Proceedings

15th International PEAT Congress 2016

Peatlands in Harmony

-Agriculture, Industry and Nature-

POSTER PRESENTATIONS

15th - 19th August 2016

Kuching, Sarawak, Malaysia

Organized by:

MPS MALAYSIAN PEAT SOCIETY

In partnership with:

IPS International Peatland Society

2.2: GHG EMISSION FROM NATURAL & MANAGED PEATLANDS

Abstract No: A-265

THE EFFECT OF PESTICIDES APPLICATION ON PHENOLIC ACID CHANGES AND CO_2 AND CH_4 PRODUCTIONS FROM PEAT SOIL

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SUMMARY

Peat soil contains organic matters, in which their degradation produces phenolic acids, CO_2 and CH_4. Phenolic acids are known to be toxic to plants. This study was aimed at evaluatingeffects of two pesticides: herbicide paraquat dichloride and insecticide BPMC, on phenolic acids of peat soil. Pesticides that fall into peat soil will react with organic matters and its degradation products. Soil samples were taken from paddy field peat soil at Kanamit Jaya Village, District of Maliku, Pulang Pisau, Central Kalimantan. The pesticide dosages usedwere based on the recommended application dose, *i.e.* 4 liter ha-^{1} for paraquat and 1 liter ha^{-1} for BPMC. Treatments consisted of 3 levels of dosage (half, equal and twice): 1104 µg kg^{-1}, 2208 µg kg^{-1}, 4416 µg kg^{-1} for paraquat and 485 µg kg^{-1}, 970 µg kg^{-1}, 1940 µg kg^{-1} for BPMC with single control. After 1, 7, 14 and 28 days of incubation, soil in each treatment was analyzed for phenolic acids, pesticide residues, function groups, and CO_2 and CH_4 productions.Results showed that pesticide applications reduced total phenolic acids in peat soil. Paraquate and BPMC applications showed similar pattern. BPMC at the rate of 242.5 µg/500 g soil showed 95% residues reduction, higher than other dosages. Meanwhile, all dosages of paraquat provided 100% reduction of residues. Analysis using FTIR did not detect any additional functional groups. However, altered intensity of absorption peaks could be an indication of compositional changes of chemical substances within peat soil during incubation period. Pesticides application did not increase $CO_2$and CH_4 emissions.

Keywords: *Peat soil, paraquat, BPMC, phenolic acid, gas emission*

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INTRODUCTION

Peat soil is a suboptimal land for cultivation because it is less fertile, has low pH, high cation exchange, low base saturation, and poor drainage. Peat soils of Jambi and Central Kalimantan contained phenolic acid derivatives such as ferulic, sinapic, coumaric, vanilic, siringic, galic and hydroxybenzoic acids (Mario &Sabiham2002). As a result of population increase and limitation of land,peat soils are cultivated.

Phenolic acids are toxic to plants and reduce plant growth. At a concentration 250 µM, phenolic acids reduced potassium absorption by barley (Hartley &Whitehead 1984). Salisylic and ferulic acids at concentrations 500 – 1000 µM reduce potassium and phosphorus absorptions by wheat and soybean (Tadano *et al.,*1992). Hydroxybenzoic acids at 7 – 70 µM retard the growth of corn, wheat, and nut and at 360 µM retard growth of sugar cane roots (Wang *et al*., 1967). Because of pests the success of developing peat soil for cultivation heavily relies on pesticides. When applied, only approximately 20% of this pesticide will arrive at targets. The rest will move spatially such as leach to surface or ground waters (Sa'id 1994).

Peat organic matters contain functional groups such as carboxyl, hydroxyl and amine capable of interacting with pesticides (Yong *et al.,* 1992). Non-olar pesticides are able to bond to peat organic matters (Harrad 1996). Pedersen *et al.* (1995) revealed that bonding of pesticides to peat organic matters will influence properties and mobility of pesticides and physiologically causing the pesticides to be inactive and difficult to degrade by soil microbes. In addition, Gerstler(1991) stated that bonding of pesticides and peat organic matters reduce activity of phenolic acids.

Peat soil is carbon emitter when altered from natural forest and could be the biggest contributor of green house gases. This research was aimed at evaluating effects of pesticide addition on interactions and bonding of phenolic acids linked to $CO_2$and CH_4 emisions from peat soil.

