Testing for PFAS in yard waste bags

Total Oxidizable Precursor and Total Organic Fluorine testing

Purpose

The presence of per- and polyfluoroalkyl substances (PFAS) is a growing concern for compost facilities.

Throughout the year, but peaking each fall, brown kraft paper fiber yard waste bags filled with leaves enter compost facilities. Given the durability of yard waste bags observed by MPCA staff, the question arose of whether and to what extent PFAS-containing coatings might be applied to paper yard waste bags to enhance durability, and whether yard waste bags might be contributing environmentally significant PFAS to compost at levels lower than the 100 parts per million (ppm) limit set by the BPI certification.

To try to answer these questions, MPCA staff purchased sixteen yard waste bags, three online and thirteen from various sellers in the Twin Cities Metro Area. Some of the bags had the same manufacturers' names printed on them; most had the seller's brand name also printed on them. None of the bags appeared to be manufactured in Minnesota.

The bags were tested using both the Total Oxidizable Precursor (TOP) assay and the Total Organic Fluorine (TOF) methods. These analyses take different approaches to assessing the potential presence of PFAS in the bags.

Summary of findings

None of the bags appeared to contain intentionally added PFAS, when compared to the BPI Certified compostable product limit of 100 ppm and the general statements in literature[1] that PFAS are used at 500 ppm and usually higher levels to provide a function such as durable water repellency.

Compared to other known sources of PFAS in composting operations, yard waste bags appear to be minor contributors of PFAS.

Levels of Total Organic Fluorine were found in half of the samples at 9 to 49 ppm. MPCA recommends that the manufacturers of these products continue to monitor these levels and seek to eliminate PFAS content in their supply chain or in manufacturing equipment, or in other inputs.

Composting and PFAS background

PFAS are a class of fluorinated organic chemicals containing at least one fully fluorinated carbon atom that are persistent in the environment and human body. PFAS are used to make a variety of heat, water, oil, stain, and grease resistant coatings and products, and as a processing aid in many other types of products. Exposure to PFAS can cause harmful health impacts to humans. They persist and change form in the natural environment. Recent research from the MPCA has found PFAS in contact water at composts sites, frequently at levels exceeding health risk limits.[2]

Presumed sources of PFAS at compost facilities include some compostable paper products and yard waste in areas where air emissions and ground contamination has occurred. Other items, including yard waste collection bags or food, may be contributing sources. There is not much information currently to determine how

[1] Fluorinated Surfactants (Second Edition), Eric Kissa, Marcel Dekker, Inc., NY, 2001.

[2] https://www.pca.state.mn.us/waste/composting-and-pfas

significantly any one feedstock contributes to PFAS at compost sites. There is some concern that PFAS that may be present in compost which would re-enter the environment when compost is applied to lawns, gardens, and construction projects.

Test methods used

New PFAS are being invented, used in industry and incorporated into commercial products, and released into the environment every day. It is difficult, if not impossible to individually test for all the tens of thousands of known PFAS that exist. MPCA therefore chose two test methods, described below, which are often used to generate the most information possible.

Total Oxidizable Precursor (TOP) analysis is a method of testing for PFAS precursors by oxidizing yard waste bag samples to break down PFAS precursors into their end products which include other PFAS. This process could simulate a “worst case scenario” of the presence of PFAS after a yard waste bag breaks down in an environment like that at a composting facility.

This analysis is helpful because terminal degradation products such as PFOA, PFOS, PFHxA, or PFHxS are often better-studied than their precursors and have risk-based values in various environmental media available. However, we cannot directly compare concentrations because there are no risk-based values for any PFAS in products.

Often, investigation projects use targeted PFAS analysis together with TOP analysis to compare which compounds are present in both. However, MPCA did not have a large enough budget to have that third test conducted. We therefore are unable to say the concentration of PFAS present before oxidation.

Unlike TOF, the TOP assay provides quantitative concentrations of the terminal degradate analytes after oxidation.

While there are over 5,000 known *PFAS*, the TOP analysis MPCA contracted with SGS AXYS Labs to conduct tests for thirty-two of the most common PFAS. In this project, the lab used SGS AXYS METHOD MLA-111 Rev 03. SGS AXYS’ detection limits for TOP vary but are generally below 10 parts per billion (ppb).

Total Organic Fluorine (TOF) is a method of determining the total level of organic fluorine present in a sample. MPCA’s hypothesis was that TOF screening could catch fluorine from PFAS that TOP assay wouldn’t account for, plus as mentioned earlier, TOF is required for BPI compostable product certification.

This analysis determines TOF by performing a total fluorine analysis and an inorganic fluoride analysis and subtracting inorganic from total fluorine to come up with total organic fluorine. Total fluorine and inorganic fluoride are both determined by combusting the sample in the presence of oxygen and using an ion-selective electrode method.

