Land Application Field Study II

US EPA Biosolids Webinar
October 29, 2020

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Disclaimer

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Outline

- **Previous Research- Field Study I**
- **Experimental Design- Field Study II**
- **Data**
  - **Metals**
  - **Nonylphenol**
  - **PFAS**
- **Biosolids PFAS levels**
- **Conclusions**
- **Next Steps- Field Study III**
- **PFAS Sampling**
- **Acknowledgements**

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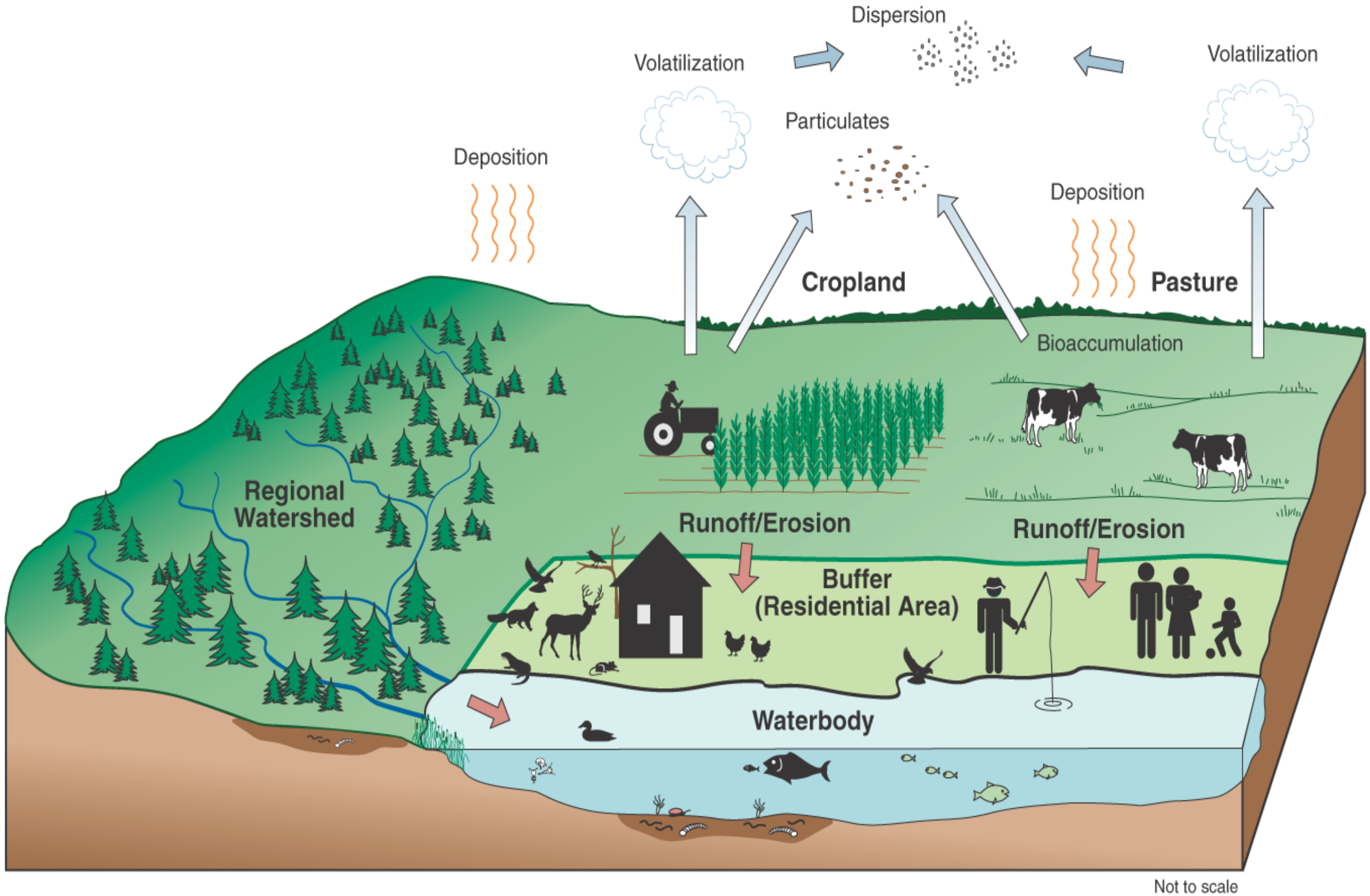

Multimedia Land Application Study: Field Study I

- Surface application by side discharge manure spreader
- Agronomic rate of 10 wet tons/acre
- Material applied
  - Anaerobically digested biosolids
  - Polymer addition during dewatering
  - Lime addition
- Application field
  - Fescue field
  - No prior application of biosolids
  - Autumn application
  - Sampled for 1 month before and 4 months after application

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Soil Study Activities

- Characterize Study Conditions
  - Weather data
  - Soil data
  - Quantity and distribution of biosolids
  - Microbial community quantity and structure
- Performance Measurements
  - Microbes: fecal coliform density, viable helminth ova, Salmonella, enteric viruses, coliphage
  - Chemicals: concentrations of alkylphenol ethoxylates and degradation products (APEs)
  - Ecotoxicity Screening

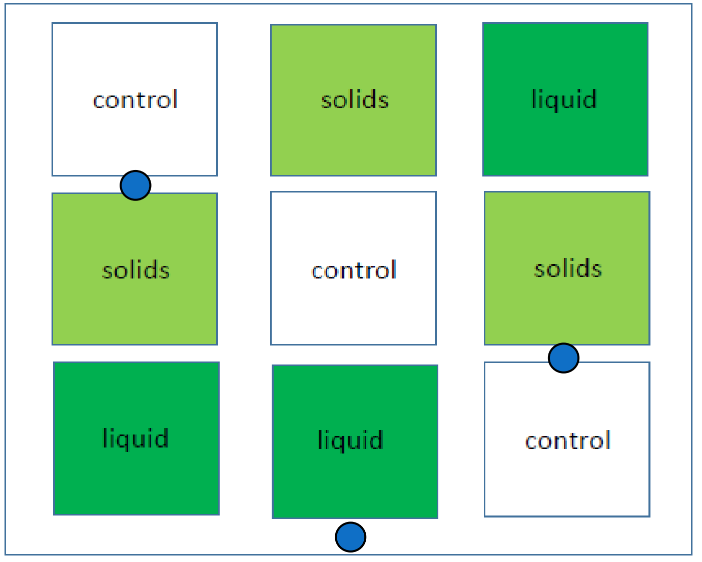
Soil Study Conclusions

- **Changes observed in shallow samples after application**
- **Microbial community shifted for about 28 days after application**
- **Total biomass, fecal coliforms, and APEs**
  - **Increased following application**
  - **Persisted for 98 day sampling period**

- **See full results in report “Multimedia Sampling During the Application of Biosolids on a Land Test Site”**
  - **Report - https://www.epa.gov/sites/production/files/2018-11/documents/multimedia-sampling-land-testsite.pdf**
  - **Summary - https://www.epa.gov/sites/production/files/2018-11/documents/study-examines-fate-agricultural-land.pdf**

Land Application Field Study II

- Research Questions
  - How are/does concentration change with time when biosolids are land applied?
  - Does the application method (Solid or Liquid) affect measured concentrations?
- Pilot/Field scale treatment plot at local WWTP on a fescue and rye grass field
- Fall application at 10 wet tons/acre
- Study Design
  - Land application techniques (liquid and solids)*
  - No application (control) and biosolids only (blue circles)*
  - 3 treatment reps of each
  - Sampled for 13 months*
- Analytes
  - Microbes: fecal coliforms, total biomass and community structure
  - Nutrients
  - Chemicals: metals, APEs, and PFAS*



* Changed from previous study (LAFS I)

Field Plots After Application

Control

Solids

Liquid

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Field Plots in Spring After Application

