Development of a Solid Phase Extraction Method for Agricultural Pesticides in Large-Volume Water Samples

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Keywords: solid phase extraction, large-volume sampling, pesticide

Abstract

An analytical method using solid phase extraction (SPE) and analysis by gas chromatography/mass spectrometry (GC/MS) was developed to determine trace levels of a variety of 41 agricultural pesticides and selected transformation products in high-elevation surface waters. Large-volume water sampling (up to 100 L) was employed because it was anticipated that pesticide contamination, if present, would be at very low levels. The target compounds comprise pesticides (and selected oxygen transformation products) known to have been extensively used in agriculture in the San Joaquin Valley, California, USA. Solid phase extraction using the polymeric resin Abselut Nexus was optimized to extract the pesticide analytes from water samples. A single determinative method using GC/MS with electron ionization was used for all analytes. Recoveries from 100 L of reagent water at 100 pg/L and 1 ng/L concentrations were generally greater than 75%, although dimethoate, disulfoton, and phorate were not recovered. Analysis of the extracts without cleanup yielded detection limits for the remaining 38 analytes between 0.1 and 30 ng/L. A silica cleanup with separate analysis of three eluant fractions improved detection limits for 37 of the compounds to between 6 and 600 pg/L in high-elevation surface waters.

1. Introduction

Methods with well established performance are available for the determination of pesticides in

fresh water at ng/L levels. They often involve solid phase extraction (SPE) of about 1 L of water, followed by GC/MS with selected ion monitoring (SIM) [1, 2]. Recently, advanced materials for SPE extraction have been investigated with separation by liquid chromatography and ultraviolet absorption detection (HPLC/UV) [3, 4].

Over the past decade, interest has grown in the occurrence and distribution of pesticides and other organic pollutants in less impacted environmental waters, such as rainwater [5], snow and ice cores [6], and remote surface water bodies [7-9]. This interest has driven the development of more sensitive analysis methods, generally using one of three general approaches: improving sensitivity and selectivity of the determinative instrumental method, increasing the fraction of extracted target compound that is analyzed, or increasing the total volume of water extracted. Selectivity of GC/MS for pesticides with high electron affinities can be enhanced by using negative chemical ionization (NCI), rather than the more common electron ionization (EI) [10]. Selectivity with either NCI or EI can be improved by the use of tandem mass spectrometry [11].

Microextraction can increase the fraction of extracted water sample analyzed. The most common variant of this approach is solid-phase microextraction (SPME) using a fiber coated with polydimethylsiloxane [12]. Saraji and Esteki achieved detection limits in the low ng/L range for derivatized carbamate pesticides using the single-drop liquid microextraction approach [13]. Derouiche et al. used headspace SPME with ion-trap MS/MS to detect as little as 0.4 ng/L of chlorinated pesticides in 2 mL of water [14]. Dispersive liquid-liquid microextraction (DLLME) was used by Berjani et al. to determine 13 pesticides at the low ng/L level in 5 mL water [15]. DLLME uses a dispersing solvent to produce a suspension of about 5 μL of dense organic

extracting solvent in the water sample. The extracting solvent is separated by centrifugation and about 10% of the total volume is injected into the GC/MS. Reguiero et al. used ultrasonification to form similar dispersions and obtained low ng/L detection limits for pesticicdes and musks in 10 mL of water (16). Xiong and Hu compared DLLME to hollow fiber liquid phase microextraction for the determination of organosulfur pesticides [17].

Large-volume injection (LVI) can increase the fraction of extracted analyte to the GC. Almeida et al. analyzed 20 μL of estuarine water extracts by LVI-GC/MS for 9 pesticides at low ng/L levels [18]. Sabik et al. injected 40 μL of a 250-μL SPE extract of water and obtained detection limits of 100-800 pg/L for 13 pesticides in river water [19].

Finally, large-volume water extraction can also increase sensitivity of pesticide determinations. Foster et al. used a Goulden liquid-liquid extraction system to sample or extract up to 120 L of water and obtained detection limits as low as 0.28 ng/L for lindane [20-21]. However, most large-volume water extractions use SPE due to its simplicity and ruggedness. Alegria and Shaw [22] used an XAD-2 SPE procedure originally employed by Ko and Baker [23] for the determination of polyaromatic hydrocarbons and polychlorinated biphenyls to analyze 76 L of sea water for sub-ng/L levels of triazine and organophosphate pesticides.

The large-volume water extraction method presented in this paper was developed for a study (Bradford et al., to be published) to evaluate the occurrence and temporal variation of airborne pesticides in high-elevation lakes of the Sierra Nevada Mountains in California, USA. Previous researchers have established the occurrence of trace levels of a few current-use pesticides and

several persistent discontinued organochlorine pesticides in multiple media in those mountains, presumably from airborne transport originating in the nearby Central Valley agricultural districts [10, 24, 25]. Recently, Usenko et al. developed a large-volume SPE method for 75 semivolatile compounds, including approximately 30 current-use pesticides and a variety of historic-use pesticides, as well as other persistent organochlorine compounds, in precipitation and surface water [26]. Using that method, Hageman et al. found chlorpyrifos and its oxon, dacthal (also known as DCPA), α- and β-endosulfan and their sulfate transformation products, and lindane, as well as four organochlorine compounds in snowpack at two sites in the Sierra Nevada [27].

The target analyte list for our method was 41 current-use pesticides (Table 1) of a wide range of polarities. The target detection limit range was less than 100 pg/L. Microextraction methods have not been demonstrated for detection limits this low, nor have LVI-GC methods on relatively low-volume extractions. Large-volume extraction was therefore chosen. Because of concerns regarding the use of organic solvents in a pristine environment, solid phase extraction was selected as the approach. Commercially available large-volume SPE devices [22, 23] were initially considered, but were too heavy and expensive for the field study that was planned. Therefore, a SPE method using a relatively small mass of functionalized polymeric resin was developed that was capable of extracting the analytes from 100 L of water in the field. Analyses of extracts were performed using GC/MS in EI mode. A silica cleanup with separate GC/MS analysis of three fractions was developed to improve detection limits.

