Bull. Environ. Contam. Toxicol. (1998) 60:693-701

Bulletin of Environmental Contamination and Toxicology

Organic Insecticides in Airborne Suspended Particulates

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Received: 22 January 1998/Accepted: 26 March 1998

Every year about two million pilgrims gathered in the Holy city Makkah in Saudi Arabia for Hajj. As apart of Hajj performance the pilgrims stay about three days in Muna valley, it is simply a 4 km^2 valley with general alignment along the northwest- southwest direction. During this period a lot of wastes are generated due to eating, breathing and sacrificing more than one million animals. These wastes are considered the sources of many diseases, which are communicated to man, many insects, flies and microorganisms.

Cypermethrin, K-othrin, permethrin, salfac and chloropyrofos methyl insecticides are widely used for pest control of a wide range of flies and other insects in animals house , mosquitoes, cockroaches, houseflies and other insects in Holy city Makkah especially during Hajj season. About 21 tones insecticides were used during 1995, 33% from this amount was used during Hajj period. Human exposure via dermal as well as inhalation routes should be considered in assessing the risk of pesticides applied. Therefore the characterization of pesticide airborne residues is interest not only as an attenuation pathway for surface deposits, but also due to the potential for human exposure through inhalation (WHO, 1982).

The present work was conducted in Hajj Research Center at Um Al-Qura University in Makkah represent essential part for the project to study the environmental impact of some insecticides used for pest control during Hajj season of 1415H (1995 G).

MATERIALS AND METHODS

Analytical reference insecticides namely Cypermethtin cyano (3-phenoxyphenyl) methyl 3 (2,2-dichloroethenyl) 2,3 dimethyl cyclopropanecarboxylate, Deltamethrine (K-othrin) cyano(3-phenoxyphenyl) methyl-3 (2,2-dibromoethenyl)-2,3dimethycyclo-propanecarboxylate, Permethrin cyano (3-phenoxyphenyl) methyl 3-(dichloroethenyl) - 2,3 dimethyl cyclopropanecarboxylate and Salfac (cyfluthrin .5%) cyano (4-floro 3-phenoxyphenyl) methyl 3-(2,2-dichloroethenyl)- 2,3 dimethyl cyclopropane-carboxylate and Rosfin (chlorpyrophos methyl) O,O dimethyl O-3,5,6-trichloro-2 pyridyl phosphorthioate.

