Department of Resources Recycling and Recovery

SCOPE OF WORK

Assessment of 6PPD-Q Pollution Risk from Rubberized Asphalt Mixes in California

I. BACKGROUND

Recycled tire rubber is used by the California Department of Transportation (Caltrans) in two types of asphalt mixes: rubberized hot mix asphalt gap-graded (RHMA-G) and rubberized hot mix asphalt open-graded (RHMA-O). Both are used exclusively as pavement surface layers. Recycled tire rubber is also used by California local agencies, cities and counties, mainly in gap-graded asphalt rubber mixtures similar to Caltrans RHMA-G and occasionally, in dense-graded hot mix asphalt (HMA) through a process called terminal blend (TB). However, there are new and emerging concerns about potential environmental impacts from tire constituents, such as 6PPD-Quinone, that warrant further investigation. This research project aims to assess the potential environmental risk of 6PPD-Q and other compounds being released from rubberized asphalt mixes.

The common ingredient of the three (3) rubberized mixes referenced above (RHMA-G, RHMA-O, and TB) is the crumb rubber modifier (CRM), also called ground tire rubber (GTR).

In the RHMA-G and RHMA-O mixes, the CRM is typically incorporated using a process known as “wet process–low agitation”. The resulting product is a rubberized binder referred to as “asphalt rubber binder” (ARB). The ARB contains 18 to 20% recycled tire rubber, approximately 2% extender oil, and the remainder is traditional asphalt binder.

In the terminal blend, rubber is reacted with asphalt binder at a very high temperature, on the order of 315°C (600°F). The elevated temperature breaks the sulfur vulcanization bonds, reducing the rubber into micrometric-sized particles that can be uniformly dispersed in the asphalt binder. The resulting product is a TB concentrate with rubber content that typically varies from 10 to 40%, depending on the technology. The concentrate is blended with asphalt binder and other polymers in an industrial facility, typically a binder terminal, to produce the rubber-modified asphalt binder, frequently referred to as “TB asphalt binder”. The TB asphalt binder can be used to produce a rubberized dense-graded mix referred to as hot mix asphalt dense-graded (RHMA-D).

New approaches for adding the recycled tire rubber in dense-graded mixes are currently under investigation by the University of California Pavement Research Center (UCPRC), funded by Caltrans and CalRecycle. The new approaches under investigation consider the RHMA-D use in both surface and intermediate pavement layers. These new approaches include:

- Wet process–low agitation, although using CRM with a small particle size, passing #40 sieve (< 0.4 mm).
- Engineered crumb rubber modifier (ECRM), which is CRM that has been treated with asphalt binder or other oils in an industrial facility or added through a process referred

to as “*dry process*”. In the dry process, the ECRM is handled the same as the reclaimed asphalt pavement (RAP), i.e., added directly to the asphalt plant mixing unit.

Nearly all of Caltrans’ use of recycled tire rubber in paving materials is through RHMA-G and RHMA-O mixes. Similarly, most California cities and counties’ use of recycled tire rubber in paving materials is through gap-graded asphalt rubber mixtures, similar to Caltrans RHMA-G, but also through rubberized dense-graded mixes produced using the TB process. The TB process is similar to the conventional HMA asphalt design and construction processes, which local engineers are already very familiar with.

II. INTRODUCTION/OBJECTIVES

Overall, rubberized asphalt mixes have been proven to increase the durability of roads and keep thousands of tires out of landfills with every paved mile.

However, new and emerging concerns about potential environmental impacts from tire constituents warrant further investigation. One such concern is the recent discovery of 6PPD-Quinone (6PPD-Q), a transformation product of 6PPD, a chemical used to protect tires from degradation. As tires wear and age, 6PPD reacts with ozone to form 6PPD-Q, which is released as part of Tire and Road Wear Particles (TRWP)—a mixture of tire rubber and road material. These particles can enter waterways through dust, rain, and stormwater runoff, where they negatively impact fish and other aquatic organisms. Coho salmon are highly sensitive to 6PPD-Q, and recent studies show that brook trout and rainbow trout are also affected.

While researchers know that chemicals like 6PPD-Q can leach from TRWPs, it is unclear whether tire rubber in California's rubberized asphalt pavements is a source of 6PPD-Q. This research project aims to assess the potential environmental risk of 6PPD-Q and other compounds being released from rubberized asphalt mixes.

Primary Objectives:

I. Review literature – and provide an up-to-date survey of rubberized asphalt mix use in California, the established occurrence of 6PPD-Q and related compounds of concern listed above, mitigation measures, and laboratory methodologies.

