

## PRODUCTION AND NEUTRALISATION OF ATMOSPHERIC ACIDITY DURING BIOMASS BURNING

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**ABSTRACT.** Cationic and anionic species present in tropical wood and its ashes were determined using Inductively Coupled Plasma Atomic Emission Spectrometry and Ion Chromatography respectively. The cationic species were found to consist of a mixture of elements with major elements (K, Ca and Mg) dominated the cationic composition, whereas anions included mainly sulphate, chloride, nitrate, carbonate, oxalate, formate and acetate. It has been postulated that the presence of mineral acids such as sulphuric acid and nitric acid might have made a major contribution towards the atmospheric acidity. Oxides of alkali and alkaline earth elements produced during the combustion process of wood might be responsible for the neutralization of the atmospheric acidity near the burning site while far from the burning site the neutralization is uncertain due to its difficulty in assessing the loss of alkaline particles from the plume.

**KEYWORD.** Acidity, alkali elements, anions, atmosphere, forest fire, neutralizing capacity

### INTRODUCTION

Several authors have suggested that biomass burning may have an acidifying effect on rainwater (Lacaux *et al.*, 1992; Sanhueza *et al.*, 1992; Cachier & Ducret, 1991; Crutzen and Andreae, 1990). Previous study on the chemical composition of rainwater in equatorial forests in Congo immediately after the biomass burning showed that hydrogen ion ( $H^+$ ) is the most abundant, indicating the general acidic character encountered in equatorial precipitation (Lacaux *et al.*, 1987). The mean acidity of the precipitation was very high and originated from a mix of mineral acids (such as  $HNO_3$  and  $H_2SO_4$ ) and organic acids (such as formic and acetic acids) (Lacaux *et al.*, 1992). It was reported by Lacuax *et al.* (1992) that nitrate ( $NO_3^-$ ) from biomass burning contributes the highest percentage (87%) to the precipitation acidity in Southern Congo followed by hydrogen ( $H^+$ ) and organic acids (formic and acetic acids) which registered 68% and 30% respectively.

Sanhueza (1991) also had observed high acidity in rain during the biomass burning and concentration of nitrate ( $NO_3^-$ ), ammonium ( $NH_4^+$ ), phosphate ( $PO_4^{3-}$ ) were much larger



during burning compared with during the non-burning period. In addition, higher concentrations of formaldehyde (HCHO), formic acid (HCOOH), and acetic acid (CH<sub>3</sub>COOH) were also observed during burning periods. It was also observed that the concentrations of formic acid were higher than acetic acid. According to Talbot *et al.* (1988), biomass burning emits ten times more acetic acid than formic acid.

However, an investigation by Radojevic & Tan (2000) showed that analysis of rainwater in Brunei Darussalam during severe haze episodes in Borneo in 1994, 1997 and 1998 failed to reveal any significant impact on rainwater acidity or wet deposition of hydrogen ion. The monthly contributions of H<sup>+</sup> deposition during the periods of biomass burning to the annual wet deposition of H<sup>+</sup> varied between 0.0 and 5.35% with pH between 4.63 and 5.91, and these results suggested that forest fire is a minor source of precipitation acidity. Williams *et al.* (1997) have also observed that the biomass burning did not significantly influence the acidity of the rainfall and the finding agrees closely with the earlier findings by Andreae *et al.* (1988b). Ward & Hardy (1991) have explained that, although biomass burning produces many acidifying compounds, for example, SO<sub>2</sub>, NO<sub>2</sub>, and organic acids such as formic acids, it also produces ions such as Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup>, which may act to neutralize the acidity.

Based on the two different conclusions of the previous studies on the role of biomass burning emission to the atmospheric acidity, a preliminary investigation on the anions emission from the biomass burning was carried out with the aim of studying their potential role to the atmospheric acidity. Investigation was also expanded to study the potential of alkaline compounds emitted during the biomass burning to neutralize the production of acidity in the atmosphere.

## METHODOLOGY

### Samples Preparation and Analyses

Samples of tropical hard wood originated from Malaysian tropical rainforest were used for this study. The dry wood chips were ground into a powder. The powdered samples were dried at 85°C for 24 hours. For ash preparation, the weighed wood chips were pyrolysed in an open crucible by heating at 320°C. The residual chars were weighed and put in the crucible and burnt in the furnace at 550°C for 5-8 hours. The ash generated from the combustion was used to determine the cations and anions.

