

Determination of Tire Additive Transformation Products in Environmental Samples by LC-MS/MS

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NEMC

Introduction

About our laboratory

A full-service environmental lab

Large list of Analyses

Organics

Inorganics

Microbiology

Radiochemistry

POPs

Emerging contaminants



Microplastics and tire additives

Microplastics

Primary microplastics

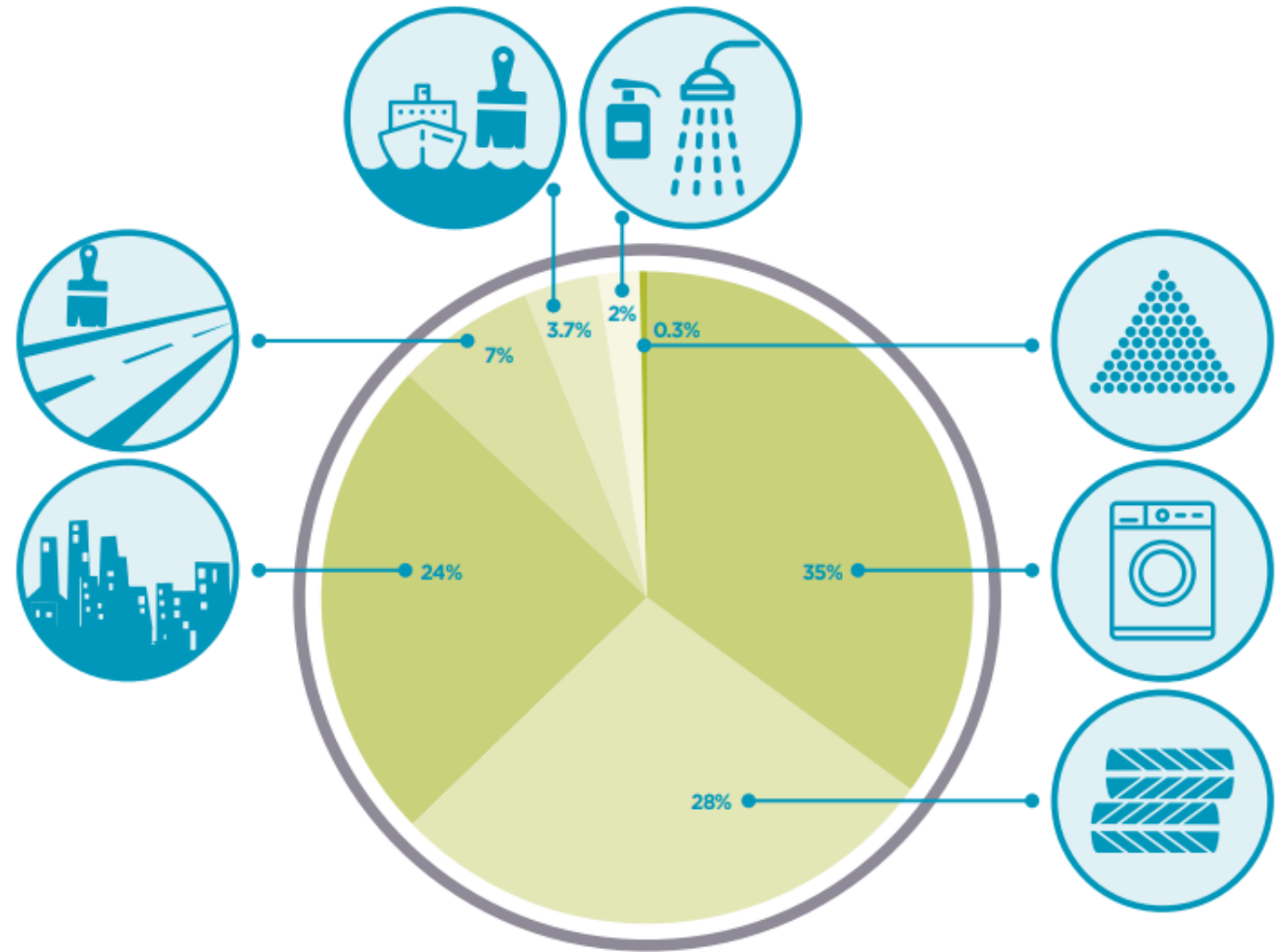


Primary Microplastics in the Oceans:

a Global Evaluation of Sources

Authors: Julien Boucher, Damien Friot

Tire and road wear particles



Microplastics

Primary microplastics

Microfibers (40-50%)

Hard plastics (30-35%)

Soft plastics (10-15%)

Secondary microplastics (2-5%)

