molecules

MDPI

Supplementary Materials

Article

Evaluation of the possibility of using hydroponic cultivations for the removal of pharmaceuticals and endocrine disrupting compounds in municipal sewage treatment plants

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Tables and Figures content:

Table S1 Literature data concerning on the studies of usefulness of hydroponically cultivated plants for removing target compounds from sewage stream

Pharmaceuticals/EDCs	Type of CW / laboratory system / full-scale system in WWTP	Plant	Method of determining target compounds in plant material			MQL [ng/g d.w.]	Concentration in plant material [ng/g d.w.]	Concentration in untreated sewage [ng/L]	Concentration in treated sewage [ng/L]	Elimination efficiency from wastewater stream (EE%)	Ref.
			Extraction	Clean-up	Detection						
18 analytes e.g. Ibuprofen Ketoprofen Naproxen Diclofenac Salicylic acid Caffeine Carbamazepine	*Mesocosm-scale*	*Typha angustifolia Phragmites australis*	Only roots ASE acetone/hexane, 1:1; v/v; two extraction cycles of 13.5 min at a temperature of 104 °C	Clean-up A florisil column with different elution of the neutral/acidic fractions. Neutral fraction directly analysed, and the acidic fraction derivatized with TMSH	GC-MS/MS	17 20 29 30 19 31 22	Detail in Fig. 3 Ibuprofen Salicylic acid Caffeine detected Ketoprofen Naproxen Diclofenac Carbamazepine not detected Salicylic acid - the main substance detected in root tissues (123-2560 ng/g)	Detail in Table 1 in the range 250-19 000	Detail in Table 1 in the range 10 -5740	*T. angustifolia* a better performance	[27]
Paracetamol	*Pilot scale*	*Phragmites australis Typha latifolia*	Not detected in plant material			-	nd	Fig. 3.	Fig. 3.	The P*hragmites* bed 51.7% for a Hydraulic Loading Rate (HLR) of 240	[29]

										mm/d to 87% with 120 mm/d HLR and 99.9% with 30 mm/d. The *Typha* bed a similar behavior with percentages of removal slightly lower, ranging from 46.7% (HLR of 240 mm/d) to >99.9% (hydraulic loading rate of 30 mm/d). At the same HLR values the unplanted bed removed between 51.3% and 97.6%	
86 pharmaceuticals e.g. Diclofenac Ibuprofen Ketoprofen Naproxen Alpha Ethinylestradiol	*Full-scan*	*Salix alba* *Iris pseudacorus* *Juncus effuses* *Callitriche palustris* *Carex caryophyllea*	20 g dry weight of each sample 1 L acetonitrile with 0.5% formic acid (v:v) under gentle	SPE SiO_2 cartridge system	UPLC-MS/MS		Ibuprofen was detected in all plant samples	in the range 1 ng/ L and 1000000 ng/L 6483 5004 604 22464 EE2 1140626	7377 3129 319 19904 EE2 901618	In detail Fig. 6. drug removal efficiency within the SFTW followed a seasonal trend, with the best	[32]

Beta Estradiol Estriol			mixing over a period of 24 h at 4 °C					- E3 17245	- E3 2860	results occurring in the summer	
8 Compounds, e.g. Caffeine Carbamazepine Ibuprofen Fluoxetine Gemfibrozil	*Full-scan*	*Typha angustifolia*	The root and shoot samples anhydrous sodium sulfate and methanol; UAE 35°C for 15 min. and then centrifuged at 3500 rpm for 5 min.	SPE	LC-MS/MS	nd	Bioconcentration factors (BCFs) in *Typha angustifolia*, ranged between 60 to 2000 Up to several hundred ng/g for caffeine	Detail in Figs. 1 and 2	Detail in Figs. 1 and 2	Between -1588% and 95.1%	[33]
Sulfamethoxazole Atenolol Dilantin Carbamazepine Diazepam Diclofenac Naproxen Triclosan	Full-scale	*Typha sp.*	MAE	SPE (nd)	LC-MS/MS	nd	<2.5 <2.5 <10 <5.0 <5.0 <2.5 <5.0 <10	nd	in the range 0-900	Atenolol/Carbamazepine/Diclofenac/Triclosan 60–100% Dilantin/Diazepam/Sulfamethoxazole 0-60%	[34]
Triclosan	Pilot-scale	*Ceratophyllum demersum Lemna sp. Paspalum spp. Pontederia cordata Potamageton spp.*	QuEChERS 30 mL 1:1 hexane:ethyl acetate	The lipid clean-up	GC-MS	MDL: 17 (shoot) 6 (root)	26 Triclosan readily accumulates in the root tissues of free living	-	-		[35]

		Sagittaria graminea *Typha sp.*					wetland plants and show species specific differences				
Diclofenac	Laboratory system	*Typha latifolia*	QuEChERS 1 ml 0.1 M HCl:ACN (1:1, v/v)	SPE, StrataX 30 mg	LC-MS	nd	0.2% of the initial amount of diclofenac (1 mg/L) detected in roots and leaves during one week exposure	nd	nd	nd	[36]
65 pharmaceuticals e.g. Diclofenac Ibuprofen Naproxen	Full-scale	*Ceratophyllum demersum* *Elodea spp.* *Glyceria maxima* *Myriophyllum spicatum* *Nymphaeaceae* *Schoenoplectus lacustris* *Typha sp.*	Not detected in plant material			-	-	 380 – 510 660 – 1500 64 – 290	 290 – 350 80 – 740 16 - 190	 24 – 36 5 – 88 34 – 75 (estimated removal rates)	[40]
Carbamazepine Clofibric acid Ibuprofen	Microcosm-scale	*Typha sp.*	Not detected in plant material			-	-	nd	nd	97 75 96	[41]
Carbamazepine Clofibric acid Diclofenac Ibuprofen Ketoprofen	Full-scale	*Phragmites australis* *Typha latifolia*	Not detected in plant material			-	-	370 70 1250 40 2100 340	23 46 188 2 42 95	39 34 85 96 98 72	[42]

