Testing Florida Surface Waters for Pesticides

Calendar Year 2015

Prepared by the Florida Department of Environmental Protection Water Quality Evaluation and TMDL Program and the Florida Department of Agriculture and Consumer Services Bureau of Scientific Evaluation and Technical Assistance

Acknowledgments: *This project has been conducted through a team effort of staff within two agencies. Specialists with FDACS and FDEP developed the plan. FDEP samplers in the Division of Environmental Assessment's Regional Operating Centers collected the samples. The FDEP Laboratory Support Section and Chemistry Section provided laboratory services. The FDEP Office of Watershed Services provided Geographic Information System mapping. Their willingness to add this task to their existing efforts allowed this valuable information to be gathered.*

INTRODUCTION

This report summarizes the results from second year of surface water monitoring for pesticides under a project jointly implemented by the Florida Department of Environmental Protection (FDEP) and the Florida Department of Agriculture and Consumer Services (FDACS). The U.S. Environmental Protection Agency (EPA) defines pesticide as any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. Pests can be insects and insect-like organisms, mice and other vertebrate animals, unwanted plants (weeds), or fungi, bacteria and viruses that cause plant diseases. Though often misunderstood to refer only to insecticides, the term pesticide encompasses herbicides, fungicides, and various other substances used to control pests. Pesticides applied in the environment can be transported to surface water and ground water where the pesticide can degrade water quality. The EPA and FDACS evaluate and mitigate the chances of these chemicals impacting water resources. Nevertheless, pesticides can reach water resources as a result of misapplication, spills, improper disposal, or unique environmental conditions. Pesticide concentrations in surface water and ground water can vary widely and are influenced by many factors, such as the amount and timing of the pesticide applications and the soils, climate, and hydrology where they are applied.

Florida's Department of Environmental Protection is statutorily responsible for protecting and restoring Florida's water quality, while FDACS is statutorily responsible for ensuring that pesticides are properly registered and used in accordance with federal (Federal Insecticide, Fungicide, and Rodenticide Act) and state laws (Chapter 487, Florida Statutes). As part of its pesticide registration review process, FDACS conducts computer simulations using environmental fate models to estimate whether environmental concentrations of pesticide active ingredients are likely to pose unreasonable risk to human health and the environment. This includes both an assessment of risk to surface and ground water, and if unreasonable risks are identified, including risk to human health, wildlife, plants, fish and aquatic

invertebrates, FDACS can impose mitigation measures through more stringent use instructions on the pesticide product label, or potentially through rulemaking and voluntary stewardship programs between the registrant and farmer.

Although FDACS relies primarily on environmental modeling in their registration process to predict levels of pesticides in surface water, FDACS does have access to a relatively small amount of in-state surface water quality monitoring data to support its role in pesticide regulation. Most of this data had been collected by Florida's water management districts, primarily the South Florida Water Management District. Additionally, some data has also been provided by the USGS National Water Quality Assessment program (http://water.usgs.gov/nawqa/). The limited amount of relevant surface water monitoring data for pesticides restricts the ability of both FDEP and FDACS to more accurately determine whether current mitigation measures are adequate to protect Florida surface waters. Both FDEP and FDACS laboratories have been active in testing ground water for pesticide residues, but resource constraints limited FDACS's ability to actively collect and analyze surface water samples for pesticides. The need to evaluate Florida surface water quality with respect to pesticides has grown in importance, since many of the newer pesticides have chemical properties and toxicity profiles that render them more apt to move to surface waters and potentially affect aquatic organisms, despite their lower risks to humans. Moreover, these newer chemistries generally have relatively low mammalian toxicity, but can be highly toxic to certain aquatic taxa at low concentrations. Also the rise in use in suburban areas of pesticides with lawn and garden products provides the opportunity for pesticides to reach surface waters.

In 2012, FDACS and FDEP agreed to cooperatively implement a project to monitor and evaluate a representative subset of Florida's surface waters for the presence of pesticides. FDEP maintains a program to monitor and assess the quality of surface water bodies throughout the state. As part of its mission to assess the water quality of all of Florida's surface waters as required by the Federal Clean Water Act and the Florida Watershed Restoration Act (per Section 403, F. S.), FDEP strategically monitors surface waters statewide on a rotating schedule. This work is being carried out by the department's Watershed Assessment Program, which includes regionally based monitoring staff in district offices. In this program, water bodies are assessed in terms of their general health, nutrient load, inorganic constituent, and overall water quality. Taking advantage of this existing sampling program and adding pesticide sampling and analysis added minimal work burden –and sampling cost.

WATER BODY IDENTIFICATION, SAMPLNG, ANALYTICAL METHODS

FDEP assigns surface water body segments numeric codes called Water Body ID's (WBIDs). FDEP's Watershed Assessment Program maintains a schedule for all WBIDs to be sampled in a given year under their Strategic Monitoring Plan. For the list of WBIDs to be sampled during calendar year 2015, the Watershed Assessment Program then identified those waterbodies that exceed nutrient and/or copper water quality criteria. Nutrients are often associated with the use of fertilizer, and where there is fertilizer use there is often pesticide use in both suburban and agricultural settings. Elevated levels of

copper could be associated with copper-containing algaecides or fungicides. Copper is also used as a micronutrient in fertilizer, or its presence could be related to non-agronomic sources. Staff from FDACS and FDEP met and reviewed maps and aerial photos of each of the WBIDs identified as impaired for either nutrients or copper. From that smaller set, those WBIDs that were surrounded by native vegetation (forest and range land) were eliminated as candidates for pesticide sampling. WBIDs that were in proximity to land uses that potentially applied pesticides (suburban and agriculture) were included as candidates to be tested for pesticides by the FDEP laboratory. The 2015 candidate list of WBIDs for pesticide monitoring contained a balance of WBIDs in urban and agricultural land uses, although such a balance was not intentional but a result of how integrally mixed agriculture and suburban areas have become throughout the state. Fifteen surface water bodies across the state were identified for pesticide analysis in 2015 (Table 1.0). Maps of these surface water bodies and the distribution of land use within 1,000 feet of their shores are listed in the Appendix. The location of each surface water body is also shown in Figure 1.

Choosing specific analytes to test presented a challenge since there are over 400 active ingredients registered for agricultural, and urban use in Florida. Not all registered pesticides are candidates for analysis since many are disinfectants, or are associated with use patterns unlikely to impact surface water. In developing the analytical approach, staff from FDACS and FDEP considered existing analytical capabilities of the FDEP laboratory, detections of pesticides in other States, commonly used pesticides, and considered the likelihood of these pesticides exceeding U.S. EPA Office of Pesticide Program aquatic life benchmarks (http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm). The final list of pesticides reported in the analytical results includes both the identified pesticides of interest and ancillary pesticides that are automatically reported as part of the same analytical method.

Table 1.0 Surface water bodies sampled for pesticides during Calendar Year 2015.

WBID#	WBID Name	County
697	Bayou Marcus Creek	Escambia
624	Eight Mile Creek	Escambia
135	Boggy Creek	Escambia
176	Pond Creek	Santa Rosa
3322A	Cherry Lake	Madison
2161	Thomas Creek	Duval
2666	Unnamed Ditch	Volusia
2666A	Sweetwater Creek	Volusia
2674	Spruce Creek	Volusia
3098B	Holly Hill	Volusia
1508A	Kosterman Bayou Run	Pinellas
1633A	Taylor Lake	Pinellas
3254	Hillsboro Canal	Palm Beach
3238	West Palm Beach Canal	Palm Beach
S3251	S-3	Palm Beach

