



Full Length Article

Airborne Paraquat Measurement and its Exposure to Spray Operators in Treated Field Environment

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ABSTRACT

Airborne residue was collected for 12 h day time (4 h sampling intervals) before and after from a paraquat treated field using passive patch samplers (cotton gauge, cellulose filter & PUF patches) and active samplers (quartz filter for particulates & PUF plug for vapor). Paraquat residue was detected by high performance liquid chromatography (HPLC) with UV detector after extracting the samples according to “NIOSH method 5003” with some modification. Pre-spray measurements by both passive and active sampling showed no detection of paraquat, whereas in post-spray measurement, peak average residue level (15.56 ng cm⁻²) were detected on cotton gauge patches in first 0–4 h post-spray passive sampling, whereas the average residue levels detected in the second post spray event were not significantly different among the three passives patch samplers. In post spray active sampling, paraquat was detected only on quartz filter samples (not on PUF plug) revealed that in the air paraquat is associated with particles rather than vapour and paraquat air concentration was detected at higher level in first 0–4 h and sharply decline in second 4–8 post-spray period. The highest paraquat air concentration measured during the 25 min spray application at operator's breathing zone was 125 µg m⁻³ that was slightly above the TLV (*threshold limit value*) and REL (recommended exposure limit) (100 µg m⁻³) of ACIGH (American Conference of Government Industrial Hygienists) and NIOSH (National Institute for Occupational Safety & Health, 1994). In addition, potential dermal and inhalation exposure dose (theoretically) estimated by extrapolating air residue data showed higher value than the proposed acceptable operator exposure level (0.0005 mg kg⁻¹day⁻¹). © 2010 Friends Science Publishers

Key Words: Paraquat; Airborne residue; Active sampling; Passive sampling

INTRODUCTION

Paraquat (*N,N'*-dimethyl-4,4'-bipyridinium dichloride) is a non-selective acutely toxic herbicide and one of the most commonly used herbicide in the world with a variety of agricultural uses, because of its rapid action, relatively low cost and broad spectrum of its activity (Lee, 1982). Due to human and environmental toxicity, paraquat has been banned or restricted in 13 countries (Pesticide Action Network Asia & the Pacific, 2003). Humans are vulnerable to paraquat exposure by ingestion or inhalation. However, the main route of paraquat exposure for agricultural workers is through skin, especially when skin is injured or diseased (Wesseling *et al.*, 1997).

Exposure of workers to paraquat by inhalation is considered to be usually negligible as the fraction of respirable particles is very low (Garnier, 1995). But inhalation may also be important under some climatic conditions and when backpacks motorised is used increasing the respirable fraction of paraquat. On the other hand, oral exposure can occur when the operator swallows

the run-off on the face when working in a spray mist (Wesseling *et al.*, 2001). Several reports found that paraquat is known to be concentrated and act principally in the lung regardless of the route of administration, producing several immediate and delayed effects due to lung fibrosis (Smith & Heath, 1976).

Malaysia was banned in 2002 considering serious health hazards after paraquat exposure to humans and later ban was temporary lifted for extensive toxicological studies (The Malaysian Pesticides Board, 2002). Still paraquat is being widely used in Malaysian plantation crops (Wibawa *et al.*, 2009), field crops and in forestry through knapsack sprayers—either lever operated or motorized (PAN-AP, 2003). Mist-blowers either mounted on a tractor or carried by workers, produce droplets with relatively small sizes (50–100 µm). Typical mists (with a median droplet diameter of 57 µm) contain about 0.1% droplets with a size of 15 µm (World Health Organization, 1990) those can easily enter the bronchi (but not alveoli if greater than 5–7 µm) (Rando 1999; Deutsche Forschungsgemeinschaft, 2004). US Environmental Protection Agency (1997) also

reported sprayers using knapsacks are more likely to be exposed to high levels of paraquat. Swan (1969) identified the exposure of knapsack spray operators as representing the highest exposure to paraquat in Malaysia's tropical agricultural practices.

