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

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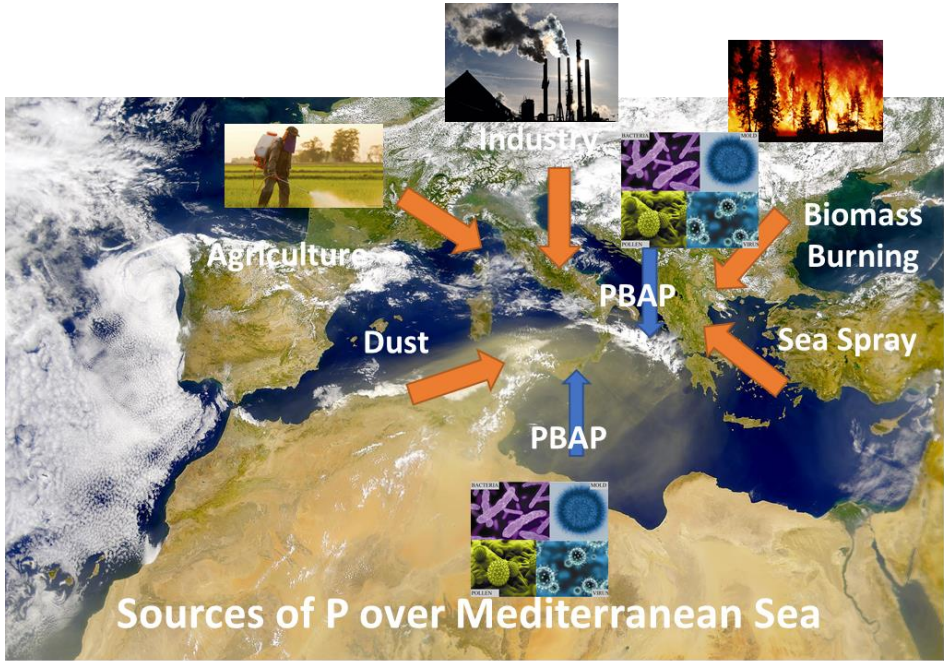
Why is important the speciation of **org-P** for Mediterranean Sea

The atmosphere is considered as an important external nutrient source for the pelagic marine organisms, 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. Decoding the chemical structure of the Org-P fraction could reveal valuable information regarding their bioavailability in the marine environment and better understanding the sources and fate of Org-P compounds in the atmospheric chemistry.



Anthropogenic org-P

The anthropogenic perturbation of the phosphorus (P) marine biogeochemical cycle due to synthetic organophosphorus compounds remains unexplored.
The last century, an increasing number of synthetic organic compounds containing P have been introduced into the environment such as organophosphorus pesticides, herbicides and organophosphate triesters (OPEs) which are persistent organic pollutants (POPs) currently used as flame retardants and plasticizers in consumer products.
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, Chlorpyrifos-Me, Chlorpyrifos-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-nbutyl phosphate (TnBP), triphenyl phosphate (TPhP), 2-ethylhexyl diphenyl phosphate (EHDPP)).

Sources of OPEs

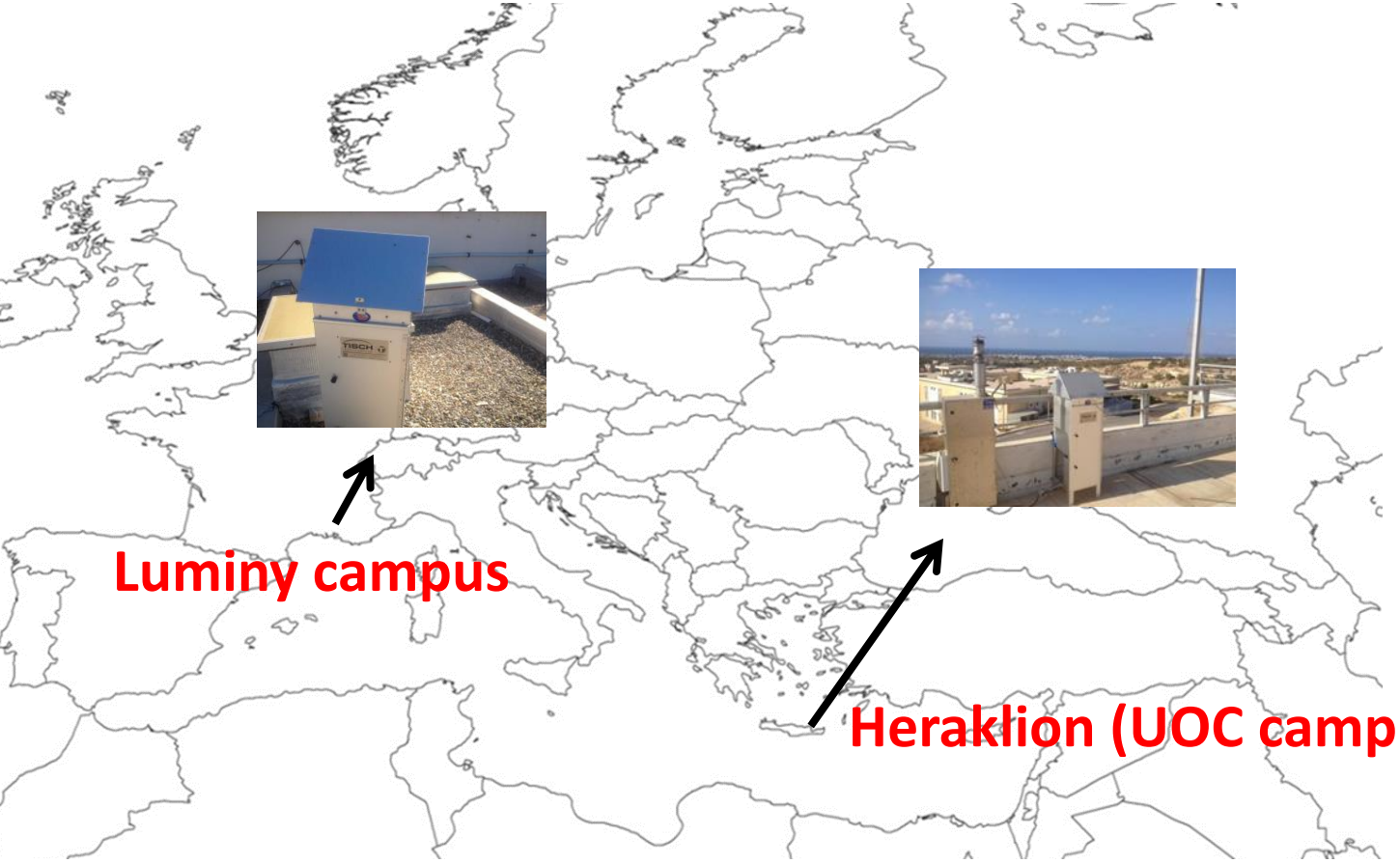
The organophosphorus flame retardants and plasticizers (OPEs) which are nowadays widely employed in many industrial applications including the manufacture of electronic equipment, textiles, plastic polymers and in the car industry and household products.

OPEs are easily released into the environment due to their use as additive flame retardants into the materials, where they are not chemically bound. The occurrence of OPEs has been reported in various environmental matrices, such as water, sediment, air, dust, biota, and food samples.