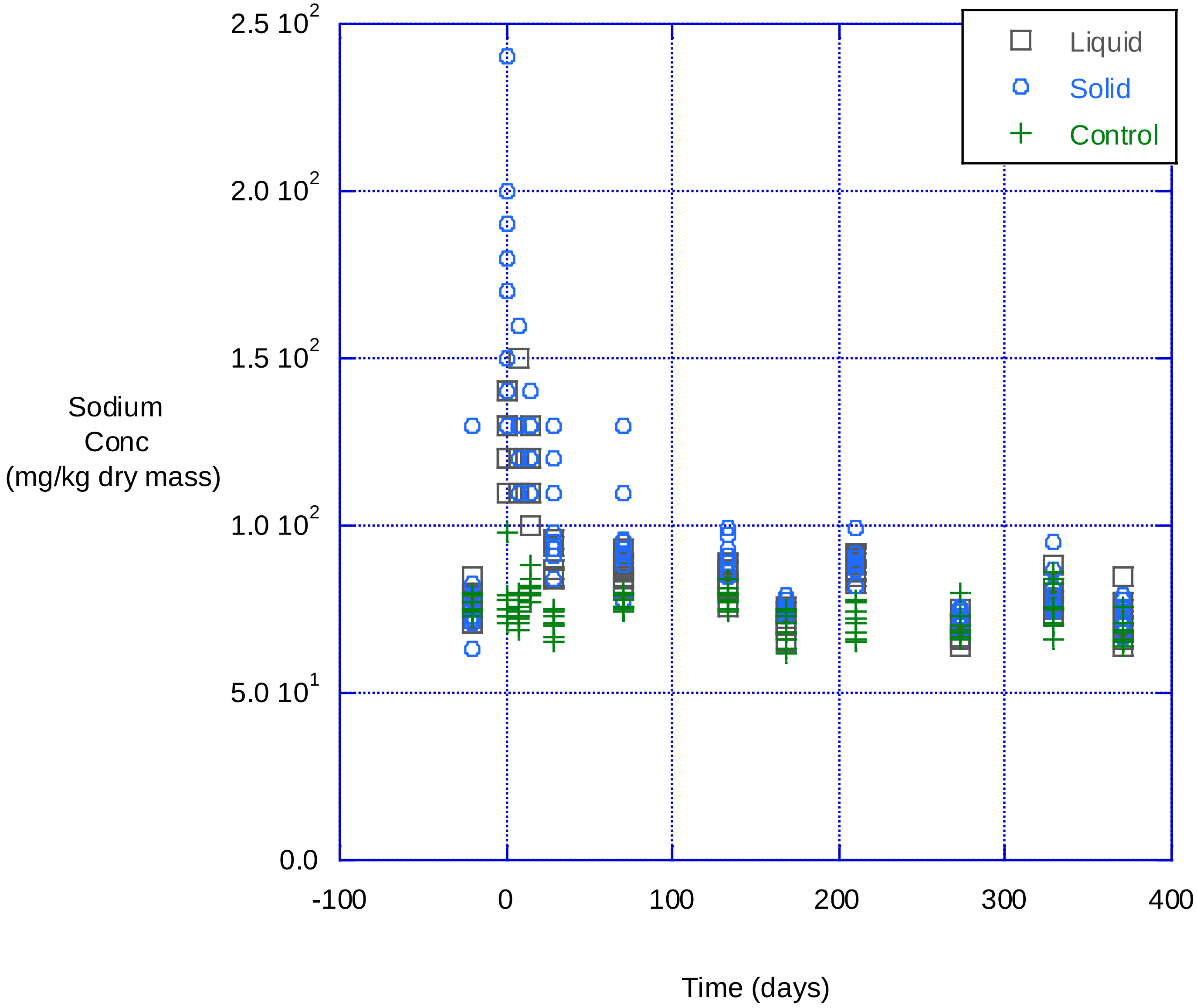
Samples From Plots

Control **Solid** **Liquid**

Sodium Data

Concentrations

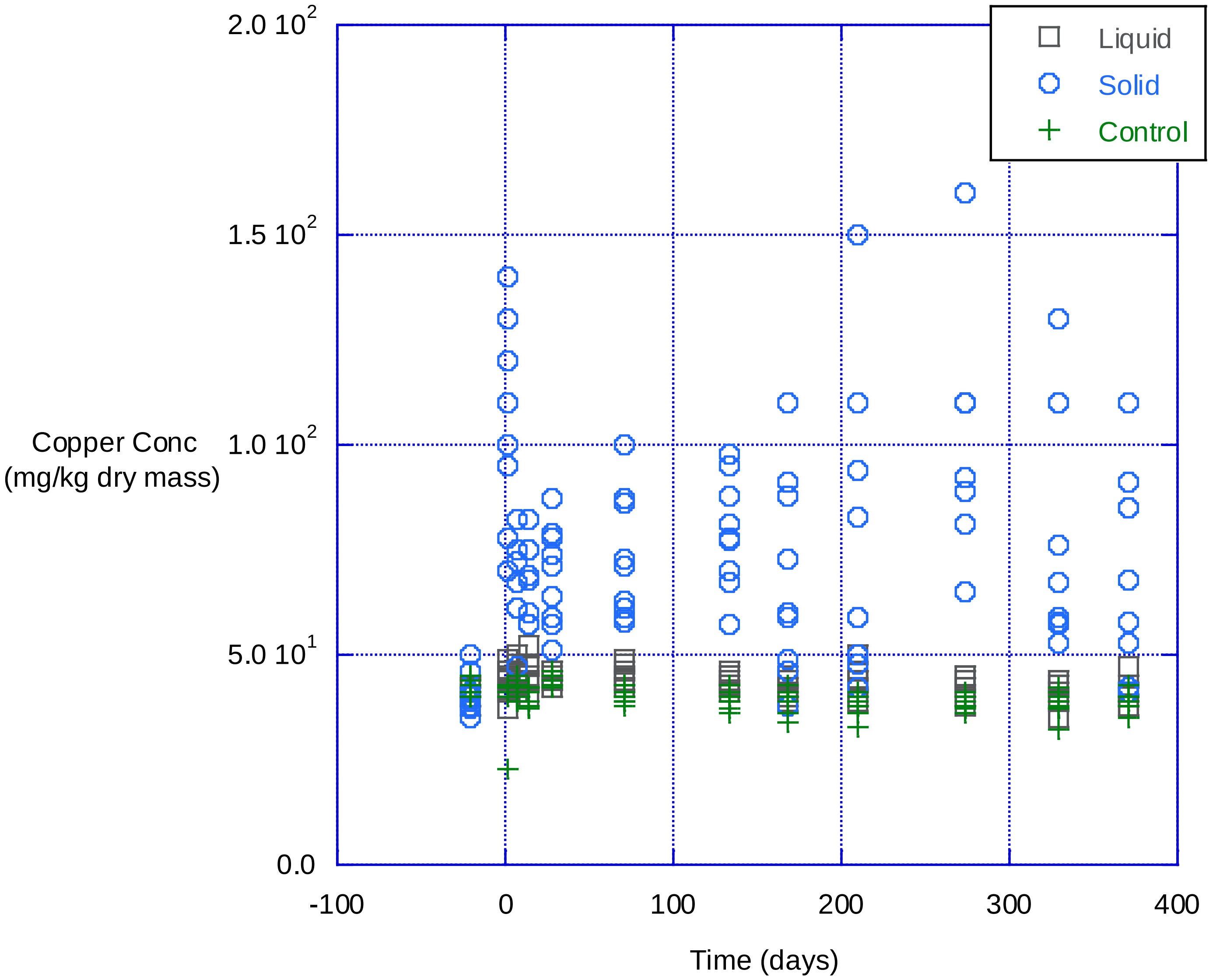
- **Elevated in the solids and liquid trmts after application**
- **By day 120 near control levels**



