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Northeast Biosolids and Residuals Conference

Burlington, Vermont

October, 25, 2017

PFAS in Wastewater Residuals: What we know!

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Topics to Be Covered

- Background
- PFAS Chemistry
- Analysis of PFAS
- Risk to Public Health from Land Application
  - Occurrence and concentrations in residuals
  - Occurrence and concentrations in the soil resulting from land application
  - Mobility/leaching

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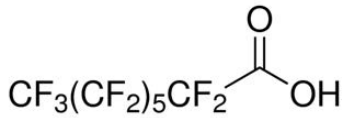
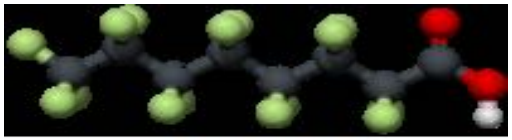
Background (general info)

- Per- and polyfluoroalkyl substances (PFAS)



Perfluorooctanoic Acid (PFOA)


PFOA

- Large group of chemicals with many subgroups
- Man-made highly fluorinated alkyl (C2-C16) chemicals with unique properties
- Hydrophobic and Lipophobic
- No natural counterparts

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Background (Why we're talking about PFAS)

- Mobile and ubiquitous (arctic, human blood & serum)
- Detected in groundwater in a number of states
- Found in groundwater near land application sites
- Legislatures and state environmental agencies expressing increased concern about PFAS
  - Establishing regulatory limits
  - Attempting to identify sources other than industry (landfills and wastewater residuals)
- PFAS have been found in residuals and land applied soils **not** impacted by industrial sources.

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PFAS Chemistry/Fate

Buck et al. 2011. *Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins*.

Large number of chemical groups and individual chemicals (>3000 used on the global market)

- Similar properties valuable in commerce
- Variable behavior in the environment

PFAS products may contain multiple isomers of the intended ingredients, residual intermediary compounds, byproducts, and – after release –degradation products.

Background (general info)

- Lowers surface tension and enhances spreading
- High chemical and thermal stability (C-F bonds)
- Very useful compounds
  - Stain-resistant carpets and fabrics
  - Food cartons, containers, wrappers
  - Surfactants and lubricants
  - Aqueous film-forming foams (AFFFs)
  - Flame retardants

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PFAS Chemistry/Fate

- Two production methods that yield different products:
  - Electro-chemical fluorination (ECF)
    - Electrolysis of organic compound in HF
    - Breaking and branching of C-chain
    - ~70% linear/30% branched in PFOA/PFOS synthesis
  - Telomerization
    - Multiple step reaction
    - PFEI – PFAI – FTI – FTOH – variety of PFAS products
    - Linear reactants yield linear alkyl chain products (PFAI)
- Perfluoroalkyl acids (PFAAs) are the metabolites of PFAS precursors

PFAS Chemistry/Fate

- As acids and esters, PFAS compounds susceptible to ionization/dissociation and increased mobility
- Ionized forms likely to predominate in the environment and biota (including humans)
- Some PFAS compounds may degrade in the environment or biota, but will ultimately transform to very stable and persistent perfluoroalkyl acids (PFAAs)
- The yield rate of PFAAs from biotic and abiotic degradation depends on the precursors and degradation conditions
- Increasing C-chain length reduces leachability and increases bioaccumulation

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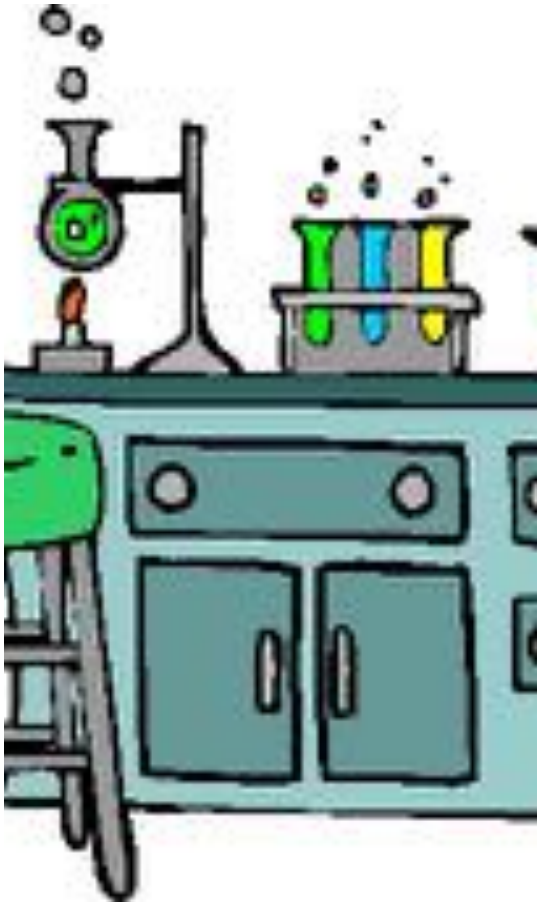
PFAS Analysis



