Supplementary Information (SI) for Environmental Science: Processes & Impacts.
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Electronic Supplementary Information (ESI)

Instrumentation

Laboratory preparation included use of an Eberbach shaker (Michigan, USA), a Branson B-52 ultrasonic bath (Danbury, USA), and a Sorvall ST 40R centrifuge (Thermo Scientific, Canada). A Zymark Turbovap LV-ZW700 evaporator (Biotage, USA) was used. The three MP method samples were analyzed using an ultra-high-performance liquid chromatographic (UPLC)–photodiode array (PDA) system consisting of an Acquity UPLC coupled to both a PDA and an Aquity QDA system from Waters (USA). The column was an Ascentis Express RP-Amide 4.6 mm x 100 mm, 2.7 µm from Supleco (Canada). The software used to operate the system and analyze the data was Empower, also from Waters.

Asset samples were analyzed using an ultra-high-performance liquid chromatographic–mass spectrometry (UPLC-MS/MS) system consisting of a Waters Acquity UPLC coupled with a Waters Xevo TQ triple quadrupole MS (USA) equipped with an electrospray source and an autosampler with a partial loop and a needle overfill feature (10 µL). The column was an Acquity UPLC BEH C18, 1.7 µm, 2.1 mm x 100 mm, from Waters (Santry, Ireland). The software used to operate the system and analyze the data was Masslynx, V4.1, from Waters (USA).

Sampling Material Preparation

Solutions of MP (4 mg/L and 20 mg/L), all in toluene, were prepared. Impregnation was performed manually by adding the solution to each filter with a volumetric pipette, as described in Table S1. The filters were placed on aluminum foil contained in an opaque Plexiglas box in which nitrogen was maintained at positive pressure. The filters were allowed to dry for at least 12 hours. The impregnated filters were immediately placed in sampling devices or stored away from light at 4°C for a maximum of 1 month.

Table S1. Parameters used for GFF impregnation

Type of filters	Dimensions (mm)	Method	MP Concentration (mg/L)	Volume transferred (µL)
Filtering membrane	37	MP-37	4	500
Top filter (inner wall)	35	MP-37	4	425
Rim filter (inner wall)	6 x 100	MP-37	4	400
Filtering membrane	13	MP-Swin + Impinger	20	2 x 50

Analysis

Impinger method (solution)

Calibration standards were prepared by mixing HDI solutions of various concentrations in toluene with MP in toluene at 0.1 mg/mL in glass tubes. The resulting HDI-MP derivative standard solutions, with concentrations

ranging from 0.05 µg/mL to 5.24 µg/mL, were obtained by evaporating the toluene followed by redissolving in 1 mL of 0.5% acetic anhydride in ACN. The mobile phase consisted of sodium acetate buffer 0.1% in water at pH 6 (acetic acid) (eluent A) and ACN (eluent B), respectively. The LC method used an isocratic elution program, 34% A and 66% B, at 1 mL/min, 5 µL sample injection and column maintained at 45°C. PDA detection was performed at λ = 242 nm. The run time for each analysis was 45 minutes. Impinger solution samples were quantitatively transferred to glass tubes and the toluene was evaporated. The samples were then dissolved in 1 mL of 0.5% acetic anhydride in ACN. All calibration standards and samples were filtered to 0.22 µm prior to transfer to 2 mL vials.

MP-Swin and 37-Swin

Calibration standards were prepared by mixing HDI solutions of various concentrations in ACN with MP in ACN at 1.3 mg/mL in 30 mL sample jars. After mixing, the solutions were allowed to react for 30 minutes and then 0.5 mL of a solution of 2.5% v/v acetic anhydride in ACN was added to each solution. An aliquot of each resulting HDI-MP derivative standard solution, ranging in concentration from 0.02 µg/mL to 8.64 µg/mL, was analyzed by LC-UV using the same procedure described in the Impinger method section. All filter samples were transferred to 30 mL sample jars containing 2 mL ACN immediately after sampling. At the time of analysis, 0.5 mL of a 2.5% v/v acetic anhydride solution in ACN was added to each sample, followed by brief agitation. All samples were filtered at 0.22 µm prior to transfer to 2 mL vials.

