# Micro and Nanoplastics in wastewater – from sink to source

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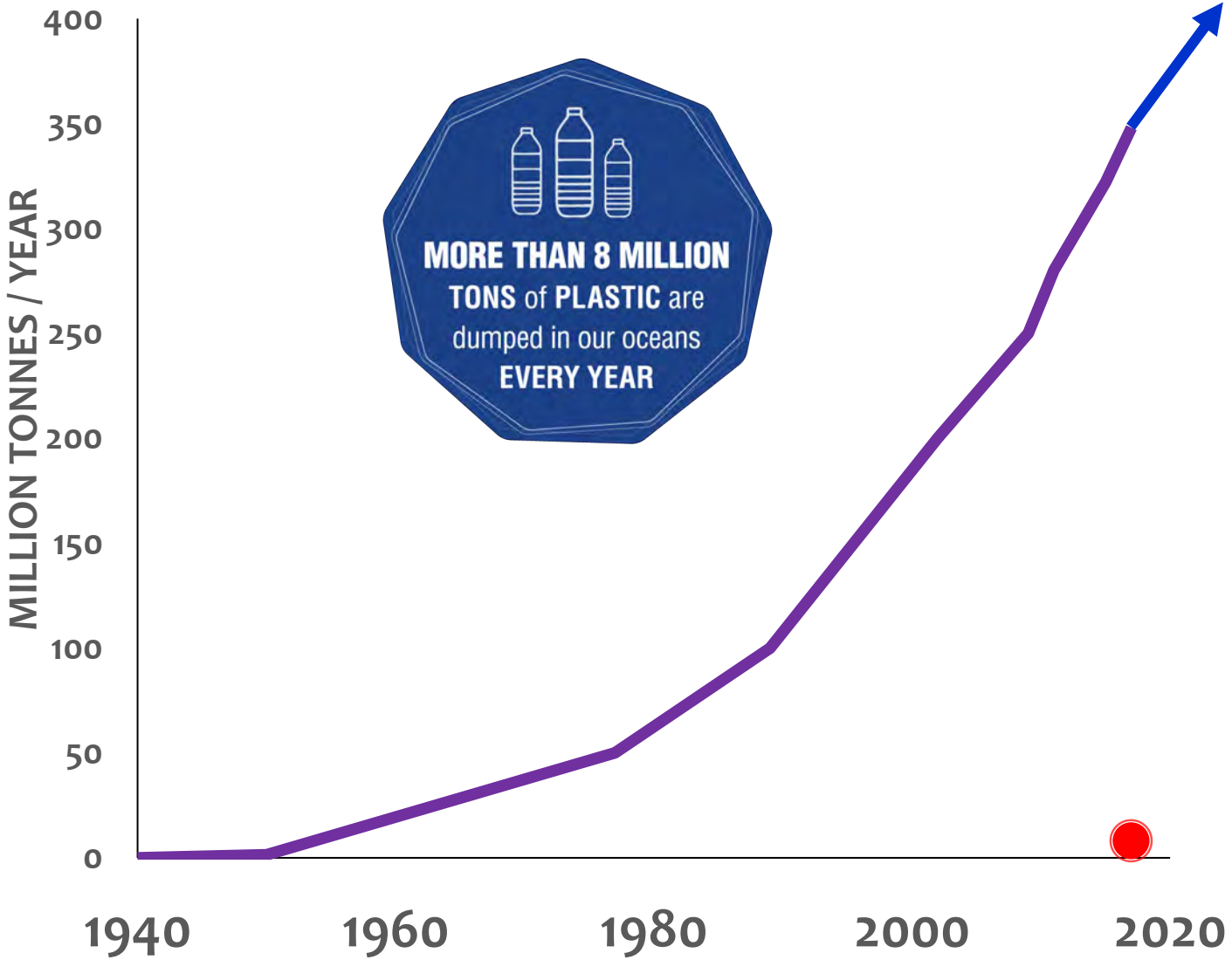
*Queensland Alliance for Environmental Health Sciences (QAEHS),*
*The University of Queensland*

HyTECH
ARC Training Centre

# Global plastics production

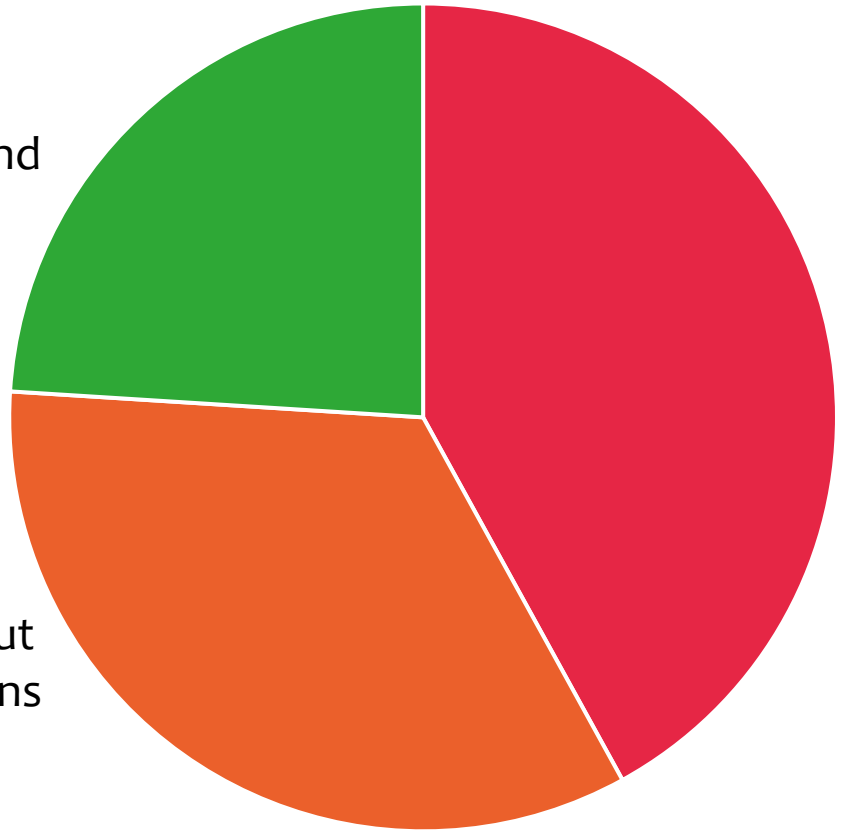




Bråte et al., 2017 MPB, 112, 105

Microplastics =
Tiny plastic pieces
< 5 mm

# How familiar are Aussies with the term “microplastics”?





*Preliminary data from collected questionnaire responses from a sample of the Australian population showing self-reported knowledge of microplastics.*



Burrows et al., In prep.

# Microplastic particles (MP) < 5mm

THE UNIVERSITY OF QUEENSLAND
AUSTRALIA

## Primary MP


## Secondary MP


# Why do we care about plastics?


- Biosolids
- Soil – croplands

Plastic fibres found in tap water around the world, study reveals

Exclusive: Tests show billions of people globally are drinking water contaminated by plastic particles, with 83% of samples found to be polluted

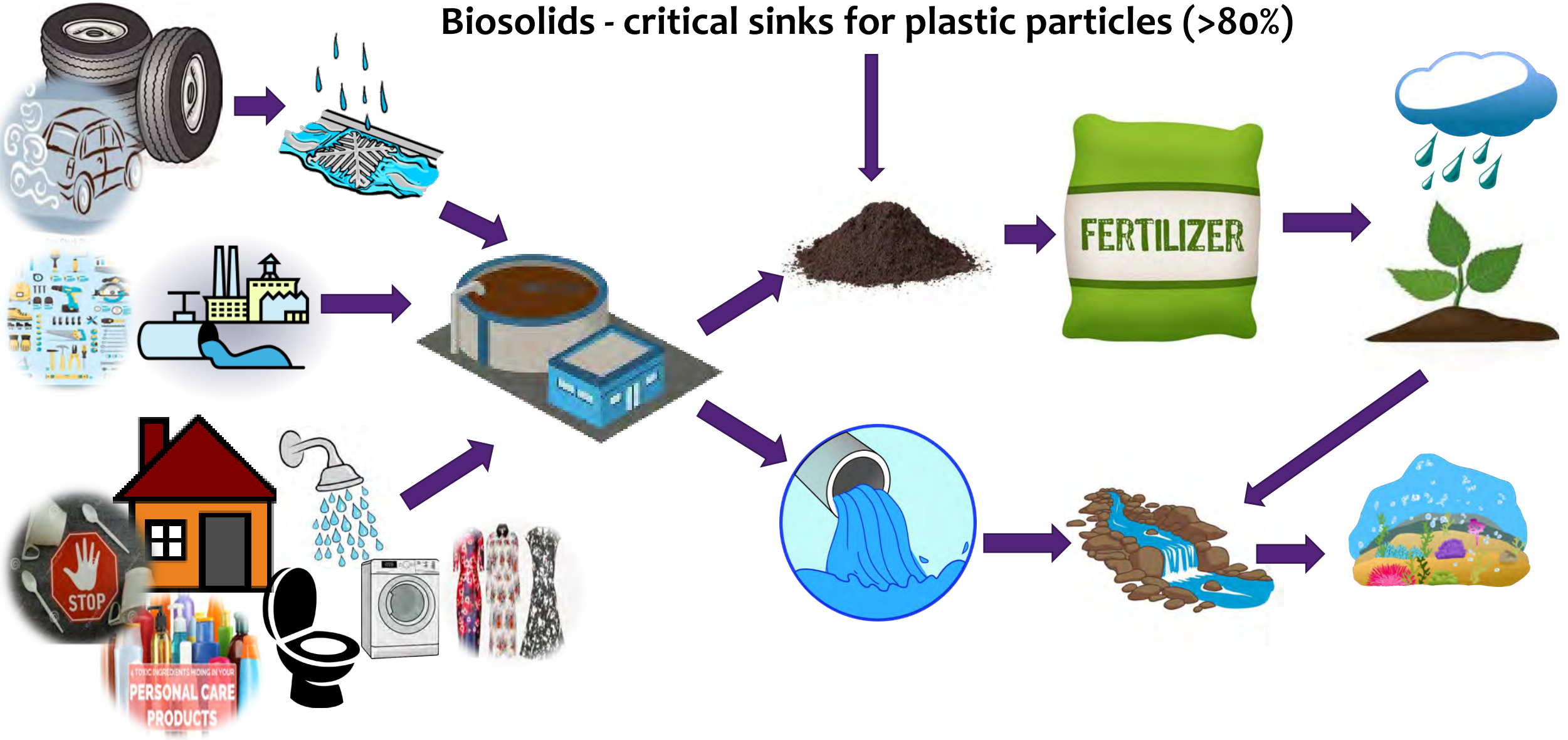
We are living on a plastic planet. What does it mean for our health?

▲ The average number of fibres found in each 500ml sample ranged from 4.8 in the US to 1.9 in Europe.

Okoffo et al., 2020. ES&T 54, 15556; Ribeiro et al., 2020 ES&T 54, 9408

# Plastics to WWTPs






Okoffo et al., 2019, ES:WR&T. 5, 1908-1931.

# Biosolids production and end-use in Australia?

- **349,000 tons in 2021**
- **83% beneficially used**
- **Around 70% for Agriculture**

❖ **Compares to:**

- Around 60% in USA and Canada are recycled via land application
- Around 50% in Europe **(NOT ALL COUNTRIES)** and China


AWA 2019; Nizzetto et al. 2016; Eurostat, 2016

https://civileats.com/2020/01/30/questions-remain-about-using-treated-sewage-on-farms/

Okoffo et al., 2020. ES&T 54, 15556

# Application of biosolids

- Beneficial – fertilizer/soil improver
- Sinks and pathway for plastics into the soil environment
- up to 430,000 Mt of plastics in soils- Europe and North America

https://civileats.com/2020/01/30/questions-remain-about-using-treated-sewage-on-farms/

# Common analytical options and analytical challenge

< 150 µm

Harmonizing detecting methodologies for micro and nanoplastics

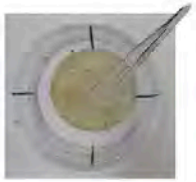
Microplastics analysis techniques

- Naked eye
- Optical microscopy

Simple, fast and easy

~ 50 µm

Individual particle picking



Time consuming

- FTIR
- Raman spectroscopy

Simple, efficient, non-destructive method

10 – 20 µm

- Pyrolysis- GCMS

Complex samples

Concentration per gram of tissue

Nanoplastics!

5

- ✓ Particle count, numbers, sizes, color, shape and not mass of plastics
- ✓ Sorting is operator dependent
- ✓ Size dependent (over or underestimations)
- ✓ Sample pre-treatment (time consuming)

5,000 µm

150 µm

50 µm

10 µm

1 µm

1 nm

Increasing challenge (uncertainty)

# Quantifying polymers

Pyrolysis-Gas Chromatography Mass Spectrometry

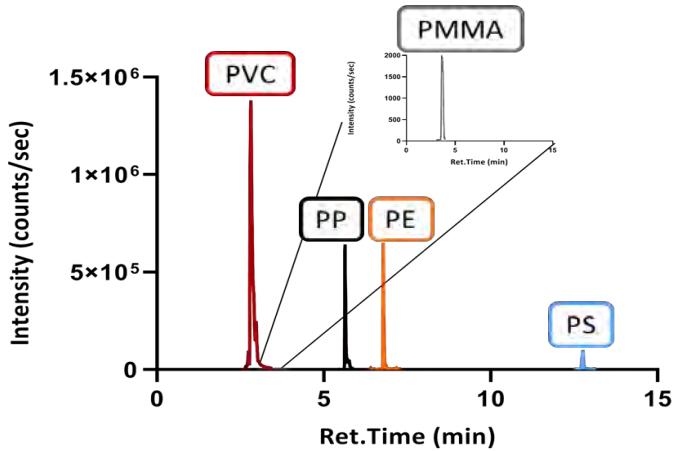
- Quantifies mass of plastics in the entire sample
- Plastic is ‘burnt’ at 650°C - breaks down into smaller molecules
- Specific ions of small molecules monitored
- Results reported as <u>total mass</u> of each plastic in a sample

