Tentatively Identified Compounds

Characterization and Data Usage Issues

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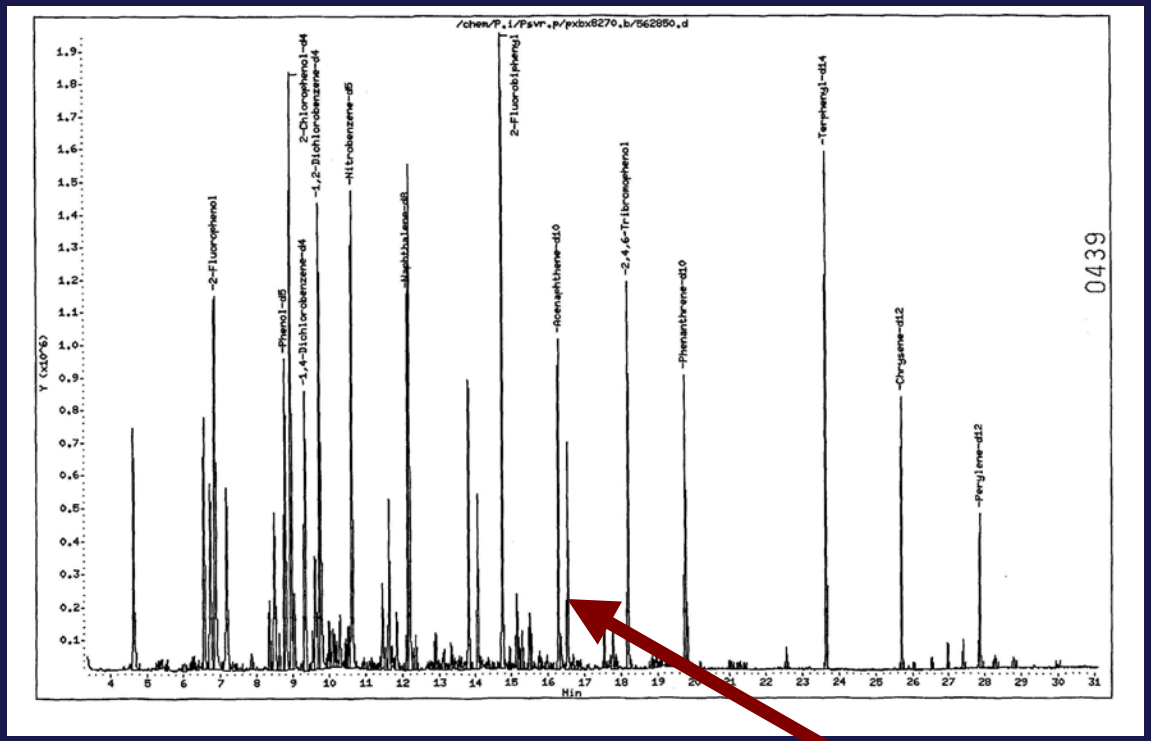
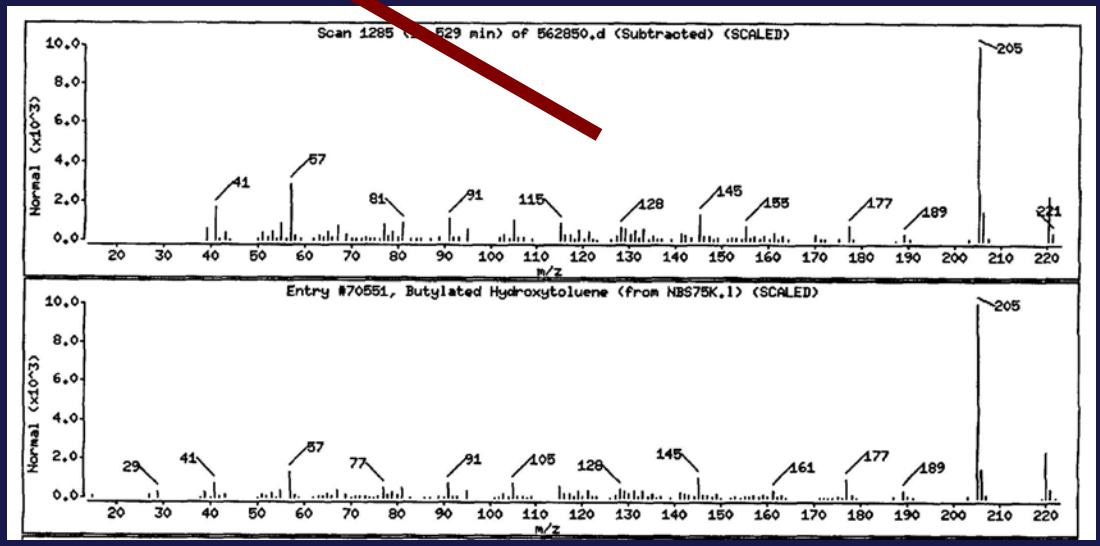
Tentatively Identified Chemicals (TICs)

