

Full Length Research Paper

Determination of glyphosate through passive and active sampling methods in a treated field atmosphere

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The study was carried out to determine the atmospheric residues of glyphosate (N-phosphonomethylglycine) using both passive and active sampling methods in Malaysia's tropical weather conditions. The field was treated with Roundup (Monsanto) @ 2L ha⁻¹ using Mistblower (Solo 412). Glyphosate was sampled in 12 h day time pre and post-spray sampling events using three simple and low-cost passive air samplers (cotton gauze, cellulose filter, and PUF) and active sampling using PUF plug and quartz filter cartridges. In pre-spray sampling event, no glyphosate detection was shown in both passive and active sampling. On the other hand, post-spray passive samples data revealed that only cotton gauze among the three passive air samples showed detection in both post-spray events during which the first post-spray (2.49 ng/cm²) showed significantly higher residue measurement than that of second post-spray period (0.84 ng/cm²). In active sampling, however, no glyphosate residue was detected in any of the PUF plug samples but detected only in quartz filter samples, revealing that glyphosate is associated with particles rather than vapour in the air. The highest concentration of glyphosate (42.96µg/m³) was measured in the air at operator's breathing zone during the 25 min spray application period. In the post-spray active sampling periods, glyphosate residue was significantly far below compared to the spray period concentration. Furthermore, in paired comparison between active and passive sampling methods in terms of residue uptake performance, passive sampling showed significantly better performance than the active sampling method in this study.

Key words: Glyphosate, active sampling, passive sampling, atmospheric residue.

INTRODUCTION

Glyphosate (N-phosphonomethylglycine) is a broad-spectrum, foliar-applied herbicide used to kill unwanted plants in a wide variety of agricultural crops, lawn and garden, aquatic, and forestry situations (Humphries et al., 2005). Glyphosate is registered in more than 130 countries and is believed to be the world's most heavily used pesticide (Duke and Powles, 2008), with over 600 thousand tonnes used annually (CCM International, 2009). Based on the registration eligibility data on toxicology and exposure study (USEPA, 1993), glyphosate

is under toxicity category III (low toxicity). Moreover, poor absorption through skin and rapid elimination of glyphosate upon normal exposure (WHO, 1994) might convince the occupational safety regulators not to set any occupational exposure limits for glyphosate. However, workers in a variety of occupations on exposure to glyphosate, develops acute illness. It has been revealed that glyphosate exposure was reported as the third most commonly-reported cause of pesticide illness among agricultural workers in California (Cox, 1995). In Malaysia, glyphosate is the predominant herbicide used in different cropping systems through motorised knapsack sprayers in low volume spray (increased herbicide concentration) for increased herbicide efficacy. This intensive use of

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glyphosate has resulted into serious contamination of the environment because substantial amount of applied pesticides have been shown to become airborne during and after application (Seiber et al., 1980). These airborne residues present a potential exposure route for field workers and other individuals dwelling close to agricultural sites.

Unlike the sampling of solid and liquid matrices, air sampling has always posed unusual challenges because of the ever changing nature of the components in the atmosphere. However, understanding the physical properties of the pesticide (that is, primarily its vapour pressure) and environmental conditions is the key to the selection of an appropriate field sampler and its sampling strategy (Woodrow et al., 2003). In the atmosphere, pesticides are distributed between particle and vapor phases based on the vapor pressure of the chemical, ambient temperature, and concentration of suspended particulate matter in the air (Gioia et al., 2005). To determine the residue level in air, both passive and active sampling methods are commonly used. Active sampling enable the pesticides present in the air to be trapped by pumping air through filter and solid adsorbent media (Tadeo, 2008), whereas passive sampling methods are conceptually simple. It is based on free flow of analyte molecules from the sampled medium to a collecting medium resulting from different physical principles (Gorecki and Namiesnik, 2002). Numerous passive air samplers are being used commercially and all of them are designed to perform sampling keeping various factors in mind, including, the matrix (air, water, soil), physico-chemical properties of the target analytes, sampling duration, environmental variability, cost and easy availability (Seethapathy et al., 2007). Despite having some limitations (possible environmental effects on analyte uptake), passive samplers could be an attractive alternative to more established sampling procedures due to its simplicity and cost-effectiveness (Kot-Wasik et al., 2007)

In Malaysia, several efforts have been made over the years to determine glyphosate in the environmental samples (soil and water) but the air compartment is still overlooked. Moreover, very little information exists in the literature on studies quantifying glyphosate residues in the air following spray application. Therefore, the objective of this study was to measure the airborne residue present during and after glyphosate application in the field.

