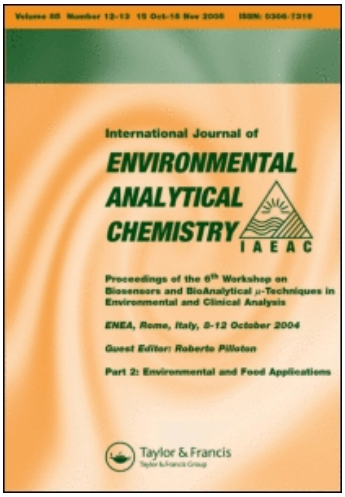

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A new design of equilibrium hollow fibre liquid phase microextraction (HF-LPME) was developed for the determination of three freely dissolved organophosphorus pesticides (OPPs), i.e. diazinon (*O*,*O*-diethyl-*O*-2-isopropyl-4-methyl-6-pyrimidyl thiophosphate), chlorpyrifos (*O*,*O*-diethyl-*O*-[3,5,6-trichloro-2-pyridyl] phosphorothioate), and fenthion (*O*,*O*-dimethyl-*O*-4-methylthio-*m*-tolyl phosphorothioate) as model compounds. In this new design a 1.2–1.4 cm length of a hollow fibre (HF), inserted to the end of 20 cm copper wire and impregnated with organic solvent, was used to extract the freely dissolved concentration of OPPs in various water samples. The limits of detection (LOD) in reagent water using gas chromatography-mass spectrometry in the selected ion monitoring (SIM) mode was in the range of 15–80 ng L^{-1}. The relative standard deviations of the analysis (inter- and intra-day) were 8.7–30%. The method was applied to the extraction of spiked lake and ground water samples. The ground water sample was spiked at 0.1 and 0.2 μg L^{-1} concentrations of the analytes under study and the average extraction efficiency at the two concentrations was below 1% showing the non-depletive nature of the extraction, meaning that the freely dissolved concentrations are measured as opposed to total concentrations. Good linearity was obtained for all of the analytes in both reagent water and lake water samples with correlation coefficients, R^2, ranging from 0.991 to 0.996, in the concentration ranges of 25–400 ng L^{-1}. The method was found to be very simple and inexpensive, with the possibility of running hundreds of samples in parallel with very minimal expenses for the determination of freely dissolved OPPs.

Keywords: freely dissolved concentration; hollow fibre liquid phase microextraction; organophosphorus pesticides; GC-MS; non-depletive extraction

1. Introduction

Urban and rural aquatic ecosystems are often polluted by a wide variety of contaminants from agricultural, industrial or municipal activities. The usual approach of environmental risk assessment regarding these contaminants is to collect a given quantity of matrix from one of the environmental compartments (i.e. water, sediment, soil and air) and determine

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the quantity of contaminants or analytes present in the sample. The determined concentrations from the analysis can be compared with objectives set or can be used to approximate the extent to which the given organism is exposed to the contaminant in that particular environmental compartment and deduce certain conclusion [1]. This approach actually does not distinguish between the amount of the contaminant available to the organism and amount which is bound to different media in that particular element of the environment.

There are considerable behavioural differences between bound and unbound environmental contaminants. In other words, the compounds' behaviour regarding aqueous mobility, biological uptake, bioaccumulation [2], sediment sorption [3,4] and potential toxic effect [5] would be changed notably when bound to dissolved organic matter (DOM) or other media in the matrix under investigation.

Therefore, from toxicological point of view it is very important to quantitatively determine the freely dissolved fraction of chemical contaminants in the environmental elements in order to evaluate and characterise their bioavailability. Hence, the values of these bioavailable fractions can be used for risk assessment studies and to estimate the maximum achievable degradation levels of these contaminants in different matrices [6–8].

Different methodologies have been developed for estimating the bioavailable fractions. The use of organisms or cells seems to be the preferred option [9], but they are typically slow and imprecise [7]. The application of non-exhaustive extraction techniques [7] is the other alternative to overcome the main limitations of the use of organisms.

