



# PARKS AND RECREATION COMMISSION

# **Regular Meeting**

Tuesday, June 29th, 2021 6:00 PM City Council Chambers

Public is welcome.



### \*\*424-7282 for additional information.

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## PARKS AND RECREATION COMMISSION

Regular Meeting,

Tuesday, 06/29/2021 6:00 PM / Council Chambers / Cordova Civic Center

Cordova Parks and Recreation is essential for providing and fostering parks, programs, and facilities for all in pursuit of a healthy sustainable community.

## <u>AGENDA</u>

<u>Commission Chair</u> Wendy Ranney <u>Commission Members</u> Karen Hallquist, Marvin Van Den Broek, Henk Kruithof, Dave Zastrow, Ryan Schuetze, Kirsti Jurica <u>Interim Parks and Recreation Director</u> Micah Renfeldt

#### 1. CALL TO ORDER

2. **ROLL CALL:** Wendy Ranney, Karen Hallquist, Marvin Van Den Broek, Henk Kruithof, Dave Zastrow, Ryan Schuetze, Kirsti Jurica, Micah Renfeldt

#### 3. APPROVAL OF AGENDA

- 4. VISITOR COMMUNICATIONS
  - a. Regarding Agenda Items (3-minute limit)

#### 5. CONSENT CALENDAR

- a. 04/27/2021 Regular Commission Meeting Minutes
- b. 05/25/2021 Regular Commission Meeting Minutes
- 6. **REPORTS** 
  - a. Director's Report

#### 7. UNFINISHED BUSINESS

- a. Bear Resistant Trash Receptacles
- b. Soccer Goals/Volleyball Court

#### 8. NEW BUSINESS

- a. Fee Schedule Changes for Youth Athletics
- b. Proposal of Covered Picnic Area at New Fill Area Adjacent to City T Dock
- c. SCORP Proposed Project List
- d. Review of Orca Inlet Recreation Area (Little League Baseball Field) Master Plan

#### 9. PENDING AGENDA

- **10. COMMISSION COMMENTS**
- 11. ADJOURNMENT

#### Minutes of Parks and Recreation Commission Meeting

Tuesday April 27, 2021 DRAFT

A. Wendy Ranney called the meeting to order at 6:00 pm.

#### B. Roll Call In Attendance: Dave Zastrow, Marvin VanDenBroek, Kirsti Jurica, Henk Kruithof, Wendy Ranney, Karen Hallquist, Micah Renfeldt, Ryan Schuetze

C. Approval of Agenda: M/ H. Kruithof S/ D.Zastrow V/ Unanimous

#### D. Visitor Communications: None

E. Consent Calendar:

Minutes from 3.30.21 M/ M.VanDenBroek S/ K. Jurica V/ Unanimous

#### F. Reports

#### 1. Director's Report

- a. Trainings at the pool, survival suit training and local fire department training.
- **b.** Tot Lot Play Surface –Discussed options. Replace surface with shredded rubber or something comparable.
- c. Bidarki increasing capacity as COVID policies relax.
- **d.** Discussed the Parks Department Logo- Most in favor of the one with mountains and birds.
- e. Need 15 bear resistant garbage containers. Cost prohibitive. Looking for funds and/or handy downs from other entities.

#### G. Unfinished Business

**a.** Hollis Hendricks Master Plan- Soccer Goals and Volley Ball Court -Canneries input and financial help?

#### H. New Business

#### I. Pending Agenda

- 1. Regular meeting, scheduled May 25, 2021
- 2. Update from the Trails Committee.

#### J. Commission Comments

K.Jurica – Can the trails committee absorb the maintenance/mitigation plan of the frisbee golf course? There is resource damage that needs to be mitigated.

- K. Hallquist No comments
- R. Schuetze No comments
- W. Ranney No comments
- M. VanDenBroek Micah you are doing a great job!
- H.Kruitof Concerned with the latch on the Tot Lot gate.

#### Adjournment

M/H. Kruithof S/K.Jurica V/Unanimous Meeting adjourned at 6.59 pm

#### Minutes of Parks and Recreation Commission Meeting

Tuesday May 25, 2021 DRAFT

A. Karen Hallquist called the meeting to order at 6:10 pm.

#### B. Roll Call

**In Attendance:** Dave Zastrow, Marvin VanDenBroek, Kirsti Jurica, Henk Kruithof, Karen Hallquist, Micah Renfeldt, Ryan Schuetze

Absent: Wendy Ranney

- C. Approval of Agenda: M/ R. Schuetze S/ K.Jurica V/ Unanimous
- D. Visitor Communications: None
- E. Consent Calendar: None

#### F. Reports

- 1. Director's Report
- a. Odiak Camper Park Only 6 campers so not going to open shower trailer.
- b. Tot Lot Play Surface Shredded Rubber is here and will be installed!
- c. Multi-Purpose Field- Picnic areas have been brushed out.

