PFAS IN BIOSOLIDS

PFAS in biosolids have emerged as a very serious problem

Biosolids is the "term" often used for the solid residues produced by sewage treatment plants. PFAS are found in the biosolids and liquid effluent produced by sewage plants.

A review of National Sewage Sludge Inventory stored data documents what we know about the nationwide occurrence of PFAS in sewage sludges <u>https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3776589/</u>

This is the first study to report nationwide occurrence and concentrations of perfluoroalkyl substances (PFAS) in U.S. biosolids.

Ten out of thirteen PFAS analyzed were consistently detected in all biosolids samples. PFOS was the most abundant PFAS in biosolids, followed by PFOA. PFASs in biosolids show no significant difference between pre- and post-phase out period. US PFAS levels are higher than those reported in Spain and Germany

To evaluate their nationwide occurrence in biosolids archived composite biosolids from nationals sewage sludge inventories were analyzed for PFASs to determine baseline concentrations. "Ten out of thirteen PFASs analyzed were consistently detected in all composite biosolids samples except for PFBA, PFHpA, and PFBS (Table 2). The most abundant PFAS in biosolids was PFOS, detected at a concentration of 403 ± 127 ng/g dw, followed by PFOA (34 ± 22 ng/g dw). The remaining eleven PFASs ranged between 2 and 26 ng/g (Table 2) and the mean total concentration of PFASs (ΣPFAS) detected in the five composite samples was 539 ± 224 ng/g dw. The levels detected in U.S. biosolids are more than an order of magnitude higher than levels detected in sewage sludge samples collected from Spain and Germany [35]."

EPA biosolids regulations are very weak – They regulate only 9 metals and have never regulated PFAS or most other toxic chemicals. EPA promotion of "beneficial reuse" of biosolids and industrial wastewater residuals has worsened the situation, spreading the contamination nationwide. Municipal wastewater treatment does not destroy PFAS molecules and has transformed some to more dangerous forms. Waste exits the plant in either effluent or sludge, which may be incinerated but is usually land applied. Short chain PFAS in particular move right into effluent because they are so soluble. Effluent is released to surface waters or used for irrigation. During sludge digestion PFAS have been found to be released to air.

The Interstate Technology and Regulatory Council has documented the presence of PFAS in biosolids and effluent and that they then enter the food chain.

(ITRC), a public-private coalition working to reduce barriers to the use of innovative air, water, waste, and remediation environmental technologies and processes, has developed a series of fact sheets summarizing the latest science and emerging chronologies regarding PFAS chemicals. Chapter 4.4.2 Biosolids of Interstate Technology and Regulatory Council's Factsheet "History and Use of PFAS "<u>https://pfas-1.itrcweb.org/wp-</u>content/uploads/2017/11/pfas_fact_sheet_history_and_use__11_13_17.pdf

"PFAS (measured as PFCAs and PFSAs) have been found in domestic sewage sludge (Higgins et al. 2005). USEPA states that more than half of the sludge produced in the United States is applied to agricultural land as biosolids, therefore biosolids application can be a source of PFAS to the environment (USEPA 2017n). The most abundant PFAS found in biosolids (PFOS and PFOA) are the same as in WWTP effluent; however, biosolids may also contain other long-chain PFAS (Hamid and Li 2016). Application of biosolids as a soil amendment can result in a transfer of PFAS to soil (Sepulvado et al. 2011). These PFAS can then be available for uptake by plants and soil organisms. There are indications that PFAAs can enter the food chain through the use of biosolids-amended soil (Lindstrom et al. 2011; Blaine et al. 2013; Blaine et al. 2014; Navarro et al. 2017). Further studies show that PFAS concentrations can be elevated in surface and groundwater in the vicinity of agricultural fields that received PFAS contaminated biosolids for an extended period of time (Washington et al. 2010)."

PFAS contamination has been found to move from land applications of sludges to edible crops, to forage for animals, into dairy products, and into groundwater and surface waters. Studies show that PFAS concentrations can be elevated in surface and groundwater in the vicinity of agricultural fields that received PFAS contaminated biosolids for an extended period of time (Washington et al. 2010)."

