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Detection of Organophosphorus Esters (Opes) in Groundwater †

Lucija Plantak *, Anita Ptiček Siročić, Ivana Grčić and Ranko Biondić

Faculty of Geotechnical Engineering, University of Zagreb, Hallerova Aleja 7, 42000 Varaždin, Croatia
* Correspondence: lucija.plantak@gfv.unizg.hr
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Abstract: Organophosphate esters (OPEs), are used as flame retardants and plasticizers to protect or enhance the properties of plastics, textiles, and many other materials. Sampling was carried out in groundwater from the karst aquifer Bokanjac–Poličnik near the city of Zadar, Croatia. To determine their continuous presence, samples were taken once during each season through one year. In collected samples nine OPEs were identified: tris(2-butoxyethyl) phosphate-TBEP, tricresyl phosphate-TCP, triphenyl phosphate-TPPA, tris(1-chloro-2-propyl) phosphate-TCPP, (tris(2-chloroethyl) phosphate-TCEP, tris(1,3-dichloroisopropyl) phosphate-TDCPP, diethyl phthalate-DEP, tri-n-butyl phosphate-TBP, and di(2-ethylhexyl) adipate-DEHA.

Keywords: organic pollutants; OPEs; groundwater quality; karst aquifer

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1. Introduction and Background

Groundwater is essential for water supply of settlements in many countries in the world, and especially in Croatia where 90 % of withdrawal is from underground aquifers. In Croatia quality of groundwater must be in line with EU commission Water Framework Directive (WFD) [1] as well as Groundwater Directive (GWD) [2]. Emerging pollutants, in particular, organic pollutants in groundwater are not enough researched due to the absence of monitoring regulations, nevertheless, monitoring is on a voluntary base [3].

Organophosphate esters (OPEs), triesters, are used as flame retardants and plasticizers to protect or enhance the properties of plastics, textiles, and many other materials. They are high-production volume chemicals with large variations in physical-chemical properties widely used in many human activities and can be detected in groundwater due to their insolubility in water, especially in wastewater. In [4] was cleared that OPEs have been used for decades, so their occurrence in the environment is not a new issue because since the 1980s, they find reports on their detection in surface waters, in groundwaters influenced by wastewater, and in drinking water. OPEs can be health hazard for humans due to their toxicity and some of them have shown carcinogenic properties i.e., Chlorinated OPEs such as TCEP, TCPP and TDCPP can accumulate in the liver, testis, thereby inducing tumors [5].

There are developed analytical methods for the determination of OPEs in water i.e., various extraction techniques followed the gas chromatography with mass spectrometry (GC-MS) and liquid chromatography with mass spectrometry (LC-MS) [6].

Sampling was carried out in groundwater from the karst aquifer Bokanjac–Poličnik near the city of Zadar, Croatia in order to detect some of the OPEs. To determine their continuous presence in the case study aquifer, samples were taken during the entire hydrological year, that is, once during each season through one year. Preparation of samples was made with the Solid Phase Extraction (SPE) method and analyzed with liquid chromatography with mass spectrometry and quadrupole time of flight (LC-MS/QTOF). In collected samples nine OPEs were identified with Water Screening Personal Compound Database and Library (PCDL): tris(2-butoxyethyl) phosphate-TBEP, tricresyl phosphate-TCP, triphenyl phosphate-TPPA, tris(1-chloro-2-propyl) phosphate-TCPP, (tris(2-chloroethyl) phosphate-TCEP, tris(1,3-dichloroisopropyl) phosphate-TDCPP, diethyl phthalate-DEP, tri-n-butyl phosphate-TBP, and di(2-ethylhexyl) adipate-DEHA. Their properties and usage are listed in Table 1.

Table 1. OPEs properties and usage detected in case study aquifer.

