Accurate mass screening and identification of emerging contaminants & their transformation products in environmental samples

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What Makes a "Contaminant of Emerging Concern"?

In general, **ECs** are a structurally diverse and heterogeneous group of chemical compounds, which have widely varying fate properties and adverse effects on environmental ecosystems **and can be classified into the following categories**:

- ***"new"* ECs,** which are chemicals that are recently manufactured and suddenly appear everywhere, and therefore, **are not currently covered by existing regulations or legislation**
- ***"old"* ECs,** which are the ones that were actually around for several decades, **but simply were not under regular investigation or for which analytical methods did not exist until recently.**
- ***"ECs within complex mixtures",*** such as industrial effluents, oil residues, hospital effluent, etc. **of which either the mixture itself or newly identified (subgroups) of components within may be considered ECs.**

Emerging pollutants

NORMAN

Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances

enhances the exchange of information on emerging environmental substances

web-based databases for the collection & evaluation of data

EMPODAT: a database of geo-referenced monitoring / occurrence data on emerging substances;

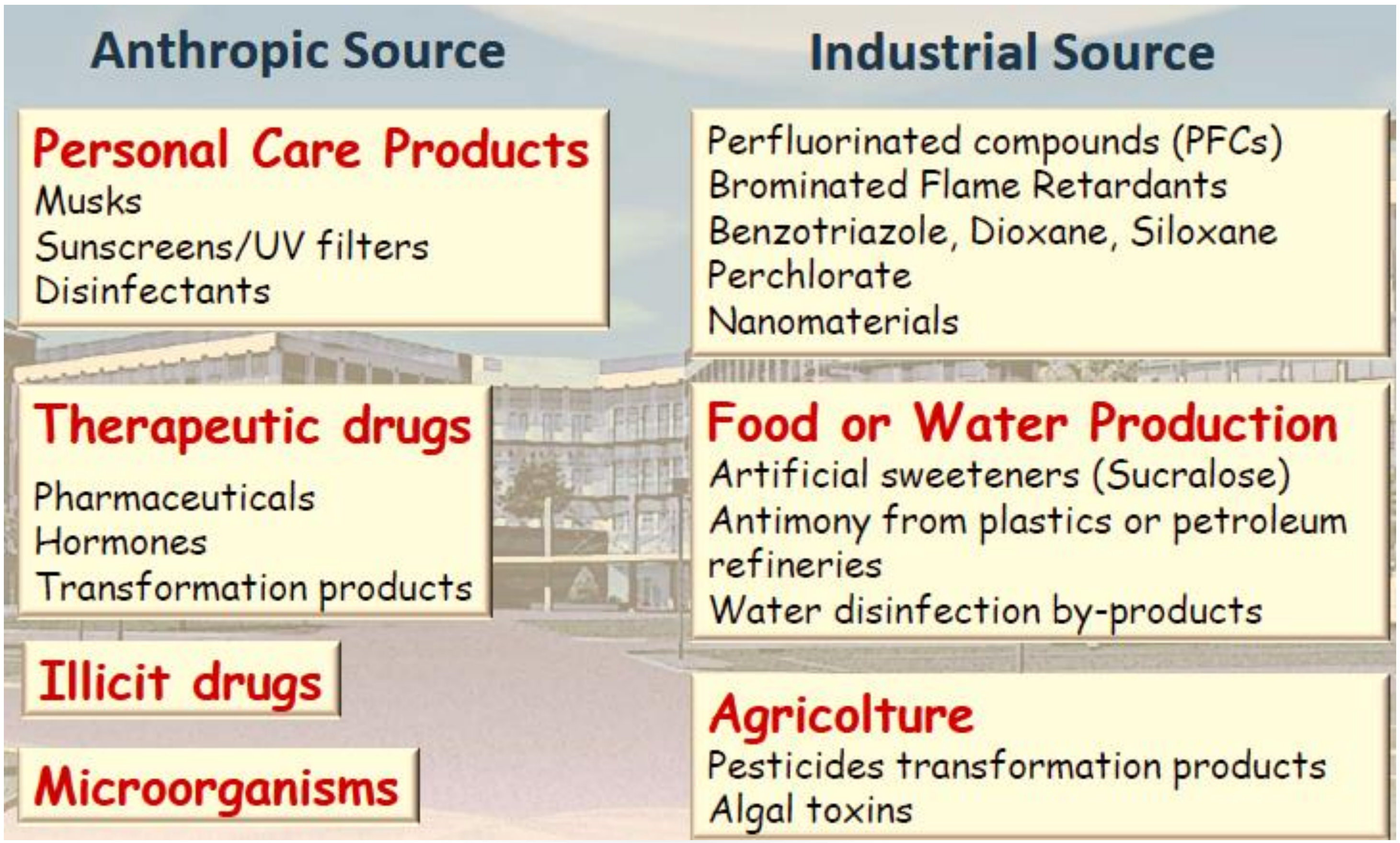
NORMAN MassBank: a database of mass spectra of unknown or provisionally identified substances.

NORMAN Suspect List Exchange: a central website to access various lists of substances for suspect screening.

Network of reference laboratories for monitoring of emerging environmental pollutants

Emerging pollutants

(Richardson and Ternes, *Anal. Chem.* 2011, 83, 4614)



Transformation Products (TPs)

New emerging contaminants in the water cycle

Transformation Products of ECs?

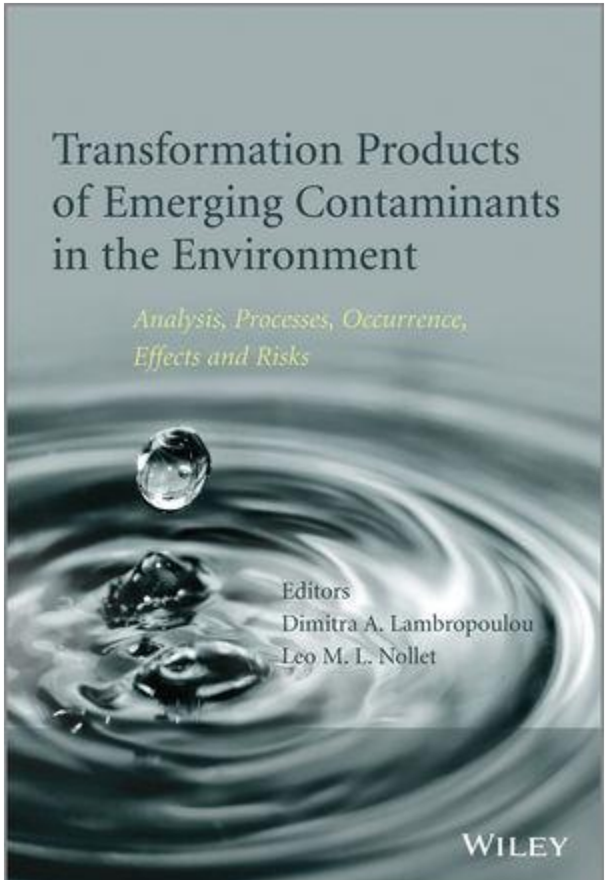
- Despite the increasing number of published studies covering EC input, occurrence, fate and effects, there is still a lack of understanding and knowledge about these substances in the aquatic environment.

- **Even more,** we know very little about the impacts of the environmental exposure to trace concentrations of their ***transformation products*** (TPs) and/or ***metabolites***, but the detection of TPs in the environment is worrying.

- TPs of ECs in aquatic environments **are still rarely considered in water quality and chemical risk assessment**, although they have been found in concentrations that are of concern.

- Since many different TPs can potentially be formed in the environment and analytical standards are typically lacking for these compounds, **knowledge on the prevalence of TPs in aquatic environments is fragmentary**.

Transformation Products of Emerging Contaminants in the Environment:
Analysis, Processes, Occurrence, Effects and Risks



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Transformation Products of Emerging Contaminants in the Environment
Analysis, Processes, Occurrence, Effects and Risks

Editors:

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Hogeschool Gent, Belgium

- Emerging contaminants include pharmaceuticals and personal care products, veterinary medicines, pesticides, brominated flame retardants, perfluorinated compounds, disinfectants, and engineered nanoparticles
- One of the first books to cover transformation products (i.e. breakdown products), rather than primary compounds
- Hot area in environmental research, because of their adverse effects on human health and environment
- Also critical for European REACH regulations
- Important for industries involved in chemistry, toxicology, water and environment
- Includes contributions from all the key international researchers

Classification of Transformation Products of ECs?

Biotic Processes | **Abiotic Processes**

Biotic TPs

- Human metabolites
- Animal metabolites
- Microbial metabolites

in Engineered & Natural Systems

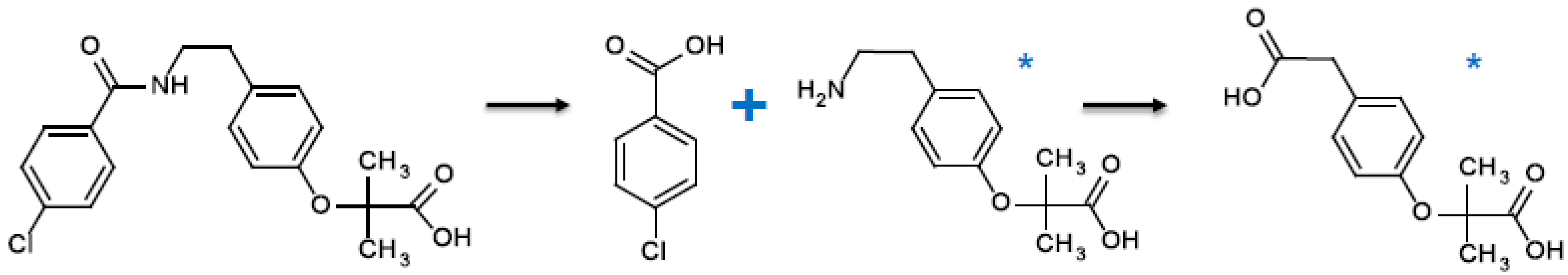
Abiotic TPs

- Hydrolysis
- Photolysis
- Chlorination
- Ozonation
- Advanced Oxidation

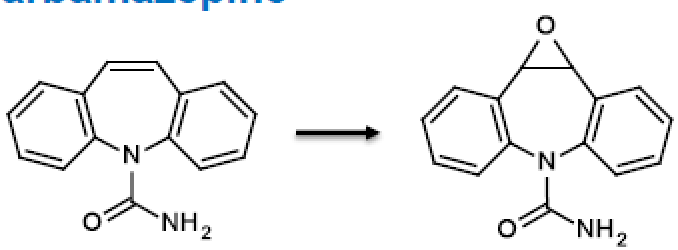
Natural Environment & Water-Treatment Processes

Proposed Transformation pathways

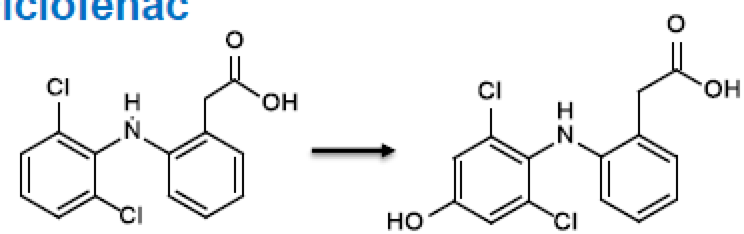
Bezafibrate



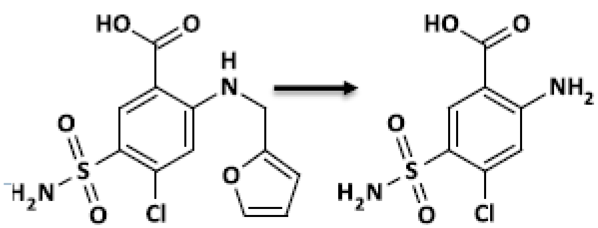
Carbamazepine



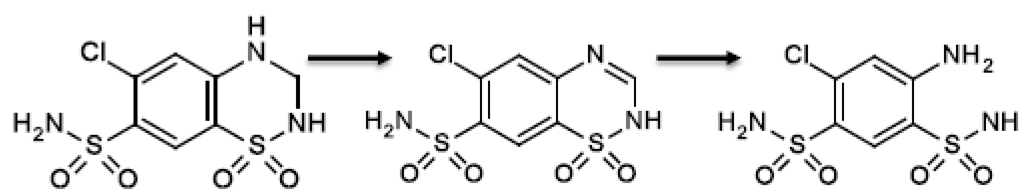
Diclofenac



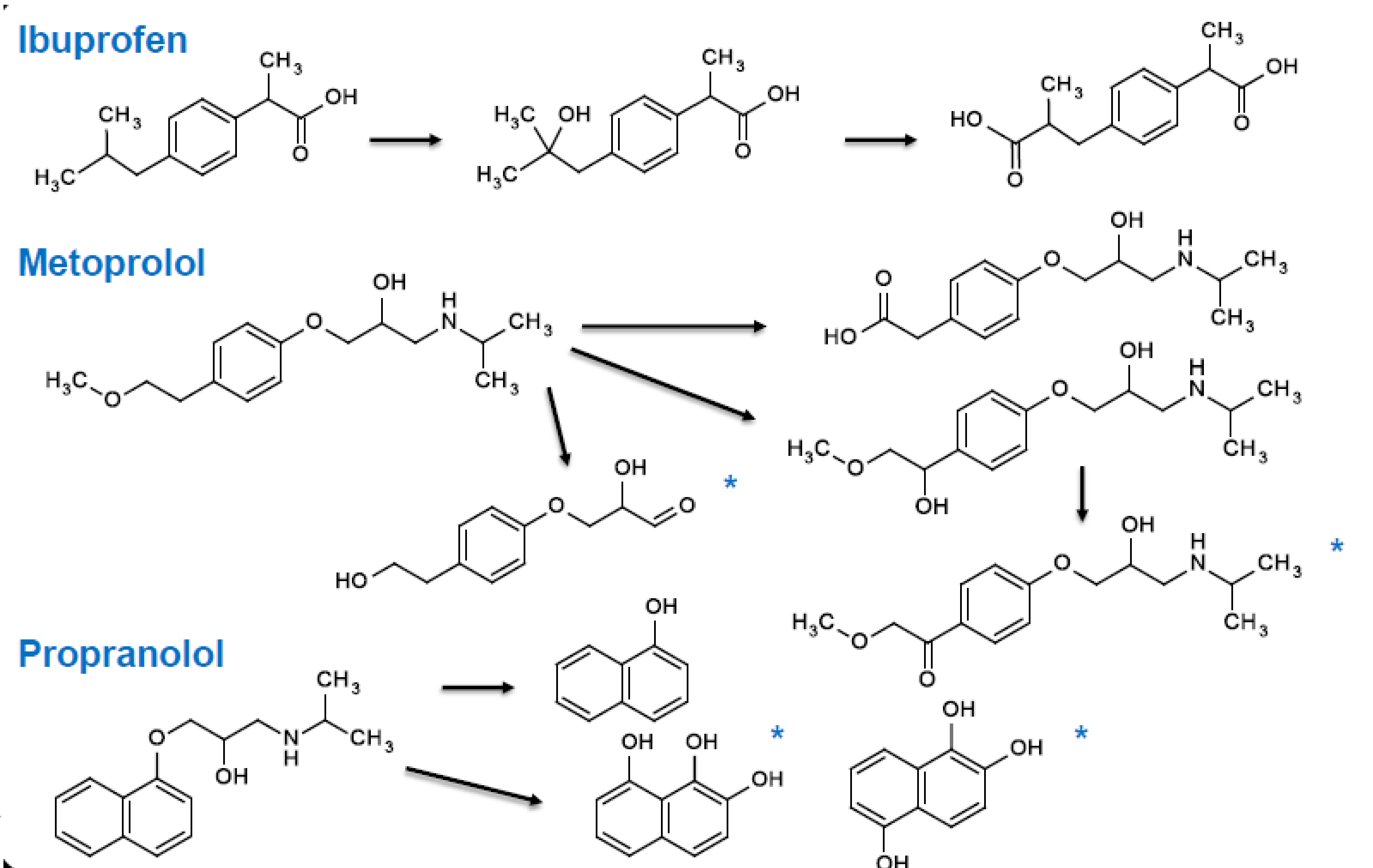
Furosemide



Hydrochlorothiazide

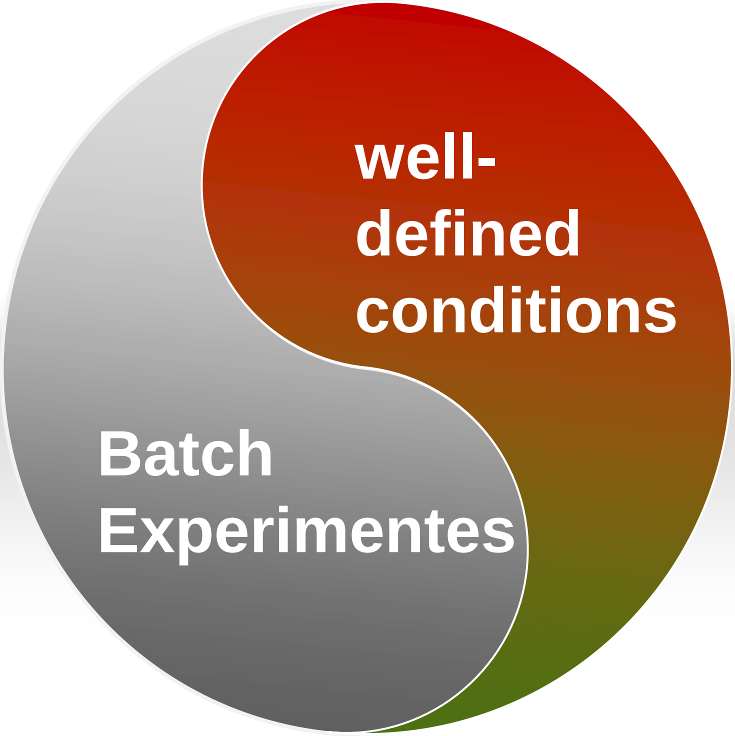


Proposed Transformation pathways



Identification approaches – laboratory studies

Simulation of the transformation processes in batch experiments under well-defined conditions with appropriate controls is a very common first approach for the identification of TPs.



Batch experiments can be applied under biotic and abiotic conditions at high concentrations of the parent ECs.

Identification and Structure elucidation of TPs

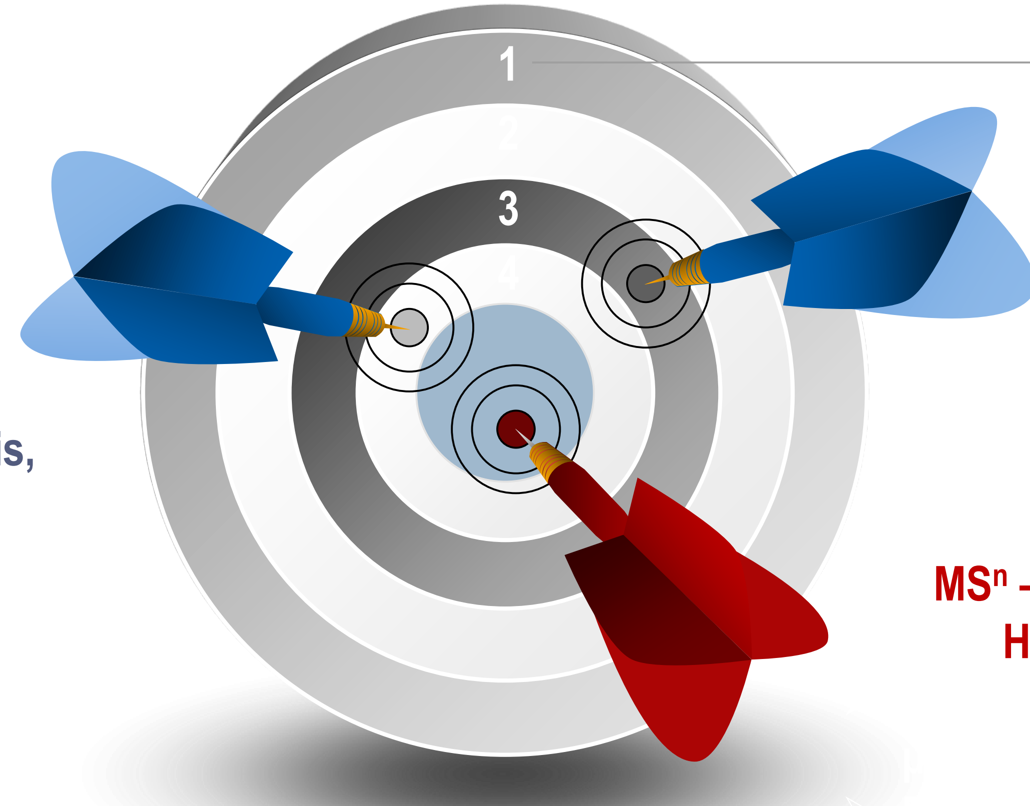
ANIMATED

Lab experiments:

Hydrolysis, Photolysis,

Photocatalysis,

Biodegradation



"Exact masses"

↓

Chemical composition

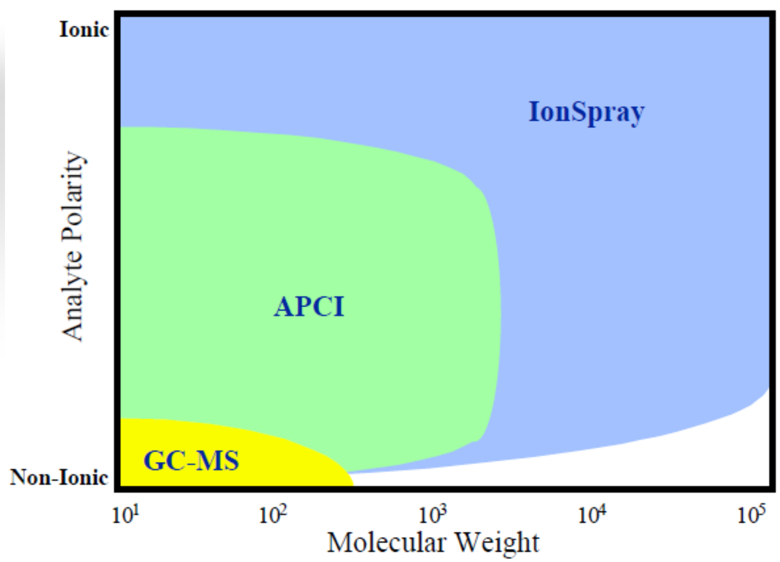
MS^n – Fragmentation
HR-MS, Q-MS

Identification of TPs in WWTs, underground water, natural water, drinking water

Identification approaches – analytical techniques

Nowadays, liquid chromatography (LC) coupled to MS (LC-MS) using a variety of mass analyzers is the technique of choice for the investigation of ECs and TPs in environmental samples.
LC is a suitable chromatographic technique **for polar, thermolabile compounds,** thus for the identification of TPs, which are generally more polar than their parent molecules.

GC-MS vs. LC-MS



Mass analyzers commonly employed

quadrupole-linear ion trap

Q-LIT

time-of-flight

TOF

linear ion trap-Orbitrap
or
quadrupole-Orbitrap

OrbiTrap

triple quadrupole

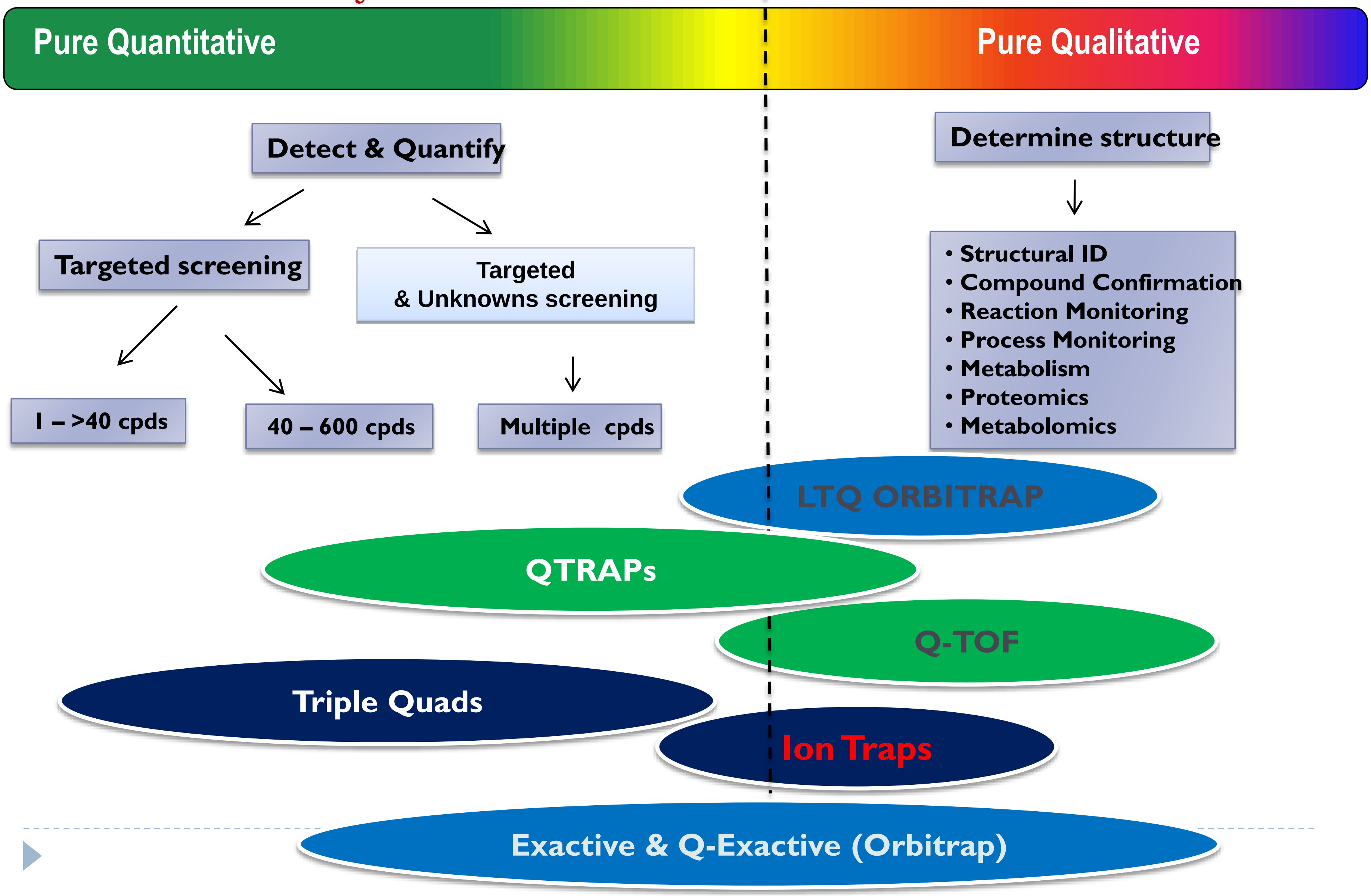
QQQ

quadrupole
time-of-flight

Q-TOF

Ion Trap

Which LCMS Analyzer Do I Choose?



