Munitions Constituents as Emerging Contaminants and IRIS Update

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April 9, 2014

US Army Corps of Engineers

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Emerging Contaminant Watch List

- 1,4-dioxane
- **Antimony**
- *Cadmium and Compounds*
- *Cobalt and Compounds*
- Decabromodiphenyl ether
- Diisocyanates
- **2,4-Dinitroanisole (DNAN)**
- **Dinitrotoluene (DNT)**
- Dioxins
- *Manganese and Compounds*

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Emerging Contaminants Watch List (cont.)

- Nanomaterials – carbon
- Nanomaterials-metals
- *Nickel*
- N-nitrosodimethylamine (NDMA)
- **5-Nitro-1,2,4-triazol-3-one (NTO)**
- **Perchlorate**
- Perfluorooctane Sulfonic Acid (PFOS)
- Perfluorooctanoic Acid (PFOA)
- N-Propyl Bromide
- Trichloroethylene (TCE)
- *Tungsten and Alloys*
- *Vanadium*

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Emerging Contaminants Action List

- **Lead compounds**
- Chromium VI
- Beryllium
- Naphthalene
- **Cyclotrimethylenetrinitramine (RDX)**
- Sulfur Hexafluoride (SF6)
- Phthalate Esters

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DNAN and NTO; Basis for Inclusion on EC Watch List

- Insensitive munitions replacements for RDX and TNT, for example IMX 101, IMX 104, OSX-12, PAX 21, and PAX 48
- Currently not highly regulated
  - TSCA limits discharge
  - Army Institute of Public Health has recommended occupational exposure levels (OEL)

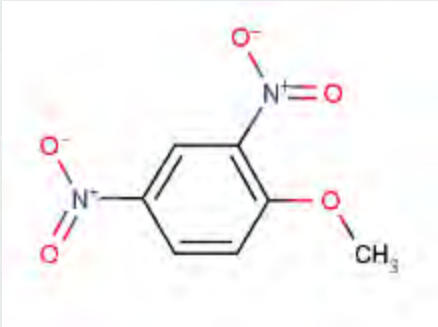
Studies Ongoing by DOD to Understand Toxicity, Fate & Transport

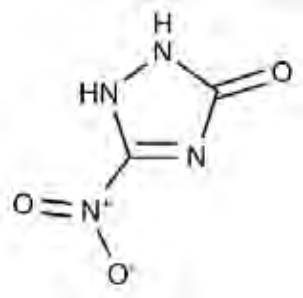
Initial findings:

§ DNAN likely less toxic than TNT

§ NTO -

- ► Male reproductive impacts
- ► Low bioaccumulation potential
- ► Has capacity to migrate





Phase I Impact Assessments

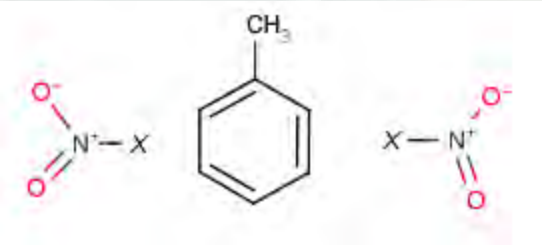
- § DNAN will be performed fourth quarter FY14
- § NTO Results:
  - ► DoD is using NTO and insensitive munitions containing the compound responsibly.
    - Health and safety protocols are in place at production and Load-Assemble-Pack (LAP) facilities
    - Waste streams carefully controlled.

Phase I Impact Assessment

§ Identified risks associated with NTO:

- ► Improve wastewater treatment systems to accommodate greater nitrogen load from increased production
- ► Occupational – current environment exposure well below the proposed OEL of mg/m^3, but as operations move to full-rate production, there may be increased exposure

NTO remains on the Watch List.



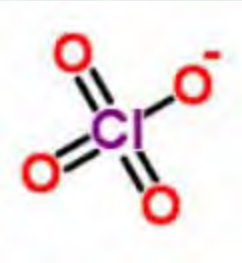
Dinitrotoluene

- New screening provisional peer reviewed toxicity value issued by EPA for technical grade DNT
- The mixture is assumed to be 76% 2,4-DNT and 19% 2,6-DNT, the remaining 5% of the mixture is assumed to be a mixture of 2,3-, 2,5-, 3,4- and 3,5-DNT

Dinitrotoluene

- § EPA Regional Screening Levels for technical grade DNT are 3x higher than 2,6-DNT
- § Values not published for 2,3-, 2,5-, 3,4- and 3,5-DNT separately; screening level applied to total DNTs
- § DNTs are regulated as totals by State of Wisconsin: 0.05 µg/L

Perchlorate



- Moved from EC Action List to Watch List several years ago
- Reference dose published in EPA's Integrated Risk Information System (IRIS) 2005
- Several States have MCLs; Federal MCL under development
  - CA MCL is 6 ppb; in 2012 released a public health goal of 1 ppb

Perchlorate MCL Timeline

- 2005 - National Research Council: *Health Implications of Perchlorate Ingestion,* establishes reference dose (RfD) for perchlorate
- Oct. 2008 – EPA published preliminary determination not to regulate perchlorate
- Jan. 2009 – EPA published interim health advisory level of 15 µg/L
- Aug. 2009 – EPA published health reference levels for various life stages of 1 to 47 µg/L for comment
- Feb. 2011 – EPA published final determination to regulate perchlorate

Perchlorate MCL Timeline

- May 2012 – EPA Science Advisory Board (SAB) publishes advice on development of the MCL
- Sept. 25, 2012 – EPA shares information regarding analytical methods and treatment technologies in public meeting
- ~~Feb. 2013~~; ~~Dec. 2013~~ – Statutory deadline to publish MCLG and MCL proposal
- ~~Aug. 2013~~; Aug. 2014– Statutory deadline to publish final MCL

Major Conclusions in Draft SAB Advisory Report

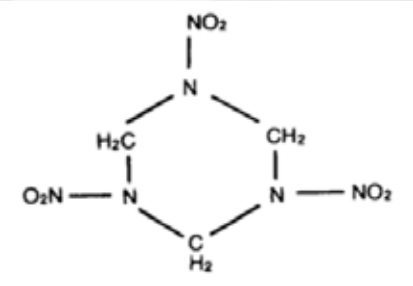
- § Sensitive Life Stage
  - ► Change from NRC 2005: From pregnant women with hypothyroidism to hypothyroxinemic pregnant women (and their fetus/infant)
- § Epidemiology and Biomonitoring Data
  - ► Insufficient but meta- or pooled analysis might provide important information
- § PBPK Modelling
  - ► Integrate mode of action

Lead

- Center for Disease Control (CDC) now uses a reference level of 5 µg/dL blood lead level (BLL). Is based upon upper 2.5% tile of 1-5 year olds tested in the U.S.
- Previously 10 µg/dL BLL was a "level of concern"
- EPA may adopt the new value; associated soil level may be 150 mg/kg

RDX

- § DoD invested in RDX toxicity research that has been published and will be used in the ongoing IRIS reassessment of its toxicity.
- § Drinking water level of concern 0.61 µg/L based upon cancer effects. Newer data suggest that a cancer value may not be warranted.



RDX

- Data supporting a change in the cancer toxicity value
  - Large body of evidence suggest it is not genotoxic or mutagenic
  - Two year rat study was negative
  - No human data link RDX to cancer
- Neurotoxicity or prostate inflammation will likely drive the noncancer reference dose

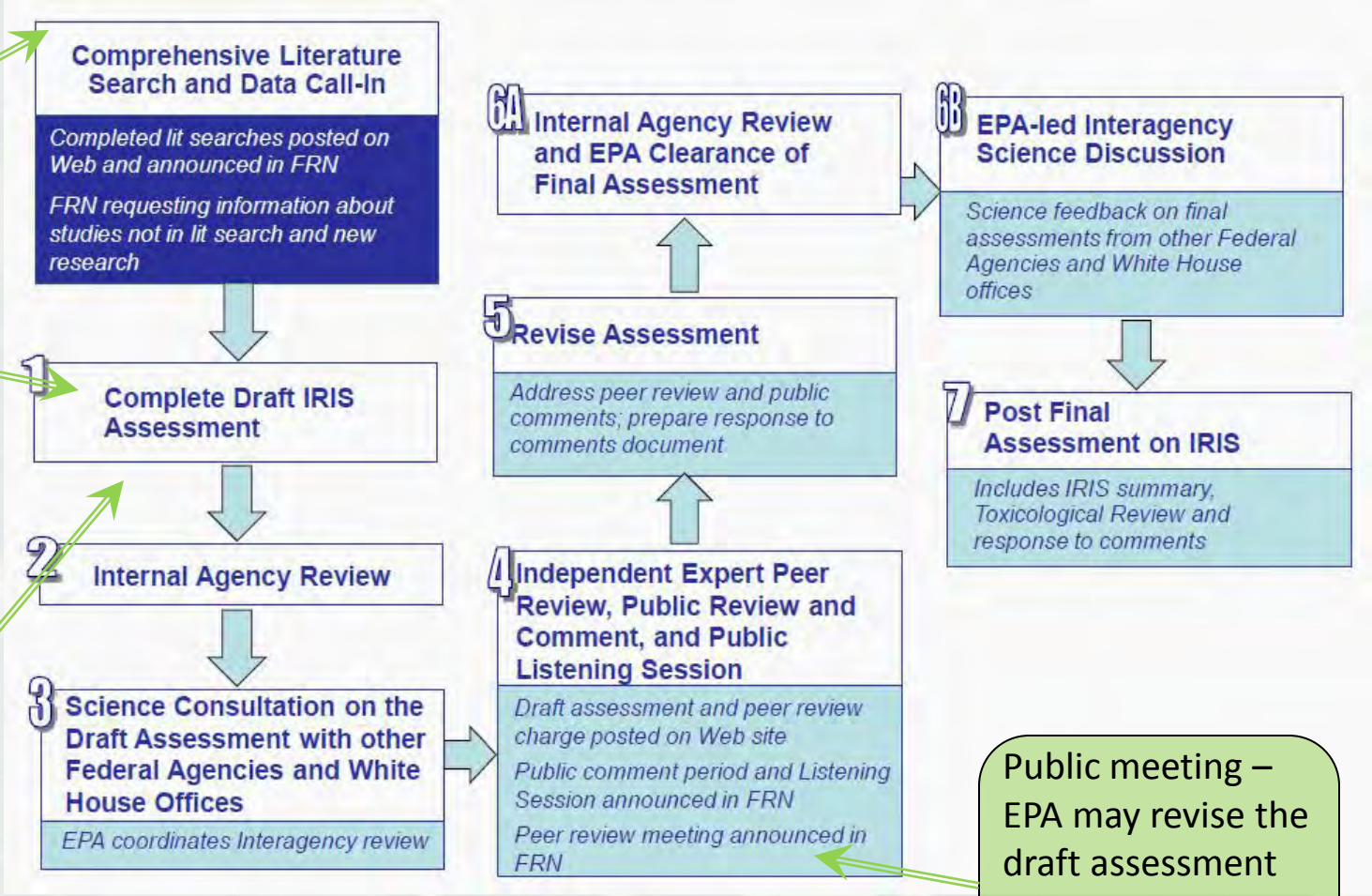
IRIS Update

IRIS Process Steps with Enhancements

EPA scoping meeting

Public meeting on problem formulation

Public meeting on literature search, evidence tables, key issues



Public meeting – EPA may revise the draft assessment and charge to be responsive to public comments

Current Chemicals of DoD Interest Undergoing Assessment

- § RDX
- § Diethyl Phthalate
- § Hexabromocyclododecane (HBCD)
- § Inorganic Arsenic
- § Benzo(a)pyrene (BaP)
- § Hexavalent Chromium
- § Trimethylbenzenes

B(a)P Undergoing Public and Peer Review

- New dermal slope factor, noncancer oral and inhalation toxicity values; existing oral slope factor was modified
- Inclusion of dermal SF decreases soil RSL by 28x
- New inhalation RfC yields an RSL equivalent to the 10^{-6} -based RSL, includes a developmental endpoint.

Risk-Based Screening Levels*		
	Existing	Proposed
Resident Soil (mg/kg)	0.015	0.1
Resident Water Use (µg/L)	0.003	0.002
Resident Air (µg/m^3)	0.00087	0.002

*Using EPA Regional Screening Level Calculator; basis 10^{-6} risk goal. Basis of existing air RSL CalEPA inhalation unit risk.

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Health Effects Documents for PFOA and PFOS

Developed by EPA Office of Water

- Chronic noncancer reference doses developed for each chemical.

Basis for values:

- PFOA - Increased liver, kidney and spleen weight; developmental effects in rodents
- PFOS - Liver and developmental effects in monkeys and rodents
- Associations seen in human epidemiological data for some effects

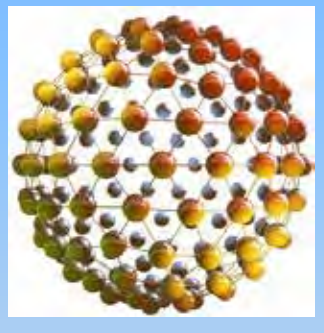
Risk-Based Screening Levels		
	Water (µg/L)	Soil (mg/kg)
PFOA	0.31	1.2
PFOS	0.47	1.8

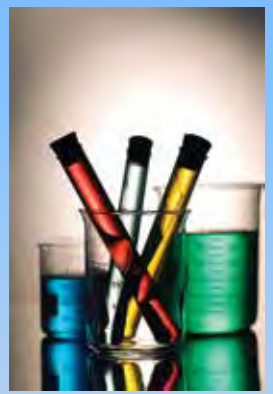
Current Provisional Short-Term Health Advisories:
PFOA – 0.4 µg/L
PFOS – 0.2 µg/L

Managing Chemical & Material Risks

Acquisition, Technology and Logistics

DoD Emerging Contaminants Program
-Emerging Risks-





Briefing for EMDQ Workshop

Paul Yaroschak, P.E.
Deputy for Chemical & Material Risk Management
Office of the Deputy Under Secretary of Defense
(Installations & Environment)

