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The environmental degradability of DEMNUM, a typical PFPE polymer

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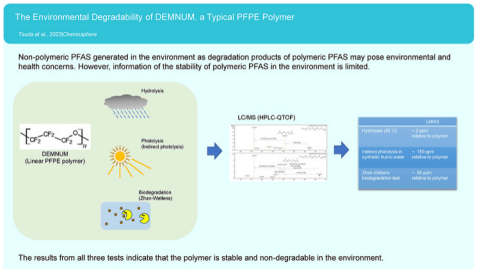
HIGHLIGHTS

- Fluorinated polymers are under the scope of the EU restriction proposal on PFAS compounds.
- The environmental stability of perfluoropolyether polymers was unknown.
- Hydrolysis, indirect photolysis and Zahn-Wellens microbial degradation tests were conducted on a linear perfluoroether polymer.
- The degradation products were structurally identified and quantified using LC-MS.
- The polymer was found stable under the tests' conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

The three environmental degradation tests of hydrolysis, indirect photolysis and Zahn-Wellens microbial degradation were conducted according to the OECD and the US EPA guidelines on DEMNUM, a typical linear perfluoropolyether polymer. Low mass degradation products that formed in each test were structurally characterized and indirectly quantified by liquid chromatography mass spectrometry (LC/MS) using a reference compound and an internal standard of similar structure. The degradation of the polymer was assumed to directly correlate with the appearance of lower mass species. The hydrolysis experiment at 50 °C showed the appearance of less than a dozen low mass species with increasing pH but at the negligible total estimated amount of ~2 ppm relative to polymer. A dozen low mass perfluoro acid entities also appeared following the indirect photolysis experiment in synthetic humic water. Their maximum total amount was at ~150 ppm relative to polymer. The largest total amount of low mass species formed during the Zahn-Wellens biodegradation test amounted to only ~80 ppm relative to polymer. The Zahn-Wellens conditions tended to produce larger low mass molecules than the ones formed under photolysis. The results from all three tests indicate that the polymer is stable and non-degradable in the environment.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large class of highly fluorinated aliphatic substances that are divided into two main categories, polymers and non-polymers (Buck et al., 2011, 2021). According to the Organization for Economic Co-Operation and Development

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(OECD), polymers are large molecules consisting of a sequence of monomer units covalently bound to one another as a result of a relevant polymerization reaction (OECD, 1993). The non-polymer category includes per- and polyfluoroalkyl surfactants with varying functional groups such as perfluoroalkyl sulfonic acids and perfluoroalkyl carboxylic acids, to which the two infamous compounds, perfluorooctane sulfonic acid (PFOS) and perfluorooctane carboxylic acid (PFOA) belong (OECD, 2022). The polymer category of PFAS includes fluoropolymers, perfluoropolyether (PFPE) polymers, and side-chain fluorinated polymers (OECD, 2013).

Non-polymeric PFAS compounds are being increasingly regulated by various organizations around the globe (OECD, 2022; EPA, 2022). The initial trend was to regulate individual compounds such as PFOA, PFOS and perfluorohexane sulfonic acid (PFHxS) (EPA, 2000; Stockholm Convention Decision SC-4/17, 2009; ECHA, 2013) but has now shifted towards regulating PFAS as a group (POPRC-17 Final, 2022; ECHA, 2022a; ECHA, 2022b). A European Union restriction proposal on PFAS substances was published by ECHA in February of 2023 that will affect around 10,000 PFAS substances including polymers (ECHA, 2022a; ECHA, 2022b; ECHA, 2023).

In recent years a lot of environmental research has focused on developing technologies that efficiently degrade PFAS compounds. Removal of PFAS contamination from the environment is traditionally accomplished using adsorption and membrane-based methods (Ochoa-Herrera and Sierra-Alvarez, 2008; Tang et al., 2006) but photochemical methods such as ultraviolet photolysis of aqueous solutions containing sensitizers such as sulfite and iodide ions (Liu et al., 2022; Hori et al., 2004) have been applied to degrade PFASs. The mechanism commences with the generation of hydrated electrons by UV photolysis of added sensitizers that then reductively eliminate fluoride ions from PFASs (Fennell et al., 2022; Park et al., 2009; Tenorio et al., 2020). Hydrothermal treatment methods have also been investigated to efficiently degrade these compounds (Yu et al., 2020). Alkaline water at high temperature and pressure consecutively defluorinated a wide class of PFASs with the end products being fluoride and carbonate ions (Hao et al., 2021).

Fluoropolymers have thermal, chemical, photochemical, hydrolytic, oxidative, and biological stability making them highly stable in the environment (Henry et al., 2018; Ameduri, 2023; Korzeniowski et al., 2023). However, low molecular weight substances (LMWS) contained within certain PFAS polymeric species as manufacturing impurities or generated from them in the environment as degradation products may pose environmental and health concerns similar to those of non-polymer PFASs (Lohmann et al., 2020). Fluorotelomer polymers with the fluorinated side groups attached through ester or urethane bonds to the polymer backbone readily degrade and release for example, fluorotelomer alcohols that then oxidize to form perfluorocarboxylic acids (Russell et al., 2008, Russell et al., 2009). More recently, the vulnerability of PFAS carboxylic acids to degradation has been investigated in activated sludge. Aerobic microbial defluorination of short-chain fluorinated carboxylic acids was found to be limited to PFAS structures that have hydrogens on the carbon next to the carboxylic acid group (Che et al., 2021).

Perfluoropolyethers (PFPE) polymers that have repeating units consisting of ether linked perfluoroalkylene groups, have been used as liquid lubricants for over 30 years, primarily in the aviation industry. The ether bond in PFPE polymers has been shown to undergo degradation at high temperatures in the presence of Lewis acids (Kasai, 1992), however, there haven't been any reports on the stability of PFPE polymers in natural environments in the presence of water, light, or microorganisms.

In this study, a linear PFPE polymer, DEMNUM underwent hydrolysis, indirect photolysis, and microbial degradation tests according to OECD and EPA guidelines. This polymer (Fig. 1a) has >24 ($CF_2CF_2CF_2O$) monomer repeating units in its backbone and can be considered as a representative example of the environmental behavior of linear PFPE polymers in general. The degradation of this polymer was indirectly measured using mass spectrometry by monitoring the appearance of LMWS during each environmental test.

