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Reference Methods and Materials

Determination of selected organophosporous contaminants in marine sediments

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INTRODUCTION

Organophosphorus (OP) compounds consist of a group of roughly 250 chemicals manufactured all over the world. Approximately 140 of these compounds are pesticides, and the remaining are mainly industrial chemicals used as flame retardants, plasticizers and industrial hydraulic fluids and solvents.

Annex 1 summarizes some of the OP pesticides. They are commonly used worldwide in agriculture or animal husbandry for crop protection and/or elimination of ectoparasites to substitute the persistent organochlorine pesticides which are currently restricted. Generally, the OP insecticides are compounds more toxic for the mammals and less toxic for the fishes (Ramade, 1977). They are also more specific than the organochlorine (Galgani et al, 1990), and they are considered to be less persistent and lipofilic (Carvahlo *et al.*, 1992; Schimmel et al, 1983).

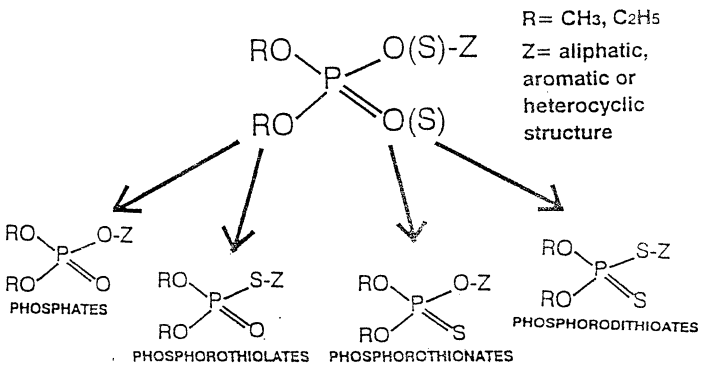
The types of marine areas at risk from contamination by organophosphorus discharges are river mouths and estuaries, lagoons, shallow waters and marshes.

The largest input of OP's in the marine environment comes through transportation of the compounds to the sea *via* surface waters. Industrial effluents containing OP residues may, however, also be discharged directly into shallow waters through pipelines from on-shore plants. Others sources of pollution may arise from spraying of crops with OP pesticides on fields nearby the sea. Finally, atmospheric transport from point or non-point sources also contributes to the pollution of coastal waters, lagoons and marshes.

Chemical structures and properties

OP compounds can be considered as derivatives of inorganic phosphorus compounds in which one or more hydrogen atoms have been replaced by organic groups. With a few exceptions (the RO group is substituted by NHiPr in some compounds, such as fenamiphos and isofenphos), the OPs can be described by the same general structural formula

In this formula R may be the methyl or the ethyl group and all combinations of oxygen and sulphur atoms attached to phosphorus as indicated are realized. The moiety Z exhibits a great diversity from aliphatic to aromatic and heterocyclic structures with additional substituents. The OPs can be classified into four main groups:



The diversity of physical properties of OP insecticides, due to the different structures and chemical composition (atoms of S, O, N, Cl, Br) (see annex 1), presents some challenges in developing a comprehensive multiresidue screen. The molecular weights of the pesticide compounds range from 141 to 466 and from 140 to 698 for the non-pesticides. The vapor pressures for the pesticides spans six order of magnitudes (from <0.001 to 1600 mPa (at 20 ^{0}C). For the non-pesticides the range spans four orders of magnitude: from less than 0.02 to 127 mm Hg. The water solubility of the pesticides also varies widely from one compound to another: from 0.14 mg/L for the least soluble, to 4 x 10^6 mg/L for the most soluble. A large range is also found in the non-pesticides: from 0.36 mg/L to 7000 mg/L. The OP pesticides usually exhibit log K_{ow} values of between 3-4, although the range varies from 0.5 for trichlorfon to 5.95 for temephos (Bowman and Sans, 1983). For the non-pesticides, the lowest log K_{ow} value is for tris(2-chloroethyl)phosphate, and the highest, 6.08 for cumylphenyl diphenyl phosphate (Muir, 1984). OP pesticides in general, do not have a high bioaccumulation potential and, consequently they do not present a high hazard to biota from this point of view.

Toxicity

OP compounds are toxic because of their action on the nervous system. OP pesticides inhibit the enzyme acetylcholinesterase (AChE), leading to accumulation of toxic levels of endogenous acetylcholine in nervous tissue and effector organs which disturbs the correct functioning of the nervous system. Non-pesticide OP's are

disturbs the correct functioning of the nervous system. Non-pesticide OP's are dangerous compounds since they are known to induce a delayed neurotoxicity in warm-blooded vertebrates by interfering with another enzyme: the neuropathy target esterase (NTE), which hydrolyses phenylacetate or phenylvalerate. All OPs pesticides are very toxic to aquatic biota. Insects and particularly crustaceans are extremely sensitive to intoxication by these pesticides, although they are wide differences between different species of the same group. Acute effects on marine crustaceans have been reported at concentrations of 1 µg/L for several OP pesticides (Schimmel *et al.*, 1983) and 150-200 µ/L for non-pesticide OP's. Chronic effects in the most sensitive aquatic biota have been found in the two groups at levels as low as 0.1 µg/L.

Degradation

The persistence of these compounds in the marine environment depend on the different degradation pathways including chemical, photochemical and biological processes. Although photolysis and hydrolysis are significant dissipative processes, the more hydrophobic OPs (chlorpyriphos, parathion) rapidly partitions into bottom materials and suspended sediment where photolysis is hampered and biotransformation is slow. The high microbial biomass in the sediment plays a role in the degradation of these pesticides (Pritchard *et al.*, 1987), but it does not compensate for the protective effect afforded by pesticide sorption onto sediment particles (Carvalho *et al.*, 1992). It appears that once OPs compounds are sorbed onto sediments they are less easily degraded (Carvalho *et al.*, 1992; Katan *et al.*, 1976) but might still be biologically active (Carvalho *et al.*, 1992). In generally, the half-live of these compounds in sediment-soil samples range from few days to few weeks (0.5 days to 30 days) (Schimmel *et al.*, 1983; Walker *et al.*, 1988; Cotham and Bidleman, 1989; Durand and Barceló, 1992), being the microbial activity the more rapidly degradation pathway. Redox transformations of OPs compounds can also be an important degradation pathway for those compounds which suffer nitro reductive process (Wolfe *et al.*, 1986).

The relatively instability or short half-life of the OPs is beneficial to the environment, but it also causes analytical problems. As many of these compounds can react to give toxic metabolites by oxidation and isomerization before hydrolysis and detoxification occurs, the analyst is confronted with a problem of great complexity.

1. SCOPE AND FIELD APPLICATION

This reference method describes the determination of organophosphorous compounds in marine sediments using capillary column gas chromatography.

Different extraction procedures are described: Soxhlet or sonication extraction after freeze-drying the sample or after drying the sample with sodium sulphate. Before analysis by GC-FPD, GC-NPD or GC-MS, elemental sulphur is adsorbed onto activated copper or elemental mercury. Organophosphorous are then purified using traditional column chromatography using Florisil and a alternative procedure using gel permeation chromatography is provided for the compounds adsorbing in the Florisil.

Among OPs pesticides that may be determined individually using Florisil cleanup are the following:

azinphos-ethyl, azinphos-methyl, chlorpyrifos, chlorthion, coumaphos, diazinon, dichlorvos, dimethoate, EPN, ethion, fenamiphos, fenitrothion, fenthion, leptophos, malathion, methidathion, methylchlorpyrifos, methylparathion, monocrotophos, parathion, sulfotep, tetrachlorvinphos. Other organophosphorus compounds may also be determined by these method, but the great variation in their physico-chemical properties makes mandatory that every analyst test his own recovery and analytical reproducibility for his selected OPs compounds.

Gas chromatography (GC) has undoubtedly been the most common technique for analysing these compounds because it can be combined with very sensitive detectors, such as nitrogen-phosphorus detector, flame photometric detector and atomic emission detector. Characterization by mass spectrometric analysis are also necessary for a reliable identification of the compounds on the chromatograms.

On the other hand, high-performance liquid chromatographic (HPLC) methods have grown in this application field due to possibility of determining thermally labile and polar compounds that are not GC amenable. LC detectors include UV scanning and diode array type detectors, electrochemical, MS and MS-MS. However, the use of HPLC is not really satisfactory because many OPs do not have a chromophoric group and, in general, UV absorption does not provide sufficient selectivity and/or sensitivity in environmental trace analysis. It should be taken into account that detection in LC-UV and LC-MS are usually at least 2.5 orders of magnitude lower than in GC-NPD

and GC-MS (Durand *et al*, 1989). For this raison, to carry out the environmental monitoring of organophosphorous pesticides at the low ng/g level, only the GC methods can be employed.

In these reference methods, only gas chromatographic methods using flame photometric, nitrogen/phosphorus thermionic and mass spectrometry detector are described to screen the compounds.

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3. PRINCIPLES

Organophosphorous compounds are extracted from an aliquot of a sample using a mixture of ethyl acetate/acetone as solvent. Extracts are treated with mercury or activated copper to remove the sulphur and then further cleaned by Florisil adsorption chromatography. An alternative cleanup procedure using gel permeation chromatography is provided for those compounds adsorbing in Florisil. Detection is achieved by capillary gas chromatography (GC-FPD, GC-NPD, GC-MS).

4. REAGENTS, SOLVENTS AND STANDARDS

4.1. Acetone, hexane, ethyl acetate, methylene chloride, cyclohexane solvents (nanograde, redistill in glass if necessary).

