


**EnviroMail™ #99**
**November 2015**

# Super Trace PAHs & OCPs to meet ADWG & ANZECC 99% protection limits plus improve precision and accuracy

## BACKGROUND

For many years laboratories have been testing OC pesticides and PAHs to trace levels. One of the challenges for industry is that every lab offers different LORs and chemicals (OCPs in particular) and that comparing results to regulatory limits was difficult across different levels of protection with no one method meeting all levels.

ALS had generally offered OC Pesticide LORs of 2-10 ppt (0.002-0.010µg/L) and PAHs at 5 to 20ppt depending on the matrix (e.g. drinking water or other clean matrices).

This allowed industry to meet ADWG however complying with ANZECC 99% or even 95% protection for fresh and marine waters was often out of reach. Industry also commented that the ALS Benzo(a)pyrene LOR of 0.005 µg/L was only half of the limit and that they would really like a better margin between the LOR and the guideline. This limited the monitoring of some pristine environments or provided a situation where any positive detect at LOR could immediately present as a guideline breach. This was less than desirable when assessing some POPs.

## NEW ALS SUPER ULTRA-TRACE CAPABILITIES

The ALS R&D team has successfully validated methods across multiple water matrices and now offer NATA accredited testing down to low ppt levels. One pleasing aspect of this methodology is the phenomenal precision, accuracy and quality benefits achieved, thereby delivering increased confidence for practitioners assessing the data.

In keeping with ALS manual handling objectives, the LORs are achieved using standard ALS 500ml Amber bottles and prices will be at about the same level as the ultra-trace rates of 2014 to avoid significant cost increases.

## METHOD AND LOR INFORMATION

PAHs - EP132-ST            LORs: 0.001-0.004 µg/L  
 OCPs - EP131A-ST        LORs: 0.001-0.002 µg/L

## LORS FOR SELECT OC PESTICIDES VS ANZECC

One of the most challenging suites of ultra-trace tests for persistent organics pollutants (POPs) in water are the OC pesticides. This is in part due to the incredibly low limits needed, but also due to the range of interfering chemicals and impact of even the smallest traces of sediment. Much like the potential false positive scenario impacting PAHs in EnviroMail™28, even a trace of sediment can have a significant positive impact on OC Pesticide analyses. Sample quality is therefore imperative.

The other key consideration with ultra-trace analysis is how accurate and precise is the laboratory data? Lower recoveries or poor precision can occur with some ultra-trace methods.

Table 1 below is familiar to many industry experts and not all limits could be met in the past. New ALS methods substantially overcome this issue with many LORs five or ten times below 99% trigger levels for both fresh and marine waters. In addition the PAH LORs have also reduced (see overleaf (P3) for full reporting).

**Table 1 - Australian and New Zealand Guidelines for Fresh and Marine Water Quality - October 2000.**

3.4.2 How guidelines are developed for toxicants									
Chemical	Trigger values for freshwater (µg/L <sup>-1</sup> )				Trigger values for marine water (µg/L <sup>-1</sup> )				
	Level of protection (% species)				Level of protection (% species)				
	99%	95%	90%	80%	99%	95%	90%	80%	
Isophorone	ID	ID	ID	ID	ID	ID	ID	ID	ID
<b>ORGANOCHLORINE PESTICIDES</b>									
Aldrin	B	ID	ID	ID	ID	ID	ID	ID	ID
Chlordane	B	0.03	0.08	0.14	0.27 <sup>c</sup>	ID	ID	ID	ID
DDE	B	ID	ID	ID	ID	ID	ID	ID	ID
DDT	B	0.006	0.01	0.02	0.04	ID	ID	ID	ID
Dicofol	B	ID	ID	ID	ID	ID	ID	ID	ID
Dieldrin	B	ID	ID	ID	ID	ID	ID	ID	ID
Endosulfan	B	0.03	0.2 <sup>A</sup>	0.6 <sup>A</sup>	1.8 <sup>A</sup>	0.005	0.01	0.02	0.05 <sup>A</sup>
Endosulfan alpha	B	ID	ID	ID	ID	ID	ID	ID	ID
Endosulfan beta	B	ID	ID	ID	ID	ID	ID	ID	ID
Endrin	B	0.01	0.02	0.04 <sup>c</sup>	0.06 <sup>A</sup>	0.004	0.008	0.01	0.02
Heptachlor	B	0.01	0.09	0.25	0.7 <sup>A</sup>	ID	ID	ID	ID
Lindane	B	0.07	0.2	0.4	1.0 <sup>A</sup>	ID	ID	ID	ID
Methoxychlor	B	ID	ID	ID	ID	ID	ID	ID	ID
Mirex	B	ID	ID	ID	ID	ID	ID	ID	ID
Toxaphene	B	0.1	0.2	0.3	0.5	ID	ID	ID	ID

