The Fate of 6PPD-Quinone in Soil and Water-Sediment Systems using a ^{14}C Radiotracer

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Abstract

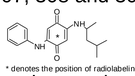
The antiozonant and antioxidant 6PPD (N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine) and its transformation product 6PPD-quinone (6PPD-Q) are believed to be carried from tire and road wear particles (TRWP) and washed into watercourses. Some publications have identified 6PPD-Q as a contributor to Urban Runoff Mortality Syndrome (URMS) of a single specific fish species, Coho salmon.

The environmental fate in soils, water-sediment systems and surface-waters has been investigated using ^{14}C-6PPD-Q to track the partitioning and transformation products.

This presentation focuses on the initial results, including identification and quantification of transformation products generated during these studies. The studies are ongoing, so preliminary data is presented here.

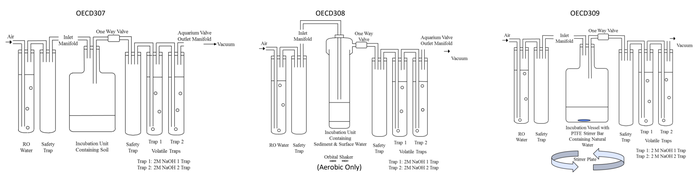
Materials and Methods

- Experiments were set up according to OECD Guidelines 307, 308 and 309.
- Radiolabeled 6PPD-Q was custom-synthesized with the universal labeling position in the quinone ring.



* denotes the position of radiolabeling

- Soils and sediments were selected to have different properties, such as pH, textural classification and biomass content.
- For the OECD 307, 308 and 309 the same general experimental setup was used with sodium hydroxide traps to collect any CO_2 that was evolved.



- Nitrogen was passed through anaerobic systems instead of air.
- In the OECD 307 study anaerobic conditions will be initiated once the half-life (DT_{50}) is reached under aerobic conditions or after 30 days incubation under aerobic conditions. Soil units are flooded with water and nitrogen passed through at this stage.
- 6PPD-Q was applied to soils (OECD 307 study) at a concentration of 29.2-29.8 µg/100 g dry equivalent weight of soil and 29.3 µg/143 ml of water in the water-sediment systems (OECD 308 Study).
- 6PPD-Q was applied at a concentration of 1.5 and 15 µg/L for the mineralization study (OECD 309). The higher concentration follows the guidance of approximately half of the water solubility and the 1.5 µg/L level has environmental relevance to many of the published papers.
- Samples were extracted with appropriate solvents and concentrated prior to reverse phase radio-HPLC or high-resolution LC-MS.

Results

Soil Transformation (OECD 307)

- Data from the preliminary study (aerobic only) on soil showed that the radioactivity became increasingly bound to the soils with time. Levels of CO_2 were fairly consistent at 7 and 14 days after treatment (DAT). Table 1 below summarizes the findings.

Soil Type	Silt Loam, pH 5.5			Clay, pH 7.7			Sandy Loam, pH 5.5			Sandy Loam pH 7.5		
Organic matter (%)	6.2			5.3			1.9			1.9		
Biomass (µg/g dry weight equiv.)	539			888			218			238		
Time-Days After Treatment (DAT)	0	7	14	0	7	14	0	7	14	0	7	14
Recovery Of Radioactivity (%)												
In soil extracts	94.4	75.6	71.3	91.2	72.1	55.0	97.6	83.8	82.8	95.9	81.2	62.3
Trapped as CO_2	NA	8.0	6.1	NA	9.4	10.7	NA	6.9	4.5	NA	7.3	8.3
Non-Extractable Residue (NER)	NA	16.4#	22.6#	NA	18.5#	34.3#	NA	9.3#	12.7#	NA	11.5#	29.4#
Total recovered in extracts/CO_2	94.6	83.6	77.4	91.2	81.5	65.7	97.6	90.7	87.3	95.9	88.5	70.6
% Remaining as 6PPD-Q in extracts	92.8	73.4	71.3	89.1	68.3	50.6	95.9	81.6	80.9	94.3	76.7	60.8
Estimated half-life/ 90% transformation time in days	31.9 /106.0			16.3/54.0			50.3/167			21.2/70.4		

Table 1: Distribution of radioactivity from soil treated with ^{14}C-6PPD-Q
NA = Not Applicable
# = by calculation,
CAKE 3.6 used to calculate transformation times; Single First Order (SFO) Model used.

6PPD-Q has a half-life of 25 vs 106 days in aerobic or anaerobic water-sediment systems.

