MIGRATION OF HIGHLY FLUORINATED CHEMICALS FROM CONTAMINATED SOILS INTO FOOD CROPS

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EARTH ENERGY ENVIRONMENT

In memory of Prof. Andrea C. Blaine

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1975-2016

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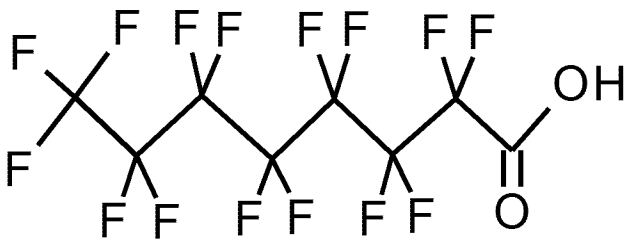
Terminology and Acronyms

PFC = perfluorinated chemical, “perfluorochemical”

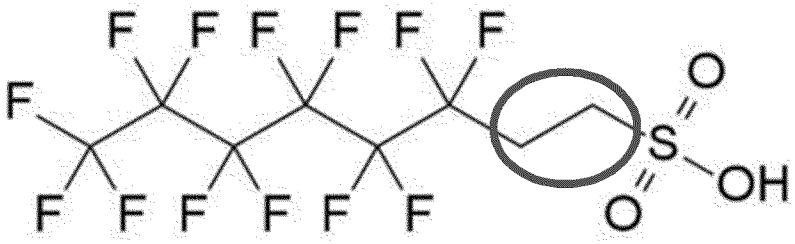
PFC = perfluorocarbons, a family of greenhouse gases

***Poly*- and per**fluoroalkyl substances = **PFASs**

Perfluoroalkyl acids = **PFAAs (a subclass of PFASs)**



Perfluoroalkyl acid

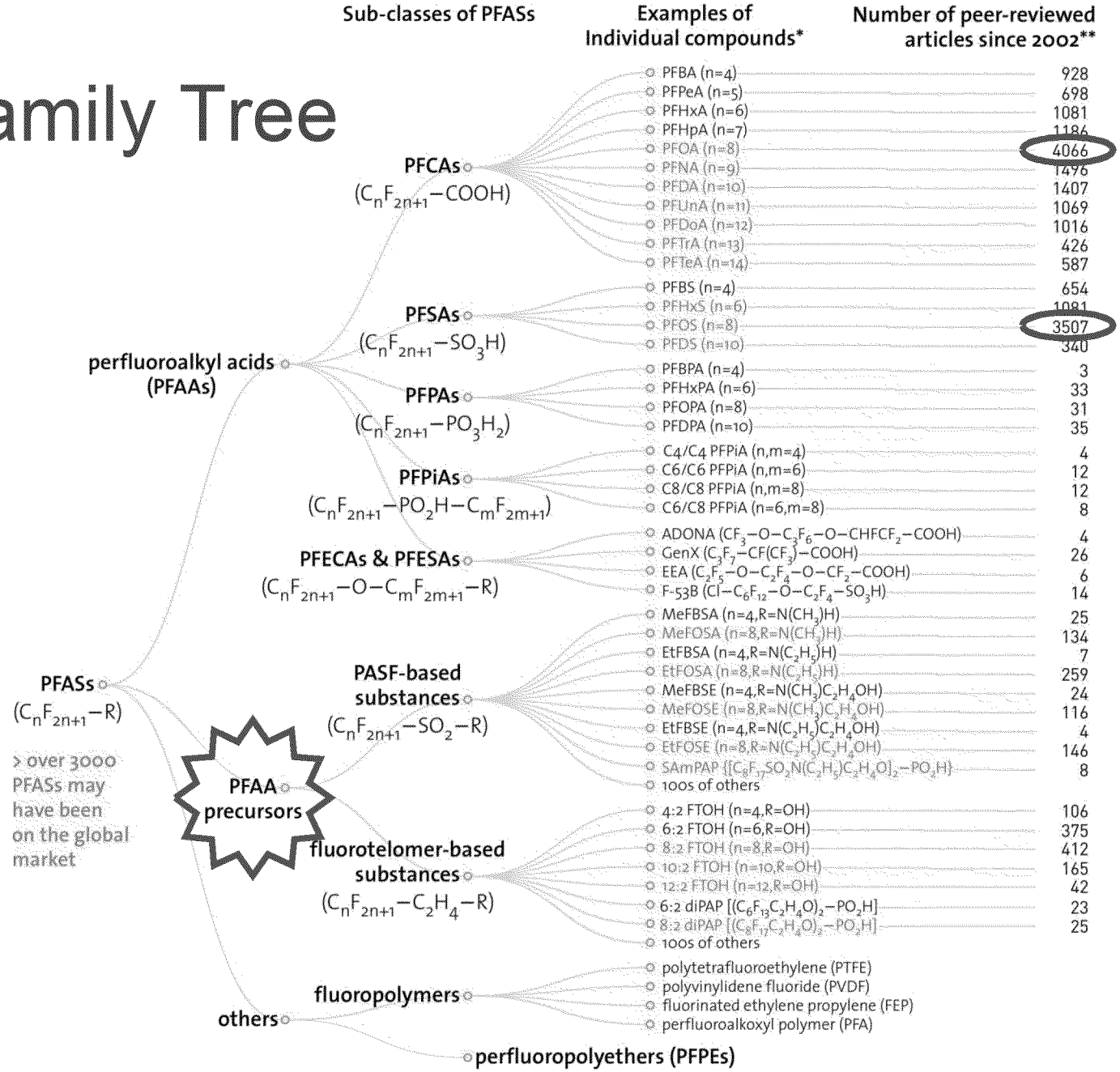


Polyfluoroalkyl acid

Buck *et al.*, 2011, *IEAM*.

PFAS Family Tree

It's not just PFOS and PFOA



Wang *et al.* 2017, *ES&T*.

