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- Title and Author Search

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[Volumes and Issues](#) [Contents of Issue 12](#)

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Processes controlling the concentration of hydroperoxides at Jungfrauoch Observatory, Switzerland

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Abstract. An automated, ground-based instrument was used to measure gas-phase hydroperoxides at the Jungfrauoch High Altitude Research Station as part of the Free Tropospheric EXperiment (FREETEX) during February/March 2003. A nebulising reflux concentrator sampled ambient air twice hourly, prior to on-site analysis by HPLC speciation, coupled with post-column peroxidase derivatisation and fluorescence detection. Hydrogen peroxide (H_2O_2) concentrations reached up to 1330 pptv over the 13-day period with a mean of 183 ± 233 pptv (\pm one standard deviation). Methyl hydroperoxide (CH_3OOH) reached up to 379 pptv with a mean of 51 ± 55 pptv. No other organic hydroperoxides were detected. The lack of an explicit diurnal cycle suggests that hydroperoxide concentrations are chiefly influenced by transport processes rather than local photochemistry at this mountainous site. There was some evidence that elevated concentrations of H_2O_2 existed in air-masses originating from the south-west, suggesting higher concentrations of HO_x due to more active photochemistry. Air which had been recently polluted exhibited low H_2O_2 concentration due to a combination of suppression of HO_2 by NO_x and deposition. The concentrations of H_2O_2 sampled here are consistent with previous box modelling studies of hydroperoxides, except in periods influenced by the boundary layer, where agreement required a depositional sink.

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