

## References

- Aldridge, W.N., and Davison, A.N. 1952. The inhibition of erythrocyte cholinesterase by tri-esters of phosphoric acid. J. of Biochem. 51-62.
- Balinova, A. 1993. Solid-phase extraction followed by high-performance liquid chromatographic analysis for monitoring herbicides in drinking water. J. of Chromatography. 643: 203-207.
- Bardalaye, P.C., and Wheeler, W.B. 1986. Solid-phase extraction and capillary gas chromatographic determination of triazine herbicides in water. Intern. J. Environ. Anal. Chem. 25: 105-113.
- Barnes, K.A. 1995. Determination of the pesticide diflufenzuron in mushrooms by high-performance liquid chromatography-atmospheric pressure chemical ionisation mass spectrometry. J. of Chromatography A. 712: 85-93
- Bidlingmeyer, B.A. 1984. Guidelines for proper usage of solid phase extraction devices. LC-GC. 2: 8.
- Biggar, J.W., and Seiber, J.N. 1987. Organophosphorus and Carbamate Esters : The Anticholinesterase Insecticides. Fate of Pesticides in the Environment. 5-18.
- Brooks, M.W. Tessier, D., and Soderstrong, D. 1990. A Rapid method for the simultaneous analysis of Chlorpyrifos, Isofenphos, Carbaryl, Iprodione and Triadimefon in groundwater by solid- phase extraction. J. of Chromatographic Science. 28: 330-339.
- Buchheit, A. J., and Witzendacher, M. 1996. Pesticide monitoring of drinking water with the help of solid-phase extraction and High Performance Liquid Chromatography- atmospheric pressure chemical ionisation mass spectrometry. J. of Chromatography A. 712: 85-93.
- Capel, P.D., Ma, L., Schroyer, B.R., Larson, S.T., and Gilchrist, T.A. 1995. Analysis and detection of the new corn herbicide acetochlor in river water and rain. Envi. Sci. Tech. 29: 1702-1705.
- Cheremisionoff, N.P., and King, J.A. 1991. Toxic properties of pesticides. Environmental Science and Pollution control Series. 58-70.
- Dauterman, W.C. 1971. Biological and nonbiological modifications of organophosphorus compounds. Bull. W.H.O. 44-133.

- Driss, M.R., Hennion, M.C., and Bouguerra, M. L. 1993. Determination of Carbaryl and some organophosphorus pesticides in drinking water using on-line liquid chromatographic preconcentration techniques. J. of Chromatography. 639: 352-358.
- Edwards, C.A. 1987. Nature and origins of Pollution of Aquatic systems by pesticides. 11-20.
- Eto, M. 1974. Organophosphorus pesticides. Cleveland: CRC Press. 30-33.
- Font, G., Manes, J., Molto, J.C., and Pico, Y. 1993. Solid phase extraction in multi-residue pesticide analysis of water. J. of Chromatography. 642: 135-161.
- Fukuto, T.R. 1987. Organophosphorus and Carbamate Esters. Fate of Pesticides in the Environment. 52-66.
- George, W.W. 1978. The Pesticides Book. University of Arizona USA. 34-38.
- Glajch, J.L. and Kirkland, J.J. 1990. Stable, sterically protected, monofunctional-silane bonded- phase columns for high performance liquid chromatography. LC-GC. 8: 140-150.
- Hanks, A.R. 1992. Liquid chromatographic method for determination of Methamidophos in technical products and pesticide Formulations : CIPAC Collaborative Study. J. of AOAC International. 75: 220-226.
- International Programme on Chemical Safety. 1986. Environmental Health Criteria 63. Organophosphorus insecticides : A General Introduction. 25-30.
- J.T. Baker Inc. 1991. Solid phase extraction for sample preparation. Bakerbond Application Note. 3-6.
- Kobayashi, H., Ohyama, K., Tomiyama, N., Jimbo, Y., Matano, O., and Goto, S. 1993. Determination of pesticides in river water by gas chromatography-mass spectrometry selected ion monitoring. J. of Chromatography. 643: 197-202.
- Larson, R.D., and Houglum, J.E. 1991. Liquid chromatography of pesticide formulations containing Dicamba, 2,4-D, and MCPP. J. ASSOC. OFF. Anal. Chem. 74: 113-122.
- Lindsay, S. 1987. High Performance Liquid Chromatography. London : 244 p.
- Liska, I., Krupcik, J. and Leclercq., P.A. 1989. The use of solid sorbents for direct accumulation of organic compounds from water matrices. J. High Resol. Chromatogr. 12: 577-590.
- Majors, M.E. 1986. Sample preparation for HPLC and Gas Chromatography using solid phase extraction. LC-GC. 4: 981-982.
- Markell, C., Hagen, D. F., and Bunnelle, V.A. 1985. New technologies in solid-phase extraction. LC-GC. 9: 10-15.