- EPA Method 537 is the only validated and approved method for PFAS analysis
- Method 537 is only approved for drinking water, and any modifications are not approved.
- Numerous commercial labs are using a modified version of Method 537 on matrices other than drinking water (wastewater, soils, residuals, etc.)
  - The term “modified” could mean anything
  - Potential for unreliable data (screening vs regulation)
  - Need for close scrutiny of data and QA/QC practices

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PFAS Analysis

- Two ASTM methods have been developed and multi-lab validated for PFAS analysis in non-drinking water matrices
  - ASTM D7968, Determination of Polyfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)
  - ASTM D7979, Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)
- These methods have not been finalized or approved by EPA for regulatory use, but EPA hopes to finalize and validate similar methods in the next 6 months under the solid waste program.

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PFAS Analysis

Significant changes in ASTM methods from Method 537:

- No solid phase extraction (SPE) or extract concentration
- Direct injection of sample extract
- External standard calibration and quantitation
- Addition of isotopically-enhanced surrogates for additional evaluation of matrix interference (no correction to data)
- Uses multiple reaction monitoring (MRM) and ion ratio for improved analyte identification
- Establishes sample collection, handling, and storage procedures for solids and non-drinking water aqueous samples

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PFAS Analysis

- NEBRA has developed a guidance document focused specifically on sampling and analysis for PFAS
- Provides guidance on how to prepare a PFAS sampling plan
- Worksheet format with specific guidance for ease of completion
- Covers analytical methods, data quality objectives, lab contacts, target analyte lists, sampling SOPs, sampling challenges, relevant regulatory requirements
- Updated (version 2.0) based on the most recent information – coming soon….

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PFAS Risk and Wastewater Residuals

- NEBRA has drafted a proposal calling for research to address the **potential** risk to public health from land application of wastewater residuals containing PFAS
- The proposal seeks to answer the following question:

"Does land application of wastewater residuals (paper mill solids, municipal biosolids, etc.) at fertilizer rates with current common regulatory requirements and proper industrial source controls represent a risk to public health from PFAS contamination of groundwater via leaching and/or surface water via runoff?"

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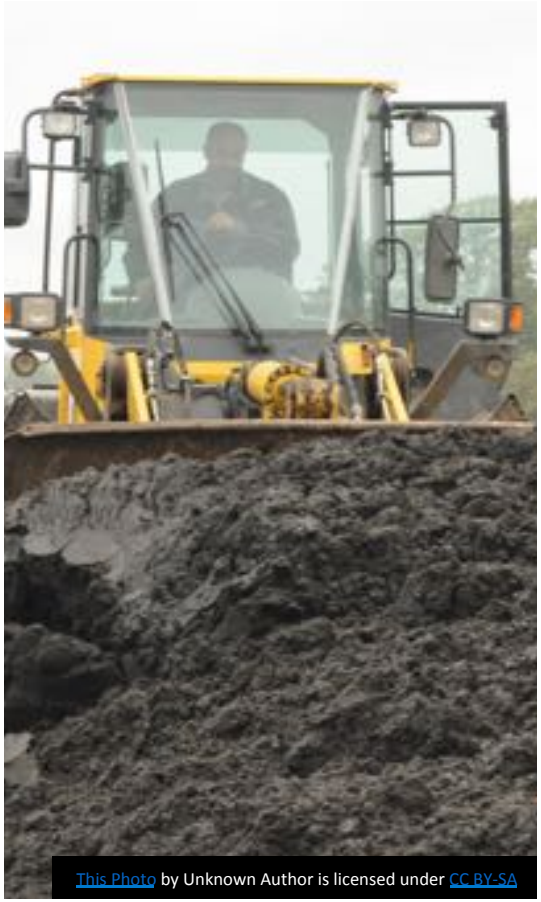
PFAS Risk and Wastewater Residuals (PFAS in Residuals)



