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## OH in the coastal boundary layer of Crete during MINOS: Measurements and relationship with ozone photolysis

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**Abstract.** Hydroxyl radical (OH) concentrations were measured in August 2001 at Finokalia Station on the northeastern coast of Crete during the Mediterranean Intensive Oxidant Study (MINOS). OH was measured based on selected ion chemical ionization mass spectrometry (SI/CIMS) with a time resolution of 30 sec and signal integration of 5 min. The corresponding accuracy, precision, and detection limit were 20% (1 $\sigma$ ), 11% (1 $\sigma$ ), and  $2.4 \times 10^5$  molecules cm<sup>-3</sup> (2 $\sigma$ ), respectively. OH levels showed a strong diurnal variability with high maxima (approximately  $2 \times 10^7$  molecules cm<sup>-3</sup>) occurring around 13:30 LT (10:30 UTC) and nighttime values below the detection limit. Daily 24-hour average concentrations varied between  $3.6$ – $6.7 \times 10^6$  cm<sup>-3</sup>. For the total measurement period (6–21 August) the mean and standard deviation were  $4.5 \pm 1.1 \times 10^6$  cm<sup>-3</sup>. The OH data set is analyzed based on a classification into three periods: I: Aug 6–8, II: Aug 9–11, III: Aug 13–18. For each of the three periods the measured OH concentrations are described by the empirical function  $[OH] = a J(O^1D)^b$ , with  $J(O^1D)$  being the ozone photolysis frequency and  $a = 1.4 \times 10^{10}$  s cm<sup>-3</sup>,  $1.7 \times 10^{10}$  s cm<sup>-3</sup>,  $2.2 \times 10^{10}$  s cm<sup>-3</sup>, and  $b = 0.68$ , respectively. Taking into account the estimated precision of the OH measurements this empirical function using three values for  $a$  and one value for  $b$  explains 99% of the observed variance of OH. A detailed sensitivity analysis using a CH<sub>4</sub>-CO box model was performed to interpret this relationship, in particular the meanings of the pre-exponential factor  $a$  and the exponent  $b$ . It was found that the value of  $b$  which represents the total logarithmic dependence of  $[OH]$  on  $J(O^1D)$  includes the individual contributions from the photolysis of O<sub>3</sub>, NO<sub>2</sub>, HCHO, HONO, and H<sub>2</sub>O<sub>2</sub> which could be determined using the box model. For the conditions prevailing during the MINOS campaign the exponent  $b$  was found to be dominated by the contributions from O<sub>3</sub>- and NO<sub>2</sub>-photolysis. For the individual functional dependences between  $[OH]$  and  $J(O^1D)$ ,  $[OH]$  and  $J(NO_2)$ , and  $J(NO_2)$  and  $J(O^1D)$  the partial logarithmic derivatives were determined to be 0.5, 0.6, and 0.3, respectively. Overall, the box model yields a value of 0.70 for the exponent  $b$  in very good agreement with the corresponding value derived from the empirical analysis of the measurements. This empirical approach in which the chemical air mass characteristics influencing the OH radical

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balance and thereby, the self-cleansing efficiency of the atmosphere, are represented by only two parameters which are constant over quite substantial time periods may be used in future experiments to test and compare OH measurements made in different atmospheric environments.

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