Discovery of contaminated milk at dairies - Maine from sludge, and New Mexico from contaminated water <u>https://www.buzzfeednews.com/article/nidhisubbaraman/pfas-food-farms-</u> milk-produce

Stone's milk tested at 690 parts per trillion for PFAS, nearly 10 times the Environmental Protection Agency's guidelines for two of the chemicals. Activists say Maine's detection limit of 50 parts per trillion was too high.

Despite pressure from the wastewater industry saying PFAS problems are not serious and too little is known, states are now addressing biosolids. Some like Michigan, Wisconsin, and Maine are calling for testing. One city Wisconsin banned land application because of high levels of PFAs in its biosolids. Maine is the only state with sludge application limits for biosolids: 2.5 ppb for PFOA, 5.2 ppb for PFOS, 1900 pb for PFBS. Soil at application sites must be tested but application is allowed if no PFAS are detected. In September 2017 the Michigan DEQ suspended approval of spreading biosolids from Lapeer's WWTP based on levels of PFOS found in their biosolids – which had been used as fertilizer since 2001.

An example of the problem in just one Michigan city, Lapeer Plating & Plastics, a decorative chrome plating facility pre-treats and discharges its industrial process wastewater to the City of Lapeer's wastewater treatment plant (WWTP). This treatment plant has had approval from Michigan's Department of Environmental Quality (DEQ) since 2001 to spread the biosolids it generates on land as fertilizer. Lapeer's WWTP historically used mist suppressants containing PFOS, one of the best-known PFAS compounds, in their industrial processes to comply with hexavalent chromium air emission requirements. In 2017 the DEQ found elevated levels of PFOS in Lapeer Plating & Plastics' process wastewater.

PFAS contamination is now a global environmental justice problem. All over the planet people and wildlife have been contaminated without their consent. We elaborate on this in the section on "FOOD CONTAMINATION" but here are a couple of examples:

Concentrations of PFOS in San Francisco Bay wildlife have historically been among the highest reported globally. The contamination may be from facilities such as factories, military bases and airports or from atmospheric deposition or contaminated waters spread globally.

In the far Arctic wolves and caribou are contaminated with PFAs from air and water. Wolves and people rely on caribou for food. PFAS contamination found there in people is linked to disease. Concentrations of PFOS in San Francisco Bay wildlife have historically been among the highest reported globally.

FOOD CONTAMINATION

Food consumption is a major pathway of exposure to PFAS. They have been detected in human serum samples from all around the world and are ubiquitous in the global environment and wildlife. They do not biodegrade, they bioaccumulate and they biomagnify in the food chain.

<u>https://www.researchgate.net/publication/285758359_Human_dietary_exposure_to_per-</u> _and_poly-fluoroalkyl_substances_PFASs.

Michigan has issued "do not eat fish" advisories for PFAS and also for deer.

One deer out of 20 tested around the former Wurtsmith Air Force Base had high levels of PFOS in muscle (547 parts per billion, exceeding Michigan's action level of 300 ppb)

A 2019 Food and Drug Administration study of PFAS in foods found PFAS in nearly half of the meat and fish tested at levels two or more times over existing federal advisory levels.

The FDA tested produce bought at farmers' markets near a PFAS production plant and other food purchased in the eastern United States, as well as dairy products from a farm near an Air Force base in New Mexico. Many of the items contained levels of PFAS well above the Environmental Protection Agency's current health advisory level for consumption in drinking water. There are currently no enforceable environmental or health standards for PFAS in the U.S. The level in the chocolate cake was more than 250 times the only federal guidelines, which are for some PFAS in drinking water. FDA study: <u>https://www.fda.gov/food/chemicals/and-polyfluoroalkyl-substances-pfas</u>

There have now been many studies of how plants take up PFAS from contaminated water and biosolids. Levels of PFAS documented in foods (milk, vegetables etc.) are linked to applications of sewage and papermill sludges or effluents.