II. Conduct a comprehensive laboratory investigation into the potential risk of releasing 6PPD-Q and related compounds, including metals, from different rubberized asphalt mixes and formulations.

Research Questions:

1. What is the potential risk of releasing 6PPD-Q and related compounds and metals from different types of rubberized asphalt mixes and formulations?
2. How does the potential risk vary with the type of asphalt mix, including rubberized hot mix asphalt gap-graded (RHMA-G), rubberized hot mix asphalt open-graded (RHMA-O), and rubberized hot mix asphalt dense-graded (RHMA-D)?
3. How does the potential risk depend on climate factors, including ambient temperature, amount of rainfall, and asphalt mix aging?

4. Using available scientific data for TRWP, what is the contribution of 6PPD-Q in stormwater from rubberized asphalt mixes compared to TRWP?

III. WORK TO BE PERFORMED

The Contractor shall conduct research to assess the potential environmental risk of 6PPD-Q and related compounds, including selected metals, leaching from rubberized asphalt mixes in California. All deliverables produced for CalRecycle under this contract shall adhere to the CalRecycle Contractor Publications Guide.

Work to be performed shall include, but is not limited to, the following:

- Review existing literature to provide a current overview of rubberized asphalt mix usage in California, including documented presence of 6PPD-Q and related compounds of concern, mitigation strategies, and applicable laboratory analysis methods. The findings from the literature review shall be included in Task 3, Final Report.

- Conduct a laboratory-scale experimental investigation and simulation to evaluate the release of 6PPD-Q and related compounds and metals from rubberized asphalt mixes. Prepare a final report documenting all activities, findings, conclusions, and recommendations for potential future CalRecycle research initiatives.

IV. Experimental Design

6PPD-Q Release Simulation

The laboratory simulation of 6PPD-Q and related compounds released from the rubberized asphalt mixes requires the simulation of stormwater runoff on the asphalt mix and, depending on the source, the application of a mechanical action as explained in Table 1 below.

Table 1. Simulation of the release mechanisms

<table>
<tr><th colspan="2">Source</th><th>Release Mechanisms</th><th>Laboratory Simulation</th></tr>
<tr><td rowspan="3">Rubberized asphalt mix</td><td>Asphalt binder surface film</td><td>Tire-pavement interaction</td><td>a) Mix surface abrasion with water runoff</td></tr>
<tr><td>Asphalt mix wearing</td><td>Tire-pavement interaction</td><td>b) Mix wearing followed by water runoff</td></tr>
<tr><td>Body of the Asphalt Slab mix</td><td>Leaching</td><td>c) Water runoff</td></tr>
</table>

Three (3) laboratory simulation procedures are listed in Table 1: a) mix surface abrasion with water runoff, b) mix wearing followed by water runoff, and c) water runoff. The three (3) procedures shall be conducted in this research as follows:

- Mix surface abrasion: An asphalt specimen will be compacted in the laboratory. Then, a drill brush will be used to wear off the asphalt binder film that covers the aggregates.

The brushing will continue until the asphalt binder film is removed and the aggregates are exposed. The operation will be conducted while water is running on the specimen in the runoff apparatus described below.

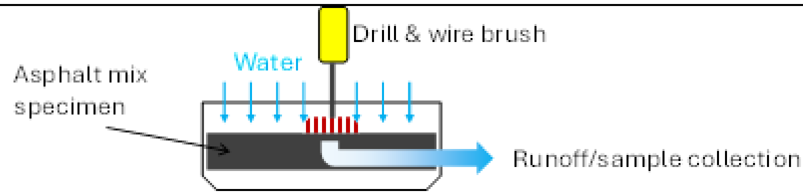
- Mix wearing: Mix wearing will be simulated following the Cantabro test. The Cantabro test consists of wearing an asphalt mix specimen in the Los Angeles abrasion machine without steel spheres. The specimen is subjected to a certain number of revolutions, and the resulting mass loss is measured to assess material resistance. In this research, the worn asphalt mix specimens and the fractured mix particles will be collected and subjected to wash out in the runoff apparatus described below.

- Water runoff: A runoff apparatus was developed for a research study conducted by UCPRC for Caltrans in the early 2000s. The apparatus includes a tray for holding the asphalt mix, a control-flow water pumping system that delivers a predetermined amount of water on the asphalt surface, and a runoff water collection and sampling system (Figure 1). Nine apparatuses were developed for the aforementioned research. The apparatuses will be restored and used for the research included in this proposal.

