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Chemical characterization and oxidative potential of particles emitted from open burning of cereal straws and rice husk under flaming and smoldering conditions

Akihiro Fushimi [a, b, *], Katsumi Saitoh [a, c], Kentaro Hayashi [d], Keisuke Ono [d], Yuji Fujitani [a], Ana M. Villalobos [b], Brandon R. Shelton [b], Akinori Takami [a], Kiyoshi Tanabe [a], James J. Schauer [b]

[a] National Institute for Environmental Studies, 16–2 Onogawa, Tsukuba, 305–8506, Japan
[b] University of Wisconsin-Madison, 660 North Park Street, Madison, WI, 53706, USA
[c] Environmental Science Analysis and Research Laboratory, 1-500-82 Matsuo-yosegi, Hachimantai, Iwate, 028-7302, Japan
[d] National Institute for Agro-Environmental Sciences, 3–1–3 Kannondai, Tsukuba, 305–8604, Japan

HIGHLIGHTS

- Particulate emission factors and their chemical compositions of rice husk were firstly shown.
- Levoglucosan/OC ratios among crop species were more stable than K^+/PM ratios.
- Stigmasterol and β-sitosterol could also be used as markers of biomass burning.
- Oxidative potential of open burning was firstly obtained experimentally.
- Oxidative potential correlated well with water-insoluble organic species.

GRAPHICAL ABSTRACT

Actual open burning situations in Japan

Rice straw *Rice husk*

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ABSTRACT

Open burning of crop residue is a major source of atmospheric fine particle emissions. We burned crop residues (rice straws, barley straws, wheat straws, and rice husks produced in Japan) in an outdoor chamber and measured particle mass, composition (elemental carbon: EC, organic carbon: OC, ions, elements, and organic species), and oxidative potential in the exhausts. The fine particulate emission factors from the literature were within the range of our values for rice straws but were 1.4–1.9 and 0.34–0.44 times higher than our measured values for barley straw and wheat straw, respectively. For rice husks and wheat straws, which typically lead to combustion conditions that are relatively mild, the EC content of the particles was less than 5%. Levoglucosan seems more suitable as a biomass burning marker than K^+, since levoglucosan/OC ratios were more stable than K^+/particulate mass ratios among crop species. Stigmasterol and β-sitosterol could also be used as markers of biomass burning with levoglucosan or instead of levoglucosan. Correlation analysis between chemical composition and combustion condition suggests that hot or flaming combustions enhance EC, K^+, Cl^- and polycyclic aromatic hydrocarbons emissions, while low-temperature or smoldering combustions enhance levoglucosan and water-soluble organic carbon emissions. Oxidative potential, measured with macrophage-based reactive oxygen species (ROS) assay and dithiothreitol (DTT) assay, of open burning fine particles per particulate mass as well as fine particulate emission factors were the highest for wheat straws and second highest

* Corresponding author. National Institute for Environmental Studies, 16–2 Onogawa, Tsukuba, 305–8506, Japan.
E-mail address: fushimi.akihiro@nies.go.jp (A. Fushimi).

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for rice husks and rice straws. Oxidative potential per particulate mass was in the lower range of vehicle exhaust and atmosphere. These results suggest that the contribution of open burning is relatively small to the oxidative potential of atmospheric particles. In addition, oxidative potential (both ROS and DTT activities) correlated well with water-insoluble organic species, suggesting that OC components, especially water-insoluble OC components emitted under non-flaming combustion, have a major impact on oxidative potential.

1. Introduction

Fine particulate matter (particles with diameter below 2.5 μm: $PM_{2.5}$) in the atmosphere is of high priority for air quality management efforts due to observed associations with adverse effects to humans (Cassee et al., 2013; Dockery et al., 1993; Haberzettl et al., 2016; Meng et al., 2016; Pope and Dockery, 2006; U. S. Environmental Protection Agency (U. S. EPA), 2012; Wittkopp et al., 2016). Therefore, origin and environmental behavior of $PM_{2.5}$ needs to be investigated. $PM_{2.5}$ is a complex mixture emitted from various sources. Even in developed countries, open burning of crop (agriculture) residue along with emissions from factories and automobiles are important sources of atmospheric particulate matter. Studies indicate that biomass burning contributes to 9–55% of total carbon (TC), organic carbon (OC), or elemental carbon (EC) (Hagino et al., 2006; Heo et al., 2013; Morino et al., 2010), and 3–21% of $PM_{2.5}$ (Takahashi et al., 2011; Villalobos et al., 2015) in the atmosphere.