"Human dietary exposure to per- and poly-fluoroalkyl substances (PFASs)" <u>https://www.researchgate.net/publication/285758359_Human_dietary_exposure_to_per-</u> _and_poly-fluoroalkyl_substances_PFAS

"Accumulation of perfluorinated alkyl substances (PFAS) in agricultural plants: A review" a 2017 analysis of the literature indicated a direct correlation between PFAS concentrations in soil and bioaccumulation in plants. Low accumulations of perfluorooctanoic acid (PFOA) and perfluorooctane <u>sulfonic acid</u> (PFOS) have been found in peeled potatoes and cereal seeds, while short-chain compounds can accumulate at high levels in leafy vegetables and fruits.

A 2010 Minnesota Department of Health study (Occurrence of perfluoroalkyl substances (PFAS) in garden produce at homes with a history of PFAS-contaminated drinking water. Outdoor tap water, garden soil, and garden produce was collected at homes impacted by the contamination. They found short-chain PFAS in water impacted produce levels more than long-chain PFAS in soil. Perfluorobutanoic acid (PFBA) was the primary PFAS present in water, followed by perfluoropentanoic acid (PFPA). Although PFBA, perfluorooctanoic acid (PFOA) and perfluorooctane_sulfonate (PFOS) were present in 100% of soil samples at higher concentrations compared to other PFAS, only PFBA was readily translocated to plants. Significant_determinants of PFBA concentration in produce were the amount of PFBA applied to the garden via watering and the type of produce tested. Results from this real-world study are consistent with experimental findings that short-chain PFAS have the highest potential to translocate to and bioaccumulate in edible plants. These findings are globally relevant, as short-chain PFAS serve as commercial substitutes for longer-chain compounds and are increasingly detected in water due to their relatively high_solubility_and mobility.

The Minnesota Department of Health studied foods grown in PFAS contaminated water (Occurrence of perfluoroalkyl substances (PFAS) in garden produce at homes with a history of PFAS-contaminated drinking water.)

Wisconsin - https://madison.com/wsj/news/local/govt-and-politics/wisconsin-case-shows-howsewage-plants-spread-unregulated-toxins-across/

Studies of contaminated milk and food :https://www.buzzfeednews.com/article/nidhisubbaraman/pfas-food-farms-milk-produce Stone's milk tested at 690 parts per trillion for PFAS, nearly 10 times the Environmental Protection Agency's guidelines for two of the chemicals. Activists say Maine's detection limit of 50 parts per trillion was too high.

Michigan has issued "do not eat" fish advisories for PFAS and also for deer. Near the former Wurtsmith Air Force Base One deer out of 20 tested had high levels of PFOS in muscle (547 parts per billion, exceeding Michigan's action level of 300 ppb). Contaminated of milk from contaminated soils or groundwater was reported in Maine, Georgia, and New Mexico. Milk had to be destroyed.

"Uptake of perfluoroalkyl acids into edible crops via land applied biosolids: Field and greenhouse studies" found PFAS in lettuce and tomatoes

It concluded "Furthermore, due to the persistence of PFAAs, repeated agricultural biosolids applications may present a potential exposure route for terrestrial food webs if PFAAs contaminate surface or ground water destined for animal or human consumption or bioaccumulate in the edible portion of crops.

" https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NHEERL&dirEntryId=307369

