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Comparison of commercially available MBIX resins for UPW production using measuring techniques described in SEMI C93 and beyond

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AGENDA

1) Problem statement
2) Test methods
3) Test results
4) Comparison of Mixed Bed Ion Exchange (MBIX) resins
5) Further findings from the experiments: What combines all resins
6) Key takeaways

PROBLEM STATEMENT

- Mixed Bed Ion Exchange (MBIX) resins are a key component to produce Ultrapure Water in a Polishing System.

- While MBIX resins are designed to remove ions from the water, all MBIX resins also shed ions, organics, particles and particle precursors. In fact, it is not so much the ion removal rate that defines the quality of the water produced with a Mixed Bed in a Polishing System, but the various shedding rates (metals, particles, organics).

- The focus of this presentation is on a comparative study of the different resins rather than on absolute values.

TEST METHODS

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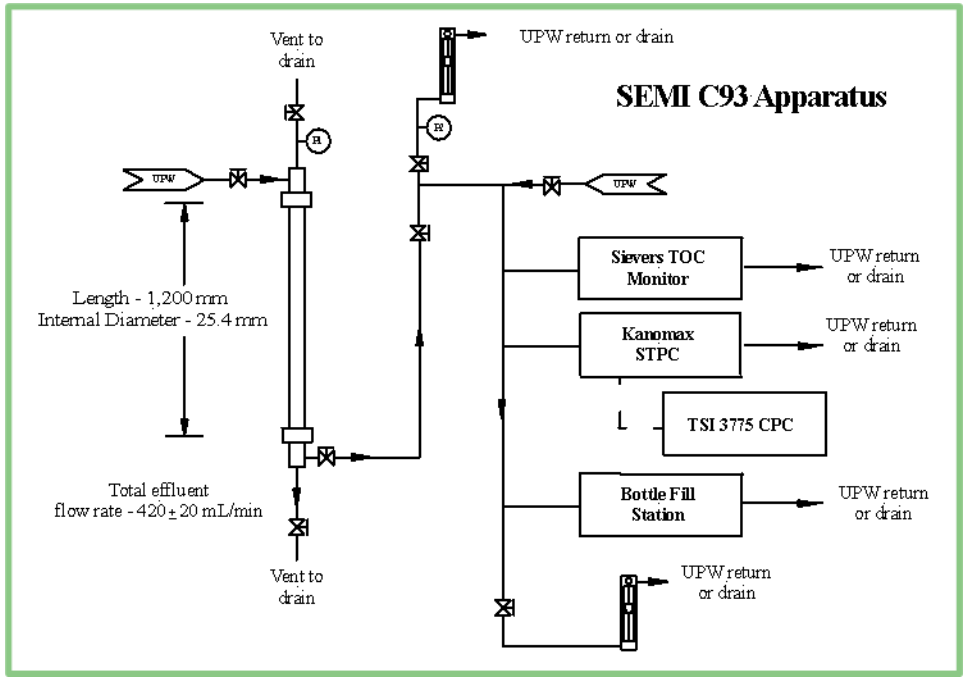
Off-line

4) CTA Sequential Spin Coating (SSC) / UNISERS Surface Enhanced Particle Sizing (SEPS)

6) DOC-Labor LC-OCD-OND Organic Speciation



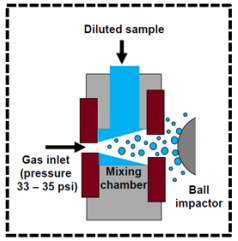
7) CTA Jasco 6600 Fourier-Transform Infrared Spectroscopy (FTIR)

1) Static leach analysis of the resin per SEMI C93-0522 with 3:1 UPW: 35% HCl by ICP/MS.

Online

5) CTA Sievers 500 RL Total Organic Carbon (TOC)

3) CTA Kanomax FMT STPC Nanoparticle Analyzer



2) CTA Ultrafine Nebulizer/ TSI Model 3775 CPC Nanoparticle Analyzer

TEST METHODS

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Method according to SEMI C93
SEMI C93 method adapted
New method

Static HCl leach test

1. Metals analysis

Dynamic IX resin rinse test

2. Particles > 4 nm were measured using ultrafine nebulization supplying a TSI 3775 4 nm condensation particle counter (CPC)
3. Particles > 7, 12 and 18 nm were measured using a Kanomax FMT Model 9010 Scanning Threshold Particle Counter (SEMI C93 presents particle analysis on MBIX resin for particles > 10 nm)
4. Measuring the accumulation and distribution of nanoparticles on wafer surfaces, involving a combination of sequential spin coating (SSC) and surface enhanced particle sizing (SEPS) using a UNISERS surface inspection. The lower particle size detection limit is 8 nm
5. TOC was measured using a Sievers Model 500 RL TOC analyser
6. Enhanced organics speciation with LC-OCD-OND analysis by DOC-Labor Huber with a DL of 5 ppt C (lower DL compared to analyses presented in SEMI C93)
7. Qualitative analysis of non-volatile residue chemistry from FTIR -ATR spectra of MBIX (Effluent - Influent) and comparisons to the other measuring techniques