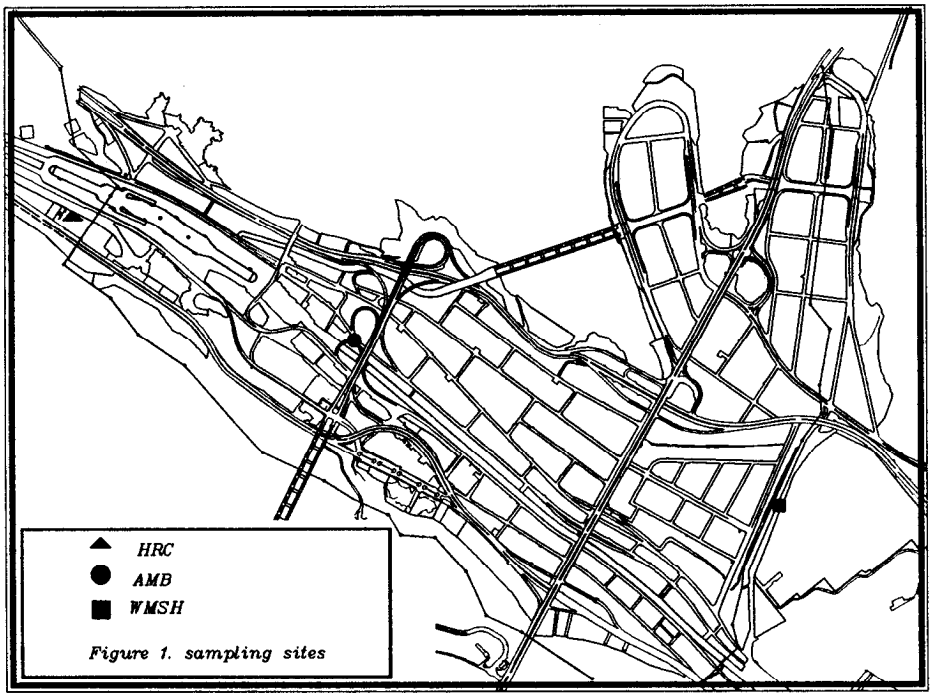

Figure 1. sampling sites

Three Staplex high volume sampler, model CKHV810 - Brooklyn, New York 11232 - 1695 USA, were used in the collecting of air suspended particulate (ASP). The first one was fixed in the Hajj Research Camp (HRC). HRC is located on a high mountain area (345m above the sea level). This mountain is situated in the narrow neck area at western end of the valley. The second one is fixed on Al-Mashaer Municipality building (AMB). This building is located in a narrow zone of the valley, surrounded by mountains and a group of buildings. It represents the middle of the valley and the nearest location to the stoning area.The third station is fixed on Wadi Mohaser Slaughter House (WMSH). This location is considered a land scape, with unique topographic characteristic, and it is selected to show the effect of the most predominant western winds, which they carry dust and sand (Fig. 1).

Previously weighed filters were placed inside the plate of each sampler and was used to collect the air samples over 24 hours. After this time the volume of air which had passed through the filter was calculated according the following equation:

$$V_m = \frac{Q_1 + Q_2}{2} \times T$$

Where:

V_m = Air volume, m^3

Q_1 = Initial air flow rate, m^3/min.

Q_2 = Final air flow rate , m^3/min.

T = Sampling time, min.

Calculation of ASP Loads:

$$ASP\ (ug\ m^3) = \frac{a - b}{Vm} \times 1000$$

Where:

a is the weighed of filter paper in, mg.

b is the weighed of filter paper after exposure time, mg.

V_m is the air volume.

Dust deposition was collected by using a semiconical polyethylene bucket with an opening of 20 cm diameter, half tilled with distilled water and mounted on iron tripods at a hight of 1m above the ground level to avoid the collection of resuspended dusts. The samplers were placed on roofs of the previously buildings. Dustfall samples were washed and screened through sieve No.10 (2mm) to remove insects and feathers, then dried at 80 °C and weighed to determine the dust deposition rates.

Particulate and dust deposited samples were extracted by using a soxhlet extractor with a mixture of 25% CH_2Cl_2 in n-hexane for 24 hours. The extracts were concentrated to 5ml, elemental sulphur was removed by reaction with mercury and the extract was quantitatively transferred to a column chromatography for separation into two fractions using 3 g of 5% deactived alumina. Fraction one(FI), which contains chloropiphenyls chlorobenzenes and hexachlorocyclohexane, was eluted with 16 ml of n-hexane. Second fraction(FII), includes permetharin, cypermethrin, deltamethrin and chloropyrophos (rosfin) was eluted with 6 ml of 20% ether in hexane. (Allchin et al.,l989) Chromatographic analysis of hydrocarbons were carried out on Auto System Perken Elmer gas chromatograph equipped with ECD detector, a BB5 Capillary column and splitless injector. The initial column temperature was 80°C. After an initial hold time for 2 min, the temperature was programmed to rise at 8°C/min to 280 °C for 30 min. The injector and detector temperatures were 250 °C and 350 °C, respectively. Nitrogen was used as a carrier, at a flow rate of 2ml/ min.

RESULTS AND DISCUSSION

The daily dust deposition per unit area throughout Muna valley was calculated and listed in Table (1). The mean rates over Muna's atmosphere were 2.07, 1.53 and 1.84 g/m^2/day for HRC, AMB and WMSH, respectiely. These rates are 15.9, 11.8 and 14.8 times the permissible limit for residental area (0.13g /m^2/day) and could cause several problems for pilgrims, such as soiling and skin irritation. This is aggravated by high temperature and relative humidity that cause sweating and enhances the deposition of soluble compounds. Nasralla and Youns(1986) reported that the rate of soluble particulate during Hajj season was 64.7 mg/m^2 /day while, its background rate was less than 10 mg/m^2/day. Moreover, the particulates deposited contained high levels of sulphate and its concentration was three times higher than the concentration in dustfall samples collected befor or

Table 1. Dust-deposition rate and the levels of some organic pollutants in its particulates.

Site	Dustfall-rates $g/m^2/day$	PCB's ng/g	Organophos-phorus, ug/g	Pyrethorid ug/g
	Range *Mean	Range Mean	Range Mean	Range Mean
HRC	1.72-2.71 2.07	367-2355 1200	33.5-50.0 41.0	196-1404 744.8
AAB	1.39-1.84 1.53	57-662 417	11.0-39.0 21.0	88-1196 538.7
WASH	1.31-2.09 1.84	152-687 444	7.4-30.9 15.4	74-522 468.0

*Mean is the average of five samples

after the Hajj period. The present study demonstrated that the mean rates of dust deposition over Muna's atmosphere during the period of study was 1.81 $g/m^2/day$. This figure is lower than the value recorded in 1981 (2.18 $g/m^2/day$) and higher than the rate reported in 1982 (294 $mg/m^2/day$). Generally, the rates of dust deposition are among the highest values detected in other any area of the world (Nasralla et al 1986 and Badawy et al 1992) and may be cause many diseases (Chrisp and Fisher, 1980).

