



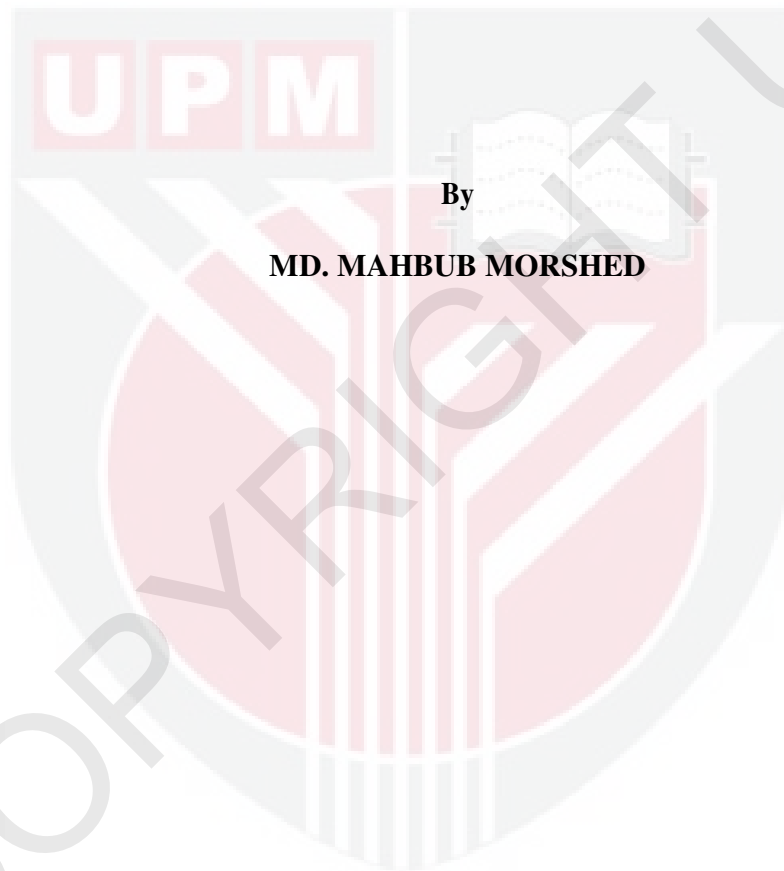
UNIVERSITI PUTRA MALAYSIA

**AIRBORNE RESIDUES OF PARAQUAT, GLYPHOSATE AND
CHLORPYRIFOS IN RICE FIELDS OF SUNGAI BESAR,
SELANGOR, MALAYSIA**

MD. MAHBUB MORSHED

FP 2011 9

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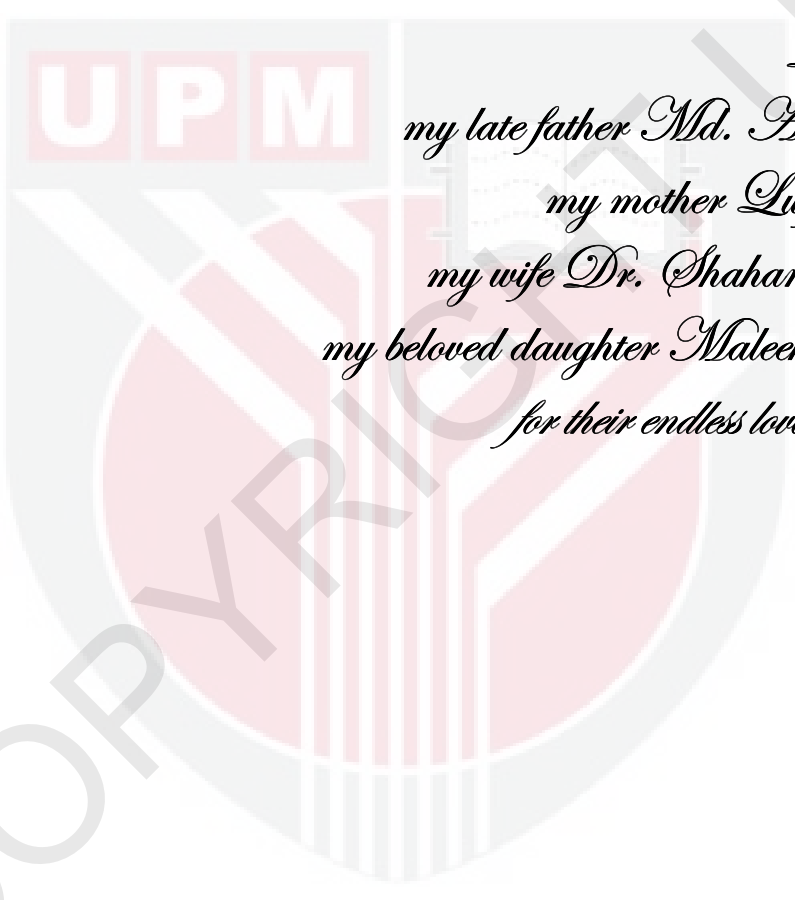


By

MD. MAHBUB MORSHED

**Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

July 2011

The logo of the University of Peshawar (UPM) is a shield-shaped emblem. At the top, the letters 'UPM' are written in a bold, sans-serif font within a red rectangular box. Below this, the shield is divided into several sections: a central vertical section with red and white stripes, and two side sections with red and white diagonal stripes. The shield is set against a light grey background.