MATERIALS AND METHODS

Experimental site

The study was conducted from February to April, 2009 at field 2 located inside the University Putra Malaysia (UPM), and the test plot size was 1000 m² which was a weedy harvested corn field. The site is bit down compared to the surrounding area. It is completely open to the west and south where prevailing winds originate, and is

not adversely affected by natural trees or shelterbelts on this side. North of the site is a hay field which extends for 0.2 km before the start of the urban area. East of the site has office building and some shed housing facilities for research studies. No fields in close proximity to this site were treated with glyphosate for pre-seeding, post-emergent or pre-harvest weed control.

Glyphosate application

Glyphosate herbicide 41% a.i. (Roundup, Monsanto Sdn. Bhd., Malaysia) was applied with a calibrated mist blower (Solo Master 412) set at a discharge rate of 0.64 L min⁻¹. Glyphosate was applied at a field dosage rate of 2 L ha⁻¹ with a spray volume of 160 L. Spray droplet diameter of this sprayer were measured using microscope fitted with Porton G12 Graticule, as described by Matthews (2000). The estimated VMD (volume median diameter) and NMD (number median diameter) for spray droplet size were 67 and 35.5 µm respectively, and these droplets diameters are considered as fine droplets (Matthews, 1999).

Air sampling procedures

Three types of passive air samplers with an exposed surface area of roughly 16 cm², namely Cotton gauze (Gasmel Sdn. Bhd., Malaysia), Cellulose filter patches (Whatman grade 41, England), and Polyurethane Foam (PUF) (SKC Inc., USA) were used for passive air sampling and each type of samplers was taped on five surfaces of an identical dimensions foil-covered box (15x15x15cm) – vertically on west (W), East (E), North (N), South (S), and horizontally on Top (T). These boxes were placed 1 m above the ground surface at three randomly selected points nearer to downwind edges of the test plot.

Active sampling was done using field air sampling pump (Model 1067) supplied by Supelco, USA calibrated to a flow rate of 10L min⁻¹ using bubble flow meter. The sampling pump was connected by tygon tube to polyurethane foam (PUF) plug cartridge (ORBO™ 1000, Supelco, USA) containing 0.022 g/cm³ density PUF plug in the glass housing, fitted in front with a Quartz fibre filter cartridge (Supelco, USA). The PUF plug will work mainly for the vapour and the quartz filter for particulate phase of airborne glyphosate (Van Dijk and Guicherit, 1999). After starting sampling, the pump operation was observed for a short time to make sure that it is operating correctly. The pump was powered by electricity through long extension cable to avoid fluctuations in the pump flow rate that have a significant effect on measurement accuracy when air is sampled.

Personal air sampling is done to determine the concentration level that a spray worker is exposed to during a full work shift or task by measuring the breathing zone concentration of the worker. Battery-operated personal air sampling pump (Model PAS-500, Supelco Inc. USA) calibrated to a flow rate of 0.3 L min⁻¹ was used during spraying. The sampling pump was fixed at the sprayer's waist belt and the sampling head fitted with PUF plug and quartz filter cartridges (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 a stopwatch.

Sampling frequency and duration

Air sampling was carried out in 12 h day time from 6:30 am to 7 pm at 4 h interval which was as follows: 4 h pre-spray, during spray (25 min), and post-spray periods (0 to 4 and 4 to 8 h). After sampling, active samplers (PUF and Quartz filter cartridges) were capped and passive samplers were collected in centrifuge falcon tubes. All samples were put in ice box at reduced temperature for transport.

