U.S. NAVAL RESEARCH LABORATORY

The chemistry of odor and odor detection

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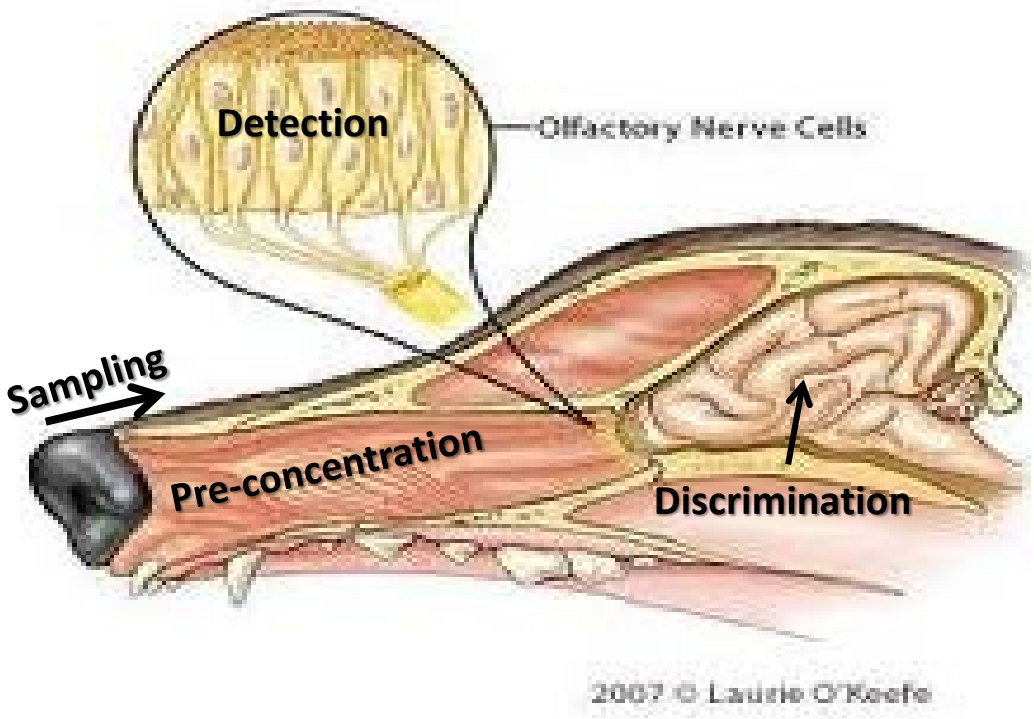
Canine as a Detector



Canine = *field detector*

- Sampling = *sniff*
- Pre-concentration = *nasal cavity*
- Detection = *olfactory nerves*
- Discrimination = *olfactory bulb*

Strengths and limitations of the canine detector

- Strengths
  - Sensitivity
    - Generally unmeasured, but considered to be below the detection limits of most instruments*
  - Selectivity
    - Ability to "see" unique odor signature and ignore background
  - Ability to follow scent to source
- Limitations
  - Lack of standardization and calibration
  - Odor targets to many analytes unknown

*Estimated LOD for nitromethane in ppt range – Kurry et. al., 2003

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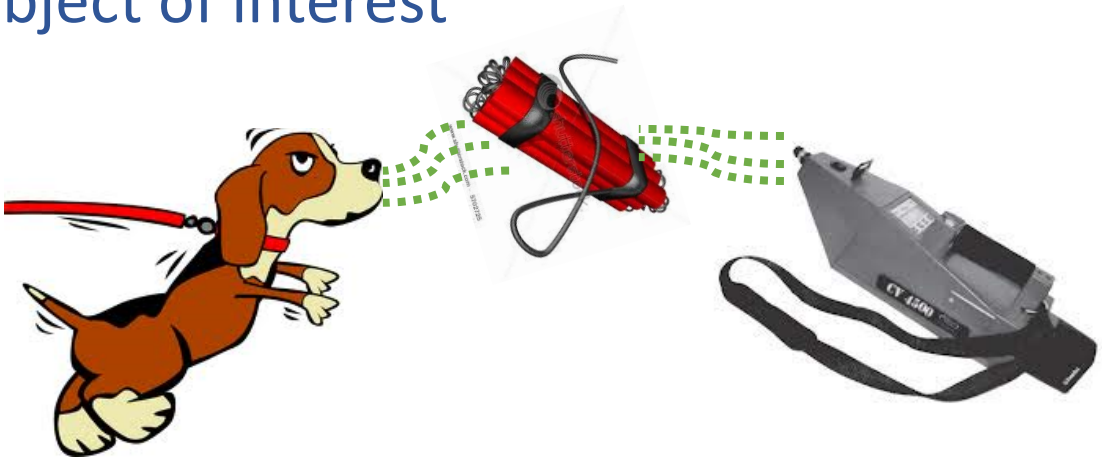
➢ **Research should be carried out to improve canine efficiency, training, and acceptance in the scientific community**