Flow chart of screening procedure of TPs

There are various workflows in the literature

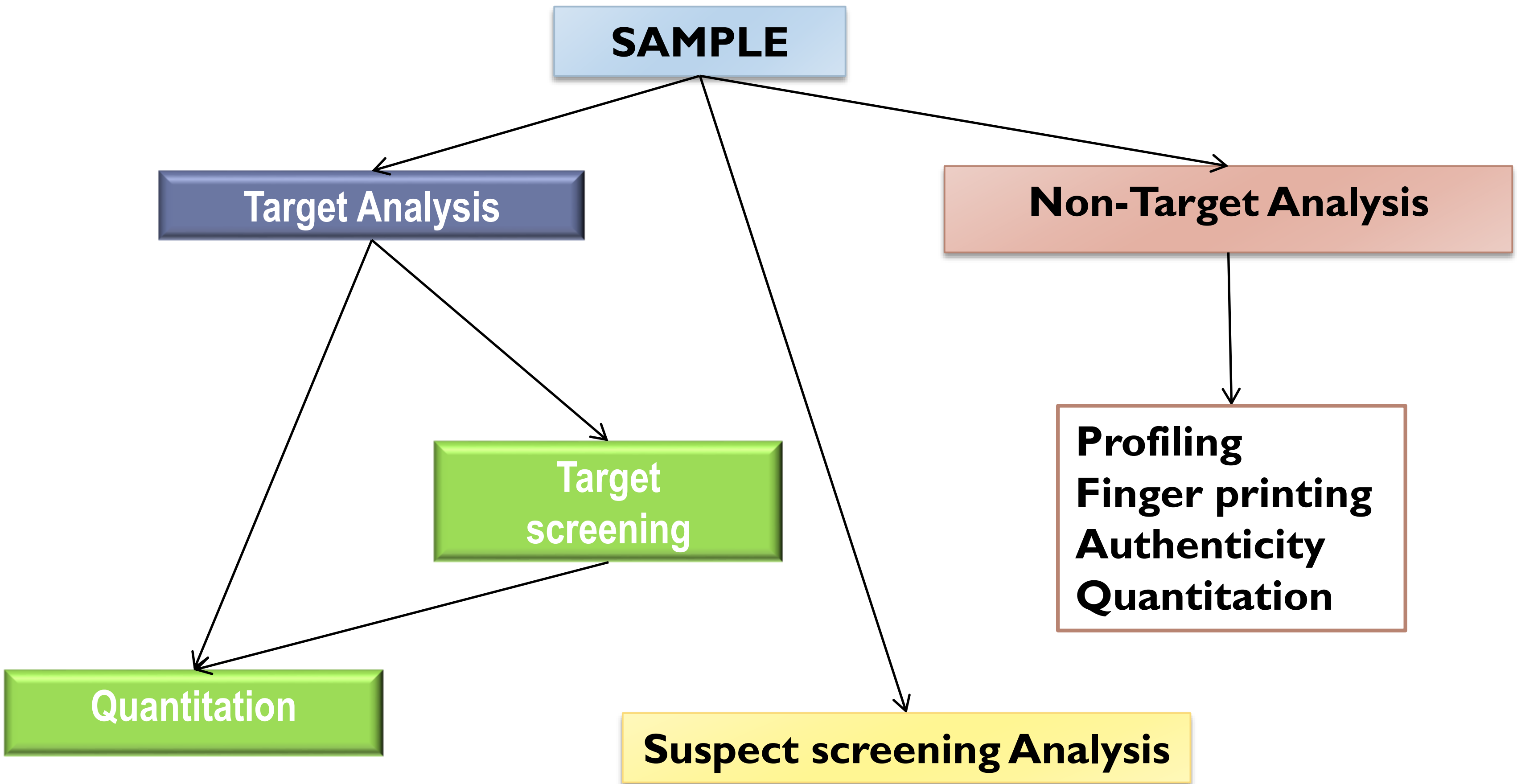
for the identification of TPs,

depending indispensably on the instrumentation and

the available software

- Bletsou, A.A., Jeon, J., Hollender, J., Archontaki, E., Thomaidis, N.S. Targeted and non-targeted liquid chromatography-mass spectrometric workflows for identification of transformation products of emerging pollutants in the aquatic environment (2015) TrAC - Trends in Analytical Chemistry, 66, pp. 32-44.
- E.L. Schymanski, J. Jeon, R. Gulde, K. Fenner,M. Ruff, H.P. Singer, et al., Identifying small molecules via high resolution mass spectrometry: communicating confidence, Environ. Sci. Technol. 48 (2014) 2097–2098.
- Aurea C. Chiaia-Hernandez & Emma L. Schymanski & Praveen Kumar & Heinz P. Singer & Juliane Hollender Suspect and nontarget screening approaches to identify organic contaminant records in lake sediments, Anal Bioanal Chem, September 2014.
- C. Hug, N. Ulrich, T. Schulze, W. Brack, M. Krauss, Identification of novel micropollutants in wastewater by a combination of suspect and nontarget screening, Environ. Pollut. 184 (2014) 25–32.
- Dimitra A. Lambropoulou (Editor), Leo M. L. Nollet (Editor), Transformation Products of Emerging Contaminants in the Environment: Analysis, Processes, Occurrence, Effects and Risks, ISBN: 978-1-118-33959-6, 964 pages, February 2014

Target or Non-target analysis workflow



Workflows of screening procedure of TPs

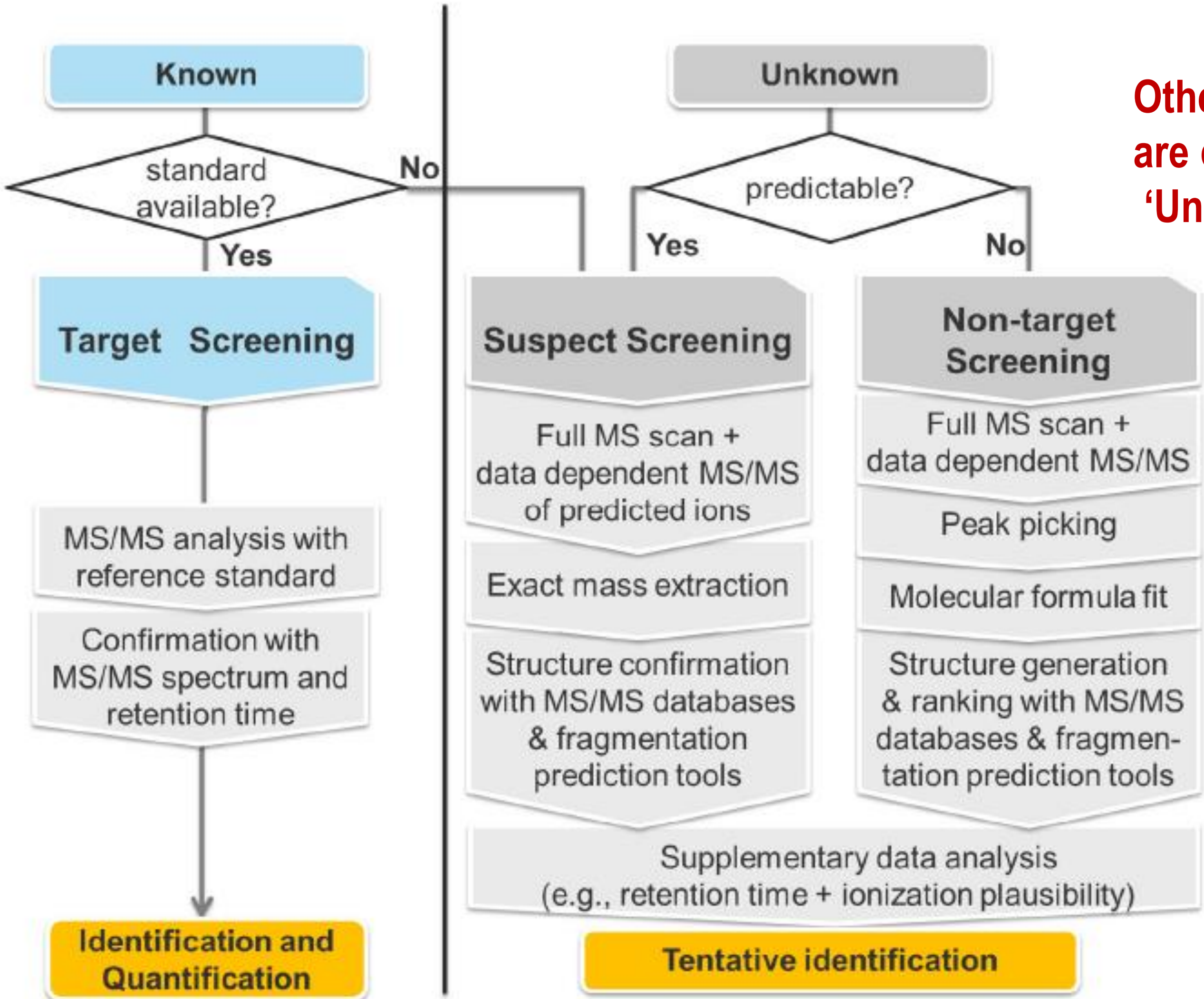
(a) **target analysis *(Known TPs)*,** which is based on the determination of already known TPs, and identification is carried out with standard solutions;

(b) **suspect screening *(Known unknown TPs)*,** with a list of possible TPs assembled from the literature or from prediction models, and the samples are screened for those candidates; and,

(c) **non-target screening *(Unknown TPs - de novo* identification of truly novel compounds*)*,** with identification of novel TPs being carried out with sophisticated post-acquisition data tools and supplementary analytical techniques.

Flow chart of screening procedure of TPs

'Known' TPs have been confirmed or confidently identified before



Other TPs are considered 'Unknown'

A.A. Bletsou et al./Trends in Analytical Chemistry 66 (2015) 32–44

Suspect screening

- **Suspect screening** is the technique of choice for the identification of TPs, when the confirmation of the analytes with a reference standard is impossible, **but molecular formula and structure of suspected molecules can be predicted**
- In suspect screening, **an important step of the identification workflow is the prediction of possible TPs using computational (*in silico*) prediction tools.**

Data processing for screening

- **Peak detection by extracting those ions matched with entries in a database**
  - Can be psuedo molecular ions and fragments
- **Recognition is based upon measurement of:**
  - Accurate mass
  - Isotope pattern
  - Retention time (if available)
  - A response threshold

Mass analyzers commonly employed

High Resolution Mass Spectrometers

time-of-flight

TOF

quadrupole
time-of-flight

Q-TOF

linear ion trap-Orbitrap
or
quadrupole-Orbitrap

OrbiTrap

The benefits of high resolution MS in high throughput screening of TPs

Home made Database for TPs of pharmaceuticals

IDEA

The scope was to build a home made database

in order to provide an integrated knowledge on the presence of TPs of pharmaceuticals in influent and effluent wastewaters from Greece using LTQ-Orbitrap- MS.

OrbiTrap

Laboratory Simulated Methods

- Photolysis
- AOPs (e.g. Photocatalysis)

M

·OH

TPs

Target Compounds / Photolysis/ AOPs (32 Parent Compounds)

Analgesics-anti-inflammatories

- Diclofenac
- Ketoprofen
- Ibuprofen
- Paracetamol
- Nimesulide
- Naproxen
- Tramadol

Antibiotics

- Ciprofloxacin
- Moxifloxacin
- Norfloxacin
- Erythromycin
- Lincomycin
- Sulfadiazine
- Sulfamethoxazole
- Trimethoprim

Phsychiatrics-antidepressants

- Bupropion
- Carbamazepine
- Duloxetine
- Fluvoxamine
- Olanzapine
- Risperidone
- Sertraline
- Venlafaxine

Beta - Blockers

- Atenolol
- Metoprolol
- Nadolol
- Pindolol
- Propranolol

Cytostatics

- Cytarabine
- 5-Flouoruracil

Antidiabetics

- Metformin

Beta-agonists

- Salbutamol

Database used for TPs of pharmaceuticals

A home-made database

>350 compounds

(corresponding to metabolites/TPs)

A customized database was compiled containing :

- ❑ TPs for which reference standards were available
- ❑ compounds identified in experiments performed at laboratory under laboratory-controlled conditions

A second home-made database was also compiled, including :

theoretical exact masses of human metabolites /TPs reported in the literature

The presence of 28 TPs/human metabolites was confirmed in the samples

mass twin

Photocatalysis of Venlafaxine

TPs	Rt	Elemental Formula	Mass (m/z) Theor.	Mass (m/z) Exper.	Error mDa	Error ppm	D
VNF	**8.72**	$C_{17}H_{27}NO_2$	278.2115	278.2115	0.05	-0.20	
342A	**3.06**	$C_{17}H_{26}NO_5$	342.1911	342.1915	0.39	1.12	
342B	**3.21**	$C_{17}H_{26}NO_5$	342.1911	342.1915	0.39	1.12	
342C	**3.40**	$C_{17}H_{26}NO_5$	342.1911	342.1915	0.39	1.12	
342D	**3.55**	$C_{17}H_{26}NO_5$	342.1911	342.1915	0.39	1.12	
342E	**6.21**	$C_{17}H_{26}NO_5$	342.1911	342.1915	0.39	1.12	
342F	**11.21**	$C_{17}H_{26}NO_5$	342.1911	342.1915	0.39	1.12	
340A	**3.33**	$C_{17}H_{26}NO_5$	340.1754	340.1758	0.33	0.99	
340B	**3.88**	$C_{17}H_{26}NO_5$	340.1754	340.1758	0.33	0.99	
326A	**5.82**	$C_{17}H_{28}NO_5$	326.1950	326.1950	-1.20	-3.68	
326B	**6.24**	$C_{17}H_{28}NO_5$	326.1950	326.1950	-1.20	-3.68	
326C	**6.66**	$C_{17}H_{28}NO_5$	326.1950	326.1950	-1.20	-3.68	
326D	**7.03**	$C_{17}H_{28}NO_5$	326.1950	326.1950	-1.20	-3.68	
324A	**3.94**	$C_{17}H_{26}NO_5$	324.1805	324.1794	-1.15	-2.43	
324B	**4.74**	$C_{17}H_{26}NO_5$	324.1805	324.1794	-1.15	-2.43	
324C	**6.36**	$C_{17}H_{26}NO_5$	324.1805	324.1794	-1.15	-2.43	
324D	**6.57**	$C_{17}H_{26}NO_5$	324.1805	324.1794	-1.15	-2.43	
312A	**3.56**	$C_{16}H_{26}NO_5$	312.1805	312.1796	-0.95	-3.04	
312B	**3.70**	$C_{16}H_{26}NO_5$	312.1805	312.1796	-0.95	-3.04	
312C	**4.38**	$C_{16}H_{26}NO_5$	312.1805	312.1796	-0.95	-3.04	
310A*	**3.18**	$C_{16}H_{24}NO_5$	310.1648	310.1638	-1.10	-3.54	
310B*	**3.53**	$C_{16}H_{24}NO_5$	310.1648	310.1638	-1.10	-3.54	
310C*	**7.74**	$C_{16}H_{24}NO_5$	310.1648	310.1638	-1.10	-3.54	
310A	**5.25**	$C_{17}H_{28}NO_4$	310.2012	310.2007	-0.58	-1.88	
310B	**5.49**	$C_{17}H_{28}NO_4$	310.2012	310.2007	-0.58	-1.88	
310C	**6.21**	$C_{17}H_{28}NO_4$	310.2012	310.2007	-0.58	-1.88	
310D	**6.56**	$C_{17}H_{28}NO_4$	310.2012	310.2007	-0.58	-1.88	
310E	**7.17**	$C_{17}H_{28}NO_4$	310.2012	310.2007	-0.58	-1.88	
310F	**8.55**	$C_{17}H_{28}NO_4$	310.2012	310.2007	-0.58	-1.88	
310G	**8.61**	$C_{17}H_{28}NO_4$	310.2012	310.2007	-0.58	-1.88	
308A	**5.69**	$C_{17}H_{28}NO_3$	308.1856	308.1846	-1.03	-3.35	
308B	**5.72**	$C_{17}H_{28}NO_3$	308.1856	308.1846	-1.03	-3.35	
308C	**5.85**	$C_{17}H_{28}NO_3$	308.1856	308.1846	-1.03	-3.35	
308D	**6.36**	$C_{17}H_{28}NO_3$	308.1856	308.1846	-1.03	-3.35	
306A	**5.31**	$C_{17}H_{24}NO_4$	306.1699	306.1693	-0.68	-2.2	
306B	**6.08**	$C_{17}H_{24}NO_4$	306.1699	306.1693	-0.68	-2.2	
296A	**2.8**	$C_{16}H_{26}NO_4$	296.1856	296.1855	-0.13	-0.46	
296B	**7.56**	$C_{16}H_{26}NO_4$	296.1856	296.1855	-0.13	-0.46	

42 TPs
(OH-isomers, demethylated, dehydrated and further oxidized TPs etc)

D. Lambropoulou et al. / Journal of Hazardous Materials, February 2017, Pages 513-526

Photocatalysis of Venlafaxine

TPs	Rt	Elemental Formula	Mass (m/z)		Error		
			Theor.	Exper.	mDa	ppm	DBE
VNF	8.72	$C_{17}H_{27}NO_2$	278.2115	278.2115	0.05	-0.20	4.5
		$C_{17}H_{26}NO$	260.2008	260.2012	0.31	1.87	5.5
		$C_{16}H_{24}NO$	246.1852	246.1861	0.86	3.49	5.5
		$C_{15}H_{19}O$	215.1430	215.1437	0.66	3.06	6.5
		C_8H_9O	121.0647	121.0644	-0.39	-3.23	4.5
		C_7H_9	93.0695	93.0698	-0.37	-4.04	3.5
294C	7.71	$C_{17}H_{28}NO_3$	294.2063	294.2053	-1.07	-3.64	4.5
		$C_{17}H_{26}NO_2$	276.1958	276.1951	-0.71	-2.55	5.5
		$C_{17}H_{24}NO$	258.1852	258.1863	1.05	4.10	6.5
		$C_{15}H_{19}O_2$	231.1379	231.1372	-0.75	-3.27	6.5
		$C_{14}H_{15}O$	199.1111	199.1117	-0.64	-3.22	7.5
292B	6.41	$C_{17}H_{26}NO_3$	292.1907	292.1899	-0.82	-2.81	5.5
		$C_{17}H_{24}NO_2$	274.1801	274.1797	-0.46	-1.66	6.5
		$C_{15}H_{17}O_2$	229.1223	229.1215	-0.81	-3.52	7.5
		C_8H_9O	121.0647	121.0644	-0.39	-3.23	4.5
274	7.27	$C_{17}H_{24}NO_2$	274.1801	274.1793	-0.86	-3.12	6.5
		$C_{15}H_{17}O_2$	229.1223	229.1216	-0.71	-3.08	7.5
		$C_{15}H_{15}O$	211.1117	211.1113	-0.44	-2.09	8.5
		$C_{14}H_{11}$	179.0849	179.0855	-0.62	-3.50	9.5
		$C_{12}H_{11}O$	171.0804	171.0802	-0.24	-1.41	7.5
		C_8H_9O	121.0647	121.0644	-0.39	-3.23	4.5
O-DES-	7.33	$C_{16}H_{26}NO_2$	264.1958	264.1954	-0.40	-1.54	4.5
VNF		$C_{16}H_{24}NO$	246.1852	246.1861	0.86	3.49	5.5
		$C_{14}H_{17}O$	201.1273	201.1270	-0.39	-1.94	6.5
		$C_{11}H_{11}O$	159.0822	159.0824	1.20	2.46	6.5
		C_9H_9O	133.0647	133.0644	-0.39	-2.94	5.5
		C_8H_9O	121.0647	121.0644	-0.39	-3.23	4.5
		C_7H_7O	107.0491	107.0489	-0.241	-2.25	4.5

42 TPs
(OH-isomers, demethylated,etc)

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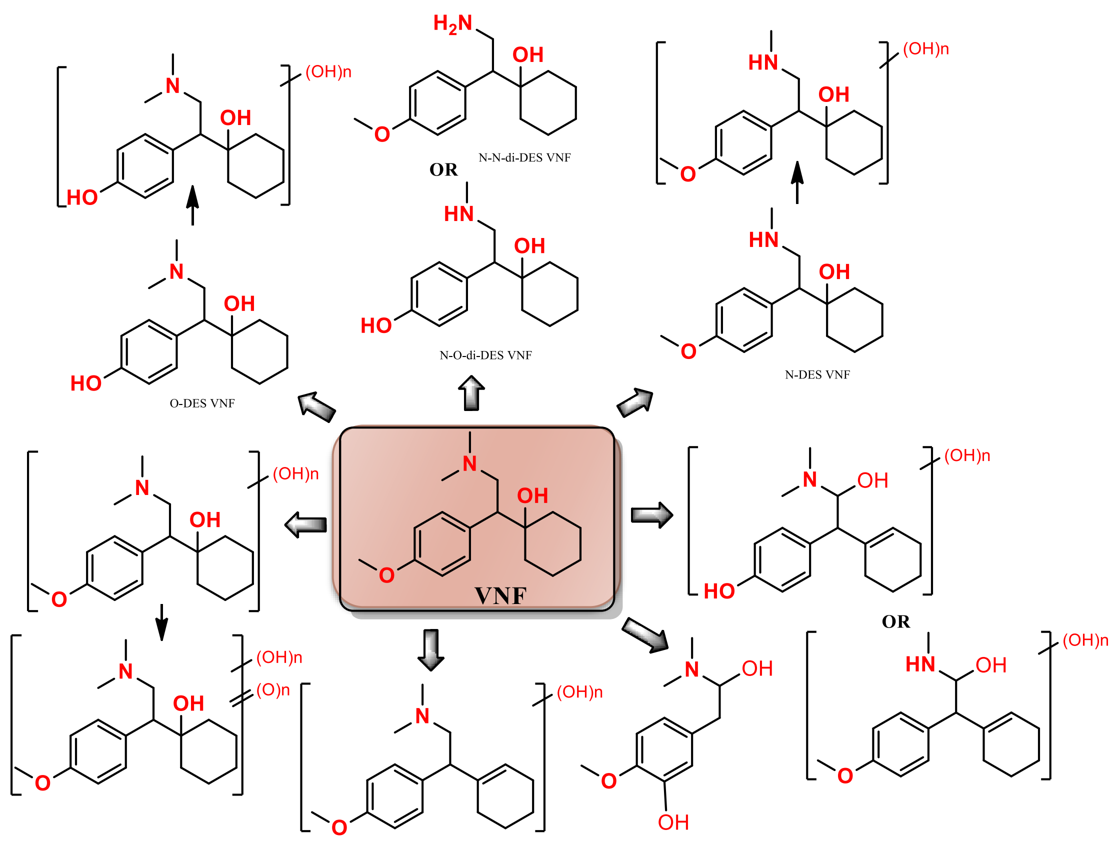
Photocatalysis of Venlafaxine



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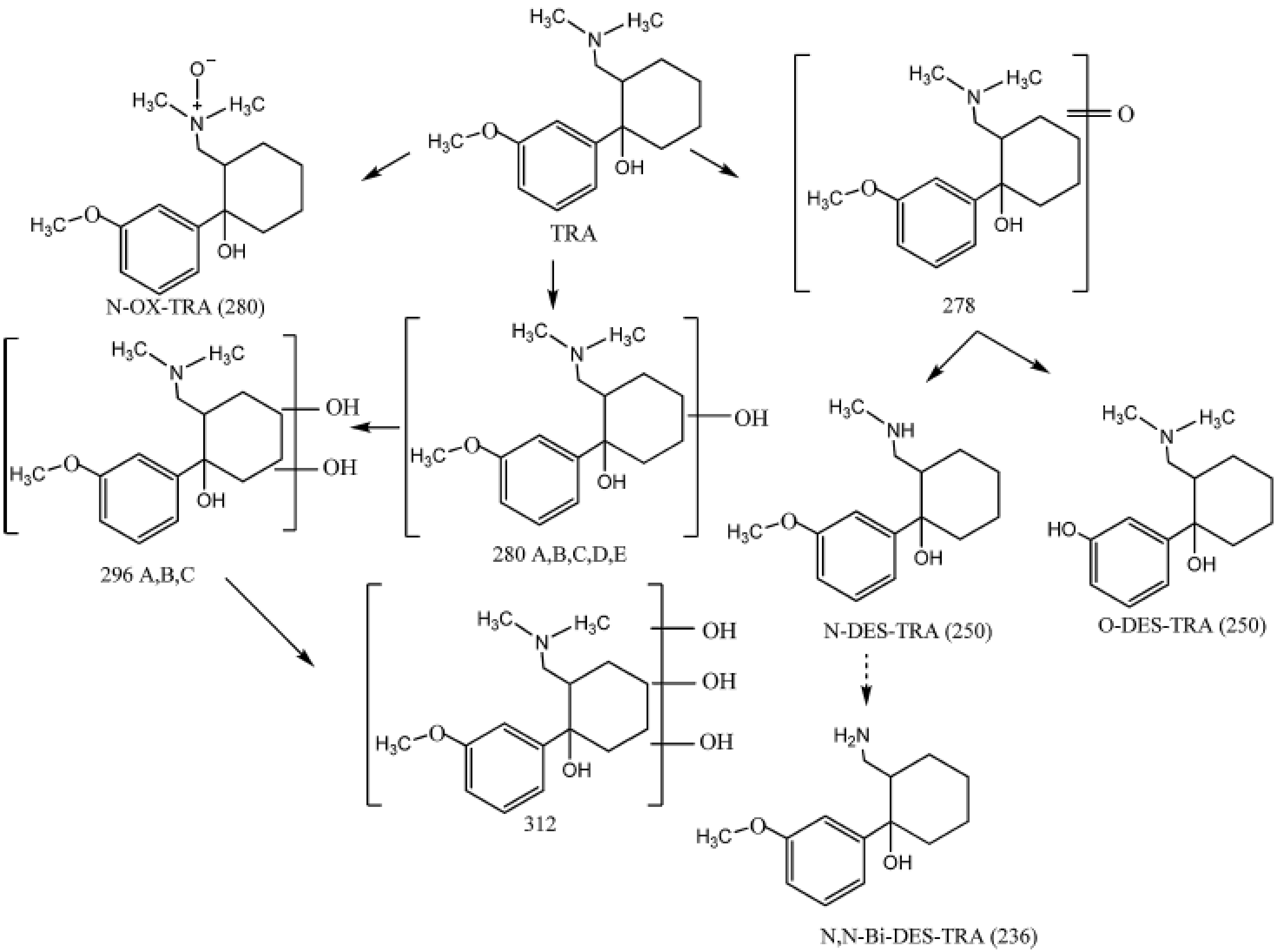
Photocatalysis of Tramadol

R_t	Molecular Formula	m/z $[M+H]^+$ / Fragments	Δ (ppm) (RDB)	MS^2 fragmentation	RDB
7.30	$C_{16}H_{26}NO_2$	$[M+H]^+$ 264.1949 (TRA)	-3.617 (4.5)	246.1852 $C_{16}H_{24}NO$ (-H_2O)	0.565 (5.5)
5.60	$C_{16}H_{26}NO_3$	$[M+H]^+$ 280.1888 (280-A)	-1.880 (4.5)	262.1803 $C_{16}H_{24}NO_2$ (-H_2O)	0.114 (5.5)
		264.1941 $C_{16}H_{26}NO_2$	-1.746 (4.5)	217.1225 $C_{14}H_{17}O_2$ (-H_2O -C_2H_7N)	0.662 (6.5)
		250.1785 $C_{15}H_{24}NO_2$	-1.626 (4.5)		
6.24	$C_{16}H_{26}NO_3$	$[M+H]^+$280.1894 (280-B)	-1.300 (4.5)	262.1804 $C_{16}H_{24}NO_2$ (-H_2O)	0.894 (5.5)
		264.1946 $C_{16}H_{26}NO_2$	-4.715 (4.5)	217.1221 $C_{14}H_{17}O_2$ (-H_2O -C_2H_7N)	-1.134 (6.5)
				149.0237 $C_8H_5O_3$	2.748 (6.5)
6.62	$C_{16}H_{26}NO_3$	$[M+H]^+$ 280.1903 (280-C)	-1.535 (4.5)	262.1804 $C_{16}H_{24}NO_2$ (-H_2O)	0.834 (5.5)
		264.1946 $C_{16}H_{26}NO_2$	-4.715 (4.5)	217.1224 $C_{14}H_{17}O_2$ (-H_2O -C_2H_7N)	0.524 (6.5)
				149.0241 $C_8H_5O_3$	5.096 (6.5)
6.84	$C_{16}H_{26}NO_3$	$[M+H]^+$280.1904 (280-D)	-1.250 (4.5)	262.1804 $C_{16}H_{24}NO_2$ (-H_2O)	0.834 (5.5)
		264.1946 $C_{16}H_{26}NO_2$	-4.715 (4.5)	217.1224 $C_{14}H_{17}O_2$ (-H_2O -C_2H_7N)	0.524 (6.5)
				149.0230 $C_8H_5O_3$	-2.084 (6.5)
7.06	$C_{16}H_{26}NO_3$	$[M+H]^+$ 280.193 (280-E)	-1.607 (4.5)	262.17996 $C_{16}H_{24}NO_2$ (-H_2O)	-0.017 (5.5)
		264.1946 $C_{16}H_{26}NO_2$	-4.715 (4.5)	217.1218 $C_{14}H_{17}O_2$ (-H_2O -C_2H_7N)	-2.470 (5.5)
				149.0235 $C_8H_6O_3$	1.070 (6.5)
5.43	$C_{16}H_{24}NO_3$	$[M+H]^+$ 278.1887 (278)	-4.586 (5.5)		
4.98	$C_{16}H_{26}NO_4$	$[M+H]^+$ 296.1844 (296A)	-4.101 (4.5)	278.1749 $C_{16}H_{24}NO_3$ (-H_2O)	-0.504 (5.5)
		278.1738 $C_{16}H_{24}NO_3$	-4.566 (5.5)	260.1635 $C_{16}H_{22}NO_2$ (-2H_2O)	-3.826 (6.5)
		264.1946 $C_{16}H_{26}NO_2$	-4.525 (4.5)	223.1567 $C_{13}H_{21}NO_2$ (-$C_3H_5O_2$)	-0.092 (4.0)
				114.0913 $C_6H_{12}NO$ (-$C_{10}H_{14}O_3$)	-0.180 (1.5)
5.89	$C_{16}H_{26}NO_4$	$[M+H]^+$ 296.1844 (296B)	-4.101 (4.5)	278.1749 $C_{16}H_{24}NO_3$ (-H_2O)	-0.504 (5.5)
		280.1894 $C_{16}H_{26}NO_3$	-4.747 (4.5)	260.1635 $C_{16}H_{22}NO_2$ (-2H_2O)	-3.826 (6.5)
		264.1945 $C_{16}H_{26}NO_2$	-5.093 (4.5)	223.1567 $C_{13}H_{21}NO_2$ (-$C_3H_5O_2$)	-0.092 (4.0)
				114.0913 $C_6H_{12}NO$ (-$C_{10}H_{14}O_3$)	-0.180 (1.5)
7.92	$C_{16}H_{26}NO_3$	$[M+H]^+$ 280.1893 (N-OX-TRA)	-5.069 (4.5)	262.1802 $C_{16}H_{24}NO_2$ (-H_2O)	0.208 (5.5)
				201.1274 $C_{14}H_{17}O$ (-C_2H_7NO -H_2O)	0.041 (6.5)
				135.0441 $C_8H_7O_2$ (-$C_8H_{19}NO$)	0.548 (5.5)

14 TPs (OH-isomers, demethylated, oxidized TPs etc)

M. Antonopoulou, I. Konstantinou / Applied Catalysis A: General 515 (2016) 136–143

Tramadol Transformation pathways…..