Owing to public concern regarding possible exposure to paraquat, air sampling methods both active and passive were used for determining the levels of paraquat in the paraquat treated field. Active sampling methods for airborne residue involve aspirating air at a known flow rate over time through suitable trapping media, which become harmonised procedures for sampling in Europe and North America. Based on active methods, inhalation standards are now available for potentially hazardous materials (Soutar *et al.*, 2000). On the other hand, passive sampling methods are conceptually simple that based on free flow of analyte molecules from the environment medium to a collecting medium resulting from different physical principles (Gorecki & Namiesnik, 2002). This sampling is commonly used for assessing dermal exposure, which often give variable results, because of different mechanism involved in sample collection (Schneider *et al.*, 1999). Several research were carried out in past to determine airborne paraquat drift and its exposure to spray operators using active and passive methods, but airborne paraquat concentrations following spray has been rarely reported. The present study was, therefore undertaken to determine the airborne paraquat residues in the field during and after application using knapsack mist blowers and its potential exposure assessment to field operators.

MATERIALS AND METHODS

Experimental site and spray application: The study was conducted in July, 2009 at field two, Universiti Putra Malaysia (UPM) and the test plot size was 1000 m². Paraquat dichloride herbicide 13% a.i., (Capayam, Syngenta Corporation Sdn. Bhd., Malaysia) was applied with a previously calibrated mist blower (Solo Master 412) set at a discharge rate of 0.64 L min⁻¹ and resulted in an average droplet diameter of VMD (volume median diameter) of 67 and (number median diameter) 35.5 µm. Droplet diameter was measured by microscope fitted with Porton G.12 Graticule and was calculated according to Omar *et al.* (1996). Paraquat was applied at a field dosage of 2 L ha⁻¹ with spray volume of 160 L. During the study, there were no multiple applications of paraquat taken place in nearby fields of the experimental sites.

Air sampling procedures: Three types of passive patch samplers with an exposed surface area of roughly 16 m², namely Cotton gauze patches (Brand: Medicot, Gasmed Sdn. Bhd., Malaysia), Cellulose filter patches (Whatman grade 41, England), and polyurethane foam (PUF) patches (SKC Inc., USA) were used and each type of patches was taped on five surfaces—west (W), East (E), North (N), South (S) and Top (T) of an identical dimensions foil-covered Box (6 x 6 x

6 inch), located 1 m above the ground surface at three randomly selected points nearer to downwind edges of the test plot.

For active sampling, field air sampling pump (Model 1067, Supelco, USA) calibrated to a flow rate value of 1 L min⁻¹ was used for sampling before and after paraquat spraying. The sampling pump was connected by tygon tube to commercially available polyurethane foam (PUF) cartridge (ORBO™ 1000, Supelco, USA) containing 0.022 g/cm³ density PUF plug in glass housing and fitted in front with quartz filter cartridge (Supelco, USA). The PUF plug was used mainly for the vapour phase and the quartz filter for particulate phase of the airborne paraquat.

Battery-operated personal air sampling pump (Model PAS-500, Supelco Inc. USA) was used during spraying and calibrated using a bubble flow meter to a flow rate of 0.3 L min⁻¹. The sampling pump was fixed at the sprayer's waist belt and the sampling head fitted with quartz filter cartridge (32 mm diameter, Supelco, USA) was attached at sprayer's collar bone area in downward position to cover the breathing zone. The duration of spraying was recorded using stopwatch.

Sampling frequency and duration: Samples were collected for 4 times as follows: 4 h pre-spray, during spray, and 0–4, 4–8 h post-spray periods. PUF and quartz filter cartridges were capped and passive patches were collected in centrifuge falcon tubes during sample collection. The tubes were placed in ice box at reduced temperature for transport.

Micrometeorological measurements: Air temperature and wind speed were recorded per hour during sampling period by using thermo-anemometer (Extech Instruments, USA). Relative humidity was also measured at similar intervals using humidity indicator (Airguide Instrument Co., USA). Wind directions, cloud cover and incidence of rain were also noted during the study period. Meteorological data showed that mean air temperature and relative humidity measured during the study was 33°C and 68%, respectively. The mean wind speeds were 2.7 m h⁻¹ that was relatively higher during morning and gradually decreased afternoon.

Statistical analysis: Data collected were analyzed following analysis of variance (ANOVA) technique and means separation were done by Tukey using statistical analysis system (SAS) (Table I & II). Differences were considered significant ($p < 0.05$).

