Liquid chromatography-tandem mass spectrometry determination of synthetic cathinones and phenethylamines in influent wastewater of eight European cities

Bade, R.; Bijlsma, L.; Sancho, J.V.; Baz-Lomba, J.A.; Castiglioni, S.; Castrignanò, E.; Causanilles, A.; Gracia-Lor, E.; Kasprzyk-Hordern, B.; Kinyua, J.; McCall, A.-K.; van Nuijs, A.L.N.; Ort, C.; Plósz, B.G.; Ramin, P.; Rousis, N.I.; Ryu, Y.; Thomas, K.V.; de Voogt, P.; Zuccato, E.; Hernández, F.

DOI
10.1016/j.chemosphere.2016.10.107

Publication date
2017

Document Version
Other version

Published in
Chemosphere

Supporting Information (S.I)

Liquid chromatography-tandem mass spectrometry determination synthetic cathinones and phenethylamines in wastewater of eight European cities

Richard Bade[a], LubertusBijlsma[a], Juan V. Sancho[a], Jose A. Baz-Lomba[b,c], Sara Castiglioni[d], Erika Castrignanò[e], Ana Causanilles[f], Emma Gracia-Lor[d], Barbara Kasprzyk-Hordern[e], Juliet Kinyua[h], Ann-Kathrin McCall[i], Alexander van Nuijs[h], Christoph Ort[i], Benedek G. Plósz[j], PedramRamin[j], Nikolaos I. Rousis[d], YeonsukRyu[b,c], Kevin Thomas[b], Pim de Voogt[f,g], Ettore Zuccato[d]Felix Hernandez[a,]*

[a]Research Institute for Pesticides and Water, University Jaume I, Avda. SosBaynat s/n, E-12071 Castellón, Spain.

[b]Norwegian Institute for Water Research (NIVA), Gaustadalléen 21, 0349 Oslo, Norway

[c]Faculty of Medicine, University of Oslo, PO box 1078 Blindern, 0316, Oslo, Norway

[d]Environmental Biomarkers Unit, Department of Environmental Health Sciences, IRCCS—Istituto di RicercheFarmacologiche "Mario Negri", Via La Masa 19, 20156 Milan, Italy

[e] University of Bath, Department of Chemistry, Faculty of Science, Bath BA2 7AY, UK

[f]KWR Watercycle Research Institute, Chemical Water Quality and Health, P.O. Box 1072, 3430 BB, Nieuwegein, The Netherlands

[g] Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, P.O. Box 94248, 1090 GE, Amsterdam, The Netherlands

[h] Toxicological Center, Department of Pharmaceutical Sciences, Campus DrieEiken, University of Antwerp, Universiteitsplein 1, 2610 Antwerp, Belgium

[i]Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-8600, Dübendorf, Switzerland

[j]Department of Environmental Engineering, Technical University of Denmark, Miljøvej, Building 115, DK-2800 Kgs. Lyngby, Denmark

*Corresponding author: felix.hernandez@uji.es Tel.: +34 964 387366 Fax: +34 964 387368

List of Supporting Information

Section 2.1: Chemicals and Materials

Table S1: *Filtration recovery for all compounds using vacuum filter (%)*

Figure S1:*Structures of all compounds in this study*

Figure S2: *SRM of a selection of compounds, after extraction with HLB (LEFT) and MCX (RIGHT) cartridges. From top to bottom: methedrone, butylone, mephedrone, MDPV and N-ethylcathinone.*

Figure S3: *Recoveries for all compounds using HLB and MCX cartridges. Legend shows different washing/drying steps used. Black lines are shown at the threshold limits for satisfactory recovery (70-120%)*

HLB: no washing, 10 min drying; MCX 1: 6 mL H_2O, 6 mL methanol, no drying; MCX 2: 5 mL methanol (pH 2), no drying; MCX 3: 5 mL methanol (pH 2), 10 min drying; MCX 4: 5mL methanol, 10 min drying

Figure S4: *Stability of all compounds in filtered IWW (pH2), with acceptable intervals of 70-120% (black lines).*

Figure S5: *Stability of all compounds in filtered IWW (natural pH) with acceptable intervals of 70-120% (black lines).*

Figure S6: *Stability of all compounds in Milli-Q water with acceptable intervals of 70-120% (black lines).*

