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**SUPPLEMENTARY MATERIAL to the paper entitled:**

# Priority organic compounds in wastewater effluents from the Mediterranean and Atlantic basins of Andalusia (Spain)

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This document provides more detailed information to the main paper mentioned above. The following information is included


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**Apparatus, instruments, solvents and standards used in the analytical procedures.**

*Chemical and reagents*. Pesticide analytical standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany), as well as the isotopically labelled pesticides parathion ethyl-$d_{10}$ and simazine-$d_5$, which were employed as internal standards (ISs) for non-polar and polar pesticides, respectively.

A mix solution (200 mg $L^{-1}$) of acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, chrysene, dibenz[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, pyrene and 2-bromonaphthalene (purities ≥ 96.6%) in dichloromethane (DCM) was provided by Supelco (Bellefonte, PA, USA). 5-Methylchrysene (99.6% purity), benzo[j]fluoranthene (98.6% purity), benzo[k]fluoranthene (99.5% purity) and fluoranthene-$d_{10}$, which was used as IS, were also obtained from Supelco. Dibenzo[a,e]pyrene, dibenzo[a,i]pyrene, dibenzo[a,h]pyrene, dibenzo[a,l]pyrene and cyclopenta[c,d]pyrene (purities ≥ 99%) were obtained from Dr. Ehrenstorfer.

A customized mix solution containing benzene, bromodichloromethane, bromoform, chloroform, carbon tetrachloride, dibromochloromethane, ethylbenzene, hexachlorobutadiene, m-xylene, methylene chloride, o-xylene, p-xylene, tetrachloroethene, toluene, trichloroethylene, 1,2-dichloroethane, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, and 1,3,5- trichlorobenzene (purity > 96.7%) at a concentration of 1 μg $mL^{-1}$ in methanol (MeOH) was obtained from Supelco.

Phenolic compounds standards, 2-nitrophenol, 4-nitrophenol, 2,4-dimethylphenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol and 4-n-nonylphenol were obtained from Fluka (Steinheim, Germany). On the other hand, 3-nitrophenol, 4-chloro-3-methylphenol, 4-tert-octylphenol and pentachlorophenol were supplied by Supelco. Purities were always > 97%. Isotopically labeled pentachlorophenol ([$^{13}C_6$]-pentachlorophenol) was used as IS and it was obtained from Dr. Ehrenstorfer.

Ethyl acetate (EtOAc), acetonitrile (ACN) and MeOH were supplied by J.T. Baker (Deventer, Holland). Acetone was purchased from Fluka and DCM was obtained from Riedel-de Haën (Seelze, Germany). All organic solvents were of analytical grade.

Ultrapure water was obtained from a Milli-Q Gradient water system (Millipore, Bedford, MA, USA). Liquid chromatography-mass spectrometry (LC-MS)-grade water was purchased from Scharlab (Sentmenat, Spain). Formic acid (purity > 98%), sulfuric acid ($H_2SO_4$, purity 96%) and magnesium sulphate anhydrous ($MgSO_4$) were purchased from Panreac (Barcelona, Spain). Sodium chloride (NaCl), and hydrochloric acid (HCl, purity 37–38%) were obtained from J.T. Baker. Anhydride acetic acid (AAA) (purity 99.9%), and pyridine (Py) (purity 99.8%) were purchased from Sigma–Aldrich (Madrid, Spain).

47-mm glass microfibre filters from Whatman (Maidstone, England, UK) and 0.45-µm HNWP nylon membrane filters from Millipore (Carrigtwohill, County Cork, Ireland) were also available for filtration stages.

For solid phase extraction (SPE), $C_{18}$ Sep-Pak cartridges (500 mg, 6 cc) as well as Oasis HLB (200 mg, 6 cc) cartridges, obtained from Waters (Milford, MA, USA), were employed. Florisil SPE cartridges were purchased from Varian (Habour City, CA, USA).

30-mm cellulose filters (Whatman) and Hydromatrix (Varian) were used for pressurized liquid extraction (PLE).

For stir bar sorptive extraction (SBSE) experiments, 10-mm long stir bars coated with a 0.5 mm film thickness layer of PDMS (Model TwisterTM) were purchased from Gerstel (Mülheim an der Ruhr, Germany).

*Instrumentation.* Non-polar pesticide, PAHs, phenolic compounds and VOCs analyses were carried out using a GC system Varian 3800 (Varian Instruments, Sunnyvale, CA, USA) equipped with electronic flow control (EFC). Samples were injected into an SPI/1079 split/splitless programmed-temperature injector, utilizing the large volume injection (LVI) technique and a Combi Pal (CTC Analytics AG, Zwingen, Switzerland) autosampler, using a 100-µL syringe. The glass liner was equipped with a plug of carbofrit (Resteck, Bellefonte, PA, USA). A fused-silica untreated capillary column (2 m × 0.25 mm i.d.) from Supelco was used as pre-column connected to a Factor Four Capillary Column VF-5ms (30 m × 0.25 mmi.d. × 0.25 µm film thickness). The carrier gas was helium (99.9999%) at a constant flow rate of 1 mL $min^{-1}$. The GC was interfaced to a 1200 L QqQ mass spectrometer (Varian Instruments) operating in electron ionization (EI) at 70 eV. Argon (99.999%) was used as collision gas. The mass

spectrometer was calibrated every four days with perfluorotributylamine. Varian Workstation software was used for instrument control and data analysis.

Polar pesticide analyses were performed in an Acquity UPLC system using an Acquity UPLC BEH $C_{18}$ column (100 mm × 2.1 mm), with a 1.7 µm particle size (both from Waters). Chromatographic separations were carried out using gradient elution with eluent A, being MeOH, and eluent B, consisting of an aqueous solution of formic acid (0.01%, v/v). MS analysis was carried out using a Waters Acquity TQD QqQ mass spectrometer (Waters, Manchester, UK). The instrument was operated using positive electrospray ionization (ESI+). Data acquisition was performed using MassLynx 4.0 and QuanLynx software (Waters).

For VOCs analyses a 4552 Archon purge-and-trap autosampler system (Varian Instruments) connected to a Velocity XPT accelerated purge-and-trap sample concentrator (Teledyne Tekmar Instruments, OH, USA) was employed. A 250-µL syringe from Hamilton (Bonaduz, Switzerland) and standard 40 mL VOC vials were used during sample preparation.

PLE was performed using an ASE 100 Accelerated Solvent Extraction system (Dionex, Sunnyvale, CA, USA) equipped with 34-mL stainless steel extraction cells. A magnetic multi-stirrer from Velp Scientifica (Usmate, Italy) was used for SBSE experiments. A Reax-2 rotary agitator from Heidolph (Schwabach, Germany) was used for agitation of the derivatization mixture of phenolic compounds. An analytical balance AB204-S from Mettler Toledo (Greifensee, Switzerland) and a Büchi Syncore line (Flawil, Switzerland) were used during extraction and standard preparation.

