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Optimization of in-cell accelerated solvent extraction technique for the determination of organochlorine pesticides in river sediments

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ABSTRACT

Organochlorine pesticides (OCPs) are ubiquitous environmental contaminants with adverse impacts on aquatic biota, wildlife and human health even at low concentrations. However, conventional methods for their determination in river sediments are resource intensive. This paper presents an approach that is rapid and also reliable for the detection of OCPs. Accelerated Solvent Extraction (ASE) with in-cell silica gel clean-up followed by Triple Quadrupole Gas Chromatograph Mass Spectrometry (GCMS/MS) was used to recover OCPs from sediment samples. Variables such as temperature, solvent ratio, adsorbent mass and extraction cycle were evaluated and optimized for the extraction. With the exception of Aldrin, which was unaffected by any of the variables evaluated, the recovery of OCPs from sediment samples was largely influenced by solvent ratio and adsorbent mass and, to some extent, the number of cycles and temperature. The optimized conditions for OCPs extraction in sediment with good recoveries were determined to be 4 cycles, 4.5 g of silica gel, 105 °C, and 4:3 v/v DCM: hexane mixture. With the exception of two compounds (α -BHC and Aldrin) whose recoveries were low (59.73 and 47.66% respectively), the recovery of the other pesticides were in the range 85.35–117.97% with precision < 10% RSD. The method developed significantly reduces sample preparation time, the amount of solvent used, matrix interference, and is highly sensitive and selective.

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1. Introduction

Sediment plays an important role in the quality of aquatic ecosystems as it has long residence time and serves as an archive for pollution indexing [1]. However, post-depositional actions (such as water flow velocity, floods, tides or wave, desorption and various diagenetic processes) can mobilize and release back sediment bound pollutants into the overlying waters or transport them from the point of entry to other areas, where they can negatively impact the environment [2].

Among sediment pollutants, organochlorine pesticides have attracted wide attention over the years due to their ubiquitous anthropogenic origin, persistence, bioaccumulative and long range transportation [3]. Nine out of the initial “dirty dozen” persistent organic pollutants (POPs) identified by the Stockholm Convention on POPs in 2001 are organochlorine pesticides (OCPs) [4]. Together with their degradation products, OCPs are potentially toxic and have adverse impacts on aquatic biota, wildlife and human health [5–7].

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Although most OCPs were banned about three decades ago, their presence and effects still linger on due to their resistance to photochemical, biological and chemical degradation in the environment. In the aquatic environment, OCPs tend to accumulate in sediments and biota because of their hydrophobic character and low solubility in water [8].

Sediment is also a complex heterogeneous matrix with varying physical, chemical and biological characteristics [9] and as such, appropriate preparation procedures and techniques are necessary to detect and quantify their OCPs content. Although there are conventional methods for the determination of OCPs in sediment, most of them are long, laborious, and costly [10]. They also require constant operator attention as each step involves manual transfer of sample, which eventually increases the likelihood of introducing error that could affect the analytical results [11]. Sample preparation techniques alone have been demonstrated to account for greater than 30% of all laboratory error [12].

Soxhlet extraction is the most common and efficient method for the extraction of semi-volatile compounds from solid samples, and is used as a reference method for newly developed methods. However, the extraction time is relatively long. Up to 48 h of extraction has been observed in literature [13]. Ultrasonic extraction

is often used for extraction of solid samples because of its simplicity. Nevertheless, analytes are usually under recovered and recovery of < 60% has been encountered [14]. Microwave-assisted extraction is a more convenient method in terms of sample throughput and recoveries between 79.78% and 117.70% have been observed [15]. However, in terms of safety, extreme caution has to be exercised when microwave-assisted extraction is used for the extraction of organic compounds.

Therefore, a sample preparation technique that is quick, reliable, safe and automated for the detection of OCPs in sediments is highly desirable. Compared to established techniques such as Soxhlet and sonication, accelerated solvent extraction (ASE) generates results in a much shorter time. In addition, filtration and clean-up of solid samples can also be achieved as part of the solvent extraction process in a single step [16], which is lacking in microwave-assisted extraction. However, till date, extraction and clean-up are done separately when utilizing ASE for the extraction of OCPs in sediment [17–19].

To evaluate the possibility of combining the extraction and clean-up steps into a single ASE step for the extraction of OCPs, a 2⁴ factorial design of experiments was employed to screen and optimize the most significant factors that affect the analytical recovery of eighteen (18) OCPs in sediment. The variables considered were: ratio of dichloromethane in dichloromethane: n-hexane mixture, extraction temperature, extraction cycle and adsorbent mass. The optimized method was used for the extraction of OCPs in certified sediment (SRM 941b). All extracts were analysed using gas chromatography coupled with tandem mass spectrometry (GCMS/MS) operated in multiple reaction monitoring (MRM) mode and an optimum determination method for the mass spectrometric assays was also developed. This allows the detection of some organochlorine pesticides down to parts per trillion (ppt) levels. The method is very selective as well as highly sensitive and reduces the cost and time of analysis drastically.

