

# METHOD STATEMENT



## Determinand:

Trace level Pesticides and selected non-polar organic compounds

## Matrix:

Surface, Ground and Saline waters, Final effluents (TBT only)

## Principle of Method:

Approximately 400mls of sample is treated with sodium tetraethylborate (STEB) to ethylate TBT cation and is then extracted with 20mls of iso-hexane. The extract is analysed by GC-MSMS with electron impact (EI) ionisation.

## Sampling and Sample Preparation:

Samples should be taken in a 500ml amber or green glass bottle with 25mls of methanol as a preservative.

Samples are stored at  $3 \pm 2^{\circ}\text{C}$  and analysed within 14 days of sampling for all compounds except those listed below. (In-house stability data)

Benzo (a) pyrene	9 days (in-house data)
Hexachlorobutadiene	7 days (in-house data)
Total BDE	8 days (in-house data)
BDE-153	8 days (in-house data)
Tributyl Tin (TBT)	9 days (in-house data)

## Interferences:

MS/MS is an extremely selective technique and interferences should only be encountered very rarely, however in theory, any compound which is extracted by the procedure, which has a chromatographic retention time similar to the compound of interest and which produces both precursor and product ions similar to that of the compounds in question, may interfere

## Performance of Method:

Precision, Bias and Limit of Detection

Compound	LOD (ng/L)	MRL(µg/l)	Range of Method	Low Standard		High Standard	
				Bias	RSD	Bias	RSD
1,3,5-Trichlorobenzene	0.1060	0.00030	0.00020 - 0.04000	-5.85%	14.30%	-0.64%	8.06%
1,2,4-Trichlorobenzene	0.0834	0.00030	0.00020 - 0.04000	-0.83%	11.87%	-0.37%	8.67%
1,2,3-Trichlorobenzene	0.1011	0.00030	0.00020 - 0.04000	2.56%	7.08%	1.49%	9.84%
TCB - Total	0.2400	0.00050	0.00060 - 0.12000	-1.27%	8.47%	0.18%	8.54%
Hexachlorobutadiene	0.0627	0.00020	0.00010 - 0.02000	-4.26%	8.68%	0.12%	10.10%
Tributyl Tin	0.0205	0.000030	0.00002 - 0.00400	0.90%	9.24%	0.25%	5.94%
Pentachlorobenzene	0.0388	0.000050	0.00005 - 0.01000	2.22%	4.79%	2.23%	6.15%
Trifluralin	0.1901	0.00030	0.00020 - 0.04000	-2.59%	9.47%	1.62%	6.38%
Hexachlorobenzene	0.0132	0.000050	0.00005 - 0.01000	-1.66%	6.42%	0.98%	4.81%
alpha-HCH	0.0204	0.000050	0.00010 - 0.02000	1.69%	3.60%	2.73%	5.12%
gamma-HCH	0.0244	0.000050	0.00010 - 0.02000	-1.18%	4.69%	1.84%	5.20%
beta-HCH	0.0455	0.000050	0.00010 - 0.02000	-2.68%	4.71%	0.70%	4.12%