- PFAS is present in residuals
  - Variable compounds (results for 19 tabulated)
  - Variable concentrations
- Highest concentrations are found in residuals with direct industrial input:

	4 WWTF	Decatur, AL
• PFOA (ng/g):	<17	244
• PFOS (ng/g):	58-159	3000
• FOSA (ng/g):	<44	244

- PFAS are also found in residuals without industrial input, but at lower concentrations.

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PFAS Risk and Wastewater Residuals (PFAS in Residuals)

- In the 2000s, PFAS were found in typical biosolids in concentrations of tens of parts per billion (ppb), with a U. S. average of 34 ppb for PFOA and 403 ppb for PFOS (Venkatesan and Halden, 2013). Recent tests of land applied New England biosolids and residuals found average concentrations of 2.3 and 5.3.
- Recent studies including wastewater sludge

Study	PFOA (ug/Kg)	PFOS (ug/Kg)
Zareitalabad et al., 2013 (median)	37	69
Sepulvado et al., 2011 (range)	8 – 68	80 – 219

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PFAS Risk and Wastewater Residuals (PFAS in Residuals)

2017 PFAS data compiled by NHDES and NEBRA,

22 facilities from NH and Northeast, 27 data points

Chemical	% detection	Conc. Range (ug/Kg)	Ave. Conc. (ug/Kg)
PFBA	20	0.54 – 140	34.6
PFPeA	8	18 – 27	22.5
PFHeA	84	0.21 – 75	11.0
PFHpA	26	0.077 – 2.8	1.1
PFOA	32	1.1 – 15	6.7
PFNA	30	1 – 3.6	2.6
PFBS	7	5.2 – 6.2	5.7
PFHxS	22	0.24 – 73	13.3
PFOS	62	0.59 - 390	34

PFAS Risk and Wastewater Residuals (PFAS in Soil)

- Land application of PFAS contaminated residuals results in detectable PFAS concentrations in the soil.
- Soil concentrations following land application reported in the literature:

Source	Type of loading	PFOS (ug/Kg)	PFOA (ug/Kg)
Washington et al., 2009	High PFAS	30 – 410	50 – 320
Sepulvado et al., 2011	Short-term Long-term	2 – 11 5.5 – 483	No data
Gottschall et al., 2017	One-time	0.2 – 0.4	0.1 – 0.8

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PFAS Risk and Wastewater Residuals (PFAS in Soil)

- PFAS soil concentrations can be correlated to residuals loading rate
- Correlation is especially strong for longer chain (>C8) PFCA.
- For short chain PFCA, soil concentration may correlate better with time from last application.
- PFAS concentrations in well water and surface water can be correlated to loading rate of short chain PFAS.
- Soil PFAS concentrations at depth may increase over time.
- Soil PFAS concentration can change as a result of precursor degradation.

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PFAS Risk and Wastewater Residuals (Mobility/Leaching)

- Little direct evidence that residuals without obvious industrial PFAS contributions are a risk to public health via groundwater contamination following land application
- A determination of public health risk is influenced by several factors:
  - Type and quality of wastewater residuals,
  - PFAS compounds to be considered,
  - Field conditions (climate, soil type, depth to groundwater, etc.), and
  - Regulatory requirements (loading limits, land application restriction, drinking water standards, required setback, application rates).
- Differences in these factors from state to state can lead to different conclusions regarding public health risk

