



Tentatively Identified Compounds

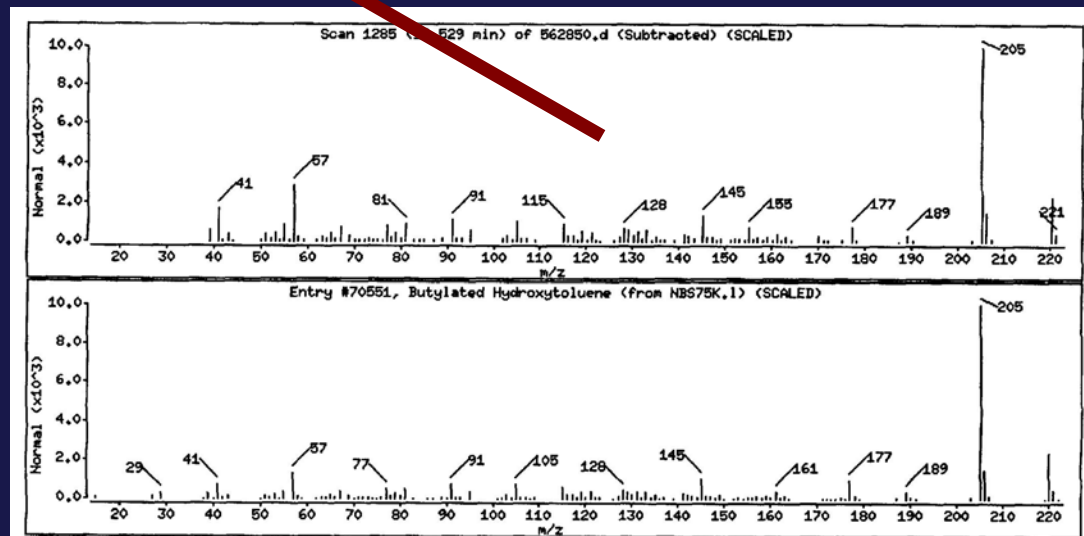
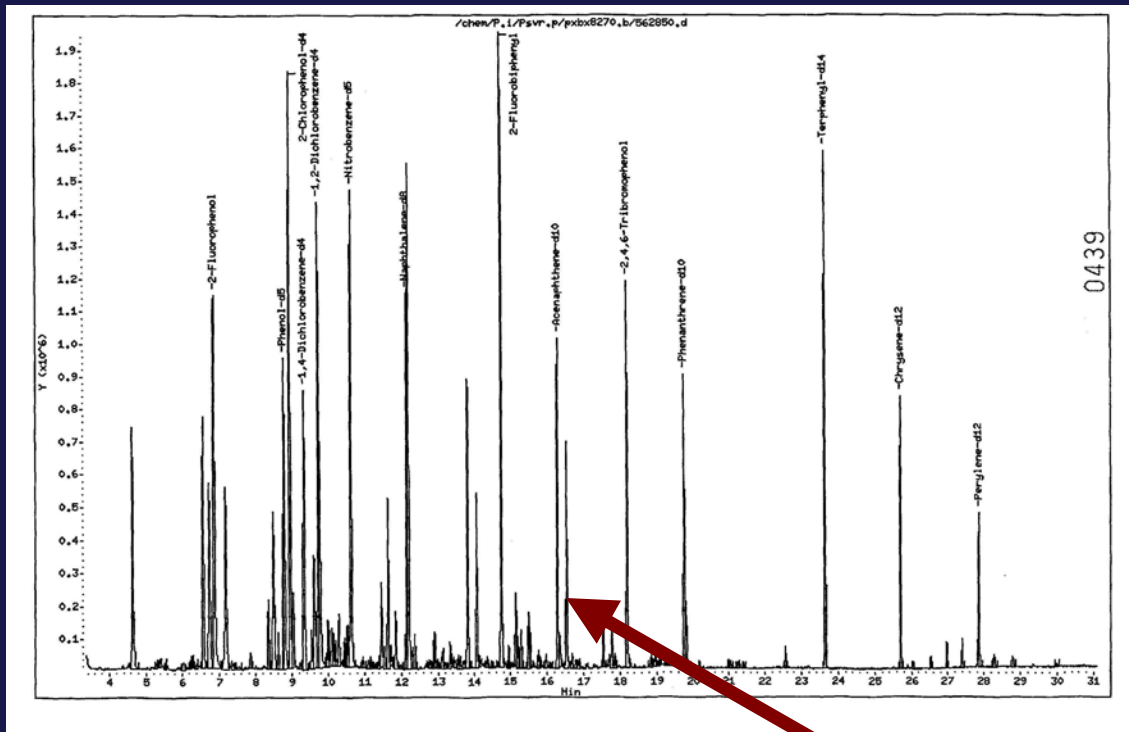
Characterization and Data Usage Issues