**Table S-1**
Compounds evaluated in this study and normative involved.

| Compound | Description | log Kow | Listed in | Compound | Description | log Kow | Listed in | Compound | Description | log Kow | Listed in |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Pesticides* | | | | Hexaconazole | FUNG | 3.9 | | Transfluthrin | INS | 5.5 | |
| 2-Phenylphenol | FUNG[a] | 2.9 | | Iodosulfuron-methyl | HB | 1.1 | | Triadimefon | FUNG | 3.1 | |
| Acrinathrin | INS/ACA | 5.6 | | Isodrin | INS | 6.7 | | Triasulfuron | HB | 1.1 | |
| Alachlor | HB | 3.1 | EU[b] | Isophenphos | INS | 4.0 | | Vinclozoline | FUNG | 3.0 | |
| Aldrin | INS | 6.2 | EPA[c],POPs[d] | Isoproturon | HB | 2.5 | EU | *PAHs* | | | |
| Atrazine | HB | 2.5 | EU | Kresoxim methyl | FUNG | 3.4 | | Acenaphthene | UB | 4.0 | EPA |
| Atrazine desethyl | TP | 1.5 | | α-Lindane | INS | 3.5 | EPA,POPs | Acenaphthylene | UB | 3.9 | EPA |
| Atrazine desisopropyl | TP | 0.4 | | β-Lindane | INS | 3.5 | EPA | Anthracene | UB | 4.5 | EU,EPA |
| Azinphos ethyl | INS/ACA | 3.2 | | δ-Lindane | INS | 3.5 | EPA | Benz[*a*]anthracene | UB | 5.6 | EPA |
| Azinphos methyl | INS | 2.9 | | γ-Lindane | INS | 3.5 | EU,EPA | Benzo[*a*]pyrene | UB | 6.0 | EU,EPA |
| Benalaxyl | FUNG | 3.5 | | Lenacil | HB | 2.3 | | Benzo[*b*]fluoranthene | UB | 6.3 | EU,EPA |
| Benfluralin | HB | 5.3 | | Linuron | HB | 3.0 | | Benzo[*k*]fluoranthene | UB | 6.4 | EU,EPA |
| Bensulfuron methyl | HB | 2.2 | | Malathion | INS/ACA | 2.7 | | Benzo[*ghi*]perylene | UB | 6.7 | EU,EPA |
| Bifenox | HB | 4.5 | | Mecarbam | INS/ACA | 2.3 | | Benzo[*j*]fluoranthene | UB | 6.1 | |
| Bifenthrin | INS/ACA | 6.0 | | Metalaxyl | FUNG | 1.7 | | 2-Bromonaphthalene | UB | 4.1 | |
| Bromophos ethyl | INS | 6.1 | | Metamitron | HB | 0.8 | | Chrysene | UB | 5.7 | EPA |
| Bromophos methyl | INS | 5.2 | | Metazachlor | HB | 2.1 | | Cyclopenta[*cd*]pyrene | UB | 4.9 | |
| Bromopropylate | ACA | 5.4 | | Methidathion | INS/ACA | 2.2 | | Dibenzo[*a*,*e*]pyrene | UB | 7.4 | |
| Bupirimate | FUNG | 3.9 | | Methoxychlor | INS | 4.9 | | Dibenzo[*a*,*h*]anthracene | UB | 6.9 | EPA |

| | | | |
|---|---|---|---|
| Buprofezin | INS/ACA | 4.3 | |
| Carbophenothion | INS/ACA | 4.7 | |
| Clodinafop propargyl | HB | 3.9 | |
| Chlordane-cis | INS | 5.6 | EPA,POPs |
| Chlordane-trans | INS | 5.6 | EPA,POPs |
| Chloridazon | HB | 1.2 | |
| Chlorfenson | INS | 4.5 | |
| Chlorfenvinphos | INS/ACA | 3.8 | EU |
| Chlormephos | INS | 3.1 | |
| Chloropropylate | ACA | 4.8 | |
| Chlorpyriphos methyl | INS/ACA | 4.2 | |
| Chlortal dimethyl | HB | 4.3 | |
| Chlorthion | INS | 3.5 | |
| Chlortoluron | HB | 2.5 | |
| Chlozolinate | FUNG | 3.1 | |
| Cycloate | HB | 3.9 | |
| Cinidon-ethyl | HB | 4.5 | |
| Cinosulfuron | HB | 2.0 | |
| γ-Cyhalothrin | INS | 6.9 | |
| Cyanofenphos | INS | 4.2 | |
| Cycloxydim | HB | 1.4 | |
| Cyfluthrin | INS | 6.0 | |
| Cypermethrin | INS | 6.6 | |

| | | | |
|---|---|---|---|
| Metobromuron | HB | 2.4 | |
| Metolachlor | HB | 2.9 | |
| Metoxuron | HB | 1.6 | |
| Metribuzin | HB | 1.6 | |
| Metsulfuron methyl | HB | 0.01 | |
| Mevinphos | INS/ACA | 0.1 | |
| Mirex | INS | 5.3 | POPs |
| Monolinuron | HB | 2.2 | |
| Norflurazon | HB | 2.4 | |
| *o,p*-DDD | TP | 5.9 | |
| *o,p*-DDT | INS | 6.8 | |
| Oxadixyl | FUNG | 0.6-0.8 | |
| Oxyfluorfen | HB | 4.5 | |
| *p,p'*-DDD | TP | 6.0 | EPA |
| *p,p'*-DDE | TP | 6.5 | EPA |
| Parathion ethyl | INS/ACA | 3.8 | |
| Parathion methyl | INS/ACA | 3.0 | |
| Penconazole | FUNG | 3.7 | |
| Pendimethalin | HB | 5.2 | |
| Pentachlorobenzene | FUNG | 5.2 | EU,POPs |
| Permethrin | INS | 6.1 | |
| Phenthoate | INS/ACA | 3.7 | |
| Phorate | INS/ACA/NEM | 3.9 | |

| | | | |
|---|---|---|---|
| Dibenzo[*a,h*]pyrene | UB | 7.4 | |
| Dibenzo[*a,i*]pyrene | UB | 7.4 | |
| Dibenzo[*a,l*]pyrene | UB | 7.4 | |
| Fluoranthene | UB | 5.1 | EU, EPA |
| Fluorene | UB | 4.1 | EPA |
| Indeno[1,2,3-*cd*]pyrene | UB | 7.1 | EU,EPA |
| 5-Methylchrysene | UB | 6.3 | |
| Naphthalene | UB | 3.3 | EU,EPA |
| Phenanthrene | UB | 4.5 | EPA |
| Pyrene | UB | 5.1 | EPA |
| *Phenolic compounds* | | | |
| 2,4,5-Trichlorophenol | IP/TP | 3.7 | |
| 2,4,6-Trichlorophenol | IP/TP | 3.7 | EPA |
| 2,4-Dimethylphenol | IP/TP | 2.3 | EPA |
| 4-Chloro-3-methylphenol | IP/TP | 3.1 | |
| 2,4-Dichlorophenol | IP/TP | 3.2 | EPA |
| 2-Chlorophenol | IP/TP | 2.1 | EPA |
| 4-Chlorophenol | IP/TP | 2.4 | |
| 2-Nitrophenol | IP/TP | 1.8 | EPA |
| 3-Nitrophenol | IP/TP | 2.0 | |
| 4-Nitrophenol | IP/TP | 1.9 | EPA |
| 4-n-Nonylphenol | IP/TP | 5.7 | EU |
| Pentachlorphenol | IP/TP | 5.2 | EU,EPA |

| | | | |
|---|---|---|---|
| Cyproconazole | FUNG | 3.1 | |
| Cyprodinil | FUNG | 3.9 | |
| Deltamethrin | INS | 4.6 | |
| Diazinon | INS/ACA | 3.3 | |
| Dichlobenil | HB | 2.7 | |
| Dichloran | FUNG | 2.8 | |
| Dieldrin | INS | 4.8 | EPA,POPs |
| Diethofencarb | FUNG | 3.0 | |
| Difenoconazole | FUNG | 4.4 | |
| Dimetomorph | FUNG | 2.6 | |
| Diniconazole | FUNG | 4.3 | |
| Diuron | HB | 2.8 | EU |
| Endosulfan $\alpha$ | INS | 4.7 | EU,EPA, POPs |
| Endosulfan $\beta$ | TP | 4.8 | EU,EPA, POPs |
| Endosulfan eter | TP | 4.0 | POPs |
| Endosulfan lactone | TP | 4.1 | POPs |
| Endosulfan suphate | TP | 3.8 | EU,EPA, POPs |
| EPN | INS/ACA | 4.7 | |
| Ethion | INS/ACA | 4.3 | |
| Ethofumesate | HB | 2.7 | |
| Ethoprophos | INS /NM | 3.6 | |
| Etrimfos | INS | 3.4 | |
| Fenamiphos | NEM | 3.3 | |