2. Material and methods

2.1. Reagents and standards

Hexane, methanol and acetone used were all SupraSolv[®], ECD and FID grade and purchased from Merck Millipore (VIC, Australia). Dichloromethane, Honeywell Burdick and Jackson ACS/HPLC grade was purchased from Chem-Supply (SA, Australia).

Standard stock mixture (in hexane: toluene 2000 µg/mL) containing Alpha-benzene hexachloride (α -BHC), Beta-benzene hexachloride (β -BHC), Gamma-benzene hexachloride (γ -BHC), Delta-benzene hexachloride (δ -BHC), Heptachlor, Aldrin, Heptachlor-exo-epoxide, α -endosulfan, 1, 1-dichloro-2, 2-bis (p-chlorophenyl) ethylene (p,p'-DDE), Dieldrin, Endrin, β -endosulfan, p,p'-dichlorodiphenyldichloroethane (p,p'-DDD), p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT), Endrin aldehyde, Endosulfan sulfate, Endrin ketone, and Methoxychlor was purchased from Supelco Sigma-Aldrich Pty. Ltd (NSW, Australia). Pentachloronitrobenzene (5000 µg/mL in methanol) and 2, 4, 5, 6-Tetrachloro-M-Xylene (TMX) (200 µg/mL in methanol) from Supelco Sigma-Aldrich Pty. Ltd (NSW, Australia) were used as internal and surrogate standards, respectively. Intermediate standard solutions of 2 and 1 µg/mL each from the standard composite and surrogate solutions respectively as well as 50 µg/mL from internal standard solution were prepared from their respective stock standards by pipetting 10, 50 and 100 µL aliquots into 10 mL volumetric flasks and diluting to the mark with hexane and methanol, as appropriate. Six calibration standards ranging from 1 to 500 ng/mL were prepared by diluting the intermediate mixture and surrogate standard solutions while keeping the concentration of internal standard constant at 500 ng/mL throughout in the same manner as described above. All solutions were

stored in polytetrafluoroethylene (PTFE)-sealed glass vials covered with aluminum foil and kept under refrigeration at 4 °C. All solutions were used within nine months after receipt, which is less than the one year recommended for storage by the supplier and USEPA [20]. Calibration checks were routinely run to check the stability of the analytes.

Silica gel (230–400 mesh ASTM), copper (> 230 mesh ASTM) and acid washed calcined sea sand were purchased from Merck Millipore (VIC, Australia). Diatomaceous earth was obtained from Thermo Fisher Scientific Australia Pty Ltd (VIC, Australia). Silica gel was activated at 130 °C for 16 h, cooled in a desiccator and deactivated using 3.3% ultrapure water (UPW) with 18.2 M Ω cm resistivity before being used. Sea sand and diatomaceous earth were baked at 450 °C for 4 h, and then allowed to cool down in a desiccator. Copper was rinsed with hydrochloric acid and solvents (water, methanol, and dichloromethane) and then used to remove any sulfur that might be present in the sediment that would have interfered with chromatogram of the analytes.

3. Design of study and optimization

Univariate optimization approach involving changing one variable at a time in a systematic way and noting its effect on the analyte recovery is lengthy and ignores the possibility of interactions between the variables under investigation [21]. It is complex and protracted when large number of variables are involved [22] and, does not necessarily lead to robust extraction conditions nor does it provide reliable, quantitative models of the process that can be used for analyte recovery, optimization and quality control [23,24].

According to Kazmer et al. [23], the identification of optimal extraction conditions is best accomplished with Design of Experiments (DoE) approaches. DoE is a structured, efficient method that simultaneously investigates multiple experimental variables using a minimal number of experiments. DoE measures the response of every possible combination of factors and factor levels to evaluate the significance of the factors and their interactions at the lowest experimental costs [25].

A simplified overview of the design and analysis of two-level screening experiments is given in [26,27]. The main steps in the approach are to: identify the purpose of the design; identify the factors and factors settings that affect response; select a design to generate treatment combinations (design matrix) and experimentally run all treatments to obtain the responses; export response results into the design matrix and perform statistical analysis for obtaining the influence order of all factors and screening insignificant factors using ANOVA; use response surface methodology (RSM) to generate simulation cases with the remaining significant factors and run all simulations using a reservoir simulator; export simulation results for calculating response and perform statistical analysis for obtaining the response surface model; and perform further optimization to obtain and validate the optimal design [27]. Detailed mathematical and statistical theories behind DoE and RSM can be found in [28].

The preliminary evaluation of the significance of the variables and optimization process for the recovery of 18 OCPs in sediment were carried out using a two level factorial design. Maximum and minimum levels of each factor (Table 1) were established using data from previous unpublished experiments. The variables chosen were ratio of dichloromethane in dichloromethane: n-hexane mixture, extraction temperature, extraction cycle and adsorbent mass resulting in 16 treatments (Table 2). A pressure of 1500 psi (10,342.14 kPa) has been observed as the optimum extraction pressure for all ASE applications [29]. Therefore, a fixed pressure of 1500 psi (1034.21 kPa) is used for all ASE extractions in this study and pressure was not varied in the screening process. All the

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