4.2. Doubly distilled water

4.3. Anhydrous sulphate sodium

4.4. Florisil, PR grade, 60-100 mesh.

4.5. Elemental mercury or elemental copper (fine powder 40 mesh) and concentrated hydrochloric acid (HCl).

4.6. Glass wool

4.7. Cellulose extraction thimbles

4.8. Carbon boiling chips

4.9. Sulphochromic mixture containing 4 g potassium dichromate ($K_2Cr_2O_7$) in 1 L of sulphuric acid.

4.10. Detergent

4.11. Individual stock solutions of standards containing 50 mg/100 mL of each OP pesticide are prepared in ethyl acetate and kept at 4°C in the dark. Calibration standards for the gas chromatographic analysis are also prepared, by appropriate dilution, in ethyl acetate at the concentration of 0.5 ng/µL. Chlorthion, who is used as internal standard, is prepared in acetone.

CAUTION: Because OPs are acetylcholinesterase inhibitors in mammals, extreme care must be exercised in their use. They should be handled with extreme care to avoid skin contact or inhalation.

5. APPARATUS

5.1. Soxhlet extraction apparatus, heaters and cooling water for condenser.

5.2. Rotary evaporator, cooling water for condenser and heated water bath for sample (never set to exceed 30°C).

5.3. Gas chromatograph (GC) equipped with capillary split/split-less or on-column injectors and an electronic data capture system. Either must have a nitrogen-phosphor detector or a flame photometric detector. Gas chromatography columns are described under section 9. Glass syringes 10 µL for injection into GC.

5.4. High purity carrier gas for the as chromatograph including molecular traps to remove trace contaminants and moisture and supply of clean dry nitrogen.

5.5. Muffle furnace for precombusting reagents.

5.6. Drying oven for glassware and reagents.

5.7. Freezedryer and porcelain mortar and pestle.

5.8. Dessicator

5.9. Glassware:

A range of volumetric flasks, graduated measuring cylinders, boiling flask, ground glass stoppers, beakers, Erlenmeyer flasks, glass and sealed Teflon centrifuge tubes, Pasteur pipettes and glass syringes, 10 mL burettes with teflon keys.

5.10. Analytical balance with a precision of 0.0001 g and and electrobalance with a precision of at least 1 μg

5.11. Deep freezer (-18 to -20 °C) for sample preservation

5.12. Stainless tweezers, spatulas, aluminum foil

5.13. High performance liquid chromatography or gel permeation system as described in section 7.7.2.

5.14. Sedimentological sieves, stainless steel: 120 and 1000 μm.

5.15. Ultrasonic bath

5.16. Supply of dry nitrogen

6. SAMPLING, SAMPLE PREPARATION AND STORAGE

For a sampling plan follow UNEP/FAO/IAEA, and for sampling follow UNEP/FAO/IAEA (19?).

The sediments must be kept at the deep-freezer (-20 °C) to preserve the sample from microbiologic degradation.

6.1. Freeze-drying procedure

The freeze-drying procedure has been always questioned because might remove some of the volatile compounds. Some recent studies (Lartigues, 1994) have evaluated the possible volatilization losses of OPs compounds in the freeze-drying procedure and have shown that no losses were found for the following OPs tested: azinphos-ethyl, azinphos-methyl, bromophos, coumaphos, diazinon, dimethoate, fenitrothion, fenthion, isofenphos, malathion, parathion-ethyl, parathion-methyl, phosmet and triazophos. Therefore, it appears that freeze-drying procedure might be used in the analysis of OPs.

Special care must be taken, however, in this procedure to ensure that does not contaminate the samples. The freeze drying procedure should be tested by drying Na_2SO_4 as a blank and extracting this as a sample. Pulverize the freeze-dried subsample carefully in a cleaned pestle and mortar and store it in a sealed jar at -20 °C until extraction.

7. PREPARATIVE ANALYTICAL PROCEDURES

7.1. Cleaning of glassware

Scrub all non-volumetric glassware vigorously with brushes in hot water and detergent. Clean it in an ultrasonic bath containing a non-posphate detergent for 15 minutes. Rince with tap water, acetone and hexane. Bake overnight in an oven at 240 °C.

Volumetric glassware should be cleaned overnight in sulfo-chromic acid, rinced with tap water, acetone and hexane.

All clean glassware should be tightly sealed with precleaned aluminium foil and solvent-rinced before using it.

CAUTION: Care should be taken to avoid skin contact or inhalation of the sulpho-chromic acid and solvents.

7.2. Cleaning and treatment of reagents

The Florisil, glass wool and carbon boiling chips should be pre-extracted in the Soxhlet apparatus with hexane/acetone to remove any contaminants. It is then dried at low heat (50 °C) in an oven, preferably under vacuum. All these items must be stored in air tight glass jars.

Na_2SO_4 used to dry samples must be precleaned by solvent extraction and/or precombusted by heating at 400 °C in a muffle furnace overnight. Precombustion should be repeat once a week.

Extraction thimbles are pre-extracted in the Soxhlet with acetone/ethyl acetate for 8 hours before extracting the sediment sample.

Precleaned florisil must be activated for 8 hours by heating at 130 °C. It is then partially deactivated with 5% of precleaned water by weight and stored in a tightly sealed jar in the dessicator. The water is added slowly, mixed well into the adsorbent and the mixture is allowed to equilibrate for one night before use. The activation/desactivation procedure must be done one or two days before using the Florisil.

7.3. Extraction of samples

7.3.1. Extraction procedure for freeze-dried samples

The freeze-dried sediment might be sieved through 120 μm mesh to remove the big particles.

Accurately weigh about 10 g of pulverized dry sediment and place it compactly into a precleaned extraction thimble in a Soxhlet apparatus. Add a few carbon boiling chips to the extraction flask. Add the internal standard (about 100-200 ng chlorthion in acetone solvent) and some compact glass wool on top of the filled extraction thimble. Pour the mixture of ethyl acetate:acetone (50:50) at about twice the volume of the Soxhlet apparatus and extract the sample for 8 hours. Extract an empty precleaned thimble containing the freeze dried Na_2SO_4 as a procedural blank of the freeze-dryer.

As an alternative to Soxhlet extraction, sonic or shaker extraction may be applied as follow: 4-5 g sediment is placed into a sealed Teflon centrifuge tube of 50 mL. Add surrogate standard and pour 25 mL of 1:1 v/v ethyl acetate:acetone. Sonicate for about 10 min at settings appropriate to yield efficient extraction. Alternatively, the extracts can be shaken several hours on a mechanical shaker. After extraction, centrifuge and filter the extract through glass wool and sodium sulphate into a clean flask. Repeat the extraction two more times, combining all extracts into the flask.

7.3.2. Extraction procedure without freeze-drying.

Decant excess water from the sediment surface then homogenize it stirring. Discard large pebbles, seaweed, wood, animals and other debris.

20 g of wet sediment is slowly and carefully mixed and blended with three-times the wet weight of precombusted Na_2SO_4. Transfer the well blended and dry mixture to a precleaned extraction thimble. Add internal standards (about 100-200 ng chlorthion in acetone solvent) and some compact glass wool on top of the filled extraction thimble. Pour the mixture of ethyl acetate:acetone (50:50) at about twice the volume of the Soxhlet apparatus and extract the sample for 8 hours. Extract an empty precleaned thimble containing the same amount of Na_2SO_4 as a procedural blank.

Similar to section 7.3.1, sonic or shaker extraction may be used as an alternative to Soxhlet extraction. In this case, a bigger Teflon centrifuge tube or a 250 mL glass or Teflon jars can be used to adequate the volumes for extracting 10 g of wet sediment mixed with Na_2SO_4..

7.4. Concentration of extract

For both extraction procedures, the extracts are concentrated on a rotary evaporator to about 10 mL. The temperature of the water bath must not exceed 30°C.

7.5. Sulphur removal

In certain types of samples such as anaerobic sediments, the presence of sulphur and sulfur compounds is commonly encountered. These compounds can cause some interferences in the analysis of organophosphorous compounds, specially by GC-FPD. A popular method to remove sulfur is to treat the sample extract with tetrabutylammoniumhydrogenosulfate (Kjolholt, 1985b, Erickson, 1986), activated copper (Smith et al, 1984), or elemental mercury (Goerlitz and Law, 1971; Mattson and Nygren, 1976). Only the last two procedures are offered here, because the one using tetrabutylammoniumhydrogenosulfate is not recommended due to the lower recoveries reported for some OPs compounds (Lartigues, 1994).

7.5.1. Treatment with elemental copper

In the same flask where the extract has been rotaevaporated to 10 mL, add a slurry of activated copper with a Pipete Pasteur and leave it all night to react with the

sulphur. When the Cu adsorbs sulphur it turns black. Transfer the extract and the rinces of the copper to a test tube of 15 mL. The final volume is decreased to 3-4 mL by a stream of dry nitrogen before measuring the extractable organic matter.

Another alternative is to pass the extract through a column filled with the activated copper at a flow rate of several mL per minute (Lartigues, 1994). Always remove traces of acid and water before passing samples through it.

NOTE: Activated copper can be prepared as follows: Stir elemental copper in fine particles (40 mesh) with concentrated HCl in a ultrasonic bath for 10 minutes. Decant most of acid preventing the very fine Cu particles to escape. This procedure is repeated 2 times more until the particles become red. Wash these activated particles several times with distilled water until pH of the water is neutral. Stir and rince the copper several times with acetone to remove the water (ultrasonic bath is recommended to be used). Stir and rince the copper several times with hexane. Keep this activated copper in the solvent to prevent exposition of the copper to the air and consequently its oxidation. It is recommend to activate the copper when it is needed to be use the same day of activation.

7.5.2. Treatment with mercury

Transfer the 10 mL rotaevaporated extract in a calibrated test tube of 15 mL along with three rinses of ethyl acetate. The final volume is decreased to 5-6 mL by a stream of dry nitrogen before removing the sulphur.

The 5-6 mL of extract is shaken a few minutes[1] with drops of precleaned elemental mercury. Carefully transfer the extract and the rinces of the mercury to a centrifuge tube. Centrifuge and recover the extract to another test tube. If the mercury is tarnished, repeat the procedure until the surface of mercury remain brilliant. The final volume is decreased to 3-4 mL by a stream of dry nitrogen before measuring the extractable organic matter.

