Emerging Information on Emerging Contaminants

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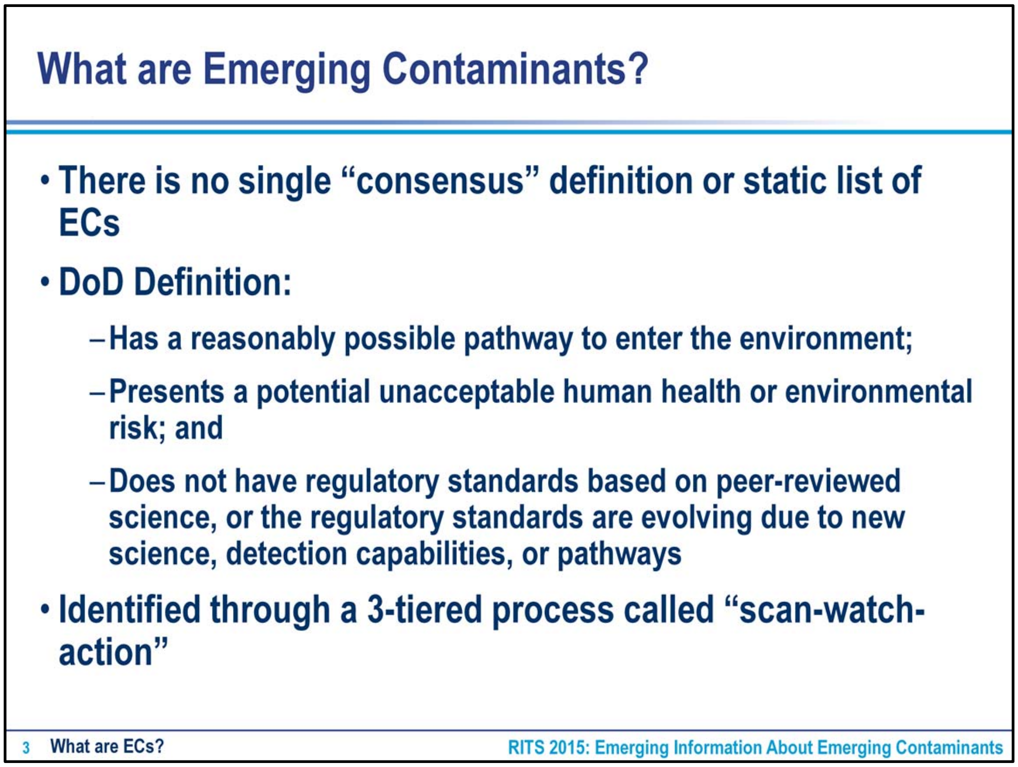
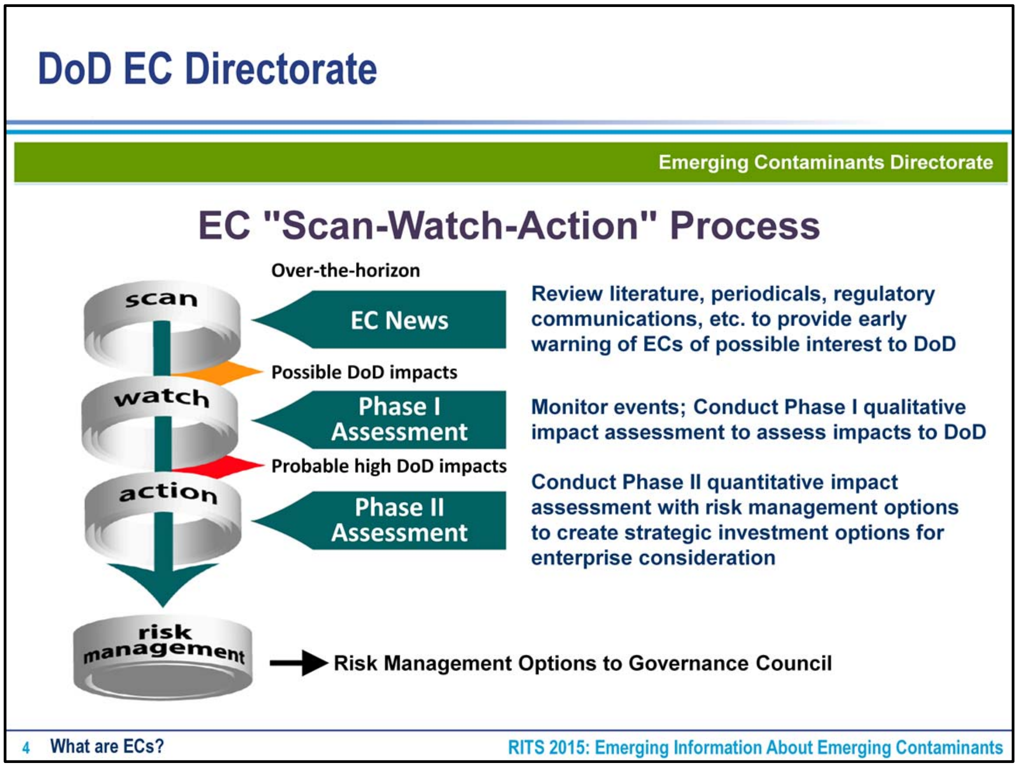
Presentation Overview

- **What are Emerging Contaminants (ECs)?**
- 1,4-Dioxane
- Cobalt
- Hexavalent Chromium
- Perfluorinated Compounds (PFCs)



- The 3-tiered process is a DoD directorate



- The DoD directorate created this process and it is how they identify DoD ECs
- Phase I impact assessments are conducted with DoD SMEs from various disciplines to evaluate if the chemical should simply remain on the ‘watch’ list or needs to be potentially elevated
- Phase II impact assessment is similar to Phase I but much more detailed

DoD EC Directorate – Scan

Emerging Contaminants Directorate

- **DoD ECs in the news**
  - Monthly compilation of news/updates on ECs for RPMs
- **RPMs can register at:** https://www.ecportalinfo.org/distlist_new.aspx

November 2014

EMERGING CONTAMINANTS IN THE NEWS

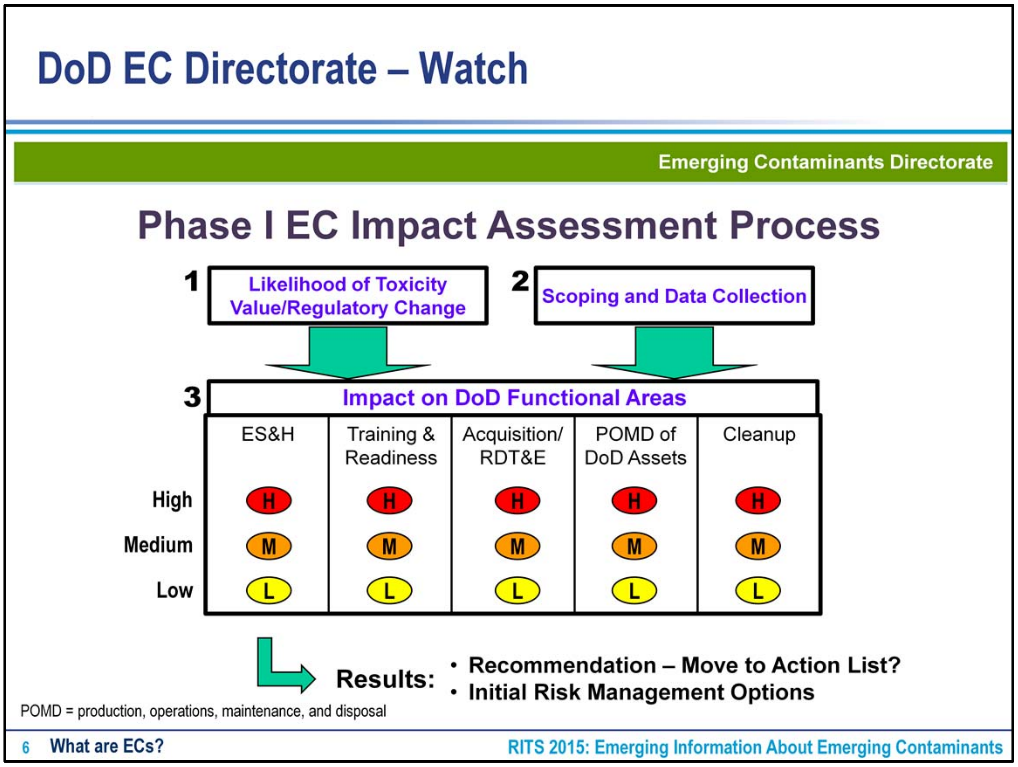
The following are brief summaries of recent developments related to emerging contaminants. When available, links and references to other sources of information are provided for readers seeking more detailed information on the topic. Individuals can register to receive the EC in the News at https://www.ecportalinfo.org/distlist_new.aspx. Prior copies of EC in the News can be found on AKO*, but you must be a registered user (*https://www.us.army.mil/suite/portal/index.jsp*). Distribution authorized to the Department of Defense and U.S. DoD contractors only. Other requests for this newsletter shall be referred to Paul Yaroschak,* Paul.J.Yaroschak.civ@mail.mil.

In this issue: Arsenic, 1-Bromopropane, Cadmium and compounds, Flame Retardants, Greenhouse Gases (GHGs), Hydrochlorofluorocarbons (HCFCs), Nonylphenol, PAH Mixtures, Nanomaterials, Perfluorooctanoic Acid (PFOA), Polybrominated Diphenyl Ethers (PBDEs), Strontium, Multi-Chemical/Risk Assessment and Policy, Upcoming Conferences

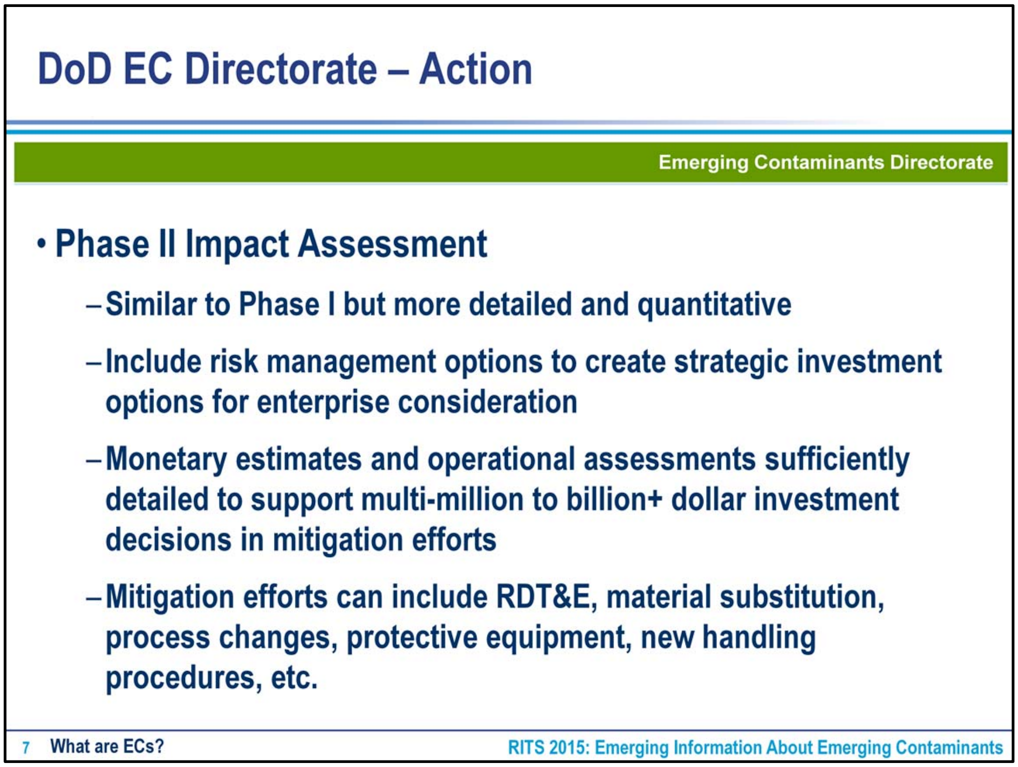
Screen List Chemicals

Arsenic *(Used for hardening copper and lead alloys, as a decolorizing and refining agent in glass, and as a component of electrical devices)*

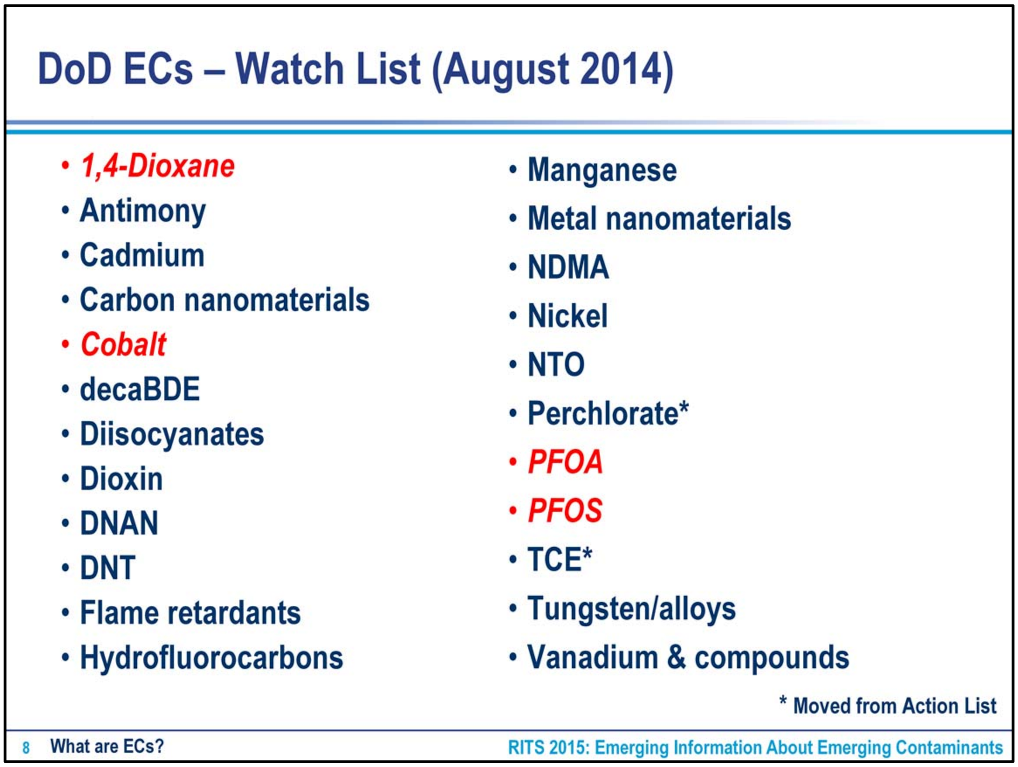
A nine year study following over 52,000 participants concluded that long-term exposure to low-level arsenic in drinking water may contribute to the development of diabetes.