OPEs	CAS No.	Formula	Usage	Literature
TBEP	78-51-3	$C_{24}H_{51}O_4P$	Adhesives, sealant chemicals, Flame retardants, Paint and coating additives, Plasticizers, Cleaning-furnishing care products	[6,7]
TCP	78-32-0	$C_{21}H_{21}O_4P$	Plasticizer, flame-retardant, solvent for nitrocellulose, as additive to extreme pressure lubricants, fluid in hydraulic systems, as lead scavenger in gasoline, to sterilize certain surgical instruments, In flexible PVC.	[8,9]
TPPA	115-86-6	$C_{18}H_{15}O_4P$	Flame retardants, Paint and coating additives, Plasticizer in automobile upholstery, fireproofing agent, for impregnating roofing paper, component of lubricating oil and hydraulic fluids.	[6,10]
TCPP	13674-84-5	$C_9H_{18}Cl_3O_4P$	Adhesives and sealants, Building/construction materials-wood products, Electrical and electronic products, Fabric, textile, and leather products, Flame retardant, Foam seating and bedding products, Insulating foam, Plastic, and rubber products	[6]
TCEP	115-96-8	$C_6H_{12}Cl_3O_4P$	Additive plasticizer and flame retardant in plastics, especially in flexible foams used in automobiles and furniture, and in rigid foams used for building insulation.	[11,12]
TDCPP	13674-87-8	$C_9H_{15}Cl_6O_4P$	Flame retardant, Plasticizer, used in polyvinyl chloride, rigid PUF, epoxy resin, and polyester fiber.	[13]
DEP	84-66-2	$C_{12}H_{14}O_4$	Adhesives and sealants, Air care products, Automotive care products, Cleaning and furnishing care products, laundry and dishwashing products, Personal care products, toys, playground, and sporting equipment, aroma chemicals	[6]
TBP	126-73-8	$C_{12}H_{27}O_4P$	Flame retardants, Functional fluids (closed and open systems), Plasticizer, Building/construction materials, Hydraulic Fluid, Ink, toner, and colorant products	[6,12]
DEHA	103-23-1	$C_{22}H_{42}O_4$	Bis(2-ethylhexyl) adipate is a diester. It is used as a plasticizer in the preparation of various polymers. Adhesives and sealants, Automotive care products, Building/construction materials, Electrical and electronic products, Fabric, textile, and leather products. Food packaging, Fuels and related products, Furniture and furnishings, Lubricants and greases, Metal products, Paints and coatings, Personal care products	[6]

