The Environmental Professional’s Guide to DoD Emerging Contaminants Laboratory Data Assessment and Usability

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Presentation Overview

- What are DoD emerging contaminants (ECs) and why are they important?
- Focus on hexavalent chromium (Cr$^{+6}$), 1,2,3-trichloropropane (TCP), 1,4-dioxane, n-nitrosodimethylamine (NDMA) and perchlorate
- Analytical methods used for detection, their pitfalls and potential false or biased reporting
- How do I assess the validity and usability of my laboratory data?
Definition of ECs

- No single definition or commonly-accepted definition of emerging contaminants
- Working definition for this presentation: “An emerging contaminant is a chemical or material that is characterized by a perceived, potential or real threat to human health or the environment or a lack of published health standards.”
What are ECs?

The range of ECs includes:

- Toxic chemicals, including persistent organic pollutants (POPs)
- Pharmaceuticals and personal care products (PPCPs)
- Veterinary medicines
- Endocrine-disrupting chemicals (EDCs)
- Disinfection By-Products
- Metals
- Nanomaterials
Why are ECs important?

- We introduce ECs into the environment through the use of industrial and household chemicals.
- Each year ~50 million pounds of PPCPs are distributed that end up in surface water.
- Wastewater and drinking water treatment can remove some of these, but not all.
- Children are most exposed to nanoparticles in candy (Westerhoff, et al., ES&T, 2012).
Origins and Fate of PPCPs in the Environment

Pharmaceuticals and Personal Care Products

1. Sources of PPCPs
   - Usual by individuals (1a) and pets (1b): Metabolic excretion (unmetabolized parent drug, parent-drug conjugates, and bioactive metabolites); sweat and vomitus. Excretion exacerbated by disease and slow-dissolving medications
   - Disposal of unused/outdated medication to sewage systems
   - Underground leakage from sewage system infrastructure
   - Disposal of euthanized/medicated animal carcasses serving as food for scavengers (1c)

2. Release of treated/untreated hospital wastes to domestic sewage systems (weighted toward acutely toxic drugs and diagnostic agents, as opposed to long-term medications); also disposal by pharmacists, physicians, humanitarian drug surplus

3. Release to private septic/leach fields (3a)
   - Treated effluent from domestic sewage treatment plants discharged to surface waters, re-injected into aquifers (recharge), recycled/reused (irrigation or domestic use) (3b)
   - Overflow of untreated sewage from storm events and system failures directly to surface waters (3b)

4. Transfer of sewage solids ("biosolids") to land (e.g., soil amendment/fertilization)
   - "Straight-piping" from homes (untreated sewage discharged directly to surface waters)
   - Release from agriculture: spray drift from tree crops (e.g., antibiotics)
   - Drug to medicated domestic animals (e.g., feed) - CAFOs (confined animal feeding operations)

5. Direct release to open waters via washing/bathing/swimming

6. Discharge of regulated/controlled industrial manufacturing waste streams
   - Disposal/release from clandestine drug labs and illicit drug usage

7. Disposal to landfills via domestic refuse, medical wastes, and other hazardous wastes
   - Leaching from defective (poorly engineered) landfills and cemeteries

8. Release to open waters from aquaculture (medicated feed and resulting excreta)
   - Future potential for release from molecular pharming (production of therapeutics in crops)

9. Release of drugs that serve double duty as pest control agents
   - Examples: 4-aminopyridine, experimental multiple sclerosis drug used as avicide; warfarin, anticoagulant; rat poison; azachlorotol, antiparasites; avian rodent reproductive inhibitors; certain antibiotics used for orchard pathogens, acaricides, analogs - brown tree snake control; caffeine, stimulant - copra frog control

10. Ultimate environmental transport/fate:
   - Most PPCPs eventually transported from terrestrial domain to aqueous domain
   - Phototransformation (both direct and indirect reactions via UV light)
   - Physicochemical alteration, degradation, and ultimate mineralization
   - Volatilization (mainly certain anesthetics, fragrances)
   - Some uptake by plants
   - Resappable particulates containing sorbed drugs (e.g., medicated-feed dusts)

Christian E. Dingeman, U.S. EPA-Las Vegas
March 2006
(original February 2001)
Environmental Impacts of ECs