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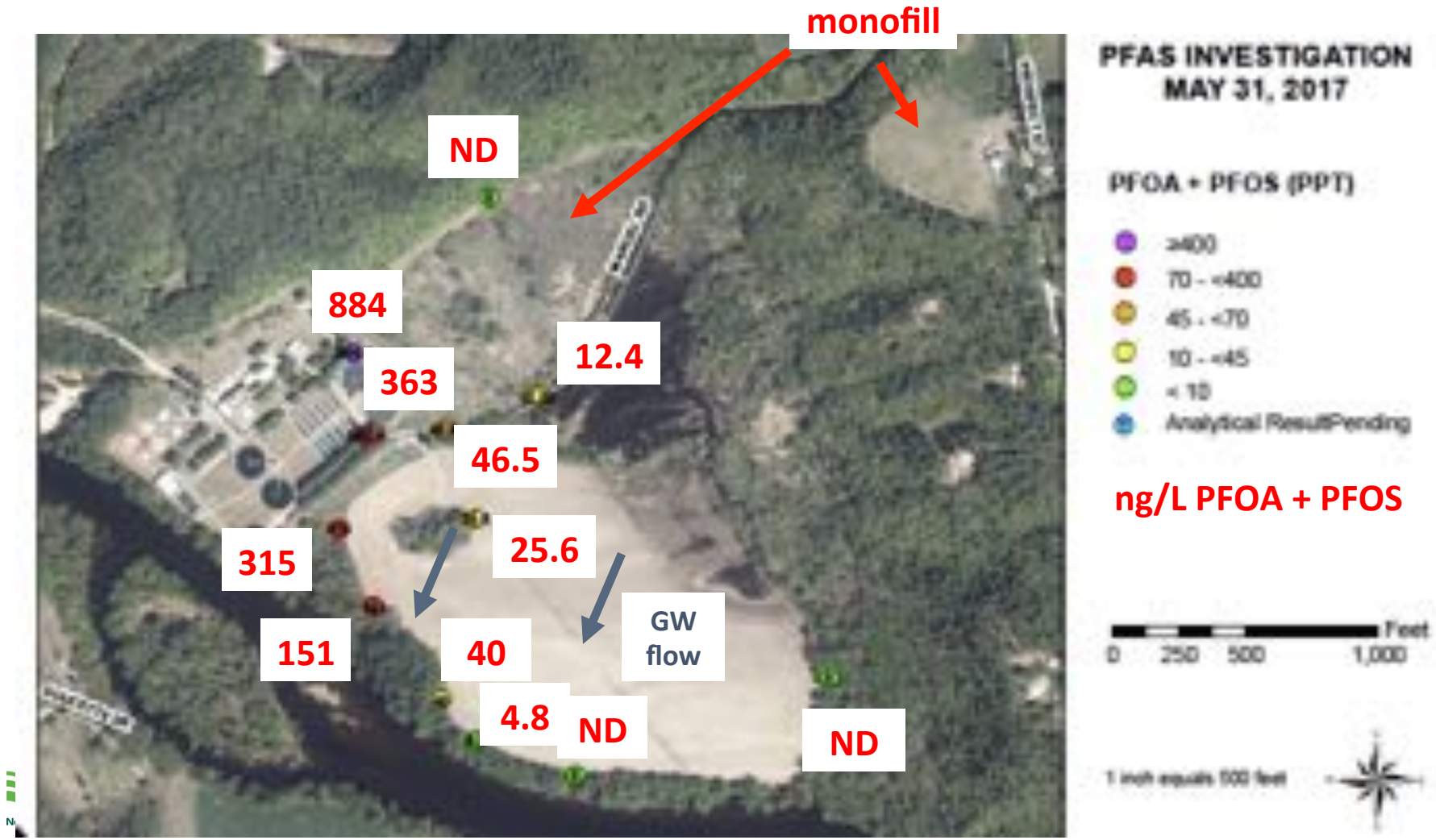
Monitoring well testing at biosolids monofill

- Monofill used in 1980s. Since ~1996, all biosolids from WWTP (11.5 MGD) have been land applied, some on farm field shown.
- Likely a worst-case scenario



Residuals management is being negatively impacted right now.

Regulatory response in March 2017 drives recycle paper mill residuals to landfill and composting business to laying off workers.