Naproxen									
Carbamazepine Clofibric acid Diclofenac Flunixin Ibuprofen Ketoprofen Naproxen	Full-scale	*Phragmites australis* *Typha latifolia*	Not detected in plant material	-	-	370 70 1250 1060 40 2100 340	-	30-47 32-36 73-96 0-64 95-96 97-99 52-92	[43]
Caffeine Diclofenac Ibuprofen Naproxen Triclosan Clofibric acid	Microcosm-scale	*Salvinia molesta* *Lemna minor* *Ceratophyllum demersum Elodea canadensis*	Not detected in plant material	-	-	nd	nd	81-99 99 44-77 40-53 96-99 16-23	[44]
73 target pharmaceuticals and e.g. Paracetamol Diclofenac Ibuprofen Naproxen Nadolol	Pilot-scale	*Phragmites australis*	Not detected in plant material	-	-	 30 284 81 178 < LOD	 16 271 58 114 < LOD	 98 38 94 86 100	[45]
Paracetamol Diclofenac Ibuprofen	*Mesocosm-scale*	*Phragmites australis*	Not detected in plant material	-	-	1500 – 34000 1900 – 2800 39900 – 83900	6390 760 18110	>95 32 - 70 52 - 85	[46]
Cotinine Caffeine Fluoxetine Paracetamol Naproxen Ibuprofen	*Full-scale*	*Phragmites australis* *Hydrocottle spp.*	Not detected in plant material	-	-	1097 25567 - 39300 10418 9922	12 28 - 10 90 38	>99 >99 - >99 >99 >99	[47]

Gemfibrozil Atenolol Nadolol Propranolol Metoprolol Sotalol						1652 1442 30 - 211 174	600 99 7 - 17 121	95 >99 >99 - >99 82	
Ketoprofen Naproxen Ibuprofen Diclofenac Salicylic acid Carbamazepine Caffeine	*Mesocosm-scale*	*Typha angustifolia* *Phragmites australis*	Not detected in plant material	-	-	1790; <890 3530; 1350 24190; 8380 830; 370 9930; 10290 1360; 1520 67340; 22590	nd	Winter / Summer 33-50 / 100 27-66 / 27-83 51-54 / 85-96 17 – 52 76-85 / 87-89 24-36/ 48 58-65 / 99 *P. australis* a better performance	[48]
Ketoprofen Naproxen Ibuprofen Diclofenac Salicylic acid Carbamazepine Caffeine	*Mesocosm-scale*	*Typha latifolia* *Salix atrocinerea*	Not detected in plant material	-	-	Table 1 concentrations at each sampling point	<890 160 990 430 1650 <1250 3570	77 – 81 73 – 85 42 – 99 65 – 87 94 – 97 - 83 - 96	[49]
Atenolol Caffeine Carbamazepine Diclofenac Glimepriride	Full-scale	*Acorus spp.* *Typha sp.*	Not detected in plant material	-	-	nd	nd	Presented in Fig. 2 Compounds with greater hydrophilicity could be more	[50]

Ibuprofen Naproxen Sulfamethoxazole								efficiently removed than hydrophobic compounds	
Carbamazepine Diclofenac Ibuprofen Naproxen	Pilot-scale A Membrane Biological Reactors (MBR) and an Activated Sludge (AS) unit, combined with vertical flow reed beds (VFRB)	nd	Not detected in plant material	-	-	VFRB AS / VFRB MBR nd / nd nd / nd 3110 / 800 1810 / 840	nd / nd nd / nd 530 / 90 270 / 150	Both systems reduced the discharge of micropollutants at comparable rates, ranging from 0.3 to 0.9 ppb for acidic drugs. A green emerging technology used for post-treatment, filtration through vertical flow reed-beds, led to a general improvement of effluent quality	[51]
Diclofenac Ibuprofen Naproxen	*Pilot-scale*	*Phragmites australis*	Not detected in plant material	-	-	20 – 260 23600 - 46800 1530 – 3940	nd	97-99	[52]

nd – Not described in detail in cited literature

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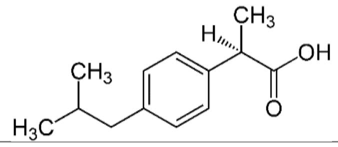
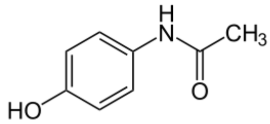
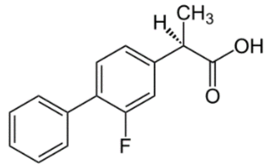
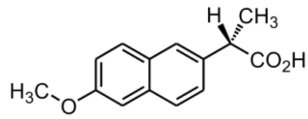
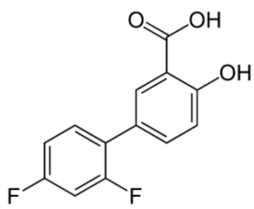
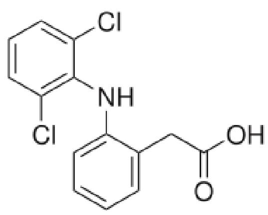
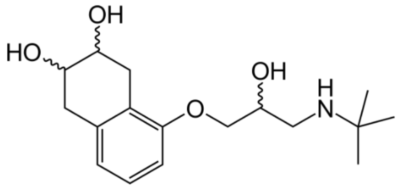
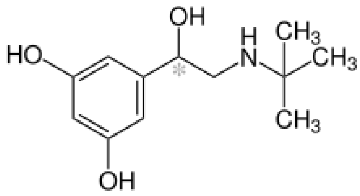
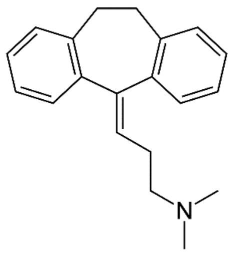
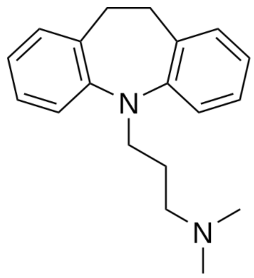
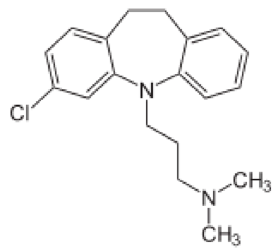
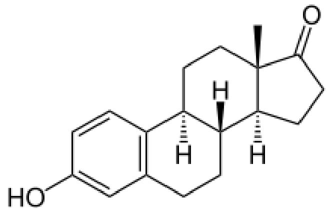
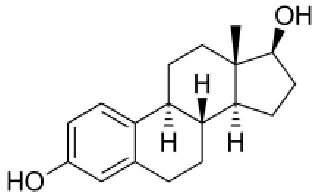
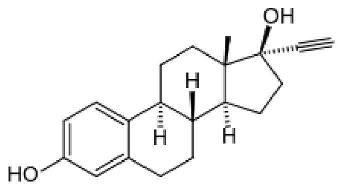
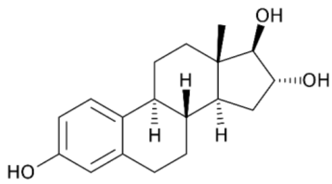
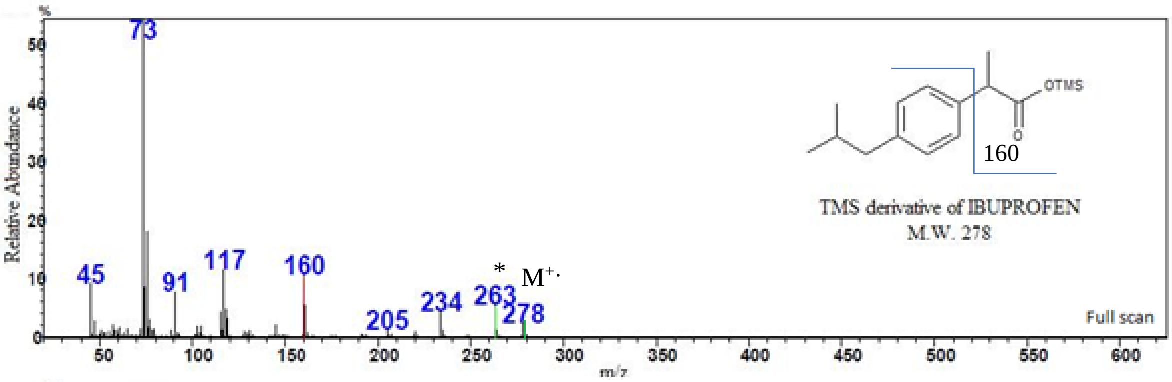
Table S2 Chemical structures and physical and chemical properties of selected non-steroidal anti-inflammatory drugs (NSAIDs), analgesics, β-blockers, β-agonists, antidepressant drugs and estrogen-based hormones

