

Appendix J

Naturally Occurring Fresh Groundwater/Salt Water Distribution Evaluation

Section 1.0 Background

In coastal aquifers, the density gradient between fresh groundwater and salt water results in the inland migration of salt water. In the idealized scenario developed by the USGS (1964), freshwater flowing toward salt water bodies is forced upwards, since it cannot flow out through the denser saline water. The fresh groundwater and salt water are separated by a transition zone within which there is mixing between the fresh groundwater and salt water. The width of the transition zone varies depending on many factors, but may be on the order of hundreds to over a thousand feet in coastal aquifers (Barlow, 2003). In the idealized scenario, the transition zone will be present at greater depths further inland. This scenario forms the basis for the simplified conceptual model of the fresh groundwater/salt water distribution at the Site.

The density-driven groundwater flow from both the anthropogenic density plume (ADP) and salt water has a significant influence on the overall groundwater flow at the Site. As a result, it has the potential to affect subsurface contaminant transport. Therefore, in order to create a comprehensive hydrologic and fate and transport model it is necessary to determine the three-dimensional extent of the natural transition zone within the subsurface.

To represent the distribution of salt water at the Site, the amount of salt water at each sampling point was calculated based on the geochemical composition of the samples collected. The following sections describe the methods and results for the calculation of the percentage of salt water in each groundwater sample.

Section 2.0 Calculation Methods

The fresh groundwater/salt water transition zone was determined by calculating the percent salt water composition for each groundwater sample using the concentrations of geochemical parameters in each groundwater sample. A set of mixing calculations were performed to determine the percentage of salt water and fresh groundwater in each of the groundwater samples collected from the Site. The evaluation required the determination of the geochemistry of the fresh groundwater (background) at the Site, as well as the geochemistry of salt water in the adjacent waterways. These two water “sources” were used as the end-members for the mixing calculation. Groundwater and surface water samples were analyzed for twenty-nine parameters, ten of which are generally associated with salt water: boron, bromide, calcium, chloride, iodide, magnesium, potassium, sodium, strontium, and sulfate. However, as explained below, several of these analytes were unsuitable for use in the evaluation.

The evaluation to determine the fresh groundwater/salt water distribution incorporated the following assumptions:

- i) pH values that are significantly greater than salt water are due to the anthropogenic activities.
- ii) Any groundwater samples that have a salt water composition significantly greater than 100 percent salt water likely have anthropogenic influences.
- iii) The salt water that has naturally infiltrated into the formation beneath the Site from the waterways historically is chemically consistent with the salt water composition of the waterway water sampled in 2012.
- iv) Background groundwater concentrations in the absence of salt water and ADP influences are chemically similar to concentrations measured in the shallow groundwater near the center of the peninsula on the 709/721 properties.

- v) The concentrations of geochemical parameters in a sample is directly related to the proportions of salt water and fresh groundwater as described in the equation below:

$$V_s = \left(\frac{(C_u \times V_u) - (C_b \times V_u)}{(C_s - C_b)} \right) \times 100$$

Where:

- V_s is the percent volume of salt water of the sample
 V_u is the percent volume of the sample, equal to 1.0 in all cases
 C_s is the concentration of the geochemical parameter in salt water [mg/L]
 C_u is the concentration of the geochemical parameter in the sample [mg/L]
 C_b is the concentration of the geochemical parameter in Site fresh groundwater [mg/L]

Section 3.0 Initial Conditions

In order to determine calculated salt water percentage, both the geochemistry of the background fresh groundwater and the salt water had to be determined. The wells used to establish the background concentration had to meet several criteria. They must be: free of elevated concentrations of salt water indicators; not show signs of ADP influence; and, be close enough to the Site as to have similar hydrologic and geologic conditions. Two different sources were considered for the background value.

- i) The former production well (FPW):

The FPW was a deep pumping well located on the Hylebos Peninsula, all analytes except for sodium and chloride were within the expected range for natural groundwater. The sodium and chloride values were elevated, which could indicate the presence of salt water at depth. The FPW was not used as a background sample for this reason.

- ii) 709 and 721 shallow wells:

The shallow upgradient wells on the 709 and 721 properties are located directly adjacent to the Site. Many of these wells are not impacted by salt water (as evidenced by the generally low chloride concentrations), nor ADP impacts. Thirteen shallow wells were selected from 709 and 721 that had chloride concentrations less than 30 mg/L and were no deeper than 25 feet (ft) BGS. These criteria created a contiguous area of fresh groundwater wells that is located in the central portion of the peninsula. The average concentrations from these wells are presented in Table 1. The bromide concentration at 709-MW21-25 (1 mg/L) was considered a statistical outlier and was omitted from the average freshwater calculation.

The salt water composition adjacent to the Site was determined by collecting water samples from the Hylebos Waterway, Blair Waterway, and Commencement Bay. Samples were collected at 3 ft and 25 ft below the water surface, and near the bottom of the Waterway. One sample was also collected from near the Tide Gauge (at 25 ft below water surface), and one sample from the Hylebos Waterway was collected in 2010 (depth unknown). In total, eleven samples were collected, eight of which were used to calculate the salt water chemistry used in the evaluation. The three samples not used were those collected at 3 feet below the water surface. These samples had concentrations of sodium and chloride that were significantly below the concentrations of the deeper samples. It was therefore concluded that the shallow samples were affected by freshwater runoff and were not representative of the salt water entering the subsurface from the waterways. There was also one sample (Hylebos 2010) where the

bromide concentration (91 mg/L) was considered a statistical outlier and this sample was rejected. An average of the remaining samples was used as representative of salt water for this evaluation, as shown on Table 2.

An average of values from several locations was used for both the salt water and freshwater groundwater concentrations. Some calculated salt water percentage values for wells at the Site were slightly below 0 percent salt water (below average background value) or slightly above 100 percent salt water, due to uncertainty in the geochemical analysis. Values below 0 percent and above 100 percent were dealt with as described in the Final Results Calculation Section.

Section 4.0 Selection of Geochemical Parameters

Groundwater and surface water samples were analyzed for 29 parameters, 10 of which are generally associated with salt water: boron, bromide, calcium, chloride, iodide, magnesium, potassium, sodium, strontium, and sulfate. Several of the geochemical parameters normally associated with salt water could not be included in the evaluation due to ADP influences on some parameters and/or Site geochemical conditions interfering with the fate and transport of the parameters. The following section describes the evaluation of each of the geochemical parameters excluded from the evaluation and the reasons for their exclusion.

Sodium chloride was used as a primary raw material for the production of both chlorine gas, and caustic soda. Since sodium chloride was stored on the salt pad and several other locations on the property it was a known anthropogenic input into the subsurface. There is no definitive way to determine if the sodium and chloride concentrations in the samples are from salt water, brine, or both. The evaluation relies on the removal of all anthropogenic influences; therefore, sodium and chloride were excluded from the analysis.

Various calcium salts (e.g., calcium carbonate, calcium chloride, calcium hydroxide) were by-products of the chemical processes conducted on the Site. Therefore, similarly to sodium and chloride, there is no definitive way to distinguish anthropogenic from salt water calcium. Due to the apparent influence of anthropogenic inputs, calcium was excluded from the evaluation.

Iodide is generally considered a reliable parameter for determining the point of salt water equilibrium. However, the reporting limit for iodide in the groundwater samples was consistently above the concentration expected in salt water, meaning that the iodide results were not useful for this evaluation.

Magnesium is known to precipitate at pH greater than 11.2 (USEPA, 1999). Due to the presence of groundwater with pH values greater than 11.2 over much of the Site, the magnesium concentrations in many groundwater samples will be lower than expected because of precipitation of magnesium oxide (brucite). Therefore magnesium was excluded from the evaluation.

Initial salt water percentage calculations were completed for each of the remaining five geochemical parameters (boron, bromide, potassium, strontium, and sulfate) and the spatial distribution of the salt water percentages were evaluated for any obvious spatial relationships between the geochemical parameters and the ADP. This evaluation was done to determine if the ADP has affected the concentrations of the five remaining salt water geochemical parameters. If a geochemical parameter was determined to be influenced by the ADP, then that parameter was eliminated from the mixing calculations. The salt water percentage values for chloride were also calculated, to show the percentages of a parameter that has known anthropogenic influences. The distribution of chloride was used as a reference when evaluating the distributions of the other parameters. The salt water percentage values were placed on maps according to the seven zone grouping planes (15 ft, 25 ft, 50 ft, 75 ft, 100 ft, 130, and 160 ft-zones), which can be seen on Figures 1-35.

Anthropogenic influences in the chloride distribution become obvious in the 75-foot zone at well 75-75, where the calculated percentage of salt water was determined to be over 200 percent. The average chloride concentration in salt water was approximately 17,000 mg/L meaning that a 100 percent increase (up to 34,000 mg/L) cannot be attributed to analytical uncertainty or natural variations. The evidence of anthropogenic influence is most pronounced at the 100-ft and 130-ft zones, where percentages of over 200 percent were calculated at several locations, mostly near or downgradient of the Salt Pad, where anthropogenic brine input is expected to be greatest. This distribution of anthropogenic impact was used to determine if the other geochemical parameters have been impacted by anthropogenic sources as well.

The results of the boron calculations (Figures 1-7) showed that there is an area of high salt water percentage values near and downgradient of the Salt Pad. Several of the values are over 200 percent salt water, and because they are close to the known ADP, these samples have likely been affected by anthropogenic sources. Boron was therefore eliminated from the evaluation due to anthropogenic influences.

The results of the potassium calculations showed that there is an area of very high salt water percentage values near and downgradient of the Salt Pad with several of the values over 200 percent salt water (Figures 8-14). The location near the ADP and the elevated values means that the samples have likely been affected by anthropogenic sources. Potassium was therefore eliminated from the evaluation due to anthropogenic influences.

The results of the sulfate calculations showed an area of high salt water percentage values near and downgradient of the Salt Pad (Figures 15-21). This correlation was particularly noticeable in the -100 ft and -130 ft zones, where locations downgradient of the salt pad had calculated seawater percentages greater than 100. Furthermore, the groundwater adjacent to the Blair Waterway and Commencement Bay does not exceed 10% seawater at any depth zone. Significant concentrations of sulfate, related to the inland migration of natural salt water would be expected below -75 ft. Given these relationships, sulfate was considered unreliable and was therefore eliminated from the evaluation.

The calculated salt water percentages for bromide are presented on Figures 29 through 35. The calculated salt water percentages for strontium are presented on Figures 22 through 28. These figures show that the calculated distribution of salt water for these two parameters is reasonably consistent. The figures do not show an area of greatly elevated calculated salt water percentages near the Salt Pad, like for boron and potassium. However, the calculated percentage values for strontium show more variation than for bromide, (higher highs and lower lows), which is likely attributable to the fact that the concentrations of strontium are much lower (6 mg/L), meaning that any uncertainty in the analysis can cause a larger error in the calculated result. Therefore strontium was not retained for the final calculations.

Section 5.0 Final Calculation Procedures

The salt water percentage calculations were performed using only bromide alone. The mixing calculation was done for each sample. Any sample that had a calculated salt water percentage below zero (background) was assigned a salt water percentage value of zero. Any sample that had a calculated salt water percentage greater than 100 percent (salt water) was assigned a value of 100 percent. The values where this correction was applied were relatively few and there was no apparent relationship with the anthropogenic plume for the values above 100 percent. This indicates that the variation is likely due to the use of average background and salt water values, the variations in natural water concentrations, and the error inherent in any laboratory analysis.

At locations where multiple samples were taken within the same depth zone, an average was taken of all salt water percentages. At locations with non-detect values, bromide samples where the reporting limit was 0.2 mg/L were set to equal the reporting limit. This procedure resulted in fifteen bromide samples being set to 0.2 mg/L, fourteen of these samples were taken in the -15 ft and -25 ft depth zones. This is a reasonable method to perform on non-detect

values since a bromide value of 0.2 mg/L corresponds with a salt water percentage of 0.16%, which is essentially fresh groundwater. Any value less than the reporting limit would have a negligible impact on the overall fresh groundwater/salt water distribution. Non-detect samples where the reporting limit for bromide was greater than 0.2 were removed from the evaluation. Setting these samples to equal the elevated reporting limit would be highly speculative. Therefore, the inclusion of these samples would introduce unacceptable levels of uncertainty into the evaluation. This procedure resulted in the removal of 9 samples (see Table 3).

Section 6.0 Final Calculation Results

A 3-dimensional model was created of salt water composition determined with bromide data using the Mining Visualization System/Environmental Visualization System (MVS/EVS) software package, developed by CTech development Corporation. The salt water data was interpolated using the kriging algorithm with control points placed along the seafloor of the Hylebos Waterway, Blair Waterway and Commencement Bay. These control points were placed at -10 ft NGVD and -40 ft NGVD and were assigned salt water percentages of 100 percent. The purpose of these points was to eliminate extrapolation of fresh and brackish water into known bodies of natural salt water.

The MVS/EVS model is included as Attachment A and indicates:

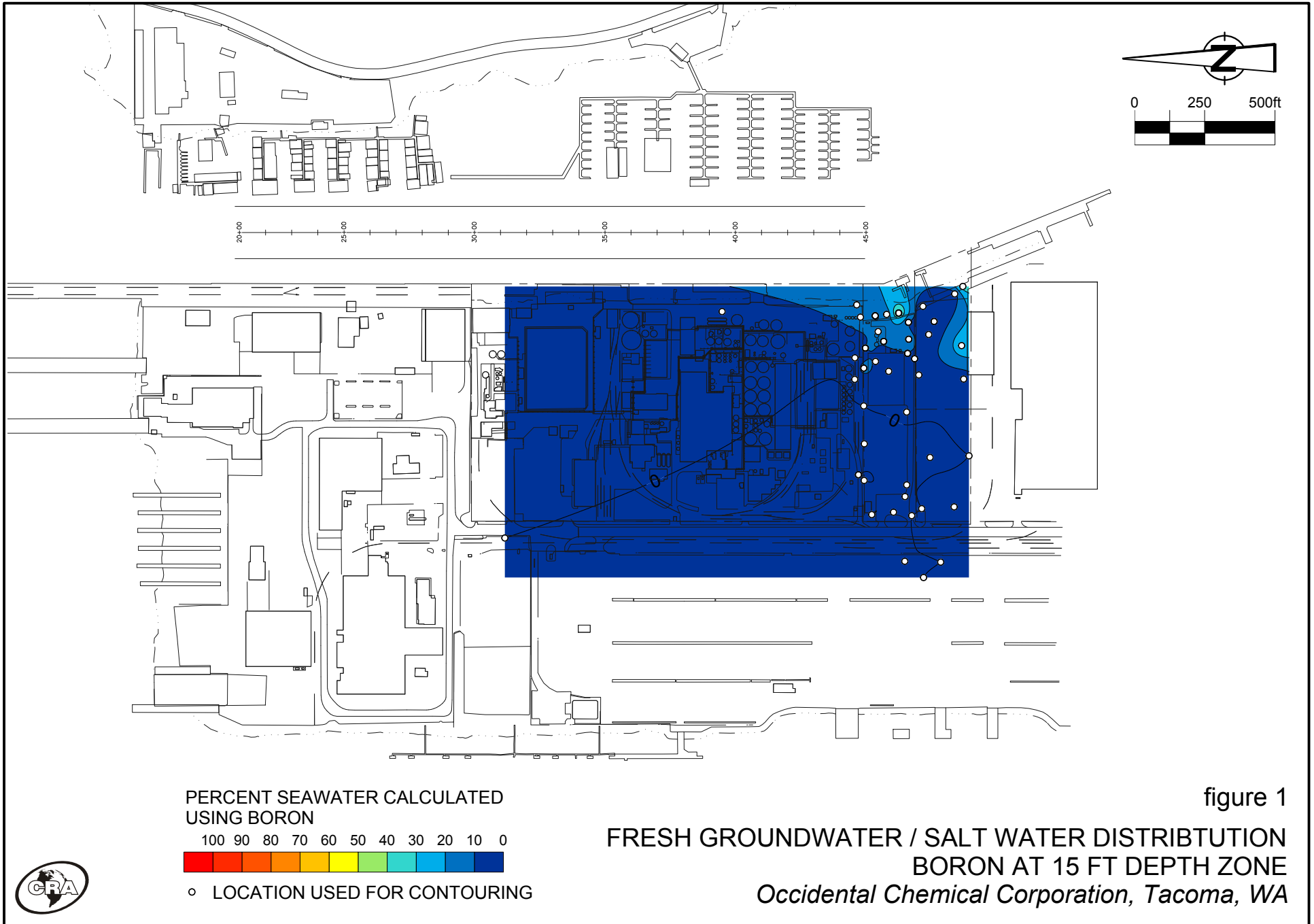
- There is a shallow lens of fresh groundwater in the middle of the peninsula between 5 ft NGVD and -35 ft NGVD, which lies on top of the denser saline water that has infiltrated into the peninsula along the Blair Waterway, Hylebos Waterway, and Commencement Bay.
- Groundwater with greater than 80 percent calculated salt water values extend under the 721 Alexander Avenue property from both the Blair and Hylebos Waterways.
- Between -115 ft NGVD and -155 ft NGVD there is a significant freshening underneath the east side of the peninsula, with calculated salt water percentages less than 20 percent.

The simplified conceptual model of the Site predicts that salt water would be present to depth beneath the entire Site peninsula and would extend to the plant-east under the Hylebos waterway to the top surface of the glacial material, sloping downward underneath the bluffs. The geochemical evaluation identified the presence of salt water to depth adjacent to the Hylebos, Blair and Commencement bay, which extended downwards and laterally across the site. However, below -85 ft NGVD the actual distribution of salt water and fresh groundwater is more complex than the conceptual model due to the deep fresh groundwater found under the peninsula. This difference could be attributed to freshwater upwelling and displacing the denser saline water. Contributions to this groundwater flow could be supplied by flow from the bluffs. Furthermore, the stratigraphy of the Site exhibits significant heterogeneity, which likely alters the fresh groundwater/salt water distribution. The zone of apparent confining effects could be limiting the extent of inland salt water migration, and could potentially provide a conduit for fresh groundwater flow from the bluffs.