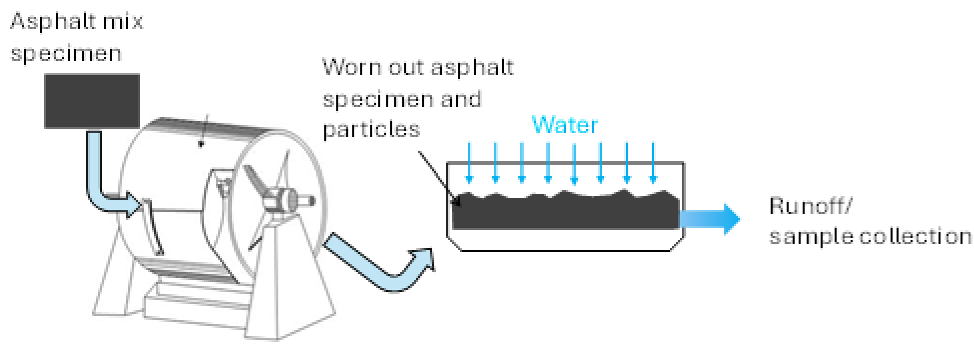
Figure 1. Runoff apparatuses

As a summary, the laboratory simulation of the release of the 6PPD-Q and related compounds is depicted in Figure 2.

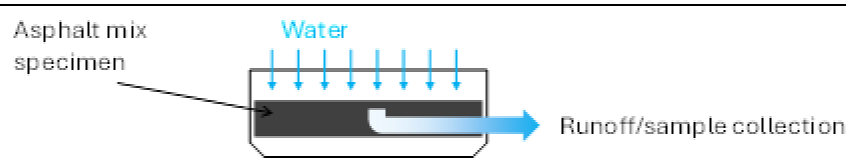
Figure 2. Laboratory simulation of 6PPD-Q release



a. Mix surface abrasion with water runoff (asphalt binder surface film)



b. Mix wearing in Los Angeles abrasion machine followed by water runoff (asphalt mix wearing)



c. Water runoff (leaching from the body of the mix)

Runoff Experiments

The runoff apparatuses will be housed at UC Davis Controlled Environment Facility (CEF) so that the runoff experiments can be conducted under controlled temperature and humidity conditions.

Water samples will be collected in pre-cleaned 500 mL amber borosilicate jars, filled completely (no headspace air), with two jars per sample to provide 1 L for laboratory analysis of the 6 PPD-Q and related compounds. Samples will be stored at 4°C in the dark until delivered to the laboratory. Additionally, 10 mL will be collected in a polypropylene tube for metals analysis by ICPMS (at the UC Davis Interdisciplinary

Center for Plasma Mass Spectrometry, icpms.ucdavis.edu) – As, Cd, Cr, Cu, Fe, Pb, Ni, V, and Zn.

Test Variables

The experimental design focuses on the key variables that may influence the leaching potential of 6PPD-Q and related compounds from rubberized asphalt mixes in California. The variables and the levels that will be tested in this experiment are listed below.

- Material (mix type):
  - HMA (control mix with no recycled tire rubber)
  - RHMA-G (wet process-low agitation)
  - RHMA-O (wet process-low agitation)
  - RHMA-D with CRM
  - RHMA-D with terminal blend
  - CRM, around 2 mm particle size

    CRM, less than 0.25 mm particle size (passing #60), or smaller

- Compaction level:
  - Standard, representative of field compaction of the mixes: HMA, RHMA-G, and RHMA-D at 7% air voids (Va) and RHMA-O at 15% Va.
  - Uncompacted mix (loose mix), lower-bound limit of the compaction variable.

- Mix aging:
  - Unaged mix (representative of the asphalt mix after paving): This condition is simulated by using a plant-produced mix that is reheated in the laboratory to the compaction temperature to produce the testing specimens. California Test 320 (2025) will be followed for reheating the mix.
  - Laboratory-aged mix: This condition is simulated by using a plant-produced mix that is conditioned in the laboratory at 100°C for 40 hours to reproduce long-term aging in the field. Then the mix is heated to the compaction temperature to produce the testing specimens. California Test 320 (2025) will be followed, except for the duration of the 100°C conditioning, which will be 40 hours instead of 20.
  - Field-aged mix: This condition is simulated by cutting the testing specimens from a field project where the asphalt mix has been in service for at least five (5) years. An attempt will be made to extract the slab from a test site with minimal traffic exposure, ensuring that any runoff pollution is attributed primarily to the rubberized mix rather than to vehicle tire wear.

