Supporting Information

Statewide Surveillance and Mapping of PFAS in Florida Surface Water

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Supporting Information 1: Example of Sampling Instructions Provided to Student/Citizen Samplers

Sampling instructions:

*Please do not sample alone. Please be careful, if needed, we can always alter sampling plans and sites. Watch out for weather, wildlife and other water hazards. Make sure to avoid wearing makeup, personal care products and clothing (and other materials) which might have water/stain resistant chemicals. Please read sampling guidelines document (Pace Field Sampling Guidelines, https://info.pacelabs.com/pfas-sampleguide) about what not to wear or use during sampling water. Avoid sampling on days after heavy rain (make note of rain events in excel file). For a video on how to collect the samples from our laboratory, please watch this video:

https://m.youtube.com/watch?v=rA_rOWuP4lg

In brief, at the site, use a grabber to hold the bottle just below the water surface, rinse out the bottle with lid off at least three times with surface water. Then, fill up the bottle 90% full and cap. On the cap (using super permanent sharpie provided), write down your initials, date, and unique sample number in permanent sharpie (take any notes as necessary). For field blanks, pour the PFAS-free water into the empty blank water bottle, cap and treat like rest of samples. Please note that at each site, you need to collect two 250 mL bottles and 1 50-mL vial. When at each site, please record date/time, site #ID, GPS coordinate, and take pictures with your phone. To keep pictures organized, one idea is to take a picture of the labeled bottle, then site photo, then repeat (this allows you to keep pictures organized by site ID). When sampling is finished, please freeze the bottles standing up in freezer or place in a fridge (if neither are an option, then at least keep out of sun and heat and in a cool/dry place). Please keep me updated on your progress and if you have any questions or concerns. When sampling is concluded, we will then discuss options to get the samples and sampling equipment back to Gainesville.

Supporting Information 2: Detailed SPE Workflow

The SPE cartridges were attached to a 24-port vacuum manifold and pre-conditioned with 4 mL of 0.3% ammonium hydroxide in methanol, 3 mL of methanol, and 4 mL of acetic acid/ammonium acetate aqueous buffer solution. PFAS-free tubing affixed to cartridge caps were attached to each of the cartridges on the manifold. The other end of each piece of tubing was placed directly into the sample bottle, and a low vacuum was initiated to allow the sample to pass slowly (approximately 1 drop per second) through the cartridge. Once all of the sample had passed through their respective cartridges, the tubing/caps were removed. The cartridges were then washed with 4 mL of the buffer solution to remove any salts and further purify the extracts. Then, full vacuum was applied for 15 min to dry the cartridges. After drying, 15 mL Falcon tubes were placed inside the vacuum manifold under each cartridge to capture the eluent. PFAS were eluted with 4 mL of methanol and 4 mL of 0.3% ammonium hydroxide in methanol for a final elution volume of 8 mL. Before the extract was removed, full vacuum was applied for 15 min. The samples were then concentrated to 1 mL using nitrogen evaporation, with 200 μL of each extract transferred to polypropylene autosampler vials for mass spectrometric analysis.

Supporting Information 3: Data Processing Workflow for PFAS Automated Quantitation (PAQ)

This data processing workflow, PFAS Automated Quantitation (PAQ), was built in R version 4.3.2 to *automate the quantitation of target PFAS in large data sets* via isotope dilution. The workflow is publicly available in Github (https://github.com/alex-antonison/PFAS-Automated-Quantitation). Briefly, PAQ takes the resultant data (as obtained below) and automatedly performs quantitation across data sets (and batches), as described below, with considerations regarding quality control. An internal standard of known concentration is spiked into samples prior to extraction. Additionally, a calibration curve is built by preparing a series of synthetic samples (i.e. calibrant solutions) of increasing concentration of target analytes with a constant concentration of their corresponding internal standards. These solutions are randomly distributed within the sample queue for data acquisition. The peak areas (i.e. signal response) for target analytes and internal standards, in the calibration solutions, are then utilized with their known concentrations to build curves for each target analyte. These calibration curves are then used to evaluate the concentrations of target analytes in unknown samples using their peak areas and the known amounts of internal standards spiked into each sample. Various quality assurance measures (blank filtering, percent recovery, evaluating the precision and accuracy of QC samples, etc.) can be evaluated once concentrations are quantified. After all calculations have been made, additional logic in the workflow allows for these concentration values to be normalized to the amount of material extracted and set to a specified unit. Then, any desired qualitative information can be linked to the quantitative data before it is organized into an output file. Validating the success of the processing method was achieved by comparing the resultant data of a sample set quantified by hand to the resultant data of the same sample set pushed through the developed automated quantitation method. The automated workflow was able to produce the same resultant data, in addition to showcasing the reproducibility that was not equally achieved when quantitation was performed by hand. This processing method utilizes several types of data/information files that will typically be unique each time a new project/data set is to be analyzed. For example, the logic for generating a calibration curve is embedded into the code of the processing method, but most studies will have unique calibration curves. Thus, a file containing relevant information about the calibration curve used in a specific study (e.g. concentration data) will need to be provided by the end user to successfully generate a curve. The largest file type is typically the raw data being quantified. There are also multiple steps throughout the workflow that require source files; these can contain internal standard concentrations, calibration curve concentrations, qualitative information about the samples, etc. Mapping files (generally for naming) are also utilized to join different files together and configuration files were implemented to have adaptability within the workflow to accommodate multiple data sets. In addition to requiring source files along with the raw data, the workflow also produces its own files which are carried through the process and implemented at different steps, allowing the workflow to be continuous.

Supporting Information 4: Florida Heat Map Modeling

A spatially enhanced excel dataset containing all surface water samples with at least one PFAS measured >LOQ (n=2,056), along with their locations, was cleaned. The dataset's combined latitude and longitude column values were checked and reformatted in preparation for ingestion into a geographic information system (GIS). ESRI's ArcGIS Pro (AGP) version 3.1.3 was used to ingest the spatially enabled data table and create a GIS point shapefile. The shapefile was then exported and projected from latitude and longitude into the Florida modified Albers coordinate system, a coordinate system used by the Florida Geographic Data Library (fgdl.org). One extreme total PFAS value in Miami was removed from the spatial analysis. AGP was then used to explore the data's (n=2,055) total PFAS spatial autocorrelation. The exploration revealed there was a correlation between the data value and its location, and that the data was clustered, Moran's Index 0.19, z-score 20.16, p-value <0.001. Eight new shapefiles, one for each of the eight parameters, were created from the projected shapefile. The point shapefiles and AGP's Natural Neighbors interpolation program were used to produce a predictive surface for each of the eight shapefiles. The Natural Neighbors interpolation method uses irregularly distributed measured values to predict a surface.[1,2]

Ancillary spatial data shapefiles were collected from FGDL and used in analysis. Those layers included state and county boundaries, American Community Survey demographics, airports, military facilities, and wastewater treatment plants (WWTP) permits. Since many of the sampled locations occurred in marine environments outside of the state boundary, the state outline layer was spatially buffered 12 km. The predictive surfaces were then clipped to the buffered state outline. Symbology for the predictive surfaces used the quantile method and varying class sizes based upon the number of records for each parameter. AGP's Generate Near Table function was used to collect the straight-line distance from each sampling location to the closest location in airports, military facilities, National Pollutant Discharge Elimination System (NPDES), and wastewater layers. The distances and nearest ancillary locations from the near tables were added to the cleaned excel dataset. Separate ancillary data maps were created that showed the facilities distribution. Airport density per square kilometer and WWTP density per square kilometer maps were also created. Sampled locations' PFAS layer value ranges were then displayed on the density maps to facilitate visual analysis.

A wastewater spill incident location table (n=11,007) was obtained (https://prodenv.dep.state.fl.us/DepPNP/reports/viewIncidentDetails?page=1) and modified. Spill gallons per incident report were extracted and added to a new column. Columns qualifying the type of spill were defined and populated. Incidents were classified as either: Raw Sewage, Untreated/Partially WW, Various Liquids, Treated WW/Reclaimed, and Processed Sludge/Biosolids. Prior to ingesting in GIS, the table was cleaned and eliminated 49 records where locations were either more than 1,25 km away from the Florida boundary layer or were in a different state. Additional records were deleted that had no coordinates or were duplicates. Separate GIS point layers were created for each incident type and whether the incident type occurred before 2022. Each layer's points were buffered 2km and the buffer's boarders were dissolved to create larger polygons around groups of points. Aggregated gallon summary statistics of points that fell within the buffer were calculated and added to the polygons. Polygon spill volume maps by type and year range (all years, or before 2022) were created using 10 classes and natural breaks (Jenks).

References

(1) ESRI. *How Natural Neighbor works*. https://pro.arcgis.com/en/pro-app/latest/tool-reference/spatial-analyst/how-natural-neighbor-works.htm#GUID-81A67F31-5180-4721-AF52-BCE7B6AFB761%20Accessed%2011/7/2023 (accessed 2023-11-06).

(2) Sibson, R. A Brief Description of Natural Neighbour Interpolation. In *Interpreting Multivariate Data*; John Wiley & Sons: New York, 1981; pp 21–36.

Supporting Information 5: List of Additional PFAS Monitored in Study and not Part of EPA Method 1633

These additional PFAS beyond EPA Method 1633 (and their respective frequencies detected >LOD) included perfluorobutane sulfanomide (FBSA, 11%), perfluorohexylphosphonic acid (PFHxPA, 16%), FHxSA (2%), sodium bis(perfluorohexyl)phosphinate (6:6PFPi, <1%), perfluropropanesulfonic acid (PFPrS, 5%), perfluoro-4-methyloctanoic acid (P4MOA, 2%), n-decafluoro-4-ethylcyclohexanesulfonic acid (PFECHS, 3%), 7H-perfluoro-4-methyl-3,6-dioxaoctanesulfonic acid (Syn32), perfluorobutanesulfinic acid (Syn34), perfluoro-3,7-dimethyloctanoic acid (Syn35), perfluoro-3,6-dioxaoctane-1,8-dioic acid (Syn40), dodecafluorosuberic acid (Syn45), perfluoro-3,6,9-trioaundecane-1,11-dioic acid (Syn53), potassium perfluoro(4-methyl-3,6-dioxaoctane)sulfonate (Syn72), 7H-dodecafluoroheptanoic acid (Oak6), hexadecafluorosebacic acid (Oak8), and 9H-hexadecafluorononanoic acid (Oak10).

Supporting Information 6: Determination of PFAS Mass Release from WWTP Spill Events

This section outlines the steps taken to estimate the mass release of PFOA and PFOS from reported WWTP spill events. In short, this was done by multiplying the concentration of PFOA and PFOS within WWTP influent, effluent, and sludge by the reported volume of these matrices spilled (https://prodenv.dep.state.fl.us/DepPNP/reports/viewIncidentDetails?page=1). Influent was considered as raw sewage and untreated/partially treated WW spill reports. Effluent was considered as treated WW spill reports. Wet sludge was considered as solids/sludge spill reports. The concentrations of PFOA and PFOS in effluent were sourced from a meta-analysis of 68 WWTPs between 2013 and 2020, excluding industrial sources (Thompson et al., 2022). The same study also provided similar values for influent, albeit with less data available (less than 30 WWTPs). Additionally, this study offered data for dry sludge. However, it's highly improbable that dry sludge would be spilled during these events since WWTPs typically do not manage the drying of sludge past a 5% solids content. Thus, for more conservative calculations, it was assumed that all spilled sludge had a 5% solids content. The concentration was then adjusted from a dry basis to a wet one by multiplying the average sludge concentration of these compounds by 0.05 to account for dilution with water prior to drying. The concentrations and the volumes used as well as the mass of PFAS calculated are presented in Supporting Information Table S10.

Supporting Information Figure S1. Surface water sampling kit, which included a reach/grabber tool, 3 HDPE bottles (250 mL), one for collection of surface water, one that was filled with Optima water used for field blank and last bottle was the clean bottle used to pour the Optima water into to serve as the field blank. A 50-mL falcon tube was also collected for a separate study.

Supporting Information Figure S2A. Geographical representation of all Florida counties (n=67)