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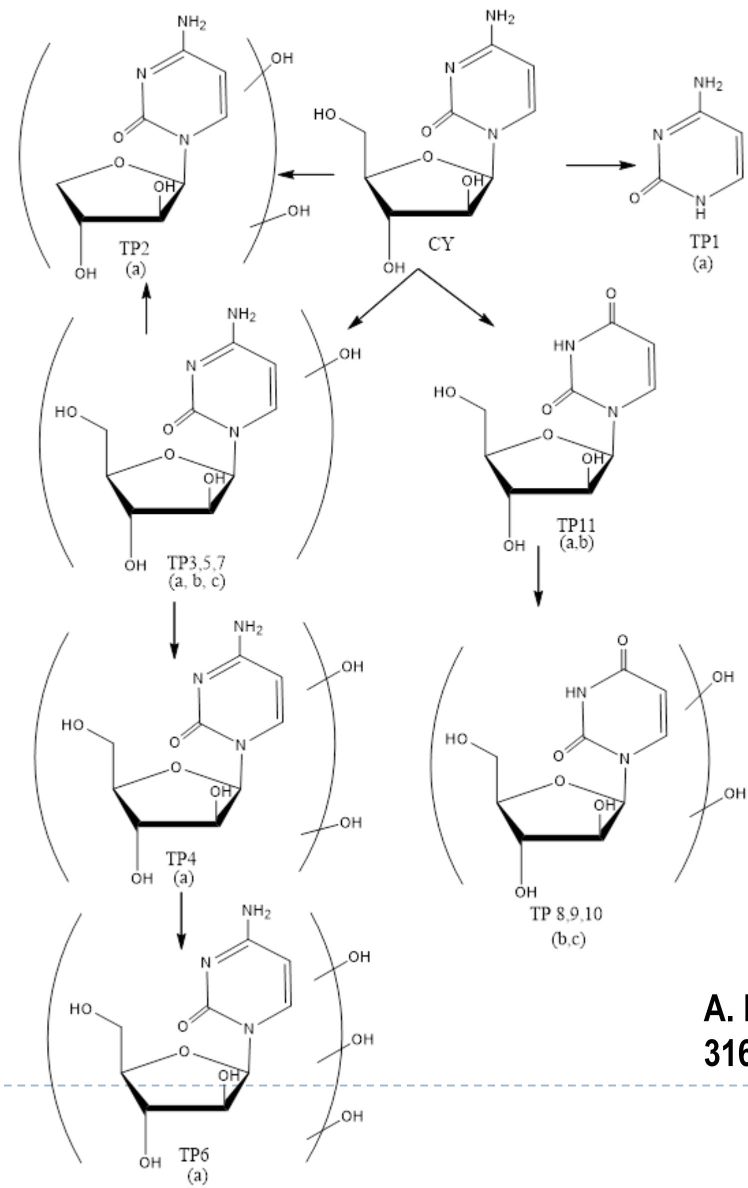
Cytarabine Transformation Products

t_R (min)	Code name	Pseudo-molecular ion formula	Theoretical m/z $[m+H]^+$	Experimental m/z $[m+H]^+$	Δ (ppm)	RDBE
1.51	CY	$C_9H_{14}N_3O_5$	244.0928	244.0922	2.4	4.5
		$C_4H_6N_3O$	112.0505	112.0506	-0.6	3.5
0.79	TP1	$C_4H_6N_3O$	112.0505	112.0505	-0.3	3.5
		$C_4H_3N_2O$	95.0240	95.0233	-7.25	4.5
		$C_3H_5N_2$	69.0447	69.0441	-9.05	2.5
0.83	TP2	$C_9H_{14}N_3O_8$	292.0775	292.0773	0.8	4.5
		$C_9H_{12}N_3O_7$	274.0670	274.0659	-3.9	5.5
		$C_8H_{11}N_2O_6$	231.0612	231.0601	-4.6	4.5
0.95	TP3	$C_9H_{14}N_3O_6$	260.0877	260.0874	0.5	1.2
		$C_9H_{12}N_3O_5$	242.0771	242.0764	-3.08	5.5
		$C_4H_6N_3O$	112.0505	112.0500	-0.3	3.5
1.25	TP4	$C_9H_{14}N_3O_6$	260.0877	260.0874	0.5	1.2
		$C_9H_{12}N_3O_5$	242.0771	242.0764	-3.08	5.5
		$C_4H_6N_3O$	112.0505	112.0500	-0.3	3.5
0.75		$C_9H_{14}N_3O_7$	276.0826	276.0820	2.3	4.5
		$C_9H_{12}N_3O_6$	258.0721	258.0718	-1.0	5.5
0.74	TP5	$C_9H_{14}N_3O_8$	292.0775	292.0760	5.3	4.5
		$C_9H_{12}N_3O_7$	274.0670	274.0659	-3.9	5.5
		$C_8H_{11}N_2O_6$	231.0612	231.0601	-4.6	4.5
0.83	TP7	$C_9H_{11}N_2O_8$	275.0510	275.0508	-0.7	5.5
0.87	TP8	$C_9H_{13}N_2O_8$	277.0666	277.0662	-1.6	4.5
		$C_9H_{11}N_2O_7$	259.0561	259.0565		
0.91	TP9	$C_9H_{11}N_2O_8$	275.0510	275.0508	-0.7	5.5
0.95	TP10	$C_9H_{13}N_2O_8$	277.0666	277.0662	-1.6	4.5
		$C_9H_{11}N_2O_7$	259.0561	259.0560	-0.59	5.5
1.16	TP11	$C_9H_{12}N_3O_7$	274.0666	274.0667	-1.0	5.5
0.78	TP12	$C_9H_{16}N_3O_7$	278.0983	278.0979	-1.4	3.5
		$C_9H_{14}N_3O_6$	260.0877	260.0874	0.5	1.2
		$C_4H_6N_3O$	112.0505	112.0503	-2.1	3.5

12 TPs (OH-isomers, etc)

Cytarabine Transformation pathways…..



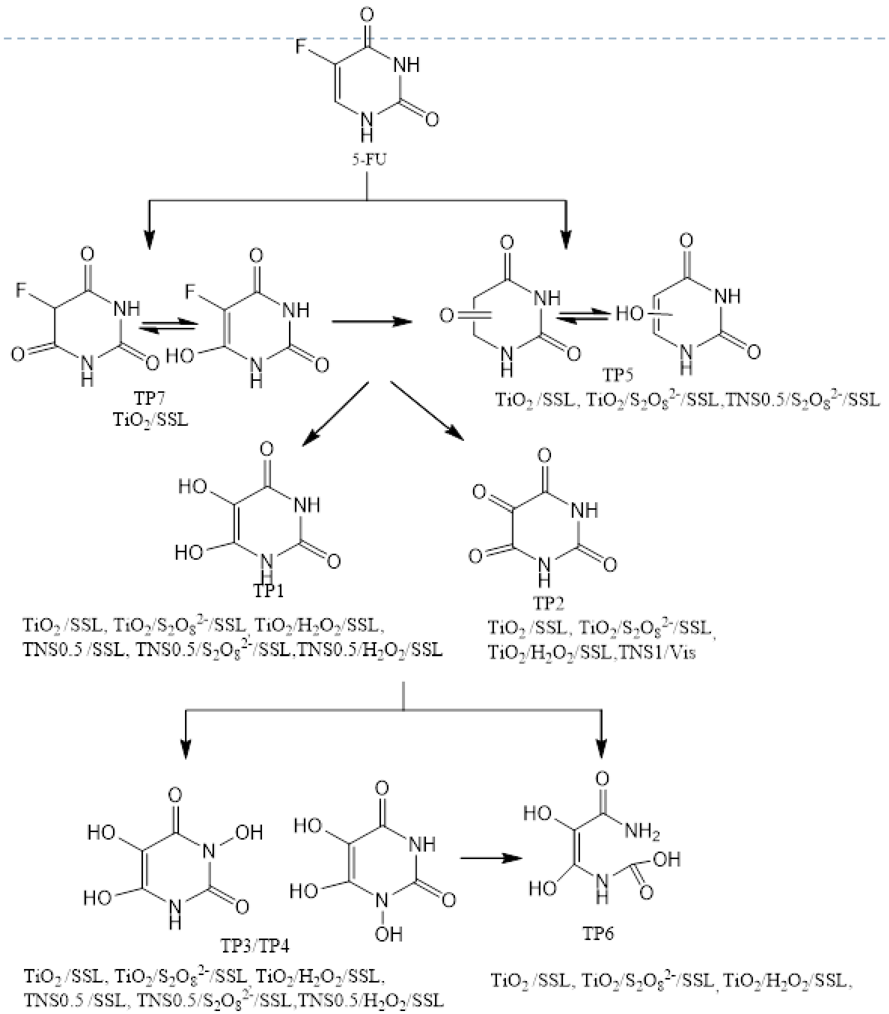
A. Koltsakidou et al. / Chemical Engineering Journal 316 (2017) 823–831

5-Flouorouracil Transformation pathways…..

t_R (min)	Code name	Pseudo-molecular ion formula	Theoretical m/z $[m\text{-}H]^-$	Experimental m/z $[m\text{-}H]^-$	Δ (ppm)	RDBE
2.0	5-FU	$C_4H_2FN_2O_2$	129.0106	129.0105	0.3	4.5
1.0	TP1	$C_4H_3N_2O_4$	143.0098	143.0103	-3.0	4.5
1.2	TP2	$C_4HN_2O_4$	140.9942	140.9950	-5.6	5.5
1.1	TP3	$C_4H_3N_2O_5$	159.0047	159.0047	0.0	4.5
1.3	TP4	$C_4H_3N_2O_5$	159.0047	159.0048	-0.2	4.5
1.5	TP5*	$C_4H_3N_2O_3$	127.0149	127.0152	-2.3	4.5
t_R (min)	Code name	Pseudo-molecular ion formula	Theoretical m/z $[m\text{+}H]^-$	Experimental m/z $[m\text{+}H]^-$	Δ (ppm)	RDBE
2.0	5-FU*	$C_4H_4FN_2O_2$	131.0251	131.0254	-1.8	3.5
1.0	TP6	$C_4H_7N_2O_5$ $C_4H_5N_2$	163.0350 145.0244	163.0352 145.0249	-1.3 -3.8	2.5 3.5
1.5	TP5*	$C_4H_5N_2O_3$	129.0295	129.0296	-0.9	3.5
2.1	TP7	$C_4H_4FN_2O_3$	147.0201	145.0198	1.7	3.5

A Koltsakidou et al. / Science of the Total Environment 578 (2017) 257–267

5-Flourouracil Transformation pathways…..



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Database…..

Data from

32 parent Compounds

Bibliographic Research
(TPs, Human Metabolites)

Home Made Library
TPs (Photolysis, AOPs)

Excel spreadsheet
Compound name, Theoretical Exact mass, t_R

Feeding masses into MS method

Sample Analysis by LC LTQ Orbitrap

Data processing

Automatic Screening
- Accuracy: Error ≤ 5 ppm
- Isotopic score >80%
- Threshold intensity > 500
- Area >2000
- Blank substraction

Manual Screening
- Gaussian Peak shape>0.7
- tR for identified TPs
- Hypothetic elution order on Theoretical LogPs

Final Library

✓ tR of TPs with available pure standards
✓ tR of identified TPs (tR ± 0.05 min)
✓ MS^2 fragments

Database used for metabolites / TPs of pharmaceuticals

A broad investigation on the presence of TPs/metabolites of pharmaceuticals in effluent **wastewaters from Greece using LTQ-Orbitrap- MS.**

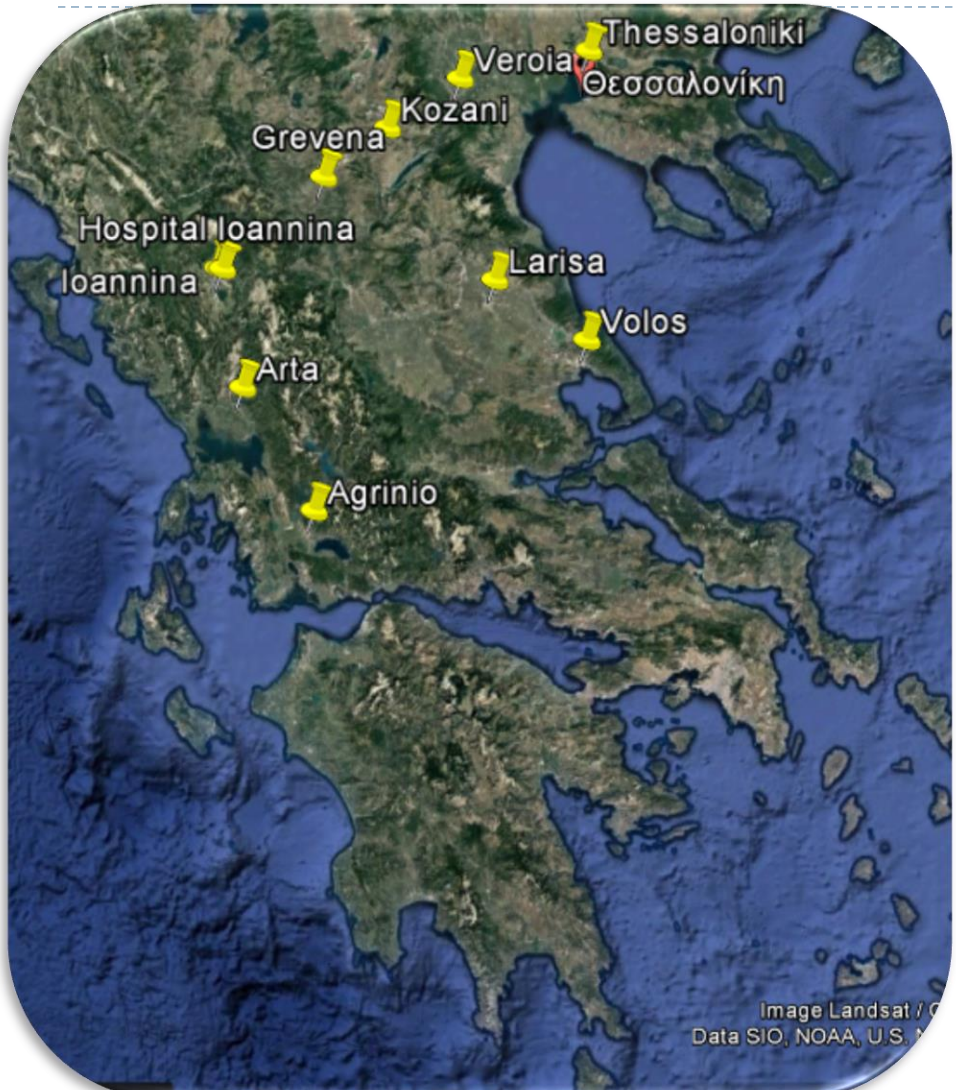
A home-made database

Up to >350 compounds,

including theoretical exact masses

(corresponding to metabolites/TPs)

Application to real wastewater samples from Greece



Location: 8 WWTPs in Greece, 7 Municipal, 1 Hospital

Samples: 24-h composite samples
Influents and effluents

Period : 1 year, 3 consecutive days/month

Ch. Kosma, D. Lambropoulou, T. Albanis, Science of The Total Environment, Vol. 466–467, 1 2014, 421-438

Ch. Kosma, D. Lambropoulou, T. Albanis, *Water Research, Volume 70, 1 March 2015, Pages 436-448*

Ch. Kosma, D. Lambropoulou, T. Albanis, *Science of The Total Environment, 590–591, 2017, 592-601*

Experimental procedure

WWTPs

Sampling

Representative sample

Filtration of the sample

Laboratory sample

-Extraction (OASIS HLB SPE)
- Elution

Eluted sample

- Evaporation to dryness
- Reconstitution in the final solvent

Analytical sample

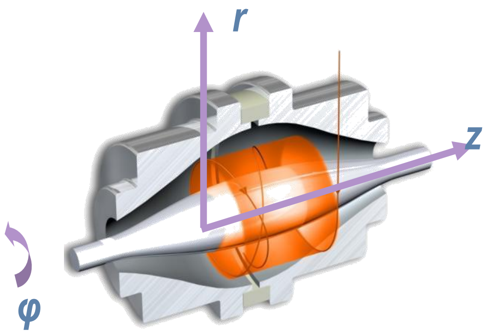
Chromatographic analysis (LTQ Orbitrap…)

Analytical result

Application to real wastewater samples from Greece

Orbitrap

- ✓ **Samples analyzed in positive (PI) and negative (NI) ionization mode**
- ✓ **Gradient program**



28 transformation products were detected

TPs of Analgestics/antiinflamatory drugs

1-Hydroxy ibuprofen

2-Hydroxy ibuprofen

4-Hydroxy-diclofenac

5-Hydroxy-diclofenac

Hydroxy-ketoprofen

N-desmethyl-tramadol

O-desmethyl-tramadol

TPs of Antibiotics

Anhydro-erythromycin

Desmethyl-clarithromycin

Metabolite N-acetyl sulfamethoxazole

N-acetyl ciprofloxacin

(2 TPs of Trimethoprim - 2,4-diaminopyrimidin-5-yl)(3,4,5-trimethoxyphenyl)methanone) /2,4-diaminopyrimidine-5-carbaldehyde)

TPs of Antidiabetics

Guanylurea

TPs of β-blockers

Hydroxy propranolol

TPs of Antidepressants /psychiatrics

O-Desmethyl venlafaxine

N-Desmethyl venlafaxine

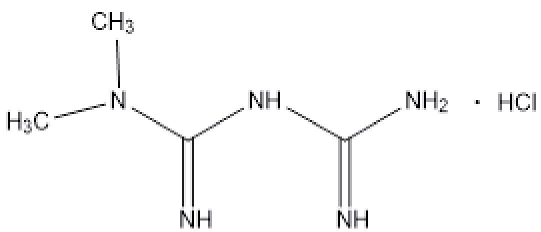
10-hydroxycarbazepine

7 **TPs of Omeprazole**

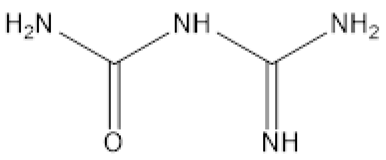
4 **Human Metabolites of Omeprazole**

Application to real wastewater samples from Greece

The case study of Metformin



Metformin



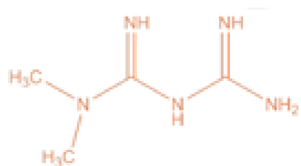
Gunylurea

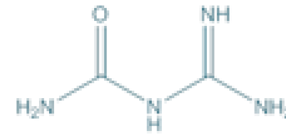
In some countries metformin **is in the top twenty list** of prescribed, produced and environmentally loaded pharmaceutically active compounds

It was reported that concentrations of **metformin and guanylurea together, account for more than half of the total load of pharmaceuticals in surface waters.**

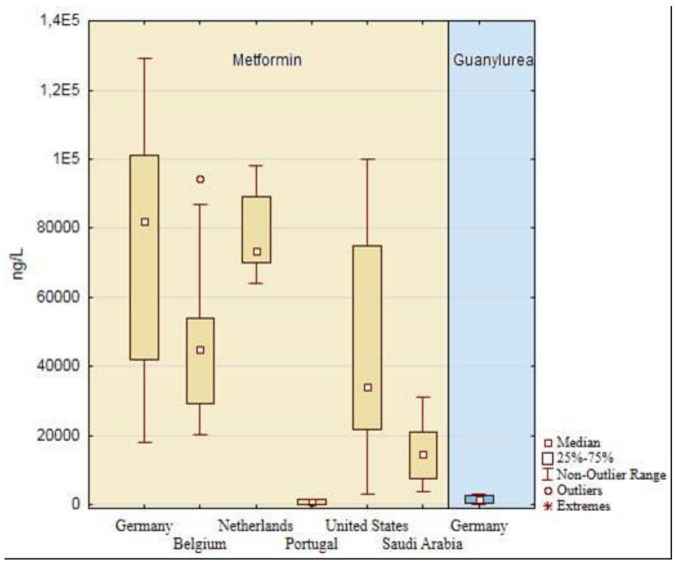
Ch. Kosma, D.Lambropoulou, T. Albanis, *Water Research*, *Volume 70, 1 March 2015, Pages 436-448*

Metformin/Guanylurea in real wastewater samples from Greece

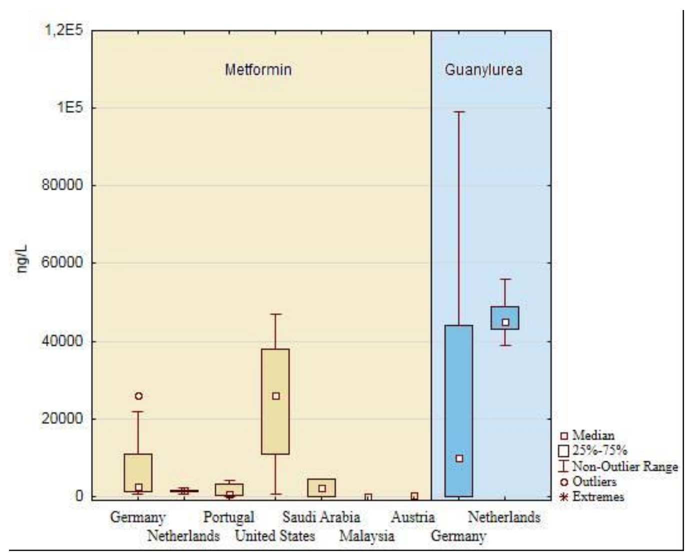




A



B



Concentration levels of metformin and guanylurea in (A) the influents and (B) the effluents of WWTPs, worldwide

