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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Influence of functional groups on toxicity of carbon nanomaterials: implication for toxicological evolution during atmospheric relevant aging of soot" *by* Yongchun Liu et al.

Anonymous Referee #2

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In this work, the authors study the DTT and cytotoxicity response of several carbon nanomaterials and correlate them to their morphology and chemical composition. The main finding is that the epoxide content of graphene oxide is particularly high and also results in high apparent oxidative potential. This specificity is confirmed with thermal treatment of this substance to reduce the epoxide abundance (though also accompanied by morphological changes in the process). The manuscript is generally well-written and addresses a current topic to interest of many researchers. The measurements appear technically sound, though further comments below could be addressed

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Discussion paper

to make the manuscript suitable for publication.

General comments.

First question is regarding the XPS measurements:

* How do the authors go from counts per second to oxygen content in (%) in Figure 5? If no calibration is performed, then is it possible to state absolute differences among functional groups or only C-O-C content among different materials?

* How are epoxides distinguished from ethers?

* It's not clear that these functional group characterizations are representative of the overall OC that is separately measured given the small probing depth of XPS. Can the authors comment on this?

The oxidation of SO2 by epoxides 2016 is cited as support for ROS generation observed in this work, but the cited work of He and He (2016) proposes a surface binding mechanism that is different from the mechanism by which oxidative potential of ROS is meant to be measured by DTT. The authors may wish to clarify this point as this may also be related to the discrepancy with the lack of difference in apparent cytotoxicity.

As with the other reviewer I agree that the connection to atmospheric soot particles is quite tenuous; due to my delay in response I already see that the authors have proposed changes in this regard (which makes the work less relevant for ACP?). One additional point on this is that the authors refer to "BC" but perhaps "soot" is more suitable, and the "surface functionalization" of soot have been characterized previously (including ethers) - e.g., Cain et al. 2010, Vander Wal et al. 2011, Popovicheva et al. 2014. However, atmospheric aging not includes surface functionalization but also condensation of co-emitted species and photochemical oxidation products which are particularly rapid under conditions of soot emissions (Johnson et al. 2005 and Adachi et al. 2010); it is unclear how much of the oxidation potential attributable to functional groups would be dependent on the carbon nanomaterial itself in the environmental

context.

Cain, J. P.; Gassman, P. L.; Wang, H. & Laskin, A. Micro-FTIR study of soot chemical composition-evidence of aliphatic hydrocarbons on nascent soot surfaces, Physical Chemistry Chemical Physics, 2010, 12, 5206-5218

Johnson, K. S.; Zuberi, B.; Molina, L. T.; Molina, M. J.; Iedema, M. J.; Cowin, J. P.; Gaspar, D. J.; Wang, C. & Laskin, A. Processing of soot in an urban environment: case study from the Mexico City Metropolitan Area, Atmospheric Chemistry and Physics, 2005, 5, 3033-3043

Adachi, K.; Chung, S. H. & Buseck, P. R. Shapes of soot aerosol particles and implications for their effects on climate Journal of Geophysical Research-atmospheres, 2010, 115, D15206

Popovicheva, O. B.; Kireeva, E. D.; Shonija, N. K.; Vojtisek-Lom, M. & Schwarz, J. FTIR analysis of surface functionalities on particulate matter produced by off-road diesel engines operating on diesel and biofuel, Environmental Science and Pollution Research, 2014, 22, 4534-4544

Vander Wal, R. L.; Bryg, V. M. & Hays, M. D. XPS Analysis of Combustion Aerosols for Chemical Composition, Surface Chemistry, and Carbon Chemical State, Analytical Chemistry, 2011, 83, 1924-1930

Minor comments:

The methods section is very sparse in citations except a few of the authors own work, but citations to primary sources would be relevant here.

There are typographical and grammatical errors which can be corrected during the editorial process of Copernicus.

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