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Radiocarbon determination of fossil and contemporary carbon contribution to aerosol in the Pacific Islands

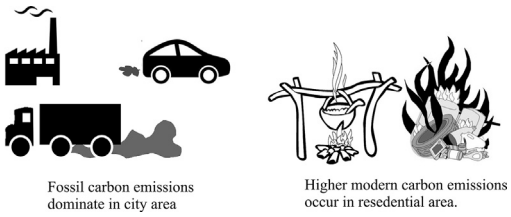
C.F. Isley [a,*], P.F. Nelson [a], M.P. Taylor [a], A.A. Williams [b], G.E. Jacobsen [b]

[a] Department of Environmental Sciences, Macquarie University, Sydney, NSW 2109, Australia
[b] Australian Nuclear Science and Technology Organisation, Sydney, NSW 2234, Australia

HIGHLIGHTS

- Aerosol elemental and organic carbon were determined for a Pacific Island location
- Fossil and modern components of carbon were quantified
- City areas were dominated by fossil carbon, from industry, vehicles and power generation
- Residential areas showed greater modern carbon, from biogenic emissions, waste burning and cooking
- Prior city-based studies have not captured the impact of open burning in residential areas

GRAPHICAL ABSTRACT



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ABSTRACT

Combustion emissions are of growing concern across all Pacific Island Countries, which account for >10,000 km^2 of the earth's surface area; as for many other small island states globally. Apportioning emissions inputs for Suva, the largest Pacific Island city, will aid in development of emission reduction strategies. Total suspended particulate (TSP) and fine particulate ($PM_{2.5}$) samples were collected for Suva City, a residential area (Kinoya, TSP) and a mainly ocean-influenced site (Suva Point, TSP) from 2014 to 2015. Percentages of contemporary and fossil carbon were determined by radiocarbon analysis (accelerator mass spectrometry); for non carbonate carbon (NCC), elemental carbon (EC) and organic carbon (OC). Source contributions to particulate matter were identified and the accuracy of previous emissions inventory and source apportionment studies was evaluated. Suva Point NCC concentrations (2.7 ± 0.4 μg/m^3) were four times lower than for City (13 ± 2 μg/m^3 in TSP) and Kinoya (13 ± 1 μg/m^3 in TSP); demonstrating the contribution of land-based emissions activities in city and residential areas. In Suva City, total NCC in air was 81% (79%–83%) fossil carbon, from vehicles, shipping, power generation and industry; whilst in the residential area, 48% (46%–50%) of total NCC was contemporary carbon; reflecting the higher incidence of biomass and waste burning and of cooking activities. Secondary organic fossil carbon sources contributed >36% of NCC mass at the city and >29% at Kinoya; with biogenic carbon being Kinoya's most significant source (approx. 30% of NCC mass). These results support the previous source apportionment studies for the city

Abbreviations: ANSTO, Australian Nuclear Science and Technology Organisation; ^{14}C, carbon 14 isotope; $ø_{blank}$, correction factor for blanks; EC, elemental carbon; $EC_{biomass}$, elemental carbon from biomass burning; $EC_{contemporary}$, elemental carbon from contemporary sources; F_C, fraction contemporary carbon; $F_{M(corrected)}$, corrected fraction of modern carbon; $F_{M(measured)}$, measured fraction of modern carbon; $F_{M(blank)}$, fraction of modern carbon in the blank; NCC, non carbonate carbon; $NCC_{contemporary}$, non carbonate carbon from contemporary sources; OC, organic carbon; $OC_{biogenic}$, organic carbon from biogenic sources; $OC_{P\_bimoass}$, organic carbon from primary biomass burning emissions; $OC_{contemporary}$, organic carbon from contemporary sources; OC_{P_fossil}, fossil organic carbon from primary sources; OC_{S_fossil}, organic carbon from secondary organic fossil sources; $PM_{2.5}$, particulate matter < 2.5 μm effective aerodynamic diameter; PNC, particle number concentration; SE, standard error; TSP, total suspended particulate.

* Corresponding author.
E-mail address: cynthia-faye.isley@hdr.mq.edu.au (C.F. Isley).

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area; yet show that, in line with emissions inventory studies, biomass combustion contributes more $PM_{2.5}$ mass in residential areas. Hence air quality management strategies need to target open burning activities as well as fossil fuel combustion.

1. Introduction

There is evidence that combustion-related atmospheric particles (which are largely carbon) are more hazardous than for particles from other sources (Hoek et al., 2013; Betha et al., 2014; Grahame et al., 2014; Lippmann, 2014; Mauderly et al., 2014; Vermeulen et al., 2014; Chung et al., 2015; Hime et al., 2015; Kioumourtzoglou et al., 2015; Oeder et al., 2015; Raspanti et al., 2016; Samoli et al., 2016). Diesel exhaust has been classified by the International Agency for Research on Cancer (2012) as carcinogenic to humans. The World Health Organisation (Janssen et al., 2011; Janssen and WHO, 2012) suggests the use of carbon as an indicator in reducing population exposure to combustion particulate matter. Shindell et al. (2012) argue that in addition to health benefits, reducing black carbon in the atmosphere also mitigates climate change impacts.