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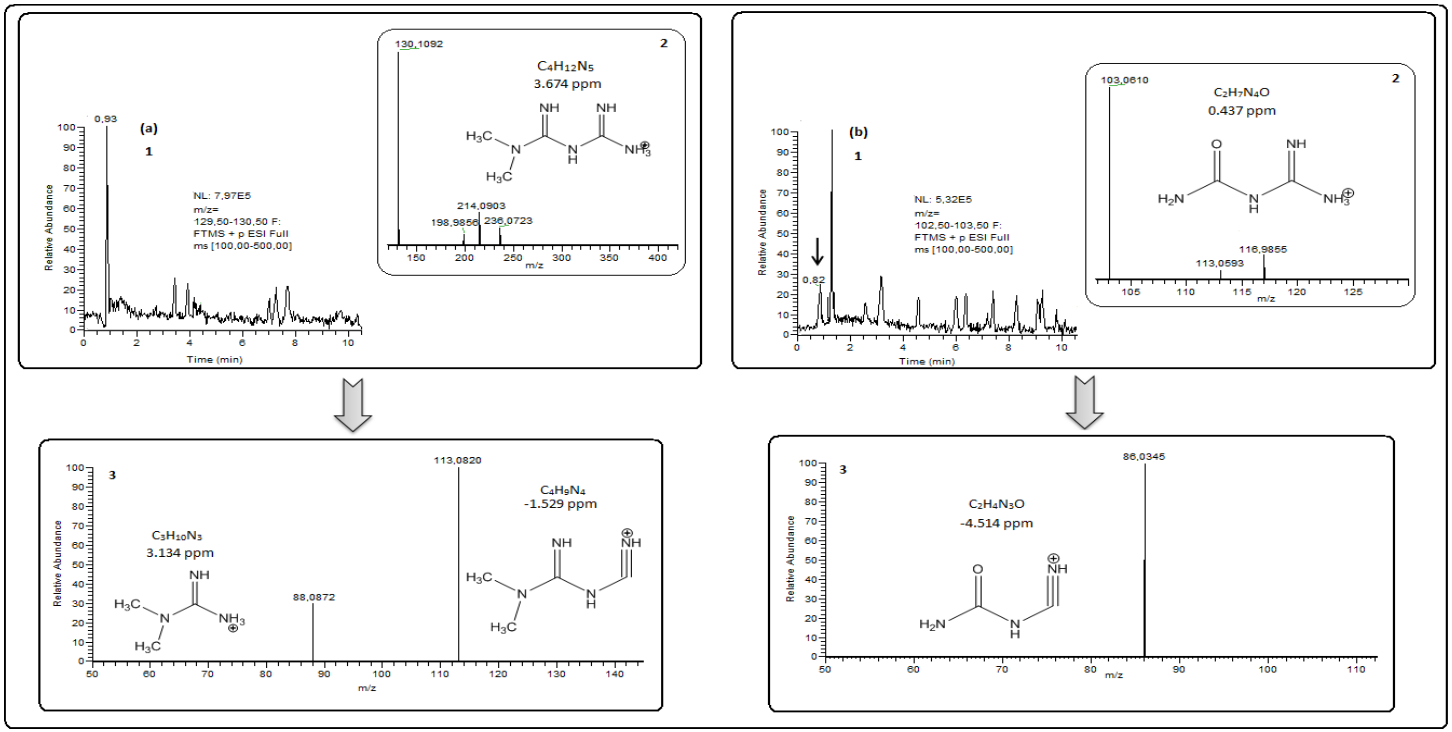
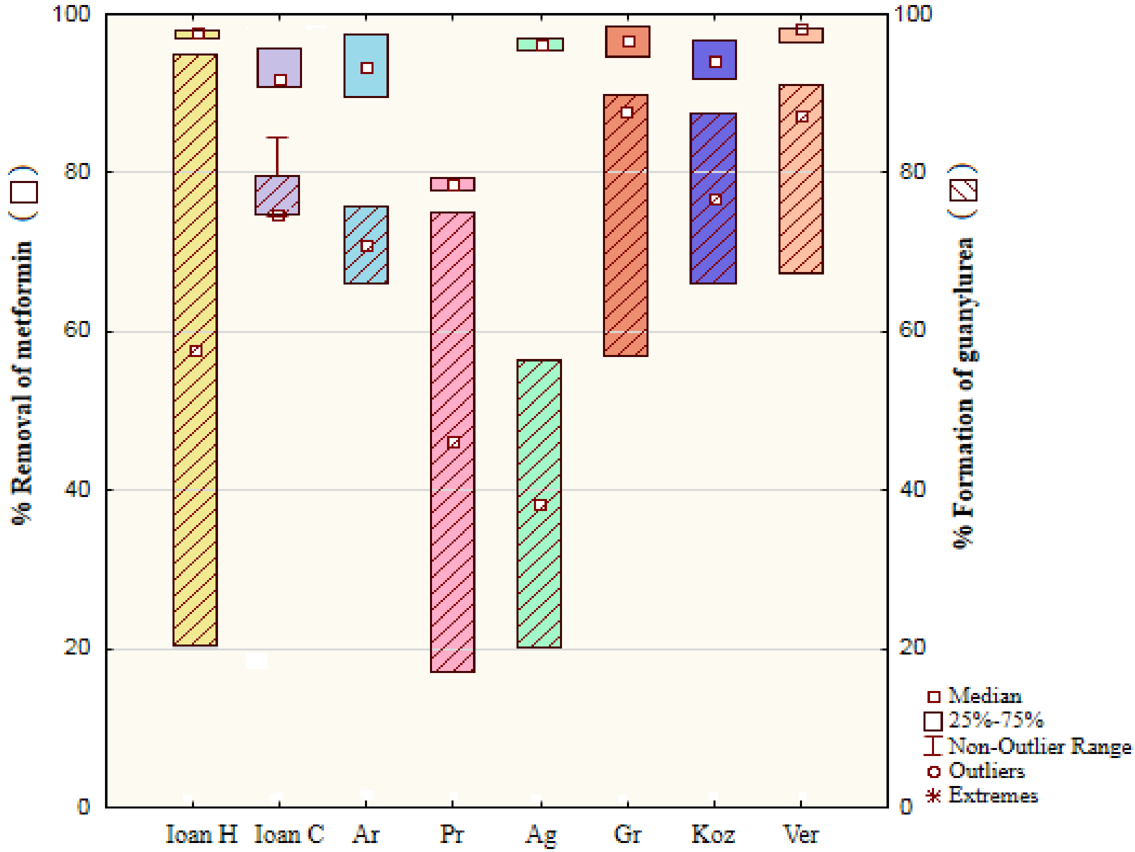
Metformin/Guanylurea in real wastewater samples from Greece



Chromatogram, (2) full scan accurate mass product ion spectrum and (3) MS/MS data obtained using Orbitrap MS targeting the corresponding ions, for (a) metformin and (b) guanylurea, espectively, found in the influent of Ioannina hospital WWTP in winter.

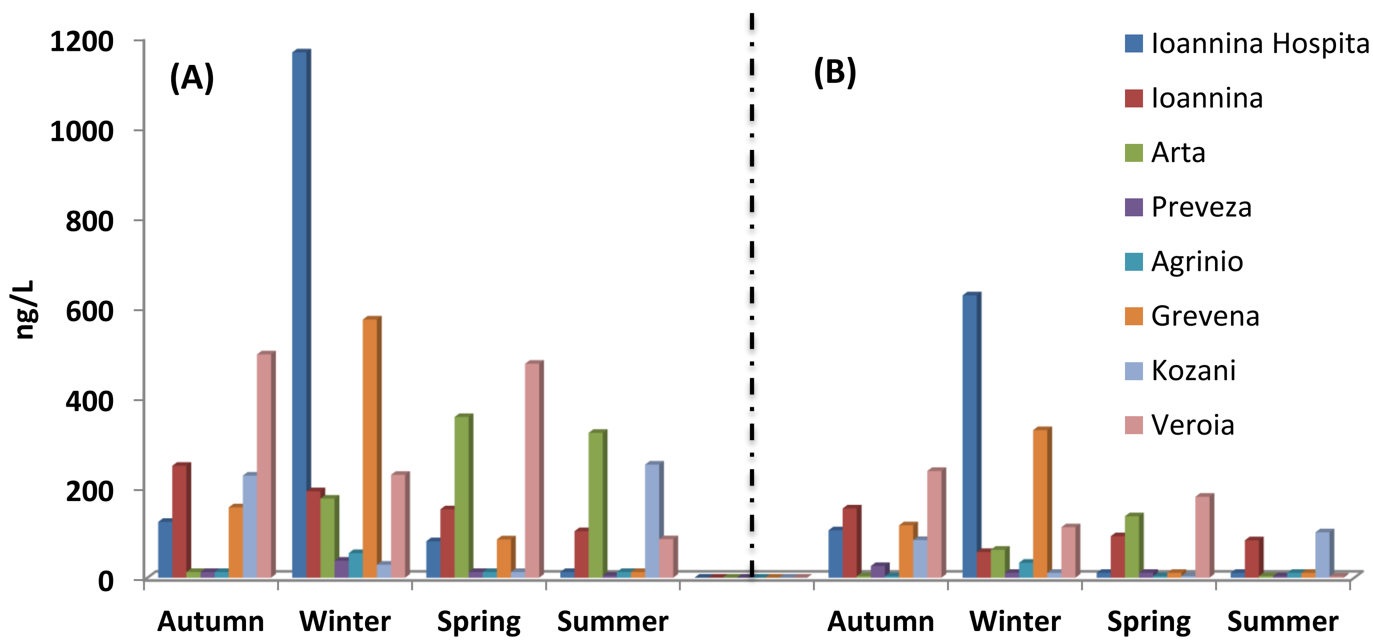
Metformin/Guanylurea in real wastewater samples from Greece



- Box and Whisker graphs showing the removal efficiencies (%) of metformin and the formation of guanylurea (%), in the eight WWTPs (Ioan C: Ioannina City, Ioan H: Ioannina Hospital, Ar: Arta, Pr: Preveza, Ag: Agrinio, Gr: Grevena, Koz: Kozani, Ver: Veroia).

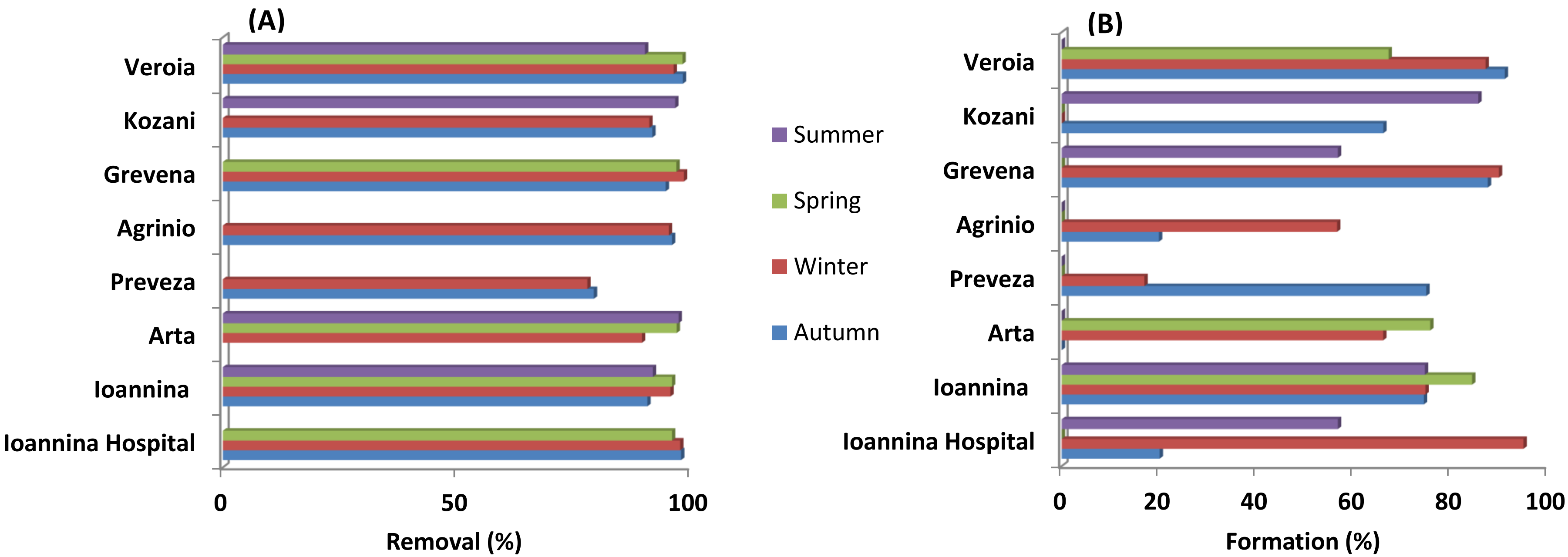
Ch. Kosma, D.Lambropoulou, T. Albanis, *Water Research*, *Volume 70, 1 March 2015, Pages 436-448*

Seasonal occurrence of (A) metformin in the influents and (B) guanylurea in the effluents



Ch. Kosma, D.Lambropoulou, T. Albanis, *Water Research*, *Volume 70*, *1 March 2015*, *Pages 436-448*

Metformin/Guanylurea in real wastewater samples from Greece



Seasonal removal efficiency (%) of metformin and (B) Seasonal formation (%) of guanylurea

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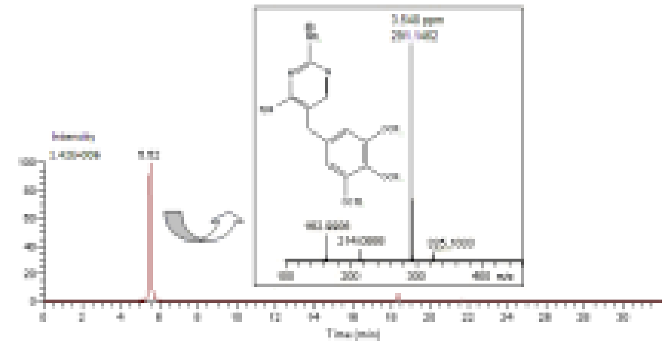
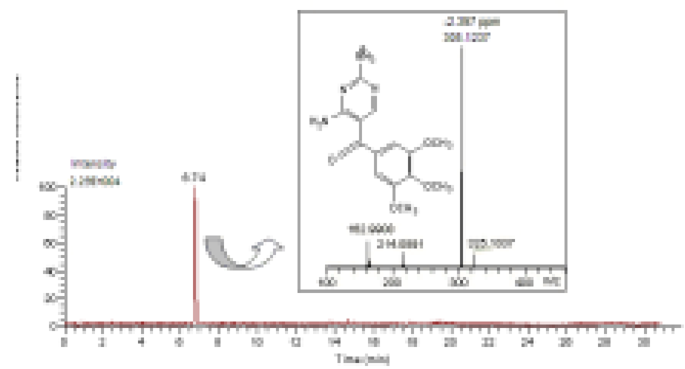
Application to real wastewater samples from Greece

The case study of Trimethoprim





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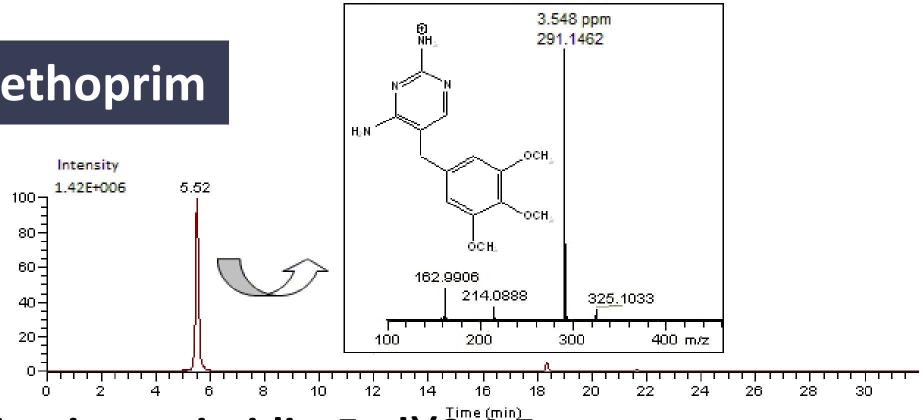
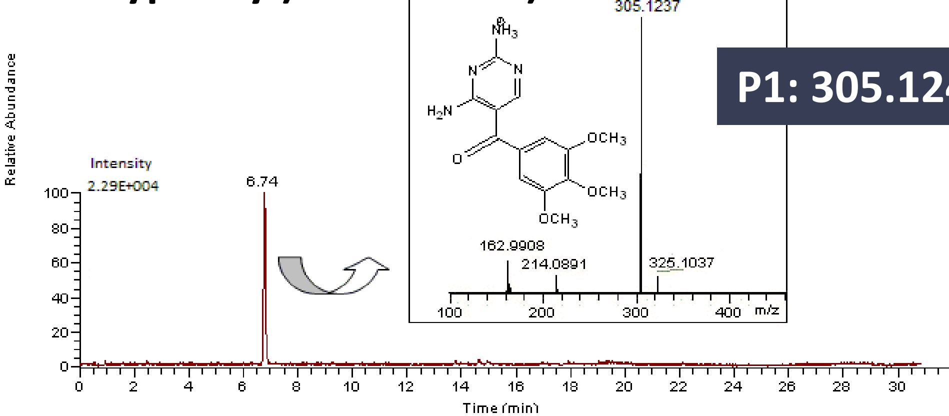
Transformation products (TPs) of Trimethoprim in WWTPs

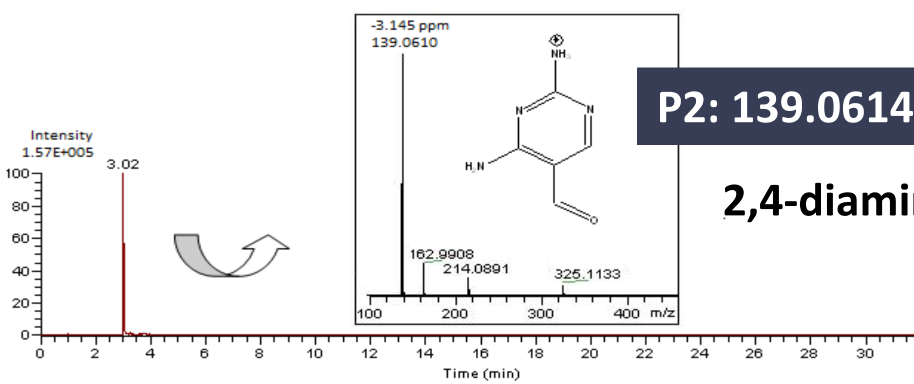
Trimethoprim



2,4-diaminopyrimidin-5-yl)(3,4,5-trimethoxyphenyl)methanone)



P1: 305.1244 m/z



P2: 139.0614 m/z

2,4-diaminopyrimidine-5-carbaldehyde)

LTQ Orbitrap MS

Suspect screening analysis

WWTP Effluent

(Ioannina – Veroia in Summer)

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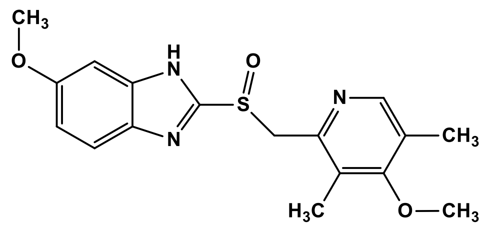
Application to real wastewater samples from Greece

The case study of Omeprazole



Omeprazole belongs **in the top twenty** prescribed and produced pharmaceuticals worldwide

It is **the first of the "proton pump inhibitors"** widely used in the treatment of dyspepsia, peptic ulcer disease etc

Environmental Fate

It can undergo various natural biotic and abiotic transformations (i.e. biodegradation, hydrolysis, photolysis etc.).

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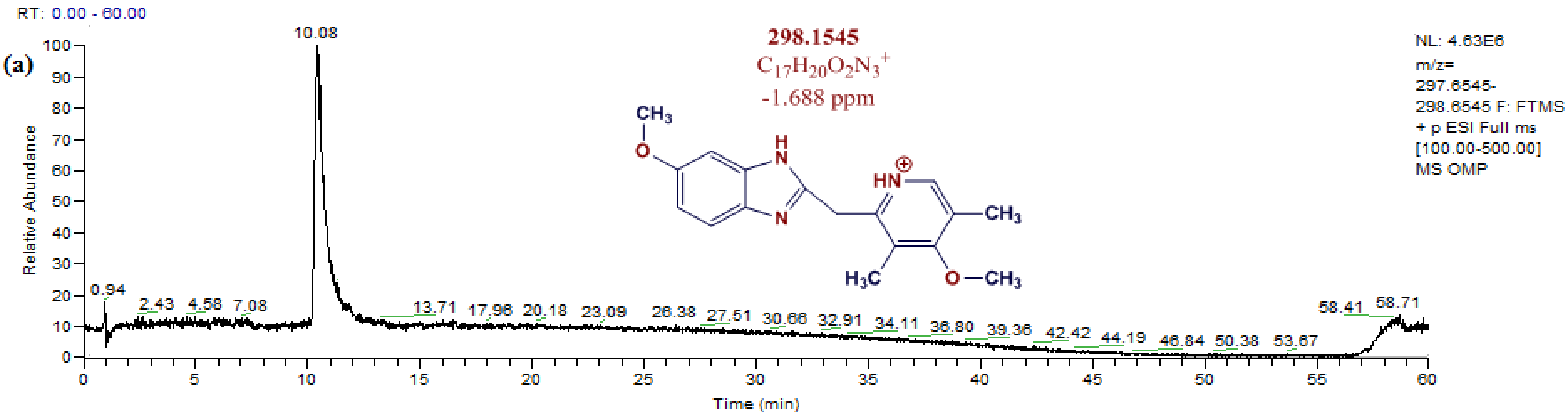
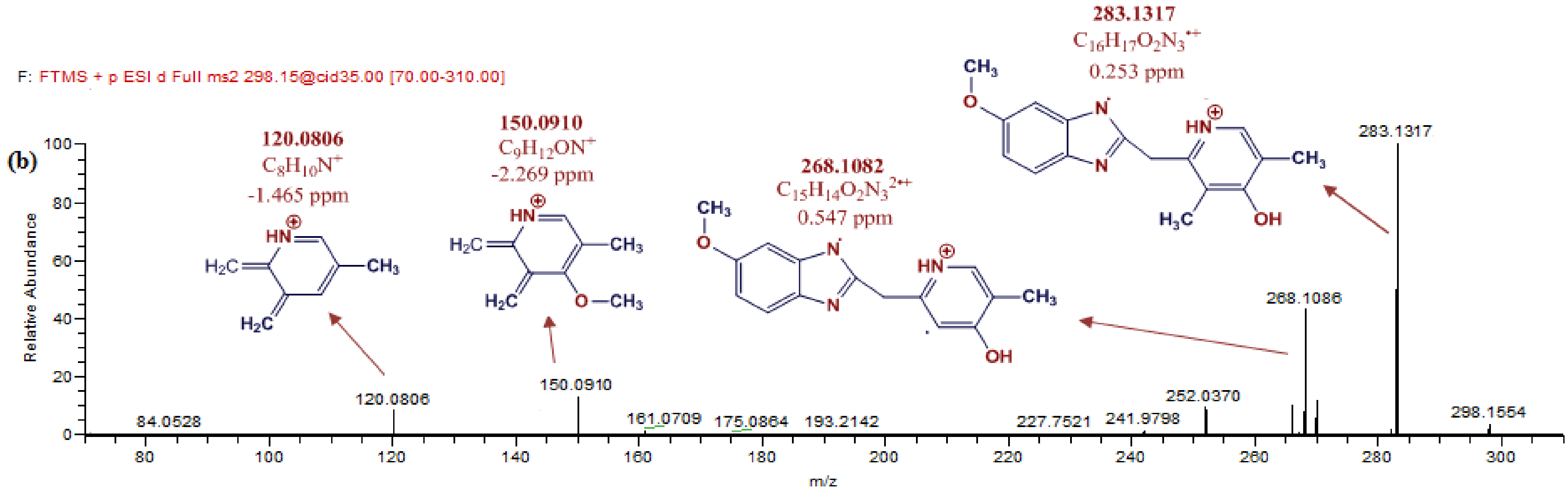
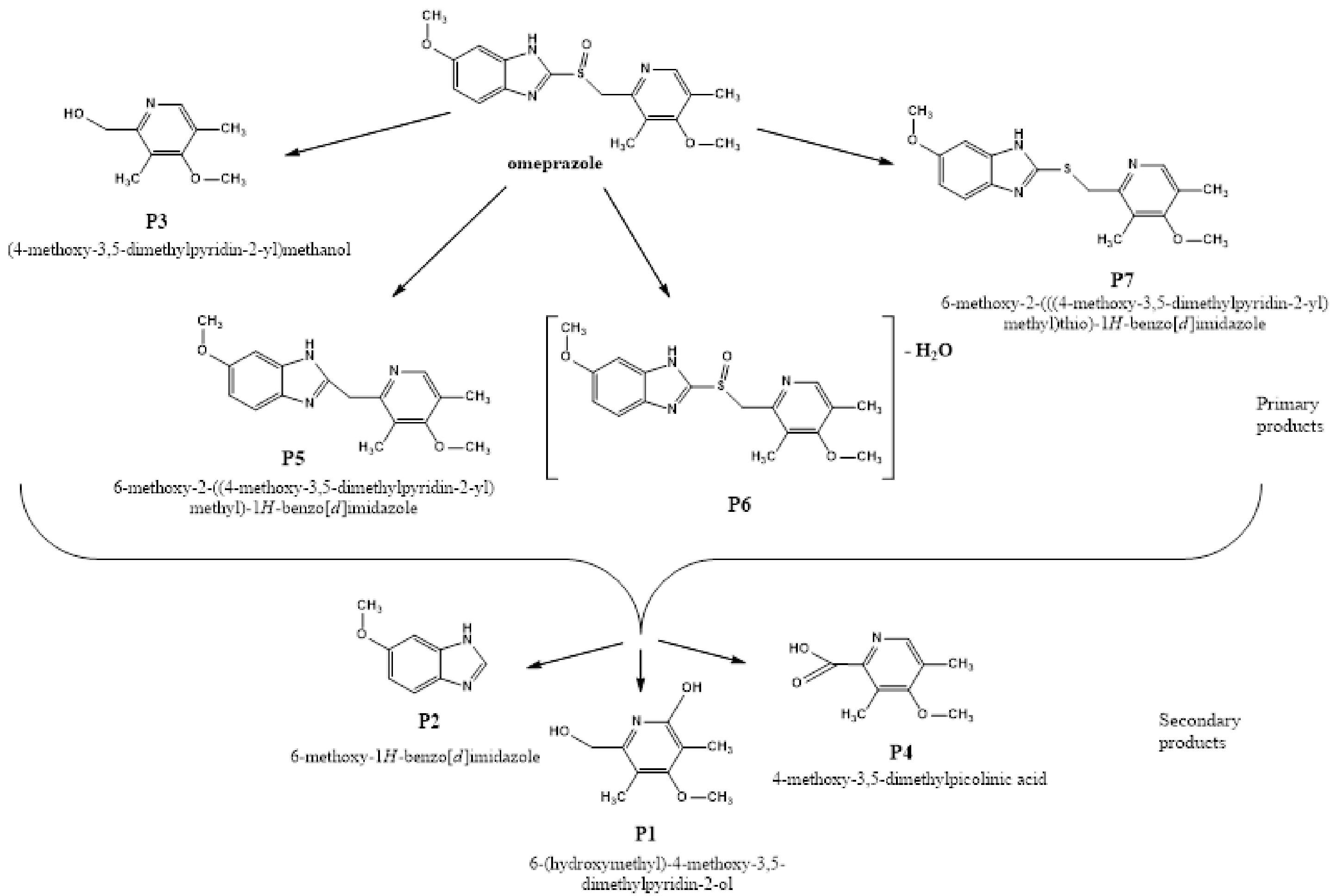
Omeprazole/ Metabolites/TPs in real wastewater samples from Greece





 Ch. Kosma, D.Lambropoulou, T. Albanis, *Science of The Total Environment, 590–591, 2017, 592-601*

