Dermal absorption of fumigants during HAZMAT exposure scenarios

Risk-Based Decision Making for Skin Decontamination for HAZMAT Incidents

Dr Sharyn Gaskin sharyn.gaskin@adelaide.edu.au, Prof Dino Pisaniello, Dr Linda Heath
Occupational & Environmental Hygiene Laboratory, University of Adelaide, Australia.

In collaboration with:
Dr Michael Logan, Queensland Fire & Emergency Services, Australia
Dr Susan Shahin, Department of Defence, Melbourne, Australia
Objectives

• Gases/vapours most common HAZMAT incident = injury

• Little known on extent and kinetics of skin absorption in HAZMAT involving toxic GASES and VAPOURS.

• **AIM:** to provide experimental data to assist in appropriate decision-making by first responders regarding skin decontamination
  • Skin decontamination should be risk-based & evidence-based

• Fumigants: phosphine, sulfuryl fluoride, methyl bromide, chloropicrin

• The data generated will be incorporated into the risk-based decision support tool ([www.chemicalcompanion.org](http://www.chemicalcompanion.org)).

Source: www.orchidsproject.eu
Why important?

• By using evidence-based approach:
  - Focus on people requiring assistance
  - Minimize number of people to be decontaminated
  - Reduced logistical and resource burden on emergency services

NOTE: focus is skin absorption of chemicals in the “worried well”. People with acute symptoms or signs will receive medical treatment as a priority.
Approach

• What is already known? Evidence for permeation?

• Chemical priorities (experiments): gas/vapours
  • using an OECD in vitro toxicology protocol using human skin and gas/vapour

• Concentrations of airborne contaminant
  = Lethal concentration (LCLo), IDLH, Exposure standards. (physiologically relevant for CBR incidents)
  • Up to 30 min exposures

• i.e. HAZMAT Exposure Scenario
How?

- Fresh human skin from cosmetic reduction surgery (abdomen)
How? cont...

- *In vitro* Franz diffusion cells – modified for gas delivery
- Detection: in/on & through skin
How? cont...

- Gas mixture delivery – dynamic atmosphere generator; certified gas
- Off-gassing from fabric e.g. ppbRAE PID (calibrated)
What are we measuring?

Potential species formed and physicochemical properties in relation to flux.

- Phosphoric acid (H₃PO₄)
- Phosphorous acid (H₃PO₃)
- Phosphonium ions
- Orthophosphates (insoluble)

We measure the chemical itself, a specific dissociation/ionisation/breakdown product, or a proxy as appropriate.
Modifying factors

- Influence of:
  - Different concentrations
  - Exposure time (up to 30 min)
  - Post-exposure ventilation (open atmosphere)
  - Temperature & relative humidity
  - Light, medium, heavy ‘street’ clothing (e.g. denim)
    - Note: protective clothing not included at this time
Outcomes: Grouped

Results for gases can be grouped into the following:

• **Brute force reactive gases** i.e. skin destruction, oxidise/ionise
  – Ammonia, chlorine, hydrogen chloride, sulphur dioxide

• **More subtle gases** which interfere **biochemically** e.g. redox, methylation, \( \text{O}_2 \) transport.
  – Hydrogen cyanide, hydrogen sulphide, nitrogen dioxide

• **Fumigant gases**
  – Phosphine, sulphuryl fluoride, methyl bromide, chloropicrin

Publications so far:
Gaskin, Baxter, Logan et al., JHazMat 2013 vol. 252-253 p338-346. (\( \text{NH}_3 \))
Gaskin, Baxter, Logan et al., JHazMat 2013 vol. 262 p759-765. (\( \text{Cl}_2, \text{HCN} \))
Gaskin, Baxter, Logan et al., ToxMechMethod 2014 vol.24 p70-72. (method)
Gaskin, Baxter, Logan et al., ToxIndustHealth, 2016 in press (\( \text{PH}_3, \text{H}_2\text{S} \))
# Outcomes - Fumigants