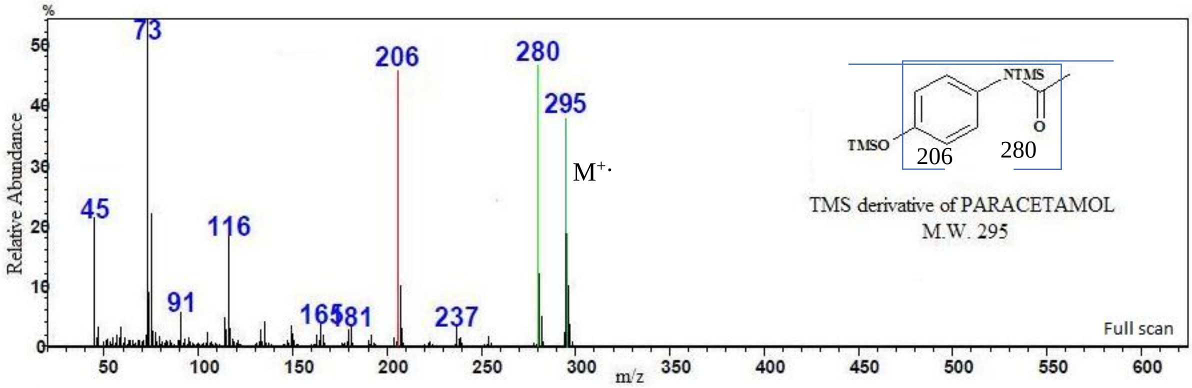
Number	Trade name/CAS number	Function	pK_a	LogP	Chemical structure
1	Ibuprofen 15687-27-1	Analgesic/ NSAIDs	4.91	3.97	
2	Paracetamol 103-90-2	Analgesic	9.38	0.46	
3	Flurbiprofen 5104-49-4	Analgesic/ NSAIDs	4.42[a]	4.16	
4	Naproxen 22204-53-1	Analgesic/ NSAIDs	4.15	3.18	
5	Diflunisal 22494-42-4	Analgesic/ NSAIDs	2.69[a]	4.44	
6	Diclofenac 15307-86-5	Analgesic/ NSAIDs	4.15	4.51	

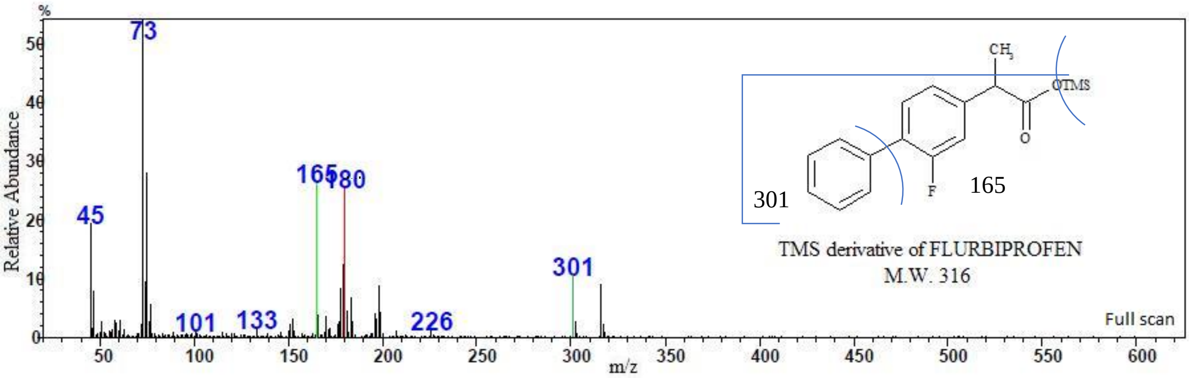
7	Nadolol 42200-33-9	β-blockers	9.67	0.81	
8	Terbutaline 23031-25-6	β_2-agonists	8.86 [a]	0.90	
9	Amitriptyline 50-48-6	Antidepressant drugs/analgesic	9.40	4.92	
10	Imipramine 50-49-7	Antidepressant drugs	9.40	4.80	
11	Clomipramine 303-49-1	Antidepressant drugs	9.20 [a]	5.19	

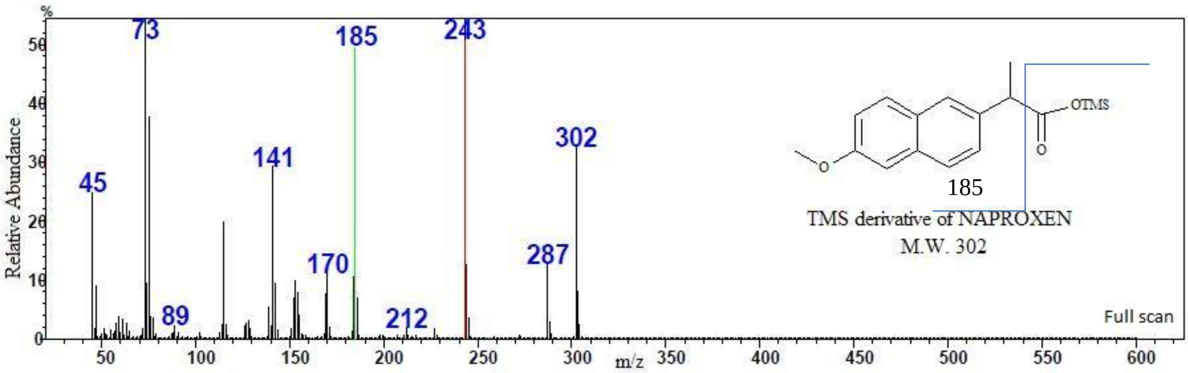
12	Estrone (E1) 53-16-7	Hormones	10.33[a]	3.13	
13	17β-estradiol (E2) 50-28-2	Hormones	10.33[a]	4.01	
14	17α-ethinylestradiol (EE2) 57-63-6	Hormones	10.33[a]	3.67	
15	Estriol (E3) 50-27-1	Hormones	10.54	2.45	