Copper Data

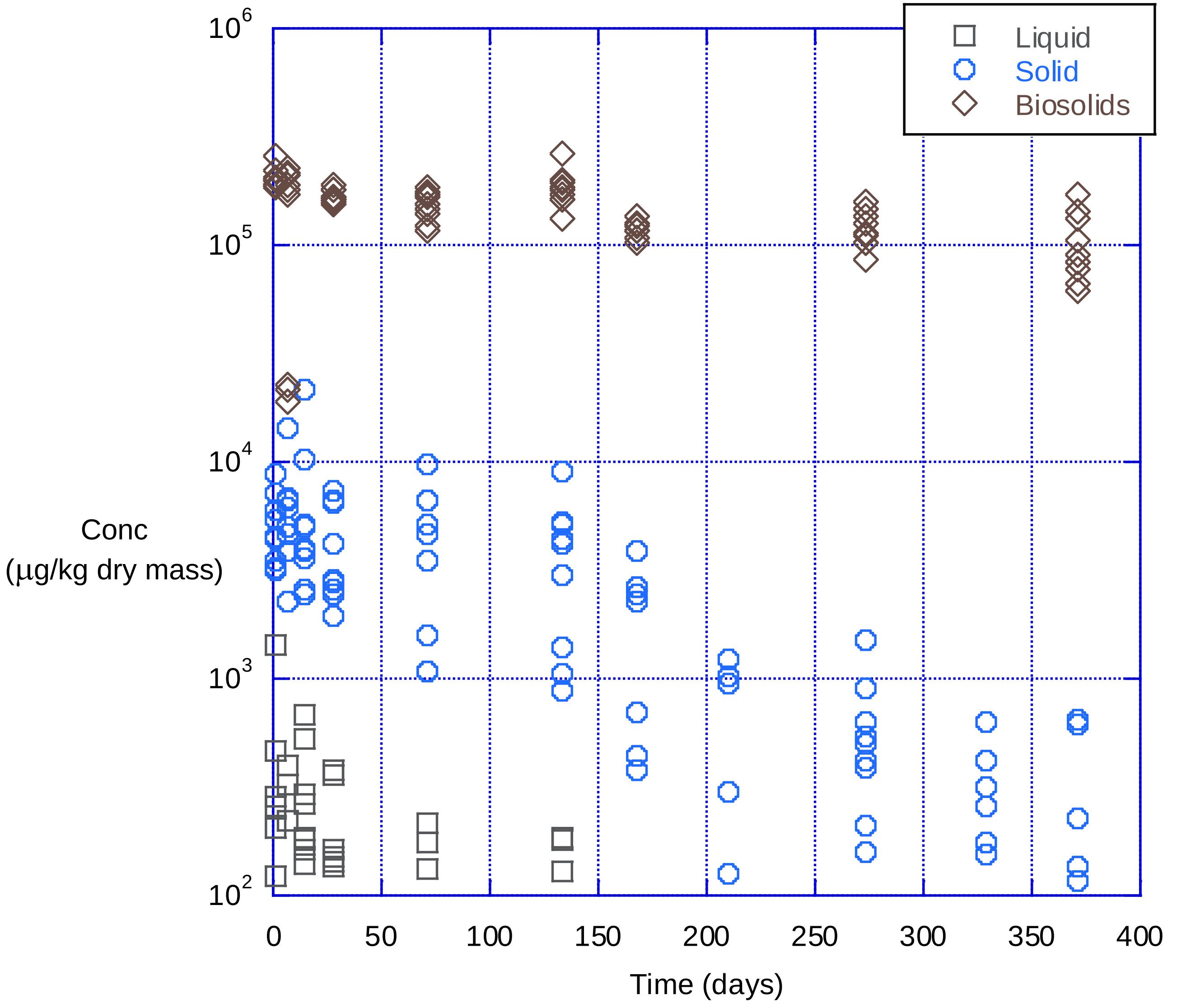
Concentrations

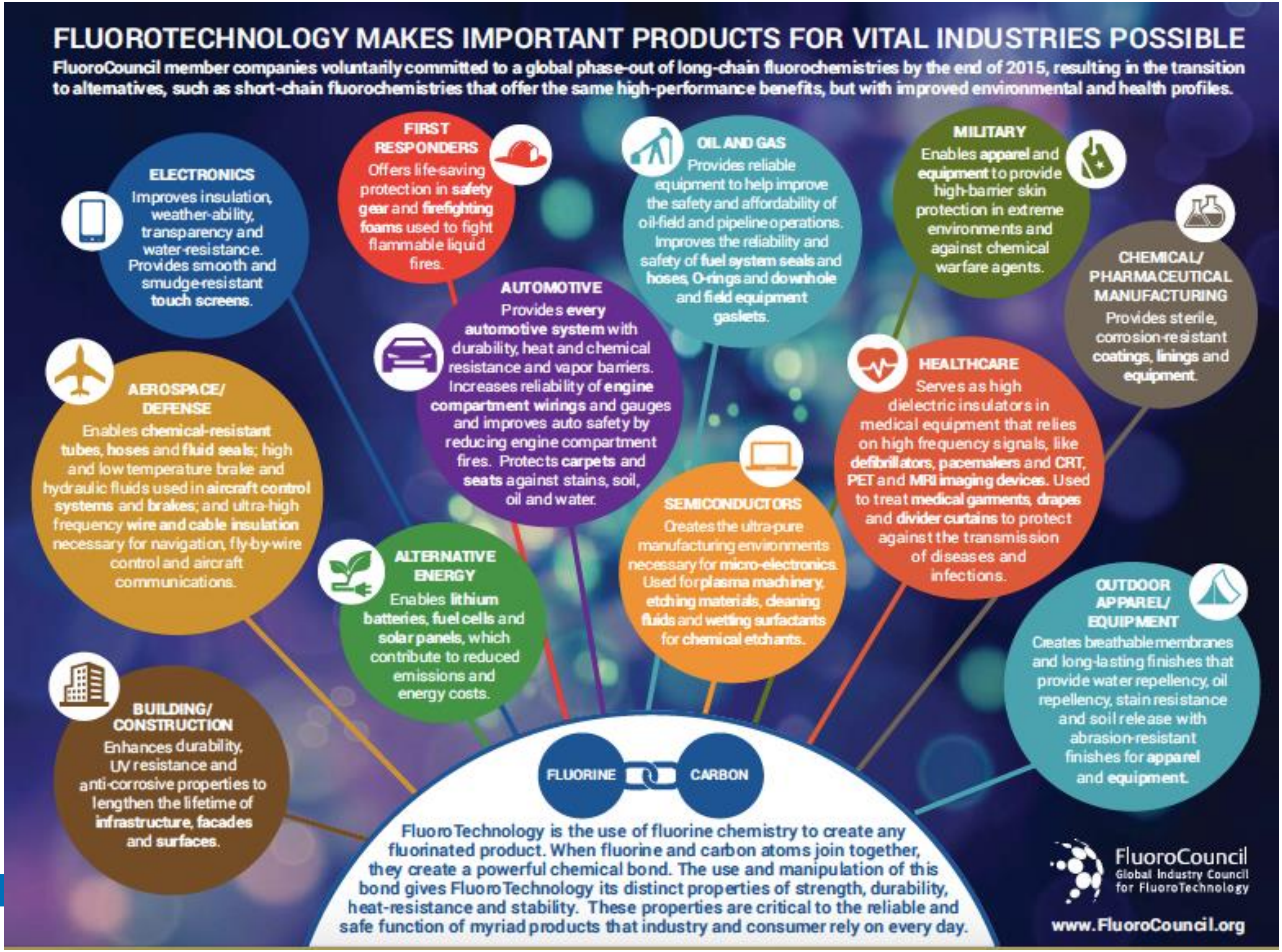
- **Higher in the solid trmt throughout the study**
- **Liquid and control similar**



Nonylphenol (NP) Data

- **Aerobically degradable surfactant, weakly estrogenic**
- **Only concentrations above the reporting limit (RL) are shown**
- **Liquid – no data > RL after 120 days**
- **NP persists in solid and biosolids throughout the study**





FLUOROTECHNOLOGY MAKES IMPORTANT PRODUCTS FOR VITAL INDUSTRIES POSSIBLE
FluoroCouncil member companies voluntarily committed to a global phase-out of long-chain fluorochemistries by the end of 2015, resulting in the transition to alternatives, such as short-chain fluorochemistries that offer the same high-performance benefits, but with improved environmental and health profiles.
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FIRST RESPONDERS
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Enables apparel and equipment to provide high-barrier skin protection in extreme environments and against chemical warfare agents.
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HEALTHCARE
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PFAS – More Than Just PFOA and PFOS

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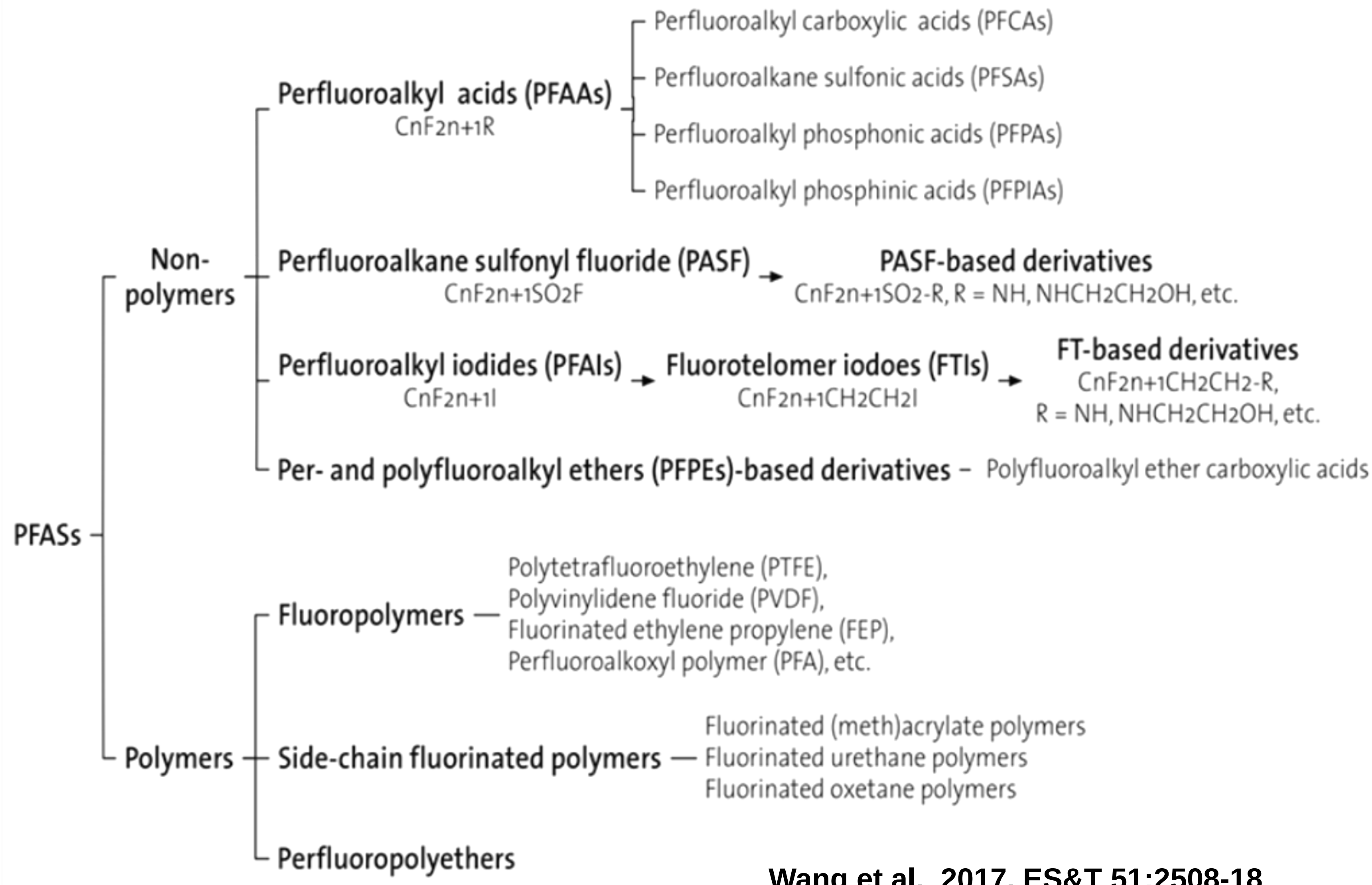


