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Landfills

Be Aware of Emerging Contaminants!

Sampling for PFAS at the Four Hills Landfill.
Photo courtesy of Sanborn, Head & Associates, Inc.

Landfill operations have long been regulated for contaminants such as heavy metals and toxic organic compounds. However, environmental professionals must now become aware of certain additional contaminants of emerging concern that are associated with landfills and are receiving new scrutiny for posing potential environmental risks.

Emerging contaminants generally arise from the Unregulated Contaminant Monitoring Rule (UCMR), a portion of the U.S. Safe Drinking Water Act used by the U.S. Environmental Protection Agency (EPA) to identify additional contaminants that may present a public health risk. Every five years, EPA develops a list of suspected contaminants that could be present in drinking water and requires sampling for them by large public drinking water systems. EPA examines the sampling results on a national basis to characterize the frequency with which each contaminant is detected and the percentage of samples greater than risk-based target levels. If EPA determines a significant public risk, it can engage in rulemaking to develop a federally enforceable Maximum Contaminant Level (MCL) for the nation's drinking water supply.

EPA is presently implementing its fourth UCMR sampling round. Although no new MCLs have resulted from the first three rounds, previous sampling has drawn attention to a number of contaminants, and in some cases have prompted state-specific regulatory actions that are presently affecting the solid waste industry.

In particular, a growing number of states are focusing on 1,4-dioxane and per- and polyfluoroalkyl substances (PFAS), which were included as part of the third UCMR sampling round (UCMR3). Both 1,4-dioxane and PFAS are of concern because people exposed to them may potentially be at elevated risk for cancer and other health effects, although such a link has yet to be clearly demonstrated. A summary of the UCMR3 sampling results for the nation's water supplies is provided in Table 1.[1]

About 37,000 samples were analyzed for 1,4-dioxane and PFAS. The results indicate that 1,4-dioxane was found above the reporting limit of 0.07 micrograms per liter (µg/l) in 11% of samples nationally, and 2.9% of samples were above the 0.35 µg/l risk-based screening concentration (RSC). PFAS sampling included 6 different compounds, and these compounds were detected less frequently, ranging among compounds between 0.05% and 1% of samples. PFOA (perfluorooctanoic acid) and PFOS (perfluorooctane sulfonic acid) exceeded their 0.07 µg/l RSC in only 0.3% and 0.09% of samples, respectively. Since multiple samples were collected from each of the approximately 4,900 public water supplies, the percentages of water supplies that detected 1,4-dioxane and PFAS in at least one sample are higher. For example, 1,4-dioxane was detected in 22% of the public water supplies tested.

Evolving Toxicity of Emerging Contaminants

Though detected relatively infrequently in the UCMR, 1,4-dioxane and PFAS have garnered considerable attention. The term "emerging" implies a dynamic and incomplete process, and this description befits contaminants such as 1,4-dioxane and PFAS. In each case, there are indications of health concerns that originated many years ago, but data uncertainties and limitations prevent robust characterization. While studies continue, citizens and politicians are pressuring (and in some cases requiring) state environmental agencies to develop standards in the absence of federal MCLs.

In 1987, EPA issued a Lifetime Health Advisory (LHA) of 200 µg/l for 1,4-dioxane in drinking water, which in time prompted some states to add it to contaminant sampling lists. For example, groundwater near landfills is monitored for landfill-related contaminants including 1,4-dioxane, because groundwater contaminated by landfill leachate can degrade the local water supply. As one consequence, such monitoring near landfills has indicated 1,4-dioxane to be a useful marker for groundwater impact delineation as its complete miscibility places it at the leading edge physically of contaminant plumes from landfill leachate releases.

Concerns over lower concentrations of 1,4-dioxane ensued with

Table 1. U.S. National Sampling Data (UCMR Data) for 1,4-dioxane and PFAS.[1]

