



Tentatively Identified Compounds

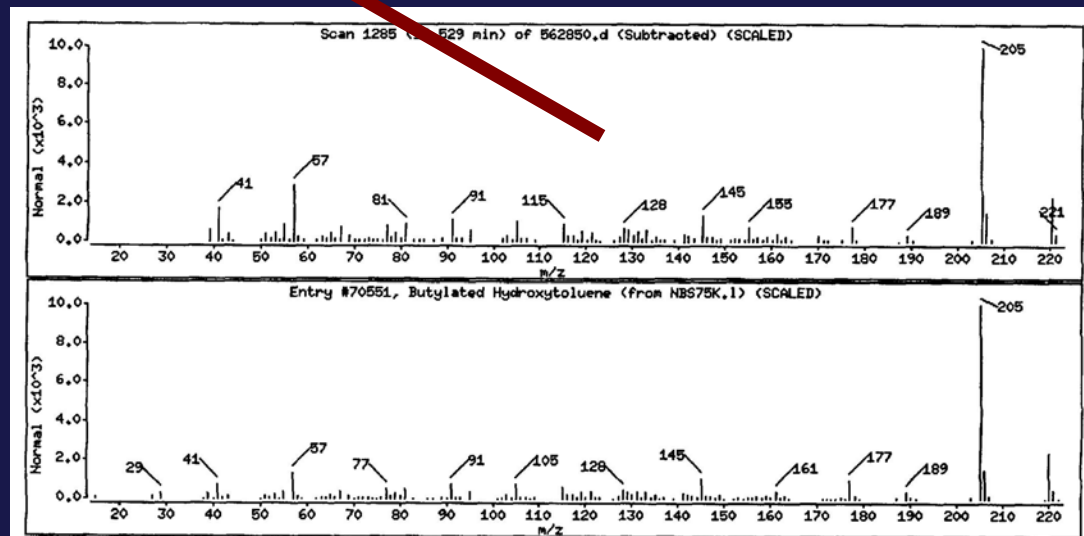
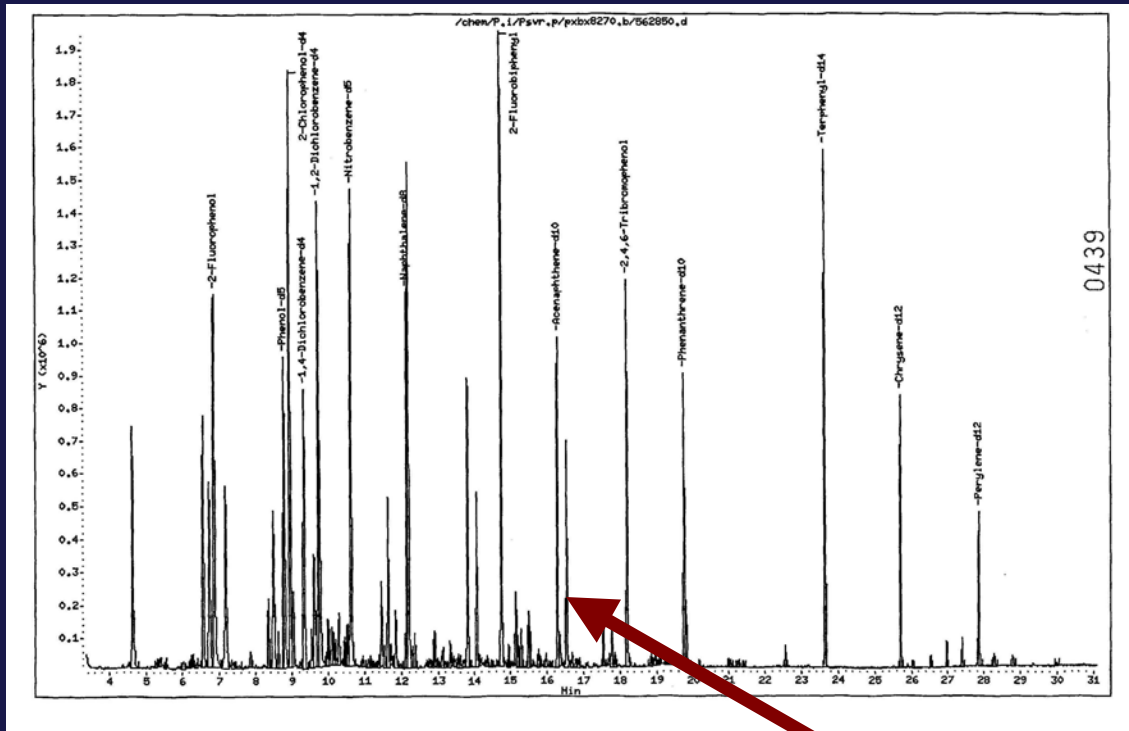
Characterization and Data Usage Issues