*Dedicated to
my late father Md. Abdul Haque
my mother Lutfun Nahar
my wife Dr. Shahnaz Sultana
my beloved daughter Maleeha Muniyat
for their endless love and sacrifices*

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

**AIRBORNE RESIDUES OF PARAQUAT, GLYPHOSATE AND
CHLORPYRIFOS IN RICE FIELDS OF SUNGAI BESAR,
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July 2011

Chairman : Professor Dzolkhifli Omar, PhD

Faculty : Agriculture

Due to government subsidies and lack of labour, rice farmers in Malaysia generally use large amount of pesticides in a season starting from land preparation until maturity. The intensive use of pesticides has resulted into serious contamination of the environment, because substantial amount of agriculturally applied pesticides have been shown to become airborne during and after application that ultimately cause acute and chronic health hazards to field workers. In this study, airborne residue levels of three widely used pesticides (paraquat, glyphosate, and chlorpyrifos) were determined in two rice seasons (wet and dry) at three sampling locations (Kampung Pasir Panjang, Kampung Simpang Lima and Kampung Sungai Panjang) in Sungai Besar, Malaysia. Air was sampled in 12h day time with a 4h sampling intervals at both pre-and post-spray sampling events by using three simple and low-cost passive samplers (cotton gauze, cellulose filter, and polyurethane foam (PUF) samplers) and two active samplers (PUF plug and quartz filter cartridges). Moreover, air was pumped in the breathing zone of the

spray operator to measure the possible amount of pesticides breathed in during field spraying. For accurate residue analysis of air samples, analytical method validation was performed that showed the fitness of methods for each compound undertaken in this study. Studies on passive sampler's performance validation showed that the performance of passive samplers were consistent. Satisfactory correlation coefficient ($r^2 = 0.979$) was observed in paired comparison between active and passive sampling methods, and passive sampling showed significantly better performance over active sampling method with respect to airborne residue measurement. Among the three passive air samplers, cotton gauze showed significantly the highest deposition for particle-bound pesticides – paraquat and glyphosate (15.56 and 2.49 ng/cm², respectively), whereas PUF sampler showed the highest for vapor-bound pesticide – chlorpyrifos (48.80 ng/cm²). In active air samplers, paraquat and glyphosate residues were detected only in quartz fibre filter cartridges (0.52 and 0.10 µg/m³, respectively); on the other hand, chlorpyrifos was detected on PUF plug cartridges (2.54 µg/m³). Data on airborne residue measured in the rice growing area revealed that among the three compounds, glyphosate was measured in the lowest amount in the air followed by paraquat and chlorpyrifos. In day-long sampling events, however, virtually no residue was detected in any of the samples exposed in the pre-event sampling, and obviously, the highest airborne residue was measured during spraying at breathing zone of the spray operator, and subsequently the residue levels were drastically dropped in the post-spray sessions. Moreover, in post-spray sampling sessions, the residue level was consistently higher during first 0-4 hours relative to that of second 4-8 hrs sampling events. Furthermore, residue amounts showed spatial (location-wise) as well as seasonal

variations during which local environmental conditions, physiochemical properties of the compound and its application technique played very important role on pesticides atmospheric deposition. In comparison between rice seasons, residue amounts measured by passive and active sampling methods showed higher detection in dry season (18.83, 8.59 ng/cm² and 0.76, 0.28 µg/m³ for paraquat; 2.82, 1.03 ng/cm² and 0.28, 0.06 µg/m³ for glyphosate; 48.62, 19.71 ng/cm² and 4.19, 1.54 µg/m³ for chlorpyrifos, respectively) than that of wet season (13.68, 4.84 ng/cm² and 0.56, 0.19 µg/m³ for paraquat; 1.62, 0.55 ng/cm² and 0.13, 0.00 µg/m³ for glyphosate; 21.28, 9.36 ng/cm² and 1.79, 0.54 µg/m³ for chlorpyrifos, respectively). However, seasonal variations showed insignificant effects on airborne residue for paraquat and glyphosate, but significant effect for chlorpyrifos. Interestingly, seasonal effect was insignificant for paraquat, glyphosate and chlorpyrifos on respirable residues (109.74, 32.50, 153.50 µg/m³ in wet season and 108.66, 31.73, 186.68 µg/m³ in dry season, respectively) in the air around the spray operator's breathing zone during spraying in the field. In extrapolated field operators exposure assessment, both potential dermal (5 to 7 and 15 to 30 times, respectively) and inhalation (40 and 100 times, respectively) doses were higher than the proposed acceptable operators exposure level (AOEL) for paraquat and chlorpyrifos, whereas, both doses were far below the proposed AOEL for glyphosate.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**SISA UDARA PARAQUAT, GLYPHOSATE DAN CHLORPYRIFOS DI
SAWAH PADI SUNGAI BESAR, SELANGOR, MALAYSIA**