2. Experimental

2.1. Chemicals and reagents

Mixed pesticide standards and internal standards for GC/MS analysis were purchased from Chem Services Inc. (West Chester, PA, USA). Organic solvents were obtained from Mallinckrodt and J.T. Baker (Phillipsburg, NJ). Working standards were prepared by appropriate dilution with Ultra Resi-Analyzed® grade ethyl acetate (ETAC). All standards were stored in a freezer at -15°C. Anhydrous, granular sodium sulfate (Tracepur) obtained from EM Science (Gibbstown, NJ) was baked in the oven at 400°C for 6 hours. Glasswool treated with dimethyldichlorosilane was purchased from Alltech Associates (Arlington Heights, IL). Solid phase sorbents: PPL (functionalized styrene-divinylbenzene polymer), Abselut Nexus [polystyrene crosslinked with 50% divinylbenzene and poly(methylmethacrylate)] silica, and C_{18}-funtionalized silica were obtained from Varian Inc. (Harbor City, CA). Amberlite XAD-2 (divinylbenzene styrene copolymer) was purchased from Axys Environmental Systems Ltd. (Sidney, British Columbia, Canada). Polypropylene cartridges (12, 60 and 140 mL) and matching polyethylene frits (20-µm pore size) were also purchased from Varian. Glass cartridges (8 mL) and PTFE frits (pore size 20-µm), used to prepare the silica columns, were obtained from Mallinckrodt Baker.

2.2. Extraction and evaporation apparatus

Large-volume water samples (100 L) were pumped *in situ* through the resin column using a ceramic, valveless pump (QB pump, Q1CKC pump head; Fluid Metering Inc., Syosset, NY)

powered by a 12-volt, 12-amp hour battery. Lake and stream water samples were filtered on-line with a 142-mm diameter, 0.7 μm glass fiber filter (Whatman, Inc., Florham Park, NJ) before extraction by the resin sorbent. All tubing was made of PTFE or PFA Teflon™. The column was attached to the sampling tubing by a laboratory-constructed stainless steel bung fitting. A stainless steel Swagelok tee (Arizona Valve & Fitting, Phoenix, AZ) fitted with a silicon septum (Supelco/Sigma-Aldrich, St. Louis, MO) was placed just before the column to allow analyte amendment of the water. Non-phosphate detergent solution (Micro 90, Cole-Parmer, Vernon Hills, IL), deionized water and HPLC grade methanol were used to clean the extraction assembly between sampling. The Turbo-Vap II and Turbo-Vap 500 used for evaporating eluants were purchased from Zymark (Hopkinton, MA).

2.3. Extraction sorbent selection procedure

Pre-cleaned sorbent material (C_{18} functionalized silica, Amberlite XAD-2 resin, Bond Elut PPL, or Abselut Nexus) was obtained in bulk.

One liter reverse osmosis water (RO or reagent water)containing 5 μg of each pesticide was passed through 2g of each solid phase sorbent at a flow rate of 40 mL/min. Pesticide analytes were eluted with successive portions of 15 ml each of n-hexane, n-hexane/ethyl acetate (1:1, v/v) and ethyl acetate. The excess water trapped in the resin was removed mainly in the n-hexane fraction. The aqueous layer was pipetted out of the n-hexane solvent, and extracted three times with 2-mL portions of n-hexane. The eluates and n-hexane washes were combined and dried

over anhydrous sodium sulfate, concentrated to 1 mL and solvent exchanged to ethyl acetate using the Turbo-Vap II evaporator at 30°C under a gentle stream of nitrogen.

2.4. Final large-volume water extraction and analyte elution procedure

All water extractions were conducted at approximately 250 mL/min using 8 g of Nexus resin packed in the 140-mL polypropylene syringe barrels. Reagent water and surface waters were used for recovery and method detection limit studies. Surface water samples were pumped in the field from one high-elevation (3091 m) lake and two lower elevation (500-900 m) streams in the southern Sierra Nevada.

Analyte recoveries in 100 L RO water samples were performed in triplicate and at two fortification levels (100pg/L and 1ng/L). Surface water samples were collected in duplicate. After extraction, the Nexus columns were wrapped in baked aluminum foil and stored at -25 ºC until elution. Prior to elution, resin columns were brought to room temperature and dried under ca. 0.5-L/min ultra-pure nitrogen for at least 1 hour, until the resin was free-flowing and no evaporative cooling of the syringe barrel was noticeable. Analytes were eluted with 400 mL of dichloromethane (DCM) by gravity. The eluant was reduced to a final volume of ca. 1 mL at 23 ºC with the Turbo-Vap 500 closed cell concentrator and exchanged to n-hexane for silica cleanup as described in section 3.2.3.

2.5. Instrumentation

All analyses were performed using an Agilent 6890A capillary gas chromatograph and 5973N mass selective detector (Agilent Technologies, Palo Alto, CA) using EI SIM mode. The gas chromatograph was fitted with a 30-m x 0.25-mm ID fused silica capillary column coated with a 0.25-µm film of crossbonded 5% diphenyl - 95% dimethyl polysiloxane (Restek Corporation, Bellefonte, PA) with an integrated deactivated guard column of 5-m x 0.25-mm ID fused silica. The injector used was a Gerstel CIS 4 inlet (Mühlheim, Germany), equipped with a programmable temperature vaporizer (PTV) and a 71-mm x 2.0-mm ID deactivated baffled liner. Pesticide-grade, deactivated, packed liner was initially investigated and found to be very susceptible to creating active sites. Sample extracts were introduced into the GC injector using a Gerstel MPS 2 autosampler equipped with a 10-µL syringe.

A 1-µL sample was injected into the inlet liner in a pulsed-splitless mode. Ultrapure helium was used as carrier gas. The initial injector temperature was at 200°C and rapidly heated to 300°C (in approx. 8 s). A pulsed pressure of 174 kPa (25 psi) was applied during injection and held for 0.75 min. After the initial pressure pulse, the carrier gas flow was held constant at 1 mL/min. The oven temperature program was: 50 °C for 1 min, 35 °C/min to 150 °C, 7 °C/min to 290 °C, 100 °C/min to 300 °C, and held 1 min. The total program required 24.96 min. The ions listed in Table 1 were monitored in the SIM mode.

