Leaching of Additives from Polyvinyl Chloride (PVC) Pipe & Microplastics

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Microplastics and Chemical Additives

Do microplastics and associated chemical additives (not removed during treatment) pose a potential health risk?

- Associated physical, biological, and chemical hazards?

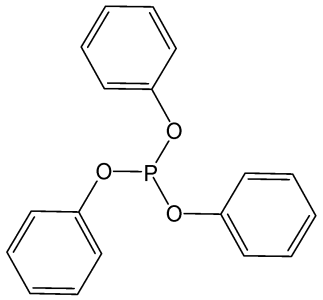
Chemical additives can constitute up to 75% of plastic mass

- Need to identify specific microplastic polymer types containing chemical additives that may be potentially toxic

What Do We Mean By “Chemical Additives”?

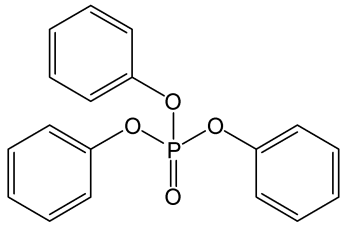
Chemicals added during manufacturing to improve plastic properties
(some of which may potentially be toxic)

Antioxidants



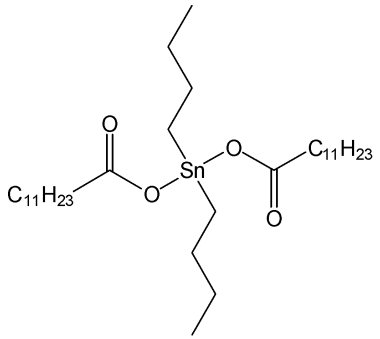
Triphenyl phosphite

Flame Retardants



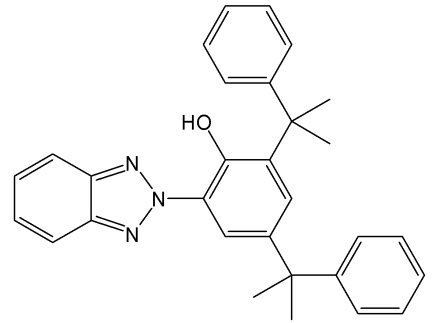
Triphenyl phosphate

Heat Stabilizers



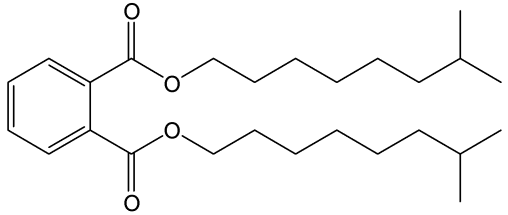
Dibutyltin dilaurate

Light Stabilizers



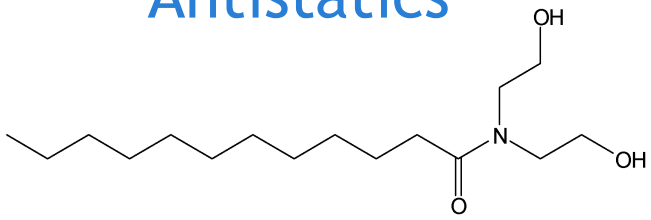
2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol

Plasticizers



Diisononylphthalate

Antistatics



N,N-bis(2-hydroxyethyl)dodecanamide

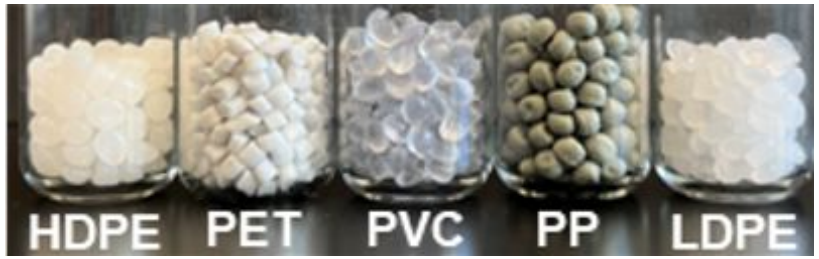
Objectives

Quantify toxicity of *chemical additives* that may potentially impact drinking water:

1) Identify *chemical additives which* are present
   - Apply screening and non-targeted analysis
2) Determine which *chemical additives* contribute to toxicity
   - Use human protein, gene, and cell bioassays
3) Assess leaching of chemical additives into water

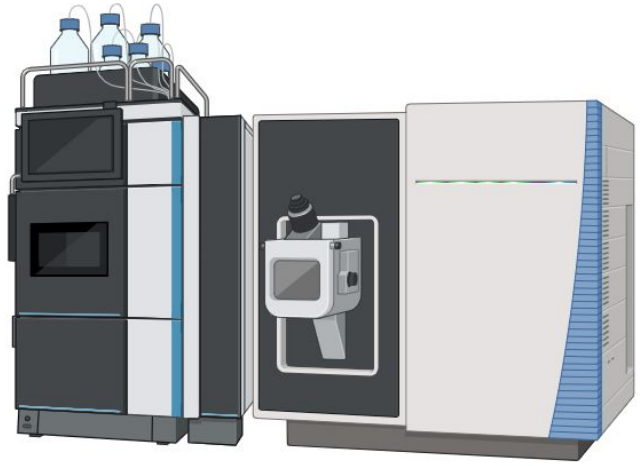
Select plastic (polymer) types

- High-density polyethylene (HDPE)
- Polyethylene terephthalate (PET)
- Polyvinyl chloride (PVC)
- Polypropylene (PP)
- Low-density polyethylene (LDPE)
- PVC pipe