Toxicity of OPEs

Mainly the chlorinated OPEs such as the tris(1-chloro-2-propyl) phosphate (TCPP), the Tris-(2-chloroethyl)phosphate (TCEP) and the Tris(1,3-dichloro-2-propyl) phosphate (TDCP) ***have toxic effects*** (Van der Veen and De Boer, 2012). Moreover, TCPP is considered potentially carcinogenic and could accumulate in human livers and kidneys. TCEP is toxic to aquatic organisms, carcinogenic for animals, and has adverse effects on human health, such as hemolytic and reproductive effects. TDCP is harmful when inhaled and can easily enter the bloodstream acting as endocrine disruptor.

Sampling Sites



Information for the sampling

Site: Crete (Heraklion), South Greece and Luminy Campus (Marseille), South France.

Sampling Period: 1) East Mediterranean: one-year period starting from October 2016 (N=68)
2) NW Mediterranean: February-July 2018 (N=23).

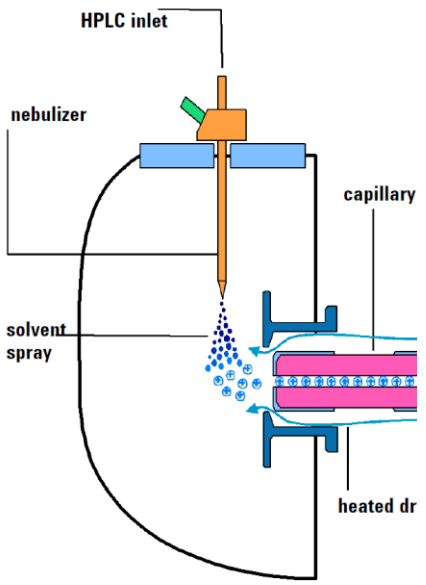
Sampler: High Volume Total Suspended Particulate (TSP) sampler (TISCH Environ.) The sampling resolution was 48 hours at a flow rate of 85 m^3/h.
Collection on pre-combusted 8×10 in. quartz filters (Pall, 2500QAT-UP).

OPEs Analysis

Agilent 6530: Q-TOF-LC/MS

HPLC conditions:

Column: Eclipse Plus (Agilent) (50mm×2.1mm I.D., 1.8 µm particle size). **Mobile phase:** 5 mM ammonium acetate in water (eluent A) and Acetonitrile with 5mM ammonium acetate (eluent B). The gradient elution was: 1) 10% (A) from 0-2.5 min, 2) 50% (A) from 2.5-10 min, 3) 50% (A) from 10-12 min 4) 10% (A) from 12-14 min, 5) 10% (A) from 14-17 min. The flow rate was set at 100 µl min^{-1}. The column temperature was set at 25°C and a 2 µl volume injection was used.