Oleh

MD. MAHBUB MORSHED

Julai 2011

Pengerusi : Profesor Dzolkhifli Omar, PhD

Fakulti : Pertanian

Oleh kerana subsidi kerajaan dan kekurangan buruh, pesawah padi di Malaysia amnya menggunakan sejumlah besar racun perosak pada musim yang bermula dari penyediaan tanah sehingga matang. Penggunaan intensif racun perosak telah membawa kepada pencemaran alam sekitar yang serius, kerana jumlah yang besar racun perosak pertanian yang diguna menunjukkan udara semasa dan selepas penggunaan yang akhirnya menyebabkan bahaya kesihatan yang akut dan kronik kepada pekerja-pekerja lapangan. Dalam kajian ini, tahap sisa-sisa udara tiga racun perosak yang digunakan secara meluas (paraquat, glyphosate, dan chlorpyrifos) telah ditentukan dalam dua musim padi (basah dan kering) di tiga lokasi pensampelan (Kampung Pasir Panjang, Kampung Simpang Lima dan Kampung Sungai Panjang) di Sungai Besar, Malaysia. Udara disampel dalam masa sehari 12 jam dengan selang pensampelan 4 jam di kedua-dua sebelum dan selepas pensampelan semasa semburan dengan menggunakan tiga contoh pasif yang mudah dan kos yang rendah (kapas kain kasa, selulosa penapis, dan busa polyurethane (PUF) patch) dan dua sampel yang aktif contohnya (plug PUF dan kuarza kartrij penapis).

Selain itu, udara dipam dalam zon pernafasan pengendalian semburan untuk mengukur jumlah yang mungkin racun perosak ditiupkan dalam semasa bidang penyemburan. Untuk analisis sisa-sisa yang tepat sampel udara, pengesahan kaedah analisis yang telah dilakukan dengan menunjukkan kesesuaian kaedah setiap kompaun yang dijalankan dalam kajian ini. Kajian ke atas pengesahan prestasi persampelan pasif menunjukkan bahawa prestasi contoh pasif yang konsisten. Pekali korelasi yang tepat ($r^2 = 0.979$) diperhatikan dalam perbandingan berpasangan antara kaedah pensampelan yang aktif dan pasif, dan pensampelan pasif menunjukkan prestasi yang jauh lebih baik kaedah pensampelan aktif berkenaan dengan pengukuran sisa-sisa udara. Antara ketiga-tiga contoh pasif udara, kain kasa kapas menunjukkan pemendapan tertinggi bagi sebatian yang terikat dengan zarah-- paraquat dan glyphosate (15.56 and 2.49 ng/cm², masing-masing), manakala sampler PUF menunjukkan tertinggi bagi sebatian- chlorpyrifos wap terikat (48.80 ng/cm²). Dalam udara aktif, sisa-sisa paraquat dan glyphosate dikesan hanya dalam kartrij penapis gentian kuarza (0.52 and 0.10 µg/m³, masing-masing), selain itu, chlorpyrifos dapat dikesan pada katrij palam PUF (2.54 µg/m³). Data mengenai sisa-sisa udara yang diukur di kawasan padi yang semakin meningkat menunjukkan bahawa di antara ketiga-tiga sebatian ini, glyphosate diukur dalam jumlah yang paling rendah di udara diikuti oleh paraquat dan chlorpyrifos. Walau bagaimanapun, dalam pensampelan sepanjang hari, hampir ada sisa-sisa yang tidak dapat dikesan dalam mana-mana sampel yang terdedah dalam pensampelan pra-event, dan jelas sekali, baki udara tertinggi adalah diukur semasa menyembur pada pensampelan zon pernafasan pengendali semburan, dan seterusnya tahap residu telah menurun secara drastik dalam sesi selepas semburan. Selain itu, dalam sesi persampelan

