Bull. Environ. Contam. Toxicol. (1984) 32:469–477

Bulletin of Environmental Contamination and Toxicology

Spill of Methyl Parathion in the Mediterranean Sea: A Case Study at Port-Said, Egypt

Mohamed I. Badawy, Mohamed A. El-Dib, and Osama A. Aly

Water Pollution Control, National Research Center, Dokki, Cairo, Egypt

Massive production and use of organic pesticides lead to the wide distribution of such toxic chemicals in the biotic and abiotic environment. Residues of pesticides in the aquatic ecosystem have raised much concern due to their hazardous effects on life and man.

Accidental spills of pesticides during their production and transportation may result in more serious and localized toxic effects (Lussen and Sechlimme 1971; Willmann 1976; Lafornara 1978).

In Egypt, the collision of two ships, namely "Garnet" and "Molaventure" took place near the northern entrance of Suez Canal at Port-Said, in February 1982. As a result, Garnet which was loaded with 31000 kg of methyl parathion slowly sank and was towed to shallow water. More than 10000 kg of methyl parathion found their way into the Mediterranean sea. Methyl parathion (O,O dimethyl-O-p-nitrophenyl phosphorothioate) is one of the most toxic organophosphorus insecticides (Webbe 1961; Morgan 1977).

The present work followed the concentration of methyl parathion in sea water, sediments and some fish species collected from the polluted area.

MATERIALS AND METHODS

The sampling area extended along a distance of approximately 5 km from the ship. Garnet was towed to an area defined by latitude 31°, 20 and longtitude 32°, 20. Sub-surface water samples were collected from all sampling sites during the period of study (February 2nd to June, 14, 1982). Bottom sediments were obtined from the first three sampling sites. Composite fish and water samples were collected together from site No 4 along a distance of 2 km on both sides of the latter site, Fig 1.

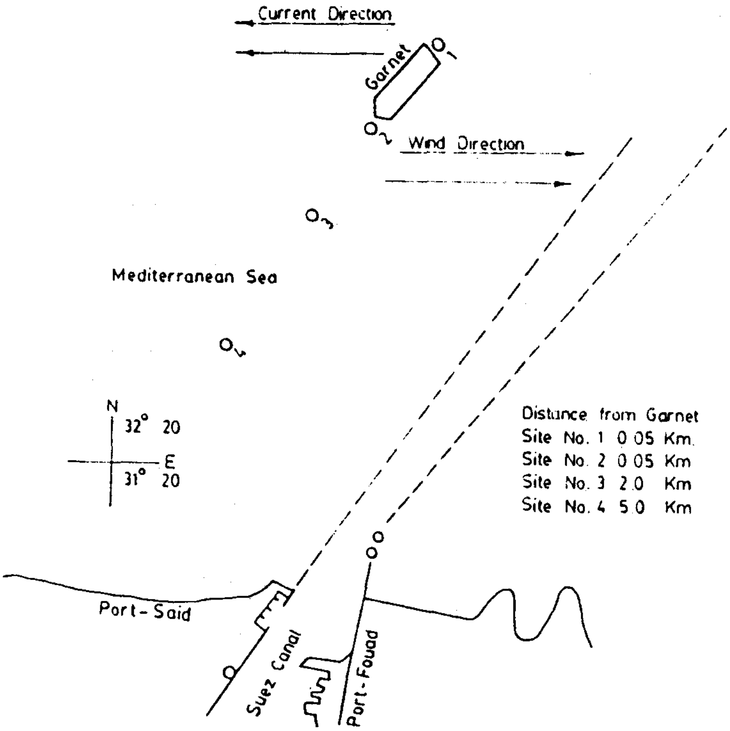

Fig 1. Schematic map showing sampling sites and location of Garnet

An adequate volume of sea water (250 mL) was transferred to a 500 mL separatory funnel and extracted twice with a 50 mL portions of 15% methylene chloride in hexane (v/v). The combined extracts were dried over anhydrous sodium sulphate and concentrated to 2 mL in a Kuderna-Danish evaporator.

A Known weight of air-dried sediments (50 g) was mixed with 50 g anhydrous sodium sulphate. The mixture was transferred to a glass chromatographic column. Further extraction and clean-up procedures were followed according to the US Environmental Protection Agency (EPA) method (1974).