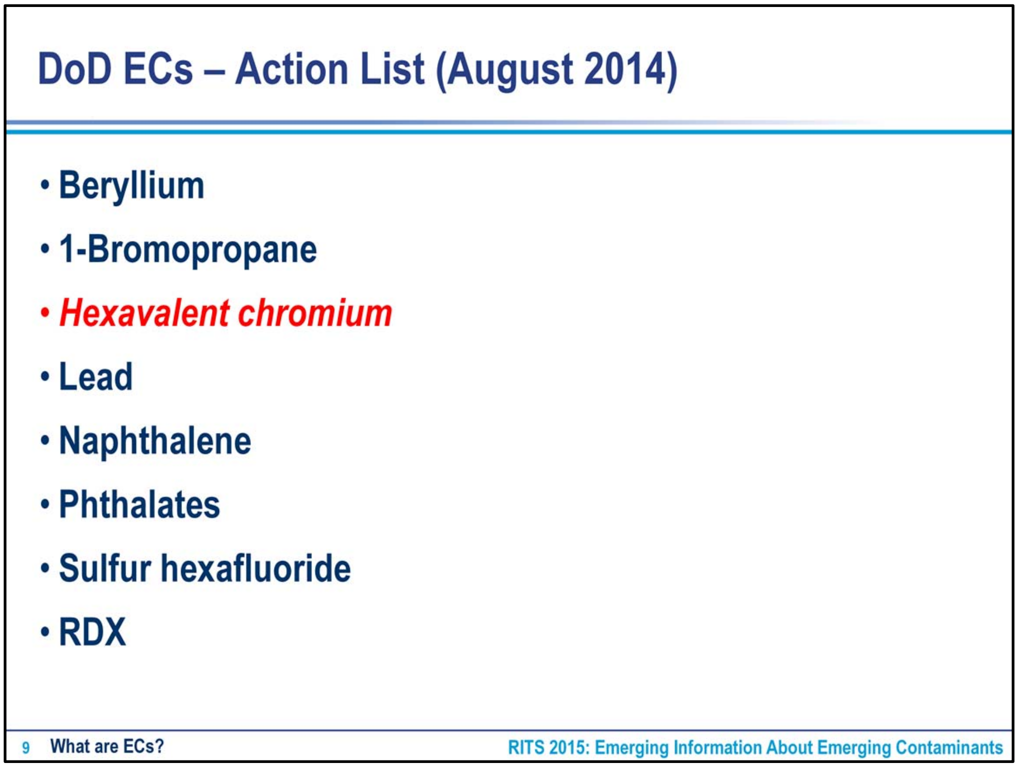
- DoD SME performs this assessment – more qualitative
- Evaluate impacts on 5 DoD functional areas
- Briefly point out that this group considers other inputs besides just the cleanup program, hence not all the "action" ECs are relevant to RPMs (e.g., SF6)



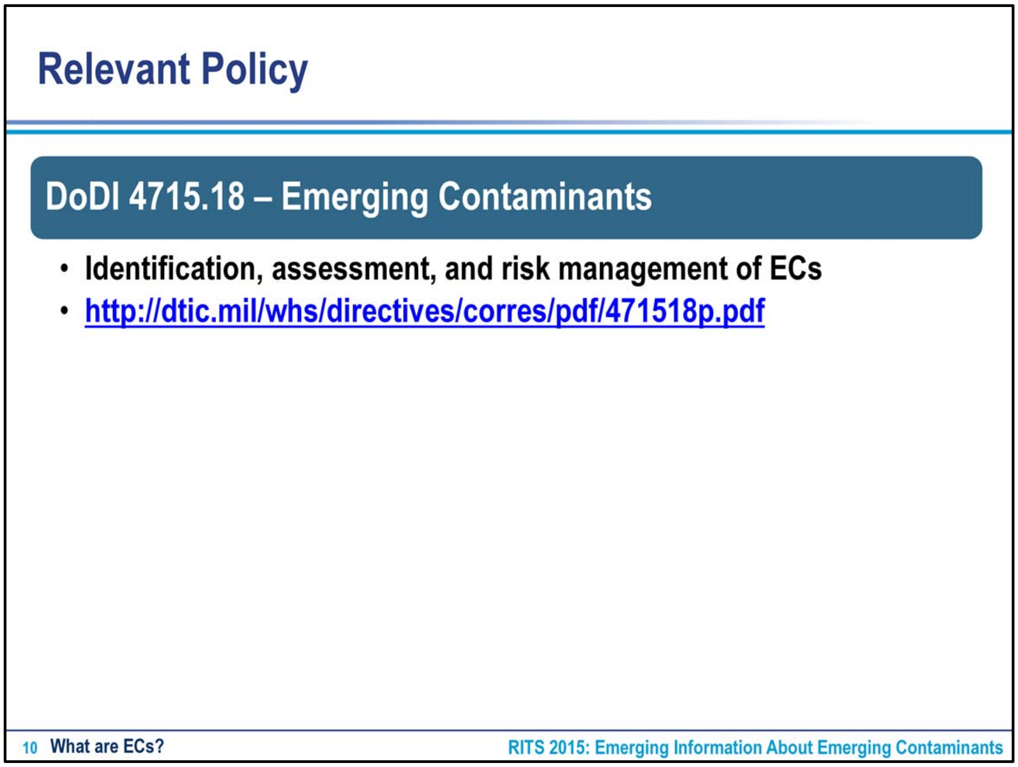
- Results determine whether EC stays on action list or moves back to watch list



- Phase I assessment evaluates these ECs
- Notice that some of these are marked as having been moved from the Action List
- Just because a chemical does not require additional action, doesn't mean that DoD "forgets" about it
    - They continue to evaluate and keep track of it to determine if other changes occur that would require it to be moved up to the action list again



- Phase II assessment for these ECs
- Again, not all of these are issues for RPMs
- Lead is on here because DoD is trying to get it out of the supply chain



- The first two are broad and cover any "ECs" while the third is specific to PFCs, which will be discussed in part 2 of this presentation

Relevant Resources

ECOS "resource trigger" paper

- Guidelines regarding initiation of actions in response to ECs
- http://www.ecos.org/section/committees/cross_media/ecos_dod_sustainability_work_group/

DoD (CMRMP)

- http://www.denix.osd.mil/cmrmd/ECMR/ECProgramBasics.cfm

EPA

- http://www2.epa.gov/fedfac/emerging-contaminants-and-federal-facility-contaminants-concern

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Relevant Resources (cont.)

NAVFAC Lead Based Paint Guidance/FAQs

- http://www.navfac.navy.mil/content/dam/navfac/Specialty%20Centers/Engineering%20and%20Expeditionary%20Warfare%20Center/Environmental/Restoration/er_pdfs/gpr/navfac-ev-guid-lbp-20140131f.pdf

NAVFAC Asbestos Guidance/FAQs

- http://www.navfac.navy.mil/content/dam/navfac/Specialty%20Centers/Engineering%20and%20Expeditionary%20Warfare%20Center/Environmental/Restoration/er_pdfs/gpr/navfac-ev-guid-asbestos-20120517.pdf

NAVFAC PFC Guidance/FAQs

- http://www.navfac.navy.mil/content/dam/navfac/Specialty%20Centers/Engineering%20and%20Expeditionary%20Warfare%20Center/Environmental/Restoration/er_pdfs/gpr/don-ev-guid-pfc-faq-20150129i.pdf

NAVFAC 1,4-Dioxane Guidance/FAQs (under development)

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Presentation Overview

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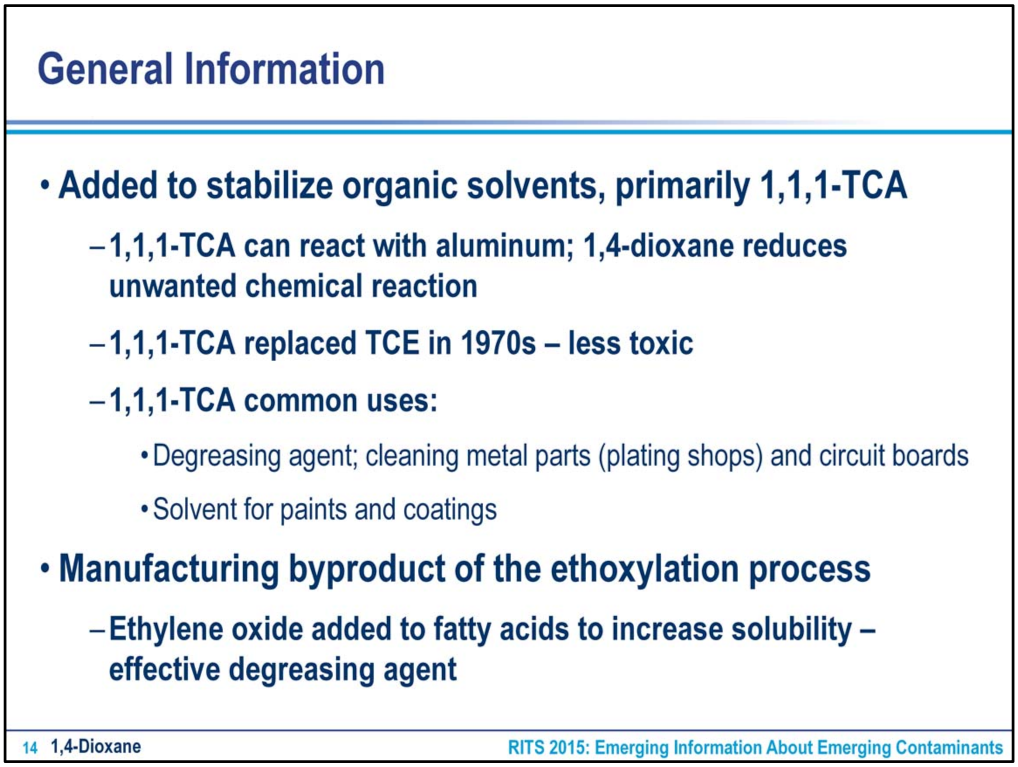
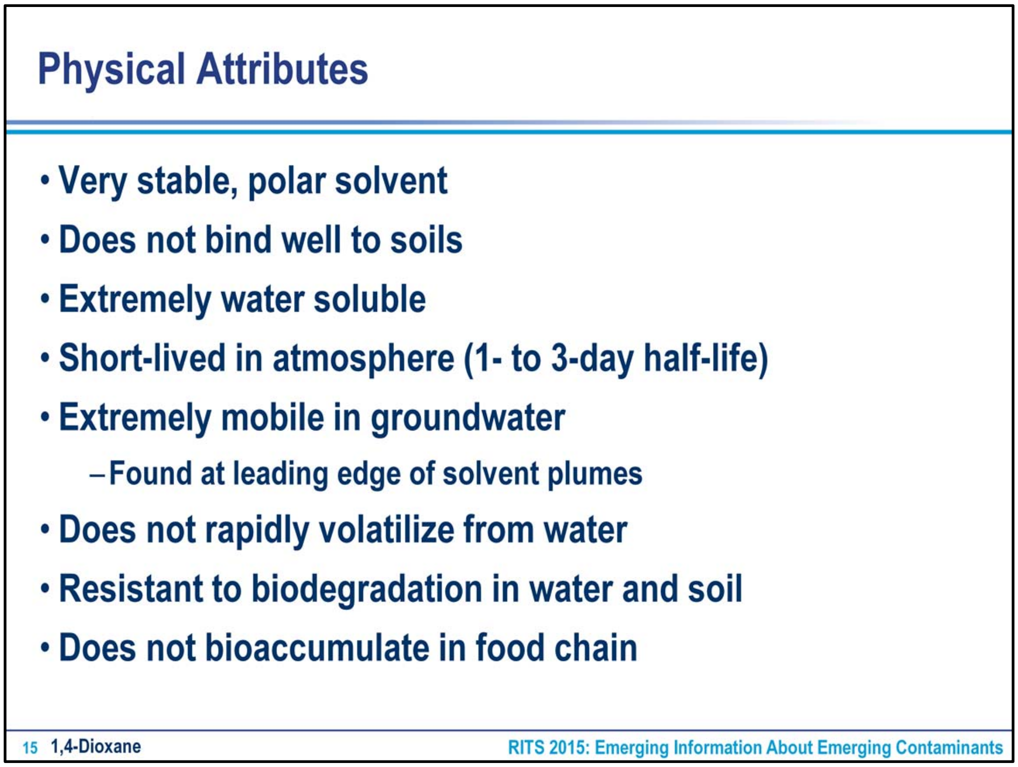
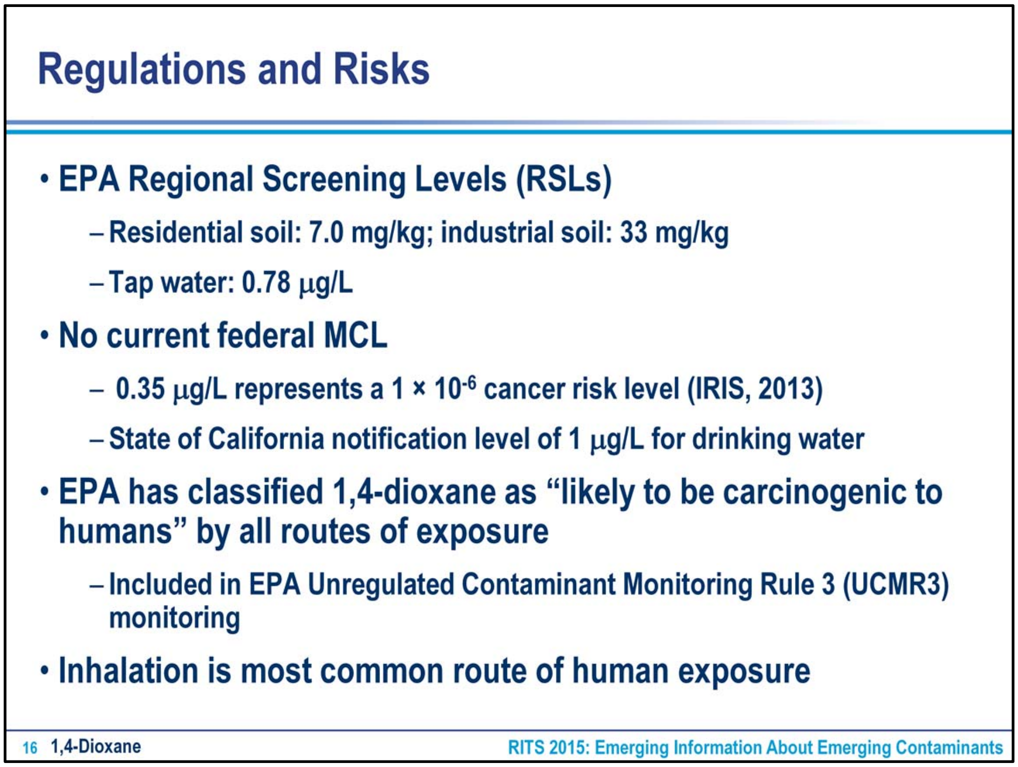


- 1,4-dioxane is a synthetic industrial chemical – typically added to stabilize at 2-3% by volume
- Reduces reaction by scavenging the HCl produced by hydrolysis of solvents and oils
- Note NOT associated with TCE
- Accidental byproduct of ethoxylation process – not Navy-related but more for information here
- Ethoxylation process makes degreasing agents such as sodium lauryl sulfate less abrasive and gives products enhanced foaming properties



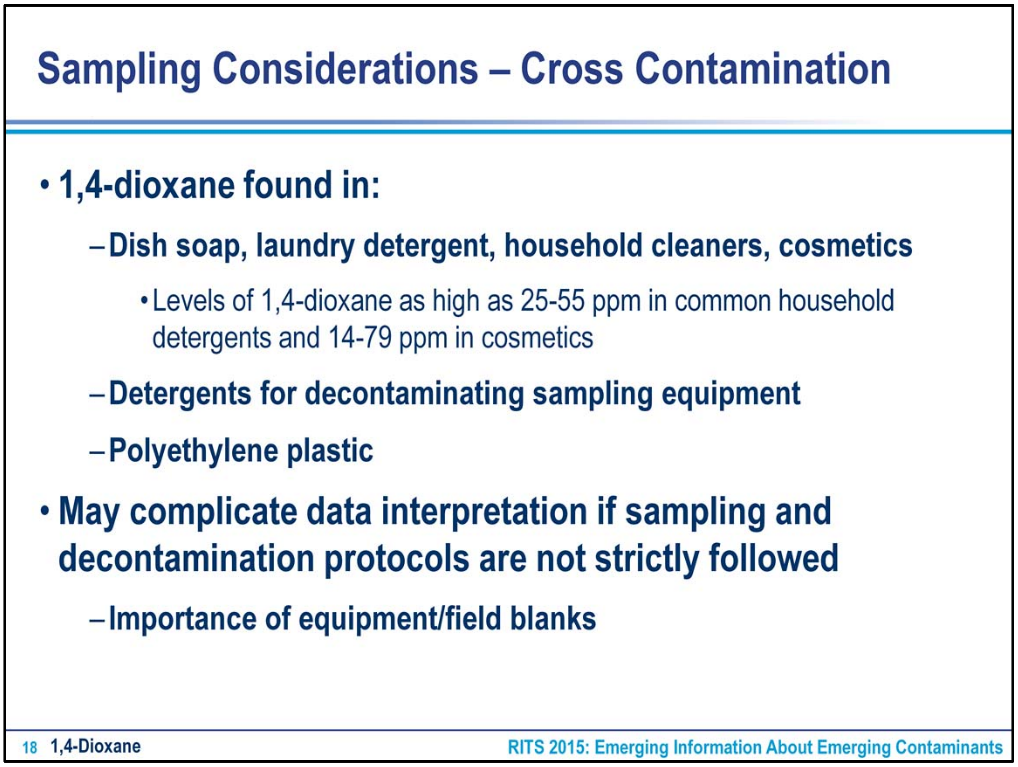
- Clear liquid at ambient temperature
- In the human body, it is quickly metabolized to b-hydroxyethoxyacetic acid (HEAA) and because of high solubility it is flushed out of the body quickly



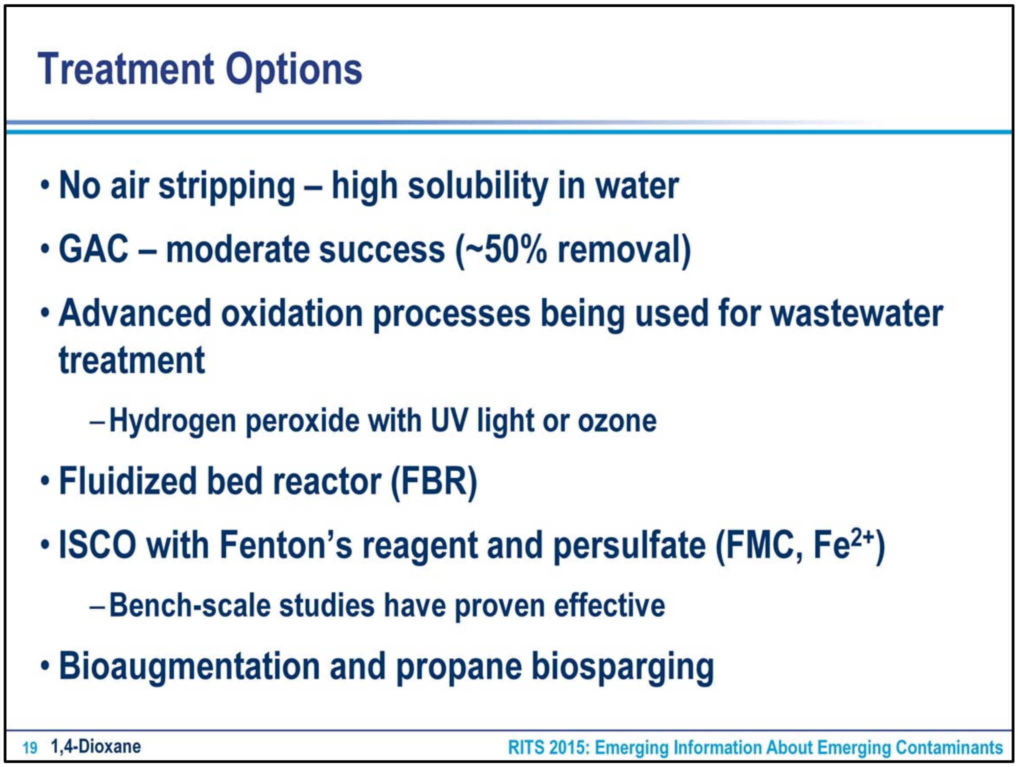
- Also listed on 2008 EPA contaminant candidate list 3 (CCL3)