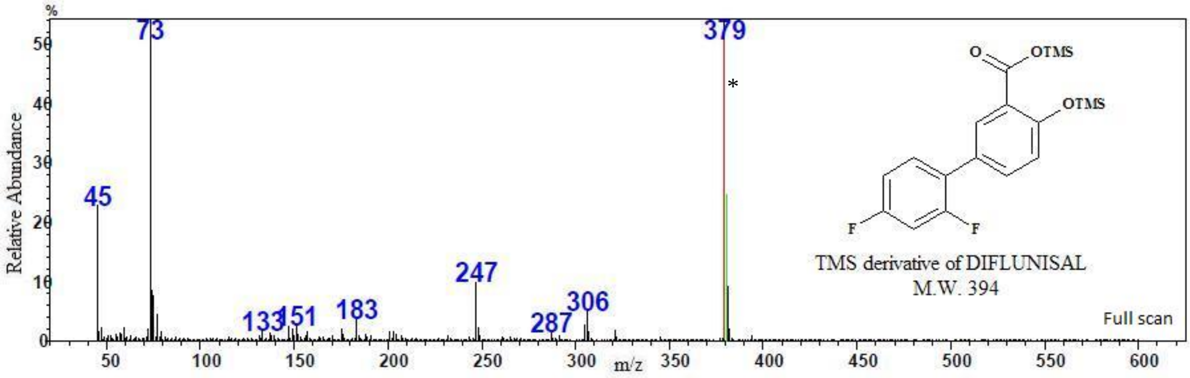
[a] Predicted property based on ChemAxon


%
Relative Abundance
73
45
91
117
160
205
234
263
278
* M+·
Full scan
m/z
160
OTMS
O
TMS derivative of IBUPROFEN
M.W. 278

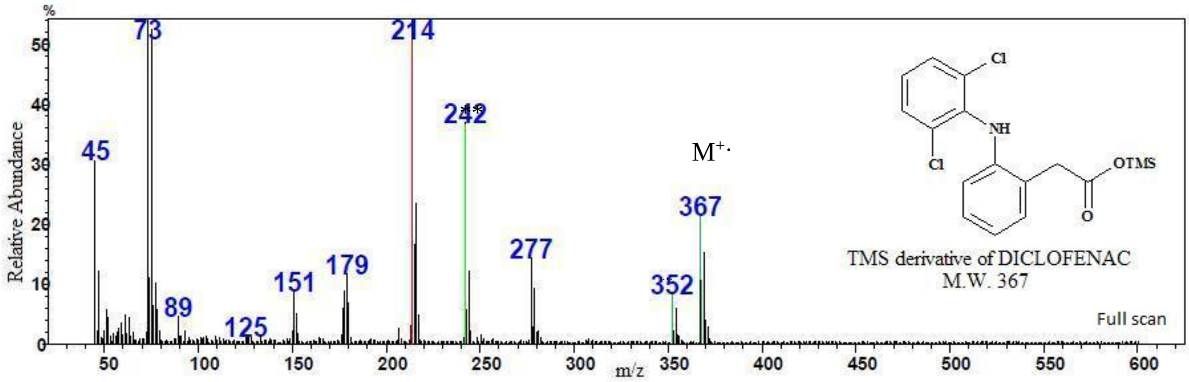

%
Relative Abundance
73
206
280
295
M+·
45
116
91
165
181
237
Full scan
m/z
NTMS
O
TMSO
206
280
TMS derivative of PARACETAMOL
M.W. 295


%
Relative Abundance
73
45
165
180
301
101
133
226
Full scan
m/z
CH3
OTMS
O
F
301
165
TMS derivative of FLURBIPROFEN
M.W. 316

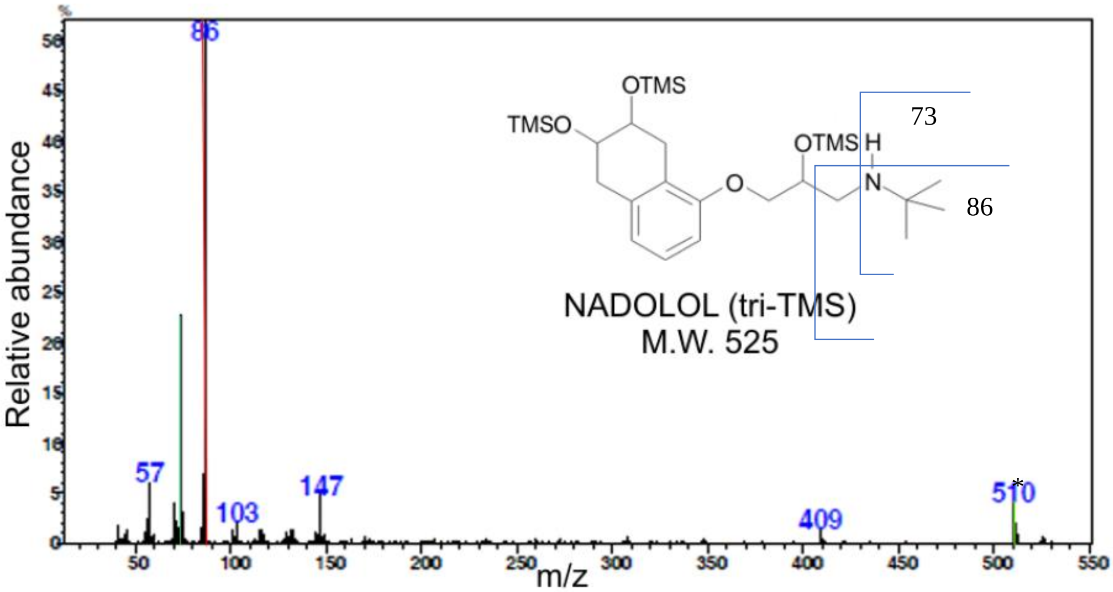

%
Relative Abundance
73
185
243
302
45
141
170
287
89
212
Full scan
m/z
OTMS
O
O
185
TMS derivative of NAPROXEN
M.W. 302



