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Efficacy of scalp hair decontamination following exposure to vapours of sulphur mustard simulants 2-chloroethyl ethyl sulphide and methyl salicylate

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ABSTRACT

Chemical warfare agents are an actual threat and victims' decontamination is a main concern when mass exposure occurs. Skin decontamination with current protocols has been widely documented, as well as surface decontamination. However, considering hair ability to trap chemicals in vapour phase, we investigated hair decontamination after exposure to sulphur mustard simulants methyl salicylate and 2-chloroethyl ethyl sulphide. Four decontamination protocols were tested on hair, combining showering and emergency decontamination (use of Fuller's earth or Reactive Skin Decontamination Lotion RSDL®). Both simulants were recovered from hair after treatment, but contents were significantly reduced (42–85% content allowance). Showering alone was the least efficient protocol. Concerning 2-chloroethyl ethyl sulphide, protocols did not display significant differences in decontamination efficacy. For MeS, use of emergency decontaminants significantly increased showering efficacy (10–20% rise), underlining their usefulness before thorough decontamination. Our results highlighted the need to extensively decontaminate hair after chemical exposure. Residual amounts after decontamination are challenging, as their release from hair could lead to health issues.

1. Introduction

Despite international regulation through the Chemical Weapons Convention [1], recent history has shown that military or civilians exposure to chemical warfare agents (CWA) can still occur [2]. Among CWA, sulphur mustard (SM or HD) is one of the most famous as it was massively used during World War I. It is a highly reactive agent which quickly penetrates skin [3] and alkylates numerous molecules, including DNA [4,5]. First symptoms of skin contamination, *i.e.* irritation followed by vesication, usually appear only 30 min to several hours after exposure [6].

Following exposure to CWA, emergency decontamination and care are of primary importance. Decontamination consists in neutralizing and/or removing the contaminant from the body surface. Emergency decontamination kits such as fuller's earth (FE) and Reactive Skin Decontamination Lotion (RSDL®) have been shown to be quite effective on pig skin when used even 45 min following exposure to the nerve agent VX [7]. Thorough decontamination will then consist in disrobing, showering with water containing detergent or soap, rinsing with water, and finally drying [8,9].

Effectiveness of skin decontamination procedures has been largely investigated through the use of *in vitro* and *in vivo* human skin models [10–15], including human volunteers studies involving non-toxic CWA simulants [16,17]. However, wounds, hair or eyes decontamination have been much less studied and is important to consider. Previous studies have shown that following vapour exposure, scalp hair can trap external contaminants such as cocaine

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and cannabinoids [18,19] but also the chemical warfare agent simulants methyl salicylate (MeS) [20] and 2-chloroethyl ethyl sulphide (CEES) [21]. To our knowledge, health issues related to chemicals trapping ability of hair and their subsequent decontamination have not been investigated. Indeed, once trapped in hair, chemicals could actually be released and intoxicate more people, including rescuers. As a matter of fact, secondary exposure to sarin has been observed during Tokyo subway attack in 1995 [22–24], highlighting the need for proper decontamination and protection when dealing with chemically contaminated people. Keeping that in mind, it is essential that decontamination procedures take the hair matrix into account, and that efficacy of standard decontamination protocols be evaluated for hair.

In this work, hair locks were exposed to MeS or CEES vapours, then decontaminated with various procedures in order to evaluate their efficacy on hair. These chemicals were selected as SM simulants according to their physicochemical properties. MeS shows similar vapour pressure to SM (see Table 1) and was then chosen to mimic SM's behaviour in vapour phase. Given that octanol/water partition coefficients are similar for both compounds (Table 1), MeS is also expected to behave similarly to SM towards the hair lipid phase. However, as opposed to MeS, the chemical structure and, as a result, electrophilic properties of CEES are similar to that of SM (Table 1). Furthermore, the main interest of using MeS as SM simulant is that it is far less toxic than SM or CEES. Therefore, it can safely be used to test experimental set-up.

Four decontamination procedures were evaluated and compared. They combined emergency decontaminants (FE and RSDL®) and thorough decontamination (shower).

