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Riot Control Agent Stormwater and Catch Basin Sampling Summary

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Report prepared by the
City of Portland Bureau of Environmental Services
Portland, Oregon

For More Information
Barb Adkins
Barbara.Adkins@portlandoregon.gov

Introduction

In response to Oregon Department of Environmental Quality's (DEQ) letter dated July 30, 2020 (Svetkovich 2020) and in accordance with the Stormwater Monitoring Plan (BES 2016) prepared for compliance with requirements included in the City's National Pollutant Discharge Elimination System (NPDES) Municipal Separated Storm Sewer System (MS4) Permit #101314 (BES 2016), the Bureau of Environmental Services (BES) prepared a Sampling and Analysis Plan (SAP) for conducting stormwater sampling to evaluate potential impacts to the City's storm system from Riot Control Agents (RCAs). The SAP was submitted to DEQ on August 20, 2020 (Adkins 2020).

The SAP focuses on collecting stormwater grab samples to evaluate whether there are indications of RCA residuals reaching the City's storm system. A small storm was forecasted and successfully sampled by BES' Field Operations staff on August 6, 2020. As directed by DEQ and the SAP, this storm represented a first flush rain event with discharge to the Willamette River and satisfies the sampling required by DEQ (Svetkovich 2020). All sampling and associated analyses were completed in compliance with the SAP and DEQ's requirement to conduct additional water quality monitoring per Schedule F, Section A, 3 of the City's current NPDES MS4 Permit. No previous pollutant-specific monitoring has been conducted at the sampling locations identified in the SAP. As such, only the results from the August 6 sampling are presented here.

In addition to the stormwater sampling required by DEQ, BES collected sediment samples from seven stormwater catch basins located in the same stormwater basin. The intent of the sediment sampling was to characterize the material accumulated in the catch basins and to evaluate whether there are any indications of RCA residuals in the material prior to removal. This report provides a summary of the results from the stormwater sampling conducted by BES on August 6, 2020 as well as the catch basin sediment sampling results conducted by BES on July 31, 2020.

Sampling Approach

RCA products were deployed by the Portland Police Bureau (PPB) and federal agents at, and in the vicinity of, the Multnomah County Justice Center and Mark O. Hatfield US District Courthouse (US Courthouse) in downtown Portland. RCA usage that informed the stormwater and catch basin sampling effort included the RCA usage that began at the end of May 2020 and continued through the end of July 2020. Though RCA use in downtown Portland has been well-documented through the news and social media, BES also evaluated citizen-generated Geographical Information System (GIS) data to confirm the approximate geographical extent of RCA use (Brumbaugh-Smith 2020). GIS data were generated through video footage from local journalists and not collected by the City. Therefore, although the accuracy of the data cannot be assessed or confirmed, the data appeared to be of sufficient quality, based on news reports, to set approximate boundaries for the study area. RCA deployment locations documented by Brumbaugh-Smith (2020) from late May through July 18 are included in Maps 1–4.

The stormwater sampling approach described in the SAP was structured to include a site (SW 3rd and Salmon; ABQ484; Map 1) where the heaviest and most frequent RCA deployment was known to have repeatedly occurred (Adkins 2020), as well as a control site within the same stormwater basin where RCA usage is thought to have not occurred (SW Park and Salmon; ABQ669; Map 2). The SW 3rd and Salmon site (ABQ484) is also the location in the City's storm system that likely captures runoff from cleaning activities in front of the US Courthouse. These two sites have similar sized catchments and analogous land uses, allowing for a direct comparison between samples. The stormwater sampling site located at SW 1st and Jefferson (ABQ608) is located close to the outfall within the same stormwater basin and represents the characteristics of the stormwater that reaches the Willamette River. The catch basin sediment sampling approach was also designed to include samples from areas of known RCA deployment (Map 3), as well as a control site (SW 3rd and Clay; AMU048; Map 4). Through extensive routine stormwater monitoring, BES has found that the concentration of pollutants in stormwater can be highly variable in the city. Given the anticipated variability, control sites were included in the sampling effort to provide a dataset suitable for direct comparison.

As noted in the SAP, specific analytical methods are not available for the primary active agents used in RCA products—o-chlorobenzylidene malononitrile (CS gas) and oleoresin capsicum (pepper spray/OC gas). Consequently, the SAP focused on collecting and analyzing samples for analytes associated with RCA dispersion: CS gas dispersion byproducts, additives, and pyrotechnic compounds.

BES reviewed available material safety data sheets (MSDSs) for the RCA products used by PPB to identify potential analytes that may indicate the presence of RCA residuals. BES also determined through information provided by the public that federal agents used additional RCA products not used by PPB. BES used the MSDS review of RCA products to provide additional guidance on the selection of appropriate analytes and analytical methods in the SAP. The RCA chemicals and additives identified in Appendix A should not be considered a complete list of all possible RCA residuals as BES was unable to obtain and review MSDSs for two RCA products on the list provided by PPB. Additionally, while the published MSDSs do provide some information regarding the composition of the reviewed RCA products, the amounts of each chemical used in a product are considered trade secrets and are not disclosed by the manufacturers. Furthermore, a list of RCA products used by federal agents was not available to support BES' development of the SAP and subsequent data analysis. BES is expecting to received information on the types and amounts of RCA products used by federal officials from the Department of Homeland Security (DHS). The anticipated RCA product list from DHS is not expected to include all federal RCA usage. This information was not available at the time of this report.

Table 1. Common stormwater pollutants and potential pollutant sources. Adapted from BES' UIC Ground Protectiveness Demonstration (GWPD) Framework (2008).

Stormwater Pollutant Category	Potential Pollutant Sources
Petroleum Hydrocarbons	Automobile drippage (fuel, oil, grease), asphalt wear, tires
Polycyclic Aromatic Hydrocarbon (PAHs) and Semi-Volatile Organic Compounds (SVOCs)	Fuels, automobile exhaust (fuel combustion), air deposition, asphalt, tires, wood preservatives
Pentachlorophenol	Treated wood, wood preservatives
Phthalates	Used automotive oil, automotive belts, brake pads, tires
Metals	Automobiles, roof runoff, native soil, pesticides
Pesticides/Herbicides	Insecticides and herbicides applied in or near rights-of-way
Nutrients (Nitrates, phosphorus)	Fertilizers, landscaped areas
Bacteria (e.g. *E. coli*, fecal coliform)	Animal waste

The presence or abundance of metals and other constituents at any of the sampling locations may be due to the use of RCA products; however, it is important to note that many analytes are routinely found in stormwater (e.g. metals), while others (e.g. cyanide, hexavalent chromium, and perchlorate) are not generally found in stormwater, and thus are not commonly sampled. Many of the pollutants commonly found in stormwater are associated with sources and activities that are found in the sampled stormwater basin (Table 1). It is important to recognize that given the range of potential pollutant sources in the basin, as well as incomplete knowledge of the precise area or quantity of RCA deployment, detecting pollutants associated with RCA residuals does not mean that RCA products are the exclusive source of these pollutants.

Sampling Events

All stormwater grab samples were analyzed for the complete list of analytes requested by DEQ, as well as the additional analytes identified by BES (Table 2). Though most RCA components do not have specific analytical methods available, all the products reviewed by BES contained metals that are reportable by EPA Method 200.8. To supplement the analyses requested by DEQ, BES also included additional analyses based on readily available analytical methods and/or stormwater and surface water quality screening criteria.

All catch basin sediment samples were analyzed for the same list of analytes requested by DEQ for the stormwater sampling (Svetkovich 2020). Based on BES' RCA product review additional analytes were also analyzed (Table 2).

Table 2. Analytes, analytical methods, and laboratories utilized for the August 6, 2020 stormwater sampling and the July 31, 2020 catch basin sediment sampling.

Analytes	Method	Laboratory
DEQ Requested Analytes (Stormwater)		
Total Metals (Ba, Cr, Cu, Pb, Zn)*	EPA 200.8	BES Water Pollution Control Lab, Portland, OR
Hexavalent Chromium	EPA 218.6	ALS Rochester, NY
Perchlorate	EPA 6850	ALS Houston, TX
BES Identified Analytes (Stormwater)		
Dissolved Metals (Ba, Cr, Cu, Pb, Zn)*	EPA 200.8	BES Water Pollution Control Lab
Dissolved Hexavalent Chromium	EPA 218.6	ALS Rochester, NY
Chloride	EPA 300.0	BES Water Pollution Control Lab
Cyanide	SM 4500-CN E	BES Water Pollution Control Lab
Semi-Volatile Organic Compounds (SVOCs)	EPA 8270	BES Water Pollution Control Lab
BES Identified Analytes (Catch Basin Sediment)		
Total Metals (Ba, Cr, Cu, Pb, Sb, Zn)*	EPA 6020	BES Water Pollution Control Lab
Hexavalent Chromium	7196A	ALS Rochester, NY
Cyanide	SM 4500-CN E	BES Water Pollution Control Lab
Perchlorate	EPA 6850	ALS Houston, TX
Total solids	SM 2540G	BES Water Pollution Control Lab

* Ba: barium; Cr: chromium; Cu: copper; Pb: lead, Sb: antimony; Zn: zinc

Stormwater Sampling

A small storm was forecasted and successfully sampled by BES field staff on August 6, 2020. The storm resulted in a rainfall total of 0.12" over a duration of 5 hours with a peak intensity of 0.07" per hour. BES field staff collected water quality grab samples from the three manholes listed in Table 3. They were unable to collect samples from outfall 8A (ABQ663) as the outfall was submerged and insufficient positive flow was observed by staff; consequently, samples were collected from the first alternate location (ABQ608). The two targeted manholes (ABQ484 and ABQ669; Table 3) were also sampled.

