Testing Florida Surface Waters for Pesticides

Calendar Year 2014

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 Regional Operations 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 2014, 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 than as a fertilizer application, although it can also be a plant micronutrient or 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 2014 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. Twenty three surface water bodies across the state were identified for pesticide analysis in 2014 (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 other classes of pesticides or 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 2014.

WBID#	WBID Name	County
4	Brushy Creek	Escambia
35	Pond Creek	Santa Rosa
18	Big Coldwater Creek	Santa Rosa
846B	Jackson Creek	Escambia
1320	Blue Run	Marion
1399	Dade City Canal	Pasco
1466	Lake Agnes	Polk
1488D	Lake Alfred	Polk
3170F6	Reedy Creek	Orange
3170P	Sawyer Lake	Orange
3169E	Lake Marsha	Orange
3169G1	Clear Lake	Orange
1938G	Lake Francis	Polk
1813C	Lake Letta	Highlands
1619B	Lake Easy	Polk
3201A1	Fisheating Creek	Highlands
3277C	North New River Canal	Broward
3287	C-7 (Little River) Canal	Miami Dade
2153	Alligator Creek	Nassau
2097K	St. Mary's River N. Prong	Nassau
2921D	Lake Woodruff Outlet	Volusia
3245B	Lake Clarke	Palm Beach
1618	Lake Seminole	Pinellas

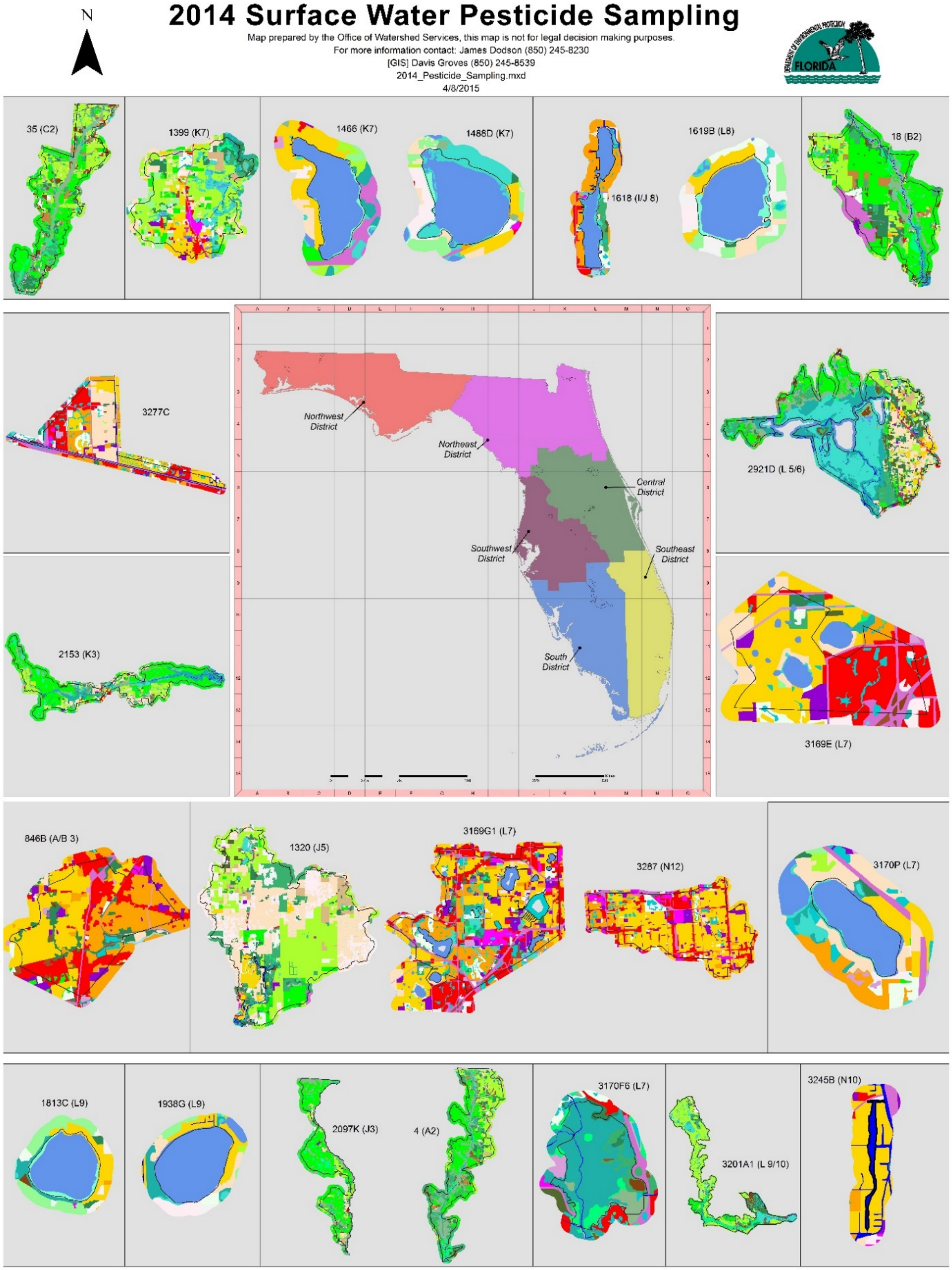


Figure 1. Locations of water bodies selected for pesticide analysis. Landuse Maps of individual water bodies are in the Appendix.

RESULTS

Samples were collected between March and December 2014. As mentioned earlier, bottles for pesticide samples accompanied the sampling crews that were scheduled to visit water bodies according to the 2014 monitoring schedule for individual WBIDs. Consequently water bodies tested for pesticides were visited at different frequencies. Most water bodies were sampled three to six times during the year. 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 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. Forty-two of the 64 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 2014 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 2015 following the same process and including new WBIDs. In January 2015, staff from both departments met to review where the Strategic Monitoring Program would be sampling during the 2015 calendar year and identified 16 WBIDs for pesticide analysis during calendar year 2015. Year 2015 monitoring is currently underway.

Table 2 Analytical Results (continued)

Pesticide Name	**Pesticide Class**	Number Detects	Number Samples	MDL (µg/L)	Range (µg/L)	Benchmark Fish (µg/L)		Benchmark Inverts (µg/L)		Benchmark (µg/L) Algae | Plants	
						Acute	Chronic	Acute	Chronic	Acute	Chronic
2,4,5-T	**Herbicide**	0	43	0.002	--	--	--	--	--	--	--
2,4-D	**Herbicide**	35	43	0.002	0.0027-0.79	12,075	14,200	12,500	16,050	3880	13.1
2,4-DB	**Herbicide**	0	7	0.002	--	--	--	--	--	--	--
Acifluorfen	**Herbicide**	0	43	0.002	--	--	--	--	--	--	--
Aldrin	**Insecticide**	0	43	0.002	--	--	--	--	--	--	--
Alpha-BHC	**Insecticide**	0	43	0.002	--	--	--	--	--	--	--
Ametryn	**Herbicide**	35	43	0.00019	0.00023-0.023	1,800	700	14,000	240	3.67	10
Atrazine	**Herbicide**	42	43	0.00024	0.00026-0.4	2,650[1]	65	360[1]	60	1[2]	37
Atrazine Desethyl	**Degradate**	36	43	0.00024	0.00028-0.04	--	--	--	--	1,000	
Bentazon	**Herbicide**	22	43	0.002	0.0023-0.18	>50,000	--	>50,000	--	4,500	5,350
Beta-BHC	**Insecticide**	0	43	0.0019	--	--	--	--	--	--	--
Bromacil	**Herbicide**	27	43	0.005	0.0052-0.089	18,000	3,000	60,500	8,200	7	45
Carbophenothion	**Insecticide**	0	43	0.0056	--	--	--	--	--	--	--
Chlordane	**Insecticide**	0	40	0.008	--	--	--	--	--	--	--
Chlorothalonil	**Fungicide**	0	43	0.0075	--	--	--	--	--	--	--
Chlorpyrifos Ethyl	**Insecticide**	24	43	0.000094	0.00012-0.0055	0.9[3]	0.57[4]	0.05[3]	0.04[4]	140	--
Chlorpyrifos Methyl	**Insecticide**	0	43	0.00012	--	--	--	--	--	--	--
Cypermethrin	**Insecticide**	0	43	0.011	--	--	--	--	--	--	--
DDD-p,p'	**Insecticide**	0	43	0.0038	--	--	--	--	--	--	--
DDE-p,p'	**Insecticide**	0	43	0.0038	--	--	--	--	--	--	--
DDT-p,p'	**Insecticide**	0	43	0.0038	--	--	--	--	--	--	--
Delta-BHC	**Insecticide**	0	43	0.0019	--	--	--	--	--	--	--
Dichlorprop	**Herbicide**	0	5	0.002	--	--	--	--	--	--	--
Dicofol	**Insecticide**	0	43	0.023	--	--	--	--	--	--	--
Dieldrin	**Insecticide**	2	43	0.0019	0.003-0.037	2.5[6]	11[6]	4.5[6]	0.7[6]	--	--
Dinoseb	**Herbicide**	0	6	0.02	--	--	--	--	--	--	--
Disulfoton	**Insecticide**	0	43	0.00047	--	--	--	--	--	--	--

Table 2 Analytical Results (continued)

Pesticide Name	Pesticide Class	Number Detects	Number Samples	MDL (µg/L)	Range (µg/L)	Benchmark Fish (µg/L)		Benchmark Inverts (µg/L)		Benchmark (µg/L) Algae | Plants	
						Acute	Chronic	Acute	Chronic	Acute	Chronic
Diuron	**Herbicide**	24	43	0.002	0.0022-0.042	200	26	80	200	2.4	15
Endosulfan I	**Insecticide**	0	43	0.0019	--	--	--	--	--	--	--
Endosulfan II	**Insecticide**	0	43	0.0019	--	--	--	--	--	--	--
Endosulfan Sulfate	**Degradate**	0	43	0.0038	--	--	--	--	--	--	--
Endrin	**Insecticide**	0	43	0.0038	--	--	--	--	--	--	--
Endrin Aldehyde	**Degradate**	0	43	0.0038	--	--	--	--	--	--	--
EPTC	**Herbicide**	0	43	0.28	--	--	--	--	--	--	--
Ethion	**Insecticide**	0	43	9.4E-05	--	--	--	--	--	--	--
Ethoprop	**Insecticide**	0	43	9.4E-05	--	--	--	--	--	--	--
Fenuron	**Herbicide**	0	6	0.008	--	--	--	--	--	--	--
Fipronil	**Insecticide**	5	43	0.00047	0.00064-0.0068	41.5	6.6	0.11	0.011	140	>100
Fipronil Sulfide	**Degradate**	14	43	0.00019	0.00022-0.0027	41.4	6.6	1.07	0.11	140	>100
Fipronil Sulfone	**Degradate**	17	43	0.00019	0.00021-0.015	12.5	0.67	0.36	0.037	140	>100
Gamma-BHC	**Insecticide**	0	43	0.0019	--	0.85	2.9	0.5	54	--	--
Heptachlor	**Insecticide**	0	43	0.0019	--	--	--	--	--	--	--
Heptachlor Epoxide	**Degradate**	1	43	0.0019	0.02-0.024	--	--	--	--	--	--
Hexazinone	**Herbicide**	20	43	0.00094	0.0011-0.26	137,000	17,000	75,800	20,000	7	37.4
Imidacloprid	**Insecticide**	30	43	0.002	0.0026-0.16	>41,500	1,200	35	1.05	>10,000	--
Linuron	**Herbicide**	0	43	0.002	--	--	--	--	--	--	--
Malathion	**Insecticide**	21	43	0.00012	0.00014-0.039	16.4	8.6[5]	0.3	0.035[5]	2,400	--
MCPP	**Herbicide**	0	6	0.002	--	--	--	--	--	--	--
Methoxychlor	**Insecticide**	0	43	0.0094	--	--	--	--	--	--	--
Metribuzin	**Herbicide**	8	43	0.00024	0.00028-0.019	--	--	--	--	--	--
Mevinphos	**Insecticide**	0	43	0.00024	--	--	--	--	--	--	--
Mirex	**Insecticide**	0	43	0.0038	--	--	--	--	--	--	--
Molinate	**Herbicide**	0	43	0.00028	--	--	--	--	--	--	--
Norflurazon	**Herbicide**	14	43	0.00094	0.0012-0.16	--	--	--	--	--	--
Pendimethalin	**Herbicide**	11	43	0.00047	0.00055-0.0053	69	6.3	140	14.5	5.2	12.5