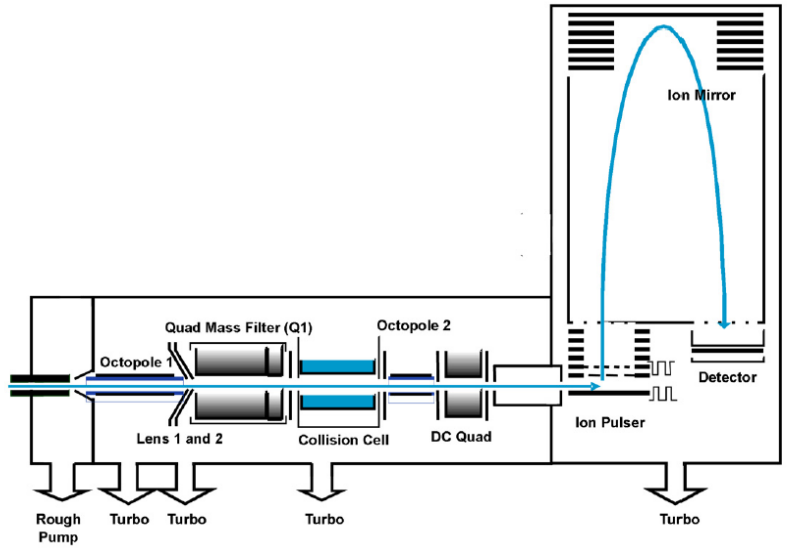


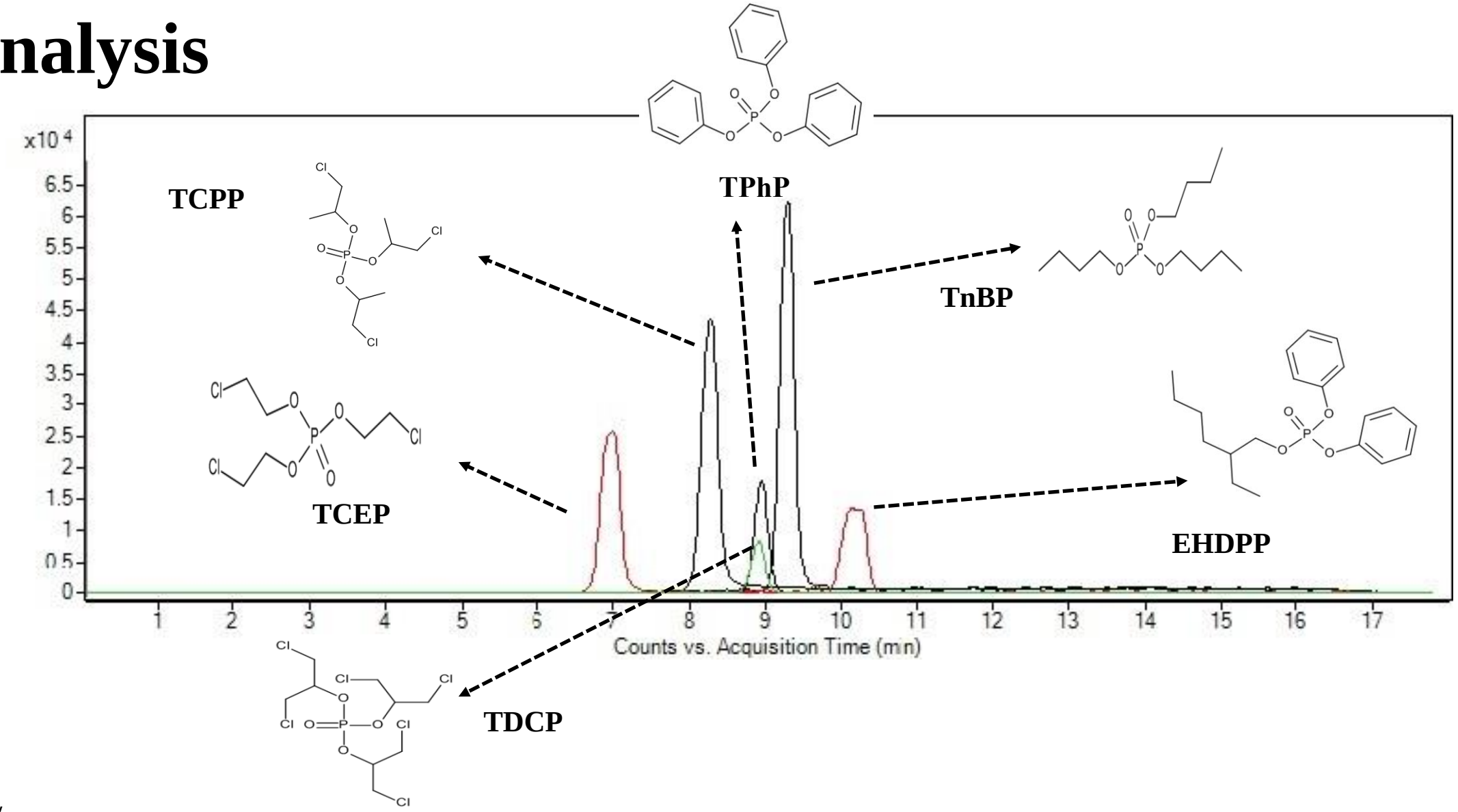
Figure 1 Electrospray ion source

MS conditions: positive ESI ionization

Source Temp: 350^{0}C, **Capillary voltage:** 3500 V

Extraction Protocol: Atmospheric quartz filters (1/10 of surface:~ 40 cm^2) were extracted in **Ethyl Acetate** by sonication within 60 min. The extracted solution was centrifuge at 5000g for 10 min and the supernatant was injected in the LC-QTOF system.
The detection limits were calculated 2-10 pg for 10 ul injection volume.

OPEs Analysis



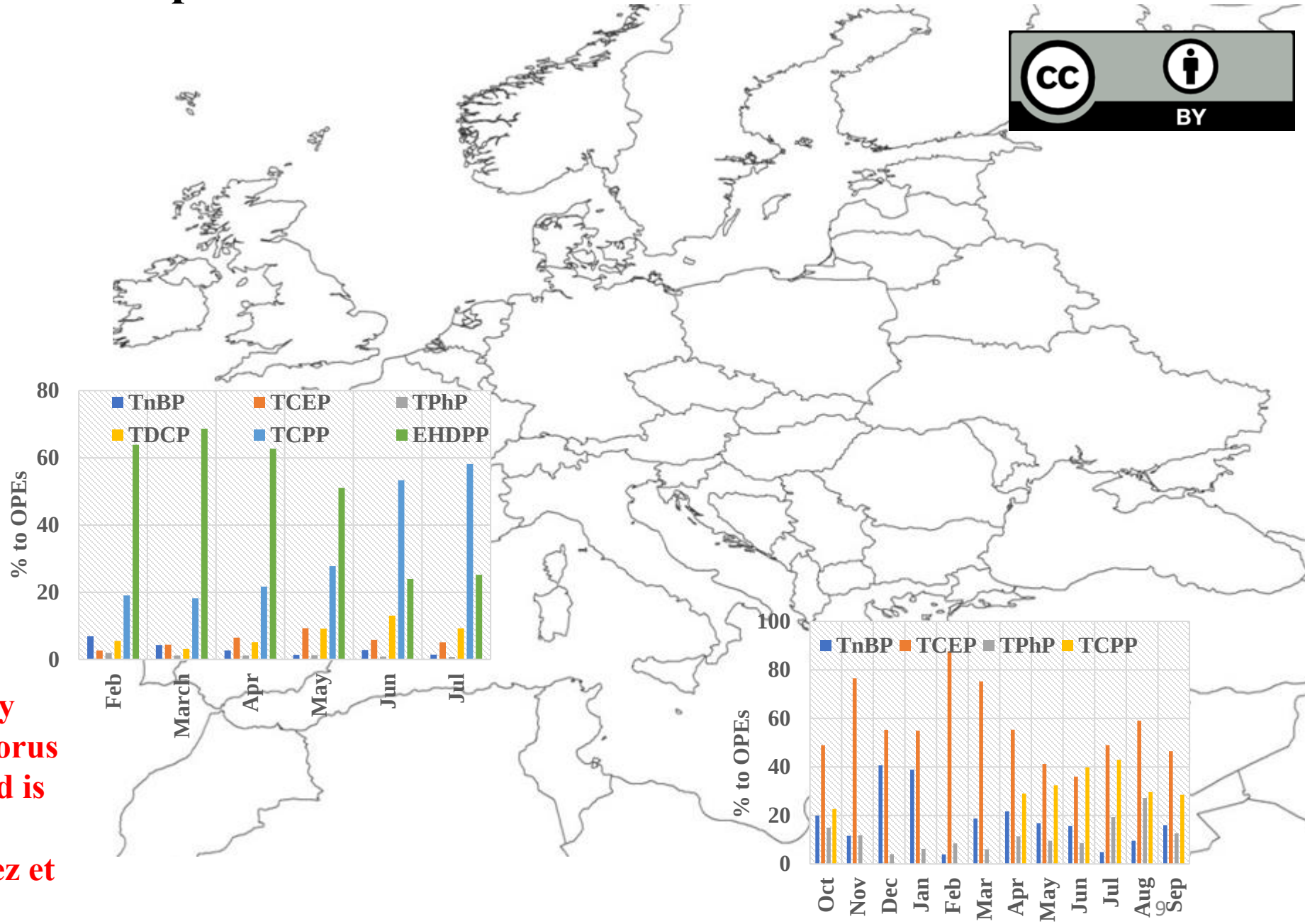
$[M+H]^+$
TCEP:284.9599 m/z
TCPP:327.0090 m/z
TDCP:428.8839 m/z
TPhP: 327.0793 m/z
TnBP: 267.1715 m/z
EHDPP: 363.1711 m/z

OPEs atmospheric pattern and spatial distribution in East and NW Mediterranean

Different pattern in percentage distribution of OPEs was observed:

- ✓ **In NW Med. most abundant are the EHDPP (49%) and TCPP (33%).**
- ✓ **In East Med. most abundant are the TCEP (57%) and TCPP (32%), while was not detected the EHDPP and TDCP.**

TCPP represents approximately 80% of the chlorinated phosphorus flame retardants in Europe, and is by production volume the most important OPE (Castro-Jiménez et al., 2016)