Omeprazole/ Metabolites/TPs in real wastewater samples from Greece



Proposed photolysis transformation pathways of omeprazole in natural waters

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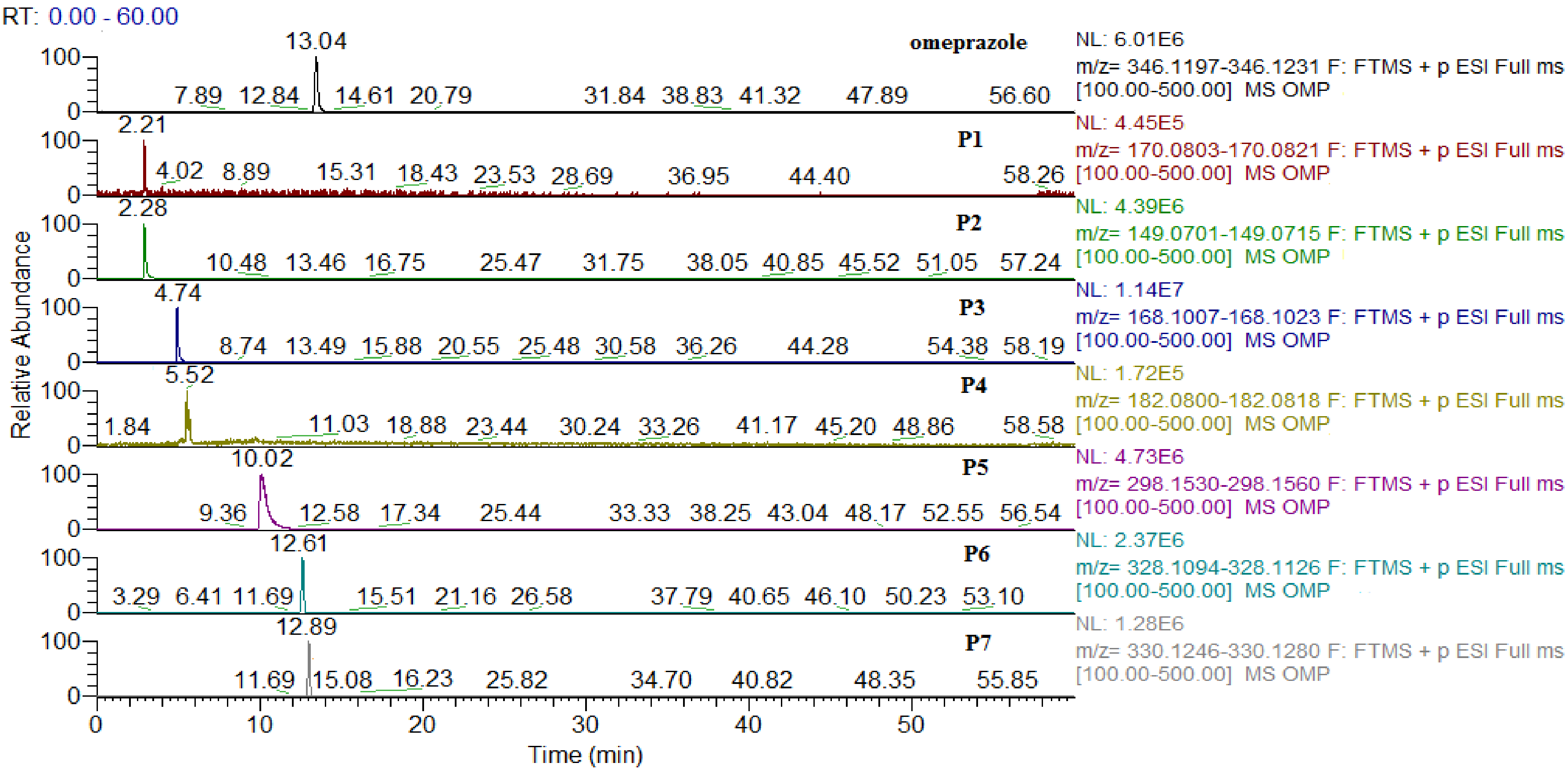
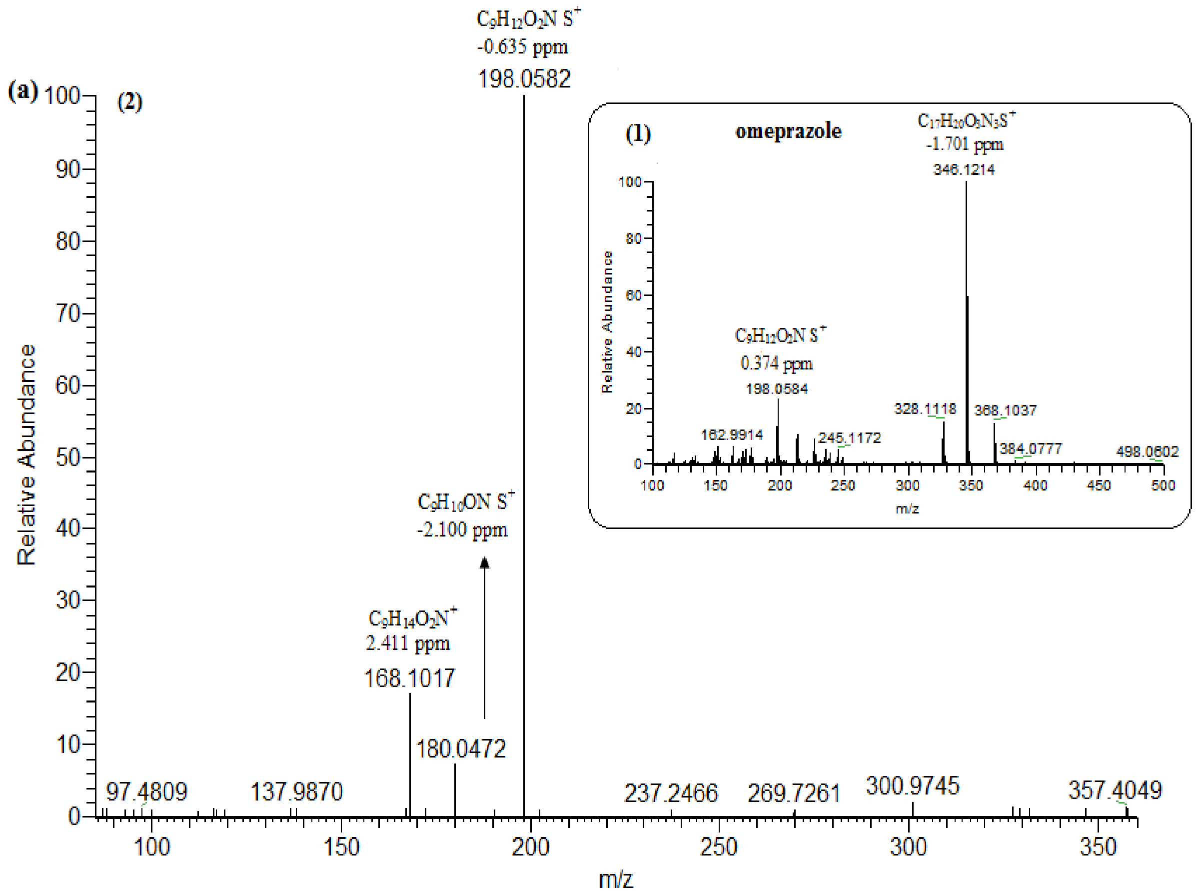
Omeprazole/ Metabolites/TPs in real wastewater samples from Greece



Extracted ion chromatogram (XIC) of omeprazole and its TPs (P1, P2, P3, P4, P5, P6 and P7) obtained after photolysis under natural irradiation, in distilled water

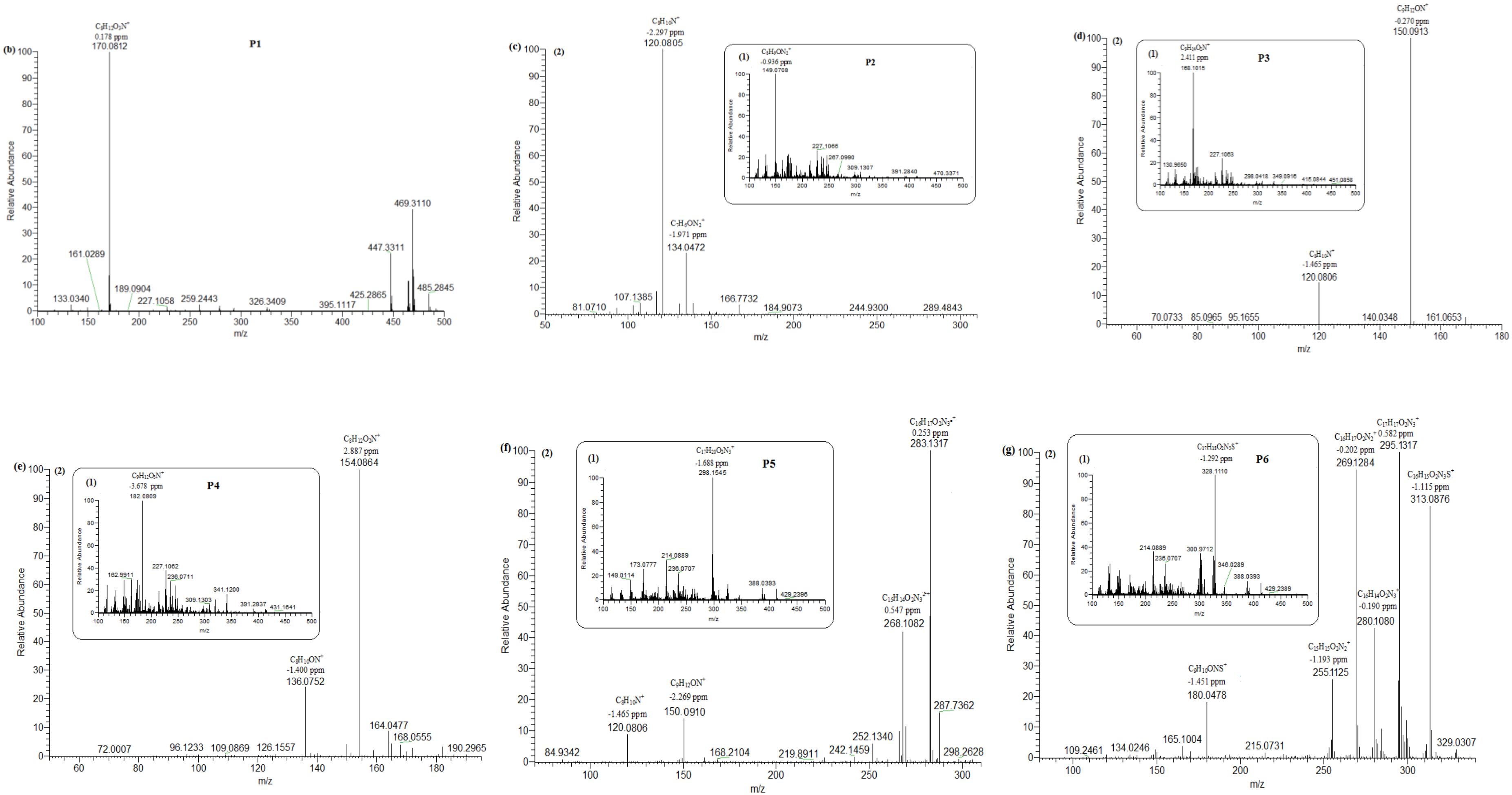
 Ch. Kosma, D.Lambropoulou, T. Albanis, *Science of The Total Environment, 590–591, 2017, 592-601*

Omeprazole/ Metabolites/TPs in real wastewater samples from Greece



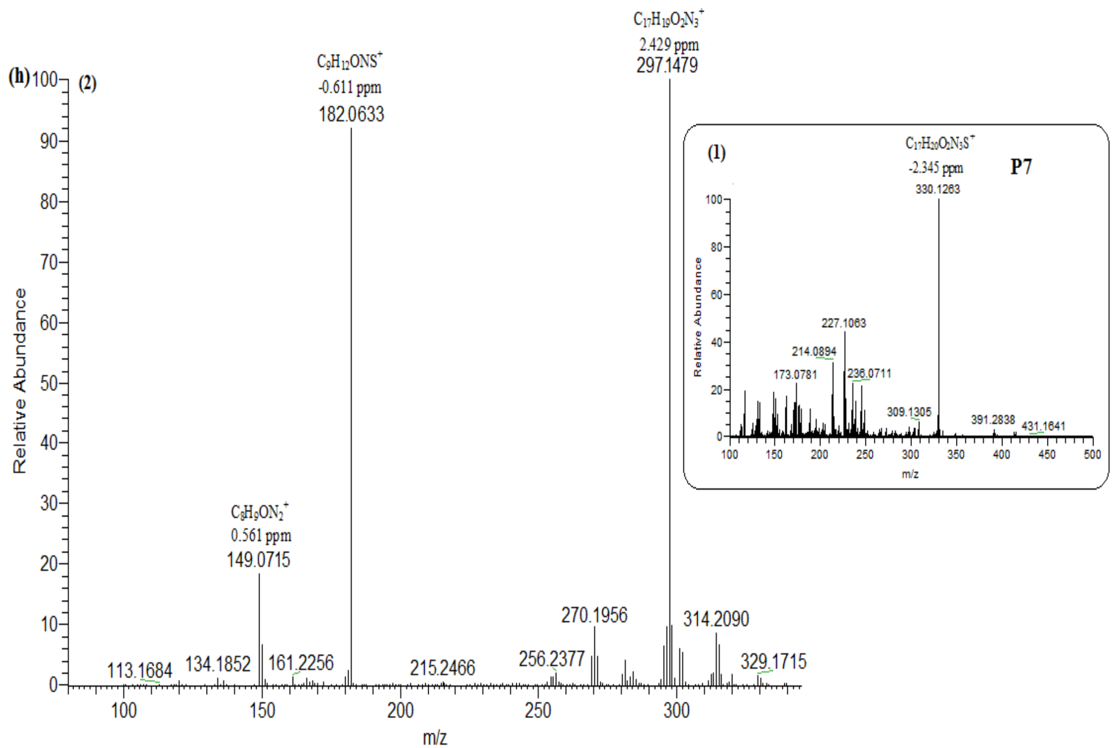
54 Ch. Kosma, D.Lambropoulou, T. Albanis, *Science of The Total Environment, 590–591, 2017, 592-601*

(1) Full scan accurate mass product ion spectrum and (2) MS/MS data obtained using Orbitrap MS targeting the corresponding ions, for (a) omeprazole and its TPs



Ch. Kosma, D.Lambropoulou, T. Albanis, *Science of The Total Environment, 590–591, 2017, 592-601*

(1) Full scan accurate mass product ion spectrum and (2) MS/MS data obtained using Orbitrap MS targeting the corresponding ions, for (a) omeprazole and its TPs



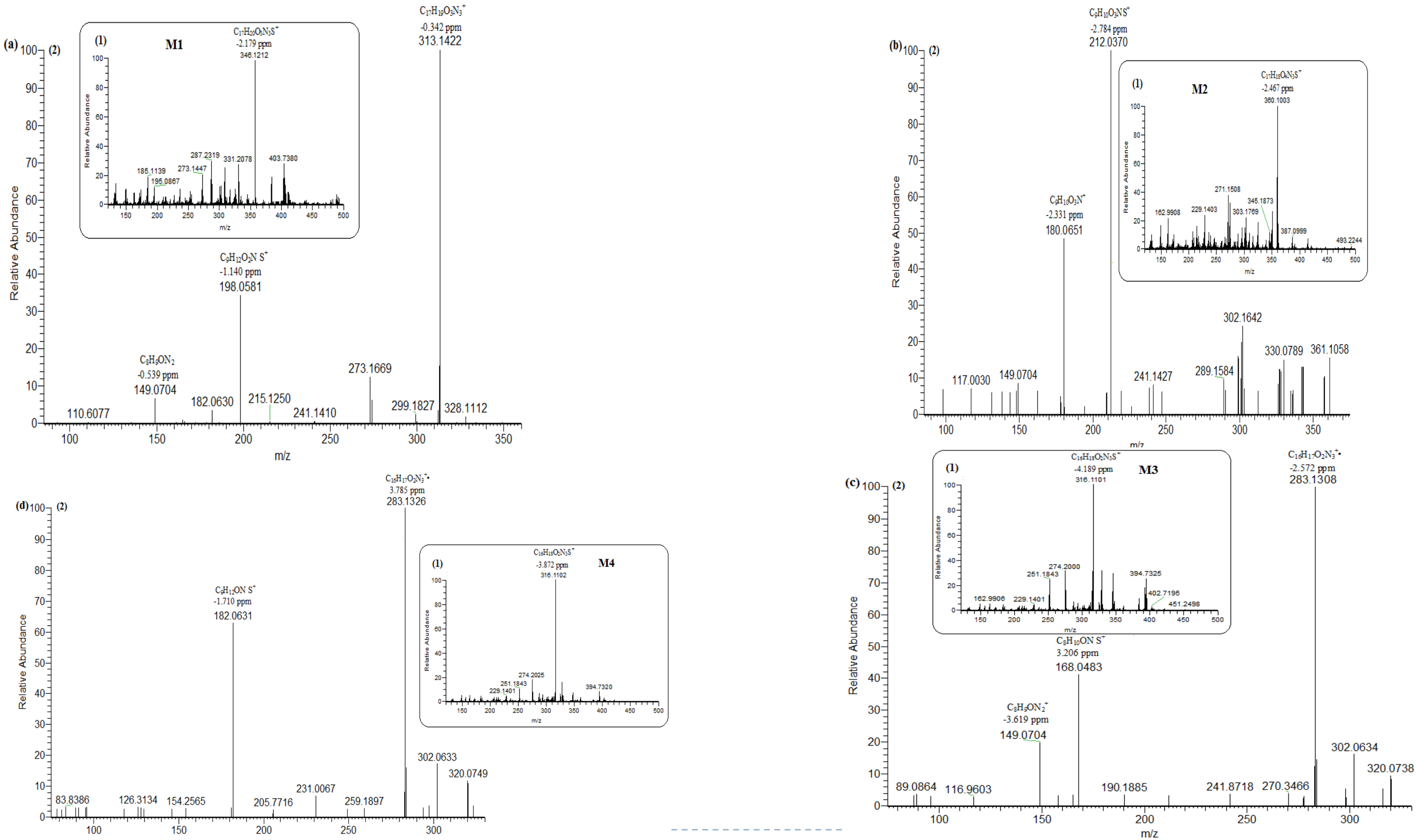
 Ch. Kosma, D.Lambropoulou, T. Albanis, *Science of The Total Environment, 590–591, 2017, 592-601*

Omeprazole/ Human Metabolites in real wastewater samples from Greece

Compound	RT (min)	Elemental composition	Mass				
			Experimental	Theoritical	RDB	Error (ppm)
M1	17.40	$C_{17}H_{20}O_3N_3S^+$	346.1212	346.1220	9.5	-2.179
		$C_{17}H_{19}O_3N_3^+$	313.1422	313.1421	10	-0.342
		$C_9H_{12}O_2N\ S^+$	198.0581	198.0583	4.5	-1.140
		$C_8H_9ON_2$	149.0704	149.0709	5.5	-0.539
M2	12.01	$C_{17}H_{18}O_4N_3S^+$	360.1003	360.1013	10.5	-2.467
		$C_9H_{10}O_3NS^+$	212.0370	212.0376	5.5	-2.784
		$C_9H_{10}O_3N^+$	180.0651	180.0655	5.5	-2.331
M3	11.36	$C_{16}H_{18}O_2N_3S^+$	316.1101	316.1114	9.5	-4.189
		$C_{16}H_{17}O_2N_3^{+\bullet}$	283.1308	283.1315	10.0	-2.572
		$C_8H_{10}ON\ S^+$	168.0483	168.0478	4.5	3.206
		$C_8H_9ON_2^+$	149.0704	149.0709	5.5	-3.619
M4	9.03	$C_{16}H_{18}O_2N_3S^+$	316.1102	316.1114	9.5	-3.872
		$C_{16}H_{17}O_2N_3^{+\bullet}$	283.1326	283.1315	10.0	3.785
		$C_9H_{12}ON\ S^+$	182.0631	182.0634	4.5	-1.710

Ch. Kosma, D.Lambropoulou, T. Albanis, *Science of The Total Environment, 590–591, 2017, 592-601*

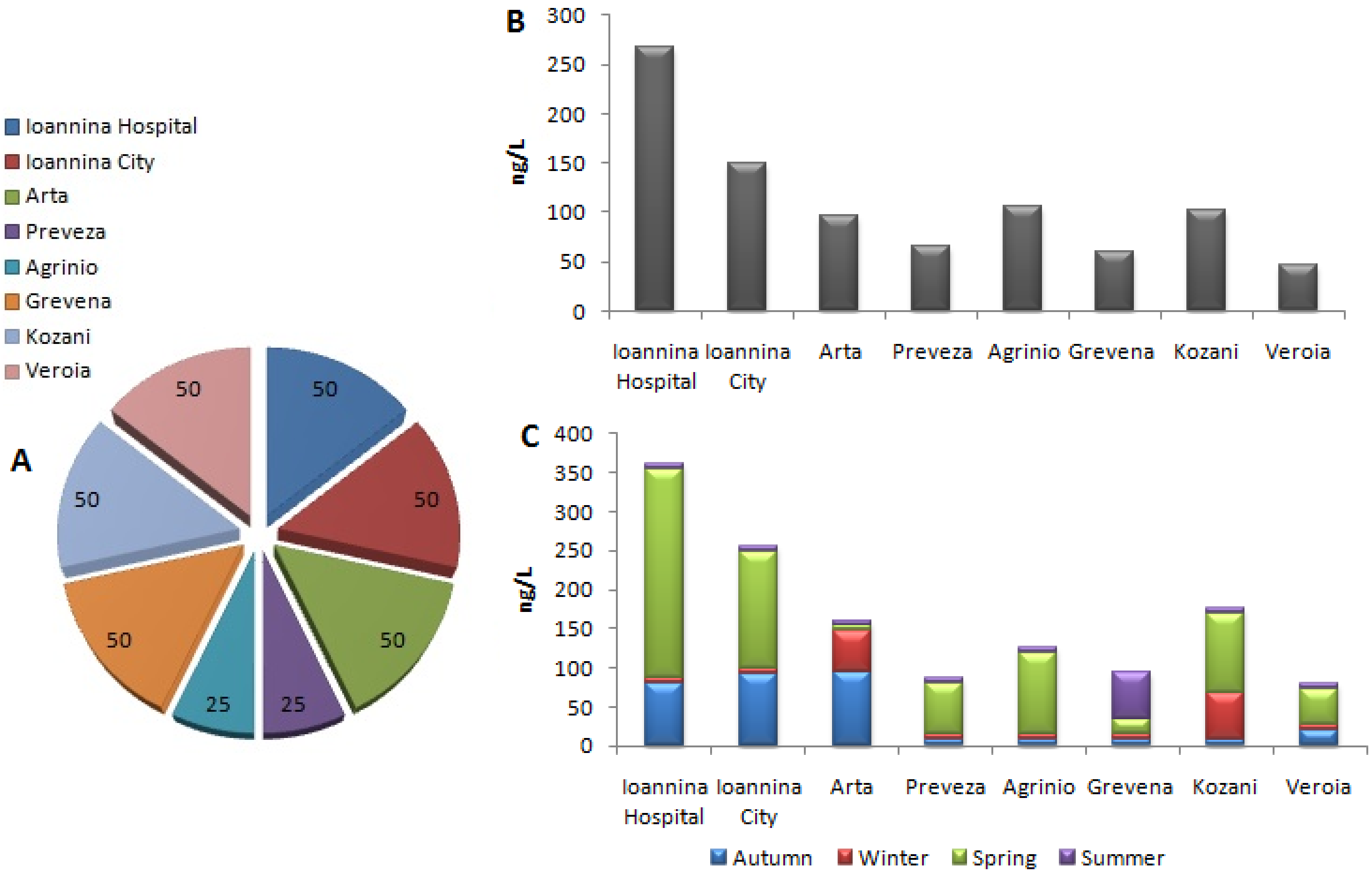
(1) Full scan accurate mass product ion spectrum and (2) MS/MS data obtained using Orbitrap MS targeting the corresponding ions, for the metabolites



 Ch. Kosma, D.Lambropoulou, T. Albanis, *Science of The Total Environment, 590–591, 2017, 592-601*

Omeprazole/ Metabolites/TPs in real wastewater samples from Greece

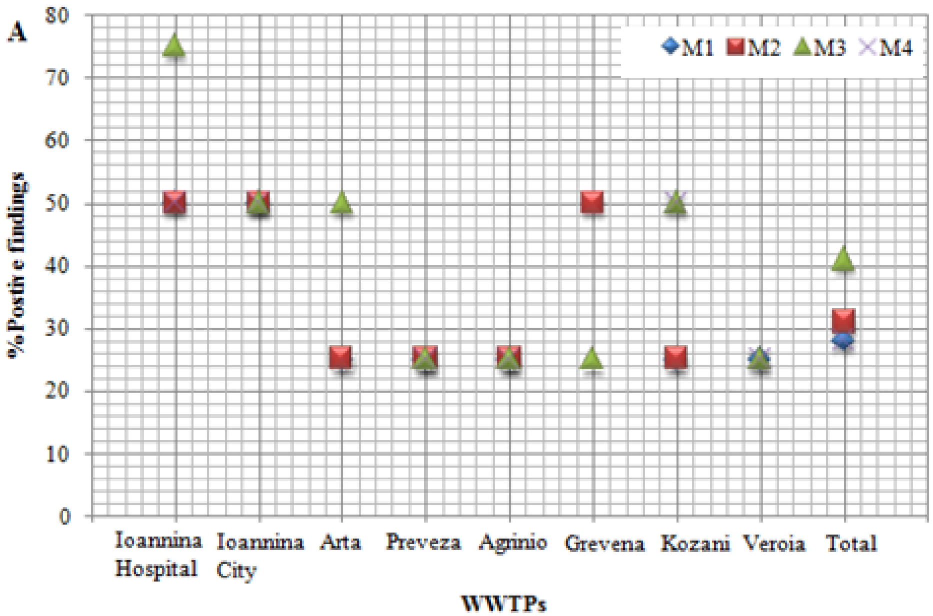
Fig. 4. A: Positive findings (%); B: Concentration ranges (ng/L) and C: Seasonal variation of omeprazole found in the influents of the eight WWTPs.