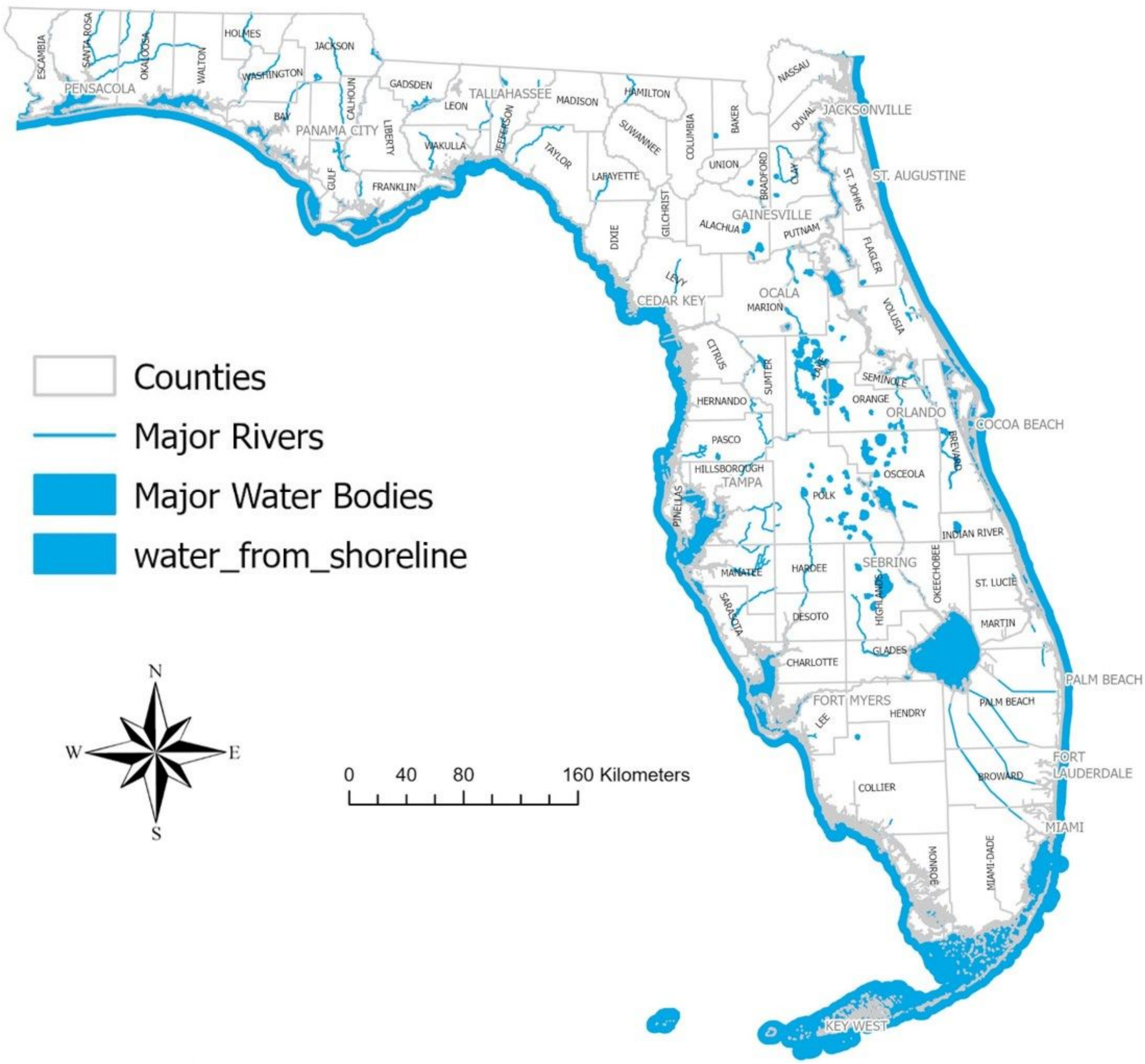
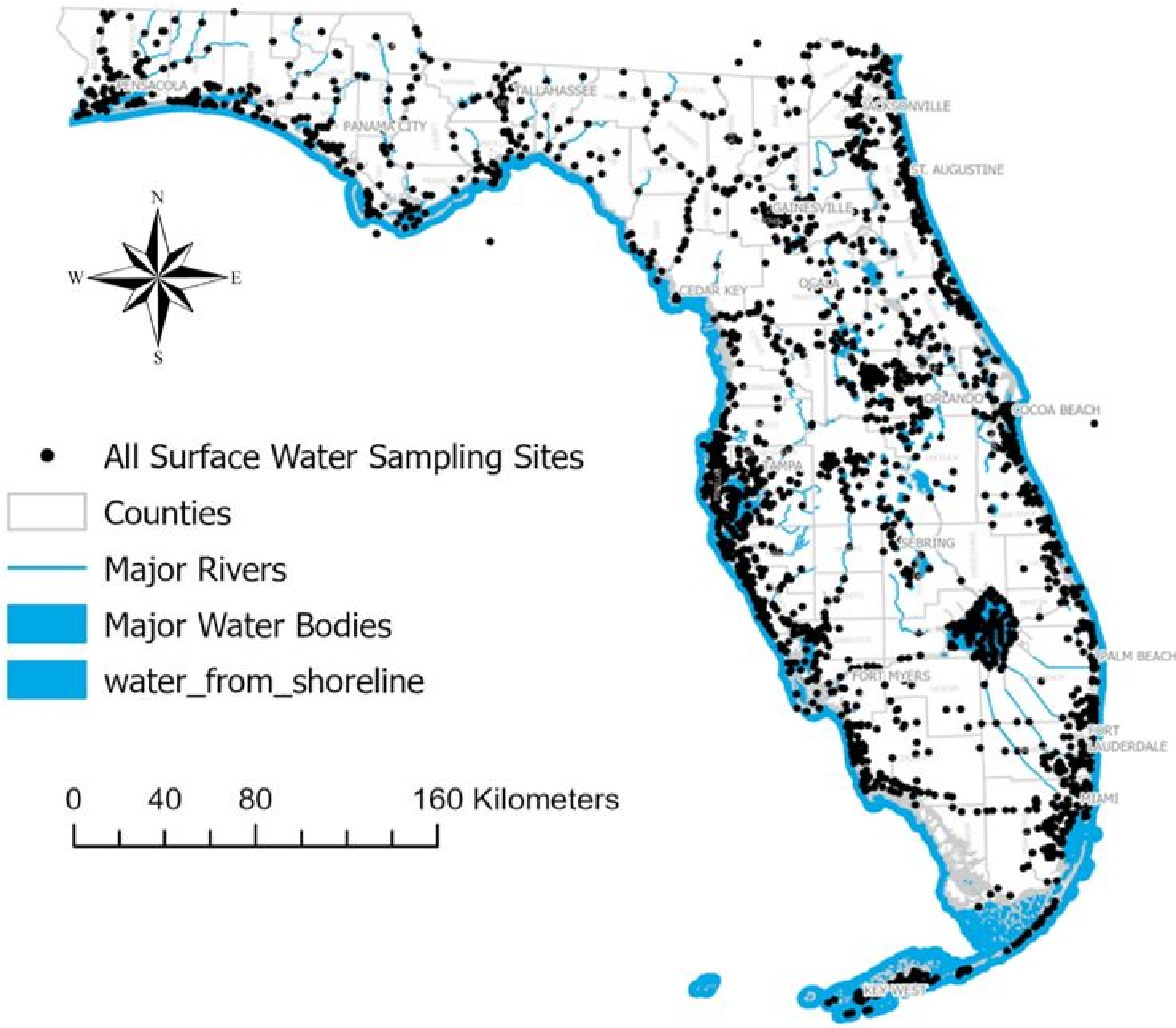
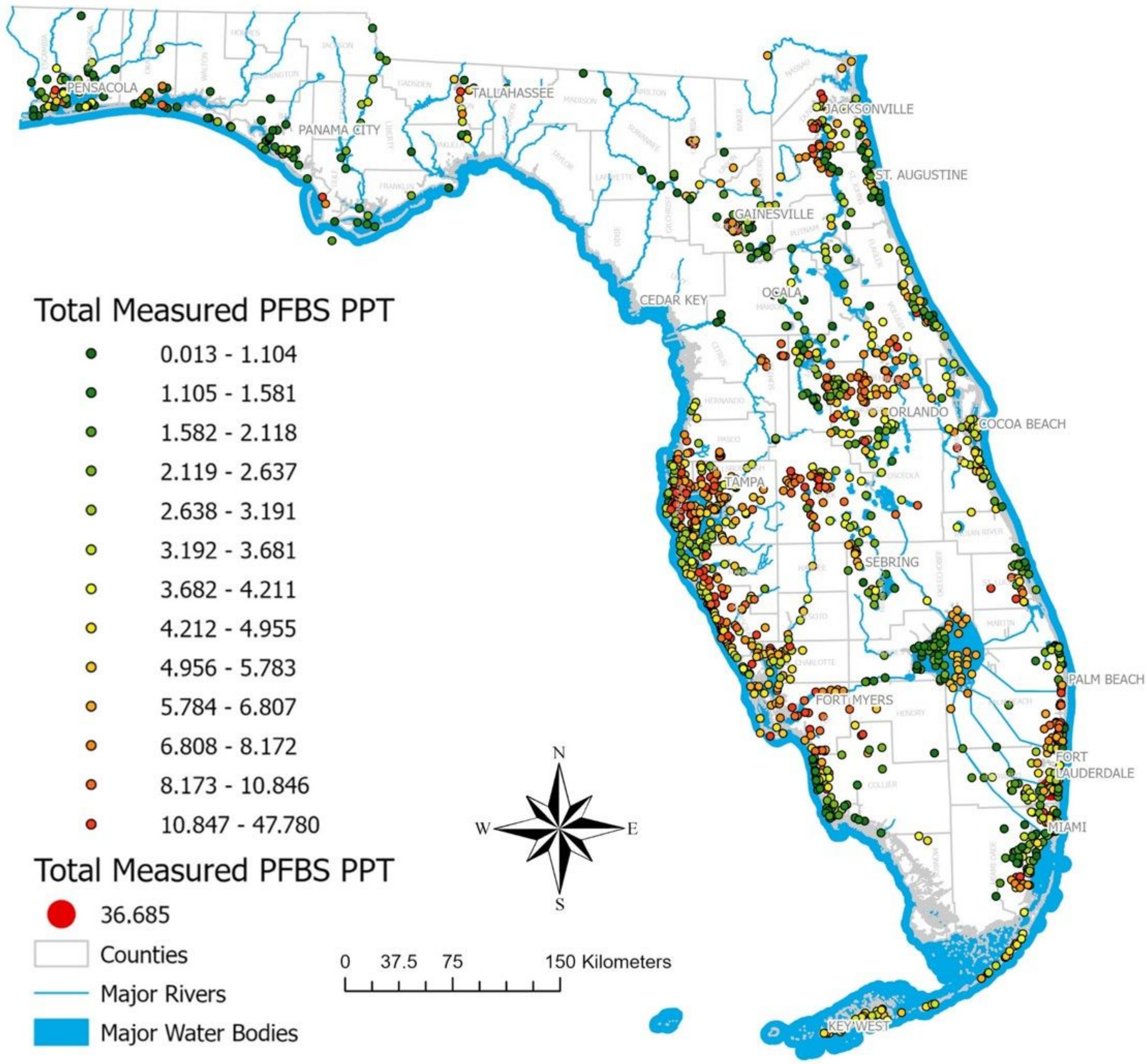


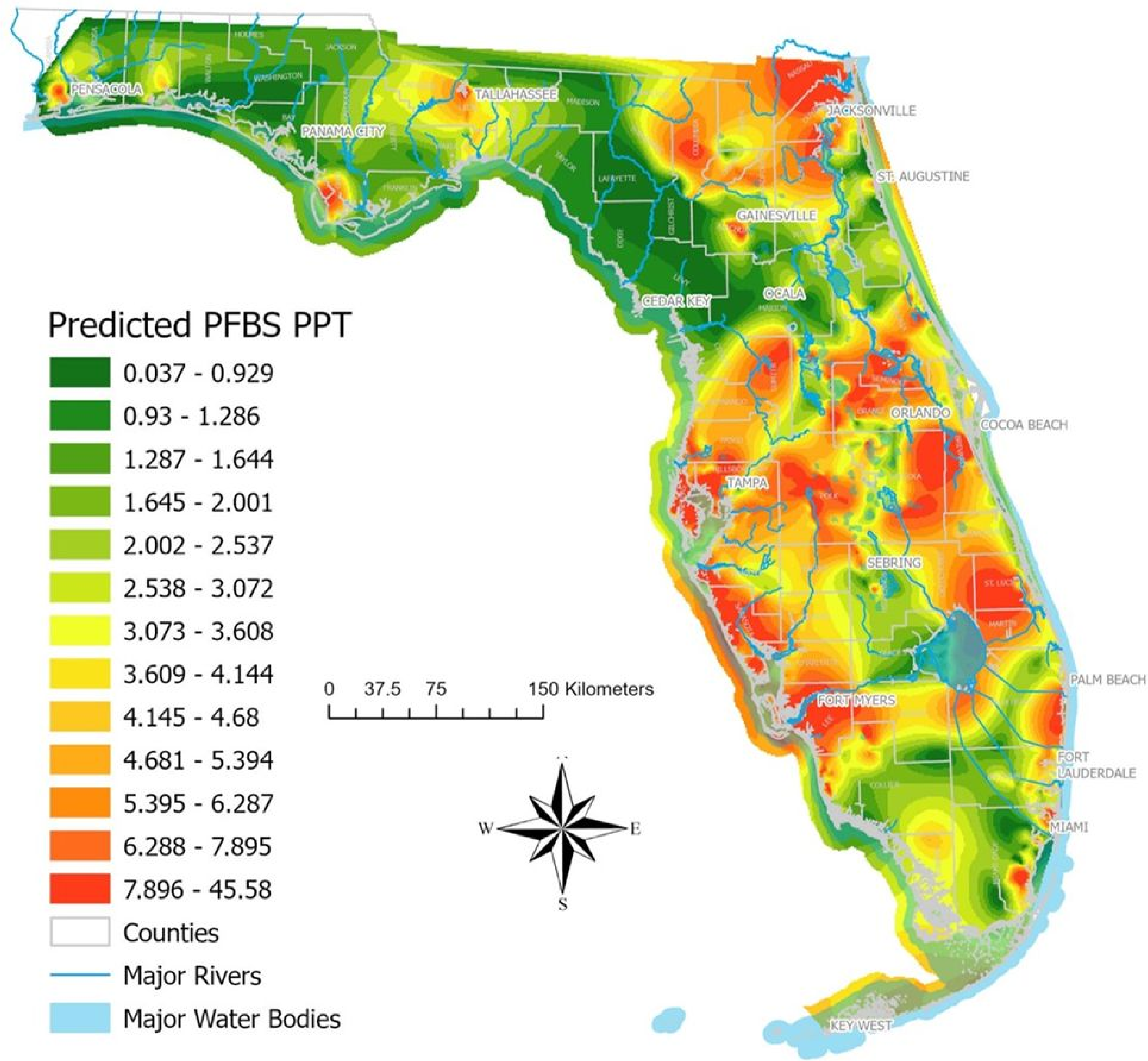
Figure 2B. Map of Florida showing all surface water sampling sites (n=2,323).



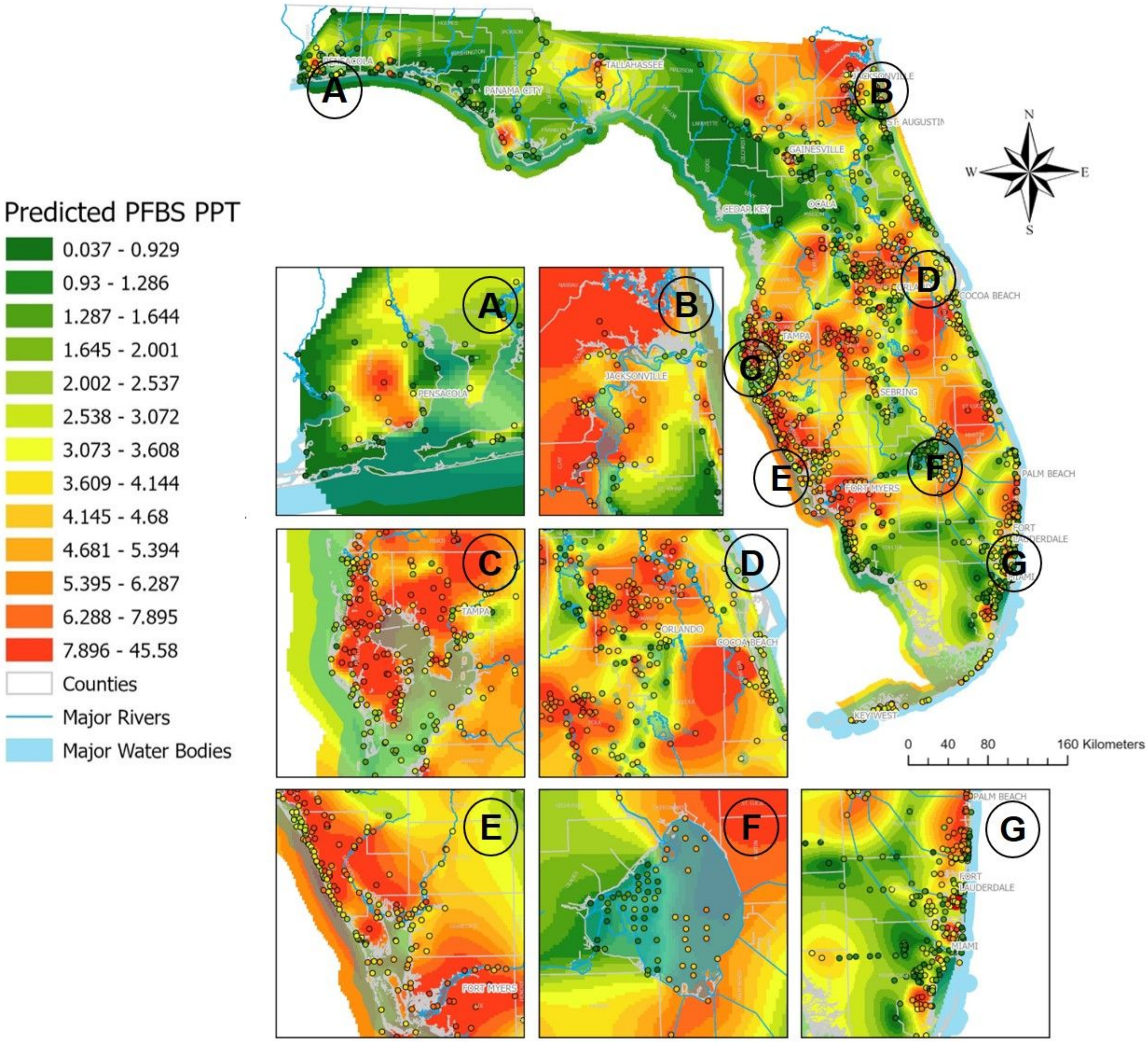
Supporting Information Figure S3A. Geographical representation of each location where PFBS was quantified (>LOQ), with each color representing the range of calculated concentration (ng/L).



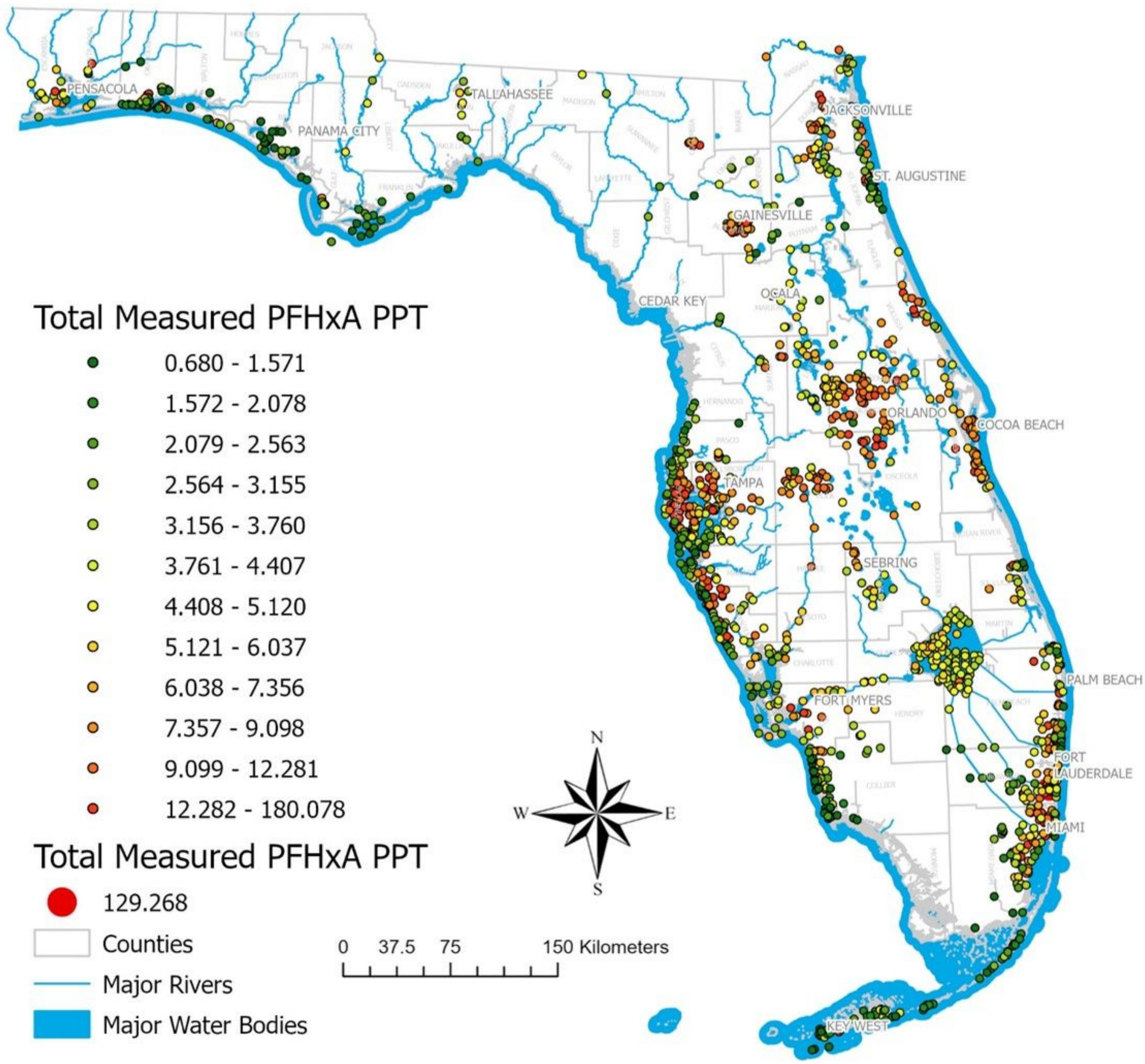
Supporting Information Figure S3B. Predictive heat map for PFBS using the Natural Neighbors interpolation method.



