

High Molecular Weight PAHs in Microplastic Samples Collected Following the Sinking of the Container Ship X-Press Pearl

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### X-Press Pearl Microplastics Spill

# WAMU 88.5 I NEWS **V CULTURE** J MUSIC O PODCASTS & SHOWS Q SEARCH ENVIRONMENT LISTEN & FOLLOW 🕅 🖨 🥼 Sri Lanka Faces An Environmental **Disaster As A Ship Full Of Chemicals** Starts Sinking JUNE 2 2021 - 2-08 PM FT Laurel Wamsley

Smoke billows from the Singapore-registered container ship X-Press Pearl on Wednesday. The ship carries more than 80 containers of dangerous goods, including 25 tons of nitric acid.

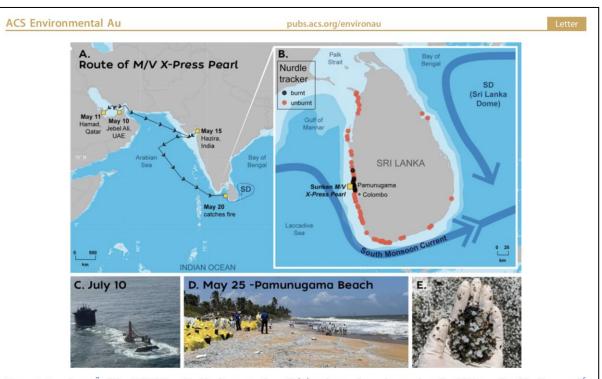
#### ENVIRONMEN 🔤 😳 💽 pubs.acs.org/environau The M/V X-Press Pearl Nurdle Spill: Contamination of Burnt Plastic and Unburnt Nurdles along Sri Lanka's Beaches Asha de Vos,\* Lihini Aluwihare, Sarah Youngs, Michelle H. DiBenedetto, Collin P. Ward, Anna P. M. Michel,\* Beckett C. Colson, Michael G. Mazzotta, Anna N. Walsh, Robert K. Nelson, Christopher M. Reddy, and Bryan D. James Cite This: ACS Environ. Au 2022, 2, 128–135 Read Online ACCESS Metrics & More Article Recommendations Supporting Information ABSTRACT: In May 2021, the M/V X-Press Pearl cargo ship May 25, 2021 - Pamunugama Beach, Sri Lanka caught fire 18 km off the west coast of Sri Lanka and spilled ~1680 tons of spherical pieces of plastic or "nurdles" (~5 mm; white in color). Nurdles are the preproduction plastic used to manufacture a wide range of end products. Exposure to combustion, heat, and chemicals led to agglomeration, fragmentation, charring, and chemical modification of the plastic, creating an unprecedented complex spill of visibly burnt plastic and unburnt nurdles. These unburnt burnt nurdle continuun nurdle pieces span a continuum of colors, shapes, sizes, and densities with high variability that could impact cleanup efforts, alter transport in the ocean, and potentially affect wildlife. Visibly burnt plastic was 3-fold more chemically complex than visibly unburnt nurdles. This added chemical complexity included combustion-derived polycyclic aromatic hydrocarbons. A portion of the burnt material contained petroleum-derived biomarkers, indicating that it

cyclic aromatic hydrocarbons. A portion of the burnt material contained petroleum-derived biomarkers, indicating that it encountered some fossil-fuel products during the spill. The findings of this research highlight the added complexity caused by the fire and subsequent burning of plastic for cleanup operations, monitoring, and damage assessment and provides recommendations to further understand and combat the impacts of this and future spills.

KEYWORDS: microplastic, pyroplastic, pollution, ship fire, contaminants, oil, maritime accident, citizen science