Part 1 – Context, Trends, & Emerging Contaminants (ECs) Program Refresher

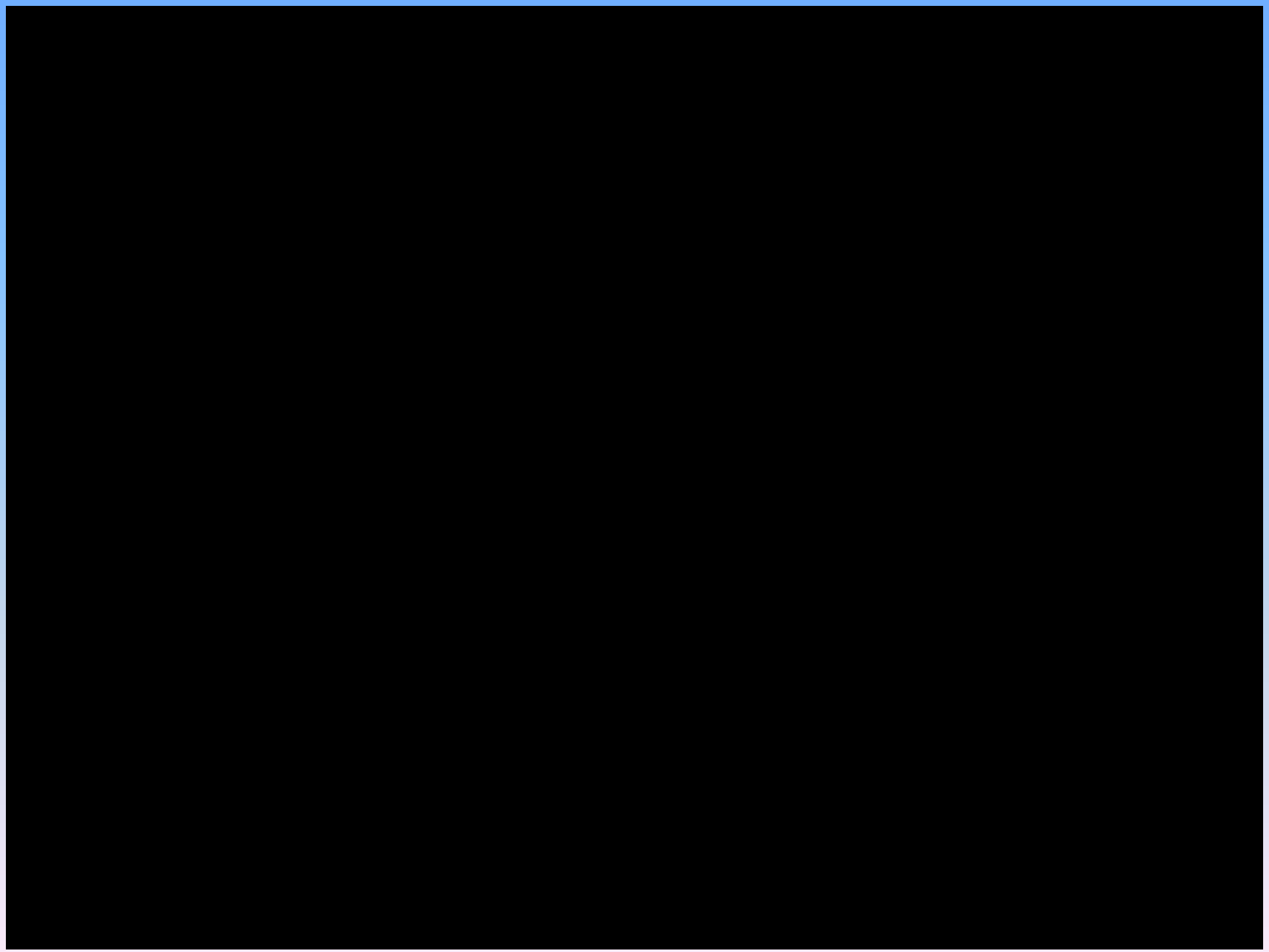
Trends

- **Use of Precautionary Principle**
  - Must understand health & environmental effects before using chemicals
- **Biomonitoring – What's showing up in humans?**
  - Centers for Disease Control's national bio-monitoring & California voluntary program
- **Evolving Risk Assessment Science & Process**
- **Strict Chemical Management & Green Chemistry**
  - Cradle to grave
- **International, Federal, & State Toxic Substances Laws**
  - Restrictions or banning of chemicals/materials (e.g., flame retardants)
  - California Green Chemistry Law & Proposition 65 Litigation
  - EU's REACH[1]
  - Pending TSCA[2] reform

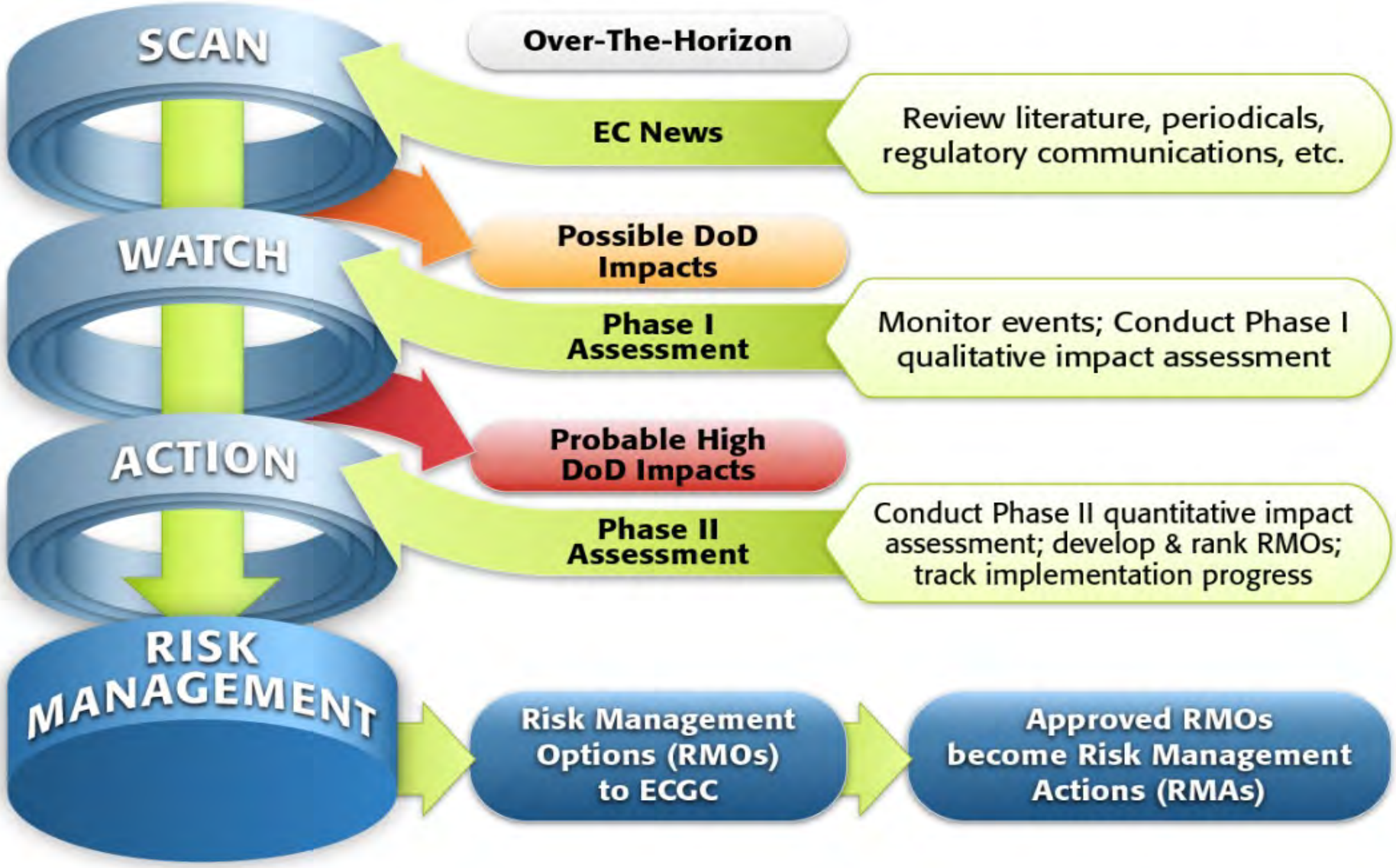
[1] Registration, Evaluation, Authorization & Restriction of Chemicals

[2] Toxic Substances Control Act

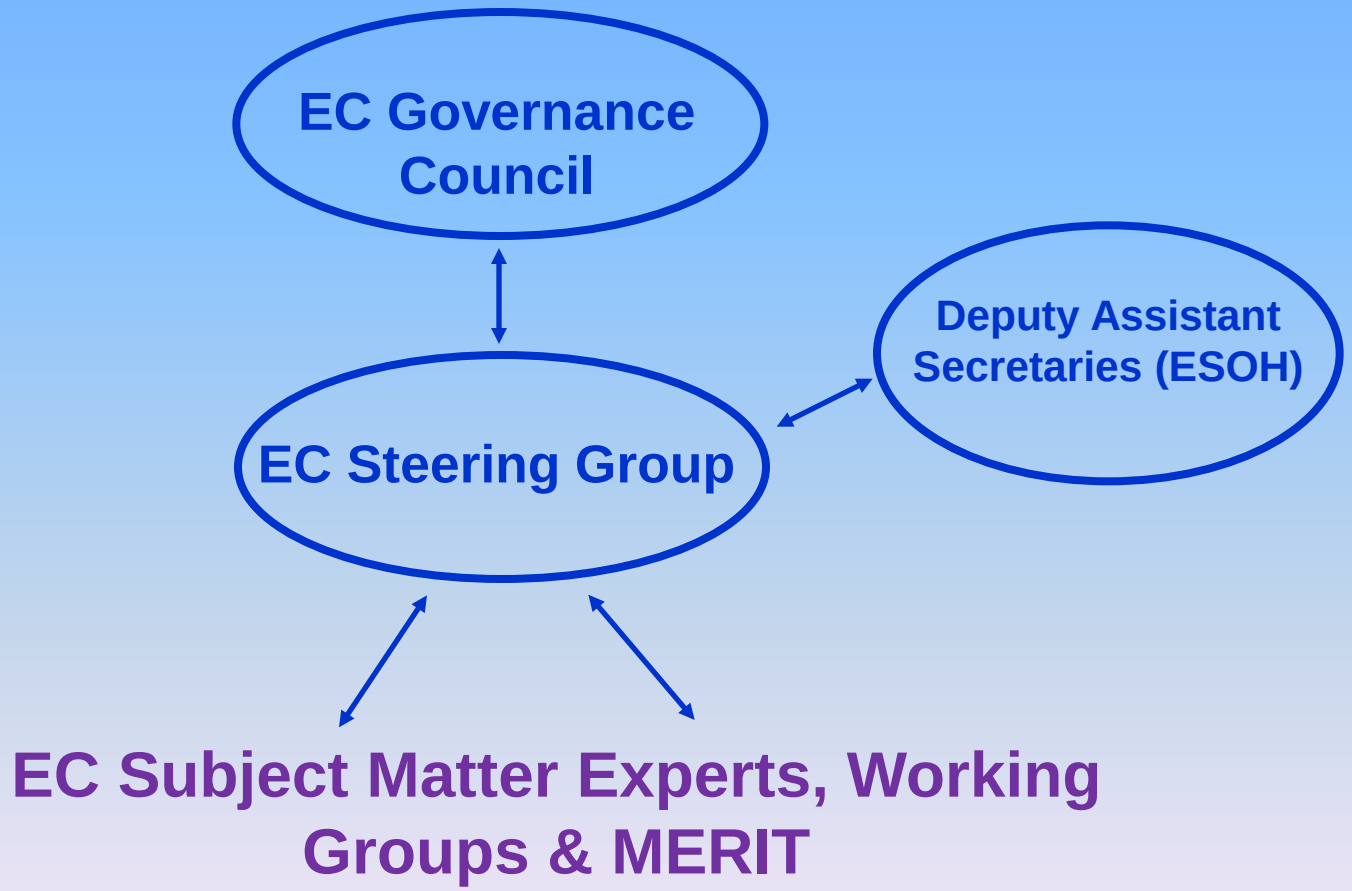
Automobile Industry Perspective (video)



EC "Scan-Watch-Action" Process

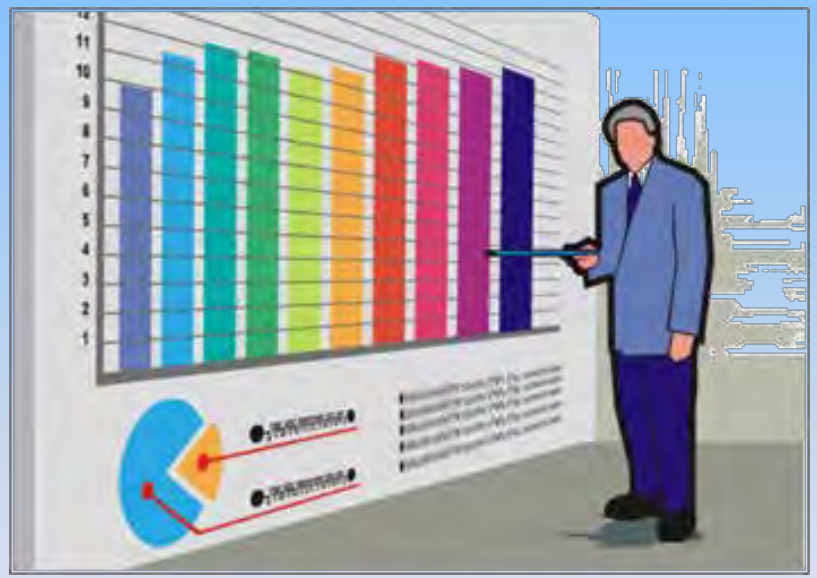


Program Governance



MERIT= Materials of Evolving Regulatory Interest Team – a virtual DoD-wide team

Part 2 – Progress Report

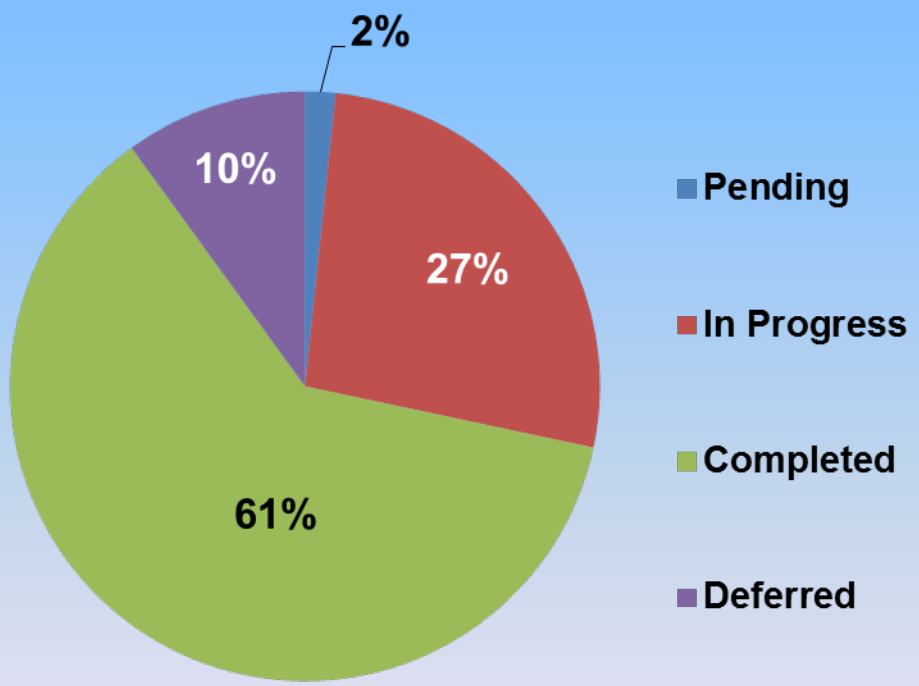


Program Scorecard – Cumulative

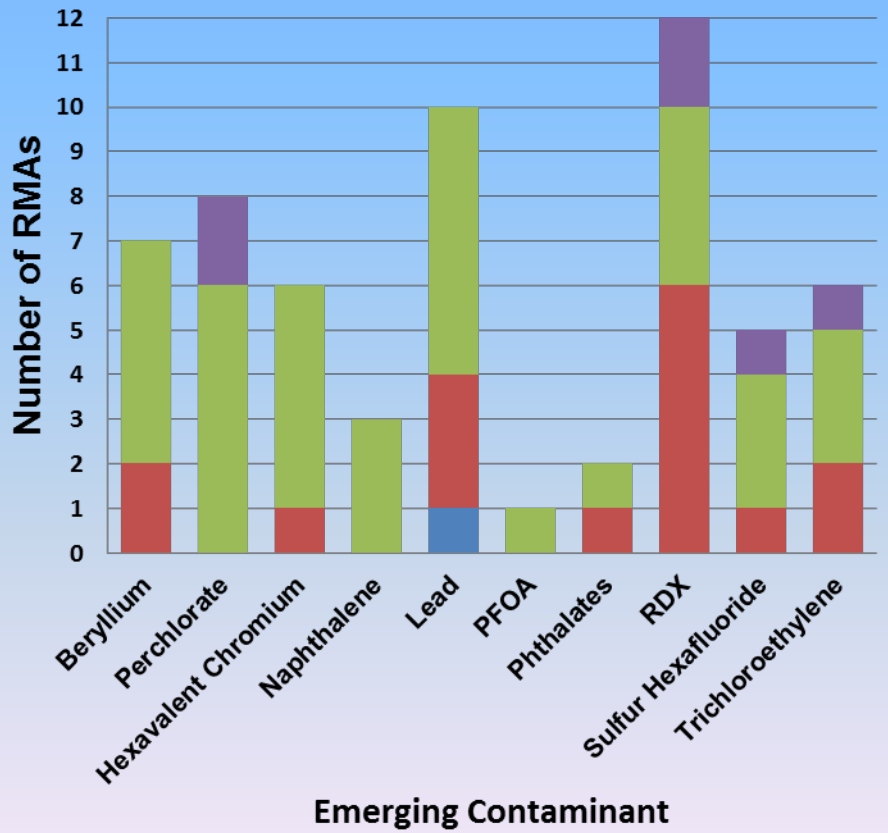
- **Potential ECs screened --- over 500**
- **Phase I Impact Assessments completed --- 36**
- **Phase II Impact Assessments completed --- 10**
  - All current/former action list chemicals completed.
- **60 Risk Management Options (RMOs) developed & turned into Risk Management Actions (RMAs)**