TOF may detect some sources of organic fluorine that are not always considered PFAS, however, MPCA has not been able to find any references to other sources of organic fluorine in papermaking.

For this project, Total Organic Fluorine analysis was performed by Galbraith Laboratories, Inc. using methods E9-1 and E9-3. Galbraith’s detection limit for TOF is generally 5-10 ppm, making it around 1000 times less sensitive than TOP testing. Once again though, TOF will identify organic fluorine from PFAS which are not on specific lists of analytes in TOP or targeted PFAS analysis.

Results

Total Oxidizable Precursor (TOP) results

Using the TOP assay, low-level PFAS were detected in all sixteen yard waste bag samples, anywhere from one PFAS compound up to as many as nine. The highest amount detected was 56.3 ppb, with 80 other detections ranging down to 0.204 ppb. The rest of the results, totaling 431, were below detection limits. Additional details on TOP results are presented in Table 1 below.

Since the BPI standard’s limit for intentionally added PFAS is 100 ppm (100,000 ppb), and MPCA research indicates levels of 500 ppm and much higher are common to provide functionality such as water or grease resistance, our TOP results suggest that PFAS were not intentionally added to any of our yard waste bag samples. What is present is therefore likely to be the result of contamination in the manufacturers' supply chains, or in their manufacturing equipment.

Table 1

Total Oxidizable Precursor (TOP) results – PFAS presence in 16 yard waste collection bags

Top analyte	Frequency of detection* (number of samples detected)	Max. Concentration (ng/g or ppb)	Range of detection limits (ng/g or ppb)
PFPeA	100% (16)	56.3	0.389 - 0.726
PFBA	100% (16)	28.6	0.777 - 0.866
PFHxA	100% (16)	13	0.194 - 0.216
PFOA	68.75% (11)	1.87	0.194 - 0.216
PFHpA	68.75% (11)	1.58	0.194 - 0.216
6:2 FTS	12.5% (2)	6.95	0.701 - 0.780
PFNA	12.5% (2)	0.383	0.194 - 0.216
PFOS	12.5% (2)	0.23	0.194 - 0.216
8:2 FTS	6.25% (1)	1.48	0.777 - 0.866
4:2 FTS	6.25% (1)	1.15	0.777 - 0.866
PFDA	6.25% (1)	0.264	0.194 - 0.216
PFUnA	6.25% (1)	0.249	0.194 - 0.216
PFDoA	0%	--	0.194 - 0.216
PFTrDA	0%	--	0.194 - 0.216
PFTeDA	0%	--	0.194 - 0.216
PFBS	0%	--	0.194 - 0.216
PFPeS	0%	--	0.195 - 0.217
PFHxS	0%	--	0.194 - 0.216
PFHpS	0%	--	0.194 - 0.216
PFNS	0%	--	0.194 - 0.216
PFDS	0%	--	0.194 - 0.216
PFDoS	0%	--	0.194 - 0.216
PFOSA	0%	--	0.194 - 0.216
N-MeFOSA	0%	--	0.223 - 0.249
N-EtFOSA	0%	--	0.486 - 0.541
MeFOSAA	0%	--	0.194 - 0.216
EtFOSAA	0%	--	0.194 - 0.216
N-MeFOSE	0%	--	1.94 – 2.16
N-EtFOSE	0%	--	1.45 - 1.62
3:3 FTCA	0%	--	0.777 - 0.866
5:3 FTCA	0%	--	4.86 - 5.41
7:3 FTCA	0%	--	4.86 - 5.41

* J flagged results are considered detections for this calculation

Complete results are available by request to p2.pca@state.mn.us.

TOP totals for each sample ranged from 1.858 ppb to 100.6 ppb, with an average total of 17.119 ppb. All these totals are 1000 times lower than a presumed intentionally added threshold of 100 ppm.

The first five analytes in Table 1 are perfluoroalkyl carboxylates (PFCAs) containing four to eight carbon atoms. TOP breaks down many compound groups to PFCAs. In addition, many studies indicate that fluorotelomer sulfonate (FTS) compounds have aerobic, anaerobic, or photolytic degradation pathways to C4-C8 PFCAs, as do many other fluorotelomer and electrochemical fluorination-based groups. Therefore, it may not be surprising that those five compounds showed the highest detection frequency (3 at 100%; 2 at 68.75%). However, we cannot be sure if these detections were of the reported compounds or were oxidation products of other precursor PFAS, or a combination of the two possibilities.

