

A New Benchmark Method for Trace Level Organochlorine Pesticides in Sediments & Soils



Dredging of sediments containing historical contaminants such as OCPs can pose environmental risks

Background

Organochlorine pesticides (OCPs) are synthetic chemicals that have had worldwide historical use for pest control, primarily as agricultural insecticides. Of the original twelve Persistent Organic Pollutants listed in the Stockholm Convention, eight are OCPs. Although restrictions against their use have been in place for decades in most industrialized nations, OCPs are highly persistent, and remain prevalent in the sediments of harbours and waterways near cities or sources of agricultural runoff. These compounds are hydrophobic, strongly associated with carbon and fine sediment, and bioaccumulative. Their deleterious effects occur primarily through ecotoxicological impacts, even at trace levels. Comparing environmental concentrations of these contaminants to applicable guidelines and ecological criteria is important for the protection of sediment dwelling (benthic) organisms and to prevent bioaccumulation and biomagnification to higher trophic levels of the food chain. Canadian and US sediment guidelines for OCPs are very low, often in the low partsper-trillion range. Measurement of OCPs at such low levels in soils or sediments poses significant challenges, particularly due to the potential for co-extracted interferences.

GC-MS/MS: The New Benchmark for OCP Testing

Until recently, the most reliable method to measure OCPs in soils and sediments at such challenging regulatory levels utilized gas chromatography with high resolution mass spectrometry (GC-HRMS), based on US EPA Method 1699, as offered by ALS Canada through our Burlington laboratory. The GC-HRMS method is extremely valuable to achieve the lowest possible reporting limits (more than 10x below the lowest guidelines) with exceptional selectivity, but it is a complex and labour-intensive test. Following innovative method development and extensive validation, ALS Canada (Waterloo laboratory) now offers a new option for a highly selective, accurate, and precise method using gas chromatography with tandem mass spectrometry (GC-MS/MS) to achieve trace level OCP detection limits in soils and sediments with near-zero potential for interferences. This new GC-MS/MS method meets most soil and sediment standards across Canada and the USA. While not achieving as low detection limits as GC-HRMS, the new procedure is more efficient, with a comparable degree of confidence and certainty. This provides environmental practitioners with the opportunity to test more samples to better delineate soil or sediment contaminant hotspots, potentially allowing for a reduction in quantities and costs for treatment or disposal. The delivery of faster results is a further benefit to clients managing major projects.



Port dredging: commercially important, but risks must be managed.

Classical OCP Test Methods

OCPs are often found in sediments and soils that contain hydrocarbons or other organics at much higher levels. With classical test methods using gas chromatography with either electron capture detection (GC-ECD) or single quadrupole mass spectrometry (GC-MS), co-extracted organic compounds often interfere with the detection of OCPs and can cause false positives,

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false negatives, or raised reporting limits. Prior to the availability of GC-MS/MS, high resolution mass spectrometry (HRMS) was the only option to overcome these analytical challenges for trace level analysis.

The Selectivity of MS/MS

The use of MS/MS detection greatly reduces the possibility of false positives or false negatives, especially for trace analysis. This is clearly shown in Figure 1 below with a comparison of mass chromatograms for methoxychlor spiked at 10 µg/kg in a soil sample and analyzed by routine GC-MS and by the new GC-MS/MS method. With the classical GC-MS method, co-extracted organic components present large interference peaks and background that creates uncertainty regarding the presence and concentration of methoxychlor. What could have been disregarded as background by classical GC-MS is clearly and unambiguously identified as methoxychlor by GC-MS/MS. The MS/MS detector provides highly selective and definitive measurements because it detects only those substances that generate a unique fragment ion (daughter ion) that originated from a specific parent ion. The measurement of "mass transitions" gives a second dimension of selectivity versus classical GC-MS, where only the parent ion is quantified.

Figure 1. Selectivity Example of GC-MS/MS





Dredged sediments may transfer legacy contaminants to terrestrial sites.

Data Quality of GC-MS/MS Method

Together with its vastly improved selectivity and sensitivity versus classical methods, the precision and accuracy of the Trace GC-MS/MS method sets a new benchmark for data quality, as illustrated by method validation results shown in Table 1. The benefits of the GC-MS/MS method for OCP testing are substantial: significantly improved accuracy and precision, with much lower detection limits, and greatly improved confidence due to near-elimination of interferences and background. The new method is currently accredited to the ISO 17025 quality standard for 29 OCP analytes; please refer to ALS Waterloo's current <u>CALA Scope of Accreditation</u> for details. Initial blind Proficiency Test results for the method were excellent, averaging

92% of reference values for OCPs in four soil samples. Independent 3rd party verification of performance gives additional confidence for the use of the GC-MS/MS method for new or ongoing projects where data quality assurance is crucial.

