Ultrafine Aerosol Size Distribution: A Study of New Particle Formation in the Atmosphere

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This project involved studies pertinent to the formation of new particles by homogeneous nucleation in the atmosphere. The research focused on (1) the development of instrumentation to measure size distributions of freshly nucleated particles in the 3 to 10 nm diameter range, (2) laboratory studies of particle thermodynamic and transport properties relevant to nucleation in the atmosphere, and (3) field measurements of new particle formation by homogeneous nucleation. We completed all of our proposed objectives, and have published peer reviewed articles on all of this work. A complete list of publications and presentations supported by this grant are given at the end of the report. Highlights of our achievements are briefly summarized below.

Highlights of our work funded by DE-FG02-91ER61205

Instrumentation Development:

- We developed the PHA-UCPC technique for measuring size distributions of freshly nucleated 3-10 nm aerosol size distributions. This technique utilizes the observations that as particle size decreases from10 nm, the droplet size formed by condensation in the ultrafine condensation particle counter also decreases. Therefore, by measuring the final droplet size it is possible to infer the initial size (Saros, Weber et al. 1996). We also showed that the pulse height distribution formed by a polydisperse aerosol in the 3 to 10 nm diameter range can be mathematically inverted to determine the size distribution of the measured aerosol (Weber, Stolzenburg et al. 1998). We showed how the commercial TSI 3025 could be modified to permit PHA measurements (Marti, Weber et al. 1996). With separate funding we developed these modifications. This modified instrument is now available commercially. Based on measurements carried out in the Arctic Ocean on the Swedish icebreaker Oden, we compared the performance of four different approaches (including the PHA-UCPC) for measuring 3 to 10 nm particle size distributions (Wiedensohler, Aalto et al. 1994).

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•As a result of his instrumentation development research on this DOE project and other related atmospheric aerosol research, Peter McMurry was invited to write a major review article on atmospheric aerosol measurements, as a part of the NARSTO assessment (McMurry 2000).

Laboratory Research:

•Theoretical predictions of particle nucleation rates require information on thermodynamic and transport properties including vapor pressures, mass accommodation coefficients, etc. We measured the vapor pressure of sulfuric acid over aerosol solutions consisting of sulfuric acid and ammonium in known ratios and at known relative humidities (Marti, Jefferson et al. 1997). These represent the first reported vapor pressures of sulfuric acid over neutralized or partially neutralized solutions.

Atmospheric Observations:

•We showed that sulfuric acid almost certainly participates in new particle formation (Weber, McMurry et al. 1995) and that terpenes may also play a role (Marti, Weber et al. 1996).

•We showed that rates of new particle formation in the atmosphere greatly exceed nucleation rates that are predicted by the binary theory for sulfuric acid-water nucleation (Weber, Marti et al. 1996; Eisele and McMurry 1997; Weber, Marti et al. 1997).

•We showed that freshly nucleated particles grow by factors of 2 to 10 faster than can be explained by the condensation of sulfuric acid vapor and its associated water and ammonia (Weber, Marti et al. 1997).

•We also showed that care must be taken when measuring ultrafine particle size distributions near clouds with aircraft. This is because cloud droplets can easily be shattered near the sampling inlet, leading to apparent high concentrations of ultrafine particles (Weber, Clarke et al. 1998).

Publications and Presentations from DOE DE-FG02-91ER61205

The following publications and presentations are based on research that was supported entirely or in part by funding from the DOE-ACP program to the McMurry-Eisele research team:

Journal Publications on research supported directly by DOE DE-FG02-91ER61205

Weber, R. J., P. H. McMurry, F. L. Eisele, and D. J. Tanner (1995) "Measurement of expected nucleation precursor species and 5 to 500 nm diameter particles at Mauna Loa Observatory, Hawaii," J. Atmos. Sci., **52**(12) 2242-2257.