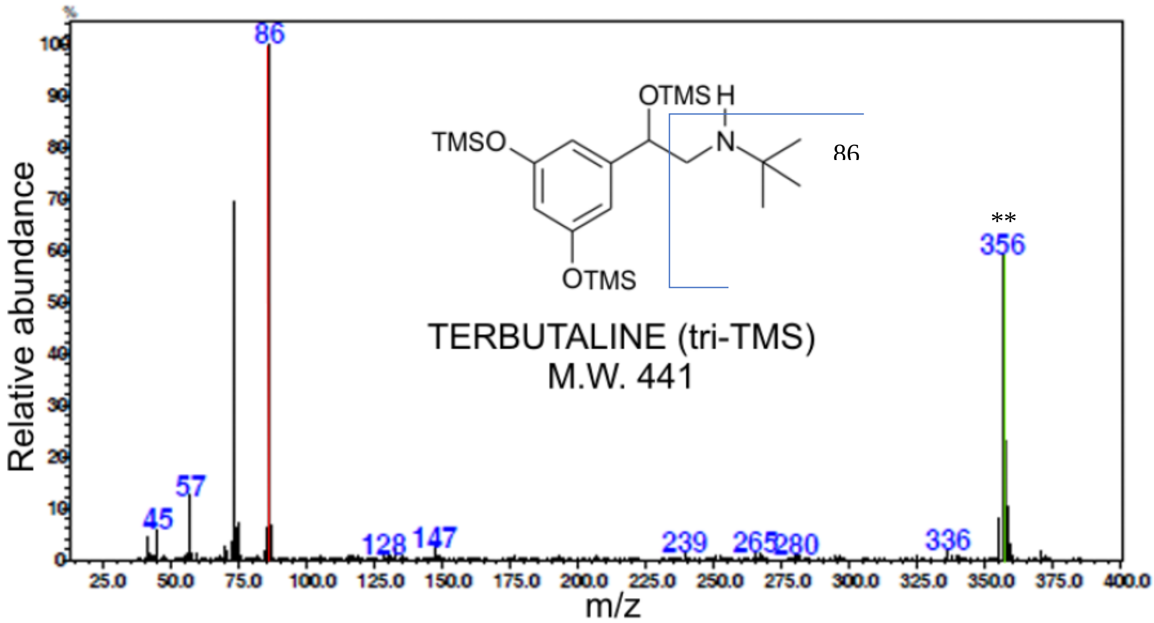
Relative Abundance
m/z
73
379
45
247
133
151
183
287
306
TMS derivative of DIFLUNISAL
M.W. 394
Full scan



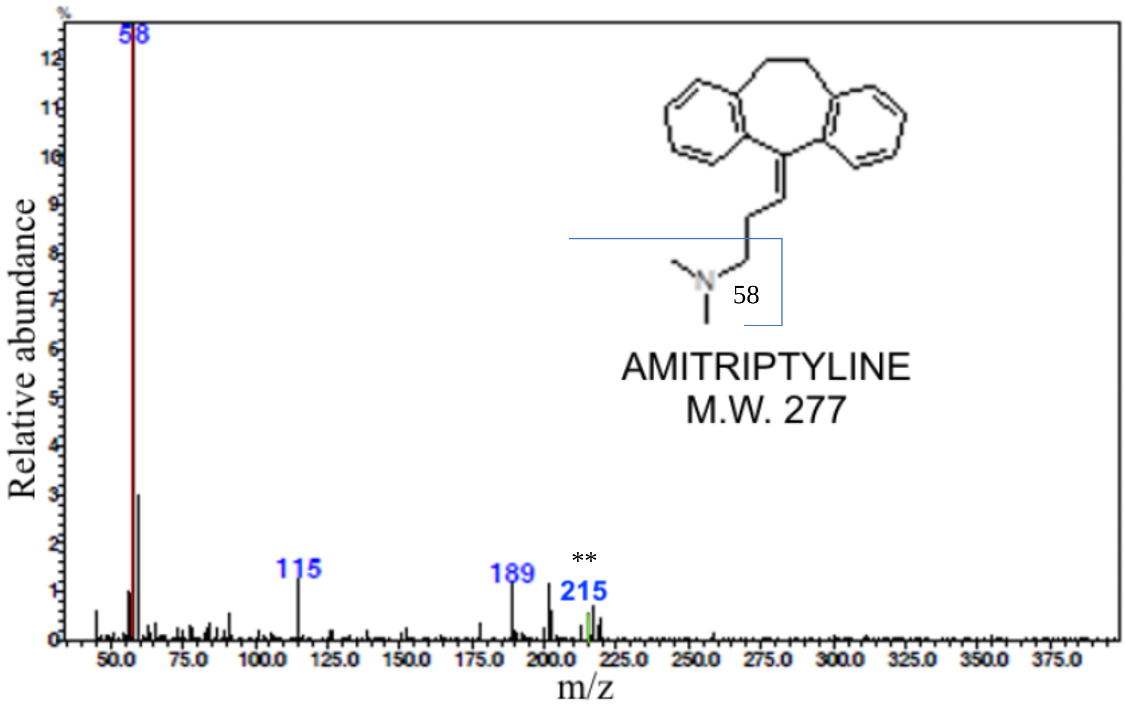
Relative Abundance
m/z
73
214
242
45
M+·
367
89
125
151
179
277
352
TMS derivative of DICLOFENAC
M.W. 367
Full scan



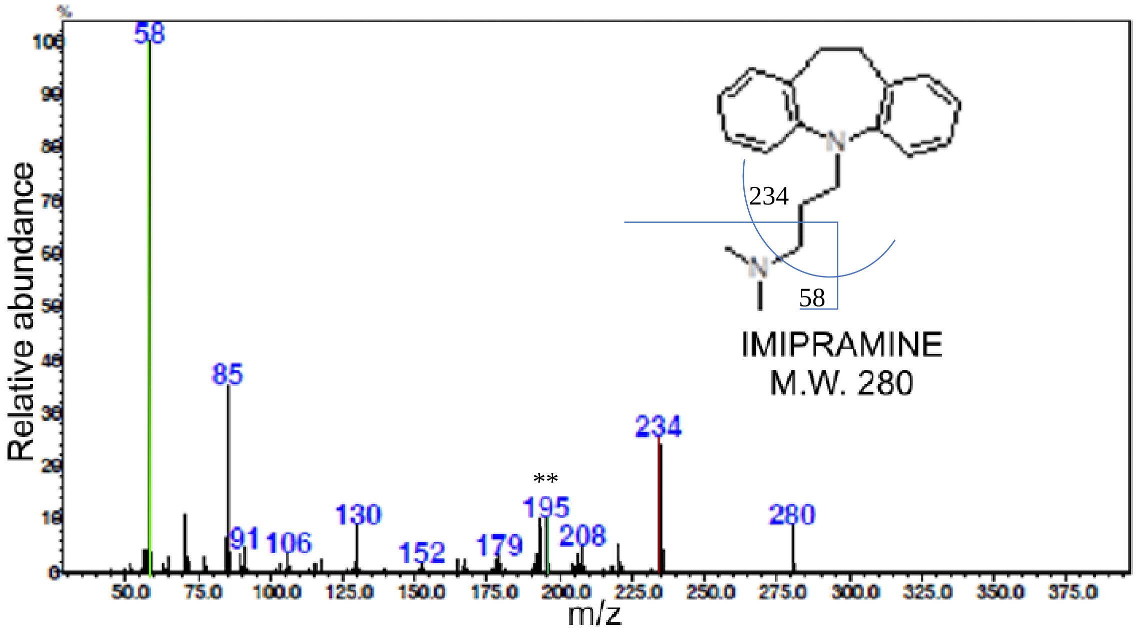
Relative abundance
m/z
86
57
103
147
409
510
OTMS
TMSO
OTMS
H
N
73
86
NADOLOL (tri-TMS)
M.W. 525

