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Trace Organic Compounds of Emerging Concern and their Removal During Onsite Wastewater Treatment

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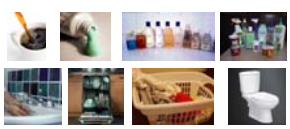
Context and Motivation

- In the past, wastewater systems were mostly focused on treatment of organic matter, nutrients, and pathogens
- Recently, there has been growing interest in contaminants of emerging concern, including trace organic compounds
  - Trace organic compounds can be present at very low levels (e.g., ng/L), but with potential for serious harmful effects
  - Trace organic compounds originate from human activities including use of:
    - Consumer product chemicals
    - Pharmaceuticals
    - Pesticides
    - Chlorinated flame retardants



  - What about occurrence & fate in onsite wastewater systems?

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CSM Research

- Initial research into trace organics in onsite systems
  - Focused on consumer product chemicals
  - Research objectives
    - Characterize trace organics in onsite wastewaters
    - Determine removals in different unit operations and systems
    - Integrate the findings and assess the implications
  - Scope of work
    - Methods development for wastewater effluents
    - Field monitoring of operating onsite systems in Colorado, USA
    - Field research at the CSM Mines Park Test Site
    - Laboratory experiments at CSM
  - CSM collaboration with U.S. Geological Survey

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CSM Field Monitoring

- Research approach
  - Monitoring at 30 operating onsite wastewater systems in CO
    - Sampling of septic tank contents near the inlet to the tank
    - Plus sampling at different locations within each onsite system
    - Sampling 2 to 3 times from 45 unique locations over 2 years
  - Ancillary sampling of drinking water and receiving waters
    - Groundwater wells (9) and surface water sites (9)

Source: Conn *et al.* 2006.

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- Monitoring different sources and within treatment units

Residence (n=16)

Convenience Store (n=2)

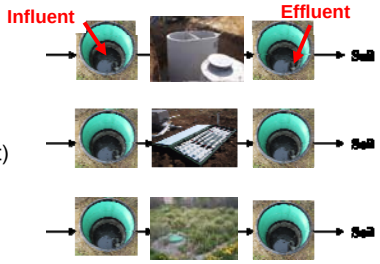
Human Institution (n=3)

Food Establishment (n=3)

Retail Stores (n=3)

Veterinary Hospital (n=3)

- Septic tanks -
  - *Sorption, anaerobic biotransformation*
- Biofilters -
  - *Sorption, volatilization, aerobic biotransformation*
- Constructed wetlands -
  - *Sorption, aerobic or anaerobic biotransformation, plant uptake*



- Water use
  - 130 L/day (vac. home) to 13,500 L/day (restaurant)
- Occupants or visitors per day
  - 2 (single-family home) to 1,100 (conv. store)
  - Also up to 40 animals (veterinary kennel)

- Results ~ a few highlights
  - Overall occurrence in septic tank <u>influents</u>: ng/L - mg/L

Compound	Use	Detection	Concentration Range (µg/L)
Caffeine	Stimulant	100%	0.5 – E 9,300
Coprostanol	Animal sterol	100%	0.5 – E 7,100
Cholesterol	Animal sterol	100%	0.5 – E 2,200
Ethylenediaminetetraacetic acid (EDTA)	Metal chelator	100%	0.5 – 1,700
4-Methylphenol	Disinfectant	98%	0.5 – E 4,500
4-Nonylphenolethoxycarboxylates (NPEC)	Surf. metabolite	95%	2 - 320
Nitrilotriacetic acid (NTA)	Metal chelator	82%	0.5 - 130
4-Nonylphenol (NP)	Surf. metabolite	77%	2 – 340
4-Nonylphenolethoxylates (NPEO)	Surf. metabolite	75%	2 – 170
5-chloro-2-(2,4-dichlorophenoxy)phenol (Triclosan)	Antimicrobial agent	68%	0.5 – 82

