

## Characterizing Ionic Species of PM<sub>2.5</sub> Derived from Agricultural Biomass Burning on Paddy Commodity

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**Abstract.** Indonesia is an agrarian country where a majority of the population is consuming rice as a staple food for daily use. However, farmers tend to do open burning of their agricultural biomass waste. This action proved to be an easy, inexpensive, and trustworthy way that can handle the accumulation of the remaining agricultural biomass waste rapidly. Besides, it could be a way of controlling the wild grass and restoring nutrients to the soil in a short period. The agricultural biomass burning practice emitted particulate matter with a size of less than 2,5  $\mu\text{m}$  (PM<sub>2.5</sub>) which causes air pollution. Several studies identified the concentration and contribution of PM<sub>2.5</sub> and black carbon (BC) from this burning activity. However, characterizing ionic species of PM<sub>2.5</sub> derived from agricultural biomass burning on paddy commodities is scarce, especially in Indonesia. In response to this problem, this research aims to characterize the ionic species of PM<sub>2.5</sub> derived from agricultural biomass burning on paddy commodities. This research continues the previous research by conducting ionic characterization from her samples of research. Sampling was performed on the field and the chamber after harvesting time at the smoldering burning phase. Samples were collected using a Minivol sampler with flowrate 5 lpm. The sample filter was analyzed in the laboratory using an ion chromatography (IC) instrument. The results showed that five dominant ions of PM<sub>2.5</sub> are K<sup>+</sup>, Mg<sub>2</sub><sup>+</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and SO<sub>4</sub><sup>2-</sup>. The t-test was performed between field burning samples and chamber burning samples. It elucidated the p-value above 0,05. Hence, the average ionic species concentration and/or contribution of PM<sub>2.5</sub> derived from agricultural biomass burning on paddy commodity at field burning and chamber burning are the same, statistically.

**Keywords:** biomass burning, chamber burning, field burning, ionic species, paddy

### 1. Introduction

Fine particulate matter in the form of PM<sub>2.5</sub> is one of the main pollutants emitted from burning agricultural waste (rice straw) and is considered the main cause of harmful effects on humans [1] and changes in the earth's climate [2]. Characterization of the chemical elements contained in particulates is one of the efforts to identify health hazards for humans and sources of pollution [3]. According to the USEPA, the purpose of speciation is to assess trends in mass component concentrations and associated emissions, including specific sources, and also to assist the interpretation of health studies by relating effects to PM<sub>2.5</sub> constituents [4]. The typical chemical composition for fine aerosol in the lower troposphere is mainly composed of water-soluble inorganic ions, insoluble mineral dust, and carbonaceous material [5]. Water-soluble inorganic ions are the major components of atmospheric

aerosols and can comprise up to a large fraction of particulate matter (PM) [6-9]. Detailed characterizations of ionic species will provide unique information on sources and atmospheric chemistry that will be served as part of the database for region acid rain and atmospheric haze studies [10].

Indonesia is an agrarian country where a majority of the population is consuming rice as a staple food for daily use. However, farmers tend to do open burning of their agricultural biomass waste. This action proved to be an easy, inexpensive, and trustworthy way that can handle the accumulation of the remaining agricultural biomass waste rapidly. Besides, it could be a way of controlling the wild grass and restoring nutrients to the soil in a short period. The agricultural biomass burning practice emitted particulate matter with a size of less than 2,5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ) which causes air pollution. The latest research in Indonesia reported the emission factor of  $\text{PM}_{2.5}$  and BC from agricultural biomass burning in West Java Province. The results showed that the emission factor of  $\text{PM}_{2.5}$  from rice straw biomass burning was 0.55 g/kg and sugarcane biomass burning was 0.49 g/kg [11]. However, the previous study has not yet analyzed the chemical characteristics of  $\text{PM}_{2.5}$  which are closely related to the toxic nature of the particulate. Therefore, this study seeks to continue the previous study by conducting ionic characterization of  $\text{PM}_{2.5}$  from agricultural biomass burning in the paddy community.