Physical degradation

Photochemical degradation

Tire and road wear particles

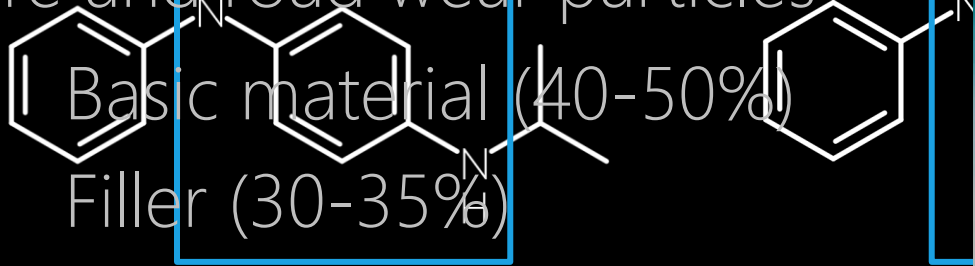
Plasticizers

Anti-oxidants



Anti-oxidants

Tire and road wear particles



Basic material (40-50%)

Filler (30-35%)

Softeners (10-15%)

Vulcanization agents (2-5%)



Additives (5-10%)

Preservatives

Desiccants

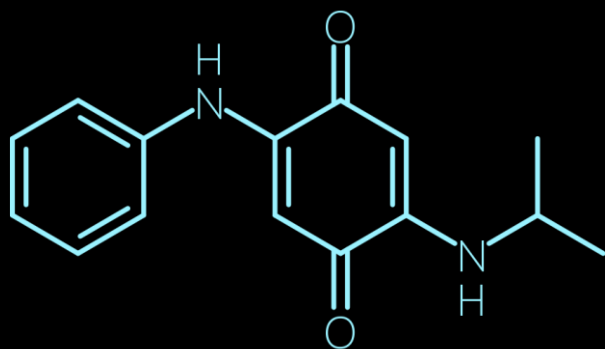
DPBD

Plasticizers

Anti-oxidants



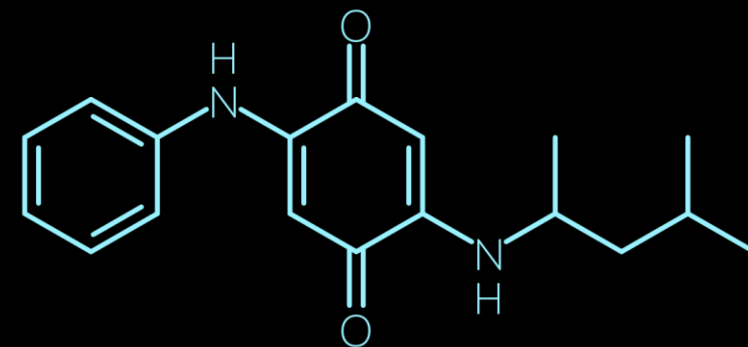
Transformation products



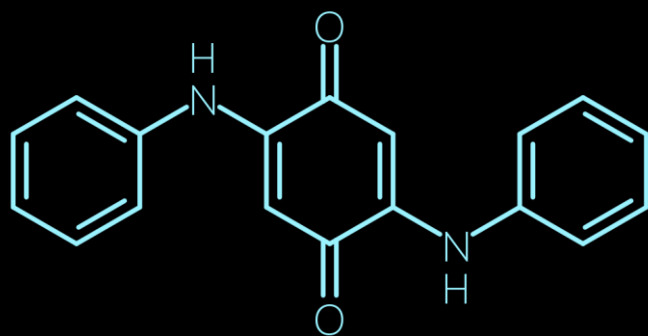
IPPD-Q



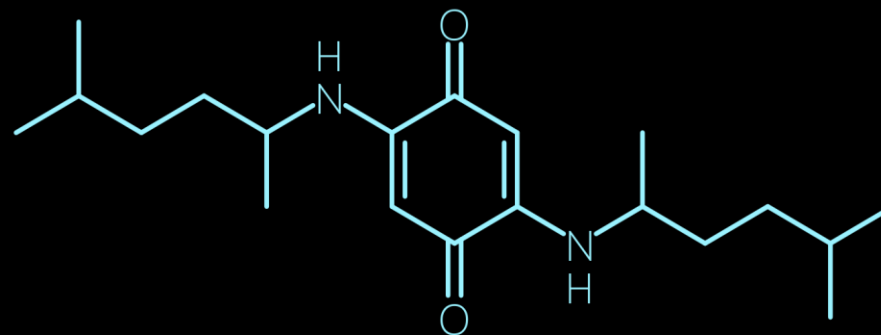
CPPD-Q



6PPD-Q



DPPD-Q



77PD-Q

6PPD-quinone

Science

HOME > SCIENCE > VOL. 371, NO. 6525 > A UBIQUITOUS TIRE RUBBER-DERIVED CHEMICAL INDUCES ACUTE MORTALITY IN COHO SALMON

REPORT

A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon

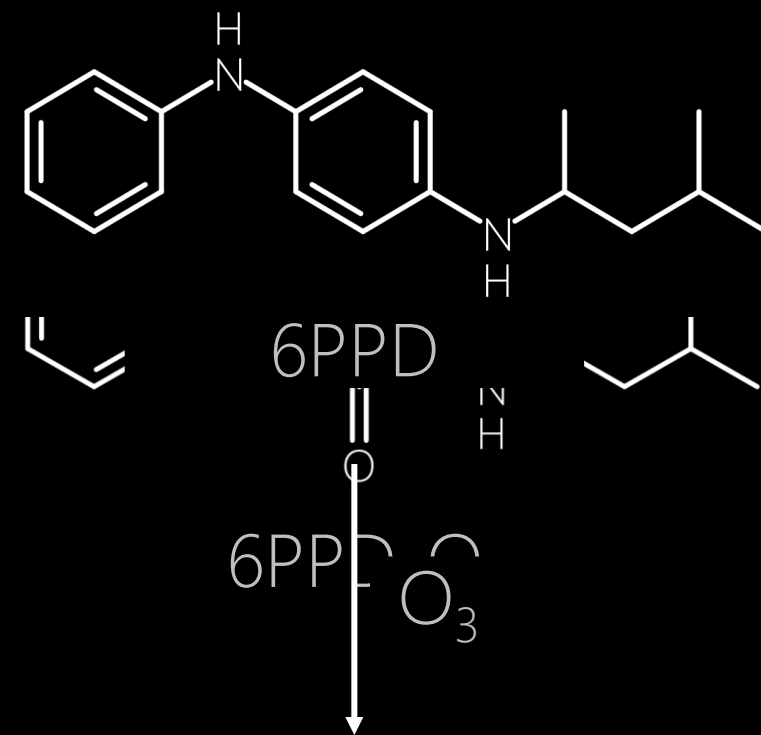
ZHENYU TIAN , HAOQI ZHAO , KATHERINE T. PETER , MELISSA GONZALEZ, JILL WETZEL , CHRISTOPHER WU, XIMIN HU , JASMINE PRAT .

EMMA MUDROCK, RACHEL HETTINGER , ALLAN E. CORTINA, RAJSHREE GHOSH BISWAS , FLÁVIO VINICIUS CRIZÓSTOMO KOCK , RONALD SOONG, AMY JENNE .