Odor Detection: Defined

- Odor detection = vapor sampling/analysis
  - Volatile organic compounds (VOCs) from scent object are released into the environment → detected
- Odorant = analyte to be detected
  - VOC that gives off an odor
- Odor profile = Unique group of odorants associated with object of interest



Odor Detection Challenges

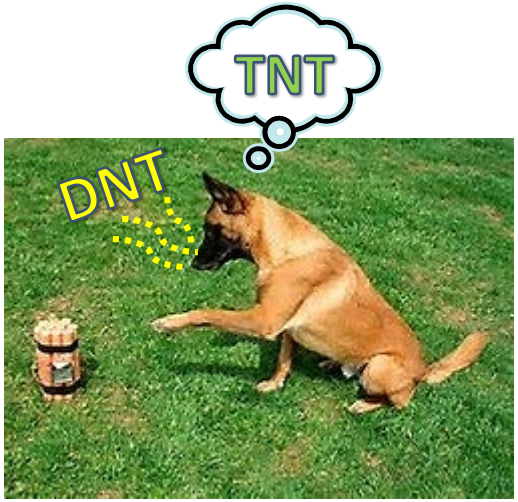
- Target compound may have low volatility
  - Low concentration of target available in headspace
  - Ex. TATP >> TNT > PETN / RDX > HMTD (?)
- Odor profiles may change with time / environment
  - Changes due to temp / humidity (i.e. increased /decreased volatility)
  - Changes due to degradation
- Odor profiles may be complicated
  - May contain many components → which ones are unique/important?
  - Ex. Human remains, some drugs / explosives

Odor Detection Challenges

- All of these challenges are complicated by field conditions
  - Sensitivity issues due to dilution in air
    - Also burial, wrapping, etc.
  - Selectivity issues due to background odors
  - Inability to control environmental conditions
    - High/low temp or humidity
    - Rain
    - Sunlight (photochemical changes)

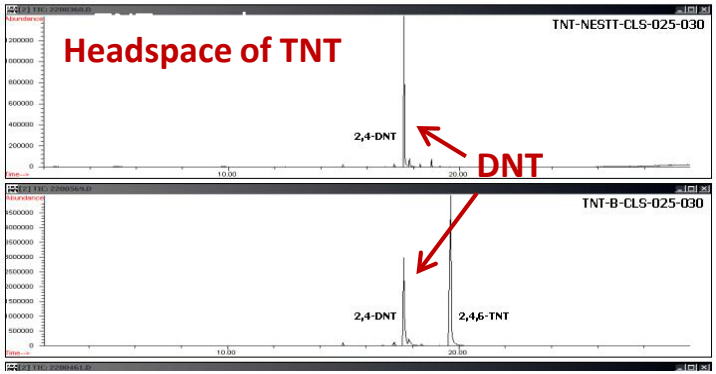
Odor Profiles

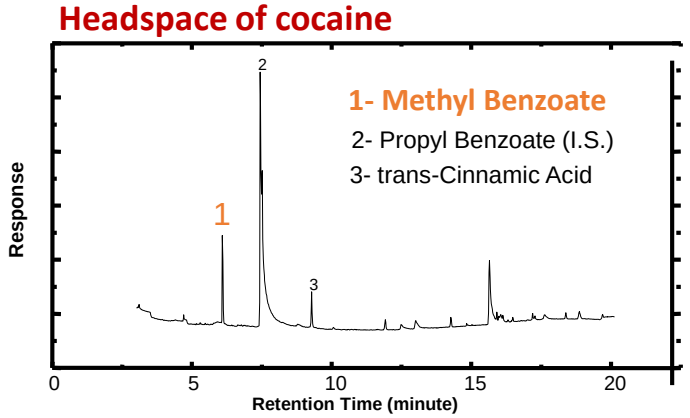
- Low volatility explosives
  - Challenges:
    - Minimal availability of parent compound
    - Real-world sampling conditions compound difficulties
  - Utilize whole odor profile:
    - Canines utilize the whole odor profile instead of parent compound alone
    - Detect the most unique and abundant volatiles associated with parent compound
  - Maximizes sensitivity and selectivity
- Researchers should understand odor profile of target compounds
  - Improve training / training aids
  - Enhance scientific understanding of canine abilities