The complete details of the field collection effort, including maps, field notes, and event photographs are included in BES' Stormwater Sampling and Analysis Plan and Sampling Event Summary letter dated August 20, 2020 (Adkins 2020).

Table 3. Basin 8A sampling locations and descriptions for the August 6, 2020 sampling event. Sampling locations are included in Maps 1 and 2.

Stormwater Sampling Location	Stormwater Location Description
Manhole ABQ608 (*Outfall alternate*)	Manhole at intersection of SW 1st and Jefferson. Alternate location to outfall 8A (ABQ663) that was inaccessible due to high river levels. This location collects stormwater from the entire outfall basin except for a two-block segment along SW Naito Parkway south of the outfall.
Manhole ABQ484	Manhole at intersection of SW 3rd and Salmon. Located in front of the US Courthouse (up-pipe from ABQ608). Intended to represent the area of heaviest RCA use.
Manhole ABQ669 (*Control site*)	Manhole at intersection of SW Park and Salmon. Located up-pipe from ABQ484. Intended to be the control site because its location up-pipe and west of the areas of noted RCA usage in the outfall 8A basin.

Catch Basin Sampling

BES field staff collected sediment samples from seven catch basins on July 31, 2020 (Table 4). Four catch basins at the intersection of SW 3rd and Main and two catch basins at SW 3rd and Salmon were sampled. An additional catch basin at SW 3rd and Clay was sampled—a location outside of the drainage area with regular RCA deployment which is intended to serve as a control site.

The catch basin located at the south corner of SW 3rd and Salmon (AQY841) was not sampled during the July 31 effort as the placement of fencing and concrete barriers surrounding the US Courthouse at SW 3rd and Salmon prevented field staff from accessing the catch basin. BES requested temporary access to the catch basin from General Services Administration (GSA), the operators of the federal facility, for sampling and cleaning, but the request was denied.

All sediment samples were collected following the Guidance for Sampling of Catch Basin Solids standard operating procedure.[1] Samples were collected from the accumulated sediment within the catch basin or from areas of sediment accumulation adjacent to the catch basin. All catch basins were cleaned by BES

[1] CH2M Hill. 2003. *Standard Operating Procedure Guidance for Sampling of Catch Basin Solids*. Prepared for City of Portland. https://www.oregon.gov/deq/FilterDocs/ph-CatchBasinSolids.pdf

after sediment samples were collected, but prior to the August 6 storm. The catch basin control site (AMU048) was not cleaned out as it was located outside the RCA use area.

Table 4. Sediment sampling locations and descriptions for the July 31, 2020 sampling event.

Catch Basin Location	Intersection	Catch Basin Intersection Location	Catch Basin Location Notes
AMU048	SW 3rd & Clay	North corner	Control site
AQL327	SW 3rd & Main	South corner	25% of sample from catch basin grate lip, 75% from bottom of catch basin
AQL328	SW 3rd & Main	West corner	
AQL329	SW 3rd & Main	West corner, 20 feet NW of AQL328	
AQL330	SW 3rd & Main	North corner	
AQY839	SW 3rd & Salmon	North corner	
AQY840	SW 3rd & Salmon	West corner	No catch basin accumulation, sample collected from adjacent street surface

Results

All analyzed metals were detected at the three stormwater sampling locations. The highest total metal stormwater concentrations were observed at SW 3rd and Salmon (ABQ484). Concentrations of dissolved barium and dissolved chromium (total and hexavalent) were also highest in the stormwater at SW 3rd and Salmon (ABQ484), while dissolved copper, dissolved lead, and dissolved zinc concentrations were highest at the SW Park and Salmon control site (ABQ669).

Only 3 of the 66 semi-volatile organic compounds (SVOCs) were detected during the August 6 stormwater sampling event: bis(2-ethylhexyl) phthalate, pentachlorophenol, and phenol. Bis(2-ethylhexyl) phthalate was not detected at the SW Park and Salmon control site (ABQ669) but was detected at the two stormwater sampling locations closer to outfall 8A (ABQ484 and ABQ608). Conversely, pentachlorophenol and phenol were detected in stormwater only at the SW Park and Salmon control site (ABQ669), but at concentrations only slightly higher than the detection limit.

The highest chloride stormwater concentration was observed at SW 1st and Jefferson (ABQ608), the manhole closest to outfall 8A, and the lowest at the SW Park and Salmon control site (ABQ484). Cyanide was not detected in any of the August 6 stormwater samples. Perchlorate stormwater samples were highest at SW 3rd and Salmon (ABQ484) and lowest at the SW Park and Salmon control site (ABQ669).

All of the sampled metals were detected at the seven catch basins with the exception of hexavalent chromium, which was detected at only three of the seven (AQY839, AQY840, and AQL330; Table 6). The lowest catch basin sediment metals concentrations were typically observed at the SW 3rd and Clay control site (AMU048) and at the catch basin on the west corner of SW 3rd and Salmon (AQY840).

Cyanide was detected in the sediment from all seven catch basins. The highest concentration was observed at the west corner of SW 3rd and Main (AQL329; 7.72 mg/kg) and the lowest concentration at the SW 3rd and Clay control site (AMU048; 0.28 mg/kg). Perchlorate was detected at four of the seven sites, including the SW 3rd and Clay control site (AMU048). The highest perchlorate sediment concentration of 0.292 mg/kg was detected at the west corner of SW 3rd and Salmon (AQY840).

Table 5. Analytical results from the water quality samples collected on August 6, 2020 from the three stormwater sampling locations. Samples from all three locations were analyzed for 66 semi-volatile organic compounds (SVOCs). The three SVOCs that were observed above the detection limit are presented here. Sampling locations are ordered in the table based on their position in the stormwater collection system—see Table 3 for complete location descriptions.

Analytes			**ABQ669** (Control Site) *SW Park & Salmon*	**ABQ484** (RCA use area) *SW 3rd & Salmon*	**ABQ608** (Near Outfall) *SW 1st & Jefferson*
Metals	Barium (µg/L)	*Total*	49.0	3,540.0	113.0
		Dissolved	39.8	77.0	56.9
	Chromium (µg/L)	*Total*	2.8	24.8	4.4
		Dissolved	2.14	4.05	1.26
	Chromium, Hexavalent (µg/L)	*Total*	0.35	1.80	0.27
		Dissolved	0.24	2.33	0.16
	Copper (µg/L)	*Total*	143.0	191.0	84.9
		Dissolved	127.0	54.5	55.6
	Lead (µg/L)	*Total*	5.7	49.2	11.8
		Dissolved	2.11	0.57	1.02
	Zinc (µg/L)	*Total*	621	2,540	506
		Dissolved	565	281	304
SVOCs	Bis(2-ethylhexyl) phthalate (µg/L)		<4.5	13.0	6.7
	Pentachlorophenol (µg/L)		3.3	<3.0	<3.0
	Phenol (µg/L)		3.6	<3.0	<3.0
Other	Chloride (mg/L)		13.9	34.6	84.2
	Cyanide (mg/L)		<0.010	<0.010	<0.010
	Perchlorate (µg/L)		10.2	320.0	49.2

Table 6. Analytical results from the catch basin sediment samples collected on July 31, 2020 from the seven sampling locations and DEQ's clean fill screening level values and background metals concentrations. See Table 4 for complete location descriptions.

Analytes (mg/kg)	**SW 3rd & Clay**	**SW 3rd & Salmon**		**SW 3rd & Main**				**DEQ Clean Fill Screening Levels (mg/kg)***
	AMU048 *Control Site*	AQY839 *North Corner*	AQY840 *West Corner*	AQL327 *South Corner*	AQL328 *West Corner*	AQL329 *NW of AQL328*	AQL330 *North Corner*	
Cyanide	0.28	2.15	0.75	1.42	0.48	7.72	1.60	--
Perchlorate	0.0182	<0.0177	0.292	0.0046	0.0028	<0.0253	<0.0193	55
Total solids (% W/W)	85.1	44.0	66.2	68.4	69.9	49.5	50.4	--
Metals								
Antimony	2.33	9.13	0.58	3.54	1.25	4.28	5.02	0.56
Barium	125	1,280	515	733	469	1,690	669	790
Chromium	17.8	71.1	11.9	31.2	25.7	42.0	31.3	76
Chromium (Hexavalent)	<0.50	2.00	0.65	<0.60	<0.11	<0.90	0.90	--
Copper	45.9	202.0	23.7	195.0	85.3	133.0	94.1	34
Lead	21.7	84.2	4.4	24.6	21.2	52.7	38.3	28
Zinc	292	785	156	1,070	382	5,340	1,570	180

* DEQ clean fill screening level values for the Portland Basin from Tables 1 and 2 of Oregon DEQ's 2019 *Clean Fill Determinations*, https://www.oregon.gov/deq/Filtered%20Library/IMDcleanfill.pdf. The screening level values for the metals included in the table represent background concentrations for the Portland Basin.