Status-Risk Management Actions

Overall Status



Status per EC



EC Watch List – April 2014

- Ü Tungsten/alloys
- Ü 1,4-dioxane
- Ü Metal Nanomaterials
- Ü Carbon Nanomaterials
- Ü PFOS
- Ü PFOA
- Ü DNT
- Ü Nickel
- Ü Cadmium
- Ü Manganese
- Ü Dioxin

- Cobalt
- Antimony
- Ü Diisocyanates
- Ü TCE ...moved from action list
- Ü Perchlorate ...moved from action list
- Ü decaBDE
- Ü Vanadium & compounds
- Ü NDMA
- Ü DNT
- DNAN
- Ü NTO

Energetic Compounds

Ü Phase I Impact Assessment completed

Notes:
- Di-nitrotoluenes (DNT)
- Perfluorooctanoic acid (PFOA)
- Perfluorooctyl sulfonate (PFOS)
- decabromodiphenyl ether (decaBDE)
- 5-Nitro-1,2,4-triazol-3-one (NTO)
- N-Nitrosodimethylamine (NDMA)
- Trichloroethylene (TCE)
- 2,4 dinitroanisole (DNAN)

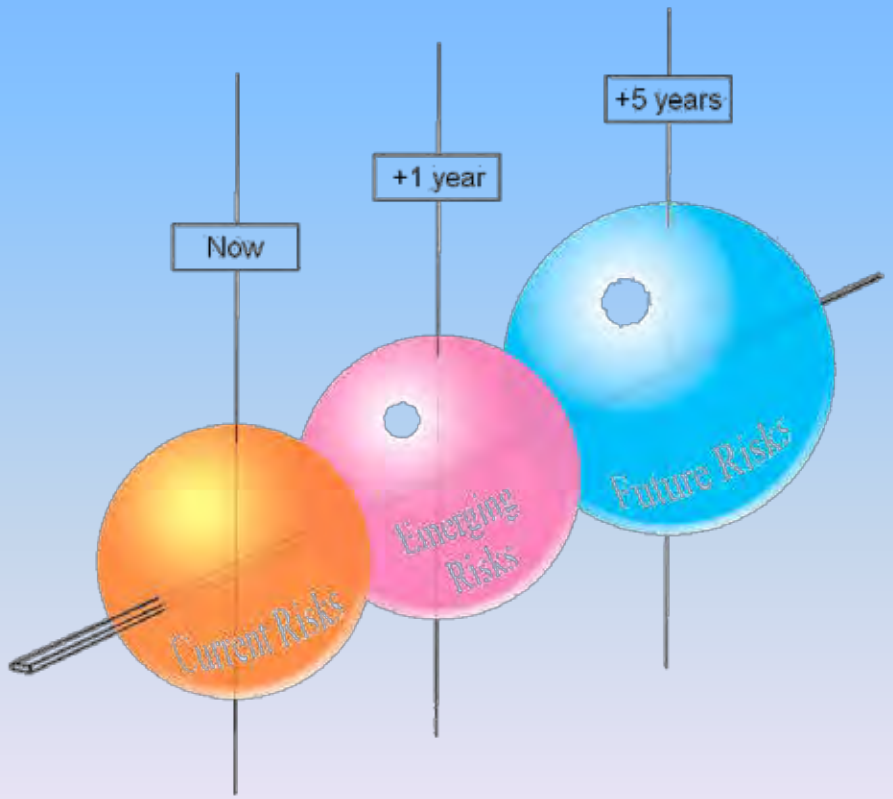
EC Action List – April 2014

- ü Royal Demolition eXplosive (RDX)
- ü Hexavalent Chromium (Cr6+)
- ü Naphthalene ...pending downgrade to watch list
- ü Beryllium
- ü Sulfur Hexafluoride (SF6)
- ü Lead
- ü Phthalates
- 1-Bromopropane ...pending ECGC approval

ü Phase II Impact Assessment completed.

RDX = Cyclotrimethylenetrinitramine

Part 3 – Risks & Risk Management Actions



Key Risk Management Actions Completed

- **Perchlorate RDT&E; Congressional Mythbusters brief**
- **Hexavalent chromium RDT&E; USD(AT&L) policy; Defense Federal Acquisition Regulation**
- **SF6[1] policy on capture & recycling**
- **Beryllium life cycle study**
- **Development of innovative naphthalene dosimeter for fuel handlers**
- **RDX[2] toxicological studies**
- **Coordination with PEO/PM for chem/bio protection equipment related to phase-out of phthalates**

[1] Sulfur Hexafluoride [2] Cyclotrimethylenetrinitramine

Lead – Why on the Action List?

- **Evolving science & regulations may pose a risk to personnel & range operations…most munitions contain lead**

Range Instructor

- **Lead-free electronics pose a risk to DoD supply chain…short-circuiting in components**

Lead Risk Management Actions

- **RDT&E on lead free munitions**
- **DoD-Industry Consortium on lead-free electronics**
  - **Develop technologies to detect lead-free circuit boards**
  - **Develop viable lead-free solders**
- **National Academy of Sciences Study**
  - **Concern: Lead exposures to personnel such as small-arms range instructors given new human health science**
  - **Conclusion:** "A review of the epidemiologic and toxicologic data allowed the committee to conclude that there is overwhelming evidence that the OSHA standard provides inadequate protection for DOD firing-range personnel and for any other worker populations covered by the general industry standard."

- **Underway: Development of DoD BLL standards**
  - **Surveillance & action levels**

Evolving Risks/Issues

- **New science on human health effects of ECs**
  - NAS[1] study for lead DoD concludes: "OSHA standard is inadequate to protect personnel"
  - NAS study has implications for range personnel; work group developing DoD-specific Blood Lead Level standards
  - Most munitions use lead; changes in air and groundwater standards have implications for range management

- **New explosive compounds are ECs (e.g., DNAN[2])**
  - Toxicology & fate/effects not fully understood; presents risks to ranges due to residual contamination
  - EC program conducting Phase I Impact Assessments to assess and mitigate risk

[1] National Academy of Sciences [2] 2,4-Dinitroanisole, an energetic compound replacement for TNT

Evolving Risks/Issues

- **Serious chemical availability issues with potential impacts on readiness…hard to quantify impacts**
  - Flame retardants: used in systems, platforms, equipment; phased out prematurely due to EPA pressure on manufacturers
  - Sulfur hexafluoride (SF6): a global warming gas, used in mission critical systems (e.g., AWACs aircraft; MK-50 torpedo; fire control systems); likely SF6 ban/restrictions; no substitutes on horizon for DoD applications
  - Phthalates: used as plasticizers; being phased-out; risks for DoD is use in DoD Chem/Bio protection equipment and munitions

- **Lack of supply chain visibility for chemicals/materials**
  - Difficult to assess risk and pinpoint risk management actions

Department of Defense Emerging Contaminants Program

INNOVATIONS IN AMERICAN GOVERNMENT AWARD
Harvard University – Ash Institute for Democratic Governance & Innovation

Backup Slides

Emerging Contaminants Program Genesis

- **~2004 – Perchlorate[1] detections in groundwater & drinking water cause national concern**
  - Disputes between DoD and regulators over response actions
  - Training/testing on 2 ranges curtailed
- **2005/6 – DoD forms EC Work group with EPA & Environmental Council of States**
  - EC Definition agreed & three policy papers developed
- **2008 – DoD creates EC funding line in FYDP**
- **2009 – DoD issues EC policy instruction**

[1] An oxidizer chemical found in munitions, pyrotechnics, and rockets

What is an Emerging Contaminant?

- Chemicals & materials that have pathways to enter the environment and present real or potential unacceptable human health or environmental risks…

and either

  - do not have peer-reviewed human health standards

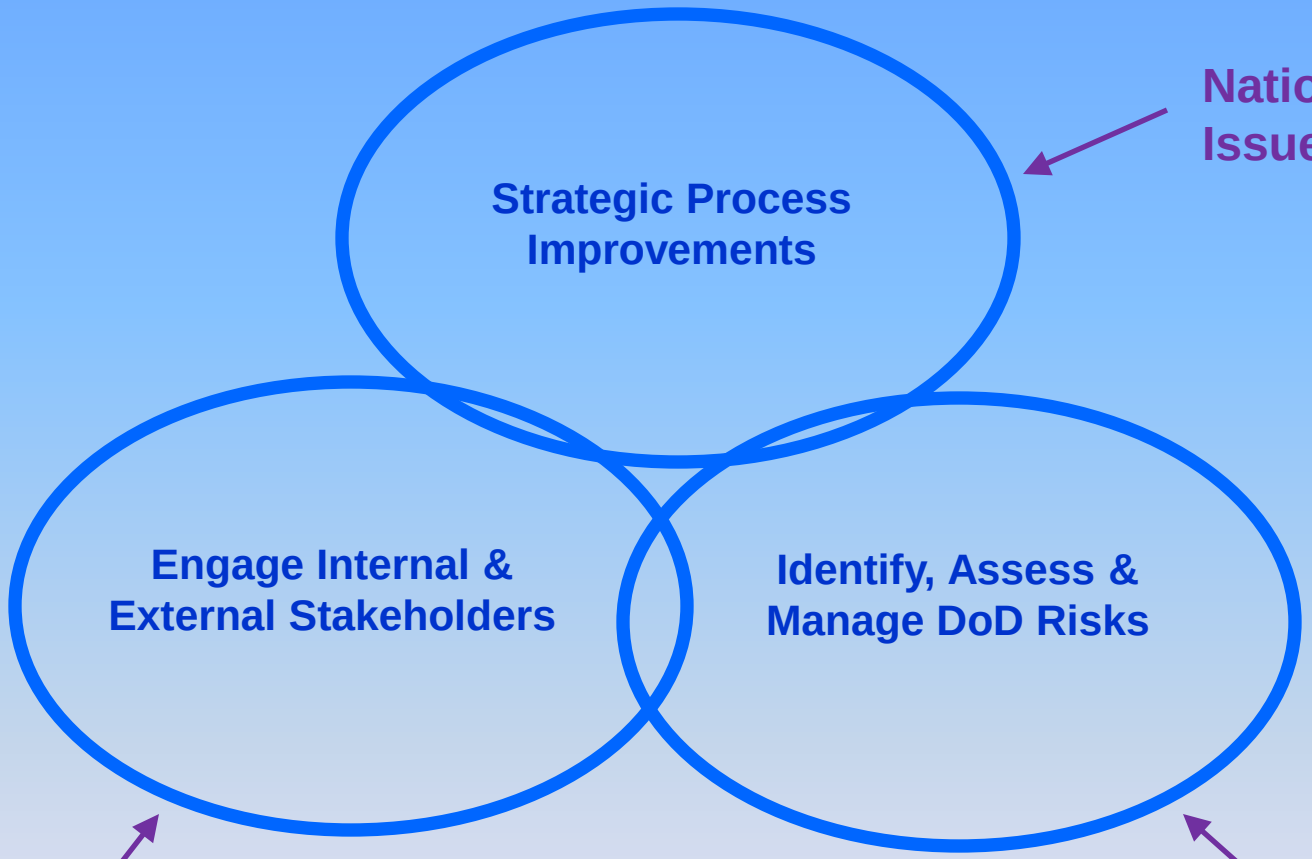
or

  - Standards/regulations are evolving due to new science, detection capabilities, or pathways.

How Can ECs Affect DoD?

- **Cause adverse health effects on operating forces, DoD employees, and/or public**
  - Human health protection paramount
- **Reduce training/readiness**
  - Restrictions on use of ranges
- **Restrict availability and/or cost of materials or chemicals**
  - Adverse impact on mission-critical applications & industrial base community
- **Increase O&M and/or cleanup costs**
  - Resource drain from mission needs

Program Strategic Priorities



National Level Issues

DoD, Federal, State, NGOs, & Industry

Internal DoD & Industry Partners

Phase I Impact Assessment Completed

- ü **Perchlorate**
- ü **Hexavalent Chromium (Sept 2006)**
- ü **Naphthalene (Sept 2006)**
- ü **Trichloroethylene (TCE) (Oct 2006)**
- ü **1,2,3-Trichloropropane (TCP) (Nov 2006)**
- ü **n-Nitrosodimethylamine (NDMA) (Nov 2006)**
- ü **1,4-Dioxane (Dec 2006)**
- ü **Dinitrotoluenes (DNT) (Dec 2006)**
- ü **Perfluorooctanoic Acid (PFOA) (Jan 2007)**
- ü **Perfluorooctyl Sulfonate (PFOS) (Jan 2007)**
- ü **Polybrominated Diphenyl Ethers (PBDEs) (Jan 2007)**
- ü **Dioxins (Feb 2007)**
- ü **Tetrachloroethylene (PCE) (Feb 2007)**
- ü **Beryllium (Mar 2007)**
- ü **Lead (Mar 2007)**
- ü **RDX (Royal Demolition eXplosive) (Mar 2007)**
- ü **Tungsten (Mar 2007)**
- ü **Nickel (May 2007)**
- ü **Hexavalent Chromium (Jul 2007)**
- ü **Tungsten Alloy (Dec 2007)**
- ü **Sulfur Hexafluoride (SF6) (Jan 2008)**
- ü **Naphthalene (Apr 2008)**
- ü **Cadmium (May 2008)**
- ü **Lead (July 2008)**
- ü **Cerium (May 2009)**
- ü **Cadmium (Sept 2010)**
- ü **Dinitrotoluenes (DNT) (Jan 2011)**
- ü **Nanomaterials (Metal-Based) (Feb 2011)**
- ü **Manganese (May 2011)**
- ü **Diisocyanates (Jun 2011)**
- ü **Phthalate Esters (Jun 2011)**
- ü **Nanomaterials (Carbon-Based) (Nov 2011)**
- ü **Decabromodiphenyl Ether (Apr 2012)**
- ü **Vanadium and Compounds (Oct 2012)**
- ü **1-Bromopropane (1-BP) (Jan 2013)**

This summary is for chemicals on which all three parts of a Phase I Impact Assessment were completed.