Contaminant	Number of samples	Number of public water supplies	Minimum Reporting Limit (MRL) (µg/l)	Percentage (%) of samples > MRL	Percentage (%) of public water supplies with a detect > MRL	Risk-Based Screening Concentration (RSC) (µg/l)	Percentage (%) of samples > RSC	Percentage (%) of public water supplies with a detect > RSC
1,4-dioxane	36,810	4,915	0.07	11	22	0.35	2.9	6.9
PFBS (perfluorobutanesulfonic acid)	36,972	4,920	0.09	0.05	0.0	-	-	-
PFHxS (perfluorohexanesulfonic acid)			0.03	0.06	1.1	-	-	-
PFHpA (perfluoroheptanoic acid)			0.01	0.6	1.8	-	-	-
PFOA (perfluorooctanoic acid)			0.02	1.0	2.4	0.07	0.09	0.3
PFOS (perfluorooctanesulfonic acid)			0.04	0.8	1.9	0.07	0.3	0.9
PFNA (perfluorononanoic acid)			0.02	0.05	0.3	-	-	-

time, and use of more sensitive analytical methods has led to more widespread detections of 1,4-dioxane in groundwater. In September 2013, EPA categorized 1,4-dioxane as a likely human carcinogen and established, using its standard guidance, a risk factor based on an assumed lifetime exposure via the ingestion exposure pathway. Application of EPA's standard risk-assessment model (a "zero threshold" model) results in a drinking water Risk Screening Level (RSL) of 0.35 µg/l, and similar values have recently been adopted in state regulations by agencies such as the New Hampshire Department of Environmental Services (0.32 µg/l) and the Massachusetts Department of Environmental Protection (0.3 µg/l). While such RSLs are not contaminant limits as such, they are intended to flag contaminant levels indicating the need for further case-specific risk assessment.

A similar evolution is in progress with PFAS. In 2009, EPA issued provisional health advisories of 0.4 µg/l for PFOA and 0.2 µg/l for PFOS, then in 2016 issued a LHA for drinking water of 0.07 µg/l for the combination of the two compounds.[2,3] Numerous states have adopted EPA's drinking-water LHA to also prescribe requirements for groundwater cleanup levels, and some states have issued lower standards and/or have expanded coverage to include additional PFAS. As an example, Vermont's 0.02 µg/l health advisory covers the sum of PFOA, PFOS, PFHxS (perfluorohexane sulfonic acid), PFHpA (perfluoroheptanoic acid), and PFNA (perfluorononanoic acid).[4]

Although the tendency has been toward lower and lower risk-based criteria, not everyone is convinced that 1,4-dioxane and PFAS require part-per-trillion standards to protect public health. Evidence from laboratory animal studies suggests that 1-4-dioxane requires a threshold level of exposure before that exposure promotes cancer (rather than a zero-exposure threshold), and that a level 1,000-fold higher than the 0.35 µg/l LHA is health protective.[5]

Similar doubts over toxicity have been noted for PFAS. A recent review commissioned by the Australian Government Department of Health concluded that "there is mostly limited, or in some cases no evidence, that human exposure to PFAS is linked with human disease," and "there is no current evidence that suggests an increase in overall cancer risk." But at the same time, the Australian panel was unwilling to declare PFAS exposure safe, noting that "even though the evidence for PFAS exposure and links to health effects is very weak and inconsistent, important health effects for individuals exposed to PFAS cannot be ruled out based on the current evidence."[6]

The trend toward more stringent health advisories reflects the need for regulatory agencies to act in the face of uncertainty and the application of the precautionary principle. However, the price of protection may be steep, as the costs associated with compliance and treatment to meet standards for 1,4-dioxane, PFAS, and other future emerging contaminants could be substantial, and overly protective standards may yield little in the way of health benefits.

Concerns for Landfills

Both 1,4-dioxane and PFAS have been widely used in commerce and consumer products, and hence, have numerous sources in the municipal solid waste stream. Both 1,4-dioxane and PFAS have been detected in landfill leachate, in some cases at levels considerably higher than EPA's LHAs. Environmental monitoring programs around unlined landfills have also identified PFAS in groundwater and surface water, also in some cases at concentrations well in excess of EPA's LHAs.

Published concentrations of 1,4-dioxane in groundwater have been reported in the 10–100 µg/l range, though data are scarce.[7] 1,4-Dioxane is increasingly being required as an analyte in groundwater monitoring programs as states react to its designation as a carcinogen by EPA, and because it is not unusual to detect it above EPA's 0.35 µg/l screening level.

Table 2 provides a summary of the concentrations of the six UCMR3 PFAS detected in landfill leachate sampling in two

Table 2. PFAS Sampling of Landfill Leachate.