The internal organs, head and tail of fish samples were removed and muscles were used for subsequent analyses. Extraction and clean up procedures were followed according to EPA method (1974).

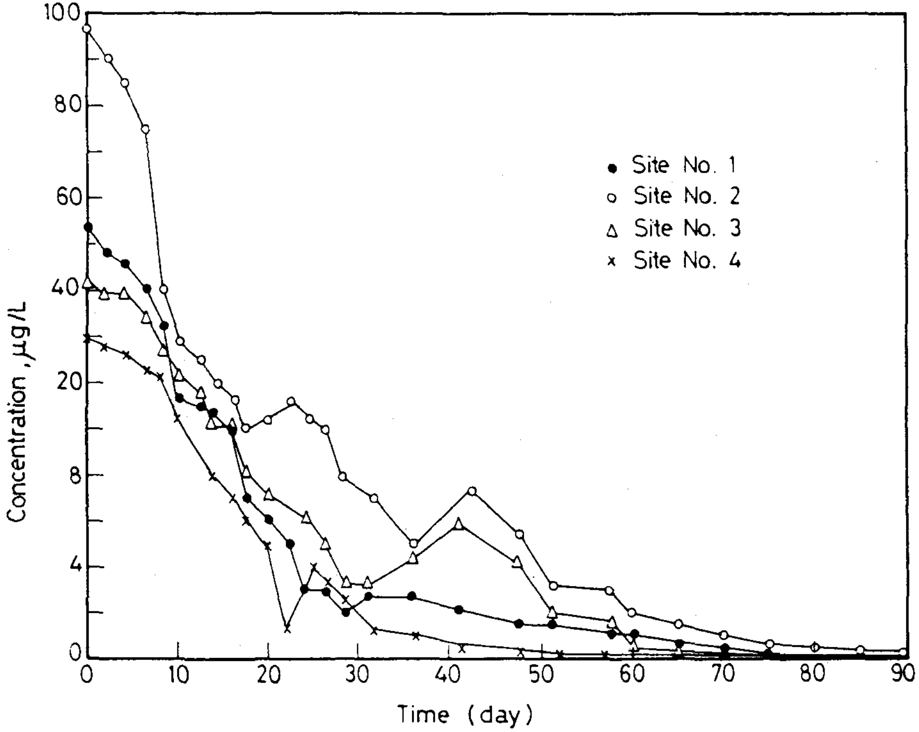

Fig 2. Concentration levels of methyl parathion in sea water at the various sites.

Residues of methyl parathion were identified and quantified using a Varian 3700 fitted with Ni^{63} electron capture detector and a glass column (4 mm I.D. and 2 meter length), packed with 5% OV 225 on 80/100 chromosorb W. The column, injector and detector temperatures were $180^{\circ}C$, $220^{\circ}C$, and $250^{\circ}C$, respectively. Nitrogen was used as a carrier gas at a flow rate of 40 mL/min. The detection limit, estimated as twice the signal to noise ratio, was 0.1 µg/L.

RESULTS AND DISCUSSION

Results presented in Fig 2, indicate the general trend of distribution and concentration levels of methyl parathion in the studied area. Maximun concentration of 96 µg/L was reached at site No 2. In general, the concentration of the insecticide decreased by distance and time to reach its lowest level of µg/L after 50 and 80 days at sites No. 4 and 2, respectively. The follow up of the distribution of methyl parathion concentration at the various sampling

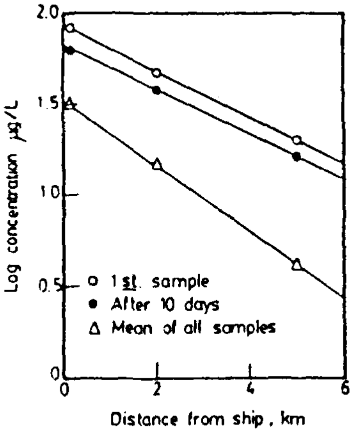

Fig 3. Logarithm of concentration of methyl parathion Vs distance.

sites indicated that the prevailing meteorological conditions (surface current and wind) have an influence in drifting the spilled insecticide towards the south - west direction.