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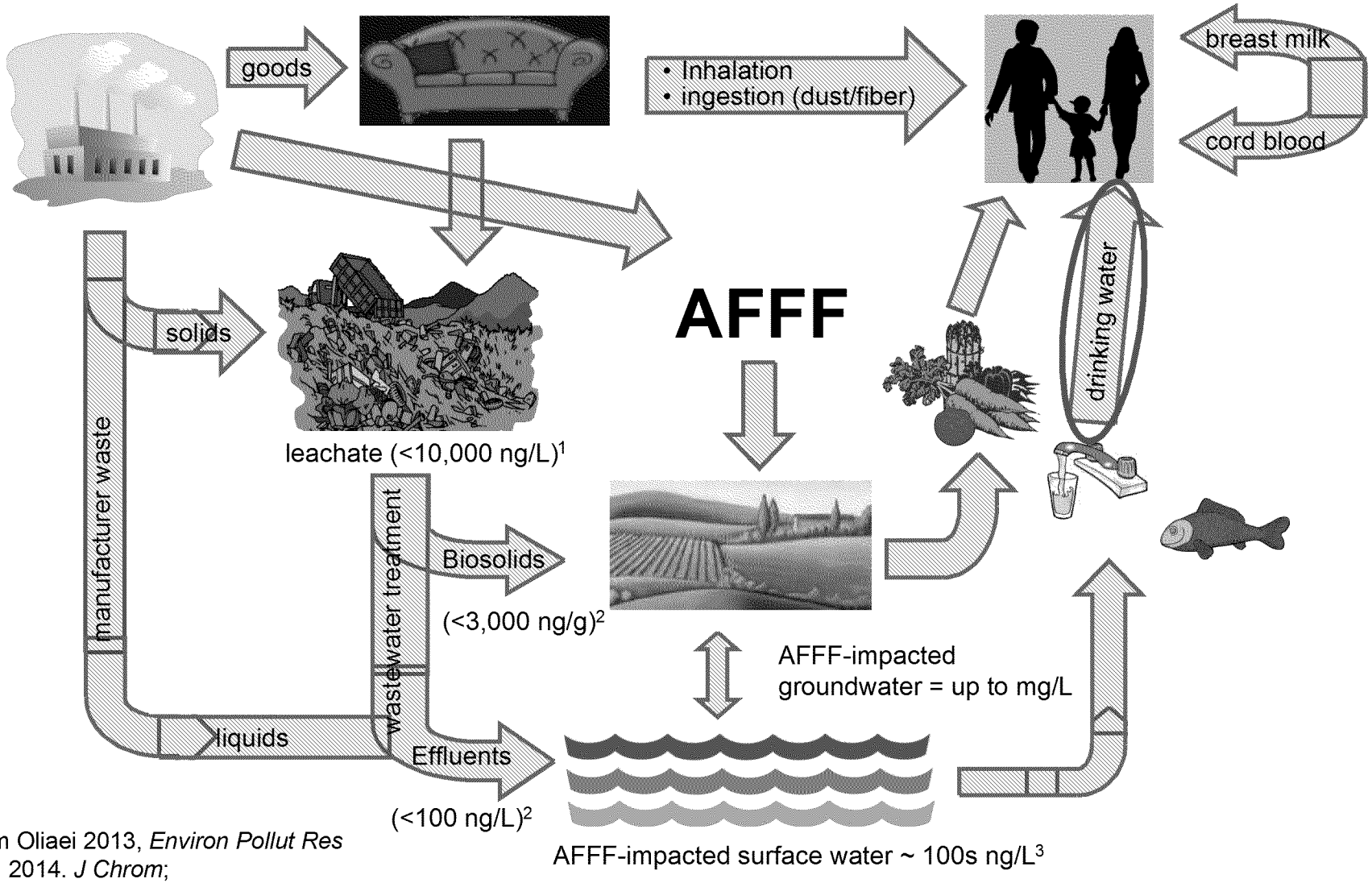
Human Exposure to PFASs



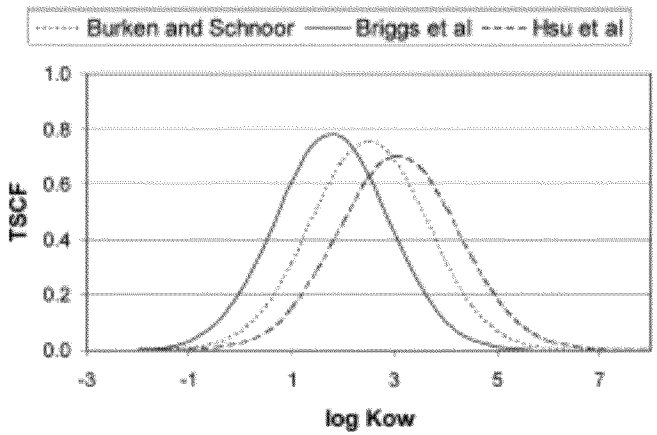
Adapted from Oliaei 2013, *Environ Pollut Res*
[1]Allred *et al.*, 2014. *J Chrom*;
[2]Schultz *et al.* 2006, *ES&T*; Higgins et al. 2005, *ES&T*;
[3]Ahrens *et al.* 2015, *Chemosphere*

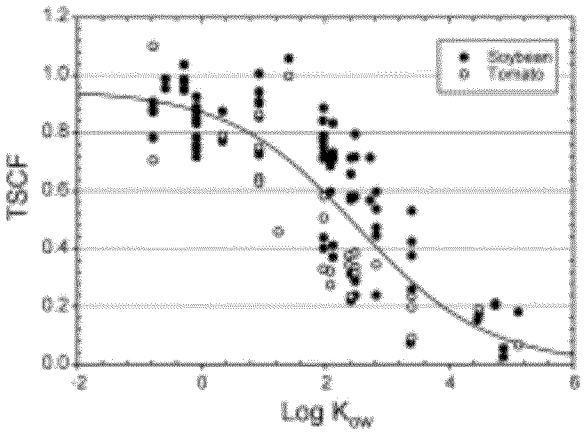
Why be concerned?

Transpiration Stream Concentration Factor (TSCF):

$$TSCF = \frac{[\text{[illegible]}]}{[\text{[illegible]}]}$$

- Plant uptake models suggest maximal TSCF at log K_{ow} ~ 2





- New model suggests sigmoidal relationship with log K_{ow}
- Many CECs of interest are small, polar, and/or charged and have low log K_{ow} values (if measureable)

Collins *et al.*, 2006. *ES&T*; Dettenmaier *et al.*, 2009. *ES&T*.