Asset Method

Asset standards and samples were prepared according to Halpenny et al.(1) The prepared solutions were injected (1 µL) into the UPLC-MS via its autosampler, set at 15°C. The mobile phase was composed of water + 0.1% FA (eluant A) and ACN + 0.1% FA (eluant B). The run started with a gradient of 50% eluant B (0.1 min.), ramped to 90% eluant A (3.0 min.), held at 90% eluant B (2 min.), and finally equilibrated at 50% eluant B (2.90 min.). The flow rate in the column was 0.6 mL/min. and the temperature was maintained at 50°C. The Xevo TQ was used in positive mode with the capillary voltage set at 0.5 kV and the source temperature at 150°C. The desolvation temperature and flow were 500°C and 1000 L/h, respectively, while the collision gas flow was set at 0.15 mL/min. The data were acquired in multiple reaction monitoring (MRM) mode (Table S2). Manual adjustments were made on the integrations to ensure that the entire peak was covered before the data were recorded. The results were used to create a regression calibration curve with linear fit.

Table S2. MRM species calculated and measured.

Substances	Calculated [M+H]+	MRM transitions	Cone (V)	Collision energy (eV)
HDI-DBA	427.2	427.2–130	40	30
HDI-DBA-d9	445.2	445.2–139	40	30
Biuret-DBA	866.2	866.2–130	40	55
Biuret-DBA-d9	893.2	893.2–139	40	55
Isocyanurate-DBA	892.4	892.4–130	40	45
Isocyanurate-DBA-d9	919.4	919.4–139	40	45

Quality Control

For each method, all analytical sequences incorporated quality control samples (QCS). For each sequence, the calibration standards were analyzed, followed by a reagent blank (RB), a QC at a value representing 50% of the dynamic range (QC50%) and then followed by the samples. Every 10 samples, the QC50% was analyzed to verify the calibration of the analytical run. At the end of the sequence, the RB, and QC50% were analyzed again, followed by the calibration standards. Each result was reported considering the fact that the QCS were in the acceptable range, which were ± 20% for the QC50.

Quantification bias determination for HDI monomer

A quantity of HDI monomer was dissolved in ACN. An aliquot of this solution was then analyzed in triplicate according to the two analytical procedures described above (MP-Swin /37-Swin and Asset methods) with a time of reaction > 12 hours. A correction factor was calculated by comparing the measured concentrations. All HDI monomer results obtained from the Asset method were multiplied by 2.46.

Conversion factor for the calculation of isocyanurate concentration in MP methods

A known amount of activator PF698C was dissolved in 100 mL of toluene. An aliquot of this solution was added to a solution of 0.01 M MP or DBA in toluene. The samples were allowed to react overnight, and the dilutions were then analyzed by the analytical procedure described above (Impinger and Asset methods). The resulting concentration of isocyanurate measured by the Asset method was used as the standard concentration attributed to the isocyanurate peak observed in the activator samples generated by MP derivatization. A conversion factor was calculated by dividing the mean slope of the calibration curve (liner regression) obtained for the HDI monomer for all LC-UV analyses by the slope of the specific isocyanurate calibration curve determined herein. A conversion factor of 2.24 was applied to all isocyanurate results obtained by the MP methods (Impinger, MP-Swin, and MP-37).