Wiedensohler, A., P. Aalto, D. Covert, J. Heintzenberg, P. H. McMurry (1994) "Intercomparison of four methods to determine size distributions of low concentration (~100 cm^{-3}), ultrafine aerosols ($3<D_p<10$ nm) with illustrative data from the Arctic," Aerosol Sci. Technol., **21**:95-109.

Weber, R. J., J. J. Marti, P. H. McMurry, F. L. Eisele, D. J. Tanner, A. Jefferson (1995) "Measured atmospheric new particle formation rates: Implications for nucleation theory," Chem. Eng. Comm., **151**:53-64.

Weber, R. J. and P. H. McMurry (1996) "Fine particle size distribution measurements at Mauna Loa Observatory, Hawaii," J. Geophys. Res., **101**(D9):14767-14775.

Saros, M., R. J. Weber, J. Marti, P. H. McMurry (1996) "Ultrafine aerosol measurement using a condensation nucleus counter with pulse height analysis," Aerosol Sci. Technol., **25**:200-213.

Marti, J. J., R. J. Weber, M. T. Saros, P. H. McMurry (1996) "Modification of the TSI 3025 condensation nucleus counter for pulse height analysis," Aerosol Sci. Technol., **25**:214-218.

Marti, J. J., R. J. Weber, P. H. McMurry, F. Eisele, D. Tanner, A. Jefferson (1997) "Particle formation at a remote continental site: Assessing the contributions of SO_2 and terpene precursors," J. of Geophys. Res., **102**(D5):6331-6339.

Marti, J. J., A. Jefferson, X. Cai, C. Richert, P. H. McMurry, F. Eisele (1997) "The H_2SO_4 vapor pressure above sulfuric acid and ammonium sulfate solutions," J. Geophys. Res., **102**(D3):3725-3735.

Eisele, F. L. and P. H. McMurry (1997) "Recent progress in understanding particle nucleation and growth," Phil. Trans. R. Soc. Lond. B **352**: 191-201.

Weber, R. J., M. R. Stolzenburg, S. N. Pandis, P. H. McMurry (1998) "Inversion of ultrafine condensation nucleus counter pulse height distributions to obtain nanoparticle (~3 to 10 nm) size distributions," J. Aerosol Sci., **29**:601-615.

Weber, R. J., P. H. McMurry, A. D. Clarke, M. Litchy, J. Li, G. Kok, D. Baumgardner (1998) "Spurious aerosol measurements when sampling from aircraft in the vicinity of clouds," J. Geophys. Res. **103**(D21): 28337-28346.

McMurry, P. H. (2000) "A review of atmospheric aerosol measurements," Atmos. Environ. **34**:1959-1999. (Invited NARSTO review paper).

Journal Publications on research that followed developments from DOE DE-FG02-91ER61205

Wiedensohler, A., P. Aalto, D. Covert, J. Heintzenberg, P. H. McMurry (1993) "Intercomparison of Three Methods to Determine Size Distributions of Ultrafine Aerosols with Low Number Concentrations," J. of Aerosol Sci., **24**: 551-554.

Weber, R. J., J. J. Marti, P. H. McMurry, F. L. Eisele, D. J. Tanner, A. Jefferson (1997) "Measurements of new particle formation and ultrafine particle growth rates at a clean continental site," J. Geophys. Res. **101** (D4): 4375-4385.

Jefferson, A., F. L. Eisele, P. J. Ziemann, J. J. Marti, R. J. Weber, and P. H. McMurry (1997) "Measurements of the H_2SO_4 Mass Accommodation Coefficient onto Polydisperse Aerosol," J. Geophysical Res, **102**(D15): 19021-19028.

Weber, R. J., P. H. McMurry, L. Mauldin, D. J. Tanner, F. L. Eisele, F. J. Brechtel, S. M. Kreidenweis, F. L. Kok, R. D. Schillawski, D. Baumgardner (1998) "A study of new particle formation and growth involving biogenic trace gas species measured during ACE-1," J. Geophys. Res. **103**(D13):16385-16396.