Figure S7: *Stability of all compounds in unfiltered WW (natural pH) with acceptable intervals of 70-120% (black lines).*

Figure S8: *The false positive detections of butylone in Bristol (LEFT) and MDPV in Zurich (RIGHT). The uppermost transition is the quantification (Q) transition in the QC (low, 5ng/L), while the lowermost is the Q of the ILIS (in sample). All transitions are shown, together with the q/Q ratios.*

2.1 Chemicals and Materials

Reference standards of all analytes: N-ethylcathinone, MDPV, methylone, butylone, methedrone, mephedrone, naphyrone, 25-C-NBOMe, 25-I-NBOMe and 25-B-NBOMe were purchased from Cerilliant (Round Rock, TX, USA) at a concentration of 1 mg/mL in methanol for the analytes. Standard stock solutions of each compound were prepared at 100 mg/L.

Mixed working solutions containing all analytes were prepared from stock solutions at different concentrations by appropriate dilution with water, and were used for preparation of the aqueous calibration standards and for spiking samples in the validation study.

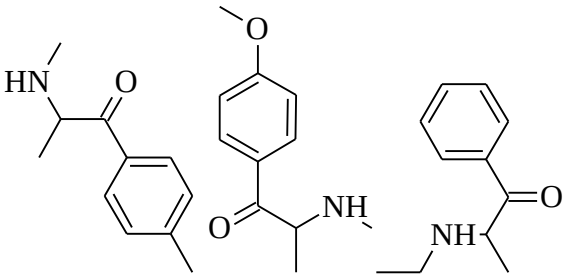
Deuterated analogues: MDPV-d_8, methylone-d_3, butylone-d_3, mephedrone-d_3, naphyrone-d_5, 25-C-NBOMe-d_3, 25-I-NBOMe-d_3 and 25-B-NBOMe-$d_3$were also purchased from Cerilliant (Round Rock, TX, USA) at a concentration of 100 µg/mL in methanol. Standard stock solutions of each compound were prepared at 10 mg/L. Mixed standard solutions containing all compounds were made with appropriate dilution with water.

All standard solutions were stored in amber glass bottles in the dark at -20°C.

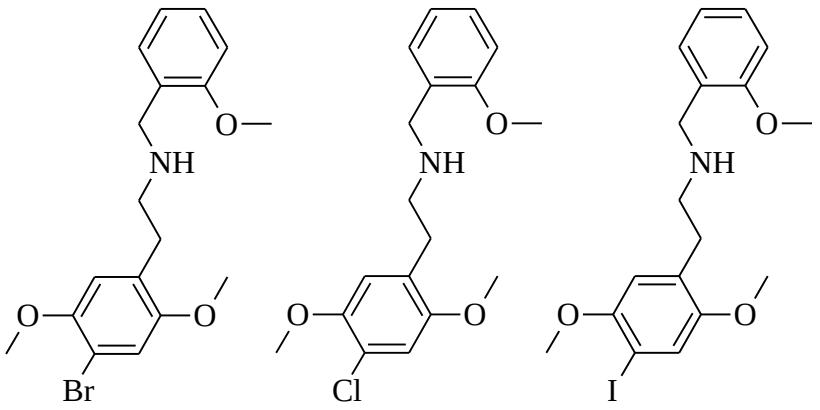
HPLC-grade methanol (MeOH), ammonium acetate, ammonia solution (25 %) and formic acid (HCOOH, 98–100 %) were acquired from Scharlau (Barcelona, Spain) HPLC-grade water was obtained by purifying demineralised water in a Milli-Q plus system from Millipore (Bedford, MA, USA). SPE cartridges used were Oasis HLB 3cc (60mg) and Oasis MCX 6cc (150 mg) from Waters (Milford, MA, USA).

