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Land Application Field Study II

MWEA Biosolids Conference



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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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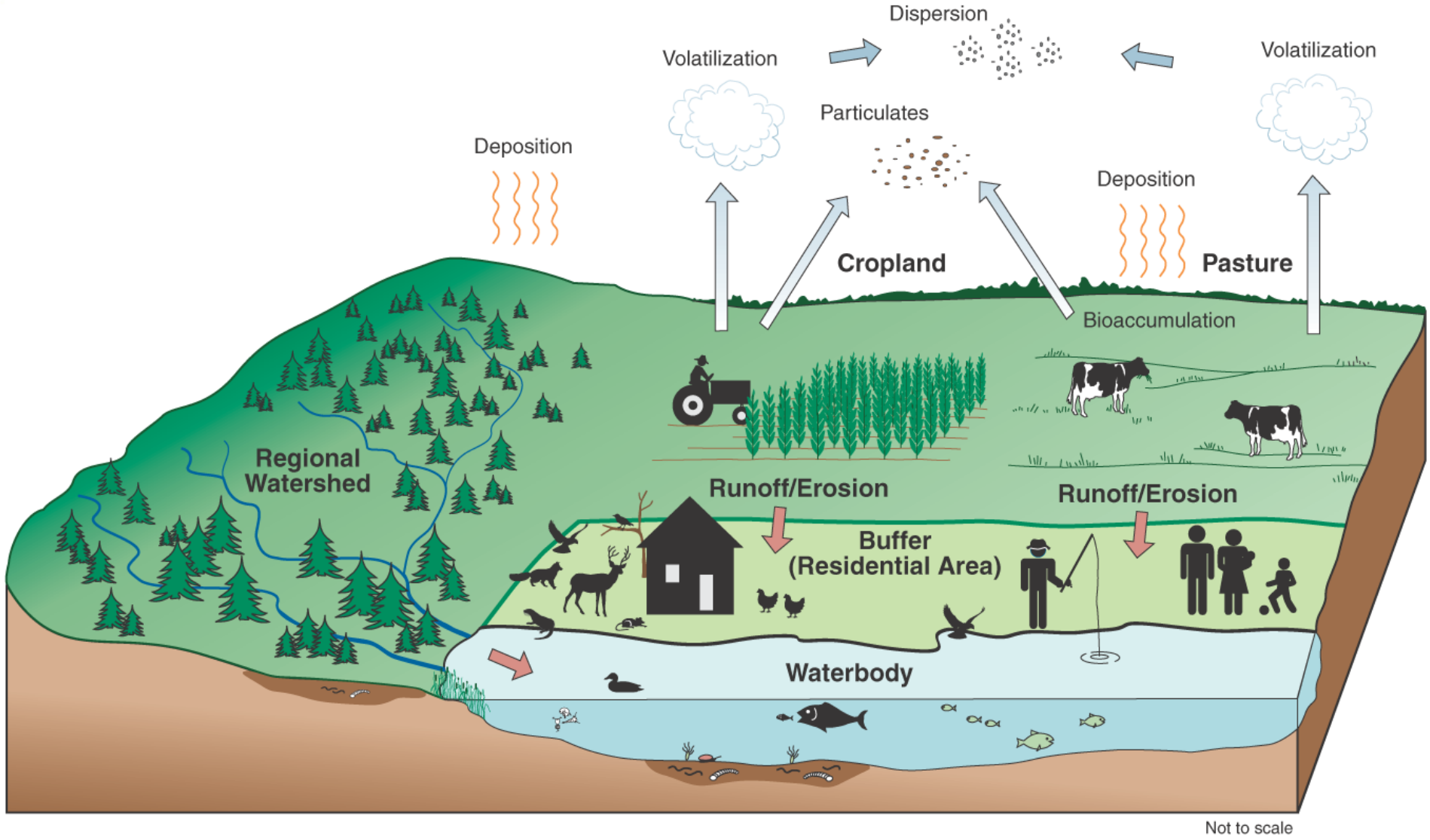


Multimedia Land Application Study: Field Study I

- 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

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**

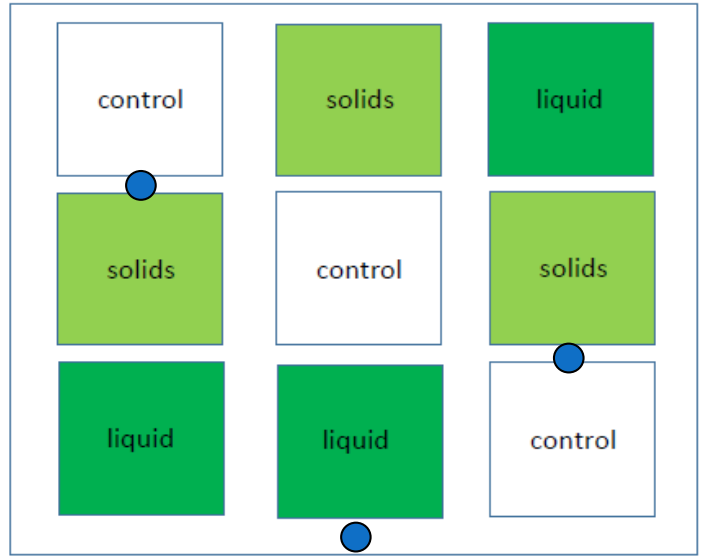
Soil Study Conclusions

- 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)

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Field Plots After Application

Control

Solids

Liquid

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• Field Plots in Spring After Application