Section 7.0 References

Barlow, P.M., 2003. Ground Water in Freshwater-Saltwater Environments of the Atlantic Coast, United States Geological Survey (USGS) Circular 1262

United States Geological Survey (USGS), 1964. Sea Water in Coastal Aquifers, Geological Survey Water Supply Paper 1613-C



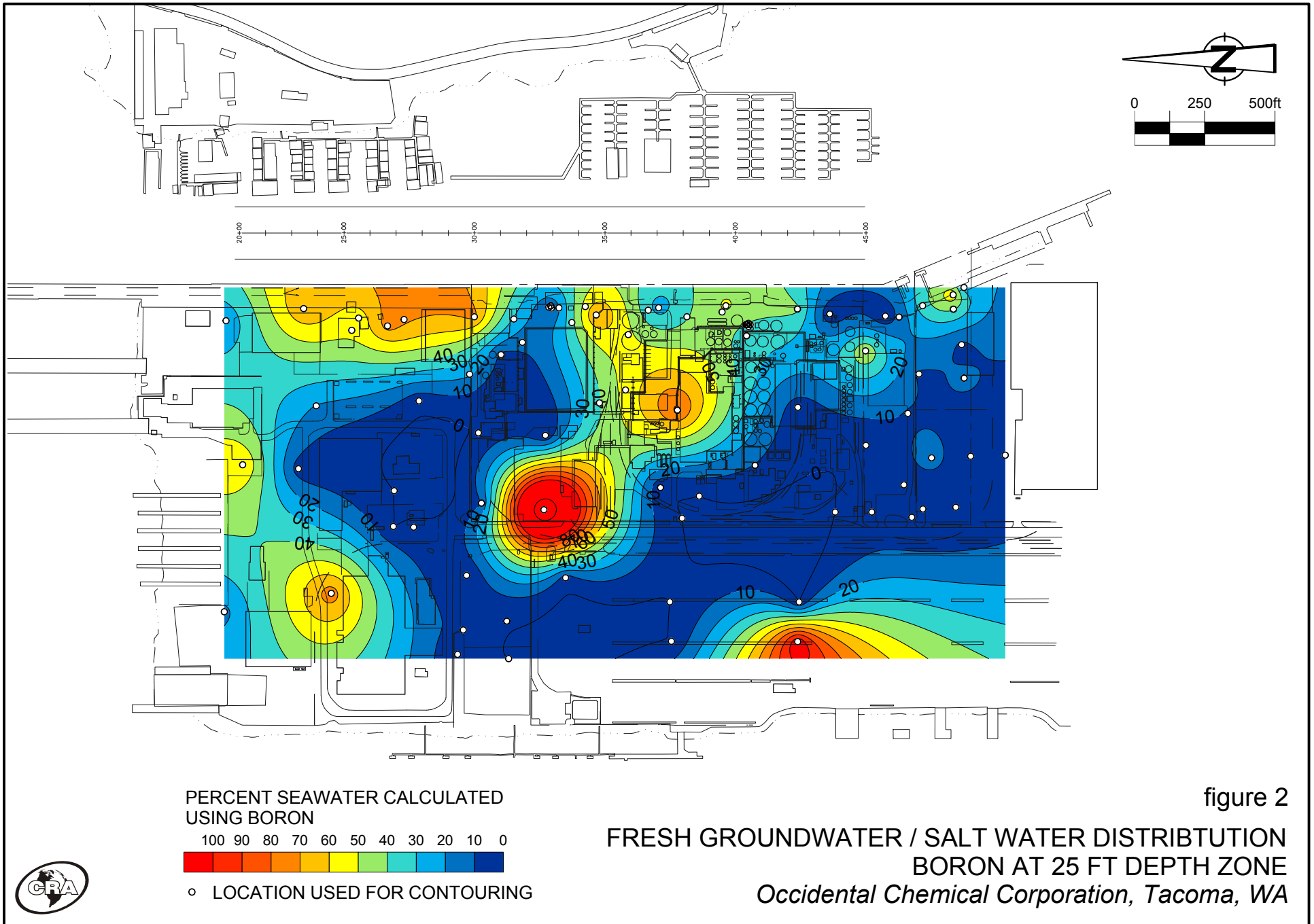
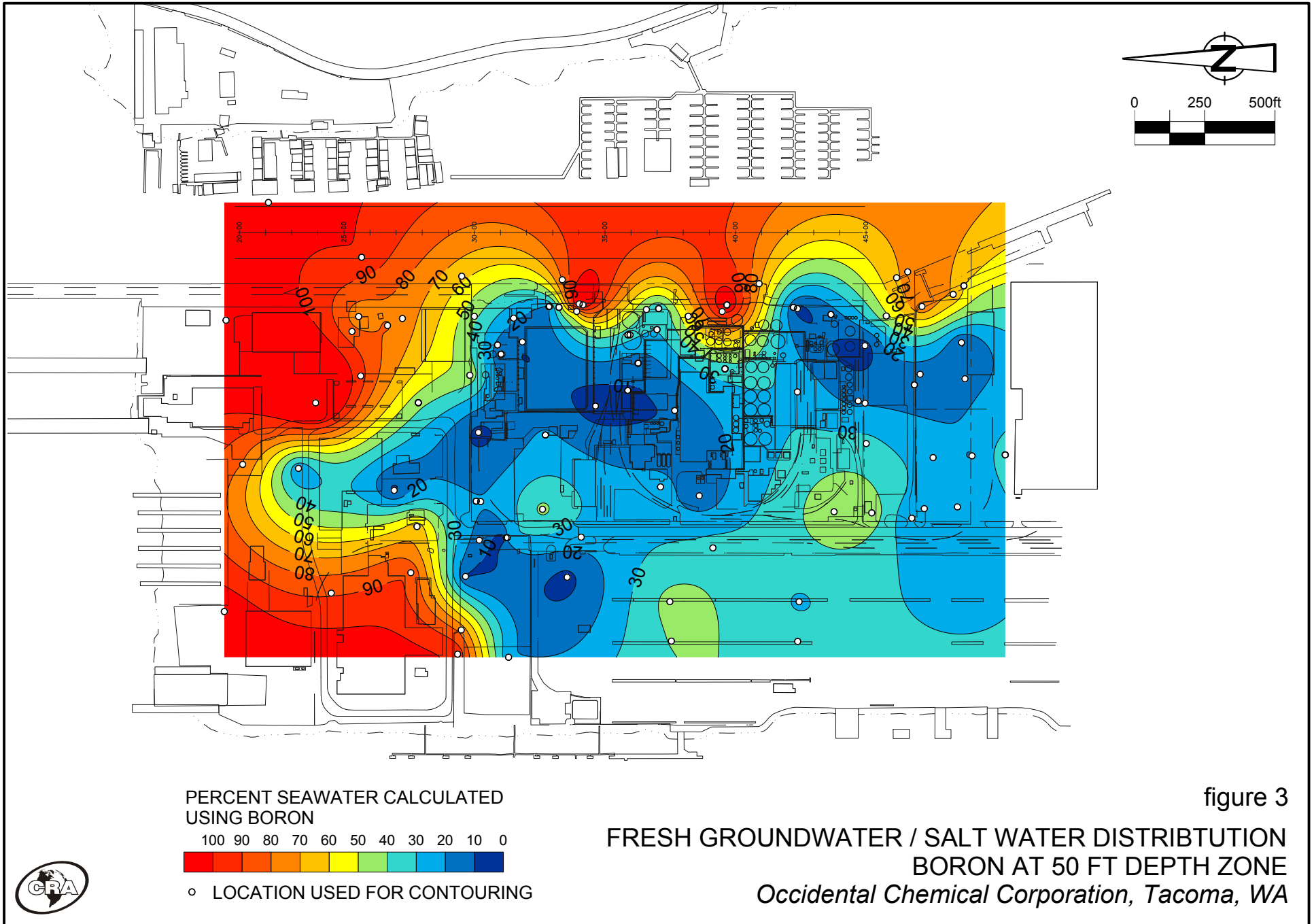
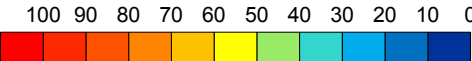


figure 2



PERCENT SEAWATER CALCULATED
USING BORON



◦ LOCATION USED FOR CONTOURING

FRESH GROUNDWATER / SALT WATER DISTRIBUTION
BORON AT 50 FT DEPTH ZONE

Occidental Chemical Corporation, Tacoma, WA

figure 3



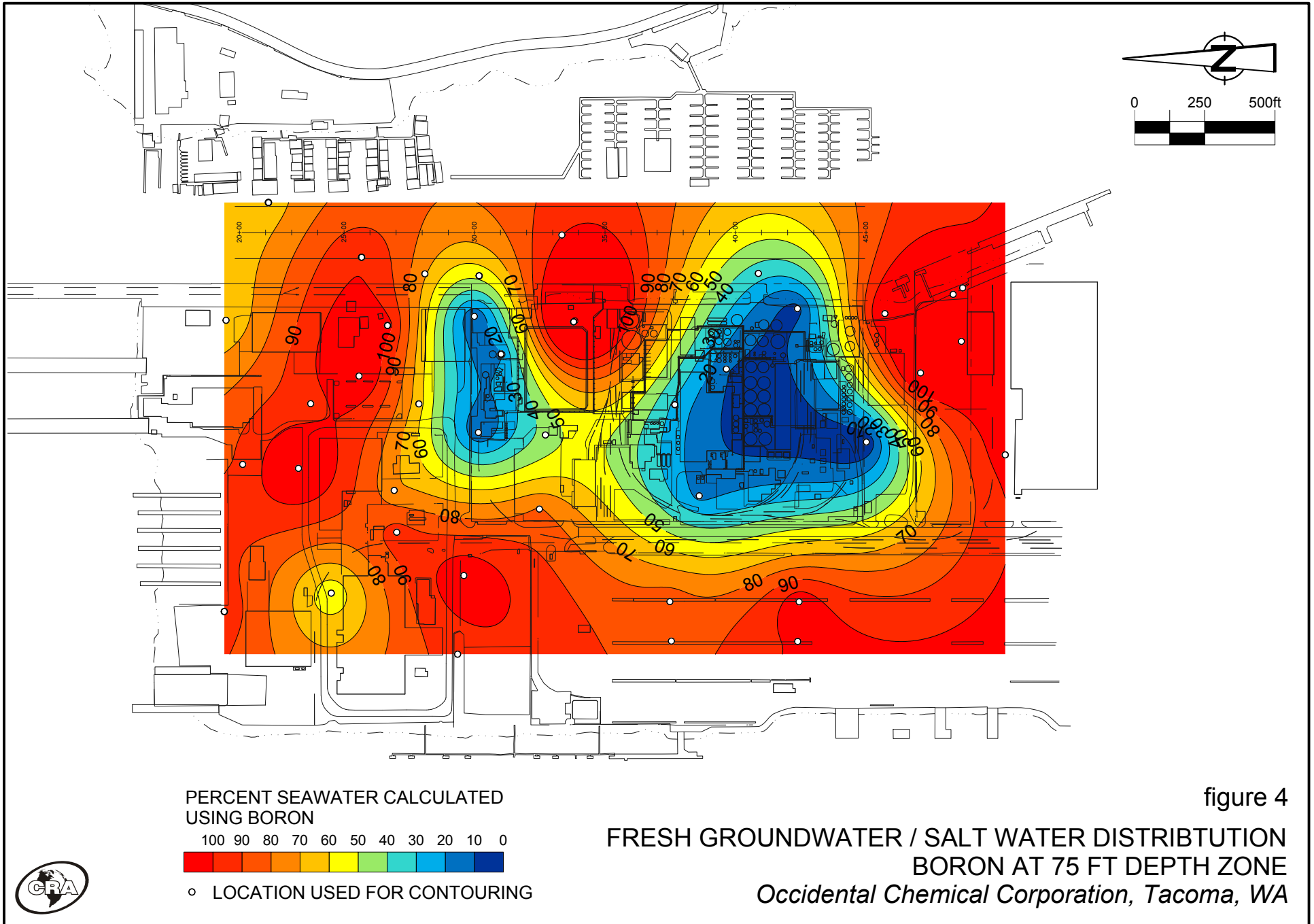


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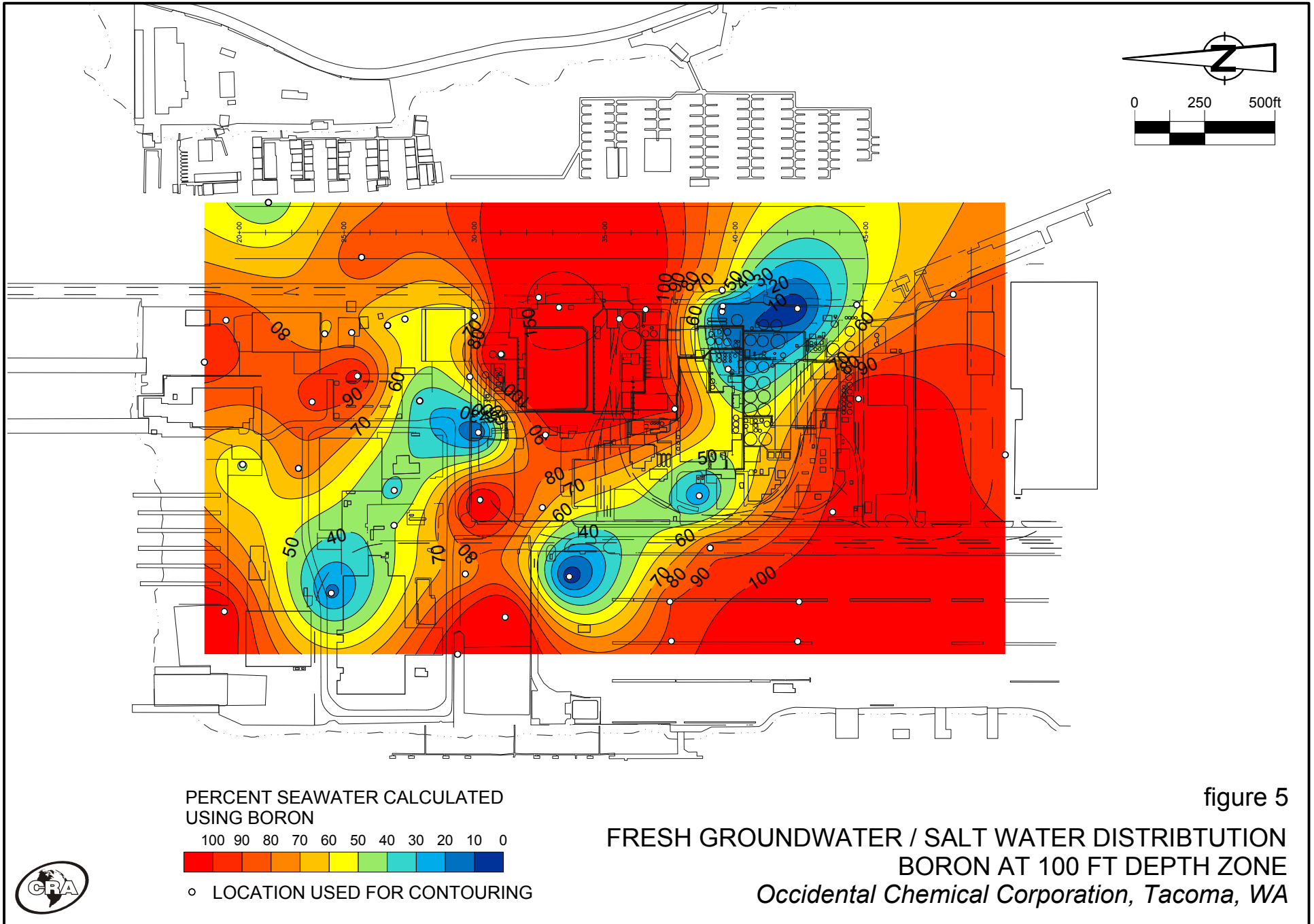


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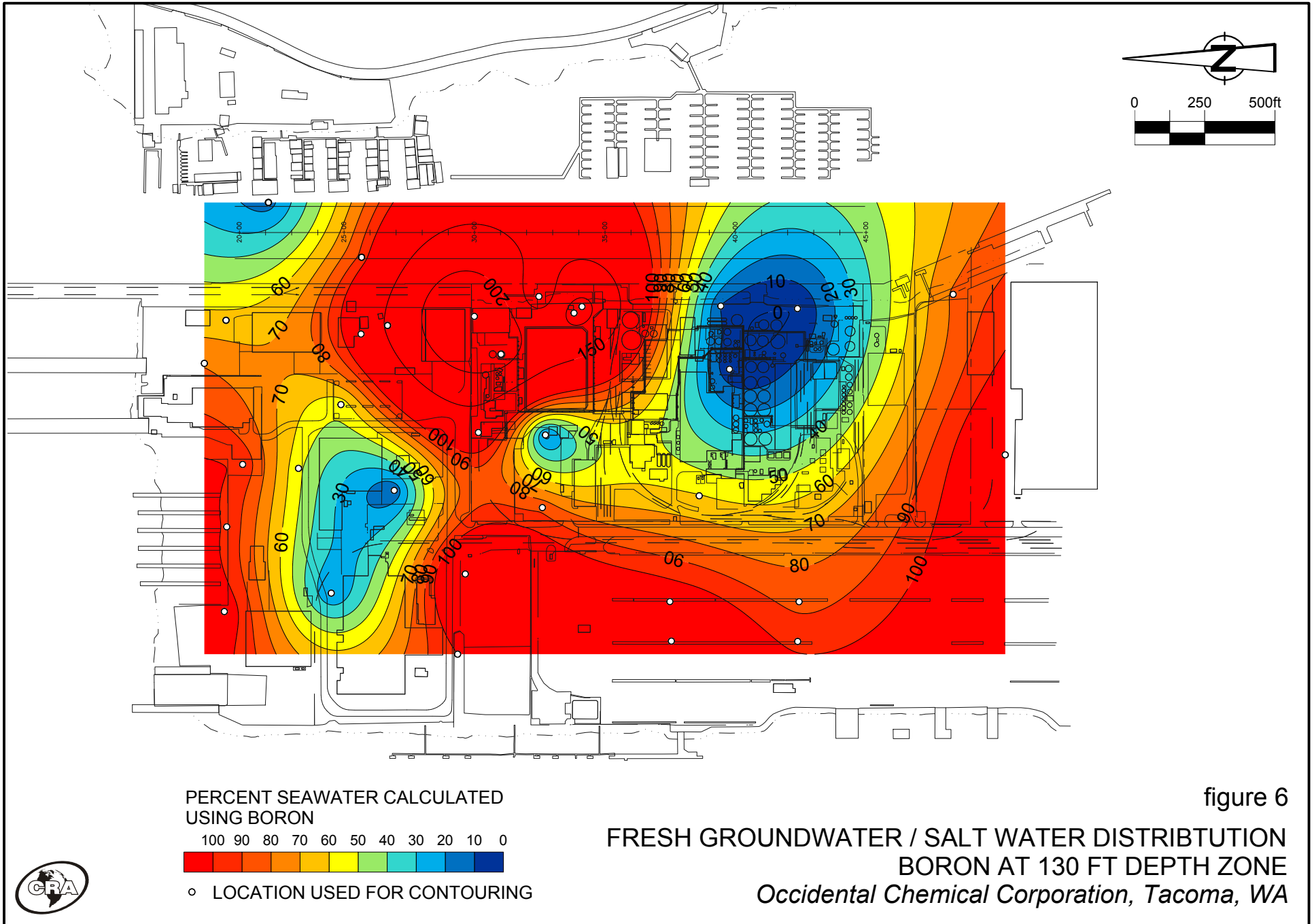