Background: Plant Uptake

Bioaccumulation Factor (BAF)

$$\mathrm{BAF} = \frac{\text{PFAA in plant } \left(\frac{\text{ng PFAA}}{\mathrm{g_{dw}}\text{plant}}\right)}{\text{PFAA in soil } \left(\frac{\text{ng PFAA}}{\mathrm{g_{dw}}\text{soil}}\right)}$$

- Assumption - non-volatile
  - Eliminates air-plant pathway
- Passive transport from soil to plant (via porewater)
  - Most likely dominant uptake pathway

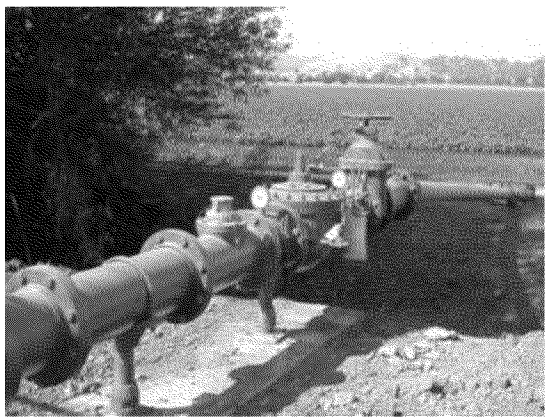
Overall Approach

Biosolids Studies

- Greenhouse-based studies of lettuce, radishes, tomatoes, celery, and snap peas
- Pilot-scale field trials of lettuce, tomatoes
- Field-based corn study

Reclaimed Water Studies

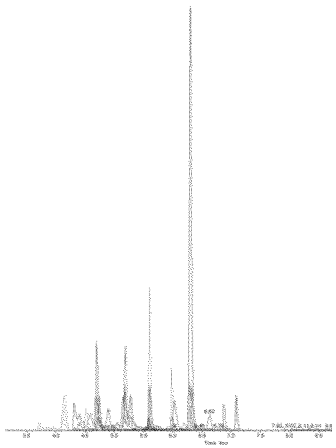
- Greenhouse-based studies of lettuce and strawberries



Blaine *et al.*, 2013. *ES&T*. 47: 14062-14069
Blaine *et al.*, 2014a. *ES&T.* 48: 7858–7865.
Blaine *et al.*, 2014b. *ES&T.* 48: 14361-14368.

Robust Analytical Methods Needed

- Need to measure PFAAs in a wide variety of matrices (soil, water, different plant tissues)
  - Non matrix-matched approach needed
- All PFAAs measured using liquid chromatography tandem mass spectrometry (LC-MS/MS)
  - Stable isotope surrogates employed whenever possible



Biosolids: Greenhouse Experiments

Crops

- Edible root: radish (*Raphanus sativus*)
- Edible stem/leaf: celery (*Apium graveolens* var. *dulce*)
- Edible leaf: lettuce (*Lactuca sativa* 'Multy')
- Edible fruit: tomato (*Lycopersicon lycopersicum* 'Stupice')
- Edible fruit/seed: sugar snap pea (*Pisum sativum*)

Soils

- "Control" - Field-collected unamended soil
- "Industrially-Impacted" - Control + composted biosolids (10% mass)
- "Municipal Soil" - Field-collected biosolids-amended soil

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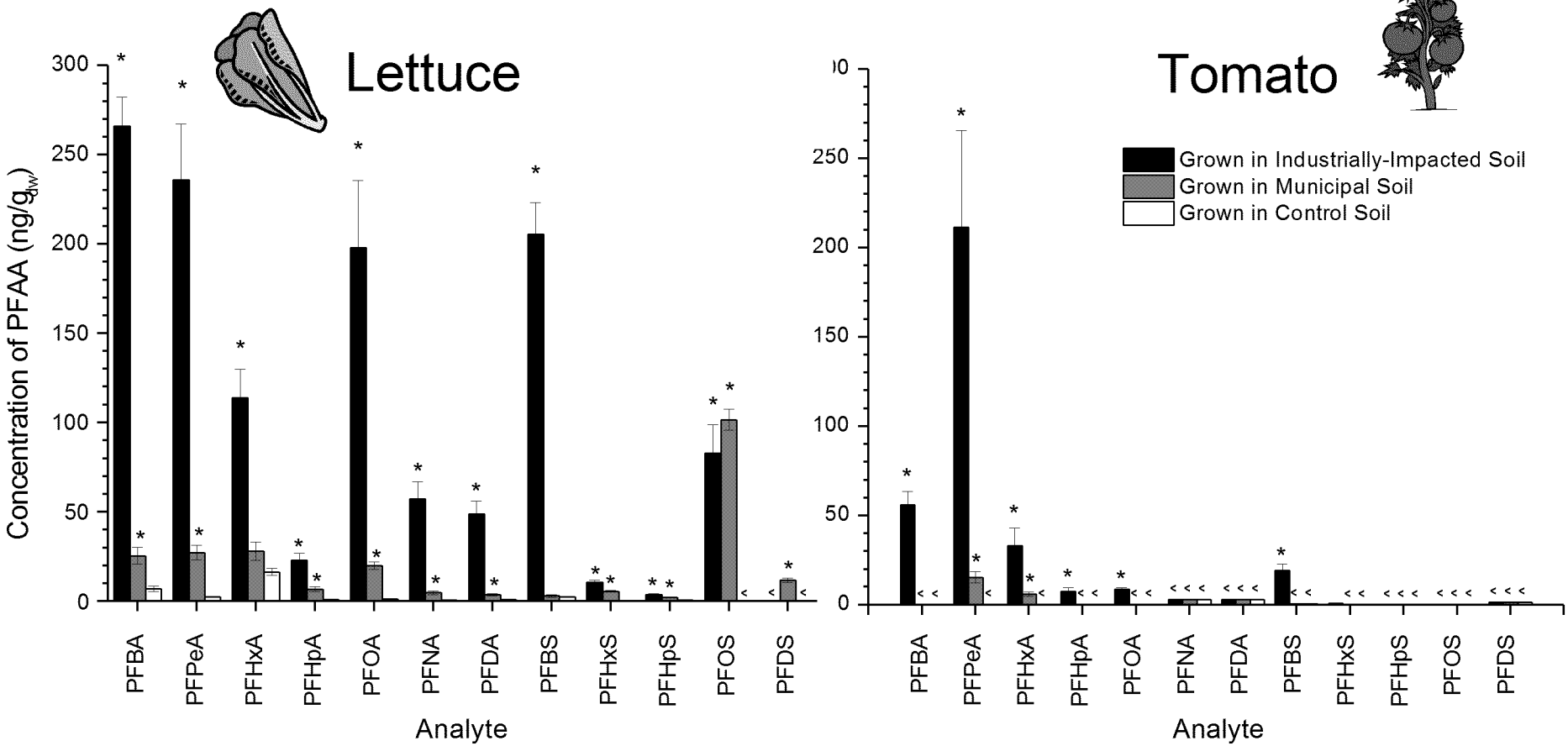
Biosolids: PFAAs in Lettuce in Tomato



Mean and standard error are shown (n = 5)
Values marked with an asterisk are significantly different (α = 0.05) than the control treatment
Values less than the LOQ are denoted by <.

Blaine *et al.*, 2013. *ES&T*. 47: 14062-14069.

