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## Evaluation of Ammonia, Greenhouse Gas Emissions and Characterization of Different Particulate Matter During Sugarcane Production in Southern Louisiana

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EVALUATION OF AMMONIA, GREENHOUSE GAS EMISSIONS AND  
CHARACTERIZATION OF DIFFERENT PARTICULATE MATTER DURING  
SUGARCANE PRODUCTION IN SOUTHERN LOUISIANA

A Dissertation

Submitted to the Graduate Faculty of the  
Louisiana State University and  
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requirements for the degree of  
Doctorate of Philosophy

in

The School of Plant, Environmental and Soil Sciences

by

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## Abstract

Application of N fertilizers and special land management practices during agricultural production could have significant implication in influencing the air quality. In this study, field experiments were established at different research sites in Louisiana to evaluate the emission of ammonia ( $\text{NH}_3$ ), greenhouse gases (GHG), and fine particulates from sugarcane cultivation and harvesting. Specifically, this study was planned to (i) evaluate the effect of different N sources (urea and urea ammonium nitrate) and residue management schemes (residue burned, RB; and residue retained, RR) on  $\text{NH}_3$  and GHG emissions, (ii) characterize the chemical and morphological characteristics of fine particles generated during sugarcane harvesting operations (regular harvesting, RH; ground burn, GB; standing burn, SB; and combine harvesting, CH), and (iii) evaluate the micrometeorological study of  $\text{NH}_3$  flux above sugarcane crop canopy. Ammonia ( $\text{NH}_3$ ) and greenhouse gas samples were collected through active and passive chamber methods, respectively, following N application in the field. Then those  $\text{NH}_3$  and GHG samples were analyzed using ion chromatography (IC) and gas chromatography, respectively. Organic/elemental carbon, water soluble species, elemental species, and morphological features were determined using thermal carbon analyzer, ion chromatography, inductively-coupled plasma-optical emission spectroscopy, and scanning electron microscopy, respectively. Volatile organic carbon and polycyclic aromatic hydrocarbons were analyzed using gas chromatography-mass spectroscopy. Bi-directional  $\text{NH}_3$  emission was obtained from two installed denuders (at 10 ft and 18 ft) equipped with meteorological tower in the sugarcane field and the captured  $\text{NH}_3$  was analyzed in IC. Field experiments showed that urea treatment produced almost 2.8 times and 1.6 times higher  $\text{NH}_3$  and  $\text{N}_2\text{O}$ , respectively, as compared to UAN plots. However, N had little effect on  $\text{CH}_4$  and  $\text{N}_2\text{O}$  emissions. Overall, majority of total  $\text{NH}_3$  and  $\text{N}_2\text{O}$  emission was observed

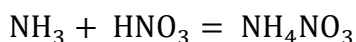
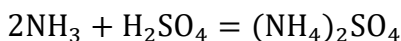
within 3-4 weeks after N application in the field. On the other hand, residue retained treatment resulted significantly higher  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_4$  emissions as compared to RB treatments over the years. Ammonia and  $\text{N}_2\text{O}$  emissions were highly correlated with water filled pore space (%), but higher correlation was found in 2012 due to higher rainfall received within 3 weeks of N application. Particulates released during different sugarcane harvesting operations showed that carbonaceous compounds contributed about 30-70% of the total particle mass. Ammonia was the major cation found in the burning particulates (GB and SB) and showed high correlation with  $\text{SO}_4^{2-}$  ions. Overall, organic carbon, major ionic species, elemental species were significantly higher in GB particles than SB particles. Low molecular weight polycyclic aromatic hydrocarbons were mainly released during sugarcane residue burning operations. Molar ratio of standing burn smoke samples was found lower than ground burn samples over four years. Ammonia emission above sugarcane crop canopy was highly dependable on different meteorological parameters such as temperature, rainfall, and wind speed. Major  $\text{NH}_3$  emission peaks were found during heavy rainfall days combined with favorable temperature. Higher rainfall increased anaerobic soil conditions and thus released more  $\text{NH}_3$  from soil surface. Daytime  $\text{NH}_3$  emission was significantly higher than nighttime emission because of higher temperature during day which helps in  $\text{NH}_3$  volatilization both from soil and crop surface. Higher wind speed created turbulence in atmospheric boundary layer and thus helped more  $\text{NH}_3$  emissions. Overall, these results are useful in managing sugarcane production while minimizing  $\text{NH}_3$ , GHG and particle matter emissions.

## **Chapter 1. Introduction**

### **1.1 Background**

Greenhouse gases adsorb and emit thermal infrared radiation and thus gradually increase the atmospheric air temperature. Different GHGs present in the ambient air are carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), ozone ( $\text{O}_3$ ), water vapor ( $\text{H}_2\text{O}$ ) and others (hydrofluorocarbon, per fluorocarbon, and sulfur hexafluoride). In general,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  are considered as the major GHGs and their emission from agricultural field is a major concern nowadays. Emissions of GHGs from agricultural sectors are mainly influenced by different cropping system, tillage management, nutrient sources and fertilizer treatments (GGWG, 2010). Inputs of nitrogen to agricultural soils occurred from commercial N fertilizer applications, organic manures, biological nitrogen fixation and green manures of crop residues (Eichner, 1990). Carbon dioxide has the shortest atmospheric life and occupies almost 84% of the total GHGs emissions (IPCC, 2011). Methane is a long lived GHG with a global warming potential (GWP) of 21 and mainly released from agriculture through animal production, manure management, and rice cultivation (GGWG, 2010; Johnson et al., 2007). Nitrous oxide is a potent GHG and has GWP of 310. Agricultural soil management activities were estimated to cause around 68% of the total  $\text{N}_2\text{O}$  emissions in US during 2010 (USEPA, 2012) and the most influencing factor is nitrogenous fertilizer application (Yamulki and Jarvis, 2002; Dalal et al., 2003). Carbon dioxide concentration has increased from 350 ppm during 1990 (Wood, 1990) to 370 ppm in 2004 (Keeling and Whorf, 2005) and expected to reach 750 ppm by the end of 21<sup>st</sup> century (IPCC, 2007a; Sachs, and Ladd, 2010).

Ammonia is colorless with highly pungent odor, lighter than air and easily volatilized from soil surface. It plays a vital role in neutralizing atmospheric acids generated by oxides of S and N, and in typical climatic conditions it produce secondary particles after reacting with SO<sub>2</sub> and NO<sub>x</sub>. Those fine secondary particles are considered as harmful fine particles and are responsible for different respiratory problems in human beings.



Particulate matter (PM) is mixture of solid particles and liquid droplets suspended in the air which originate from a variety of sources, such as power plants, industrial processes, and agricultural operations. The concentration of NH<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and water vapor largely influence the composition of aerosols in any particular area (Cadle et al., 1982; Lee et al., 1993; Baek and Aneja, 2004). Most often, importance is given to organic particulates, but it is well documented that inorganic compounds such as Cu and Fe could cause oxidative stress of human health (Baulig et al., 2004; Limbach et al., 2005). Small airborne particles have a high probability of deposition in the respiratory tract and thus increase human mortality and morbidity (Hughes et al., 1998; Morawska et al., 1998). It is also reported that inhalation of PM<sub>10</sub> can cause pathological diseases in the deeper respiratory tract region of human beings (Berico et al., 1997). High concentration of PM<sub>10</sub> is a concern because PM<sub>10</sub> is small enough to be inhaled and with prolonged exposure can cause decreased lung function, cardiac arrhythmia and heart attacks (Madden et al., 2009). Another major health concern is from the fact that most of the toxic trace metals like lead, zinc, copper etc. in the air are in the form of fine particles with size distribution equivalent to that of aerosols with 1.0 um or less in diameter (Fang et al., 1999).

Primarily the residues of sugarcane, rice, wheat, cotton, lentils, corn, and soybean are burned in US (McCarty, 2009) and it has been reported that on an average, 32% of the sugarcane crop area was burned during 2010 (USEPA, 2012). Biomass burning of sugarcane is one of the major agronomic practices for Louisiana and it accounts for a major part of air quality issues. It is one of the most significant sources of gaseous and particulate matter emissions into the troposphere. Biomass is mainly composed of carbon (~45% by weight), hydrogen, oxygen and small amounts of nitrogen, sulfur, phosphorus and potassium (Andreae, 1991) and during the burning of biomasses, CO<sub>2</sub> and water vapor are generally produced (Levine, 1996). Burning also releases the greenhouse gases like CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O. Beyond that, biomass burning also producer of chemically active gases such as sulphur dioxide, nitric oxide, carbon monoxide and volatile organic compounds (Koppmann et al., 2005). It has been reported that agricultural residue burning contributes approximately 9.5% of total global biomass burning emissions and roughly around 9% of total CO<sub>2</sub> released from global biomass burning (Andreae and Merlet, 2001; McCarty, 2009). Burning of sugarcane is practiced in Louisiana to reduce the cost of processing. The burning practice of sugarcane residues varies widely throughout the World. Pre-harvest burning is very common in Brazil, Mexico, and Costa Rica but in US and Philippines sugarcane trashes are burned either before or after harvest (Franca et al., 2012). At sugarcane harvesting time, from May to November, the crops (mainly the leaves) are burnt in order to make the process of harvesting easier and also, to increase the sugarcane content by weight (Santos et al., 2002). A common pre-harvest practice of sugarcane is to burn off the leaves, dry cane tops, and ground trash aiding in the stalk harvest by minimizing unwanted biomass in the field (Clements, 1980). Studies show that the concentrations of fine particles in the atmosphere increase significantly in the season of foliage burning. This current research

project was planned to evaluate the emission of different greenhouse gases ( $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{CO}_2$ ),  $\text{NH}_3$ , and fine particulates from sugarcane cultivation in Louisiana.

## **1.2 Sugarcane production in Louisiana**

Sugarcane (*Saccharum officinarum*) is a tall perennial crop belongs to the Poaceae (grass) family and is generally grown in tropical and subtropical climatic conditions. It is one of the most important row crops grown in Louisiana and have been a major part of the Louisiana agricultural economy for more than 200 years (USDA-NRCS, 2012). Sugarcane is commercially grown in Louisiana, Florida, Texas and Hawaii in the US and with 23 sugarcane growing parishes, Louisiana contributes around 20% of the total sugar production in the United States (Salassi et al., 2009). Around 390 thousands acreages of sugarcane was harvested in Louisiana during 2009 (Salassi et al., 2009) and its acreage is expected to increase. In Louisiana, sugarcane is usually planted using whole stalks (4 to 8 nodal buds) or billets (2 to 4 buds) and the planting is done during August for better yield as compared to the planting during September and October (Viator et al., 2005). Sugarcane yield in Louisiana has been increased significantly in recent years after introduction of new varieties with higher yield potential and higher pest resistance (Legendre et al., 2001). Typically, seven sugarcane varieties are used in Louisiana (HoCP 96-540, L 99-226, HoCP 00-950, L 01- 283, L 01-299, L 03-371, and HoCP 04-838) and HoCP 04-838 performed better in terms of cane yield followed by variety L 03-371 (Sugarcane Production Handbook, 2014).

Sugarcane produces huge biomass and needs an intense fertilizer application and special land management practices (Yadav et al., 2009). The worldwide nitrogen (N) application rate for sugarcane varies from 45 to 300 kg ha<sup>-1</sup> (Srivastava and Suarez, 1992). Typically, in Louisiana,

N is applied at the rate of 120-140 and 140-160 lb acre<sup>-1</sup> for light and heavy soil, respectively, in stubble sugarcane crops (Sugarcane Production Handbook, 2014) and mainly in the form of urea, urea ammonium nitrate (UAN), and ammonium nitrate. Special land management such as residue burning is an important agricultural operation often practiced in Louisiana. Left over sugarcane residues drastically reduce the yield of subsequent sugarcane crop and thus Louisiana farmers are more interested in burning the residues in the field. Burning of the residues can be done before harvesting (standing burn) or after harvesting of sugarcane (ground burn). These fertilizers and residue burning operations during sugarcane cultivation can produce significant amount of ammonia (NH<sub>3</sub>) and different greenhouse gases (GHGs) which adversely affect air quality (Ernst and Massey, 1960; Venterea et al., 2005; Blanco-Conqui and Lal, 2008; Davidson, 2009; Serrano-Silva et al., 2011).

### **1.3 Greenhouse gases and their importance**

According to Wien's displacement law, the peak wavelength of solar radiation is in visible range i.e. nearly 500 nm while for earth it is in thermal infrared range i.e. 11000 nm (Mohanakumar, 2008). Because of the increasing concentration of GHGs the balance between the amount of solar energy received and the amount of thermal infrared red energy emitted by the earth surface is getting highly affected (Ramanathan, 1988). Additionally, due to uneven temperature rising of the earth surface, there is a possibility of change in air circulation pattern and subsequent impacts on rainfall, crop production, and other meteorological parameters in different areas (Ramanathan, 1988). Nitrous oxide is considered as the most potent GHG with global warming potential (GWP) of 296 as compared to CH<sub>4</sub> (GWP 23) for 100 year time frame (IPCC, 2001; Snyder et al., 2009). Intergovernmental Panel on Climate Change (IPCC) and United Nation Framework Convention on Climate Change (UNFCCC) are the two major

international organizations which documented the most scientific and efficient way of calculating GHGs emissions from different sectors.

According to Carbon Dioxide Information Analysis Center (CDIAC), in 2008, China was the largest emitter of carbon di oxide followed by USA which included fossil fuel burning, cement production, and gas flaring (Boden et al., 2011). According to IPCC report (2007) based on 2004 total greenhouse gas emission, carbon dioxide, methane, nitrous oxide, and fluorinated gas contributed 77%, 14%, 8%, and 1 %, respectively. This report also stated that energy production through burning coal, natural oil, and gas produced maximum GHG i.e. 26% which is followed by industry with 19% contribution. Agriculture contributed 9% of the total GHG emission in the US during 2013 (USEPA, 2015).

#### **1.4 Factors influencing greenhouse gas emissions**

Soil temperature, N content in organic matter, land use change, source of nutrient (manures or fertilizers), tillage, residue incorporation in soil, soil compaction can influence GHG emission by favoring soil microbial population responsible for GHG emissions (Mosquera et al., 2007; Snyder et al., 2009). It was reported that the amount of CO<sub>2</sub> emission from the respiration of heterotrophic soil microbes and plant roots increases exponentially with increasing temperature (Smith et al., 2003). However, Xia et al. (2009) found that warm day temperature had no effect on soil respiration while, warm night had significant effect on it. Also, higher diurnal temperature variation has positive relation with soil respiration and CO<sub>2</sub> flux (Smith et al., 2003). Recently it was reported that N sources did not produce any significant impact on CO<sub>2</sub> emission (Tian et al, 2015). Watling (1998) found that summer tilled sandy loam soil produced approximately 8 times higher CO<sub>2</sub> as compared to no tilled soil (So et al., 1999). Similarly,



Thornton (1998) found that tilled soil produced higher ( $34.5 \text{ gm m}^{-2}$ )  $\text{CO}_2$  than untilled soil ( $20 \text{ gm m}^{-2}$ ).

Nitrous oxide emission from soil is highly influenced by N application (Maljanen et al., 2003; Zhang and Han, 2008; Tian et al., 2015), soil temperature (Horvath et al., 2006; Zhang and Han, 2008), soil moisture content (Ma et al., 2010) and other meteorological parameters such as air temperature, rainfall etc. According to Ball et al. (1999), heavy soil compaction increased nitrous oxide emission as compared to light and zero compaction plots and the increment was higher under wet soil condition in winter barley in Scotland. It was also reported that least compacted soil produced less  $\text{N}_2\text{O}$  and  $\text{CH}_4$  irrespective of tillage status of soil (Yamulki and Jarvis, 2002). Decaying of plants materials facilitated by termites can also produces methane (Martius et al., 1996; Fearnside, 2000). According to Lubbers et al. (2013), the presence of earth worm in soil increases the greenhouse gas emission. When soil moisture is not limiting factor and sufficient to support microbial activity (volumetric soil moisture content  $>20\%$ ), temperature is the limiting factor for soil respiration and GHG emission (Smith et al., 2003). Under dry warm condition soil respiration is low due to lack of available moisture (Smith et al., 2003). Under saturated or water logged soil condition, emission of GHGs like nitrous oxide and methane are predominant. Higher  $\text{N}_2\text{O}$  emission was found under zero tilled condition than conventional tillage (Burford et al., 1981; Linn and Doran, 1984; MacKenzie et al., 1997). This is because of the lack of macro pore space and gas diffusion in no tilled soil than conventional tilled soil (O,Sullivan and Ball, 1993; Breland and Hansen, 1996; Ball et al. 1997 a,b; Ball et al. 1997 a). Another study in eastern Canada showed that under humid condition the  $\text{N}_2\text{O}$  emission was highest from conventional tillage than no tillage and vice versa (Helgason et al., 2005; Malhi et al., 2006). According to some studies incorporation of some N rich residues like leguminous

crops (Aulakh et al., 1991; Baggs et al., 2000; Huang et al., 2004) increase nitrous oxide emission. Type of crops can also affect amount of nitrous oxide from soil. Kaiser et al. (1998) found that nitrous oxide emission from winter wheat was lower than sugar beet. Additionally, removal of plant residue is helpful in reducing N<sub>2</sub>O emission rather than incorporating in soil (Hao et al., 2001; Malhi et al., 2006).

Wetlands are one contributor of total global methane production (IPCC, 2007; Bhullar et al., 2013). Rice cultivation also contributes methane production from agriculture sector (Schütz et al., 1989a; Nouchi et al., 1990; Khalil et al., 1998). Methane flux in rice cultivation is influenced by soil temperature, water level, sky cover, and wind speed. Higher soil temperature leads to higher methane emission (Seiler et al., 1984; Schütz et al., 1990; Sass et al., 1991; Parashar et al., 1993; Khalil et al., 1998). As a result, cloud cover decreases the methane flux by reducing the incoming solar radiation (Khalil et al., 1998). Wind speed has a positive relationship with methane emission from rice field (Khalil et al., 1998). Intermittent flooding reduced methane emission over continuous flooding (Khalil et al., 1998; Jain et al. 2000).

### **1.5 Emissions from agricultural production**

In 2004, globally agriculture produced 14% GHG (International Panel for Climate Change, 2007). Agriculture produced 9% of total GHG in USA in 2013 which is 17% higher than the amount produced in 1990 (USEPA, 2015). According to Reynolds (2013), global agriculture GHG emission was 4.7 billion ton of carbon dioxide equivalent which increased 13% over 1990. Also among all the sectors for GHG production, agriculture serves as third highest. In 2010, among different agriculture sources, enteric fermentation produced highest GHG 40% followed by manure in the pasture, chemical fertilizer, biomass burning, rice cultivation, and

manure management, respectively (Tubiello et al., 2013). In 2008, N<sub>2</sub>O emission was 4% of total US GHG emission (Bracmort, 2010). Though its magnitude of emission is less, it has very high global warming potential and can also destroy ozone layer. It also has a long life time in atmosphere i.e. approximately 114 years. Among total US N<sub>2</sub>O production, agriculture contributes 75% (USEPA, 2011; Cavigelli et al., 2012). Because of the introduction of high yielding varieties and exhaustive application of synthetic fertilizers, the atmospheric concentration of N<sub>2</sub>O is continuously increasing 0.6–0.9 parts per billion per year (Cavigelli et al., 2012). The life time of methane in atmosphere is 10 years (Smith et al., 2003). In 2013, methane emission was 10% of total GHG emission in the US (USEPA, 2015). Total 46% methane was produced by agriculture system (26 % from enteric fermentation or normal digestion by cattle and 10% from manure) (USEPA, 2015). It also can be produced by water logged condition, natural water body, leakage from natural gas system etc.

## **1.6 Mitigation strategies of GHG emissions**

Agricultural soil acts as a carbon (C) sink and can store C for few years (labile C pools) to several hundred years (recalcitrant C pools) (Monreal et al., 1997a; Munoz et al., 2010). Conservation tillage and residue retention improve soil carbon content and helps in C sequestration (Sá et al., 1999; Bayer et al., 2006). Additionally, no tillage reduces CO<sub>2</sub> emissions from fossil fuel burning. It was also found that no tillage over moldboard ploughing could save 20 kg C ha<sup>-1</sup>yr<sup>-1</sup> by reducing fossil fuel combustion (Johnson et al., 2007). According to USEPA, the land use, land use change, and forestry in USA improve the carbon sequestration by 16% as compared to 1990 and act as net carbon sink. Carbon sequestration can be increased by preserving forest area and preventing its conversion for settlement purposes, Converting crop land into forest land, preventing land degradation (e.g. soil erosion). Different measures like

optimum N application, use of nitrification inhibitor (prevent conversion of ammonium to nitrate), prevent soil compaction or water stagnation can reduce N<sub>2</sub>O emission from soil (Saggar et al., 2009). Tilled or aerated soil produced lower N<sub>2</sub>O than no tilled soil (Ball et al., 2008; Bhatia et al., 2010). Drainage in high rainfall areas reduces water stagnation, enhance aeration and thus reduce CH<sub>4</sub> and N<sub>2</sub>O emission (Monteny et al., 2006). Studies showed that nitrification inhibitor reduces N<sub>2</sub>O emission by preventing nitrate production which is the substrate for denitrification (Weiske et al., 2001; Zerulla et al., 2001; Majumdar et al., 2002; Cui et al., 2011; Liu et al., 2013). Similarly nitrification inhibitor can also be applied on manures (e.g. cattle slurry, urine) to reduce N<sub>2</sub>O emission (Zaman et al., 2009; Di and Cameron, 2012; Moir et al., 2012).

### **1.7 Particulate matter emission from agricultural production**

Particulates are ubiquitous and agricultural contributions in the formation of fine particles are an important area of research. Particulates can either be primary (directly emitted from the source) or secondary (formed during chemical reaction) depending on their origin. Different agricultural operations such as fertilizer application and land management practices can largely influence the emission of particulates in the air. Different field operations like biomass burning, land preparation, planting, and harvesting during sugarcane production contributes respirable soil and plant particles into the atmosphere. These particles contain carbonaceous compounds (Hall et al., 2012; Rajput et al., 2014; Paraskevopoulou et al., 2014), water soluble ionic species (Turn et al., 1997; Kim Oanh et al., 2011), and heavy metals (Li et al., 2007) and can cause human health issues when deposited deeper in the respiratory track. An intensive chemical and physical characterization is necessary in order to understand the chemistry of these airborne particles. Depending on the origin, airborne particulates can be classified as primary and secondary

particles. Primary particles directly released to the atmosphere from different sources like industry, traffic, agriculture etc and secondary particles generally formed within the atmosphere by chemical reactions like ammonium nitrate, ammonium sulfate etc (Chung et al., 2008; Giere and Querol, 2010).  $PM_{2.5}$  and  $PM_{10}$  can be also be classified (Pilinis and Seinfeld, 1987; Chow et al., 1998; Chong et al., 2002) by their chemical composition like: (1) Metal oxides (Al, Si, Ca, Ti, Fe, and other metal oxides), (2) Sulfates and nitrates (ammonium sulfate, ammonium bisulfate, and ammonium nitrate), (3) Polycyclic aromatic hydrocarbons (volatile organic compounds, acetaldehyde, formaldehyde, nitro-PAHs, oxygenated PAHs, and PAH diones), (4) Sodium chloride, (5) Sodium nitrate, and (6) Particulate organic carbon. Individual particles have different chemical composition and morphological characteristics; and their characterization will help to provide us the information on their source, atmospheric history and reaction mechanism (Chung et al., 2008).

## **1.8 General objective**

The objective of this study is to evaluate the different air quality issues from sugarcane production in southern Louisiana. Ammonia, greenhouse gases and particulate matter are the key factors for air quality concerns. Application of N fertilizers and residue management has significant impacts on emissions of ammonia and greenhouse gases throughout the growth of sugarcane and a systematic study is necessary to better understand the science of these gas emissions from the field. Also close inspection on the release pattern and chemistry of respirable particulate matter which generates during sugarcane harvesting and biomass burning is essential.

## 1.9 Specific objectives

The specific objectives of this study are:

- to evaluate the effect of N fertilization and residue management practices on NH<sub>3</sub> volatilization loss in Louisiana
- to quantify greenhouse gas emissions influenced by N fertilization and residue management practices from subtropical sugarcane production
- to characterize the elemental composition and morphological features of particulates emitted from sugarcane production
- to evaluate the micrometeorological study of diurnal NH<sub>3</sub> flux and the concentration of PM<sub>2.5</sub> from sugarcane production in Louisiana.

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## **Chapter 2. Effect of Nitrogen Fertilization and Residue Management Practices on Ammonia Emissions from Subtropical Sugarcane Production**

### **2.1 Introduction**

Gaseous ammonia ( $\text{NH}_3$ ) emission following N fertilization is one of the major pathways of nitrogen (N) loss from a soil profile which leads to the reduction in N use efficiency by plants. It plays an important role in atmospheric chemistry by neutralizing precipitation and aerosol formation (Anderson et al., 2003; Behera et al., 2013). Ammonia itself is not considered a major air pollutant according to the Clean Air Act (CAA), but it acts as an active precursor of  $\text{PM}_{2.5}$  formation in the air and a secondary source for nitrous oxide ( $\text{N}_2\text{O}$ ) emissions when present in the soil. Under typical atmospheric conditions,  $\text{NH}_3$  reacts with gaseous sulfur dioxide ( $\text{SO}_2$ ) and oxides of nitrogen ( $\text{NO}_x$ ) to form secondary fine and ultrafine particles like ammonium sulfate  $[(\text{NH}_4)_2\text{SO}_4]$  and ammonium nitrate  $[\text{NH}_4\text{NO}_3]$ , which are highly responsible for different human health issues, especially respiratory problems (Seinfeld and Pandis, 1998; Anderson et al., 2003). It has been reported that ammonium sulfates contribute more than 40% of the total  $\text{PM}_{2.5}$  of the southeastern part of the United States (USEPA, 2014). In addition, sulfate and nitrate aerosols can influence global radiation budget by acting as cloud condensation nuclei (CCN) and scattering incoming solar radiation (Bauer et al., 2007; Myhre et al., 2009; Behera et al., 2013).

Major sources of  $\text{NH}_3$  emission include livestock production, fertilizer application; human and animal waste, biomass burning, and soil biogenic processes (Bouwman et al., 1997; Wu et al., 2008). Agricultural application of synthetic fertilizers can contribute about 12 to 16% of the total global atmospheric  $\text{NH}_3$  emissions (Pain et al., 1998; Stephen and Aneja, 2008). Although there have been emission factors (EFs) of  $\text{NH}_3$  from agricultural uses of N fertilizers in the past, many current available EFs did not consider specific agricultural production systems and contained various inaccuracies (Goebes et al., 2003). The magnitude of  $\text{NH}_3$  emissions from

N fertilizers is influenced by various factors including type and quantity of fertilizers used, timing and techniques of fertilizer application, soil moisture content as well as other soil & meteorological conditions. The majority of  $\text{NH}_3$  emissions from agricultural fields usually occur within a few days of fertilizer application (Ruijter et al., 2010; Turner et al., 2012; Tian et al., 2015). However, the accurate measurement of atmospheric  $\text{NH}_3$  concentration is often very difficult because  $\text{NH}_3$  is a sticky gas and can easily be adsorbed by almost all surfaces (Anderson et al., 2003; Behera et al., 2013). In addition, under particular inorganic aerosol system (such as ammonium-sulfate-nitrate-water), nitrate and sulfate compete for available  $\text{NH}_3$ . At sulfate concentration of  $> 9 \mu\text{g m}^{-3}$ , ammonium-nitrate aerosol concentration was found to be near zero (West et al., 1999). Therefore, understanding  $\text{NH}_3$  emission from different agricultural production systems is very important for assessing the impact of management practices on potential air quality in that region.

Sugarcane is one of the major row crops grown in many parts of the world. In the mainland U.S., sugarcane production is concentrated in Louisiana, Florida, and Texas. Sugarcane produces large biomass and requires significant amounts of nutrients especially N and K and special land management practices (Fageria et al., 1997; Franca et al., 2012). Solid urea has traditionally been used for agricultural crop production but application of liquid urea ammonium nitrate (UAN) is increasingly becoming popular especially in southern USA for sugarcane production in recent years. This change in N fertilizer source likely has different effects on  $\text{NH}_3$  loss dynamics and subsequently the air quality.

Field management of sugarcane residues also varies widely across the globe. For instance, in Australia, sugarcane harvest residues (trash) are generally kept as such in the field to conserve soil moisture needed for better ratoon production (Wood, 1991; Fageria et al., 1997), whereas,

in-situ biomass burning of the sugarcane residues is a common practice in Brazil and major parts of the U.S. (Franca et al., 2012). Two open-field burnings of sugarcane residues are often carried out in U.S. sugarcane production, before-harvest burning of standing cane and after-harvest ground burning of combine residue. The former is to eliminate leafy trash for easy combining (cutting) and sugar milling processing, whereas the latter is to prevent the yield loss of subsequent ratoon crops if the residue is not removed (Viator et al., 2008, 2009a,b, Udeigwe et al., 2010). The latter is especially true in subtropical sugarcane production, such as in Louisiana, due to negative soil water-temperature relations of relatively cold and wet winter, production of allelochemicals, and high populations of overwintering sugarcane borers and sugarcane beetles (Richard, 2001; Kennedy and Arceneaux, 2006; Viator et al., 2008). Although sweeping residue after combine harvesting has recently been suggested as an alternative solution to this issue, the limited harvest time window in a wet winter, especially for the late-harvested plant cane and first stubble cane crops, makes such an option difficult to be realized (Viator et al., 2009b). An approximate 38% of the sugarcane crop area was burned during 2013 in the US (USEPA, 2015). While various studies have investigated impacts of residue retention on runoff water quality (Southwick et al., 2001; Viator et al., 2009a; Udeigwe et al., 2010), there has been very little information concerning the effect of these sugarcane residue management practices on ammonia emission from soil, an important factor that has both N efficiency and air quality implications. Few studies have focused on other crops under different climate regions (Hutchings et al., 2001; Hyde et al., 2003; Zhang et al., 2011; Gong et al., 2013; Bosch-Serra et al., 2014; Yang et al., 2015). Therefore, the goal of this study was to evaluate the emission losses of ammoniacal N from sugarcane production as impacted by two common N fertilizer sources (urea and UAN) and two

residue management practices (residue retained, RR and residue burn, RB) in the subtropical region of southern U.S.A.

