

RMP REGIONAL MONITORING PROGRAM FOR WATER QUALITY IN SAN FRANCISCO BAY

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Summary for Managers: Non-targeted Analysis of Stormwater Runoff following the 2017 Northern San Francisco Bay Area Wildfires

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Highlights

- Chemicals potentially related to wildfires were identified via non-targeted analysis
 of stormwater samples from watersheds in the City of Santa Rosa and Sonoma
 and Napa Counties after the three most destructive fires of the October 2017
 Northern California firestorm.
- Comparing samples from fire-impacted sites versus unburned reference sites led to high-confidence identifications of 76 potentially fire-related compounds. Authentic standards were available for 48 of these analytes, and 46 were confirmed by matching mass spectra and gas chromatography retention times. Of these 46 compounds, 37 had known commercial and industrial uses as intermediates or ingredients in plastics, personal care products, pesticides, and as food additives. Nine compounds had no known uses or sources and may be oxidation products resulting from burning of natural or anthropogenic materials.
- Limitations in the available data prevent selection of a specific list of contaminants for targeted monitoring following wildfires. However, study results still yield insights relevant to study design and interpretation, including a need for broad regional monitoring strategies to overcome variation across regions and reference sites that are sufficiently far from burned areas such that they are minimally impacted by the migration of fire-related chemicals. Pre- and post-fire monitoring of the same watershed could more easily identify fire-related contaminants and eliminate the need for reference sites. Non-targeted analysis spectra from any stormwater samples collected by the RMP should be archived for future use.

Background: The Potential Need for Expanded Contaminant Monitoring after Fires

Urban-wildland interfaces in the western US are increasingly threatened by the growing number and intensity of wildfires, potentially changing the type of contaminants released into the landscape as more urban structures are burned. In October 2017, the Tubbs, Nuns, and Atlas wildfires devastated communities in Northern California (Figure 1), burning over 8,500 buildings and 210,000 acres of land in the span of 24 days (California Department of Forestry and Fire Protection 2017). Together, these wildfires were the most destructive and costliest fires in the history of California at that time (California Department of Forestry and Fire Protection 2019).

Post-wildfire monitoring efforts in impacted watersheds typically focus on a few well-established water quality and chemistry concerns (McKee et al. 2018). Few studies go beyond these limited targeted analyses and attempt to identify the multitude of other fire-related compounds that are released from or form as the result of combustion of residential, commercial, and industrial structures in urban-wildland interfaces. Some of these unidentified compounds may be toxic to aquatic ecosystems or human health, and may pose risks to wildlife or in water bodies that act as drinking water supplies to nearby communities.

Following the 2017 Northern California wildfires, targeted monitoring of metals, nutrients, and up to 16 conventionally monitored PAHs in stormwater from burned watersheds in the City of Santa Rosa and in Sonoma and Napa Counties indicated a limited number of exceedances of toxicity thresholds, mostly for metals (North Coast Regional Water Quality Control Board 2018; San Francisco Bay Regional Water Quality Control Board 2018a; San Francisco Bay Regional Water Quality Control Board 2018b). However, this suite of chemicals evaluated did not encompass the wide range of fire-related chemicals produced during these destructive wildfires.

To better understand the contaminant-related risks of these events, it is important to expand the scope of monitoring. Non-targeted analysis is a cutting-edge technique based on high-resolution mass spectrometry that allows an expansive, open-ended look at thousands of chemicals at a time to determine their presence or absence. Non-targeted analysis can be used to broaden our understanding of the impacts of wildfires, thereby improving ecological risk assessment and management responses. California state guidance on emerging contaminants in aquatic ecosystems recommends non-targeted analysis as an essential means of assuring focus on the contaminants with greatest potential to impact an ecosystem, by seeking to remove a "knowledge bias" on previously identified problem chemicals (Dodder et al. 2015). The Regional Monitoring

Program for Water Quality in San Francisco Bay (RMP) Emerging Contaminants Strategy uses non-targeted analysis to create inventories of unanticipated contaminants in tissues, sediment, or water that can be used to direct targeted chemical monitoring or identify toxicity data gaps (Sutton et al. 2017). This type of approach has been used to identify novel contaminants in San Francisco Bay waters (Overdahl et al. 2021), marine mammal blubber and bivalve tissue (Sutton and Kucklick 2015), and wastewater effluent (Overdahl et al. 2021). Data from these non-targeted analysis studies has been integrated with toxicological risk screening methods to inform priorities for further work on contaminants of emerging concern.

This project represents one of the first applications of non-targeted analysis to identify novel contaminants released by or associated with wildfires (Chang et al. 2021).

Project Objectives

The objectives of this project were to:

- establish a sampling, analytical, and interpretive framework for more effectively monitoring contaminants of emerging concern derived from wildfires in environmental water samples, and
- identify additional potentially significant contaminants that are not routinely monitored after wildfires that may be of interest to monitor in future targeted analysis of wildfire-impacted waters.