In this study no attempt was made to measure the diffusion rate of the spilt insecticide. Several factors are also expected to take part in the decrease of methyl parathion concentration such as evaporation, chemical and biological degradation and adsorption on suspended matter and sediments (Kaufman and Plimmer 1972). A direct approach to assess the effects of dilution and transportation of pollutants, is the use of the first order decay equation: $C = C_i e^{-kt}$ where Ci = initial concentration C = concentration at time t and k is a constant (Baumgartner and Callaway 1972). On such basis, Hashimoto et al (1978) developed the equation: $Y_o = Ye^{-kx}$ where Y the concentration of pollutant at a distance "x" km; Y_o is the concentration at a source point, and "k" is a constant related to dilution. Such an equation leads to the derivation of the distance required to reduce the initial concentration of pollutant to its half value ($x_{\frac{1}{2}}$), where: $x_{\frac{1}{2}} = 0.693/k$. Results presented in Fig 3 indicate that obtainable data were in agreement with the given equation. The distance required to decrease methyl parathion concentration to its half value at site No.2, under the prevailing meteorological conditions, was 1.2 km during the first 10 days of sampling. However, when the mean values of concentrations attained at each sampling site were considered, the value of $x_{\frac{1}{2}}$ was only 0.8 km. Results reached by this study add to the validity of the mathematical derivations given by Hashimoto et al (1978) in estimating the distance necessary to reduce the initial concentration of spilt insecticide to its half value.

Table 1 shows the concentration levels of methyl parathion in sediments together with its concentration in water collected simaltaneously from the same sampling sites. It is evident that the residue levels in sediments gradually increased during the first 20 days of sampling. Residue levels of methyl parathion in sediments reached their highest values at site No. 2 whereas lowest values were found at site No 1. The decrease in residue levels in water coincide with the general increase in methyl parathion in sediments. Such a trend may be attributed to the uptake and adsorption of the insecticide by the suspended matter and sediments. The concentration factor given in Table 1 reached its maximum value of 49.5 at sampling site No.3, after 20 days of the spill. Meanwhile, values of the concentration factor at site No 3 were higher than its values at site No 2 which were still higher than values obtained at site No 1.

Residue levels of methyl parathion in water (Fig 2) and in sediments (Table 1) tend to show that the spilt insecticide was drifted towards the south - west direction under the influence of surface current and wind.

Variations in concentration levels of methyl parathion in fish and composite water samples collected from site No. 4 are presented in Table 2. Maximum concentration was found in the first sample of Anguilla species and amounted to 195.5 µg/L. Thereafetr, residue of methyl parathion in Anguilla species decreased to 72.5 µg/kg. In case of Sardine, Scidena and Mugil species, residues of the insecticide attained their highest values in the second fish sample. Worth to be noted that the concentration of methyl parathion in sea water decreased by time whereas values of the concentration factor showed a general trend to increase and a maximm level of 6.9 was found in case of Anguilla species. In general, values of the concentration factor followed to order, Anguilla > Mugil > Sardin> Scidena.

Available results revealed that the uptake of methyl parathion was subject to variation according to fish species concerned, time of exposure and the concentration of the insecticide in water. According to Kanazawa (1978) the biococentration of diazinon in fish increased as the concentration of the compound and exposure time increased. Residue levels were also reported to decrease as the fish was transfered to clean water. Matihiessen et al (1982) indicated that residue levels of endosulfan in fish increased with increase of lipid content. Other investigators (Hamelink et al 1971

Table 1. Distribution of methyl parathion in sediments and sea water

Date of sampling	Concentration								
	Site No.1			Site No.2			Site No.3		
	Sediments µg / kg	Water µg/L	CF *	Sediments µg / kg	Water µg/L	CF	Sediments µg / kg	Water µg/L	CF
18/2/82.	269.0	54.0	5.5	400.5	96.0	4.2	303.0	43.0	7.0
28/2/82.	325.0	32.0	10.2	450.0	40.1	11.2	350.0	32.0	12.5
10/3/82.	144.0	6.9	20.8	481.2	10.8	44.5	396.6	7.8	49.5
28/3/82.	80.2	3.2	62.8	145.2	4.4	32.9	101.2	4.4	23.0
6/4/82.	22.9	1.6	12.0	40.3	5.4	7.4	20.8	1.4	14.3
24/4/82.	5.10	1.0	5.1	7.4	1.6	4.1	4.5	1.2	3.7