TEST RESULTS - METALS

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Total Metals concentration

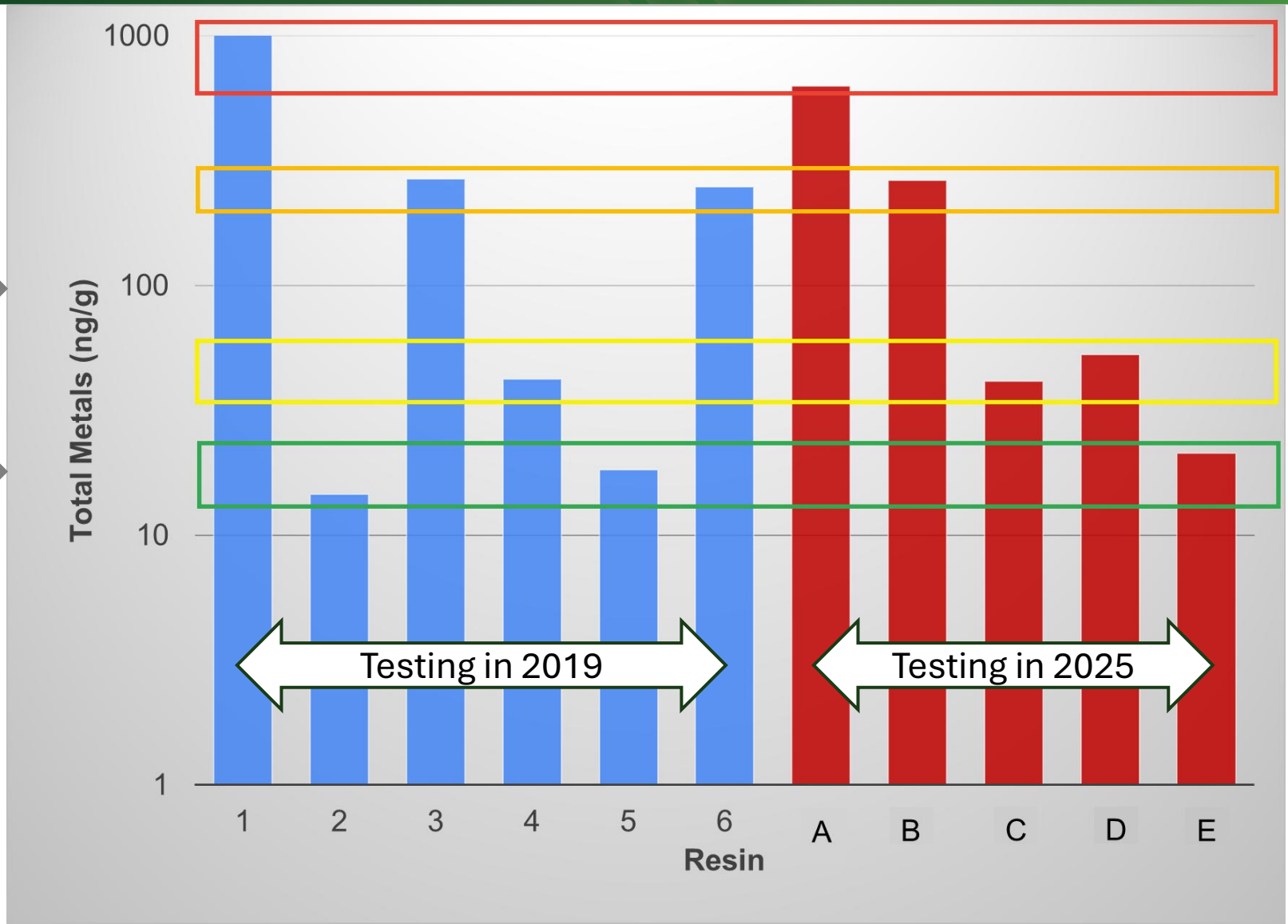
Resins 1 – 6 tested in the rev. of SEMI C93 released 2019

Resins A – E tested in 2025

Results

⇒ We found a factor 30 between resins A to E for total metals content.

⇒ We found the total metal content to be in the same range compared to the last testing 2019.



TEST RESULTS – ONLINE PARTICLES

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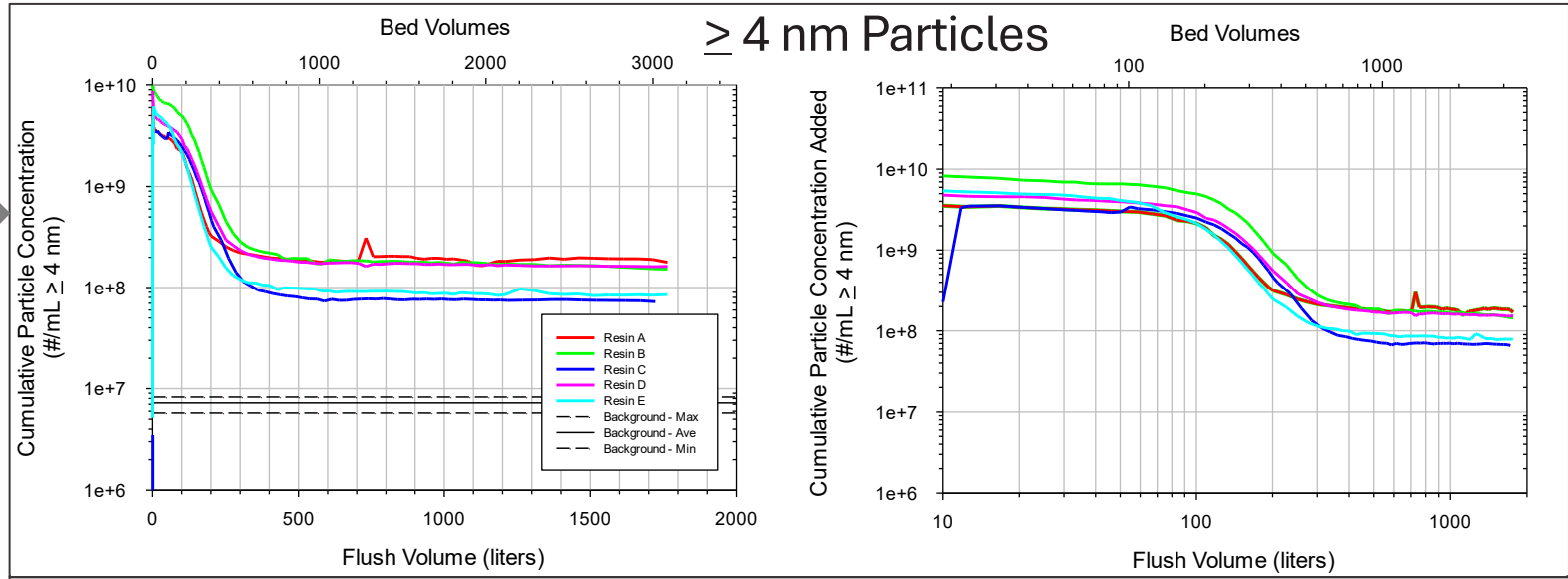
Particles ≥ 4 nm for resins A-E measured with a CPC