### Fate of the Ship and Nurdles

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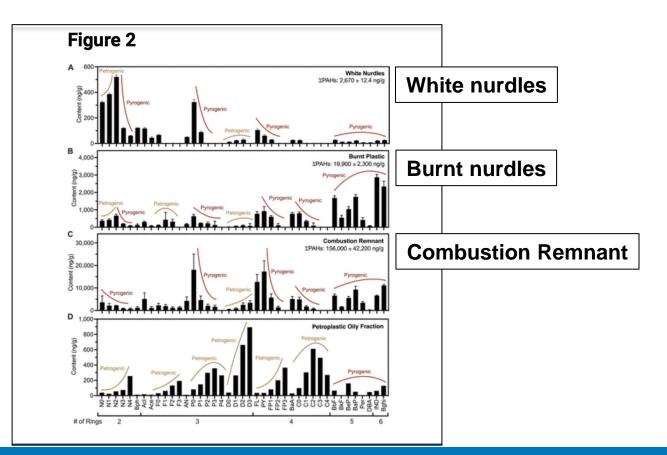
**Figure 1.** Travel route<sup>7</sup> of the M/V X-Press Pearl leading up to the spill (A) and map of crowd-sourced nurdle sightings collated by Oceanswell<sup>5</sup> between May 29 to July 11, 2021 (B). Photographs of (C) the ship after sinking taken on July 10 (photo credit: Conor Bolas, ITOPF), of (D) burnt plastic and unburnt nurdles that washed ashore onto Pamunugama beach, and of (E) a handful of them both; photographs were taken on May 25. Full-sized photographs are available in Figures S1 and S2.

# Spill Response: Characterization of Microplastics

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Divergent Forms of Pyroplas	pubs.acs.org/environau Article
X-Press Pearl Ship Fire	Fire and Oil Led to Complex Mixtures of PAHs on Burnt and Unburnt
<mark>Bryan D. James</mark> ,* Asha de Vos, Lihini I. Al Anna D. M. Michal Madr F. Hahn and Ch	Plastic during the M/V X-Press Pearl Disaster
Anna P. M. Michel, Mark E. Hahn, and Cl Cite This: ACS Environ. Au 2022, 2, 467–479	<mark>Bryan D. James</mark> ,* Christopher M. Reddy, Mark E. Hahn, Robert K. Nelson, Asha de Vos,* Lihini I. Aluwihare, Terry L. Wade, Anthony H. Knap, and Gopal Bera
ACCESS   III Metrics & More	Cite This: https://doi.org/10.1021/acsenvironau.3c00011
ABSTRACT: In late May 2021, the M/V X-Press Pe ship caught fire while anchored 18 km off the coast of Lanka and spilled upward of 70 billion pieces of plastic	ACCESS   Metrics & More Article Recommendations Supporting Information
(~1680 tons), littering the country's coastline. combustion, heat, chemicals, and petroleum produc apparent continuum of changes from no obvious effe consistent with previous reports of melted and bu (pyroplastic) found on beaches. At the middle of this nurdles were discolored but appeared to retain morphology, resembling nurdles that had been weat environment. We performed a detailed investigation of and surface properties of discolored nurdles collected	leading to the largest maritime spill of resin pellets (nurdles). The disaster was exacerbated by the leakage of other cargo and the ship's underway fuel. This disaster affords the unique

# **Differentiating Pyrogenic and Petrogenic PAHs**





# Why Look for More Than the US EPA 16 PAHs?

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Contents lists available at ScienceDirect

#### **Environmental Pollution**

journal homepage: www.elsevier.com/locate/envpol

#### Invited paper

Source-oriented risk assessment of inhalation exposure to ambient polycyclic aromatic hydrocarbons and contributions of non-priority isomers in urban Nanjing, a megacity located in Yangtze River Delta, China☆

Shaojie Zhuo<sup>a</sup>, Guofeng Shen<sup>a, d, \*</sup>, Ying Zhu<sup>b</sup>, Wei Du<sup>a</sup>, Xuelian Pan<sup>a</sup>, Tongchao Li<sup>a</sup>, Yang Han<sup>a</sup>, Bengang Li<sup>a</sup>, Junfeng Liu<sup>a</sup>, Hefa Cheng<sup>a</sup>, Baoshan Xing<sup>c</sup>, Shu Tao<sup>a</sup>

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- <sup>b</sup> Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YO, United Kingdom

"...inclusion of non-priority PAHs could be valuable for both PAH source apportionment and health risk assessment."