- Non-target chemicals detected during analyses for volatile and semivolatile organics by GC/MS
- Tentatively identified by forward computer search against NIST library (75,000-147,000 compounds)
- Reported with “Quality” factor for match
- May be reported as specific chemical or member of chemical family


/chem/P.i/Psvr.p/pxbx8270.b/562850.d
Y (x10^6)
Min
0439
2-Fluorophenol
Phenol-d5
2-Chlorophenol-d4
1,4-Dichlorobenzene-d4
1,2-Dichlorobenzene-d4
Nitrobenzene-d5
Naphthalene-d8
2-Fluorobiphenyl
Acenaphthene-d10
2,4,6-Tribromophenol
Phenanthrene-d10
Terphenyl-d14
Chrysene-d12
Perylene-d12


Scan 1285 (
529 min) of 562850.d (Subtracted) (SCALED)
Normal (x10^3)
m/z
205
41
57
81
91
115
128
145
155
177
189
221
Entry #70551, Butylated Hydroxytoluene (from NBS75K.l) (SCALED)
Normal (x10^3)
m/z
205
29
41
57
77
91
105
128
145
161
177
189

Laboratory Responsibilities

- Conduct computer search against library spectra
- Review results, select best match to report
- Estimate concentrations
- Flag TICs if in blank

Program Responsibilities

- No clear guidance for TIC data usage
- Need to determine possible importance
  - Artifact from sampling or analysis?
  - Background?
  - Natural product?
  - Previously unrecognized contaminant at site?
  - Related to known compounds of interest?
- Decide how to use information

Case Study – Eastern US Site

- Military training range
- Sole source aquifer
- Basic CLP list for VOC and SVOC
- Additional target organics selected afte review of potential chemicals released from training activities
  - Explosives and explosive degradation products
  - Propellants
  - Ordnance fillers, additives
  - Smokes, dyes

Site TICs

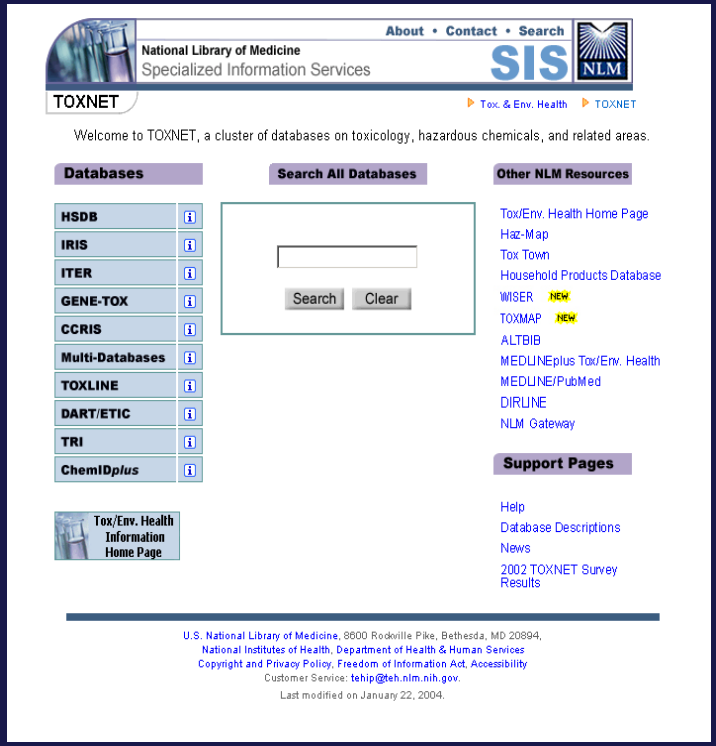
- 3,600 Groundwater samples 4,700 TIC detections
- 7,700 Soil samples, 106,000 TIC detections
- Over 600 different chemicals reported more than once
- Many intimidating long chemical names
- Agency and public concern for the unknown – potential toxicity

