These data and analyses support the research article "Mass balance of emerging contaminants in the water cycle of an highly urbanized and industrialized area of Italy" by Castiglioni et al. (2018) [1].

The occurrence of 80 emerging contaminants in waste and surface water was investigated in an highly urbanised area of Italy, the River Lambro basin. The data presented here include: (1) concentrations in untreated and treated wastewater of different wastewater treatment plants (WWTPs); (2) concentrations in surface water collected along the river Lambro, in the north and south of the city of Milan (main urban center in the area). These concentrations indicate the distribution and fate of emerging contaminants in the environment.

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**Specifications Table**

| Subject area | Analytical Chemistry |
|--------------|----------------------|
| More specific subject area | Emerging Contaminants in the environment |
| Type of data | Tables |
| How data was acquired | Mass spectrometry (API 3000 QqQ, ABSciex; 6410 QqQ Agilent Technologies) |
| Data format | Raw data |
| Experimental factors | Samples were filtered and extracted by solid phase extraction |
| Experimental features | Samples were collected in the influents and effluents of three wastewater treatment plants in Milan, and in rivers receiving discharges from the plants and the surrounding urbanised area. Wastewater effluents were collected taking into account the wastewater resident time in the plant. |
| Data source location | Milan and River Lambro basin; North of Italy |
| Data accessibility | The data are available within this article. |
| Related research article | This data article is a companion paper of the research article: Castiglioni, S.; Davoli, E., Riva F., Palmiotto, M. Camporini, P. Manenti, A., Zuccato E. 2018. Mass balance of emerging contaminants in the water compartment of an highly urbanized and industrialized area of Italy. Water Research. 131, 287-298. |

**Value of the Data**

- These data offer a comprehensive overview of the occurrence of a wide panel of emerging contaminants in waste and surface water in a urban area and can be compared with other studies.
- These data may help to understand the distribution and fate of the emerging contaminants in the environment.
- These data may contribute to the need of monitoring data to support future prioritisation exercises and guidelines development by national and international authorities.
- The occurrence and distribution of contaminants may help to identify the sources of contamination in a urban area.

1. **Data**

The presented data were obtained during a comprehensive monitoring study in the most urbanised and industrialized area of Italy. The occurrence of about 80 emerging contaminants was investigated in wastewater (WW) and surface water in the river Lambro basin. The fate of these contaminants during wastewater treatment was assessed by analysing influents and effluents in three wastewater treatment plants (WWTPs) which collect wastes from the entire city of Milan. Data presented include: (1) concentrations of emerging contaminants in influent wastewater collected before any treatment (Tables 1–3); (2) concentrations in effluent wastewater collected immediately before the discharge in surface water (Tables 4–6); (3) concentrations in rivers Olona, Seveso and Lambro collected before Milan (O1,S1,L1) and in the Lambro River after discharges from the city of Milan (L2,3,4) and at the closure of the basin (L5) (Tables 7–9). Refer to [1] for detailed interpretation and discussion.
### Influent WW