Note: The high toxicity and potential contamination of mercury obliges technicians to operate with caution.

[1] After about 10 min, some OPs can react with the mercury (Goerlitz and Law, 1971)

7.6. E.O.M. determination

The extractable organic matter (EOM) is determined by evaporating a mea small volume of this extract on the pan of an electrobalance in the following mann

Evaporate 5 to 10 µl of the 3-4 mL extract on the weighing pan of an ele balance and weigh the residue to ±1 µg

The quantity of E.O.M. is:

$$E.O.M.(mg/g) = \text{weight of residue (mg)} \times \frac{\text{volume of extract (ml)}}{\text{amount evaporated } (\mu l)} \times \frac{1000}{\text{quantity of sample e}}$$

Note: Extreme care must be taken to ensure balance and pans are clean, dry and sta obtain accurate reading of ±1 µg. A small hot plate is used to warm pans and forceps an keep these instrument dry after solvent cleaning.

If no electro-balance is available a known volume of the extract can be trans into a clean pre-weighed beaker. The solvent is evaporated with dry nitrogen ga a constant weight of ± 5 mg is reached. The amount of "lipids" in the sample account the volume of the lipid extract which was dried.

7.7. Cleanup

Because organophosphorous compounds might be destroyed by strong acid and (Viana *et al*, 1993; Bernal et al, 1992), non-destructive methods involving partit solvents and column chromatography with silica gel, Florisil, alumina, gpc or r phase are preferred.

The primary objective of using an adsoption chromatographic clean-up in pe residue analysis is to remove pigments, waxes, polar impurities and small amou fats from the sample extract. However, OP pesticides are difficult to separate fr fatty acids and esters by adsorption chromatography because of their similar pola The adsorbents most extensively used for residue analysis are silica-gel, alumi Florisil. Silica-gel requires a wide range of solvent polarities to elute all C carbophenoxon, disulfoton, edifenphos, IBP, methamidophos, monocrot oxydemeton methyl, phosmet, pyridaphention are adsorbed on silica (Thompso

1977; Sasaki et al, 1987). However, conditioning of the silica gel with acetic acid improves the recovery because the acid can activate the sites on the silica gel, preventing the OP pesticides from binding with these sites (Lores *et al.*, 1987). Neutral alumina can degrade some OP compounds. Florisil has been recommended by EPA, even if it may retain some OP insecticides (mercapto functionality, oxigenated analogs and dimethoate) and oxidize OP with thio-ether groups [Neicheva et al, 1988]. Whichever procedure is followed, it must be calibrated by running through a series of standards and quantifying their recovery in the eluate.

The proposed reference method suggests and offers an adsorption chromatography procedure using Florisil. For compounds adsorbing on this adsorbent, gel permeation chromatography (GPC) is recommended and offered as an alternative to the adsorption chromatography. Usually, the coextractives are not quantitatively removed from the final extract but the concentration of these materials are sufficiently reduced so that there is not a significant interference in the chromatography using element-specific detectors (FPD, NPD, MS-SIM).

7.7.1. Adsorption chromatography by Florisil

Glass burettes of 10 mL with teflon stopcoks are convenient adsorption columns. They can be plugged with pre-extracted cotton or glass wool. The Florisil adsorbant must be precleaned, activated and desactivated according to section 7.2. Columns should be prepared immediately before use.

A slurry method of layering the Florisil into the column is recommended. 5 g of 5% deactivated Florisil is placed into a beaker and covered with hexane. A slurry is made by agitation. The column is partially filled with hexane and the agited slurry is poured into the glass column with the open stopcock. The Florisil is allowed to settle into an even bed tapping regularly with a rubber stopper attached to the end of a pencil. Any Florisil adhering to the column sides is rinced down with hexane. Finally, 1 g of precombusted Na_2SO_4 is layered on top of the adsorbant bed. Drain the solvent to the top of the adsorbant, taking care to ensure the bed is never allowed to run dry.

About 500 µl of the extract is transferred by Pasteur pipette on top of the Florisil packed column and is drained into the adsorbant. The tube containing the extract is rinced three times with about 500 µl of the eluent mixture. Most of the organophosphorus compounds (azinphos-ethyl, azinphos-methyl, chlorpyrifos,

chlorthion, coumaphos, diazinon, dichlorvos, EPN, ethion, fenitrothion, leptophos, malathion, methidathion, methylchlorpyrifos, methylparathion, parathion, sulfotep, tetrachlorvinphos) are eluted with 30 ml hexane: ethyl acetate (75:25). Fenamiphos and fenthion are recovered in a second fraction, which is eluted with 30 mL hexane: ethyl acetate (50:50). Finally, the extracts are concentrated to a 250-400 µL and then analysed by gas chromatography.

7.7.2. Gel permeation chromatography (GPC)

GPC is a cleanup method where sample components are separated based on their molecular size in solution. Large biogenic compounds such as lipids are excluded from the pores of the polymeric material and eluted before smaller analytes, which are retained in the pores. Separation mechanisms other than size exclusion, adsorption and partition, must be considered depending of the mobile phase and the pore size of the packing chosen. The packings more used are 200 to 400 mesh Bio-Bead SX-3 resins (2000 Mr exclusion limit) and the highly crosslinked spherical polystyrene divinylbenzene matrix with particles sizes as small as 5 microns (< 1000 Mr exclusion limit). Two suggestions for GPC procedures are offered here: the first using low efficiency column technology (200-400 mesh packings: Bio-beads SX-3) and the second using a high resolution GPC columns. The use of these higher efficiencies enable the same separation to be done with much smaller columns, greatly increasing the speed of the process while simultaneously reducing solvent consumption.

Apparatus

1.-Filtration device for solutions, 5 mL syringe with Luer-Lok tip, fitted with 13 mm diameter Swinny stainless steel filter holder and 13 mm diameter filters, 5.0 µm LS-type.

2.- A high performace liquid chromatography (HPLC) or GPC apparatus which must include:

2.1. sample introduction valve (Rheodyne7125) and stainless steel loops.

2.2. pump, low pressure, suitable for use with organic solvents, capable of 5 mL/min flow.

2.3. pulse dampener is pump is not pulseless

2.4. UV-VIS detector at 254 nm

3. Glass syringes 100, 250 and 500 µL for injection into the HPLC or GPC.

Low-resolution polystyrene columns: Bio-Beads SX-3

The procedure given here is the one described in soil samples by Durand et al, (1
and in biota samples by Barceló et al, (1991).

Samples are injected via 150 µl loops from Rheodyne. A stainless steel col
(450 mm x 10 mm i.d.) packed with Bio-Beads SX-3 is used. The eluent is a mi
of ethyl acetate/cyclohexane (1:1) pumped at 1 mL/min through a high-pressure p
coupled with a UV-VIS detector at 254 nm. The collection time is from 22 to 34
and the mean recovery varied from 64% to 85% (RSD< 12%) for the follo
compounds: dioxathion, fenitrothion, malathion, tetrachlorvinphos, azinphos-e
ronnel and coumaphos.

High resolution GPC columns (PLgel)

Extracts are filtered through filtration device and injected with a 500 µl loops
Rheodyne 7125. A 300 x 7.5 mm PL-Gel column (5µm, 50 °A) with a a capaci
50-100 mg fatty lipids can be used. Elute with CH_2Cl_2 100% pumped at 1 ml/min.
colecction time is from 6 to 8 min and the recovery of OPs is higher than 70%.
methylene chloride contained in the GPC eluate should be exchanged to ethyl ac
before injecting the organophosphorus in the gas chromatograph.

7.8. Precision and accuracy

The recovery of individual organophosphorous compounds spiked in
organophosphorous-free sediment at a concentration of about 40 ng/g, follc
Florisil cleanup, was found to be higher than 70% (RSD< 10%; n=3) for the follc
selected organophosphorous pesticides: azinphos-ethyl, azinphos-methyl, chlorpy
chlorthion, coumaphos, diazinon, dichlorvos, EPN, ethion, fenamiphos, fenitro
fenthion, leptophos, malathion, methidathion, methylchlorpyrifos, methylpara
parathion, sulfotep, tetrachlorvinphos.

8. DETERMINATION OF FRESH WEIGHT/DRY WEIGHT RATIO

A subsample of 1-2 g is introduced into a baker and heated in an oven at 105 °C for 24 hours. The baker is then transferred to a desicator to cool and then weighed again. The procedure is repeated until a constant weight is reached.

9. GAS CHROMATOGRAPHIC DETERMINATIONS

The identification of the organophosphorous compounds by selective gas chromatographic separation may be corroborated through the use of two or more capillary columns of different polarity. The so-called primary column, generally a DB-1701 (14% cyanopropyl-phenyl-methylpolysiloxane), and a second column, called a confirmatory column, such a DB-5 (5% diphenyl and 95% dimethyl polysiloxane) are recommended to be used. However, some polar OP insecticides, such as acephate and methamidophos, do not chromatograph well on the nonpolar DB-5.

Multiresidue GC analysis is generally performed by hot splitless injection because of the ease of exchanging the injector inlet when it becomes contaminated with non-volatile deposits from the matrix. However, this injection technique is less precise and suitable for thermolabile OPs (temephos and trichlorfon) than cold on-column injection (Stan and Goebel, 1984).