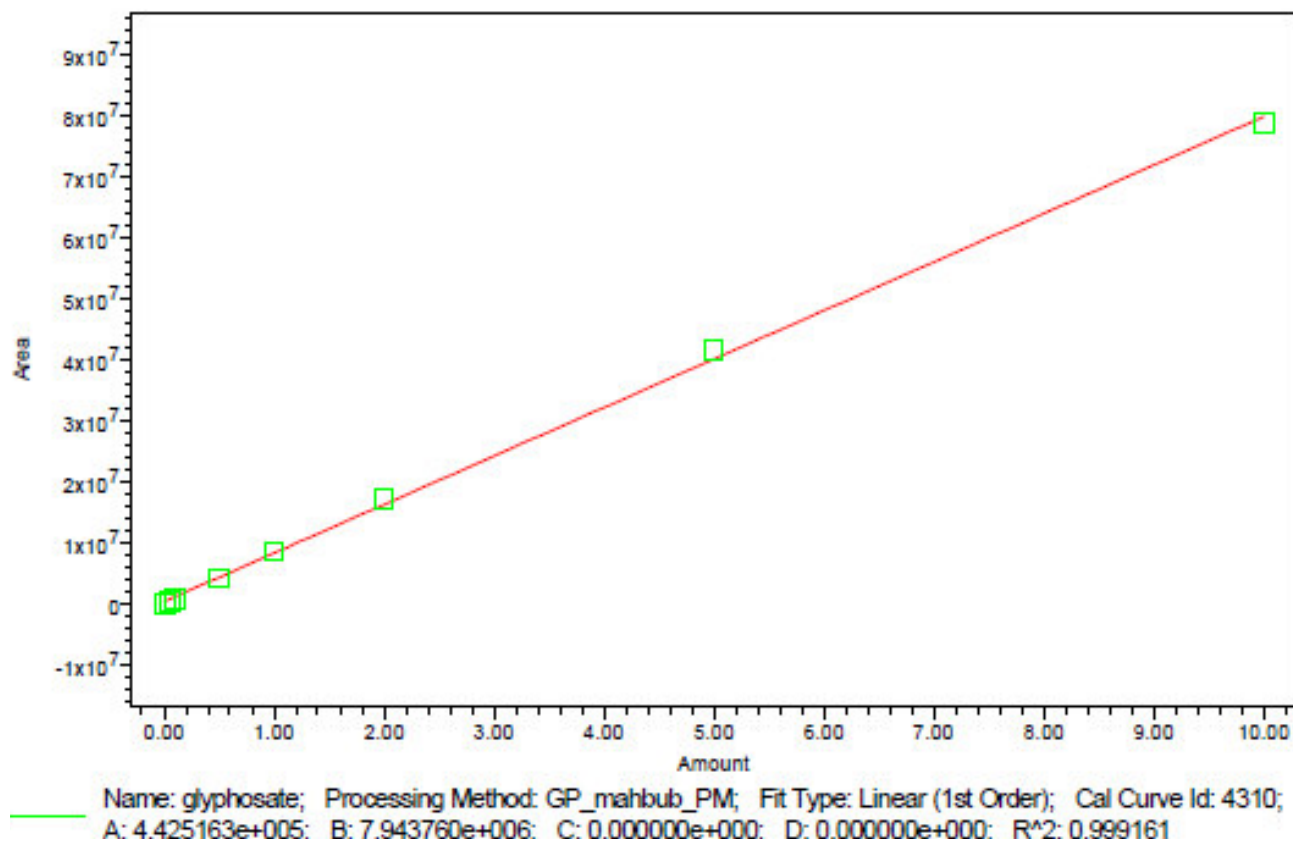


Figure 1. Linear calibration curve for glyphosate (N = 9; $Y = 7.94 \times 10^6 x + 4.43 \times 10^5$ and correlation coefficient $r^2 = 0.999$).

Micrometeorological measurements

Air temperature and wind velocity were recorded on 'sampling data sheet' at every one hour during sampling period by using Thermo-Anemometer (Extech Instruments, USA). Relative humidity was also measured at same intervals using Humidity Indicator (Airguide Instrument Co., USA). During the period wind directions, cloud cover, and incidence of rain were also noted.

Chemical analysis

Preparation of standard solution and curve

Standard stock solution (400 ppm) was prepared by dissolving 0.004 g glyphosate standard (Sigma-Aldrich, USA, purity 99.7%) in 10 ml 0.025 M sodium borate buffer (pH 9) solution. Nine working standards of 10.0, 5.0, 2.0, 1.0, 0.5, 0.1, 0.05, 0.01 and 0.005 ppm were prepared taking the corresponding aliquots from the stock solution followed by dilution with sodium borate buffer for the preparation of standard curve to estimate the linearity and sensitivity of response. Prior to HPLC injection, each working solutions were pre-column derivatized with a derivatizing agent (0.002M FMOC-Cl) as described in the pre-column derivatization step. The lowest calibration level (LCL), which runs on an instrument with acceptable response (area) is 0.005 ppm. Standard curve (Figure 1) for glyphosate was found to be linear over the above range through the evaluation of the correlation coefficient, which was 0.999. Chromatogram of working standard solution of glyphosate (10.00 ppm) was shown in Figure 2.

Sample preparation

The sample preparation method was done according to 'Method PV2067' with some modification as proposed by Occupational Safety and Health Administration (OSHA) analytical laboratory, USA. Both active and passive samplers were carefully transferred to 50 mL centrifuge tubes by clean tweezers. 10 ml borate buffer was added to each tube and then the tubes were capped and allowed to stand for 30 min to soak samples completely. The centrifuge tubes were placed on an orbital shaker at 200 rpm for 1 h followed by ultra sonication (Cole Parmer, USA) for 2 h to desorb the analyte.

Pre-column derivatisation

The derivatizing agent (0.002M FMOC-Cl) was prepared by adding 0.1293g 9-fluorenylmethoxycarbonyl chloride (obtained from ACROS Organics, USA; purity 98%) in 250 ml acetone. Before injecting into HPLC, 1 mL aliquot of each sample extract was transferred in a silanized vial and derivatized with 1 mL of derivatizing agent to produce a highly fluorescent derivative. The vials were shaken to mix for 30 sec on a mini-shaker and subsequently allowed them to sit at room temperature in a dark place for 30 min. Then 1 mL of each sample was transferred in HPLC vial and subsequently labeled and injected to HPLC-FD for analysis.