Odor Profiles

- Odor profile = collection of odorants that make up the *unique* odor a target object
- Canines do not necessarily alert to the parent
  - Examples:
    - TNT → 2,4-DNT
    - Cocaine → methyl benzoate

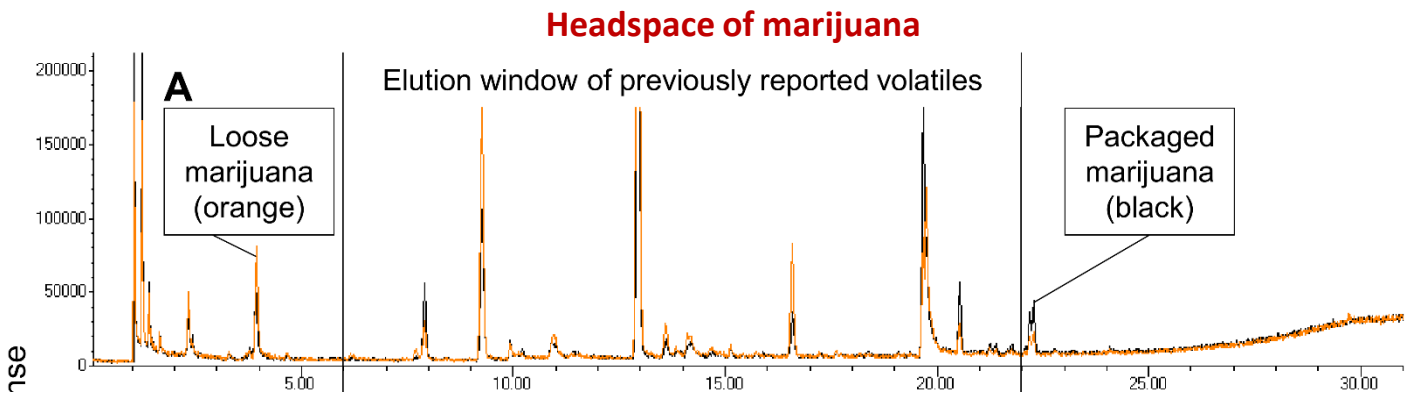




Courtesy of Dr. Kenneth Furton and Dr. Michael Macias

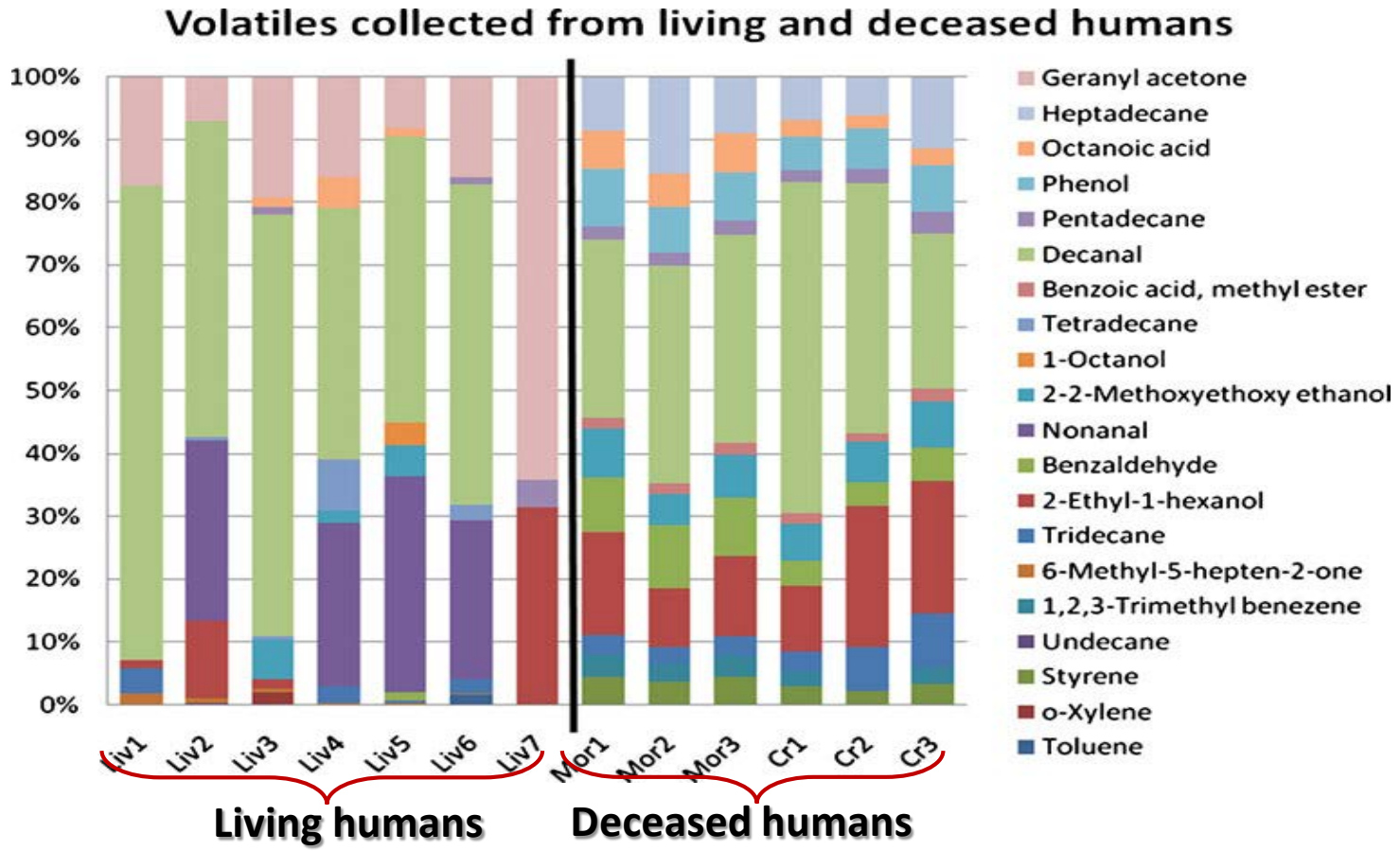
Odor Profiles

- Odor profiles of some profiles are simple (single component)
  - Example: TNT → 2,4-DNT
- Others are more complicated with many components composing the odor profile