METHOD

Cultivated peat soil samples were taken from Kanamit Jaya Village, Maliku District, Pulang Pisau Regency, Central Kalimantan Province. The sampling coordinates were 2^0 55'46" north latitude and 114^0 10'16" east latitude. The sampling techniques followed. Composite samples were taken at depth 0 - 25 cm. Physical and chemical analyses include pH, C-organic content, N-total, fiber content, colorand level of decomposition.

This study included 2 types of pesticide and 3 dose levels (half, equal, and twice dose of application). Pesticide dose refer to recommended application, *i.e.* 4 liter ha^{-1} for paraquat and 1 liter ha^{-1} for BPMC. With peat soil *bulk density* 0.25 g cm^{-3} and soil depth 10 cm then such the dose will equal to active compounds 2208 μg kg^{-1} for paraquat and 970 μg kg^{-1} for BPMC. Treatments were labeled: K/kontrol (peat soil without pesticide addition); A1(soil + paraquat 552 μg); A2 (soil + paraquat 1104 μg); A3 (soil + paraquat 2208 μg); B1 (soil + BPMC 242.5 μg); B2 (soil + BPMC 485 μg) and B3 (soilt + BPMC 970 μg). Analyses were include phenolic acids, pesticide residues, functional groups, CO_2 and CH_4. Effects of phenolic acids and pesticides interaction was studied with 0.00389 mmol paraquat and 0.00482 mmol BPMC and 0.005 mmol pure phenolic acids.

Incubation and sampling

To 500 g soil sample, pesticide was added and incubated at room temperature. Samplings were done at 1, 7, 14 and 28-day based on pesticide *degradation time* (DT_{50}) as referenced from EPA (1998). CO_2 and CH_4 were sampled in dark room at room temperature after incubation for 24 h in closed chamber. Prior to closing the chamber, a bottle contained 5 mL 0.2N KOH was placed in the chamber. To sampling CH_4 gas the bottle lid was modified through addition of capillary hose equipped with a stop cock.

Phenolic acids analysis

Sample of weight 5 gram was added with 25 mL methanol and shaken for 60 minutes. The extract then was centrifuged at 3000 rpm, filtered through millipore of size 0.2 μm. Aliquot was analysed by HPLC equipped with reverse phase column C18 and ultraviolet (UV) detector. Aliquots were read at a wavelength 280 nm. The HPLC system was operated at column temperature 30°C, flow rate 0.7 mL $minute^{-1}$ and mobile phase consisted of TFA 0.1% and metanol mixture (75:25) (Deptan 2003).

Pesticide residues analysis

Peat soil sample of 20 g weight was added with 50 mL of acetone and dichlorometane mixture, shaken for 8 h and then eluted through florisil and sodium sulphate (1:1) column. After evaporation for 15 minutes the aliquot was redissolved in 25 mL metanol for paraquat residues determination by HPLC 20A. The operating temperature was 30°C, mobile phase a mixture of methanol-water (60:40) set at flow rate 0.5 mL $minute^{-1}$, and using UV detector. BPMC residues were determined by using GC operated at temperature 60°C using mobile phase helium gas set at flow rate 1 mL $minute^{-1}$ (Deptan 2003).

$CO_2$and CH_4 measurement

According to Anas (1989), CO_2 concentration can be measured by using acid-base titration method. After the sample was incubated, to the 5 mL KOH solution in an erlenmeyer which was placed in the incubated closed container was added with 2 drops of phenolphtalein indicator (PP) then was titrated with HCl which was already standardized with sodium borate until the color changed from pale red to clear. Then methyl orange indicator was added and back titrated with HCl until the liquid color change from orange-yellow to red. The added volume of HCl was then recorded. The production of $CH_4$was measured using GC operated at column temperature 48°C, injector and *Flame Ionization Detector* (FID) temperature 140°C, with helium carrier gas set at flow rate47 mL $minute^{-1}$.

RESULTS AND DISCUSSION

Physical and chemical properties of peat soil

The soil samples were classified as very acidic soil (Table 1). This in accordance to Salampak (1999) findings where the pH of peat soil of Central Kalimantan wasin the range 3.25–3.75. Acidity of peat soil is correlated to organic acids humic and fulvic. The levels of organic-Cwas 52.07% and total-Nwas 0.94%. Ash and organic matter contents were correlated with maturity of peat soil (Noor 2001). Indonesian peat soil is an ombrogen peat soil consisted of thick soil peat but less nutrients.

