Concentration and Distribution of Tire-Derived Chemicals in Tamsui River watershed

Yu-Ching Cheng[1], Cheng-Shiuan Lee[2]

(1) Department of Agricultural Chemistry, National Taiwan University, Taipei, Taiwan
(2) Research Center for Environmental Changes, Academia Sinica, Taipei, Taiwan

Introduction

Tire wear particles (TWPs) are an important but often overlooked source of microplastic pollution. A tire antioxidant **6PPD** transforms in the environment into **6PPD-quinone (6PPD-Q)**, a compound linked to acute mortality in Coho salmon and potentially harmful to other aquatic life, which has attracted increasing concerns globally. However, its occurrence in subtropical urban rivers is poorly understood. We investigated 6PPD-Q in **suspended particulate matter (SPM)** from **23 sites** across the Dahan, Xindian, Keelung, and Tamsui rivers in northern Taiwan, with one Tamsui River site sampled hourly from 08:00–20:00. Concentrations (0.6–25.8 ng/g, d.w.) were measured using **LC–MS/MS**, and additional **tire-derived chemicals (TDCs)** were identified with **IMS QToF MS**. Our study confirmed that 6PPD-Q is widespread throughout the Tamsui River watershed. A clear spatial pattern emerged: higher concentrations occurred in upstream, low-salinity zones. Correlation analysis indicated that distance to the river mouth (r = 0.37) and salinity (r = –0.51) are key environmental drivers of 6PPD-Q distribution. The partition coefficient (K_d) ($10^{2.68}$ – $10^{5.19}$)—the ratio of 6PPD-Q concentration in SPM to that in water—was significantly positive correlated with salinity (r = 0.52). This suggests that although 6PPD-Q is more water-associated overall, seawater intrusion could enhance 6PPD-Q enrichment on SPM. Furthermore, we found a strong positive correlation (r = 0.68) between the proportion of 6PPD-Q concentration in SPM relative to the total concentration in both SPM and sediments, and the distance from the river mouth, suggesting that 6PPD-Q bound to SPM progressively settles out of the water column as it moves downstream. This work provides a foundational understanding of 6PPD-Q behavior in northern Taiwan urban rivers and underscores the need for further research on its ecological impacts.

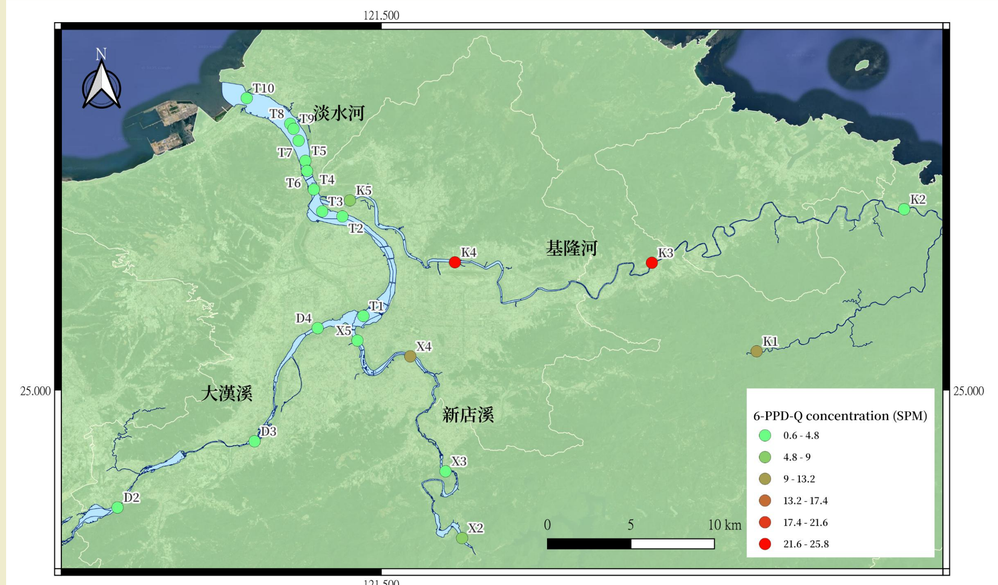
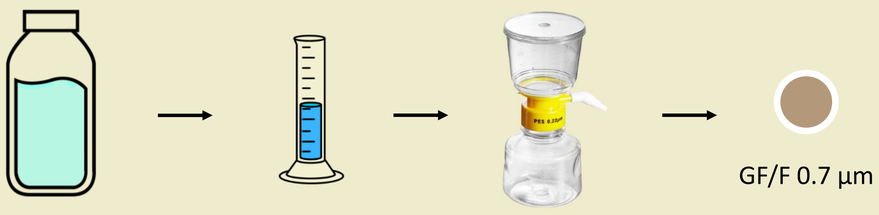


