

Greenpeace Research Laboratories Analytical Results 2018-05

Organic contaminants and metals in water, sediment and sludge samples from two hydraulic fracturing sites in Argentina

September 2018

Introduction

10 samples (4 water samples and 6 sediment and/or sludge samples) were received from Greenpeace Argentina for analysis at the Greenpeace Research Laboratories on 25 May 2018. According to documentation supplied, all samples were collected between 17th and 20th of May, 2018, from locations in the vicinity of hydraulic fracturing sites in the regions of Neuquen (six samples) and Rio Negro (4 samples), Argentina.

Details of the samples received are provided in Table 1a, together with GPS coordinates for the sample collection location in Table 1b.

Materials and methods

Concentrations of metals and metalloids were determined for all samples by ICP mass spectrometry (MS) following acid digestion and using appropriate certified reference samples and laboratory reference samples. For water samples, concentrations of dissolved metals and metalloids were determined in filtered samples.

Semi volatile organic chemicals (sVOCs) were isolated from samples using solid phase extraction (SPE) with ethyl acetate, followed by a mixture of pentane and toluene (for water samples) or Accelerated Solvent Extraction (ASE) with a mixture of pentane and acetone (for sediment and sludge samples). Extracted compounds were subsequently identified as far as possible using gas chromatography/mass spectrometry (GC/MS) operated in SCAN and SIM modes.

Volatile organic chemicals (VOCs) were identified in subsamples of all samples as received (with no pre-treatment) using GC/MS with Headspace sample introduction technique.

More detailed descriptions of the sample preparation and analytical procedures are presented in Appendix 1.

**Greenpeace Research Laboratories
School of Biosciences
Innovation Centre Phase 2
Rennes Drive
University of Exeter
Exeter EX4 4RN, UK**

Sample code	Sample type	Date & time	Location	Analyses conducted
VM18001	Fresh water (pumped from Well)	14:00, 17.05.2018	Tratayen, Neuquen, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)
VM18002	Sludge (from an abandoned sludge repository)	18:12, 17.05.2018	Calera, Neuquen, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)
VM18003	Sediment (Dirt from a water/chem spill site)	13:30, 18.05.2018	South Allen, Rio Negro, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative) Extractable Petroleum Hydrocarbons /EPH (quantitative)
VM18004	Sediment (Dirt from a water/chem spill site)	13:35, 18.05.2018	South Allen, Rio Negro, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative) EPH (quantitative)
VM18005	Water (from a channel next to a School)	15:00, 18.05.2018	South Allen, Rio Negro, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)
VM18006	Fresh water (Community's drinkable water)	15:50, 18.05.2018	Costa Blanco, Rio Negro, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)
VM18007	Sediment (from an abandoned cutting repository)	17:48, 19.05.2018	Loma de la Lata, Neuquen, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative) EPH (quantitative)
VM18008	Sediment (from an abandoned cutting repository)	17:55, 19.05.2018	Loma de la Lata, Neuquen, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative) EPH (quantitative)
VM18009	Sediment (from an active cutting repository)	19:40, 19.05.2018	Loma Campana, Neuquen, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative) EPH (quantitative)
VM18010	Fresh water (Community's drinkable water)	unknown, 20.05.2018	Campo Maripe, Neuquen, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)

Table 1a: details of samples received and analysed at the Greenpeace Research Laboratories

Sample code	S			W		
	degree (°)	minutes (')	seconds (")	degree (°)	minutes (')	seconds (")
VM18001	38	27	08,2	68	36	23,5'
VM18002	38	21	21.69	68	58	25.05'
VM18003	39	0	24.75	67	48	53.72
VM18004	39	0	24.00	67	48	56.17
VM18005	39	1	31.18	67	47	45.70
VM18006	39	2	5.90	67	47	36.84
VM18007	38	24	55.25	68	50	46.98
VM18008	38	24	55.25	68	50	46.98
VM18009	38	20	27.40	68	43	7.82
VM18010	38	23	35.37	68	53	59.98

Table 1b: GPS coordinates of sample collection location

Results and Discussion

The results for the samples are outlined in the following sections. The concentrations of metals and metalloids in solid samples as well as filtered water samples are reported in Table 2a and 2b respectively. In addition, the organic chemicals identified in individual samples are summarised in Tables 3 (for VOCs and Extractable Petroleum Hydrocarbons (EPHs) results). Chromatograms and detailed lists of organic chemicals that could be identified in each sample using GC-MS are provided in Appendix 2.

3.1 Metals

Though not directly comparable, reported average concentrations of metals and metalloids in continental crust and in shale are included for comparison (Krauskopf & Bird 1994). In most cases, concentrations of metals and metalloids in the samples were not notably higher than average continental crust and/or shale concentrations. There were, however, notable exceptions; concentrations of barium and strontium in three samples of sediment from either an abandoned cutting repository (VM18007 and VM18008) or an active cutting repository (VM18009) were considerably higher than average continental crust and/or shale concentrations. In addition, concentrations of cadmium and lead in the sample from the active cutting repository (VM18009) were higher than the other solid samples, and somewhat higher than average continental crust or shale concentrations.

For the water samples, the concentrations of the metals and metalloids showed little sign of elevation in concentrations above typical background concentrations for uncontaminated surface freshwaters (ATSDR 2005a/b, ATSDR 2007, ATSDR 2008, Comber *et al.* 2008, Salomons & Forstner 1984).

Sample code	VM18002	VM18003	VM18004	VM18007	VM18008	VM18009	Average abundance in continental crust ^(a)	Average abundance in shale ^(a)
Aluminium	6300	40400	38000	18100	20100	23900	81300	80000
Arsenic	1.07	14.0	10.7	4.5	3.50	11.5	1.8	13
Beryllium	0.10	1.14	1.09	0.76	0.82	0.88	2.8	3
Barium	272	764	372	7600	9430	7360	425	580
Cadmium	0.04	0.16	0.26	0.17	0.13	0.62	0.2	0.3
Chromium	3.42	16.1	16.4	20.5	23.6	19.8	100	90
Cobalt	1.38	7.85	8.77	4.21	3.24	5.97	25	19
Copper	2.5	19.3	23.2	10.4	9.0	39.5	55	45
Gallium	1.63	10.5	10.1	5.71	5.95	7.30	15	19
Iron	5030	33100	33800	15950	13200	28900	50000	47200
Lead	3.64	20.1	14.3	29.5	23.9	70.8	13	20
Manganese	63.0	452	509	276	266	480	950	850
Mercury	<0.08	<0.08	<0.08	<0.08	0.08	<0.08	0.08	0.4
Nickel	0.4	8.2	9.2	7.7	10.1	14.8	75	68
Selenium	0.3	1.9	2.0	1.0	1.0	1.4	0.05	0.6
Strontium	200	213	212	10950	13800	1460	375	300
Vanadium	17.6	67.9	76.2	51.5	43.5	91.6	135	130
Zinc	11.7	49.0	49.8	46.2	36.8	73.9	70	95

Table 2a: Concentrations of metals and metalloids (mg/kg DW) in sediment and sludge samples, together with the average abundances in continental crust and in shale (Krauskopf & Bird 1994)

Sample code	VM18001	VM18005	VM18006	VM180010
Aluminium	2	1	12	11
Arsenic	2.6	4.8	1.5	3.6
Beryllium	<0.05	<0.05	<0.05	<0.05
Barium	94.9	44.7	18.0	94.4
Cadmium	<0.05	<0.05	<0.05	0.07
Chromium	<0.2	<0.2	<0.2	<0.2
Cobalt	0.16	0.18	<0.05	0.15
Copper	<0.4	<0.4	3.2	<0.4
Gallium	<0.2	<0.2	<0.2	<0.2
Iron	17	38	10	2
Lead	<0.2	<0.2	<0.2	<0.2
Manganese	<0.2	6.1	1.0	0.4
Mercury	<0.2	<0.2	<0.2	<0.2
Nickel	<0.2	0.4	0.4	0.4
Selenium	<0.5	<0.5	<0.5	<0.5
Strontium	831	529	107	760
Vanadium	2.8	17.1	3.6	7.5
Zinc	<1	7	9	4

Table 2b: Concentrations of metals and metalloids ($\mu\text{g/l}$) in filtered water samples

3.2 Organic contaminants

3.2.1 Semi-volatile organic compounds (sVOCs, determined by GC-MS)

Solid samples: compared to the corresponding method blanks, which are included for quality control purposes, (Appendix 2), the chromatograms of these samples are characterised either by substantial 'hills' of complex and only partially resolvable hydrocarbon mixtures throughout much of the analytical run (VM18002, VM18007, VM18008, and VM18009), or with a baseline of hydrocarbon contamination that rises prominently towards the middle and the end of their respective runs (VM18003 and VM18004). Such properties make it extremely difficult to identify individual compound in those areas of the chromatograms, but indicate nonetheless that the majority of these samples contain significant levels of hydrocarbon contaminants. This was investigated further through quantitative analysis for Extractable Petroleum Hydrocarbons (EPH) as described below.

Water samples (VM18001, VM18005, VM18006 & VM18010): In these cases, there were no significant differences between the chromatograms obtained from analysis of the samples and those from their corresponding method quality control blanks (see Appendix 2), even after concentrating up the extracts and those of the method blanks by a further factor of 10 in order to investigate the possible presence of trace contaminants. It was not possible in this case to analyse the same water samples for the presence of more water soluble, polar organic chemicals. Such analyses would necessitate the collection of additional samples in order to provide the volume required for separate sample preparation, as well as the preparation of a target list of possible polar organic contaminants, based on information regarding the chemical formulations used in industrial activities in the area.

3.2.2 Volatile organic compounds (VOCs)

No volatile organic compounds were identified in either of the two freshwater samples from Neuquen (VM18001 & VM18010). In the four samples collected from Rio Negro (the sediment/soil samples VM18003 and VM18004, and the water samples VM18005 & VM18006), only between 1 to 5 VOCs were isolated, many being at trace levels and therefore only identified via the more sensitive selective ion monitoring (SIM) mode of GC-MS analysis (Appendix 2). In the case of the water samples, it is important to note that the samples were collected and stored in containers in which there was a small headspace above the level of the liquid, which could have led to some loss of volatile compounds during transportation and storage and, therefore, possible underestimation of VOC contamination. To address the significance of this potential loss, it would be necessary to collect further samples from the same locations in specialised stoppered bottles that could be sealed without headspace.

The remaining four samples (VM18002, VM18007, VM18008 & VM18009), all of which were identified as sludges or sediments collected from waste repositories in Neuquen, each showed the presence of highly complex mixtures of volatile organic compounds (VOCs), consistent with the results described above for the semi-volatile (solvent-extractable) organic compounds.

For example, a total of 183 VOCs were isolated from sample VM18009 (sediment from an active cutting repository at Loma Campana), though only 35 of them (19%) could be reliably identified (i.e.

greater than 90% quality match following verification by expert interpretation). Another 84 compounds (46%) could only be tentatively identified (i.e. with a quality match between 50% and 90%). Taking these reliably and more tentatively identified compounds together (119 compounds in total), the majority were hydrocarbons, including linear hydrocarbons and their derivatives, cyclohexane derivatives, benzene derivatives and naphthalene derivatives. The patterns of contamination identified for these samples in the GC-MS analyses match those for petroleum hydrocarbon content (table 3).