This project examined post-fire stormwater discharges under the assumption that combustion residue from the North Bay fires deposited on the surrounding landscape, and subsequent rainstorms flushed the accumulated wildfire-related chemicals into waterways, introducing known and previously unknown contaminants to downstream surface waters. We sampled sites downstream of burned areas, as well as reference sites downstream of unburned areas. We used comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GCxGC/TOF-MS) to identify fire-related contaminants to inform future post-fire stormwater monitoring efforts. Chemicals that were potentially related to wildfires were selected from the thousands of chemicals preliminarily detected in the dissolved phase via non-targeted analysis by implementing a screening method based on comparison between samples from fire-impacted sites and unburned reference sites. Two classes of chemicals were identified: those that were uniquely present in the fire-impacted sites ("fire-specific"), and those that were present in both the fire-impacted and reference sites in one region ("region-wide"). We used the results to test the hypothesis that burned areas with greater urban

and suburban development would yield higher numbers of unique fire-related analytes. Upon tentative identification via comparison with a mass spectral library, the identities of selected chemicals were confirmed with authentic standards. Contaminants were examined for associations with combustion, and screened to determine possible sources and available ecotoxicological information.

Finally, with this summary we provide wildfire-related monitoring recommendations to the RMP. Because this study is a novel effort to provide qualitative occurrence information (not quantitative concentration data), and because many of the compounds identified have little to no toxicity data, it is not yet possible to establish a specific list of emerging contaminants suitable for targeted stormwater monitoring following wildfires. Nevertheless, the findings provide insights that can inform future study design.

Sample Collection and Analysis

Stormwater samples were collected from 12 sites: four sites from each of three regions, the City of Santa Rosa, and Sonoma and Napa Counties north of the San Francisco Bay Area (Figure 1). For two of three regions, reference sites were monitored concurrently to allow comparison of the burn-impacted areas to unburned reference areas in the vicinity. Sampling sites were a subset of those selected by two Regional Water Quality Control Boards (San Francisco Bay and North Coast) for targeted monitoring related to wildfire impacts, with selection based on factors including land use and density of burned structures, proximity to vulnerable aquatic habitat, availability of prior water quality data, and site accessibility (Table 1). Fire-impacted sites were all downstream of burned areas, although for a few with larger watersheds, the percentage of land burned was less than 20%. Reference sites were downstream of entirely unburned watersheds; however, atmospheric transport and deposition of unknown amounts of fire-related contaminants to the reference sites may be expected. The watersheds of reference sites do not contain significant development, while many of the watersheds of fire-impacted sites include developed areas.

Figure 1. Map of the study area (upper left) and each region (Tubbs Fire and the City of Santa Rosa, upper right; Nuns Fire in Sonoma County, lower left; and Atlas and Nuns Fires in Napa County, lower right) indicating sampling sites and fire-affected areas.

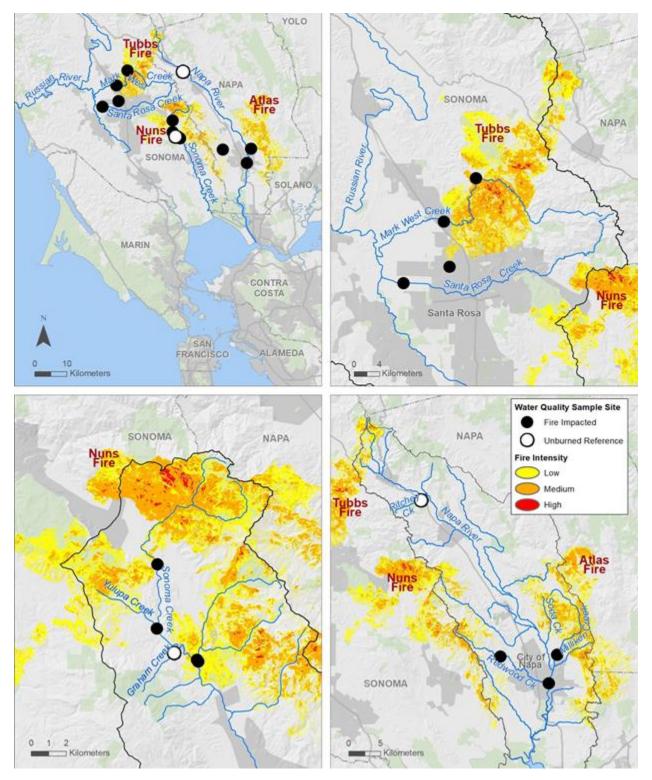


Table 1. Site information including coordinates, watershed area, and percentages of development and wildfire impacts.

Site	Coordinates (latitude, longitude)	Watershed Area* (km²)	Percentage Developed** (low, medium, high intensity)	Percentage Burned*** (low, medium, high intensity)	Turbidity [†] (ntu)
Sonoma					
Reference: Graham Creek 300 m upstream of Sonoma Creek confluence	38.36704 -122.541	4.92	0.05% Low	N/A	Storm 1 17.6 Storm 2 192 Baseline 0.48
Sonoma Creek at Cypress Ave	38.4122 -122.554	38.01	3.42% Low 1.22% Medium 0.02% High	25.8% Low 41.6% Medium 2.68% High	Storm 1 7.45 Storm 2 32.4 Baseline 0.56
Yulupa Creek above confluence with Sonoma Creek at Warm Springs Rd	38.3793 -122.553	17.21	0.30% Low	25.1% Low 14.% Medium 0.166 % High	Storm 1 2.52 Storm 2 302 Baseline NS
Sonoma Creek at Glen Ellen (includes all Sonoma watersheds above)	38.36376 -122.526	84.01	2.21% Low 0.66% Medium 0.02% High	21.7% Low 24.9% Medium 1.32% High	Storm 1 3.98 Storm 2 286 Baseline 0.52