| | | | |
|---|---|---|---|
| Pyridaben | INS/ACA | 6.4 | |
| Pyrifenox | FUNG | 3.4 | |
| Pirimicarb | INS | 1.7 | |
| Pirimiphos ethyl | INS | 5.0 | |
| Pirimiphos methyl | INS/ACA | 4.2 | |
| Pyriproxyfen | INS | 5.4 | |
| Procymidone | FUNG | 3.1 | |
| Prometryn | HB | 3.1 | |
| Propachlor | HB | 2.3 | |
| Propazine | HB | 2.9 | |
| Propiconazole | FUNG | 3.7 | |
| Propyzamide | HB | 3.2 | |
| Pyrazophos | FUNG | 3.8 | |
| Quinalphos | INS/ACA | 4.4 | |
| Quinmerac | HB | -1.1 | |
| Quinoxyfen | FUNG | 4.7 | |
| Quintocene | FUNG | 5.1 | |
| S421 | INS | 5.3 | |
| Sebuthylazine | HB | 3.2 | |
| Sethoxydim | HB | 4.5 | |
| Silafluofen | INS | 8.2 | |
| Simazine | HB | 2.1 | EU |
| Sulfotep | INS/ACA | 3.9 | |

| | | | |
|---|---|---|---|
| 4-Tertoctylphenol | IP/TP | 4.1 | EU |
| *VOCs* | | | |
| 1,2,3-Trichlorobenzene | UB | | EU |
| 1,2,4- Trichlorobenzene | UB | | EU, EPA |
| 1,2-Dichloroethane | UB | | EU, EPA |
| 1,3,5-Trichlorobenzene | UB | | EU |
| Benzene | UB | | EU, EPA |
| Bromodichloromethane | UB | | EPA |
| Bromoform | UB | | EPA |
| Carbon tetrachloride | UB | | EPA |
| Chloroform | UB | | EU, EPA |
| Dibromochloromethane | UB | | EPA |
| Ethylbenzene | UB | | EPA |
| Hexachlorobutadiene | UB | | EU,EPA |
| m-Xylene + p-Xylene | UB | | |
| o-Xylene | UB | | |
| Tetrachloroethene | UB | | |
| Toluene | UB | | EPA |
| Trichloroethylene | UB | | EPA |

| | | | | | | |
|---|---|---|---|---|---|---|
| Fenitrothion | INS | 3.4 | | Tau fluvalinate | INS/ACA | 4.3 |
| Fenoxaprop-P-ethyl | HB | 4.6 | | Tebufenozide | INS | 4.2 |
| Fenpropathrin | INS/ACA | 6.0 | | Tebufenpirad | ACA | 5.0 |
| Fenthion | INS | 4.8 | | Tebutam | HB | 3.0 |
| Fenarimol | FUNG | 3.6 | | Tecnazene | FUNG | 4.0 |
| Fipronil | INS | 4.0 | | Tepraloxydim | HB | 1.5 |
| Fluacipop-butyl | HB | 4.5 | | Terbumeton | HB | 3.0 |
| Flucythrinate | INS | 4.7 | | Terbutryn | HB | 3.6 |
| Fluorochlorhidrone | HB | 3.4 | | Terbuthylazine | HB | 3.2 |
| Fludioxonil | FUNG | 4.1 | | Terbuthylazine desethyl | TP | 1.9 |
| Fonophos | INS | 3.9 | | Tetrachlorvinphos | INS/ACA | 3.9 |
| Formothion | INS | 1.5 | | Tetraconazole | FUNG | 3.6 |
| Furalaxyl | FUNG | 2.7 | | Tetradifon | ACA | 4.6 |
| Heptachlor | INS | 5.4 | EPA,POPs | Tetramethrin | INS | 4.6 |
| Heptachlor epoxide | TP | 4.2 | EPA | Thiazopyr | HB | 3.9 |
| Heptenophos | INS | 2.3 | | Thifensulfuron methyl | HB | 1.1 |
| Hexachlorobenzene | FUNG | 5.7 | EU,EPA, POPs | Tolcophos methyl | FUNG | 4.6 |

[a]Abbreviations: ACA: Acaricide; FUNG: Fungicide; HB: Herbicide; INS: Insecticide; IP: Industrial product; NEM: Nematicide; TP: Transformation product; UB: Ubiquitous contaminant.
[b] Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001, establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. Off. J. Eur. Communities L 331/1, 16.12.2001, available on http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2001:331:0001:0005:EN:PDF (last accessed April 2013).
[c] List of the 129 priority pollutants by United States Environmental Protection Agency (U.S. EPA). Appendix A to part 423, available on http://www.epa.gov/waterscience/methods/pollutants.htm (last accessed April 2013).
[d] Stockholm Convention on Persistent Organic Pollutants, Secretary-General of the 451 United Nations, 22 May (2001), available on http://chm.pops.int/ (last accessed April 2013).

**Table S-2**

Summary of the analytical method employed for the measurement of the target compounds in WW samples.

| Compound | Extraction method | Determination technique | Injection | Column | Program | Analyzer | Parameters | Recovery (%) | Precision[b] | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| Non-polar pesticides | Aqueous phase: SPE[a] - Volume: 250 mL - Cartridges: $C_{18}$ - Elution: 3 mL AcOEt + 3 mL MeOH + 3 mL MilliQ water SPM: PLE (AcOEt/MeOH, 3:1 v/v, 75 ºC) | GC | 10 µL, LVI+PTV (Carbofrit) | Varian FactorFour VF-5ms (30 m × 0.25 mm × 0.25µm) | Injector: 70 ºC (0.5 min)→310ºC (100ºC/min, 10 min) Oven: 70ºC (3.5 min) →180ºC (35ºC/min)→300ºC (10ºC/min, 7 min) | QqQ | EI (70eV), transfer line (300 ºC), manifold (40 ºC), source (280 ºC) | 50-120 | Intra-day: < 25 | [1] |
| Polar pesticides | SPE -Volume: 250 mL - Cartridges: OASIS - Elution: 5 mL MeOH + 5 mL AcOEt/DCM | UHPLC | 5 µL | $C_{18}$ (100mm × 2.1mm,1.7µm) | A (MeOH), B (Water, 0.01% HCOOH) 10% A→90% (5 min, kept 2 min)→25% A (over 1.5 min), flow (0.35 ml/min), column (35ºC) | QqQ | ESI+, capillary (3.5 kV), extractor (5 V), source (110 ºC), desolvation (350 ºC), cone gas (80 L/h), desolvation gas (600 L/h) | 50-120 | Intra-day: < 25 | [1] |
| PAHs | SBSE (4 h, 850 rpm); desroption 15 min (1 mL AcOEt) | GC | 10 µL, LVI+PTV (Carbofrit) | Varian FactorFour VF-17ms (20 m × 0.15 mm × 0.05µm) | Injector: 70ºC (0.5 min)→325ºC (200ºC/min, 20.23 min) Oven: 70ºC (5 min) →180ºC (70ºC/min, 1 min) →245ºC (5ºC/min, 1 min) →270ºC (4ºC/min, 1.5 min) →310ºC (15ºC/min, 5.01 min) | QqQ | EI (70eV), transfer line (300 ºC), manifold (40 ºC), source (280 ºC) | 53-120 | Intra-day: < 28 Inter-day: < 28 | [2] |
| Phenolic compounds | SPE -Volume: 250 mL -Cartridges: OASIS -Elution: 3 mL acetone + 3 mL DCM | GC | 10 µL, LVI+PTV | Varian FactorFour VF-5ms (30 m × 0.25 mm × 0.25 µm) | Injector: 70ºC (0.5 min)→310ºC (100ºC/min, 10 min) Oven:70ºC (3.5 min) →300ºC (20ºC/min, 4 min) | QqQ | EI (70eV), transfer line (300 ºC), manifold (40 ºC), source (280 ºC) | 70-120 | Intra-day: < 28 Inter-day: < 27 | [3] |
| VOCs | PTE (purge time, 13 min; desorption time, 2 min, desorption temp, 250 ºC) | GC | --- | Varian FactorFour VF-5ms (30 m × 0.25 mm × 0.25 µm) | Injector:250ºC Oven:50ºC (2 min)→70ºC (5ºC/min)→250ºC (100ºC/min, 5 min) | QqQ | EI (70eV), transfer line (300 ºC), manifold (40 ºC), source (280 ºC) | 73-112 | Intra-day: < 25 Inter-day: < 25 | [4] |