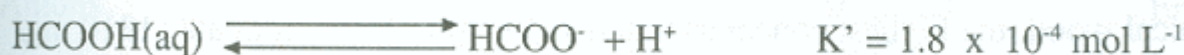
For the determination of major elements (K, Ca, and Mg) in wood and ash samples, samples were homogenized and digested in the Parr Bomb® with concentrated HNO<sub>3</sub> (Merck)

and heated in the oven at 110°C for about 4 hours. After cooling, the sample solutions were filtered, quantitatively transferred into standard flasks and analyzed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Meanwhile for anions [chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), carbonate ( $\text{CO}_3^{2-}$ ), oxalate ( $\text{COO}^{2-}$ ), formate ( $\text{HCOO}^-$ ), and acetate ( $\text{CH}_3\text{COO}^-$ )] determination, wood and ash samples were extracted with Mili-Q water and allowed to equilibrate for 15 hours in the water bath (25°C) under continuous stirring. The solutions were filtered, quantitatively transferred into standard flasks and analyzed using Ion Chromatography (Dionex). Titrimetric technique was used to determine carbonate in both the samples.

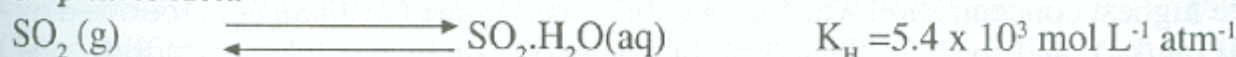
### Determination of $[\text{HCOO}^-]/[\text{HSO}_3^-]$ and $[\text{HCOO}^-]/[\text{SO}_4^{2-}]$ Ratios

The role of organic acid (e.g formic acid) and mineral acid (e.g sulphuric acid) in atmospheric acidification near and far from the source was investigated based on the ratio of organic and mineral acids. The appropriate values of Henry's Law and the equilibrium constants that were used in the determining the ratios are based on values provided by Brimblecombe (1996). The ratios of  $[\text{HCOO}^-]/[\text{HSO}_3^-]$  were calculated to determine the main contributor to the atmospheric acidity. At a greater distance from the burning site, it was assumed that complete oxidation of sulphur dioxide to sulphuric acid have occurred and, therefore, the ratios of  $[\text{HCOO}^-]/[\text{SO}_4^{2-}]$  were used to determine the main contribution of the atmospheric acidity away from the burning site using the following reactions for determination of their ratios.

#### Formic Acid



#### Sulphuric Acid





## RESULTS AND DISCUSSION

### Elements in Tropical Wood and Ash

Among the three major elements, K (143.80 g/kg) was found to have the highest concentration in the tropical wood followed by Ca (5.13 g/kg) and Mg (0.4 g/kg). Whereas in wood ash, the highest concentration was found to be of Ca (2.67 g/kg) followed by K (2.48 g/kg) and Mg (0.18 g/kg). Based on these results, the amount of elements that were lost into the atmosphere during the biomass burning can be estimated and the results are shown in Table 1. It is also noted that 50 to 98% of the metallic elements were lost into atmosphere during the combustion process.

**Table 1. Concentrations of some metals in tropical wood and ash samples and their estimated loss during biomass burning**

Elements (g/kg)	Wood (g/kg)	Ash	Estimated (g/kg)	Loss [%]
Potassium (K)	143.80	2.48	141.32	[98]
Calcium (Ca)	5.13	2.57	2.56	[50]
Magnesium (Mg)	0.41	0.18	0.23	[56]

### Anions in Tropical Wood and Ash

In tropical wood, the highest concentration was found to be of sulphate (1310 mg/kg) followed by chloride (70 mg/kg), acetate (60 mg/kg), formate (30 mg/kg), and nitrate (20 mg/kg). Carbonate and oxalate were not detected in the wood sample. Whereas in ash samples, the highest concentration was found to be of carbonate (2190 mg/kg) followed by formate (10 mg/kg), and oxalate (2 mg/kg). Other anions such as sulphate, chloride, and nitrate were found to be less than 1 mg/kg. However, acetate was not detected in the ash. Based on the concentration values in wood and ash, the loss of anions during the biomass burning were calculated and the results are shown in Table 2.