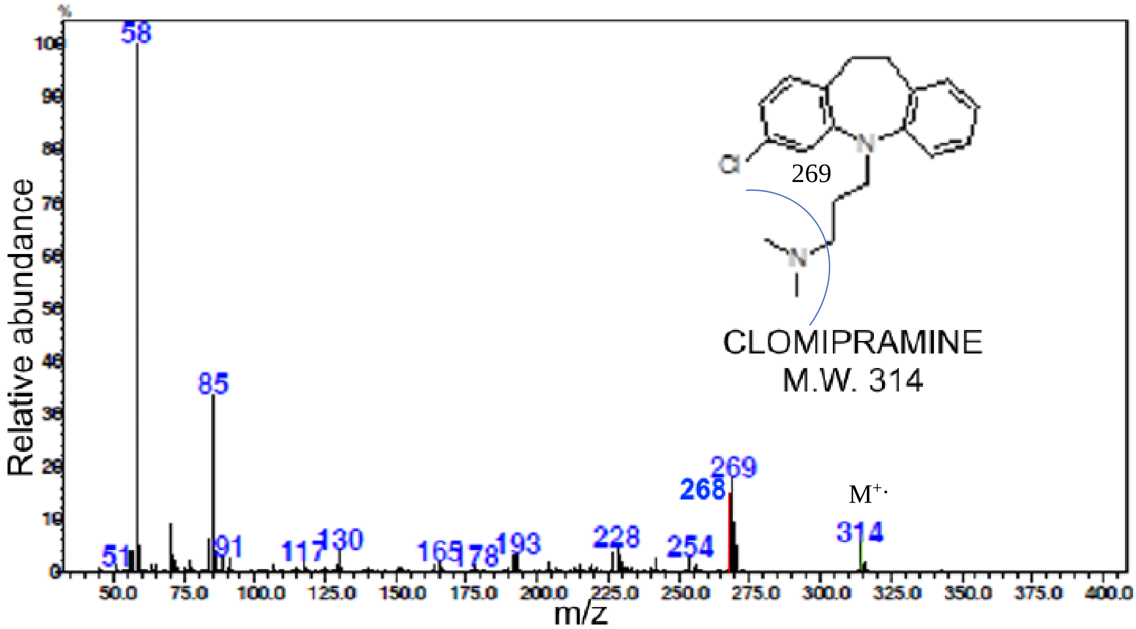


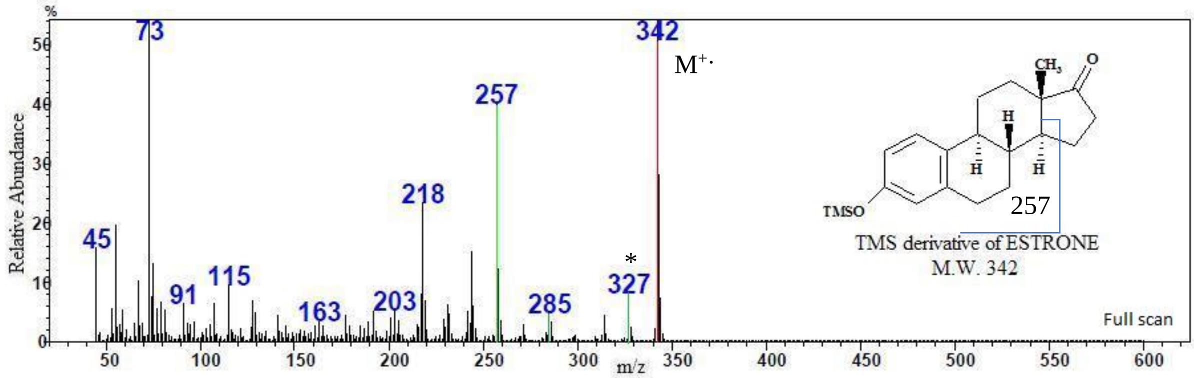
Relative abundance
m/z
86
57
45
128
147
239
265
280
336
**
356
OTMS H
TMSO
N
86
OTMS
TERBUTALINE (tri-TMS)
M.W. 441

