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Assessing environmental impact in an industrial site using an unmanned aerial vehicle with multi-spectral image camera

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Experimental

Metabolomic Analysis by Hydrophilic Liquid Interaction Chromatography Hi-Resolution Mass Spectrometry (Data dependent analysis)

Hydrophilic liquid interaction chromatography (HILIC) metabolite profiling was performed on a Vanquish Liquid Chromatography chromatographic separation system connected to an ID-X High Resolution Mass Spectrometer (Thermo Scientific, Hemel Hempstead, UK). The HILIC positive (ESI+) and negative (ESI-) MS data sets were acquired using the AcquireX acquisition workflow (data dependent analysis). The MS parameters were set as follows: MS¹ mass resolution 30 K, for MS² 30 K stepped energy (HCD) 20, 35, 50 scan range 100–1000, RF lens (%) 35, automatic gain control (AGC) gain, intensity was set to 25% and minimum intensity threshold was set to 20,000 with an maximum injection time of 50 ms. An extraction blank was used to create the background MS/MS exclusion list and a pooled quality control (QC) was used to create the MS/MS inclusion list. Hydrophilic Liquid Interaction Chromatography (HILIC) separation was performed on a Waters Acquity UPLC BEH amide column (2.1 × 150 mm with particle size of 1.7 µm) operating at 45 °C with a flow rate of 200 µL/min. The liquid chromatography (LC) gradient consisted of a binary buffer system, buffer A (LC/MS grade water) and buffer B (LC/MS grade ACN), both containing 10 mM ammonium formate. Independent buffers systems were used for positive and negative ionization mode acquisition respectively; for positive ionization mode buffers pH was adjusted using 0.1% formic acid, whereas for negative ionization mode buffers pH was adjusted using 0.1% ammonia solution. The LC gradient was identical for both polarities, namely 95% B at T_0 , hold for 1.5 min, followed by a linear decrease to 50% B in 11 min, a hold for 4 min, return to the starting conditions, and hold for further 4.5 min (column stabilization). The voltage applied for positive (ESI+) and negative (ESI-) ionization modes was 3.5 kV and 2.5 kV, respectively. Injection volumes used were 3 µL for positive ionization mode (ESI+) and 5 µL for negative ionization mode (ESI–).

Element	Calibration range (µg/g) ^{&}	Number of data points	Y= MX + C#	R ²	Intra-precision (lowest concentration) %RSD (n = 6)	Intra-precision (highest concentration) %RSD (n = 6)	LLOD (µg/g)*	LOQ (µg/g)*
V	59.5 - 334	5	0.4529x +16.512	0.9867	2.4	2.1	3.7	11.3
Ni	22.1 - 129	6	1.3465x – 28.702	0.9843	1.2	0.8	1.2	3.8
Zn	29.7 - 9191	6	0.7695x + 158.37	0.9857	0.9	0.8	24.3	73.6
As	5.3 - 658	6	0.9643x + 5.4947	0.9975	2.1	0.3	2.7	8.2
Rb	83.6 - 227	5	1.0391x + 0.6971	0.9983	0.2	0.4	0.9	2.7
Sr	35.8 - 220	5	1.079x + 2.8082	0.9889	0.3	0.5	0.5	1.4
Y	15.9 - 111	5	0.9213x + 1.4721	0.9984	0.5	0.5	0.5	1.5
Zr	171 - 264	5	0.9887x + 9.0014	0.9858	0.5	0.1	6.6	20.0
Ва	371 - 8803	6	0.507 – 231.94	0.9778	1.6	1.1	4.8	14.5
Pb	27.0 - 2706	5	0.9948x + 15.897	0.9994	0.7	0.4	10.8	32.8

Table S1. Quality Control of XRF using Certified Reference Materials

[&] minimum and maximum concentration of CRMs

used to correct sample data

* Determined using CRM calibration data. The lower limit of detection (LLOD) and limit of quantification (LOQ) were determined using replicate preparation of the calibration curve using the equations: LOD = $3.3\sigma/s$ and LOQ = $10\sigma/s$, where σ is the standard deviation of the intercept and s is the slope.

Table S2. Concentration (μ g/g) of elements (a) Main Site Teesside Terminal (Site A)[#], and (b) Greatham Oil Storage Depot (Site B)[#].

