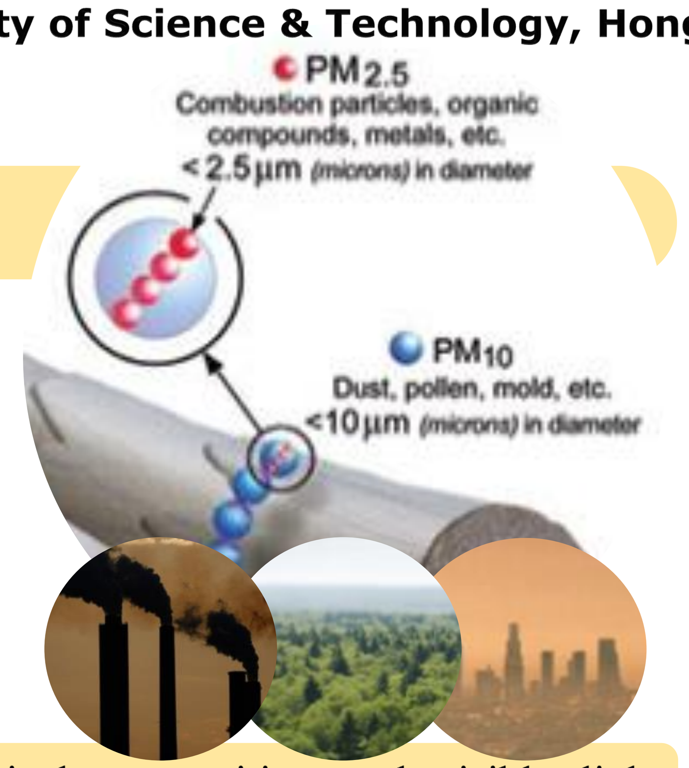
Quantifying the relationship between visibility degradation and PM2.5 constituents at a suburban site in Hong Kong:

Differentiating contributions from hydrophilic and hydrophobic organic compounds

Yugen Li[1], Hilda X. H. Huang[2], Stephen M.Griffith[3], Cheng Wu[1], Alexis K. H. Lau[1], Jian Zhen Yu[1,2,3*]

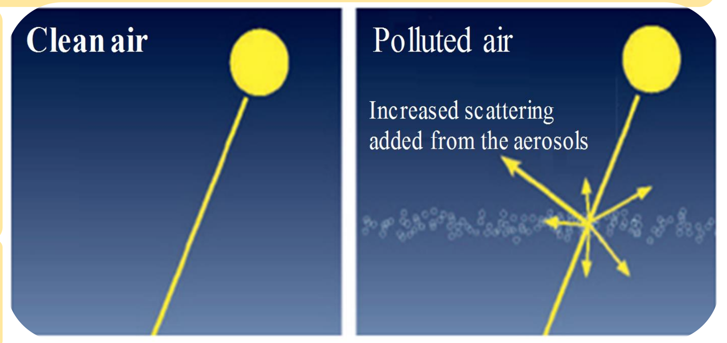
[1] Division of Environment and sustainability, Hong Kong University of Science & Technology, Hong Kong, China
[2] Institute of Environment, Hong Kong University of Science & Technology, Hong Kong, China
[3] Department of Chemistry, Hong Kong University of Science & Technology, Hong Kong, China
*Corresponding author email: jian.yu@ust.hk

Background



- Atmospheric aerosol plays a key role in air pollution and climate change issues. Aerosols directly influence the solar radiation balance and cause visibility degradation through absorption and scattering of light. Any sample of ambient air has an associated light extinction coefficient, σ_{ext}, which defines how efficiently light is attenuated by gases and aerosols in the air sample.
- For analyzing the relationship between aerosol chemical composition and visible light extinction, Mie theory is the first and most robust approach, but requires a long period of size-resolved sampling of ambient aerosols. A more practical approach is to use multilinear regress -ion to link measured light extinction coefficients (dependent variable) with collocated aerosol chemical compositions (independent variables). The widely used **IMPROVE** formula is an example of this method and is designed to reconstruct the light extinction coefficient for gases and particles:

$$\sigma_{ext} = 3.0f(RH)[AS] + 3.0f(RH)[AN] + 4.0R_{OC}*[OC] + 1.0[Soil] + 0.6[CM] + 1.7f(RH)[SS] + 10[EC] + \sigma_{Rayleigh}$$