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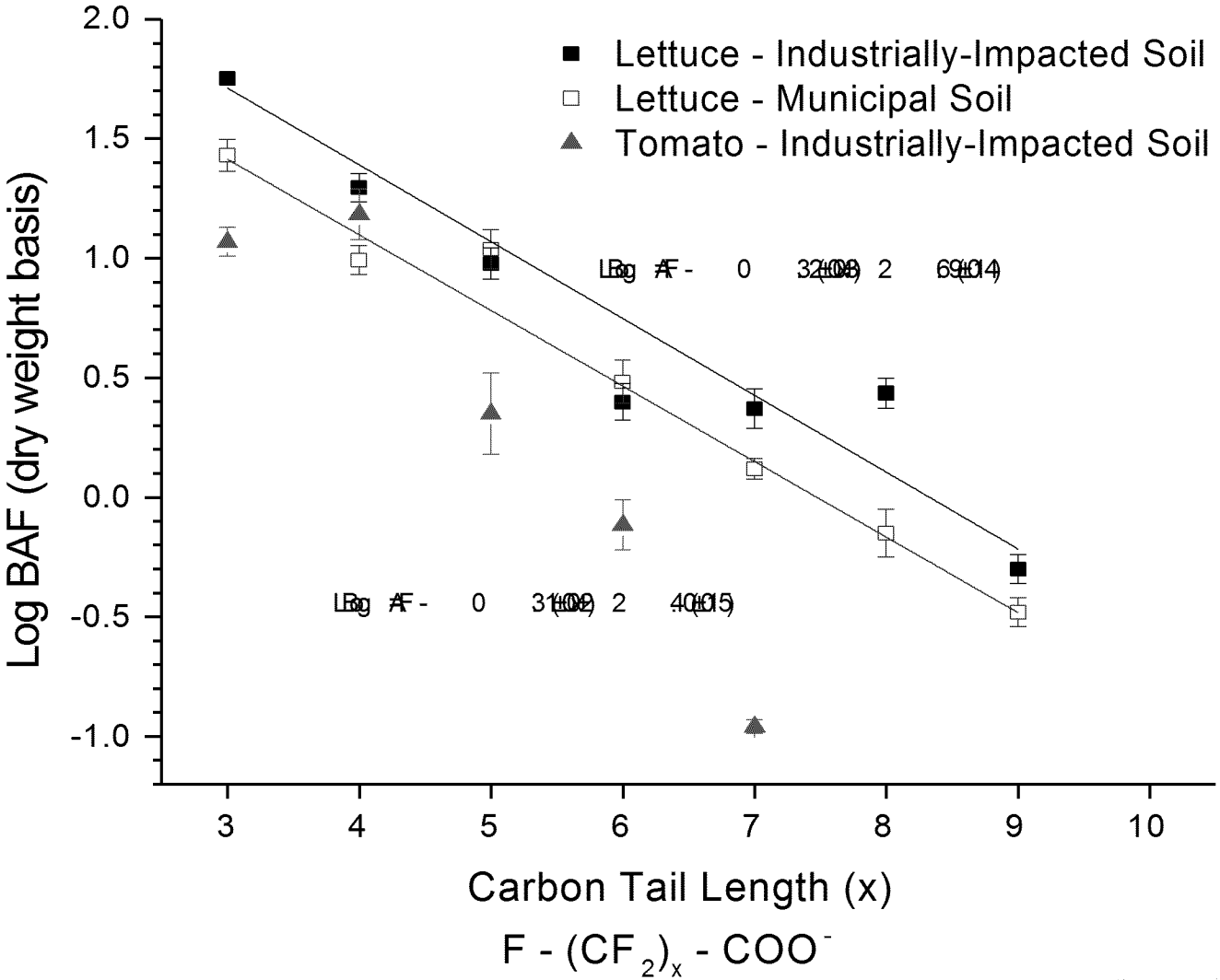
Biosolids: BAFs for PFAAs in Lettuce and Tomato



Blaine *et al.*, 2013. *ES&T*. 47: 14062-14069.

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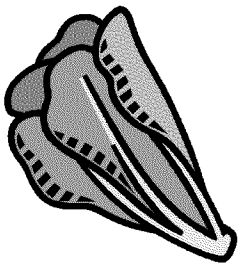
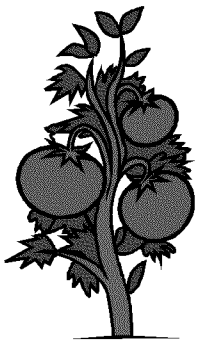
Field Trial Plots

Crops

- Edible Leaf (lettuce)
- Edible Fruit (tomato)





Biosolids-Amended Plots – 3 replicate plots each

- Control (unamended)
- 0.5X agronomic rate for N (single application)
- 1X agronomic rate for N (single application)
- 2X agronomic rate for N (single application)
- 4X agronomic rate for N (single application)

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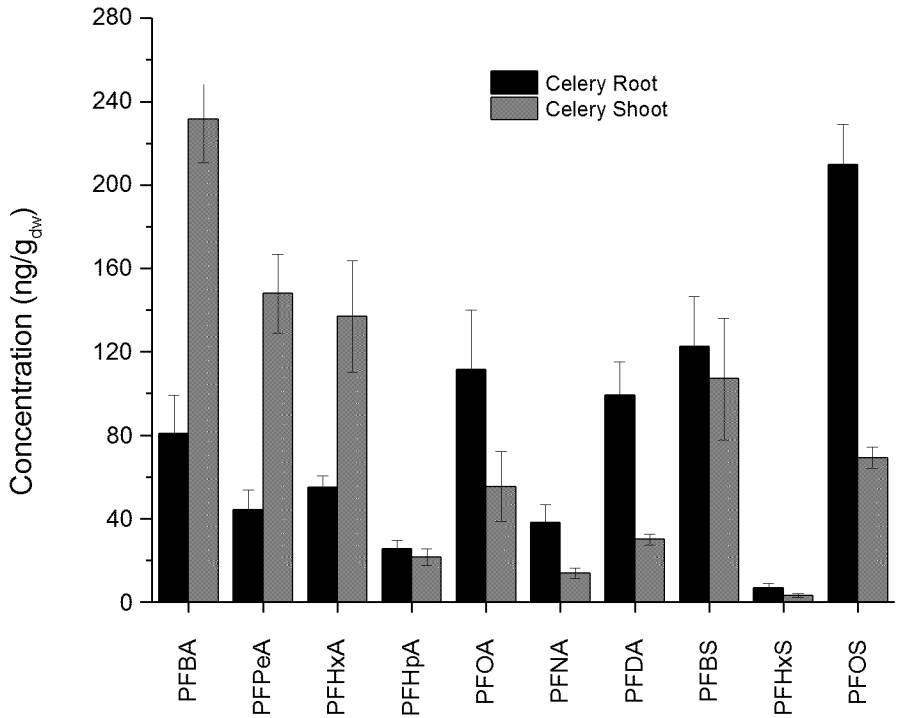
BAFs for PFAAs: Greenhouse vs. Field