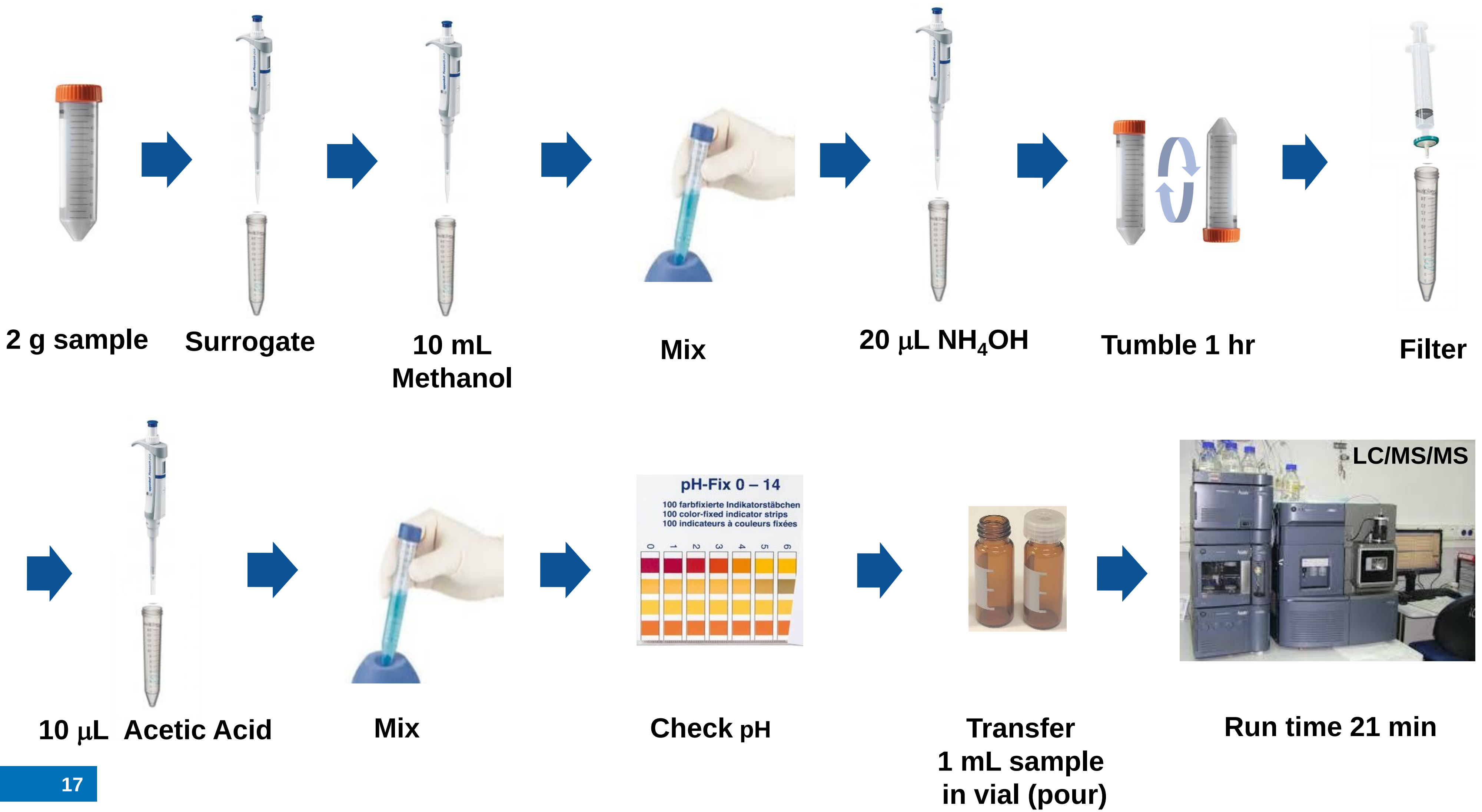
Wang et al. 2017. ES&T 51:2508-18

PFAS by ASTM D7968 (LC/MS/MS)

- Matrix - Environmental solids such as soils, sediments, and sludges
  - Developed by Larry Zintek (Reg 5 Chicago Regional Laboratory)
  - Single lab validated

- Method
  - Solvent extraction
  - Analysis by LC/MS/MS with MRMs and ion ratios
- Target Analytes:
  - 11 Perfluorinated Carboxylic Acids (PFCAs): C4 - C14
  - 3 Perfluorinated Sulfonic Acids (PFSAs): C4-C10
  - Intermediates
    - 6 PFCAs - 6:2, 8:2, 10:2, & 7:3 FTCA; and 6:2 & 8:2 FTUCA
- Surrogate standards (isotopically labeled compounds): 9 PFCAs and PFSAs
  - Used to monitor analytical method performance/quality
  - Not used to “correct” the data

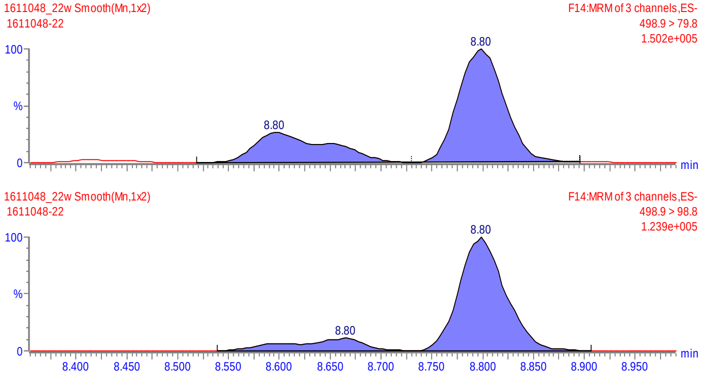
LC/MS/MS Analytical Method – ASTM D7968



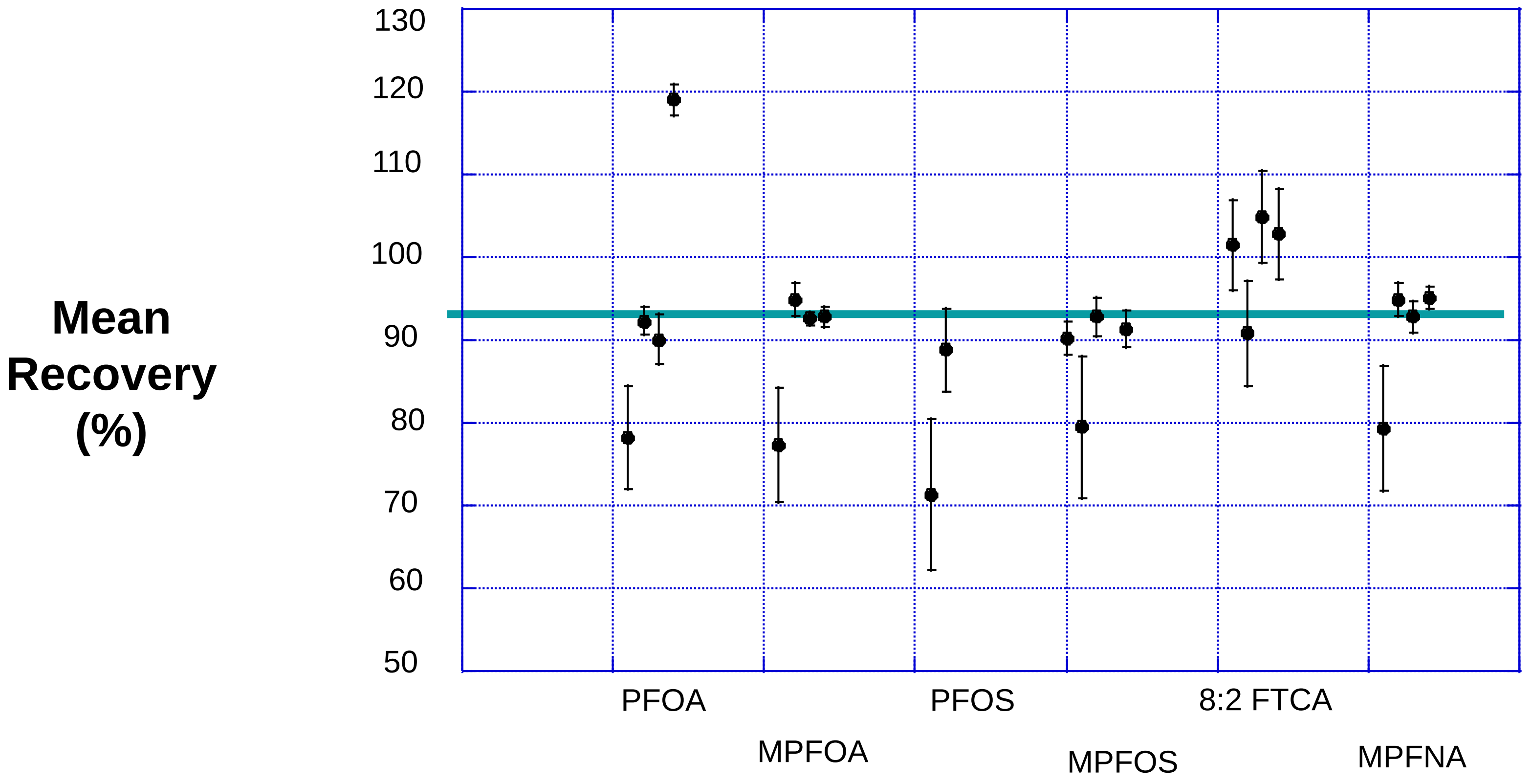
Based on schematic by William Lipps, Shimadzu