Phase I Impact Assessment Results Summary

Recommended for Watch List

- Cadmium and Compounds
- Cerium ***
- Cobalt and Compounds
- Decabromodiphenyl Ether (deca-BDE)
- Diisocyanates
- Dinitrotoluenes (DNT)
- 1,4-Dioxane
- Dioxins
- Manganese and Compounds
- Nanomaterials (Metal- and Carbon-Based)
- Nickel
- Perfluorooctyl Sulfonate (PFOS)
- Tetrachloroethylene (PCE) ***
- Tungsten
- Tungsten Alloy
- Vanadium and Compounds

Dropped After Phase I

- Dichlorobenzenes
- n-Nitrosodimethylamine (NDMA)
- Polybrominated diphenyl ethers (PBDEs)
- 1,2,3-Trichloropropane (TCP)

Recommended for Phase II / Action List

- Beryllium
- Hexavalent Chromium
- Lead
- Naphthalene
- Perchlorate *
- Perfluorooctanoic Acid (PFOA) **
- Phthalate Esters
- RDX
- Sulfur Hexafluoride (SF6)
- Trichloroethylene (TCE) **
- 1-Bromopropane (1-BP) *(proposed)*

Future Assessments (anticipated date)

- 1,4-Dioxane (Inhalation only) (TBD)
- n-Nitrosodimethylamine (NDMA) (TBD)
- 2,4-Dinitroanisole (DNAN) and 5-Nitro-1,2,4-triazol-3-one (NTO) (components in insensitive explosive formulations) (TBD)
- Cobalt (pending IRIS review) (TBD)

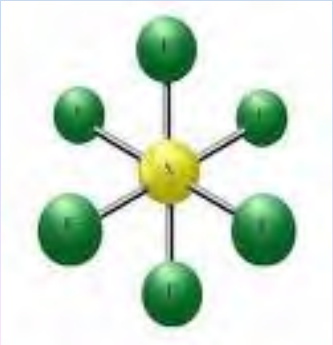
Determining Need for Phase I Assessment

- Antimony

* Demoted to Watch List in September 2010
** Subsequent Phase II Impact Assessment recommended delisting from the Action List and adding to the Watch List
*** Regulatory developments supported delisting from the Watch List

Sulfur Hexafluoride (SF6) Background

- A non-flammable, non-toxic gas – no human health concerns
- Extremely stable, with excellent dielectric properties (electrical insulation and arc-quenching)
- A high global warming potential – 22,800 times more potent than carbon dioxide (CO_2) – long lasting in the atmosphere
- Average global SF6 concentration has increased by about 7 percent per year during the 1980s and 1990s

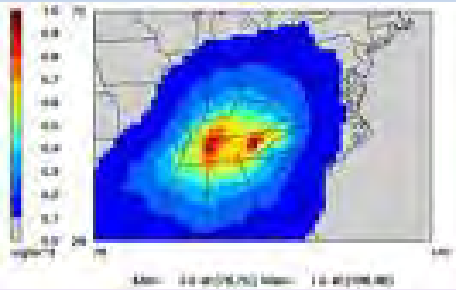


SF6 Commercial Uses

- High-voltage electrical switchgear & transformers
- High-energy imaging equipment
- Research - atomic particle tandem accelerators

SF6 Military Uses

- Pressurization/dielectric for aircraft targeting pods/avionics -- Airborne Warning and Control System (AWACS) radar (e.g., E-3 Aircraft)
- Waveguide pressurization for shipboard targeting radar (e.g., MK 92 Fire Control System)
- Comprehensive Nuclear Test Ban Treaty monitoring and nuclear event detection
- MK-50 Torpedo propulsion



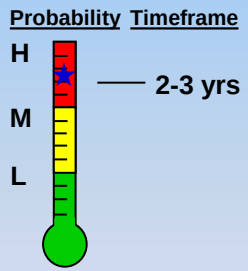
SF6 Phase I Impact Assessment

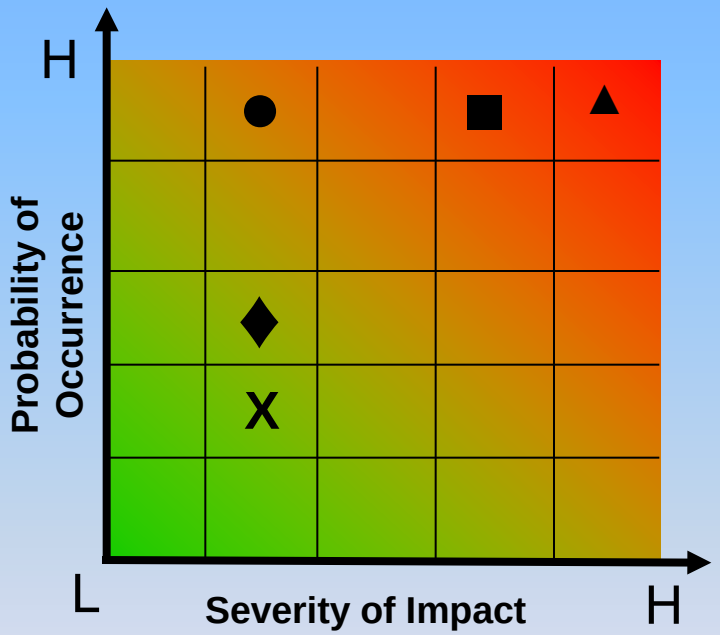
Completed January 2008

Sulfur Hexafluoride (SF6) is used in radar systems (e.g., AWACS aircraft); helicopter rotor-blade leak tests; discharge testing in fire suppression systems; electrical switch gear; and propulsion systems for specific weapons (e.g., MK-50 torpedo) in service and under design.

Likelihood of Toxicity Value/ Regulatory Change

1. **Probability that Greenhouse Gas emission initiatives will restrict use/availability of SF6**





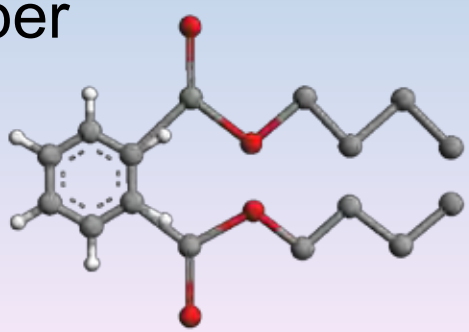
- ♦ ES&H
- ■ Training & Readiness
- ▲ Acquisition/RDT&E
- ● PO&MD of Assets
- X Cleanup

SF6 Risk Management Actions

- **DoD Policy issued on SF6 capture & recycling**
- **RDT&E on substitutes for mission critical applications**
- **Coordination with Electric Power Research Institute on substitutes for electrical infrastructure**

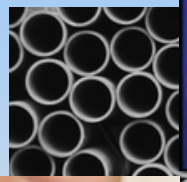
Phthalates Background

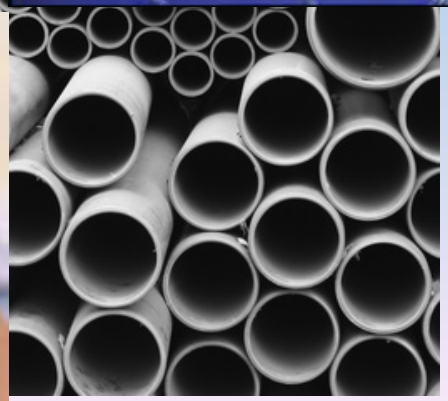
- Organic compounds derived from petroleum…phthalates are esters of phthalic acid
- Main uses:
  - Plasticizers to increase flexibility, durability and transparency of plastic products and to soften polyvinyl chloride (PVC) products
  - Solvents for oil-based dyes and nitrocellulose-based lacquers and coatings
- Due to their universally beneficial qualities, phthalates have found their way into a wide variety of consumer products
- Widespread human exposure…a number of phthalates appear in human biomonitoring surveys



Phthalates Commercial Uses

- The specific phthalates in a product depends on the properties the phthalates impart and their cost
- Phthalate-containing products include:
  - **Medical supplies and devices** (i.e., intra-venous (IV) tubing and blood bags)
  - Dental materials
  - Paints, wood varnishes and lacquers
  - Anti-corrosion and anti-fouling paints
  - Wire and cable applications
  - Sealing compounds
  - Vinyl tile
  - Textiles and textile inks
  - Cosmetics
  - **Food packaging**





Phthalates Military Uses

- Solid rocket fuel binder
- Rocket motors & cartridges
- Plastics, rubber and vinyl components
- Wire insulation

- CBRN equipment (protective masks, gloves, boots, hoods) ??

Phthalates Risk Drivers

- CPSC[1] assessments and/or EPA Chemical Action Plan (CAP) for phthalates may result in requirements to label, restrict, or ban specific phthalates
- Three phthalates[2] included on the *REACH Authorisation List* (Annex XIV) cannot be placed on the market or used after 21 July 2015 without authorization
- Bottom line: Production of certain phthalates discontinued in U.S….additional suppliers may stop producing specialty phthalates critical to DoD applications
  - Time/cost intensive RDT&E needed for phthalate substitutes
  - Items made with new materials may require re-qualification

[1] Consumer Product Safety Commission

[2] BBP—Butyl benzyl phthalate; DEHP—Di(2-ethylhexyl) phthalate; DBP—Dibutyl phthalate

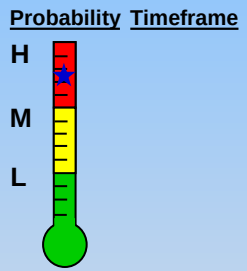
Phthalates Phase I Impact Assessment

Completed June 2011

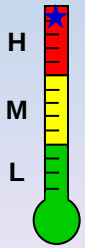
Phthalates are used as a plasticizer to create preferable physical properties in plastic products. Critical DoD phthalate-containing items include CBR equipment (protective masks, gloves, boots, hoods), propellant mixtures used in numerous munitions products, and a variety of sealers, paints, and resins.

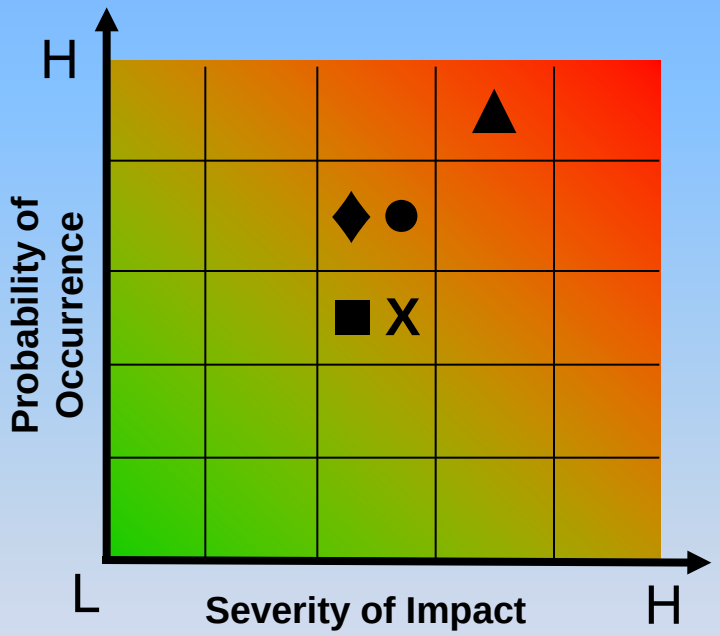
Likelihood of Toxicity Value/ Regulatory Change

1. **Probability that USEPA TSCA chemical management regulations will restrict use/availability of phthalates**



2. **Probability that EU REACH chemical management regulations will restrict use/availability of phthalates.**





- ♦ ES&H
- ■ Training & Readiness
- ▲ Acquisition/RDT&E
- ● PO&MD of Assets
- X Cleanup

Phthalates Risk Management Actions

- **Issued early Risk Alert**
- **Completed Phase II Impact Assessment**
- **Worked with Joint Program Executive Office for Chemical & Biological Defense (JPEO-CBD) to minimize risk to protective equipment**
- **Issued Risk Memo to DoD Acquisition Executives**
  - **Locate critical applications requiring phthalates**
  - **Take risk management actions (e.g., testing substitutes)**

EC "Scan-Watch-Action" Process

Over -the- horizon

EC News

Review literature, periodicals, regulatory communications, etc.

Possible DoD impacts

Phase I Assessment

Monitor events; Conduct Phase I qualitative impact assessment

Probable high DoD impacts

Phase II Assessment

Conduct Phase II quantitative impact assessment; develop & rank RMOs

Risk Management Options (RMOs) to ECGC

Approved RMOs become Risk Management Actions (RMAs)

decaBDE[1]
An Example of Material Availability Risk

- A **flame retardant** used in electronics, wire and cable insulation, textiles, automobiles & aircraft
- EPA: "Studies have shown that decaBDE persists in the environment, potentially causes cancer and may impact brain function."
- EPA & companies agree to **phase-out production** & sales for most uses 31 Dec 2012 & end all uses by end of 2013
- DoD, FAA, NASA, and industry believe phase-out is premature; substitutes not fully verified for performance or health risks

[1] decabromodiphenyl ether

Flame Retardants in Aerospace Products Have Increased Survivability

- **Assures safety in flight, if fire occurs**
- **Assures ability to escape, if aircraft crash occurs**
- **Meets FAA requirements**
  - 14 CFR Part 25 regulations:
    - Section 25.853, Compartment Interiors
    - Section 25.855, Cargo/Baggage Compartment
    - Section 25.856, Thermal/Acoustic Insulation
    - Section 25.869, Wire Flammability
    - Appendix F, Detailed Test Requirements
      - Materials and parts must successfully pass test/s in order to show compliance
      - Nine (9) different tests specified; some materials/parts must pass multiple tests
      - Variations of configurations require individual testing

2008 Continental Airlines 737
0 fatalities, 115 survivors

DecaBDE has become integral to meeting stringent aviation safety requirements

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Use by DoD Approved by The Boeing Company

DecaBDE is Used in Many Applications in Most Boeing Products

- Adhesives and Tapes
- Composites
- Ducting & Molded Parts
- Electrical/Electronics
- Emergency Equipment
- Fabrics & Films
- Insulation
- Interiors
- Sealants

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Boeing has a Global, Multi-Tiered Supply Chain

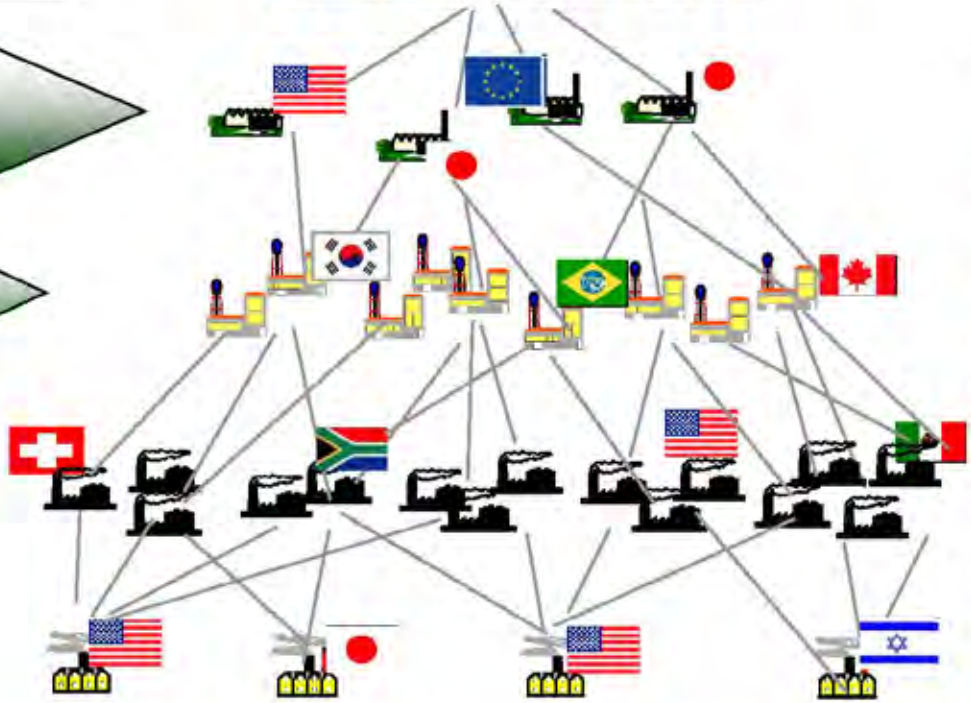
Boeing
Aircraft with a Lavatory

Commodity Supplier-
Supplier Owned Design:
Lavatories with Panels

Part Mfg
Panel with Edge Potting

Material Mfg
Potting Compound

Chemical Mfg
DecaBDE



Global Supply Chain

737 Lavatory

DecaBDE alternative manufacturers & compounders drive the replacement timetable

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The Boeing Company – Distribution to OIRA – 16 February 2011

decaBDE Risk Management Actions

- **Issued "EC Risk Alert" to DoD & prime contractors**
  - **Difficult to locate decaBDE in supply chain**
- **Working with OMB, EPA, FAA, Aerospace Industries Association on reducing risk and evaluating substitutes**
  - Commented on EPA proposed rule on flame retardants
  - Possible joint testing on substitutes
- **Convened stakeholders roundtable on larger public policy issue of chemical phase-out process**

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PFOS, PFOA and Other Fluorinated Compounds:

Overcoming Sampling and Analytical Challenges

Author: Terry Obal, Ph.D., C.Chem.

