Source-related smart suspect screening in the aqueous environment: search for tire-derived persistent and mobile trace organic contaminants in surface waters

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| number | proposed compound         | $m/z$ of molecular ion or adduct ion | RT [min] | $m/z$ of fragment ions | assigned elemental composition |
|--------|---------------------------|---------------------------------------|----------|------------------------|-------------------------------|
| Positive mode | [M+H]$^+$ / [M+Na]$^+$ | cations                              |          |                        |                               |
| 1      | C19H42N6O11Na             | 553.283                               | 6.83     | 385.1818               | C19H42N6O11Na                |
|        |                           |                                       |          | 337.2134               | C13H26N6O6Na                 |
|        |                           |                                       |          | 283.1531               | C12H22N6O4Na                 |
|        |                           |                                       |          | 177.0876               | C11H19N6O3                   |
|        |                           |                                       |          | 163.0715               | C7H9N6                       |
| 2      | diformylated HMMM         | 473.232                               | 9.32     | 207.1003               | C17H34N6O8Na                 |
|        |                           |                                       |          | 177.0876               | C8H11N6O                     |
|        |                           |                                       |          | 163.0715               | C7H9N6                       |
| 3      | formylated HMMM           | 443.223                               | 9.01     | 315.1776               | C16H32N6O7Na                 |
|        |                           |                                       |          | 283.152                | C12H23N6O4                   |
|        |                           |                                       |          | 177.0876               | C11H19N6O3                   |
|   |   |   |   |
|---|---|---|---|
| 4 | 4 | 239.126 | C9H15N6O2 |
|   |   | 177.0890 | C7H9N6 |
|   |   |   |   |
| 4 | diformylated PMMM | 429.206 | 8.18 |
|   |   |   |   |
| 5 | HMM | 413.213 | 8.64 |
|   |   |   |   |
|   |        |      |     |                        |                        |
|---|--------|------|-----|------------------------|------------------------|
| 6 | formylated PMMM | 399.196 | 7.75 | C14H28N6O6Na          | C14H28N6O6Na          |
|   |        |      |     |                        |                        |
|   |        |      |     | 369.1862 C13H26N6O5Na | 369.1862 C13H26N6O5Na |
|   |        |      |     | 337.1593 C12H22N6O4Na  | 337.1593 C12H22N6O4Na  |
|   |        |      |     | 315.1784 C12H23N6O4    | 315.1784 C12H23N6O4    |
|   |        |      |     | 283.1511 C11H19N6O3    | 283.1511 C11H19N6O3    |
|   |        |      |     | 239.1243 C9H15N6O2     | 239.1243 C9H15N6O2     |
|   |        |      |     | 207.0983 C8H11N6O      | 207.0983 C8H11N6O      |
|   |        |      |     | 177.0876 C7H9N6        | 177.0876 C7H9N6        |
|   |        |      |     | 163.0715 C6H7N6        | 163.0715 C6H7N6        |
| 7 | C13H26N6O6Na | 385.182 | 6.95 | C13H26N6O6Na          | C13H26N6O6Na          |
|   |        |      |     | 283.1531 C11H19N6O3    | 283.1531 C11H19N6O3    |
|   |        |      |     | 177.0876 C7H9N6        | 177.0876 C7H9N6        |
|   |        |      |     | 163.0715 C6H7N6        | 163.0715 C6H7N6        |
| 8 | PMMM    | 369.186 | 7.61 | C13H26N6O5Na          | C13H26N6O5Na          |
|   |        |      |     | 315.1784 C12H23N6O4    | 315.1784 C12H23N6O4    |
|   |        |      |     | 239.1263 C9H15N6O2     | 239.1263 C9H15N6O2     |
|   |   |   |   |
|---|---|---|---|
|   |   |   |   |
| 9 | TMMM | 349.154 | 6.32 |
|   |   |   |   |
| 10 | HMMM TP 311 | 311.144 | 5.20 |
|   |   |   |   |
| 11 | DMMM | 215.124 | 3.03 |
|   |   |   |   |
| 12 | unknown | 351.132 | 5.75 |