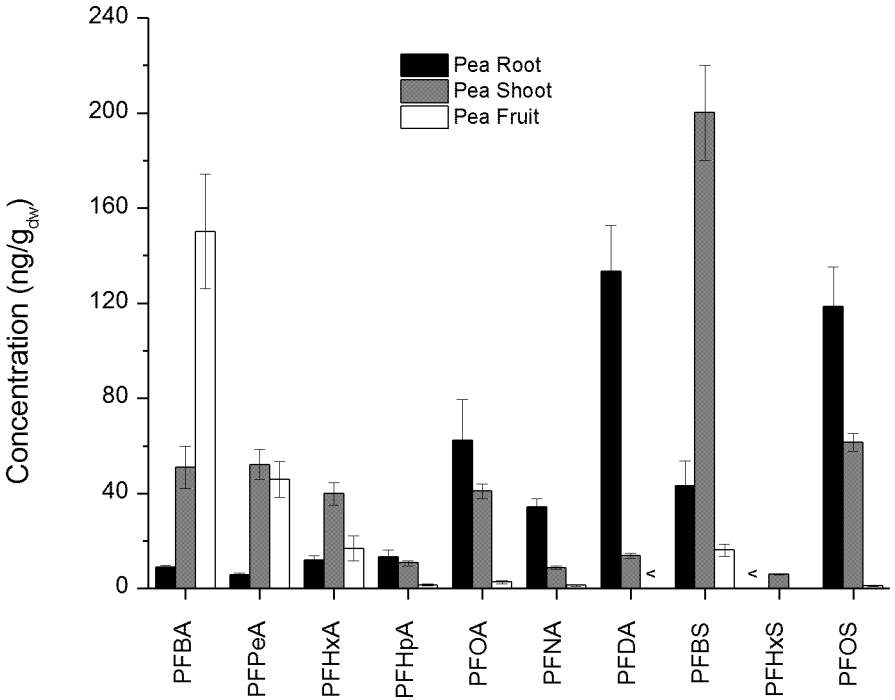
Analyte	Greenhouse Lettuce (Municipal Soil)	Greenhouse Lettuce (Industrially-Impacted Soil)	Field Trial Lettuce (4X Soil)	Greenhouse Tomato (Industrially-Impacted Soil)	Field Trial Tomato (4X Soil)
PFBA	28.38 ± 5.21	56.84 ± 3.45	39.89 ± 2.41	12.16 ± 1.71	18.22 ± 5.34
PFPeA	10.21 ± 1.52	20.43 ± 2.70	16.29 ± 2.35	17.06 ± 3.74	14.85 ± 1.96
PFHxA	11.66 ± 2.11	9.90 ± 1.37		2.90 ± 0.87	6.84 ± 0.81
PFBS	14.47 ± 3.84	4.22 ± 0.37	2.02 ± 0.32	0.42 ± 0.08	
PFHxS	1.08 ± 0.11	7.56 ± 0.86	1.51 ± 0.11	0.50 ± 0.04	
PFOS	0.32 ± 0.02	1.67 ± 0.32	0.10 ± 0.01		

Plant distribution: PFAAs in Celery and Peas

- Two compartment crop grown in biosolids-amended soil



- Three compartment crop grown in biosolids-amended soil



Blaine *et al.*, 2014a. *ES&T.* 48:7858–7865.

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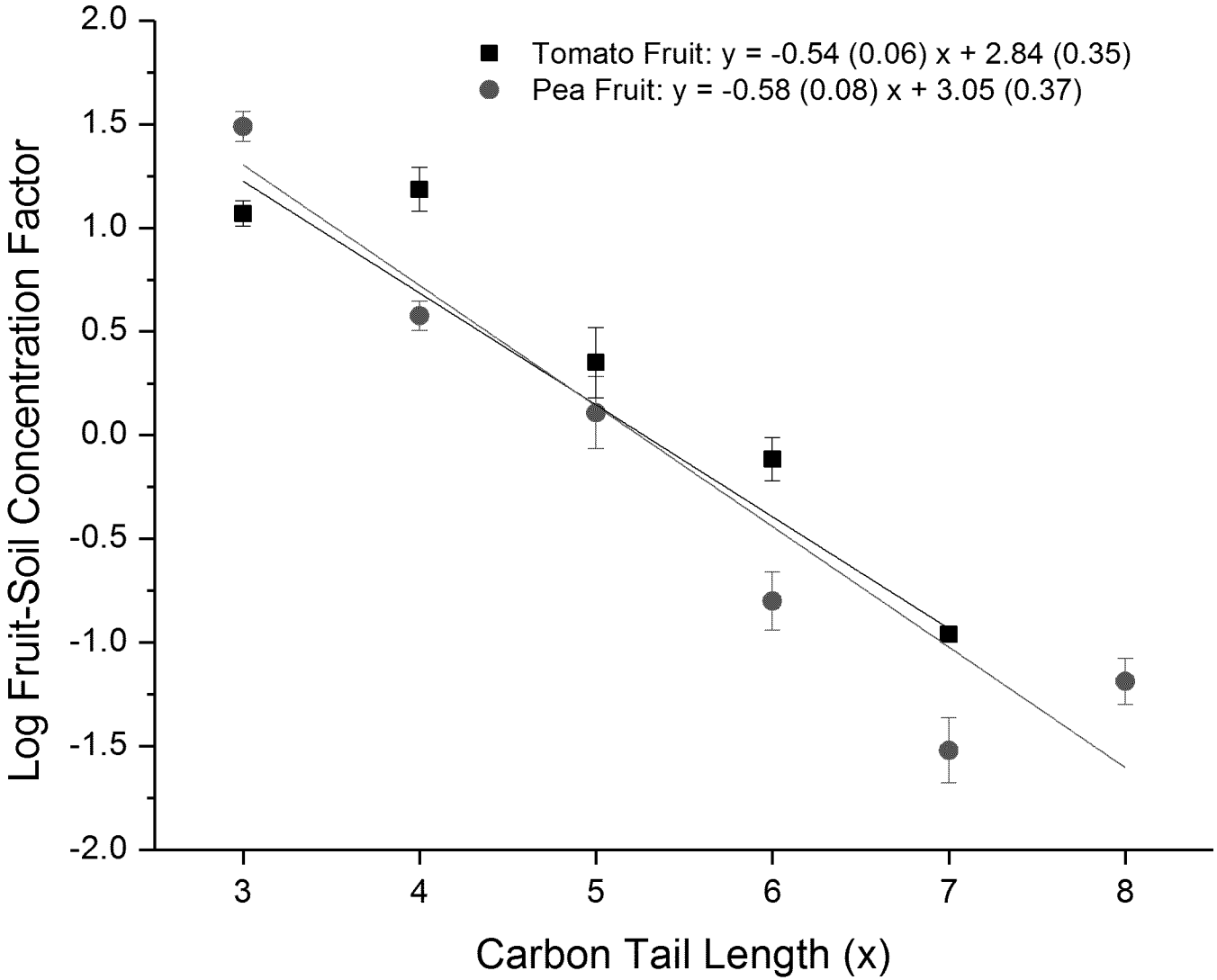
Biosolids: PFAA Fruit-Soil Concentration Factors



$F - (CF_2)_x - COO^-$

Blaine *et al.*, 2014a. *ES&T.* 48:7858–7865.

