Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.


# Supporting Information

# High-throughput and reliable determination of 13 haloacetic acids and dalapon in water and evaluation of control strategies

Cristina Postigo [a*], Pere Emiliano[b], Fernando Valero[b]

[a] *Water, Environmental and Food Chemistry Unit (ENFOCHEM), Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), C/Jordi Girona 18-26, 08034 Barcelona, Spain*

[b] *Department of R+D+i & Process Control. Ens d'Abastament d'Aigua Ter-Llobregat (ATL), Sant Martí de l'Erm 30, 08970, Sant Joan Despí, Barcelona, Spain*

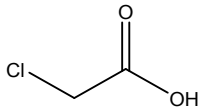
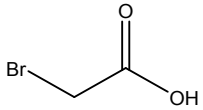
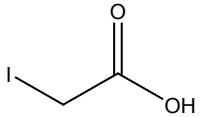
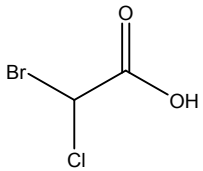
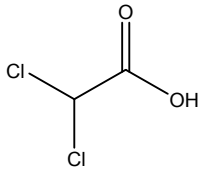
***Corresponding Author**: Cristina Postigo (0000-0002-7344-7044)
Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Dept. of Environmental Chemistry
C/ Jordi Girona 18-26, 08034 Barcelona, Spain.
cprqam@cid.csic.es
Tel: +34-934-006-100, Fax: +34-932-045-904

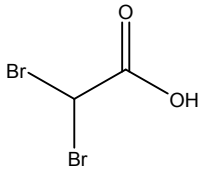
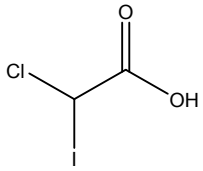
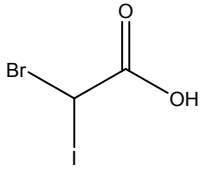
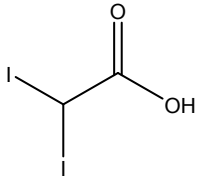
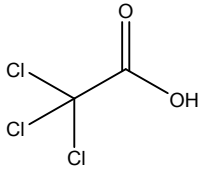
**LIST OF TABLES**

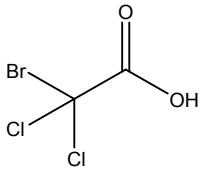
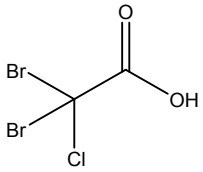
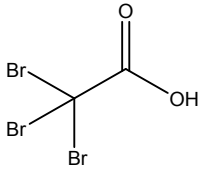
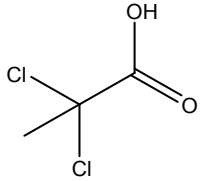
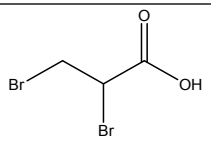