**PE, PP, PET, Nylon 6, Nylon 66, PMMA, PC, PS, PVC, ABS, SBR, PU**


**Sample cup**



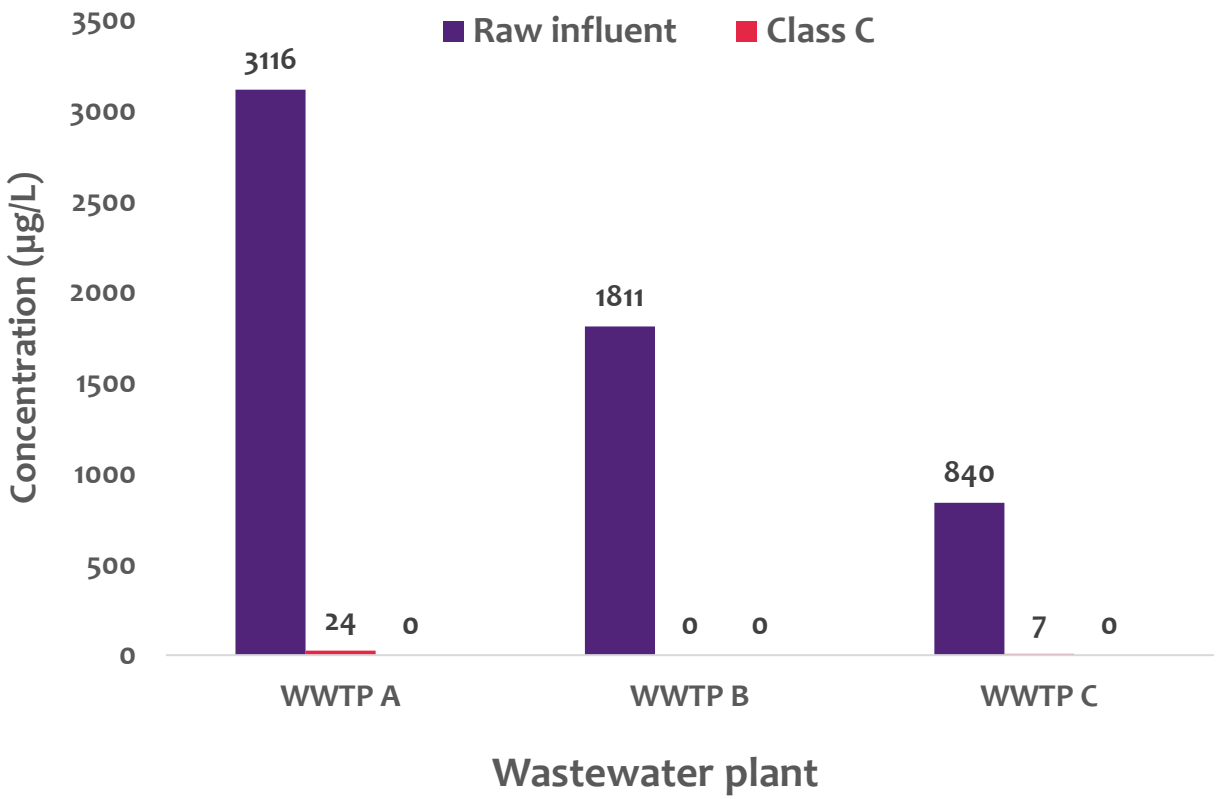
**Pyr-GCMS Analysis**




**ID and concentration of different polymers**

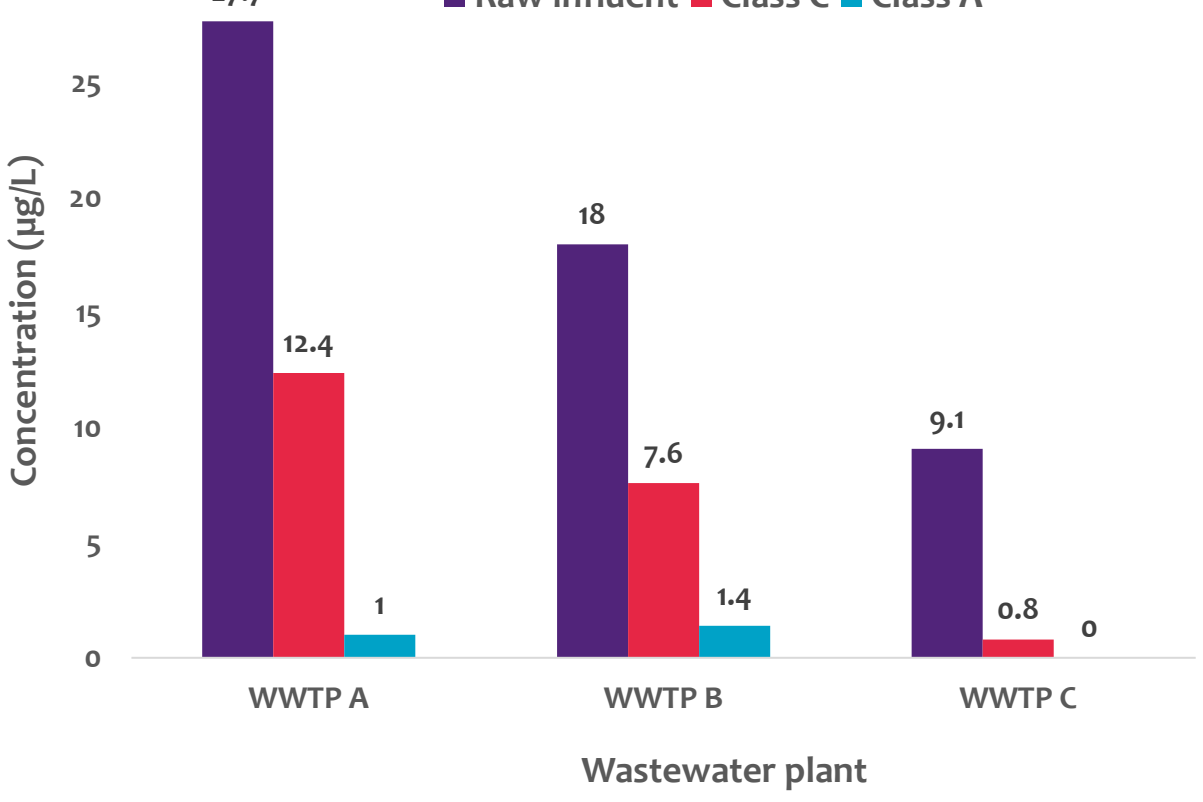
# MPs and NPs in Wastewater influent/effluent

A




**PE, PVC, PET, PP, PMMA**

B




**Nylon 66, PE, PP, PET, Nylon 6, PMMA, PC, PS**

Okoffo et al. 2023, 159251, STOTEN



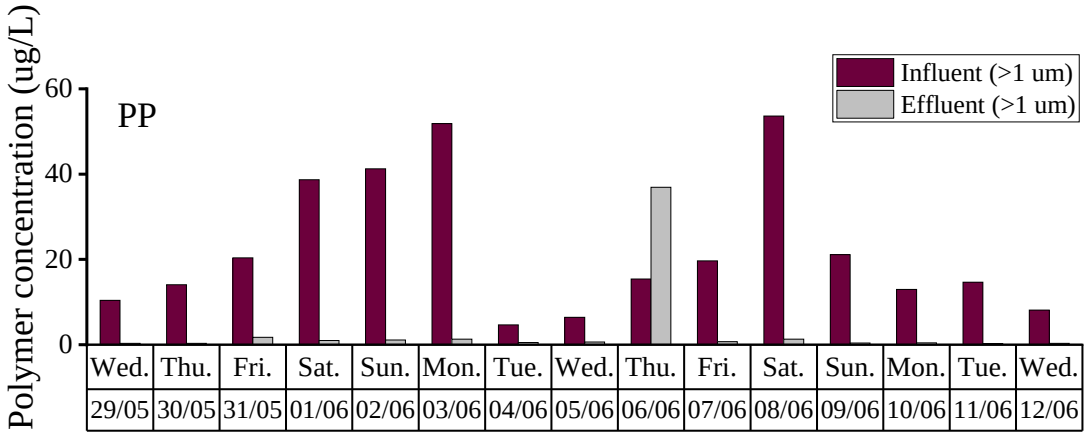
Okoffo et al. 2024

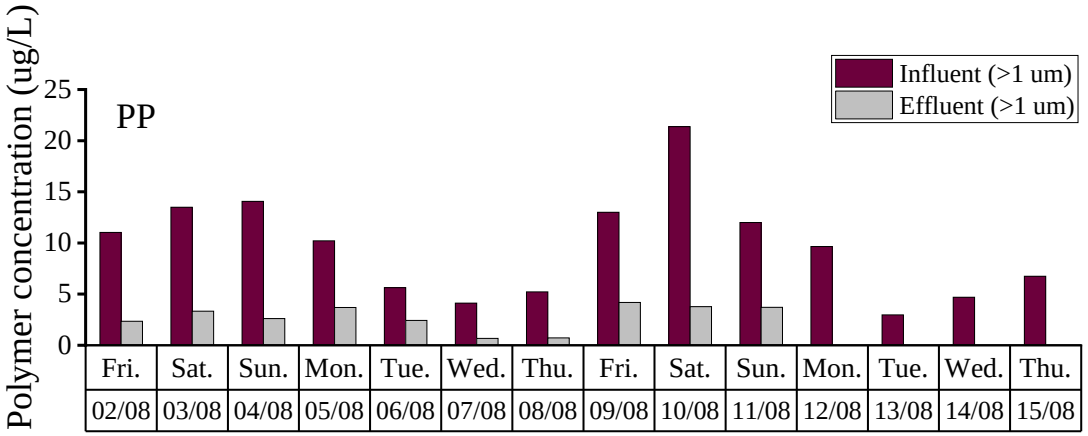
# PP

## WWTP (A)

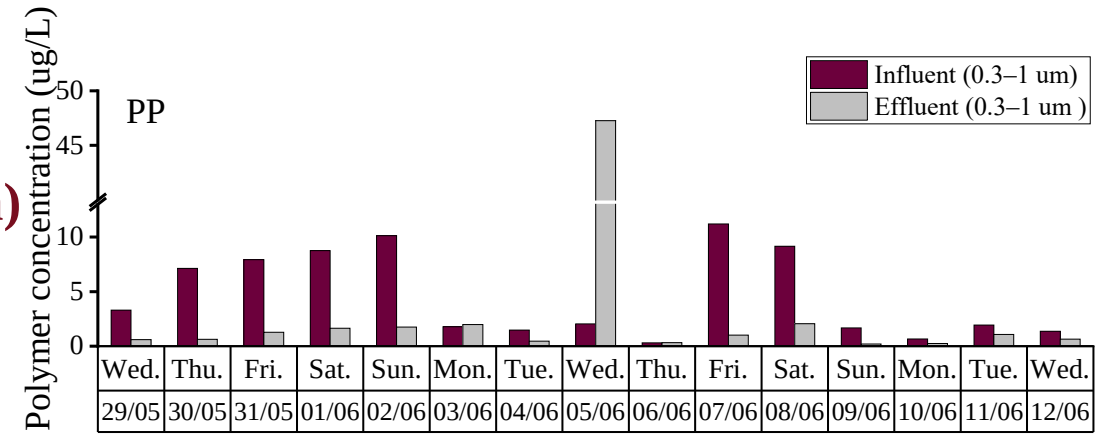
## WWTP (B)

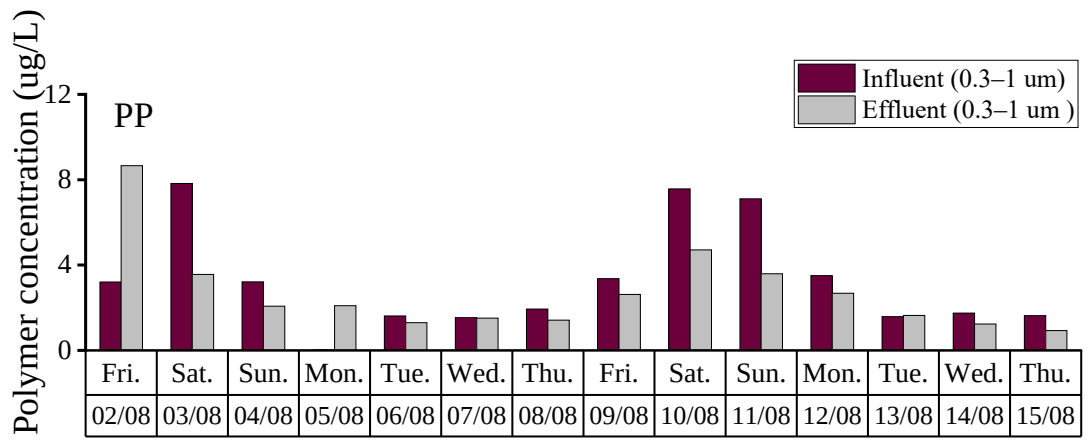
**(> 1µm)**




**(0.3–1µm)**





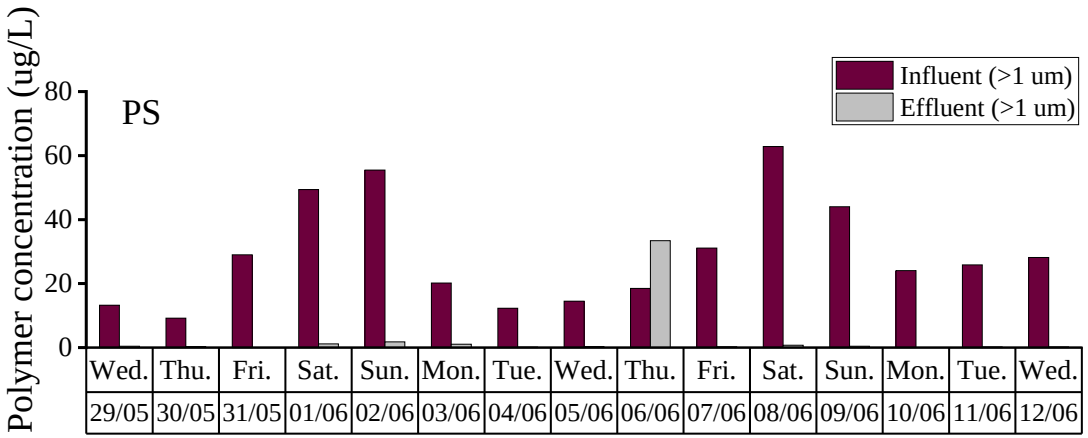

Okoffo et al., Unpublished

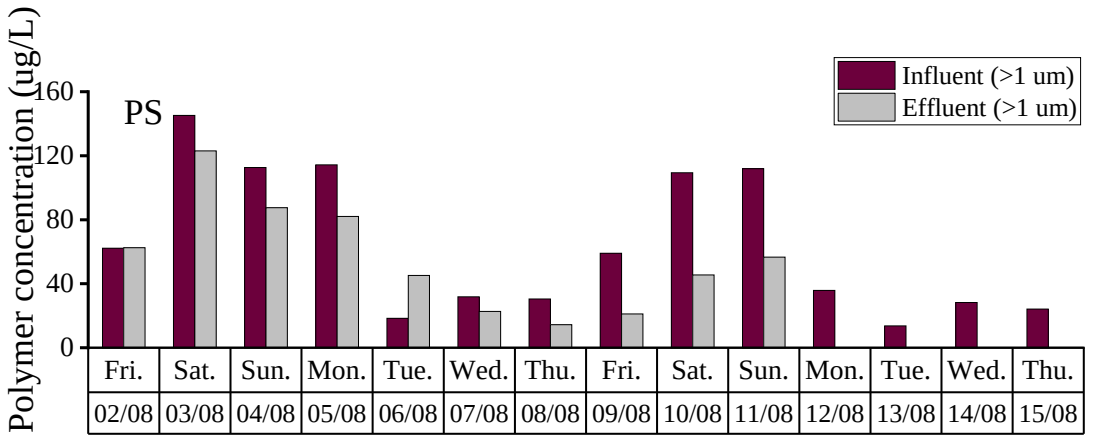
# PS

## WWTP (A)

## WWTP (B)

**(> 1µm)**

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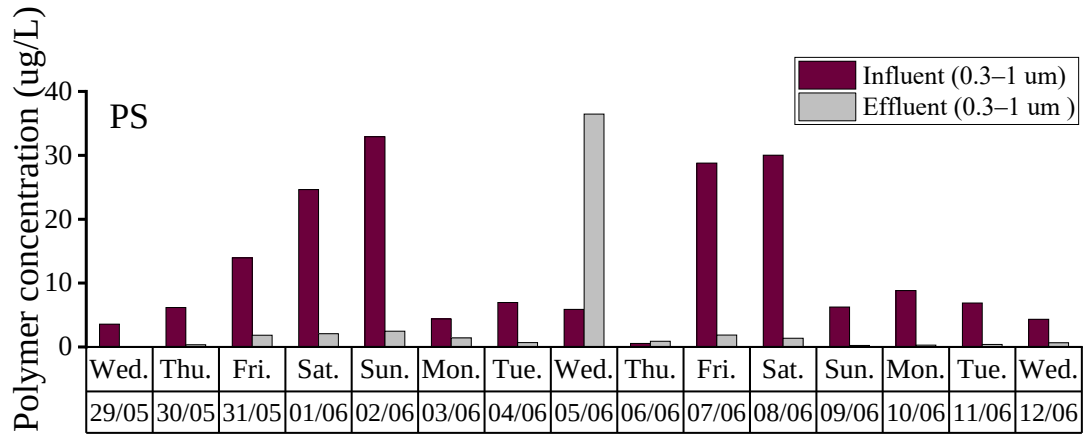
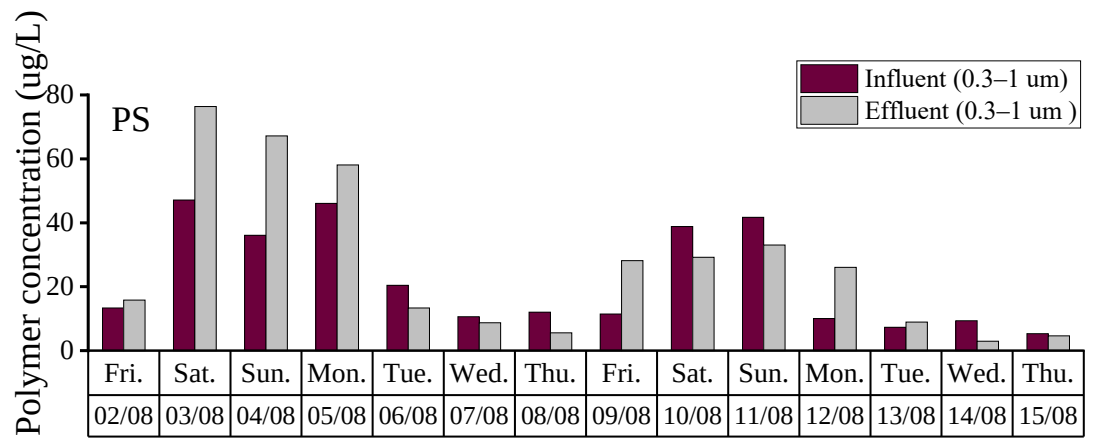


