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

Supporting Information

Manuscript Title: Recovery of Per- and Polyfluoroalkyl Substances After Solvent Evaporation

Authors:

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Supplemental Methods

UPLC-MS analysis- All samples were run on an Agilent 6495C triple quadrupole mass spectrometer with a 1290 Infinity II liquid chromatograph system. A 100 µL aliquot of each sample is injected onto an LC system with 100 µL sample loop and separated on a Phenomenex Kinetex F5 analytical column (2.1 x 100 mm, 2.6 µm particle size; Phenomenex, Torrance, CA). The aqueous mobile phase (A) is 5% HPLC-grade acetonitrile in water with 0.1% formic acid and the organic mobile phase (B) is 5% water in HPLC-grade acetonitrile with 0.1% formic acid. Gradient: initial 20% B to 99% B at 7 min and held 99% B until 8 min, then to 20% B at 8.01 min and held at 20% B until 10 min for a total analysis time of 10 min. Flow rate was 0.5 mL/min at a column temperature of 45 °C. A 3 second needle wash was included before each injection to eliminate cross contamination. The LC had also been retrofitted with non-Teflon tubing and an InfinityLab Poroshell HPH-C18 delay column (3.0 x 50 mm, 4µm; Agilent, Santa Clara, CA) installed in the solvent path prior to the sample injection to delay any PFAS present in the LC eluent. A dynamic multiple reaction monitoring (DMRM) method was used to measure the quant and qual ions of the analytes (**Table S2**) with instrument parameters as follows: Drying gas temperature: 100°C; Drying gas flow rate: 15 L/min; Sheath gas temperature: 300°C; Sheath gas flow rate: 11 L/min; Nebulizer pressure: 15 psi; Capillary voltage: 2,000 V (-) and 3,000 V (+); Nozzle voltage: 0 V (-) and 1,500 V (+); High Pressure RF: 90 V (-) and 150 V (+); Low Pressure RF: 60 V (-) and 60 V (+); Delta EMV: 200 (-) and 0 (+). For this LC method (solvents and column) previous validation data (Enders et al Rapid Commun Mass Spectrom 2022, 36(11):e9295) showed no carryover up as high as 10,000 ng/L. Samples were run in increasing concentration order to further minimize the potential for carryover. All samples with a high concentration were run with three subsequent solvent blanks.

Data analysis- Samples were analyzed using Agilent Quantitative Analysis software version 10.0. Peak areas were exported for the comparison analysis. The comparison was done by averaging the controls responses and then normalizing each treatment replicate to the control to obtain a ratio that can be compared among analytes. Those ratios were then plotted in GraphPad Prism (version 9.3.0) as a bar graph with replicates shown as seen in supplemental **Figures S1-S10**. A non-normalized heat map showing the average normalized ratio for each treatment per compound and concentration was used to show trends across compound class and concentrations, **Figure 3**. For the recovery study, **Figure 1**, the same normalization was performed, and either an unpaired two-tailed student T test or a Welch's T Test were used to determine the significance difference between the reconstitution methods. Welch's T test was employed when p-value for the F-test was significant ($P< 0.05$) which indicated that the variance between the two treatments was not equal and therefore a T test with a correction factor needed to be employed. See supplementary **Table S3** for statistical results of related figures.

Data Repository- The raw data can be found in an online repository at panoramaweb.org or by clicking this link. If the link does not work, navigate to https://panoramaweb.org/ using a web browser of your choice. Then click the Home button in the upper left-hand corner to drop down a list of projects. Scroll down to and click "NCSU- METRIC", click METRIC Public Data, click the folder labeled "RECOVERY OF PER- AND POLYFLUOROALKYL SUBSTANCES AFTER SOLVENT EVAPORATION", and finally click the "Raw Data" button in the upper right hand corner of the page to access the raw files.

Table S1- Analyte list with CAS #, full chemical name and vendor source.

Abbreviation	Analyte	CAS #	CCL*	Vendor †
Perfluoroalkyl carboxylic acids (PFCA)				
PFBA	Perfluorobutanoic acid	375-22-4	4	CIL
PFPeA	Perfluoropentanoic acid	2706-90-3	5	CIL
PFHxA	Perfluorohexanoic acid	307-24-4	6	CIL
PFHpA	Perfluoroheptanoic acid	375-85-9	7	CIL
PFOA	Perfluorooctanoic acid	335-67-1	8	CIL
PFNA	Perfluorononanoic acid	375-95-1	9	CIL
PFDA	Perfluorodecanoic acid	335-76-2	10	CIL
PFUnDA	Perfluoroundecanoic acid	2058-94-8	11	CIL
PFDoDA	Perfluorododecanoic acid	307-55-1	12	CIL
PFTrDA	Perfluorotridecanoic acid	72629-94-8	13	CIL
PFTeDA	Perfluorotetradecanoic acid	376-06-7	14	CIL
PFHxDA	Perfluorohexadecanoic acid	67905-19-5	16	CIL
PFODA	Perfluorooctadecanoic acid	16517-11-6	18	CIL
Perfluoroalkyl sulfonic acids (PFSA)				
PFBS	Perfluorobutanesulfonic acid	375-73-5	4	CIL
PFPeS	Perfluoropentanesulfonic acid	2706-91-4	5	CIL
PFHxS	Perfluorohexanesulfonic acid	355-46-4	6	CIL
PFHpS	Perfluoroheptanesulfonic acid	375-92-8	7	CIL
PFOS	Perfluorooctanesulfonic acid	1763-23-1	8	CIL
PFNS	Perfluorononanesulfonic acid	68259-12-1	9	CIL
PFDS	Perfluorodecanesulfonic acid	2806-15-7	10	CIL
Perfluoroether carboxylic acids (PFECA)				
PFMOAA	Perfluoro-2-methoxyacetic acid	674-13-5	-	CIL
PMPA	Perfluoro-2-methoxypropanoic acid	377-73-1	-	CH
PEPA	Perfluoro-2-ethoxypropanoic acid	267239-61-2	-	FL
PFO2HxA	Perfluoro-3,5-dioxahexanoic acid	39492-88-1	-	CH
PFO3OA	Perfluoro-3,5,7-trioxaoctanoic acid	39492-89-2	-	FL
Gen-X	Perfluoro-2-propoxypropanoic acid	13252-13-6	-	CIL
PFO4DA	Perfluoro-3,5,7,9-butaoxadecanoic acid	39492-90-5	-	FL
PFO5DoDA	Perfluoro-3,5,7,9,11-pentaoxadodecanoic acid	39492-91-6	-	FL
Hydro-EVE	2,2,3,3-Tetrafluoro-3-{[1,1,1,2,3,3-hexafluoro-3-(1,2,2,2-tetrafluoroethoxy)propan-2-yl]oxy}propanoic acid	773804-62-9	-	CH
ADONA	4,8-Dioxa-3H-perfluorononanoic acid	919005-14-4	-	CIL