(a)

SAM	IPLE [@]	V	Ni	Zn	As	Rb	Sr	Y	Zr	Ва	Pb
2.1	mean	341.3	54.4	93.7	12.2	63.2	169.3	21.7	218.9	10729	90.8
5.1	replicates	363.0, 319.7	55.3, 53.5	99.6, 87.8	13.0, 11.4	64.8, 61.6	177.3, 161.3	22.4, 21.0	212.6, 225.2	10992, 10465	99.4, 82.2
2.2	mean	336.0	50.9	ND	13.1	63.1	274.8	20.3	213.1	20763	90.1
5.2	replicates	364.7, 307.3	51.8, 50.0	ND, ND	13.8, 12.3	64.0, 62.2	278.5, 271.2	20.3, 20.2	206.5, 219.6	20477, 21049	95.0, 85.2
2.2	mean	335.7	52.6	52.7	12.6	62.4	281.6	22.7	223.1	19688	86.7
5.5	replicates	367.6, 303.8	53.7, 51.5	62.5, 42.9	14.0, 11.1	63.5, 61.3	291.6, 271.6	23.5, 22.0	230.1, 216.0	19763, 19613	96.1, 77.3
2.4	mean	348.9	55.0	205.9	12.8	64.6	273.4	23.3	239.1	18955	99.2
5.4	replicates	381.1, 316.8	56.0, 54.1	216.5, 195.2	13.8, 11.7	65.4, 63.8	267.1, 279.1	23.1, 23.4	238.1, 240.1	17840, 20069	104.2, 94.1
2 5	mean	322.0	54.3	149.2	11.2	64.9	243.0	22.4	230.8	17216	70.9
5.5	replicates	379.1, 264.9	55.3, 53.3	162.6, 135.7	12.4, 9.9	66.5 <i>,</i> 63.2	245.9, 240.1	21.8, 22.9	238.8, 222.8	16801, 17631	78.8, 62.9
26	mean	366.1	68.0	497.7	15.5	61.2	288.8	25.0	222.8	16965	104.5
3.0	replicates	408.9, 323.2	68.9, 67.0	520.8, 474.6	14.2, 16.7	61.1, 61.3	285.6, 291.9	25.4, 24.7	230.4, 215.2	16398, 17532	102.1, 107.0
2 7	mean	326.5	52.7	56.4	13.6	60.8	276.6	19.0	233.3	20488	86.8
5.7	replicates	368.0, 285.0	54.7, 50.6	74.9, 37.9	15.4, 11.8	63.3, 58.3	292.9, 260.2	19.6, 18.5	231.0, 235.6	21246, 19730	95.7, 77.8
2.0	mean	381.8	56.3	227.8	14.7	67.4	383.8	23.4	238.6	26631	95.6
5.8	replicates	419.9, 343.8	56.6, 56.0	230.8, 224.9	14.8, 14.5	66.7, 68.0	362.9, 404.6	22.5, 24.2	224.4, 252.8	24619, 28643	98.1, 93.1
2.0	mean	330.6	53.8	172.4	12.2	61.3	298.3	20.9	213.3	20030	84.6
5.9	replicates	366.3, 295.0	55.4, 52.2	197.8, 147.0	13.7, 10.8	63.9, 58.7	316.5, 280.1	21.8, 20.0	227.2, 199.5	20448, 19613	93.4, 75.8
2 10	mean	273.5	51.7	ND	14.3	63.9	287.2	21.5	225.0	8401	105.6
3.10	replicates	228.7, 318.4	52.1, 51.3	ND, ND	14.7, 13.9	64.4, 63.3	284.1, 290.4	21.5, 21.4	233.7, 216.3	6611, 10190	107.6, 103.6
2 1 1	mean	337.9	47.8	ND	13.9	60.2	402.1	15.4	203.5	30132	100.1
5.11	replicates	384.8, 291.0	48.2, 47.4	ND, ND	14.7, 13.1	62.0, 58.3	426.4, 377.7	16.0, 14.8	217.4, 189.7	30832, 29432	108.0, 92.2
2 1 2	mean	335.9	47.5	ND	14.2	60.8	356.0	15.1	212.7	26177	96.8
3.12	replicates	383.1, 288.8	48.1, 46.9	ND, ND	14.9, 13.5	61.7, 59.9	355.5, 356.5	15.7, 14.6	219.7, 205.6	25941, 26414	103.0, 90.5

