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# Determination of organochlorine pesticides in sediment using graphitized carbon black solid-phase extraction and gas chromatography/mass spectrometry

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ABSTRACT

An analytical method for the determination of organochlorine pesticides (OCPs) in sediment samples involves ultrasonic extraction, solid-phase extraction (SPE), gas-chromatography (GC)/electron-capture detection (ECD), and GC/mass spectrometry (MS). OCPs were extracted from sediment samples by ultrasonication in mixtures of *n*-hexane and acetone. Several SPE sorbents [Florisil, silica gel, C18, Oasis HLB, and graphitized carbon black (GCB)] were evaluated as means of preliminary purification. GCB SPE cartridges successfully removed major contaminants such as non-polar hydrocarbons when eluted with an acetone–acetonitrile mixture. After purification, the extract was preferentially screened using GC/ECD and confirmed and quantified using GC/MS. The percentage recovery of samples spiked with 10 or 100 ng/g OCP ranged from 73.9% to 106.0% with a relative standard deviation of 0.4–5.7%. Detection limits ranged from 0.002 to 0.005 ng/g for GC/ECD and from 0.03 to 0.50 ng/g for GC/MS detection. The linear dynamic range extended from 0.2 to 20 ng/g, with a correlation coefficient ($R^2$) greater than 0.995. The method was validated using a standard reference material (SRM 1941b) and spiked sediment samples. Real sediment samples collected from a river near a Korean industrial area exhibited low levels of several OCPs when analyzed using this method.

## 1. Introduction

Organochlorine pesticides (OCPs) and other persistent organic pollutants are of great concern due to their longevity, endocrine-disrupting effects, and bioaccumulation [1–3]. Despite a ban on OCP production effective since the mid-1970s, OCPs have recently been found in air [4], water [5], soil [6], and sediment [7,8]. In aqueous and marine environments, OCPs tend to have strong affinities for suspended particulates and accumulate in sediment. The determination of OCP levels in sediment can therefore indicate the level of contamination and bioaccumulation in aquatic organisms. Recently, many countries have developed analytical methods for monitoring persistent organic pollutants and OCPs in the environment.

Numerous analytical methods have been reported to not only detect the presence of pesticides in soil and sediment, but also to measure their concentrations with both precision and accuracy [9–11]. The conventional approach to analysis of chlorinated compounds in environmental samples involves extraction followed by a multi-step purification using various adsorbents. Typical extraction techniques include Soxhlet extraction [12], supercritical fluid extraction (SFE) [13], pressurized liquid extraction (PLE) [14], microwave-assisted extraction (MAE) [15], and ultrasonic extraction (UE) [16]. Although Soxhlet extraction requires several hours and large volumes of organic solvents, it is relatively inexpensive and typically yields satisfactory analyte recovery. SFE, PLE, and MAE do not require as much solvent or extraction time, but these methods are expensive and involve other complex parameters.

UE is rapid, simple, and amenable to multiple, simultaneous extractions. In addition, UE has been widely applied to the extraction of chlorinated organic pollutants from sediment, soil, and biological samples due to its relatively short extraction time, easy operation, and flexible solvent requirements [17,18].

During the extraction of chlorinated pollutants from solid environmental samples such as soil, sediment, and sludge, less polar interferents may be co-extracted in large amounts along with the