Result

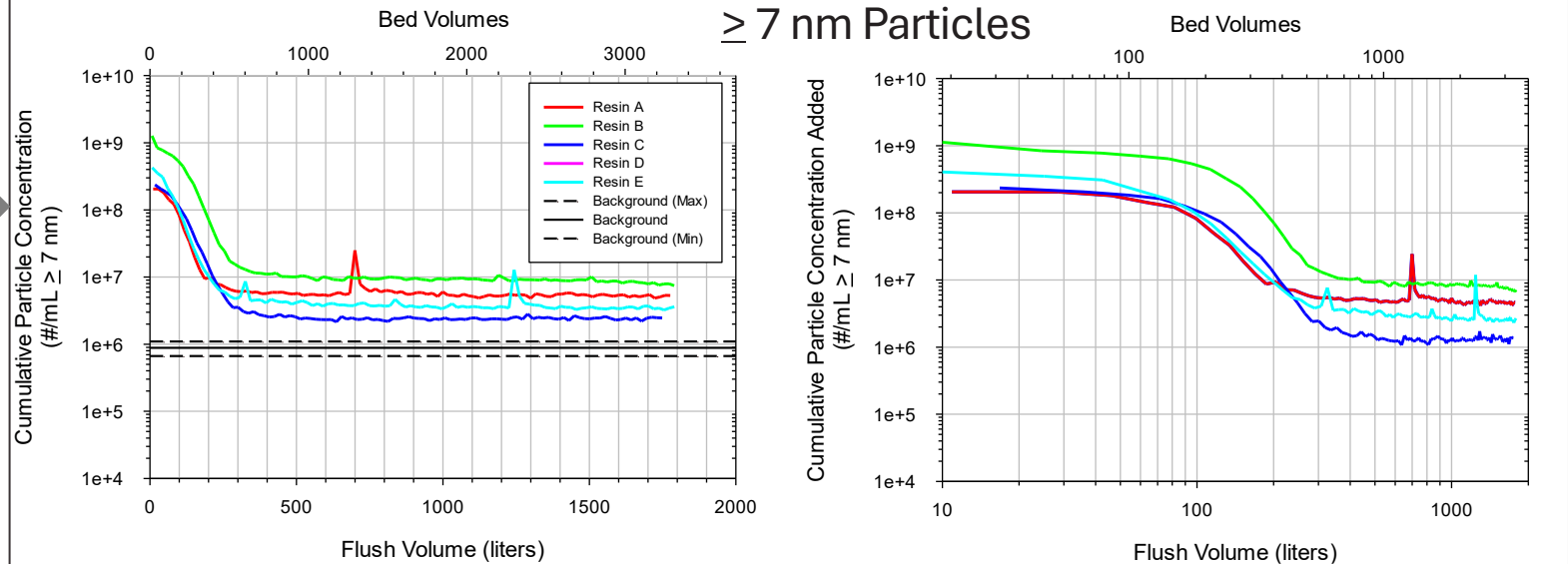
=> We found a factor 2.4 between resins A to E for particles ≥ 4 nm