2 1 2 *	mean	330.5	49.6	0.0	12.4	59.9	267.6	17.2	221.0	18856	96.7
3.13*	replicates										
3.14	mean	335.7	48.3	0.0	12.8	58.3	346.2	18.1	221.5	24471	90.1
	replicates	371.4, 300.0	49.0 <i>,</i> 47.5	ND, ND	13.3, 12.3	58.6, 57.9	356.6, 335.8	19.5, 16.7	228.2, 214.8	24678, 24264	93.7, 86.6
2.45	mean	346.4	50.5	0.0	13.3	62.5	259.2	20.3	207.8	20655	102.1
5.15	replicates	376.7, 316.2	51.3, 49.6	ND, ND	13.9, 12.8	62.5, 62.5	260.9, 257.5	21.0, 19.7	209.8, 205.8	20714, 20596	111.1, 93.1
2.16	mean	350.5	55.8	126.0	13.1	67.3	206.1	23.4	243.2	13127	97.5
5.10	replicates	364.5, 336.5	55.6, 55.9	122.7, 129.2	13.8, 12.4	66.0, 68.6	206.9, 205.4	23.4, 23.4	231.8, 254.7	13211, 13043	98.6, 96.3
2 17	mean	342.4	62.3	340.6	13.0	62.2	342.0	20.8	227.4	21798	90.9
3.17	replicates	366.3, 318.6	66.7, 58.0	346.4, 334.9	13.9, 12.0	62.4, 62.1	342.2, 341.9	20.7, 20.9	221.9, 232.8	19134, 24461	96.8, 84.9
2 1 0	mean	310.9	56.0	297.6	11.4	58.4	317.8	19.6	207.2	20822	82.8
5.18	replicates	347.3, 274.4	56.2, 55.7	299.8, 295.4	12.2, 10.6	58.6, 58.2	319.2, 316.4	19.7, 19.6	206.9, 207.4	20339, 21306	<i>87.9, 77.7</i>
2 10	mean	324.9	51.7	165.0	11.9	59.7	409.9	19.2	226.7	33781	89.8
5.19	replicates	362.3, 287.5	51.7, 51.7	161.1, 169.0	12.7, 11.2	59.8, 59.6	399.5, 420.3	19.4, 19.1	230.2, 223.2	31601, 35960	99.1, 80.4
2 20	mean	283.3	53.5	313.2	9.4	52.7	367.7	20.0	187.7	24747	78.4
5.20	replicates	340.0, 226.5	54.5, 52.6	341.6, 284.8	10.7, 8.1	55.5 <i>,</i> 49.9	385.8, 349.6	21.7, 18.3	191.6, 183.9	24580, 24915	90.4, 66.4
2 21	mean	311.6	53.6	116.3	10.7	61.5	221.6	21.5	233.3	17164	88.3
5.21	replicates	341.3, 281.9	54.1, 53.1	125.4, 107.3	11.1, 10.3	62.3, 60.8	229.1, 214.1	21.4, 21.5	229.8, 236.8	17599, 16728	92.8, 83.8
2.22	mean	338.5	51.7	ND	11.9	61.5	302.1	21.1	223.8	24540	92.5
5.22	replicates	357.4, 319.5	52.7, 50.8	ND, ND	12.6, 11.3	61.1, 62.0	307.2, 297.0	21.3, 20.9	218.9, 228.8	25586, 23495	96.5, 88.6
2 22	mean	328.4	54.9	99.5	12.3	59.5	373.4	20.7	209.5	26700	94.0
5.25	replicates	351.7, 305.1	53.6, 56.1	84.2, 114.8	13.1, 11.5	59.8, 59.3	380.3, 366.4	21.0, 20.4	213.3, 205.6	26690, 26710	96.2, 91.8
2.24	mean	319.1	51.5	ND	13.3	57.6	311.6	20.3	214.1	20562	88.4
5.24	replicates	351.9, 286.4	52.3, 50.7	ND, ND	13.6, 13.1	57.7 <i>,</i> 57.5	313.9, 309.3	20.0, 20.7	220.5, 207.7	21089, 20035	90.9, 85.9
2.25	mean	325.8	55.3	115.8	12.3	63.9	157.4	22.3	237.9	10981	92.5
5.25	replicates	359.9, 291.6	56.7, 53.9	<i>132.2, 99.5</i>	13.4, 11.3	65.6 <i>,</i> 62.2	164.8, 149.9	22.8, 21.8	235.9, 239.9	11633, 10329	99.1, 85.8
2.76	mean	312.5	53.3	137.1	10.9	59.9	270.9	20.7	218.3	19598	85.5
5.20	replicates	352.1, 272.9	54.6, 51.9	158.2, 116.1	12.1, 9.8	62.1, 57.6	302.1, 239.8	21.2, 20.1	229.1, 207.4	21917, 17278	94.3, 76.8
3.27	mean	296.8	53.6	127.5	11.4	59.4	291.6	22.3	219.4	20228	95.8