‘Blinky’ compared with real 3-eyed fish caught in Argentina in 2011 (Kuweight 64, 2011)

(Groening, 1990)
Environmental Impacts of ECs

- There is evidence to suggest aquatic organisms and wildlife may be affected by endocrine disrupting chemicals (EDCs) – “He/She fishes” (Brown, et al., USGS, 2004-2005)
- Humans have shown EDC-related health issues, but there is some debate if chemicals at environmental concentrations are also having an effect (Pomati, et al., ES&T, 2006)
- USGS Study detected 63 of 100 ECs in at least 1 water sample (taken from 74 untreated drinking water (DW) locations) (Focazio, et al., 2008)
- AP Investigative Reports found pharmaceuticals in the DW of 46 million Americans and some resist DW and wastewater treatment processes (Donn, et al., 2008)
- Bottom Line: More studies are needed
Focus on 5 ECs

- Hexavalent Chromium (Cr\(^{+6}\))
- 1,2,3-Trichloropropane (TCP)
- 1,4-Dioxane
- N-nitrosodimethylamine (NDMA)
- Perchlorate
Hexavalent Chromium (Cr\(^{+6}\))

- Complex anions: CrO\(_4^{2-}\), Cr\(_2O_7^{2-}\) (Motzer, 2005)
- First emerged: late 1990s (Erin Brockovich)
- Naturally occurring (geogenic):
  - Soquel Creek Water District
  - Cr(VI) in groundwater aquifer
  - hydrogeologic conditions (Motzer and McCraven, 2003)
- Anthropogenic: plating shops, etc.
- Carcinogenic: inhalation, ingestion (both)
- CA PHG = 0.02 \(\mu g/L\) (20 ng/L)
- No current CA primary MCL
Environmental Impacts of Cr$^{+6}$

- Carried in air as particles or dust
- Rain removes particles from atmosphere, where they are deposited in the ground or carried by wind
- Airborne particles settle in <10 days
- Will contaminate soil and water as it settles with small amounts dissolving
Detection Methods for Cr\(^{6+}\)

- Modified EPA 218.6 (DW)
- EPA 218.7 – New!
- EPA 7196A (Colorimetric)
- EPA 7199 (Ion Chromatography (IC))
- EPA 6800 (Isotope Dilution)
- USGS Cation Exchange (field)
- Cr(VI) Speciation by IC-ICP/MS (lab)

Analysis of Cr(VI) by Ion Chromatography (IC)

Column: Dionex IonPac AS7
Flow Rate: 1.5 mL/min.
Eluant: 250 mM \((NH_4)_2SO_4\), 100 mM NH\(_4\)OH

Post Column Reactor: 2 mM Diphenylcarbohydrazide
10\% Methanol
1 NH\(_2\)SO\(_4\)

Detector: Vis 520 nm
Potential Problems With Cr$^{+6}$ Analysis

- Interferences (buffer/de-chlorinating agent preservative added in EPA 218.7)
- 24-hour holding time for EPA 218.6, 7196A, and 7199
- HT problem alleviated with promulgation of EPA 218.7 (HT= 14 days)

(Macler, 2012)
1,2,3-Trichloropropene (TCP)

- Anthropogenic: used historically as a paint and varnish remover, cleaning and degreasing agent, and in pesticides formulations
- Carcinogenic: Under Prop. 65, added to list of chemicals known to the state to cause cancer or reproductive toxicity (Title 22, California Code of Regulations, Section 12000)
- OEHHA published PHG of 0.0007 µg/L in August 2009
- As of November 15, 2011, detections of 1,2,3-TCP in two or more samples were reported in 337 sources, belonging to 89 water systems in 17 counties
- No current MCL, but NL = 0.005 µg/L per CDPH (Mazzera, 2012).
Environmental Impacts of TCP

- **Not** likely to sorb to soil based on its low soil organic carbon-water coefficient; likely to leach from soil into ground water
- **Will** sink to the bottom of a ground water aquifer because its density is greater than that of water; likely to exist as a DNAPL in its pure form
- **Found** typically at industrial or hazardous waste sites
- **Evaporates** from surface soil and water
- **Is** subject to photodegradation when in the atmosphere, with a half-life of 15 days
- **Unlikely** to become concentrated in plants, fish or other seafood because of its low bioconcentration factor (BCF ~9.2)
Detection Methods for TCP