2. Materials and methods

DEMNUM polymer was supplied by Daikin Industries, Ltd. Reference compound Perfluoro-3,6,9-trioxadecanoic acid (CAS Number: 151772-59-7) (used as a calibrant) and reference compound Perfluoro-3,6-dioxaheptanoic acid (CAS Number: 151772-58-6) (used as an internal

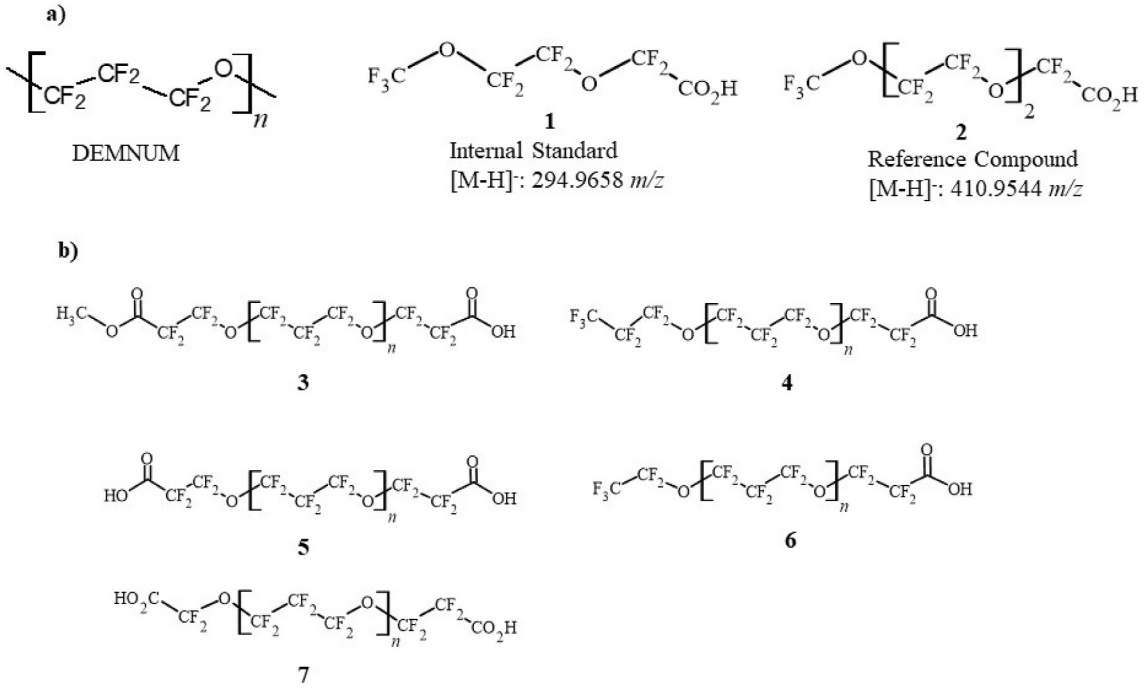

Fig. 1. a) Structures of DEMNUM and the two standards. b) Structures of identified low molecular weight species (LMWS).

standard) were purchased from Exfluor (Purity 98% by SDS). Their structures are shown in Fig. 1a.

DEMNUM was washed with methanol in the following manner: Approximately 2 g of DEMNUM polymer were shaken for 10-min intervals with 35 mL of methanol and the supernatant methanol layer discarded following centrifugation at 4000 rpm for 10 min. This procedure was repeated five times. The 5th methanol layer was removed and analyzed for remaining LMWS using LC/MS. DEMNUM was then dried under a gentle stream of nitrogen and weighed. No weight losses were observed due to extraction. This "washed" polymer material was used in all three studies described in this work. The three tests presented in this work are the following:

2.1. Hydrolysis as a function of pH

This test was conducted according to the OECD guideline for the testing of chemicals, 111: Hydrolysis as a function of pH (OECD, 2004). Buffer solutions at pH 4, 7 and 9 (details are in the Supplementary Document) were autoclaved, degassed with nitrogen and sterilized by passing through a sterile 0.2 μm PTFE membrane. All vials and pipettes used to transfer solutions were also autoclaved to minimize the potential for microbial degradation of the test material. The polymer was dosed at ~500 ppm (500 μg/mL) in each vial. Aliquots (~6.25 mg or 3.34 μL) of polymer were placed in 18 10-mL vials. The solution in each vial was topped with 12.5 mL of the appropriate buffer (6 vials per buffer) and the headspace of each vial was flushed with sterilized (filtered) nitrogen. The vials were sealed with autoclaved Teflon-lined caps, vortexed, and labeled. One vial from each pH level was checked on Day 0 and on day 5 for pH. All remaining vials were analyzed by LC-MS/MS (two on Day 0 and two on Day 5 for each pH treatment). Two vials from each dosed pH solution were taken for LC-MS/MS analyses before and after the 5-day incubation at 50.0 ± 0.5 °C. The pH and temperature of each test solution had been checked on Day 0 (at test initiation) and on Day 5 (at test termination) (Tables S2 and S3).

2.2. An evaluation of the indirect photolysis in synthetic humic water by artificial sunlight

This test was conducted according to the OPPTS guideline 835.5270 (EPA, 1998; EPA, 1996) and the OECD guideline for testing of chemicals (OECD, 1981, OECD, 2000)

Six "Light-exposed" and six "Dark-control" quartz tubes containing ~1.00 mg/mL each of the polymer in synthetic humic water (SHW) were prepared. Light-exposed test tubes were irradiated continuously for ~17 days at 25 ± 2 °C under a filtered xenon arc lamp while Dark control samples were wrapped with aluminum foil and maintained in a temperature-controlled incubator to assess whether factors other than light contributed to the formation of LMWS. Duplicate samples from each group were analyzed at selected time intervals that correspond to Days 0, 3, 7, 14, 21, and 30 of natural light exposure by LC/MS. The Supplementary Document contains all the experimental details.

2.3. An evaluation of inherent biodegradability using the Zahn-Wellens/EMPA test

This test was conducted according to the OECD guideline for testing of chemicals, Method 302 B (OECD, 1992), and U.S. EPA test guidelines, OPPTS 835.3200 (EPA, 2009a,b). The biodegradation of the DEMNUM polymer in an aqueous medium containing activated sludge prepared in accordance to the Zahn-Wellens test guidelines was evaluated over a period of 28 days. Four groups of test vessels were prepared:

1. A blank untreated control group (3 test vessels) in order to measure the dissolved organic carbon (DOC) background concentration of the activated sludge.
2. A positive control group (3 test vessels) containing diethylene glycol in order to evaluate the viability of the sludge.
3. A treatment group containing the polymer at a concentration of 0.1 mg/mL (3 test vessels) in order to evaluate its biodegradability.
4. A toxicity control vessel containing both the polymer and diethylene glycol used to evaluate the toxicity of the polymer towards the inoculum. The Supplementary Document contains all the experimental details.