**LIST OF FIGURES**

**Table S1.** Target haloacetic acids and main physical-chemical properties.

| *Target I-HAAs* | *Abr.* | *CAS #* | *Monoisotopic mass (Da)* | *Molecular formula (SMILES)* | *Molecular structure* | *pKa[a]* | *Log P[b]* | *Solubility (mg/L)[b]* | *Vapor pressure (mm Hg)[b]* | *Source* | *Purity (%)* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Chloro-acetic acid | CAA | 79-11-8 | 93.9822 | $CH_2Cl$-COOH (C(C(=O)O)Cl) |  | 3.1 | 0.34 (0.22) | 1.953e5 (8.58e5) | 0.247 (6.50e-2) | Sigma-Aldrich (EPA 552.2 mix) | 98.1 |
| Bromo-acetic acid | BAA | 79-08-3 | 137.9316 | $CH_2Br$-COOH (C(C(=O)O)Br) |  | 2.6 | 0.43 (0.41) | 9.379e4 (1.75e6) | 0.131 (0.118) | Sigma-Aldrich (EPA 552.2 mix) | 99.9 |
| Iodo-acetic acid | IAA | 64-69-7 | 185.9178 | $CH_2I$-COOH (C(C(=O)O)I) |  | 3.0 | 0.85 | 2.426e4 | 0.0323 | Sigma-Aldrich | >98.0 |
| Bromochloro-acetic acid | BCAA | 5589-96-8 | 171.8927 | CHBrCl-COOH (C(C(=O)O)(Cl)Br) |  | 2.0 | 0.61 | 4.427e4 | 0.137 | Sigma-Aldrich (EPA 552.2 mix) | 99.9 |
| Dichloro-acetic acid | DCAA | 79-43-6 | 127.9432 | $CHCl_2$-COOH (C(C(=O)O)(Cl)Cl) |  | 2.3 | 0.52 (0.92) | 3.776e4 (1 e6) | 0.00667 (0.179) | Sigma-Aldrich (EPA 552.2 mix) | 99.0 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Dibromo-acetic acid | DBAA | 631-64-1 | 215.8421 | $CHBr_2$-COOH (C(C(=O)O)(Br)Br) |  | 1.6 | 0.70 | 2.14e4 | 0.023 | Sigma-Aldrich (EPA 552.2 mix) | 97.0 |
| Chloroiodo-acetic acid | CIAA | 53715-09-6 | 219.878799 | CHICl-COOH (C(C(=O)O)(Cl)I) |  | 2.3 | 1.03 | 1.132e4 | 0.0181 | CanSyn | 100.0 |
| Bromoiodo-acetic acid | BIAA | 71815-43-5 | 263.8283 | CHIBr-COOH (C(C(=O)O)(Br)I) |  | 1.9 | 1.12 | 5414 | 0.00464 | CanSyn | 93.9 |
| Diiodo-acetic acid | DIAA | 598-89-00 | 311.8144 | $CHI_2$-COOH (C(C(=O)O)(I)I) |  | 2.3 | 1.53 | 1282 | 0.00045 | CanSyn | 95.1 |
| Trichloro-acetic acid | TCAA | 76-03-9 | 161.9042 | $CCl_3$-COOH (C(=O)(C(Cl)(Cl)Cl)O) |  | 1.7 | 1.44 (1.33) | 1.99e4 (5.46e4) | 0.196 (6.00e-2) | Sigma-Aldrich (EPA 552.2 mix) | 99.9 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Bromodichloro-acetic acid | BDCAA | 71133-14-7 | 205.8537 | $CBrCl_2$-COOH (C(=O)(C(Br)(Cl)Cl)O) |  | 1.5 | 1.53 | 4869 | 0.036 | Sigma-Aldrich (EPA 552.2 mix) | 99.6 |
| Chlorodibromo-acetic acid | DBCAA | 5278-95-5 | 249.8032 | $CBr_2Cl$-COOH (C(=O)(C(Br)(Br)Cl)O) |  | 1.1 | 1.62 | 2353 | 0.00519 | Sigma-Aldrich (EPA 552.2 mix) | 86.0 |
| Tribromo-acetic acid | TBAA | 75-96-7 | 293.7527 | $CBr_3$-COOH (C(=O)(C(Br)(Br)Br)O) |  | 0.7 | 1.71 | 1102 | 0.00028 | Sigma-Aldrich (EPA 552.2 mix) | 98.1 |
| Dalapon | DPN | 75-99-0 | 141.9588 | $CH_3$-$CCl_2$-COOH (CC(C(=O)O)(Cl)Cl) |  | 2.6 | 1.68 | 7432 (5.02e5) | 0.67 (0.151) | Sigma-Aldrich | >90 |
| 2,3Dibromo-propanoic acid | DBPA | 600-05-5 | 229.8578 | $CH_2Br$-CHBr-COOH C(C(C(=O)O)Br)Br |  | 2.24 | 1.19 | 7092 | 0.00637 | Sigma-Aldrich | >90 |

[a]ACE and JChem acidity and basicity calculator – www.chemicalize.com

***b*** US Environmental Protection Agency's EPISuite - Predicted values (experimental values)

**Table S2.** TOC, turbidity, UV absorbance and dissolved aluminum in source and clarified waters.

| | Source water | Clarified water (pH 7.1) | Clarified water (pH 7.8) |
|---|---|---|---|
| TOC [mg/L] | 3.22 | 2.47 | 2.49 |
| Turbidity [NTU] | 60 | 0.87 | 1.09 |
| $UV_{254}$ [$m^{-1}$] | - | 4.26 | 4.07 |
| Dissolved aluminum [mg/L] | - | 0.02 | 0.13 |

**Table S3.** Residual free chlorine (mg/L) in the HAA formation potential test samples collected at different times.

| | Clarified water (ph 7.1) | Clarified water (pH.7.8) |
|---|---|---|
| 0 h | 8.0 | 8.0 |
| 24 h | 3.4 | 3.1 |
| 48 h | 3.1 | 2.6 |
| 72 h | 2.4 | 2.1 |

