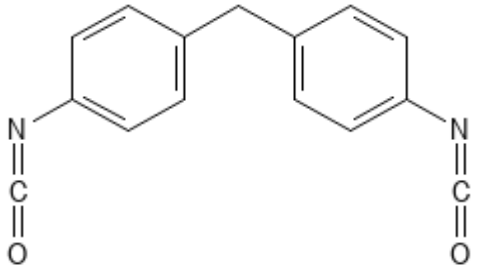
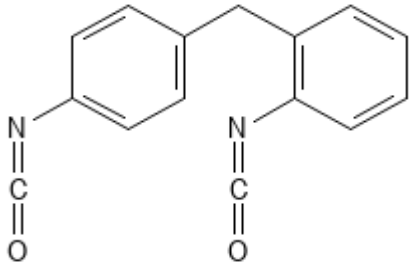
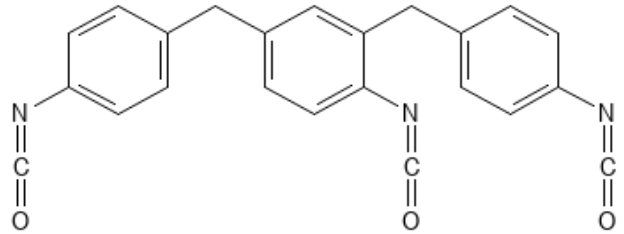
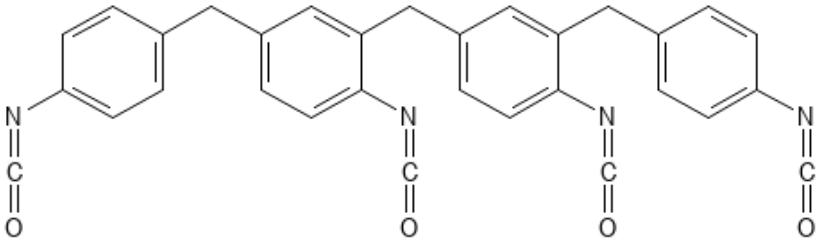
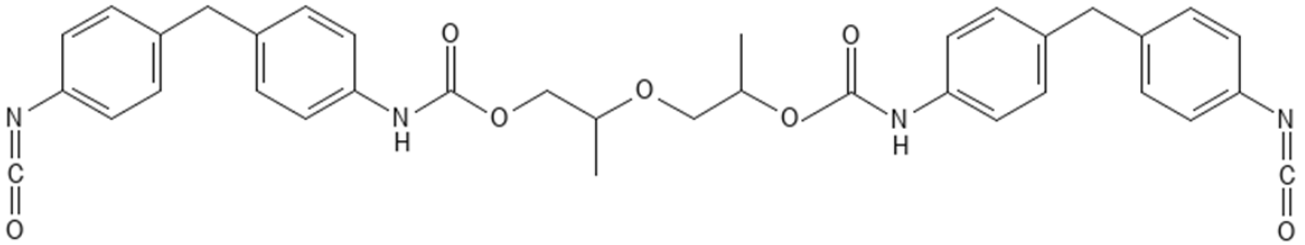
Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

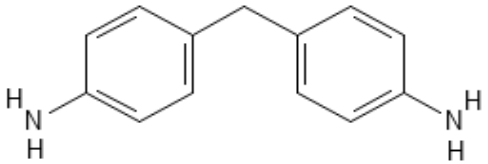
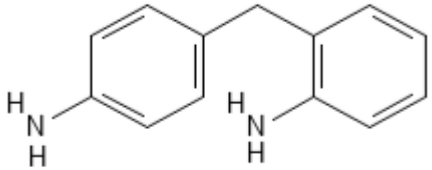
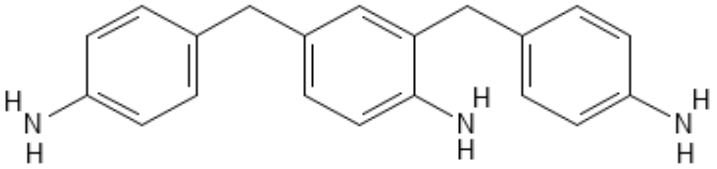
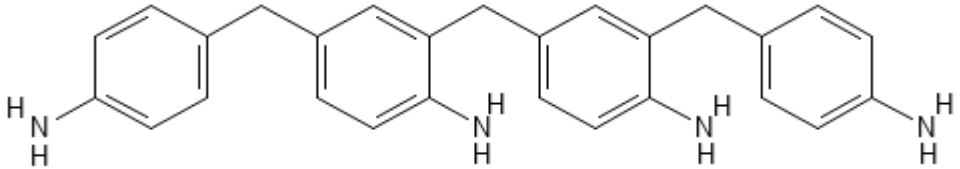
Supplemental Information – 1 – Tables and Figures

