SUMMARY

The atmospheric particulate matter has a large impact on climate, atmospheric chemistry in the biosphere and human health. It is a complex system because of the large number of species and its continuous evolution. This thesis extends the knowledge of the composition and properties of the organic fraction and contaminants that generate it to degrade in the troposphere. For that, we have developed various methodologies of analysis, performing studies of different atmospheric degradation processes using high volume atmospheric simulation chambers (EUPHORE) and there have been various environmental sampling campaigns.

First, we have studied the polycyclic aromatic hydrocarbons that are important components of the primary particulate matter. It has developed a method for its determination, quantifying atmospheric levels with different sampling locations. Furthermore, their presence has been characterized in lightdiesel engine emissionsand significant differences depending on the nature of the fuel and operating regimes as engines have been observed.

Secondly, we have developed a new methodology for the determination of multi-oxygenated compounds, used successfully in characterizing the secondary particulate contaminants from biogenic compounds (isoprene and monoterpenes), identifying new products. This method has also been used to determine empirically mistakes on monitoring systems of particulate matter. The results indicate the existence of a sub-estimation of the mass concentration and have provided information on the species involved. Finally, seasonal variations have established multi-oxygenated compounds with different origins and sources of pollution.

Thirdly, it has been interpreted in depth the effect of the oxidizing conditions in the photo-oxidation reactions of aromatic compounds, based on data on the chemical composition and physical properties of the particulate matter produced. In the case of toluene, has provided information on the formation of particulate matter at low levels of NO_x, improving the characterization of multi-oxygenated compounds

formed. In the case of benzene, have contributed to the development of atmospheric degradation mechanism. The determination of yields, densities, etc., and the identification of new several products have led to propose the key compounds that act as precursors to particulate matter. The study carried out with its main degradation products (phenol and catechol) confirmed these findings and have established that the formation of particles is a function of the relative importance of two reaction channels controlled by the concentration of NO_x.

Fourthly, we have developed a methodology for the analysis of pesticides in atmospheric samples, allowing the analysis of the different families most commonly used in the Mediterranean Area. The methodology has been validated through testing in simulation chamber and through analysis of environmental samples. Being semi-volatile compounds they have been observed both in the gas phase and in the particulate material. Finally, we studied the contribution of the degradation products of pesticides. Photochemical experiments have shown that the degradation of pesticides leading to a high yield in the formation of secondary material. The determination of the chemical composition of the organic fraction has shown that pesticides are a significant source of multi-oxygenated compounds and enabled to make proposals on pathways of degradation in the troposphere.

In conclusion, the studies in this thesis have improved in the description of the physical properties and chemical composition of atmospheric organic particulate matter, identifying about 325 species of different chemical families. The quality of the data obtained allows advance knowledge of the chemical processes involved in the reactivity of several prominent atmospheric pollutants, and highlights the need for a review of the programs of pollution monitoring to ensure air quality.