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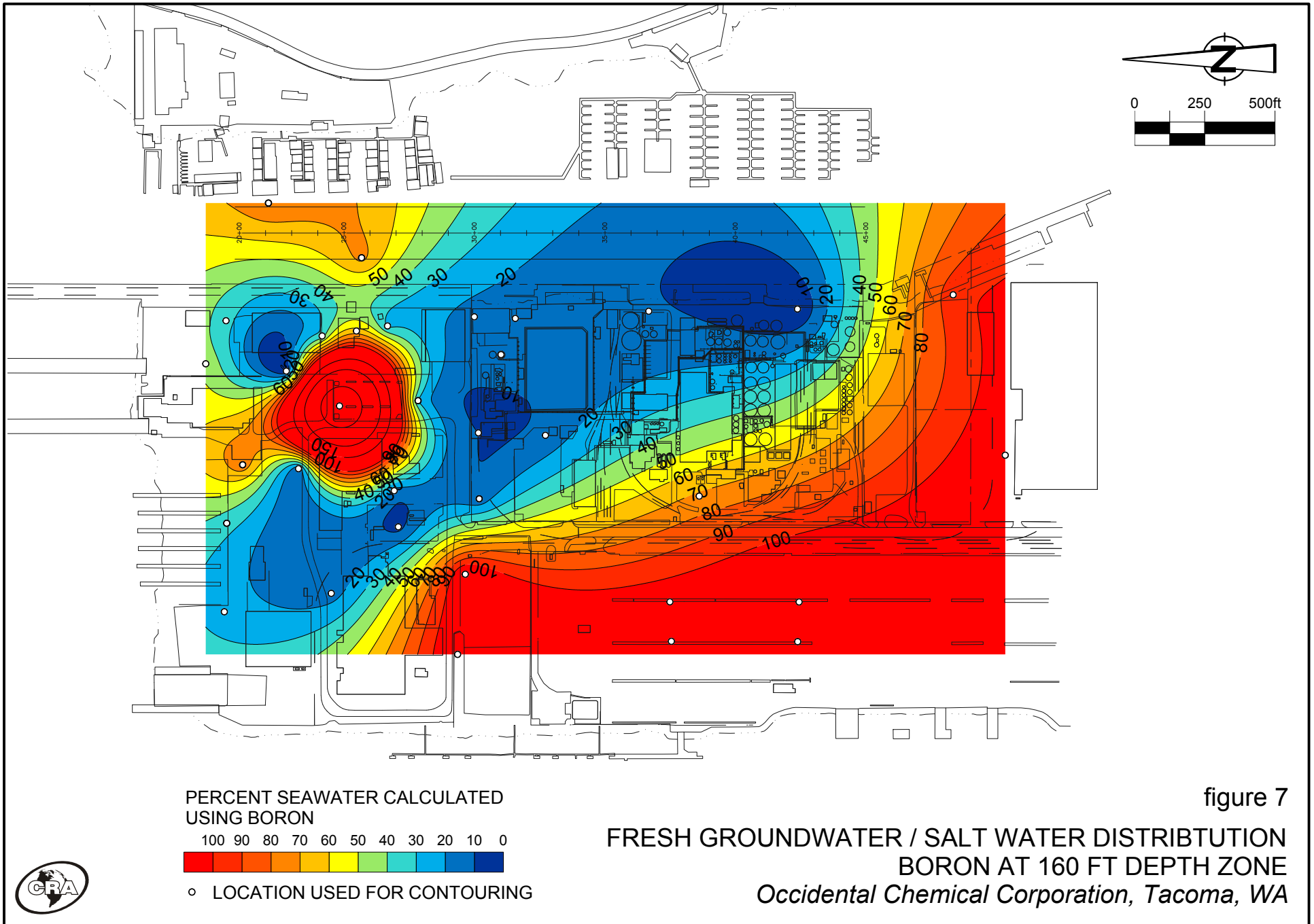


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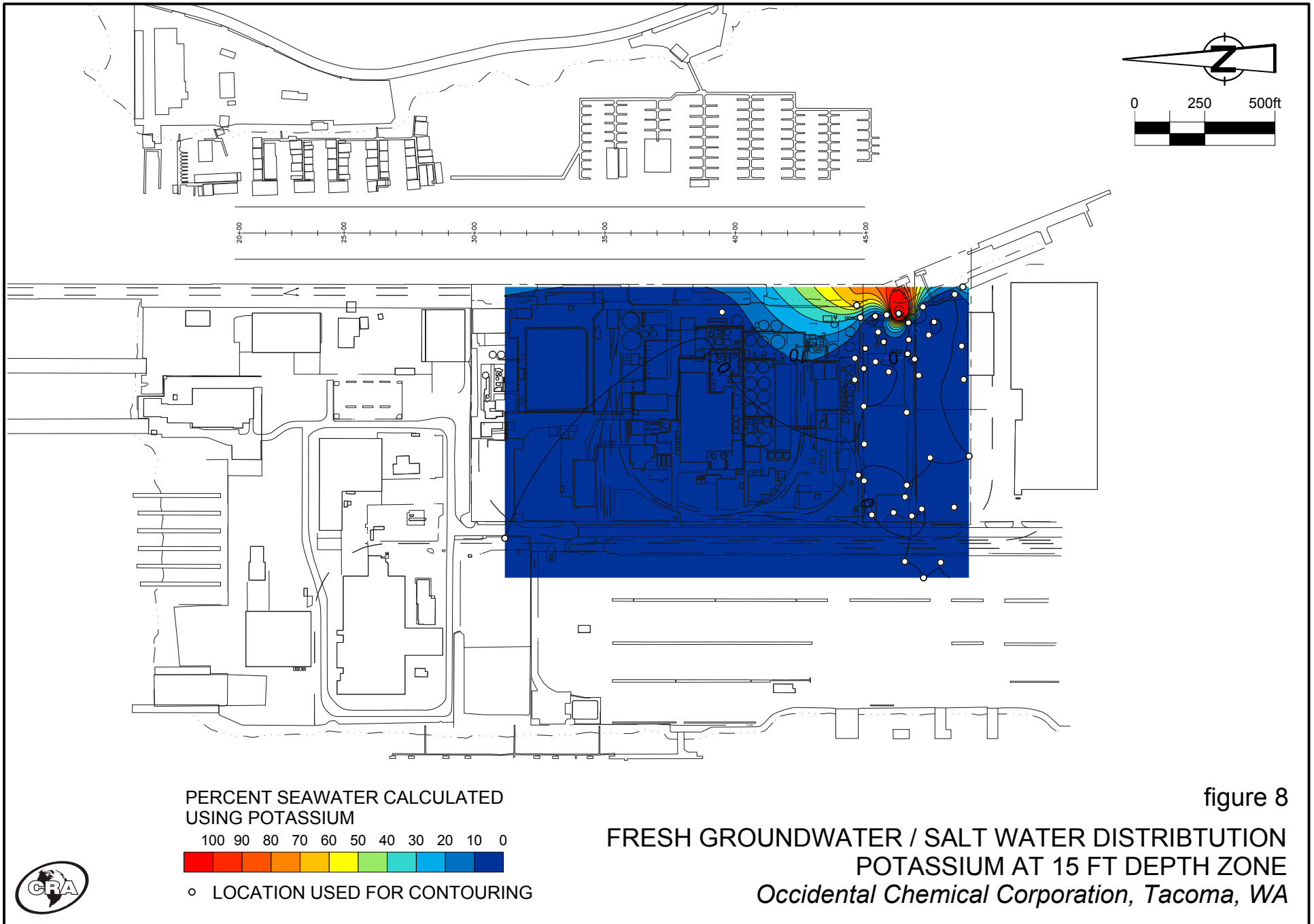


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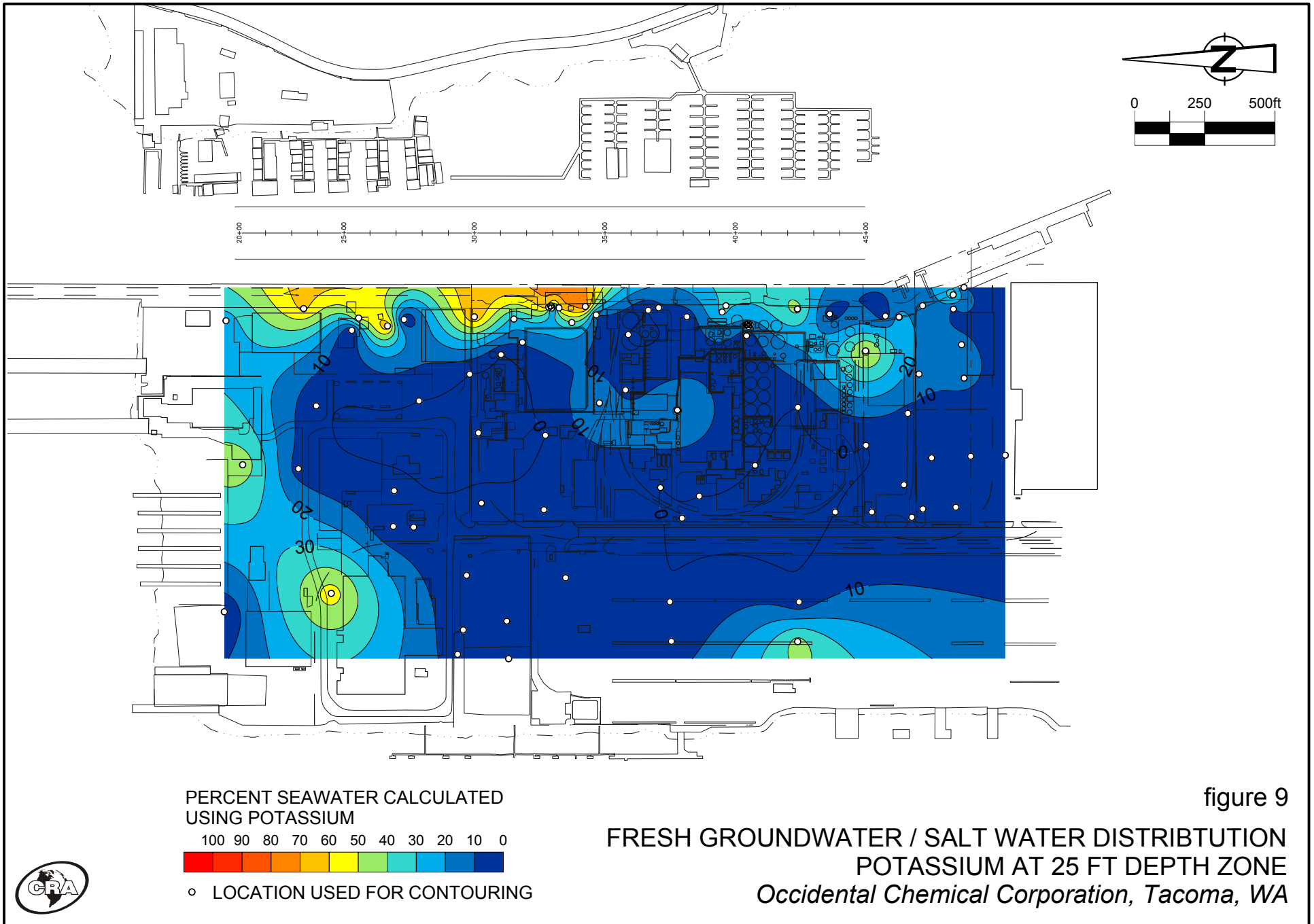


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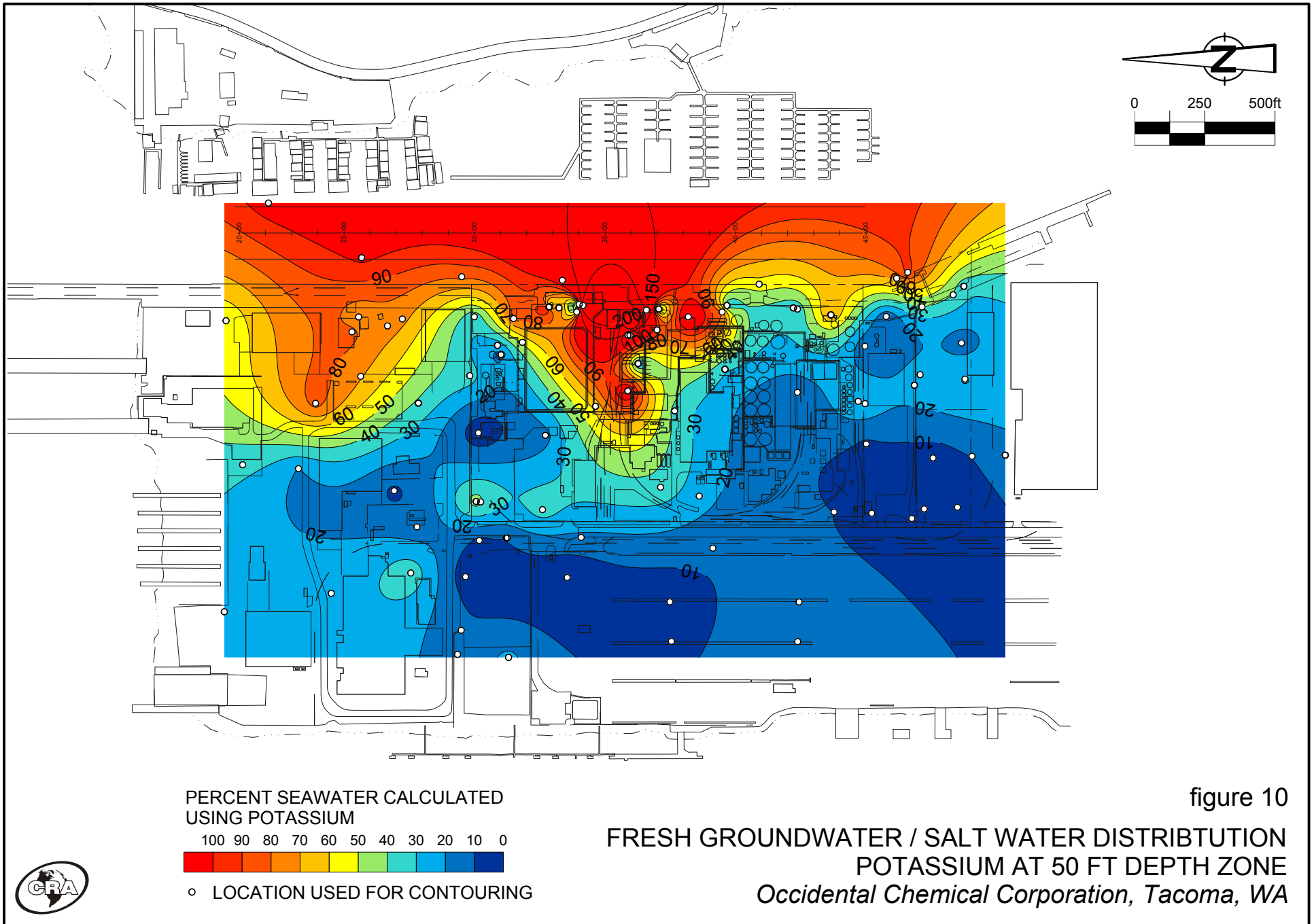


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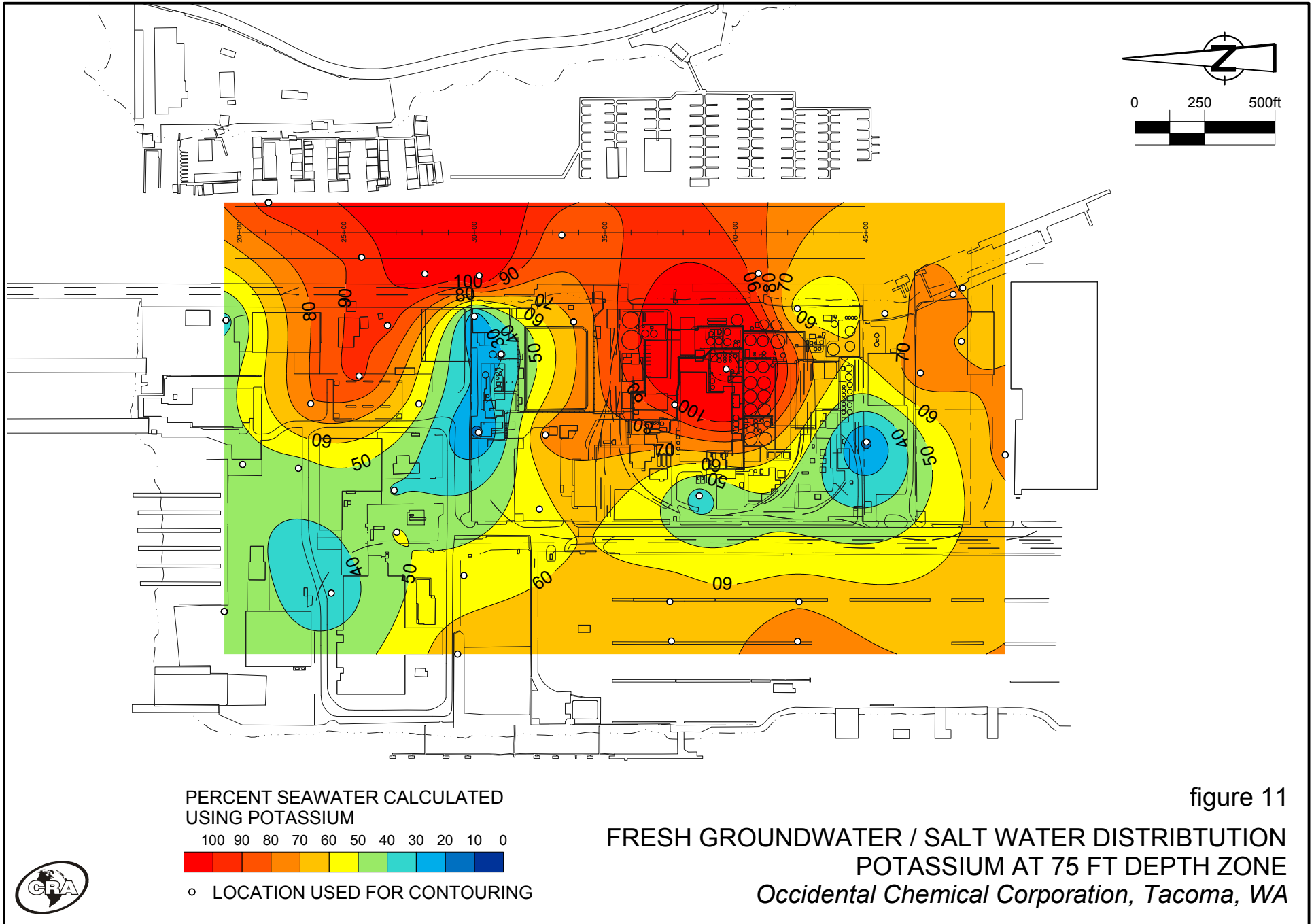