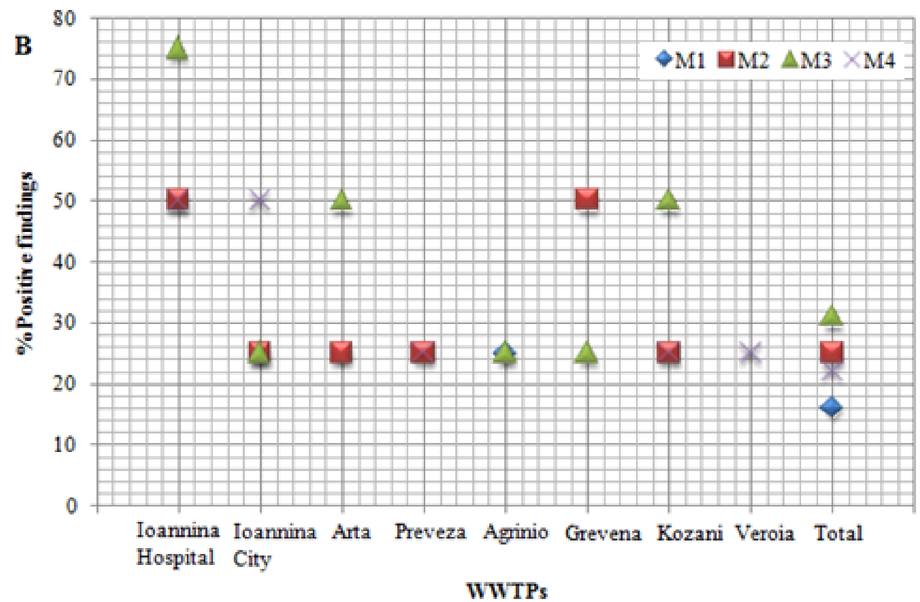


[59] Ch. Kosma, D.Lambropoulou, T. Albanis, *Science of The Total Environment, 590–591, 2017, 592-601*

Omeprazole/ Metabolites/TPs in real wastewater samples from Greece

Positive findings of omeprazole metabolites in the (A) influents and (B) effluents of the eight WWTPs





[60] Ch. Kosma, D.Lambropoulou, T. Albanis, *Science of The Total Environment, 590–591, 2017, 592-601*

28 transformation products were detected

TPs of Analgestics/antiinflamatory drugs

1-Hydroxy ibuprofen

2-Hydroxy ibuprofen

4-Hydroxy-diclofenac

5-Hydroxy-diclofenac

Hydroxy-ketoprofen

N-desmethyl-tramadol

O-desmethyl-tramadol

TPs of Antibiotics

Anhydro-erythromycin

Desmethyl-clarithromycin

Metabolite N-acetyl sulfamethoxazole

N-acetyl ciprofloxacin

(2 TP of Trimethoprim - 2,4-diaminopyrimidin-5-yl)(3,4,5-trimethoxyphenyl)methanone) /2,4-diaminopyrimidine-5-carbaldehyde)

TPs of Antidiabetics

Guanylurea

TPs of β-blockers

Hydroxy propranolol

TPs of Antidepressants /psychiatrics

O-Desmethyl venlafaxine

N-Desmethyl venlafaxine

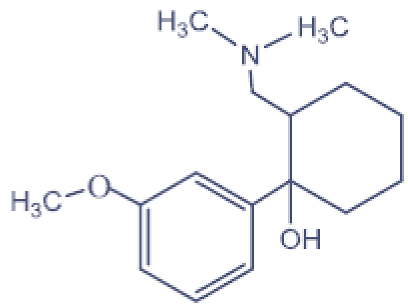
10-hydroxycarbazepine

7 TPs of Omeprazole

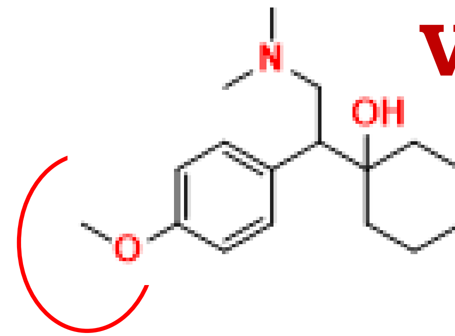
4 Human Metabolites of Omeprazole

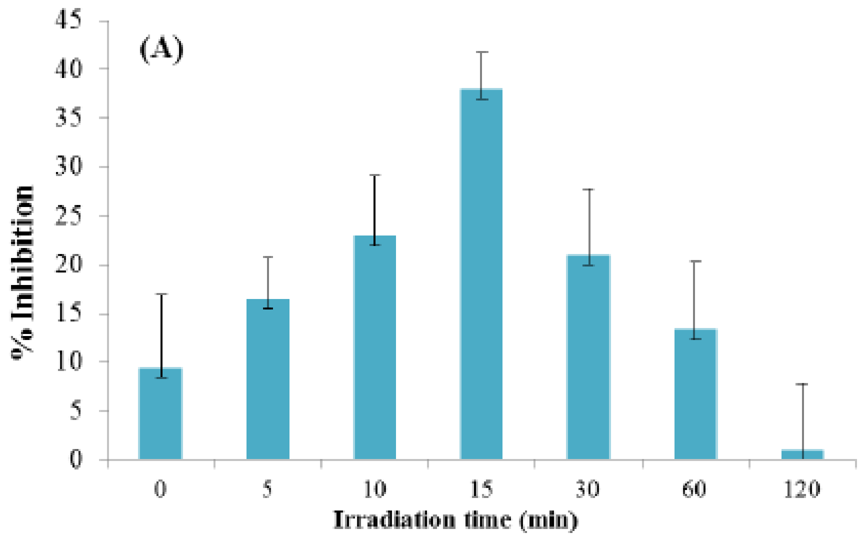
Prioritization of TPs

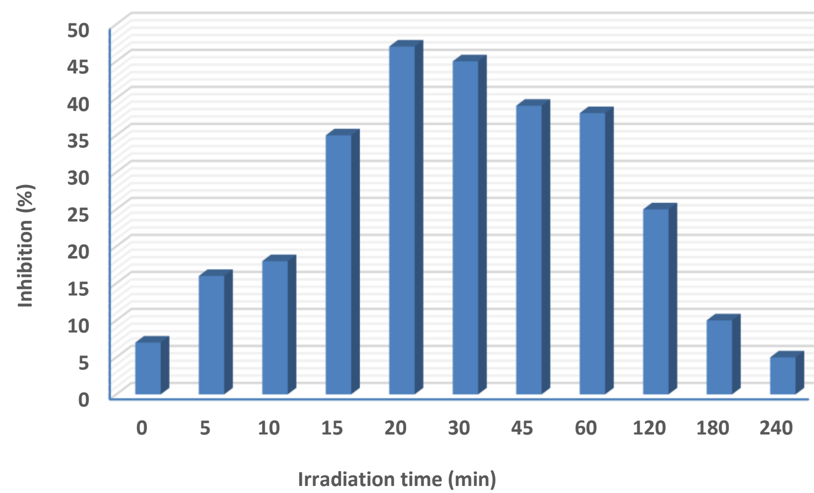
Tramadol



VNF







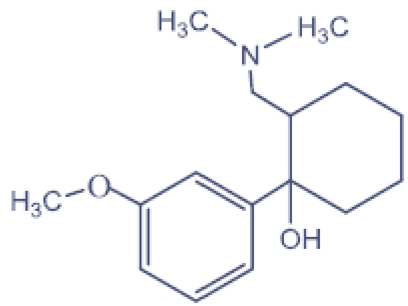
Inhibition of *Vibrio fischeri* bioluminescence as a function of photocatalytic treatment of TRA, and VNF

M Antonopoulou et al. / Science of the Total Environment 545–546 (2016) 476–485

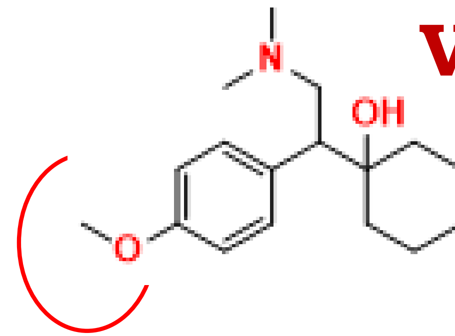
D. Lambropoulou et al. / Journal of Hazardous Materials, February 2017, Pages 513-526

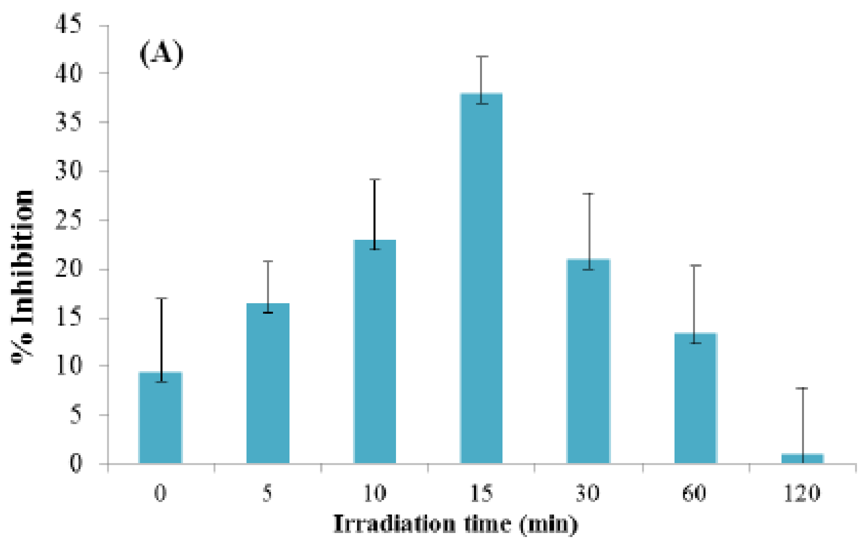
Prioritization of TPs

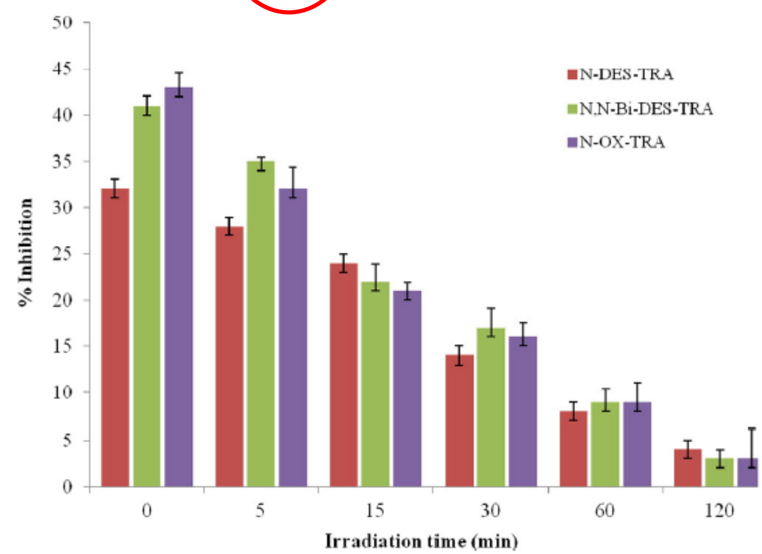
Tramadol



VNF







Inhibition of *Vibrio fischeri* bioluminescence as a function of photocatalytic treatment of TRA, N-DES-TRA, N,N-Bi-DES-TRA, N-OX-TRA

M Antonopoulou et al. / Science of the Total Environment 545–546 (2016) 476–485

Application to real wastewater samples from Greece

Location: 4 WWTPs in Greece, 4 Municipal
Samples: 24-h composite samples
Influents and effluents

Period : 2 year, 3 consecutive days/month

More TPs

The work is in progress….

Databases used for metabolites / TPs of pharmaceuticals

Transformation Products
LSM, Literature

Human Metabolites
Literature

High Resolution Mass Spectral Libraries for MS/MS data
(MassBank, MetFrag, MZmine etc)

High Quality Mass Spectral Library — MassBank

In silico fragmentation for computer assisted identification of metabolite mass spectra — MetFrag

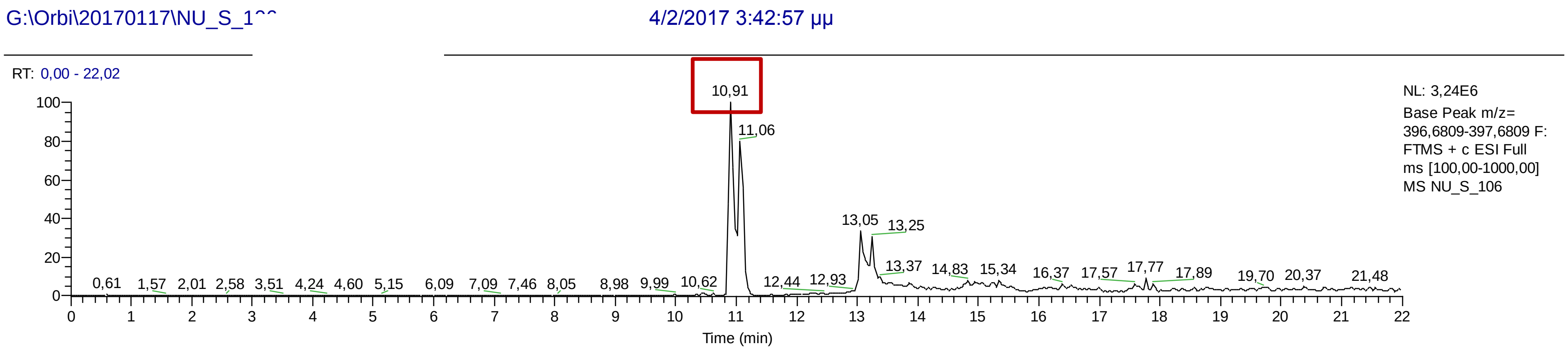
Open-source software for mass-spectrometry data processing — MZmine 2

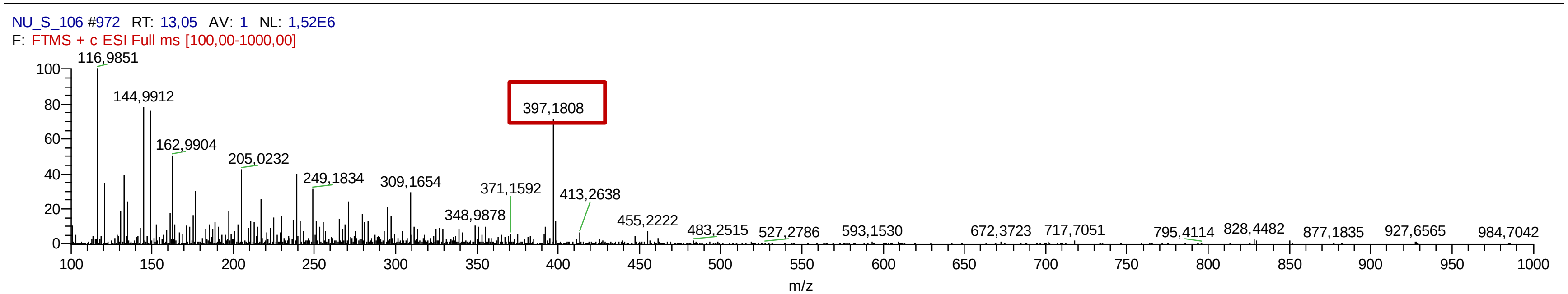
The use of Databases

MZmine 2

Open-source software for mass-spectrometry data processing

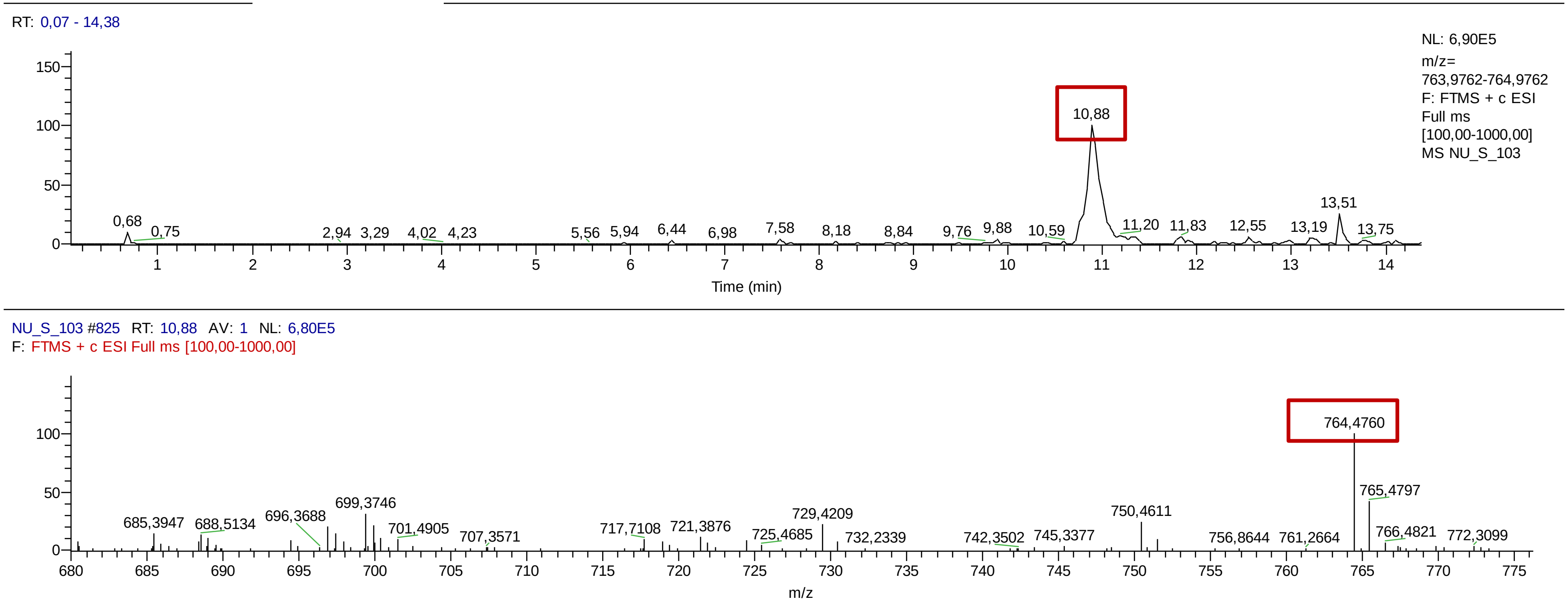
fluticasone 17beta-carboxylic acid, Rt: 13,05





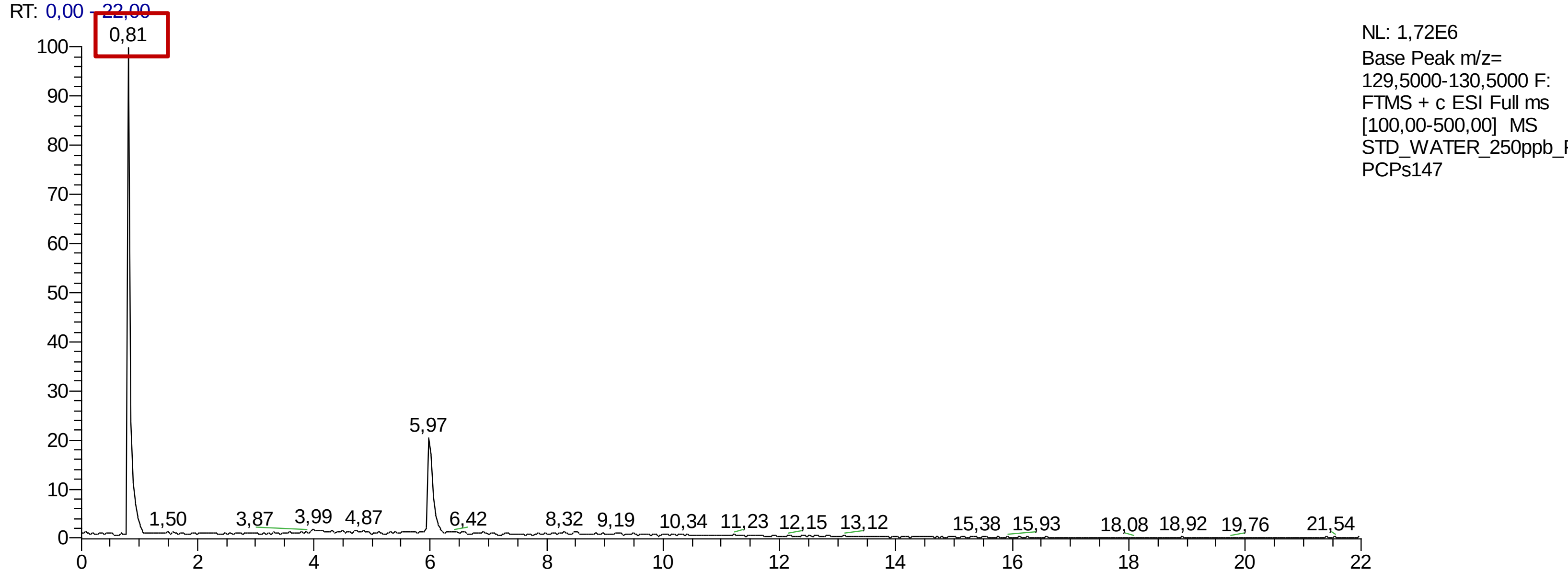
14-hydroxyclarithromycin, Rt: 10,88

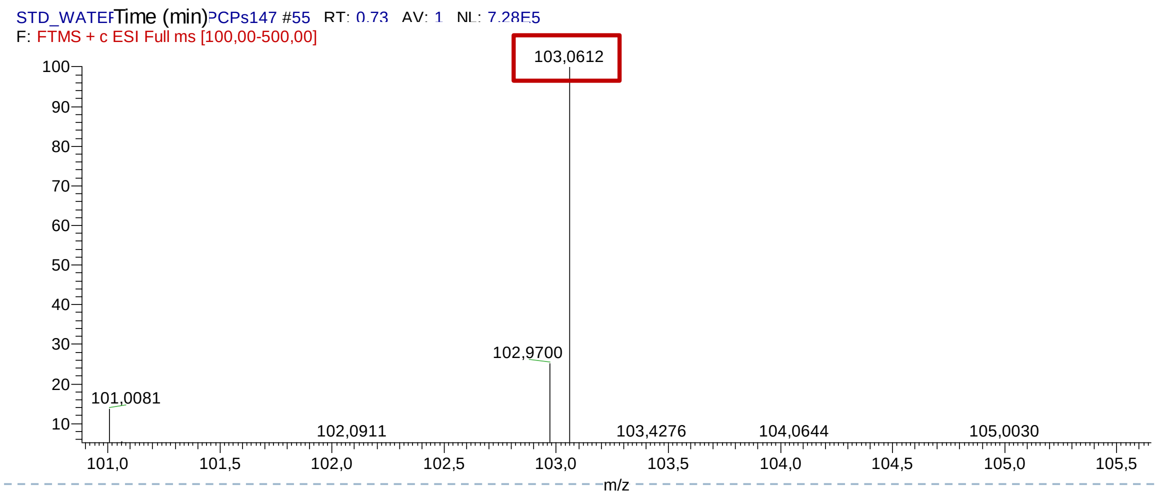
C:\Users\...\Orbi\20170117\NU_S_103 4/2/2017 9:32:33 μμ



Quanylurea, Rt: 0,81

7/12/2016 6:51:49 μμ





Target screening

Data from
>500 parent Compounds

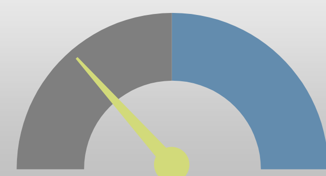
HRMS
Multiresidue Method

1 **Pesticides**

Edit this text here.

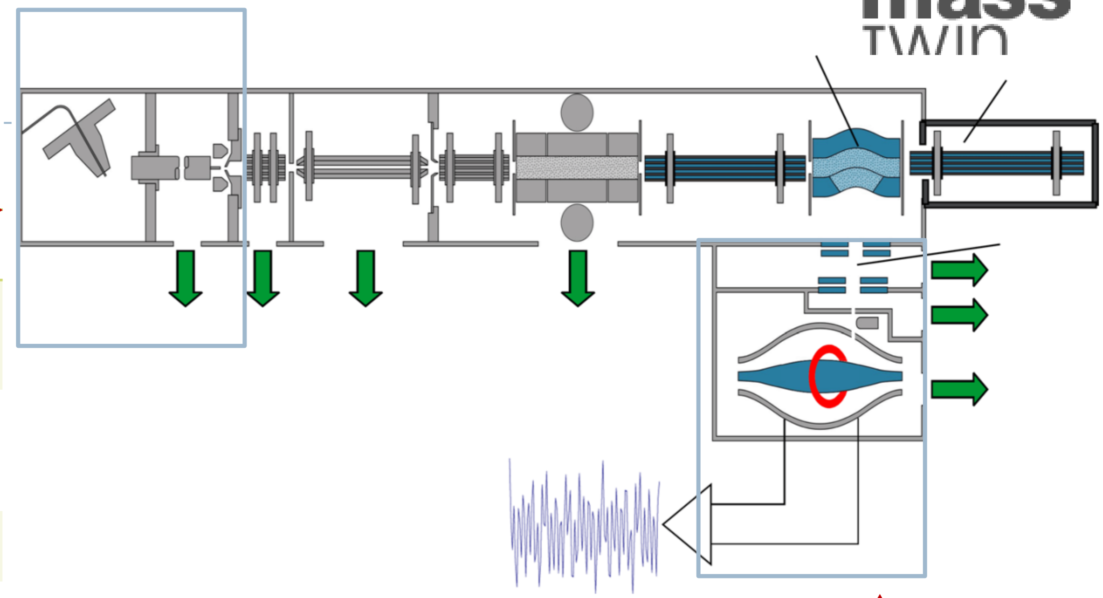
2 **PPCPs**

Edit this text here.



