Oxidative Potential and Chemical Characteristics of Ambient $PM_{2.5}$ in Guangzhou, China

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Abstract

The dithiothreitol (DTT) assay is widely used to characterize the Oxidation Potential (OP) of atmospheric particulate matter (PM), which can cause adverse effects on human health. However, it's under debate which chemical species determines the consumption rate of DTT. During January and April 2018, we measured the improved DTT assay of daily PM2.5 samples collected in Guangzhou, China with complimentary measurements of water-soluble ions, organic/elemental carbon (OC/EC) and metal elements. The average sampled air volume normalized consumption rate of DTT (DTTv) was 4.67 ±1.06 and 4.45 ± 1.02 nmol min-1 m-3, in January and April, respectively while the average PM2.5 mass normalized consumption rate of DTT (DTTm) was 13.47 ± 3.86 and 14.66 ± 4.49 pmol min-1 µg-1. Good correlations were found between DTTv and concentration of PM2.5, OC, and EC while no correlation was found between DTTm and concentrations of water-soluble ions, OC, EC or metal element, which is consistent with most early observations. We also evaluated the contribution of soluble metals to DTT assay by addition of EDTA, a strong metal chelator. We found that nearly 90% of DTTv and DTTm were reduced by EDTA, suggesting a dominant role of soluble metals in determining the response of DTT to ambient PM2.5. Based on responses of DTT to soluble metals in literature, we found that Cu(II) and Mn(II) are the major contributors to OP of PM2.5 in Guangzhou. The correlation coefficient between DTTm and OC shows a clear increase after addition of EDTA, implying that the response of DTT to quinones is not strongly suppressed by EDTA.

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Introduction

Oxidation potential that determines the capability of reactive oxygen species (ROS) generation is widely used to characterize the impact of $PM_{2.5}$ on human health. In January and April 2018, we measured the dithiothreitol (DTT) assay of daily $PM_{2.5}$ samples collected in Guangzhou, China with complimentary measurements of water-soluble ions, organic/elemental carbon (OC/EC) and metal elements. Correlations between DTT and chemical compositions of $PM_{2.5}$ were analyzed. Contribution of soluble metals to DTT assay was also evaluated by addition of EDTA.

Materials & Methods

The DTT assay is used to characterize the Oxidation Potential (OP) of atmospheric particulate matter (PM). Agitation, instead of ultrasonication was adopted as the extraction method to avoid ROS generation during sample preparation. EC/OC were measured on-line. Water-soluble ions and heavy metals were analyzed by IC and ICP-MS, respectively.