3. Results and discussion

3.1 Sorbent Selection

The pesticide compounds (Table 1) exhibit a wide range of polarities [28, 29] however; they do not fall into the highly-polar or the non-polar category. With this in mind, C_{18}-functionalized silica, XAD-2, PPL and Abselut Nexus were chosen as potential solid phase sorbents. Preliminary extraction experiments were first conducted with C_{18}-functionalized silica and XAD-2 solid phase sorbents. Recoveries were fair for most of the analytes, but somewhat variable, especially for the more polar compounds. PPL and Abselut Nexus yielded similar average recoveries: 95% and 97%, respectively, for the analytes evaluated. Recoveries with Nexus were more consistent between compounds, with a standard deviation of 12%, compared with 19% for PPL. In addition, Nexus was designed for extractions without the need for preconditioning with methanol, which is an advantage for field work. Therefore, Nexus was chosen for further evaluation, and no preconditioning was used after the initial solid phase comparison study.

3.2 Development of the solid phase extraction procedure using Abselut Nexus

After selecting Abselut Nexus as the most suitable sorbent for the target pesticides, an extraction procedure for large volume water samples was developed and optimized. The complete extraction protocol is outlined in Figure 1. Analyte amendment was performed using an injection port located just before the Nexus cartridge. A battery powered metering pump (section 2.2.) was used to deliver the large volume water samples to the Nexus cartridges. The amount of resin necessary for optimum extraction of pesticide analytes from a 100 L water sample was

determined by conducting a breakthrough experiment in which large volume water samples amended with 5 µg of each analyte were pumped through 8-g Nexus columns followed by 4-g Nexus columns. The cartridges were then separated and treated separately. For every analyte except dimethoate, the initial 8-g of resin recovered >97% of the compound. The 8-g column recovered ~60% of the dimethoate.

3.2.1 Solvent selection for analyte elution

Recoveries by three elution procedures were evaluated: sequential 160-mL volumes of n-hexane, n-hexane/ethyl acetate (1:1, v/v), and ethyl acetate (procedure 1); 400-mL of dichloromethane (procedure 2); and 400-mL acetone (procedure 3). The extracts from each procedure were solvent exchanged into 1 mL of ethyl acetate and analyzed by GC/MS to determine the recoveries for 5 µg of each pesticide. Dichloromethane provided higher recoveries on average (95% vs. 87% and 88% for the sequential hexane-ethyl acetate system and the acetone eluant, respectively) and more consistency among the analytes (8% vs. 12% and 18%, respectively). Remaining experiments were therefore conducted with dichloromethane as the elution solvent.

3.2.2. Sorbent drying and eluant evaporation temperature studies

Initial analyte elutions were performed on extraction sorbents that had been briefly purged with nitrogen to remove excess moisture. In addition, the remaining water in the eluant required extensive drying with sodium sulfate. More complete removal of water from the sorbent with

nitrogen without subsequent sodium sulfate drying was evaluated. One liter of reagent water, fortified with the suite of pesticide compounds (5 µg each), was applied to each Nexus cartridge. Before elution using solvent procedure 1, approximately 0.5 L/min of nitrogen was passed through the extraction cartridges for drying periods of 60 and 150 minutes. Passing N_2 over the 8-g Nexus bed for 1 hour removed almost all the water trapped in the resin. As shown in Figure 2, there was little difference between those recoveries and the recoveries obtained after 2.5 hours drying, except for the carbamates among which EPTC, butylate, and pebulate were the most affected. Recoveries improved for these analytes with the 2.5 hour gas purge, after which the Nexus was visibly free flowing, indicating nearly complete water removal. Apparently, even small amounts of residual water affect GC analysis of the early-eluting analytes. As an added drying step, 300-mg sodium sulfate was added to the silica clean-up column in the final procedure.

The effect of solvent evaporation temperature was studied to see if evaporation time could be reduced. Duplicate samples of 400 mL of dichloromethane containing 5 µg of each analyte were concentrated in the Turbo-Vap 500 apparatus at 23, 35 and 58 ºC. Figure 2 shows the recoveries obtained for the three evaporation temperatures. Aside from the eight most volatile analytes (EPTC, butylate, pebulate, prophos, ethylfluralin, trifluralin, benfluralin, and phorate), there was no trend among the three temperatures for the rest of the analytes. For the eight most volatile compounds analyzed, significant losses occurred at temperatures above 23 ºC, and that temperature was used in the final method.

3.2.3. Silica fractionation cleanup

A multi-solvent cleanup on silica was developed to isolate the pesticide analytes from water matrix coextractants. The pesticides were eluted from the silica column based on increasing order of polarity and were collected in several solvent fractions (Figure 1).

The initial elution with n-hexane removed polymer residues and other lipophilic matrix components but none of the target analytes. The pyrethroids (cis- and trans- permethrin), DCPA and most of the carbamate-, aniline-, and organochlorine- pesticides were eluted in the 8:2 and 4:6 n-hexane-dichloromethane fractions. Hexanedioic acid and other interfering compounds were collected in the dichloromethane fraction. The 1:1 DCM-ETAC solvent mixture eluted the organophosphate pesticides and oxygen analogues, leaving chlorophyll and other organics on the column.

3.2.4. Holding time study

We mentioned earlier, that the large-volume water extraction method was developed for a study to evaluate the occurrence and temporal variation of airborne pesticides in high elevation lakes of the Sierra Nevada Mountains in California. Because of the remoteness of the sampling locations, it was anticipated that field samples may not be analyzed within the first days of collection but will be kept frozen to await analysis. The short term and long term stability of the pesticide analytes on the Nexus sorbent was then studied. This was performed using Nexus cartridges spiked with 5 ug each pesticide in water. The wet cartridges were kept in a freezer at -25C and analyzed after two, fifteen and 30 days of storage. One of the samples was kept for one year.

The recoveries obtained for a two-day and one-year old samples are presented in Table 2. Prolonged storage of the Nexus cartridges did not affect the recovery of the majority of the pesticide compounds. The eluate from the 1-year old sample extract was accidentally evaporated to dryness and reconstituted in ethyl acetate. Fractions of the more volatile species could have been lost during the evaporation process which could explain in part the lower recoveries obtained for butylate, ethalfluralin and pebulate. Recoveries for disulfoton and phorate were 50 and 66%, respectively. These two compounds were later dropped in the study because of erratic recoveries in standard mixtures and sample extracts.