**Molecular Formulas:**

|   |   |   |   |
|---|---|---|---|
|   |   |   |   |
| 9 | C13H22N6O4Na | 349.154 | 6.32 |
|   | C11H22N6O4Na | 349.154 | 6.32 |
|   | C9H17N6O3 | 349.154 | 6.32 |
|   | C8H15N6O2 | 349.154 | 6.32 |
|   | C7H11N6O | 349.154 | 6.32 |
|   | C6H9N6 | 349.154 | 6.32 |
|   | C5H7N6 | 349.154 | 6.32 |
|   | C10H20N6O4Na | 349.154 | 6.32 |
|   | C6H9N6 | 349.154 | 6.32 |
|   | C5H7N6 | 349.154 | 6.32 |
|   | C7H15N6O2 | 349.154 | 6.32 |
|   | C6H13N6O2 | 349.154 | 6.32 |
|   | C5H7N6 | 349.154 | 6.32 |
|   | C4H7N6 | 349.154 | 6.32 |

**Composition:**

|   |   |   |   |
|---|---|---|---|
|   |   |   |   |
| 9 | C7H9N6 | 177.0876 |
|   | C6H7N6 | 163.0715 |
|   |   |   |   |
| 10 | C10H20N6O4Na | 311.144 | 5.20 |
|   | C6H9N6 | 165.0877 |
|   | C5H7N6 | 151.0727 |
|   |   |   |   |
| 11 | C7H15N6O2 | 215.124 | 3.03 |
|   | C6H13N6O2 | 201.1087 |
|   | C5H7N6 | 151.0727 |
|   | C4H7N6 | 139.0699 |
|   |   |   |   |
| 12 | unknown | 351.132 | 5.75 |

**Unknown Molecules:**

|   |   |   |   |
|---|---|---|---|
|   |   |   |   |
| 13 | C17H16N3O3 | 310.118 | 4.09 | 305.1274 | -CH2O2 |
|    |            |         |      | 235.0798 | -C6H8N |
|    |            |         |      | 193.0695 | -C6H8N,-C2H2O |
| 14 | C16H18N3O2 | 284.139 | 6.20 | C16H18N3O2 | |
|    |            |         |      | 145.075  | C9H9N2 |
|    |            |         |      | 195.091  | C13H11N2 |
| 15 | C16H16N3O  | 266.128 | 4.62 | C16H16N3O | |
|    |            |         |      | 195.091  | C13H11N2 |
|    |            |         |      | 92.049   | C6H6N  |
| 16 | PA6 Dimer* | 249.157 | 4.57 | C12H22N2O2Na |
|    |            |         |      | 209.165  | C12H21N2O |
|    |            |         |      | 100.1110 | C6H14N  |
| 17 | C15H22NO2  | 248.164 | 5.80 |          | |
| 18 | C15H16NO   | 226.123 | 9.58 |          | |
| 19 | 1.3-dicyclohexylurea | 225.197 | 9.72 | C13H25N2O |
|   | Name                          | Molecular Weight | Relative Intensity | Molecular Formula | Molecular Weight     |
|---|-------------------------------|-------------------|-------------------|--------------------|----------------------|
| 20| N-Cyclohexyl-N'-phenylurea    | 219.149           | 9.19              | C6H14N             | 100.111              |
|   |                               |                   |                   |                    | 83.085               |
|   |                               |                   |                   |                    | C6H11                |
| 21| C13H13N2O                     | 213.102           | 7.99              | C13H13N2O          | 184.0760             |
|   |                               |                   |                   |                    | 129.068              |
|   |                               |                   |                   |                    | C6H8N2               |
| 22| 1.3-Diphenylguanidine         | 212.119           | 4.95              | C13H14N3           | 195.0917             |
|   |                               |                   |                   |                    | 94.0641              |
|   |                               |                   |                   |                    | C6H8N                |
| 23| C12H16N2Na                    | 211.124           | 8.49              | C13H26N           | 114.127              |