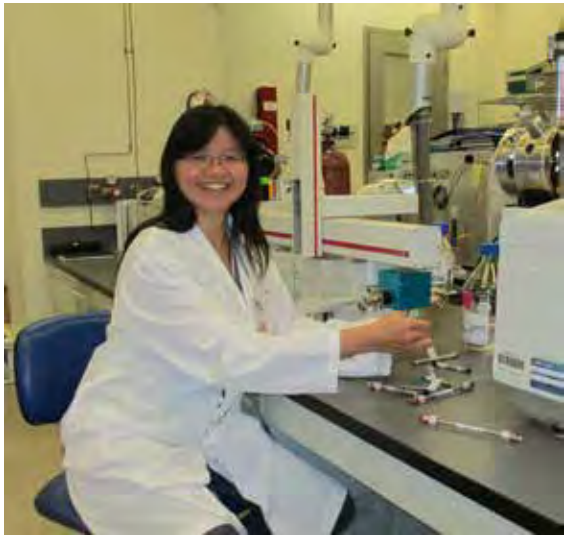
Date: 2014 DoD Environmental Monitoring Data Quality Workshop

April 8-10, 2014

Acknowledgments

Success Through Science®

Adam Robinson

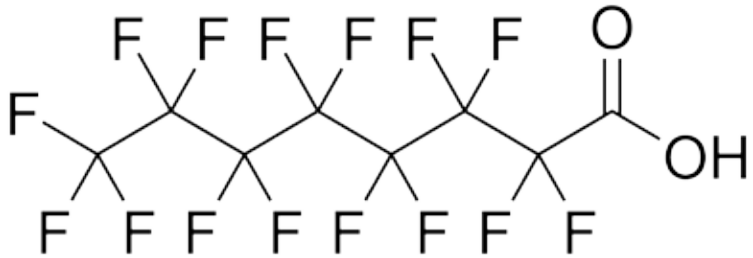


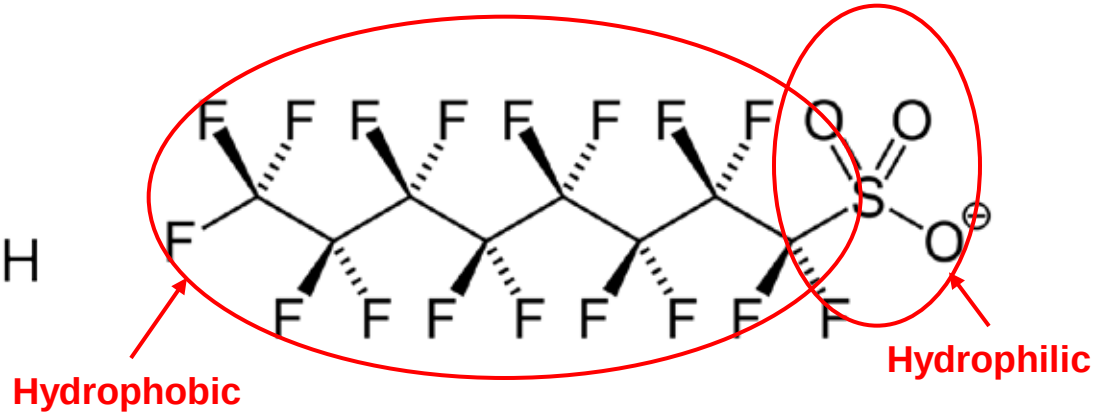
Sin Chii Chia

Outline

- Overview
  - History
  - Environmental Significance
- Sampling, Analytical and Reporting Considerations
  - Sampling Challenges
  - Analytical Methods
  - “Understanding” the results

What are they?





Perfluorooctanoic Acid (PFOA)

Teflon®

Perfluorooctane Sulfonate (PFOS)

Scotchguard®

Chemical and Physical Properties

- Very stable and persistent – do not degrade
- Low volatility
- Soluble in water
- Readily bind (sorb) to variety of materials (hard to predict partitioning)
- Bioaccumulation
- Ubiquitous (“they’re everywhere”)

Fluoropolymers vs. Fluorinated Telomers

Fluoropolymers

- Long chain molecules
- Fire resistant
- Repel oil, grease, stains and water
- Used to provide non-stick surface in cookware and waterproof breathable membranes for clothing
- Hundreds of other uses in virtually all industry segments (e.g. aerospace, automotive, chemical, electronics, textile, etc.)

Fluorinated Telomers

- Surfactants and surface treatment chemicals in many products (e.g. repellent coatings on textiles, leather and paper)
- High performance surfactants in products that need to flow evenly (e.g. paints, coatings, fire fighting foams, engineering coatings in the manufacture of semi-conductor coatings)

PFC Naming Conventions

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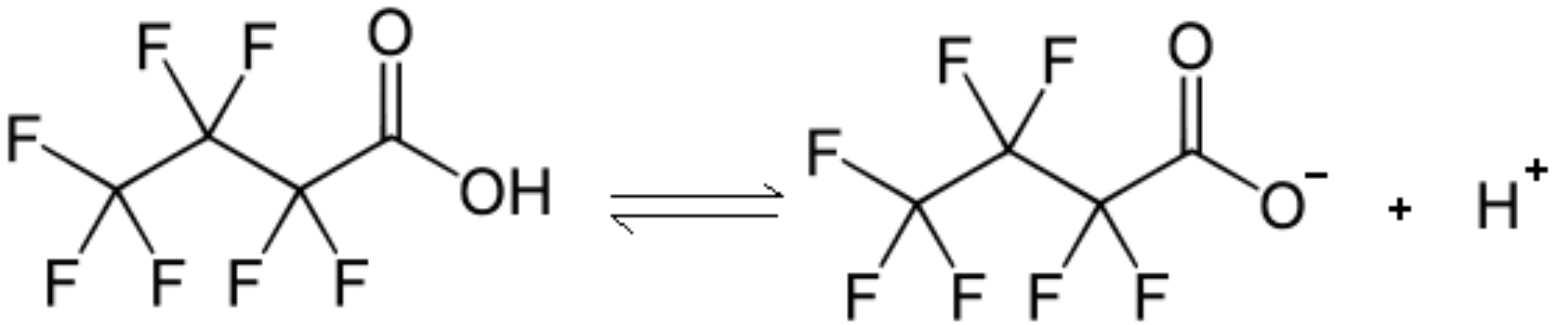

Perfluorobutanoic Acid
aka
Perfluorobutyric Acid

Perfluorobutanoate

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Naming Conventions

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Abbreviation	Acid	Conjugate
PFBA	Perfluorobutanoic Acid	Perfluorobutanoate
PFBS	Perfluorobutanesulfonic Acid	Perfluorobutanesulfonate
PFPA	Perfluoropentanoic Acid	Perfluoropentanoate
PFHxA	Perfluorohexanoic Acid	Perfluorohexanoate
PFHxS	Perfluorohexanesulfonic Acid	Perfluorohexanesulfonate
PFHpA	Perfluoroheptanoic Acid	Perfluoroheptanoate
PFOA	Perfluorooctanoic Acid	Perfluorooctanoate
PFOS	Perfluorooctanesulfonic Acid	Perfluorooctanesulfonate
PFNA	Perfluorononanoic Acid	Perfluorononanoate
PFDA	Perfluorodecanoic Acid	Perfluorodecanoate
PFDS	Perfluorodecanesulfonic Acid	Perfluorodecanesulfonate
PFUdA	Perfluoroundecanoic Acid	Perfluoroundecanoate
PFDoA	Perfluorododecanoic Acid	Perfluorododecanoate
PFTrDA	Perfluorotridecanoic Acid	Perfluorotridecanoate
PFTeDA	Perfluorotetradecanoic Acid	Perfluorotetradecanoate
PFOSA	Perfluorooctanesulfonamide	Perfluorooctanesulfonamide

Key Dates for PFOS and PFOA

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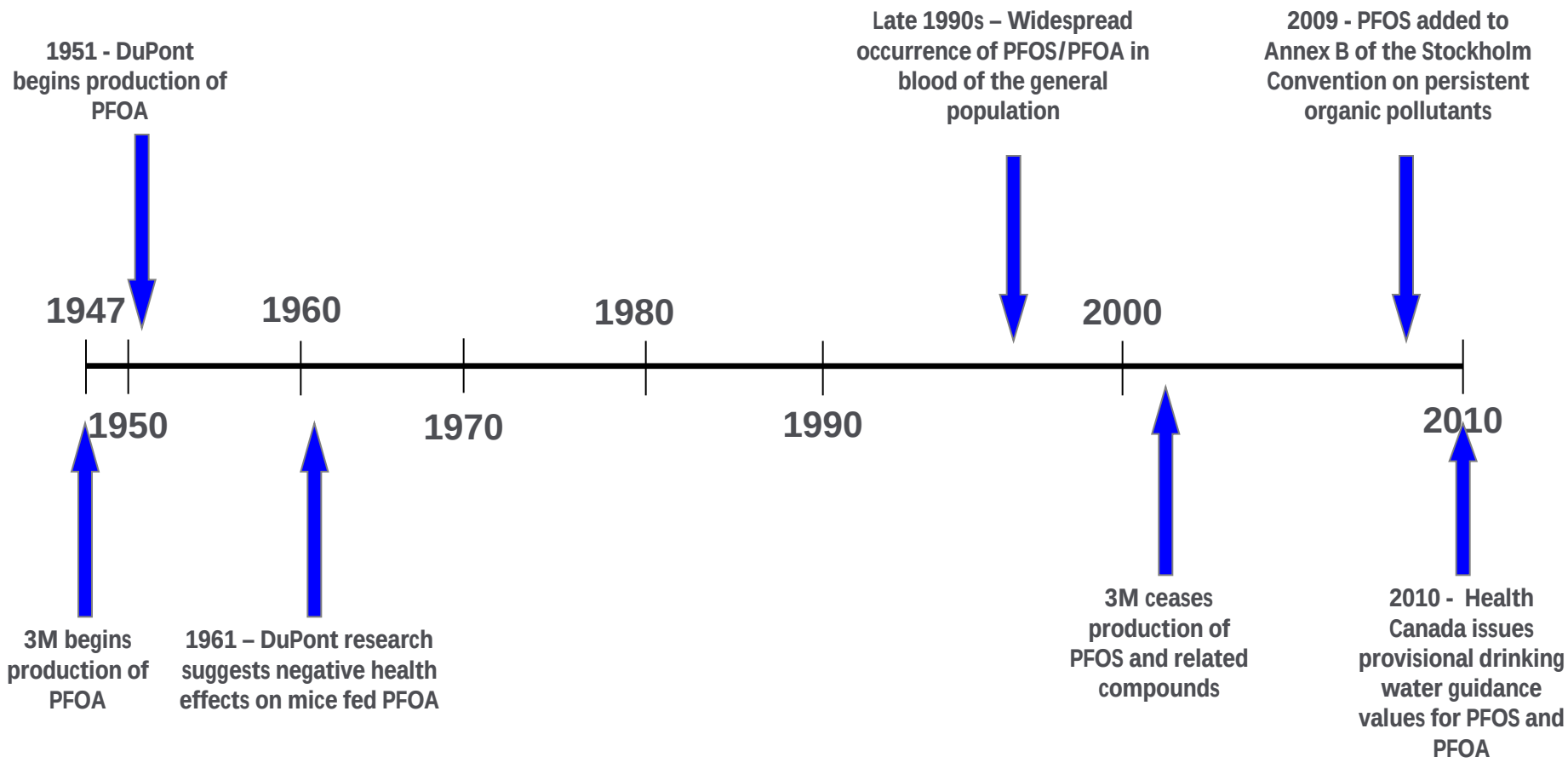

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Environmental Pathways for PFC Exposure

- Commercially used perfluorinated compounds (PFCs) have been widely detected in humans, but the sources of human exposure are not fully characterized

- Suggested sources of exposure
  - Drinking Water
  - Dust/Ambient Air
  - Food

How are PFC finding their way into people?

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White Castle

Key Dates for PFOS and PFOA

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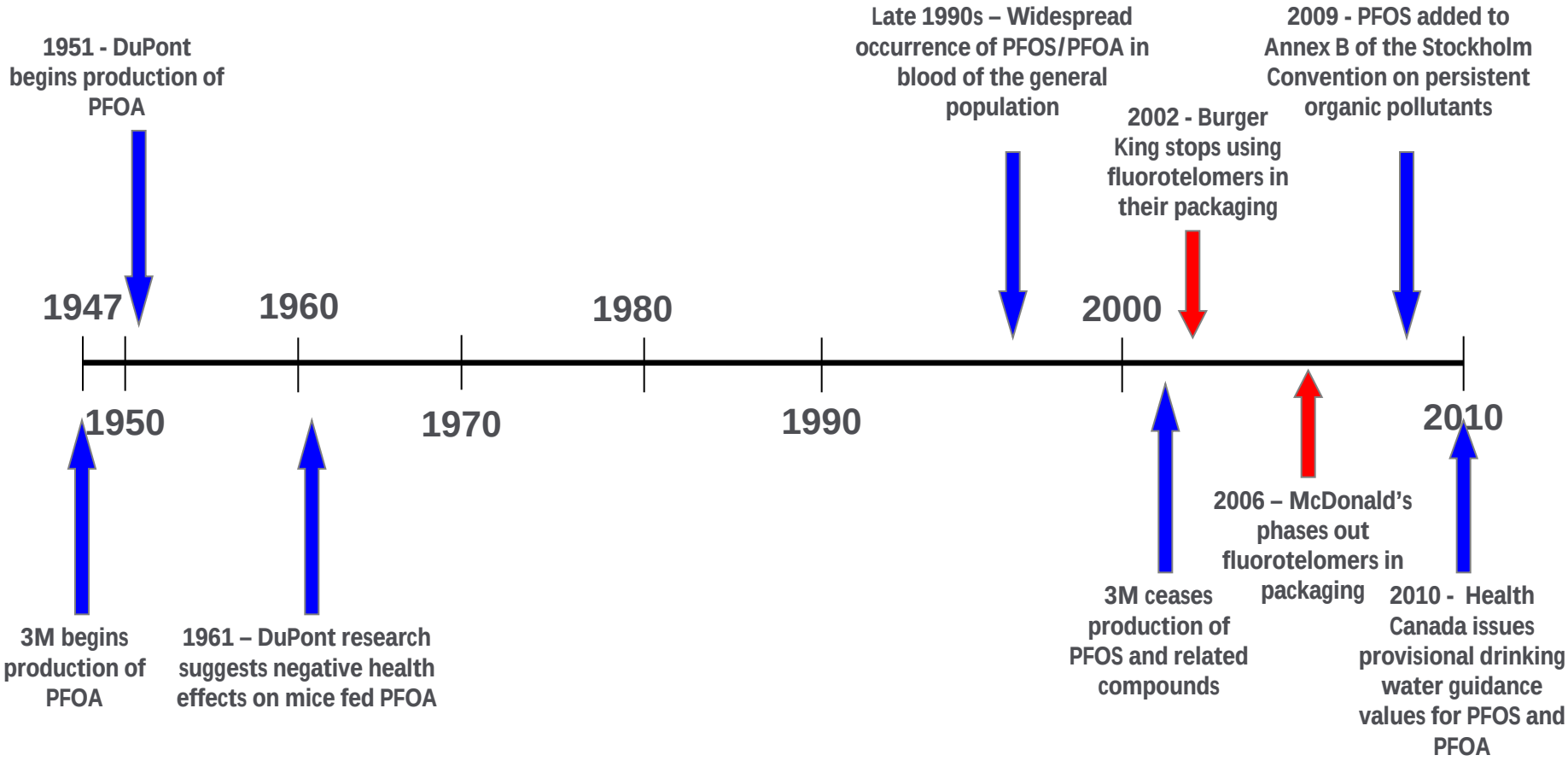

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Where are they being found?