Analytical Method Quality Controls

- **Analyte Identification**
  - **Each batch: Initial calibration, Calibration check, and Second source check**
  - **Each analyte: Retention time, Primary and Confirmation ion masses, and Ion ratio**
- **Accuracy – 2 of each/batch unless specified**
  - **Surrogate spiking - All samples and blanks**
    - **Used to assess method performance**
    - **Not used to alter reported concentrations**
  - **Matrix spike samples – MS and MS duplicates**
  - **Spiked blanks**
  - **Method reporting limit checks**
- **Precision - 2 of each/batch**
  - **Duplicate samples**
  - **Matrix spike duplicates**
  - **Spiked blanks**
- **Laboratory Contamination – method blanks – 2/batch**



ASTM D7968 Performance Data



- Error bars are % RSD
- 6 replicates of each matrix
- Spiked at 400 ng/kg dry soil all except 8:2 FTCA 8000 ng/kg dry soils
- 4 ASTM soil matrices: CL-1; CH-1; SP-1; ML-16
  - PFOS not shown for SP-1 and ML-1 because the matrices had background conc comparable to spike conc

Treatment Plots - November

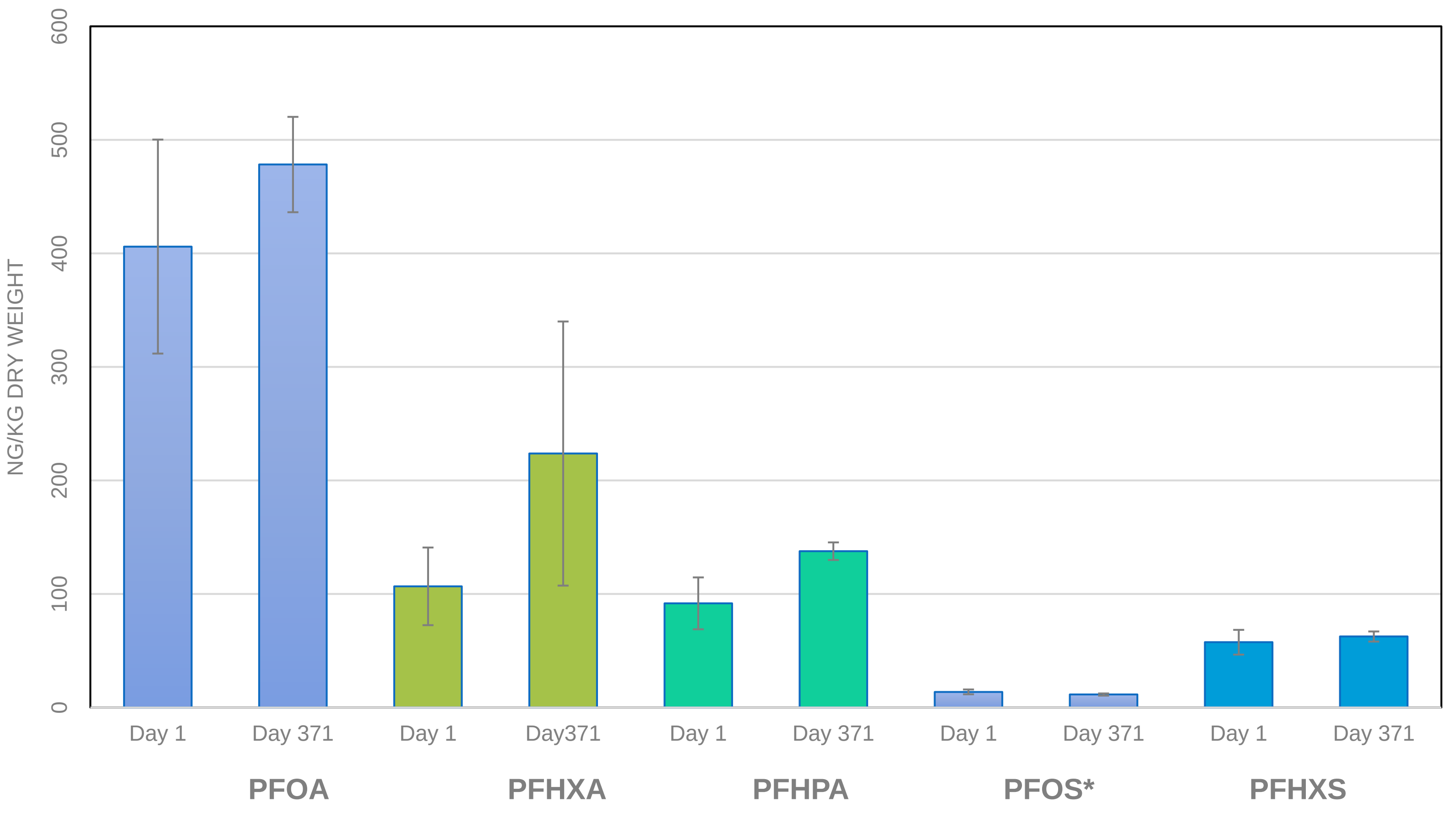
Liquid

Solid

Control

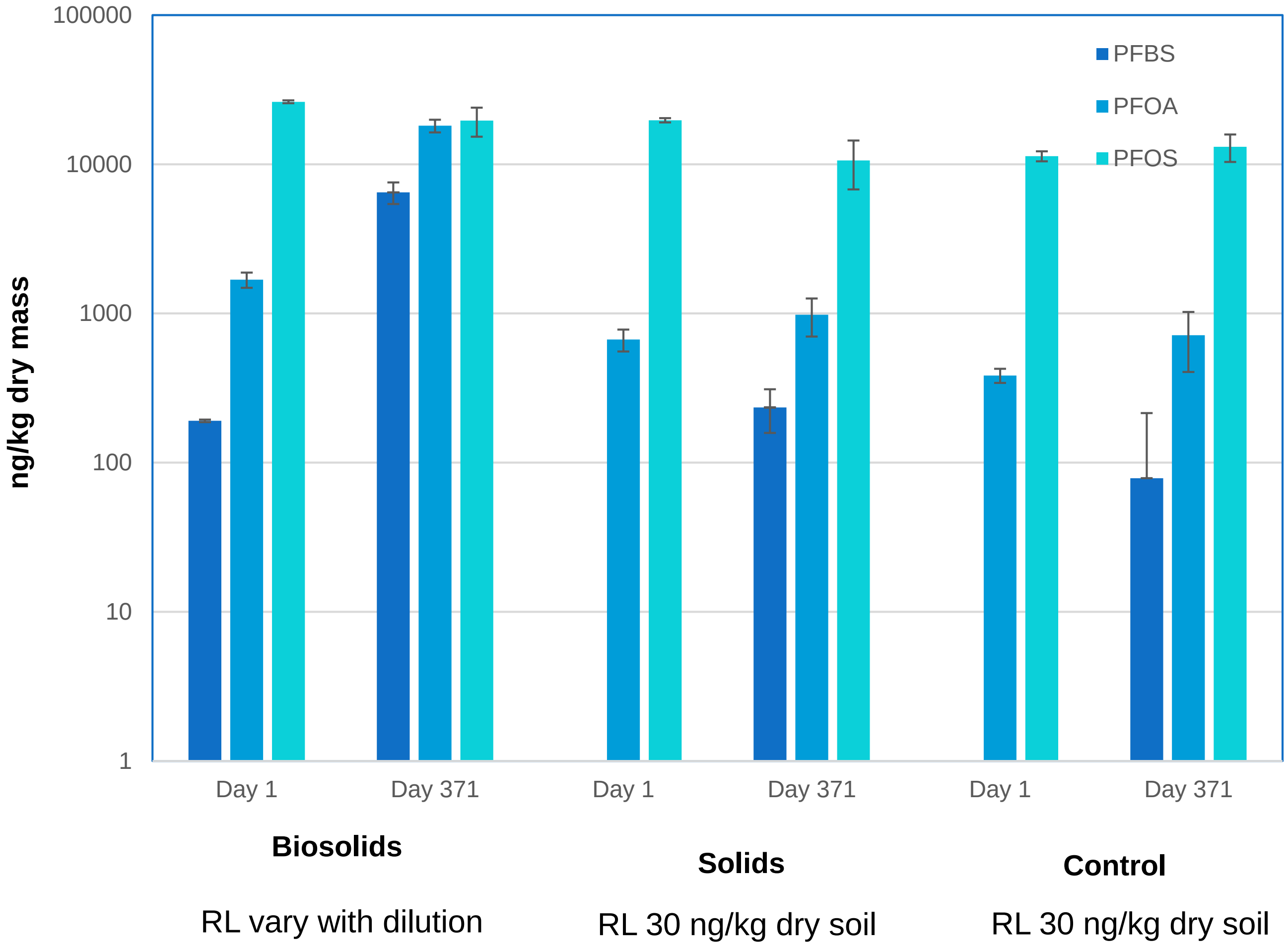
Control Plot PFAS Levels

- Control plot had biosolids last applied 10 years earlier
- There were no intermediates present
- PFOS* is in ng/g (ppb)
- No observed differences