Identify additives

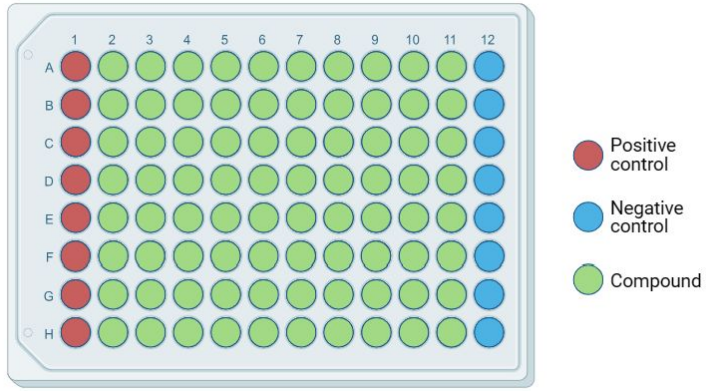
1. Extract additives
2. Use liquid chromatography mass spectrometry (LC/MS)



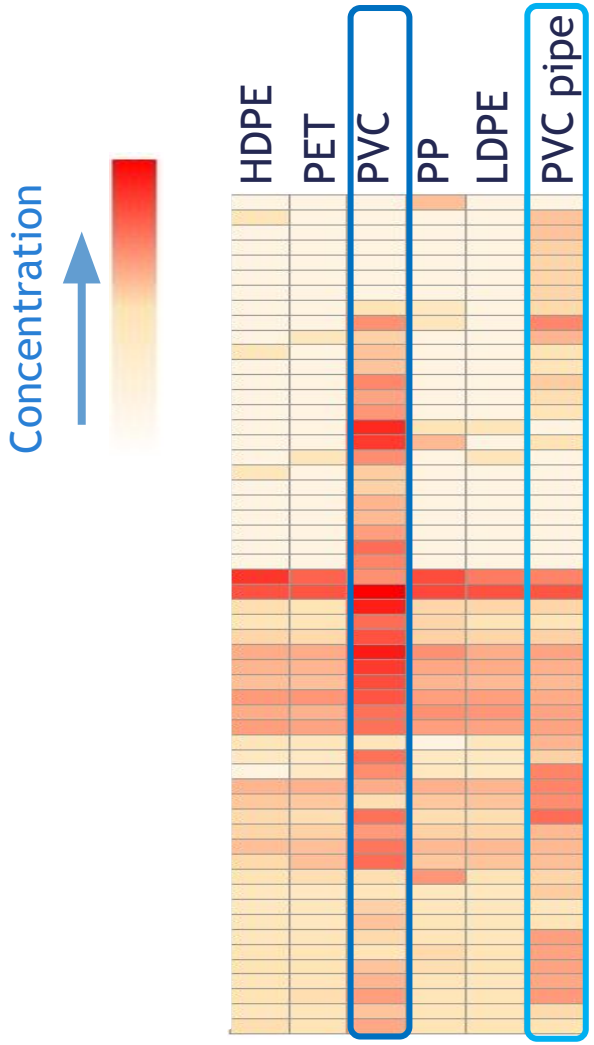
Identify toxicity drivers

Human cell bioassays:

- hCES1 inhibition
- PPARγ activity
- HEK293 cell viability



Results – Identify Additives



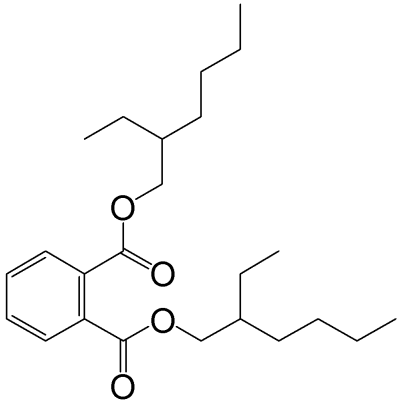
Results from non-targeted analysis:

1. 56 chemicals identified in polymers
2. PVC contained highest number of additive types, as well as highest concentrations
3. PVC pipe had 2nd highest number of additive types, but *at lower concentrations*

Results – Identify Additives

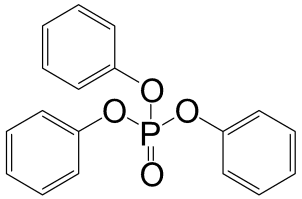
Toxic chemicals among 56 additives

Phthalates

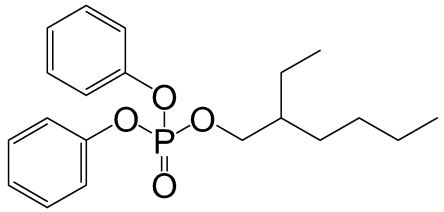


Di(2-ethylhexyl) phthalate
(DEHP)

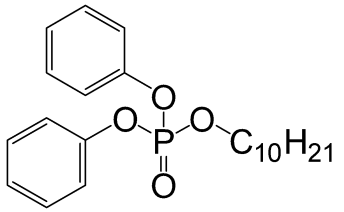
Organophosphate flame retardants (OPFRs)



Triphenyl phosphate
(TPHP)