2.4. Liquid chromatography/mass spectrometry (LC/MS) analysis

Quantitative and structural analyses of LMWS were performed on a high-resolution accurate mass Bruker Daltonics maXis impact quadrupole time-of flight (QToF) mass spectrometer interfaced with a Dionex (Thermo) UltiMate 3000 HPLC. The mass spectrometer was operated in negative ESI ion mode using a data dependent method where one full mass spectrometric (MS) scan is followed by three collision induced dissociation (CID) scans of the three most intense ions. Active exclusion was employed. Reversed phase HPLC conditions using a C_{18} column were employed to separate the LMWS. Additional experimental details can be found in the Supplementary Document (Table S1). The scan range of the mass spectrometer was 50–1500 *m/z*. Manual interrogation of the data using the Bruker software DataAnalysis 4.2™ in conjunction with a non-targeted automated data analysis method using a Visual Basic script that looked for *m/z* values with intensities greater than 3000 counts and a mass defect between 0.9 and 1.1 were employed to screen the MS data for perfluorinated compounds. Each possible ion was then structurally characterized from its MS/MS spectrum. Once the various types of LMWS classes were identified, a second targeted Visual Basic script that contained all possible ions in Fig. 1b whose negative ion masses were between 50 and 1500 *m/z* was employed. This script generated extracted ion chromatograms (EICs) for these ions from the MS spectra and integrated their EIC peaks to obtain the peak areas. Calibration standards of the internal standard (IS) **1** and reference substance **2** (calibrant) (Fig. 1a) were made in the range 1–100 μg/L in pure acetonitrile. The IS concentration was maintained at 100 μg/L (nominal) in all standards and samples. Linear regression equations (weighted 1/x) were generated from the ratio of the calibrant peak area to the IS peak area using the Bruker software QuantAnalysis™. The LOQ of the method is set to 0.1 μg/L (1/10 of the lowest calibration point) and the LOD is estimated at 1/10 of that (0.01 μg/L). It should be noted that the concentrations of LMWS measured in this work are estimates as they were calculated using calibration curves for reference compounds **1** and **2**. Since it is not possible to obtain reference standards for each of the unknown LMWS found in this work, and since molecules that have similar structure and functional groups tend to have similar ionization efficiency, this semi-quantitative approach was adopted. Methods on the quantification of PFASs that do not have reference standards have been previously reported (Cao et al., 2023; Nickerson et al., 2020). Fig. S3 of the Supplementary Document contains the extracted ion chromatograms (EICs) for the two reference compounds used in this study at the same concentration of 100 μg/L each. Despite their structural difference, the LC/MS peak heights and peak areas were very close for both ions supporting this approach. A representative calibration curve from 1 to 100 μg/L of **2** is also included in the Supplementary Document (Fig. S4).

3. Results

3.1. LMWS impurities present in the DEMNUM polymer material

DEMNUM's 1-H and 19-F NMR spectra are provided in the Supplementary Document in Figs. S1 and S2, respectively and provide proof of the purity of the polymer material. However, residual impurities and low molecular weight substances (LMWS) were detected by mass spectrometry as it has lower detection limits (LODs) than 1H NMR which is about 10 ppm. These species consisted of perfluoroalkyl ether carboxylic

acids of different sizes and were minimized by consecutive methanol extractions of LMWS present in the polymer. The purpose in this context is to differentiate between LMWS already present as impurities or byproducts within the polymer material itself and those formed because of polymer degradation under the three test conditions described in this work. The identity and estimated concentrations of LMWS remaining in the fifth methanol extraction layer are summarized in Table 1 and their structures are included in Fig. 1b. Fig. 2 shows the decrease in ion abundance of select ions from Table 1 as a function of methanol washes. The figure indicates that washing the polymer with methanol is an effective way of removing residual LMWS. The structures in Table 1 were deduced from both the parent accurate mass and collision-induced dissociation (CID) mass spectrometric spectra when possible. Low molecular weight perfluoroalkyl ether carboxylic acids have a signature fragmentation pattern from which the repeating units and the end groups can be deduced (Strynar and Miller, 2022; Spool and Kasai, 1998). It has been observed in this work that some of the LMWS underwent in-source fragmentation. However, these species could be easily identified as they would either yield ions with a terminal alcohol as the likely structure which is unstable in solution or they would undergo decarboxylation such as the starred ions at the bottom of Table 1. In addition, although small, a parent signal is usually observed together with the in-source fragment at the same retention time.

The terminal groups found in these LMWS consisted of either CF_3CF_2O-, $CF_3CF_2CF_2O$-, CH_3O- or $–CO_2H$ on one end of the molecule, and $–CO_2H$ on the other end. Methyl ester formation is due to the reaction of the methanol extraction solvent with the carboxylic acid terminal of the LMWS. Therefore, detection of a methyl ester ion indicates the presence of a dicarboxylic acid species in the polymer material. The difference in rates of decrease between the methyl esters (*m/z* 651 and 817) and the other LMWS in Fig. 2 is probably due to the incomplete conversion of di-acids to methyl esters in the first wash or the differences in methanol extraction efficiencies between the two classes of compounds. The relative amount (ng/g) of the majority of LMWS in Table 1 is relatively low. The higher concentrations in the table are for species of type **3** in Figure.

Table 1
Identity and concentration of the main LMWS remaining in the 5th methanol extract.

Structure[a]	Formula	RT (min.)[b]	*m/z* [M − H]⁻	(μg/L)[c]	ng/g polymer[d,e]
3, $n = 0$	$C_7H_4F_8O_5$	10.6	318.9858	2.2 ± 0.2	42 ± 4[e]
3, $n = 1$	$C_{10}H_4F_{14}O_6$	14.1	484.9712	12.4 ± 0.5	241 ± 10[e]
3, $n = 2$	$C_{13}H_4F_{20}O_7$	17.8	650.9565	62.3 ± 3.7	1210 ± 72[e]
3, $n = 3$	$C_{16}H_4F_{26}O_8$	24.4	816.9418	173.7 ± 10.1	3375 ± 192[e]
3, $n = 4$	$C_{19}H_4F_{32}O_9$	28.3	982.9279	78.8 ± 2.9	1497 ± 55[e]
3, $n = 5$	$C_{22}H_4F_{38}O_{10}$	33.2	1148.9119	25.2 ± 1.3	479 ± 24.7[e]
4, $n = 2$	$C_{12}HF_{23}O_5$	23.0	660.9386	0.8 ± 0.1	15 ± 2
4, $n = 3$	$C_{15}H_1F_{29}O_6$	28.2	826.9259	0.9 ± 0.5	17 ± 10
4, $n = 4$	$C_{18}H_1F_{35}O_7$	33.9	992.9102	21.9 ± 1.8	416 ± 34
5, $n = 3$	$C_{15}H_2F_{26}O_8$	14.5	802.9262	0.3 ± 0.0	6 ± 1
5, $n = 4$[f]	$C_{15}H_2F_{28}O_6$	25.2	808.9332	12.7 ± 0.7	241 ± 13
5, $n = 5$[f]	$C_{18}H_2F_{34}O_7$	29.1	974.9185	9.8 ± 1.2	186 ± 23
5, $n = 6$[f]	$C_{21}H_2F_{40}O_8$	34.4	1140.9038	6.7 ± 0.5	127 ± 10
6, $n = 4$	$C_{17}H_1F_{33}O_7$	31.8	942.9115	0.3 ± 0.1	6 ± 2

[a] Refer to Fig. 1 for structures.
[b] RT is the LC/MS retention time in minutes.
[c] The LOQ of the method is 0.1 μg/L and the LOD is 0.01 μg/L. The uncertainties are for 3 samples.
[d] ~1.8 g of polymer were extracted in 35 mL of methanol.
[e] The ionization efficiency of the methyl esters was observed to be much larger than that of reference compound 2 thus yielding unusually high values for type 3 species (refer to text for explanation).
[f] The reported formula and *m/z* are that of the parent di-acid having undergone the neutral losses of both CO_2 and $CF_3CF{=}O$.