Perfluoroether sulfonic acids (PFESA)				
NBP 1	Perfluoro-3,6-dioxa-4-methyl-7-octene-1-sulfonic acid	29311-67-9	-	CIL
NBP 2	Perfluoro-2-{[perfluoro-3-(perfluoroethoxy)-2-propanyl]oxy}ethanesulfonic acid	749836-20-2	-	CIL
NBP 4	Pentanoic acid, 2,2,3,3,4,5,5,5-octafluoro-4-(1,1,2,2-tetrafluoro-2-sulfoethoxy)-	2416366-18-0		CH
NVHOS	1-(1,1,2,2-tetrafluoro-2-sulfoethoxy)-1,2,2,2-tetafluoroethane	1132933-86-8		CH
F53B Major	9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	73606-19-6	-	CIL
F53B Minor	11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	83329-89-9	-	CIL
Perfluoroalkyl sulfonamides (PFSAm)				
FBSA	Perfluorobutane sulfonamide	30334-69-1	4	CIL
FHxSA	Perfluorohexane sulfonamide	41997-13-1	6	CIL
NMeFOSAA	N-methyl perfluorooctanesulfonamidoacetic acid	2355-31-9	8	CIL
NEtFOSAA	N-ethyl perfluorooctanesulfonamidoacetic acid	2991-50-6	8	CIL
FOSA	Perfluorooctane sulfonamide	754-91-6	8	CIL
MeFOSA	N-Methylperfluorooctanesulfonamide	31506-32-8	8	CIL
Fluorotelomer sulfonic acids (FTS)				
4:2 FTS	4:2 Fluorotelomer sulfonic acid	757124-72-4	6	CIL
6:2 FTS	6:2 Fluorotelomer sulfonic acid	27619-97-2	8	CIL
8:2 FTS	8:2 Fluorotelomer sulfonic acid	39108-34-4	10	CIL
10:2 FTS	10:2 Fluorotelomer sulfonic acid	120226-60-0	12	CIL
Zwitterions				
N-AP-FHxSA	N-(3-dimethylaminopropan-1-yl)perfluoro-1-hexane-sulfonamide	50598-28-2	6	CIL
N-TAmP-FHxSA	N-[3-(perfluoro-1-hexanesulfonamido)propan-1-yl]-N,N,N-trimethylammonium	38850-51-0	6	CIL
N-CMAmP-62FOSA (62 FTAB)	6:2 Fluorotelomer sulfonamide betaine	34455-29-3	8	CIL

***Abbreviations**: Carbon Chain Length (CCL)
†**Source:** CIL- Cambridge Isotope Laboratories, CH- Chemours, FL-Fluoryx

Table S2- DMRM transition list. Quant ions are listed first and bolded.

Compound Name	Precusor Ion	MS1 Resolution	Product Ion	MS2 Resolution	Fragment (V)	Collision Energy (V)	Cell Acceler ator (V)	Retention Time (min)	Retention Window	Polarity
Perfluoroalkyl carboxylic acids (PFCA)										
PFBA	212.98	Wide	**168.90**	Widest	166	10	4	3.3	6	Negative
PFBA	212.98	Wide	212.98	Widest	166	0	4	3.3	6	Negative
PFPeA	262.97	Wide	**219.04**	Widest	166	9	4	6.9	1.5	Negative
PFPeA	262.97	Wide	262.97	Widest	166	0	4	6.9	1.5	Negative
PFHxA	312.97	Wide	**118.90**	Widest	166	22	4	8.44	1.5	Negative
PFHxA	312.97	Wide	268.90	Widest	166	10	4	8.44	1.5	Negative
PFHpA	362.97	Wide	**318.80**	Widest	166	10	4	9.5	1.5	Negative
PFHpA	362.97	Wide	168.90	Widest	166	18	4	9.5	1.5	Negative
PFOA	412.96	Wide	**368.80**	Widest	166	10	4	10.39	1.5	Negative
PFOA	412.96	Wide	168.90	Widest	166	18	4	10.39	1.5	Negative
PFNA	462.96	Wide	**419.00**	Widest	166	10	4	11.18	1.5	Negative
PFNA	462.96	Wide	218.90	Widest	166	14	4	11.18	1.5	Negative
PFDA	512.96	Wide	**469.00**	Widest	166	10	4	11.9	1.5	Negative
PFDA	512.96	Wide	268.80	Widest	166	18	4	11.9	1.5	Negative
PFUnDA	562.95	Wide	**518.90**	Widest	166	10	4	12.61	1.5	Negative
PFUnDA	562.95	Wide	268.80	Widest	166	18	4	12.61	1.5	Negative
PFDoDA	612.95	Wide	**568.80**	Widest	166	10	4	13.3	1.5	Negative
PFDoDA	612.95	Wide	318.80	Widest	166	22	4	13.3	1.5	Negative
PFTrDA	662.95	Wide	**618.90**	Widest	166	10	4	13.96	1.5	Negative
PFTrDA	662.95	Wide	168.90	Widest	166	30	4	13.96	1.5	Negative
PFTeDA	712.94	Wide	**668.80**	Widest	166	10	4	14.49	1.5	Negative
PFTeDA	712.94	Wide	168.80	Widest	166	30	4	14.49	1.5	Negative
PFHxDA	812.94	Wide	**768.90**	Widest	166	14	4	14.75	1.5	Negative
PFHxDA	812.94	Wide	218.90	Widest	166	30	4	14.75	1.5	Negative
PFODA	912.93	Wide	**868.90**	Widest	166	14	4	15.03	1.5	Negative
PFODA	912.93	Wide	218.90	Widest	166	34	4	15.03	1.5	Negative
Perfluoroalkyl sulfonic acids (PFSA)										

PFBS	298.94	Wide	**80.00**	Widest	166	38	4	8.29	1.5	Negative
PFBS	298.94	Wide	99.00	Widest	166	30	4	8.29	1.5	Negative
PFPeS	348.94	Wide	**80.00**	Widest	166	46	4	9.45	1.5	Negative
PFPeS	348.94	Wide	99.00	Widest	166	42	4	9.45	1.5	Negative
PFHxS	398.93	Wide	**79.90**	Widest	166	40	4	10.18	1.5	Negative
PFHxS	398.93	Wide	98.80	Widest	166	38	4	10.18	1.5	Negative
PFHpS	448.93	Wide	**79.90**	Widest	166	46	4	11.12	1.5	Negative
PFHpS	448.93	Wide	98.80	Widest	166	46	4	11.12	1.5	Negative
PFOS	498.93	Wide	**80.00**	Widest	166	58	4	11.59	1.5	Negative
PFOS	498.93	Wide	99.00	Widest	166	42	4	11.59	1.5	Negative
PFNS	548.92	Wide	**80.00**	Widest	166	50	4	12.45	1.5	Negative
PFNS	548.92	Wide	99.00	Widest	166	54	4	12.45	1.5	Negative
PFDS	598.92	Wide	**80.00**	Widest	166	58	4	13.05	1.5	Negative
PFDS	598.92	Wide	99.00	Widest	166	54	4	13.05	1.5	Negative
Perfluoroether carboxylic acids (PFECA)										
PFMOAA	178.97	Wide	**84.90**	Widest	166	0	4	1.94	3	Negative
PMPA	228.97	Wide	**184.90**	Widest	166	10	4	4.8	4	Negative
PMPA	228.97	Wide	84.90	Widest	166	26	4	4.8	4	Negative
PEPA	234.98	Wide	**135.00**	Widest	166	18	4	7.2	4	Negative
PEPA	234.98	Wide	119.00	Widest	166	10	4	7.2	4	Negative
PFO2HxA	244.97	Wide	**85.10**	Widest	166	10	4	6.3	3	Negative
PFO2HxA	244.97	Wide	151.00	Widest	166	5	4	6.3	3	Negative
Gen-X	284.59	Wide	**168.90**	Widest	166	10	4	8.76	1.5	Negative
Gen-X	284.59	Wide	184.80	Widest	166	14	4	8.76	1.5	Negative
PFO3OA	310.96	Wide	**85.00**	Widest	166	10	4	8.6	1.5	Negative
PFO3OA	310.96	Wide	310.96	Widest	166	0	4	8.6	1.5	Negative
ADONA	376.96	Wide	**250.90**	Widest	166	10	4	9.86	1.5	Negative
ADONA	376.96	Wide	85.00	Widest	166	30	4	9.86	1.5	Negative
PFO4DA	376.95	Wide	**85.00**	Widest	166	10	4	10	1.5	Negative
PFO4DA	376.95	Wide	376.95	Widest	166	0	4	10	1.5	Negative
PFO5DoDA	442.94	Unit	**85.00**	Widest	166	18	4	10.9	2	Negative
PFO5DoDA	442.94	Unit	442.94	Widest	166	0	4	10.9	2	Negative
Hydro-EVE	426.96	Wide	**283.00**	Widest	166	10	4	10.12	1.5	Negative