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<sup>&</sup>lt;sup>d</sup> Jiangsu Key Laboratory of Environmental Engineering, Jiangsu Provincial Academy of Environmental Sciences, Nanjing 210036, China

# Why Look for HMW PAHs? Toxicity





Aquilina "Evaluation of the cancer risk from PAHs by inhalation: Are current methods fit for purpose? Env.Intl. (2023)

# Why Look for HMW PAHs? Source Apportionment

nature About the journal ∽ Publish with us ∨ Explore content ~ nature > letters > article Letter | Published: 08 December 1983 **Retene**-a molecular marker of wood combustion in ambient air Thomas Ramdahl *Nature* **306**, 580–582 (1983) Cite this article

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## Adapting for HWM PAHs – GC-APCI

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#### **GC/MS Conditions:**

# Column: Rxi-5HT 15m x 0.25mm x 0.10 µm (Restek)

Temp Program: 31 min runtime

Carrier Gas: Nitrogen

Injection: Split 10:1, SSL at 380°C, 100% graphite o-ring, 4 mm straight liner with wool, graphite ferrules on head and tail of column, high temp BTO septum

Mass Spectrometer: Xevo™ TQ Absolute tandem quadrupole system

Ionization: GC-APCI+ , dry source, charge exchange

Corona current: 2.0  $\mu$ A Cone gas: 270 L/hr (N<sub>2</sub>) Make up gas: 350 L/hr (N<sub>2</sub>) Aux Gas: 200 L/hr (N<sub>2</sub>) CID Gas: 0.40 mL/min (N<sub>2</sub>)

Ramp (°C/min)	Temp °C	Hold (min)								
Initial	40	0.5								
14	160	0								
22	395	11								
Ramp (mL/min per min)	Flow (mL/min)	Hold (min)								
Initial	0.60	0								
0.015	0.90	0								
0.150	3.0	0								



# Acquisition Scheme: MRM Method Development

Compound Name	Parent (m/z)	Daughter	(m/z)	Α	Dv	vell (s)	Co	ne (	V)	Collision	(eV)	PIC	Co	omments	]		
coronene	300.0500	296.0500			0.002		50			100			N2				
coronene	300.0500	298.0500			0.002		50			75			N2				
Experiment Setup - c:\masslynx\xevo tq absolute.pro\a File Edit View Options Toolbars Functions Help	Compound	Name	Pare	ent	(m/z)	Daughte	er (m/z)	Α	D	well (s)		Cone (	V)	Collisio	n (eV)	PIC	Comments
	398		398.10	000		394.1000			0.005		60			95			N2
SIR MRM RadarScan R Points Per Peak: 32.787	398		398.10	000		396.1002			0.005		60			75			N2
Total Run Time: 24.00							10			1			20mir	s			
No.         Type           31         Image: MRM of 2 mass pairs, Time 15.20 to 16.50, API           32         Image: MRM of 2 mass pairs, Time 15.00 to 17.50, API           33         Image: MRM of 2 mass pairs, Time 16.00 to 17.50, API           34         Image: MRM of 2 mass pairs, Time 16.00 to 17.50, API           35         Image: MRM of 2 mass pairs, Time 16.00 to 17.50, API           36         Image: MRM of 2 mass pairs, Time 16.00 to 17.50, API           37         Image: MRM of 2 mass pairs, Time 16.00 to 17.50, API           38         Image: MRM of 2 mass pairs, Time 16.00 to 17.50, API           39         Image: MRM of 2 mass pairs, Time 17.00 to 18.50, API           39         Image: MRM of 2 mass pairs, Time 17.00 to 18.50, API           40         Image: MRM of 2 mass pairs, Time 17.00 to 18.50, API           41         Image: MRM of 2 mass pairs, Time 17.00 to 18.50, API           42         Image: MRM of 2 mass pairs, Time 18.00 to 19.50, API           43         Image: MRM of 2 mass pairs, Time 18.00 to 19.50, API           44         Image: MRM of 2 mass pairs, Time 19.00 to 21.00, API           45         Image: MRM of 2 mass pairs, Time 19.00 to 21.00, API           46         Image: MRM of 2 mass pairs, Time 19.00 to 21.00, API           47         Image: MRM of 2 mass pairs, Time 19.00 to 21.00, API <td< td=""><td>I+ (dah anth d14) I+ (coronene) I+ (ae ai ah pyr) I+ (314) I+ (314) I+ (324) I+ (3228) I+ (328) I+ (328) I+ (340) I+ (328) I+ (350) I+ (352) I+ (350) I+ (352) I+ (366) I+ (376) I+ (376) I+ (400)</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>Time</td><td></td><td></td><td></td><td></td><td></td><td></td><td>^</td></td<>	I+ (dah anth d14) I+ (coronene) I+ (ae ai ah pyr) I+ (314) I+ (314) I+ (324) I+ (3228) I+ (328) I+ (328) I+ (340) I+ (328) I+ (350) I+ (352) I+ (350) I+ (352) I+ (366) I+ (376) I+ (376) I+ (400)									Time							^
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### Pseudo-MRM for EI GC/MS of PAHs