During biomass burning, the emission of sulphate into the atmosphere was found to be in high concentration as compared with other anions. In terms of percentage loss, all the anions were lost into the atmosphere by more than 75% except carbonate and oxalate. The loss of these anions could be through association with the ash particles or/and volatilization. Previous studies have also found the high concentrations of these anions along with some sulphate and chloride in particulate matter during biomass burning in tropical rainforest (Andreae *et al.*, 1988a). Silva *et al.* (1999).

**Table 2. Concentrations of anions in tropical wood and ash samples and their estimated loss during biomass burning**

Anions (mg/kg)	Wood (mg/kg)	Ash (g/kg) [%]	Estimated	Loss
Sulphate ( $\text{SO}_4^{2-}$ )	1310	<1	>1309	[>99]
Chloride ( $\text{Cl}^-$ )	70	<1	>69	[>99]
Acetate ( $\text{CH}_3\text{COO}^-$ )	60	ND	>59	[>99]
Nitrate ( $\text{NO}_3^-$ )	10	<1	>9	[>99]
Formate ( $\text{HCOO}^-$ )	20	5	>1.5	[>75]
Oxalate ( $\text{COO}^{2-}$ )	ND	2190	*	
Carbonate ( $\text{CO}_3^{2-}$ )	ND	2	*	

\* Anion is higher in ash than in wood

Based on the average biomass of dense tropical rainforest of about 412 MT/ha or  $4.12 \times 10^5$  kg/ha estimated by Fearnside (1991), the amount of anions emitted in the tropical forest fire has been estimated. As shown in Table 3, the highest emission of anion was sulphate (543 kg/ha) which accounted for about 89%, while other anions were emitted in relatively small amounts. The importance of the bulk release of these anions into the atmosphere has always been associated with rainfall acidification as previously reported elsewhere (Lacaux *et al.*, 1992; Sanhueza *et al.*, 1992; Cachier and Ducret, 1991; Crutzen and Andreae, 1990; Talbot *et al.*, 1988).

**Table 3. Estimated emission of anions into the atmosphere during the tropical forest fire**

Anions	Estimated (kg/ha)	Emission [%]
Sulphate ( $\text{SO}_4^{2-}$ )	543	[89]
Chloride ( $\text{Cl}^-$ )	28	[5]
Acetate ( $\text{CH}_3\text{COO}^-$ )	26	[4]
Nitrate ( $\text{NO}_3^-$ )	8	[1]
Formate ( $\text{HCOO}^-$ )	7	[1]
Oxalate ( $\text{COO}^{2-}$ )	*	
Carbonate ( $\text{CO}_3^{2-}$ )	*	

\*Higher concentration in ash than in wood



## Acidity and Neutralising Capacity from Biomass Burning

The acidity contributions of sulphate, nitrate, chloride as well as the organic acids which are characterized by formate and acetate were estimated based on the values of anion concentrations that were lost during biomass burning with the exclusion of other sources in the form of organic compound (e.g organic sulphur) as shown in Table 4. It was further assumed that there was no contribution from any other source.

**Table 4. Organic and mineral acids contributions (Mean-Weighted Concentration, MWC) to the atmospheric acidity**

Acids	MWC ( $\mu\text{eq/kg}$ )	% Acidity
<b><u>Organic Acids</u></b>		
Acetic acid	1	3
Formic acid	0.4	1
		} 4
<b><u>Mineral Acids</u></b>		
Sulphuric acid	28	88
Hydrochloric acid	2	7
Nitric acid	0.3	1
		} 96
Total	31.7	

Mineral acids and organic acids from the emission of biomass burning of tropical wood have contributed to the atmospheric acidity of about 96 and 4% respectively. The estimate of acidity contributions in the atmosphere during biomass burning is comparable to the estimate of the anion contributions to precipitation acidity in tropical forest of Congo by Lacaux *et al.* (1992) in which the mineral acids (sulphuric and nitric acids) and the organic acids (formic and acetic acids) contributed about 64% and 36% respectively. However, the opposite results were found in other tropical regions, for example, in Amazonian and Australia, where the organic acids contributed 65-85% to the precipitation acidity (Andreae *et al.*, 1990; Andreae *et al.*, 1988b).