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Compound	LOD (ng/L)	MRL(µg/l)	Range of Method	Low Standard		High Standard	
				Bias	RSD	Bias	RSD
delta-HCH	0.0433	0.000050	0.00010 - 0.02000	-6.78%	6.76%	-0.39%	6.24%
epsilon-HCH	0.0388	0.000050	0.00010 - 0.02000	-3.82%	5.41%	-1.38%	6.59%
Total HCH	0.0936	0.00020	0.00050 - 0.10000	-2.55%	4.16%	0.70%	4.62%
Anthracene	0.0907	0.00030	0.00020 - 0.04000	1.40%	7.46%	3.59%	6.59%
Heptachlor	0.0118	0.000030	0.00002 - 0.00400	11.06%	10.12%	-3.83%	10.31%
cis-Heptachlor Epoxide (isomer B)	0.0280	0.000030	0.00006 - 0.01200	-3.01%	10.76%	0.41%	8.96%
trans-Heptachlor Epoxide (isomer A)	0.0210	0.000030	0.00002 - 0.00400	-0.41%	10.80%	-0.62%	7.48%
Sum Heptachlor/Heptachlor Epoxide	0.0426	0.000090	0.00006 - 0.01200	-4.83%	8.67%	-1.35%	7.30%
Alachlor	0.1983	0.00030	0.00020 - 0.04000	0.00%	8.54%	1.35%	5.60%
Aldrin	0.0723	0.00030	0.00020 - 0.04000	-5.98%	8.59%	-0.01%	6.78%
Isodrin	0.0800	0.00030	0.00020 - 0.04000	-2.75%	5.46%	0.96%	9.07%
Dieldrin	0.0919	0.00030	0.00020 - 0.04000	-5.39%	8.22%	0.58%	8.45%
Endrin	0.1436	0.00030	0.00020 - 0.04000	-0.96%	5.52%	1.09%	4.10%
Sum - Cyclo diene Pesticides	0.2312	0.00050	0.00080 - 0.16000	-3.77%	5.02%	0.66%	5.82%
Terbutryn	0.1273	0.00030	0.00020 - 0.04000	1.51%	6.04%	3.86%	5.89%
Chlorpyrifos	0.0604	0.00010	0.00010 - 0.02000	-4.96%	6.90%	-1.07%	6.45%
Dicofol	0.0491	0.00010	0.00010 - 0.02000	12.15%	11.14%	15.16%	13.00%
Chlorfenvinphos	0.1257	0.00020	0.00020 - 0.04000	2.20%	12.64%	2.68%	5.34%
Cybutryne (Irgarol)	0.0511	0.00010	0.00010 - 0.02000	-1.34%	9.03%	2.85%	6.85%
Fluoranthene	0.1376	0.00030	0.00020 - 0.04000	-0.70%	4.57%	4.38%	5.58%
pp-DDE	0.0407	0.000200	0.00010 - 0.02000	2.48%	10.47%	5.57%	8.52%
op-DDT	0.0707	0.00020	0.00010 - 0.02000	-3.75%	4.44%	2.14%	2.83%
pp-TDE (DDD)	0.0620	0.00020	0.00010 - 0.02000	1.29%	9.77%	5.36%	7.01%
pp-DDT	0.0985	0.00020	0.00010 - 0.02000	-2.64%	5.70%	1.18%	3.21%
DDT - Total	0.1736	0.00040	0.00040 - 0.08000	-0.67%	5.31%	3.57%	3.53%
Diflufenican	0.0601	0.0020	0.00010 - 0.02000	0.68%	8.15%	4.26%	5.69%
Quinoxifen	0.0461	0.000100	0.00020 - 0.04000	-0.02%	6.38%	1.83%	5.94%
Aclonifen	0.1126	0.00030	0.00020 - 0.04000	1.79%	18.22%	-3.87%	11.13%
BDE 28	0.0195	0.000030	0.00002 - 0.00400	-0.79%	5.42%	-0.62%	4.35%
BDE 47	0.0260	0.000030	0.00002 - 0.00400	-2.48%	13.56%	3.21%	6.43%
BDE 100	0.0131	0.000030	0.00002 - 0.00400	-0.97%	8.05%	2.70%	2.67%
BDE 99	0.0181	0.000030	0.00002 - 0.00400	-1.22%	5.53%	1.73%	3.94%
BDE 154	0.0293	0.000080	0.00002 - 0.00400	-3.45%	10.88%	6.19%	8.87%
Sum BDE Congeners	0.0476	0.00010	0.00012 - 0.02400	-1.45%	4.57%	2.62%	3.44%
Benzo(a)Pyrene	0.0160	0.000030	0.00002 - 0.02500	0.61%	5.79%	0.24%	6.96%
Benzo(b)Fluoranthene	0.0933	0.00020	0.00020 - 0.04000	-0.20%	7.64%	1.46%	10.37%
Benzo(k)Fluoranthene	0.0994	0.00020	0.00020 - 0.04000	-0.04%	7.99%	4.05%	8.07%
Indeno(123cd)Pyrene	0.0668	0.00020	0.00020 - 0.04000	-0.54%	10.54%	-1.07%	9.46%
Benzo(ghi)Perylene	0.0689	0.00020	0.00020 - 0.04000	-1.81%	11.90%	1.15%	11.38%

Compound	Accreditation	LOD (ng/L)	MRL(µg/l)	Range of Method	Low/CLOI Standard		High Standard	
					Bias	RSD	Bias	RSD
Tributyl Tin	MCERTS	0.0435	0.000100	0.00002 - 0.00400	-3.70%	8.92%	-1.91%	8.99%