Table 1: GC-MS/MS Method Precision & Accuracy

	Mid-Level Spike Performance 0.01 ug/g	
Parameter	Average Recovery	Precision RSD
Aldrin	96%	1.7%
alpha-BHC	98%	1.7%
beta-BHC	98%	1.8%
gamma-BHC (Lindane)	96%	1.7%
delta-BHC	99%	0.5%
alpha-Chlordane	105%	2.9%
gamma-Chlordane	99%	0.4%
oxy-Chlordane	102%	2.3%
o,p-DDD	102%	0.3%
p,p-DDD	102%	0.9%
o,p-DDE	101%	0.5%
p,p-DDE	99%	0.8%
o,p-DDT	103%	1.6%
p,p-DDT	102%	1.5%
Dieldrin	101%	2.4%
alpha-Endosulfan	99%	2.8%
beta-Endosulfan	104%	1.9%
Endosulfan Sulfate	100%	1.1%
Endrin	94%	2.8%
Endrin Aldehyde	94%	2.3%
Endrin Ketone	104%	1.3%
Heptachlor	97%	1.2%
Heptachlor-Epoxide	98%	1.7%
Hexachlorobenzene	97%	2.3%
Hexachlorobutadiene	100%	1.7%
Hexachloroethane	98%	3.7%
Methoxychlor	102%	1.6%
Mirex	105%	0.3%
trans-Nonachlor	107%	3.5%
Pentachloronitrobenzene	99%	2.5%
Average:	100%	1.7%

Applications

ALS has designed this method to meet the most commonly used Canadian federal and provincial guidelines and standards, as well as some example sediment guidelines from the USA, as listed below:

- » CCME Sediment Quality Guidelines for the Protection of Aquatic Life, Freshwater and Marine Interim Sediment Quality Guidelines (ISQGs) and Probable Effect Levels (PELs), 1998.
- » BC Contaminated Sites Regulation, Schedule 3.1 Soil Standards and Schedule 3.4 Sediment Standards, 2019.
- » Alberta Tier 1 Soil and Groundwater Remediation Guidelines, 2019.
- » Saskatchewan Environmental Quality Guidelines, 2015.
- » Ontario Reg. 153/04 Table 1, Full Depth Background Site Condition Standards, Sediment, 2011.
- » Ontario Provincial Sediment Quality Guidelines (PSQG) for Confined and Unconfined Fills, 2011.

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- » Sediment Evaluation Framework for the Pacific Northwest, Proposed Screening Levels (Freshwater Benthic, Marine Benthic, and Water Quality), 2018.
- » US EPA Regional Implementation Manual for the Evaluation of Dredged Material Proposed for Disposal in New England Waters (2004).

Guidelines and standards in the USA vary by state, region, and disposal type, but the Limits of Reporting (LORs) for ALS Waterloo's Trace GC-MS/ MS method will meet all but the lowest and most challenging limits. Table 2 compares our Trace GC-MS/MS and Ultra-Trace GC-HRMS LORs to the Guidelines and Regulations mentioned above. ALS Burlington's EPA 1699 GC-HRMS method is recommended where the absolute lowest possible detection limits are required; reporting limits for this method vary by sample as per EPA 1699 guidance (MDLs are shown in Table 2).

Table 2: ALS OCP Reporting Limits Compared to Regulations/Guidelines

Sampling and Contact Information

Soil or sediment samples submitted for Trace OCPs require a 120 mL glass jar with Teflon lined lid. The same jar may also be used for other tests such as PAHs, metals and mercury analysis, and for TOC if required for normalization of data. Particle sizing and leaches require additional sample. Default LORs shown for the ALS GC-MS/MS method are on a dry sample weight basis, for up to 50% moisture content in the sediment or soil sample. LORs will be increased for samples with higher moisture contents; to minimize potential LOR increases, we recommend to discard any overlying water during sampling or prior to submission of sediment samples.

Please contact your ALS Account Manager or <u>ALSWTInfo@alsglobal.com</u> for more information about the new Trace GC-MS/MS sediment/soil Method.



^b Pacific Northwest proposed WQ based screening level (0.007 μg/g).

Pacific Northwest Total Chlordane screening level is for alpha-chlordane + gamma-chlordane + oxy-chlordane + cis-nonachlor + trans-nonachlor

Legend

ALS Waterloo Trace Method LOR is at least 10X lower than the regulation / guideline ALS Waterloo Trace Method LOR is at least 5x lower than the regulation / guideline ALS Waterloo Trace Method LOR is equal to or below the regulation / guideline