Many studies revealed that airborne particulate from both urban and rural sites are mutagenic in the *S. typhimurium* reversion system (Takeda et al. 1984, Nardini and Clonfero, 1992, Crebllil et al, 1995). Data represented in Table (2) demonstrated that the atmosphere over Muna area was highly polluted with ASP during the period of study. These particulates are blown up into the air dispersed and then brought down by the action of gravity force. The means average of ASP were found 457± 266, 339± 171 & 280±151ug/m3 compared with the values of 615± 467±, 328±176, 282±199 $\mu g/m^3$ at WASH, AMB, HRC stations in 1993, respectively (Badawy and Al- Samady, 1996). These values indicated that the levels of ASP in the valley exceeded the permissible limit (80 $\mu g/m^3$) and may cause respiratory infections. The previous study showed that the mortality rates for tuberculosis, asthma, influenza, pneumonia and bronchitis were positively related to the level of ASP, in addition to the heart attack and cancer of the lung (Holland 1972, Chrisp and Fisher, 1980)

The highest concentration of ASP was detected at WMSH station, while the lowest was found at HRC station. This variations in ASP values are due to many factors such as the topographic feature of the stations, human activity, wind

Table 2. Level of airborne suspended particulates, μg/ m^3

Date From : To		HRC	AMB	WMHS
04/12	05/12	96	193	193
05/12	06/12	186	228	328
06/12	07/12	157	486	536
07/12	08/12	357	346	414
08/12	09/12	457	489	536
09/12	10/12	540	457	920
10/12	11/12	392	440	711
11/12	12/12	393	414	910
12/12	13/12	482	479	702
13/12	14/12	372	*	246
14/12	15/12	188	*	312
15/12	16/12	165	180	157
16/12	17/12	143	188	244
17/12	18/12	138	171	175
Mean		280±151	339±171	457± 266

*not analysed

direction, rain fall and traffic volumes. In general, the levels of ASP increased considerably during Tashreek days (10-12 th Zul Hijjah) reaching 1075 ug/m^3 compared with the value recorded on 4/12 to 5/12 (85ug/m3). This value can be considered as the background level because it was detected before Pilgrims occupancy of Muna area. The highest values detected at WMSH station are related to the mass movement of pilgrims to and from Arafat. In addition to the WMSH station is located in a wide sandy land scape and downward of the south western winds which occur in summer time and they carry dust and sand from south. The second mean value was found at AMB station. This station is located in a narrow zone of the valley surrounded by mountain and a group of building . The lowest value was detected at HRC station . This site is in mountainous area (345m above the sea level) and upward of the western winds effect.

Generally, the results demonstrated that the levels of ASP during the period of investigation are higher than those detected in several areas of the world (WHO , 1982, Badawy et al, 1992) and may be the cause of many diseases (Holland, 1972, Chrisp and Fisher, 1980), taking into account the synergistic effects associated with the presence of other contaminants. Therefore, the plantating of the valley with shade trees should be considered, especially at the area near to Mouzdlfa, to decrease the levels of ASP.

Results represented in Table (3) showed that the mean concentrations of chloropyrophos (organophosphorus insecticides) in airborne particulate were 6.7± 1.2, 7.3± 2.1 and 3.7 ± 1.4 ug/m3 for HRC, AMB and WMSH stations,

Table3 Residue levels of some organic pesticides(ug/m^3), and PCBs in air particulate, ug/m3