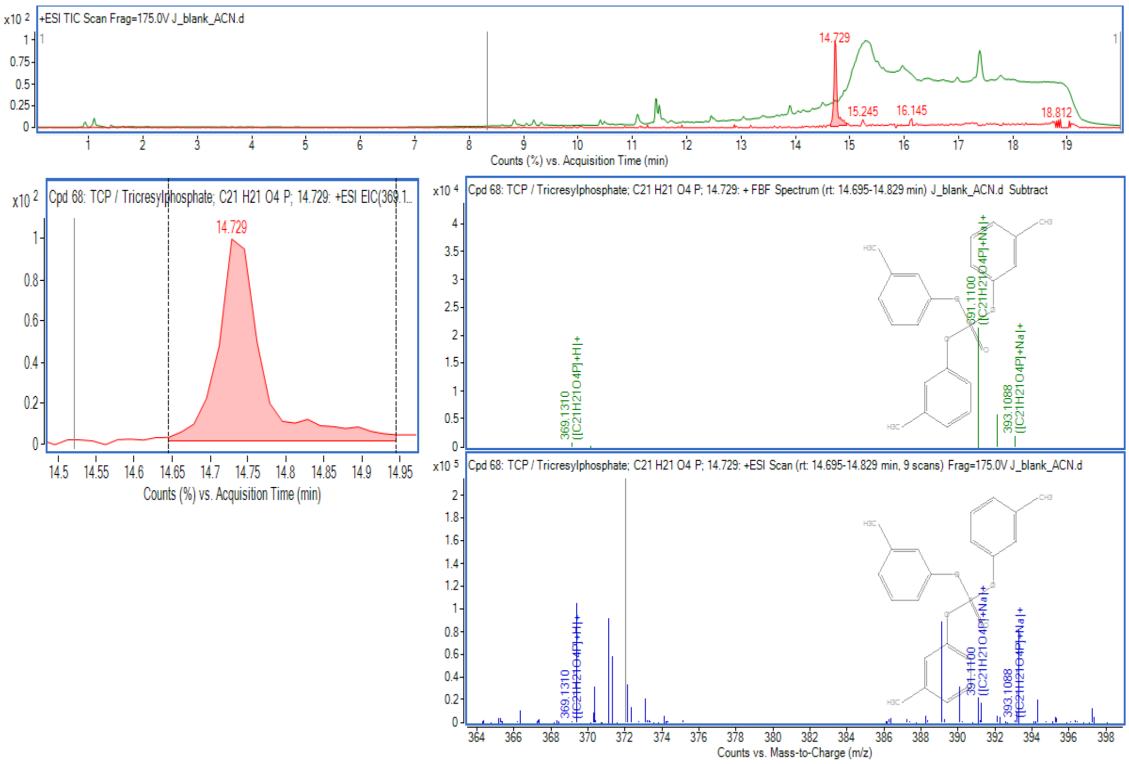
2. Methodology

Sampling of groundwater is caried out from three piezometer wells on Bokanjac–Poličnik basin near city of Zadar in Croatia. Samples was taken four times in one year in order to have all seasons covered i.e., to have samples from one hydrological year. For sampling, sterile glass bottles was used and they were refrigerated through transport and until sample preparation began. Three sites where samples were taken are marked with: J, B and B4. Due to the complexity of the groundwater samples that is relatively clear and great quality according to the parameters regulated for human consumption, and due to the small concentrations of expected organic pollution that can't be directly measured there is need for concentration. Prepared analyte for analysis is concentrated trough Solid Phase Extraction (SPE) method just to increase selectivity of the method. SPE method is used to eluate concentrated analyte in order to easier identification and quantification of expected compounds in extremely low concentrations. Cartridges used for SPE are Bond elut plexa C18 and the samples was eluted with methanol (MeOH) and filtered through KX syringe filter PET 25 mm, 0,22. Filtered samples are analyzed in Agilent 6530 LC/MS QToF device that detects ion masses (M/z) and relative abundance of isotopes i.e., with this device we determine which ions are in samples based on masses that are detected [14].

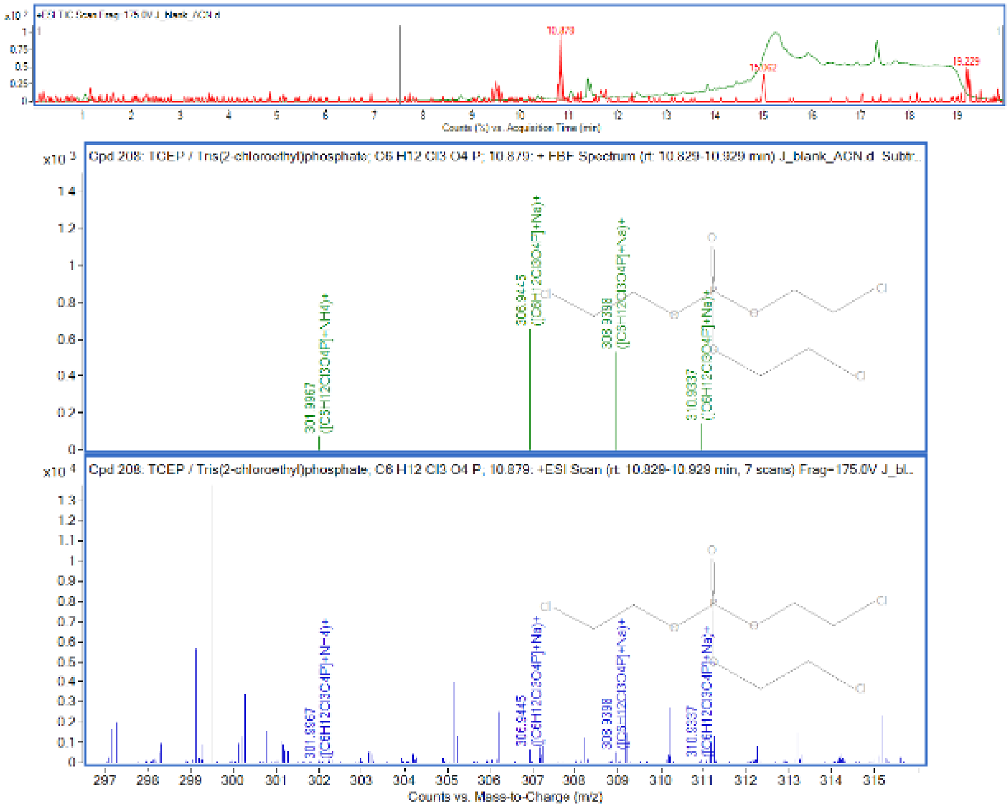
LC/MS QToF analysis was performed with a InfinityLab Poroshell 120 EC–C18 (3.0 × 100 mm), 2.7 µm, Agilent Technologies, Inc. column. Injecting 0,4 mL/min of analyte with mobile phases: (A) deionized water with 0.1 % formic acid, (B) MeOH with 0.1 % formic acid, (C) acetonitrile (ACN) with 0.1 % formic acid. These mobile phases were used in 20 min run in positive ionization mode and with column temperature of 35 °C.