Discussion

As noted above, many of the pollutants analyzed as part of this effort are commonly found in stormwater, making it difficult to definitively determine whether RCA residuals are present in the samples. To support the evaluation, both the stormwater and sediment catch basin sampling efforts were designed to include control sites. Given the range of potential confounding factors, the analysis presented below focuses on comparing the results of the stormwater and sediment samples to those from the nearby control sites.

Many of the analytes included in Table 2 have associated water quality criteria (OAR 340-041-8033 Table 30 and Table 40). While these criteria can provide some context when evaluating the stormwater results presented in Table 5, it is important to emphasize that these water quality criteria only apply to waters of the state—lakes, rivers, and streams. Notably, the criteria do not apply to stormwater samples collected from a pipe in a storm system, including the samples collected during the August 6 event. Any samples with concentrations above the water quality criteria would not represent an exceedance of Oregon's in-stream water quality standards.

DEQ's clean fill screening level values and background soil concentrations for the Portland Basin are used by DEQ Materials Management staff to evaluate whether material meets DEQ's definition of clean fill for purposes of reuse or disposal. These screening levels serve as guidance for DEQ staff when evaluating whether a waste material is clean fill or if it needs to be regulated as a solid waste. Sediment concentrations above DEQ's clean fill screening level values do not translate to an exceedance of any state standard. Rather the values provide a useful comparison for the catch basin sediment results and inform how any removed material should be handled and disposed.

Metals

Total barium in stormwater was substantially higher at SW 3rd and Salmon (ABQ484; 3,540 µg/L) than at the SW Park and Salmon control site (ABQ669; 49 µg/L). Barium sediment concentrations were also higher in the catch basins located at the intersections with observed RCA deployment, compared to the SW 3rd and Clay control site (AMU048). The elevated stormwater and sediment barium concentration at SW 3rd and Salmon and the elevated sediment concentrations at SW 3rd and Main may indicate the presence of RCA residuals as barium was noted on the MSDSs for most of the RCA products reviewed, either as barium chromate or barium nitrate. While elevated barium concentrations are seen in close proximity to the area with heavy RCA usage, they are not observed at the location nearest the outfall of the basin at SW 1st and Jefferson (ABQ608), suggesting that the stormwater contribution from the area of known RCA usage represents a small component of the total stormwater in the basin that discharges to the Willamette River. The total barium concentration of 113 µg/L observed at SW 1st and Jefferson (ABQ608) is within the range of concentrations measured in stormwater from other parts of the city.

Both total chromium and hexavalent chromium stormwater concentrations were substantially higher at the SW 3rd and Salmon site (ABQ484) than at the SW Park and Salmon control site (ABQ669). Sediment chromium concentrations were higher at five of the six catch basins located in the area of RCA usage, compared to the SW 3rd and Clay control site (AMU048). Hexavalent chromium was consistently observed above the detection limit at the two SW 3rd and Salmon catch basins but was below laboratory method reporting limits at the SW 3rd and Clay control site (AMU048). As with barium, these elevated concentrations suggest that RCA residuals may be present as many of the RCA products reviewed by BES include chromium compounds as well as California Proposition 65 warnings[2] indicating that use of these products may result in exposure to hexavalent chromium. Past permit-related stormwater monitoring for chromium indicates that concentrations are typically less than 2 µg/L and rarely exceed 20 µg/L. While both stormwater and sediment chromium concentrations were higher at SW 3rd and Salmon, the elevated concentrations did not appear to persist through the system, with lower stormwater concentrations observed at SW 1st and Jefferson (ABQ608).

The stormwater concentration of total zinc was substantially higher at SW 3rd and Salmon (ABQ484; 2,540 µg/L) than at the other two locations. Compared to the SW 3rd and Clay control site (AMU048; 292 mg/kg), the catch basin sediment concentrations of zinc were higher in the samples from the other two intersections (382–5,340 mg/kg), with the exception of the sample from the west corner of SW 3rd and Salmon (AQY840; 156 mg/kg). Zinc and zinc oxide are listed on the MSDSs for many of the RCA products reviewed by BES, suggesting that the higher levels of zinc at SW 3rd and Salmon and at SW 3rd and Main may be due to the use of RCA products in the drainage area. Zinc is also a common stormwater pollutant and is frequently detected at elevated concentrations in stormwater samples collected by BES. The stormwater zinc concentration at SW 3rd and Salmon (ABQ484; 2,540 µg/L) is substantially higher than the mean concentration of 168 µg/L identified by the Oregon Association of Clean Water Agencies (ACWA) for stormwater[3] associated with commercial land use (Strecker et al. 1997), but it is not outside of range of concentrations measured in Portland's stormwater. Zinc stormwater concentrations over 1,000 µg/L are not common, but have been observed; however, these are typically confined to areas of the city with industrial land uses. Total zinc was also approximately ten times the dissolved zinc stormwater concentration, which is not typical for stormwater, and indicates the zinc detected at SW 3rd and Salmon (ABQ484) is measured primarily in particulate form. As with barium and chromium, the concentration of zinc nearest the outfall at SW 1st and Jefferson (ABQ608) was lower than at SW 3rd and Salmon, indicating that the stormwater contribution from that location represents a small component of the stormwater in the basin that discharges to the Willamette River.

The highest stormwater concentration of total lead was observed at SW 3rd and Salmon (ABQ484; 49.2 µg/L) and was approximately ten times higher than the concentration observed at the SW Park and Salmon control site (ABQ669; 5.7 µg/L). The highest lead catch basin sediment concentration was also observed at the north corner of SW 3rd and Salmon (AQY839; 84.2 mg/kg) and was approximately four times higher than the SW 3rd and Clay catch basin control site (AMU048; 21.7 mg/kg). Lead was listed as a component in every RCA MSDS reviewed by BES, including lead chromate, lead salts, and lead styphnate, which suggests that the higher observed concentration at SW 3rd and Salmon may be from RCA residuals. As with zinc, lead is also a common stormwater pollutant and is regularly seen in stormwater samples. While the SW 3rd and Salmon (ABQ484) stormwater sample appears to be elevated, the total lead concentrations observed at the SW Park and Salmon stormwater control site (ABQ669) and at SW 1st and Jefferson (ABQ608) are within the range of concentrations commonly measured in stormwater in Portland.

Unlike the other metals, there was less variation between the total copper concentrations measured at the three stormwater locations. The concentration of total copper at SW 3rd and Salmon (ABQ484; 191.0 µg/L) was higher than at the other two locations but by substantially less than the other metals. A

[2] Proposition 65 warning: the chemical is known to the State of California to cause cancer, birth defects, or other reproductive harm. Nearly all RCA MSDSs included a warning that product use could result in exposure to methylene chloride, tetrachloroethylene, and hexavalent chromium.

[3] ACWA sponsored a project to evaluate water quality data collected from land-use-based stormwater monitoring in Oregon (Strecker et al. 1997). The results from the ACWA stormwater evaluation provide a benchmark against which stormwater sample can be evaluated.

similar copper pattern was seen in the catch basin sediment samples. Concentrations of copper were higher in the samples from the catch basins at both SW 3rd and Main and at SW 3rd and Salmon when compared to the SW 3rd and Clay control site (AMU048). As with lead and zinc, copper is a common stormwater pollutant that is frequently measured at elevated concentrations in Portland. While copper is a component of some RCA products, of those reviewed by BES, copper was listed on only half of the MSDSs. The use of RCA products in the SW 3rd and Salmon (ABQ484) drainage area may have contributed to the higher concentration of total copper concentration compared to the SW Park and Salmon control site (ABQ669), but they did not result in substantially higher concentrations of total copper.

The catch basin sediment samples were also analyzed for antimony. Antimony was detected in all the catch basin sediment samples. Concentrations were typically higher in samples from the areas with known RCA deployment, but concentrations did not vary substantially between samples and were not substantially different from the SW 3rd and Clay control site (AMU048). Antimony was listed on only one of the MSDSs reviewed by BES and it is not a common stormwater pollutant; however, it is common in metal alloys and is often used as a lead hardener. As noted above, all the RCA products reviewed contained lead in some form, suggesting that antimony may be an unlisted RCA component. It is unclear whether the antimony detected in the catch basin samples is associated with RCA usage.

All the metals were primarily observed in their particulate form in the stormwater collected at SW 3rd and Salmon (ABQ484)—the dissolved concentration of the metal was substantially lower than the total concentration. This tendency was particularly strong for barium, chromium, lead, and zinc where the dissolved metal fraction for each was less than 20%.[4] The differences in concentrations, as well as form (primarily as particulate rather than dissolved metals), suggest that RCA residuals may be present in the samples collected from SW 3rd and Salmon (ABQ484).

RCA Dispersion Byproducts

Cyanide was included in the list of analytes based on BES' review of the MSDSs for the RCA products used by the PPB and other available literature. Research by Kluchinsky et al. (2002) found that hydrogen cyanide (HCN) and particulate cyanide (CN^-) were produced under the high temperatures used in CS gas dispersion. While the presence of cyanide may have indicated the presence of RCA residuals in the stormwater, cyanide was not detected in any of the stormwater samples. Cyanide was detected in all catch basin sediment samples. Cyanide concentrations varied between the catch basins, but the concentrations in the sediment collected from the six catch basins at SW 3rd and Main and at SW 3rd and Salmon were approximately 2–28 times higher than at the SW 3rd and Clay control site (AMU048). Cyanide is not a common stormwater pollutant. As such, the higher cyanide catch basin sediment concentrations may be indicative of an accumulation of RCA residuals.