Average concentration of detected OPEs over Mediterranean

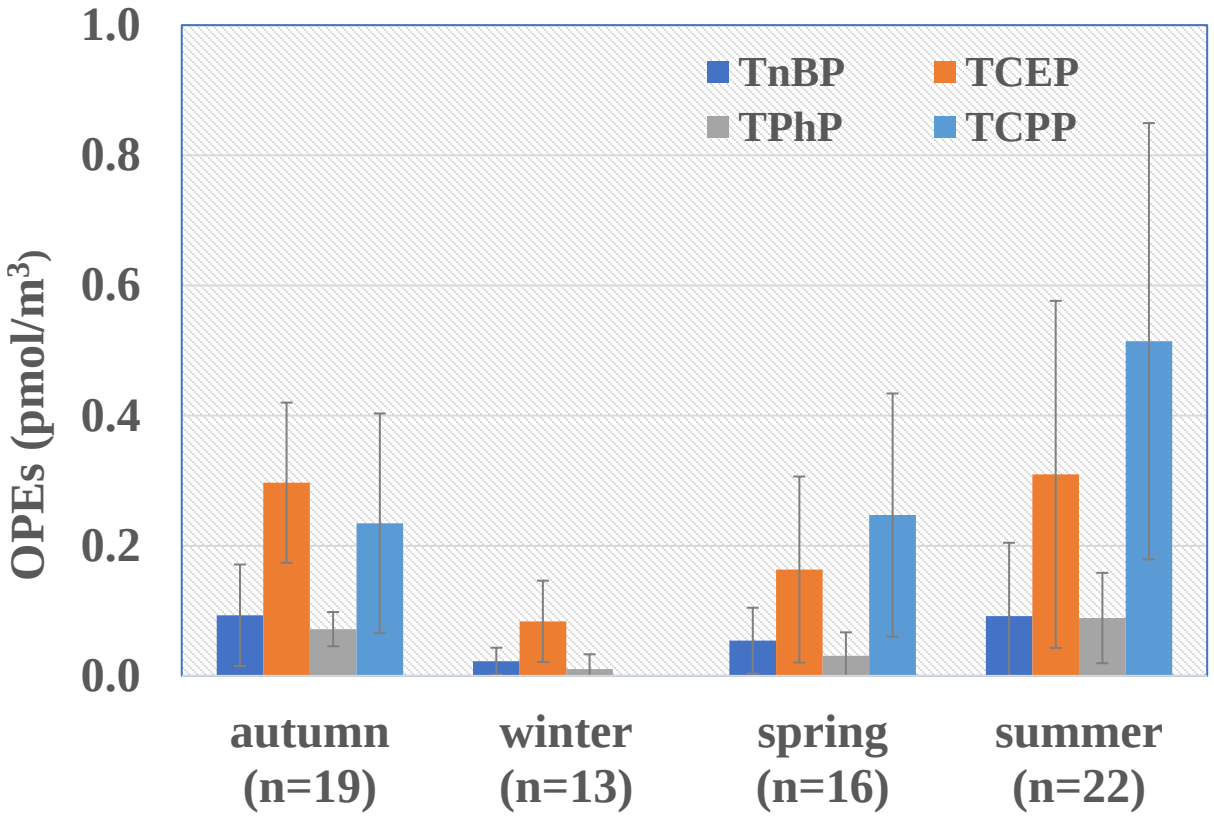
OPEs (pmol/m^3)	East Med. (N=67)	NW Med. (N=23)
TCPP	0.35±0.28	1.71±1.28
TCEP	0.23±0.20	0.29±0.31
TDCP	n.d	0.32±0.20
TnBP	0.07±0.08	0.18±0.21
TPhP	0.06±0.05	0.06±0.06
EHDPP	n.d	3.04±4.17

The percentage contribution of OPEs to the organic P* was calculated.

- **for East Med. at 0.4± 0.5%**
- **for NW Med. at 8.4± 8.9%**

** Organic P for East Med. was calculated at 0.24±0.32 nmol P/m^3 and for NW Med. was at 0.11±0.09 nmol P/m^3 (Violaki et al., unpublished data).*

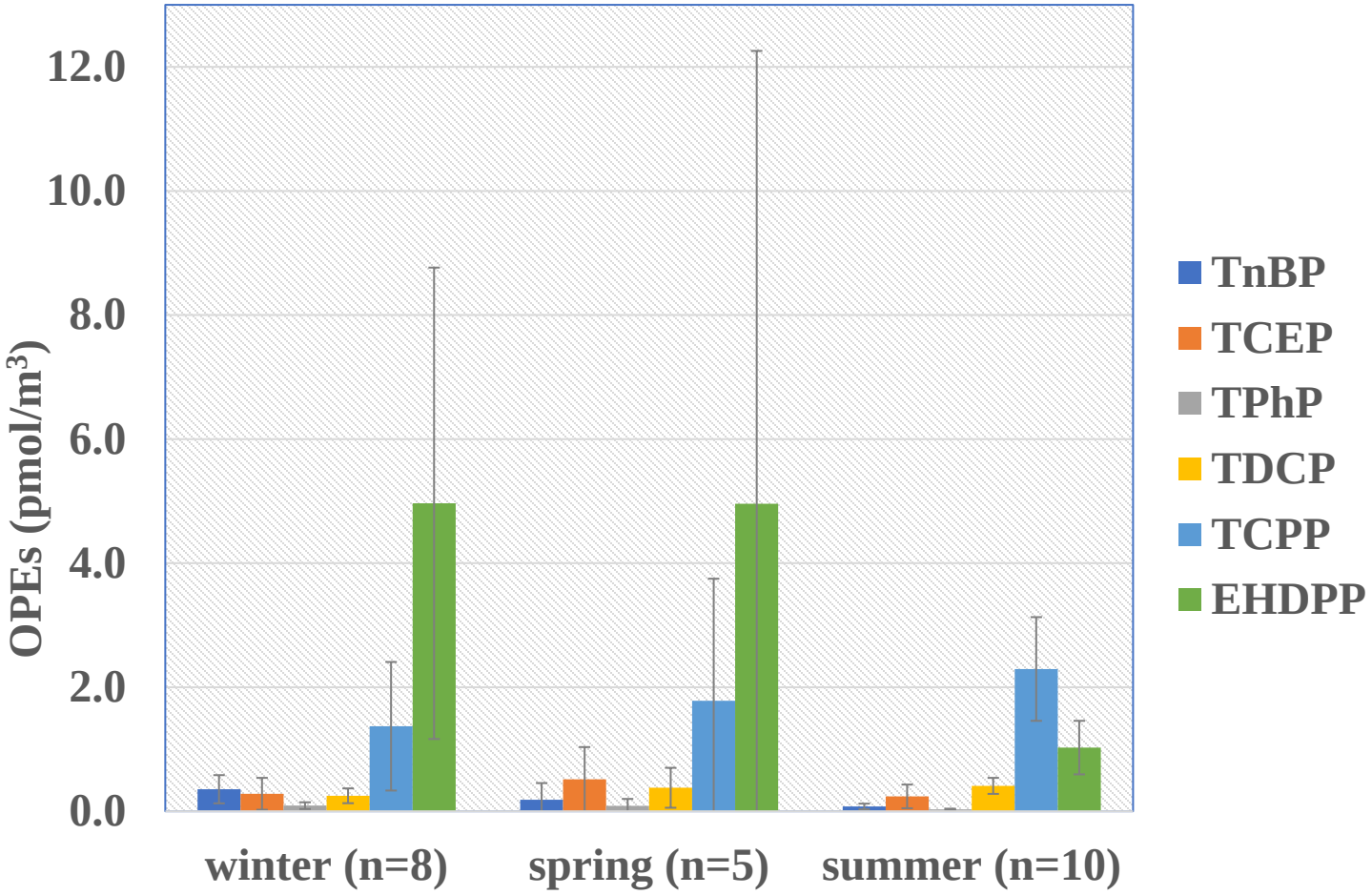
Seasonal variability in East Med.



TCPP is peaked in summer (0.51 pmol/m^3), while all OPEs have lower concentration during winter most probably due to rain wash out.

TCEP is peaked in summer and winter (0.31 & 0.31 pmol/m^3, respectively), The same trend with TCEP follows the TnBP with same maximum concentration at 0.09 pmol/m^3.

Seasonal variability in NW Med.