Sampling Methods

EPA Sampling Method	Target Media	Detection Limit	Approximate Cost ($)
8260	Water	~100 µg/L	75
8015	Water	15 µg/L	75
8260-SIM	Water	0.5 – 10 µg/L	90
8270-SIM	Soil	2 µg/kg	90
522	Water	0.020 – 0.036 µg/L	125



- As mentioned earlier, it is an accidental byproduct of the ethoxylation process used to manufacture household cleaners and cosmetics
- Found in Dawn, Tide, Liquinox, cosmetics, etc…



- ISCO uses sodium persulfate and iron catalyst

1,4-Dioxane – Path Forward

- **Update/evaluate conceptual site model (CSM)**
- **Analyze for 1,4-dioxane if plume contains 1,1,1-TCA and/or daughter products 1,1-DCA (biotic) or 1,1-DCE (abiotic)**
- **Analysis of 1,4-dioxane *not* recommended at sites where *only* TCE has been detected**
  - **Several studies suggest 1,4-dioxane is strongly associated with 1,1,1-TCA and not other solvents such as TCE**
    - Mohr (2001). *1,4-Dioxane and other Solvent Stabilizers*
    - EPA Clu-In

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1,4-Dioxane Case Study – Former NAS Brunswick, ME

- Site location and history
- Site CSM
- Treatment of 1,4-dioxane and other ECs

Site Location and History

- Former Naval Air Station (NAS) Brunswick, ME
- ~20 miles northeast of Portland, ME
- Supported antisubmarine warfare ops from 1940s to 2010
- Base closure in 2011 (based on 2005 BRAC)

Site CSM

Former NAS Brunswick, ME

- Complex geology – interbedded layers of sand, silt, and clay overlying basal clay (aquitard) and bedrock
- Groundwater flow toward the east – discharges to streams
- 1990 RI identified PCE, TCE, and 1,1,1-TCA in groundwater
  - Sources include Site 4 (acid/caustic pit), Site 11 (former Fire Training Area), and Site 13 (DRMO area)
- Groundwater extraction and treatment system (GWETS) installed in 1995 – 7 extraction wells (EWs)
  - 1995-2000 metals removal and UV oxidation
  - 2000-2011 air stripper and GAC

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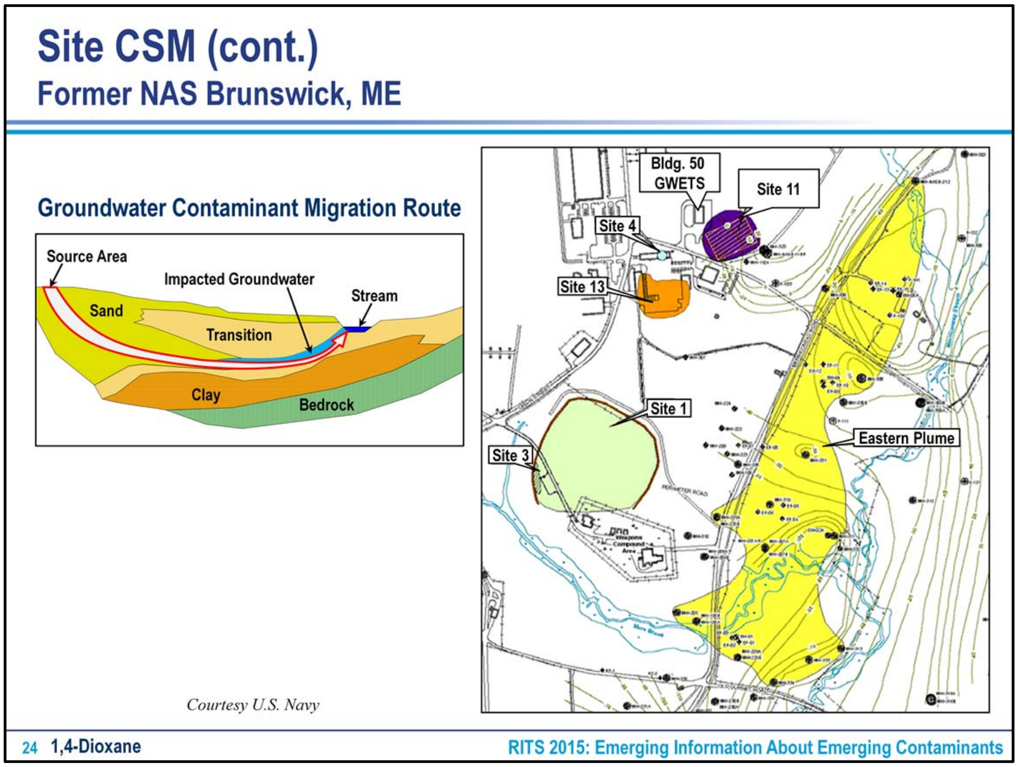
- GWETS has 7 extraction wells
- GWETS installed under an interim ROD



- Bowl-shaped migration pathway – dictated by geology
- Groundwater discharging near stream
- Plume has remained stable due to geologic constraints and stream boundaries

1,4-Dioxane Investigation
Former NAS Brunswick, ME

- Initially identified in 2004
- Initiated 1,4-dioxane RI in 2008
  - Identified dissolved 1,4-dioxane concentrations nearing 100 μg/L
  - State of ME maximum exposure guideline (MEG) of 32 μg/L
- GWETS O&M indicated 1,4-dioxane not treated
  - GWETS 1,4-dioxane influent concentrations up to 33 μg/L
  - Influent concentrations were expected to increase further above MEG due to new EWs installed in 1,4-dioxane hot spots

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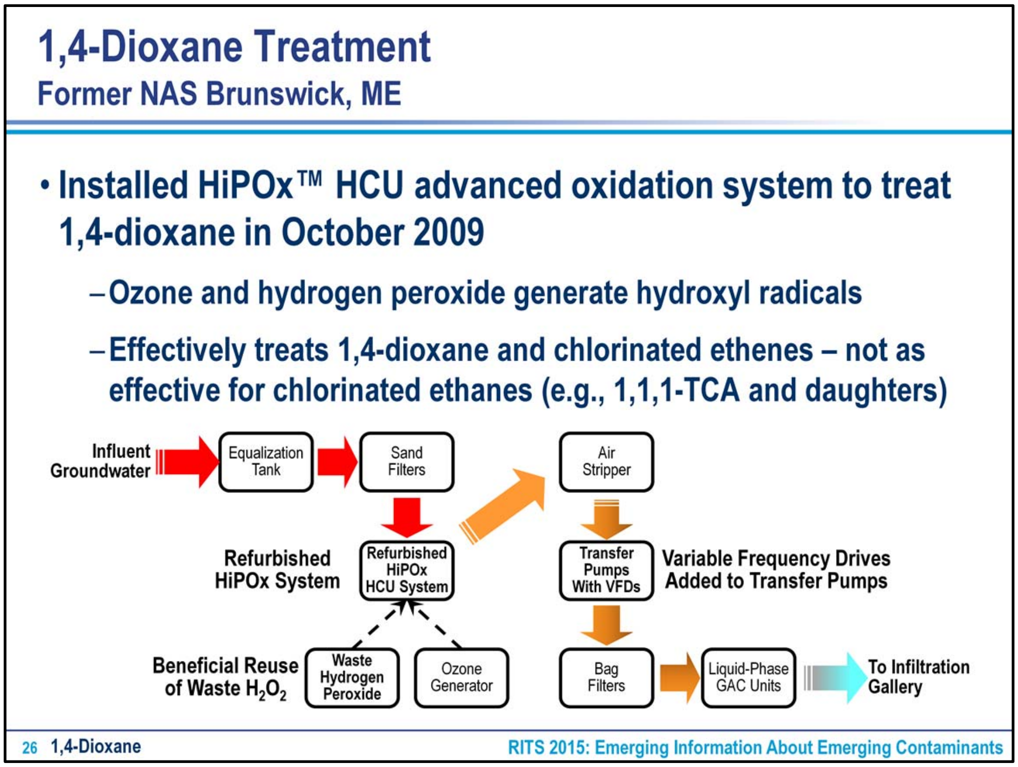

- Air stripper and GAC still included to treat residual chlorinated ethenes and chlorinated ethanes
- System further modified in 2011 - air stripper taken off line since there was a huge annual electrical usage cost and it did not provide added value to contaminant reductions on effluent

1,4-Dioxane and other EC Treatment

Former NAS Brunswick, ME

- **Pilot testing**
  - **Influent concentrations of up to 27 μg/L**
  - **100% 1,4-dioxane removal in 13 of 16 samples**
    - Remaining samples below system design goal of 10 μg/L

Date	Influent Concentration (μg/L)	Effluent Concentration (μg/L)
September 2011	7.7	ND
April 2013	1.4	ND
May 2014	7.7	ND
January 2015	4.1	ND

- **Developed risk-based remedial goal of 3.5 μg/L in 2010**
- **System being adapted to treat other ECs (PFCs)**

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- Navy is adapting the plant to meet future EC treatment requirements – will be conducting a pilot study in 2015 at the GWETS Treatment plant to assess PFC treatment which is currently found throughout the base in GW and in the Eastern plume at levels well above the provisional EPA advisories

1,4-Dioxane – Additional Information

- EPA fact sheet (January 2014)
  - http://www2.epa.gov/sites/production/files/2014-03/documents/ffrro_factsheet_contaminant_14-dioxane_january2014_final.pdf
- EPA Clu-In
  - http://clu-in.org/contaminantfocus/default.focus/sec/1,4-Dioxane/cat/Policy_and_Guidance/
- EPA 1,4-dioxane treatment technologies document
  - http://www.epa.gov/tio/download/remed/542r06009.pdf
- NAVFAC 1,4-Dioxane Guidance/FAQs (under development)

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1,4-Dioxane – Additional Information (cont.)

- Air Force primer (August 2008)
  - http://www.eosremediation.com/download/1,4Dioxane/2008%20AFCEE%20A%20 Primer%20for%20AF%20RPMs%20AFD-081010-028.pdf
- ASTDR toxicological profile (April 2012)
  - http://www.atsdr.cdc.gov/ToxProfiles/TP.asp?id=955&tid=199
- California State Water Resources Control Board
  - http://www.swrcb.ca.gov/water_issues/programs/gama/docs/coc_1_4_dioxane.pdf
- Federal Remediation Technologies Roundtable (FRTR)
  - http://costperformance.org/remediation/

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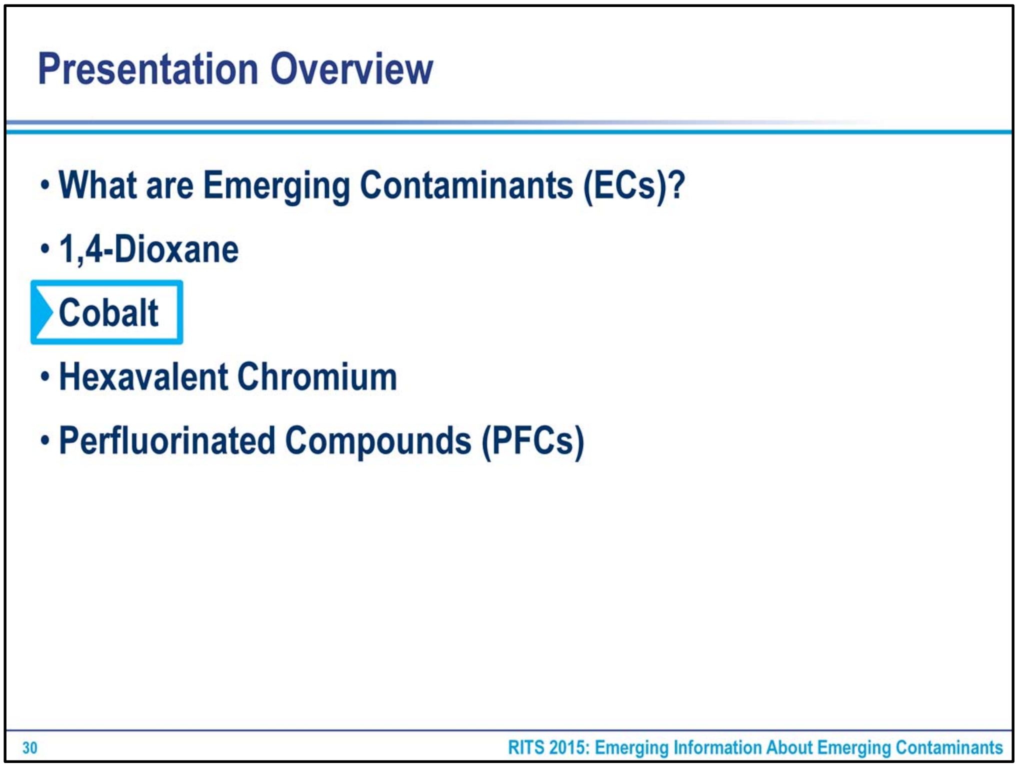
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Change in Cobalt Tier 2 Toxicity Value

- **2002 oral reference dose (RfD) = 0.02 mg/kg-day**
  - **Based on increased red blood cells in a 1976 study – administered as a *treatment* to anemic patients**
- **2008 RfD = 0.0003 mg/kg-day**
  - **Based on decreased iodine uptake study from 1956**
    - Single dose; no No-Observed-Adverse-Effect Level (NOAEL); 2-week exposure

Year	RfD (mg/kg-day)	Uncertainty Factor	EPA Confidence Level	Residential Soil RSL (mg/kg)	Tap Water RSL (μg/L)
2002	0.02*	10	Low-medium	1,600	730
2008	0.0003	3,000	Low	23	6.0

*Note: To a lesser extent, the different values are also impacted by updates in exposure factors. Values above based on a target hazard index of 1.

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- On “Watch” list
- Primary Navy use is based on the temperature stability of cobalt alloys – used in aircraft engines and is corrosion- and wear-resistant
- Basically different studies preferred by different sets of regulators
- 2008 – only a single dose – long-term effects not evaluated
- NOAEL = no observed adverse effect level

Possible Risk Management Strategies for Cobalt

- RfD change means cobalt is screening into risk assessment as a COPC, and may be a risk driver – very conservative
- Possible risk management strategies
  - Use site-specific background conditions to demonstrate cobalt is not related to a release
  - Use CSM to demonstrate no evidence of historical use
  - Present estimated dietary intakes for comparison and reality check
  - Present range of risks
    - Evaluate old/new RfD, reasonable maximum exposure (RME) and central tendency exposure (CTE); include several exposed receptors

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- Remember in 2002 study it was administered as a treatment

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Background and Toxicity Values

- On DoD's "Action List" of ECs
  - Primary Navy-related use is in the chrome plating of metals
- Toxicity values in IRIS (Tier 1) from 1998
  - Oral RfD = 0.003 mg/kg-day
    - No critical effect; NOAEL identified but not a Lowest-Observed-Adverse-Effect Level (LOAEL)
  - Inhalation reference concentration (RfC) = 0.001 g/m^3
  - Cancer weight-of-evidence: Class A for inhalation
  - Inhalation unit risk = 0.084 $(mg/m^3)^{-1}$
    - Study assumes 1:6 ratio of hexavalent:trivalent chromium

- Discussed here because of new Tier 3 oral CSF (cancer slope factor)
- NOAEL = no observed adverse effect level
- LOAEL = lowest observed adverse effect level

Toxicity Values

- **Other toxicity values**
  - **Tier 3 oral cancer slope factor (CSF) = 0.5 $(mg/kg\text{-}day)^{-1}$ from a study by NJ DEP, 2009**
    - Ingestion of Cr-VI started to drive risks based on cancer endpoint
    - EPA determined it may have a mutagenic mode of action and recommended the use of age-dependent adjustment factors, which result in more conservative estimates of risk
- **Draft IRIS Update issued for public comment in 2010**
  - **Oral route of exposure only (ingestion from drinking water)**
  - **Peer reviewers urged EPA to consider recent research efforts**

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Regulatory Levels

- **EPA MCL for *total chromium* of 0.1 mg/L**
  - **Based on the assumption that all chromium is hexavalent**
  - **Given recent toxicological research, MCL revision is likely**
    - Some debate over carcinogenicity by oral exposure
  - **Hexavalent chromium included in EPA's UCMR3 list**
    - Comparison just to method reporting limit (MRL); no health-based comparison value
    - As of July 2014, detected in ~75% of all samples collected above the MRL
- **California MCL for *hexavalent chromium* of 0.04 mg/L**