[a] Abbreviations: AcOEt: Ethyl acetate; DCM: Dichloromethane; EI: Electronic ionization; ESI: Electrospray ionization; GC: Gas chromatography; LVI: Large volumen injection; MeOH: Methanol; PLE: Pressurized liquid extraction; PTE: Purge and trap extraction; PTV: Pressure temperature vaporization; QqQ: Triple quadrupole; SPE: Solid phase extraction; SPM: Suspended particulate matter; UHPLC: Ultra high performance liquid chromatography

[b] Expressed as Relative Standard Deviation (%).

**Table S-3**

Total concentration (aqueous phase + particulate matter) of the non-polar pesticides detected in each WWTP effluent evaluated.

| WWTP | Effluent No[a] | Concentration (µg L$^{-1}$) | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 2-Phenylphenol | Chlorfenvinphos | Cyproconazole | Cyprodinil | Diazinon | Dimetomorph | Endosulfan lactone | Ethoprophos | Fludioxonil | Isodrin | Penconazole | Permethrin | Terbutryn |
| WWTP1 | 1 | 0.08 | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | < LOQ | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP2 | 2 | N.D.[b] | < LOQ[c] | N.D. | N.D. | N.D. | < LOQ | N.D. | < LOQ | < LOQ | N.D. | N.D. | N.D. | N.D. |
| WWTP3 | 3 | 0.99 | < LOQ | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP4 | 4 | N.D. | 0.10 | N.D. | N.D. | N.D. | < LOQ | N.D. | 0.04 | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP5 | 5 | 0.17 | N.D. | N.D. | 0.09 | N.D. | 0.66 | 0.08 | 0.03 | 0.43 | N.D. | N.D. | N.D. | N.D. |
| WWTP6 | 6a | 0.10 | 0.03 | N.D. | N.D. | 0.07 | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. | N.D. | N.D. |
| | 6b | 0.35 | 0.04 | N.D. | N.D. | 0.06 | N.D. | N.D. | 0.02 | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP7 | 7 | N.D. | 0.08 | N.D. | N.D. | 0.04 | N.D. | N.D. | 0.01 | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP8 | 8 | 0.12 | 0.03 | N.D. | N.D. | 8.63 | N.D. | N.D. | 0.03 | N.D. | N.D. | N.D. | N.D. | < LOQ |
| WWTP9 | 9 | 0.12 | 0.28 | N.D. | N.D. | 0.22 | N.D. | N.D. | 0.03 | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP10 | 10 | N.D. | 0.14 | N.D. | N.D. | < LOQ | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP11 | 11 | 0.10 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP12 | 12 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP13 | 13 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP14 | 14 | N.D. | 0.15 | N.D. | N.D. | < LOQ | N.D. | N.D. | 0.02 | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP15 | 15 | 0.38 | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. | 0.03 | N.D. | N.D. | N.D. | 0.03 | N.D. |
| WWTP16 | 16 | 0.15 | < LOQ | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.08 | N.D. | N.D. | N.D. | N.D. |
| WWTP17 | 17 | 0.09 | N.D. | N.D. | N.D. | 1.06 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP18 | 18 | 0.25 | 0.03 | N.D. | N.D. | 0.18 | N.D. | N.D. | 0.07 | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP19 | 19 | N.D. | 0.96 | N.D. | N.D. | 0.08 | N.D. | N.D. | < LOQ | N.D. | 0.17 | N.D. | N.D. | N.D. |
| WWTP20 | 20 | 0.21 | 0.03 | N.D. | N.D. | 0.10 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP21 | 21a | N.D. | < LOQ | < LOQ | N.D. | 0.08 | N.D. | N.D. | 0.03 | N.D. | N.D. | 0.32 | N.D. | N.D. |
| | 21b | N.D. | 0.10 | 0.08 | N.D. | 0.09 | N.D. | N.D. | 0.03 | N.D. | 0.06 | < LOQ | N.D. | N.D. |
| | 21c | N.D. | < LOQ | < LOQ | N.D. | 0.27 | N.D. | N.D. | N.D. | N.D. | N.D. | 0.23 | N.D. | N.D. |
| | 21d | N.D. | 0.03 | 0.06 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| | 21e | N.D. | 0.05 | 0.03 | N.D. | 0.08 | N.D. | N.D. | N.D. | N.D. | 0.04 | < LOQ | N.D. | N.D. |
| | 21f | 8.26 | 0.20 | 0.09 | N.D. | 0.07 | N.D. | N.D. | N.D. | N.D. | 0.05 | N.D. | N.D. | N.D. |
| | 21g | 0.08 | < LOQ | N.D. | N.D. | 0.92 | N.D. | N.D. | 0.02 | N.D. | N.D. | 0.13 | N.D. | N.D. |
| | 21h | 0.24 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| | 21i | N.D. | 0.05 | 0.05 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.11 | 0.11 | N.D. | N.D. |

[a]The treatment corresponding to each effluent number is shown in Table 1
[b]N.D.: not detected
[c]LOQ: limit of quantification

**Table S-4**

Total concentration (aqueous phase) of the polar pesticides detected in each WWTP effluent evaluated.