PFAS with EPA Screening Levels

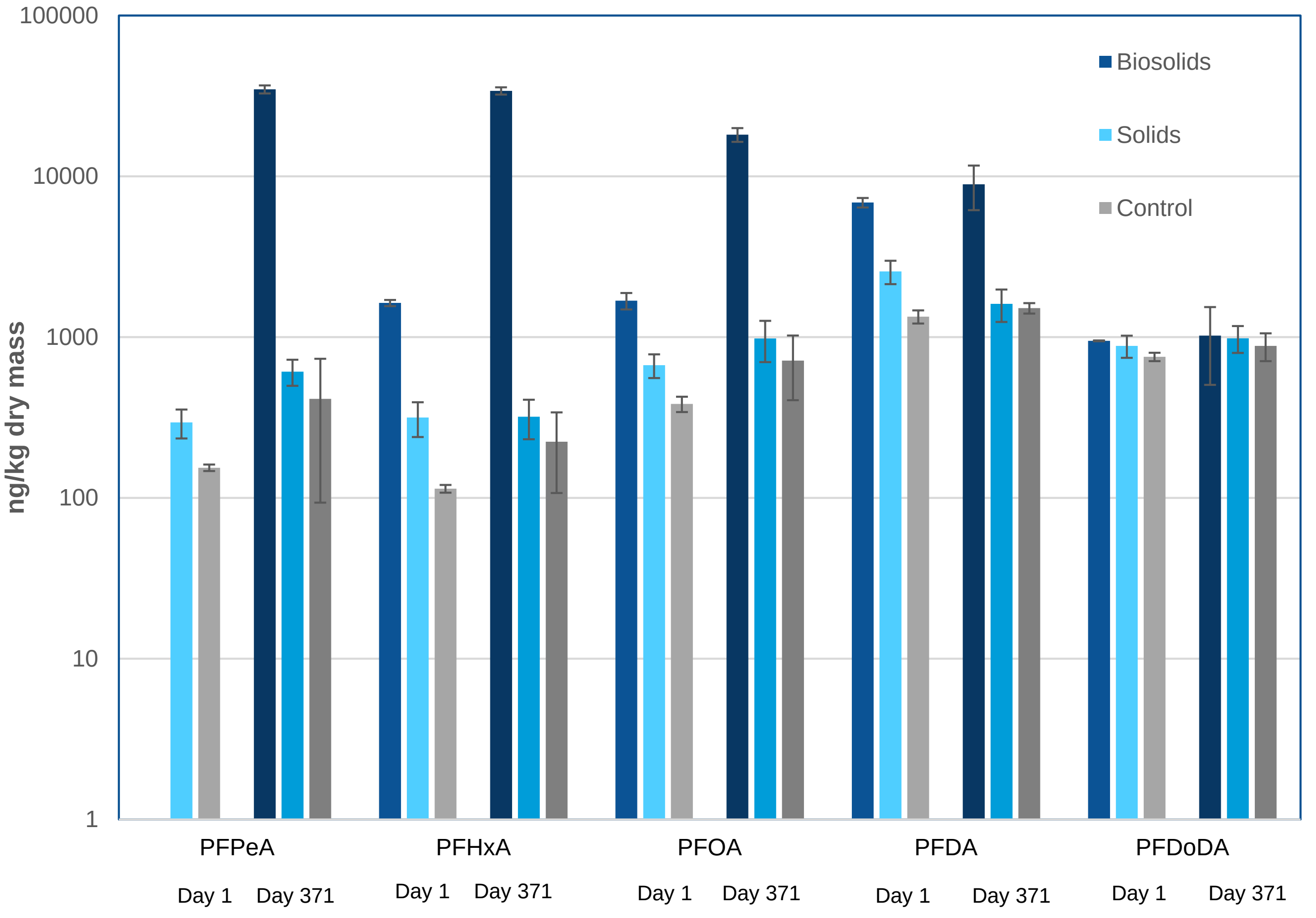
- **Conc above RL are shown**
- **Control soils have PFAS**
- **Conc increase with time for PFBS and PFOA in all trmts**
- **Superfund screening levels**
  - **PFBS 1.6x10^9 ng/kg dry soil**
  - **PFOA 1,260,000 ng/kg dry soil**
  - **PFOS 1,260,000 ng/kg dry soil**
- **Some samples did not meet QA acceptance criteria**
  - **Biosolids controls 56 %**
  - **Solids application 23%**
  - **Control soil 8 %**



Superfund Values at OLEM website (https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables)

Other Observed PFAS

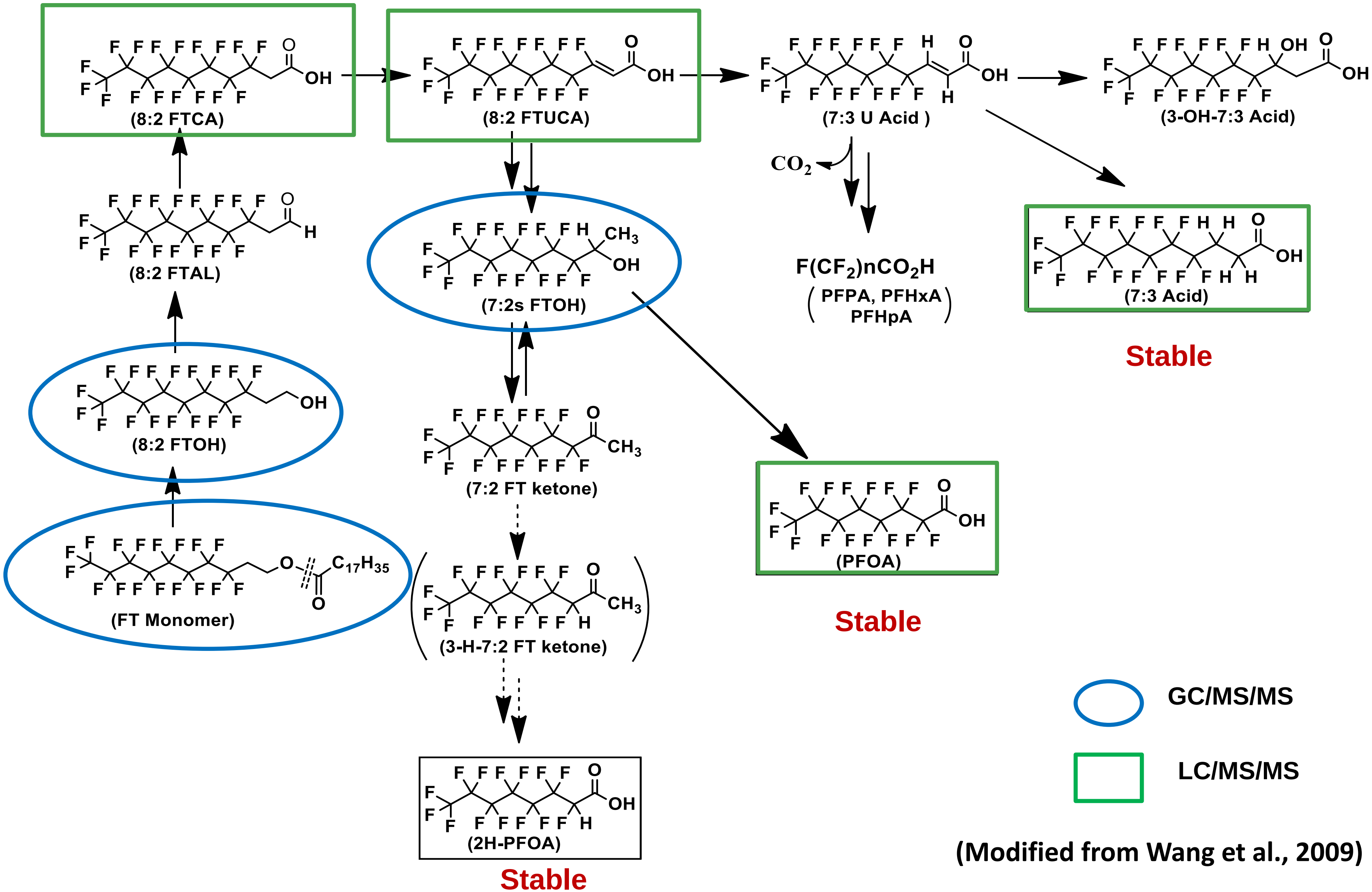
- **Conc above RL are shown**
- **Biosolids show increasing conc with time**
  - **PFPeA**
  - **PFHxA**
  - **PFOA**
- **Solids show increasing conc with time**
  - **PFPeA**
  - **PFOA**
- **Control**
  - **Similar levels over time**
  - **Often similar to solids**



Biosolids Control

- Biosolids placed in buried 5 gallon bucket. Approximately 3 gallons
- Sampled periodically throughout study
- Was vented but protected from rain.
- Material was sampled from interior of mass