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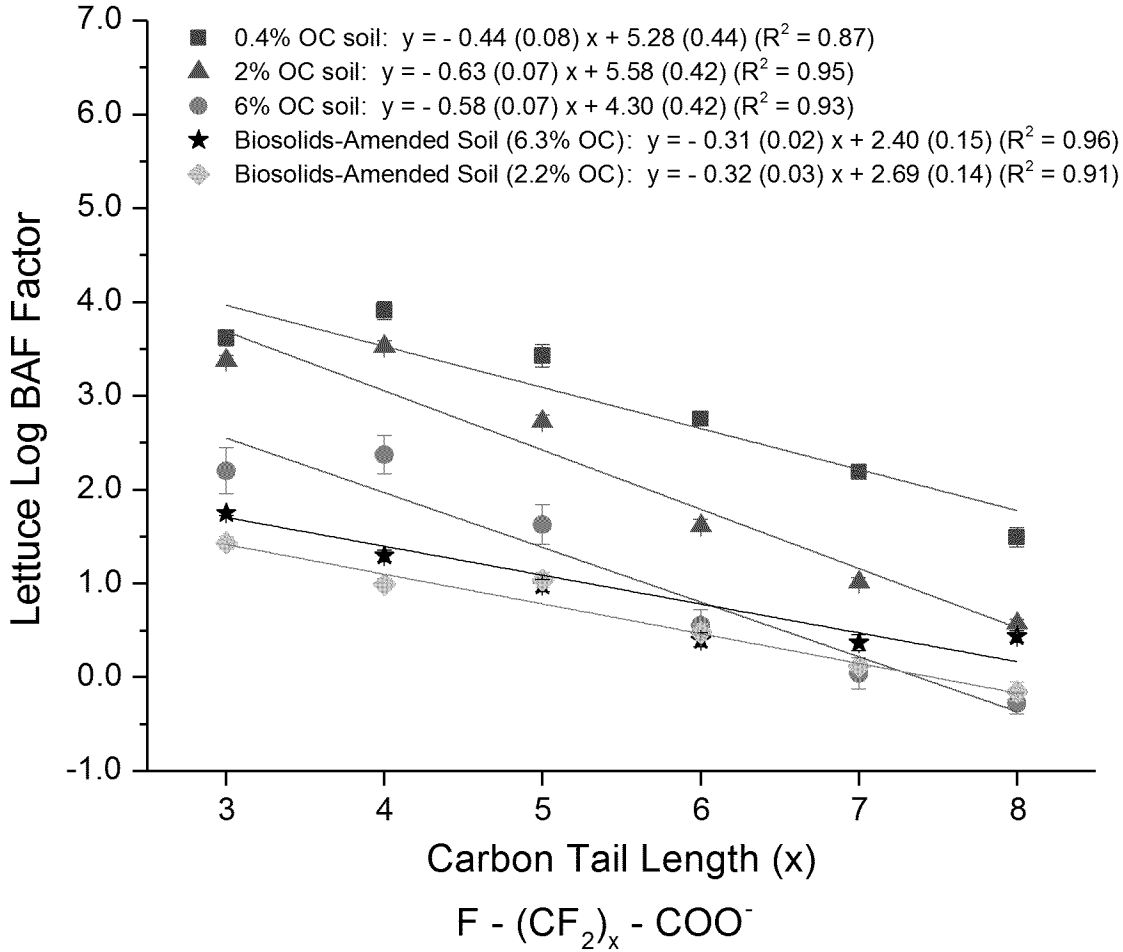
Lettuce: Reclaimed Water Studies

BAFs Relative to Soil

- Assumed equilibrium
- Varied soil OC
  - Soil OC ↑, BAF ↓
- Comparison to biosolids-amended soil:
  - Reclaimed water NOT in equilibrium with soil
  - PFAAs **more bioavailable** in reclaimed water than in biosolids-amended soil



Blaine *et al.*, 2014b. *ES&T.* 48: 14361-14368.

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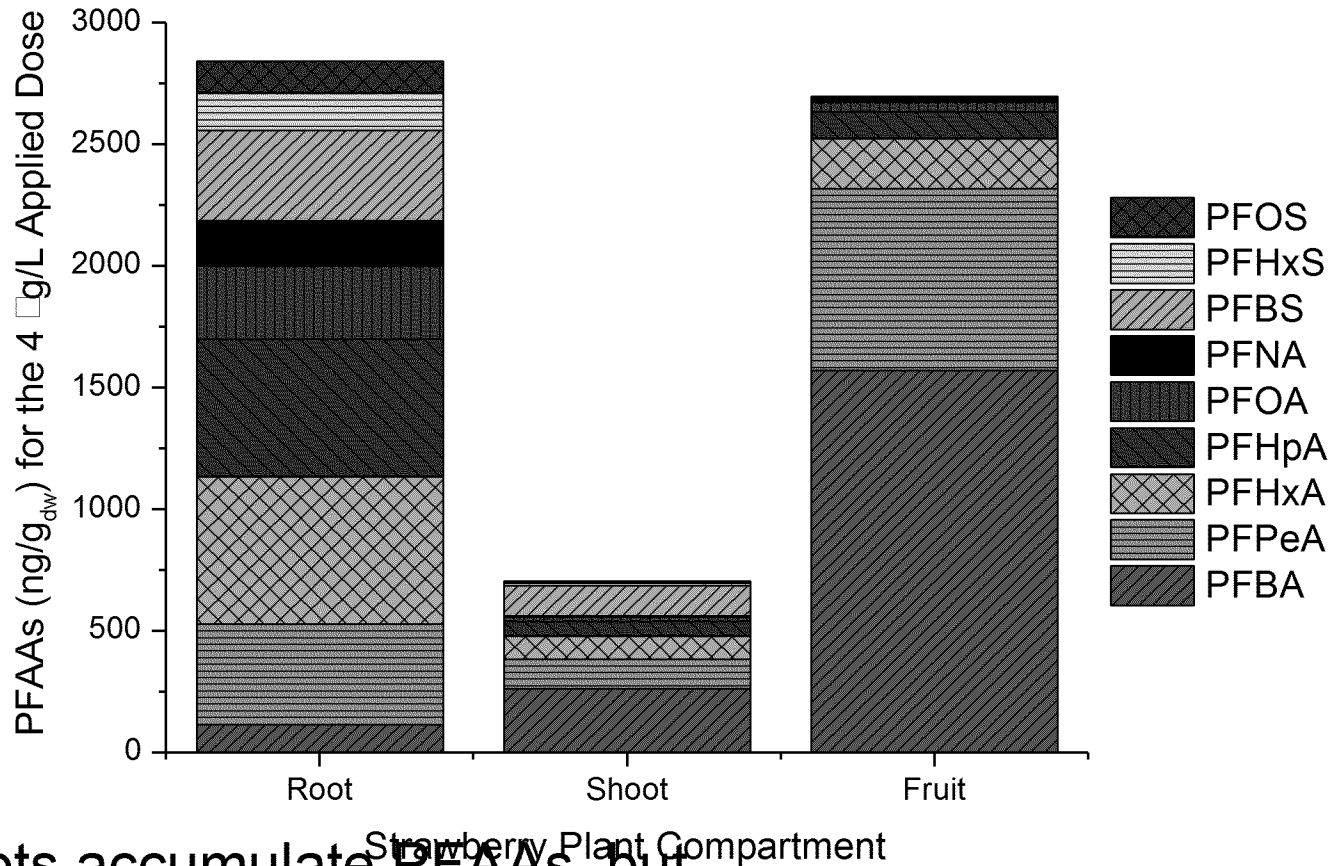
PFAA Distribution in Strawberry Plant