| Concentrations (ng/L) | WWTP A | WWTP B | WWTP C |
|-----------------------|--------|--------|--------|
| **Antibiotics**       |        |        |        |
| Amoxicillin           | 2.0    | 1.0    | < LOQ  | < LOQ  | < LOQ  |
| Ciprofloxacin         | 655.6  | 632.7  | 220–1120 | 666.7 | 656.5 | 492–876 | 531.9 | 693.2 | 114–905 |
| Clarithromycin        | 1012.0 | 909.1  | 715–1510 | 976.1 | 976.8 | 404–1617 | 892.9 | 960.8 | 698–1075 |
| Dehydro-erythromycin  | 307.8  | 297.6  | 170–517 | 303.8 | 313.9 | 43–636  | 196.4 | 215.5 | 136–219 |
| Erythromycin          | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   |
| Lincomycin            | 29.5   | 29.7   | 14–40   | 28.1  | 28.3  | 17–40   | 13.9  | 14.3  | 10.4–173 |
| Ofloxacin             | 487.8  | 469.3  | 144–830 | 682.3 | 631.9 | 580–908 | 467.1 | 624.3 | 85–738  |
| Oxytetracycline       | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   |
| Spiramycin            | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   |
| Sulfamethoxazole      | 170.0  | 93.9   | 32–1057 | 10.5  | 5.9   | 11–36.8 | < LOQ  | < LOQ  | < LOQ   |
| Vancomycin            | 64.9   | 58.3   | LOQ–127 | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   |
| **Anticancer**        |        |        |        |
| Cyclophosphamide      | 2.9    | 2.9    | LOQ–5.5 | 1.8   | 1.0   | LOQ–4.2 | 4.9   | 3.6   | LOQ–10  |
| Methotrexate          | 3.5    | 1.4    | 0.9–28  | < LOQ  | < LOQ  | < LOQ   | 3.0   | 2.3   | LOQ–8   |
| Tamoxifen             | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   |
| **Antinflammatory**   |        |        |        |
| Diclofenac            | 798.5  | 611.9  | 214–2198 | 494.5 | 449.7 | 333–841 | 731.2 | 546.5 | 426–1794 |
| Ibuprofen             | 1709.7 | 1707.0 | 975–2377 | 1643.4| 1641.8| 1194–2114| 863.9| 873.7| 660–1049 |
| Ketoprofen            | 1209.5 | 1262.9 | 708–1924 | 964.2 | 917.6 | 792–1242| 859.0| 792.4| 685–1283 |
| Naproxen              | 1192.5 | 1207.7 | 706–1688 | 1407.9| 1072.6| 701–5921| 571.1| 534.1| 517–668 |
| Paracetamol           | 3095.8 | 3328.3 | 1961–3960| 2471.4| 2349.2| 1481–3737| 2578.4| 2683.3| 1661–3099 |
| **Bronchodilator**    |        |        |        |
| Salbutamol            | 6.9    | 6.8    | 5.1–9.8 | 12.4  | 10.5  | 6.6–23.6 | 8.3   | 8.4   | 7.1–10  |
| **Cardiovascular**    |        |        |        |
| Atenolol              | 1519.0 | 1564.7 | 1142–1789| 1913.7| 1910.4| 1368–2888| 1614.2| 1615.3| 1448–1745|
| Enalapril             | 62.9   | 65.5   | 41–86   | 106.2 | 75.2  | 57–324  | 91.1  | 92.3  | 71–114  |
| **CNS drug**          |        |        |        |
| Carbamazepine         | 286.3  | 285.1  | 184–429 | 309.2 | 314.1 | 248–370 | 1313.7| 275.5| 221–3487 |
| Demetyl-diazepam      | 3.7    | 3.7    | 2.9–4.3 | 4.5   | 4.7   | 2.2–6.3 | 3.7   | 4.0   | 2.7–4.5 |
| Diazepam              | 1.7    | 1.6    | 1.0–2.3 | 1.4   | 1.2   | 1.0–2.7 | 6.3   | 3.7   | 3.2–22  |
| **Diuretics**         |        |        |        |
| Furosemide            | 544.8  | 474.9  | 304–1083 | 429.5 | 412.8 | 165–662 | 548.7 | 446.1| 279–934 |
| Hydrochlorothiazide   | 667.6  | 740.8  | 341–848 | 547.5 | 528.4 | 116–1001| 377.6 | 369.0| 317–523 |
| **Estrogens**         |        |        |        |
| 17-β estradiol        | 15.8   | 11.8   | LOQ–37  | 6.1   | 4.6   | LOQ–15  | 15.6  | 15.1  | 12.4–19.5 |
| Estrone               | 41.2   | 41.6   | 25–57   | 53.4  | 44.6  | 20–104  | 36.3  | 35.9  | 34–41   |
| 17-α ethinylestradiol | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   |
| **Gastrointestinal**  |        |        |        |
| Omeprazole            | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   |
| Ranitidine            | 115.7  | 106.4  | 41–234  | 117.2 | 114.8 | 32–217  | 112.0 | 109.9| 83–165  |
| **Lipid Regulators**  |        |        |        |
| Atorvastatine         | 79.1   | 65.9   | 24–153  | 56.2  | 52.7  | 28–98   | 55.5  | 49.0  | 18–108  |
| Bezafibrate           | 148.1  | 155.5  | 70–281  | 156.3 | 156.1 | 91–278  | 2181.7| 1780.5| 353–6045|
| Clofibric acid        | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   |
| Gemfibrozil           | 263.3  | 204.4  | 90–787  | 215.7 | 229.2 | 114–295 | 155.4 | 154.5 | 107–197 |
| **Erectile dysfunction drug** | < LOQ   | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   |
### Table 2
Means, medians and ranges of illicit drugs (IDs) measured in influent wastewater.

