QUESTIONS & ANSWERS
USDA Webinar on PFAS & Biosolids

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Presented by Dr. Linda Lee (Purdue Univ.) and Ned Beecher (NEBRA)
http://conservationwebinars.net/webinars/pfas-in-agricultural-operations/

Responses, in italics, were written by the presenters listed above, April 2021.

PFAS in Food containers

- Are PFAS associated with bulk packaging used for fruits and vegetables, meats, etc. (i.e.., coated boxes)?
    - *Probably in some cases. We know it is used in many types of packaging and containers used in food packaging, but details of this kind of information is hard to get from manufacturers of such products. You really have to look into it on a case-by-case basis.*

PFAS in Biosolids

- When you refer to the use of biosolids as well regulated, are there any places in the US where tests for PFAS in biosolids are required?
    - *Yes, several states are testing biosolids to determine typical levels and identify anomalies. Sampling and testing for PFAS at such low levels in a complex matrix like wastewater solids / biosolids is not easy, and analytical methods are still being developed and refined. States that have required testing already include CA, MA, ME, MI, NH, VT.*
- Are there any treatment / bioremediation methods for PFAS in biosolids and compost? How effective are these processes? What is the resulting waste from that process and how is it best handled or disposed?
    - *There are no methods proven at field scale. Research is ongoing. Blending biosolids with low PFAS-containing materials helps reduce loads to the soil, and thus leachable concentrations. Although data are limited on current methods being tested specifically on biosolids, so far they have not proven very successful. The concept of bioremediation is dangerous with PFAS because, as was presented, biodegradation of PFAS leads to more PFAS and the latter are the ones more typically quantified. Other approaches are to pretreatment of influent high in PFAS coming into our water resource recovery facilities to reduce PFAS in the biosolids. Of course, destruction of the whole biosolids matrix and the PFAS all at once may be possible with several developing technologies, all of which require considerable energy and are not sustainable from a larger perspective, including goals to increase carbon sequestration in soils. Incineration is one well-known option, but the required temperature to break the C-F bonds is likely over 1000 degrees C. There are many concerns about the products being produced during incineration, which has led to suits against incinerators in some states. See other developing options here: https://www.epa.gov/chemical-research/pfas-innovative-treatment-team-pitt.*
- Are there any cover crops that can be used on biosolids applied lands that may have the potential to remediate PFAS?
    - *Whatever gets taken up by a plant is not destroyed and thus the plant still needs to be dealt with. In addition. plant uptake varies between different PFAS (e.g. more uptake of*

short chain PFAS) and different crop species (e.g. grass seems to take up some PFAS; corn takes up little). But remember the levels of PFAS in soils are very low in most situations, even where biosolids or wastewater irrigation have been used for decades, so extracting those minimal levels will require considerable effort. It's important to determine if the mere presence of low levels of PFAS create any significant risk or not. Some PFAS will be sequestered / sorbed and not generally available to cause any impact. Others may leach slowly to groundwater, which may or may not cause unacceptable impacts.

- Some states allow staging of a heat dried granular biosolids on a farm field for days to months before agronomically applied. What are your thoughts on that?
    - *The potential pollutants of concern in this situation are N & P. Those are why the biosolids are being used as fertilizer. They are in the biosolids at levels of 2 – 6 percent. Field stockpiling of biosolids is common. The key is what the climate is like and how the stockpiles are managed to reduce N and P runoff and leaching. In comparison, PFAS, some of which are leachable and some not much, are in typical biosolids in 1s – 10s parts per billion – 7 orders of magnitude smaller amounts than the nutrients.* Release of PFAS from heat-dried material is no different than other biosolids. However, these heat-dried granules, when applied for their nutrient value, usually resulted in a lower loading of PFAS to the soils because less is needed than other biosolids that have lower nutrient value.
- Are there any areas in the US where produce and animal feed grown in fields treated with biosolids is being systematically tested for PFASs?
    - *Not that we are aware of, except in research projects.*
- How were the samples of biosolids collected and processed in the examples given?
    - *Refer to the methods section in published journal articles, such as https://pubs.acs.org/doi/abs/10.1021/acs.estlett.9b00280.*
- You mentioned that reducing biosolid application on cropland is not a realistic solution. Why not? In areas with manure nutrient surpluses, would replacing biosolids with manure help reduce PFAS exposure?
    - *We didn't mean to suggest that reducing land application of biosolids is not a reasonable option in some specific local situations. What we meant is that a broad policy of reducing biosolids use as fertilizers and soil amendments is not necessarily a sustainable solution for the management of wastewater solids. These materials have to be managed, and incineration and landfill disposal, the other options, have significant environmental impacts too. Transferring small amounts of PFAS into soil may not create significant risk. More research is needed.*
    - *Yes, using manures instead of biosolids will likely mean less PFAS being applied to soil. One main difference may be that biosolids may serve as a slower release source of macro-nutrients, other trace nutrients, and higher in more persistent carbon, so aids in carbon sequestration more than manure.*
- PFAS is the concern today. With new chemicals being created every day, why would one promote the use of biosolids being land applied on agricultural land when there are so many knowns and unknowns (contamination, biosecurity, food safety)? (EPA 503 Self Audit in Nov 2018 352 pollutants and 61 acutely hazardous).
    - *Biosolids provide many benefits to soils and farms, just as composts and manures do. And wastewater solids have to be managed in some way. Landfill disposal and incineration are the other options, and those have significant environmental impacts too. Why not try our best to put the nutrients and organic matter in biosolids – which is*