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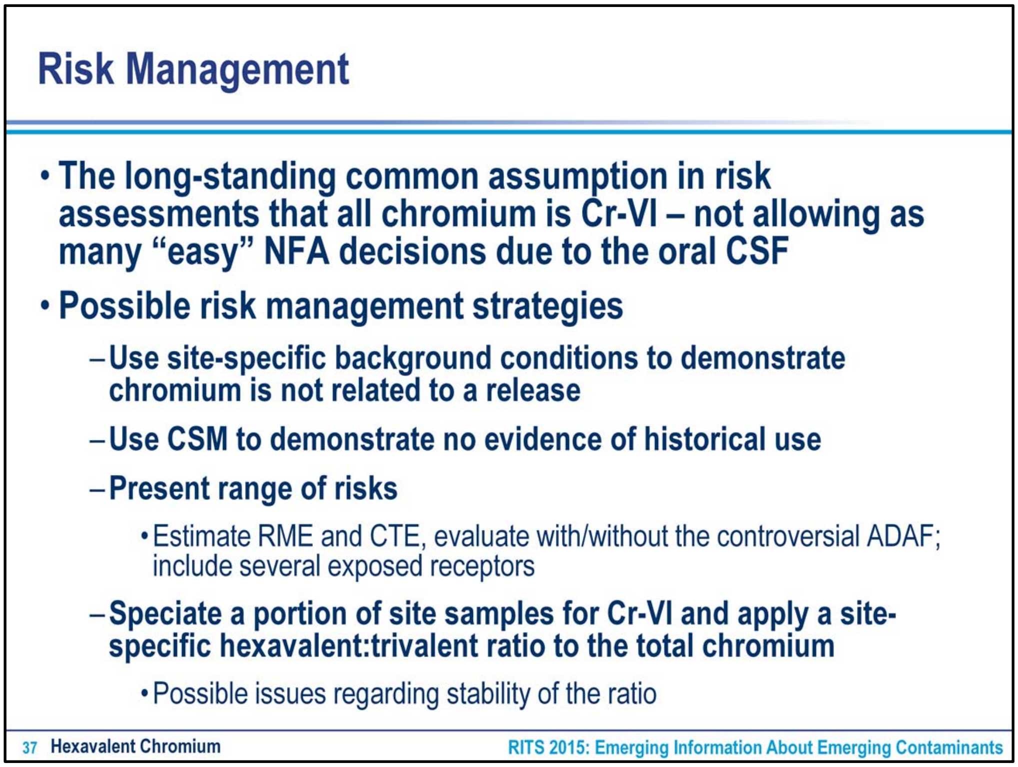

- ADAF = age-dependent adjustment factor

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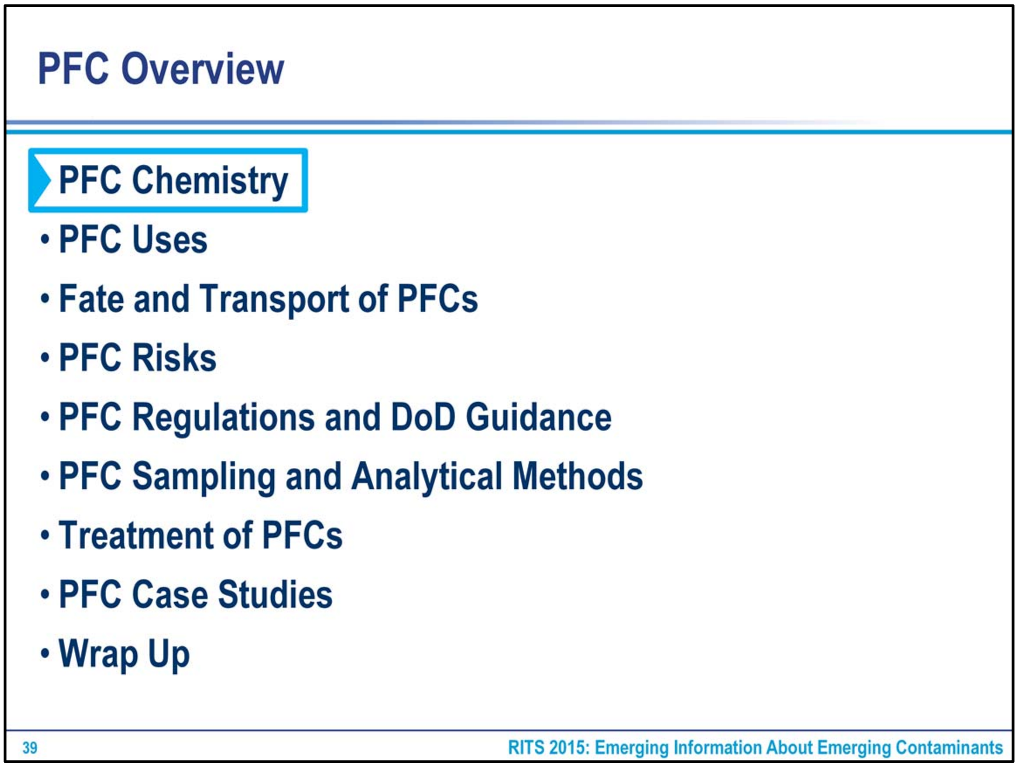
PFC Overview
PFC Chemistry
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• Fate and Transport of PFCs
• PFC Risks
• PFC Regulations and DoD Guidance
• PFC Sampling and Analytical Methods
• Treatment of PFCs
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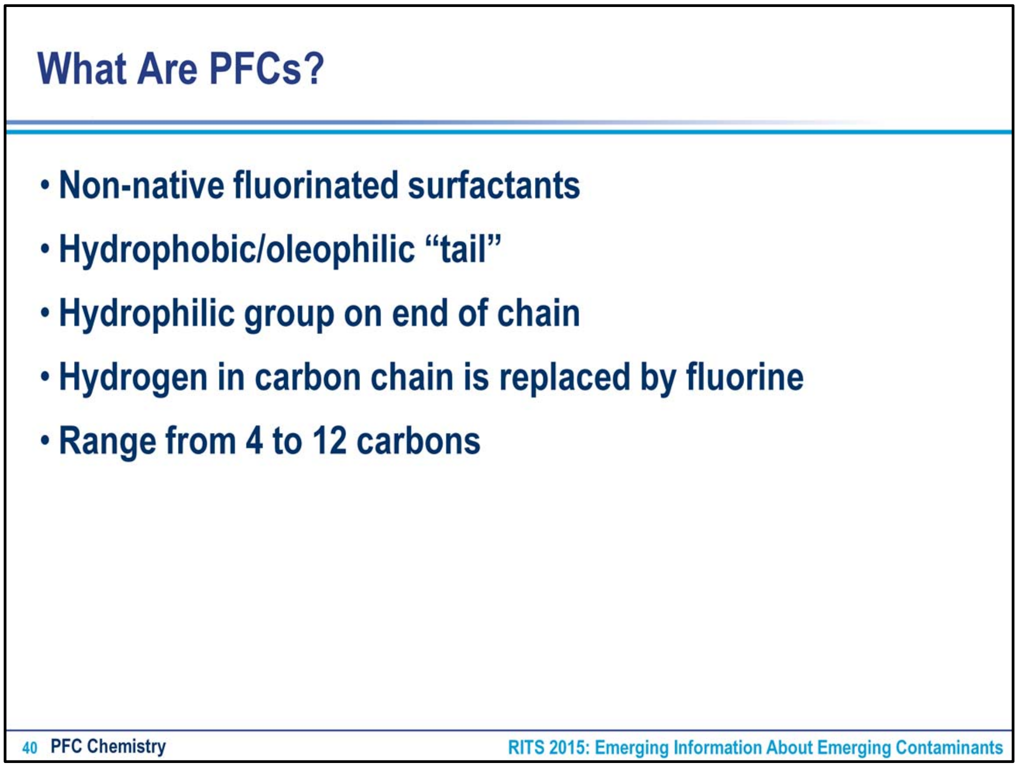
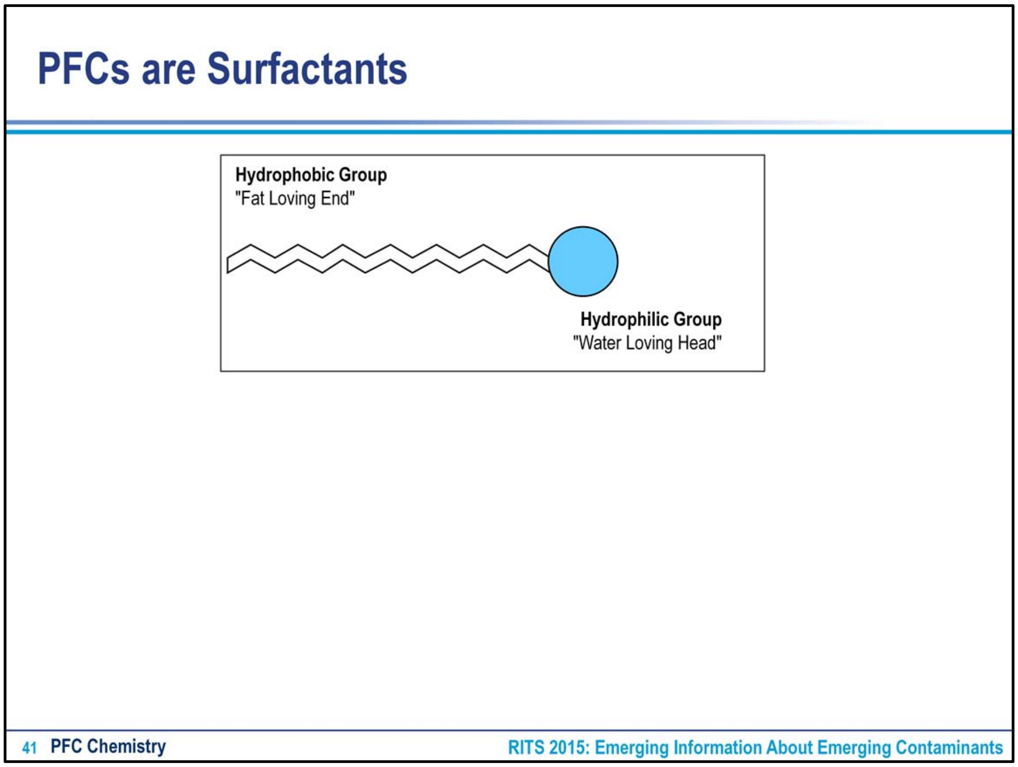


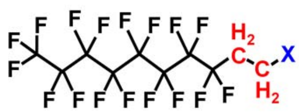
- All of this information presented can be found on the EPA fact sheet and NAVFAC PFC guidance
- Compound consisting of molecules consisting of polar water soluble group attached to a water insoluble hydrocarbon chain – sits on border between oil and water
- Typically in a surfactant, C is surrounded by H – in PFCs, C surrounded by F – a VERY strong bond that gives PFCs extra properties including thermal resistance
- Always an even # of carbons



- Head – prefers aqueous phase
- Tail – prefers oil phase
- Form micelles

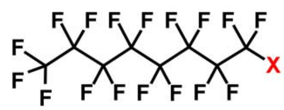
Classification of PFCs

Polyfluorinated	Perfluoroalkyl
Carbon backbone partially surrounded by fluorine	Carbon backbone fully surrounded by fluorine
Fluorotelomer alcohols 8:2 FTOH	Perfluorinated carboxylates (CO_2H)
Fluorotelomer sulphonates	Perfluorinated sulfonates (SO_3H)
Precursor to perfluoroalkyl compounds	Perfluorinated phosphonates/phosphinic (POOH)



X = halides, alcohol, olefin, ester

Polyfluorinated Compounds (Fluorotelomer)



X = carboxyl, sulfonyl

Perfluorinated Compounds

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- Precursors – 2 of Cs still have H. H reacts quickly and is easily broken down by aerobic bacteria – replaced by a functional group
- If you see precursors, likely the release is fairly recent

PFC Naming Convention

Abbreviation	Name	No. of Carbons	Functional/ Hydrophilic Group
PFBA	perfluorobutanoic acid	4	carboxyl
PFBS	perfluorobutanesulfonic acid	4	sulfonyl
PFPA	perfluoropentanoic acid	5	carboxyl
PFHxS	perfluorohexanesulfonic acid	6	sulfonyl
PFHxA	perfluorohexanoic acid	6	carboxyl
PFOA	perfluorooctanoic acid	8	carboxyl
PFOS	perfluorooctanesulfonic acid	8	sulfonyl
PFOSA	perfluorooctanesulfonamide	8	sulfonamide
PFNA	perfluorononanoic acid	9	carboxyl
PFDA	perfluorodecanoic acid	10	carboxyl
PFUdA	perfluoroundecanoic acid	10	carboxyl
PFDoa	perfluorododecanoic acid	12	carboxyl

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- These are all perfluoroalkyl or perfluorinated compounds
- PFOA – Teflon
- PFOS – Scotchgard
- From name you can figure out number of carbons

PFC Overview

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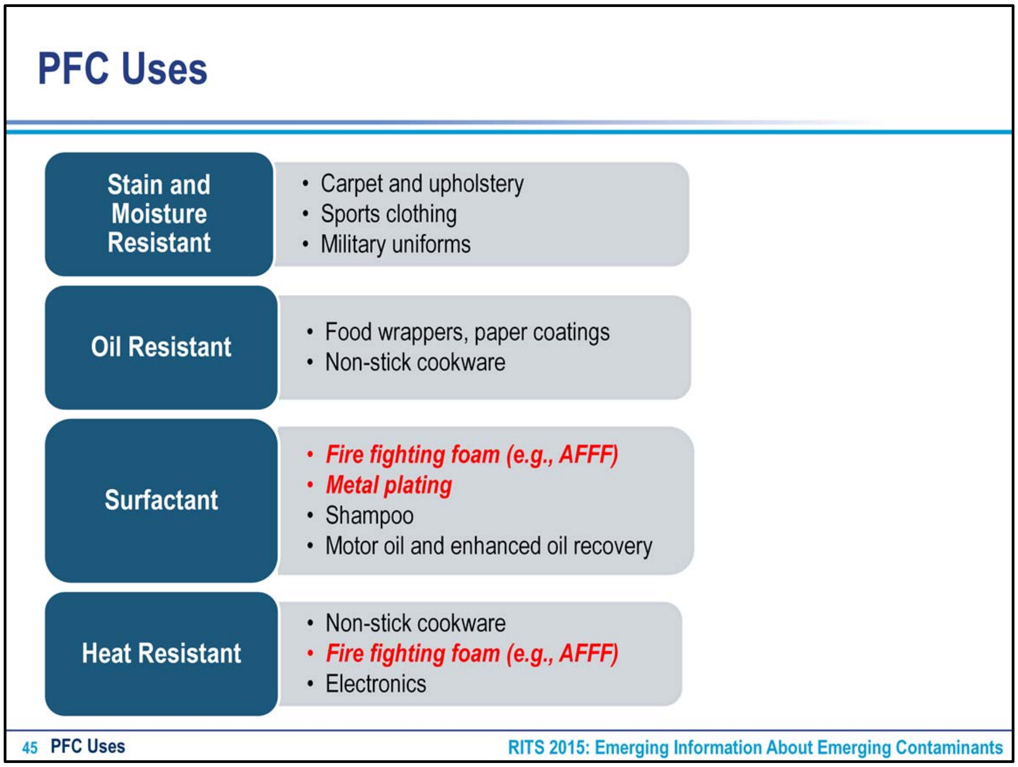
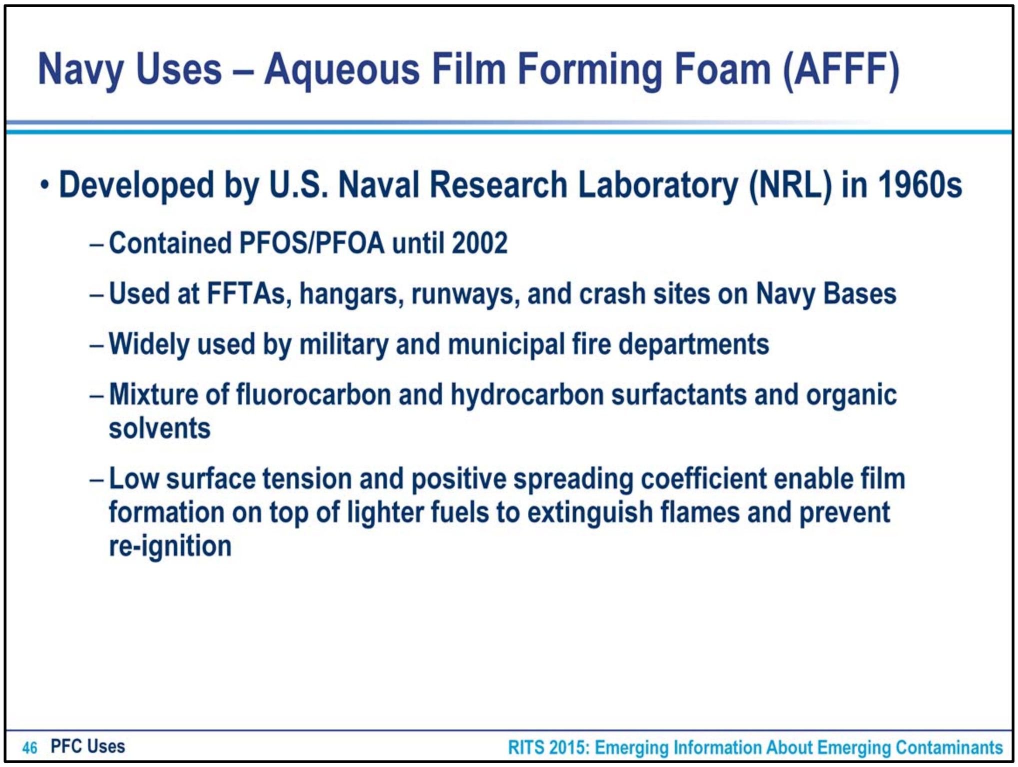


- Navy uses are highlighted in red



- Oregon State University has done extensive research on makeup of PFC-laden water from AFFF releases
    - Article in ES&T
- Poly- and perfluorinated compounds in AFFF initially – poly (precursors) break down quickly once dispersed

Navy Uses – AFFF (cont.)

