Biodiversity restoration and conservation of inland water ecosystems for environmental and human well-being

BioReset

BiodivRestore-406

2020 - 2021 Joint Call
Joint COFUND Call on “Conservation and restoration of degraded ecosystems and their biodiversity, including a focus on aquatic systems”

Deliverable 1.1.4

Data from monitoring of microplastics in the environment

Lead Beneficiary	Work package	Delivery month
IFE	**1**	**24**

1. Executive Summary

BioReset proposes to advance treatment processes (chemical, physical, biological and their combination) to promote ecosystem recovery and conservation and to develop assessment strategies. Diatoms will be used to model ecosystem conservation and restoration since their communities show high levels of biodiversity. The diatoms will provide an expeditious method to compare different recovery strategies and water treatment processes, allowing to address timescale and key conservation/restoration questions. The full environmental, economic, and social viability of the upgraded and innovative treatment technologies will be assessed. Based on this knowledge, scale-up studies in geographically different sites (Portugal and Spain) will be performed to ascertain the technical and economic feasibility at a larger scale and recommended action guidelines will be issued.

BioReset also envisages the creation of a representative space-time picture of the presence of emerging contaminants in inland waters and its correlation to effects on diatom communities. For this, powerful analytical techniques, such as gas- and liquid chromatography, will be used. Besides these methods, and to obtain real-time information, miniaturized analytical platforms that can perform fast, and on-site monitoring will also be employed.

Deliverable 1.1.4 provides details about microplastics in the environment in a landfill's case study and the analytical characterization of selected points near the old Brånåsen landfill, located in Skedsmo (Lillestrøm municipality). There is a need to develop, test and implement new methods to find and characterize sources of emissions of environmentally hazardous compounds. This report demonstrates source tracking based on chemical analyzes of landfill runoff and water upstream and downstream the large recipient (the Nitelva river).

2. Task description

WP1 regards analytical methods to analyse emerging contaminants (EC, pharmaceuticals and microplastics) in inland waters using established and novel methods. Task 1.1 focuses on monitoring pharmaceuticals with ultra-high performance liquid chromatography with tandem mass spectrometry (UHPLC-MS/MS) and microplastics with GC-Pyr-MS/MS. Only water samples that were accessible to collect by laboratory equipment were taken at this study. The approach employed made use of a suspect screening methodology based on Gas chromatography coupled to MS/MS, Ultra High-Performance Liquid Chromatography coupled to High Resolution Mass Spectrometry, and GC-Pyr-MS/MS. The objective was to understand the potential diffuse leakage from the landfill site that it is not collected in the urban sewage system and may reach to the immediate water recipients, the Nitelva river. A list of suspected contaminants is presented, that will serve to select the target contaminants that are cause of concern for the future monitoring and for achieving a better selection of the landfill leachate method or technology to be implanted in the area. The study will serve as decision-making tool for performing extra measures such as construction of new boreholes for advanced monitoring or implementation of mitigation strategies, and as a demonstration of a method for chemical source tracking of environmentally harmful compounds.

Brånåsdalen waste landfill was established in 1970 and closed in around 1990. From 1992, residential construction was permitted in the area and several detached houses were built right up to the edge of the landfill. In 2000, the Haugen and Lillehaugen housing associations were built. In 2006, today's Nitteberg garden was included in the municipal plan as regulated as a residential area - family housing. The regulatory plan was adopted in 2012 and the establishment of the housing estate began immediately afterwards. In 2015, the municipality (Skedsmo) became aware that conditions had arisen in a single-family house, which was thought to have been flushed to the landfill. Relatively large amounts of landfill gas were measured, and the house had large distortions. This led to the redemption of the home and Skedsmo municipality contacted the County Governor in Oslo and Akershus to discuss what measures should be implemented in the years to come. Since then, it is being thoroughly assessed by specialists, scientists and consultants which measures should be implemented.

For a more detailed description of the Brånåsen landfill and the last years' data for leachate monitoring, we refer to this web page: https://www.lillestrom.kommune.no/energi-klima-og-miljo/deponier/branasdalen-nedlagte-avfallsdeponi/

3. WP1 - Task 1.1 team members

The Team members in WP1, Task 1.1, regarding microplastic analysis, were:

Name	Organization	Role
Laura Ferrando Climent	IFE	Task coordinator
Mario Silva	IFE	Researcher
Vian Yasin	IFE	Researcher

4. Developed activities

Sampling

Samples were taken as random samples on 29.09.2022. The weather conditions were cloudy, with little rain showers and temperature of 9 ºC. No abnormal rains or overflows were registered before the sampling collection. Samples from landfill leachate in source point (point 1) are presented in Figure 1. The sampling was performed in the points described in Figure 2.

5 liter of water sample were taken at every point (Figure 2) in glass bottles prewashed and preserved with sodium azide (1%) to stop further degradation of organic components. Bottles were filled to the top avoid oxygen gap and transported to the IFE laboratory right after the sampling. For the sample collection, a manual pump system connected to a 6-m water hose was used.

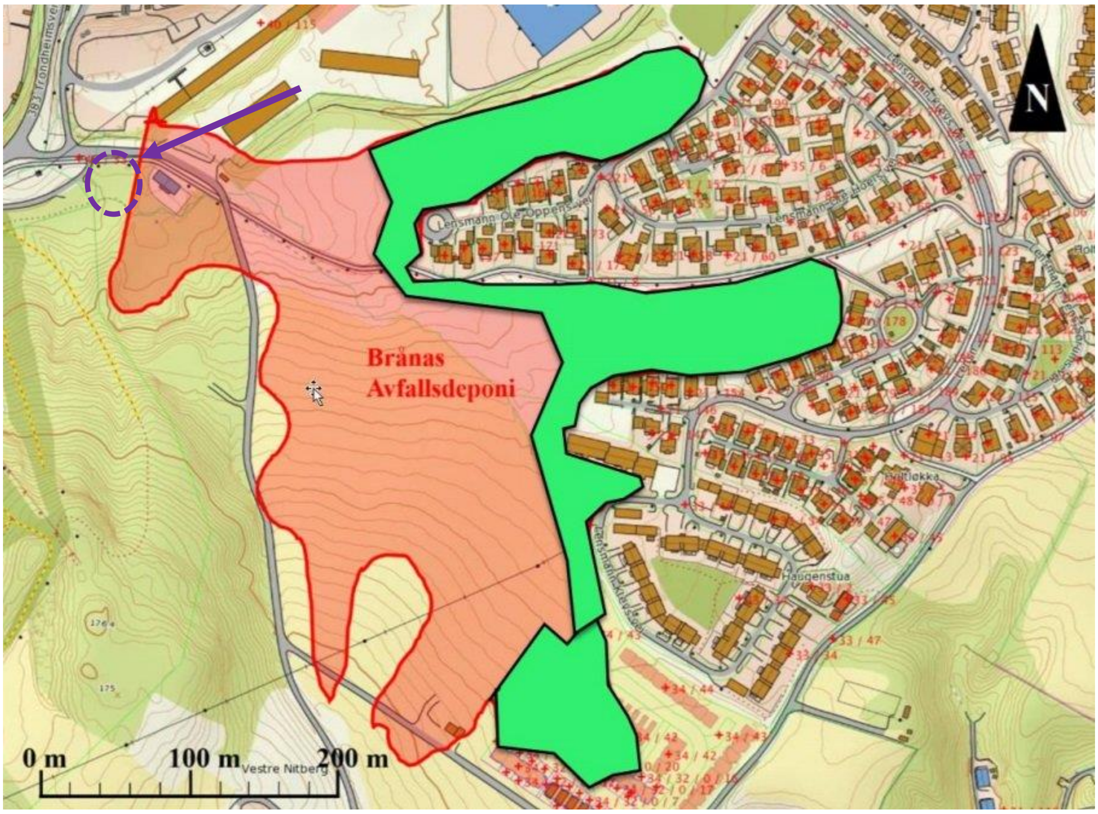


Figure 1. Brånåsen area and sampling point 1 (raw landfill leachate, *point where urban system collects the landfill leachate,*)