- Marvin, H.C., and Brindle, I.D. 1990. Automated high performance liquid chromatography for the determination of pesticides in water using solid phase extraction. Anal. Chem. 62: 1495-1498.
- MC. Doneld, T., and Rosenfeld, J. 1993. Solid - phase sample preparation of natural water with reversed-phase disk. J. of Chromatography. 629: 41-53.
- McLafferty, F.W. 1980. Interpretation of Mass Spectra. 3 d ed. University science books. 86-90.
- Mills, M.S., and Thurman, E.M. 1993. Application of mixed-mode, solid-phase extraction in environmental and clinical chemistry. J. of chromatography. 629: 11-21.
- Naidong, W.K., Roets, V.E., and Hoogmartens, J. 1991. Determination of metacycline and related substances by column liquid chromatography on poly (styrene-divinylbenzene). J. of chromatography. 586: 61-66.
- Okumura, T., and Nishikawa, Y. 1995. Determination of organophosphorus pesticides in environmental samples by capillary gas chromatography - mass spectrometry. J. of Chromatography. 709: 319-331.
- Prasad,S.S. 1992. Predicting the environmental distribution of compounds with unknown physicochemical properties from known pesticide properties. J. of AOAC.75: 20-25.
- Richardson, M.L., and Gangolli, S. 1996. The Dictionary of Substances and their Effects. England. 2: 460-462.
- Richardson, M.L., and Gangolli, S. 1996. The Dictionary of Substances and their Effects. England. 5: 304-309.
- Richardson, M.L., and Gangolli, S. 1996. The Dictionary of Substances and their Effects. England. 6: 259-417.
- Schuster, R. 1994. Application note. Hewlett packard. 35-37.
- Snyder, L.R.,and Kirkland, J.J.1979. Introduction to Modern Liquid Chromatography. 2d ed. 15-30.
- Stenhagen, E., Abrahamsson, S., and McLafferty, F.W. 1974. Registry of Mass Spectral Data. Wiley. 3358 pp.
- Stephen,H., Spencer, S. and Seager,L. 1976. Environmental chemistry: air and water pollution. Water Pollution. 168-171.
- Van Horne, K.C., et al. 1985. Sorbent extraction technology. Harbor city: Analytichem International, Inc.13-16.

## **APPENDIX**

### Appendix-A

The results of optimum conditions (Table)

**Table A-1** The effect of sorbent mass on the percent recovery for each OPs in mixture solution at 1.00 ppm

Compounds	C <sub>18</sub> SPE mass (mg)	Conc. before extraction(ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
Malathion	100	1.00	20.91	104.55	±3.93
	200	1.00	19.89	99.48	±5.90
	300	1.00	19.06	95.30	±4.08
	400	1.00	19.86	99.32	±6.03
	500	1.00	20.45	20.45	±2.46
Methyl parathion	100	1.00	20.29	101.45	±1.30
	200	1.00	20.43	102.13	±3.97
	300	1.00	19.69	98.4	±4.79
	400	1.00	19.21	96.06	±6.22
	500	1.00	19.37	96.88	±5.58
Profenofos	100	1.00	20.44	102.22	±2.65
	200	1.00	16.27	81.35	±2.03
	300	1.00	6.77	33.85	±3.54
	400	1.00	2.69	13.47	±3.48
	500	1.00	ND	-	-
Chlorpyrefos	100	1.00	70.60	70.60	±2.35
	200	1.00	40.78	40.78	±1.13
	300	1.00	ND	-	-
	400	1.00	ND	-	-
	500	1.00	ND	-	-

Remark : ND = Not Detectable

Triplicate analysis

**Table A-2** The effect of volume of mixture solution on the percent recovery for each OPs at 1.00 ppm (100 mg C<sub>18</sub>SPE)

Compounds	Volume of aq.sol (mL)	Conc. before extraction(ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
Malathion	500	1.00	9.72	48.64	±2.03
	400	1.00	13.32	80.91	±0.69
	300	1.00	9.67	80.60	±1.07
	200	1.00	6.68	83.56	±0.56
	100	1.00	3.44	86.07	±0.52
Methyl parathion	500	1.00	9.18	45.93	±0.78
	400	1.00	16.07	100.43	±1.57
	300	1.00	8.58	99.34	±0.61
	200	1.00	7.50	93.78	±0.58
	100	1.00	3.57	89.16	±0.40
Profenofos	500	1.00	19.99	99.96	±0.91
	400	1.00	14.55	90.97	±0.64
	300	1.00	10.18	84.87	±0.49
	200	1.00	7.99	99.91	±0.66
	100	1.00	3.98	99.57	±0.71
Chlorpyrefos	500	1.00	6.38	31.88	±0.47
	400	1.00	4.50	28.15	±1.17
	300	1.00	3.09	25.71	±1.44
	200	1.00	1.33	20.82	±2.45
	100	1.00	2.05	51.19	±1.13

Remark : ND = Not Detectable  
 Triplicate analysis

**Table A-3** The effect of volume of mixture solution on the percent recovery for each OPs at 1.00 ppm (500 mg C<sub>18</sub> SPE)