## **2.2 Materials and methods**

### **2.2.1 Site location and characteristics**

The field experiments were carried out at the Louisiana State University AgCenter St. Gabriel research station (USA, 30°15'13"N 91°6'5"W) in 2012 and 2013. First year and second year stubble sugarcane (*Saccharum officinarum*) was used as the planting material for 2012 and 2013, respectively. The soil of the experimental site was a commerce silt loam (Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts). Surface soil samples (15 cm depth) from the site were taken before the field experiment and analyzed for particle size distribution, cation exchange capacity (CEC), pH, electrical conductivity (EC), total N, total C and different nutrients (P, K, Ca, Mg, and S). Physical and chemical characteristics of the background soil of the field experiment are presented in Table 2.1. Soil and air temperature were measured using portable thermometer probe.

Additional soil samples were also collected throughout the seasons in both 2012 and 2013 to determine water filled pore space (WFPS) during each NH<sub>3</sub> collection. Composite soil samples were taken (n = 8) from each treatment plots using stainless soil probes and kept it in the plastic bags. Those plastic bags are then weighed using a microbalance in a humidity-temperature controlled room and recorded as initial soil weight (W<sub>I</sub>) in gm. Those soil samples were then oven dried at 105°C for 24 hours and final soil weight was noted (W<sub>F</sub>) in gm. The difference in soil weight (W<sub>I</sub>-W<sub>F</sub>) after drying indicates the weight of the total moisture content (gm) in the soil and eventually soil moisture content (%Φ<sub>m</sub>) was calculated. The volumetric water content

( $\Phi_v$ ) was then calculated as  $\% \Phi_m \times BD$  (bulk density of the soil). Finally, the WFPS percentage was calculated using the formula:

$$\Psi = (\Phi_v/TP) \times 100;$$

Where  $\Psi$  is the WFPS (%),  $\Phi_v$  is the volumetric water content (%) and TP is the total porosity (%) of the soil. Percentage TP was calculated as  $TP = (1 - BD/PD) \times 100$ ; where BD, and PD are the bulk density and particle density of the soil.

Table 2.1. Selected soil physical and chemical properties of the experimental field

Parameters	Avg. values
pH (1:1)	$6.1 \pm 0.5$
<sup>§</sup> CEC (meq/100 gm)	$15.1 \pm 2.9$
<sup>¶</sup> Sand (%)	22
<sup>¶</sup> Silt (%)	62
<sup>¶</sup> Clay (%)	16
<sup>‡</sup> C (%)	$0.9134 \pm 0.087$
<sup>‡</sup> N (%)	$0.0878 \pm 0.923$
<sup>ψ</sup> P (mg kg <sup>-1</sup> )	$28.7 \pm 4.8$
<sup>ψ</sup> K (mg kg <sup>-1</sup> )	$105.1 \pm 15.5$
<sup>ψ</sup> Ca (mg kg <sup>-1</sup> )	$2006.2 \pm 252$
<sup>ψ</sup> Mg (mg kg <sup>-1</sup> )	$415.3 \pm 41.8$
<sup>ψ</sup> S (mg kg <sup>-1</sup> )	$44.9 \pm 6.8$

<sup>§</sup>Cation exchange capacity (CEC) was analyzed using ammonium acetate replacement method

<sup>¶</sup>Particle size distribution (sand, silt and clay) was done using pipette method

<sup>‡</sup>Carbon and N was analyzed in Carbon-nitrogen analyzer

<sup>ψ</sup>Elemental analysis was done using Mehlich-3 extraction followed by ICP analysis

### **2.2.2 Fertilizer treatments and residue managements**

Field experiments consisting of 6 treatments (one control, two N sources, and two residue management approaches;  $3 \times 2 = 6$ ) were established in 2012. For two N fertilizer source treatments, it was applied at the rate of  $135 \text{ kg N ha}^{-1}$  in the form of granular urea (45.9% N) and liquid urea ammonium nitrate (UAN; 31.9% N). The control plots (no N was added) were used to obtain the background  $\text{NH}_3$  concentration. Urea was surface broadcasted followed with soil cover and UAN was injected directly into the soil through applicator and worked into the shoulders of the rows. Two different types of residue management schemes including the residue burned (RB) treatment (harvested sugarcane trash was burned in the field) and the residue retained (RR) treatment (residue from the previous sugarcane harvest was left as such on the soil surface) were implemented. In 2013, separate field experiments were conducted to evaluate the effects of fertilizers and residue management separately on  $\text{NH}_3$  volatilization. Experiments of N fertilizer source comparisons were conducted in the more commonly RB residue management plots, whereas residue management approaches were compared in the more popular UAN fertilized plots. In both cases, N fertilizer was applied at a rate of  $157 \text{ kg N ha}^{-1}$  due to the second stubble of the ratoon crop. In both years, randomized complete block design (RCBD) was used for the evaluation. Fertilizers were applied on May 22 in 2012 and on May 20 in 2013, respectively. All field experiments were conducted in sugarcane plots of 3 rows (5.5 m) wide by 15.2 m long each and replicated 4 times.

### **2.2.3 Ammonia collection and analysis**

Ammonia was collected using an active chamber method with continuous flushing of the  $\text{NH}_3$ -free pure outside air into the closed chamber systems installed in the experimental fields. It has been shown by various studies that active chamber methods are much more efficient on

measuring  $\text{NH}_3$  emission as compared to the passive chambers (Marshall and Debell, 1980; Ruess and McNaughton, 1988; Frank and Zhang, 1997; Harper, 2005; Hou et al., 2007; Das et al., 2008). In addition, flushing or air circulation can also be used to collect enough  $\text{NH}_3$  volatilization in a very short period of time by creating sufficient air turbulence inside the chambers (Marshall and Debell, 1980; Harper, 2005). In this study, stainless steel top ( $0.3 \times 0.3 \times 0.26 \text{ m}^3$ ) and bottom chambers ( $0.3 \times 0.3 \times 0.2 \text{ m}^3$ ) were used to collect  $\text{NH}_3$  emitted from the soil (Fig. 2.1). Inner walls of the chambers were coated with polytetrafluoroethylene (PTFE) sheets to prevent  $\text{NH}_3$  from reacting with the stainless steel because  $\text{NH}_3$  is very reactive and could react with measurement equipment (Roelle and Aneja, 2002; Das et al., 2008). The bottom chambers were placed 10 cm deep in the soil of the sugarcane rows and were kept undisturbed for the whole sampling season. During each sampling event, the top chambers were connected with the bottom chambers using clamps and the whole chamber system in the field was covered with reflective insulation sheets, which prevent the metal chamber from heating due to direct sun light. Ethylene propylene diene monomer (EPDM) rubber weather strips were placed on top of both the chambers for close sealing when clamped during sampling. The outside air was drawn in a dilute citric acid (4%) trap through teflon tubing to eliminate the  $\text{NH}_3$  in the air before flowing into the closed chamber. The  $\text{NH}_3$ -free air then flushed the chamber gas into the second citric acid trap for collecting volatilized  $\text{NH}_3$ . The flushing and collection system was powered by an air sampling pump (LaMotte company, Maryland) and operated at a flow rate of 1.5 litres per minute (LPM) for 90 minutes.

The first  $\text{NH}_3$  sample was taken 2 hours after fertilizer application followed by every alternate day for first three weeks and then once a week for two and half months in 2012 and for about 4 months in 2013.

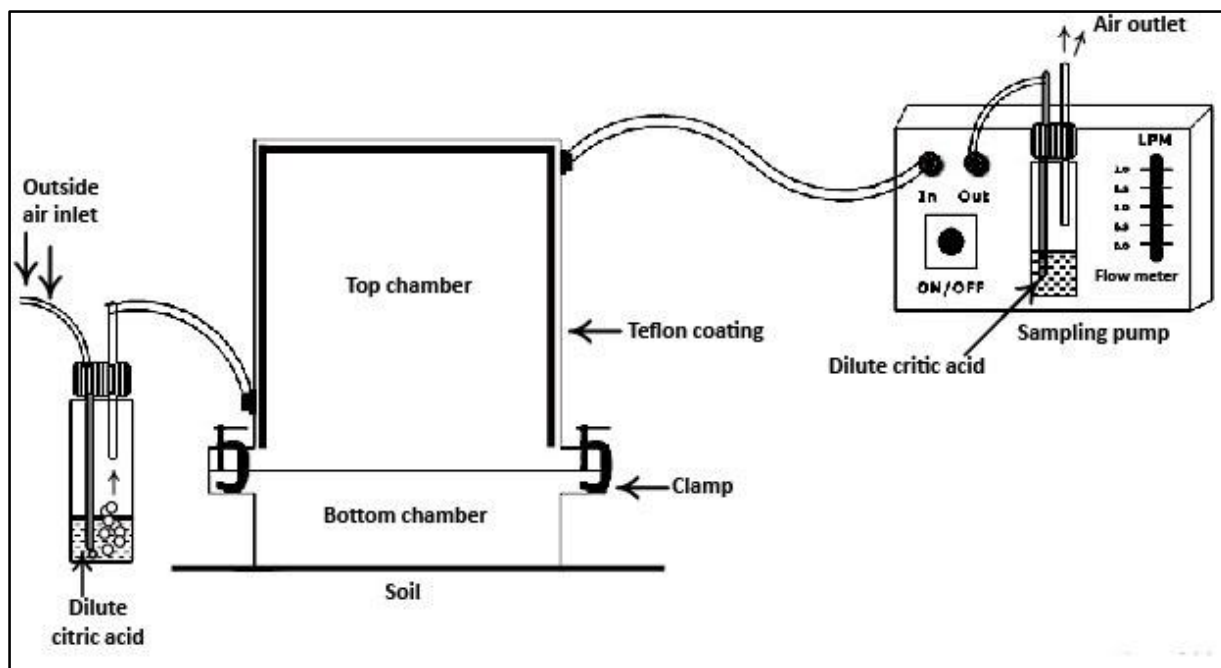


Fig 2.1. Schematic diagram of an active chamber system used for ammonia collection

One  $\text{NH}_3$  sampling was missed from residue plot (at 11 DAN) due to some technical problems in 2013. All  $\text{NH}_3$  samples collected in dilute citric acid were analyzed using ion chromatography (Dionex, ICS-2000). Soil and air temperatures were taken by portable soil temperature probe with every  $\text{NH}_3$  sampling. Composite surface soil samples were also collected and analyzed for soil moisture content. Rainfall data were obtained for the experiment sites from the LSU AgCenter weather station website for St Gabriel research station.

## 2.2.4 Emission factor (EF) analysis

The emission factor (EF) of  $\text{NH}_3\text{-N}$  for the entire sugarcane growing season was analyzed using the following formula:

$$\text{EF (\%)} = \frac{\sum(\text{NH}_3 - \text{N})_{\text{fertilizer}} - (\text{NH}_3 - \text{N})_{\text{control}}}{\text{Applied available N source}} \times 100$$



Where  $\text{NH}_3\text{-N}_{\text{fertilizer}}$  and  $\text{NH}_3\text{-N}_{\text{control}}$  are the total  $\text{NH}_3\text{-N}$  emissions from the fertilized field and from the control plot, respectively. Applied available N source is the amount of N applied in the field ( $\text{kg ha}^{-1}$ ).

### **2.2.5 Statistical analysis**

Statistical analyses were done using SAS 9.3 (SAS Institute. 2012, Cary, NC) for analysis of variance (ANOVA) with PROC MIXED and mean separation was done by Tukey-Kramer method at a  $P < 0.05$  level.

## **2.3. Results and discussion**

### **2.3.1 Soil and environmental parameters**

High soil and air temperatures occurred throughout the whole sampling season. Average soil and air temperature was very similar for both the years (Fig. 2.2 and 2.4). Year 2013 received twice the number of rainfall days as compared to 2012. But half of the rainfall was received within 3 weeks of fertilization in 2012, whereas, 75% of the rainfall was received after 3 weeks of fertilizer application in 2013. Bulk density of the RR treatment plots was found to be 6.5% lower than the RB plots which indicated that residue retention improved soil structure by adding organic matter to the soil (Blanco-Canqui et al., 2009; Kornecki and Fouss, 2011). Average soil moisture content, as expressed as WFPS of RR plots, was 5-6% higher as compared to that of RB plots in 2012 and 2013, respectively.

### **2.3.2 Ammonia volatilization from 2012 field experiment**

Ammonia volatilization as impacted by different fertilizer applications and residue management treatments is presented in Fig 2.2.

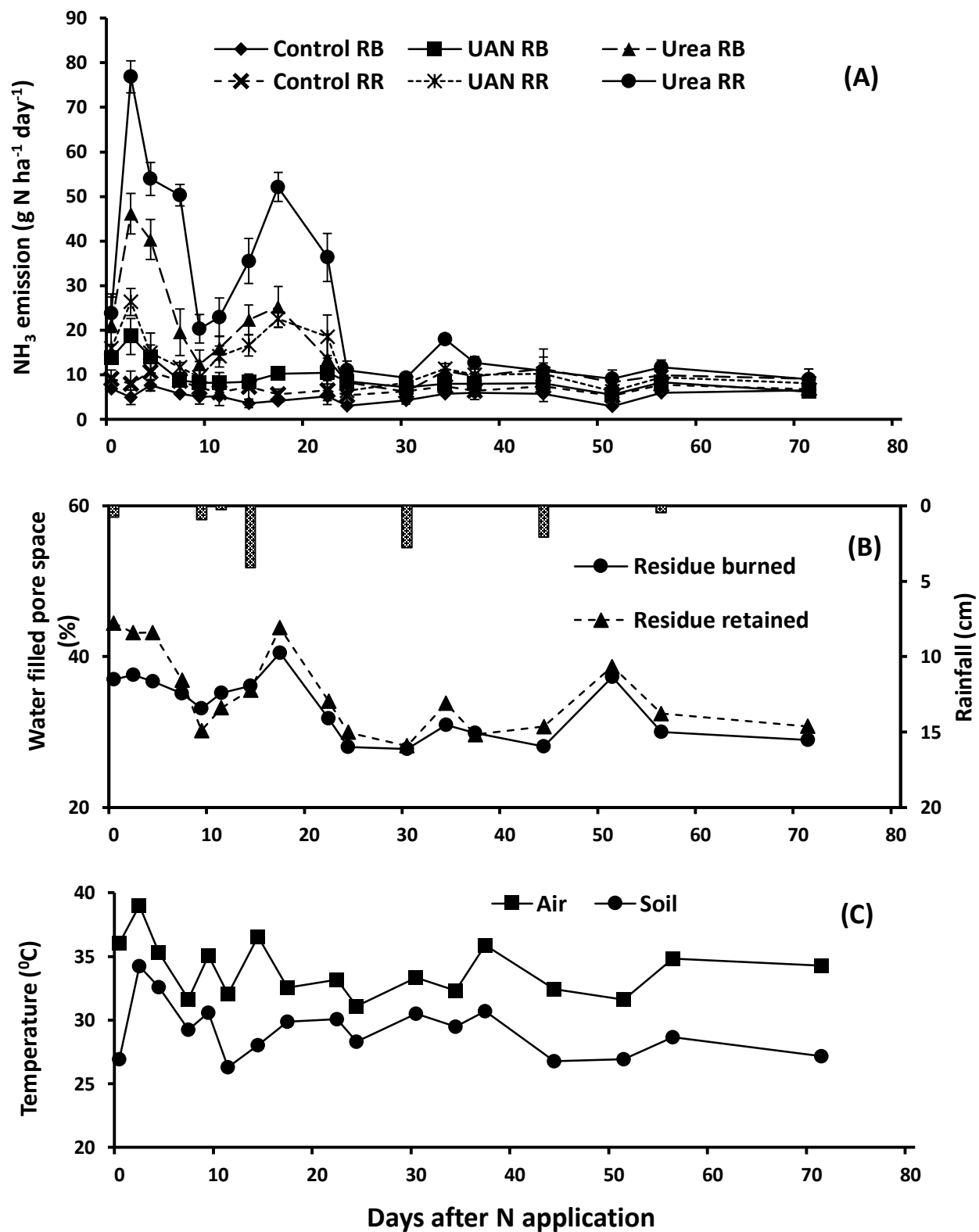


Fig 2.2. 2012 field observations following N applications: (A) daily  $\text{NH}_3\text{-N}$  losses, (B) rainfall and water filled pore space, and (C) air and soil temperatures.

Ammonia samples were collected till 71 DAN from all field plots due to Hurricane Isaac in 2012 which caused significant lodging of sugarcane plants. Nonetheless, major portion of  $\text{NH}_3$  emission was captured before the hurricane occurred. Significant  $\text{NH}_3\text{-N}$  loss began a day after fertilizers were applied with sharp emission peaks at 2 and 17 DAN, which corresponded to higher soil moisture levels after rainfall events (Fig. 2.2B) and higher soil and air temperatures (Fig. 2.2C). The majority of the volatilization losses were found within 3 weeks after N application. This was especially true for urea treated plots in both RB and RR management schemes, accounting for 67-69% of the total seasonal cumulative  $\text{NH}_3\text{-N}$  losses from the field. After 3 weeks, the  $\text{NH}_3$  emission decreased significantly. Several studies also found significant loss of  $\text{NH}_3$  within the first 3 weeks following N fertilizer application for paddy rice and cereal crops (Hou et al., 2007; Ruijter et al., 2010; Turner et al., 2012). On the other hand, the general decline in  $\text{NH}_3$  emission with time could be due to lower availability of ammonia caused by nitrification and  $\text{NH}_4^+$  fixation in clay lattices as well as by decreased soil pH (Black et al., 1985; Sommer and Jensen, 1994).

Different N sources had considerable impacts in  $\text{NH}_3$  emission from the sugarcane field. Urea-treated plots showed significantly higher  $\text{NH}_3\text{-N}$  emission ( $P < 0.05$ ) than UAN and the control irrespective of the residue management treatments within the first 30 days of N application (Fig.2.2A). As cumulatively for the season, urea plots produced about an average of 2.1 times higher  $\text{NH}_3\text{-N}$  emissions than UAN plots over the sample collection period ( $8.1 \text{ kg N ha}^{-1} \text{ season}^{-1}$  vs.  $3.8 \text{ kg N ha}^{-1} \text{ season}^{-1}$ ) (Fig. 2.3). Other studies also reported 1.5-2.4 times higher emissions from urea application than from UAN fertilization for pasture wheat and barley (Vaio et al., 2008; Turner et al. 2012). The UAN plots had generally higher cumulative  $\text{NH}_3$  emissions

than the control plots but the difference was not statistically significant, indicating the relative advantage of using UAN to minimize  $\text{NH}_3$  volatilization by N fertilizer application in sugarcane production.

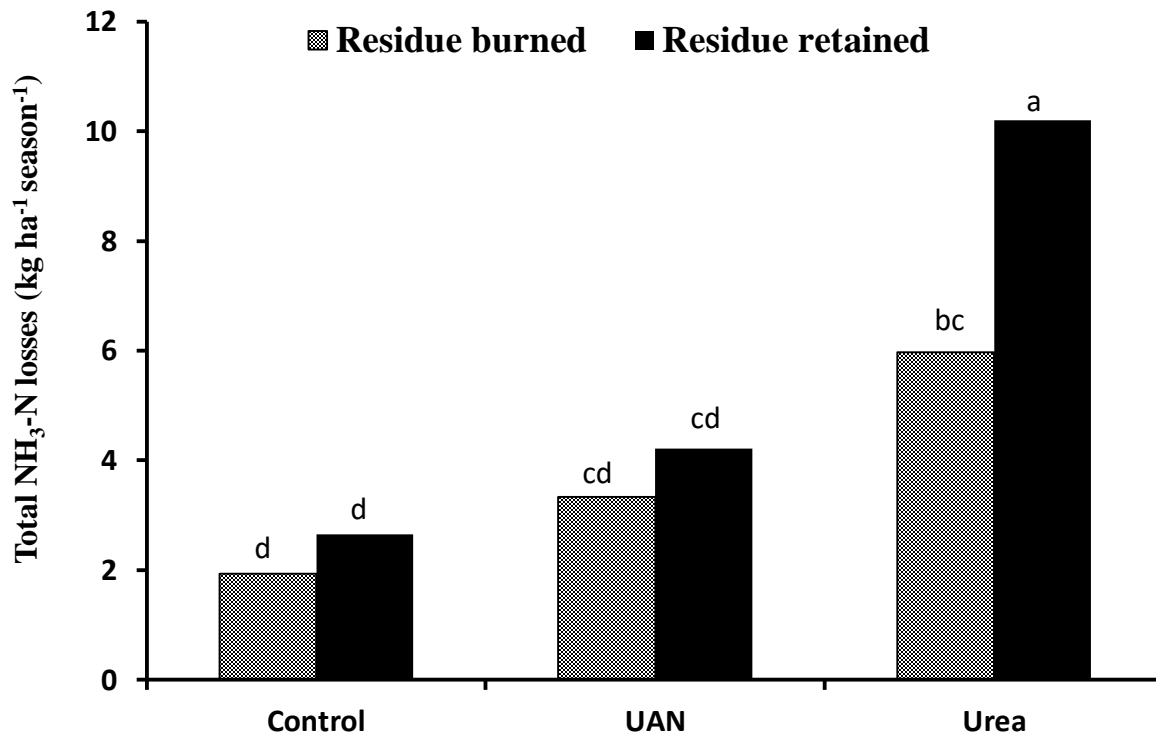


Fig 2.3. Accumulated seasonal  $\text{NH}_3\text{-N}$  losses from the sugarcane field under different residue and fertilizer treatments in 2012. The same lowercase letters on top of the bar diagram represents statistically insignificant at  $\alpha = 0.05$  level

Significant effects of residue management schemes on  $\text{NH}_3\text{-N}$  emission were also seen from daily observations (Fig. 2.2A). The RR treatments had an average daily emission of  $16.2 \text{ g NH}_3\text{-N ha}^{-1} \text{ day}^{-1}$ , which was significantly ( $P < 0.05$ ) higher than the average daily  $\text{NH}_3$  loss of  $10.6 \text{ g N ha}^{-1} \text{ day}^{-1}$  from RB plots over the season. This difference was particularly significant when urea was applied (Fig. 2.3). This was likely due to the generally higher soil water moisture

under the RR management scheme (Mulumba and Lal, 2008), which facilitates the urease to hydrolyze urea into  $\text{NH}_3\text{-N}$ . Leaving crop residues as a blanket on the soil has been found to increase  $\text{NH}_3$  volatilization significantly compared to the residues incorporated in the soil (Manheim et al., 1997; Ruijter et al., 2010). On the other hand, soils with retained stubbles were showed to have generally higher C/N ratios, which could help soil microorganisms such as ammonifiers to produce more  $\text{NH}_3$  through the decomposition of organic matter (Riedo et al., 2002; Ruijter et al., 2010). Nonetheless, in this study, we did not find any statistically significant interactive effects of residue management and fertilizer source on gaseous  $\text{NH}_3$  losses.

### **2.3.3 Ammonia volatilization from 2013 field experiment**

Ammonia fluxes from fertilizer source and residue management schemes were examined separately in 2013 to assess the impact of individual treatments. Gas flux samples were collected till 112 DAN (Fig. 2.4). Similar to 2012, significant  $\text{NH}_3\text{-N}$  losses began one day after fertilizer application regardless of the experiments for fertilizer source or residue management scheme evaluations (Figs. 2.4 A and 2.4B). As for the experiment comparing fertilizer sources within the RB treatment, the most commonly employed residue management practice in the Louisiana, average  $\text{NH}_3\text{-N}$  emission from urea plots was  $14.8 \text{ g N ha}^{-1} \text{ day}^{-1}$  or  $5.7 \text{ kg N ha}^{-1} \text{ season}^{-1}$  which was significantly ( $\alpha = 0.05$ ) higher than  $12.2$  and  $7.0 \text{ g N ha}^{-1} \text{ day}^{-1}$  or  $4.4$  and  $2.2 \text{ kg N ha}^{-1} \text{ season}^{-1}$ , respectively, for both the UAN plots and the control (Fig. 2.5A). This result, unlike that of 2012 in the combined fertilizer source and residue management treatment experiment which showed only the significant difference in the RR residue management practice, further confirms the difference between urea and UAN applications in affecting  $\text{NH}_3\text{-N}$  loss. Nonetheless, major portion of the volatilization losses (55% of the total loss) was within 4 weeks after N application.

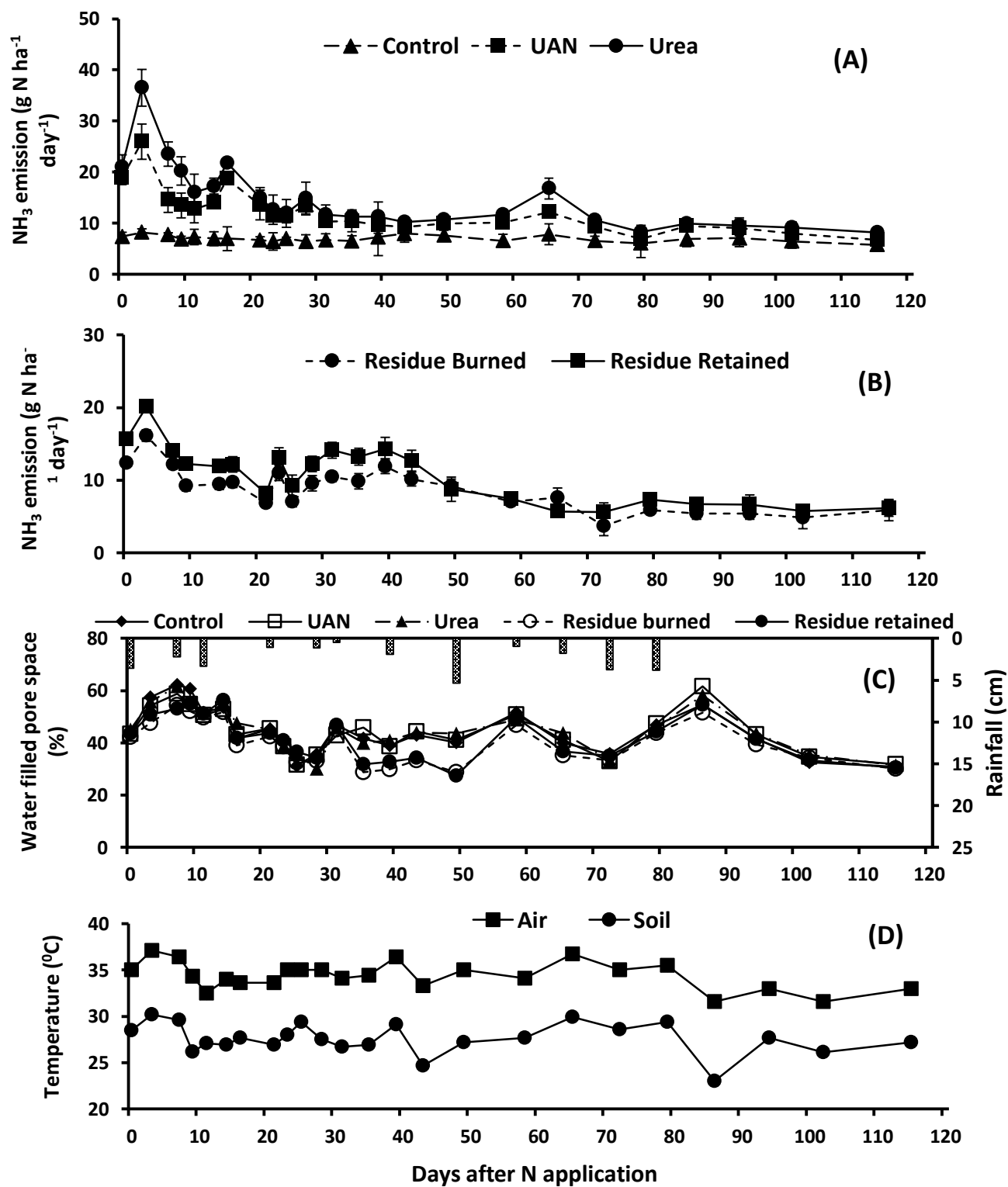


Fig 2.4. 2013 field observations following N applications: (A) daily  $\text{NH}_3$ -N losses, (B) rainfall and water filled pore space, and (C) air and soil temperatures.

As for the experiment comparing two residue management schemes, the RR practice generally had higher  $\text{NH}_3\text{-N}$  daily loss than the RB treatment during the whole sampling season (Fig. 2.4). Cumulatively,  $\text{NH}_3\text{-N}$  emission from the RR plots was significantly higher with 26% greater than that from the RB plots for the season (Fig. 2.5B). Approximately 70-75% of the total volatilization loss was observed within 42 days after N application. The latter was slightly longer than that observed in the year 2012, which generally showed the major emissions within the first 30 days of N fertilization. Relatively low soil temperature could be the cause for these slightly prolonged  $\text{NH}_3\text{-N}$  emissions in 2013, which seems to be more associated with the RR plots.