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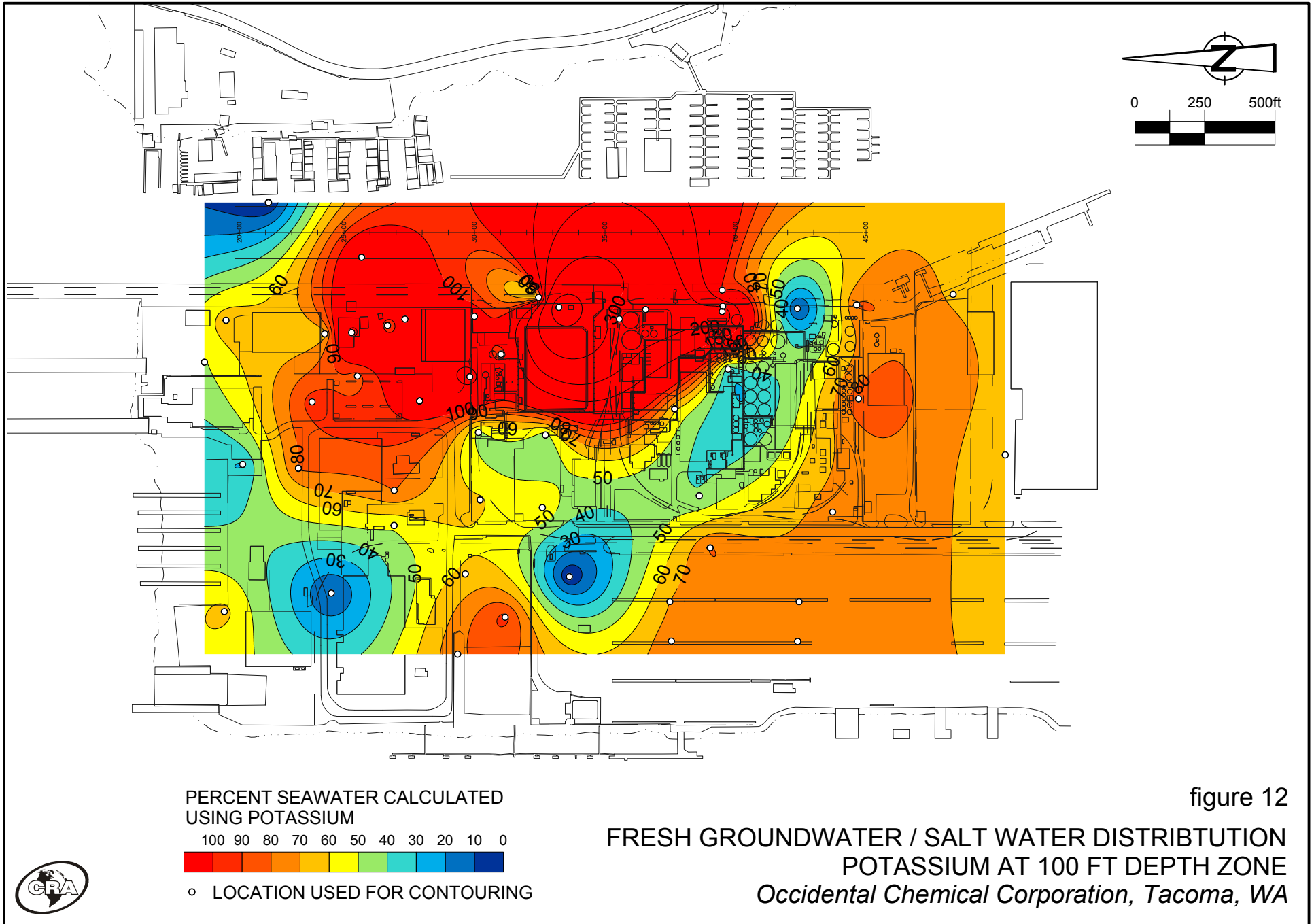


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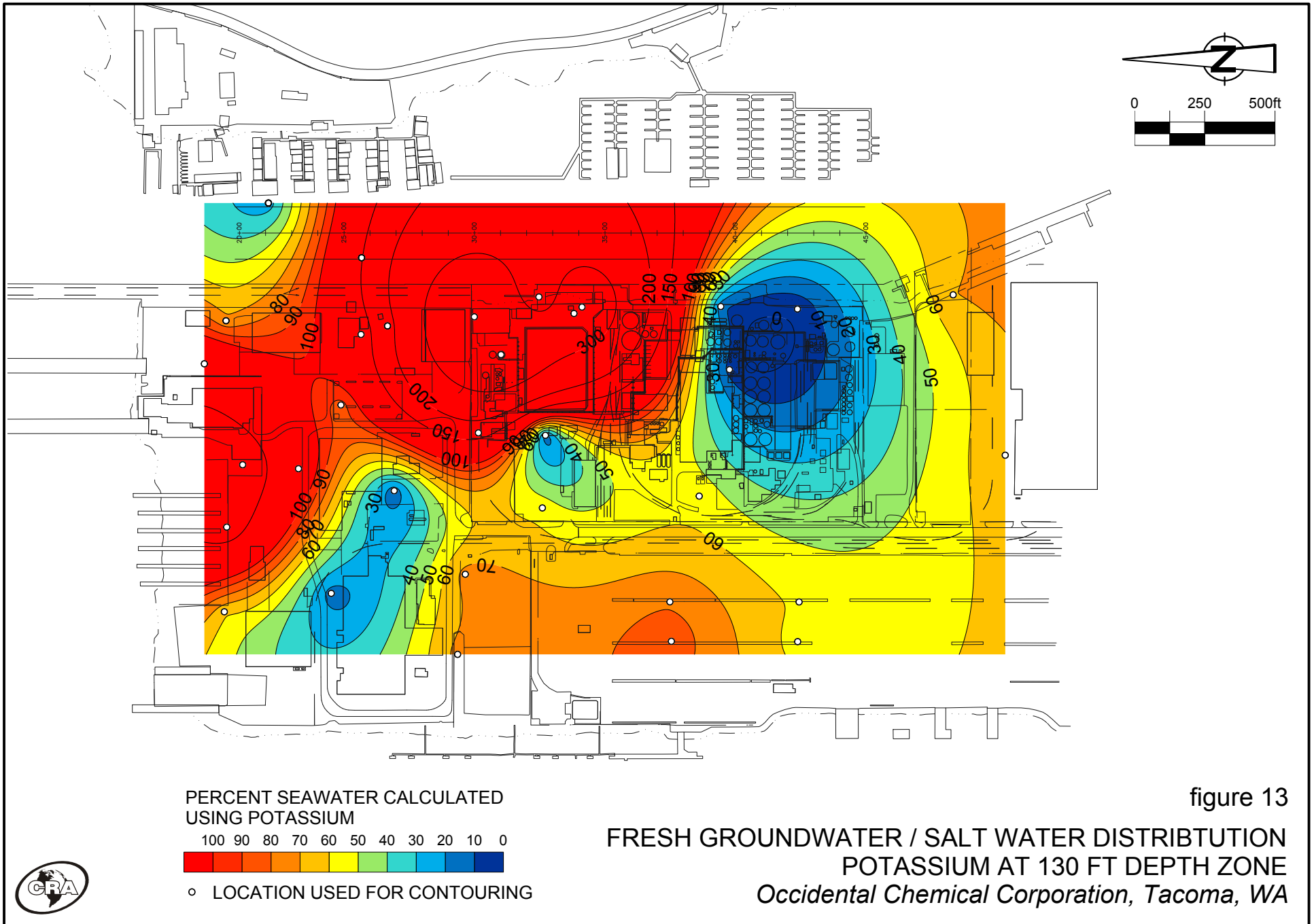


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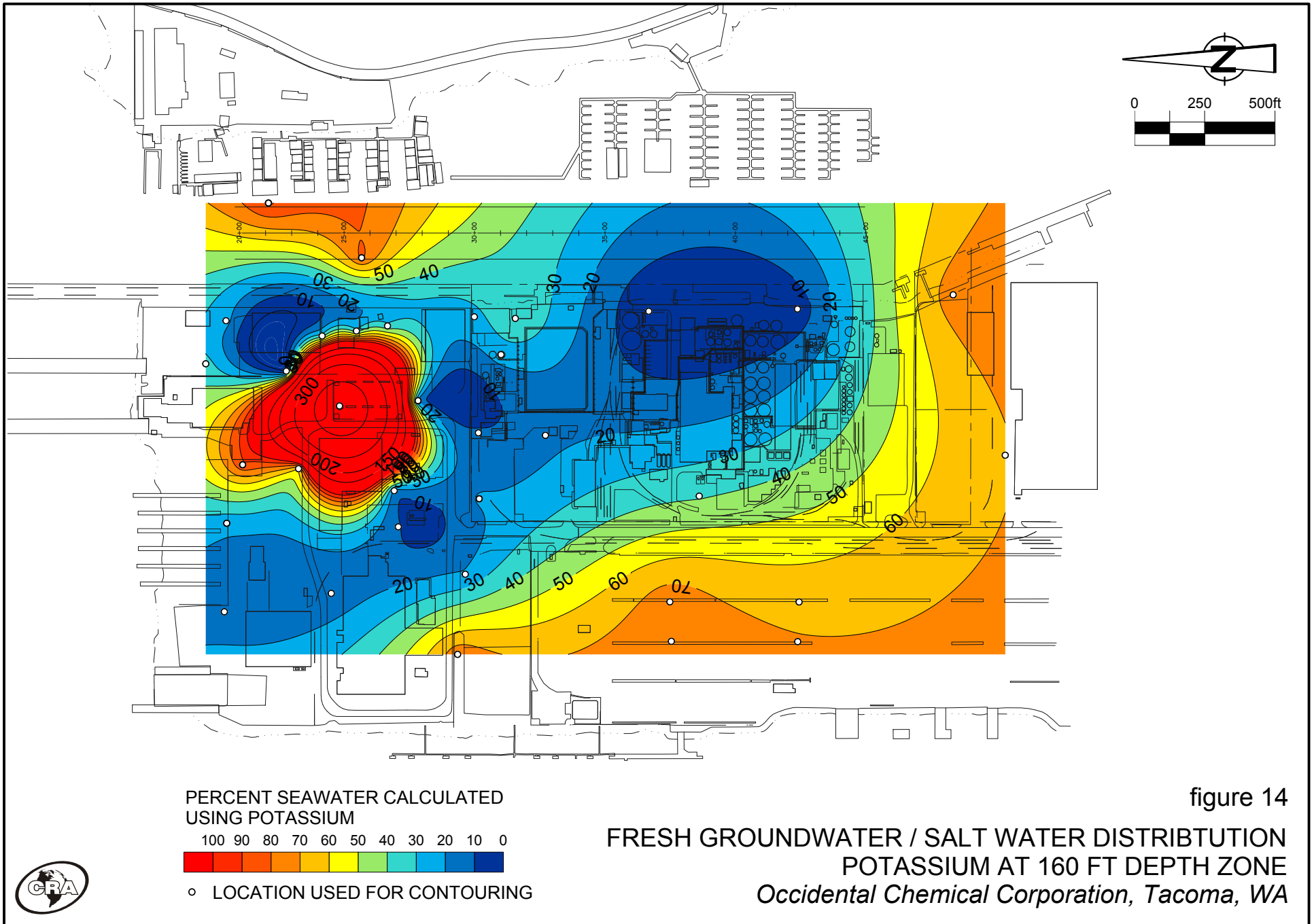
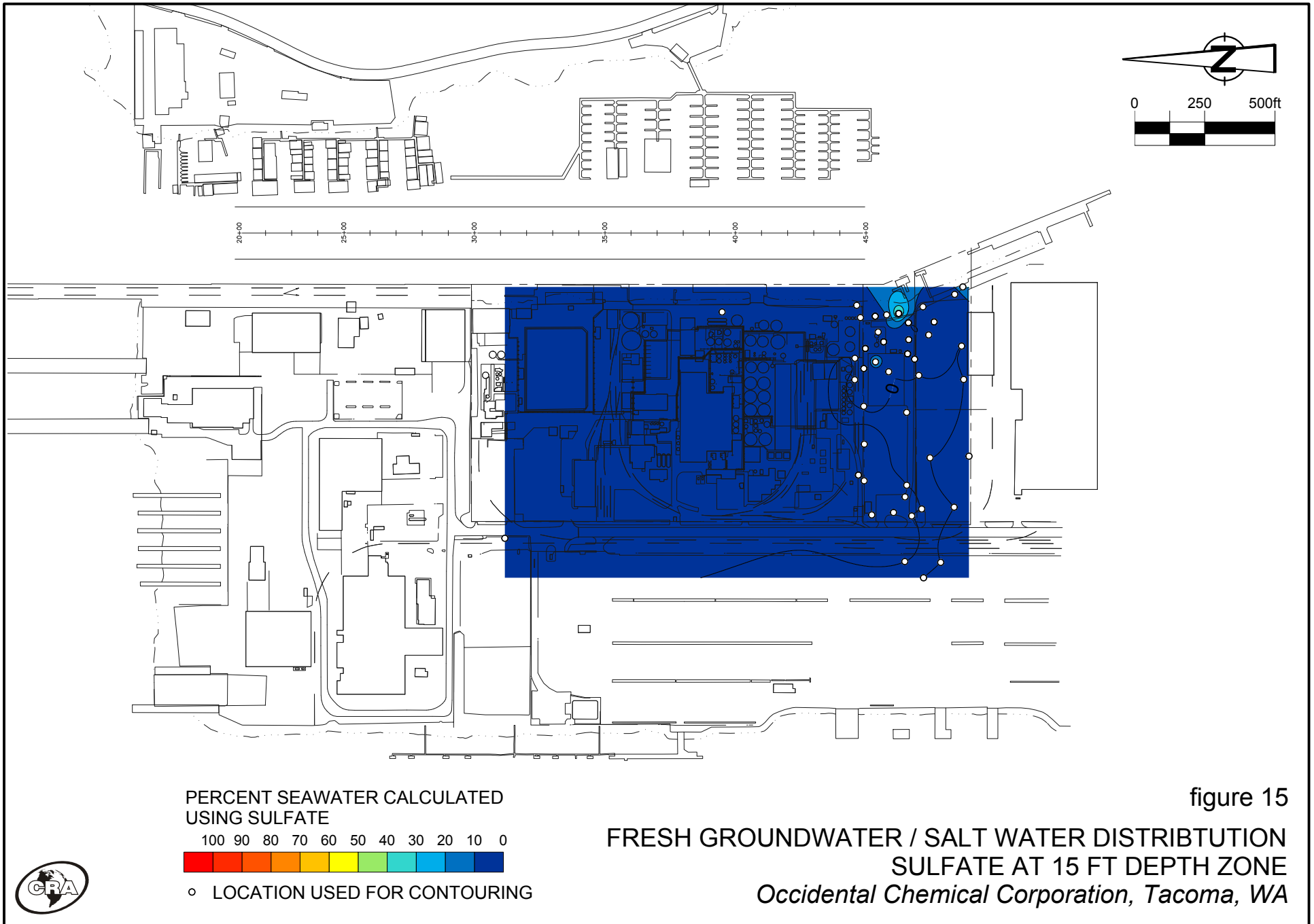


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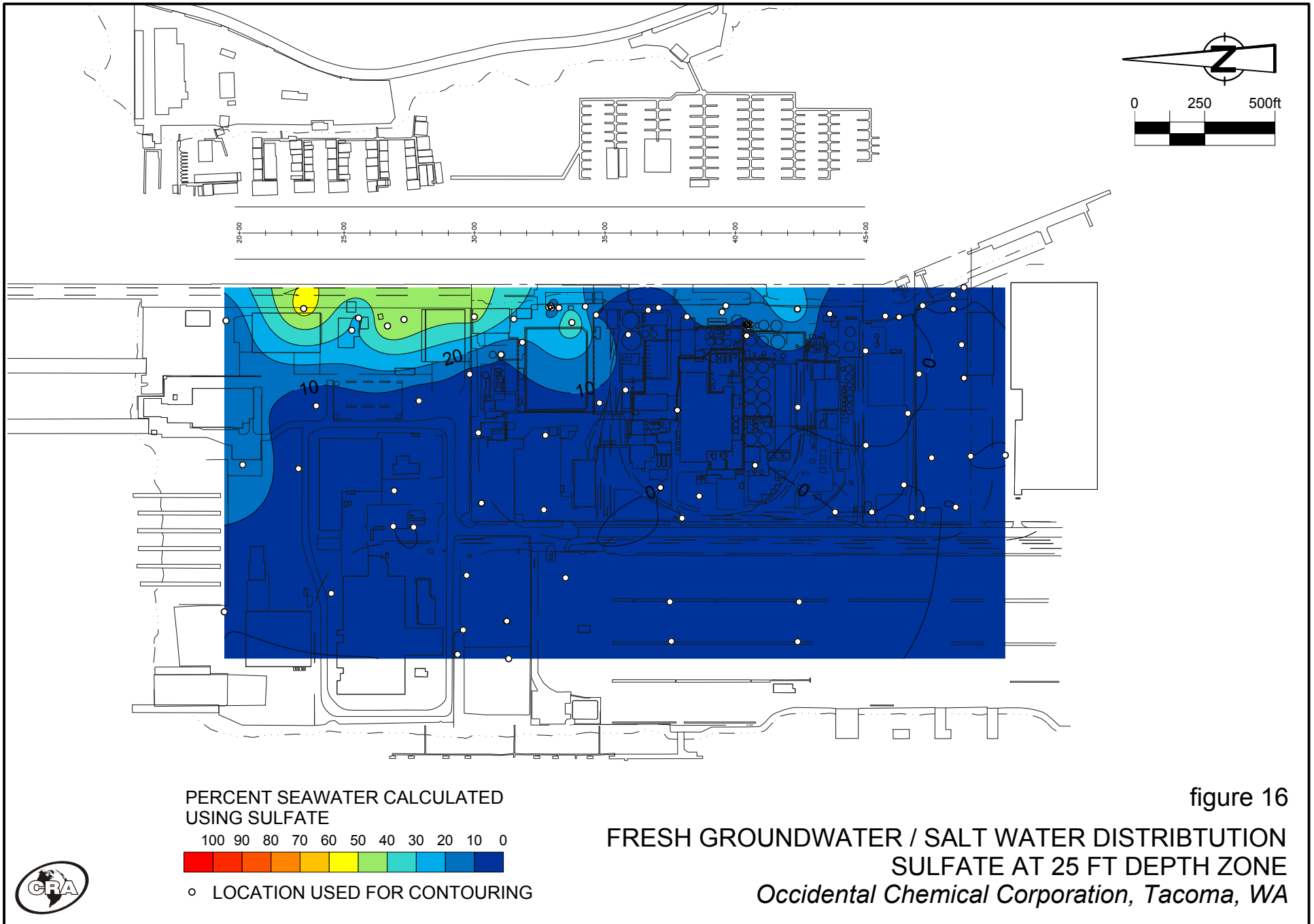


figure 16

FRESH GROUNDWATER / SALT WATER DISTRIBUTION
 SULFATE AT 25 FT DEPTH ZONE
Occidental Chemical Corporation, Tacoma, WA