- With only limited success of IMPROVE or similar equations to model light extinction coefficients in Asia, there is still a need to explore 'localized' equations to describe visibility degradation in relation to the chemical composition and optical properties of aerosols.
- Furthermore, the light extinction contributions from speciated OC components has been largely unexplored. This study aims to attribute light extinction coefficients in greater depth to the OC components

Aerosol sampling and chemical analysis

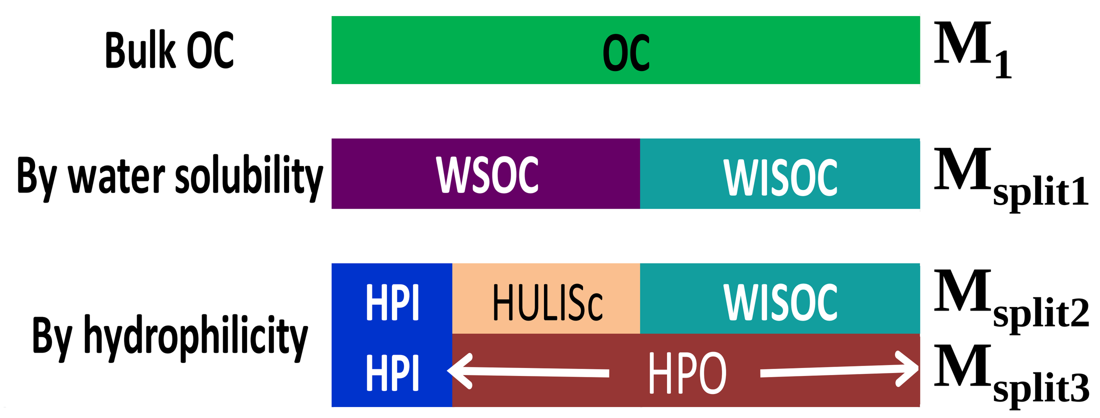
- In this study, we collected around 120 ambient $PM_{2.5}$ samples at a suburban site of Hong Kong over a course of two years. Location is at the Hong Kong University of Science and Technology Air Quality Research Supersite (HKUST Supersite, 22°20.272"N, 114°16.049" E).
- Major chemical components obtained include ions, elements, different carbon fractions. Daily averaged mass scattering coefficients (σ_{sp}) and mass absorption coefficients (σ_{ap}) were measured with a nephelometer (Aurora 3000, EcoTech Pty Ltd., Australia) and aethalometer (AE-31, Magee Scientific Company, Berkeley, CA, USA), respectively.
- This comprehensive data set was used to generate 'localized' equations similar to IMPROVE to reconstruct light extinction coefficients for aerosols in Hong Kong and investigate the role of different aerosol compositions in visibility degradation.

✓ Light scattering
✓ Light absorption

Localized equations

✓ Ions
✓ Metals
✓ EC
✓ OC

Methodology



- In addition to determining the bulk OC scattering efficiency, a stepwise separation of organic matter (OM) was performed according to water solubility: dividing water soluble organic carbon (WSOC) and water insoluble organic carbon (WISOC); alternatively according to water affinity: hydrophilic carbon (HPI) and hydrophobic carbon (HPO), the latter being the sum of humic-like substance carbon (HULISc) and WISOC. M_1 to M_{split3} as shown in the above schematic are different representations of the OC mass.

$$\sigma_{ext} = \sum_i (a_i m_i)$$

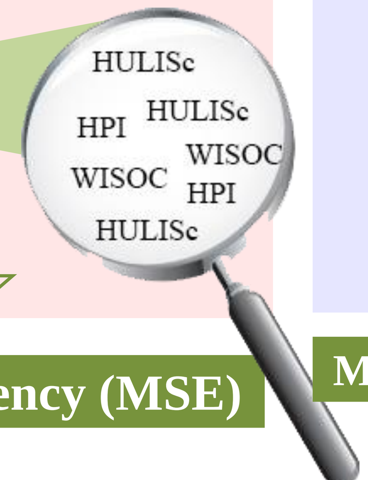
Multiple Linear Regression (MLR)

