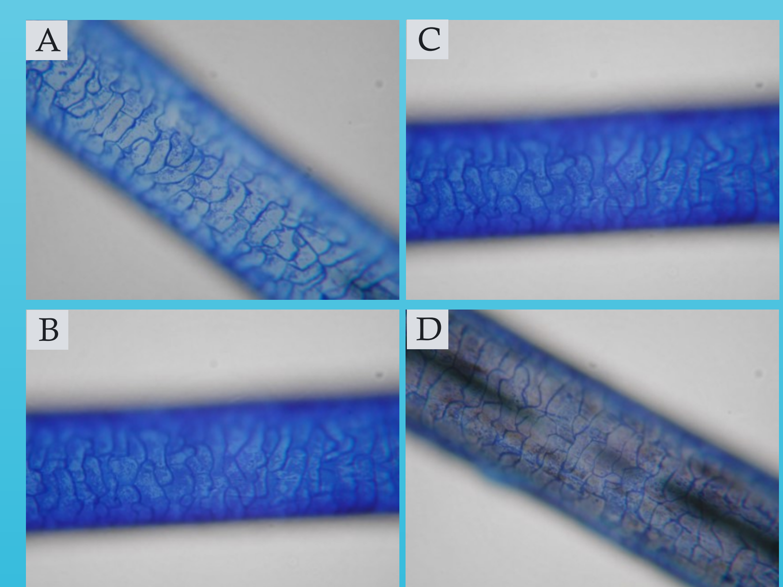

Figure 3. Several hair samples exposed for 5 seconds. All stained with methylene blue. Note the degree of staining varies between the different hairs even though they are all from the same donor.

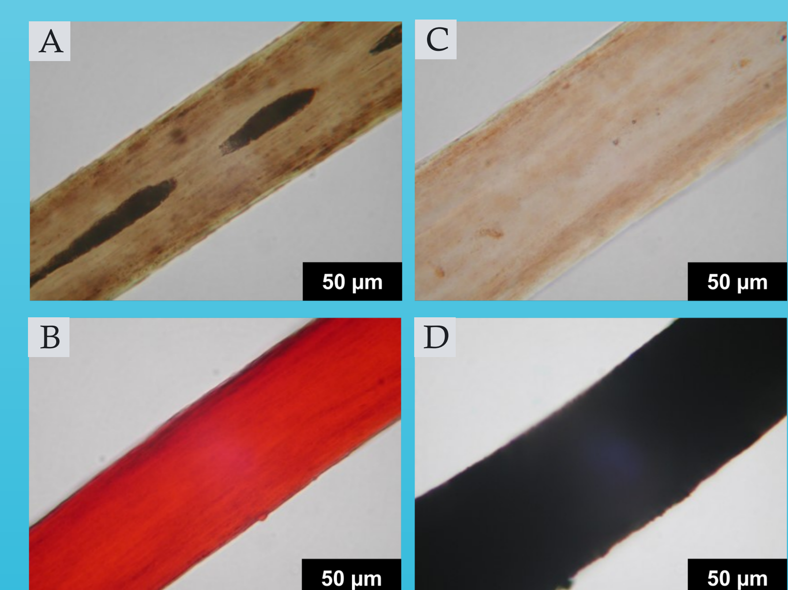

Figure 4. Appearance of the treated hair after 10 mins exposure. (A) Hair before exposure, stained with Neocarmine. (B) Neocarmine stained after exposure. (C) Hair without staining, after exposure. (D) Hair after exposure, stained with methylene blue. Note the hair shown in (D) was so strongly stained that it appears almost black.

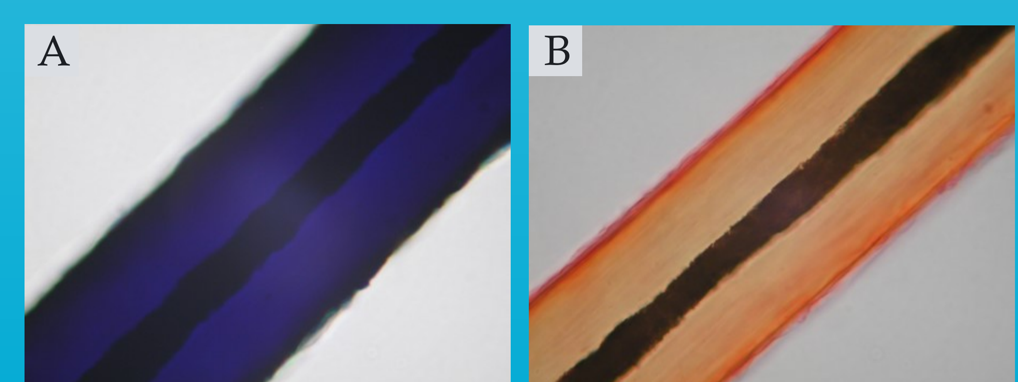

Figure 5. Hair after 30 seconds exposure to chlorine gas. (A.) Stained with methylene blue and (B.) Stained with Neocarmine.