BOWEN DU , FAN HOU , HUAN HE , RACHEL LUNDEEN , ALICIA GILBREATH , REBECCA SUTTON , NATHANIEL L. SCHOLZ , JAY W. DAVIS .

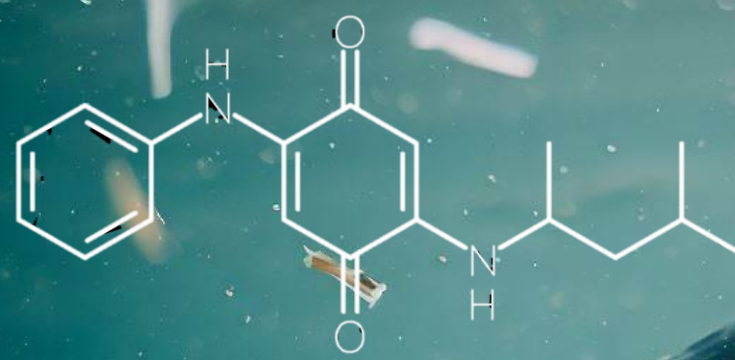
MICHAEL C. DODD , ANDRE SIMPSON , JENIFER K. MCINTYRE , AND EDWARD P. KOLODZIEJ  [fewer](#) [Authors Info & Affiliations](#)

SCIENCE • 3 Dec 2020 • Vol 371, Issue 6525 • pp. 185-189 • DOI: 10.1126/science.abd6951



6PPD-quinone toxicity

Chemical	Lowest LC ₅₀	Species
Parathion	40 ng/L	Crayfish
6PPD-Q	95 ng/L	Coho salmon
Mirex	100 ng/L	Crayfish
Guthion	100 ng/L	Crustacean
Chlorpyrifos	110 ng/L	Crustacean
Endrin	150 ng/L	Yellow perch
4,4'-DDT	180 ng/L	Crayfish
Diazinon	250 ng/L	Water flea
Cadmium	350 ng/L	Golden trout



Analytical method

Analytical challenges

Low reporting limits

LC₅₀ of 95 ng/L

Matrix

Urban watersheds

Stormwater runoff

Logistics

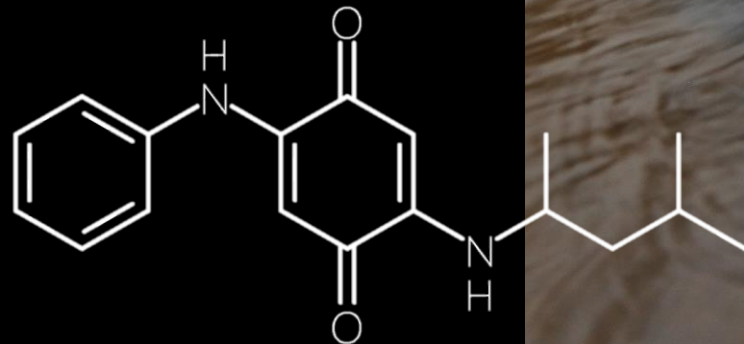
Sample shipments



Analytical challenges

- ✓ Low reporting limits
- ✓
- ✗ Matrix

Online Solid Phase Extraction
Concentration
Logistics
Cleanup?