	replicates	345.1, 248.6	55.3, 51.8	147.4, 107.5	12.8, 10.1	61.0, 57.7	263.2, 319.9	21.7, 22.8	217.6, 221.3	18203, 22252	97.8, 93.8
2 20	mean	322.8	53.2	84.2	12.2	61.7	257.8	21.3	233.7	17884	96.9
5.20	replicates	350.6, 295.0	54.2, 52.2	91.7, 76.7	13.0, 11.4	61.9, 61.5	254.2, 261.4	21.4, 21.1	218.4, 249.1	17974, 17793	99.5, 94.3
2.20	mean	312.3	50.6	ND	10.8	56.9	392.0	19.2	207.9	28613	77.4
5.29	replicates	339.6, 285.0	51.2, 50.1	ND, ND	11.3, 10.4	56.3, 57.5	395.1, 389.0	18.6, 19.9	201.2, 214.7	29807, 27420	79.2, 75.6
2 20	mean	335.1	48.1	ND	11.6	58.4	463.5	16.7	206.7	38808	87.7
5.50	replicates	376.6, 293.6	49.3, 46.9	ND, ND	13.0, 10.3	59.5, 57.3	483.7, 443.3	17.3, 16.2	212.0, 201.4	40747, 36868	95.1, 80.2
2 21	mean	294.4	63.7	1074	13.7	46.8	256.8	26.6	174.0	18251	106.4
5.51	replicates	323.0, 265.8	65.4, 61.9	1103, 1044	14.1, 13.4	<i>48.0, 45.5</i>	259.3, 254.2	27.1, 26.2	172.5, 175.5	18682, 17820	111.8, 101.0
2 2 2	mean	339.8	56.4	199.5	12.3	63.8	323.7	22.3	238.7	23939	88.7
5.32	replicates	367.6, 312.0	57.3, 55.6	205.0, 194.1	13.1, 11.6	63.3, 64.3	314.4, 333.0	22.0, 22.6	227.0, 250.5	23771, 24106	90.9, 86.5
2.22	mean	322.5	52.6	144.0	10.9	60.5	261.9	20.7	230.2	20631	86.2
5.55	replicates	361.2, 283.7	53.5, 51.7	159.6, 128.3	12.6, 9.2	62.1, 58.9	279.4, 244.3	20.9, 20.5	224.8, 235.6	21286, 19976	91.7, 80.7
2.24	mean	324.1	53.6	123.0	11.9	61.7	227.9	21.5	228.2	16170	89.0
5.54	replicates	341.8, 306.4	53.5, 53.7	123.0, 123.1	11.7, 12.0	61.4, 62.1	224.5, 231.3	21.0, 22.1	236.7, 219.8	16515, 15826	90.9, 87.1
2.25	mean	313.3	54.1	ND	12.6	62.0	190.6	22.1	230.0	13862	91.2
5.55	replicates	364.3, 262.3	57.0, 51.2	ND, ND	13.4, 11.8	64.8, 59.3	187.5, 193.8	22.2, 22.1	232.5, 227.6	13392, 14331	100.4, 81.9
2.26	mean	318.0	54.3	117.8	11.5	60.6	265.6	22.1	216.8	19078	85.4
5.50	replicates	349.5, 286.6	55.0, 53.5	127.7, 108.0	11.8, 11.2	62.0, 59.3	246.3, 284.8	22.6, 21.6	223.6, 210.1	18327, 19828	87.8, 83.1
Me	ean	327.1	53.7	142.2	12.4	60.8	295.0	20.9	220.5	21017	91.3
S	SD		4.2	196.4	1.3	3.7	69.1	2.4	14.5	5950	7.8