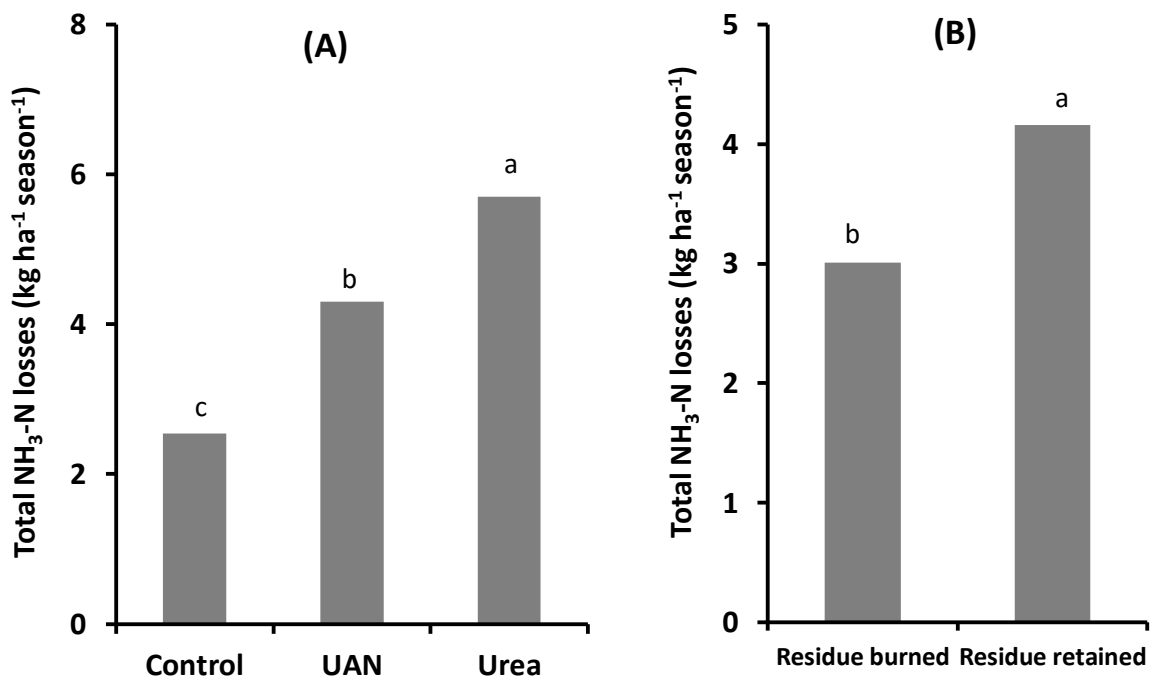


Fig 2.5. Accumulated seasonal  $\text{NH}_3\text{-N}$  losses in 2013 from the sugarcane field under (A) different fertilizer treatments and (B) residue managements. The same lowercase letters on top of the bar diagram represents statistically insignificant at  $\alpha = 0.01$  or 0.05 level.

### 2.3.4 Emission factors

The average seasonal  $\text{NH}_3\text{-N}$  EF, which considers only the emission from applied N after eliminating background process observed from the control plots, for different fertilizer applications under different residue management schemes are presented in Table 2.2. The EF values of urea application were clearly much greater than the UAN application. This was especially true under RR residue management scheme in which  $\text{NH}_3\text{-N}$  EF from urea was approximately 3.3 folds of that from UAN as compared to 2.0 times under the RB management practice. This result suggests that granular urea application in sugarcane production systems generally has more than doubled  $\text{NH}_3\text{-N}$  loss even though urea was immediately covered by soil after application through disking. The liquid nature of UAN through knifing in the soil clearly has the advantage of low volatility loss as  $\text{NH}_3$  emissions. On the other hand, the RR residue management had generally higher  $\text{NH}_3\text{-N}$  EF than the RB residue management practice (1.7% vs. 1.2% for UAN and 5.6% vs. 2.4% for urea), a result that is consistent with greater moisture as observed in the residue retained plots (Figs. 2.2B and 2.4C), which helps the hydrolysis of urea and facilitates  $\text{NH}_3$  emission loss (Manheim et al., 1997; Ruijter et al., 2010).

Table 2.2. Average emission factor (EF) of  $\text{NH}_3\text{-N}$  of different N treatments from sugarcane field

Treatment	Emission factor (%)	
	Residue burned	Residue retained
Control	--	--
UAN	$1.2 \pm 0.15$	$1.7 \pm 0.26$
Urea	$2.4 \pm 0.32$	$5.6 \pm 0.82$



It should be pointed out that the previous research reported that keeping the residue blanket on soil surface reduced subsequent yield of sugarcane crops as compared to the residue burned treatment and one of main reasons for this decrease was often attributed to unfavorable negative soil water-temperature relations due to relatively cold winter as well as production of allelochemicals and overwintering sugarcane borers and sugarcane beetle (Richard, 2001; Kennedy and Arceneaux, 2006; Viator et al., 2008, 2009a). However, our study indicates that the greater loss of nutrient N as  $\text{NH}_3$  emission, facilitated by the residue blanket could be also a potentially contributing factor to this decreased yield phenomenon. In addition, toxicity of ammonia to plants has been reported at concentrations higher than  $600 \mu\text{g NH}_3 \cdot \text{m}^{-3}$  for 24 h and  $10,000 \mu\text{g mg NH}_3 \cdot \text{m}^{-3}$  for 1 h (Van Der Eerden, 1982). While we did not measure the open air  $\text{NH}_3$  concentration, relatively high intensity of  $\text{NH}_3\text{-N}$  emissions observed immediately following the fertilizer application in this study with urea under the residue retained management practice suggests it is not unlikely that  $\text{NH}_3$  concentration could reach the toxic level under the microclimate environment and cause the reduction of plant growth. This could be another factor contributing to the loss of sugarcane yield of subsequent sugarcane, which has not been adequately investigated.

The  $\text{NH}_3\text{-N}$  EF values (2.4-5.6%) reported in this study were higher than the 1.9% observed by Tian et al. (2015) in a granular urea-treated cotton field in the same region, suggesting sugarcane production tend to facilitate  $\text{NH}_3$  loss even though the soil used in this study has a pH 6.1 which is similar to pH 6.2 of the soil in the cotton study. On the other hand, these EFs are much lower than the 17-39%  $\text{NH}_3\text{-N}$  loss of applied urea-N directly applied on trash (residue) covered sugarcane fields as observed in Queensland, Australia (Freney et al.,

1992), suggesting that the soil incorporation of urea as practiced in Louisiana sugarcane production can dramatically reduce  $\text{NH}_3$  volatilization. These observed EFs are also much lower than the 23% of applied N reported for pasture soils (Van Der Weerden and Jarvis, 1997) and 13.7% of average estimate of the loss for urea applications from many other upland crop production studies (Yan et al., 2003). These results clearly demonstrate the effects of crop systems and associated field management practices on  $\text{NH}_3\text{-N}$  emissions.

### **2.3.5 Relationship between $\text{NH}_3$ emissions and soil WFPS**

Higher peaks of  $\text{NH}_3$  emissions were generally observed immediately after high rainfall events such as days 2, 17 and 34 in 2012 and days 2 and 12 in 2013 especially when N fertilizers were just applied. Previous research has showed that rainfall and resulting soil water dynamics highly influences the hydrolysis of urea and eventually  $\text{NH}_3$  volatilization particularly as soil begins to dry due to an increase in diffusion (Corre et al., 2002; Arnibar et al., 2004; Tian et al., 2015). In this study, while we did not find direct statistically significant correlation between rainfall amount and  $\text{NH}_3\text{-N}$  emission over a sampling season, there was significant correlation between the soil moisture content as expressed by WFPS (%) and the magnitude of daily  $\text{NH}_3\text{-N}$  emission for each season (Fig. 2.6). Average WFPS in 2013 was about 25% higher than 2012 because of more frequent rainfall events and greater overall total amounts of precipitation received during the sampling period in 2013. However, the results showed that the average WFPS had much higher correlation with average  $\text{NH}_3$  emission of combined N fertilizers in 2012 ( $R^2 = 0.61$ ,  $P < 0.01$ ) than 2013 ( $R^2 = 0.27$ ,  $P < 0.05$ ). Most rainfall events in 2013 occurred 3 weeks after fertilization, when  $\text{NH}_3$  emissions were already very low. Whereas, in 2012, more than half of

the rainfall events were within 3 weeks of fertilization, when, the  $\text{NH}_3$  emissions were relatively higher than rest of the sampling period. Separately, WFPS showed slightly greater correlation with  $\text{NH}_3\text{-N}$  emission from urea ( $R^2 = 0.48$ ) than from UAN ( $R^2 = 0.32$ ) for both the years.

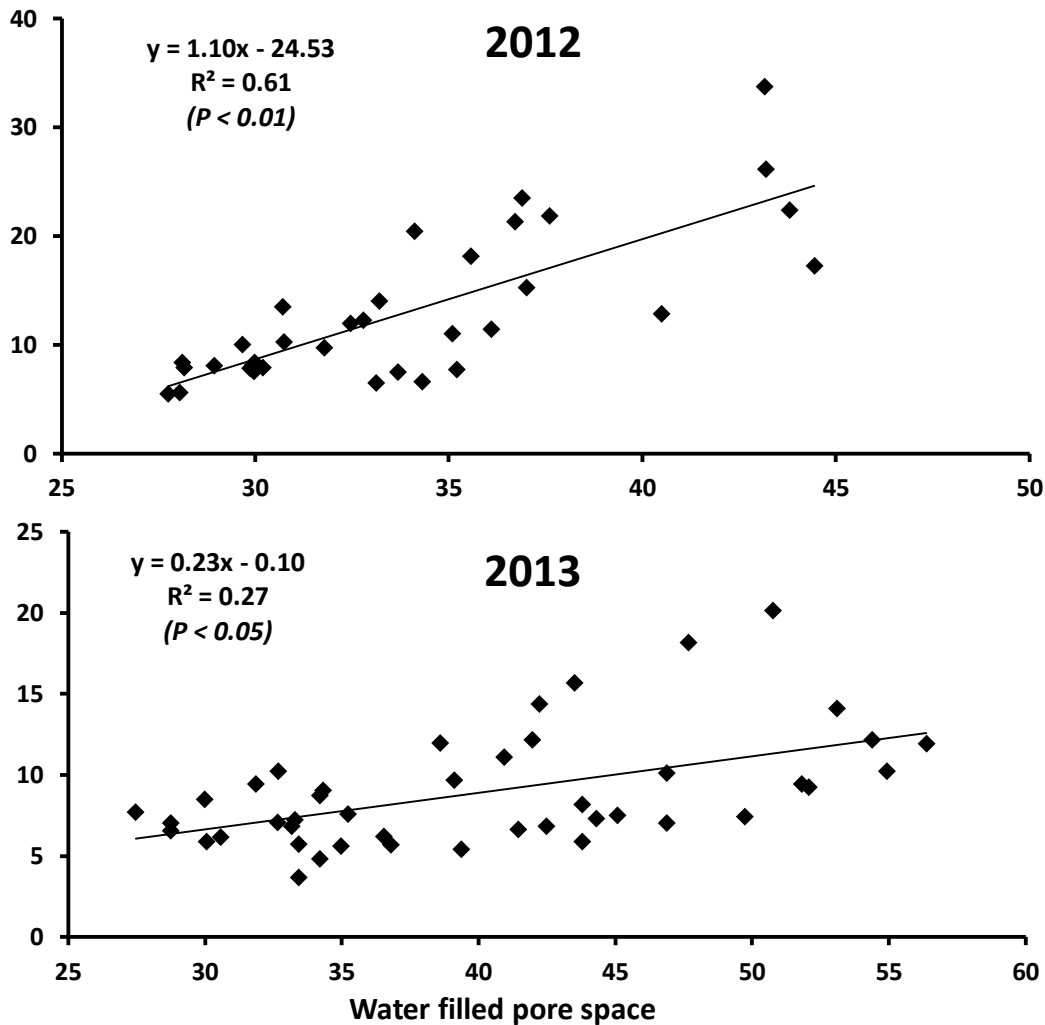


Fig 2.6. Relation between daily ammonia losses and water filled pore space (%) in 2012 and 2013

Also, it was found that the plots with RR treatments had generally higher correlations with WFPS ( $R^2 = 0.67$  in 2012 and 0.29 in 2013) than RB plots ( $R^2 = 0.47$  in 2012 and 0.21 in 2013) because the residue blanket in the field retained more soil moisture and thus subsequently

increased the WFPS(%). Previous studies of different N fertilizer sources have showed that WFPS did not significantly influence  $\text{NH}_3$  emissions from soil or that higher emissions were only found in a WFPS range primarily between 8-30% (Fenn and Escarzaga, 1976; Bouwmeester et al., 1985; Akiyama et al., 2004). Our study appears to indicate that  $\text{NH}_3$ -N emissions in N fertilizer-treated sugarcane fields generally increased with increasing WFPS up to 45-55% observed in the field.

Overall, we did not observe any statistically significant relationship between soil and air temperatures with  $\text{NH}_3$  volatilization, even though some higher  $\text{NH}_3$  emissions corresponded to high soil and air temperatures on certain days.

## **2.4. Conclusions**

Two years of field experiments clearly showed that N fertilizer source had a significant impact on  $\text{NH}_3$  emissions from soil under sugarcane production. Urea application produced significantly higher  $\text{NH}_3$  volatilization with emission factor of twice or more than the application of UAN depending on the harvest residue management of proceeding crops. The residue retention management approach showed generally higher average  $\text{NH}_3$  emission than that of the ground burning of harvested residue following N fertilizer application, due to higher soil moisture retained by the former, which helped hydrolysis of urea and subsequently  $\text{NH}_3$  emissions. The significantly highest amount of  $\text{NH}_3$  volatilization was measured within 4 weeks after N application and it was generally increased with increasing WFPS up to 45-55%. This study demonstrates the importance of both fertilization applications and harvest crop residue management approaches in affecting  $\text{NH}_3$  emission factors from sugarcane production.

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## **Chapter 3. Quantitative Study of Greenhouse Gas Emissions Influenced by Nitrogen Fertilization and Residue Management Practices from Subtropical Sugarcane Production**

### **3.1. Introduction**

Nitrous oxide ( $\text{N}_2\text{O}$ ) and methane ( $\text{CH}_4$ ) are potent greenhouse gases (GHG) with higher global warming potential (GWP) than  $\text{CO}_2$ . Agriculture accounts for about 58 and 47% of the total anthropogenic emissions of  $\text{N}_2\text{O}$  and  $\text{CH}_4$ , respectively, and the concentration of these two gases increased by nearly 17% from 1990 to 2005 (Smith et al., 2007). Nitrous oxide from soil is generally produced through nitrification and denitrification processes by different aerobic and anaerobic microorganisms. Nitrous oxide emission from soil is greatly influenced by type of N fertilizer used (Venterea et al., 2005), tillage methods (Venterea et al., 2005), soil temperature (Maljanen et al., 2003), soil moisture content (Davidson, 1992; Ma et al., 2010) and other meteorological factors. However, N application for crop production is reported as the major factor for  $\text{N}_2\text{O}$  emission from soil (Yamulki and Jarvis, 2002; Dalal et al., 2003). Methane biosynthesis generally occurred in anaerobic soil through reduction of  $\text{CO}_2$  (Henckel et al., 2000; Ramirez et al., 2009). Agricultural soils can act as a net sink or source of  $\text{CH}_4$ , depending on soil moisture, N content, and ecosystem (Chan and Parkin, 2001; Gregorich et al., 2005; Liebig et al., 2005) because  $\text{CH}_4$  can be consumed by methanotrophic bacteria (McLain and Martens, 2006) or produced by methanogenic bacteria in soil (Chan and Parkin, 2001). Carbon dioxide released from soil is mainly through microbial decomposition of organic matter (Janzen, 2004; Smith et al., 2008). Sugarcane is an important row crop grown in major parts of the world and produced commercially in Louisiana, Florida, and Texas in the US. It is a high biomass producing crop and requires intensive supply of different nutrients especially N during the growth season. While

urea has been widely used in the past; liquid Urea Ammonium Nitrate (UAN) is gaining popularity as a primary N source for sugarcane production in recent days.

Proper management of sugarcane residues (in-situ vs off-situ) has been an important factor for subsequent crop production in different parts the World. Sugarcane residues can be left in the field (residue retained, RR) or can be burned in the field (residue burned, RB) depending on the agro climatic conditions of that region (Wood, 1991; Fageria et al., 1997; Franca et al., 2012). Harvested sugarcane residue is retained in Australia because it conserves soil moisture and thus increase crop yield (Wood, 1991; Fageria et al., 1997), whereas, in Brazil harvest residues of sugarcane burned in the open field for better sugar production. Both of these residue management techniques have been practiced in the US. It is reported that approximately 38% of the sugarcane crop area was burned during 2010 (USEPA, 2015). There are published research on the influence of these different residue managements on GHG emissions specifically  $N_2O$  fluxes from sugarcane field. Research study reported that with 70% water holding capacity (WHC), the application of wheat straw mulch can significantly reduce  $N_2O$  emission as compared to the soil without straw in Northern Ireland (Cai et al, 2001). Research conducted in Western Canada, stated that removal of straw from the field would significantly reduce  $N_2O$  loss from the soil (Hao et al, 2001). On the other hand, application of rice straw in wheat fields resulted in higher emission of  $N_2O$  in northern India (Pathak et al, 2006). From another study conducted in northeast China, Liang et al (2007) reported that straw application can significantly enhanced  $N_2O$ -N emission from agricultural field. But researches on  $N_2O$ -N flux measurement from agricultural crop production in tropical US climate is very limited (Tian et al., 2015) and further research is needed for better understanding of residue application methods (with or

without N supply) on N<sub>2</sub>O emission from soil. This current research project was planned with the objective of quantifying GHG emission under the influence of different N sources and residue management schemes from subtropical sugarcane production.

### **3.2. Materials and methods**

#### **3.2.1 Site location and characteristics**

The field experiments were done at Louisiana State University AgCenter research station in St Gabriel, Louisiana (USA, 30°15'13"N 91°6'5"W) for two years. First and second year sugarcane stubbles were used for planting in a commerce silt loam soil (silt 62%, sand 22%, and clay 16%) in 2012 and 2013, respectively. Background soil samples were collected with core sampler at 15 cm depth (n = 8) a week before fertilizer application and were analyzed for pH, texture, CEC, EC, total N, total C and different other nutrients (P, K, Ca, Mg, and S). Cation exchange capacity and particle size distribution of the soil were measured by ammonium acetate replacement method and pipette, respectively. The soil of the experimental field was found slightly acidic (pH, 6.1) with moderate cation exchange capacity (CEC, 15.1 meq/100gm). Other physiochemical properties of the background soil were presented in Table 3.1. More soil samples were also collected through cylindrical core auger for measuring the bulk density of the soil. Bulk density of the soil was used to calculate water filled pore space (%) with the formula  $\Psi = (\Phi_v/TP)*100$ ; where  $\Psi$  is the WFPS (%),  $\Phi_v$  is the volumetric water content (%) and TP is the total porosity (%) of the soil. Additional details of measuring WFPS were described in previous chapter (section 2.2.1).

### **3.2.2 Nitrogen application and residue managements**

Urea (45.9% N) and UAN (31.9% N) were the main N sources for this experiment. Control plots were also established in both 2012 and 2013 to get the background GHG concentrations. Nitrogen was applied at the rate of 135 kg ha<sup>-1</sup> and 157 kg ha<sup>-1</sup>, respectively, for the first and second year of the experiment. Fertilizers were applied on May 22 in 2012 and on May 20 in 2013. First GHG samples were taken 2 hours after N application for both years which are represented as 0 days after N application (DAN) in the results. Urea was surface broadcasted followed with soil cover and UAN was injected directly into the soil through UAN applicator. Two different types of residue managements namely residue retained (RR) and residue burned (RB) were established in 2012 to compare fertilizer and residue interactions on GHG emissions. Residues from last year harvesting were kept as such for half of the experimental field and the residue on the other half of the field was burned. Split plot in randomized complete block design (RCBD) with 2 replications in the main plots and 4 replications in the sub-plots was used in 2012. However, two field experiments were done in 2013 to evaluate the separate effect of fertilizers and residues on GHG emissions. Nitrogen was applied at the rate of 157 kg ha<sup>-1</sup> in the form of granular urea and liquid UAN. Randomized complete block design (RCBD) with 4 replications was used for these experiments in 2013.

### **3.2.3 Gas sample collection and analysis**

Greenhouse gases were collected using a closed chamber system installed in the experimental field. In this study, stainless steel top (0.3 x 0.3 x 0.4 m<sup>3</sup>) and bottom chambers (0.3 x 0.3 x 0.2 m<sup>3</sup>) were used to collect greenhouse gas emissions from the soil. The bottom chambers were placed 10 cm deep in the soil of the fertilized rows and were kept undisturbed for the whole

sampling season. During each sample collection, the top chambers fitted with sampling port were used to connect the bottom chambers using iron clamps and the whole chamber system in the field was covered with reflective aluminum insulation sheets which prevent heating of the metal chamber from direct sun light. Ethylene propylene diene monomer (EPDM) rubber weather strips were placed on top of both chambers for tight sealing when clamped during sampling. The first GHG samples were taken 2 hours after fertilizer application, followed by every alternate day for first three weeks and then once a week for two and half months in 2012 and for about 4 months in 2013. Gas samples were collected from the head space of the whole chamber system using 15 ml syringes at 0, 30, and 60 min intervals and the collected samples were stored in pre-vacuumed vials fitted with rubber septa. To avoid the diurnal variations, gas sampling was done during same time of the day whenever possible. Gas samples were then analyzed using Varian CP-3800 gas chromatograph (GC) equipped with flame ionization detector (FID for CO<sub>2</sub> and CH<sub>4</sub>) and electron capture detector (ECD for N<sub>2</sub>O). Soil and air temperatures were taken by portable soil temperature probe with every NH<sub>3</sub> sampling. Soil samples were also collected with each gas sampling to determine gravimetric moisture content. Rainfall data for this experiment site was obtained from the LSU AgCenter weather station website.

#### **3.2.4 Emission factor (EF) analysis**

The emission factor (EF) of N<sub>2</sub>O-N for the sugarcane growing season was analyzed using the following formula:

$$EF (\%) = \frac{\sum (N_2O - N)_{fertilizers} - (N_2O - N)_{control}}{\text{Applied available N source}} \times 100$$

Where  $N_2O-N_{\text{fertilizers}}$  and  $N_2O-N_{\text{control}}$  are the total  $N_2O-N$  emissions from the fertilized field and from the control plot, respectively. Applied available N source is the amount of N applied in the field ( $\text{kg ha}^{-1}$ ).

### **3.2.5 Statistical analysis**

Statistical analyses were done using SAS 9.3 (SAS Institute. 2012, Cary, NC) for analysis of variance (ANOVA) with PROC MIXED and mean separation was done by Tukey-Kramer method at a  $P < 0.05$  level.

## **3.3 Results and discussion**

### **3.3.1 Soil and environmental conditions**

The average air temperature was found to be very similar in both years with the value of 34 and  $34.3^{\circ}\text{C}$  for 2012 and 2013, respectively. However, the average soil temperature for 2012 ( $29.2^{\circ}\text{C}$ ) was found little higher than 2013 ( $27.1^{\circ}\text{C}$ ). Almost two times higher rainfall was received in second year of sugarcane production as compared to the first year. The majority of the rainfall (more than 50%) was received within 3 weeks of sample collection during 2012, whereas, in 2013 almost 75% of the rainfall was received after 3 weeks of sampling. Bulk density of residue plots ( $1.23 \text{ g cm}^{-3}$ ) were found 6.5% lower than nor-residue treatment plots ( $1.31 \text{ g cm}^{-3}$ ) which is due to the reason that residues added organic matter in the soil and thus improved the soil structure (Kornecki and Fouss, 2011). Average WFPS of RR plots (41.8%) were found 14% higher as compared to RB plots (36.7%) for both 2012 and 2013; similar findings have been reported in the past (Jacinthe and Lal, 2003).

### 3.3.2 Nitrous oxide fluxes

Daily N<sub>2</sub>O emissions under different N sources and residue management schemes observed in 2012 were presented in Fig 3.1A. Greenhouse gas samples were only be able to collect till 71 DAN because of high impact of hurricane Isaac in Louisiana during August, 2012 and almost 90-95% of the sugarcane crop in the experimental field was lodged. Significant N<sub>2</sub>O-N loss was started a day after fertilizer application and overall, major emission was found within 24 DAN (Fig 3.1A). Higher peaks of N<sub>2</sub>O emission on 17 and 34 DAN were corresponding to relatively high soil moisture content (Fig. 3.1D) on those particular days. Several studies indicated that soil temperature have influence on N<sub>2</sub>O emission because of the higher microbial induced nitrification and denitrification processes in the soil (Dobbie and Smith, 2003b; Wang et al., 2005; Horvath et al., 2006; Zhang and Han, 2008). However, in our experiment temperature (Fig 3.1E) did not show much significant relation with N<sub>2</sub>O loss except there are some data points (for example 4, 17, and 34 DAN) where high air and soil temperature may have attributed more gas emissions.

Different N sources produced considerable impacts on N<sub>2</sub>O emissions from fertilizer plots in 2012 (Fig 3.2A). Average N<sub>2</sub>O emissions from urea treated plots (7.3 kg N ha<sup>-1</sup> season<sup>-1</sup>) were significantly higher ( $P < 0.05$ ) than UAN plots (5.0 kg N ha<sup>-1</sup> season<sup>-1</sup>), and control (2.4 kg N ha<sup>-1</sup> season<sup>-1</sup>). Studies indicated that N application in general increase N<sub>2</sub>O emission from soil (Maljanen et al., 2003; Zhang and Han, 2008). Average nitrous oxide emissions from cotton and wheat-maize field were found 2.2 and 5.1 kg N ha<sup>-1</sup> year<sup>-1</sup>, respectively, in northern China (Liu et al., 2014). A field experiment conducted in wheat field of northern India, where yearly N<sub>2</sub>O-N emission ranged from 4.5 to 6.0 kg N ha<sup>-1</sup> from urea treated plots (Pathak et al., 2006).



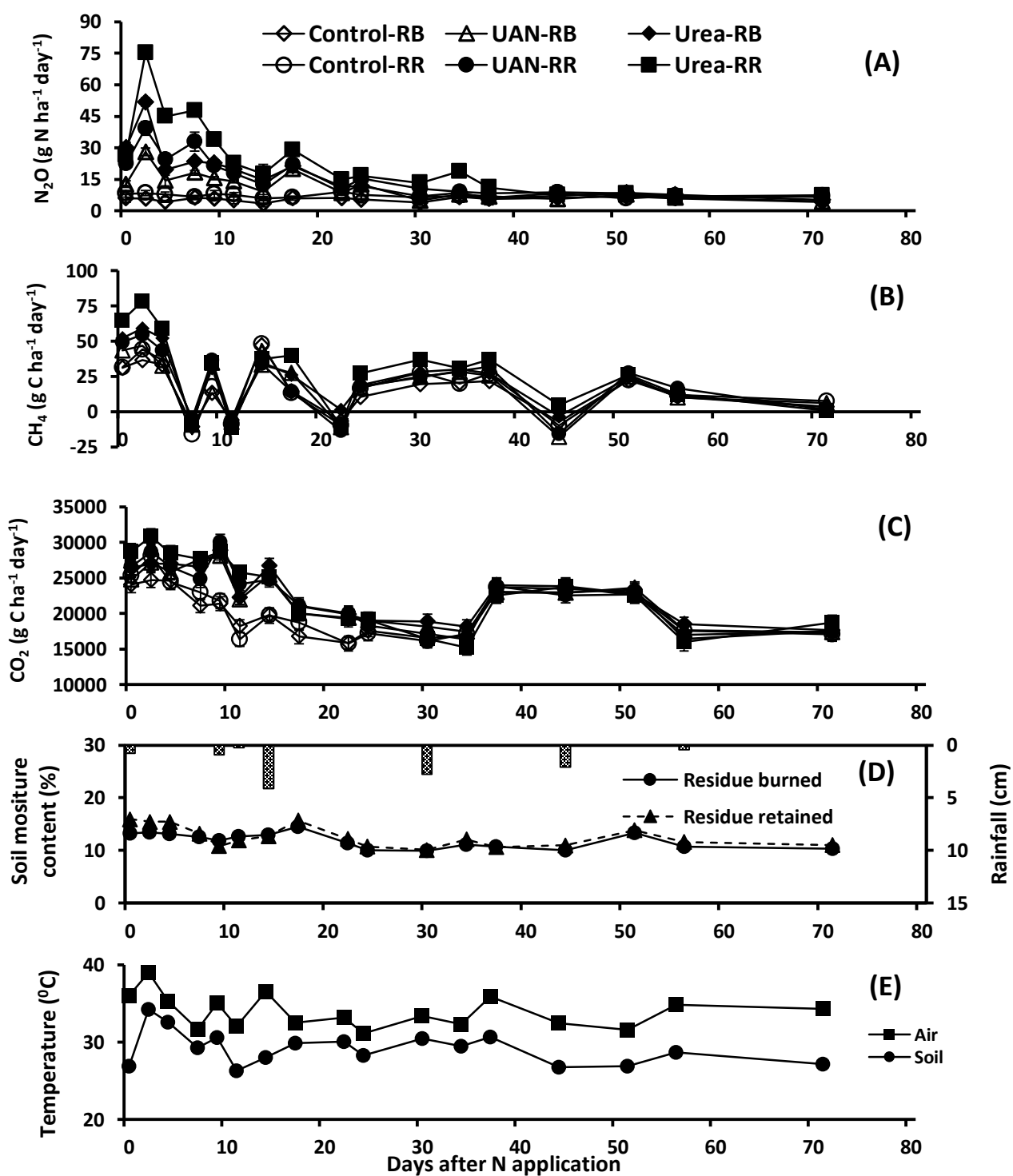


Fig 3.1. Daily greenhouse gas emissions (A, B, C), rainfall and soil moisture content (D), and air and soil temperatures (E) following N applications in 2012

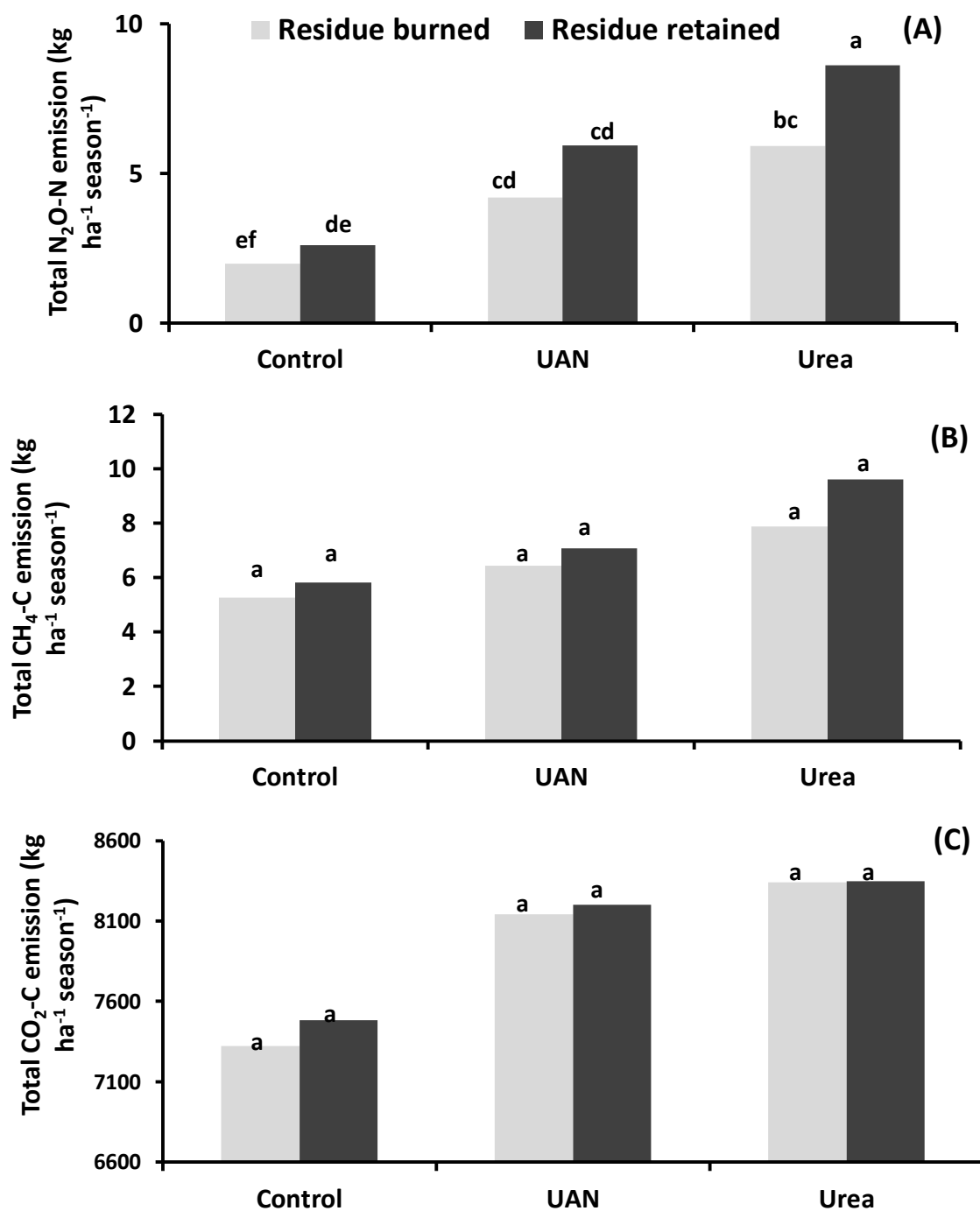


Fig 3.2. Total seasonal emission of  $N_2O$  (A),  $CH_4$  (B), and  $CO_2$  (C) from sugarcane field in 2012. The same lowercase letters on top of the bar diagram represents statistically insignificant at  $\alpha = 0.01$  or  $0.05$  level.