|   |                               |                   |                   |                    | 83.085               |
|   |                               |                   |                   |                    | C6H11                |
| 24| N-Methylocyclohexylamine      | 196.207           | 5.62              | C13H26N           | 108.068              |
|   |                               |                   |                   |                    | C6H8N                |
| 25| Tributylamine                 | 186.220           | 6.02              | C6H11              | 111.0443             |
|   |                               |                   |                   |                    | 94.0641              |
|   |                               |                   |                   |                    | C6H8N                |
|   | Compound                          | MW    | LogP | Molecular Formula       |
|---|-----------------------------------|-------|------|-------------------------|
|26 | Dicyclohexylamine                 | 182.191 | 5.85 | C12H24N                |
|   |                                   |       |      |                         |
|   |                                   |       |      | C6H14N                  |
|   |                                   |       |      |                         |
|   |                                   |       |      |                         |
|27 | C8H10NO_Acetanilide ?             | 136.075 | 5.81 |
|28 | cyclohexylethylamine              | 128.144 | 2.89 |
|29 | caprolactam                       | 114.091 | 4.17 |
|30 | C6H8N                             | 94.064 | 1.36 |
|31 | heptaethylene glycol monoethyl ether | 395.158 | 6.28 | C14H30NO8NaS           |
|   |                                   |       |      |                         |
|   |                                   |       |      | 333.1880                |
|   |                                   |       |      | -NOS                    |
|   |                                   |       |      | 175.0795               |
|   |                                   |       |      | -C6H16O5               |
|32 | unknown                           | 377.214 | 6.72 |
|33 | hexaethylene glycol monoethyl ether | 333.188 | 5.92 |
|34 | hexaaoxaoctadecane/ propoxylated glycerol | 289.162 | 5.47 |
|35 | hexaaoxaoctadecane/ propoxylated glycerol | 289.162 | 5.81 |
|36 | tetraethylene glycol dimethyl ether | 245.135 | 4.83 |
|37 | unknown                           | 249.009 | 6.56 |
|   |     |          |        |        |
|---|-----|----------|--------|--------|
| 38 | unknown | 158.151 | 8.96   |        |
| 39 | mercaptobenzothiazole | 167.993 | 7.48   |        |
| 40 | hydroxybenzothiazole | 152.016 | 7.05   |        |
| 41 | aminobenzothiazole | 151.032 | 3.93   |        |
| 42 | benzothiazole | 136.020 | 7.19   |        |
|   | negative mode | [M-H]⁻ | anions |        |
| 43 | benzothiazolsulfonic acid | 213.9645 | 4.80   | 121.0293 C7H4NS |
| 44 | unknown | 178.0537 | 4.16   |        |
| 45 | C7H5O2 | 121.0294 | 4.73   |        |
| 46 | C9H17O3 | 173.1188 | 7.56   |        |
| 47 | unknown | 309.1026 | 8.71   |        |
| 48 | unknown | 309.1027 | 9.48   |        |
Table S2: Detected relative peak areas in the TCR and the RD samples, in River Parthe at dry weather, after some and after heavy rainfall, and in the influent and effluent of a wastewater treatment plant (3 dates)

