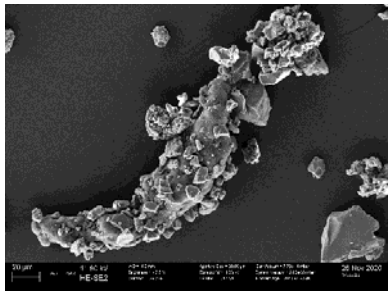
UFZ HELMHOLTZ Centre for Environmental Research

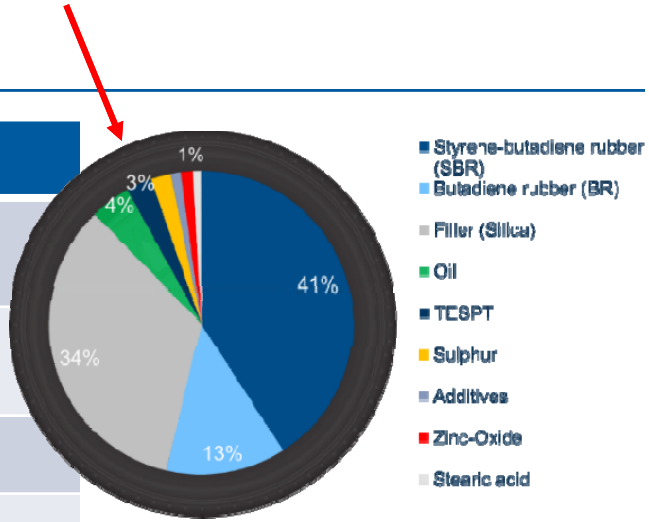
Tire Wear Particles and Associated Chemicals in the Environment

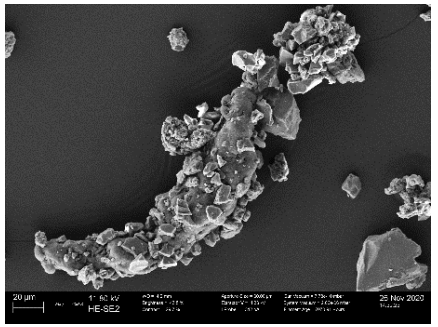


Thorsten Reemtsma

Additives in Tires

Class of chemicals	Chemicals*	function
phenylendiamines	6-PPD, 7-PPD, IPPD, BENAPT	antioxidants
benzothiazoles	OBS, CBS, MTBT etc	vulcanization accelerators
methoxymethyl melamines	HMMM etc	adhesive
guanidines	DPG	vulcanization accelerators

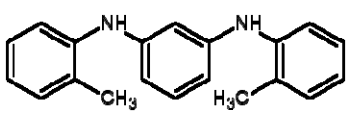




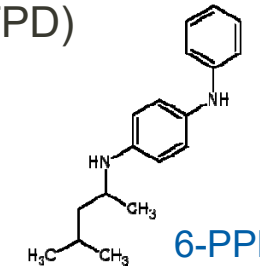
- *) and their transformation products formed during tire production and use
- Tire and Road wear particles (TRWPs) contain constituents
  - of tires
  - and of roads!

Phenylendiamines as Antioxidants

- 6-PPD
- 7-PPD
- IPPD
- BENAPT (DPPD, PTPD, DTPD)



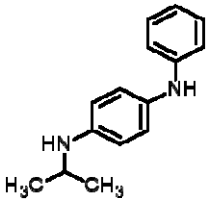
DTPD



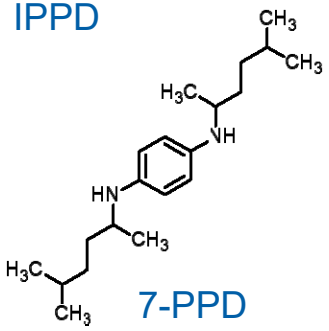
6-PPD

- To prevent degradation and cracking due to oxidation of the rubber
  - Formation of transformation products of antioxidant inevitable