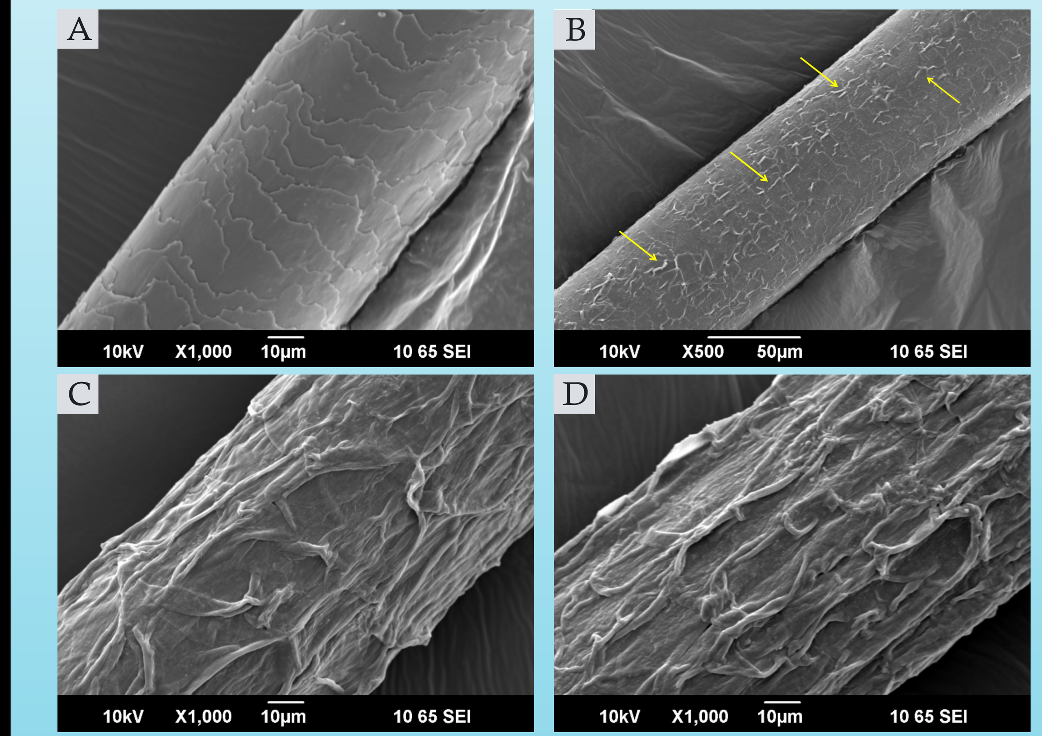

Figure 6. High-magnification SEM micrographs of a subset of the human hair samples. (A) Appearance of an untreated hair, (B) hair exposed for 5 seconds, (C) exposed for 30 seconds, and (D) exposed for 5 minutes. The yellow arrows in (B) indicate areas where the cuticle is starting to wrinkle.

DISCUSSION AND CONCLUSIONS

The results from the initial study showed that significant damage occurred to the cuticle layer of the exposed hairs when the samples were subjected to very high apparent dosages. This can readily be seen in the photomicrographs of the hairs which show significant stain uptake (Figures 3 – 5). In addition, the damage to the cuticle can be directly observed when the hairs are examined at high magnification using SEM (Figure 6). It is important to note that dosage (Cl_2 concentration x time) was not precisely known for this set of experiments.

The follow-on study, which used Cl_2 gas concentrations of 1,000 and 1,200 ppm for 15- and 30-min intervals, did not show any apparent damage to the cuticle layers of the hairs. In addition, no observable damage was observed in the cotton and silk textile fibers. No stain infiltration was observed for the hair and textile fibers at these known dosage levels. It is noted that a concentration of 1,200 ppm is much higher than what is estimated for the exposure of victims during Cl_2 gas attacks.

The results from this research show that it is possible for hairs to be sufficiently affected, by high concentrations of Cl_2 gas, such that they provide evidence of CW exposure. However, at known concentrations as high as 1,200 ppm, no morphological evidence was observed to detect Cl_2 exposure. Thus, for hairs (and potentially textiles) to confidently record Cl_2 exposure, the gas concentration must be higher than 1,200 ppm. Additional research is needed to see if other markers (morphological or chemical) may be used to detect Cl_2 exposure in hair and textile fibers.

ACKNOWLEDGEMENTS

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