Site	Date	Perme-thrine	K. othrine	Cyper-methrine	Total conc. Chloropyrophs		PCBs*
HRC	19/11-24/11*	2.32	0.24	0.34	2.900	8.44	3.70
	24/11-28/11	8.20	0.93	0.74	9.87	5.80	3.75
	28/11-2/12	18.24	0.69	1.80	20.73	5.88	5.94
	2/12 - 5/12	10.95	0.54	1.67	13.16	4.71	6.44
	Mean	9.93	0.60	1.14	11.61	6.21	4.96
		±6.61	± 6.29	± 0.71	----	± 1.58	±1.43
AMB	19/11-24/11	4.75	0.27	0.36	5.38	6.70	1.11
	24/11-28/11	10.89	0.61	0.60	12.10	5.57	1.22
	28/11-2/12	30.70	1.81	3.61	36.12	11.84	2.36
	2/12-5/12	16.33	1.00	0.81	18.14	6.50	5.53
	Mean	15.67	0.92	1.35	17.94	7.2	2.56
		±11.10	± 0.66	± 1.52	-----	± 2.1	± 2.06
WMH	19/11-24/11	5.4	0.3	0.30	6.00	2.15	0.56
	24/11-28/11	7.94	0.48	0.94	9.36	5.50	1.26
	28/17-2/12	10.20	0.18	0.28	10.65	3.86	1.59
	2/12 - 5/12	1.84	0.58	0.86	3.28	3.10	2.33
	Mean	6.35	0.39	0.60	7.34	3.65	1.44
		±3.57	± 0.18	± 0.36		± 1.4	± 0.74

* ng/m^3

Each result is the average of three samples

Table 4 . Residue levels of some organic pesticides and PCBs in soil samples

Site	Date	Permetrine	K-othrine	Cyperme-thrine	Chloropyro-phos	PCBs
		ug/ g	ug/ g	ug/ g	ug/ g	ng/ g
1	26/11	57.40	41.00	64.60	14.00	11.24
	02/12	28.25	33.60	45.35	12.40	6.40
2	26/11	424.92	429.50	556.96	20.0	41.16
	2/12	304.96	261.72	440.24	18.0	22.20
3	26/11	239.40	167.77	276.60	9.20	8.60
	2/12	128.90	119.70	211.80	4.60	5.70

* 1 (HRC), 2 (AMB), 3 (WMSH)

respectively. These results indicate that no ambient air level above the National Academy of Science (NAS) proposed guideline level of 10.0 ug/m^3 were recorded except the samples collected in the period of 28/11-2/12 from AMB site. On the other hand when a comparison of the present data with the levels reported in the other areas of the world suggests that the current levels of airborne insecticide in Muna's atmosphere are not exceptionally high and are within the range as reported in other areas (Wright et al, 1991, Iwata et al, 1994).

Chloropyrophos detected in soil samples collected from site adjacent to the airborne particulate sampling stations ranged from 4.6 to 20 ug/g g. However, the concentration detected in North Carolina ranged from 16 to 499 ug/g (Wright et al, 1991). The low levels detected in soil samples are related to the soil in Muna area is sandy and contains gravel, therefor its adsorption capacity is very low.

The presence of airborne residues of pyrethroid insecticides such as K-othrine, Cypermethrine and Permithrine was investigated after their application during Hajj Season of 1415 H (1995 G), which about 8.5 tones of insecticides applied. Data in Table (3) show that the mean concentration of these insecticides ranged between7.34 and 17.94 ug/m^3. The highest concentration was detected in samples collected from AMB station (36.12 ug/m^3). This finding is related to the location of this site, which is down wind direction in narrow zone of valley represented the middle of the valley where most of insecticides were applied by using air craft.

The total concentrations of PCBs were calculated as Aroclor 1221 plus Aroclor 1242 and Aroclor 1245 and presented in Table (3). The data of the present study revealed that the mean concentration of total PCBs are 4.96,2.56 and 1.44 ng/m^3 for HRC, AMB and WMSH stations, respectively. The highest concentration was detected in samples collected during the period of 2/12 - 5/12 (6.44 ng/m^3) from

HRC site. Assuming a level of 5 ng/m^3 in urban air, a breathing rate of 22 m^3/day, retention and absorption of inhaled particles / vapour of 50%, and a mean residence time of PCBs in the body of 3 years air would contribute 0.8 ug/kg to the PCBs concentration in the body (WHO, 1993). Also the results of the present study indicated the levels of PCBs over Muna's atmosphore are among the highest levels reported in the other areas of the world. Manchester and Andren (1988) studied the levels of PCBs in a remote site in the Great Lakes Region. They found that the total PCBs concentations varied from 1.82 ng/m^3 in the summer to 0.135 ng/m3 in the winter.

Acknowledgments. The author is grateful to the Hajj Research Center Authorities, Umm Al Qura University, Saudi Arabia, for their financial support and providing facilities. Also the author wishes to thank Dr. M.M. Harery the General Director of Hajj Research Center and Dr. O.F. El Bar the Head of Environmental Department for their invaluable guidance and discussions. Thanks to engineer Magbul of Dallah Co. for supplying materials and informations of insecticides used

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