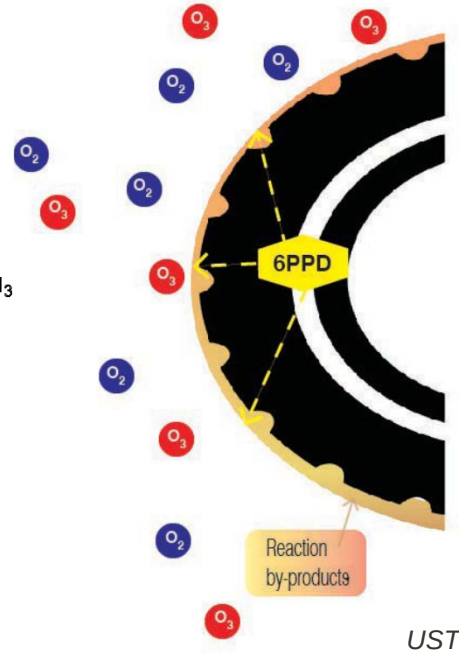
- Not homogenously distributes in the tire



IPPD



7-PPD



USTMA

6-PPDQ – Aspects of This Presentation

- Amounts
- Reactivity
- Availability

Amounts – What are we talking about?

Region	tire wear emission rates [x10^3 t/a][a]					
	passenger cars	trucks[b] & busses	urban	rural	highway	total
EU (2014)	264[c, d]	1063[c, d]	n/a	n/a	n/a	1327[c,d]
Germany (2014)	52	81	40	45	48	133
USA (2010)	500	620	750	370		1120

Wagner et al. (2019) Water Research 139, 83-100

6-PPD
13
11

- Assuming 1% of 6-PPD in tire rubber
- LC_{50} of 6-PPDQ for coho salmon: 95 ng/L
  - Tian et al. (2022) Environ. Sci. Technol. Lett.

- How do 11 x 10^3 t/a of 6-PPD potentially (!) spread with TRWPs on roads in the US
- compare to 95 ng/L of 6-PPDQ toxic to coho salmon in surface water?

Determination of TRWPs in the Environment – Analytical Challenges

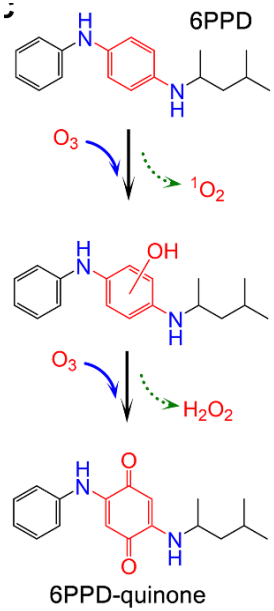
TRWPs difficult to detect

- Py-GC-MS
  - Information on the amount of rubber (SBR/NR)
- Single particle analysis (SPA)
  - Kovochich et al. (2021) Environ. Sci. Technol. Lett. 8, 1057.
- Zn after density separation
  - Kloeckner et al. (2019) Chemosphere 222, 714.
- Organic markers
  - e. g. Kloeckner et al. (2021) Environ. Sci. Technol. 55, 11723