#### G. Unfinished Business

#### H. New Business

#### I. Pending Agenda

- 1. Update from the Trails Committee.
- 2. Baseball Field/Municipal Park Master Plan.

#### J. Commission Comments No comments

#### Adjournment

**M**/ H. Kruithof **S**/ K.Jurica **V**/ Unanimous Meeting adjourned at 6:55 pm.



#### From the Administrative Office of the City of Cordova/ Parks and Recreation Dept.

Date: 06/29/2021
To: Mayor and Parks and Recreation Commission
From: Micah Renfeldt / Interim Director of Parks and Recreation

Dear Mayor and Commissioners,

We are pleased to announce that the Dept. of Parks and Recreation will have a new Director, Duncan Chisolm, starting the second week of July. This will be my last official Director's report. I would like to express my sincere gratitude to the Commissioners for their support during my short tenure and this transition.

#### **CAYAC Partnerships**

I attended a regular meeting of the non-profit, Cordova Amateur Youth Athletics Corporation (CAYAC) to discuss usage of Bidarki for their youth basketball and youth soccer programs. The topic of pricing was a common concern. It has come up also with other user groups. As a public facility, we do not want to become cost prohibitive, especially to groups that provide programming, for which we are no longer funded adequately, and that the community desperately wants and needs. Any change in our fee schedule requires an act of Council and it is my suggestion to make a change to help possibly relieve this financial burden for youth athletics. We are still in discussions about scheduling.

On another note, it is the opinion of CAYAC that an outdoor basketball court is a high priority for their organization and the community and has approached us about land usage. An area of Hollis Henrichs Park was proposed. We are in continued discussion on this matter.

I am of the opinion of that we should continue fostering our relationship with this organization to help provide Cordova better programming for youth athletics.

#### Outdoor Picnic Area/History of Salmon Fishing/Processing in Cordova

Paula Payne has written a proposal for an outdoor picnic site on the new fill area in between Ocean Beauty and the current Science Center, adjacent to the T Dock. This site would serve the community at large and provide a historic account of commercial fishing and processing in Cordova. I have attached a copy of this proposal to this report in the appendix.

#### Salmon Runs

I met with Kristin Carpenter about assisting with signups and shirt distribution for the Salmon Runs. We have provided this service for the event in the past and will continue to do so.

#### State Comprehensive Outdoor Recreation Plan (SCORP)

I have been contacted to be a representative on the Prince William Sound Working Group to help update Alaska's SCORP. I will be serving this group in two capacities; that of the Parks and Recreation Director, until Duncan arrives; and that of the Cordova Disc Golf Club President. These work sessions provide a guiding framework that Federal administrators use for the Land Water Conservation Fund, and to where these resources are allocated. Shovel ready projects will have the highest priority.

As the President of the Club, I have proposed, and am working on (in my off-time), along with the Club Board and members, the creation of a budget for improvements on our course. I feel strongly that we should create a Parks project to propose and have shovel ready to be on this list as well. Skaters' Cabin would be high on my short list as a contender. The Michael O'Leary Trail is currently on this list, as well as several other projects from various communities around the Sound.

#### **Fish Cleaning Station**

The water lines to the Fish Cleaning Station have been dug and installed. It is set to be moved very shortly. Short of any major complications in our other Parks, we are confident it will be in its final location, with the water on, before this meeting takes place. This is our highest Park priority, as we continue seeing more and more fish come into town, without an easily accessible place to clean them. On a side note, I will be coordinating a meeting this summer with Rich Sorenson about collaborating the construction of an additional station to be placed adjacent to the existing structure.

#### Multipurpose Field Picnic Area

We are ready to add fill, do some grading/leveling, and install box steps and some retaining rocks. Picnic tables, a fire ring, and a sign will finalize this project. Projected timeline pushed back into the middle or end of July.

#### Noel Pallas Children's Memorial Playground

The maintenance access gate has been installed. There are a few additional elements needing done in preparation for the final surface material installation. Relocation of existing surface material; installation of barrier fabric to mitigate gravel/rubber mixing and weed control.

In relation to this project, The Copper River Watershed Project contacted our office, expressing uncertainty over a recent study of tire tread wear particles and their impact on spawning Coho Salmon. I contacted one of the researchers to obtain a copy of the full article and read it. It applies to several physio/chemical reactions. Specifically those between a UV protectant chemical additive in tires, the wear process of creating tire tread wear particles, reaction with ozone attributed to vehicle exhaust, and the resulting road surface runoff into spawning streams. Through my reading, I have concluded that this study does not apply to our Tot Lot as follows; there are no Coho spawning streams downhill from the Tot Lot, the material will no longer be subjected to driving conditions, thusly, the material will no longer contact the many varied substances found on road surfaces or be exposed to high levels of potential chemical reactions. I will attach the study for your perusal.