HPLC systems

HPLC (High performance liquid chromatography) was consisted of

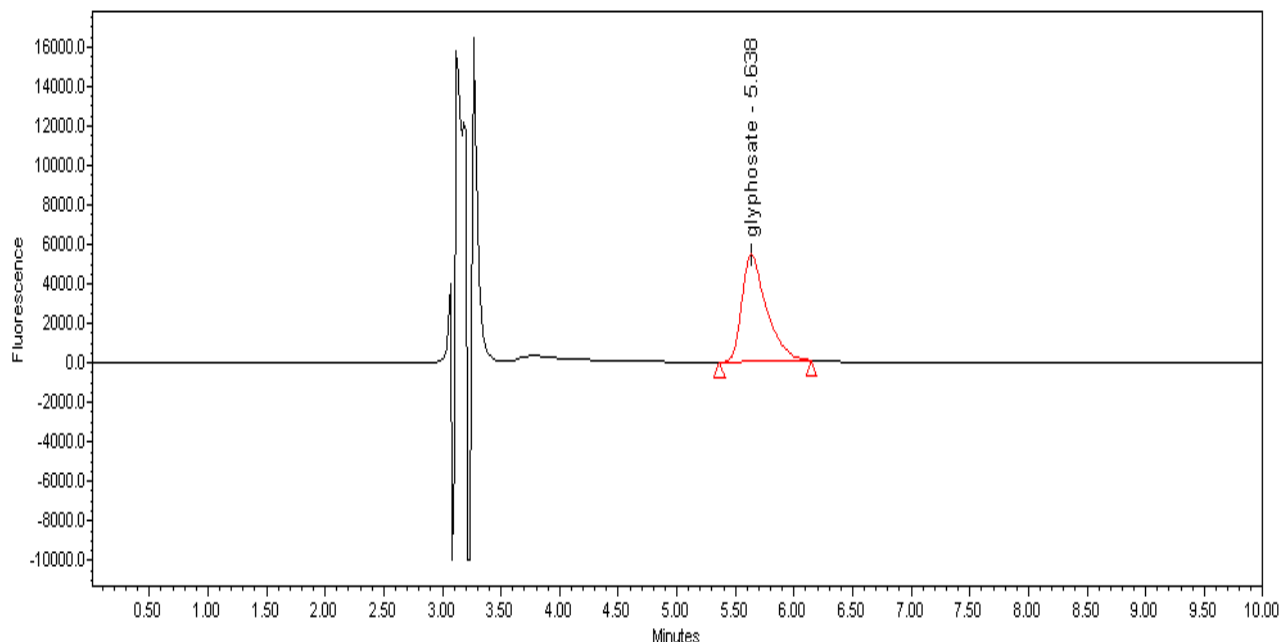


Figure 2. Chromatogram of glyphosate obtained at 10 ppm standard concentration with the recommended HPLC-Fluorescence conditions.

Waters 600 controller pump equipped with Waters 717 auto sampler and a fluorescence detector (Waters 4174). The detector was set with an emission wavelength of λ 320 nm and an excitation wavelength of λ 206 nm that was operated in single channel mode with photomultiplier gain at 1, attenuation at 64 and output data sensitivity (EF) at 5000. The stationary phase was 250 mm \times 4.6 mm i.d 5 μ A⁰ Hypersil NH₂ column (APS-2) and the mobile phase was comprised of 50% Acetonitrile and 50% Phosphate buffer (0.05M Potassium phosphate monobasic KH₂PO₄ adjusted to pH 6.0 with 7N KOH). The mobile phase flow rate (isocratic) was 1 ml/min. All the solvents and solutions used in the mobile phase were previously filtrated and degassed by ultrasonic application. The injection volume was 25.0 μ L. Total sample run time was 10 min and analyte retention time was 5.6 min.

Fortification and recovery studies

The percentage of analyte recovery from fortified samples generally represents the extraction efficacy of the method. Fortification was done in triplicates by applying 100 μ L of three spiking concentrations (1.0, 5.0 and 10.0 ppm) over the surface of three fresh unused samplers (cotton gauge, cellulose filter, and PUF). Then the fortified (spiked) samples were capped and allowed to keep at 4°C inside freeze drawer overnight to equilibrate. The following day, the fortified samples were extracted and analyzed to HPLC-FD as same as field samples. Mean recovery percentages from fortified samples were comprised between 88.8 to 97.2% with a relative standard deviation (RSD) value of 4 to 6% (Table 1). Chromatogram of glyphosate fortified at the concentration of 10.0 ppm showed the same peak retention time (5.6 min) as standard peak (Figure 3).