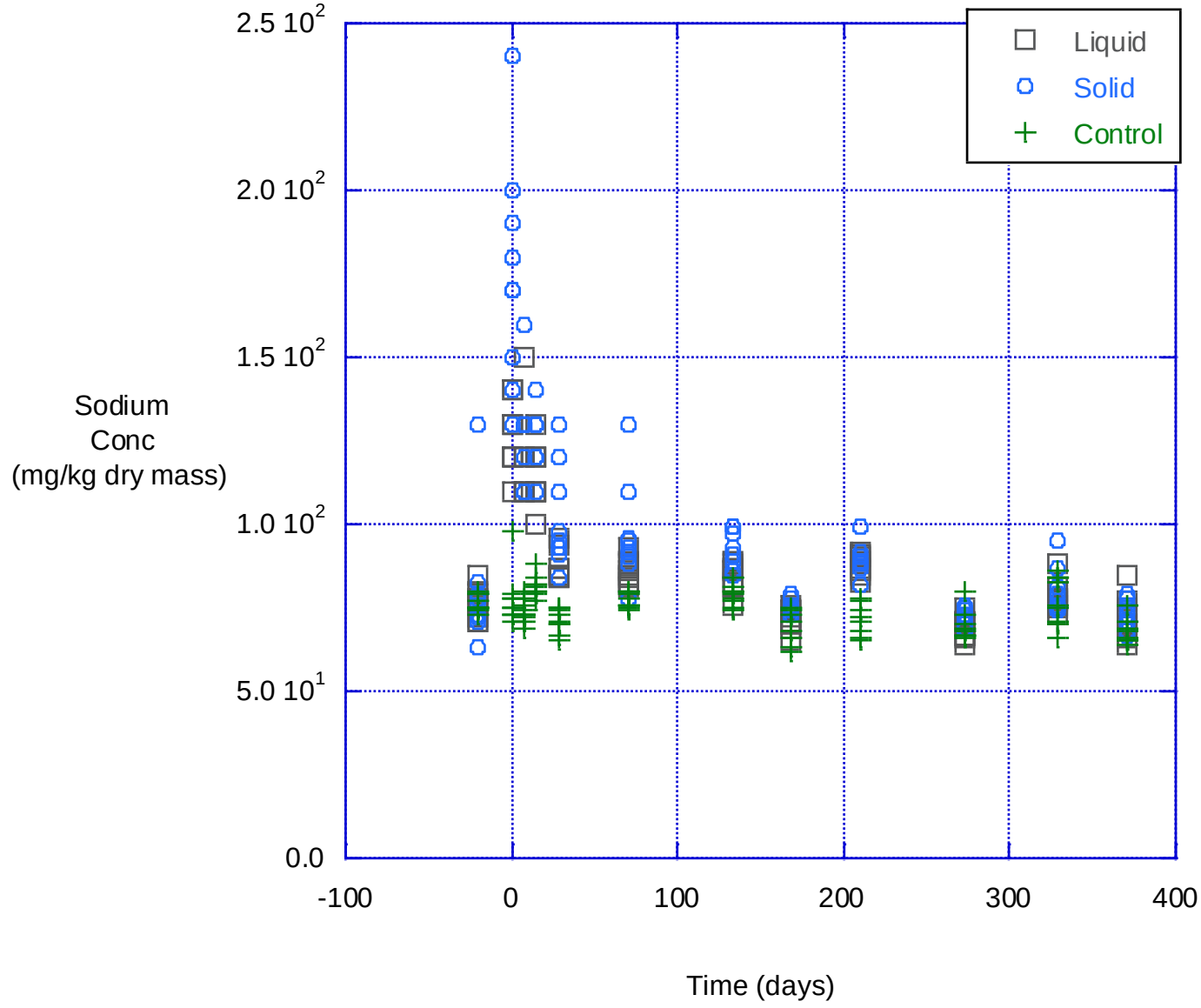
Samples From Plots

Control Solid Liquid

Sodium Data

Concentrations

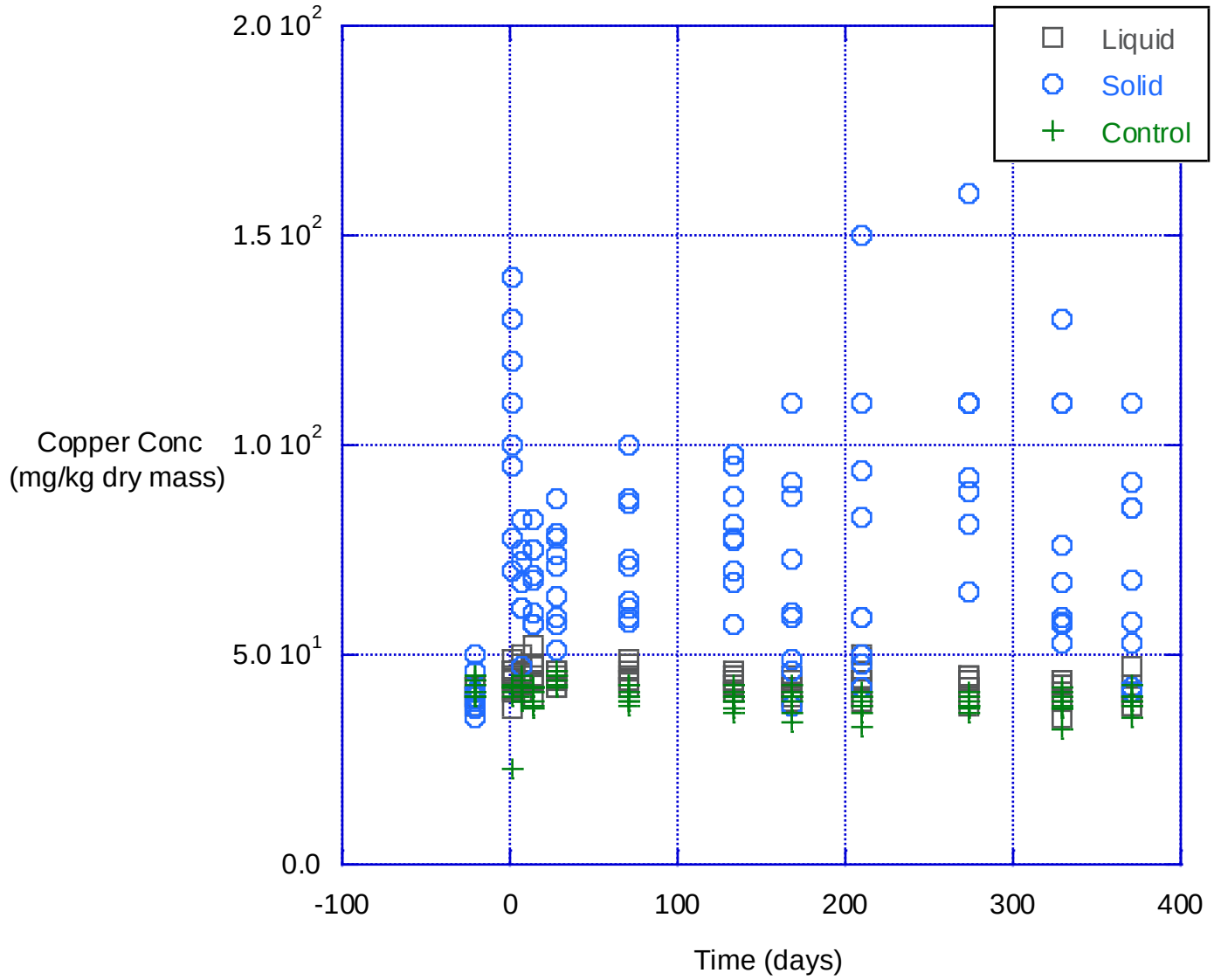
- **Elevated in the solids and liquid trmts after application**
- **By day 120 near control levels**