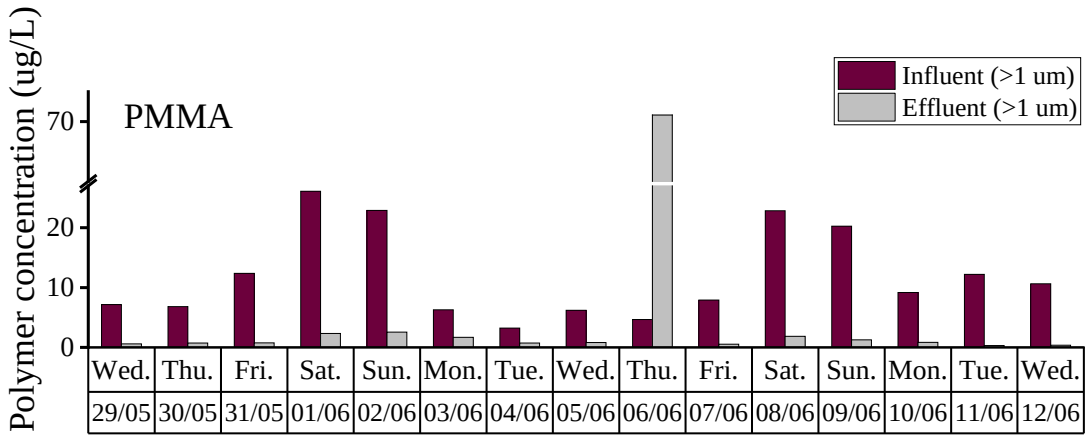

Okoffo et al., Unpublished

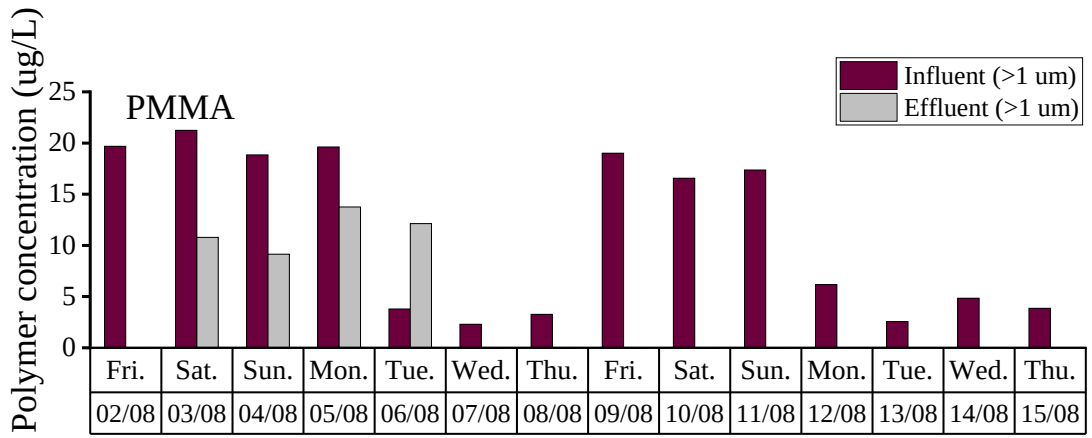
# PMMA

## WWTP (A)

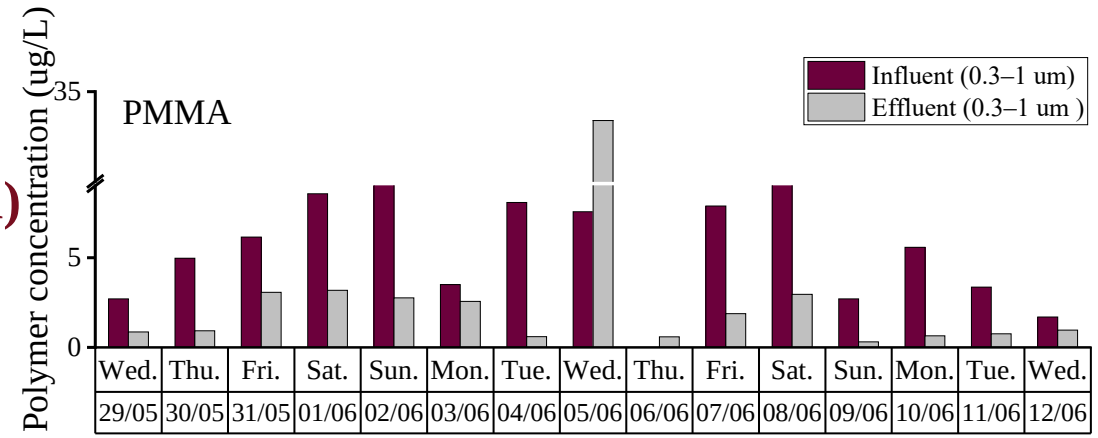
## WWTP (B)

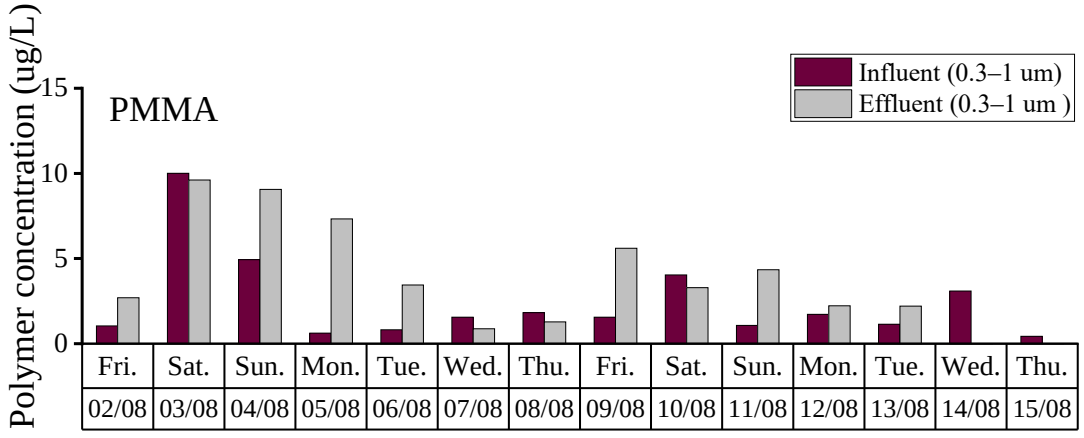
**(> 1µm)**




**(0.3–1µm)**



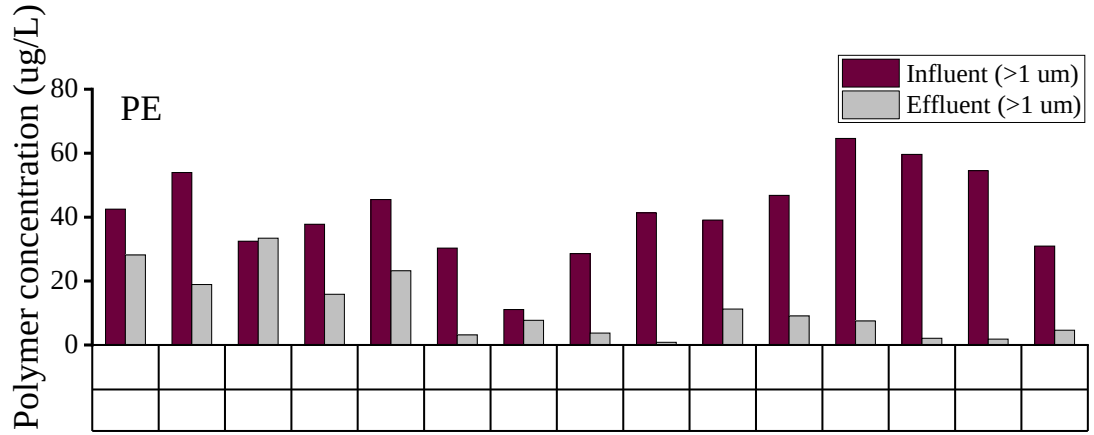

Okoffo et al., Unpublished

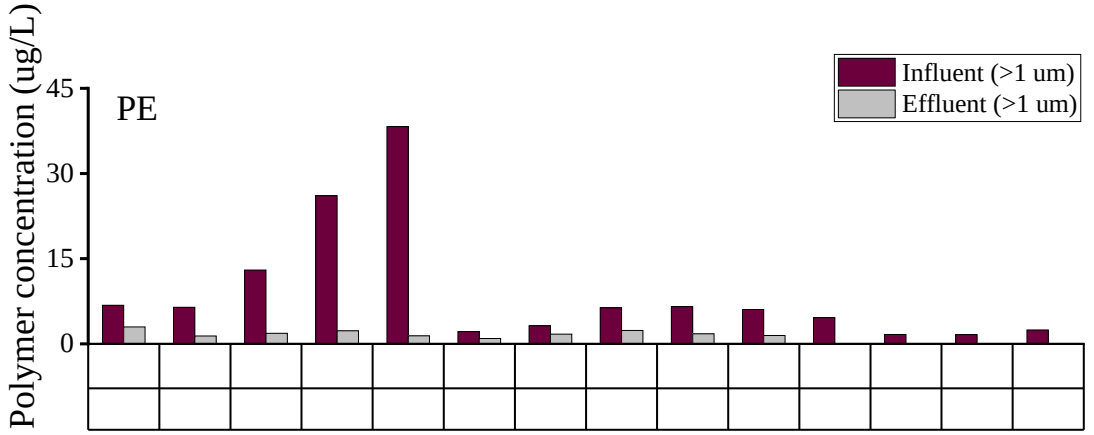
# PE

## WWTP (A)

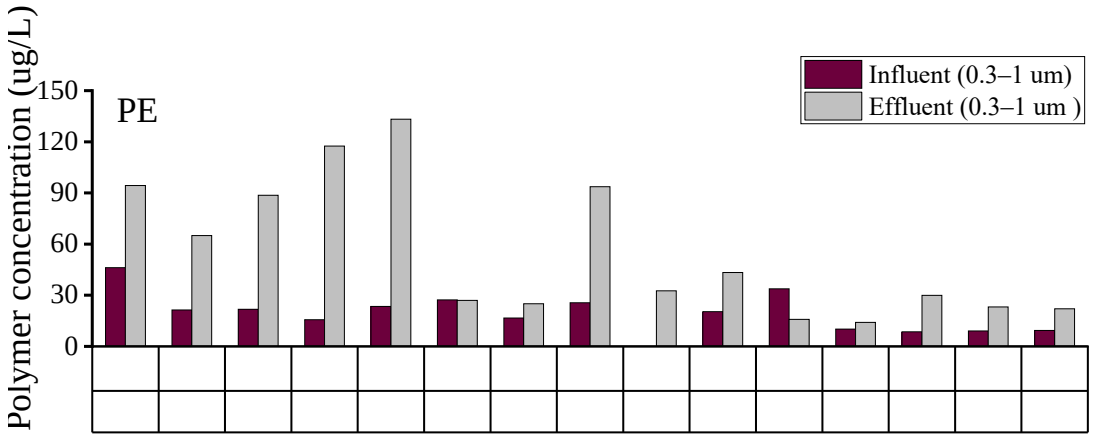
## WWTP (B)

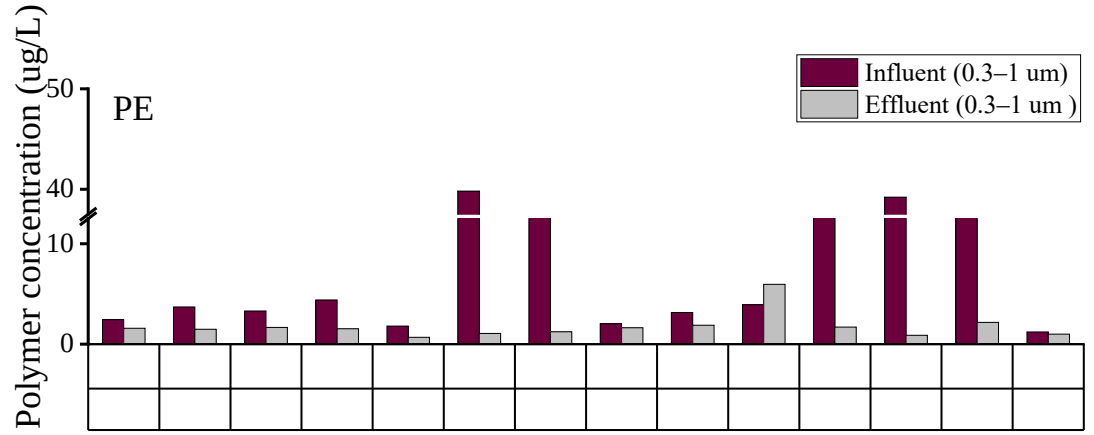
**(> 1µm)**




**(0.3–1µm)**

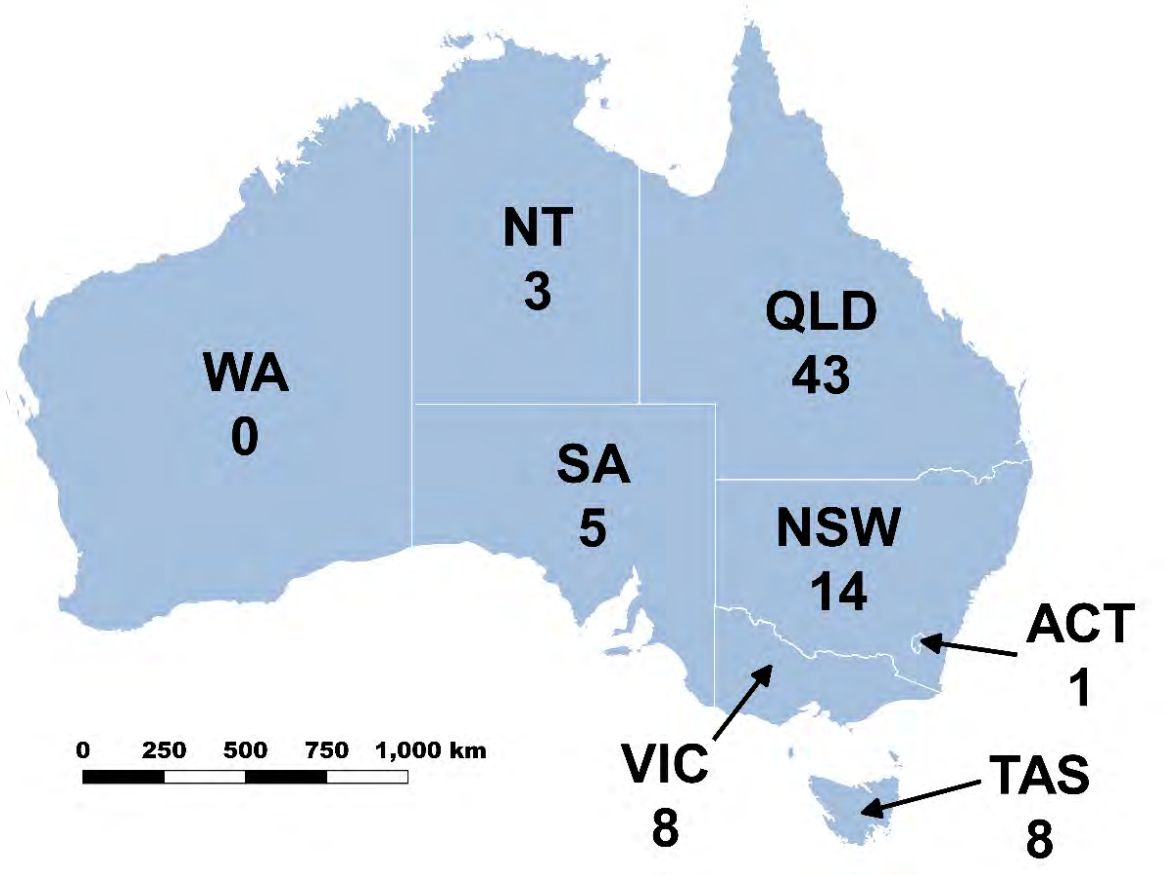



Okoffo et al., Unpublished

# Australian Biosolid samples

Australian Research Council Linkage Project (LP150100364)