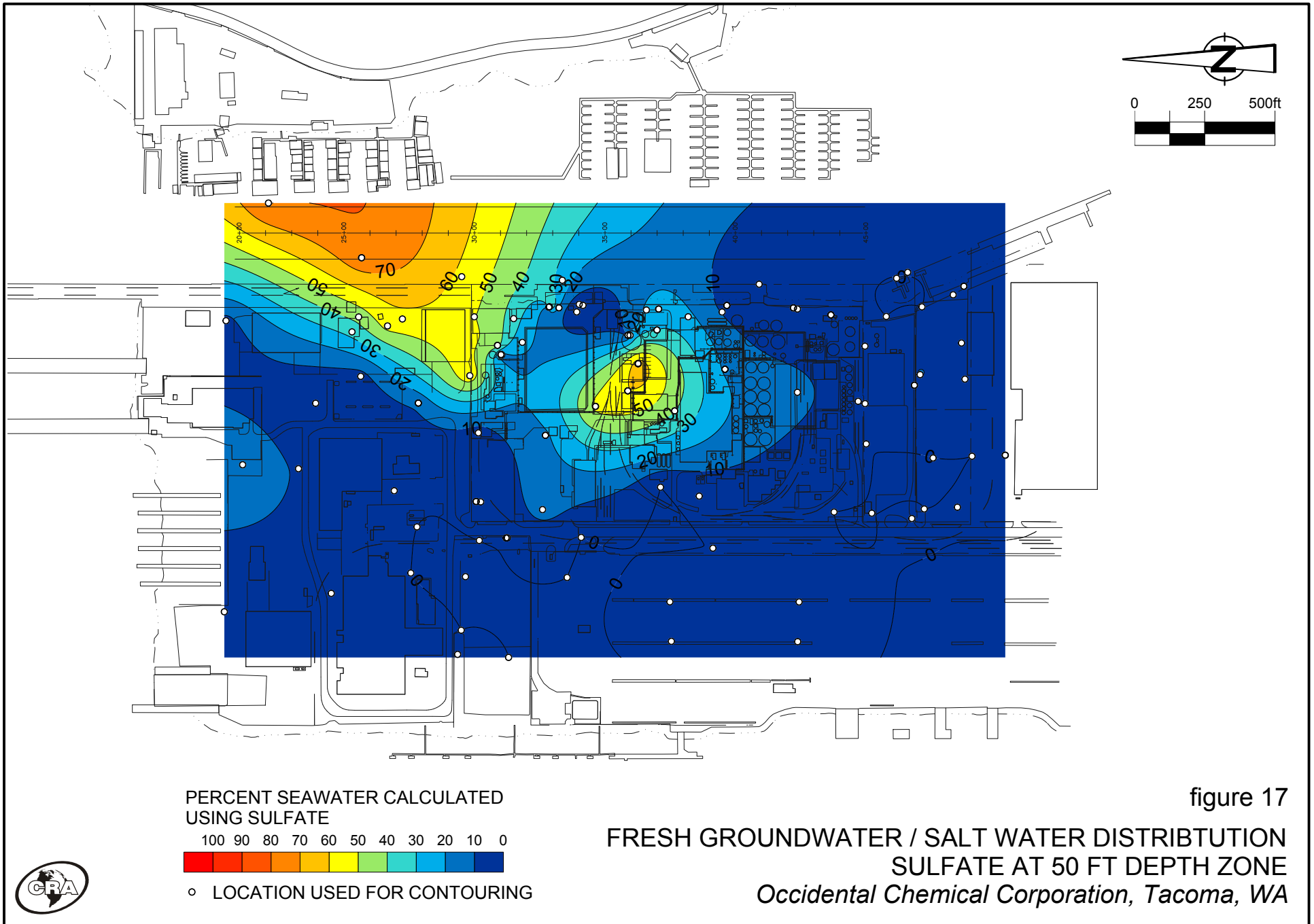
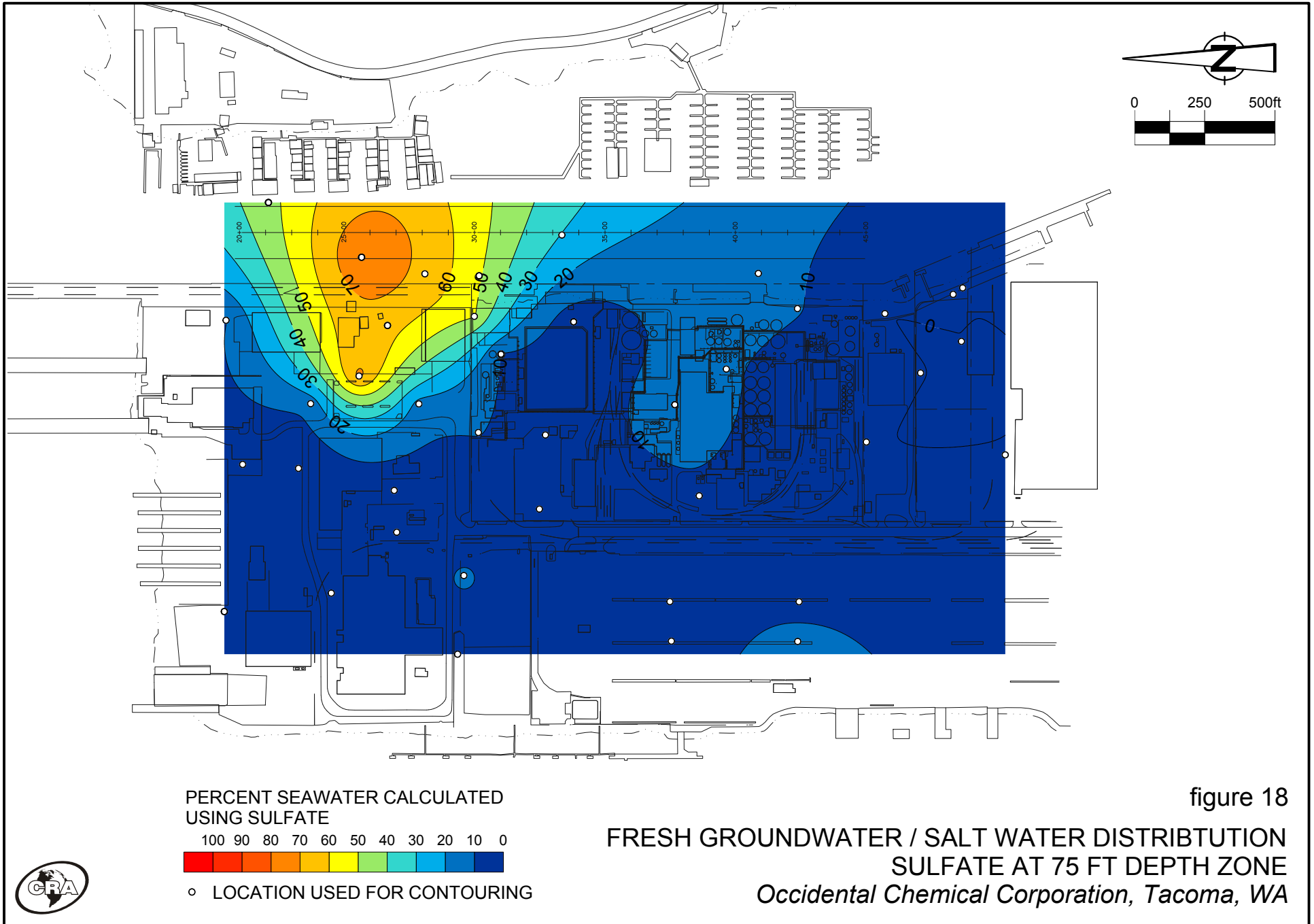


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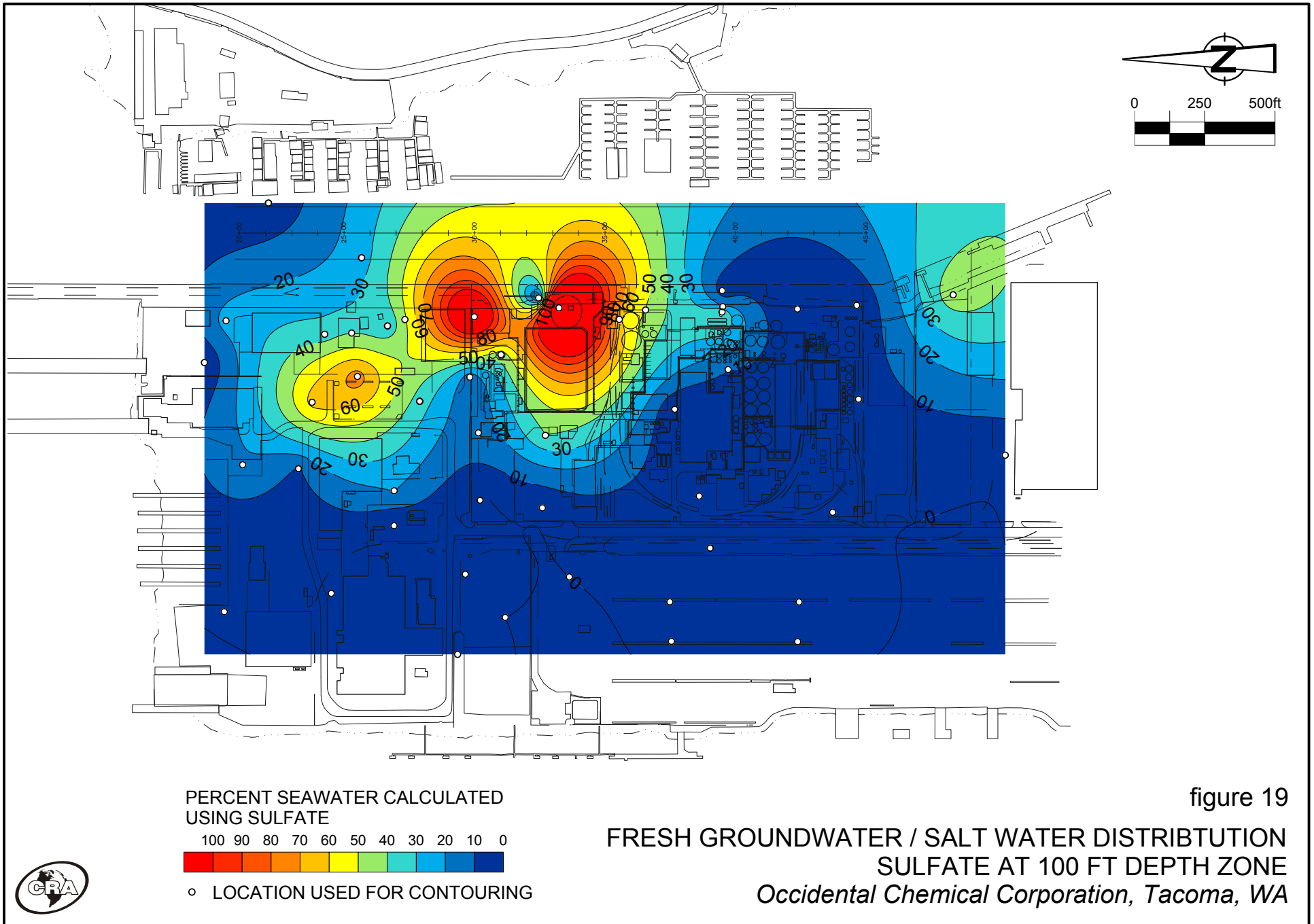


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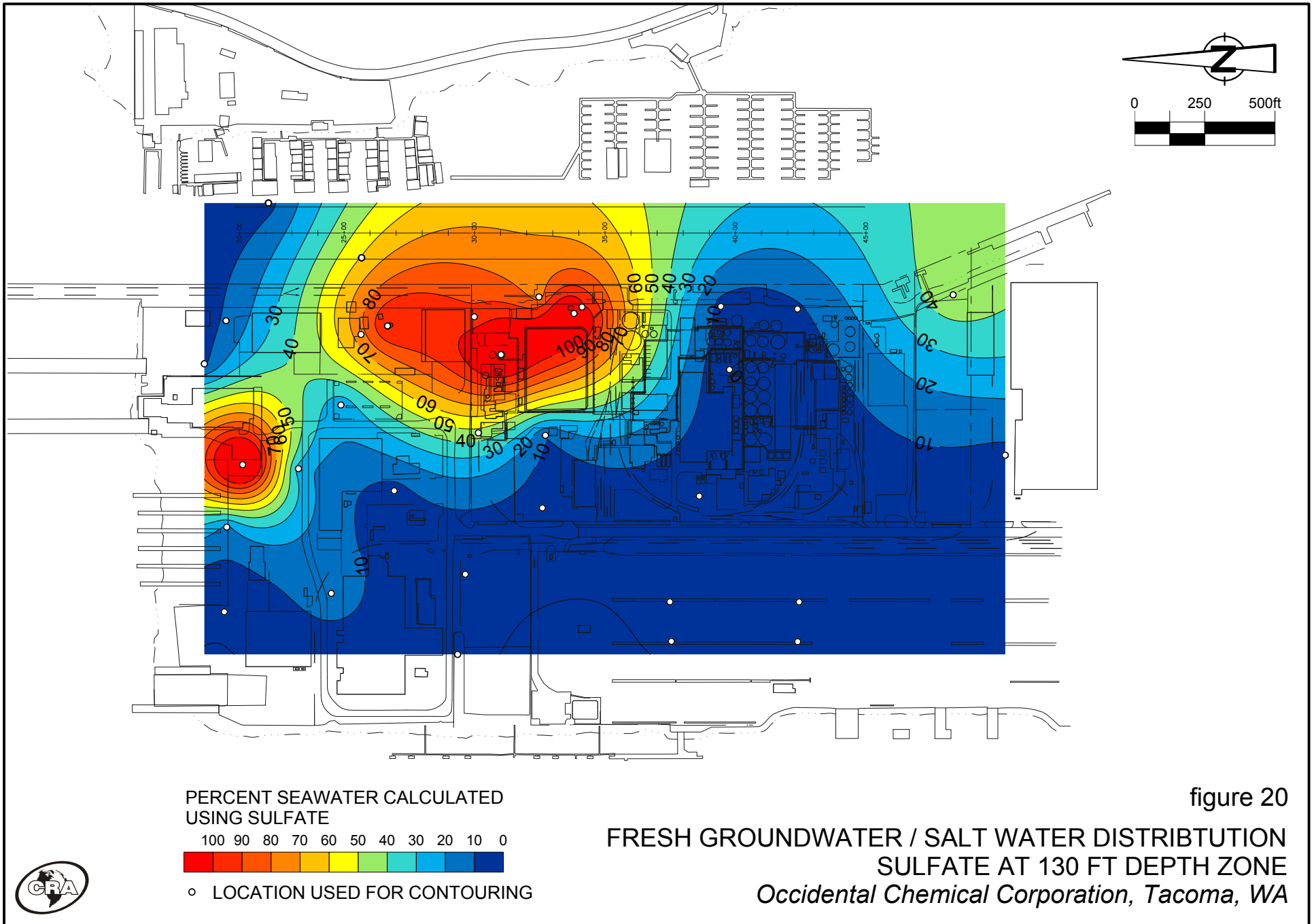


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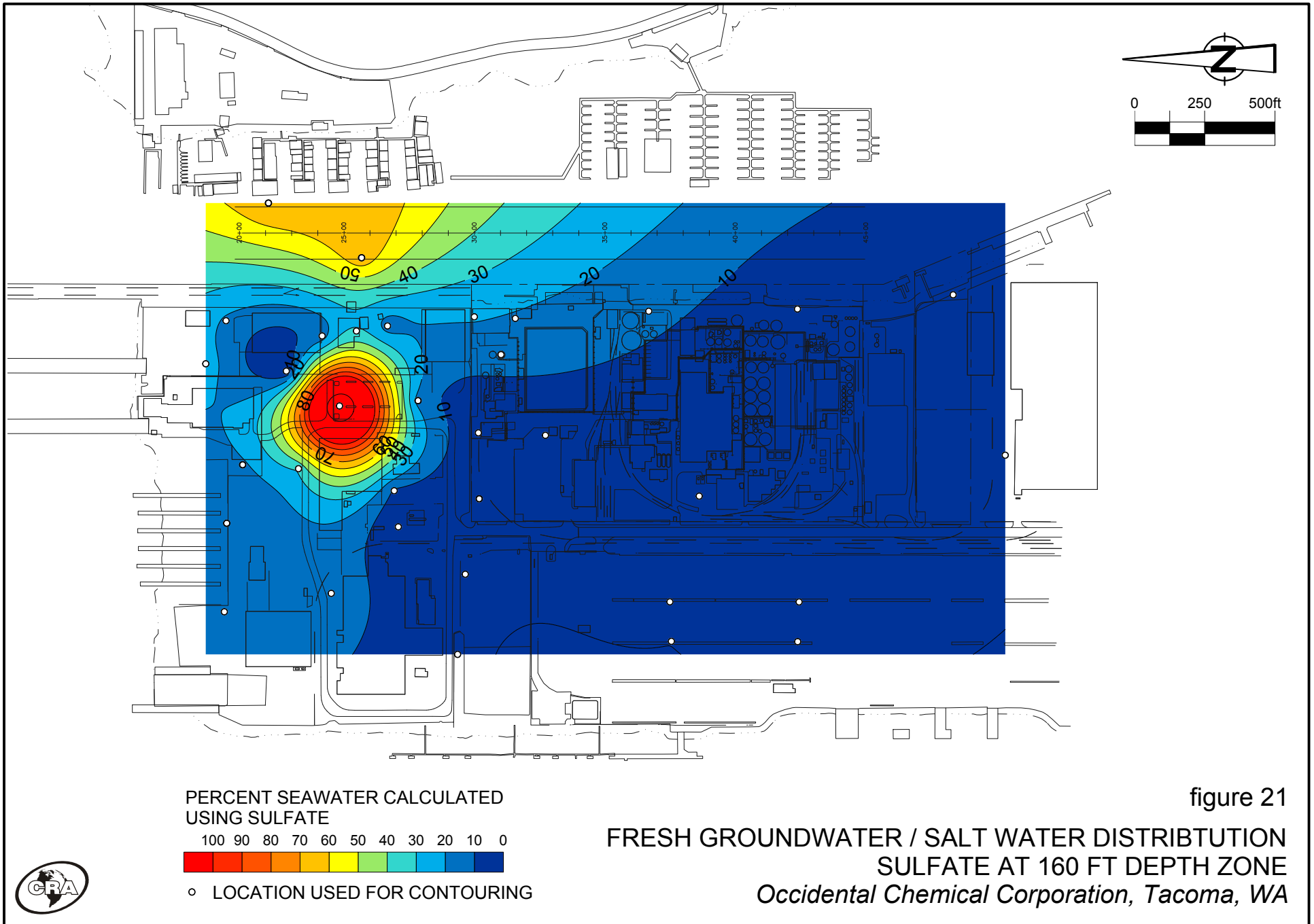