Copper Data

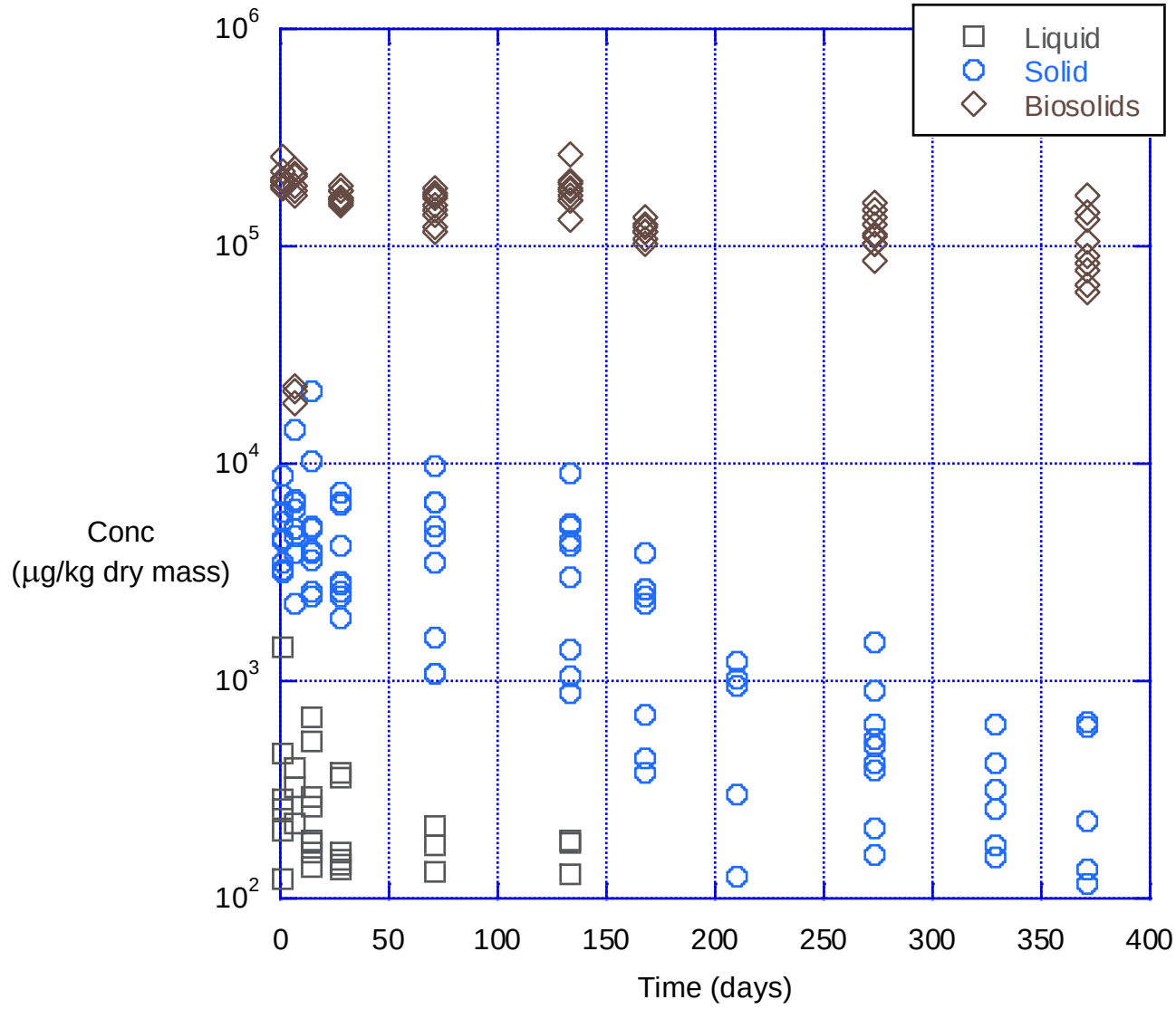
Concentrations

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



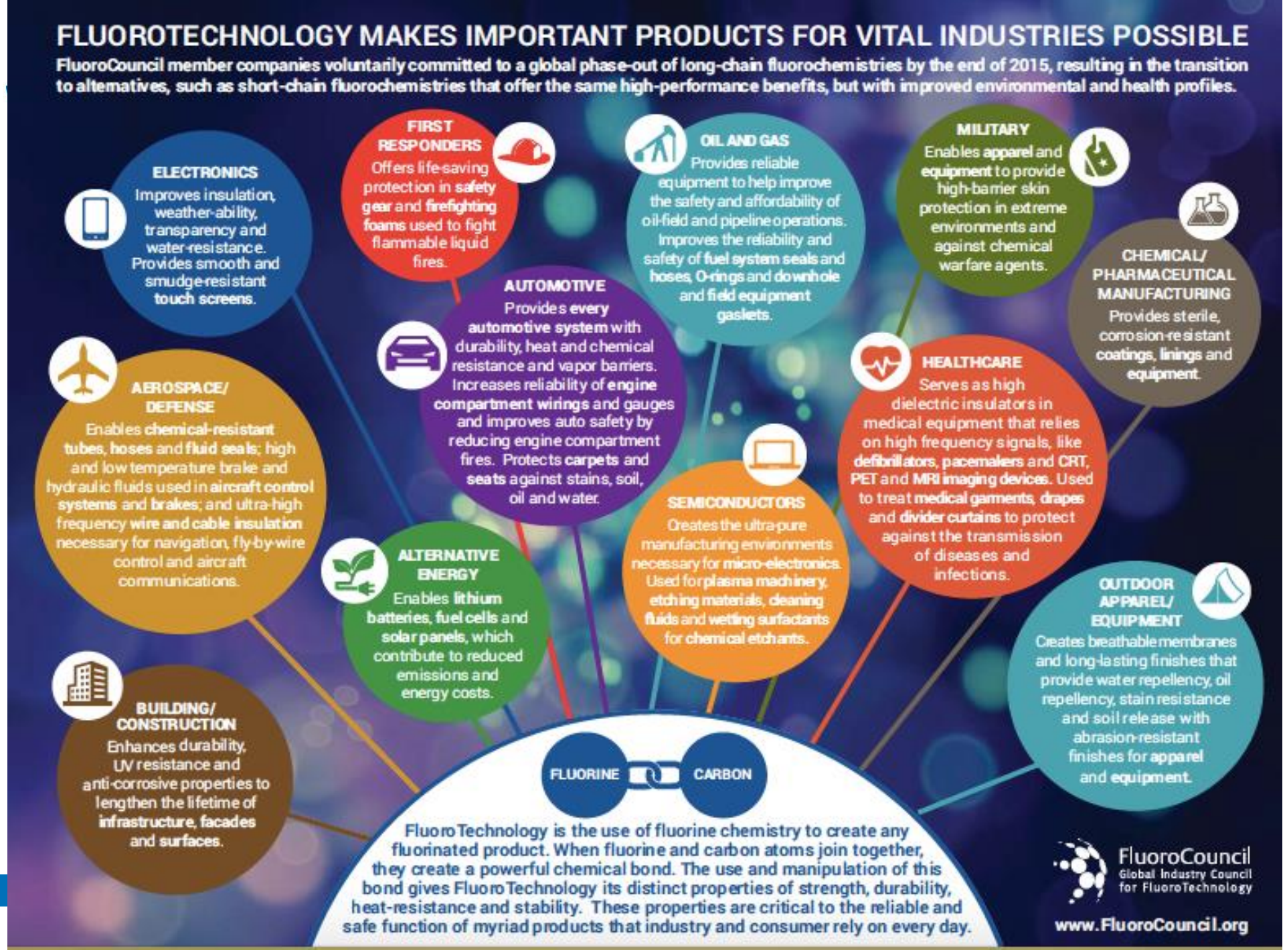
Nonylphenol (NP) Data

- **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.