However, in 2012, N<sub>2</sub>O emissions from UAN and control plots were not significantly different from each other. On the other hand, RR plots (5.8 kg N ha<sup>-1</sup> season<sup>-1</sup>) produced significantly higher ( $P < 0.05$ ) N<sub>2</sub>O than RB (4.0 kg N ha<sup>-1</sup> season<sup>-1</sup>) plots. This is because retained residues in the field can work as a blanket in the soil and hold more soil moisture which helps the denitrification and subsequently more N<sub>2</sub>O emissions. However, the interaction effect of residues and fertilizers for N<sub>2</sub>O emission was statistically insignificant ( $P > 0.05$ ). Results showed that cumulative NH<sub>3</sub>-N losses from both RB and RR plots within 3 weeks after N application represents 76 and 78% of the total cumulative N<sub>2</sub>O-N losses from the field, respectively. However, urea contributed almost 2 times higher N<sub>2</sub>O-N than UAN within first 24 days of fertilizer application.

Nitrous oxide emission fluxes from fertilizers and residue management practices were evaluated separately in 2013 to find out the impact of individual treatments on gas emission. Samples from both treatments were collected till 115 days after N application (Figs. 3.3A & 3.4A). Similar to 2012, significant amount of N<sub>2</sub>O loss from N treated plots was started a day after N application in the soil and overall, about 70% of the emission occurred within 3 weeks after N application (Fig. 3.1A) which is very similar to the findings of experiments done at United Kingdom by Baggs et al (2003) where they found up to 48% of the N<sub>2</sub>O emitted during first 3 weeks of N fertilizer and residue application. Nitrous oxide peaks from urea and UAN plots were become flat after 24 DAN and almost similar to control except on 31, 43, and 58 DAN when higher soil moisture (Fig. 3.3D) could have attributed more N<sub>2</sub>O-N emissions. High nitrous oxide emissions from residue field was occurred a day after fertilizer was applied and about 74-77% of the total N<sub>2</sub>O emission happened within 25 DAN (Fig. 3.4A).

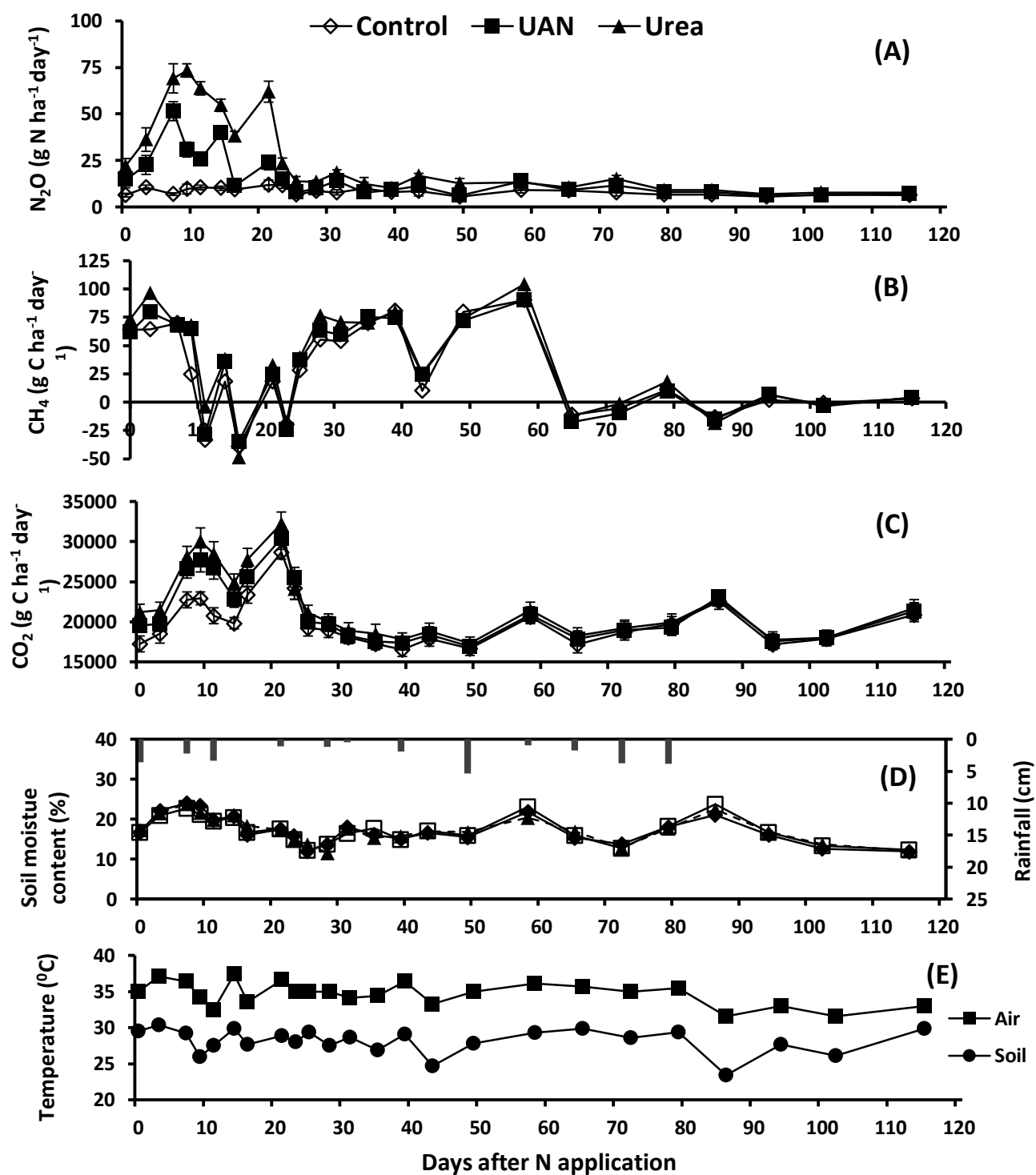


Fig 3.3. Daily greenhouse gas emissions (A, B, C), rainfall and soil moisture content (D), and air & soil temperatures (E) following N applications from fertilizer field in 2013

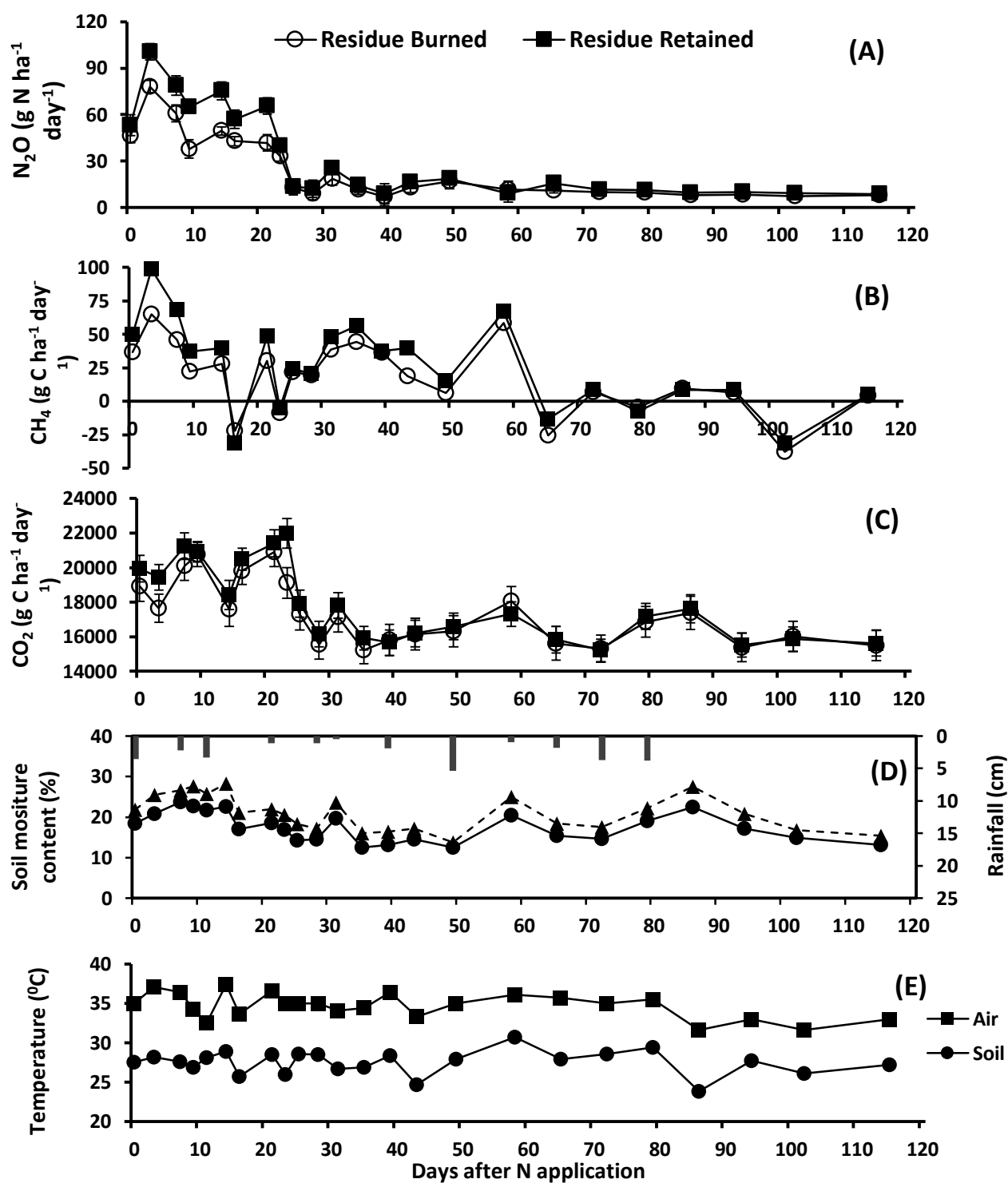


Fig 3.4. Daily greenhouse gas emissions (A, B, C), rainfall and soil moisture content (D), and air & soil temperatures (E) following N applications from residue field in 2013

Higher N<sub>2</sub>O peaks at 14, 21, and 31 DAN were corresponded with higher soil moisture on those days. Soil and air temperature did not have any significant influence on N<sub>2</sub>O emission in this experiment.

Average N<sub>2</sub>O-N emission from N treated plots was found to be highest from urea (9.5 kg N ha<sup>-1</sup> season<sup>-1</sup>) followed by UAN (5.6 kg N ha<sup>-1</sup> season<sup>-1</sup>) and control (3.0 kg N ha<sup>-1</sup> season<sup>-1</sup>) in 2013 (Fig. 3.5A). The statistical analysis showed that N<sub>2</sub>O emissions from control, UAN, and urea were significantly different from each other's ( $P < 0.05$ ) which depicts that unlike in 2012, UAN produced significantly higher N<sub>2</sub>O emissions than control in 2013. It indicates that residues probably had a masking impact on N<sub>2</sub>O emission when applied in combination with synthetic N fertilizers. Shan and Yan (2013) stated that crop residues combined with fertilizers can reduce 12% N<sub>2</sub>O-N emission from the soil. However, they also noted that residue plots without any fertilizers can significantly increase N<sub>2</sub>O emission as compared to control plots. On the other hand, average emission of N<sub>2</sub>O-N from RR plots (11.9 kg N ha<sup>-1</sup> season<sup>-1</sup>) was found significantly higher ( $P < 0.05$ ) than RB plots (8.3 kg N ha<sup>-1</sup> season<sup>-1</sup>) in 2013 (Fig. 3.5B). Studies in the past stated that retained residues can have considerable influence on nitrous oxide emission as compared to the bare land or cultivated soil without any residue treatments. A field experiment in Ohio, USA indicates that residue treatments produced almost two times higher N<sub>2</sub>O-N than bare soil (Jacinthe and Lal, 2003). Some recent studies observed that retained residue plots emitted 1.6 to 1.8 times higher N<sub>2</sub>O from wheat field (Ma et al., 2010) and about 2.2 times higher N<sub>2</sub>O from agricultural soils (Shan and Yan, 2013) as compared to burned residue plots which indicates the similarity to the results found in our experiment.

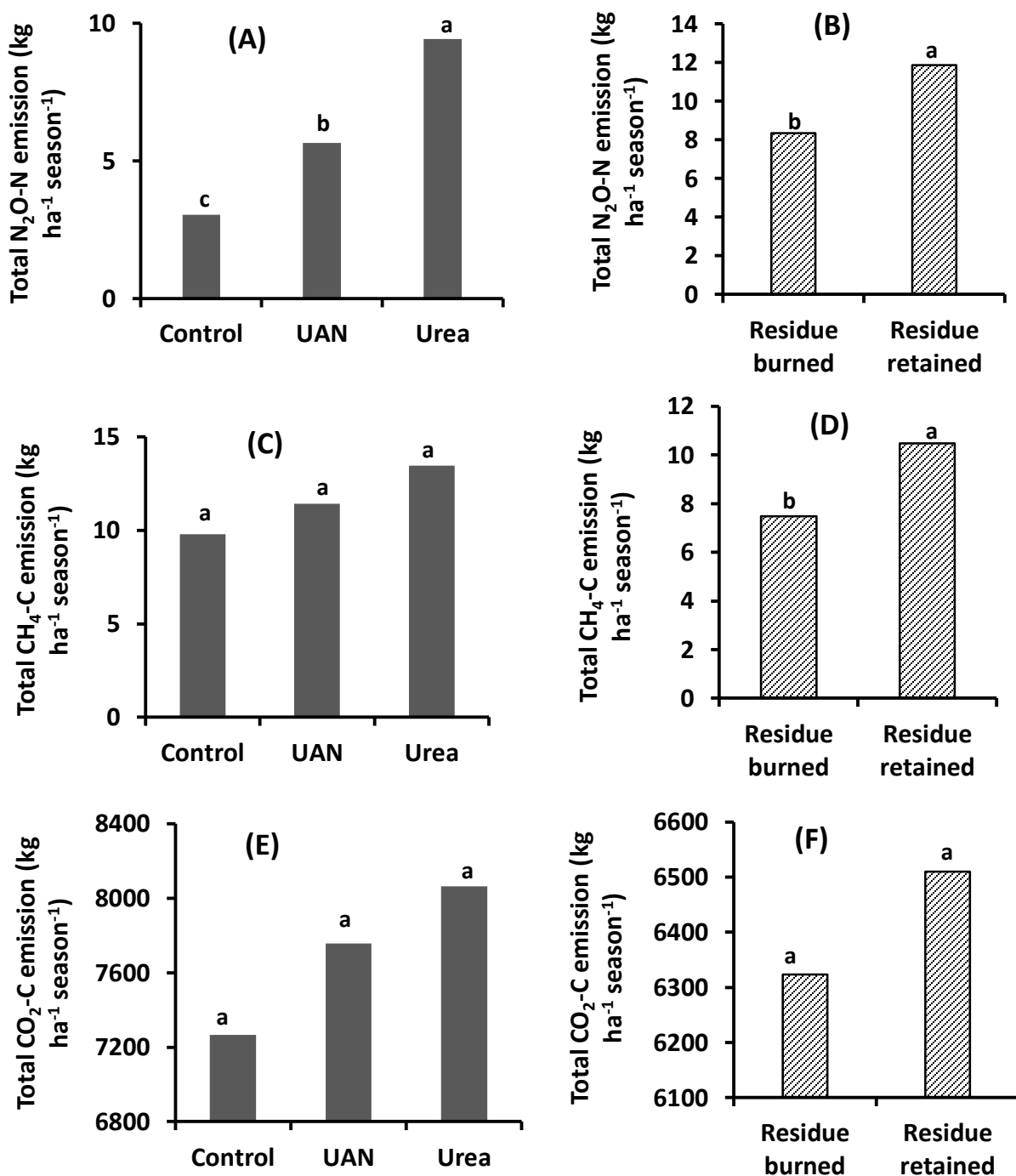


Fig 3.5. Total seasonal emission of N<sub>2</sub>O (A, B), CH<sub>4</sub> (C, D), and CO<sub>2</sub> (E, F) from sugarcane field in 2013. The same lowercase letter in a bar represents statistically insignificant at alpha 0.05 or 0.01 level.

The significant effect of residues on N<sub>2</sub>O-N emission was also observed from 1.5 times higher EF value of residue treated plots as compared to the burned plots (2.77% vs 1.90%) in 2012 (Table 3.1). The results also showed that on an average, 2% and 2.7% of the applied N was lost as N<sub>2</sub>O-N from UAN and urea, respectively, which is comparable to another recent study reported from subtropical cotton production (Tian et al., 2015). The average N<sub>2</sub>O EF of urea (2013) plots was found to be more than 1.7 times higher than that of UAN plots.

Table 3.1. Average emission factor (EF) of N<sub>2</sub>O-N of different N treatments from sugarcane field

Treatment	Emission factor (%)	
	Residue burned	Residue retained
Control	--	--
UAN	1.67 ± 0.27	2.46 ± 0.38
Urea	3.52 ± 0.32	4.45 ± 0.46

### 3.3.3 Methane and Carbon Dioxide fluxes

Results from two year field experiments showed both emission and absorption peaks for CH<sub>4</sub> (Figs 3.1B, 3.3B, and 3.4B). Major positive peaks (9, 14, 17, 34, 37, and 51 DAN) were corresponding to higher WFPS and soil and air temperature in 2012 (Fig 3.1B). This is due to the reason that CH<sub>4</sub> emission is mainly occurs in anaerobic soil conditions (Wang et al., 1993; Liang et al., 2007). In a field study at New Zealand, CH<sub>4</sub> emission was observed immediately after heavy rainfall (Saggar et al., 2008). Negative peaks (7, 11, 22, and 44 DAN) were found during dries days with relatively lower soil temperature. Similar to 2012, higher positive CH<sub>4</sub> peaks in



2013 (14, 21, 31, 58, and 79 DAN) were also corresponded to high WFPS and soil temperature (Fig 3B). However, more negative CH<sub>4</sub> peaks (11, 16, 23, 65, and 72 DAN) were also noticed in 2013 than 2012 corresponding to drier days and lower soil temperature. Almost all major CH<sub>4</sub> peaks were found within 60 days after N application, which was very similar observed from a cotton field in Louisiana (Tian et al, 2015).

Average CH<sub>4</sub>-C emission from urea treated plots (8.7 kg C ha<sup>-1</sup> season<sup>-1</sup>) was little higher than UAN (6.8 kg C ha<sup>-1</sup> season<sup>-1</sup>) and control (5.5 kg C ha<sup>-1</sup> season<sup>-1</sup>) plots but the difference was not statistically significant. Application of N fertilizers did not produce any significant impact on CH<sub>4</sub> emission from soil (Jacinthe and Lal, 2003). However, RR plots showed almost 1.3 times higher CH<sub>4</sub> emission as compared to RB plots. Average CH<sub>4</sub> emission from fertilizer field (control, UAN, and urea) in 2013 was much higher than 2012 may be because of higher rainfall days in 2013. However, no significant difference was found between different N sources and control plots for CH<sub>4</sub> emission in 2013 (Fig. 5C). Residue retained plots (10.5 kg C ha<sup>-1</sup> season<sup>-1</sup>) produced significantly higher ( $P < 0.05$ ) CH<sub>4</sub> emission (Fig. 5D) as compared to RB plots (7.4 kg C ha<sup>-1</sup> season<sup>-1</sup>), most likely due to residues providing more organic matter for methanogenic organisms in the soil (Liang et al., 2007) and 20% higher WFPS in RR plots also created more anaerobic soil conditions which favored methane forming bacteria present in the soil and subsequently emitted more CH<sub>4</sub>.

Average CO<sub>2</sub> emissions from urea (8344 kg C ha<sup>-1</sup> season<sup>-1</sup>) and UAN treated plots (8172 kg C ha<sup>-1</sup> season<sup>-1</sup>) were very similar to control plots (7402 kg C ha<sup>-1</sup> season<sup>-1</sup>) in 2012 (Fig. 3.2C). Recently it was reported that N sources did not produce any significant difference on CO<sub>2</sub> emission (Tian et al, 2015). However, carbon dioxide emission for first few days after N

application was little higher probably because of initial higher C/N ratio in the field increased microbial activity and more CO<sub>2</sub> was produced as a byproduct of organic matter degradation. As likely fertilizer plots, residue treatment differences did not show any considerable CO<sub>2</sub> emission difference as well in 2012. Fertilizer urea treated plots emitted 10% higher CO<sub>2</sub> than control plots in 2013 (Fig. 3.5E) which was statistically insignificant ( $P > 0.05$ ). Similar observation was found by Nikiema et al (2011) where they found that application of N in the soil had higher CO<sub>2</sub> than control but the emission was not significant. Residue retained plots and RB plots showed almost similar daily CO<sub>2</sub> emissions in 2013 (Fig. 3.4C). In general, CO<sub>2</sub> emission in 2013 was little higher than 2012 likely due to more rainfall days in 2013.

#### **3.3.4 Relationship between N<sub>2</sub>O emissions and soil WFPS**

The emission of N<sub>2</sub>O from soil is highly influenced by the soil moisture content. The relation between average N<sub>2</sub>O emission and soil WFPS (%) for both years was presented in Fig 3.6. Higher amount of rainfall received in 2013 which resulted in almost 25% higher WFPS than 2012. However, regression showed that the WFPS was much higher correlated with average N<sub>2</sub>O emissions in 2012 ( $R^2 = 0.52$ ) as compared to 2013 ( $R^2 = 0.36$ ). This is because majority of the rainfall in 2013 was received 3 weeks after N application when the N<sub>2</sub>O concentration was already very low. On the other hand, almost 50% of the total rainfall was received within 21 DAN in 2012 when N<sub>2</sub>O emission flux was very high. The relationship between WFPS and urea or UAN was found linear for both years. Previous studies reported that the relationship of N application and N<sub>2</sub>O emission is in general linear (Bouwman, 1996; Gregorich et al., 2005; IPCC, 2006; Jarecki et al., 2009) and sometime shows a threshold effect (McSwiney and Robertson, 2005). However, urea had little higher correlation ( $R^2 = 0.45$ ) as compared to UAN

( $R^2 = 0.40$ ) probably because soil moisture helps urea hydrolysis (Black et al., 1987) to produce more  $\text{NH}_3$ , which is the primary source of nitrification and denitrification pathways for  $\text{N}_2\text{O}$  emission.

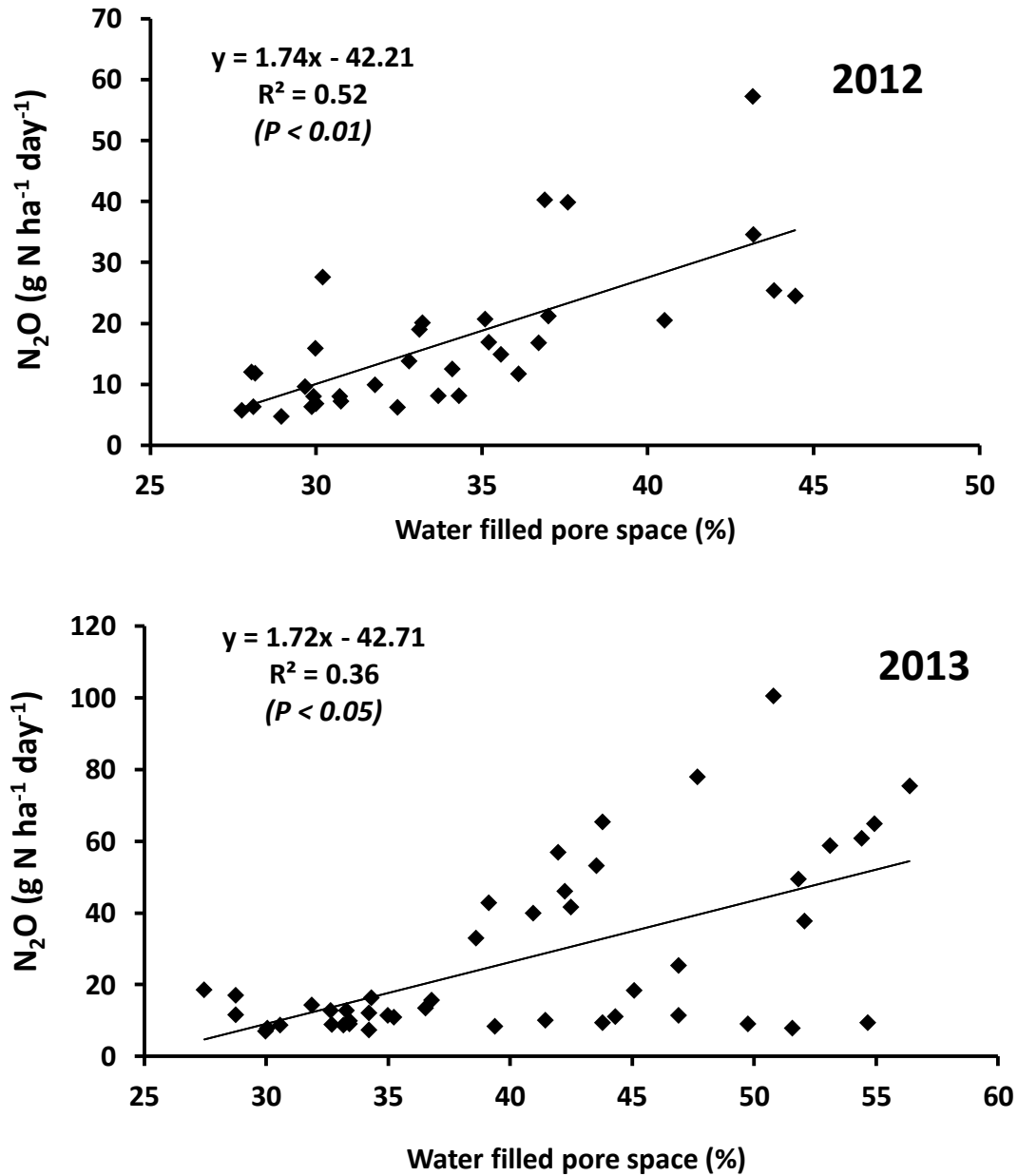


Fig 3.6. Relation between daily nitrous oxide losses and water filled pore space (%) in 2012 and 2013

Also, RR plots showed higher correlation ( $R^2 = 0.46$ ) with WFPS than RB plots ( $R^2 = 0.40$ ). Water filled pore space in RR plots was 20% higher than RB plots which (Fig. 4D) leads to more anaerobic condition and thus generates more  $N_2O$  through denitrification. In addition, relatively high soil moisture content in RR plots increase the availability of soil  $NH_4^+$  and favors denitrifying microorganisms present in the soil (Davidson, 1992; Ma et al., 2010).