Fig. 1. Spatial distribution of 6PPD-Q concentrations in suspended particulate matter (SPM) across the Dahan, Xindian, Keelung, and Tamsui Rivers in northern Taiwan.

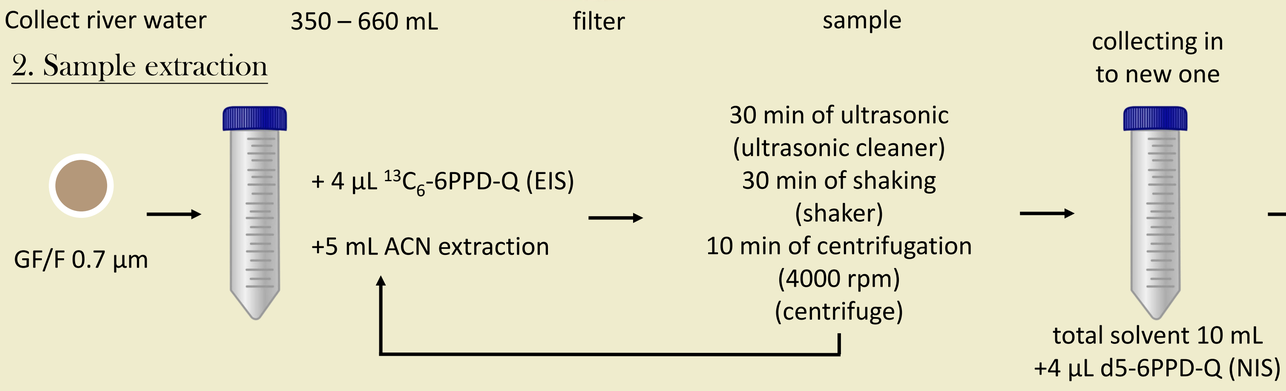
Experimental process

1. Sample collection



Collect river water → 350 – 660 mL → filter → GF/F 0.7 µm sample

2. Sample extraction



3. Sample analysis

Waters TQ-Absolute UPLC–MS/MS
This system was used for the quantitative analysis of 6PPD-Q and its isotopic internal standard.

Waters Vion IMS QToF MS
This high-resolution mass spectrometer was used to perform non-target analysis for the identification and confirmation of other TDCs besides 6PPD-Q.

Results

1. UPLC-MS/MS (Target Analysis)

Distribution

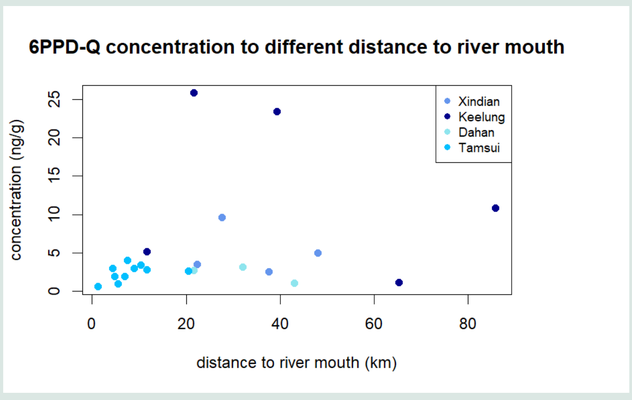


Fig. 2. The data points are color-coded by river. The overall trend indicates that 6PPD-Q concentrations tend to increase at locations further from the river mouth (i.e., upstream regions), especially in the Keelung and Xindian rivers.