| Concentrations (ng/L) | WWTP A | WWTP B | WWTP C |
|-----------------------|--------|--------|--------|
|                       | Mean   | Median | Range  | Mean   | Median | Range  | Mean   | Median | Range  |
| **Cocaine and metabolites** |        |        |        |        |        |        |        |        |        |
| Benzoylecgonine       | 638.9  | 631.3  | 480–880| 685.9  | 867.3  | 630–1300| 660.2  | 618.6  | 580–860|
| Norbenzoyleconeine    | 22.6   | 21.9   | 16–31  | 29.8   | 29.5   | 20–50  | 22.1   | 19.5   | 18–32  |
| Cocaine               | 262.2  | 251.4  | 190–325| 346.9  | 337.6  | 180–615| 242.8  | 246.2  | 174–293|
| Norcocaine            | 4.1    | 3.9    | 2.4–5.8| 6.7    | 6.1    | 4.0–13.0| 4.4    | 4.2    | 3.8–5.7|
| Cooethyllene          | 6.4    | 5.5    | 3.9–10.7| 9.2    | 9.0    | 5.0–20.0| 4.7    | 4.7    | 4.0–7.0|
| Ecgonine methyl ester | 157.9  | 153.0  | 113–228| 255.9  | 244.8  | 160–405| 115.3  | 123.4  | < LOQ-208|
| Ecgonine              | 125.3  | 122.3  | < LOQ-300| 192.9  | 189.8  | 94–312 | 97.9   | 115.3  | < LOQ-126|
| Anhydroecgonine       | < LOQ  | < LOQ  | < LOQ  | 2.6    | 0.4    | < LOQ-10| < LOQ  | < LOQ  | < LOQ  |
| Anhydroecg. methylster| < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  |
| **Opioids**           |        |        |        |        |        |        |        |        |        |
| Morphine              | 59.1   | 57.7   | 34–85  | 49.8   | 47.4   | 34–80  | 68.5   | 69.7   | 49–99  |
| 6-acetylmorphine      | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  |
| Morphine 3j glucuronide| 2.5    | 0.6    | < LOQ-7.5| 6.4    | 7.0    | < LOQ-19| 3.9    | 4.2    | < LOQ-12|
| Morphine 6j glucuronide| 2.2   | 1.5    | < LOQ-5| 2.0    | 1.5    | < LOQ-4.2| 2.8    | 1.5    | < LOQ-5.1|
| Oxycodone             | 8.7    | 2.3    | < LOQ-91| 31.6   | 23.6   | < LOQ-412| < LOQ  | < LOQ  | < LOQ  |
| Hydrocodone           | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  |
| Codeine               | 94.9   | 72.4   | 50–390 | 105.1  | 108.8  | 53–153 | 76.5   | 75.7   | 66–91  |
| 6-acetylmorphine       | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  |
| Methadone             | 9.5    | 9.4    | 6.0–14.0| 17.3   | 18.0   | 14–22  | 8.4    | 9.4    | 3.0–11.0|
| EDDP                  | 12.8   | 10.6   | 7.0–21.0| 22.4   | 22.4   | 15–33  | 9.2    | 10.3   | 4.0–12.0|
| **Amphetamines and Ketamine** |        |        |        |        |        |        |        |        |        |
| Amphetamine           | 25.2   | 21.3   | < LOQ-45| < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  |
| Methamphetamine      | 146.5  | 141.3  | 112–210| 84.5   | 64.3   | 8–240  | 10.7   | 9.8    | 9.0–14.0|
| MDA                   | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  |
| MDMA                  | 13.0   | 10.2   | < LOQ-33| 7.0    | 7.6    | < LOQ-31| 6.2    | 1.6    | < LOQ-18|
| MDEA                  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  |
| MBDB                  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  |
| Ketamine              | 6.8    | 7.0    | 4.0–9.5| 6.8    | 6.6    | < LOQ-16| 3.0    | 3.7    | < LOQ-5.3|
| **Cannabinoids**      |        |        |        |        |        |        |        |        |        |
| THC-COOH              | 67.12  | 61.07  | 50–120 | 64.59  | 63.15  | 41–90  | 91.73  | 74.17  | 41–164 |
| OH-THC                | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  |
| THC                   | 6.48   | 5.64   | < LOQ-15| < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  |

## 2. Experimental design, materials, and methods

### 2.1. Sample extraction and analysis

#### 2.1.1. Pharmaceuticals (PHARM) and illicit drugs (IDs)

PHARM and IDs were analysed using methods already published [2–4]. Briefly, samples (50 mL of influent wastewater; 100 mL of effluent wastewater; 400 mL of surface water; 500 mL of groundwater) were acidified to pH 2.0 with 37% HCl, spiked with labeled internal standards and SPE-extracted using mixed reverse-phase cation exchange cartridges (Oasis MCX). Cartridges were conditioned before use by washing with 5 mL of methanol, 3 mL of ultrapure (MilliQ) water and 3 mL of water acidified to pH 2. Samples were passed through the cartridges at a flow rate of 5–15 mL/min.
depending on the volume. Cartridges were then vacuum-dried for 10 min and eluted with 2 mL of methanol and 2 mL of a 2% ammonia solution in methanol. The eluates were pooled, dried under a nitrogen stream and redissolved in ultrapure water (200 µL) for instrumental analysis.