Table 2 Analytical Results (continued)

Pesticide Name	Pesticide Class	Number Detects	Number Samples	MDL (µg/L)	Range (µg/L)	Benchmark Fish (µg/L)		Benchmark Inverts (µg/L)		Benchmark (µg/L) Algae | Plants	
						Acute	Chronic	Acute	Chronic	Acute	Chronic
Permethrin	**Insecticide**	0	43	0.0094	--	--	--	--	--	--	--
Phorate	**Insecticide**	0	43	0.00024	--	--	--	--	--	--	--
Prometryn	**Herbicide**	2	43	0.00024	0.00042-0.0018	1,450	620	9,295	1,000	1	11.8
Silvex	**Herbicide**	0	43	0.002	--	--	--	--	--	--	--
Simazine	**Herbicide**	28	43	0.00024	0.00027-0.0097	3,200	960	500	2,000	36	140
Terbufos	**Insecticide**	0	43	9.4E-05	--	--	--	--	--	--	--
Terbuthylazine	**Herbicide**	4	43	0.00019	0.00074-0.0045	1700	--	25,450	--	--	--
Toxaphene	**Insecticide**	0	40	0.094	--	--	--	--	--	--	--
Trifluralin	**Herbicide**	0	40	0.0076	--	--	--	--	--	--	--

[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 = **0.041 ppb**
[5]Malathion Aquatic Life Criteria CCC = 0.1 ppb
[6]Dieldrin not to Exceed 1.0 µg/L in freshwater and 0.71 µg/L in salt water

Detected in >10% of samples collected
Exceeded a benchmark value

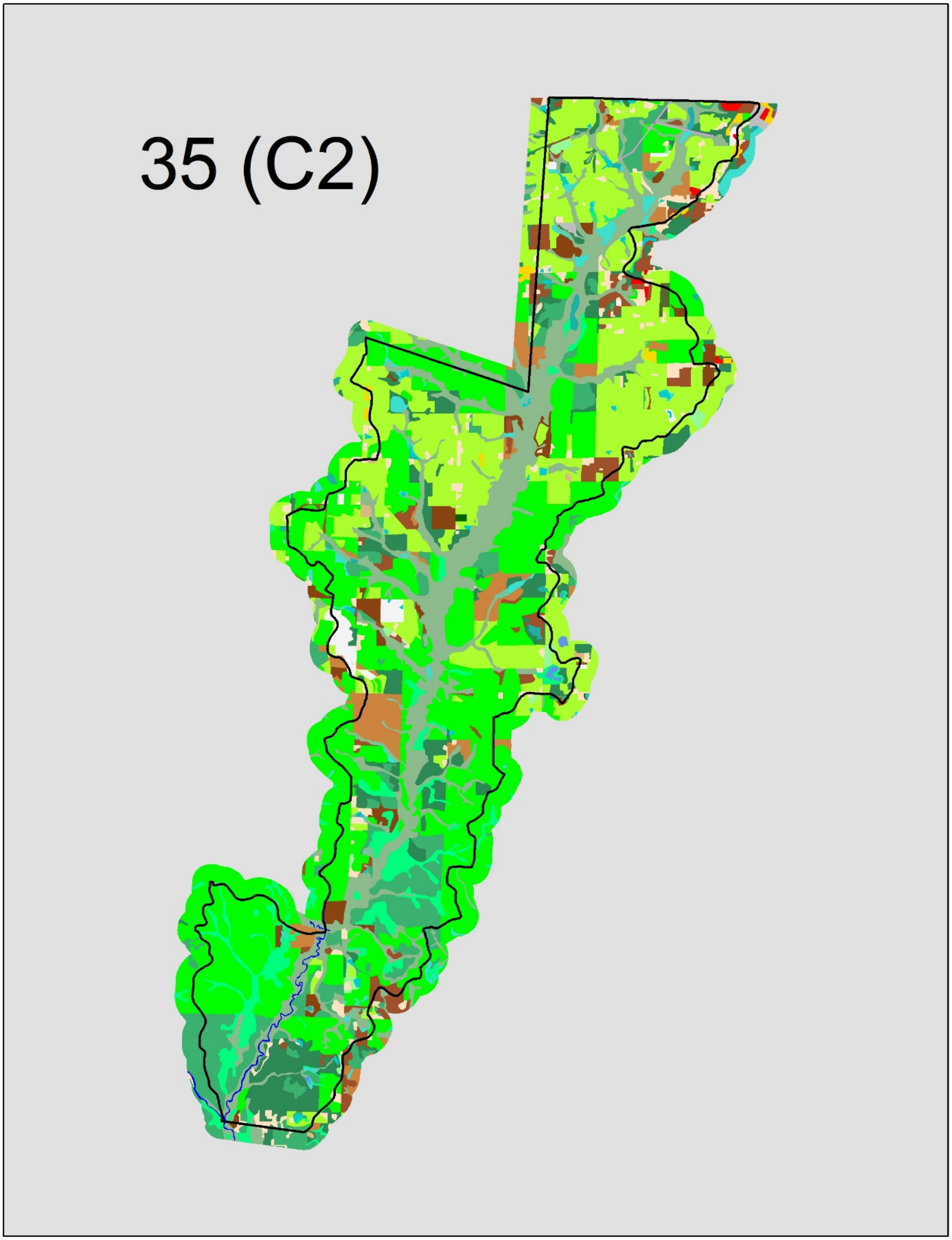
Benchmark values from: http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm
http://water.epa.gov/scitech/swguidance/standards/criteria/current/upload/2001_10_12_criteria_ambientwqc_aldrindieldrin.pdfAtrazine Aquatic Life Criteria CMC = 1,500 ppb

[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
Detected in >10% of samples collected
Exceeded a benchmark value

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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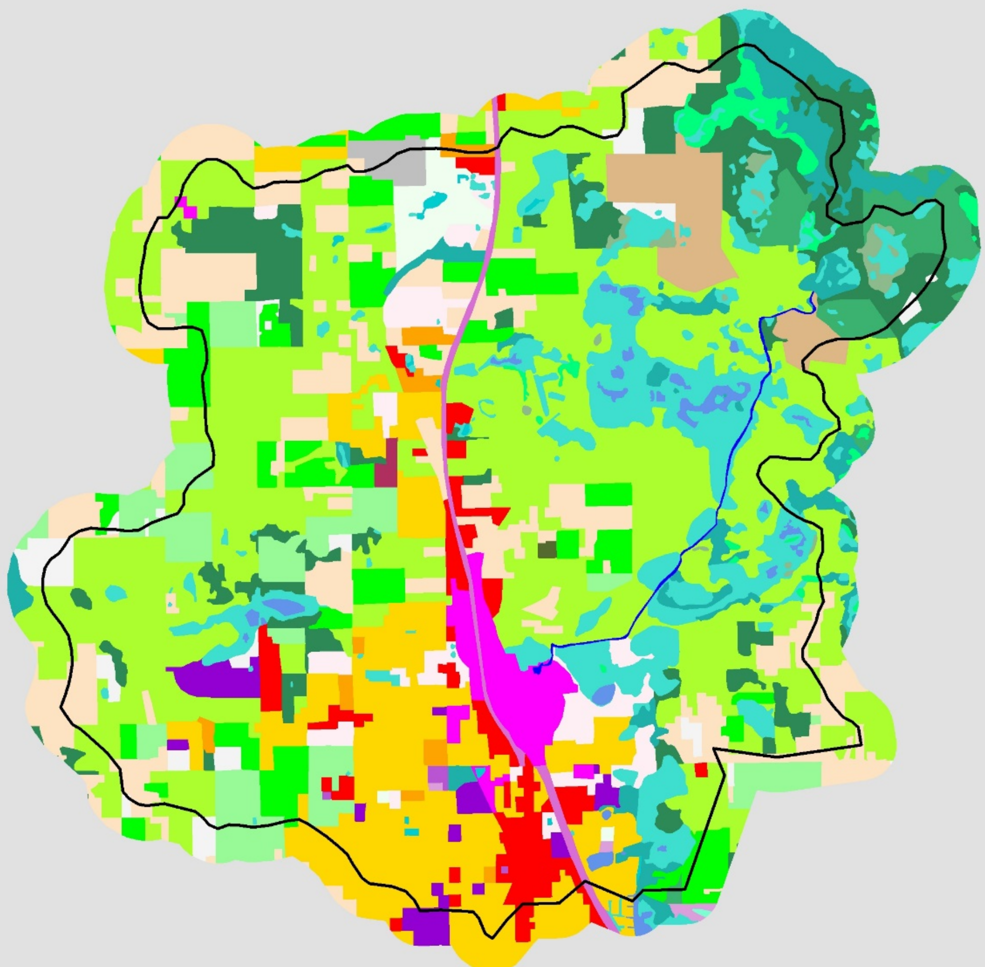