Particles ≥ 7 nm for resins A-E measured with a STPC

Result

=> We found a factor 3.3 between resins A to C, E for particles ≥ 7 nm



TEST RESULTS – PARTICLES ON WAFER

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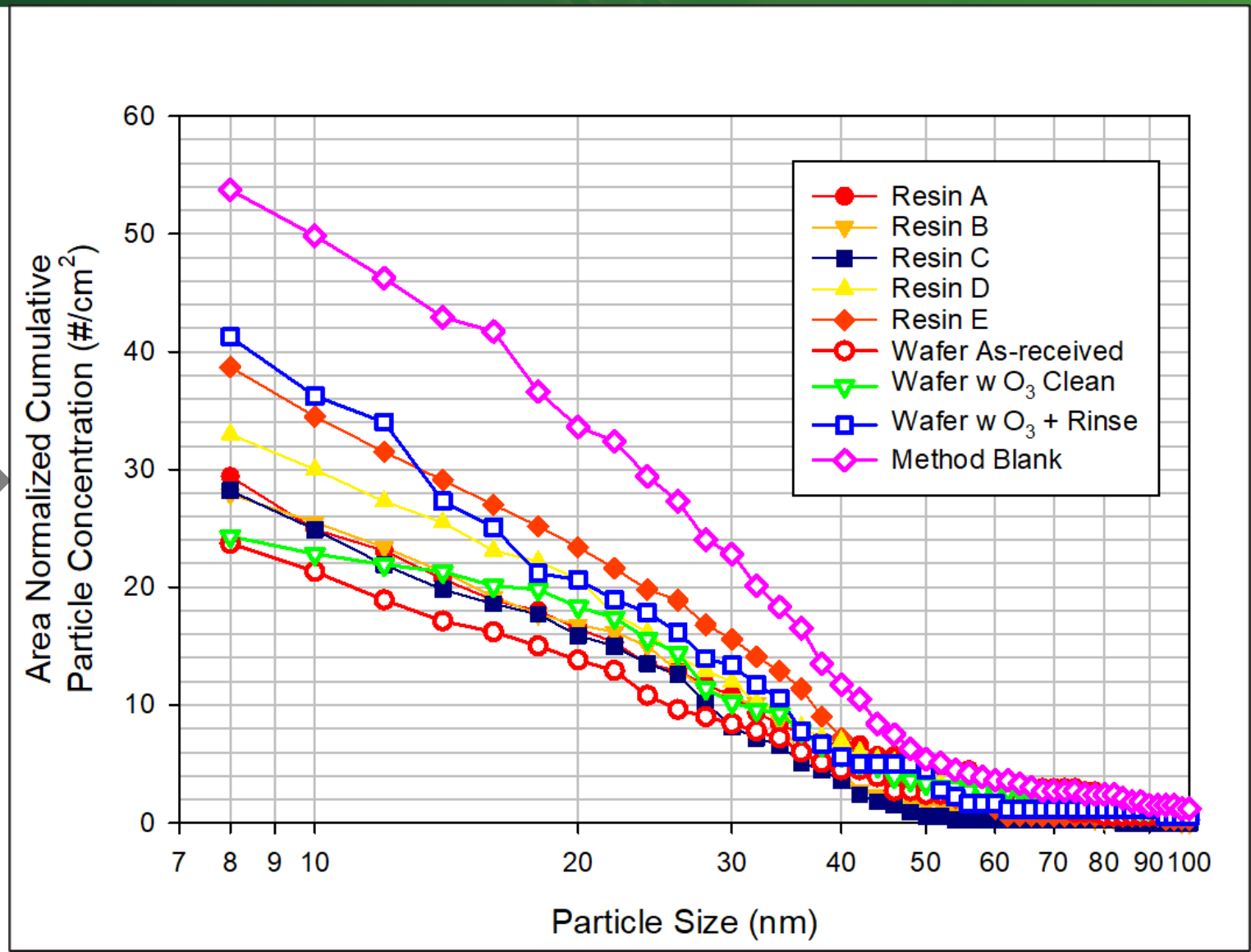
Particles ≥ 8 nm on wafer surfaces, involving a combination of sequential spin coating (SSC) and surface enhanced particle sizing (SEPS) using a UNISERS surface inspection tool

Observations:

- Increase handling steps increase background levels.
- Unable to detect a coorelation between particle precursor concentration to on-wafer defects likely due to the low signal-to-noise.