In the splitlless mode, full efficiency of the column is realized by reconcentration of the sample components in a narrow band on the column prior to analysis, either by using a solvent effect or the effect of condensation of the solutes at the column inlet. The latter mechanism operates effectively for compounds with boiling points about 150 °C above the column temperature. Compounds with lower boiling points need a solvent effect for reconcentration. The solvent effect focuses the analytes on the head of the column. The oven temperature should be set to 10-30 °C below the boiling point of the solvent. The column temperature can then be raised to the temperature required. The temperature of injector should allow a rapid evaporation of solvent and solutes but it should be low enough to avoid destruction of sensitive components. The splitless mode allows a relatively large amount (0.5-3 µl) of dilute sample to be injected into a simple open glass tube liner in the injector port. The volume of this insert liner must accommodated quantitatively the vapour volume of the sample to avoid loss of

analytes and memory peaks. It should also be periodically cleaned in chromic acid mixture overnight, followed by rincing with water, acetone, hexane and desactivation by sililization. Aliquots of 1-2 µl might be injected in the splitless mode using a "hot needle technique".

The on-column technique allows the injection of a liquid sample directly into the inlet of the column, and this eliminates the possibility of sample loss during vaporization and transfer from the vaporizer to the column. The needle of the syringe must reach far enough into the column to avoid the sample components being transferred back into the injector block. To avoid a fast deterioration of the column a deactivated retention gap is recommended to couple in front of the analytical column via a press fit connector.

Detection and measurement are best accomplished by flame photometric gas chromatography using a phosphorus specific filter. The nitrogen-phosphorous detector, may also be used but with less specificity, and electron capture detector for those compounds to which it responds. Confirmation of the identity of the compounds should be made by GC-MS in the electron impact mode or negative chemical ionisation for those compounds to which it responds. Confirmation with a detector other than mass spectrometry requires the use of a second column that exhibits a different retention time for all analytes.

9.1. Detection with flame photometric detector (GC-FPD)

The FPD is a highly sensitive and selective detector for sulfur and phosphorus compounds. When a sulfur or phosphorus containing compound is combusted in a hydrogen-rich flame, chemiluminescent species such as S_2 or HPO are produced. By monitoring the characteristic emission of these species (394 nm for sulfur and 526 nm for phosphorus), detection and quantification of sulfur or phosphorus containing pesticides can be made. The FPD detects sulfur or phosphorus compounds by burning the column effluent in a tuned flame and measuring a selected spectral portion of the emission above the flame. Light emission at a wavelength characteristic of the

phosphorus species passes through the 526 nm optical filter to a photomultiplier tube where it is converted to a current and amplified.

As the dynamic range of FPD is rarely more than two decades, the linearity of the FPD must be checked for each analyte. The detection limit of this detector with the phosphorous filter is about 10-100 pg.

Carrier gas can be hydrogen, helium or nitrogen depending on the availability of high quality grades. Hydrogen carrier, generally show the better chromatographic resolution but safety cut offs must be included when it is used.

Table 1 exemplifies the cromatographic conditions that may be applied to analyse the OP compounds by GC-FPD. Figure 1 illustrates the example of chromatogram for selected OPs using these conditions.

Table 1. Conditions for a capillary GC-FPD.

Carrier gas: helium at a flow-rate of 1.5 mL/min

Column: 25 m x 0.25 mm I.D. x 0.20 μm Chrompack OV-1701.

Injector temperature: Splitless: 250 ^{o}C

Detector temperature: 225 ^{o}C.

Temperature programme: 60 ^{o}C for 1 min; 60 ^{o}C to 190 at 25 ^{o}C/min, 190 ^{o}C to 225 ^{o}C at 2 ^{o}C/min, 225 ^{o}C to 280 ^{o}C at 5 ^{o}C/ min, 280 ^{o}C isothermal for 10 min;

9.2. Detection with nitrogen-phosphour detector (GC-NPD).

The nitrogen-phosphorus detector (NPD) uses a jet and collector similar to the universally employed FID. However, the collector contains a small alumina cylinder coated with a rubidium salt (the active element) and heated electrically. In the presence of this thermoionic source, nitrogen and phosphorus containing organic molecules are efficiently ionized. Ions are collected and the resulting current measured.

Hydrogen and air are required, but at flows significantly less than normal FID operation. Thus, the flame is not actually ignited but it glows on the surface of the heated alkali source (rubidium salt) to produce dissociation of ions. The advantage of this arrangement is that normal hydrocarbon ionization reactions associated with the FID do not proceed efficiently and thus the detector provides high selectivity towards

nitrogen and phosphorus containing compounds. However, accurate control of the hydrogen flow rate is important due to the fact that the NPD response depends on the concentration of the H atoms in the gaseous boundary layer of the bead.

As, the NPD is a destructive and mass flow-rate dependent detector, "the constant-flow" mode should preferably be used or co-injection of internal standards is recommended to increase quantitative accuracy.

Care should be taken to turn off the collector voltage while the detector gases are interrupted (i.e. during changing of the septum, column, gas cylinders, etc.). Gas supplies must be free of moisture to avoid a fast deterioration of the active element.

The selection of the carrier gas is also important. When helium is used, the NPD response may decrease to only 10% of that measured using nitrogen because of increased cooling of the alkali source and incomplete decomposition of the sample.

The NPD offers a dynamic range of 2 to 3 decades and the detection limit for OPs is about 30 to 200 pg.

Figure 2 and 3 illustrates two chromatograms obtained by GC-NPD with different conditions and different columns.

9.3 Quantification

The chromatograph is first calibrated by injecting an appropriate standard mixture which includes the surrogate standard (chlorthion) used in the analysis. Prior to use as a quantitative instrument, the linear range of response must be determined by injecting a series of standard mixtures of OPs and constructing calibration curves. Quantitative analysis can only be conducted when the concentrations of analytes are within the linearly calibrated range. Response factors (RFs) are calculated in terms of area. ng^{-1}

Organophosphorus in samples are determined by injecting a known aliquot of the organic extracts into the GC. Peak areas are integrated and amounts calculated from the RFs of the external standards. Recoveries of the surrogate standard should also be evaluated for losses through the analytical procedure. These values should be better than 70% recovery, otherwise the analytical procedure must be checked.

The external standard method uses absolute response factors, the internal standard method is calibrated in terms of response ratios. In external standard methods, the sample amount injected must be highly reproducible. The method is well suited to automatic mechanical methods of injection. On the other hand, the internal standard method is independent of sample size and compensates for any slight instrumental drift. When used properly, it is the most accurate method of calculation.

The calculations are exemplified below:

External standard method

Compute RFs from external standard run as area. ng^{-1}.

Compute XF (dilution factor) as total extract volume (μL) divided by μL injected.

$$\text{Recovery of chlorthion (REC)} = \text{Peak area on GC} \times \frac{1}{\text{RF of chlorhion}} \times \text{XF} \times \frac{1}{\text{total ng chlorhion added to sample}}$$

$$\text{[paration] (ng / g)} = \text{Peak area on GC} \times \frac{1}{\text{RF of parathion}} \times \text{XF} \times \frac{1}{\text{REC chlorthion}} \times \frac{1}{\text{g sample}},$$

Internal standard method:

$$\text{[paration] (ng / g)} = \frac{\text{Peak area parathion}}{\text{Peak area chlorthion}} \times \frac{\text{RF chlorthion}}{\text{RF parathion}} \times \frac{\text{total ng chlorthion added to sample}}{\text{g sample}}$$

9.4. Confirmation by mass spectrometry

In order to avoid "false positives" in the determination of pesticides in sediment samples, GC-MS, in electron impact (EI) mode by the selective ion monitoring or the full scan mode, is the most widely used confirmation technique. GC/MS on negative or positive chemical ionization can be also successfully applied to those compounds to which it responds.

Peak confirmation is achieved by evaluating the retention time of the peaks on the chromatograms and evaluation of the associated spectrum. In the case of quantification by GC/MS/EI, the spectra are also used to determine if any coeluting substances are contributing to the areas of target ions to be used for the quantification.

The practical detection limit for GC/MS/EI analysis in scan mode is generally in the range of 5 to 10 ng per compound injected. Sensitivity is greatly increased by acquiring the data in the selected ion monitoring or SIM mode. In this procedure, the time windows for ion monitoring are established with scan data for pure compounds. For routine EI-SIM acquisition, Table 2 lists some confirmatory ions and the approximate percent relative abundances, which can be used as a first level of confirmation of peak identity for SIM data. However, as these percentages can vary significantly from one instrument to another, depending on the calibration tune and conditions, it is recommended to calibrate your mass spectrometer with real standards to confectioner your own percent relative abundances. The detection limit for OPs in electron impact and SIM mode is generally in the range of 50 to 200 pg per compound injected.

For the OPs compounds exhibiting a high electronic affinity, the mass spectrometry in the chemical ionization (CI) mode may facilitate the identification of these compounds at trace levels due to the high selectivity of this technique. Interferences are found to be less dominant than in EI mode, specially in the negative mode (NICI). Sensitivity for the determination of OPs is in general much better in NICI than in positive mode (PICI) or in EI ionization, depending on the electron affinity of the compound. Table 2 lists some confirmatory ions and the approximate percent relative abundances in the NICI technique using methane as a reagent gas. Caution should be taken with these abundances because they are dependent on the instrumental

parameters, pressure and temperature of the ion source, concentration of the compound, presence of oxygen and instrument type.