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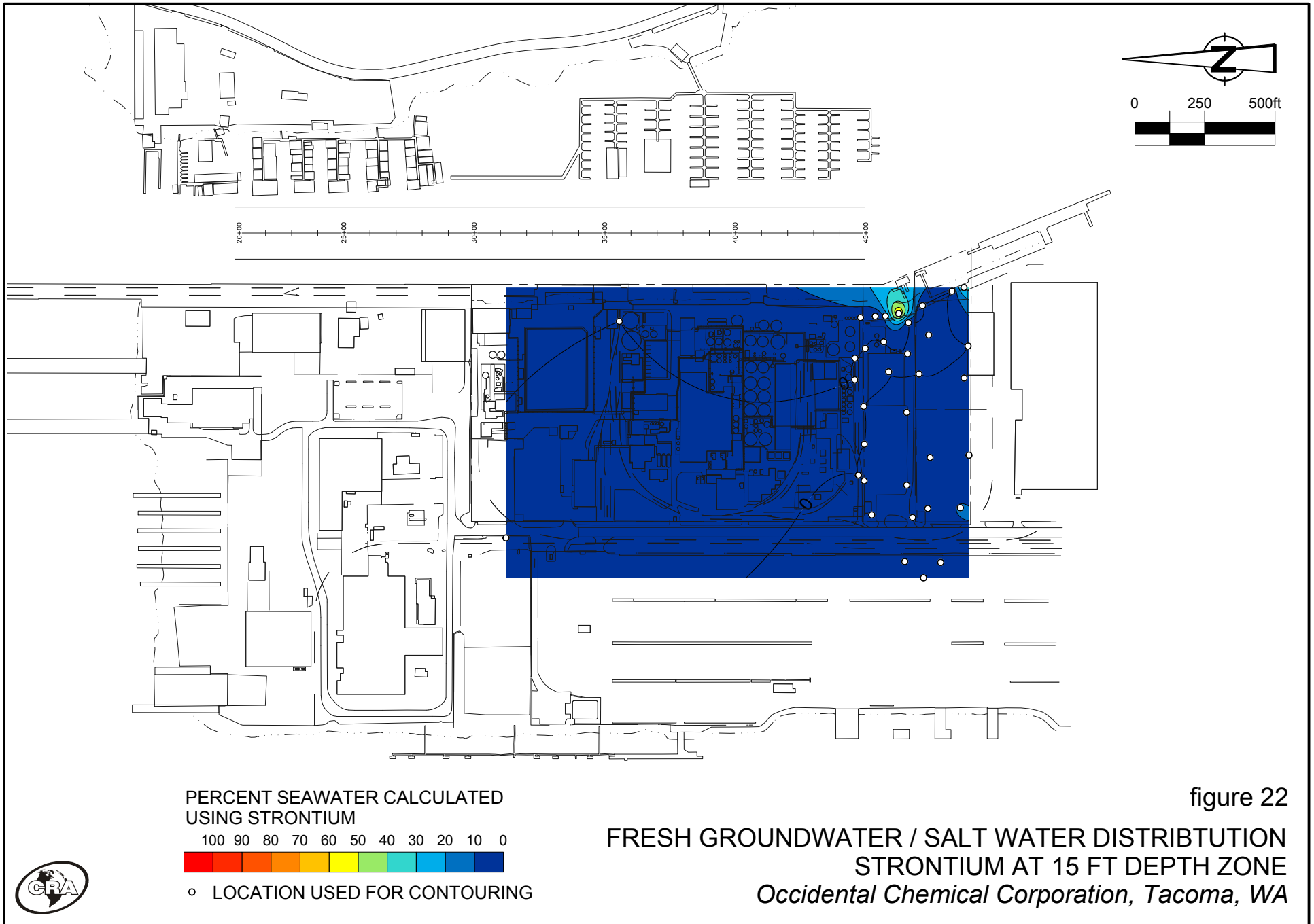


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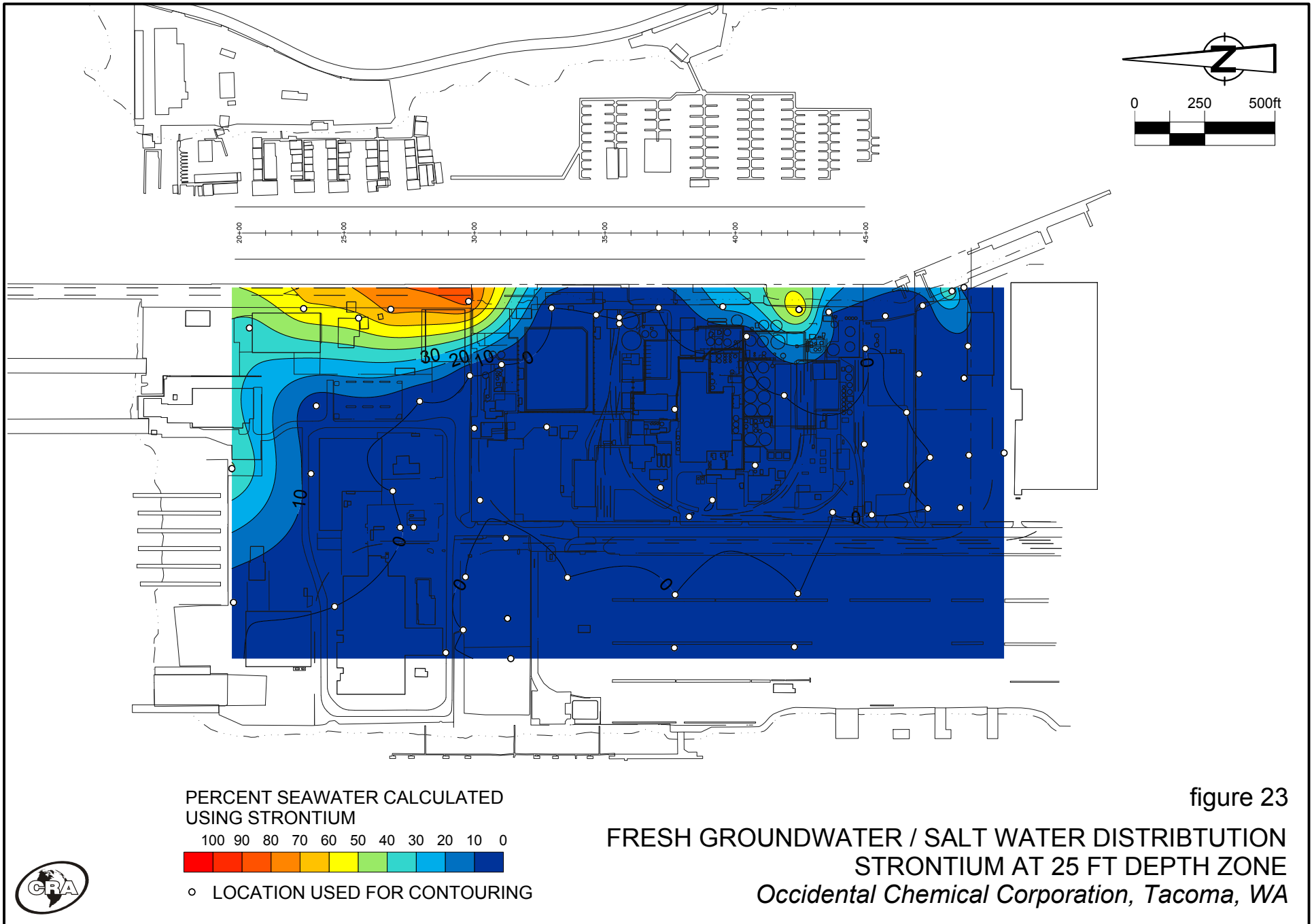


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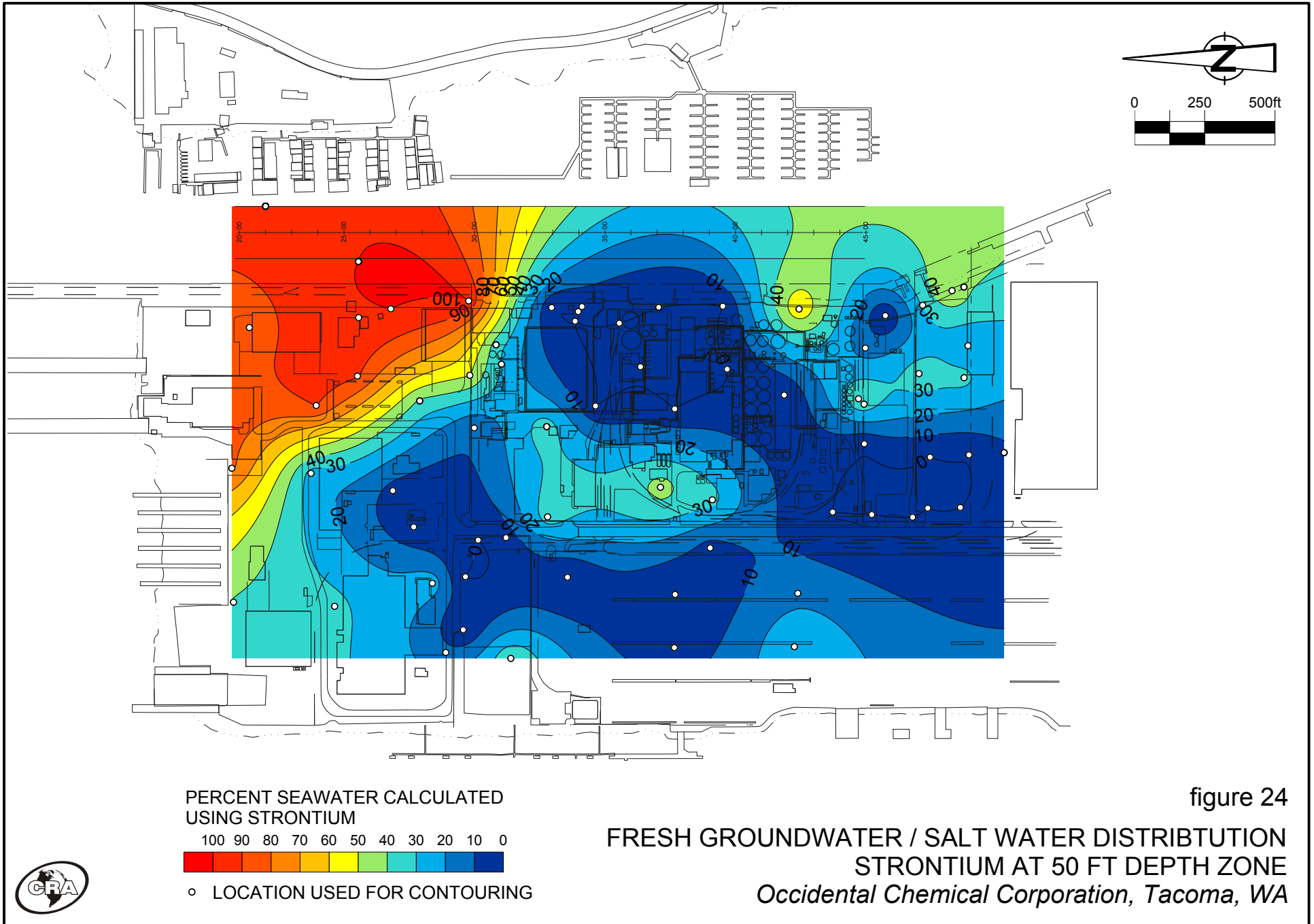


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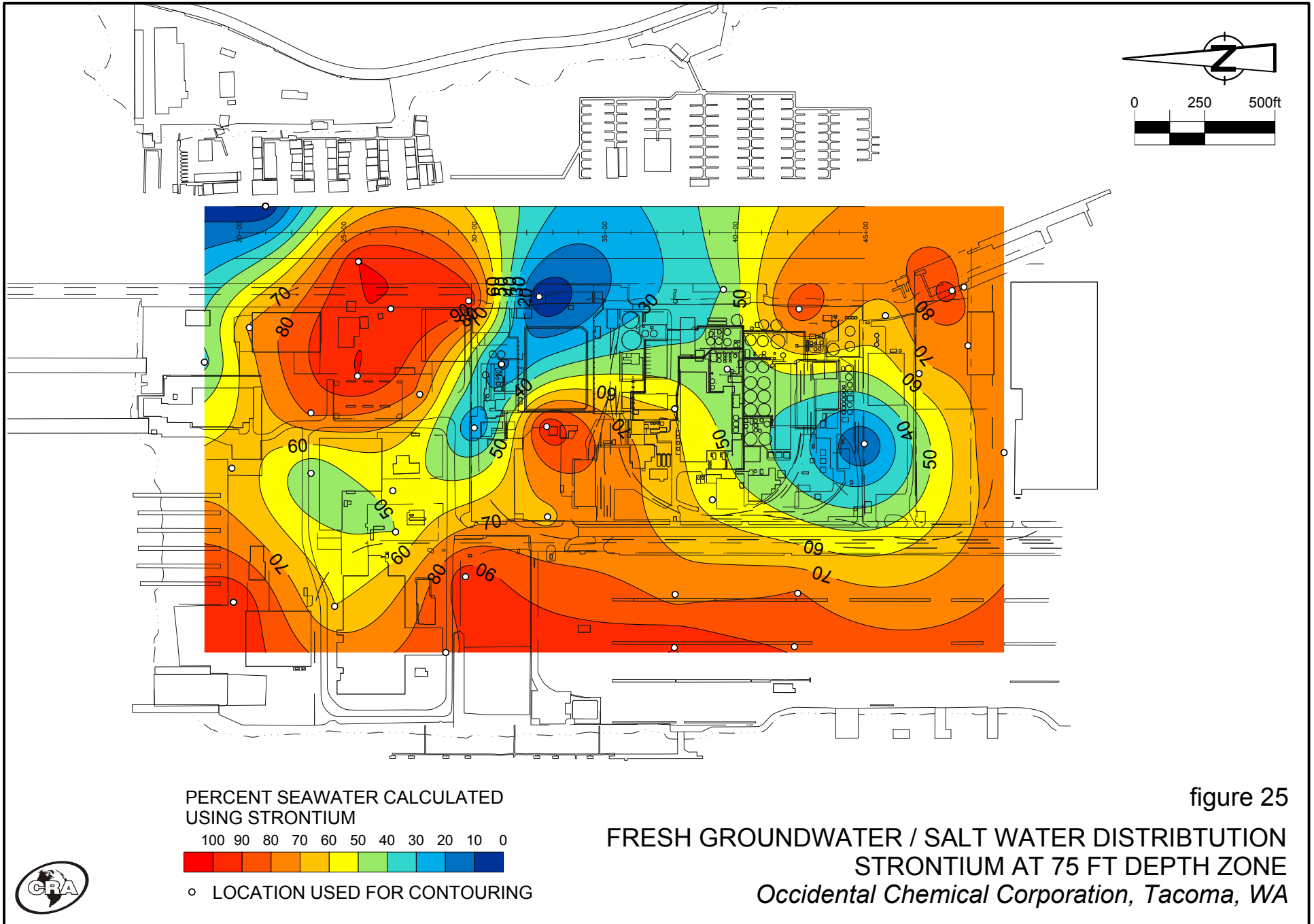


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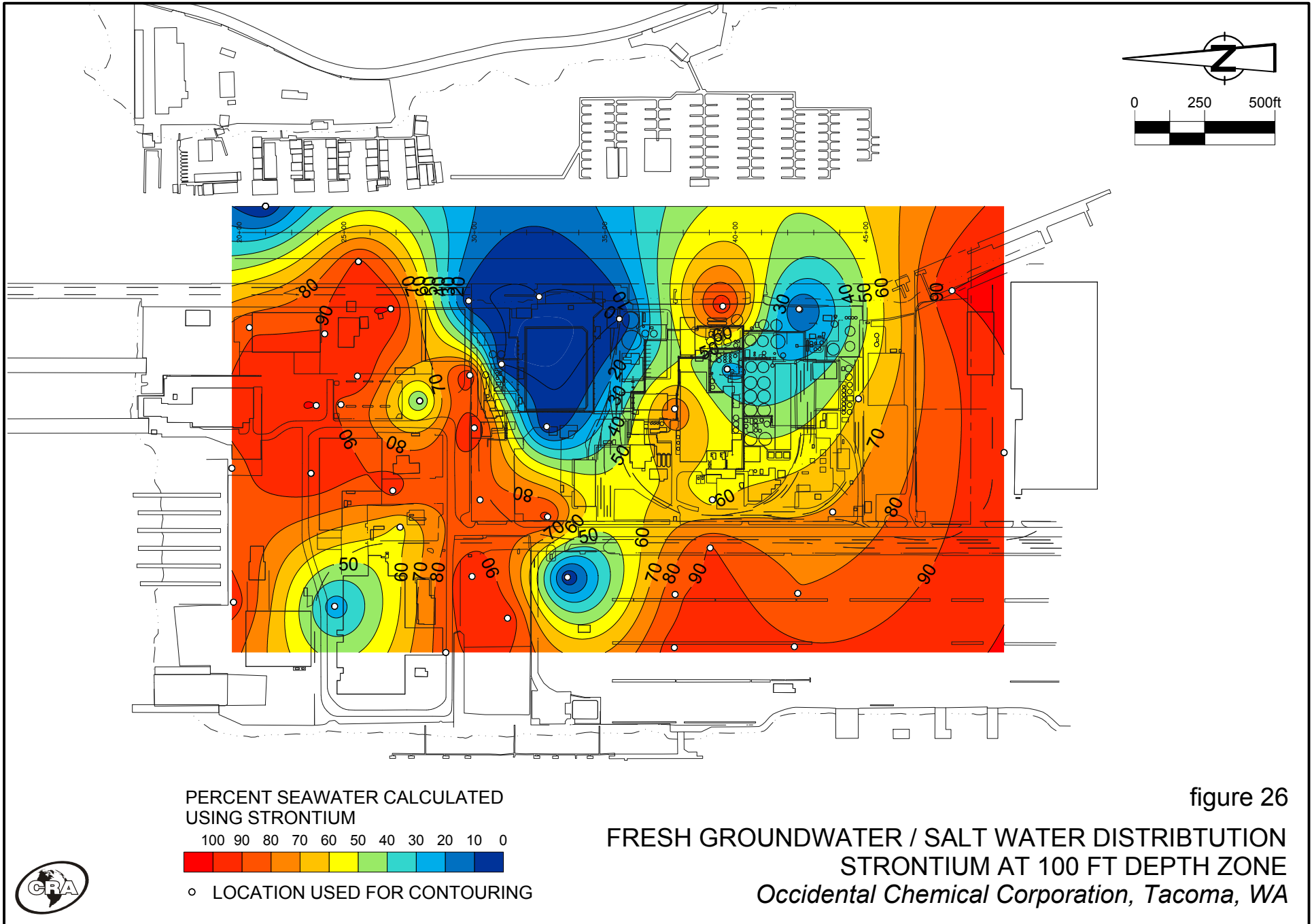