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



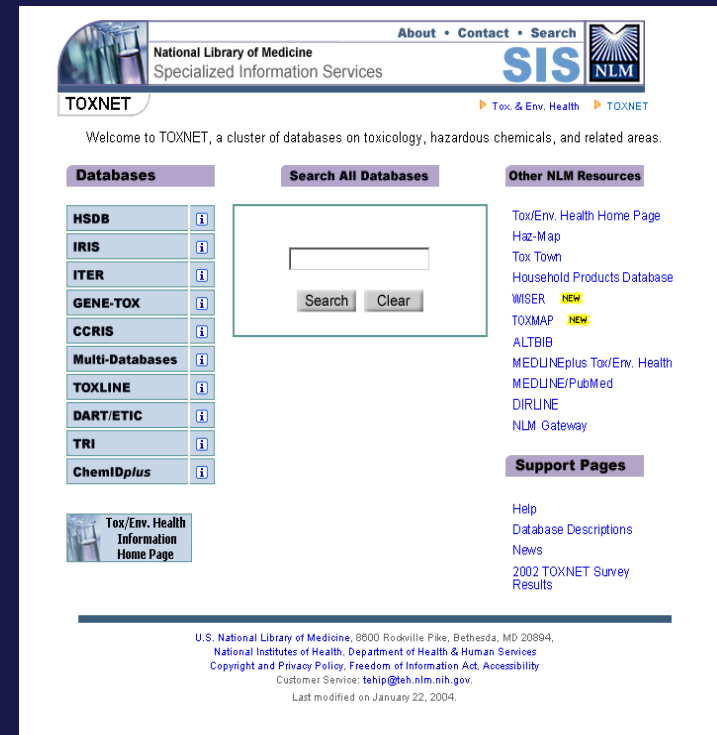
TIC Evaluation-Information Needs



- 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



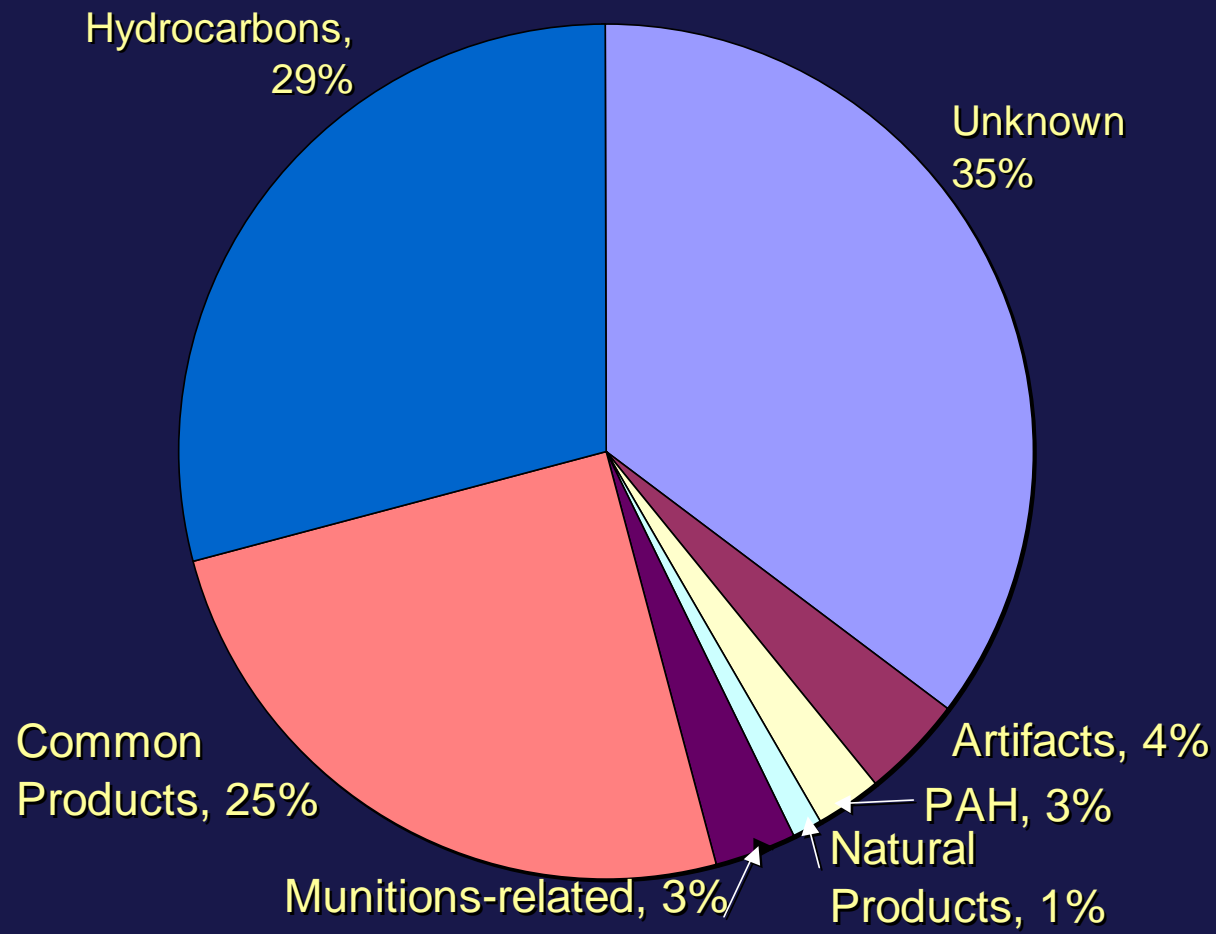
The screenshot shows the TOXNET website interface. At the top, there is a navigation bar with links for 'About', 'Contact', and 'Search'. The National Library of Medicine (NLM) logo is visible on the right. Below the navigation bar, the TOXNET logo is displayed, along with a welcome message: 'Welcome to TOXNET, a cluster of databases on toxicology, hazardous chemicals, and related areas.' The main content area is divided into three columns. The left column lists various databases: HSDB, IRIS, ITER, GENE-TOX, CCRIS, Multi-Databases, TOXLINE, DART/ETIC, TRI, and ChemIDplus. The middle column features a search box with 'Search' and 'Clear' buttons. The right column lists 'Other NLM 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. Below the search box, there is a 'Support Pages' section with links for 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, phone number, and email.