For environmental purposes, the most commonly used non-exhaustive methods for sensing the freely dissolved concentrations (C_{free}) of pollutants include diffusion gradients in thin films (DGT) [10] for metals and semipermeable membrane devices (SPMDs) [11] as well as solid-phase microextraction (SPME) [12–14] for organic compounds. Most of the time the DGT and SPMDs are operated in the kinetic uptake regime as they need long time to reach equilibrium, while SPME was successfully used as an equilibrium sampling device due to its relatively short equilibration time [13]. In addition, Ramos *et al*. [15] have also found out that negligible depletion SPME was a good technique to determine bioavailable concentrations of hydrophobic chemicals in aquatic environments. The main drawback of SPME is its low extraction capacity for some polar analytes.

Over the last one decade a number of non-exhaustive, miniaturised liquid–liquid extraction (LLE) techniques have been introduced [16,17]. The most representative procedures of micro-LLE which are easy, fast and utilise only microlitres of toxic solvents are: single-drop microextraction (SDME) [18–23], continuous-flow microextraction (CFME) [24], supported-liquid membrane extraction (SLME) [25,26], liquid-phase microextraction (LPME) [21,27–30], hollow-fibre LPME (HF-LPME) [27–34], extracting-syringe technique (ESy) [35], microporous-membrane liquid–liquid extraction (MMLLE) [25] and membrane assisted solvent extraction (MASE) [36]. These sample preparation techniques are by their nature non-exhaustive or semi-exhaustive, and hence can be utilised for equilibrium extraction of freely dissolved analytes.

Recently, the freely dissolved concentrations (C_{free}) of chlorophenols [37] and copper ions [38] were determined by the use of equilibrium sampling through membranes (ESTM), based on HF-SLME in environmental water samples in our group. These works clearly showed the application potential of HF-LPME for the determination of freely dissolved organic and inorganic contaminants in environmental compartments. Moreover, the use of HF-LPME was found to be attractive because of the low-cost, disposable nature

of the polypropylene porous polymers [33,34,37–39] and the selectivity of the hollow fibre (HF) membrane because of the pores in its wall. Rasmussen and co-workers [33] have reviewed the developments in such HF-based liquid phase microextraction, its basic extraction principles, technical set-up, recovery, enrichment, extraction speed, selectivity, applications and the future trends.

In the majority of applications of HF-LPME, i.e. the two phase mode, a piece of HF of porous polypropylene (1.5–10 cm) was inserted at the end of the needle of microsyringe containing few microlitres of the organic solvent immiscible with water. Then the HF was impregnated with the organic solvents (1–2 μL) and placed in a sample vial containing 0.1–4 mL sample, depending on the application. At the end of extraction, the content of the HF lumen was injected into the separating instruments. In this kind of design a problem is that the extraction process needs the use of expensive microsyringes for its applications. Therefore, the analysis of a large number of environmental samples would be expensive as it requires many microsyringes for parallel runs or the sample preparation takes a very long time with limited number of microsyringes

One of the limiting factors, when it comes to developing countries where there is shortage of funds for environmental researchers, is the cost required to carry out the analysis of the type explained above. To partially overcome such problems, a new design of HF-LPME for the determination of freely dissolved organophosphorus pesticide, as model compounds, has been developed. The design explained in the current study was found to be simpler and inexpensive. We have also demonstrated the possibility of running hundreds of samples in parallel, with very minimal expenses, in each series of experiments.

2. Experimental

2.1 *Reagents and standards*

The pesticide standards, namely, diazinon, fenthion and chlorpyrifos were purchased from Dr Ehrenstorfer GmbH, Wesel, Germany.