**Table S4.** Linearity figures (i.e, linearity range and coefficient of determination of weighted (1/x) linear regression models) obtained in matrix-matched calibration curves constructed using the internal standard method.

| | ***Linearity*** | | | |
|---|---|---|---|---|
| | ***Clarified water*** | | ***Tap water*** | |
| | *Range [µg/L]* | *$R^2$* | *Range [µg/L]* | *$R^2$* |
| CAA | 6-100 | 0.9953 | 6-100 | 0.9962 |
| BAA | 1-100 | 0.9981 | 1-100 | 0.9952 |
| IAA | 0.6-100 | 0.9982 | 0.6-100 | 0.9944 |
| DCAA | 0.6-100 | 0.9984 | 0.6-100 | 0.9933 |
| DBAA | 0.6-100 | 0.9938 | 0.6-100 | 0.9939 |
| DIAA | 0.06-60 | 0.9987 | 0.3-60 | 0.9979 |
| BCAA | 0.6-100 | 0.9930 | 0.3-100 | 0.9964 |
| BIAA | 0.6-100 | 0.9966 | 0.6-100 | 0.9909 |
| CIAA | 0.3-100 | 0.9931 | 0.3-100 | 0.9935 |
| TCAA | 3-100 | 0.9977 | 3-100 | 0.9927 |
| TBAA | 3-100 | 0.9967 | 1-100 | 0.9939 |
| DCBAA | 6-100 | 0.9951 | 6-100 | 0.9934 |
| DBCAA | 3-100 | 0.9962 | 3-100 | 0.9926 |
| DPN | 3-100 | 0.9991 | 1-100 | 0.9947 |