Table S1: Filtration recovery for all compounds using vacuum filter (%)

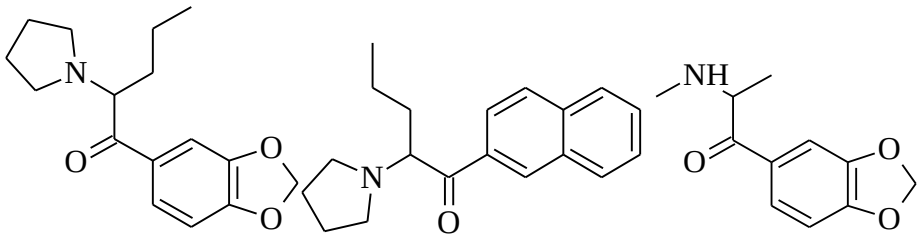
Compound	Natural pH	pH = 2
N-ethylcathinone	98	106
MDPV	55	71
Mephedrone	97	102
Methylone	88	104
Butylone	84	104
Methedrone	90	102
Naphyrone	1	4
25-B-NBOMe	1	1
25-I-NBOMe	0	1
25-C-NBOMe	1	1



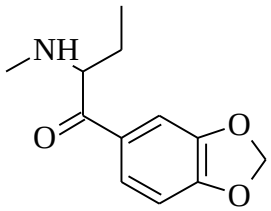
Mephedrone Methedrone N-ethylcathinone



25-B-NBOMe 25-C-NBOMe 25-I-NBOMe



MDPV Naphyrone Methylone



Buytlone

Figure S1: Structures of all compounds in this study

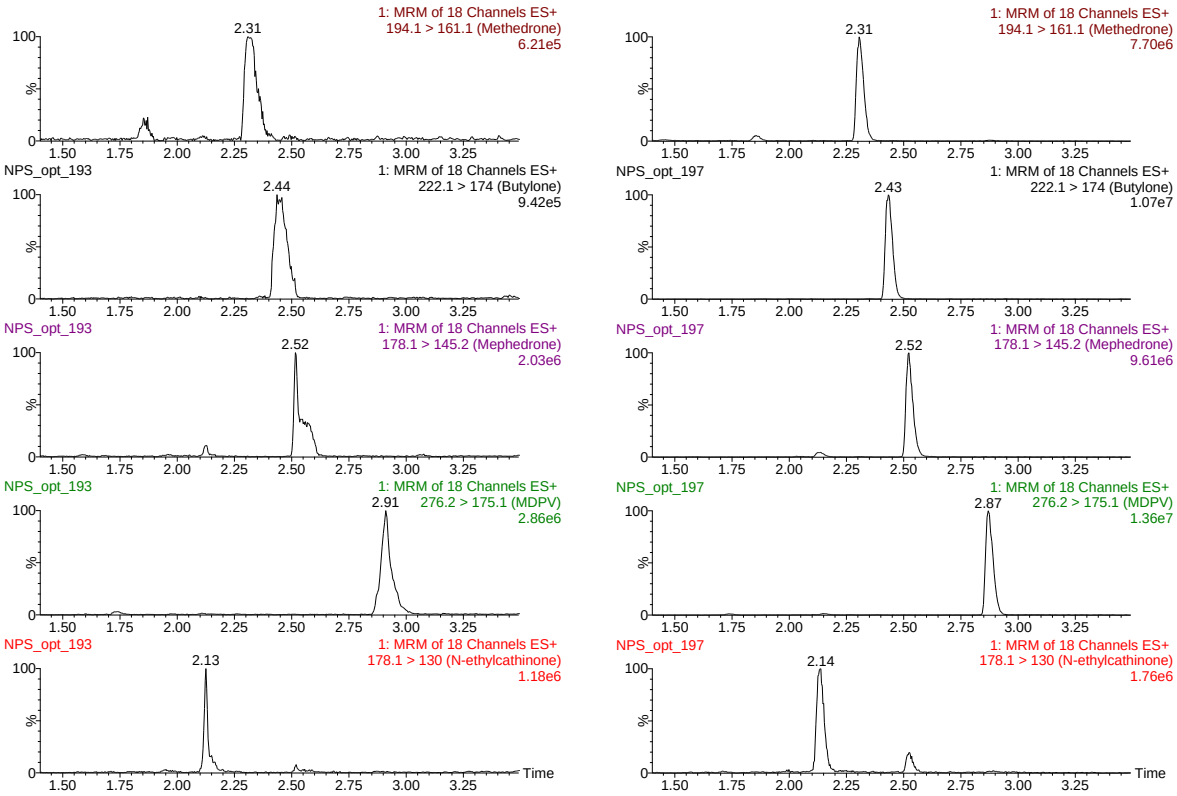


Figure S2: SRM of a selection of compounds, after extraction with HLB (LEFT) and MCX (RIGHT) cartridges. From top to bottom: methedrone, butylone, mephedrone, MDPV and N-ethylcathinone.