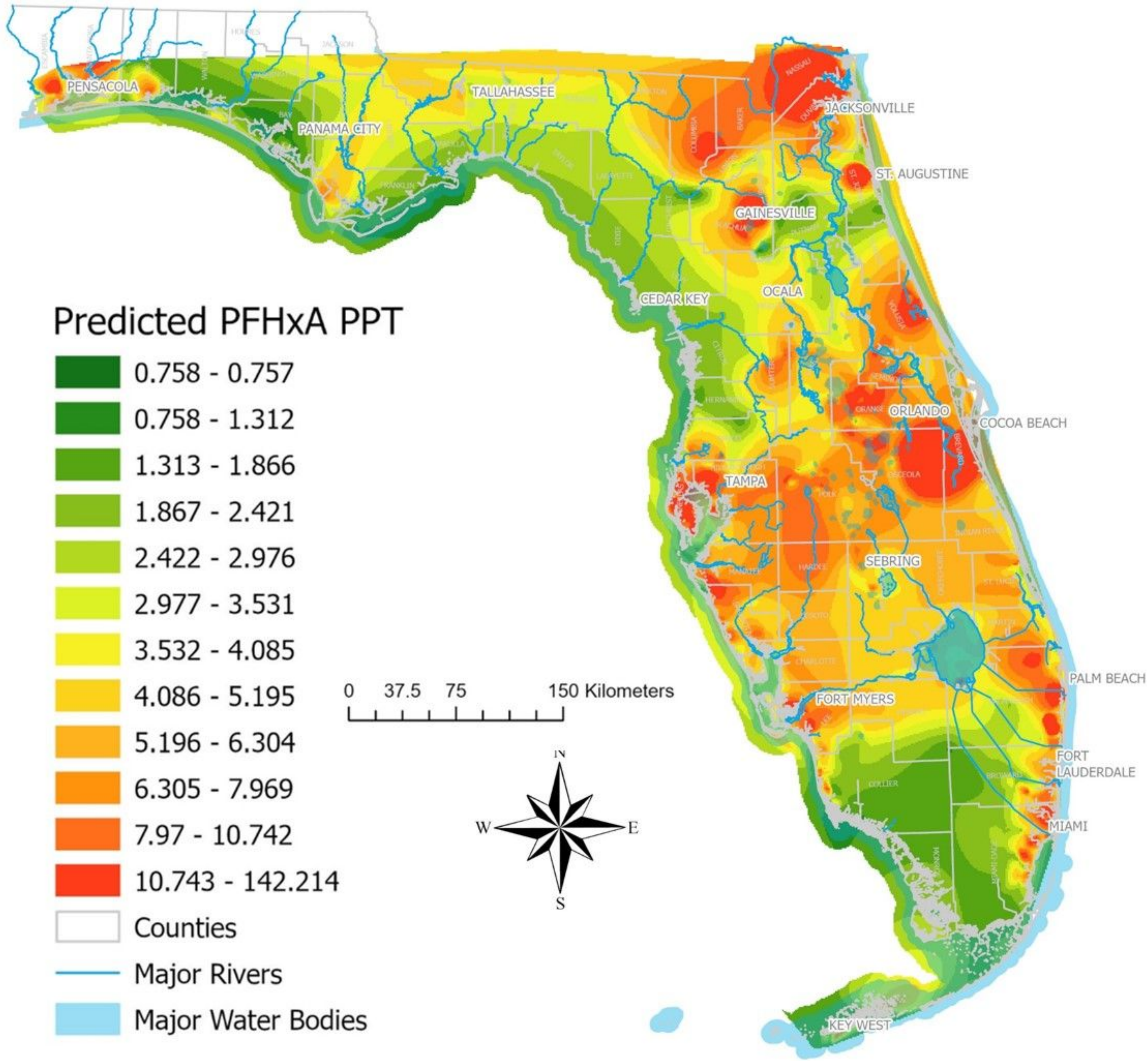
Supporting Information Figure S3C. Prediction heat map for PFBS with regional inserts around (A) Pensacola, (B) Jacksonville, (C) Tampa Bay, (D) Orlando/Cocoa Beach, (E) Sarasota/Ft Myers, (F) Lake Okeechobee and (G) Miami/Ft Lauderdale.



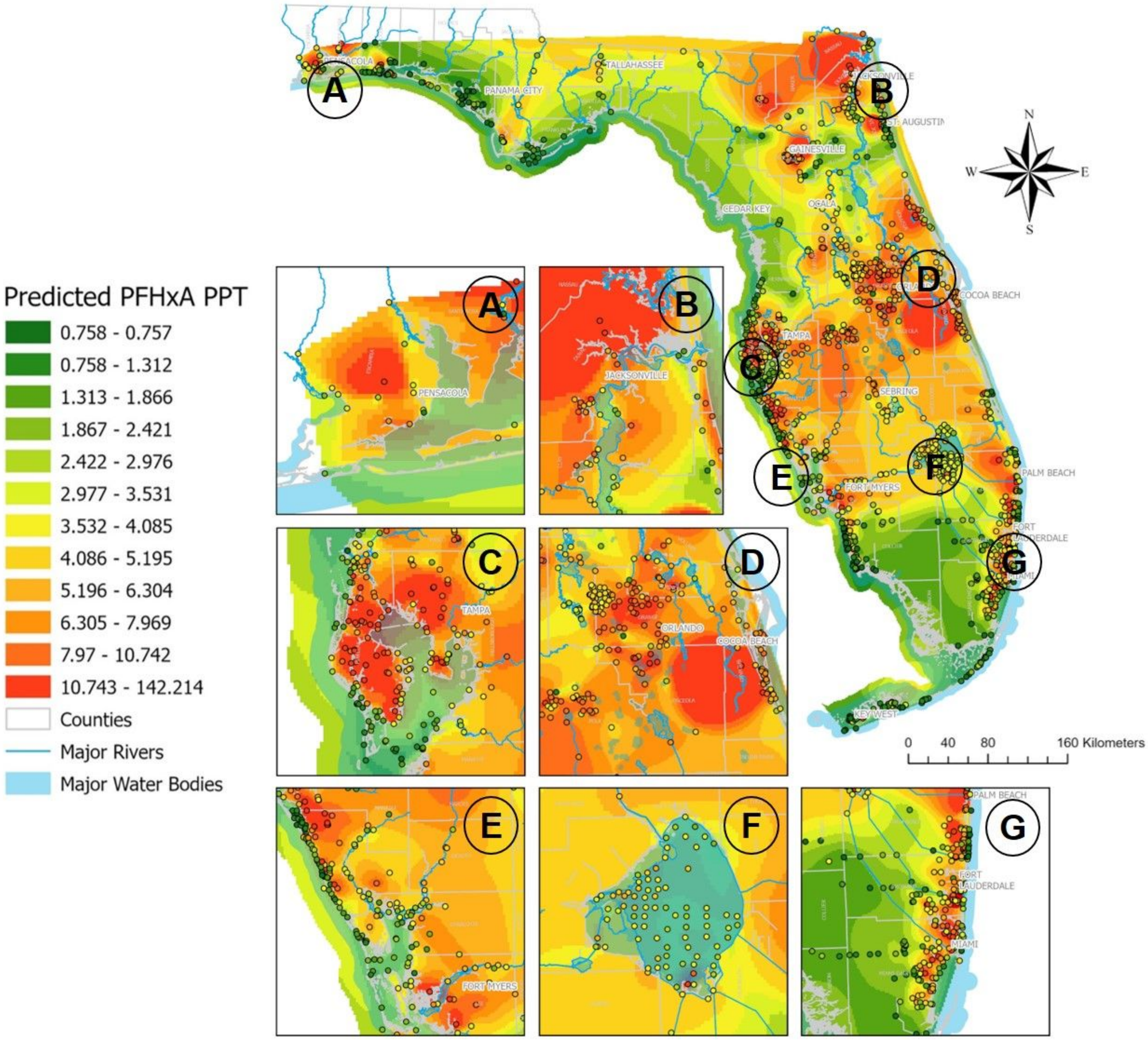
Supporting Information Figure S4A. Geographical representation of each location where PFHxA was quantified (>LOQ), with each color representing the range of calculated concentration (ng/L).



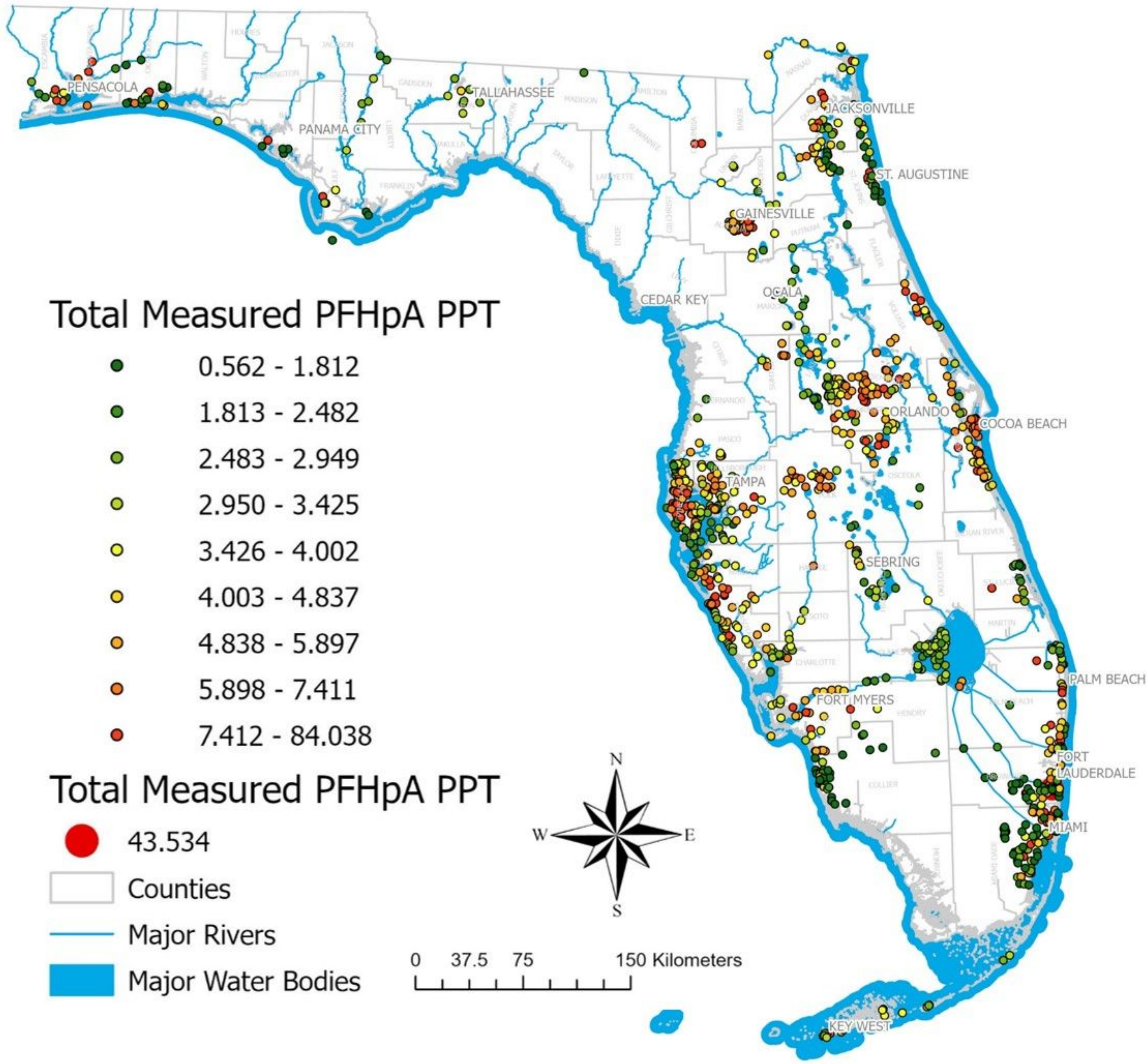
Supporting Information Figure S4B. Predictive heat map for PFHxA using the Natural Neighbors interpolation method.



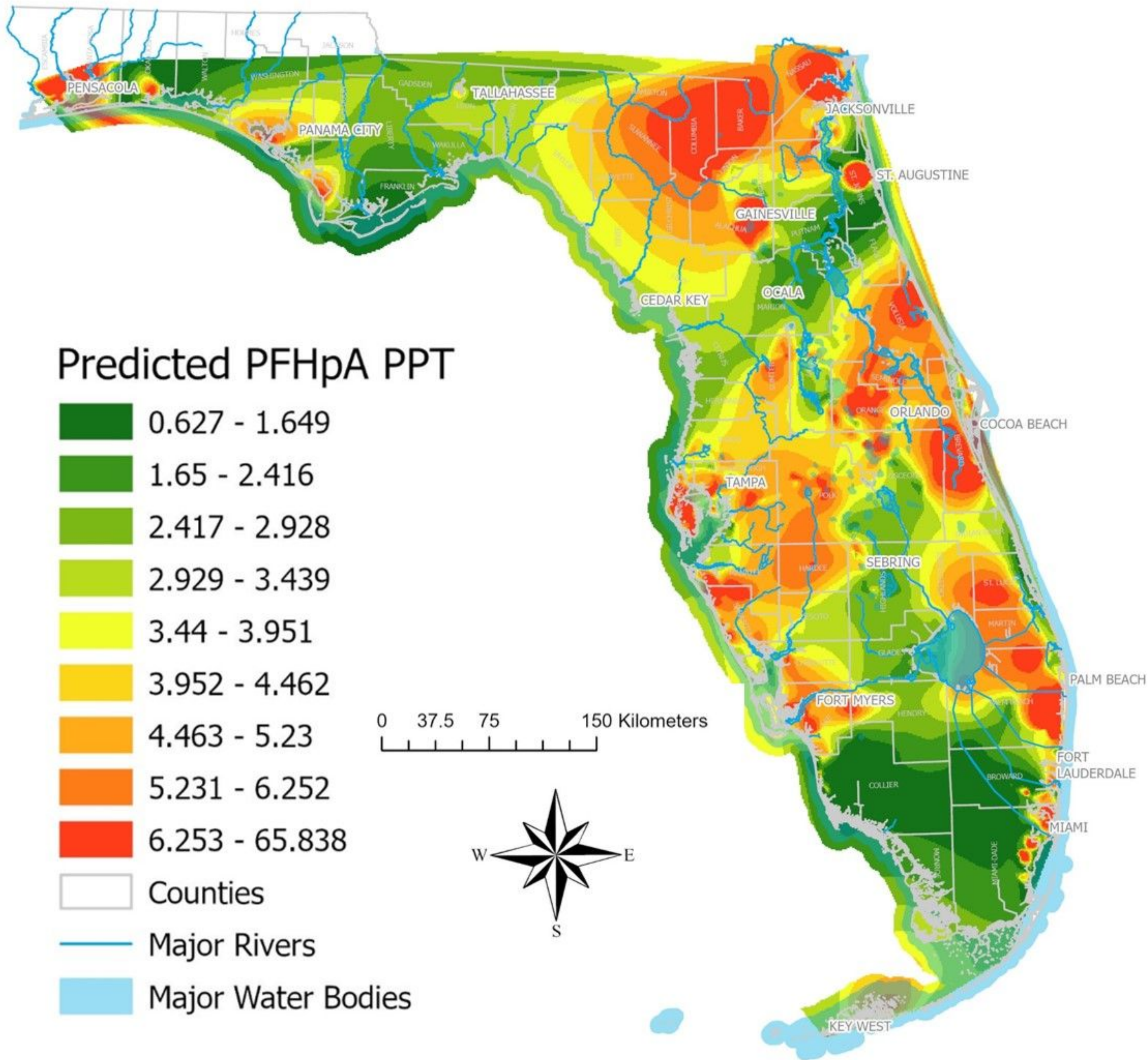
Supporting Information Figure S4C. Prediction heat map for PFHxA with regional inserts around (A) Pensacola, (B) Jacksonville, (C) Tampa Bay, (D) Orlando/Cocoa Beach, (E) Sarasota/Ft Myers, (F) Lake Okeechobee and (G) Miami/Ft Lauderdale.