#### Appendix:

#### Letter for covered picnic tables/BBQ area at the fill lot at Harbor entrance

#### The Back Story

Cordova has a very rainy climate, about 160 inches of rain per year. Cordova used to have covered picnic areas with multiple picnic tables within walking distance to town at: Nirvana Park and Hollis Hendrichs Park, and a world class covered picnic facility out the road at Child's Glacier. Over the last 20 years we have lost all three of these covered picnic areas and they have not been replaced.

#### The Issue

Cordova desperately needs covered outdoor picnic areas that are walking distance to town. This became even more evident during the Covid Pandemic with so many people and young families wanting to gather outside. Comparatively, Sitka and Juneau have many covered picnic areas throughout their towns. Sitka has covered picnic areas all along its waterfront including a large waterfront multi table covered facility in town.

#### The Solution

The land fill at the entrance to the Harbor (where "The Jump" currently resides and across from the Science Center) is the perfect location to create a community covered picnic and BBQ area and waterfront park. Envision a sturdy well-built outdoor covered picnic area with BBQ grills like we had at Childs Glacier on this location. This would include planting trees, some outside picnic tables, and a covered BBQ area with multiple picnic tables underneath. Cordovans and tourists could gather, picnic, and watch our fishing fleet come and go.

Outside of the fill there is space to park food trucks for the summer to enhance the park experience, provide opportunity for a few small local businesses, and provide rent to the city to offset costs of the picnic area. The Pavilion could also be rented out for special events. We could place a kiosk outlining the history of fishing in Cordova at this picnic area location for tourists and residents to read and enjoy. (Rendering of the proposed area to follow.)

#### **Conclusion**

This is a wonderful community-oriented solution for the marvelous community of Cordova! In the past this location has been contentious because it is a visible and prominent waterfront space located at the entrance to Cordova's harbor, the heart of our community. What better could we do with a space at the heart of our community, than to create a beautiful, covered community picnic area and park for all Cordovans and visitors to Cordova to enjoy?











# A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon

Zhenyu Tian<sup>1,2</sup>, Haoqi Zhao<sup>3</sup>, Katherine T. Peter<sup>1,2</sup>, Melissa Gonzalez<sup>1,2</sup>, Jill Wetzel<sup>4</sup>, Christopher Wu<sup>1,2</sup>, Ximin Hu<sup>3</sup>, Jasmine Prat<sup>4</sup>, Emma Mudrock<sup>4</sup>, Rachel Hettinger<sup>1,2</sup>, Allan E. Cortina<sup>1,2</sup>, Rajshree Ghosh Biswas<sup>5</sup>, Flávio Vinicius Crizóstomo Kock<sup>5</sup>, Ronald Soong<sup>5</sup>, Amy Jenne<sup>5</sup>, Bowen Du<sup>6</sup>, Fan Hou<sup>3</sup>, Huan He<sup>3</sup>, Rachel Lundeen<sup>1,2</sup>, Alicia Gilbreath<sup>7</sup>, Rebecca Sutton<sup>7</sup>, Nathaniel L. Scholz<sup>8</sup>, Jay W. Davis<sup>9</sup>, Michael C. Dodd<sup>3</sup>, Andre Simpson<sup>5</sup>, Jenifer K. McIntyre<sup>4</sup>, Edward P. Kolodziej<sup>1,2,3</sup>\*

In U.S. Pacific Northwest coho salmon (*Oncorhynchus kisutch*), stormwater exposure annually causes unexplained acute mortality when adult salmon migrate to urban creeks to reproduce. By investigating this phenomenon, we identified a highly toxic quinone transformation product of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), a globally ubiquitous tire rubber antioxidant. Retrospective analysis of representative roadway runoff and stormwater-affected creeks of the U.S. West Coast indicated widespread occurrence of 6PPD-quinone (<0.3 to 19 micrograms per liter) at toxic concentrations (median lethal concentration of  $0.8 \pm 0.16$  micrograms per liter). These results reveal unanticipated risks of 6PPD antioxidants to an aquatic species and imply toxicological relevance for dissipated tire rubber residues.

umans discharge tens of thousands of chemicals and related transformation products to water (1), most of which remain unidentified and lack rigorous toxicity information (2). Efforts to identify and mitigate high-risk chemical toxicants are typically reactionary, occur long after their use becomes habitual (3), and are frequently stymied by mixture complexity. Societal management of inadvertent, yet widespread, chemical pollution is therefore costly, challenging, and often ineffective.