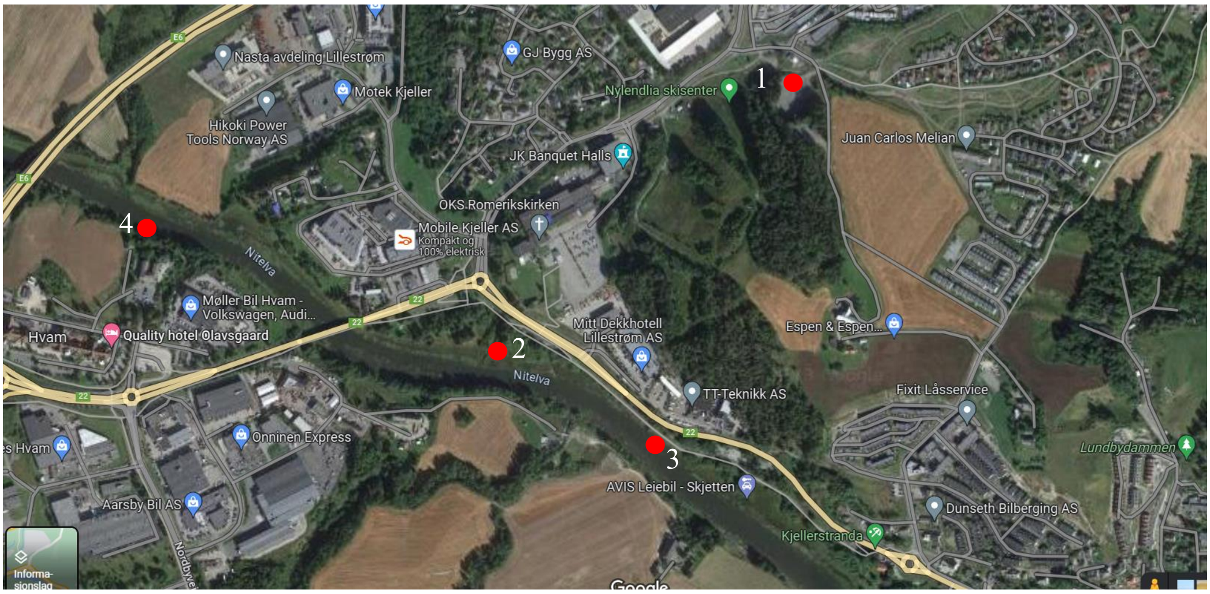


Figure2. Sampling points in Brånåsen area: (1) Brånåsen landfill leachate, (2) municipal outlet stream to Nitelva, (3) 500 m downriver after point 2 and (4) 500 m upriver before point 2.

Sample preparation and extraction

The samples were conserved at 5 °C for further use. Samples were centrifuge at 3000 rpm for 10 min and filtered through sequential filters sizes, glass fiber filters of 1mm followed by a 47-µm filter. They were transferred to 500-mL glass tubes containing 200 µL of HCl (1M), and prepared for solid phase extraction (SPE). The SPE procedure was performed with ISOLUTE ENV+ sorbent (Supelco ® 200mg/6mL) columns using a vacuum system and involved several steps: 1) conditioning with methanol (2mL) followed by MilliQ water (2 mL) at 2 mL/min, 2) loading 500 mL of sample at 1 mL/min, 3) washing with 1 mL milliQ water, and 4) elution in 1,5 mL of acetonitrile (AcN). The extracts were dried with N_2 and reconstituted in 1 mL of AcN, and later a portion was transferred into a chromatographic vial with insert (300 µl aliquots) and analyzed through GC-MS/MS and UPLC-HRMS.

Analytical methods

Samples extracted were submitted to two different analytical methods: 1) Screening by GC-MS/MS and 2) Screening by UPLC-HRMS. A third method is being considered for further exploration of microplastics, that it will employ GC-Pyr-MS/MS. The characterization of suspected components in the samples was performed using existing libraries (NIST) and data processing tools such as Compound Discoverer ®.

Screening analysis by GC-Pyr-MS/MS

This analysis was performed using a Thermo Scientific TraceTM 1310 gas chromatograph (Thermo Fischer Scientific, Waltham, MA, USA) equipped with a Restek Rtx®-5MS column (30 m X 0.25 mm X 0.25 µm) and coupled to a triple quadrupole mass spectrometer Thermo Scientific TSQ 8000 (Thermo Fischer Scientific, Waltham, MA, USA). The temperature program of the oven was as follows: initial temperature 50 °C kept for 3 min, followed by a ramp of 20 °C/min to 110 °C, and another ramp of 15 °C/min to 290 °C, and finally 7 min at 290 °C. Helium with a purity of 99.999% (Praxair Norway AS, 0663 Oslo) was used as carrier gas at a constant flow of 1 mL/min. The temperature of the injector was 250 °C and the temperatures of the ion transfer line and ion source were 290 °C and 320 °C, respectively. The injector was operated in split-less mode for 2 min returning to split mode after this time. The mass spectrometer (MS) was operated in electron impact (EI) ionization mode (+70 eV) and full scan mode was used to monitor suspected molecules within the range of 75-600 Da. The operation conditions of the MS were standard for all screening purposes.

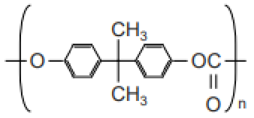
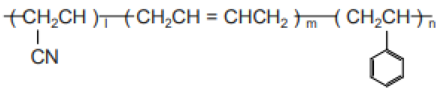
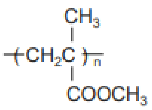
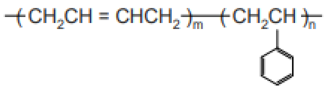
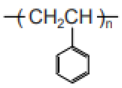
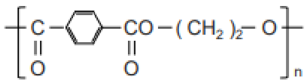
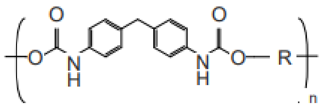
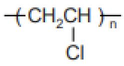
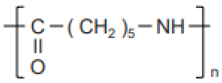
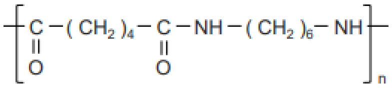
Screening analysis by UPLC-HRMS

The analysis was performed using an UPLC (Ultimate 3000 chromatograph with autosampler) coupled to a QExactive detector from Thermo Scientific. The MS analysis was performed with an electrospray ionization (ESI) interface in positive ionization mode. Chromatographic separation was performed using an Acquity BEH C18 column (150 mm × 2.1 mm i.d. 1.7 µm particle size; Waters Corp. Mildford, MA, USA) where the separation was performed in 28 min using a binary mobile phase of formic acid 0.1% (solvent A) and acetonitrile (solvent B) at 0.4 mL/min. The gradient elution started with 98% A and then increasing B to 100% in 28 min: Solvent A, held for 5 min; 5–10 linear rate to 100% B, 10–26 linear rate to 100% B, held for 0.5 min; reconditioning with a linear rate to 98% A, 26–28 min. Due to the chemical structure of suspect substances (cationic surfactants with large straight-chain and branched alkanes), the gradient was performed using a ramp in the flow rate (0.4 mL/min from 0 to 5 min, 0.5 mL/min from 5 to 10 min, 0.5 mL/min held for 15 min and coming back to 0.4 mL/min). 5 µl of extracted sample was directly injected in the system. For the MS detection, an acquisition method based on full scan mode at 70,000 resolution power was performed using a wide range of masses (100–1000 Da) in order to acquire the maximum amount of data. Parallel to full-scan MS acquisition, data-dependent acquisition (DDA) was used where the threshold of intensity (1000 counts) was used for triggering the ion masses to a MS/MS experiment (35,000 resolution power). The chromatograms obtained were compared with blank samples.