1b. These methyl ester type species have resulted from partial esterification of dicarboxylic acids and are expected to have higher ionization efficiencies in the ESI source of the mass spectrometer than either reference compound **1** or **2**. This has resulted in artificially higher concentration values for these methyl ester species than for the rest of the compounds in Table 1. However, even the highest value in the table, which is for ion **3**, $n = 3$, corresponds to only ~0.002 mol percent of the washed polymer. This was calculated assuming a MW of 5000 Da for DEMNUM. The sum of the amounts found in Table 1 indicate that, at the maximum, only ~8×10^{-4} wt/wt percent (8 ppm) of LMWS to polymer remained after the 5th wash but the actual amount is probably much lower. This was calculated by summing all the concentrations in Table 1 and multiplying by the methanol volume in the 5th wash (35 mL) and dividing by the 1.8 g of DEMNUM that were washed.

3.2. Hydrolysis as a function of pH

The hydrolysis of DEMNUM polymer was assessed by incubating it in sterile aqueous pH 4, 7, and 9 buffers at 50 °C for 5 days at a concentration of ~0.5 mg/mL. The details of this experiment can be found in the Supplementary Document. At the beginning of the study.

(Day 0) and after 5 days of incubation (Day 5), duplicate quartz test tubes were analyzed by LC MS to determine whether any LMWS degradants formed and to estimate their amounts. Polymer-containing Day 0 samples from all three buffers did not contain any LMWS by LC/MS analysis. Day 5 samples in contrast showed a handful of LMWS (Table 2) however, none of their concentrations was above the LOQ of the method (0.1 μg/L). Since the initial concentration of polymer in each sample was 0.5 mg/mL, it is clear that they were formed at negligible quantities Table 2. LMWS detected by LC/MS in hydrolysis buffers following five days of polymer incubation at 50 °C.

(~0.2×10^{-4} % wt/wt each or a total of ~2 ppm referred to the polymer) assuming the LOQ limit, and therefore subjecting DEMNUM to hydrolysis conditions does no result in the formation of low molecular weight perfluoroalkyl ether carboxylic acids hydrolysis products to any notable extent. According to OECD 111 Guideline, there is no need to continue the experiment if the substance does not hydrolyze by more than 10% of its initial concentration in all 3 pH's by day 5 of incubation at 50 °C (OECD, 2004).

3.3. Indirect photolysis in synthetic natural water by artificial sunlight

Indirect photolysis of DEMNUM polymer in synthetic humic water (SHW) adjusted to pH 7.0 to form lower molecular weight species (LMWS) was examined. None of the "dark" control samples contained any observable amounts of LMWS even after 30 days of incubation. Light-irradiated samples on the other hand showed the presence of LMWS from Day 3 of natural light exposure. About a dozen species were found in the photolysis samples. These are listed in Table 3 together with their structures and estimated average concentrations. The data in Table 3 shows that the concentration of most of the species formed increased slowly with continuing irradiation up to.

Day 14 then leveled off or slightly decreased. The two main perfluoroalkyl ether carboxylic acids in the table (*m/z* 329 and *m/z* 495) were species with a $CF_3CF_2CF_2O$- end group on one terminus and a $–CF_2CF_2CO_2H$ on the other. The rest of the species formed had carboxylic acid groups on both ends. Interestingly, dicarboxylic acid species

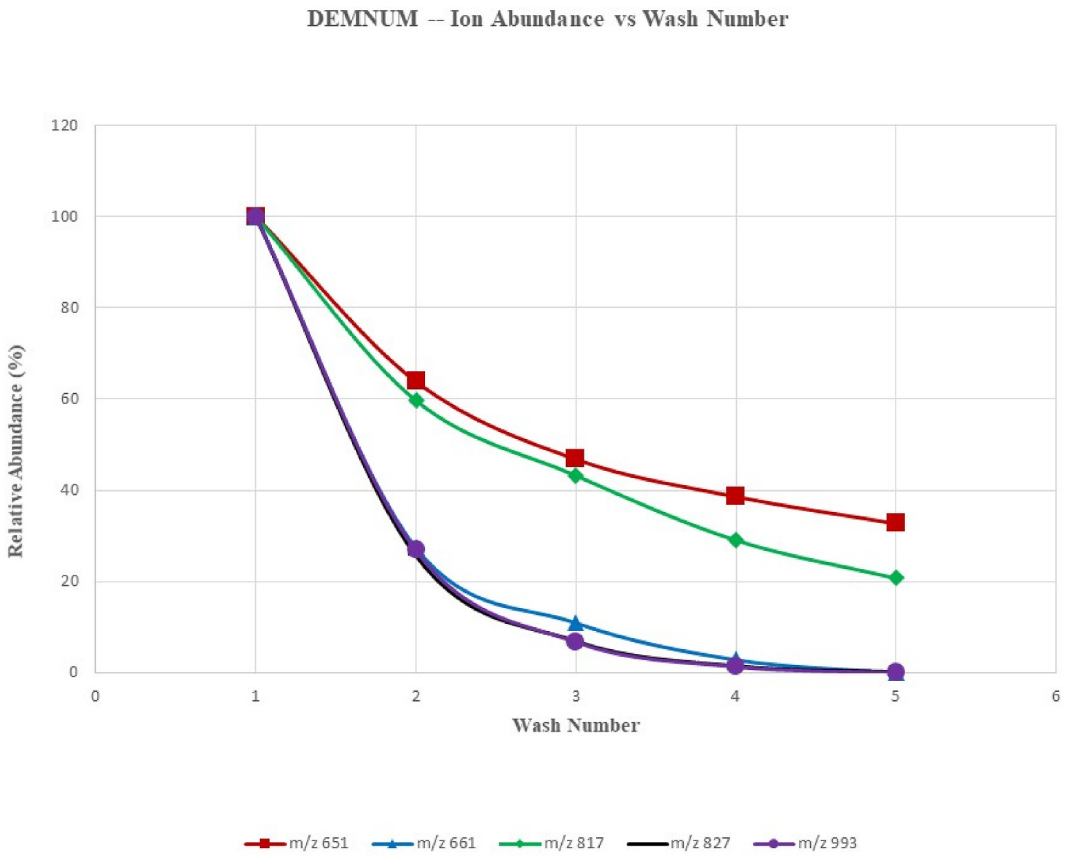

Fig. 2. Decrease in ion abundance for 5 LMWS (Table 1) as a function of the number of methanol extractions performed on DEMNUM.