PFAS – More Than Just PFOA and PFOS

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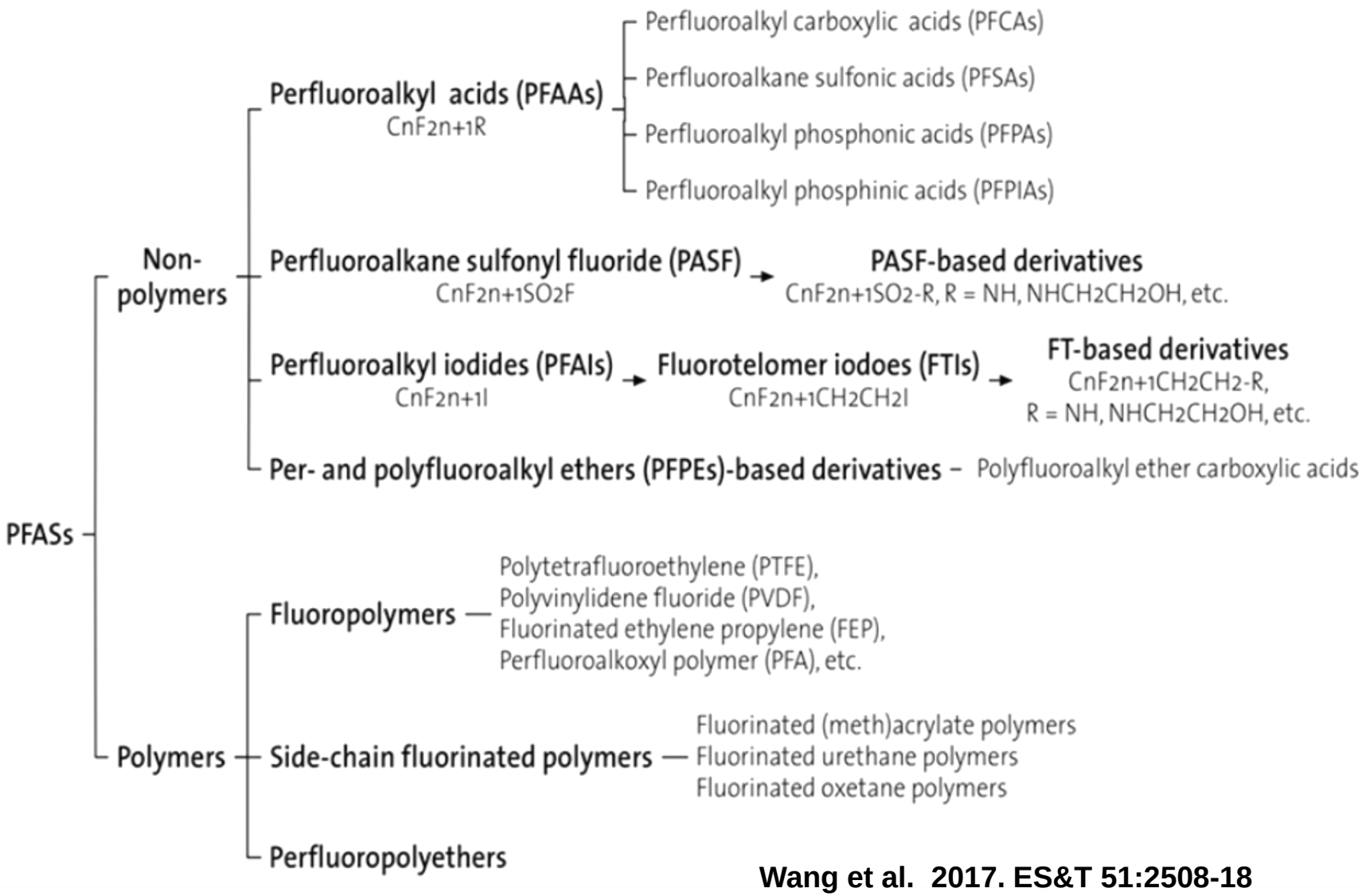


Wang et al. 2017. ES&T 51:2508-18

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

2 g sample

Surrogate

10 mL Methanol

Mix

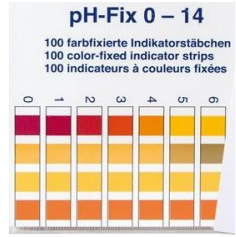
20 µL NH_4OH

Tumble 1 hr

Filter

10 µL Acetic Acid

Mix



Check pH

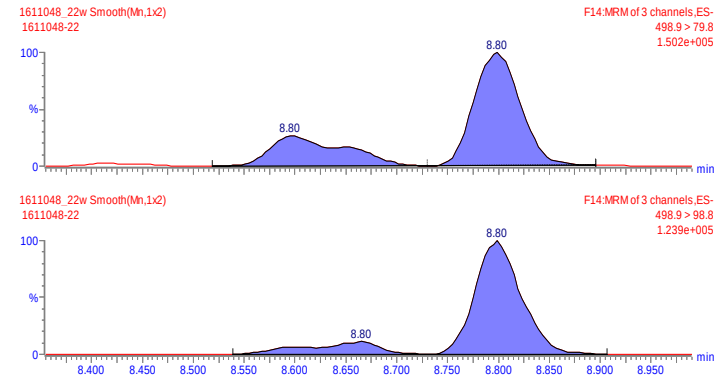
Transfer 1 mL sample in vial (pour)

Run time 21 min

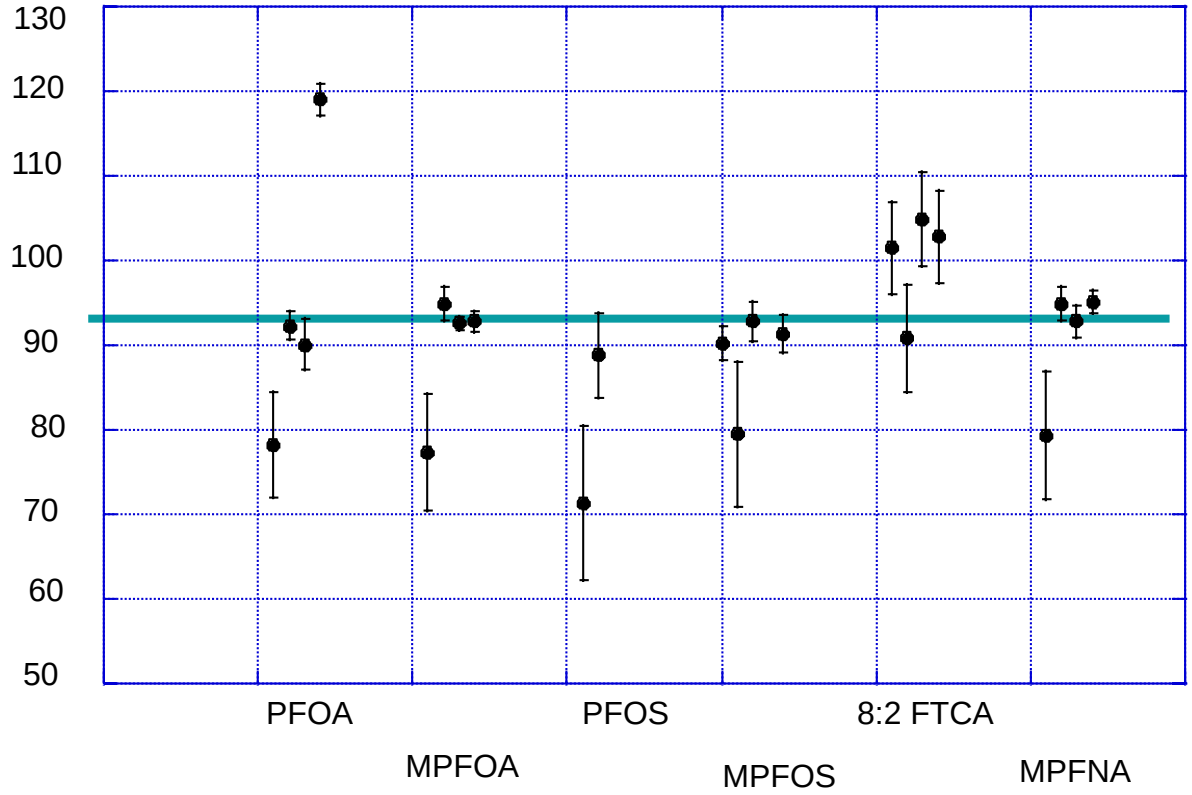
Based on schematic by William Lipps, Shimadzu