Hydro-EVE	426.96	Wide	213.00	Widest	166	30	4	10.12	1.5	Negative
Perfluoroether sulfonic acids (PFESA)										
NBP 1	442.92	Wide	**262.90**	Widest	166	18	4	10.87	1.5	Negative
NBP 1	442.92	Wide	147.00	Widest	166	30	4	10.87	1.5	Negative
NBP 2	462.93	Wide	**263.00**	Widest	166	26	4	10.82	1.5	Negative
NBP 2	462.93	Wide	213.00	Widest	166	38	4	10.82	1.5	Negative
NBP 4	440.93	Wide	**240.80**	Widest	166	26	4	7.4	1.5	Negative
NBP 4	440.93	Wide	196.90	Widest	166	34	4	7.4	1.5	Negative
NVHOS	296.94	Wide	**116.90**	Widest	166	30	4	7.4	1.5	Negative
NVHOS	196.94	Wide	80.00	Widest	166	42	4	7.4	1.5	Negative
F53 Major	530.89	Wide	**350.90**	Widest	166	30	4	12.2	1.5	Negative
F53 Major	530.89	Wide	83.10	Widest	166	30	4	12.2	1.5	Negative
F53 Minor	630.89	Wide	**450.90**	Widest	166	30	4	13.39	1.5	Negative
F53 Minor	630.89	Wide	98.80	Widest	166	34	4	13.39	1.5	Negative
Perfluoroalkyl sulfonamides (PFSAm)										
FBSA	297.96	Wide	**77.90**	Widest	166	26	4	10.13	1.5	Negative
FBSA	297.96	Wide	63.90	Widest	166	60	4	10.13	1.5	Negative
FHxSA	397.95	Wide	**77.90**	Widest	166	30	4	12.09	1.5	Negative
FHxSA	397.95	Wide	168.80	Widest	166	30	4	12.09	1.5	Negative
FOSA	497.94	Wide	**78.10**	Widest	166	38	4	13.57	1.5	Negative
FOSA	497.94	Wide	48.10	Widest	166	60	4	13.57	1.5	Negative
MeFOSA	511.96	Wide	**169.00**	Widest	166	30	4	14.4	1.5	Negative
MeFOSA	511.96	Wide	218.90	Widest	166	26	4	14.4	1.5	Negative
NMeFOSAA	569.96	Wide	**418.80**	Widest	166	22	4	14.1	1.5	Negative
NMeFOSAA	569.96	Wide	511.80	Widest	166	22	4	14.1	1.5	Negative
NEtFOSAA	583.98	Wide	**419.00**	Widest	166	18	4	14.4	1.5	Negative
NEtFOSAA	583.98	Wide	526.00	Widest	166	18	4	14.4	1.5	Negative
Fluorotelomer sulfonic acids (FTS)										
4:2 FTS	326.97	Wide	**307.00**	Widest	166	18	4	7.95	1.5	Negative
4:2 FTS	326.97	Wide	81.00	Widest	166	30	4	7.95	1.5	Negative
6:2 FTS	426.97	Wide	**407.00**	Widest	166	26	4	9.86	1.5	Negative
6:2 FTS	426.97	Wide	81.00	Widest	166	38	4	9.86	1.5	Negative

8:2 FTS	526.96	Wide	**506.90**	Widest	166	30	4	11.35	1.5	Negative
8:2 FTS	526.96	Wide	81.10	Widest	166	34	4	11.35	1.5	Negative
10:2 FTS	626.95	Wide	**606.90**	Widest	166	34	4	12.71	1.5	Negative
10:2 FTS	626.95	Wide	81.10	Widest	166	46	4	12.71	1.5	Negative
Zwitterions										
N-AP-FHxSA	485.06	Wide	**85.10**	Widest	166	38	4	11.4	1.5	Positive
N-AP-FHxSA	485.06	Wide	58.10	Widest	166	60	4	11.4	1.5	Positive
N-TAmP-FHxSA	499.07	Wide	**59.10**	Widest	166	60	4	10.2	1.5	Positive
N-TAmP-FHxSA	499.07	Wide	60.10	Widest	166	38	4	10.2	1.5	Positive
N-CHAmP-6:2FOSA	571.10	Wide	**58.10**	Widest	166	54	4	10.34	1.5	Positive
N-CHAmP-6:2FOSA	571.10	Wide	104.00	Widest	166	34	4	10.34	1.5	Positive

Table S3. One-way ANOVE data for associated figures

One-Way ANOVA							
Compound	**Figure**	**Comparison**	**Mean Diff.**	**95.00% CI of diff.**	**Below threshold?**	**Summary**	**Adjusted P Value**
PFBA	Fig. 1 & S1A	MeOH No Heat vs. NH_4OH No Heat	-0.4237	-0.7731 to -0.07435	Yes	*	0.015
PFPeA	Fig. 1 & S1A	MeOH No Heat vs. NH_4OH No Heat	-0.3255	-0.5046 to -0.1463	Yes	***	0.0005
PFHxA	Fig. 1 & S1A	MeOH No Heat vs. NH_4OH No Heat	-0.2818	-0.4255 to -0.1380	Yes	***	0.0002
PFHpA	Fig. 1 & S1A	MeOH No Heat vs. NH_4OH No Heat	-0.2843	-0.4348 to -0.1338	Yes	***	0.0003
PFOA	Fig. 1 & S1A	MeOH No Heat vs. NH_4OH No Heat	-0.3056	-0.4450 to -0.1663	Yes	****	<0.0001
PFNA	Fig. 1 & S1A	MeOH No Heat vs. NH_4OH No Heat	-0.2627	-0.4067 to -0.1186	Yes	***	0.0004
N-AP (100)	Fig. 1 & S7A	MeOH Heat vs. MeOH No Heat	-0.151	-0.5063 to 0.2043	No	ns	0.626
N-AP (1k)	Fig. 1 & S7B	MeOH Heat vs. MeOH No Heat	-0.328	-0.4175 to -0.2384	Yes	***	<.001
N-AP (10k)	Fig. 1 & S7C	MeOH Heat vs. MeOH No Heat	-0.592	-0.7957 to -0.3884	Yes	****	<0.0001

Figure S1. Process efficiencies of PFCA compounds under heat, no-heat, methanol, and ammonium hydroxide conditions for three concentrations (**A**) 100 ng/L, (**B**) 1,000 ng/L and (**C**) 10,000 ng/L.