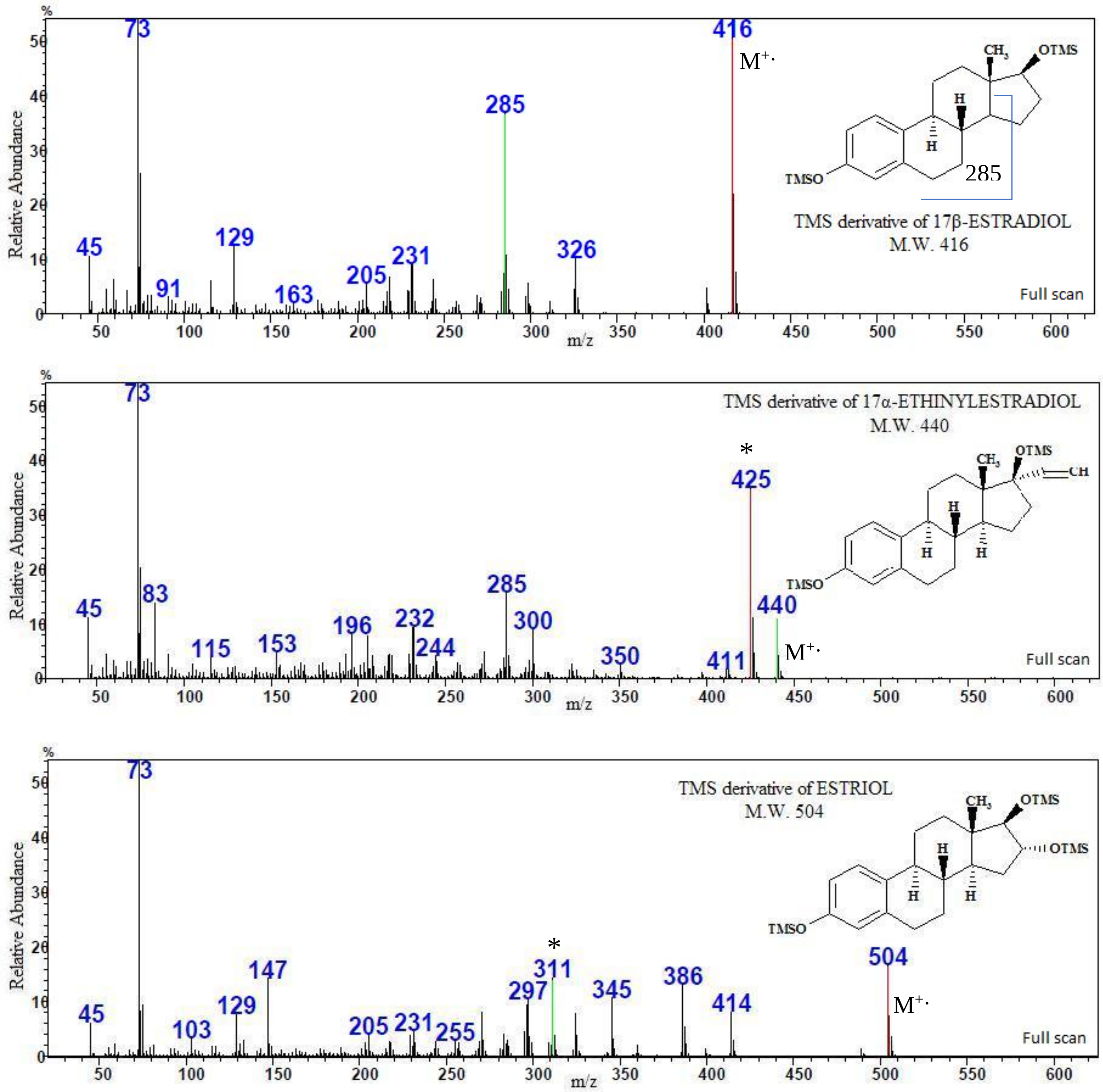


Relative abundance
m/z
58
115
189
**
215
N
58
AMITRIPTYLINE
M.W. 277


IMIPRAMINE
M.W. 280
234
58
**
Relative abundance
m/z


CLOMIPRAMINE
M.W. 314
Cl
269
M+·
Relative abundance
m/z


TMS derivative of ESTRONE
M.W. 342
TMSO
257
M+·
*
Full scan
Relative Abundance
m/z



* ion [M-15] where 15 is derived from detachment of one CH_3 group from TMS

** The ion is formed in a complicated process of intramolecular rearrangement

Figure S1 The mass spectra of target compounds with the MS fragments assignation

Figure S2 Activated sludge chamber with a system of constructed wetlands in the investigated Municipal Wastewater Treatment Plant in Sochaczew (Mazowieckie Voivodeship, Poland)

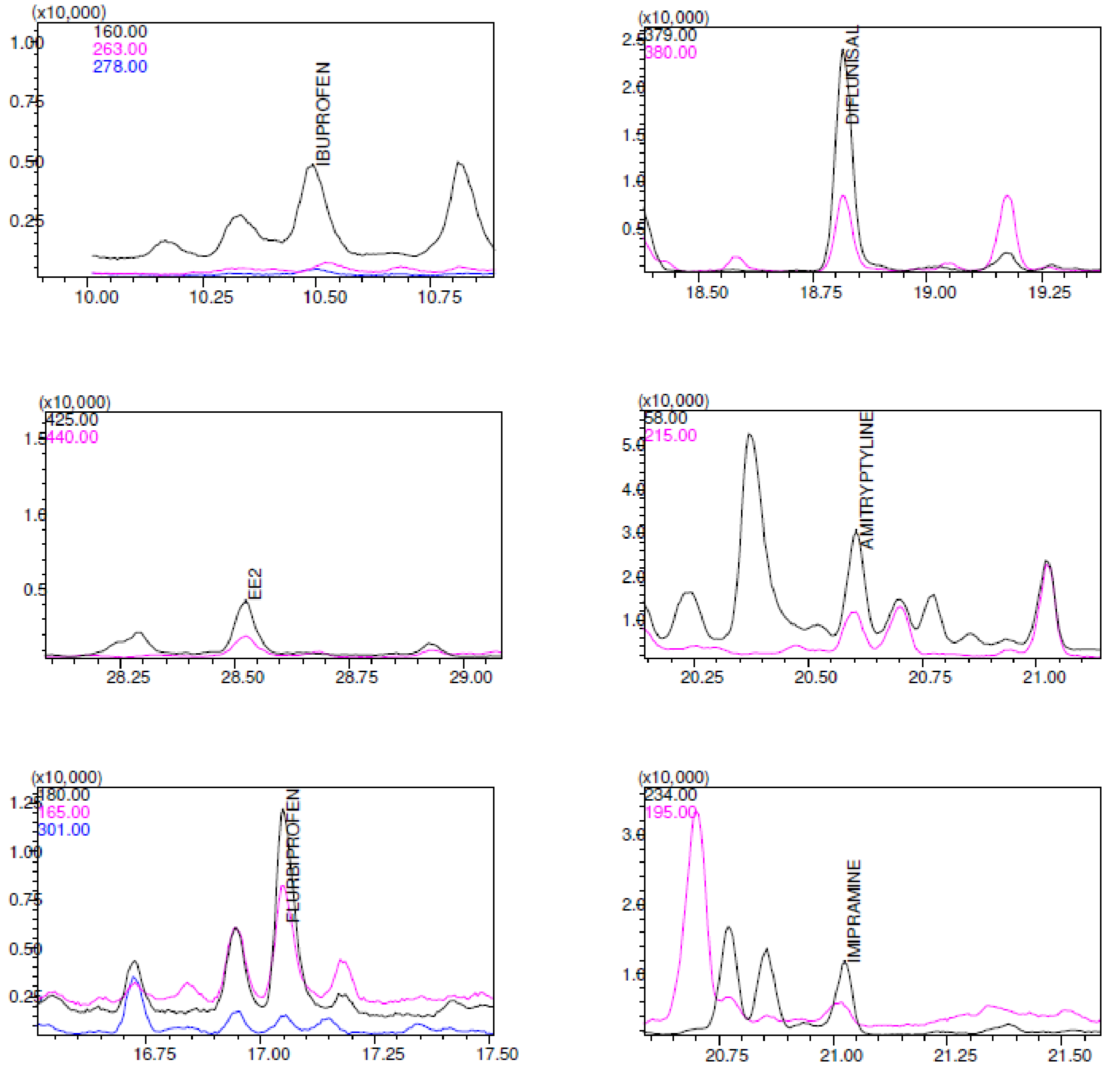


Figure S3 Example chromatogram with marked SIM ions for determined target compounds in real Papyrus (*Cyperus papyru*) samples