Brisbane, Sydney, Melbourne (Springvale), Perth, Newcastle, Roma, Darwin, Adelaide, Townsville, Mackay, Gladstone, Wollongong, Nowra, Mudgee, Chinchilla, Emerald Water Resources Group: Canberra, Bendigo, Geelong, Melbourne (Scoresby), Wangaratta, Traralgon

## PRECISION, ACCURACY AND LORS FOR SELECT OCPs AND PAHS

This new ALS methodology has significant benefits with respect to Quality as follows;

- The Previous ALS Super Ultra Trace PAH method had an average recovery across the 16 PAHs of 97% with an average RSD of 14% at 5ppt. The new Super Trace PAH method has an average recovery of 99-106% over three matrices at the LOR of 1ppt with an incredibly tight overall average RSD of 7.8% at 1ppt.
- The Previous ALS Super Ultra Trace PAH method had an average recovery for Benzo(a)pyrene of 88% with an average RSD of 10% at 5ppt. The new ST method has an average recovery of 87-96% and an average RSD of 6.4% at 1ppt.
- The Previous ALS UT OC Pesticides method had an average recovery across the OCPs of 81% with an average RSD of 13% at 1ppt. The new Super Trace OC Pesticide method has an average OCP recovery of 97, 102 and 105% for each of the three matrices validated at the LOR of 1ppt with an incredibly tight overall average RSD of 6.3%

This method performance not only provides lower LORs but significant benefits to quality (precision and accuracy) and enhances overall confidence in the results for comparison to guidelines given the lower reporting limits.

## REPORTING AND LORS FOR SELECT OCPs AND PAHS

The new OCP EP131A-ST method reports 22 OC Pesticides plus two summed analytes. Key analytes are shown below with limits and ALS LORs. The ALS objective was reporting an LOR of less than half the Limit with a method MDL of less than a tenth of the lowest guideline limit. This objective was achieved as shown below.

The new PAH method reports 21 PAHs plus a sum of the 16 priority PAHS and a PAH TEQ.

Analyte	MDL <sup>(1)</sup> (µg/L)	LOR (µg/L)	Trigger Value Fresh Water 99% protection (ANZECC)	Trigger Value Marine Water 99% protection (ANZECC)
Aldrin	<0.0001	0.001	ID	ID
Chlordane	~0.0001	0.001	0.03	ID
DDT	~0.0003	0.002	0.006	ID
Dieldrin	~0.0002	0.002	ID	ID
Endosulfan	~0.0002	0.002	0.03	0.005
Endrin	~0.0002	0.002	0.01	0.004
Heptachlor	~0.0002	0.002	0.01	ID
Lindane	<0.0001	0.001	0.07	ID
Benzo(a)pyrene	~0.0002	0.001	ID (0.01 ADWG guideline)	-
Phenanthrene	0.0001	0.002	ID	-
Chrysene	0.0001	0.001	ID	-

<sup>(1)</sup> MDL is provided as a rounded average value across three matrices validated. .

## SAMPLING CONSIDERATIONS, SAMPLE CONTAINERS AND TEST COMMUNICATION

With ultra-trace testing, it is very important to consider whether the samples are likely to be of a 'pristine' nature. Samples should not be submitted containing high levels of TRH and other organics (without discussion) and PAH LORs may be raised for dirty matrices. High levels of TRH will also result in LOR increases for OCPs. Another key consideration is the impact of even the smallest traces of sediment as discusses in [EnviroMail 28 \(link follows\) EnviroMail28 Super Ultra-Trace PAHs in water July 2008](#)

This new ALS methodology can only be performed using ALS traceable 500mL Amber bottles. Both OC Pesticides and PAHs can be simultaneously extracted for analysis and therefore one bottle will meet both combined analytical needs. Additional bottles should be provided for lab duplicates (1 in 10) and matrix spikes (1 in 20) however for simplicity it is recommended that one sample in every batch have three bottles provided every 10 samples or part thereof. To avoid confusion with other ultra-trace methods please record the method codes EP132-ST and EP131A-ST on COCs.