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PFAS Risk and Wastewater Residuals (Mobility/Leaching)

What does the scientific literature tell us about leachability of PFAS:

- PFAS can and does move through the vadose zone to groundwater
- Correlations between biosolids/PFAS loading and observed groundwater and surface water concentrations have been observed
- One potential set of conservative soil screening levels for protection of groundwater were calculated for PFOS (3 ug/kg) and PFOA (3 ug/kg) (Xiao et al. 2015)
- Observation in groundwater can follow release to surface soils by years if not decades, especially for longer chain PFAS (C8 and higher)

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PFAS Risk and Wastewater Residuals (Mobility/Leaching)

- Sorption in the soil does occur and is best described as a sorption equilibrium reaction
- PFAS sorption equilibria are influenced by:
  - **PFAS carbon chain length**
  - **Organic carbon content**
  - pH
  - [Ca^{+2}]
  - Clay content
  - Specific surface area

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PFAS Risk and Wastewater Residuals (Mobility/Leaching)

Conclusions on PFAS risk:

- The ubiquitous presence of PFAS in plant, animal, and human tissue as well as air, soil, and water resources confirms the obvious mobility of these chemicals
- However, there is little information to answer our original question
- A little perspective on PFAS risk from wastewater residuals:
  - PFAS are in residuals because they have been widely used for decades and persistent in the environment
  - Presence in residuals is not evidence of risk or even significant exposure in excess of current everyday exposure
  - Uncertainty on extent of public health risk

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NEBRA Response to PFAS Issue

- NEBRA pursuing answers via facilitation of relevant research and guidance:
  - Sampling and Analysis Guidance
  - Proposal for PFAS Research
  - PFAS Advisory Group
  - Webinars on PFAS issues
- Working with state agencies and legislatures to deal with PFAS risk in a measured and thoughtful manner (need to avoid regulatory over-reach)
- NEBRA as a information resource on PFAS issues

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NEBRA Resources

(see members-only page: click button on right side of https://www.nebiosolids.org)

HOT TOPIC:
PFAS (PFOA, PFOS, etc.) in Biosolids & Residuals

(Last updated September 18, 2017.)

NEBRA is collecting background information & data, communicating with state & federal regulatory agencies, researchers, and stakeholders around the continent, to provide up-to-date information & advice on this growing issue of concern.

"THANK YOU!
NEBRA's work on PFAS is supported through the generous support of...
SCA/Essity
Lystek
Resource Management Inc.
Chittenden Solid Waste District
Town of Merrimack, NH
Waste Management"

NEW!

Sept. 14, 2017: Webinar - Analyzing PFAS in Wastewater, Solids, & Soils

Recording of Webinar
Slides (PDF, ~16 MB download)
Questions & comments with presenter responses (9/21/17)

Current methods of analyzing PFAS in waters other than drinking water and solids, soils, & sediments are fraught. We are updating our sampling guidance document accordingly. It appears that ASTM methods D7968 (for soils) and D7979 (for wastewater, liquid sludges, surface water and groundwater) are best for now while U. S. EPA works toward validating and approving applicable methods. You can ask each laboratory to use these methods instead of their modified Method 537. If they suggest using their modified Method 537, you should get their full quality control data and thoroughly review it. (See NEBRA's letter to labs, below, which provides details on what QC information you should ask for.) The only current EPA-approved method is Method 537 v. 1.1 for drinking water. It is likely the only legally defensible and regulation-applicable method currently available. Contact the NEBRA office for the latest details.

Additional NEBRA Actions & Documents re PFAS...

- **NEBRA Comments: CT DEEP Draft Comprehensive Energy Strategy**, Sept. 25, 2017
- **NEBRA Letter to Labs Requesting PFAS Analysis Quality Data**, August 22, 2017
- **NH Public Radio's *The Exchange* discusses PFASs**, August 14, 2017
- **NEBRA Comments to National Groundwater Association re their draft PFAS report**, 7/31/17 see the **NGWA draft report here...**

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Join us Friday at lunch:

Further details and discussion regarding…

- PFAS in biosolids & residuals
- What NEBRA is doing
- Proposed next steps

Stay at 12:30, as the conference ends, and enjoy your box lunch with a discussion of PFAS. Location of the discussion to be announced…

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References

- Analyzing PFAS in Wastewater, Solids, & Soils: State of the Science Webinar, NEBRA Webinar, Sept. 14, 2017
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QUESTIONS?

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