In far Arctic wolves and caribou contaminated with PFAs from air and water. People eat caribou and fish. PFAS found in their blood linked to breast

cancer., https://pubs.acs.org/doi/abs/10.1021/es201353v

The biomagnification behavior of perfluorinated carboxylates (PFCAs) and perfluorinated sulfonates (PFSAs) was studied in terrestrial food webs consisting of lichen and plants, caribou, and wolves from two remote northern areas in Canada. Six PFCAs with eight to thirteen carbons and perfluorooctane sulfonate (PFOS) were regularly detected in all species. Lowest concentrations were found for vegetation (0.02–0.26 ng/g wet weight (ww) sum (Σ) PFCAs and 0.002–0.038 ng/g ww PFOS). Wolf liver showed highest concentrations (10–18 ng/g ww ΣPFCAs and 1.4–1.7 ng/g ww PFOS) followed by caribou liver (6–10 ng/g ww ΣPFCAs and 0.7–2.2 ng/g ww PFOS). Biomagnification factors were highly tissue and substance specific. Therefore, individual whole body concentrations were calculated and used for biomagnification and trophic magnification assessment. Trophic magnification factors (TMF) were highest for PFCAs with nine to eleven carbons (TMF = 2.2-2.9) as well as PFOS (TMF = 2.3-2.6) and all but perfluorooctanoate were significantly biomagnified. The relationship of PFCA and PFSA TMFs with the chain length in the terrestrial food chain was similar to previous studies for Arctic marine mammal food web, but the absolute values of TMFs were around two times lower for this study than in the marine environment. This study demonstrates that challenges remain for applying the TMF approach to studies of biomagnification of PFCAs and PFSAs, especially for terrestrial animals.

Contamination of wildlife is found throughout the world – from the US to the Arctic to the Antarctic.

"Concentrations of perfluorooctane sulfonate (PFOS) in San Francisco Bay (SF Bay) wildlife have historically been among the highest reported globally.

Per- and polyfluoroalkyl substances (PFASs) in San Francisco Bay wildlife: Temporal trends, exposure pathways, and notable presence of precursor compounds." <u>Chemosphere</u>. 2017 Oct;185:1217-1226. doi: 10.1016/j.chemosphere.2017.04.096. Epub 2017 Apr 21. <u>Sedlak MD1</u>, <u>Benskin JP2</u>, <u>Wong A3</u>, <u>Grace R4</u>, <u>Greig DJ</u>5.

To track continuing exposures to PFASs and assess the impact of the 2002 phase-out of production of PFOS and related chemicals in the US, nine perfluoroalkyl carboxylic acids (PFCAs; C4-C12), three perfluoroalkyl sulfonic acids (PFSAs; C4, C6, C8) and perfluoroactane sulfonamide (PFOSA, a PFOS precursor) were measured in SF Bay cormorant eggs in 2012 and harbor seal serum sampled between 2009 and 2014. PFOS remained the dominant perfluoroalkyl acid (PFAA) in both cormorant eggs (36.1-466 ng/g) and seals (12.6-796 ng/g) from 2012 and 2014, respectively. Concentrations in seal and bird eggs from the South Bay have declined approximately 70% in both matrices. To elucidate potential pathways of exposure, prey fish, sediments and wastewater effluent were analyzed for PFASs, and in the case of sediment and effluent, a suite of PFAA precursors. PFOS was the dominant PFAA in prey fish and sediment. In effluent, different mixtures of PFAAs were measured, with PFOS, PFHxA, and PFOA detected in the highest concentrations. Polyfluoroalkyl phosphate diesters (PFCA-precursors) were observed at concentrations over an order of magnitude higher than PFCAs in sediment, highlighting their importance as a potential, on-going source of PFCAs to SF Bay wildlife. These findings suggest that the PFOS phase-out has resulted in reduced burdens to wildlife in SF Bay, but that exposure to diverse and incompletely characterized PFASs continues. Nine perfluoroalkyl carboxylic acids (PFCAs; C4-C12), three perfluoroalkyl sulfonic acids (PFSAs; C4, C6, C8) and perfluorooctane sulfonamide were measured in SF Bay cormorant eggs in 2012 and harbor seal serum sampled between 2009 and 2014. PFOS remained the dominant perfluoroalkyl acid (PFAA) in both cormorant eggs (36.1-466 ng/g) and seals (12.6-796 ng/g) from 2012 and 2014, respectively. Polyfluoroalkyl phosphate diesters (PFCA-precursors) were observed at concentrations over an order of magnitude higher than PFCAs in sediment, highlighting their importance as a potential, on-going source of PFCAs to SF Bay wildlife.