Sediments

Homogenize/weigh sample (0.5 g)



Solvent leach (5 mL acetonitrile)



Solvent leach (5 mL acetonitrile)



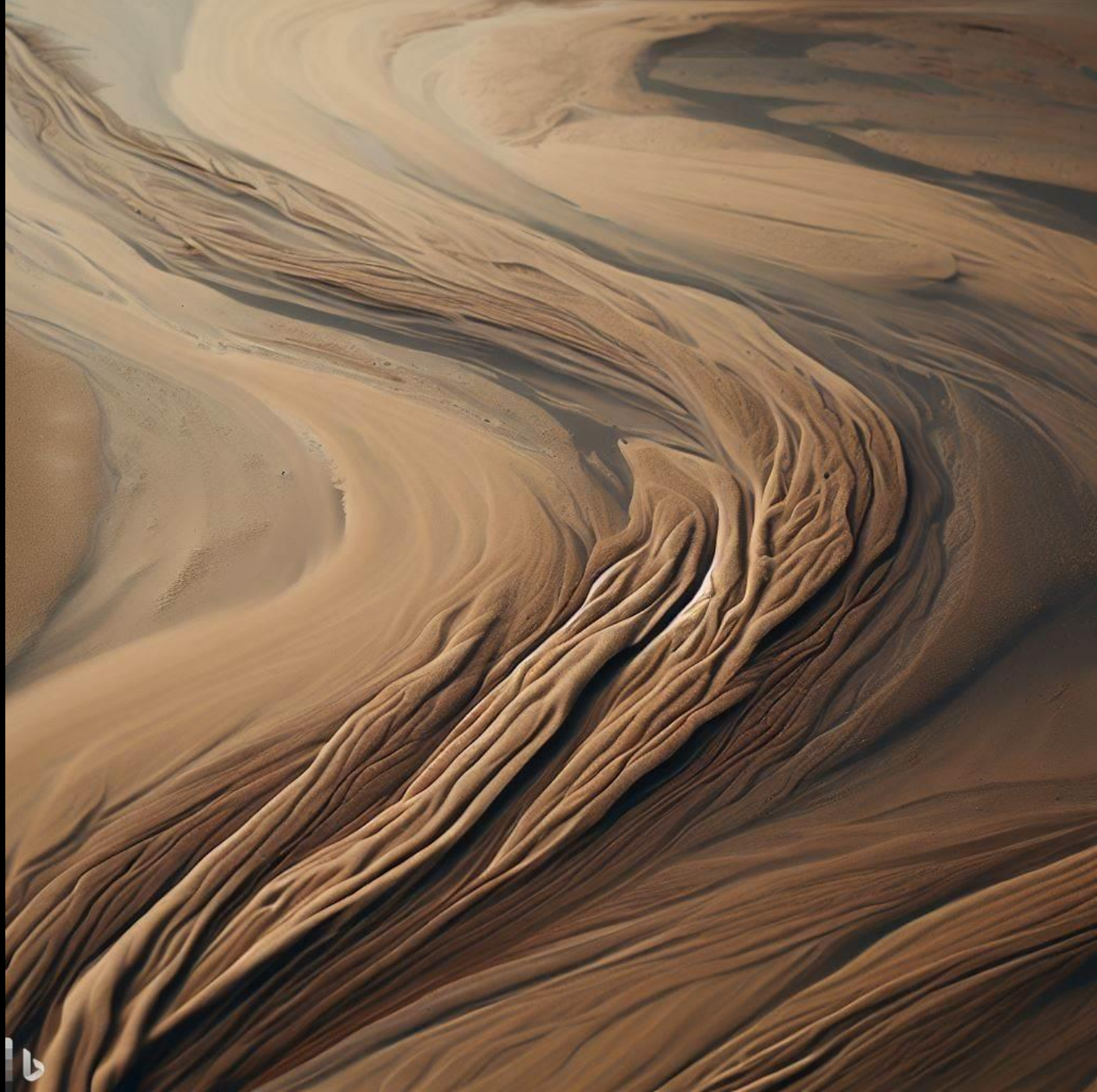
Winterize overnight



SPE pass-through



Analyze



Chromatography

Column: Poroshell Phenylhexyl 100x2.1mm 2.7 μm

Mobile phase A: 5 mM $\text{NH}_4\text{CH}_3\text{COOH}$ in water

Mobile phase B: Methanol

Flow rate: 650 $\mu\text{L}/\text{min}$

Time program:

0.0 min 30%B

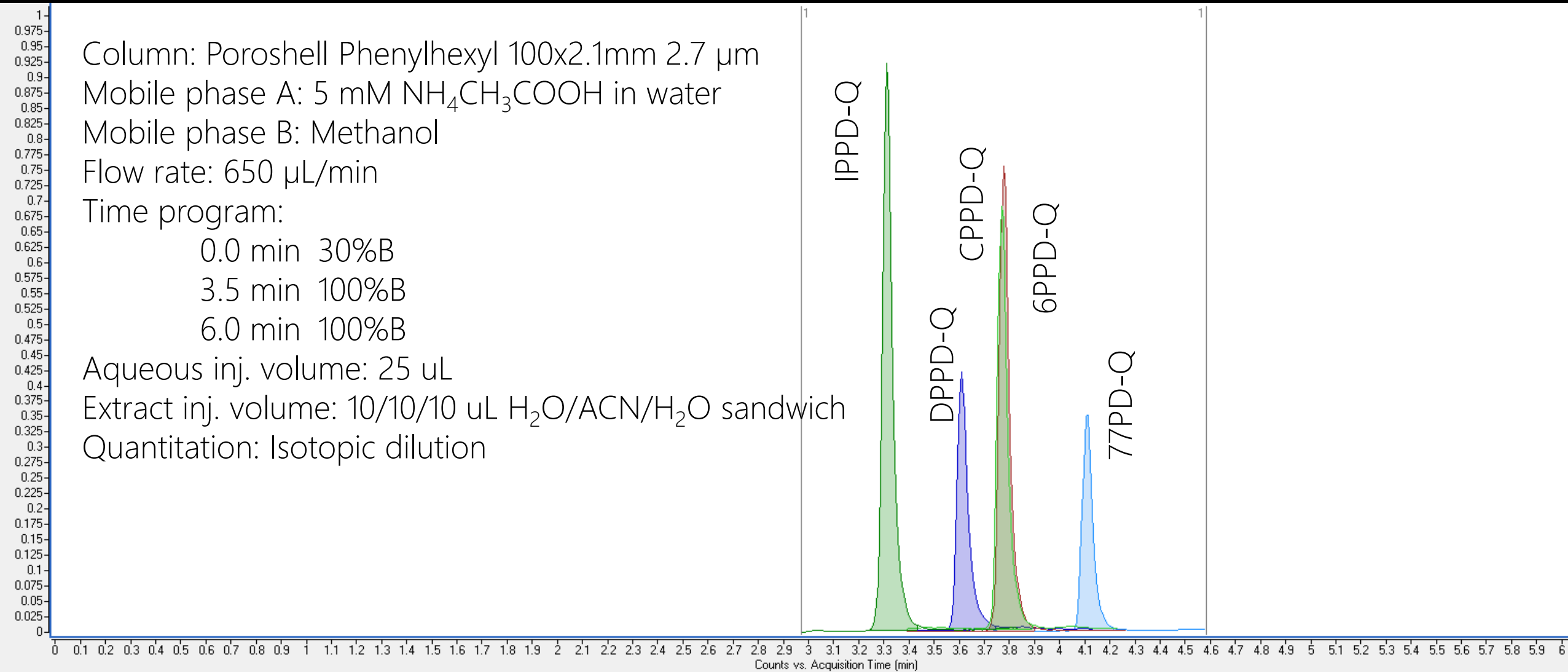
3.5 min 100%B

6.0 min 100%B

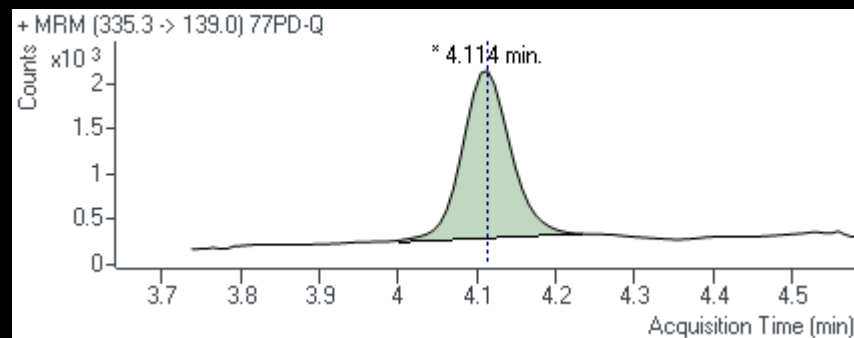
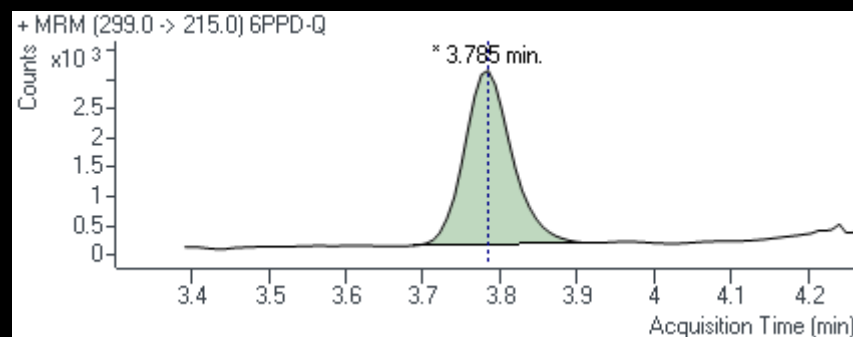
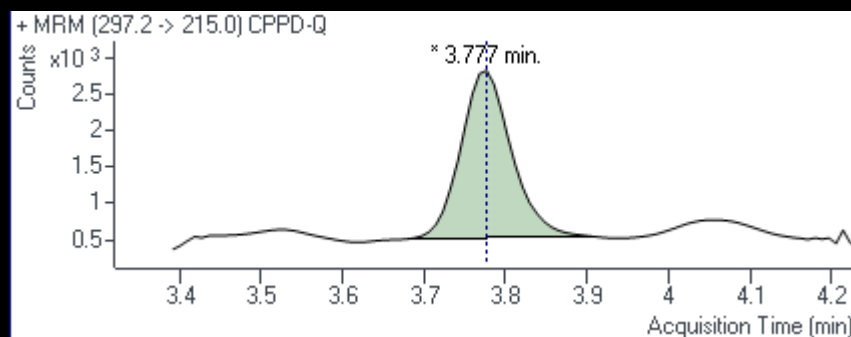