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 glyphosate established at 5 concentration levels with three replicates (ICH, 1996). The LOD for this method was 0.015 μ g ml⁻¹ and the LOQ was determined to be 0.05 μ g ml⁻¹.

QC/QA considerations: Laboratory and solvent blanks were prepared and extracted as same as the field samples which showed no contamination in solvent and samplers. One field blank sample for every 15 samples was used for analysis along with the field samples. All field blank samples were below the analytical limit of detection (LOD) for glyphosate tested.

Statistical analysis

The study was repeated three times in the same location. Data collected were analyzed following analysis of variance (ANOVA) technique under RCBD (factorial) experimental design and means separation were done by Turkey's Studentized range (HSD) using statistical analysis system (SAS). Differences were considered significant at $p < 0.05$.

RESULTS AND DISCUSSIONS

During the entire sampling period, the weather was clear and sunny. Temperatures were warm, ranging from 82 to 97°F. Relative humidity ranging from 84 to 55% was observed. However, relative humidity was high in the morning and evening, and decreased as temperature increased in the mid-day periods. Wind velocity was almost same throughout the day blowing predominantly from south and south-west direction, ranging between 2 to 5 mil/h. However, there was no incidence of rainfall on the sampling days during the study period.

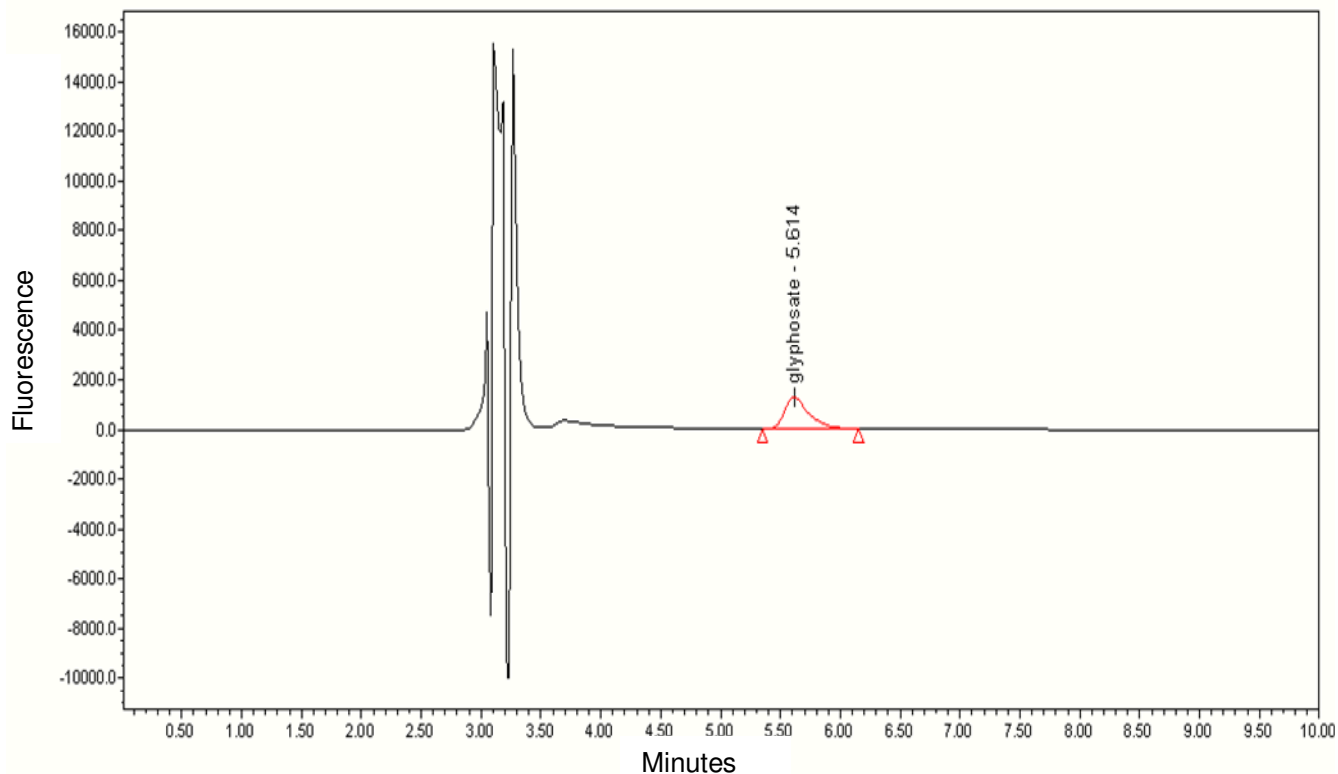


Figure 3. Chromatogram of glyphosate obtained at 10 ppm fortification concentration with the recommended HPLC-Fluorescence conditions.