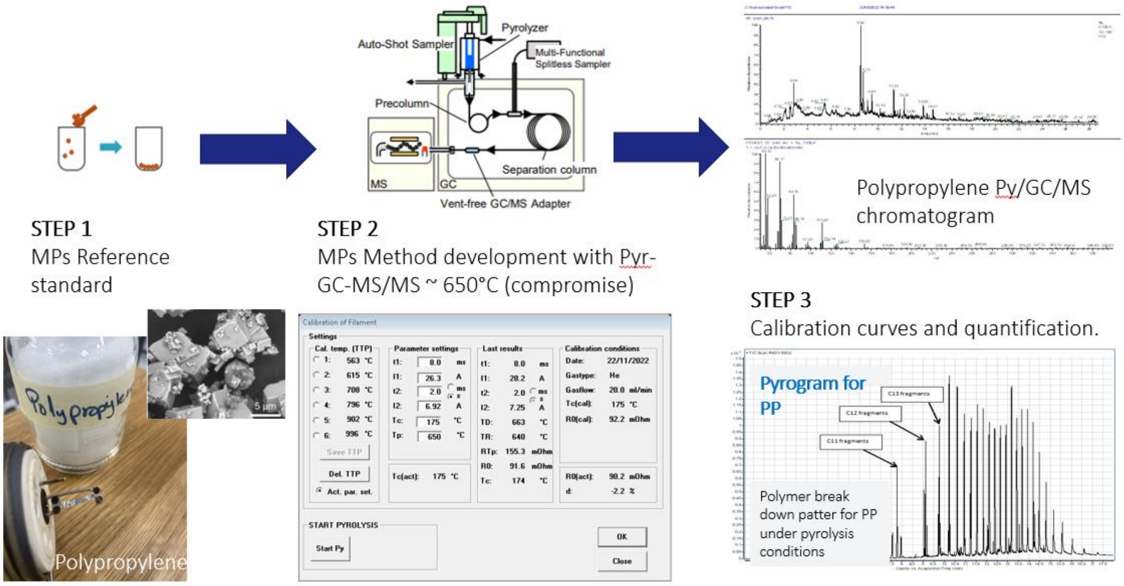
Screening of microplastics by GC-Pyr-MS/MS

The method developed was based on Pyrolysis coupled to GC-MS/MS. Pyrolysis is an analytical technique that involves the thermal decomposition of a sample by heating it to 550-1000 °C. When a Pyrolysis instrument is connected to a GC/MS it is possible to identify plastic particles, by analyzing the thermally degraded larger molecules into smaller molecules in an inert atmosphere. Depending on the pyrolysis temperature, this can lead to characteristic, volatile degradation products that either resemble or can be traced back to the predecessor molecule. Sample material is placed on a Pt filament in a closed chamber with an inert atmosphere. The sample will then thermally fragment and sent into the GC with the He mobile phase.

The microplastics Calibration Standard set employed contained 12 polymers which are homogeneously dispersed with a solid diluent for easy weighing on semi-microbalances. The diluents weare SiO_2 and $CaCO_3$. The microplastics substances targeted were:

$-(CH_2CH_2)_n-$		
Polyethylene (PE)	Polycarbonate (PC)	Acrylonitrile-butadiene-styrene resin (ABS)
$-(CH_2CH(CH_3))_n-$	 $-(CH_2\overset{CH_3}{\underset{COOCH_3}{C}})_n-$	
Polypropylene (PP)	Poly(methyl methacrylate) (PMMA)	styrene-butadiene rubber (SBR)
		
Polystyrene (PS)	Polyethylene terephthalate (PET)	Polyurethane* (PU)
 $-(CH_2\underset{Cl}{CH})_n-$	 $-[\underset{O}{\underset{\|}{C}}-(CH_2)_5-NH]_n-$	 $-[\underset{O}{\underset{\|}{C}}-(CH_2)_4-\underset{O}{\underset{\|}{C}}-NH-(CH_2)_6-NH]_n-$
Polyvinyl chloride (PVC)	Nylon 6 (N6)	Nylon 66 (N66)

The calibration procedure for MP analysis by GC-Pyr-MS/MS is depicted in Figure 3.



STEP 1
MPs Reference standard

STEP 2
MPs Method development with Pyr-GC-MS/MS ~ 650°C (compromise)

```
Calibration of Filament
Settings
Cal. temp. (TTP)   Parameter settings   Last results          Calibration conditions
○ 1:  563 °C       t1:  [ 8.0]  ms      t1:   8.0   ms        Date:      22/11/2022
○ 2:  615 °C       I1:  [26.3]  A       I1:  28.2   A         Gastype:   He
○ 3:  708 °C       t2:  [ 2.0] ○ ms     t2:   2.0 ○ ms        Gasflow:   20.0 ml/min
○ 4:  796 °C                   ● s                ● s         Tc(cal):   175 °C
○ 5:  902 °C       I2:  [6.92]  A       I2:  7.25   A         R0(cal):   92.2 mOhm
○ 6:  996 °C       Tc:  [ 175]  °C      TD:   663   °C
                   Tp:  [ 650]  °C      TR:   640   °C
  [Save TTP]                            RTp: 155.3  mOhm
  [Del. TTP]       Tc(act):  175 °C     R0:   91.6  mOhm      R0(act):   90.2 mOhm
● Act. par. set.                        Tc:   174   °C        d:         -2.2 %

START PYROLYSIS
  [Start Py]                                                  [OK]
                                                              [Close]
```

Polypropylene Py/GC/MS chromatogram

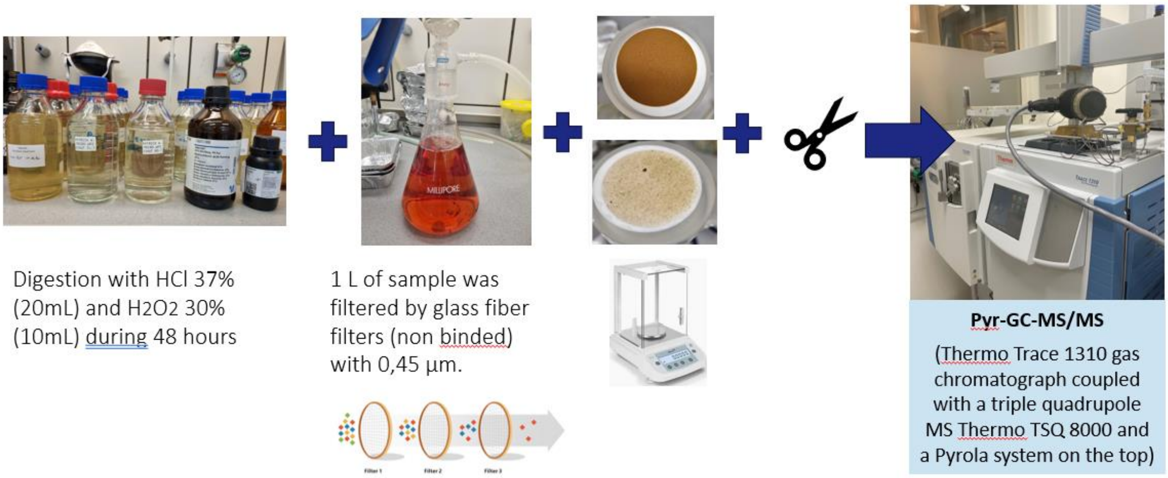
STEP 3
Calibration curves and quantification.

Pyrogram for PP

Polymer break down patter for PP under pyrolysis conditions

Figure 3. Calibration procedure for MP analysis by GC-Pyr-MS/MS.

The sample preparation of MPs and analysis in water samples is depicted in Figure 4.



Digestion with HCl 37% (20mL) and H_2O_2 30% (10mL) during 48 hours

1 L of sample was filtered by glass fiber filters (non binded) with 0,45 µm.

Pyr-GC-MS/MS

(Thermo Trace 1310 gas chromatograph coupled with a triple quadrupole MS Thermo TSQ 8000 and a Pyrola system on the top)

Figure 4. Sample preparation and MP analysis by GC-Pyr-MS/MS.

5. Results

The suspect screening was performed using a wide spectrum of components commonly used in domestic household and the existing information of the industry activities before the landfill was closed (Lillestrøm municipality).