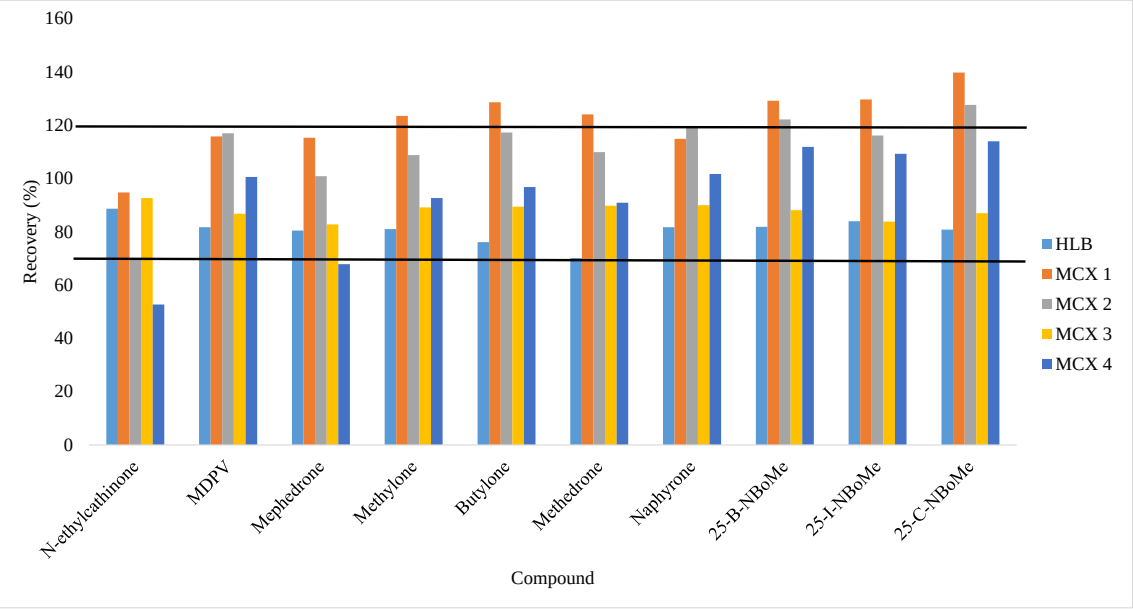


Figure S3: Recoveries for all compounds using HLB and MCX cartridges. Legend shows different washing/drying steps used. Black lines are shown at the threshold limits for satisfactory recovery (70-120%)

HLB: no washing, 10 min drying; MCX 1: 6 mL H_2O, 6 mL methanol, no drying; MCX 2: 5 mL methanol (pH 2), no drying; MCX 3: 5 mL methanol (pH 2), 10 min drying; MCX 4: 5mL methanol, 10 min drying