Compounds	Volume of aq.sol(mL)	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
Malathion	500	1.00	20.42	102.07	±2.10
	400	1.00	16.16	101.01	±1.37
	300	1.00	8.59	71.57	±0.95
	200	1.00	6.86	85.68	±0.74
	100	1.00	3.20	80.13	±0.45
Methyl parathion	500	1.00	20.21	100.84	±2.48
	400	1.00	15.90	99.39	±0.94
	300	1.00	11.82	98.56	±0.39
	200	1.00	7.21	90.06	±0.79
	100	1.00	3.45	86.24	±0.48
Profenofos	500	1.00	ND	-	-
	400	1.00	ND	-	-
	300	1.00	ND	-	-
	200	1.00	ND	-	-
	100	1.00	ND	-	-
Chlorpyrefos	500	1.00	ND	-	-
	400	1.00	ND	-	-
	300	1.00	ND	-	-
	200	1.00	ND	-	-
	100	1.00	ND	-	-

Remark : ND = Not Detectable  
TriPLICATE analysis

**Table A-4** The effect of elution solvent (MeOH/H<sub>2</sub>O) on the percent recovery for Malathion and Methyl parathion in mixture solution at 1.00 ppm using 100 mg C<sub>18</sub> SPE cartridge

Compounds	Ratio of MeOH/H <sub>2</sub> O	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
Malathion	90:10	1.00	18.04	90.19	±0.54
	80:20	1.00	17.39	86.97	±0.38
	70:30	1.00	16.73	83.66	±0.57
	60:40	1.00	16.19	80.95	±1.01
	50:50	1.00	15.66	75.69	±0.70
	40:60	1.00	8.81	44.08	±0.75
	30:70	1.00	ND	-	-
	20:80	1.00	ND	-	-
	10:90	1.00	ND	-	-
Methyl parathion	90:10	1.00	18.97	94.86	±0.84
	80:20	1.00	18.19	90.98	±0.79
	70:30	1.00	17.15	85.75	±0.49
	60:40	1.00	16.42	82.10	±0.18
	50:50	1.00	15.79	78.96	±0.71
	40:60	1.00	5.55	27.73	±1.58
	30:70	1.00	ND	-	-
	20:80	1.00	ND	-	-
	10:90	1.00	ND	-	-

Remark : ND = Not Detectable

Triplicate analysis



**Table A-5** The effect of elution solvent (MeOH/H<sub>2</sub>O) on the percent recovery for Profenofos and Chlorpyrifos in mixture solution at 1.00 ppm using 100 mg C<sub>18</sub> SPE cartridge

Compounds	Ratio of MeOH/H <sub>2</sub> O	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
Profenofos	90:10	1.00	16.44	82.20	±0.36
	80:20	1.00	15.95	79.77	±0.60
	70:30	1.00	14.82	74.12	±0.31
	60:40	1.00	8.16	40.78	±1.08
	50:50	1.00	ND	-	-
	40:60	1.00	ND	-	-
	30:70	1.00	ND	-	-
	20:80	1.00	ND	-	-
	10:90	1.00	ND	-	-
Chlorpyrefos	90:10	1.00	16.43	82.14	±0.43
	80:20	1.00	14.97	74.83	±1.04
	70:30	1.00	9.20	46.01	±1.91
	60:40	1.00	ND	-	-
	50:50	1.00	ND	-	-
	40:60	1.00	ND	-	-
	30:70	1.00	ND	-	-
	20:80	1.00	ND	-	-
	10:90	1.00	ND	-	-

Remark : ND = Not Detectable

Triplicate analysis

**Table A-6** The effect of elution solvent (ACN/H<sub>2</sub>O) on the percent recovery for Malathion and Methyl parathion in mixture solution at 1.00 ppm using 100 mg C<sub>18</sub> SPE cartridge

Compounds	Ratio of ACN/H <sub>2</sub> O	Conc. before extraction(ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
Malathion	90:10	1.00	20.06	100.31	±0.95
	80:20	1.00	19.97	99.87	±1.11
	70:30	1.00	19.75	98.75	±0.39
	60:40	1.00	20.00	100.00	±1.13
	50:50	1.00	18.80	94.00	±0.94
	40:60	1.00	7.66	38.30	±1.67
	30:70	1.00	0.29	1.46	±4.13
	20:80	1.00	ND	-	-
	10:90	1.00	ND	-	-
Methyl parathion	90:10	1.00	18.59	92.96	±0.40
	80:20	1.00	18.61	93.05	±0.76
	70:30	1.00	19.22	96.09	±0.16
	60:40	1.00	20.19	100.96	±1.51
	50:50	1.00	19.84	99.21	±0.67
	40:60	1.00	12.08	60.41	±0.69
	30:70	1.00	9.71	4.85	±3.29
	20:80	1.00	ND	-	-
	10:90	1.00	ND	-	-

Remark : ND = Not Detectable

TriPLICATE analysis

**Table A-7** The effect of elution solvent (ACN/H<sub>2</sub>O) on the percent recovery for Profenofos and Chlorpyrifosin mixture solution at 1.00 ppm using 100 mg C<sub>18</sub> SPE cartridge