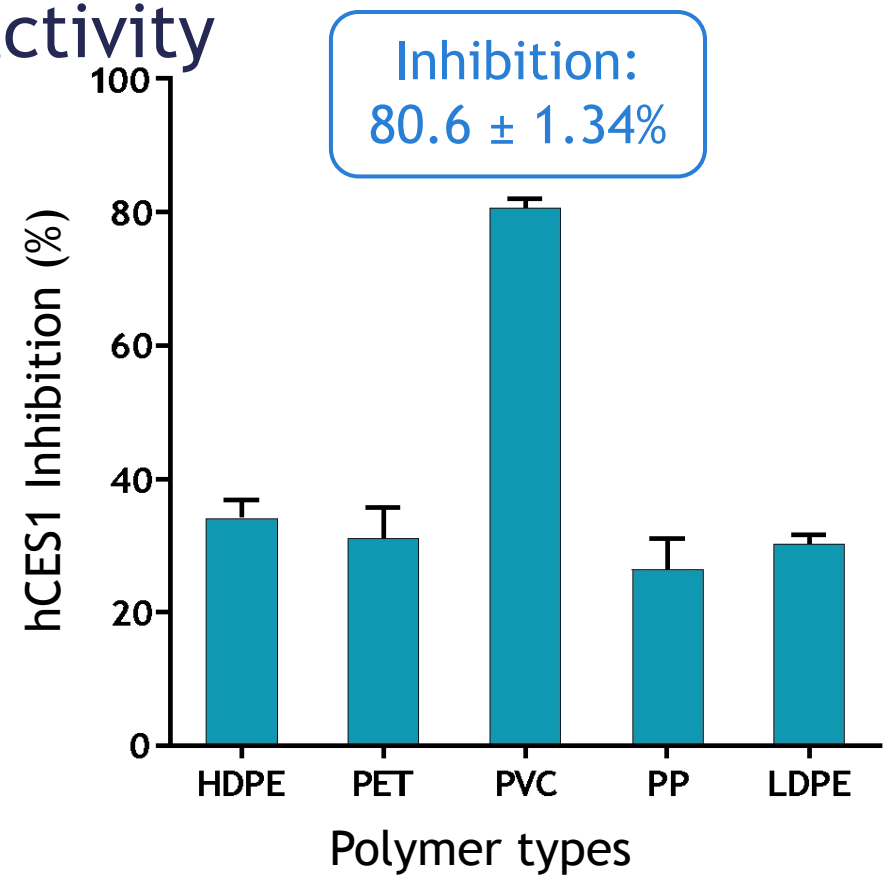
2-ethylhexyl diphenyl phosphate
(EHDPP)



Decyl diphenyl phosphate
(DDPHP)

Results – Human Liver Assay (Test 1)

Chemical additives (from PVC) - significantly inhibit liver enzyme activity



Which specific chemicals in PVC cause toxicity?

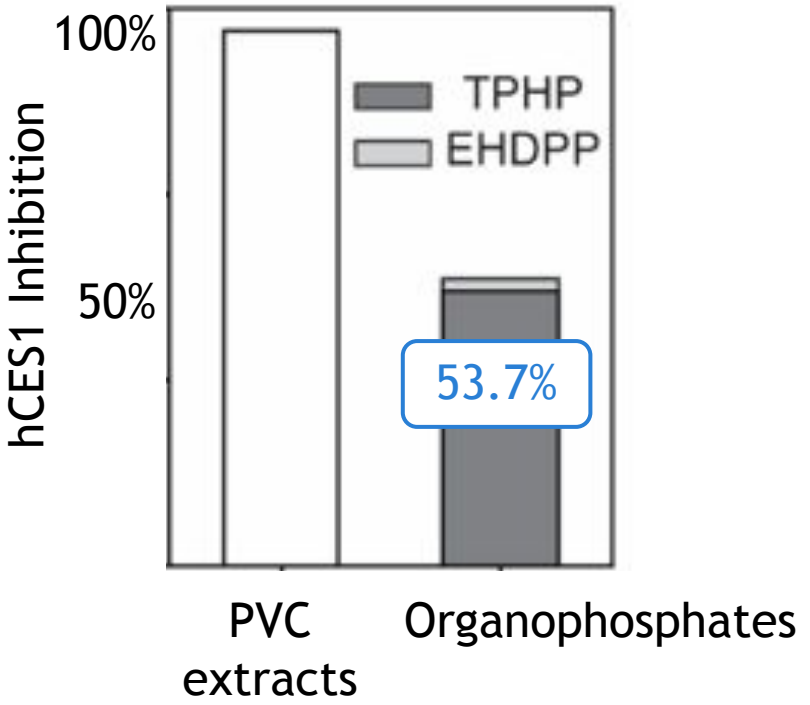
Out of 56 additives identified, begin with the most toxic: *organophosphates*

Results – Human Liver Assay (Test 1)

Organophosphates observed in PVC:

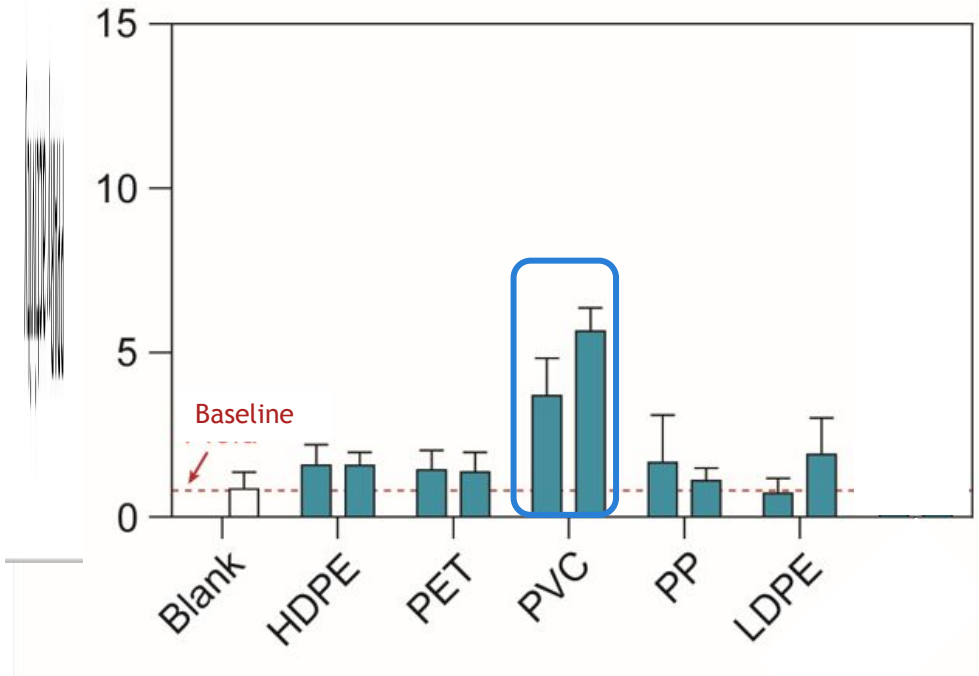
1) TPHP *(Triphenyl phosphate)* = 96.6 µg/g
2) EHDPP *(2-ethylhexyl diphenyl phosphate)* = 22.8 µg/g