Site	Coordinates (latitude, longitude)	Watershed Area* (km²)	Percentage Developed** (low, medium, high intensity)	Percentage Burned*** (low, medium, high intensity)	Turbidity [†] (ntu)
Napa					
Reference: Ritchie above gabion wall in Napa- Bothe State Park	38.55078 -122.521	6.32	0.03% Low 0.01% Medium	N/A	Storm 1 1.88 Storm 2 28.9 Baseline 1.29
Redwood Creek downstream of Pickle Creek at Mt Veeder and Redwood Rd. intersection	38.33388 -122.371	22.92	0.07% Low 0.02% Medium 0.01% High	13.3% Low 11.0% Medium 0.409% High	Storm 1 12.8 Storm 2 284 Baseline 1.51
Milliken Creek at Hedgeside Ave	38.33827 -122.269	44.66	2.74% Low 0.74% Medium 0.01% High	29.9% Low 32.9% Medium 0.774% High	Storm 1 7.12 Storm 2 51.3 Baseline 1.33
Napa River at public dock, Main and 3rd (includes all Napa watersheds above)	38.298 -122.283	732.78	3.04% Low 2.24% Medium 0.23% High	6.82% Low 5.2% Medium 0.147% High	Storm 1 30.1 Storm 2 43.5 Baseline NS

Site	Coordinates (latitude, longitude)	Watershed Area* (km²)	Percentage Developed** (low, medium, high intensity)	Percentage Burned*** (low, medium, high intensity)	Turbidity [†] (ntu)				
Santa Rosa									
Upper Mark West Creek	38.54958 -122.720	78.71	0.19% Low 0.016% Medium 0.001% High	9.26% Low 18.0% Medium 0.800% High	Storm 1 43 Baseline 0.575				
Lower Mark West Creek (includes Upper Mark West watershed)	38.50925 -122.770	111.11	1.23% Low 0.43% Medium 0.04% High	14.1% Low 26.6% Medium 0.854% High	Storm 1 19.6 Baseline 1.96				
Pine Creek	38.46264 -122.750	12.76	20.24% Low 31.30% Medium 7.40% High	25.4% Low 14.2% Medium 0.0137% High	Storm 1 89.3 Baseline 5.56				
Santa Rosa Creek	38.44517 -122.806	198.91	11.61% Low 12.17% Medium 1.74% High	9.33% Low 5.51% Medium 0.0365% High	Storm 1 75.7 Baseline 1.61				

^{*}Upstream contributing areas, or watersheds, for each sample point were calculated by using the ESRI "Watershed" tool for each point using a filled 10 m NED (Nation Elevation Model) to create flow direction and flow accumulation rasters. For each sample point, all upstream areas were merged into a single contributing area/watershed polygon, used to calculate acreage of the contributing area for each sample point.

**For each sample point's contributing area, NLCD2016 (National Land Cover Database 2016) land use data was used in a summary statistical analysis to assess the acreage and percent cover for each land use type.

^{***}The USDA Forest Service Geospatial Technology and Applications Center (GTAC)'s Burned Area Reflectance Classification (BARC) rasters for the Atlas, Nuns, and Tubbs Fires were used in a summary statistical analysis to assess the acreage and percent cover of low, moderate, and high severely burned areas.

†Turbidity data provided by the San Francisco Bay (Sonoma and Napa) and North Coast (Santa Rosa) Regional Water Quality Control Boards. Baseline turbidity was measured Nov. 1 (Santa Rosa) and Nov. 2 (Sonoma and Napa); NS = not sampled.

One-liter grab samples were collected directly into amber glass bottles from the surface of the water during up to two storm events after wildfire cessation. A storm event was considered suitable for sampling after passing the threshold of ≥ 1 in of precipitation in a span of 24 hr. The first two storms to meet these criteria were relatively small, and occurred on November 15, 2017, and January 8, 2018, resulting in modest increases above base flow. Samples were collected during the rising limb of the hydrograph. Turbidity measurements indicated the first storm (turbidity range 1.4-89 ntu) was lower energy than the second storm (turbidity range 28.9-302 ntu; Table 1). All regions were sampled during the first storm; during the second storm, the North Coast Regional Water Quality Control Board opted not to collect samples for non-targeted analysis in the Santa Rosa region. A field blank was collected during the sampling events in each region.

Samples were analyzed as the dissolved phase at San Diego State University, where they were vacuum filtered to remove sediment particles and concentrated via solid phase extraction using OASIS® HLB cartridges and dried using sodium sulfate. Final sample extracts were analyzed by Pegasus 4D comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC/TOF-MS). This approach focuses on nonpolar compounds.