2. Materials and methods

2.1. Chemicals, materials and hair

Methyl salicylate (99% purity), 2-chloroethyl ethyl sulphide (98% purity) and N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) were purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France). Internal standard (IS) methyl salicylate-d_4 was purchased from Cluzeau Info Labo (Sainte-Foy-la-Grande, France). Suprasolv® dichloromethane (DCM) and acetone were supplied by VWR (Fontenay-sous-Bois, France), as well as Teflon® ribbon used to hang hair locks for exposure.

Standard MeS (1182 μg mL^{-1}) and CEES (1605 μg mL^{-1}) solutions were freshly prepared in DCM, and calibration solutions were prepared by subsequent dilution of standard solutions. Preparation of spiking IS solution in acetone (58.6 μg mL^{-1}) was previously described [20].

One-liter two-neck round-bottom flasks were manufactured by the glasswork service of Aix-Marseille University (Marseille, France).

FE (particle size 90% ≤ 100 μm) was purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France). RSDL® kits were obtained from E-Z-EM Canada Inc. (Anjou, Canada). The OpCell® sponge contained in those kits was cut into 2.5 × 3.5 cm pieces. Liquid Marseille soap from Le Sérail (Marseille, France) was used for showering experiments. *In vitro* hair showering was performed as already described by Josse and colleagues [28]. Water temperature and flow rate could be modulated from 15 to 50°C, and from 0.1 to 5 L min^{-1}, respectively. Liquid soap concentration was adjustable from 0.2 to 10% (v/v). Absorbing paper (Fouque Chimie, Marseille, France) was used to remove FE from hair and to dry hair after showering.

Natural blond hair was supplied by Sécher-Fesnoux (Chaville, France). Hair samples were prepared as 5-g locks (~30-cm long). In order to avoid hazardous chemicals projections, hair showering was performed in a CaptairPyramid glove box from Erlab (Val-de-Reuil, France) disposed in a fume hood.

2.2. Hair exposure to MeS or CEES

Hair locks were weighed then hung at the top of a 1-L closed two-neck round-bottom flasks. Pure MeS (20 μL *i.e.* 23.6 mg) or pure CEES (100 μL *i.e.* 107 mg) was loaded at the bottom of the tank via a lateral neck. After closure, the tank was placed for 2 h in an oven at 40°C in order to speed up the evaporation process.

Control experiments were conducted in the same way. Contaminated hair was extracted just after exposure in order to evaluate initial contamination (initial content Q_0).

2.3. Hair decontamination

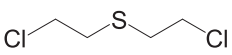
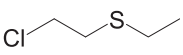
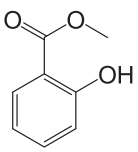
After exposure, hair locks were removed from the tank then transferred into a crystallizer. They were subjected to decontamination according to the procedures described in the following sections. Steps combination for each procedure is detailed in Table 2.

During showering, we did not apply any physical cleaning of hair surface, *i.e.* use of a sponge or flannel, in order to avoid variability due to human action.

2.3.1. Hair powdering with FE

A relatively large amount of FE, *i.e.* 5 g, was poured on the hair in order to entirely cover them. Then, hair was wiped 5 times from top to bottom by using a cotton pad. This allowed enhancing FE

Table 1
Physicochemical properties and chemical structures for SM and simulants CEES and MeS.

	Sulphur mustard (SM) CAS 505-60-2	2-Chloroethyl ethyl sulphide (CEES) CAS 693-07-2	Methyl salicylate (MeS) CAS 119-36-8
Molecular mass (g mol^{-1})	159.08	124.63	152.15
Vapour pressure (Pa, at 25 °C)	14.1–14.7	453	4.6–15
Vapour density	5.4–5.6	4.3[a]	5.2
Log $K_{o/w}$	2.41	2.2[b]	2.55
Chemical structures			

Data from Refs. [6,25–27].
[a] Fisher Material Safety Data Sheet.
[b] Estimated with EPISuite v4.11 ©2000–2012 EPA.

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