Two types of stock solutions of 100 mg L^{-1} for each pesticide (diazinon, fenthion, chlorpyrifos) were prepared. One kind was prepared in ethyl acetate (BDH, Laboratory Chemicals Division, England) for calibration and the other in acetone (Analytical reagent, Techno Pharmchem, Bahadurgarh, India) for spiking during the method development. Mixed standard solutions of 10 mg L^{-1}, containing each of the pesticides was prepared in ethyl acetate and acetone. The working solutions with concentrations ranging from 0.025 to 0.25 mg L^{-1}, at five points, were prepared every week from the 10 mg L^{-1} stock solution for calibration. Another 10 μg L^{-1} mixture containing all pesticides was prepared in a mixture of water and acetone for spiking. Then, different concentrations of the organophosphorus pesticides (OPPs) mixture were prepared from the 10 μg L^{-1}. Methidathion (Dr Ehrenstorfer) was used as an internal standard for the gas chromatography-mass spectrometry (GC-MS) analysis. *n*-Undecane (Sigma-Aldrich, St. Louis, MO, USA), dihexyl ether (Fluka, Switzerland) and 1-octanol (Fluka, Chemie GmbH, Buchs, Germany) were tested for use as membrane solvents. All other chemicals; humic acid (Aldrich), sodium chloride (Labmerk Chemicals PVT Ltd, India), ethyl acetate (Sigma-Aldrich), acetone (Techno Pharmchem, Bahadurgar, India) and heptane (BDH, Poole, England) were of HPLC grade or of analytical grade. The HF used was of medium sized Q3/2 type with 0.2 μm pore size, 200 μm wall thickness and 600 μm inner diameter (Membrana GmbH, Wuppertal, Germany).

2.2 *Extraction procedure*

Twenty centimetre copper wire was inserted into one end of 2 cm long HF to the approximate depth of 0.5 cm. After that, the other end of the HF was sealed using a cigarette lighter flame. Then, the effective length of HF was about 1.2–1.4 cm.

The sealed HF was sonicated in the membrane solvent for about 1 min to clean the HF. Afterwards, it was impregnated with the same extraction solvent for about 4–5 min to fill up the wall as well as the lumen of the HF (Figure 1a). The soaked extraction unit (Figure 1b) was then rinsed with distilled water in a small beaker to remove excess organic solvent. Subsequently, the copper wire containing the HF was allowed to suspend in the sample bottle by tying it to a clamp or a rope which was tied to two stands, as shown in Figure 1c. The sample container for all types of extraction was an amber bottle to avoid any possible light interaction with the analytes. The sample bottle was with nearly zero headspace and also covered with aluminium foil. The extraction unit was inserted into the sample bottle through a small orifice, prepared in the middle of the foil covering the top of the bottle. The orifice was then completely covered with additional piece of aluminium foil. Then, at the end of the extraction the copper wire was removed from the sample bottle and put into a vial with insert (From Agilent Technologies) containing 40 μL ethyl acetate and internal standard. This was followed by sonication of the vial to washout all of the

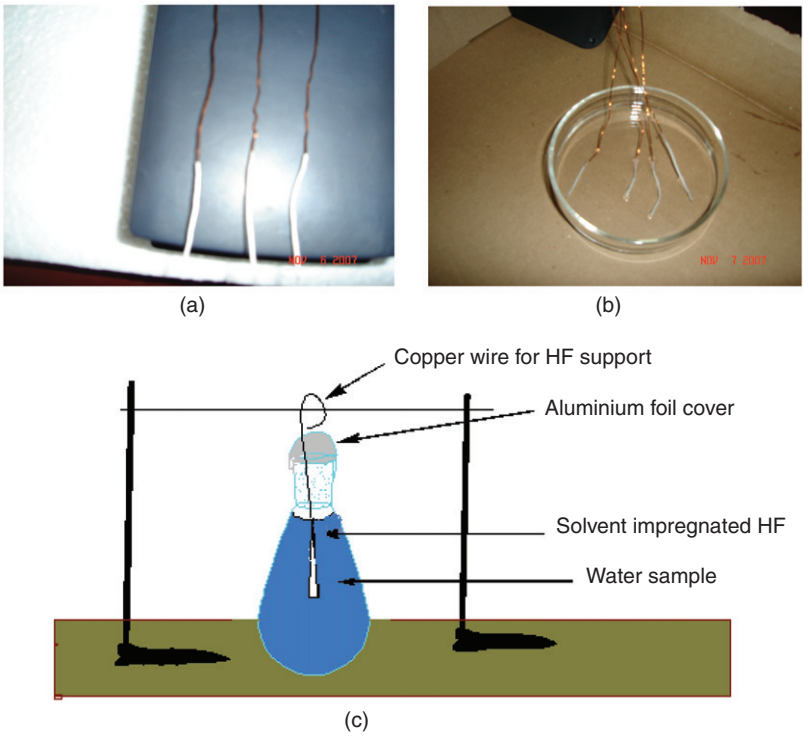

Figure 1. Extraction procedure using HF-LPME: (a) Copper wire was inserted into one of the HF for support; (b) impregnation of the HF in the extraction solvent and (c) hanging of the impregnated HF in the sample bottle covered with aluminium foil.