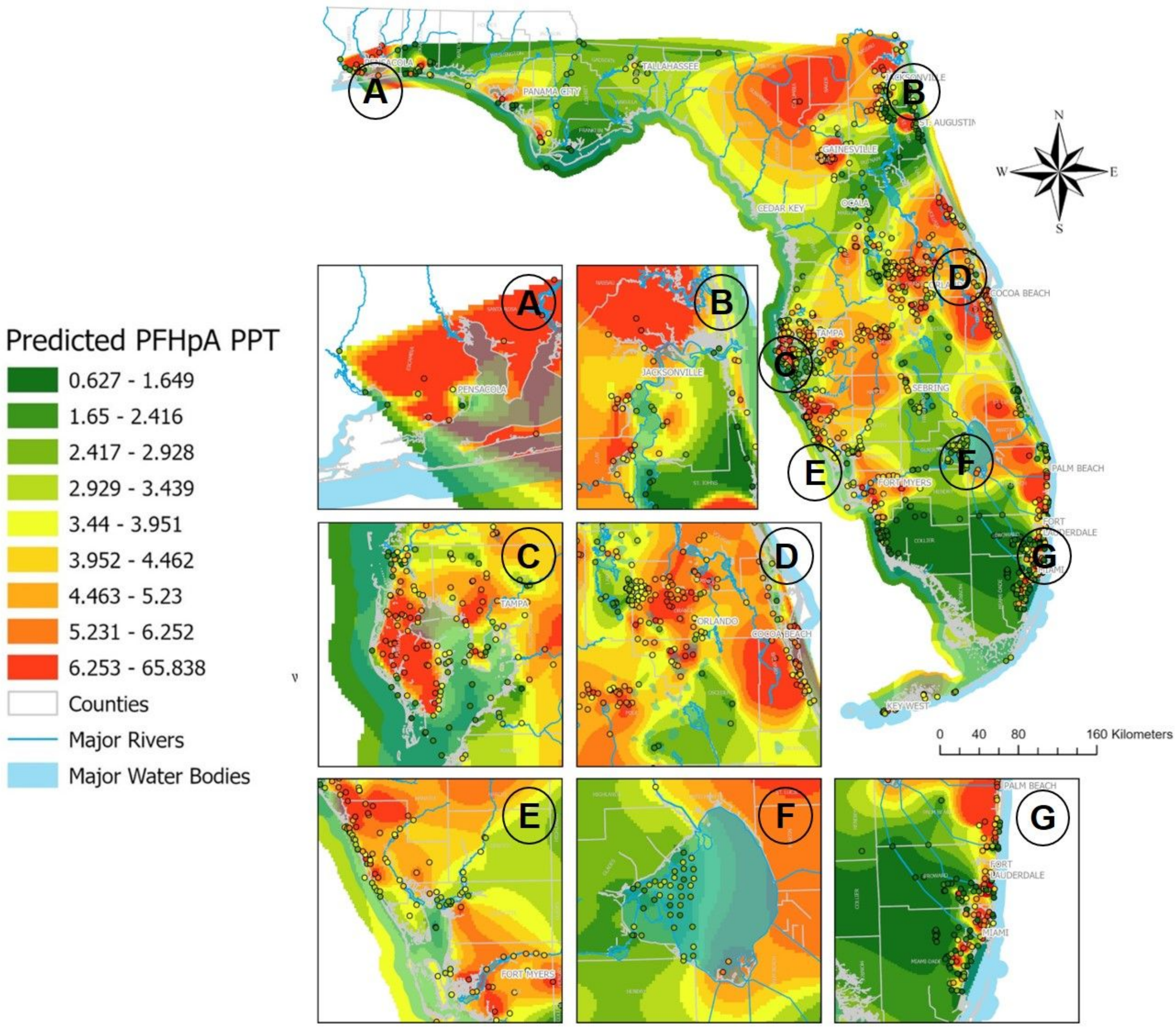
Supporting Information Figure S5A. Geographical representation of each location where PFHpA was quantified (>LOQ), with each color representing the range of calculated concentration (ng/L).



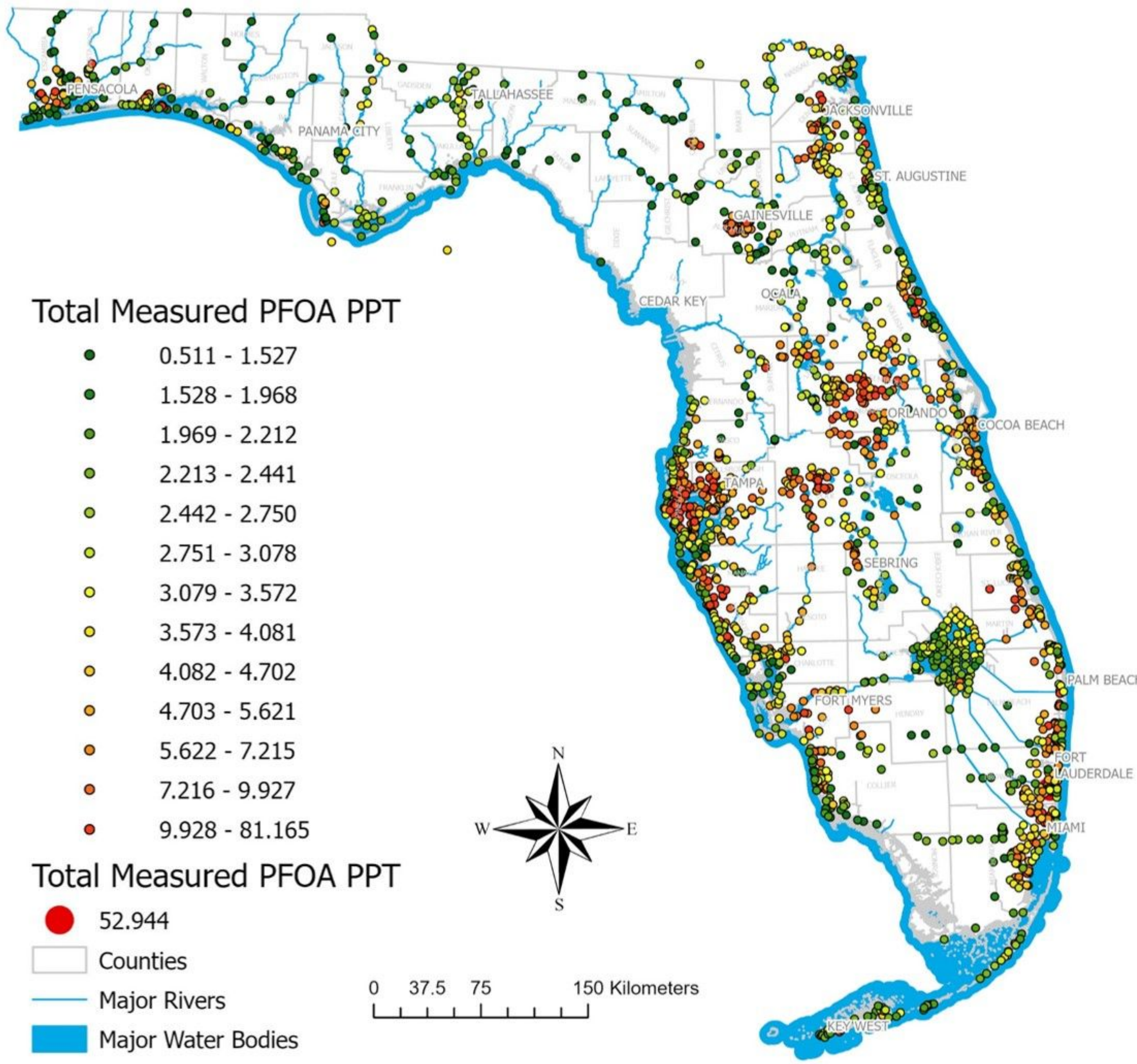
Supporting Information Figure S5B. Predictive heat map for PFHpA using the Natural Neighbors interpolation method.



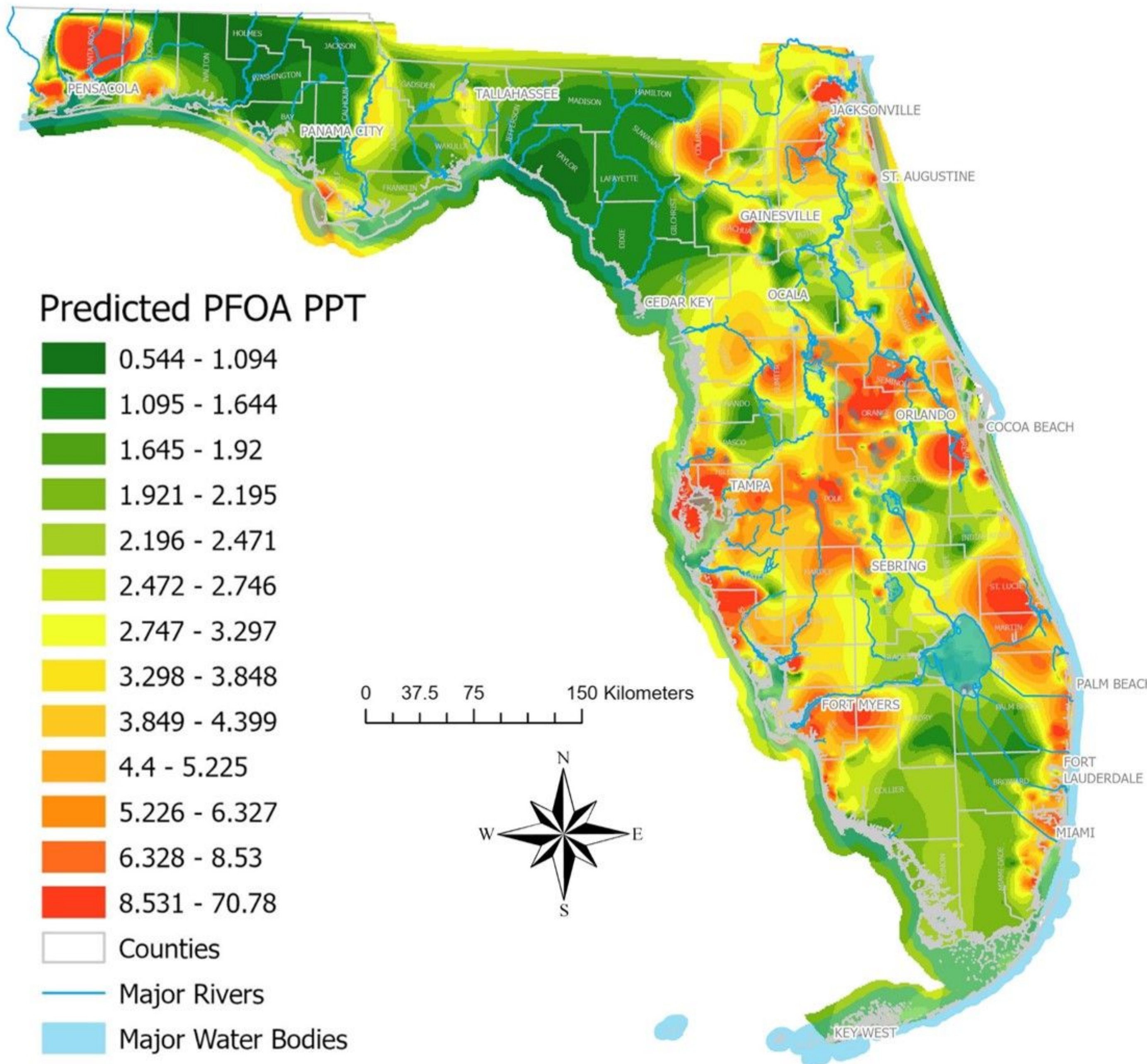
Supporting Information Figure S5C. Prediction heat map for PFHpA with regional inserts around (A) Pensacola, (B) Jacksonville, (C) Tampa Bay, (D) Orlando/Cocoa Beach, (E) Sarasota/Ft Myers, (F) Lake Okeechobee and (G) Miami/Ft Lauderdale.



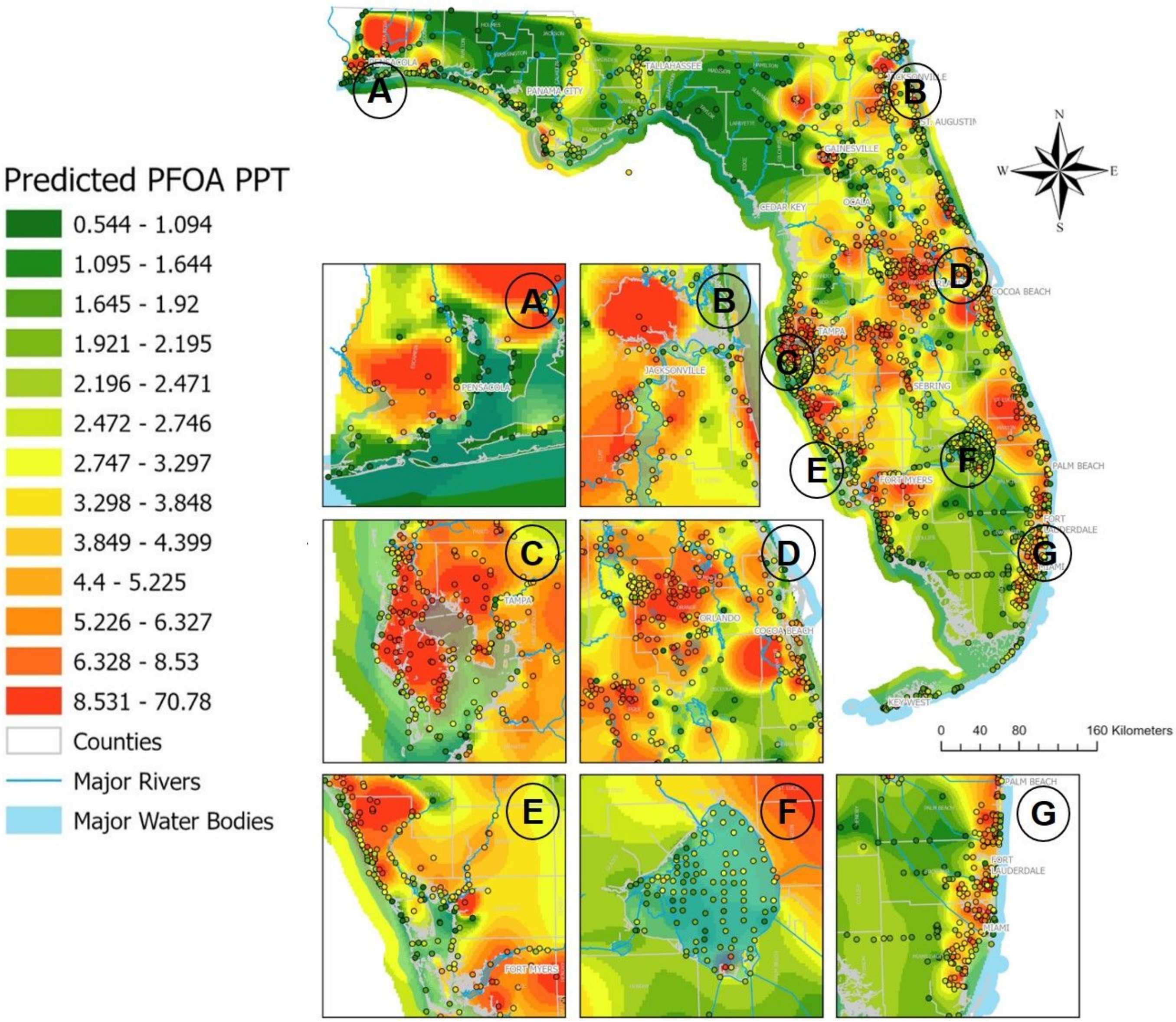
Supporting Information Figure S6A. Geographical representation of each location where PFOA was quantified (>LOQ), with each color representing the range of calculated concentration (ng/L).