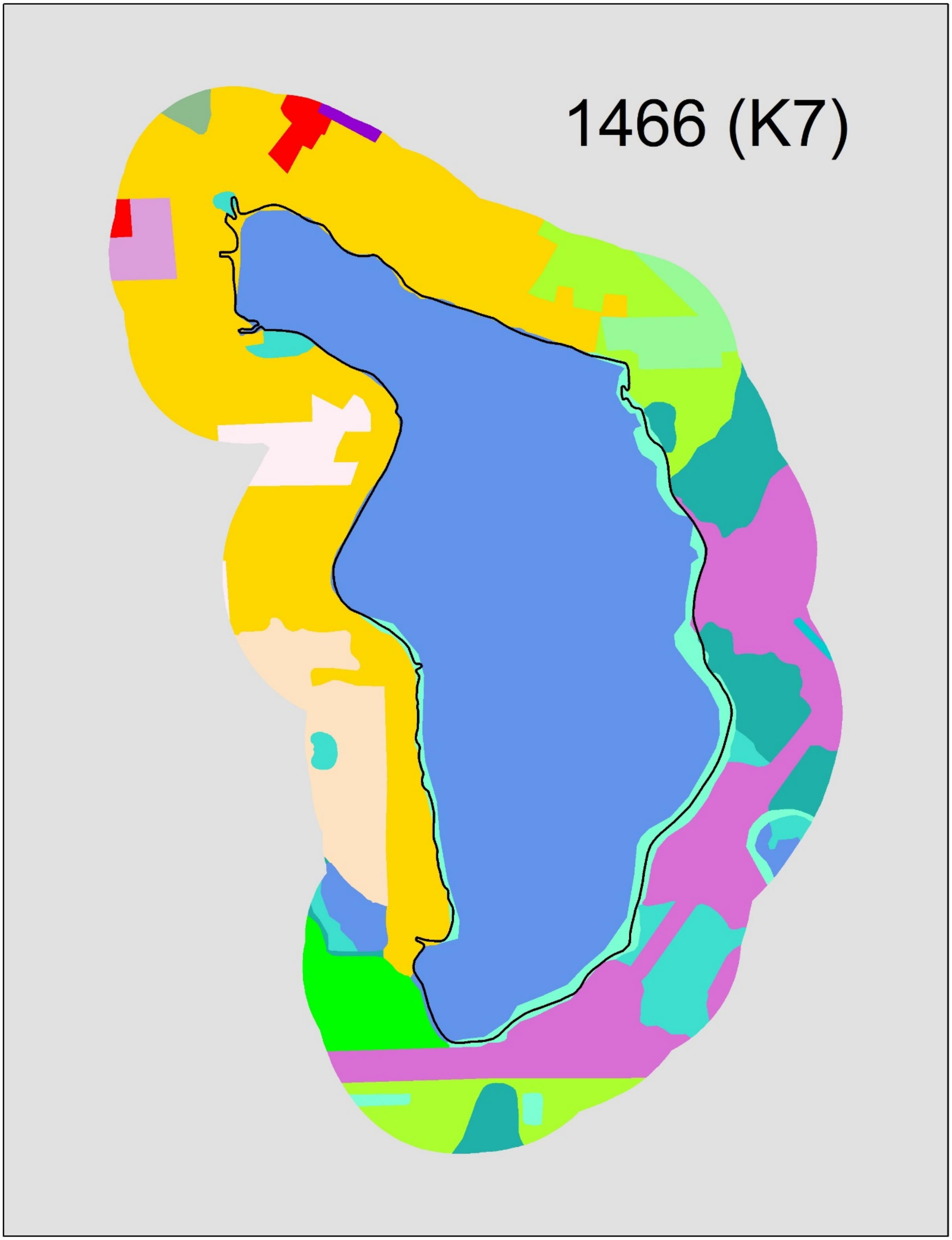
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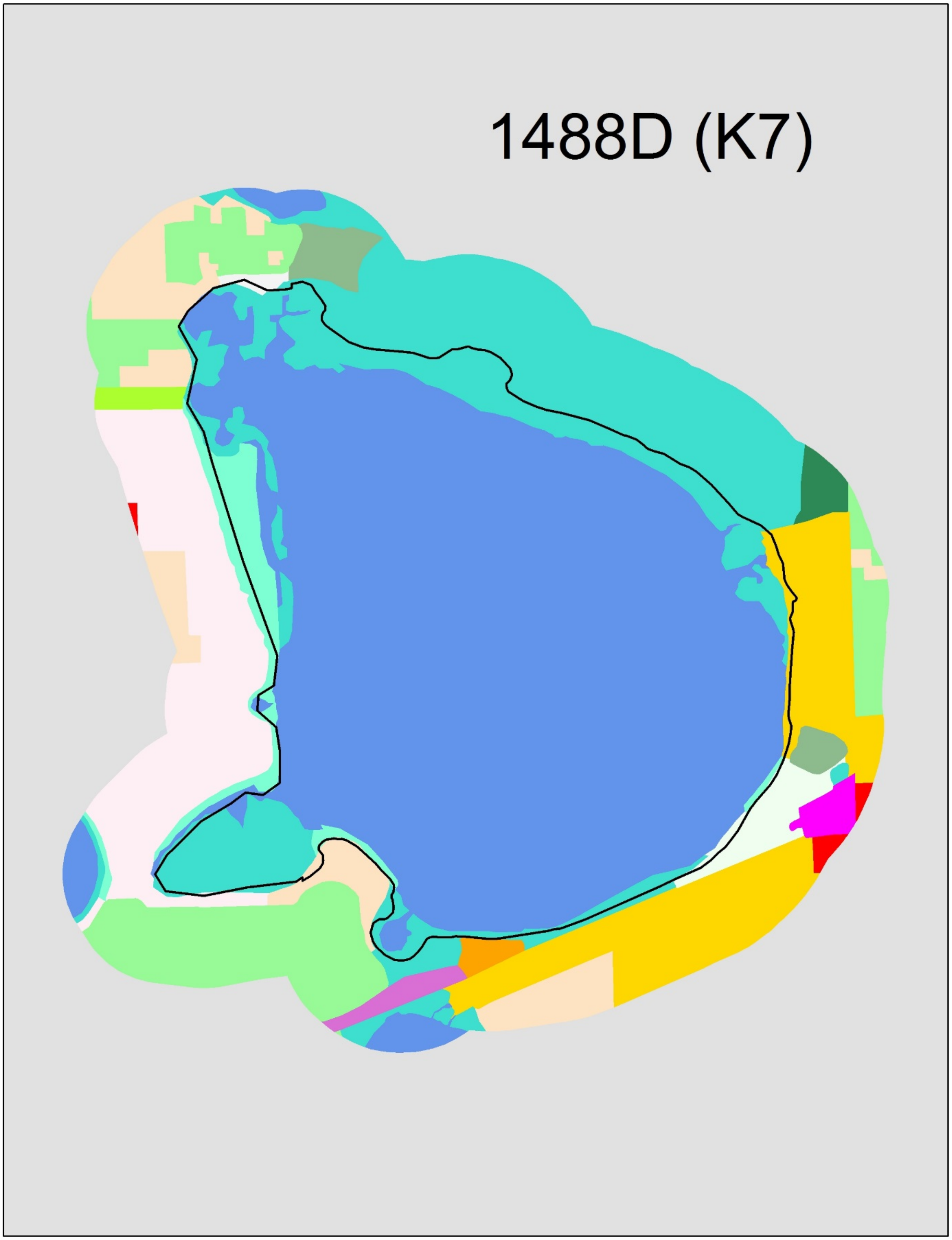
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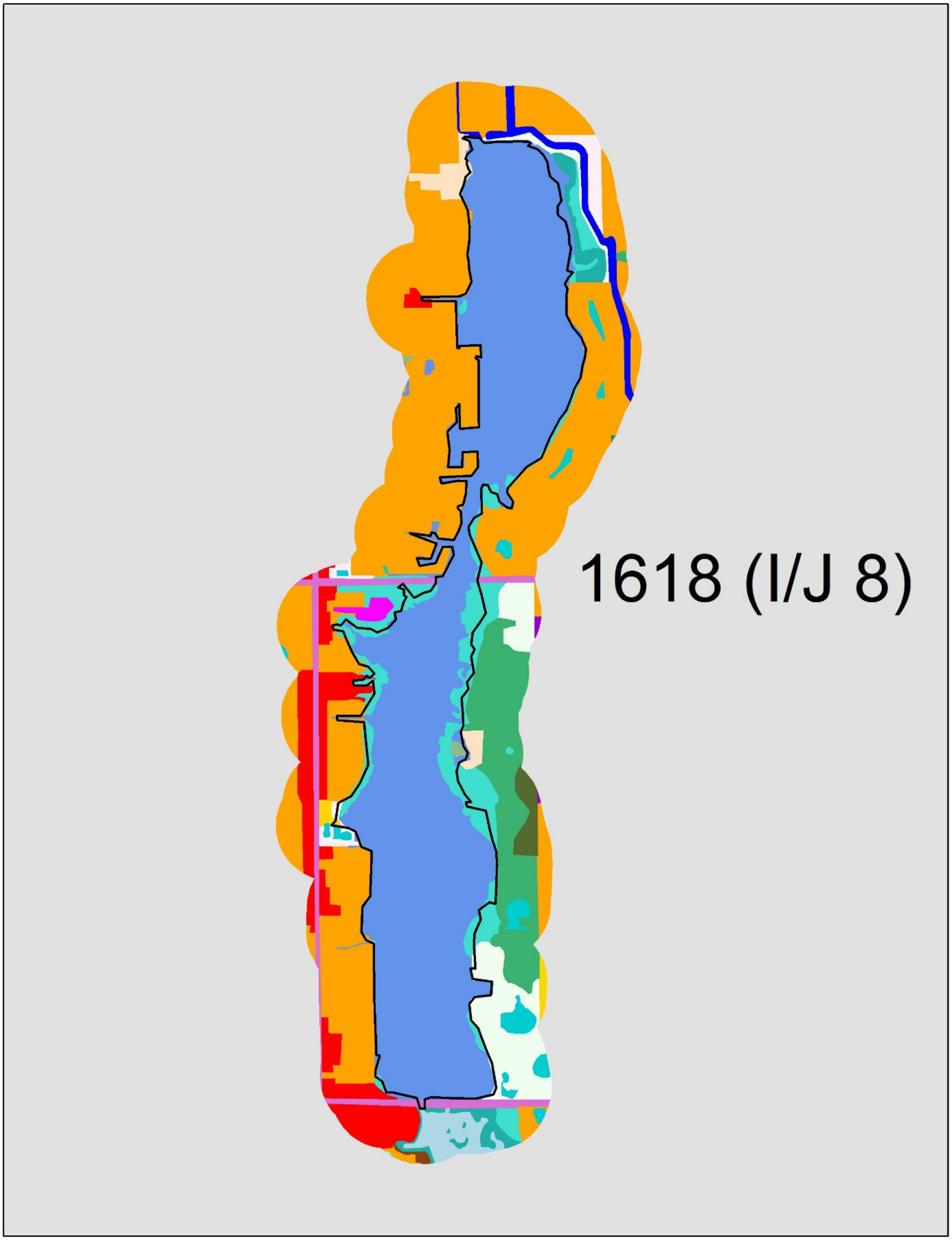
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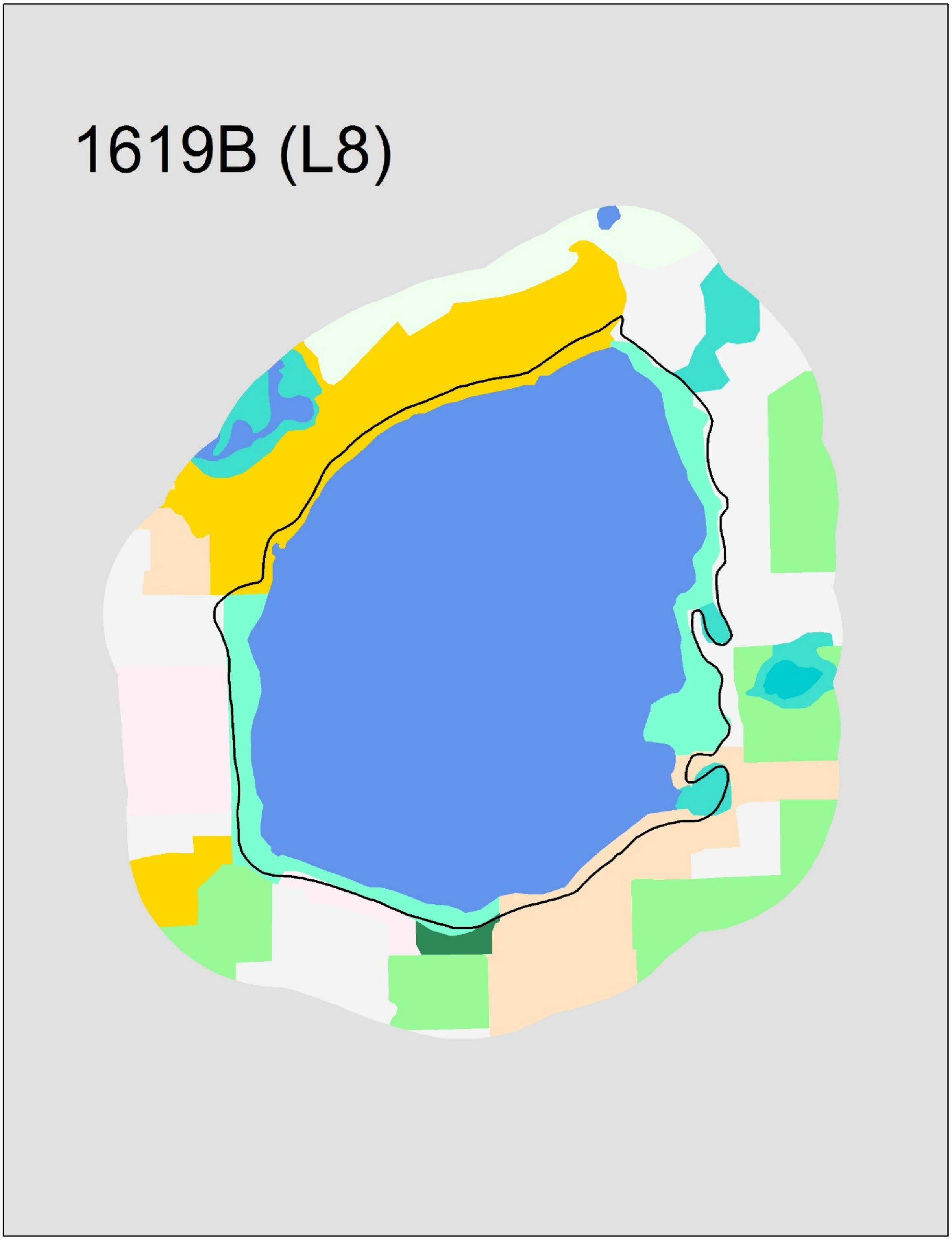