Concern regarding combustion emissions is common across the Pacific Islands, particularly those due to diesel fuels (Gleye, 2010; Dornan and Jotzo, 2012; Pacific Energy Summit, 2013; Escoffier et al., 2016; Taibi et al., 2016) and from waste burning (Thaman et al., 2003; Periathamby et al., 2009; Mataki, 2011; Owens et al., 2011; Woodruf, 2014; Mohee et al., 2015). This study has relevance not only for Fiji and other Pacific Islands, but for other small island states affected by open burning of waste (Mohee et al., 2015; Marra, 2016; Riquelme et al., 2016) and reliance on diesel combustion (Mishra et al., 2009; Lucas et al., 2017). Indeed, these combustion sources are significant issues globally for cities in developing countries (Guerrero et al., 2013; Mitra, 2014; The World Bank, 2014; Wiedinmyer et al., 2014).

Studies in Suva, Fiji (Isley et al., 2017a) indicate significant black carbon concentrations (2.2 ± 0.1 μg m^{-3} annual mean). Source apportionment studies for Suva (Isley et al., 2018a; Isley et al., 2018b) have been based, in part, on black carbon concentration determined by the laser integrating plate method (Taha et al., 2007). Variability in the composition of atmospheric particles may affect black carbon measurements (Janssen et al., 2012). Here carbon content is tested using a thermal method, to verify previous results. Elemental (EC) and organic carbon (OC) components are also quantified, as these are useful for source apportionment (Zheng et al., 2006; Zhang et al., 2012; Bernardoni et al., 2013; Liu et al., 2014).

Further, radiocarbon analysis allows identification of fossil and contemporary carbon components (Zencak et al., 2007). Radiocarbon analysis is a method widely used in scientific studies and by environmental regulatory authorities to determine biomass burning contributions (Sheesley et al., 2009; Department for Environment Food and Rural Affairs, 2012; Belis et al., 2014). The 5730 yr. half-life of ^{14}C makes it an ideal tracer for identifying combustion products derived from fossil fuels (^{14}C-free) versus those from biomass (Reddy et al., 2002). In contrast to elemental and molecular tracers; e.g., potassium and chlorine, methyl chloride and levoglucosan, which may exhibit high emission variability, radiocarbon (^{14}C) measurements provide unambiguous source apportionment (Currie, 2000) of contemporary and fossil carbon aerosol, since it retains its identity throughout atmospheric chemical changes (Krecl et al., 2008). Use of ethanol from biomass sources in motor vehicle fuels can complicate this, however ethanol was not being added to Fijian motor vehicle fuels at the time of the air sampling (World Data Atlas, 2018).

Fijian source-apportionment studies (Isley et al., 2018b) have focussed on the inner city and indicate that diesel fuels are the most significant anthropogenic source. Emissions inventory studies (Isley et al., 2016) estimate wood and waste burning to contribute 35% of $PM_{2.5}$ (particulate matter < 2.5 μm effective aerodynamic diameter) emissions in the greater Suva area. Conversely, Suva City air sampling results (Isley et al., 2018b) show open burning to only represent 8% of $PM_{2.5}$ mass. In south Asia, Gustafsson et al. (2009) noted a similar difference between the particle emissions inventory and elemental composition studies, which used black carbon. Interestingly, radiocarbon analyses showed a larger contribution from biomass combustion (Gustafsson et al., 2009). Accurate information on biomass contributions is necessary for effective air quality management. It was surmised (Isley et al., 2018b) that open burning source contributions to atmospheric particulate may be higher in Suva's residential areas, where open burning of waste is common practice (McDowall, 2005).

In this study, using the radiocarbon method, fossil and contemporary carbon ratios were determined for Suva, as well as whether these are consistent between inner city, residential and background locations. These data can be used to identify source contributions to total particulate concentration; evaluate the accuracy of emissions inventory and previous source apportionment studies and provide a solid scientific basis for the development of effective pollutant control measures.

2. Method

2.1. Locations

Airborne particulate samples were collected at three ambient monitoring sites in Suva: Suva City, Kinoya and Suva Point as shown in Fig. 1. The Suva bus terminal, city markets, an industrial precinct and shipping port activities all lay within 1 km of the Suva City site. Kinoya lies within Nasinu, Fiji's most densely populated area, containing a mixture of formal and informal (squatter) settlements. Suva Point is a mainly ocean-influenced site, with winds mainly from the southeast (Isley et al., 2017a); hence less influenced by city emissions than the other locations.

2.2. Sampling

Samples were collected during intensive sampling campaigns in October 2014, April to May 2015 and October 2015, as detailed in Supplementary Table S1. $PM_{2.5}$ samples were collected at Suva City using an Aerosol Sampling Program (ASP) cyclone sampler (Cohen, 1996) operating at 22 L/min flowrate. Total particulate samples, at Suva City, Kinoya and Suva Point, were collected using a low-volume Ecotech Microvol sampler with flowrate 3 L/s (Australian/New Zealand Standard, 2006). In each case, quartz fibre filters were used (47 mm for TSP, 15 mm for $PM_{2.5}$), precleaned at 900 °C to ensure carbon contaminants were removed. Samples were chilled during transport to prevent volatilisation of organic carbon components.

2.3. Sample preparation

Sixteen air particulate filter samples were prepared. Each sample represents an average of 3 days of sampling for $PM_{2.5}$ samples (City, 5 samples) and 16 days for TSP samples (all sites, 11 samples). Samples were placed in a desiccator with 30 mL of concentrated HCl for 24 h and exposed to HCl fumes to remove carbonates (Jordan et al., 2006). All remaining carbon, which includes organic carbon (OC) and elemental carbon (EC), is termed total "non carbonate" carbon (NCC) in this paper. Twelve of the samples were divided into half, one half to be analysed for NCC and the other for EC. These fractions were prepared as shown in Supplementary Fig. S1.