For analysis, samples were grouped by region, with analytes categorized as "fire-specific" and "region-wide." Analytes were considered fire-specific if present in all the fire-afflicted sites of a particular region but not present in the corresponding reference site(s) and field blank. Analytes were also considered fire-specific if the ratio between the lowest peak area among the fire-afflicted sites was at least three times greater than the corresponding reference site peak area. Analytes that met the 3:1 peak area ratio threshold were considered to be present at a higher concentration in the burned sites, with the possible implication that they were produced during the fire and were introduced into the nearby waterways via distributive migration of fire residue during and after the fire events (Stein et al. 2012). Analytes meeting these criteria are referred to as "detected" in the discussion below.

In contrast, region-wide analytes were present in all fire-afflicted sites and the corresponding reference site(s) of a region, but not present in the field blank. For the

Santa Rosa region, where no specific reference site was sampled, the reference sites from both the Napa and Sonoma regions were used for these comparisons.

Detected analytes were mass spectra matched to an assigned library hit from the 2011 NIST Electron Ionization Mass Spectral Library, and were considered tentatively identified if they had a Similarity Score ≥ 700 (max 999), showed the top three most prominent ions from the NIST Library hit present, and had a similar pattern of intensity of ions to the NIST Library hit. Of the 177 fire-specific analytes detected, 76 were tentatively identified. Only tentatively identified analytes categorized as fire-specific were considered for confirmation with an authentic standard. Based on commercial availability, 48 authentic standards were obtained for identity confirmation. Among the 48 with available standards, the identities of 46 analytes were confirmed by matching mass spectra and retention time; a verification success rate of 96%. The remaining two analytes had mismatches in either retention time or mass spectra. The high identification accuracy is promising in that the non-targeted analysis results can provide a basis for reliable ecotoxicity assessment. It also serves as a foundation that supports enhanced efficiency of future non-targeted monitoring of environmental water samples. The main objective of the analyte identity confirmation step was to ensure further chemical reviews were conducted on reliable data.

Fire-specific contaminants with confirmed identities were further examined for associations with combustion, possible sources, and available ecotoxicity information; tentatively-identified region-wide analytes were not subjected to confirmation and, therefore, were not examined further.

Findings

Fire-Specific and Region-Wide Contaminants

The number of fire-specific analytes detected varied greatly by region, with Santa Rosa showing the highest number of detections followed by Napa and Sonoma in decreasing order (Table 2). In terms of fire-specific analytes detected across multiple regions, three were found in Napa and Santa Rosa samples for the first storm event, and three were found in Sonoma and Napa samples across the first and second storm events.

Table 2. Number of detected analytes in each region for each sampling event. NA = not available, samples not collected.

1st Storm Event (Nov. 15,	2017)		
	Sonoma	Napa	Santa Rosa
Fire-specific	3	40	97
Region-wide	163	178	307
2nd Storm Event (Jan. 8, 2	018)		
	Sonoma	Napa	Santa Rosa
Fire-specific	3	42	NA
Region-wide	114	91	NA

As the number of structures damaged or destroyed by the wildfires in the region increased, so did the number of detected analytes. The City of Santa Rosa experienced the highest numbers of structures destroyed or damaged (Tubbs Fire, 5953 structures) and also had the highest number of fire-specific analytes (97), followed by Napa (Atlas and Nuns Fires, 2431 structures) and Sonoma (Nuns Fire, 1528 structures) (California Department of Forestry and Fire Protection 2017; California Department of Forestry and Fire Protection 2019). This trend supported our hypothesis that there would be more contaminants from the more expansive chemical complexity of materials that make up anthropogenic structures and their contents compared to undeveloped areas. Some of these contaminants were likely discharged as a result of the wildfires, while others may have been present due to the higher levels of development at wildfire-impacted sites relative to reference sites. In addition to the number of structures burned, the types of structures burned also likely plays a role in the number and types of fire-related contaminants, and may explain why there were so few fire-specific contaminants in Sonoma compared to the other regions.

In every region for both sampling events, there were more detected analytes in the region-wide category than the fire-specific category. This difference was most prominent in Sonoma, where the number of region-wide analytes exceeded the number of fire-specific analytes by 54-fold for the first storm event and 38-fold for the second. The numbers of region-wide compounds were similar for Napa and Sonoma and higher in Santa Rosa, possibly reflecting the higher levels of development in the latter region. These findings suggest there can be considerable variation across neighboring regions,

indicating a need for broad regional monitoring strategies when applying non-targeted analysis. Upon cross-referencing, 55 analytes were found in all three regions for the first storm event samples and 48 were found in both regions for the second storm event samples.

It is possible some region-wide compounds were formed during wildfires. Dry and wet deposition (Sabin et al. 2005) of wildfire-induced chemicals could disperse them to the unburned reference areas beyond the perimeters of burned areas. Plumes of smoke from these fires blanketed not only the North Bay but also much of the Bay Area (Nauslar et al. 2018), resulting in poor air quality (Gupta et al. 2018). Diablo winds, a San Francisco Bay Area meteorological phenomenon that is characterized by warm, dry gusts of wind that rapidly spread the initial ignitions into mega-fires (Werth et al. 2011; Smith et al. 2018), likely induced transport of wildfire residue during and after the fire events. These winds have the capacity to lift off burning biomass, ash, and smoke from the ground and disperse them in multiple directions.