Skin (undamaged) = excellent barrier

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Phosphine</th>
<th>Sulfuryl fluoride</th>
<th>Methyl bromide**</th>
<th>Chloropicrin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IDLH = 50 ppm</td>
<td>IDLH = 200 ppm</td>
<td>IDLH = 250 ppm</td>
<td>IDLH = 2 ppm</td>
</tr>
<tr>
<td></td>
<td>LCLo = 1000 ppm</td>
<td>LCLo = 5000 ppm</td>
<td>LCLo = est. 1600 ppm</td>
<td>LCLo = 300 ppm</td>
</tr>
<tr>
<td>Concentration</td>
<td>Negligible Penetration at LC&lt;sub&gt;LO&lt;/sub&gt;</td>
<td>No Penetration at LC&lt;sub&gt;LO&lt;/sub&gt;</td>
<td>No Penetration at LC&lt;sub&gt;LO&lt;/sub&gt;</td>
<td>No Penetration at LC&lt;sub&gt;LO&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>Negligible* Absorption at LC&lt;sub&gt;LO&lt;/sub&gt;</td>
<td>No Absorption at LC&lt;sub&gt;LO&lt;/sub&gt;</td>
<td>No Absorption at LC&lt;sub&gt;LO&lt;/sub&gt;</td>
<td>Absorption at LC&lt;sub&gt;LO&lt;/sub&gt; for 10+ min exposures</td>
</tr>
<tr>
<td>Post-exposure ventilation</td>
<td>No effect</td>
<td>No effect</td>
<td>No effect</td>
<td>No effect (bound)</td>
</tr>
<tr>
<td>High temperature, humidity</td>
<td>No effect</td>
<td>No effect</td>
<td>No effect</td>
<td>No effect</td>
</tr>
<tr>
<td>Clothing</td>
<td>No effect</td>
<td>No effect</td>
<td>No effect</td>
<td>Reduced absorption, but fabric sink</td>
</tr>
</tbody>
</table>

* flux of 1.12 µgPH<sub>3</sub>/cm<sup>2</sup>/hr at 30 min
** Evidence (occupational exposure) of skin absorption & blistering (10,000 ppm 40 min) √SK notation
Major outcomes

• Set of practical guidelines can be derived. These are diagrammatically represented for each chemical as actions corresponding to different concentrations.

• Can we group "like" chemicals for which similar advice may be adopted?

- At high concentrations and exposure times (e.g. ≥ IDLH) if wearing bulky clothing or denim, remove outer layer.
- Decontaminate with enhanced ventilation or washing with water.
- Add fans, if available, to enhance the speed of ventilation.
Emergency Response Decision Support System

www.chemicalcompanion.org

Features:
The Chemical Companion provides first responders with decision support for hazardous environments contaminated with chemical agents. This software tool, which operates on Windows, Android, and iOS, is provided free-of-charge to the military, law enforcement, and fire departments.

Features include:

• Detailed information on 2,000 common chemicals and synonyms
• Personal Protective Equipment (PPE) including respirators
• Hazardous Concentration Levels and Exposure Guidelines
• Isolation and Protective Action Distances
• ERG and Emergency Medical Information
• Identify unknown chemicals using physical properties or exposure symptoms
• Decision Support Tools and more...

Development team:
Emergency Response
Decision Support System

- www.chemicalcompanion.org

**Sulfuryl fluoride**

**Person: Direct Gas Contact** - Move to Fresh Air

There is no decontamination requirement for this chemical. There is no evidence that skin is an entry route for Sulfuryl fluoride, but it may be a respiratory irritant.

**Warning:** For individuals whose skin is damaged or have visible signs of eczema, decontamination is recommended.

**Object: Direct Gas Contact** - Move to Fresh Air

There is no decontamination requirement for this chemical.

**Selection Details:**
- Gas, Sulfuryl fluoride, 2000 ppm
- Skin was directly affected by contaminate.
- Objects were directly affected by contaminate.

**Warnings:**
- Fresh air readily removes any Sulfuryl fluoride trapped within clothing.
- Move person upwind from affected area.
- Medical assessment of affected person required.
- Sulfuryl fluoride is classified as per the GHS/OSHA values for acute dermal toxicity, skin corrosivity and eye corrosivity.
- Sulfuryl fluoride is unlikely to present acute dermal toxicity, eye corrosivity, or skin corrosivity based on provided input.
- Follow Agency policy, adopt appropriate skin and respiratory protection and seek expert advice.
- All ppm values are measured by volume unless otherwise noted.
Ammonia (anhydrous)

**Person: Direct Gas Contact - Decon**
Decontaminate in accordance with agency policy.

**Object: Direct Gas Contact - Decon**
Decontamination of the object is required. Ammonia (anhydrous) poses a health risk to persons, and may affect the integrity of the object.

Selection Details:
- Gas, Ammonia (anhydrous), 1000 ppm
- Skin was directly affected by contaminant.
- Skin Contact: Unknown
- Donned Clothing: Shirt/trousers or dress
- Exposure Time: Unknown
- Objects were directly affected by contaminant.

Warnings:
- Move person upwind from affected area.
- Medical assessment of affected person required.
- Ammonia (anhydrous) is classified as per the GHS/OSHA values for acute dermal toxicity, skin corrosivity and eye corrosivity.
- Ammonia (anhydrous) causes severe skin burns and serious eye damage, but is unlikely to present acute dermal toxicity based on provided input.
- Follow Agency policy, adopt appropriate skin and respiratory protection and seek expert advice.
- All ppm values are measured by volume unless otherwise noted.

www.chemicalcompanion.org
• Thank you

• Question?