Time	H2O + 0.1% f.a. (%)	MeOH + 0.1% f.a (%)	µl/min
0.00	90	10	500
1.50	90	10	500
4.00	40	60	500
8.00	30	70	500
11.00	0	100	500
12.00	0	100	500
12.01	90	10	500
15.00	90	10	500

ESI source	
Shealth Gas Flow rate (arb)	40
Aux Gas Flow rate (arb)	8
Sweep Gas Flow rate (arb)	.
Spray Voltage (kV)	3.60
Capillary Temperature (°C)	320
Capillary Voltage (V)	40
Tube Lens:	120



Injection control	
Full MS	5.00e + 05
SIM	5.00e + 04
MSn	3.00e + 05

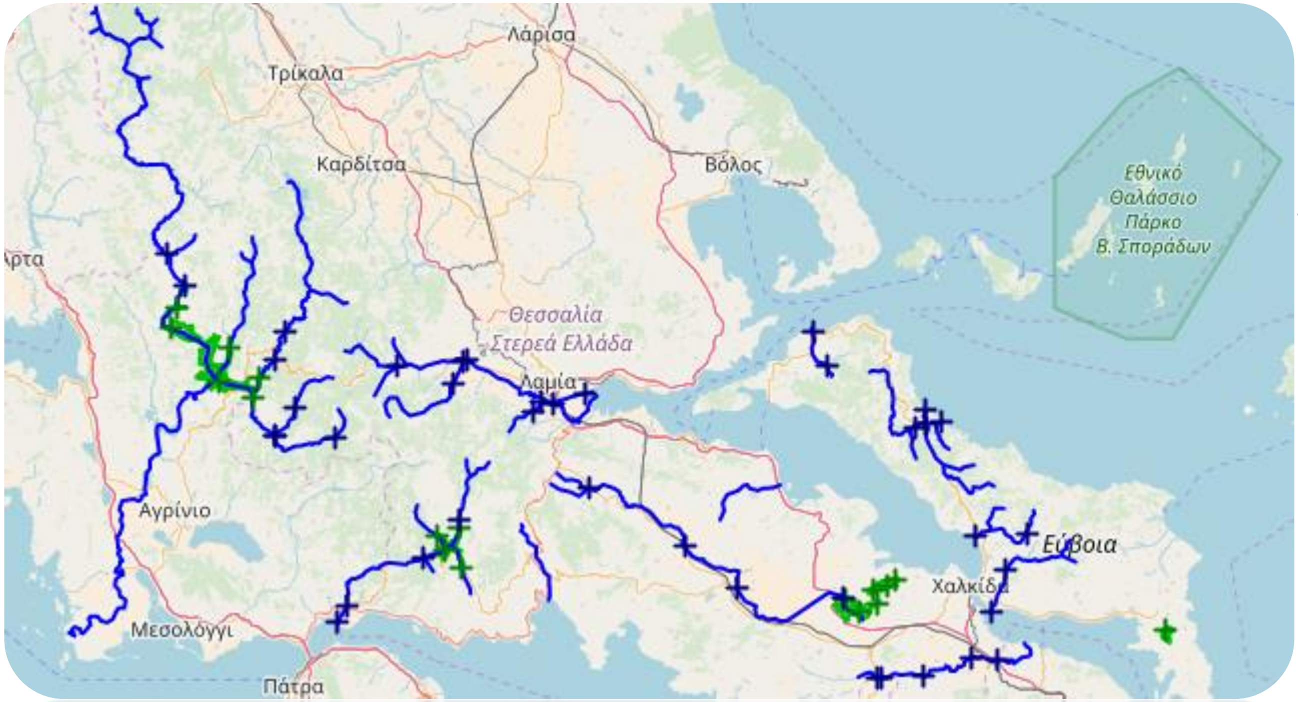
Application to real wastewater samples from Greece

Monitoring in 2 WWTPs

Thessaloniki (Greece)

WWTP-Sindos located in the west part of Thessaloniki, serves 363.987 citizens

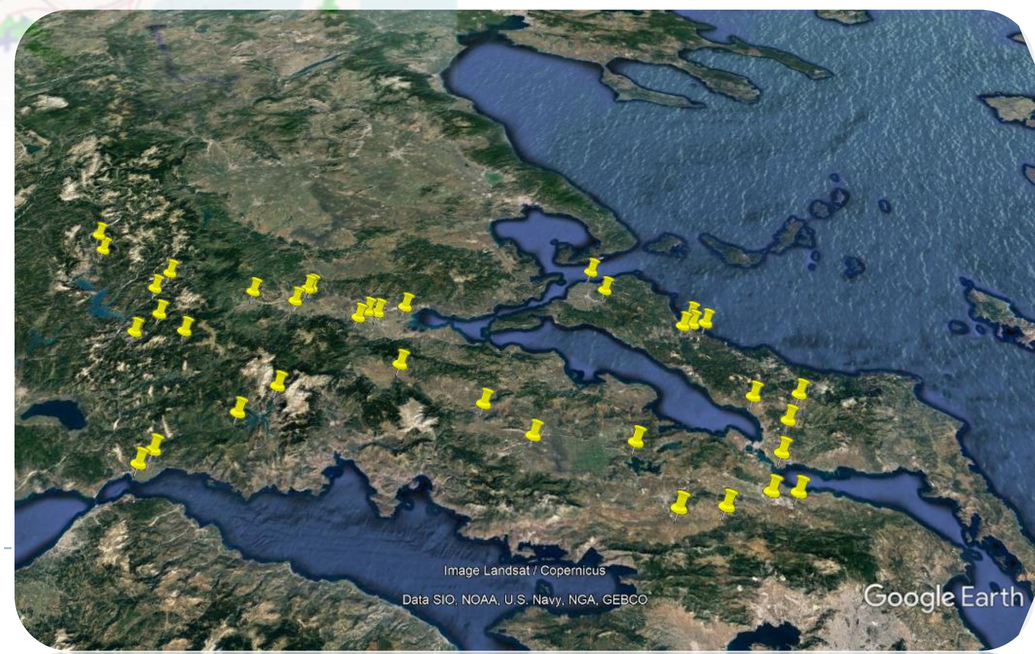
WWTP-Aineia located in the southeast coastal part of Thessaloniki, serves 50.264 citizens



- ✓ **Rivers**
- ✓ **Lakes**
- ✓ **Canals**

Monitoring for Pesticides/PPCPs/PFCs/OPFRs

In progress

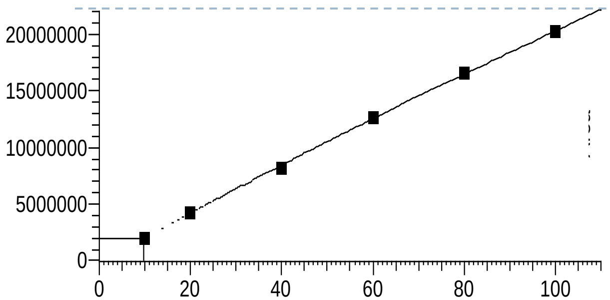


Pesticides

mass twin

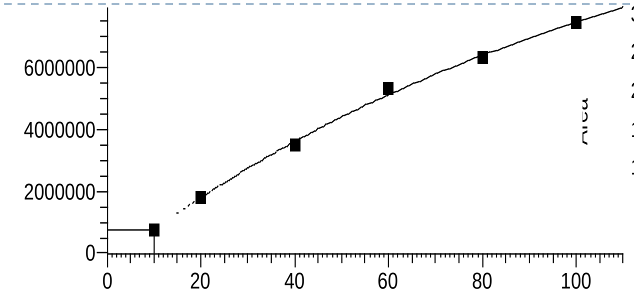
Mexacarbate

$\log(Y) = 5.14049+1.2381*\log(X)-0.0775164*(\log(X))^2 \quad R^2 = 0.9994$



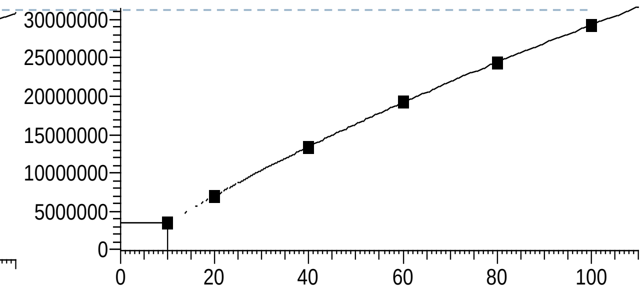
Nitenpyram

$\log(Y) = 4.28683+1.91158*\log(X)-0.309451*(\log(X))^2 \quad R^2 = 0.9992$



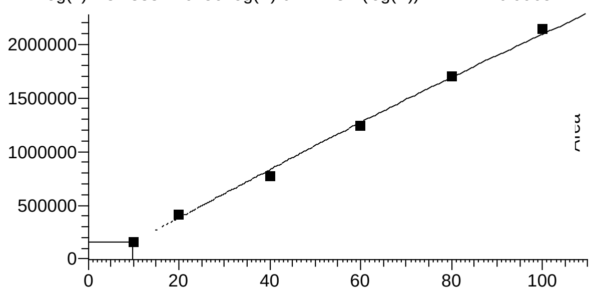
Carbendazim

$\log(Y) = 5.35816+1.30602*\log(X)-0.12592*(\log(X))^2 \quad R^2 = 0.9999$



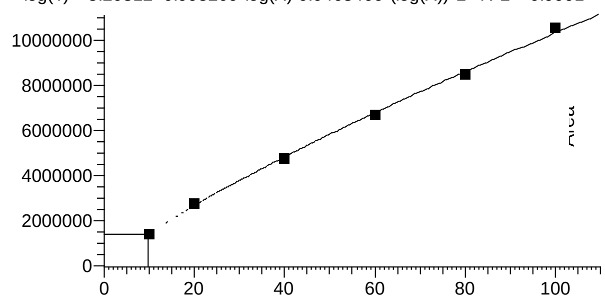
Thiamethoxam_Na

$\log(Y) = 3.7388+1.6456*\log(X)-0.177431*(\log(X))^2 \quad R^2 = 0.9965$



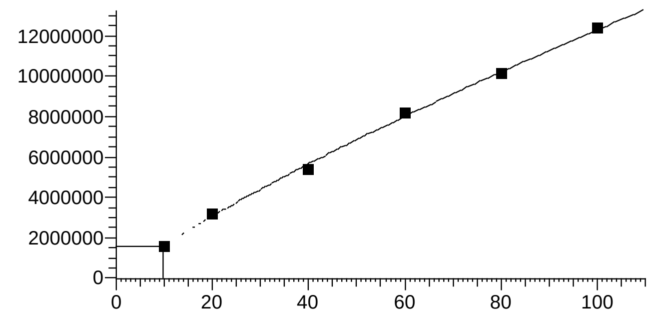
Dicrotophos

$\log(Y) = 5.20812+0.995209*\log(X)-0.0463466*(\log(X))^2 \quad R^2 = 0.9991$



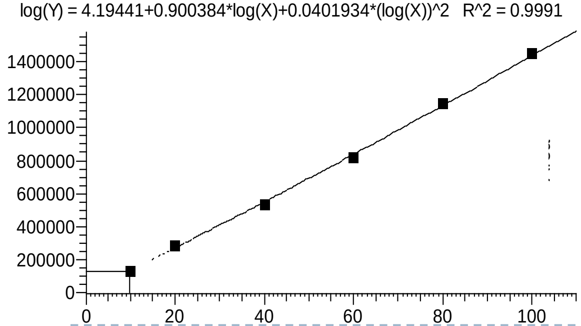
Fenuron

$\log(Y) = 5.21658+1.04504*\log(X)-0.0543577*(\log(X))^2 \quad R^2 = 0.9984$



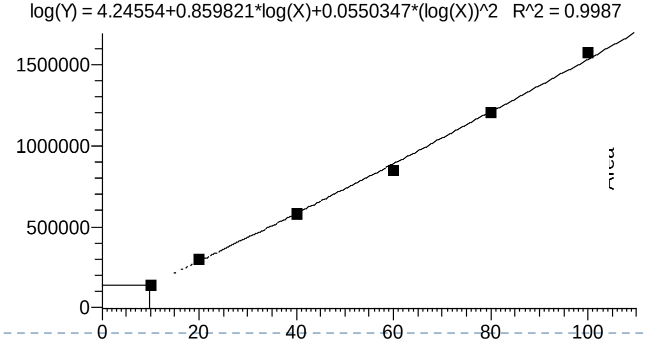
Clothianidin

$\log(Y) = 4.19441+0.900384*\log(X)+0.0401934*(\log(X))^2 \quad R^2 = 0.9991$



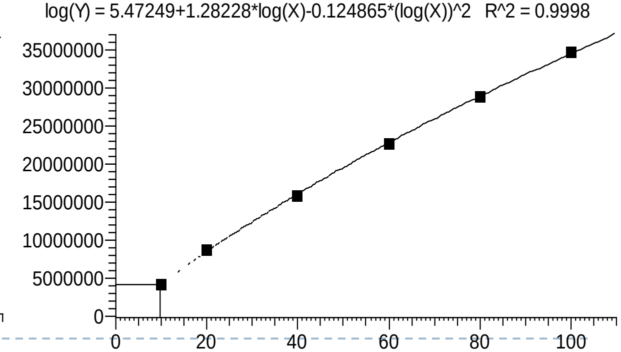
Imidacloprid

$\log(Y) = 4.24554+0.859821*\log(X)+0.0550347*(\log(X))^2 \quad R^2 = 0.9987$

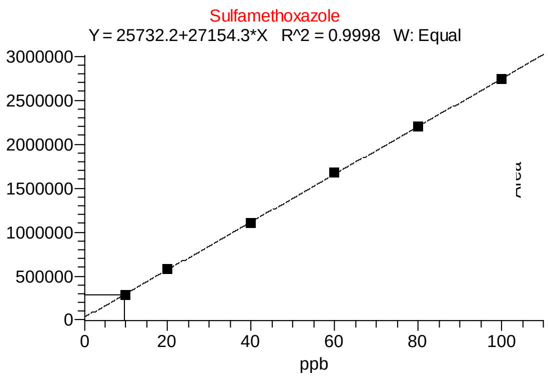


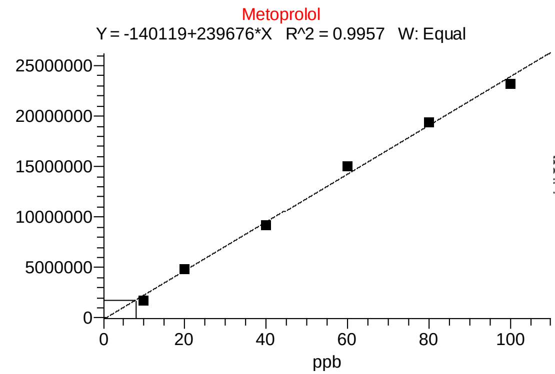
Formetanate

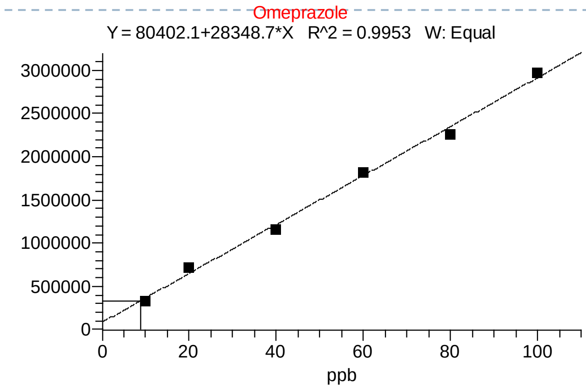
$\log(Y) = 5.47249+1.28228*\log(X)-0.124865*(\log(X))^2 \quad R^2 = 0.9998$

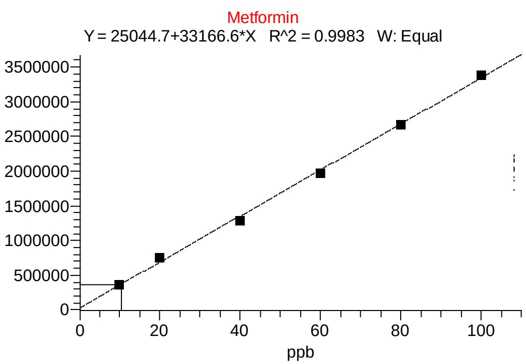


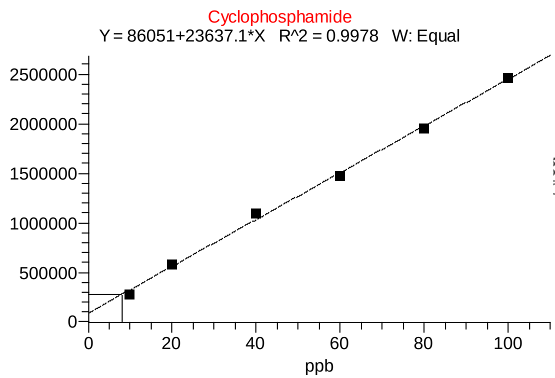
PPCPs

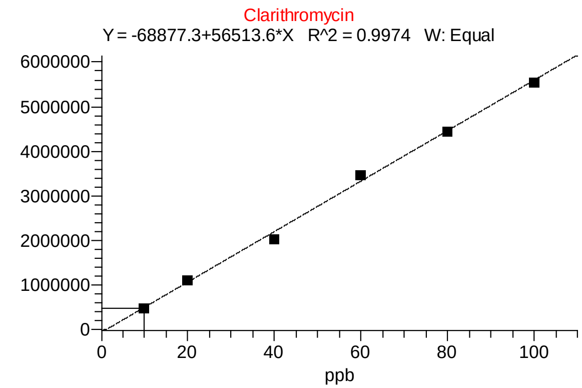

Sulfamethoxazole
Y = 25732.2+27154.3*X R^2 = 0.9998 W: Equal
ppb

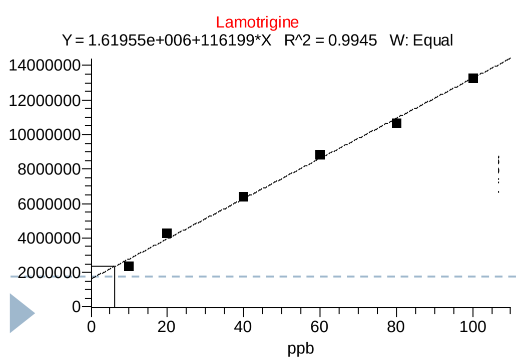

Metoprolol
Y = -140119+239676*X R^2 = 0.9957 W: Equal
ppb

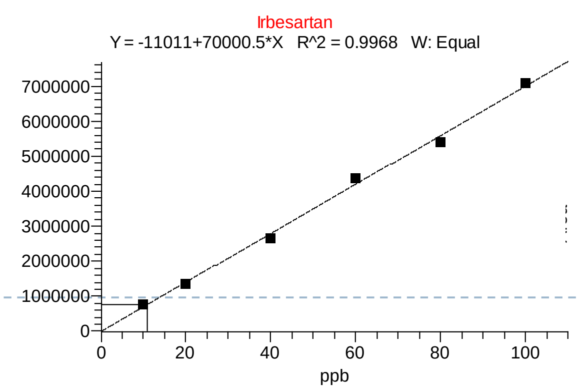

Omeprazole
Y = 80402.1+28348.7*X R^2 = 0.9953 W: Equal
ppb

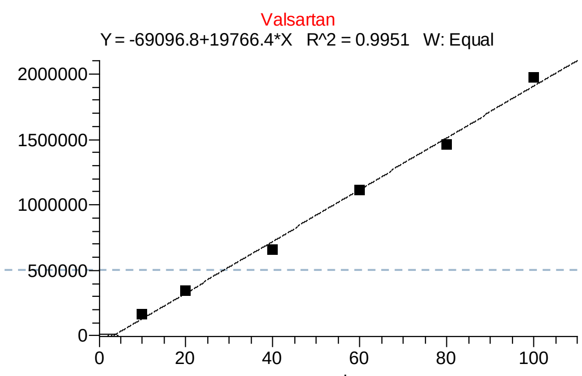

Metformin
Y = 25044.7+33166.6*X R^2 = 0.9983 W: Equal
ppb


Cyclophosphamide
Y = 86051+23637.1*X R^2 = 0.9978 W: Equal
ppb


Clarithromycin
Y = -68877.3+56513.6*X R^2 = 0.9974 W: Equal
ppb


Lamotrigine
Y = 1.61955e+006+116199*X R^2 = 0.9945 W: Equal
ppb


Irbesartan
Y = -11011+70000.5*X R^2 = 0.9968 W: Equal
ppb

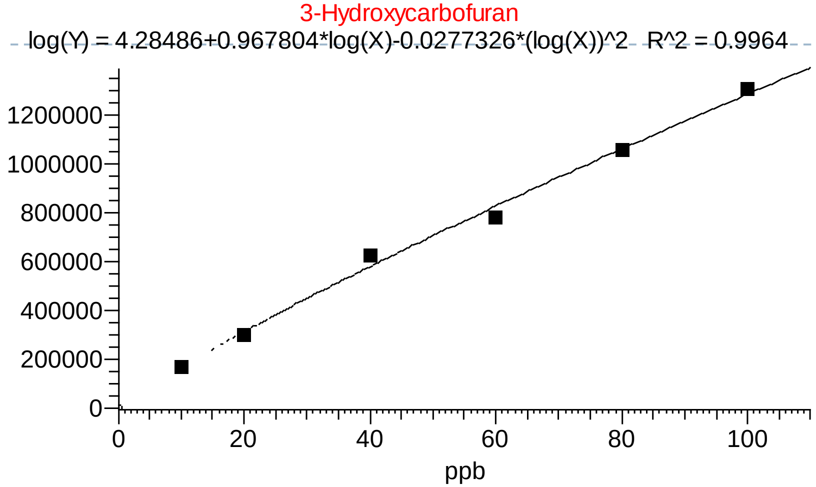

Valsartan
Y = -69096.8+19766.4*X R^2 = 0.9951 W: Equal

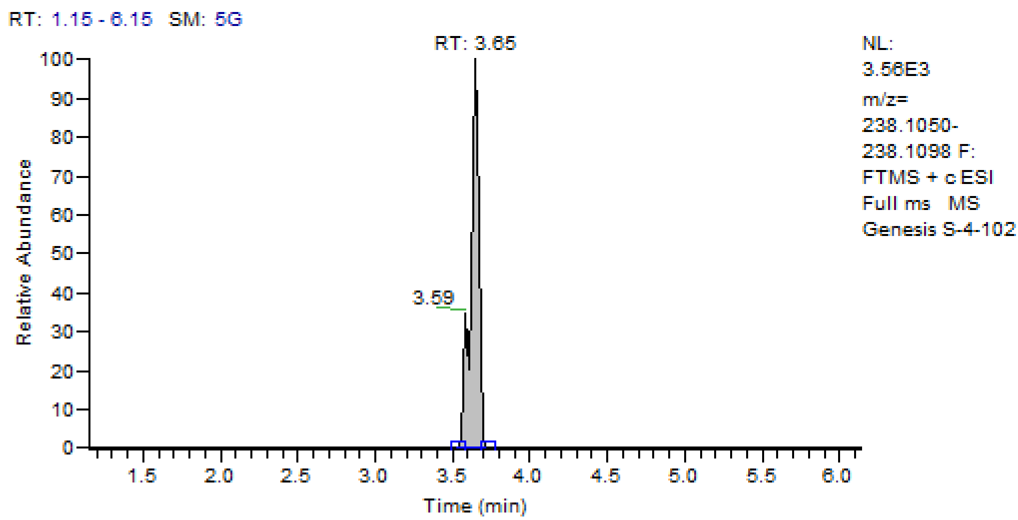
PPCPs

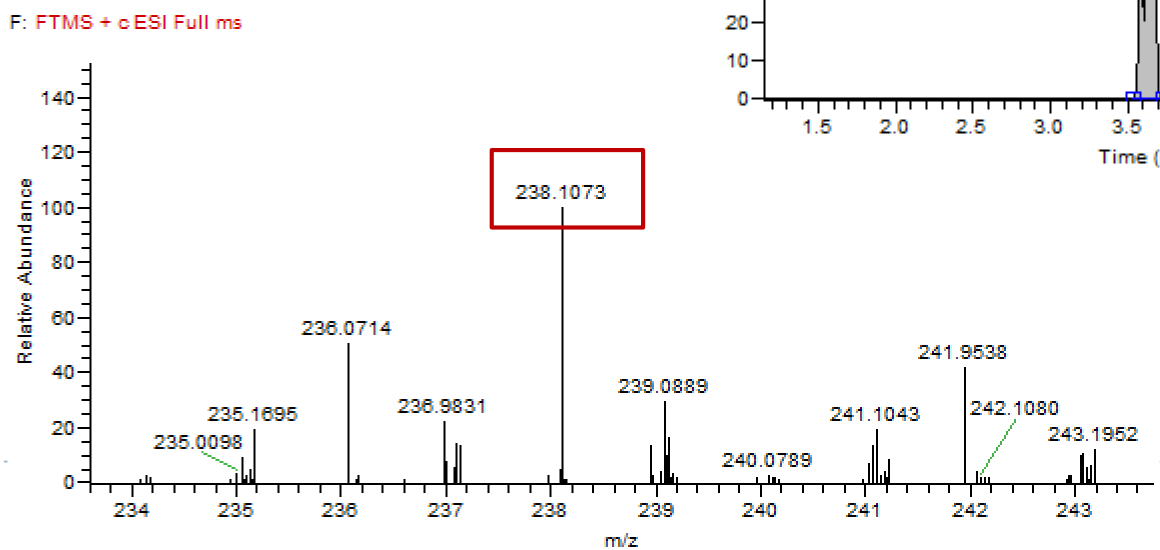
37 different therapeutic classes and TPs

1. Anesthetic
2. Amine ergot alcaloids
3. Antibiotics
4. Antidiabetics
5. Antidiarrheal
6. Antiepileptic
7. Antifungal
8. Antineoplastic
9. Antiplatelet agent
10. Anti-vertigo agent
11. Antiviral
12. Anti-angina agents
13. Anti-inflammatory-analgesics
14. Antiparkinsonian agent
15. Antiseptics
16. Antioxidants
17. Beta-blockers
18. Beta-agonists
19. Brominated flame reductant
20. Calcium channel blocker
21. Diuretic
22. Thyroid Hormones
23. Inotropic agent
24. Insect repellent
25. Antihistamines
26. Antihypertensive agent
27. Laxative drug
28. Lipid regulators
29. Muscarinic antagonist
30. Mucolytic agent
31. Proton pump inhibitors
32. Proton pump V inhibitor
33. Psychomotor stimulant
34. Psychiatric drugs
35. Steroid hormones
36. UVA/UVB absorbers
37. α_1 receptor antagonist