Table 2. Target compounds analysis by gas chromatography-mass spectrometry in the electron impact (EI) and negative ion chemical ionization (NICI) scanning from m/z 100 to 500. (From Busch *et al.*, 1978; Stan and Kellner, 1982; Liao *et al.*, 1991; Lacorte *et al.*, 1993; Hites, 1992; Agüera *et al.*, 1993)

Compound name	M.W.	EI	NICI
		m/z, % relative abund.	m/z, % relative abund.
Acephate	183	136(100), 125(12), 183(7)	
Amidithion	273		157(100)
Azinphos-ethyl	345	132(100), 160(82), 104(19)	185(100), 133(4)
Azinphos-methyl	317	160(100), 132(84), 104(30)	157(100), 133(12)
Bromophos	364	331(100), 329(80), 125(65)	257(100), 141(66), 270 (47)
Bromophos-ethyl	392	303, 359	257(100), 358(59), 330(12)
Carbophenothion	342	157(100), 121(48), 342(30)	185(100), 143(52)
Chlorfenvinphos	358	267(100), 323(76), 269(63)	153(100)
Chlorpyrifos	349	197(100), 199(92), 314(54)	313(100), 212(61), 169(48)
Chlorphyriphos methyl	321	125(100), 109(25), 286(60)	
Chlorthion	297	109(100), 125(97), 297(40)	188(100), 297(20), 153(13)
Coroxon	346	109(100), 346(91), 210(80)	
Coumaphos	362	362(100), 109(95), 226(78)	225(100), 362(28), 169(11)
Coumithoate	368	216(100), 368(90), 125(76)	
Cyanofenphos	303	157(100), 149(55), 169(55)	
Cyanophos	243	109(100), 125(45), 243(40)	
Cythioate	297	125(100), 109(94), 297(40)	
Demeton-O	258	115(100),171(90), 143(70)	169(100), 229(8), 95(5)
Demeton-S	258	114(100), 170(80), 143(65)	169(100), 229(8), 95(5)
Demeton-S-methyl	230	109(100), 142(70)	141(100), 215(64), 95(9)
Demeton-S-methylsulfon	262		141(100), 247(13)
Dialifor	393	208(100), 210(42), 347(10)	185(100), 173(51)
Diazinon	304	137(100), 179(75), 152(65)	169(100)
Dicapthon	300	262(100), 125(64), 216(20)	
Dichlofenthion	314	279(100), 223(50), 281(42)	285(100), 278(81), 250(60)
Dichlorvos	220	109(100), 185(25), 145(7)	125(100), 134(28), 205(23)
Dicrotophos	237	127(100), 193(15)	125(100), 224(14)
Dimethoate	229	125(100), 143(20), 229(10)	157(100)

Compound name	M.W.	EI	NICI
		m/z, % relative abund.	m/z, % relative abund.
Dioxathion	456	125(100), 153(30), 270(30)	153(100), 185(<1)
Disulfoton	274	142(100), 186(70), 274(75)	185(100)
EPN	323	157(100), 169(65), 185(38)	138(100), 323(38)
Ethion	384	231(100), 153(85), 125(80)	185(100)
Ethoprop	242	158(100), 139(58), 126(40)	199(100)
Etrimfos	292	125(100), 109(43), 292(36)	
Famphur	325	218(100), 125(61)	
Fenamiphos	303	154(100), 303(87), 217(54)	153(100)
Fenchlorphos	320	285(100), 125(65), 109(28)	211(100), 141(37), 270(13)
Fenitrooxon	261		261(100)
Fenitrothion	277	109(100), 125(97), 277(67)	168(100), 277(84), 141(29)
Fensulfothion	308	125(100), 141(85), 293(80)	169(100), 293(19), 171(14)
Fenthion	278	278(100), 125(70), 169(30)	263(100), 141(52), 277(10)
Fonofos	246	109(100), 137(60), 246(46)	169(100), 109(72)
Formothion	257	125(100), 126(70), 170(20)	157(100)
Heptenophos	251	124(100), 109(40), 250(7)	
Iodofenphos	412	377(100), 125(44), 379(37)	
Iprobenfos	288	204(100), 288(18), 246(18)	
Lepthophos	410	171(100), 377(62), 375(45)	241(100), 239(61), 243(46)
Malaoxon	314	127(100), 109(30), 195(15)	141(100), 172(9)
Malathion	330	127(100), 125(100), 173(95)	157(100)
Mecarbam	329	131(100), 125(49), 329(12)	
Menazon	281	156(100), 125(24), 281(19)	
Methamidophos	141	141(100), 111(19)	
Methidathion	302	145(100), 125(20)	157(100)
Mevinphos-beta	224	127(100), 192(24), 109(32)	125(100)
Mevinphos-alpha	224	127(100), 192(30), 109(25)	
Monocrotophos	223	127(100), 109(22), 192(7)	125(100), 208(9)
Naled	378	109(100), 145(53)	251(100), 205(43), 160(33)
Omethoate	213	110 (100), 125 (17), 213(4)	141(100), 198(7)
Parathion	291	109(100), 139(40), 291(35)	154(100), 291(28), 169(14)

Compound name	M.W.	EI	NICI
		m/z, % relative abund.	m/z, % relative abund.
Parathion-methyl	263	263(100), 149(64), 109(99)	154(100), 263(67), 141(22)
Paraoxon	275	109(100), 220(20), 275(20)	275(100), 153(40), 152(25)
Paraoxon-methyl	247		247(100)
Phenkapton	376		177(100), 185(89)
Piperophos	353	122(100), 140(80), 320(50)	
Pirimiphos-ethyl	333	333(100), 318(82), 304(58)	
Pirimiphos-methyl	305	290(100), 276(90), 305(65)	
Phorate-O		171(100), 111(75), 143(45)	
Phorate	260	121(100), 260(38), 231(29)	185(100)
Phosalone	367	182(100), 184(35), 121(65)	185(100)
Phosmet	317	160(100), 161(15), 317(2)	157(100), 207(14), 161(9)
Phosphamidon	299	127(100), 264(46), 138(35)	125(100), 178(46), 249(41)
Phoxim	298	129(100), 157(78), 298(15)	169(100)
Profenofos	374	139(100), 208(75), 339(30)	
Prothoate	285	115(100), 285(8), 121(18)	
Pyrazophos	373	221(100), 232(31), 373(22)	373(100), 169(40), 236(9)
Pyridafenthion	340	199(100), 188(89), 340(79)	340(100), 169(40)
Quinalphos	298	146(100), 298(170)	
Ronnel	320	125(100), 285(97), 287(64)	211(100), 213(99), 141(20)
RPA-400629	368	171(100), 121(31), 215(30),	185(100), 169(49)
Stirofos	366	109(100), 331(66),	125(100)
Sulfotepp	322	322(100), 202(53), 266(39)	293(100), 169(38), 277(12),
Temephos	466	466(100), 125(51), 203(10)	
Terbufos	288	103(100), 231(59), 153(45)	
Tetrachlorvinphos	364	109(100), 329(84), 331(80)	125(100)
Thiomethon	246	125(100), 158(10)	
Thionazin	248	107(100), 106(73), 143(52)	
Triamiphos	294		293(100)
Triazophos	313	161(100), 162(80), 257(30)	95(100), 312(31), 169(29)
Trichlorfon	256	109(100), 110(75), 139(60)	147(100), 170(19), 134(14)
Vamidothion	287	145(100), 142(53), 109(53)	141(100), 272(10), 259(10)

10. QUALITY ASSURANCE

Guidelines for data acquisition and data quality evaluation in environmental chemistry are published by UNEP (Reference Method 57) and by the American Chemical Society (ASC, 1980).

It has been recommended that a reference material should be analysed periodically to check on the quality of analytical data. Nowadays, there is no a reference material for OPs compounds in sediments, and consequently, the accuracy of the method can not be checked. However, analysts should use their own specially prepared reference material for quality control purposes to check the precision of their measurements.

One approach consist on the *recovery test method*, which can be determined by analysing samples to which have been added known amounts of analyte. This procedure has the limitation that the added analyte is not necessarily in the same form as that naturally present in the sample matrix and, because of its more availability , may give unduly optimistic recovery figures.

Recovery test method

Make a recovery test by spiking three subsamples of a sediment sample with appropriate amount of pesticides (between 200 and 1000 ng/g depending on the expected concentration). Analyse the unspiked and spiked subsamples in the same way as is described for the samples. Calculate the recoveries according to the 9.3 section. For those analytes naturally present in the unspiked sediment, corrected recoveries of analytes should be calculated by substracting the amount of analyte naturally present in the unspiked sample.