Figure 5 shows the total ion chromatogram (TIC) for the relevant sampling points using GC-MS/MS after sample extraction. Relevant similarities were observed in the composition of the point 1, point 2 and point 3 samples, as well as differences from point 4 and all the controls (tap water, blanks).

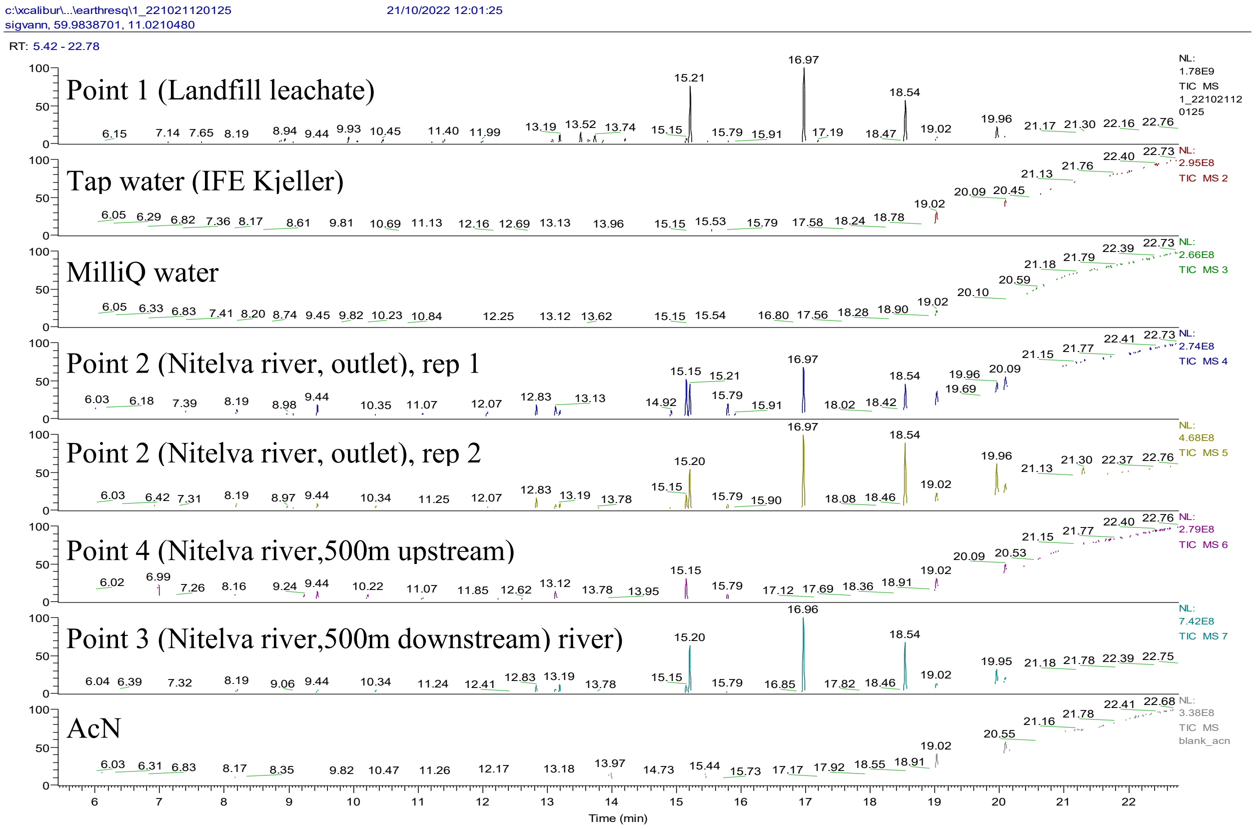


Figure 5. Total ion chromatogram (TIC) of Point 1,2, 3, 4, Tap water, MilliQ water and can used during the sample preparation.

The data processing work based on previous author strategies (Ferrando-Climent et al. 2016, Jaen-Gil et al 2020), allowed to identify suspect components at samples collected at point 1, 2 and 3 that were not detected at samples collected in point 4, neither in blanks (tap water, milliQ water and AcN).

A peak with high chromatographic intensity (10^8) was detected at 13.19 min. After data processing, the peak was tentatively identified as Diethylenglycol dimethacrylate with a molecular mass (MW) of 242 and molecular formula of $C_{12}H_{18}O_5$ (90% match by NYST library). The tentative identification of this component is presented in Figures 6 and 7 (NIST library) and named as COMP242.

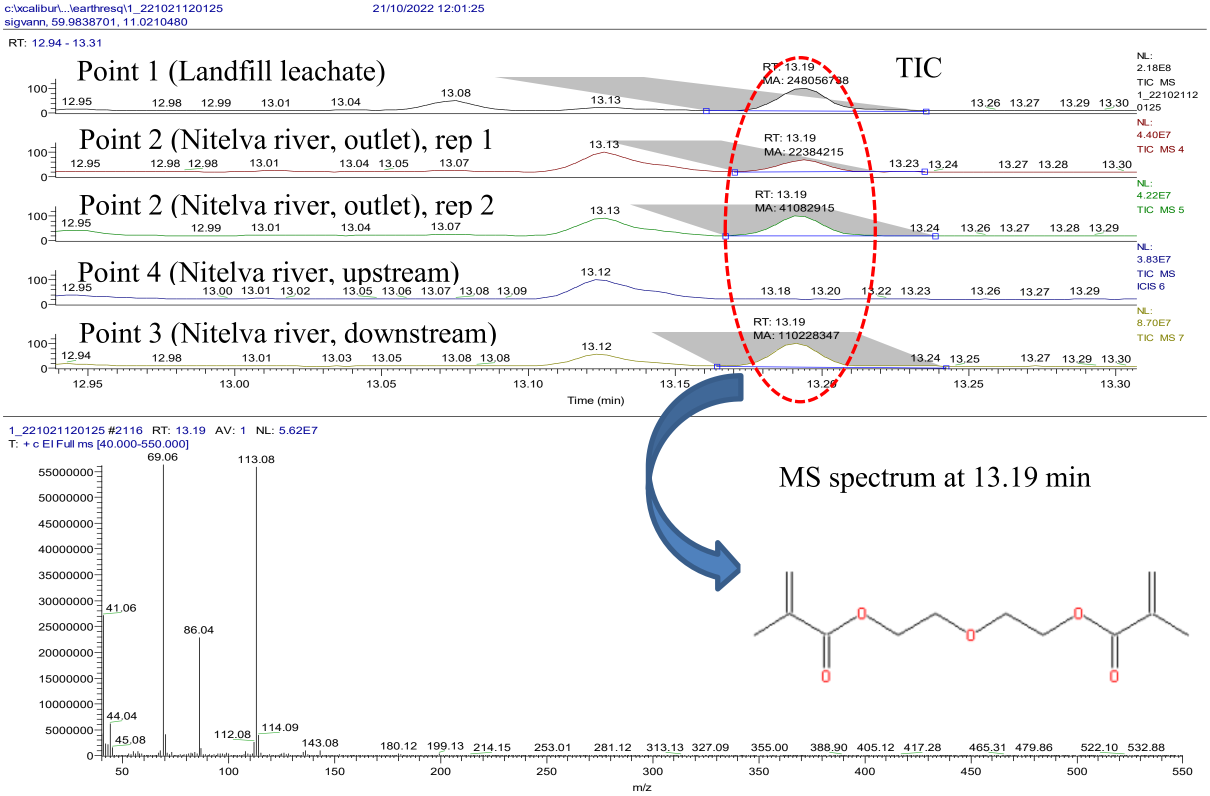


Figure 6. Tentative identification of Diethylenglycol dimethacrylate (COMP242) at point 1, 2, and 3: Peak at 13.19 min with MS spectrum at 13.19 min.