TIC Evaluation-Information Needs

- Common name
- Possible relationship to training activities
- Common uses/sources
- Potential toxicity
- Fate and transport – potential groundwater threat?

Information Sources

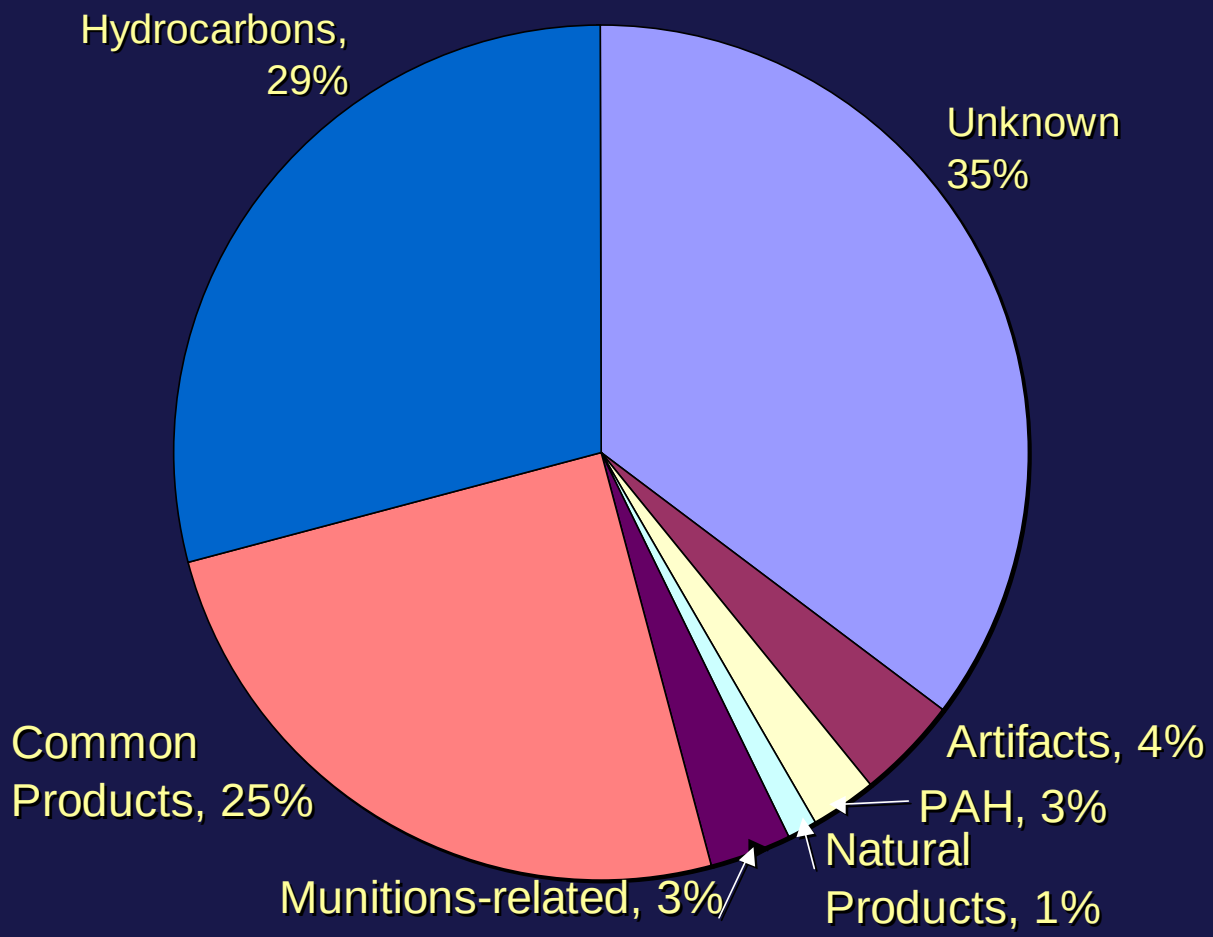
- Merck Index
- TOXNET -HSDB
- Encyclopedia of Explosives,
  US Army R&D Command
- Google
- US Patent Database
- Literature search
  - Medline
  - ACS journals