Oxidative Transformation to Form PFOA



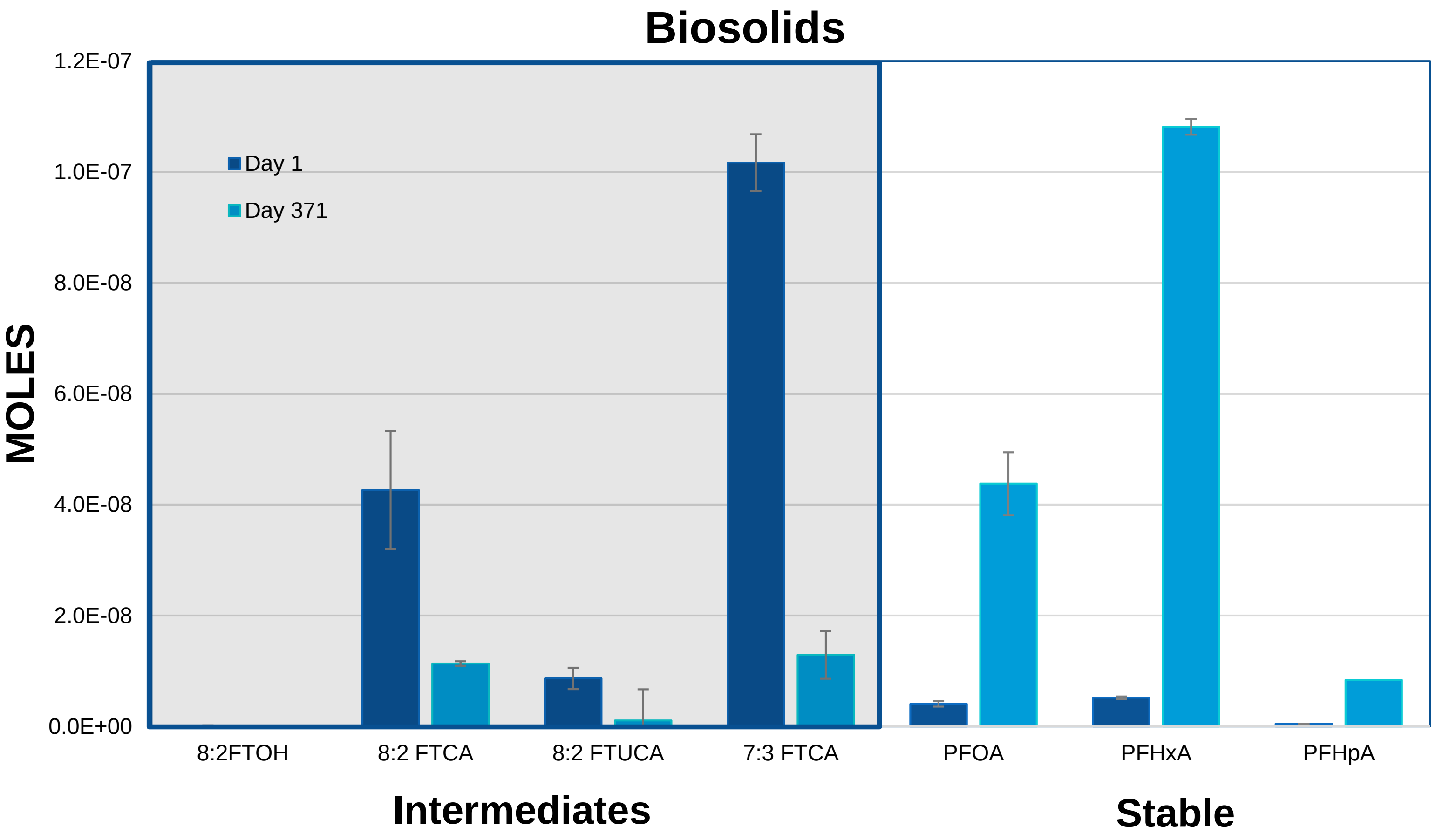
GC/MS/MS

LC/MS/MS

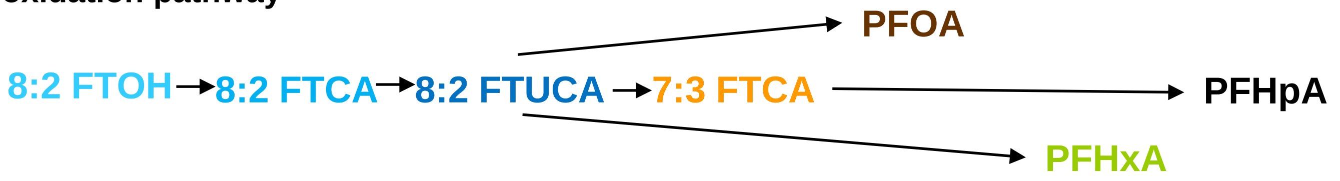
(Modified from Wang et al., 2009)

PFAS Transformation Products

- Intermediates concentration range similar to PFAA concentrations
- Intermediates concentrations decrease with time
- Stable PFAAs increased
- **85% mole balance**

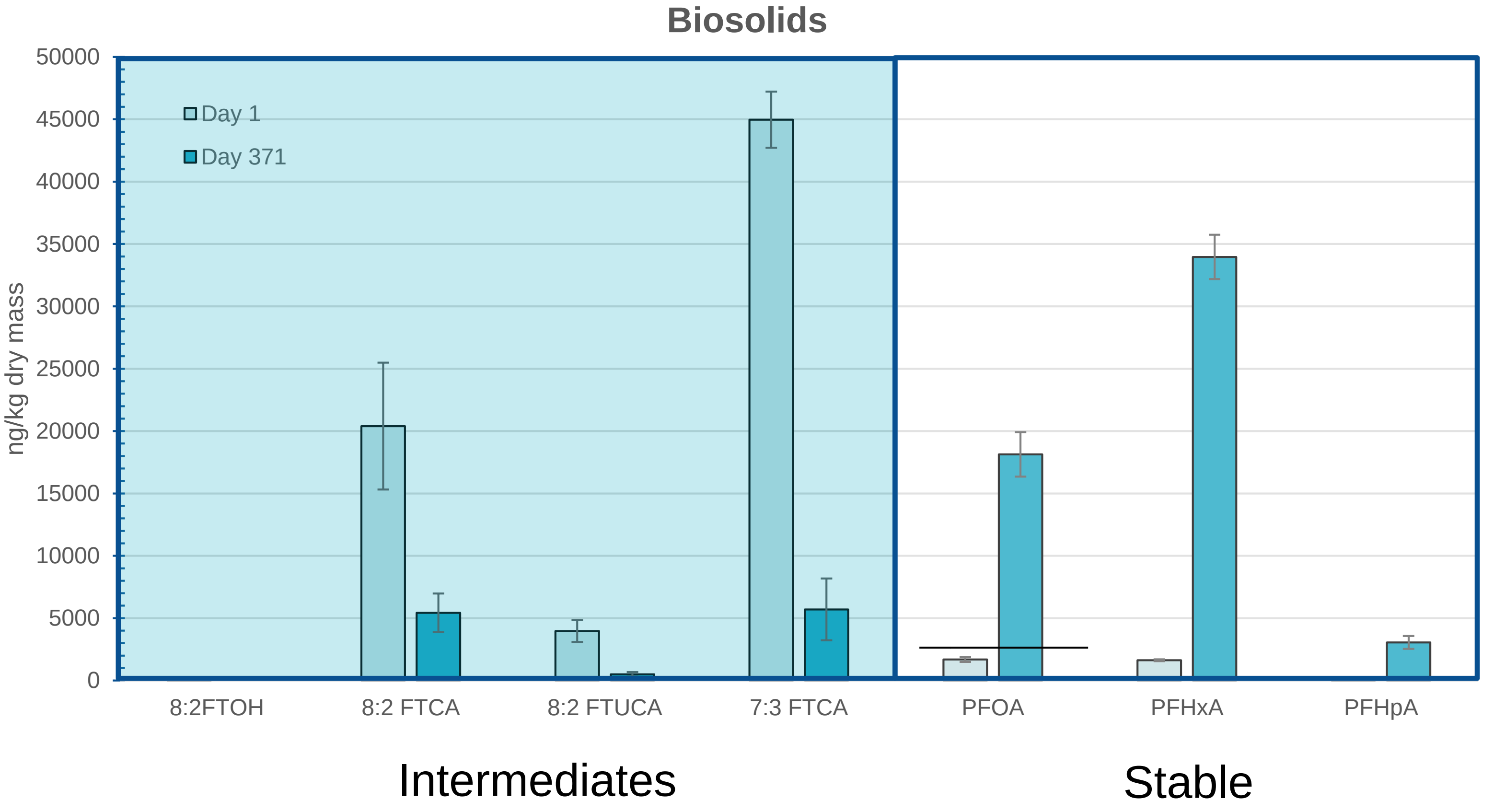


C8 oxidation pathway



Intermediates to Stable Products Percentages

- Intermediates Day 1 account for 95% of PFAS mass in C8 path
- Stable PFAAs Day 371 account for 83% of PFAS mass in C8 path
- Maine biosolids limit 2500 ppt for PFOA
- PFOA 10 times PFHxA 21 times PFHpA 17 times increase over year
- **Intermediates Matter**



Conclusions

- Metals
  - Sodium at background levels in 120 days
  - Copper conc in solids > control and liquids throughout the study
- NP
  - Liquids - removed after 120 days
  - Solids
    - Consistent with previous study, little change in conc for 1st 100 days
    - Slow decline throughout the study
  - Biosolids conc similar throughout the study
- PFAS
  - Observed in all trmts
  - Lower Molecular Weight (MW) conc > higher MW conc
  - Intermediates present and appear to convert to stable end products

Land Application of Biosolids

More studies needed to evaluate PFAS and land application of biosolids to assess potential risks. Next study:

- Field site operated for more than 20 years
- Measure PFAS concentration as a function of depth and biosolids application loadings
- Measure PFAS in plants from the application sites
- Measure other chemicals to characterize the site
- Develop conceptual model of biosolids application sites and compare to real world data with the goal of predicting PFAS concentrations