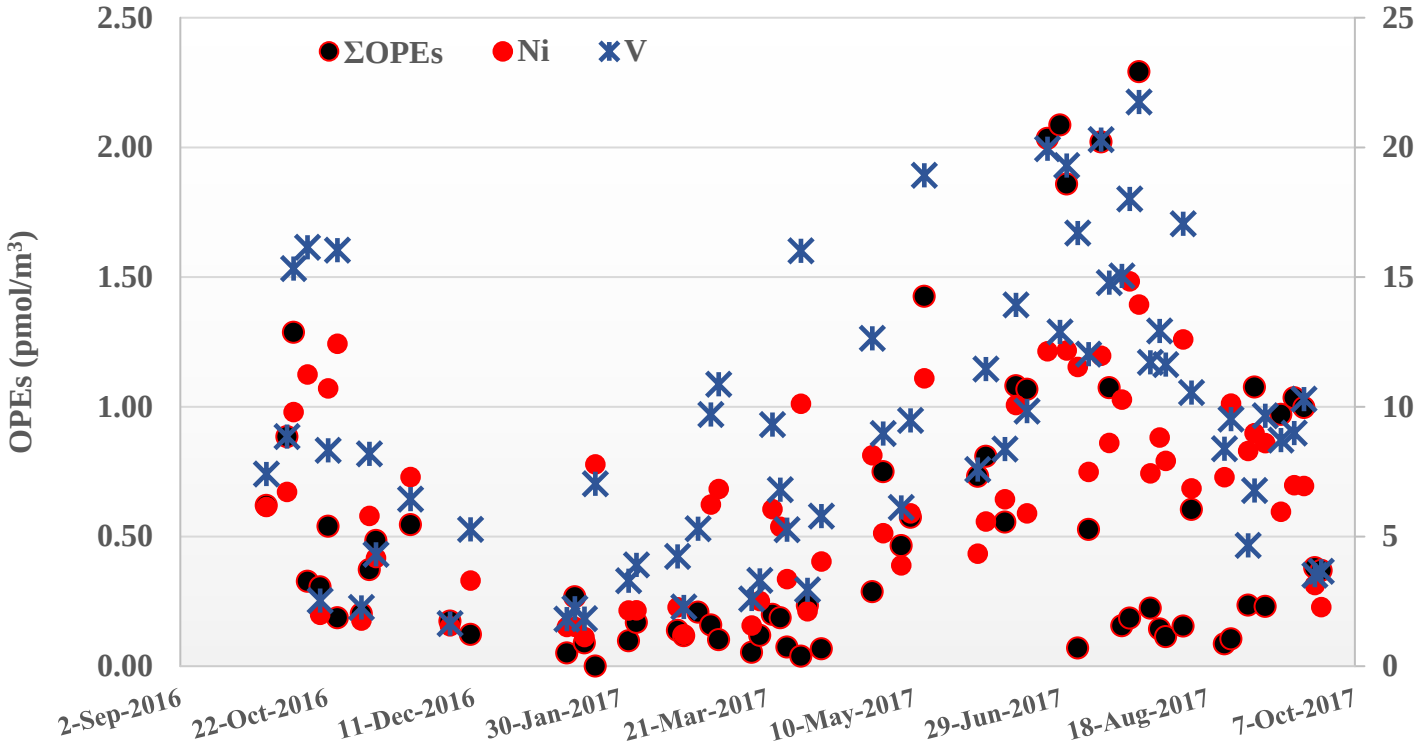


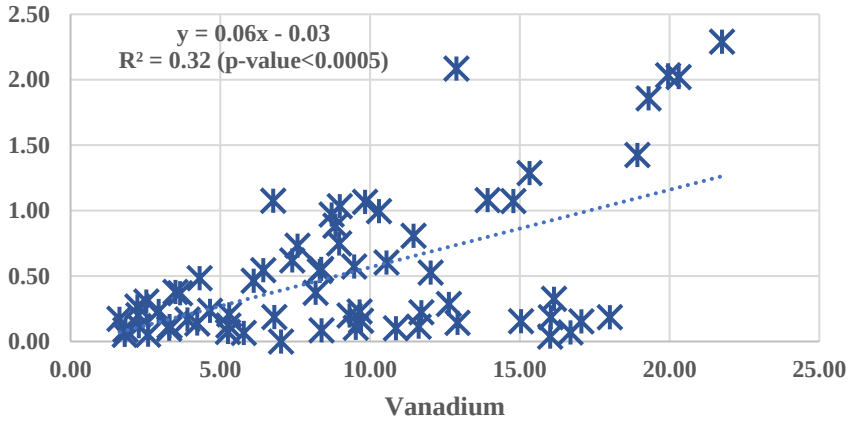
EHDPP is peaked in winter and summer (4.97 & 4.96 pmol/m^3 , respectively). The same trend follow also the TCPP with concentrations 2.29 and 1.78 pmol/m^3, respectively.

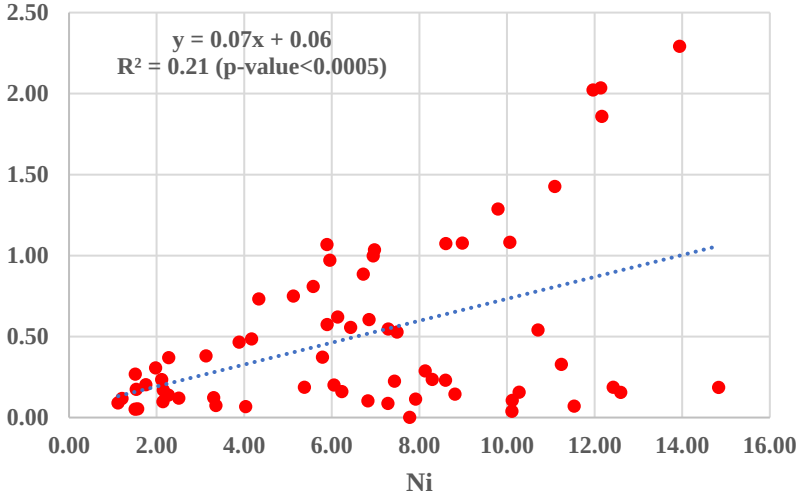
TCEP and TPhP are peaked in spring with concentrations 0.52 & 0.09 pmol/m^3, respectively. TDCP maximized during the summer with 0.41 pmol/m^3 and TnBP in winter with concentration at 0.36 pmol/m^3.

Sampling was not performed during the autumn.

East Med.