Table 2
LMWS detected by LC/MS in hydrolysis buffers following five days of polymer incubation at 50 °C.

m/z $[M-H]^-$	Structure [a]	Molecular Formula	RT (min)[b]	pH 4[c,d]	pH 7	pH 9
304.9702	**5**, $n=0$	$C_6H_2F_8O_5$	5.1	≤ LOD	≤ LOD	≤ LOQ
420.9587	**7**, $n=1$	$C_8H_2F_{12}O_6$	8.6	≤ LOD	≤ LOQ	≤ LOQ
470.9555	**5**, $n=1$	$C_9H_2F_{14}O_6$	9.5	≤ LOD	≤ LOQ	≤ LOQ
586.9440	**7**, $n=2$	$C_{11}H_2F_{18}O_7$	11.3	≤ LOD	≤ LOQ	≤ LOQ
636.9408	**5**, $n=2$	$C_{12}H_2F_{20}O_7$	11.9	≤ LOD	≤ LOD	≤ LOQ
802.9262	**5**, $n=3$	$C_{15}H_2F_{26}O_8$	14.4	≤ LOQ	≤ LOQ	≤ LOQ
494.9531	**4**, $n=1$	$C_9H_1F_{17}O_4$	15.8	≤ LOD	≤ LOQ	≤ LOQ
610.9403	**6**, $n=2$	$C_{11}H_1F_{21}O_5$	19.2	≤ LOD	≤ LOQ	≤ LOQ
660.937	**4**, $n=2$	$C_{12}H_1F_{23}O_5$	22.3	≤ LOQ	≤ LOQ	≤ LOQ

[a] Refer to Fig. 1 for structures.
[b] RT is the LC/MS retention time in minutes.
[c] No LMWS were detected on Day 0 in any of the buffers.
[d] LOQ and LOD of the method are 0.10 μg/L and 0.01 μg/L, respectively. The polymer concentration in each sample was ~0.5 mg/mL.

with one $-CF_2CO_2H$ terminus were also formed (Fig. 1b, **7**). Upon CID in the mass spectrometer, these acids had a neutral loss of trifluoroacetic acid (CF_3CO_2H) whereas acids with both termini being $-CF_2CF_2CO_2H$ groups showed the neutral loss of $CF_3CF_2CO_2H$ and a distinctive loss of ~188 (Fig. 3).

This difference in CID fragmentation along with the accurate mass measurement allowed the two species to be differentiated. Fig. 4 demonstrates the LC/MS spectrum of Day 21 of light exposure. The internal standard peak (reference compound **1**) is the tallest peak in the figure. Since its ionization efficiency is expected to be similar to that of potentially forming LMWS, it can be estimated from Fig. 4 that all LMWS formed by light exposure had concentrations less than 100 μg/L. The total amount of observed LMWS following 30 days of light exposure is at 0.01% (wt/wt) or ~0.1 mol% of the initial amount of polymer (~150 ppm referred to the polymer). The data in Table 3 shows that the trend for formation of LMWS following photolysis is a fast initial formation followed by a slow decrease. Arbitrarily fitting the initial three data points to a first order rate equation results in an upper estimate of the photolysis rate constant that is in the 10^{-6} order of magnitude. The actual photolytic rate constant for DEMNUM would be even lower.

3.4. An evaluation of inherent biodegradability using the Zahn-Wellens test

Dissolved organic carbon (DOC) measurements on the positive control test vessels confirmed the viability of the Zahn-Wellens matrix. Almost 100% of diethylene glycol (250 mg Carbon/L) was transformed in the positive control vessels by Day 14 of the experiment confirming the viability of the inoculum and validity of the test (Fig. S9 in the Supplementary Document). The percent degradation (DOC removal) in the toxicity control vessel was also almost 100% by day 14. According to the Zahn-Wellens test guidelines, 25% degradation by Day 14 for the toxicity control vessel indicates that the test material is non-inhibitory to the inoculum under the experimental conditions (OECD, 1992).

Table 3
Measured concentrations (μg/L) of potential LMWS in dosed light-irradiated synthetic humic water samples.[a]

m/z	Structure	Molecular	RT (min)	Day 3	Day 7	Day 14	Day 21	Day 30
				μg/L				
420.9587	7, *n* = *1*	$C_8H_2F_{12}O_6$	8.7	4.2 ± 0.3	5.3 ± 0.4	5.6 ± 0.2	4.7 ± 0.1	4.4 ± 0.2
470.9555	5, *n* = *1*	$C_9H_2F_{14}O_6$	9.5	7.1 ± 0.2	9.3 ± 0.1	9.8 ± 0.1	7.7 ± 0.4	7.2 ± 0.3
586.9440	7, *n* = *2*	$C_{11}H_2F_{18}O_7$	11.3	5.8 ± 0.4	7.3 ± 0.4	7.9 ± 0.2	6.2 ± 0.1	5.6 ± 0.2
328.9677	4, *n* = *0*	$C_6H_1F_{11}O_3$	11.8	25 ± 1	32.9 ± 0.1	33 ± 1	34.0 ± 0.3	34.3 ± 0.9
636.9408	5, *n* = *2*	$C_{12}H_2F_{20}O_7$	12.0	9.5 ± 0.2	12.2 ± 0.2	13.7 ± 0.6	10.54 ± 0.02	10.0 ± 0.4
752.9294	7, *n* = *3*	$C_{14}H_2F_{24}O_8$	13.7	3.1 ± 0.4	4.6 ± 0.3	5.2 ± 0.5	5.2 ± 0.2	4.5 ± 0.4
802.9262	5, *n* = *3*	$C_{15}H_2F_{26}O_8$	14.6	2.6 ± 0.3	4.1 ± 0.6	5.3 ± 0.2	6.2 ± 0.8	4.9 ± 0.6
444.9563	6, *n* = *1*	$C_8H_1F_{15}O_4$	14.7	6.9 ± 0.1	8.4 ± 0.7	9 ± 1	8.0 ± 0.2	7.08 ± 0.02
494.9531	4, *n* = *1*	$C_9H_1F_{17}O_4$	15.9	52.6 ± 0.5	57 ± 4	63 ± 6	56 ± 2	52 ± 3
918.9147	7, *n* = *4*	$C_{17}H_2F_{30}O_9$	17.1	–	2.2 ± 0.2	2.6 ± 0.3	3.2 ± 0.3	3.2 ± 0.2
610.9416	6, *n* = *2*	$C_{11}H_1F_{21}O_5$	19.8	2.1 ± 0.1	2.41 ± 0.04	2.3 ± 0.1	2.7 ± 0.2	2.6 ± 0.4
660.9384	4, *n* = *2*	$C_{12}H_1F_{23}O_5$	22.9	7 ± 1	9 ± 4	12 ± 5	14 ± 2	8 ± 2
Sum (μg/L)				126 ± 2	155 ± 6	169 ± 8	159 ± 3	144 ± 4

[a] LOQ and LOD of the method are 0.10 μg/L and 0.01 μg/L, respectively. The polymer concentration in each sample was ~1 mg/mL. Refer to Fig. 1.