Table 1. Percent recovery (mean \pm S.D.) and relative standard deviation (% RSD) for the glyphosate fortified samples (N = 27).

Compound	Fortification concentration (ppm)	Fortification level ($\mu\text{g}/\text{sample}$)	% mean recovery \pm S.D.	% RSD
Glyphosate	1.0	0.1	88.8 \pm 5.75	6.61
	5.0	0.5	98.7 \pm 4.28	4.31
	10.0	1.0	97.2 \pm 4.50	4.66

Passive air samplers

The results for each passive air sampler showed very little amount of glyphosate detection only on cotton gauge samples as summarized in Table 2. Since glyphosate has no significant vapour pressure and therefore, the loss of glyphosate to the atmosphere via volatilization from treated surfaces is nonexistent (Franz et al., 1997). The main emission pathway for non-volatile particulate-phased compounds like glyphosate into atmosphere occurred through wind erosion process of dust particles on treated surfaces loaded with pesticides (Van Dijk and Guicherit, 1999). In this study, pre-spray air sampling was taken for 4 h period prior to spraying and glyphosate was not detected in any of the three samplers in this pre-event sampling. The absence of detection at pre-spray sampling in the morning could be due to the complete

removal of residual atmospheric glyphosate via wet deposition mainly by night dew/fog, since glyphosates low Henry's Law Constant ($4.6 \times 10^{-10} \text{ Pa m}^3 \text{ mol}^{-1}$) indicates that it tends to partition in water versus air (Franz et al., 1997) and thereby efficiently removed from the air (Chang et al., 2011). On the other hand, post-event sampling was carried out in 8 h periods with an interval of 4 h that started immediately after completion of spraying, and among the three passive samplers, very little glyphosate was detected mainly on cotton gauge passive samplers in both post-spray sampling periods. However, glyphosate was also detected on the PUF samples only in the first post-spray sampling event (0 to 4 h periods) that was found below the limit of quantitation (LOQ) levels and in contrast, no glyphosate was detected on cellulose filter samples in both post-spray sampling periods. The amount of glyphosate deposition by cotton

Table 2. Glyphosate residue amount mean \pm S.D deposited on three passive air samplers before and after application in the treated field air.

Passive air samplers	Samplers orientation	Deposition amount (ng/cm ²)			
		Pre-spray	Post-spray		
		4 h	0-4 h	4-8 h	8 h TWA ^a
PUF	West	ND	<LOQ ^b	ND	-
	East	ND	<LOQ	ND	-
	North	ND	<LOQ	ND	-
	South	ND	<LOQ	ND	-
	Top	ND	<LOQ	ND	-
	Average	-	-	-	-
Cellulose filter	West	ND	ND	ND	-
	East	ND	ND	ND	-
	North	ND	ND	ND	-
	South	ND	ND	ND	-
	Top	ND	ND	ND	-
	Average	-	-	-	-
Cotton gauge	West	ND	3.42 \pm 1.11 ^{ab}	1.95 \pm 0.24 ^a	2.68 \pm 0.67 ^a
	East	ND	1.79 \pm 0.68 ^{ab}	<LOQ ^b	0.89 \pm 0.34 ^b
	North	ND	1.97 \pm 0.65 ^{ab}	<LOQ ^b	0.98 \pm 0.32 ^b
	South	ND	4.16 \pm 0.70 ^a	2.25 \pm 0.47 ^a	3.20 \pm 0.58 ^a
	Top	ND	1.12 \pm 0.92 ^b	ND ^b	0.56 \pm 0.46 ^b
	Average	-	2.49 \pm 1.12	0.84 \pm 1.03	1.66 \pm 1.07

^a TWA, time-weighted average = sum of the products of concentration and time for each sampling period, divided by total sampling time. ^b <LOQ = below limit of quantitation. Values followed by the same letter (s) column wise, are not significantly different at (P < 0.05). Samples that produced undetected results have been assigned as 'ND'.

gauze samplers could be explained by the findings of OECD (1997) which recommended cotton fabrics 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. In first 0 to 4 h post-spray event, cotton gauze samples yielded higher average glyphosate deposition (2.49 ng/cm²) than that of second 4 to 8 h post spray sampling event (0.84 ng/cm²). Obviously, the low levels of glyphosate detection may account for its insignificant post-application volatilization from treated surfaces. Furthermore, once glyphosate had been sprayed, the resulting fine pesticides particles tends to adsorbed onto dust particles present in the air and subsequently partitioned to particulate phase in the atmosphere. Therefore, the nature and concentration of dust particles in the air would determine the atmospheric loading as glyphosate in the air is associated with particulate matter (dust), assuming that this particulates are removed by gravitational settling or wind erosion. But this atmospheric loading into particles is dependent upon many factors in which environmental factors (such as wind speed, temperature and humidity) are of importance (Van Dijk

and Guicherit, 1999). However, in the tropical weather of Malaysia, prevailing high temperature and humidity as well as high precipitation plays very important role in glyphosate atmospheric deposition. The amount of dust particles in the air is reduced as a result of high atmospheric humidity and frequent precipitation events (UN-ECE, 1979). This resulted to lower levels of atmospheric glyphosate deposition.