Chloride was also added to the list of analytes as the literature indicated that high temperature CS gas dispersion may produce hydrogen chloride (HCl; Kluchinsky, et al., 2002). Unlike all of the other analytes, chloride concentrations were highest at SW 1st and Jefferson (ABQ608; 84.2 mg/L). The lowest concentration was observed at the SW Park and Salmon control site (ABQ669; 13.9 mg/L). BES does not routinely analyze stormwater samples for chloride, and so no stormwater data are available for comparison; however, DEQ has established instream water quality criteria for chloride. The acute and chronic instream water quality criteria for chloride are 860 mg/L and 230 mg/L respectively (OAR 340-041-8033 Table 30). All of the samples were below the instream chronic chloride criterion. It is unclear

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[4] Dissolved fractions for barium, chromium, lead, and zinc were 2%, 16%, 1%, and 11% respectively.

whether the increase in chloride at SW 1st and Jefferson (ABQ608) and SW 3rd and Salmon (ABQ484) is due to the use of RCA products or other activities within the basin.

Semi-Volatile Organic Compounds

As noted above, only three (out of 66) of the SVOCs were detected during the August 6 stormwater sampling event: bis(2-ethylhexyl) phthalate, pentachlorophenol, and phenol. Bis(2-ethylhexyl) phthalate is commonly used as a plasticizer and hydraulic fluid. Pentachlorophenol is used as a pesticide and disinfectant, commonly used to preserve wood. Phenol is also commonly used in the production of plastics, as well as in detergents and pharmaceutical drugs. All three of the SVOCs were detected at low levels. While the concentration of bis(2-ethylhexyl) phthalate was higher at SW 3rd and Salmon (ABQ484; 13.0 µg/L), the difference was not substantial and was within the range of concentrations observed in the City's routine permit-related stormwater monitoring.

Hexachloroethane, an ingredient in one of the RCA products used in the vicinity of the US Courthouse, was not detected. Diphenylamine, a common ingredient in RCA products (reportable as the sum of diphenylamine and 1,4,5 N-nitrosodiphenylamine), was also not detected. In addition, malononitrile, o-chlorobenzylaldehyde, and 1,3 diethyldiphenylurea were not detectable as tentatively identified compounds (TICs). Malononitrile and o-chlorobenzylaldehyde are formed through hydrolosis of o-chlorobenzylidene malononitrile, the main ingredient in CS gas, a component of many of the RCA products used in the US Courthouse area. CS gas has a half-life of approximately 15 minutes in liquid at a pH of 7 with half-life shortening as alkalinity increases (NRC 2014). As such, it does not appear that RCA usage has contributed to an increase in SVOCs to the City's storm system.

Perchlorate

Perchlorate is commonly used as a propellent and was noted on many of the MSDSs reviewed by BES. Consistent with many of the other analytes, perchlorate stormwater concentrations were highest at the site with the greatest RCA usage (ABQ484; 320.0 µg/L) and lowest at the SW Park and Salmon control site (ABQ669; 10.2 µg/L). The concentration of perchlorate closest to the outfall at SW 1st and Jefferson (ABQ608; 49.2 µg/L) was lower than at SW 3rd and Salmon, suggesting that the stormwater from the SW 3rd and Salmon drainage area represents a small component of the stormwater in the basin that discharges to the Willamette River. The elevated concentration of the perchlorate observed in the August 6 stormwater samples may indicate the presence of RCA residuals.

Perchlorate is not commonly sampled in stormwater. Concerns related to elevated concentrations of perchlorate are more often associated with drinking water which is regulated by the U.S. Environmental Protection Agency (EPA) under the Safe Drinking Water Act. EPA's 2019 proposed rulemaking for the regulation of perchlorate in public drinking water systems included a maximum contaminant level and a health-based maximum contaminant level goal of 56 µg/L. Ultimately, in July 2020 EPA decided to withdraw its 2011 determination to regulate perchlorate in drinking water. As a result, EPA does not currently regulate perchlorate as a drinking water contaminant (EPA 2020).

The highest sediment concentration of perchlorate was seen at the catch basin on the west corner of SW 3rd and Salmon (AQY840; 0.292 mg/kg). As noted in Table 4, the sample from this catch basin was not collected from the basin, but from material that had accumulated on the street surface next to the catch basin grate. Due to the design of the catch basin, no material can accumulate within the basin. BES field staff noted that unlike the other six catch basin samples, the sample from AQY840 was composed entirely of a gray ash/charcoal-like fine material. The source of the accumulated material is not known; however, given that the material had accumulated on the street surface, it is likely to have recently accumulated. The higher concentration of perchlorate may be an indicator of RCA residuals in the material collected from the west corner of SW 3rd and Salmon (AQY840).

Conclusion

The extent of the conclusions that can be drawn from the collected stormwater and catch basin samples is limited as the results are from a single set of sampling events and the contribution from RCA residuals to total sample concentrations is unknown. To address this, the analysis presented here focuses on a comparison between the samples collected from an area of high known RCA use (US Courthouse) and those collected at nearby control sites to evaluate whether there are indications of RCA residuals reaching the City's storm system. The results from the August 6 stormwater sampling identified higher concentrations of metals and analytes not commonly found in stormwater at the sampling location associated with the greatest RCA deployment. Similarly, higher concentrations were also observed in the catch basin sediment sample compared to the nearby control site. These higher concentrations may suggest that some residuals from the RCA products used in the downtown area entered the City's storm system; however, the sampling also indicates that the elevated concentrations were not observed near the outlet of the storm basin.

The City is actively implementing multiple management practices in the downtown area to minimize possible impacts to the City's storm system and to minimize the amount of pollutants that reach the river.

A. The City continues to implement standard management activities, including street sweeping five times a week in the downtown core. In addition to standard practices, the City has taken additional steps to protect receiving waters and the City's storm system. BES staff actively worked with property owners in the downtown area, providing guidance on cleaning techniques to minimize the impact to the storm system.
B. BES contacted GSA about illicit discharges associated with power washing of debris and residue from the US Courthouse. GSA representatives confirmed their knowledge of and agreed to implement appropriate cleanup methods including proper disposal of wastewater from cleaning activities. BES continues to regularly inspect and investigate complaints of illicit discharges in the downtown corridor.
C. BES has taken proactive steps to remove potential pollutants before they reach the Willamette River. BES contract crews cleaned out all six catch basins by the US Courthouse shortly after the sediment samples were collected, as well as three catch basins located at SW 3rd and Madison.

These cleaning efforts were conducted after sample collection, but before the forecasted storm on August 6 out of an abundance of caution. The catch basin on the east corner of SW 3rd and Salmon (AQY841) has not been cleaned or sampled as BES was denied access by GSA to collect samples and to clean out the catch basin. This asset is inaccessible to BES as it is located behind the fence and concrete barriers surrounding the US Courthouse. BES is evaluating City Code enforcement options for denial of access to the City storm catch basin.

The results from the sampling suggests that possible RCA residuals are primarily observed in particulate form. As such, best management practices that address particulate pollutants (e.g. street sweeping, cleaning pipes and catch basins) may be effective at capturing RCA residuals and preventing them from impacting the City's storm system. The City will use the results of this sampling effort to inform the ongoing implementation of routine or additional best management practices as well as their effectiveness under wet weather conditions.

