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## Atmospheric phosphorus characterization by $^{31}\text{P}$ -NMR during dust events and bioavailability implications

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Phosphorus is a critical nutrient affecting primary productivity in large areas of oceanic oligotrophic and ultraoligotrophic ecosystems. The principal source of externally supplied inorganic-P in such ecosystems is the atmosphere with dust considered as an important source. However, recent work showed that organic-P originating from bioaerosols and dust can supply as much bioavailable P as inorganic P in dust, and is thus critical for primary productivity. The presence of organic-P in atmospheric samples is typically inferred by subtraction of the amount of inorganic phosphorus from the total amount of phosphorus. At present, there is no direct method for organic-P determination. Direct speciation methods point to important sources (e.g., phospholipids from bioaerosol), but cannot account for the total amount of P in organic form. There is a need therefore to develop a method to directly identify P that are associated with organic compounds. Nuclear magnetic resonance ( $^{31}\text{P}$ -NMR) spectroscopy can provide such a capability, as it has proven to be a powerful analytical tool for the molecular characterization of organic-P in marine plankton, sinking particles, high molecular weight dissolved organic matter and sediment. The  $^{31}\text{P}$ -NMR technique, however, has never been applied to atmospheric samples and is the focus of this study.

Here we analyze Total Suspended atmospheric Particles (TSP) collected during dust events ( $n=5$ ) in the eastern Mediterranean by using a high-volume air sampler. These particles were then analyzed using magic angle spinning solid-state  $^{31}\text{P}$ -NMR. The results showed the typical functional groups in P speciation which were: orthophosphate and monophosphate esters sharing the same chemical shift ( $\text{H}_3\text{PO}_4$  and  $\text{RH}_2\text{-PO}_4$ ), phosphate diesters ( $\text{R}_1\text{R}_2\text{ HPO}_4$ ) and pyrophosphate ( $\text{H}_4\text{P}_2\text{O}_7$ ). No phosphonates were detected (C-P bond) in TSP samples. Monophosphate esters and diesters are mainly found in nucleotides and their derivatives (e.g., DNA, RNA, AMP, ADP, and ATP), phospholipids and flame retardants (OPEs), and as such they constitute the majority of atmospheric organic-P. The above-mentioned P-organic compounds have C-O-P bonds therefore they are easily hydrolysable in the marine environment by the alkaline phosphatase enzyme providing an important source of P in aquatic ecosystems. Finally, the results showed that the

amount of organic-P estimated colorimetrically is about equal to that estimated by  $^{31}\text{P}$  NMR indicating that the latter technique can be successfully employed in atmospheric studies for P speciation.