what 90+% of what's in biosolids – to use, for sustainable cycling? Parts per billion of PFAS in biosolids and soil may not be a significant risk – so far, research seems to indicate this is the case. Yes, it's unfortunate to have any PFAS in soil, but it is getting there by many ways, including aerial deposition, and it is found widely even in areas with no obvious source (see Vermont background study: https://anrweb.vt.gov/PubDocs/DEC/PFOA/Soil-Background/PFAS-Background-Vermont-Shallow-Soils-03-24-19.pdf).

- *The EPA Inspector General report you mention has been widely criticized by researchers and other experts. See https://www.nebiosolids.org/w4170-scientific-rebuttal-to-epa-oig.*
- *Yes, biosolids contain traces of myriad chemicals that are in our daily living environments. Most of these chemicals are not persistent in a land-applied scenario, especially fertile agricultural croplands, thus they do not build up in the environment. Also, humans are exposed to these chemicals far more in ways other than through biosolids recycling to soils, including use in their homes (chemicals form personal care products, antimicrobials, fragrances, etc.) or taken orally (e.g., antibiotics, etc.). See https://nwbiosolids.org/sites/default/files/2017-07/1705_8461w_NWbiosolids_RISKbro_web.pdf*
- *"PFAS is the concern today..." – Yes, but PFAS are clearly a worst-case contaminant – highly persistent, somewhat leachable, and with some toxicity at apparently very low levels*. Most other trace chemicals in biosolids are decomposed in the soil. Others are sequestered/sorbed in soil. The ideal, of course, is to keep working to reduce inputs of concerning contaminants into wastewater, and that is what required industrial pretreatment programs do at wastewater treatment facilities.*

  **There is continued scientific debate about how toxic PFAS are; humans have been living with them in our bodies for decades.... that sounds scary, but it's reality, and human longevity and quality of life have improved during that period, so they and all the other chemicals, etc. we are exposed to are not killing us the way cholera did when we had little or no wastewater treatment ~100+ years ago.*

Concentrations in Humans

- What levels of PFAS/PFOS are found in people and what are the health implications of these chemicals?
  - *See the graph at the bottom of this page for examples of measurements of some PFAS in human blood: https://nwbiosolids.org/sites/default/files/2017-07/1705_8461w_NWbiosolids_RISKbro_web.pdf You can see more where that came from; look up NHANES, part of the U. S. CDC.*
  - *Health implications: Look to the health research literature regarding health implications of PFAS.*
  - *One important note is that as certain PFAS are phased out, we are seeing substantial decreases in human blood samples, which supports regulation at the use and product end of 'forever' chemicals.*

Biochar

- Do PFOAS interact with biochar, bind to it?

- *Yes to some degree, and this varies with biochar source. Research is still limited.. Dr. Lee is conducitng research on this specific to biosolids-based biochar.*

- Would pyrolysis during biochar production be enough to take apart these compounds?
  - *What appears to be most important in that scenario is the temperature reached in the gas phase treatment in the pyrolysis system. If the temperature is high enough in the gas phase treatment, then the C-F bonds are broken. In most cases, it is more likely the PFAS that leaves the system is in the syngas and fate in burning the syngas is not yet known. Research on all this is limited. Dr. Lee's research to date in this area shows that when biosolids are pyrolized at low temperature and low oxygen, PFAS loads are not necessarily lower BUT the PFAS released to water in contact with biosolids is < 6 ppt for the short chain and in most cases not detectable (eg., PFOA, PFOS, etc.).*