Total Organic Fluorine (TOF) results

Total Organic Fluorine analysis for yard waste bags resulted in a detection limit of 10 ppm for all but one of the 16 samples, which had a detection limit of 9 ppm. Seven out of the 16 yard waste bags had detections of TOF from 9 ppm up to 49 ppm while the results for the remaining 9 bags were below detection limits. None of the samples detected inorganic fluoride above the 5 ppm detection limit, however, the 5 ppm detection limit introduces an equal amount of uncertainty about the TOF result, which is arrived at by measuring total fluorine and inorganic or mineralized fluorine, then subtracting the inorganic result to arrive at total organic fluorine.

It is unclear how much of the detected TOF in these samples comes from PFAS. While MPCA staff haven't found references to other sources of organic fluorine in paper, it is possible that some from non-PFAS sources are present.

With no results higher than 49 ppm, our TOF results appear to support the implication of the TOP results that PFAS were not intentionally added to the yard waste bags. As was mentioned in the TOP results section, 100 ppm PFAS is commonly thought to be a minimum amount needed to provide the function of water resistance. The BPI certification makes this same assumption, so MPCA's yard waste bag purchases would all meet that standard. PFAS detected in the yard waste bags, if not intentionally added, may be the result of contaminated equipment or water in the manufacturing process, PFAS in recycling paper content, background PFAS present in virgin paper fiber, or a combination of these factors.

Result conclusions

There is not a clear relationship between the results for Total Oxidizable Precursor (TOP) and Total Organic Fluorine (TOF) for each sample. Yard waste bag samples with higher detections of TOF do not necessarily correspond with samples that have higher individual or total TOP detections. Samples with higher TOF detections and lower TOP detections may be detecting PFAS that is not accounted for in the 32 analytes in the TOP analysis.

Both TOP and TOF showed our yard waste bags would pass the BPI standard but also contribute low levels of PFAS to compost or other management methods: anywhere from less than 1 ppb of thirty-two PFAS to 49 ppm organic fluorine, which typically comprises about 60-70% of many PFAS.

While these contributions are environmentally relevant over time, they are relatively less significant than paper products coated with resistant chemical layers, or vegetation originating from PFAS contaminated areas. This suggests prioritizing PFAS elimination in other compost inputs first, however, yard waste bags will have a cumulative impact and should remain on the list for eventual PFAS elimination. Manufacturers of yard waste bags may have contamination in their process which they should monitor and seek to eliminate, and in the short term, buyers of yard waste bags may seek out manufacturers without detectable contamination.

Consumers who are interested in product-specific results may request them through p2.pca@state.mn.us.

Next steps

To better understand the sources of PFAS at compost facilities, additional testing and research should be conducted. Ultimately, prioritizing other feedstocks – beyond yard waste bags - to screen for PFAS likely makes sense given the limited resources available to assess PFAS sources at compost sites.

To the extent that further analysis of PFAS in yard waste bag is worthwhile several additional steps could enhance our knowledge.

First, more research focused on potential sources of fluorine that may be reported in a TOF analysis of yard waste bags is needed. This will give a clearer picture of how much of the reported organic fluorine may be attributed to PFAS versus other types of fluorine compounds present in the material being tested.

Second, completing standard PFAS analysis on the same yard waste bags could provide a better understanding of what PFAS are present in bags, prior to oxidation, that could break down into different PFAS at a compost facility. But if those post-oxidation compounds are not showing up in standard analysis, we will still not know the identity of the precursor compounds.

Third, we should continue to survey the testing market to find providers offering greater sensitivity for existing methods. The history of environmental testing methods has seen the development of ever-lower detection limits, and that can be expected to continue for PFAS. For instance, MPCA is now in touch with a lab in the U.S. which can deliver TOF detection limits of 300 ppb for some materials. We will continue to look for method improvements like this.

Fourth, MPCA anticipates that in time non-targeted analytical techniques for PFAS will develop more fully and become more widely available and affordable. These techniques should help identify PFAS not found or specified in TOP or TOF methods.

Fifth, testing for PFAS in additional composting inputs - compostable products, food, and yard waste – will help to determine the primary sources of PFAS at compost facilities. Additional efforts to monitor PFAS in food packaging are coming soon as Minnesota’s prohibition on the manufacturing or sale of intentionally added PFAS in food packaging becomes effective in 2024. MPCA and partners can plan and budget for testing of paper, food, yard waste, and other typical inputs to compost.

Lastly, compost facilities require a holistic PFAS approach since there are several potential PFAS contributors. For example, if the compost site is near a facility with air emissions or receives yard waste or food grown in an airshed with an emitter, air deposition could be a significant source of PFAS. Similarly, food or plants grown in areas with PFAS soil contamination or biosolids application could be a significant source of PFAS. Strategic interventions to reduce PFAS levels in compost or contact water should be informed by site-specific considerations of likely significant sources.