IMPROVE equation M_{ori}

$$\sigma_{sp} = 3.0*f(RH)[AS] + 3.0*f(RH)[AN] + 1.7*f(RH)[SS] + 7.2*[OC] + 1.0*[Soil] + 0.6*[CM] + \sigma_{Rayleigh}$$

$$\sigma_{ap} = 10[EC]$$

Mass Scattering Efficiency (MSE)



Localized 'Speciated OC' equation M_{split2}

$$\sigma_{sp} = 3.2*f(RH)[AS] + 3.7*f(RH)[AN] + 1.1*f(RH)[SS] + 11.0*[HULISc] + 16.1*[HPI] + 12.8*[WISOC] + \sigma_{Rayleigh}$$

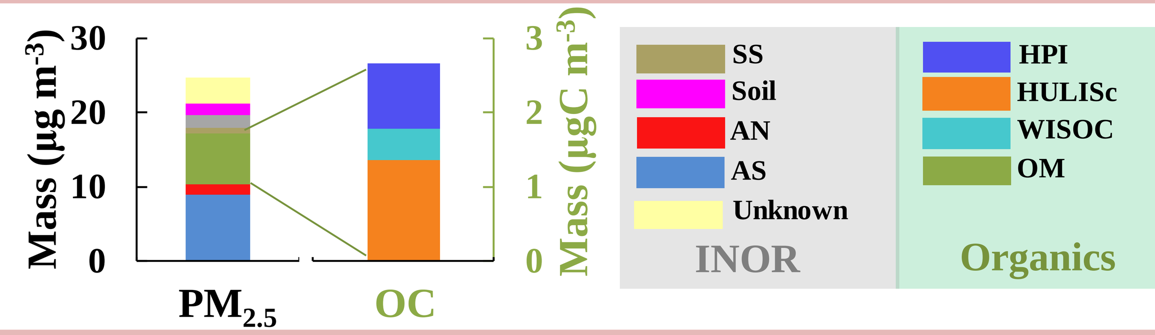
$$\sigma_{ap} = 5.8[EC] + 1.6[HULISc] + 2.4[HPI] + 1.5[WISOC]$$

Mass Scattering Efficiency (MSE)

Mass Absorption Efficiency (MAE)

Lack of speciating OC for MSE and MAE estimations revealed the inaccurate presentation by IMPROVE of OC contributions to both light scattering and absorption.

Results and Discussion



- The annual average OC concentration was 3.88±2.82 µgC m^{-3}, with 2.11±2.01 µgC m^{-3} as WSOC and 1.79±1.48 µgC m^{-3} as WISOC. HULISc was the dominant component of WSOC, with an average of 1.36±1.39 µgCm^{-3}. HPI fraction constituted 0.87±0.88 µgC m^{-3}.

$$M_{ori}: \sigma_{sp,525} = 3.0f(RH)[AS] + 3.0f(RH)[AN] + 1.7f(RH)[SS] + 7.2[OC] + 1.0[Soil] + 0.6[CM]$$

$$M_1: \sigma_{sp,525} = 3.2f(RH)[AS] + 3.7f(RH)[AN] + 1.1f(RH)[SS] + 13.1[OC]$$

- The MSEs of AS and AN (3.2 and 3.7 m^2 g^{-1}) for M_1 are comparable to 3.0 in the IMPROVE formula. Higher OC (13.0 m^2 g^{-1}) vs value of 7.2 m^2 g^{-1} in the IMPROVE formula indicate that the OC component at our site might have a significantly different composition from the U.S. sites, leading to the higher MSE.