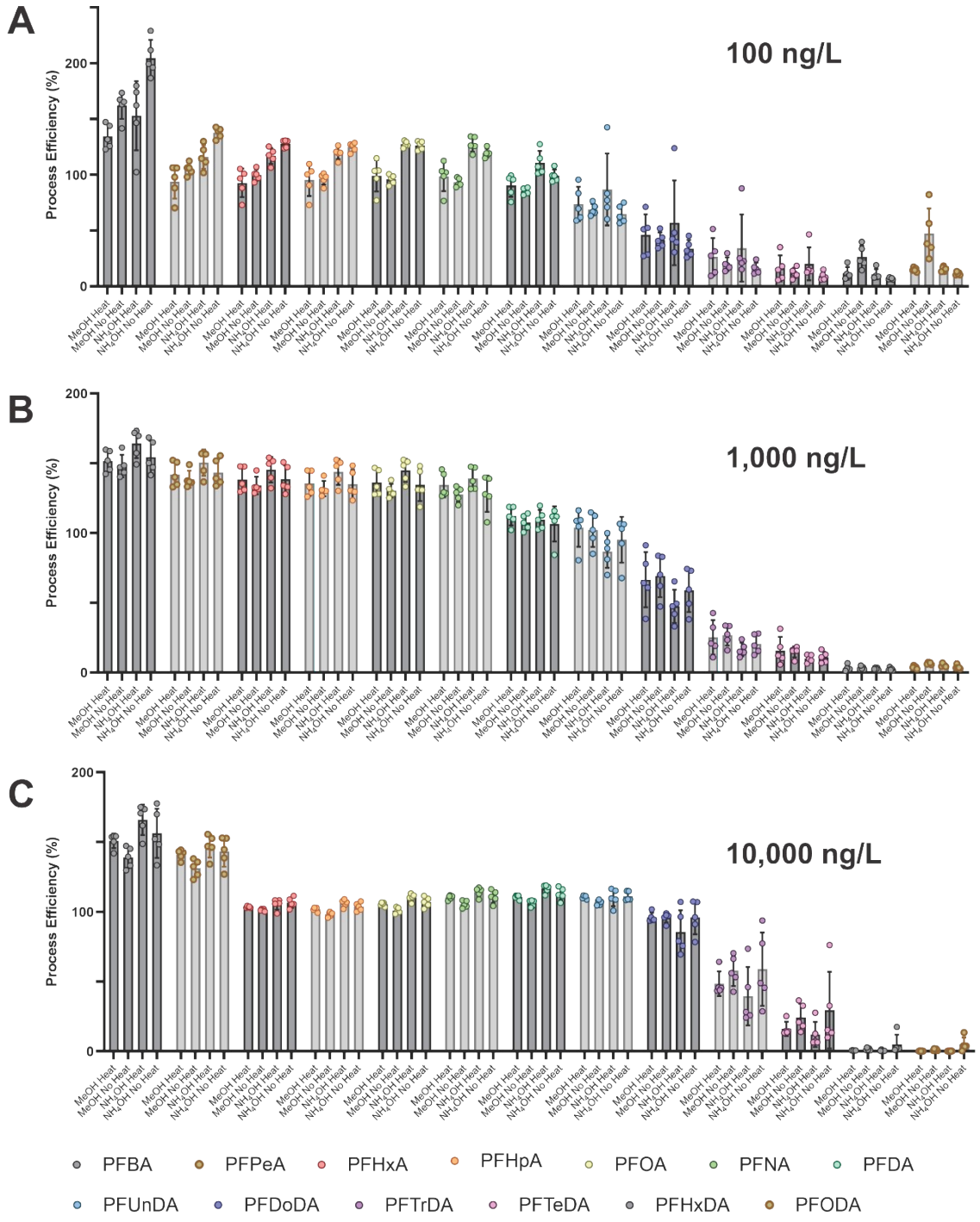

Figure S2. Process efficiencies of PFSA compounds under heat, no-heat, methanol, and ammonium hydroxide conditions for three concentrations (**A**) 100 ng/L, (**B**) 1,000 ng/L and (**C**) 10,000 ng/L.

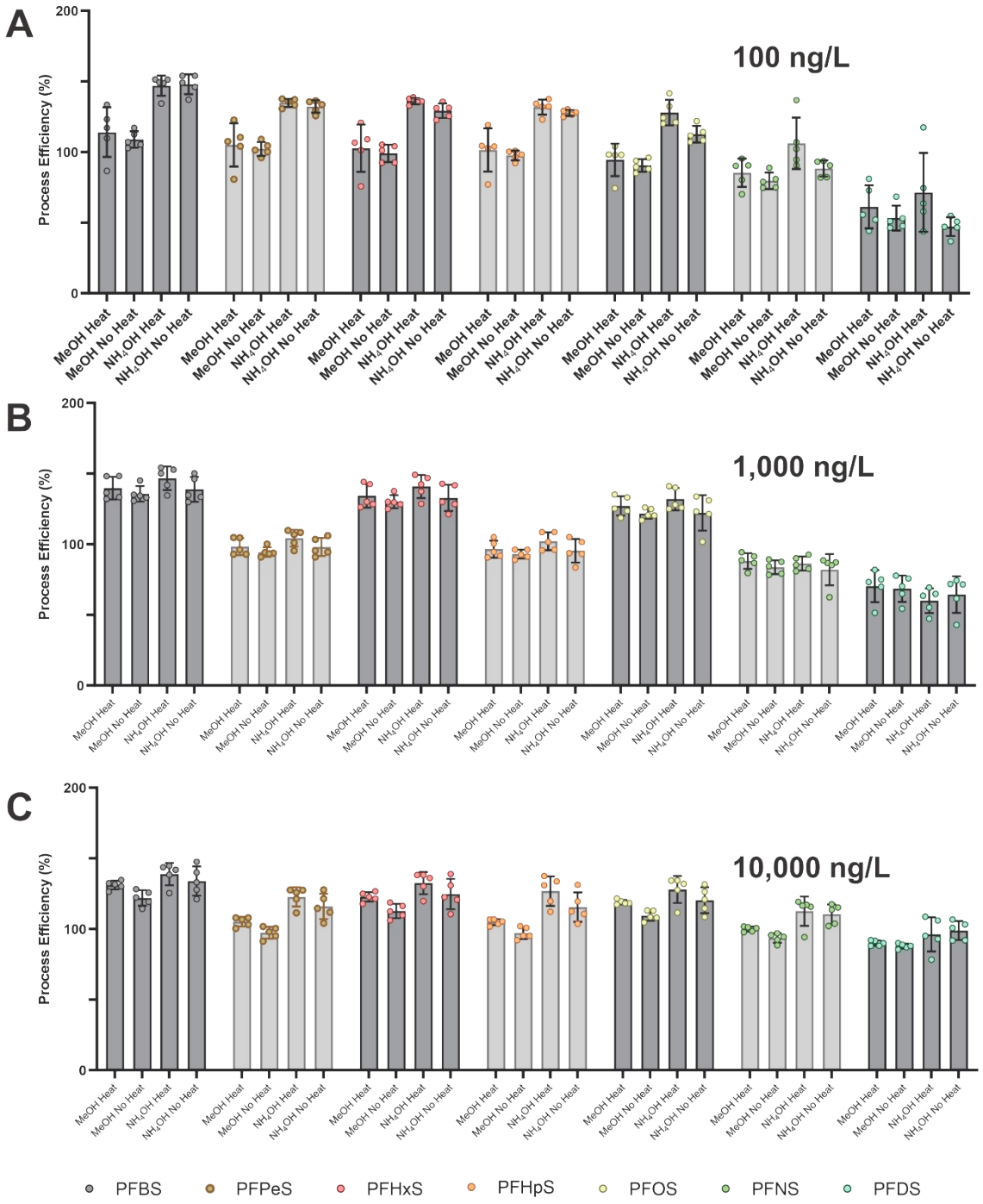

Figure S3. Process efficiencies of PFECA compounds under heat, no-heat, methanol, and ammonium hydroxide conditions for three concentrations (**A**) 100 ng/L, (**B**) 1,000 ng/L and (**C**) 10,000 ng/L.