- Typically purchased and stored as a concentrate (1 to 6%)
  - Mixed with water and then air to disperse as a foam

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Navy Uses – AFFF (cont.)

- Continued use of stockpiled PFOS-based AFFF not currently restricted under U.S. regulations
- AFFF now produced using smaller chain PFCs (<C6)

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Navy Uses – Other

- **PFCs often used at metal plating shops**
  - Added to metal plating baths to reduce surface tension, thereby reducing the amount of splatter in order to meet air emissions
- **Also associated with sludge disposal areas and oil-water separators in vicinity of historical releases**

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Fate and Transport

- Chemicals are extremely stable – C-F bond is high energy and difficult to break
  - Do not hydrolyze, photolyze, or biodegrade under typical environmental conditions
  - Are extremely persistent in the environment
  - High potential to bioaccumulate (long chain)
  - Very soluble – migration in groundwater depends on flow rate and charge of the substrate
- **Much is still unknown about these chemicals**
  - Several research projects currently underway to evaluate fate and transport properties (e.g., SERDP)

51 Fate and Transport of PFCs RITS 2015: Emerging Information About Emerging Contaminants

- Highlight that much is still unknown about these compounds – consult with NAVFAC HQ if questions

Physical/Chemical Properties of PFOS and PFOA

Property	PFOS (Potassium Salt)	PFOA
CAS number	2795-39-3	335-67-1
Physical description	White powder	White powder/waxy white solid
Molecular weight (g/mol)	538	414
Water solubility (µg/L at 25°C)	570 (purified) 370 (freshwater)	9,500 (purified)
Melting point (°C)	>400	45 to 50
Boiling point (°C)	Not measurable	188
Vapor pressure at 20°C (mm Hg)	2.48×10^{-6}	0.017
Organic carbon partition coeff. (log K_{oc})	2.57	2.06
Henry's Law constant (atm m^3/mol)	3.05×10^{-9}	Not measurable
Half-life in water at 25°C (years)	**41**	**92**

Source: ASTDR, 2009; Brooke et al., 2004; Cheng et al., 2008; EFSA, 2008; EPA, 2002; UNEP, 2006

- Highlight solubility and half-life

Presentation Overview

- PFC Chemistry
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Health Risks

- **High potential to bioaccumulate**
  - PFOS and PFOA accumulate in protein-rich blood and related organs – not fats
- **Potential health effects are being extensively evaluated**

54 PFC Risks RITS 2015: Emerging Information About Emerging Contaminants

Risk Assessment

- EPA RSL tables do not include PFOA of PFOS
  - No Tier 1 or Tier 2 toxicity values
- Potential screening levels calculated based on RSL residential and industrial worker exposure scenarios and Tier 3 subchronic toxicity values developed by EPA (2009)

Media	PFC	Residential Exposure*	Industrial Exposure*
Groundwater (µg/L)	PFOA	4.0	NA
	PFOS	1.6	NA
Soil (mg/kg)	PFOA	12	165
	PFOS	4.9	66

* Values calculated using RfD derived by EPA in their short term provisional HAL (2009) and the exposure assumptions used to calculate EPA RSLs in May 2014)

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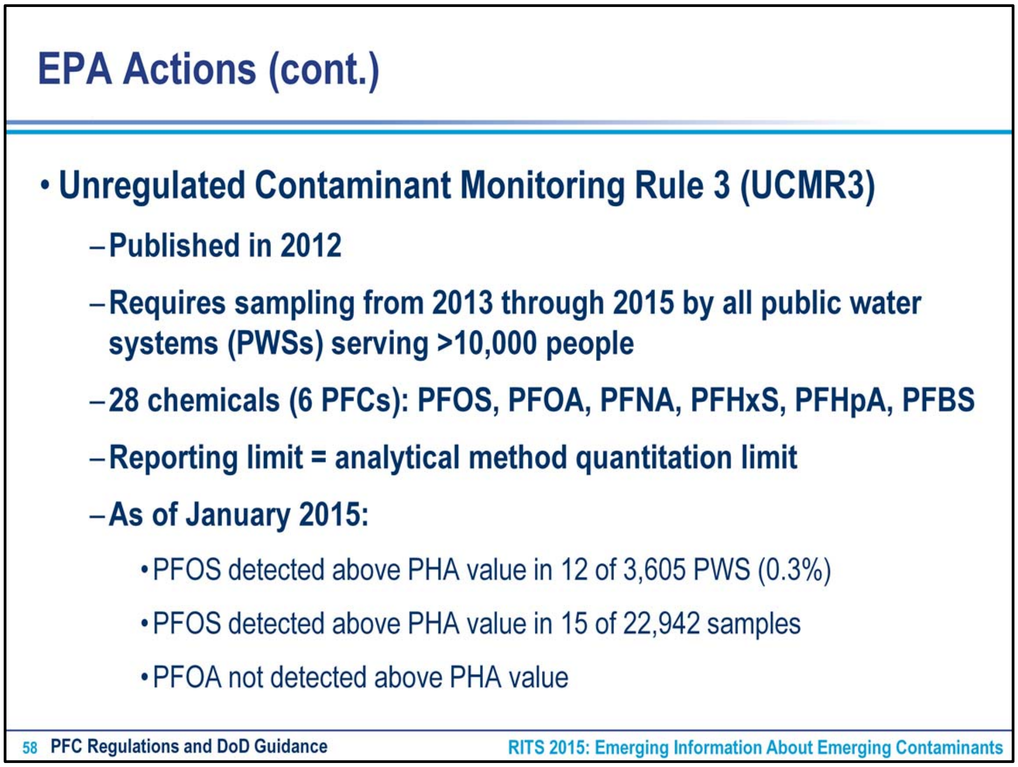
EPA Actions

- 2010/2015 Stewardship Program
  - Minimize potential impact of PFOA on environment
  - Reduce facility emissions and product content of PFOA and related chemicals by 95% before 2010; eliminate by 2015
- PFOS and PFOA are listed on EPA's Contaminant Candidate List (CCL 3)
- Provisional Health Advisory (PHA) values issued for PFOA (0.4 μg/L) and PFOS (0.2 μg/L) in January 2009
  - Assess potential exposure through drinking water
  - Not promulgated (not ARARs)

57 PFC Regulations and DoD Guidance RITS 2015: Emerging Information About Emerging Contaminants

- 3M began to phase out C8 chemistries in 2000. Discontinued use of PFOS in 2001
- ARAR = Applicable or Relevant and Appropriate Requirements



Unregulated Contaminant Monitoring Rule 3 (UCMR3)

- Data available on EPA UCMR3 Website
- PFBS has a Tier 2 toxicity value

Navy Policy – October 2014

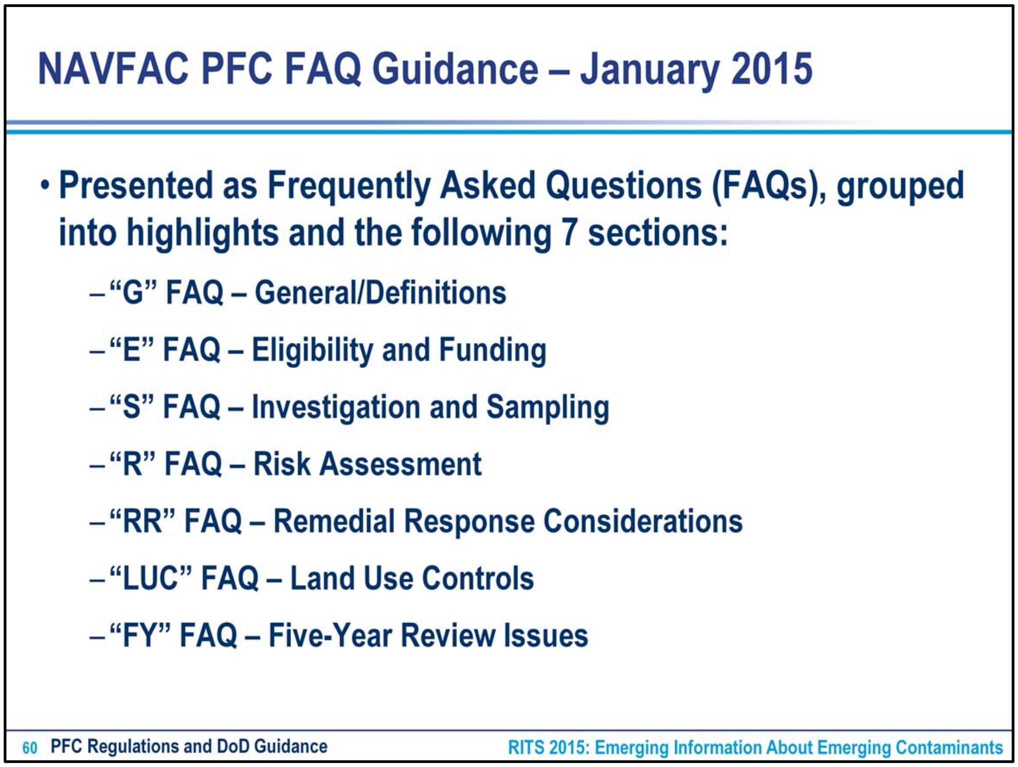
- Identify all known and suspected sites where PFOS/PFOA may have been released on active and Base Realignment and Closure (BRAC) installations
- UCMR3 sampling at all Navy PWSs by December 2015
- For Navy PWSs not under UCMR3, sample finished drinking water for PFOS/PFOA within 1 mile of an upgradient PFC source

DEPARTMENT OF THE NAVY
THE ASSISTANT SECRETARY OF THE NAVY
(ENERGY, INSTALLATIONS AND ENVIRONMENT)
1000 NAVY PENTAGON
WASHINGTON DC 20350-1000

October 21, 2014

MEMORANDUM FOR DEPUTY CHIEF OF NAVAL OPERATIONS (FLEET READINESS AND LOGISTICS) (N4)
DEPUTY COMMANDANT OF THE MARINE CORPS (INSTALLATIONS AND LOGISTICS)

SUBJECT: Perfluorinated Compounds (PFCs) – An Emerging Environmental Issue

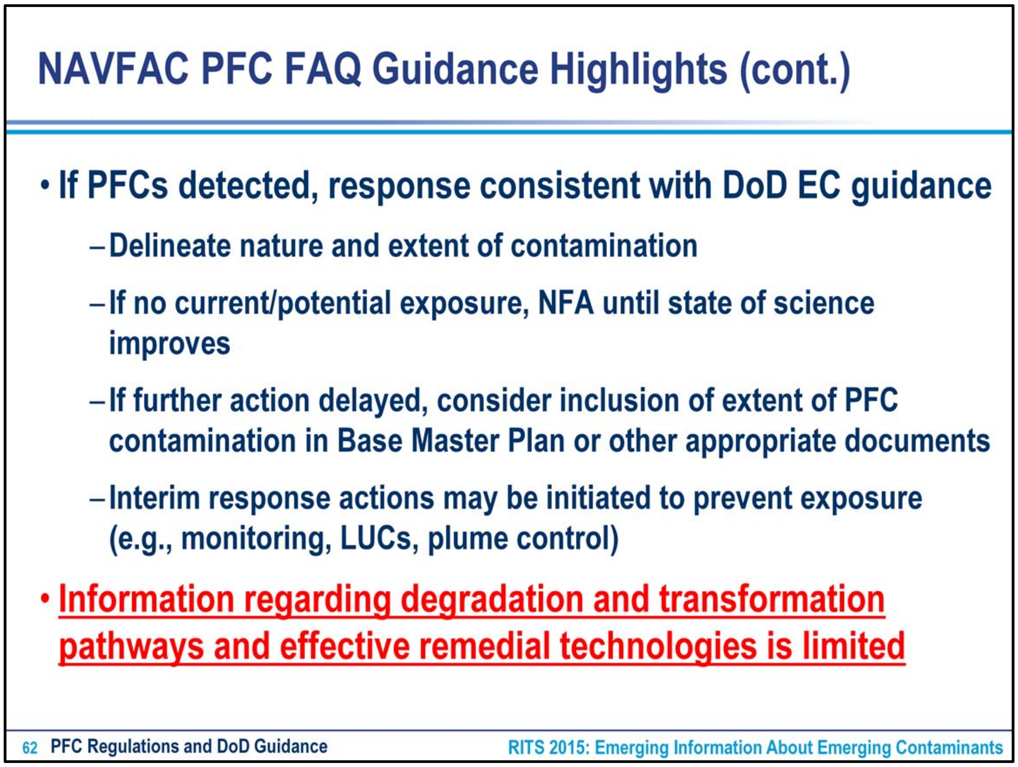


- Navy funding historical release evaluations only – no ongoing releases

NAVFAC PFC FAQ Guidance Highlights

- Investigate for PFCs when CSM indicates:
  - Historical release/use of AFFF – prioritize FFTA and crash sites
  - Historical use of an area for other industrial activities (e.g., plating operations) that may have released PFCs
- Focus initial sampling on PFOA and PFOS
  - Sampling of additional PFCs may be included to facilitate remedial design or when state of science improves
- Currently Tier 3 non-cancer toxicity values for PFOA/PFOS
  - Estimate risk-based screening levels (Tier 1A or 1B)
  - Estimate non-cancer hazards from oral exposure in Tier 2 HHRA

61 PFC Regulations and DoD Guidance RITS 2015: Emerging Information About Emerging Contaminants



- Contact NAVFAC HQ for assistance

Regulatory Levels – PFOA and PFOS

Organization	Media	PFOA (μg/L)	PFOS (μg/L)
EPA PHA value	Drinking water	0.4	0.2
MN Health Based Advisory	Groundwater	0.3	0.3
NJ Preliminary Health Based Guidance	Drinking water	0.04	NA
NC Interim Maximum Allowable Concentration	Groundwater	1	NA
NC Public Health Goal	Private drinking water well	0.63	0.63
Michigan	Drinking water	0.42	NA
ME Maximum Exposure Guideline	Groundwater	0.1	NA

Key Point Not all levels are promulgated; check with Navy legal counsel to identify ARARs

63 PFC Regulations and DoD Guidance RITS 2015: Emerging Information About Emerging Contaminants

- Some states (MN, NJ) have also set groundwater levels for other PFCs besides PFOA/PFOS
- Some states, (MN, TX) have derived toxicity values for either PFOA and/or PFOS, but also other PFCs
  - However, since these values have not been reviewed/adopted by EPA as Tier 3 toxicity values, just because you can FIND a toxicity value for another PFC doesn't mean you should use it to assess your site
- Check with LANT, the Risk Assessment Workgroup (RAW), or HQ before using some of these other values

