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Health Risk Assessment of Poly- and Perfluoroalkyl Substances in Soils and Crops from the Land Application of Biosolids

Linda Hall, Tina Hoang, and ***Robert Scofield*** (rscofield@gsi-net.com)
(GSI Environmental, Oakland, CA, USA)

ABSTRACT: Land application is the primary method of biosolids management in the United States. Municipalities have attempted to ban the land-application of biosolids due to questions over human exposure to chemicals; poly- and perfluoroalkyl substances (PFASs) are among the most frequently-cited. PFASs are chemically-stable. Waste water treatment processes do not remove or degrade many PFASs, and they are common constituents of biosolids. Land-application of biosolids has been reported as a source of PFASs in soil, thus we evaluated the potential human health impacts for a hypothetical site where biosolids had been applied to soil for years. We considered direct exposure to PFASs in soils, and also evaluated human health impacts from the consumption of meat and milk from cows fed crops grown on those soils. Separate calculations addressed exposures from ingestion of homegrown produce. Soil screening levels and hazard quotients (HQs) demonstrated that soil exposures and ingestion of meat and/or milk from animals fed crops grown on biosolids-amended soil did not present concerns for human health under our assumed conditions. Ingestion of homegrown produce resulted in an elevated HQ for PFOS, indicating that ingestion of homegrown produce grown on soils amended with biosolids warranted further analysis for our assumed conditions.

INTRODUCTION

Land application is the primary method of biosolids management in the United States, with nearly 4 million dry tons applied annually (WERF, 2010). Increasingly, some concerned municipalities have attempted to ban the land-application of biosolids due to questions over human exposure to chemicals of emerging concern. Of these chemicals, poly- and perfluoroalkyl substances (PFASs) are among the most frequently-cited (NBRA, 2017), given their persistence and toxicity. Many PFASs are ubiquitous in the environment due to their long-standing and widespread use in industrial and consumer products (ATSDR, 2015).

Conventional waste water treatment processes do not effectively remove or degrade many PFASs, and as a result, they are common constituents of treated effluent, sludge, and biosolids (Venkatasen and Halden, 2013). Land-application of biosolids has been reported as a source of PFASs in soil (Higgins et al., 2005).

Humans may be exposed to PFASs in land-incorporated biosolids via direct contact with soil or surface runoff; inhalation of re-suspended particulates; ingestion of meat and milk from cattle fed crops grown on biosolids-amended soils; or direct ingestion of homegrown vegetables. In spite of these concerns, few site-specific health risk assessments for PFASs in land-applied biosolids have been performed.

Our objective was to evaluate the potential health risks to humans from the land application of Class A biosolids from a municipal source for a hypothetical, but realistic situation. Class A biosolids have been heat-treated to reduce pathogens to virtually non-detectable levels; these biosolids must also comply with requirements regarding the level of select organic chemicals, metals, odors, and vector attractions as per the U.S. Environmental Protection Agency (U.S. EPA), Part 503 Rule (U.S. EPA, 1993). Because the majority of crops grown on biosolids-amended soils are used as livestock feed, our primary focus was to evaluate exposure of humans who may ingest meat and milk from these animals. We also estimated potential human exposure to PFASs in homegrown vegetables grown on biosolids-amended soils. For both exposure scenarios, we addressed direct soil-based exposures by comparison to screening levels calculated with the U.S. EPA Regional Screening Level Calculator (U.S. EPA, 2017).

MATERIALS AND METHODS

We evaluated potential human exposures to the PFASs perfluorooctanoic acid (PFOA), perfluorosulfonic acid (PFOS), and perfluorobutane sulfonate (PFBS) – the three PFASs that have U.S. EPA-derived reference doses (RfDs) (U.S. EPA, 2014, 2016a, 2016b). We estimated exposures for a hypothetical site assumed to be used for either agricultural crop production or residential purposes. Our conceptual site model (CSM) (Figure 1) for both land use scenarios depicts the complete, potentially complete, or incomplete exposure pathways associated with the land-incorporation of biosolids. We address the ingestion of meat, milk, and homegrown produce quantitatively, but evaluate contact with surface runoff and inhalation or particulates qualitatively because runoff and dust mitigation practices minimize exposures from these routes. We did not evaluate the ingestion of groundwater, given that there is no clear evidence to indicate that PFASs from biosolids derived from municipal waste treatment facilities impact groundwater. While there are two reports which show that PFASs from biosolids impacted by industrial wastes have contaminated groundwater, these appear to be isolated instances that are not relevant to conventional municipal biosolids (Holzer et al., 2008; Lindstrom et al., 2011). Soil-based exposures were evaluated by comparison to screening levels calculated with the U.S. EPA Regional Screening Level Calculator (U.S. EPA, 2017). These screening levels (SLs) address incidental ingestion and dermal contact with soil.