Table 1: The main properties of peat soil used in this experiment. Samples were taken from 0-25 cm depth

Parameter	Value
pH	3,50
Organic-C (%)	52,07
Total-N (%)	0,94
C/N ratio	55,39
Ash (%)	10,24
Water (%)	70,87
Fiber volume (%)	46
Munsell color	10 YR 3/1 (very dark grey)
Decomposition level	hemic

Phenolic acids

Phenolic acids prior to treatments demonstrated domination of ferulic and vanilic each at 1.327 and 1.291 mg kg^{-1}. Other phenolic acids such as galic, protocatechuic, hydroxybenzoic, siringic, and fumaric were in the range 0.4 – 0.6mg kg^{-1} (Table 2).

Table 2:Concentrations of various phenolic acids in the soil prior to pesticide application

Phenolic acid	Concentration (mg kg^{-1})
Ferulic	1,32
Vanilic	1,29
Coumaric	0,57
Hydroxybenzoic	0,54
Siringic	0,54
Protocatechuic	0,47
Galic	0,43
Total	5,16

Phenolic acids after treatments

Results of A1 (Figure 1) showed that protocatechuic decreased 46.7% (highest) and ferulic 20.04% (lowest). This indicated that addition of 552 µg paraquat did not influence phenolic acid biodegradation by soil microbes. Ferulic and vanilic consistently demonstrated decreasing concentrations for the whole incubation period. However, other phenolic acids showed increasing concentration at 14-days of incubation. Ferulic and vanilic dominated phenolic acids composition for the whole incubation period. Compared to control, phenolic acids demonstrated decreasing concentrations at 28-days of incubation.

The same pattern was developed by B1. Phenolic acids demonstrated a decreasing tendency in the range 16.4–39.4%.At 242.5 µg,BPMC treatment showed the highest reduction of phenolic acids to protocatechuic meanwhile the lowest was ferulic acid.

For A2, at 28-days of incubation, the phenolic acid concentrations showed increasing pattern except for protocatechuic and galic acids. Significant increment happened to ferulic acid, i.e. 21%. Galic acid decreased significantly at 31%. For 4 weeks incubation, vanilic and ferulic concentrations dominated the composition of phenolic acids. At 14-days incubation phenolic acid concentrations decreased and start to increase while approaching 28-days incubation. It is predicted that at 14-day incubation the 1104 µg paraquat addition induced toxicity to soil microbes producing enzyme for phenolic acids biodegradation. In general results of B2 demonstrated fluctuating concentration changes of phenolic acids for the whole incubation period except ferulic acid that tend to decrease. For B2 the highest reduction was ferulic acid, i.e 15.2%.

Results of A3 showed fluctuating concentration changes during 28-days of incubation. On the other hand,B3 showed decreasing concentrations of phenolic acids. The highest reduction was galic acid at 39.1% and the lowest was siringic at5.9%. Ferulic and vanilic acids dominated the phenolic acids composition for the whole incubation period.

Eventhough decreasing concentrations of phenolic acid derivatives was fluctuating, however, the total concentrations decreased. Paraquat treatment for A1, A2 and A3 were each 21.4%, 20.8% and 13.6%, respectively, and for BPMC were 26.5%, 20.3% and 25.8%, consecutively.