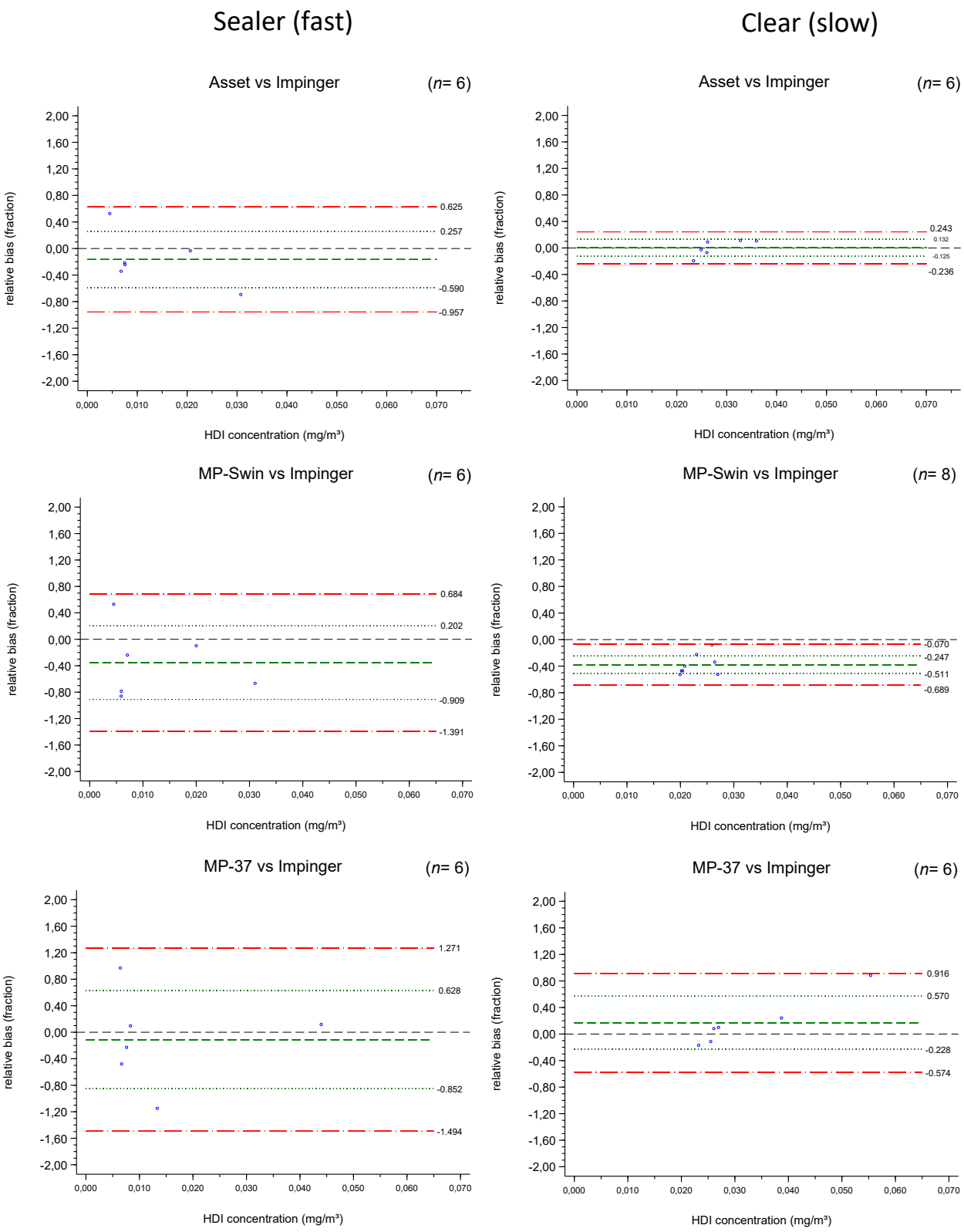

Figure 1. Bland–Altman plots comparing the MP-37, MP-Swin and Asset methods with the impinger method for HDI, grouped by the product applied (left = sealer (fast), right = clear (slow))