#	Lib.	Match	R.Match	Prob. (%)	Name
1	M	864	871	82.1	Diethyleneglycol dimethacrylate
⊞2	R	801	821	13.8	2-Propenoic acid, 2-methyl-, 1,2-ethanediylbis(oxy-2,1-ethanediyl) est
3	M	747	757	2.69	2-Propenoic acid, 2-methyl-, oxybis(2,1-ethanediyloxy-2,1-ethanediyl)
4	M	713	736	0.69	N,N'-Methylenebismethacrylamide
⊞5	M	655	674	0.12	2-Propenoic acid, 2-methyl-, 1,2-ethanediyl ester
⊞6	R	653	712	0.11	2-Propenoic acid, 2-methyl-, 2-chloroethyl ester
⊞7	M	631	650	0.04	α-Methyl-α-propylsuccinimide
8	M	622	651	0.03	2H-Pyrrol-2-one, 1,5-dihydro-4-methoxy-
9	M	617	649	0.02	Spiro[bicyclo[2.2.1]heptane-2,2'-[1,3]dioxolane]-3-one, 1,7,7-trimethyl
⊞10	M	613	643	0.02	3,4-Methylpropylsuccinimide
⊞11	M	612	628	0.02	2,5-Pyrrolidinedione, 3-methyl-4-propyl-, cis-
12	M	611	685	0.02	3,5,5-Trimethylhexyl ethylphosphonofluoridate
13	M	610	631	0.02	Imidazolidin-4-one, 2-t-butyl-3,5-dimethyl-
⊞14	M	610	624	0.02	4-Ethyl hydrogen itaconate
15	M	608	687	0.01	4-Methylpentyl ethylphosphonofluoridate
16	M	608	643	0.01	2-(tert-Butylamino)ethyl methacrylate
17	M	604	724	0.01	Phosphonofluoridic acid, ethyl-, decyl ester
18	M	602	691	0.01	Phosphonofluoridic acid, ethyl-, nonyl ester
19	M	599	632	0.01	3-Methylpentyl ethylphosphonofluoridate
20	M	599	621	0.01	Butanoic acid, 3-oxo-, 2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl ester
21	M	596	630	0.01	Pyrimidine, 2-fluoro-4-amino-
22	M	596	608	0.01	Cyclopropanecarboxamide, N-cycloheptyl
23	M	594	612	0.01	Diethylene glycol monomethyl ether methacrylate
24	M	589	709	0.00	Phosphonofluoridic acid, ethyl-, octyl ester
25	M	589	692	0.00	β-Phenoxyethyl methacrylate
26	M	589	614	0.00	(3-Methylpyrrolidin-2,5-dion-3-yl)-acetic acid, methyl ester
27	M	588	599	0.00	Mono-butyl itaconate
28	M	587	693	0.00	1H-Azepin-1-amine, hexahydro-N-(1-methyl-2-propenyl)-
29	M	583	602	0.00	Cyclopropanecarboxamide, N-(2-octyl)
30	M	582	598	0.00	Heptanoic acid, 2-vinyl-, ethyl ester
31	M	580	685	0.00	1,3-Dimethylbutyl ethylphosphonofluoridoate
32	M	580	617	0.00	3-[Tetrahydro-3-thienyl]-2-oxazolidinone-S,S-dioxide
⊞33	R	579	587	0.00	Dibutyl itaconate

InLib = -117, Hit List

Name: 1_221021120125#2116 RT: 13.19 AV: 1
MW: N/A ID#: 4 DB: Text File
Comment: T: + c EI Full ms [40.000-550.000]
10 largest peaks:
69 999 | 113 993 | 41 482 | 86 406 | 44 109 |
40 75 | 70 72 | 114 70 | 112 46 | 42 40 |
Synonyms:
no synonyms.

Difference MF=864 RMF=871
Diethyleneglycol dimethacrylate
864 871R 82.1P

Name: Diethyleneglycol dimethacrylate
Formula: $C_{12}H_{18}O_5$
MW: 242 Exact Mass: 242.115423 CAS#: 2358-84-1 NIST#: 232648 ID#: 32988 DB: mainlib
Other DBs: Fine, TSCA, HODOC, EINECS
Contributor: Japan AIST/NIMC Database- Spectrum MS-NW-5180
10 largest peaks:
69 999 | 113 840 | 41 563 | 86 271 | 39 131 |
70 81 | 114 58 | 40 48 | 42 36 | 45 35 |
Synonyms:
1.2-Propenoic acid, 2-methyl-, oxydi-2,1-ethanediyl ester
2.3-Oxapentane-1,5-diyl dimethacrylate
3.Ageflex DEGDMA
4.MFM-418
5.2-[2-(Methacryloyloxy)ethoxy]ethyl 2-methylacrylate #

Estimated non-polar retention index (n-alkane scale):
Value: 1559 iu
Confidence interval (Diverse functional groups): 89(50%) 382(95%) iu

Figure 7. Identification of component COMP242 via NIST MS library.

Diethylenglycol dimethacrylate is used as a monomer to prepare Hydroxyapatite/Poly methyl methacrylate composites that have applicability in bone cement, coatings, adhesives etc. A recent publication pointed out that ethylene glycol dimethacrylate and diethylene glycol dimethacrylate exhibit cytotoxic and genotoxic effect on human gingival fibroblasts via induction of reactive oxygen species (Bielecka-Kowalska et al. 2018).

A second component (COMP 286) with a high chromatographic peak intensity (10^8) was detected at 15.21 min. After data processing, the peak was tentatively identified as Triethylene glycol dimethacrylate with a molecular mass (MW) of 286 and molecular formula of $C_{14}H_{22}O_6$ (97% match by NYST library). The tentative identification of this component is presented in Figures 8 and 9 (NIST library).

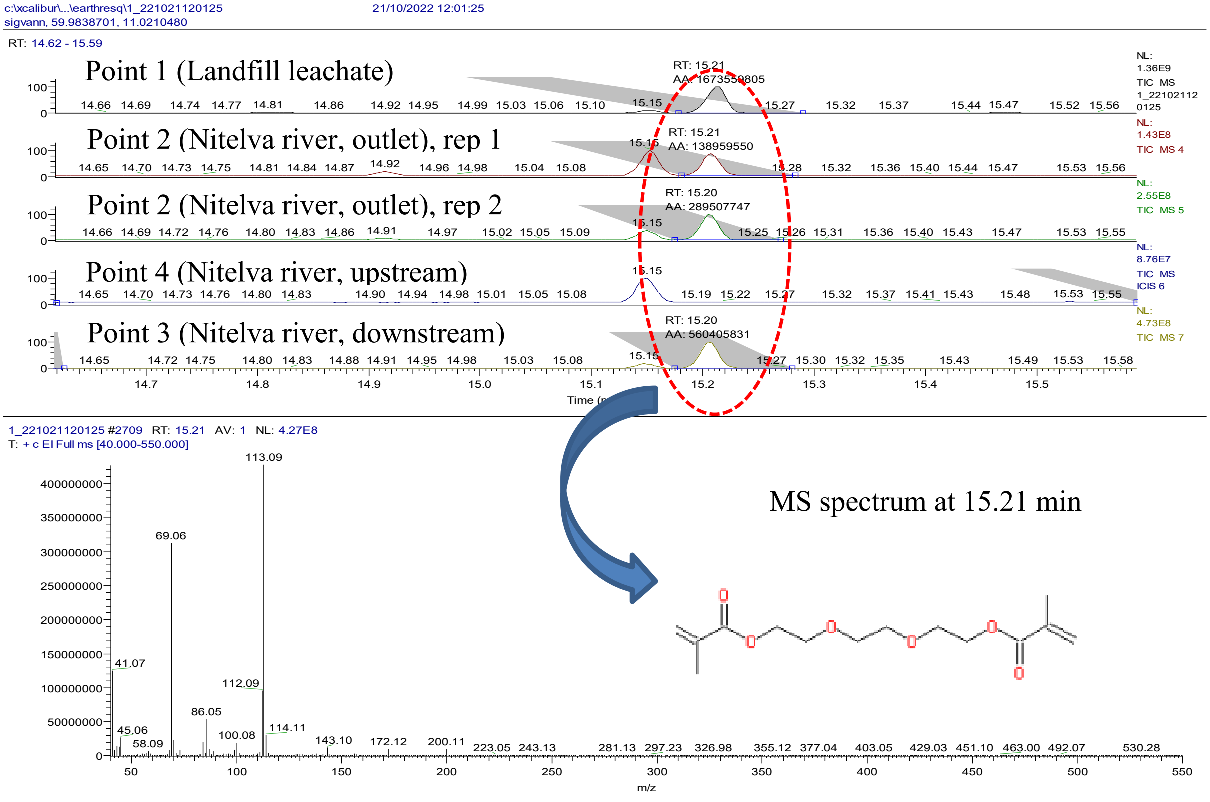


Figure 8. Tentative identification of Diethylenglycol dimethacrylate at point 1, 2, and 3: Peak at 15.21 min with MS spectrum at 15.21 min.