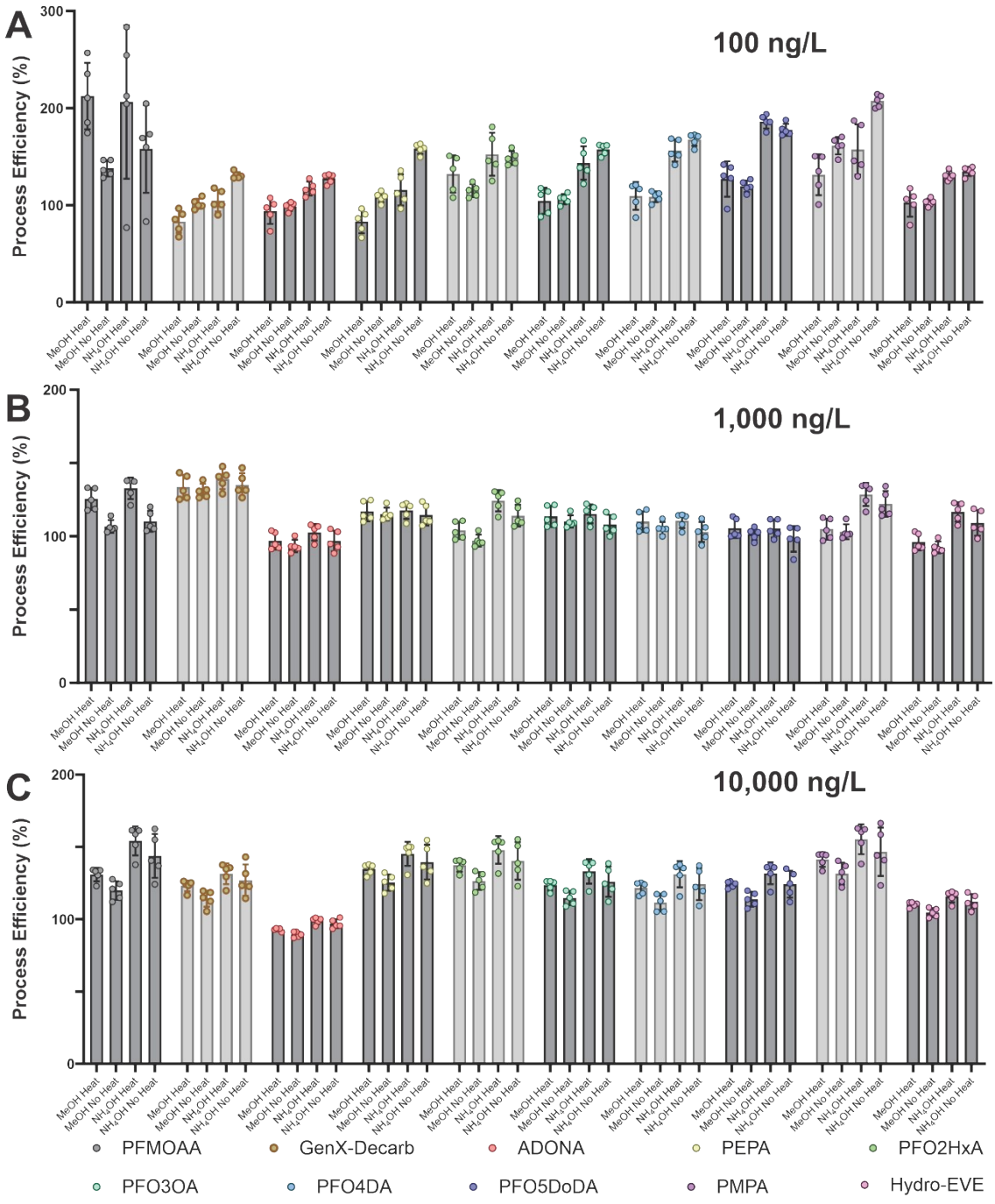

Figure S4. Process efficiencies of PFESA compounds under heat, no-heat, methanol, and ammonium hydroxide conditions for three concentrations (**A**) 100 ng/L, (**B**) 1,000 ng/L and (**C**) 10,000 ng/L.