Analyses were done using an API 3000 QqQ equipped with a Turbo Ion Spray source (AB-Sciex, Thornhill, Ontario, Canada), two Series 200 pumps and Series 200 auto-sampler (Perkin-Elmer, Norwalk, CT). Chromatographic separation was done using a Luna C8 50 mm × 2 mm, 3 µm particle size (Phenomenex, Torrance, CA, USA) for PHARM and an XTerra MS C18, 100×2.1 mm, 3.5 µm (Waters Corp., Milford, MA) for IDs. Analytical conditions and validation parameters are described elsewhere [2–4].

Specific extraction and analytical conditions were adopted for a group of small polar metabolites of cocaine (called ecgonines) as detailed in an earlier publication [5]. The main differences were the volumes of extraction (20, 40 and 100 mL respectively for influent, effluent and surface water); the SPE cartridges (Oasis-MCX 150 mg); and sample reconstitution (eluates were dried to 20 µL and 80 µL of acetonitrile were added). In view of the high polarity of these substances, chromatographic separation was done with an XBridge HILIC 100×2.1 mm, 3.5 µm (Waters Corp., Milford, MA). Analytical conditions and validation parameters are described elsewhere [5].

### Table 3
Means, medians and ranges of the other classes of ECs measured in influent wastewater.

| Concentrations (ng/L) | WWTP A | WWTP B | WWTP C |
|-----------------------|--------|--------|--------|
|                       | Mean   | Median | Range  | Mean   | Median | Range  | Mean   | Median | Range  |
| Personal Care Products (PCPs) |       |        |        |        |        |        |        |        |        |
| PBSA                  | 185.1  | 183.0  | 60–327 | 387.1  | 361.7  | 185–573 | 309.9  | 316.9  | 202–458 |
| Benzophenone-4        | 404.8  | 392.4  | 154–638 | 548.1  | 512.4  | 236–1000 | 186.9  | 185.9  | 99–275  |
| Benzophenone-3        | 48.2   | 45.2   | 20–82  | 53.6   | 53.5   | 33–74   | 35.8   | 45.1   | < LOQ-58 |
| 4-MBC                 | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   |
| Disinfectants (DIS)   |        |        |        |        |        |        |        |        |        |
| Triclosan             | 1195   | 1144   | 505–2210 | 976.1  | 840.9  | 645–1705 | 1405   | 1609   | 706–1930 |
| Triclocarban          | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   |
| Perfluorinated compounds (PERF) |       |        |        |        |        |        |        |        |        |
| PFOS                  | 3.4    | 2.6    | 1.6–9.1 | 3.4    | 3.3    | 3.0–4.5 | 19.9   | 16.4   | 16–36   |
| PFOA                  | 7.8    | 7.6    | 6.6–10 | 11.2   | 10.2   | 6.6–24  | 9.4    | 8.8    | 8.5–11  |
| Alkylphenols and Bisphenol A (Alk-BPA) |       |        |        |        |        |        |        |        |        |
| Bisphenol A           | 443.0  | 450.9  | 400–470 | 326.9  | 354.7  | 170–385 | 1059   | 1162   | 756–1312 |
| 4-teroctylphenol      | 176.9  | 171.7  | 161–202 | 137.9  | 98.0   | 77–239  | 160.1  | 188.7  | < LOQ–410 |
| Nonylphenol           | 1492   | 1360   | 1304–1790 | 2006   | 1736   | 1187–3531 | 1059   | 1162   | 756–1312 |
| 4-octylphenol         | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ  | < LOQ   | < LOQ  | < LOQ  | < LOQ   |
| Anthropogenic Biomarkers (AM) |       |        |        |        |        |        |        |        |        |
| Caffeine              | 92337  | 85747  | 75000–113000 | 49178  | 49965  | 43000–55000 | 31795  | 34192  | 22400–36000 |
| 1-methylxanthine      | 1346   | 1235   | 1100–1700 | 3748   | 3790   | 3200–4400 | 9445   | 9663   | 4800–16400 |
| Paraxanthine          | 28395  | 29678  | 24000–32000 | 24565  | 23896  | 21400–31000 | 11939  | 11836  | 9450–14200 |
| Nicotine              | 21568  | 21253  | 17000–26000 | 9245   | 8769   | 4300–13400 | 6855   | 5437   | 1500–11700 |
| Cotinine              | 1522   | 1507   | 1450–1650 | 1818   | 1838   | 1600–2000 | 941    | 927    | 800–1100 |
### Table 4
Means, medians and ranges of pharmaceuticals (PHARM) measured in effluent wastewater.