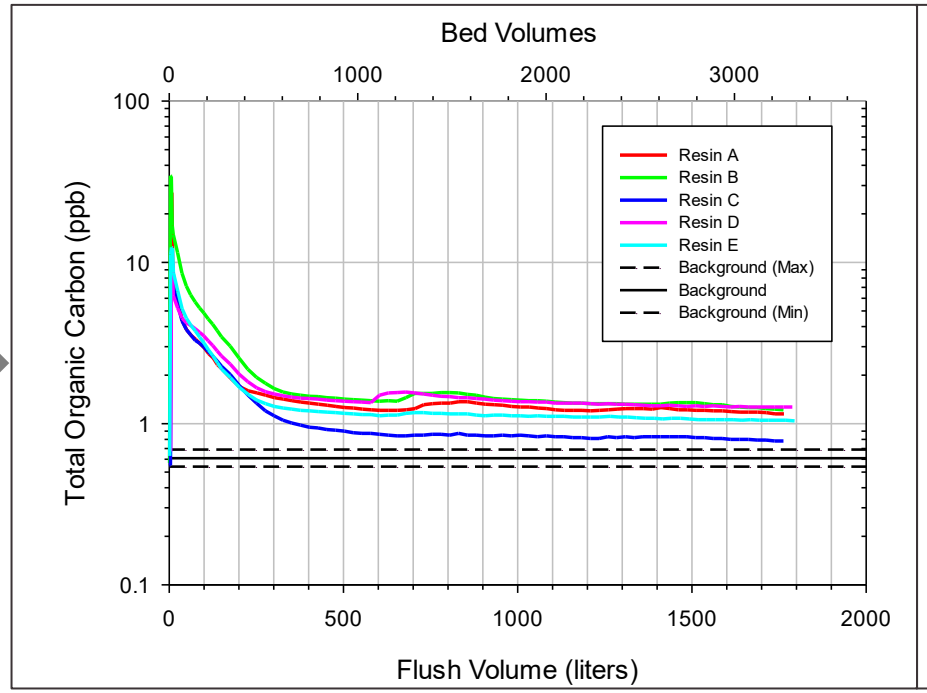


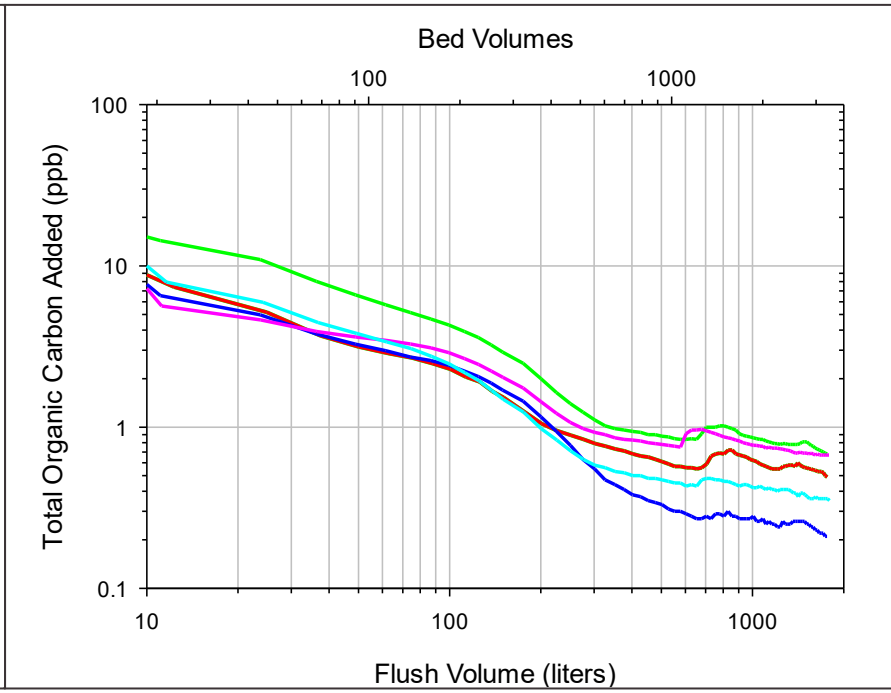
TEST RESULTS – ONLINE TOC

Online TOC after 3,200 bed volumes have passed through the resin column

Result

=> We found a factor 1.6 for the final water quality after rinse down between resins A to E