  - Example: marijuana



Rice et. al. "Characterizing the Smell of Marijuana by Odor Impact of Volatile Compounds: An Application of Simultaneous Chemical and Sensory Analysis" *Plos One;* **2015**, 10: 1-17.

Odor profiles:
Living vs. deceased human odor humans



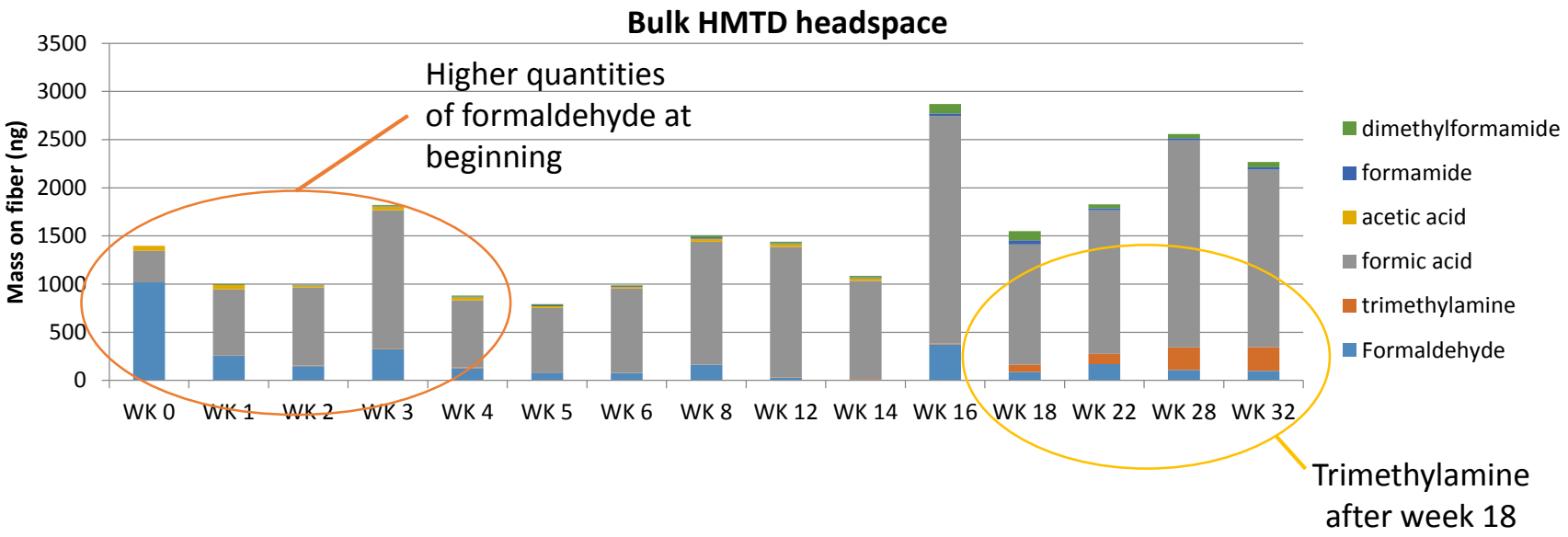
DeGreeff, L.E. et al. "Collection and identification of human remains volatiles by non-contact, dynamic airflow sampling and SPME-GC/MS using various sorbent materials." *Analytical and Bioanalytical Chemistry*, **2011**, 401: 1295-1307.