3. Results

OPEs that was detected with above mentioned methodology are identified with Agilent Water Screening Personal Compound Database and Library (PCDL) and are shown on Figures 1–6.



(**a**)



(**b**)

Figure 1. OPEs in sample J (**a**) TCP; (**b**) TCEP.

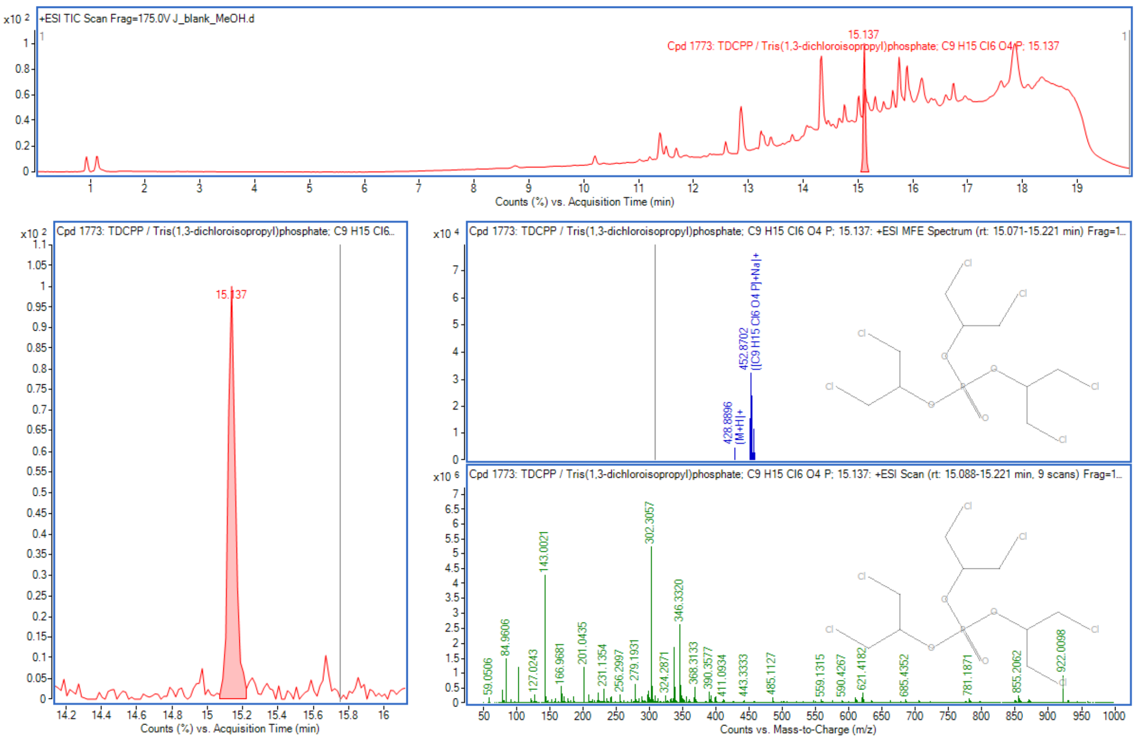
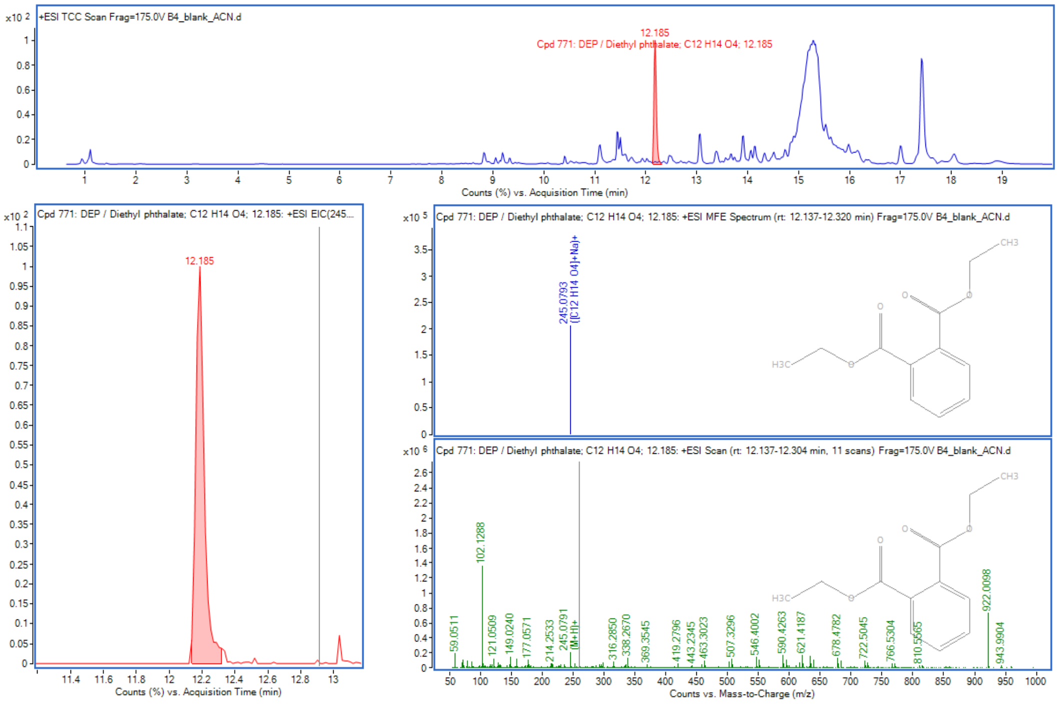
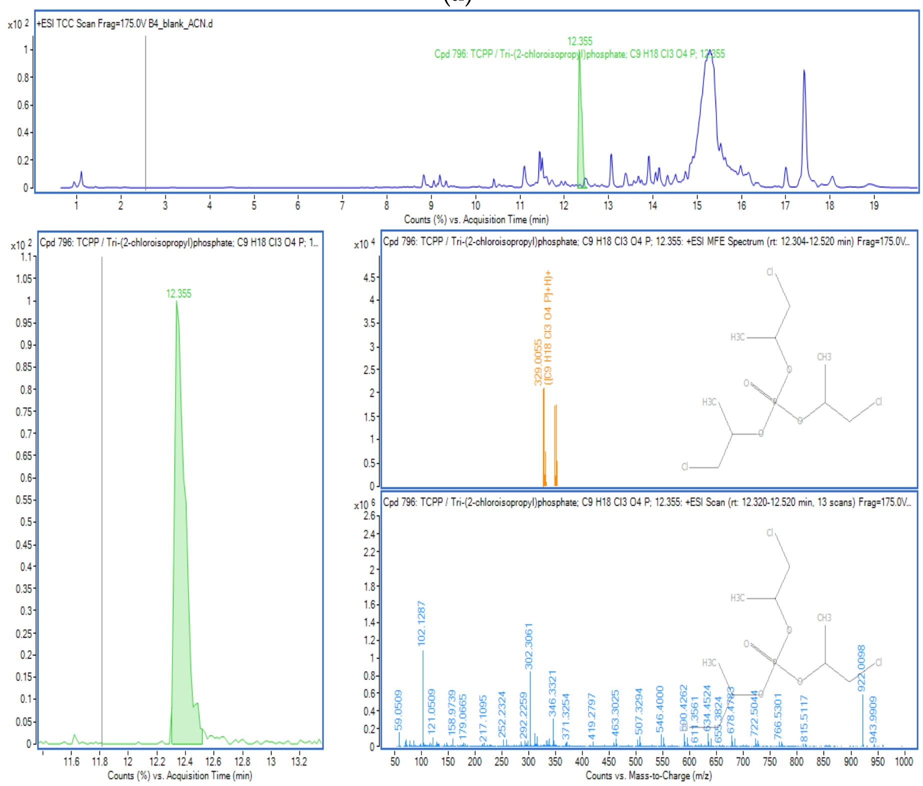


Figure 2. TDCPP in sample J.