3.2.3 Extractable Petroleum Hydrocarbons (EPH)

Of the six solid or semi-solid samples provided, five (VM18003 & 4, VM18007, 8 & 9) were subjected to analysis for Extractable Petroleum Hydrocarbons (EPH) by an accredited independent external laboratory, using GC-FID. This method measures total concentrations of hydrocarbon chemicals in the molecular size range C10-C40, and therefore includes both lighter and heavier oil fractions. The remaining sludge sample, VM18002, was rejected for analysis by this external laboratory as it was judged to be too heavily contaminated for the methods applied and could have contaminated other procedures in the laboratory.

Extractable petroleum hydrocarbons (EPH) were detected in all five samples analysed, though at much higher levels in the three solid waste materials collected from either the Loma de la Lata (VM18007 & 8) or Loma Campana (VM18009) sites than were found in the two samples of sediment/soil from the Rio Negro region (VM18003 & 4).

The EPH value in sample VM18004 (78.2 mg/kg) was less than the 100 mg/kg often considered to be a 'normal' or background reference value for uncontaminated soils (Potra et al. 2013), recognising that the EPH method responds to some naturally occurring hydrocarbon substances in soils and vegetation. The EPH concentration in sample VM18003, also at the Rio Negro site, was significantly higher, at 688 mg/kg, perhaps indicating some past contamination of the site with oil-related materials. This concentration is clearly above expected background levels for uncontaminated soils, but below thresholds for further screening that are, or have in the past been, applied in a number of countries around the world, for soils for residential, commercial or agricultural use. For example, a threshold value of 1000 mg/kg total petroleum hydrocarbons (TPH, which includes a wider range of compounds than those that are captured by EPH alone) has been applied to potentially contaminated sites (former vehicle fuel/gas stations) in New South Wales, Australia (NSW EPA 2003)¹. Nonetheless, given that this sample was collected from surface sediment/soil in an apple orchard, the presence of such elevated levels in itself justifies further investigation of possible sources and effects, as well as remedial action to reduce contaminant levels where possible.

Solid waste samples collected from storage ponds at Loma de la Lata (VM18007 & 8) and Loma Campana (VM18009) contained far higher levels of EPH (between 59 500 and 128 000 mg/kg, or between 5.95 and 12.8% of the total weight of the sample), indicative of very high levels of

¹ The same value was in the past used as a screening value for potential leaching of hydrocarbons from contaminated soil into groundwater under the ICRL initiative in the UK, though this has since been superseded by more complex risk-based approaches.

hydrocarbon contamination in these materials and strongly suggestive that these materials are wastes arising directly from industrial operations.

It is not clear whether there are regulations or other limit values applicable to the hydrocarbon content of such wastes in Argentina, or, therefore, specific conditions or management actions that would normally be required. Some guidance levels or limit values have been set for EPH in soils or wastes in certain other countries or regions and, while these are clearly not directly applicable to Argentina, they are nonetheless useful as reference points for comparative purposes

For example, levels of EPH in all three samples exceeded the widely recognised Dutch Intervention Level for hydrocarbons in soil (5000 mg/kg) (NSW EPA 2003) by more than 10 times, more than 20 times in the case of VM18008. Similar thresholds have been applied in certain US states to screen hydrocarbon pollution levels in soils for residential use (e.g. 5100 mg/kg in New Jersey) (NJAC 2012) and for surface layers of soils in agricultural areas (e.g. 4000 mg/kg in New Zealand) (NZ MftE 2011). Levels of EPH in all three samples also exceed the higher thresholds set by the New Zealand Ministry for the Environment for soils in residential or commercial areas (>20 000 mg/kg), as well as the still higher threshold applicable in New Jersey for sites that are to be used for non-residential developments (54 000 mg/kg). Although it must be recognised that samples VM18007, 8 & 9 were collected from waste repositories rather than from ambient soils, the storage of such wastes in relatively open and poorly controlled conditions clearly raises concerns regarding potential contamination of the surrounding environment, including air, soil, surface waters and groundwater. More detailed surveys to determine whether the handling and storage of these oily wastes is leading to contamination of the surrounding environment are clearly warranted.

The concentrations of hydrocarbons in these samples are so high that they should be handled through proper containment, treatment and disposal, rather than by simple evaporative storage in open ponds. According to UK technical guidance on classification of waste within the Europe (SEPA/NIEA/CNC/EA 2015), wastes containing petroleum hydrocarbons (TPH) at levels above 3% of the total mass would normally be required to be labelled as 'toxic to reproduction', while at greater than 10%, materials are identified as being even more acutely toxic, including through risks of inhalation/aspiration. Wastes generated through prospecting for mineral resources are addressed under a different Directive than wastes from many other industrial sources within the EU, but the level of hazard presented by a waste is categorised in similar ways.

Irrespective of the equivalent regulations that apply in Argentina, all three of these waste materials, collected from easily accessible open sites, are clearly highly contaminated with oily residues, with the potential to generate odour nuisance and possible health and fire risk for local communities and wildlife.

For more information please contact:

Kevin Brigden, Iryna Labunska, Melissa Wang, Jorge Casado, David Santillo or Paul Johnston

Sample Code	VM18001	VM18002	VM18003	VM18004	VM18005	VM18006	VM18007	VM18008	VM18009	VM18010
Location	Tratayen , Neuquen	Calera , Neuquen	South Allen , Rio Negro,	South Allen , Rio Negro,	South Allen , Rio Negro,	Costa Blanco , Rio Negro	Loma de la Lata , Neuquen	Loma de la Lata , Neuquen	Loma Campana, Neuquen	Campo Maripe , Neuquen
Sample type	Fresh water	Sludge	Sediment	Sediment	Water	Fresh water	Sediment	Sediment	Sediment	Fresh water
EPH (Range > C10 - C40, mg/kg)	N.Q.	N.Q.?	688	78.2	N.Q.	N.Q.	59600	128000	59500	N.Q.
Number of VOCs Isolated	0	N.I.	1	1	1	5	N.I.	N.I.	183	0
Number of VOCs identified to >90%	0	N.I.	0	1	1	5	N.I.	N.I.	35	0
Percentage of VOCs identified to > 90% (%)	N.A.	N.A.	0	100	100	100	N.A.	N.A.	19	N.A.

Table 3: Summary of organic contaminant results in samples: VOCs screening and Extractable Petroleum Hydrocarbons (EPH) quantification.

N.Q.: not quantified; N.A: not applicable; N.I.: not interpreted

References

- ATSDR (2005a) Toxicological profile for nickel. Agency for Toxic Substances and Disease Registry, US Public Health Service, August 2005, Available at: <https://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=44>
- ATSDR (2005b) Toxicological profile for zinc. Agency for Toxic Substances and Disease Registry, US Public Health Service, August 2005, Available at: <https://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=54>
- ATSDR (2007) Toxicological profile for barium. Agency for Toxic Substances and Disease Registry, US Public Health Service, Available at: <http://www.atsdr.cdc.gov/ToxProfiles/tp.asp?id=327&tid=57>
- ATSDR (2007) Toxicological profile for barium. Agency for Toxic Substances and Disease Registry, US Public Health Service, August 2007, Available at: <https://www.atsdr.cdc.gov/toxprofiles/TP.asp?id=327&tid=57>
- ATSDR (2008) Toxicological profile for aluminium. Agency for Toxic Substances and Disease Registry, US Public Health Service, September 2008, Available at: <https://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=191&tid=34>
- Comber, S.D.W., Merrington, G., Sturdy, L., Delbeke, K., van Assche, F. (2008) Copper and zinc water quality standards under the EU Water Framework Directive: The use of a tiered approach to estimate the levels of failure. *Science of the Total Environment* 403(1-3): 12-22
- Krauskopf, K.B. & Bird, D.K. (1994) *Introduction To Geochemistry*, 3rd Edition. ISBN 0-07-113929-X
- NJAC (2012) Technical requirements for site remediation, New Jersey Administrative Code 7:26E., publ. New Jersey Department of Environmental Protection: 96 pp.
- NSW EPA (2003) Guidelines for Assessing Service Station Sites. Contaminated Sites EPA 94/119, publ. New South Wales Environment Protection Agency, Australia: 38 pp.
- NZ MftE (2011) Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand, MODULE 4: Tier 1 soil acceptance criteria, publ. New Zealand Ministry for the Environment, 1999 (updated 2011): 76 pp.
- Potra, A.F., Micle, V. & Babut, C.S. (2013) Bioremediation of petroleum hydrocarbon-contaminated soil by composting technology. *ProEnvironment* 6: 411-415
- Salomons, W. & Forstner, U. (1984) *Metals in the hydrocycle*. Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, ISBN 3540127550
- SEPA/NIEA/CNC/EA (2015) *Waste Classification: Guidance on the classification and assessment of waste* (1st edition 2015), Technical Guidance WM3, publ. Scottish Environment Protection Agency / Northern Ireland Environment Agency / Cyfoeth Naturiol Cymru / Environment Agency: 185 pp.

Appendix 1: Details of methodologies

Analysis for Volatile Organic Compounds (VOCs)

Methods

VOCs were analysed using an Agilent 7890B gas chromatograph with an Restek Rxi-624Sil column (30m, 0.25mm ID, 1.4µm film thickness) connected to an Agilent 7697A Headspace Sampler and linked to an Agilent 5977A MSD operated in EI mode. The GC oven temperature program included an initial temperature of 43°C (held for 4min), rising to 55°C at 5°C/min, and then to 210°C at 15°C/min (held for 2.5min). The carrier gas was helium, supplied at 1.5ml/min.

A 10ml portion from each water sample, and a small portion from each sediment and/or sludge sample was sub-sampled into a 20ml headspace vial. They were analysed with the GC-MS in total ion monitoring (SCAN) mode to identify as many of the volatile organic compounds present as possible. Identification of compounds was carried out by matching spectra against the Wiley7N Library, employing expert judgment in order to avoid misidentifications. In addition, this sub-sample was also analysed at the same time with the GC-MS in selective ion monitoring (SIM) mode, in order to match the GC-MS spectra obtained against those of mixed standard preparations containing a range of volatile aromatic organic compounds and halogenated alkanes.

Quality control

A number of blanks of laboratory air capped at the time that sub-sampling had taken place were also analysed. Any background contaminants detected in blanks are subtracted from the chromatograms obtained for the samples before mass spectra are interpreted.

Analysis for extractable organic compounds

Preparation

20 µg of deuterated naphthalene was added as an Internal Standard (IS) to each portion of sample that was subject to extraction.

Water sample extraction: Water samples (500ml) were prepared using solid phase extraction technique with Dionex AutoTrace workstation, eluting with ethyl acetate followed by a mixture of pentane and toluene (95:5). Obtained extracts were concentrated to a volume of 3ml with a stream of clean nitrogen and cleaned up prior to analysis. 2.5 ml of the extracts and the blank were further concentrated for another 10 times.