### **3.4. Conclusions**

Two year field experiment showed that fertilizer urea significantly influence  $N_2O$  emissions as compared to other treatments from sugarcane production. However, N sources did not show any impact for other two GHG emissions. Major portion of the  $N_2O$  emission occurred with 3-4 weeks after N application and then returned to background level. Residues left as such in the field hold more soil moisture and subsequently released more  $N_2O$  and  $CH_4$  than burned residue plots by providing higher organic matter in the soil and creating anaerobic soil conditions. Methane showed both emission and absorption peaks throughout the years which clearly indicate the involvement of methanogenic or methanotrophic organisms in the soil. Overall, higher correlation of  $N_2O$  release and WFPS was observed in 2012 than 2013 because of higher rainfall days within 3 weeks after N application in 2012. Year 2013 has relatively higher GHG emissions than 2012 due to favorable weather conditions.

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## **Chapter. 4 Characterization of Elemental Composition and Morphological Features of Particulates Emitted from Sugarcane Production**

### **4.1. Introduction**

Particulate matter (PM) of size 10 microns ( $PM_{10}$ ) and less (in particular  $PM_{2.5}$ ) are the major contributors of air pollution and are highly responsible for human health diseases, specifically respiratory problems. Particulate matter along with ozone ( $O_3$ ), carbon monoxide (CO), nitrogen oxides, sulfur dioxide ( $SO_2$ ), and lead (Pb) are considered as the six “criteria pollutants” by United States Environmental Protection Agency (USEPA) under Clean Air Act. Particulates are generally the combination of solid particles and liquid droplets that are present everywhere in the atmosphere. Because of its great variability in chemical, physical, and mineralogical characteristics, PM represents an important and existing research field for mineralogists, geologists, and agriculturists. Airborne particulates are generally classified as primary or secondary depending on their origins. Primary particles are directly emitted to the atmosphere whereas; the secondary particles are generally formed within atmosphere through gas-to-particle conversion (Chung et al., 2008; Giere and Querol, 2010). Particles can also be categorized based upon their size or aerodynamic diameter (Wardoyo, 2007) such as, coarse particles (particle diameter of 2.5 to 10  $\mu m$  size:  $PM_{10}$ ), fine particles (particle diameter of 0.1 to 2.5  $\mu m$  size:  $PM_{2.5}$ ), and ultrafine particles (particle diameter < 0.1  $\mu m$ ). Major sources of  $PM_{2.5}$  (Funk, 2010) are direct emissions from industry, agriculture, vehicle, and secondary formation from sulfur dioxide ( $SO_2$ ), nitrogen oxides ( $NO_x$ ), ammonia ( $NH_3$ ) and volatile organic compounds (VOCs). The primary and secondary particulates contains with harmful carbonaceous compounds (Hays et al., 2005; Dhammapala et al., 2006; Hall et al., 2012; Rajput et al., 2014; Paraskevopoulou et al., 2014), different water soluble ionic species (Turn et al.,

1997; Kim Oanh et al., 2011; Zhang et al., 2012), heavy metals (Li et al., 2007), elemental species (Zhang et al., 2012), and polycyclic aromatic hydrocarbons (Kim Oanh et al., 2011). These fine particles also contain many different trace elements which play a major role in cytotoxicity or inflammation in humans (Dockery et al., 1993) and most of the toxic metals are mainly associated with PM<sub>2.5</sub> as compared to PM<sub>10</sub>. Health problems associated with PM exposure are chronic obstructive pulmonary diseases, asthma, fibrosis, and lung cancer (Fubini and Fenoglio, 2007; Giere and Querol, 2010). In addition to affecting human health, PM has direct and indirect effects on climate (cloud condensation nuclei), ecosystems, and visibility both locally and globally (Giere and Querol, 2010).

Under the National Ambient Air Quality Standards (NAAQS), the average primary (provide public health protection) and secondary standards (provide public welfare protection) for PM<sub>2.5</sub> and PM<sub>10</sub> are 35 and 150  $\mu\text{g m}^{-3}$ , respectively, for 24 hours' time period. However, particles produced during the burning of fossil fuels or plant biomass are most likely to exceed this limit in the source region and can cause serious air quality issues. In addition to that, coarse particles released during biomass burning also create nuisance to the local human community and can reduce the aesthetic value of properties. Release of fine and coarse particles from biomass burning generally depends on the source of the burning materials (Conde et al., 2005). Models and methods like principal component analysis (Thurston and Spengler, 1985), chemical mass balance (USEPA, 2006), and positive matrix factorization (Paatero and Tapper, 1994) have been developed in the past to identify the source and distribution of the air pollutants, however, due to the complexity and unique behavior of the particulates, it is often required to better understand the origin and distribution of the particulates for its physiochemical characterizations.

Agricultural production especially harvest crop residue burning has a major role in releasing these particles into the atmosphere, impairing regional and global air quality (Hobbs et al., 1997; Posfai et al., 2003). Agricultural contribution to the release of fine particulates have been reported in various places including open-air leaf burning in Austria (Schmidl et al., 2008), wood burning in China (Zhang et al., 2012), rice and wheat straw burning in India (Rajput et al., 2014) and also wheat and rice residue burning in California, USA (Hays et al., 2005). However, the impact of biomass burning of row crops such as sugarcane on air quality has not been adequately documented in the past. Sugarcane is an important row crop in major parts of the World. Its production in the US involves different harvesting operations that potentially contribute to the PM emissions into the atmosphere. Particularly two types of residue burning are practiced during sugarcane harvesting, namely standing burn (burning of leaves and trashes of standing sugarcane crops before harvesting) and ground burn (burning of left over sugarcane trashes in the field after harvesting). Burning of standing sugarcane residues facilitates easy harvesting and increase sugar concentration (Arbex et al., 2000; Le Blond et al., 2008), whereas, ground burn of harvesting residue avoids the yield loss of subsequent crop (Richard, 2001; Kennedy and Arceneaux, 2006; Viator et al., 2008).

Chemical characterization of particulates originated from burning different household fuels (such as wood leaves, cook stove) was reported in the past (Zhang et al., 2012), but the information on in-situ residue burning of agricultural crops was very limited (Rajput et al., 2014; Singh et al., 2014), specifically from subtropical sugarcane production. Therefore, the objective of this paper was to characterize the chemical and morphological features of harmful particulates originate from different sugarcane harvesting operations.

## 4.2. Materials and methods

### 4.2.1 Sampling sites and sample collection

Particle samples were collected during sugarcane harvesting in 2012 and 2013 from two sites located at Louisiana State University AgCenter research stations in New Iberia (Iberia parish; 30°00'13"N 91°49'06"W) and in St. Gabriel, Louisiana (Iberville parish, 30°15'13"N 91°6'5"W), respectively. Particulates were collected during four major sugarcane harvesting operations such as regular harvesting (RH) without any burn, standing burn (SB), combine harvesting after standing burn (CH), and ground burn (GB) of harvested residues.

The size distribution of particles (total suspended particulates) was monitored using a Met One optical particle 212 profiler (Met One Instruments Inc, Oregon). The instrument used scattered laser light to count individual particles in the range of 0.5 to 10 µm (8 channels size distribution) and was operated at a sample air flow rate of 1 LPM. The profiler was maintained at about 15 meters away from the harvesting row during RH and CH operations. The collected particle distribution was processed using *profiler utility* software. The profiler was operated 5 minutes before actual harvesting or burning to get the background particle concentration in the ambient air (which was denoted as 0 min in the results) and was kept running for additional 5 minutes after the particle concentration went down to the background level after harvesting or burning.

Particulates for chemical and morphological characterization were collected on Whatman quartz microfibre filters (Whatman International Ltd.) using a Tisch TE-6070 high volume air

sampler (HVAS; Tisch Environmental Inc., Ohio, USA) at downwind position in the field (Fig. 4.1) and operated at a flow rate 40 CFM (1133 LPM).



Fig 4.1. High volume air sampler (HVAS) installed in the field for collecting particles from burning sugarcane residues

The air sampler was kept in downwind position throughout the harvesting event and the sampling time for each harvesting operation was recorded. An example of particulate sample collected on a quartz microfiber filter for ground burn of residues was shown in Fig. 4.2. In addition, gas samples during standing or ground burn of residues were collected in 1 lit PVF tedlar bags (equipped with screw cap) using a portable air sampling pump (LaMotte company, Maryland, USA).



Fig 4.2. Quartz microfiber filter (20.3 x 25.4 cm<sup>2</sup>) after collecting particles from sugarcane residue burning

#### 4.2.2 Laboratory analysis

The collected particulate mass was determined by difference between filter weight before and after sample collection. Soluble ions of particulates were quantified by extracting known portion of the filter paper after sample collection through sonication in 10 ml ultrapure water for 1 hour. The extracts were filtrated using 0.1  $\mu\text{m}$  syringe filter. Cations ( $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ) and anions ( $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ) in the filtrates were then analyzed using a Dionex ICS-2000 ion chromatography (Thermo Fisher Scientific, California, USA) following ASTM method D6919-03 and EPA method 300.0 (Part A), respectively. Organic and elemental carbon of the particulates was analyzed using a Thermal Carbon Analyzer (Sunset Laboratory, Forest Grove, OR, USA) following the National Institute for Occupational Safety and Health (NIOSH) Method 5040 protocol. Total contents of other elements in the particulates were determined by digesting pre-weighed sample-containing filters in an environmental express hot block at  $115^\circ\text{C}$  using 2:1 mixture of  $\text{HNO}_3$ : $\text{HCl}$  followed by analysis in Varian Vista-MPX Simultaneous CCD ICP-OES. Polycyclic Aromatic Hydrocarbons (PAH) in the collected filters were analyzed using gas chromatography-mass spectroscopy (GC-MS) following standard EPA 8270 PAH method and carried out by Test America Inc, (Pensacola, Florida, USA). Volatile organic compounds of the gas samples (tedlar bags) were analyzed using GC-mass spectroscopy (CHEMTEX, Environmental and Industrial Hygiene Services, Texas, USA). Morphological features of particulates were carried out using a JSM-6610LV scanning electron microscope (JEOL Corporation Ltd, MA, USA). A small portion of the sample filter paper was mounted in SEM stub using double side carbon conductive tape and coated with platinum (10 nm) using sputter (EMS 550X) before SEM analysis.

### 4.2.3 Statistical analysis

Analysis of variance (ANOVA) was carried out using SAS 9.3 (SAS Institute. 2012, Cary, NC) and mean separation was done by Tukey-Kramer method at a  $P < 0.05$  level. Regression analysis was also performed to obtain the relation between  $\text{NH}_4^+$  and sulfate ion concentrations.

## 4.3. Results and discussion

### 4.3.1 Size distribution and morphology of particulates

Typical distributions of coarse size (2.5-10  $\mu\text{m}$  diameter) and fine size fraction (<2.5  $\mu\text{m}$  diameter) particles emitted during different sugarcane harvesting operations (RH, GB, SB, and CH) are presented in Figs. 4.3 and 4.4, respectively. Average count of coarse particles released was the highest from CH ( $1.3 \times 10^4 \text{ L}^{-1}$ ), followed by RH ( $5.8 \times 10^3 \text{ L}^{-1}$ ), SB ( $5.0 \times 10^3 \text{ L}^{-1}$ ), and GB ( $4.5 \times 10^2 \text{ L}^{-1}$ ) (Fig. 4.3). However, average number of fine particles emitted was the highest from GB ( $1.8 \times 10^6 \text{ L}^{-1}$ ) followed by SB ( $1.1 \times 10^6 \text{ L}^{-1}$ ), CH ( $2.9 \times 10^5 \text{ L}^{-1}$ ), and RH ( $6.6 \times 10^4 \text{ L}^{-1}$ ).

The result was an obvious indication that burning of sugarcane residues produced significantly higher fine particles as compared to harvesting operations. Clearly, the burning of sugarcane residues (GB and SB) produced significantly higher ( $P < 0.05$ ) fine particles than non-burning harvesting operations. During that burning period GB and SB actually released about 35-55 times more fine particulates hourly average PM emission standard established by NAAQS, which signifies the air pollution of the region during the harvesting operations. While GB and SB had sustained peaks of fine particulate emissions during burning events, RH and CH showed multiple peaks of particle emissions (Figs. 4.3 and 4.4), which was due to the change of distance between the OPD and the harvester during combining.



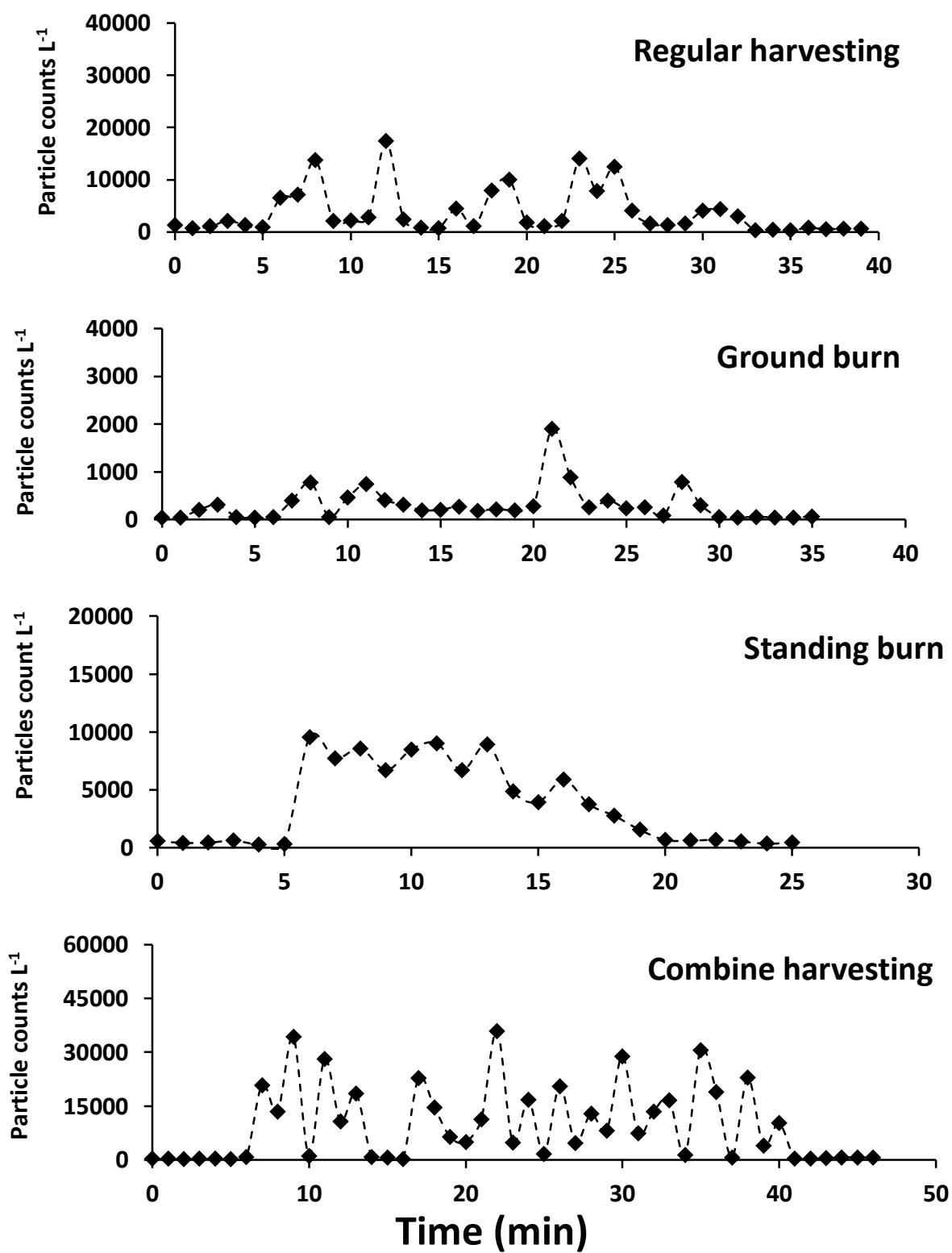


Fig 4.3. Distribution of particle size 2.5-10  $\mu\text{m}$  from different harvesting operations in Louisiana

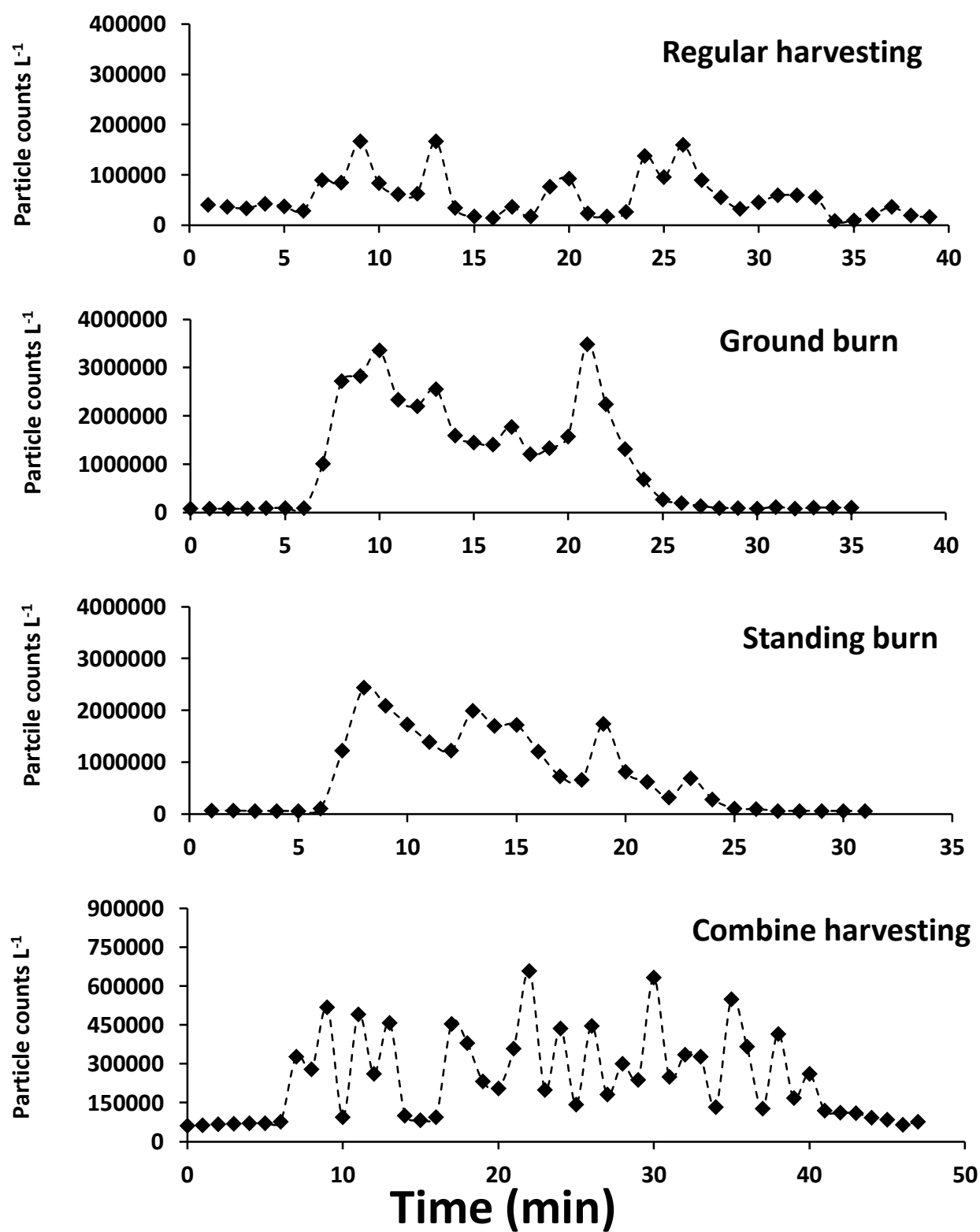


Fig 4.4. Distribution of particles size  $<2.5 \mu\text{m}$  from different harvesting operations in Louisiana

Normal photographic image and SEM images of the collected particles are presented in Fig. 4.5 and Fig. 4.6, respectively. In general, RH looked like the mixture of diluted black color with fade green color (Fig. 4.5) which was probably because of particles collected from RH being mixture of plant and soil dust particles during combining harvesting process (Arslan and Aybek, 2012). On the other hand, GB and SB filter paper looked dark grey and dark black color, respectively, clearly indicating burned carbon particles. The CH photographic image showed loosened black patches, which was due to collection of burned harvesting particles in patches during harvesting after standing burn.

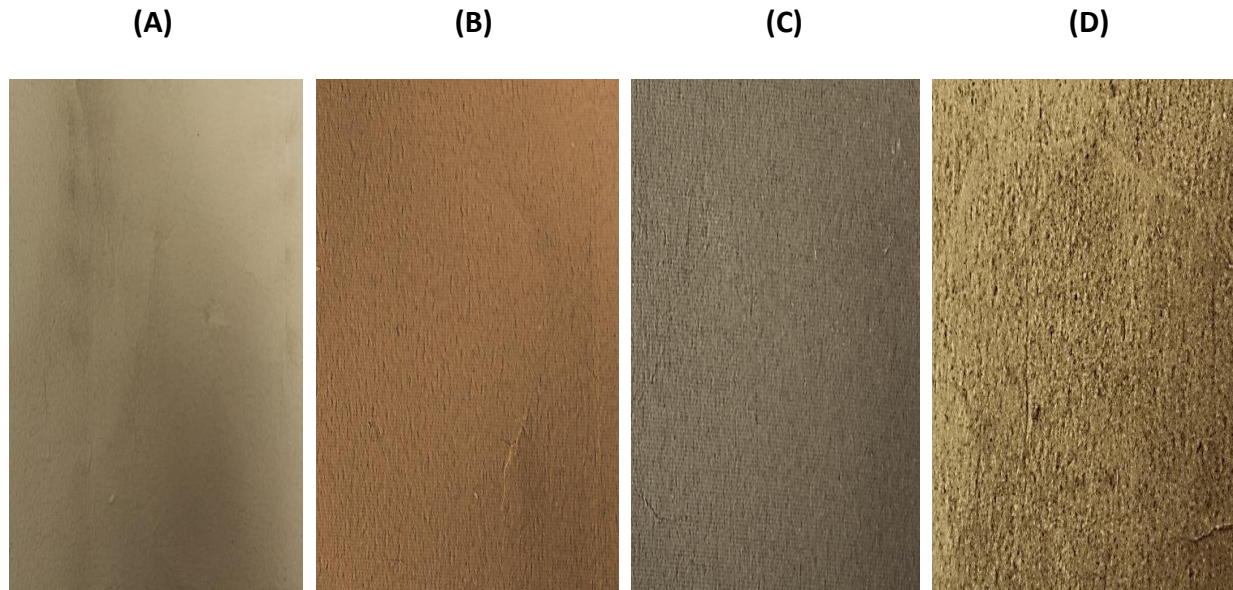
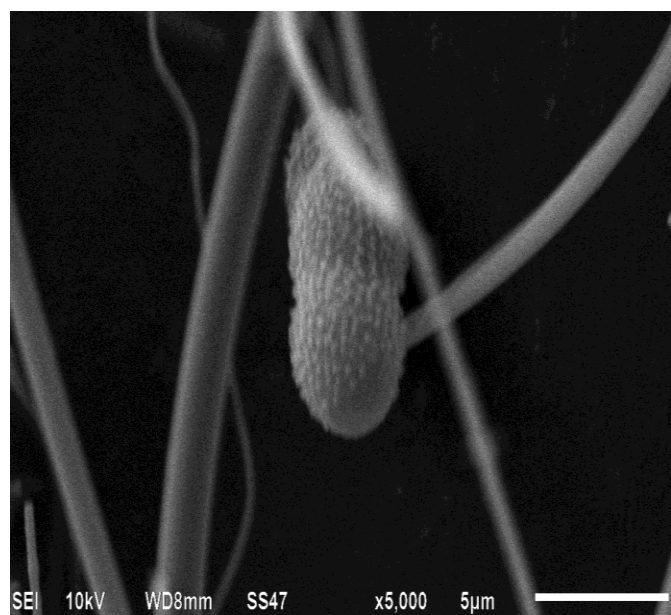
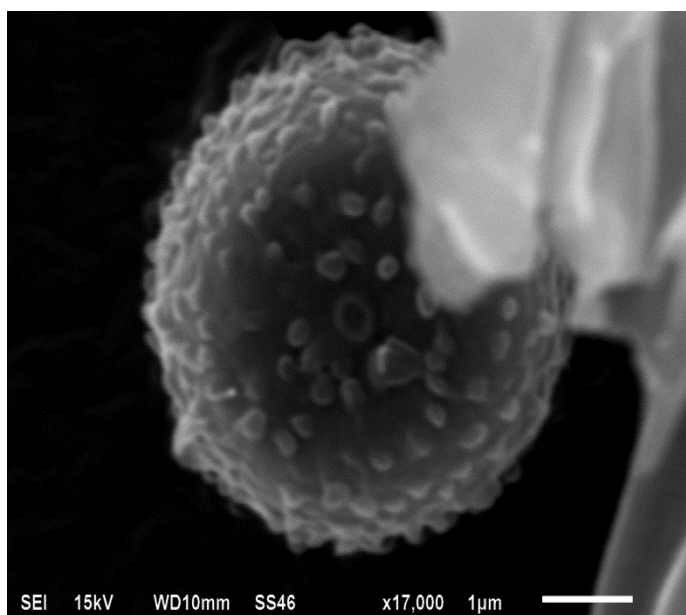
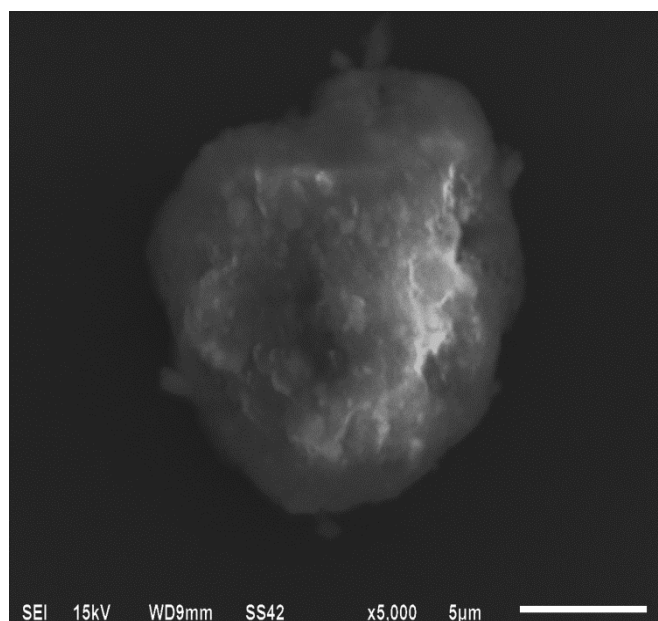
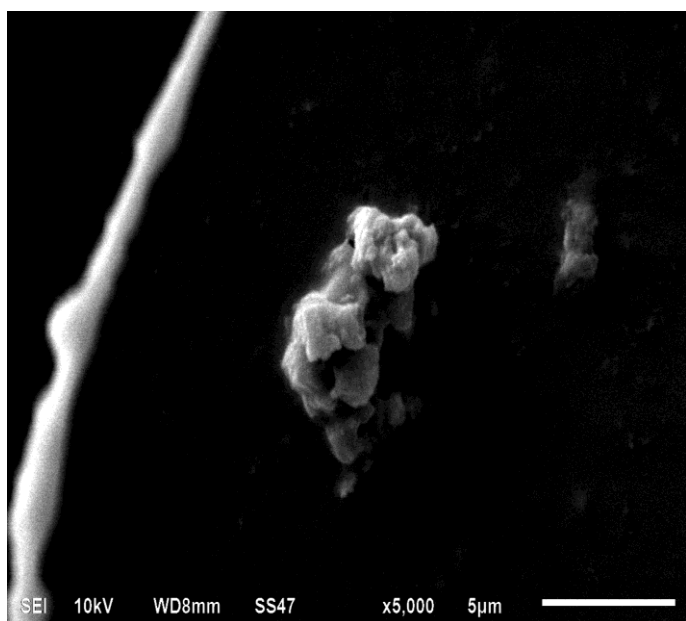


Figure 4.5. Typical photographic images of particulate matter collected in quartz microfibre filters (20.3 x 25.4 cm<sup>2</sup>) from (A) regular harvesting, (B) ground burn, (C) standing burn, and (D) combine harvesting during sugarcane harvesting operations

Scanning electron microscopy images of RH samples showed the plant particles of different shapes (Fig 4.6A). The general shape of the plant particles were circular or elongated tubular.