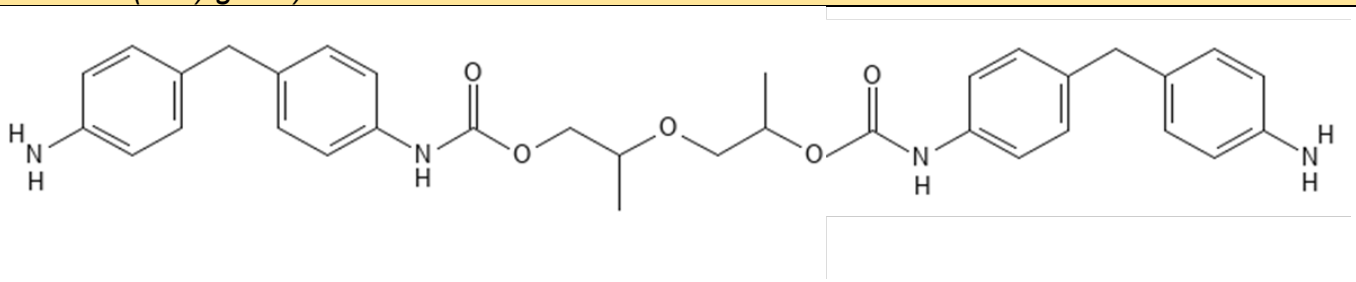
Table S1 – Nomenclature and structure of selected MDI monomers, homologues, and oligomers. Structures drawn by the authors with PubChem Sketcher V2.4.

DPG = di-propylene glycol; MDA = methylene dianiline; MDI = methylene diphenyl diisocyanate. Log K_{ow} (octanol-water partition coefficient) values: MDI monomers (measured by Yakabe, 1997); MDA monomers (measured by Macnab, 1999, Yakabe, 1997); MDI homologues and oligomers (calculated by Muuronen et al., 2018); MDA homologues and oligomers (estimated from the corresponding MDI homologues and oligomers by subtracting 1.5 units per NH_2-group). References included in main article or below.

Compound	Log K_{ow}	Structure
MDI monomers (MW = 250 g/mol)		
4,4'-MDI	4.5	
2,4'-MDI	4.5	

MDI homologues (MW = 250 + 131 x [number of rings - 2] g/mol)		
3-Ring MDI	7.3	
4-Ring MDI	9.6	
MDI oligomer (MW = 2 x 250 + MW diol (134) g/mol)		
MDI-DPG	10.4	

MDA monomers (MW = 198 g/mol)		
4,4'-MDA	1.55	
2,4'-MDA	1.8	
MDA homologues (MW = 198 + 105 x [number of rings – 2] g/mol)		
3-Ring MDA	ca 2.8	
4-Ring MDA	ca 3.6	

MDA oligomer (MW = 2 x 224 + MW diol (134) g/mol)		
MDA-DPG	ca 7.4	
MDI-based ureas (MW and log K_{ow}: see reference)		
Please refer to:	https://www.diisocyanates.org/sites/dii/files/visual_select_file/properties_of_mdi-_and_tdi-ureas_1.pdf	

Macnab, J. I. (1999). *Determination of physical properties of 4,4'-MDA*. International Isocyanate Institute. Available from: https://www.bl.uk/onlinegallery/ . Summary available at: https://www.diisocyanates.org/sites/dii/files/visual_select_file/phys-chem_amines.pdf .