analytes extracted into the organic phase out of the HF pores and lumen. Afterwards, the vial was capped and put in an autosampler of GC-MS for injection into GC.

2.3 *Water sample collection*

Lake water and ground water samples were collected from Lake Awassa and nearby residential houses in Awassa town, respectively. The sampling sites were located in Southern Ethiopia, 275 km away from the capital city of the country. Blank and spiked extraction of the analyte from the water samples were performed as soon as the samples were brought to the Analytical Laboratory at the Department of Chemistry, Addis Ababa University. To investigate the impact of suspended particles, the real water samples were spiked without prior filtrations.

2.4 *Gas chromatography-mass spectrometric analysis*

The GC-MS analyses were performed using Agilent-6890 Gas Chromatograph (GC) interfaced with Agilent 5975 Mass Selective Detector (MSD), all from Agilent Technologies. The analytes were separated on a HP-5MS (30 m × 0.25 mm I.D., 0.25 μm film thickness) capillary column from Agilent (S & W Scientific, USA). The column was initially maintained for 1 min at 50°C, subsequently it was increased to 193°C at a rate of 50°C min^{-1}, then increased to 205°C at a rate of 1°C min^{-1} and finally increased to 260°C at a rate of 60°C min^{-1}. Helium was used as a carrier gas with a flow rate of 1 mL min^{-1} (6 min solvent delay). The inlet temperature was set to 250°C while interface and source temperatures were set to 280°C and 250°C, respectively. A split–splitless injector in the splitless mode was used for the injection of the standards and extracts. The injection volume was 1 μL. All concentrated sample extracts and standard solutions were analysed by 70 eV electron impact ionisation mode. The instrument was operated in the selected ion monitoring (SIM) mode for the quantitative analysis of the analytes. Four fragment ions were monitored for each compound, in order to maximise the detector signal, the most abundant and characteristic ion in the spectrum was selected for quantification, and three other peaks for confirmation purposes. Peak identification was based upon the scan mode of the GC-MS. Data acquisition and processing were made using the Chemstation software, obtained from Agilent Technologies.

3. Results and discussion

3.1 *General information and evaluation of extraction parameters*

The compounds studied are listed in Table 1 along with their log P and water solubility data. It is to be noted that the compounds are reasonably hydrophobic and have low solubility in water.

In the HF liquid phase microextraction (HF-LPME) procedure, a HF of certain length, containing the membrane liquid phase in its pores and the lumen, is immersed in the aqueous sample solution containing the analyte of concern. Then, the analytes partition between the two immiscible solvents. The extraction is completed when the system reaches equilibrium. In this kind of extraction, it is assumed that the dynamics of extraction is limited by diffusion [41]. Therefore, parameters related to this equilibrium conditions should be used to optimise the method of extraction. In this regard,

Table 1. List of the studied analytes along with their log P and water solubility data.

Compound name	log P[a]	Water solubility[b] (mg L^{-1})
Diazinon	3.44 ± 0.37	60
Fenthion	3.21 ± 0.34	4.2
Chloropyrifos	4.77 ± 0.40	1.4

Notes: [a]Calculated by ACD/Chemsketch (Advanced Chemistry Development Inc. Toronto, Canada).
[b]Obtained from reference [40].

the extraction of analyte can be expressed as the enrichment factor or extraction efficiency, as these parameters express the relationships between the amount extracted and amount originally present in the matrix of concern. In this study, enrichment factor was used to investigate the parameters governing the effectiveness of the method for the non-depletive extraction of the three OPPs. The enrichment factor (E_e) of the analyte can be evaluated using the formula [42]:

$$Ee = \frac{C_{org}}{C_i} = \frac{V_{aq} \times (K_{org/aq} \times V_{org})}{\left[(K_{org/aq} \times V_{org}) + V_{aq}\right]} \quad (1)$$

where C_{org} is the concentration of the analyte in the acceptor organic phase at the end of extraction, C_i is the initial concentration of the analyte in the sample, V_{aq} is the volume of the sample and V_{org} is the volume of extracting phase. $K_{org/aq}$ is the organic aqueous partition coefficient.