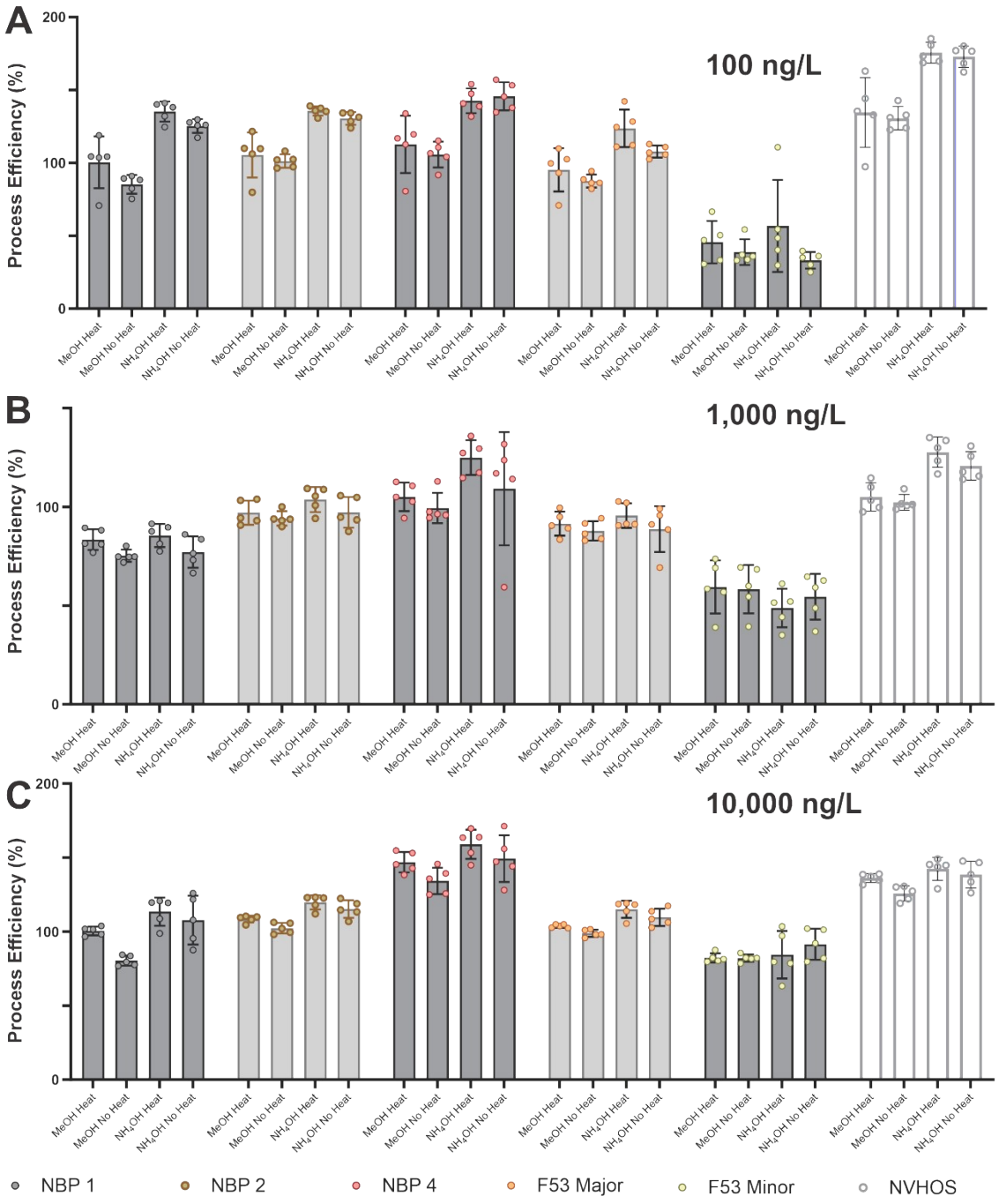

Figure S5. Process efficiencies of PFSAm compounds under heat, no-heat, methanol, and ammonium hydroxide conditions for three concentrations (**A**) 100 ng/L, (**B**) 1,000 ng/L and (**C**) 10,000 ng/L.

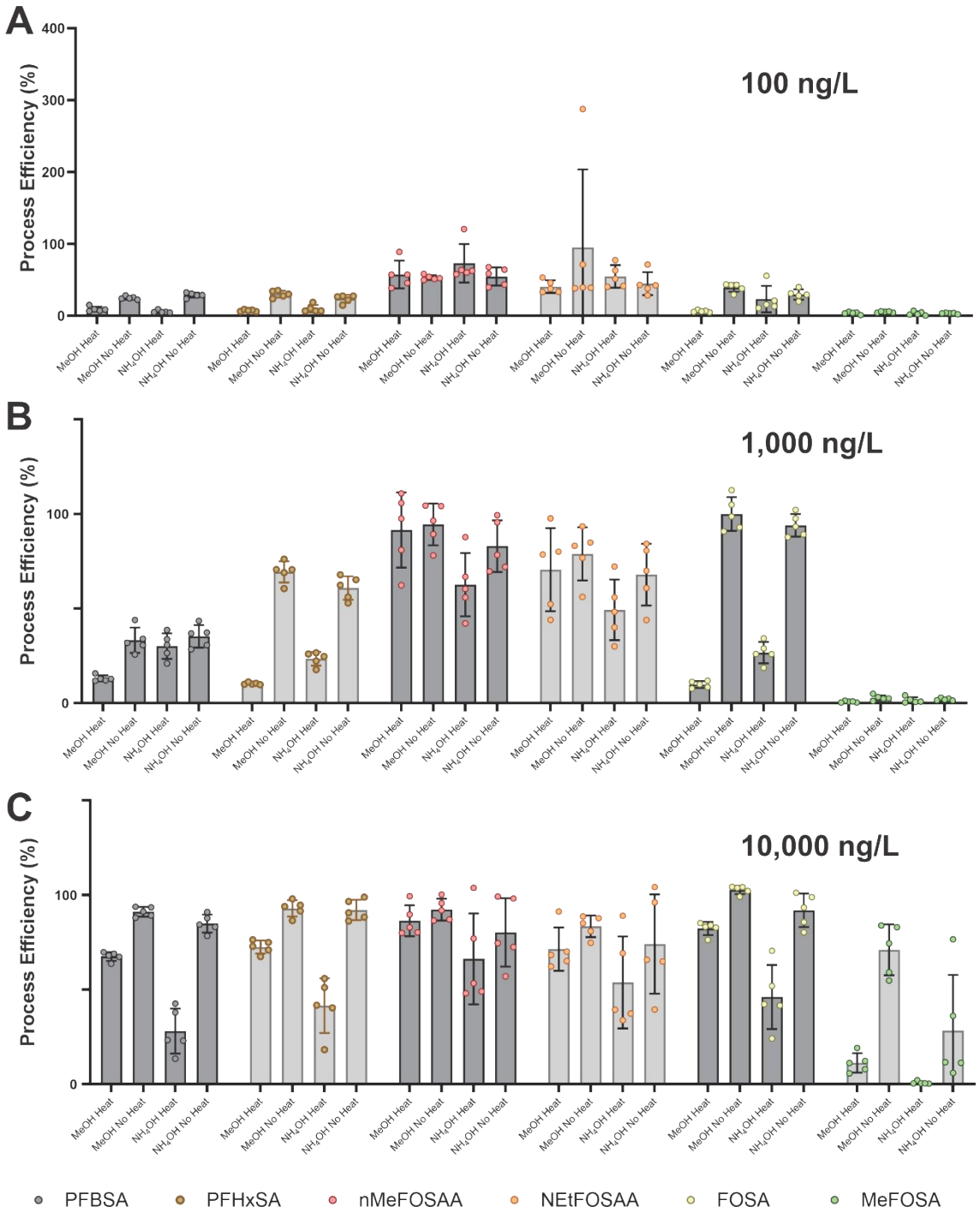

Figure S6. Process efficiencies of FTS compounds under heat, no-heat, methanol, and ammonium hydroxide conditions for three concentrations (**A**) 100 ng/L, (**B**) 1,000 ng/L and (**C**) 10,000 ng/L.