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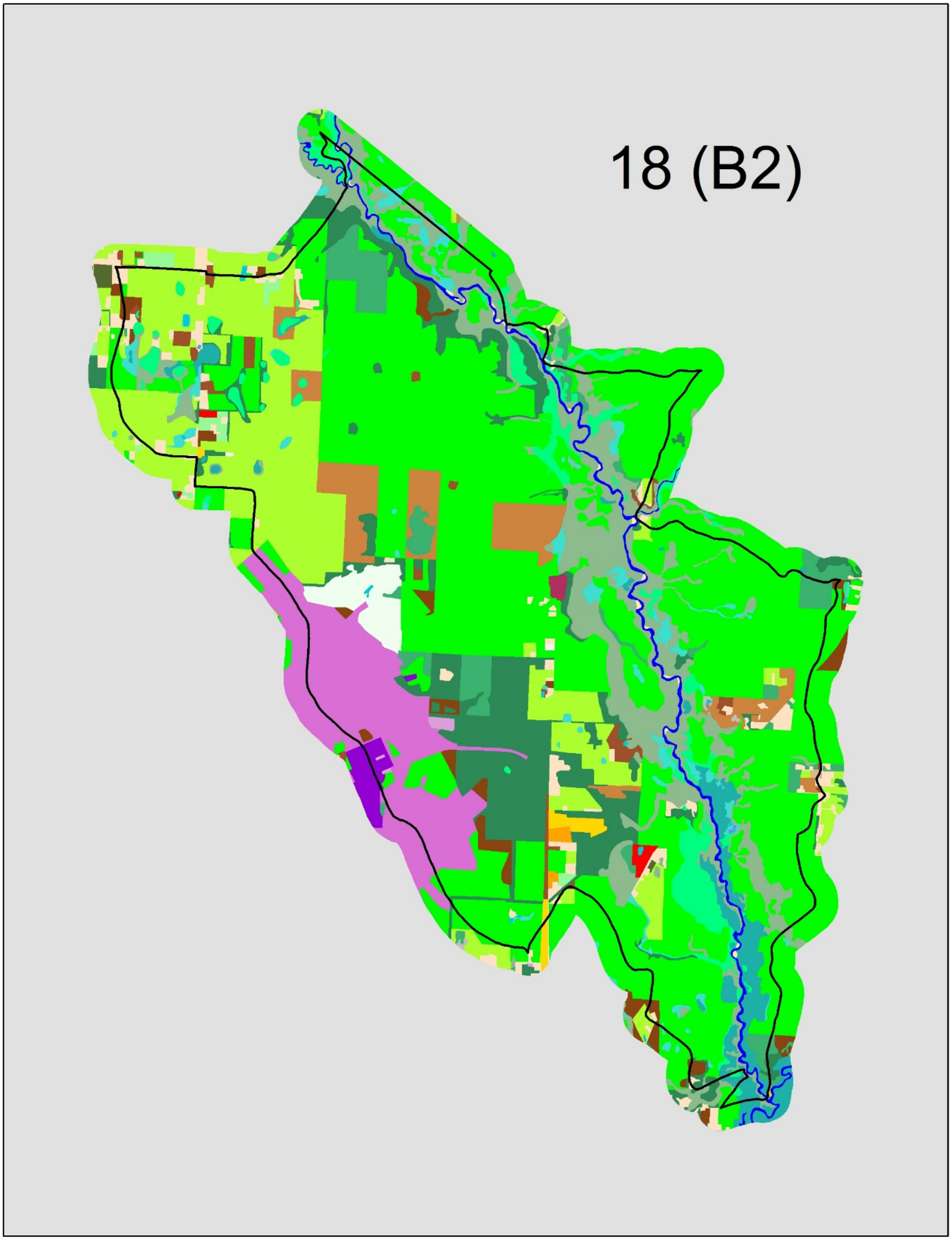
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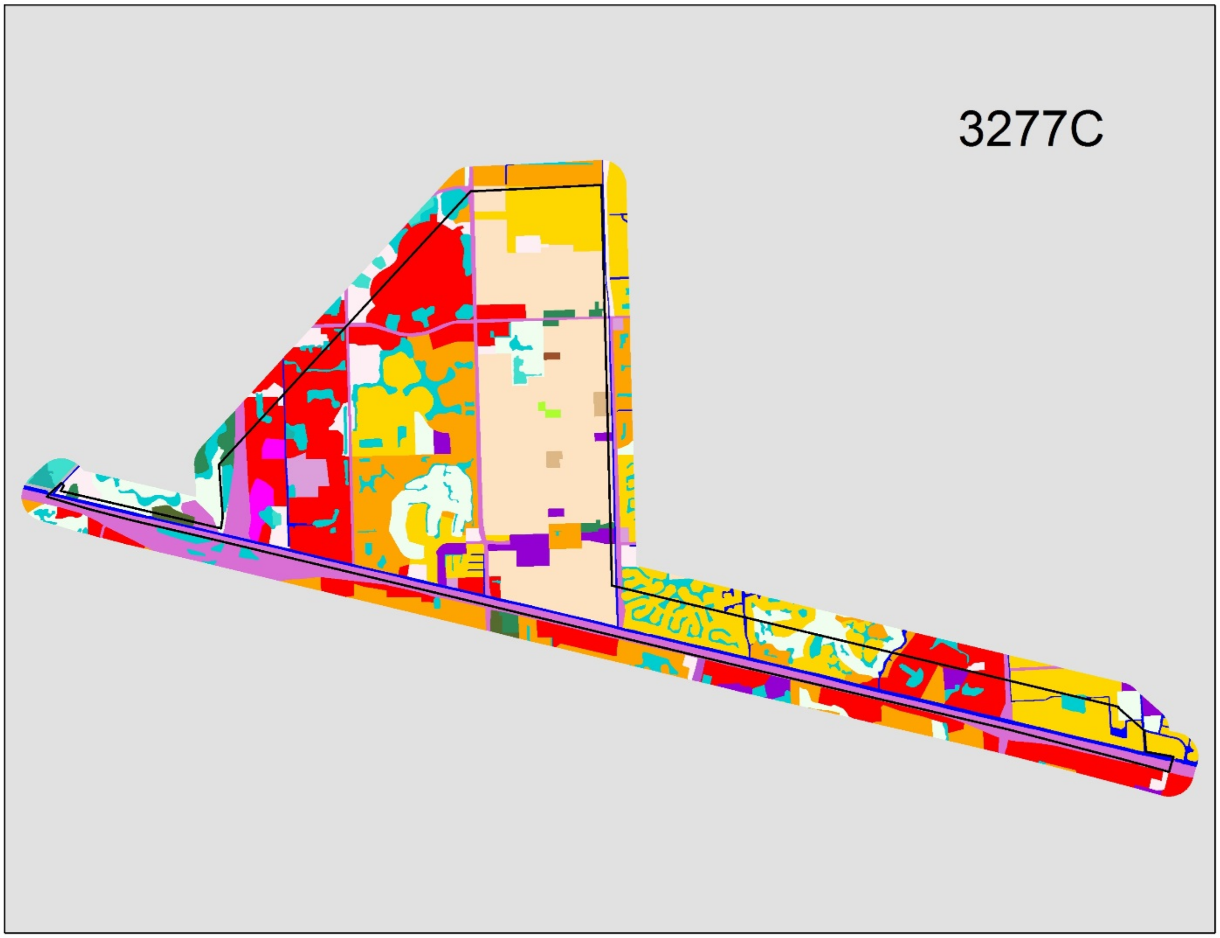
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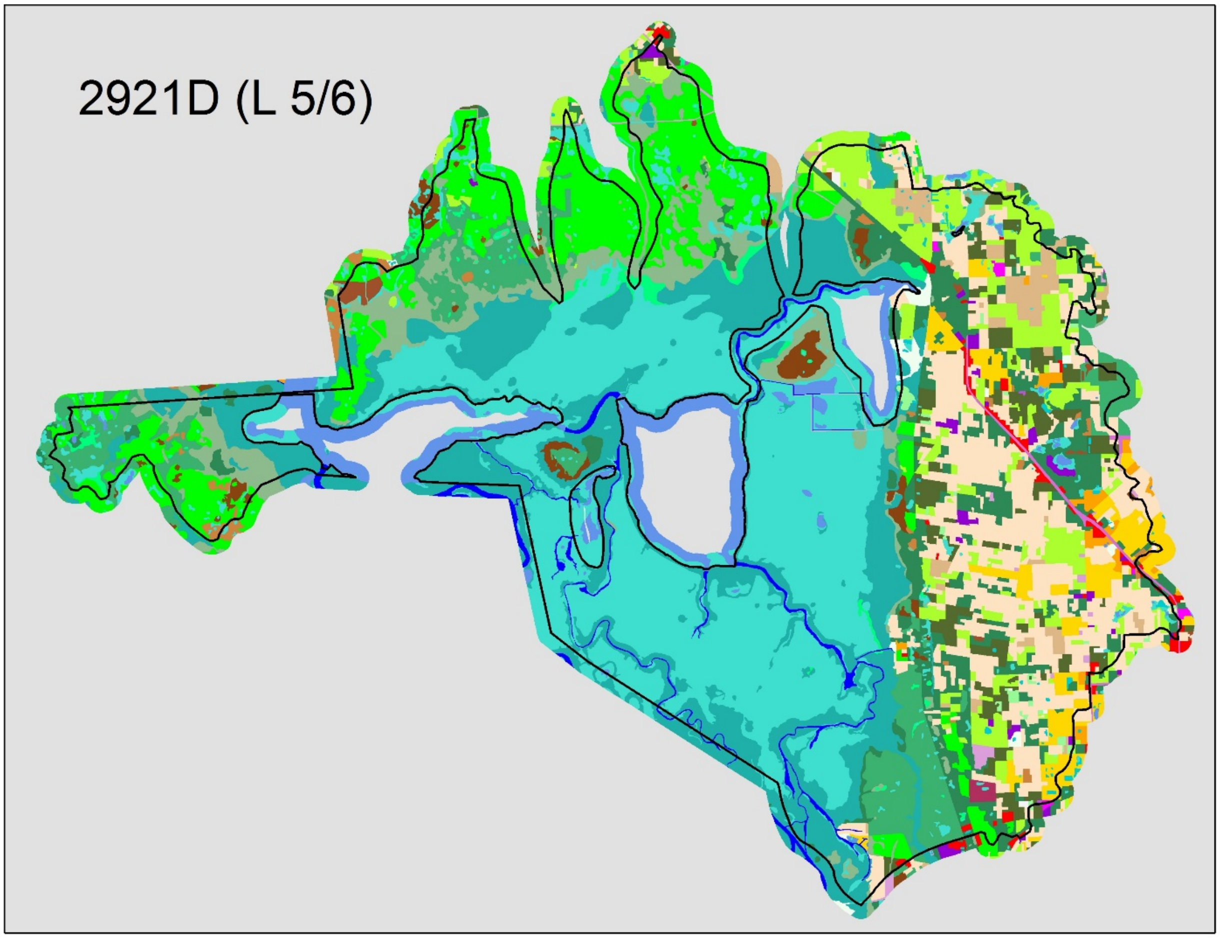
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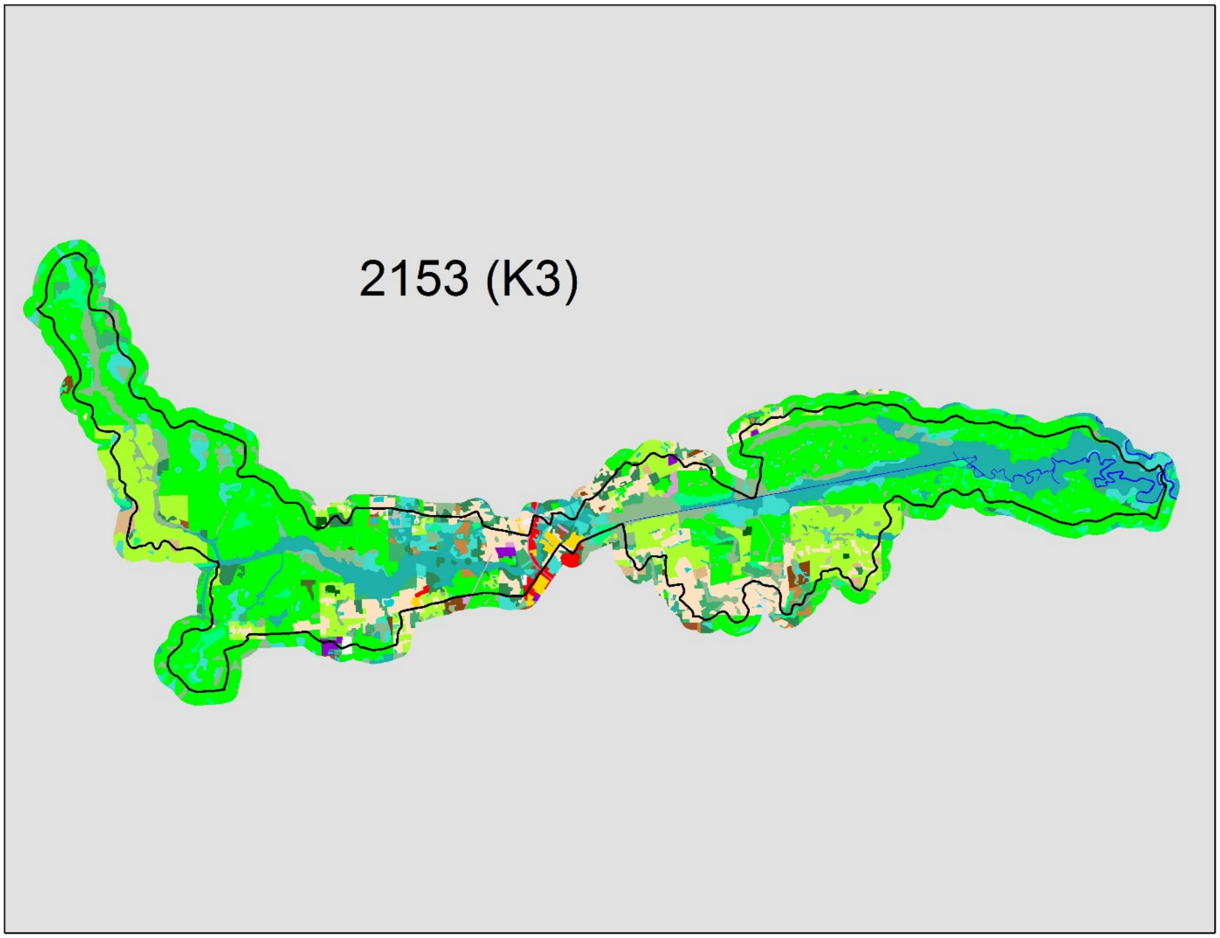