3.2 *Volume of the extracting phase*

For method optimisation, validation and application studies in non-depletive extraction of the analyte, the volume of extracting phase plays a significant role. According to Mayer and co-workers [1], the non-depletive extracted amount of an analyte on solid phase microextraction fibre should be kept below 5% of the amount dissolved in the sample medium and mathematically expressed as:

$$\left(\frac{V_{sampler} \times K_{sampler/medium}}{V_{medium}}\right) \leq 0.05 \quad (2)$$

where $V_{sampler}$ and V_{medium} are the volume of the sampler and that of the medium from which the analytes are extracted, respectively. Here, $K_{sampler/medium} = K_{org/aq}$.

An incomplete trapping, which is similar to the SPME discussed above, was followed in this work. The sampler volume, i.e. the volume of the organic liquid in the HF, therefore, had to be appropriately chosen. The volume of the sampler can then be calculated from the length, internal diameter and thickness of the HF used. Since the internal diameter and thickness of the HF are constant for a given type of HF, the sampler volume used for a given sample varies with the length of the HF used for the extraction. Therefore, in this study, an effective length of 1.2–1.4 cm of the HF with the dimensions indicated above was used. This corresponds to the approximate volume of the sampler (the lumen and the pores) of 9.4–11 μL.

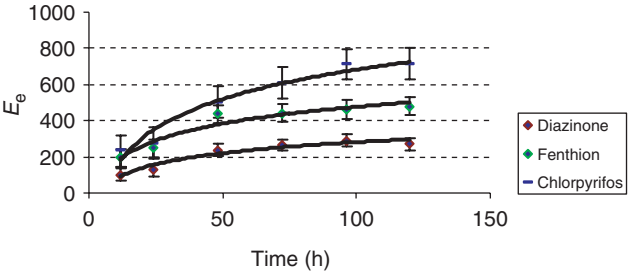

Figure 2. Determination of equilibrium uptake time for the analytes studied using HF-LPME. Extraction conditions: 0.4 μg L^{-1} of the analytes under study spiked in reagent water. The extraction solvent was *n*-undecane. The extraction sample volume was kept at about 80 mL.

3.3 *Extraction time*

Application of any passive sampler for environmental sampling can be carried out in any one of the three regimes [1]: kinetic, intermediate and near equilibrium. Passive samplers, which require a long time to attain thermodynamic equilibrium, are usually operated in the kinetic uptake regime [1]. Despite the fact that it will take long time, equilibrium uptake regime will be appropriate for biomimetic approaches. Therefore, we have chosen to work at the equilibrium uptake regime so that the measurements were not affected by potential interferents from the matrix on the absorption kinetics [15].

In equilibrium sampling method, determination of the time at which this thermodynamic equilibrium has reached is critical. The amounts of mass transfer and hence the enrichment factor increases with increasing time until it reaches the equilibrium. In this study, the determination of equilibrium extraction time was performed by following the enrichment factor of each analyte with increasing extraction time. Figure 2 shows the effect of extraction time on the enrichment factors of the three OPPs. The time to reach equilibrium is more or less similar for all of the three analytes. As it could also be seen from Figure 2, an equilibrium uptake regime was practically achieved for all of the analytes under study after 72 h of extraction and thus for the subsequent experimental works 72 h was chosen.