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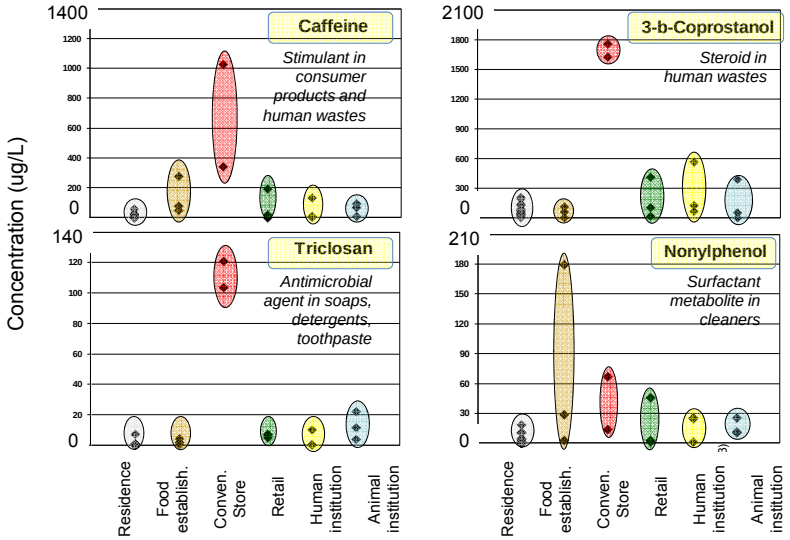
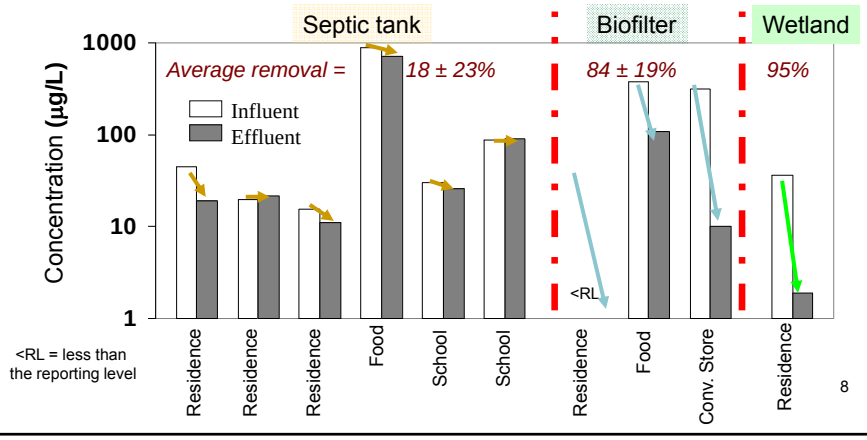
E = estimated value (concentration exceeded maximum value on standard curve).

- Occurrence of trace organics varies by type of source, e.g.:



- Removal efficiencies depend on compound properties and process conditions within treatment units, e.g.:
  - Caffeine - removal enhanced by aerobic biotransformation
    - Triclosan, dichlorobenzene, NTA,…similar



<RL = less than the reporting level

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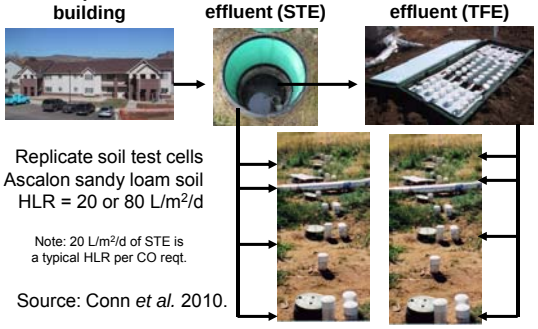
Controlled Field Research

- Research approach
  - Controlled field research at the CSM Mines Park Test Site
  - Monitoring of treatment unit effluents and soil pore water at different vadose zone depths

8-unit apartment building → **Septic tank effluent (STE)** → **Textile biofilter effluent (TFE)**

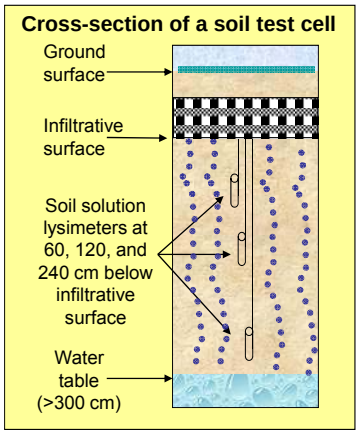


Replicate soil test cells
Ascalon sandy loam soil
HLR = 20 or 80 L/m^2/d

Note: 20 L/m^2/d of STE is a typical HLR per CO reqt.

Source: Conn *et al.* 2010.