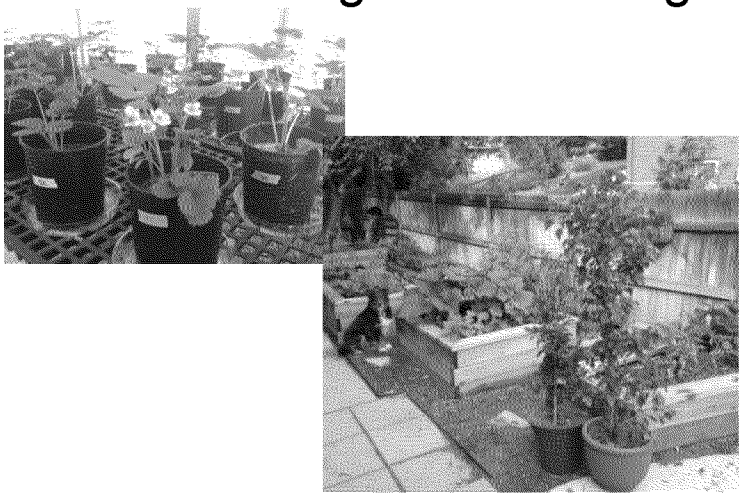


- Roots accumulate PFAAs, but…
- Bias against longer chain carboxylates and **ALL** sulfonates in fruit

Blaine *et al.*, 2014b. *ES&T.* 48: 14361-14368.

Implications

- PFAAs can bioaccumulate into plants from PFAA contaminated soils and reclaimed water
- Plant uptake factors for PFAAs dependent on chain length and head group
  - short-chain > long-chain
  - carboxylates > sulfonates
- PFAA distribution within plants
  - short-chain in fruit crops
  - long-chain in shoot or root crops



- Concentration-dependent uptake suggests passive uptake
- Data suggest new plant accumulation models and further toxicological studies on short-chain PFAAs may be needed
  - What about other PFASs present in AFFF-impacted groundwater?

Disclaimer & Acknowledgements

"The opinions expressed are those of the speaker. Findings, opinions, and conclusions in this presentation do not represent and should not be construed to represent any U.S. EPA determination or policy."

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ReNUWIt: The Urban Water Engineering Research Center

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Human Health Risks for PFOS & PFOA in Homegrown Produce

Jason Conder, Jenn Arblaster, Emily Larson | August 10,2017
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Introduction

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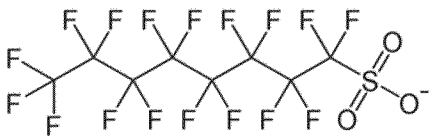
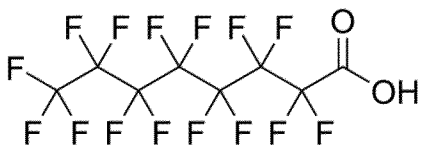
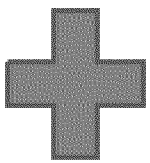
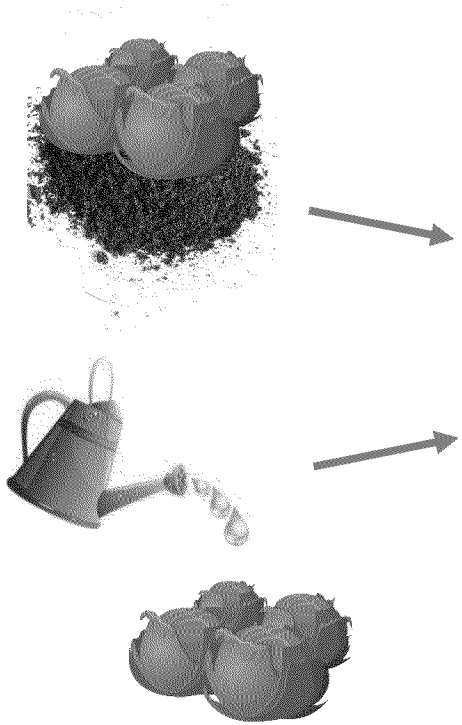
- Produce grown in PFAS contaminated soils or irrigated with PFAS-impacted water may result in a exposure pathway for consumers of home grown produce near PFAS contaminated sites









Exposure Modeling

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- Homegrown produce consumption pathways considered for human health risk assessments at contaminated sites (e.g., perchlorate, metals, etc.)
- Two scenarios for the consumption of home grown produce were modeled to evaluate potential risks to human health
  - Produce (lettuce) grown in PFOS/PFOA contaminated soils
  - Produce (lettuce) grown using PFOS/PFOA contaminated water
- Key goal: what are concentrations in lettuce, soil, and water that might lead to exposure levels of concern?