Compounds	Ratio of ACN/H <sub>2</sub> O	Conc. before extraction(ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
Profenofos	90:10	1.00	12.22	61.12	±0.75
	80:20	1.00	12.37	61.87	±0.24
	70:30	1.00	13.75	68.76	±1.49
	60:40	1.00	19.98	99.89	±1.92
	50:50	1.00	12.39	61.99	±1.31
	40:60	1.00	1.93	9.65	±0.21
	30:70	1.00	ND	-	-
	20:80	1.00	ND	-	-
Chlorpyrefos	90:10	1.00	12.15	60.74	±0.81
	80:20	1.00	12.74	63.71	±0.72
	70:30	1.00	13.59	67.98	±0.72
	60:40	1.00	16.96	84.81	±0.47
	50:50	1.00	11.00	55.03	±0.25
	40:60	1.00	2.56	12.80	±0.86
	30:70	1.00	ND	-	-
	20:80	1.00	ND	-	-
	10:90	1.00	ND	-	-

Remark : ND = Not Detectable

Triplicate analysis

**Table A-8** The results of volume of elution solvent (60%acetonitrile)on the percent recovery for Malathion and Methyl parathion in mixture solution at 1.00 ppm

Compound	Volume of 60/40(ACN/H <sub>2</sub> O) (ml)	Conc. before ) extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
Malathion	1.0	1.00	2.74	27.45	±1.89
	2.0	1.00	7.66	76.63	±2.07
	3.0	1.00	13.58	82.46	±0.25
	4.0	1.00	22.24	88.94	±1.79
	5.0	1.00	18.34	91.68	±0.62
	6.0	1.00	11.60	68.24	±0.56
	7.0	1.00	8.21	57.41	±0.43
	8.0	1.00	6.91	55.31	±1.89
	9.0	1.00	6.22	55.99	±0.68
	10.0	1.00	5.39	53.95	±1.43
Methyl parathion	1.0	1.00	4.01	40.11	±2.39
	2.0	1.00	7.90	79.04	±3.89
	3.0	1.00	14.09	85.42	±0.59
	4.0	1.00	22.06	88.27	±0.45
	5.0	1.00	19.71	98.55	±2.40
	6.0	1.00	15.82	93.07	±1.91
	7.0	1.00	9.58	67.00	±1.43
	8.0	1.00	8.14	65.10	±0.23
	9.0	1.00	7.09	63.80	±0.64
	10.0	1.00	6.00	60.02	±1.62

Remark : ND = Not Detectable  
TriPLICATE analysis

**Table A-9** The results of volume of elution solvent (60%acetonitrile) on the percent recovery for Profenofos and Chlorpyrifos in mixture solution at 1.00 ppm

Compound	Volume of 60/40(ACN/H <sub>2</sub> O) ( ml )	Conc. before ) extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
Profenofos	1.0	1.00	ND	-	-
	2.0	1.00	1.93	19.33	±2.14
	3.0	1.00	7.91	47.96	±1.27
	4.0	1.00	16.17	64.71	±0.69
	5.0	1.00	17.76	88.84	±0.43
	6.0	1.00	14.89	87.58	±0.49
	7.0	1.00	12.77	89.32	±0.70
	8.0	1.00	11.63	93.07	±0.32
	9.0	1.00	10.60	95.46	±0.53
	10.0	1.00	9.74	97.42	±0.25
Chlorpyrefos	1.0	1.00	ND	-	-
	2.0	1.00	ND	-	-
	3.0	1.00	3.61	21.89	±1.23
	4.0	1.00	10.50	42.00	±1.31
	5.0	1.00	15.71	78.55	±0.73
	6.0	1.00	13.76	80.96	±1.01
	7.0	1.00	11.97	83.75	±0.41
	8.0	1.00	10.94	87.57	±0.55
	9.0	1.00	10.25	92.22	±0.35
	10.0	1.00	9.61	96.11	±0.43

Remark : ND = Not Detectable

Triplicate analysis

**Table A-10** The effect of SPE vacuum pump (in.Hg) on the percent recovery for OPs in mixture solution at 1.00 ppm

Compounds	SPE pump (in.Hg)	Conc. before extraction(ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
Malathion	3.0	1.00	18.69	93.46	±0.27
	5.0	1.00	18.79	93.97	±0.45
	7.0	1.00	19.11	95.55	±0.51
	10.0	1.00	19.35	96.77	±0.36
	12.0	1.00	19.48	97.39	±0.51
	15.0	1.00	19.35	96.78	±0.74
	17.0	1.00	19.61	98.04	±0.41
	20.0	1.00	19.72	98.59	±0.56
	22.0	1.00	19.18	95.91	±0.38
Methyl parathion	3.0	1.00	18.46	92.32	±1.39
	5.0	1.00	18.95	94.73	±0.34
	7.0	1.00	19.06	95.31	±0.50
	10.0	1.00	19.09	95.44	±0.32
	12.0	1.00	18.89	94.45	±0.74
	15.0	1.00	19.33	96.67	±0.58
	17.0	1.00	19.81	99.06	±0.67
	20.0	1.00	19.96	99.82	±1.31
	22.0	1.00	19.40	97.02	±0.49
Profenofos	3.0	1.00	13.66	68.31	±1.77
	5.0	1.00	15.32	76.57	±0.61
	7.0	1.00	16.96	84.80	±0.55
	10.0	1.00	16.85	84.24	±1.07
	12.0	1.00	17.03	85.15	±0.21
	15.0	1.00	17.76	88.78	±1.02
	17.0	1.00	18.16	90.78	±0.75
	20.0	1.00	17.18	85.91	±0.59
	22.0	1.00	15.92	79.58	±0.77
Chlorpyrefos	3.0	1.00	4.93	24.98	±2.84
	5.0	1.00	7.97	39.83	±2.01
	7.0	1.00	8.32	41.06	±1.23
	10.0	1.00	8.61	43.05	±1.97
	12.0	1.00	8.95	44.76	±2.63
	15.0	1.00	11.25	56.24	±0.64
	17.0	1.00	14.50	71.51	±0.73
	20.0	1.00	9.51	47.57	±1.24
	22.0	1.00	8.98	44.92	±1.74