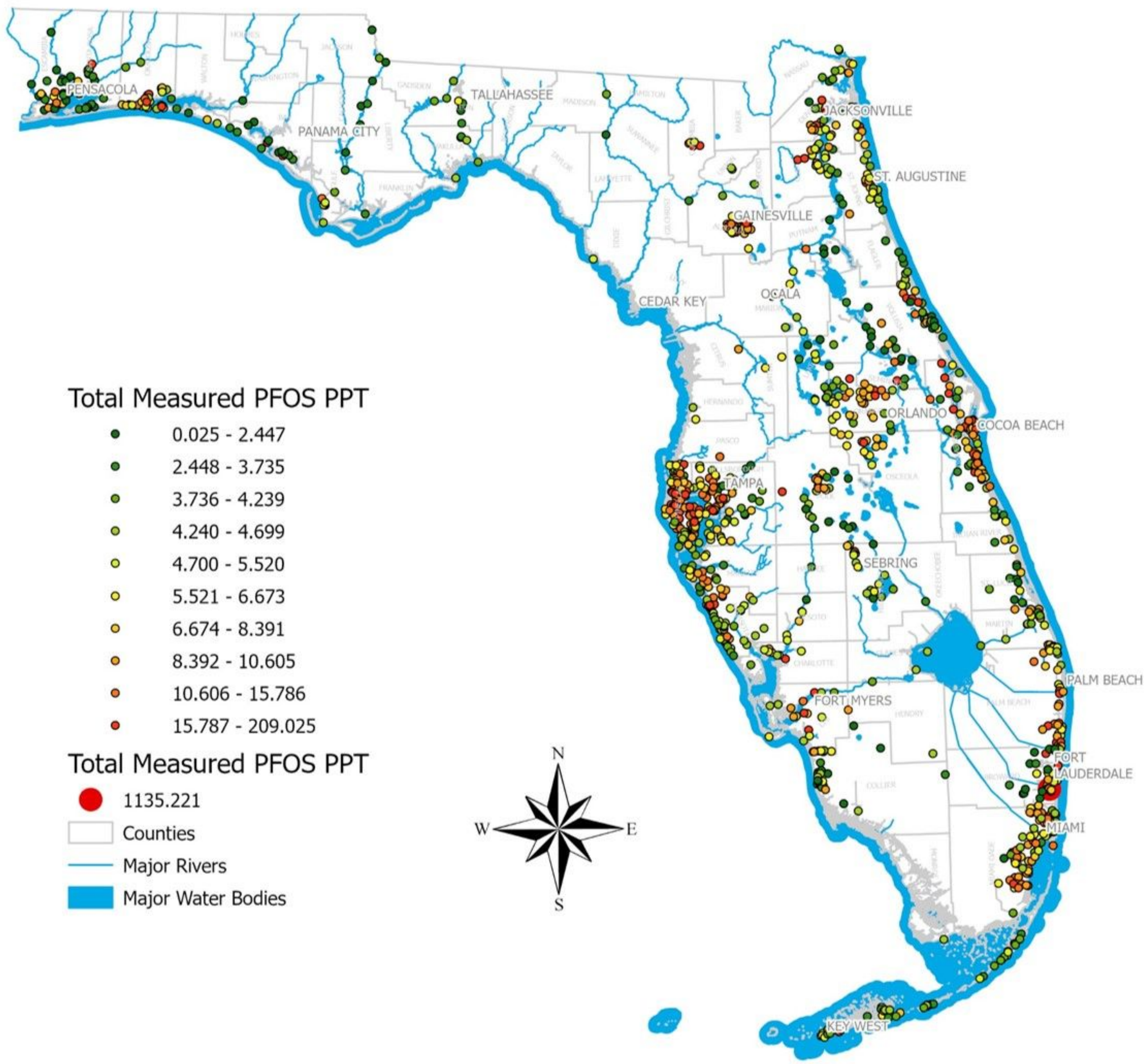
Supporting Information Figure S6B. Predictive heat map for PFOA using the Natural Neighbors interpolation method.



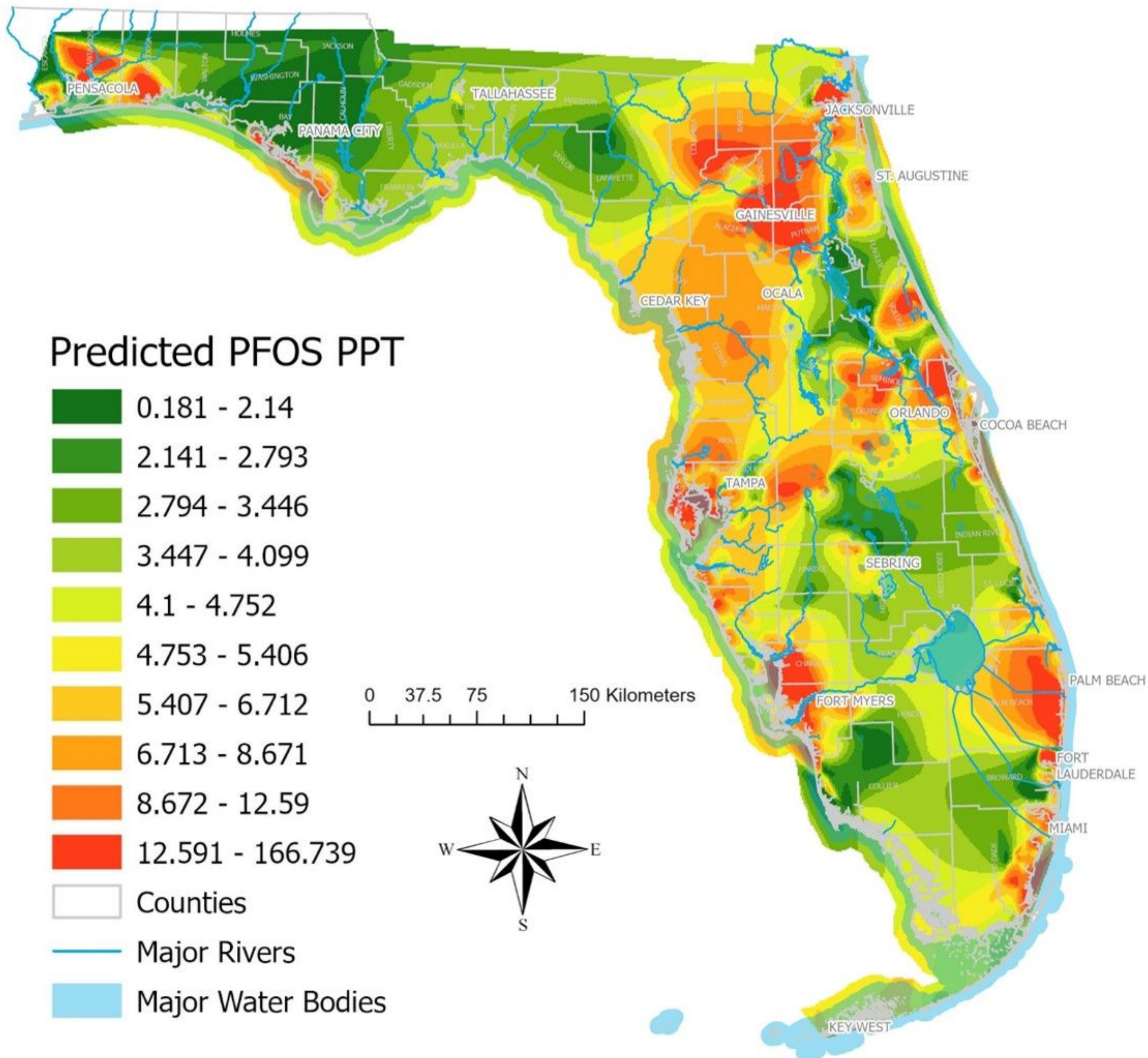
Supporting Information Figure S6C. Prediction heat map for PFOA with regional inserts around (A) Pensacola, (B) Jacksonville, (C) Tampa Bay, (D) Orlando/Cocoa Beach, (E) Sarasota/Ft Myers, (F) Lake Okeechobee and (G) Miami/Ft Lauderdale.



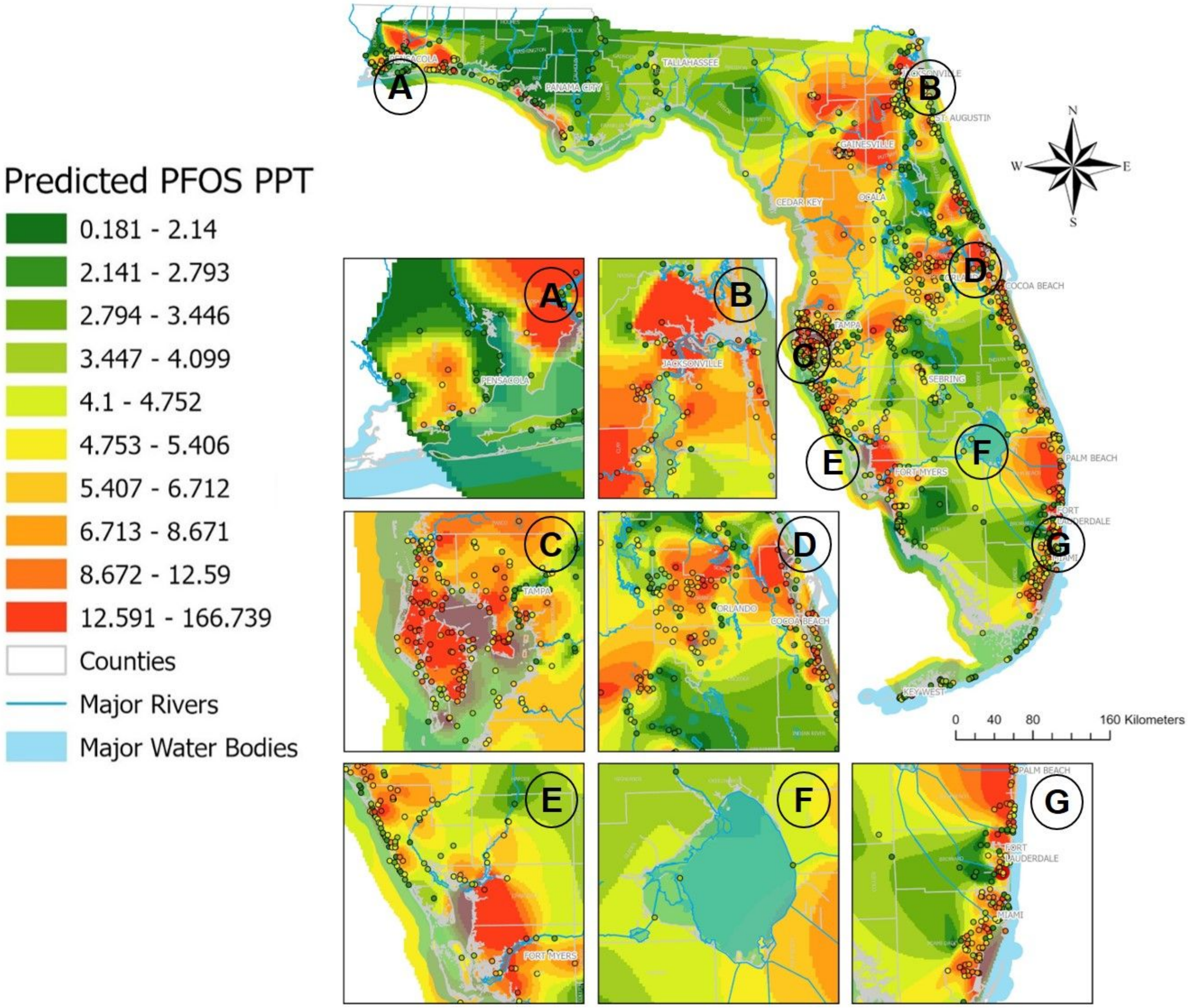
Supporting Information Figure S7A. Geographical representation of each location where ΣPFOS was quantified (>LOQ), with each color representing the range of calculated concentration (ng/L).



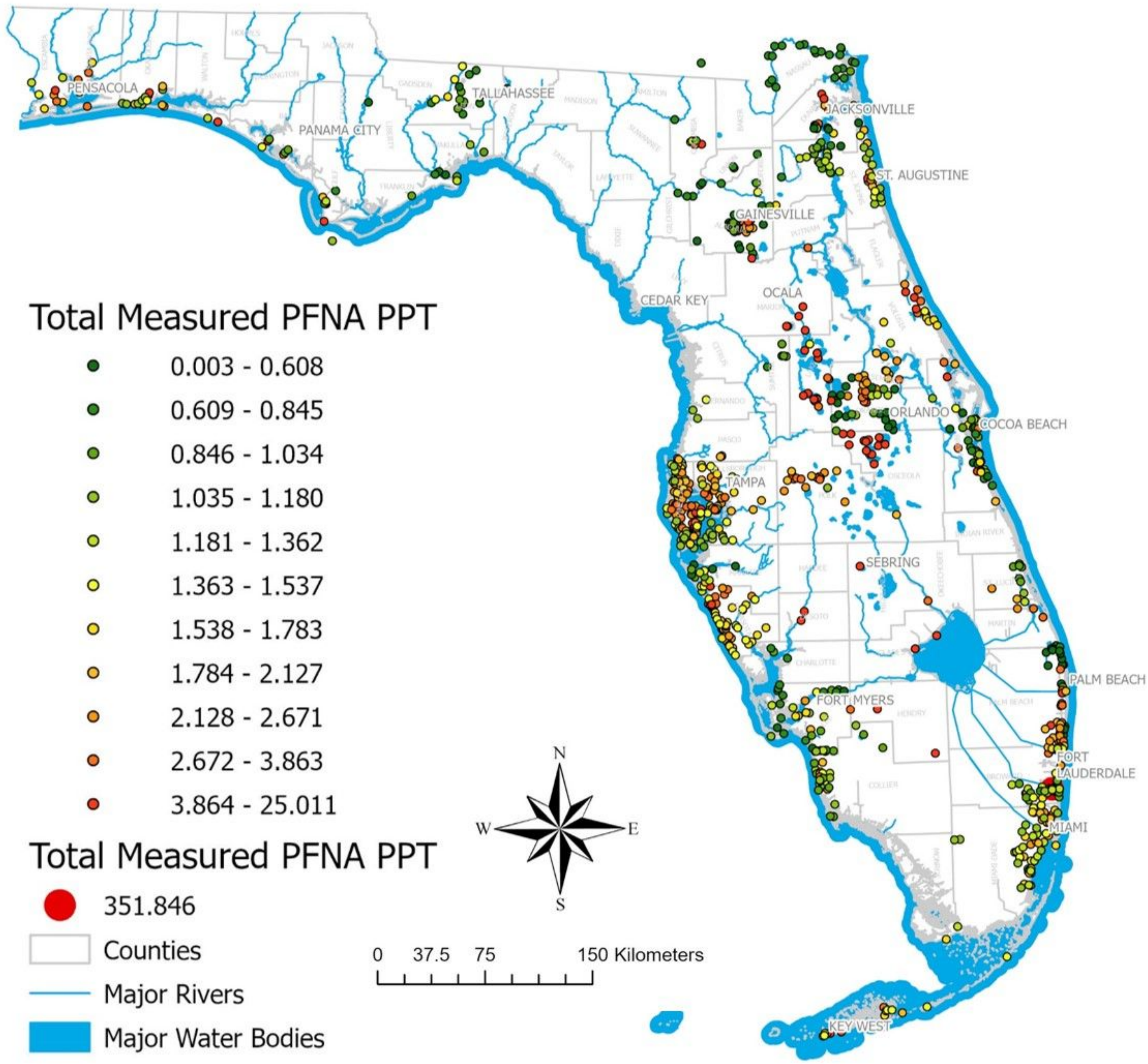
Supporting Information Figure S7B. Predictive heat map for ΣPFOS using the Natural Neighbors interpolation method.



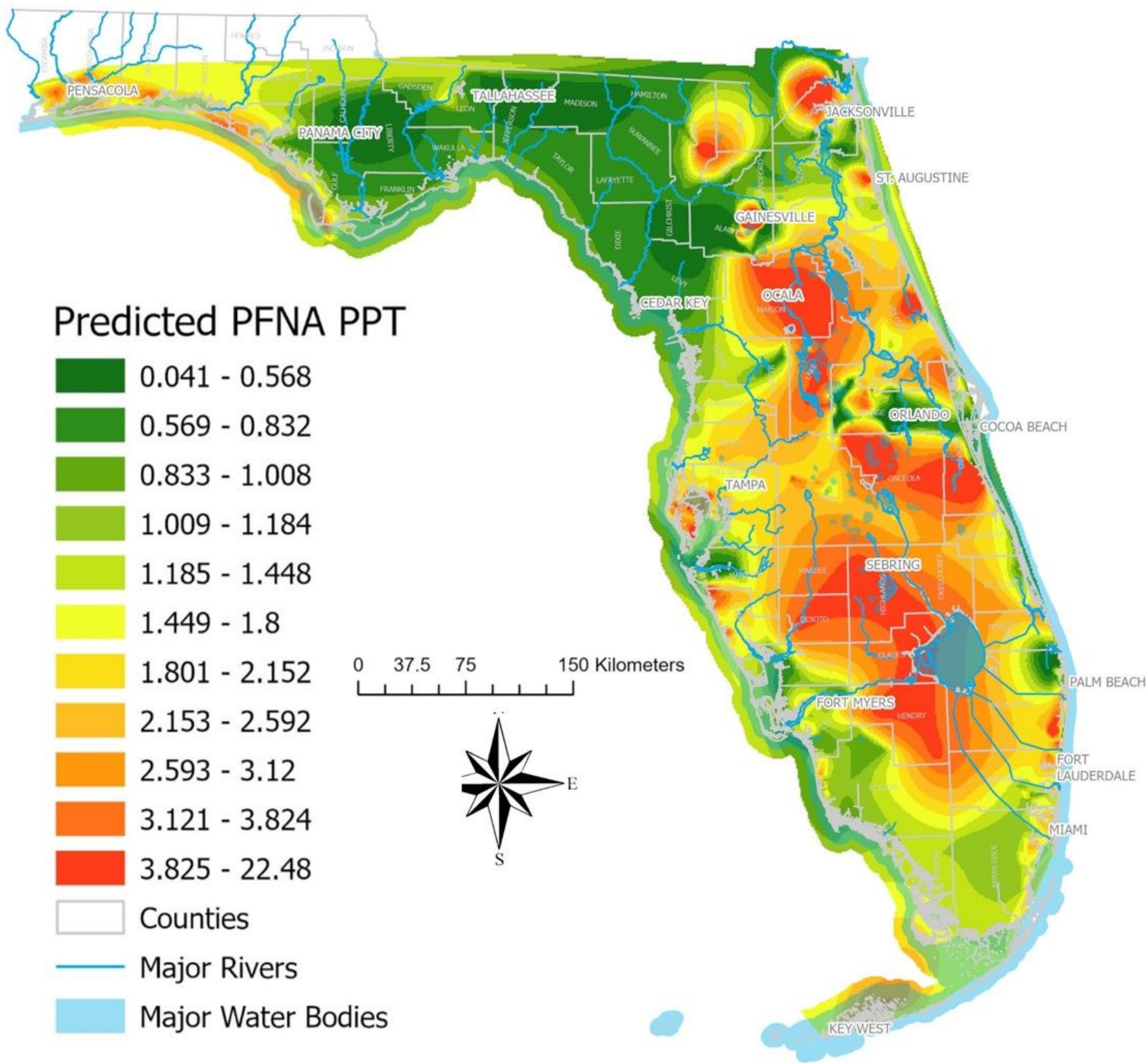
Supporting Information Figure S7C. Prediction heat map for ΣPFOS with regional inserts around (A) Pensacola, (B) Jacksonville, (C) Tampa Bay, (D) Orlando/Cocoa Beach, (E) Sarasota/Ft Myers, (F) Lake Okeechobee and (G) Miami/Ft Lauderdale.