Weber, R. J., P. H. McMurry, T. S. Bates, A. D. Clarke, D. S. Covert, F. J. Brechtel, G. L. Kok (1999) "Intercomparison of airborne and surface-based measurements of condensation nuclei in the remote marine troposphere during ACE-1," J. Geophys. Res. **104**(D17):21673-21683.

Clarke, A. D., V.N. Kapustin, F. L. Eisele, R. J. Weber, P. H. McMurry (1999) "Particle nucleation near marine clouds: Sulfuric acid and predictions from classical binary theory," Geophys. Res. Lett. **26**:2425:2428.

Ball, S. M., D. R. Hanson, F. L. Eisele, P. H. McMurry (1999) "Laboratory studies of particle nucleation. Initial results for H_2SO_4, H_2O and NH_3 vapors," J. Geophys. Res. **104**(D19):23709-23718.

Weber, R. J., P. H. McMurry, R. L. Mauldin, D. J. Tanner, F. L. Eisele, A. D. Clarke, and V. N. Kapustin (1999) "New particle formation in the remote troposphere: A comparison of observations at various sites," Geophys. Res. Lett. **26**:307-310.

Publications in press or under review (supported by DOE DE-FG02-91ER61205 or based on developments from that grant):

Dick, W. D., P. H. McMurry, R. J. Weber, F. Quant (2000) "White-light detection for nanoparticle sizing with the TSI 3025A UCPC," J. Nanoparticle Res., in press.

McMurry, P. H., K. S. Woo, R. Weber, D.-R. Chen, D. Y. H. Pui (2000), "Size distributions of 3 to 10 nm atmospheric particles: Implications for nucleation mechanisms," Phil. Trans. of the Royal Society London, submitted.

McMurry, P. H. and M. Kulmala (2000) "Review of atmospheric nucleation," prepared as part of the IGAC report, edited by S. Schwartz, J. Heintzenberg and F. Raes, in press.

Theses supported wholely or in part by DE-FG02-91ER61205:

Richert, C. A. (1991) "Measurements of the relative humidity dependent vapor pressure of sulfuric acid using the tandem differential mobility analyzer," M.S. Thesis, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455

Weber, R. J. (1995) "Studies of new particle formation in the remote troposphere," Ph.D. Thesis, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455

Saros, M. T. (1995) "Sensitivity of pulse heights to pressure for ultafine particles in the ultrafine condensation particle counter (UCPC)," M.S. Thesis, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455

Vollmers, K. (1998) "Separation and collection of ultrafine aerosols for near real time chemical analysis," M.S. Project, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455

Invited Lectures and Conference Presentations based on work supported wholely or in part by DE-FG02-91ER61205:

Aalto, P., P. H. McMurry, A. Wiedensohler, D. S. Covert, J. Heintzenberg, "Measurement of 3 to 8 nm Diameter Atmospheric Particles with an Ultrafine Aerosol CNC using the Pulse Height Analysis Mode," AAAR Annual Meeting, San Francisco, CA October 12-16, 1992.

Weber, J. J., P. H. McMurry, F. L. Eisele, and D. J. Tanner "Measurement of Expected Nucleation Precursor Species and Ultrafine and Fine Particles at Mauna Loa Observatory, Hawaii," AAAR Annual Meeting, Oak Brook, IL, October 11-15, 1993

Weber, J. J., P. H. McMurry, F. L. Eisele, and D. J. Tanner "Measurement of Expected Nucleation Precursor Species and Ultrafine and Fine Particles at Mauna Loa Observatory, Hawaii," AMS Meeting, Nashville, TN, January 24-28, 1994.

Weber presented papers at the 1993, 1994 and 1996 AGU meeting and Marti presented a papers at the 1994 AGU meeting on work supported by our DOE-ACP project.

Weber, R. J., J. J. Marti, P. H. McMurry, F. L. Eisele, and D. J. Tanner, "Growth rates of ultrafine particles at remote marine and continental sites," AAAR Annual Meeting, Pittsburgh, PA, October 9-13, 1995.