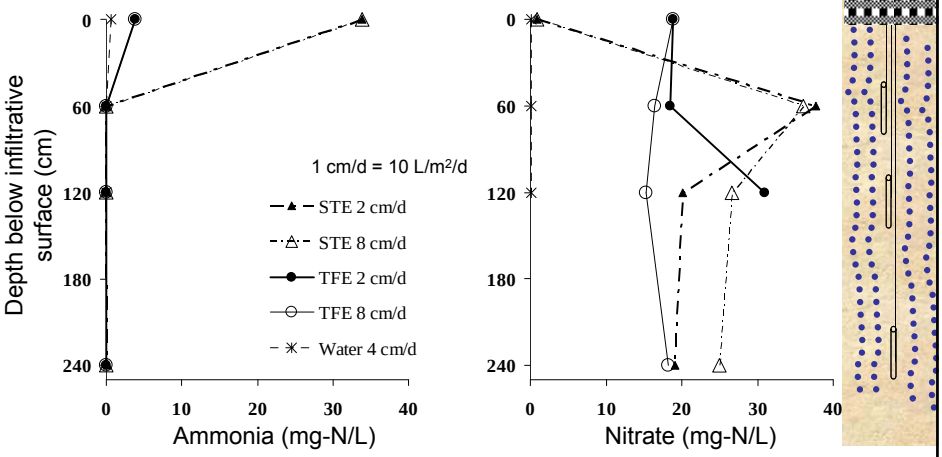
Cross-section of a soil test cell



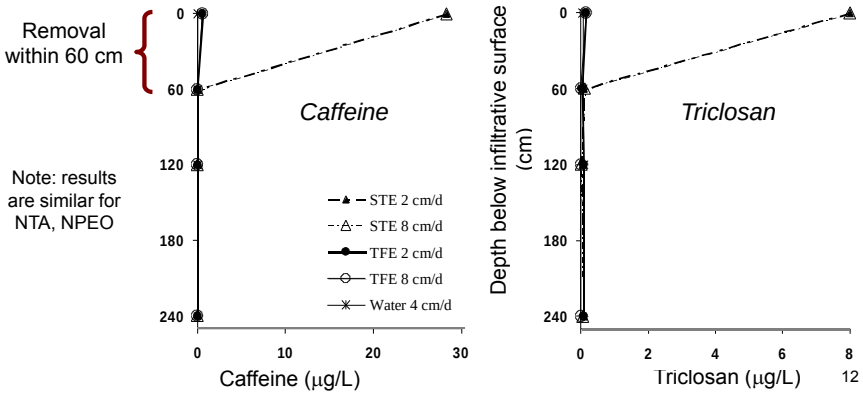
- Results ~ a few highlights
  - Effluent composition (average (*std. dev.*), n=14 over 13 mo.)

Parameter	Units	Septic tank	Textile biofilter
pH	pH	7.39 *(0.16)*	6.17 *(0.92)*
Alkalinity	mg-$CaCO_3$/L	190 *(29)*	21 *(12)*
DOC	mg/L	30 *(8.4)*	16 *(4.2)*
NH_4	mg-N/L	34 *(7.5)*	3.8 *(1.1)*
NO_3	mg-N/L	0.85 *(0.48)*	19 *(3.8)*
Caffeine	µg/L	34 *(8.7)*	0.87 *(0.49)*
EDTA	µg/L	24 *(1.0)*	33 *(13)*
Nitrilotriacetic acid (NTA)	µg/L	3.7 *(2.3)*	4.0 *(1.9)*
4-Nonylphenol	µg/L	3.3 *(1.4)*	<RL of 2
4-NP1EC	µg/L	63 *(23)*	7.3 *(3.6)*
4-NP1EO	µg/L	1.6 *(0.97)*	<RL of 1
Triclosan	µg/L	9 *(3.3)*	<RL of 0.2

- Nitrogen species
  - Primary mechanism: biotransformation



- Caffeine and Triclosan (also NPEO, NTA)
  - Removal within ≤60 cm below effluent infiltrative surface



- Caffeine and NTA removal
  - Primary mechanism: Aerobic biotransformation
    - Co-metabolism of trace organics under mg/L DOC levels
    - Zero-order attenuation rates

$$k_{APP} = \frac{(C_o - C)}{t}$$

k_{APP} = zero-order attenuation rate, ug/L per day
C_o = applied effluent concentration, ug/L
C = pore water concentration at 60 cm, ug/L
t = vadose zone travel time, days (22 to 32 days)

Parameter	STE	TFE
Caffeine	1.1 - 1.5 ug/L-d	0.02 – 0.04 ug/L-d
NTA	0.12 – 0.18 ug/L-d	

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- Triclosan removal
  - Primary mechanisms: Sorption and aerobic biotransformation
    - Sorption to organic matter and biofilms
      - Sorption estimates by equilibrium partitioning
      - 99.9% of Triclosan would be sorbed
    - Co-metabolism after sorption
      - Half-life of sorbed Triclosan = about 18 days

$$K_d = \frac{C_s}{C_w} = K_{oc} f_{oc} f_{HA}$$

$$f_{HA} = (1 + 10^{(pH - pKa)})^{-1}$$

K_d = equilibrium partition coefficient, ug/L per day
K_{oc} = Organic carbon partition coefficient, 47,000
f_{oc} = fraction organic carbon content, 0.028
f_{HA} = fraction in neutral protonated form, STE = 0.76, TFE = 0.98