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## Matrix Spike Recoveries

Compound	Surface Water		Ground Water		Saline Water	
	Recovery	RSD	Recovery	RSD	Recovery	RSD
1,3,5-Trichlorobenzene	99.52%	9.54%	100.03%	8.20%	98.58%	11.08%
1,2,4-Trichlorobenzene	100.94%	10.28%	98.01%	8.68%	99.32%	11.04%
1,2,3-Trichlorobenzene	102.10%	10.60%	101.42%	9.28%	99.85%	10.96%
TCB - Total	100.89%	9.75%	99.79%	7.47%	99.30%	10.81%
Hexachlorobutadiene	99.53%	11.37%	100.30%	8.54%	98.87%	11.82%
Tributyl Tin	97.04%	9.00%	101.31%	6.59%	98.19%	5.58%
Pentachlorobenzene	102.61%	7.22%	104.41%	5.20%	102.85%	6.14%
Trifluralin	97.89%	7.60%	97.50%	6.19%	100.93%	7.98%
Hexachlorobenzene	99.46%	6.75%	102.90%	5.07%	101.88%	4.43%
alpha-HCH	102.50%	5.41%	102.23%	3.27%	102.56%	3.58%
gamma-HCH	100.26%	7.46%	101.71%	4.42%	101.19%	6.00%
beta-HCH	99.81%	5.99%	100.24%	6.97%	98.57%	6.96%
delta-HCH	97.28%	9.45%	100.29%	8.33%	97.55%	8.04%
epsilon-HCH	98.39%	8.21%	100.85%	6.27%	99.12%	5.64%
Total HCH	99.65%	6.85%	101.06%	5.14%	99.80%	5.23%
Anthracene	103.88%	8.70%	100.74%	5.25%	104.38%	6.72%
Heptachlor	95.06%	9.77%	98.18%	8.65%	95.92%	8.32%
cis-Heptachlor Epoxide (isomer B)	100.60%	8.42%	101.03%	10.11%	100.83%	8.72%
trans-Heptachlor Epoxide (isomer A)	96.16%	8.53%	98.17%	9.00%	97.42%	6.66%
Sum Heptachlor/Heptachlor Epoxide	96.30%	9.01%	99.12%	8.26%	98.06%	6.92%
Alachlor	102.49%	9.17%	103.98%	5.91%	104.91%	9.67%
Aldrin	96.12%	9.01%	100.99%	7.47%	97.98%	6.54%
Isodrin	97.14%	8.04%	100.32%	7.13%	98.61%	5.01%
Dieldrin	98.16%	10.26%	101.79%	9.51%	99.93%	8.85%
Endrin	99.64%	6.85%	101.07%	4.01%	100.09%	4.08%
Sum - Cyclo diene Pesticides	97.41%	7.92%	101.04%	6.24%	99.15%	5.26%
Terbutryn	103.37%	5.56%	102.87%	4.54%	101.83%	4.99%
Chlorpyrifos	102.16%	10.78%	101.82%	7.43%	99.03%	7.32%
Dicofol	113.97%	11.33%	114.61%	12.44%	112.75%	12.88%
Chlorfenvinphos	107.36%	9.08%	104.11%	7.51%	104.54%	9.32%
Cybutryne (Irgarol)	102.93%	13.08%	102.01%	6.84%	101.46%	4.79%
Fluoranthene	104.79%	6.73%	104.89%	4.86%	106.47%	7.73%
pp-DDE	100.78%	8.53%	106.98%	8.99%	107.95%	11.31%
op-DDT	100.86%	4.69%	101.45%	3.55%	101.88%	2.75%
pp-TDE (DDD)	101.82%	9.90%	101.39%	10.03%	99.87%	6.54%
pp-DDT	101.23%	4.61%	102.79%	2.74%	101.48%	2.40%
DDT - Total	100.67%	5.20%	102.77%	3.53%	102.61%	3.34%
Diflufenican	101.00%	8.46%	104.19%	7.06%	103.31%	8.89%
Quinoxifen	103.14%	5.83%	103.69%	5.65%	101.87%	5.84%
Aclonifen	98.18%	15.81%	98.63%	11.71%	94.83%	9.62%
BDE 28	98.07%	4.39%	100.33%	5.27%	101.09%	4.47%
BDE 47	100.74%	11.35%	104.15%	8.68%	98.48%	7.44%
BDE 100	99.70%	4.99%	102.60%	4.75%	99.81%	3.81%