Sediment and sludge sample extraction: approximately 10 g of each sample (wet weight) was extracted employing an Accelerated Solvent Extraction (ASE) technique, using a Dionex ASE-350, with a mixture of pentane and acetone in a ratio of 3:1, and at a temperature of 100°C. Obtained extracts were concentrated to a volume of 3ml with a stream of clean nitrogen and cleaned up prior to analysis.

For the clean-up stage, each extract was shaken with 3ml isopropyl alcohol and 3ml TBA-reagent (mixture of 3% tetrabutylammonium hydrogen sulphate and 20% sodium sulphite in deionised water) and left to stand until the aqueous and organic phases had separated. The pentane phase was collected and eluted through a Florisil column, using a 95:5 pentane:toluene mixed eluent, and the cleaned extract concentrated to a final volume of 1ml as before. 20 µg of bromonaphthalene was added to each extract as a second IS prior to GC-MS analysis.

Analysis

For the total organic compounds screening, samples were analysed using an Agilent 6890 Series II GC with Restek Rtx-17Sil column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5973 Inert MSD operated in EI mode and interfaced with an Agilent Enhanced Chem Station data system. The GC oven temperature program employed was as follows: an initial temperature of 40°C, raised to 260°C at 10°C/min, then to 295°C at 50°C/min (held for 5 min), then to 325°C at 50°C/min (held for 4 min), finally raised to 330°C at 50°C/min. The carrier gas was helium, supplied at 1ml/min. Identification of compounds was carried out by matching spectra against both the Wiley 7N and Pesticides Libraries, using expert judgment as necessary in order to avoid misidentifications.

Quality control

A number of extraction and solvent blanks were also analysed to ensure the detection of any possible contamination resulting from sample handling in the laboratory. Any background contaminants detected in blanks are subtracted from the chromatograms obtained for the samples before mass spectra are interpreted.

Quantification of Extractable Petroleum Hydrocarbons (EPH):

Subsamples of VM18003, VM18004, VM18007, VM18008, and VM18009 were analysed in an independent third party accredited analytical laboratory for the quantification of Extractable Petroleum Hydrocarbons (EPH Range >C10 - C40) by GC-FID, according to method TM061 of the

Massachusetts Department of Environmental protection (1998). Further details of methods and quality control could be provided upon request.

Analysis for metals

Preparation

For water samples, a portion of each sample was filtered through a 0.45 micron filter and then acidified by the addition of concentrated nitric acid to give a final concentration of 5% v/v, to enable determination of dissolved metal concentrations. 25 ml of each acidified sample was digested firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180°C over 15 minutes followed by holding at 180°C for a further 15 minutes. Cooled digests were filtered and made up to 25 ml with deionised water.

For solid (sediment and sludge) samples, a representative portion of each sample was air dried to constant weight, homogenised and then ground to a powder using a pestle and mortar. Approximately 0.25 g of the ground sample was accurately weighed and digested with 0.5 ml concentrated hydrochloric acid and 5.0 ml concentrated nitric acid, firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system with temperature ramping: heating to 110°C over 20 minutes, held at 110°C for 20 minutes, heating to 170°C over 20 minutes, held at 170°C for 20 minutes, heating to 220°C over 20 minutes, held at 220°C for 20 minutes. Following cooling, some samples remained notably coloured and therefore 2.5 ml hydrogen peroxide (30% v/v) was added dropwise to each sample resulting in decoloured solutions. The samples were subsequently treated to a second microwave-assisted digestion using the same temperature ramping as before. Following cooling, each digest solution was filtered and made up to 25 ml with deionised water. Prior to analysis, each digest solution was diluted 1:4 using deionised water.

Analysis

Prepared sample digests were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an Agilent 7900 Spectrometer utilizing a collision cell with helium as the collision gas to minimize polyatomic interferences. Multi-element standards, matrix matched to the samples, at concentrations of 1, 10, 100, 1000 and 5000 $\mu\text{g/l}$ respectively, other than for mercury (1, 2, 5, 20 $\mu\text{g/l}$ respectively) were used for instrument calibration. Analysis employed in-line addition of an internal standard mix at 1000 $\mu\text{g/l}$ (Scandium, Germanium, Yttrium, Indium and Terbium). Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Quality control

For water samples, one sample was prepared for ICP analysis in duplicate and analysed to verify method reproducibility, along with a blank sample. Two mixed metal quality control solution of 80 and 800 $\mu\text{g/l}$ for each metal, other than mercury at 4 and 16 $\mu\text{g/l}$, were digested and analysed. All control samples were prepared in an identical manor to the samples.

For solid samples, one sample was prepared for ICP analysis in duplicate and analysed to verify method reproducibility, along with a blank sample. To check the method efficiency, two certified reference material (CRM) samples were prepared in an identical manner; GBW07311 stream sediment and GBW07406 soil, certified by the China National Analysis Centre for Iron and Steel, Beijing, China.

Calibration of the ICP-MS was validated by the use of quality control standards at 80 $\mu\text{g/l}$ and 800 $\mu\text{g/l}$ (4 $\mu\text{g/l}$ and 16 $\mu\text{g/l}$ for mercury) prepared in an identical manner but from different reagent stocks to the instrument calibration standards.

Further details of the methods employed can be provided on request.

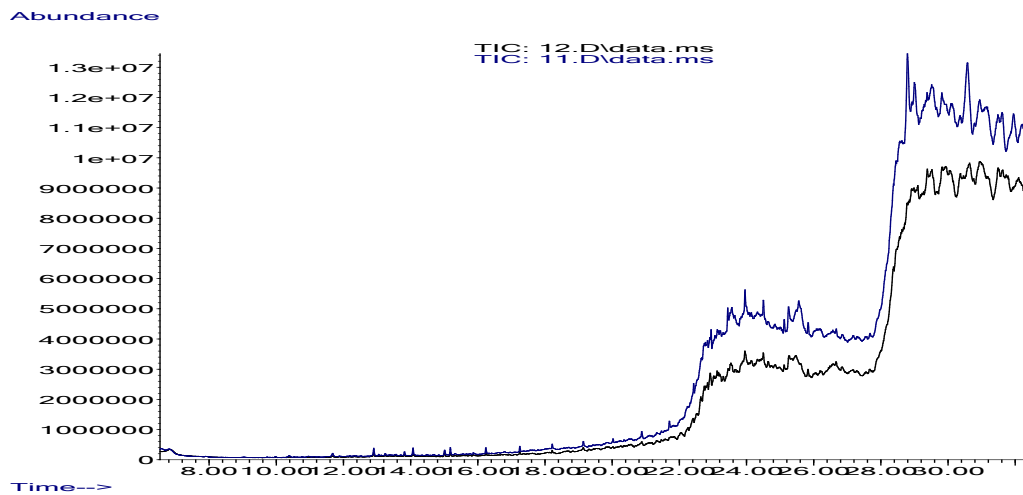
Appendix 2: Detailed semi-volatile organic (sVOCs) and volatile organic (VOCs) chromatograms and analytical screening data

Chromatograms and detailed screening data arising from GC-MS analysis of some samples are presented below. These data list separately semi-volatile organic compounds (sVOCs) identified following solvent extraction and volatile organic compounds (VOCs) identified through separate headspace GC-MS analysis.

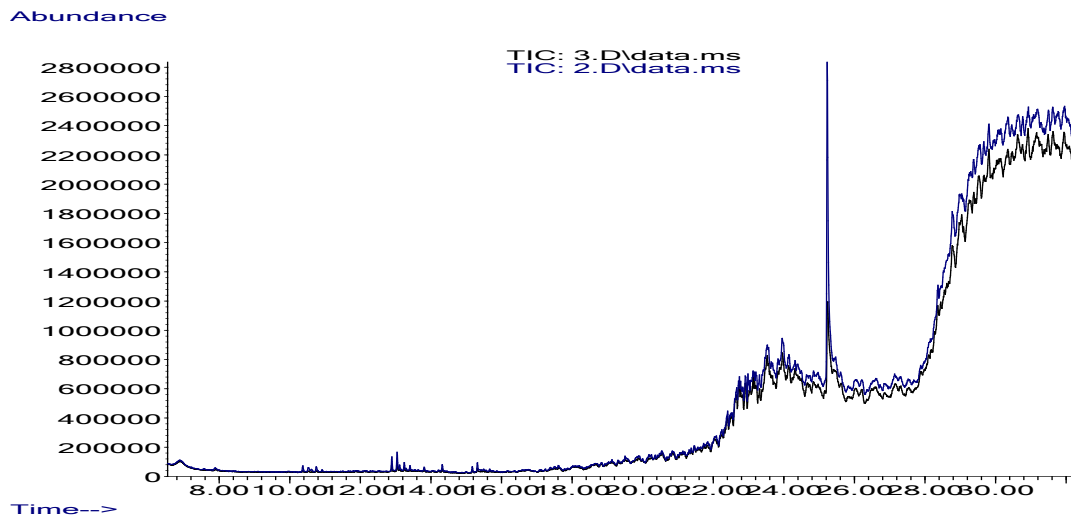
Semi-volatile organic analysis results (sVOCs)

Sample code	VM18001
Location	Tratayen, Neuquen, Argentina
Sample type	Fresh water
Date & time	14:00, 17.05.2018
Description	Fresh water pumped from well, no colour, no smell

VM18001 (Black) v.s. Extraction Blank (Blue)

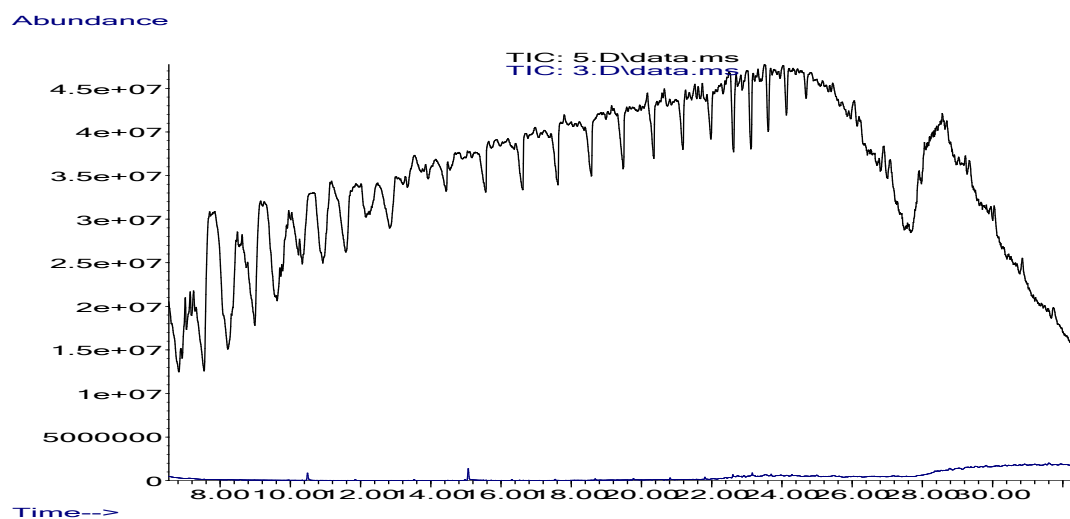


VM18001- 10x concentrated (Black) v.s. Extraction Blank – 10x concentrated (Blue)