## Appendix-B

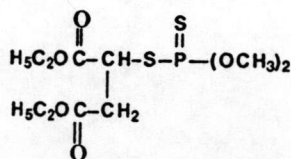
### Characteristic of the four OPs pesticides

**Malathion** (Richardson and Gangolli, 1994)

**Function** : Insecticides

**Chemical Name** : S-(1,2-bis(ethoxycarbonyl)ethyl O,O-dimethyl phosphorodithioate;

**Formula** :  $C_{10}H_{19}O_6PS_2$  **Mol.Wt.** 330.36



**Trade Name** : carbofos, mercaptothion, phosphothion, moldison, sodophos

**Physical properties** :

**M.Pt.**  $2.9^{\circ}\text{C}$ ; **B.Pt.**  $156-157^{\circ}\text{C}$ ; **Specific gravity**  $d_4^{25}$  1.2315; **Partition coefficient**  $\log P_{ow}$  2.36(1); **Volatility** v.p.  $4 \times 10^{-5}$  mm Hg at  $30^{\circ}\text{C}$ .

**Solubility** :

Water:  $145 \text{ mg l}^{-1}$  at  $20^{\circ}\text{C}$ . Organic solvent: esters, alcohols, ethers, ketones, aromatic and alkylated aromatic hydrocarbons, vegetable oils.

**Occupational exposure:**

**US TLV (TWA)**  $10 \text{ mg m}^{-3}$ ; **UK Long-term limit**  $10 \text{ mg m}^{-3}$ ; **Supply classification** harmful. **Risk phrases** Harmful if swallowed. **Safety phrases** avoid contact with skin.

**Ecotoxicity:****Fish toxicity:**

LD<sub>50</sub> (96 hr) bluegil sunfish, bass, brown trout, rainbow trout 0.1-0.29 mg l<sup>-1</sup>

LC<sub>50</sub> (48) carp 9.80-10.04 mg l<sup>-1</sup>

Snakehead fish ( 6 months resulting to spawning phase) 0.02 mg l<sup>-1</sup>

**Invertebrate toxicity:**

LC<sub>50</sub> (24, 48, 72, 96 hr) freshwater carb 8.9, 6.5, 3.8 ppm, respectively.

*Anabaena oryzae* and *Phormidium fragile* 93.5% and 85.7% of applied dose recovered in respiration the metabolited were mono-and dicarboxylic acid, mercaptoethyl succinate, mono- and di-ethylsuccinate.

**Bioaccumulation:**

Bioconcentration factor for carp in muscle, liver and kidney 2.7-17.3

Bioconcentration factor coho salmon 29.3

**Degradation studies:**

The time required for complete biodegradation in a model river water were 8, 12 and 18 days for 5, 10 and 15 mg dm<sup>-3</sup>, respectively. Rate of degradation in 10 days 81-92% in various non-sterile loam soil and 5-19% in various sterile loam soils. Unsterile seawater and sedimented cores under laboratory light at 20<sup>0</sup> C, pH 8 t<sub>1/2</sub> 2.6 and 20 days, respectively.

**Mammalian and avian toxicity****Acute data**

LD<sub>50</sub> oral mouse, rat 190, 290 mg kg<sup>-1</sup>, respectively

LC<sub>50</sub> oral redwing blackbird 400 mg kg<sup>-1</sup> diet.

LC<sub>50</sub> (4 hr) inhalation rat 84.6 mg m<sup>-3</sup>

LD<sub>50</sub> (24 hr) dermal rabbit 4100 mg kg<sup>-1</sup>

LD<sub>50</sub> intraperitoneal rat, mouse 193, 250 mg kg<sup>-1</sup>, respectively.

**Legislation:**

Limited under EC Directive on Drinking Water Quality 80/778/EEC.

Pesticieds: maximum admissible concentration 0.1 µg l<sup>-1</sup>. Included in



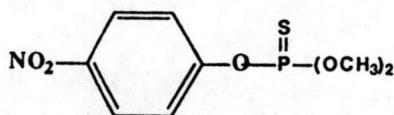
Schedule 6 (Release into Land: Prescribed Substances) Statutory Instrument  
No. 472, 1991.UK Department of Environment advisory value for drinking  
water  $7 \mu\text{g l}^{-1}$ .