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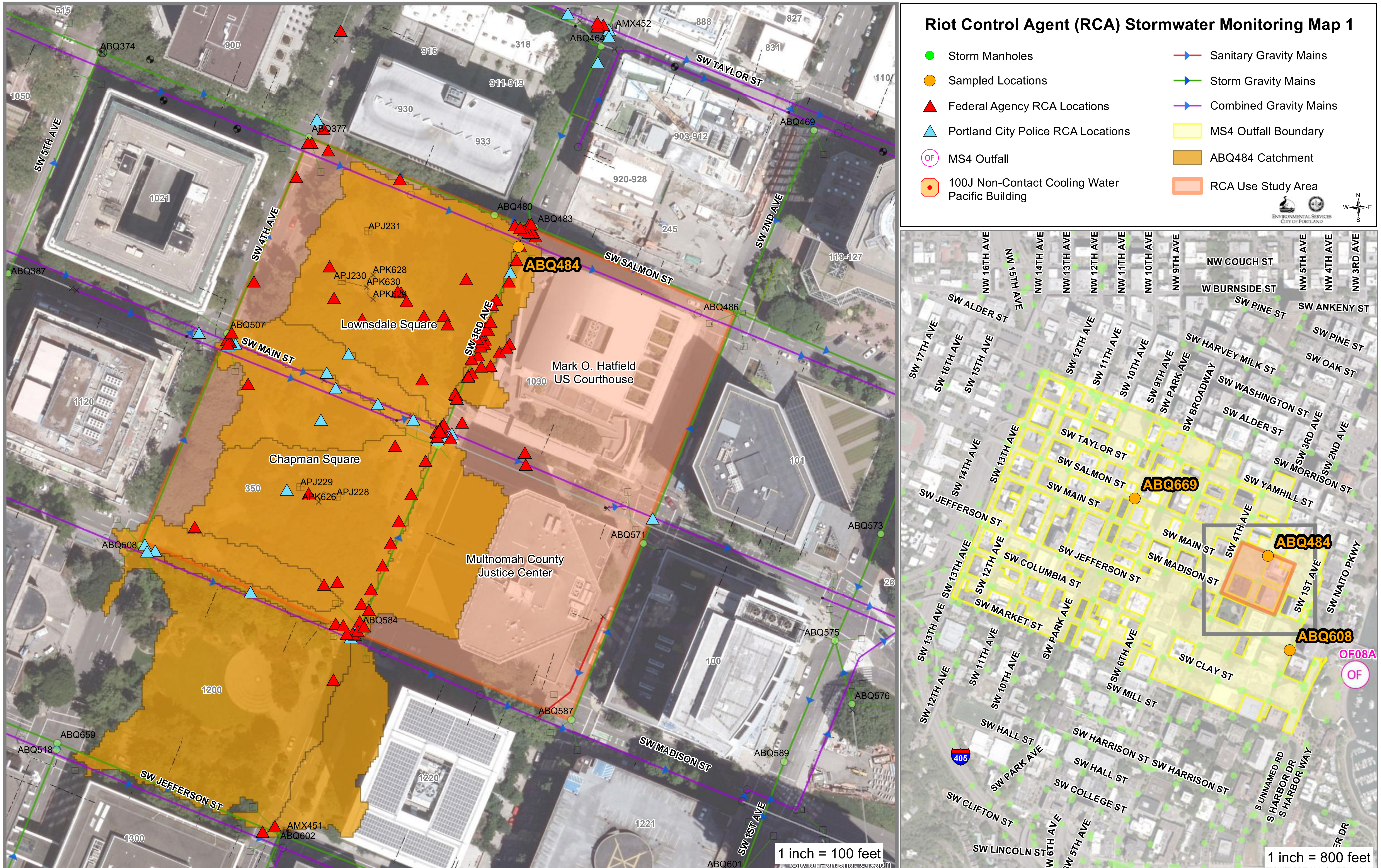
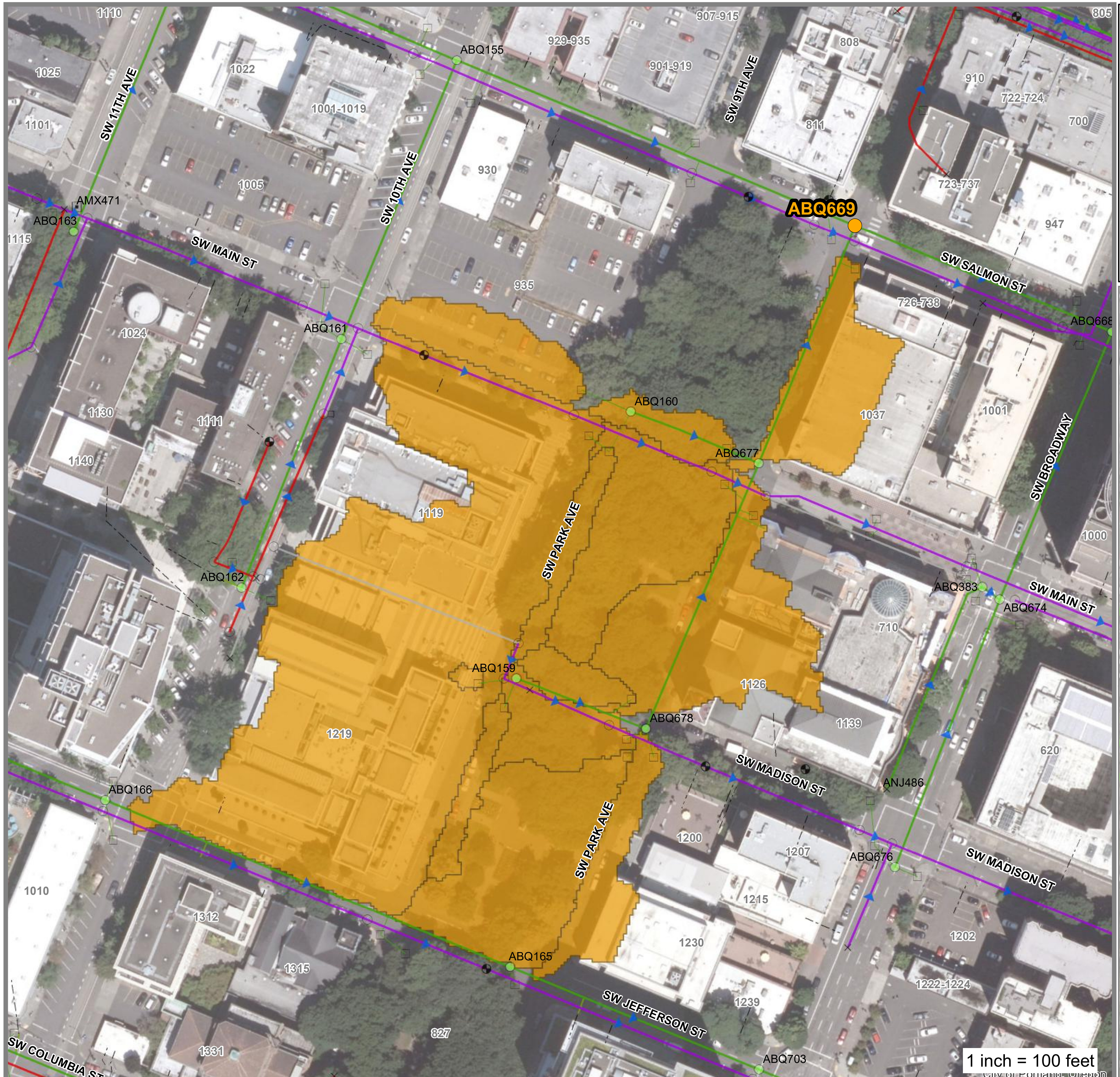


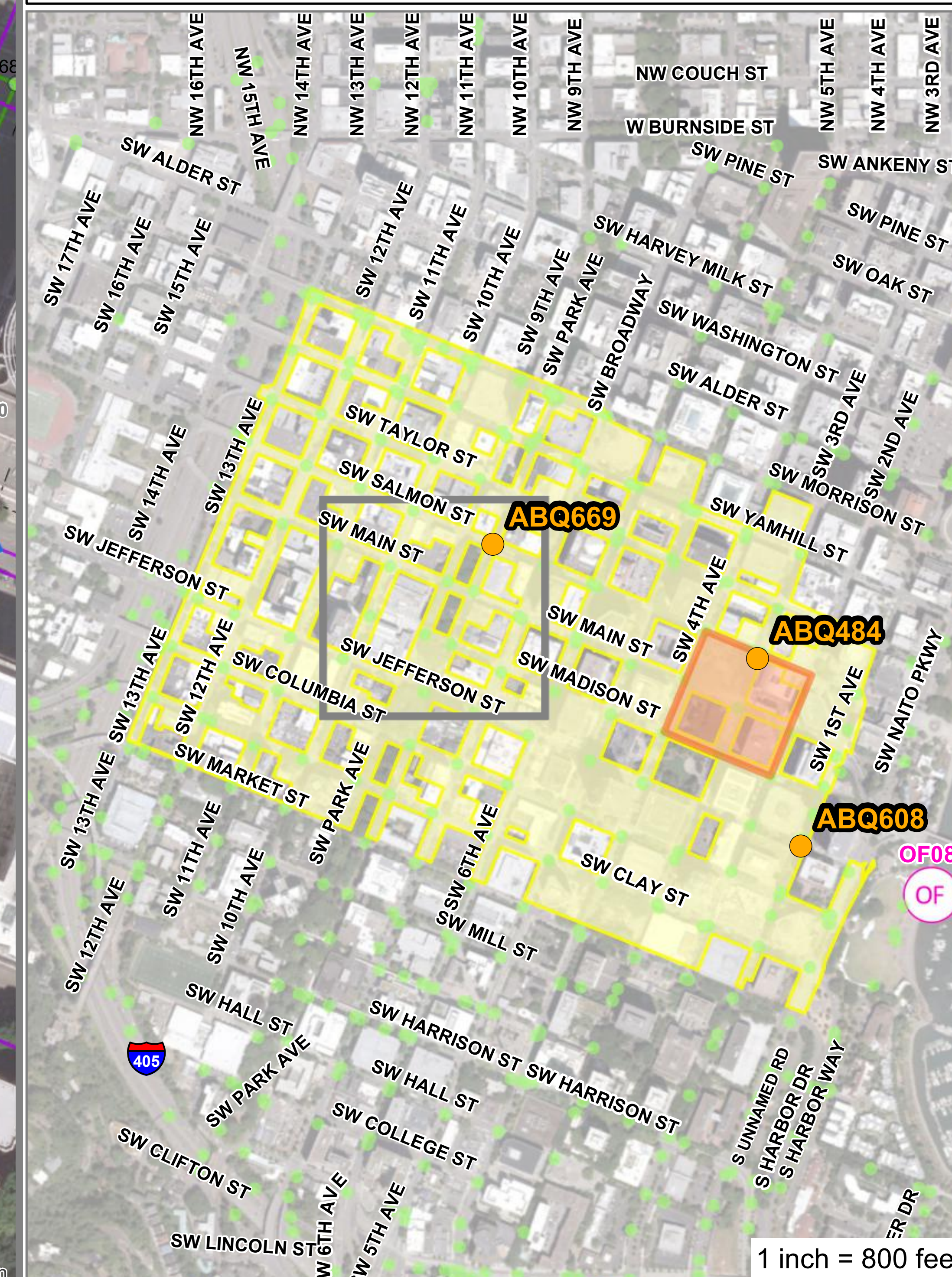
Riot Control Agent (RCA) Stormwater Monitoring Map 1
Storm Manholes
Sampled Locations
Federal Agency RCA Locations
Portland City Police RCA Locations
MS4 Outfall
100J Non-Contact Cooling Water Pacific Building
Sanitary Gravity Mains
Storm Gravity Mains
Combined Gravity Mains
MS4 Outfall Boundary
ABQ484 Catchment
RCA Use Study Area
Environmental Services City of Portland
ABQ484
Lownsdale Square
Chapman Square
Mark O. Hatfield US Courthouse
Multnomah County Justice Center
SW SALMON ST
SW MAIN ST
SW MADISON ST
SW JEFFERSON ST
SW TAYLOR ST
SW 5TH AVE
SW 4TH AVE
SW 3RD AVE
SW 2ND AVE
SW 1ST AVE
ABQ374
ABQ377
ABQ387
ABQ464
AMX452
ABQ469
ABQ480
ABQ483
ABQ486
ABQ507
ABQ508
ABQ571
ABQ573
ABQ575
ABQ576
ABQ584
ABQ587
ABQ589
ABQ601
ABQ602
AMX451
ABQ518
ABQ659
APJ231
APJ230
APK628
APK630
APK629
APJ229
APK626
APJ228
1 inch = 100 feet
City of Portland, Oregon
ABQ669
ABQ608
OF08A
NW COUCH ST
W BURNSIDE ST
SW ALDER ST
SW PINE ST
SW ANKENY ST
SW OAK ST
SW HARVEY MILK ST
SW WASHINGTON ST
SW YAMHILL ST
SW MORRISON ST
SW COLUMBIA ST
SW MARKET ST
SW CLAY ST
SW MILL ST
SW HALL ST
SW HARRISON ST
SW COLLEGE ST
SW CLIFTON ST
SW LINCOLN ST
SW PARK AVE
SW BROADWAY
SW NAITO PKWY
S HARBOR DR
S HARBOR WAY
1 inch = 800 feet