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

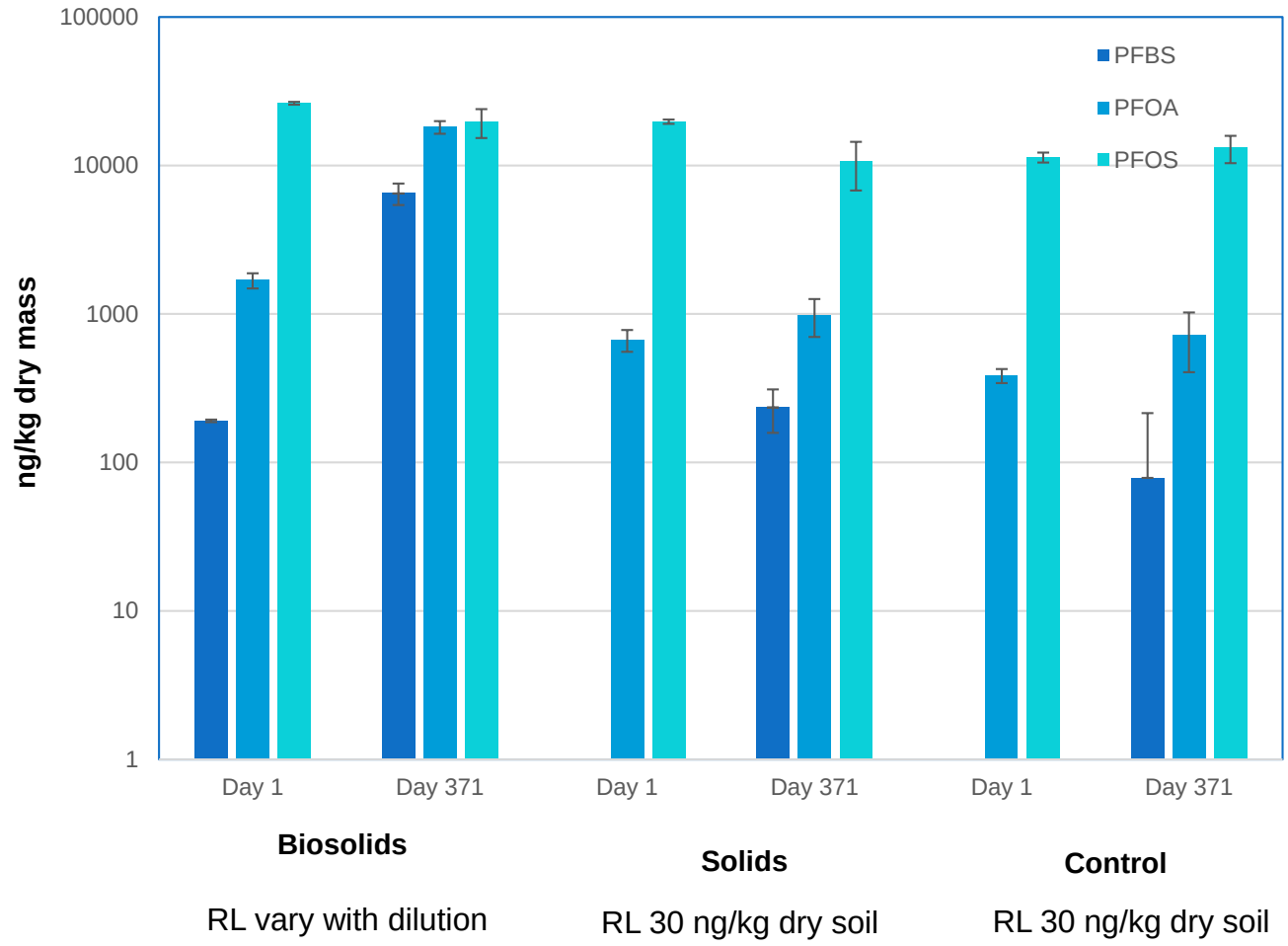
Liquid

Solid

Control

PFAS with EPA Screening Levels

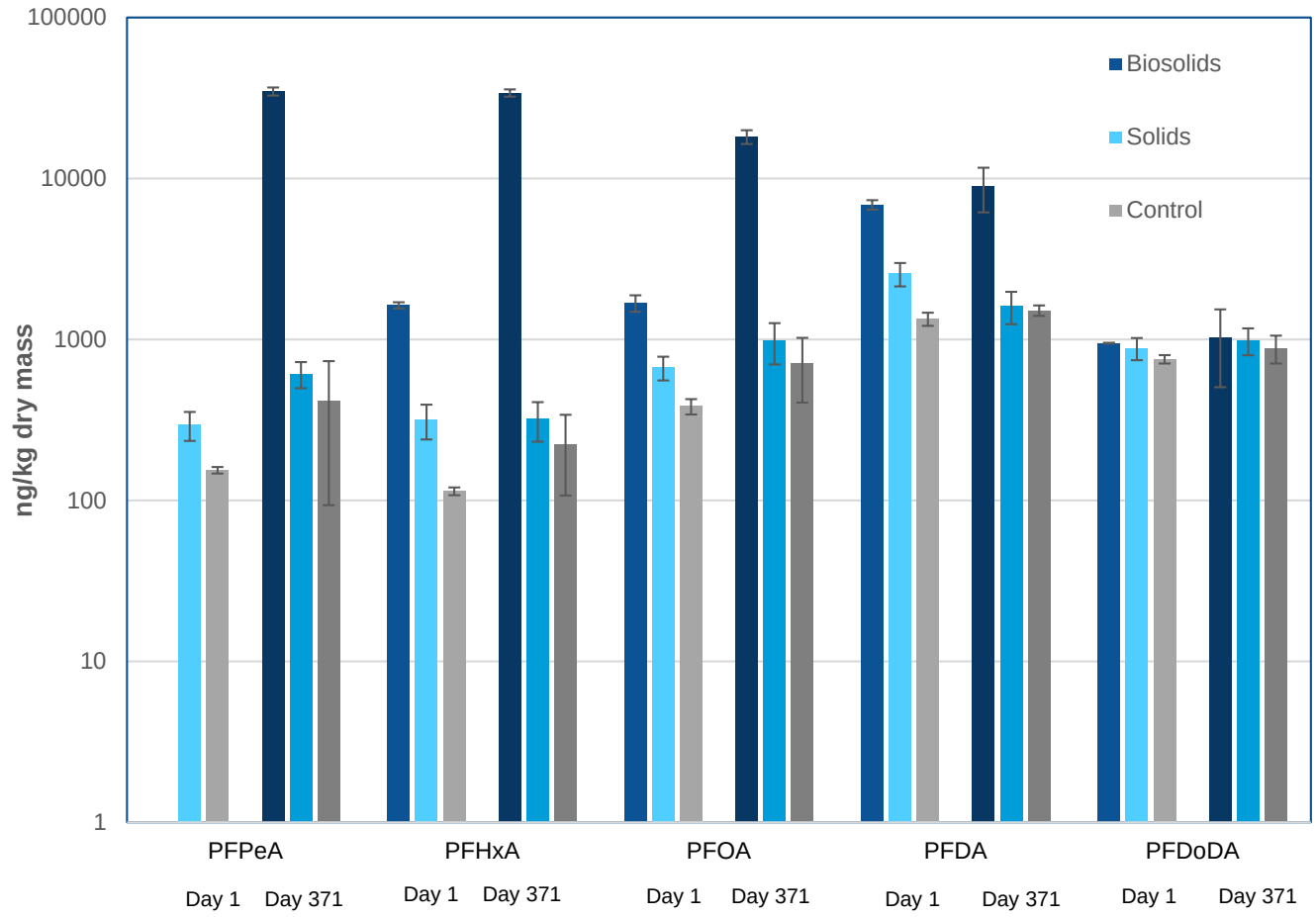
- Conc above RL are shown
- Control soils have PFAS
- Conc increase with time for PFBS and PFOA in all trmts
- Superfund screening levels
  - PFBS 1.6x10^9 ng/kg dry soil
  - PFOA 1,260,000 ng/kg dry soil
  - PFOS 1,260,000 ng/kg dry soil
- Some samples did not meet QA acceptance criteria
  - Biosolids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