Produce Grown in PFAS Contaminated Soils

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- Bioaccumulation Factors (BAFs) for soil to plant (kg dw soil/kg dw plant) were used from Blaine et al. (2014) study
  - Converted to wet weight basis for consumption model
  - Concentrations in produce were predicted using BAF for lettuce

- PFOS = 0.7 kg dw soil/kg dw plant
  0.1 kg ww soil/kg ww plant

- PFOA = 1.9 kg dw soil/kg dw plant
  0.3 kg ww soil/kg ww plant

Produce Grown using PFAS Contaminated Water

Geosyntec consultants

- Bioaccumulation Factors (BAFs) for water to plant (kg dw soil/kg dw plant) were used from Blaine et al. (2014) study
  - Converted to wet weight basis for consumption model
  - Concentrations in produce were predicted using BAF for lettuce

- PFOS = 6.5 L/kg dw plant
  0.97 L/kg ww plant

- PFOA = 35 L/kg dw plant
  5.2 L/kg ww plant

Exposure Assumptions

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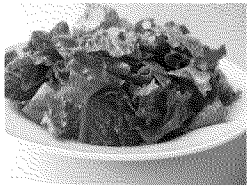
- Exposure model assumes:
  - Exposure Frequency (EF) = 4 month (120 days) growing season (June-September)
  - Ingestion Rate (IR) = 0.3 kg ww consumed per day (adults)
    - Based on the 95% UCL for homegrown produce for average 80kg adult (USEPA 2011)
    - About 2 salads per day



  - Standard human health exposure parameters
    - Exposure Duration (ED) =26 years (adult)
    - Averaging time (AT) = 365 *ED
    - Body Weight (BW) = 80 kg (adult)
    - **Relative Source Contribution (RSC) = 1 (or 0.2)**

Toxicity and Risk Characterization

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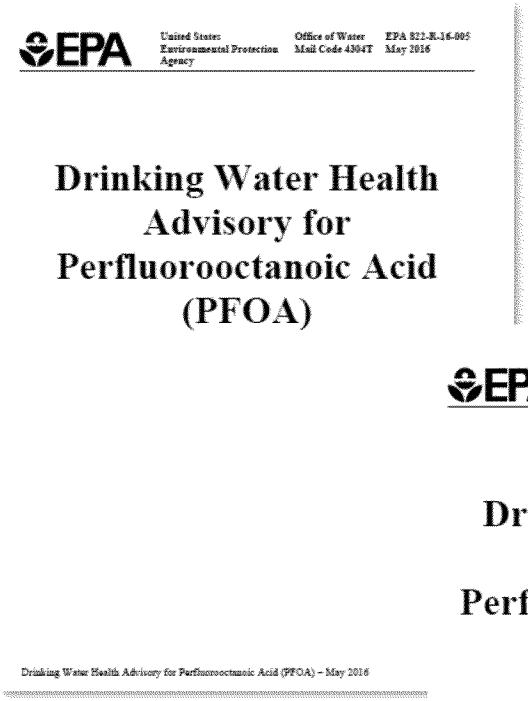
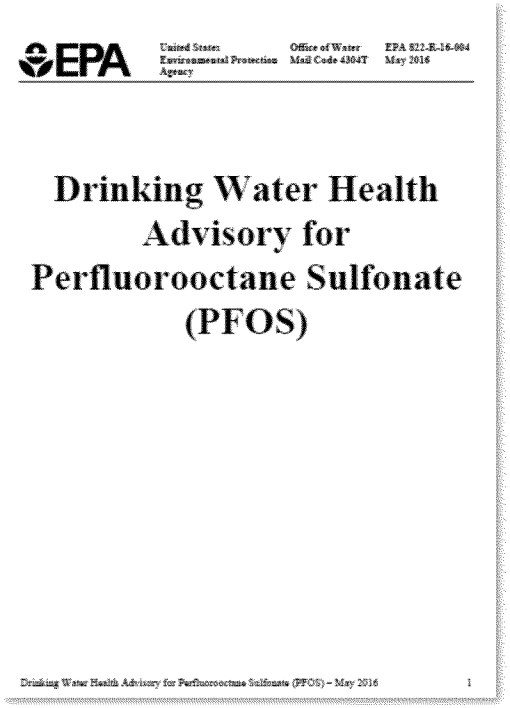
- Effects
  - PFOS: reduced birth weight
  - PFOA: developmental effects in bones, accelerated puberty
- Non-cancer Reference Dose (RfD) for PFOS & PFOA = 0.00002 mg/kg bw-day (USEPA, 2016)
  - Non-cancer hazard for PFOA occurs at lower exposures than cancer (no slope factor for PFOS)



EPA United States Environmental Protection Agency | Office of Water Mail Code 4304T | EPA 822-R-16-005 May 2016

Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA)

Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA) – May 2016



EPA United States Environmental Protection Agency | Office of Water Mail Code 4304T | EPA 822-R-16-004 May 2016

Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS)

Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS) – May 2016 1

Risk Based Concentrations

Geosyntec consultants

Chemical	Risk-based screening value in lettuce (µg/kg lettuce, ww)		Risk-based screening value in soil (mg/kg soil, dw)		Risk-based screening value in water (ng/L water)	
	RSC = 1	RSC = 0.2	RSC = 1	RSC = 0.2	RSC = 1	RSC = 0.2
PFOS	16	3.3	0.16	0.031	17000	3400
PFOA	16	3.3	0.057	0.011	3100	620
	Similar range as identified by Australia food standards (1-9 µg/kg)		More conservative than EPA residential soil guidelines for direct consumption (6-16 mg/kg, dw)		Less conservative than drinking water health advisory (70 ng/L)	

DRAFT (WORK IN PROGRESS)

- Initial modeling results indicate risk-based screening levels for soil may be lower than EPA's current residential guidelines
- Drinking water health advisory level (70 ng/L) likely protective of homegrown produce pathway

Conclusions

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- Potential for produce consumption pathway to influence risk-based decision-making
- Initial modeling results indicate risk-based screening levels for soil may be lower than EPA's current residential guidelines
- Drinking water health advisory level (70 ng/L) likely protective of homegrown produce pathway
- Caveats
  - Uptake of other produce may be different than lettuce
  - Screening levels assume PFAS in soil or water (not both)
  - Additivity of PFOA and PFOS (EPA)
  - Measurement of PFASs in produce more accurate than the model
  - Organic matter in soil decreases uptake factors (current BAFs conservative)

Disclaimer

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- The risk-based screening levels (and general risk-based approach for homegrown produce) presented here is for example purposes only and should not be applied in site decision-making without a full consideration and analysis of the uncertainties of the model assumptions and parameters
- Although levels of PFOA and PFOS below the draft risk-based screening levels is likely to indicate an absence of risk, exceedance of the levels does not imply unacceptable risk; these levels should not be used as enforceable criteria or as cleanup levels