Challenges

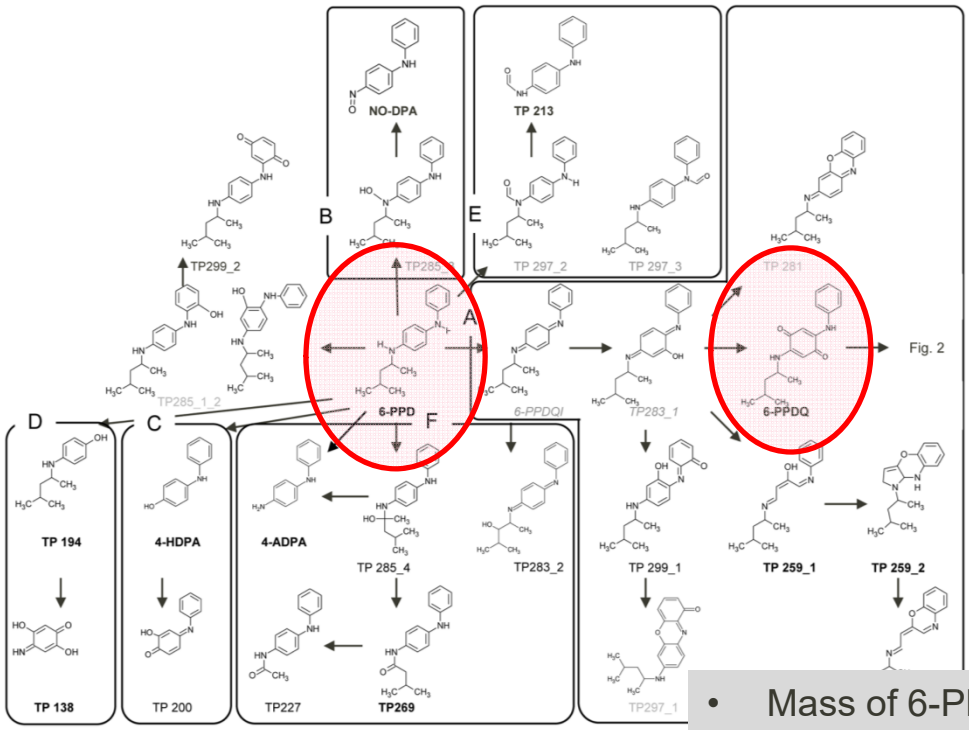
- Influence of mineral matrix on monomer formation
- Monomer formation from organic matter
- Effort and costs
- Appropriate density window for aged TRWPs
- Limited sensitivity
- Not established
- Once released from TRWPs chemicals move around independently

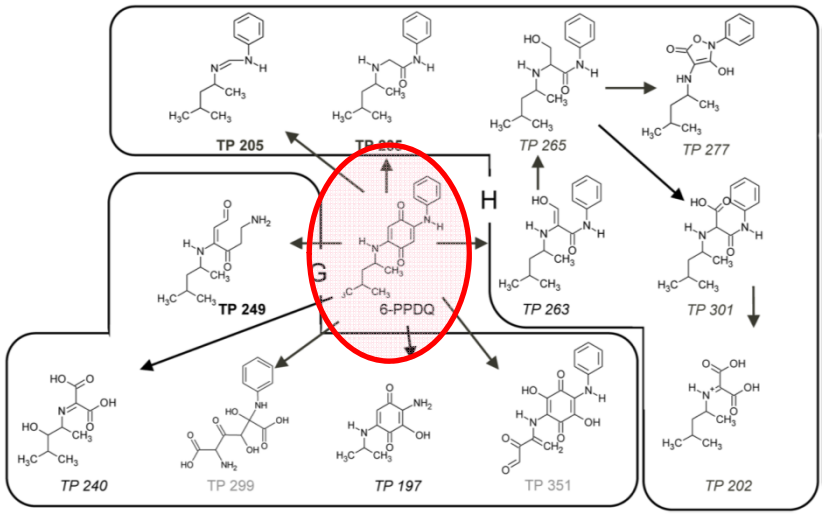
Oxidative Abiotic Transformation of 6-PPD



- It‘s more complex than this!