3.2.5. Large-volume water extraction recoveries

Pesticide analytes spiked into alpine lake water extracts and laboratory reagent waters were effectively recovered after silica clean up. There was no significant difference between the alpine lake water matrices and the reagent water in the fractions analyzed.

Recoveries obtained with the final large-volume water analysis procedure were evaluated at both 100 pg/L and 1ng/L analyte concentrations. Each amendment level was extracted in triplicate. The results, presented in Table 2, indicate average recoveries of 70%-130% at both concentrations for 22 analytes. Eight compounds had moderately elevated recovery (130%-150%) at one of the concentrations. Azinphos-methyl and the oxygen analog of chlorpyrifos exhibited recoveries in excess of 150% and high variabilility at the higher amendment concentration. The three most volatile analytes (EPTC, butylate, and pebulate), as well as lindane and fonofos, gave lower recoveries (50%-67%), although the precision of the recovery

was generally better than 10% (absolute standard deviation). This precision was similar for most of the analytes and indicated that determinations of these compounds could be useful, depending on data quality objectives. The oxygen analogs of azinphos-methyl and phosmet did not exhibit acceptable chromatographic sensitivity for analysis below 1 ng/L, and they were deleted from the method. Recoveries for dimethoate, disulfoton, and phorate were near zero at both concentrations. Interestingly, the results of the breakthrough experiment and sample holding time study, conducted at higher analyte concentrations, indicated incomplete retention only for dimethoate. The poor recoveries obtained for the three compounds at these lower concentrations indicate that the incomplete retention was not due to exceeding the capacity of the Nexus but rather to low partitioning of the analytes to the solid phase.

3.3. Estimated method detection limits

The instrument and method detection limits were determined as the concentrations at which the peak heights for the quantification ion and two other ions exceed 10 σ of the background at the analyte retention time, and the ratios of the qualifying ions to the quantification ion meet an intensity ratio criterion of ±30 %. In addition, the retention time of the peak must match the expected retention time within ±0.05 min. Instrument detection limits were estimated in ethyl acetate. Method detection limits for reagent water were determined using pooled data of four 100-L reverse osmosis water extractions. Method detection limits for surface waters were

estimated from the pooled data of two high-elevation lakes and two low-elevation stream water extractions.

Estimated instrument detection limits (IDLs) ranged from 0.6 to 60 pg/μL (Table 3), and IDLs for 40 of 41 analytes were ≤20 pg/ μL. These correspond to ≤200 pg/L equivalent water concentration (a 1-μL GC-MS injection contains the analytes extracted from ca. 0.1% of the water sample, or 0.1 L of water). Oxygen analogs of organophosphate pesticides had generally higher IDLs than the parent compounds.

Method detection limits (MDLs) for reagent water and surface water averaged 100 and 140 pg/L, respectively, for 37 of the 38 compounds that exhibited significant recovery. A large m/z interference near the retention time of cyanazine limited reliable detection of that compound to concentrations exceeding about 1000 pg/L in all samples.

The effectiveness of the fractionated silica clean-up procedure in reducing matrix interferences can be seen in Table 3 by comparing the MDLs for the reagent water and surface water with the MDLs in the last column estimated from the peak-to-peak noise of lake water extracts that were analyzed without fractionation of the clean-up eluants. The MDLs without cleanup are at least 3 times greater than those with cleanup for 31 of the 38 recovered compounds. MDLs for 16 analytes were improved by at least a factor of 10 by cleanup. The improvement in the MDL achieved by discarding some fractions of the silica cleaned extract is illustrated in Figure 3 for the DCPA extracted from 100 L of lake water.

The detection limits obtained with this method were sufficient to conduct a large scale study to measure agricultural pesticides in four lakes at high elevation in Sequoia and Kings Canyon National Park which were selected to represent sites relatively near and far the San Joaquin Valley. Chlorothalonil, chlorpyriphos, DCPA, endosulfan I, endosulfan II, simazine and trifluralin were detected in multiple samples collected at these sites during June and October. Four of the compounds were found at concentrations and at frequencies that allowed the evaluation of temporal patterns (results of the temporal variation study are presented in a paper by Bradford et al, to be published).

4. Conclusions

The large-volume water extraction presented in this paper provides recoveries and detection limits sufficient to permit the detection of 38 of 41 targeted current-use pesticides and transformation products at concentrations at or below 500 pg/L in surface water. Detection of 29 analytes was possible at or below 100 pg/L. Recoveries of four target compounds (azinphos-methyl, chlorpyrifos oxon, disulfoton and phorate) were poor, and those compounds are not suitable for analysis at pg/L levels by this method. The detection limits reported here were suitable for our intended use, so no attempts were made to further lower them. However, about 20 of the 38 compounds recovered by this method yielded MDLs essentially unaffected by matrix in the cleaned-up analysis, as demonstrated by the agreement between the IDL and the MDL (Table 3). This indicates that either further reducing the final extract volume or using LVI-GC could significantly reduce those MDLs. Finally, alternative determinative methods to GC-MS, such as GC coupled with inductively coupled plasma mass spectrometry, could be

investigated as a complementary technique for the analysis of phosphorus- and other heteroatom-containing pesticides.

This method is well suited to field studies of trace concentrations of 38 pesticides and degradates, covering a wide range of agricultural and domestic uses. It has superior detection limits to microextraction techniques used to improve sensitivity. It does not require the large volumes of organic solvent required for liquid-liquid extraction. The SPE resin used does not require the preconditioning needed with other solid phases, so there is no need for the use of organic solvents at environmentally sensitive sites. The method is particularly advantageous for sampling in remote locations accessible only on foot because the field extraction units are light. They are also inexpensive, facilitating parallel duplicate extractions. The field water extraction procedure is easily learned by sampling personnel with no chemistry background, and it can run unattended while other tasks are performed by the field teams. The fact that many analytes are stable on the resin for extended periods is advantageous for studies where resources or logistics result in long holding times. Finally, although saline waters were not examined in this study, the resin has been used for extraction of many diverse media. Therefore, it is likely the method could be applied to a broad range of environmental waters, including brackish, estuarine, or marine systems.