In addition to the above findings, the glyphosate detection was showed in higher amount on cotton gauze samplers oriented on south approach (4.16 and 3.42 ng/cm²) followed by west (2.24 and 1.95 ng/cm²) in post sampling periods indicating the correlation of wind movement with atmospheric deposition of glyphosate during which wind was predominantly blown from south and south-west direction across the face of samplers. This wind movement might influence the gravitational settling and inertial impaction of wind blown particulates at the time of deposition on samplers. In agreement with the effect of wind movement on airborne pesticides, Thistle (2000) asserted that the dispersion of pesticide droplets in the air is influenced by the droplet size, atmospheric stability and wind movement (vertical and

Table 3. Glyphosate residue amount mean \pm S.D measured on active air samplers before, during and after application in the treated field air.

Spray periods	Active sampling			
	Air volume (m ³)	Air concentration ($\mu\text{g}/\text{m}^3$)		
		Quartz filter	PUF plug	Total air concentration
Pre- spray (4 h)	0.24	ND	ND	ND
During spray(25 min)	0.0075	42.8	ND	42.96 \pm 7.96 ^a
Post- spray	0-4 h	0.24	0.10	0.10 \pm 0.013 ^b
	4-8 h	0.24	0.051	0.051 \pm 0.007 ^b

Samples that produced undetected results have been assigned as 'ND'. Values followed by the same letter (s) column wise, are not significantly different at ($P < 0.05$).

horizontal components).

Active air samplers

The air concentrations of glyphosate measured by active sampling were presented in Table 3. The result showed that glyphosate was not detected in any of the air samples collected with polyurethane foam (PUF) plug samples but it was detected only in quartz filter samples. The absence of glyphosate in the PUF plug indicates that glyphosate is not released as the vapour into the atmosphere but rather is carried by particulate matter (Humphries et al., 2005). In the pre-spray sampling event, no glyphosate was detected in both quartz filter and PUF plugs, this indicates that glyphosate is no longer in the atmosphere in the wet and high humid morning but have been removed through wet deposition.

The highest air concentrations of glyphosate (42.96 $\mu\text{g}/\text{m}^3$) occurred during 25 min spray application period that was collected through personal air sampling pump operated at operator's breathing zone. The result was within a range of 0.41 to 48 $\mu\text{g}/\text{m}^3$ glyphosate residue levels in the working air depending upon the method of application and rate of applications which was revealed in a study conducted in Ukraine (Chmil and Kuznetsova, 2009). The high concentration measured during spray application period was due to fine droplets produced by mist blower sprayer that remain in the surrounding air due to their lower terminal velocity (Matthews, 1999). Most importantly, a significant proportion of these fine droplets are inhalable particles that pose serious risk of health injury to spray operators. On the post spray sampling done by field air sampling pump, glyphosate was detected in small amounts in quartz filter samples that were drastically lower than the spray period concentration. However, glyphosate concentrations were markedly higher during 0 to 4 h post spray (0.10 $\mu\text{g}/\text{m}^3$) and decline during 4 to 8 h period (0.051 $\mu\text{g}/\text{m}^3$). However, this post spray results were far below the reported residue range of 10 to 17 $\mu\text{g}/\text{m}^3$ during 24 h post

spray fine filter sampling to measure Alberta's atmospheric glyphosate deposition conducted by Water research group of Alberta Environment (Humphries et al., 2005). Concentration of glyphosate in air was found very small at post-spray sampling, and this occurrence might be because of negligible volatility after spray application. Furthermore, this might be due to the total volume of air sampled with the field air sampling pump.

Paired comparison of passive sampling method performance with active sampling

In field situations, there is a considerable variability of the concentrations of airborne residues during sampling periods in which the performance of both active and passive sampling methods also showed different performance in terms of residue uptake. Active air samplers have been widely accepted as the reference method for the evaluation of the performance of passive air samplers. Hence, both active and passive samplings were done side-by-side in all sampling events in this study to do the paired comparison between the active and passive sampling methods. This paired comparison is important for the performance evaluation of passive samplers by assessing the magnitude and direction of differences between passive and active air samplers.