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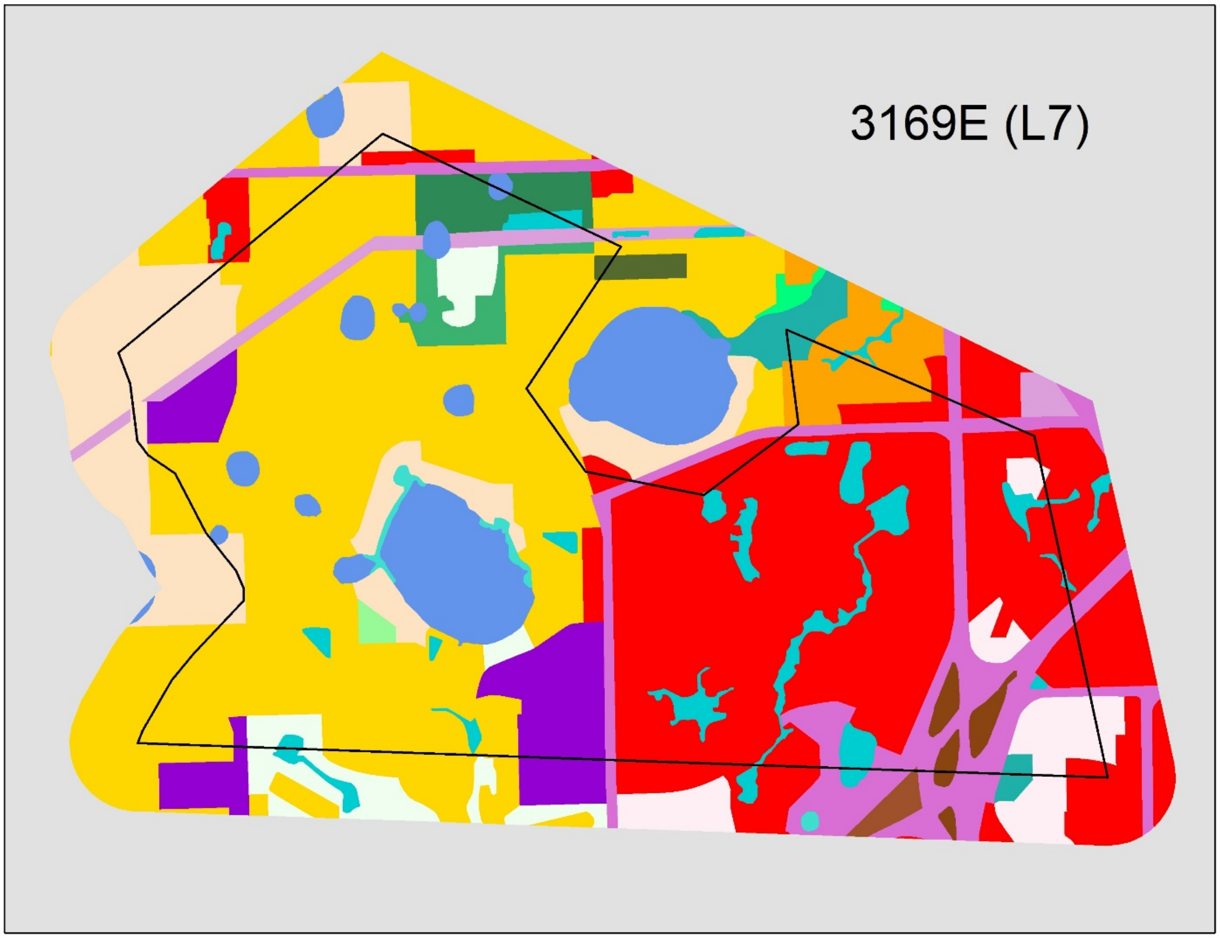
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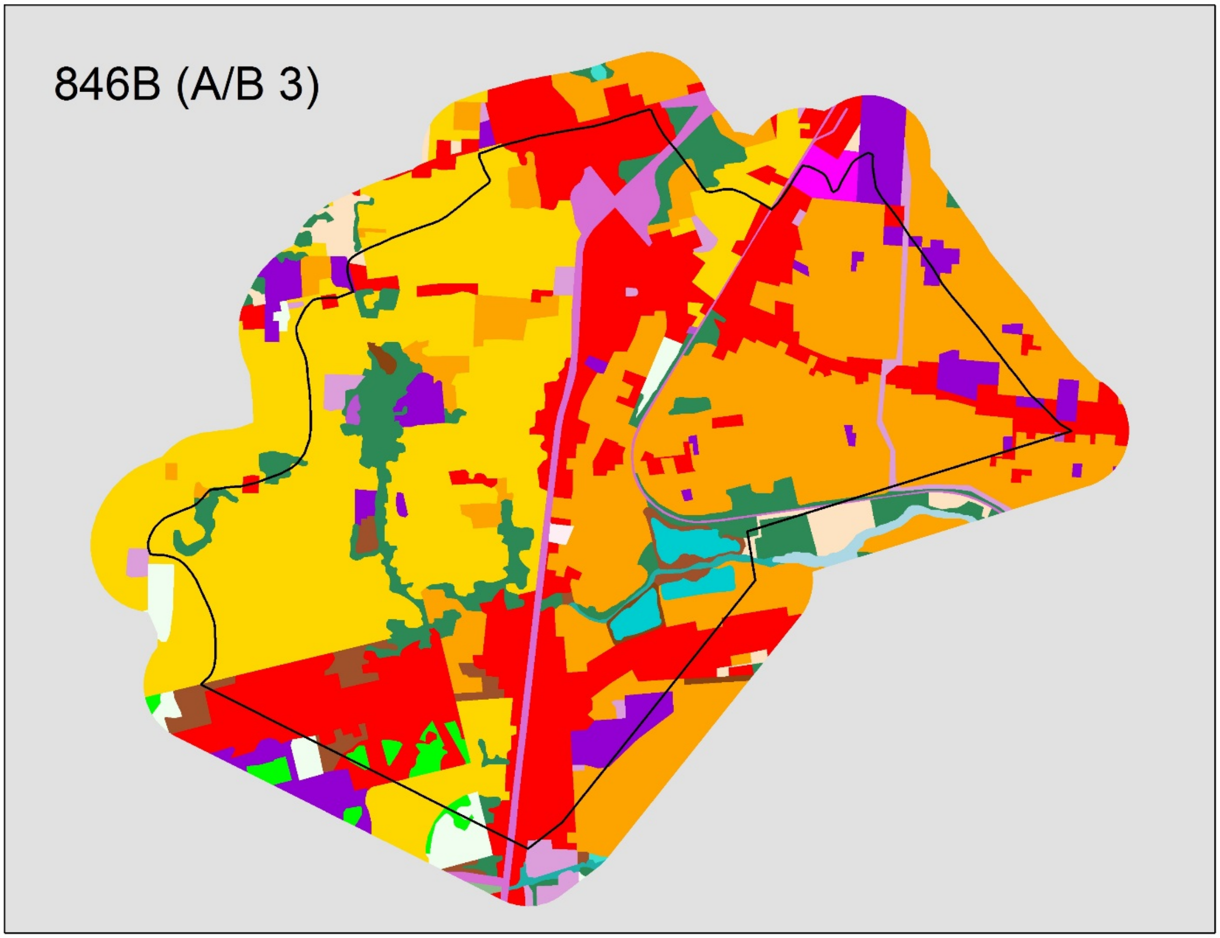
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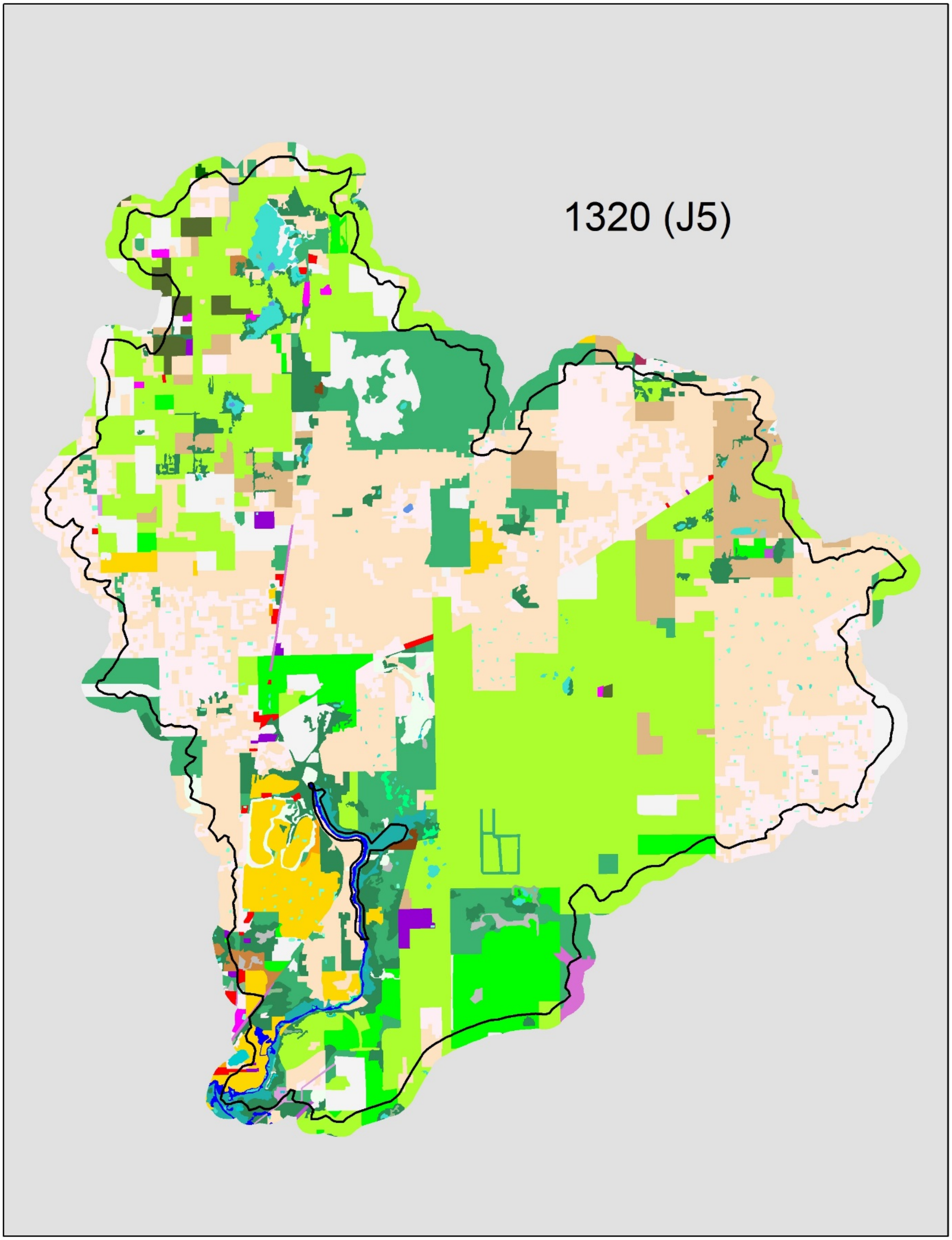
