Supplementary information

Improving the detectability of microplastics in river waters by single particle inductively coupled plasma mass spectrometry

Celia Trujillo [1], Josefina Pérez-Arantegui [1], Ryszard Lobinski [2,3] and Francisco Laborda [1] *

[1] Group of Analytical Spectroscopy and Sensors (GEAS), Institute of Environmental Sciences (IUCA), University of Zaragoza, Pedro Cerbuna 12, 50009, Zaragoza, Spain; ctrujillo@unizar.es

[2] Université de Pau et des Pays de L'Adour, E2S UPPA, CNRS, IPREM UMR 5254, Hélioparc, 64053, Pau, France; ryszard.lobinski@univ-pau.fr

[3] Chair of Analytical Chemistry, Department of Chemistry, Warsaw University of Technology, ul. Noakowskiego 3, 00-664 Warszawa, Poland; ryszard.lobinski@pw.edu.pl

* Correspondence: flaborda@unizar.es; Tel.: +34 976762252

2.3. River water samples.

**Table S1.** List of rivers studied and locations of the sampling points.

Sample identification	River	Location	Longitude	Latitude	Additional information
RW01	Segre	Torres de Segre	0⁰ 30' 46,035'' E	41⁰32' 8,665'' N	rural area
RW02	Noguera Ribagorzana	Corbins	0⁰ 41' 44,807'' E	41⁰ 41' 42,562'' N	rural area
RW03	Clamor Amarga	Zaidín	0⁰ 9' 23,535'' E	41⁰ 31' 32,533'' N	rural area
RW04	Cinca	Fraga	0⁰ 8' 55,230'' W	41⁰ 47' 29,677'' N	rural area
RW05	Alcanadre	Sariñena	0⁰ 8' 55,230'' W	41⁰ 47' 29,677'' N	rural area
RW06	Flumen	Albalatillo	0⁰ 9' 42,000'' W	41⁰ 44' 5,000'' N	rural area
RW07	Gállego	San Mateo de Gállego	0⁰ 48' 50,780'' W	41⁰ 43' 59,406'' N	rural area
RW08	Arba de Ríquel	Ejea de los Caballeros	1⁰ 13' 18,312'' W	42⁰ 7' 57,812'' N	rural area
RW09	Aragon Subordan	Javierregay	0⁰ 42' 19,17'' W	42⁰ 37' 47,026'' N	rural area
RW10	Aragón	Caparroso	1⁰ 38' 31,757'' W	42⁰ 21' 2,191'' N	rural area
RW11	Irantzu	Estella	2⁰ 0' 6,691'' W	42⁰ 38' 49,283'' N	rural area
RW12	Arakil	Irañeta	1⁰ 36' 3,279'' W	42⁰ 59' 28,331'' N	rural area
RW13	Queiles	Novallas	1⁰ 41' 18,153'' W	41⁰ 56' 56,288'' N	rural area
RW14	Alhama	Alfaro	1⁰ 45' 39,234'' W	42⁰ 10' 41,501'' N	rural area
RW15	Ega	Estella	2⁰ 0' 43,720'' W	42⁰ 38' 57,873'' N	upstream WWTP
RW16	Ega	Estella	2⁰ 0' 40,040'' W	42⁰ 38' 52,060'' N	downstream WWTP
RW17	Ega	Pamplona	1⁰ 43' 6,810'' W	42⁰ 48' 38,690'' N	upstream WWTP
RW18	Arga	Pamplona	1⁰ 43' 11,970'' W	42⁰ 48' 44,950'' N	downstream WWTP
RW19	Ebro	Tudela	1⁰ 34' 15,510'' W	42⁰ 3' 20,390'' N	upstream WWTP
RW20	Ebro	Tudela	1⁰ 33' 43,410'' W	42⁰ 3' 12,140'' N	downstream WWTP
RW21	Biadasoa	Bera de Bidasoa	1⁰ 41' 56,640'' W	43⁰ 16' 48,540'' N	upstream WWTP
RW22	Biadasoa	Bera de Bidasoa	1⁰ 41' 47,420'' W	43⁰ 16' 44,120'' N	downstream WWTP
RW23	Adour	Bayonne	1⁰ 21' 54'' W	43⁰ 29' 36'' N	rural area
RW24	Gabas	Poursiugues-Boucoue	0⁰ 21' 6'' W	43⁰ 33' 16'' N	rural area
RW25	Garonne	Toulouse	1⁰ 23' 17'' E	43⁰ 30' 41'' N	rural area
RW26	Save	Le Castéra	1⁰ 8' 60'' E	43⁰ 39' 9'' N	rural area
RW27	Echez	Maubourguet	1⁰ 1' 53'' E	43⁰ 28' 5'' N	rural area
RW28	Baïse	Fontrailles	0⁰ 23' 24'' E	43⁰ 20' 35'' N	rural area

3.2. Acid pre-treatment of river water samples.

Table S2. Mean size and recovery of microparticles subjected to pre-treatments with nitric acid.