## REFERENCES

*Australian and New Zealand Guidelines for Fresh and Marine Water Quality - October 2000*

Brisbane, Sydney, Melbourne (Springvale), Perth, Newcastle, Roma, Darwin, Adelaide, Townsville, Mackay, Gladstone, Wollongong, Nowra, Mudgee, Chinchilla, Emerald  
Water Resources Group: Canberra, Bendigo, Geelong, Melbourne (Scoresby), Wangaratta, Traralgon



OC Pesticides - Super Trace Analytes, CAS Numbers and LORs				
Method	Analyte	CAS Number	LOR	Units
EP131A-ST	Aldrin	309-00-2	0.001	µg/L
	alpha-BHC	319-84-6	0.001	µg/L
	beta-BHC	319-85-7	0.001	µg/L
	gamma-BHC (Lindane)	58-89-9	0.001	µg/L
	delta-BHC	319-86-8	0.002	µg/L
	cis-Chlordane	5103-71-9	0.001	µg/L
	trans-Chlordane	5103-74-2	0.001	µg/L
	4,4'-DDD	72-54-8	0.002	µg/L
	4,4'-DDE	72-55-9	0.002	µg/L
	4,4'-DDT	50-29-3	0.002	µg/L
	Dieldrin	60-57-1	0.002	µg/L
	alpha-Endosulfan	959-98-8	0.002	µg/L
	Endosulfan sulfate	1031-07-8	0.002	µg/L
	beta-Endosulfan	33213-65-9	0.002	µg/L
	Endrin	72-20-8	0.002	µg/L
	Endrin ketone	53494-70-5	0.002	µg/L
	Endrin aldehyde	7421-93-4	0.002	µg/L
	Heptachlor	76-44-8	0.002	µg/L
	Heptachlor epoxide	1024-57-3	0.002	µg/L
	Hexachlorobenzene (HCB)	118-74-1	0.002	µg/L
Methoxychlor	72-43-5	0.002	µg/L	
Oxychlordane	27304-13-8	0.002	µg/L	
Sum of Aldrin + Dieldrin	309-00-2/60-57-1	0.002	µg/L	
Sum of cis- and trans-Chlordane	57-74-9	0.001	µg/L	
Sum of DDD + DDE + DDT	72-54-8/72-55-9/50-2	0.002	µg/L	
Sum of alpha- and beta-Endosulfan	115-29-7	0.002	µg/L	
PAHs - Super Trace Analytes, CAS Numbers and LORs				
Method	Analyte	CAS Number	LOR	Units
EP132-ST	Acenaphthene	83-32-9	0.002	µg/L
	Acenaphthylene	208-96-8	0.002	µg/L
	Anthracene	120-12-7	0.001	µg/L
	Benzo(a)anthracene	56-55-3	0.002	µg/L
	Benzo(a)pyrene	50-32-8	0.001	µg/L
	Benzo(b+j)fluoranthene	205-99-2 205-82-3	0.004	µg/L
	Benzo(e)pyrene	192-97-2	0.001	µg/L
	Benzo(g,h,i)perylene	191-24-2	0.002	µg/L
	Benzo(k)fluoranthene	207-08-9	0.004	µg/L
	Chrysene	218-01-9	0.001	µg/L
	Coronene	191-07-1	0.002	µg/L
	Dibenz(a,h)anthracene	53-70-3	0.001	µg/L
	7,12-Dimethylbenz(a)anthracene	57-97-6	0.002	µg/L
	Fluoranthene	206-44-0	0.001	µg/L
	Fluorene	86-73-7	0.002	µg/L
	Indeno(1,2,3,cd)pyrene	193-39-5	0.002	µg/L
	3-Methylcholanthrene	56-49-5	0.004	µg/L
	2-Methylnaphthalene	91-57-6	0.002	µg/L
	Naphthalene	91-20-3	0.004	µg/L
	Phenanthrene	85-01-8	0.002	µg/L
	Perylene	198-55-0	0.002	µg/L
	Pyrene	129-00-0	0.001	µg/L
	Sum of 16 US EPA Priority PAHs	None	0.001	µg/L
	Benzo(a)pyrene TEQ (zero)	None	0.001	µg/L
	Benzo(a)pyrene TEQ (half LOR)	None	0.001	µg/L
	Benzo(a)pyrene TEQ (LOR)	None	0.001	µg/L

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