Dinitrogen pentoxide ($N_2O_5$) plays key roles in a number of nocturnal chemical processes within the troposphere, including the sink of nitrogen oxides ($NO_x$). However, accurate measurement of this atmospheric trace compound remains as a challenging task, especially in polluted environment like China. We initially deploy a thermal dissociation chemical ionization mass spectrometry (TD-CIMS) for $N_2O_5$ field measurement in Hong Kong from 2010-2012. Unusual high $N_2O_5$ signal measured as $NO_3^-$ (62 amu) were frequently observed. Various interference tests and correction were conducted to verify the data, but we caution the use of 62 amu for measuring ambient $N_2O_5$ in a high $NO_x$ environment like Hong Kong. Therefore, we optimized the CIMS to measure $N_2O_5$ as ion cluster of $I(N_2O_5)^-$ at 235 amu with some minor improvements and demonstrated to has the ability for simultaneous in situ measurements of $N_2O_5$ at an urban site. Then, the CIMS was deployed to another field study at a mountain-top site (Tai Mo Shan). A comparison of $N_2O_5$ measurement with a cavity ring-down spectrometry was performed and found to be in good correlation with the CIMS. High concentration of $N_2O_5$ was observed between the boundary layer and there are some occasions where $N_2O_5$ exceeds several ppb, which is among the highest values ever reported. These results provide deeper understanding on the chemistry of $NO_x$ in a polluted environment. Furthermore, our first observation of nitryl chloride ($ClNO_2$) and its co-existence with $N_2O_5$ also implies an active heterogeneous reactivity between $N_2O_5$ and chloride particles in an Asian environment. Thus, $N_2O_5$ is an important nocturnal intermediate and has the potential in jump-starting the atmospheric photochemistry in this region.