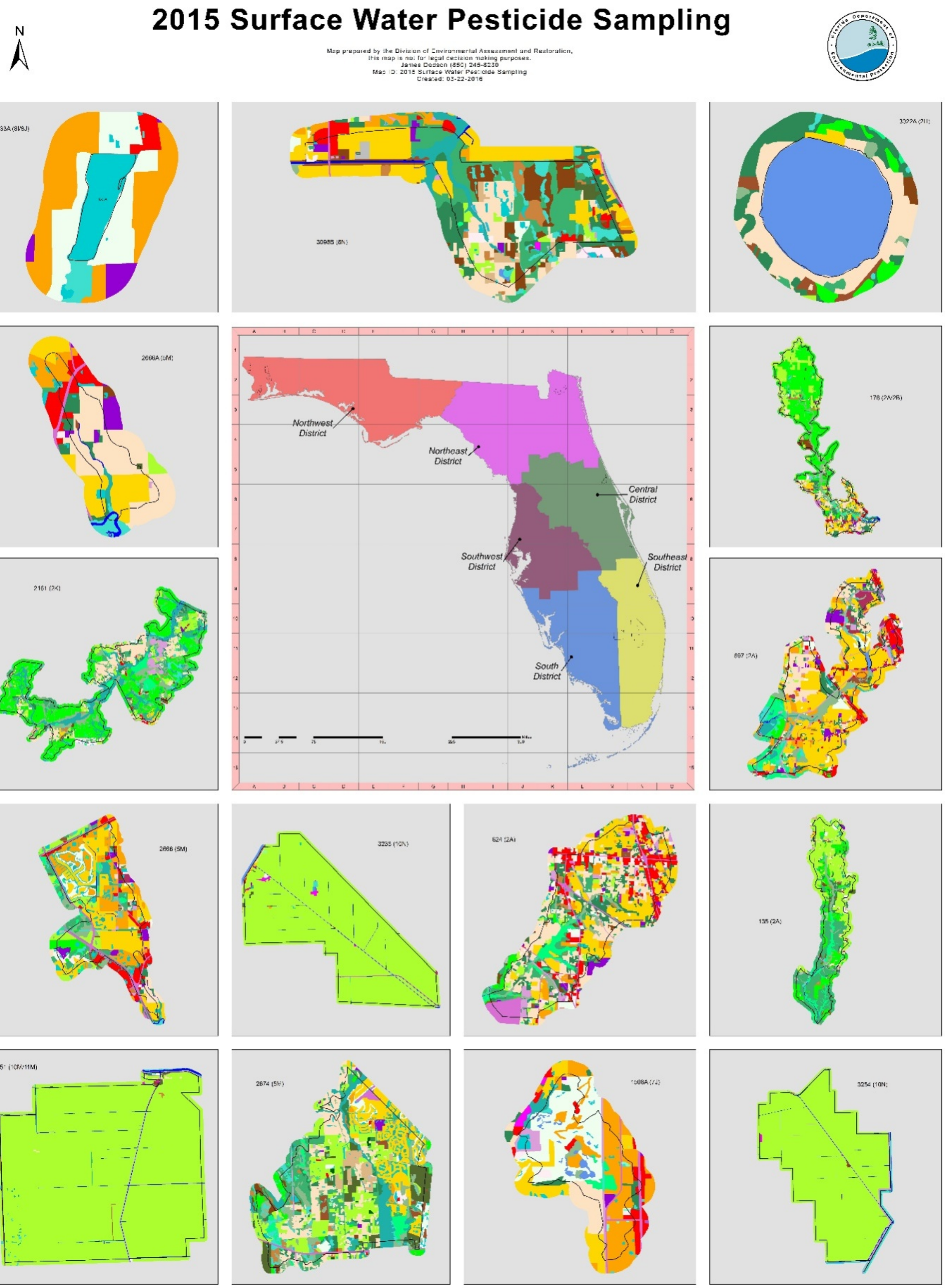


Figure 1. Locations of water bodies selected for pesticide analysis. Landuse Maps of individual water bodies are in the Appendix.

RESULTS

Samples were collected between March and December 2015. As mentioned earlier, bottles for pesticide samples accompanied the sampling crews that were scheduled to visit water bodies according to the 2015 monitoring schedule for individual WBIDs. As a result, water bodies tested for pesticides were visited at different frequencies. The typical reason for fewer samples collected from a particular water body was lack of access on the scheduled sampling date, often due to low water levels at the time of the visit. In effect, this created a random distribution of samples for the entire effort.

Laboratory analysis was completed by FDEP's Bureau of Laboratories Chemistry Section located in Tallahassee. The pesticide analytical methods were highly sensitive, making the detection limits very low. The result was Minimum Detection Limits often less than 0.5 part per trillion (nanogram per liter [ng/L]). For a little perspective, 1 part per trillion is roughly equal to a single drop of water, equally distributed, in an Olympic sized swimming pool.

For example, with a detection limit of 0.00024 micrograms per liter, 98 percent of the samples collected contained detectable concentrations of the herbicide atrazine. This indicates that atrazine is a widely used herbicide and residues from its use can often be found in the environment, albeit at low levels.

Table 2 summarizes the detections observed. **No detections exceeded an EPA aquatic benchmark**. (http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm)

Other observances of note from the data set include:

1. Thirteen herbicides, 3 insecticides, 2 insecticide degradates, and 1 herbicide degradate were detected in this program.
2. The herbicides atrazine, 2,4-D, desethyl atrazine, ametryn, bromacil, norflorazon, and simazine were detected in more than 70% of the samples taken, but at levels far below benchmark levels of concern for fish, aquatic invertebrates, alga and plants. The high percentage of herbicide detections is due the widespread use of herbicides in the targeted residential and agricultural watersheds and due to the very low minimum level of detection (LOD) of the method.
3. Insecticides detected include fipronil (in 12% of the samples), imidacloprid (in 70% of the samples), malathion (in 49% of the samples) and chlorpyrifos (in 56% of the samples). Despite their frequent occurrence, detected concentrations were all below published ecological levels of concern.
4. This second year of sampling included the addition of glyphosate due to the popularity of its use. Of the 44 samples tested for glyphosate there was only one detection.
5. Fifty-three of the 80 analytes included in the lab testing methods were not detected in the surface waters samples.

Summary and Follow-up

Overall, these results showed that several analytes were present in a high percentage of analyses but at concentrations lower than published ecological or human health risk thresholds.

Implementation of the 2015 sampling program was successful and the results have been useful in terms of developing a better understanding of the variety and distribution of residual pesticides in surface waters. As a result, the project is being continued for 2016 following the same process and including new WBIDs. In January 2016, staff from both departments met to review where the Strategic Monitoring Program would be sampling and identified 27 WBIDs for pesticide analysis during calendar year 2016. It is expected that approximately six of these WBIDs will be unavailable for sampling due to the same accessibility problems encountered in previous years. Taking this into allowance it is anticipated that pesticide data will be collected from 21 WBIDs. Year 2016 monitoring is currently underway.

Table 2 Analytical Results (µg/L)

Pesticide Name	Pesticide Class	Number Detects	Number Samples	MDL (µg/L)	Range (µg/L)	Fish Acute (µg/L)	Fish Chronic (µg/L)	Invert Acute (µg/L)	Invert Chronic (µg/L)	Algae Acute (µg/L)	Plants Acute (µg/L)
2,4,5-T	Herbicide	0	54	0.002	--	--	--	--	--	--	--
2,4-D	Herbicide	42	59	0.002	0.0024 - 0.4	12,075	14,200	12,500	16,050	3880	13.1
2,4-DB	Herbicide	0	12	0.002	--	--	--	--	--	--	--
Acetochlor	Herbicide	0	18	0.002	--	--	--	--	--	--	--
Acifluorfen	Herbicide	0	55	0.002	--	--	--	--	--	--	--
Alachlor	Herbicide	0	18	0.25	--	--	--	--	--	--	--
Aldrin	Insecticide	0	10	0.0019	--	--	--	--	--	--	--
Alpha BHC	Byproduct	0	10	0.0019	--	--	--	--	--	--	--
Ametryn	Herbicide	32	55	0.00019	0.00033 – 0.046	1,800	700	14,000	240	3.67	10
Atrazine	Herbicide	54	55	0.00024	0.00035 – 0.65	2,650[1]	65	360[1]	60	1[2]	37
Atrazine desethyl	Degradate	45	55	0.00024	0.0016 – 0.047	--	--	--	--	1,000	--
Azinphos methyl	Insecticide	0	18	0.0015	--	--	--	--	--	--	--
Bentazon	Herbicide	39	54	0.002	0.0024 – 0.7	>50,000	--	>50,000	--	4,500	5,350
Beta-BHC	Byproduct	0	10	0.0019	--	--	--	--	--	--	--
Bromacil	Herbicide	23	55	0.00048	0.0006 – 0.015	18,000	3,000	60,500	8,200	6.8	45
Butylate	Herbicide	0	10	0.0004	--	--	--	--	--	--	--
Carbophenothion	Insecticide	0	10	0.0057	--	--	--	--	--	--	--
Chlorothalonil	Fungicide	0	10	0.0076	--	5.25	3	1.8	0.6	6.8	630
Chlorpyrifos ethyl	Insecticide	12	55	0.0001	0.00015 – 0.00075	0.9[3] (n=1)	0.57[4] (n=1)	0.05[3] (n=1)	0.04[4] (n=1)	140	--
Chlorpyrifos methyl	Insecticide	0	55	0.00012	--	--	--	--	--	--	--
Cyanazine	Herbicide	0	18	0.0005	--	--	--	--	--	--	--
Cypermethrin	Insecticide	0	10	0.011	--	--	--	--	--	--	--
DDD	Herbicide	0	10	0.0038	--	--	--	--	--	--	--
DDE	Herbicide	0	10	0.0038	--	--	--	--	--	--	--

Table 2 Analytical Results (µg/L)

Pesticide Name	Pesticide Class	Number Detects	Number Samples	MDL (µg/L)	Range (µg/L)	Fish Acute (µg/L)	Fish Chronic (µg/L)	Invert Acute (µg/L)	Invert Chronic (µg/L)	Algae Acute (µg/L)	Plants Acute (µg/L)
DDT	Herbicide	0	10	0.0038	--	--	--	--	--	--	--
Delta-BHC	Byproduct	0	10	0.0019	--	--	--	--	--	--	--
Demeton	Insecticide	0	18	0.0001	--	--	--	--	--	--	--
Diazinon	Insecticide	0	18	0.00012	--	--	--	--	--	--	--
Dichlorprop	Herbicide	4	12	0.002	0.018 – 0.038	500	1700	--	--	7000	63
Dicofol	Insecticide	0	10	0.023	--	--	--	--	--	--	--
Dieldrin	Insecticide	0	18	0.0001	--	--	--	--	--	--	--
Dinoseb	Herbicide	0	12	0.02	--	--	--	--	--	--	--
Disulfoton	Insecticide	0	55	0.00047	--	--	--	--	--	--	
Diuron	Herbicide	21	61	0.002	0.0021 – 0.28	200	26	80	200	2.4	
Endosulfan I	Insecticide	0	10	0.0019	--	--	--	--	--	--	
Endosulfan II	Insecticide	0	10	0.0019	--	--	--	--	--	--	
Endosulfan sulfate	Degradate	0	10	0.0038	--	--	--	--	--	--	
Endrin	Insecticide	0	10	0.0038	--	--	--	--	--	--	
Endrin aldehyde	Degradate	0	10	0.0038	--	--	--	--	--	--	
EPTC	Herbicide	0	55	0.00028	--	--	--	--	--	--	
Ethion	Insecticide	0	55	0.000094	--	--	--	--	--	--	
Ethoprop	Insecticide	0	55	0.000094	--	--	--	--	--	--	
Fenamiphos	Insecticide	3	18	0.00025	0.00042 – 0.0017	4.75	3.8	0.95	0.12	--	
Fenuron	Herbicide	11	44	0.002	0.0086 – 0.059	200[6]	26[6]	80[6]	200[6]	2.4[6]	
Fipronil	Insecticide	22	55	0.0005	0.0003 - 0.00089	41.5	6.6	0.11	0.011	140	
Fipronil sulfide	Degradate	31	55	0.00019	0.00027 – 0.0029	41.4	6.6	1.07	0.11	140	
Fipronil sulfone	Degradate	39	55	0.00019	0.00025 – **0.012**	12.5	0.67	0.36	**0.037**	140	
Fluridone	Herbicide	22	40	0.0004	0.0014 – 0.17	2800	480	650	600	500	
Fonofos	Insecticide	0	18	0.0002	--	--	--	--	--	--	
Gamma-BHC	Byproduct	0	10	0.0019	--	--	--	--	--	--	
Glyphosate	Herbicide	1	44	5	12	21500	1800	26600	49900	12100	