Marilyn Hoyt Bill Alsop Andrew Nelson

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



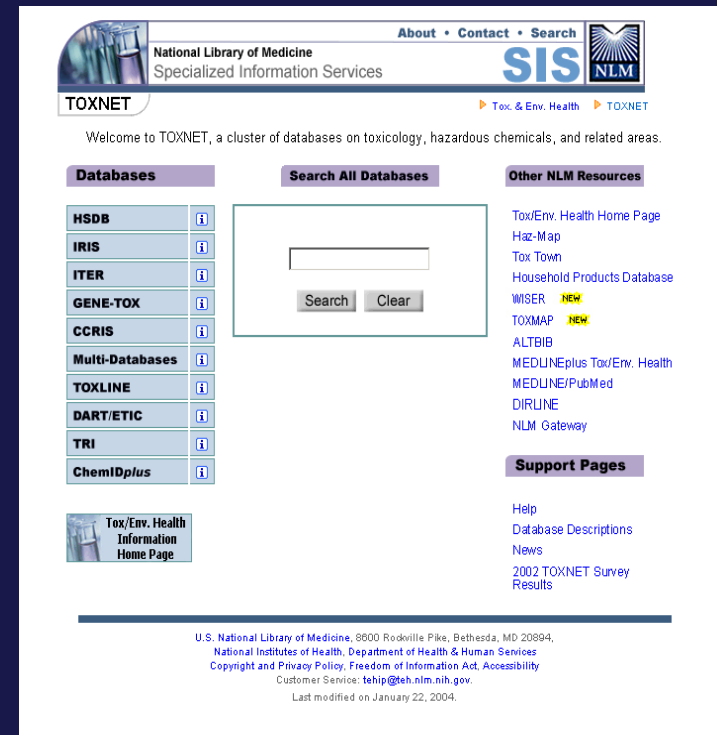
TIC Evaluation-Information Needs



- 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



The screenshot shows the TOXNET website interface. At the top, there is a header for the National Library of Medicine (NLM) Specialized Information Services (SIS). The TOXNET logo is prominently displayed. Below the header, there is a navigation bar with links for 'About', 'Contact', and 'Search'. A search box is present with 'Search' and 'Clear' buttons. The main content area is divided into several sections:

- Databases:** A list of databases including HSDB, IRIS, ITER, GENE-TOX, CCRIS, Multi-Databases, TOXLINE, DART/ETIC, TRI, and ChemIDplus.
- Search All Databases:** A search box with 'Search' and 'Clear' buttons.
- Other NLM Resources:** Links to various resources such as Tox/Env. Health Home Page, Haz-Map, Tox-Town, Household Products Database, WISER (NEW), TOXMAP (NEW), ALTBIB, MEDLINEplus Tox/Env. Health, MEDLINE/PubMed, DIRLINE, and NLM Gateway.
- Support Pages:** Links to Help, Database Descriptions, News, and 2002 TOXNET Survey Results.