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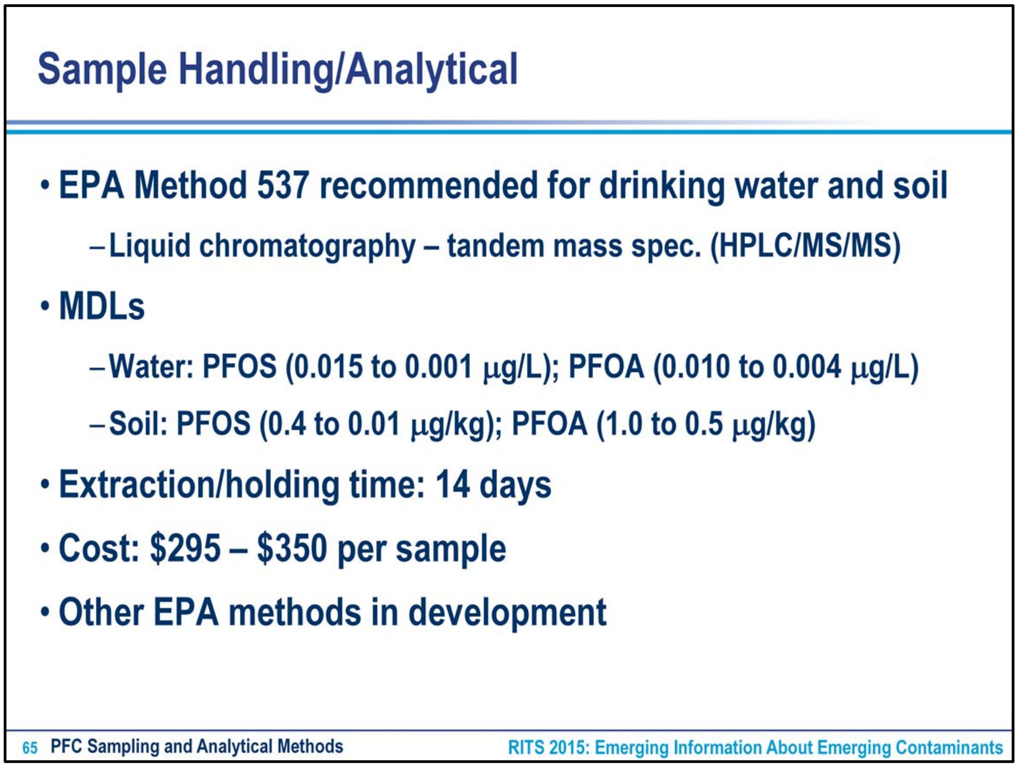
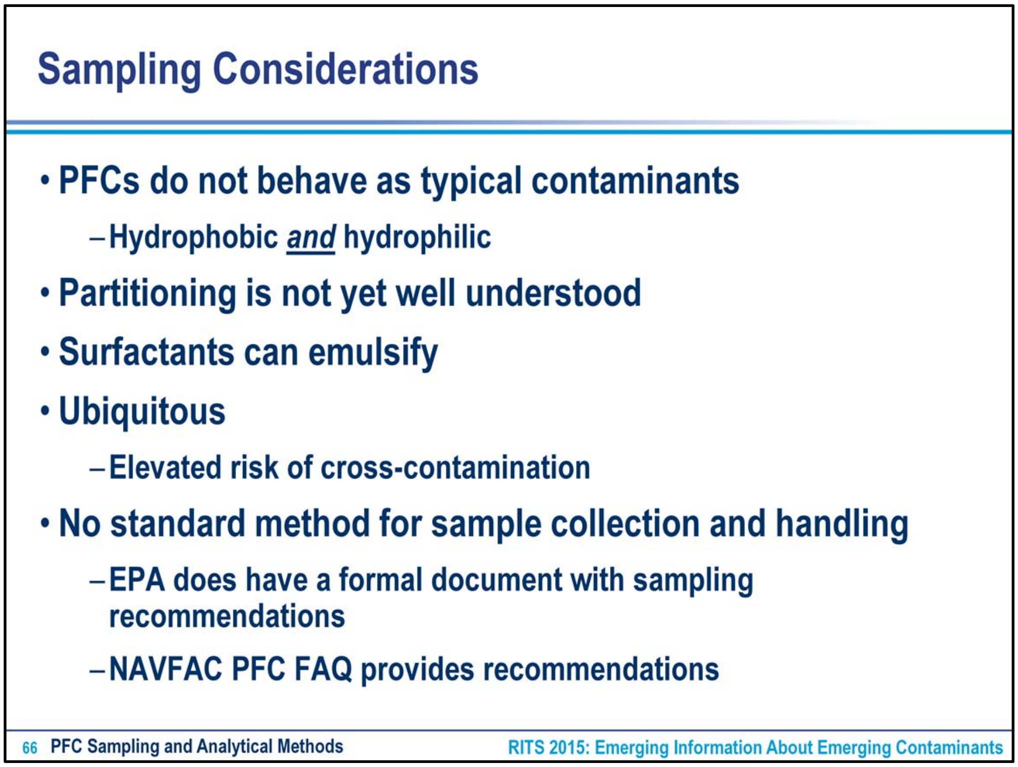
- PFC Chemistry
- PFC Uses
- Fate and Transport of PFCs
- PFC Risks
- PFC Regulations and DoD Guidance
- **PFC Sampling and Analytical Methods**
- Treatment of PFCs
- PFC Case Studies
- Wrap Up



- EPA 537 recommended in NAVFAC guidance and in EPA UMCR3 – there are other sampling methods
- Use a DoD ELAP-certified laboratory



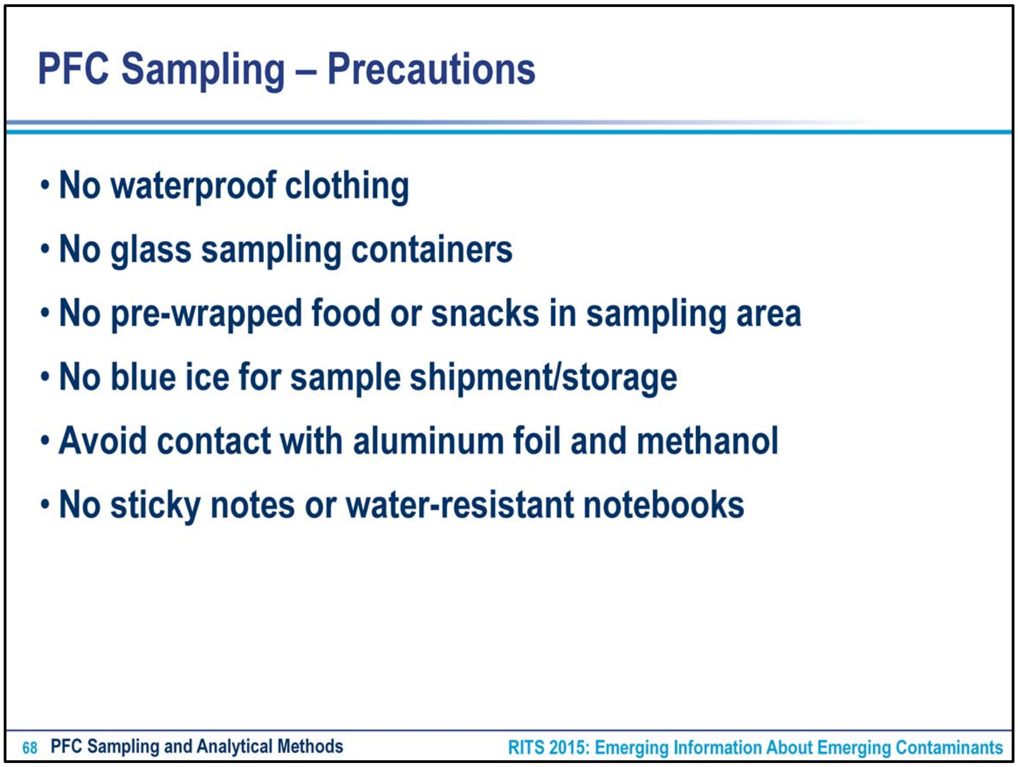
- No specific approved SOP has been developed by EPA or NAVFAC

Recommended PFC Sampling Procedures

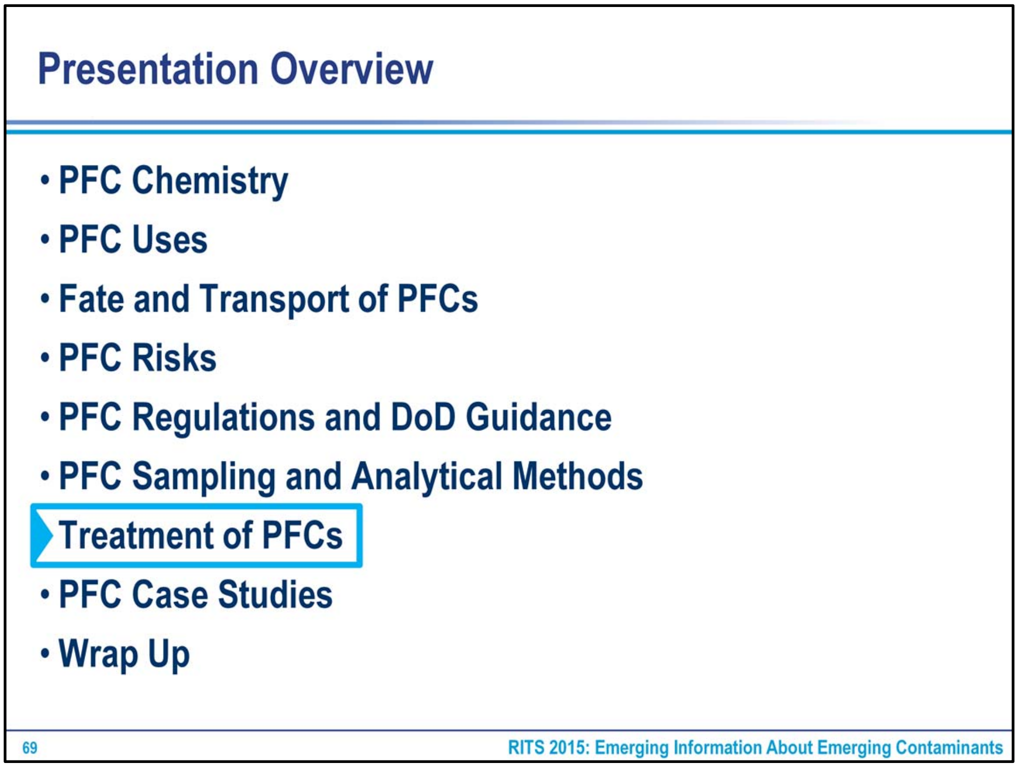
- **Dedicated stainless steel or polyethylene sampling**
- **Use nitrile gloves at all times**
- **Use DI water free of PFCs – *can be provided by laboratory***
- **Low flow, bailers, grab samplers (no components with PFCs)**
- **250 ml HDPE bottle**
- ***No preservatives***
- ***No filtering***

67 PFC Sampling and Analytical Methods RITS 2015: Emerging Information About Emerging Contaminants

- No Teflon
  - However, a recent laboratory study suggests this may not be an issue



- No Teflon, GoreTex, or Tyvek suits
- No Teflon-lined caps on sample bottles
- No Post-It notes
- Put samples in PFC-free zip-lock bags – ice could be an issue
- Well laundered clothes and careful with cosmetics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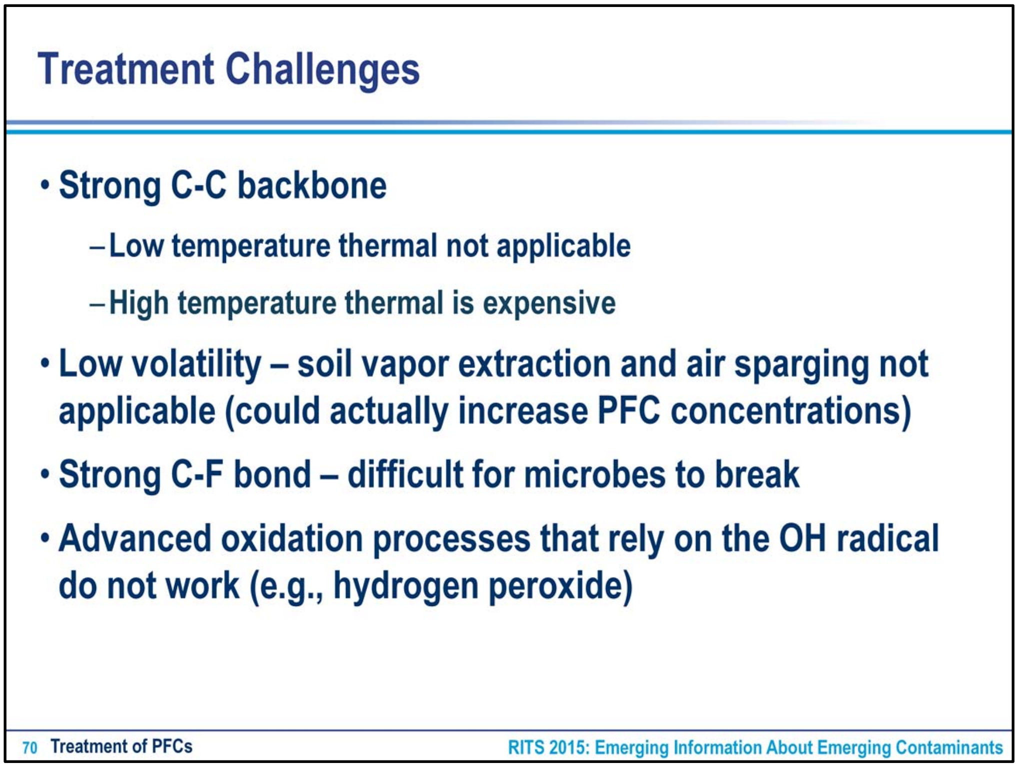

- Main treatment options are GAC, membrane filtration (nanofiltration and reverse osmosis), and oxidation-based technologies

Treatment Options

- **Adsorption** onto granular activated carbon (GAC) and ion exchange
  - Quick breakthrough for low C chain compounds (C4 and C6)
  - Higher chains (C8) have slower breakthrough

Parameter	Charge Capacity (% wt)	Annual GAC Costs ($)			
		20 gpm	44 gpm	220 gpm	440 gpm
PFOS	0.002 to 0.005	3,932	7,865	39,322	78,643
CVOCs	0.02 to 0.4	256	512	2,555	5,112
BTEX	0.1 to 2.0	52	102	512	1,022
PAH	1.3 to 2.5	29	57	284	568

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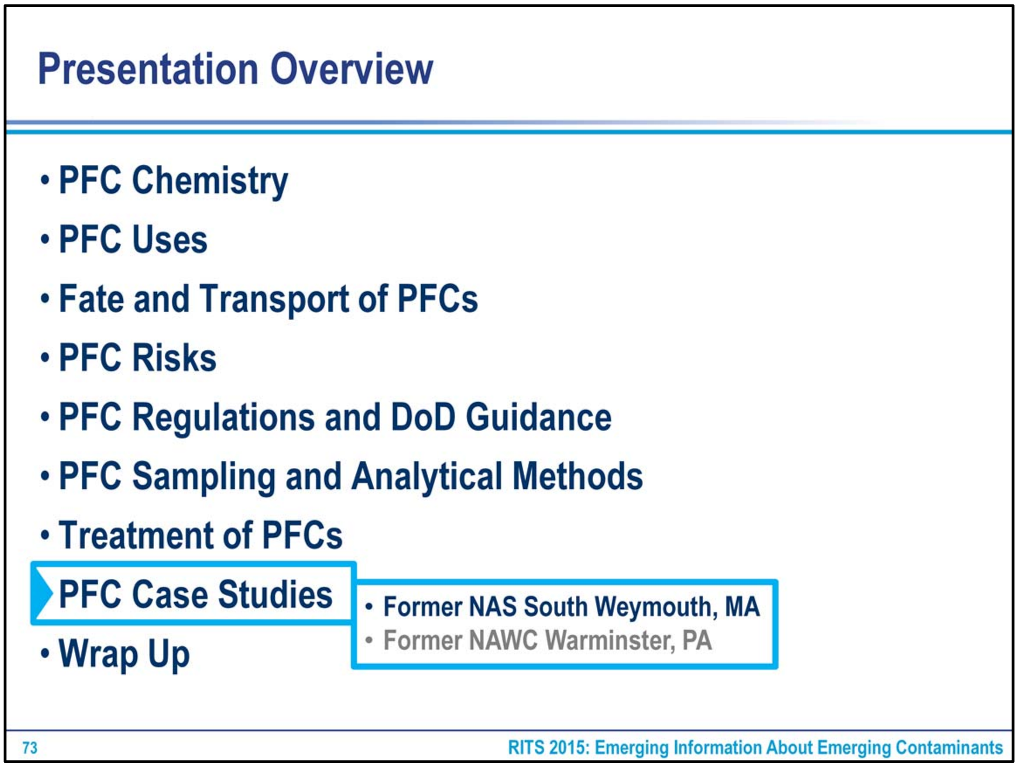
Treatment Options (cont.)