(1)



(2)

Figure 4.6A. Scanning electron microscopy (SEM) images of particulate matter collected from (1) regular harvesting (RH) and from (2) ground burn (GB) of harvested sugarcane residues

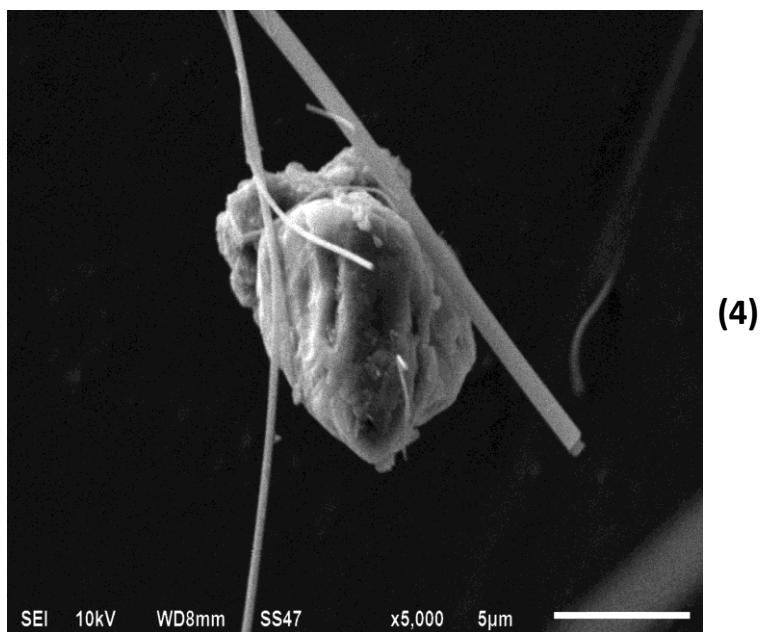
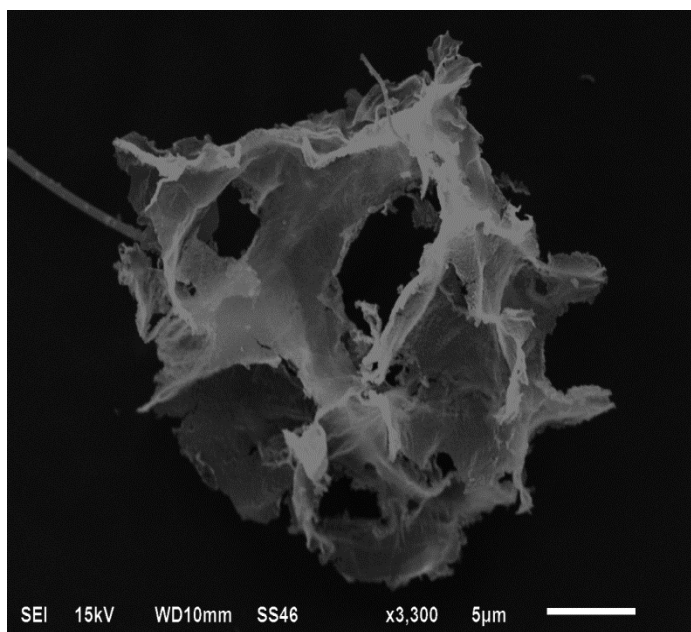
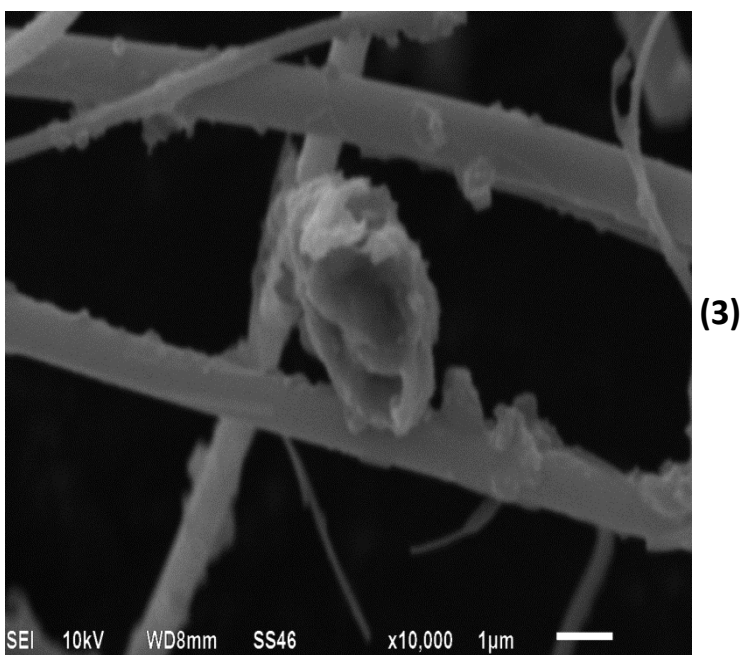
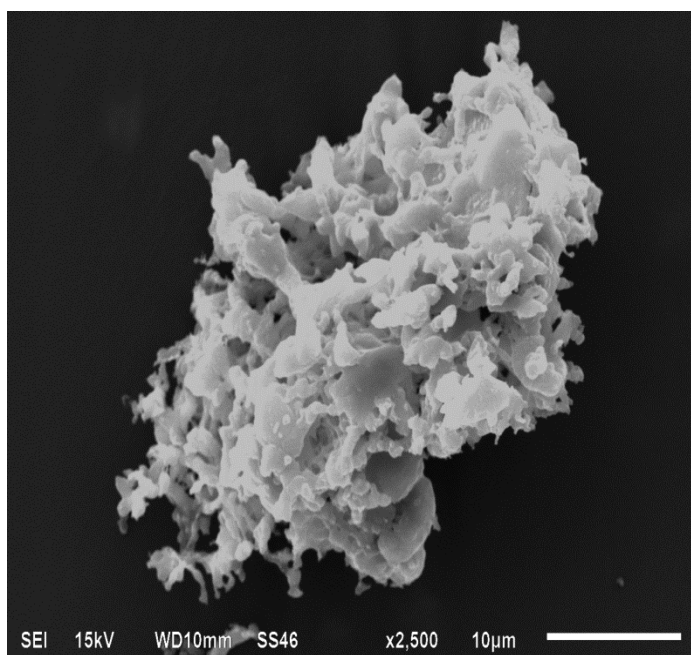


Figure 4.6B. Scanning electron microscopy (SEM) images of particulate matter collected from (3) standing burn (SB) and (4) combine harvesting operations of sugarcane residue.

On the other hand, the particles emitted from GB were more like fused and dense burned particles which occurred in different shapes. The particles collected from SB operation appeared to be agglomerates of small burned particles, which were also reported from grass burning in other research experiments (Li et al., 2004, 2010; Wagner et al., 2012). The CH samples (Fig 4.6B) showed both plant and burned particles and the particles were appeared to be fluffy. The EDX data (Fig 4.7) indicated that GB and SB samples were dominated with C and K elements whereas RH and CH samples with O and Si. These results indicated the difference between PM generated from different harvesting processes and consistent with the results obtained from ICP analysis after digestion.

#### **4.3.2 Total chemical composition of particulate matter from sugarcane harvesting**

Particulate matter of < 10  $\mu\text{m}$  size data collected from different sugarcane harvesting operations for 2012 and 2013 are presented in Table 4.1. Total carbon in PM ranged 23.4-25.9% (average 24.7%) for RH, 70.3-70.6% (average 70.5%) for GB, 60.2-61.4% (average 60.8%) for SB, and 39.3-40.3% (average 39.8%) for CH over 2 years. High C% in PM of GB and SB as compared to that of RH and CH indicated the particle carbonation during burning process. Similar observations were reported in previous studies where carbon compounds made about 42 and 84% of PM mass from rice and wheat residues burning, respectively, in California, USA (Hays et al., 2005), 67% of the total PM mass from wood burning in Austria (Schmidl et al., 2008), 41 and 55% of the total PM mass from wood and coal burning, respectively, in China (Zhang et al., 2012), 32 and 37% of the total PM<sub>2.5</sub> mass from rice-straw and wheat-straw burning, respectively, in Northern India (Rajput et al., 2014).

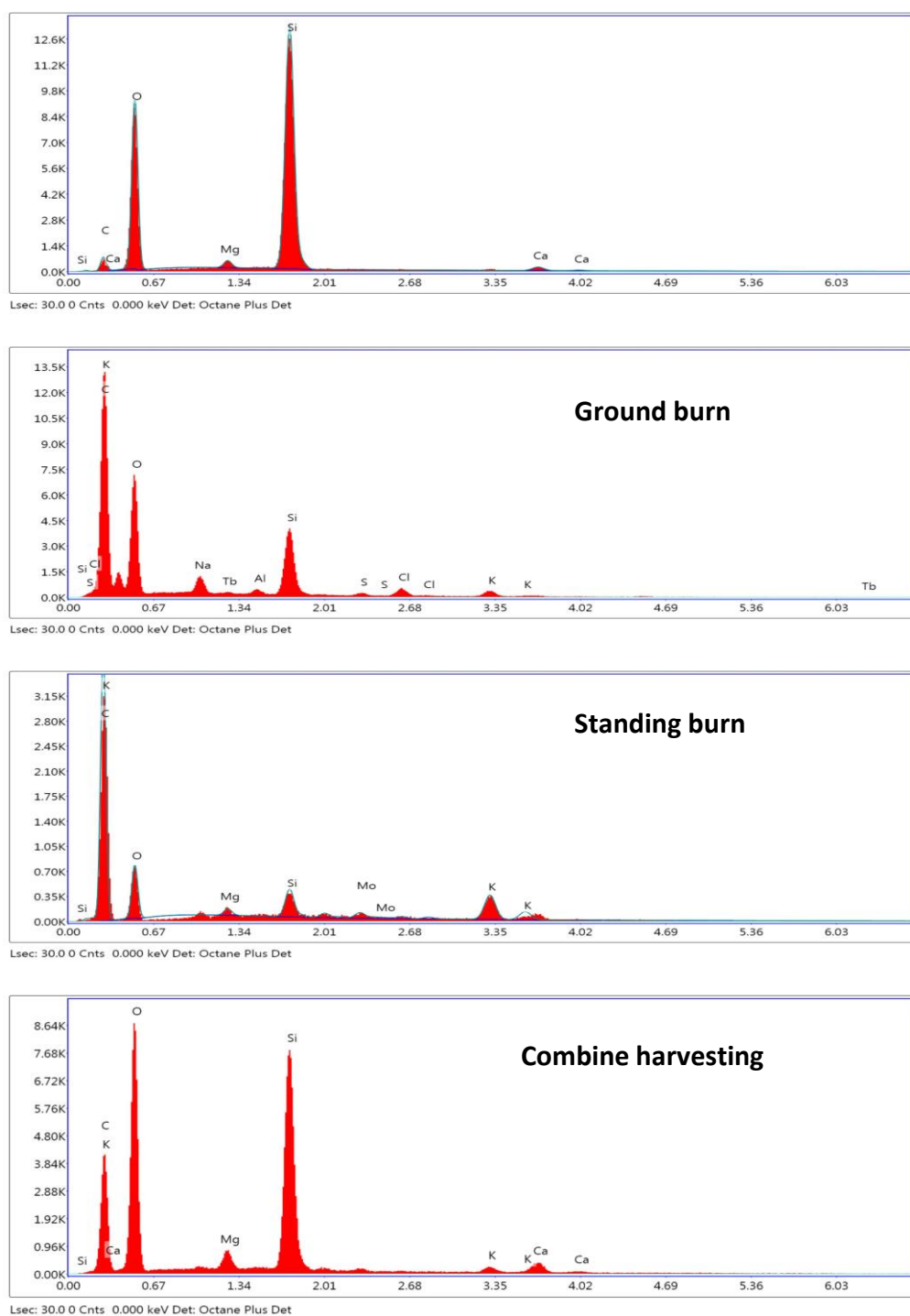


Figure 4.7. EDAX images of (A) Regular harvesting, (B) Ground burn, (C) Stand burn, and (D) Harvesting after stand burn particles collected during sugarcane harvesting

Concentration of organic carbon (OC) in all the particles were found much higher than elemental carbon (EC) concentration and the result was consistent with the findings in previous studies (Dhammapala et al., 2006; Hall et al., 2012; Rajput et al., 2014; Paraskevopoulou et al., 2014). Statistical analysis showed that PM emitted from the two sugarcane burning methods (GB and SB) had significantly higher ( $P < 0.05$ ) organic carbon (OC) as compared to other harvesting operations (RH and CH) in 2012. On the other hand, OC content in particles from all four harvesting operations were found statistically different ( $P < 0.05$ ) from each other's in 2013. However, only GB particles had significantly higher ( $P < 0.05$ ) elemental carbon (EC) as compared to other harvesting methods for both years. Previous studies reported that OC and EC are generally exists in finer particles with a diameter ranged from 0.1 to 1.0  $\mu\text{m}$  (Kleeman et al., 2000; Funaska et al., 2000; Na et al., 2005). Mkoma et al (2013) reported that OC accounted about 86% of the total carbon (TC) in  $\text{PM}_{2.5}$  fraction as compared to 13% of the TC in  $\text{PM}_{10}$  fraction. However, the abundance of EC in finer fraction was documented as much higher as compared to OC (Funaska et al., 2000) and thus EC can penetrate more easily into human respiratory tract and cause different lung and heart diseases (Na et al., 2005). Our result clearly indicates that GB released much finer particles in the air as compared to SB and the result was found consistent with particle size distribution analysis (Fig 4.4).

The OC/EC ratio ranged 6.4-10.4 (average 8.4) for RH, 6.1-6.8 (average 6.5) for GB, 10.8-11.9 (average 11.4) for SB, and 6.2-8.8 (average 7.5) for CH for two years. These ratios were very much comparable with the one found by Rajput et al. (2014) in India, where OC/EC ratio of GB particles from rice and wheat residue burning were 10.6 and 3.0, respectively. In another field study conducted in Northern India, the average OC/EC ratio was reported as 13.0



from rice residue burning (during winter season) and 4.0 from wheat residue burning (during summer season) (Singh et al., 2014). An OC/EC ratio of 11.2 was documented in particulates emitted from open burning of corn stover in Eastern China (Li et al., 2007). Relatively lower OC/EC ratio (OC/EC = 5.8) was found from rice field burning particles in Thailand (Kim Oanh et al., 2011). So, it can be concluded that the OC/EC ratio from residue burning varies considerably depending on the residue types, burning methods and analysis of the samples.

Ammonium,  $K^+$ ,  $Na^+$ , and  $Mg^{2+}$  were the major water soluble cations found in the particulates in this research study. Among water soluble ionic species,  $NH_4^+$  accounted as 2.2-2.4% (average 2.3%) for RH, 6.4-7.1% (average 6.8%) for GB, 4.5-5.1% (average 4.8%) for SB, and 2.5-2.8% (average 2.7%) for CH for 2 years. The ammonium ion concentration found in our experiment was higher than 3.0% of the total PM mass from sugarcane residue burning at California, USA (Turn et al., 1997), and 2.4% from rice straw burning at Thailand (Kim Oanh et al., 2011) and lower than 11 and 9% from wood and coal burning in China (Zhang et al., 2012), Ammonium ion concentration in GB particles was significantly higher ( $P < 0.05$ ) than SB particles in 2012 possibly because GB has more reduced condition to emit more ammonia as compared to SB. In both years, burning operations produced particulates with significantly higher  $NH_4^+$  as compared to other operations clearly indicating enrichment of  $NH_4^+$  particles during burning process. The potassium ion generally used as a tracer or marker of biomass burning (Andreae, 1983) accounts for an average of 2.6 and 2.0% for GB and SB particles as compared to 0.5 and 0.41% for RH and CH (Table 4.1), respectively, in our experiment. These results were found very similar to other experiment such as 2.5% of PM mass from wheat straw burning (Singh et al., 2014), but lower than 8.5% from corn stover burning (Li et al., 2007).

Table 4.1. Chemical compositions of particulates collected during different sugarcane harvesting operations at Louisiana, USA

Chemical composition	2012				2013			
	Regular harvesting	Ground burn	Stand burn (SB)	Combined harvest	Regular harvesting	Ground burn	Stand burn (SB)	Combined harvest
-----Weight % of total PM mass-----								
<b>A. Carbon content analysis<sup>¶</sup></b>								
OC	20.22 ± 3.29 c	60.70 ± 6.23 a	55.03 ± 6.16 a	34.67 ± 3.98 b	23.61 ± 4.15 c	61.33 ± 7.69 a	56.67 ± 5.96 a	35.26 ± 4.45 b
EC	3.14 ± 0.40 c	9.90 ± 1.55 a	5.11 ± 0.71 b	5.58 ± 0.64 bc	2.27 ± 0.61 c	8.98 ± 1.12 a	4.75 ± 0.67 b	3.99 ± 0.71 bc
TC	23.37 ± 3.69 c	70.62 ± 7.04 a	60.17 ± 8.09 a	40.27 ± 4.62 b	25.88 ± 3.54 c	70.31 ± 9.38 a	61.44 ± 6.19 a	39.25 ± 3.33 b
<b>B. Water soluble ionic species<sup>‡</sup></b>								
NH <sub>4</sub> <sup>+</sup>	2.43 ± 0.42 c	6.44 ± 0.82 a	4.48 ± 0.45 b	2.49 ± 0.47 c	2.22 ± 0.36 c	7.11 ± 1.27 a	5.1 ± 0.47 ab	2.77 ± 0.52 bc
K <sup>+</sup>	0.41 ± 0.16 b	2.24 ± 0.39 a	1.88 ± 0.54 a	0.32 ± 0.09 b	0.59 ± 0.14 b	2.86 ± 0.41 a	2.13 ± 0.33 a	0.50 ± 0.13 b
Na <sup>+</sup>	0.27 ± 0.05 c	0.55 ± 0.11 a	0.45 ± 0.11 ab	0.39 ± 0.08 ab	0.56 ± 0.13 a	0.85 ± 0.20 a	0.63 ± 0.12 a	0.48 ± 0.11 a
Mg <sup>2+</sup>	0.12 ± 0.03 b	0.43 ± 0.09 a	0.21 ± 0.05 b	0.14 ± 0.04 b	0.22 ± 0.06 c	0.61 ± 0.13 a	0.46 ± 0.08 b	0.37 ± 0.06 bc
Br <sup>-</sup>	0.09 ± 0.01 a	0.11 ± 0.03 a	0.13 ± 0.02 a	0.04 ± 0.01 a	0.06 ± 0.01 b	0.16 ± 0.03 a	0.14 ± 0.02 a	0.02 ± 0 b
Cl <sup>-</sup>	0.43 ± 0.05 b	1.88 ± 0.34 a	0.48 ± 0.13 ab	0.22 ± 0.09 b	0.47 ± 0.08 c	3.55 ± 0.62 a	2.14 ± 0.38 b	0.39 ± 0.13 c
F <sup>-</sup>	0.40 ± 0.12 c	0.96 ± 0.23 a	0.87 ± 0.24 ab	0.63 ± 0.29 bc	0.12 ± 0.04 c	0.75 ± 0.13 a	0.56 ± 0.16 ab	0.29 ± 0.10 bc
NO <sub>3</sub> <sup>-</sup>	0.28 ± 0.07 c	0.42 ± 0.12 a	0.35 ± 0.09 b	0.26 ± 0.09 c	0.36 ± 0.07 b	0.62 ± 0.17 a	0.45 ± 0.12 ab	0.39 ± 0.11 B
PO <sub>4</sub> <sup>3-</sup>	1.18 ± 0.21 a	1.49 ± 0.27 a	1.31 ± 0.19 a	1.21 ± 0.31 a	1.26 ± 0.36 a	1.40 ± 0.36 a	1.30 ± 0.13 a	1.14 ± 0.18 a
SO <sub>4</sub> <sup>2-</sup>	1.53 ± 0.37 b	3.94 ± 0.62 a	2.91 ± 0.39 a	1.34 ± 0.27 b	2.10 ± 0.40 b	3.82 ± 0.54 a	3.29 ± 0.26 a	0.94 ± 0.13 c
<b>C. Elemental composition<sup>§</sup></b>								
P	0.57 ± 0.11 a	0.59 ± 0.12 a	0.50 ± 0.09 a	0.68 ± 0.14 a	0.89 ± 0.18 a	0.49 ± 0.13 b	0.49 ± 0.11 b	0.55 ± 0.07 b
K	0.71 ± 0.14 ab	2.76 ± 0.46 a	2.58 ± 0.50 bc	0.45 ± 0.09 c	0.78 ± 0.13 c	3.93 ± 0.47 a	2.55 ± 0.41 b	0.58 ± 0.11 c
Ca	0.55 ± 0.17 b	1.23 ± 0.27 a	1.28 ± 0.29 a	0.67 ± 0.15 b	0.67 ± 0.23 b	1.52 ± 0.45 a	1.81 ± 0.30 a	0.72 ± 0.16 b

Table 4.1. Continued

Mg	0.31 ± 0.09 b	0.65 ± 0.11 a	0.57 ± 0.12 ab	0.39 ± 0.04 b	0.28 ± 0.08 c	0.97 ± 0.24 a	0.76 ± 0.24 ab	0.45 ± 0.11 bc
S	0.92 ± 0.21 b	1.87 ± 0.40 a	1.75 ± 0.28 a	0.84 ± 0.19 b	1.08 ± 0.30 b	2.15 ± 0.61 a	2.33 ± 0.56 a	0.48 ± 0.17 c
Na	1.26 ± 0.37 a	1.08 ± 0.21 a	1.31 ± 0.19 a	1.06 ± 0.22 a	1.51 ± 0.20 a	0.98 ± 0.14 a	1.02 ± 0.17 a	1.27 ± 0.23 a
Si	1.74 ± 0.56 a	0.79 ± 0.13 b	0.43 ± 0.06 b	1.48 ± 0.19 a	1.43 ± 0.16 a	0.53 ± 0.16 c	0.33 ± 0.07 c	0.88 ± 0.21 b
Fe	0.60 ± 0.10 a	0.19 ± 0.04 b	0.17 ± 0.04 b	0.39 ± 0.09 ab	0.52 ± 0.12 a	0.15 ± 0.02 b	0.27 ± 0.02 b	0.29 ± 0.10 ab
Al	0.33 ± 0.07 a	0.02 ± 0.00 a	0.09 ± 0.01 a	0.39 ± 0.06 a	0.21 ± 0.07 a	0.03 ± 0.01 a	0.19 ± 0.02 a	0.06 ± 0 a

¶ Analyzed by thermal carbon analyzer

‡ Analyzed by ion chromatography

§ Analyzed by ICP-OES

The ratio of water soluble  $K^+$  ion and OC content in PM ( $K^+/OC$ ) is often used as the indicator to differentiate between residue burning and other organic C sources (Mkoma et al., 2013), and was found with an average value of 0.04 to 0.05 (same for both SB and GB) in our experiments. The ratio was close to 0.07 from wood burning in China (Zhang et al., 2012) and 0.06 from rice straw burning in northern India (Rajput et al., 2014), but lower than 0.06 to 0.36 from crop residue burning at east Africa (Mkoma et al., 2013). Other two cations ( $Na^+$  and  $Mg^{2+}$ ) did not show any considerable differences among residue burning and harvesting methods over the years.

Sulfate was the major water soluble anion found in the particulates followed by  $PO_4^{3-}$  and  $Cl^{-1}$  (Table 4.1). On average,  $SO_4^{2-}$  contributed about 44-40% of the total water soluble anionic mass of the particulates collected over two years. Ground burn and SB operations produced significantly higher ( $P < 0.05$ )  $SO_4^{2-}$  than RH and CH. Chloride ion concentration in GB particles was also

statistically higher than SB and other harvesting operations. However, there was no difference in particulate phosphate concentrations from all harvesting operations over the two years.

It is interesting to note that strong correlation was found between  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ion concentration for this experiment (Fig 4.8). The strong correlation of these two ions with linear regression slope ranging from 0.7046 to 1.0765 indicated that sulfate ions were completely neutralized by ammonium ions for both types of residue burnings and helped in forming high number of ammonium sulfate particulates in the ambient air. A very high correlation of  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ions from particulates of wood and coal burning was also reported (Zhang et al., 2012). Ammonium sulfate is highly responsible for different human respiratory problems as well as scattering of incoming solar radiation (Andreae and Curtzen, 1997).

Among total elemental species, K, S, Si, Ca and Na contributed the most to the total PM mass for all harvesting operations. The K concentration was significantly higher ( $P < 0.05$ ) in burned particles (GB and SB) than harvesting particles for both years (Table 4.1). However, Si content in particles of RH and CH operations was significantly higher than GB and SB particles indicating potential soil dust contribution from combine harvesting. On the other hand, sugarcane (*Saccharum* sp) is a member of Poaceae (grass) family and generally accumulates higher Si in leaves and tissues (Le Blond et al., 2008; Naidoo et al., 2009). Regular harvesting released a large amount of sugarcane plant particles in the air, which could also add to the explanation why RH particles contained higher amount of Si than burning particles. Other elements (P, Mg, Fe, and Al) all together contributed less than 2% of the total PM mass in this experiment.

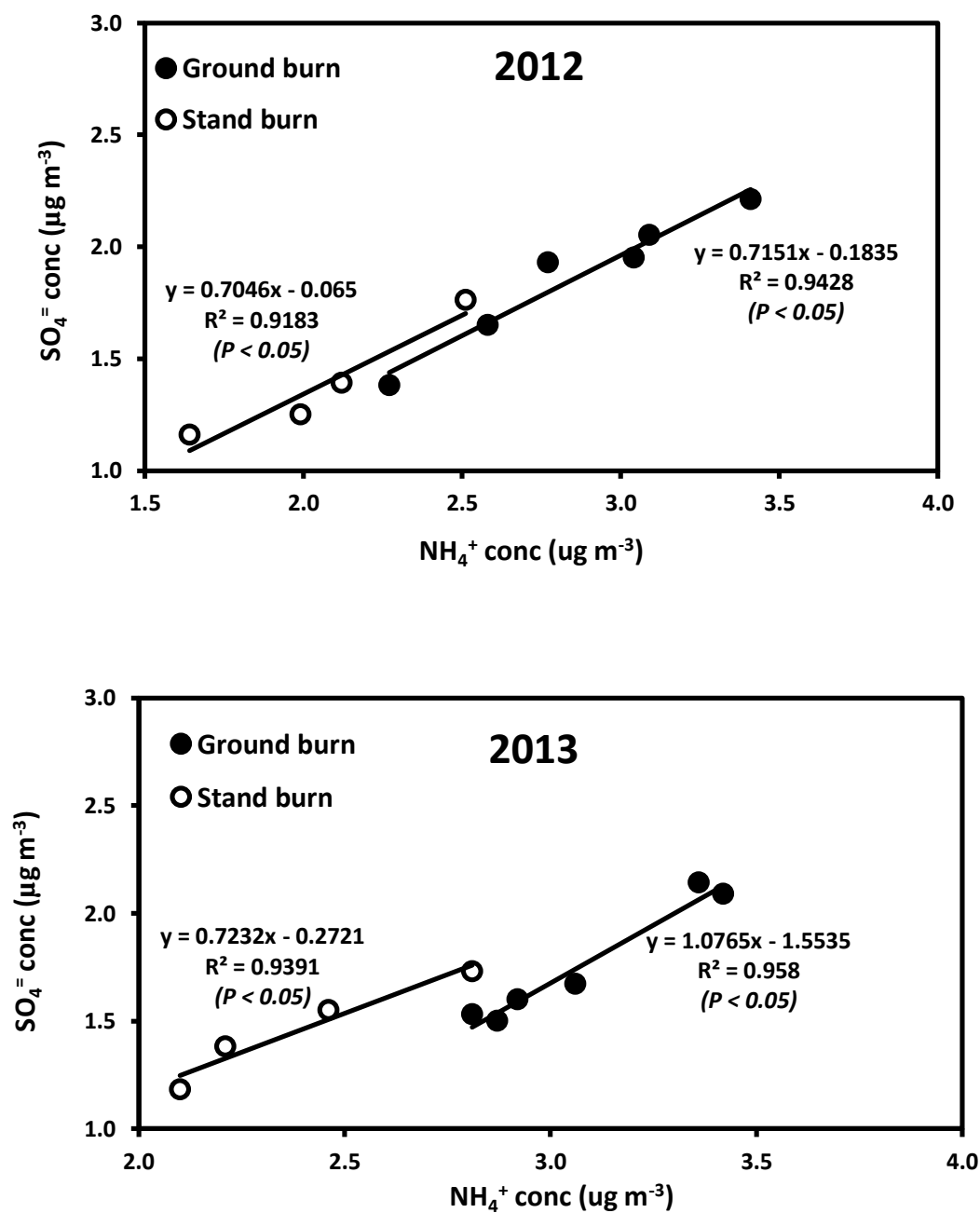


Fig 4.8. Correlation of ammonium and sulfate ion concentration from ground burn and stand burn particles emitted from sugarcane biomass burning for two years

Table 4.2. Summary of PAHs in particulate samples collected during sugarcane residue burning and combining

PAHs	Ground burn	Stand burn	Combine harvest
	----- Weight % of total PM mass -----		
Benzopyrene	0.0067 ± 0.0008	0.0008 ± 0.000	ND
Benzo[b]fluoranthene	0.0062 ± 0.0010	0.0044 ± 0.0007	ND
Benzoperylene	0.0058 ± 0.0012	0.0054 ± 0.0011	ND
Benzo[k]fluoranthene	0.0018 ± 0.0003	0.0013 ± 0.000	ND
Chrysene	0.0015 ± 0.0003	0.0020 ± 0.0004	ND
Fluoranthene	0.0009 ± 0.000	0.0023 ± 0.0006	ND
Indenopyrene	0.0056 ± 0.0007	ND	ND
Pyrene	0.0007 ± 0.000	0.0015 ± 0.0002	0.0008 ± 0.0002
Phenanthrene	0.0220 ± 0.0032	0.0143 ± 0.0019	ND
Benzo-anthracene	0.0020 ± 0.0005	0.0020 ± 0.000	ND
Acenaphthylene	0.0093 ± 0.0015	0.0087 ± 0.0009	ND
Anthracene	ND	0.0009 ± 0.000	0.0008 ± 0.000

ND: Not detected

Polycyclic aromatic hydrocarbons found in collected particles from burning residues are presented in Table 4.2. Particulate samples from RH were not analyzed. Low molecular weight PAHs (three benzene rings or less) such as phenanthrene (C<sub>14</sub>H<sub>10</sub>) and acenaphthylene (C<sub>12</sub>H<sub>8</sub>) contributed a major percentage of the total PAH concentration in the particles as compared to

pentacyclic or hexacyclic high molecular hydrocarbons such as benzopyrene ( $C_{20}H_{12}$ ), benzo-fluoranthene ( $C_{20}H_{12}$ ), and indenopyrene ( $C_{23}H_{14}$ ). Similar findings were also observed from particulates emitted from pre-harvesting sugarcane residue burning in Florida, USA (Hall et al., 2012) and from wood burning in Southern US (Conde et al., 2005). In fact, phenanthrene itself contributed about 47 and 41% of the total PAH mass for GB and SB particles, respectively. About eleven PAH was detected in both GB and SB particles, however, most of the PAHs emitted from GB particles were found significantly higher ( $P < 0.05$ ) in concentration than in SB particles. Our results also showed that particles from combined harvesting did not release any significant amount of PAH in the air. Polycyclic hydrocarbons are known for having carcinogenic and teratogenic properties (Conde et al., 2005) and can cause birth defects, cancerous tumors and developmental disorders in mammals. Our results clearly indicate that ground burning of sugarcane residues can generate significantly higher PAH-contained particulates and eventually cause more health problems for human beings living near the source regions.