SAM	IPLE [@]	V	Ni	Zn	As	Rb	Sr	Y	Zr	Ва	Pb
1.1	mean	311.9	58.2	517.5	7.8	69.1	118.1	22.9	169.6	5097	61.4
1.1	replicates	349.9, 273.8	60.6, 55.8	525.7, 509.2	8.9, 6.6	70.6, 67.7	121.6, 114.5	23.1, 22.7	177.7, 161.5	5020, 5173	68.1, 54.8
1.2	mean	293.0	56.2	260.9	7.6	64.8	86.6	20.5	198.0	3409	62.4
	replicates	318.4, 267.6	57.3, 55.1	280.4, 241.4	8.4, 6.8	65.3 <i>,</i> 64.3	91.1, 82.1	21.5, 19.6	207.6, 188.3	3345, 3473	68.6, 56.2
	mean	425.3	59.5	125.5	44.0	87.5	97.4	24.0	191.9	3261	325.7
1.3	replicates	451.7, 399.0	60.7, 58.2	136.8, 114.3	44.9, 43.1	90.3, 84.8	99.8, 94.9	24.6, 23.5	198.6, 185.1	3160, 3363	328.3, 323.2
1.4	mean	394.8	56.7	94.5	34.6	84.6	93.4	24.6	204.8	3475	239.5
	replicates	419.7, 369.8	57.3, 56.0	102.2, 86.8	36.5, 32.7	86.0, 83.2	94.6, 92.2	24.6, 24.6	207.2, 202.3	3481, 3469	243.6, 235.4
1.5	mean	398.7	58.7	ND	28.2	89.6	92.3	24.4	210.5	3239	185.0
	replicates	417.9, 379.5	58.8, 58.6	ND, ND	27.5, 28.9	90.5, 88.8	92.5, 92.0	24.3, 24.5	209.4, 211.6	3170, 3308	184.7, 185.4
1.0	mean	381.4	55.8	79.9	28.1	86.3	98.2	25.4	233.8	3333	203.5
1.0	replicates	<i>383.3, 379.5</i>	56.3, 55.3	84.8, 75.0	29.2, 27.0	87.5, 85.1	99.6, 96.8	25.9 <i>,</i> 24.9	238.3, 229.3	3371, 3296	209.4, 197.5
17	mean	360.1	64.4	655.0	11.5	80.6	122.4	25.2	164.5	4644	70.5
1.7	replicates	381.3, 338.9	65.1, 63.7	668.9, 641.1	12.2, 10.8	81.1, 80.1	124.0, 120.8	25.4, 25.0	167.8, 161.2	4631, 4657	73.9, 67.1
1.0	mean	460.3	66.5	375.7	21.8	90.7	109.8	25.6	168.5	3596	152.1
1.8	replicates	460.3, 460.3	67.7, 65.3	387.4, 363.9	22.4, 21.3	91.9, 89.4	111.5, 108.1	25.9, 25.3	168.5, 168.5	3534, 3657	154.0, 150.3
1.0	mean	375.6	58.6	125.1	9.0	84.2	111.1	24.5	191.2	4106	63.6
1.9	replicates	375.6, 375.6	60.1, 57.0	133.4, 116.7	9.6, 8.4	85.3, 83.2	115.0, 107.2	24.5, 24.6	196.5, 185.9	4091, 4122	75.6, 51.7
M	ean	377.9	59.4	254.8	21.4	81.9	103.2	24.1	192.5	3796	151.5
S	D	52.1	3.7	215.6	13.2	9.1	12.5	1.6	22.6	672	95.0

* Only one replicate

ND = <LOQ

Data corrected using CRM calibration equation

[@] Duplicate samples were determined by two different individuals on different occasions, but within one month of each other.

Site A: Conoco Phillips, Main Site Teesside Terminal, Seal Sands. A 285 acre site investigating the middle (number 3) of 5 available beds. Site B: Greatham Oil Storage Depot, Greatham. A 375 acres site investigating the periphery of the accessible area.

Figure S1. Sampling locations: Site A Main Site Teesside Refinery and B Greatham Storage Depot, (a) photograph of the main site (Site A) pre-development, in 1969, (b) photograph of Greatham Storage Deport (Site B), 1974, (c) aerial photograph of Main Site (Site A), sampling area highlighted, (d) aerial photograph of Storage Depot (Site B), sampling area highlighted, (e) ground-based photograph of sampling locations at Main Site (Site A), and (f) ground-based photograph of sampling locations at the Storage Depot (Site B).

(a)









[Note: photographs (a)-(d) courtesy of Mr Tony J. Finn, Environment Engineer, Conoco Phillips, Teesside Operations, Seal Sands, Middlesbrough.]

Figure S2. Vegetation index maps for an area of Site A (Main Site) (a) NDVI (b) GNDVI (c) SAVI and (d) CI green VI.

(a)







(c)

Figure S3. Vegetation index maps for an area of Site B (Storage Depot) (a) NDVI (b) GNDVI (c) SAVI and (d) CI green VI.

(a)











(c)













Figure S5: Relationship between VI and C12-AS in Site A and Site B (a) NDVI and C12-AS (b) GNDVI and C12-AS (c) SAVI and C12-AS and (d) CI green VI and C12-AS











Figure S6. Relationship between VI and tetradecylsulfate in Site A and Site B (a) NDVI and tetradecylsulfate in (b) GNDVI and tetradecylsulfate in (c) SAVI and tetradecylsulfate in and (d) CI green VI and tetradecylsulfate