TIC Categories at Training Range

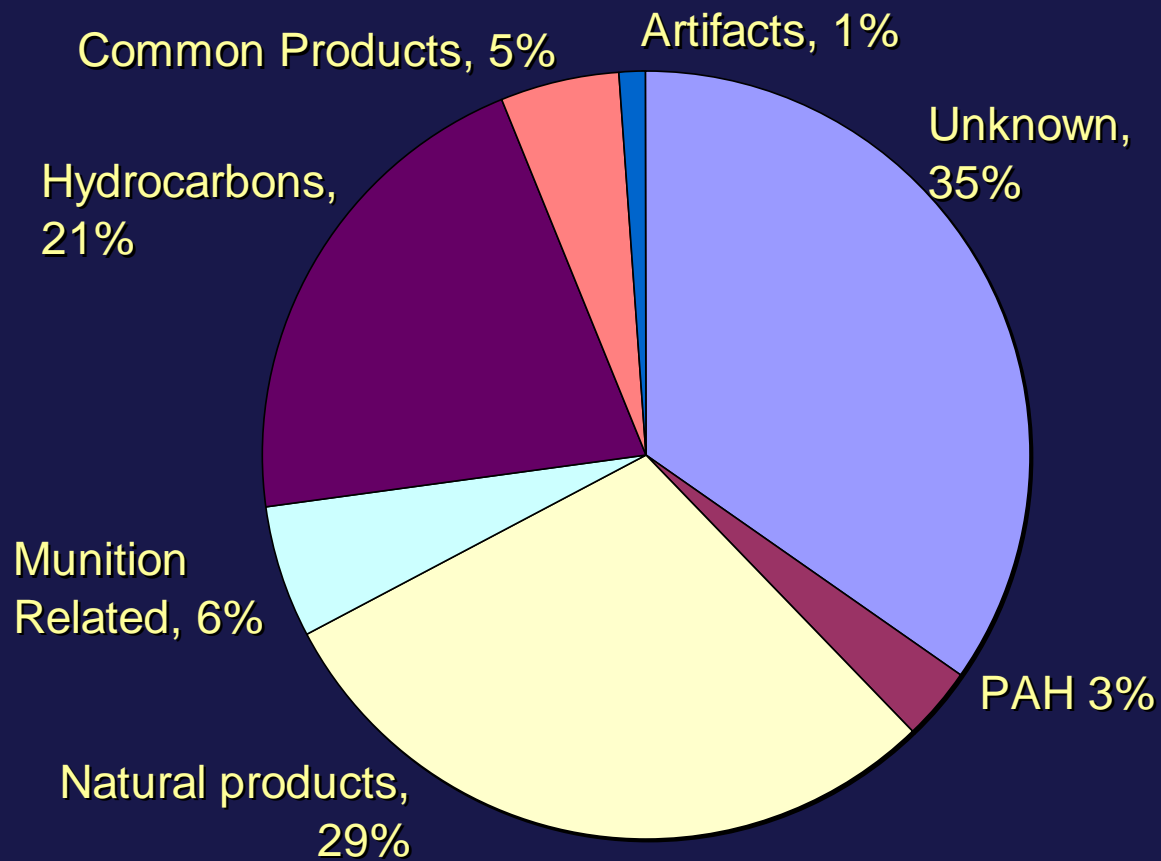


- Possible sources
 - Munitions-related
 - Common products -related to non-training site activities
 - Aliphatic hydrocarbons – petroleum fuels, natural sources
 - Polyaromatic hydrocarbons (PAH)
 - Complex natural products
 - Artifacts
- Many TICs could fit into multiple categories
- Many TICs remain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

Distribution of TICs in Groundwater



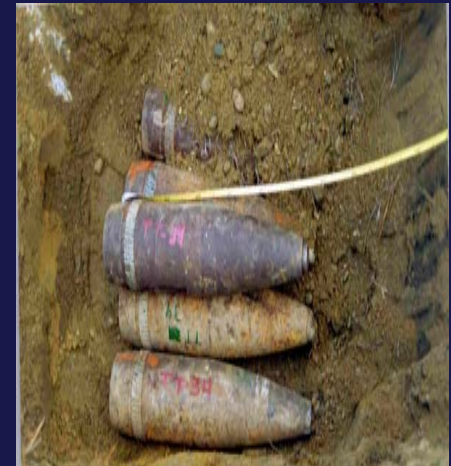
Distribution of TICs in Soils



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



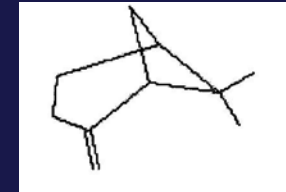
Common Product Chemical Examples



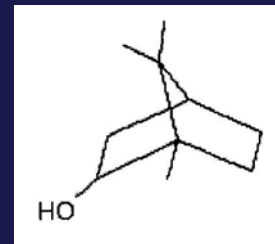
- Diethyl toluamide = DEET insect repellent
- Nonylphenol = detergent metabolite
- 1,1-oxybis-2-ethoxyethane = ethylene glycol ether, antifreeze
- Butylated hydroxytoluene = BHT, antioxidant, food additive
- Butyl hexadecanoate = ant repellent
- Natural products with known commercial applications included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

Complex Natural Products

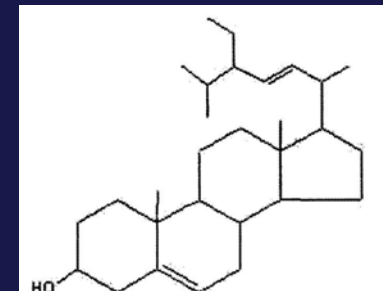
- 1% of groundwater TICs, 29% of soil TICs
- Complex hydrocarbon structures
- Terpenes
- Plant sterols
 - Testosterone
 - Progesterone



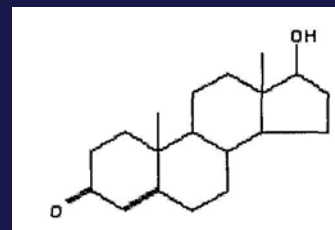
Beta-pinene (C₁₀H₁₆)



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