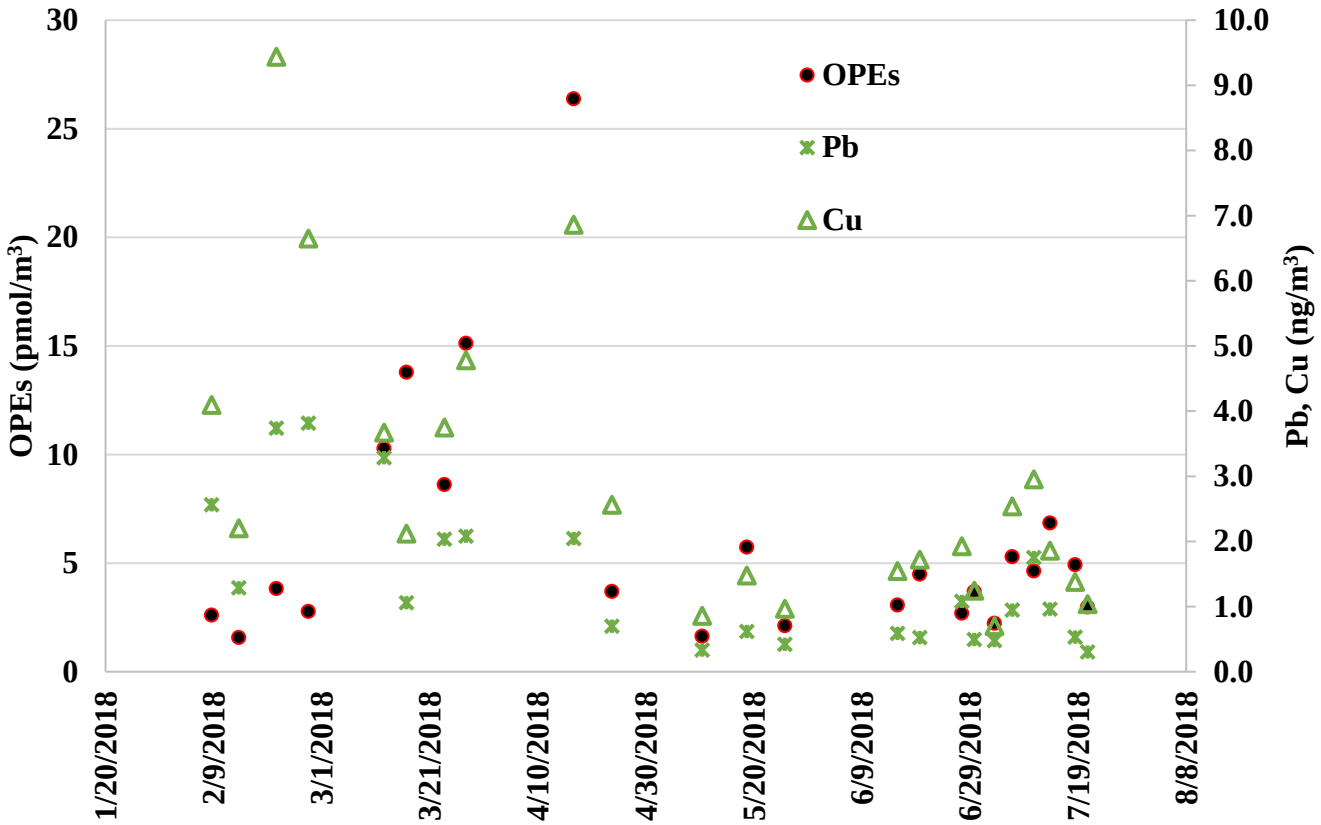


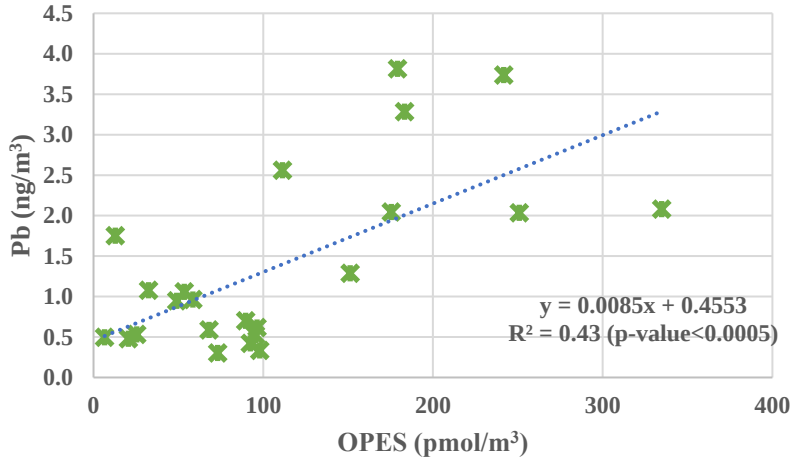


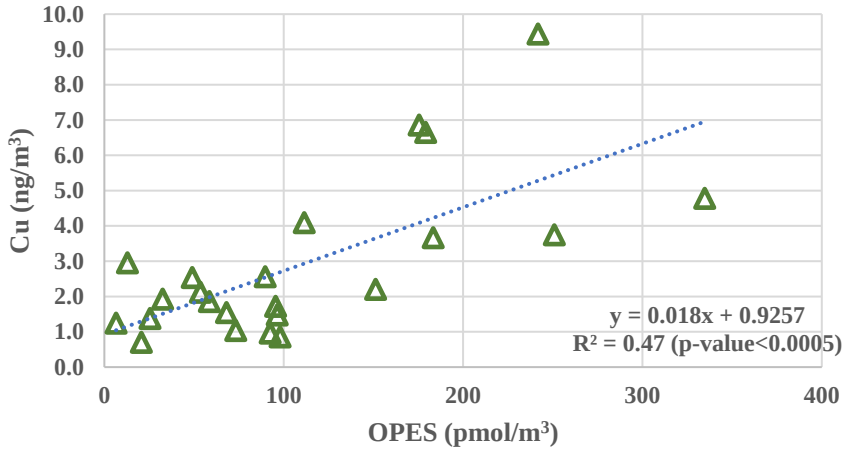


In East Med. significant correlation was found with Vanadium & Nickel, suggesting anthropogenic sources from fossil fuel oil combustions.

NW Med.







In NW Med. significant correlation was found with Pb & Cu, confirming as important sources the anthropogenic activities.

Biogeochemical Implications

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 NW Mediterranean (29 tons of P) during the same period.

Overall, the above anthropogenic compounds represented 3.7%* of the total anthropogenic P deposited during stratification period in the Mediterranean, however their toxicity and fate to the marine environment warrants further investigations.

Recent study supported that the microbial uptake of OPEs has important role on the biogeochemical cycling of P in P-limited aged seawater (Vila-Costa et al., 2019). However, the atmospheric deposition of OPEs compounds contribute only with less than 0.03% to new production of Mediterranean.