The selection of reference sites may strongly influence the identification of both fire-specific and region-wide contaminants, as these were identified based on comparisons of detections among different sites. Sonoma's reference site (Graham Creek) was located closest to the main tributary that passes through the burned area (less than 500 m); the Sonoma region was observed to contain the least number of firespecific analytes as well as greatest relative difference between the number of firespecific and region-wide analytes. Napa's reference site (Ritchie Creek) was at least 8 km away from the burned areas; the Napa region had a higher abundance of firespecific analytes overall and less relative difference between the number of fire-specific and region-wide analytes. This trend suggests an inverse relationship between the distance from the burned areas to the sampling sites and the degree of indirect wildfire influence on surface water. When the location of the reference site is positioned closer to the burned area, the site is more prone to the migration effects of fire-related chemicals, hindering the selectivity in identifying chemicals that are specific to the burned areas. For a clearer distinction between the two categories, setting the reference site location adequately far apart from the burned area is recommended for future monitoring efforts. Should broader application of non-targeted analysis be implemented generally in California streams, the potential for comparison of samples collected before and after wildfires may become possible, an alternative study design that would avoid potential limitations in interpretation that can be introduced by reference sites.

Preliminary Source Identification and Ecotoxicity Screening of Fire-Specific Analytes

We compiled information about the 46 identity-confirmed compounds from online chemical databases such as PubChem and WebWISER to establish a preliminary picture of the types and potential toxicological concerns of fire-specific chemicals in stormwater runoff (Table 3). A previous study of organic constituents of wildfire ash indicates that carbon (C) is the major organic element, but other elements are also present in smaller proportions mainly in heterocyclic compounds; organic nitrogen (N) is lost first, then oxygen (O) and hydrogen (H), and lastly C (Bodí et al. 2014). Therefore, we expected a high proportion of fire-derived compounds to be aromatic or cyclic structures, containing a small proportion of N and O compared to C. This hypothesis was confirmed. Of the 46 fire-derived compounds confirmed in this study, thirty two compounds contain a phenyl or aromatic ring. Twenty-three compounds contained a cyclic chemical structure. Only three compounds were neither cyclic nor aromatic. Thirty-six compounds contained O, 15 compounds contained N, two compounds contained sulfur, and three compounds did not contain any of these heteroatoms.

Some of the 46 compounds identified are known to be pyrogenic. For example, phthalic anhydride is found in incinerator emissions, diesel exhaust, and oak and tobacco smoke (USEPA 2019); 2,4-dimethyl-phenol is found in gas and diesel exhaust (Hoffmann and Wynder 1963) and cigarette smoke (Clark and Bunch 1996); quinoline is present in coal (Cooke and Gaikwad 1984) and tobacco smoke (Adams et al. 1983); and 2-cyclopenten-1-one, 2-methyl is found in the combustion of black tea, bread flour, and cane sugar (Sung 2013). This provides further support that many of the fire-specific compounds found in this study are associated with burning and combustion. In contrast, some of the chemicals categorized as fire-specific, such as caffeine, simply reflect the presence of higher levels of human development at fire-impacted sites relative to reference sites.

Thirty-seven compounds are used in a variety of commercial and industrial products as intermediates or ingredients in plastics, personal care products, pesticides, and as food additives. These chemicals may have originated from structures in the developed portions of the watersheds, with combustion as one possible means of release. Nine compounds had no known uses or sources. They are partially aromatic or cyclic and eight compounds contain oxygen. They may be oxidation products after burning of natural or anthropogenic materials.

Table 3. Identity-confirmed fire-specific analytes in stormwater. Compounds are listed in order of freshwater predicted no effect concentration (PNEC), from smallest to largest. This type of non-targeted analysis does not provide qualitative concentrations, so lower PNECs do not necessarily reflect higher risk. NA = not available.

Name	CAS#	Region	Use	PNEC (µg/L)	Assessment Factor	Species	Endpoint	PNEC Reference
2- Nonadecanone	629- 66-3	Napa	fatty acid (naturally occurs in saliva)	0.025	1000	Selenastrum capricornutum	QSAR- predicted growth EC50	NORMAN
Benzene, 1,1'- (1,3-butadiyne- 1,4-diyl)bis-	886- 66-8	Santa Rosa	unknown but active TSCA Commercial Activity Status	0.058	1000	Pimephales promelas	QSAR- predicted acute LC50	NORMAN
2-Benzothiazo- lamine, N- cyclohexyl-	28291- 75-0	Santa Rosa	unknown	0.093	1000	Pimephales promelas	QSAR- predicted acute LC50	NORMAN
Pentadecanoic acid	1002- 84-2	Santa Rosa	used in manufacture of paper products and plastics; adhesive; fragrance; naturally found in mammal milk	0.16	1000	Selenastrum capricornutum	QSAR- predicted growth EC50	NORMAN