Chemical Analysis

Preparation of standard solution and curve: Paraquat dichloride standard (Sigma-Aldrich, USA. Purity 99.2%) was dried on hot plate at 50°C to remove water. Standard stock solution was prepared by dissolving 0.005 g paraquat in 10 mL of water in a volumetric flask. Six working standard solutions of 10.0, 5.0, 1.0, 0.5, 0.05, 0.01 ppm were prepared. Linearity of the standard curve was confirmed by the evaluation of the regression coefficient ($r^2 = 0.99$).

HPLC conditions: HPLC chromatograms were obtained using controller pump (Waters 600) equipped with autosampler (Waters 717) and a PDA detector (Waters 2996)

set at λ 257 nm. The stationary phase (column) was C18 10 μ (150 mm x 3.9 mm i.d.) (Waters) and the mobile phase was 60% HPLC water (adjusted with pH 3 & then added 5 g NaCl) and 40% acetonitrile. The isocratic flow rate was maintained at 1 mL min⁻¹. All the solvents and solutions used in the mobile phase were previously filtrated and degassed by ultrasonic application. The injection volume was 10 μ L. Total sample run time was 5 min and analyte retention time was 1.30 min.

Sample preparation: The samples were prepared by 'Method 5003' with some modification (NIOSH Manual of Analytical Methods). Quartz filters and PUF plugs were carefully transferred to 15 mL centrifuge tubes by clean tweezers. Ten mL acidic aqueous solvent (0.01 N HCL) were added to each tubes using 5 mL pipette and then capped the tubes and allowed to stand for 30 min to soak samples completely. The centrifuge tubes were placed on an orbital shaker @ 200 rpm for 1 h followed by sonication for 2 h to desorb analyte. One mL of each sample solution was transferred to HPLC vials and subsequently labeled and analyzed.

Fortification and recovery studies: Fortification was done in triplicates by applying 100 μ L of three fortification concentrations (0.5, 1 & 5 μ g/mL) over the surface of three samplers (Cotton gauge, cellulose filter & PUF patches). The spiked samples were capped and allowed to kept at 4°C overnight to equilibrate. The following day, spiked samples were extracted and analyzed. Good recoveries were obtained by the fortification on three samplers, which ranged between 82% and 118%.

Limit of detection (LOD) and limit of quantitation (LOQ) determination: The LOD and LOQ were determined via linear regression method using linear calibration curve of paraquat test compound established at 5 concentration levels with three replicates (ICH, 1996). The LOD for this method was 0.008 μ g mL⁻¹ and the LOQ was 0.03 μ g mL⁻¹.

Quality control (QC)/quality assurance (QA) considerations: Laboratory and solvent blank samples were analyzed, which confirmed no contamination in both solvent and unused passive and active samplers (Patches, PUF & quartz filter). One field blank sample for every 15 samples was used for analysis along with the field samples. All blank samples were below the analytical limit of detection (LOD) for paraquat tested.

RESULTS AND DISCUSSION

Passive samplers: As shown in Table I, no paraquat in the air was detected on any of the passive samplers exposed before the application (i.e., pre-spray period). Seiber and Woodrow (1984) estimated the physical form of airborne pesticides based on their vapour pressure, in which reported that paraquat exists primarily in air as particulate forms and following spraying the concentrations of airborne paraquat have been shown to be very low as they strongly bound to dust particles (Taylor, 1978). Therefore airborne paraquat