In investigating the role of organic and mineral acids in contributing to the atmospheric acidity at near and away from the burning site, the ratios of  $[\text{HCOO}^-]/[\text{HSO}_3^-]$  and  $[\text{HCOO}^-]/[\text{SO}_4^{2-}]$  were determined at various pH as shown in Table 5. Based on the ratios, it is suggested that atmospheric acidity at near and away from the burning site is mostly

contributed by mineral acid (sulphuric acid). Brimblecombe (1996) suggested that organic acid such as formic acid could contribute to the acidity near the sources due to its high solubility and dissociation constant, which could make it more effective at acidifying water droplets than sulphur dioxide. However, in this study, formic acid could only make a minor contribution to atmospheric acidity near the burning site mostly due to its small amount being emitted in comparison with sulphur dioxide during biomass burning. In contrast, further away from the burning site, sulphuric acid which is more soluble could contribute to the atmospheric acidity because sulphur dioxide takes a long time to oxidize.

**Table 5. Ratios of  $[\text{HCOO}^-]/[\text{HSO}_3^-]$  and  $[\text{HCOO}^-]/[\text{SO}_4^{2-}]$  near and far away from the burning site at various pH conditions.**

pH	Near $[\text{HCOO}^-]/[\text{HSO}_3^-]$	Far away $[\text{HCOO}^-]/[\text{SO}_4^{2-}]$
3.0	0.094	0.0003
3.5	0.090	0.0010
4.0	0.080	0.0028
4.5	0.062	0.0062
5.0	0.039	0.0103
5.5	0.025	0.0130

The contributions from mineral and organic acids will raise the  $\text{H}^+$  concentration, but at the same time the presence of alkalinity in the particulate matter in the atmosphere will reduce the  $\text{H}^+$  concentration (William *et al.*, 1997). In order to determine whether the atmospheric condition is more acidic or alkaline during the biomass burning period, the balance of the sum of cations and that of anions were calculated. The alkalinity was assumed to be associated with  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . These elements were observed to constitute the major elements emitted into the atmosphere during the biomass burning. The mass-weighted concentrations (MWC) for these cations are shown in Table 6.

**Table 6. Mass-weighted concentration (MWC) of cations emitted during tropical biomass burning**

Solutes	MWC ( $\mu\text{eq/kg}$ )	%
$\text{K}^+$	3623	96
$\text{Ca}^{2+}$	128	3
$\text{Mg}^{2+}$	19	1



Based on the estimates (Table 4 and Table 6), it was found that there was an excess of cation relative to anion. The MWC ion deficit [DEF = " cations - " anions] showed that there is an anion deficit of 3738  $\mu\text{eq/kg}$  of wood. The alkali elements could present mainly in the form of oxides, hydroxides, and carbonates. The result has shown a significant imbalance between the ionic concentrations in the atmosphere. Therefore, it is postulated that the emission of alkali compounds during biomass burning could potentially neutralize all the production of atmospheric acidity particularly near the burning site. The excess of alkaline compounds emitted during biomass burning could also suggest that atmospheric conditions near the source are alkaline. Further away from the source the alkaline condition in the atmosphere would decrease due to various chemical and physical processes such as neutralization, dilution and sedimentation. Simultaneously, despite decreasing contributions of formic acid and sulphur dioxide to the atmospheric acidity (i.e. because of dispersion), the oxidation of sulphur dioxide to sulphuric acid tends to have an opposite effect. This leads to the suggestion that the atmospheric condition far from the source could be acidic (i.e. loss of alkaline elements and production of sulphuric acid). However, this finding is still inconclusive, as the degree of transport of alkaline particles over great distances is still largely uncertain.

## CONCLUSION

Mineral acids, mainly sulphuric acid was found to be the major contributor to the atmospheric acidity during the biomass burning. Preliminary investigations have also found that mineral acids are responsible to the atmospheric acidity near and far from the burning site. This was due to the larger amount of sulphur dioxide emitted from the tropical biomass burning. However, based on the balance of mass-weighted concentration between the sum of anions and cations that were lost during wood burning, it has been observed that there were enormous excess of cations. This result could suggest that the emission of alkaline compound during the biomass burning has the potential to neutralize the atmospheric acidity. Therefore, the atmospheric condition particularly near the burning site was postulated to be more alkaline. Away from the burning site, the neutralizing capacity of the alkaline particles could be less effective; however, this is inconclusive as the contribution of the alkaline particles to the atmospheric alkalinity is still uncertain.



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