Name	CAS#	Region	Use	PNEC (µg/L)	Assessment Factor	Species	Endpoint	PNEC Reference
Octocrylene	6197- 30-4	Napa	plastic additive; UV filter (sunscreen, cosmetics); used in paints/waxes/ polishes	0.266	10	Daphnia magna	measured chronic reproduction NOEC	ECHA 2020a
Benzothiazole, 2-(methylthio)-	615- 22-5	Santa Rosa	unknown but active TSCA Commercial Activity Status	1.14	1000	Daphnia magna	QSAR- predicted acute LC50	NORMAN
2- Coumaranone	553- 86-6	Napa	unknown	1.2	1000	Selenastrum capricornutum	measured growth EC10	*ECHA 2020b
Proximpham	2828- 42-4	Napa	herbicide	2.55	1000	Daphnia magna	QSAR- predicted acute LC50	NORMAN
Phenol, 2,6- dimethoxy-	91-10- 1	Santa Rosa	fragrance/ flavoring agent	2.59	1000	Daphnia magna	QSAR- predicted acute LC50	NORMAN
Phenol, 2,4- dimethyl-	105- 67-9	Santa Rosa	industrial intermediate (phosphate esters, resins, rubbers); fragrance	2.7	100	Daphnia magna	measured chronic reproduction NOEC	*ECHA 2020c

Name	CAS#	Region	Use	PNEC (µg/L)	Assessment Factor	Species	Endpoint	PNEC Reference
			(cosmetics); antimicrobial; component of coal, gas/diesel exhaust, and					
Phenol, 2-(1- methylethyl)-	88-69- 7	Santa Rosa	cigarette smoke flavoring agent	3.87	1000	Pimephales promelas	QSAR- predicted acute LC50	NORMAN
1,2,4- Trimethoxy- benzene	135- 77-3	Santa Rosa	attractant	4.36	1000	Daphnia magna	QSAR- predicted acute LC50	NORMAN
Phenol, 3,4,5- trimethoxy-	642- 71-7	Napa	consumer use, has been detected in toys	4.89	1000	Daphnia magna	QSAR- predicted acute LC50	NORMAN
5,6-Dimethyl- 1H- benzotriazole	4184- 79-6	Santa Rosa	unknown	4.94	1000	Selenastrum capricornutum	QSAR- predicted growth EC50	NORMAN
Dodecane, 2,6,10- trimethyl-	3891- 98-3	Napa	biofuel; cosmetic ingredient	5.4	10	Daphnia magna	measured chronic reproduction NOEC	ECHA 2020d
2(5H)- Furanone, 5- methyl-	591- 11-7	Santa Rosa	flavoring agent	7.38	1000	Pimephales promelas	QSAR- predicted acute LC50	NORMAN

Name	CAS#	Region	Use	PNEC (µg/L)	Assessment Factor	Species	Endpoint	PNEC Reference
4- Methylphthalic anhydride	19438- 61-0	Santa Rosa	unknown but active TSCA Commercial Activity Status	9.42	1000	Pimephales promelas	QSAR- predicted acute LC50	NORMAN
Phenol, 2- methoxy-	90-05- 1	Napa	pharmaceutical; fragrance/ flavoring agent; naturally occurring plant oil	10	1000	Selenastrum capricornutum	measured growth NOEC	*ECHA 2020e
Quinoline	91-22- 5	Santa Rosa	industrial intermediate/ solvent (pharmaceuticals, dyes, paints); flavoring agent; naturally present in coal and tobacco smoke	16	50	Daphnia magna	measured chronic reprouction NOEC	ECHA 2020f
Ethanone, 1- (2,5- dimethylphenyl)-	2142- 73-6	Napa	unknown	16.2	1000	Daphnia magna	QSAR- predicted acute LC50	NORMAN
1H-Inden-1- one, 2,3- dihydro-	83-33- 0	Santa Rosa	natural part of steroid hormone biosynthesis	22.2	1000	Daphnia magna	QSAR- predicted acute LC50	NORMAN

Name	CAS#	Region	Use	PNEC (µg/L)	Assessment Factor	Species	Endpoint	PNEC Reference
1H-Isoindole- 1,3(2H)-dione, 2-methyl-	550- 44-7	Santa Rosa	used in plastics manufacturing	22.7	1000	Selenastrum capricornutum	QSAR- predicted growth EC50	NORMAN
Ethanone, 1- (3-hydroxy- phenyl)-	121- 71-1	Santa Rosa	unknown but active TSCA Commercial Activity Status	22.8	1000	Daphnia magna	measured acute EC50	*ECHA 2020g
Pyrazine, ethyl-	13925- 00-3	Santa Rosa	fragrance/ flavoring agent	23.8	1000	Selenastrum capricornutum	QSAR- predicted growth EC50	NORMAN
Pyrazine, 2,3- dimethyl-	5910- 89-4	Napa	fragrance/ flavoring agent (including in tobacco products)	25.6	1000	Selenastrum capricornutum	QSAR- predicted growth EC50	NORMAN
2-Cyclopenten- 1-one, 3,4- dimethyl-	30434- 64-1	Santa Rosa	unknown	25.6	1000	Daphnia magna	QSAR- predicted acute LC50	NORMAN
Isophthal- aldehyde	626- 19-7	Napa	unknown	33.7	1000	Pimephales promelas	QSAR- predicted acute LC50	NORMAN
Formamide, N-cyclohexyl-	766- 93-8	Santa Rosa	unknown	35.1	1000	Selenastrum capricornutum	QSAR- predicted growth EC50	NORMAN