Riot Control Agent (RCA) Stormwater Monitoring Map 2

- Storm Manholes
- Sampled Manholes
- Federal Agency RCA Locations
- Portland City Police RCA Locations
- MS4 Outfall
- 100J Non-Contact Cooling Water Pacific Building
- Sanitary Gravity Mains
- Storm Gravity Mains
- Combined Gravity Mains
- MS4 Outfall Boundary
- ABQ669 Catchment
- RCA Use Study Area

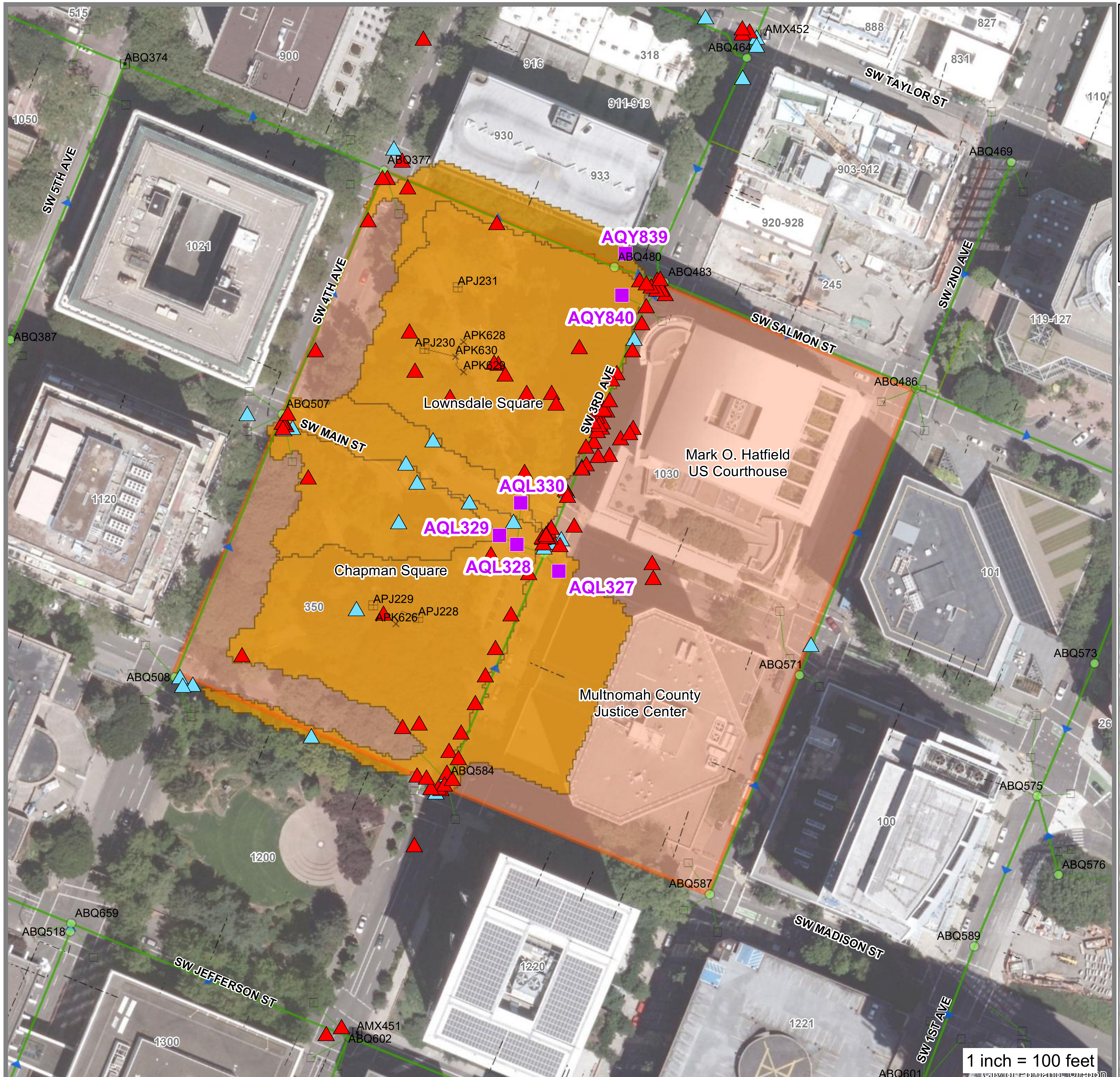
Environmental Services City of Portland

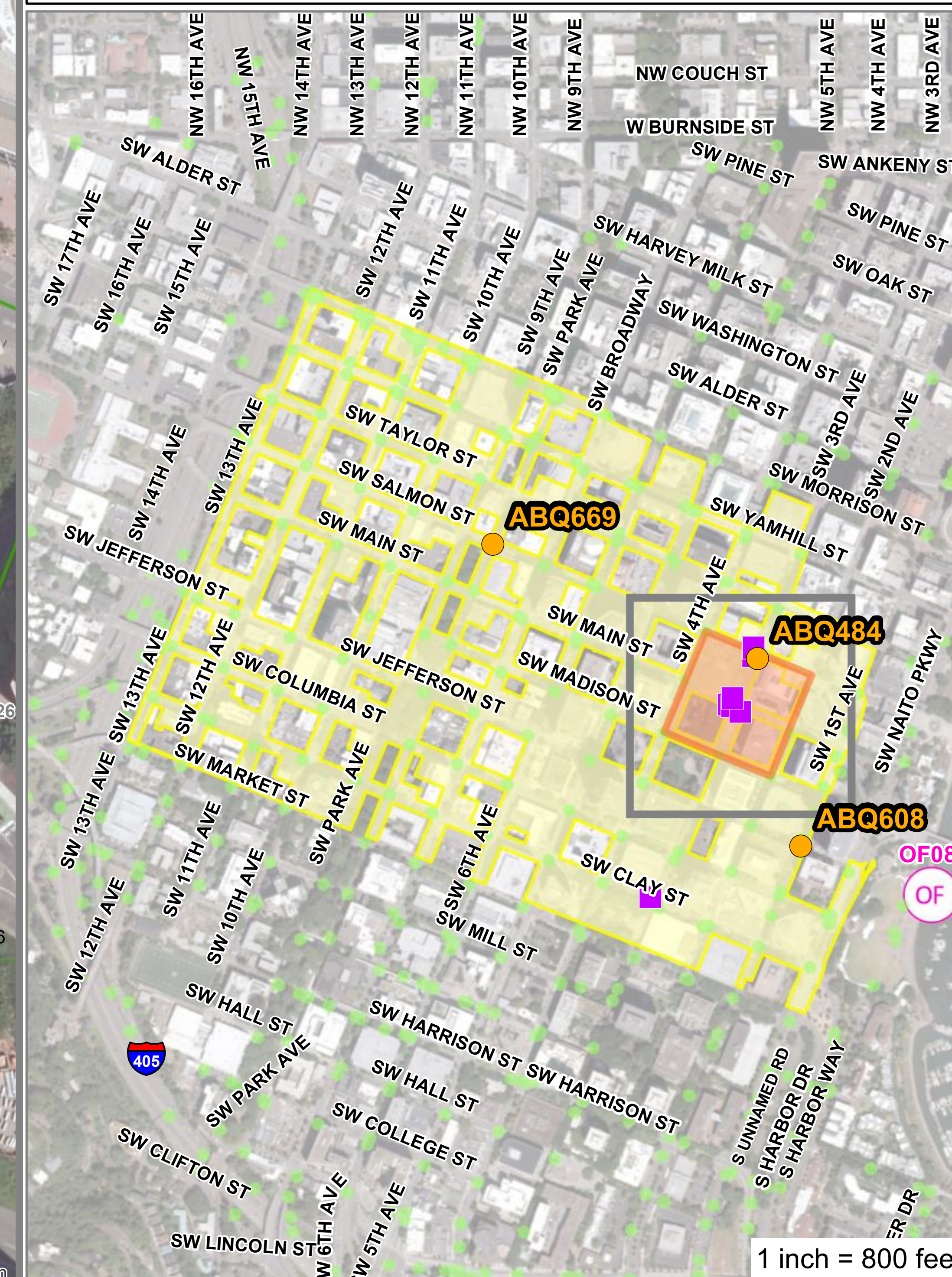




Riot Control Agent (RCA) Sediment Sampling Map 3

- Storm Manholes
- Sampled Manholes
- Sampled Catch Basins
- Federal Agency RCA Locations