#### **4.3.3 Analysis of volatile organic compounds and molar emission ratio of the smoke samples collected during burning of sugarcane residues**

Volatile organic compounds (VOC) were collected and analyzed from smoke gas samples collected during sugarcane residue burning (GB and SB) and the results are summarized in Table 4.3. Isoprene ( $C_5H_8$ ) and propylene or propene ( $C_3H_6$ ) were the major VOCs found in the sample with averaging about 0.098 and 0.168, respectively, for SB and 0.435 and 0.432, respectively, for GB. Both of these compounds were significantly higher ( $P < 0.05$ ) in GB samples than in SB samples. Benzene ( $C_6H_6$ ) was another VOC also found in both burning

particles but with relatively higher concentration in GB samples (Table 4.3). A considerable amount of butane ( $C_4H_{10}$ ), propane ( $C_3H_8$ ), and toluene ( $C_7H_8$ ) were only found in GB particles.

Table 4.3. Summary of VOC in smoke gas samples collected during sugarcane residue burning

Volatile organic compounds	Stand burn	Ground burn
	-----ppmv -----	
Isoprene	$0.098 \pm 0.019$	$0.435 \pm 0.110$
Propylene	$0.168 \pm 0.039$	$0.424 \pm 0.112$
Butane	ND	$0.120 \pm 0.028$
1-butene	ND	$0.117 \pm 0.025$
Propane	ND	$0.116 \pm 0.031$
t-2-butene	$0.05 \pm 0.01$	$0.088 \pm 0.013$
Benzene	$0.039 \pm 0.007$	$0.080 \pm 0.017$
1,3-Butadiene	$0.028 \pm 0.005$	$0.061 \pm 0.009$
Toluene	ND	$0.034 \pm 0.007$
4-Methyl-1-Pentene	ND	$0.029 \pm 0.007$
3-Methylheptane	ND	$0.029 \pm 0.005$
2-Methyl-1-Pentene	ND	$0.027 \pm 0.006$
t-2-pentene	$0.099 \pm 0.018$	ND
Pentane	$0.074 \pm 0.021$	ND
Hexane	$0.040 \pm 0.009$	ND

ND: Not detected



Toluene has often considered as the model organic compound of secondary particle emissions in previous studies (Hildebrandt et al., 2009; Stockwell et al., 2015). Major VOC were reported as benzene and toluene from sugarcane residue burning in Florida, USA (Hall et al., 2012), propene, propane, benzene, and toluene from agricultural residue burning in eastern China (Suthawaree et al., 2010), toluene from African savanna grass and US grass burning in Montana, USA (Stockwell et al., 2015). Other volatile organic compounds such as pentane and hexane were only found in SB particles. Volatile organic carbon along with nitrogen oxides can produce surface ozone (O<sub>3</sub>) through photochemical reactions (Suthawaree et al., 2010) which is responsible for skin cancer in human beings. In addition to that VOC can also cause eye and throat irritation, damage to liver, kidney, and central nervous systems.

Table 4.4. Molar emission ratios of selected carbon gases released from smoke gas samples collected during burning of sugarcane residues over four years

Year	Ground burn		Stand burn	
	CO/CO <sub>2</sub>	CH <sub>4</sub> /CO <sub>2</sub>	CO/CO <sub>2</sub>	CH <sub>4</sub> /CO <sub>2</sub>
2010	0.241	0.010	0.058	0.006
2011	0.187	0.011	0.087	0.002
2012	0.440	0.015	0.094	0.002
2013	0.204	0.012	0.062	0.002

The average emission ratio of CO/CO<sub>2</sub> during four years of available collections for SB was found 0.08 (Table 4.4) which was lower than 0.1 indicating that the burning was dominated

by flaming phase (Zhang et al., 2008a; Zhang et al., 2012). However, CO/CO<sub>2</sub> ratio of 0.26 for GB depicts the dominance of smoldering phase during burning (Hurst et al., 1994; Zhang et al., 2008a). Similar CO/CO<sub>2</sub> ratio was observed from rice and wheat straw burning in China (Zhang et al., 2008a). In addition, the average CH<sub>4</sub>/CO<sub>2</sub> ratio of SB (0.003) was found much lower than GB (0.013) which indicated that GB situation was generally under a more reduced condition than SB operation.

#### **4.4 Conclusion**

This study demonstrates that biomass burning operations (GB and SB) were dominated with higher PM<sub>2.5</sub> emission than RH and CH operations during sugarcane harvesting. Chemical characteristics of particulates emitted from sugarcane harvesting at Louisiana, USA indicated that carbonaceous particles contributed most of the total PM mass, averaging 25% for RH, 69% for GB, 59% for SB, and 40% for CH. Statistically higher elemental carbon in GB indicated much finer fraction of particles as compared to SB. Ammonium was the major water soluble cation found in all particulates and it was highly correlated with SO<sub>4</sub><sup>2-</sup> concentration, thus subsequently released higher number of secondary particles in the air. Higher concentration of Si found in harvesting particulates revealed that RH mainly produced plant particles in the air. Organic carbon, major water soluble ions and elemental species were found significantly higher in GB particles than SB particles. Particulates from sugarcane residue burning (GB, SB, and CH) were dominated by low molecular weight PAHs, and GB released significantly higher PAHs in the air than SB and CH operations. Analysis of smoke gas samples collected during burning events showed that isoprene and propylene were the major VOCs and higher numbers of VOCs were released from the GB operation than SB operation. There was much higher molar ratio of

CH<sub>4</sub>/CO<sub>2</sub> found in lower in smoke samples GB than SB, indicating generally more reduced conditions under GB than under SB of sugarcane biomass during harvesting.

#### 4.5 References

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## **Chapter. 5 Micrometeorological Study of Diurnal Ammonia Flux and The Concentration of PM<sub>2.5</sub> from Sugarcane Production in Louisiana**

### **5.1 Introduction**

Ammonia is very reactive gas and one of the most abundant nitrogen containing compounds in the atmosphere. It plays an important role in the atmospheric chemistry because of its acid neutralizing capacity and ability to form different fine secondary particles such as ammonium sulfate, ammonium nitrate, ammonium bi-sulfate, ammonium chloride etc. In order to understand the chemistry of atmospheric ammonia, it is very important to measure accurately the NH<sub>3</sub> flux and different factors controlling the flux. Land-atmosphere exchange of gaseous NH<sub>3</sub> in agricultural system is controlled by different factors such as, fertilizer source, fertilizer application rate, soil type, crop type, leaf surface water, and different meteorological parameters (Flechard et al., 2013). Vertical NH<sub>3</sub> flux can be strongly be influenced by immediate rainfall after N application (Tian et al., 2015), air temperature (Sutton et al., 2000; Sutton et al., 2013), season (Horvath et al., 2005), wind speed (Flechard et al., 2013) and wind direction (walker et al., 2006). In general, vertical wind speed increases NH<sub>3</sub> emission above crop canopy by creating unstable atmospheric conditions. However, large wind speed can also help in NH<sub>3</sub> dispersion (Loubet et al., 2009a) and subsequently reduce NH<sub>3</sub> concentrations near point sources (Flechard and Fowler, 1998a; Flechard et al., 2013). Leaf surface water (LSW) generally acts as water soluble NH<sub>3</sub> sink (Flechard et al., 2013) by blocking stomatal openings (Zhang et al., 2003), because of its acidic nature the LSW express an affinity for atmospheric NH<sub>3</sub> (Flechard and Fowler, 1998b) as well as NH<sub>3</sub> emitted from the soil (Nemitz et al., 2000a). Many methods have been used to calculate the concentration of atmospheric NH<sub>3</sub> in the past. But because of strong bi-directional flux of NH<sub>3</sub> between soil and/or plant and atmosphere, it is very important to

calculate the overall flux above the crop canopy. A lot of different methods and models such as the foot print model (Leclerc and Thurtell, 1990; Schuepp et al., 1990; Haenel and Grunhage, 1999; Horst, 2001; Schmid, 2002; Foken and Leclerc, 2004), active and passive ammonia sampling system (Sutton et al., 2001b), continuous flow denuder (Wyers et al., 1993), and V<sub>2</sub>O<sub>5</sub>-coated denuder (Keuken et al., 1989) have been developed for calculating vertical NH<sub>3</sub> flux from atmosphere.

Ammonia exchange flux in agricultural fields has been well documented in several studies (Sutton et al., 2000; Herrmann et al., 2001; Walker et al., 2006; Spirig et al., 2010). However, in-situ NH<sub>3</sub> measurement for a longer duration is often limited when crops are present in the field (Sutton et al., 2000). Ammonia flux measurements using chamber techniques (Tian et al., 2015) are not very efficient in collecting samples for every few hours and are in general limited to collect samples on occasional days (Harper et al., 1987; Sutton et al., 2000). Continuous NH<sub>3</sub> flux measurement has been successfully done in recent years using micrometeorological studies (Sutton et al., 2000; Spirig et al., 2010), specifically using the aerodynamic gradient method (AGM) and more recently relaxed eddy accumulation (Hensen et al., 2009; Spirig et al., 2010). Micrometeorological measurement of ammonia is the study of different flux measurement techniques to calculate the vertical turbulent flow of NH<sub>3</sub> within atmospheric boundary layers by using different models and equations. This technique with active samplers can measure the vertical NH<sub>3</sub> flux very successfully.

Research on micrometeorological NH<sub>3</sub> flux analysis over crop canopy is very limited (Sutton et al., 2000), particularly from subtropical crop production. Our research project has been



planned to evaluate the  $\text{NH}_3$  emission from subtropical sugarcane production and also to analyze the relation between  $\text{NH}_3$  fluxes with different meteorological parameters.

## **5.2. Materials and methods**

### **5.2.1 Annular denuder system (ADS)**

The Annular Denuder System (ADS) is an instrument used for trapping different gases ( $\text{NH}_3$ ,  $\text{HNO}_3$ ,  $\text{HONO}$ ,  $\text{SO}_2$ , and  $\text{HCl}$ ), and different atmospheric fine particles ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$ ) in the atmosphere. An USEPA approved ADS (URG-3000C, URG Corporation, Chapel Hill, NC, USA) was used for this current experiment (Fig. 5.1). Two ADS were installed at 10 ft and 18 ft heights above the ground in a meteorological tower situated in the middle of the sugarcane field (Fig. 5.2). The denuders were installed at two different heights to calculate the vertical  $\text{NH}_3$  emission flux above sugarcane crop canopy. Each ADS was consisted of 2 annular denuders (150 mm length each), 2 circular couplers for connecting the denuders, one filter pack (containing Teflon and nylasorb filters in series), and one 2.5  $\mu\text{m}$  cut size cyclone air inlet which only allowed particulates of  $\leq 2.5 \mu\text{m}$  in diameter to pass through the system and deposited in the filters. Teflon (47 mm, 2.0  $\mu\text{m}$ , Pall Corporation, NY, USA) and nylasorb (47 mm, 1.0  $\mu\text{m}$ , Pall Corporation, NY, USA) filters were separated by stainless porous screens inside the filter packs. Three concentric glass channels were connected (1 mm annular space) with each other inside each denuder and provided enough surface area for  $\text{NH}_3$  absorption. Each ADS (10 and 18 ft) was connected with air sampling pumps (URG-3000-02BB) which were operated at a flow rate of 10  $\text{L min}^{-1}$ . Two dry gas meters (Gallus 2000-G1, Actaris Metering Systems, Netherlands) were also installed to measure the volume of air passed through the ADS.

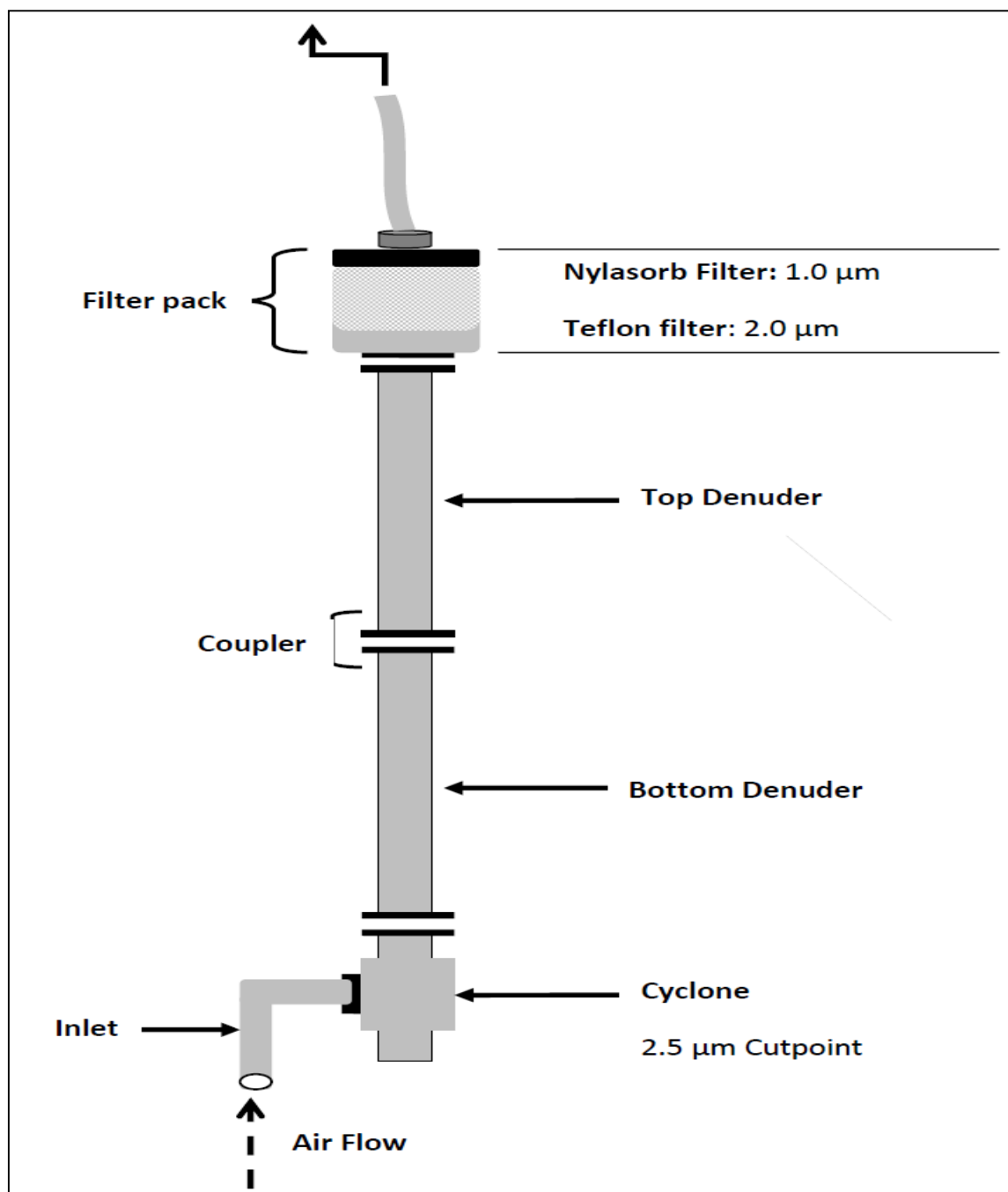


Fig 5.1. Schematic diagram of Annular Denuder System (ADS)

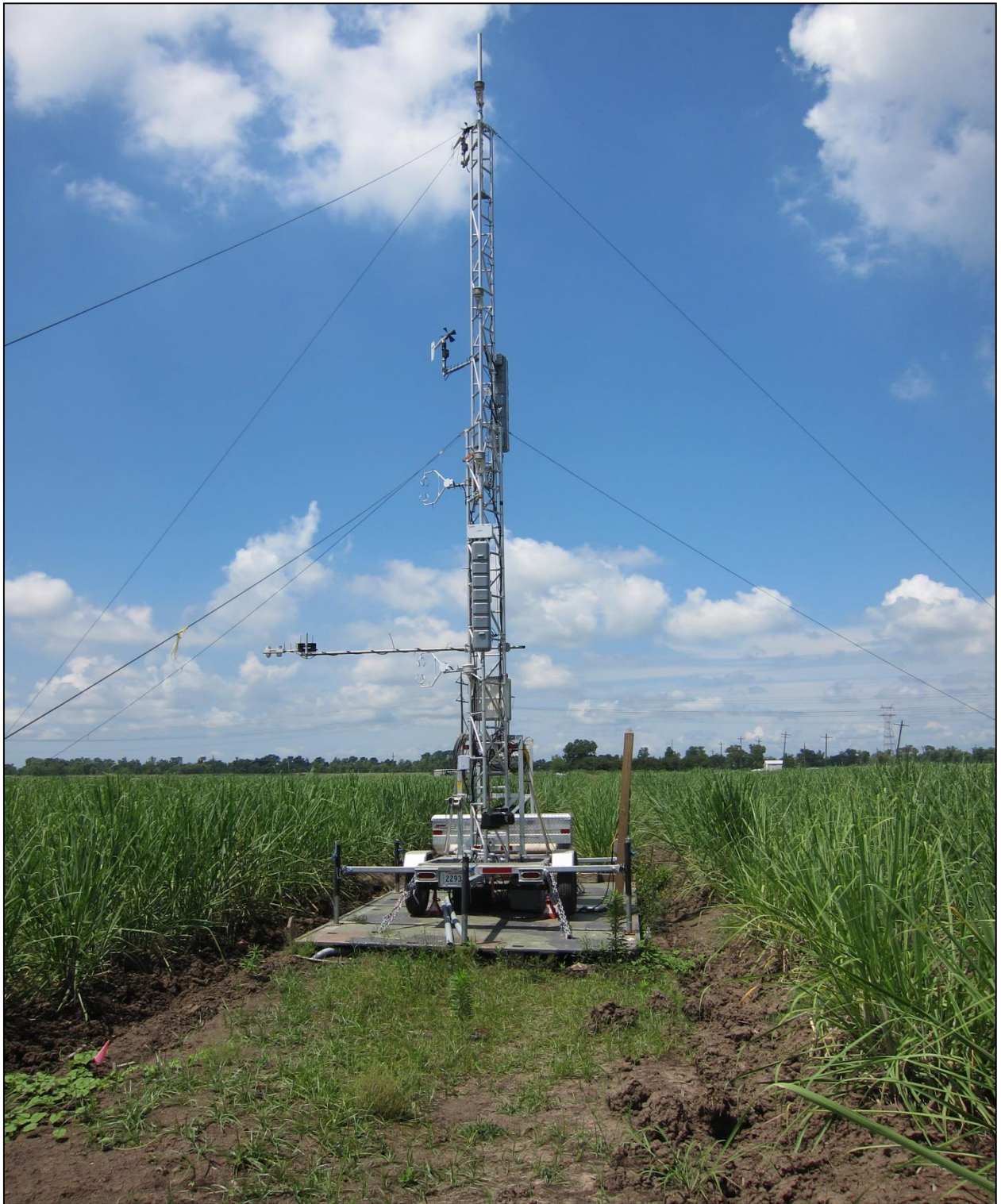


Fig 5.2. Application of ADS and micrometeorological tower in the sugarcane field

### 5.2.2 Sampling site, sample collection and analysis

Field experiments were done for 3 years at Louisiana State University AgCenter research station in St Gabriel, Louisiana (USA, 30°15'13"N 91°6'5"W). Plant cane, first year stubble, and second year stubble sugarcane crop (*Saccharum officinarum*) were used for 2011, 2012 and 2013, respectively. One time N was applied exactly the same day of our first sample collection at the rate of 135 kg ha<sup>-1</sup> for first two years and 157 kg ha<sup>-1</sup> for last year in the form of liquid UAN injected in the soil by UAN injector. The soil of the experimental site was commerce silt loam with low CEC and slightly acidic pH.

For all 3 years the first NH<sub>3</sub> sample was taken on the same day of fertilizer application (noted as 0 days after N application in the results). Samplings were done two times (day and night) every day for first two months and then twice in a week till harvesting. Day (6:00 am to 6:00 pm) and night (6:00 pm to 6:00 am) samplings (12 hours interval) were scheduled to find the diurnal variation of NH<sub>3</sub> emission from sugarcane field. Day-night NH<sub>3</sub> collection from agricultural production was reported in previous work (Baek and Aneja, 2004). Different acids (citric acid, oxalic acid, phosphoric acid) have been suggested as coating solution in previous studies (Perrino and Gherardi, 1999; Roumeliotis et al., 2010) for NH<sub>3</sub> collection. For this experiment the walls of annular denuders were coated with 10 ml denuder coating solution (1.0 gm citric acid, 99 ml methanol, and 1 ml glycerol) before sampling for trapping the gaseous NH<sub>3</sub>. The denuders were rotated for 5 minutes for uniform coating of the acidic solution and then dried using NH<sub>3</sub>-free air stream (nitrogen flow).

After sampling, the denuders were rinsed with 20 ml ultrapure water and the extracted solution was then analyzed in an ion chromatography (Dionex, ICS-2000) equipped with an Ionpac capillary column and CSRS300 suppressor, 23 mM methanesulfonic acid at a flow rate of 1.0 ml per minute. Once the analysis was done, the denuders were cleaned with 10 ml ultrapure water (2-3 time) followed by rinsing with 10 ml methanol solution and dried using nitrogen flow. The denuder were coated again with denuder coating solution and reused for another sampling. Teflon and nylon filters were weighed in a temperature-humidity controlled room using a microbalance to obtain particulate mass. Sugarcane plant height was also measured once a week starting from the day of fertilizer application till harvesting during November. Rainfall, soil and air temperature, relative humidity data was obtained from LSU AgCenter weather station located at St. Gabriel, Louisiana. One minute and 4 minutes wind speed and wind direction data for all 3 years were collected from meteorological instruments equipped with that tower. A memory card was used to collect the recorded data in every two weeks.

Teflon and nylasorb filter were pre-weighed in a temperature-humidity controlled room and the weight of the filters after sample collection was also recorded. The difference in filter weights was used for calculating particle mass. Statistical analysis was done using ANOVA (SAS, 9.3) at 5% confidence interval level.

## **5.3 Results and discussion**

### **5.3.1 Soil and environmental parameters**

Air and soil temperature for all three sugarcane production seasons were high until the end of September and started decreasing rapidly after that. Average soil and air temperatures

were highest in 2013 (air, 31.5<sup>0</sup>C; soil, 28<sup>0</sup>C), followed by 2011 (air, 29.6<sup>0</sup>C; soil, 26.6<sup>0</sup>C) and 2012 (air, 28.6<sup>0</sup>C; soil, 25.2<sup>0</sup>C). The average rainfall received was also highest in 2013 (0.90 cm) followed by 2012 (0.77 cm) and 2011 (0.25 cm). However, year 2011 received highest rainfall days during sampling and other two seasons received same number of rainfall days. More than 60% of the total rainfall was occurred within first 9 weeks after N application in 2011 and 2012; however, year 2013 received uniform rainfall throughout the sampling. Average relative humidity (RH) during sampling period was highest in 2013 (76%) possibly because of highest rainfall received in this year. However, average RH for other two years was found to be very similar.

### **5.3.2 Ammonia flux from sugarcane production**

Ammonia emissions for three years (2011, 2012, and 2013) are presented in Figs. 5.3, 5.4, and 5.5. Background NH<sub>3</sub> concentration is often found very significant such as it ranged from 0.20 to 0.90 µg m<sup>-3</sup> from a deciduous forest in Midwest USA depending on the seasons (Hansen et al., 2015). Ammonia samples were collected for 3 full days before N application to get an average level of NH<sub>3</sub> concentration in ambient air. Henceforth, background NH<sub>3</sub> concentrations were subtracted from the measured concentration and the resulted concentration was reported here for all three years. Full day NH<sub>3</sub> samples were collected till 183 DAN from sugarcane field in 2011 (Fig. 5.3B). Ammonia emission significantly started 4 days after N application and about 76% of the total NH<sub>3</sub> emission was occurred within first 67 DAN.

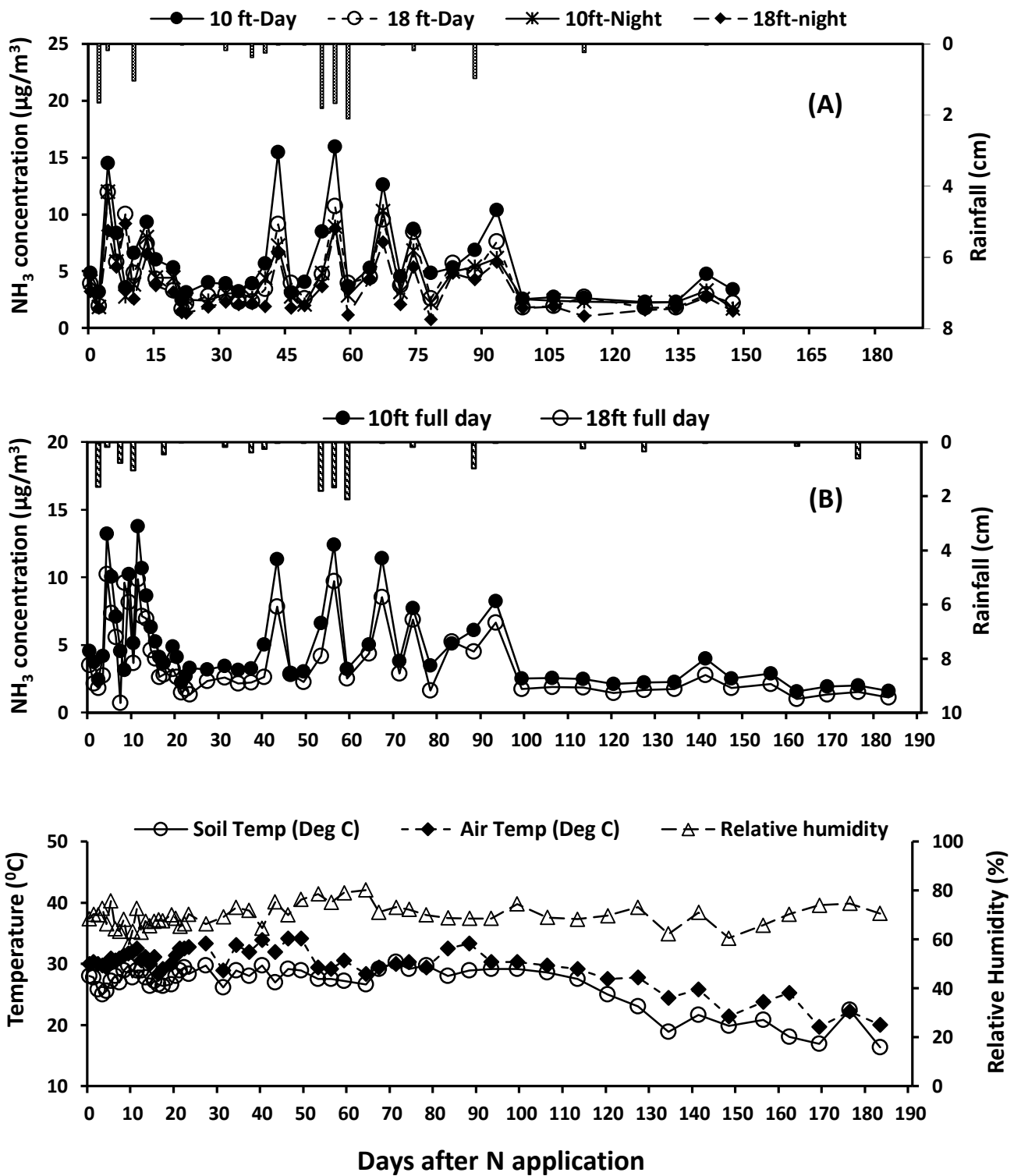


Fig 5.3. Ammonia emission from sugarcane production in St Gabriel, LA, USA in 2011