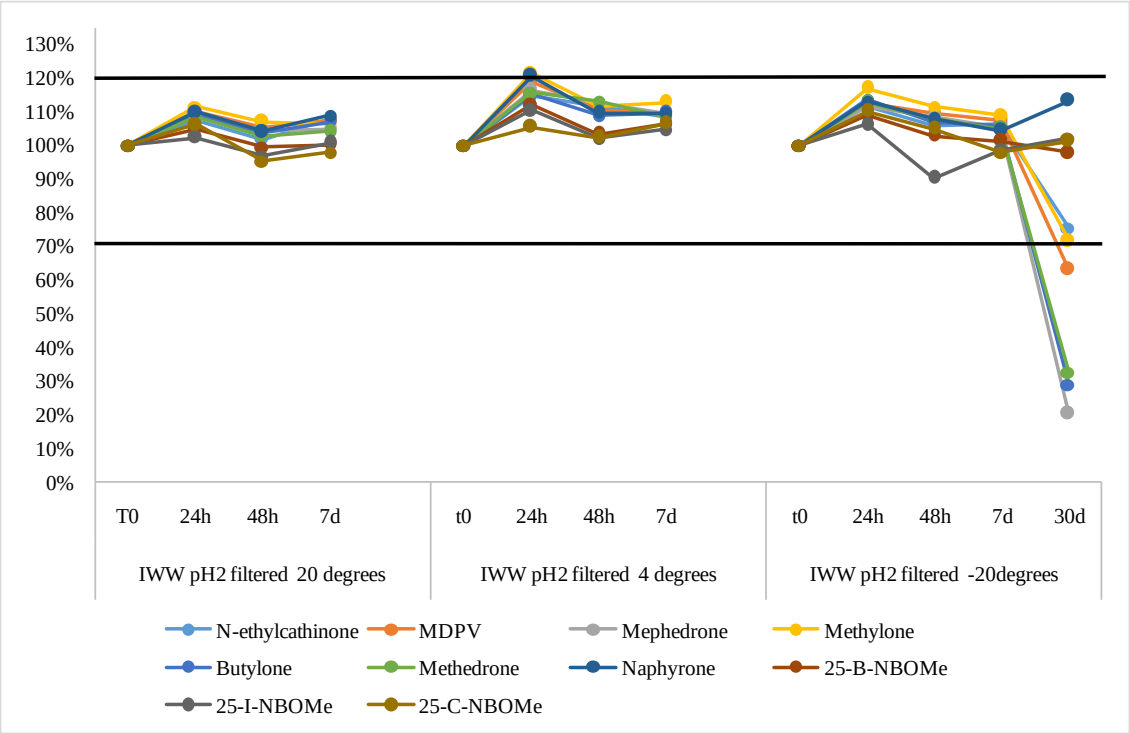


Figure S4: Stability of all compounds in filtered IWW (pH2) at 20ºC (LEFT), 4ºC (MIDDLE) and -20ºC (RIGHT), with acceptable intervals of 70-120% (black lines).

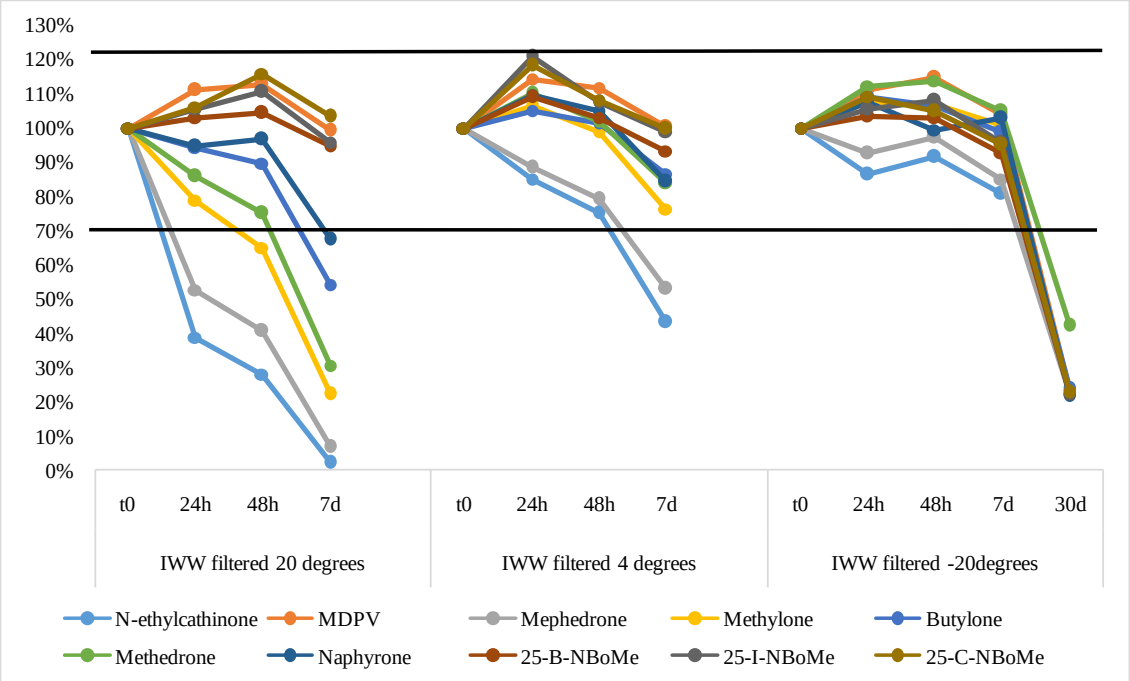


Figure S5:Stability of all compounds in filtered IWW (natural pH) at 20ºC (LEFT), 4ºC (MIDDLE) and -20ºC (RIGHT), with acceptable intervals of 70-120% (black lines).