- Pollution source (test procedure, Figure 2):

    - Asphalt binder surface film (Figure 2a).
    - Asphalt mix wearing (Figure 2b).
    - Leaching from the body of the mix (Figure 2c).
- Runoff water temperature:
    - 4°C (39.2°F)
    - 20°C (68°F)
    - 45°C (113°F)
- Time span:
    - First flush (beginning of the storm).
    - Duration of storm (a characteristic storm will be defined for this project, e.g., 0.5" total over 48 consecutive hours).
    - End of first rainy season: This condition will be simulated by running one-year rainfall on the asphalt mixes.
    - Year-to-year evolution: This condition will be simulated by running two one-year rainfalls on the asphalt mixes, with a one-month rest period in between. Then, comparing the runoff collected during the second-year rainfall simulation versus the first-year rainfall simulation.

Test Factorial

The testing factorial shown in Table 2 totals 62 tests. For each test, the runoff water will be sampled three (3) times with the standard time span (first flush, duration of characteristic storm, and end of first rainy season) and six (6) times (two (2) years with each being sampled at first flush, duration of characteristic storm, and end of first rainy season) with the year-to-year time span, which results in a total of 246 samplings and the corresponding chemical analyses.

The factorial, shown in Table 2, will be reconsidered as test results are available.

Table 2. Testing Variables and Levels

Material	Com-paction	Aging	Test Proc. (*)	Runoff Temp	Time Span (**)	Replicates
HMA	7% Va	Unaged	a	20 °C	Standard	2
			b	20 °C	Standard	2
			c	4 °C	Year-to-year	2
				20 °C	Year-to-year	2
				45 °C	Year-to-year	2
			c’	20 °C	Standard	2
	Field slab 1	Field-aged	c	20 °C	Standard	2
RHMA-G	7% Va	Unaged	a	20 °C	Standard	2
			b	20 °C	Standard	2
			c	4 °C	Year-to-year	2
				20 °C	Year-to-year	2
				45 °C	Year-to-year	2
			c’	20 °C	Standard	2
		Lab-aged	c	20 °C	Standard	2
	Loose mix	Unaged	c	20 °C	Standard	2
		Lab-aged	c	20 °C	Standard	2
	Field slab 1	Field-aged	c	20 °C	Standard	2
	Field slab 2	Field-aged	c	20 °C	Standard	2
RHMA-O	15% Va	Unaged	c	4 °C	Standard	2
				20 °C	Year-to-year	2
				45 °C	Standard	2
			c’	20 °C	Standard	2
	Field slab 1	Field-aged	c	20 °C	Standard	2
	Field slab 2	Field-aged	c	20 °C	Standard	2

Material	Com-paction	Aging	Test Proc. (*)	Runoff Temp	Time Span (**)	Replicates
RHMA-D with CRM	7% Va	Unaged	c	20 °C	Year-to-year	2
RHMA-D with TB	7% Va	Unaged	c	20 °C	Year-to-year	2
CRM (< 0.25 mm)	N.A.	Unaged	c	4 °C	Standard	2
				20 °C	Year-to-year	2
				45 °C	Standard	2
		Lab-aged	c	20 °C	Standard	2
CRM (< 2 mm)	N.A.	Unaged	c	20 °C	Standard	2
Total number of replicates:						**62**

(*) Test procedures (Figure 2): a) Mix surface abrasion with water runoff, b) Mix wearing followed by water runoff, and c) Water runoff. The c' is the same as c but conducted with 6PPD-Q-spiked water. In analytical chemistry, "spiking" means adding a known amount of a substance to a sample to test the accuracy and recovery of an analytical method, a process often called the spike-and-recovery test. In this research, deuterated 6PPD-Q (D5) will be spiked as a surrogate in all samples prior to extraction. Surrogate recoveries in recent studies with challenging environmental samples have been at least 80%.

(**) Standard time span: Collect water samples at three (3) times (first flush, duration of characteristic storm, and end of first rainy season). Year-to-year time span: Run two (2) one-year rainfalls (collecting three (3) samples first flush, duration of characteristic storm, and end of first rainy season, for each year), with a one-month rest period in between.