residue is greatly influenced by the nature and concentration of dust particles present in the air and on treated surfaces. It was observed in this study that the amount of airborne paraquat detected was low since the apparent lack of significant wind erosion of paraquat from surface deposits. In the present study, there were considerable differences in average deposition amount among three passive samplers at post spray periods and the significantly higher average value (15.56 ng cm⁻², respectively) was recorded for cotton gauge patches compared to other two patches in first 0–4 post-spray event. This increased amount of deposition by cotton gauze patches could be explained by the findings of OECD (1997), which recommended cotton patches for trapping particles constructed with layers of cotton surgical gauze as they are porous enough and have uneven surfaces that help to retain the particles landing on it. On the other hand, the average paraquat deposition detected on Cellulose patches (4.56 ng cm⁻²) was significantly higher than PUF (2.30 ng cm⁻²) in 0–4 h, whereas the amounts detected on all three passive samplers-cotton, cellulose and PUF patches (2.56, 1.18 & 1.02 ng cm⁻²) were statistically insignificant in 4–8 post-spray periods. Data presented in Table II also shown that the airborne residue level was consistently higher during 0–4 h following spray application relative to that of 4–8 h, although Seiber and Woodrow (1981) found no detectable amount of airborne paraquat at 5 to 7 h after aerial spraying. Moreover a trend of lower concentrations in all patches oriented horizontally on the top during 4–8 post spray period was observed. It was also remarkable that no paraquat was measured on the PUF patch orientated on top surfaces in both post-spraying periods but no explanation in favour is available. It was also readily apparent that paraquat was detected in lowest concentration on PUF patches as the trapping ability of polymeric materials like PUF is strongly affected by the volatility of the analyte (Woodrow *et al.*, 2003).

In addition to above, deposition trend on passive samplers in terms of samplers orientation revealed (Table I) that the deposition gave significantly highest figures in cotton and PUF patches oriented for south compared to east, west and north approaches at both 0–4 and 4–8 post-spray events, during which wind movement was mainly from south to north direction at an average speed of 2.7 m h⁻¹. Although cellulose filter patches showed highest deposition on south but no significant differences among the orientation approaches and among the all three patches highest deposition on south orientation was on cotton gauze patches in both 0–4 (31.94 ng cm⁻²) and 4–8 h (5.93 ng cm⁻²) post-spray. This certainly reflects a positive correlation between residue deposition and wind movement across the samplers face. In agreement with the effect of wind movement on this observation, Thistle (2000) asserted that the dispersion of pesticide droplets is influenced by the droplet size, atmospheric stability and wind speed (vertical & horizontal components).

Active samplers: Paraquat could not be detected in any of

Table I: Paraquat deposited on three passive samplers before and after application in the field

Passive samplers	Samplers orientation	Deposition amount (ng cm ⁻²) Mean ^c ± S.D.			
		Pre-spray	Post-spray		
		- 4 hrs	0-4 h	4-8 h	8 h TWA ^a
PUF Patches	West	ND ^b	1.38± 0.66 bc	1.44± 0.70 ab	1.41± 0.19 b
	East	ND	3.19± 0.62 ab	0.88± 0.52 ab	2.03± 0.55 b
	North	ND	2.88± 1.10 ab	0.06± 0.08 b	1.47± 0.53 b
	South	ND	4.06± 1.09 a	2.75± 1.36 a	3.45± 0.44 a
	Top	ND	ND± 0.00 c	ND± 0.00 b	ND± 0.00 c
	Average	-	2.30± 0.20 C	1.02± 0.28 A	1.66± 0.06 B
Cellulose Filter Patches	West	ND	3.81± 0.84 a	0.63± 0.58 a	2.22± 0.70 a
	East	ND	4.44± 0.54 a	ND± 0.00 a	2.22± 0.26 a
	North	ND	4.13± 1.57 a	1.93± 1.28 a	3.03± 0.80 a
	South	ND	5.19± 2.09 a	2.17± 2.17 a	3.68± 0.99 a
	Top	ND	5.25± 0.18 a	1.18± 1.18 a	3.21± 0.39 a
	Average	-	4.56± 0.28 B	1.18± 0.14 A	2.87± 0.21 B
Cotton Gauge Patches	West	ND	5.75± 2.10 b	2.06± 1.33 b	3.90± 1.43 b
	East	ND	11.50± 2.09 b	1.62± 1.12 bc	6.56± 1.45 b
	North	ND	12.44± 3.77 b	3.06± 1.29 b	7.75± 2.53 b
	South	ND	31.94± 14.45 a	5.93± 0.96 a	18.93± 7.21 a
	Top	ND	16.19± 4.60 ab	0.13± 0.16 c	8.16± 2.22 b
	Average	-	15.56± 4.62 A	2.56± 0.88 A	9.06± 2.62 A

^a TWA, time-weighted average = sum of the products of concentration and time for each sampling period, divided by total sampling time