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

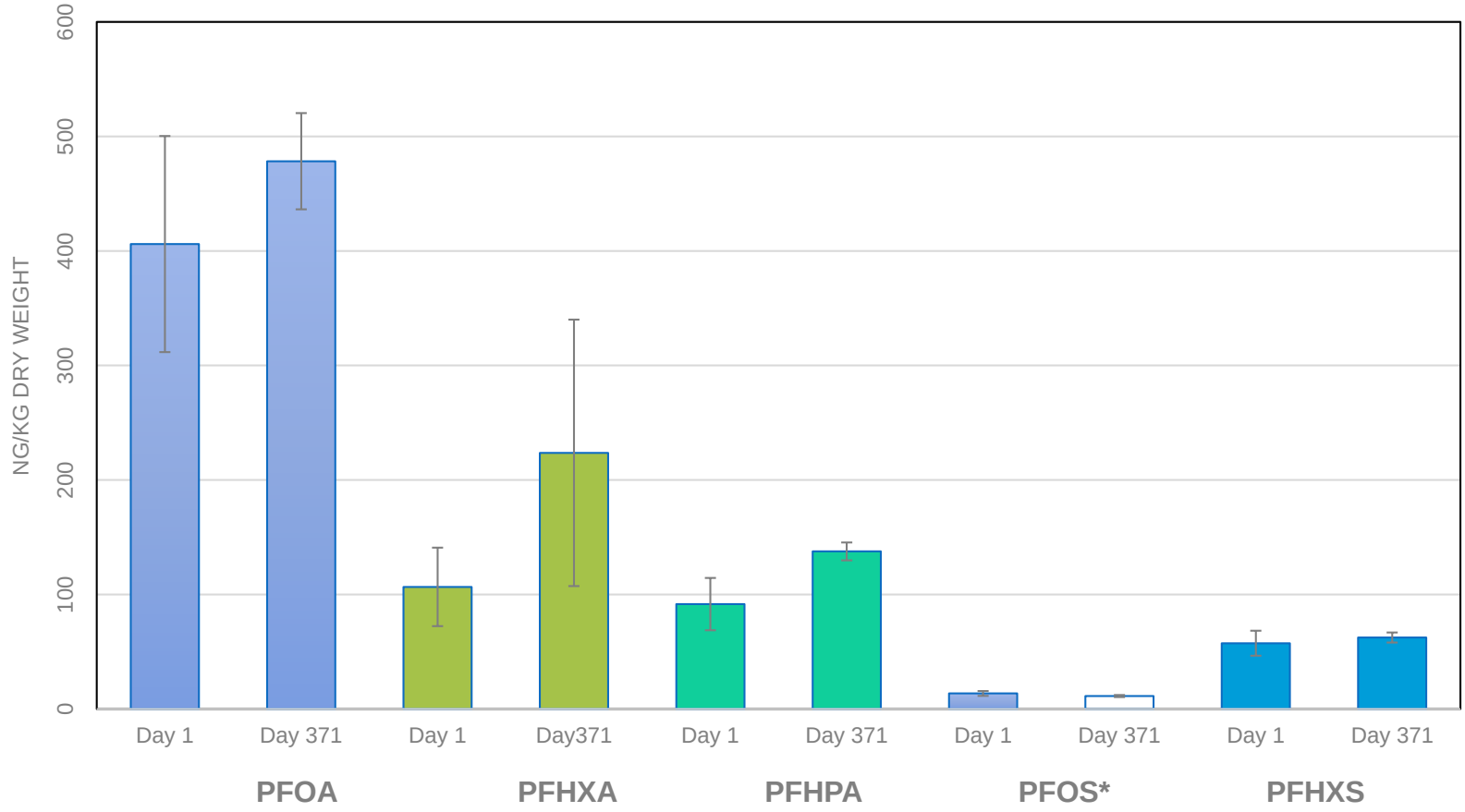
Other Observed PFAS

- **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**



Control Plot PFAS Levels

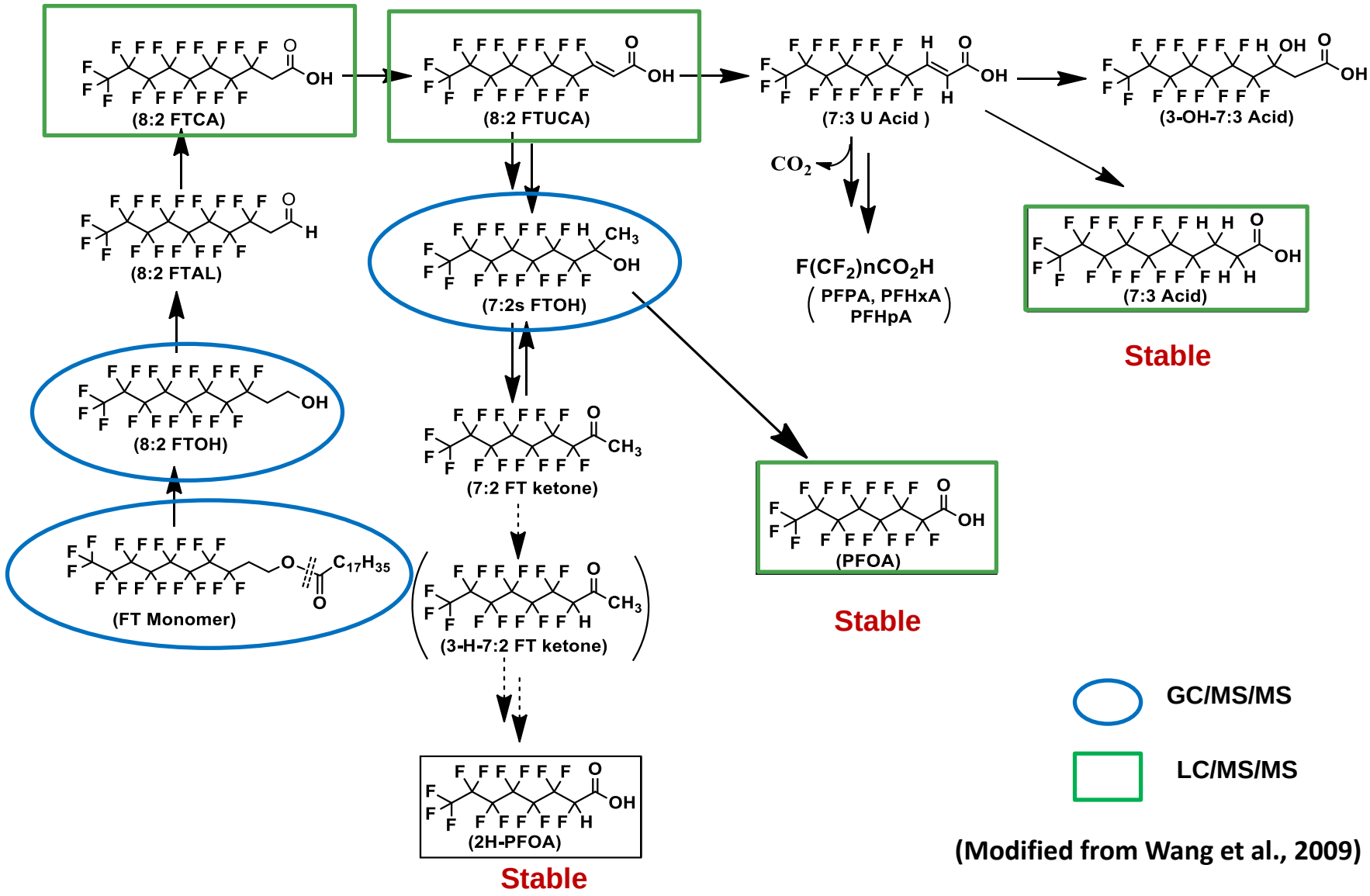
- Control plot had biosolids last applied 10 years earlier
- There were no intermediates present
- PFOS* is in ng/g (ppb)
- No observed differences