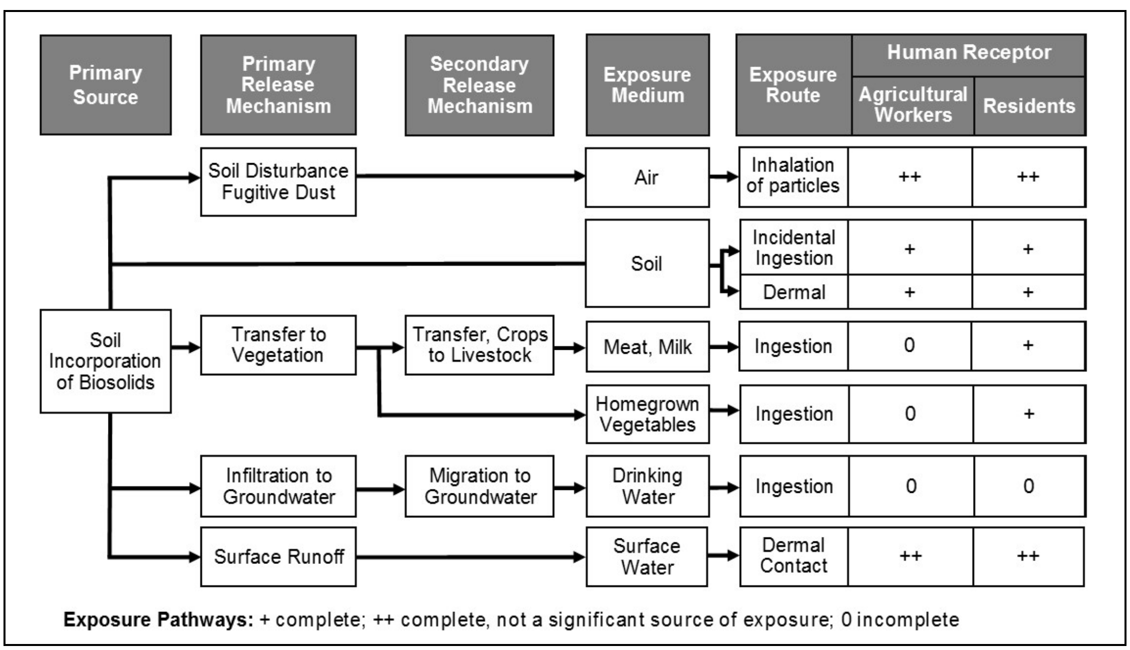

FIGURE 1. Conceptual site model, potential PFAS exposure pathways following land application of Class A biosolids.

To evaluate the magnitude of human exposure to PFASs from land-applied biosolids, we relied on PFAS soil concentration data from Sepulvado et al. (2011), summarized in

Table 1. These PFAS soil concentrations represent values from land that received agronomic applications of biosolids over a 33-year period.

TABLE 1. Concentration of PFASs in biosolids-amended soil.[1]

Chemical	Concentration (mg/kg)
PFBS	1.0E-4
PFOS	1.5E-1
PFOA	9.0E-3

[1] Source: Estimated from Sepulvado et al. 2011

Calculation of Plant, Meat, and Milk Concentrations. Soil-to-plant uptake factors, or bioaccumulation factors (BAFs), were calculated (Equation 1) for agricultural crops based on measured BAFs for corn and wheat (Blaine et al., 2013; Wen et al., 2014). BAFs for homegrown produce were calculated using the same equation, but with values from Blaine et al. (2013, 2014) for the edible portion of lettuce, radish, celery, tomato, and peas grown on municipal biosolids-amended soil (Table 2).