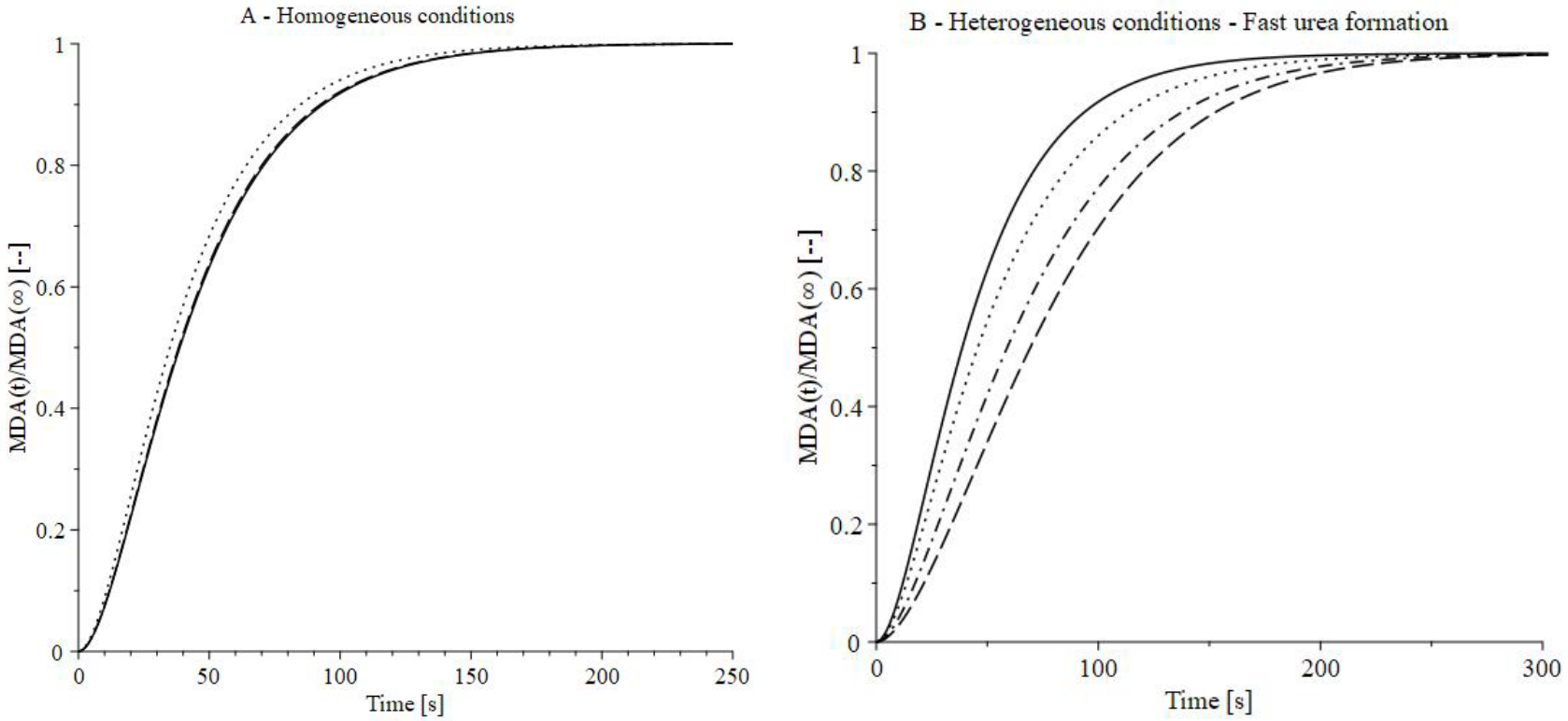


Figure S1A (left) – Ratio of MDA yield relative to ultimate MDA yield [MDA(∞)] as a function of time under hypothetical homogeneous conditions. Line types: solid = 1 µmol/L MDI concentration; dash = 10 µmol/L concentration; dot = 100 µmol/L concentration.