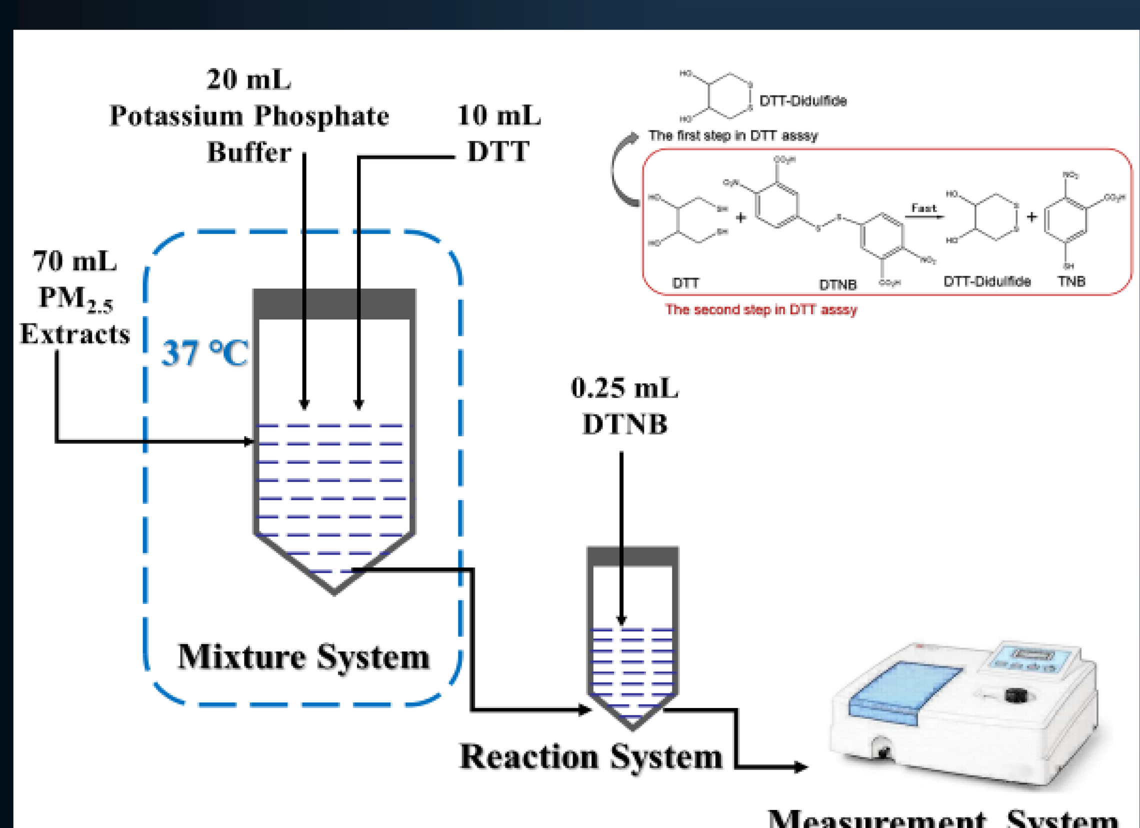

Figure 1 The experimental flow chart of the DTT assay

Results and Discussion

The average sampled air volume normalized consumption rate of DTT (DTTv) was 4.67 ±1.06 and 4.45 ± 1.02 nmol min^{-1} m^{-3}, in January and April, respectively while the average $PM_{2.5}$ mass normalized consumption rate of DTT (DTTm) was 13.47 ± 3.86 and 14.66 ± 4.49 pmol min^{-1} μg^{-1}.

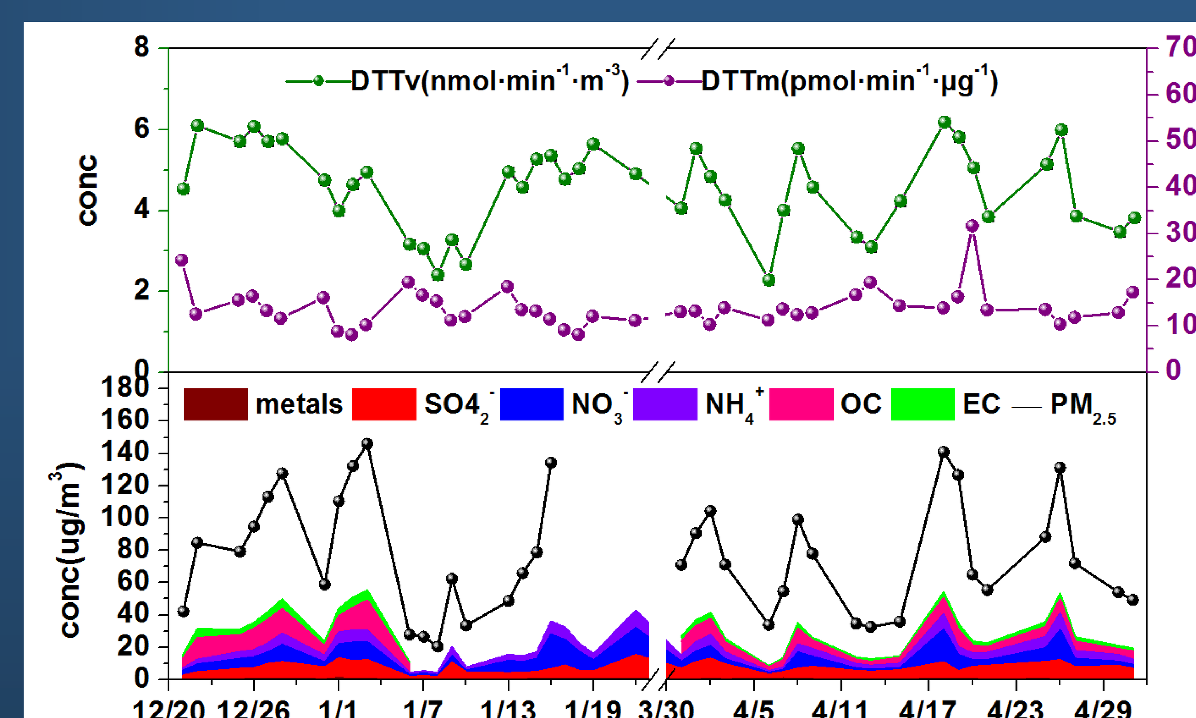

Figure 2 Temporal variations of $PM_{2.5}$ mass concentration, chemical compositions and OP values (DTTm and DTTv).

Figure 3 shows the OP values measured with and without EDTA addition. The OP of $PM_{2.5}$ in January and April (DTTv, nmol min^{-1} m^{-3}) decreased by 84.4% and 90.0%, respectively, after the addition of EDTA .