| Compound No | TCR | RD | River Parthe | Wastewater treatment plant |
|-------------|-----|----|--------------|---------------------------|
|             |     |    | Dry weather  | some rain                 | strong rain               | influent_1 | influent_2 | influent_3 | effluent_1 | effluent_2 | effluent_3 |
| 1           | 948 | 72365 | n.d. | 1002 | 3736 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 2           | 1414 | 23 | n.d. | n.d. | 17372 | 56 | 113 | 1796 | 111 | 11 | 292 |
| 3           | 9899 | 268 | 28005 | 32224 | 96285 | 2596 | 3075 | 16906 | 2552 | 385 | 5223 |
| 4           | 3273 | 173 | n.d. | n.d. | 26686 | 280 | 908 | 833 | 110 | 28 | 392 |
| 5           | 24858 | 510 | 2548793 | 5213327 | 17020433 | 18823 | 18775 | 50038 | 10446 | 2050 | 17057 |
| 6           | 14205 | 883 | 243 | 250 | 51177 | 4336 | 8645 | 6407 | 1255 | 341 | 3063 |
| 7           | 2385 | 792 | n.d. | n.d. | 9874 | 496 | 1596 | 277 | 99 | 45 | 199 |
| 8           | 680 | 112 | n.d. | n.d. | 42863 | 3136 | 1385 | 10420 | 1463 | 61 | 3278 |
| 9           | 2171 | 4297 | n.d. | n.d. | 7432 | 1450 | 2050 | 5722 | 1085 | 168 | 1036 |
| 10          | 3029 | 1289 | n.d. | n.d. | 3738 | 32 | 49 | 65 | n.d. | 13 | n.d. |
| 11          | 7764 | 2044 | 2124 | 2133 | 17458 | 553 | 2908 | 1044 | 1135 | 212 | 1693 |
|   | 12   | 13   | 14   | 15   | 16   | 17   | 18   | 19   | 20   | 21   | 22   | 23   | 24   | 25   | 26   | 27   | 28   |
|---|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|   | 388  | 651  | 4466 | 11503| 3810 | 1367 | 1971 | 65912| 31689| 68854| 149261| 1202 | 24833| 4982 | 333997| 153  | 280  |
|   | 89   | 7296 | 5706 | 7328 | 247  | 412  | 1133 | 6537 | 4422 | 281  | 311422 | 1747 | 1626 | 4386 | 27566 | 330  | 89   |
|   | n.d. | n.d. | n.d. | n.d. | 923900| n.d. | n.d. | n.d. | 306  | n.d. | 15035 | 1924 | 522  | n.d. | 2565  | n.d. | n.d. |
|   | n.d. | n.d. | n.d. | n.d. | 1185208| n.d. | n.d. | n.d. | 686  | n.d. | 15815 | 7272 | 397  | 738  | 2565  | n.d. | n.d. |
|   | 11541| n.d. | n.d. | 1216 | 2417123| n.d. | n.d. | n.d. | 764  | n.d. | 25462 | 13434| 32299| 763  | 402762| n.d. | n.d. |
|   | n.d. | n.d. | n.d. | 1616 | 864   | n.d. | n.d. | n.d. | n.d. | n.d. | 2201  | 2949 | 190  | 812  | 64196 | n.d. | n.d. |
|   | n.d. | n.d. | n.d. | n.d. | 957   | n.d. | n.d. | n.d. | n.d. | n.d. | 250   | 65   | 10   | 9    | 4647  | n.d. | n.d. |
|   | n.d. | n.d. | n.d. | n.d. | 373   | n.d. | n.d. | n.d. | n.d. | n.d. | 179   | 65   | 4256 | 10   | 33321 | n.d. | n.d. |
|   | n.d. | n.d. | n.d. | n.d. | 375   | n.d. | n.d. | n.d. | n.d. | n.d. | 703   | 30   | 14   | n.d. | 492   | n.d. | n.d. |
|   | n.d. | n.d. | n.d. | n.d. | 347   | n.d. | n.d. | n.d. | 4580 | n.d. | 144   | 38   | n.d. | 318  | n.d.   | n.d. | n.d. |
|   | n.d. | n.d. | n.d. | n.d. | 4717  | n.d. | n.d. | n.d. | 4501 | n.d. | 24    | n.d. | n.d. | n.d. | n.d.   | n.d. | n.d. |
|   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|
| 29 | 9725 | 7771 | 36218 | 28805 | 34657 | 62141 | 8373 | 35342 | 16220 | 36644 | 22521 |
| 30 | 1073 | 1339 | n.d. | n.d. | 1428 | 3575 | 2789 | 3854 | n.d. | n.d. | n.d. |
| 31 | 174  | 166  | n.d. | n.d. | 11047| n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 32 | 5515 | 851  | 763  | 1827 | 96645| 752  | 995  | 800  | n.d. | n.d. | n.d. |
| 33 | 686  | 2833 | n.d. | n.d. | 10631| 677  | 67   | 18   | n.d. | n.d. | n.d. |
| 34 | 3549 | 1008 | 663  | 3714 | 78784| 75   | 82   | 30   | 13   | 15   | 22   |
| 35 | 13340| 1204 | 690  | 1005 | 22963| 481  | 485  | 180  | 13   | 5    | 8    |
| 36 | 3088 | 608  | 638  | 700  | 21900| 751  | 27   | 36   | n.d. | n.d. | n.d. |
| 37 | 166  | 1840 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 38 | 602  | 1471 | 3180 | 3253 | 2922 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 39 | 1733 | 3537 | 1554 | 1207 | 1278 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 40 | 48672| 2009 | 523  | 815  | 1406 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 41 | 2710 | 314  | n.d. | n.d. | n.d. | 162  | 22   | 47   | n.d. | n.d. | n.d. |
| 42 | 1687 | 136  | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 43 | 2483 | 60461| 10031| 11023| 9454 | 103  | 125  | 100  | 155  | 179  | 116  |
| 44 | 27   | 245  | 1520 | 1847 | 5303 | 30616| 14632| 28449| n.d. | n.d. | n.d. |
| 45 | 115  | 826  | 852  | 936  | 902  | 204  | n.d. | 193  | n.d. | n.d. | n.d. |
|   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|
| 46 | 35 | 6952 | 187 | 423 | 408 | n.d. | n.d. | n.d. | n.d. | n.d. |
| 47 | 208 | 35395 | n.d. | n.d. | 29410 | 1171 | 388 | 2036 | n.d. | n.d. |
| 48 | 177 | 11772 | 964 | 1045 | 1180 | 21 | 14 | 39 | n.d. | n.d. |