More articles about PFAS in wildlife.

"PERFLUOROALKYL ACIDS: What Is the Evidence Telling Us?" (EHP – 2007) https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1867999/.

"The first research to suggest that the levels of PFAAs being detected in wild animals could be impacting their immune systems involved bottlenose dolphins believed to have "the highest [PFOS levels] ever reported in any wildlife species"

"Perfluorinated alkyl acids in plasma of American alligators (Alligator mississippiensis) from Florida and South Carolina." <u>Environ Toxicol Chem.</u> 2017 Apr;36(4):917-925. doi: 10.1002/etc.3600. Epub 2016 Sep 26. <u>https://www.ncbi.nlm.nih.gov/pubmed/27543836</u>.

PFAS Also found in South African crocodiles. <u>https://www.ncbi.nlm.nih.gov/pubmed/27038902</u>

How should contaminated biosolids be managed? Incineration and landfilling are bad management options.

Incineration and other thermal treatment facilities lead to air releases because few if any get hot enough to destroy PFAS. Such air emissions can travel far. Dioxin from a US incinerator has been identified in a remote Arctic village. Citizens living near the few incinerators where PFAS are sent for destruction are concerned that EPA and states do not require local testing to prove they are not being impacted.

Landfilling PFAS wastes is not a good idea. It has contaminated groundwater and also lead to air emissions. Collected leachate may be sent to sewage plants but they do not remove PFAS. They persist in effluent and biosolids and contaminate food if land applied.

Municipal wastewater treatment does not destroy PFAS molecules and can transform some to more dangerous forms. They exit the plant in either effluent or sludge (biosolids). Biosolids may be incinerated but are usually land applied. Short-chain PFAS predominate in effluent because they are extremely soluble. Effluent and biosolids contaminate food

According to "Review of the fate and transformation of per- and polyfluoroalkyl substances (PFASs) in landfills" "Studies have shown that perfluoroalkyl acids (PFAAs) are routinely detected in landfill leachate, with short chain (C4-C7) PFAAs being most abundant, possibly indicating their greater mobility, and reflecting the industrial shift towards shorter-chain compounds. Despite its restricted use, perfluorooctanoic acid (PFOA) remains one of the most abundant PFAAs in landfill leachates. Recent studies have also documented the presence of PFAA-precursors (e.g., saturated and unsaturated fluorotelomer carboxylic acids) in landfill leachates at concentrations comparable to, or higher than, the most frequently detected PFAAs. Landfill ambient air also contains elevated concentrations of PFASs, primarily semi-volatile precursors (e.g., fluorotelomer alcohols) compared to upwind control sites, suggesting that landfills are potential sources of atmospheric PFASs."

"Review of the fate and transformation of per- and polyfluoroalkyl substances (PFASs) in landfills". <u>https://www.ncbi.nlm.nih.gov/pubmed/29275271</u>

Abstract A critical review of existing publications is presented i) to summarize the occurrence of various classes of per- and polyfluoroalkyl substances (PFASs) and their sources in landfills, ii) to identify temporal and geographical trends of PFASs in landfills; iii) to delineate the factors affecting PFASs in landfills; and iv) to identify research gaps and future research directions. Studies have shown that perfluoroalkyl acids (PFAAs) are routinely detected in landfill leachate, with short chain (C4-C7) PFAAs being most abundant, possibly indicating their greater mobility, and reflecting the industrial shift towards shorter-