| Concentrations (ng/L) | WWTP A | WWTP B | WWTP C |
|-----------------------|--------|--------|--------|
| **Antibiotics**       |        |        |        |
| Amoxicillin           | < LOQ  | < LOQ  | < LOQ  |
| Ciprofloxacin         | 141.0  | 137.5  | 47–246 |
| Clarithromycin        | 281.6  | 254.4  | 101–516|
| Dehydro-erythromycin  | 176.3  | 162.5  | 44–345 |
| Erythromycin          | < LOQ  | < LOQ  | < LOQ  |
| Lincomycin            | 10.2   | 9.2    | 5.9–15.8|
| Ofloxacin             | 215.1  | 203.2  | 83–380 |
| Oxycetracycline       | < LOQ  | < LOQ  | < LOQ  |
| Spiramycin            | 10.2   | 9.2    | 5.9–15.8|
| Sulfamethoxazole      | 78.8   | 67.2   | 17–382 |
| Vancomycin            | 37.0   | 31.5   | LOQ–94 |
| **Anticancer**        |        |        |        |
| Cyclophosphamide      | 4.1    | 3.9    | 2.1–7.4|
| Methotrexte           | < LOQ  | < LOQ  | < LOQ  |
| Tamoxifen             | < LOQ  | < LOQ  | < LOQ  |
| **Antiinflammatory**  |        |        |        |
| Diclofenac            | 368.5  | 294.3  | 147–812|
| Ibuprofen             | 0.9    | 0.7    | LOQ–2.8|
| Ketoprofen            | 92.4   | 69.1   | 25–220 |
| Naproxen              | 31.0   | 28.6   | 14–58  |
| Paracetamol           | < LOQ  | < LOQ  | < LOQ  |
| **Bronchodilator**    |        |        |        |
| Salbutamol            | 5.4    | 5.2    | 2.8–11 |
| **Cardiovascular**    |        |        |        |
| Atenolol              | 183.9  | 188.2  | 128–232|
| Enalapril             | < LOQ  | < LOQ  | < LOQ  |
| **CNS drug**          |        |        |        |
| Carbamazepine         | 207.4  | 180.3  | 123–353|
| Demethyl-diazepam     | 3.9    | 3.9    | 1.8–7.3|
| Diazepam              | 1.4    | 1.4    | 0.8–2.2|
| **Diuretics**         |        |        |        |
| Furosemide            | 186.4  | 171.5  | 118–295|
| Hydrochlorothiazide   | 442.5  | 302.2  | 119–2270|
| **Estrogens**         |        |        |        |
| 17-β estradiol        | < LOQ  | < LOQ  | < LOQ  |
| Estrone               | < LOQ  | < LOQ  | < LOQ  |
| 17-α ethynlestradiol  | < LOQ  | < LOQ  | < LOQ  |
| **Gastrointestinal**  |        |        |        |
| Omeprazole            | < LOQ  | < LOQ  | < LOQ  |
| Ranitidine            | 8.0    | 7.1    | LOQ–15 |
| **Lipid Regulators**  |        |        |        |
| Atorvastatine         | 1.9    | 1.3    | LOQ–4  |
| Bezafibrate           | 9.7    | 9.6    | 4.4–16.7|
| Clofibric acid        | < LOQ  | < LOQ  | < LOQ  |
| Gemfibrozil           | 4.7    | 3.3    | 2.4–9  |
| **Erectile dysfunction drug** |  | | |
| Sildenafil            | < LOQ  | < LOQ  | < LOQ  |
Table 5
Means, medians and ranges of illicit drugs (IDs) measured in effluent wastewater.