^b Not detected

^c Mean of three trials at three times different times (7 days intervals)

Values followed by the same letter (s), are not significantly different at (P = 0.005)

Table II: Paraquat collected on active samplers before, during and after application in the field

Spray periods	Air Volume (m ³)	Air concentration (µg m ⁻³) Mean ^c ± S.D.		
		Quartz filter	PUF Plug	Total
Pre-spray (4 hrs)	0.24	ND	ND	-
During spray (25 mins)	0.0075	125.49	ND	125.49± 19.43 a
Post-spray	0-4 h	0.24	ND	0.36 ± 0.10 b
	4-8 h	0.24	0.18	0.18 ± 0.09 b
	8-h TWA	0.24	-	0.27 ± 0.08 b

^b Not detected

^c Mean of three times trial at three different times (7 days intervals)

Values followed by the same letter (s), are not significantly different at (P = 0.005)

Table III: Potential dermal dose extrapolated from average deposition amount by three patches

Passive samplers	Post-spray periods	Deposition amount ^c (ng cm ⁻²)	Potential dermal dose ^a (mg kg ⁻¹ day ⁻¹) ^b
PUF patches	8 h TWA	1.66	4.32 × 10 ⁻⁴
Cellulose filter patches	8 h TWA	2.87	7.46 × 10 ⁻⁴
Cotton gauge patches	8 h TWA	9.06	0.0024

^a 8 hr-TWA deposition amount (ng/cm²) and total body surface area (18,200 cm²), divided by 70 kg b.w

^b Calculations are usually made on the basis of an eight-hour working day

^c The value represents mean of three samples on 8h-TWA

Table IV: Potential inhalation dose calculated from air concentrations measured by personal air sampling at breathing zone

Sampler type	Spray period	Air concentration ^c (µg m ⁻³)	Potential inhalation exposure ^a (mg h ⁻¹)	Potential inhalation dose ^b (mg kg ⁻¹ day ⁻¹)
Quartz filter	During spraying 25 mins	125.49	0.22	0.025

^a Breathing rate (1.75 m³ h⁻¹) multiplied by air concentrations (125 µg m⁻³) at breathing zone

^b Potential inhalation exposure (0.22 mg h⁻¹) and 8-h working day, divided by 70 kg b.w

^c The value represents mean of three samples during spray

the air samples collected with PUF plug but it was detected only in quartz filter samples, suggesting that the pesticide was associated with particulate matter in air rather than vapor (Table III). Besides, paraquat was not detected in any of the samples prior to the spraying. The highest paraquat air concentrations measured during 25 min spray event was

125 µg m⁻³ (0.125 mg m⁻³) and this result almost conforms to the study done by Makovskii (1972), where paraquat air concentrations measured in air during spraying were between 0.13 and 0.55 mg m⁻³ depending on the mode of application. Most importantly, the level of paraquat concentrations in air found during spraying was slightly

above the TLV (*threshold limit value*) and REL (*recommended exposure limit*) ($100 \mu\text{g m}^{-3}$) of ACIGH and NIOSH. Interpretations suggested for higher paraquat air concentrations during spray application was associated with mode of application, where the droplets created by mist blower sprayer were relatively fine (as the measured NMD, $\text{Dn}_{0.5} = 35.5 \mu\text{m}$, i.e., diameter having half of the total number of droplets being smaller than $35.5 \mu\text{m}$), which did not settle quickly and therefore remained aerosolized in surrounding air. After spray application, airborne paraquat concentrations was fell off dramatically dropped because of paraquat's non-volatility. The air concentration was measured $0.35 \mu\text{g m}^{-3}$ in 0–4 h post-spray period, whereas the amount was $0.18 \mu\text{g m}^{-3}$ in subsequent sampling periods. Although paraquat concentrations measured in 0–4 h post-spray event was almost 2 times higher than that of 4–8 h post-spray sampling period, which was statistically insignificant (at $p=0.05$). Furthermore the 8 h TWA (time-weighted average) paraquat concentration ($0.27 \mu\text{g m}^{-3}$) was far below (less than 0.3%) than 8 TWA ($100 \mu\text{g m}^{-3}$) of ACIGH TLV and NIOSH REL for occupational exposure to paraquat. A similar result was reported by Chester and Woollen (1981), who found the mean paraquat concentration in air was $0.24\text{--}0.97 \mu\text{g m}^{-3}$ during the measurement of 8 h occupational exposure to paraquat in Malaysia.