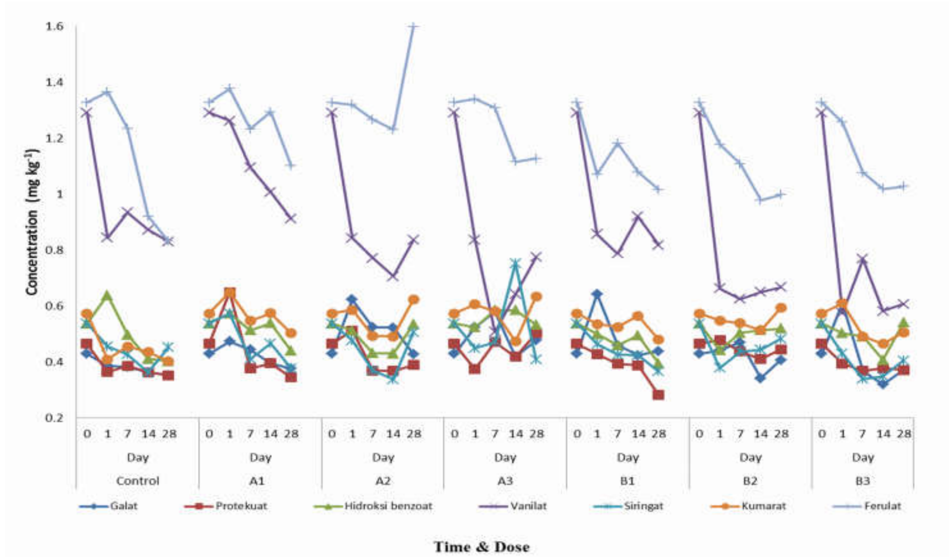

Figure 1: Composition of phenolic acids from various rates of paraquat and BPMC treatments on 1-28 days of incubation period

The decreasing of phenolic acids concentration showed that the interaction between pesticide and phenolic acid occured via covalent bonding, Van der Waals force, ion exchange, hydrogen bonding, ligand exchange, and hydrophobic interaction mechanisms (Khan 1989).According to Bollag (1992) decreasing of phenolic acids concentration might be caused by the coupling reaction between pesticide and phenolic acid. Fluctuation of phenolic acid derivatives might also caused by transformation via C oxidation of the phenolic acid.

Pure phenolic acids

Paraquat treatment on day-1 showed decreasing of phenolic acid concentration in the 19.48–30.55% (Figure 2). The highest reduction occured to ferulic acid and the lowest to protocatechuic acid. On another hand galic acid showed very high concentration rising. Such a significant rise as the result of interfering peak originated from paraquat such that overlapping the peak of galic acid. In that situation galic acid peak appeared within the interfering peak resulting in the reading for galic acids become overestimated. On day-28 coumaric and ferulic acids experienced very high concentration reduction, i.e 75% and 72%, respectively, meanwhile hydroxybenzoic acid showed the lowest reduction.

BPMC treatment on day-1 demonstrated that protocatechuic acid concentration decreased significantly at 62.66% followed by ferulic acid at 36.87%. On day-28 ferulic acid concentration experinced the highest reduction, i.e 75%. Vanilic and siringic concentration increased by 4.27% and 1.78% respectively. Similar to paraquat treatment the presence of interfering peak also happened to BPMC treatment. Splitting of ferulic and coumaric acid peaks happened in paraquat and BPMC treatments on day-14 and 28. It is suspected a new compound has been created as the result phenolic acid and pesticide reation.

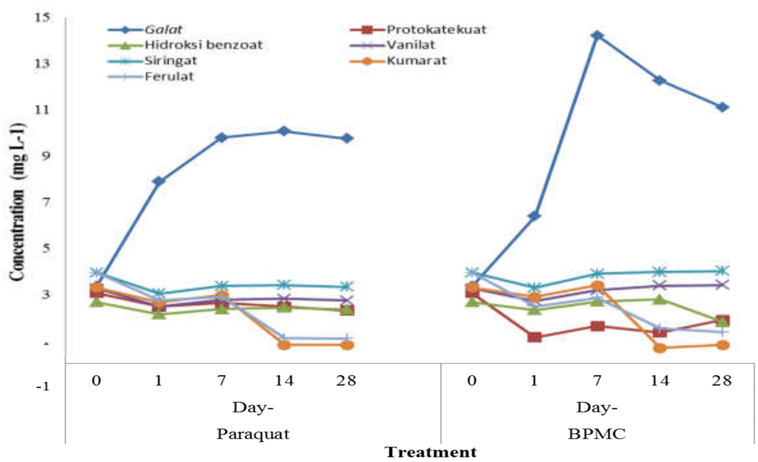

Figure 2: Composition of pure phenolic acids from various rates of paraquat and BPMC treatments on 1-28 days of incubation period

$CO_2$and CH_4 productions

Addition of paraquat and BPMC did not affect the production of $CO_2$and CH_4 (Figure 3). Incubation at day-28 revealed CO_2 emission tend to higher than at day-1, 7, and 14. Soil samples treated at half and twice BPMC dose rates for 28 days of incubation showed the highest CO_2emission. This finding was different from CO_2emisson of soil samples without pesticide addition or paraquat and BPMC additions at all dose rates but at incubation time less than 28 days (day-1, 7 dan 14).