Oxidative Abiotic Transformation of 6-PPD





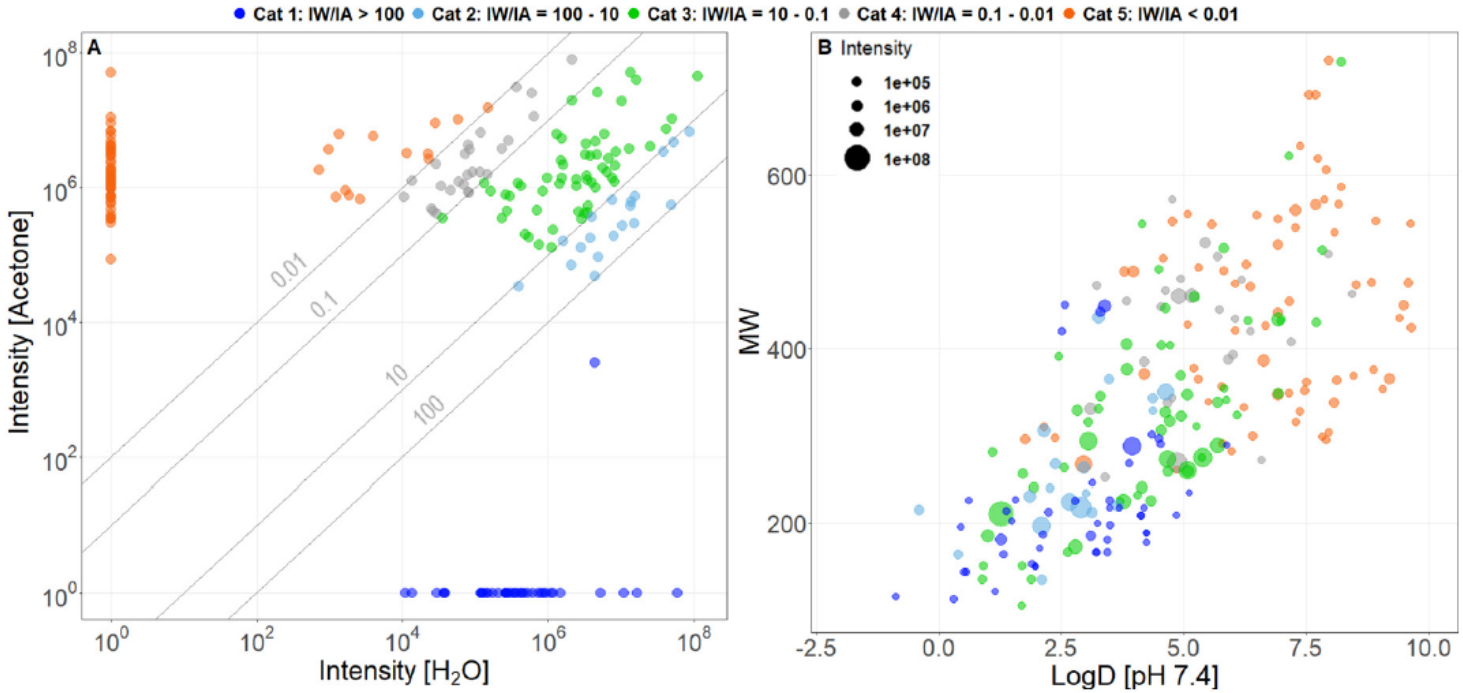
- 38 TPs detected and structures proposed
- 14 TPs detected in WWT effluent

- Mass of 6-PPD in TRWPs cannot be converted 1:1 into 6-PPDQ
- What is the conversion factor?

Seiwert et al. (2022) Water Research 212, 118122

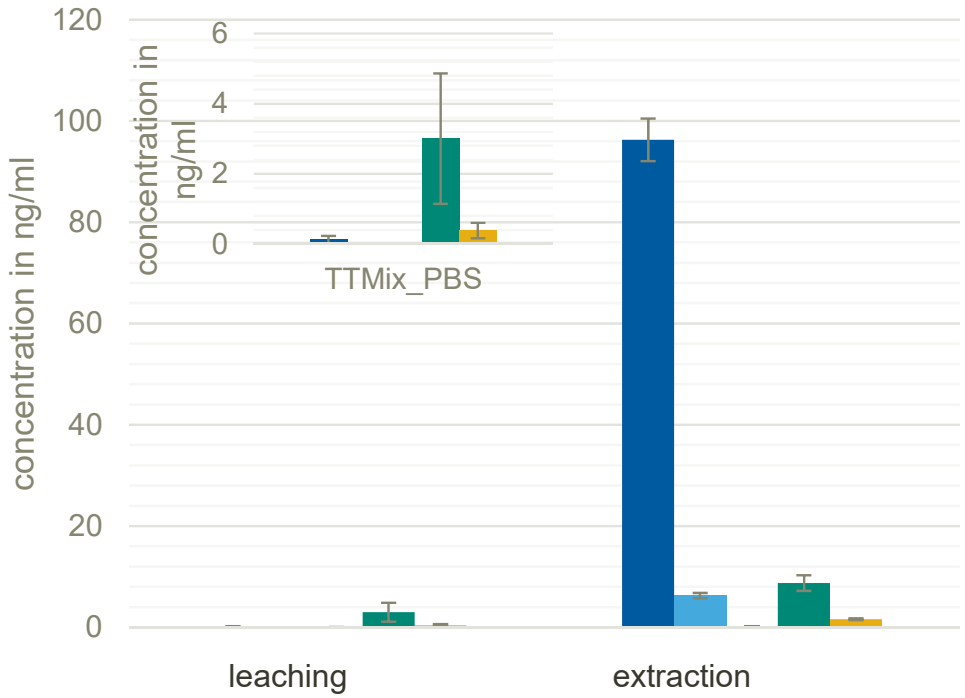
Leaching of Chemicals from Tire Particles