- Portland City Police RCA Locations
- MS4 Outfall
- 100J Non-Contact Cooling Water (Pacific Building)
- Storm Gravity Mains
- MS4 Outfall Boundary
- Sampled Inlet Catchments
- RCA Use Study Area

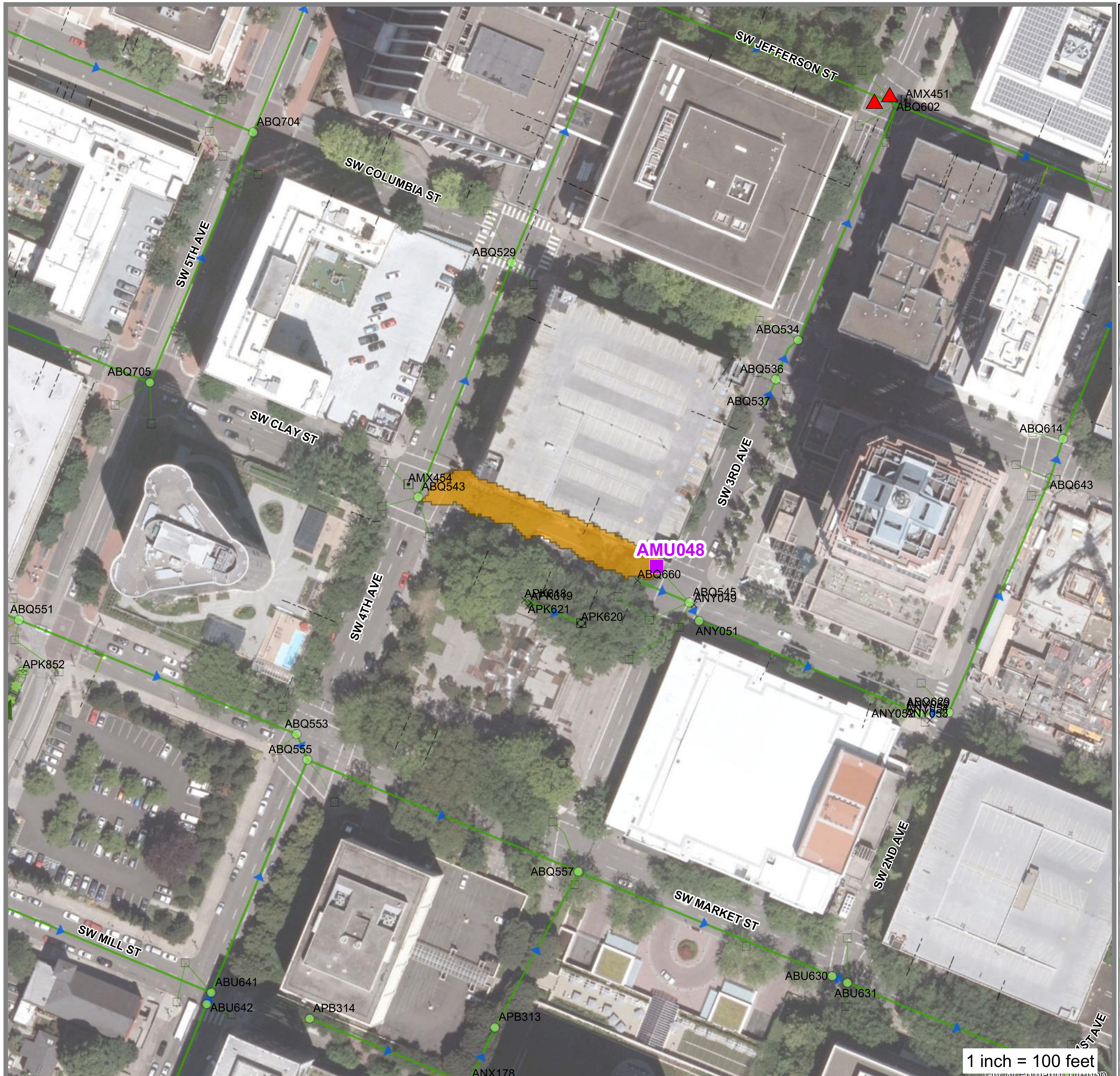


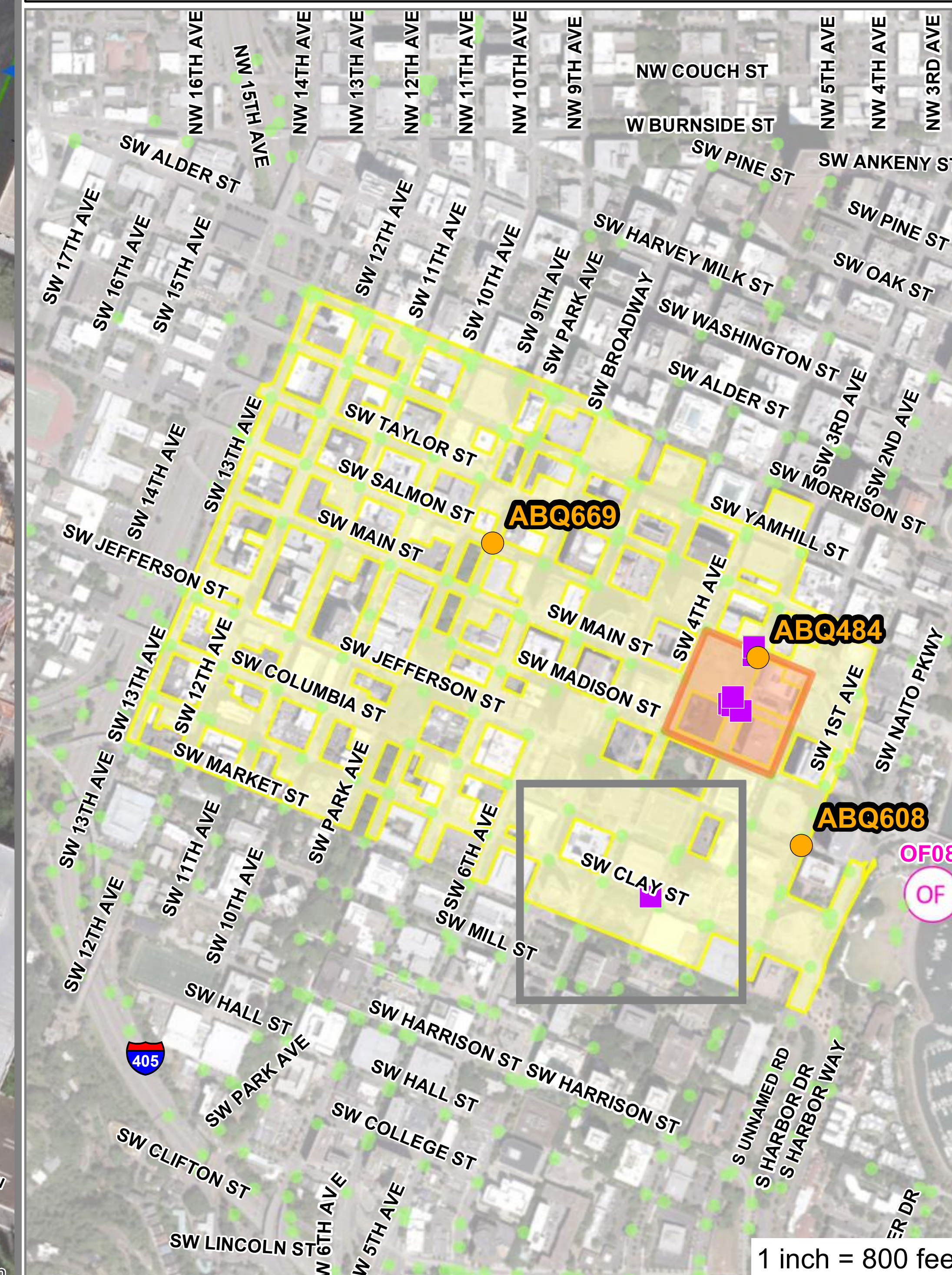


Riot Control Agent (RCA) Sediment Sampling Map 4

- Storm Manholes
- Sampled Manholes
- Sampled Catch Basins
- Federal Agency RCA Locations
- Portland City Police RCA Locations
- MS4 Outfall
- 100J Non-Contact Cooling Water (Pacific Building)
- Storm Gravity Mains
- MS4 Outfall Boundary
- Sampled Inlet Catchments
- RCA Use Study Area