- **Membrane Filtration** (nanofiltration and reverse osmosis)
- **Oxidation** with persulfate, sonolysis, and electrolysis with boron-doped diamond electrodes
  - Not with hydroxyl radical, but with per radical
  - Some laboratory studies; not yet demonstrated at field scale
    - Heat-activated persulfate and permanganate, UV-activated persulfate, ultrasonification, electrochemical oxidation, catalyzed hydrogen peroxide
- **No acceptable, cost-effective *in situ* treatment available**
  - GAC is only treatment method currently in use at sites
- **If remedy is needed, contact NAVFAC HQ for support**

72 Treatment of PFCs RITS 2015: Emerging Information About Emerging Contaminants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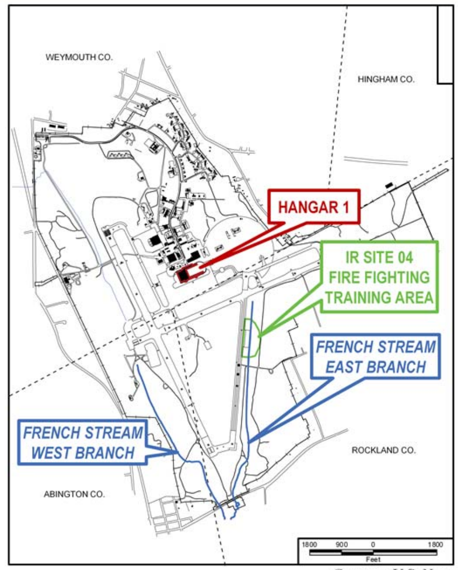
Case Study 1 – Former NAS South Weymouth, MA

- Site Location and History
- Geology/Hydrogeology
- PFC Evaluation Timeline
- Potential PFC Sources
- PFC Sampling
- PFC Data Evaluation

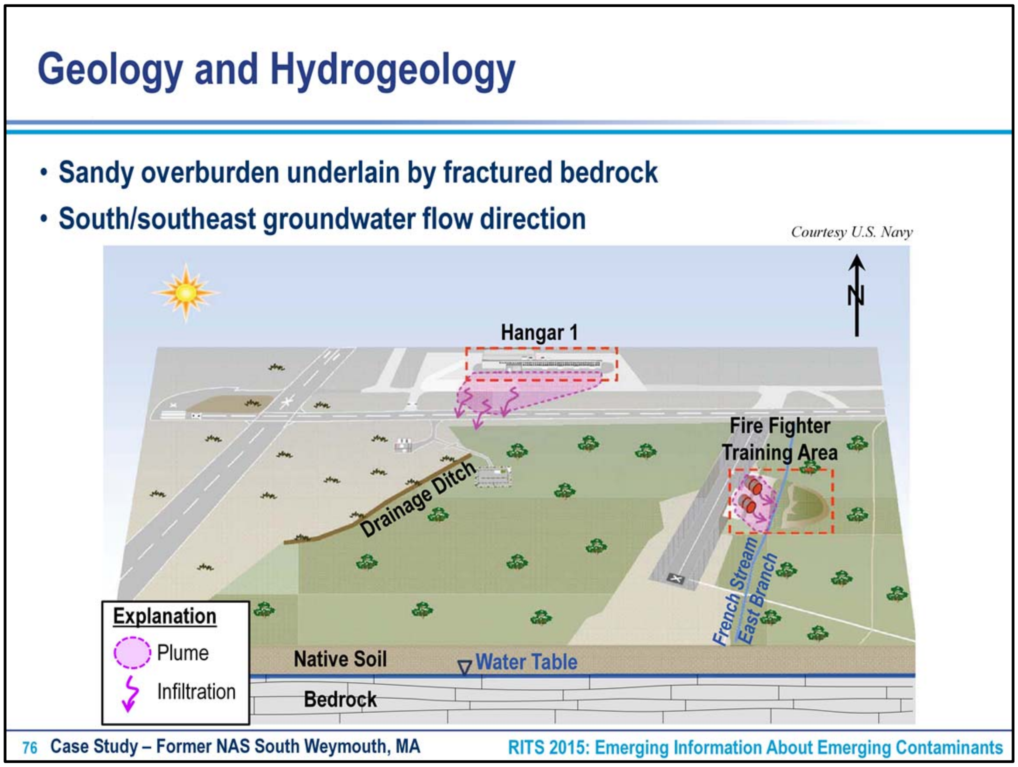
Site Location and History

- Located 15 miles southeast of Boston, MA
- Operated from 1942 to 1997 as a Naval airfield
- Added to NPL in 1993
- Closed in 1997 under BRAC
- Relevant activities included maintenance of aircraft and fire fighting training exercises

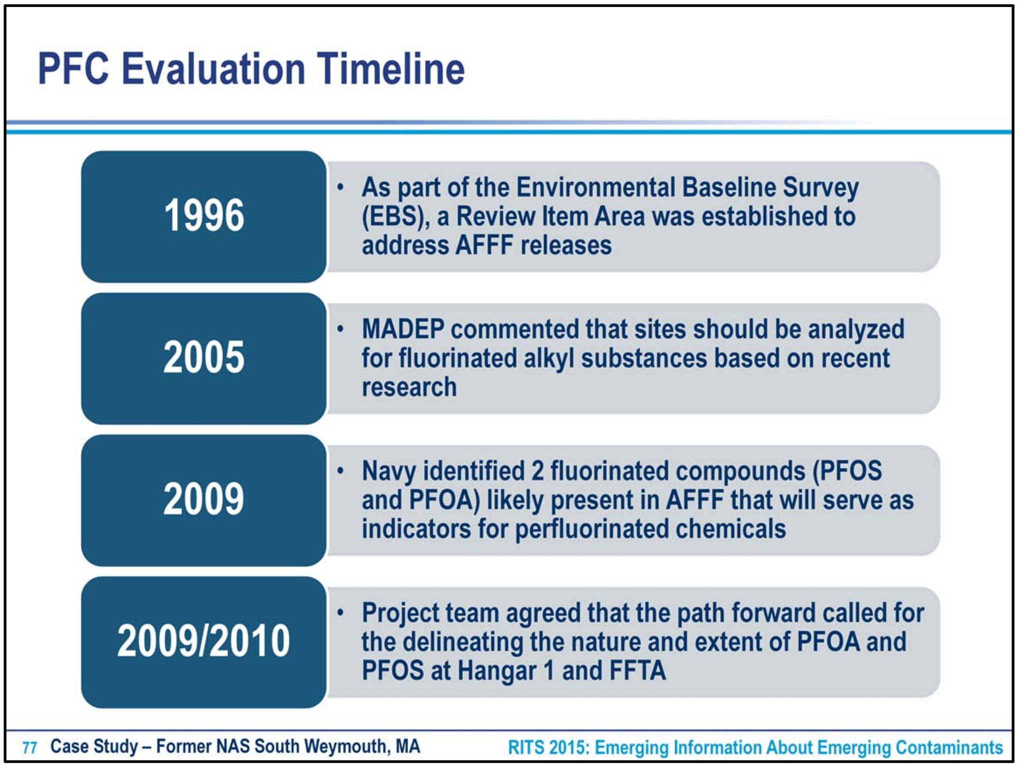


Courtesy U.S. Navy

75 Case Study – Former NAS South Weymouth, MA RITS 2015: Emerging Information About Emerging Contaminants



- 10 to 30 ft of unconsolidated overburden underlain by fractured granitic bedrock
  - Overburden consists of sand, silty sand, sand and gravel, and glacial till
- Depth to groundwater is 3 to 13 ft bgs
- Groundwater flow in overburden, shallow bedrock, and deep bedrock is toward the south/southeast


PFC Evaluation Timeline
1996
• As part of the Environmental Baseline Survey (EBS), a Review Item Area was established to address AFFF releases
2005
• MADEP commented that sites should be analyzed for fluorinated alkyl substances based on recent research
2009
• Navy identified 2 fluorinated compounds (PFOS and PFOA) likely present in AFFF that will serve as indicators for perfluorinated chemicals
2009/2010
• Project team agreed that the path forward called for the delineating the nature and extent of PFOA and PFOS at Hangar 1 and FFTA
77 Case Study – Former NAS South Weymouth, MA
RITS 2015: Emerging Information About Emerging Contaminants

Potential PFC Source Areas

- AFFF stored in Hangar 1 in above-ground storage tanks (ASTs) and used during training exercises at FFTA
- Releases:
  - Reported spill of 5,000 to 10,000 gallons of AFFF in 1987
    - Reportedly contained in the oil-water separator connected to sanitary sewer
  - Reported accidental releases from hose nozzles, ASTs, pump room
    - Likely directed to outside floor drains connected to storm water drainage system
  - AFFF used in fire fighting training exercises occurring at FFTA
- In 2010-2011, Navy sampled at Hangar 1 and FFTA areas to delineate the nature and extent of PFOA and PFOS
  - 36 groundwater, 50 soil, 5 surface water, and 6 sediment samples

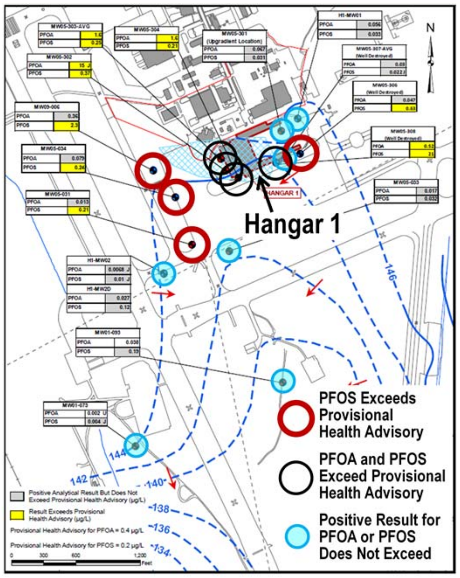
78 Case Study – Former NAS South Weymouth, MA RITS 2015: Emerging Information About Emerging Contaminants

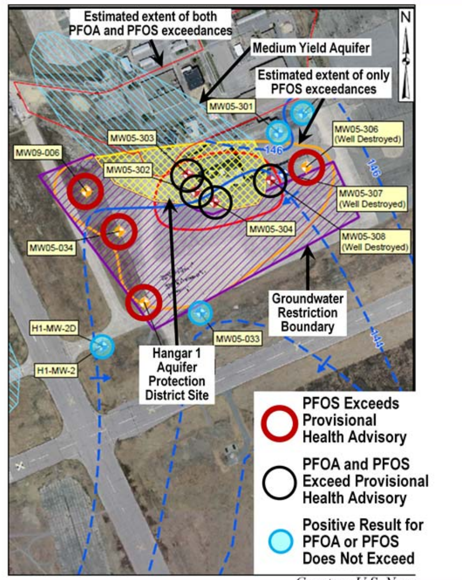
PFC Sampling – Hangar 1 Groundwater Results

- 14 wells sampled in vicinity of Hangar 1
  - Either PFOA and/or PFOS exceeded PHA value in 8 wells
- Highest concentrations of PFOA are associated with location of former ASTs and Hangar 1
- High concentrations of PFOS are more widespread
  - Detected 2,500 ft downgradient of Hangar 1; above PHA value ~500 ft downgradient of Hangar 1

PFC	PHA Value (µg/L)	Maximum Concentration (µg/L)	Median Concentration (µg/L)	Number Above PHA Value
PFOA	0.4	**15**	0.062	4
PFOS	0.2	**21**	**0.21**	8

PFC Sampling – Hangar 1 Groundwater Results (cont.)





Courtesy U.S. Navy

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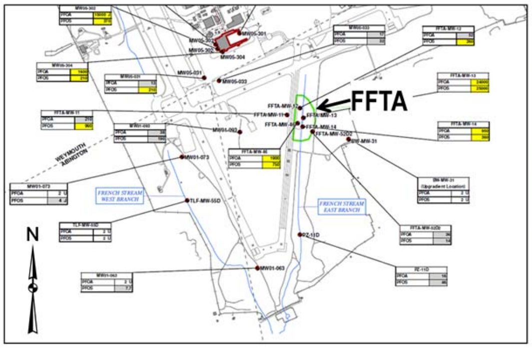
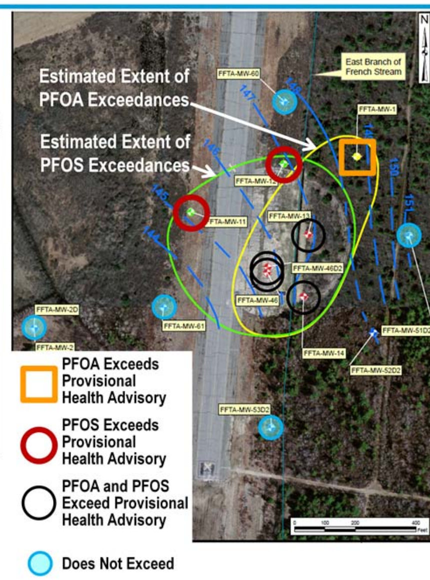
PFC Sampling – FFTA Groundwater Results

- **12 wells sampled in vicinity of FFTA**
  - **Either PFOA and/or PFOS exceeded PHA value in 5 wells**
- **Highest concentrations of PFOA and PFOS are within perimeter of FFTA**
- **High concentrations of PFOS are slightly more widespread**

PFC	PHA Value (μg/L)	Maximum Concentration (μg/L)	Median Concentration (μg/L)	Number Above PHA Value
PFOA	0.4	**24**	0.037	3
PFOS	0.2	**25**	0.118	5

PFC Sampling – FFTA Groundwater Results (cont.)





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82 **Case Study – Former NAS South Weymouth, MA** **RITS 2015: Emerging Information About Emerging Contaminants**

PFC Data Evaluation – HHRA

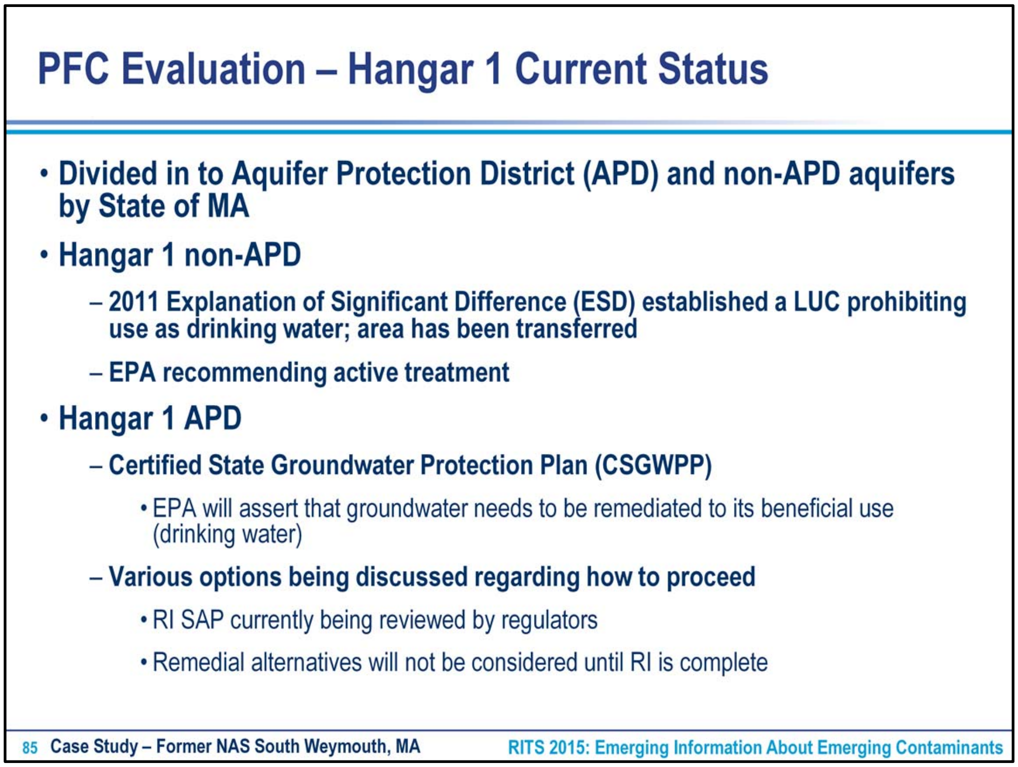
- No cancer toxicity values are currently available
- EPA Office of Water developed non-cancer toxicity values that can be used to estimate risk-based screening levels
  - Significant uncertainty associated with the toxicity values
  - Considered "Tier 3" toxicity values based on sub-chronic rather than chronic exposure

	Groundwater (µg/L)		Soil (mg/kg)	
Site-Specific Screening Criteria	PFOA	PFOS	PFOA	PFOS
Residential screening level	3.1	1.3	12	4.9
Industrial screening level	NA	NA	123	49

83 Case Study – Former NAS South Weymouth, MA RITS 2015: Emerging Information About Emerging Contaminants

PFC Data Evaluation – Ecological Risk Assessment

- Some literature available on the ecotoxicology
- For installations in EPA Region 1, ten papers were reviewed to try to determine the toxicity of PFOS and/or PFOA to aquatic organisms
  - Papers indicated acute toxicity occurs in the range of ~10 to 300 mg/L
  - Chronic toxicity was observed at concentrations as low as 10 μg/L in fish larvae and roughly 90 μg/L in midge larvae
- Approach used at South Weymouth
  - Relied on site-specific toxicity test data that was previously conducted as part of the RI; results showed no site-specific toxicity
  - All surface water sample results were less than the conservative chronic level identified in literature review



- LUC based on PHA value

PFC Evaluation – FFTA Current Status

- Attempted similar approach to Hangar 1 non-APD
- MADEP and EPA requested a broader groundwater restriction that prevents any use of the PFC impacted water
- Completed the FFTA ESD
  - Includes broader groundwater restriction language with a Long Term Monitoring (LTM) component
    - Annual groundwater sampling and 1 or 2 rounds of surface water sampling

86 Case Study – Former NAS South Weymouth, MA RITS 2015: Emerging Information About Emerging Contaminants

Case Study 1 – Summary

- Environmental investigations are ongoing to delineate the nature and extent of PFOA and PFOS at South Weymouth
- ESDs establishing LUC restricting uses of groundwater have been completed for two sites
  - Hangar 1 non-APD
  - FFTA
- Hangar 1 APD site is at a critical decision point regarding whether to consider active remediation
  - Where applicable, based on the CSM, the current Navy position is to delineate the nature and extent of contamination for PFOA and PFOS
  - Making the decision to actively remediate with uncertain criteria/ toxicological data and in the absence of a completed pathway is difficult and not recommended until more certain information is available

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- **PFC Case Studies**
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Case Study 2 – Former NAWC Warminster, PA

- Site Location and History
- Current CSM
- Timeline of Initial PFC Detections
- Evaluation of Potential PFC Sources
- PFC Treatment Evaluation
- Proposed PFC Remedial Investigation Activities
  - Public drinking water well sampling
  - Groundwater well installation
  - Groundwater, soil, surface water, and sediment sampling

89 Case Study – Former NAWC Warminster, PA RITS 2015: Emerging Information About Emerging Contaminants

Site Location

- Former Naval Air Warfare Center (NAWC) Warminster, PA
- ~20 miles north of Philadelphia, PA
- 824 acres

Site History

1944-1996	• Used for manufacturing, research, development, testing, and evaluation of Navy aircraft and aircraft components
1989	• Facility listed on NPL due to groundwater contamination; environmental studies commenced
1996-1998	• Base closure initiated under DoD BRAC program; environmental cleanup continues
Early 2000s	• Majority of property transferred to local authorities and redeveloped
2000-present	• Navy continues groundwater remediation