- **Extractable vs. leachable concentration of chemicals detected from tires**



Müller et al. (2022) Sci. Tot. Environ. 802, 149799

Leaching of Chemicals from Tire Particles

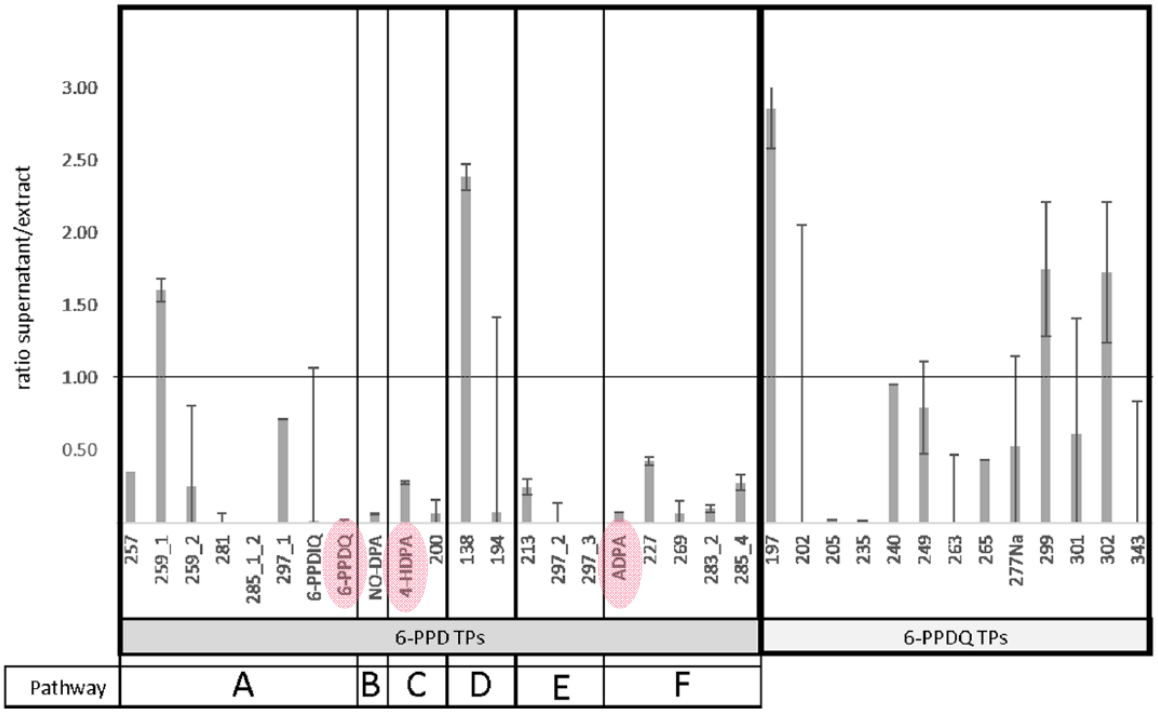


- Most of 6-PPD and 6-PPDQ remains in TRWPs after leaching for 1h in ultrasound
  - Thermodynamics
  - Kinetics?

UFZ (2022) unpubl.