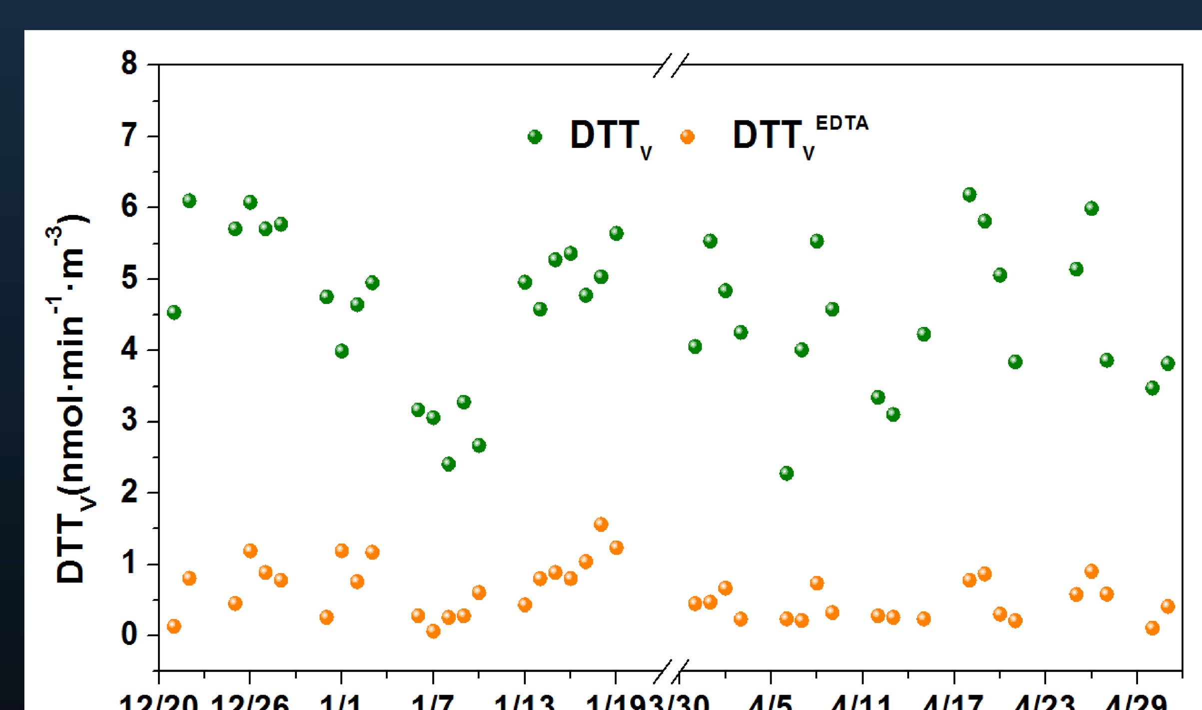

Figure 3 The change of DTTv before and after adding EDTA-Na_2

The contributions of major heavy metals to OP values was estimated based on parameterization from literature (Charrier et al., 2012). The reconstructed OP was 137% in January and 112% in April, on average 125%,which suggested that the parameterization can be applicable in our study with some uncertainties. Overall, more than 90% of OP of PM2.5 were from Cu (II) and Mn (II), while other elements such as Fe, V, Co, Ni, and Pb contributed less than 1% of OP in PM2.5 in Guangzhou.

