METHOD STATEMENT

Determinand:
Phenoxyalkanoic herbicides and phenolic compounds by GC-MSMS

Matrix:
Treated Sewage Effluent, Trade Effluent & Surface Waters

Principle of Method:
Aqueous samples are extracted using a solid phase extraction technique. Acetonitrile is added to the sample to dissolve the compounds. A suitable sub sample is diluted with acidified de-chlorinated laboratory tap water and the compounds are isolated using solid phase extraction (SPE). The sample extract is solvent exchanged and concentrated. The sample extract is reacted with a silylation reagent. The sample extract is injected by large volume injection (LVI) into a capillary column gas chromatograph (GC), the organic compounds are separated and then identified and quantified with mass spectrometric detection (MSD) in multiple reaction monitoring (MRM) mode.

Sampling and Sample Preparation:
Sampling, samples should be collected in glass bottles with PTFE lined screw caps, no sample preservative is required. Storage – samples should be analysed as soon as possible after collection. When this is not possible, they should be stored under refrigeration at 3±2˚C in the dark, until analysis can begin. The maximum permissible storage time prior to analysis is 7 days (US EPA Soil Analysis QA QC Manual 2012 Table 3-1). Wherever possible, sample extracts should be analysed on the day of preparation. If this is not possible, the extracts may be stored under refrigeration at 5 ± 3˚C in the dark and analysed within 7 days of preparation.

Interferences:
GC-MS/MS is an extremely selective technique and interferences should only be encountered very rarely. However, any compound, which passes through the extraction procedure, and has a similar gas chromatographic retention time and mass spectrometric properties to the compound of interest, may cause interference.

Performance of Method:

Precision, Bias and Limit of Detection

DETERMINAND	LOD	LOW STANDARD			HIGH STANDARD		
	(ng/litre)	MEAN	RECOVERY	RSD	MEAN	RECOVERY	RSD
4-Chloro-2-methylphenol	13.6	2041	102.1%	5.12%	8036	101.18%	2.83%
2,4-Dichlorophenol	8.82	2007	100.4%	1.15%	7981	99.8%	1.25%
2,4,6-Trichlorophenol	36.0	2017	100.8%	2.52%	7994	99.9%	2.27%
4-Chlorophenoxyacetic acid	74.3	978.4	97.8	17.0%	4112	102.8%	9.50%
MCPP	35.6	1149	115.0%	13.7%	4158	104.0%	5.72%
Paratertoctylphenol	25.5	1043	104.3%	7.95%	3980	99.5%	9.96%
MCPA	38.5	1121	112.1%	10.5%	4162	104.1%	4.49%
2,4-DP (Dichlorprop)	43.9	1129	112.9%	12.7%	4159	104.0%	4.81%
2,4-D	41.9	1101	110.1%	15.6%	4194	104.9%	4.68%
Bromoxynil	28.1	1136	113.6%	16.0%	4190	104.8%	9.04%
2,4,5-TP (Fenoprop)	19.9	1179	117.9%	14.5%	4237	105.9%	5.90%
Pentachlorophenol	22.4	1067	106.7%	6.43%	4038	101.0%	8.00%
MCPB	32.9	1021	102.2%	5.26%	4012	100.3%	3.77%
4-Paranonylphenol	18.3	1025	102.5%	5.21%	4068	101.7%	3.40%
2,4-DB	15.5	1030	103.1%	2.84%	4003	100.1%	3.11%

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Matrix Spike Recoveries

Final Effluent Results

DETERMINAND	FINAL EFFLUENT LOW SPIKE			FINAL EFFLUENT HIGH SPIKE		
	MEAN	RECOVERY	RSD	MEAN	RECOVERY	RSD
4-Chloro-2-methylphenol	2038	100.5%	5.81%	8038	100.1%	3.62%
2,4-Dichlorophenol	2012	100.0%	1.54%	8066	100.7%	1.53%
2,4,6-Trichlorophenol	2160	100.0%	4.73%	8216	100.7%	2.75%
4-Chlorophenoxy acid	1047	100.1%	8.71%	4226	104.5%	10.2%
MCPP	1015	99.5%	5.05%	3881	96.5%	5.28%
Paratertoctylphenol	1000	99.1%	11.1%	3901	97.3%	9.54%
MCPA	1038	99.8%	3.80%	3994	98.9%	4.47%
2,4-DP (Dichlorprop)	1009	99.7%	4.86%	3935	98.1%	4.51%
2,4-D	1053	100.8%	11.1%	4106	101.5%	3.67%
Bromoxynil	1049	104.3%	6.09%	4074	101.7%	6.29%
2,4,5-TP (Fenoprop)	1039	102.3%	6.68%	3995	99.5%	5.37%
Pentachlorophenol	1040	103.5%	6.76%	4035	100.7%	6.17%
MCPB	1011	99.9%	4.82%	4019	100.2%	3.04%
4-Paranonylphenol	1027	101.4%	5.37%	4148	103.4%	3.45%
2,4-DB	1038	102.3%	5.04%	4091	101.9%	3.45%