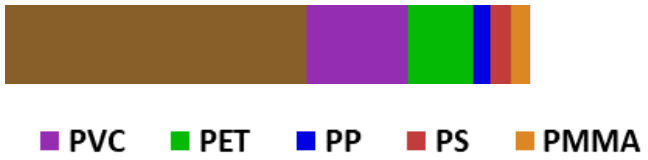


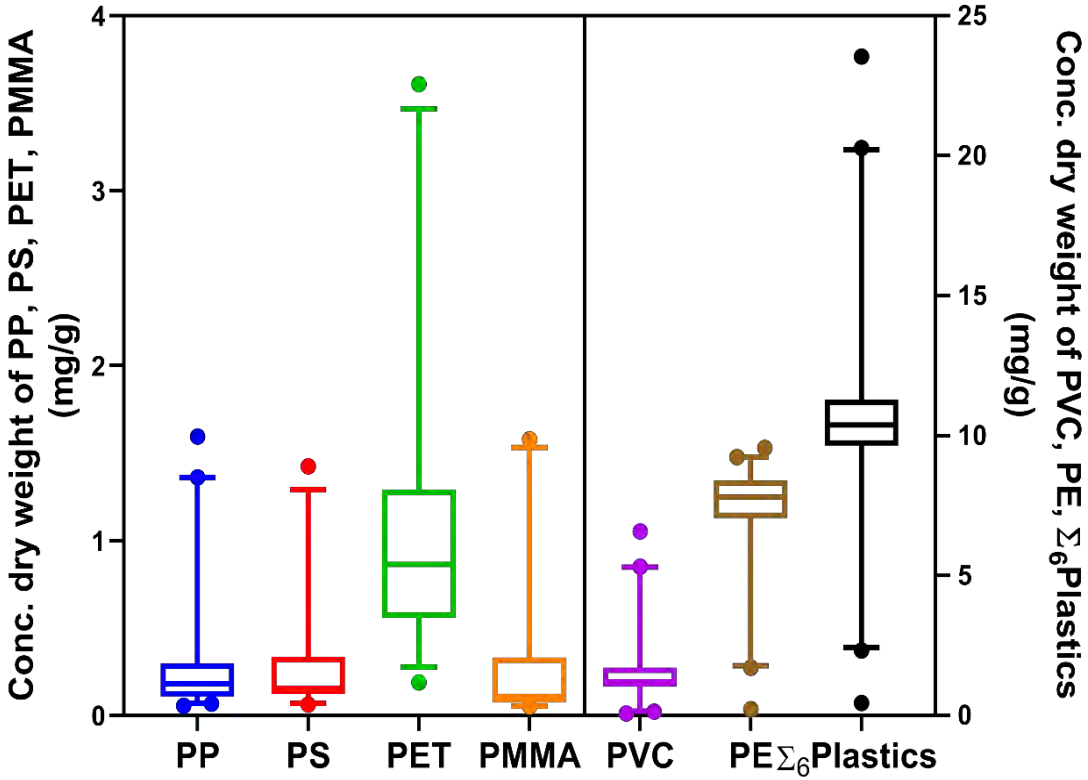

- Biosolids from 82 WWTPs (2016)
- 34% of the population during census week in 2016
- 7 plastics quantitatively analyzed
- Operators provided data for the 82 WWTPs

Okoffo et al., 2020. ES&T 54, 15556

# Plastics in Australian Biosolids

- Plastics detected in 99% of biosolids (81/82 sites)
- 6 plastics (PS, PP, PE, PVC, PMMA, PET) in all biosolids samples (0.4 and 23.5 mg/g dry weight ). PC was not detected
- PE predominant plastic (69%) by mass of Σ6Plastics, followed by PVC at 15% and PET at 9%.

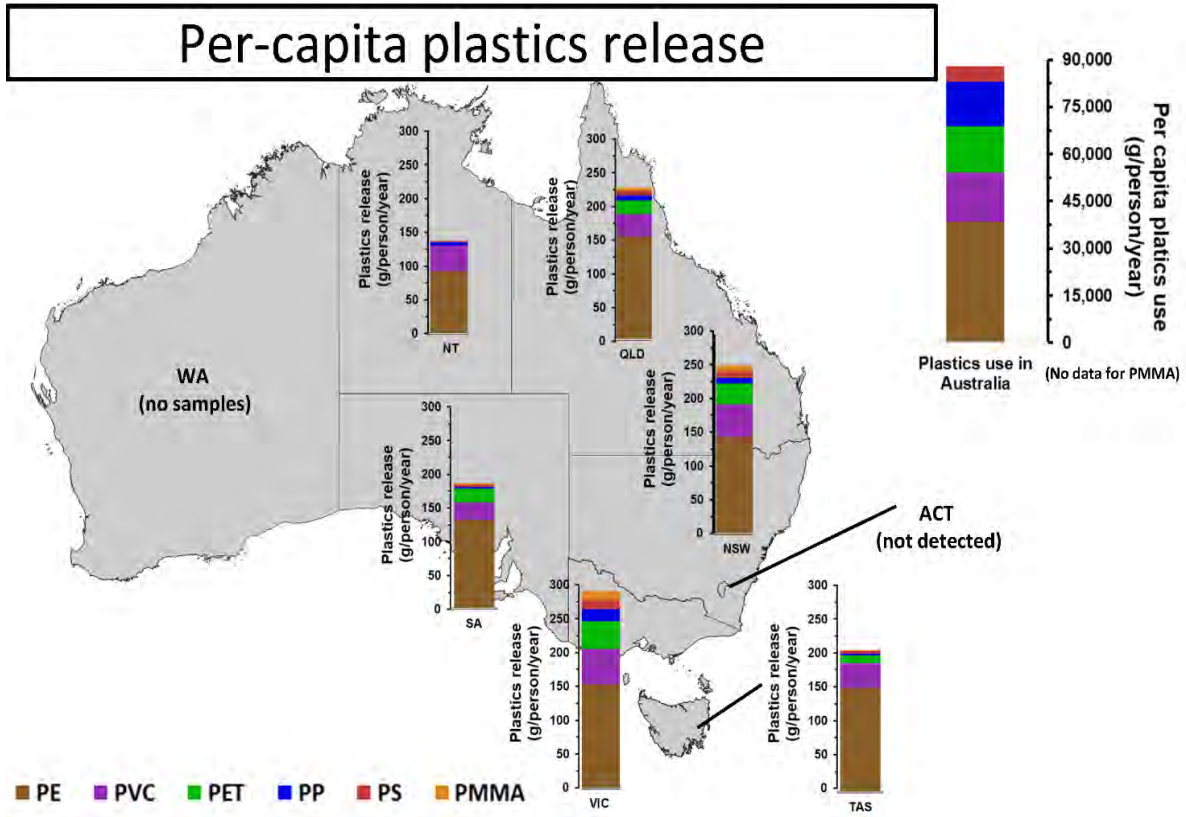



Okoffo et al., 2020. ES&T 54, 15556

# How much plastic do you release through sewage?

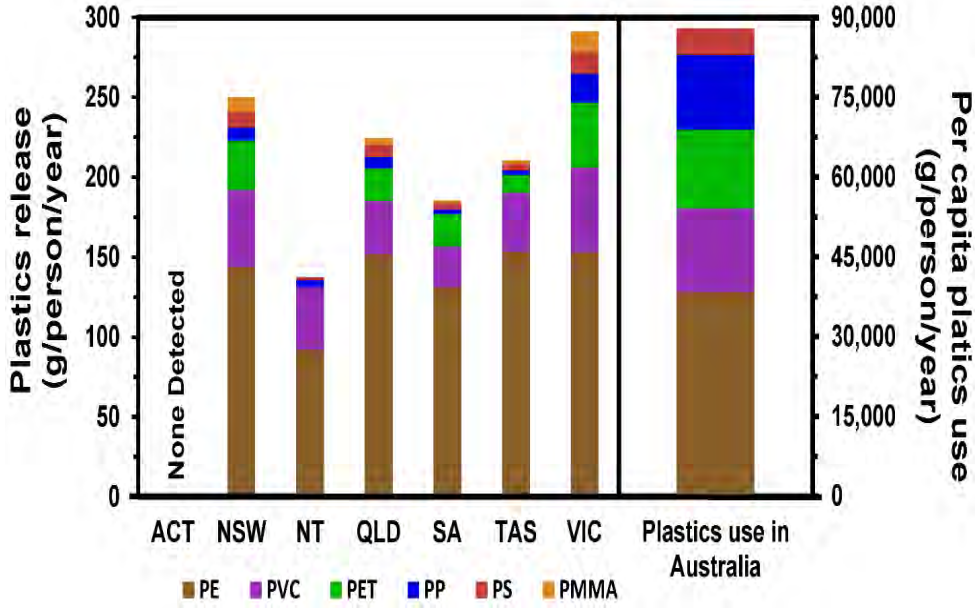
- Per-capita Σ6Plastics across sites were between 8 and 877 g/person/year!
- Mean 200 g/person/year
- PMMA & PET release corelates with socio-economic factors.



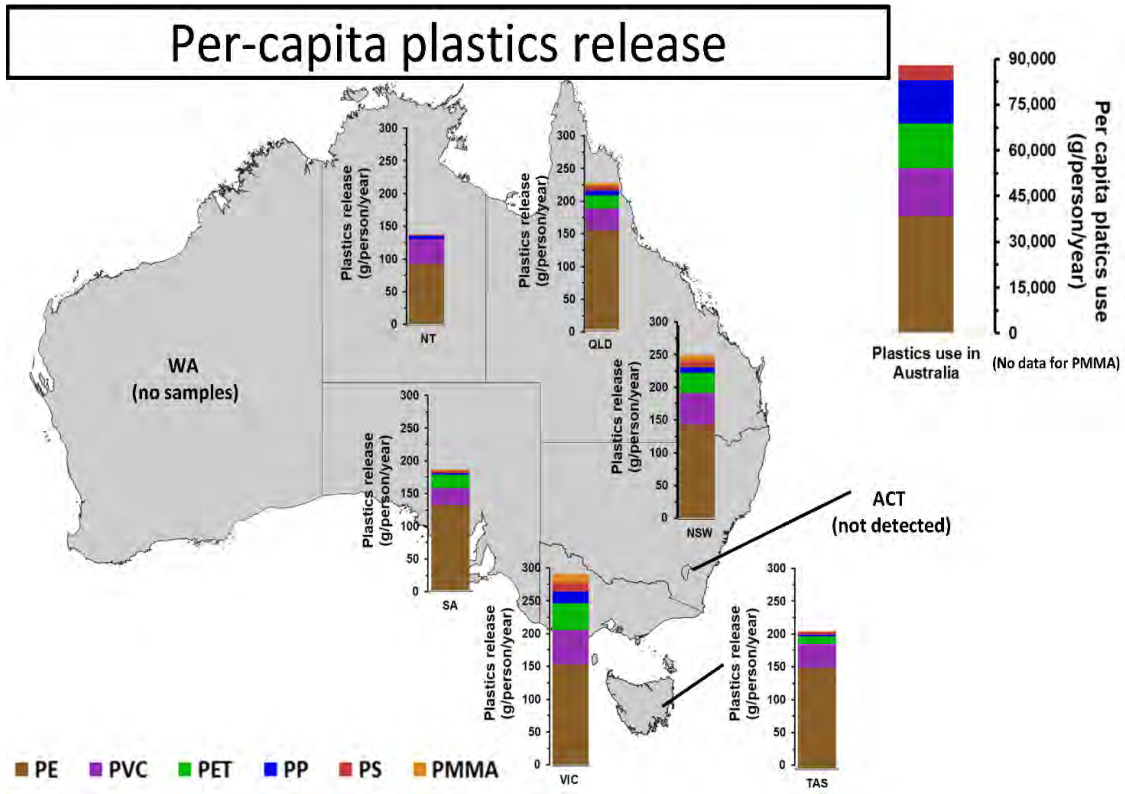

Okoffo et al., 2020, ES&T

# How much plastic do you release through sewage?

**A**




**B**




- Per-capita plastics released from WWTPs in Australian jurisdictions, compared to plastics consumption data in Australia for 2016/17

- No significant difference
  - per-capita mass loads and size of WWTP
  - states and territories
- No relationship % industrial area and per-capita loads

Okoffo et al., 2020. ES&T 54, 15556

# Emissions of plastics through Biosolids

**Table 1. Estimated Annual Emissions of Plastics through Biosolids End-Use Categories in Australia**[a]

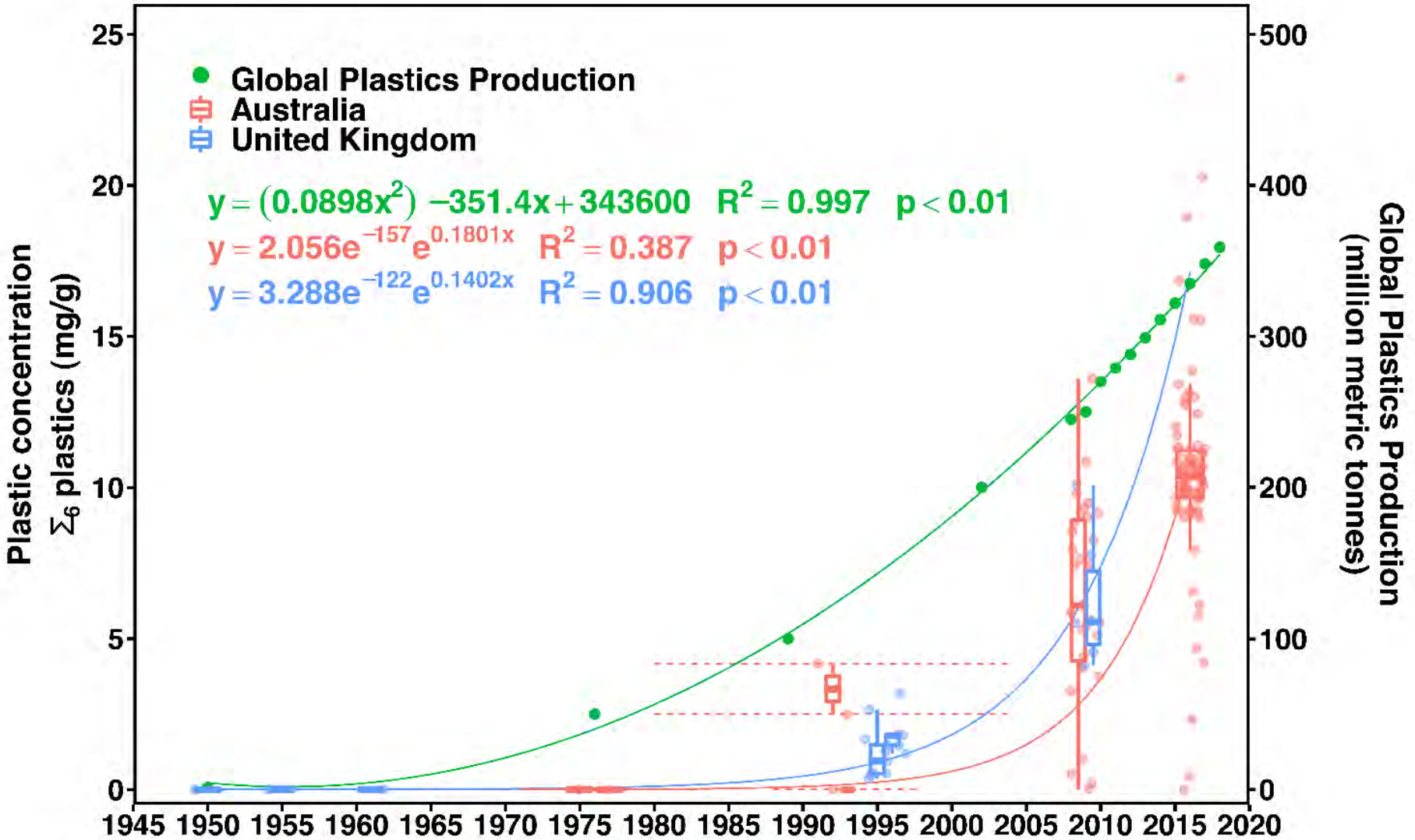
| | Mt/year | | | | | |
|---|---|---|---|---|---|---|
| plastics | agriculture | landfill | stockpile | composting | others | sum |
| biosolids end-use estimated for Australia | 349,900 | 2200 | 1900 | 13,000 | 76,300 | 443,000 |
| percentage (%) biosolids end-use for Australia | 78.9 | 0.5 | 0.4 | 3.0 | 17.2 | 100 |
| PP | 100 | 1 | 1 | 4 | 23 | 130 |
| PS | 100 | 1 | 1 | 4 | 22 | 130 |
| PET | 360 | 2 | 2 | 13 | 80 | 460 |
| PVC | 540 | 3 | 3 | 20 | 120 | 680 |
| PMMA | 120 | 1 | 1 | 4 | 25 | 150 |
| PE | 2580 | 17 | 15 | 100 | 570 | 3200 |
| $\Sigma_6$plastics | 3700 | 24 | 21 | 140 | 810 | 4700 |

[a]PP: polypropylene, PS: polystyrene, PET: polyethylene terephthalate, PMMA: poly-(methyl methacrylate), PVC: polyvinyl chloride, PE: polyethylene and $\Sigma_6$plastics: the total quantified plastic across all sites, other includes: biosolids sent for further processing (external contractor/company), mine rehabilitation, and landfill rehabilitation.