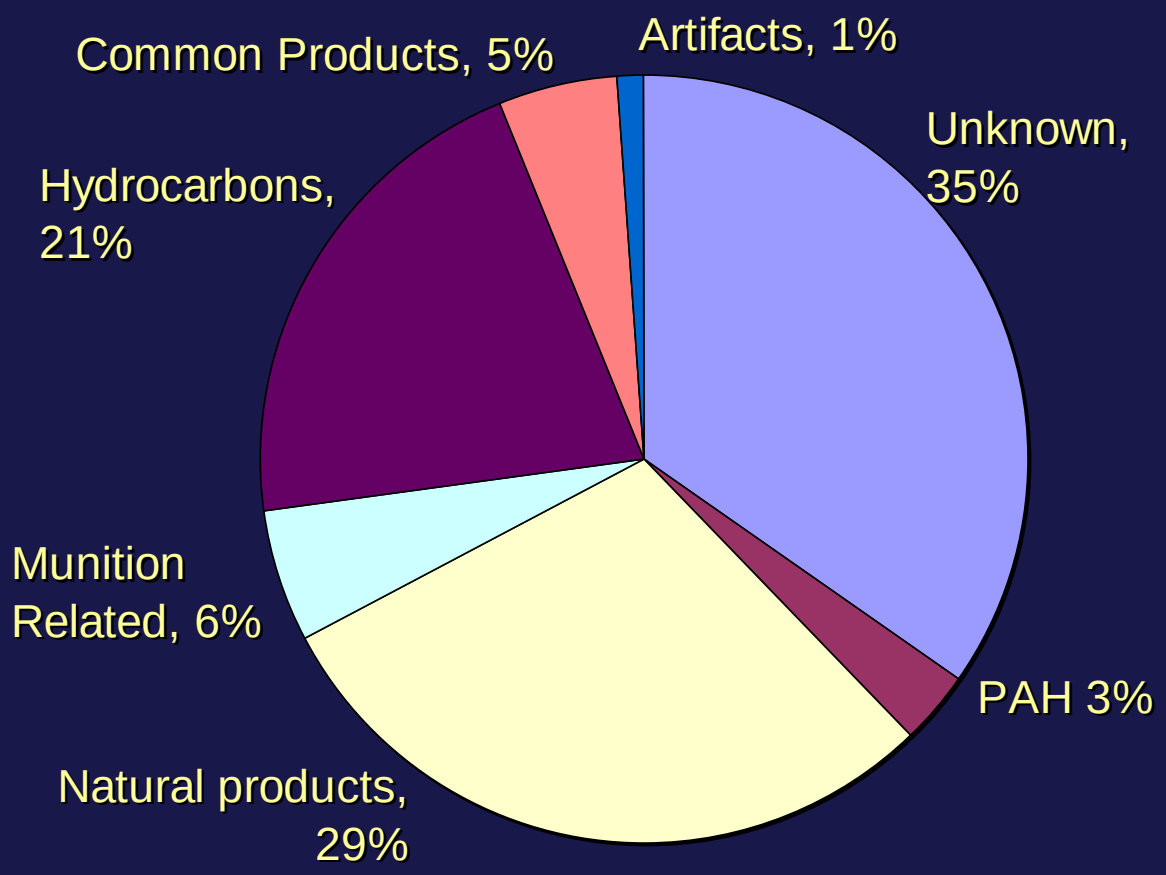
TIC Categories at Training Range

- Possible sources
  - Munitions-related
  - Common products -related to non-training site activities
  - Aliphatic hydrocarbons – petroleum fuels, natural sources
  - Polyaromatic hydrocarbons (PAH)
  - Complex natural products
  - Artifacts
- Many TICs could fit into multiple categories
- Many TICs remain as unknowns