The pervasive biological degradation of contaminated waters near urban areas ("urban stream syndrome") (4) is exemplified by an acute mortality phenomenon that has affected Pacific Northwest coho salmon (*Oncorhynchus kisutch*) for decades (5–9). "Urban runoff mortality syndrome" (URMS) occurs annually among adult coho salmon returning to spawn in freshwaters where concurrent stormwater exposure causes rapid mortality. In the most urbanized watersheds with extensive impervious surfaces, 40 to 90% of returning salmon may die before spawning (9). This mortality

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threatens salmonid species conservation across ~40% of the Puget Sound land area despite costly societal investments in physical habitat restoration that may have inadvertently created ecological traps through episodic toxic water pollution (9). Although URMS has been linked to degraded water quality, urbanization, and high traffic intensity (9), one or more causal toxicants have remained unidentified. Spurred by these compelling observations and mindful of the many other insidious sublethal stormwater impacts, we have worked to characterize URMS water quality (10, 11).

Previously, we reported that URMS-associated waters had similar chemical compositions relative to roadway runoff and tire tread wear particle (TWP) leachates, providing an opening clue in our toxicant search (10). In this work, we applied hybrid toxicity identification evaluation and effect-directed analysis to screen TWP leachate for its potential to induce mortality (a phenotypic anchor) in juvenile coho salmon as an experimental proxy for adult coho (6). Using structural identification by means of ultrahigh-performance liquid chromatography-high-resolution tandem mass spectrometry (UPLC-HRMS/MS) and nuclear magnetic resonance (NMR), we discovered that an antioxidant-derived chemical was the primary causal toxicant. Retrospective analysis of runoff and receiving waters indicated that detected environmental concentrations of this toxicant often exceeded acute mortality thresholds for coho during URMS events in the field and across the U.S. West Coast.

Aqueous TWP leachate stock (1000 mg/liter) was generated from an equal-weight mix of tread particles ( $0.2 \pm 0.3 \text{ mm}^2$  average surface area) (fig. S1) from nine used and new tires (table S1). TWP leachate (250 mg/liter positive controls) was acutely and rapidly (~2 to

6 hours) lethal to juvenile coho (24 hours exposures, 98.5% mortality, n = 135 fish from 27 exposures) (data file S1), even after heating (80°C, 72 hours; 100% mortality, n = 10 fish from two exposures), indicating stability during handling. Behavioral symptomology (circling, surface gaping, and equilibrium loss) (fig. S2 and movie S1) of TWP leachate exposures mirrored laboratory and field observations of symptomatic coho (5, 6). No mortality occurred in negative controls, including solvent- and process-matched method blanks subjected to identical separations (0 of 80 fish, 16 exposures) or exposure water blanks (0 of 45 fish, nine exposures).

Mixture complexity [measured here as number of UPLC-HRMS electrospray ionization (ESI+) chemical features] was a substantial barrier to causal toxicant identification because 250 mg/liter TWP leachate typically contained more than 2000 ESI+ detections. Our fractionation studies, optimized over 2-plus years through iterative exploration of toxicant chemical properties, focused on reducing these detection numbers to attain a simple, yet toxic, fraction amenable to individual compound identifications. Throughout this fractionation procedure, observed toxicity remained confined to one narrow fraction, which is consistent with a single compound or a small, structurally related family of causal toxicants. In initial studies, TWP leachate toxicity was unaffected by silica sand filtration, cation and anion exchange, and ethylenediaminetetraacetic acid (EDTA) (114 µM) addition (12), indicating that toxicant(s) were not particle-associated, strongly ionic, or metals, respectively, and validating prior studies that eliminated candidate pollutants (13, 14) as primary causal toxicants.

Mixture complexity was reduced by using cation exchange, two polarity-based separations (XAD-2 resin and silica gel), and reversephase high-performance liquid chromatography (HPLC) on a semipreparative C18 column (250 by 4.2 mm ID, 5 µm particle size). After C18-HPLC generated 10 fractions, only C18-F6 (10 to 11 min) was toxic; it contained ~225 ESI+ and ~70 ESI- features (Fig. 1). Having removed ~90% of features, we began to prioritize and identify candidate toxicants by abundance (peak area), followed by fish exposures with commercial standards at fivefold higher concentrations (mixtures at 1 to  $25 \mu g$ /liter) than those estimated in C18-F6. We identified 11 plasticizers, antioxidants, emulsifiers, and various transformation products, including some wellknown environmental contaminants [such as tris(2-butoxyethyl) phosphate] and some that are rarely reported [such as di(propylene glycol) dibenzoate and 2-(1-phenylethyl)phenol] (table S2). We also detected several bioactive, structurally related phenolic antioxidants and their transformation products (2,6-di-t-

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butyl-4-hydroxy-4-methyl-2,5-cyclohexadienone, 3,5-di-*t*-butyl-4-hydroxybenzaldehyde, and 7,9-di-*tert*-butyl-1-oxaspiro[4,5]deca-6,9diene-2,8-dione) (*15*). However, over many rounds of identification and subsequent exposure to juvenile coho, none of these identified chemical exposures reproduced URMS symptoms or induced mortality. Because these identifications used exhaustive environmental scientific literature searches (*10*, *16*, *17*), we suspected a previously unreported toxicant.