Compare bioassay response to calculated response from individual chemicals



TPHP *(Triphenyl phosphate)* an organophosphate flame retardant - responsible for majority of human liver assay toxicity

Results – Human Gene Assays (Test 2)



PVC exhibited highest toxicity

Which chemicals were responsible?

Triphenyl Phosphate (TPHP) caused 1.5% of the response, compared to >50% in liver assay

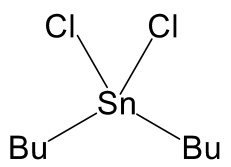
- Suggests toxicity due to other chemicals

PVC pipe material - unexpectedly exerted strong toxicity

Results – Human Gene Assays (Test 2)

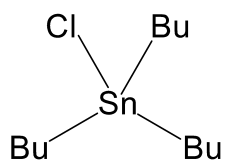
Major chemical additives identified in PVC pipe:

Organotins



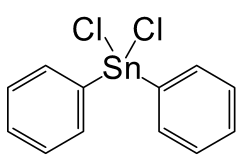
Dibutyltin dichloride (DBT)

92.1 µg/g



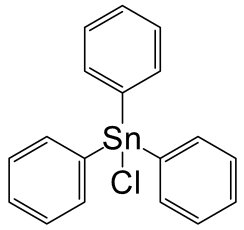
Tributyltin chloride (TBT)

0.15 µg/g



Diphenyltin dichloride (DPT)

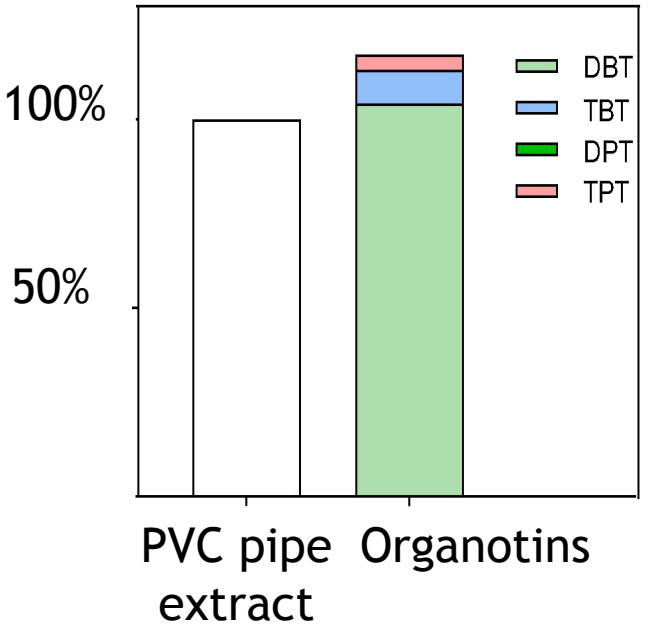
0.005 µg/g



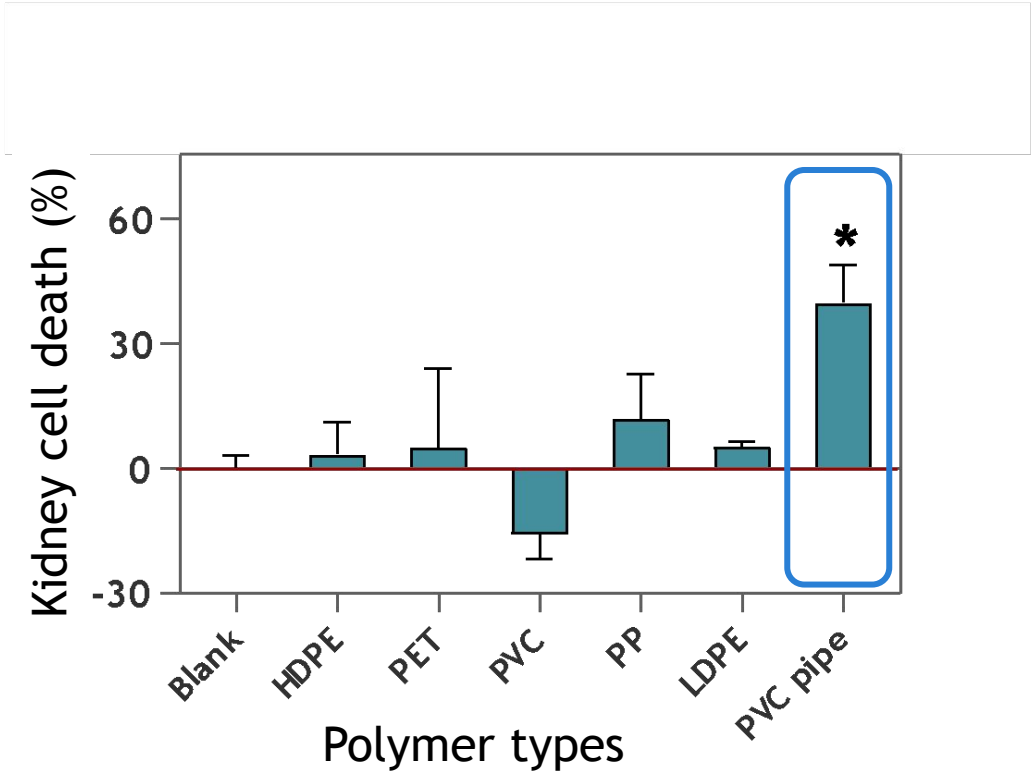
Triphenyltin chloride (TPT)