$$BAF_{soil-vegetation} = C_{vegetation} / C_{soil} \quad \text{(Eq. 1)}$$

where

$BAF_{soil\text{-}vegetation}$ = Bioaccumulation factor for PFASs that transfer from soil to agricultural crops or homegrown produce, unitless
$C_{vegetation}$ = Mean concentration of PFAS in agricultural crops or produce
C_{soil} = Concentration of PFAS in soil

The concentration of PFOA, PFOS, and PFBS in agricultural crops or homegrown produce was estimated (Equation 2) as the product of the soil concentration and BAF (OEHHA, 2015). We assumed that deposition does not contribute significantly to plant tissue concentrations, and that the uptake of PFASs from soil was the dominant transfer mechanism from soil to plant tissue.

$$C_{vegetation} = C_{soil} \times BAF_{soil-vegetation} \quad \text{(Eq. 2)}$$

where

$C_{vegetation}$ = PFAS concentration in crops or homegrown produce (mg/kg)
C_{soil} = PFAS concentration in soil (mg/kg)
$BAF_{soil\text{-}vegetation}$= BAF for PFAS uptake from soil to crops or homegrown produce (unitless)

Milk and meat (beef) concentrations of PFASs were calculated (Equation 3) from plant-to-milk and plant-to-meat biotransfer factors (BTFs) for PFOA and PFOS measured by Vestergren et al. (2013). In the absence of an experimentally-determined BTF for PFBS, we assumed that PFBS transferred to meat and milk in the same proportion as PFOS. BTFs are summarized in Table 2; concentrations of PFAs in crops, meat, milk, and produce are provided in Table 3.

$$C_{meat,milk} = Intake_{feed} \times C_{vegetation} \times BTF_{vegetation-meat,milk} \quad \text{(Eq. 3)}$$

where

$C_{meat,milk}$ = PFAS concentration in meat or milk (mg/kg)
$Intake_{feed}$ = Feed (crop) ingestion rate of beef cattle (9 kg/d) or dairy cattle (22 kg/d) (OEHHA, 2015)
$C_{vegetation}$ = PFAS concentration in crops (mg/kg)
$BTF_{vegetation\text{-}meat,milk}$ = BTF for PFAS uptake from crops to animals (d/kg)

TABLE 2. PFAS bioaccumulation factors (BAF) and biotransfer factors (BTFs).[a]

Analyte	Meat and Milk Pathway			Produce Pathway
	$BAF_{soil\text{-}crops}$[a] (unitless)	$BTF_{vegetation\text{-}meat}$[b] (d/kg)	$BTF_{vegetation\text{-}milk}$[b] (d/kg)	$BAF_{soil\text{-}produce}$[c] (unitless)
PFBS	1.25	0.071	0.021	3.75
PFOS	0.10	0.071	0.021	0.49
PFOA	0.53	0.012	0.011	0.61

[a] Average BAFs were calculated from corn (grain and stover) and wheat (husk, straw, and grain) concentrations, assuming non-detected concentrations were equivalent to the detection limit and the below limit-of-quantification (LOQ) concentrations were equivalent to one half the LOQ (Blaine et al., 2013, Wen et al., 2014).
[b] BTF values for PFOS and PFOA are from Vestergren et al., 2013. There were no data for PFBS, so the value for PFOS was used as a surrogate.
[c] Average BAFs were calculated from greenhouse lettuce grown from biosolids-amended soil from municipal sources (Blaine et al., 2013); and radish roots, celery shoots, tomato fruit, and pea fruit (Blaine et al., 2014), where LOQ concentrations were assumed to be equivalent to zero.

TABLE 3. Estimated PFAS concentrations in vegetation, meat, and milk.

Analyte	Concentration (mg/kg)			
	Crops	Meat	Milk	Produce
PFBS	1.3E-4	8.0E-5	5.9E-5	3.8E-4
PFOS	1.5E-2	9.6E-3	7.1E-3	7.4E-2
PFOA	4.8E-3	5.2E-4	1.2E-3	5.5E-3

Ingestion of Meat and Milk or Homegrown Produce. Human intake of PFOA, PFOS and PFBS from the ingestion of meat and milk (Equation 4) or of homegrown produce (Equation 5) was calculated based on methods from the U.S. EPA (1989) and the exposure parameters listed in Table 4.