- **EPA 8260B** - Gas Chromatography/Mass Spectrometry (GC/MS) for solid matrices
- **EPA 502.2** - GC / photoionization electrolytic conductivity detectors in series (PID)
- **EPA 504.1** - microextraction and GC for drinking water and ground water
- **EPA 551.1** - liquid-liquid extraction and GC with Electron Capture Detection (ECD)
- **EPA 524.2** – GC/MS for surface water, ground water and drinking water in any stage of water treatment
Potential Problems With TCP Analysis

- Since it is subject to photodegradation when released to air, sample collection using amber glass containers may be a useful precaution.
- Like any other VOC, holding time may be an issue (7 days for unpreserved samples, 14 days for preserved samples) due to degradation.
1,4-Dioxane

- $\text{C}_4\text{H}_8\text{O}_2$; CAS = 123-91-1
- First emerged: 2001 SCVWD white paper by Tom Mohr
- Solvent and stabilizer for other solvents (e.g., TCA)
- Solubility: miscible
- Highly mobile and recalcitrant
- Plumes: well down-gradient from more degradable contaminants: TCE and TCA
- Toxic: probably carcinogenic
- NL = 3.0 $\mu$g/L; RL = 300 $\mu$g/L
Environmental Impacts of 1,4-Dioxane

- Typically found at solvent release sites and polyethylene terephthalate (PET) plastic manufacturing facilities*
- Short-lived in the atmosphere, with a 6-10 hour half-life*; Breakdown products include aldehydes and ketones
- May migrate rapidly in ground water and does not volatilize rapidly from surface water bodies
- Relatively resistant to biodegradation and does not bioconcentrate in the food chain*

*(Mohr 2001)
Detection Methods for 1,4-Dioxane

- **EPA 522** (Drinking water, SPE and GC/MS SIM)
- **EPA 8260 and 8270** (Ground water and hazardous waste)
- **Modified 8270** (Liquid-liquid extraction and isotope dilution GC/MS SIM)
- **EPA 1624** (Isotope dilution GC/MS)
- **EPA 8261A** (Vacuum distillation and GC/MS SIM)
Common Problems with 1,4-Dioxane Analysis

- “Poor performer” in conventional GC/MS instrument calibration (very low relative response factors)
- Conventional methods produce sensitivity levels ~100x greater for dioxane as compared to other VOCs
- Poor recovery of dioxane (poor extraction efficiency)
### COMPARISON OF COMMONLY USED VOC TECHNIQUES FOR THE ANALYSIS OF 1,4-DIOXANE

<table>
<thead>
<tr>
<th>EPA Approval</th>
<th>EPA 8260C</th>
<th>EPA Approval</th>
<th>EPA 8260C</th>
<th>EPA 1624</th>
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<tr>
<td><strong>MDL</strong></td>
<td>EPA 8261A</td>
<td>Selected Ion Monitoring</td>
<td>Modified Method</td>
<td>EPA 1624</td>
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<tr>
<td><strong>PQL</strong></td>
<td>EPA 8270</td>
<td>0.5-10.0 ug/L</td>
<td>20-100 ug/L</td>
<td>-</td>
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<tr>
<td><strong>Sample Volume</strong></td>
<td>5 mL or 25 mL</td>
<td>10-0.23 ug/L</td>
<td>2 samples 40 mL each</td>
<td>2 samples 40 mL each</td>
</tr>
<tr>
<td><strong>Sample prep technique</strong></td>
<td>Vacuum distillation</td>
<td>Liquid-Liquid extraction</td>
<td>Purge &amp; Trap</td>
<td>Purge &amp; Trap Heated</td>
</tr>
<tr>
<td><strong>Method drawbacks</strong></td>
<td>NONE</td>
<td>Very time consuming</td>
<td>Poor Purging efficiency</td>
<td>Poor Purging efficiency</td>
</tr>
<tr>
<td><strong>Cost per sample</strong></td>
<td>LOWEST</td>
<td>HIGHEST</td>
<td>HIGH</td>
<td>HIGH</td>
</tr>
<tr>
<td><strong>EPA Approval</strong></td>
<td>APPROVED</td>
<td>NOT APPROVED</td>
<td>APPROVED</td>
<td>APPROVED</td>
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</table>
NDMA