To sharpen our search, we used multidimensional semipreparative HPLC using two additional structurally distinct column phases [pentafluorophenyl (PFP) and phenyl]. Parallel fractionations (same column dimensions, mobile phase, and gradient as for C18-HPLC) (18) of the toxic silica gel fraction generated toxic fractions of PFP-F6 (10 to 11 min; ~204 ESI+, 60 ESI- features) and phenyl-F4 (8 to 9 min; ~237 ESI+, 75 ESI- features); all other fractions were nontoxic. Across these separations (C18, PFP, phenyl), only four ESI+ and three ESI- HRMS features co-occurred in all three toxic fractions (fig. S3). Of these, one unknown compound [mass/charge ratio (m/z)299.1752, C18H22N2O2, RT 11.0 min on analytical UPLC-HRMS] dominated the detected peak area (10-fold higher intensity in both ESI+ and ESI-). To further resolve candidate toxicants for synthetic efforts, we converted the three-dimensional chromatography workflow from parallel to serial through sequential C18, PFP, and phenyl columns (C18-F6 to PFP-F6 to phenyl-F4; with solvent removal by means of centrifugal evaporation and toxicity confirmation between separations). The purified final fraction was chemically simple (four ESI+, three ESI- detections), highly lethal (100% mortality in 4 hours; n = 15 coho, three exposures), and was again dominated by  $C_{18}H_{22}N_2O_2$ . Drying this fraction yielded a pink-magenta precipitate (Fig. 1).

Published characterizations of crumb rubber (16) and receiving waters (10, 17) did not mention C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>. UPLC-HRMS/MS spectra indicated C4H10 and C6H12 alkyl losses (M-58 and M-84 fragments) (Fig. 2B), but MS<sup>3</sup> and MS<sup>4</sup> fragmentation yielded no additional structural insights (fig. S4). Additionally, in silico fragmentation (MetFrag, CSI:FingerID) of C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> compounds in PubChem and ChemSpider (15,624 and 17,105 structures, respectively) failed to match observed fragments. Thus, to the best of our knowledge, C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> was not described in environmental literature or databases and posed a "true unknown" identification problem (19). We then assumed a transformation product; industrial manufacturing (such as high heat or pressure, or catalysis) and diverse reactions in environmental systems generate many undocumented transformation products, most of which lack commercial standards.



**Fig. 1. Tire rubber leachate fractionation scheme.** As a metric of mixture complexity and separation efficiency, the numbers above gray bars represent distinct chemical features detected in solid-phase extracted fish exposure water (1 liter) and subsequent fractions by means of UPLC-HRMS. Blue indicates nonlethal fractions; red indicates lethal fractions. All fractionation steps and exposures were replicated at least twice; positive and negative controls were included throughout fractionations. (**Inset**) Purified product (~700  $\mu$ g from 30 liter of TWP leachate) in the final lethal fraction. TWP, tire tread wear particles; CEX, cation exchange; EA, ethyl acetate; EtOH, ethanol; H<sub>2</sub>O, water; Hex, hexane; DCM, dichloromethane; RT, retention time.



**Fig. 2. 6PPD-quinone identification and a proposed formation pathway.** (**A**) Extracted ion chromatograms of 6PPD-quinone from UPLC-HRMS (ESI+); red data indicate the final fraction from TWP leachate, and black data indicate the purified 6PPD ozonation mixture. (**B**) Observed MS/MS fragmentation (integrated from 10, 20, and 40 eV) of 6PPD-quinone in the final toxic fraction from TWP leachate (red spectra) and 6PPD ozonation (black spectra). (**C**) One proposed reaction pathway from 6PPD to 6PPD-quinone (alternate proposed formation pathways are provided in fig. S13). Red highlights indicate key changes in the diphenylamine structure during ozonation.

Our breakthrough came by assuming that abiotic environmental transformations commonly modify active functional groups by preferentially altering the numbers of hydrogen and oxygen atoms relative to carbon and nitrogen. By searching a recent U.S. Environmental Protection Agency (EPA) crumb rubber report (16) for related formulas (C18H0-xN2-4O0-y), several characteristics of the C18H24N2 anti-ozonant "6PPD" [N-(1,3dimethylbutyl)-N'-phenyl-pphenvlenediamine] matched necessary attributes. First, 6PPD is globally ubiquitous (0.4 to 2% by mass) in passenger and commercial vehicle tire formulations (20), indicating sufficient production to explain mortality observations within large and geographically distinct receiving water volumes. 6PPD was present in TWP leachate but was completely removed during fractionation through cation exchange. 6PPD crystals are purple, similar to the pink-magenta precipitate obtained after fractionation. Most compellingly, neutral losses in 6PPD gas chromatography (GC)-MS spectra matched the C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> GC-HRMS spectra (fig. S5), and the predicted logKow of 6PPD (5.6) (Kow, noctanol-water partition coefficient) was close to that for  $C_{18}H_{22}N_2O_2$  (5 to 5.5) (11). Last, literature detailing the industrial chemistry of 6PPD reactions

with ozone [7 days, 500 parts per billion volume (ppbv)] described a  $C_{18}H_{22}N_2O_2$  product (21), leading us to hypothesize that 6PPD was the likely protoxicant (Fig. 2C).