- Although PFOS, PFOA and other PFCs are likely to be found anywhere, at differing concentrations, typical areas where these are compounds of concern, at elevated concentrations, are:
  - AFFF
  - Airports
  - Run-off from incidents of fire
  - Landfill leachate
  - WWTP Effluent

…and now they're making the news

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THE KINGS COUNTY ADVERTISER
THE KINGS COUNTY REGISTER

The Register/Advertiser > News

Contaminated water in Greenwood

Nancy Kelly
Published on March 25, 2010

Chemical found in 14 Wing well

Environment International 39 (2012) 19–26

Contents lists available at SciVerse ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

ELSEVIER

Highly elevated levels of perfluorooctane sulfonate and other perfluorinated acids found in biota and surface water downstream of an international airport, Hamilton, Ontario, Canada

S.R. de Solla [a,*], A.O. De Silva [b], R.J. Letcher [c]

[a] Wildlife and Landscape Science Directorate, Environment Canada, 867 Lakeshore Road, Burlington, ON, Canada
[b] Water and Science Technology Directorate, Environment Canada, 867 Lakeshore Road, Burlington, ON, Canada
[c] Wildlife and Landscape Science Directorate, Environment Canada, Ottawa, ON, Canada

Documents show widespread PFOS pollution at Hamilton's airport

The toxic firefighting chemical polluting Hamilton's airport has been found at more than 10 airports and military sites across Canada, according to a federal petition response.

Documents provided in a response to a petition filed with the auditor general's office by local biologist Joe Minor also say Transport Canada is still deciding whether it will help Hamilton deal with perfluorooctane sulfonate (PFOS) pollution at the city airport, which was once federally owned.

nada is spending millions of dollars cleaning up historic pollution at a municipal airport in British Columbia even as it me help to Hamilton.

udying PFOS (perfluorooctane sulfonate) contamination at an old firefighting training pad at its airport, which Transpor Canada owned until 1996. The toxic chemical has also been found downstream in fish and turtles in the Binbrook reservoir (http://www.thespec.com/news/local/article/794613-low-level-pollution-riddles-reservoir-bottom).

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Toxicology

- Still being evaluated- a range of toxicological effects have been reported in a variety of species
- Several agencies around world have developed aquatic risk values for PFOS and PFOA, and terrestrial risk values are being developed
- Not yet confirmed as human carcinogen
- Readily absorbed and accumulates in all tissues, especially target organs (e.g. liver)
- Not metabolized and eliminated slowly
- PFOS exposure has been associated with many health problems including some cancers
- Several agencies have derived human toxicity reference values – all suggest high potential human toxicity

Regulatory Status in Canada (PFOS Focus)

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- Risk management strategies seek to have environmental PFOS concentrations as low as possible, prevent re-introduction to market, and address remaining uses (restrictions, exemptions, BMP etc.)
- PFOS still in AFFF (allowed at 0.5 ppm); AFFF with PFOS >0.5 ppm is prohibited on and after May 30, 2012 (certain military operations are excluded)
- On and after May 29, 2013, manufacture, use, sale and import of PFOS and PFOS-containing products is prohibited in Canada
- Other PFCs (polyfluorotelomer sulphonates) are used in newer AFFF formulations
- January 2013: EC Consultation document describes existing RM actions in Canada and globally, requests input on exemptions, and sets next steps and timelines

Regulatory Status

- 2010/2015 PFOA Stewardship Program:
  - Eight (8) global suppliers agree to:
  - 95% reduction in PFOA (and related precursor) levels in emissions relative to 2000 levels
  - Total elimination of PFOA (and related precursor) levels in emissions
- September 30, 2013 – USEPA Significant New Use Rule (SNUR) relating to perfluoroalkyl sulphonates (PFASs)
- SNUR related to perfluoroalkyl carboxylates (PFACs) (in-process)

Regulatory Limits – Drinking Water

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Jurisdiction	PFOA (ug/L)	PFOS (ug/L)	PFBA (ug/L)	PFBS (ug/L)
Canada – Health Canada	**0.7**	**0.3**	N/V	N/V
U.S.A - EPA	**0.4**	**0.2**	N/V	N/V
U.S.A. – Minnesota	**0.3**	**0.2**	**7**	**7**
U.S.A. – New Jersey	**0.04**	N/V	N/V	N/V
U.S.A. – North Carolina	**2**	N/V	N/V	N/V
Europe – United Kingdom	**10**	**0.3**	N/V	N/V
Europe - Germany	**0.1 (PFOA and PFOS)**		N/V	N/V

Regulatory Limits – UCMR3

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Compound	Minimum Reporting Level (ug/L)
Perfluorooctane sulphonate (PFOS)	0.04
Perfluorooctanoic Acid (PFOA)	0.02
Perfluorononanoic Acid (PFNA)	0.02
Perfluorohexanesulfonate (PFHxS)	0.03
Perfluoroheptanoic Acid (PFHpA)	0.01
Perfluorobutane sulphonate (PFBS)	0.09

Provisional Soil Levels - PFOS

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Jurisdiction	Residential (ug/g)	Commercial (ug/g)	Industrial (ug/g)
Canada – Health Canada[1]	**0.7**	**1**	5
U.S.A – EPA Region IV	**6**	N/V	N/V

1) CCME Guidelines for PFOS anticipated 2014/2015

Problem Statement(s)

- Inconsistent approaches to analysis for PFCs in simple and complex environmental matrices
- High risk of sample cross contamination due to ubiquitous nature of PFCs and the tendency to be found at high concentrations
- Sample matrices range from simple to complex
- Data comparability between laboratories is difficult
  - High variability
  - Lack of confidence in the results
  - Inability to make supportable remedial decisions

Sampling, Analytical and Reporting Considerations

Sample Containers

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Sampling: Best Practices

- Sampling and field quality assurance plans must address the concern for false positives
- Sampling methods MUST address potential sources of PFOS, PFOA and other PFCs:
  - No Teflon®
  - No Gore-tex®
  - No water proof field note books
  - No glass sampling containers
- Water for blanks MUST be PFC free.

Analytical Methods
The “Basics”

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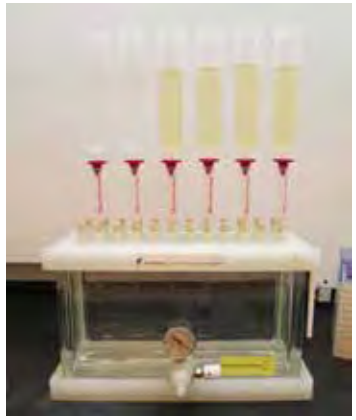

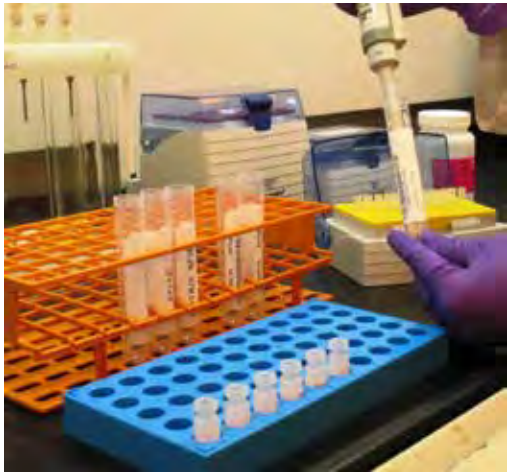

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Importance of Isotope Dilution…

- If the isotopically labeled analogue is added to the sample at the very beginning of the analytical process (i.e. before any sample homogenization, extraction, clean-up etc.), it enables exact compensation for variances at all stages of the analysis, from sample preparation through to the final instrumental measurement.

- IDMS provides greater accuracy than other calibration methods because it compensates for any matrix effects that may suppress recovery of the parameters being measured.

Importance of Isotope Dilution…

- Simply put…

  …the recovery of the labeled compound, which is not naturally present in the sample, is an exact representation of the recovery of the native compound which is present in the sample.

- Using PFOS as an example, the $^{13}C_4$-labelled analog of PFOS is used to correct for varying recovery of the native (^{12}C) PFOS from the sample. So if the recovery of the labeled PFOS is 60%, the recovery of the native PFOS being measured will also be 60%.

Branched (technical) vs. Linear PFOS

- When interpreting PFOS data, it is important to understand if it is being quantified as the linear or branched chain isomers
- Technical PFOS is a mixture of linear and branched chain PFOS isomers
- Linear PFOS is typically pure
- Branched chained PFOS contains at least 3 isomers
- This is an important differentiation because if linear PFOS is used as the calibration standard, the quantitative results on real-world samples (containing a mix of linear and branched PFOS) can be off by as much as 40%

Limits of Quantitation (LOQs)

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Compound	LOQs	
	Water (ug/L)	Soil (ug/kg)
Perfluorobutanoic Acid (PFBA)	0.02	0.1
Perfluorobutanesulfonic Acid (PFBS)	0.02	0.1
Perfluoropentanoic Acid (PFPA)	0.02	0.1
Perfluorohexanoic Acid (PFHxA)	0.02	0.1
Perfluorohexanesulfonic Acid (PFHxS)	0.02	0.1
Perfluoroheptanoic Acid (PFHpA)	0.02	0.1
Perfluorooctanoic Acid (PFOA)	***0.02***	***0.1***
Perfluorooctanesulfonate (PFOS)	***0.02***	***0.1***
Perfluorononanoic Acid (PFNA)	0.02	0.1
Perfluorodecanoic Acid (PFDA)	0.02	0.1
Perfluorodecanesulfonate (PFDS)	0.02	0.1
Perfluoroundecanoic Acid (PFUdA)	0.02	0.1
Perfluorododecanoic Acid (PFDoA)	0.02	0.1
Perfluorotridecanoic Acid (PFTrDA)	0.02	0.1
Perfluorotetradecanoic Acid (PFTeDA)	0.02	0.1
Perfluorooctanesulfonamide (PFOSA)	0.02	0.1

Sampling Protocols and Analytical Methods: Key Areas for Consideration

- Sample Collection Protocols:
  - Low flow, bailers, passive samplers
  - Cross-contamination
  - Minimize exposure of samples/extracts to potential sources of PFCs
  - Fill containers completely
- Minimize transfer of sample aliquots
  - (i.e. as much as is possible, avoid subsampling prior to addressing adsorption)
- Sample Preparation:
  - Homogenization/Filtration

Sampling Protocols and Analytical Methods: Key Areas for Consideration

- Sample Extraction/Clean-up
  - Direct injection/solid phase extraction (SPE)
- Analysis:
  - "Isotope Dilution" LC/MS/MS
  - Calibration: solvent based standards/matrix matched standards
- Data Reduction:
  - Linear vs branched chain PFOS

What to expect when requesting analyses

- Laboratory Accreditation (ISO Guide 17025):
  - SCC (Canada)
  - DoD (USA)
- Calibration Range:
  - Water: 0.02 – 50 ug/L
  - Soil: 0.1 – 10 ug/kg
- Standard Turnaround Time – 10 working days
- Rush Analyses – Minimum 3 days

Questions?

eurofins | Lancaster Laboratories Environmental

The Use of Advanced Instrumental Techniques to Address Emerging and Unique Circumstance Contaminants.

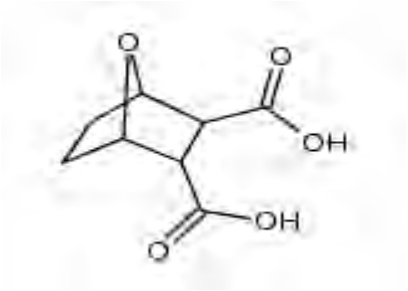
Chuck Neslund, Technical Director

2014 DoD Environmental Monitoring & Data Quality Workshop
April 8-10, 2014

Providing comprehensive scientific resources to environmental clients worldwide.

Case Study #1

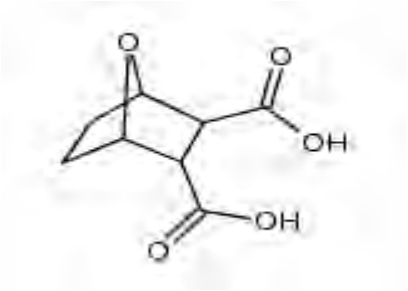
Endothall



- Widely used herbicide for control of aquatic weeds and algae
- Also used with sugar beets, hops, cotton and alfalfa.
- EPA has MCL of 100 ug/l in drinking water
- EPA Method 548.1 used for analysis in water

Case Study #1

Endothall



EPA Method 548.1

§ Extract 100 mls of water with ion exchange SPE

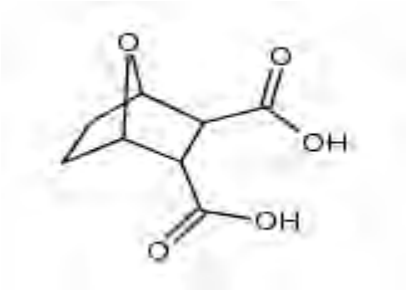
§ Derivatize with acidic methanol

§ Analyze by GC/MS

§ Method MDLs listed around 2 ug/l

Case Study #1

Endothall

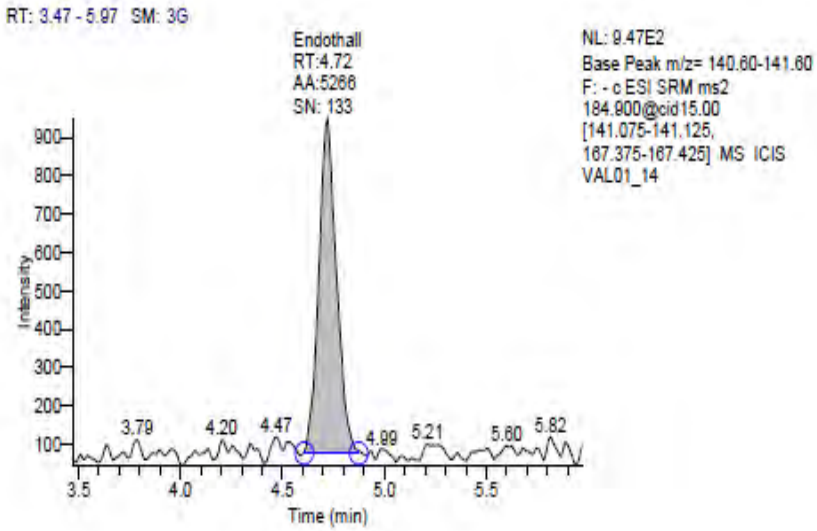


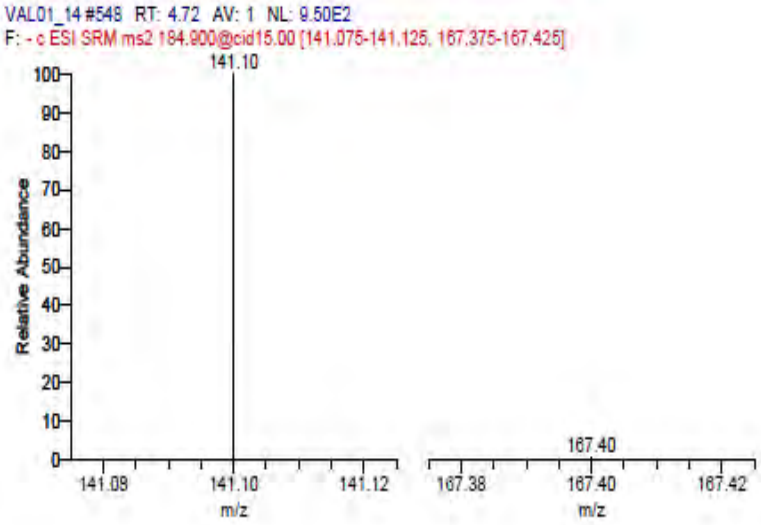
- Client needed soil samples analyzed in addition to waters
- No proven methodology for soil
- Dicarboxylic acid functionality looked suitable for LC/MS/MS approach
- Extract from soil? Optimally use water...maybe ion pairing reagent