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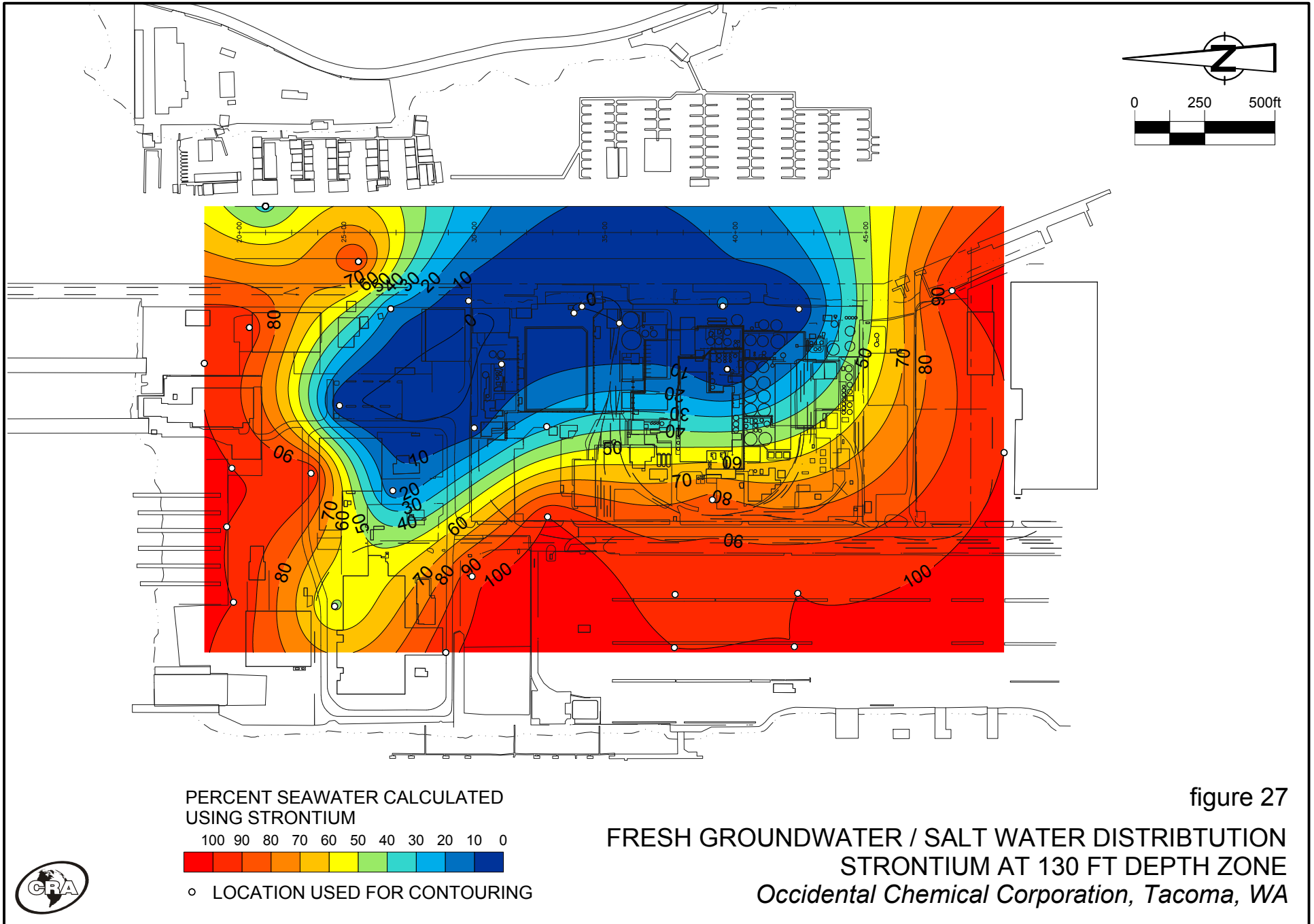


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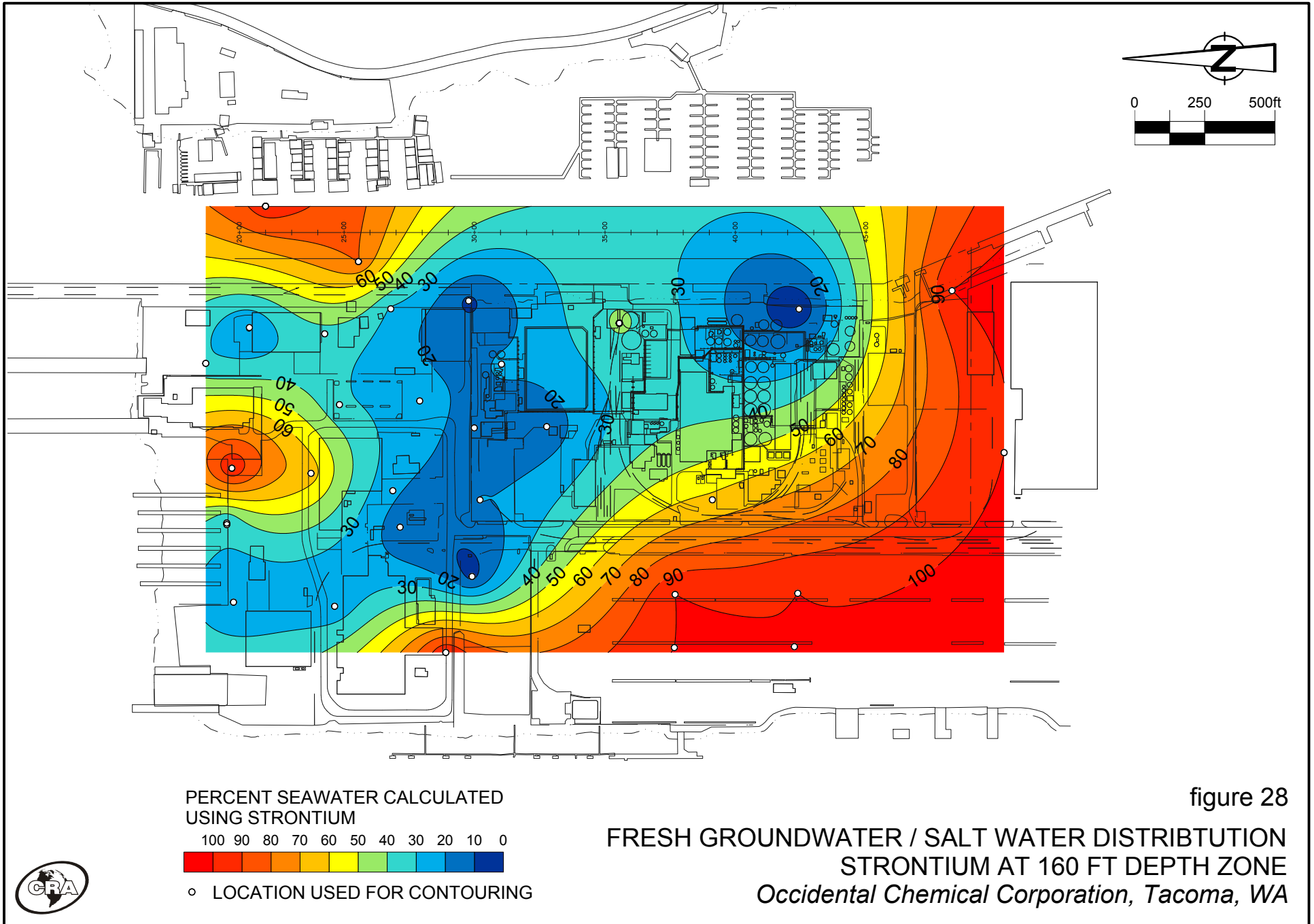


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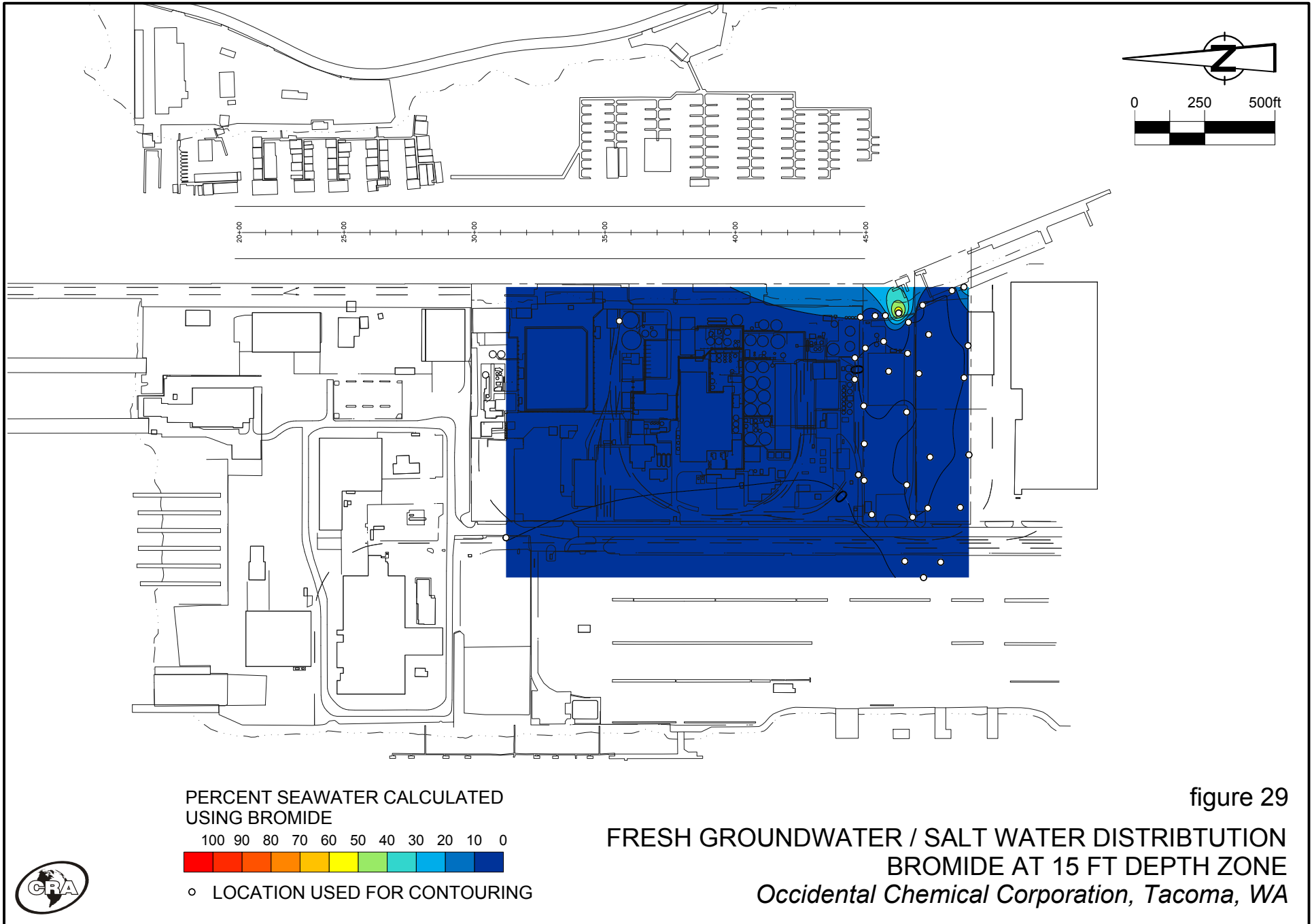


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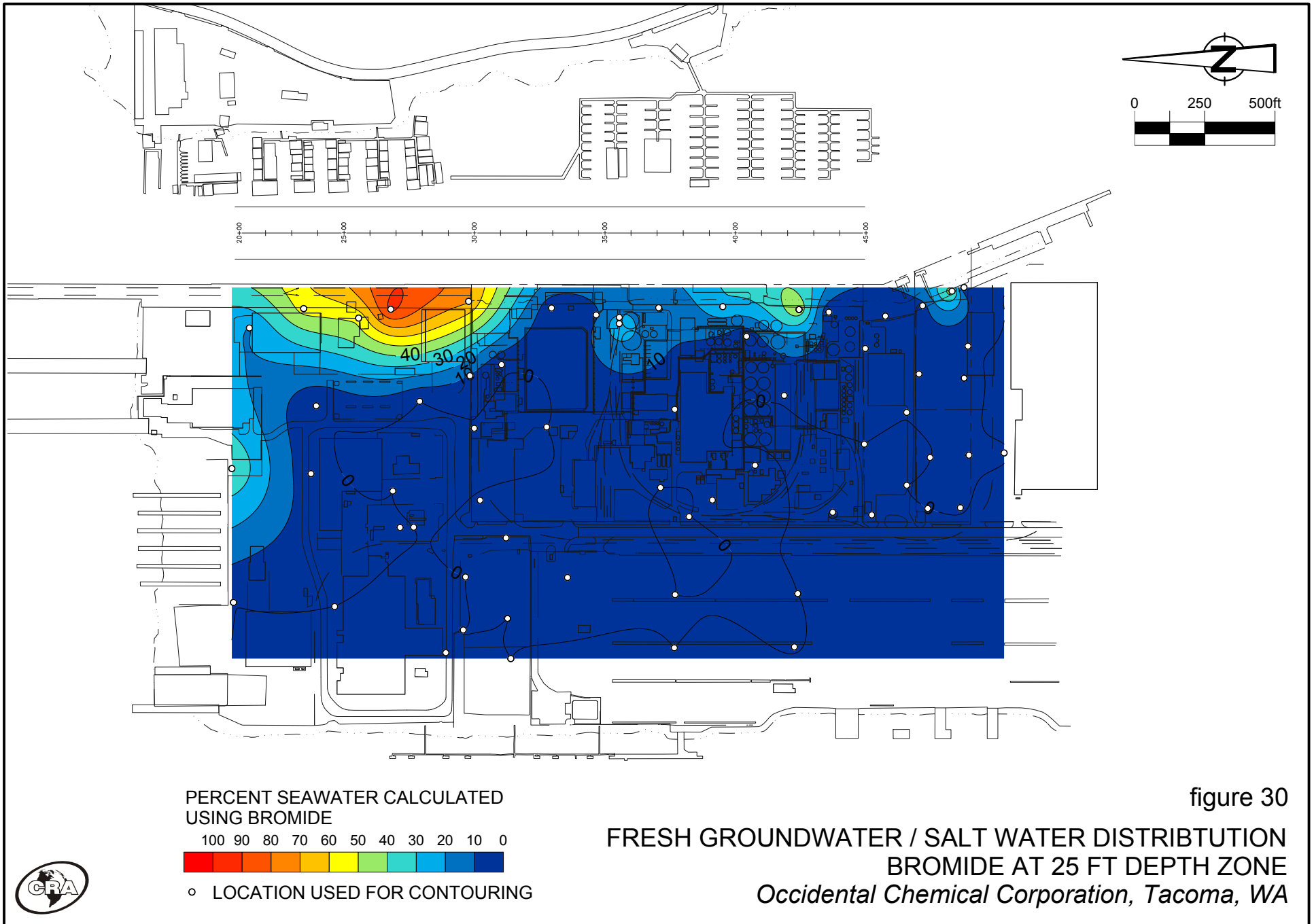
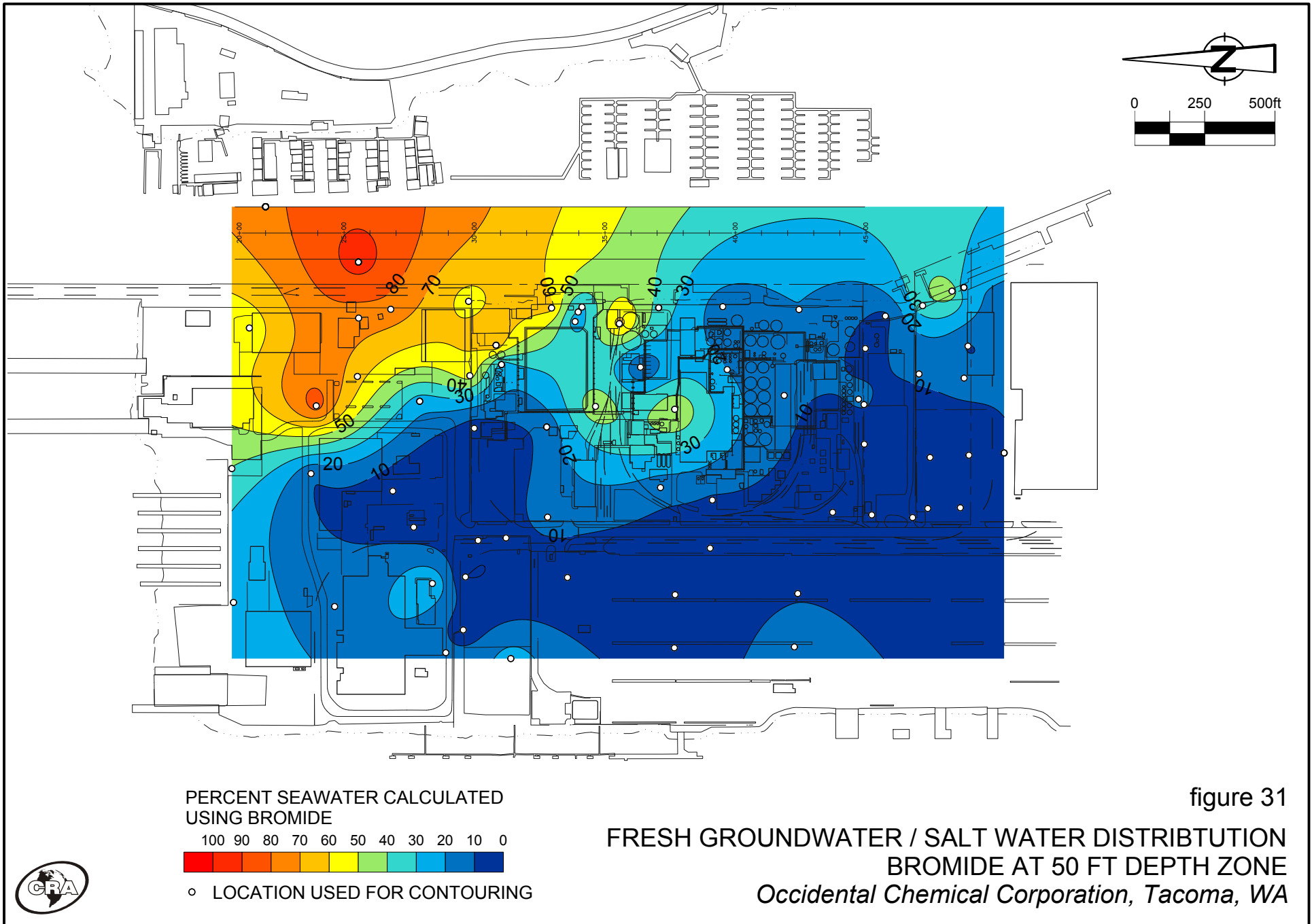
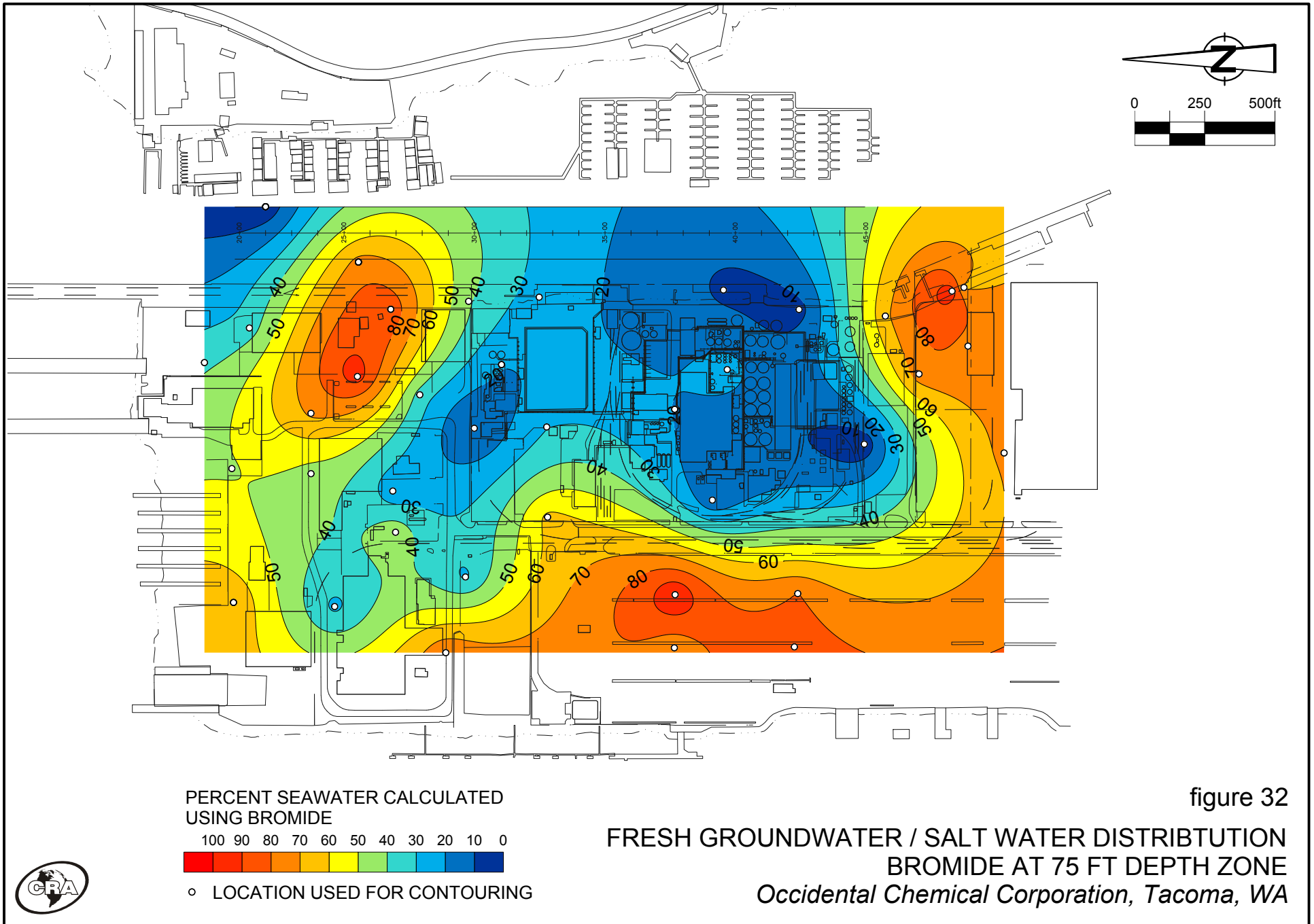