Trade Effluent Results

DETERMINAND	TRADE EFFLUENT LOW SPIKE			TRADE EFFLUENT HIGH SPIKE		
	MEAN	RECOVERY	RSD	MEAN	RECOVERY	RSD
4-Chloro-2-methylphenol	2293	100.6%	4.22%	8069	97.4%	5.41%
2,4-Dichlorophenol	2219	99.8%	1.05%	8251	100.3%	1.05%
2,4,6-Trichlorophenol	2005	99.1%	2.35%	7988	99.6%	1.96%
4-Chlorophenoxy acid	1040	101.4%	10.5%	4313	107.2%	7.51%
MCPP	1063	104.4%	8.26%	3953	98.4%	6.80%
Paratertoctylphenol	954.9	95.0%	11.3%	3703	92.5%	8.81%
MCPA	1221	106.7%	4.92%	4159	100.1%	5.80%
2,4-DP (Dichlorprop)	1055	104.8%	5.63%	3955	98.7%	5.76%
2,4-D	1083	104.7%	5.84%	4096	101.5%	4.36%
Bromoxynil	1073	107.2%	10.1%	4042	101.0%	6.43%
2,4,5-TP (Fenoprop)	1099	109.2%	7.4%	4004	99.9%	7.44%
Pentachlorophenol	1065	106.2%	8.00%	4104	102.5%	6.37%
MCPB	1025	101.5%	4.29%	4027	100.5%	3.48%
4-Paranonylphenol	1005	99.7%	5.07%	3966	98.9%	4.24%
2,4-DB	1039	100.6%	3.39%	4035	100.6%	3.39%

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Surface Water Results

DETERMINAND	SURFACE WATER LOW SPIKE			SURFACE WATER HIGH SPIKE		
	MEAN	RECOVERY	RSD	MEAN	RECOVERY	RSD
4-Chloro-2-methylphenol	2047	101.6%	5.54%	8013	100.0%	2.51%
2,4-Dichlorophenol	2006	100.0%	1.41%	8049	100.6%	1.32%
2,4,6-Trichlorophenol	2032	99.8%	2.27%	8086	100.6%	2.17%
4-Chlorophenoxy acid	1010	98.1%	14.0%	4108	102.0%	9.59%
MCPP	1106	109.6%	13.9%	4117	102.7%	6.74%
Paratertoctylphenol	961.5	95.5%	10.2%	3714	92.7%	8.08%
MCPA	1109	108.4%	9.78%	4139	102.8%	6.31%
2,4-DP (Dichlorprop)	1092	108.2%	11.8%	4106	102.4%	5.49%
2,4-D	1072	103.4%	8.93%	4141	102.6%	4.98%
Bromoxynil	1094	109.0%	15.8%	4096	102.3%	6.42%
2,4,5-TP (Fenoprop)	1140	113.2%	16.6%	4168	104.0%	6.31%
Pentachlorophenol	1059	105.5%	9.39%	4084	102.0%	5.98%
MCPB	1029	102.1%	4.06%	4064	101.4%	2.80%
4-Paranonylphenol	1024	101.1%	4.68%	3979	99.2%	4.63%
2,4-DB	1036	102.6%	4.08%	4059	101.2%	2.25%

Uncertainty of Measurement

The reported uncertainty is an expanded uncertainty calculated using a coverage factor of 2, which gives a level of confidence of approximately 95%

Determinand	Uncertainty of Measurement %
4-Chloro-2-methylphenol	15.29
2,4-Dichlorophenol	5.36
2,4,6-Trichlorophenol	6.31
4-Chlorophenoxy acid	33.60
MCPP	29.09
Paratertoctylphenol	24.95
MCPA	20.75
2,4-DP (Dichlorprop)	23.51
2,4-D	23.74
Bromoxynil	32.30
2,4,5-TP (Fenoprop)	31.37
Pentachlorophenol	26.40
MCPB	11.96
4-Paranonylphenol	13.72
2,4-DB	13.56

References:
In-house method.