- Equating to approximately 200 g/person/year in Australia
- Represents 0.13% of total plastics use in Australia

Okoffo et al., 2020. ES&T 54, 15556

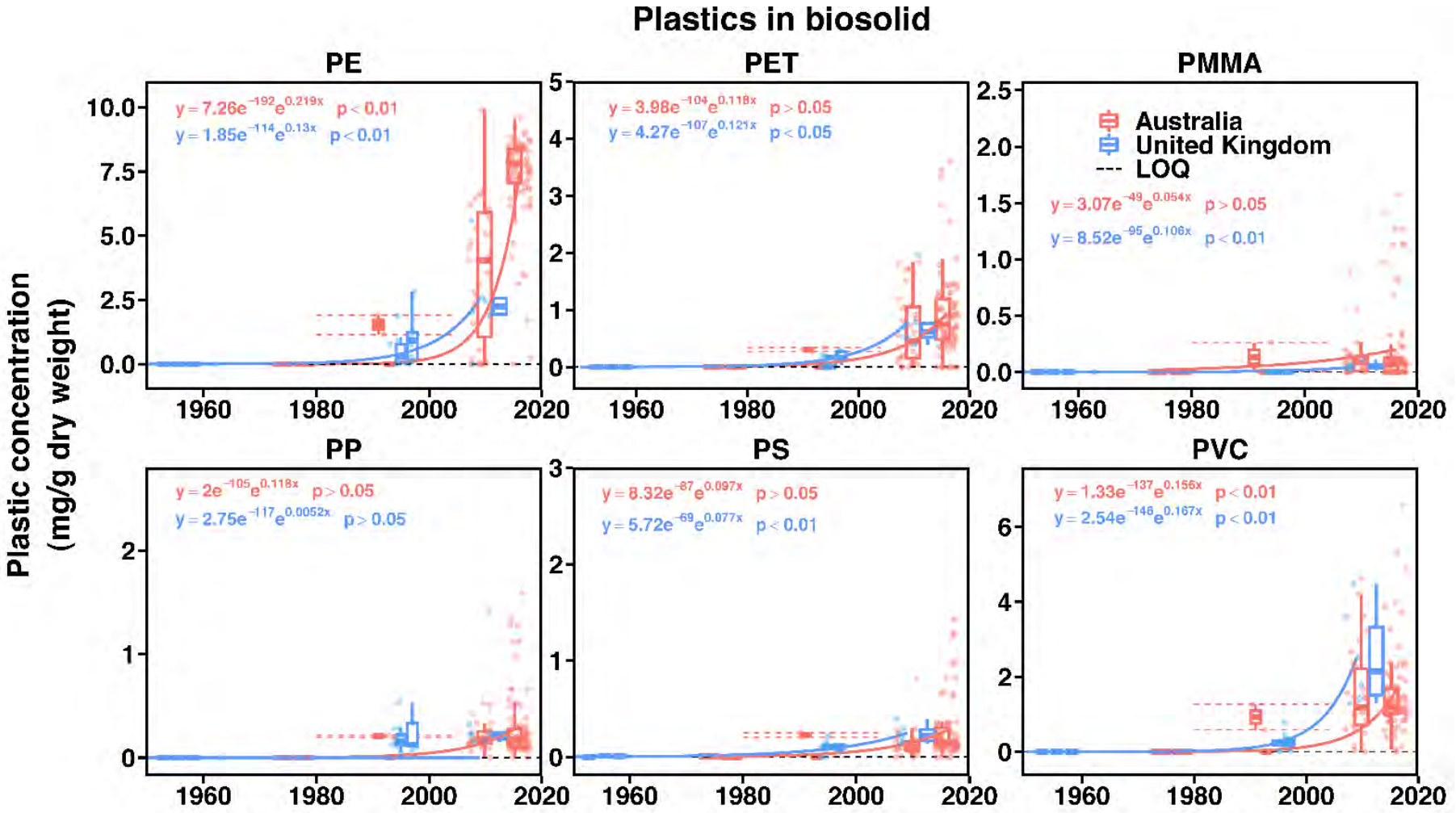
# Biosolids: Plastics in archived samples from 1950 to 2016




- ✓ Concentrations of plastics closely correlate with production and consumption

Okoffo et al. (2021) Wat Res 201, 117367

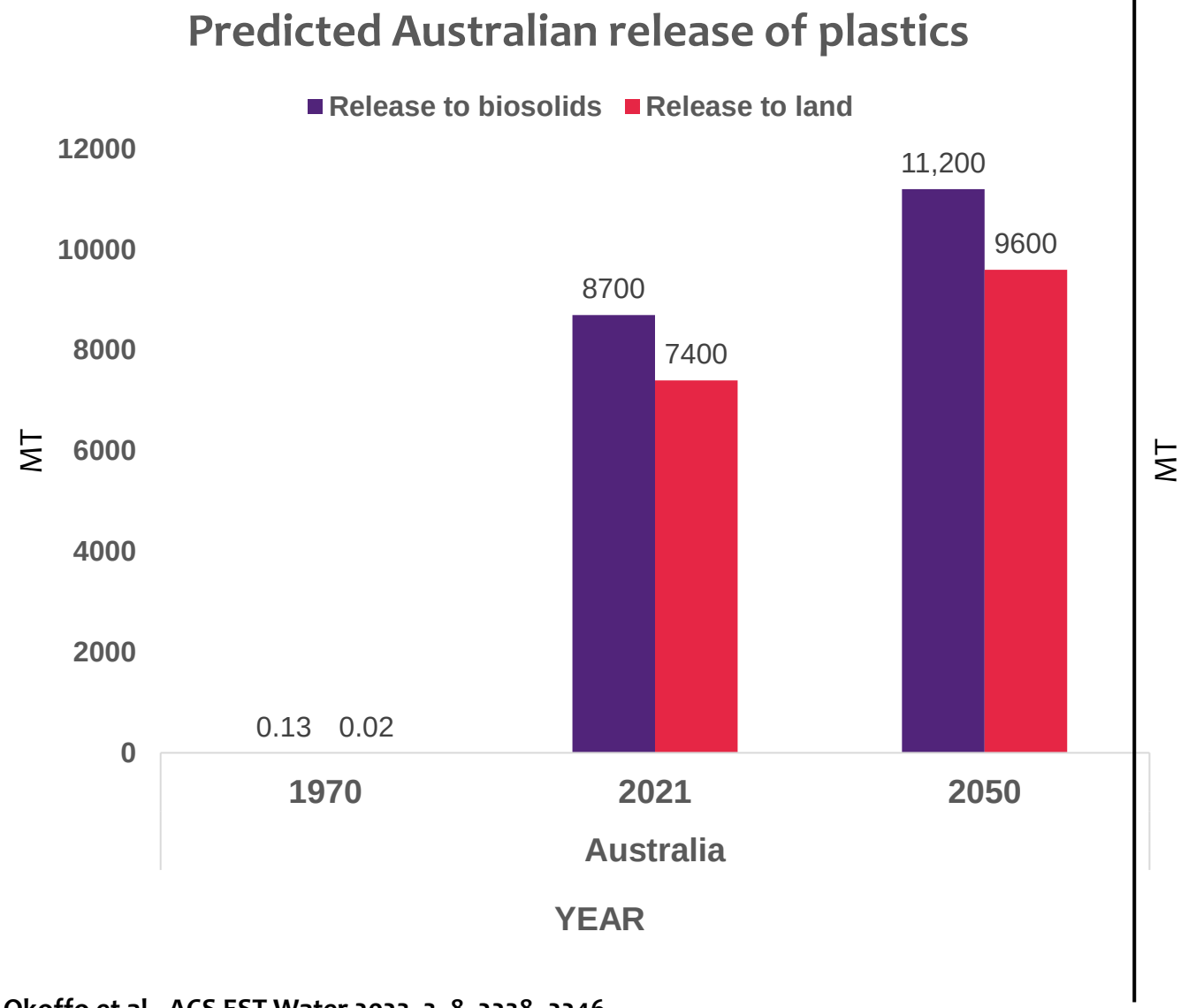
# Increase in specific plastics- what happened in the 90's?

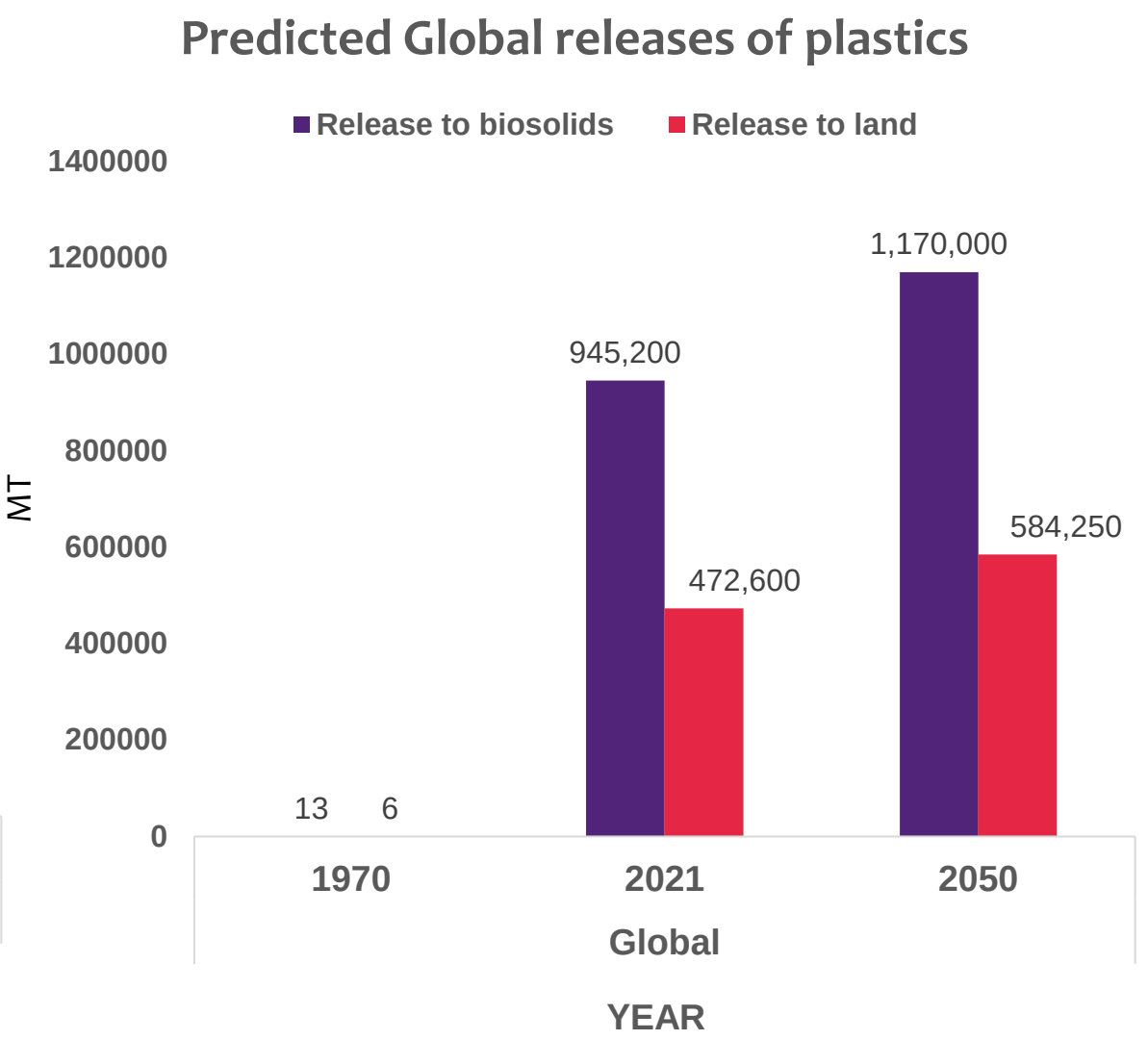



- ✓ Prior to the 1990s, leakage of plastics into biosolids was limited except for PS.
- ✓ Leakage from 1990s driven by increased production and consumption of PE, PET, PVC.

Okoffo et al. (2021) Wat Res 201, 117367

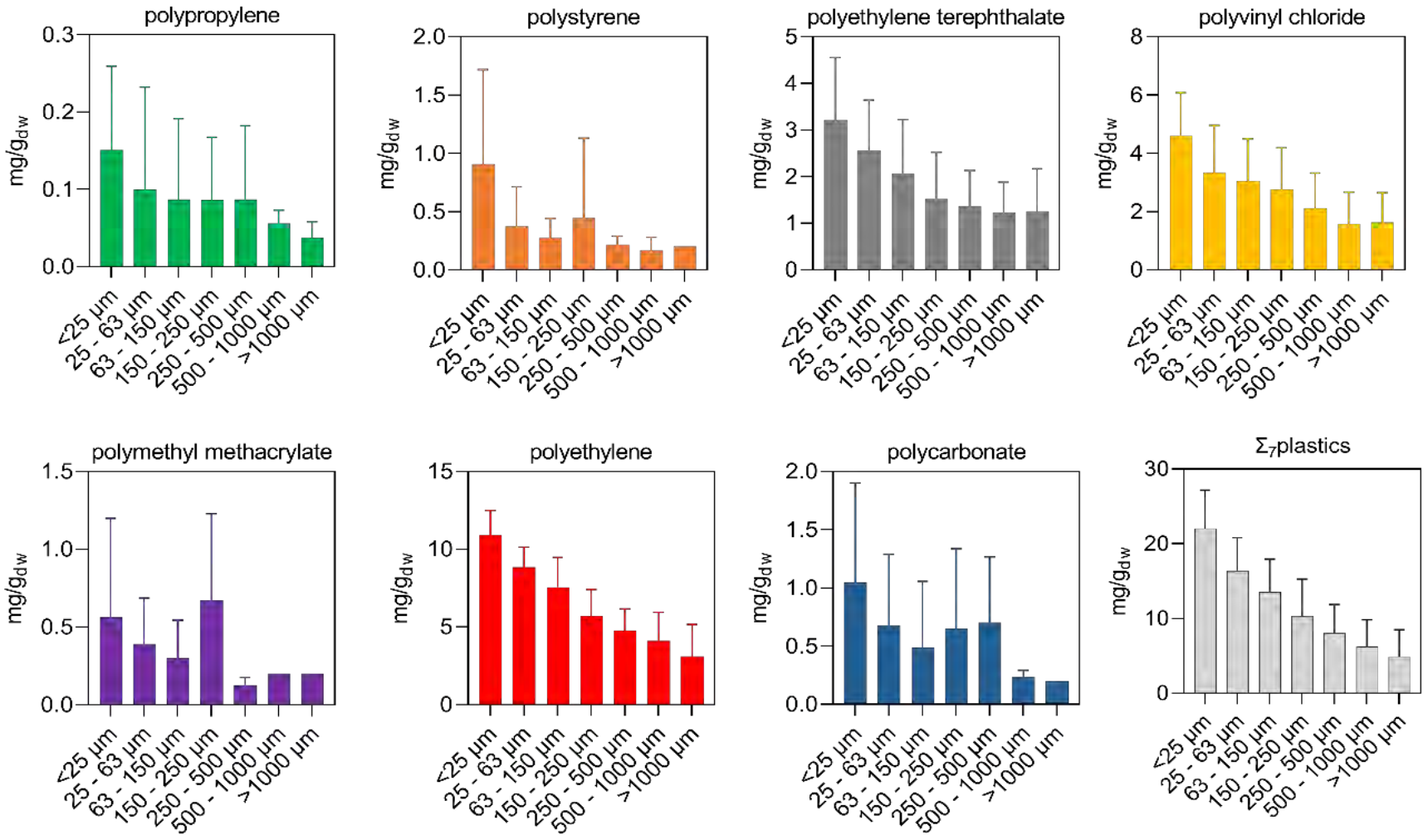
# Predicted release of plastics to Australian/Global biosolids and land (1970-2050)




Okoffo et al., ACS EST Water 2023, 3, 8, 2238–2246

# Size fractionated biosolids samples




Okoffo et al., STOTEN

# Micro-bioplastics in wastewater and biosolids

Table 6. Concentration of Micro-Bioplastics in Several Environmental Samples (mg/g for Solids and mg/L for Aqueous Samples)[a]

| samples | PLA | PBAT |
|---|---|---|
| wastewater influent A[b] | 0.15 | 0.07 |
| wastewater influent B[b] | 0.09 | <0.03 |
| wastewater influent C[b] | <MDL | <0.03 |
| biosolids A | 0.13 | <MDL |
| biosolids B | 0.09 | 0.09 |
| biosolids C | 0.18 | 0.10 |
| marine sediment A | <MDL | <MDL |
| marine sediment B | 0.09 | <0.03 |
| marine sediment C | 0.10 | <MDL |
| drinking water | <MDL | <MDL |
| reservoir water | <MDL | <MDL |
| stormwater | <MDL | <MDL |
| road dust A | <MDL | <MDL |
| road dust B | <MDL | <MDL |

**Polylactic acid (PLA)**

**Polybutylene adipate terephthalate (PBAT)**

Okoffo et al., EST

# What next?

- Biosolids treatment – post WWTPs treatment but pre-land application

  Pyrolysis; Gasification; Incinerating of biosolids?