*CSW: Clarified surface water, TW: tap water

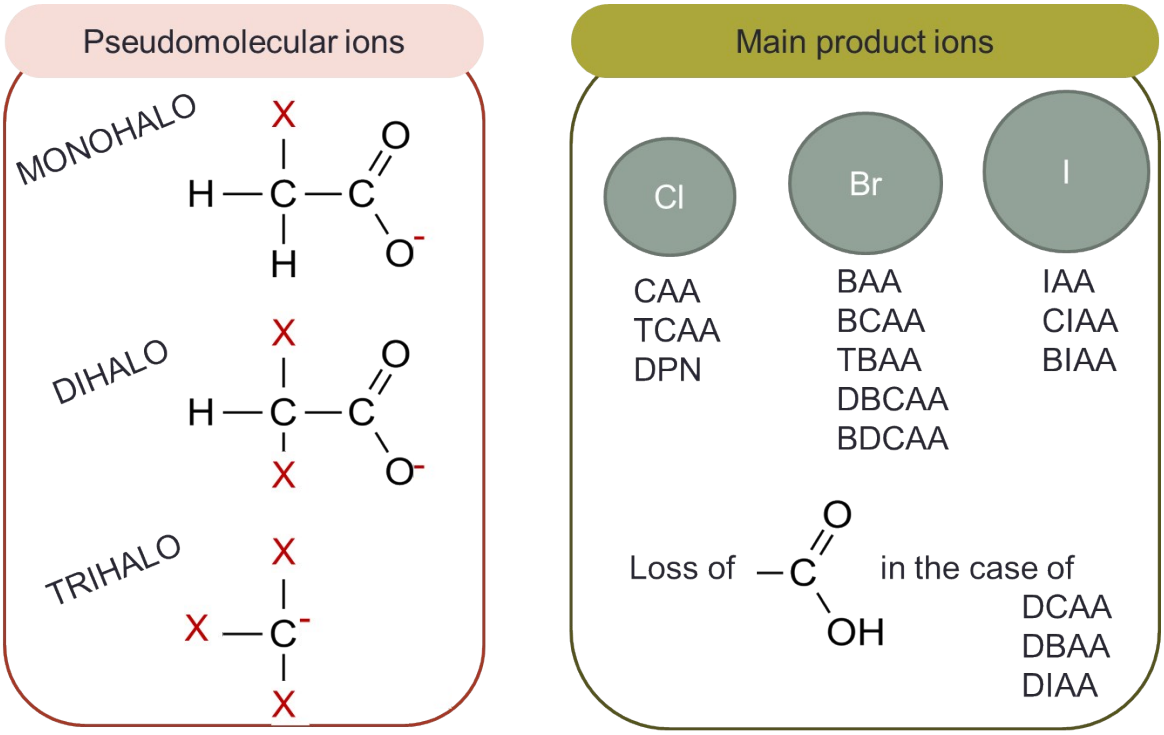



**Figure S1.** Formation of pseudomolecular ions and main product ions of HAAs under electrospray negative ionization.

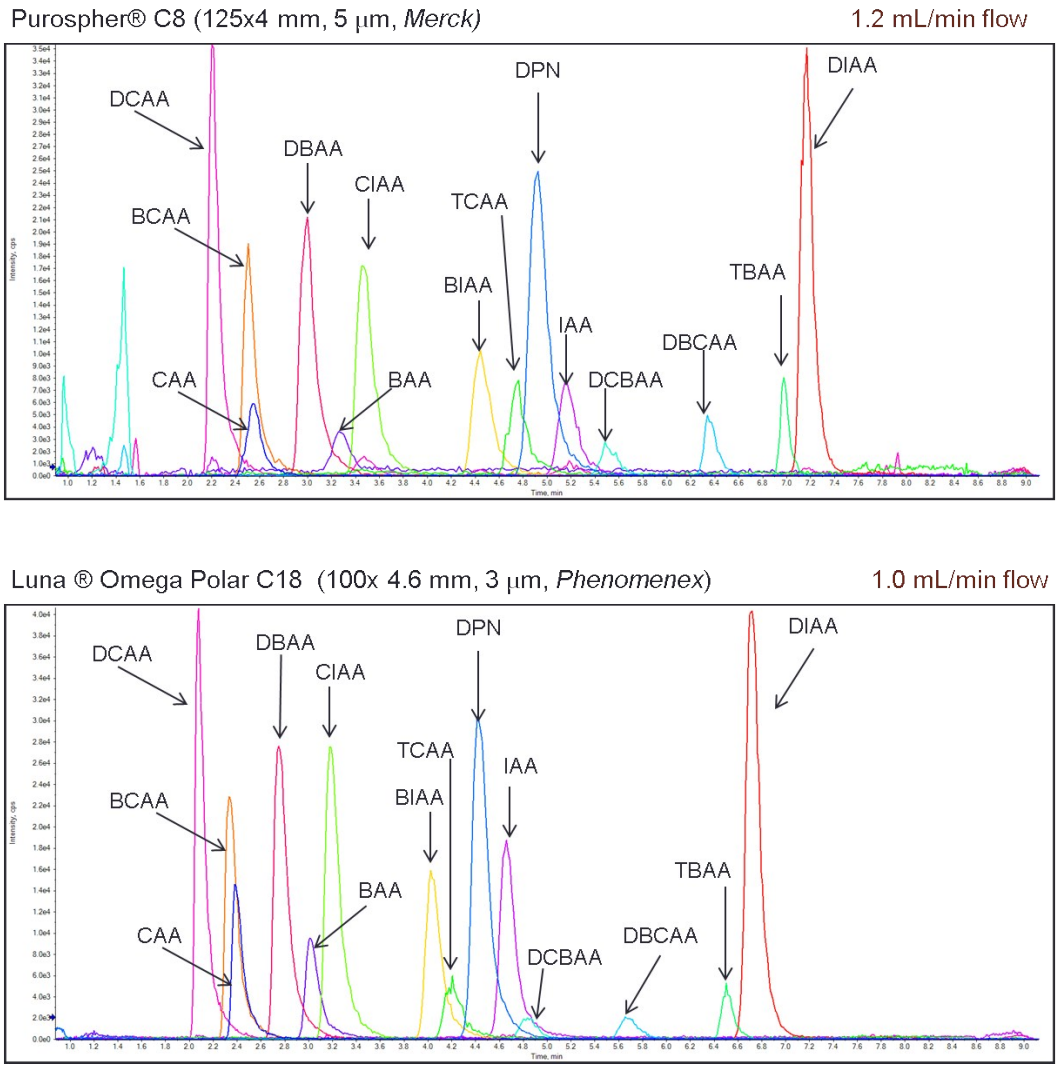
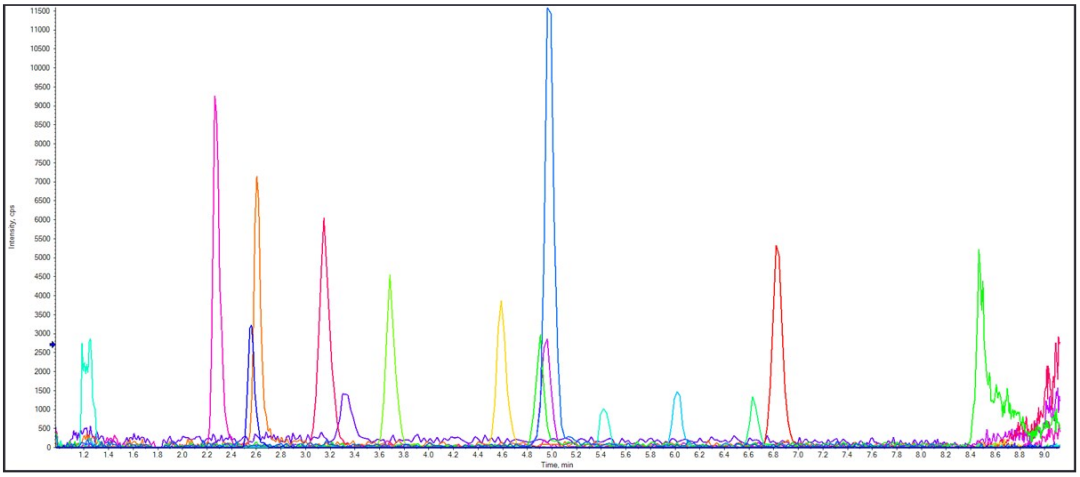