6-PPD and Transformation Products in Snowmelt

- **Ratio of mass in water phase to mass in particles**

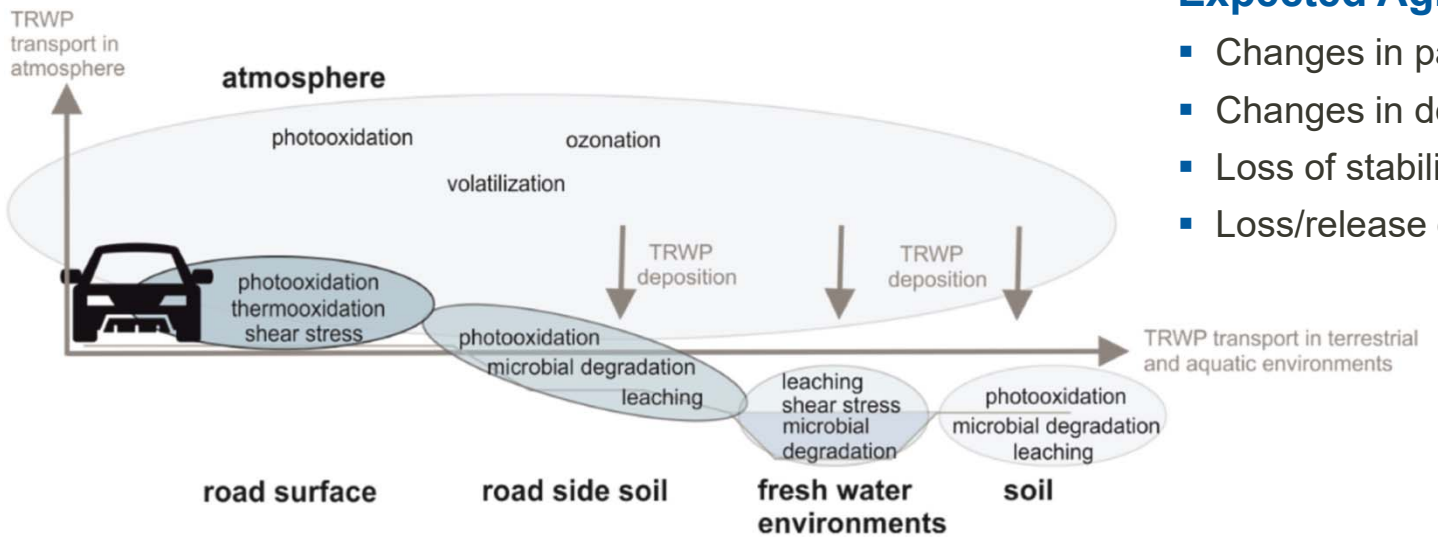


majority in water

majority in particles

Seiwert et al. (2022) Water Res.