Ionic characterization analyzed both cation and anion content which indicates the reactivity of an element/molecule to bond and form a complex compounds/secondary pollutant. The ionic content of  $\text{PM}_{2.5}$  can be developed into a source profile as an input in the local receptor model. Research on the case of burning agricultural residues in China stated that the main cations and anions from burning agricultural biomass residues in China are  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  [12]. Due to the urgency of understanding the ionic species of  $\text{PM}_{2.5}$  derived from agricultural biomass burning in Indonesia, therefore this research is needed.

## 2. Materials and Methods

Samples of this research were obtained from the previous study [11]. Since the previous study analyzed the concentration of  $\text{PM}_{2.5}$  and BC only. Hence, we used the samples and conducted further characterization of ionic species of  $\text{PM}_{2.5}$  derived from agricultural biomass burning of paddy commodity.

### 2.1. Sampling site

A sampling site was located in Cianjur Regency, West Java Province, Indonesia. This location represents a high activity of biomass burning as a post-harvest solution to eradicate unused biomass stockpiles in fields. Besides, West Java Province is well known for its national granary as its rice production contributed up to 15,25% nationally.

### 2.2. Sample collection

Sampling was performed on the field and the chamber after harvesting time at the smoldering burning phase. Samples were collected using a Minivol sampler with flowrate 5 lpm.

### 2.3. Sample preservation

Samples were placed in a 47 mm diameter – Petri dish and stored at a controlled room temperature of 22-23°C and relative humidity (RH) of 41-55%.

### 2.4. Ionic species analysis

A quarter of the filtered sample was put in to test tube with 30 ml of de-ionized water. The test tube was placed in an ultrasonic bath with normal water at 55-60 °C for 120 minutes. The extracted ionic water from the test tube was filtered using Whatman 42 after being cooled down for 24 h at room temperature. This extraction of ionic species was conducted in PT. Ganesha Environmental & Energy Services (PT. GEES) laboratory. Eight major ionic species ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ) were measured by ion chromatography (Metrohm 883 basic IC) with a detection limit for cation

is 0.02 mg/L; anions is 0.04 mg/L at Isotope Application and Radiation Center Laboratory BATAN, Jakarta. The extracted ionic water from a blank filter was used to correct the concentration of ionic species.

### 3. Results and Discussion

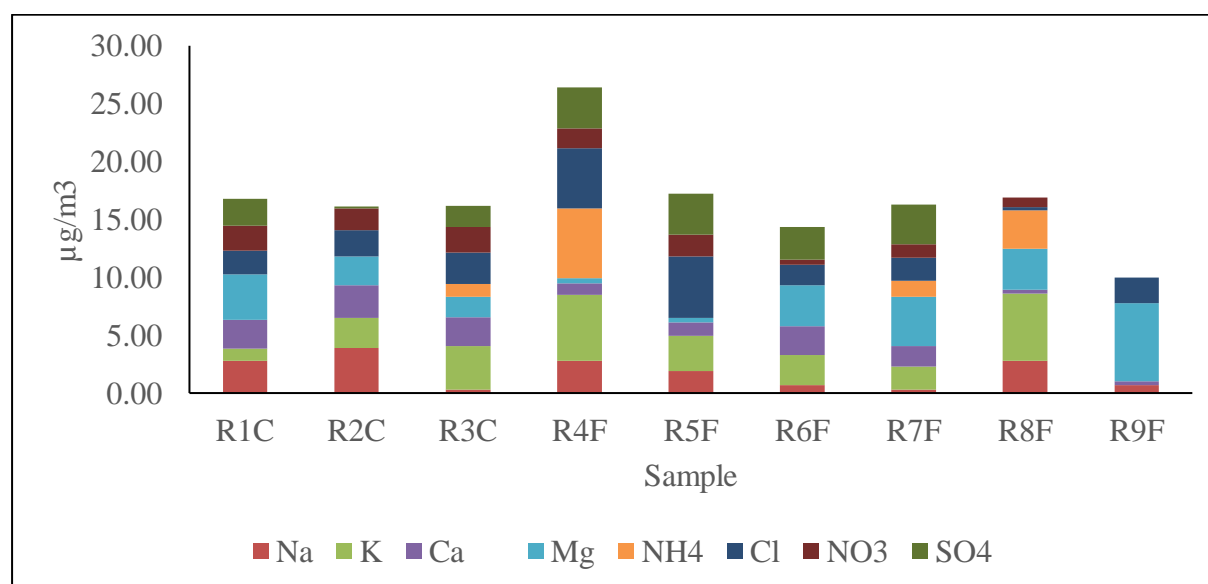
#### 3.1. Ion concentration in $PM_{2.5}$