TEST RESULTS – LC-OCD

Amino Acids from LC-OCD

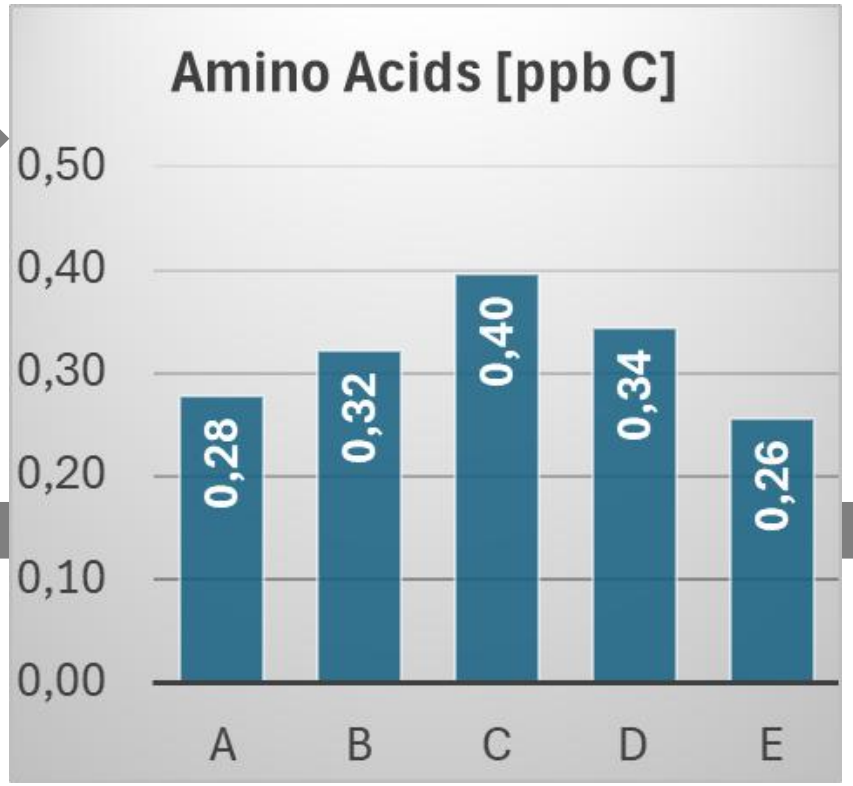
Result

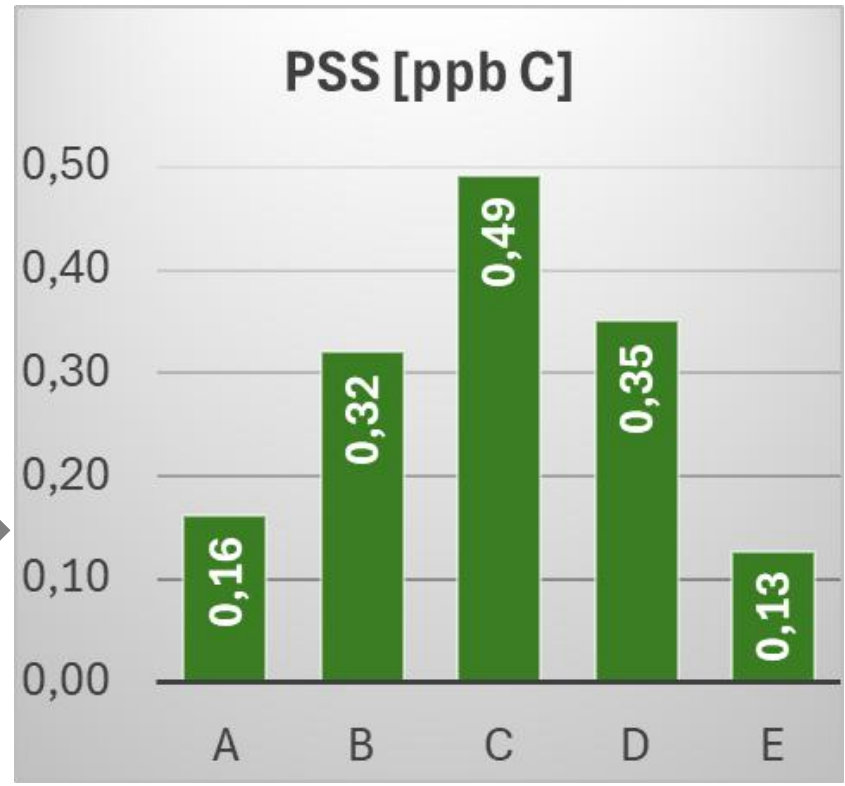
=> We found a factor 1.55 between resins A to E

PSS (Polystyrene sulfonate) from LC-OCD

Result

=> We found a factor 3.7 between resins A to E





RESIN COMPARISON (QUALITATIVE)

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	Metals	Particles			Organics			Result
Variability	30	2.4	3.3		1.60	1.55		
Test	M1	P1	P2	av. P	O1	O2	av. O	av. M/O/P
Resin A	0	1	1	1	1	3	2	0.8
Resin B	1	1	0	0.5	0	1	0.5	0.8
Resin C	2	3	3	3	3	0	1.5	2.0
Resin D	2	1	*	1	1	1	1	1.5
Resin E	3	2	2	2	2	3	2.5	2.7

* no data

x3 x1 x2 → Weighted Average

M1 - Total Metals, P1 - 4 nm Particles, P2 - 7 nm Particles, O1 - Online TOC, O2 - LC-Amino Acids

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AMINO ACIDS VS PSS

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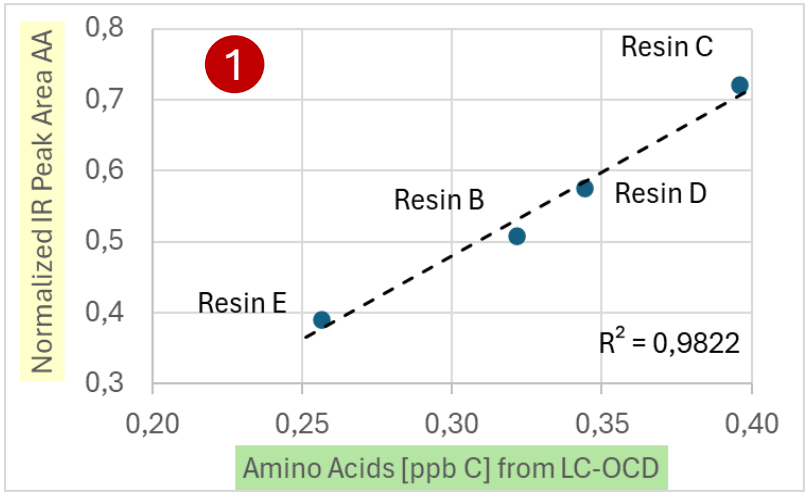
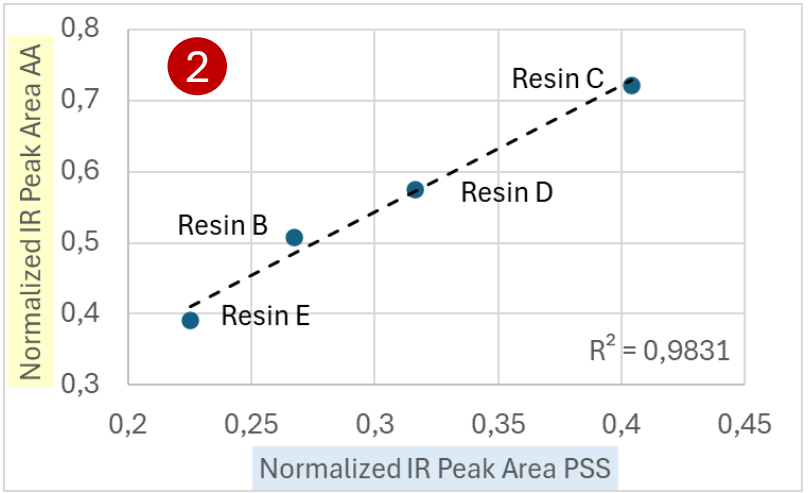
1 Data for Amino Acids from FTIR and LC are very well aligned

