Science of the Total Environment xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Ground-level air pollution changes during a boreal wildland mega-fire☆

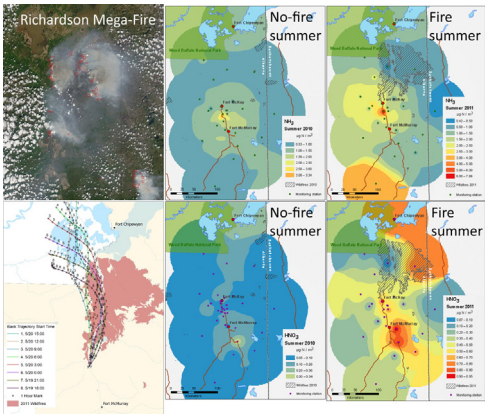
Andrzej Bytnerowicz [a,*], Yu-Mei Hsu [b], Kevin Percy [b], Allan Legge [c], Mark E. Fenn [a], Susan Schilling [a], Witold Frączek [d], Diane Alexander [a]

[a] USDA Forest Service, Pacific Southwest Research Station, 4955 Canyon Crest Drive, Riverside, CA 92507, USA
[b] Wood Buffalo Environmental Association, #100-330 Thickwood Blvd., Fort McMurray, Alberta, T9K 1Y1, Canada
[c] Biosphere Solutions, Calgary, Alberta, T2N 1H7, Canada
[d] Environmental Systems Research Institute, Redlands, CA 92373, USA

HIGHLIGHTS

- Boreal mega-fire increased $PM_{2.5}$, NH_3, HONO, HNO_3, NH_4^+ and NO_3^- at receptor site.
- Elevated ambient NH_3 and HNO_3 lasted several months across northern Alberta.
- Higher NH_3 and HNO_3 contributed to increased N deposition to boreal forests.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 May 2016
Received in revised form 6 July 2016
Accepted 7 July 2016
Available online xxxx

Editor: Elena Paoletti

Keywords:
Fine particulate matter
Reactive nitrogenous species
Sulfur dioxide
Sulfate
Ozone

ABSTRACT

The 2011 Richardson wildland mega-fire in the Athabasca Oil Sands Region (AOSR) in northern Alberta, Canada had large effects on air quality. At a receptor site in the center of the AOSR ambient $PM_{2.5}$, O_3, NO, NO_2, SO_2, NH_3, HONO, HNO_3, NH_4^+ and NO_3^- were measured during the April–August 2011 period. Concentrations of NH_3, HNO_3, NO_2, SO_2 and O_3 were also monitored across the AOSR with passive samplers, providing monthly summer and bi-monthly winter average values in 2010, 2011 and 2012. During the fire, hourly $PM_{2.5}$ concentrations >450 μg m^{-3} were measured at the AMS 1 receptor site. The 24-h National Ambient Air Quality Standard (NAAQS) of 35 μg m^{-3} and the Canada Wide Standard (CWS) of 30 μg m^{-3} were exceeded on 13 days in May and 7 days in June. During the fire emission periods, sharp increases in NH_3, HONO, HNO_3, NH_4^+, NO_3^- and total inorganic reactive N concentrations occurred, all closely correlated with the $PM_{2.5}$ changes. There were large differences in the relative contribution of various N compounds to total inorganic N between the no-fire emission and fire emission periods. While in the absence of fires NO and NO_2 dominated, their relative contribution during the fires was ~2 fold smaller, mainly due to increased NH_3, NH_4^+ and NO_3^-. Concentrations of HONO and HNO_3 also greatly increased during the fires, but their contribution to the total inorganic N pool was relatively small. Elevated NH_3 and HNO_3 concentrations affected large areas of northern Alberta during the Richardson Fire. While NH_3 and HNO_3 concentrations were not at levels considered toxic to plants, these gases contributed

☆ Capsule: Boreal mega-fire caused a sharp increase in ambient $PM_{2.5}$, NH_3, HONO, HNO_3, NH_4^+ and NO_3^- near the fires as well as long-lasting and widespread occurrence of elevated NH_3 and HNO_3.

* Corresponding author.
E-mail addresses: abytnerowicz@fs.fed.us (A. Bytnerowicz), mfenn@fs.fed.us (M.E. Fenn).

http://dx.doi.org/10.1016/j.scitotenv.2016.07.052
0048-9697/Published by Elsevier B.V.

significantly to atmospheric N deposition. Generally, no significant changes in O_3 and SO_2 concentrations were detected and their ambient concentrations were below levels harmful to human health or sensitive vegetation.

Published by Elsevier B.V.

1. Introduction

Large wildland fires burning over 10,000 ha are termed mega-fires. Such fires cause severe degradation of air quality, impacting human health and ecological processes to varying degrees (Stephens et al., 2014). Mega-fires are also major sources of greenhouse gases with severe consequences for climate change (Liu et al., 2014). The Richardson Fire was the second largest wildland mega-fire in the history of Alberta, Canada. It was located north of the city of Fort McKay in an area known as the Richardson Backcountry. The fire started on May 15th, 2011 and reached 16,000 ha overnight (Gregory, 2012). The fire rapidly spread through the Athabasca Oil Sands Region (AOSR) until the end of June (Fig. 1) when its progression slowed as rain and cooler weather prevailed in the region. Large areas of boreal forest, especially on the eastern flanks of the AOSR, were allowed to burn into August due to the absence of human settlements or oil facilities in those areas. By the end of summer 2011 when the fire was fully contained, over 700,000 ha of forest burned (https://en.wikipedia.org/wiki/Richardson_fire).