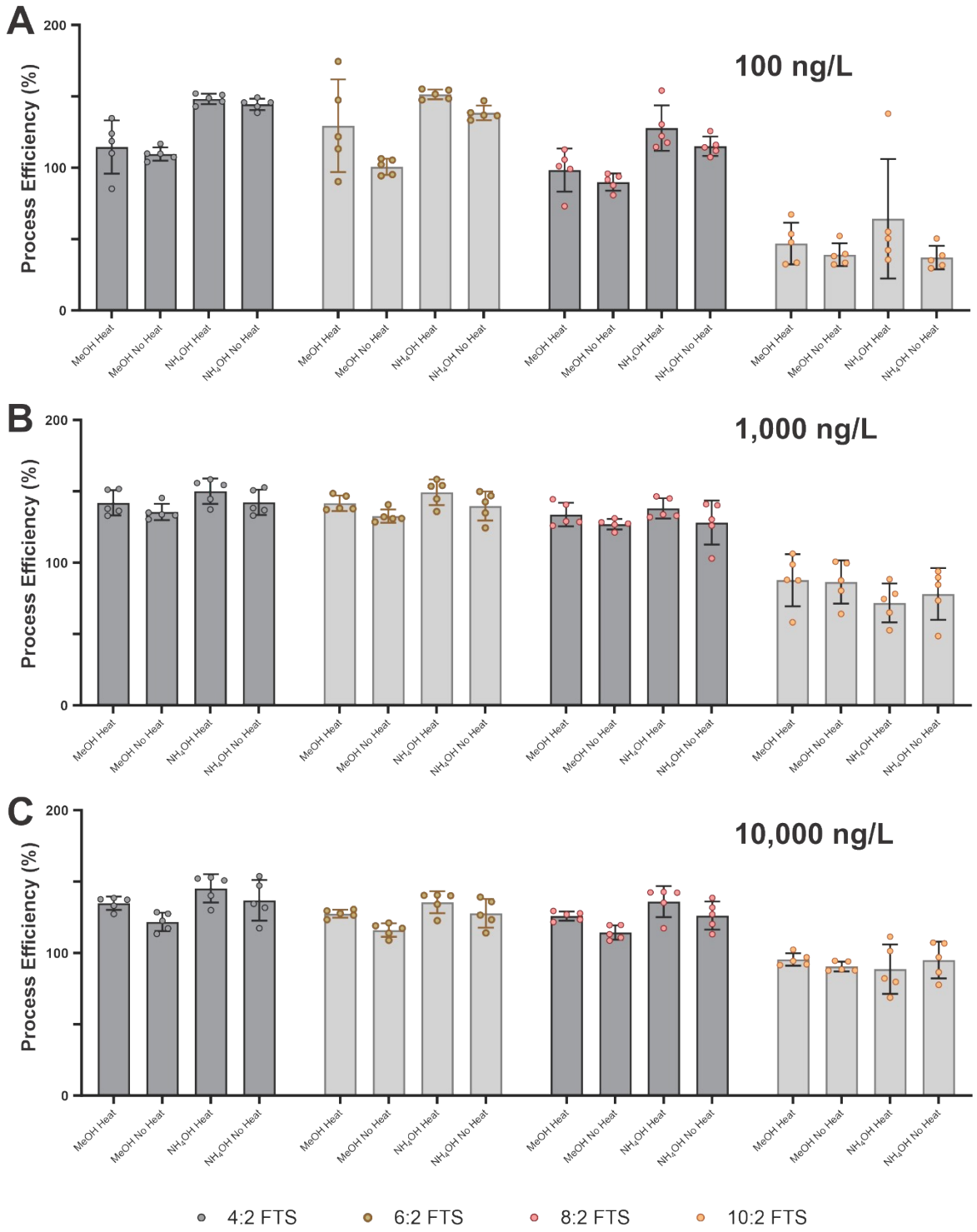

Figure S7. Process efficiencies of Zwitterionic compounds under heat, no-heat, methanol, and ammonium hydroxide conditions for three concentrations (**A**) 100 ng/L, (**B**) 1,000 ng/L and (**C**) 10,000 ng/L.

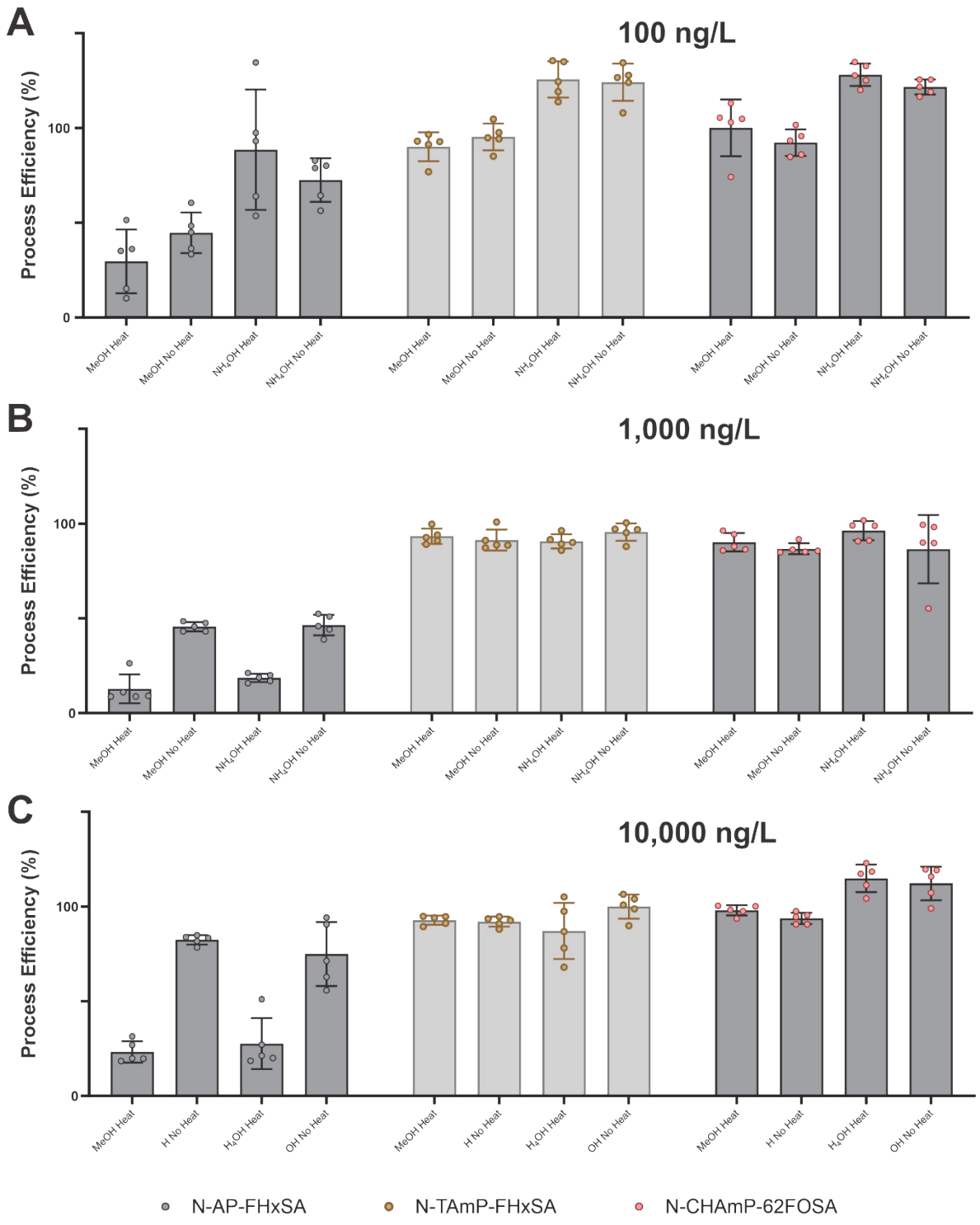

Figure S8. Process efficiencies of reconstituting extracts with 1 mL of 50:50 methanol water or 500 µL of 100% methanol and then 500 µL of 100% water for (**A**) PFCA & (**B**) PFSA. All replicates were run in MeOH with no heat applied.