Disclaimer

The United States Environmental Protection Agency funded the research described here. It has been subjected to Agency review and approved for publication. Mention of trade names and commercial products does not constitute endorsement or recommendation for use.

Acknowledgement

We are most grateful to Nellie Dujua and Pamela Pilger of the USEPA SEEP program for meticulously preparing the glassware and field extraction materials. We also thank Elizabeth Gentry, Patrick L. Ferguson, Tammy Jones-Lepp, Jason Scheick and Dr. Lantis Osemwengie for considerable help.

References

[1] S.D. Zaugg, M.W. Sandstrom, S.G. Smith, K.M. Fehlberg, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory— determination of pesticides in water by C-18 solid-phase extraction and capillary- column gas chromatography/mass spectrometry with selected-ion monitoring. U.S. Geological Survey, Open-File Report 95-181, 1995, 49 pp.

[2] USEPA. 2004. EPA Method 527--Determination of Selected Pesticides and Flame Retardants in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS). EPA 815-R-05-005. April 2005.

[3] Al-Degs, S. Yahya, Al-Ghouti, A.Mohammad, Int. J. Environ. Anal. Chem. 88 (2008) 487-498.

[4] N. Fontanals, R.M. Marce, P.A.G. Cormack, D.C. Sherrington, F. Borrull, J. Chromatogr. A 1191 (2008) 118-124.

[5] Malik, A., Singh, V. K., Singh, K. P., *Bull. Environ. Contam. Toxicol.* 2007, 79, 639-645.

[6] Wang, Xiao-ping; Yao, Tan-dong; Wang, Peng-ling; Wei, Yang; Tian, Li-de., *Sci. Total Environ.* 2008, 394, 134-143.

[7] Thurman, E. M.; Cromwell, A. E., *Environ. Sci. Technol.* 2000, 34, 3079-3085.

[8] Yao Zi-wei, Jiang Gui-bin, Xu Heng-zhen, Distribution of organochlorine pesticides in seawater of the Bering and Chukchi Sea, *Environ. Pollut*. 2002, 116, 49-56.

[9] Carroll, J., Savinov, V., Savinova, T., Dahle, S., McCrea, R., Muir, D. C. G., *Environ. Sci. Technol*. 2008, 42, 69-74.

[10] McConnell, L. L., LeNoir, J. S., Datta, S., Seiber, J. N., *Environ. Sci. Technol.* 1998, 17, 1908-1916. CODEN: ETOCDK ISSN:0730-7268. CAN 129:249930 AN 1998:634304 CAPLUS.

[11] Pitarch, E., Medina, C., Portoles, T., Lopez, F. J., Hernandez, F., Anal. Chim. Acta. 2007, 538, 46-258.

[12] Sauret-Szczepanski, N., Mirabel, P., Wortham, H., *Environ. Pollut. (Amsterdam, Neth.)* 2006, 139, 33-142.

[13] Saraji, M., Esteki, N., *Anal. Bioanal. Chem.* 2008, 391, 1091-1100.

[14] Derouiche, A., Driss, M. R., Morizur, J. P., Taphanel, M. H., *J Chromatogr. A* 2007, 1138, 231-243.

[15] Berijani, S., Assadi, Y., Anbia, M., Milani M. R., Aghaee, E., *J. Chromatogr. A* 2006, 1123, 1-9.

[16] Regueiro, J., Llompart, M., Garcia-Jares, C., Garcia-Monteagudo, J. C., Cela, R., *J. Chromatogr. A* 2008, 1190, 27-38.

[17] Xiong, J., Hu, B., *J. Chromatogr. A* 2008, 1193, 7-18.

[18] Almeida, C., Serodio, P., Florencio, M. H., Nogueira, J. M. F., *Anal. Bioanal. Chem.* 2007, 387, 2569-2583.

[19] Sabik, H., Rondeau, B., Gagnon, P., Jeannot, R., Dohrendorf, K., *Int. J. Environ. Anal. Chem.* 2003, 83, 457-468.

[20] Foster, G. D., Rogerson, P. F., *Int. J. Environ. Anal. Chem.* 1990, 41, 105-117.

[21] Foster, G. D., Gates, P. M., Foreman, W.T., McKenzie, S. W., Rinella, F. A., *Environ. Sci. Technol*. 1993, 27, 1911-1917.

[22] Alegria, H. A., Shaw, T. J., *Environ. Sci. Technol.* 1999, 33, 850-856.

[23] Ko, F. C., Baker, J. E., *Mar. Chem.* 1995, 49, 171-188.

[24] LeNoir, J. S., McConnell, L. L., Fellers, G. M.; Cahill, T. M.; Seiber, J. N., *Environ. Toxicol. Chem.* 1999, 8, 2715-2722.

[25] Fellers, G. M., McConnell, L. L., Pratt, D., Datta, S., *Environ. Toxicol. Chem.* 2004, 23, 2170-2177.

[26] Usenko, S., Hageman, K. J., Schmedding, D. W., Wilson, G. R., Simonich, S. L., *Environ. Sci. Technol*. 2005, 39, 6006-6015.

[27] Hageman, K. J., Simonich, S.L., Campbell, D. H., Wilson, G. R., Landers, D. H., *Environ. Toxicol. Chem*. 2006, 40, 3174-3180.

[28] Finizio, A., Vighi, M., Sandroni, D., *Chemosphere* 1997, 34, 131-161.

[29] U.S. Department of Agriculture. 2006. The ARS pesticide properties database. http://www.ars.usda.gov/Services/docs.htm?docid=14199.

Figure Captions

Figure 1. Schematic for extracting and purifying water samples before GC-MS Analysis

Figure 2. Average Recoveries of Pesticide Classes in Various Solvent Evaporation Temperatures and Solid Phase Drying Times

Figure 3. Quantitation ion chromatogram at (m/z 301) for DCPA of (a) combined fractions 2 and 3 of the extract of 100 L of alpine lake water after silica cleanup (as analyzed in final method), and (b) raw extract. DCPA concentration in lake water, was approximately 50 pg/L.