It should be further noted that under diffusion controlled conditions, it is possible to reduce equilibration time by stirring or agitating the sample at certain constant speed and it was found that stirring significantly reduced the time to reach the equilibrium. However, if biomimetic approach is required or if application to real environmental situation is targeted, static conditions are preferred to stirring or agitation [37]. Therefore, we have chosen static conditions where there was no disturbance of any kind. This will obviously take a very long time, but since the extraction set up developed was so simple and inexpensive, it is possible to run many parallel extractions at the same time, which compensates for the length of time. Hence, it is possible to apply this sample preparation technique to the analysis of very large number of environmental water samples.

3.4 *Choice of the membrane solvent*

The choice of organic solvent for the HF-LPME technique plays a significant role for efficiently and selectively isolating analytes from various matrices. For attaining

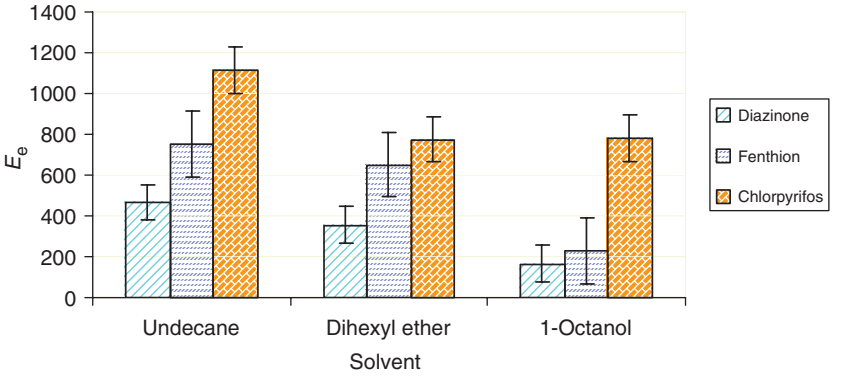

Figure 3. Enrichment factor, E_e of the OPPs for various membrane solvents investigated. Extraction conditions: 0.4 μg L^{-1} analyte mixture spiked in reagent water and sample volume was adjusted to 1125 mL.

maximum permeation, the analytes in question should appreciably be dissolved in the chosen solvent; in a similar manner to the common principle of LLE, i.e. 'like dissolves like'. Accordingly, the particular solvent chosen should offer high solubility for the target analyte, be efficiently immobilised in the HF pores and be compatible with the capillary GC column [33]. Based on these considerations, three organic solvents; namely, *n*-undecane, dihexyl ether and 1-octanol were evaluated for their performances. Figure 3 shows the differences in the enrichment factors of the analytes using these organic solvents. The more non-polar solvent (*n*-undecane) provided the highest enrichment factor among the solvents investigated. Therefore, *n*-undecane was used as an extraction solvent for the subsequent experimental works.

3.5 *Effects of the sample volume*

The other important variable, influencing the non-depletive extraction behaviour of the analyte is the sample volume. Evaluation of the extent to which it may affect the enrichment factor is particularly significant when the focus of the research is aiming towards the real environmental conditions. This is for the reason that the analyte amount extracted into the extracting phase increases with increasing sample volume [43]. One of the conditions used for the non-depletive equilibrium extraction is using very large sample volume so that the extracted amount in small volume of the sampler will be kept to the minimum [1]. Figure 4 shows the effect of sample volume on the enrichment factor of the contaminants from reagent water. Equilibrium has been achieved at about 500 mL of the sample volume. But to entirely avoid any kind of depletion, as indicated by Equation (2) above and the convenience of measurement for the amber bottles, 1000 mL of sample volume was chosen for all subsequent extractions. Furthermore, to work with zero headspace the actual sample volume used during the whole extraction process was adjusted to 1125 mL.

3.6 *Effect of humic acid*

Dissolved organic carbon (DOC), which usually occurs in natural waters as humic acid, HA, mainly ranges in concentration from 0.5 to 50 mg L^{-1} [15]. These substances can

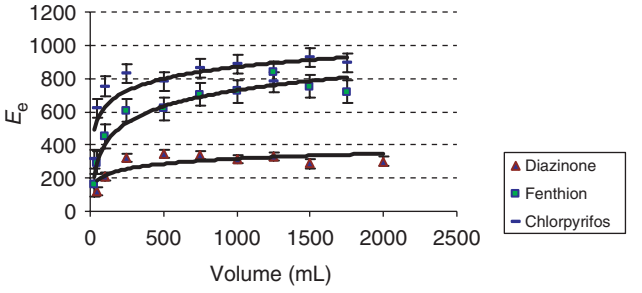

Figure 4. Effect of sample volume on the enrichment factor of the pesticides studied. Extraction conditions: 0.4 μg L^{-1} of the OPPs mixture was spiked in reagent water.