- Formerly used in production of liquid rocket fuel, antioxidants, and softeners for copolymers.
- Industrial sources: tanneries, pesticide and rocket fuel manufacturing plants, rubber and tire manufacturers, alkylamine manufacture and use sites, fish processing facilities, foundries, and dye manufacturers.
- Also an unintended byproduct of chlorination of wastewater and drinking water at treatment plants that use chloramines for disinfection.
Environmental Impacts of NDMA

- May be found in air, water and soil
- Completely miscible in water and does not sorb onto solid particles or sediment
- Can be highly mobile when released to soil and can leach into ground water
- Broken down very quickly by sunlight when released to air
- Has been found at high concentrations (~3,000 ng/L) in ground water near rocket testing facilities and downgradient of DW wells, especially where wastewater effluent was used for aquifer recharge
Detection Methods for NDMA

- **EPA 607** (wastewater) uses MeCl$_2$ extraction, GC and a nitrogen phosphorus detector
- **EPA 1625** (wastewater) uses isotope dilution and high resolution GC/MS
- **EPA 521** (drinking water) uses solid phase extraction (SPE), and capillary column GC with large-volume injection and chemical ionization tandem MS (GC/MS/MS)
Common Problems With NDMA Analysis

- Method blank contamination due to the process of producing “clean” water (resins)
- Poor extraction efficiency (low recovery of NDMA-d6)
Perchlorate

- A naturally occurring and man-made anion that consists of 1 chlorine atom bonded to 4 oxygen atoms
- Commonly used as an oxidizer in solid propellants, munitions, airbags for cars, etc., and also found in some disinfectants and herbicides
- Used by the Department of Defense (DoD) as an oxidizer in munitions and missiles since the 1940s (Mendiratta, et al., 1996)
Environmental Impacts of Perchlorate

- Recent surveys have detected perchlorate in food crops and milk (FDA, 2008)
- Highly soluble, relatively stable and mobile in water (plumes can be extensive)
- Does not volatilize from water to air
- Detected at current and Formerly Used Defense Sites (FUDS) primarily involved in the manufacture, maintenance, use, and disposal of ammunition and rocket fuel
- Has been detected at nearly 270 sites; more than 45 of these are on the EPA’s National Priorities List (NPL)
Detection Methods for Perchlorate

- **EPA 314.0** - Ion Chromatography (IC)
- **EPA 314.1** - Inline Column Concentration/ Matrix Elimination IC with Suppressed Conductivity Detection
- **EPA 332.0** - IC with suppressed conductivity and electrospray ionization (EI) MS
- **EPA 331.0** - Liquid Chromatography (LC)/ EI/MS
- **EPA 6850** – High performance liquid chromatography (HPLC)/EI/MS
- **EPA 6860** - IC with electrospray ionization (EI) mass spectrometry (MS) or tandem mass spectrometry (MS/MS)
Problems With Perchlorate Analysis

- False positive results due to other compounds with similar retention times
- Potential interferences from p-chlorobenzenesulfonic acid (p-CBSA) and its salts; brackish water samples should be diluted prior to IC analysis to reduce interferences
- Failure to confirm a positive result obtained from IC analysis with MS
Perchlorate Confirmation

20 µg/L Perchlorate - EPA Test Sample

Ion chromatography (IC)

IC-MS/MS

Perchlorate
0.1 ppb
Data Assessment and Usability

How do I assess the validity and usability of my laboratory data?