Sample code	VM18002
Location	Calera, Neuquen, Argentina
Sample type	Sludge
Date & time	18:12, 17.05.2018
Description	Sludge from an abandoned sludge repository, yellow-brown, strong smell

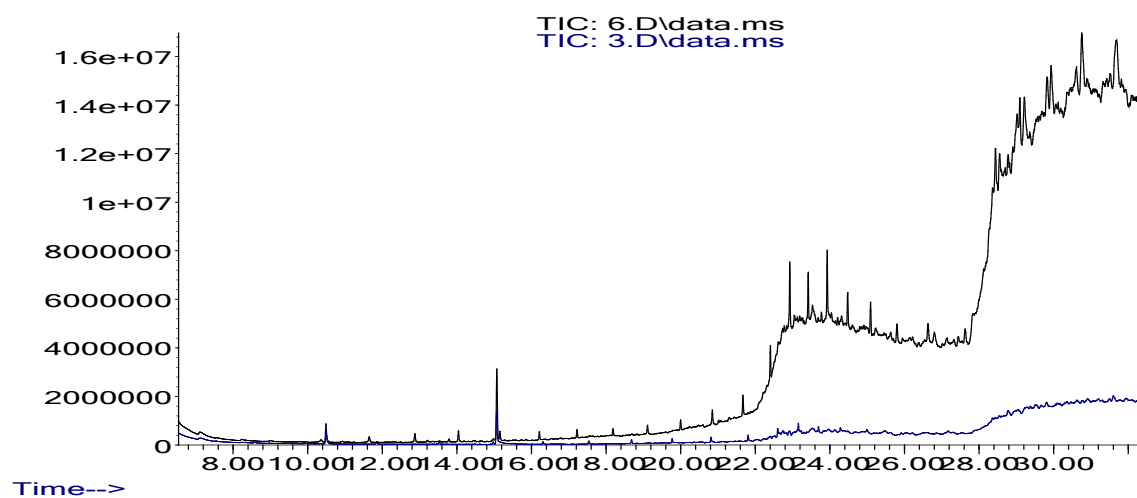
VM18002 (Black) v.s. Extraction Blank 1 (Blue)



Sample code	VM18003
Location	South Allen, Rio Negro, Argentina
Sample type	Sediment
Date & time	13:30, 18.05.2018
Description	Sediment/soil from a water/chemical spill site, brown, no smell

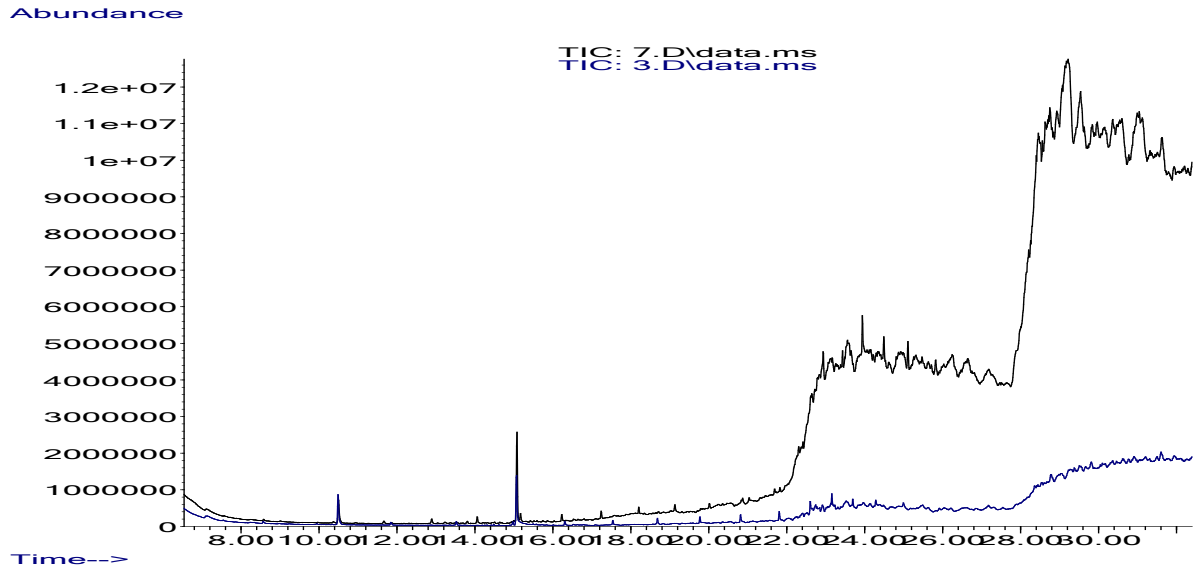
VM18003 (Black) v.s. Extraction Blank 1 (Blue)

Abundance



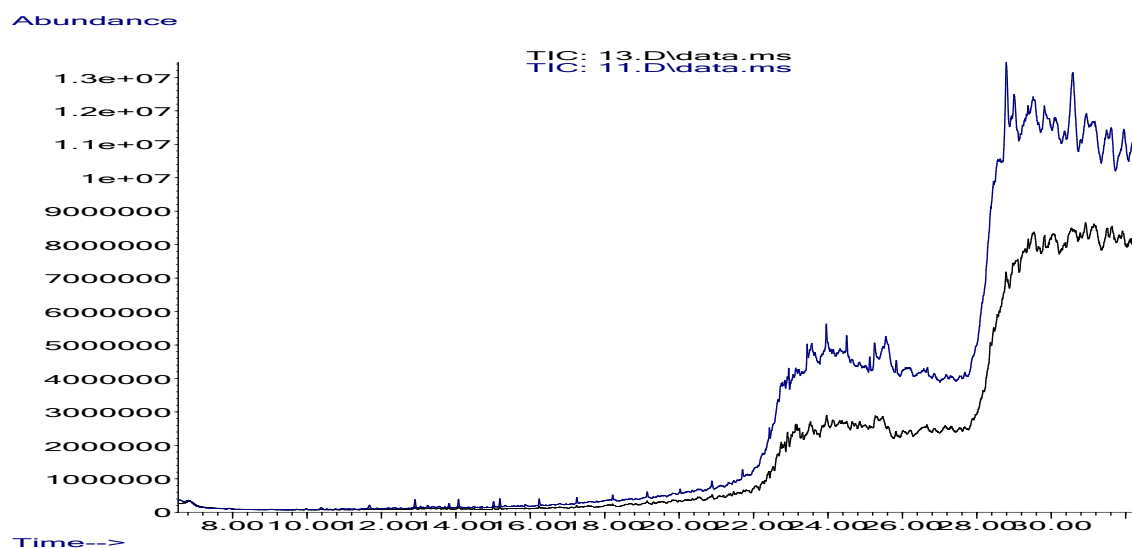
Sample code	VM18004
Location	South Allen, Rio Negro, Argentina
Sample type	Sediment
Date & time	13:35, 18.05.2018
Description	Sediment/soil from a water/chemical spill site, brown, no smell

VM18004 (Black) v.s. Extraction Blank 1 (Blue)

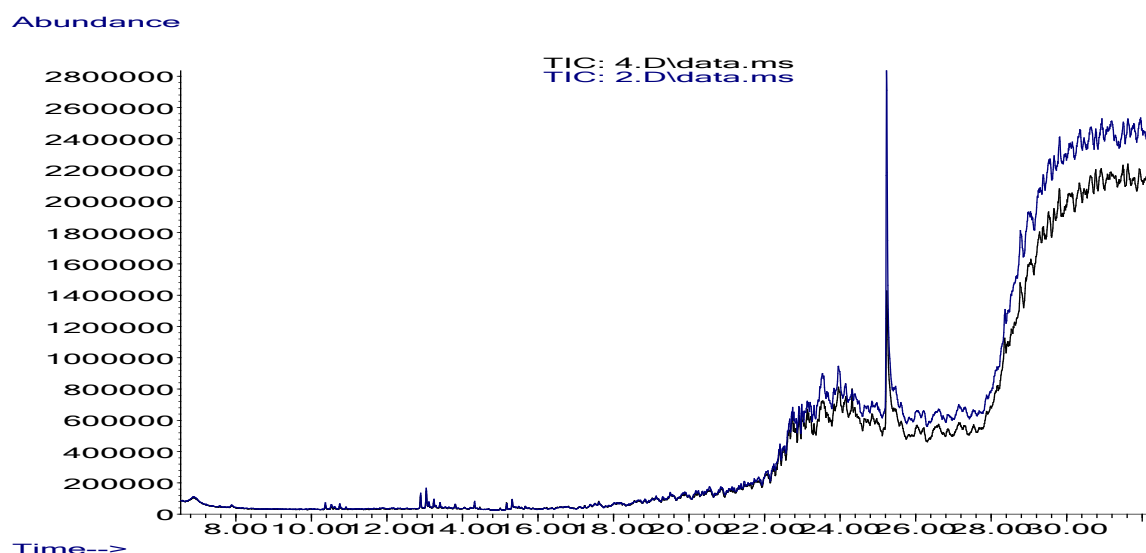


Sample code	VM18005
Location	South Allen, Rio Negro, Argentina
Sample type	Water
Date & time	15:00, 18.05.2018
Description	Water from a channel next to a School, milky, nauseating smell

VM18005 (Black) v.s. Extraction Blank (Blue)

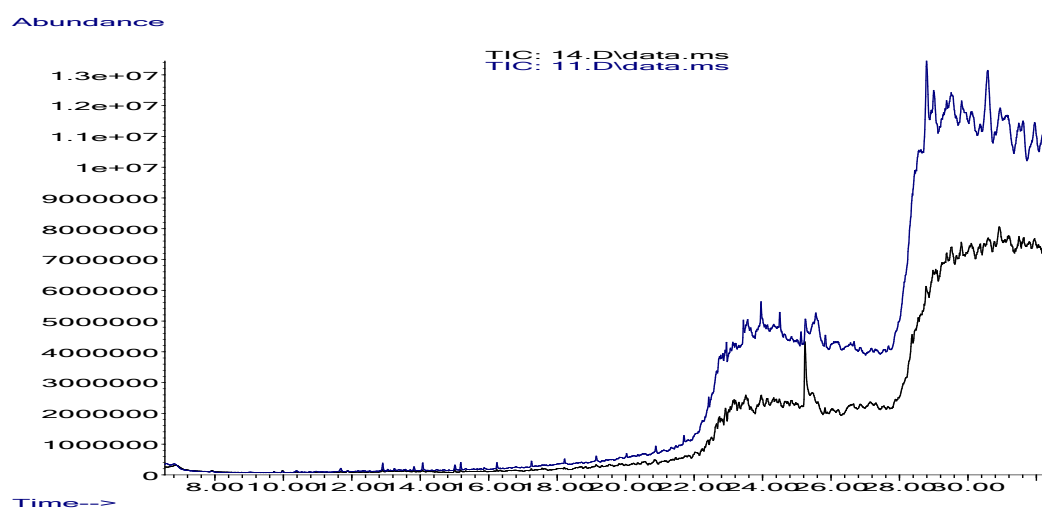


VM18005 – 10x concentrated (Black) v.s. Extraction Blank – 10x concentrated (Blue)