Ionic concentrations are summarized in Table 1 and total ionic concentrations are in Figure 1. High ionic concentration found in sample R4F>R5F>R1C>R2C>R3C, respectively. The concentrations followed an order of  $Mg^{2+}>Ca^{2+}>K^{+}>Cl^{-}>Na^{+}>NO_3^{-}>SO_4^{2-}>NH_4^{+}$  (2,717  $\mu g/m^3$ , 2,599  $\mu g/m^3$ , 2,480  $\mu g/m^3$ , 2,348  $\mu g/m^3$ , 2,330  $\mu g/m^3$ , 2,077  $\mu g/m^3$ , 1,455  $\mu g/m^3$ , 1,063  $\mu g/m^3$ ) in chamber and  $K^{+}>Mg^{2+}>Cl^{-}>NH_4^{+}>SO_4^{2-}>Na^{+}>Ca^{2+}>NO_3^{-}$  (3,816  $\mu g/m^3$ , 3,153  $\mu g/m^3$ , 2,811  $\mu g/m^3$ , 2,680  $\mu g/m^3$ , 2,212  $\mu g/m^3$ , 1,533  $\mu g/m^3$ , 1,184  $\mu g/m^3$ , 0,985  $\mu g/m^3$ ) in field burning. Higher concentration of  $Mg^{2+}$  may happened due to the influence of agricultural machinery fuel usages.

**Table 1.** Ion concentration in  $PM_{2.5}$

Location	Sample	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Chamber	R1C	2.81	1.06	2.48	3.90	nd	2.03	2.17	2.34
	R2C	3.87	2.63	2.84	2.48	nd	2.26	1.85	0.22
	R3C	0.32	3.75	2.48	1.77	1.06	2.75	2.21	1.80
	Avg±stdv	2.33±1.80	2.48±1.35	2.60±0.20	2.72±1.08	1.06	2.35±0.37	2.08±0.19	1.46±1.10
Field	R4F	2.81	5.67	1.00	0.42	6.03	5.24	1.70	3.56
	R5F	1.90	3.04	1.14	0.42	0.00	5.32	1.85	3.53
	R6F	0.68	2.63	2.48	3.54	nd	1.77	0.43	2.78
	R7F	0.32	1.96	1.77	4.25	1.42	1.99	1.13	3.40
	R8F	2.81	5.78	0.35	3.54	3.28	0.33	0.79	0.00
	R9F	0.68	nd	0.35	6.74	nd	2.21	0.00	0.00
Avg±stdv	1.53±1.12	3.82±1.78	1.18±0.82	3.15±2.42	2.68±2.60	2.81±2.02	0.98±0.72	2.21±1.73	