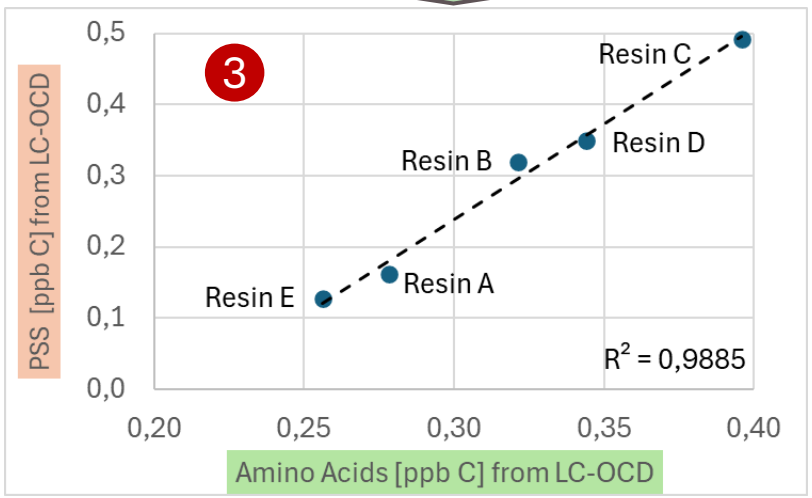
4 Data for Polystyrene Sulfonate (PSS) from FTIR and LC are very well aligned

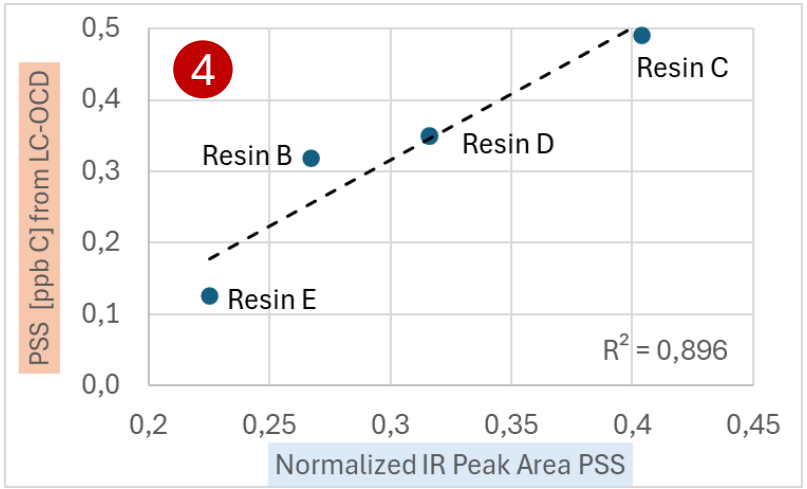
3 We also see a strong correlation between PSS and Amino Acids from LC,

2 as well as between PSS and Amino Acids from FTIR

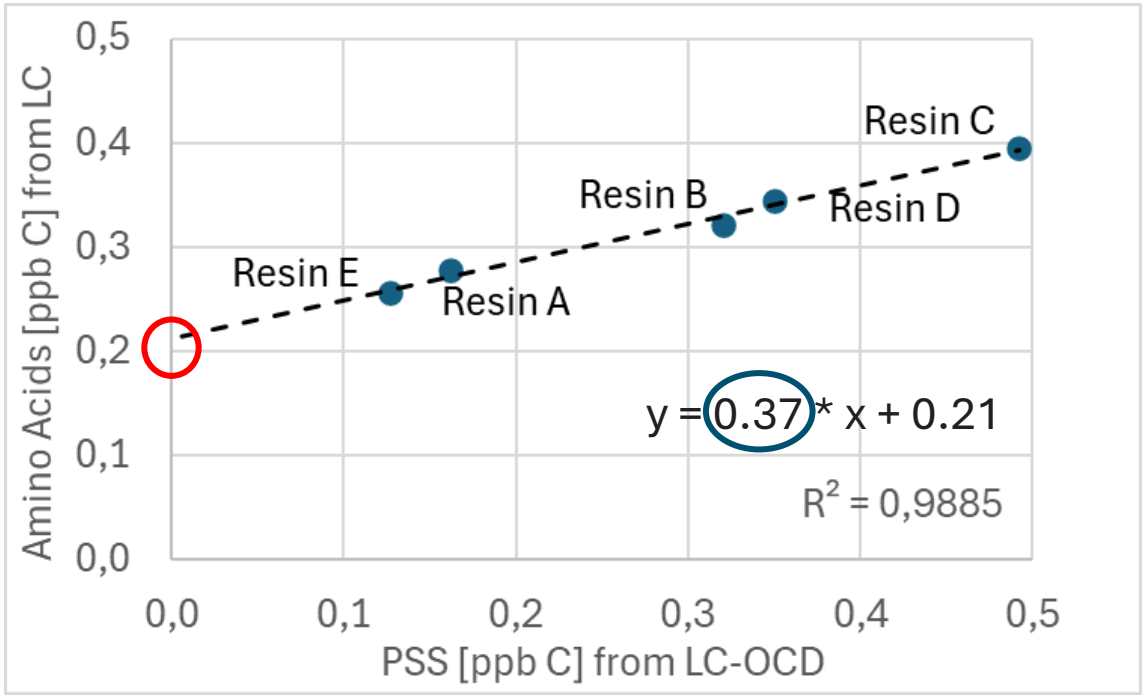








AMINO ACIDS VS PSS



Resin test data after approx. 3 days rinse time suggest for **ALL** resins, that 0.21 ppb C from Amino Acids can generally be found in the MBIX product **without** link to PSS.

Resin test data after approx. 3 days rinse time suggest for **ALL** resins, that the shedding rates for PSS and Amino Acids are strongly correlated.