Table 2 Analytical Results (μg/L)

Pesticide Name	Pesticide Class	Number Detects	Number Samples	MDL (μg/L)	Range (μg/L)	Fish Acute (μg/L)	Fish Chronic (μg/L)	Invert Acute (μg/L)	Invert Chronic (μg/L)	Algae Acute (μg/L)	Plants Acute (μg/L)
Heptachlor	Insecticide	0	10	0.0019	--	--	--	--	--	--	
Heptachlor epoxide	Degradate	0	10	0.0019	--	--	--	--	--	--	
Hexazinone	Herbicide	28	55	0.00095	0.0011 – 0.032	137,000	17,000	75,800	20,000	7	
Imidacloprid	Insecticide	32	48	0.002	0.0043 – 0.13	>41,500	1,200	35	1.05 (n=1)	>10,000	
Linuron	Herbicide	0	61	0.002	--	--	--	--	--	--	
Malathion	Insecticide	4	55	0.00012	0.00096 – 0.021	16.4	8.6[5]	0.3	0.035[5]	2,400	
MCPA	Herbicide	0	12	0.002	--	--	--	--	--	--	
MCPP	Herbicide	5	13	0.002	0.0073 – 0.037	11000	180000	> 45500	50800	115000	
Metalaxyl	Fungicide	5	18	0.0002	0.00034 – 0.029	65000	9100	14000	100	140000	
Methoxychlor	Insecticide	0	10	0.0095	--	--	--	--	--	--	
Metolachlor	Herbicide	8	18	0.0002	0.00037 – 0.001	1900	6000	550	3200	10	
Metribuzin	Herbicide	23	55	0.00024	0.00045 – 0.029	21,000	3,000	2,100	1,290	8.7	
Mevinphos	Insecticide	0	55	0.00024	--	--	--	--	--	--	
Mirex	Insecticide	0	10	0.0038	--	--	--	--	--	--	--
Molinate	Herbicide	0	55	0.00028	--	--	--	--	--	--	--
Norflurazon	Herbicide	1	55	0.0005	0.001	4,050	770	>7,500	1,000	9.7	58.2
Parathion ethyl	Insecticide	0	10	0.00025	--	--	--	--	--	--	--
Parathion methyl	Insecticide	0	10	0.00025	--	--	--	--	--	--	--
Pendimethalin	Herbicide	5	55	0.00025	0.00069 – 0.0045	69	6.3	140	14.5	5.2	12.5
Permethrin	Insecticide	0	10	0.0095	--	--	--	--	--	--	--
Phorate	Insecticide	0	55	0.00024	--	--	--	--	--	--	--
Picloram	Herbicide	0	1	0.05	--	--	--	--	--	--	--
Prometon	Herbicide	0	18	0.0009	--	--	--	--	--	--	--
Prometryn	Herbicide	2	55	0.00024	0.00057 - 0.0045	1,450	620	9,295	1,000	1	11.8
Silvex	Herbicide	0	54	0.002	--	--	--	--	--	--	--
Simazine	Herbicide	28	55	0.00024	0.00089 – 0.13	3,200	960	500	2,000	36	140
Terbufos	Insecticide	0	55	0.000094	--	--	--	--	--	--	--

Table 2 Analytical Results (μg/L)

Pesticide Name	Pesticide Class	Number Detects	Number Samples	MDL (μg/L)	Range (μg/L)	Fish Acute (μg/L)	Fish Chronic (μg/L)	Invert Acute (μg/L)	Invert Chronic (μg/L)	Algae Acute (μg/L)	Plants Acute (μg/L)
Terbuthylazine	Herbicide	0	56	0.00019	--	--	--	--	--	--	--
Triclopyr	Herbicide	0	2	0.0084	--	--	--	--	--	--	--

[1]Atrazine Aquatic Life Criteria CMC = 1,500 ppb
[2]Atrazine Chronic Aquatic Community Benchmark is 17.5 ppb
[3]Chlorpyrifos Aquatic Life Criteria CMC = **0.083 ppb**
[4]Chlorpyrifos Aquatic Life Criteria CCC = **0.041 ppb**
[5]Malathion Aquatic Life Criteria CCC = 0.1 ppb
[6]Fenuron Benchmarks are based on Diuron Aquatic Life Benchmark; fenuron is an analog of diuron and has been shown to be less toxic to fish than diuron.
Detected in >10% of samples collected
Exceeded a benchmark value

Notable Detects

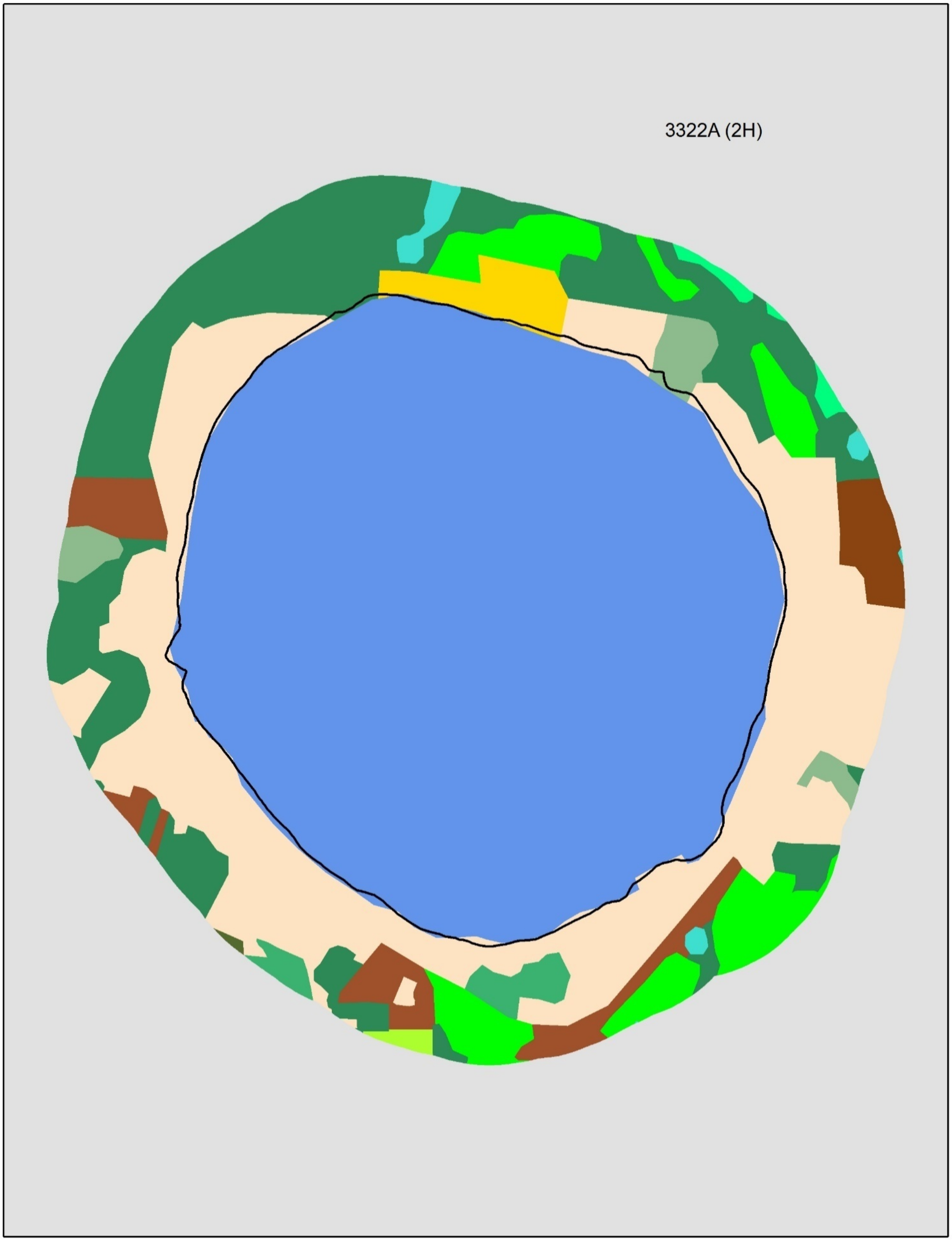
Pesticide	Analysis	Result	Units	MDL	Sample Date	Location	Comment

No exceedance in this calendar year.