We tested this hypothesis with gas-phase ozonation (500 ppbv  $O_3$ ) of industrial grade 6PPD (96% purity) (21). A C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> product formed: UPLC-HRMS analysis demonstrated exact matches of retention time (11.0 min) and MS/MS spectra between this synthetic C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> and the TWP leachate fractionationderived C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> (Fig. 2, A and B). When purified, the ozone-synthesized  $C_{18}H_{22}N_2O_2$ formed a reddish-purple precipitate. Onedimensional <sup>1</sup>H NMR structural analysis confirmed identical TWP leachate-derived and ozone-synthesized C18H22N2O2 structures (figs. S6 to S7). Two-dimensional NMR spectra and related simulations revealed isolated tertiary carbons and carbonyl groups (figs. S8 to S12), clearly indicating a quinone structure for C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> rather than the dinitrone struc-



**Fig. 3. Dose-response curves. (A)** Dose-response curve for 24-hour juvenile coho exposures to roadway runoff and TWP leachate (n = 365 fish). Error bars represent three replicates of eight fish (except TWP leachate 2, n = 5 fish; Seattle site 1, duplicate of n = 10 fish). 6PPD-quinone concentrations were from retrospective quantification. (**B**) Dose-response curves for 24-hour juvenile coho exposures to ozone-synthesized 6PPD-quinone (10 concentrations, two replicates, n = 160 fish). Curves were fitted to a four-parameter logistic model. Cl, confidence interval.

ture reported in the past 40 years of literature describing 6PPD ozonation products (21). Therefore, the  $C_{18}H_{22}N_2O_2$  candidate toxicant was unequivocally "6PPD-quinone" {2-anilino-5-[(4-methylpentan-2-yl)amino]cyclohexa-2,5-diene-1,4-dione}. Consistent with environmental 6PPD ozonation, reported 6PPD ozonation products  $C_{18}H_{22}N_2O$  (formula-matched) and 4-nitrosodiphenylamine ( $C_{12}H_{10}N_2O$ , standard-confirmed) (21) also were detected in ozonation mixtures and nontoxic TWP leachate fractions.

Exposures to ozone-synthesized and tire leachate-derived 6PPD-quinone (~20  $\mu$ g/liter nominal concentrations) both induced rapid (<5 hours, with initial symptoms evident within 90 min) mortality (n = 15 fish, three exposures) (fig. S2 and movie S2), which matched the 2 to 6 hours mortality observed for positive controls. Behavioral symptomology in response to synthetic 6PPD-quinone exposures matched that from field observa-

tions, roadway runoff, bulk TWP leachate, and final toxic TWP fraction exposures, confirming the phenotypic anchor (5-9). Using synthetic 6PPD-quinone (purity ~98%), we performed controlled dosing experiments (10 concentrations, n = 160 fish in two independent exposures). 6PPD-quinone was highly toxic [median lethal concentration (LC<sub>50</sub>)  $0.79 \pm 0.16 \,\mu\text{g}/$ liter] to juvenile coho salmon (Fig. 3B). Estimates of LC<sub>50</sub> through controlled exposures closely matched estimates derived from bulk roadway runoff and TWP leachate exposures (LC<sub>50</sub>  $0.82 \pm 0.27 \mu g/liter)$ , indicating the primary contribution of 6PPD-quinone to observed mixture toxicity (Fig. 3A). Direct comparisons with 6PPD were performed  $(LC_{50} 250 \pm 60 \mu g/liter through no$ minal concentrations) (fig. S14), but confident assessment of 6PPD toxicity was precluded by its poor solubility, high instability, and formation of products during exposure.

To assess environmental relevance, we used UPLC-HRMS to retrospectively quantify 6PPD-quinone in archived extracts from roadway runoff and receiving water sampling (fig. S15 and table S4) (10). In Seattle-region roadway runoff (n =16 of 16 samples), 0.8 to 19 µg/liter 6PPD-quinone was detected (Fig. 4A). During seven storm events in three Seattle-region watersheds highly affected by URMS, 6PPDquinone occurred at <0.3 to 3.2 µg/ liter (n = 6 of 7 discrete storm events; n = 6 of 21 samples when

including samples collected across the full hydrograph). These samples included three storms with documented URMS mortality in adult coho salmon; 6PPD-quinone was not detected in pre- and poststorm samples, but concentrations were near or above  $LC_{50}$  values during storms. We also detected 6PPD-quinone in Los Angeles region roadway runoff (n = 2 of 2 samples, 4.1 to 6.1 µg/liter) and San Francisco region creeks affected by urban runoff (n = 4 of 10 samples, 1.0 to 3.5 µg/liter).