| WWTP | Effluent No[a] | Concentration (µg L$^{-1}$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Atrazine desisopropyl | Diuron | Isoproturon | Linuron | Metribuzin | Propyzamide | Sebuthylazine &Terbuthylazine | Terbumeton | Terbuthylazine desethyl |
| WWTP1 | 1 | N.D.[b] | 0.19 | N.D. | N.D. | N.D. | N.D. | < LOQ | < LOQ | N.D. |
| WWTP2 | 2 | N.D. | 0.15 | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | < LOQ |
| WWTP3 | 3 | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | < LOQ | N.D. | 0.03 |
| WWTP4 | 4 | N.D. | 0.19 | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | < LOQ |
| WWTP5 | 5 | N.D. | 0.15 | N.D. | < LOQ | < LOQ | N.D. | < LOQ | < LOQ | 0.04 |
| WWTP6 | 6a | N.D. | 1.67 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| | 6b | N.D. | 1.01 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP7 | 7 | N.D. | 1.01 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP8 | 8 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.02 | N.D. | N.D. |
| WWTP9 | 9 | N.D. | 0.62 | 0.05 | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. |
| WWTP10 | 10 | N.D. | 0.23 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP11 | 11 | N.D. | 0.39 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP12 | 12 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | < LOQ |
| WWTP13 | 13 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. |
| WWTP14 | 14 | N.D. | 0.19 | N.D. | N.D. | N.D. | N.D. | 0.04 | N.D. | < LOQ |
| WWTP15 | 15 | N.D. | 0.45 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP16 | 16 | N.D. | 0.09 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP17 | 17 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.13 | N.D. | 0.09 |
| WWTP18 | 18 | N.D. | 0.09 | < LOQ[c] | N.D. | N.D. | N.D. | 0.06 | < LOQ | < LOQ |
| WWTP19 | 19 | 0.01 | 0.29 | N.D. | N.D. | N.D. | N.D. | 0.14 | N.D. | 0.07 |
| WWTP20 | 20 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.19 | < LOQ | 0.16 |
| WWTP21 | 21a | N.D. | 0.05 | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. |
| | 21b | N.D. | 0.06 | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. |
| | 21c | N.D. | 0.06 | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. |
| | 21d | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. |
| | 21e | N.D. | 0.04 | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. |
| | 21f | N.D. | 0.06 | N.D. | N.D. | N.D. | N.D. | 0.02 | N.D. | N.D. |
| | 21g | N.D. | 0.09 | N.D. | N.D. | N.D. | N.D. | 0.01 | N.D. | N.D. |
| | 21h | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| | 21i | N.D. | 0.05 | N.D. | N.D. | N.D. | N.D. | 0.03 | N.D. | < LOQ |

[a]The treatment corresponding to each effluent number is shown in Table 1
[b]N.D.: not detected
[c]LOQ: limit of quantification

## Table S-5

Total concentration (aqueous phase + particulate matter) of the PAHs detected in each WWTP effluent evaluated.

| WWTP | Effluent No[a] | Concentration (μg L$^{-1}$) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | ACP | BaA | BaP | BbF | BghiP | BjF | BkF | CHR | FLR | FLU | IP | NPH | P | PYR |
| WWTP1 | 1 | N.D.[b] | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.04 | 0.07 | N.D. | N.D. | 0.05 | 0.04 |
| WWTP2 | 2 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.03 | 0.07 | N.D. | N.D. | 0.05 | 0.04 |
| WWTP3 | 3 | < LOQ[c] | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | 0.80 | N.D. | 1.20 | 0.44 | 0.01 |
| WWTP4 | 4 | N.D. | 0.04 | 0.10 | N.D. | N.D. | N.D. | 0.05 | 0.04 | 0.06 | 0.07 | N.D. | N.D. | 0.06 | 0.05 |
| WWTP5 | 5 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.04 | N.D. | N.D. | 0.06 | < LOQ |
| WWTP6 | 6a | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | 0.06 | N.D. | N.D. | 0.03 | < LOQ |
| | 6b | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.04 | N.D. | N.D. | 0.07 | < LOQ |
| WWTP7 | 7 | N.D. | 0.02 | N.D. | 0.01 | 0.02 | N.D. | N.D. | 0.02 | 0.03 | 0.06 | 0.03 | N.D. | 0.09 | 0.03 |
| WWTP8 | 8 | N.D. | 0.03 | N.D. | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.03 | 0.03 | 0.02 | N.D. | 0.06 | 0.02 |
| WWTP9 | 9 | N.D. | 0.01 | N.D. | 0.01 | N.D. | < LOQ | 0.01 | 0.01 | 0.02 | 0.04 | N.D. | N.D. | 0.05 | 0.02 |
| WWTP10 | 10 | N.D. | 0.01 | N.D. | N.D. | 0.01 | < LOQ | 0.01 | 0.01 | 0.03 | 0.04 | N.D. | N.D. | 0.04 | 0.02 |
| WWTP11 | 11 | N.D. | N.D. | N.D. | 0.01 | N.D. | N.D. | N.D. | 0.01 | 0.02 | 0.03 | N.D. | N.D. | 0.04 | 0.02 |
| WWTP12 | 12 | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. | N.D. | 0.01 | 0.02 | 0.04 | N.D. | N.D. | 0.05 | 0.02 |
| WWTP13 | 13 | N.D. | 0.03 | N.D. | 0.01 | 0.02 | 0.01 | 0.01 | 0.02 | 0.05 | 0.08 | N.D. | N.D. | 0.09 | 0.05 |
| WWTP14 | 14 | N.D. | N.D. | N.D. | 0.01 | N.D. | N.D. | N.D. | 0.01 | 0.02 | 0.04 | N.D. | N.D. | 0.05 | 0.03 |
| WWTP15 | 15 | N.D. | N.D. | N.D. | 0.01 | < LOQ | N.D. | N.D. | 0.01 | 0.02 | 0.05 | N.D. | N.D. | 0.07 | 0.02 |
| WWTP16 | 16 | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. | N.D. | 0.01 | 0.02 | 0.05 | N.D. | N.D. | 0.04 | 0.02 |
| WWTP17 | 17 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.01 | 0.01 | 0.03 | N.D. | N.D. | 0.03 | 0.01 |
| WWTP18 | 18 | N.D. | 0.01 | N.D. | < LOQ | N.D. | N.D. | N.D. | N.D. | 0.01 | 0.03 | N.D. | N.D. | 0.04 | 0.02 |
| WWTP19 | 19 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.01 | 0.04 | N.D. | N.D. | 0.05 | 0.01 |
| WWTP20 | 20 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.01 | 0.01 | 0.04 | N.D. | N.D. | 0.03 | 0.01 |
| WWTP21 | 21a | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.01 | 0.11 | N.D. | N.D. | 0.04 | 0.01 |
| | 21b | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.01 | 0.09 | N.D. | N.D. | 0.03 | 0.01 |
| | 21c | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.01 | 0.11 | N.D. | N.D. | 0.05 | 0.01 |
| | 21d | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.01 | 0.08 | N.D. | N.D. | 0.03 | 0.01 |
| | 21e | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | <LOQ | 0.62 | N.D. | N.D. | 0.11 | 0.01 |
| | 21f | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.01 | 0.08 | N.D. | N.D. | 0.02 | 0.01 |
| | 21g | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.01 | 0.07 | N.D. | N.D. | 0.03 | 0.01 |
| | 21h | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.03 | N.D. | N.D. | 0.03 | 0.01 |
| | 21i | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | 0.03 | N.D. | N.D. | 0.03 | 0.01 |

[a]The treatment corresponding to each effluent number is shown in Table 1
[b]N.D.: not detected
[c]LOQ: limit of quantification
Abbreviations: ACP: acenaphthene; BaA: benz[*a*]anthracene; BaP: benzo[*a*]pyrene; BbF: benzo[*b*]fluoranthene; BghiP: benzo[*ghi*]perylene; BjF: benzo[*j*]fluoranthene; BkF: benzo[*k*]fluoranthene ; CHR: chrysene; FLR: fluoranthene; FLU: fluorene; IP: indene[1,2,3-*cd*]pyrene; NPH: naphthalene; P: phenanthrene; PYR: pyrene.