- How does this source compare to other agriculture plastic uses/sources;

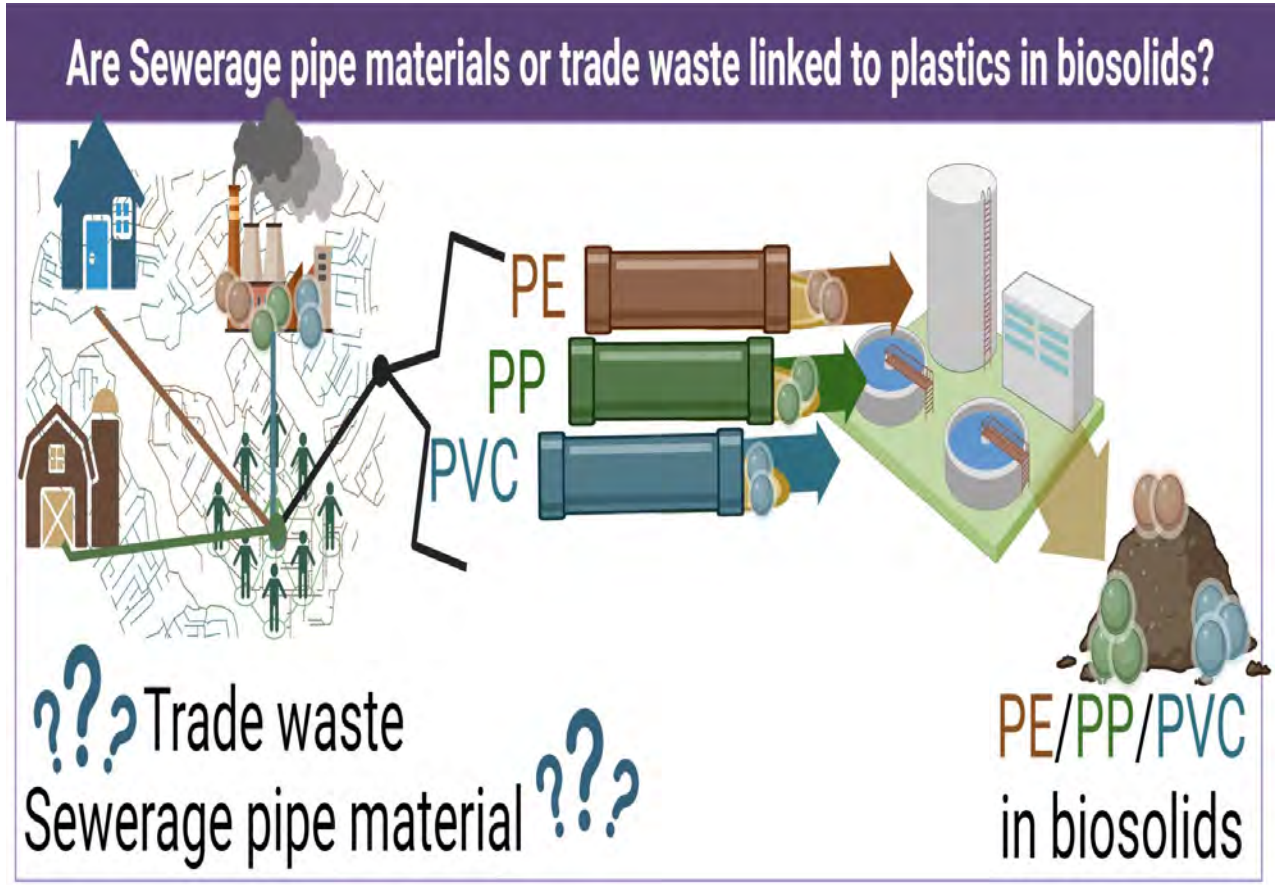
  Compost? Mulch films? Fertilizers?

- Plastic removal technologies?
- Source tracking and control (started)
- Fate of plastics within WWTPs - mass balance; size distribution? (Started at 3 QLD plants)
- Application to land and its impacts?

# Source tracking of plastics to wastewater

- Domestic sources/Household wastewater
  - personal care products, washing machine wastewater (laundering synthetic clothing), **dishwasher**
- PVC pipes in sewer networks
- Industrial wastewater/trade waste sources
- Landfill sites
- Deposition (shower, sinks, toilets)
- Stormwater sources??
- **Controlling the source of all plastics**

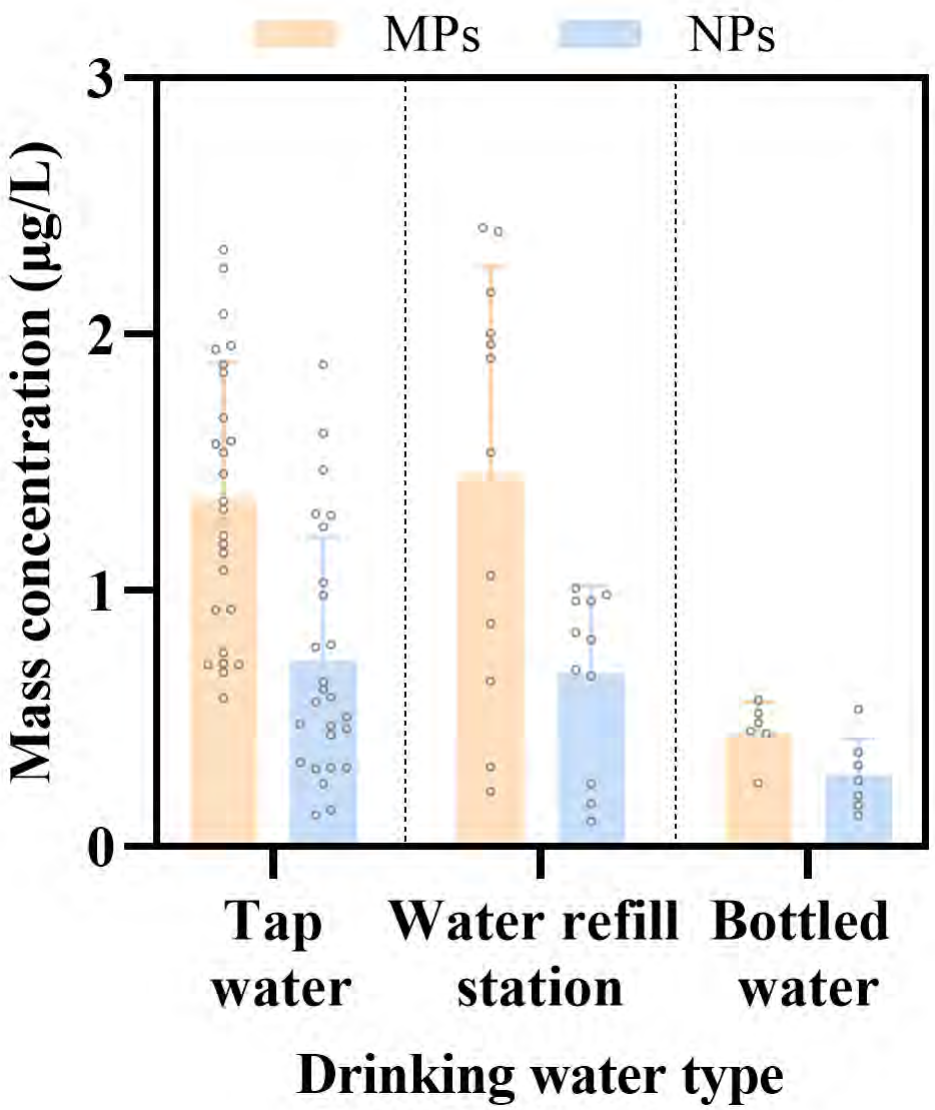
# The role of sewerage pipe materials and trade waste

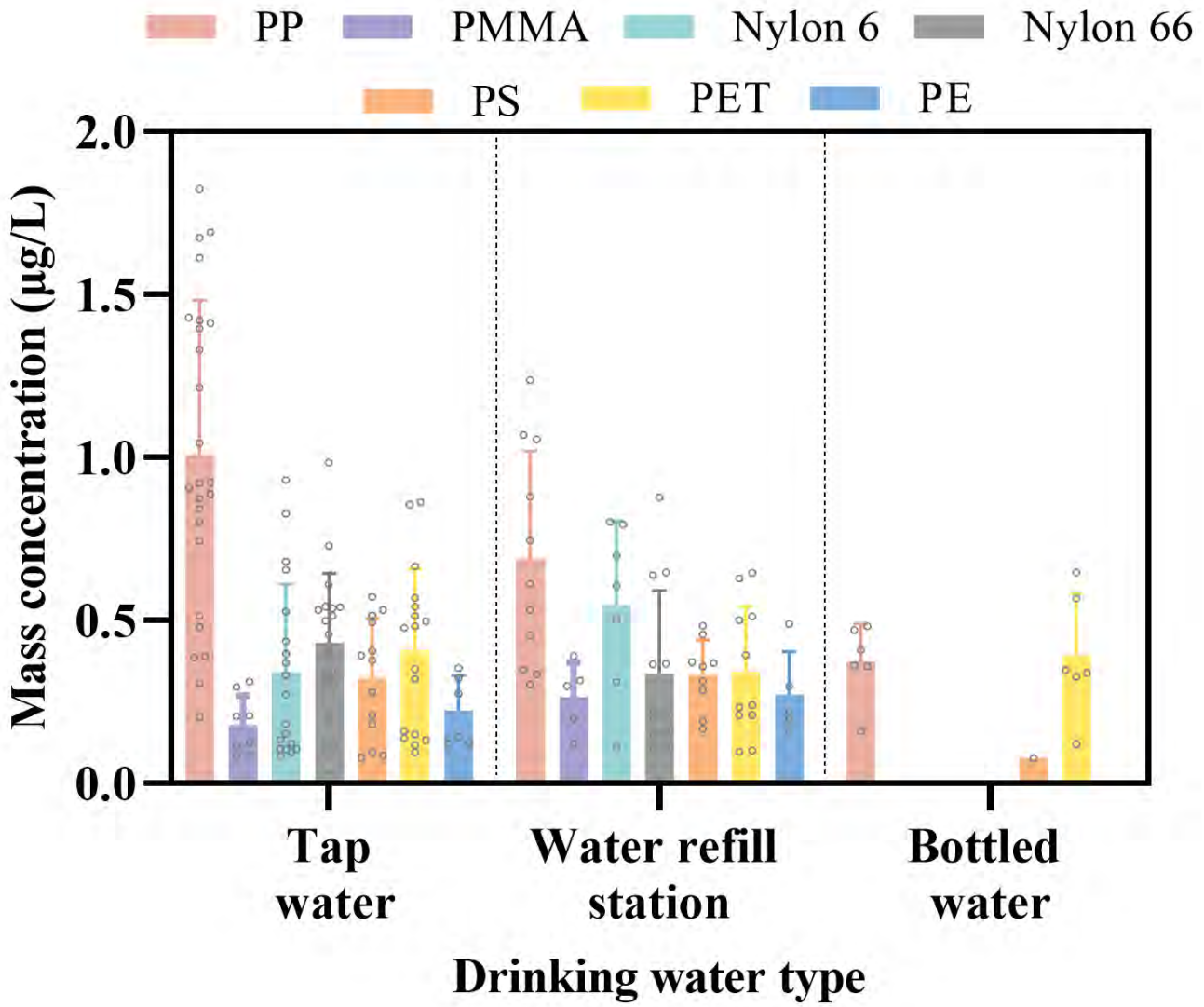



- Biosolids plastics concentrations compared with sewage pipe materials.
- Proportion of plastic material in sewerage pipes did not correlate with plastics concentrations in biosolids.
- Sewerage infrastructure likely not a key source of PVC, PE or PP entering biosolids.
- Plastics in biosolids correlated with trade waste categories such as **automotive wash bays, general manufacturing, hospitals, laboratories, food manufacturing and food service, laundry and dry cleaning.**

Okoffo et al. STOTEN

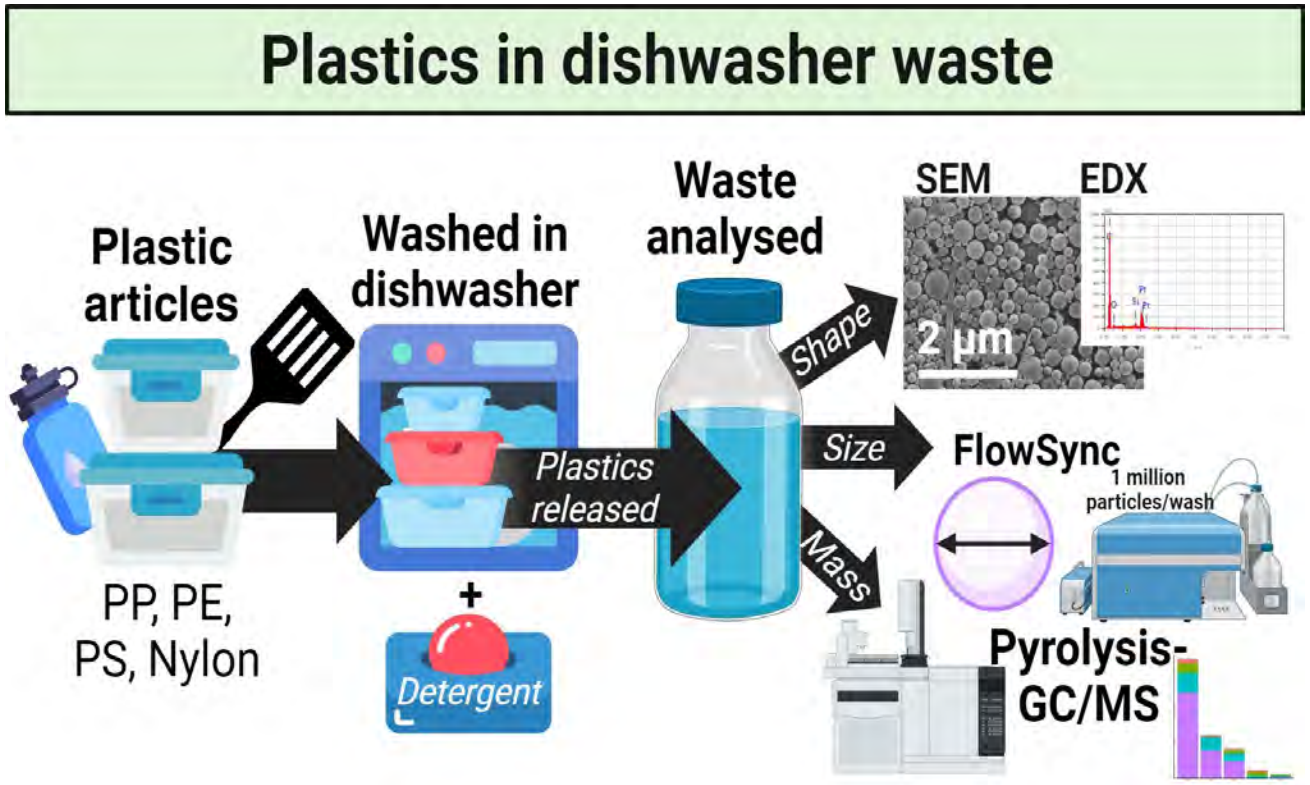
# Drinking water (Tap water)?