Appendix

Land Use Legend

- Residential Low Density
- Residential Medium Density
- Residential High Density
- Commercial and Services
- Industrial
- Extractive
- Institutional
- Recreational
- Open Land
- Cropland and Pastureland
- Tree Crops
- Feeding Operations
- Nurseries and Vineyards
- Specialty Farms
- Other Open Lands <Rural>
- Herbaceous
- Shrub and Brushland
- Mixed Rangeland
- Upland Coniferous Forests
- Upland Hardwood Forests
- Tree Plantations
- Streams and Waterways
- Lakes
- Reservoirs
- Bays and Estuaries
- Major Springs
- Slough Waters
- Wetland Hardwood Forests
- Wetland Coniferous Forests
- Wetland Forested Mixed
- Vegetated Non-Forested Wetlands
- Non-Vegetated
- Sand Other Than Beaches
- Disturbed Lands
- Riverine Sandbars
- Transportation
- Communications
- Utilities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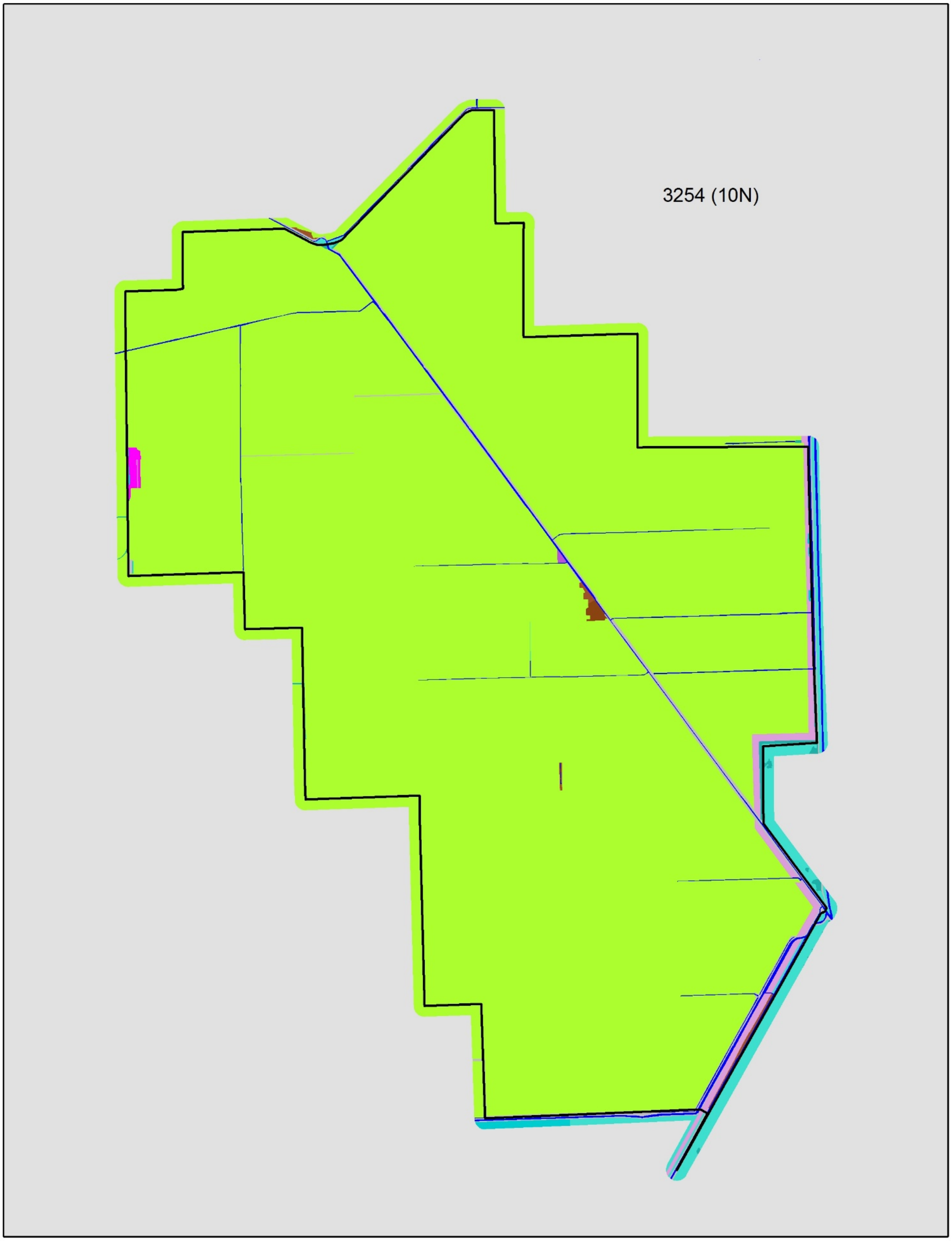
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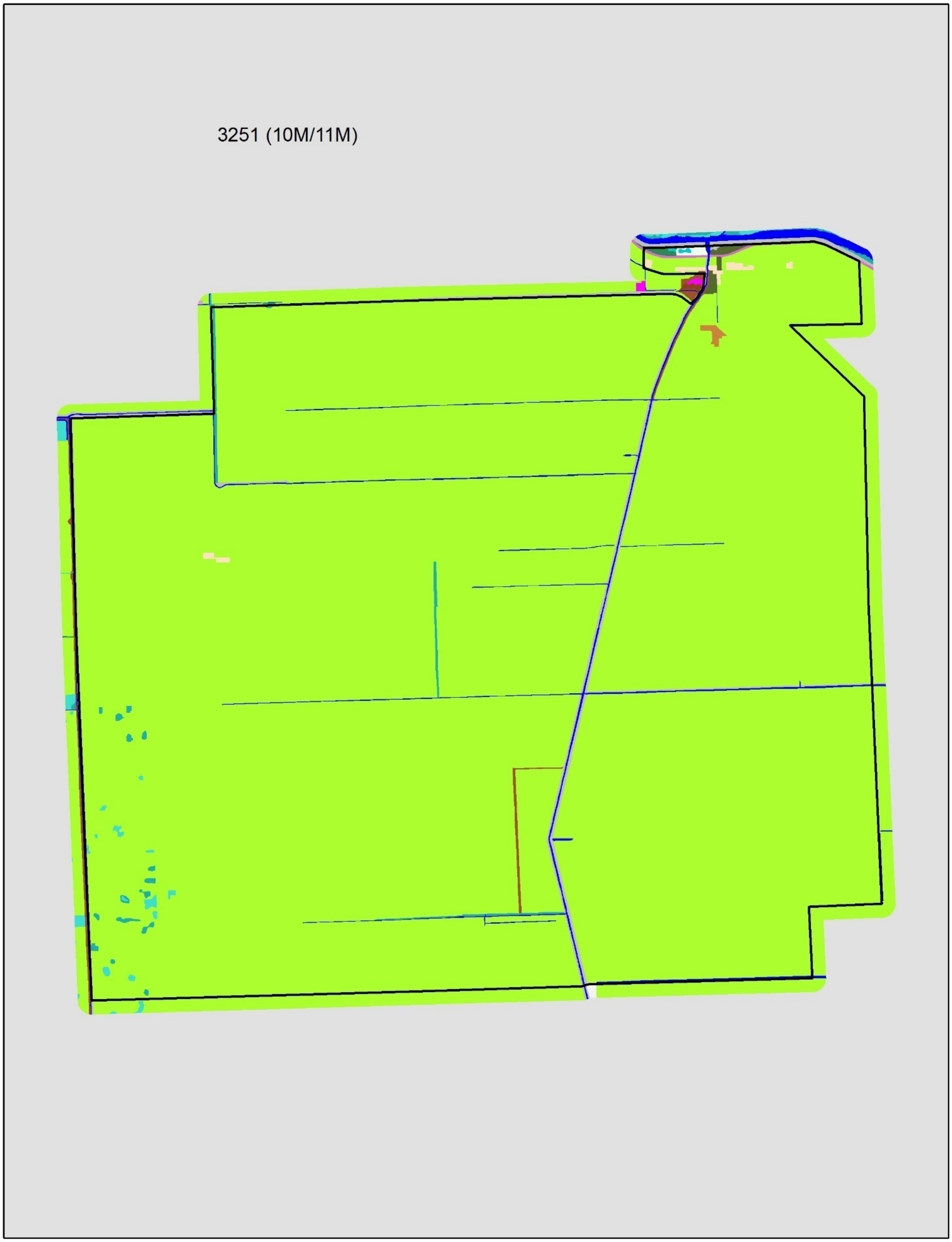
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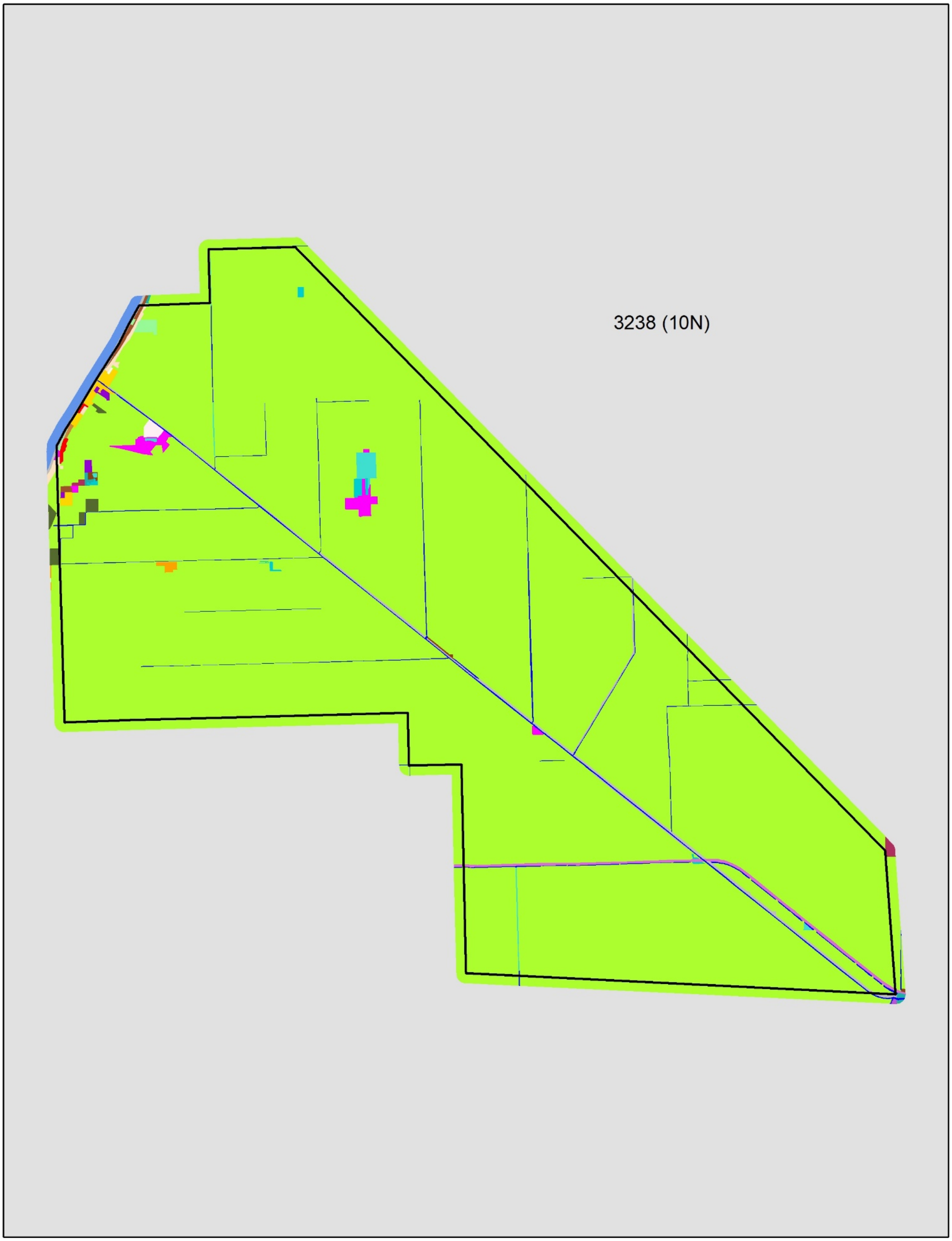
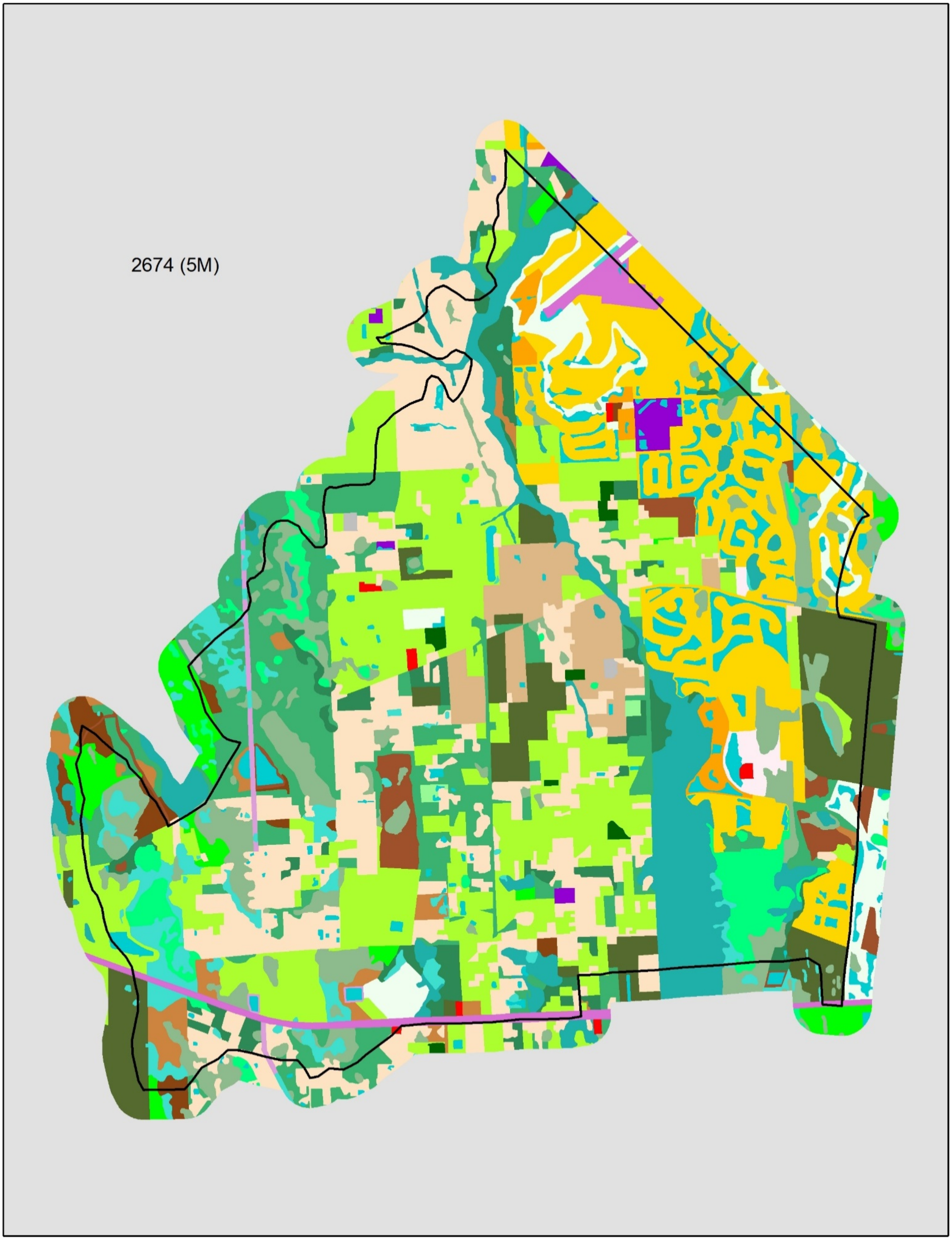