However, current National Institute for Occupational Safety and Health (NIOSH), Health and Safety Executive (HSE), and European Committee for Standardization (CEN) validation protocols have used Student's *t*-tests, paired sample Student's *t*-tests, and linear regression as the statistical methods for evaluating the performance of passive samplers. In this context, linear regression analysis would be preferable providing a measure of the degree of association between the two methods (that is, the correlation of coefficient) on the assumption that a linear relationship exists between them, over the range of conditions covered by the field tests. Basically, these tests can only investigate whether in general the mean concentrations measured by active and passive sampling

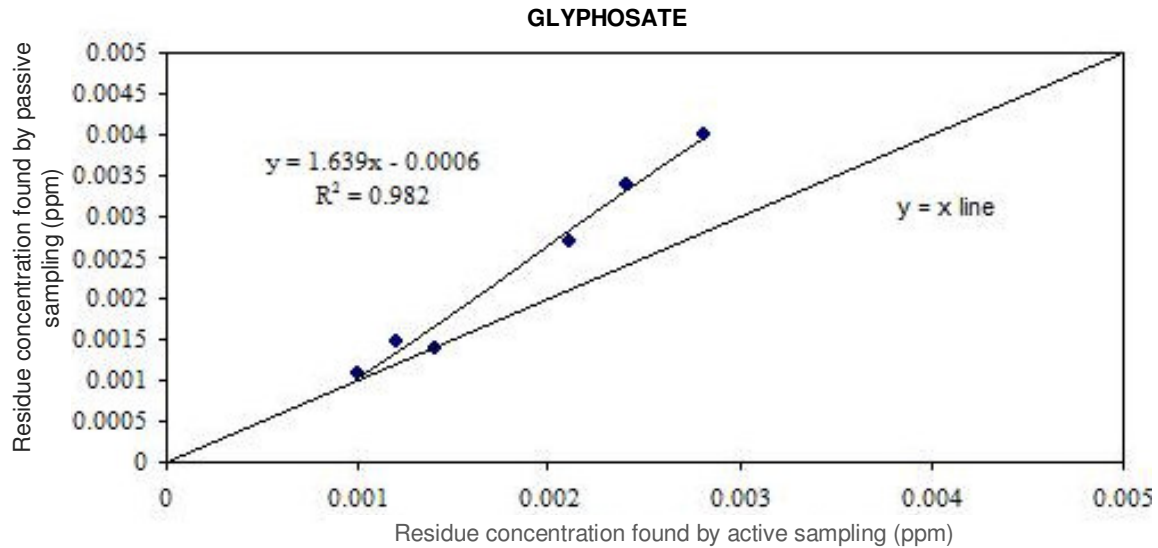


Figure 4. Paired relationship between the active and passive sampling methods -based on the results of airborne glyphosate residue uptake concentration (ppm).

methods are statistically different from each other, but not identify the source of the differences (Shih et al., 2000).

The linear relation determined by the regression analysis is taken the following equation form:

$$y = a + bx$$

Where y and x are the residue concentrations measured by the passive and active sampling methods respectively. For perfect agreement between the two methods, the true values of the intercept (a) and slope (b) parameters should be respectively 0 and 1.

From the field performances of three passive samplers in terms of glyphosate residue uptake, it was quite evident in this study that only cotton gauze samplers showed residue uptake in comparison to other two passive samplers. Therefore, passive (cotton gauze) and active (quartz fibre filter) air samplers (a total of 6 pairs of residue concentrations in ppm) were used for determining the agreement between passive and active sampling methods.

In regression analysis (Figure 4), linear correlation was found between pair-wise ($n = 6$) comparison of residue concentrations measured by active and passive sampling methods over the range of 0.001 – 0.004 ppm. The linear regression line equation showed satisfactory correlation coefficient ($R^2 = 0.98$) with a moderate slope ($b = 1.63$) and a negative intercept ($a = -0.0006$). It was also observed that residue concentration found at the second post-spray events (4 to 8 h) were very close to standard line ($y = x$ line). In contrast, the residue concentrations found during the first post-spray sampling events (0 to 4 h) were far above the standard line. Hence, it can be

inferred that residue uptake by passive sampling was much higher than active sampling method in the first post-spray sampling event immediately after spraying, and with passage of time the performance of two methods became almost similar in the second sampling event.

Conclusion

The study of airborne glyphosate residue in post-spray application showed that in the air, glyphosate is associated with particles rather than vapour. It was also noted that meteorological conditions play a significant role in atmospheric sampling. Among the three passive samplers used in this study, only cotton gauze passive sampler showed atmospheric glyphosate detection in both post-spray sampling events and could be suitably used for non-volatile pesticides residue measurement in the air. In paired comparison between active and passive sampling methods, it was quite evident that passive sampling showed significantly better performance than the active sampling. Although occupational safety organizations have not yet established any threshold limits for glyphosate exposure, but the air concentration during spray application at sprayer's breathing zone was substantially higher that suggesting the use of personal protective equipments (PPEs) for persons in charge of application.

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