TABLE 4. Exposure parameters.

Exposure Parameter			Animal Product		Homegrown Produce
Variable	Description	Units	Beef	Milk	
$IR_{meat,\ milk\ or\ produce}$	Ingestion Rate	kg/meal	0.062[a]	0.24[b]	0.053[c]
$FI_{meat,\ milk,\ or\ produce}$	Ingestion Fraction	unitless	0.12[d]	1.0	1.0
EF	Exposure Frequency	meals/year	350		
ED	Exposure Duration	years	13[e]		
BW	Body Weight	kg	80		
AT	Averaging Time	days	4,745[f]		

[a] An 80-kg individual consumes the average of 7.7E-4 kg/kg-d beef (U.S. EPA, 2011. Table 11-5) for one meal/day.
[b] An average of 0.24 kg/d of fluid milk (U.S. EPA, 2011. Table 11-12) is consumed for one meal/day.

[c] An 80-kg individual consumes an average of 6.6E-4 kg/kg-d home-grown vegetables for one meal/day. Value is applicable to populations that garden, and has been adjusted to account for preparation losses and post-cooking losses (U.S. EPA, 2011. Table 13-70).
[d] Assumed that all dairy cows that were slaughtered for beef were fed biosolid-amended crops (USDA, 2016).
[e] Mean current residence time of 13 years (U.S. EPA, 2011. Table 16-5).
[f] AT = ED x 365 days/year

$$Intake_{meat,milk} = \frac{C_{meat,milk} \times IR_{meat,milk} \times FI_{meat,milk} \times EF \times ED}{BW \times AT} \qquad \text{(Eq. 4)}$$

where

Intake$_{meat,milk}$ = Daily intake of meat or milk (mg/kg-d)
$C_{meat,\ milk}$ = Concentration of PFAS in meat or milk (mg/kg)
Intake$_{meat,milk}$ = Ingestion rate of meat or milk (kg/meal)
$FI_{meat,milk}$ = Fraction of meat or milk ingested from contaminated source (unitless)
EF = Exposure frequency (meals/year)
ED= Exposure duration (years)
BW = Body weight (kg)
AT = Averaging time (period over which the exposure is averaged) (days)

$$Intake_{produce} = \frac{C_{produce} \times IR_{produce} \times FI_{produce} \times EF \times ED}{BW \times AT} \qquad \text{(Eq. 5)}$$

where

$Intake_{produce}$ = Human daily intake of homegrown produce (mg/kg-d)
$C_{produce}$ = Concentration of PFAS in homegrown produce (mg/kg)
$IR_{produce}$ = Ingestion rate of homegrown produce (kg/meal)
$FI_{produce}$ = Fraction ingested from contaminated source (unitless)
EF = Exposure frequency (meals/year)
ED= Exposure duration (years)
BW = Body weight (kg)
AT = Averaging time (period over which the exposure is averaged) (days)

Soil-based Exposure. The U.S. EPA Regional Screening Level (RSL) calculator (U.S. EPA, 2017) incorporates default exposure parameters for direct exposure to soils via incidental ingestion, and dermal contact. RSLs were calculated for workers and for residents and compared to concentrations of PFASs in soil.

Dermal Contact with Surface Runoff; Inhalation of Particulates. Federal regulations for the management of biosolids mandate practices that minimize surface runoff (U.S. EPA, 1993; NRC, 2002) and as a consequence, limit potential human exposure. For land application, the U.S. EPA stipulates that biosolids cannot be (1) stored on site for more than six hours; (2) applied to flooded, frozen, or snow-covered land, or (3) applied to land with slopes above 6%. Additional requirements (e.g., dust mitigation measures) may also be stipulated by local permitting authorities.

As a result of these management practices, the potential for human exposure to surface runoff or particulate matter is limited and is not likely to result in significant exposure.