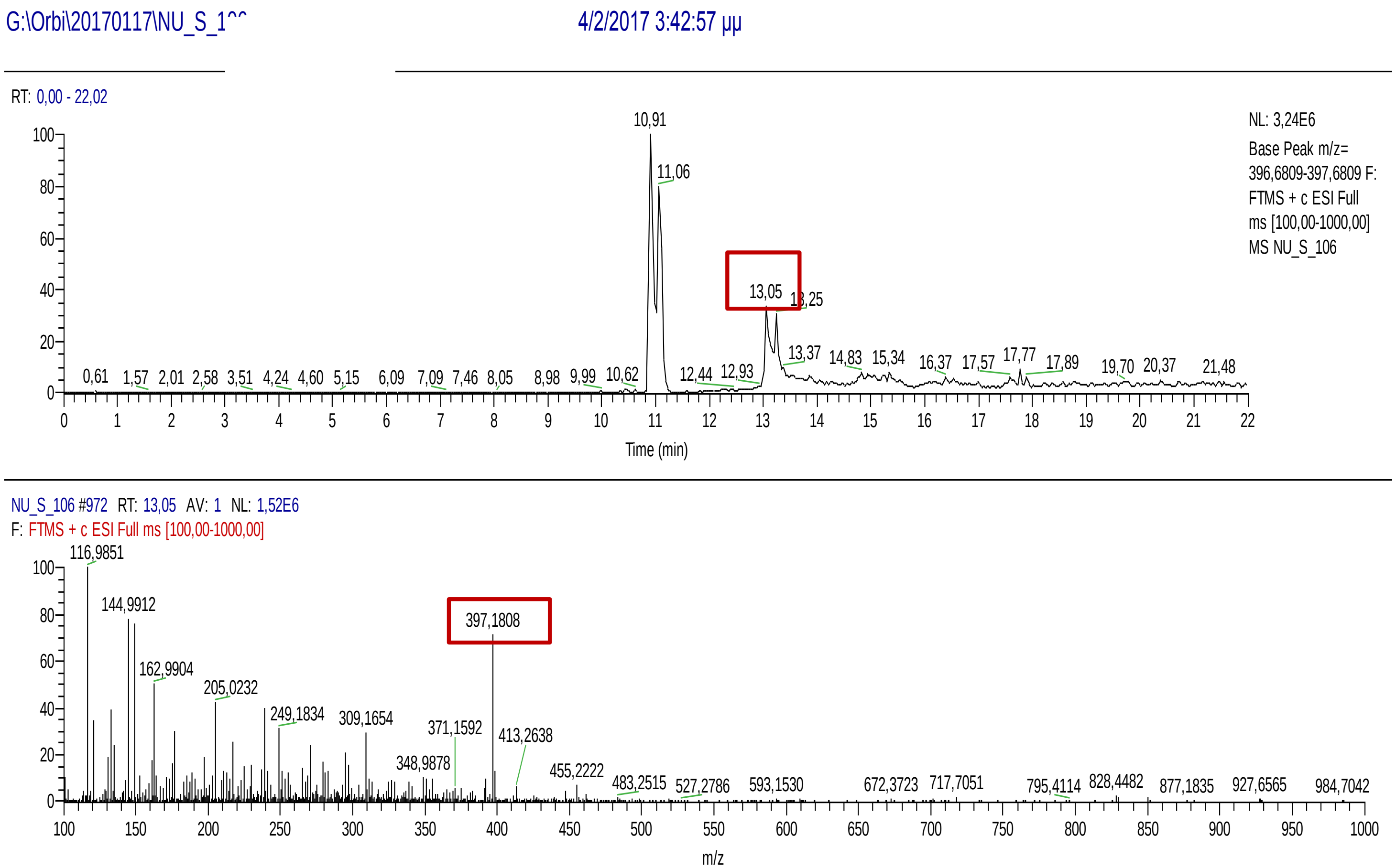
Results for TPs and metabolites







Results for TPs and metabolites



Results for TPs and metabolites

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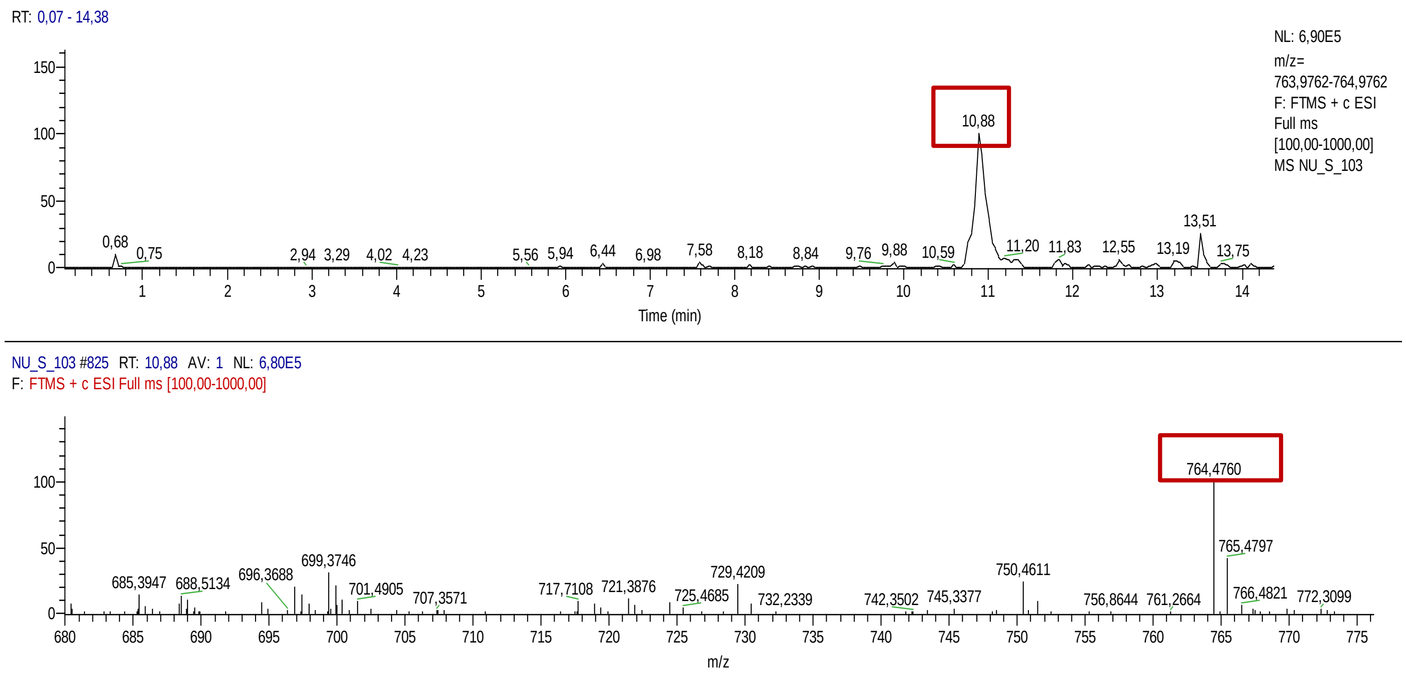
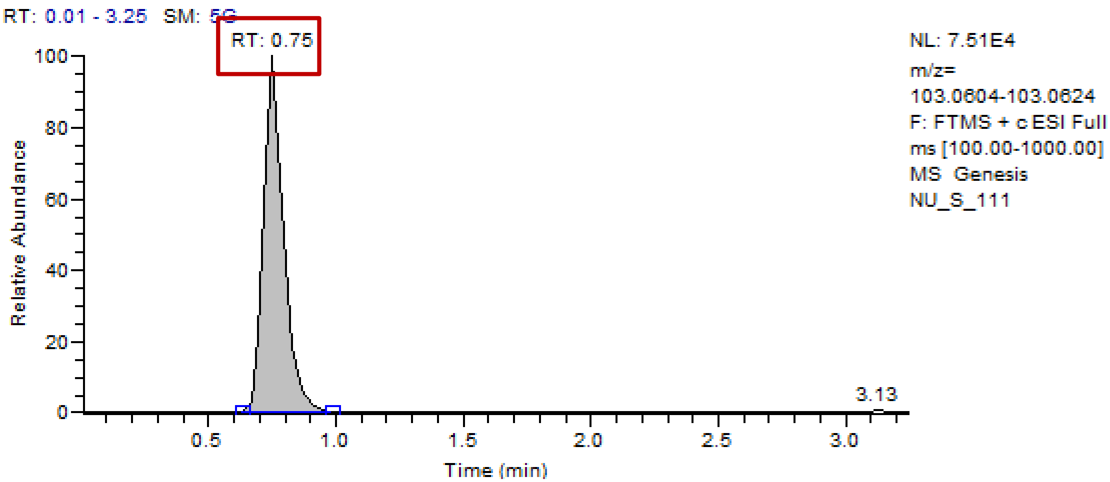
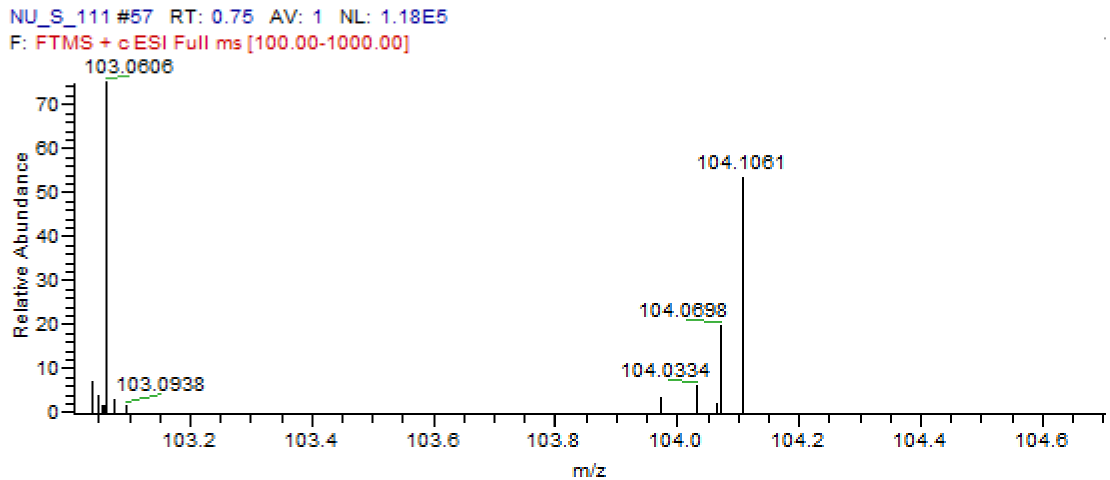


Results for TPs and metabolites

Quanylurea, Rt: 0.75

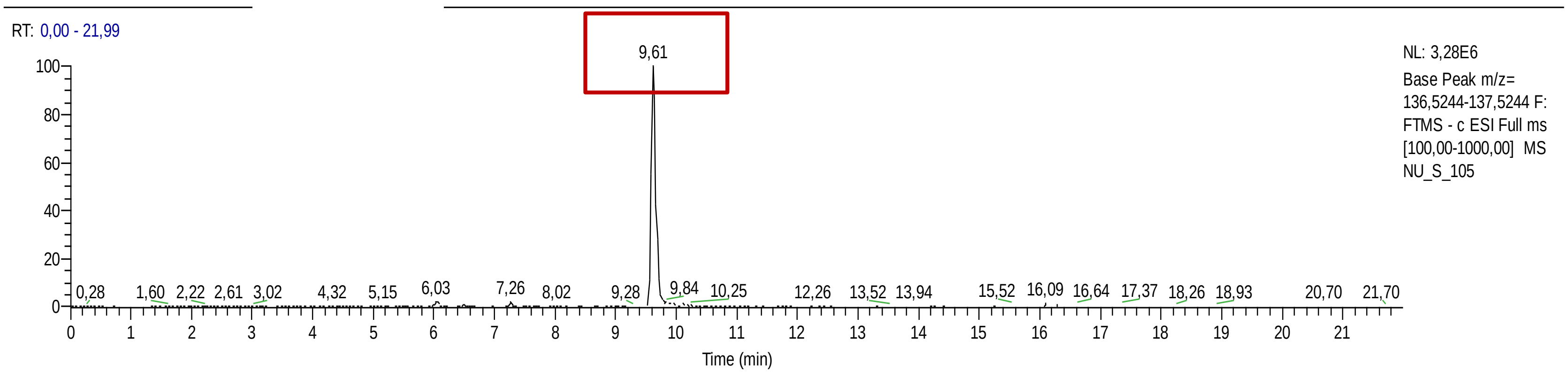


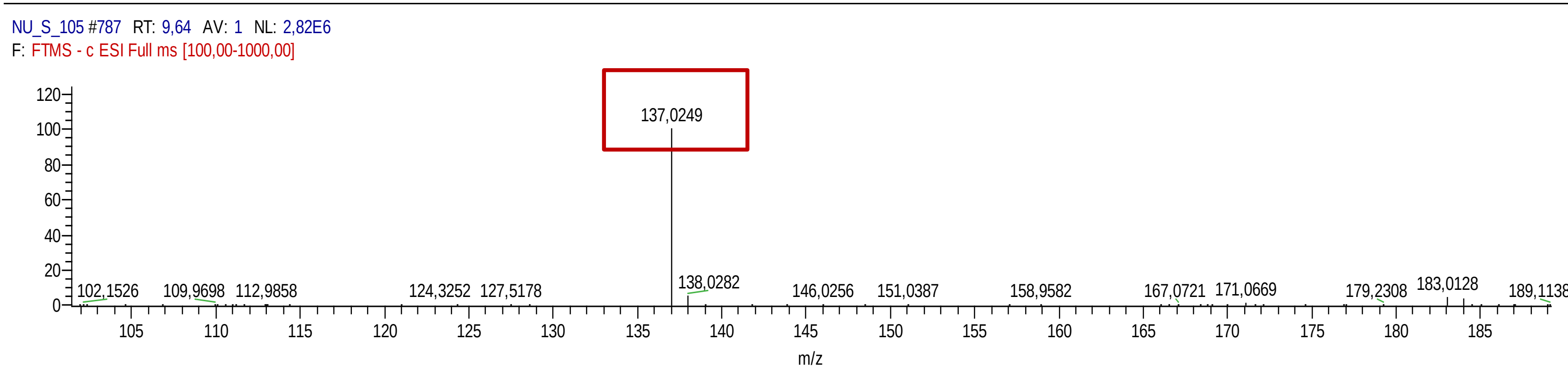


Salicylic acid, Rt: 9.61

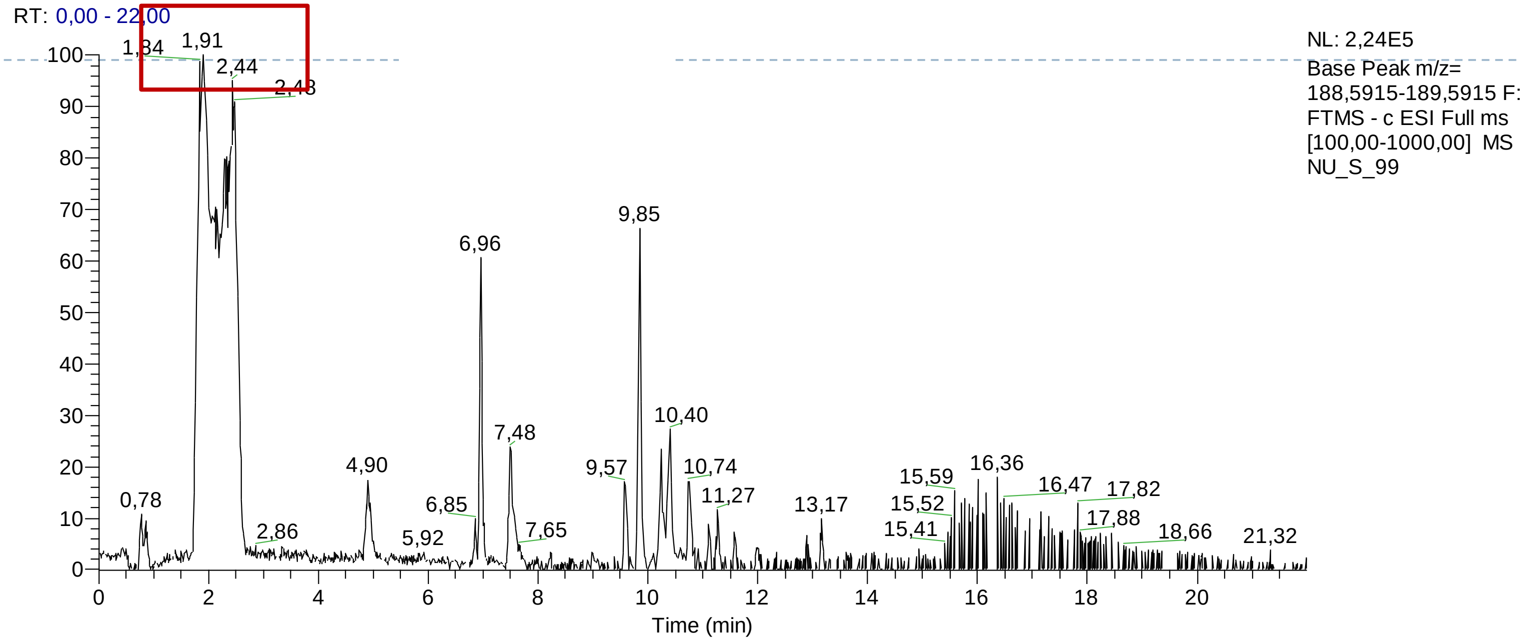
G:\Orbi\20161207\Negative

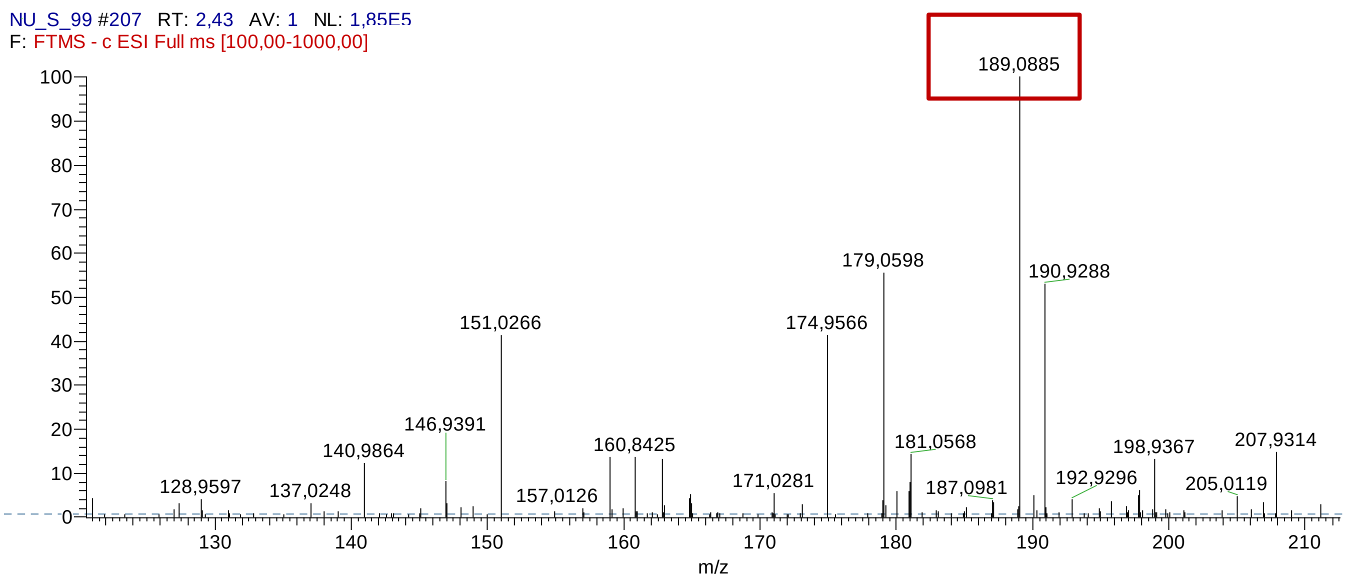
21/12/2016 10:09:31 μμ





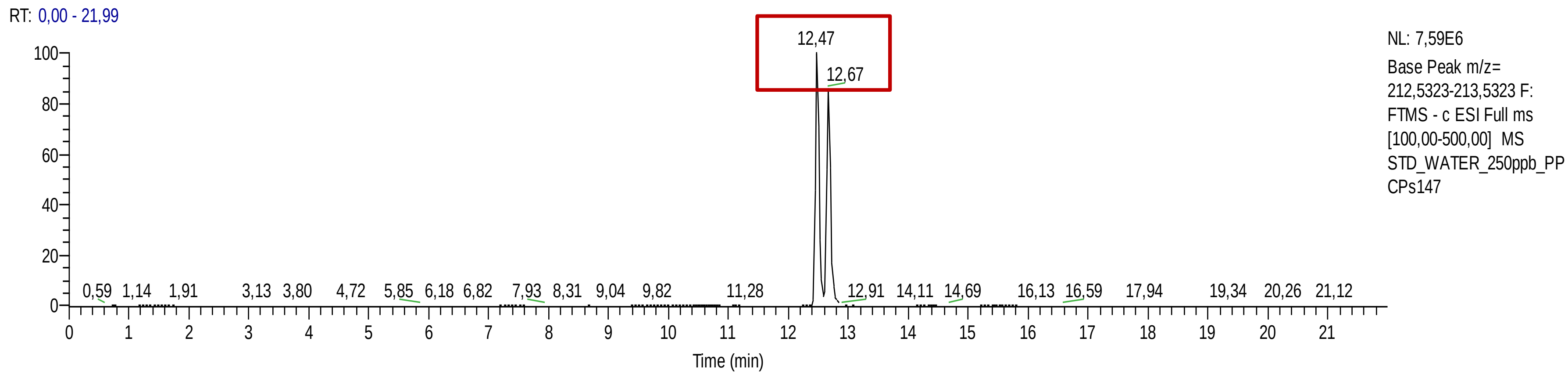
1-OH Ibuprofen, Rt: 1.91

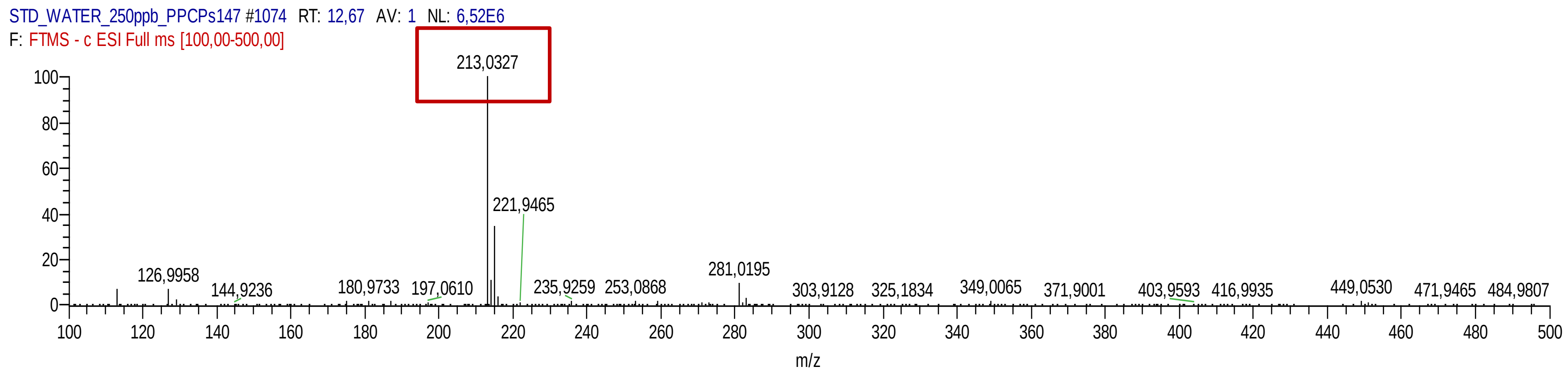




Clofibric acid, Rt: 12.6

15/12/2016 4:39:52 πμ





HRMS
Multiresidue Method

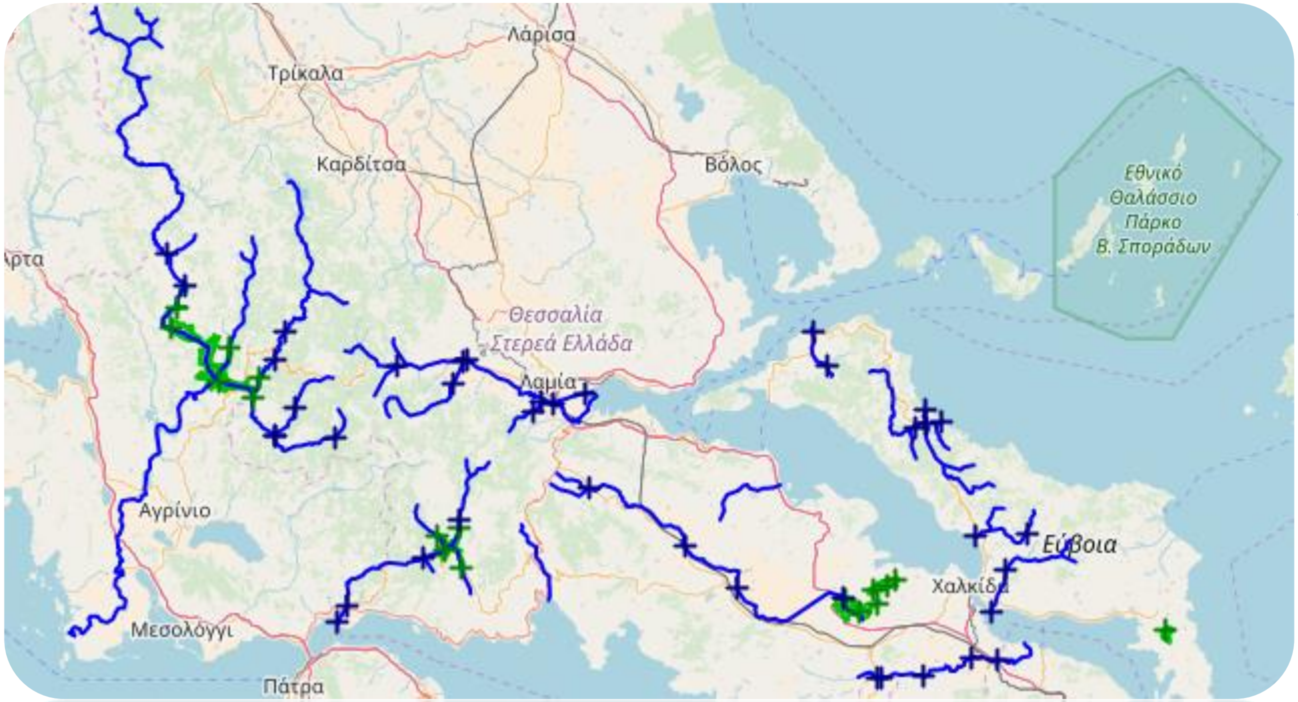
Target + Suspect Screening

A home-made database
>350 compounds

Data from
>500 parent
Compounds

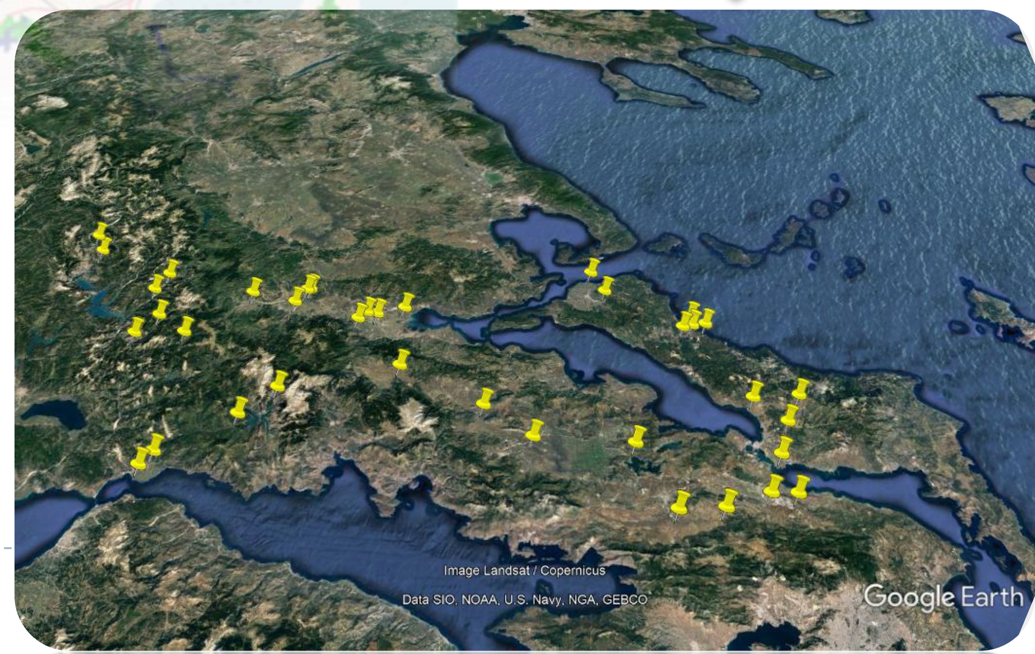
The work is in progress....

>850
Compound Screening



- ✓ Rivers
- ✓ Lakes
- ✓ Canals

The work is in progress….



To conclude

The application of rapid screening methods for the identification and detection of unknown ECs by LC–HRMS is still under development

Suspect screening is a promising tool for the tentative detection of emerging contaminants for which pure standards are not available, such as transformation products

Open source and commercial software such as Mass Frontier and Mass Fragmenter are available to predict mass spectral fragments using different fragmentation rules, but they need a lot of improvement.

To conclude

From recent published data it is evident that the presence of TPs in the aquatic environment is not negligible and that TPs clearly contribute to the environmental and human health risk of Pharmaceuticals

A tentative method to prioritize TPs is very important, especially due to the large number of TPs that may form through various environmental transformation processes

conclusions….

Research in the field of ECs & TPs is ongoing

&

a great progress is anticipated in the near future!!

Acknowledgments….

The Unit of high resolution analysis-ORBITRAP-LC-MS of the Aristotle University of Thessaloniki for providing access to the facilities

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Advanced Microextraction Approaches Based on Novel nano- Polymers to Measure Pharmaceuticals, Personal Care Products (PPCPs) and their Transformation Products (TPs) in the Aquatic Environment

Ευρωπαϊκή Ένωση
Ευρωπαϊκό Κοινωνικό Ταμείο
ΕΠΙΧΕΙΡΗΣΙΑΚΟ ΠΡΟΓΡΑΜΜΑ
ΕΚΠΑΙΔΕΥΣΗ ΚΑΙ ΔΙΑ ΒΙΟΥ ΜΑΘΗΣΗ
επένδυση στην κοινωνία της γνώσης
ΥΠΟΥΡΓΕΙΟ ΠΑΙΔΕΙΑΣ, ΔΙΑ ΒΙΟΥ ΜΑΘΗΣΗΣ ΚΑΙ ΘΡΗΣΚΕΥΜΑΤΩΝ
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ΕΣΠΑ 2007-2013
πρόγραμμα για την ανάπτυξη
ΕΥΡΩΠΑΪΚΟ ΚΟΙΝΩΝΙΚΟ ΤΑΜΕΙΟ
Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

Thank you for your attention!

dlambro@chem.auth.gr

Ευχαριστώ!


Thessaloniki


thank you
danke
謝謝
ngiyabonga
teşekkür ederim
gracias
dank je
спасибо
bedankt
dziękuje
obrigado
sukriya
kop khun krap
go raibh maith agat
mochchakkeram
tapadh leat
arigatō
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grazie
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sagolun
ありがとう
takk
taiku