3238 (10N)


3098B (8N)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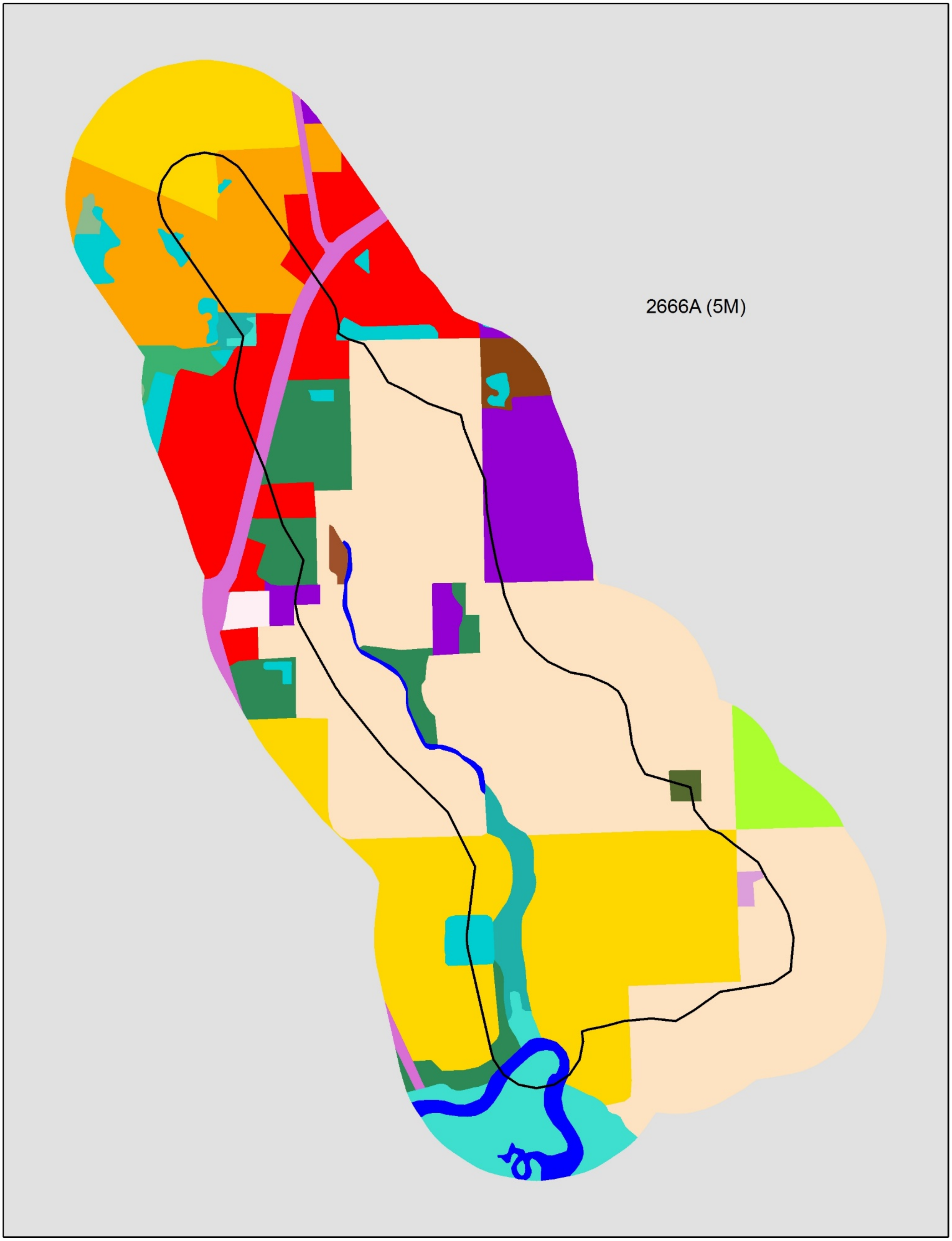
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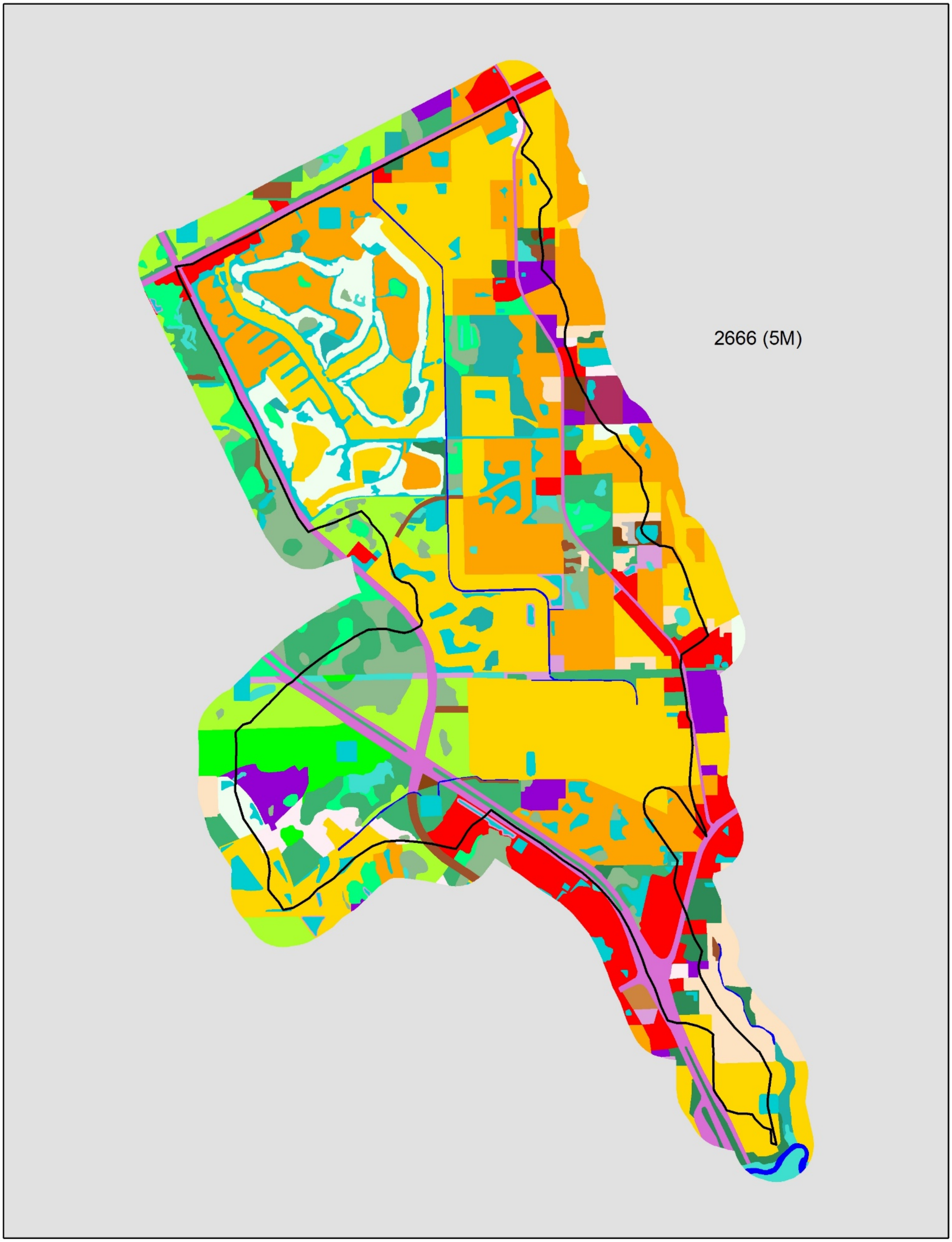
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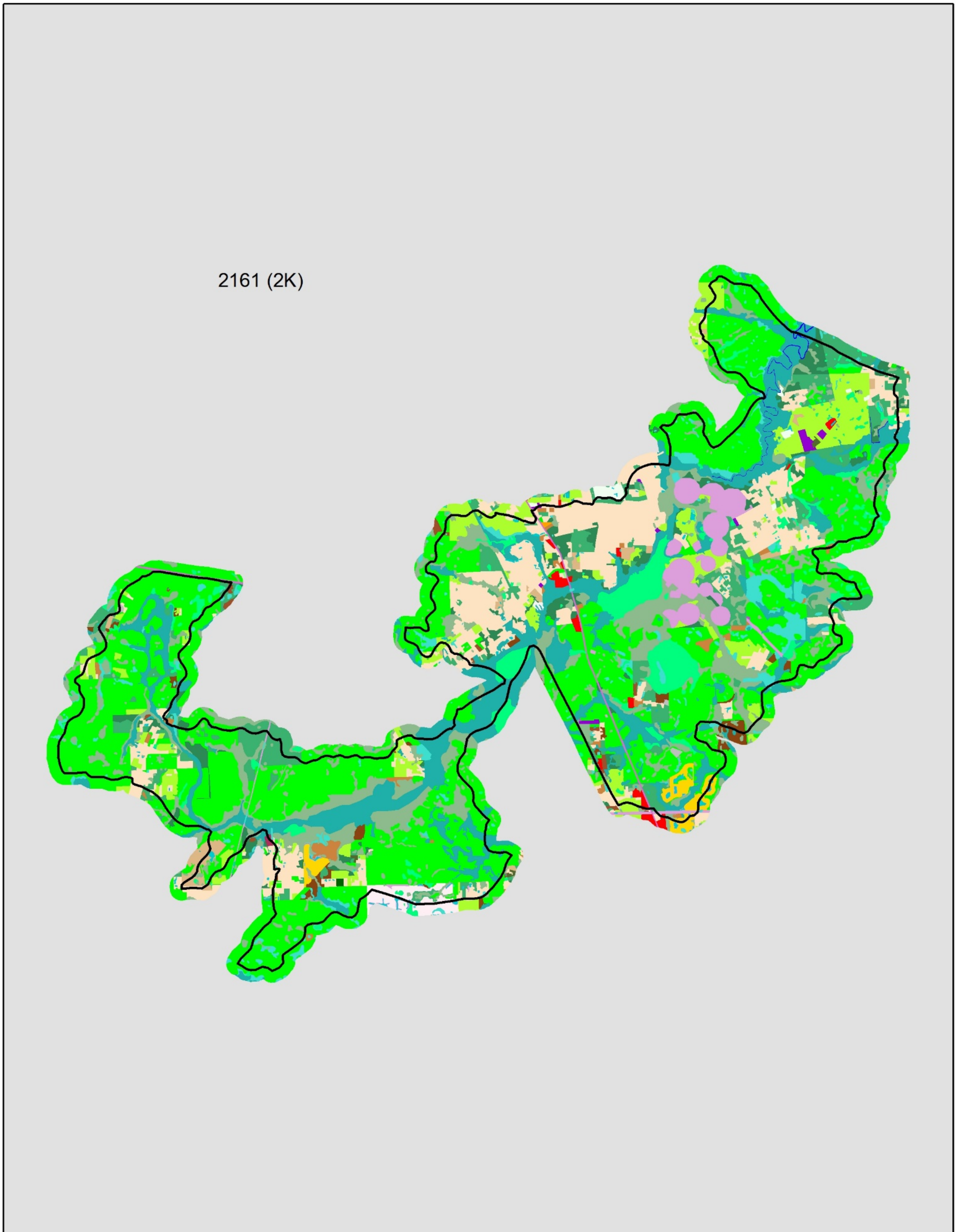