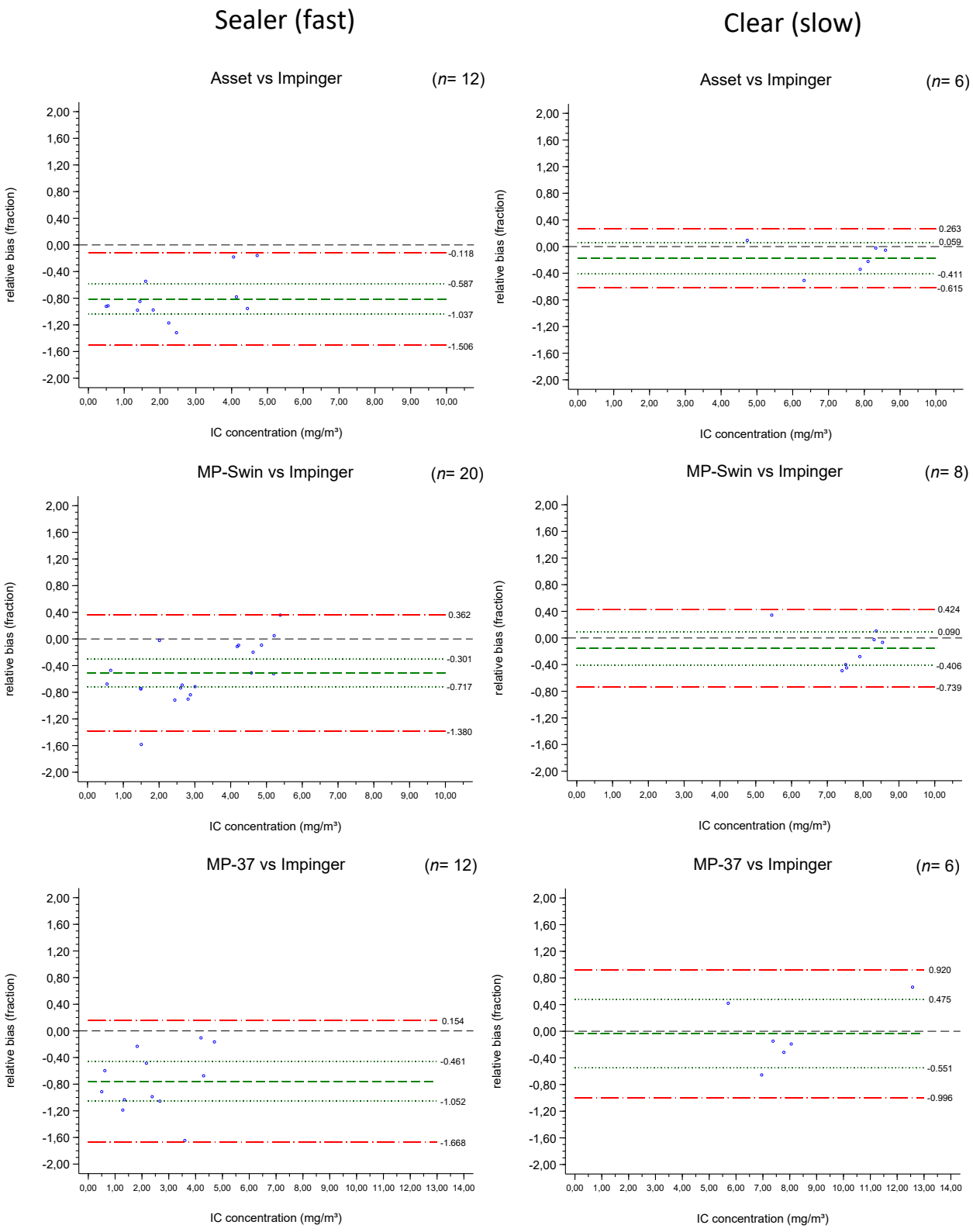

Figure 2. Bland–Altman plots comparing the MP-37, MP-Swin and Asset methods with the impinger method for isocyanurate (IC), grouped by the product applied (left = sealer (fast), right = clear (slow))

References

1. Halpenny M, Brown J. ASSET™ EZ4-NCO Dry Sampler Extraction Procedure: Sigma-Aldrich; 2013 [Available from: https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Supelco/Instructions/1/ASSET_EZ4-NCO_Extraction.pdf.