Wildland fires produce large amounts of smoke which is defined as an aerosol consisting mainly of water vapor, primary gases, volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs) and particles (Andreae and Merlet, 2001). Primary gases released from fires include carbon monoxide (CO), carbon dioxide (CO_2) as well as nitrogen oxides (NO_x), ammonia (NH_3) and sulfur dioxide (SO_2) (Conard and Ivanova, 1998; Goldammer et al., 2009). Secondary gases, produced during reactions of the primary gases, include ozone (O_3) formed by complex photochemical reactions of VOCs and NO_x (Urbanski et al., 2009), and nitric acid (HNO_3) generated by reactions between nitric oxide (NO), nitrogen dioxide (NO_2), as well as the oxygen and hydroxyl radicals (O and OH, respectively) (Seinfeld and Pandis, 2006). Particles in wildland fire smoke are predominantly in the fine mode (diameter ≤ 2.5 μm) (http://www3.epa.gov/airtrends/aqtrnd04/pmreport03/pmunderstand_2405.pdf; Saarnio et al., 2010) and mainly consist of elemental carbon (soot), organic carbon and various organic compounds (Goldammer et al., 2009). The less-prominent inorganic fraction of fine smoke particles includes ammonium (NH_4^+), nitrate (NO_3^-) and sulfate (SO_4^{2-}) ions forming semi-volatile compounds such as NH_4NO_3 and $(NH_4)_2SO_4$ (Schaap et al., 2004). These compounds result from complex reactions of NO_x, sulfur oxides (SO_x), nitrous acid (HONO), HNO_3 and NH_3 in smoke plumes (Akagi et al., 2012). The inorganic fraction of smoke particulate matter also contains water-soluble ions such as potassium, sodium, magnesium, calcium, and chloride as well as various trace elements (Goldammer et al., 2009; Hays et al., 2002). Carbon monoxide, CO_2, VOCs, SVOCs, elemental carbon and NO_x emitted from wildland fires contribute significantly to changing global temperatures either directly or indirectly by producing such compounds as O_3 (a greenhouse gas) or particulate NO_3^-, the latter causing negative radiative forcing (IPCC, 2013).

Various air pollutants released directly from wildland fires, and those formed during secondary reactions in smoke plumes, negatively affect human health. These toxic compounds include NO_x, SO_x, O_3 and numerous organic gases and aerosols, many of them carcinogenic (Fowler, 2003; Goldammer et al., 2009). Biomass burning that leads to elevated levels of $PM_{2.5}$ is associated with serious human health problems (Kinney, 2008; Koelemeijer et al., 2006). Significant impacts on ecosystem health can be caused by elevated concentrations of O_3, NO_2, SO_2 and HNO_3 well-known for their phytotoxic effects on sensitive vegetation (Bytnerowicz et al., 2007). Nitrogen oxides, NH_3, HONO, HNO_3, as well as particulate NH_4^+ and NO_3^- are important components of reactive atmospheric nitrogen and major drivers of atmospheric dry deposition of nitrogen (N) to forests and other ecosystems (Hanson and Lindberg, 1991; Lovett, 1994; Pinder et al., 2012). Knowledge of ambient concentrations of N air pollutants is important for understanding their potential phytotoxic effects on sensitive vegetation and for estimates of N dry deposition to forests and other ecosystems. Ambient air quality of the AOSR has been monitored from a perspective of potential impacts of emissions from oil exploration and processing on the boreal forest and wetland ecosystems (Percy, 2013; Percy et al., 2012). For that purpose, a passive sampler monitoring network for ecologically important air pollutants such as NO_2, HNO_3, NH_3, SO_2 and O_3 has been developed (Bytnerowicz et al., 2010b; Fenn et al., 2015; Hsu and Bytnerowicz, 2015; Hsu and Clair, 2015). No indications of direct

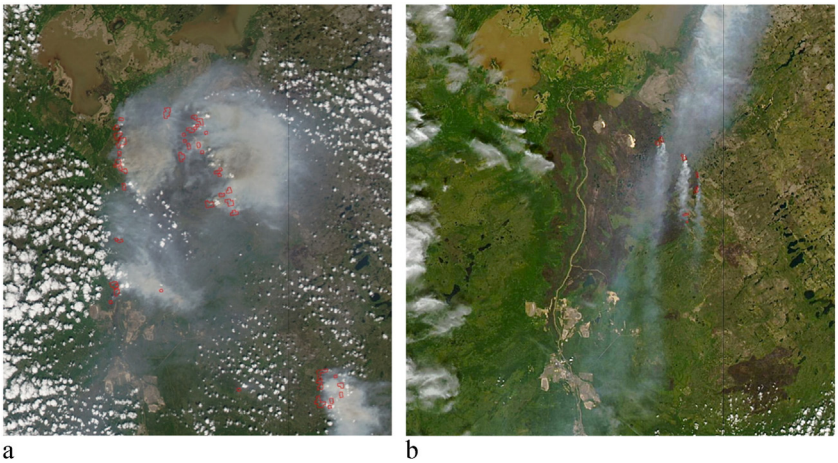


Fig. 1. Progression of the Richardson Fire shown as images obtained on June 8, 2011 (a) and June 26 (b) from the Moderate Resolution Imaging Spectroradiometer (MODIS), the Aqua satellite. Under thick smoke a cluster of wildfires are outlined in red. Dark brown burn scars seen on the June 26th image define the areas burned by the Richardson Fire (center of the AOSR), and in Saskatchewan (SE section of the image).

Please cite this article as: Bytnerowicz, A., et al., Ground-level air pollution changes during a boreal wildland mega-fire, Sci Total Environ (2016), http://dx.doi.org/10.1016/j.scitotenv.2016.07.052