Changes in odor

- Changes in odor profile
  - With time or storage condition
    - Examples:
      - Explosives: HMTD
      - Human odor: decomposition / blood
  - With formulation or brand
    - Examples:
      - Explosives
      - Narcotics
  - Need to be aware and train appropriately
    - Consider how the canine generalizes / discriminates like odors
    - May need multiple training aids

Changes in odor

- Changes in odor profile- HMTD
  - With time, storage condition, and formulation



DeGreeff, L.E. et al. "Variation in the headspace of bulk HMTD with time, environment, and formulation." *Forensic Chemistry*, **2017** *in press.*

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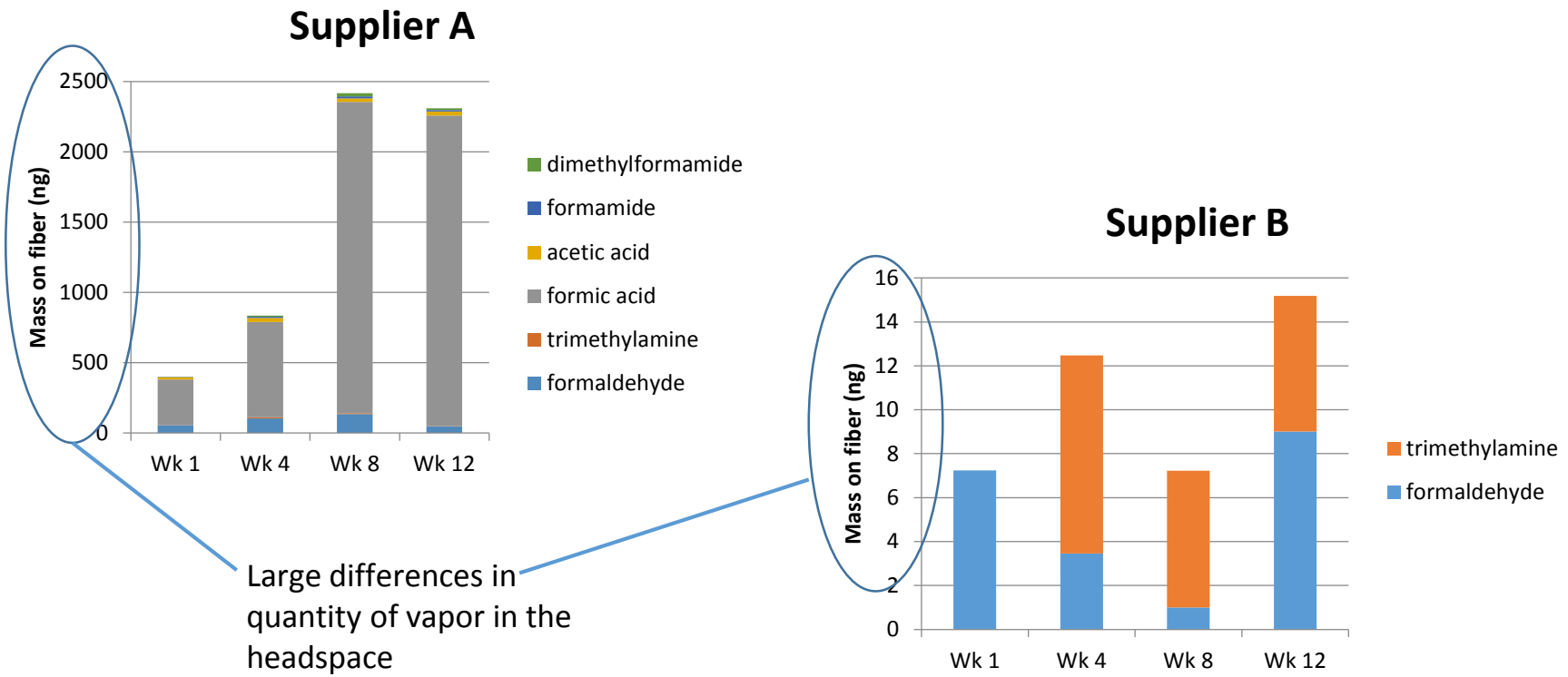
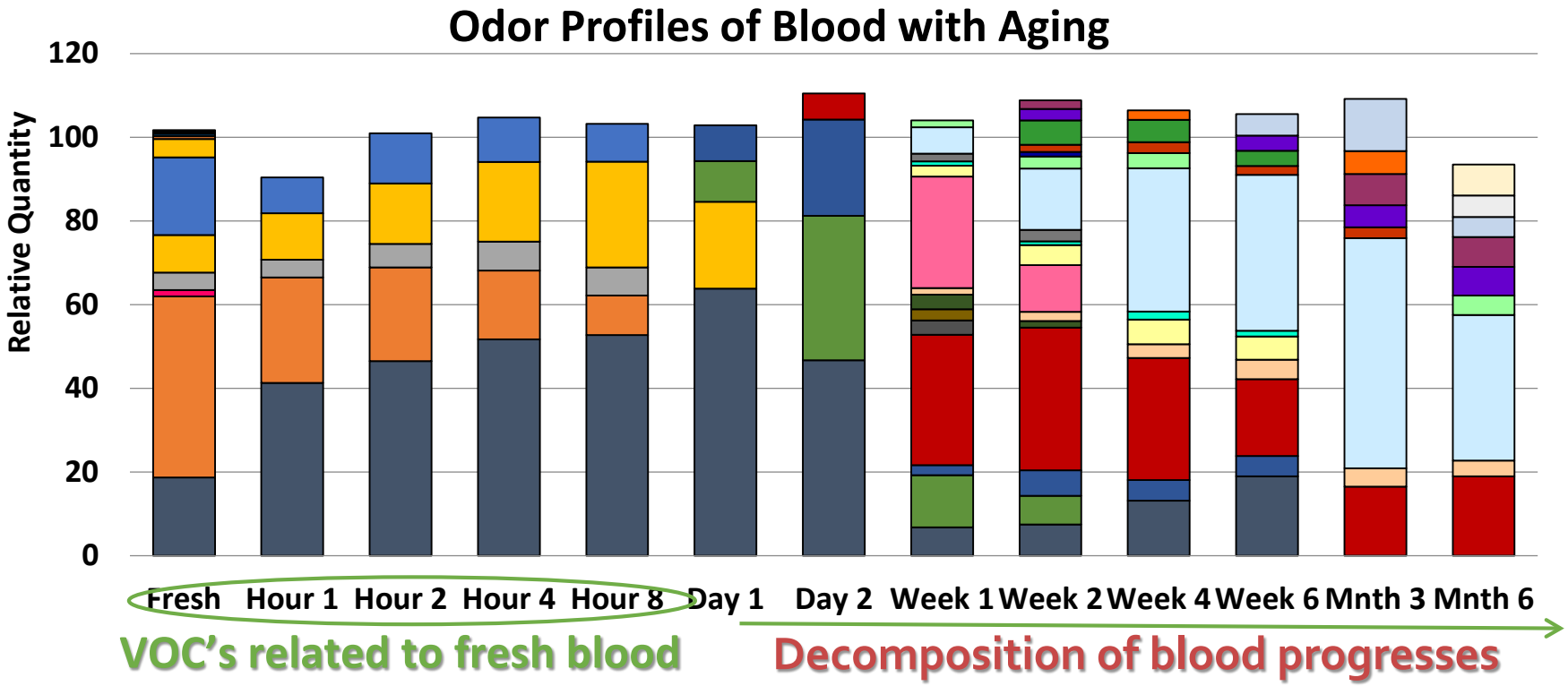