Name	CAS#	Region	Use	PNEC (µg/L)	Assessment Factor	Species	Endpoint	PNEC Reference
Ethanone, 1,1'- (1,4- phenylene)bis-	1009- 61-6	Napa	fragrance	40.9	1000	Daphnia magna	QSAR- predicted acute LC50	NORMAN
Phthalimide	85-41- 6	Santa Rosa	used in the production of dyes; found in rubber tires; fungicide	76	100	Daphnia magna	measured chronic reproduction NOEC	*ECHA 2020h
Caffeine	58-08- 2	Sonoma	stimulant	87	1000	Leuciscus idus	measured acute LC50	ECHA 2020i
1,2- Cyclohexane- dione	765- 87-7	Napa	flavoring agent	94.1	1000	Daphnia magna	QSAR- predicted acute LC50	NORMAN
Pyridine, 2- methyl-	109- 06-08	Santa Rosa	industrial intermediate for rubber, dyes, and resins	300	1000	Selenastrum capricornutum and Daphnia magna	measured growth EC50 and acute LC50	ECHA 2020j
Phthalic anhydride	85-44- 9	Napa	intermediate in the manufacture of plasticizers, resins, pigments/dyes, agricultural, pharmaceutical, and other	1000	10	Oncorhynchus mykiss	measured chronic embryotoxici ty NOEC	ECHA 2020k

Name	CAS#	Region	Use	PNEC (µg/L)	Assessment Factor	Species	Endpoint	PNEC Reference
			commercial					
			chemicals; found					
			in incinerator					
			emissions, diesel					
			exhaust, and					
			smoke (oak,					
			tobacco, etc.);					
			may form as an					
			artifact in GC					
			analysis					
Ethanone, 1- (3,4-dimethyl- phenyl)-	3637- 01-02	Napa	used in petroleum production	NA				
1,3-			unknown but					
Dicyclohexyl-	2387-	Santa	active TSCA	NA				
urea	23-7	Rosa	Commercial	INA				
ulea			Activity Status					
2-Cyclopenten-	1120-	Santa	found in					
1-one, 2-	73-6	Rosa	combustion of	NA				
methyl-	75 0	11034	food products					
Benzamide, N,N-diethyl-4- methyl-	2728- 05-04	Sonoma	unknown	NA				
1-Propyne, 3- phenyl-	10147- 11-2	Napa	unknown	NA				

Name	CAS#	Region	Use	PNEC (µg/L)	Assessment Factor	Species	Endpoint	PNEC Reference
Cyclohexanone , 3-methyl-, (R)-	13368- 65-5	Santa Rosa	unknown	NA				
4,4-Dimethyl-2-cyclopenten-1-one	22748- 16-9	Santa Rosa	unknown	NA				
2H-Pyran-2- one, 5,6- dihydro-	3393- 45-1	Santa Rosa	unknown	NA				
2-Cyclohexen- 1-one, 3,5- dimethyl-	1123- 09-07	Santa Rosa	unknown	NA				
7-Methylindan- 1-one	39627- 61-7	Santa Rosa	unknown	NA				
1(3H)- Isobenzo- furanone, 5- methyl-	54120- 64-8	Santa Rosa	unknown	NA				
1(2H)- Acenaphthyl- enone	2235- 15-6	Santa Rosa	unknown	NA				

^{*}PNEC calculated from data provided in the cited reference following standard guidance (ECHA 2008).

As a preliminary screening of potential toxicological risk to aquatic systems, we compiled available predicted no effect concentrations (PNECs) for freshwater (Table 3). All available PNECs were deterministically derived. The species, endpoint, and assessment factors used to derive the PNECs give an idea of their level of uncertainty; for example, a PNEC derived from a quantitative structure-activity relationship (QSAR)-predicted estimate of an acute LC50 is more uncertain than a PNEC derived from a measured chronic endpoint such as reproduction. Similarly, the larger the assessment factor, the more uncertainty associated with the final PNEC value. Nevertheless, comparing PNECs allows an initial assessment of the potential risks of the confirmed analytes. Of the 34 PNECs compiled, 28 had assessment factors of 1000, indicating considerable uncertainty and the need for further study to better characterize toxicity. Twelve of the 46 identified compounds did not have available PNECs and their potential toxicity is therefore unknown; the majority of these compounds also had no clear source or use, suggesting they may be novel pyrogenic products.

Risk assessment typically involves comparison of occurrence levels with thresholds for adverse effects; because this non-targeted analysis did not focus on yielding quantitative concentrations, we cannot directly compare PNECs with measured concentrations. Many identified compounds have little to no toxicological data available, and could be combustion products that have, to date, not been studied. However, this does not mean they are not potentially toxic to aquatic ecosystems or human health. This work, along with future fire monitoring efforts, may indicate a need for further toxicological study of these contaminants.