**Methyl Parathion** (Richardson and Gangolli, 1994)

**Function :** Insecticide

**Chemical Name :** O,O-dimethyl O-4-nitrophenyl phosphorothioate

**Formula :**  $\text{C}_8\text{H}_{10}\text{NO}_5\text{PS}$       **Mol.Wt.** 263.21



**Trade Name :** Dalf (Bayer), Nitrox 80 (Bayer), Bladan (Bayer), Tekwaisa  
Folidoc M (Bayer), Metron  
Metacide (Bayer), Patron M

**Occurrence:** Residues have been isolated from water, sediments, soil, crops and in  
fish tissues.

**Physical properties:**

**M.Pt.**  $35 - 38^{\circ}\text{C}$ ; **B.Pt.**  $154^{\circ}\text{C}$ ; **Specific gravity**  $d_4^{20}$  1.358; **Partition  
coefficient**  $\log P_{ow}$  3.11; **Volatility** v.p.  $9.7 \times 10^{-6}$  mmHg at  $20^{\circ}\text{C}$ .

**Solubility:**

Water:  $50 \text{ mg l}^{-1}$  at  $20^{\circ}\text{C}$ . Organic solvent; acetone, benzene  
chloroform, diethyl ether, dichloromethane, carbon tetrachloride, ethanol,  
mineral oils.

**Occupational exposure:**

**UK Long-term limit**  $0.2 \text{ mg m}^{-3}$ ; **UK Short-term limit**  $0.6 \text{ mg m}^{-3}$ ;  
**UN No.2783; Supply classification** very toxic. **Risk phrases** Toxic in contact with skin very toxic if swallowed. **Safety phrases** After contact with skin, wash immediately with plenty of soap and water. Water suitable protective clothing and gloves. In case of accident or if you feel unwell, seek medical advice immediately.

**Ecotoxicity****Fish toxicity:**

LC<sub>50</sub> (96 hr) golden orfe, rainbow trout, flathead minnow, large-mouth bass  
 $2.7\text{-}8.9 \text{ mg l}^{-1}$

**Invertebrate toxicity:**

LC<sub>50</sub> (96 hr) sand shrimp, grass shrimp, hermit crab  $2\text{-}7 \text{ } \mu\text{g l}^{-1}$

**Degradation studies**

Degraded to carbon dioxide and water by a *Bacillus sp.* isolated from soil. A mixed bacterial culture from the soil, including a *Pseudomonas sp.* could not utilise methyl parathion as a sole carbon source. In anaerobic sediments, aminomethyl parathion was identified as the reduction product. In heat-sterilised sediments the rate of reduction was halved.

**Mammalian and avian toxicity****Acute data**

LD<sub>50</sub> oral rat, mouse  $14,200 \text{ mg kg}^{-1}$ , respectively.

LD<sub>50</sub> oral starling, redwing blackbird  $7.5, 10 \text{ mg kg}^{-1}$ , respectively.

LD<sub>50</sub> (4 hr) inhalation rat  $34 \text{ mg m}^{-3}$ .

LD<sub>50</sub> dermal mouse  $1200 \text{ mg kg}^{-1}$ .

LD<sub>50</sub> subcutaneous rat, mouse  $6, 18 \text{ mg kg}^{-1}$ , respectively.

LD<sub>50</sub> intraperitoneal rat, mouse  $2.8, 5.4 \text{ mg kg}^{-1}$

LD<sub>50</sub> intravenous rat, mouse  $9.0, 9.8 \text{ mg kg}^{-1}$

**Legislation**

Limited under EC Directive on Drinking Water Quality 80/778/ EEC.

Pesticides: maximum admissible concentration  $0.1 \mu\text{g l}^{-1}$ . Included in Schedule 6 (Release into Land: Prescribed Substances) Statutory Instrument No. 472, 1991.

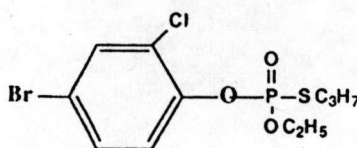
EEC maximum residue level for fruit and vegetables 0.2 ppm. Tolerable daily intake (TDI) human  $0.02 \text{ mg kg}^{-1}$ .

**Profenofos** (Richardson and Gangolli, 1994)

**Function** : Insecticide and acaricide

**Chemical Name** : O-(4-Bromo-2-chlorophenyl) O-ethyl-S-propyl phosphorothioate

**Formula** :  $\text{C}_{11}\text{H}_{15}\text{BrClO}_3\text{PS}$       **Mol.Wt.** 373.64



**Trade Name** : CGA-15324 (Ciba Geigy)  
Curacron (ciba-Geigy)

**Physical properties:**

**B.Pt**  $110^{\circ}\text{C}$ ; **Specific gravity**  $d^{20}$  1.455; **Partition coefficient**  $\text{l}^{-1}$  at  $20^{\circ}\text{C}$ ;  
**Volatility** v.p.  $9.75 \times 10^{-6}$  mmHg at  $20^{\circ}\text{C}$ .