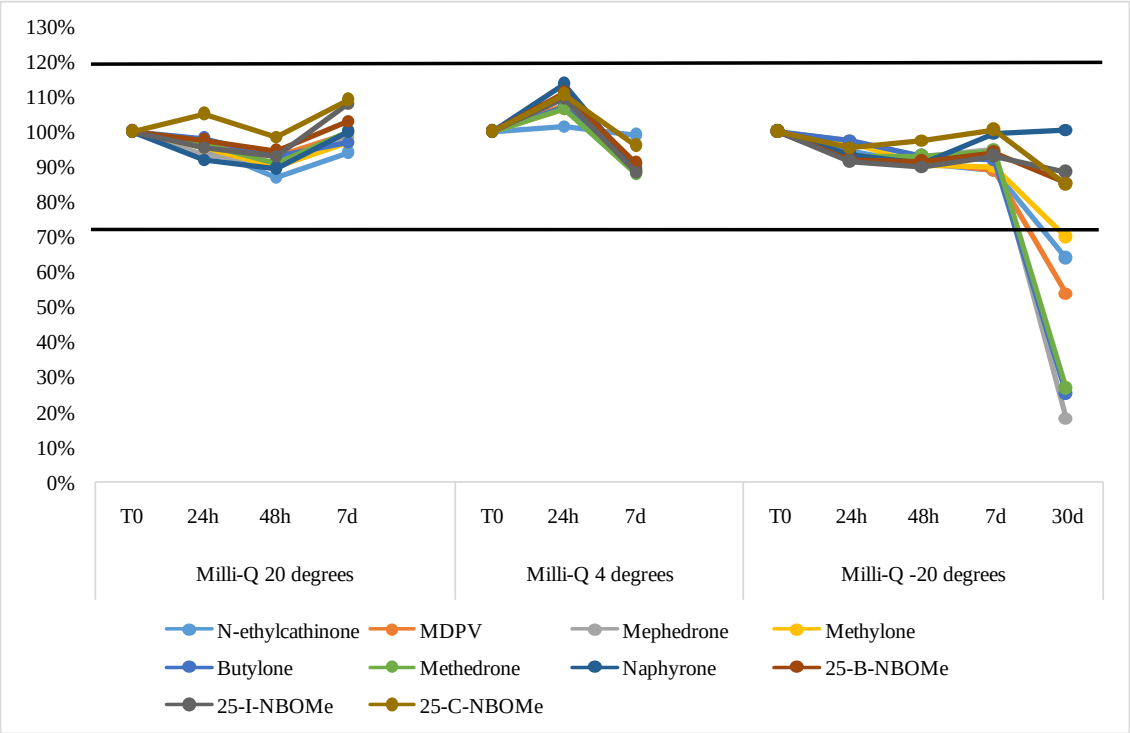


Figure S6: Stability of all compounds in Milli-Q water at 20ºC (LEFT), 4ºC (MIDDLE) and -20ºC (RIGHT), with acceptable intervals of 70-120% (black lines).