RESULTS

We evaluated the likelihood of non-cancer effects from exposure to PFBS, PFOS, and PFOA via the ingestion of meat and milk from cattle fed a diet of crops grown on biosolids-amended soil for a hypothetical, but realistic situation. We also considered a separate scenario in which residents consumed homegrown produce grown on biosolids-amended soil. The potential for non-cancer effects for each PFAS was estimated by calculating a hazard quotient (HQ) which is the ratio of the pathway-specific intake to the RfD.

The results, summarized in Table 5, indicate that the daily ingestion of beef or milk are not likely to result in exposure at levels of concern, as all HQs are either below or equal to the threshold HQ of one.

Hazard quotients from the ingestion of homegrown produce grown on biosolids-amended soils indicate that the intake of PFOS is associated with a HQ of 2.3; the HQs for PFBS and PFOA are both below one. The results for PFOS suggest that daily ingestion of homegrown produce grown on soils impacted by the long-term incorporation of biosolids may warrant further, site-specific analysis. This analysis could include the application of local (site-specific) exposure parameters, the measurement of PFAS concentrations in soil, or the measurement of PFAS concentrations in homegrown produce.

Soil-based exposure to PFASs was examined by using the U.S. EPA RSL Calculator (U.S. EPA, 2017) to calculate soil SLs for residents and workers. These SLs are based on default exposure assumptions, and address incidental ingestion and dermal contact with soils. The SLs and PFAS soil concentrations given in Table 6 indicate that soil-based exposures associated with the land application of biosolids do not appear to present a concern for human health.

DISCUSSION

The calculations described here are based on a number of assumptions regarding the uptake and transfer of PFASs from soil to plants, from plants to meat and milk, from meat and milk to humans, and plants to humans. The calculations utilized PFAS soil concentrations from a site that had received biosolids over a 33-year period.

In considering the selection of soils data for this assessment, we identified a considerable range of PFAS concentrations in biosolids-amended soils (Sepulvado et al., 2011; Blaine et al., 2013 and 2014; Yoo et al., 2011; Wen et al., 2014). The variability is due to differing sources of biosolids (municipal vs. industrial; urban vs rural), and differing rates and time periods of application. As a result of this variability, the concentration of PFASs in biosolids that are available for plant uptake – and ultimately for human ingestion – will depend on the biosolids source(s), the land application rate, and the number of biosolid applications. We note that PFOS and PFOA concentrations in biosolids are also likely to decline in the future due to the phase-out of these chemical by most large U.S. manufacturers and expanded regulation under the Toxic Substances Control Act (TSCA) (U.S. EPA, 2015).

We identified variability in the soil-to-plant BAFs that have been measured or estimated for PFASs. While short chain PFASs such as PFBS transfer to plant tissues to a greater extent than the long-chain PFOS and PFOA, plant uptake also varies with the species and portion of the plant, with roots and shoots acquiring greater concentrations of PFASs than fruits or grains (Blaine et al., 2014; Wen et al., 2014).

Thus, while our calculations represent reasonable estimations of potential PFAS intake, the presence of different PFAS concentrations in soil, the production of different crops, or the cultivation of different homegrown produce could all affect the results.

Additionally, the exposure parameters we selected may or may not represent local conditions. Collectively, all of these factors suggest that site-specific evaluations may be warranted when crops or homegrown produce are grown on soils where the long-term land application of biosolids is practiced.

TABLE 5. Oral toxicity factors and hazard quotients.

Analyte	RfD (mg/kg-d)	Hazard Quotient (unitless)		
		Beef	Milk	Produce
PFBS	2.0E-2[a]	3.4E-7	8.3E-6	1.2E-5
PFOS	2.0E-5[b]	4.1E-2	1.0	2.3
PFOA	2.0E-5[c]	2.2E-3	0.17	0.17

[a] US EPA (2014)
[b] US EPA, 2016a
[c] US EPA, 2016b

TABLE 6. Summary of PFAS soil concentrations and soil screening levels (mg/kg).

Analyte	Soil[b]	Agricultural Worker[a]	Resident[a]
PFBS	1.0E-4	1.82×10^4	1.26×10^3
PFOS	1.5E-1	18.2	1.26
PFOA	9.0E-3	18.2	1.26

[a] U.S. EPA Regional Screening Level Calculator (US EPA, 2017)

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