Plastic microparticles: 2 μm PS (BCR). Mean ± standard deviation (n = 3).

Pre-treatment	HNO₃ (% *v/v*)	Mean size (μm)	Particle concentration ($\times 10^6$ L^{-1})	Particle recovery (%)
no	-	2.12 ± 0.02	-	-
heating (100ºC 5 min)				
	0.2	2.12 ± 0.03	189 ± 12	60
	1	2.12 ± 0.02	218 ± 13	69
	10	2.12 ± 0.02	207 ± 9	66
	50	2.04 ± 0.02	86 ± 17	27
without heating (room temperature, 24h)				
	10	2.20 ± 0.01	220 ± 5	65

Figure S1. Time scan corresponding to the analysis of bacteria *E.coli* labelled with Ag. (a) corresponds to the bacteria time scan without the treatment. (b) corresponds to the bacteria time scan with the treatment.
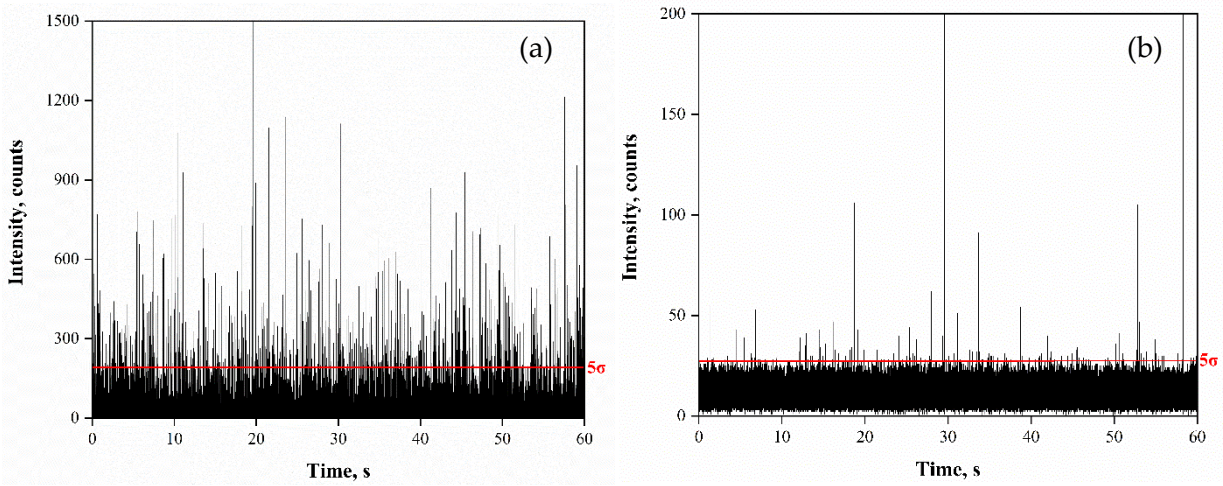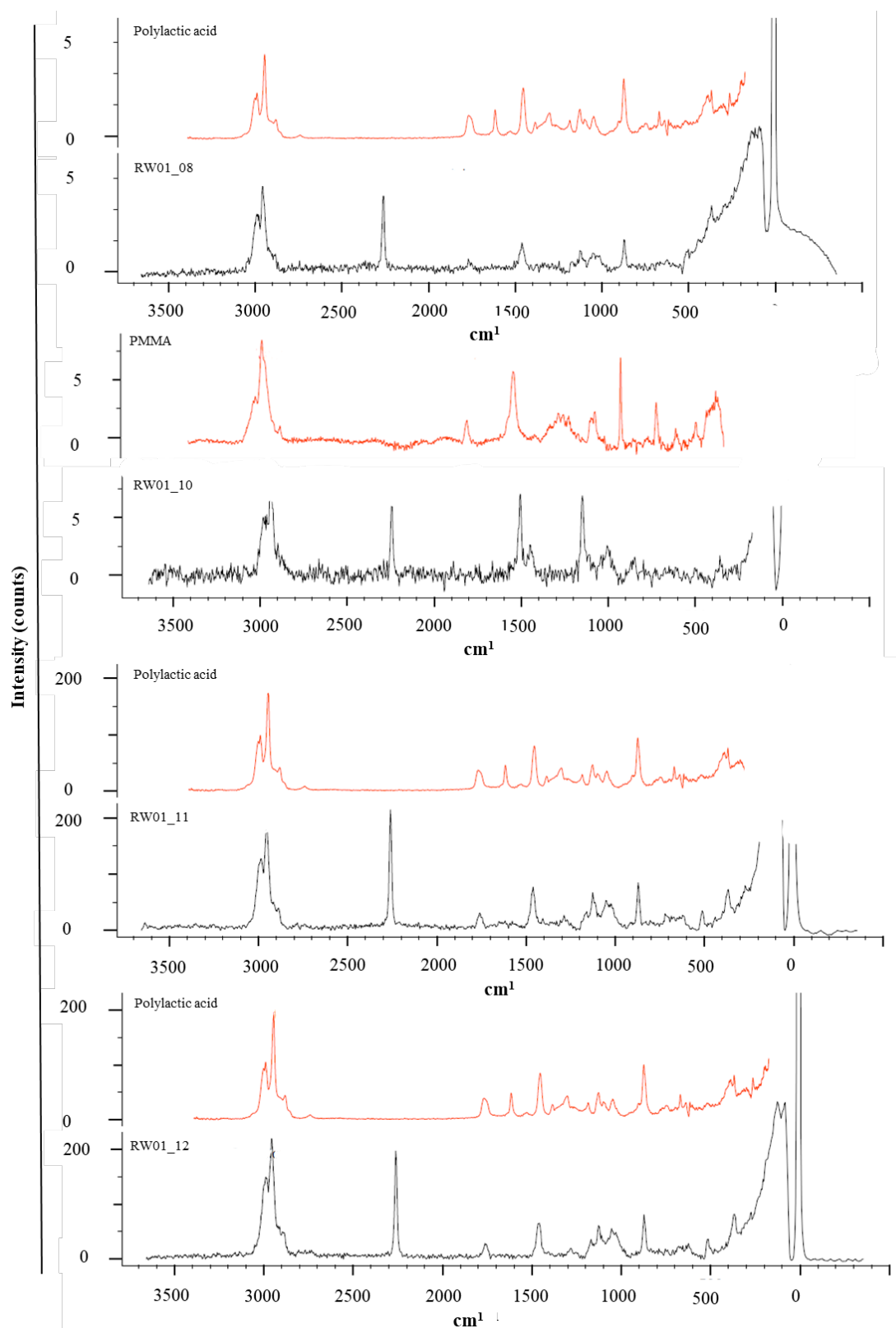
Figure S2. FESEM image of bacteria form river water filtered on glass fibre.