ENVIRONMENTAL SERVICES CITY OF PORTLAND





Appendix A: Riot Control Agent (RCA) Chemicals and Additives

	Chemical	Associated Water Quality Criteria	Toxicity	Triple Chaser OC Model 1020	Triple Chaser CS Model 1026	Triple Chaser Saf-Smoke Model 1027	Flameless Tri-Chamber CS Model 1032	Skat Shell 40MM CS Model 6172	Skat Shell 40MM OC Model 6170	Han-ball Grenade OC Model 1099	Low Roll II Distraction Device *	Military Style Maximum Smoke HC*	Stinger Rubber Ball 40mm Smokeless Round*	Skat Shell 40MM Smoke Model 6173*	Notes
Riot Control Agents	o-chlorobenzylidene malononitrile (CS Gas)		LD50 (rat, oral): 178 mg/kg		X		X	X							
	Oleoresin capsicum (pepper spray - OC Gas)			X					X	X					
	1-Chloroacetophenone (CN Gas)														Usage mostly replaced by OC and CS Gas
	Dibenz (b.f.)-1,4-oxazepine (CR Gas)														Usage mostly replaced by OC and CS Gas
	Hexachloroethane (HCE)											X			Smoke is considered toxic due to HCE and zinc oxide reacting to form zinc chloride (Wikipedia)
RCA Biproducts/Additives	Cyanide (HCN & CN^{-}) **	CN: 5.2 µg/L [AL]			X		X	X							Hydrogen cyanide (HCN) and particulate cyanide (CN^{-}) are produced during high temperature CS gas dispersion (Kluchinsky, et al., 2002)
	Hexavalent Chromium	Cr VI: 11 µg/L [AL]		X	X	X	X	X	X	X	X	X	X		
	Hydrogen Chloride	Cl: 230 mg/L [AL]													Hydrogen chloride (HCl) is produced during high temperature CS dispersion (Kluchinsky, et al., 2002)
	Lead salts	Pb: varies w/ hardness		X	X	X	X	X	X	X	X	X	X		
	Methylene Chloride	Cl: 230 mg/L [AL]		X	X	X	X	X	X	X	X	X	X		Solvent carrier for CS Gas
Pyrotechnic Chemicals	Aluminum powder	Al: varies w/ pH, DOC, hardness		X	X		X			X	X	X		X	MSDSs indicate stabilized or pyrophoric
	Antimony sulfide	Sb: 1600 µg/L [G]												X	
	Barium chromate	Ba: 1000 µg/L [HH] Cr III: varies w/ hardness Cr VI: 11 µg/L [AL]			X	X	X			X	X	X			
	Barium nitrate	Ba: 1000 µg/L [HH]						X						X	
	Bismuth														Purportedly less toxic lead substitute used in non-lethal rounds
	Centralite (1,3-diethyldiphenylurea)		LC50 (zebra fish): 15.6 µg/L LD50 (rat, oral): 780 mg/kg					X	X				X		Burning rate moderator
	Charcoal						X							X	
	Copper	Varies w/ ions, pH, temp			X		X		X		X		X	X	
	Diphenylamine		LD50 (rat, oral) 1120 mg/kg		X		X	X	X				X		
	Freon														Possible propellant
	Glycerol trinitrate (nitroglycerin)		LD50 (rat, oral): 105 mg/kg LD50 (rat, dermal): 29 mg/kg					X	X						
	Graphite													X	
	Iron **	Fe: 1000 µg/L [AL]						X	X				X	X	
	Lead Azide													X	

	Chemical	Associated Water Quality Criteria	Toxicity	Triple Chaser OC Model 1020	Triple Chaser CS Model 1026	Triple Chaser Saf-Smoke Model 1027	Flameless Tri-Chamber CS Model 1032	Skat Shell 40MM CS Model 6172	Skat Shell 40MM OC Model 6170	Han-ball Grenade OC Model 1099	Low Roll II Distraction Device *	Military Style Maximum Smoke HC*	Stinger Rubber Ball 40mm Smokeless Round*	Skat Shell 40MM Smoke Model 6173*	Notes
	Lead chromate	Pb: varies w/ hardness Cr III: varies w/ hardness Cr VI: 11 µg/L [AL]	LD50: (mouse): 12000 mg/kg		X	X	X			X		X			
	Lead dithiocyanate	Pb: varies w/ hardness CN: 5.2 µg/L [AL]			X	X	X	X			X	X		X	
	Lead 2,4,6-trinitro-m-phenylene dioxide (Lead styphnate)	Pb: varies w/ hardness	LD50 (rat, oral): 650 mg/kg					X	X				X	X	
	Magnesium carbonate			X	X	X	X			X					
	Magnesium distearate			X	X		X								
	Magnesium oxide				X		X	X	X						
	Manganese	100 µg/L [HH]								X					
	Nitrocellulose			X	X	X	X	X	X	X		X	X	X	
	Potassium chlorate		LD50 (rat, oral): 1870 mg/kg	X	X	X	X			X	X			X	
	Potassium nitrate			X	X		X	X	X	X		X		X	
	Potassium perchlorate						X	X	X		X			X	
	Rosin								X					X	
	Silica				X		X	X	X						
	Silicon			X	X		X			X		X			
	Sucrose			X	X	X	X			X				X	
	Sulfur				X		X	X	X					X	
	Terephthalic acid			X		X				X				X	
	Tetracene													X	
	Tetrachloroethylene														Possible propellant
	Triiron tetraoxide	Fe: 1000 µg/L [AL]			X		X								
	Zinc	Zn: varies w/ hardness			X		X		X		X		X	X	
	Zinc Oxide	Zn: varies w/ hardness										X			
	Zirconium dioxide							X							

Table Notes:

Amounts of each chemical used in each product are trade secrets and are not disclosed by the manufacturers

[AL] indicates aquatic life chronic criterion; OAR 340-041-8033 Table 30: https://www.oregon.gov/deq/Rulemaking%20Docs/tables303140.pdf

[HH] indicates human health criterion for water + organism or organism only; OAR 340-041-8033 Table 40: https://www.oregon.gov/deq/Rulemaking%20Docs/tables303140.pdf

[G] indicated aquatic life chronic guidance value; OAR 340-041-8033 Table 31: https://www.oregon.gov/deq/Rulemaking%20Docs/tables303140.pdf

* Product not listed by Portland Police Bureau, but product noted in photos from public, included here for completeness

** Willamette River is listed as impaired for the pollutant in DEQ's 2018/2020 Integrated Report

X = Proposition 65 warning: the chemical is known to the State of California to cause cancer, birth defects or other reproductive harm.

Table Reference:

Kluchinsky, T. A., Savage, P. B., Fitz, R., & Smith, P. A. (2002). Liberation of hydrogen cyanide and hydrogen chloride during high-temperature dispersion of CS riot control agent. *AIHA Journal*, *63*(4), 493-496.

Appendix B: Riot Control Agent Product List

Portland Police Bureau product list:

- FN303 Pava/OC Powder 40MM
  https://fnamerica.com/products/less-lethal/projectiles/
- Combined Systems OC-CS Vapor Grenade Model 6343
  https://www.combinedsystems.com/product/6343-oc-cs-vapor-grenade/
- Defense Technology Triple Chaser OC Model 1020
  https://www.defense-technology.com/product/triple-chaser-separating-canister-oc/
- Defense Technology Triple Chaser CS Model 1026
  https://www.defense-technology.com/product/triple-chaser-separating-canister-cs/
- Defense Technology Triple Chaser Saf-Smoke Model 1027
  https://www.defense-technology.com/product/triple-chaser-separating-canister-saf-smoke/
- Defense Technology Flameless Tri-Chamber CS Model 1032
  https://www.defense-technology.com/product/flameless-tri-chamber-cs-grenade/
- Defense Technology Skat Shell 40MM CS Model 6172
  https://www.defense-technology.com/product/skat-shell-40-mm-multiple-projectile-round-cs/
- Defense Technology Skat Shell 40MM OC Model 6170
  https://www.defense-technology.com/product/skat-shell-40mm-multiple-projectile-round-oc/
- Defense Technology Han-ball Grenade OC Model 1099
  https://www.defense-technology.com/product/han-ball-grenade-oc/

Other products identified from photos from public:

- Sabre Red 1.33% MK9 Fogger
  https://www.sabrered.com/pepper-spray/sabre-red-133-mc-185-oz-fog-mk-9
- Low Roll II Distraction Device
  https://www.defense-technology.com/product/low-roll-ii-11-gram-non-reloadable-distraction-device-w-safety-clip/
- Military Style Maximum Smoke HC
  https://www.defense-technology.com/product/maximum-smoke-hc-military-style-canister/
- Stinger Rubber Ball 40mm Smokeless Round
  https://www.defense-technology.com/product/stinger-40-mm-60-caliber-rubber-balls-round/
- Skat Shell 40MM Smoke Model 6173
  https://www.defense-technology.com/product/skat-shell-40-mm-multiple-projectile-round-saf-smoke/