Baklanov, A. M., S. N. Dubtsdov, R. Caldow, M. M. Havlicek, G. J. Sem, P. H. McMurry, J. Marti, M. Saros, R. Weber, "Ultrafine aerosol size distribution measurement workshop at TSI," AAAR Annual Meeting, Pittsburgh, PA, October 9-13, 1995.

McMurry, P. H. "Frontiers in Aerosol Measurement," invited plenary lecture, International Aerosol Conference, Los Angeles, CA, August 29-September 2, 1994, Los Angeles, CA.

McMurry, P. H. "Measurement of Ultrafine Aerosols in the Remote Troposphere: Implications for Nucleation Mechanisms," Gordon Conference, Atmospheric Chemistry, June 20, 1995 (Invited Plenary Lecture).

McMurry, P. H., "Chemistry, Measurement of Ultrafine Aerosols in the Remote Troposphere: Implications for Nucleation Mechanisms," Max Plank Institute for Atmospheric Physics, Heidelberg, Germany, September 25, 1995.

Saros, M., P. H. McMurry, M. R. Stolzenburg, "Sensitivity of pulse heights to pressure for ultrafine particles in the UCPC," Abstracts of the AAAR Annual Meeting, Pittsburgh, Pa, October 9-13, 1995.

Marti, J. J., P. H. McMurry, A. Jefferson, F. Eisele, "The H_2SO_4 vapor pressure of sulfate solutions approximating atmospheric aerosols," Abstracts of the AAAR Annual Meeting, Pittsburgh, Pa, October 9-13, 1995.

McMurry, P. H., R. Weber, J. Marti, F. Eisele, D. J. Tanner, A. Jefferson, "Experimental studies of nucleation and growth in the free troposphere," J. Aerosol Sci. 26 Supplement 1, pp S205-S206, 1995; European Aerosol Conference, Helsinki, Finland, September 18-22, 1995.

Weber, R. J., M. R. Stolzenburg, S. N. Pandis, P. H. McMurry, "Inversion of ultrafine condensation nucleus counter pulse height distributions to obtain nanoparticle (~3 to 10 nm) size distributions," American Association for Aerosol Research, October, 1996.

McMurry, P. H. , "Atmospheric nucleation phenomena," Hiroshima University, Japan, April, 1997.

Weber, R. J., P. H. McMurry, F. L. Eisele, L. Mauldin, D. Tanner, "Evidence for new sulfate particle formation in the remote troposphere involving biogenic trace gas species, 5th International Aerosol Conference, Edinburgh, Sept. 12-18, 1998.

Weber, R. J., P. H. McMurry, F. L. Eisele, L. Mauldin, D. Tanner "Rapid growth rates of freshly formed nanoparticles in the remote troposphere," 5th International Aerosol Conference, Edinburgh, Sept. 12-18, 1998.

McMurry, P. H. (1998) "State of the art in Atmospheric Aerosol Measurement" EPA/NARSTO Workshop.

McMurry, P. H.(1998) "Field Measurements of atmospheric aerosols," DOE/PNL Workshop on Atmospheric Aerosols.

Dick, W. D., D. Lappen, F. R. Quant, R. J. Weber, P. H. McMurry, "New pulse height analysis modifications to the TSI 3025 condensation particle counter," American Association for Aerosol Research, Tacoma, WA, October 11-15, 1999.

McMurry, P. H. "Penguins, DRAM and Nucleation," Carleton College, January 22, 1999.

McMurry, P. H. "Ultrafine Atmospheric Aerosols: Measurement and Behavior," EPRI Advisory Board, September 29, 1999.

McMurry, P. H. "Atmospheric Nucleation," University of Delaware, November 5, 1999.

McMurry, P. H. "Size distributions of 3 to 10 nm atmospheric particles: Implications for Nucleation Mechanisms," Discussion Meeting on Ultrafine Particles in the Atmosphere, March 15-16, 2000 (Invited plenary lecture).