- Data should be reported and validated to the equivalent of EPA Level III or higher in order to be legally defensible.
- Preferably validated by a third party using EPA National Functional Guidelines for Organic and Inorganic Data Review if no other project guidance document is available to eliminate potential or perceived bias.
NDMA Example 1

- Lab reported NDMA data by EPA 8270C SIM with positive detections above the reporting limit of 10 μg/L
- Lab analyzed a 1-point initial calibration curve (method specifies 5-point ICal) at 100 μg/L
- Lab analyzed continuing calibration verification standard at 100 μg/L
Response Factor Report  GC-MS #29

Method : E:\MSCHEM\1\METHODS\NDMA-J14.M (Chemstation Integrator)
Title : NDMA by GC\MS_SIM
Last Update : Fri Oct 14 17:38:43 2005
Response via : Initial Calibration

Calibration Files
100 =1014002A.D = =

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<thead>
<tr>
<th>Compound</th>
<th>100</th>
<th>Avg</th>
<th>%RSD</th>
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<tbody>
<tr>
<td>1) IR</td>
<td>NDMA-d6</td>
<td>0.725</td>
<td>0.725</td>
</tr>
<tr>
<td>2)</td>
<td>NDMA</td>
<td>1.048</td>
<td>1.048</td>
</tr>
<tr>
<td>3)</td>
<td>NDEA</td>
<td>2.126</td>
<td>2.126</td>
</tr>
</tbody>
</table>
Usable or Not?

- Usable, but the data is qualified as estimated (J detects/UJ non-detects) due to use of single-point initial calibration at 10x the reporting level.
NDMA Example 2

- Lab reported a detected result of 230 ng/L of NDMA using EPA 1625 Modified
- Lab reported internal standard recovery of 3.8% for NDMA-d6.
- Method 1625 specified recovery limits are 25%-150%
Trace Level Organic Compounds

Lot-Sample #: G6F290345-001  Work Order #: H3G0W1AA  Matrix: WATER
Date Sampled: 06/27/06  Date Received: 05/29/06
Prep Date: 07/03/06  Analysis Date: 07/13/06
Prep Batch #: 6184218
Dilution Factor: 1

<table>
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<tr>
<th>PARAMETER</th>
<th>RESULT</th>
<th>LIMIT</th>
<th>UNITS</th>
<th>METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-Nitrosodimethylamine</td>
<td>230</td>
<td>2.0</td>
<td>ng/L</td>
<td>CFR136A 1625 Modi</td>
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</tbody>
</table>

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<thead>
<tr>
<th></th>
<th>PERCENT</th>
<th>RECOVERY</th>
<th>LIMITS</th>
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<tbody>
<tr>
<td>INTERNAL STANDARDS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-Nitrosodimethylamine-d6</td>
<td>3.8</td>
<td>(25 - 150)</td>
<td></td>
</tr>
</tbody>
</table>

NOTE(S):

* Surrogate recovery is outside stated control limits.
Usable or not?

- Usable. Data was not rejected but qualified as estimated (J detects/UJ non-detects) due to recovery correction through the use of isotope dilution.
1,4-Dioxane Example

- Lab reported 1,4-dioxane by 8270C SIM as not detected (ND) at a reporting limit of 10 μg/L
- Lab did not include 1,4-dioxane in the initial calibration
- Lab injected a single-point standard at the end of the analytical run (method specifies CCVs be run at the beginning and end of each 12-hour analytical sequence) at 100 μg/L
1,4-Dioxane Analysis

Abundance

Ion 88.00 (87.70 to 88.70): 1019041A.D

Abundance

Ion 58.00 (57.70 to 58.70): 1019041A.D

Time-> 2.70 2.75 2.80 2.85 2.90 2.95 3.00 3.05 3.10 3.15 3.20 3.25 3.30 3.35 3.40 3.45

2.75

2.74
Usable or Not?

- Usable, but qualified as estimated (J detects/UJ non-detects)
- Data can be used as a screen for presence only due to lack of appropriate instrument calibration
Summary

- Make sure field personnel are properly trained in sample collection techniques to minimize contamination and false positive results.
- Select a laboratory that is certified for the analysis and request EPA Level III deliverables for legally defensible data.
- Know the pitfalls and limitations of each analytical method and select a method that will achieve your project goals.
Acknowledgements

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- Bruce Macler, EPA Region IX
References


USEPA. (2012). “EPA’s recommendations for enhanced monitoring for Hexavalent Chromium (Chromium-6) in Drinking Water.”
http://water.epa.gov/drink/info/chromium/guidance.cfm

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