Figure S1B (right) - Ratio of MDA yield relative to ultimate MDA yield as a function of time under heterogeneous conditions and at the assumed MDI solubility of 1 µmol/L. Line types: solid = base case at assumed solubility limit (1 µmol/L); dot = 2 µmol/L loading; dash-dot = 5 µmol/L loading; dash = 10 µmol/L loading. "Fast" urea formation scenario.

Model substance: pure 4,4'-MDI. MDA = methylene dianiline; MDI = methylene diphenyl diisocyanate.

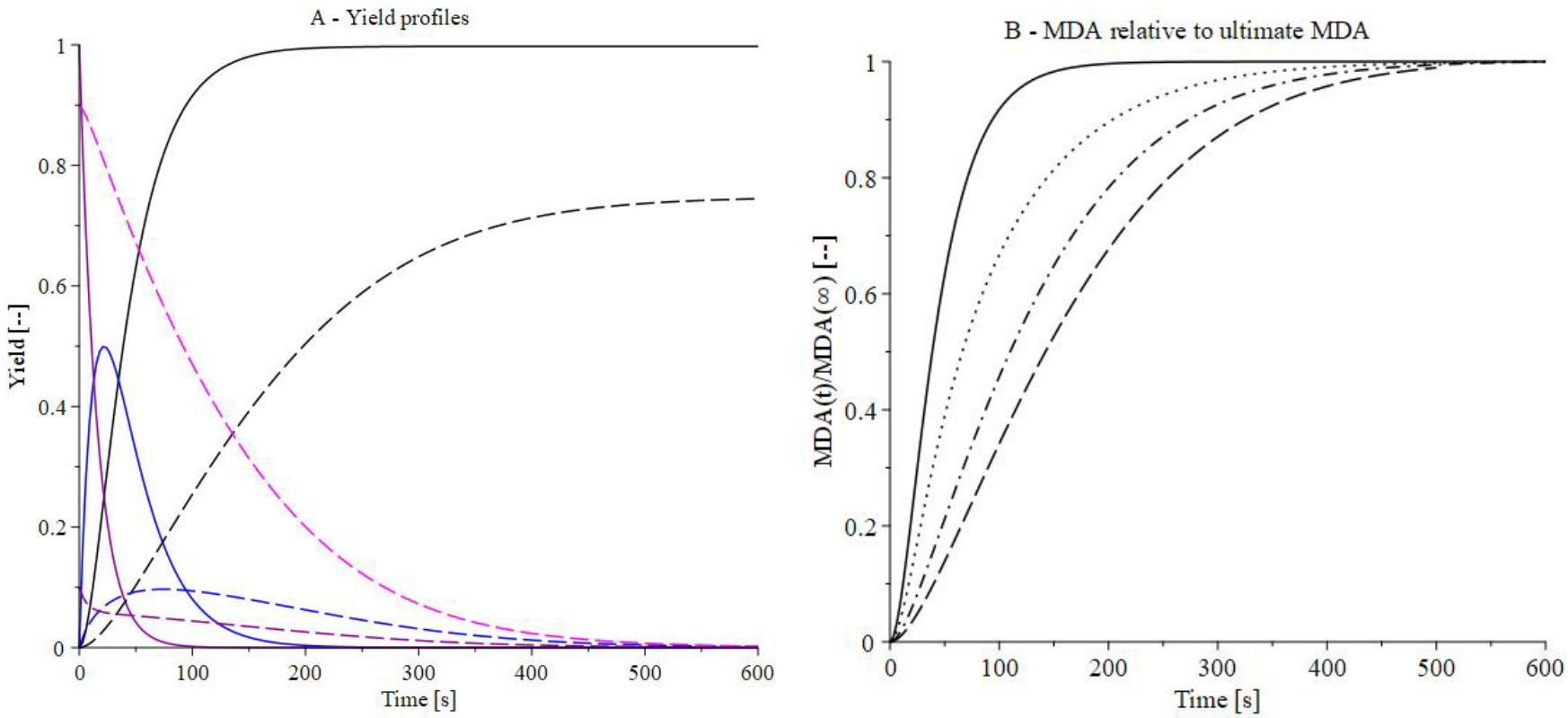


Figure S2A (left) - Hydrolysis yields as a function of time under heterogeneous conditions at 10 µmol/L (2.5 mg/L) and at the assumed MDI solubility of 1 µmol/L (0.25 mg/L).