* CF (Concentration factor) = $\dfrac{\text{concentration in sediment}}{\text{concentration in water}}$

Table 2. Concentration of methyl parathion in fish samples and sea water

Date of Sampling	Fish species	No of Fish	Mean concen. in fish µg / kg	Mean concen. in water	Concentration factor (CF*)
18/2/82.	Sardin	30	131.5	53.9	2.4
	Mugil	30	151.2	53.9	2.8
	Anguilla	30	195.5	53.9	2.6
	Scidena	30	119.0	53.9	2.2
28/2/82.	Sardin	30	149.2	26.7	5.5
	Mugil	30	160.0	26.7	6.0
	Anguilla	30	174.0	26.7	6.5
	Scidena	30	137.8	26.7	5.2
10/3/82.	Sardin	30	49.5	10.47	4.7
	Mugil	30	61.9	10.47	5.9
	Anguilla	30	72.3	10.47	6.9
	Scidena	30	46.7	10.47	4.6

$$* \ \text{CF (Concentration Factor)} = \frac{\text{concentration in sediment}}{\text{concentration in water}}$$

Neely et al. 1974; Crosby 1975) reported that partition of pesticides between animal fats and the surrounding water depends on the water solubility of the compounds. Such a partition will be independant of fish species in question. Results given by this study, however, showed the variation in the ability of fish species to accumulate the same insecticide even when present in the same aquatic eco-system. Consequently, the metabolic activities and/or excreation may contribute to the final concentration of a given compound in fish species (Eisler 1967).

REFERENCES

Baumgartner DJ, Callaway RJ (1972) Marine Pollution and sea life, Fishing News Books, London, England.

Crosby DG (1975) The toxicant wildife complex. Pure. Appl. Chem. 42 : 233 - 239.

Eisler R (1967) Tissue changes in puffer exposed to methoxychlor and methyl parathion. USDI Burea of Sport Fisheries and Wildlife, Technical Paper 17 : 3 - 14.

Environmental Protection Agency, EPA, (1974) Pesticide residue analysis in water, Method No. 430/1 - 74 - 012 (USA).

Hamelink JL, Waybrant RC, Ball RC (1971) A proposal : Exchange equilibria control the dgree of chlorinated hydrocarbons are biological magnified in lentic environments. Trans. Am. Fish Soc. 100 : 207 - 215.

Hashimoto A, Kozima T, Shakino H, Akiyama (1979) Occurence and determination of dinitrotoluene isomers in sea water. Water Res. 13 : 509 - 513.

Kaufman DD, Plimmer JR (1972) Approaches to the synthesis of soft pesticides. In Michell R. (ed) Wiley Interscience, New York.

Kanazowa J (1978) Bioconcentration ratio of diazinon by fresh water fish and snail. Bull. Environ. Contam. Toxicol. 20 : 613 - 617.

Lafernara JP (1978) Cleanup after spill of toxic substances. Jour. Water Poll. Control Fed. 50 : 617 - 627.

Lussen H., Schlimme (1971) Lokolisierung des pflozen schutzmittles enduosulfan in Rhein und dessen wirkung auf fische Gas-Wasserfach, Wasser-Abwasser. 112 : 18 -21.

Matthiessen P, Fox PJ, Douthwaite RJ, Wood AB (1982) Accumulation of endosulfan residues in fish and their prrdators after aerial sprial spraying for the control of testse fly in Botswana. Pestic. Sci. 13 : 39 - 48.

Morgan H (1977) Biomonitoring with fish and cud to industrial effluent and surface water quality control. Prog. Wat. Tech. 9 : 703 - 711.

Neely WB, Branson DR, Blau GE (1974) Partion coefficient to measure bioconcentration potential of organic chemicals in fish. Environ. Sci. Technol. 8 : 1113 - 1118.

Webbe G (1961) Field trials of phosphoric acid esters as larvicides and their toxicity to fish. Ann. of Trop. Med and parasit. 55 : 187 - 191.

Willmann JC (1976) PCB spill in the Duwamish - seattle, Wa. Proc. 1976 National Conf. Control of hazordous material spills, Information Transfer. Inc, Rockville Md. Water proc.

Received July 18, 1983; accepted August 18, 1983