chain compounds. Despite its restricted use, perfluorooctanoic acid (PFOA) remains one of the most abundant PFAAs in landfill leachates. Recent studies have also documented the presence of PFAA-precursors (e.g., saturated and unsaturated fluorotelomer carboxylic acids) in landfill leachates at concentrations comparable to, or higher than, the most frequently detected PFAAs. Landfill ambient air also contains elevated concentrations of PFASs, primarily semi-volatile precursors (e.g., fluorotelomer alcohols) compared to upwind control sites, suggesting that landfills are potential sources of atmospheric PFASs. The fate of PFASs inside landfills is controlled by a combination of biological and abiotic processes, with biodegradation releasing most of the PFASs from landfilled waste to leachate. Biodegradation in simulated anaerobic reactors has been found to be closely related to the methanogenic phase. The methane-yielding stage also results in higher pH (>7) of leachates, correlated with higher mobility of PFAAs. Little information exists regarding PFAAprecursors in landfills. To avoid significant underestimation of the total PFAS released from landfills, PFAA-precursors and their degradation products should be determined in future studies. Owing to the semi-volatile nature of some precursor compounds and their degradation products, future studies also need to include landfill gas to clarify degradation pathways and the overall fate of PFASs.

Landfilling has been suggested as an interim solution because it can be monitored and leachate sent to sewage plants for treatment. We know, however, that sewage plants do little or nothing to remove them. Recall that "Recent studies have also documented the presence of PFAA-precursors (e.g., saturated and unsaturated fluorotelomer carboxylic acids) in landfill leachates at concentrations comparable to, or higher than, the most frequently detected PFAAs." Biodegradation in the landfill releases most of the PFASs from landfilled waste into the leachate. If sent to sewage plants the PFAS are again released in biosolids and effluent. That effluent is usually land applied or put into surface waters. Not a final solution!

Treatment technologies are being studied. "Forever chemicals' no more?" - March 25: C&E News March 2019 <u>https://cen.acs.org/environment/persistent-pollutants/Forever-chemicals-technologies-aim-destroy/97/i12</u>

"Plasma, on the other hand, can break down PFAS molecules much faster but may not degrade them completely. In some cases, these destruction technologies—sound waves, plasma, and the like—that are being developed for highly contaminated water might be paired with a filter material like granular activated carbon or an ion-exchange resin to eliminate the problem of long-term waste when treating larger volumes of less-contaminated water. For example, an ion-exchange resin could be regenerated with a solvent rinse, then the concentrated rinse solution treated with plasma or an electrochemical approach to destroy the PFAS. Chris Higgins of the Colorado School of Mines, who studies emerging contaminants like PFAS, says he sees these "treatment trains" as key in the future of PFAS treatment. "

Excavation with offsite disposal in a landfill is relevant for PFAS-impacted source zones; however, in addition to cost, the potential long-term liability of this option should be carefully considered given PFASs persistence and limited PFAS treatment or monitoring in

most landfill leachates. Landfill operators in several countries (notably Australia and Sweden) are becoming increasingly restrictive regarding PFAS-impacted wastes. Excavated soils may be incinerated at high temperatures (>1,100 °C) to destroy PFASs, although this may be prohibitively expensive for many sites. In the United Kingdom, wastes containing PFOS (characterized as a persistent organic pollutant) above 50 milligrams per kilogram may require destruction even if classified as Nonhazardous (ATP3 1342/2014). Capping of soil impacts left in situ or containment of excavated soil within engineered stockpiles to prevent infiltration and leaching to groundwater have both been implemented and require long-term management. For this management approach, continued liability as well as restrictions on redevelopment are key considerations. Soil washing, or aggressively leaching PFAS from soil particles ex situ to capture the PFAS-

soil washing, or aggressively leaching PFAS from soil particles ex situ to capture the PFASrich leachate, may be suitable to minimize volumes of PFAS-impacted soil. Applicable PFASimpacted soils typically have relatively low fines content, as leachate treatment and fines treatment/disposal may be complex and expensive.

The need for more data should not be used as a justification for delaying risk mitigation actions.

The inability of current technologies to destroy PFAS reminds of the immediate need to stop the production and use of fabrics, carpets, shoes and clothing containing PFAS. Though biomonitoring studies from several countries have shown that the concentrations of PFOS and PFOA have decreased because of their voluntary phaseouts from 2000 to 2002, levels of short-chain PFAS used as substitutes are increasing.