Water-Sediment Transformation (OECD 308)

- Initial results from the water-sediment study showed that under aerobic conditions 6PPD-Q quickly partitioned to the sediment by 7 DAT. Under anaerobic conditions this was notably slower (Table 2).
- Formation of CO_2 was faster in the aerobic system which produced 3-4 times more CO_2 than the anaerobic systems by 14 DAT.

Sediment System	Silt Sediment, pH 7.6								Loamy Sand Sediment, pH 6.8							
Organic Matter (%)	7.1								4.3							
Time (days after treatment (DAT)	0		7		14		29		0		7		14		29	
Aerobic	✓	×	✓	×	✓	×	✓	×	✓	×	✓	×	✓	×	✓	×
Recovery Of Radioactivity (%)																
Extracted from Sediment (%)	10.0	7.6	66.7	38.7	60.4	45.6	55.0	53.8	12.8	6.0	51.3	21.2	53.5	58.5	46.3	44.9
Surface Water (%)	89.9	91.0	20.0	57.9	18.4	45.9	7.6	32.8	86.0	94.0	35.4	76.3	22.4	35.3	9.6	43.1
Trapped as CO_2 (%)	NA	NA	2.3	0.6	3.9	1.2	TBC	TBC	NA	NA	1.8	0.5	3.7	0.9	TBC	TBC
Non-extractable Residue (NER)	NA	NA	11.0#	2.8#	17.3#	7.4#	TBC	TBC	NA	NA	TBC	2.1#	31.4#	5.3#	TBC	TBC
Total Recovered in extracts/CO_2	99.9	98.5	89.0	97.2	82.7	92.6	62.6	86.6	98.7	100.0	88.5	97.9	79.6	94.7	55.9	87.9

Table 2: Distribution of radioactivity from Water-Sediment vessels treated with ^{14}C-6PPD-Q
TBC = To Be Confirmed, NA = Not Applicable
# = by calculation, remaining residue confirmation still to be performed

- In the preliminary experiment 6PPD-Q accounted for 68-71% of the total extracted radioactivity from the water and sediment in the aerobic systems and 89-90% in the anaerobic systems.
- The water contained some transformation products of 6PPD-Q while the sediment extract was almost entirely 6PPD-Q.
- The total system half-life (DT_{50}) was calculated to be 25 (aerobic) to 106 days (anaerobic) from the preliminary data.

Mineralization Study (OECD 309)

- Study mass balance (radioactive recovery) was 97.8-104.9% for the 1.5 µg/L dose and 96.2-98.4% for the 15 µg/L dose, indicating good mass balance for the first 45 days.
- Mineralization to CO_2 accounted for up to 31.9% and 36.2% for the 1.5 and 15 µg/L application groups, respectively, by 45 days.
- In radio-HPLC analysis two major polar transformation products were observed UK1a & UK1b (Figure 1).
- Several minor transformation products were observed UK2-UK5 (Figure 1). Identification of the transformation products is ongoing but UK2-UK5 have tentatively been identified as hydroxylation products.
- Irrespective of the test concentration, 6PPD-Q accounted for approximately 37% of the radioactivity after 28 days. Graph 1 shows the decline of 6PPD-Q and formation of the transformation products over time, for the 15 µg/L incubation group. Results for both groups were similar.
- The DT_{50} was calculated to be 12.6 to 17.5 days respectively for the 1.5 and 15 µg/L application groups (SFO model). DT_{50} was 136-2770 days in sterile natural water.

Figure 1: Example Radio-HPLC chromatogram from the mineralization of 6PPD-Q Study (28 Days)

Graph 1: Decline of 6PPD-Q and formation of transformation products over time in the mineralization of 6PPD-Q study.

Conclusions

- Preliminary data in soils indicated 6PPD-Q was bound to the soil, the most being bound in the clay soil. Transformation of 6PPD-Q was also greatest in the clay soil with a half-life estimated to be 16 days and longest in the low pH sandy loam at 50 days (preliminary values).
- Transformation in soil appears to be pH dependent, with longer DT_{50} in acidic soil.
- In water-sediment systems, 6PPD-Q partitions to the sediment faster in aerobic systems than anaerobic systems. 6PPD-Q also transforms faster in aerobic water-sediment systems.
- In surface waters, 6PPD-Q transforms to polar products and CO_2 with minor intermediate hydroxylation products formed.
- 6PPD-Q transforms faster in active water than by hydrolysis alone (12.6 -17.5 days vs. 136-2700 days)

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