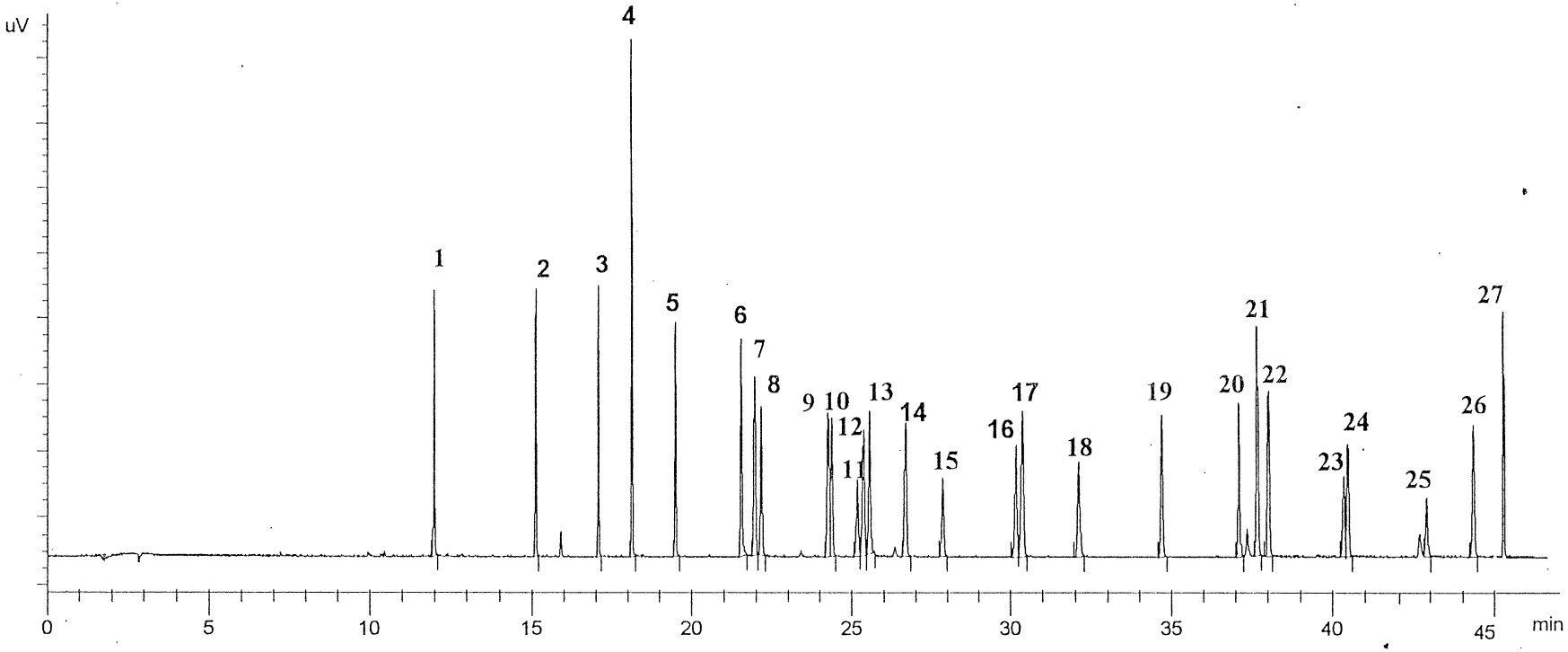


Fig. 1. GC-FPD chromatogram for organophosphorous standards. Peaks: 1= Dichlorvos; 2= TiBP; 3= TBP; 4= Sulfotep; 5= Diazinon; 6 = Monocrotophos; 7= Methylchlorpyrifos; 8= Dimethoate; 9= Chlorpyrifos; 10= Parathion-methyl; 11= Fenthion; 12= Malathion; 13 = Fenitrothion; 14= Parathion-ethyl; 15= Chlorthion; 16= Tetrachlorvinphos; 17= Methidathion; 18= Fenamiphos; 19= Ethion; 20= Tris(2ethylhexyl)phosphate; 21= Triphenylphosphate; 22= Tributoxiethylphosphate; 23= Leptophos; 24= EPN; 25= Azinphos-methyl; 26= Azinphos-ethyl; 27= Coumaphos.

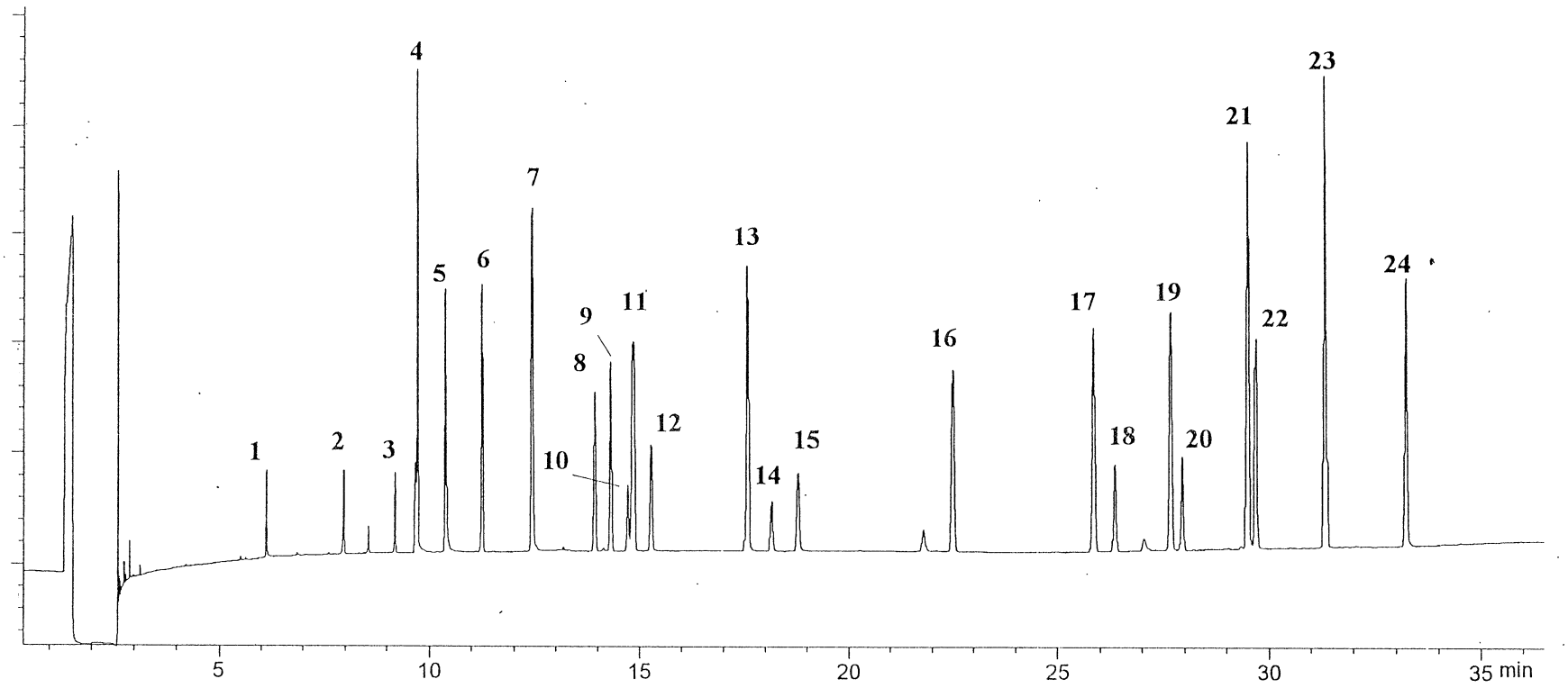


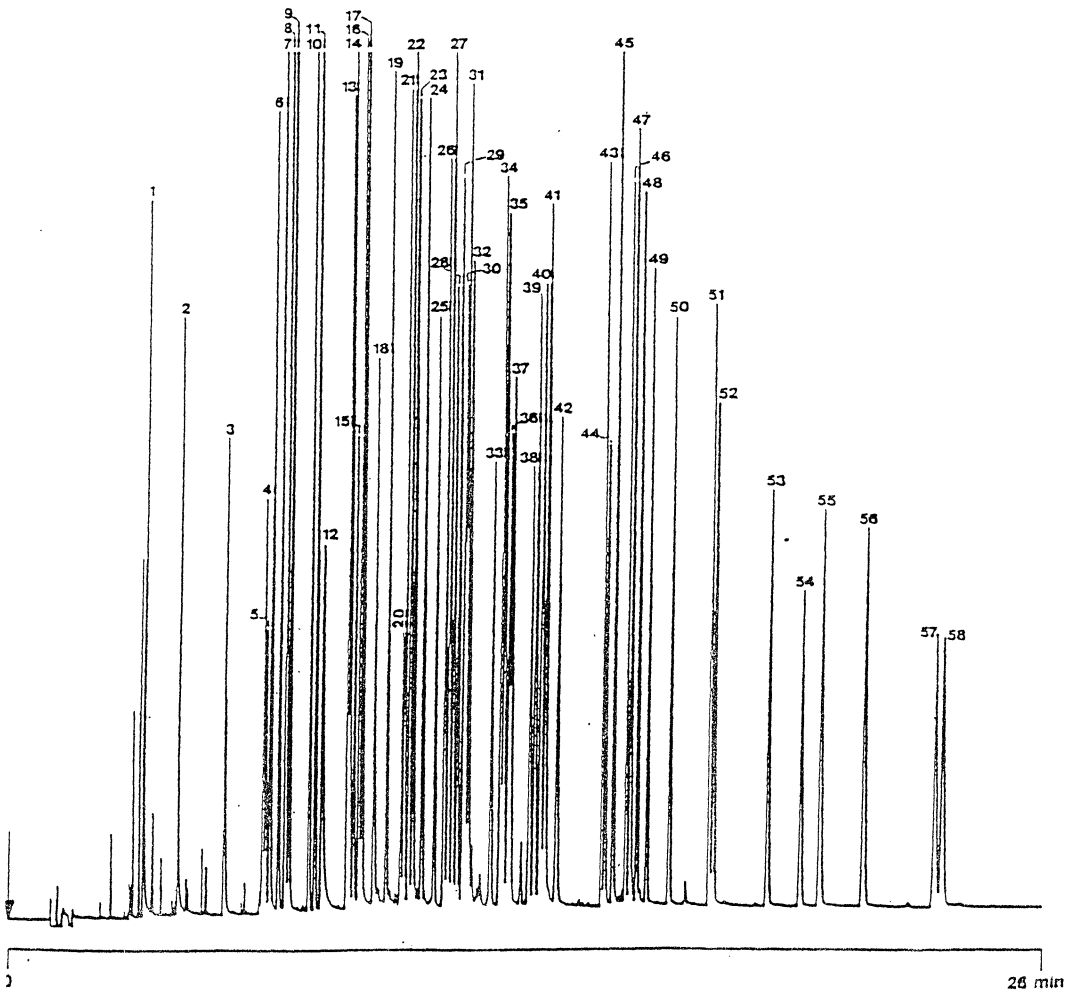
Fig. 2. GC-NPD chromatogram for organophosphorous standards. Peaks: 1= Dichlorvos; 2= TiBP; 3= TBP; 4= Monocrotophos and Sulfotep; 5= Dimethoate; 6= Diazinon; 7= Methylchlorpyrifos and Parathion-methyl; 8= Fenitrothion; 9= Malathion; 10= Fenthion; 11= Chlorpyrifos and Parathion-ethyl; 12= Chlorthion; 13= Methidathion;14= Tetrachlorvinphos; 15= Fenamiphos; 16= Ethion; 17= Triphenylphosphate; 18= Tributoxiethylphosphate; 19= EPN; 20= Tris(2ethylhexyl)phosphate; 21= Azinphos-methyl; 22= Leptophos; 23= Azinphos-ethyl; 24= Coumaphos.