figure 30





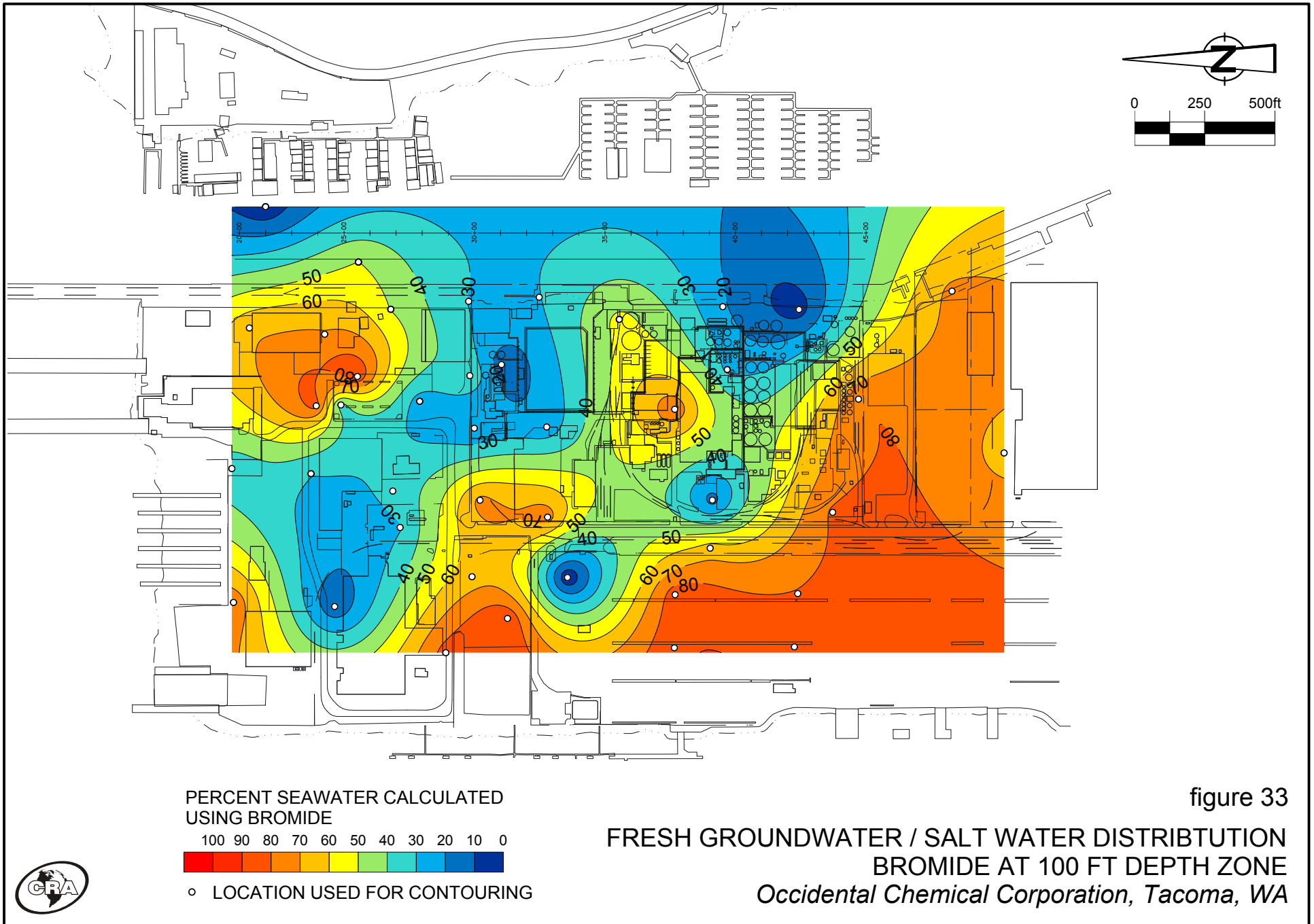


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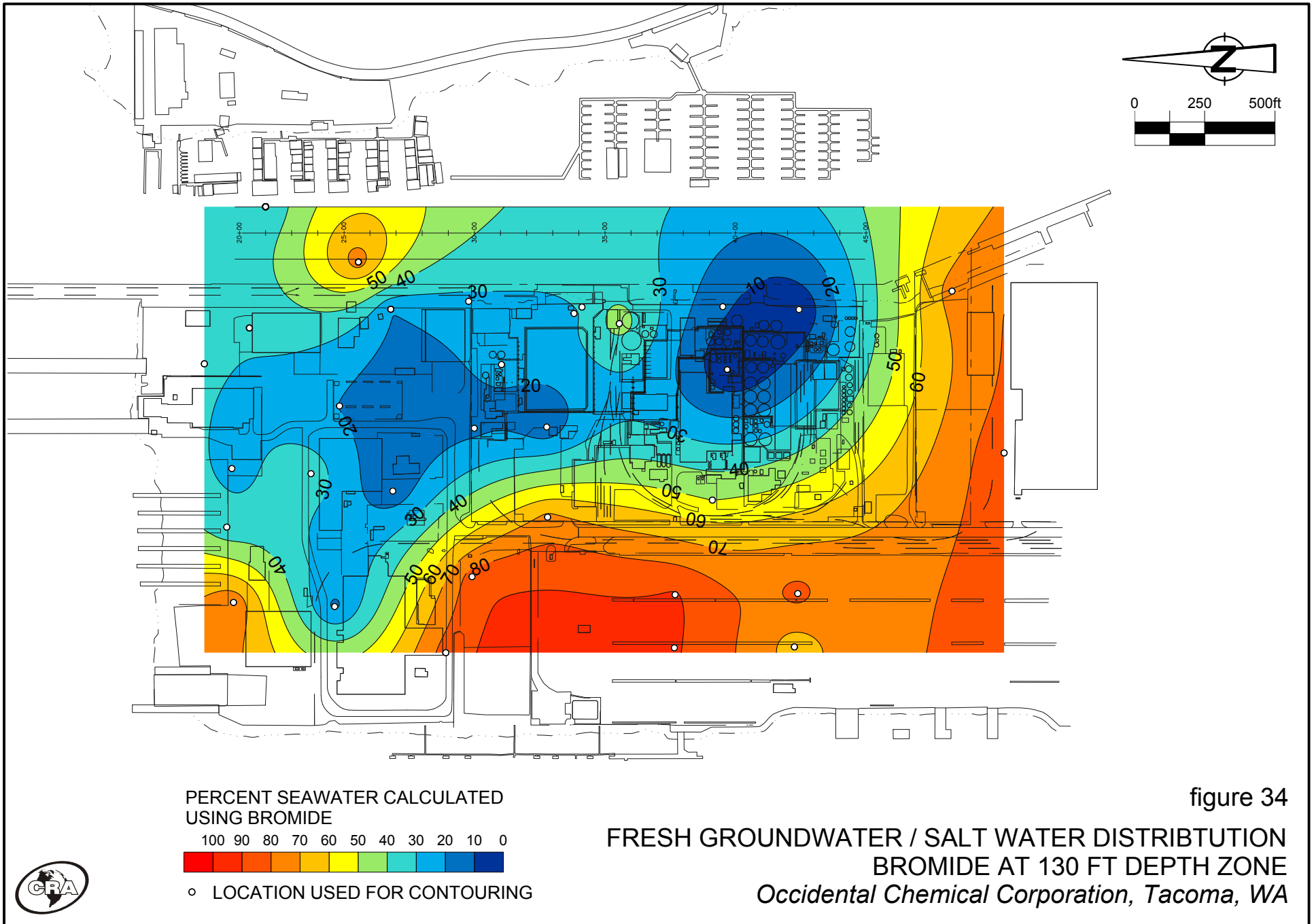


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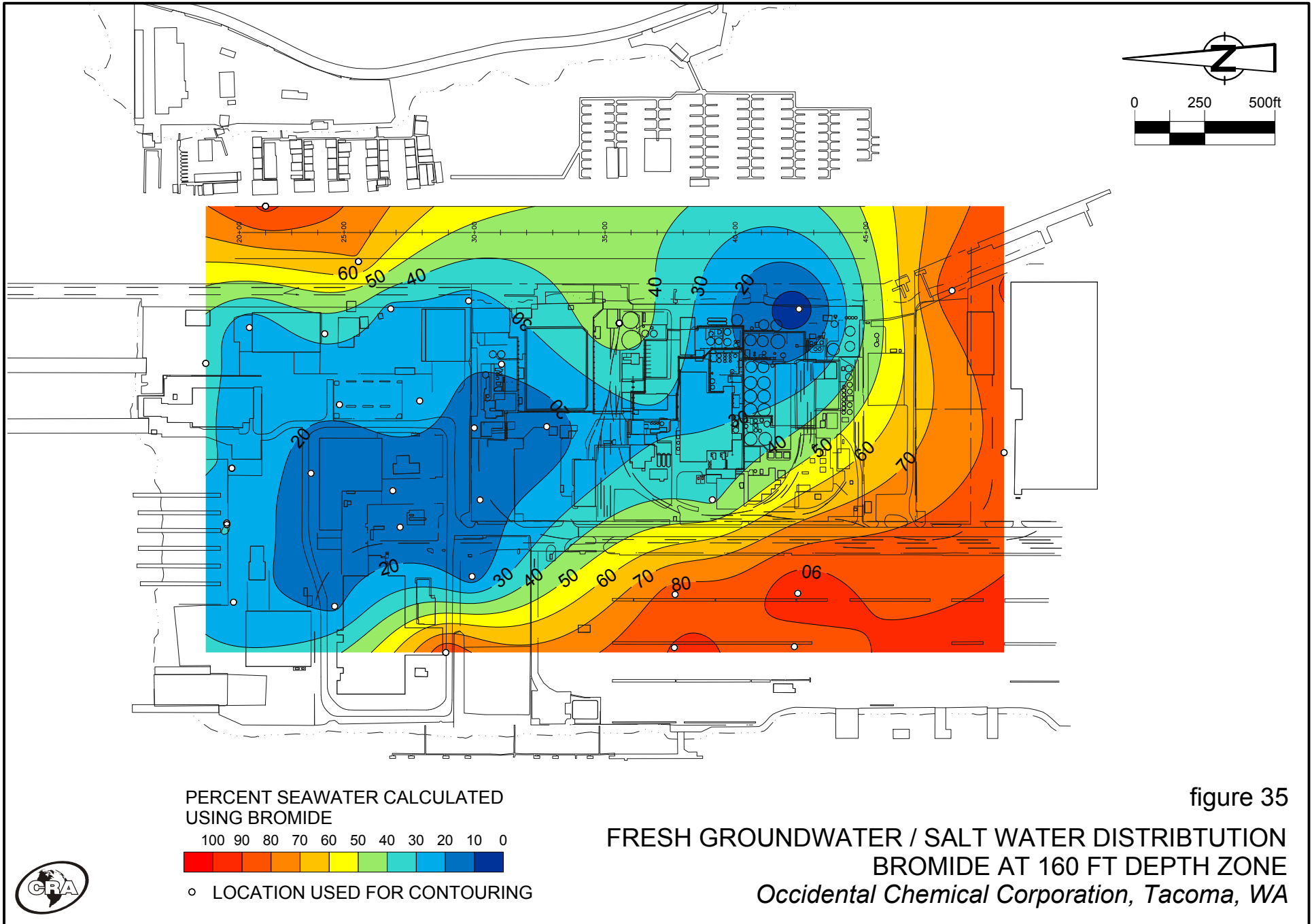


figure 35

TABLE 1
 BACKGROUND (FRESHWATER) WELLS AND VALUES
 SALT WATER EQUILIBRIUM EVALUATION

Occidental Chemical Corporation
 Tacoma, Washington

Sample Location	Boron (mg/L)	Bromide (mg/L)	Calcium (mg/L)	Chloride (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Strontium (mg/L)	Sulfate (mg/L)
52-15	0.02	0.20	62.3	1.69	1.8	1.53	6.18	0.334	10.6
52-15	0.03	0.20	63.3	1.52	1.83	1.58	6.37	0.341	10.5
709-MW11-15	0.06	0.02	42.4	1.7	10.1	2.19	10.3	0.201	1.88
709-MW11-25	0.21	0.03	33.8	3.8	8.88	13.8	170	0.256	4.64
709-MW17-15	0.06	0.01	111	1.6	6.05	4.01	11.2	0.666	1.28
709-MW18-15	0.04	0.20	80.2	2.12	2.11	2.66	7.63	0.468	19.6
709-MW18-25	0.29	0.04	37.5	13.7	10.8	16	96.9	0.241	1.11
709-MW21-15	0.06	0.02	78.9	1.6	7.65	5.17	14.6	0.43	0.54
709-MW21-25	0.13	1.00	17.3	1.42	1.36	7.24	161	0.129	8.41
721-MW12-15	0.08	0.03	90.9	4.41	8.38	5.73	21.9	0.582	0.59
721-MW12-25	0.51	0.03	39.4	2.41	2.72	11.3	182	0.224	1.11
721-MW13-15	0.06	0.20	39.7	5.39	6.37	4.4	11.6	0.073	18.3
721-MW13-25	0.07	0.02	73.7	26.7	7.23	6.52	11.6	0.344	4.09
721-MW14-15	0.03	0.01	110	5.12	5.55	5.39	6.84	0.681	0.76
721-MW14-25	0.16	0.04	35.5	2.07	2.93	11.9	179	0.285	0.72
93C-25	0.15	0.20	34.2	19.4	9.46	5.85	14.4	0.198	6.64
HC-NC11-5	0.04	0.20	121	2.65	4.01	5.41	7.77	0.735	0.79
HC-NC11-6	0.03	0.20	124	2.41	3.77	5.09	5.78	0.725	0.9
HC-NC11-8	0.03	0.20	98.2	4.42	3.03	2.46	5.67	0.57	1.55
Average	0.109 Not used	0.103	68.07 Not used	5.48 Not used	5.48 Not used	6.22 Not used	48.99 Not used	0.39	4.95 Not used

Statistical outlier - not used in end-member average

TABLE 2
SALT WATER LOCATIONS AND VALUES
FRESH GROUNDWATER / SALT WATER DISTRIBUTION

Occidental Chemical Corporation
Tacoma, Washington

Sample Location	Sample Depth (ft BWS)	Boron (mg/L)	Bromide (mg/L)	Calcium (mg/L)	Chloride (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Strontium (mg/L)	Sulfate (mg/L)
Hylebos 2010	unknown	3.38	91.6	324	16000	1040	350	8720.00	6.28	2160
TG-001	25	2.69	61.0	310	17200	1010	307	8420.00	5.98	3210
Blair Waterway Middle	25	2.80	60.0	317	17100	1030	317	8580.00	6.21	3120
Blair Waterway Bottom	50	2.79	61.0	317	17600	1030	321	8620.00	6.09	3040
Commencement Bay Middle	25	2.69	60.0	307	17200	1030	304	8540.00	5.98	3180
Commencement Bay Bottom	49	2.79	61.0	325	17300	1060	321	8860.00	6.41	3250
Hylebos Waterway Middle	22	2.79	61.0	320	17200	1050	312	8700.00	6.23	3340
Hylebos Waterway Bottom	41	2.48	59.0	286	17400	939	276	7800.00	5.60	3640
WW SAMPLES AVERAGE	--	2.80	60.4	313	17125	1024	314	8530.00	6.10	3118
		Not used		Not used	Not used	Not used	Not used	Not used		Not used

Notes:

91.6

Statistical outlier - not used in end-member average

TABLE 3
 EXCLUDED GROUNDWATER SAMPLES
 FRESH GROUNDWATER / SALT WATER DISTRIBUTION

Occidental Chemical Corporation
 Tacoma, Washington

Sample Location	Sample Elevation (ft NGVD)	Chemical Parameter	Result	Reporting Limit (mg/L)	RL Description (RL, QL)	Sample Collection Date
709-MW21-25	-13.32	Bromide	U	1.00	RL	7/27/2012
82-230	-97.21	Bromide	U	2.50	QL	6/11/2010
82-230	-62.21	Bromide	U	5.00	QL	6/10/2010
82-230	-77.21	Bromide	U	5.00	QL	6/10/2010
82-230	-62.21	Bromide	U	5.00	QL	6/10/2010
75-75	-62.77	Bromide	U	10.00	QL	7/27/2010
82-150	-117.57	Bromide	U	12.50	QL	7/7/2010

Notes:

RL: Reporting Limit

QL: Quantitation Limit

U: Analyte was not detected