Name: 1_221021120125#2709 RT: 15.21 AV: 1
MW: N/A ID#: 5 DB: Text File
Comment: T: + c EI Full ms [40.000-550.000]
10 largest peaks:
113 999 | 69 729 | 41 290 | 112 223 | 86 125 |
114 70 | 45 60 | 70 54 | 84 46 | 100 43 |
Synonyms:
no synonyms.

#	Lib.	Match	R.Match	Prob. (%)	Name
⊞1	R	943	945	96.6	2-Propenoic acid, 2-methyl-, 1,2-ethanediylbis(oxy-2,1-ethanediyl) est
2	M	787	809	2.49	Diethyleneglycol dimethacrylate
3	M	753	754	0.63	2-Propenoic acid, 2-methyl-, oxybis(2,1-ethanediyloxy-2,1-ethanediyl)
4	M	663	687	0.05	Butanoic acid, 3-oxo-, 2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl ester
5	M	648	683	0.03	N,N'-Methylenebismethacrylamide
⊞6	M	647	682	0.03	2-Propenoic acid, 2-methyl-, 1,2-ethanediyl ester
⊞7	R	642	701	0.02	2-Propenoic acid, 2-methyl-, 2-chloroethyl ester
⊞8	M	629	658	0.01	4-Pyrimidinecarboxylic acid, hexahydro-2,6-dioxo-, methyl ester
⊞9	R	614	634	0.01	Creatine
10	M	613	634	0.00	Diethylene glycol monomethyl ether methacrylate
11	M	602	722	0.00	1,3-Dimethylbutyl ethylphosphonofluoridoate
12	M	599	631	0.00	2-Propenamide, N,N,2-trimethyl-
⊞13	M	596	609	0.00	L-2-Aminobutyric acid, N-dimethylaminomethylene-, methyl ester
14	M	591	681	0.00	3-Methylpentyl ethylphosphonofluoridate
15	M	591	646	0.00	Spiro[bicyclo[2.2.1]heptane-2,2'-[1,3]dioxolane]-3-one, 1,7,7-trimethyl
16	M	587	630	0.00	2H-Pyrrol-2-one, 1,5-dihydro-4-methoxy-
17	M	586	652	0.00	4-Methylpentyl ethylphosphonofluoridate
⊞18	M	586	608	0.00	1,3,2-Dioxaborolane, 2-ethyl-4,5-dimethyl-
19	M	580	613	0.00	β-Guanidinopropionic acid
⊞20	M	580	609	0.00	α-Methyl-α-propylsuccinimide
⊞21	M	579	646	0.00	Heptanoic acid, anhydride
22	M	579	607	0.00	Imidazolidin-4-one, 2-t-butyl-3,5-dimethyl-
⊞23	M	579	592	0.00	4-Ethyl hydrogen itaconate
24	M	578	644	0.00	2-(tert-Butylamino)ethyl methacrylate
25	M	578	637	0.00	3,5,5-Trimethylhexyl ethylphosphonofluoridate
⊞26	M	578	626	0.00	3,4-Methylpropylsuccinimide
27	M	577	607	0.00	Cyclopropanecarboxamide, N-(2-octyl)
28	M	577	592	0.00	Heptanoic acid, 4-octyl ester
⊞29	M	576	599	0.00	Ribitol, 1,3:4,5-di-O-(ethylboranediyl)-2-deoxy-
30	M	573	621	0.00	2-Furancarboxylic acid, decyl ester
⊞31	R	572	635	0.00	2-Furancarboxylic acid, octyl ester
32	M	571	689	0.00	1H-Azepin-1-amine, hexahydro-N-(1-methyl-2-propenyl)-
⊞33	M	569	609	0.00	Creatinine

InLib = 497, Hit List

Difference MF=943 RMF=945
2-Propenoic acid, 2-methyl-, 1,2-ethanediylbis(oxy-2,1-ethanediyl) ester
943 945R 96.6P

Name: 2-Propenoic acid, 2-methyl-, 1,2-ethanediylbis(oxy-2,1-ethanediyl) ester
Formula: $C_{14}H_{22}O_6$
MW: 286 Exact Mass: 286.141638 CAS#: 109-16-0 NIST#: 71271 ID#: 16520 DB: replib
Other DBs: Fine, TSCA, RTECS, HODOC, NIH, EINECS
Contributor: RADIAN CORP
Related CAS#: 72145-92-7; 664995-57-7; 64641-52-7; 77302-65-9; 107869-00-1; 113723-03-8; 116117-65-8; 120415-48-7; 121150-61
10 largest peaks:
113 999 | 69 929 | 41 417 | 112 176 | 39 124 |
86 111 | 45 76 | 114 73 | 70 63 | 43 47 |
Synonyms:
1. Methacrylic acid, diester with triethylene glycol
2. Ethylenebis(oxyethylene) methacrylate
3. NK Ester 3G
4. Polyester TGM-3
5. Triethylene dimethacrylate
6. Triethylene glycol dimethacrylate
7. TGM 3
8. TGM 3PC
9. TGM 35
10. 1,2-Bis[2-(Methacryloyloxy)ethoxy]ethane
11. TEDMA
12. TGM 3S
13. 2-{2-[2-(Methacryloyloxy)ethoxy]ethoxy}ethyl 2-methylacrylate #
14. 2-Propenoic acid, 2-methyl-, 1,1'-[1,2-ethanediylbis(oxy-2,1-ethanediyl)] ester
15. NSC 84260
16. Bisomer TEGDMA
Estimated non-polar retention index (n-alkane scale):

[Text File] 1_221021120125#2709 RT: 15.21 AV: 1
(replib) 2-Propenoic acid, 2-methyl-, 1,2-ethanediylbis(oxy-2,1-ethanediyl) ester

Figure 9. Identification of component COMP286 via NIST MS library.

Triethylene glycol dimethacrylate also called Polyester resin,black or TGM 3 is an unsaturated polyester resin (UPR) and one of the three most widely used matrix resin materials in resin matrix composites. It is widely used in epoxy/polyester mixed coatings, including dental applications. To the date, insufficient data are available to determine the rate or importance of biodegradation of triethylene glycol methacrylate in soil or water. If released to water, triethylene glycol dimethacrylate may adsorb to suspended solids and sediment based on an estimated K_{oc} value of 250. Triethylene glycol dimethacrylate will be non-volatile from water surfaces based on an estimated Henry's Law constant of 1.7×10^{-12} atm-cu m/mol. An estimated BCF value of 16 suggests that bioconcentration in aquatic organisms is low (public data from publichem.com). A third component was tentatively identified (COMP286a) at 16.97 min with similar chemical structure that COMP286 (Figures 10 and 11). This component is very likely a positional isomer of COMP286. Two more positional isomers, COMP286b and COMP286c were identified at 18.54 and 19.96 min (Figures 12 to 15).