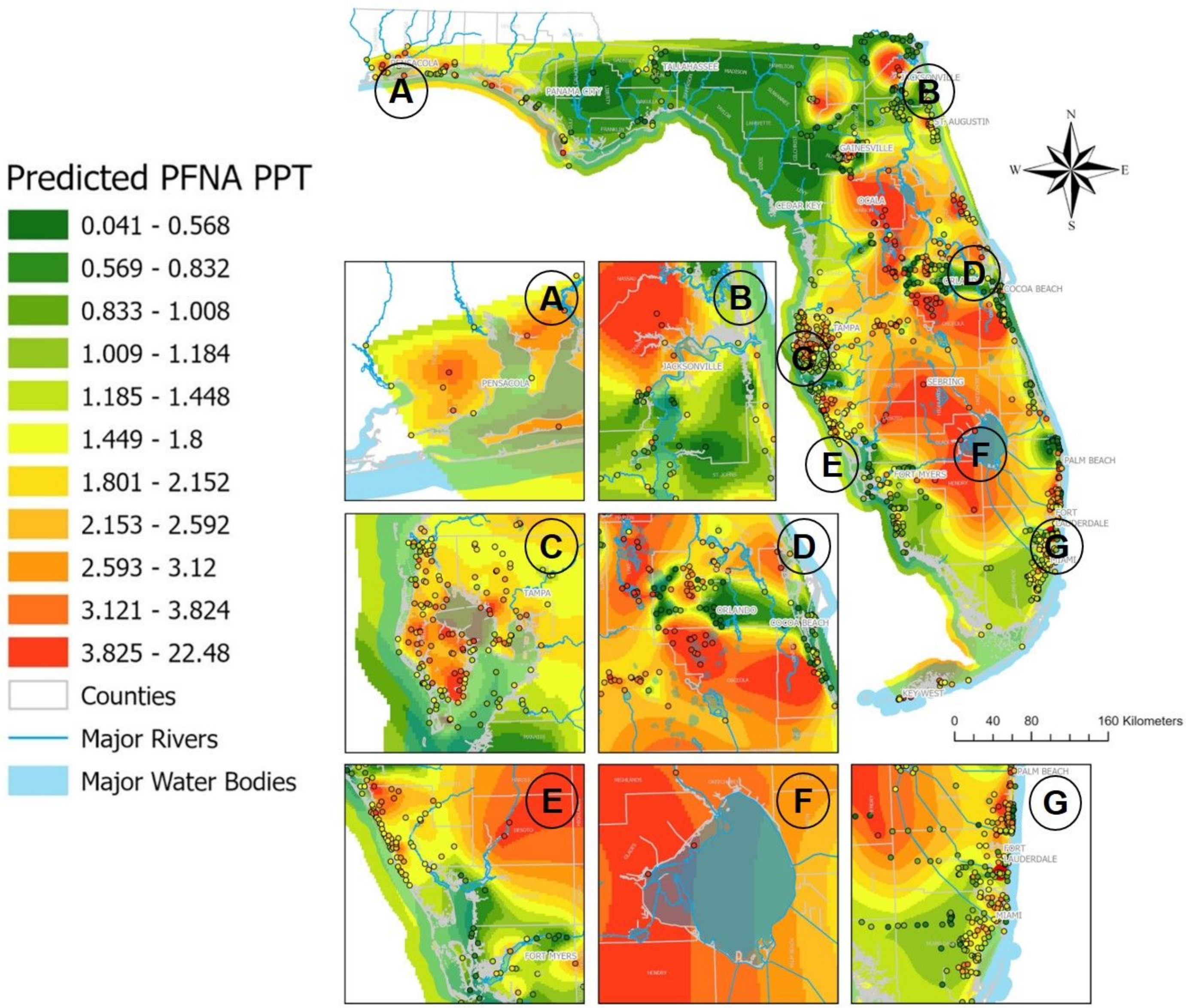
Supporting Information Figure S8A. Geographical representation of each location where PFNA was quantified (>LOQ), with each color representing the range of calculated concentration (ng/L).



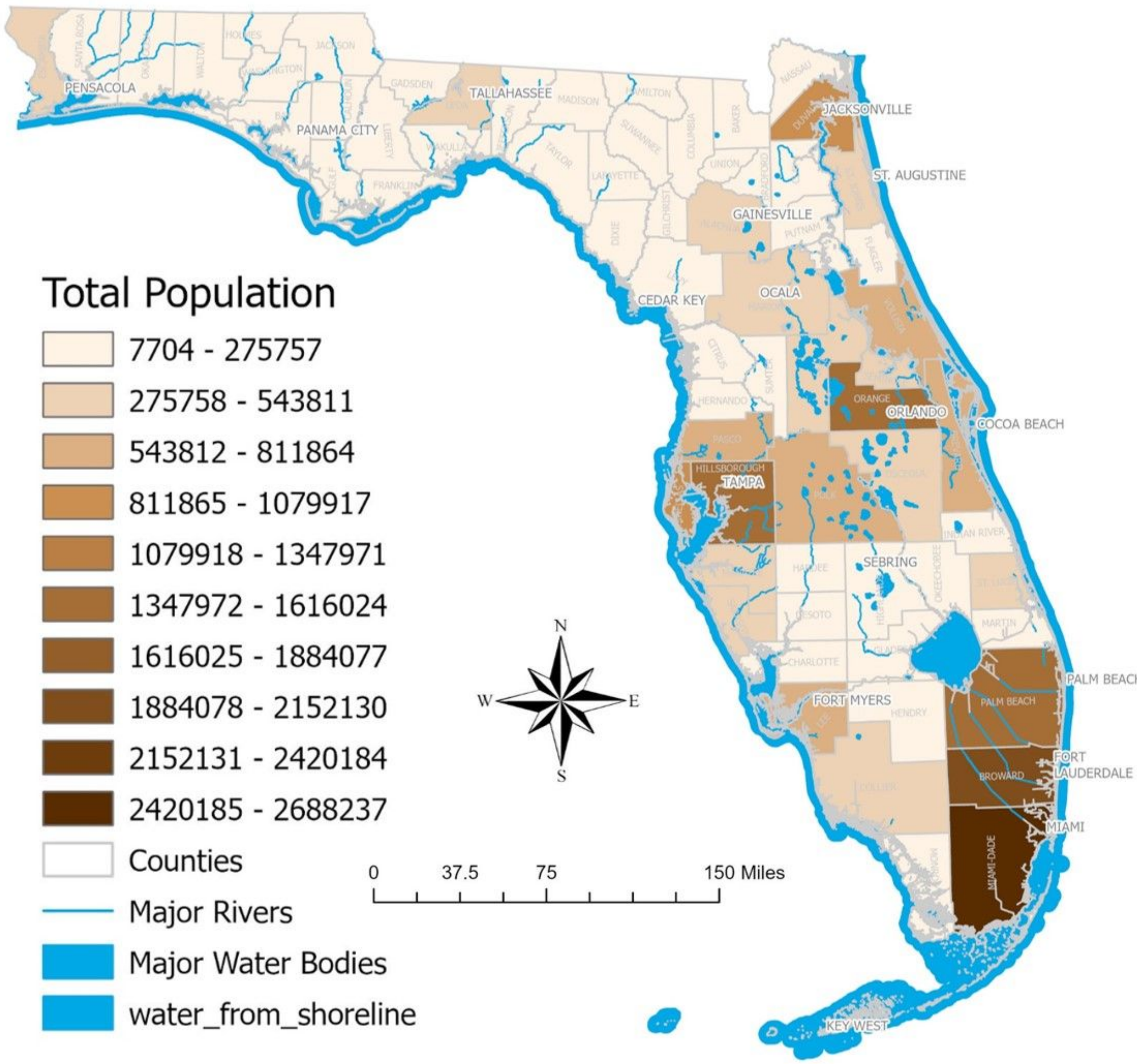
Supporting Information Figure S8B. Predictive heat map for PFNA using the Natural Neighbors interpolation method.



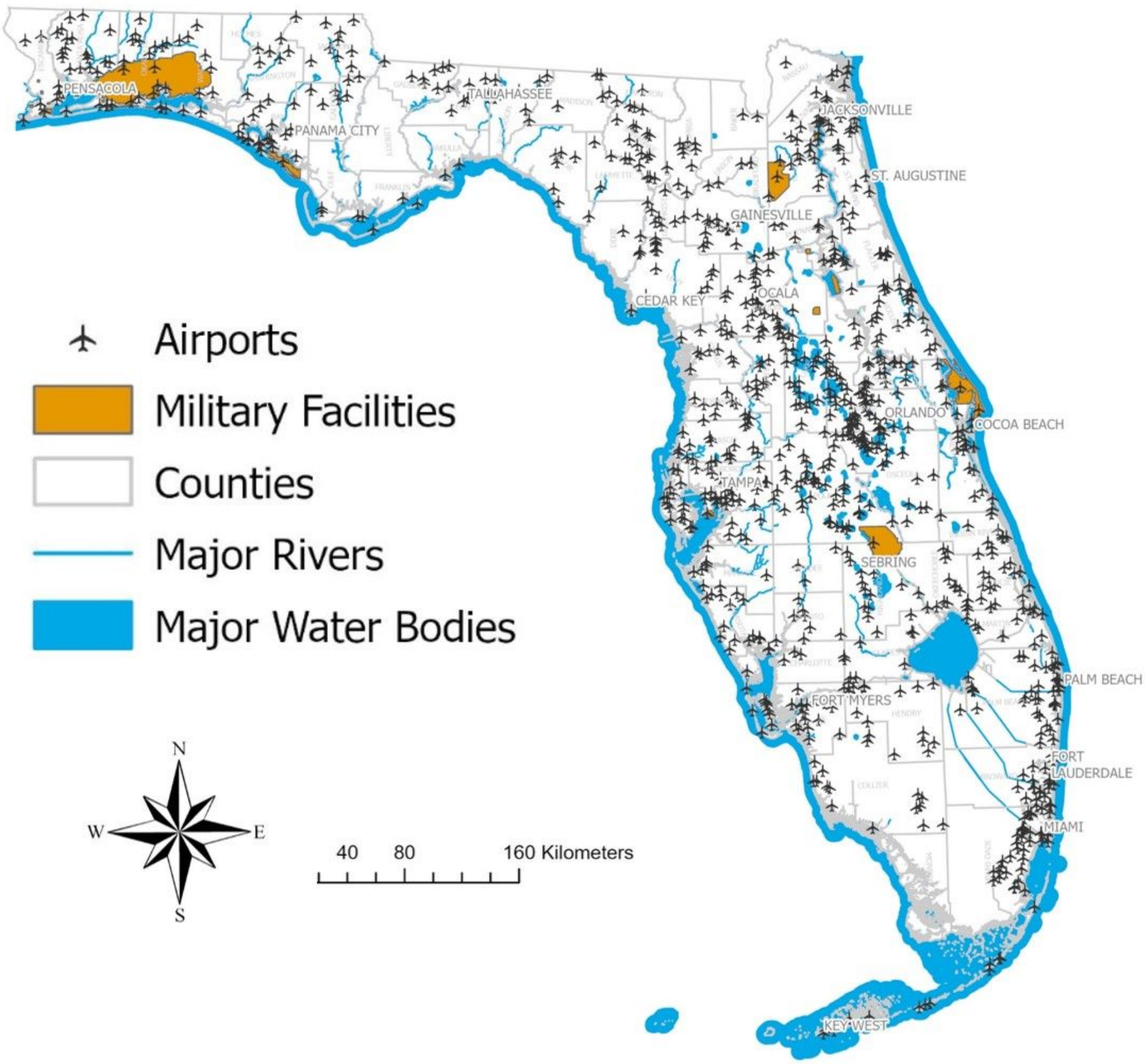
Supporting Information Figure S8C. Prediction heat map for PFNA with regional inserts around (A) Pensacola, (B) Jacksonville, (C) Tampa Bay, (D) Orlando/Cocoa Beach, (E) Sarasota/Ft Myers, (F) Lake Okeechobee and (G) Miami/Ft Lauderdale.



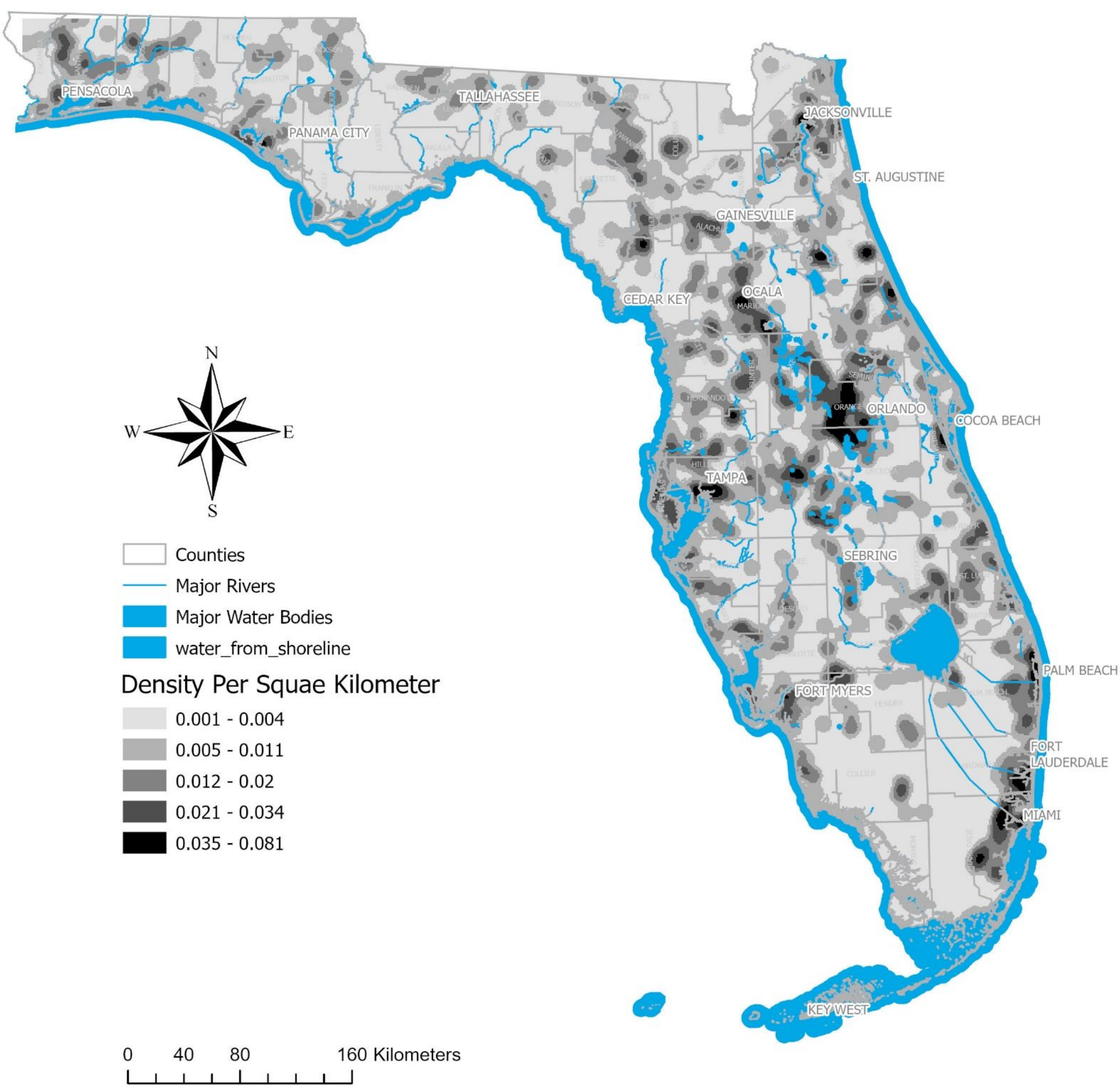
Supporting Information Figure S9. Total population map (units) for the state of Florida, segmented by county.