Conditions:30 m x 0.25 mm i.d.x 0.25 μm PTE-5 (5% phenylmethylsilixone). Injector temperature: Splitless: 250 ^{o}C; Detector temperature: 225 ^{o}C; Temperature programme: 60 ^{o}C for 1 min; 60 ^{o}C to 190 at 25 ^{o}C/min, 190 ^{o}C to 225 ^{o}C at 2 ^{o}C/min, 225 ^{o}C to 280 ^{o}C at 5 ^{o}C/ min, 280 ^{o}C isothermal for 10 min.

Separation of organophosphorous pesticides

Chromatogram 4

Column	:	CP-Sil 13 CB fused silica WCOT 50 m x 0.32 mm; df = 0.4 µm Cat.no. 7937
Temperature	:	80°C → 270°C, 20°C/min
Carrier gas	:	H_2, 100 kPa (1.0 bar, 14 psi)
Injector	:	on-column
Detector	:	NPD
Sample size	:	1 µl
Concentration range	:	1 ng/compound
Courtesy	:	Mr. Lembacher, Hipp K.G., Pfaffenhofen Germany



Peak identification:

1. triethyl phosphate
2. dichlorvos
3. mevinphos
4. tinox
5. TCPP
6. heptenophos
7. tributyl phosphate
8. phorate oxon
9. ethoprophos
10. sulfotep
11. phorate
12. monocrotophos
13. dimethoate
14. diazinon
15. dioxathion
16. cyanophos
17. disulfoton
18. paraoxon-methyl
19. dichlophethiol
20. malaoxon
21. dursbanmethyl
22. methyl parathion
23. ronnel
24. pirimiphos methyl
25. malathion
26. dursbanethyl
27. ethyl parathion
28. trichloronate
29. pirimiphosethyl
30. cruforuate
31. chlorthion
32. bromophos-methyl
33. chlorfervinphos
34. quinalphos
35. phenthoate
36. bromophos ethyl
37. prophaphos
38. tetrachlorvinphos
39. methidathion
40. fenaminphos
41. bromfenvinphos
42. profenphos
43. ethion
44. fensulfothion
45. triaminphos
46. triazophos
47. carbophenothion
48. famphur
49. edifenphos
50. triphenyl phosphate
51. EPN
52. phenkapton
53. phosalon
54. azinphos-methyl
55. pyrazophos
56. azinphos ethyl
57. coumaphos
58. tri-p-cresyl phosphate

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Bromophos-ethyl	*O*-4-bromo-2,5-dichlorophenyl *O,O*-diethylphosphorothioate	394.0	0.14	6.1 (30)	5.7
Butamifos	*O*-ethyl *O*-6-nitro-*m*-tolyl *sec*-butylphosphoramidothioate	332.4	5	84 (27)	
Carbophenothion	*S*-(4-chlorophenylthio)methyl *O,O*-diethylphosphorodithioate	342.9	< 1	1.07 (25)	5.1
Chlorfenvinfos	2-chloro-1(2,4-dichlorophenyl)vinyl diethyl phosphate	359.6	145 (23)	0.530 (20)	3.8
Chlormephos	S-choromethyl O,O-diethyl phosphorodithioate	234.7	60	7600 (30)	
Chlorphoxim	2-(2-chlorophenyl)-2(dietoxyphosphinothioxyloxyimino)acetonitrile	332.7	1.7	< 1 (20)	
Chlorpyrifos	*O,O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate	350.6	2 (25)	2.5 (25)	5.0
Chlorpyrifos-methyl	*O,O*-dimethyl *O*-3,5,6-trichloro-2pyridyl phosphorothioate	322.5	4 (24)	5.6 (25)	4.3
Chlorthion	*O,O*-dimethyl *O*-(3-chloro-4-nitrophenyl)phosphorothioate	297.5			
Chlorthiophos	*O*-2,5-dichloro-4-(methylthio)phenyl *O,O*-diethyl phosphorothioate	361.2	0.3	0.53 (25)	
Coroxon, Coralox	*O*-3-chloro-4-methyl-2-oxo-2*H*-1-benzopyran-7-yl *O,O*-diethyl phosphate	346	ins.		
Coumaphos	*O*-3-chloro-4-methyl-2-oxo-2*H*-chroment-7-yl *O,O*-diethyl phosphorothioate	362			
Coumithoate	*O*-(7,8,9,10-tetrahydro-6-oxo-6*H*-dibenzo[*b,d*] pyran-3-yl) *O,O*-diethyl phosphorothionate	368	ins.		

Annex 1. List of the organophosphorous pesticides most used worldwide (Royal Society of Chemistry, 1987; British Crop Protection Council, 1983)

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Acephate	*O,S*-dimethyl acetylphosphoramidothioate	183.2	790000	0.226 (24)	
Amidithion	*S*-2-methoxyethylcarbamoylmethyl *O,O*-dimethyl phosphorodithioate	273			
Anilofos	*S*-4-chloro-*N*-isopropylcarbaniloylmethyl *O,O*-dimethylphosphorodithioate	367.5	13.6	2.2 (60)	
Azamethiphos	*S*-6-chloro-2,3-dihydro-2-oxo-oxazolo[4,5-b]pyridin-3-ylmethyl *O,O*-dimethyl phosphorothioate	324.7	1100	0.005 (20)	
Azinphos-ethyl	*S*-3,4-dihydro-4-oxobenzo[d]-[1,2,3]-triazin-3-ylmethyl) *O,O*-diethyl phosphorodithioate	345.4	4-5	<0.029 (20)	3.4
Azinphos-methyl	*S*-(3,4-dihydro-4-oxobenzo[d]-[1,2,3]-triazin-3-ylmethyl) *O,O*-dimethyl phosphorodithioate	317.1	29 (25)	<0.001 (20)	2.7
Bensulide	*O,O*-diisopropyl S-2-phenylsulphonylaminoethyl phosphorodithioate	397.5	25	<0.133 (25)	
Bialaphos	L-2-amino-4-[(hydroxy)(methyl)phosphinoyl]butyryl-L-alanyl-L-alanine	323.3	1000000		
Bromophos	*O*-4-bromo-2,5,-dichlorophenyl *O,O*-dimethylphosphorothioate	366.0	0.7	17 (20)	4.9

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Crotoxyphos	dimethyl (*E*)-1-methyl-2-(1-phenylethoxycarbonyl)vinyl phosphate	314.3	1000	1.9 (20)	
Cyanofenphos	*O*-4-cyanophenyl-*O*-ethyl phenylphosphonothioate	303.3	0.6 (30)	0.001 (20)	
Cyanophos	*O*-4-cyanophenyl *O,O*-dimethyl phosphorothioate	243.2	46 (30)	105 (20)	2.74
Demeton-O	*O,O*-diethyl *O*-[2-(ethylthio)ethyl]phosphorothioate	258.3	60	34 (20)	
Demeton-S	*O,O*-diethyl *S*-[2-(ethylthio)ethyl]phosphorothioate	258.3	2000	34(20)	
Demeton-S-methyl	*S*-2-ethylthioethyl *O,O*-dimethyl phosphorothioate	230.3	3300	48 (20)	
Demeton-S-methylsulphone	*S*-2-ethylsulphonylethyl *O,O*-dimethyl phosphorothioate	262.3	3300	0.66 (20)	
Dialifos, Dialifor	*S*-2-chloro-1-phthalimidoethyl *O,O*-diethyl phosphorodithioate	393.8	< 1	133 (35)	
Diazinon	*O,O*-diethyl *O*-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate	304.3	40	0.097 (20)	3.8
S,S-di-sec-butyl O-ethyl phosphorodithioate	*S,S*-di-sec-butyl *O*-ethyl phosphorodithioate	270.4	248	120 (25)	
Dicapthon	O-2-chloro-4-nitrophenyl O,O-dimethyl phosphorothioate	300			3.6
Dichlofenthion	*O*-(2,4-dichlorophenyl) *O,O*-diethyl phosphorothioate	315.2	245		5.38
Dichlorvos	2,2-dichlorovinyl dimethyl phosphate	221.0	10000	1600 (20)	1.5
Dicrotophos	(*E*)-2-dimethylcarbamoyl-1-methylvinyl dimethyl phosphate	237.2	Misc.	9.3 (20)	
Dimethoate	*O,O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate	229.2	25000	1.1 (25)	0.8

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Dioxathion	*S,S'*-(1,4-dioxane-2,3-diyl) *O,O,O',O'*-tetraethyl di(phosphorodithioate)	456.5	Ins.	Neg.	
Disulfoton	*O,O*-diethyl *S*-2-ethylthioethyl phosphorodithioate	274.4	25	24 (20)	4.0
Ditalimfos	*O,O*-diethyl phthalimidophosphonothioate	299.29	133	93 (100)	
Edifenphos	*O*-ethyl *S,S*-diphenyl phosphorodithioate	310.4	56	13 (20)	
EPBP	*O*-2,4-dichlorophenyl O-ethylphenylphosphonothioate	347.2	ins.	509000 (200)	
EPN	*O*-ethyl *O*-4-nitrophenyl phenylphosphonothioate	323.3	Ins.	0.126 (250	
Ethion	*O,O,O',O'*-tetraethyl *S,S'*-methylene bis(phosphorodithioate)	384.5	Sparingly	0.2 (25)	5.1
Ethoprophos	*O*-ethyl *S,S*-dipropyl phosphorodithioate	242.3	750	46.5 (26)	
Etrimfos	*O*-6-ethoxy-2-ethylpyrimidin-4-yl *O,O*-dimethyl phosphorothioate	292.3	40	6.5 (20)	
Famphur	O-4-dimethylsulphamoylphenyl O,O-dimethyl phosphorothioate	325.3	sparing.		
Fenamiphos	ethyl 4-methylthio-*m*-tolyl isopropylphosphoramidate	303.4	700	0.133 (30)	3.2
Fenchlorphos, Ronnel	*O,O*-dimethyl *O*-2,4,5-trichlorophenyl phosphorothioate	320			4.8
Fenitrothion	*O,O*-dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate	277.2	30	18 (20)	3.4
Fensulfothion	*O,O*-diethyl *O*-4methylsulphinylphenyl phosphorothioate	308.3	1540		2.2
Fenthion	*O,O*-dimethyl *O*-4-methylthio-*m*-tolyl phosphorothioate	278.3	55	4 (20)	4.1
Fonofos	*O*-ethyl *S*-phenyl (*RS*)-ethylphosphonodithioate	246.3	13	28 (25)	3.9