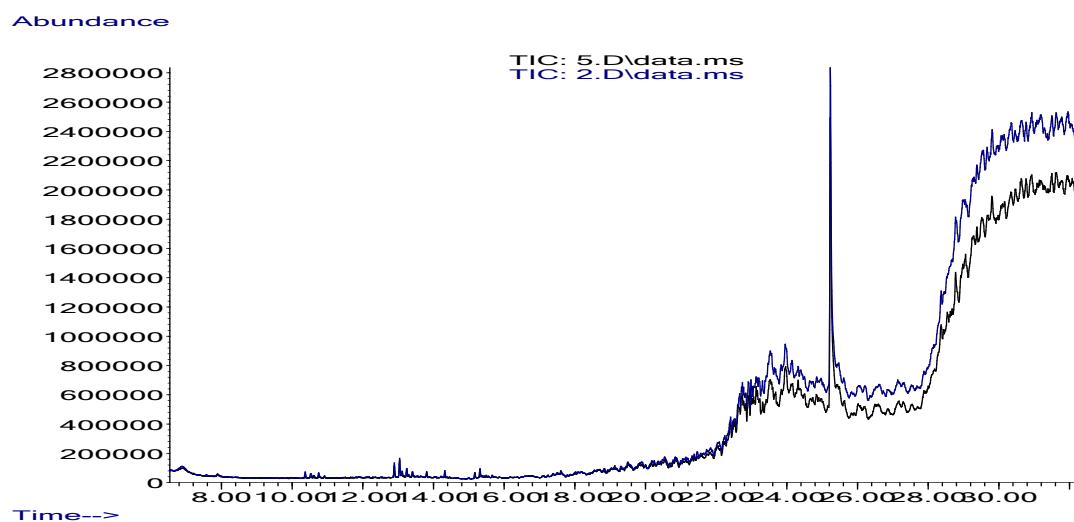


Sample code	VM18006
Location	Costa Blanco, Rio Negro, Argentina
Sample type	Fresh water
Date & time	15:50, 18.05.2018
Description	Community's drinkable water, no colour, no smell

VM18006 (Black) v.s. Extraction Blank (Blue)



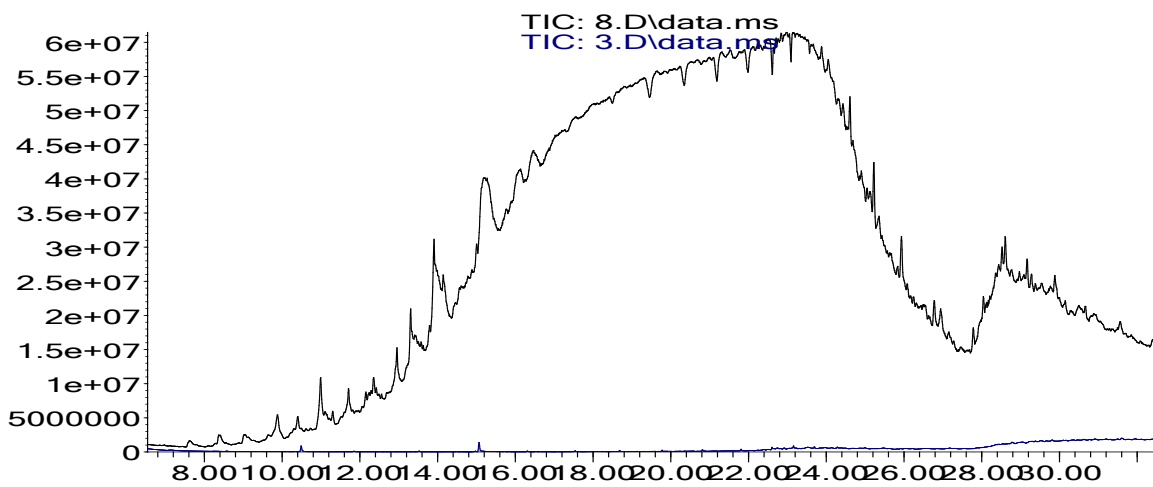
VM18006 – 10x concentrated (Black) v.s. Extraction Blank – 10x concentrated (Blue)



Sample code	VM18007
Location	Loma de la Lata, Neuquen, Argentina
Sample type	Sediment
Date & time	17:48, 19.05.2018
Description	Sediment from an abandoned cutting repository, black-brown colour, hydrocarbon smell

VM18007 (Black) v.s. Extraction Blank 1 (Blue)

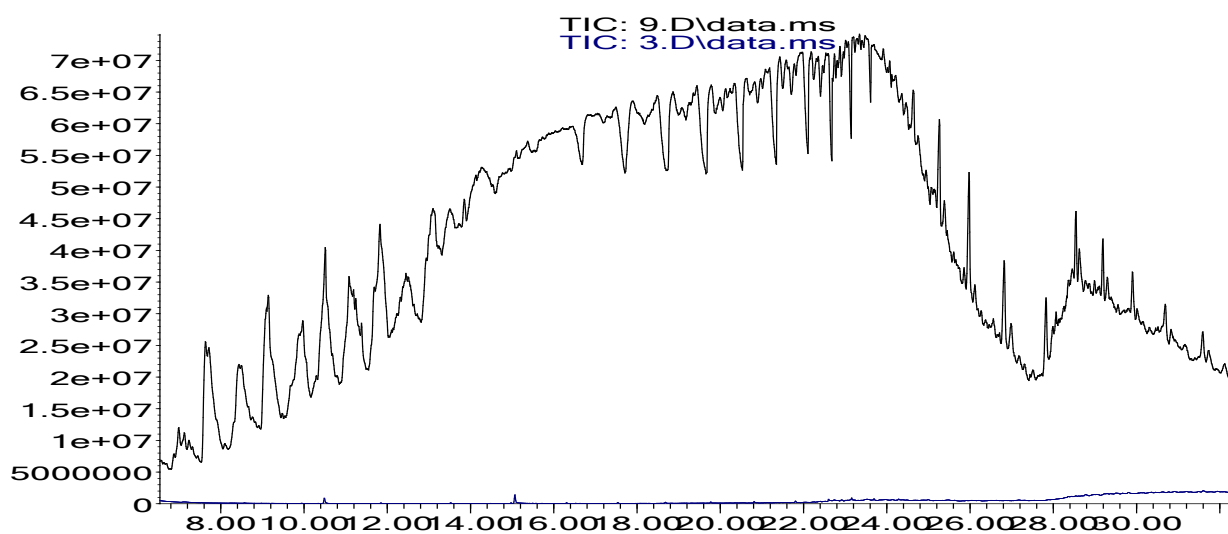
Abundance



Sample code	VM18008
Location	Loma de la Lata, Neuquen, Argentina
Sample type	Sediment
Date & time	17:55, 19.05.2018
Description	From an abandoned cutting repository, black-brown colour, hydrocarbon smell

VM18008 (Black) v.s. Extraction Blank 1 (Blue)

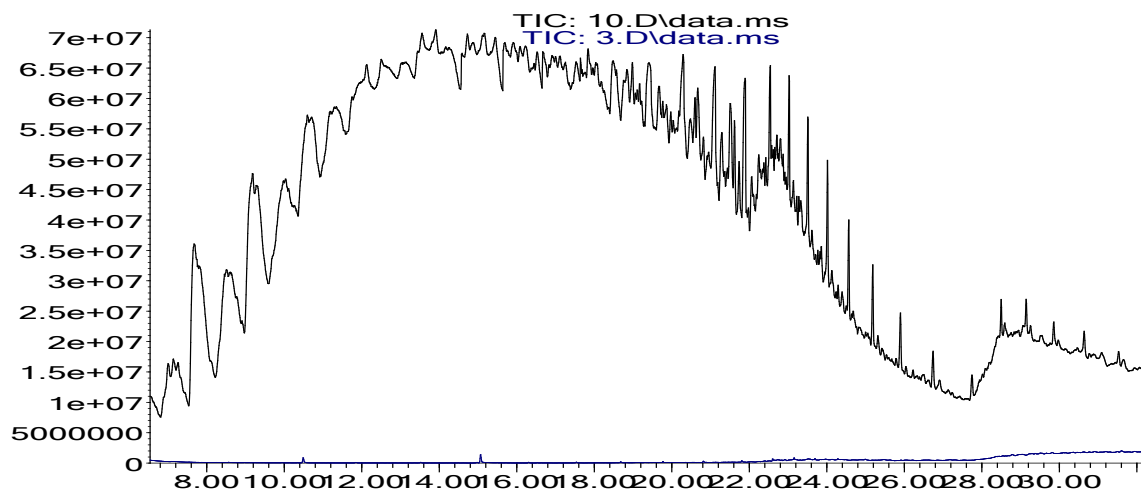
Abundance



Sample code	VM18009
Location	Loma Campana, Neuquen, Argentina
Sample type	Sediment
Date & time	19:40, 19.05.2018
Description	Sediment from an active cutting repository, black-brown colour, hydrocarbon smell

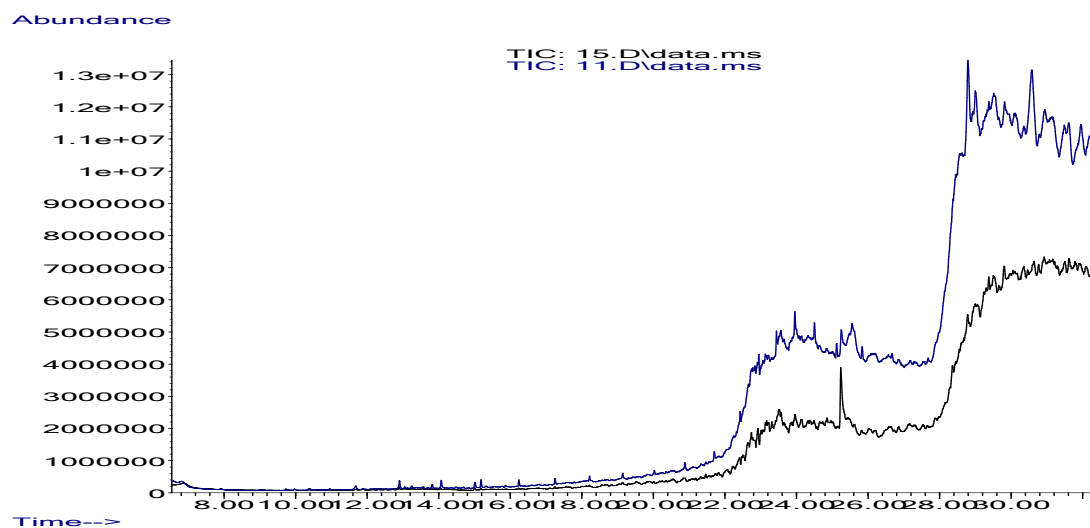
VM18009 (Black) v.s. Extraction Blank 1 (Blue)