Figure S2B (right) - Ratio of MDA yield relative to ultimate MDA yield [MDA(∞)] as a function of time under heterogeneous conditions and at the assumed MDI solubility of 1 µmol/L.

"Slow" urea formation scenario. Model substance: pure 4,4'-MDI. Line color: violet = MDI dissolved; magenta = MDI in solid phase; blue = MIA; black = MDA. Line types: solid = base case at assumed solubility limit (1 µmol/L); dot = 2 µmol/L loading; dash-dot = 5 µmol/L loading; dash = 10 µmol/L loading. MDA = methylene dianiline; MDI = methylene diphenyl diisocyanate; MIA = methylene diphenyl amino-isocyanate.

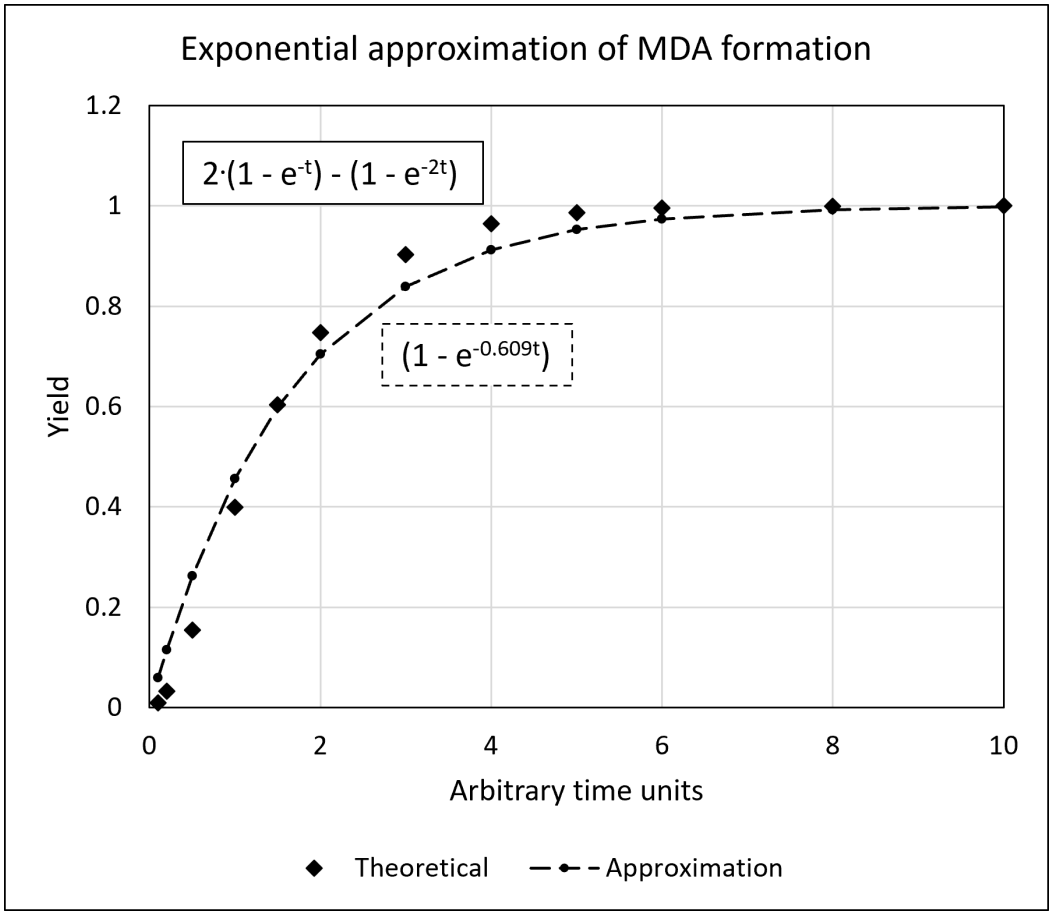


Figure S3 – Approximation of the MDA yield curve by a single exponential approach.