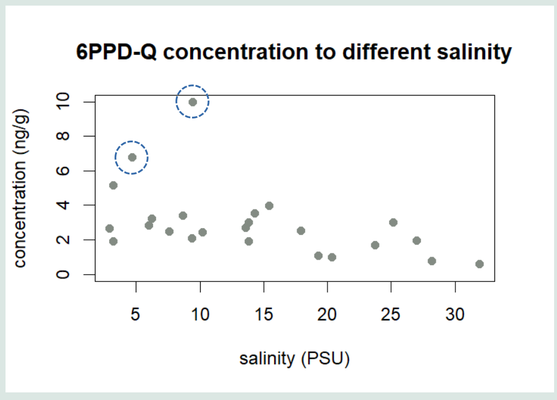


Fig. 3. Relationship between 6PPD-Q concentration and salinity. The data points indicate a general negative correlation, with higher 6PPD-Q concentrations observed in areas of lower salinity, suggesting a conservative mixing behavior of 6PPD-Q in the estuary. (Selecting the stations that salinity>1.)

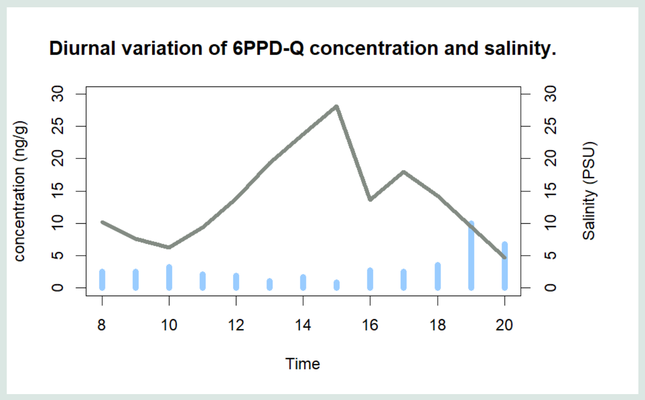


Fig. 4. Diurnal variation of 6PPD-Q concentration and salinity at the time-series station. The figure illustrates that 6PPD-Q concentration fluctuates over time, showing a negative correlation with the changes in salinity.

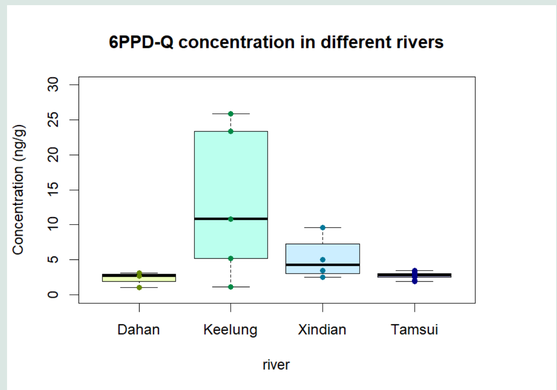


Fig. 5. Comparison of 6PPD-Q concentrations across different rivers. The figure shows that the Keelung River has a noticeably higher median 6PPD-Q concentration compared to the other rivers, while the Dahan and Tamsui Rivers have relatively lower concentrations. However, the **Kruskal-Wallis test** results indicate no statistically significant difference between the groups, which may be due to the low sample size, resulting in a lack of statistical power.