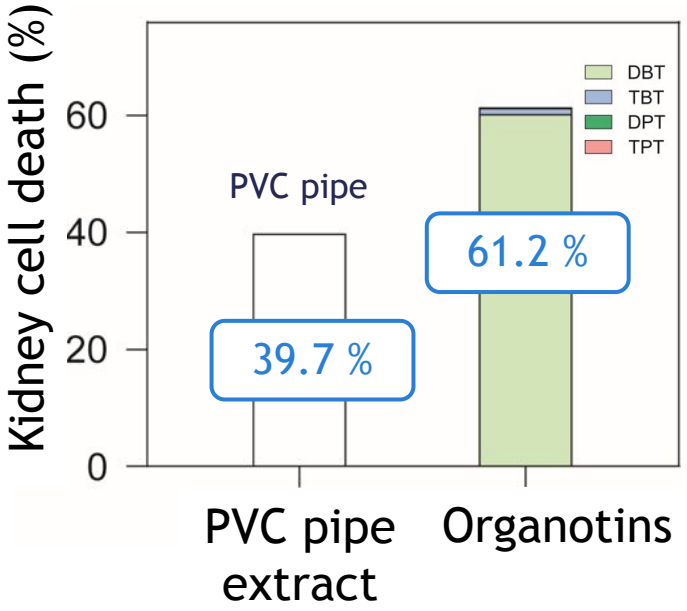
0.05 µg/g

0.01% of PVC pipe by mass



Results – Human Cell Assays (Test 3)



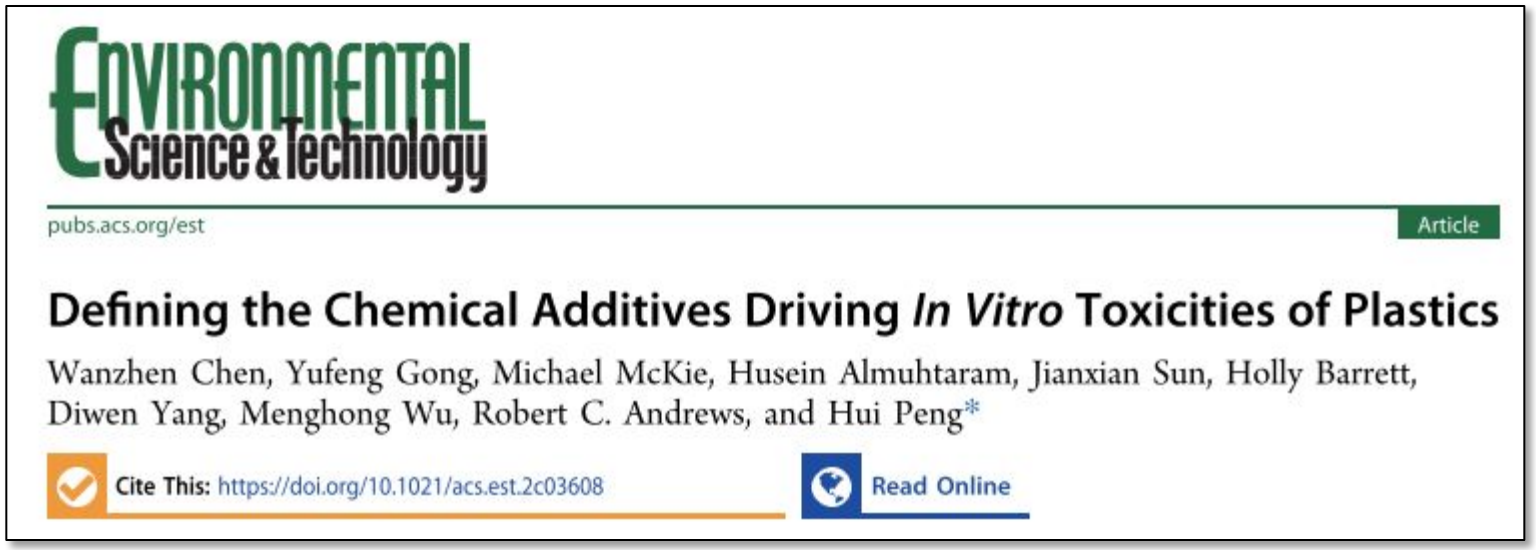


Organotins associated with PVC pipe cytotoxicity

Chemical Additives (in PVC) - Potential Health Concern

Organophosphorus compounds – *may inhibit liver enzyme activity*

Organotin compounds - *exert toxicity to human nucleic acids and cells*



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Defining the Chemical Additives Driving *In Vitro* Toxicities of Plastics

Wanzhen Chen, Yufeng Gong, Michael McKie, Husein Almuhtaram, Jianxian Sun, Holly Barrett, Diwen Yang, Menghong Wu, Robert C. Andrews, and Hui Peng*

Cite This: https://doi.org/10.1021/acs.est.2c03608 Read Online

PVC and PVC pipe materials selected for further detailed study

Objectives:

Assess leaching associated with 7 PVC materials

- 4 different PVC pre-production pellets, 3 types of PVC pipe (used in water distribution systems)
- Evaluate leaching of chemical additives into artificial freshwater (AFW)