PFAS Compound	18 Landfills in the United States[8]				6 Vermont Landfills[9]			
	Frequency of Detection	Average (µg/l)	Min Detect (µg/l)	Max Detect (µg/l)	Frequency of Detection	Average (µg/l)	Min Detect (µg/l)	Max Detect (µg/l)
PFBS	87 of 87	0.23	0.0034	3.41	6 of 6	0.63	0.0054	3.5
PFHxS	86 of 87	0.36	0.0064	1.33	6 of 6	0.22	0.012	0.41
PFHpA	87 of 87	0.59	0.032	3.13	6 of 6	0.45	0.021	0.86
PFOA	87 of 87	0.89	0.030	4.99	6 of 6	1.1	0.080	2.1
PFOS	84 of 87	0.13	0.0029	0.80	6 of 6	0.15	0.023	0.28
PFNA	86 of 87	0.05	0.0028	0.29	6 of 6	0.034	0.0013	0.13
Total PFAS	87 of 87 (69 PFAS compounds)	11.9	0.30	65.87	6 of 6 (29 PFAS compounds)	9.0	0.40	25.1

Table 3. Groundwater Sampling Results for PFAS (in µg/l) at Vermont Landfills.[10]

PFAS Compound	MSW 1	MSW 2	MSW 3	MSW 4	MSW 5	MSW 6	Paper Sludge	C&D[a]
PFOA	0.011	0.045	0.008	0.014	0.002	0.009	0.018	0.9
PFOS	ND	0.037	0.005	0.005	ND	ND	0.011	0.14
Total	0.011	0.082	0.013	0.019	0.002	0.009	0.029	1.04

[a]C&D = Construction and demolition waste.

recent studies. Levels are typically detected at concentrations above EPA's 0.07 µg/l LHA (which applies specifically to the sum of PFOA and PFOS). Also, the six UCMR PFAS account for only a small fraction of total detected PFAS concentrations. Though the studies examined different lists of PFAS (a "standard" analyte list has not yet been developed), two compounds found at levels higher than the UCMR3-specific compounds were PFBA (perfluorobutanoic acid) and PFPeA (perfluoropentanoic acid). Recalling a bit of chemistry, this might reflect the advent of shorter-chain PFAS that have replaced the C8 compounds PFOA and PFOS, which have been phased out of use in the United States. Hence, landfill leachate typically contains PFAS at levels that, if released to groundwater, could lead to exceedance of drinking water standards for PFAS in states that currently regulate PFAS. This is significant, as the number of states regulating PFAS, as well as the number of PFAS subject to regulation, are likely to grow.

Developing regulation of 1,4-dioxane and PFAS at landfills could lead to costly treatment of leachate, enhanced environmental monitoring, and potential remediation/mitigation costs that may vary across states. Many landfills currently discharge leachate to wastewater treatment plants (WWTPs). Regulatory pressures on WWTPs to reduce effluent concentrations of contaminants of emerging concern may in turn be shifted upstream to the leachate generators, through WWTP demands for leachate pre-treatment and reduced contaminant loadings as a condition of continued acceptance of leachate. Similarly, landfills that accept sewage sludge may need to consider the acceptability criteria based on concentrations of these compounds in the sludge.

The potential importance of groundwater contamination resulting from landfill leachate releases depends on neighboring land use. Drinking water ingestion is typically the most important exposure pathway to 1,4-dioxane and PFAS, and under most circumstances, the potential risks associated with off-property contamination depend on the existence or absence of affected drinking water wells. An example of the potential implications of PFAS regulations can be found in New Hampshire and Vermont, where landfills have been required to sample for PFAS in conjunction with groundwater monitoring programs. PFOA and PFOS were detected above the 0.07 µg/l LHA in groundwater monitoring samples collected at approximately 30% of active and closed landfills in New Hampshire whereas PFOA and PFOS were detected above detection limits in groundwater at 67% of landfill sites sampled. In Vermont, PFOA and PFOS were sampled in groundwater near eight closed landfills (see Table 3). PFOA was detected at all landfills, and PFOS at most of them, in two cases at levels above the EPA LHA of 0.07 µg/l.