Discussion

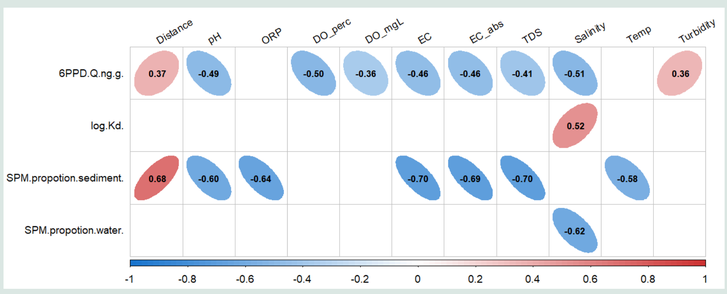


Fig. 6. Pearson correlation matrix showing the relationships between 6PPD-Q concentration and various environmental parameters with non-significant values (p>0.05) omitted.

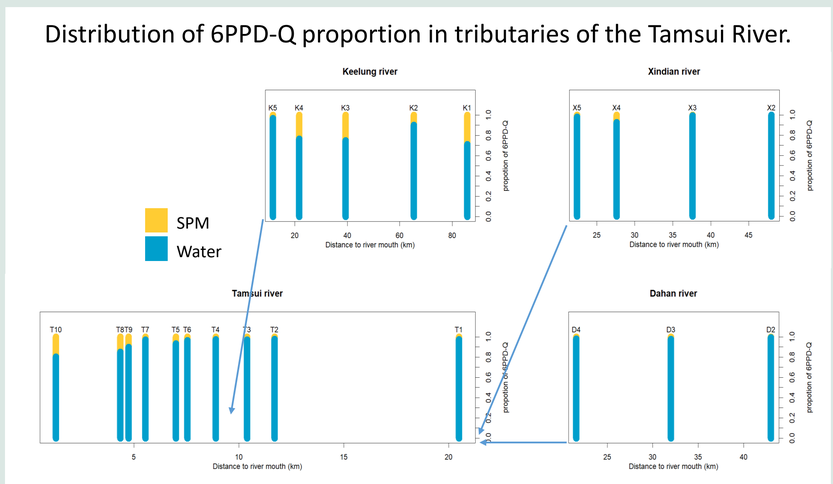


Fig. 7. This figure presents the proportion of 6PPD-Q in SPM (yellow) and water (blue) across sampling sites in the Keelung, Xindian, Dahan, and Tamsui rivers. The plot illustrates that while 6PPD-Q is predominantly found in water, a notably higher proportion of SPM-associated 6PPD-Q is observed at Keelung River and Tamsui River.

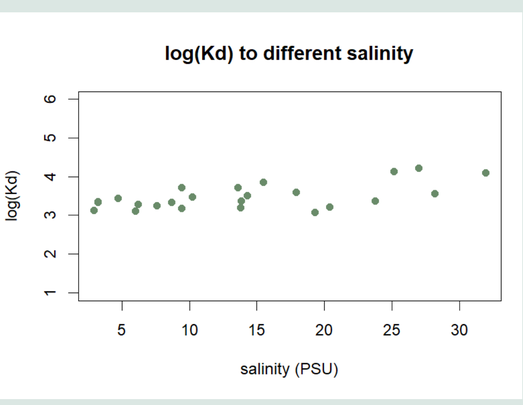


Fig. 8. The data points show a positive relationship, indicating that the tendency of 6PPD-Q to partition onto SPM increases as salinity increases. (K_d=C_{SPM}/C_{Water})

C_{water} data credit: Ching-Chieh Chen

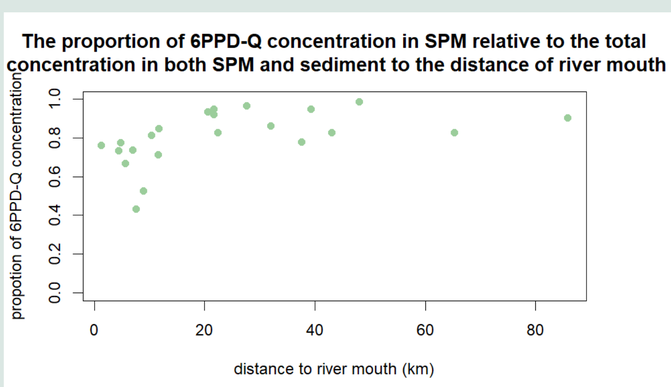


Fig. 9. This plot illustrates the relationship between the proportion, as a function of the distance (km) to the river mouth. This indicates that particles carrying 6PPD-Q move downstream with the current and gradually settle, leading to a decrease in the concentration of particle-bound 6PPD-Q in the water column.

