

The GAW-PFR aerosol optical depth network

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Aerosol optical depth (AOD) is one of a number of important parameters required to assess and predict climate change. In order to monitor AOD over the long-term and provide data of traceable quality, the World Optical depth Research and Calibration Centre (WORCC), Davos, was established by the WMO Global Atmosphere Watch (GAW) programme. Twelve existing GAW baseline stations were chosen for the deployment of PFRs (Precision Filter Radiometer; in-house manufacture). Quality controlled and assured AOD data from this GAW-PFR network (www.pmodwrc.ch/worcc) are submitted by WORCC to the World Data Centre for Aerosols (WDCA; wdca.jrc.it). This work will give an overview of WORCC activities and AOD time-series at GAW baseline stations.

GAW-PFR measurements mostly began in 1999 – 2002, although the time-series extends further back to 1993 at Hohenpeissenberg (Germany, 995 m asl), and to 1995 at Jungfraujoch (Switzerland, 3580 m) using BAS and SPM-2000 type sunphotometers, respectively. Mean AOD at $\lambda = 500$ nm generally varies according to location type and site elevation. For instance, AOD $\sim 0.02 - 0.05$ at high elevation sites (Izaña, Spain, 2370 m; and Mauna Loa, USA, 3397 m) which are influenced by the free troposphere, although desert dust episodes (Sahara and Gobi deserts, respectively) can on occasion result in increased AOD. Higher AOD values are observed in the continental boundary layer, for instance AOD $\sim 0.11 - 0.12$ at Alice Springs, (Australia, continental desert) and Bratts Lake (Canada, continental prairie). Mean AOD at Ny Alesund (Norway, arctic tundra) is ~ 0.08 , however, measurements are restricted to the sunlit March to October period.

Apart from monitoring activities, WORCC has also developed a calibration hierarchy and is actively involved in comparisons of AOD across different networks. A field comparison of 4 AOD networks co-located at Bratts Lake, Canada demonstrated good agreement, which was well within the target uncertainty of AOD = $\pm 0.005 + 0.01/\text{airmass}$. These and other inter-comparisons illustrate that the aim of achieving worldwide homogeneity in ground-based AOD observations is moving closer.

Structural variations in nanocrystalline iron oxides and sulfides

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Iron oxide and sulfide nanoparticles are ubiquitous in soils and sediments and play important roles in a number of environmental processes. Some iron minerals, including ferrihydrite and mackinawite, almost exclusively form as nanominerals. Their structures and chemical compositions may vary and are difficult to study. We used analytical transmission electron microscopy (TEM), including electron energy-loss spectroscopy (EELS), electron diffraction and electron crystallography for the structural characterization of synthetic iron oxide and sulfide nanocrystals.

We tested whether the common iron oxide minerals can be identified in nanocrystalline samples on the basis of quantitative analyses of EELS spectra and by fingerprinting the fine structure of the Fe and O core-loss edges. The results indicate that magnetite and hematite can be reliably distinguished from other iron oxides, but the identification of most other minerals are ambiguous, owing to overlapping spectral features and an insufficient energy resolution.

The structure of maghemite contains iron vacancies with respect to the magnetite structure. We found that the intensity distributions of reflections in electron diffraction patterns from magnetite/maghemite particles significantly differ from those of pure magnetite. Electron crystallographic image processing of high-resolution TEM images indicates a highly variable, nanoscale domain structure, a likely consequence of different vacancy ordering schemes. Further experiments and analyses are in progress in order to determine the possible structures of the maghemite varieties.

Freshly precipitated iron sulfide is poorly crystalline and contains 3-4-nm large particles that include both mackinawite (FeS) and greigite (Fe₃S₄) structural elements. A detailed structural and chemical characterization of these phases could be helpful for a better understanding of the roles of iron sulfides in metal cycling in marine sediments.