Aging of TRWPs



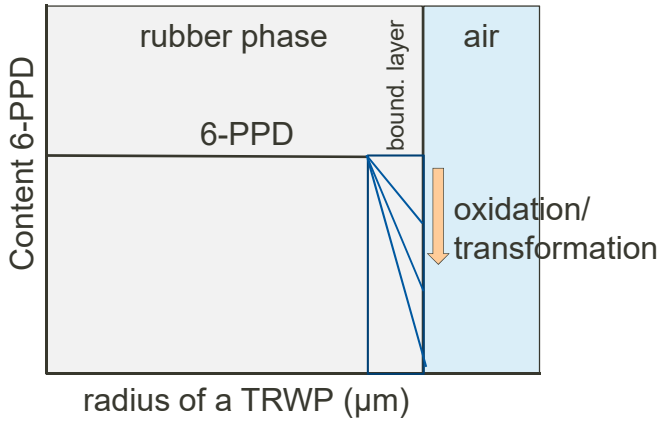
Wagner et al. (2021) Chemosphere

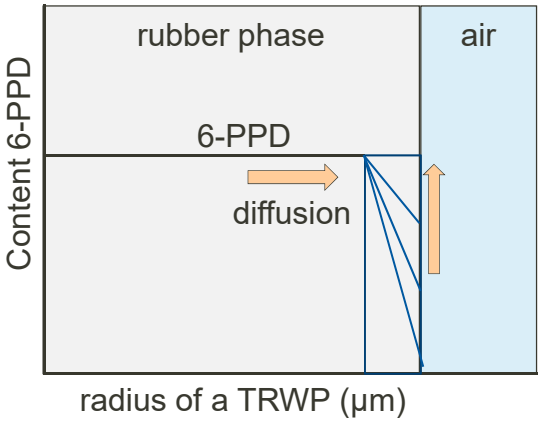
Expected Aging Effects

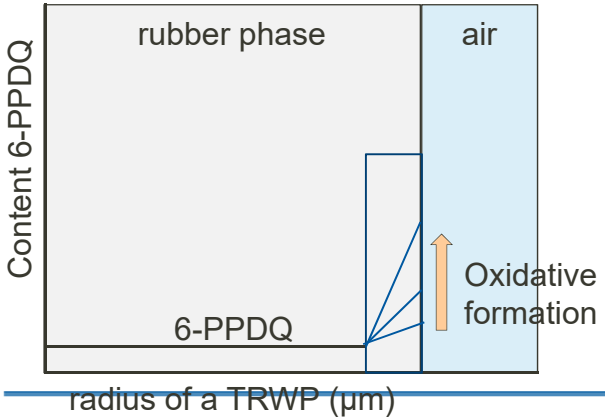
- Changes in particle size
- Changes in density
- Loss of stabilizing chemicals
- Loss/release of chemicals

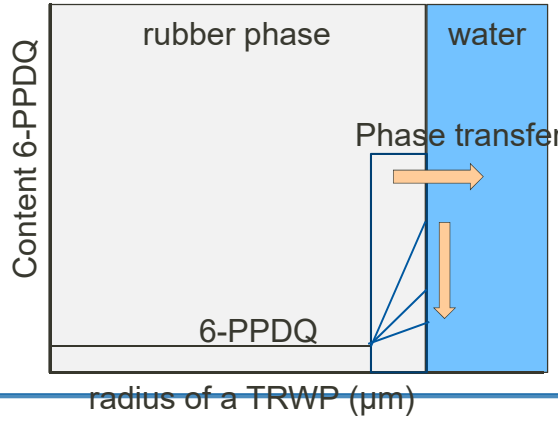
- Limited knowledge on extent and importance of aging effects in the environment

Processes Affecting 6-PPDQ Content in a TRWP









6-PPDQ Concentration in Surface Water

Influencing factors

- Amount of TRWPs deposited at a given site
- 6-PPD concentration in TRWP
- Diffusion rate to TRWP surface
- Rate of transformation to 6-PPDQ
  - Rates of competing transformations
- Rate of 6-PPDQ release from TRWP into surrounding water
- Exchange of water from the boundary layer with the bulk water
- Dilution factor with bulk water

Possible measures

- ➢ Reduced by various measures
  - ➢ e.g. street cleaning, runoff treatment, etc
- ➢ Substitution (but avoid regrettable substitution!)
- ➢ Slowed down by reduced oxygen availability
  - ➢ e.g in sediments
- ➢ Reduced by TRWPs being burried in sediments

Conclusions? / Guesses!

- Most transport of chemicals from TRWPs with road runoff occurs with the particulate phase rather than dissolved in water.
- Importance of dissolved phase increases with polarity of chemicals
- About 10 x 10^3 t/a of 6-PPD would be spread with TRWPs in the US.
  - If not transformed beforehand during use
- 6-PPD in TRPWs only partially transformed into 6-PPDQ.
  - This proportion is, likely, quite variable.
- Retaining TRWPs from road runoff certainly reduced the load of 6-PPD and 6-PPDQ arriving at surface waters.
  - There are several good reasons for runoff treatment.
- Burial of TRWPs in sediments should slow down the formation and the release of 6-PPDQ.

Acknowledgements and Contact

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- http://www.ufz.de/analytics

- Kloeckner et al. (2019) Tire and road wear particles in road environment - Quantification and assessment of particle dynamics by Zn determination after density separation. Chemosphere 222, 714.
- Kovochich et al. (2021) Characterization of individual tire and road wear particles in environmental road dust, tunnel dust, and sediment. Environ. Sci. Technol. Lett. 8, 1057.
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- Kloeckner et al.. (2021) Organic markers of tire and road wear particles in sediments and soils: Transformation products of major antiozonants as promising candidates. *Environ. Sci. Technol.* **55**, 11723.
- Seiwert et al. (2022) Abiotic oxidative transformation of 6-PPD and 6-PPD quinone from tires and occurrence of their products in snow from urban roads and in municipal wastewater. Water Res 212, 118122.