(**a**)



(**b**)

Figure 3. OPEs in sample B4 (**a**) DEP; (**b**) TCPP.

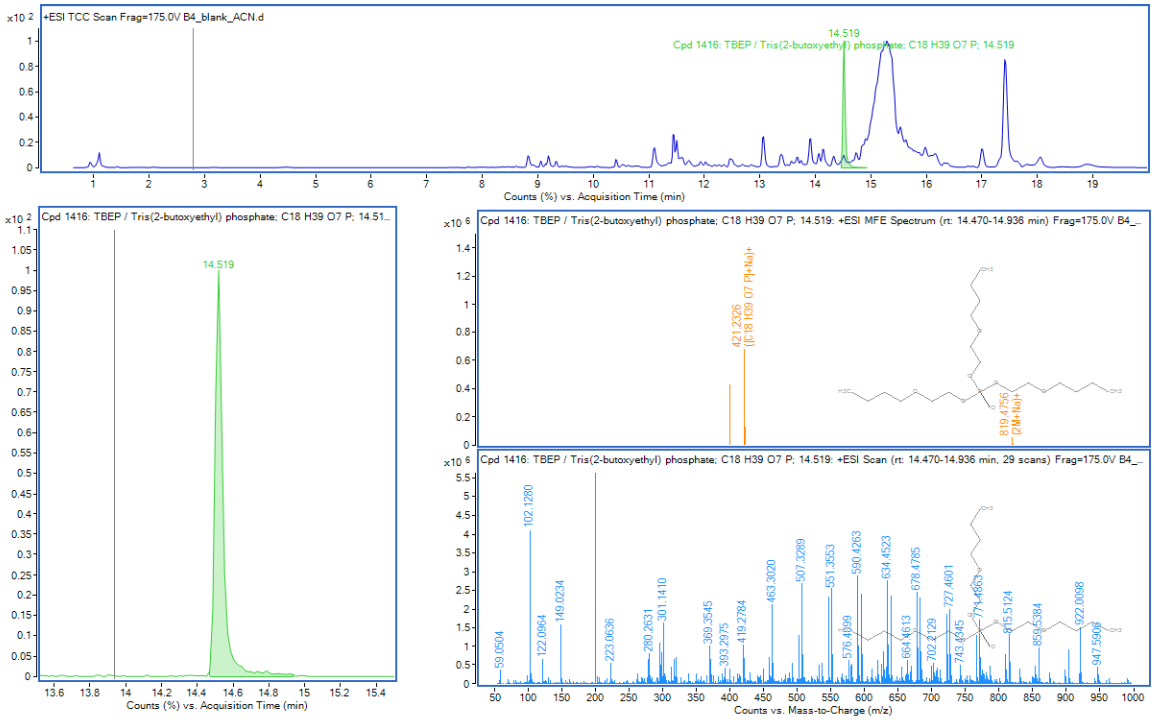
