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OH reactivity of the urban air in Helsinki, Finland, during winter

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ABSTRACT

A new instrument to measure total OH reactivity in ambient air based on the Comparative Reactivity Method (CRM) has been built and characterized at the Finnish Meteorological Institute in Helsinki, Finland. The system is based on the detection of pyrrole by a gas chromatograph with a photoionization detector and designed for long term studies. It was tested in a container close to the SMEAR III semi-urban station in Helsinki during the winter in February 2016. The sampling location next to the delivery area of the institute was influenced by local vehicle emissions and cannot be considered representative of background conditions in Helsinki. However, effects of nitrogen oxides on the measurements could be investigated there. During this campaign, 56 compounds were measured individually by 1) an in-situ gas chromatograph coupled to a mass spectrometer (GC/MS) and by 2) off-line sampling in canisters and on adsorbent filled cartridges taken at the container and subsequently analysed by GC-FID and liquid chromatography, respectively. In addition, nitrogen oxides were measured at the same location, while ozone, carbon monoxide and sulfur dioxide concentrations have been retrieved from the SMEAR III mast data. The comparison between the total OH reactivity measured and the OH reactivity derived from individual compound measurements are in better agreement for lower reactivity levels. Possible explanations for the differences are discussed in detail.

1. Introduction

The hydroxyl radical (OH) is the most important oxidant in our atmosphere (Denman et al., 2007; Lelieveld et al., 2016). Yet it is difficult to measure directly and to represent correctly in models. OH reacts with nearly all atmospheric trace gases and its lifetime is therefore short (from a few seconds to below 10 ms). OH reactivity is defined as the inverse of its lifetime and can be derived by summing the products of the concentrations [*i*] of all individual compounds *i* reacting with OH with their corresponding OH reaction rate coefficients ($k_{i,\mathrm{OH}}$):

$$R_{\mathrm{OH}} = \sum_i k_{i,\mathrm{OH}}[i] \qquad (1)$$

Kovacs and Brune (2001) originally proposed measurement of total OH reactivity as a holistic approach to verify whether the compounds that are routinely measured (in particular Volatile Organic Compounds, VOCs) are sufficient to account for the directly measured reactivity and OH concentrations in models. The basic assumption is that if reactive compounds are missing from the models, the OH concentrations in photochemical and global climate models will be overestimated, leading to inaccurate predictions.

The first OH reactivity measurement method relied on the direct observation of OH and its decay by laser induced fluorescence (LIF, Kovacs and Brune, 2001; Kovacs et al., 2003). Later Sinha et al. (2008) proposed an alternative relative rate approach based on the measurement of a VOC by mass spectrometry and termed the Comparative Reactivity Method (CRM). With this method the oxidation of a reference compound (not present naturally in the air) in an OH field is monitored with and without ambient air present. This method has been then adopted by several groups (e. g. Kim et al., 2011; Dolgorouky et al., 2012; Michoud et al., 2015; Yang et al., 2016a) and has been deployed at various sites (e. g. Zannoni et al., 2015, 2016; Hansen et al., 2015; Williams et al., 2016).

Generally studies made in urban environments have found that the difference between the total OH reactivity measured and the OH reactivity calculated from individually measured atmospheric compounds (called unexplained or *missing* reactivity) is below 40% and in some cases within the experimental error (e. g. Kovacs et al.,

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2003; Ren et al., 2003, 2006; Sadanaga et al., 2005; Shirley et al., 2006; Yoshino et al., 2006, 2012; Lou et al., 2010; Lee et al., 2009; Hansen et al., 2015; Whalley et al., 2016). This contrasts with forested sites where large fractions of the OH reactivity could not be explained. Di Carlo et al. (2004) first reported such data from the temperate forest and since then similar findings have been reported from other tropical and boreal forests (e. g. Sinha et al., 2008, 2010; Nölscher et al., 2012b, 2016; Edwards et al., 2013). These findings on the variability of OH reactivity from ambient air at various locations and from biogenic emissions have been the main drivers for the development of a new CRM system at the Finnish Meteorological Institute (FMI) suitable for semi-autonomous longer term measurements at boreal forest sites. OH reactivity measurements have been comprehensively reviewed recently (Yang et al., 2016b) and the immediate research goals for the OH reactivity community summarized (Williams and Brune, 2015). It is clear that most work to date has been performed in intensive campaigns due to the complexity of the instrumentation. Here we endeavour to construct a robust, sensitive, accurate, and precise system suitable for seasons spanning measurement intervals and we test the system with as little intervention as possible during a month of measurements.

