Developing pH nanosensors for individual cloud droplets and aerosol particles

Supervisor: Dr. Zongbo Shi, Prof. Jamie Lead, and Prof. Roy Harrison, School of Geography, Earth & Environmental Sciences, University of Birmingham (for more information and/or to apply contact z.shi@bham.ac.uk, or r.m.harrison@bham.ac.uk, or j.r.lead@bham.ac.uk)

Abstract

Aerosols and clouds affect human health and play an important role in climate change. A fundamental parameter of aerosols and clouds are their pH, which determines their chemical and physical properties. For example, pH controls nutrient dissolution in the dust, which modulates the atmospheric supply of nutrients to the global ocean and thus affects the Earth's climate. pH also determines the phase partitioning of acids and bases in the atmosphere, which directly affect global climate change. Limited indirect measurement and thermodynamic modelling provided some information on the acidity of bulk aerosol. pH measurements of bulk cloud water have also been done before. However, the pH of individual aerosol particles and droplets has never been measured directly although it is well known that particles and droplets are extremely heterogenous. This lack of information has been shown to lead to large errors in global models.

The objectives of this project are to (1) develop pH sensitive nanosensors, and (2) to apply the technology to determine the pH of laboratory-generated and real individual droplets and fresh and aged sea salt particles. The results will be compared with thermodynamic model outputs. The data obtained will contribute to the improvement of present models and our understanding of the role of atmospheric processes on global biogeochemical cycles. In this project, the student will be given full training in the project specific skills including nanoparticle (NP) synthesis and NP characterisation using AFM, TEM, STEM, EELS, XPS, and FFF. The student will also learn analytical skills for aerosol and cloud chemistry. He/she will also develop skills in thermodynamic modelling. He/she will also be given extensive training in generic skills, via a formal training programme within School of Geography, Earth and Environmental Sciences (GEES), the University of Birmingham.

Introduction. pH is a fundamental control on chemical and physical properties of aerosols and cloud droplets, which has direct implications for global climate change. In our previous work, we have clearly showed that Fe and P dissolution in the mineral dust is strongly pH dependent, and thus the pH in the dust and droplets determines the role the atmosphere processes plays in global biogeochemical cycles and the global climate change. pH in the aerosols and the clouds also determines the phase partitioning of acids and bases. The effects of pH on halogen chemistry, sulphur oxidation in the atmospheric aqueous solutions are well documented. Acidity in the aqueous solutions on the secondary organic aerosol formation is potentially important and is under intensive investigations in the world. In addition, acidity (and pH) of aerosol particles has been suggested to be directly linked with morbidity and mortality, and therefore is a potential human health threat.

Presently, the pH of aeosols was indirectly measured after dilution with water or by thermodynamic modelling or by colorimetry coupled with reflectance UV-Visible spectrometry. pH of cloud water was also widely measured. However, all these methods are bulk techniques and pH in individual droplets and particles was never measured before, although it is well known that chemical compositions and pH of these environmental entities are extremely heterogeneous. This lack of information has already been shown to lead to large errors in models. For example, a global model predicts no increase in soluble Fe in the dust assuming an average pH, whereas significant increase in the same dust with the same average pH but composed of a mixture of lower and higher pH particles.

Since pH is a critical parameter in the study of tissue metabolism, neurophysiology, cancer diagnostics, muscle contraction, and blood flow, the development of *in vivo* pH monitoring sensors has been an active research for more than 20 years. Many fluorescent probes including nanoparticle based sensors have been developed to determine the pH of living cells of micrometer sizes including human and plant cells. However, to our knowledge, this technology has never been developed to determine the pH in more complex environmental entities, e.g., individual droplets and particles.

Aims. The purpose of this project is to develop nanosensors to determine the pH of individual micrometer sized particles and droplets. The specific objectives include:

1) To synthesise and characterize well controlled, monodisperse, and pH-sensitive nonosensors;

2) To "print" the pH nanosensors in a two dimensional substrate for droplet or particle collection;

3) To apply this novel technology to measure the pH of laboratory generated single droplets and aerosol particles (e.g., sea salt particles).

The data obtained will contribute to the improvement of present thermodynamic models and our understanding of the role of atmospheric acid processing on global biogeochemical cycles.

Method: The objectives will be met in a step wise approach given the complexity of the problem at hand. The first step of the research will be to develop pH nanosensors for application in algae, which is novel but requires less development considering the existing knowledge in biomedical sciences. In addition, both algae and NPs are routinely used in our laboratories and we have a good deal of expertise with both. The second step will be to develop pH nanosensors and to physically or chemically constrain the nanosensors on a two dimensional surface. This will then be used to collect laboratory generated individual droplets for further pH quantification. The third step will be to optimize the technique to apply it to individual particles generated from laboratory, e.g., fresh and aged sea salt particles. These steps represent different levels of complexity and the first two steps will serve as the stepping stones for a successful development of nanosensors for pH measurements of individual particles with tiny amounts of water compared to droplets or living cells. Depending on the progress, the student will apply the established methodology to aerosol particles collected from the UK and overseas and the measured pHs will be compared with indirectly measured and thermodynamic model predicted pHs.

Training: Applicants should ideally have a good BSc degree in analytical chemistry and/or nanoscience although the candidates with other backgrounds should not be deterred from applying. Applications from Masters students are also welcome. The PhD student will be given extensive training in both generic and specialist skills. Generic skills will be provided by a formal training programme within GEES at UoB. This programme is intensive in the first year but runs throughout the PhD and includes a series of lectures at Masters level in appropriate areas, a set of specifically designed lectures for the PhD cohort and monitored access to staff development and other courses and seminar programmes. The student is required to give at least two formal presentations along with conference presentations and publications. Specialist training is also available in the diversified research group with a wide range of facilities including confocal laser scanning microscopy, transmission electron microscopy, FlFFF for characterizing the fluorescent embedded nanoparticles. Modelling skills are also available in the group as well as in collaborating institutions in the UK and abroad. The student will be required to attend internal group meetings and various workshops and be encouraged to attend summer schools (e.g., SOLAS, Earth System Sciences) to expand his/her visions. The student will also be encouraged to apply for further funding for more training in the UK and/or abroad.

Chinese nationals are welcome to apply with potential funding from Li Siguang Fellowship subject to successful applications to Chinese Scholarship Council. The candidate would be expected to work on this specified project.

Background reading:

Shi, Z. et al.. Atmos Chem Phys, 11, 995-1007;
Harrison, R.M., Yin, J., 2010. J Environ Monit., 12, 1404-1414;
Cumberland, S.A., **Lead, J.R.,** 2009. J Chromato. A., 1216, 9099-9105;
Han, J., Burgess, K., 2010. Chemical Reviews, 110, 2709-28;
Keene, W. C. et al., 2004. J. Geophys. Res., 109, D23307.