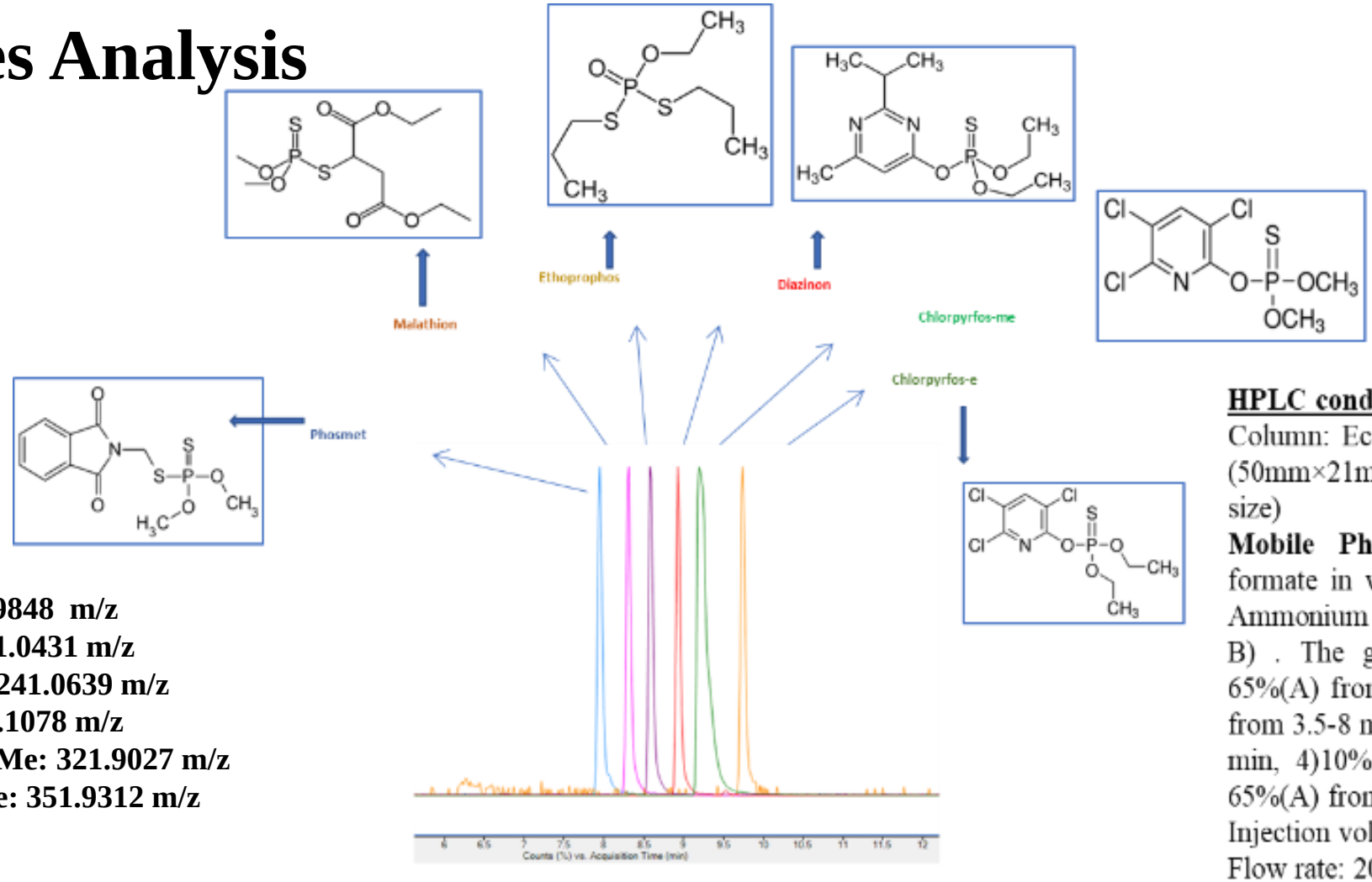
** Calculations were based on annual DP reported from Kanakidou et al., 2019 for Mediterranean (62.27 Gg-P y^{-1}) , considering the solubility as 68% and assumed ~ 3% of TP as anthropogenic (Myriokefalitakis et al., 2016, Violaki et al., 2018).*

Organophosphorous Pesticides

Pesticides are emitted in the atmosphere:

- ✓ **During application**
- ✓ **Volatilization from soil and plants after application**
- ✓ **Wind erosion of soil particles containing absorbed pesticides.**

Pesticides Analysis



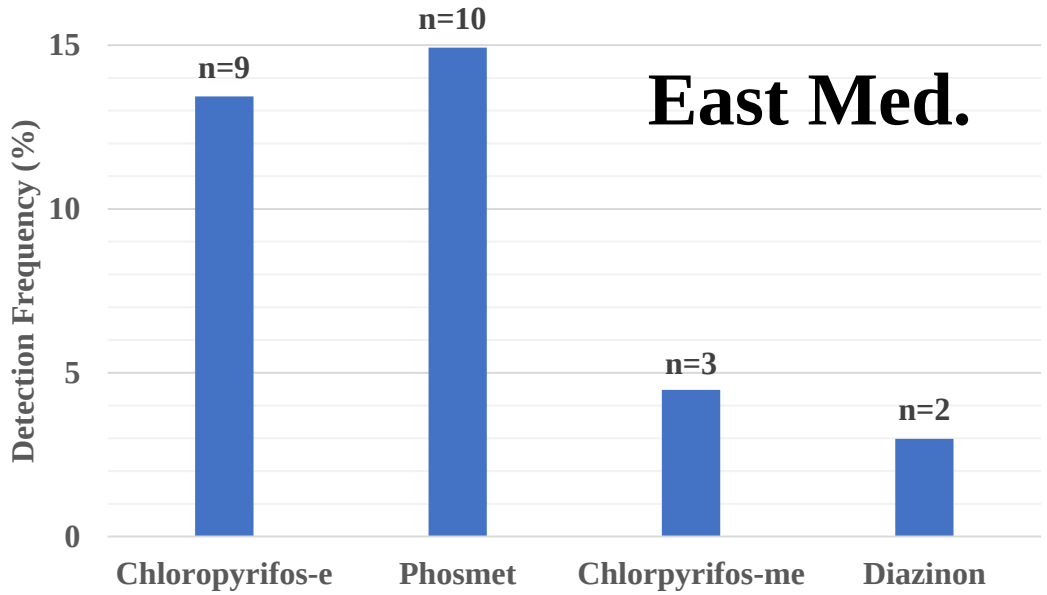
$[M+H]^+$
Phosmet:339.9848 m/z
Malathion:331.0431 m/z
Ethoprophos:241.0639 m/z
Diazinon: 305.1078 m/z
Chlorpyrifos-Me: 321.9027 m/z
Chlorpyrifos-e: 351.9312 m/z

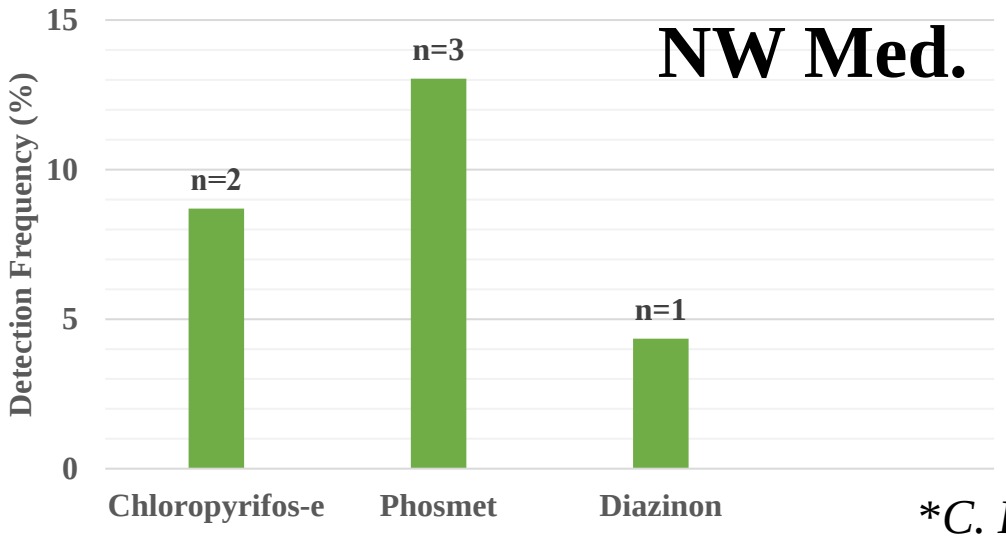
HPLC conditions
Column: Eclipse Plus C18 (Agilent) (50mm×21mm I.D., 1.8 µm particle size)
Mobile Phase: 0.8% Ammonium formate in water (eluent A) and 8% Ammonium formate in MeOH (eluent B) . The gradient elution was: 1) 65%(A) from 0-3.5 min, 2) 10% (A) from 3.5-8 min, 3) 10%(A) from 8-12 min, 4)10%(A) from 12-15 min 5) 65%(A) from 15-18 min.
Injection volume: 10µL
Flow rate: 200 µL/min