DeGreeff, L.E. et al. "Variation in the headspace of bulk HMTD with time, environment, and formulation." *Forensic Chemistry*, **2017** *in press.*

Changes in odor

- Changes in odor profile – Blood (human decomp)



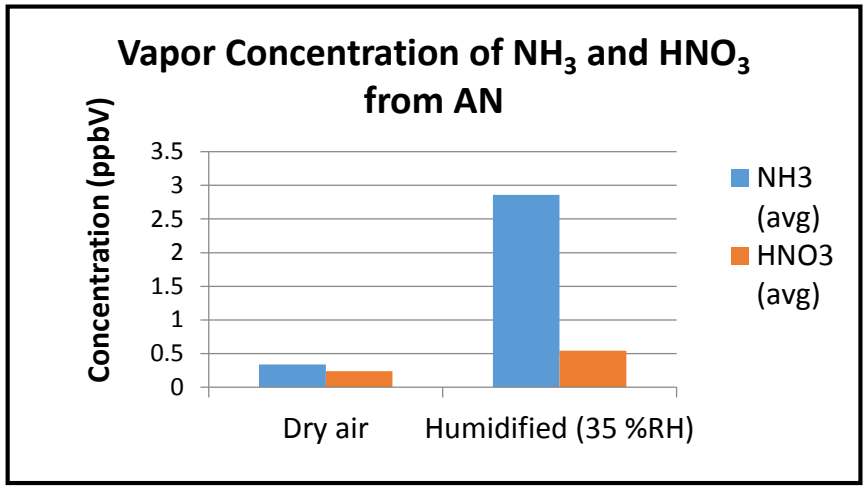
DeGreeff, L.E. et al. "Detection of VOCs in dried human blood by instrument and canine." *American Academy of Forensic Science*, **2013**, Washington, D.C.

Field conditions

- Available odor concentration may be reduced / increased by:
  - Temperature, humidity
  - Absorption - wrapping, packaging, etc.
  - Odor transport – through soil, through container, etc.

Field conditions

- Available odor concentration may be reduced / increased by:
  - **Temperature, humidity**



Ammonium nitrate vapor composition changes!

- NH_3 : HNO_3 in vapor is highly humidity dependent
  - Dry air: $NH_3 \approx HNO_3$
  - Humidified air
    - Initially $NH_3 > HNO_3$
    - NH_3 decays slowly while HNO_3 remains steady
    - New exposure to humidified air renews cycle
  - AN deliquesces (>62% RH at 25°C)

Field conditions

- Odor transport
  - Burial of target may not only reduce odor, but also change scent picture
  - Transport properties of odorants may differ
  - Example: TNT buried in sand
    - 0.1 g TNT buried in 39 g sand, in vial
    - Both TNT and 2,4-DNT were detected
    - Ratio of TNT to 2,4-DNT changed with time

TRANSPORT OF EXPLOSIVES I:
TNT IN SOIL AND ITS EQUILIBRIUM VAPOR

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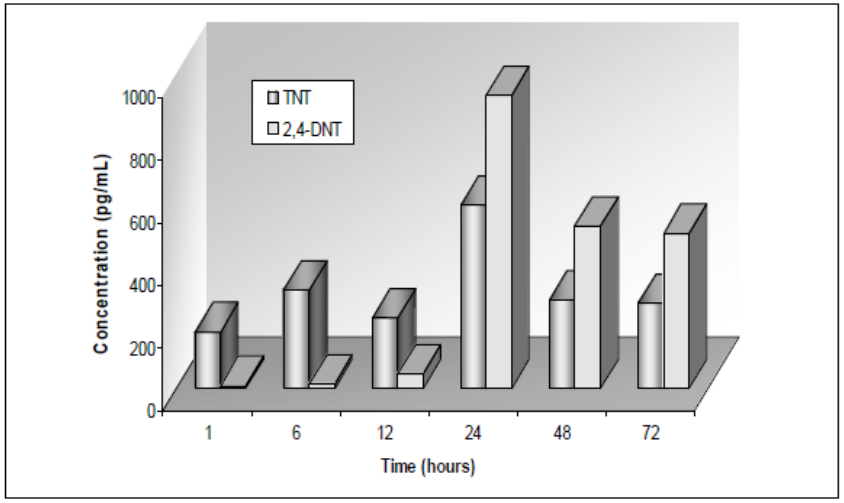

