**Supplementary materials**

Occurrence and removal of illicit drugs in different wastewater treatment plants with different treatment techniques

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Caption:

Table S1. 12 illicit drugs analyte ions and MS parameters.

Table S2. Recoveries (%) of illicit drugs and their metabolites from different matrix with spiking concentration of 10 n/L.

Table S3. Recoveries (%) of 12illicit drugs and their metabolites in waste water with different spiking concentrations.

Table S4. The structural formula, elemental composition and physicochemical properties for 12 illicit drugs and their metabolites.

Table S5. Full text abbreviations of professional terms.

Table S1 12 illicit drugs analyte ions and MS parameters

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Target | retention time(min) | precursor ion(m/z) | declustering potential(V) | quota ion | | qualitative ion | |
| collision voltage(V) | product Ion(m/z) | collision voltage(V) | product Ion(m/z) |
| AMP | 1.83 | 136.1 | 14 | 14 | 91 | 9 | 119.1 |
| METH | 1.96 | 150.1 | 22 | 16 | 91 | 10 | 119.1 |
| MC | 1.64 | 164.1 | 20 | 18 | 131 | 22 | 105 |
| MDA | 1.91 | 180 | 22 | 20 | 105 | 16 | 135.4 |
| MDMA | 2.01 | 194.1 | 22 | 12 | 163 | 24 | 105 |
| NK | 2.2 | 224 | 28 | 24 | 125 | 50 | 89.2 |
| KET | 2.27 | 232 | 16 | 24 | 125 | 16 | 179 |
| BE | 2.25 | 290 | 20 | 20 | 168.1 | 28 | 105 |
| COC | 2.71 | 304.1 | 6 | 18 | 182.1 | 28 | 82.1 |
| MTD | 3.93 | 310.1 | 4 | 24 | 105 | 48 | 77.1 |
| HER | 2.61 | 370 | 34 | 48 | 165.1 | 26 | 268.1 |
| COD | 1.74 | 300 | 28 | 26 | 215.1 | 35 | 165.1 |

Table S2 Recoveries (%) of illicit drugs and their metabolites from different matrix with spiking concentration of 10 ng/L.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Analytes | Tap water | | Milli-Q water | | Surface water | |
|  | Mean（%） | RSD（%） | Mean（%） | RSD（%） | Mean（%） | RSD（%） |
| METH | 82.7 | 1.8 | 80.8 | 9.5 | 71.8 | 4.7 |
| AMP | 94.2 | 2.6 | 78.7 | 6.1 | 75.6 | 3.9 |
| KET | 88.7 | 0.9 | 83.2 | 5.1 | 72.7 | 4.2 |
| MC | 90.4 | 1.2 | 75.6 | 4.5 | 75.8 | 3.6 |
| MDA | 83.8 | 3.5 | 82.5 | 5.8 | 74.7 | 5.7 |
| MDMA | 93.6 | 6.3 | 76.8 | 7.3 | 73.9 | 4.8 |
| NK | 79.8 | 3.7 | 84.5 | 5.6 | 72.3 | 3.4 |
| BE | 82.3 | 1.4 | 80.6 | 2.4 | 83.7 | 7.3 |
| COD | 87.1 | 7.3 | 79.7 | 1.8 | 76.2 | 8.2 |
| COC | 91.4 | 5.6 | 71.2 | 3.7 | 74.9 | 4.1 |
| MET | 73.8 | 1.9 | 80.7 | 6.9 | 87.4 | 2.8 |
| HR | 76.3 | 4.7 | 85.1 | 2.7 | 82.9 | 3.5 |