Ke Shi et al., Unpublished

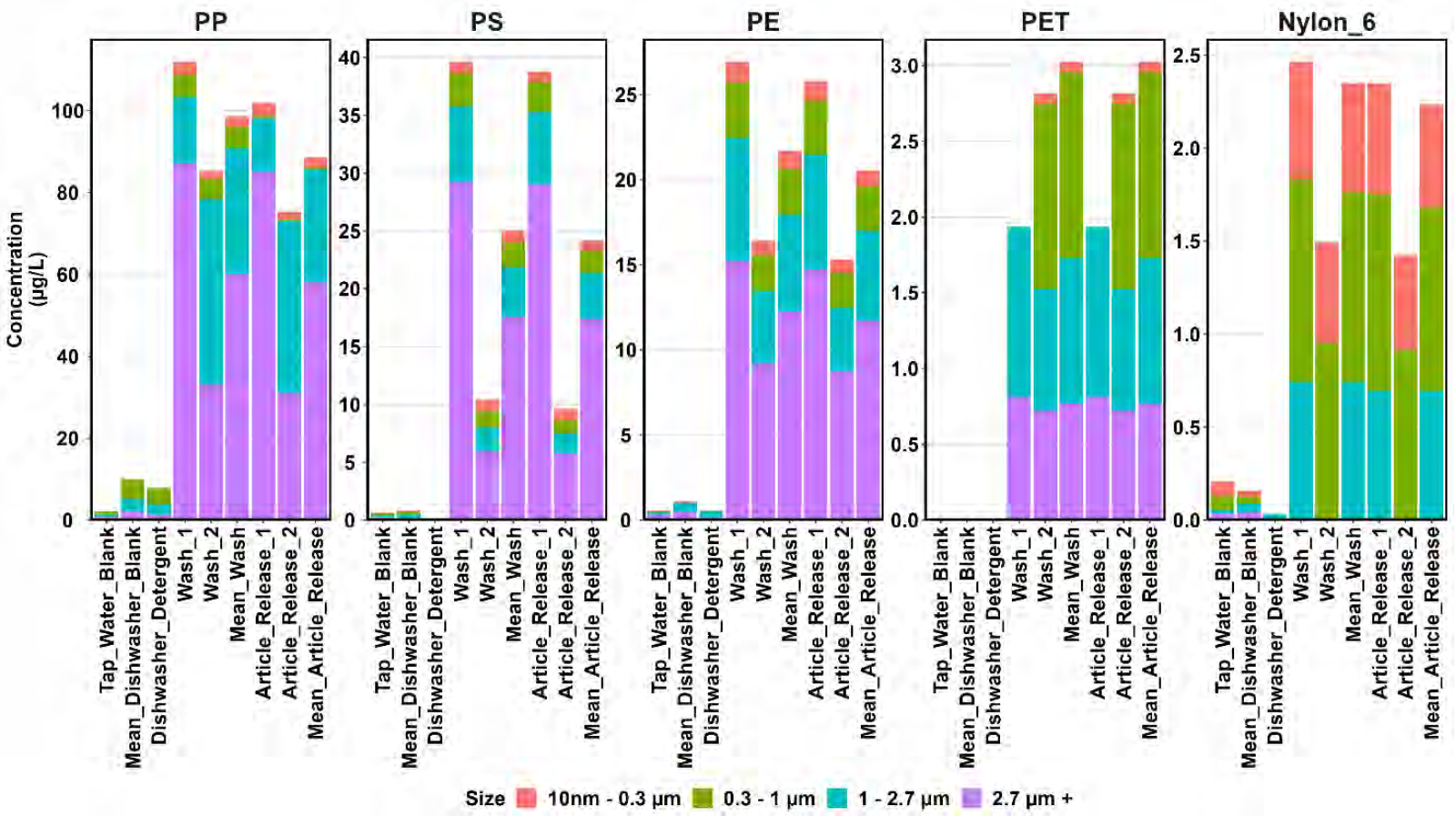
# Dishwasher?




- ✓ PP, PE, PS, PET and nylon 6 articles (washed before experiments)
- ✓ Blanks (tap water, dishwasher, detergent)
- ✓ 4 size ranges
  - > 2.7 µm
  - 1 µm – 2.7 µm
  - 0.3 µm - 1 µm
  - 0.01 – 0.3 µm
- ✓ Normalization to Surface Area
- ✓ Release Estimates (e.g.: dishwashers per household within an area, the number of households within the area, the average number of dishwasher cycles per household)

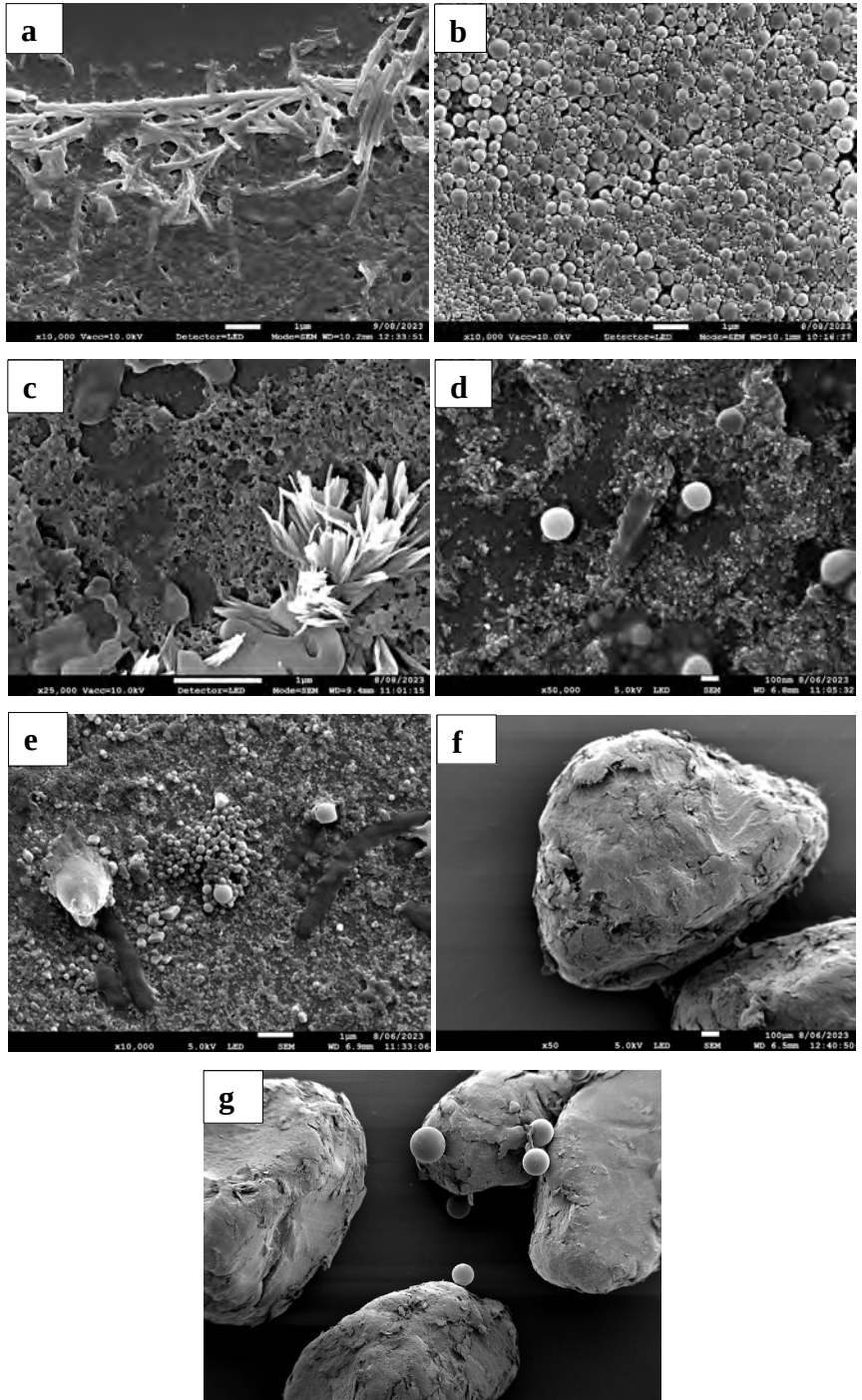
Okoffo et al., Unpublished

# Dishwasher?




- ✓ Tap water showed plastics
- ✓ Detergent showed PE and PP
- ✓ PP, PS and PE release greater amounts in larger particle size range (> 2.7 µm)
- ✓ whereas PET and nylon 6, released consistent amounts across the 4 size ranges (0.01 – 0.3 µm, 0.3 µm - 1 µm, 1 µm – 2.7 µm, and > 2.7 µm).

Okoffo et al., Unpublished

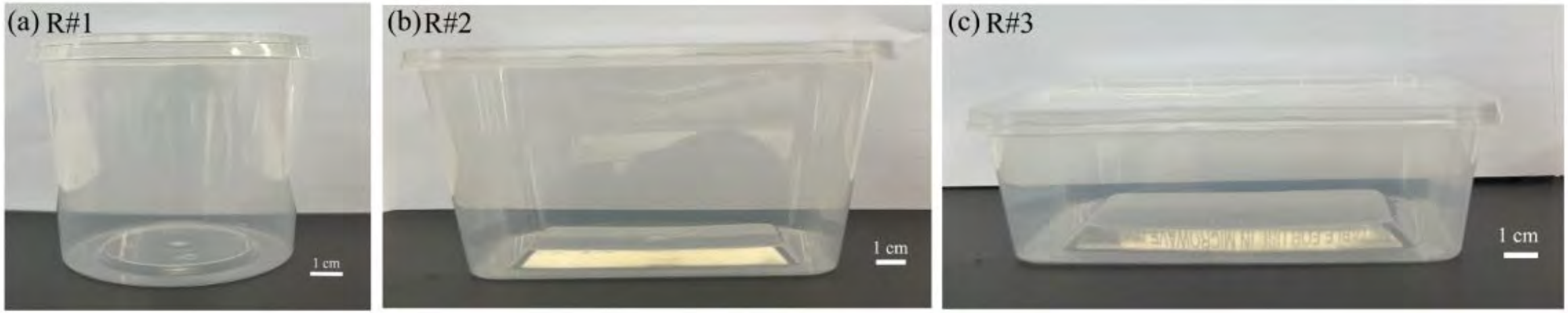


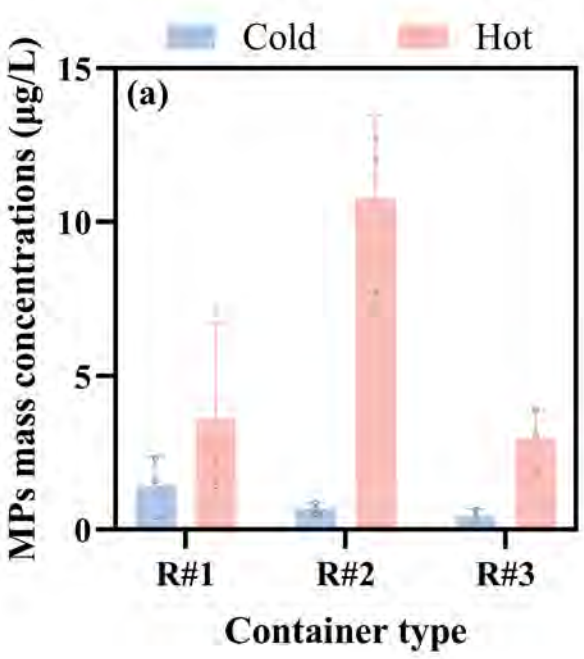

- release load of up to ~920,000 particles per cycle (full load)
- ~170 million particles per household per year
- If you wash one 1,000 cm2 (1 L container) for each of the 5 plastics (∑5plastics), then the release of plastics from dishwashers would equate to less than 30 mg/year/person, around the mass of a grain of rice

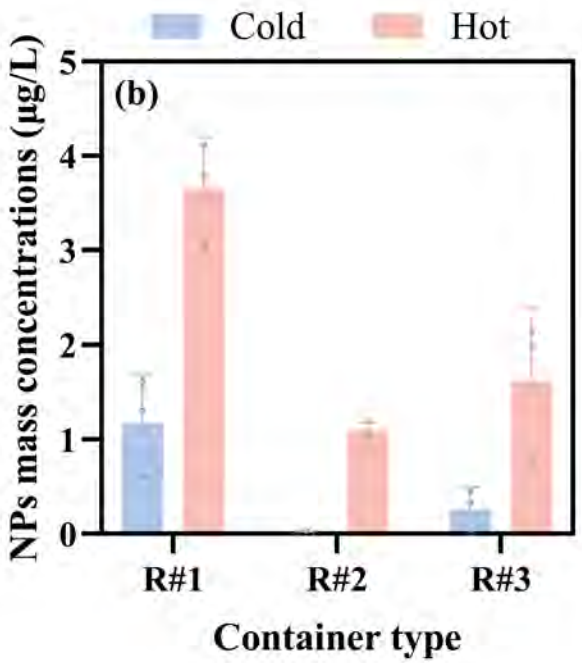
Okoffo et al., Unpublished

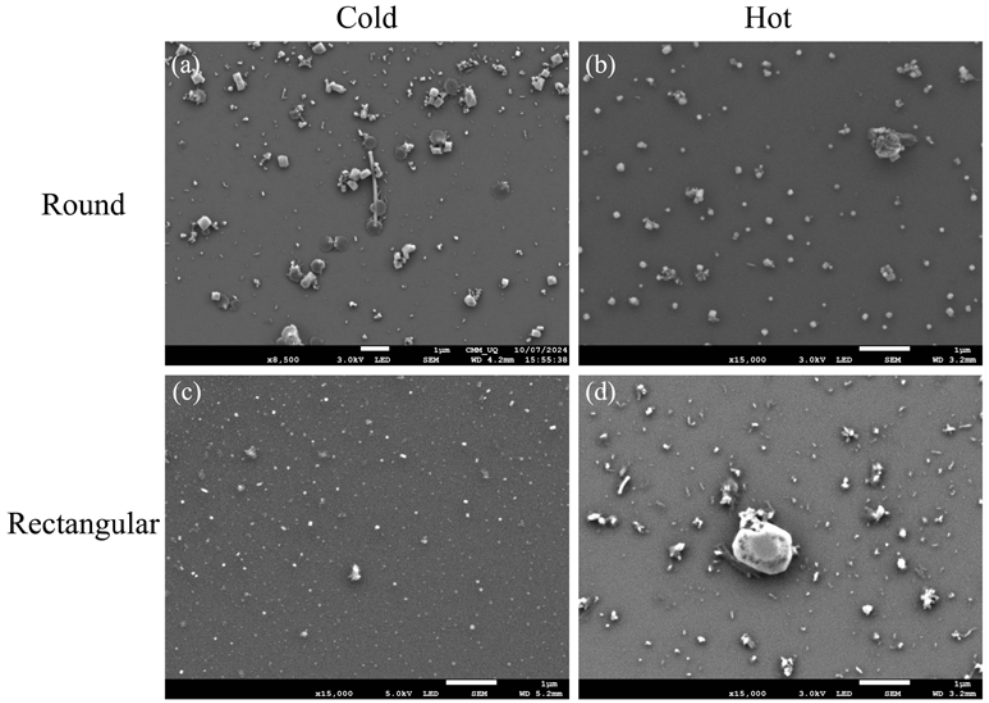
# Handwashing of containers?