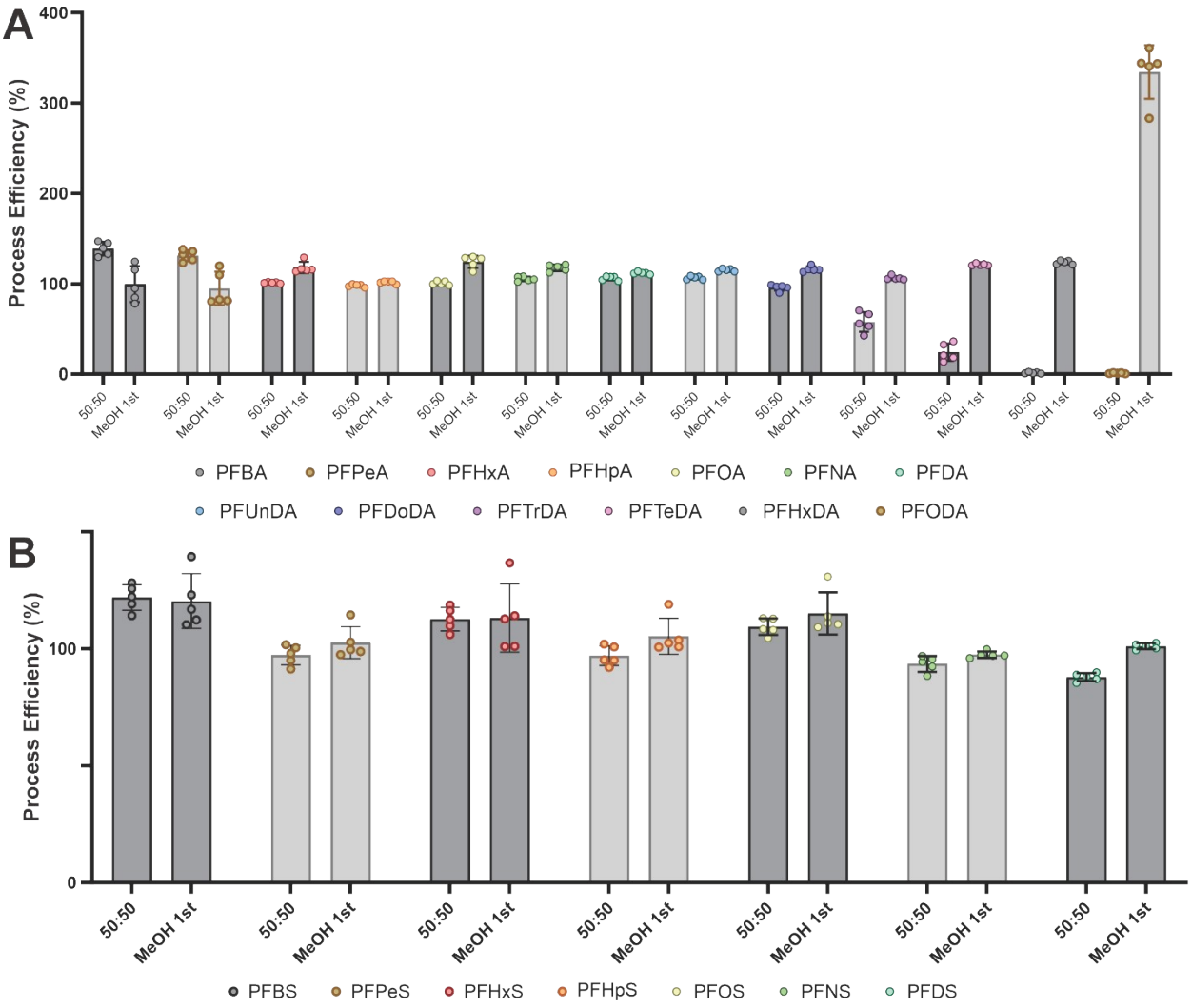

Figure S9. Process efficiencies of reconstituting extracts with 1 mL of 50:50 methanol water or 500 µL of 100% methanol and then 500 µL of 100% water for (**A**) PFECA and (**B**) PFESA. All replicates were run in MeOH with no heat applied.

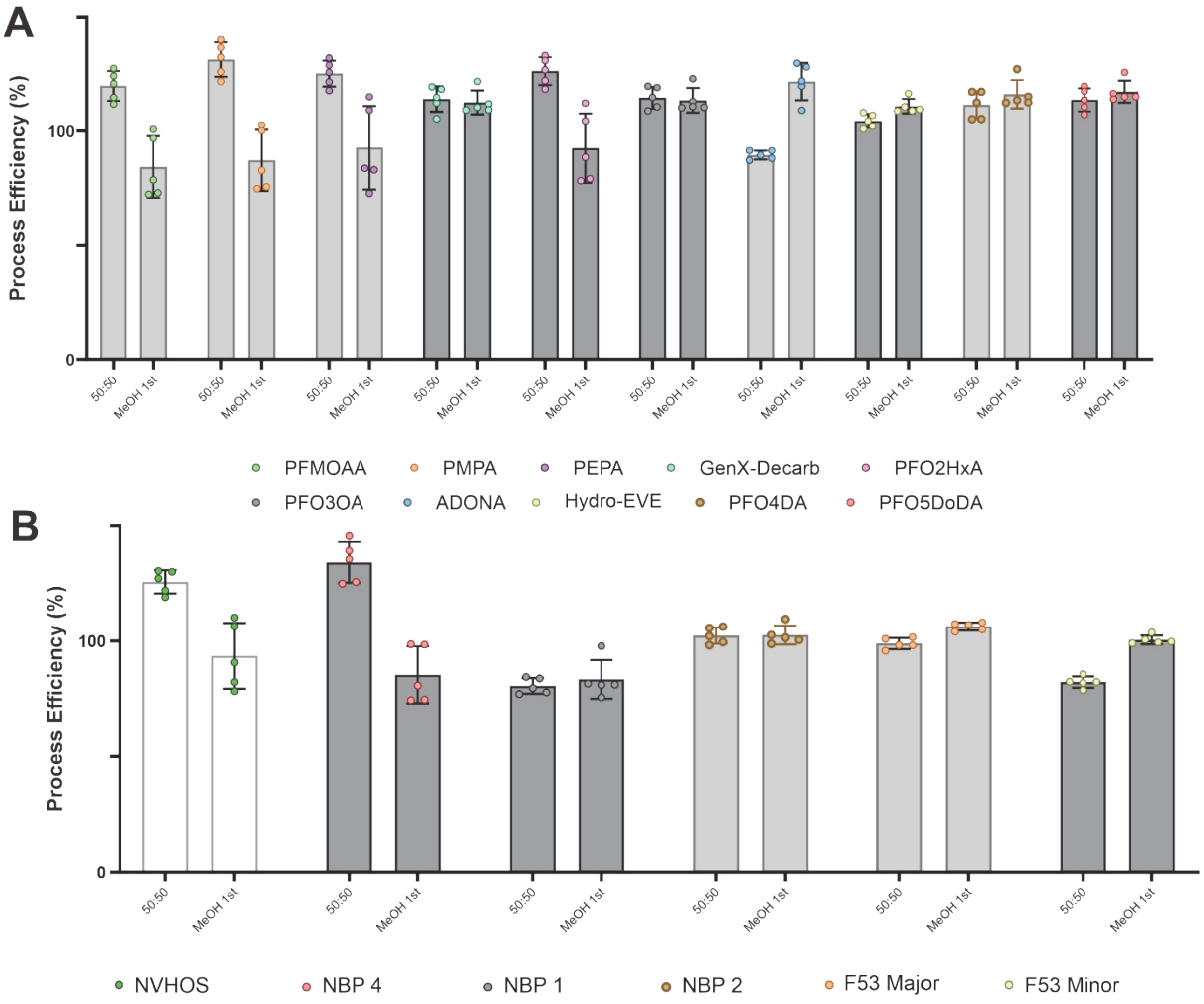

Figure S10. Process efficiencies of reconstituting extracts with 1 mL of 50:50 methanol water or 500 µL of 100% methanol and then 500 µL of 100% water for (**A**) FTS, (**B**) PFSAm, & (**C**) Zwitterions. All replicates were run in MeOH with no heat applied.