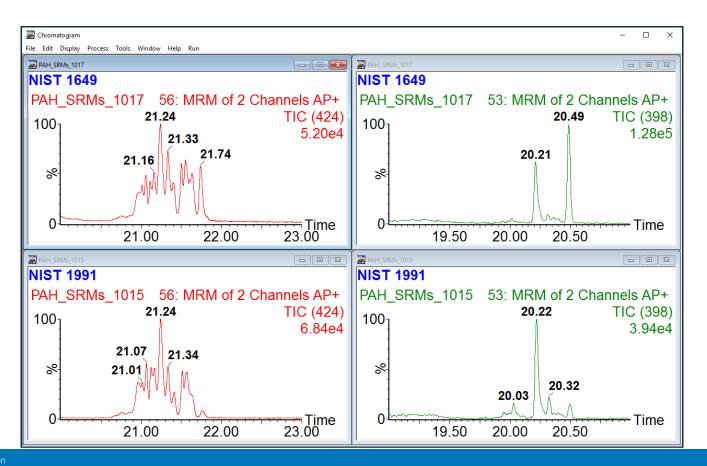


Lian (2016) Analysis of polycyclic aromatic hydrocarbons...)

#### SRM NIST 1991: Mixed Coal Tar/Petroleum Extract

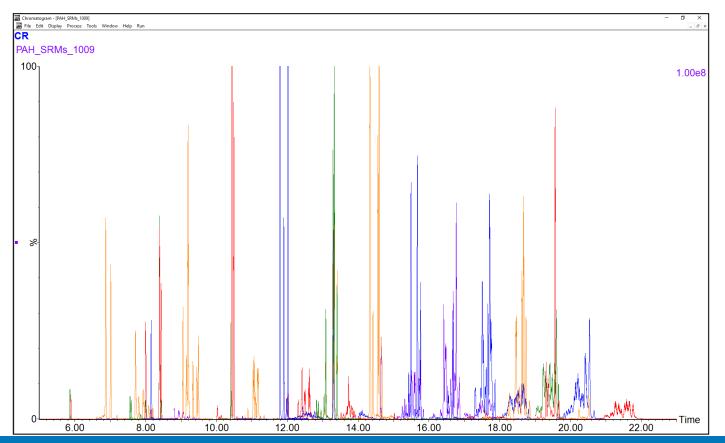
#### E Chromatogram - [PAH\_SRMs\_1015] - 🗆 X File Edit Display Process Tools Window Help Run - 8 × **NIST 1991** PAH\_SRMs\_1015 17.49 100<sub>1</sub> 17.67 314 – 424 Da PAHs % 18.27 19.22 18.65 19.55 23.00 17.00 18.00 19.00 21.00 22.00 20.00