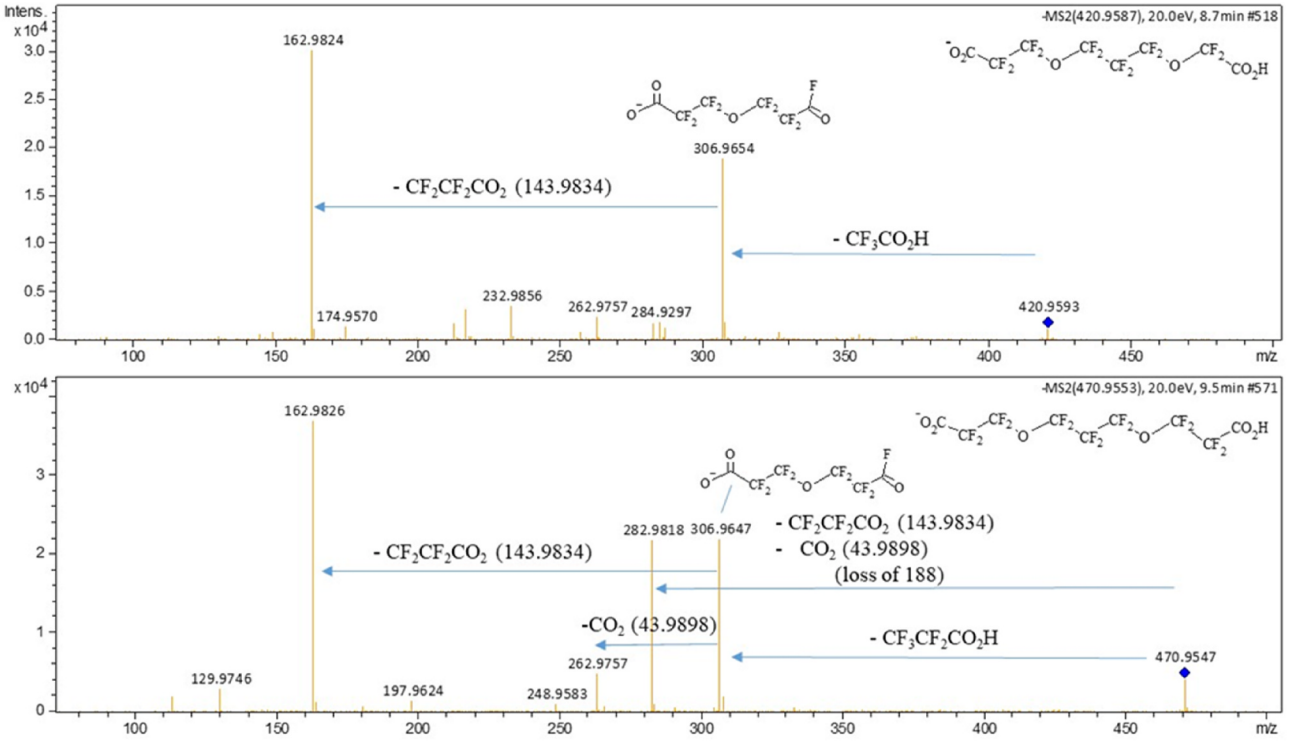

Fig. 3. CID spectra of two carboxylic acid species found following DEMNUM photolysis.

3.5. LMWS polymer degradation products in activated sludge

None of the blank control vessels had any LMWS throughout the course of the study. Samples obtained from the treatment vessels and injected directly into the LC/MS instrument did not show the presence of any LMWS. Therefore, the samples were concentrated by a factor of four and reinjected into the instrument. These concentrated samples showed the presence of less than a dozen LMWS which are listed in Table 4.

Fig. 5 is a representative LC/MS spectrum containing the extracted ion chromatograms (EICs) of these LMWS found on Day 28 of the treatment following 4-fold concentration. The structures are in Fig. 1.

The largest peak in Fig. 5 at 11.1 min is that of the added internal standard **1** at 100 μg/L nominal. The rest of the peaks are LMWS appearing following incubation of the polymer in activated sludge and are minute compared with the IS peak (they are expected to have similar ionization efficiency). The largest LMWS peak is at 29 min and belongs to a di-acid species having five $CF_2CF_2CF_2O$- repeat units (**5**, *n* = *5*). The rest of the more visible peaks belong to species having $CF_3CF_2CF_2O$- as one of the termini, a carboxylic acid (-$CF_2CF_2CO_2H$) as the other and a variable number of - $CF_2CF_2CF_2O$- repeat units (**4**, *n* = *2-4*). It is interesting to note the difference in species formed between the Zahn-Wellens and photolysis experiments. Dicarboxylic acids with structure **7** (Fig. 1) were not formed in activated sludge. In addition, degradation by sludge resulted in the formation of larger LMWS. Since the ionization efficiency of the IS is expected to be similar to that of potentially forming LMWS, it can be estimated that they are all well below 25 μg/L concentration (the samples were concentrated 4 fold prior to the addition of the IS and LC/MS analysis). Table 4 also contains an estimate of the amounts of LMWS formed at different time points averaged over the three treatment test vessels. The amounts of each LMWS are extremely low and can partially explain the high variance in the measurements as seen in the table. The sum of these LMWS (bottom row of Table 4) indicates that the plateau was reached by day 28. The highest total concentration observed was on day 27 (30 ± 5 μg/L) corresponding to an average of ~8 μg/L in the treatment test vessels or ~ 80 ppm relative to polymer. This translates to the generation of ~0.03% wt/wt LMWS to