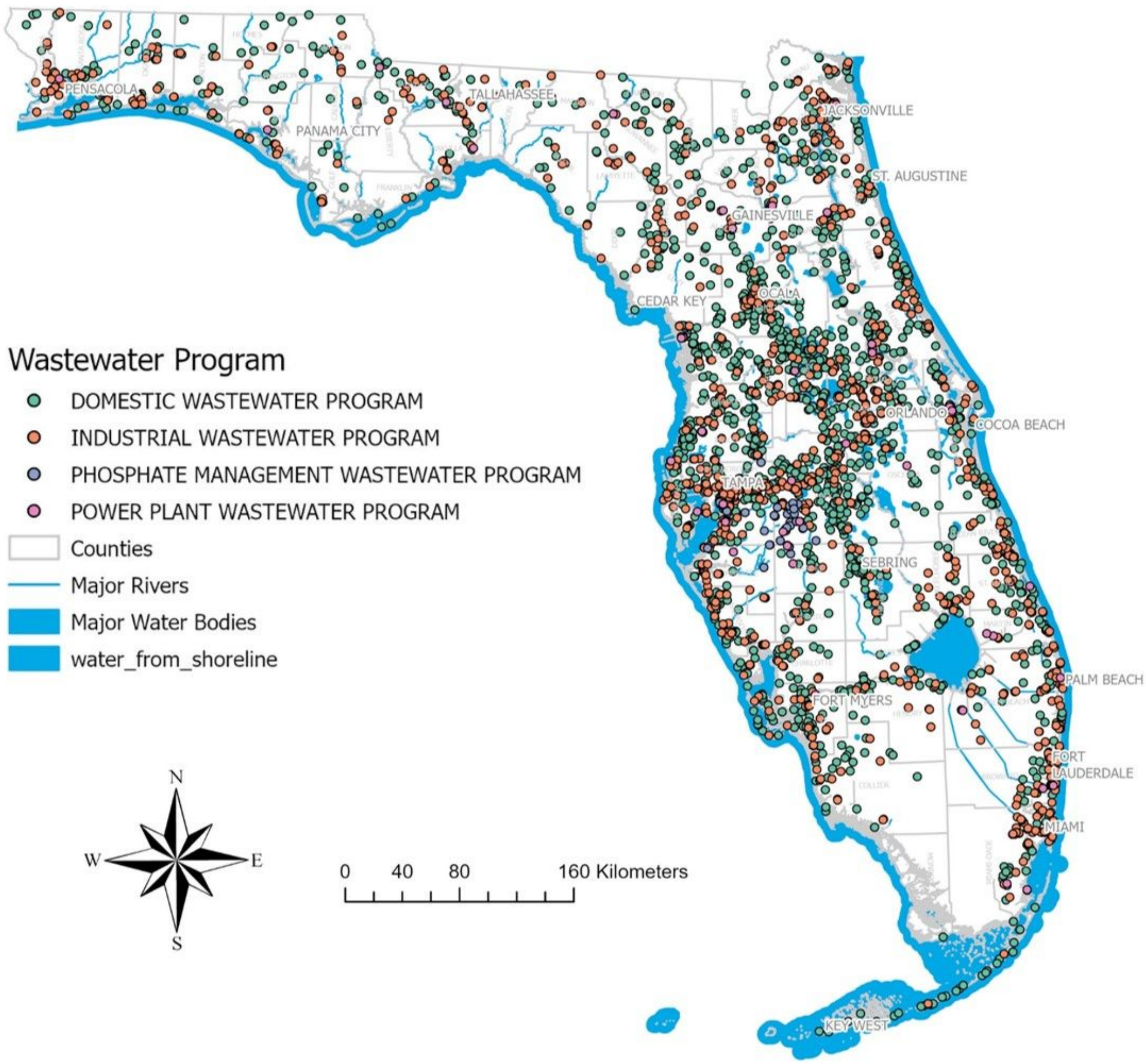
Supporting Information Figure S10. Map displaying location of military facilities and airports in Florida.



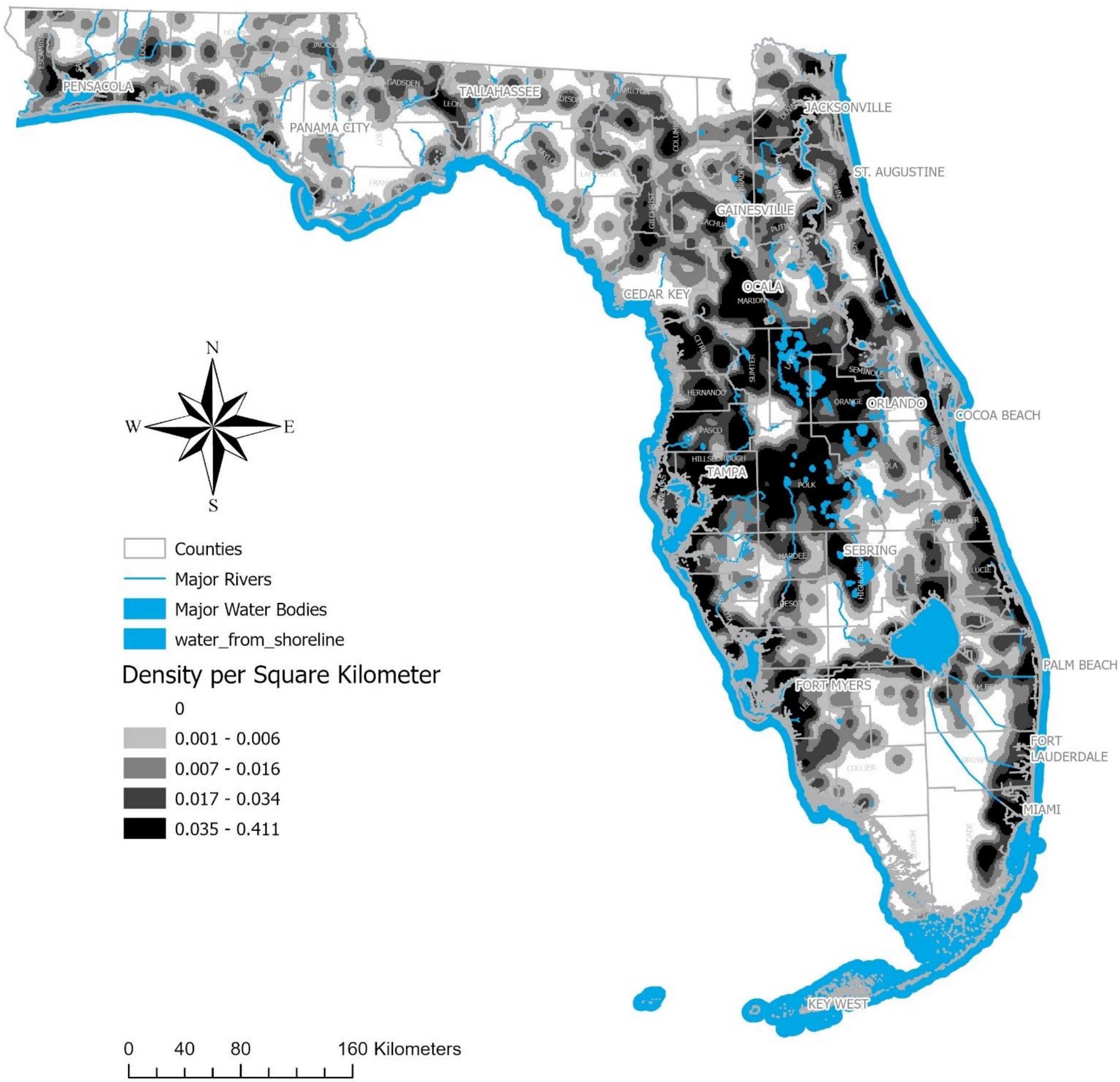
Supporting Information Figure S11. Density map of airports located within Florida.



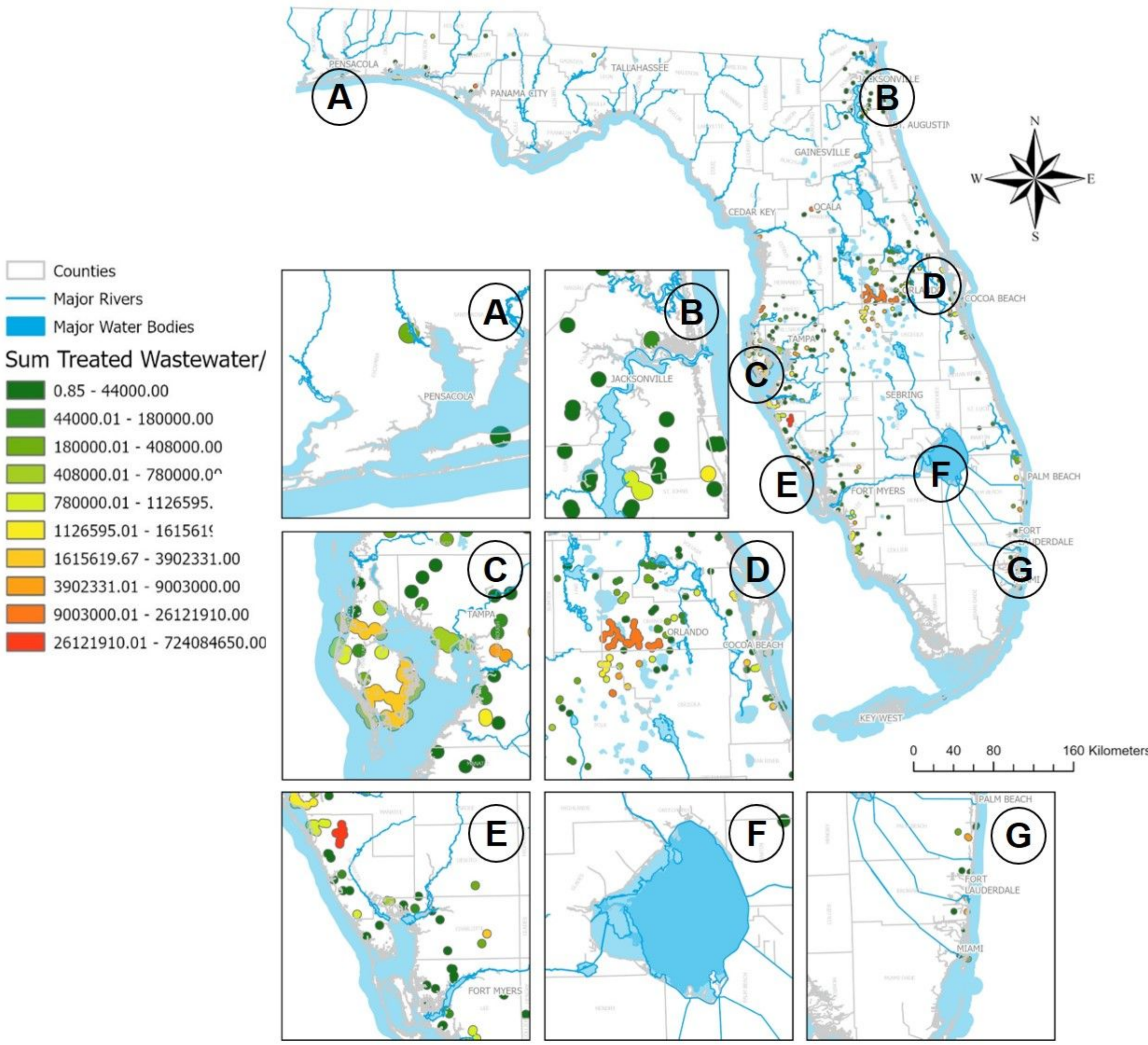
Supporting Information Figure S12. Map displaying location of WWTPs in Florida.



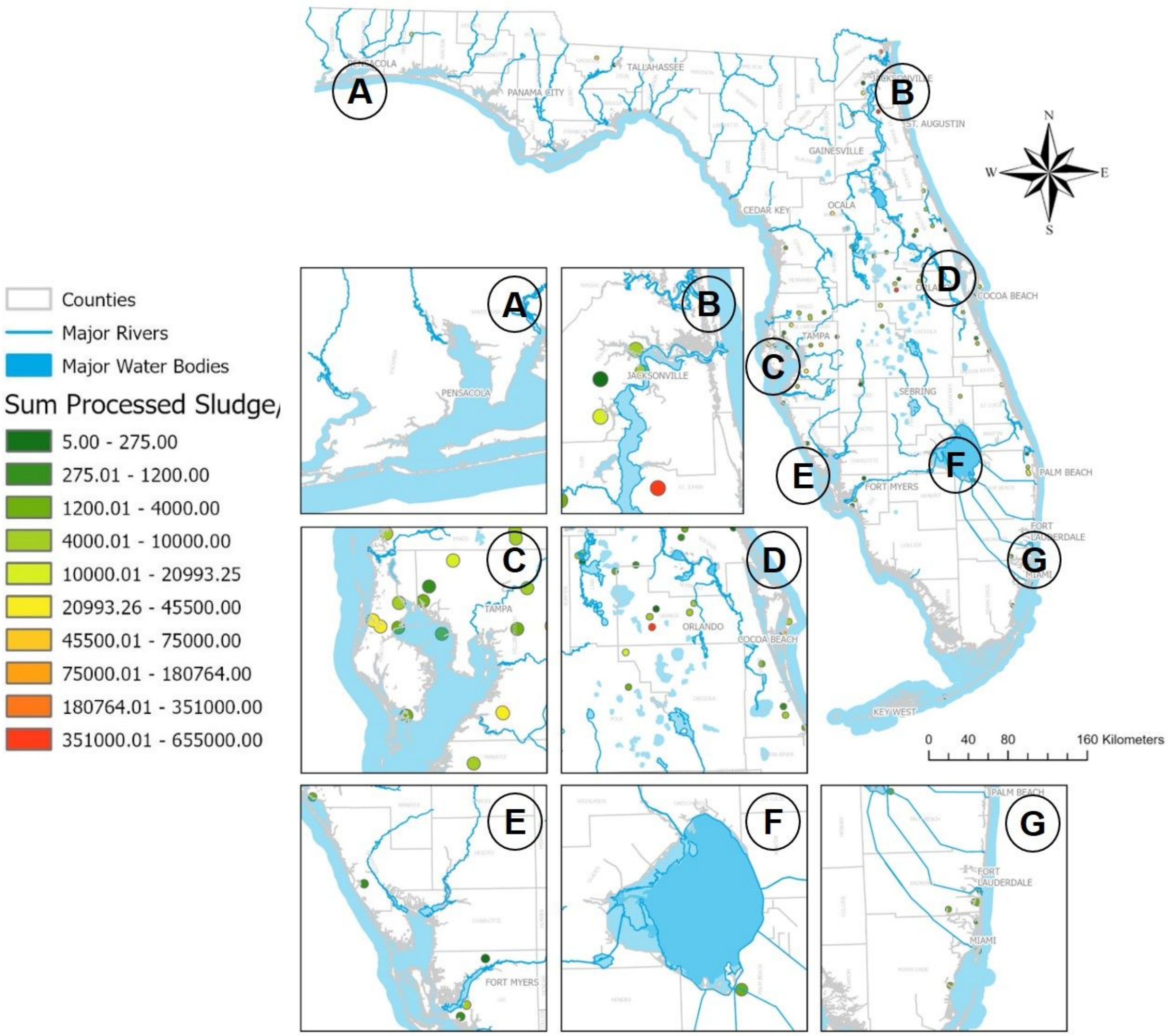
Supporting Information Figure S13. Density of WWTPs located within Florida.



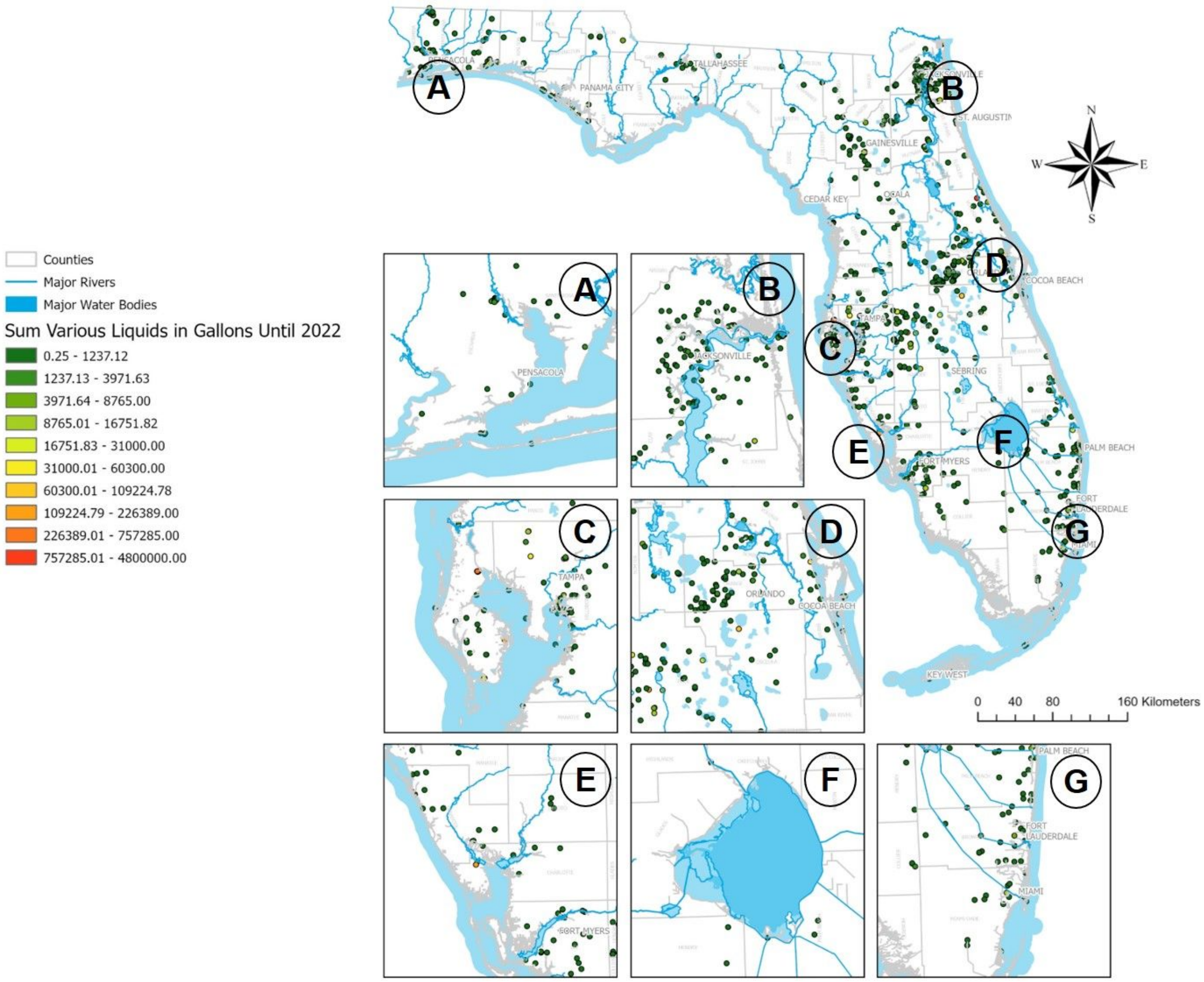
Supporting Information Figure S14. Sum of treated wastewater spills in the state of Florida (prior to 2022).