**Solubility**: Water:  $20 \text{ mg l}^{-1}$  at  $20^{\circ}\text{C}$ .

**Occupational exposure:**

**UN No.** 3018; **Supply classification** harmful.

**Risk phrases** Harmful by inhalation, in contact with skin and if swallowed.

**Safety phrases** Wear suitable protective clothing and gloves.

## Ecotoxicity

### Fish toxicity:

LC<sub>50</sub> (96 hr) rainbow trout, crucian carp, bluegill sunfish 0.08-0.3 mg l<sup>-1</sup>.

### Mammalian and avian toxicity

#### Acute data

LD<sub>50</sub> oral rat, rabbit 358, 700 mg kg<sup>-1</sup>, respectively.

LD<sub>50</sub> oral chicken 1900 µg kg<sup>-1</sup>.

LC<sub>50</sub> (4 hr) inhalation rat 3 mg l<sup>-1</sup>

LD<sub>50</sub> dermal rabbit 472 mg kg<sup>-1</sup>.

### Carcinogenicity and long-term effects

No effect level in 2 years feeding trial in rats 0.38 mg kg<sup>-1</sup> diet.

No effect level in 18 month feeding trials in mice 0.08 mg kg<sup>-1</sup> diet.

### Legislation

EC maximum residue limit in maize 0.05 ppm.

Limited under EC Directive on Drinking Water Quality 80/778/EEC.

Pesticides: maximum admissible concentration 0.1 µg l<sup>-1</sup>

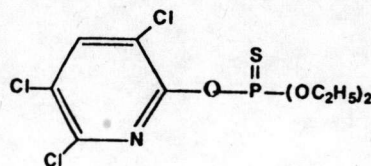
## Chlorpyrifos (Richardson and Gangolli, 1994)

**Function :** Insecticide

**Chemical Name :** O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate

**Trade Name :** Dowco 179, DursbanL, Orsban

**Formula :** C<sub>9</sub>H<sub>11</sub>Cl<sub>3</sub>NO<sub>3</sub>PS **Mol.Wt.** 350.59



**Occurrence:** Residues have been isolated from soils, crops and animal fats.

**Physical properties:**

**M.Pt.** 42<sup>0</sup> C; **B.Pt.** 160<sup>0</sup> C (decomp.); **Specific gravity**  $d_{4}^{25}$  1.398; **Partition coefficient**  $\log P_{ow}$  5.11; **Volatility** v.p.  $1.87 \times 10^{-5}$  mmHg at 25<sup>0</sup> C.

**Solubility**

Water: 2 mg l<sup>-1</sup> 25<sup>0</sup> C. organic solvent: isooctane, methanol

**Occupational exposure**

**US TLV (TWA)** 0.2 mg m<sup>-3</sup>; **UK long-term limit** 0.2 mg m<sup>-3</sup>; **UK Short-term limit** 0.6 mg m<sup>-3</sup>; **Supply classification** toxic.

**Risk phrases** Toxic in contact with skin and if swallowed.

**Safety phrases** After contact with skin, wash immediately with plenty of soap and water. Wear suitable protective clothing and gloves-If you feel unwell, seek medical advice.

**Ecotoxicity**

**Fish toxicity**

LC<sub>50</sub> (24 hr) goldfish 0.18 mg l<sup>-1</sup>.

LC<sub>50</sub> (96 hr) rainbow trout 0.003 - 0.011 mg l<sup>-1</sup>

LC<sub>50</sub> (96 hr) catfish 11.1 mg l<sup>-1</sup>

**Invertebrate toxicity**

LC<sub>50</sub> (96 hr) *Gammarus lacustris*, *Gammarus fasciatus* 0.11- 0.32 µg l<sup>-1</sup>.

**Degradation studies**

t<sub>1/2</sub> in dry loam soil 4 weeks and in silt loam 12 weeks. In both these soils sterilised by autoclaving t<sub>1/2</sub> was 24 weeks.

**Mammalian and avian toxicity**

**Acute data**

LD<sub>50</sub> oral rat 135-160 mg kg<sup>-1</sup>

LD<sub>50</sub> oral guinea pig 504 mg kg<sup>-1</sup>

LD<sub>50</sub> oral rabbit 1000-2000 mg kg<sup>-1</sup>

LD<sub>50</sub> oral redwing blackbird, starling 13-75 mg kg<sup>-1</sup>

LD<sub>50</sub> (4 hr) inhalation rat > 0.2 mg kg<sup>-1</sup>

LD<sub>50</sub> dermal rabbit ≈ 2000 mg kg<sup>-1</sup>

**Legislation:**

Limited under EC Directive on Drinking Water Quality 80/778/ EEC.

Pesticides: maximum admissible concentration 0.1 µg l<sup>-1</sup>.

## Appendix-C

### GLOSSARY OF TERMS

#### **CAPACITY :**

The total mass of isolates and/or interferences that a specific sorbent mass can retain in a given solvent environment. Capacity of a sorbent for a specific isolate is a function of the solvent or matrix environment. In general, the maximum retentive capacity of sorbent is a few percent of the sorbent mass.