Table 3. Number of Chemical Analyses

Time Span	Number of Tests	Number of Chemical Analyses
Standard	42	42 × 3 = 126
2-year rainfall (year-to-year)	20	20 × 6 = 120
Total	**62**	**246**

V. TASKS IDENTIFIED

Types of work anticipated include, but are not limited to:

Task 1: Literature review

The Contractor shall perform the following Task 1 subtasks:

- **Task 1.1**: First Kick-off Meeting: Coordinate and participate in a virtual kick-off meeting with the CalRecycle Contract Manager within fourteen (14) days of contract execution to review the tasks and timeline, and to schedule ongoing virtual quarterly meetings to review work progress and draft documents.

- **Task 1.2**: Literature Review: Provide an up-to-date survey of rubberized asphalt mix use in California, established occurrence of 6PPD-Q and related compounds of concern listed above, mitigation measures, and laboratory methodology. The literature review shall include, but not be limited to, research publications, journals, articles, and books. The Contractor shall identify the advantages, limitations, gaps in the literature, and potential areas for improvement in the existing research. Literature review findings shall be incorporated in the Final Report.

Task 2: Laboratory-scale experimental investigation on the 6PPD-Q Pollution Risk from Rubberized Asphalt Mixes in California:

The Contractor shall perform the following Task 2 subtasks:

- **Task 2.1**: Second Kick-off Meeting: Coordinate and participate in a second kick-off meeting with the CalRecycle Contract Manager to discuss and plan the experimental investigation and timeline at least thirty (30) days prior to beginning the laboratory-scale experimental investigation, and to schedule ongoing quarterly meetings to review work progress and draft documents.

- **Task 2.2**: Experimental Design: design and set up a laboratory-scale experimental apparatus to assess the risk of 6PPD-Q and related compounds and selected metals leaching from various types of rubberized asphalt mixes. All sample analysis will follow the appropriate EPA methodology.

  Task 2.3: Conduct runoff experiments. This task consists of running the control flow water on the specimens and collecting the water samples following the testing protocol. The testing factorial is shown in Table 2. The water samples will be analyzed for 6PPD-Q and related compounds at the UC Davis Civil and Environmental Engineering Department laboratory by experienced Staff Research Associates. Additionally, the metals As, Cd, Cr, Cu, Fe, Pb, Ni, V, and Zn will be analyzed by the UC Davis Interdisciplinary Center for Plasma Mass Spectrometry Core Facility.

- **Deliverable(s):**
  - Work plan detailing the experimental design.
  - Complete experimental setup.
  - Conduct runoff experiments.

Task 3: Data Analysis, Final Report, and Presentation

The Contractor shall:

- Analyze the water samples' chemical analysis data to address the research questions that are listed above.
- Prepare and submit a draft final report to CalRecycle for review and comment by January 28, 2028. The draft final report shall document all activities, findings, conclusions, and recommendations for potential future CalRecycle research initiatives. CalRecycle will review and return the draft report to the Contractor for edits within sixty (60) days of submittal.
- Revise the draft final report in response to CalRecycle refinements within thirty (30) days of receiving.
- Submit the **Final Report** on or before May 28, 2028. The report and all presentation materials shall meet the CalRecycle Contractor Publications Guide requirements so they can be posted on CalRecycle's website in advance of any conference/workshop and/or published by CalRecycle following the completion of the study.
- Prepare and deliver a final presentation of the project results to CalRecycle management no later than thirty (30) days after submission of the Final Report as directed by CalRecycle's Contract Manager. The final presentation shall cover all activities, findings, conclusions, and recommendations presented in the final report.

- **Deliverable(s):**
  - Project Final Report summarizing the work conducted in all tasks.
  - PowerPoint presentation explaining the results in the Final Report due April 2028.

VI. CONTRACT/TASK TIME FRAME

The contract is estimated to begin on May 1, 2026, and end on June 30, 2028.

Task	Deliverable(s)	Due Date(s)
Task 1: Literature Review	Initial Project kickoff meeting	Within fourteen (14) days of contract execution.
	To be included in the Final Report	Draft: January 28, 2028 Final: May 28, 2028
Task 2: Laboratory-scale experimental investigation on the 6PPD-Q Pollution Risk from Rubberized Asphalt Mixes in California	Second kick-off meeting to discuss and plan the experimental investigation and timeline.	July 1, 2026
	Laboratory-scale experimental investigation: Work plan	August 1, 2026
	Complete experimental setup	October 1, 2026
	Conduct experiments	December 1, 2026
Task 3: Data Analysis, Final Report, and Presentation	Data Analysis	June 1, 2027

	Final Report	Draft: January 28, 2028 Final: May 28, 2028
	Final Presentation	April 17, 2028