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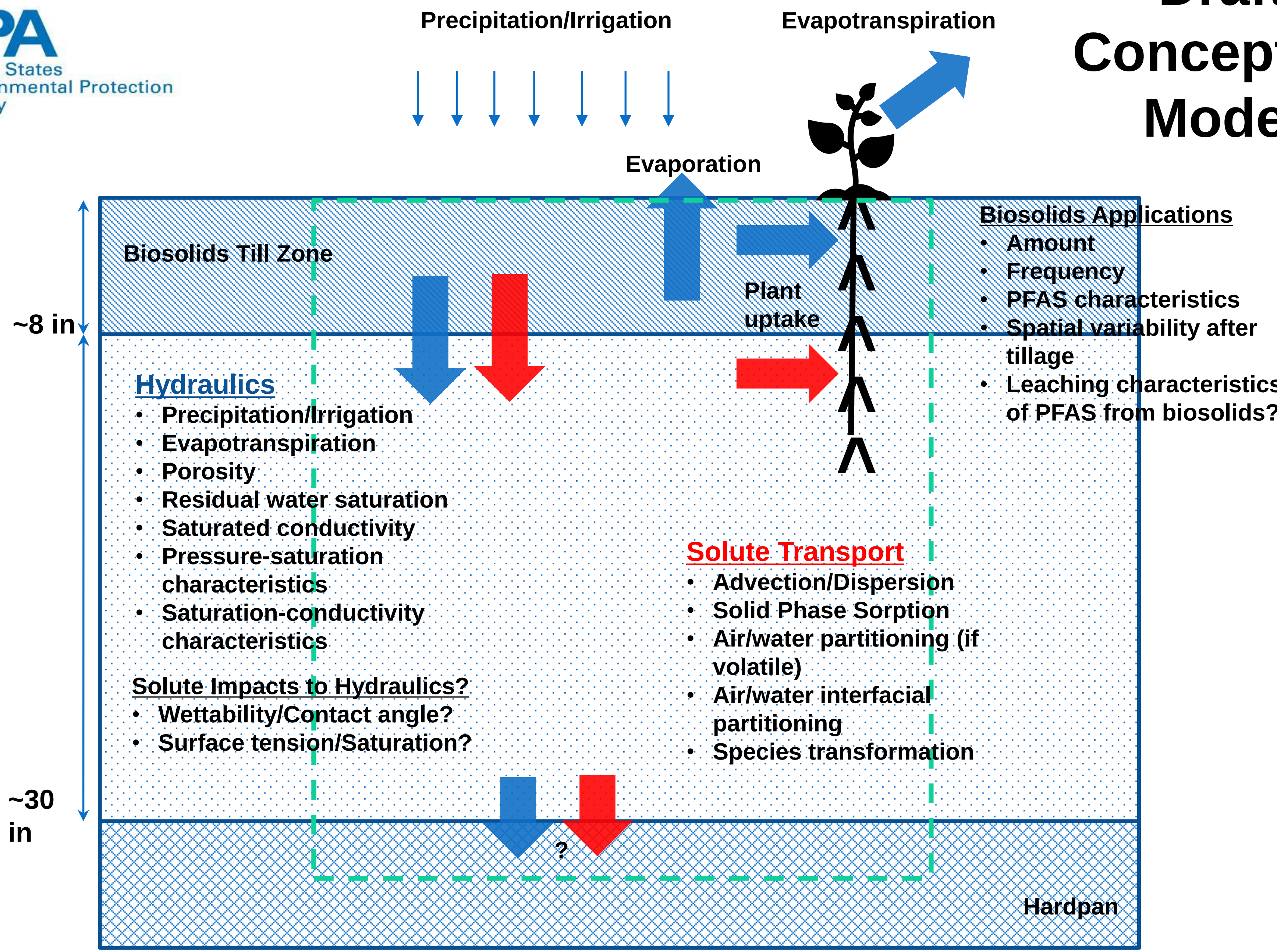
Draft Conceptual Model



Acknowledgements

- Region 5 CRL: Francis Awanya, Anna Knoebel, Nidia Fuentes, Robert Thompson, Rob Snyder, Sylvia Griffin, Dennis Wesolowski, George Schupp
- PTSI: Solidea Bonina, Raghu Venkatapathy, Keith Bisbe, and Karen Koran
- ORD, NRMRL: Laura Boczek, Eric Rhodes, Marc Mills, Robert Ford, Jim Voit, Patrick Clark, Jonathan Ricketts (resigned EPA), Gerry Henderson, Michael Moeykens, Mark Kemper, Jennifer Goetz, Elizabeth Martin (resigned EPA), and Sean Murphy (resigned EPA)
- Others: Kavitha Dasu (currently Battelle Memorial Institute), Lawrence Wong (Senior Environmental Employee, CRL), Jason Hunold, Katrin Friesen (University of Alabama)

Questions

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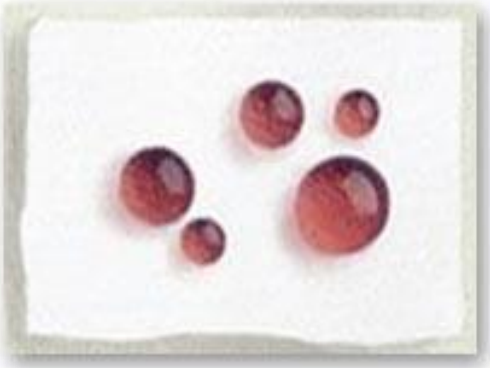
PFAS Sampling

- PFAS found in many common lab and field supplies and equipment
  - Teflon - equipment, seals, sample caps, and bottles
  - Water proof paper and PPE
  - Personal care products
  - Clothing – water and stain repellent fabrics
  - Surface treatment on aluminum foil, food wrappers
  - Blue Ice
  - Supplies – sharpies, post-it notes



- Avoid using these items when possible and pre-screen supplies and equipment
  - Claims of PFOS/PFOA free may contain C6 and other versions of PFAS
  - Read labels and product descriptions carefully

- Information is evolving – check for updates
- Be careful about reusing existing equipment because of cross contamination – Decon and check for contamination

Equipment and Supplies

Avoid:

- Teflon, PTFE, and Fluoropolymers
- Aluminum foil may have PFAS surface treatment
- Decon 90, sharpies, post-it notes, waterproof papers or books
- Blue Ice
- Coated Tyvek

Acceptable

- HDPE, polypropylene, and silicone materials
- Alconox or Liquinox
- Ball point pens
- Water ice – double bag in polyethylene bags
- Uncoated Tyvek (if necessary)
- Sample bottles follow analytical SOP (usually PP or HDPE, not glass)

Other Precautions

- Food packaging may contain PFAS treatments – careful where you eat and wash hands before returning
- Frequent nitrile glove changes
- Collect sample, field, and equipment blanks
- Spiked blanks used by some

Best practice

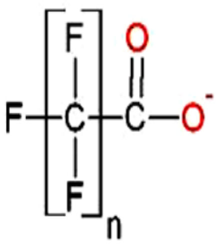
- Pretest materials and products for PFAS contamination
- Keep separate from “normal” supplies
- Test periodically for cross contamination

Acronyms

- PFAS- per- and polyfluorinated alkyl substances
- PFCAs- perfluorinated carboxylic acids
- PFSAs- perfluorinated sulfonic acids
- PFHxA- perfluorohexanoic acid
- PFOA- perfluorooctanoic acid (MPFOA- isotopic version)
- PFOS- perfluorooctane sulfonic acid (MPFOS- isotopic version)
- PFHpA- perfluoroheptanoic acid
- PFPeA- perfluoropentanoic acid
- PFBS- perfluorobutane sulfonic acid
- PFHpS- perfluoroheptane sulfonic acid
- FTUCA- fluorotelomer unsaturated acid (8:2 measured)
- FTCA- fluorotelomer saturated acid (6:2, 8:2, 7:3 and 10:2 measured)
- WWTP- wastewater treatment plant
- MRM- multiple reaction monitoring
- RSD- relative standard deviation
- PFNA- perfluorononionic acid (MPFNA- isotopic version)
- QA- quality assurance
- PFDA- perfluorodecanoic acid
- PFDoDA- perfluorododecanoic acid
- LC/MS/MS- liquid mass spectrometry
- GC/MS/MS- gas mass spectrometry
- PFAA- perfluorinated alkyl acid
- FTOH- fluorotelomer alcohol
- POTW- publicly owned treatment works
- MW- molecular weight

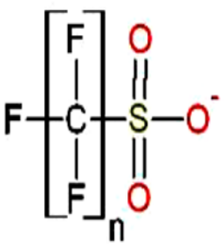
PFAS Analytes

Perfluoroalkyl Carboxylates



PFBA	n = 4
PFPeA	n = 5
PFHxA	n = 6
PFHpA	n = 7
PFOA	n = 8
PFNA	n = 9
PFDA	n = 10
PFUdA	n = 11
PFDoA	n = 12
PFTrA	n = 13
PFTeA	n = 14

Perfluoroalkyl Sulfonates



PFBS	n = 4
PFPeS *	n = 5
PFHxS	n = 6
PFHpS	n = 7
PFOS	n = 8
PFNS *	n = 9
PFDS	n = 10

Backe et al. 2013 ES&T