Abundance

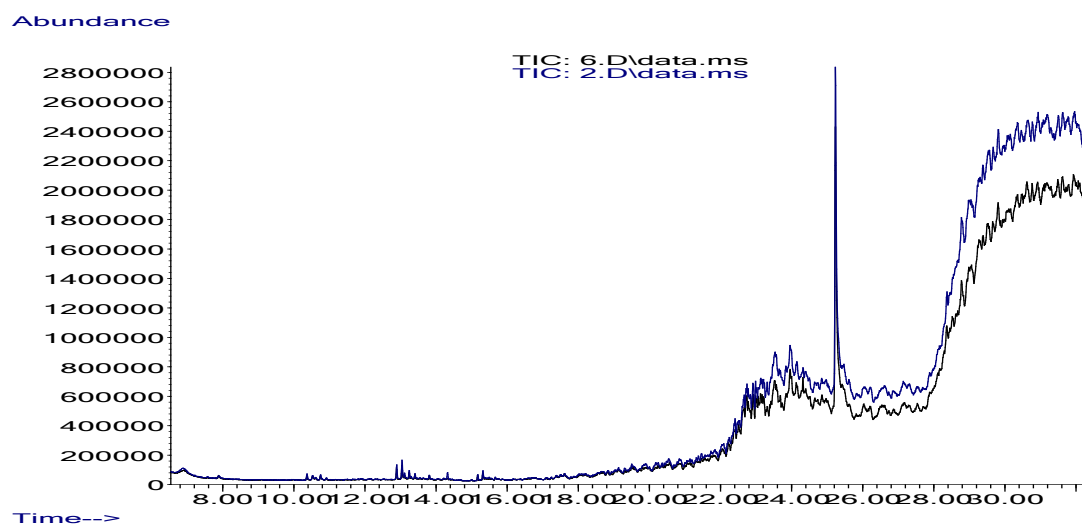


Sample code	VM18010
Location	Campo Maripe, Neuquen, Argentina
Sample type	Fresh water
Date & time	unknown, 20.05.2018
Description	Community's drinkable water, no colour, no smell

VM18010 (Black) v.s. Extraction Blank (Blue)



VM18010 - 10x concentrated (Black) v.s. Extraction Blank- 10x concentrated (Blue)

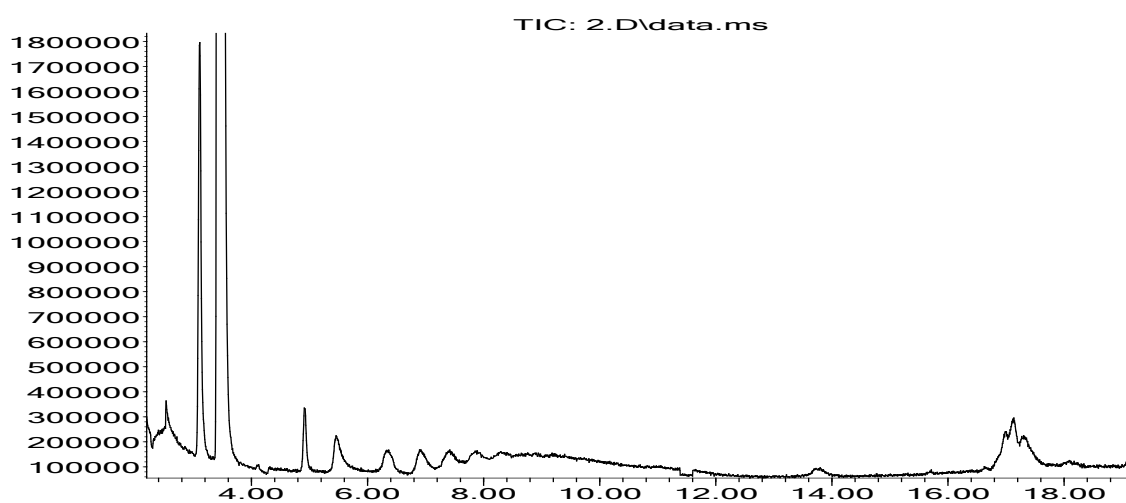


Volatile organic analysis results (VOCs)

Note: Some compounds have been identified only at trace levels using Selective Ion Monitoring (SIM) method, which is indicated below next to the name of such compounds.

Sample code	VM18001
Location	Tratayen, Neuquen, Argentina
Sample type	Fresh water
Date & time	14:00, 17.05.2018
Description	Fresh water pumped from well, no colour, no smell

Abundance



Number of compounds isolated: 0

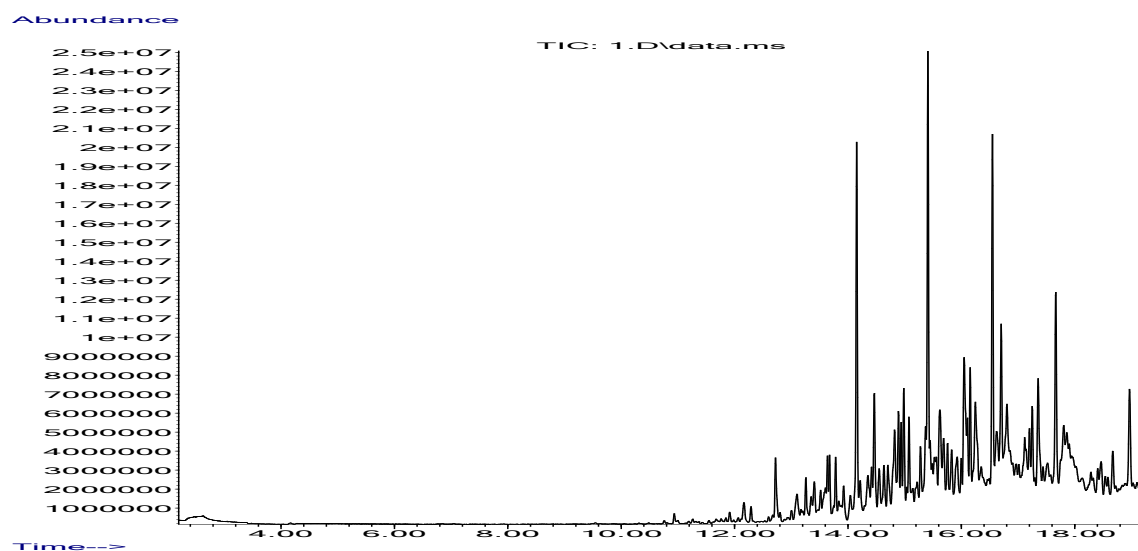
Compounds identified to better than 90%: 0

None

Compounds tentatively identified:

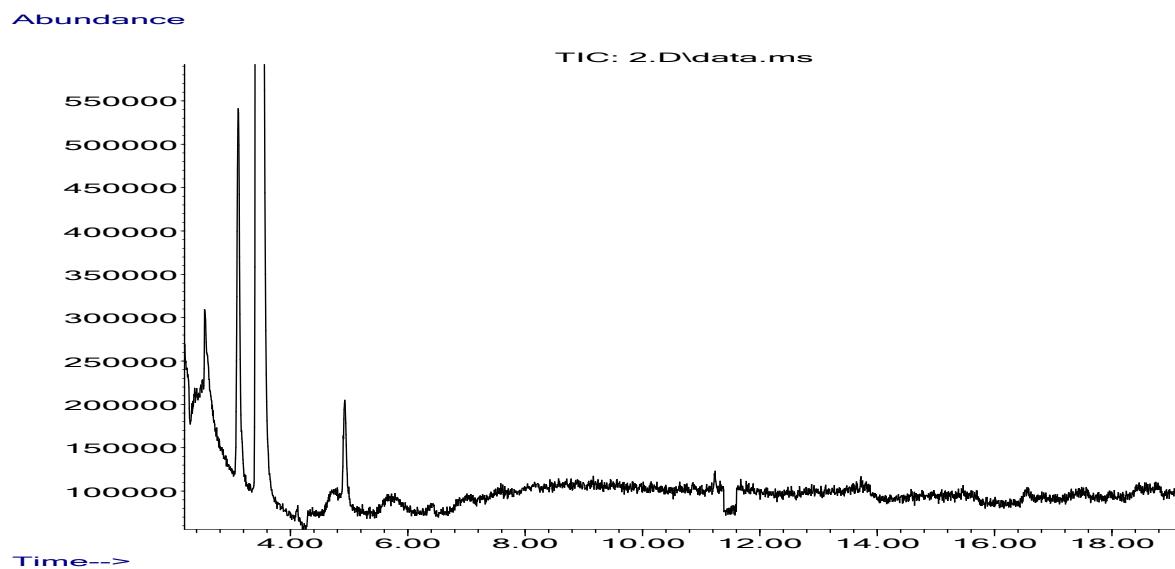
None

Sample code	VM18002
Location	Calera, Neuquen, Argentina
Sample type	Sludge
Date & time	18:12, 17.05.2018
Description	Sludge from an abandoned sludge repository, yellow-brown, strong smell



NB: Given the very high complexity of the chromatogram, detailed interpretation to identify all individual chemical constituents was not possible in this case.

Sample code	VM18003
Location	South Allen, Rio Negro, Argentina
Sample type	Sediment
Date & time	13:30, 18.05.2018
Description	Sediment/soil from a water/chemical spill site, brown, no smell



Number of compounds isolated: 1

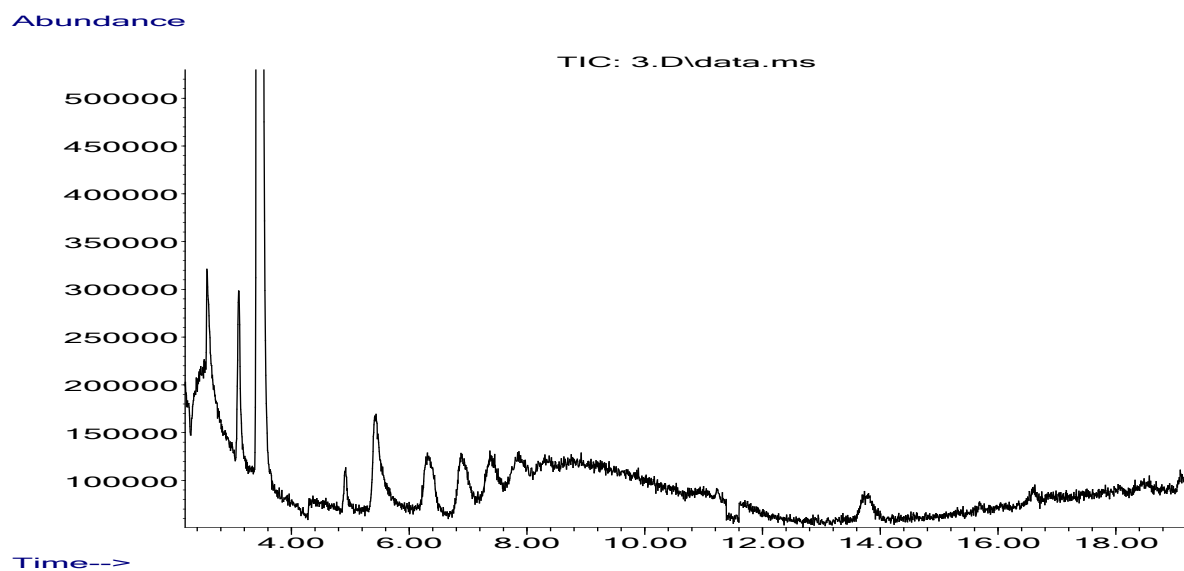
Compounds identified to better than 90%: 0

None

Compounds tentatively identified:

None

Sample code	VM18004
Location	South Allen, Rio Negro, Argentina
Sample type	Sediment
Date & time	13:35, 18.05.2018
Description	Sediment/soil from a water/chemical spill site, brown, no smell



Number of compounds isolated: 1

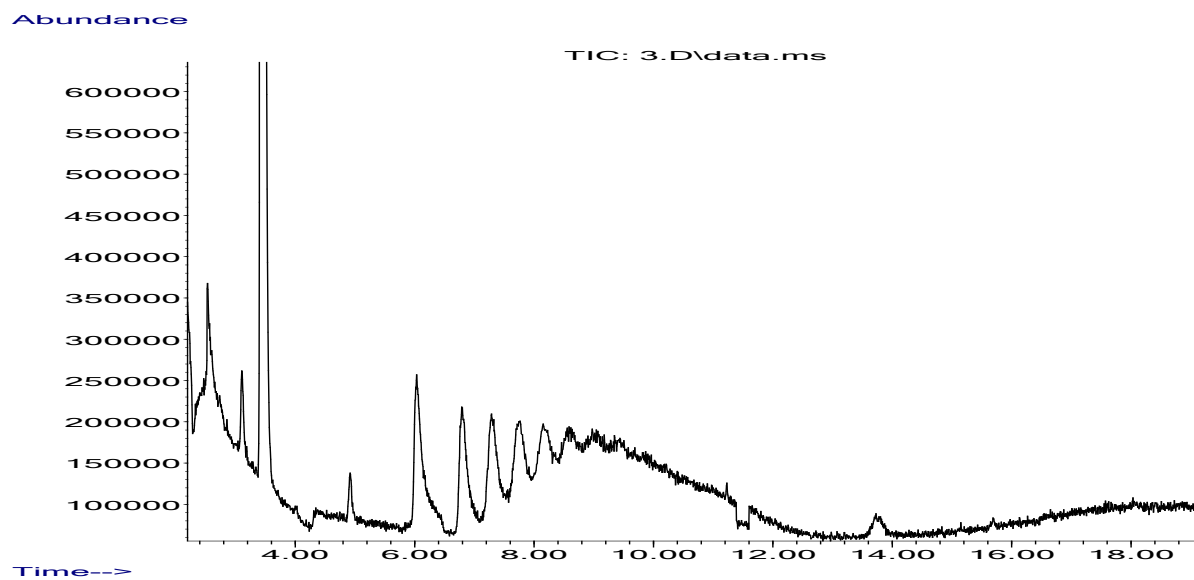
Compounds identified to better than 90%: 1

CAS#	Name
000075-15-0	Carbon disulphide (SIM)

Compounds tentatively identified:

None

Sample code	VM18005
Location	South Allen, Rio Negro, Argentina
Sample type	Water
Date & time	15:00, 18.05.2018
Description	Water from a channel next to a School, milky, nauseating smell



Number of compounds isolated: 1

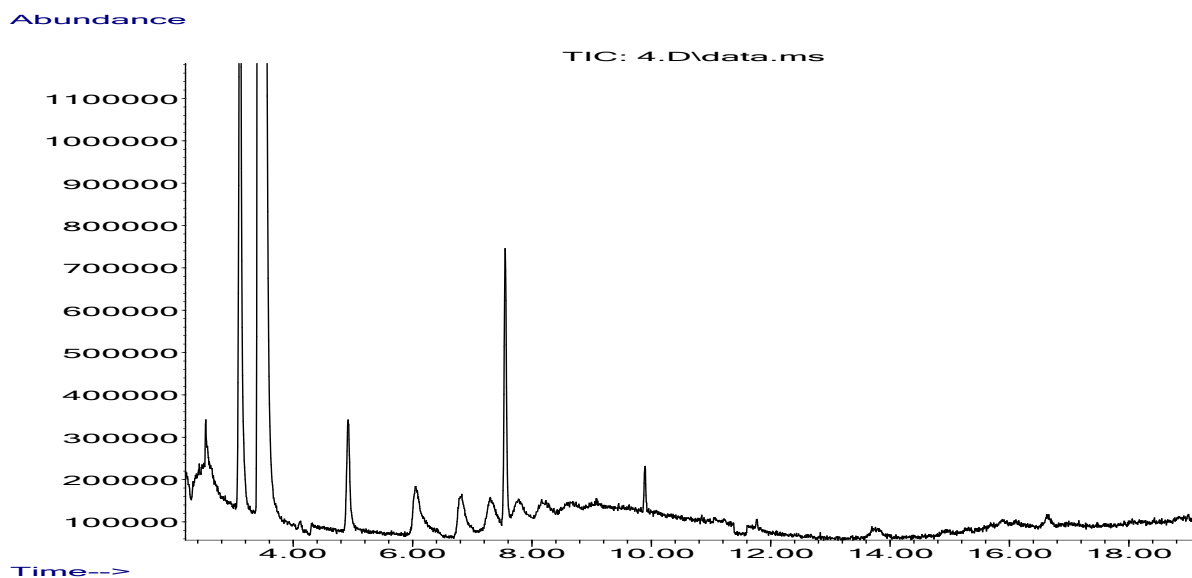
Compounds identified to better than 90%: 1

CAS#	Name
000067-66-3	Chloroform (SIM)

Compounds tentatively identified:

None

Sample code	VM18006
Location	Costa Blanco, Rio Negro, Argentina
Sample type	Fresh water
Date & time	15:50, 18.05.2018
Description	Community's drinkable water, no colour, no smell



Number of compounds isolated: 5

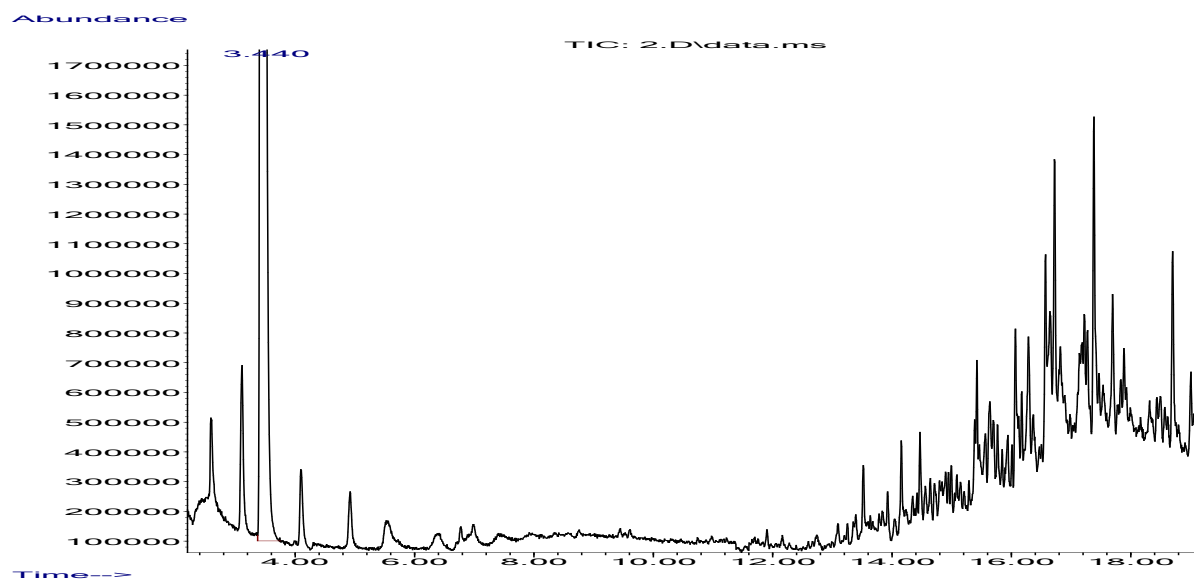
Compounds identified to better than 90%: 5

CAS#	Name
000067-66-3	Chloroform
000075-27-4	Methane, bromodichloro-
000124-48-1	Methane, dibromochloro-
000075-25-2	Bromoform (SIM)
000100-42-5	Styrene (SIM)

Compounds tentatively identified:

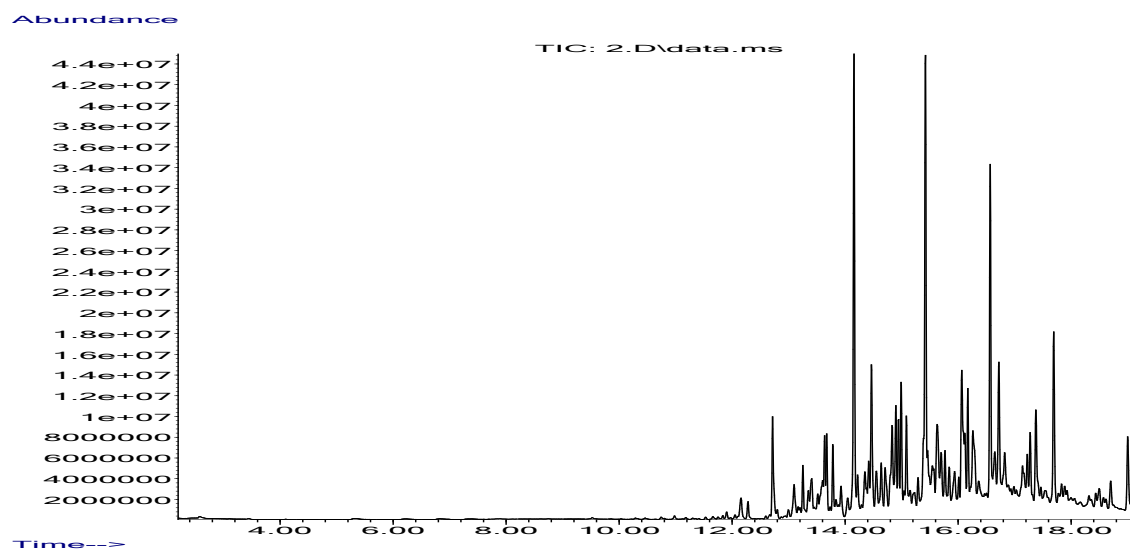
None

Sample code	VM18007
Location	Loma de la Lata, Neuquen, Argentina
Sample type	Sediment
Date & time	17:48, 19.05.2018
Description	Sediment from an abandoned cutting repository, black-brown colour, hydrocarbon smell



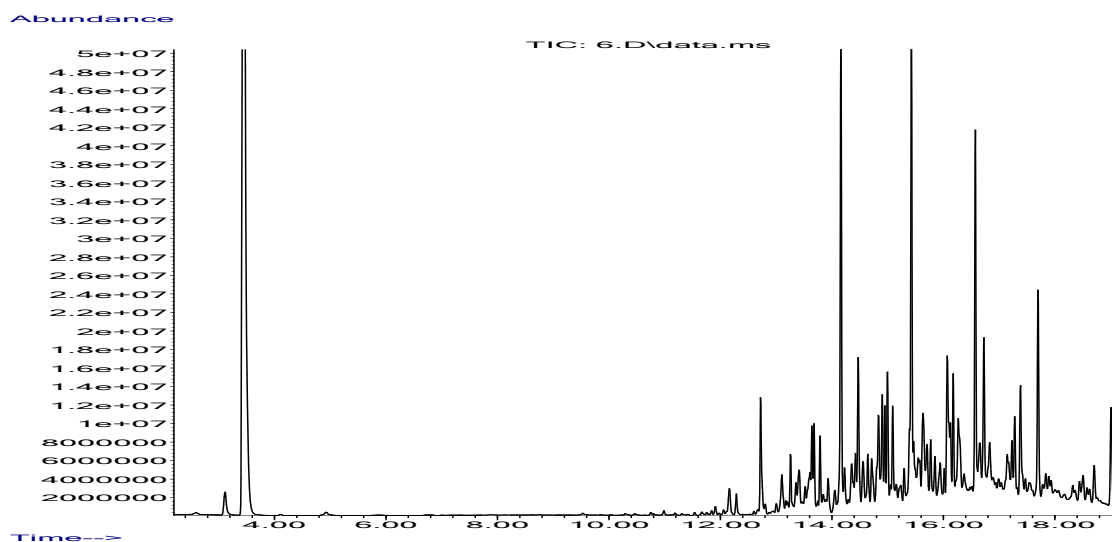
NB: Given the very high complexity of the chromatogram, detailed interpretation to identify all individual chemical constituents was not possible in this case.