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

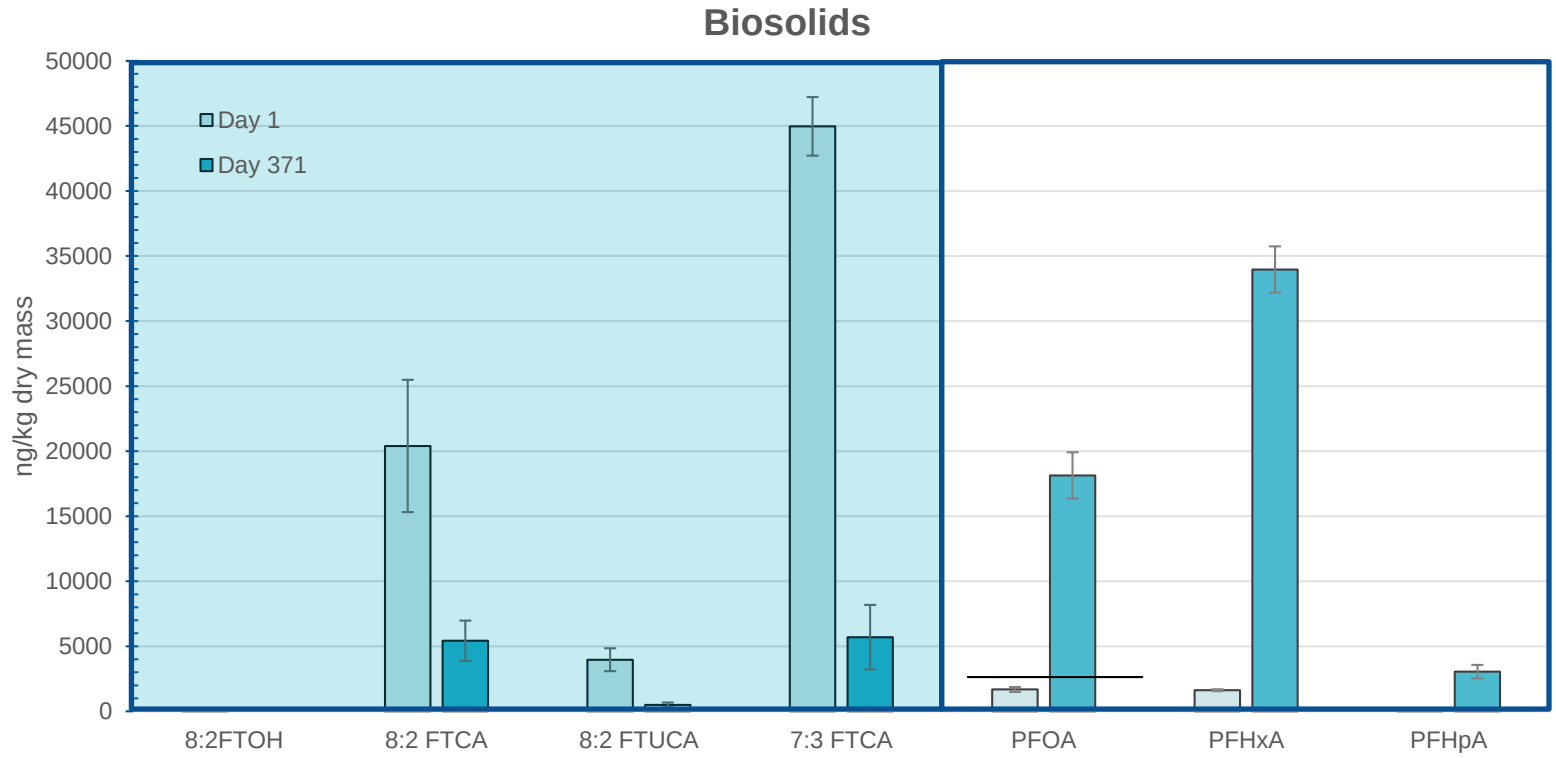
Oxidative Transformation to Form PFOA



(Modified from Wang et al., 2009)

