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The role of Organophosphate Esters Flame Retardants (OPEs) and organophosphate pesticides in Phosphorus Cycle in the atmosphere of Mediterranean Sea.

Kalliopi Violaki[1,2], Maria Tsagaraki[3], Athanasios Nenes[1,4], Richard Sempere[2], Javier Castro Jimenez[2], and **Christos Panagiotopoulos**[2]

[1]Laboratory of Atmospheric Processes and their Impacts, School of Architecture, Civil & Environmental Engineering, École Polytechnique Fédérale de Lausanne, Lausanne, 1015, Switzerland

[2]Aix-Marseille Univ., Université de Toulon, CNRS, IRD, Mediterranean Institute of Oceanography (MIO) UMR 7294, France, CNRS, MIO, France

[3]Chemistry Department, University of Crete, 71003 Heraklion, Crete, Greece

[4]Institute of Chemical Engineering Sciences, Foundation for Research and Technology Hellas, GR-26504, Patras, Greece

The atmosphere is considered as an important external nutrient source for the marine environment, especially in remote ocean waters or the oligotrophic Mediterranean Sea. Phosphorus (P) is a critical nutrient affecting primary productivity in large areas of oceanic ecosystems. Much has been placed on inorganic P, while the importance of organic P as potential pool of bioavailable P is not widely recognized. In this study we quantify and speciate the anthropogenic organic P in the West and East Mediterranean atmosphere. Several anthropogenic organophosphorus compounds are analyzed, including pesticides (Phosmet, Malathion, Ethoprophos, Diazinon, Chloropyrifos-Me, Chloropyrifos-e), organophosphorus flame retardants and plasticizers (OPEs) (Tris- (1-chloro-2-propyl) phosphate (TCPP), tris[2-chloro-1-(chloromethyl)ethyl]phosphate (TDCP), Tris-(2-chloroethyl)phosphate (TCEP), tri-n-butyl phosphate (TnBP), triphenyl phosphate (TPhP), 2-ethylhexyl diphenyl phosphate (EHDPP)).

Our analysis applied to Total Suspended atmospheric Particles (TSP) collected in Eastern (Crete, n = 67) and Western (Marseille, n = 25) Mediterranean Sea by using high-volume air sampler. The analysis performed with the liquid chromatography coupled to mass spectrometry (Q–TOF–LC/MS) after optimization of the analytical protocol for the aerosol samples. Five pesticides were found during the sampling period in East Mediterranean in total of 27 samples. The most frequent were chlorpyrifos–e (n = 9) and phosmet (n = 10) with average concentration 0.24±0.38 pmol m^{-3} and 0.24±0.45 pmol m^{-3}, respectively following by diazinon (n = 4) at 0.07±0.00 pmol m^{-3}. Higher concentration was estimated in chlorpyrifos-me at 0.91±0.93 pmol m^{-3} (n = 3) while ethoprophos was detected only in one sample (0.002 pmol m m^{-3}), malathion was below detection limit. In the West Mediterranean, the most abundant organophosphate pesticides were phosmet (n = 3) with an average concentration of 0.07±0.04 pmol m^{-3}, followed by diazinon (0.05 pmol m^{-3}, n = 1) and chloropyrifos-e (0.04 pmol m^{-3}, n = 2). Malathion, chlorpyrifos-me and ethoprophos were not detected. The average contribution of organophosphate pesticides in atmospheric organic P

detected during this study was 0.2% and 0.1% for East and West Mediterranean, respectively.

OPEs analyses in the same samples revealed higher concentrations in the West than in East Mediterranean atmosphere especially for TCPP, TCEP and TDCP, which are considered as the most potentially hazardous. In the West Med. the most abundant detected OPEs were the EHDPP (3.04±4.17 pmol m^{-3}) and the TCPP (1.71±1.28 pmol m^{-3}). In East Mediterranean, the most abundant detected OPEs were the TCPP (0.36±0.29 pmol m^{-3}) and the TCEP (0.24±0.20 pmol m^{-3}) whereas the TDCP and the EHDPP were not detected. The percentage contribution of OPEs in atmospheric organic–P over the West Mediterranean was 9%, while over East was 0.4%.

The total anthropogenic organic P deposited in East Mediterranean during stratification period (June-September) was calculated at 8 tons, which was 4 times lower comparing with West Mediterranean (29 tons of P) during the same period. Overall, the above anthropogenic compounds represented only 0.4% of the total anthropogenic P deposited during stratification period, however their toxicity and fate to the marine environment warrants further investigations.

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