**Figure S2.** Chromatographic resolution of HAA peaks after LVI (200 µl)-LC-ESI(-)-HRMS of an HPLC-grade water containing 30 µg/L of the HAAs mix in the two LC columns tested. A mobile phase consisting of ACN: H2O, both with 0.1% formic acid, was used in both injections.

$H_2O$:acetonitrile, both 0.1% FA




$H_2O$:methanol, both 0.1% FA

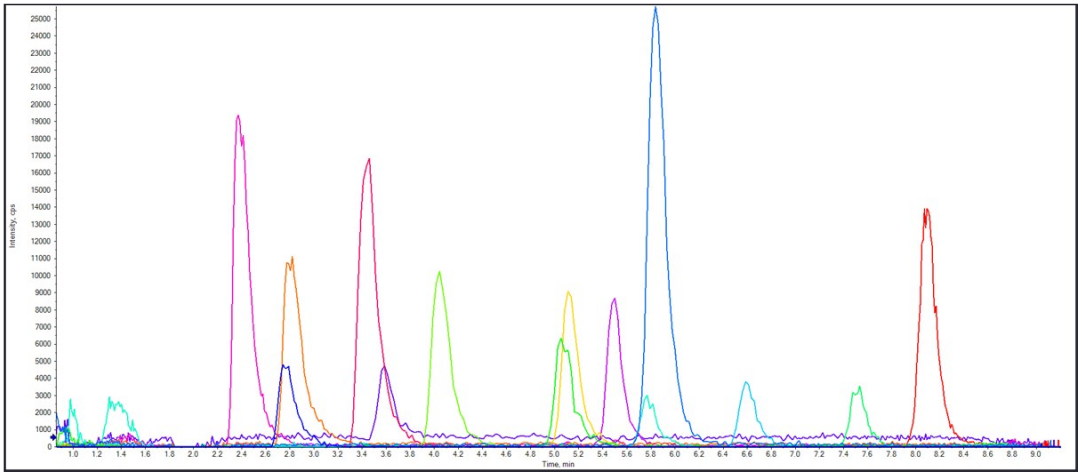



**Figure S3.** Chromatographic separation of HAAs (25 µg/L) in the Lunar Omega Polar C18 column using different mobile phase compositions: methanol or acetonitrile as organic constituent.