| Effluent WW | WWTP A | WWTP B | WWTP C |
|-------------|--------|--------|--------|
|              | Mean   | Median | Range  | Mean   | Median | Range  | Mean   | Median | Range  |
| Cocaine and metabolites |        |        |        |        |        |        |        |        |        |
| Benzoylecgonine   | 11.3   | 10.4   | 7.0–22.0| 5.8    | 0.9    | <LOQ–40 | 126.8  | 116.7  | 100–170 |
| Norbenzoylecgonine| 4.1    | 3.7    | 3.0–7.0| 8.4    | 6.5    | 3.0–25.0| 8.2    | 7.6    | 6.0–11.0 |
| Cocaine           | 0.9    | 0.8    | 0.5–1.3| 0.5    | 0.3    | <LOQ–2 | 26.8   | 24.3   | 22.0–36.0 |
| Norcocaine        | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | 0.9    | 0.8    | 0.6–1.3 |
| Cacaethyline      | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | 0.6    | 0.5    | 0.4–1.0 |
| Egonine methyl ester| <LOQ  | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ  | <LOQ   | <LOQ–48 |
| Egonine           | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | 22.9   | 19.8   | 18.0–34.0 |
| Anhydroecgonine   | 7.8    | 7.2    | 3.0–13.0| 25.0   | 24.6   | 16–38  | 16.1   | 17.9   | 12.0–19.0 |
| Anhydroecg. methylster| <LOQ | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ  | <LOQ   | <LOQ   |
| Opioids           |        |        |        |        |        |        |        |        |        |
| Morphine          | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | 41.7   | 34.6   | 27–91   |
| 6-acetylmorphine  | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   |
| Morphone 3β glucuronide | <LOQ  | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   |
| Morphone 6β glucuronide | <LOQ  | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   |
| Oxycodeone        | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   |
| Hydrocodone       | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   |
| Codeine           | 15.2   | 14.9   | 13.0–20.0| 32.1   | 28.2   | 11.0–65.0| 79.4   | 77.2   | 71–83   |
| 6-acetylcodine    | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   |
| Methadone         | 8.8    | 8.8    | 7.0–11.0| 14.9   | 15.5   | 10.0–21.0| 8.4    | 8.5    | 7.0–10.0 |
| EDDP              | 11.3   | 10.7   | 7.0–15.0| 21.4   | 21.2   | 11.0–31.0| 10.7   | 10.5   | 8.0–13.0 |
| Amphetamines and Ketamine |        |        |        |        |        |        |        |        |        |
| Amphetamine       | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   |
| Methamphetamine  | 24.9   | 24.0   | 14–37   | 27.3   | 18.3   | 1.5–79  | 4.0    | 3.6    | 3.0–6.5 |
| MDA               | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   |
| MDMA              | 4.0    | 1.6    | <LOQ–11 | 3.1    | 1.6    | <LOQ–12 | 3.9    | 1.6    | <LOQ–15 |
| MDEA              | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   |
| MBDB              | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   |
| Ketamine          | 7.3    | 7.5    | 3.0–11.0| 8.2    | 7.2    | 5.0–15.0| 3.2    | 3.1    | 2.0–6.0 |
| Cannabinoids      |        |        |        |        |        |        |        |        |        |
| THC-COOH          | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | 5.5    | 5.1    | <LOQ–11 |
| OH-THC            | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   |
| THC               | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   | <LOQ   |

2.1.2. Personal care products, disinfectants, perfluorinated substances, alkylphenols and BPA

Specific analytical methods were developed and validated adapting already published methods for PCPs [6], DIS [7] and Alk-BPA [8]. A novel method was developed for PERF, described by Castiglioni et al., [9]. All these substances were extracted using the same SPE procedure. Samples (100, 200, 400 and 500 mL respectively for influent, effluent, surface and groundwater) were extracted using 3 mL HLB cartridges (60 mg Oasis HLB resin) and maintaining a neutral pH (7). Cartridges were conditioned by washing with 5 mL methanol and 3 mL Milli-Q water and samples were loaded at a constant flow rate from 5–15 mL/min depending on the volume. Cartridges were vacuum-dried and eluted with 4 mL methanol. Eluates were divided into two parts (2 mL each) for separate mass spectrometric analysis.
The first aliquot was used for PERF analysis and an API 3000 QqQ equipped with a Turbo Ion Spray source (AB- Sciex, Thornhill, Ontario, Canada) was used in the negative ionisation mode. Eluates evaporated to dryness under a nitrogen stream were reconstituted in 200 µL of methanol and Milli-Q water (40:60, v/v). Chromatographic separation was done using an XTerra MS C18, 100 x 2.1 mm, 3.5 µm column (Waters Corp., Milford, MA) as detailed elsewhere [9].

The second aliquot was used for PCPs, DIS, Alk-BPA analysis. A 6410 QqQ (Agilent Technologies, Santa Clara, CA, USA) was used in positive and negative ionisation mode, respectively for analysis of PCPs and DIS. Eluates were dried and reconstituted in 200 µL of MilliQ water. Chromatographic separation was carried out using an Atlantis T3 column 150x2.1 mm, 3 µm (Waters Corp., Milford, MA, USA). Analytical details and method validation are reported by [10]. The same extract was used for the analysis of Alk-BPA, with an API 3000 QqQ in negative ionisation mode as detailed elsewhere [8].