Sample code	VM18008
Location	Loma de la Lata, Neuquen, Argentina
Sample type	Sediment
Date & time	17:55, 19.05.2018
Description	Sediment from an abandoned cutting repository, black-brown colour, hydrocarbon smell



NB: Given the very high complexity of the chromatogram, detailed interpretation to identify all individual chemical constituents was not possible in this case.

Sample code	VM18009
Location	Loma Campana, Neuquen, Argentina
Sample type	Sediment
Date & time	19:40, 19.05.2018
Description	Sediment from an active cutting repository, black-brown colour, hydrocarbon smell



Number of compounds isolated: 183

Compounds identified to better than 90%: 35

CAS#	Name
000080-56-8	2-Pinene
001678-91-7	Cyclohexane, ethyl-
000108-87-2	Cyclohexane, methyl-
001678-92-8	Cyclohexane, propyl-
000000-00-0	Cyclohexane, trimethyl-
000000-00-0	Cymene or xylene, ethyl- (2 isomers)
000124-18-5	Decane
000000-00-0	Decane, methyl- (3 isomers)
000112-40-3	Dodecane
000000-00-0	Dodecane, 2,6,10-trimethyl- or Hexadecane, 2,6,10,14-tetramethyl-
061141-72-8	Dodecane, 4,6-dimethyl-

000000-00-0	Dodecane, trimethyl-
000638-36-8	Hexadecane, 2,6,10,14-tetramethyl-
000091-17-8	Naphthalene, decahydro-
000111-84-2	Nonane
000871-83-0	Nonane, 2-methyl-
005911-04-6	Nonane, 3-methyl-
017301-94-9	Nonane, 4-methyl-
000095-47-6	O-xylene
000000-00-0	Octane, 2,6-dimethyl- or Nonane, 3-methyl-
005881-17-4	Octane, 3-ethyl-
000000-00-0	Tetradecane or Dodecane or Octadecane
000000-00-0	Tridecane or Tetradecane or Pentadecane
000000-00-0	Tridecane, methyl-
001120-21-4	Undecane
017301-23-4	Undecane, 2,6-dimethyl-
001002-43-3	Undecane, 3-methyl-
000100-41-4	Benzene, ethyl- (SIM)
000075-15-0	Carbon disulphide (SIM)
000110-82-7	Cyclohexane (SIM)
000108-88-3	Toluene (SIM)
000000-00-0	m- and/or p- Xylene (SIM)

Compounds tentatively identified: 84

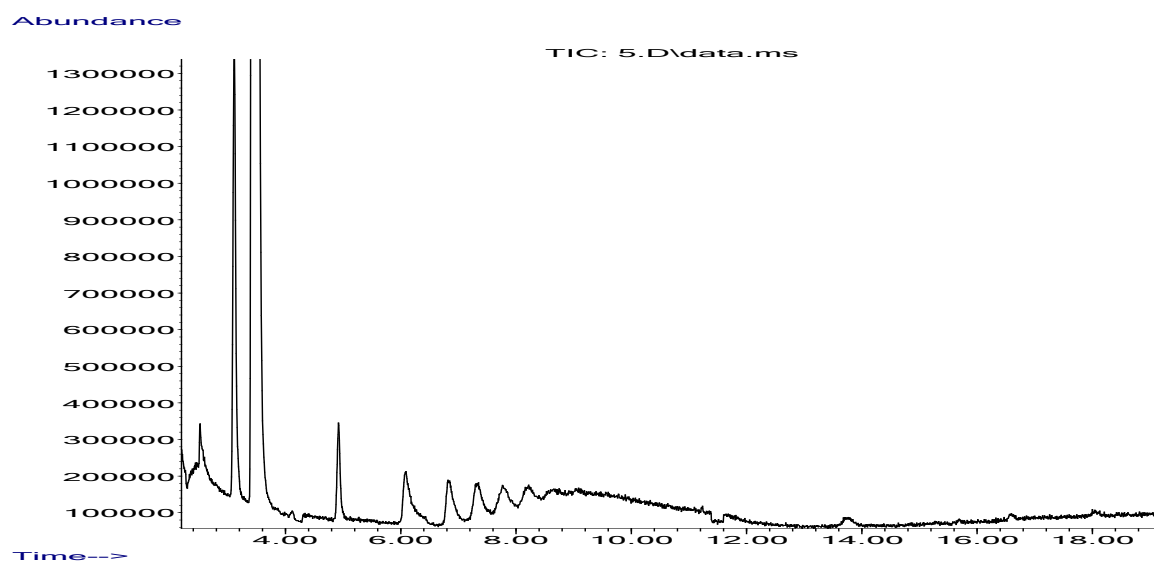
CAS#	Name
000000-00-0	2-Hexene, 4-ethyl-2,3-dimethyl-
000067-64-1	2-Propanone
091531-64-5	4-Cycloocten-1-one, 6,6-dimethyl-, (Z)-
050704-01-3	Benzene, (1,3-dimethyl-2-butenyl)-

004489-84-3 Benzene, (3-methyl-2-butenyl)-
000108-67-8 Benzene, 1,3,5-trimethyl-
004810-04-2 Benzene, 1,3,5-trimethyl-2-propyl-
000098-51-1 Benzene, 1-(1,1-dimethylethyl)-4-methyl-
001595-16-0 Benzene, 1-methyl-4-(1-methylpropyl)-
001595-05-7 Benzene, 1-methyl-4-butyl-
000078-78-4 Butane, 2-methyl-
042836-66-8 Cyclobutanecarboxylic acid, 2,2-dimethyl
000000-00-0 Cycloheptanone, 2,2,6-trimethyl-
000696-29-7 Cyclohexane, (1-methylethyl)-
006165-44-2 Cyclohexane, 1,1'-(1,4-butanediyl)bis-
050876-31-8 Cyclohexane, 1,1,3,5-tetramethyl-, trans-
003073-66-3 Cyclohexane, 1,1,3-trimethyl-
007094-27-1 Cyclohexane, 1,1,4-trimethyl-
001678-81-5 Cyclohexane, 1,2,3-trimethyl-, (1 α ,2 β ,3 α)-
002234-75-5 Cyclohexane, 1,2,4-trimethyl-
001839-63-0 Cyclohexane, 1,3,5-trimethyl-
000638-04-0 Cyclohexane, 1,3-dimethyl-, cis-
002207-03-6 Cyclohexane, 1,3-dimethyl-, trans-
000589-90-2 Cyclohexane, 1,4-dimethyl-
000624-29-3 Cyclohexane, 1,4-dimethyl-, cis-
004926-90-3 Cyclohexane, 1-ethyl-1-methyl-
000000-00-0 Cyclohexane, ethyl-dimethyl- (2 isomers)
004923-77-7 Cyclohexane, 1-ethyl-2-methyl-, cis-
006236-88-0 Cyclohexane, 1-ethyl-4-methyl-, trans-
054411-01-7 Cyclohexane, 1-methyl-2-pentyl-
001678-82-6 Cyclohexane, 1-methyl-4-(1-methylethyl)-, trans-
001678-93-9 Cyclohexane, butyl-
004259-00-1 Cyclopentane, 1,1,2-trimethyl-

000000-00-0	Cymene or xylene, ethyl- (3 isomers)
013150-81-7	Decane, 2,6-dimethyl-
017312-54-8	Decane, 3,7-dimethyl-
017312-55-9	Decane, 3,8-dimethyl-
002847-72-5	Decane, 4-methyl-
013151-35-4	Decane, 5-methyl-
013187-99-0	Dodecane, 2-bromo-
003891-98-3	Dodecane, 2,6,10-trimethyl-
001560-97-0	Dodecane, 2-methyl-
006117-97-1	Dodecane, 4-methyl-
006044-71-9	Dodecane, 6-methyl-
103982-58-7	Hept-2-ene, 2,4,4,6-tetramethyl-
000000-00-0	Heptane, dimethyl- (3 isomers)
000592-27-8	Heptane, 2-methyl-
014676-29-0	Heptane, 3-ethyl-2-methyl-
000000-00-0	Heptane, 3-ethyl-5-methylene-
004860-03-1	Hexadecane, 1-chloro-
000112-58-3	Hexane, 1,1'-oxybis-
001610-23-7	Hexane, 1,6-dicyclohexyl-
003522-94-9	Hexane, 2,2,5-trimethyl-
000591-76-4	Hexane, 2-methyl-
001075-22-5	Indan, 5,6-dimethyl-
013837-67-7	M-menthane, (1s,3s)-(+)-
003877-19-8	Naphthalene, 1,2,3,4-tetrahydro-2-methyl-
000119-64-2	Naphthalene, 1,2,3,4-tetrahydro-
021564-91-0	Naphthalene, 1,2,3,4-tetrahydro-1, 5-dimethyl-
004175-54-6	Naphthalene, 1,2,3,4-tetrahydro-1, 4-dimethyl-
013065-07-1	Naphthalene, 1,2,3,4-tetrahydro-2, 7-dimethyl-
002809-64-5	Naphthalene, 1,2,3,4-tetrahydro-5-methyl-

000000-00-0	Nonane, dimethyl- (2 isomers)
000111-65-9	Octane
007146-60-3	Octane, 2,3-dimethyl-
015869-93-9	Octane, 3,5-dimethyl-
002216-33-3	Octane, 3-methyl-
062016-18-6	Octane, 5-ethyl-2-methyl-
040710-70-1	Octatetracontane, 1-iodo-
000694-72-4	Pentalene, octahydro-
000611-14-3	Toluene, o-ethyl-
000622-96-8	Toluene, p-ethyl-
000000-00-0	Toluene, propyl- (2 isomers)
026730-12-1	Tridecane, 4-methyl-
000000-00-0	Undecane, methyl- (3 isomers)

Sample code	VM18010
Location	Campo Maripe, Neuquen, Argentina
Sample type	Fresh water
Date & time	unknown, 20.05.2018
Description	Community's drinkable water, no colour, no smell



Number of compounds isolated: 0

Compounds identified to better than 90%:

None

Compounds tentatively identified:

None