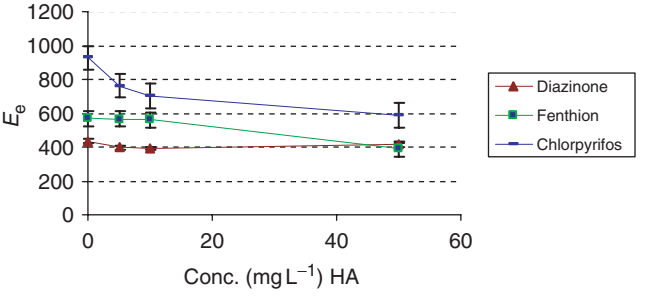

Figure 5. Influence of varied concentrations of humic acids on the enrichment factor of the pesticides investigated. Extraction conditions: 0.4 μg L^{-1} of OPPs mixture spiked in reagent water and sample volume was adjusted to 1125 mL.

possibly cause interferences when the selective extraction of freely dissolved organic pollutant from environmental water samples is targeted. Consequently, the study of effects of these substances, on the extraction efficiency and thus the analyte enrichment requires designing a systematic experimental procedure. This may be needed either to determine the extent to which they will be enriched and thus interfere and/or to minimise their accumulation along the analytes of interest. The other possible effect would be the binding of analytes to these substances and hence their non-availability for extraction. In this context, other workers [44,45] showed that a certain fraction of the freely dissolved aqueous concentration of organic pollutants can bound to humic acid and hence the freely dissolved amount was decreased in the presence of DOC.

In the current study, interfering potential of the dissolved organic carbon, i.e. HA, in the determinations of freely dissolved OPPs with HF-LPME were carried out by dissolving HA in the concentration range of 0–50 mg L^{-1} in reagent water. The resulting solution was then allowed to equilibrate for over 3 h under stirring conditions. Subsequently, the extraction was carried out in similar ways to the other spiked reagent water samples discussed above.

Figure 5 shows the effect of humic acid on the enrichment factor of the pesticides studied. The free concentration of the most hydrophobic compound decreased with increasing humic acid concentration than the other two compounds, which are relatively less hydrophobic.

Table 2. Repeatability and reproducibility of the method expressed in terms of RSD.

Analyte	Repeatability (RSD, $n = 5$)	Reproducibility (RSD, $n = 3$)	LOD ($ng\,L^{-1}$)
Diazinone	8.7	11.3	15
Fenthion	13.2	15.6	80
Chloropyrifos	14.8	30	15

Note: Concentration of the model analytes for both repeatability and reproducibility was kept at $200\,ng\,L^{-1}$.

3.7 *Analytical performances*

3.7.1 *Linearity and limit of detection*

Validation of the method is so essential in order to establish that the analytical performance parameters are acceptable for their intended use. The optimised HF-LPME conditions were used to evaluate the linearity of the proposed method over the concentration range of 25–$400\,ng\,L^{-1}$ for all of the target analytes in reagent water. Linear regression with proportional weighting was calculated for the plot of peak area *versus* concentrations of the analytes using Excel® with the DPX plug-in. The evaluated results for regression correlation coefficient and limit of detection (LOD) of the method are given in Table 2. A linearly proportional relationship between the amount of the extracted analyte and its initial concentration in the sample matrix is critical in developing any sample preparation technique. To this effect, good linearity was obtained for all of the analytes, with correlation coefficients, r^2, ranging from 0.991 to 0.996.

The LOD values were determined as three times the standard deviation of the noise from chromatograms taken at low-spiked concentrations.