Figure 3. TNT and 2,4-DNT vapors concentration in headspace from TNT buried in sand at different times after the mixture was. TNT values have been multiplied by a factor of 50 for visualization purposes.

Detection and Remediation Technologies for Mines and Minelike Targets IX, edited by Russell S. Harmon, J. Thomas Broach, John H. Holloway, Jr., Proceedings of SPIE Vol. 5415 (SPIE, Bellingham, WA, 2004) 0277-786X/04/$15 · doi: 10.1117/12.542905

Field conditions

- Absorption to surfaces
  - Wrapping / surfaces may absorb odor
  - Example: TNT with materials commonly associated with landmines
    - TNT bonds to some surfaces more strongly than to others

Surface adsorption and retention of TNT vapors

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Part of the SPIE Conference on Enforcement and Security Technologies
Boston, Massachusetts • November 1998
SPIE Vol. 3575 • 0277-786X/98/$10.00

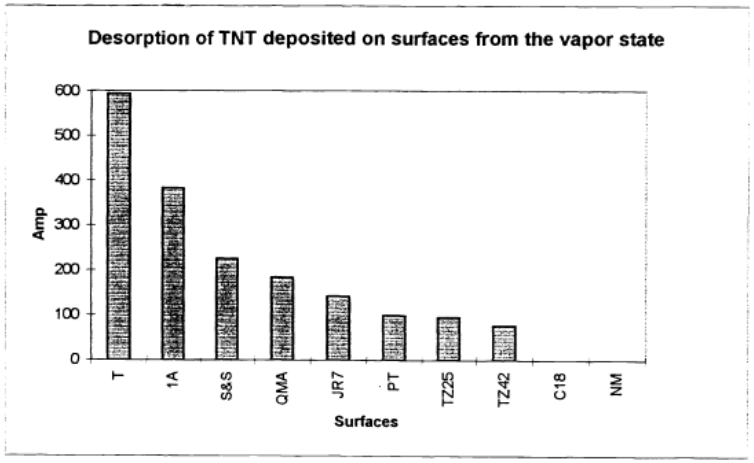

FIG. 4. IMS analysis of TNT adsorbed on various surfaces from the vapor state using 250 ng TNT in the vapor generator/collector system.

Improving detection through science

- Understand odor profile
- Understand how odor profile changes
- Encourage generalization across variants of a single target
  - Canines trained only a single variation of a target, might not detect other variations in target
  - May need multiple training aids
- Consider field conditions
- **When given the chance to train with new conditions or variants…take it!**

Knowledge gaps???

- Project: "Canine Research – Past, Present, Future; An Analysis of Gaps and User Needs"
  - Where are the knowledge gaps in canine detection?
    - To include detection of explosives, narcotics, human remains, and human tracking
    - Related research in veterinary and behavioral sciences
  - Research gaps?
  - Operational needs?
  - Average cost of research?
- To contribute:

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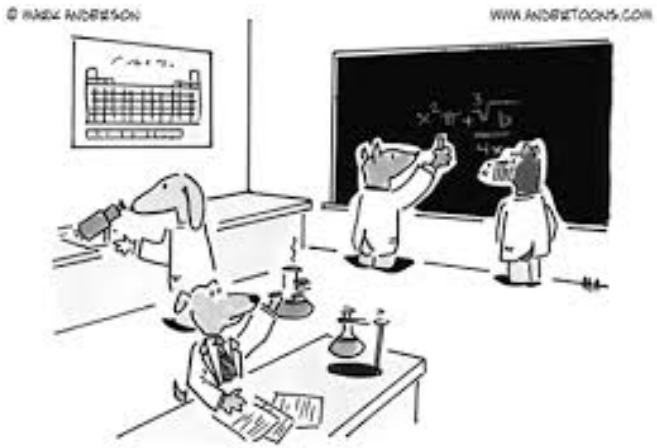
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Thank you!

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