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Formothion	*S*-(*N*-formyl-*N*-methylcarbamoylmethy) *O,O*-dimethyl phosphorodithioate	257.3	2600	0.113 (20)	
Glyphosate	*N*-(phosphonomethyl)glycine	169.1	12000	Negl.	
Heptenophos	7-chlorobicyclo[3.2.0]hepta-2,6-dien-6-yl dimethyl phosphate	250.6	2200	65 (15)	
IBP	*S*-benzyl *O,O*-di-isopropyl phosphorothioate	288.3	1000		
Iodofenphos	*O*-2,5-dichloro-4-iodophenyl *O,O*-dimethyl phosphorothioate	413.	<2	0.106 (20)	5.2
Iprobenfos	*S*-benzyl *O,O*-di-isopropyl phosphorothioate	288.3	1000	0.247 (20)	
IPSP	*S*-ethylsulphinylmethyl *O,O*-di-isopropyl phosphorodithioate	304.4	1500 (15)	2 (27)	
Isazofos	*O*-5-chloro-1-isopropyl-1*H*-1,2,4,-triazol-3-yl *O,O*-diethyl phosphorothioate	313.7	250	4.3 (20)	
Isofenphos	*O*-ethyl *O*-2-isopropoxycarbonylphenyl isopropylphosphoramidothioate	345.4	24	0.53 (20)	4.1
Isothioate	*S*-2-isopropylthioethyl *O,O*-dimethyl phosphorodithioate	260.4	97	293 (20)	
Isoxathion	*O,O*-diethyl *O*-5-phenylisoxazol-3-yl phosphorothioate	313.3	1.9	<0.133 (25)	4.58
Lepthophos	*O*-4-bromo-2,5-dichlorophenyl *O*-methyl phenylphosphonothioate	410			5.9
Malathion	*S*-1,2-bis(ethoxycarbonyl)ethyl *O,O*-dimethyl phosphorodithioate	330.3	145	5.3 (30)	2.8

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Mecarbam	*S*-(*N*-ethoxycarbonyl-*N*-methylcarbamoylmethyl) *O,O*-diethyl phosphorodithioate	329.4	<1000	Neg.	
Menazon	S-4,6-diamino-1,3,5-triazin-2-ylmethyl O,O-dimethyl phosphorodithioate	281			
Methacrifos	methyl (*E*)-3(dimethoxyphosphinothioyloxy)-2-methacrylate	240.2	400	160 (20)	
Methamidophos	*O,S*-dimethyl phosphoramidothioate	141.1	2000000	40 (30)	
Methidathion	*S*-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl *O,O*-dimethyl phosphorodithioate	302.3	240	0.13 (20)	2.4
Mevinphos	2-methoxycarbonyl-1-methylvinyl dimethyl phosphate	224.1	Misc.	17 (20)	
Monocrotophos	dimethyl (*E*)-1-methyl-2-(methylcarbamoyl)vinyl phosphate	223.2	1000000	9 (20)	
Naled	1,2-dibromo-2,2-dichloroethyl dimethyl phosphate	380.8	Ins.	266 (20)	
Omethoate	*O,O*-dimethyl S-methylcarbamoylmethyl phosphorothioate	213.2	Misc.	3.2 (20)	
Oxydemeton-methyl	*S*-2-ethylsulphinylethyl *O,O*-dimethyl phosphorothioate	246.3	Misc.	3.8 (20)	
Oxydeprofos	*S*-2-ethylsulphinyl-1-methylethyl *O,O*-dimethyl phosphorothioate	260.3	Sol.	0.625 (20)	
Parathion	*O,O*-diethyl *O*-4-nitrophenyl phosphorothioate	291.3	24	5 (20)	3.8
Parathion-methyl	*O,O*-dimetnyl *O*-4-nitrophenyl phosphorothioate	263.2	60	1.3 (20)	2.9
Phenkapton	*S*-2,5-dichlorophenylthiomethyl *O,O*-diethyl phosphorodithioate	376			

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Phenthoate	*S*-α-ethoxycarbonylbenzyl *O,O*-dimethyl phosphorodithioate	320.4	11	5 (40)	4.31
Piperophos	*S*-2-methylpiperidinocarbonylmethyl *O,O*-dipropyl phosphorodithioate	353.5	25	0.032 (20)	
Pirimiphos-ethyl	*O*-2-diethylamino-6-methylpyrimidin-4-yl *O,O*-diethyl phosphorothioate	333.4	< 1	39 (25)	4.8
Pirimiphos-methyl	*O*-2-diethylamino-6-methylpyrimidin-4-yl *O,O*-dimethyl phosphorothioate	305.3	5	15 (30)	4.2
Phorate	*O,O*-diethyl *S*-ethylthiomethyl phosphorodithioate	260.4	50	110 (20)	3.8
Phosalone	*S*-6-chloro-2,3-dihydro-2-oxobenzoxazol-3-ylmethyl *O,O*-diethyl phosphorodithioate	367.8	10	Neg.	4.4
Phosdiphen	bis(2,4-dichlorophenyl) ethyl phosphate	416.0	0.7	66 (20)	
Phosfolan	diethyl 1,3-dithiolan-2-ylidenephosphoramidate	255.3	650000		
Phosmet	*O,O*-dimethyl *S*-phthalimidomethyl phosphorodithiate	317.3	25	133 (25)	2.8
Phosphamidon	2-chloro-2-diethylcarbamoyl-1-methylvinyl dimethyl phosphate	299.7	Misc.	3.3 (200)	
Phoxim	*O,O*-diethyl α-cyanobenzylideneamino-oxyphosphonothioate	298.3	7	10 (20)	4.4
Profenofos	*O*-4-bromo-2-chlorophenyl *O*-ethyl *S*-propyl phosphorothioate	373.6	20	1.3 (20)	
Propaphos	4-(methylthio)phenyl dipropyl phosphate	304.3	125		

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Propetamphos	(*E*)-*O*-2-isopropoxycarbonyl-1-methylvinyl *O*-methyl ethylphosphoramidothioate	281.3	110	1.9 (20)	
Prothiofos	*O*-2,4-dichlorophenyl *O*-ethyl *S*-propyl phosphorodithioate	345.2	1.7	< 1(20)	
Prothoate	*O,O*-diethyl *S*-isopropylcarbamoylmethyl phosphorodithioate	285.4	2500	13 (40)	
Pyrazophos	*O*-6-ethoxycarbonyl-5-methylpyrazolo[1,5-a]pyrimidin-2-yl *O,O*-diethyl phosphorothioate	373.4	4.2	0.22 (20)	
Pyridafenthion	*O,O*-diethyl-*O*-[2-phenyl-3(2*H*)-pyridazinone-6-yl] phosphorothioate	340.3	ins.		
Quinalphos	*O,O*-diethyl *O*-quinaxalin-2-yl phosphorothioate	298.3	22	0.346 (20)	
Stirofos	*O,O*-diethyl *O*-2-chloro-1-(2,4,5-trichlorophenyl)ethenyl phosphate	364	11		
Sulfotep	*O,O,O',O'*-tetraethyl dithiopyrophosphate	322.3	25	22 (20)	
Sulprofos	*O*-ethyl *O*-4-(methylthio)phenyl *S*-propyl phosphorodithioate	322.4	< 5	< 0.1(20)	
Temephos	*O,O,O',O'*-tetramethyl *O,O'*-thiodi-p-phenylene bis(phosphorothioate)	466.5	ins.		5.9
TEPP	tetraethyl pyrophosphate	290.2	misc.	21 (20)	
Terbufos	*S*-tert-butylthiomethyl *O,O*-diethyl phosphorodithioate	288.4	4.5	35 (26)	4.5
Tetrachlorvinphos	(*Z*)-2-chloro-1(2,4,5-trichlorophenyl)vinyl dimethyl phsophate	366.0	11		

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
O,O,O',O'-tetrapropyl dithiopyrophosphate	*O,O,O',O'*-tetrapropyl dithiopyrophosphate	378.4	30	13 (25)	
Thiomethon	*S*-2-ethylthioethyl *O,O*-dimethyl phosphorodithioate	246.3	200	20 (20)	
Thionazin	O,O-diethyl O-pyrazin-2-yl phosphorothioate	248.2	1140	400 (30)	
Tolclofos-methyl	*O*-2,6-dichloro-p-tolyl *O,O*-dimethyl phosphorothioate	301.1	0.4	57 (20)	
Triamiphos	5-amino-3-phenyl-1H-1,2,4-triazol-1-yl-N,N,N',N'-tetramethylphosphonic diamide	294			
Triazophos	*O,O*-diethyl *O*-1-phenyl-1*H*-1,2,4-triazol-3-yl phosphorothioate	313.3	35	0.39 (30)	3.5
S,S,S-tributyl phosphorotrithioate	*S,S,S*-tributyl phosphorotrithioate	314.5	2.3		
Tributyl phosphorotrithioite	Tributyl phosphorotrithioite	298.5	Sparing.		
Trichlorfon	dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate	257.4	154000	1 (20)	0.43
Trichloronate	*O*-ethyl *O*-2,4,5-trichlorophenyl ethylphosphonothioate	333.6	50	2 (20)	5.2
Vamidothion	*O,O*-dimethyl *S*-2-(1methylcarbamoylethylthio)ethyl phosphorothioate	287.3	4000000	Neg.	

a: Temperature at which the vapour pressure has been measured is given in brackets
b: From Bowman and Sans, 1983 and OECD, 1989.