The calculated LODs for all of the target analytes in reagent water were in the range of 15–$80\,ng\,L^{-1}$, see Table 2.

3.7.2 *Repeatability and reproducibility*

Reproducibility and repeatability studies were conducted in order to evaluate the precision of the method. The repeatability of the method (intra-day precision) was studied by running five extractions of spiked reagent water at $200\,ng\,L^{-1}$ concentration for 72 h. The repeatability of the method, expressed as relative standard deviation (RSD), was acceptable for the extraction of all of the analytes, Table 2.

Reproducibility of the method (inter-day precision), on the other hand, was studied by extracting reagent water samples spiked at $200\,ng\,L^{-1}$ for three different days. It is evident from Table 2 that the reproducibility of the method, expressed in terms of the relative standard deviation, is different for the three analytes. It is slightly low for chlorpyrifos as compared to the remaining two analytes. This particular observation requires further investigation.

3.8 *Applications*

The optimised and validated HF-LPME method was applied to the extraction of OPPs in the lake and ground water samples.

Table 3. Linearity of HF-LPME for the extraction of freely dissolved OPPs in reagent and lake water samples.

Analyte	Conc range ($ng\,L^{-1}$)	Matrices	Linear regression equation	Correlation coefficient (r^2)
Diazinone	25–400	Reagent water	$y = 303165x - 5709.5$	0.996
	50–800	Lake water	$y = 722.14x - 13023$	0.9923
Fenthion	25–400	Reagent water	$y = 8688.3x - 120.78$	0.9908
	50–800	Lake water	$y = 1036x - 14441$	0.9947
Chloropyrifos	25–400	Reagent water	$y = 4516.2x - 43.391$	0.9915
	50–800	Lake water	$y = 444.93x - 12729$	0.9912

Diazinone and fenthion were detected in the lake water sample. Since this detection was only based on the retention time corresponding to the SIM mode of the GC-MS analysis, and since these are so small that they cannot be confirmed by the scan mode, they were not quantified. None of these pesticides were detected in the sample of the ground water.

The applicability of the method was further investigated by extracting spiked lake and ground water samples. The ground water sample was spiked at 0.1 and $0.2\,\mu g\,L^{-1}$ concentrations of the analytes under study. The average extraction efficiency at the two concentrations were below 1% showing that the method is indeed non-depletive [1] and the amount extracted were so small that the equilibrium system of the water was totally undisturbed and the concentration obtained were only those of freely dissolved ones.

The linearity of the method in the lake water samples was also compared with that of the reagent water. The comparison was made by considering the similarity between the slopes of the two water matrices. Table 3 shows the linearity of the method in reagent water compared with that of the lake water samples. All analytes exhibited good linearity with squared regression coefficients (r^2) ranging from 0.991 to 0.996, using peak area as a response variable in all of the water samples.

It is also possible to see from Table 3 that the slopes for the two water samples were significantly different from each other. This further indicates that there is significant matrix influences on the extraction of freely dissolved concentration of OPPs using HF-LPME. The difference in the slopes for the two water samples may be due to the bound of some of the analytes to the suspended particles in the lake water as these suspended particles were not filtered before spiking.

4. Conclusion

The developed non-depletive equilibrium sampling methodology based on HF-LPME renders an efficient, cost effective and simple sample preparation process for the determination of freely dissolved OPPs in environmental waters. Since the total organic solvent used in this technique per sample was only 51 μL, the technique overcomes the limitations of the conventional methods such as use of expensive and toxic organic solvents and the utilisation of tedious and cumbersome procedures. The percent recoveries of the analytes spiked in ground and lake water samples at different concentrations were all below 1% showing that the method is non-depletive. In addition, as the HF pieces are

disposable there is no carry over effect. This is, therefore, one alternative to the SPME technique in the determination of bioavailable concentration of organic contaminants in environmental water samples. The limitation of the method is the long extraction time as compared with other equilibrium extraction devices like SPME, but this is efficiently offset by the cheap materials and simple handling, permitting the extraction of many samples in a parallel way. The overall method provided satisfactory linearity and detection limits in the nanogram per litre ranges of contaminant concentrations.

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