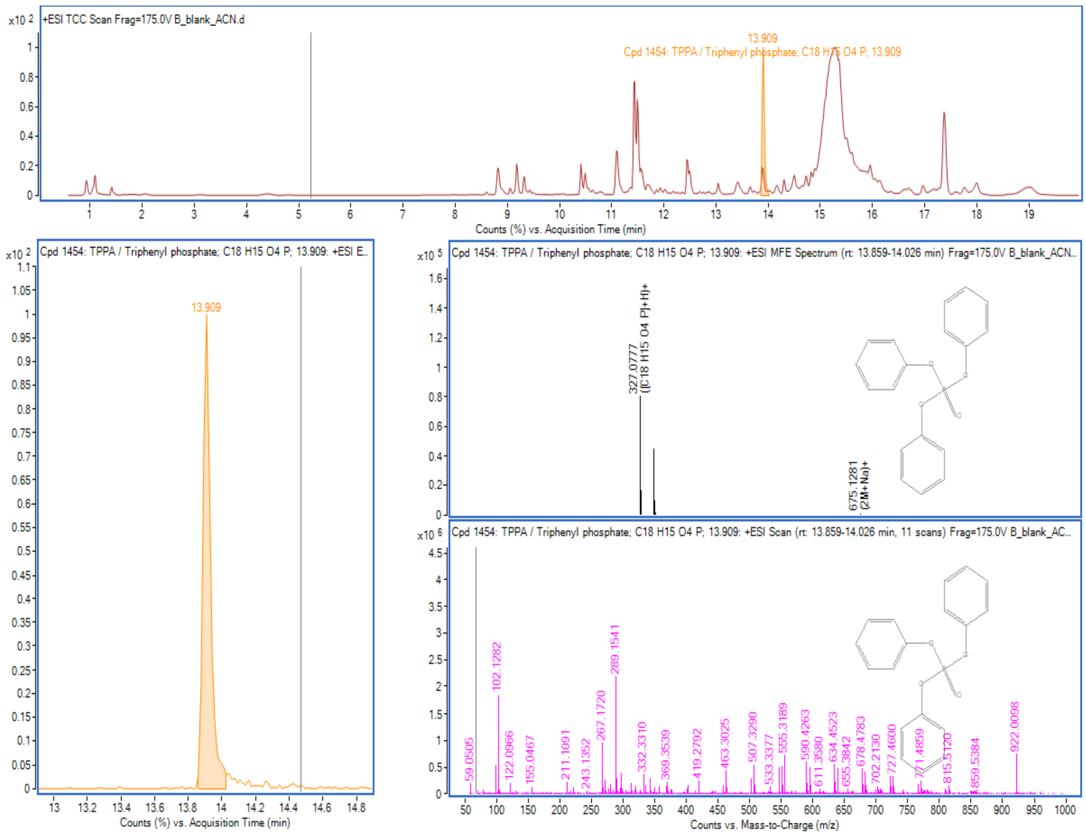
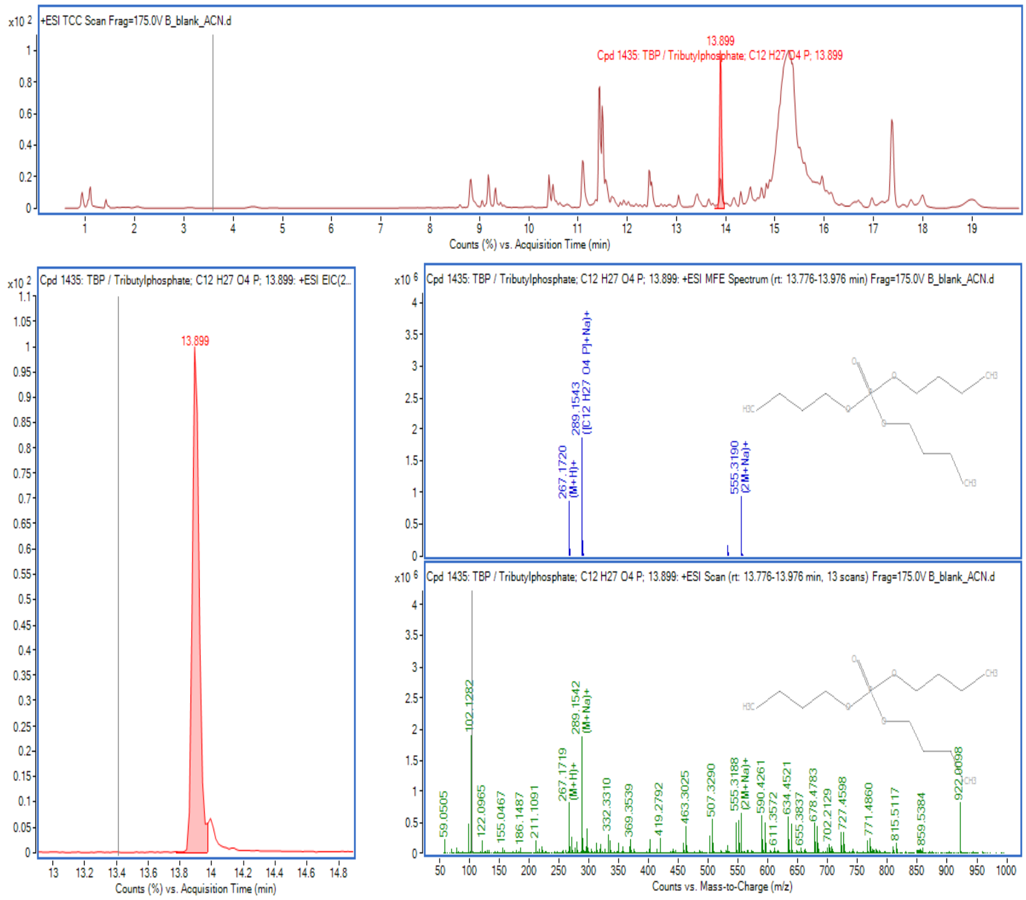


Figure 4. TBEP in sample B4.



