**Supporting Information**

**First Evidence of Widespread Occurrence and Bioaccumulation of the Antiandrogenic Fluorescent Dye 7-(dimethylamino)-4-methylcoumarin and 7-(dimethylamino)-4-methylcoumarin in Dongjiang River Basin, South China**

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**Supporting Information contains 6 pages which including 4 tables.**

**Supporting Information Table S1.** The physicochemical properties of the target analytes measured in this study (predicted using the US Environmental Protection Agency’s EPI Suite™).

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**Table S1** The physicochemical properties of the target analytes measured in this study (predicted using the US Environmental Protection Agency’s EPI Suite™).

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Compound | Abbreviation | CAS# | Structure | M.W. | Log Kowa | Solubility (mg/L) at 25 ℃b | BAFc | BCFd |
| 7-(dimethylamino)-4-methylcoumarin (sublimation purified) | DACM | 87-01-4 |  | 203.24 | 2.24 | 516.9 | 9.661 | 9.661 |
| 7-diethylamino-4-methylcoumarin (sublimation purified) | R-ADMC | 91-44-1 |  | 203.24 | 3.22 | 53.28 | 38.09 | 38.09 |

\* Based on experiment database match; a Based on KOWWINTM v1.68 estimate; b Based on WSKOWWINTM v1.42; c & d Based on BCFBAFTM v3.01.

**Table S2** Retention time, MRM transition and mass spectrometric parameters of coumarins.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Coumarins | RTa | Q1b | Q3c | DPd | CEe | EPf | CXPg |
| Linuron-d6 1 | 15.0 | 255.000  | 160.000  | 106.000  | 27.000  | 8.000  | 14.000  |
| Linuron-d6 2 | 15.0  | 255.000  | 185.000  | 106.000  | 22.000  | 8.000  | 17.000  |
| R-ADMC 1 | 15.0  | 232.000  | 188.000  | 104.000  | 41.000  | 5.000  | 17.000  |
| R-ADMC 2 | 15.0  | 232.000  | 203.000  | 104.000  | 25.000  | 5.000  | 20.000  |
| DACM 1 | 15.0  | 204.000  | 148.000  | 150.000  | 31.000  | 11.000  | 14.000  |
| DACM 2 | 15.0  | 204.000  | 132.000  | 150.000  | 48.000  | 10.000  | 13.000  |

aRT: Retention time (min); bQ1: Precursor ion; cQ3: Product ion; dDP:Declistering Potential; eCE: Collision Energy; fEP: Entrance Potential; gCXP: Cell exit Potential

**Table S3** Major parameters for the gradient flow used in the separation of coumarins.

|  |  |  |  |
| --- | --- | --- | --- |
| Time (min) | Flow rate (mL/min) | Mobile Phase A (%) | Mobile Phase B (%) |
| 0 | 0.3 | 98 | 2 |
| 1 | 0.3 | 96 | 4 |
| 6 | 0.3 | 1 | 99 |
| 8 | 0.3 | 1 | 99 |
| 9 | 0.3 | 98 | 2 |
| 10 | 0.3 | 98 | 2 |

\*0.1% formic acid in milli-Q water and 0.1% formic acid acetonitrile were separately used as mobile phase A and B.

**Table S4** Quality assurance/quality control (QA/QC) information of coumarins in each matrix.a

|  |  |  |
| --- | --- | --- |
|  | DACM | R-ADMC |
|  | ***Water samples*** |
| Recoveries (%) | 63.00  | 63.00  |
| Matrix effect (%) | 87.90  | 91.50  |
| Accuracy (%) | 55.40  | 57.70  |
| Precision (%) | 12.9 | 9.6 |
|  | ***Sediment samples*** |
| Recoveries (%) | 50.60  | 68.30  |
| Matrix effect (%) | 110.00  | 85.04  |
| Accuracy (%) | 61.16  | 64.30  |
| Precision (%) | 1.67  | 2.62  |
|  | ***Fish Samples*** |
| Recoveries (%) | 97.96 | 94.14 |
| Matrix effect (%) | 74.27 | 80.05 |
| Accuracy (%) | 72.90  | 75.57 |
| Precision (%) | 16.39 | 14.31 |
|  | ***Plant, Algae and Zooplankton samples*** |
| Recoveries (%) | 93.47 | 94.93 |
| Matrix effect (%) | 120.42 | 99.07 |
| Accuracy (%) | 112.56 | 94.04 |
| Precision (%) | 3.95 | 3.01 |

*a* For the pre-extraction matrix spike sample, randomly selected samples (n > 3) were spiked with 10 ng of the target analytes and 10 ng Linuron-d6 prior to extraction; for the post-extraction matrix spike sample, the randomly selected samples were spiked with 10 ng Linuron-d6 prior to extraction and 10 ng target analytes prior to reconstitution.