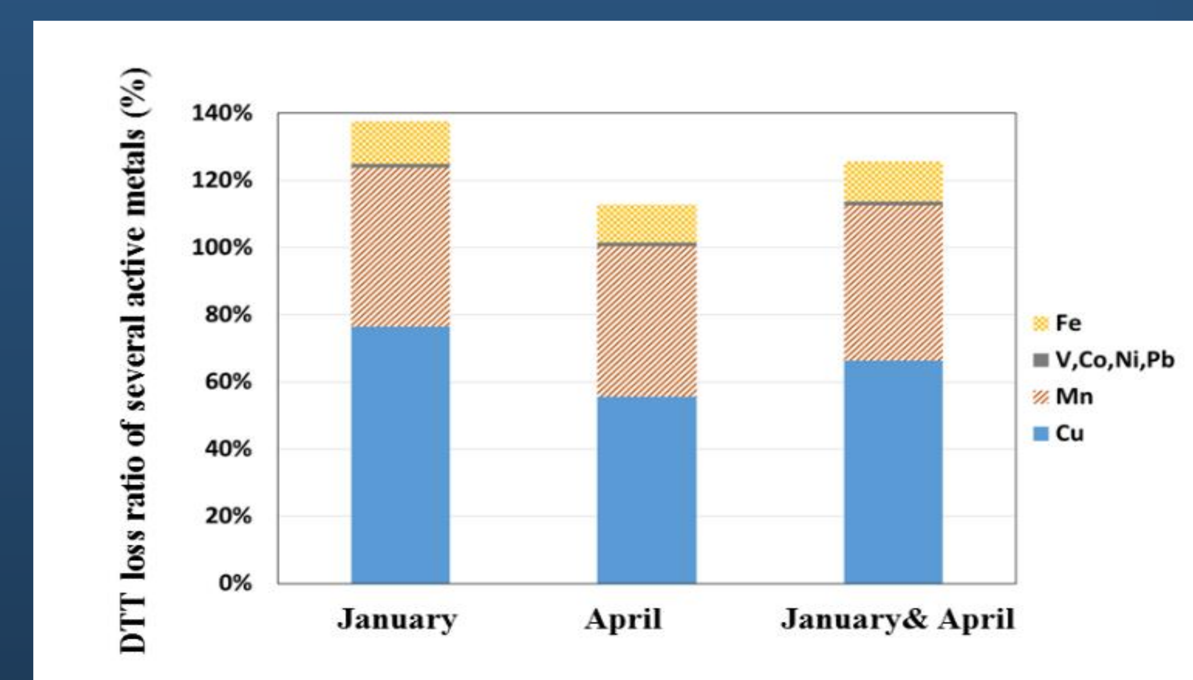

Figure 4 Calculated average contributions to DTT loss by seven metals in atmospheric $PM_{2.5}$

The correlation coefficient between DTTm and OC shows a clear increase after addition of EDTA, implying that the response of DTT to quinones is not strongly suppressed by EDTA

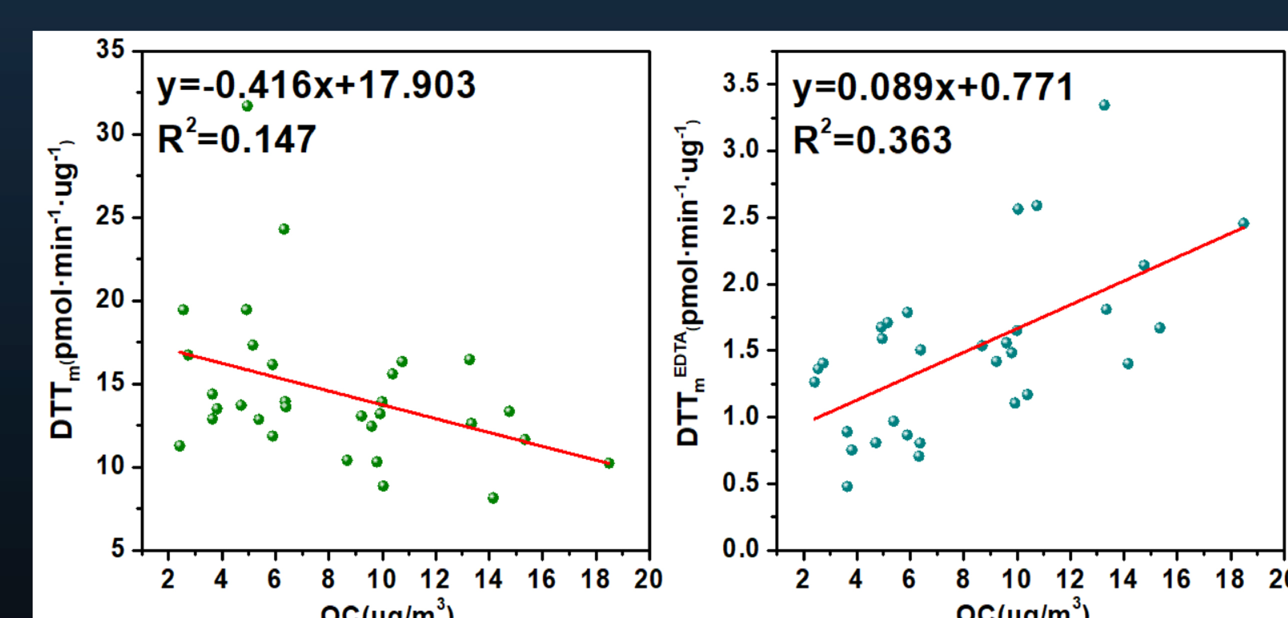

Figure 5 The change of DTTv before and after adding EDTA-Na_2

Conclusions

- The average value of DTTv was 4.67 ±1.06 and 4.45 ± 1.02 nmol min^{-1} m^{-3} in January and April respectively; and DTTm was 13.47 ± 3.86 and 14.66 ± 4.49 pmol min^{-1} μg^{-1}.
- Good correlations were found between DTTv and concentration of $PM_{2.5}$, OC, and EC while no correlation was found between DTTm and concentrations of water-soluble ions, OC, EC or metal element, which is consistent with most early observations.
- Soluble metals dominate the response of DTT to ambient $PM_{2.5}$, and Cu(II) and Mn(II) may be the major contributors to OP of $PM_{2.5}$ in Guangzhou.
- Response of DTT to quinones is much smaller than metals, and not strongly suppressed by EDTA

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References

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