Table 1. Pesticides targeted in this study

Pesticide	CAS #	Monitored Ions[a]
Aniline pesticides		
Alachlor	15972-60-8	160, 188, 146, 237
Benfluralin	1861-40-1	292, 264, 276, 318
Ethalfluralin	55283-68-6	276, 316, 292, 333
Metolachlor	51218-45-2	162, 238, 240, 146
Pendimethalin	40487-42-1	252, 281, 162, 253
Trifluralin	1582-09-8	306, 262, 307, 290
Carbamates pesticidides		
Butylate	2008-41-5	217, 146, 156, 174
EPTC	759-94-4	189, 128, 132, 86
Pebulate	1114-71-2	203, 128, 132, 161
Carbaril	63-25-2	144, 115, 116, 145
Carbofuran	1563-66-2	164, 149, 122, 131
OC pesticides		
Chlorothalonil	1897-45-6	266, 264, 268, 124
Dicofol	115-32-2	251, 139, 253, 111
Endosulfan I	959-98-8	277, 239, 170, 265
Endosulfan II	33213-65-9	241, 195, 170, 237
Lindane	58-89-9	217, 181, 183, 219
Permethrin I	54774-45-7	183, 163, 165, 184
Permethrin II	51877-74-8	183, 163, 165, 184
OP pesticides and oxons		
Azinphos-methyl	86-50-0	160, 132, 104, 161
Chlorpyrifos	2921-88-2	314, 197, 199, 316
Chlorpyrifos oxon	5598-15-2	298, 270, 197, 242
Diazinon	333-41-5	304, 137, 179, 152
Diazoxon	962-58-3	273, 137, 288, 260
Dimethoate	60-51-5	87, 93, 143, 229
Disulfoton	298-04-4	88, 142, 186, 274
Fonofos	944-22-9	246, 109, 137, 110
Malaoxon	1634-78-2	127, 99, 109, 125
Malathion	121-75-5	173, 125, 127, 93
Methidathion	950-37-8	145, 125, 85, 93
Methyl parathion	298-00-0	263, 109, 125, 79
Methyl parathion oxon	950-35-6	247, 109, 230, 200
Phorate	298-02-2	75, 121, 260, 231
Phosmet	732-11-6	160, 161, 317, 104
Prophos	13194-48-4	242, 158, 139, 200
Tribufos	78-48-8	169, 170, 202, 113
Other pesticides		
Cyanazine	21725-46-2	240, 225, 173, 198
DCPA	1861-32-1	301, 299, 303, 332
Linuron	330-55-2	248, 61, 187, 160
Simazine	122-34-9	186, 173, 158, 203
Napropamide	15299-99-7	271, 72, 128, 100
Propargite	2312-35-8	135, 173, 81, 350

[a]Quantitation based on first m/z listed.

Table 2. Pesticide recoveries from Nexus sorbents after short term and long term storage at -25° C.

Pesticide	Stored - 2 days	Stored - 1 year
Aniline pesticides		
Alachlor	108	106
Benfluralin	84	76
Ethalfluralin	88	57
Metolachlor	109	111
Pendimethalin	96	95
Trifluralin	86	71
Carbamates pesticidides		
Butylate	84	50
EPTC	85	77
Pebulate	92	64
Carbaril	93	91
Carbofuran	NA*	NA
OC pesticides		
Chlorothalonil	87	76
Dicofol	82	NA
Endosulfan I	100	97
Endosulfan II	102	99
Lindane	98	72
Permethrin I + II	96	90
OP pesticides and oxons		
Azinphos-methyl	116	97
Chlorpyrifos	97	80
Chlorpyrifos oxon	109	59
Diazinon	106	94
Diazoxon	106	94
Dimethoate	69	72
Disulfoton	102	52
Fonofos	100	84
Malathion	110	113
Methidathion	111	78
Methyl parathion	94	98
Methyl parathion oxon	91	88
Phorate	96	66
Phosmet	103	95
Prophos	105	105
Tribufos	NA	NA
Other pesticides		
Cyanazine	114	110
DCPA	98	87
Linuron	130	118
Simazine	NA	NA
Napropamide	116	100
Propargite	95	110

* Not analyze

Table 3. Pesticide recoveries at two concentrations from extraction of 100 L water, instrument detection limits and estimated method detection limits

	Recoveries		IDL[a]	MDL[b]	MDL	MDL
	1 ng/L	100 pg/L		reagent water	surface waters	without clean-up
Aniline pesticides						
Alachlor	99 ± 11	94 ± 11	1.6	80	100	200
Benfluralin	83 ± 6	91 ± 6	6	80	40	200
Ethalfluralin	87 ± 5	78 ± 3	6	120	60	300
Metolachlor	105 ± 13	111 ± 5	60	80	120	200
Pendimethalin	90 ± 10	97 ± 7	8	200	140	3000
Trifluralin	85 ± 6	90 ± 7	8	120	40	200
Carbamates pesticidides						
Butylate	54 ± 3	61 ± 6	3	120	100	600
EPTC	56 ± 5	57 ± 5	6	140	80	400
Pebulate	67 ± 7	63 ± 4	4	60	60	200
Carbaril	122 ± 10	138 ± 10	1.4	4	200[c]	3000
Carbofuran	93 ± 14	82.1 ± 0.2	3	140	300	800
OC pesticides						
Chlorothalonil	75 ± 7	92 ± 12	2	30	14	60
Dicofol	93 ± 20	110 ± 27	8	40	300	600
Endosulfan I	77 ± 14	91 ± 10	2	40	30	800
Endosulfan II	100 ± 8	96 ± 6	4	60	100	6000
Lindane	60 ± 9	52 ± 10	3	120	100	600
Permethrin I	99 ± 4	81 ± 6	3	40	40	1200
Permethrin II	100 ± 6	80 ± 5	4	60	100	1200
OP pesticides and oxons						
Azinphos-Methyl	185 ± 30	135 ± 18	16	300	300	1200
Chlorpyrifos	82 ± 5	80 ± 5	2	30	20	200
Chlorpyrifos oxon	206 ± 56	84 ± 55	8	140	80	200
Diazinon	84 ± 4	99 ± 11	2	40	20	100
Diazoxon	136 ± 11	112 ± 8	10	160	60	600
Dimethoate	16 ± 3	NR[d]	14	NR	NR	NR
Disulfoton	Trace	4 ± 6	16	NR	NR	NR
Fonofos	52 ± 4	52 ± 21	2	80	100	140
Malaoxon	127 ± 19	141 ± 7	10	400	400	1000
Malathion	111 ± 2	96 ± 4	2	40	60	600
Methidathion	94 ± 10	90 ± 3	8	300	600	16000
Methyl parathion	102 ± 14	91 ± 4	1.4	30	30	300
Methyl parathion oxon	140 ± 21	90 ± 19	18	100	80	1000
Phorate	NR	NR	12	NR	NR	NR
Phosmet	151 ± 18	113 ± 13	12	300	600	3000
Prophos	93 ± 6	106 ± 19	4	120	80	160
Tribufos	106 ± 2	93 ± 8	3	80	100	4000
Other pesticides						
Cyanazine	125 ± 11	146 ± 13	3	1000[e]	1000[e]	1000[e]
DCPA	90 ± 10	91 ± 2	0.6	8	6	60
Linuron	122 ± 8	99 ± 6	4	30	30	300
Simazine	90 ± 11	111 ± 9	6	200	200	300