Case Study #1

LOQ Level Standard for Endothall – 50 ng/g in soil

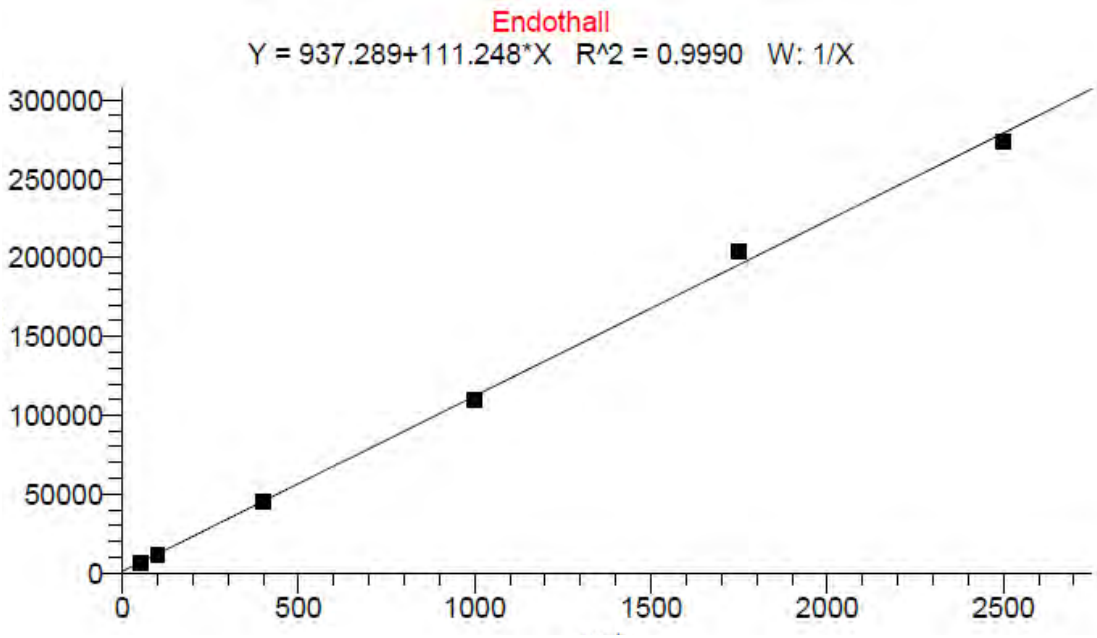
10 ng/ml in solution





Case Study #1

Calibration Curve for Endothall – 50 ng/g to 2500 ng/g in soil



Recoveries of 70-130

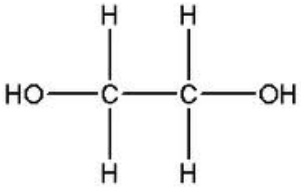
LOQ = 50 ng/g

MDL = 25 ng/g

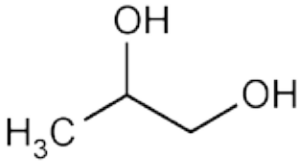
Case Study #2

Glycols

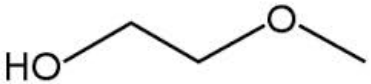
Ethylene Glycol



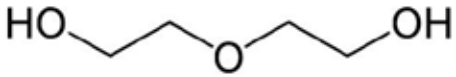
Propylene Glycol



2-methoxy ethanol

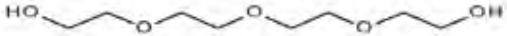


Diethylene Glycol



Triethylene Glycol

Tetraethylene Glycol



Case Study #2

Glycols

- Group of compounds is very water soluble which makes extraction and concentration difficult
- Typical approach has been to use a GC/FID method like SW-846 8015, with direct aqueous injection (DAI)
- Sample matrix can have significant impact on what is detected (false positives)
- Sensitivity not spectacular, 5-10 mg/l common, optimized systems may do a little better

Case Study #2

Glycols

- What about application of LC/MS/MS?
- Well suited for DAI, better selectivity and sensitivity?
- Concern about small size of molecules, particularly ethylene and propylene glycol
- How effectively would they ionize?

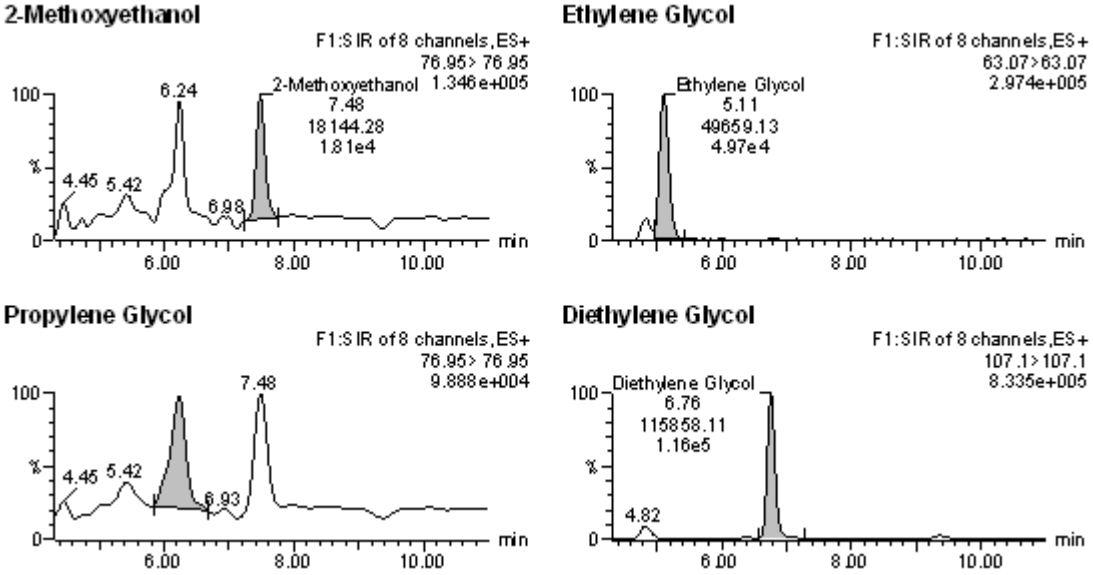
Case Study #2

Glycols

Resolution – split the analysis into two analytical runs

a. Selected Ion Reaction (SIR)

b. Multiple Reaction Monitoring (MRM)



Ethylene Glycol – 500 ug/l

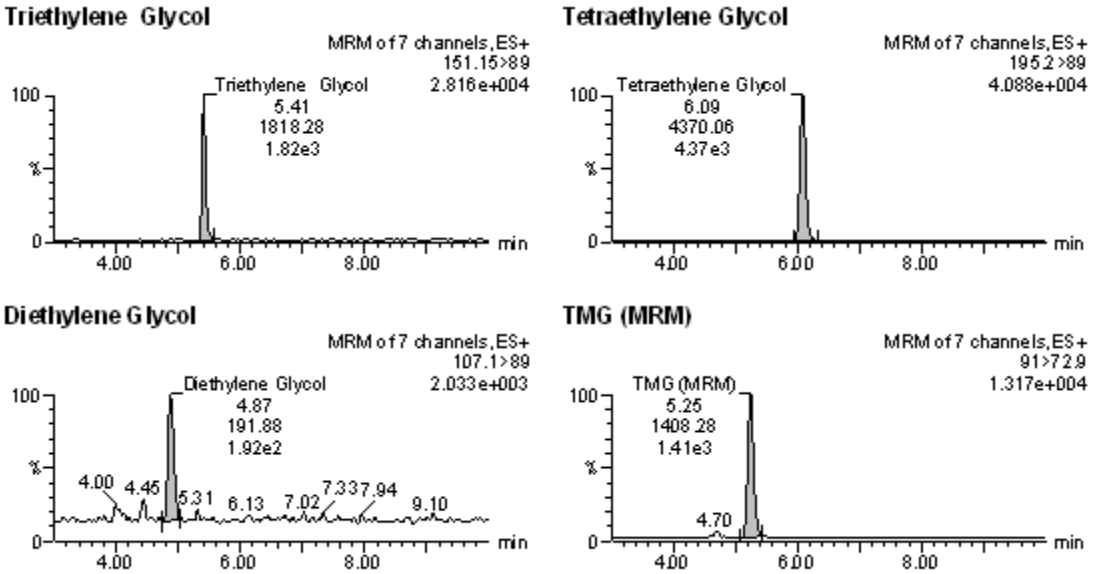
Propylene Glycol – 100 ug/l

2-methoxyethanol – 100 ug/l

Diethylene glycol – 25 ug/l

Case Study #2

Glycols



Diethylene glycol – 25 ug/l

Triethylene glycol – 25 ug/l

Tetraethylene glycol – 25 ug/l

Diethylene glycol can be reported from either mode

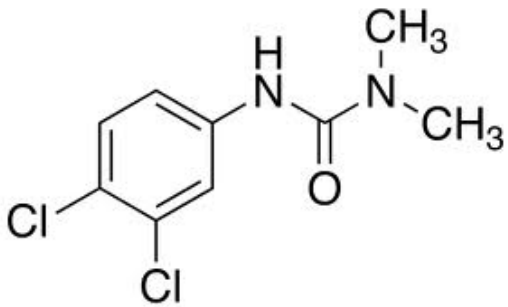
Note use of a surrogate, tetramethylene glycol

Limit for tetraethylene glycol improves

Case Study #3

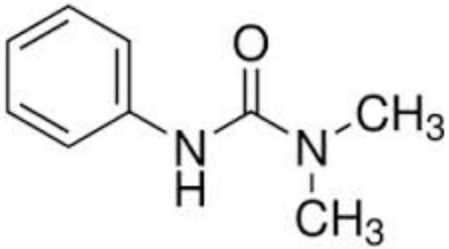
Phenyl Urea Herbicides

Diuron



Monuron

Fenuron



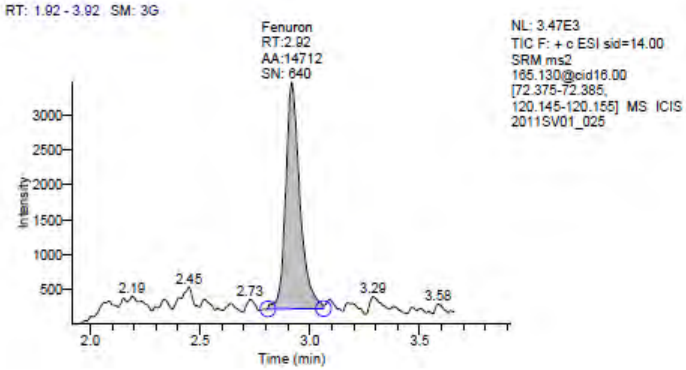
Case Study #3

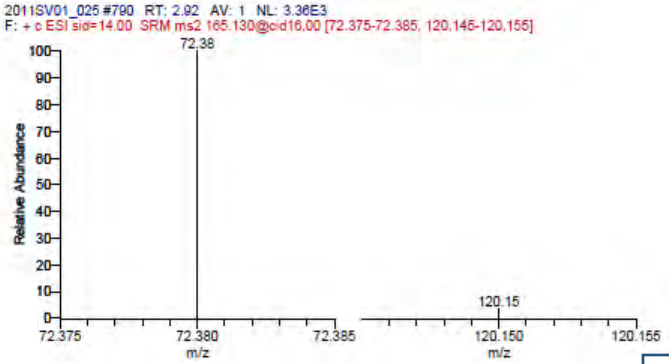
Phenyl Urea Herbicides

- Used for pre- and postemergent control of broadleaf and grassy weeds
- Also used on fruit and nut crops, grains, cotton, corn, etc.
- Analysis of compounds referenced in SW-846, Method 8321B
- Use of a generalized extraction resulted in sub-ppm limits
- Desire to optimize for low level detection

