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
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 after 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

- Hydrocarbons: 29%
- Common Products: 25%
- Natural Products: 1%
- Munitions-related: 3%
- Artifacts: 4%
- PAH: 3%
- Natural Products: 1%
- Unknown: 35%
Distribution of TICs in Soils

- Unknown, 35%
- Natural products, 29%
- Hydrocarbons, 21%
- Munition Related, 6%
- PAH, 3%
- Common Products, 5%
- Artifacts, 1%
- Unknown, 35%
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