### Comparing NIST SRM 1649 (Urban Dust) and 1991

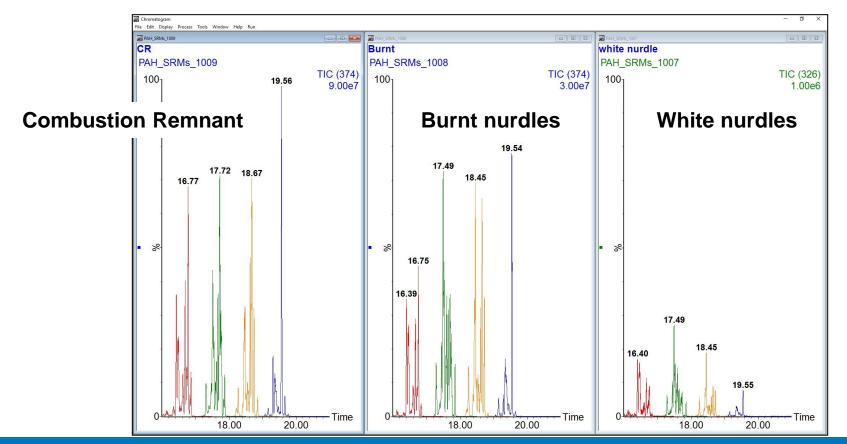


#### **Combustion Remnant Extract**

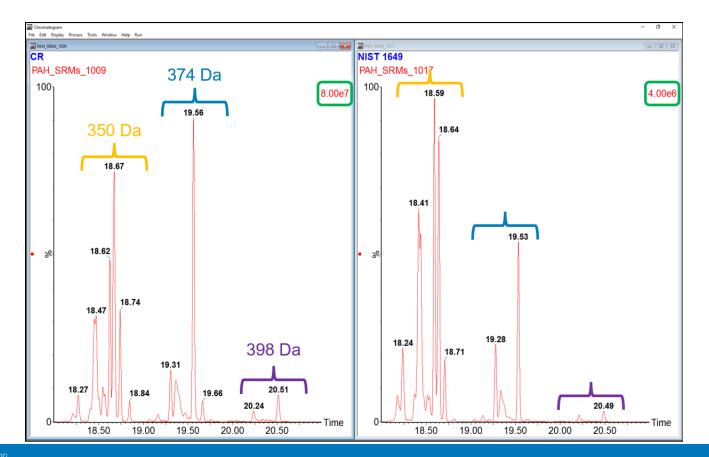




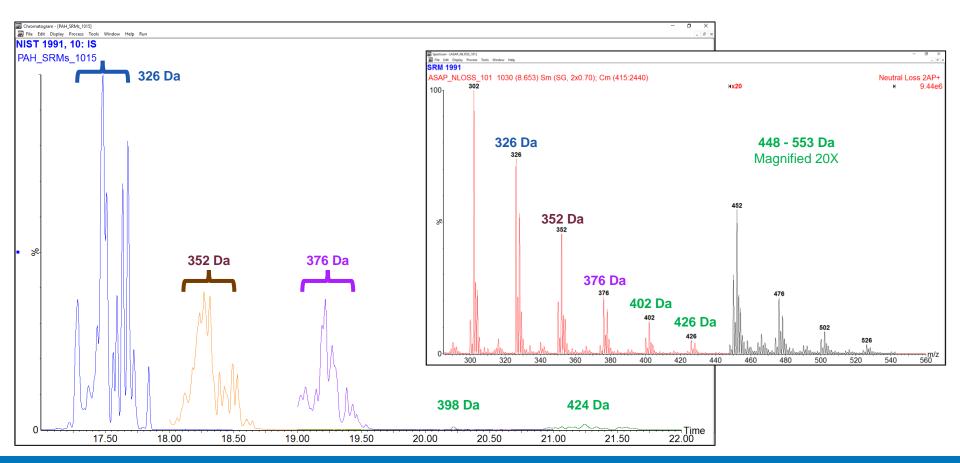
# Comparing HMW PAH Profiles of Different MPs



#### Comparing MP with NIST 1649 (Urban Dust)



#### MRM Chromatogram v. NLoss Direct Probe Spectrum



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#### Conclusions

- Analysis of an expanded range of HMW PAHs in unfractionated extracts of MPs was achieved using a standard GC-APCI QqQ configuration combined with a simple, generic microextraction
- Charge transfer, atmospheric pressure chemical ionization facilitated the implementation of a class-specific MRM acquisition scheme
- Only minor modification to the original GC method required
- Nitrogen carrier gas achieved elution of HWM PAHs with symmetric, narrow peaks through the use of flow programming
- Further investigation of HMW PAHs for potential source markers and toxic compounds is enabled with this approach

#### Acknowledgements

### Waters™

- Stephanie Crombie
- Daniel Furlong

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of Canada

# Thank you for your attention!

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