2.1.3. Anthropogenic markers

The SPE method for the selected analytes was modified from previous publications for caffeine and nicotine analyses [11,12] and included some of the main metabolites as described by Senta et al., [13]. The extraction volumes were 3, 200, 400 and 500 mL respectively for influent, effluent, surface and groundwater. Sample pH was adjusted to 7.0–7.5 using 12% HCl (v/v) and SPE was done with Oasis
HLB cartridges previously equilibrated with 6 mL of methanol and 3 mL of ultrapure water. After loading the samples, cartridges were vacuum-dried for 5 minutes then eluted with 2 mL of methanol. Dried residues were redissolved in 100 μL of water/methanol mixture (80/20, v/v). Chromatographic separation was done using a 100×1 mm X-Terra C18 column (Waters Corp., Milford, MA, USA). Chromatographic and mass spectrometric conditions for analyses are described elsewhere [13].

Table 7
Concentrations of PHARM (ng/L) in surface water samples.

| PHARM          | North of Milan | South of Milan |
|----------------|----------------|----------------|
|                | O1  | S1  | L1  | L2  | L3  | L4  | L5  |
| Antibiotics    |     |     |     |     |     |     |     |
| Amoxicillin    | 2.0 | 10.3| 4.4 | 22.7| 25.3| 13.0| 16.7|
| Ciprofloxacin  | 22.6| 60.1| 31.2| 41.2| 55.1| 19.4| 6.7 |
| Clarithromycin | 182 | 326 | 119 | 202 | 212 | 177 | 149 |
| Dehydro-Erythromycin | 61 | 94.7| 30.2| 73.3| 60.6| 58.0| 53.2|
| Lincomycin     | 3.0 | 10.2| 5.0 | 23.2| 6.8 | 4.9 | 13.8|
| Ofloxacin      | 81.0| 158 | 73.4| 117 | 150 | 69.4| 30.7|
| Sulfamethoxazole| 3.2 | 1.3 | 6.3 | 1.6 | 9.5 | 13.9| 10.1|
| Vancomycin     | 1.0 | 1.0 | 6.2 | 9.5 | 9.2 | 8.0 | 19.6|
| Antiinflammatory |    |     |     |     |     |     |     |
| Diclofenac     | 86.5| 184 | 60.0| 605 | 461 | 215 | 121 |
| Ibuprofen      | 76.5| 134 | 53.5| 174 | 107 | 62.6| 79.5|
| Ketoprofen     | 3.9 | 9.8 | 30.8| 26.8| 20.1| 8.5 | 0.9 |
| Naproxen       | 52.4| 92.7| 71.1| 124 | 122 | 75.7| 62.4|
| Paracetamol    | 1.0 | 9.5 | 10.4| 26.8| 25.7| 24.3| 18.8|
| Bronchodilator |     |     |     |     |     |     |     |
| Salbutamol     | 1.8 | 3.6 | 1.6 | 12.8| 2.2 | 339 | 205 |
| Cardiovascular |     |     |     |     |     |     |     |
| Atenolol       | 110 | 400 | 171 | 280 | 232 | 184 | 166 |
| Enalapril      | 1.5 | 6.5 | 2.6 | 7.1 | 5.7 | 4.4 | 3.6 |
| CNS drug       |     |     |     |     |     |     |     |
| Carbamazepine  | 115 | 166 | 54.2| 246 | 105 | 78.4| 86.0|
| Diazepam       | 0.4 | 0.8 | 0.3 | 2.3 | 2.7 | 125 | 53  |
| Demetyl-diazepam| 0.8 | 1.7 | 0.7 | 1.6 | 1.1 | 66.3| 38.0|
| Diuretics      |     |     |     |     |     |     |     |
| Furosemide     | 33.0| 74.3| 70.3| 72.2| 77.7| 572 | 27.0|
| Hydrochlorothiazide | 23.2| 74.1| 31.9| 46.9| 77.1| 649 | 314 |
| Estrogens      |     |     |     |     |     |     |     |
| 17-β estradiol | 1.3 | 4.0 | 2.3 | 3.2 | 2.5 | 2.5 | 1.3 |
| Estrone        | 5.0 | 12.6| 7.8 | 20.4| 11.7| 7.9 | 5.4 |
| Gastrointestinal |    |     |     |     |     |     |     |
| Ranitidine     | 7.0 | 14.4| 4.2 | 10.6| 8.5 | 4.0 | 5.1 |
| Lipid Regulators |   |     |     |     |     |     |     |
| Atorvastatine  | 1.4 | 4.2 | 1.6 | 3.3 | 2.3 | 0.8 | 0.8 |
| Bezaflibrate   | 12.3| 22.2| 9.9 | 21.3| 148 | 79.5| 28.2|
| Clofibr acid   | 5.4 | 1.4 | 0.2 | 41.2| 0.2 | 0.2 | 8.4 |
| Gemfibrozil     | 15.0| 27.5| 8.5 | 23.3| 19.0| 9.0 | 11.5|
### Table 8
Concentrations of IDs (ng/L) in surface water samples.