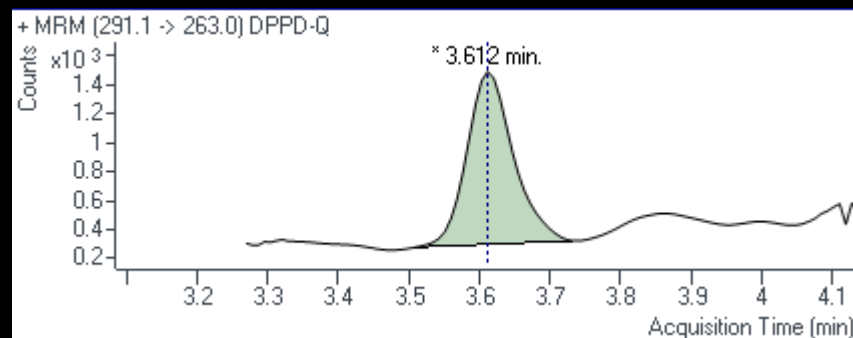
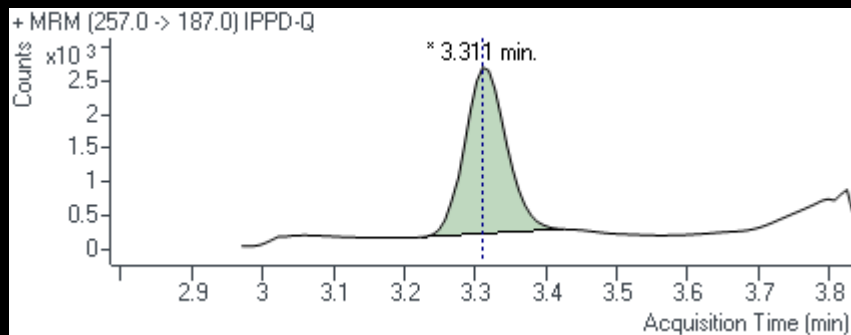
Aqueous inj. volume: 25 μL

Extract inj. volume: 10/10/10 μL $\text{H}_2\text{O}/\text{ACN}/\text{H}_2\text{O}$ sandwich