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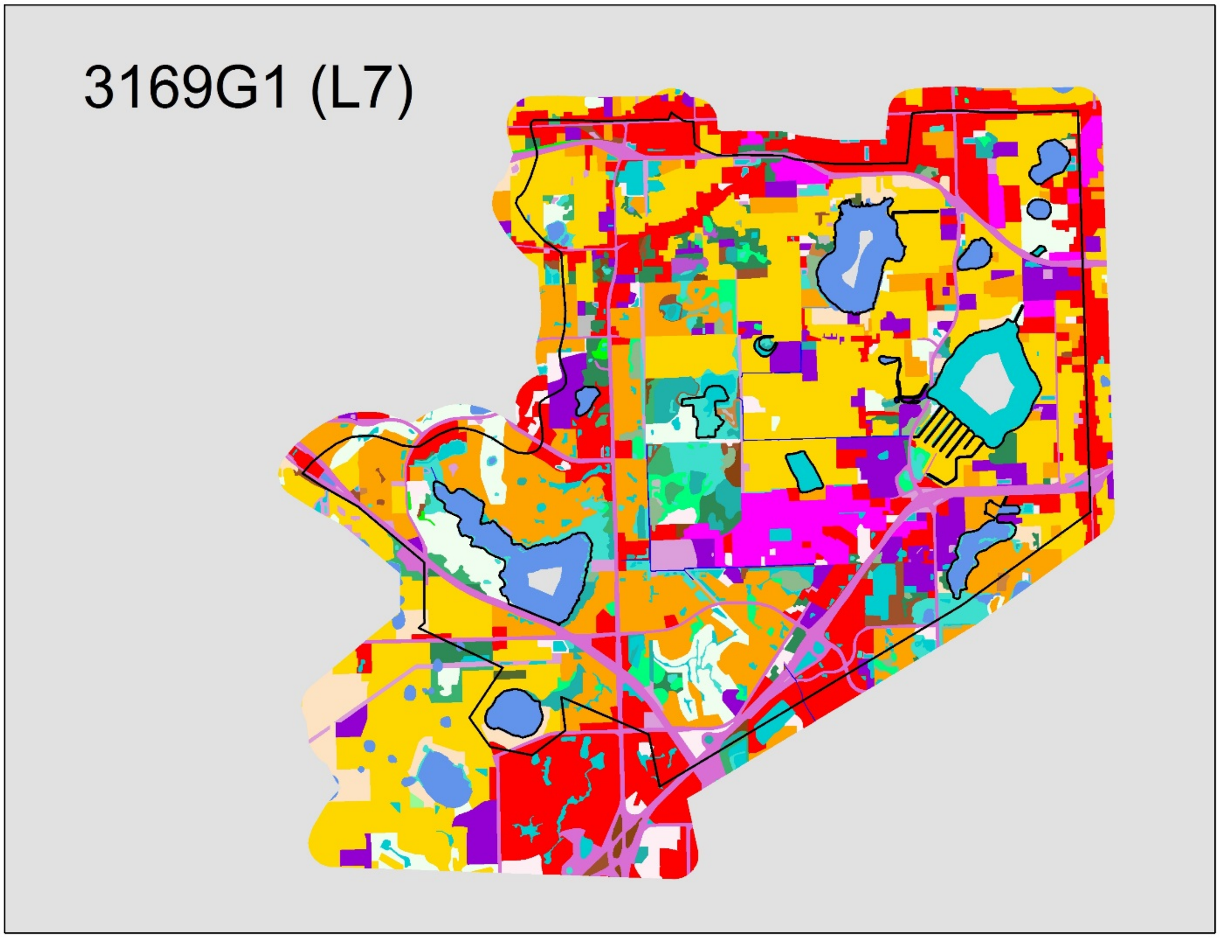
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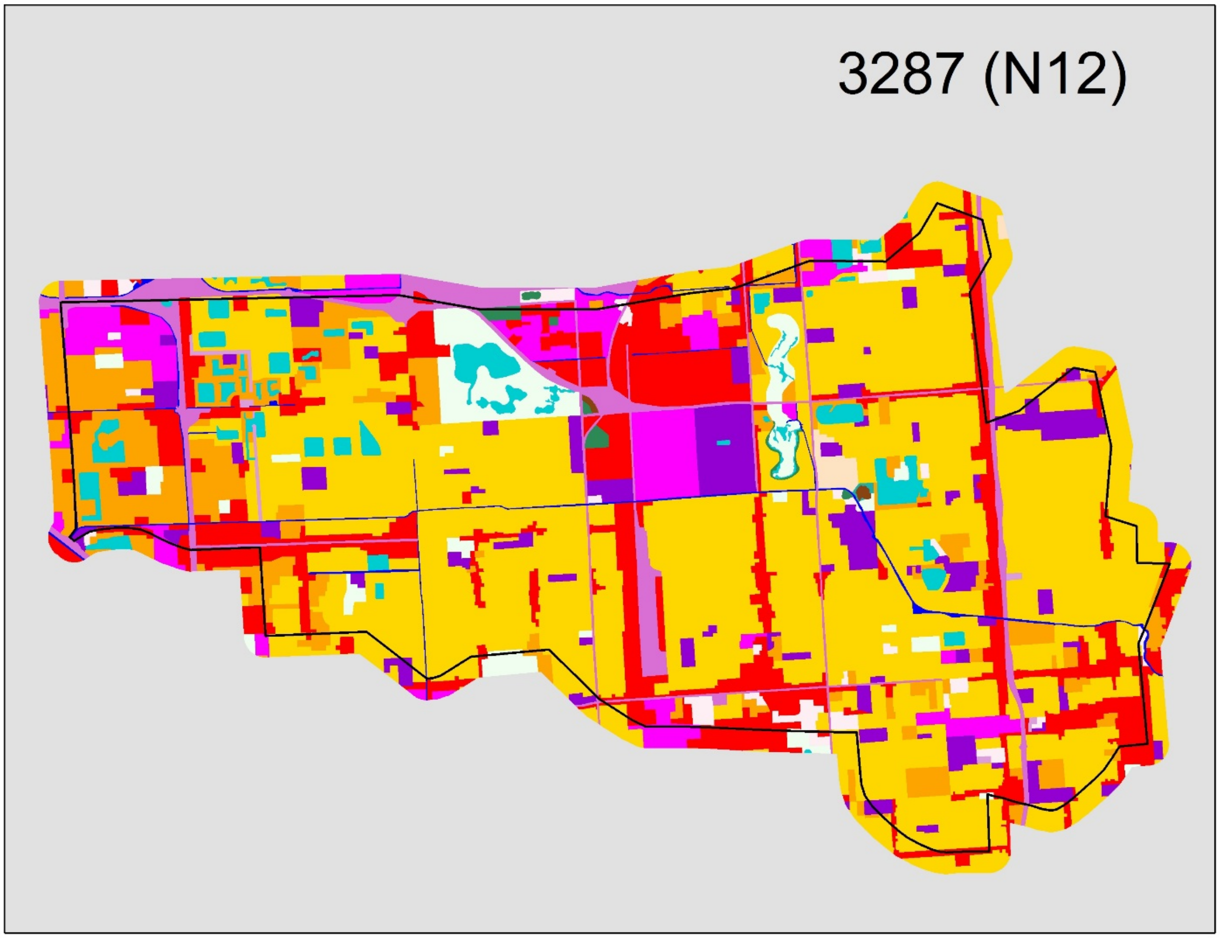
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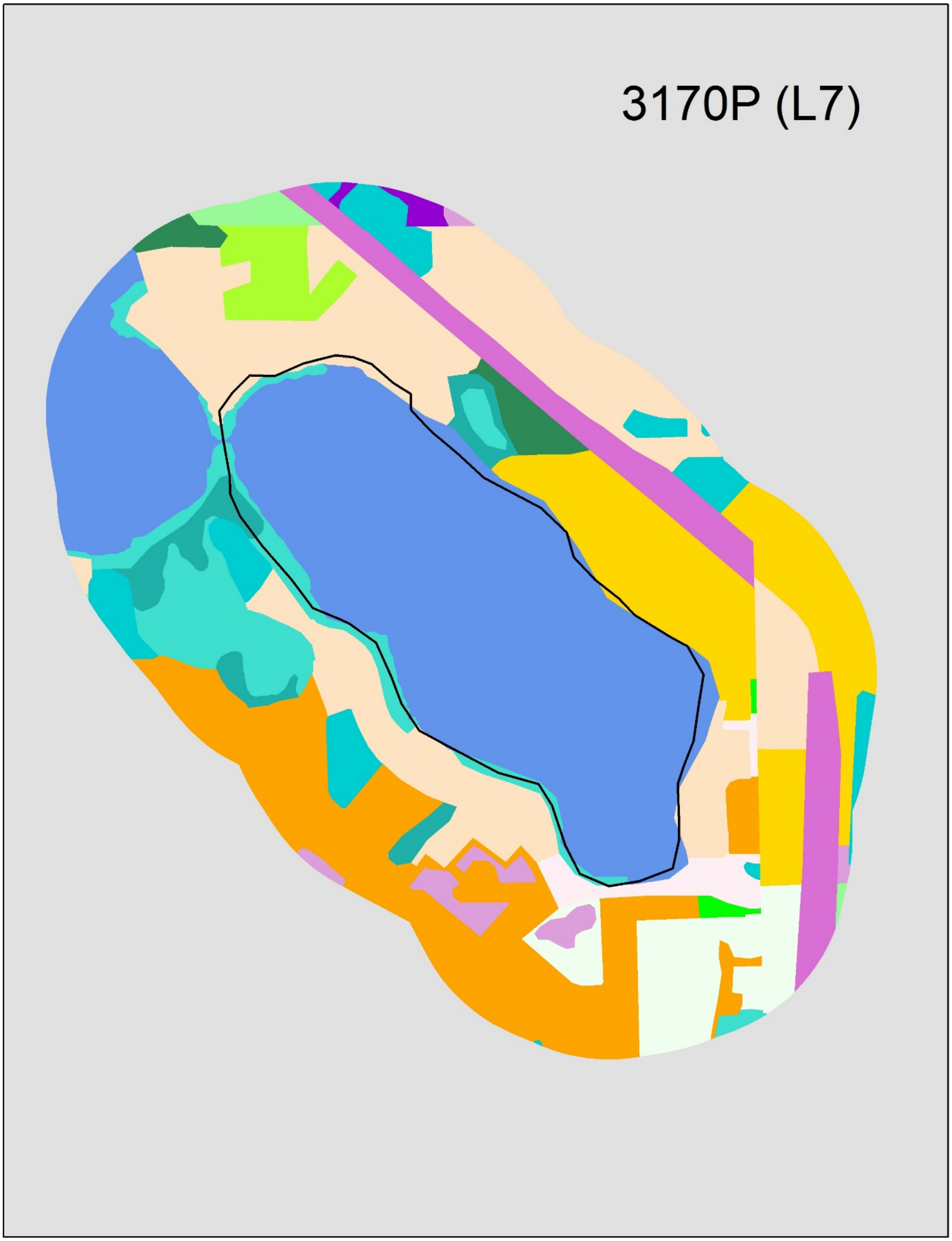
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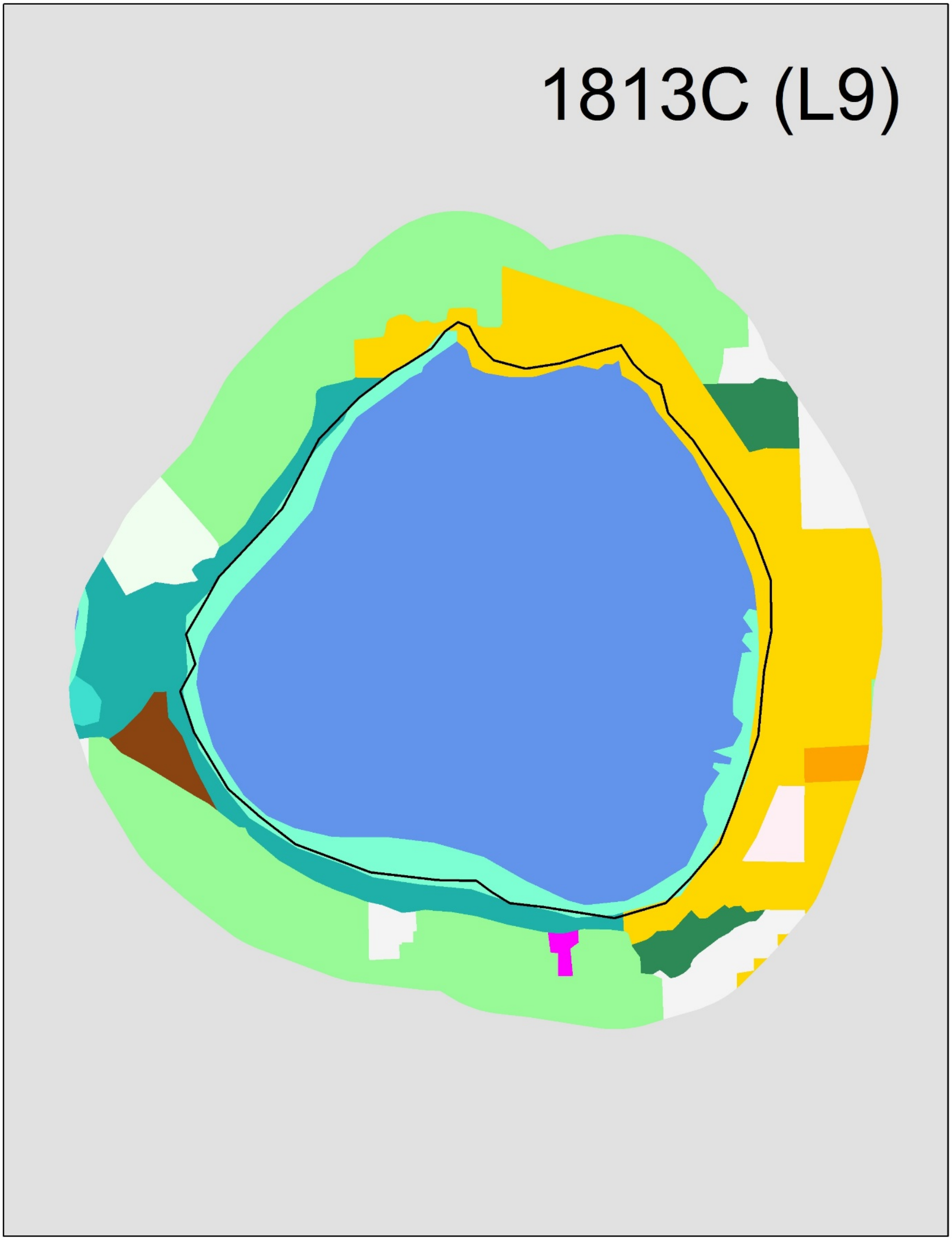