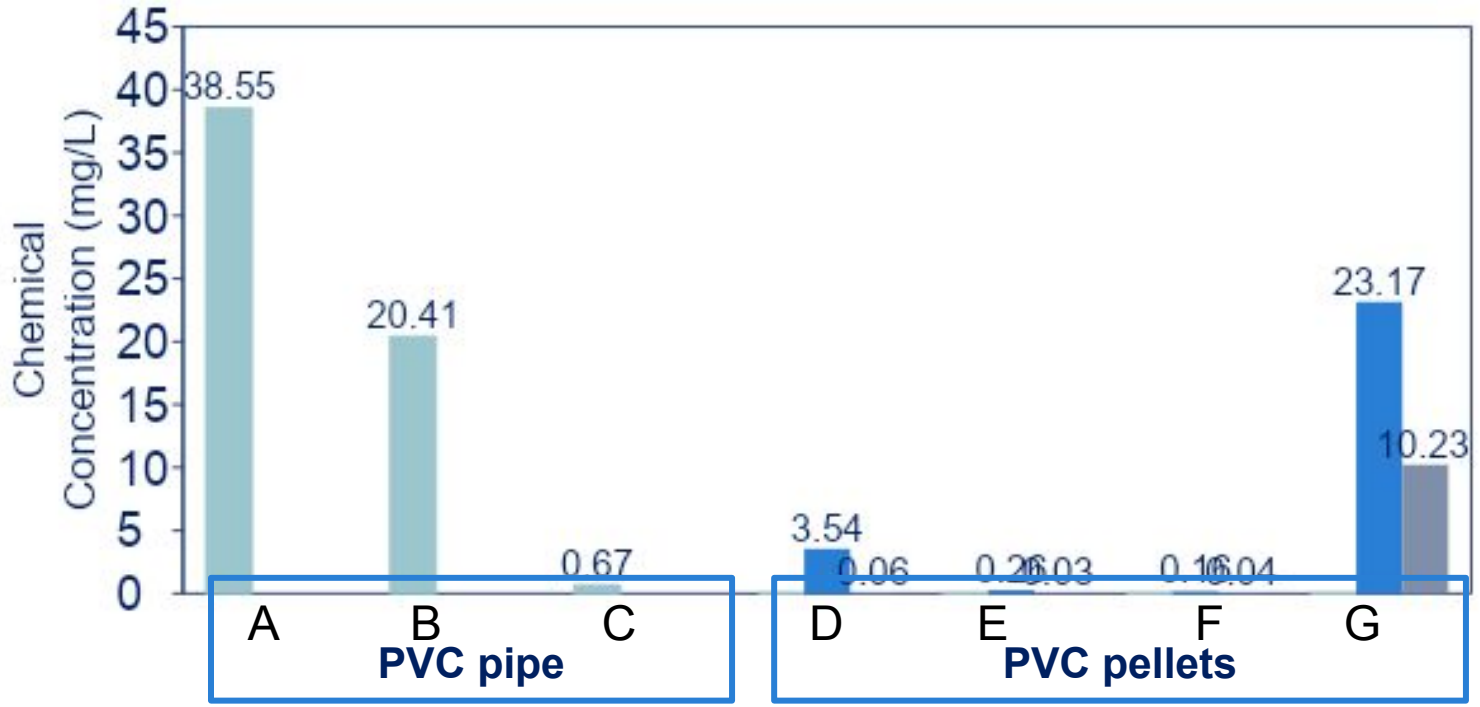
As a function of:

- Particle size
- pH
- Presence of oxidants (chlorine and chloramine)

Additive Compositions of PVC Materials

7 types of PVC - *very different chemical compositions*

- Quantified following organic solvent extraction



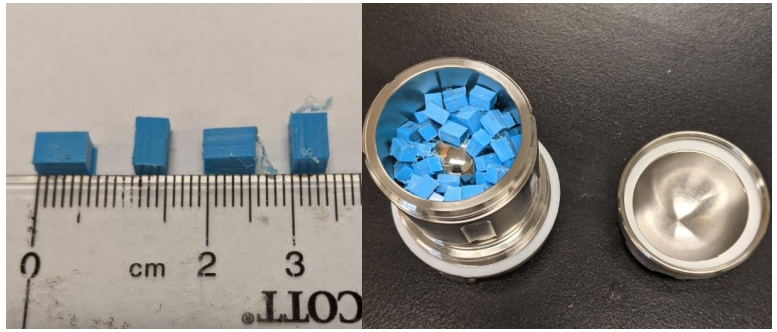
High concentration of DBT in Pipe materials A and B

High concentration of TPhP and EHDPP in Pellet G

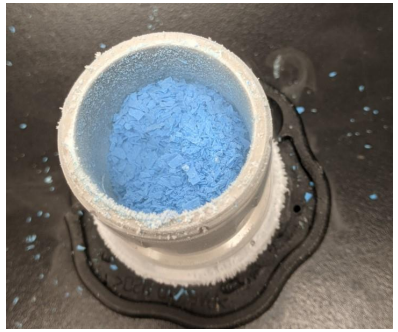
DBT - Dibutyltin dichloride TPhP - Triphenyl phosphate EHDPP - 2-Ethylhexyl diphenyl phosphate

Experimental Design:

Assessing leaching from PVC pipe and PVC pellets

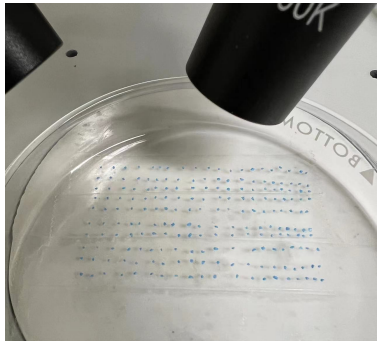


Pre-cryomilling

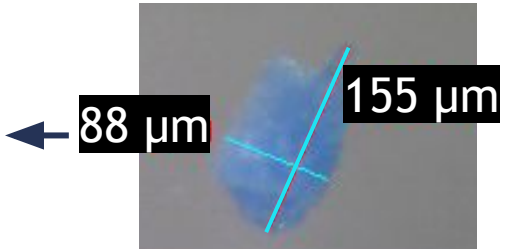


Post-cryomilling

Sieving



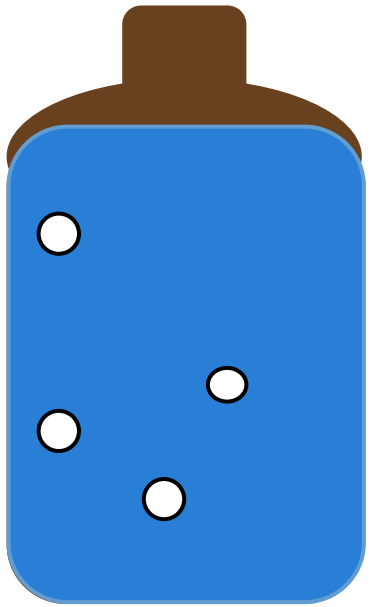
Two surface areas (sizes) prepared for each pipe:
~650 cm^2/g (45 µm)
~120 cm^2/g (500 µm)



Quantify particle size
(major and minor dims)

Leaching Method:

PVC MPs



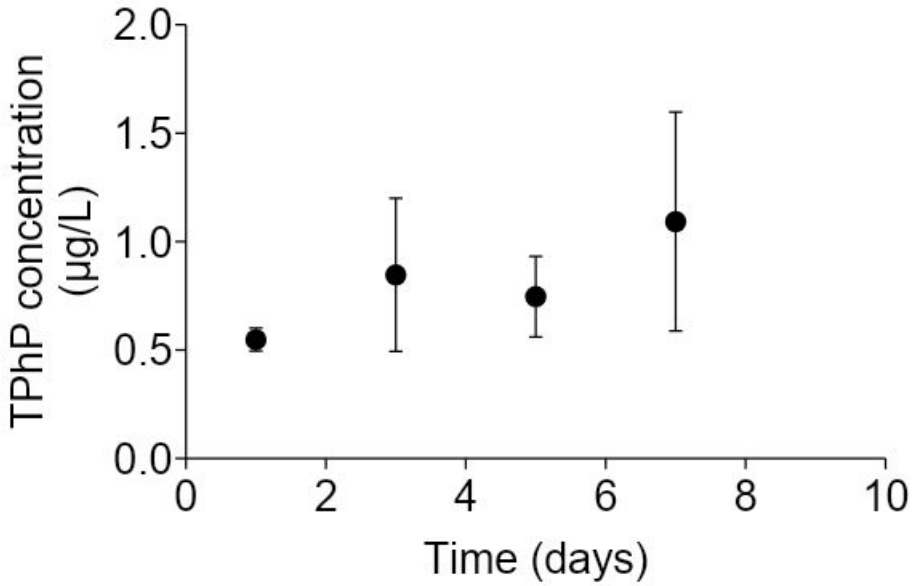
2 mL amber glass vial

Mixing

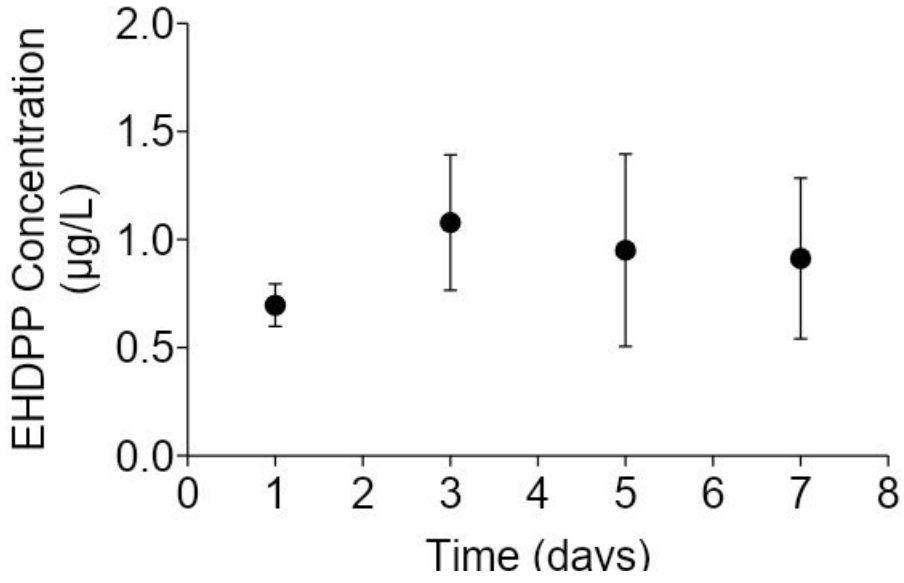
Measure residual

Organophosphorus Leaching from "Pellet G" (45 – 1000 µm)

TPhP (Triphenyl phosphate)



EHDPP (2-Ethylhexyl diphenyl phosphate)

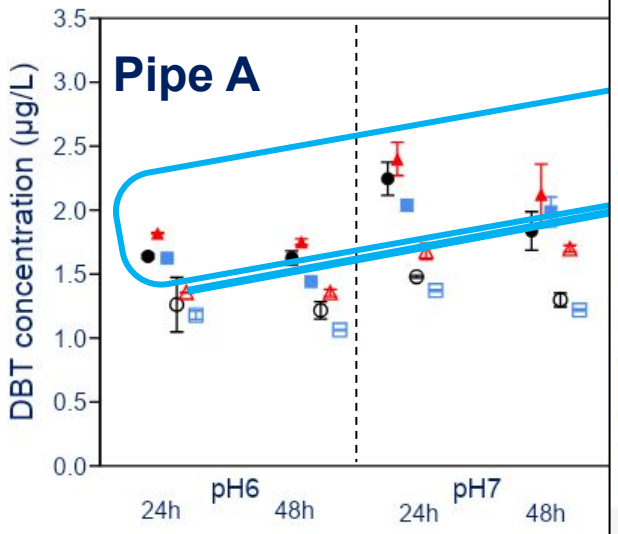


Higher standard deviation attributed to large particle size range with respect to pellets: 45 – 1000µm