selepas semburan tahap residu adalah sentiasa tinggi bermula pada 0-4 jam berbanding dengan kedua 4-8 jam acara pensampelan. Tambahan pula, jumlah sisa-sisa menunjukkan ruang (lokasi-tepat) serta variasi bermusim di mana keadaan persekitaran tempatan, sifat-sifat physiochemical sebatian dan teknik penggunaan memainkan peranan yang amat penting pada mendapan racun perosak atmosfera. Dalam perbandingan antara musim padi, jumlah sisa yang diukur dengan kaedah pensampelan yang pasif dan aktif menunjukkan pengesanan yang lebih tinggi pada musim kering (18.83, 8.59 ng/cm² dan 0.76, 0.28 µg/m³ untuk paraquat; 2.82, 1.03 ng/cm² dan 0.28, 0.06 µg/m³ untuk glyphosate; 48.62, 19.71 ng/cm² dan 4.19, 1.54 µg/m³ untuk chlorpyrifos, masing-masing) daripada musim basah (13.68, 4.84 ng/cm² dan 0.56, 0.19 µg/m³ untuk paraquat; 1.62, 0.55 ng/cm² dan 0.13, 0.00 µg/m³ untuk glyphosate; 21.28, 9.36 ng/cm² dan 1.79, 0.54 µg/m³ untuk chlorpyrifos, masing-masing). Walau bagaimanapun, variasi bermusim menunjukkan kesan sisa udara untuk paraquat dan glyphosate yang tidak ketara, tetapi kesan yang ketara untuk chlorpyrifos. Menariknya, kesan bermusim tidak penting untuk paraquat, glyphosate dan chlorpyrifos pada sisa-sisa nafas (109.74, 32.50, 153.50 µg/m³ pada musim basah dan 108.66, 31.73, 186.68 µg/m³ pada musim kering, masing-masing) dalam udara di sekeliling pernafasan pengendalian semburan zon semasa menyembur. Dalam bidang pengendalian pendedahan penilaian yang diekstrapolasi, ke atas kulit (5 hingga 7 dan 15 hingga 30 kali, masing-masing) dan penyedutan yang berpotensi (40 dan 100 kali, masing-masing) dos yang lebih tinggi daripada pengendalian yang dicadangkan oleh pendedahan tahap yang boleh diterima (AOEL) untuk paraquat dan chlorpyrifos, sedangkan, kedua-dua dos yang jauh lebih rendah daripada AOEL yang dicadangkan untuk glyphosate.

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I certify that an Examination Committee has met on 25/07/2011 to conduct the final examination of Md. Mahbub Morshed on his Ph.D thesis entitled "Airborne Residues of Paraquat, Glyphosate and Chlorpyrifos in Rice Fields of Sungai Besar, Selangor, Malaysia" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree.

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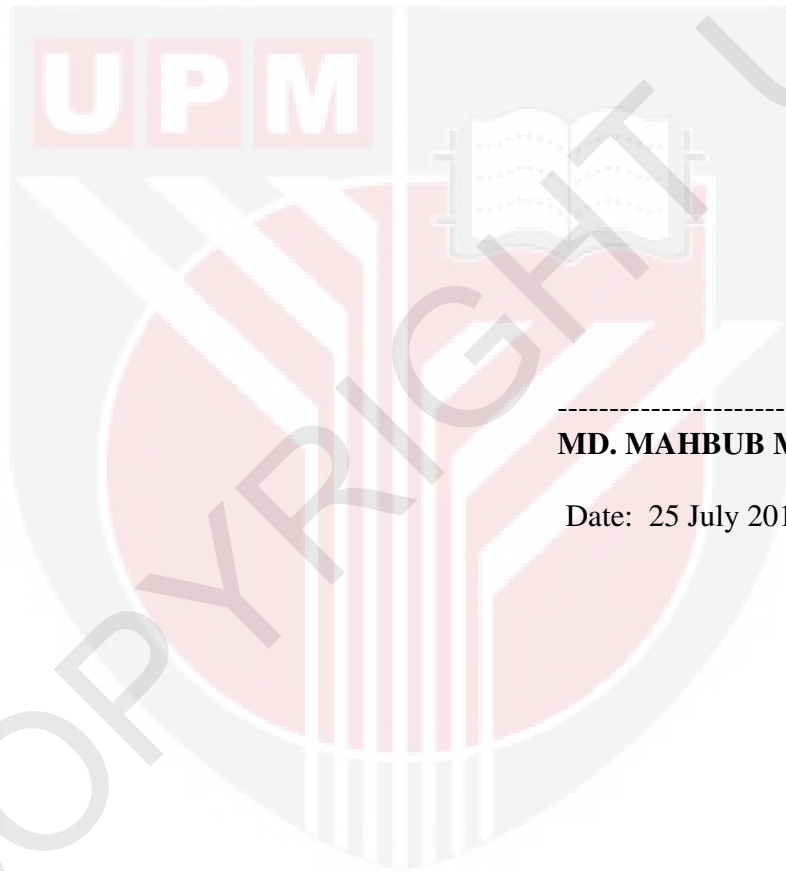
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Date: 8 September 2011

DECLARATION

I hereby declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or other institutions.



MD. MAHBUB MORSHED

Date: 25 July 2011

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