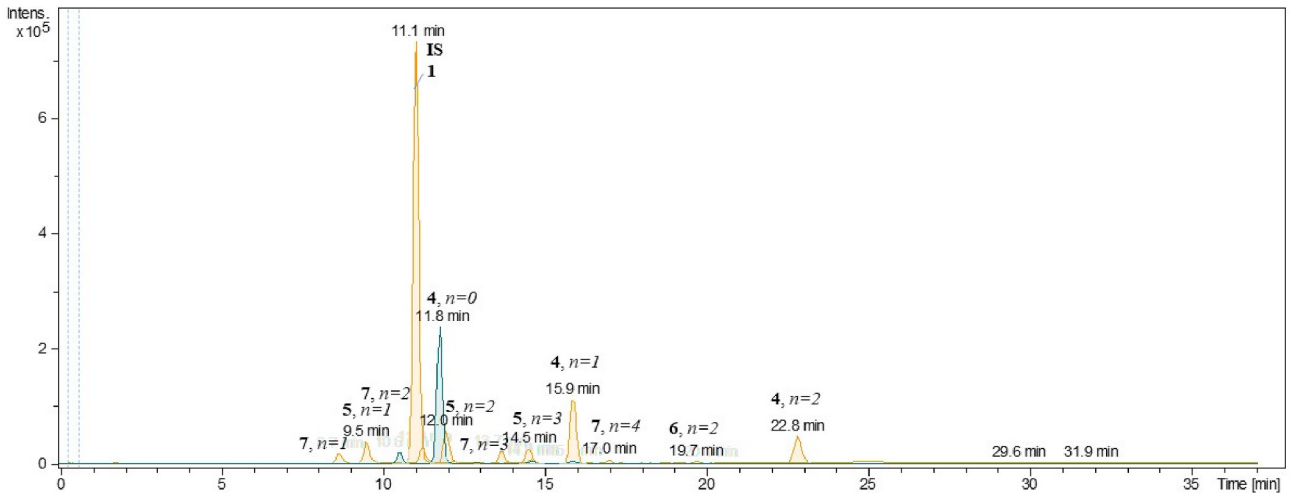

Fig. 4. LC/MS extracted ion chromatograms of LMWS found in a DEMNUM photolysis sample (Day 21). The assignments are above the figures and the structures are in Fig. 1.

Table 4
LMWS found in the Zahn-Wellens treatment vessels and their estimated amounts (μg/L) following a 4 fold concentration.

m/z	Structure[a,b]	Molecular Formula	RT (min)	3 h	Day (14)	Day (21)	Day (27)	Day (28)
776.9269	**6**, *n = 3*	$C_{14}H_1F_{27}O_6$	25.4	<LOQ[c]	<LOQ	<LOQ	0.26 ± 0.05	<LOQ
942.9123	**6**, *n = 4*	$C_{17}H_1F_{33}O_7$	29.5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
1108.8976	**6**, *n = 5*	$C_{20}H_1F_{39}O_8$	35.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
660.9384	**4**, *n = 2*	$C_{12}H_1F_{23}O_5$	22.0	1.6 ± 0.3	2.0 ± 0.6	1.6 ± 0.5	4 ± 2	3.2 ± 0.7
826.9237	**4**, *n = 3*	$C_{15}H_1F_{29}O_6$	26.6	<LOQ	0.7 ± 0.5	0.6 ± 0.4	4 ± 1	3 ± 1
992.9091	**4**, *n = 4*	$C_{18}H_1F_{35}O_7$	31.0	<LOQ	1.05 ± 0.02	0.7 ± 0.5	2.1 ± 0.6	1.9 ± 0.5
636.9408	**5**, *n = 2*	$C_{12}H_2F_{27}O_7$	12.1	<LOQ	0.3 ± 0.2	0.3 ± 0.2	<LOQ	<LOQ
802.9262	**5**, *n = 3*	$C_{15}H_2F_{26}O_8$	14.5	<LOQ	0.8 ± 0.3	0.3 ± 0.2	0.25 ± 0.05	0.4 ± 0.3
968.9115	**5**, *n = 4*	$C_{18}H_2F_{32}O_9$	19.0	<LOQ	0.24 ± 0.03	0.16 ± 0.09	<LOQ	<LOQ
1134.8968	**5**, *n = 5*	$C_{21}H_2F_{38}O_{10}$	29.1	7 ± 6	10 ± 3	9 ± 3	19 ± 4	19 ± 4
1300.8807	**5**, *n = 6*	$C_{24}H_2F_{44}O_{11}$	34.3	<LOQ	0.5 ± 0.3	0.4 ± 0.4	0.6 ± 0.4	0.9 ± 0.6
	Sum (μg/L)			9 ± 6	16 ± 3	13 ± 3	30 ± 5	28 ± 4

2The samples taken from each treatment vessel were 4 fold concentrated. The actual estimated concentrations in the vessels is a quarter of what is displayed in the table.

[a] Refer to Fig. 1.

[b] The polymer concentration in each treatment vessel was 0.1 mg/mL.

[c] The LOQ of the method is 0.1 μg/L and the LOD is 0.01 μg/L of DEMNUM incubation in activated sludge.

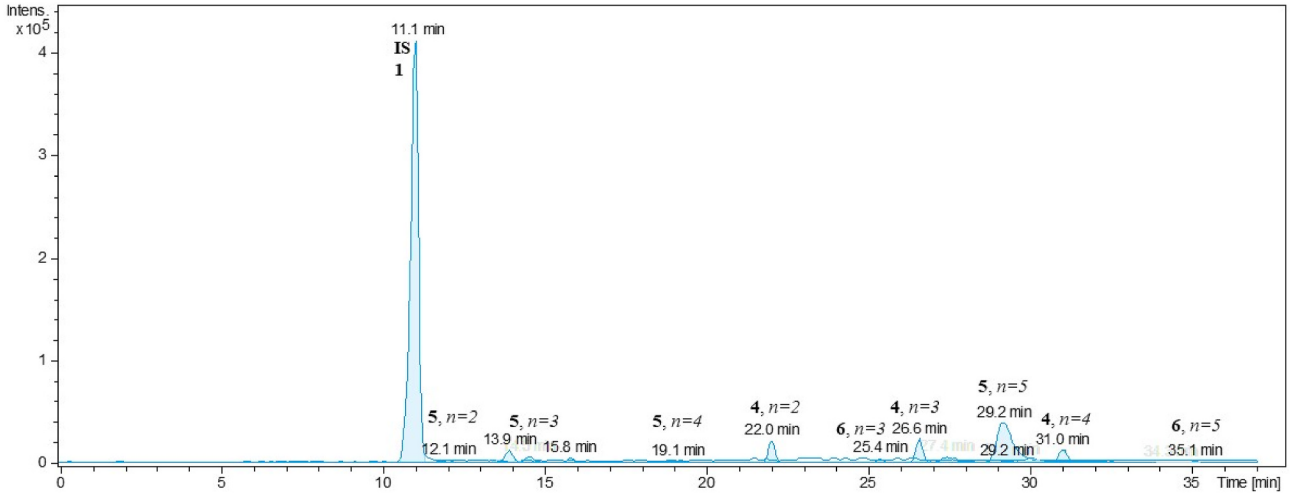

Fig. 5. LC/MS extracted ion chromatograms (EICs) of LMWS found in Zahn-Wellens Day 28 test vessels after being concentrated 4-fold. The ion assignments are above the figure and their structures can be found in Fig. 1.

polymer after 28 days.