Ke Shi et al., Unpublished



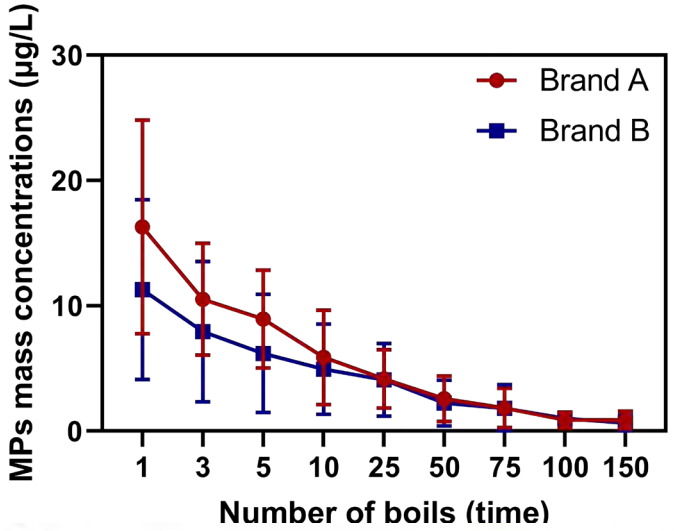
# Dishwasher Detergent?

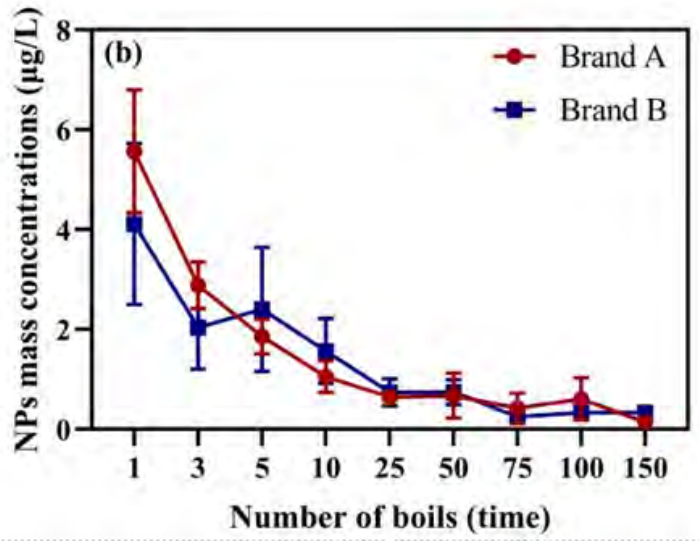

- 10 brands of dishwasher detergent
- Polyvinyl alcohol (PVA) water-soluble packaging material
- PE and PP

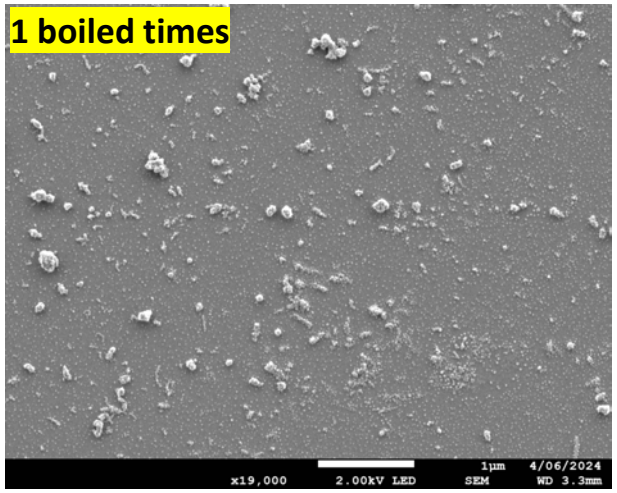
Ke Shi et al., Unpublished

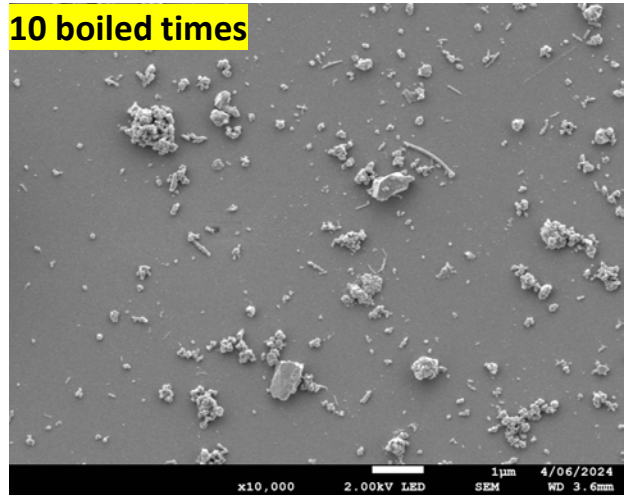
# Plastic products?

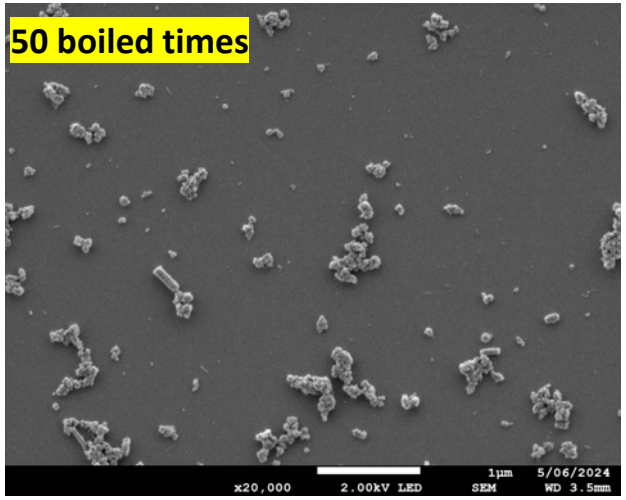
Boiling
N=150

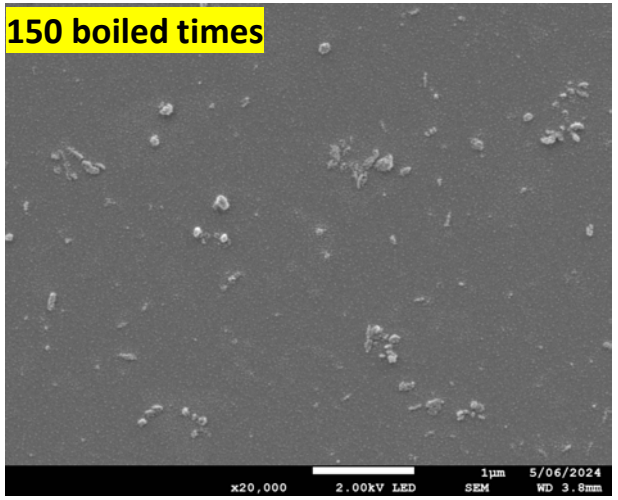


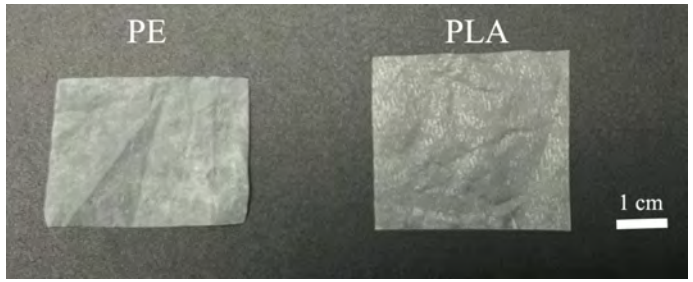



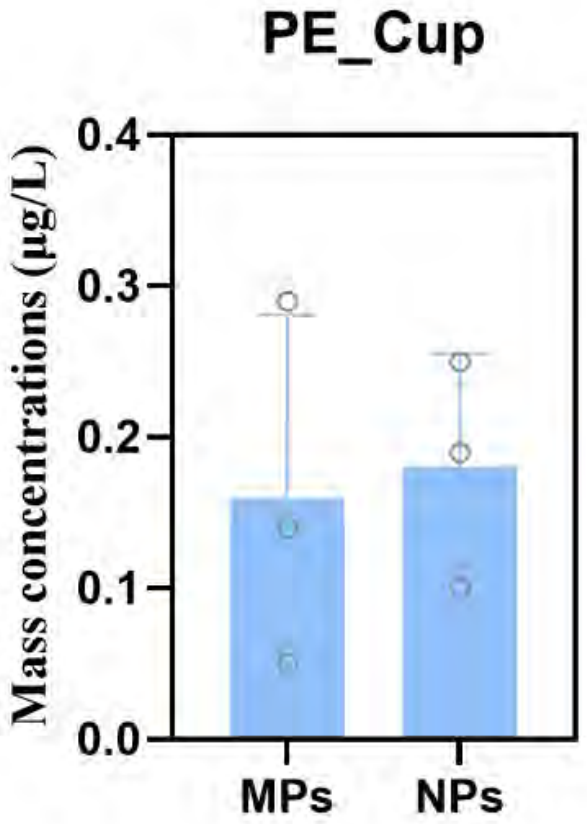



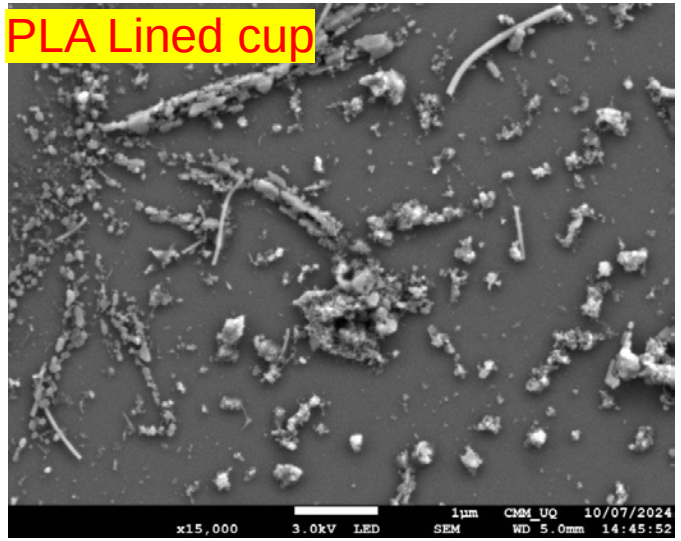

Ke Shi et al., Unpublished

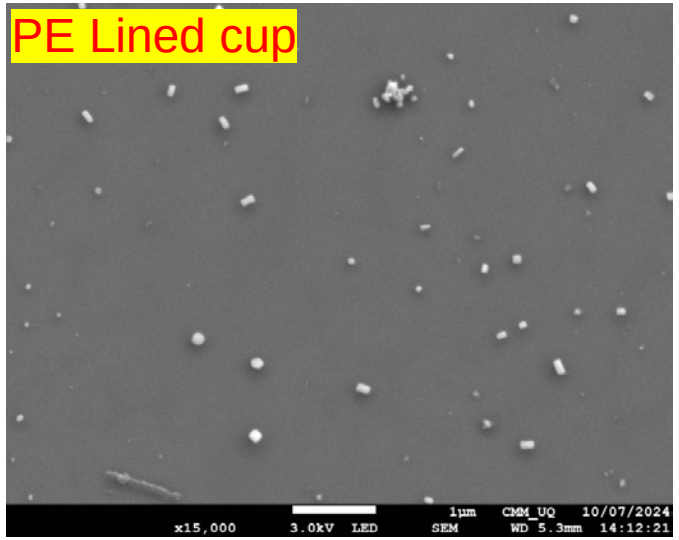
# Plastic products?




- PE or PLA cup
- 95 ℃, 20 min

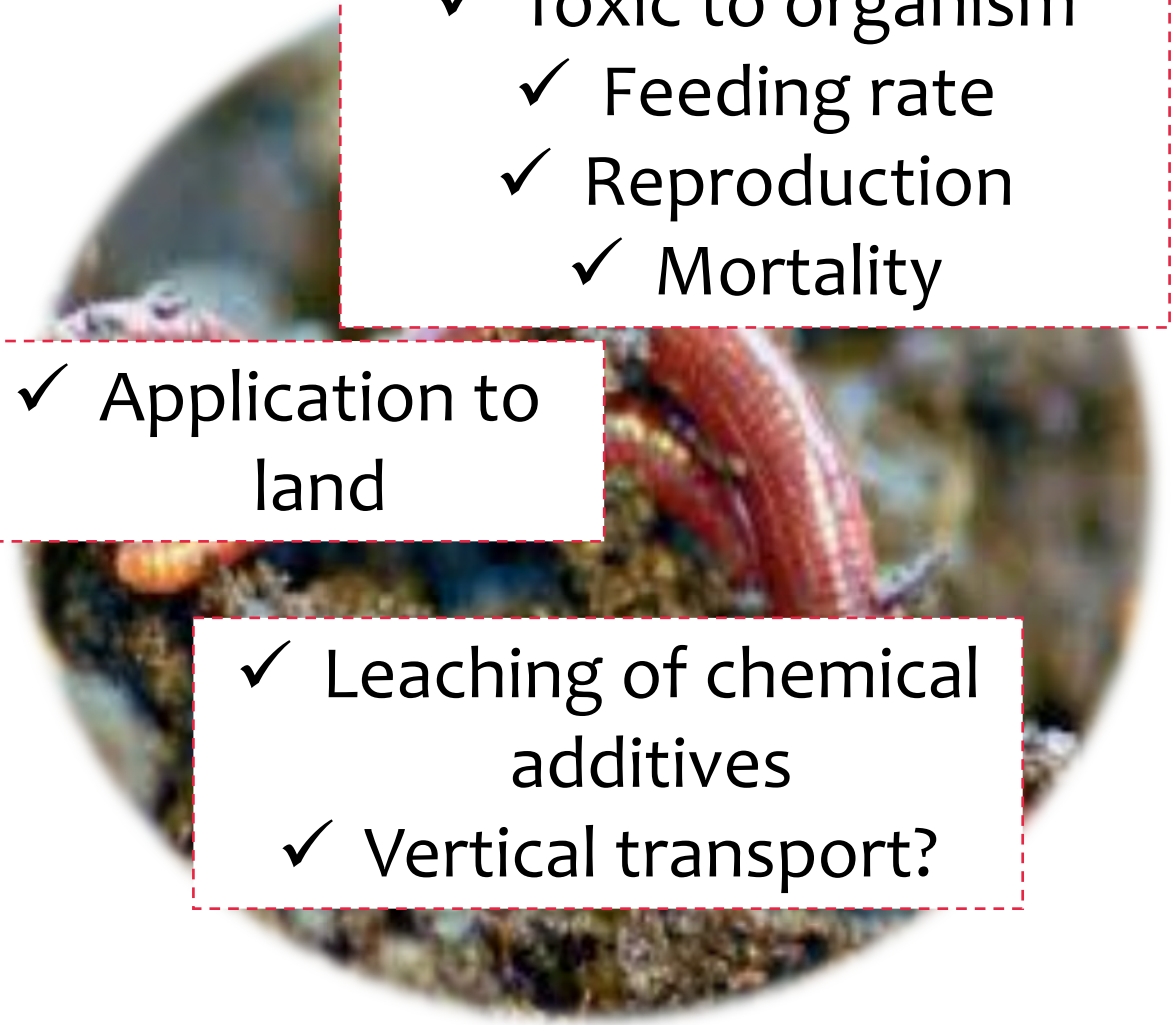



Ke Shi et al., Unpublished

# Is there actually a problem?



- ✓ Toxic to organism
- ✓ Feeding rate
- ✓ Reproduction
- ✓ Mortality

- ✓ Application to land

- ✓ Leaching of chemical additives
- ✓ Vertical transport?

➢Does uptake in organism or plants occur and if so at what size/dimension?

➢Studies on the effects of microplastic uptake by plants are starting

➢Studies on the effects of microplastic exposure on soil health are increasing

http://www.fao.org; https://www.intechopen.com; https://www.intechopen.com

# The major challenge: A balanced assessment

- Exposure assessment- progress but far from fully developed or standardized

- Uncertainties and knowledge gaps prevent the full evaluation of health impacts

  - Overall exposure concentrations vs. actual environmental concentrations
  - Size of particles
  - Virgin (pristine) vs. weathered polymers (complex and dynamic mixtures)
  - Impacts of plastic additives and not plastic particles?

# Take home

- Tiny pieces of plastic are ubiquitous in biosolids and are part of a ‘plastics cycle’

- Reducing exposure to plastic in wastewater requires a variety of solutions

  - source identification and control

- Reluctant to speculate at this stage in terms of risk based on lack of alignment between what is being tested versus what actually present

# Acknowledgements

Samples: WWTP operators

QAEHS staff and student

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**Thank you!**

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