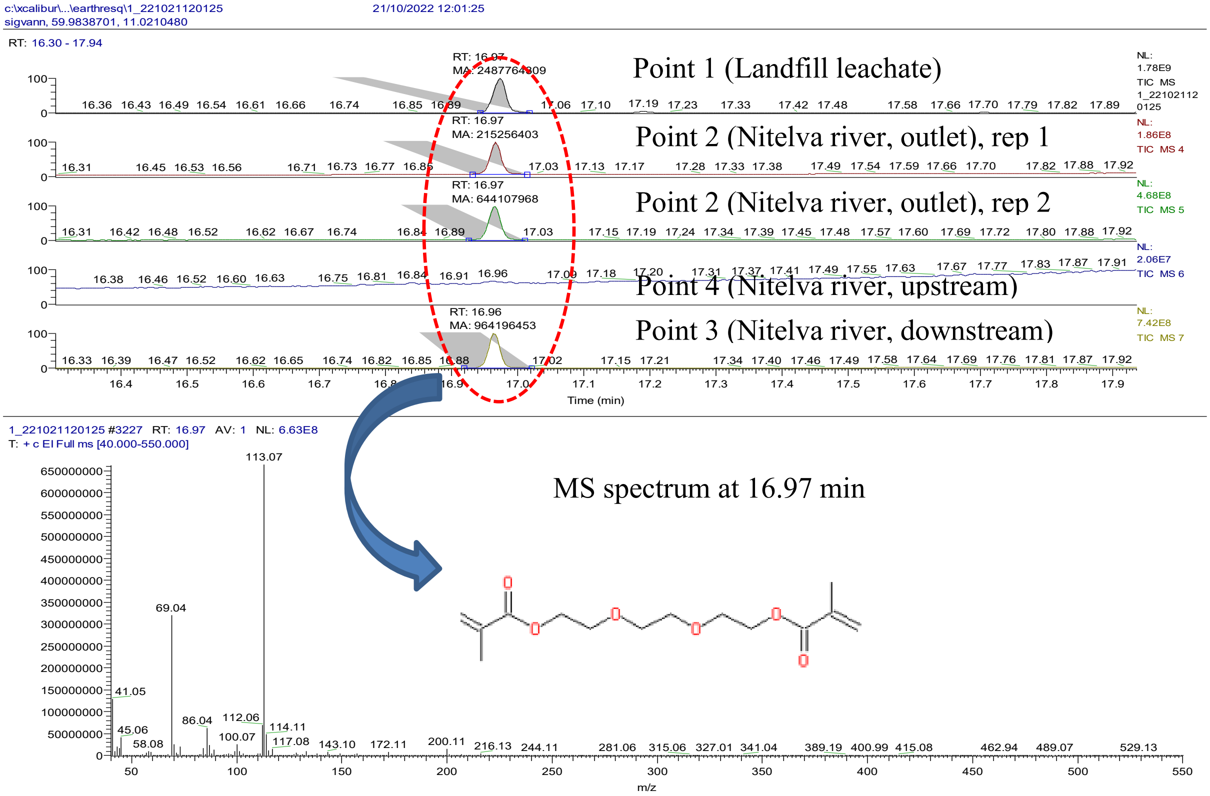


Figure 10. Tentative identification of the isomer of Diethylenglycol dimethacrylate at point 1, 2, and 3: Peak at 16.97 min with MS spectrum at 16.97 min.

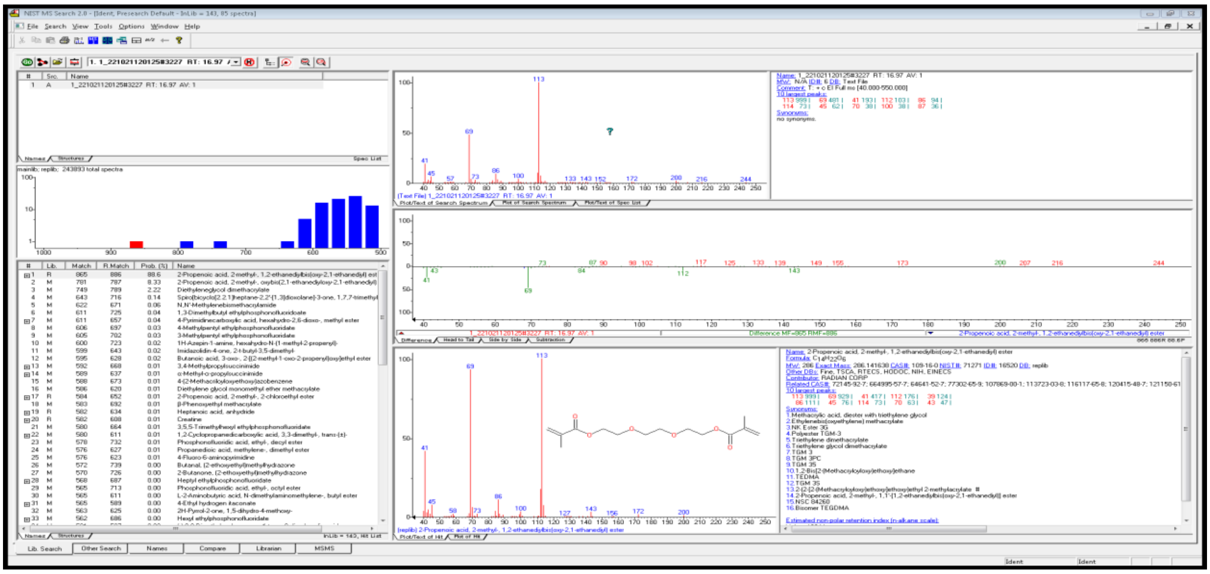


Figure 11. Identification of component COMP286a via NIST MS library.

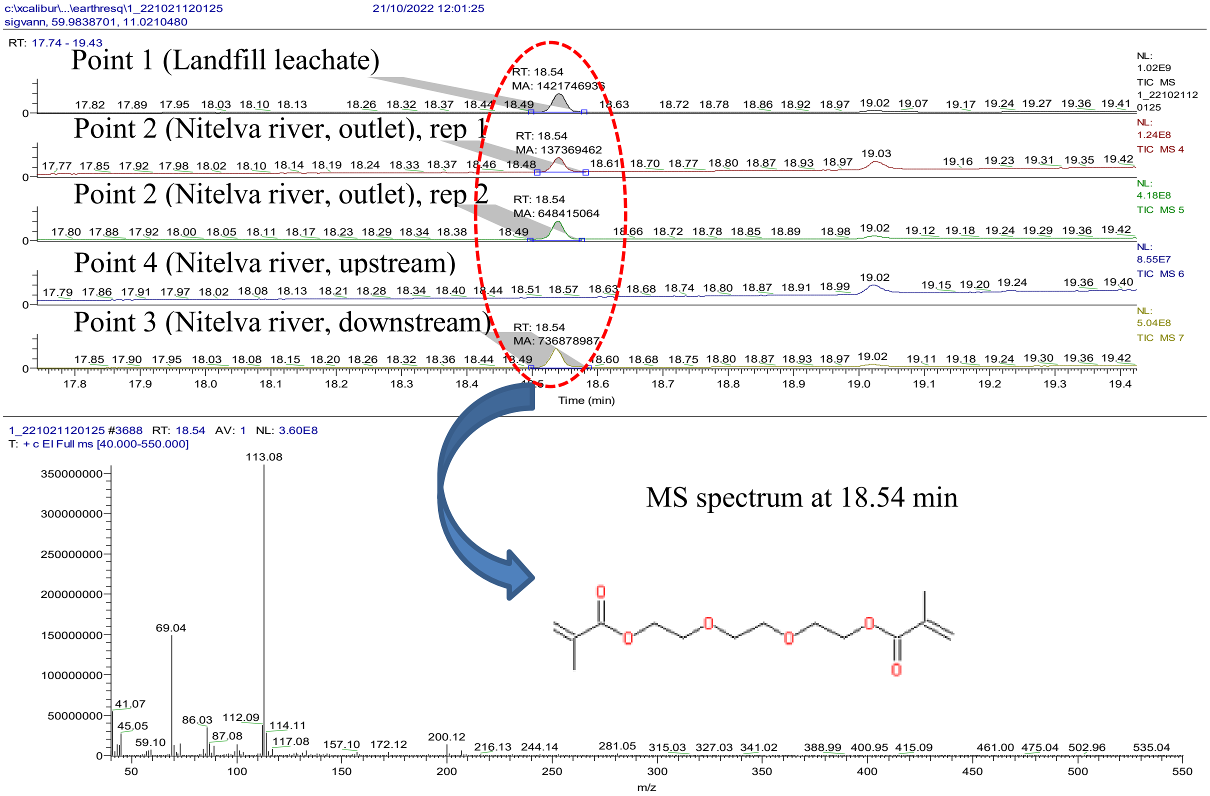


Figure 12. Tentative identification of the isomer of Diethylenglycol dimethacrylate at point 1, 2, and 3: Peak at 18.54 min with MS spectrum at 18.54 min.