2. Methods

2.1. The Comparative Reactivity Method (CRM)

Sinha et al. (2008) developed the CRM method in order to provide more affordable and transportable OH reactivity measurements requiring less ambient air inflow than those based on LIF. Its principle relies on the addition of a given compound (pyrrole, C_4H_5N) to both ambient air and zero air and exposing the mixtures to OH. The radicals are produced by the photolysis of water with a UV lamp ($\lambda < 185$ nm). A scheme of the setup is depicted in Fig. 1 with a gas chromatograph using a photoionization detector (GC-PID, GC955, Synspec b.v., Groningen, The Netherlands) as the detector rather than the original proton transfer reaction mass spectrometer (PTR-MS), similar in concept to Nölscher et al. (2012a). The whole system is therefore easy to transport for field campaigns and does not require a lot of space.

By comparing the consumption of pyrrole in both ambient and zero air mixtures after exposure to OH, it is possible to estimate the total reactivity of the compounds present in ambient air. Assuming pseudo-first order conditions ([Pyrrole]≫[OH]), the total OH reactivity in the reactor, R_{eqn}, can be derived from the following formula:

$$R_{\mathrm{eqn}} = \frac{C_3 - C_2}{C_1 - C_3} \cdot k_{\mathrm{OH,pyr}} \cdot C_1 \qquad (2)$$

where C_1 is the concentration of pyrrole in the presence of an effective OH scavenger, C_2 the concentration of pyrrole in zero air (all OH reacts with pyrrole), C_3 the concentration of pyrrole in ambient air, and $k_{\mathrm{OH,pyr}}$ the reaction rate for the reaction of pyrrole with OH.

A two minute program was used to sample and quantify pyrrole with GC-PID. C_2 and C_3 measurements were alternated sequentially every 8 min and the first point measured after switching the valve was discarded (stabilisation period). These alternate measurements take into account natural changes in the relative humidity (RH), a key parameter to determine the amount of OH produced as zero air is generated by using a catalyst (platinum on alumina, Pt/AlO_3) at ca. 500 °C to remove VOCs without altering RH significantly (see also section 3.1.2).

Under field conditions C_1 is measured approximately every other week by adding up to 60 ml min^{-1} of a 0.600% mixture of propane in nitrogen as an OH scavenger (AGA, Espoo, Finland). This has been shown to be more reliable and quicker than the original method of measuring C_1 under completely dry conditions, without scavenger (Michoud et al., 2015). C_1 takes into account the photolysis of pyrrole by UV (ca. 9–25%).

The minimum sampling flow is 325 ml min^{-1} during C_2 measurements (zero air only), and about 650 ml min^{-1} during C_3 measurements (half of which goes to the reactor). The nitrogen flow is 145 ml min^{-1} and the pyrrole input flow is about 4 ml min^{-1} from a gas cylinder (5.27 ppmv ± 10% in 6.0 N_2, Westfalen AG, Münster, Germany). Therefore the total flow through the reactor is 472 ml min^{-1} and the dilution factor D is 1.45 (ratio of sampling and total flows). The system is controlled and the data recorded with a custom-made software written in Python (pyCRM).

2.2. Laboratory characterization

For the characterization of the CRM system in the laboratory, the

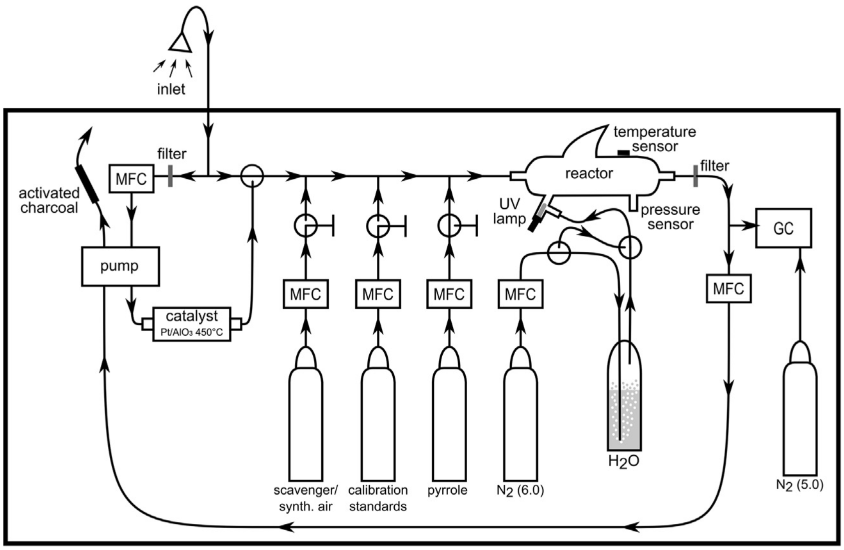

Fig. 1. Scheme of the CRM-FMI setup (MFC: Mass Flow Controller, GC: Gas Chromatograph).