**Table S-6**

Total concentration (aqueous phase) of the phenolic compounds detected in each WWTP effluent evaluated.

| WWTP | Effluent No[a] | Concentration (μg $L^{-1}$) | | | |
|---|---|---|---|---|---|
| | | 2,4,6-Trichlorophenol | 2,4,5-Trichlorophenol | 4-Tertoctylphenol | Pentachlorphenol |
| WWTP1 | 1 | N.D.[b] | N.D. | 0.20 | 0.21 |
| WWTP2 | 2 | 0.28 | 0.22 | 0.11 | 0.07 |
| WWTP3 | 3 | N.D. | N.D. | 3.17 | N.D. |
| WWTP4 | 4 | N.D. | N.D. | 443.23 | N.D. |
| WWTP5 | 5 | N.D. | N.D. | 8.27 | N.D. |
| WWTP6 | 6a | N.D. | N.D. | 3.61 | N.D. |
| | 6b | N.D. | N.D. | 3.55 | N.D. |
| WWTP7 | 7 | N.D. | N.D. | 250.48 | N.D. |
| WWTP8 | 8 | 0.26 | N.D. | 0.08 | N.D. |
| WWTP9 | 9 | N.D. | N.D. | 3.58 | N.D. |
| WWTP10 | 10 | N.D. | N.D. | 255.37 | N.D. |
| WWTP11 | 11 | N.D. | 0.13 | 0.35 | 0.05 |
| WWTP12 | 12 | N.D. | N.D. | 0.11 | 0.04 |
| WWTP13 | 13 | N.D. | 0.14 | 0.13 | 0.04 |
| WWTP14 | 14 | N.D. | 0.13 | 0.24 | N.D. |
| WWTP15 | 15 | N.D. | N.D. | 0.11 | N.D. |
| WWTP16 | 16 | N.D. | 0.12 | 0.11 | N.D. |
| WWTP17 | 17 | N.D. | N.D. | 0.09 | N.D. |
| WWTP18 | 18 | 0.08 | 0.14 | 0.16 | N.D. |
| WWTP19 | 19 | 0.12 | 0.13 | 0.11 | N.D. |
| WWTP20 | 20 | 0.12 | 0.13 | 0.12 | N.D. |
| WWTP21 | 21a | 0.11 | 0.15 | 0.10 | 0.04 |
| | 21b | N.D. | 0.16 | 0.09 | N.D. |
| | 21c | 0.14 | N.D. | 0.11 | N.D. |
| | 21d | N.D. | N.D. | 0.17 | N.D. |
| | 21e | N.D. | N.D. | 0.07 | N.D. |
| | 21f | N.D. | N.D. | 0.10 | N.D. |
| | 21g | 0.12 | N.D. | 0.18 | N.D. |
| | 21h | N.D. | N.D. | 73.45 | N.D. |
| | 21i | N.D. | N.D. | 83.71 | N.D. |

[a]The treatment corresponding to each effluent number is shown in Table 1
[b]N.D.: not detected

**Table S-7**

Total concentration (aqueous phase + particulate matter) of the VOCs detected in each WWTP effluent evaluated.

| WWTP | Effluent No[a] | Concentration (µg L$^{-1}$) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1,2,3-TCB | 1,2,4-TCB | 1,2-DCE | 1,3,5-TCB | BDM | BEN | BMF | DBC | ETB | MPX | OXYL | TCC | TCE | TOL |
| WWTP1 | 1 | 0.28 | < LOQ[c] | N.D. | N.D. | 44.25 | 0.15 | 70.79 | 80.31 | N.D. | N.D. | 0.12 | 0.16 | N.D. | N.D. |
| WWTP2 | 2 | 0.28 | < LOQ | N.D. | N.D. | < LOQ | < LOQ | 0.19 | 0.17 | N.D. | N.D. | N.D. | 0.17 | N.D. | N.D. |
| WWTP3 | 3 | N.D.[b] | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | < LOQ | 0.53 | 1.21 | 0.80 | N.D. | N.D. | 0.81 |
| WWTP4 | 4 | N.D. | < LOQ | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | < LOQ | N.D. | 0.16 | N.D. | 0.49 |
| WWTP5 | 5 | N.D. | < LOQ | N.D. | < LOQ | N.D. | N.D. | N.D. | < LOQ | N.D. | < LOQ | N.D. | N.D. | N.D. | 0.78 |
| WWTP6 | 6a | N.D. | < LOQ | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. | N.D. | N.D. | N.D. | 0.17 |
| | 6b | N.D. | < LOQ | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. | N.D. | N.D. |
| WWTP7 | 7 | N.D. | < LOQ | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP8 | 8 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | < LOQ | < LOQ | 0.12 | N.D. | N.D. | N.D. |
| WWTP9 | 9 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.12 | 0.34 | 0.17 | N.D. | N.D. | N.D. |
| WWTP10 | 10 | 0.28 | < LOQ | N.D. | N.D. | 0.12 | N.D. | N.D. | < LOQ | 0.12 | 0.29 | 0.12 | N.D. | N.D. | 0.22 |
| WWTP11 | 11 | N.D. | N.D. | N.D. | N.D. | 20.63 | N.D. | 5.70 | 18.34 | 0.14 | 0.44 | 0.15 | N.D. | N.D. | N.D. |
| WWTP12 | 12 | N.D. | N.D. | N.D. | N.D. | 3.29 | N.D. | 0.92 | 1.63 | < LOQ | 0.13 | 0.12 | N.D. | N.D. | N.D. |
| WWTP13 | 13 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | < LOQ | N.D. | N.D. | N.D. | N.D. |
| WWTP14 | 14 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | < LOQ | 0.10 | 0.12 | N.D. | N.D. | N.D. |
| WWTP15 | 15 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.14 | N.D. | < LOQ | 0.12 | N.D. | N.D. | N.D. |
| WWTP16 | 16 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP17 | 17 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP18 | 18 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP19 | 19 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | < LOQ | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP20 | 20 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| WWTP21 | 21a | N.D. | N.D. | N.D. | N.D. | < LOQ | 0.15 | < LOQ | N.D. | N.D. | 0.12 | N.D. | 0.13 | < LOQ | N.D. |
| | 21b | N.D. | N.D. | < LOQ | N.D. | < LOQ | 0.13 | < LOQ | < LOQ | N.D. | 0.12 | < LOQ | 0.13 | < LOQ | N.D. |
| | 21c | N.D. | N.D. | N.D. | N.D. | < LOQ | 0.13 | < LOQ | N.D. | N.D. | 0.12 | N.D. | 0.13 | 0.19 | N.D. |
| | 21d | N.D. | N.D. | N.D. | N.D. | < LOQ | 0.12 | < LOQ | < LOQ | N.D. | 0.12 | N.D. | 0.13 | 0.18 | N.D. |
| | 21e | N.D. | N.D. | < LOQ | N.D. | < LOQ | 0.13 | < LOQ | < LOQ | N.D. | 0.12 | N.D. | 0.13 | 0.13 | N.D. |
| | 21f | N.D. | N.D. | N.D. | N.D. | N.D. | 0.13 | < LOQ | N.D. | < LOQ | 0.13 | < LOQ | N.D. | 0.11 | N.D. |
| | 21g | N.D. | N.D. | N.D. | N.D. | < LOQ | 0.13 | < LOQ | N.D. | N.D. | 0.12 | N.D. | N.D. | < LOQ | N.D. |
| | 21h | N.D. | N.D. | < LOQ | N.D. | N.D. | 0.30 | N.D. | N.D. | 0.11 | 0.26 | 0.28 | N.D. | 0.11 | N.D. |
| | 21i | N.D. | N.D. | N.D. | N.D. | < LOQ | 0.13 | N.D. | N.D. | N.D. | 0.12 | < LOQ | N.D. | 0.12 | N.D. |

[a]The treatment corresponding to each effluent number is shown in Table 1
[b]N.D.: not detected
[c]LOQ: limit of quantification
Abbreviations: 1,2,3-TCB: 1,2,3- Trichlorobenzene; 1,2,4-TCB: 1,2,4- Trichlorobenzene; 1,2-DCE: 1,2-Dichloroethane; 1,3,5-TCB : 1,3,5- Trichlorobenzene; BDM: Bromodichloromethane; BEN: Benzene;; BMF: Bromoform; DBC: Dibromochloromethane; ETB: Ethylbenzene; MPX: *m*-Xylene + *p*-Xylene; OXYL: *o*-Xylene; TCC: Carbon tetrachloride; TCE: Tetrachloroethene; TOL:Toluene.