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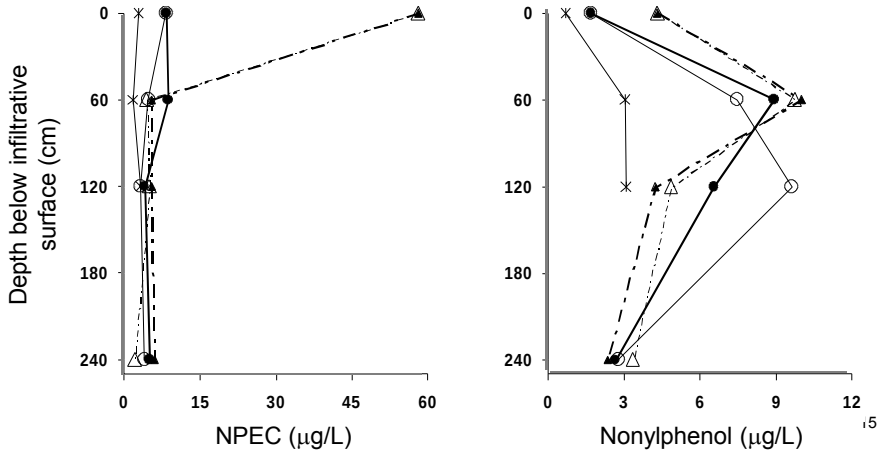
- Surfactant metabolites
  - Behavior is more complicated
  - Conversion of other trace organics to Nonylphenol and persistence



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- Removal efficiencies
  - 82% removal of DOC by 60-cm soil depth
  - 91% to >99% removal of NP1EC, Triclosan, NTA, Caffeine within 60 cm of soil
  - EDTA removal of 96% after 240-cm soil depth
  - Nonylphenol concentrations increased during shallow soil treatment, with negligible removal overall
  - For both effluent types (STE *vs.* TFE) and loading rates (20 *vs.* 80 L/m^2/day):
    - Concentrations in soil pore water at each depth (60, 120, or 240 cm) were similar
    - Higher mass removal and %removal of trace organic compounds can occur with STE (*vs.* TFE) and 80 L/m^2/day (*vs.* 20 L/m^2/day)

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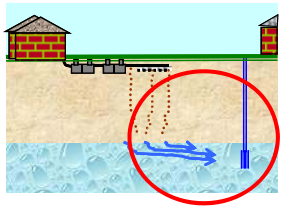
- Implications for minimum depth of unsaturated soil to groundwater…?
  - Minimum depth necessary to minimize risk to ecosystem and human health from trace organic compounds will depend on:
    - Organic compounds of interest
    - The level of treatment to be achieved before reclaimed water reaches a potential receptor, such as via:
      - Drinking water derived from groundwater
      - Surface water resources



- Example of exposure point assessment
  - Potential 4-nonylphenol (NP) levels at a point of exposure
    - Treatment by percolation through unsaturated soil
    - Treatment during groundwater transport

Depth of percolation to groundwater (cm)	Average soil pore water concentration (ug/L)[a]	NP exposure concentration (ug/L)		
		DAF[b] =1	DAF = 10	DAF = 100
60	10.	**10.0** [c]	1.0	0.10
120	4.2	4.2	0.42	0.042
240	2.3	2.3	0.23	0.023

[a] Based on sandy loam soil profile receiving STE at a design HLR of 20 L/m^2/day
[b] DAF = ratio of trace organic compound concentration in pore water to its concentration at the point of exposure.
[c] Concentration exceeds the USEPA toxicity-based water quality criteria of the 4-day average concentration in freshwater systems not to exceed 6.6 ug/L.

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Summary

- Trace organics associated with consumer product chemicals are present in onsite wastewaters
  - The types and levels depend on the source and activities
  - Concentrations can be higher than in municipal wastewaters
- Onsite system removals can be very high
  - Depends on compound properties and treatment conditions
    - For some compounds, onsite systems remove >99%
    - Some compounds may persist (e.g., 4-Nonylphenol, EDTA) and may reach shallow ground water
    - Concern over ultimate fate is dependent on site conditions
- While not presented today, onsite systems can provide comparable removal to centralized treatment plants
- Research is continuing…

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Acknowledgements

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Further Information

- Associated research publications
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- http://smallflows.mines.edu/

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