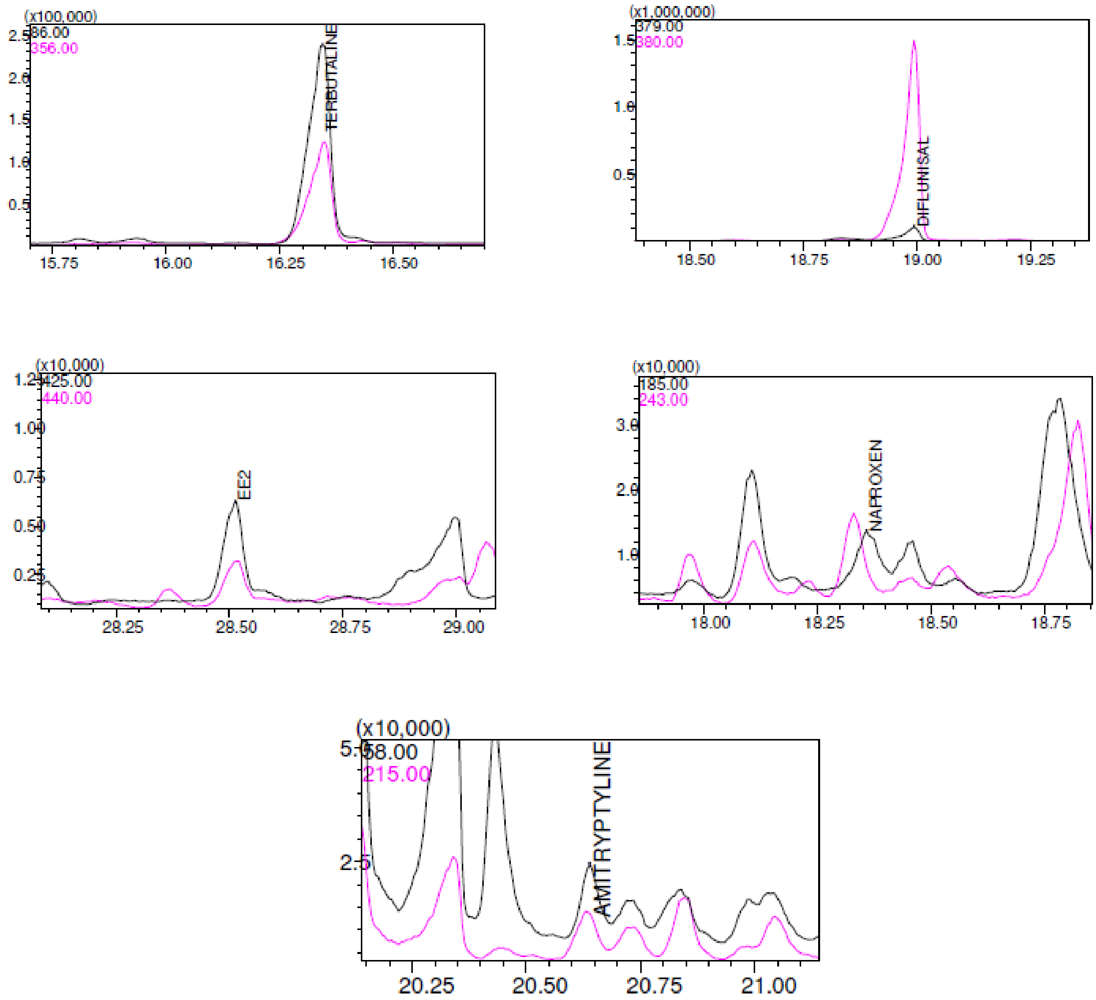


Figure S4 Example chromatogram with marked SIM ions for determined target compounds in real Yellow pimpernel (*Lysimachia nemorum*) samples

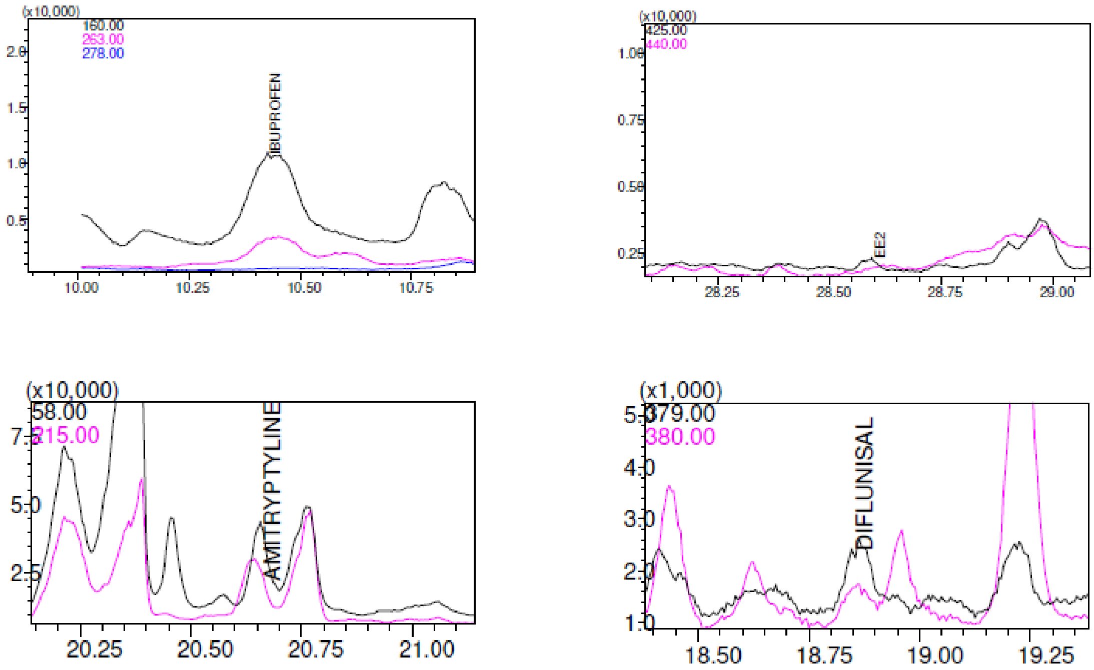


Figure S5 Example chromatogram with marked SIM ions for determined target compounds in real European spindle (*Euonymus europaeus*) samples