The highest CH_4production occured at day-28 incubation (Figure 4). Compared to others, addition of paraquat at twice dose rate of recommended value and incubated for 28 days demonstrated the highest emission of CH_4. Pesticide addition on peat soils tend to show similar production of CO_2 and CH_4. Although the addition of pesticide showed a similar pattern, however, responded to CO_2 and CH_4 productions seemed lacking. This result contradicted to those of Fitriani (2013) who stated that the adddition of pesticides at recommended dose rates and incubated for 30 days will increase CO_2production. Pesticide addition of peat soil showed a lesser CH_4 prodution compared to control incubated for less than l4 days. Reduction of emission linked to the decreasing mehtanogenic microbes population. Results of study by Cahyaningtyas (2012) showed carbamate insecticide on inceptisol soil enhanced by biochar husk CH_4 emission by 33.2%. Water logged agricultural lands (anaerobic) also produce higher CH_4.

B1 treatment (addition of half BPMC dose) demonstrated higher methane emission compared to control. Such the increasing of CH_4emission compared to control was predicted that at the dose rate application did not induce toxic effects. Kimura *et al*. (1993) reported that beside pesticides, the formation of $CH_4$was strongly inflenced by organic matter, temperature, pH, moisture and Eh of soil.

CONCLUSION

BPMC and paraquat pesticides capable of interacting with phenolic acid via condensation or coupling reactions. As the result of interaction the concentrations of phenolic acids and pesticides in peat soil decerased. The implication of this is the pesticide will have a positive impacts in reducing the negative effects of phenolic acids to plants. Differences in pesticide doses did not show linear correlation to CO_2 and CH_4 productions.

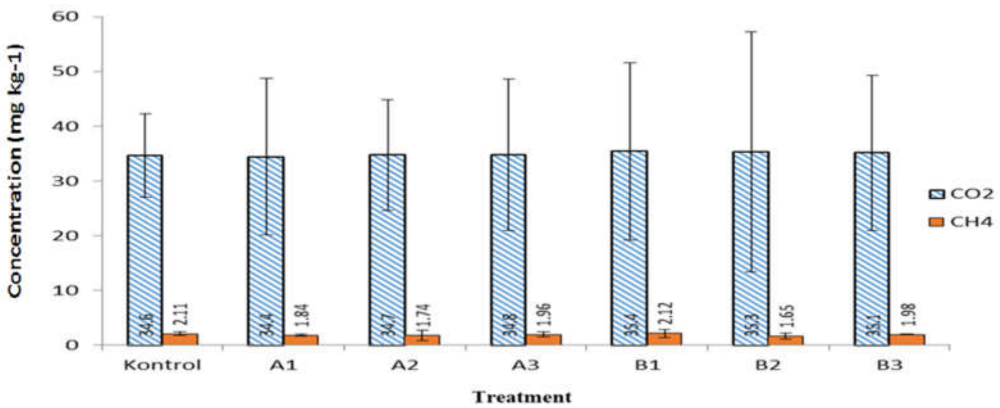

Figure 3: Emission of CO2 and CH4 from various dosages of paraquat and BPMC treatmentson 1-28 days of incubation period

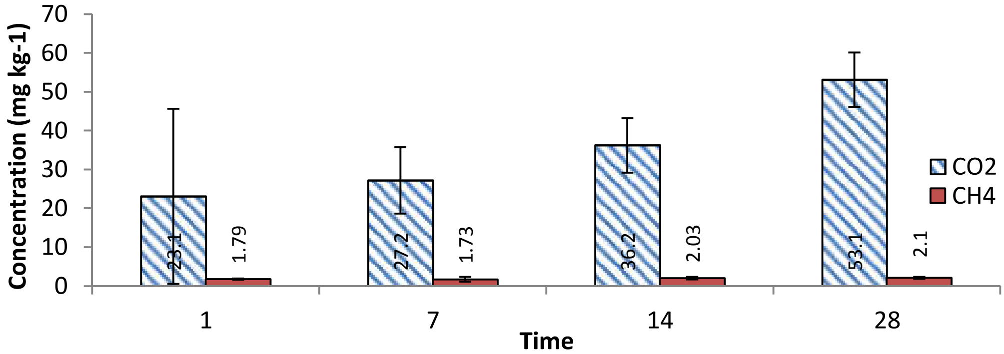

Figure 4: Emission of CO2 and CH4 from various dosages of paraquat and BPMC treatmentson 1-28 days of incubation period

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