nd = not detected



**Figure 1.** Accumulation of ion concentration per sample

### 3.2. Ion contribution in PM<sub>2.5</sub>

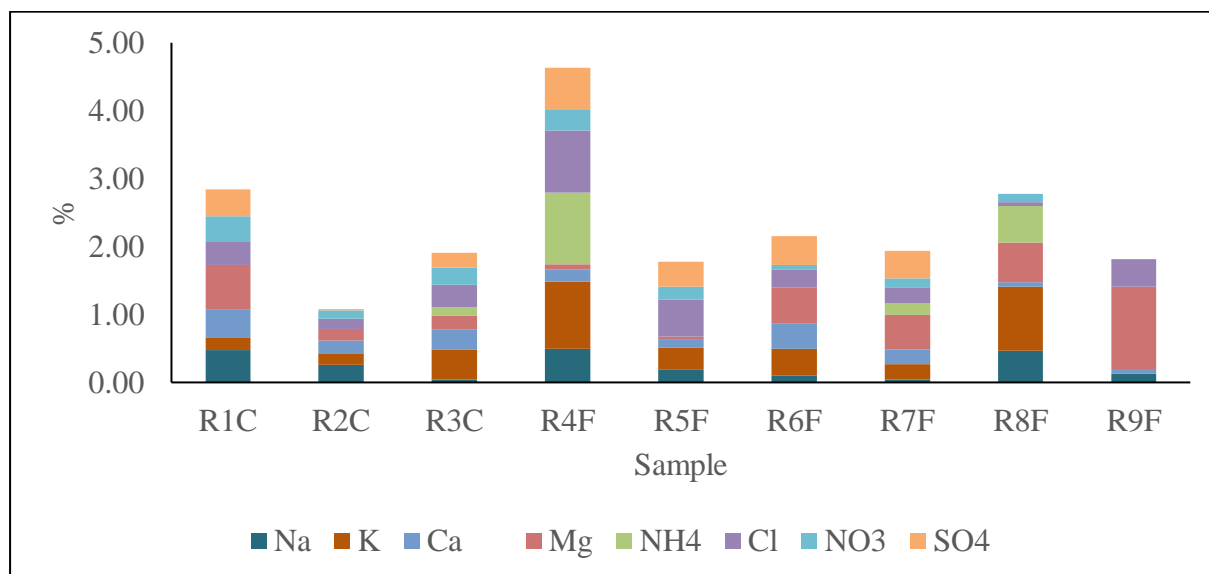
Ionic contributions are summarized in Table 2 and total ionic contributions are in Figure 2. High ionic contribution found in sample R4F>R1C>R8F>R6F>R3C, respectively. The contributions followed an order of Mg<sup>2+</sup>>Ca<sup>2+</sup>>Cl<sup>-</sup>>K<sup>+</sup>>Na<sup>+</sup>>NO<sub>3</sub><sup>-</sup>>SO<sub>4</sub><sup>2-</sup>>NH<sub>4</sub><sup>+</sup> (0,345 %, 0,301 %, 0,273 %, 0,266 %, 0,257 %, 0,251 %, 0,208 %, 0,126 %) in chamber and K<sup>+</sup>>Mg<sup>2+</sup>>NH<sub>4</sub><sup>+</sup>>Cl<sup>-</sup>>SO<sub>4</sub><sup>2-</sup>>Na<sup>+</sup>>Ca<sup>2+</sup>>NO<sub>3</sub><sup>-</sup> (0,577 %, 0,494 %, 0,441 %, 0,404 %, 0,302 %, 0,236 %, 0,167 %, 0,137 %) in field burning.

According to similar research in China, the emission of agricultural biomass burning in paddy contains several ions from the most abundant to the least sequentially: Cl<sup>-</sup>>K<sup>+</sup>>SO<sub>4</sub><sup>2-</sup>>NO<sub>3</sub><sup>-</sup>>NH<sub>4</sub><sup>+</sup>>F<sup>-</sup>>Ca<sup>2+</sup>>Na<sup>+</sup>. These ions play an important role in the formation of haze pollution. The differences in the order of abundance in this study can occur due to fertilization, and herbicides. It also reported that the accumulated contribution of ions reached up to 11% and was considered high due to the low emission factor [12].

**Table 2.** Ion contribution in PM<sub>2.5</sub>

Location	Sample	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Chamber	R1C	0,47	0,18	0,42	0,66	nd	0,34	0,37	0,40
	R2C	0,26	0,18	0,19	0,17	nd	0,15	0,12	0,01
	R3C	0,04	0,44	0,29	0,21	0,13	0,33	0,26	0,21
	Avg±stdv	0.26±0.22	0.27±0.15	0.30±0.12	0.34±0.27	0.13	0.27±0.11	0.25±0.12	0.21±0.19
Field	R4F	2.81	5.67	1.00	0.42	6.03	5.24	1.70	3.56
	R5F	1.90	3.04	1.14	0.42	0.00	5.32	1.85	3.53
	R6F	0.68	2.63	2.48	3.54	nd	1.77	0.43	2.78
	R7F	0.32	1.96	1.77	4.25	1.42	1.99	1.13	3.40
	R8F	2.81	5.78	0.35	3.54	3.28	0.33	0.79	0.00
	R9F	0.68	nd	0.35	6.74	nd	2.21	0.00	0.00
	Avg±stdv	0.24±0.19	0.58±0.37	0.17±0.12	0.49±0.43	0.44±0.47	0.40±0.30	0.14±0.10	0.30±0.25