MS conditions
Instrument: Agilent 6530 Q-TOF-LC/MS
ESI: positive ionisation
Source Temp: 300^0 C
Capillary Voltage: 2000V

Extraction Protocol: Atmospheric quartz filters (1/10 of surface :40 cm^2) were extracted in **Ethyl Acetate** by sonication within 60 min. The extracted solution was centrifuge at 5000g for 10 min and the supernatant was injected in the LC-QTOF system. The detection limits were calculated 2-10 pg for 10 ul injection volume.

Results….





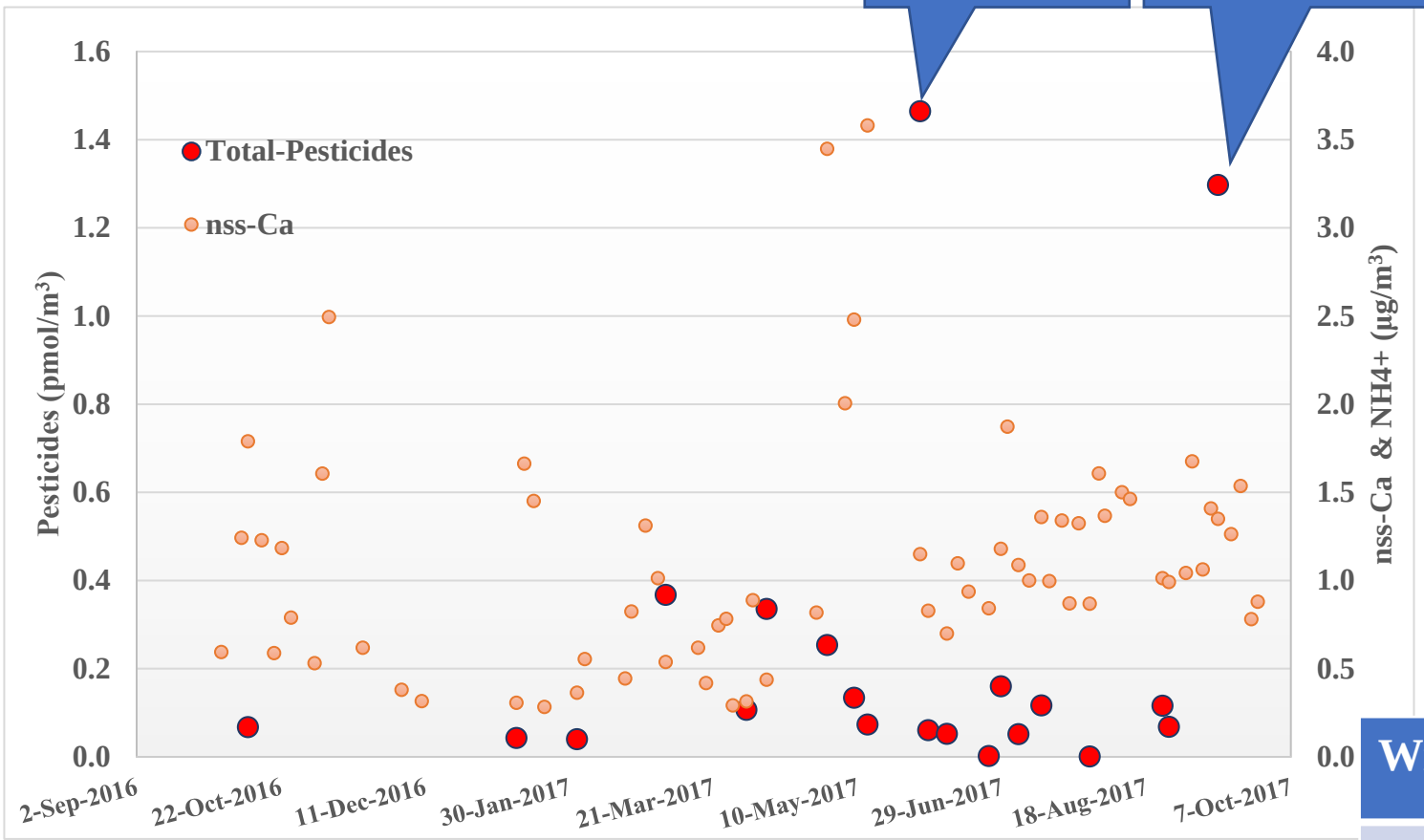
pmol/m^3	East Med.	NW Med.	Half-Life in soil* (days)	Half-Life in Air (hours)
Chlorpyrifos-e	0.24±0.38	0.04±0.01	50	6-72
Phosmet	0.24±0.45	0.07±0.04	3-12	6-72
Chlorpyrifos-me	0.91±0.93	n.d	50	6-72
Diazinon	0.07	0.05	9	4
Malathion	n.d	n.d	0.17	5

The percentage contribution of P-pesticides to the organic P was calculated.

- **for East Med. 0.1± 0.2%**
- **for NW Med. 0.1± 0.1%**

**C. Degrendele et al, Atmos. Chem. Phys., 16, 1531–1544, 2016.*

East Med.



The temporal variability of detected pesticides over East Med. show higher concentration during spring period, most probably due to the frequent application during the growing season.
Higher concentrations of pesticides were observed with airmass origin from Black sea and Sahara desert .

The total organic P deposited in East Mediterranean during stratification period (June-September) was calculated at 3.4 tons, which was 20 times higher comparing with NW Mediterranean (0.2 tons of P) during the same period.
Organophosphorus pesticides represented only 0.3% of the total anthropogenic P deposited during the same period in the Mediterranean.

Wind Sector	Pesticides	% to Org-P
Dust (N=5)	0.36±0.53	**0.5**
Central Europe (N=6)	0.14±0.17	**0.1**
Black Sea (N=7)	0.52±0.28	**0.1**

Conclusions…..

Different pattern in percentage distribution of OPEs was observed; in East Med. most abundant were the TCEP (57%) and TCPP (32%), while was not detected the EHDPP and TDCP. In NW Med. most abundant were the EHDPP (49%) and TCPP (33%).

Higher percentage contribution of OPEs to the organic P was calculated for NW Med. (8.4± 8.9%). In East Med. 0.4± 0.5% of organic P was attributed to OPEs.

The most frequent organophosphorus pesticides over Mediterranean were chlorpyrifos-ethyl and Phosmet, both are broad use insecticides. Higher contribution of pesticides in organic P was observed during dust events (0.5%).

Overall, the above anthropogenic compounds represented ~4 % of the total anthropogenic P deposited during stratification period in the Mediterranean, however their toxicity and fate to the marine environment warrants further investigations.

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