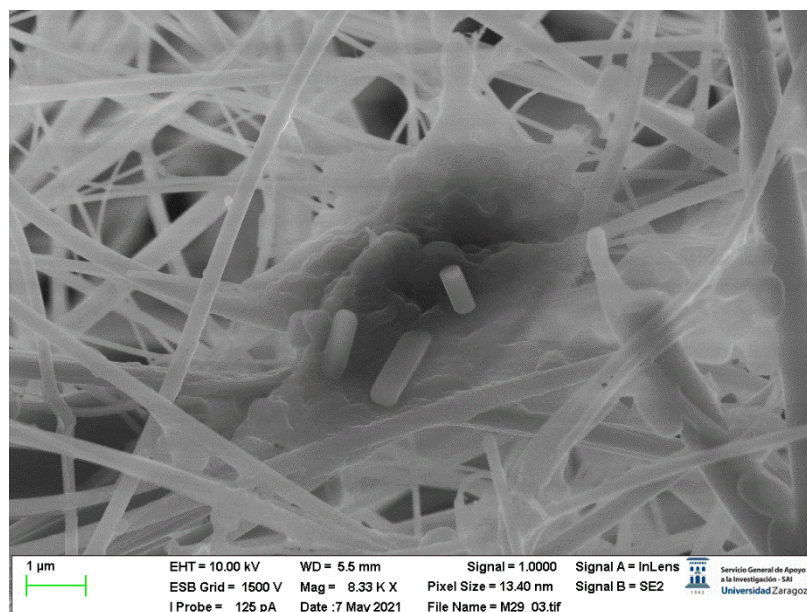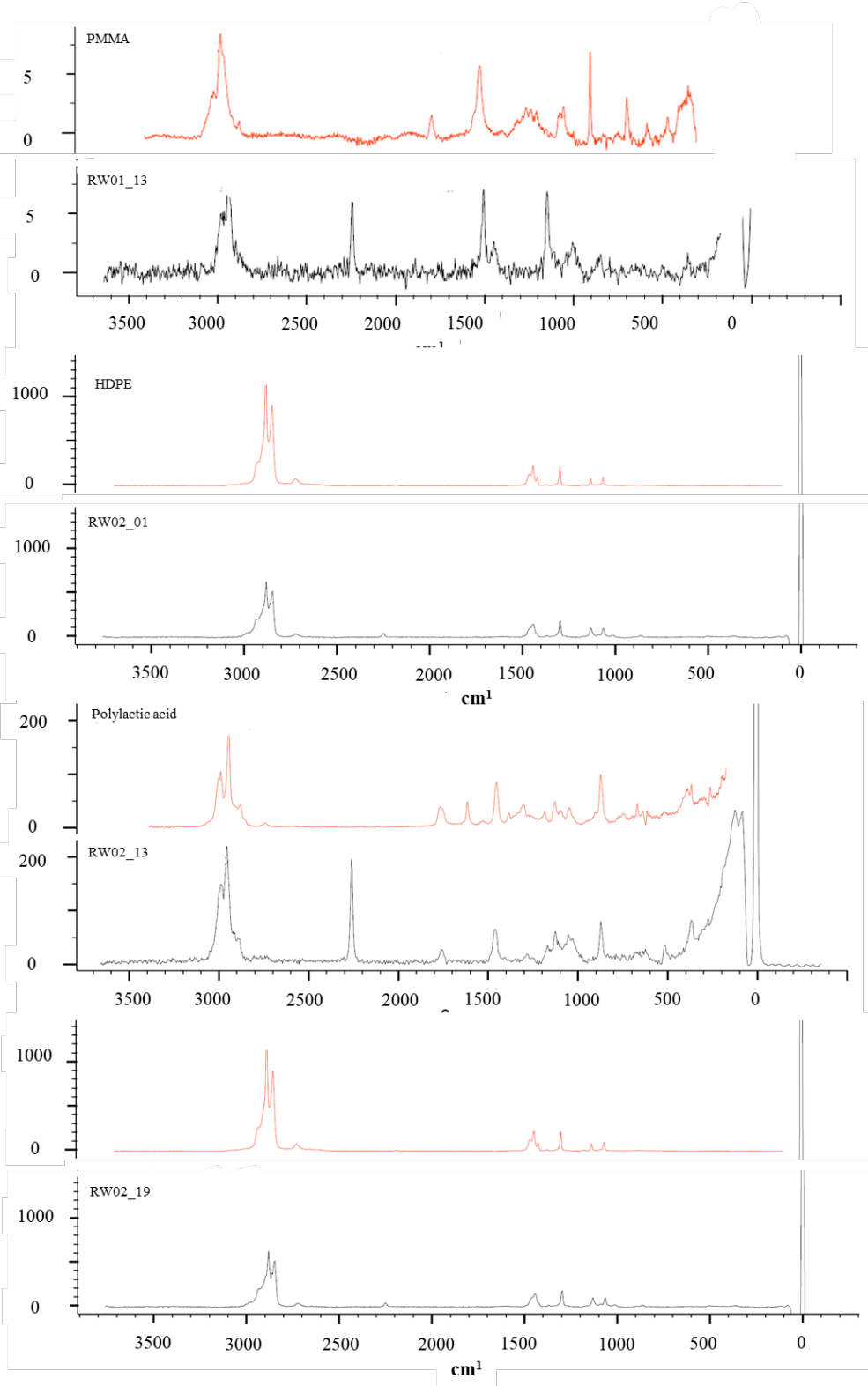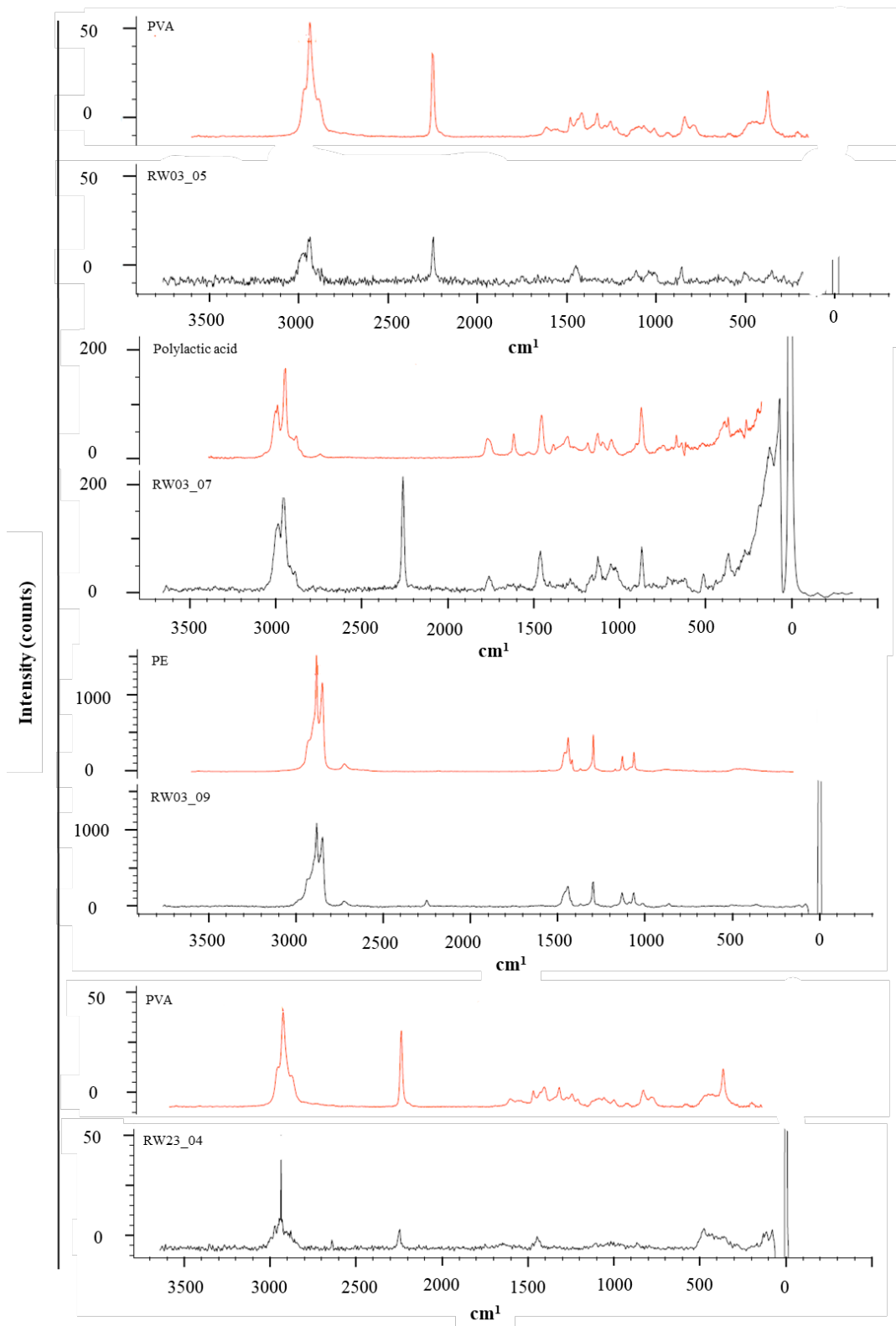
3.3. Analysis of river water samples by scanning electron and Raman microscopies.

Figure S3. Raman spectra of the plastic particles presented in Table 5. In black, spectra obtained from the analysis of the river water particles. In red spectra of the most probable compositions provided by the software KnowItAll™.

PMMA

RW01_13

HDPE

RW02_01

Polylactic acid

RW02_13

RW02_19

Intensity (counts)

PVA

RW03_05

3500 3000 2500 2000 1500 1000 500 0

cm^1

Polylactic acid

RW03_07

3500 3000 2500 2000 1500 1000 500 0

cm^1

PE

RW03_09

3500 3000 2500 2000 1500 1000 500 0

cm^1

PVA

RW23_04

3500 3000 2500 2000 1500 1000 500 0

cm^1

Intensity (counts)

PE

RW23_05

cm^1

PP

RW23_25

cm^1

PMMA

RW25_08

cm^1

Intensity (counts)