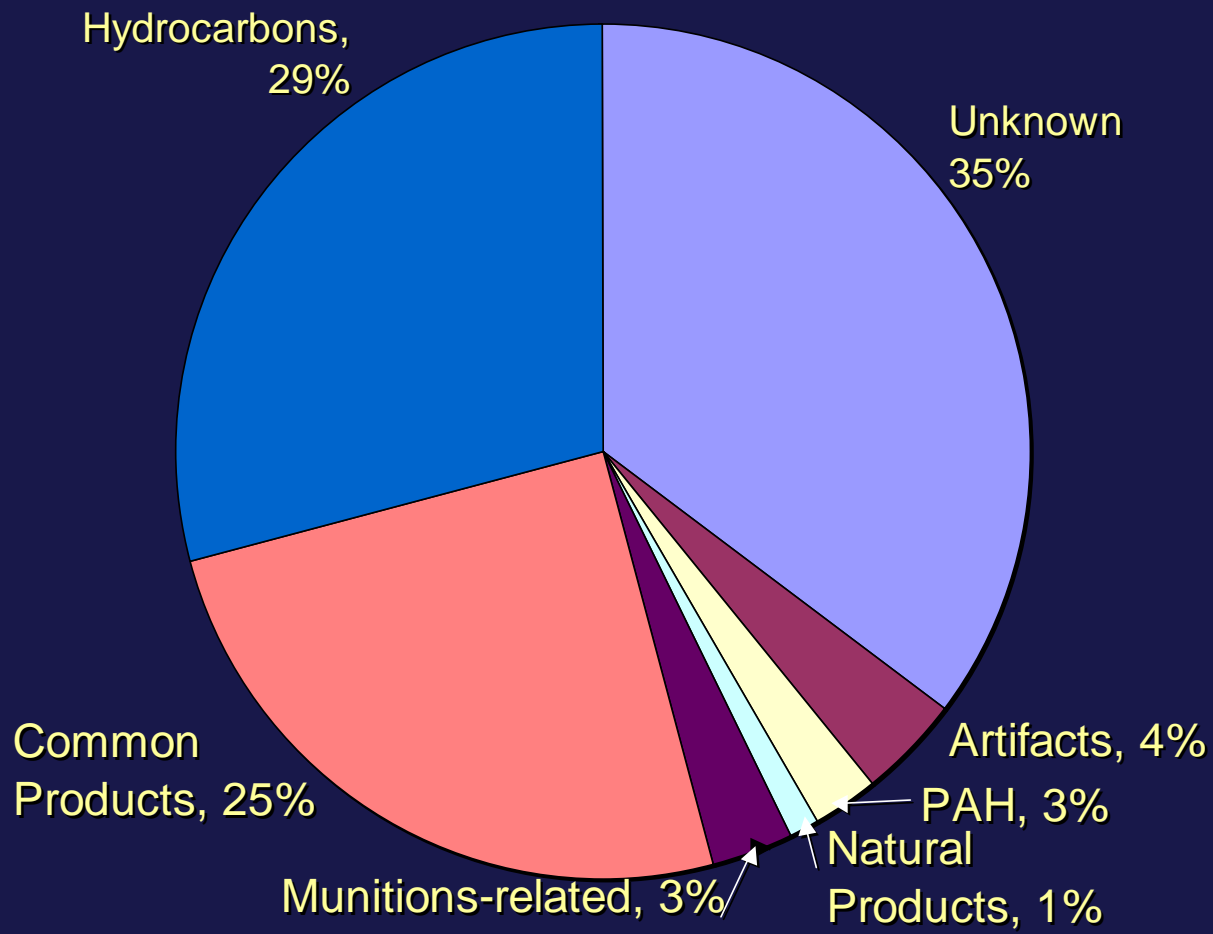
At the bottom of the page, there is a footer with contact information for the U.S. National Library of Medicine, including the address (8600 Rockville Pike, Bethesda, MD 20894), phone number (301-495-4545), and email (tehip@eh.nlm.nih.gov). The page was last modified on January 22, 2004.