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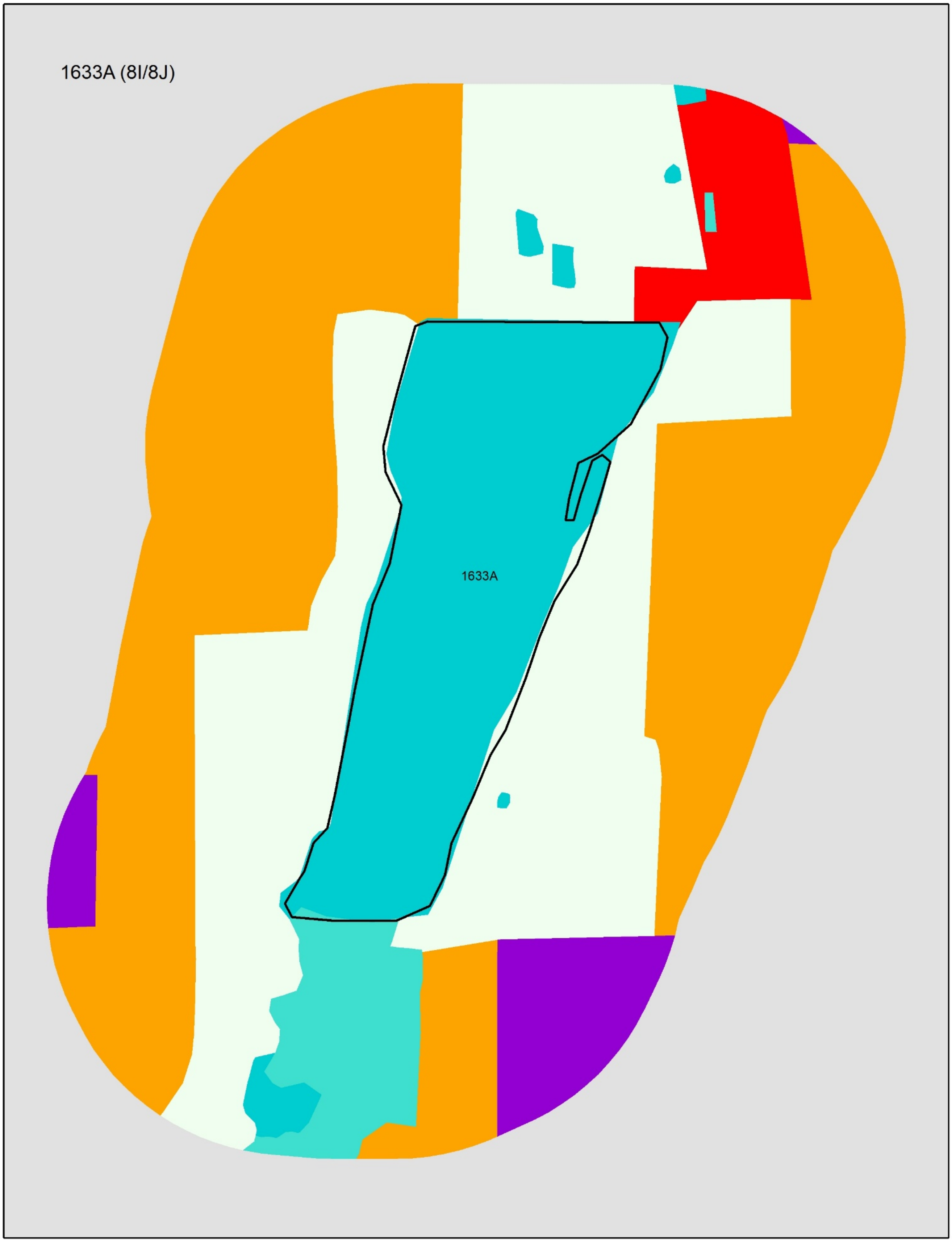
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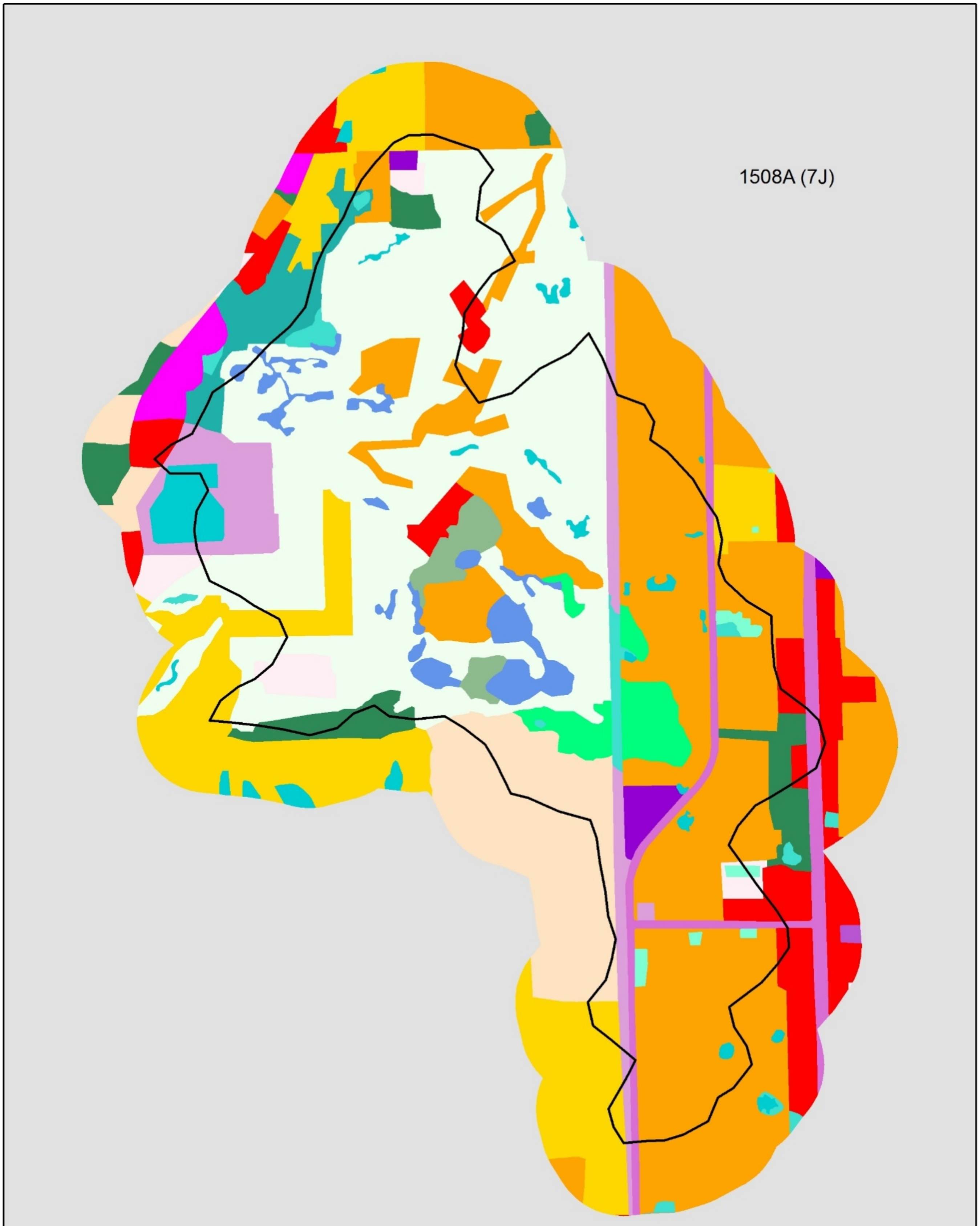
1633A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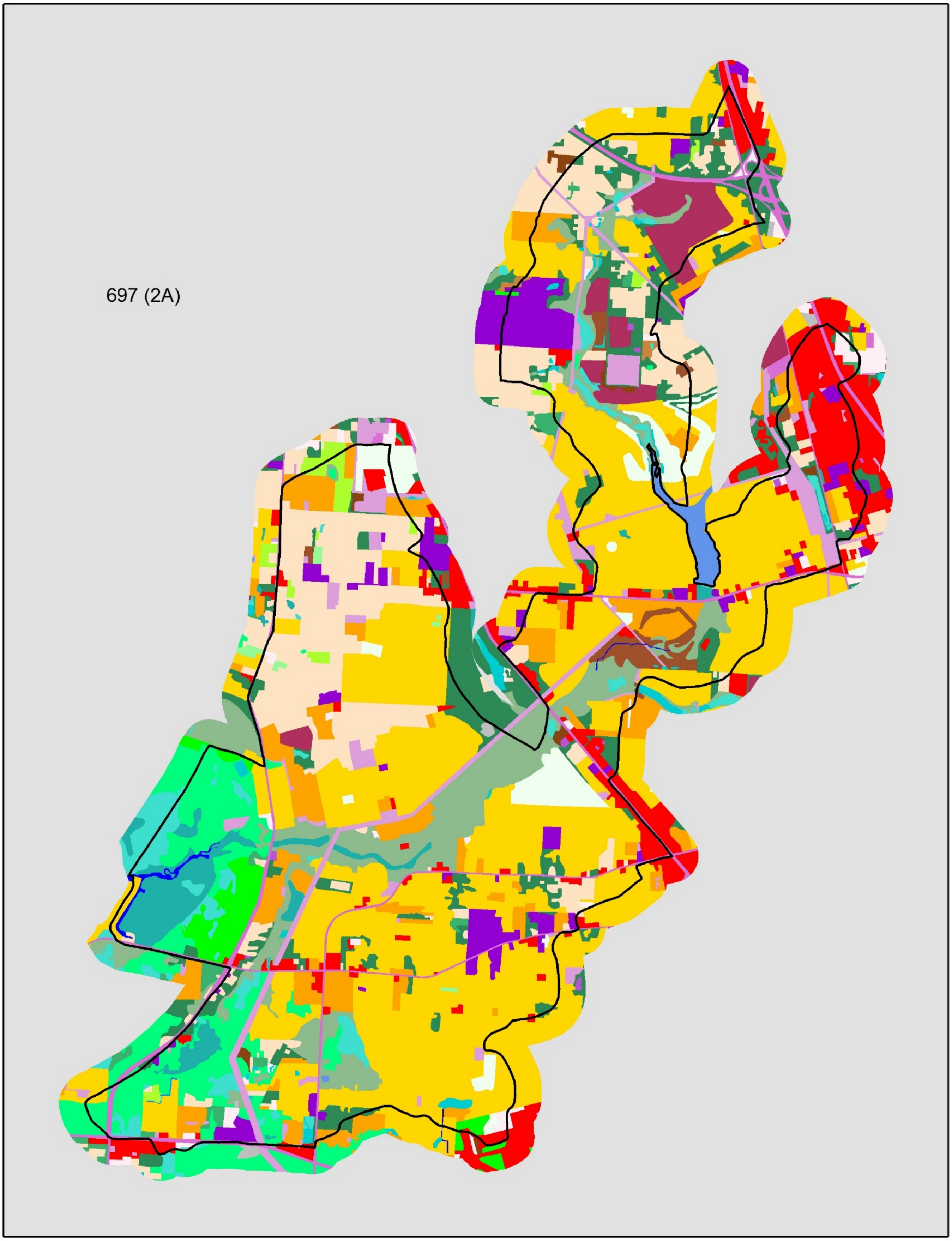