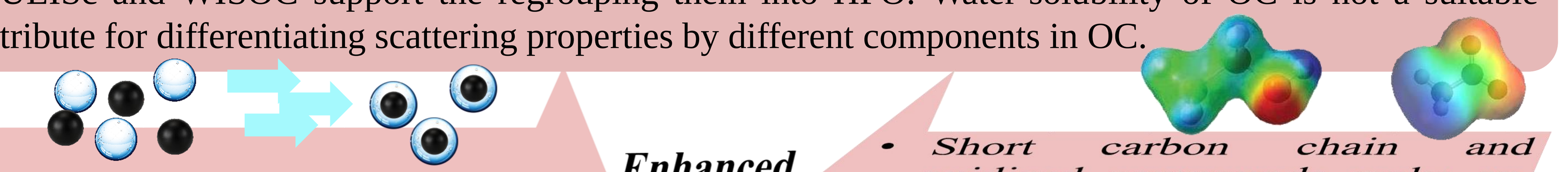
$$M_{split1}: \sigma_{sp,525} = INORG_{Msplit1} + 12.4[WSOC] + 14.0[WISOC]$$

- In M_{split1}, WSOC (12.4 m^2 g^{-1}) exhibits a lower MSE than WISOC (14.0 m^2 g^{-1}), different from the intuition that water to be associated with WSOC contribute to more scattering. It serves a motivation to further split WSOC by hydrophilicity.

$$M_{split2}: \sigma_{sp,525} = INORG_{Msplit2} + 16.1[HPI] + 11.0[HULISc] + 12.8[WISOC]$$

$$M_{split3}: \sigma_{sp,525} = INORG_{Msplit3} + 15.5[HPI] + 12.2[HPO]$$

- HPI (16.1 m^2 g^{-1}) shows a significantly greater MSE than both HULISc and WISOC. Similar MSEs of HULISc and WISOC support the regrouping them into HPO. Water-solubility of OC is not a suitable attribute for differentiating scattering properties by different components in OC.



- *A higher affinity to water vapor increase the HPI scattering ability.*

Enhanced HPI MSE

- *Short carbon chain and oxidized compounds make an uneven distribution of electrons at the molecular level.*
- *The presence of O, N make the compounds more polarizable.*

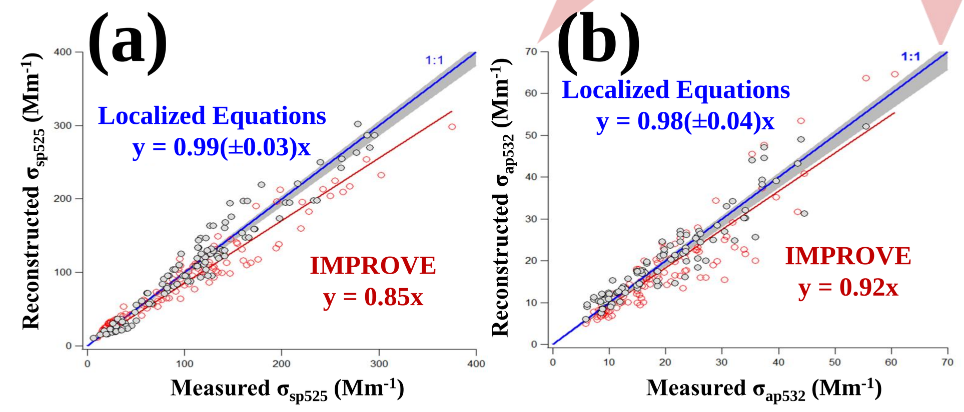


Fig. Measured vs. Reconstructed (a) scattering coefficient (b) absorption coefficient. The IMPROVE comparison (red) utilizes the whole dataset of measurements while the localized equations (grey) are a result from a randomized iterative MLR method. Only one is displayed here.

Summary

✓ This is the first effort to examine the MSEs and MAEs of specific organic carbon components separated by water solubility or water affinity.
✓ Similar MSEs for the inorganic components to those in the original IMPROVE equation.
✓ MSE for OC derived in the local formulas is significantly larger, explaining the underestimation of the measured light scattering coefficient (σ_{sp}) by the IMPROVE formula. HPI is found to have a stronger ability to attenuate light than HPO on a per carbon mass basis.
✓ OC is a key and uncertain component in accurately reconstructing light extinction from chemical composition. Speciating OC by hydrophilicity followed by determining their MSEs, is likely a more promising approach than water-solubility in reconstructing scattering contributions by OC.

Acknowledgment

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Contact

Email: ylidh@connect.ust.hk **Phone: (+852) 6356 2673**