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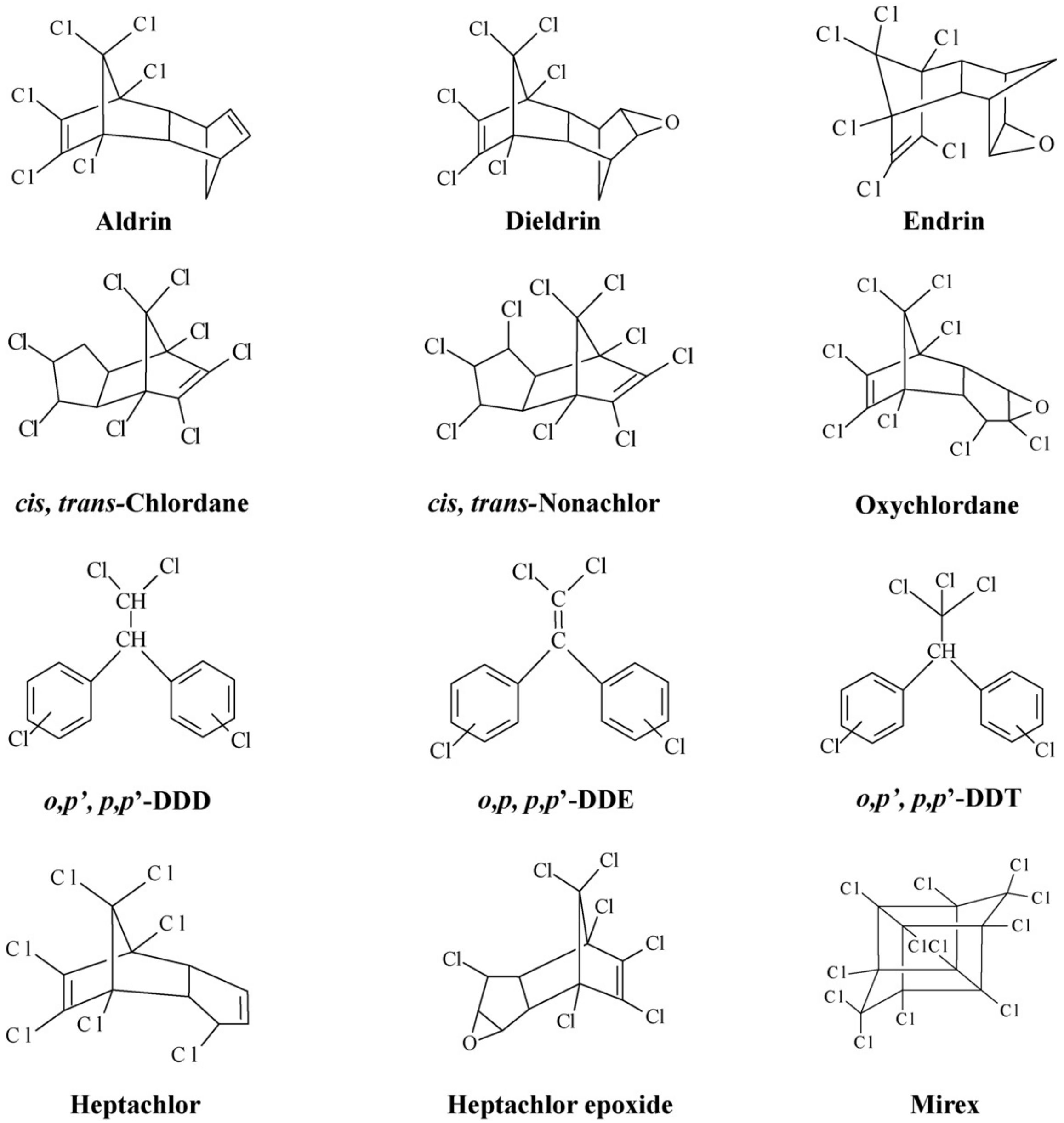

**Fig. 1.** Chemical structures of organochlorine pesticides (OCPs) investigated in this study.

target materials due to their high solubility in organic solvents. These interferents can affect chromatographic performance, resulting in analytical inaccuracies and decreased instrumental precision.

Several approaches have been developed for obtaining accurate results in gas chromatography (GC) or GC/mass spectrometry (MS) analyses while simultaneously eliminating co-extraction of undesirables, including liquid–liquid partitioning [19], size-exclusion chromatography [20], conventional column chromatography [21], and multi-step chromatography [22]. However, most of these methods are time-consuming and use large volumes of organic solvents.

Recently, solid-phase extraction (SPE) has become an important technique, boasting low cost, short processing time, and minimal solvent usage. SPE cleanup methods use various sorbents, such as Florisil, silica, and alumina, to eliminate interfering species from soil and sediment extracts [23,24]. SPE cartridges containing C18 [25], Oasis HLB [26], and graphitized carbon black (GCB) [27] have been used to isolate pesticides from environmental samples. GCB-SPE cartridges are particularly adept at removing polar materials, such as pigments, as well as non-polar constituents [28,29]. Recently, a multi-residue analytical method was developed for the determination of pesticides in soil and sediment using an SPE sorbent combination to remove undesired matrix components [30]. An alternative method, solid-phase microextraction, has been developed for rapid determination of chlorinated pesticides in environmental media [31,32].

Numerous reported methods for OCP determination use GC with electron-capture detection (ECD) [33]. GC/ECD effectively and sensitively detects halogenated compounds and other species that contain electron-withdrawing groups. It has been widely used to screen for chlorinated pollutants in samples with complex matrices. However, ECD suffers from poor discrimination of co-eluted analytes in the gas chromatogram and a narrow dynamic range. For this reason, GC/MS in selected-ion monitoring (SIM) mode has become popular for the determination of chlorinated pesticides. GC/MS-SIM is highly selective and sensitive for chlorinated compounds and can be used to identify analytes detected by GC/ECD.