**Table S-8**. Spearman correlation coefficients between the variables [a]

| | PHP | CIP | CHL | DIA | ETO | PEN | DIU | S&T | TBD | FLU | P&A | FLR | PYR | BaA | CHR | BbF | 246T | 245T | TOP | PET | TCC | BEN | BDM | DBC | TCE | ETB | MPX | OXYL | BMF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PHP | 1.000 | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| CIP | -0.276 | 1.000 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| CHL | -0.207 | 0.275 | 1.000 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| DIA | 0.083 | 0.114 | 0.328 | 1.000 | | | | | | | | | | | | | | | | | | | | | | | | | |
| ETO | 0.014 | -0.162 | 0.110 | 0.155 | 1.000 | | | | | | | | | | | | | | | | | | | | | | | | |
| PEN | **-0.401** | **0.628** | 0.051 | 0.338 | 0.007 | 1.000 | | | | | | | | | | | | | | | | | | | | | | | |
| DIU | 0.032 | -0.315 | 0.317 | -0.014 | 0.290 | -0.211 | 1.000 | | | | | | | | | | | | | | | | | | | | | | |
| S&T | -0.218 | 0.096 | 0.178 | 0.303 | 0.329 | 0.085 | **-0.448** | 1.000 | | | | | | | | | | | | | | | | | | | | | |
| TBD | 0.016 | -0.272 | 0.011 | -0.065 | 0.168 | -0.233 | -0.224 | **0.693** | 1.000 | | | | | | | | | | | | | | | | | | | | |
| FLU | -0.323 | **0.489** | 0.046 | -0.146 | -0.054 | **0.396** | -0.068 | -0.201 | -0.304 | 1.000 | | | | | | | | | | | | | | | | | | | |
| P&A | -0.026 | -0.359 | -0.079 | -0.196 | 0.117 | -0.193 | 0.125 | 0.012 | 0.096 | 0.133 | 1.000 | | | | | | | | | | | | | | | | | | |
| FLR | -0.346 | **-0.378** | 0.019 | -0.099 | 0.225 | -0.343 | 0.181 | 0.108 | -0.031 | -0.040 | 0.262 | 1.000 | | | | | | | | | | | | | | | | | |
| PYR | -0.270 | **-0.403** | 0.009 | -0.147 | 0.221 | **-0.376** | 0.170 | 0.125 | 0.007 | -0.029 | **0.414** | **0.959** | 1.000 | | | | | | | | | | | | | | | | |
| BEA | -0.133 | -0.298 | 0.271 | 0.110 | 0.124 | -0.271 | 0.130 | 0.039 | -0.133 | -0.140 | 0.353 | **0.609** | **0.569** | 1.000 | | | | | | | | | | | | | | | |
| CHR | -0.154 | **-0.453** | 0.038 | -0.059 | -0.172 | **-0.412** | 0.090 | -0.017 | -0.001 | -0.274 | **0.376** | **0.739** | **0.727** | **0.648** | 1.000 | | | | | | | | | | | | | | |
| BbF | 0.059 | **-0.376** | -0.089 | -0.017 | -0.071 | -0.342 | 0.179 | -0.108 | -0.228 | -0.288 | **0.430** | **0.556** | **0.603** | **0.520** | **0.730** | 1.000 | | | | | | | | | | | | | |
| 246T | -0.089 | -0.044 | 0.023 | **0.490** | **0.366** | 0.291 | -0.173 | **0.401** | 0.178 | -0.027 | -0.092 | 0.081 | 0.060 | 0.007 | -0.196 | -0.134 | 1.000 | | | | | | | | | | | | |
| 245T | -0.211 | 0.006 | -0.003 | -0.009 | 0.335 | 0.073 | -0.014 | 0.279 | 0.155 | 0.028 | -0.067 | 0.255 | 0.271 | -0.034 | -0.023 | 0.161 | 0.353 | 1.000 | | | | | | | | | | | |
| TOP | 0.058 | **-0.372** | 0.095 | **-0.472** | -0.121 | -0.279 | **0.435** | **-0.369** | 0.011 | -0.202 | 0.075 | -0.007 | -0.025 | 0.281 | 0.149 | 0.022 | **-0.410** | -0.303 | 1.000 | | | | | | | | | | |
| PET | -0.275 | -0.115 | **-0.499** | **-0.404** | 0.180 | -0.015 | -0.032 | -0.039 | -0.089 | 0.161 | 0.100 | **0.436** | **0.438** | -0.088 | 0.078 | 0.132 | 0.103 | **0.413** | -0.141 | 1.000 | | | | | | | | | |
| TCC | **-0.495** | **0.428** | -0.012 | -0.103 | **0.379** | **0.382** | -0.046 | 0.108 | -0.148 | **0.608** | -0.028 | 0.201 | 0.178 | -0.095 | -0.274 | **-0.409** | 0.195 | 0.205 | -0.227 | **0.378** | 1.000 | | | | | | | | |
| BEN | -0.130 | **0.676** | -0.055 | 0.029 | -0.040 | **0.632** | -0.319 | -0.071 | **-0.397** | **0.364** | **-0.392** | **-0.383** | **-0.362** | **-0.375** | **-0.571** | **-0.474** | 0.014 | -0.146 | -0.184 | 0.097 | **0.432** | 1.000 | | | | | | | |
| BDM | -0.141 | -0.213 | -0.282 | -0.342 | -0.062 | -0.194 | 0.137 | -0.216 | -0.130 | -0.119 | -0.031 | 0.343 | 0.304 | -0.049 | 0.196 | 0.082 | -0.232 | -0.068 | 0.150 | **0.587** | 0.047 | 0.005 | 1.000 | | | | | | |
| DBC | -0.016 | -0.243 | **-0.505** | **-0.409** | 0.179 | -0.221 | 0.184 | -0.181 | -0.040 | -0.031 | 0.131 | **0.392** | **0.421** | -0.243 | 0.122 | 0.199 | -0.036 | 0.106 | -0.081 | **0.739** | 0.226 | -0.049 | **0.691** | 1.000 | | | | | |
| TCE | -0.133 | **0.726** | 0.096 | -0.037 | **-0.398** | **0.392** | **-0.382** | 0.000 | -0.232 | 0.246 | -0.247 | **-0.463** | **-0.403** | -0.271 | **-0.412** | -0.342 | -0.058 | -0.341 | -0.122 | -0.246 | 0.213 | **0.652** | -0.194 | -0.221 | 1.000 | | | | |
| ETB | 0.254 | -0.243 | -0.028 | -0.205 | -0.193 | -0.221 | 0.066 | -0.316 | -0.112 | -0.115 | 0.061 | -0.039 | 0.017 | 0.105 | 0.106 | 0.083 | -0.264 | -0.117 | **0.418** | 0.023 | -0.264 | -0.099 | 0.348 | 0.072 | -0.061 | 1.000 | | | |
| MPX | -0.045 | **0.378** | 0.094 | -0.099 | -0.289 | 0.295 | -0.213 | -0.198 | -0.227 | 0.180 | -0.173 | -0.251 | -0.222 | -0.179 | -0.111 | -0.095 | -0.242 | -0.108 | 0.083 | 0.056 | -0.031 | **0.364** | 0.305 | 0.021 | 0.340 | **0.693** | 1.000 | | |
| OXYL | 0.245 | **-0.376** | -0.174 | -0.238 | -0.046 | -0.342 | -0.002 | -0.194 | -0.116 | -0.235 | 0.219 | 0.194 | 0.263 | 0.076 | 0.295 | 0.306 | -0.260 | -0.225 | 0.255 | 0.180 | -0.248 | -0.088 | **0.537** | **0.386** | -0.166 | **0.766** | **0.548** | 1.000 | |
| BMF | -0.141 | -0.213 | **-431** | **-0.420** | 0.145 | -0.194 | 0.096 | -0.082 | 0.018 | -0.038 | 0.040 | **0.374** | **0.386** | -0.213 | 0.061 | 0.082 | 0.009 | 0.169 | -0.043 | **0.827** | 0.289 | 0.005 | **0.768** | **0.910** | -0.194 | 0.114 | 0.098 | 0.349 | 1.000 |