Quantitation: Isotopic dilution



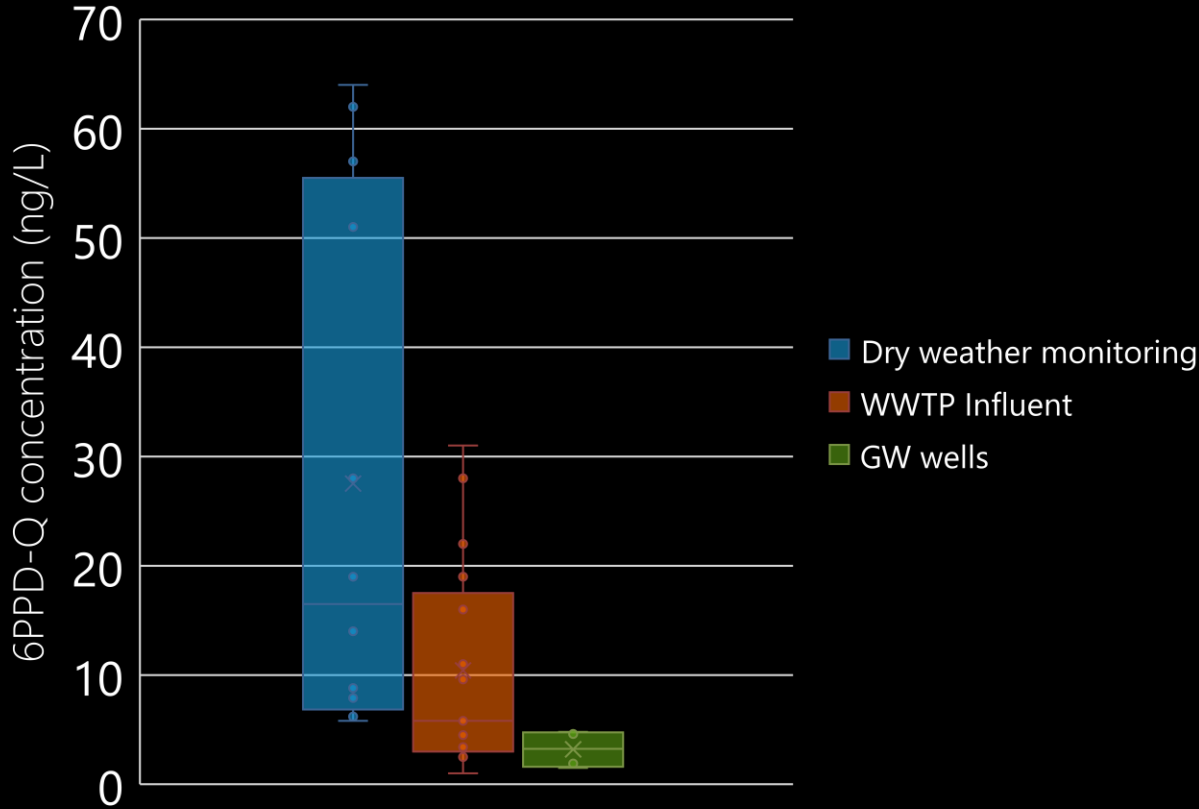
Sensitivity at 1 ng/L



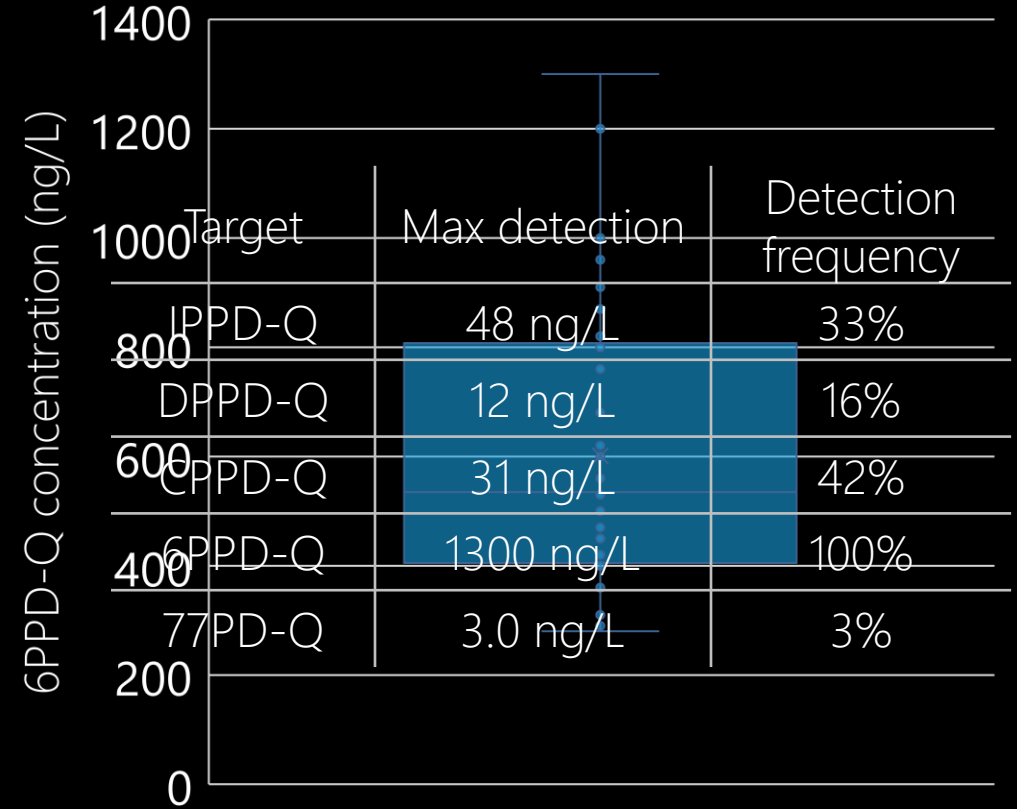
Occurrence data in Southern California

Detection frequency

6PPD-Q dry weather



6PPD-Q wet weather



6PPD-Q detection frequency:

- Wet weather: 100%
- Dry weather: 33%
- WWTP influent: 42%
- GW wells: 5%



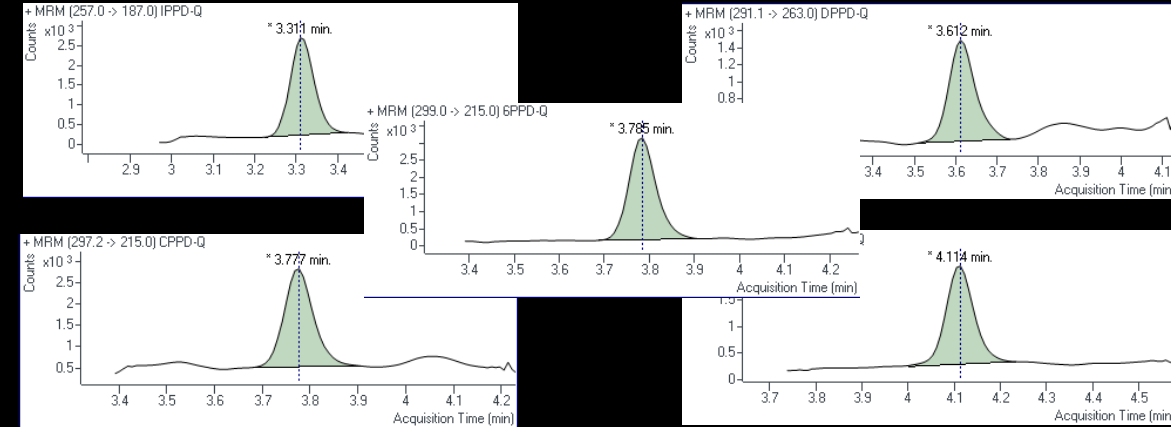
Summary

Method challenges

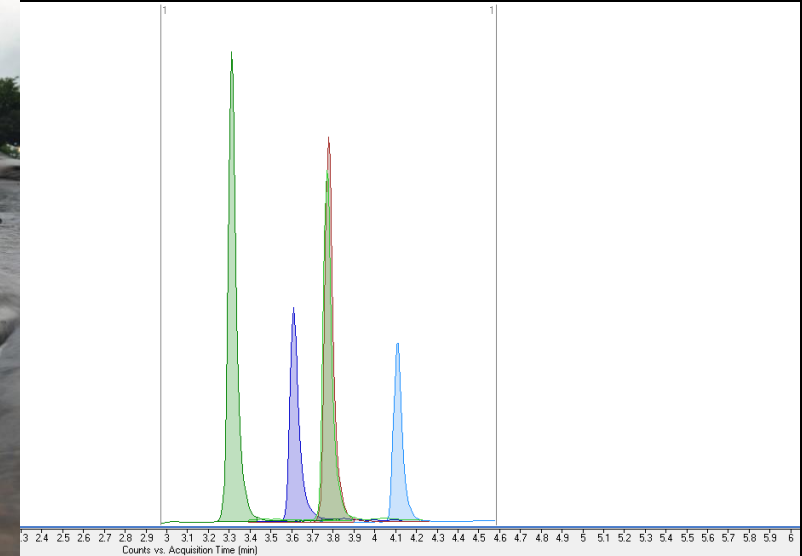
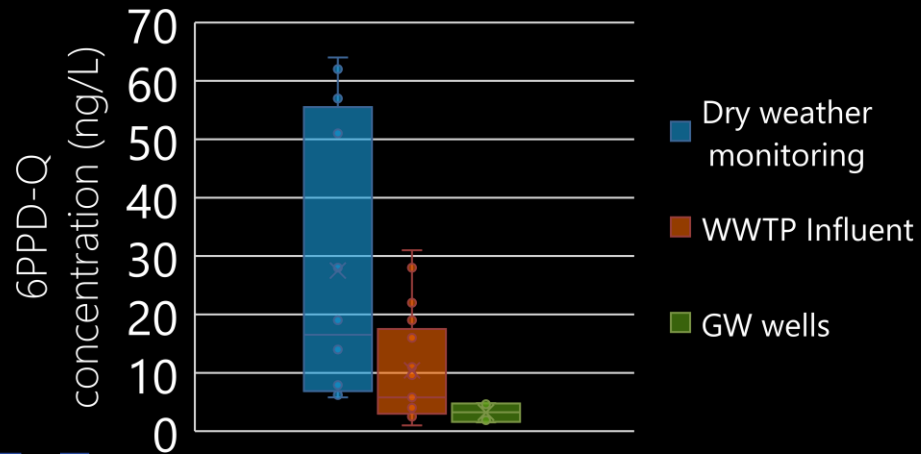
Low reporting limits

Matrix

Detection frequency



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