Napropamide	126 ± 7	139 ± 7	1.4	30	30	700
Propargite	117 ± 12	102 ± 4	20	300	400	30000

[a]Instrument detection limit, pg/L injected.
[b]Method detection limit for 100 L water extraction, pg/ L
[c]Mass interference near retention time in many surface water extracts elevated detection limit.
[d]Not recovered or poorly recovered.
[e]Mass interference precludes reliable detection below ca. 1000 pg/L.

Figure(s)

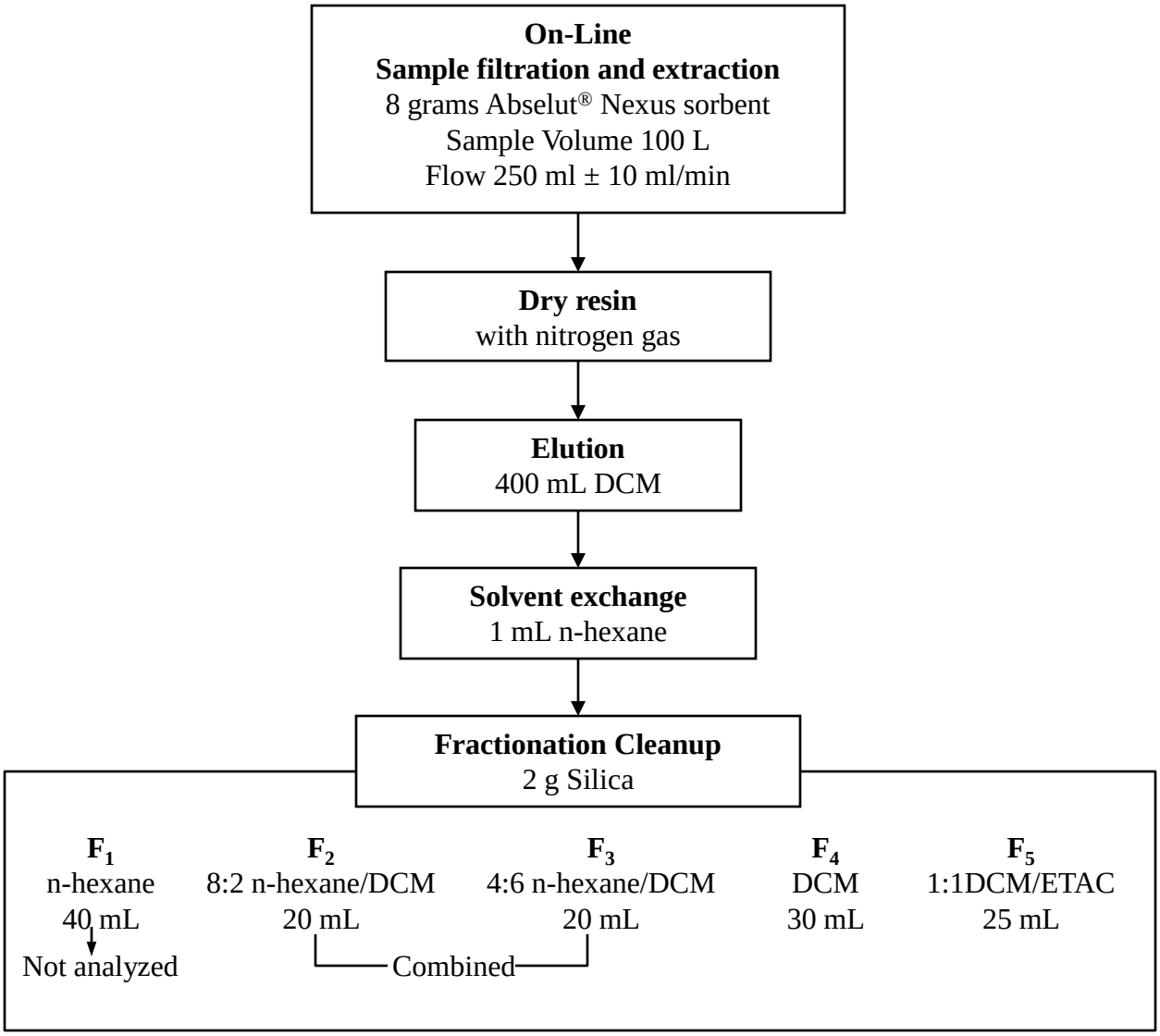

Figure 1

Figure(s)

