Background: Most of the available knowledge regarding the environmental fate of pesticides focuses on their degradation in bulk water or soil. Recently, it became clear that the degradation rate and environmental fate of pesticides are affected by photooxidation reactions when pesticides are in contact with the atmosphere. Furthermore, previous studies have mainly focused on the reactivity of the parent compound only and not of its derivatives, even though degradation products may continue to pose environmental concern.

Aims: This research provides a quantitative investigation of the photo-oxidation of thin film chlorpyrifos, an organophosphate pesticide widely used in agriculture and urban environments. This includes determination of reaction rates, quantum yields and products identification.

Methods: Chlorpyrifos degradation was studied under solar radiation in ambient and synthetic atmosphere. Actinic flux and absorbance spectra of absorbed chlorpyrifos were also measured in order to calculate the quantum yield for chlorpyrifos direct photochemistry. Photo-oxidation experiments were conducted with both analytical and technical grade chlorpyrifos, as well as with its derivative: chlorpyrifos-oxon.

Results: The photo-degradation of absorbed analytical chlorpyrifos is very fast, with half-life of 1.3 hours and quantum yield of ~0.017. While the apparent photo-degradation rate of technical chlorpyrifos is faster (0.7 hours), its quantum yield is almost the same (~0.015). The derivative chlorpyrifos-oxon is less sensitive to photo-oxidation (~0.001), and is therefore more likely to remain longer on open atmospheric surfaces. These results imply that chlorpyrifos-oxon is more likely to be found on aerosols from treated fields. Indeed, air sampling near chlorpyrifos treated field was found to contain chlorpyrifos-oxon. 3,5,6-trichloro-2-pyridinol, which is a major product of chlorpyrifos in bulk processes, was not detected in the laboratory film samples or in the air samples.

Conclusions: The present research provides new kinetic constants and shows that surface degradation processes should be considered in understanding environmental fate of pesticides.