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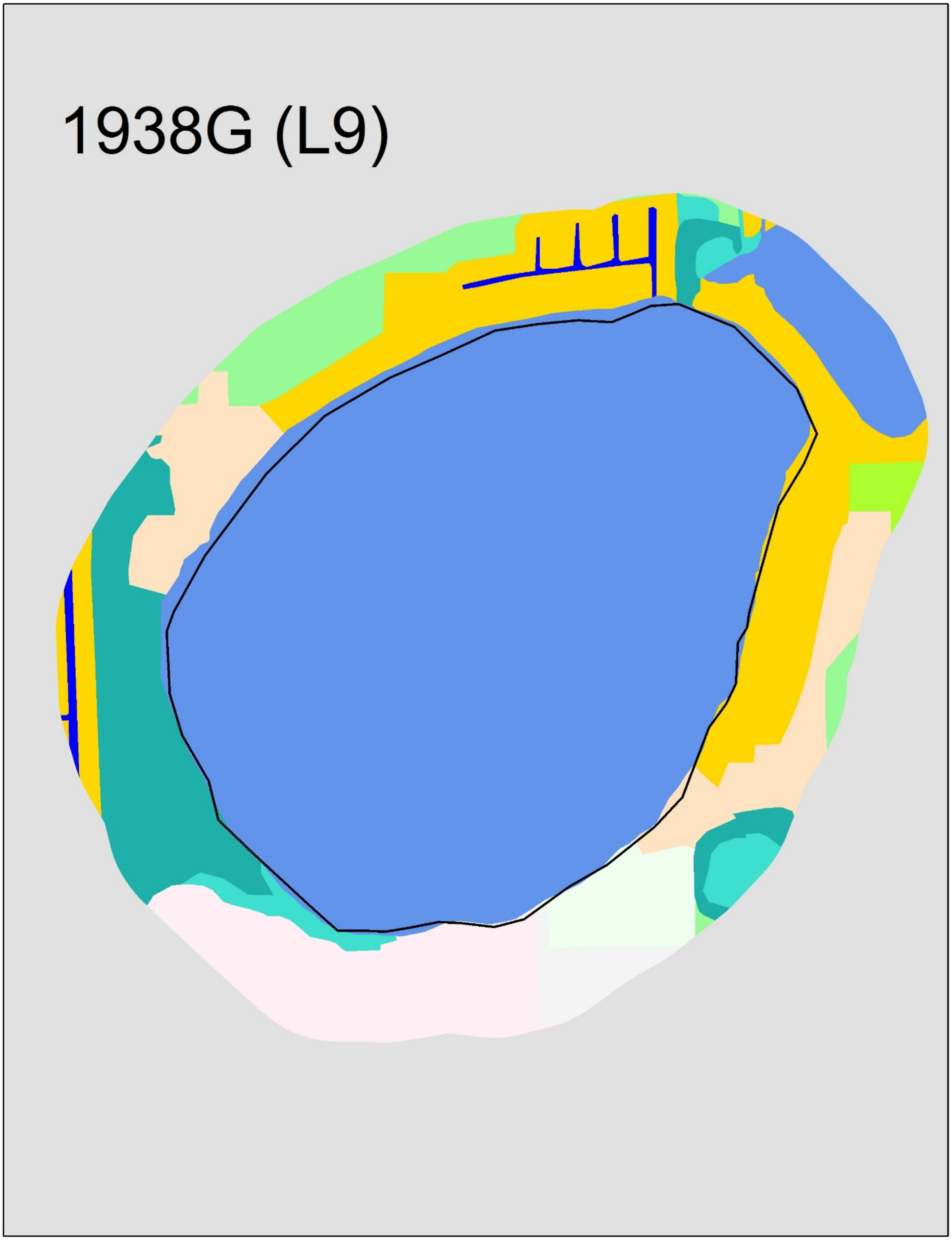
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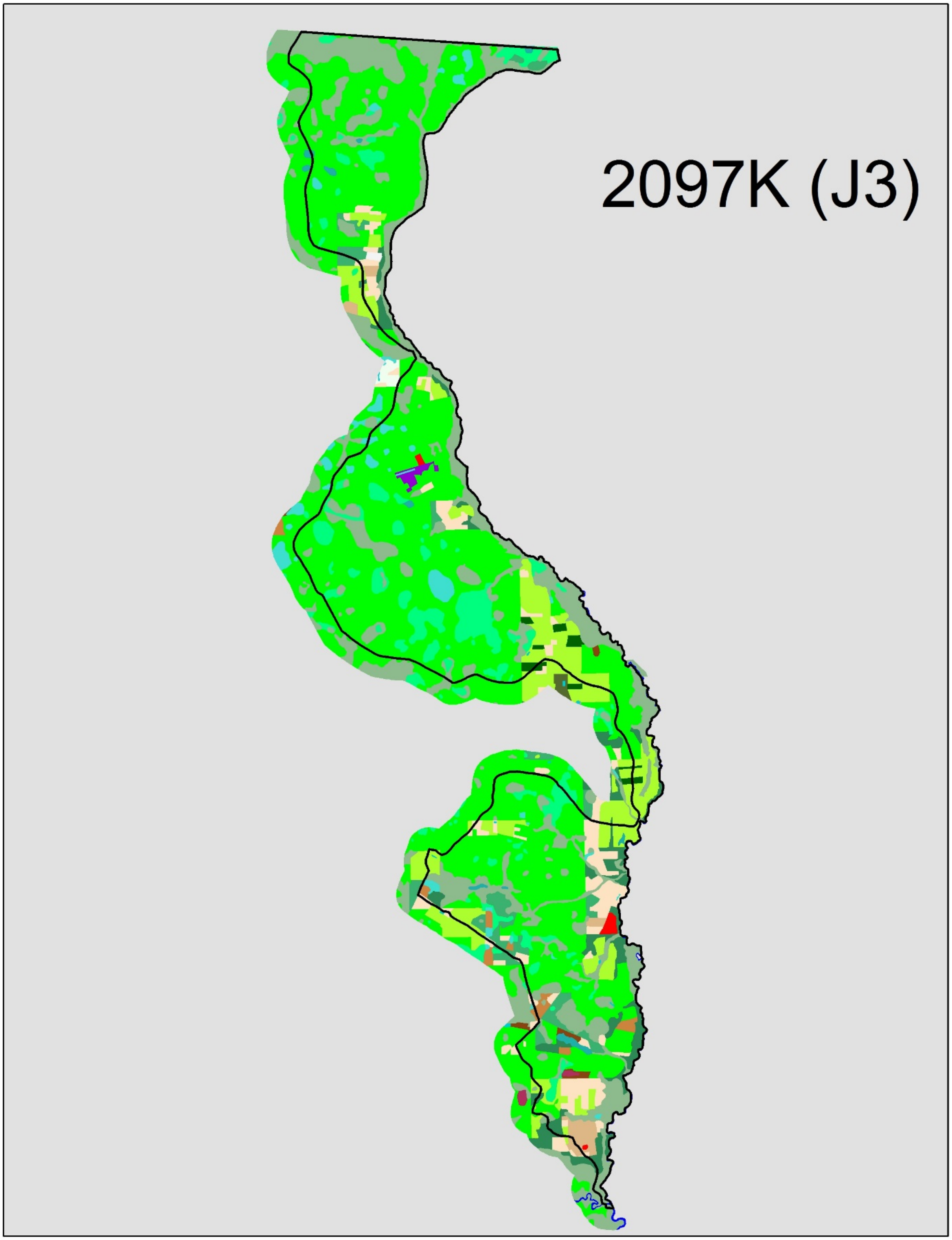
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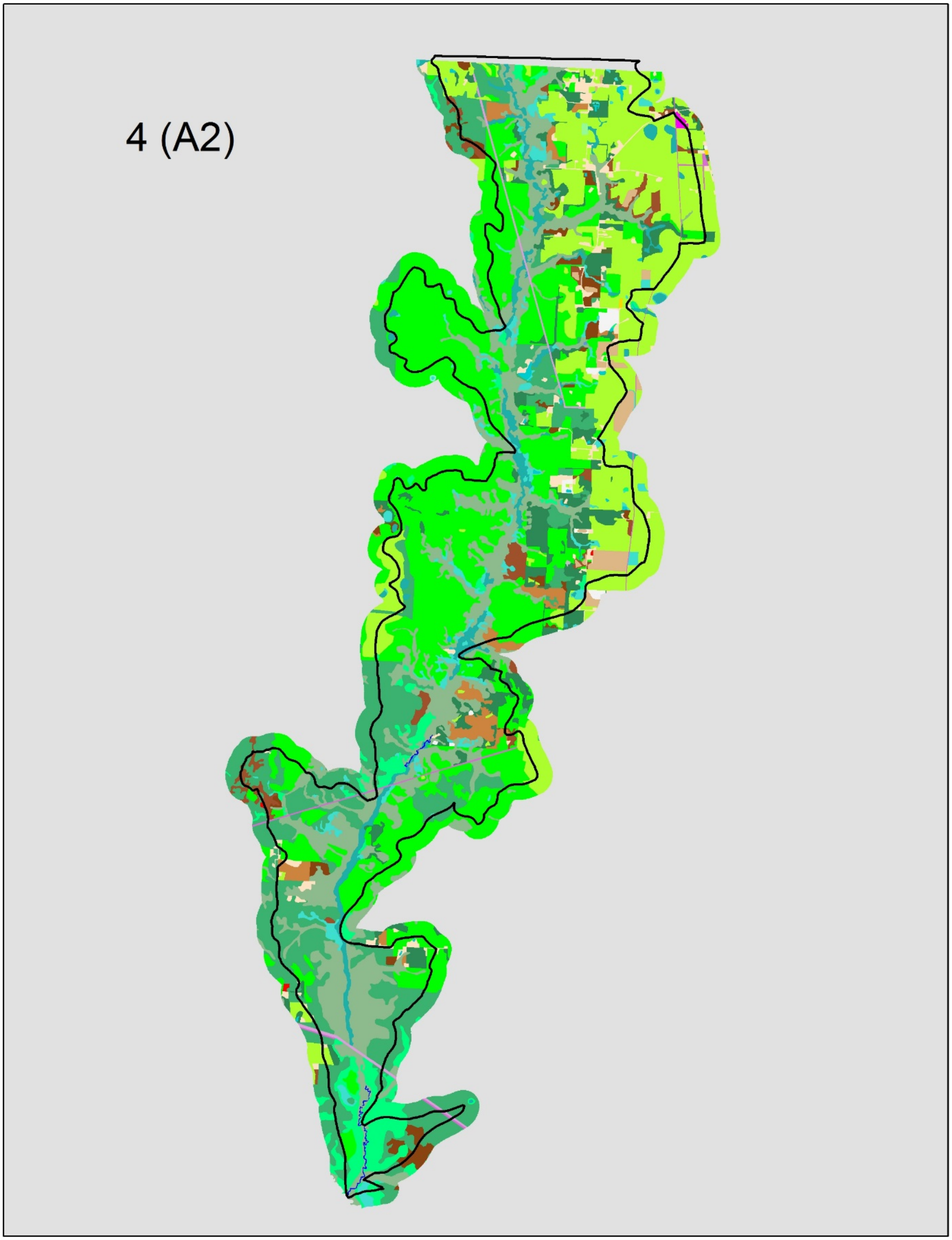
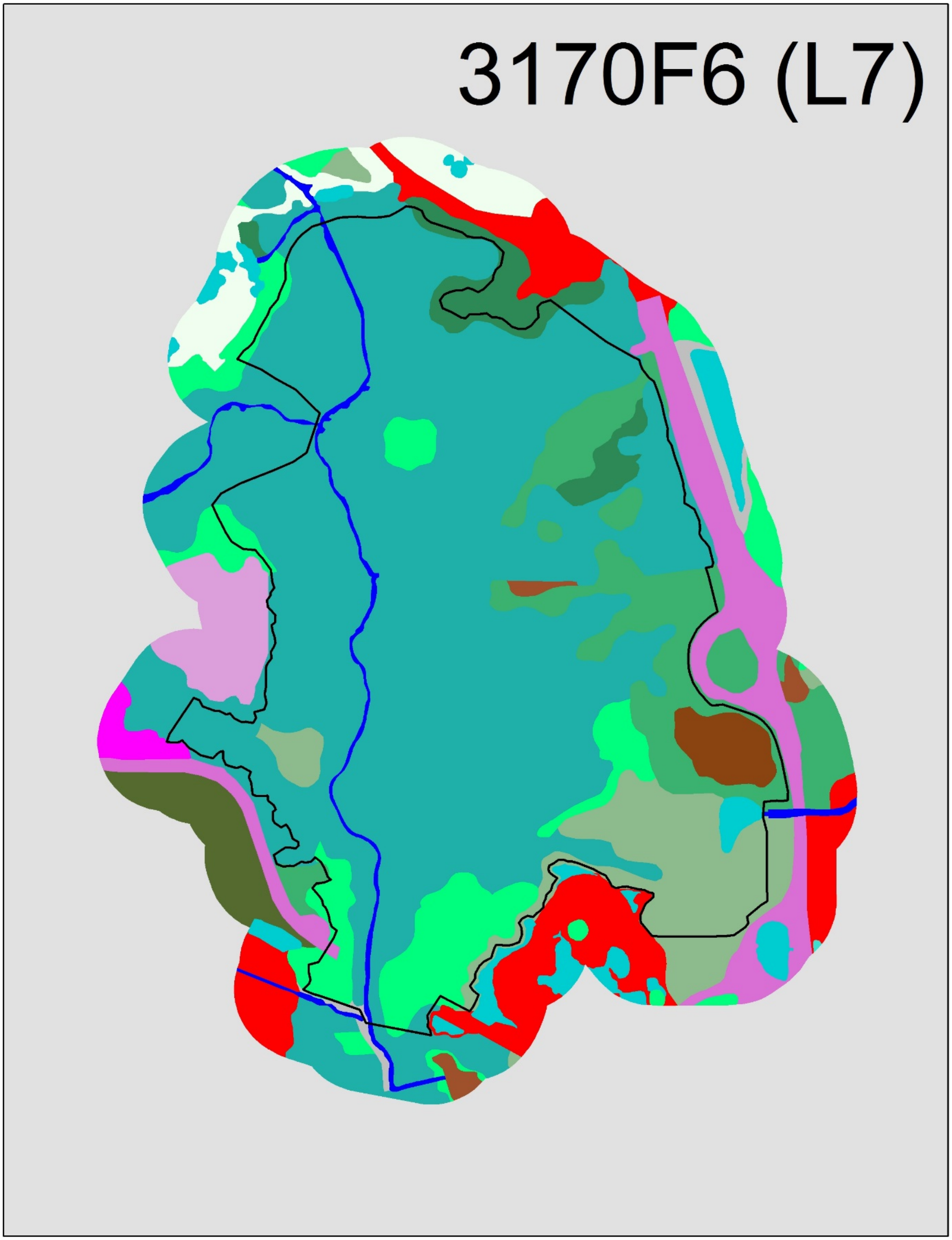