$C_{sediment}$ data credit: Wei-Hung Wang

2. Vion IMS QTof MS (Non-target Analysis)

#	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Station ID	X2	X3	X4	X5	K1	K2	K3	K4	K5	D2	D3	D4	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
compounds	8PPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	CPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	CPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	DPG
	IPPD-Q	CPPD-Q	CPPD-Q					6QDI	CPPD-Q			IPPD-Q					DPG	DPG	DPG	DPG	DPG	IPPD-Q
			6QDI					IPPD-Q										6QDI				
								CPPD														

#	23	24	25	26	27	28	29	30	31	32	33	34	35
Station ID	GT1	GT2	GT3	GT4	GT5	GT6	GT7	GT8	GT9	GT10	GT11	GT12	GT13
compounds	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	IPPD-Q	DPG	IPPD-Q	IPPD-Q
	DPG	DPG		DPG	6QDI	DPG	DPG		DPG	6QDI	IPPD-Q	DPG	DPG
					DPG					DPG	6QDI		

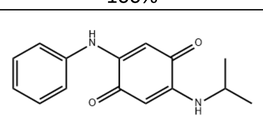
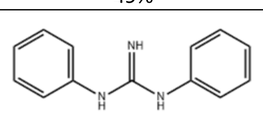
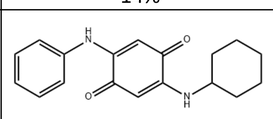
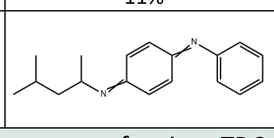
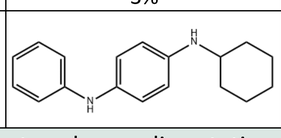
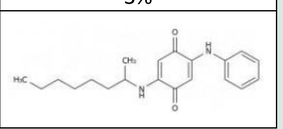
TDCs	IPPD-Q	DPG	CPPD-Q	6QDI	CPPD	8PPD-Q
Detected frequency	100%	49%	14%	11%	3%	3%
structure						

Fig. 10. Spatial distribution of other TDCs detected by **Vion IMS QToF**. This figure shows the presence of various TDCs at each sampling station, with the compounds ranked by concentration. IPPD-Q was detected at all locations, while DPG was mainly found in the downstream Tamsui River. The occurrence of CPPD-Q, 6QDI, CPPD, and 8PPD-Q was sporadic.

Conclusions

Pearson correlation matrix was used to identify key relationships between 6PPD-Q concentration, its partitioning behavior, and various environmental parameters.

- **Salinity and Dilution**

Both spatial and temporal data (Figs. 3 & 4) show a negative correlation between 6PPD-Q concentration and salinity. This is primarily due to the dilution effect as freshwater containing the contaminant mixes with a larger volume of seawater at the estuary.

- **Distribution Patterns**

While the Kruskal-Wallis test showed no statistically significant differences in 6PPD-Q concentrations between the four rivers (Fig. 5), the spatial plots (Fig. 2) indicate that the highest concentrations occur in the midstream urban areas, highlighting these as primary source zones.

- **Water-Sediment Relationship**

The data suggest a complex relationship between 6PPD-Q and particulate matter. The partition coefficient (K_d) indicates that 6PPD-Q has a medium affinity to SPM. As salinity increases, a higher proportion of 6PPD-Q is found on suspended particles (Fig. 8), likely due to flocculation and salting-out effect.

- **Other Tire-Derived Chemicals**

Our analysis identified six other TDCs in SPM, with IPPD-Q being the most widespread. This highlights the chemical complexity of tire wear particles, suggesting that a multifaceted approach is required for their effective removal and a need for further research on their potential ecotoxicological effects.