PFAS in Pesticides/Herbicides

- Are pesticides a source of PFAS onto farmland from routine use?
  - *Possibly. PFAS are beneficial as surfactants, spreaders, and they may have been or may be used as part of the "inert" ingredients in pesticides. PFAS are known to be ingredients in some ant insecticides. PFAS may also be in the coatings used in the actual container holding the pesticides and has recently been shown to leach into the pesticide.* It is a main ingredient in some roach traps. *Information about other uses in farm chemicals is not easy to find.*
- What information is available for PFAS in pesticide/herbicide use? Can you name some pesticides that have a PFAS inactive ingredient/carrier?
  - *Only one comes to mind as exemplified in the article at the following link: https://theintercept.com/2019/04/29/brazil-pfos-sulfluramid-pesticide/*
- One of slides showed PFAS are part of insecticide active ingredients. Do you have examples of any currently registered pesticide active ingredient with PFAS (example other than contamination through containers)?
  - *This has not been measured systematically yet, and it will not show up on labels.*
- Sophie Green provided a link with info on pesticide PFAS packaging 100. https://gcc02.safelinks.protection.outlook.com/?url=https%3A%2F%2Fwww.epa.gov%2Fpesticides%2Fpfas-packaging&data=04%7C01%7C%7C99cbc69061e54d73afae08d8d516c04a%7Ced5b36e701ee4ebc867ee03cfa0d4697%7C0%7C0%7C637493640987584791%7CUnknown%7CTWFpbGZsb3d8eyJWIjoiMC4wLjAwMDAiLCJQIjoiV2luMzIiLCJBTiI6Ik1haWwiLCJXVCI6Mn0%3D%7C1000&sdata=TweUxJUTOHRqJiEecXXeuYLSeXix7jOMaMWKFNs2PzI%3D&reserved=0

PFAS in Crops

- Is there a concern for PFAS uptake in crops, with seeing PFAS can bind to soil?
  - *Crop uptake of PFAS has been demonstrated in greenhouse and some field studies in various plants, and it varies depending on crop type and specific PFAS compound (e.g. short-chain PFAS show greater plant uptake). The levels of uptake are small, and the likelihood of significant contamination of food is small. USDA and other surveys of food products tested for PFAS shows minimal contamination of the food supply, and that the most significant source and exposure is from food packaging, where the PFAS in the*

packaging coating rubs off onto the food that is consumed. But more research is needed and is ongoing.

- What do we know about levels in ag. product related to the amounts in soils and forage? Is bioaccumulation/magnification a concern?
    - *Tough question, and more research is needed. There are data showing accumulation of PFOS in particular in dairy cows in a few anomalous situations where contamination from industrial or fire-fighting activities have resulted in high levels of local contamination on a farm (in soil and/or groundwater/animal water). PFAS tend to bind to proteins, so relatively high levels can accumulate in milk. However, this seems to happen only when the PFOS levels in soils and the environment are very high, not at typical low background soil levels.*
    - *See above for discussions of plant uptake.*

Byproducts of PFAS Breakdown

- Does PFAS break down into many byproducts that need to be handled?
    - *As explained by Dr. Lee, complex PFAS can decompose some and leave behind persistent PFAS such as PFOA or PFOS.*
    - *For these persistent PFAS to be further broken down, they require very high temperature treatment or some similar level of energy to break the C-F bonds. When that happens, the fluorine (F) goes into HF – hydrofluoric acid, which has to be managed depending on the situation (see https://www.sciencedirect.com/science/article/pii/S0045653519306435). Yes hydrofluoric acid does have to be dealt with in such scenarios and is a concern, but, generally, there is little concern at this time about PFAS byproducts of such high-temperature treatments, which generally result mostly in simple common compounds like CO_2.*

PFAS in Firefighting

- Do all types of fire-fighting foam contain PFAS precursors?
    - *No. Many, but not all, Class B fire-fighting foams (often called AFFF – aqueous film-forming foam) do, but there is an increasing number of PFAS-free alternatives. And other common types of fire suppressants do not contain PFAS. DOD has several funded projects right now looking to find PFAS-free alternatives that can meet military specs which are more stringent than what others have to follow.*

PFAS in Organic Production Systems

- Are there any differences in PFAS content of milk, manure, or other agriculture products that are certified 'organic'?
    - *Don't know of any research on this specifically. The amount of research on agricultural fate of PFAS is fairly small and shows minimal PFAS in milk, manure, and agricultural products in most situations that have been looked at. There are a few anomalous situations where significant industrial or fire-fighting PFAS contamination has affected farms and their products, but these are rare exceptions, fortunately.*
- Are organic growers who use solid waste for fertilizer more at risk for accumulation and contamination?