4 (A2)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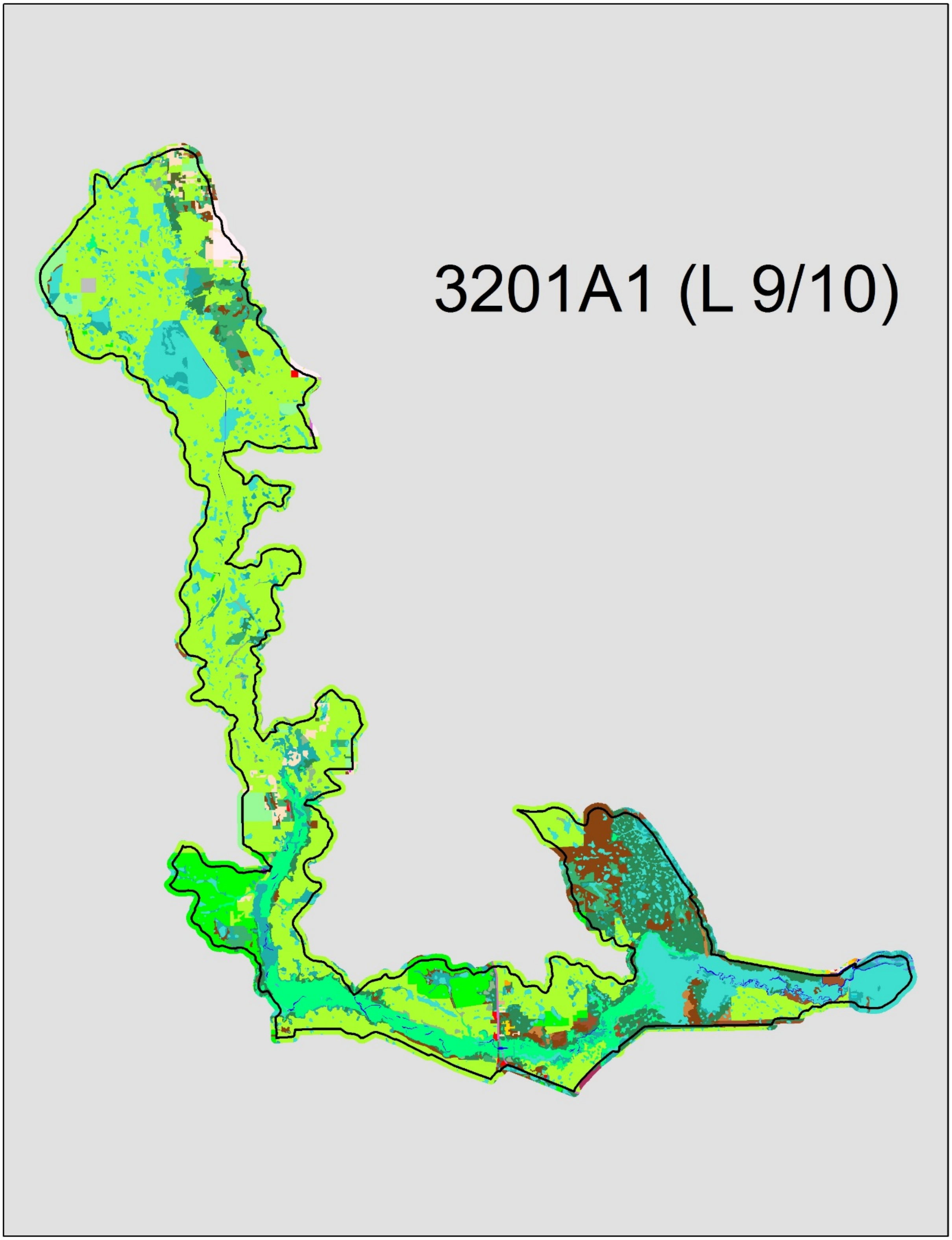
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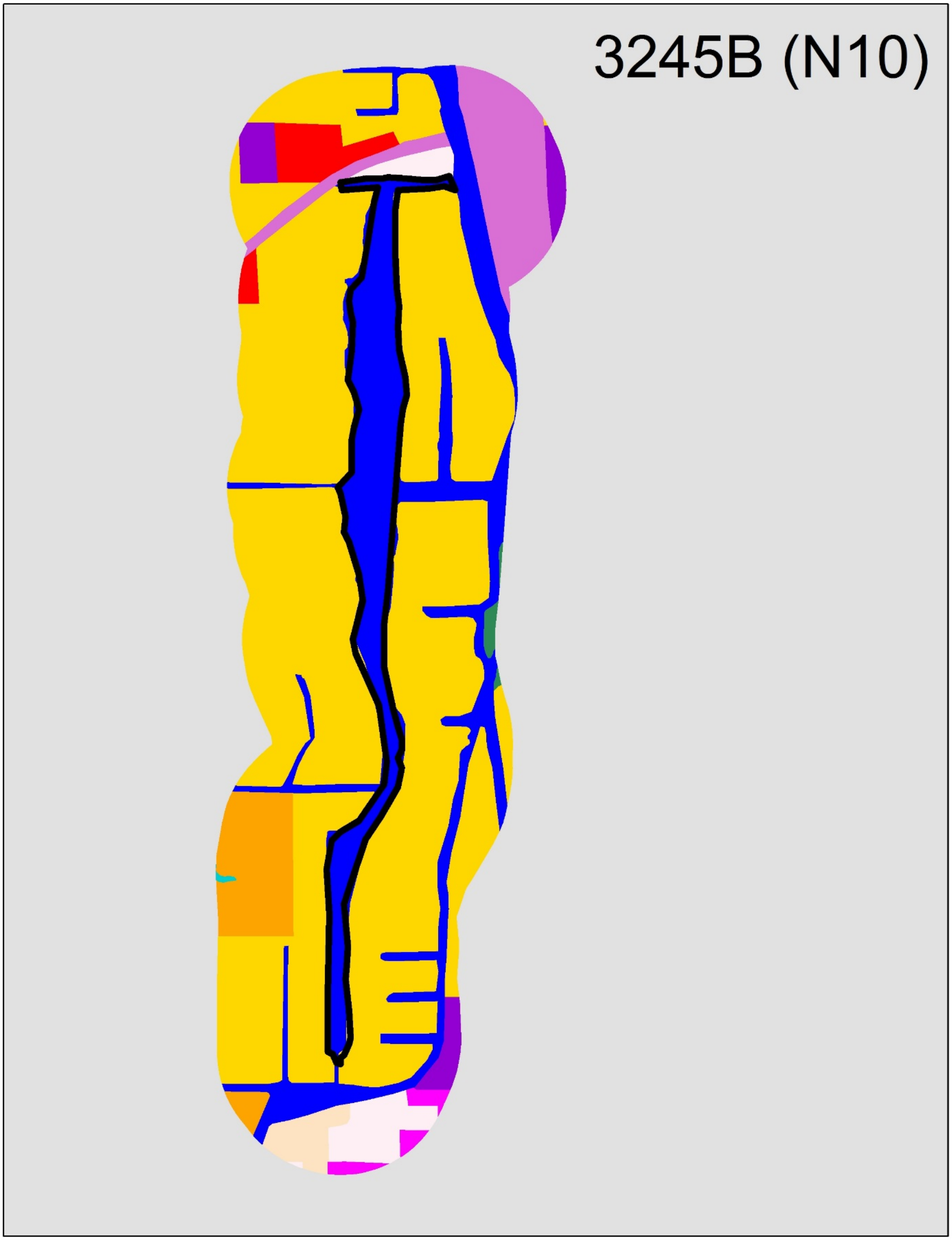
3245B (N10)