The slope of the correlation between AA and PSS is

0.37 AA/PSS or 2.7 PSS/AA

For the ion paring model, PSS molecules (n*C8) would then travel with n*C3 Amino Acids …

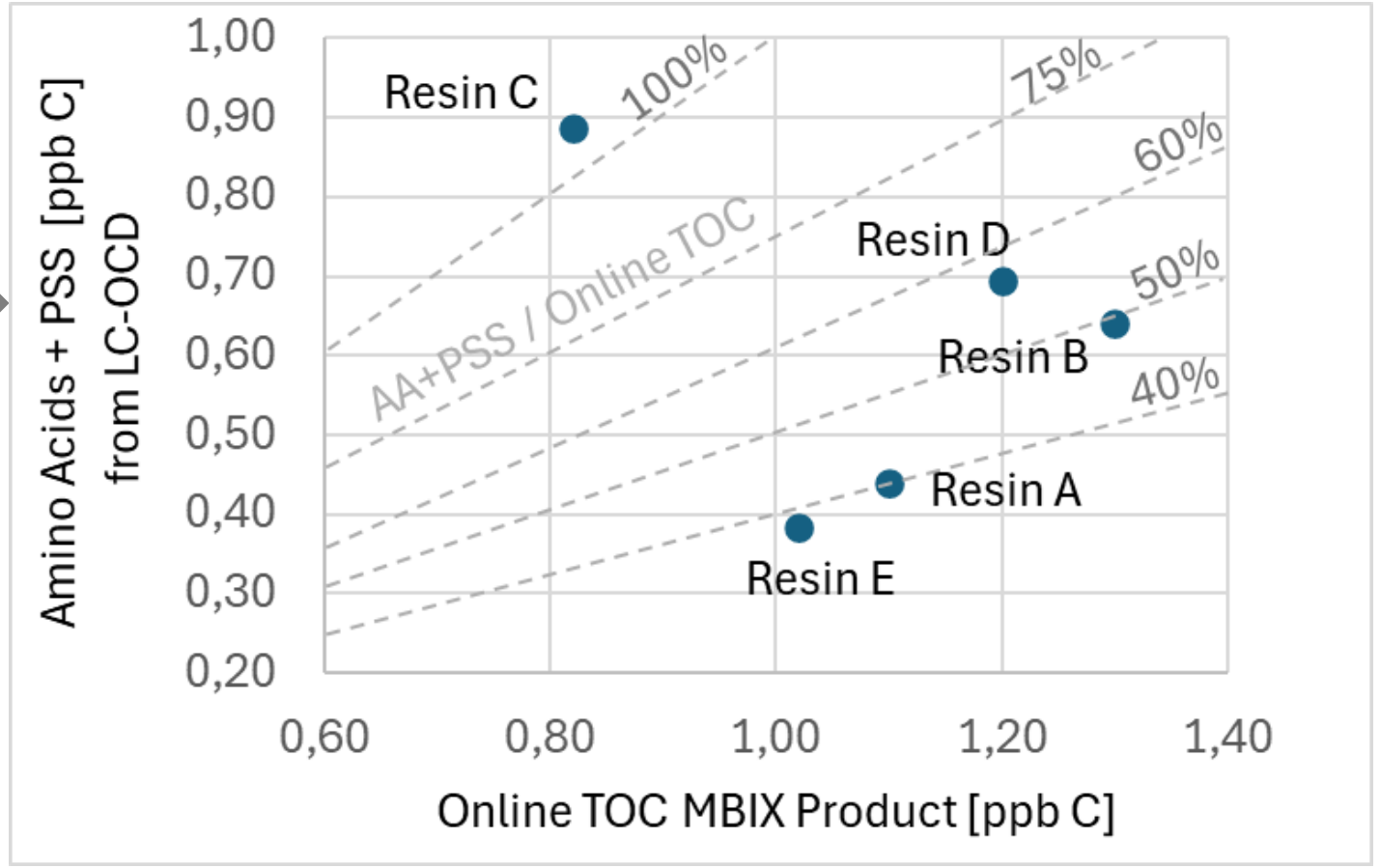
8 / 3 = 2.7

➢ This is just a potential conclusion from the data analysis!

TEST RESULTS – ORGANIC SPECIATION

This graph shows, that the Amino Acid plus the PSS fraction of the DOC from LC is in the range of 50 % of the Online TOC for most of the resins.

Only for resin C, which had the lowest online TOC after rinse down, we found a significantly higher Amino Acids plus PSS content of ~100 % of the online TOC. This would indicate, that from resin C, no other organic contaminants are released.
For all other resins, ~50% of the organic contamination is still unknown.



KEY TAKEAWAYS

- *Mixed bed resins eat and bleed*: We examined the “bleed” of 5 Semi grade MB-resins with state-of-the-art technology.
- There is no “dream” resin if we combine all parameters, but there are clear front runners when it comes to specific parameters.
- Metals were the main differentiator between the five resins, followed by TOC and particles.
- We found a strong correlation between Amino Acids and PSS from LC-OCD and from FTIR, which are seen as potential Particle Precursors (PP’s).
- Cationic and anionic PP’s correlate well with each other, suggesting that they travel together as an ion pair through the MBIX, as previously proposed by Zazzera et al..
- PP’s make up a large part of target TOC (1 ppb).

NEXT STEPS

- Veolia will use the test results as a benchmark for future testing.
- Veolia will keep on working with the vendors of MBIX resins to produce even cleaner resins.
- Veolia will keep on supporting the Microelectronics community to better understand the chemical reaction pathways from particle precursors to particles on wafers.

Thank you !

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