

Response to Editor

We are pleased that our manuscript has been accepted for publication following the corrections you suggested.

We agree with the Editor and Reviewer #3 that O/C is of general interest to atmospheric chemistry beyond particulate matter. Therefore we have revised the Abstract and Introduction to reflect a broadened discussion of reactive organic carbon and its properties.

The revised text is excerpted below, with the added text in *italics* and the line numbers provided.

Abstract (lines 10-29)

Abstract. *Due to its complexity, gas- and particle-phase organic carbon in the atmosphere are often classified by their bulk physicochemical properties. However, there is a dearth of robust, moderate-cost approaches to measure bulk chemical composition of organic carbon in the atmosphere. This is particularly true for degree of oxygenation, which critically affects the properties and impacts of organic carbon, but for which routine measurements approaches are lacking. This gap has limited understanding of a wide range of atmospheric components, including particulate matter, the mass of which is monitored worldwide due to its health and environmental effects, but the chemical characterization of which requires relatively high capital costs and complex operation by highly trained technical personnel.* In this work, we demonstrate a new approach to estimate the mass of carbon and oxygen in analytes and mixtures that relies only on robust, moderate-cost detectors designed for use with gas chromatography. Organic compounds entering a flame ionization detector were found to be converted with approximately complete efficiency to CO₂, which was analysed downstream using an infrared detector to measure the mass of carbon analysed. The ratio of FID signal generated per CO₂ formed (FID/CO₂) was shown to be strongly correlated ($R^2 = 0.89$) to the oxygen-to-carbon ratio (O/C) of the analyte. Furthermore, simple mixtures of analytes behaved as the weighted average of their components, indicating that this correlation extends to mixtures. These properties were also observed to correlate well with the sensitivity of the FID estimated by structure activity relationships (quantified as the relative Effective Carbon Number). The relationships between measured FID/CO₂, analyte O/C, and FID sensitivity allow estimation of one property from another with <15% error for mixtures and <20% error for most individual analytes. The approach opens the possibility of field-deployable, autonomous measurement of the carbon and oxygen content of particulate matter using time-tested, low-maintenance detectors, though such an application would require some additional testing on complex mixtures. *With some instrumental modifications, similar measurements on gas-phase species may be feasible.* Moreover, potential expansion to additional gas chromatography detectors may provide concurrent measurement of other elements (e.g. sulphur, nitrogen).

Introduction (lines 31- 44)

Reactive organic carbon (ROC) in the atmosphere oxidizes in the presence of natural and anthropogenic emissions to produce aerosols and ozone, air pollutants with significant health, ecosystem, and climate effects (Intergovernmental Panel on Climate Change, 2013; World Health Organization, 2016). ROC is complex, comprised of thousands of different compounds possessing a broad range of structures, volatility, and reactivity (Goldstein and Galbally, 2007). The vapor pressures of ROCs range from highly volatile gaseous compounds to essentially non-volatile species that are emitted in condensed form as primary organic aerosols (POA) or are produced through oxidation of gases to form secondary organic aerosol (SOA) (Donahue et al., 2006; Jimenez et al., 2009; Zhang et al., 2007). Similarly, solubility ranges from essentially insoluble (e.g., volatile hydrocarbons) to highly soluble polyols (Hodzic et al., 2014; Raventos-Duran et al., 2010). Given these broad ranges, there is a keen interest in classifying organic compounds by understanding their bulk physicochemical properties (Donahue et al., 2006; Kroll et al., 2011). A major parameter by which ROC is frequently classified is some measure of the degree of oxidation or oxygenation of each compound (Donahue et al., 2011; Kroll et al., 2011; Pankow and Barsanti, 2009). This is because the oxygen content of a molecule influences its volatility (Aiken et al., 2008; Huffman et al., 2009), its ability to absorb into existing particle-phase (Donahue et al., 2011), and its solubility (Raventos-Duran et al., 2010). Consequently, a robust approach to measuring O/C and properties of organic carbon would be a valuable tool for understanding the impacts of ROC.

Introduction (lines 45-52)

*Degree of oxygenation particularly affects the impacts of particle-phase organic carbon. Atmospheric particulate matter (“aerosols”) is responsible for a substantial fraction of annual global deaths (Dockery et al., 1993; Lim et al., 2012; World Health Organization, 2016) and is consequently monitored, primarily on a mass basis, throughout the world. A major fraction of these aerosols is comprised of organic compounds, which may be directly emitted or form through the atmospheric oxidation of naturally and anthropogenically emitted volatile organic compounds. Owing to the wide range of sources and formation chemistry of aerosols, the composition may vary substantially, and *the impacts of aerosols are dependent on their composition*. For example, increased oxygenation increases hygroscopicity (Massoli et al., 2010), which increases cloud formation and impacts albedo (Intergovernmental Panel on Climate Change, 2013).*

Introduction (lines 109-122)

One significant potential application of using combined FID and CO₂ measurements to measure oxygen content would be the measurement of bulk chemical properties of *organic compounds*. As a preliminary assessment of the feasibility of such an approach, we provide in the Supplementary Information (Section S1 and Table S1) an estimate of the concentrations of CO₂ generated in the combustion of atmospherically-relevant concentrations of organic aerosols. Using reasonable assumptions for a theoretical instrument *that collects and analyses organic aerosol based on this approach*, expected concentrations of CO₂ measured in the outflow of an FID of ~100 ppb to ~100 ppm, well within the detection range of current NDIR-based CO₂ instrumentation. *We focus here on organic aerosols due to*

their major atmospheric consequences and the known effects of bulk oxygen content on these consequences, but note that this approach could also be adapted to collected samples of gas-phase organic compounds.

Besides oxygen, nitrogen and sulphur are common heteroatoms occurring in *atmospheric samples, particularly* organic aerosols. Both elements are present at concentrations approximately an order of magnitude lower than oxygen or carbon (Aiken et al., 2008; Carrasquillo et al., 2014; Docherty et al., 2011; Surratt et al., 2008), with organic sulphate primarily present as organosulphates, and nitrogen present as a mixture of functional groups including nitrates (Farmer et al., 2010), N-containing heterocycles (Laskin et al., 2015), and amines (Murphy et al., 2007).