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**



C8 oxidation pathway

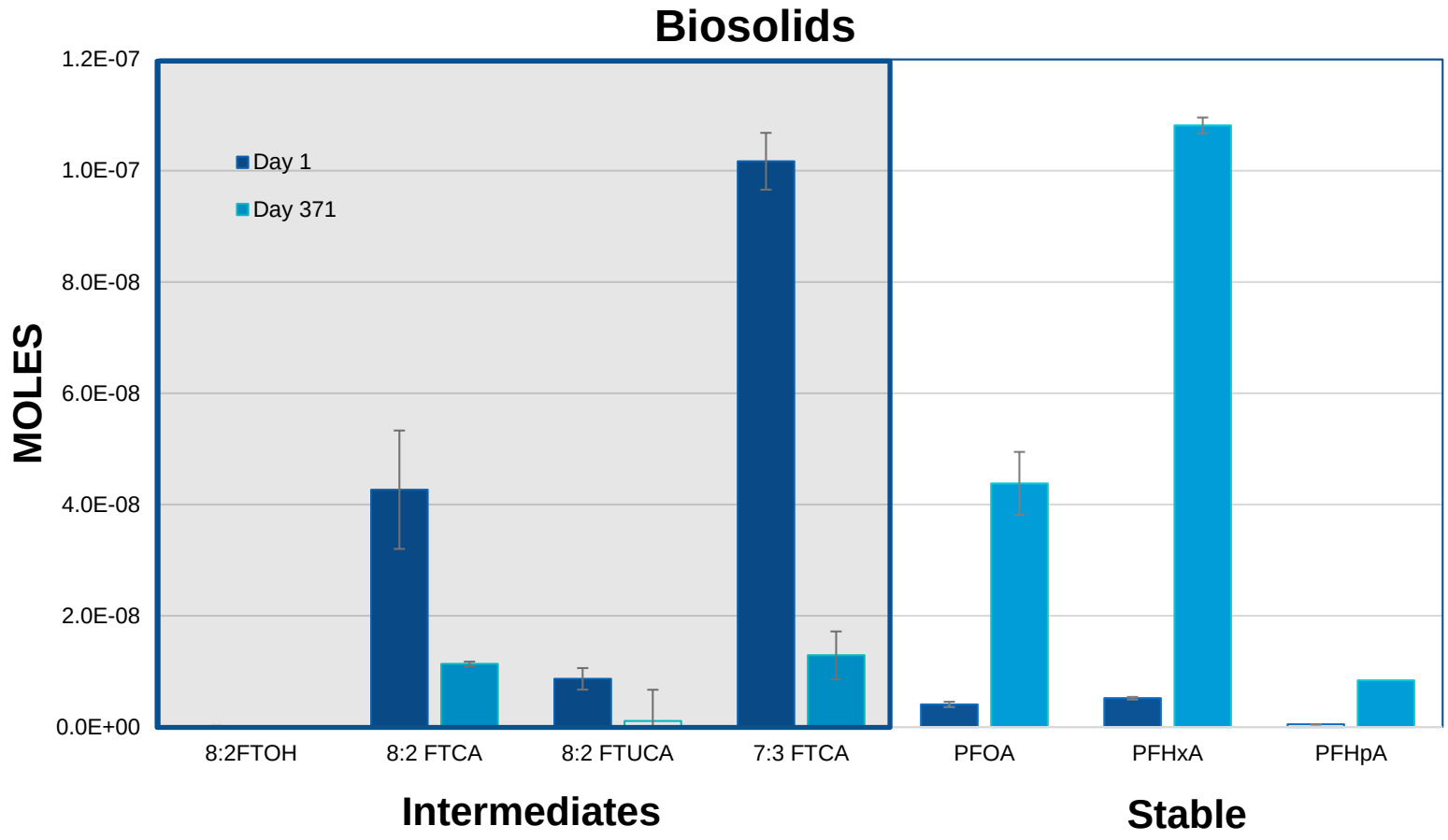
8:2 FTOH → 8:2 FTCA → 8:2 FTUCA → 7:3 FTCA → PFHpA

8:2 FTUCA → PFOA

7:3 FTCA → PFHxA

PFAS Transformation Products

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



C8 oxidation pathway

Conclusions

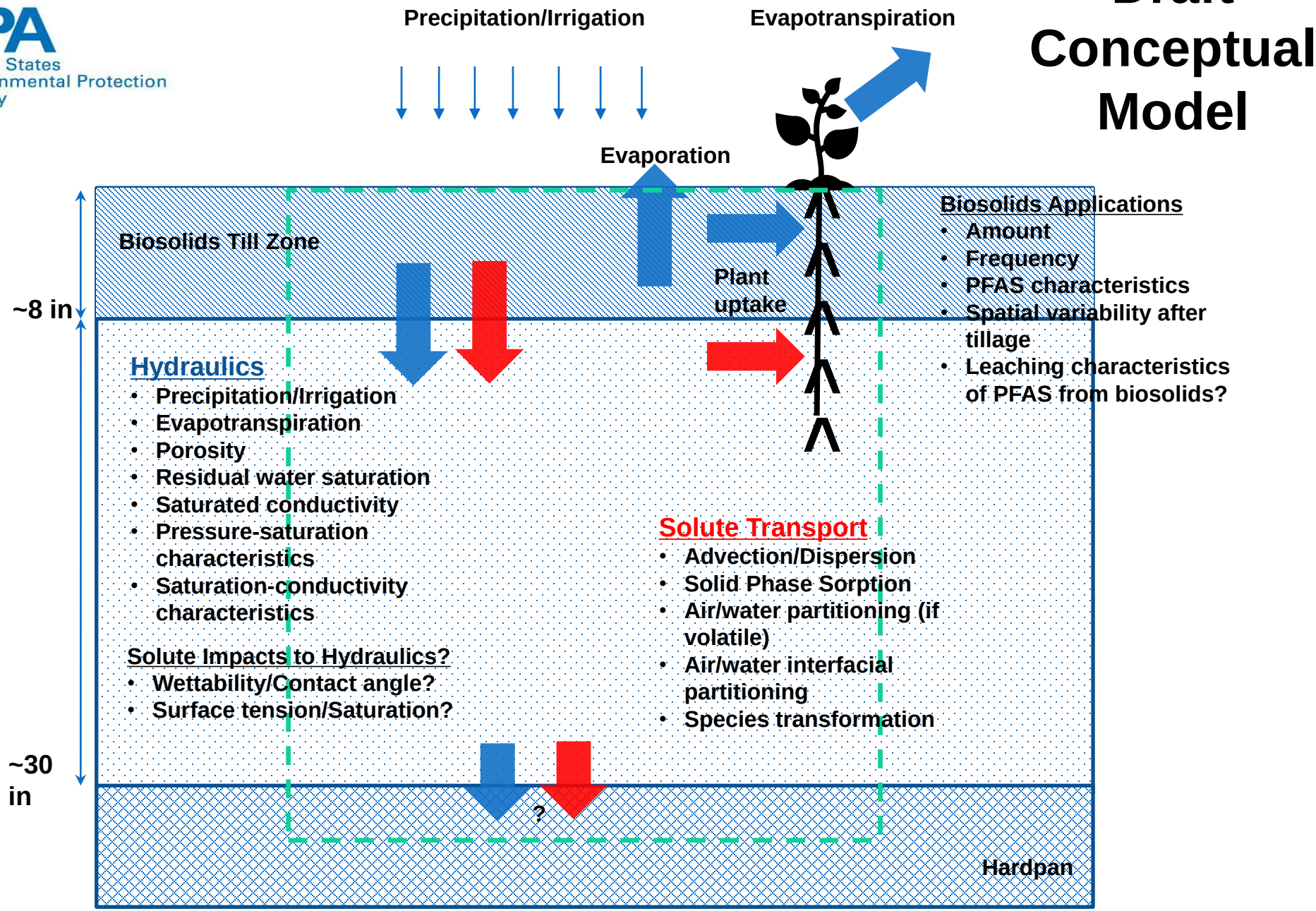
- **Metals**
  - **Sodium at background levels in 120 days**
  - **Copper conc in solids > control and liquids throughout the study**
- **NP**
  - **Liquids - removed after 120 days**
  - **Solids**
    - **Consistent with previous study, little change in conc for 1st 100 days**
    - **Slow decline 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

Draft Conceptual Model



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

Acknowledgements

- **Region 5 CRL: Francis Awanya, Anna Knoebel, Nidia Fuentes, Robert Thompson, Rob Snyder, Sylvia Griffin, Dennis Wesolowski, George Schupp**
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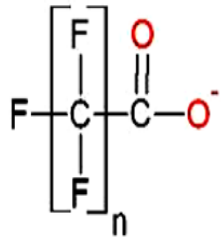
- **Others: Kavitha Dasu (currently Battelle Memorial Institute), Lawrence Wong (Senior Environmental Employee, CRL), Jason Hunold, Katrin Friesen (University of Alabama)**

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

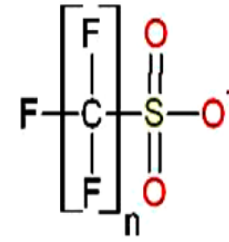
PFAS Analytes

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