

## DOCTORAL THESIS

# Investigation of chemical components, sources, and dithiothreitol (DTT) based oxidative potential of PM<sub>2.5</sub> and its humic-like substances (HULIS) fraction

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## Abstract

Air pollution caused by ambient fine particulate matter (PM<sub>2.5</sub>) is a significant global environmental problem. Pollutants that adhere to PM<sub>2.5</sub> may be transported into human respiratory system and perturb the redox equilibrium through the generation of reactive oxygen species (ROS), thus leading to myriad health effects. This mechanism has been proposed to be related with the high redox-active components in PM<sub>2.5</sub>, such as transition metals, quinones, and humic-like substances (HULIS). This thesis aims to improve the scientific understanding on the sources and health impacts of PM<sub>2.5</sub> especially its HULIS fraction. Thus, both chemical characterization and redox activity measurement of ambient PM<sub>2.5</sub> samples were conducted. Positive matrix factorization (PMF) was then performed to apportion the source-specific contributions to PM<sub>2.5</sub> and its oxidative potential. The HULIS fraction of PM<sub>2.5</sub> was also quantified and source apportioned regarding their mass concentration and oxidative potential.

The main findings are summarized below:

(1) In Chapter 2, 66 PM<sub>2.5</sub> samples collected in Hong Kong during 2016-2017 were analyzed, including carbonaceous components, major ions, metals, and some source markers. The oxidative potential of PM<sub>2.5</sub> were measured using dithiothreitol (DTT) assay. Results showed clear temporal trends for both PM<sub>2.5</sub> mass concentration and its major fraction, with higher levels observed on days under

regional pollution than on days under long range transport (LRT) pollution and local emissions. The DTT consumption of  $PM_{2.5}$  on the contrary, only showed slightly higher activity on regional and LRT days than on local days, possibly due to the comprehensive effects of different sources and species concentrations under different sampling days. We then conducted source apportionment using PMF model. Five primary sources (i.e. marine vessels, Cu-related source, Fe-Mn-Zn-related source, vehicle emissions, biomass burning) and one secondary source were resolved for both  $PM_{2.5}$  mass concentration and DTT activity. Secondary formation was found to be the most significant source responsible for  $PM_{2.5}$  mass concentration (30.3%), followed by Cu-related source (24.8%), marine vessels (17.9%) and vehicle emissions (14.5%). Biomass burning (6.8%) and Fe-Mn-Zn-related source (5.8%) were two minor sources contributing to  $PM_{2.5}$  mass concentration. For oxidative potential of  $PM_{2.5}$ , Cu-related source was the predominant contributor (39.1%). Secondary formation (23.7%) and marine vessels (20.1%) were also two significant sources responsible for the DTT consumption of  $PM_{2.5}$ . For intrinsic oxidative potential,  $PM_{2.5}$  emitted from marine vessels and Cu-related source showed highest value, indicating more toxic feature of  $PM_{2.5}$  derived from those sources regarding DTT activity.

(2) In Chapter 3 and 4, the mass concentration, optical properties, and ROS-generation potential of HULIS were investigated in  $PM_{2.5}$  samples collected in

Hong Kong during 2011-2012. They all showed higher levels on regional days than on LRT days and local days. PMF analysis was conducted regarding the mass concentration and ROS activity of HULIS. Six sources were determined, including four primary sources (i.e. marine vessels, vehicle emissions, industrial exhaust, and biomass burning) and two secondary sources (i.e. secondary organic aerosol formation and secondary sulfate). Most sources showed higher contributions to both mass concentrations and DTT activity of HULIS on regional days than on LRT and local days, except that marine vessels had a higher contribution on local days than the other two synoptic conditions. Secondary processes were the major contributor to HULIS (54.9%) throughout the year, followed by biomass burning (27.4%) and industrial exhaust (14.7%). As for the DTT activity of HULIS, biomass burning (62.9%) and secondary processes (25.4%) were found to be the top two contributors. Intrinsic ROS-generation potential of HULIS was also investigated by normalizing the DTT activity by HULIS mass in each source. HULIS from biomass burning were the most DTT-active, followed by marine vessels; while HULIS formed through secondary processes were the least DTT-active. For the optical properties of HULIS, multiple linear regression model was adopted to evaluate the contributions of various sources to the light absorbing ability of HULIS. Biomass burning was found to be the only source significantly associated with the light absorbing property of HULIS.

(3) In Chapter 5 and 6, the predominant species of water-soluble fraction of  $PM_{2.5}$ , HULIS, were measured in samples collected in Beijing from 2011 to 2012. Various HULIS species, and the redox activity of HULIS were quantified together with certain source markers of  $PM_{2.5}$ . HULIS and their redox activity showed similar temporal trend, with higher levels measured during the heating season (November to March) than during the non-heating season (April to October). Source apportionment of both HULIS and their redox activity was performed using PMF. Four combustion-related primary sources, namely coal combustion, biomass burning, waste incineration, and vehicle exhaust, and one secondary factor were resolved. In particular, waste incineration was identified as a source of HULIS for the first time. Biomass burning and secondary aerosol formation were the major contributors (>59%) to both HULIS and associated DTT activity throughout the year. During the non-heating season, secondary aerosol formation was the most important source, whereas during the heating season, the predominant contributor was biomass burning. The four combustion-related sources accounted for about 70% of HULIS and their ROS activity, implying that future reduction in  $PM_{2.5}$  emissions from combustion activities can substantially reduce the HULIS burden and their potential health impact in Beijing.

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