Source contributions are estimated by a chemical transport model or a receptor model such as the chemical mass balance (CMB) model. For source apportionment, PM emission factors and chemical compositions (source profiles) are needed, but PM emission factors and the chemical compositions of open burning can largely differ among crop types and combustion conditions, which are influenced by water content and ignition position (Oanh et al., 2011; U. S. EPA, 1995). Therefore, emission factors and chemical compositions that match the actual circumstances in each country or region are needed to accurately estimate the effect of open burning. However, the emission data for open burning is limited (Hays et al., 2005; Saito et al., 1994; Turn et al., 1997; U. S. EPA, 1995; Zhang et al., 2007). For instance, rice husks are often burned in the fields of Japan and other countries (JCAP/JATOP, 2007; Olawale et al., 2012) and have a combustion state which is quite different from that for straws, but PM emission factor and chemical composition data are not available. Therefore, for example, emission factors obtained in the literature (U. S. EPA, 1995) have been used for the emissions inventory of Japan (JCAP/JATOP, 2007; Kannari et al., 2007).

Indoor biomass smoke is categorized as a probable human carcinogen (Group 2a) according to International Agency for Research on Cancer (2010). Furthermore, studies on humans show that indoor biomass burning is associated with pulmonary dysfunction, reduced antioxidant defense, oxidative DNA damage, and inflammation of the airways (Arbex et al., 2004; Banerjee et al., 2012; Gupta et al., 2016; Mukherjee et al., 2014; Oluwole et al., 2013). The levels of PM and inflammation markers were positively associated with the generation of reactive oxygen species (ROS) (Banerjee et al., 2012; Mukherjee et al., 2014). Furthermore, biomass burning seems to have a certain impact on ambient PM oxidative potential (redox activity) (Hamad et al., 2015; Saffari et al., 2013; Verma et al., 2009b). All of these studies were conducted on humans and were analyzed based on indoor or outdoor air concentrations. No studies to date have evaluated the oxidative potential of biomass burning PM itself so as to be compared with other emission sources or the atmosphere.

There were five objectives for our study: (1) to experimentally obtain PM emission factors and chemical compositions (elemental carbon, organic carbon, ions, elements, and organic species) of crop residues (rice straws, barley straws, wheat straws, and rice husks) produced in Japan; to the best of our knowledge, this is the first report of PM emission factors and chemical compositions for rice husks, as we validated the applicability of the emission factors from the literature in the Japanese emissions inventory. (2) To examine the differences of emission factors and chemical compositions among crop species and combustion conditions. (3) To obtain source profiles of organic markers and elements for CMB. (4) To quantitatively measure the oxidative potential and compare with other sources and the atmosphere. And finally, (5) to discuss which chemical species impact oxidative potential.

2. Methods

2.1. Burning experiments

Burning experiments were conducted in January and November 2011 at the National Institute for Agro-Environmental Sciences, Tsukuba, Japan. Supplementary details of the burning experiments and the emission factors of greenhouse gases are reported elsewhere (Hayashi et al., 2014). Four kinds of crop residue with high production rates in Japan were burned: straw and husk of paddy rice and barley straw produced in cropland reclaimed from the sea in Okayama Prefecture, and wheat straw made in Hokkaido.

A portable (0.3 m^3) stainless steel combustion hood was used to simulate typical open burning of crop residue, backfiring in particular, under closed-system conditions. The back of the hood was equipped with two fan motors for stable and forced ventilation ($\approx$4 m^3 min^{-1}) of ambient air. The exhaust was blown into the atmosphere through an exhaust duct connected on the roof of hood. The hood was placed on the soil surface of a field. In each experiment, crop residues were placed on the soil surface inside the hood and ignited. Air-dried crop residues with moisture content of $\approx$10% or humidified residues with moisture content of $\approx$20% were burned to understand the effect of moisture content on PM emission factors and chemical compositions. For rice husk, however, only the dry residue was used because rice husk is hard to ignite, even if it is dry.

2.2. Sampling of exhaust particles

To collect exhaust PM from the burning experiments, a portion of the exhaust gas was continuously sampled from ignition until the end of combustion. The PM sample list and sampling conditions are shown in Table 1. The exhaust PM was collected by particle size (>7.0 μm, 2.1–7.0 μm, <2.1 μm) from the exhaust duct using two cascade impactors (AN-200, Tokyo Dylec Corp, Tokyo, Japan) simultaneously, producing a flow rate of 28.3 L min^{-1}. A stainless