| IDs                          | North of Milan | South of Milan |
|------------------------------|----------------|----------------|
|                              | O1  | S1   | L1  | L2  | L3  | L4  | L5  |
| Cocaine and metabolites      |     |      |     |     |     |     |     |
| Benzoylecgonine              | 33.5| 74.8 | 38.5| 82.1| 65.4| 39.2| 45.4|
| Norbenzylecgonine            | 2.9 | 7.5  | 3.7 | 6.6 | 4.9 | 3.2 | 3.1 |
| Cocaine                      | 3.9 | 21.2 | 10.1| 33.3| 18.9| 12.2| 12.0|
| Norcocode                     | 0.1 | 0.7  | 0.4 | 0.7 | 0.7 | 0.4 | 0.4 |
| Cocoethylene                 | 0.1 | 0.3  | 0.2 | 0.3 | 0.2 | 0.2 | 0.3 |
| Ecgonine methyl ester        | 4.9 | 6.2  | 3.7 | 20.3| 10.7| 8.8 | 9.9 |
| Anhydroecgonine              | 9.0 | 21.3 | 6.0 | 14.1| 6.6 | 12.2| 7.9 |
| Opioids                      |     |      |     |     |     |     |     |
| Morphine                     | 0.3 | 1.6  | 2.5 | 2.0 | 6.2 | 8.2 | 1.5 |
| Codeine                      | 15.4| 23.0 | 9.6 | 20.6| 15.7| 10.7| 10.2|
| Methadone                    | 2.5 | 9.7  | 1.8 | 8.0 | 3.7 | 2.6 | 2.7 |
| EDDP                         | 4.7 | 15.9 | 4.2 | 10.2| 7.3 | 4.2 | 3.3 |
| Amphetamines and Ketamine    |     |      |     |     |     |     |     |
| Methampethamine              | 0.2 | 1.1  | 0.2 | 2.7 | 0.9 | 0.8 | 0.8 |
| MDMA                         | 0.2 | 0.2  | 1.2 | 1.5 | 1.5 | 1.3 | 0.5 |
| Ketamine                     | 40.8| 4.1  | 0.6 | 3.4 | 1.4 | 1.0 | 1.8 |
| Cannabinoids                 |     |      |     |     |     |     |     |
| THC-COOH                     | 0.7 | 1.4  | 2.0 | 3.5 | 2.7 | 1.9 | 2.1 |

### Table 9
Concentrations of the others ECs (ng/L) in surface water samples.

| Personal Care Products (PCPs) | North of Milan | South of Milan |
|-------------------------------|----------------|----------------|
|                              | O1  | S1   | L1  | L2  | L3  | L4  | L5  |
| PBSA                          | 167 | 517  | 105 | 294 | 174 | 167 | 124 |
| Benzophenone-4                | 168 | 373  | 109 | 241 | 172 | 142 | 112 |
| Benzophenone-3                | 4.1 | 13.7 | 3.8 | 9.1 | 6.6 | 4.7 | 2.8 |
| Disinfectants (DIS)           |     |      |     |     |     |     |     |
| Triclosan                     | 35.4| 149  | 59.8| 52.2| 131 | 117 | 86.6|
| Perfluorinated compounds (PERF)|     |      |     |     |     |     |     |
| PFOS                          | 4.2 | 6.6  | 4.4 | 4.9 | 12.7| 6.2 | 14.2|
| PFOA                          | 25.1| 33.8 | 13.1| 26.5| 16.7| 11.7| 18.4|
| Alkylphenols and Bisphenol A (Alk-BPA) |     |      |     |     |     |     |     |
| Bisphenol A                   | 90.1| 295  | 126 | 154 | 119 | 131 | 114 |
| 4-ter-octylphenol             | 14.6| 110  | 14.1| 18.7| 22.4| 14.8| 11.1|
| Nonylphenol                   | 38.4| 277  | 33.9| 51.9| 33.7| 27.8| 24.3|
| Anthropicogenic Biomarkers (AM)|     |      |     |     |     |     |     |
| Caffeine                      | 885 | 4339 | 1519| 3344| 2903| 2126| 1644|
| 1-methylxanthine              | 5.3 | 5.3  | 5.3 | 37.7| 35.0| 5.3 | 5.3 |
| Paraxanthine                  | 105 | 367  | 180 | 300 | 329 | 236 | 184 |
| Nicotine                      | 673 | 6424 | 2259| 3334| 3015| 2033| 1254|
| Cotinine                      | 50.7| 148  | 53.2| 118 | 110 | 78.1| 70.4|
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