(**a**)



(**b**)

Figure 5. OPEs in sample B (**a**) TPPA; (**b**) TBP.

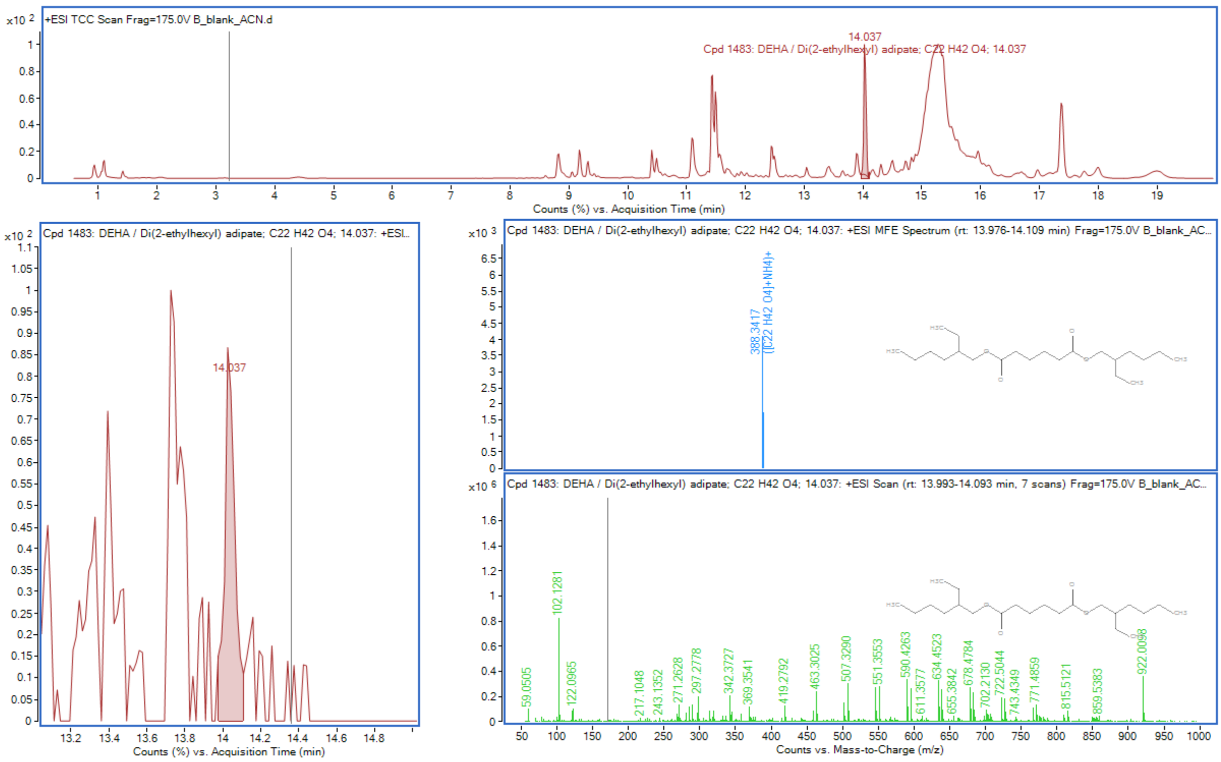


Figure 6. DEHA in sample B.

4. Conclusions and Discussion

OPEs are potential pollutants in groundwaters that are not under regulations and there are no defined maximum available concentrations for such emerging pollutant. OPEs can be find in nature in relatively small concentrations, and it is not easy to identify their presence in groundwater. In this research nine of the OPEs was detected in groundwater samples in one karst basin in Croatia trough all seasons of one year. In that part, where samples were taken, water for water supply system is withdraw form case study karst aquifer. Consequently, there is a need for raising the public awareness of usage and release of OPEs in the environment. Also, some of the OPEs found in samples are toxic i.e., dangerous for human health due to their persistent persistence in water environment. That's why research on their identification, quantification and behavior in groundwater is important.

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Conflicts of Interest: The authors declare no conflict of interest.

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