Case Study #3

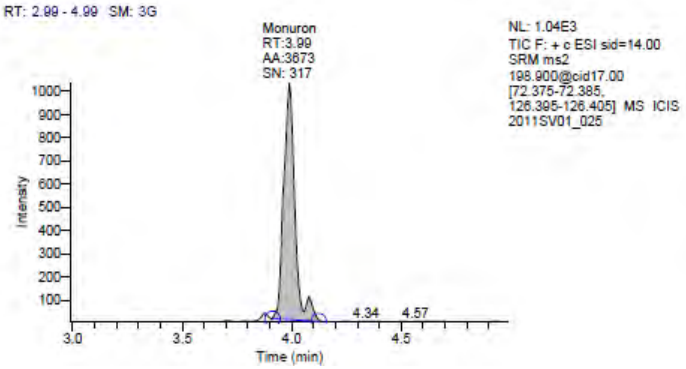
Phenyl Urea Herbicides

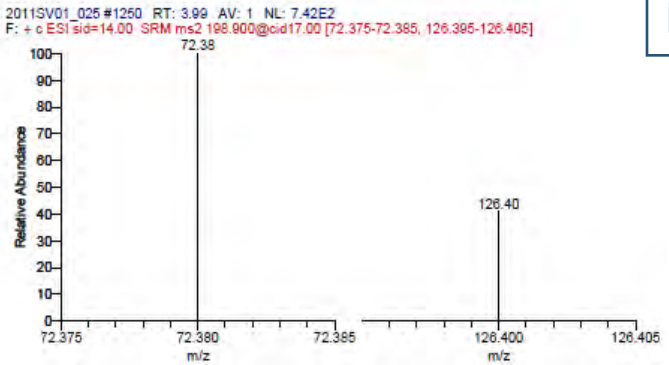




Fenuron – 1 ng/ml

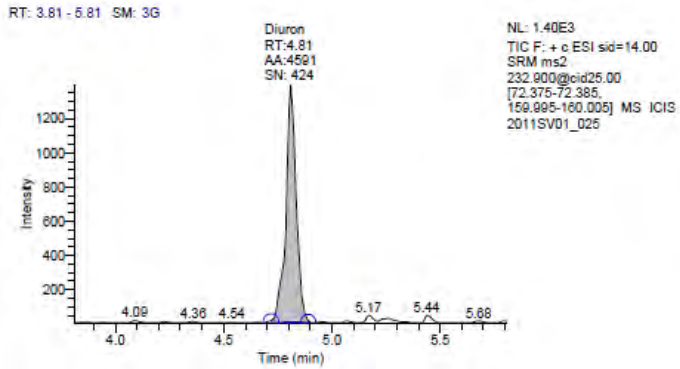
Monuron – 1 ng/ml

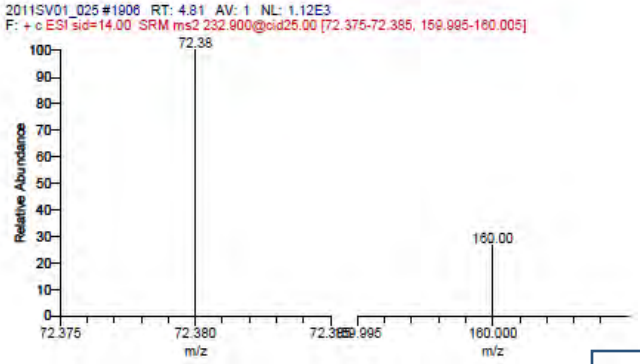


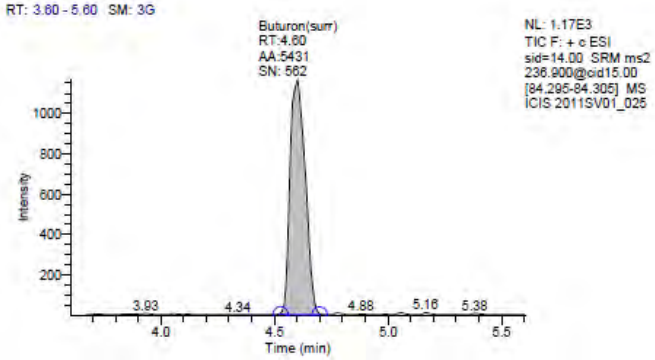


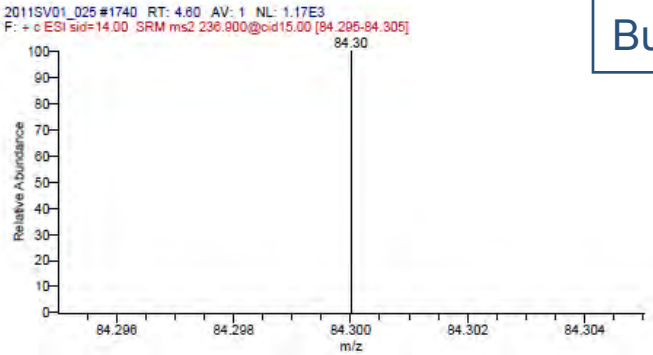
Case Study #3

Phenyl Urea Herbicides









Diuron – 1.5 ng/ml

Buturon – 1.5 ng/ml

Case Study #3

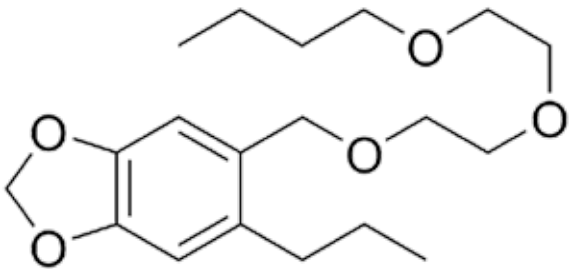
Phenyl Urea Herbicides

- 5 grams of soil blended with water and acetonitrile
- Extract cleaned up on SPE column
- Able to report low limits for analysis

	LOQ
Monuron -	0.2 ng/g
Fenuron -	0.2 ng/g
Diuron -	0.3 ng/g

Case Study #4

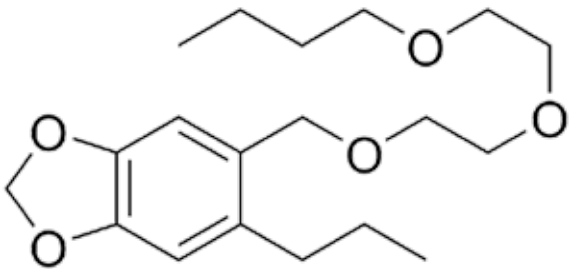
Piperonyl Butoxide



- Used as a synergist in pesticide formulations
- Enhances the potency of pesticide compounds like pyrethrins, pyrethroids and certain carbamates
- Used in over 1500 EPA registered products
- Home use and restaurants a significant consumer of products employing piperonyl butoxide

Case Study #4

Piperonyl Butoxide

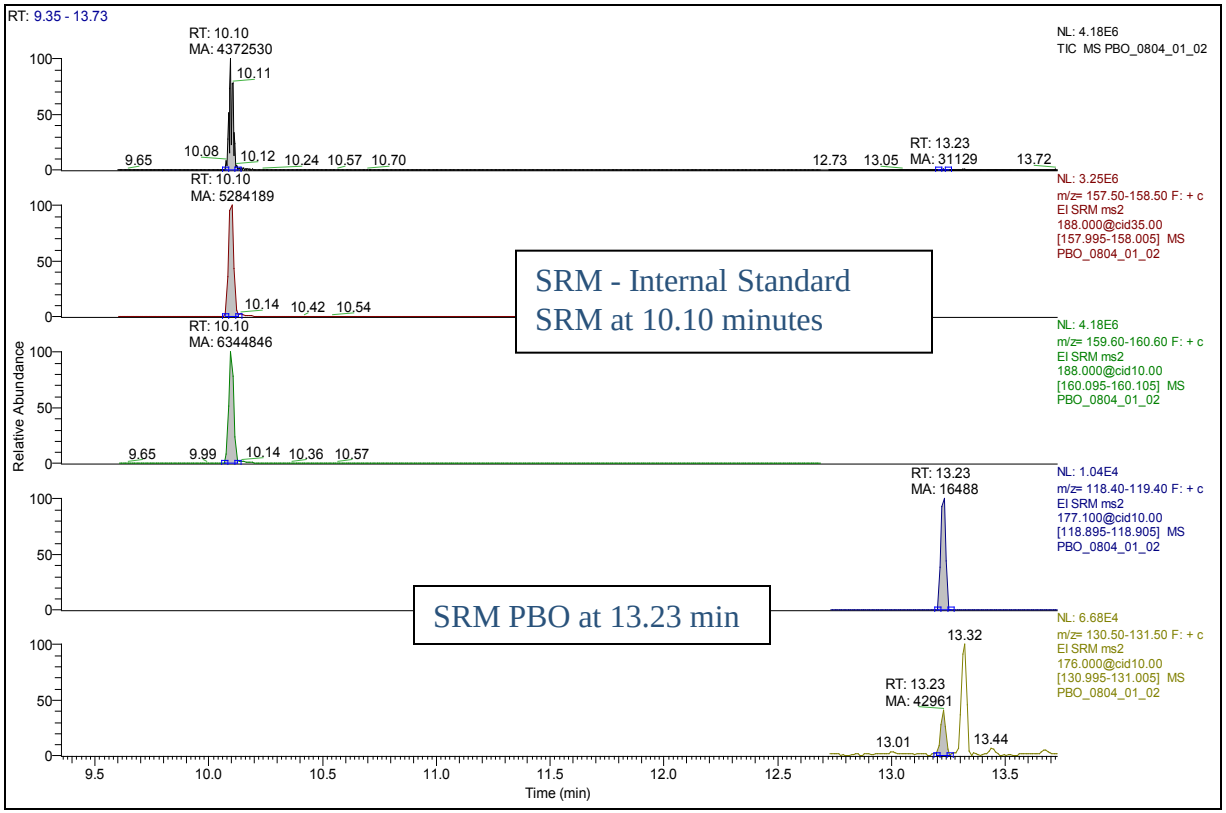


- Client with project to assess residual levels in WWTP sludges and biosolids
- Treatment of processes to degrade PBO, so need for low level analysis
- Extraction and clean-up of sludge extracts a challenge to meet low limits
- Take advantage of selectivity and sensitivity of GC/MS/MS to reach goals

Case Study #4

Piperonyl Butoxide

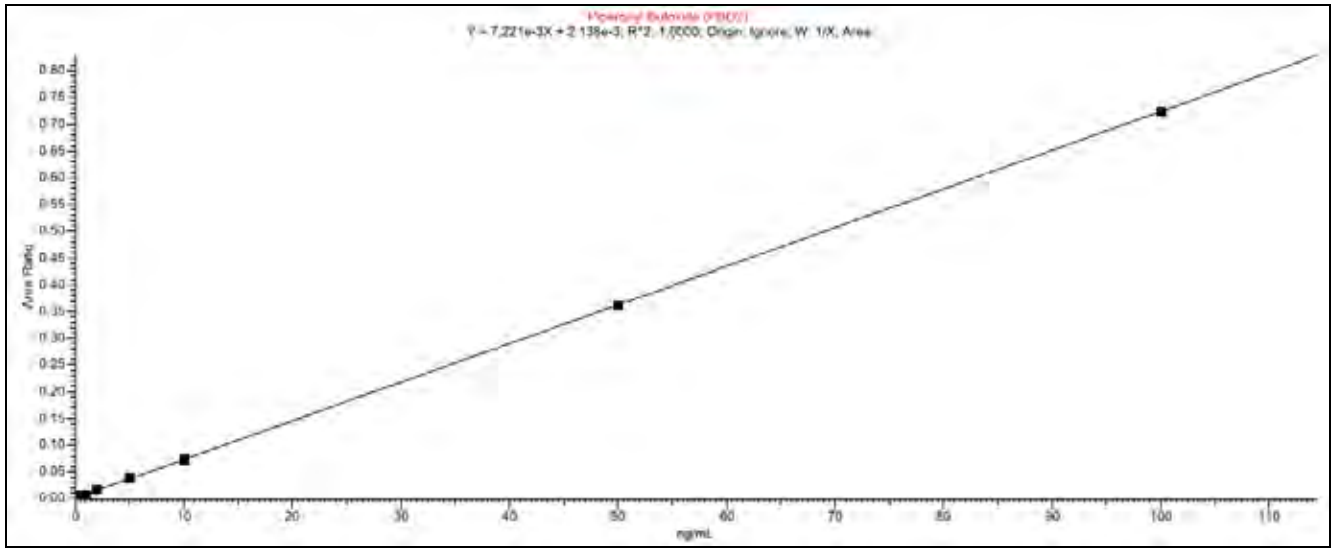
LOQ Level Standard at 0.5 ng/ml



Case Study #4

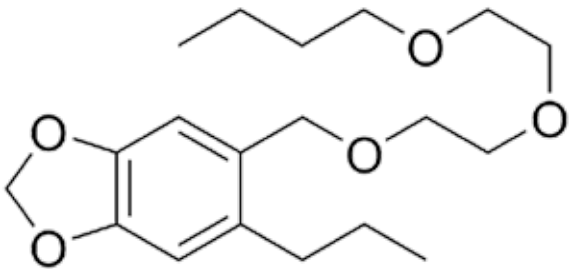
Piperonyl Butoxide

Calibration Curve - 0.5 ng/ml to 100 ng/ml



Case Study #4

Piperonyl Butoxide

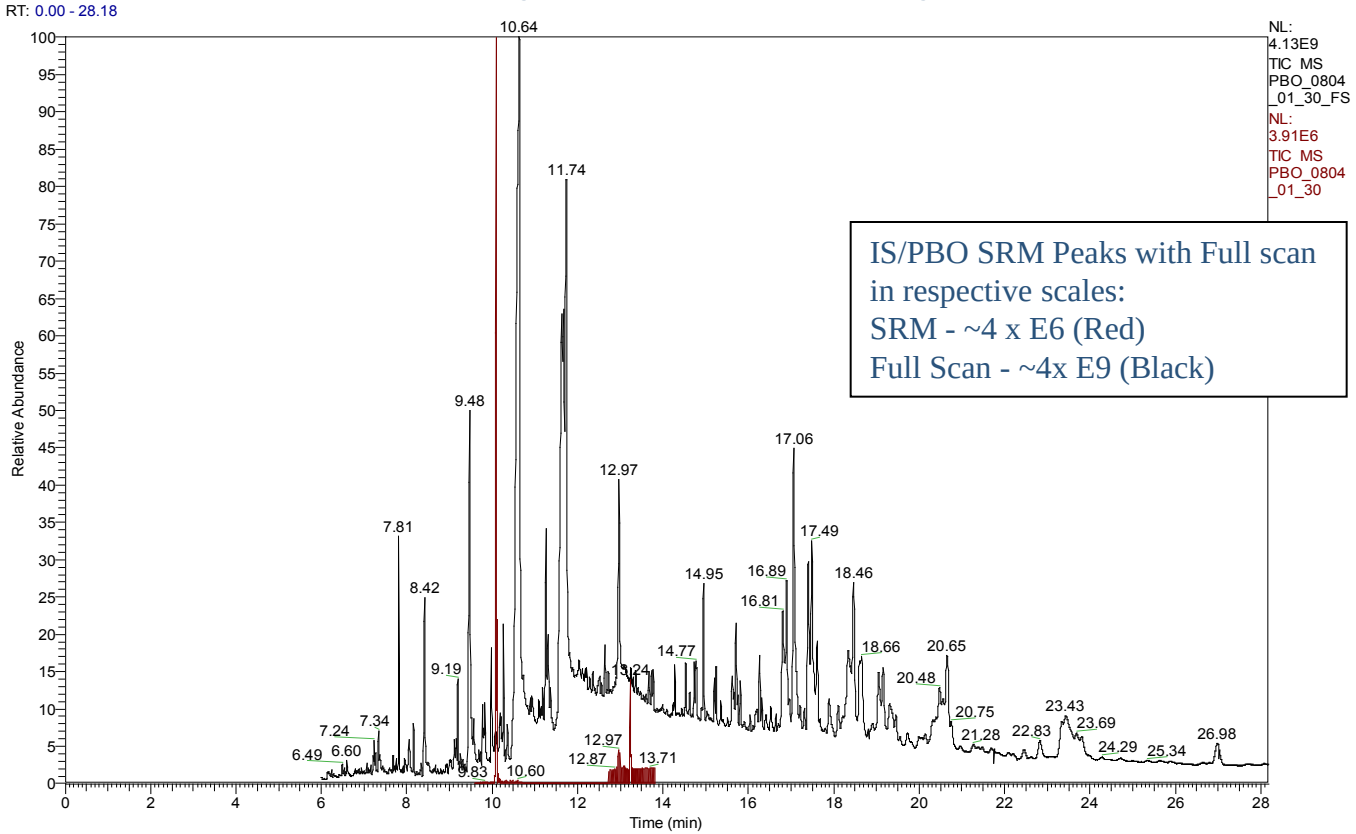


- Matrix present with the higher solids content presents problem
- Greater sensitivity and selectivity of GC/MS/MS allowed us to
  a. Use less sample for extraction (liq/liq extraction)
  b. Avoid use of column clean-ups that ultimately may have reduced recoveries.
- Under this scenario, still able to detect to 25 ng/l

Case Study #4

Piperonyl Butoxide

Full Scan Chromatogram vs SRM Chromatogram of Matrix



IS/PBO SRM Peaks with Full scan in respective scales:
SRM - ~4 x E6 (Red)
Full Scan - ~4x E9 (Black)

Conclusions

- While not exactly mainstream yet, the analytical techniques of LC/MS/MS and GC/MS/MS hold great promise
- Superior selectivity and sensitivity enable reporting in difficult matrices at lower levels
- Better sensitivity allows reduction in sample amounts and reduction in sample processing techniques
- Useful tools to consider for application to compounds not already well defined by the more standard analytical methods

Acknowledgement

- Meng Yu (Eurofins Lancaster Laboratories Environmental)
- Tim Trees (Eurofins Lancaster Laboratories Environmental).

Thank you