Table S3 Recoveries (%) of 12 illicit drugs and their metabolites in waste water with different spiking concentrations.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Analytes | | 0.1 ng/L | | | | 10 ng/L | | | | 50 ng/L | | | |
|  | | Mean（%） | | RSD（%） | | Mean（%） | | RSD（%） | | Mean（%） | | RSD（%） | |
| METH | | 81.3 | | 3.2 | | 88.9 | | 5.3 | | 81.4 | | 7.2 | |
| AMP | | 90.1 | | 8.2 | | 79.8 | | 4.6 | | 79.3 | | 9.7 | |
| KET | | 82.9 | | 0.7 | | 86.3 | | 3.9 | | 75.5 | | 8.3 | |
| MC | | 80.1 | | 2.4 | | 89.4 | | 3.1 | | 80.3 | | 5.4 | |
| MDA | | 92.2 | | 7.2 | | 95.1 | | 4.5 | | 81.2 | | 5.6 | |
| MDMA | | 79.5 | | 4.5 | | 85.3 | | 2.7 | | 73.9 | | 6.3 | |
| NK | | 83.4 | | 3.6 | | 90.1 | | 0.9 | | 70.1 | | 9.5 | |
| BE | | 75.3 | | 2.7 | | 84.2 | | 1.4 | | 74.5 | | 8.1 | |
| COD | | 72.8 | | 0.9 | | 86.5 | | 9.6 | | 79.7 | | 7.3 | |
| COC | | 93.6 | | 5.3 | | 89.4 | | 2.5 | | 83.9 | | 2.6 | |
| MET | | 70.7 | | 6.1 | | 82.7 | | 4.8 | | 82.1 | | 4.7 | |
| HR | | 87.3 | | 3.9 | | 92.6 | | 1.7 | | 90.6 | | 1.5 | |
|  |  | |  | |  | |  | |  | |  | |  |  |  |

Table S4 The structural formula, elemental composition and physicochemical properties for 12 illicit drugs and their metabolites.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Classes | Common name | CAS | Elemental composition | Monoisotopic mass | p*K*a | | Tbp(°C) | water Solubility |
|  |  | pKa(acid) | pKa(base) | (mgL-1) |
| Amphetamines | Amphetamine | 300-62-9 | C9H13N | 135.21 | - | 9.9±0.4 | 211.58 | 2.80E+04 |
| Methamphetamine | 7632/10/2 | C10H15N | 149.24 | - | 10.3 ± 0.4 | 215.79 | 1.33E+04 |
| Methcathinone | 66514-93-0 | C10H13NO·HCl | 163.22 | - | 8.5 ± 0.4 | 251.53 | 1.78E+04 |
| MDA | 4764-17-4 | C10H13NO2 | 179.22 | - | 9.5 ± 0.4 | 281.85 | 1.59E+04 |
| MDMA | 42542-10-9 | C11H15NO2 | 193.24 | - | 9.9 ± 0.4 | 285.27 | 7034 |
| Ketamine | Norketamine | 79499-59-5 | C12H14ClNO·HCl | 223.7 | - | 8.5 ± 0.4 | 337.1 | 1801 |
| Ketamine | 1867-66-9 | C13H16ClNO·HCl | 237.73 | - | 7.1 ± 0.4 | 339.74 | 3870 |
| Cocaine | Cocaine | 50-36-2 | C17H21NO4 | 303.35 | - | 8.6 ± 0.4 | 362.63 | 1298 |
| Benzoylecgonine | 519-09-5 | C16H19NO4 | 289.33 | 2.9 ± 0.5 | 9.2±0.5 | 489.11 | 1605 |
| Opioids | Codeine | 76-57-3 | C18H21NO3 | 299.36 | 14.1 ± 0.5 | 8.2 ± 0.4 | 405.72 | 1.22E+04 |
| Methadone | 76-99-3 | C21H27NO | 309.45 | - | 8.74±0.4 | 390.44 | 48.48 |
| Heroin | 561-27-3 | C21H23NO5 | 369.42 | - | 8.0 ± 0.4 | 424.35 | 2152 |

Table S5 Full text abbreviations of professional terms

|  |  |
| --- | --- |
| methamphetamine | METH |
| 3,4-methylenedioxymethamphetamine | MDMA |
| benzoylecgonine | BE |
| cocaine | COC |
| amphetamine | AMP |
| methadone | MET |
| ketamine | KET |
| codeine | COD |
| norketamine | NK |
| methcathinone | MC |
| heroin | HR |
| 3,4-methylenedioxyamphetamine | MDA |
| methamphetamine-d8 | METH-d8 |
| methanol | MeOH |
| acetonitrile | ACN |
| formic acid | FA |
| ammonium hydroxide | NH3H2O |
| the solid phase extraction | SPE |
| ultra-performance liquid chromatography equipped with tandem mass spectrometry | UPLC-MS/MS |
| electrospray ionization | ESI+ |
| multiple-reaction monitoring | MRM |
| limit of detection | LOD |
| wastewater based epidemiology | WBE |
| ethylenediaminetetraacetic acid disodium salt | EDTA-2Na |
| anoxic oxic | A/O |
| limit of detection | LOD |
| anaerobic anoxicoxic | A2/O |
| anoxic oxic | A/O |
| sequencing batch reactor activated sludge | SBR |
| wastewater treatment plants | WWTP |
| contaminants of emerging concern | CECs |