Historic Contaminant Source Areas

- **Area A – Three primary waste sites**
  - Burn pits for solvents, paints, roofing materials, and unspecified chemicals
  - Disposal trenches and unlined lagoons that received ***wastewater sludges***
- **Area B – Three primary waste sites**
  - Trenches/pits for disposal of paints, solvents, oil, and construction debris
- **Area C – Two primary waste sites**
  - Landfill trenches for disposal of non-industrial solid waste paints, oils, and metals, construction debris, solvents, and sewage sludge
  - ***FFTA***
- **Area D – Former main building complex**
  - Laboratories and shops supporting R&D; ***metal plating laboratory***

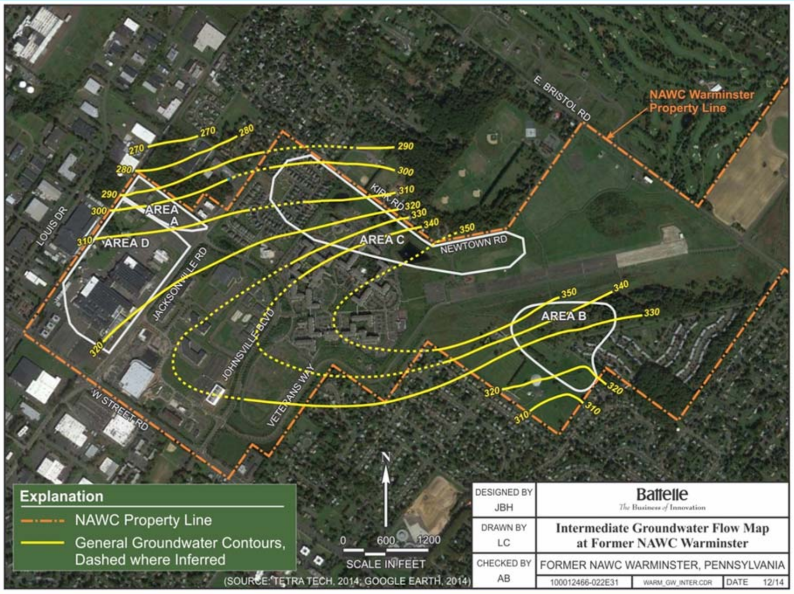
92 Case Study – Former NAWC Warminster, PA RITS 2015: Emerging Information About Emerging Contaminants

Geology and Hydrogeology

- 5-15 ft of clayey soils overlie weathered bedrock
- Weathered bedrock transitions to competent bedrock
  - Alternating units of fine-grained sandstone and siltstone/mudstone
- Groundwater present at 10-15 ft bgs
  - Former runway represents topographic high; radial groundwater flow
- Hydrogeologic units delineated based on presence of semi-continuous thin siltstone/mudstone units
  - Form interconnected, discrete groundwater flow system

Geology and Hydrogeology (cont.)

Courtesy U.S. Navy



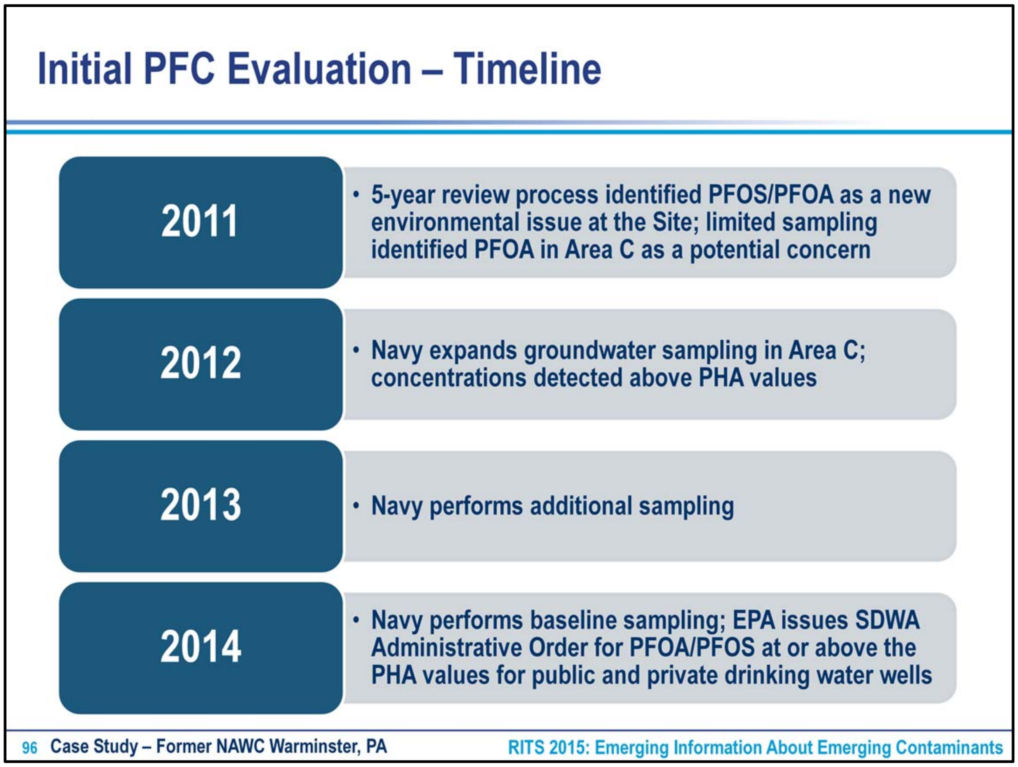
94 **Case Study – Former NAWC Warminster, PA** **RITS 2015: Emerging Information About Emerging Contaminants**

Remedial System for VOCs

- Site characterization activities identified chlorinated volatile organic compounds (CVOCs) in soil and groundwater
  - Areas A and D: TCE, PCE, carbon tetrachloride
  - Area C: PCE
- Per signed ROD, groundwater extraction and treatment system (GWETS) in place at Areas A, C, and D
  - System includes air stripper and LGAC
  - Designed to provide source area hydraulic containment and reduce concentrations below MCLs

Courtesy U.S. Navy

95 Case Study – Former NAWC Warminster, PA RITS 2015: Emerging Information About Emerging Contaminants



- 2013 – PFOS/PFOA detected in public supply well; Navy begins investigation potential sources of PFOS and PFOA at NAWC Warminster

Baseline PFC Groundwater Sampling – 2014

Area/Source	No. of Wells/ Samples	PFOA		PFOS	
		No. Above PHA Value	Maximum Concentration (µg/L)	No. Above PHA Value	Maximum Concentration (µg/L)
A	15	0	0.381	13	**0.665**
D	8	7	**1.62**	7	**2.41**
C	8	8	**2.6**	8	**16**
Area A Influent	2	0	0.215	2	**0.66**
Area C Influent	2	2	**2.6**	2	**1.5**
GWETS Effluent	2	2	**0.772**	0	0.02
PWS Well A (Area C)	3	0	0.100	2	**0.21**
PWS Well B (Area A/D)	2	0	0.349	2	**1.09**
PHA Value			**0.4**		**0.2**

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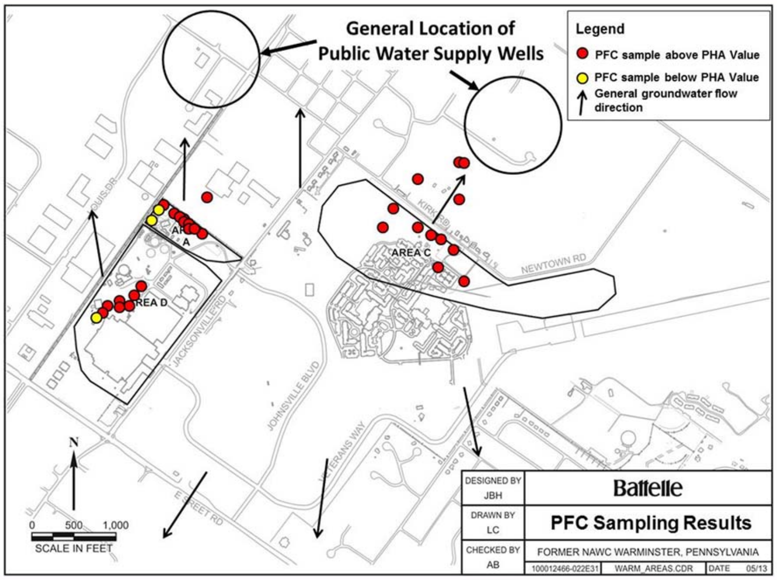
Baseline PFC Groundwater Sampling – 2014 (cont.)



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98 Case Study – Former NAWC Warminster, PA

RITS 2015: Emerging Information About Emerging Contaminants

Evaluation of PFC Sources

- Evaluation of historical records to determine where PFCs were present and/or potentially used
- PFCs used in a wide range of products related to former NAWC Warminster activities
  - Metal plating, fire fighting, application/testing of non-stick paints/coatings
- Off-site sources also identified
  - Lubricant manufacturing facilities, etching/engraving facility, plastic manufacturing facility, fire stations

99 Case Study – Former NAWC Warminster, PA RITS 2015: Emerging Information About Emerging Contaminants

Evaluation of PFC Sources (cont.)

- 14 potential on-site sources identified
  - Laboratories – metal plating shops
  - Lagoons/trenches – metal plating bath wastes
  - Burn pits – paints with surface protectors and solvents
  - FFTAs – use of AFFF
  - Landfills/trenches – AFFF and paints with surface protectors
  - Buildings – fire-retardant aviation suit testing
  - Plane crash site – use of AFFF
  - Fire stations and emergency response centers – use of AFFF
  - WWTP and GWETS – discharge of PFC-laden water

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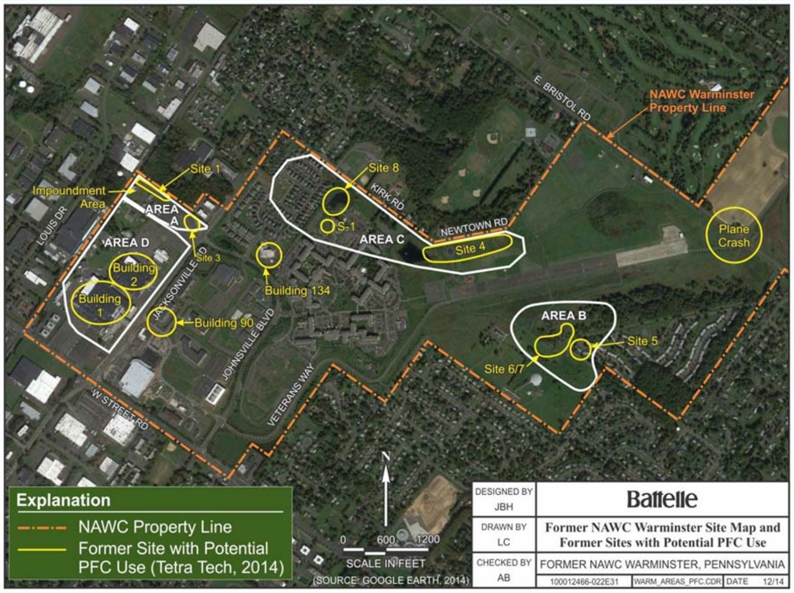
Evaluation of PFC Sources (cont.)

Courtesy U.S. Navy



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Evaluation of PFC Sources (cont.)

- **Warminster Municipal Authority (WMA) conducted PFC sampling per UCMR3 in November 2013 and June 2014**
  - **Posted to EPA UCMR3 Website in 2014**
- **Three production wells taken off line**

Area/Source	No. of Wells/ Samples	PFOA		PFOS	
		No. Above PHA Value	Maximum Concentration (μg/L)	No. Above PHA Value	Maximum Concentration (μg/L)
Supply Well A (Area C)	2	0	0.122	0	0.16
Supply Well B (Area A/D)	2	0	0.349	2	**1.09**
Supply Well C (Area A/D)	2	0	0.0885	0	0.193
PHA Value			**0.4**		**0.2**

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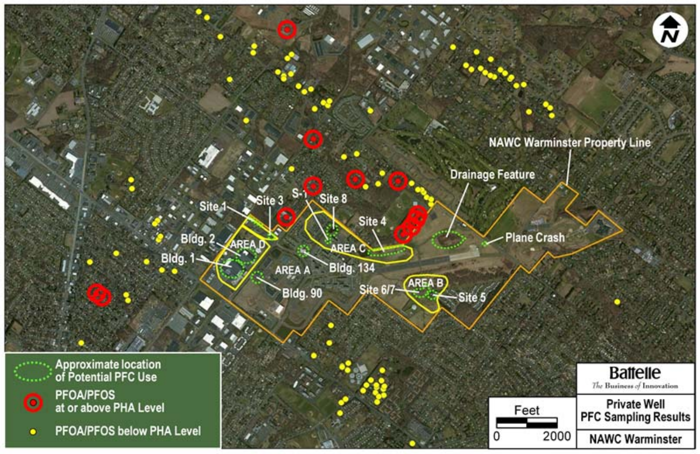
Private Well Identification

- 125 private water wells were identified and sampled by EPA through an Interagency Agreement with the Navy



Courtesy U.S. Navy

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PFC Treatment Evaluation

- Public water supply wells
  - Two currently fitted with air strippers to remove VOCs; only one operating
  - Evaluated temporary and permanent treatment system options
  - Evaluated GAC options
    - Virgin vs. regenerated carbon
    - Coconut vs. coal-based
  - Consider other PFCs during remedial design
- GWETS
  - Evaluated GAC design and changeout options
  - Virgin vs. regenerated carbon
  - Consider other PFCs during remedial design

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Proposed Remedial Investigation

- Objectives:
  - Identify/delineate PFC sources (PFOS and PFOA)
  - Delineate PFC plume (PFOS and PFOA)
- Use results from: CSM, private well sampling, PFC source evaluation, baseline on-site sampling
- Activities:
  - Monitoring well installation
  - Soil, surface water, sediment, and groundwater sampling
  - Additional private well sampling

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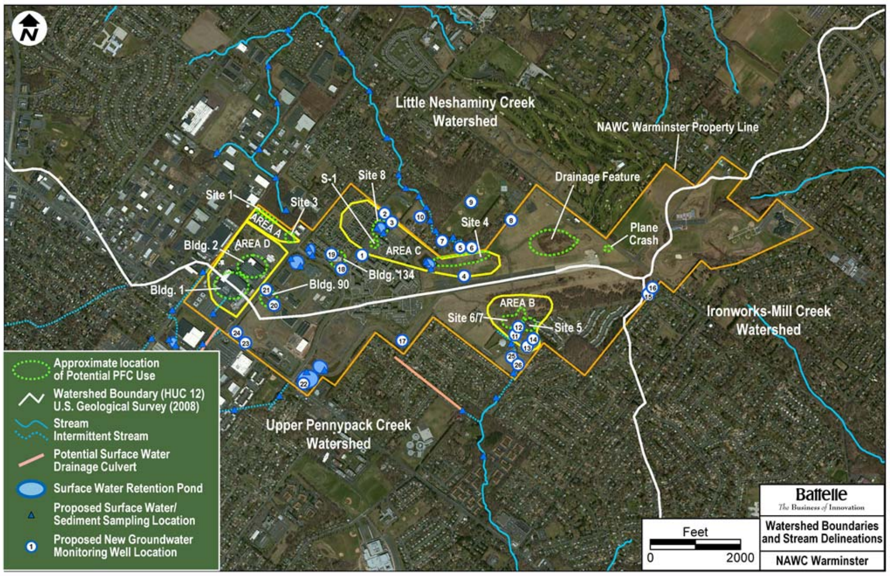
Case Study 2 – Proposed Sampling Locations

Courtesy U.S. Navy



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Presentation Overview – Part 2

- PFC Chemistry
- PFC Uses
- Fate and Transport of PFCs
- PFC Risks
- PFC Regulations and DoD Guidance
- PFC Sampling and Analytical Methods
- Treatment of PFCs
- PFC Case Studies
- **Wrap Up**

PFC Wrap Up – Key Points

- Consult NAVFAC PFC FAQs for information
- Investigate for PFCs when CSM indicates:
  - Historical release/use of AFFF – prioritize FFTA and crash sites
  - Historical use of an area for other industrial activities (e.g., plating operations) that may have released PFCs
- Focus initial sampling on PFOA and PFOS
  - Sampling of additional PFCs may be included to facilitate remedial design or when state of science improves
  - High potential for sampling cross-contamination – develop strong QA program

PFC Wrap Up

- If PFCs detected, response should be consistent with DoD EC guidance
- Information regarding degradation and transformation pathways and effective remedial technologies is limited
  - Prevent exposure by implementing LUCs
  - Initiate interim remedies (e.g., wellhead treatment)
- Consult NAVFAC HQ for guidance

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PFC Additional Information

- EPA fact sheet (March 2014)
  - http://www2.epa.gov/sites/production/files/2014-04/documents/factsheet_contaminant_pfos_pfoa_march2014.pdf
- EPA PHA value document
  - http://water.epa.gov/action/advisories/drinking/upload/2009_01_15_criteria_drinking_pha-PFOA_PFOS.pdf
- DASN (E) Memorandum: PFCs – An Emerging Environmental Issue (October 2014)
- NAVFAC PFC Guidance/FAQs
  - http://www.navfac.navy.mil/content/dam/navfac/Specialty%20Centers/Engineering%20and%20Expeditionary%20Warfare%20Center/Environmental/Restoration/er_pdfs/gpr/don-ev-guid-pfc-faq-20150129i.pdf

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