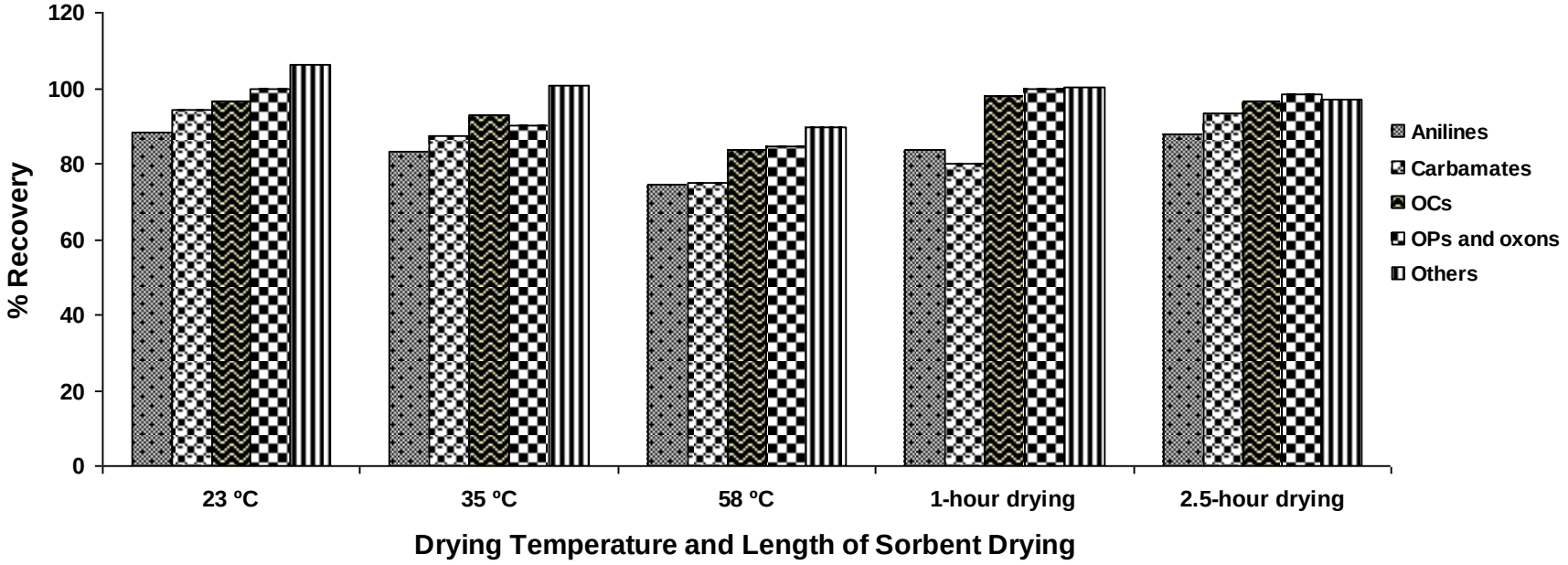

Figure 2

Figure(s)

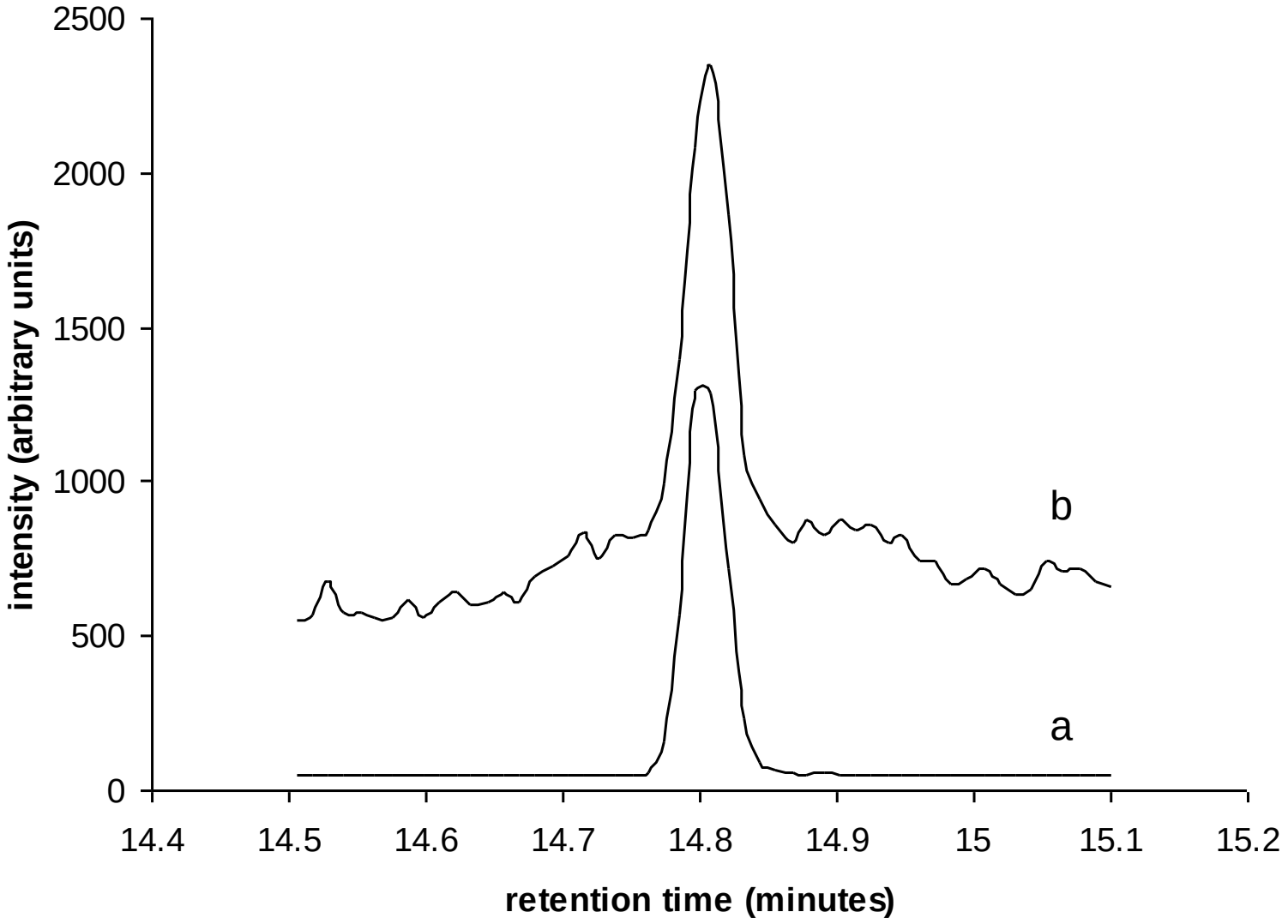

Figure 3