These data implicate 6PPD-quinone as the primary causal toxicant for decades of stormwater-linked coho salmon acute mortality observations. Although minor contributions from other constituents in these complex mixtures are possible, 6PPD-quinone was both necessary (consistently present in and absent from toxic and nontoxic fractions, respectively) and, when purified or synthesized as a pure chemical exposure, sufficient to produce URMS at environmental concentrations. Over the product





**Fig. 4. Environmental relevance of 6PPD-quinone. (A)** Using retrospective UPLC-HRMS analysis of archived sample extracts, 6PPD-quinone was quantified in roadway runoff and runoff-affected receiving waters. Each symbol corresponds to duplicate or triplicate samples, and boxes indicate first and third quartiles. For comparison, the 0.8  $\mu$ g/liter LC<sub>50</sub> value for juvenile coho salmon and detected 6PPD-quinone levels in 250 and 1000 mg/liter TWP leachate are included. **(B)** Predicted ranges of potential 6PPD-quinone mass formation in passenger

cars (for example, four tires, ~36 kg tire rubber mass) and heavy trucks (for example, 18 tires, ~900 kg of tire rubber) (represented in orange) and measured 6PPD-quinone concentrations in affected environmental compartments (represented in blue, with experimental data italicized). Predicted ranges reflect calculations applying 0.4 to 2% 6PPD per total vehicle tire rubber mass followed by various yield scenarios (1 to 75% ultimate yields) for 6PPD reaction with ground-level ozone to form 6PPD-quinone.

life cycle, antioxidants [such as PPDs, TMQs (2,2,4-trimethyl-1,2-dihydroquinoline), and phenolics] are designed to diffuse to tire rubber surfaces, rapidly scavenge ground-level atmospheric ozone and other reactive oxidant species, and form protective films to prevent ozone-mediated oxidation of structurally important rubber elastomers (21, 22). Accordingly, all 6PPD added to tire rubbers is designed to react, intentionally forming 6PPD-quinone and related transformation products that are subsequently transported through the environment. This anti-ozonant application of 6PPD inadvertently, yet drastically, increases roadway runoff toxicity and environmental risk by forming the more toxic and mobile 6PPDquinone transformation product. On the basis of the ubiquitous use and substantial mass fraction (0.4 to 2%) of 6PPD in tire rubbers and the representative detections across the U.S. West Coast (table S4), which include many detections near or above LC50 values, we believe that 6PPD-quinone may be present broadly in peri-urban stormwater and roadway run-off at toxicologically relevant concentrations for sensitive species, such as coho salmon.

Globally, ~3.1 billion tires are produced annually for our more than 1.4 billion vehicles, resulting in an average 0.81 kg per capita annual emission of tire rubber particles (23). TWPs are one of the most substantial micro-

plastics sources to freshwaters (24); 2 to 45% of total tire particle loads enter receiving waters (25, 26), and freshwater sediment contains up to 5800 mg/kg TWP (23, 24, 27). Supporting recent concerns about microplastics (24, 28), 6PPD-quinone provides a compelling mechanistic link between environmental microplastic pollution and associated chemical toxicity risk. Although numerous uncertainties exist regarding the occurrence, fate, and transport of 6PPD-quinone, these data indicate that aqueous and sediment environmental TWP residues can be toxicologically relevant and that existing TWP loading, leaching, and toxicity assessments in environmental systems are clearly incomplete (25). Tire rubber disposal also represents a major global materials problem and potential potent source of 6PPDquinone and other tire-derived transformation products. In particular, scrap tires repurposed as crumb rubber in artificial turf fields (17) suggest both human and ecological exposures to these chemicals. Accordingly, the human health effects of such exposures merit evaluation.

Environmental discharge of 6PPD-quinone is particularly relevant for the many receiving waters proximate to busy roadways (Fig. 4B). It is unlikely that coho salmon are uniquely sensitive, and the toxicology of 6PPD transformation products in other aquatic species should be assessed. For example, used tires were more toxic to rainbow trout (75% lower 96 hours  $LC_{50}$ ) relative to new tires (29), an observation that is consistent with adverse outcomes mediated by transformation products. If management of 6PPD-quinone discharges is needed to protect coho salmon or other aquatic organisms, adaptive regulatory and treatment strategies (17, 30, 31) along with source control and "green chemistry" substitutions [identifying demonstrably nontoxic and environmentally benign replacement antioxidants (22, 32)] can be considered. More broadly, we recommend more careful toxicological assessment for transformation products of all high-productionvolume commercial chemicals subject to pervasive environmental discharge.