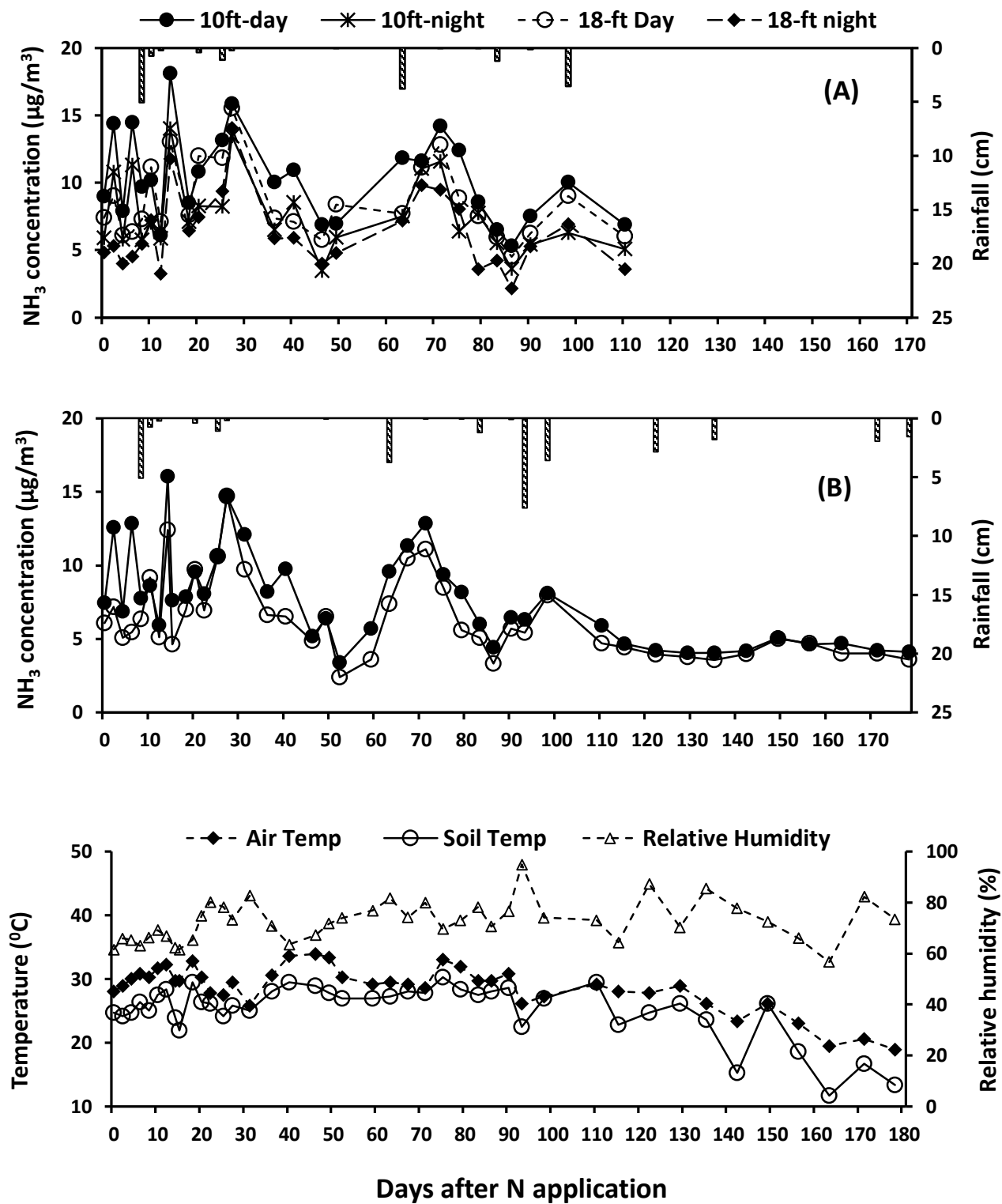


Fig 5.4. Ammonia emission from sugarcane production in St Gabriel, LA, USA in 2012



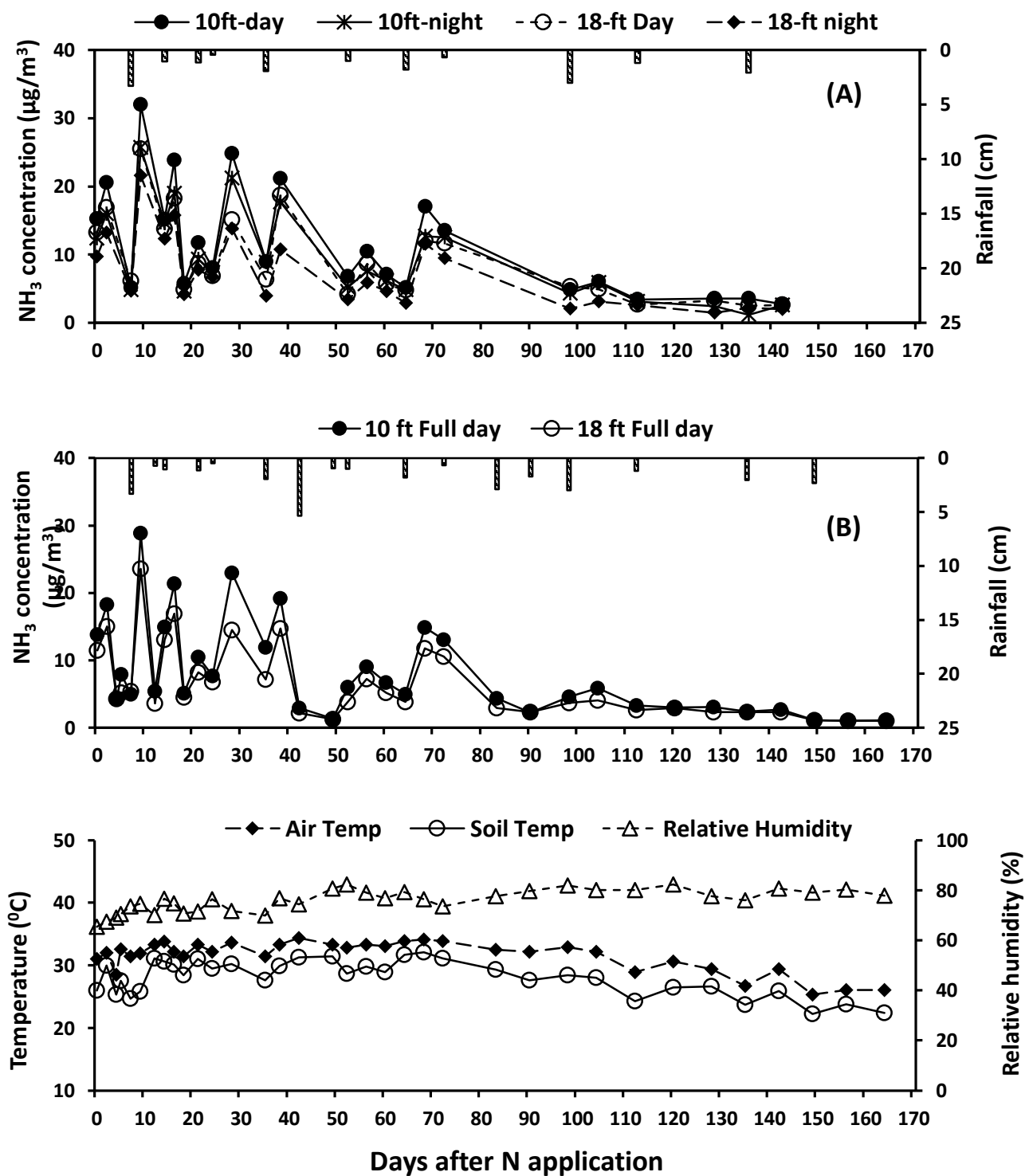


Fig 5.5. Ammonia emission from sugarcane production in St Gabriel, LA, USA in 2013

However, the general decline of  $\text{NH}_3$  emission over time possibly because of lower availability of  $\text{NH}_3$  caused by nitrification,  $\text{NH}_4^+$  fixation in clay lattices, and decreased in soil pH (Black et al., 1985; Sommer and Jensen, 1994). The average  $\text{NH}_3$  concentration for 2011 was 5.1 and 3.8  $\mu\text{g m}^{-3}$  for 10 ft and 18 ft ADS, respectively, which was much lower than the concentration measured near swine lagoon in North Carolina (Baek and Aneja, 2004). It could possibly because manure fermentation produce considerable amount of  $\text{NH}_3$  over time. Ammonia emission at 10 ft ADS was found significantly higher ( $P < 0.05$ ) than 18 ft ADS which indicates positive emission flux above the crop canopy. Major  $\text{NH}_3$  emission peaks (4, 8, 11, 43, 56, and 67 DAN) were corresponded to higher rainfall and relatively higher temperature during those high emission days. Higher rainfall resulted in higher soil moisture which helped hydrolysis of the urea form of UAN to release more  $\text{NH}_3$  in the air (Manheim et al., 1997; Ruijter et al., 2010).

Ammonia samples for full day were collected till 178 DAN from sugarcane field in 2012 (Fig. 5.4B). A few data points were missed during last week of August when Hurricane Isaac hit Baton Rouge (first landfall at August 28, 2012) and our meteorological tower recorded an average wind speed of 25.2 mph during that period and a total of 16 cm rainfall in 3 days. In this year,  $\text{NH}_3$  emission significantly started a days after N application and about 58% of the total  $\text{NH}_3$  emission was occurred within first 59 DAN. After 98 DAN, the  $\text{NH}_3$  emission was very low which could possibly because more than 90% of the sugarcane crops were lodged after Hurricane Isaac and  $\text{NH}_3$  emission from ground and plant surface after that incident were become negligible. The average  $\text{NH}_3$  concentration for 2012 was 7.7 and 6.1  $\mu\text{g m}^{-3}$  for 10 ft and 18 ft ADS, respectively, which was higher than the previous year. Similar  $\text{NH}_3$  concentration (2 to 9  $\mu\text{g m}^{-3}$ ) was reported from oilseed crop in Europe (Sutton et al., 2001b), and average 9.4  $\mu\text{g m}^{-3}$

emission from soybean field in North Carolina (Walker et al., 2006). Likely of 2011,  $\text{NH}_3$  emission at 10 ft ADS was significantly higher ( $P < 0.05$ ) than 18 ft ADS in 2012. Highest  $\text{NH}_3$  emission in 2012 was observed at 14 DAN (10 ft:  $16.1 \mu\text{g m}^{-3}$ , 18 ft:  $12.4 \mu\text{g m}^{-3}$ ) immediately after a heavy rainfall. This was also reported in other studies (Ferrara et al., 2014; Hansen et al., 2015). Other sharp emission peaks (6, 27, 40, 71, and 98 DAN) were also corresponded to higher rainfall and relatively higher temperature during those days.

Full day ammonia samples were collected till 164 DAN in 2013 (Fig. 5.5B). Like 2012,  $\text{NH}_3$  emission started a day after N application also in 2013. More than 80% of the total  $\text{NH}_3$  emission was occurred within 68 DAN in 2013. The average  $\text{NH}_3$  concentration was 8.30 and  $6.54 \mu\text{g m}^{-3}$  for 10 ft and 18 ft ADS, respectively, which was significantly higher ( $P < 0.05$ ) than the emissions found in 2011. However, the emission from year 2012 and 2013 was not significantly different from each other. Higher  $\text{NH}_3$  concentration in 2013 was possibly because of much higher rainfall & humidity, soil and air temperature as compared to 2011 and 2012. Higher air temperature can increase  $\text{NH}_3$  volatilization from soil as well as above crop canopy (Sutton et al., 2013). Highest  $\text{NH}_3$  emission in 2013 was observed at 9 DAN (10 ft:  $28.8 \mu\text{g m}^{-3}$ , 18 ft:  $23.6 \mu\text{g m}^{-3}$ ) because of higher rainfall with uniform rainfall distribution throughout the sampling period and relatively high air temperature. Average  $\text{NH}_3$  emission at 10 ft ADS was significantly higher ( $P < 0.01$ ) than 18 ft ADS in 2013.

Wind speed and variation of diurnal wind speed have very strong influence  $\text{NH}_3$  emission above sugarcane crop canopy. The correlation of  $\text{NH}_3$  emission with wind speed (MPH) and standard deviation of wind speed (MPH) is presented in Fig 5.6.

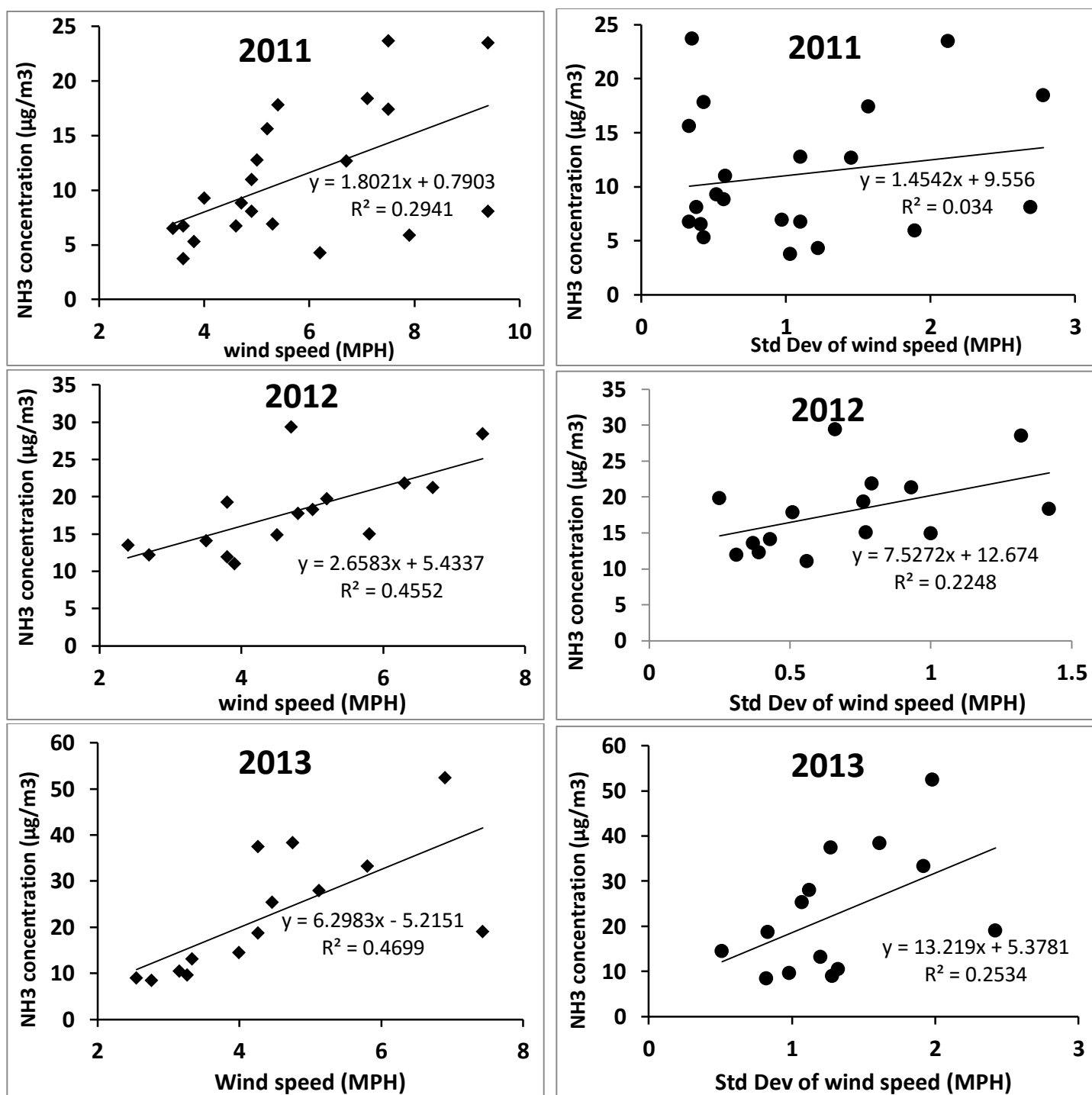


Fig 5.6 Correlation of NH<sub>3</sub> concentration (µg m<sup>-3</sup>) with wind speed (MPH) and standard deviation of wind speed (MPH) for first 30 days of sample collection over 3 years from sugarcane production

However, the correlation was only established for first 30 days of sample collection because the major portion of  $\text{NH}_3$  emission from soil is generally occurred within 4 weeks after fertilizer application and it was described in details in chapter 2.

The strong correlation of  $\text{NH}_3$  emission with wind speed was observed for this experiment with  $R^2$  value ranged from 0.29-0.47 (average 0.38) over 3 years. High wind speed increase the turbulence in the atmospheric boundary layer and thus favors  $\text{NH}_3$  emission from soil surface (Flechard et al., 2013). The sharp peaks of  $\text{NH}_3$  during 56 and 67 DAN in 2011 and were possibly because of higher wind speed (6.9 and 7.4 mph, respectively) during that day. Higher  $\text{NH}_3$  emission on 71 DAN in 2012 was also because of high amount of rainfall favored with relatively higher wind speed during that day. Ammonia emission was also correlated with wind speed variation during the sampling days with  $R^2$  ranged from 0.034-0.25 (average 0.14) for 3 years (Fig. 5.6). Higher standard deviation of wind speed actually indicated that variation of day and night wind speed is high and it can create sufficient turbulence in the boundary layer and subsequently favors more  $\text{NH}_3$  emissions.

### **5.3.3 Diurnal and seasonal variation of ammonia emission**

Day-night  $\text{NH}_3$  emission flux from 10 and 18 ft ADS were presented in Fig 5.2A, 5.3A, and 5.4A for year 2011, 2012, and 2013, respectively. Average daytime (DT) and nighttime (NT)  $\text{NH}_3$  fluxes were highest in 2013 (DT:  $10.39 \mu\text{g m}^{-3}$ , NT:  $8.45 \mu\text{g m}^{-3}$ ) followed by 2012 (DT:  $9.43 \mu\text{g m}^{-3}$ , NT:  $6.96 \mu\text{g m}^{-3}$ ), and 2011 (DT:  $5.19 \mu\text{g m}^{-3}$ , NT:  $3.82 \mu\text{g m}^{-3}$ ). Overall, DT  $\text{NH}_3$  emission was significantly higher ( $P < 0.05$ ) than NT  $\text{NH}_3$  emission for 2011 and 2012. Ammonia flux during DT was higher than NT in 2013, but the difference was not significant.

Day time  $\text{NH}_3$  flux was documented as higher than nighttime in several studies. This may be because of higher volatilization corresponds to higher soil and air temperature and stomatal closure of leaves during nighttime (Sutton et al., 2000; Horvath et al., 2005; Skjøth and Geels, 2013; Sutton et al., 2013), and nighttime rewetting of the soil surface from dew drops (Ferrara et al., 2014). In a recent study, daytime  $\text{NH}_3$  emission was found much higher than nighttime emission with a peak emission during 7:30 to 11:00 am from a sorghum field in Italy (Ferrara et al., 2014). In another study average diurnal  $\text{NH}_3$  flux was observed maximum during morning (after sunrise) and minimum during sunset (Walker et al., 2006). Horvath et al (2005) found monthly average  $\text{NH}_3$  emission ranged from 0.76 to 6.56  $\mu\text{g m}^{-3}$  during day time and 0.61 to 4.75  $\mu\text{g m}^{-3}$  during night time from grasslands in the Hungarian great plain. Our results clearly showed that  $\text{NH}_3$  emission during summer period was significantly higher ( $P < 0.01$ ) than emissions during spring and winter seasons. In a recent study summer  $\text{NH}_3$  emission was reported higher than winter  $\text{NH}_3$  emissions from deciduous forest at Midwest USA (Hansen et al., 2015).

#### **5.3.4 Particle matter emissions**

Particle emissions during three sugarcane production cycles are presented in Fig. 5.7. Average PM emission was highest in 2013 (10 ft: 19.4  $\mu\text{g m}^{-3}$ , 18 ft: 17.0  $\mu\text{g m}^{-3}$ ), followed by 2011 (10 ft: 18.7  $\mu\text{g m}^{-3}$ , 18 ft: 16.6  $\mu\text{g m}^{-3}$ ), and 2012 (10 ft: 17.6  $\mu\text{g m}^{-3}$ , 18 ft: 16.1  $\mu\text{g m}^{-3}$ ). Highest PM emission in 2013 probably due to higher amount of ammonia emission this year.

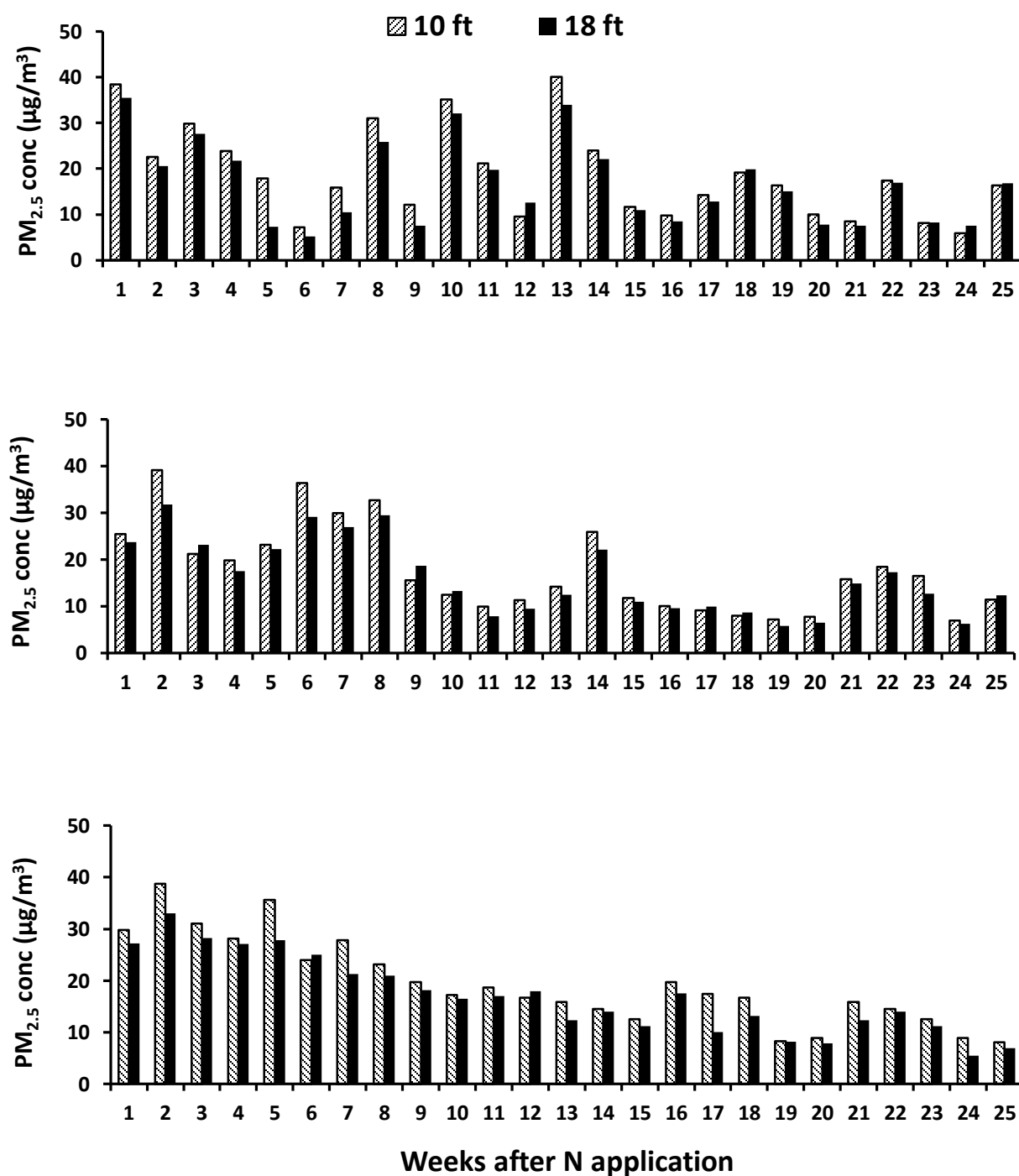


Fig 5.7. Particulate matter emission from sugarcane production for 3 years in St Gabriel, LA, USA

Ammonia can form different fine particles such as ammonium sulfate and ammonium nitrate after reacting with sulfate and N oxides. Particle emission peaks during all three years were also corresponded with higher  $\text{NH}_3$  emission during those days. The concentration of PM found in 10 ft ADS was always higher than 18 ft ADS throughout the years. Particle matter concentrations in few days were found higher than the NAAQS standard guidelines for 24 hour period ( $35 \mu\text{g m}^{-3}$ ).

## 5.4 Conclusion

Three year field experiment shows that  $\text{NH}_3$  emission at lower height ADS was significantly higher than the ADS situated in upper height, indicating a positive vertical  $\text{NH}_3$  flux from sugarcane production following N application. Rainfall played a major role on  $\text{NH}_3$  emissions by creating anaerobic soil conditions and major  $\text{NH}_3$  emission peaks were observed immediately after heavy rainfall. Both wind speed and standard deviation of wind speed were highly correlated with  $\text{NH}_3$  emission indicating higher wind speed created more mixing in the boundary layer and thus released more  $\text{NH}_3$  from soil as well as from crop canopy. Temperature was also as an important factor on  $\text{NH}_3$  emission resulting in significant higher DT emission as compared to NT emission throughout the years. Wind speed and wind direction also largely influenced the emission by creating atmospheric turbulence and  $\text{NH}_3$  transportation from point source. Higher concentration of PM was found during high  $\text{NH}_3$  emission days indicating the possibility of forming secondary particulates from  $\text{NH}_3$  reacting with oxides of S and N in the air. Overall, 2013 produced higher  $\text{NH}_3$  because of relatively higher N application rate and higher rainfall in that year. Most of the meteorological data was collected from St Gabriel AgCenter weather station which is in general a good representative of the weather condition of



our sampling site, however, more meteorological data from the actual tower instruments could have resulted a better portrait of the relation between ammonia emission and different meteorological parameters.

## 5.5 References

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## Chapter 6. Conclusions

Sugarcane is an important row crop in Louisiana and fertilizer application and special land management practices during sugarcane production can significantly influence air quality. This study was conducted to evaluate different air quality issues from sugarcane production in Louisiana. Specifically, the main aim of this research project was to quantify ammonia and different greenhouse gases from different N fertilization and special residue application (residue burned and residue retained) from sugarcane growing seasons. Micrometeorological  $\text{NH}_3$  emission flux over sugarcane crop canopy was also analyzed for three sugarcane production cycles. Characterization of morphological features and elemental composition of fine particulates generated during different sugarcane harvesting operations were also investigated for two years.

Two years of field experiments clearly showed that fertilizer source significantly influenced  $\text{NH}_3$  emissions during sugarcane production. Urea applied plots produced significantly higher  $\text{NH}_3$  as compared to UAN and control. However,  $\text{NH}_3$  emissions from UAN treated plots were significantly higher than control only in 2013 when residue and fertilizer treatments were established separately. The results indicate that possibility of negative interaction effects occurred between UAN and residues during 2012. Residue retained plots worked as a blanket in the field and conserved more soil moisture and thus helped hydrolysis of urea to produce significantly higher  $\text{NH}_3$  as compared to residue burned plots for both years. Much higher correlation between  $\text{NH}_3$  emission and WFPS was found in 2012 than 2013 due to majority of rainfall in 2012 was received within 3 weeks after N application when  $\text{NH}_3$

emissions from soil were really high. Overall, significant amount of  $\text{NH}_3$  volatilization was observed within 3-4 weeks after N application.

Fertilizer urea significantly influenced  $\text{N}_2\text{O}$  emissions as compared to other treatments from sugarcane production. However, N sources did not produce any significant impact for other two GHG emissions. About 60-70% of the total nitrous oxide emission occurred within 3 weeks after N application for both years. Residue retained plots emitted significantly higher  $\text{N}_2\text{O}$  and  $\text{CH}_4$  as compared to residue burned plots. This was probably because residues left in the field provided more organic matter in the soil and also created anaerobic soil condition by retaining more soil moisture which helped in releasing more  $\text{N}_2\text{O}$  and  $\text{CH}_4$  from soil. Results showed both absorption and emission peaks for  $\text{CH}_4$  for both years which suggests the involvement of methanogenic or methanotrophic organisms in the soil. Nitrous oxide emission was correlated much higher with WFPS in 2012 as compared to 2013 because of the higher rainfall received within 3-4 weeks in 2012. Overall, second year stubble sugarcane crop produced relatively higher  $\text{N}_2\text{O}$  as compared to first year stubble crop.

Field experiments were also conducted to determine the elemental composition and morphological features of the particulates emitted during different sugarcane harvesting operations in Louisiana. Burning of sugarcane biomass residues (GB and SB) were mainly released fine particulates in the air as compared to harvesting operations (RH and CH). A major portion of the  $\text{PM}_{2.5}$  mass was contributed by carbonaceous particles for all harvesting operations throughout the years. Statistically higher elemental carbon was found in SB particles than GB particles. Ammonium was the major cation present in the fine particulates and was highly correlated with sulfate ions ( $\text{SO}_4^{2-}$ ) suggesting the formation of secondary particles in the air

during sugarcane residue burning operations. Higher concentration of Si found in harvesting particles (RH and CH) depicts that RH and CH produced plant particles in the air. Almost same number of PAHs were detected in GB and SB particles, however, significantly higher PAH concentration was found in GB particles indicated that ground burning of sugarcane residues impaired air quality more than standing burning of sugarcane residues. Overall, GB particles had significantly higher organic carbon, major water soluble ions and elemental species than SB particles.

Three years micrometeorological field study of  $\text{NH}_3$  emission showed a positive vertical  $\text{NH}_3$  flux above sugarcane canopy following N application in the soil. Rainfall and temperature were the major factors for  $\text{NH}_3$  emissions from soil as well as from crop leaf surface. Major  $\text{NH}_3$  emission peaks were corresponded with higher rainfall throughout the years. Rainfall increase the water filled pore space in the soil and thus creating anaerobic condition in the soil and subsequently released more  $\text{NH}_3$ . Daytime  $\text{NH}_3$  emission was found significantly higher than NT emission probably because of higher temperature during day than night favors  $\text{NH}_3$  volatilization from soil. Wind speed and variation in the wind speed were other two major meteorological parameters influenced  $\text{NH}_3$  emission. Particulate matter emission was higher during high  $\text{NH}_3$  emission days suggesting acid neutralization by  $\text{NH}_3$  and thus forming fine secondary particles such as ammonium sulfate and ammonium nitrate. Overall, 2013 showed higher  $\text{NH}_3$  emission primarily because of higher N application combined with favorable meteorological parameters.

## **Vita**

Sanku Datta Mudi, a native to West Bengal, India earned his Masters' degree in Soil Science from Punjab Agricultural University, India in 2010. Thereafter, he worked as a research associate at department of soils in Punjab Agricultural University for few months. Then he joined Louisiana State University in the School of Plant, Environmental, and Soil Sciences during fall 2010. He worked with Dr. Jim Jian Wang on different air quality issues from agricultural crop productions in Louisiana. His dissertation title is "Evaluation of ammonia, greenhouse gas emissions and characterization of different particulate matter during sugarcane production in southern Louisiana".