Assuming that all the biodegradation is originating from the polymer itself (this will be further discussed), the first order biodegradation rate is on the same order of magnitude as its rate of photodegradation (10^{-6}/day) signifying that the substance, as expected, is non-degradable by common microorganisms present in the sludge.

4. Discussion

Henry and co-workers (Henry et al., 2018) reported that unlike other PFAS species (Wang et al., 2012), fluoropolymers were stable and do not degrade in the environment fulfilling the requirements for "polymers of low concern" (PLC). For example, although polytetrafluoroethylene (PTFE) rapidly degraded under ionizing radiation (e.g., gamma radiation or high-energy electron-beam radiation) it was resistant to photolysis (Drobny, 2006). In addition, it had been found inert to degradation by water (hydrolysis) and by microorganisms under oxygenated (aerobic) or anoxic (anaerobic conditions) (Arkles, 1973). In contrast, the hydrolytic properties of a commercial fluorotelomer were investigated by Washington and Jenkins (Washington et al., 2015) who found that its neutral abiotic hydrolysis proceeded with a half-life of 55–89 years whereas its base-mediated hydrolysis at pH > 10 was much faster with a half-life of less than one year (Washington and Jenkins, 2015).

In this work, the hydrolysis, photolysis and biodegradation properties of the perfluoropolyether (PFPE) DEMNUM were examined. The formation of low molecular weight substances (LMWS) consisting of perfluoroalkyl ether carboxylic acids was followed using mass spectrometry with sub ppb levels of detection. The hydrolysis study was performed at 50 °C in acidic, neutral and basic buffers. Only two LMWS were detected in acidic conditions at pH 4, but as the pH increased, 9 LMWS were detected (Table 2). However, all species detected were below the LOQ of the method (0.1 μg/L). Since the initial concentration of polymer in each buffer was 0.5 mg/mL, LMWS were formed at negligible quantities (~$0.2X10^{-4}$ % wt/wt or ~2 ppm total referred to the polymer) assuming they all were at the LOQ limit. According to OECD 111 Guideline (OECD, 2004), there is no need to continue the hydrolysis experiment beyond day 5 if the substance does not hydrolyze by more than 10% of its initial concentration in all 3 pH's by day 5 of incubation at 50 °C. Since this is the case for DEMNUM, it is found stable and will not result in the formation of low molecular weight perfluoroalkyl ether carboxylic acids hydrolysis products to any notable extent even at pH 9 and 50 °C. Its half-life ($t_{1/2}$) according to OECD guidelines is estimated to be greater than one year (OECD, 2004).

DEMNUM stability to hydrolysis at room temperature and pH 7 is also seen in the results of the photolysis experiment for the Dark samples. DEMNUM samples that were incubated in the dark in synthetic humic water did not show any LMWS even after 30 days of incubation, supporting the data obtained from the hydrolysis study. Irradiation of the polymer with artificial sunlight (xenon arc lamp) resulted in the formation of low levels of about a dozen LMWS (Table 3). The maximum total amount of observed LMWS is estimated at 0.01% (wt/wt) (~160 ppm) or ~0.1 mol % of the initial polymer concentration. Degradation was not observed throughout the study in any of the dark control samples, therefore the likely scenario for the formation of LMWS in SHW light-irradiated samples is the indirect photolytic transformation of the polymer itself. The NMR spectra for the polymer provided in the Supplementary Document indicate that the polymer material is very pure. However, since the detection limit of 1-H NMR is in the ~10 ppm order of magnitude, it is possible that the tiny amounts of degradation that are observed during photolysis are due to impurities within the polymer material which are more susceptible to degradation than the bulk of the polymer itself. This could explain the photolysis data in Table 3 that shows fast initial formation of LMWS followed by a slow decrease as the impurities in the polymer get consumed. Regardless of the source, the upper limit of the indirect photolysis first order rate constant is in the 10^{-6} order of magnitude indicating that the photolysis degradation rate in either case is negligible.

Extremely slow degradation of DEMNUM in activated sludge was also observed over the course of 28 days. Activated sludge treatment vessels had the polymer at an initial concentration of 100 mg/L, however, samples obtained from each vessel had to be concentrated 4-fold in order to detect LMWS by LC/MS. The highest total concentration observed was on day 27 (30 ± 5 μg/L) corresponding to an average of ~8 μg/L in the treatment vessels days (~80 ppm referred to the polymer). This is about half the amount that was formed during the photolysis experiment and is expected as perfluorinated species are resilient to being broken up by common bacteria found in sludge. The upper estimate of the rate constant for the bio degradation of the DEMNUM material is in the order of magnitude of 10^{-6}/day which is negligible.

Men and co-workers studied the aerobic microbial defluorination of short chain fluorinated carboxylic acids and found degradation to be limited to PFAS structures that have hydrogens on the carbon next to the carboxylic acid group (Che et al., 2021). Mabury and co-workers (Rankin et al., 2014) investigated the degradability in soil of a model fluorotelomer containing 8:2 fluorotelomer alcohols side-linked to the polymer chain through ester linkages. However, their rate constants for the model fluorotelomer under different soil conditions were in the 10^{-3} range, three orders of magnitude higher than the rate constants found here for DEMNUM.

The results of this work show that DEMNUM is a very stable polymer under environmental conditions. The polymer degradation was indirectly monitored by mass spectrometry through the appearance of LMWS and the estimation of their amounts. For future work we could employ a more direct approach starting from an ultra pure polymer sample to see if the very low degradation rates observed here for both photolysis and biodegradation can be brought even lower. For example, the polymer degradation could be monitored by NMR with before and after ^{19}F NMR spectra which would be expected to remain unchanged in terms of splitting patterns and peak heights if the polymer is stable (Tonelli et al., 1982). Mass spectrometric peak areas of the polymer itself in addition to its degradants could also be monitored by LC/MS or MALDI/MS for changes during the degradation process.

5. Conclusions

DEMNUM polymer, a linear PFPE polymer, was found stable under hydrolytic, indirect photodegradability and microbial degradability tests. The few low molecular weight species that were detected using mass spectrometry in each of the three experiments had negligible amounts relative to the amount of polymer used proving that it is resilient to environmental degradation.

Author contribution statement

Nobuhiko Tsuda: Conceptualization, Writing - Original draft preparation, Yoshitaka Honda: Conceptualization, Edward Schaefer: Project administration, Conceptualization, Supervision, Peizhi Lian: Investigation, Experimental, Asmaa Muneer: Investigation, Experimental, Timothy J. Blake: Investigation, Experimental, Reviewing, Loubna A. Hammad: Investigation, Experimental, Writing, Reviewing, Editing.

Disclaimer

N. Tsuda and Y. Honda are employees of Daikin Industries, the manufacturer of DEMNUM. The rest of the authors on this paper are employees of Eurofins EAG that was contracted by Daikin Industries to conduct this study.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.139331.

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