(Lower surface area/mass - when compared to smaller particles)

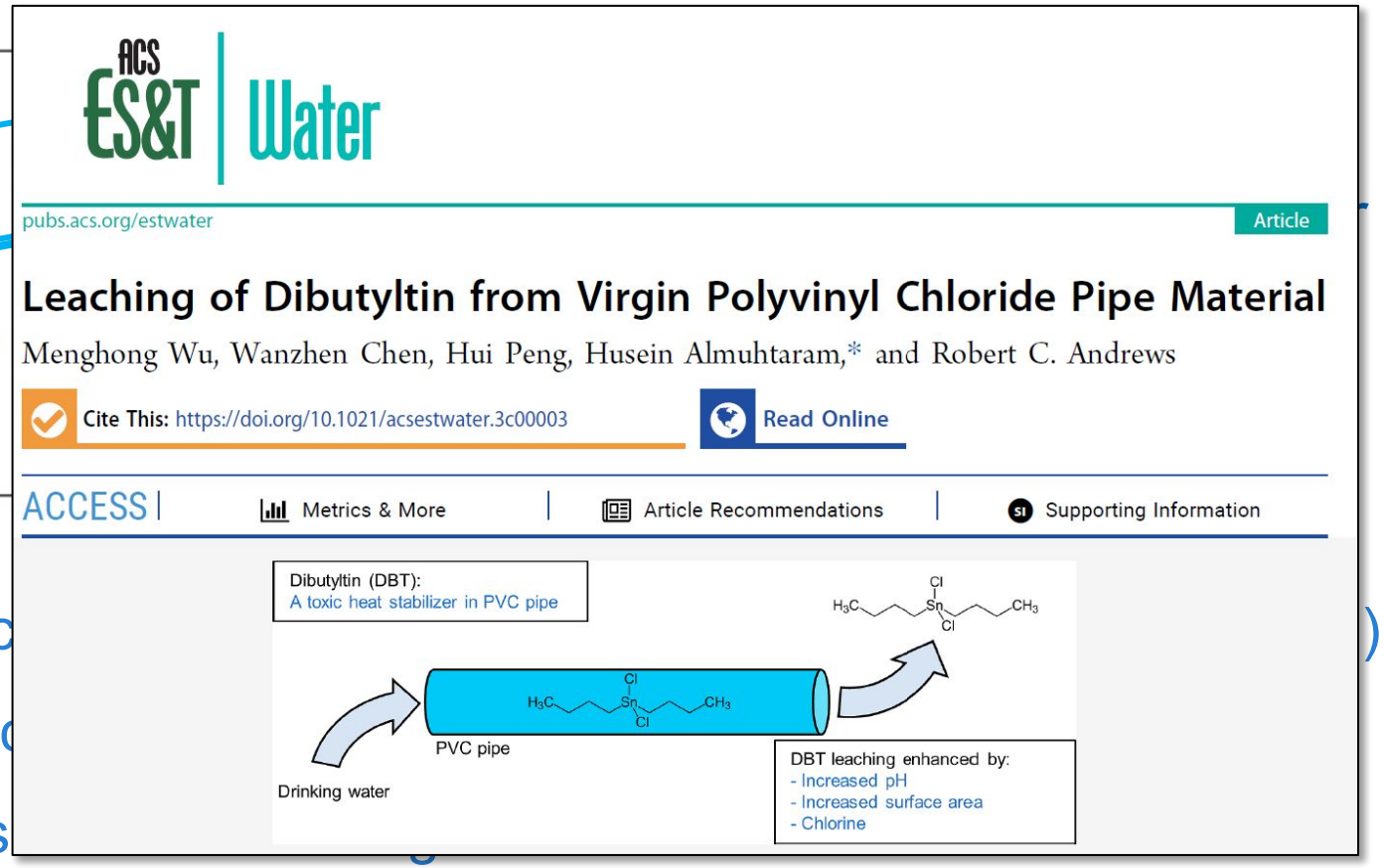
Impact of Particle Size, pH, and Presence of Chlorine/Chloramines on DBT Leaching (Pipe A, B, and C)

- Control (45 µm)



Types B & C

- Higher DBT leac) particles
- DBT leaching inc
- Chlorine increas



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Leaching of Dibutyltin from Virgin Polyvinyl Chloride Pipe Material

Menghong Wu, Wanzhen Chen, Hui Peng, Husein Almuhtaram,* and Robert C. Andrews

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Summary:

Specific composition of chemical additives for a given type of plastic (PVC) - widely vary

- Concern regarding associated toxicity

Leaching - pH dependent (for chemicals examined in this study)

- pH range 6 – 8, DBT leaching as pH

Presence of chlorine can increase leaching; chloramines did not exert appreciable effect.

Frequently Asked Questions:

1) Should we stop using PVC pipe?
   NO! Many questions yet to be answered
2) Is leaching observed in actual pipes or only particles?
   Study currently ongoing
3) What is the impact of temperature?
   Current study focused on 20 °C – other temps to be examined
4) What about PVC pipe employed in treatment processes (e.g. chlorine feed systems)?
   Potential for faster leaching, but must consider pipe lengths
5) Does leaching rate decrease over time?
   Potentially, but chemical additives part of material itself, not only on surface
   Study currently ongoing

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- Toronto Water
- York Region

Questions?

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