TIC Categories at Training Range

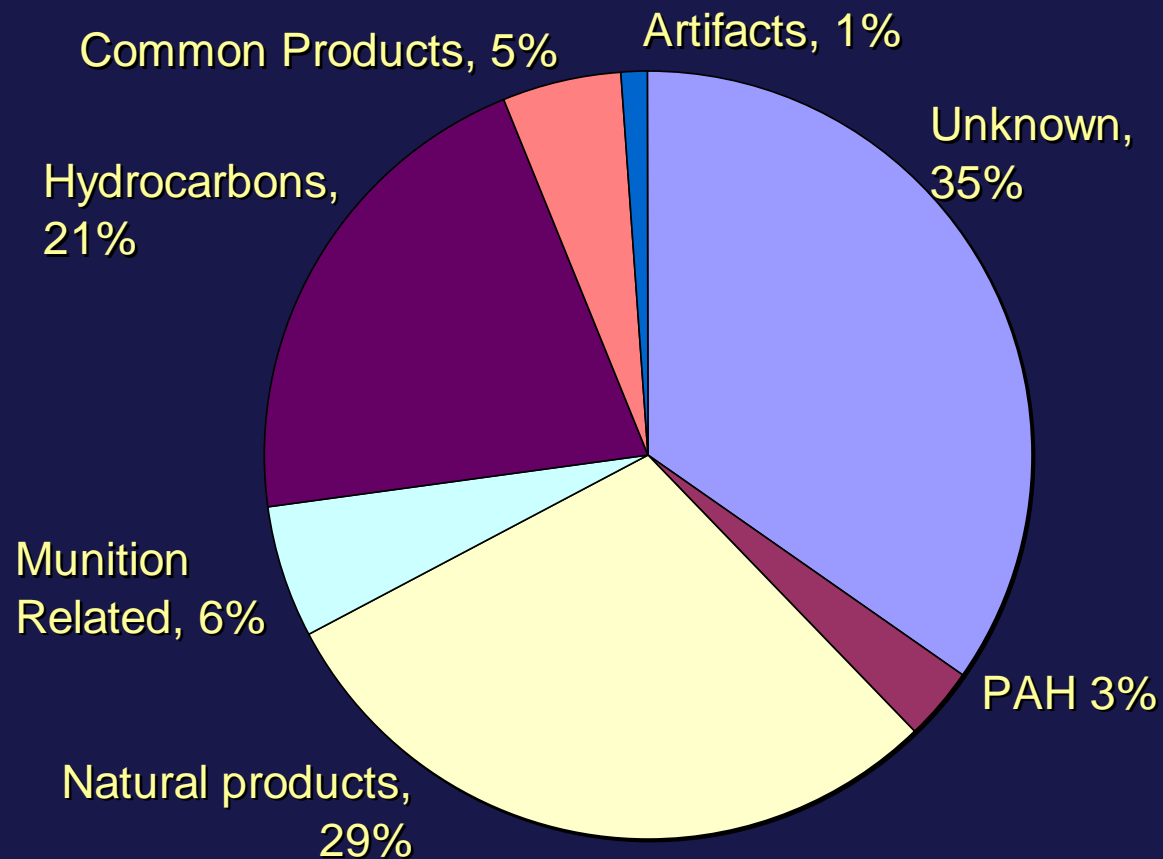


- Possible sources
 - Munitions-related
 - Common products -related to non-training site activities
 - Aliphatic hydrocarbons – petroleum fuels, natural sources
 - Polyaromatic hydrocarbons (PAH)
 - Complex natural products
 - Artifacts
- Many TICs could fit into multiple categories
- Many TICs remain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

Distribution of TICs in Groundwater



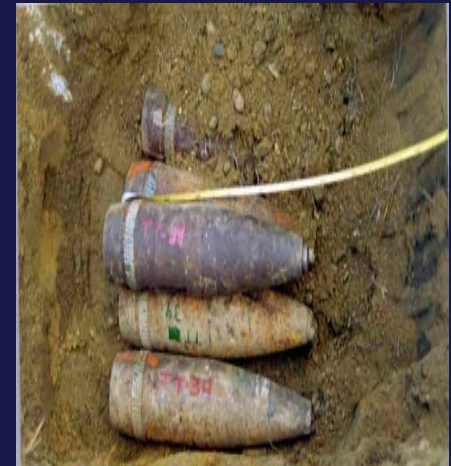
Distribution of TICs in Soils



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



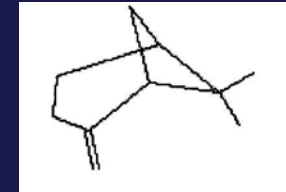
Common Product Chemical Examples



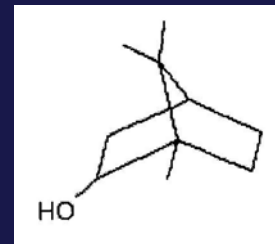
- Diethyl toluamide = DEET insect repellent
- Nonylphenol = detergent metabolite
- 1,1-oxybis-2-ethoxyethane = ethylene glycol ether, antifreeze
- Butylated hydroxytoluene = BHT, antioxidant, food additive
- Butyl hexadecanoate = ant repellent
- Natural products with known commercial applications included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

Complex Natural Products

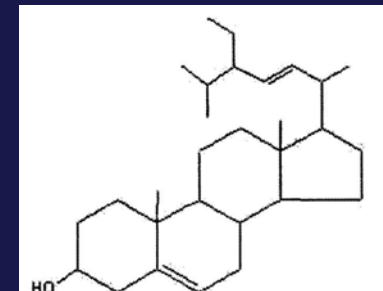
- 1% of groundwater TICs, 29% of soil TICs
- Complex hydrocarbon structures
- Terpenes
- Plant sterols
 - Testosterone
 - Progesterone



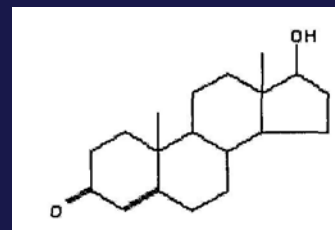
Beta-pinene (C₁₀H₁₆)



Borneol
(C₁₀H₁₈O)



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



Testosterone (C₁₉H₂₈O₂)

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