Potential exposure assessment: Health related problems resulting from paraquat occupational exposure are being reported around the world. In developing countries, paraquat is widely used under high-risk conditions as agricultural workers often wear partial protection. During mixing and spray of pesticides, 87–95% of overall exposure was seen on the skin, while inhalation accounted for 5–13% (Rutz & Krieger, 1992).

Potential dermal exposure: In calculating potential dermal exposure, 100% of the paraquat amount on a patch of known area is extrapolated to the surface areas of whole body region on the assumption of uniformity of deposition over the area. Total surface areas of whole body can be estimated by the following equation (Gehan & George, 1970; U.S. EPA, 1985) if heights and weights are known:

$$\text{Surface area (SA)} = a_0 H^a_1 W^a_2$$

$$\text{SA} = 0.0239 H^{0.417} W^{0.517} \text{ (where, H=cm, W=kg, SA=m}^2\text{)}$$

The total body surface areas of an adult (body weight 70 kg & height 168 cm) was estimated to be approximately $18,200 \text{ cm}^2$ that is composed of head and neck, trunk (front), trunk (back), arms, thighs, legs and feet and hands. The potential dermal exposure dose was then extrapolated from the 8 h TWA paraquat deposition on each three passive samplers in 'ng paraquat per cm^2 ' to 'mg paraquat per kg per day'. Even if the more realistic assumptions were made, this might give substantial under- or over-estimation of exposure. Prediction of dermal exposure from airborne contaminants would be difficult, because the many different surfaces and movements involved would create an

extremely complicated aerodynamic situation. The distribution of dermal exposure along with the body regions depends on the type and methods of application and also by the climatic conditions during application (Turnbull, 1985).

The scientific committee on plants (SCP) of European Commission (2002) proposed an acceptable operator exposure level (AOEL) of $0.0005 \text{ mg kg}^{-1} \text{ day}^{-1}$ on the risk of paraquat risk to workers taking into particular account of potential inhalation and dermal exposure. However the estimated potential dermal dose in Table III revealed that among the three patches, cotton gauze patches showed higher extrapolated dermal exposure dose ($0.0024 \text{ mg kg}^{-1} \text{ day}^{-1}$), which was around 5 times above the proposed acceptable operator exposure level ($0.0005 \text{ mg kg}^{-1} \text{ day}^{-1}$).

Potential inhalation exposure: For pesticides that are poorly absorbed via skin, the inhalation route can become the most important route of absorption (Durham & Wolfe, 1962). The inhalable fraction (all particles capable of being drawn into the nose & mouth) is the most biologically relevant fraction to measure the inhalation exposure. Therefore potential exposure by the inhalation route is best estimated using personal air sampling at breathing zone. To estimate the inhalation exposure and dose, we assumed that the average human male (70 kg b.w.) breathing rate is of $1.75 \text{ m}^3 \text{ h}^{-1}$ (Seiber & Woodrow, 1981) and absorption factor default is of 1, assuming that all of the paraquat particulate fractions entered through breaths and was entrained in the lungs.

The potential inhalation exposure dose ($0.025 \text{ mg kg}^{-1} \text{ day}^{-1}$) (Table IV) that was estimated based on paraquat air concentration at breathing zone of spray operators during spray application was 50 times higher than the proposed acceptable operator exposure level ($0.0005 \text{ mg kg}^{-1} \text{ day}^{-1}$).

CONCLUSION

The study provides important information on airborne paraquat residue before, during and following spray application in treated field atmosphere, enabling fitting these residue data to theoretical exposure assessment on field operators. Despite having some limitations of passive samplers, passive (cotton gauze patches for airborne paraquat) along with active sampling could be an attractive alternative in terms of its simplicity and low cost in measuring airborne residues in field for shorter duration of sampling. In summary, it would seem prudent to advice agriculture workers to use personal protective equipments (PPEs) during and after paraquat application in the field, since both potential dermal and inhalation exposure dose were substantially higher than the acceptable operator level for paraquat.

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