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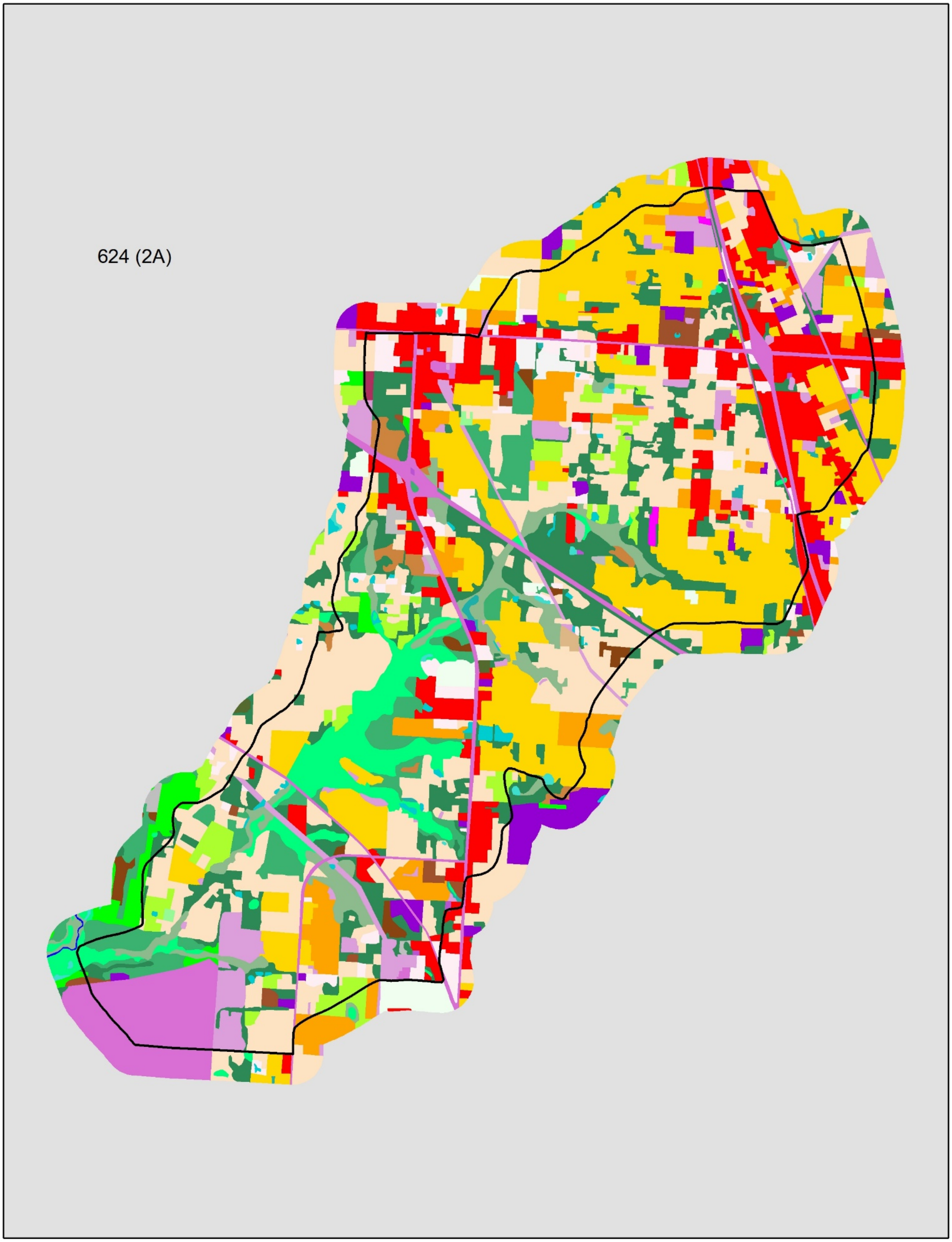
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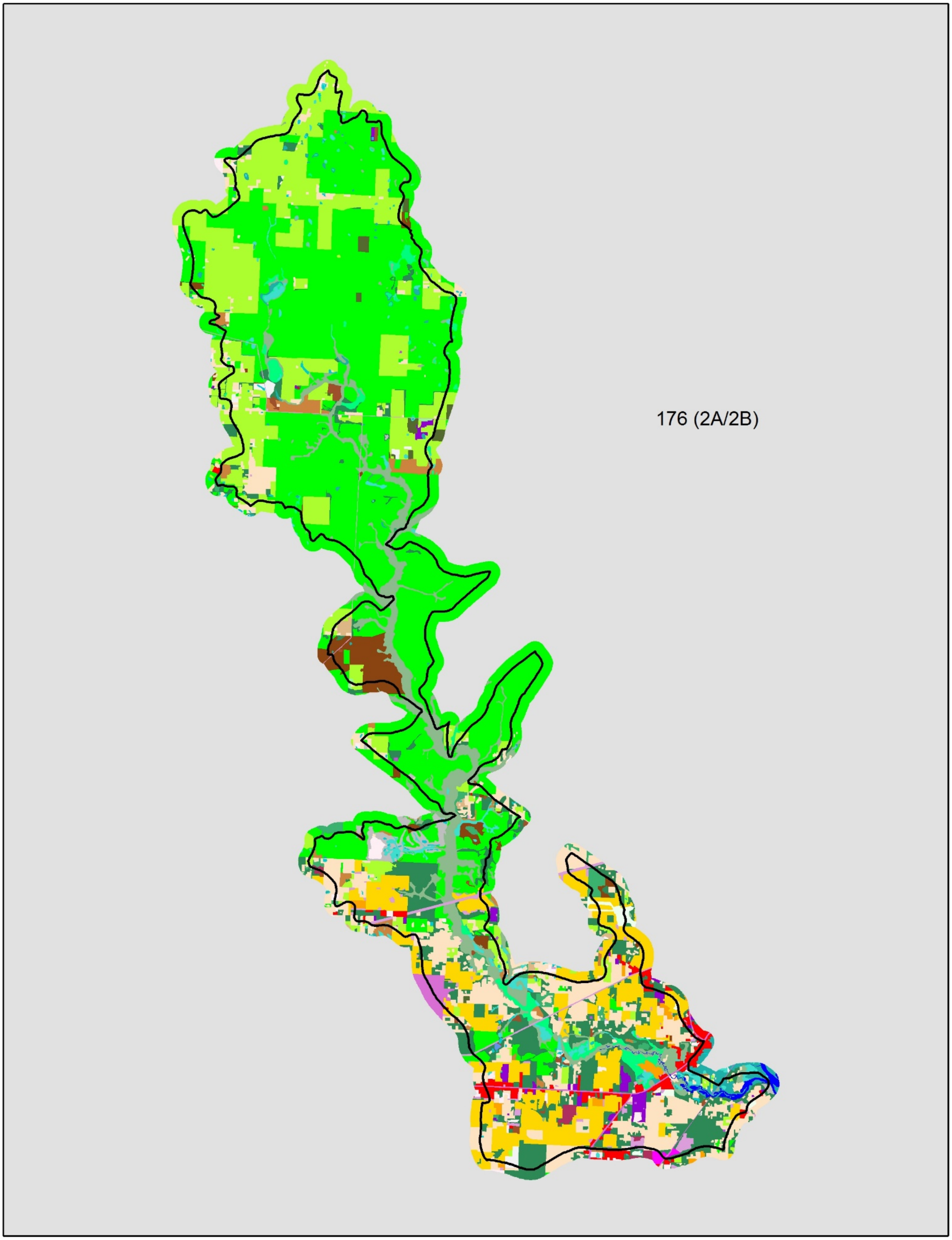
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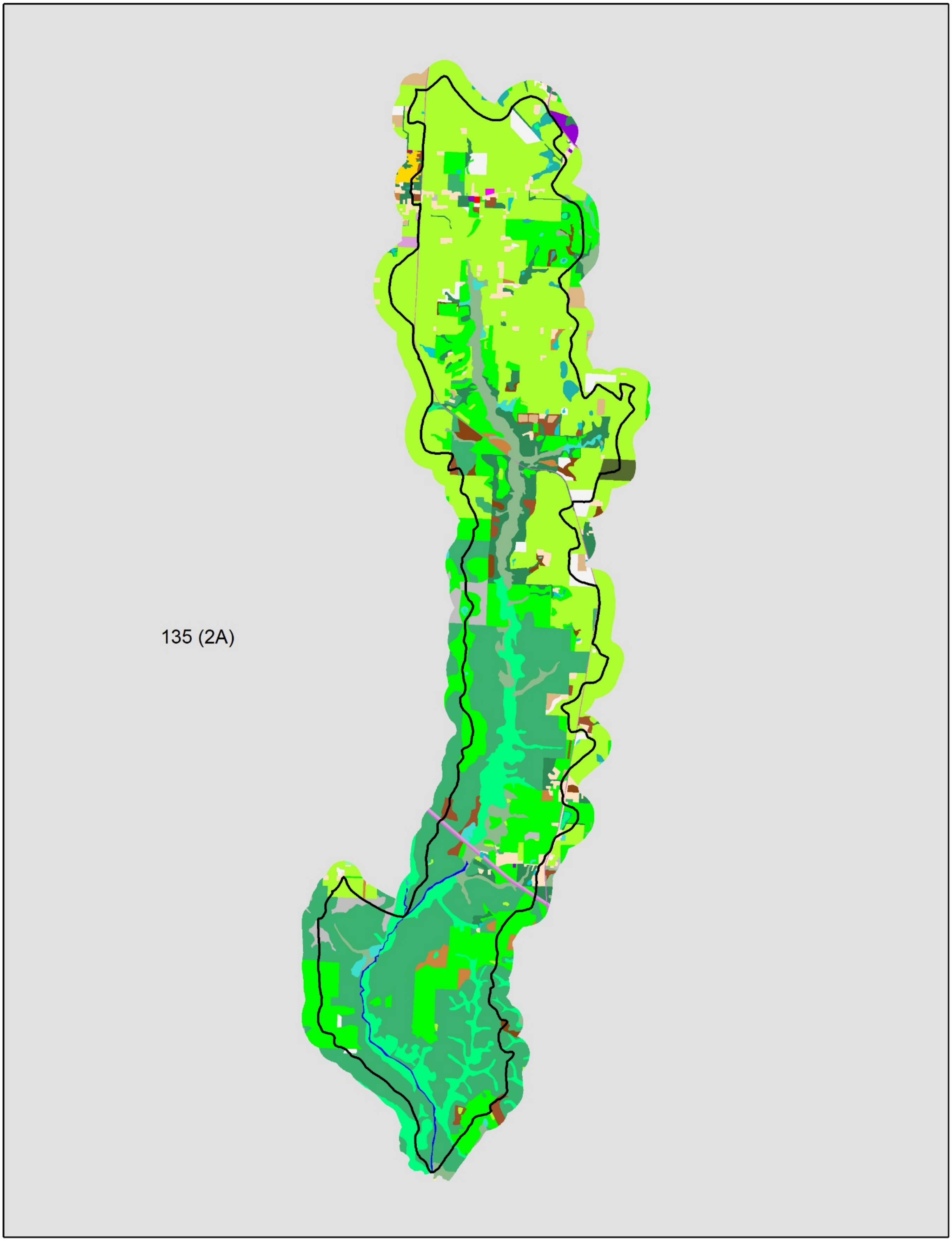
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