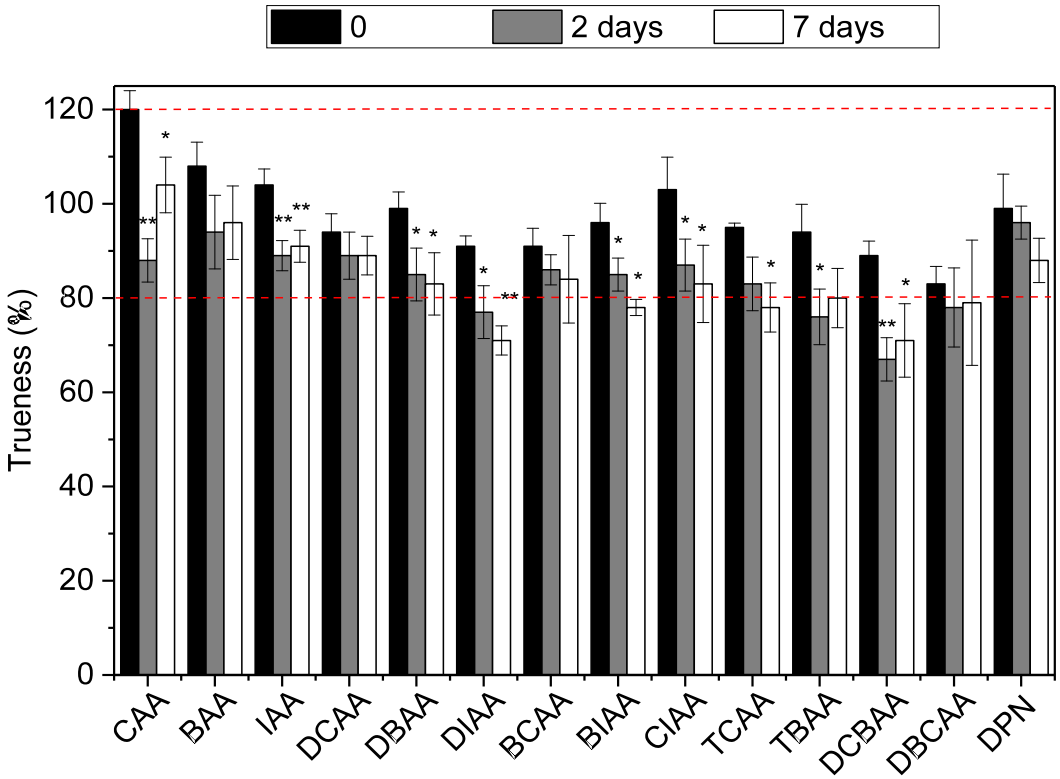



**Figure S4.** Average trueness of HAA measurements in HPLC-grade water samples (n=3) fortified at a concentration of 5 µg/L and after two and seven days stored at -20ºC in the dark. Error bars indicate RSD values of n=3 independently prepared and analyzed samples.

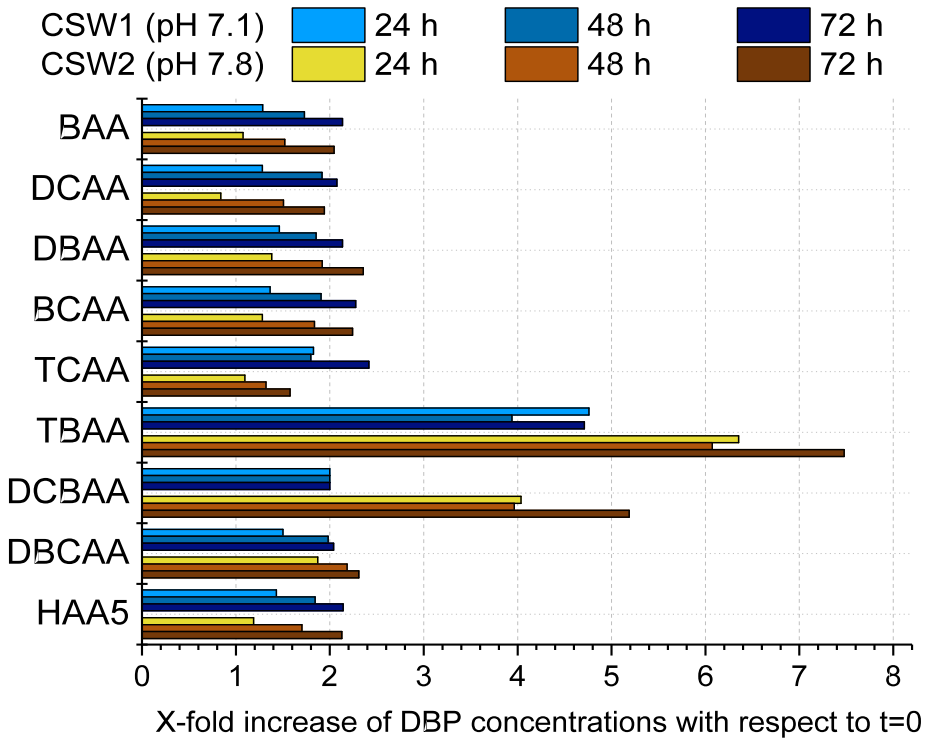



**Figure S5.** X-fold increase of DBP concentrations at different reaction times with respect to t=0, calculated as $C_t/C_0$, where $C_t$ is the concentration at time = 24 h, 48 h or 72 h and $C_0$ is the concentration at time =0.