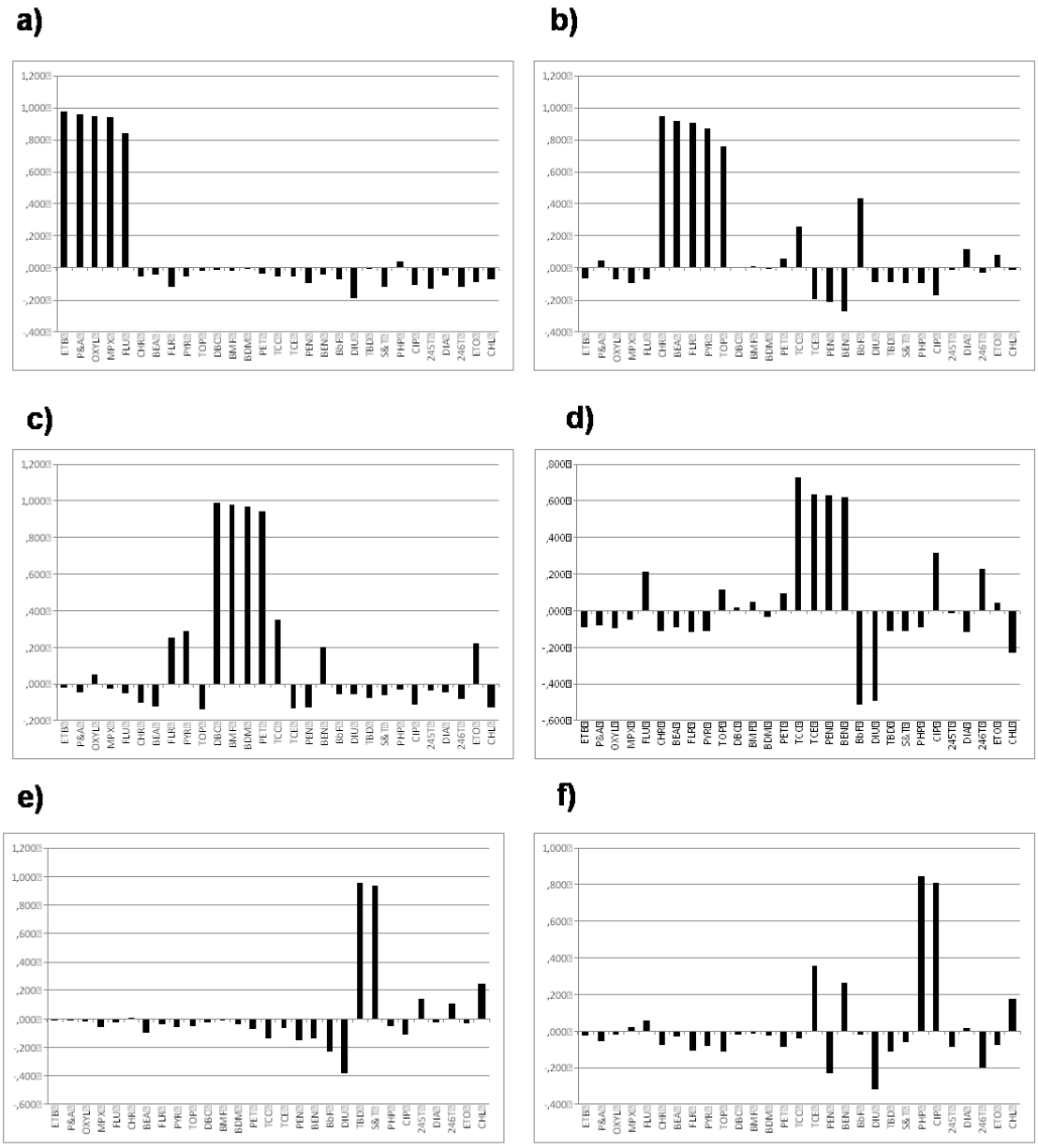
[a] Significant correlations (greater than 0.360, significance 95 %) are indicated in bold

Abbreviations: 245T: 2,4,5-Trichlorophenol; 246T: 2,4,6-Trichlorophenol; BaA: Benzo[*a*]anthracene; BbF: Benzo[*b*]fluoranthene; BDM: Bromodichloromethane; BEN: Benzene; BMF: Bromoform; CHL: Chlorfenvinphos; CHR: Chrysene; CIP: Cyproconazole; DBC: Dibromochloromethane; DIA: Diazinon; DIU: Diuron; ETB: Ethylbenzene; ETO: Ethoprophos; FLR: Fluoranthene; FLU: Fluorene; MPX: *m*-Xylene + *p*-xylene; OXYL: *o*-Xylene; P&A: Phenanthrene + anthracene; PEN: Penconazole; PET: Pentachlorophenol; PHP: 2-Phenylphenol; PYR: Pyrene; S&T: Sebuthylazine+terbuthylazine; TBD: Terbuthylazine desethyl; TCC: Carbon tetrachloride; TCE: Tetrachloroethene; TOP: 4-Tertoctylphenol

**Table S-9**
Percentages of explained variances obtained by principal component analysis.

| Principal component | Eigenvalue | Explained variance | Accumulative variance |
|---|---|---|---|
| 1 | 5.383 | 18.6 | 18.6 |
| 2 | 4.389 | 15.1 | 33.7 |
| 3 | 4.315 | 14.9 | 48.6 |
| 4 | 2.918 | 10.1 | 58.6 |
| 5 | 2.210 | 7.6 | 66.3 |
| 6 | 1.710 | 5.9 | 72.2 |
| 7 | 1.404 | 4.8 | 77.0 |
| 8 | 1.371 | 4.7 | 81.7 |
| 9 | 1.103 | 3.8 | 85.5 |

**Fig. S-1.**
Loadings for six principal components included in this study: (a) $PC_1$; (b) $PC_2$; (c) $PC_3$; (d) $PC_4$; (e) $PC_5$; (f) $PC_6$




Abbreviations: 245T: 2,4,5-Trichlorophenol; 246T: 2,4,6-Trichlorophenol; BaA: Benzo[*a*]anthracene; BbF: Benzo[*b*]fluoranthene; BDM: Bromodichloromethane; BEN: Benzene; BMF: Bromoform; CHL: Chlorfenvinphos; CHR: Chrysene; CIP: Cyproconazole; DBC: Dibromochloromethane; DIA: Diazinon; DIU: Diuron; ETB: Ethylbenzene; ETO: Ethoprophos; FLR: Fluoranthene; FLU: Fluorene; MPX: *m*-Xylene + *p*-xylene; OXYL: *o*-Xylene; P&A: Phenanthrene + anthracene; PEN: Penconazole; PET: Pentachlorophenol; PHP: 2-Phenylphenol; PYR: Pyrene; S&T: Sebuthylazine+terbuthylazine; TBD: Terbuthylazine desethyl; TCC: Carbon tetrachloride; TCE: Tetrachloroethene; TOP: 4-Tertoctylphenol

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