Figure 13. Identification of component COMP286b via NIST MS library.

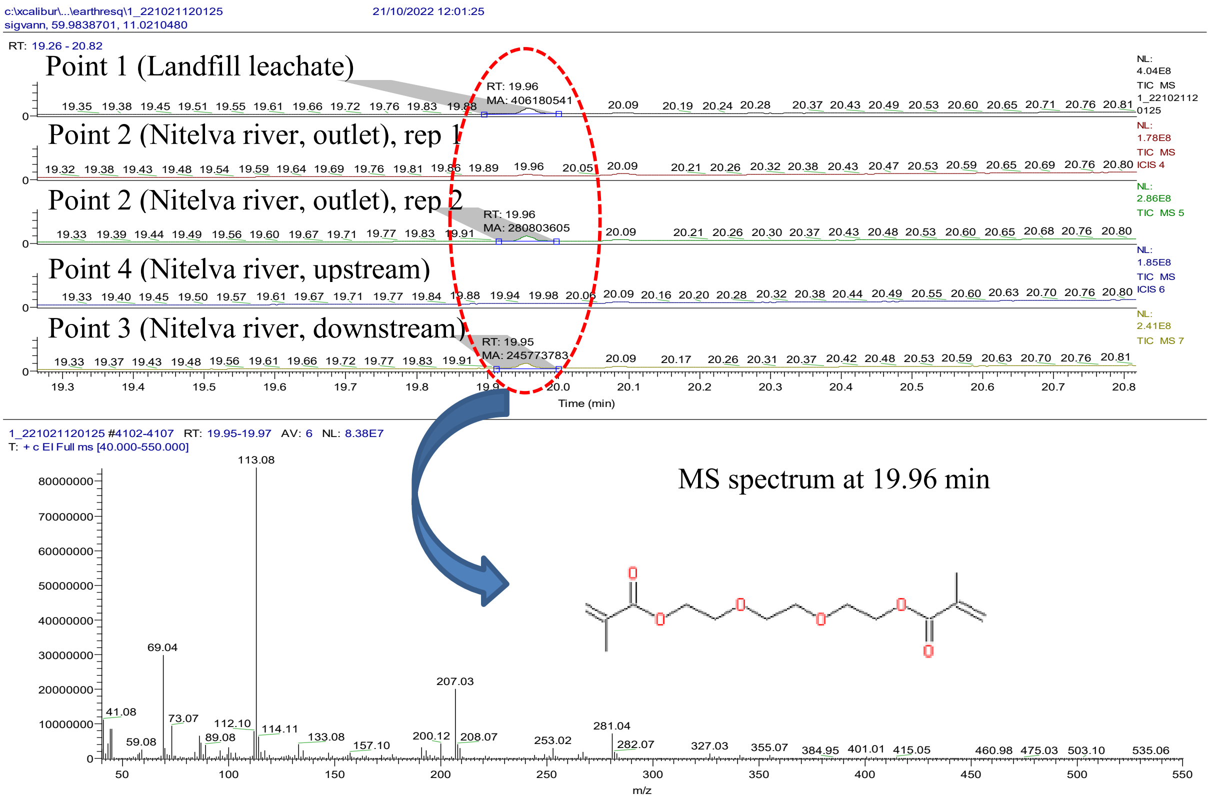


Figure 14. Tentative identification of the isomer of Diethylenglycol dimethacrylate at point 1, 2, and 3: Peak at 19.96 min with MS spectrum at 19.96 min.

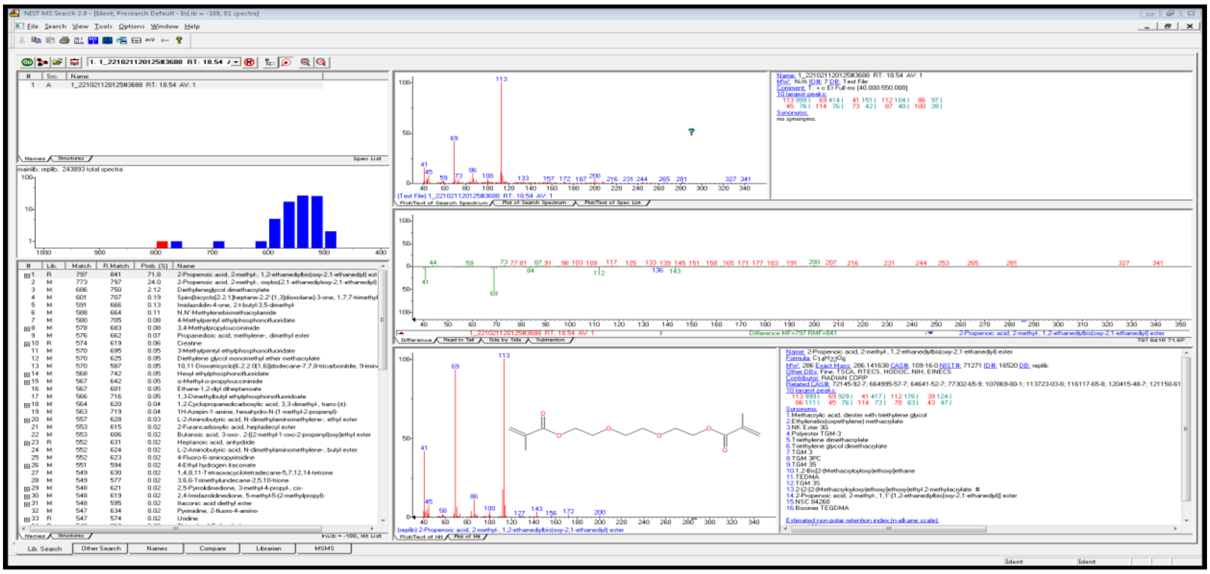


Figure 15. Identification of component COMP286c via NIST MS library.

Results from GC-Pyr-MS/MS analysis

All the sample filters were subjected to three analysis (three regions of a single filter) and the results are presented in Table1. High deviation was found in the triplicates of the filters.

Table 1. Results from GC-Pyr-MS/MS analysis.

Sample	PE	PP	PET	PS	PU	N6	N66
Landfill leachate	<LOD	**45 µg/L**	<LOD	<LOD	<LOD	<LOD	<LOD
Nitelva Outlet	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Nitelva Outlet 20m	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Nitelva river upstream	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Nitelva river downstream	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Tap water	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
LOD (µg/L)	*10.0*	*7.1*	*1.2*	*1.1*	*2.1*	*1.0*	*2.0*

6. Conclusion

The results derived from UPLC-HRMS will help to understand the degradation of such family of components that were present after landfill premises. Though, the suspect screening has pointed out that there is potentially a source of methacrylates components that are not present up in the Nitelva river and they were found at landfill leachate and later at two distances from the urban water discharge down in the Nitelva river. In view of these results, it is recommended to a further study that can help to clarify the concentration of such substances, the potential environmental risk and discard other sources for such type of components (apart of the landfill leachate).

Take aways:

- Several acrylate-type components and PP were found in the landfill leachate and the surface water recipient of Brånåsen case. However, MPs found in surface waters analyzed were below LOD or not detected.
- The results corroborate what other authors have found that the most common MPs found in environment are PS, PE and PP (*Lúcia H.M.L.M. Santos et. al 2023)*
- Landfills might be a source of MPs and other associated components
- The collection of the water samples represents a challenge to understand the occurrence of MPs since some MPs sink and others float. Larger water volumes are recommended.
- The MPs analysis might vary depending on the filter area (surface) launched for the analysis in the GC-Pyr-MS/MS. So, several analyses are required for a single same sample.
- This work has only focused on MP composition, but more efforts are required to assess the occurrence of MPs sizes.
- A more extensive monitoring has been planned in the area to quantify the acrylamides-like components.

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