As an additional indicator of potential toxicological risk, we also compiled hazard listings for each chemical from Pharosproject.net, an online catalog of key health and environmental hazard information and process chemistry developed by the Healthy Building Network (for details see Chang et al. 2021 Table S3). Four compounds, all identified as industrial intermediates and/or used in plastics manufacturing, were identified as known concerns in the US due to their toxicity to aquatic ecosystems. Three of the four compounds (phthalic anhydride, 2,4-dimethyl-phenol, and quinoline) are specifically of concern in California, as they are listed on the California Department of Toxic Substances Control (DTSC) Candidate Chemical List; quinoline is also on California's Proposition 65 list. The fourth compound, 2-methyl-1H-isoindole-1,3(2H)-dione, is a priority chemical in Minnesota and may also be of interest in other parts of the US. Other compounds, such as octocrylene, a plastic additive and sunscreen active ingredient, and 2,6,10-trimethyl-dodecane, used in biofuels and personal care products, are identified as high concern substances outside of the US.

The compounds already identified as known concerns in the US or other countries could be the focus of future targeted monitoring or method development, particularly those with relatively low PNECs and more certainty (lower assessment factors), such as octocrylene (PNEC 0.266 µg/L) and 2,6,10-trimethyl-dodecane (PNEC 5.4 µg/L). An additional aquatic toxicity concern, the compound proximpham, was once used as an herbicide but is now considered obsolete, with no registered uses in the US; this compound may have formed from breakdown of a parent compound, or possibly during combustion. Additional unrestricted compounds are also listed as potential or known hazards to aquatic environments, including caffeine, 2-methoxy-phenol, 2-(1-methylethyl)-phenol, 4-methylphthalic anhydride, and 1,3-dicyclohexylurea.

To assess ecological risk to downstream receiving waters including San Francisco Bay, the loading and fate of these contaminants must also be considered. Loading estimates require information on contaminant concentrations and stormwater flows. Upon discharge to receiving waters, physicochemical properties including partitioning and persistence can determine whether contaminants can build up to levels of toxicological concern. Non-targeted analysis can be considered a first step in developing an overall understanding of the potential for emerging contaminants from wildfires to impact water quality in the Bay.

Conclusions and Recommendations for Future Monitoring

Projected longer and fiercer fire seasons in California imply that environmental impacts of wildfires will continue to become more severe in the future (Fried et al. 2004; Westerling and Bryant 2008; Hurteau et al. 2014). In this regard, public and environmental health organizations and water agencies will need to develop and implement more advanced means to identify previously unknown contaminants and manage the growing catalog of contaminants produced from larger and increasingly frequent wildfires.

Use of novel approaches such as the non-targeted analysis method presented in this study will allow managers to make decisions based on the most current, comprehensive, and relevant information. Beyond supporting improved decision-making, data acquired using this framework can be used to develop models for more efficient identification and prediction of contaminants of emerging concern in aquatic ecosystems.

As this study represents the first application of this framework, limitations in the available data prevent selection of a specific list of contaminants for targeted monitoring

following wildfires. Nevertheless, we can draw a number of insights relevant to study design and interpretation.

Recommendations for Future Monitoring

- Employing non-targeted analysis more broadly to characterize stormwater in local tributaries can allow for comparison of pre- and post-fire water samples at the same site affected by wildfires. Using historic fire data could be useful for identifying watersheds that are most likely to be affected by wildfires for pre-fire sampling efforts. This alternative study design does not rely on reference sites for identification of contaminants potentially related to wildfires. Non-targeted analysis spectra from any stormwater samples collected by the RMP should be archived to allow for this type of use in the future.
- Broad regional monitoring strategies are needed to successfully apply nontargeted analysis and overcome variation across regions. Our comparison of the region-wide contaminants identified in each of the three neighboring regions indicated considerable diversity in detected contaminants. This suggests caution should be exercised when generalizing across regions, and that a geographically broad sampling strategy may be preferred for adequate characterization of contaminants.
- Reference sites should be adequately far from the burned areas such that they are minimally impacted by the migration of fire-related chemicals. An ideal reference site is one that is somewhat distant from fire-impacted zones and, therefore, less prone to receiving fire-related chemicals through processes including wet and dry air deposition. At the same time, it is important that the reference site is not so distant from burned areas as to be regionally distinct in its contaminant profile. Ideally, the watersheds of reference sites would contain similar levels of development as fire-impacted sites, unlike the relatively undeveloped reference sites we used in this study. Using air quality monitoring sites could also help to identify a less impacted reference site by determining the smoke plume direction and extent of air deposition during the wildfire.
- Additional studies of wildfires may provide sufficient support for targeted monitoring of some of the compounds we identified, particularly those with lower PNECs and higher levels of available toxicity data, such as octocrylene and 2,6,10-trimethyl-dodecane. At present, there is some uncertainty as to whether these contaminants were discharged as a result of the wildfires, or may have been present due to the higher levels of development at wildfire-impacted sites relative to reference sites. Further studies may supply information that can be

used to elucidate the sources of identified contaminants. For example, sampling post-post-fire (e.g., several months to years later) could help confirm both longevity of contaminants (for exposure assessment) and if observed contaminants were fire-associated or if they are always present regardless of wildfires.

Non-targeted analysis based on liquid chromatography, rather than the gas
chromatography method used in this study, can complement existing data by
providing information on the presence of polar compounds in stormwater
samples. Scientists at California's Department of Toxic Substances Control are
currently preparing a manuscript describing the results of a non-targeted analysis
of the same stormwater samples using liquid chromatography and quadrupole
time-of-flight mass spectrometry.

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