Distribution of TICs in Groundwater



Distribution of TICs in Soils



Munition-related TICs

3% of TICs in groundwater, 6% in soils

- Explosives – TNT, RDX; biodegradation products
  - All reported are current target analytes for explosives method
- Plasticizers, stabilizers, soaps, waxes
  - Phthalates
  - Soaps
  - Polychlorinated naphthalenes
  - Phosphate esters
  - Hydrocarbon waxes
- Dyes

Common Product Chemicals

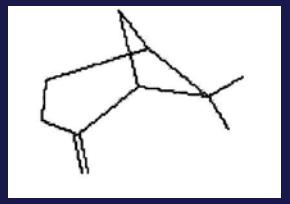
- 25% of groundwater TICs; 5% soil TICs
- Pesticides
- Ethylene glycols - antifreeze
- Detergents
- Antioxidants
- Sunscreen
- Pharmaceuticals
- Common solvents
- Several also found in USGS survey of surface waters

Common Product Chemical Examples

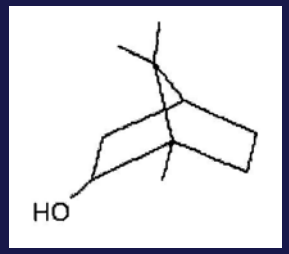
- Diethyl toluamide = DEET insect repellant
- Nonylphenol = detergent metabolite
- 1,1-oxybis-2-ethoxyethane = ethylene glycol ether, antifreeze
- Butylated hydroxytoluene = BHT, antioxidant, food additive
- Butyl hexadecanoate = ant repellant
- Natural products with known commercial applications included in this category – e.g limonene

Complex Natural Products

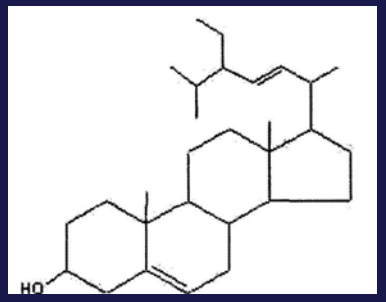
- 1% of groundwater TICs, 29% of soil TICs
- Complex hydrocarbon structures
- Terpenes
- Plant sterols
- Animal sterols
  - Testosterone
  - Progesterone



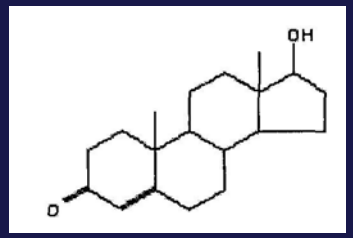
Beta-pinene ($C_{10}H_{16}$)



Borneol
($C_{10}H_{18}O$)



Stigmasterol
(stigmasta-5,22-dien-3ß-ol)



Testosterone ($C_{19}H_{28}O_2$)

Hydrocarbons

- Aliphatic and aromatic hydrocarbons
  - 29% groundwater TICs, 21% soil TICs
  - Petroleum fuels, hydrocarbon solvents
  - Some likely natural products
- PAH
  - 3% groundwater TICs, 3% soil TICs
  - Petroleum
  - On-site combustion
  - Background – atmospheric deposition

Program Uses of TIC Data

- Monthly review of TICs in groundwater with source attribution
- Confirm target analyte results
  - Many TICs are targets for other methods
    - Explosives, biodegradation products in 8330 analysis
- Additions to target analyte lists
  - Polychlorinated naphthalenes - added GC/MS/SIM method after TIC detections
  - Added HPLC/MS analysis for dyes
  - Added plasticizers, propellants to SVOC list

Risk Assessment Options

- Determine relationship to site activities
- Establish % detection criterion for consideration in risk assessment
- Research literature for toxicity, exposure and fate and transport data
- If no data available, determine if appropriate surrogate with toxicity data can be identified
- Determine if appropriate surrogate with exposure, fate and transport data can be identified
- Incorporate uncertainty in risk assessment

Conclusions

- TICs can provide information useful to:
  - Modify the target analyte list to address non-standard chemicals of potential concern
  - Understand various sources of chemicals in the environment
  - Allay fears for the unknown