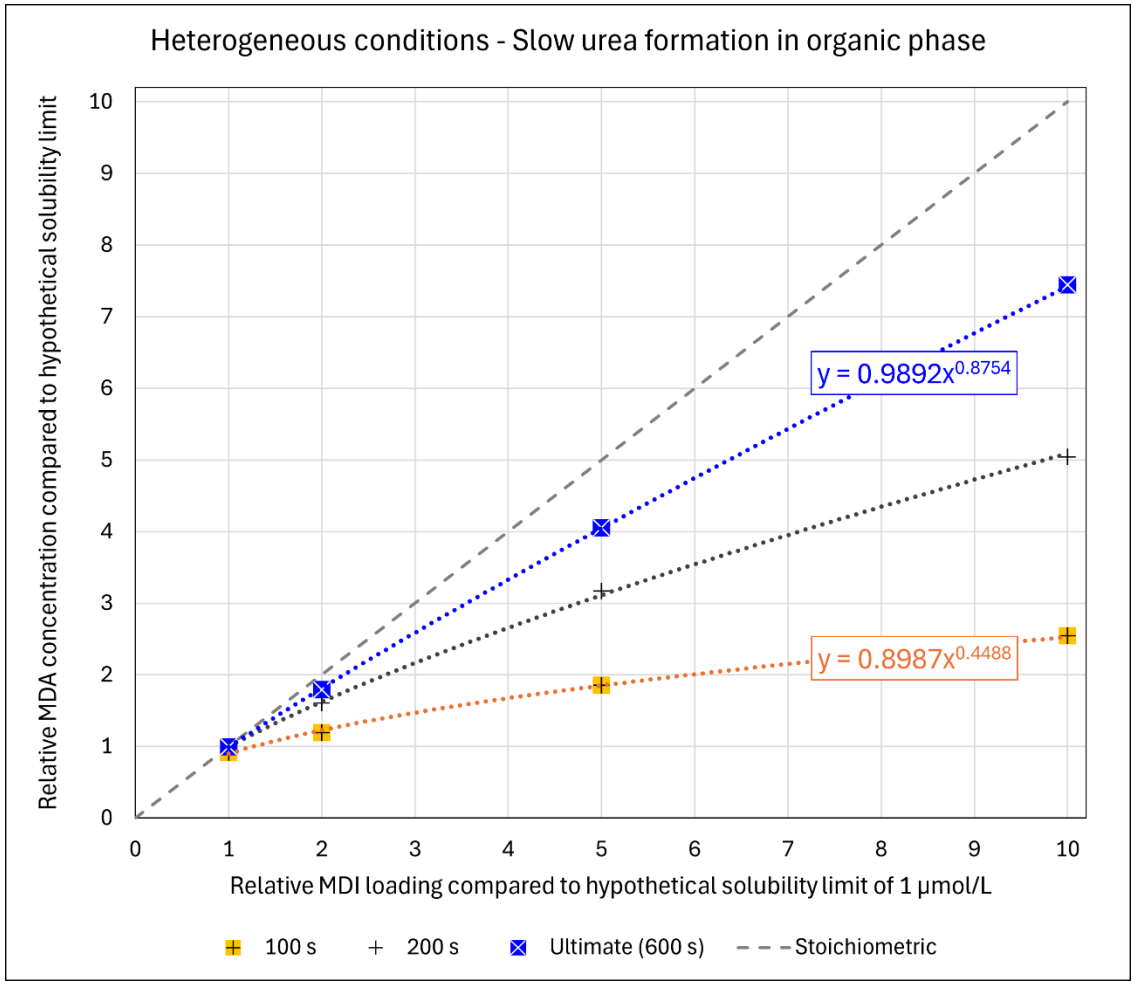


Figure S4 – Evolution of the MDA yield as a function of time and loading under heterogeneous conditions and the "slow" urea formation scenario.

Blue-filled markers indicate the ultimate yield achieved. The increasing ratio between the blue- and yellow-filled markers illustrates the gradual slowdown of MDA formation as loading exceeds the assumed solubility limit.