- *Not sure what "solid waste" is referring to here. PFAS can be found in organic soil amendments, some of which included organics diverted from the municipal solid waste stream, including (in order by relative typical PFAS levels) biosolids > food & food packaging composts > food composts > manures & manure composts ≥ yard & leaf waste composts.*

PFAS in Dairy and Other Livestock Operations

- Any recommendation on cow calf operations. Should grazing be restricted on application sites for example?
  - *No, unless significant levels of PFAS are found in milk, manure, and/or soils. Some plant uptake into grass of PFOS in particular has been found, but unless soil levels are relatively very high (high 100s to 1000s ug/kg / parts per billion), there does not seem to be much chance of significant impact on animals or milk.*
- I would love to hear more about sources and impacts of PFAS on NM and ME dairies. How much monitoring of PFAS in ag products (like milk) is happening?
  - *See "Maine Farm PFAS Concern – Information Update" at the bottom left of this page: https://www.nebiosolids.org/pfas-biosolids and https://www.newscentermaine.com/article/news/health/high-pfos-levels-detected-on-maine-farm-maine-milk-supply-deemed-safe/97-6612bb54-039f-4c9b-a6cc-45da4b0df520*
  - *NM dairy: https://nmpoliticalreport.com/2019/02/19/groundwater-contamination-devastates-a-new-mexico-dairy-and-threatens-public-health/*

  See "PFAS and Biosolids and Septage on NE Farms" fact sheets on the right side of this page: https://www.nebiosolids.org/pfas-biosolids.

PFAS Testing and Regulation

- Were "ISM" type methods used, or random "discrete" samples? What was the mass of the subsamples extracted by the laboratory?
  - *Typically 0.5-1 g samples are used. There still are not formally approved extraction methods; however, what is important is the QAQC data that goes with the data reported which includes blank controls, process controls, matrix spikes, etc. and the use of isotopically-labeled surrogates and internal standards to account for recoveries and matrix effects. The method developed by the Lee lab is more robust and time-consuming than what would typically be found acceptable by a commercial lab due to time; however, other groups have requested and been given the method developed in the Lee lab.*
- Do you anticipate increasing adoption of precursor measurements will continue to increase levels of PFOS/PFAS contamination ? And when is a standard method expected?
  - *It will take several pages to answer this suite of questions in more detail, which time does not allow – look forward to webinars on this in the future. The precursor world is large. Currently, there are a couple on the EPA 24 list, but there are many more including those that are not extracted in any standard extraction method. So other than a few of them, like the ones on the EPA 24 list, nothing will be coming anytime soon.*

- How much PFAS are we finding in precipitation?
    - *It varies. There are a couple papers out there. Link to one is below. https://www.watereducation.org/aquafornia-news/rainwater-parts-us-contains-high-levels-pfas-chemical-says-study#:~:text=New%20data%20shows%20that%20rainwater,enough%20to%20trigger%20regulatory%20action*

- What is the impact on the natural environment (all species) from these substances?
    - *Again, there is no simple quick answer to this. It usually takes substantial concentrations and effects may not be visually evident, unlike some other types of exposure. So exposures tend to have more subtle effects, but what happens on a chronic versus acute scale to communities is still not well known.*
- 45. Jean Pillo: Have there been studies done of PFAS concentration from trash to energy plants?
    - *Not sure, but I suspect the research is just getting started in this area. We did mention already that PFAS could be transferred to syngas but what happens to the PFAS in the syngas is not known or even the PFAS levels.*

General Comment

- I deal with salinity. So, to me, "ppt" is parts per thousand. Having ppt mean two very different concentrations gets confusing. Is there any thought to change this?
    - *Good point! Scientists (including regulatory fields) don't use or typically spell out one part per thousand and do not abbreviate as "ppt" (which is usually understood to represent "parts per trillion"). Published papers use the measurement: e.g. ng/kg, which is clear and precise. In our writings, we try to be sure to clarify what "ppt" means when it is first used.*
- I disagree that no one knew the consequences of PFAS. Every chemist knows that chorine and fluorine are problematic chemicals
    - *Touché! Ditto! Note that adding a halogen or two or three is very common in development of pesticides as well as pharmaceuticals, for various reasons, which includes keeping them in the right place longer to accomplish their mode of action. In the case of PFAS, the perfluorocarbon chain is what makes them more problematic, as has been the case for other highly chlorinated compounds, but those others were eventually found to be biodegradable, etc. to less toxic compounds.*