Treatment and remediation options differ for 1,4-dioxane and PFAS. Because leachate typically contains many other contaminants at higher concentrations, primary treatment may be required before treatment to remove 1,4-dioxane and PFAS. Reverse osmosis (RO) is a potential option to remove both 1,4-dioxane and PFAS, and PFAS can also be removed through use of activated carbon and resins. Concentrated RO waste streams and spent carbon/resin media must be discarded or regenerated. These same methods are applicable to ex-situ treatment of groundwater used for drinking water. In-situ groundwater remediation is more challenging and less studied, though techniques such as aggressive chemical oxidation show promise. In cases of contaminated wells, providing alternate supplies of drinking water is another potential mitigation option. Any and all of these efforts may be costly additions to operating and post-closure expenses at landfills.

Regulatory and Legal Implications

EPA is evaluating the possibility of establishing a federal MCL to limit the amount of PFAS allowable in drinking water, which could help to establish a more uniform direction among states. Establishing a federal MCL will require time, however, and states are likely to continue to move forward with individual and varying regulations. Actions regarding 1,4-dioxane and PFAS will not likely be limited to the regulatory arena.
As potential environmental sources of 1,4-dioxane and PFAS, landfills may be parties to future litigation, for example, for remediation cost recovery at Superfund sites and arising from private party tort—and such litigation is already underway at locations in Michigan and other states. Drinking water contamination and property damages are at this point the primary concerns, as the uncertainties regarding toxicity make it difficult to meet the legal standard for causality between exposure and adverse health effects.

Conclusion

Emerging contaminants such as 1,4-dioxane and PFAS will increasingly demand the attention of the solid waste management industry by raising the costs of compliance, environmental protection, and remediation at landfills. An EPA rule (i.e., the UCMR) provides the ability to identify new contaminants of concern for drinking water, based on national sampling results. But, by drawing attention to emerging contaminants and not developing maximum permissible levels (MCLs) to limit them uniformly nationwide, EPA is in effect prompting individual states to act in response to public pressure, resulting thus far in very protective and potentially very costly regulations that vary among jurisdictions. And just around the corner, it will be interesting to see if the upcoming new round of UCMR sampling draws a focus upon some other new emerging contaminant such as manganese (commonly detected in groundwater near landfills). **em**

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References

1. UCMR3 Frequency; U.S. Environmental Protection Agency (EPA), 2017; https://www.epa.gov/sites/production/files/2017-02/documents/ucmr3-data-summary-january-2017.pdf.
2. PFOA, PFOS Provisional Health Advisories; U.S. Environmental Protection Agency (EPA), 2009; https://www.epa.gov/sites/production/files/2015-09/documents/pfoa-pfos-provisional.pdf.
3. PFOA Health Advisory; U.S. Environmental Protection Agency (EPA), 2016; https://www.epa.gov/sites/production/files/2016-05/documents/pfoa_health_advisory_final_508.pdf.
4. Health Vermont, 2018; http://www.healthvermont.gov/sites/default/files/documents/pdf/ENV_DW_PFAS_HealthAdvisory.pdf.
5. Dourson, M.; Reichard, J.; Nance, P.; Burleigh-Flayer, H.; Parker, A.; Vincent, M.; McConnell, E. Mode of action analysis for liver tumors from oral 1,4-dioxane exposures and evidence-based dose response assessment; *Reg. Toxicol. Pharmacol.* **2014**, *68* (3), 387-401.
6. Expert Panel for PFAS; Australian Government Department of Health, 2018; https://www.health.gov.au/internet/main/publishing.nsf/Content/C9734ED6BE238EC0CA2581BD00052C03/$File/summary-panels-findings.pdf.
7. Toxicological Profile for 1,4-Dioxane; Agency for Toxic Substances and Disease Control (ATSDR), Atlanta, GA, 2012; https://www.atsdr.cdc.gov/toxprofiles/tp187.pdf.
8. Lang J., Allred, B., Field, J., Levis, J., Barlaz, M. (2017). National Estimate of Per– and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate; *Environ. Sci. Technol.* **2017**, *51* (4), 2197–2205.
9. Weston and Sampson. Letter report to John Schmeltzer, Vermont Department of Environmental Conservation. Wastewater Treatment Facility and Landfill Leachate PFAS Sampling at Various Locations, Northern Vermont. May 3, 2018.
10. Perfluoroalkyl Substances (PFAS) Contamination Status Report; Vermont Department of Environmental Conservation, 2018; https://dec.vermont.gov/sites/dec/files/documents/PFAS%20Sampling%20Report%207.10.18%20FINAL.pdf.