#### **C-18 :**

**Functional group:** Octadecyl

( 18-carbon straight-chain hydrocarbon )

**Primary interaction:** Non-Polar

**Secondary interactions:** Polar, Cation Exchange

**Comments:**

C<sub>18</sub> is the most non-polar sorbent available. It is the most retentive of all sorbents for isolates being retained by a non polar mechanism. Extremely non-polar compounds are often difficult to elute from C<sub>18</sub>. Conversely, C<sub>18</sub> does not retain certain very polar molecules such as carbohydrates. C<sub>18</sub> is generally regarded as the least selective sorbent, since it retains almost anything from aqueous matrices often a benefit when the isolates vary widely in structure. Because of C<sub>18</sub>'s low selectivity, final extracts are often not as pure as they are when more selective sorbents are employed. C<sub>18</sub> is excellent for desalting matrices prior to ion exchange because salts pass through it unretained. The potential for significant with C<sub>18</sub> than with any other sorbent because of the predominant effect of the long hydrocarbon chain.

#### **ELUTION :**

Removal of a chemical species from a sorbent by changing the solvent or matrix chemistry to disrupt the isolate/sorbent interaction. Strength of an elution solvent refers to the effectiveness of the solvent for eluting an isolate or interferences from a particular sorbent. For example, non-polar solvents are strong eluters for non-polar sorbents, whereas polar solvents are weak elution solvents for non-polar sorbents.

**EXTRACTION :**

Transfer of the chemical species from one phase into another. In sorbent extraction, transfer of the species of the interest from the matrix environment onto the solvent (elution). Isolate purification is effected by a series of selective extraction steps.

**INTERACTION :**

Attraction or repulsion between two chemical species in a specific chemical environment. In sorbent extraction, the three principal interactions are isolate/sorbent, matrix/sorbent, and isolate/matrix. Specific possible interactions include non-polar, polar, ion-exchange, covalent and a variety of others.

**INTERFERENCES :**

Undesired components in the sample matrix. In sorbent extraction two types of interferences exist. These are retention interferences, that inhibit isolate retention on a sorbent by competition or by interaction with the isolate, and detection interferences, that interfere with the final analysis or end use of the isolate and therefore must be removed from the sample.

**ISOLATE :**

The compounds of interest to be isolated from the sample matrix.

**MATRIX :**

The sample environment from which the isolate is to be extracted. A blank matrix is one that does not contain the isolate. The matrix is important in sorbent extraction because retention of the particular isolate on a given sorbents is strongly influenced by the chemistry of the matrix.

**NON-POLAR :**

A commonly used mechanism in sorbent extraction. Non-polar interactions occur between non-polar isolate functional groups and non-polar functional groups on the surface of the sorbent. Also refers to functional groups that exhibit predominantly van der waals interactions. Thus C18 is referred to as a non-polar sorbent because of its hydrocarbon chain.



**NORMAL PHASE :**

Silica, Diol, NH<sub>2</sub> and CN Extract-clean bonded and non-bond phases are available in this separation mode. In normal, or adsorption, phase separation, polar sample constituents are preferentially retained by the solid phase and eluted with use of polar solvent systems. Normal phase SPE systems are usually employed in sample-presituations involving a polar to moderately polar analyte in a non-polar matrix.

**POLAR :**

A commonly used mechanism in sorbent extraction. Polar interactions occur between isolate functional groups exhibiting dipole moments, and similar groups on the sorbent. Also refers to the functional groups themselves. For example unbonded silica is a very polar sorbent because of the high content of Silanols.

**RETENTION :**

The attraction of a chemical species for a sorbent such that the species is immobilized on the sorbent. The degree of this attraction is referred to as the strength of the retention. This attraction is due to one of the chemical interactions.

**REVERSE PHASE :**

C<sub>18</sub>, C<sub>8</sub>, C<sub>2</sub> and CH Extract-clean bonded phase are available in this separation mode. In reverse phase separations, non-polar sample constituents are preferentially retained by the bonded phase and eluted with use of non-polar solvent systems. Moderately polar, organic samples may also be retained by reverse phase SPE products and, since the attractive forces are not as those involved in non-polar interaction, eluted with more polar solvent systems. Reverse phase sample/sorbent/solvent interactions are very similar to those found in liquid/liquid partition systems. Reverse phase SPE systems are often the first choice for sample systems involving a non-polar to moderately polar analyte in an aqueous or polar matrix.

**SOLVATION :**

The process that prepares a sorbent for sample application. In most cases, solvation consists of 2-3 steps: first, a wetting of the sorbent with an organic solvent (this solvent should be miscible with the solvent used in the next step), followed by removal of excess wetting solvent off the sorbent using a solvent similar to the sample

matrix to be applied. A solvated sorbent is one that has been processed in this manner. Solvation is important to retention of chemical species since an improperly solvated may retain nothing.

**SORBENT :**

The porous, chemically modified silica used for selective extraction of chemical species from liquids. The sorbents described in this handbook are 40  $\mu\text{m}$  particle size, 60 angstrom porosity bonded silica gels.



## **Biography**

Miss Pranee Tethgatak received a Bachelor Degree of Science (Chemistry) from Faculty of Science, Burapha University in 1991. After graduation, she worked at Scientific and Technological Research Equipment centre (STREC) of Chulalongkorn University since 1992 to present. Then in 1994, she has continue studied in Interdisciplinary Programme in Environmental Science, Graduate school, Chulalongkorn University.