nd = not detected



**Figure 2.** Accumulation of ion contribution per sample

### 3.3. T-test performance

The results of the statistical analysis between chamber and field burning are summarized in Table 3. The null hypothesis is being accepted. The results can be interpreted as the average ionic species content (concentration and/or contribution) of PM<sub>2.5</sub> derived from agricultural biomass burning on paddy commodity at chamber and field burning are the same, statistically (95% confidence level).

These results are from previous research [13]. However, the differences in emission factors between chamber and field burning may occur due to the influence of water content, meteorological conditions, and combustion characteristics that affect the combustion process and emissions [14]. It also reported that some speciation had a difference in abundance up to more than 10x for the abundance of speciation in chamber combustion compared to field combustion [15].

$\mu_1$ : The average sample concentration and/or contribution at chamber burning

$\mu_2$ : The average sample concentration and/or contribution at field burning

H0:  $\mu_1 - \mu_2 = 0$

H1:  $\mu_1 - \mu_2 \neq 0$

**Table 3.** T-test results

Commodity	Parameter	Burning	N	Avg. Concentration ( $\mu\text{g}/\text{m}^3$ )	Stdev	P-value
Paddy	PM <sub>2.5</sub>	Chamber	3	980,00	470,00	0,42
		Field	6	700,00	168,00	
	Ion	Chamber	3	16,36	0,37	0,84
		Field	6	16,84	5,40	
Commodity	Parameter	Burning	N	Avg. Contribution (%)	Stdev	P-value
Paddy	Ion	Chamber	3	1,94	0,88	0,44
		Field	6	2,51	1,10	

N = number of samples

The results showed the potential of having more efficient sampling practices by determining one burning type only (chamber or field). It can reduce the long step of research and therefore, focus more on other specific interest matters, for example, characterizing other chemical parameters such as volatile organic compound (VOC) and hydrocarbon content. Further observations of other chemical parameters will provide richer source profile data.

#### 4. Conclusion

Ionic composition in PM<sub>2.5</sub> derived from agricultural biomass burning on paddy commodity has been investigated in two different burning types (chamber and field). The concentrations followed an order of  $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+ > \text{Cl}^- > \text{Na}^+ > \text{NO}_3^- > \text{SO}_4^{2-} > \text{NH}_4^+$  in chamber, and  $\text{K}^+ > \text{Mg}^{2+} > \text{Cl}^- > \text{NH}_4^+ > \text{SO}_4^{2-} > \text{Na}^+ > \text{Ca}^{2+} > \text{NO}_3^-$  in-field burning. The contributions followed an order of  $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Cl}^- > \text{K}^+ > \text{Na}^+ > \text{NO}_3^- > \text{SO}_4^{2-} > \text{NH}_4^+$  in chamber, and  $\text{K}^+ > \text{Mg}^{2+} > \text{NH}_4^+ > \text{Cl}^- > \text{SO}_4^{2-} > \text{Na}^+ > \text{Ca}^{2+} > \text{NO}_3^-$  in-field burning. Therefore, the five dominant ions of PM<sub>2.5</sub> are  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ , and  $\text{SO}_4^{2-}$ . The t-test was performed between field burning samples and chamber burning samples. It elucidated that all the p-value were above 0,05. Hence, the average ionic species concentration and/or contribution of PM<sub>2.5</sub> derived from agricultural biomass burning on paddy commodity at field burning and chamber burning are the same, statistically. The higher value of  $\text{Mg}^{2+}$  can indicate the influence of machinery fuel usage. Hence, further research related to the influence of agricultural machinery fuel usage on the PM<sub>2.5</sub> chemical composition in the agricultural sector is needed.

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