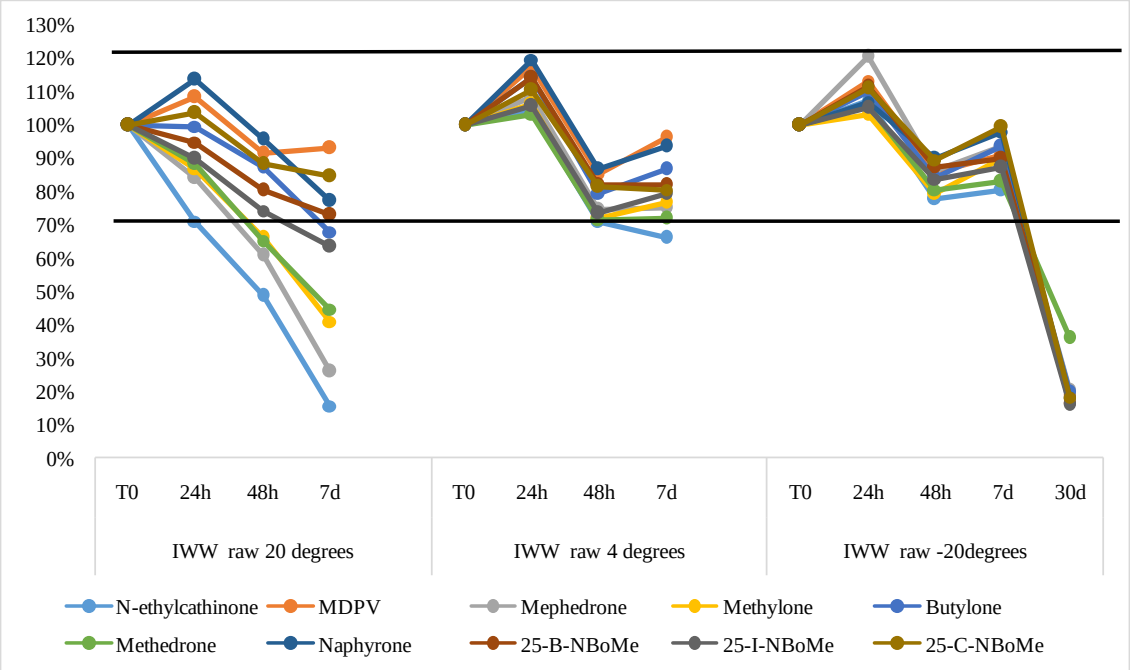


Figure S7: Stability of all compounds in rawIWW (natural pH) at 20ºC (LEFT), 4ºC (MIDDLE) and -20ºC (RIGHT), with acceptable intervals of 70-120% (black lines).

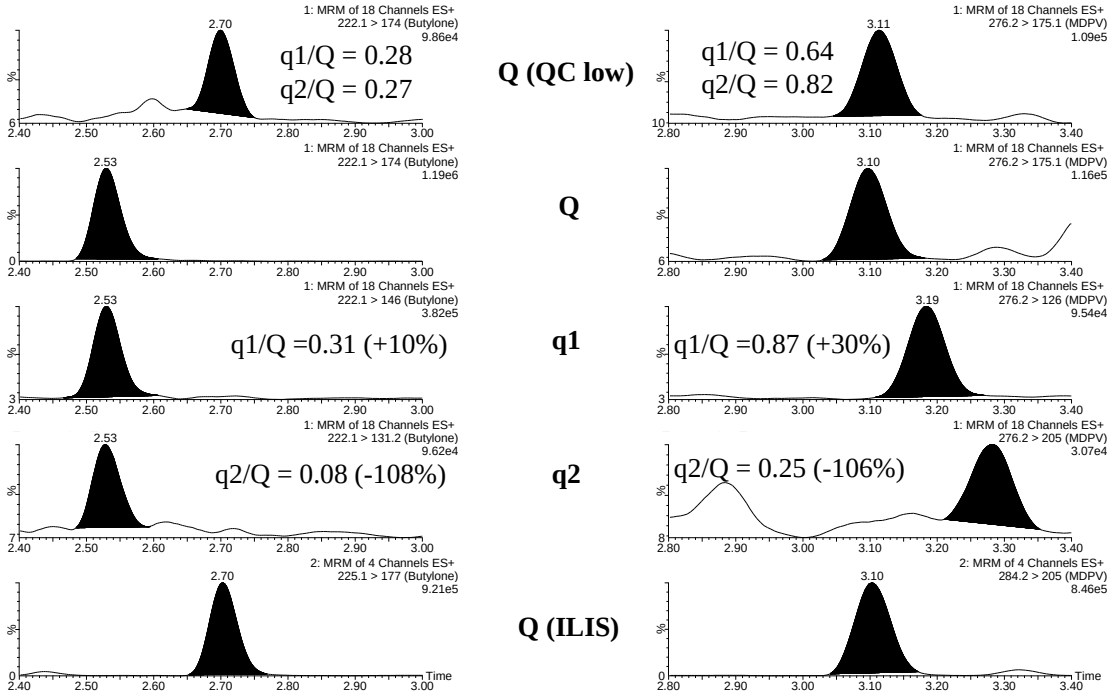


Figure S8: The false positive detections of butylone in Bristol (LEFT) and MDPV in Zurich (RIGHT). The uppermost transition is the quantification (Q) transition in the QC (low, 5ng/L), while the lowermost is the Q of the ILIS (in sample). All transitions are shown, together with the q/Q ratios.