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and do not necessarily represent the views of the sponsoring organizations. Author contributions: Z.T., H.Z., K.T.P., J.K.M., M.C.D., and E.P.K. designed research; Z.T., H.Z., M.G., K.T.P., C.W., R.H., and A.E.C. performed HRMS and data analysis; Z.T., H.Z., M.G., J.W., K.T.P., C.W., R.H., E.P.K., J.K.M., and A.E.C. conducted fish exposures; J.P., C.W., and J.W. generated TWP particles; J.W., J.P., E.M., and J.K.M. maintained the fish facility and enabled exposure studies; R.G.B., F.V.C.K., R.S., A.J., and A.S. elucidated structures by means of NMR; K.T.P., C.W., F.H., Z.T., M.G., B.D., A.G., and R.S. provided water samples; X.H., Z.T., H.Z., M.G., and J.W.D. provided perspectives and context; and J.T., H.Z., K.L.S. and J.P.M. provided perspectives and context; and J.T., H.Z., M.C.P., and E.P.K. wrote the manuscript. Competing

interests: None declared. Data and materials availability: Data file S1 includes the record of the juvenile coho salmon exposure experiments. Number of tanks and coho salmon used, mortality results, and treatment information are included in the table. All other data needed to evaluate the conclusions in the paper are present in the paper or the supplementary materials.

#### SUPPLEMENTARY MATERIALS

science.sciencemag.org/content/371/6525/185/suppl/DC1 Materials and Methods Supplementary Text Figs. S1 to S15 Tables S1 to S5 References (33–47) Movies S1 and S2 Data File S1

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#### A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon

Zhenyu Tian, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, Jasmine Prat, Emma Mudrock, Rachel Hettinger, Allan E. Cortina, Rajshree Ghosh Biswas, Flávio Vinicius Crizóstomo Kock, Ronald Soong, Amy Jenne, Bowen Du, Fan Hou, Huan He, Rachel Lundeen, Alicia Gilbreath, Rebecca Sutton, Nathaniel L. Scholz, Jay W. Davis, Michael C. Dodd, Andre Simpson, Jenifer K. McIntyre and Edward P. Kolodziej

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#### Tire tread particles turn streams toxic

For coho salmon in the U.S. Pacific Northwest, returning to spawn in urban and suburban streams can be deadly. Regular acute mortality events are tied, in particular, to stormwater runoff, but the identity of the causative toxicant(s) has not been known. Starting from leachate from new and aged tire tread wear particles, Tian *et al.* followed toxic fractions through chromatography steps, eventually isolating a single molecule that could induce acute toxicity at threshold concentrations of ~1 microgram per liter. The compound, called 6PPD-quinone, is an oxidation product of an additive intended to prevent damage to tire rubber from ozone. Measurements from road runoff and immediate receiving waters show concentrations of 6PPD-quinone high enough to account for the acute toxicity events.

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#### ORCA INLET RECREATION AREA/LITTLE LEAGUE BASEBALL FIELD:

Classification: Recreation Area / Community \* (Creation of Athletics Classification?)

#### 1. Plan phase II of the construction of this recreational area

- a. The Parks and Recreation Commission recommend a joint work session with the Planning and Zoning Commission, Cordova Little League, and the Parks and Recreation Commission to discuss any future plans for this recreational area.
- b. This Commission identifies the need for a safe approach or route to this area for foot and bike traffic, along with covered dugouts and a snack shack that is either mobile or fixed. It would be good to assess the need and expand programming in this area as well. (*Dugouts are currently covered; The Snack Shack is part of the existing structure*)
- c. Outfield fencing was constructed through a generous donation by <u>Wilson Construction</u>
- 2. \*Personal Notes:
  - a. <u>Roof metal and fascia were replaced in the Summer of 2019, at very</u> <u>little cost, with repurposed roof metal from the City Streets Shop re-</u> <u>roofing project</u>
  - b. Siding needs replacing on most of the building
  - c. <u>Restrooms were renovated the winter of 2020/2021</u>
  - d. <u>Winter cover panel for the rollup concessions counter was replaced</u> <u>Summer of 2019</u>
  - e. <u>It is the recommendation of the Parks Maintenance Supervisor that a</u> <u>mechanical sand screen be purchased to remove rocks and debris</u> <u>from the field during summer months.</u> This same unit may be used <u>for the future sand volleyball court installation/maintenance</u>
    - i. <u>Barber Sandman TT</u>
      - 1. <u>https://www.youtube.com/watch?v=MSt1itwNQNU</u>

2. Price quote as of 06/2021 = ~\$13,000 before shipping

f. <u>It should be the goal to furnish grass in the outfields</u>