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Compound	Surface Water		Ground Water		Saline Water	
	Recovery	RSD	Recovery	RSD	Recovery	RSD
BDE 99	98.86%	3.18%	100.26%	3.68%	99.34%	4.82%
BDE 154	101.87%	9.22%	101.71%	9.91%	102.58%	10.66%
Sum BDE Congeners	100.18%	5.51%	101.67%	4.04%	99.58%	3.86%
Benzo(a)Pyrene	98.93%	5.42%	103.04%	13.51%	96.53%	8.01%
Benzo(b)Fluoranthene	97.27%	12.91%	101.01%	13.30%	98.01%	12.96%
Benzo(k)Fluoranthene	98.73%	12.98%	98.75%	15.27%	101.81%	10.17%
Indeno(123cd)Pyrene	98.47%	8.80%	105.70%	11.75%	94.58%	11.97%
Benzo(ghi)Perylene	99.70%	6.73%	105.45%	13.14%	98.67%	8.49%

Compound	Balsall Common FE CLOI Spike		Balsall Common FE 80% Spike		Heanor FE CLOI Spike	
	Recovery	RSD	Recovery	RSD	Recovery	RSD
Tributyl Tin	82.6%	10.35%	80.1%	8.78	86.0%	7.06%

Compound	Heanor FE 80% Spike		Meriden FE CLOI Spike		Meriden FE 80% Spike	
	Recovery	RSD	Recovery	RSD	Recovery	RSD
Tributyl Tin	88.1%	4.46%	91.7%	8.40%	91.5%	10.02%

## 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%.

Compound	Relative UoM (%)	Minimum UoM (µg/L)
Aclonifen	34.5	0.00017
Alachlor	16.7	0.00009
Cyclodiene Pesticide (WFD sum)	18.5	0.00015
Aldrin	22.1	0.00010
Dieldrin	23.1	0.00008
Endrin	18.9	0.00011
Isodrin	16.4	0.00008
Anthracene	17	0.00021
Benzo(a)pyrene	11.9	0.000019
Benzo(b)fluoranthene	21.2	0.00007
Benzo(k)fluoranthene	24.2	0.00008
Indeno(1,2,3-c,d)pyrene	17	0.00017
Benzo(g,h,i)perylene	13.5	0.00009
Cybutryne	17.8	0.00003
DDT - Total WFD	13.3	0.00008
pp-DDE	17.9	0.000026

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Compound	Relative UoM (%)	Minimum UoM (µg/L)
pp-DDD (TDE)	21.6	0.00003
op-DDT	10.2	0.00005
pp-DDT	10.5	0.00007
Diflufenican	17.9	0.00003
Dicofol	30.2	0.00006
Fluoranthene	14.5	0.00008
Total Heptachlor (WFD)	24.5	0.000027
Heptachlor	24.5	0.000008
cis-Heptachlor Epoxide	17.4	0.000013
trans-Heptachlor Epoxide	20.9	0.000017
Hexachlorobenzene	18.1	0.000013
Hexachlorobutadiene	23.2	0.00006
HCH - Total WFD	15	0.00012
alpha-HCH	14.5	0.000025
beta-HCH	14.1	0.000057
gamma-HCH (Lindane)	12.9	0.000085
delta-HCH	23.2	0.000026
epsilon-HCH	19.4	0.000029
Quinoxifen	11.1	0.000044
Chlorfenvinphos	25.5	0.00007
Chlorpyrifos	15.4	0.00005
Pentachlorobenzene	12.3	0.000025
PBDEs - Total WFD	8.8	0.00004
BDE 28	13.8	0.000008
BDE 47	21.9	0.000012
BDE 99	11.6	0.000016
BDE 100	13	0.000010
BDE 153	22.6	0.000016
BDE 154	18.3	0.000018
Terbutryn	12.8	0.00006
Tributyltin	14.6	0.000018
Trifluralin	17.3	0.00010
Trichlorobenzene - Total WFD	21.7	0.00031
1,2,3-Trichlorobenzene	19.6	0.00014
1,2,4-Trichlorobenzene	21.5	0.00014
1,3,5-Trichlorobenzene	23.3	0.00011
Tributyl Tin (MCERTS)	36.9	-

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## References:

EU Priority Substances Directive 2013  
Directive 2013/39/EC

EQS Substance Datasheet - Priority Substance No. 18. 2005

EQS Substance Datasheet - Priority Substance No. 14. 2005

Heptachlor EQS Dossier 2011