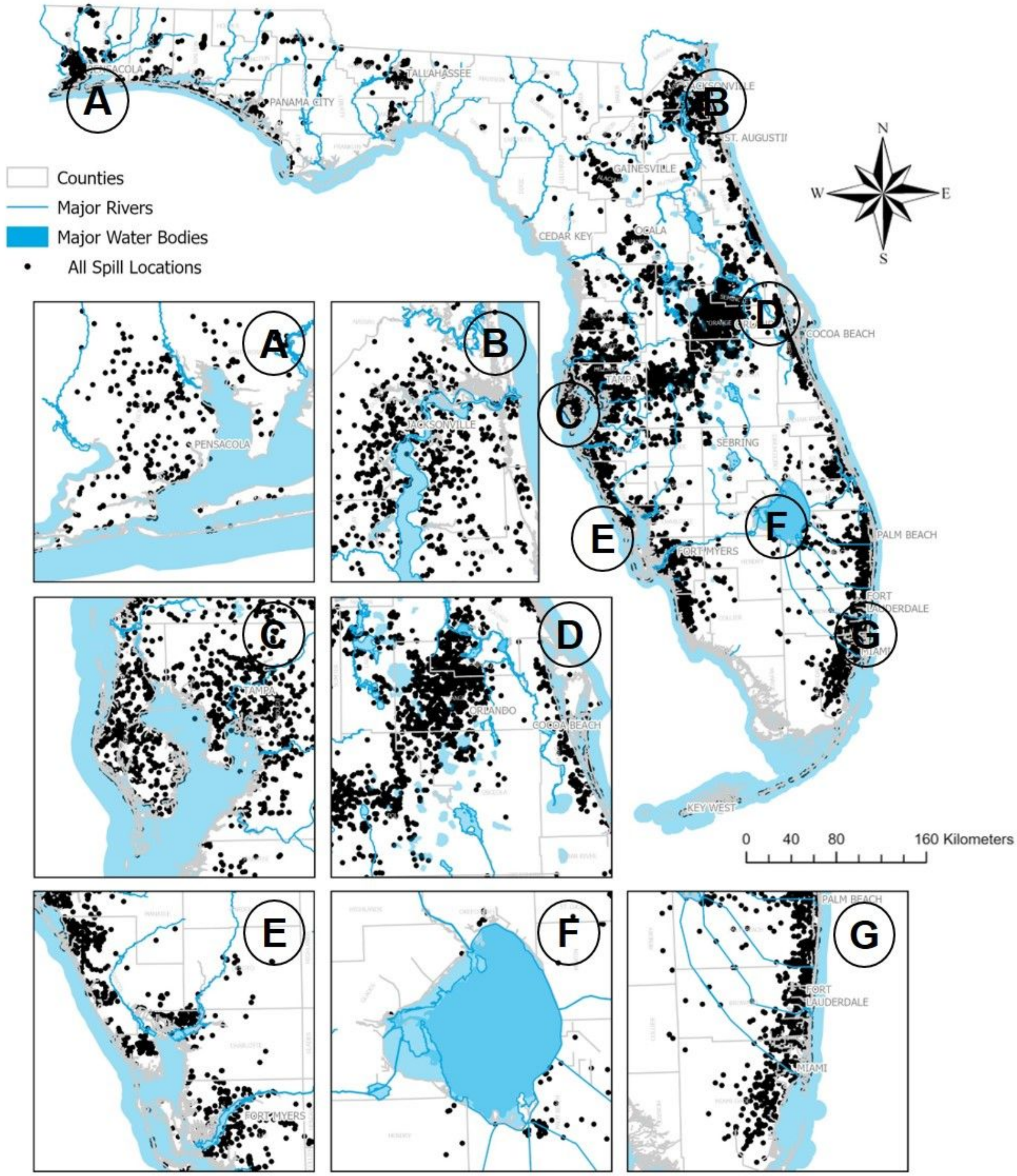
Supporting Information Figure S15. Sum of sludge/solid spills in the state of Florida (prior to 2022).



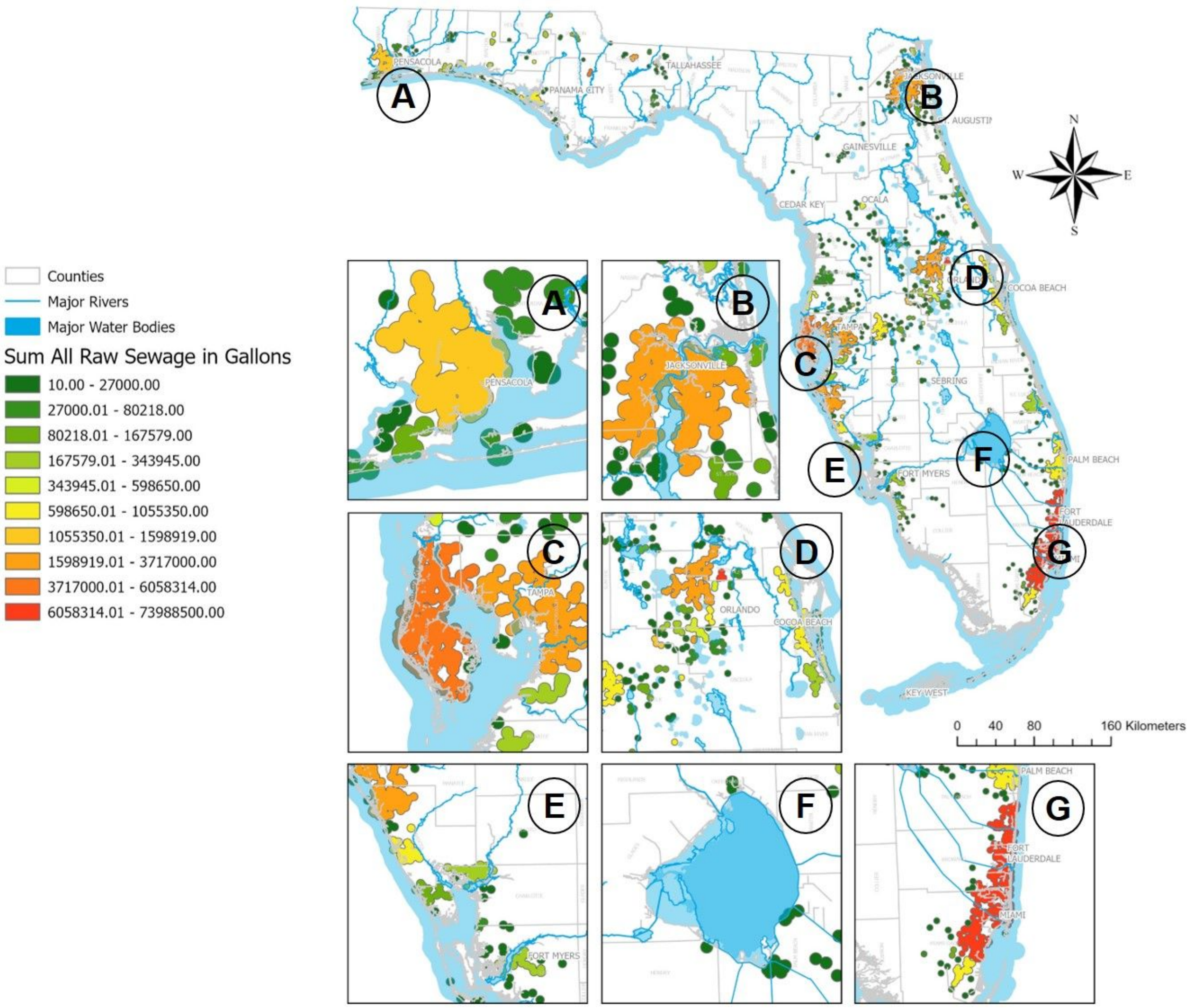
Supporting Information Figure S16. Sum of various liquid spills in the state of Florida (prior to 2022).



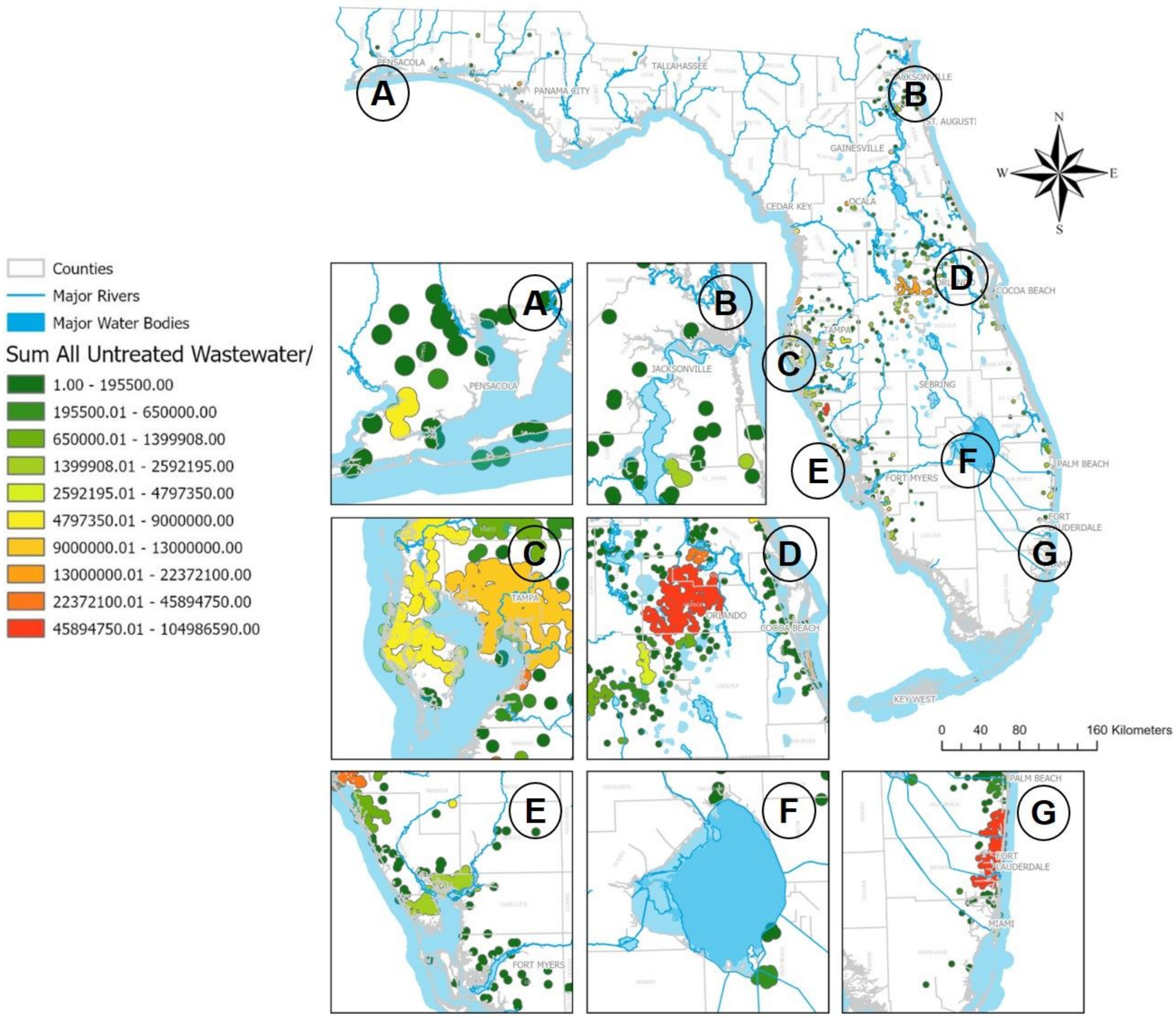
Supporting Information Figure S17. Pollutions spills in Florida from 2017 to date.



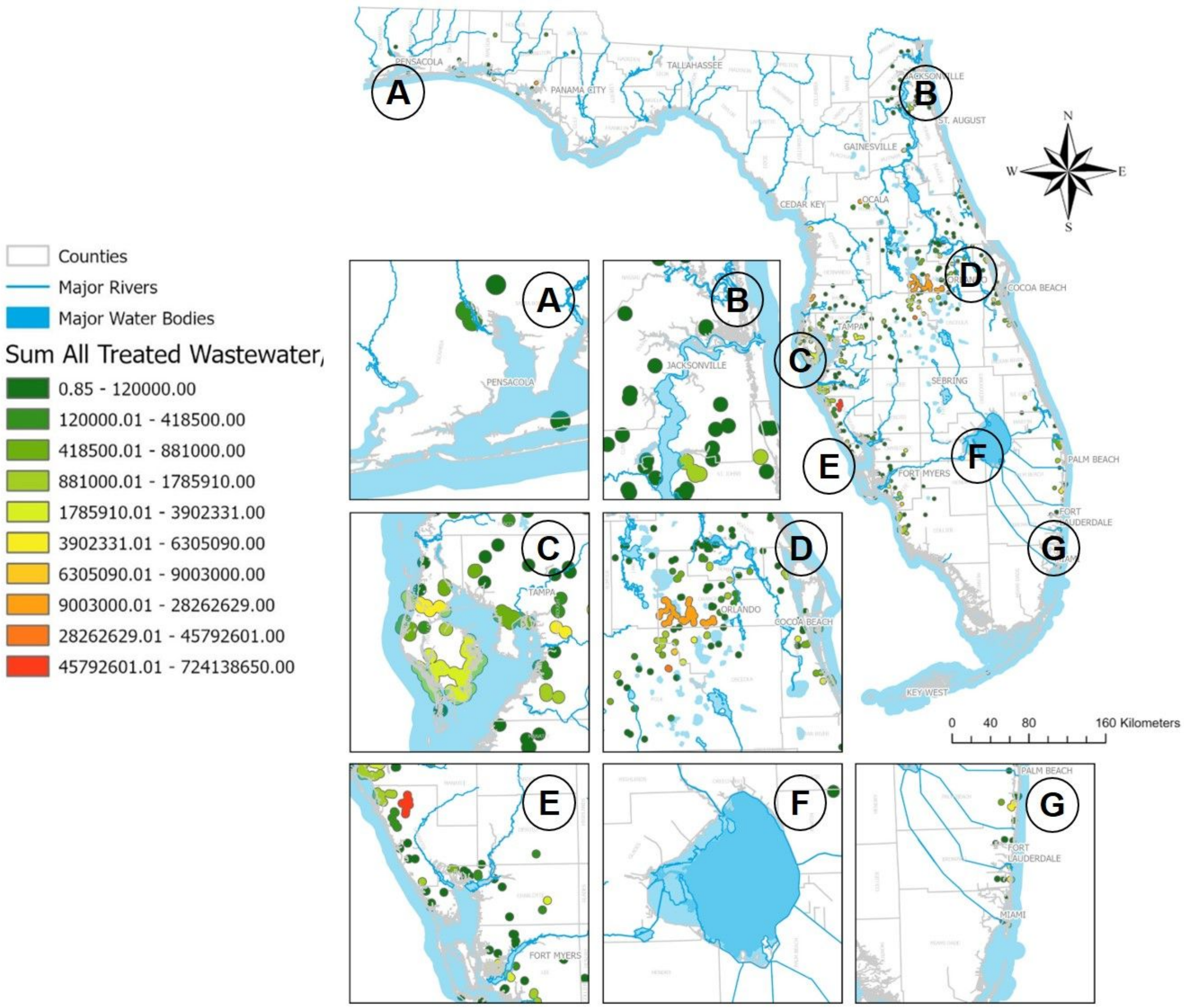
Supporting Information Figure S18. Sum of raw sewage spills in the state of Florida (to date).



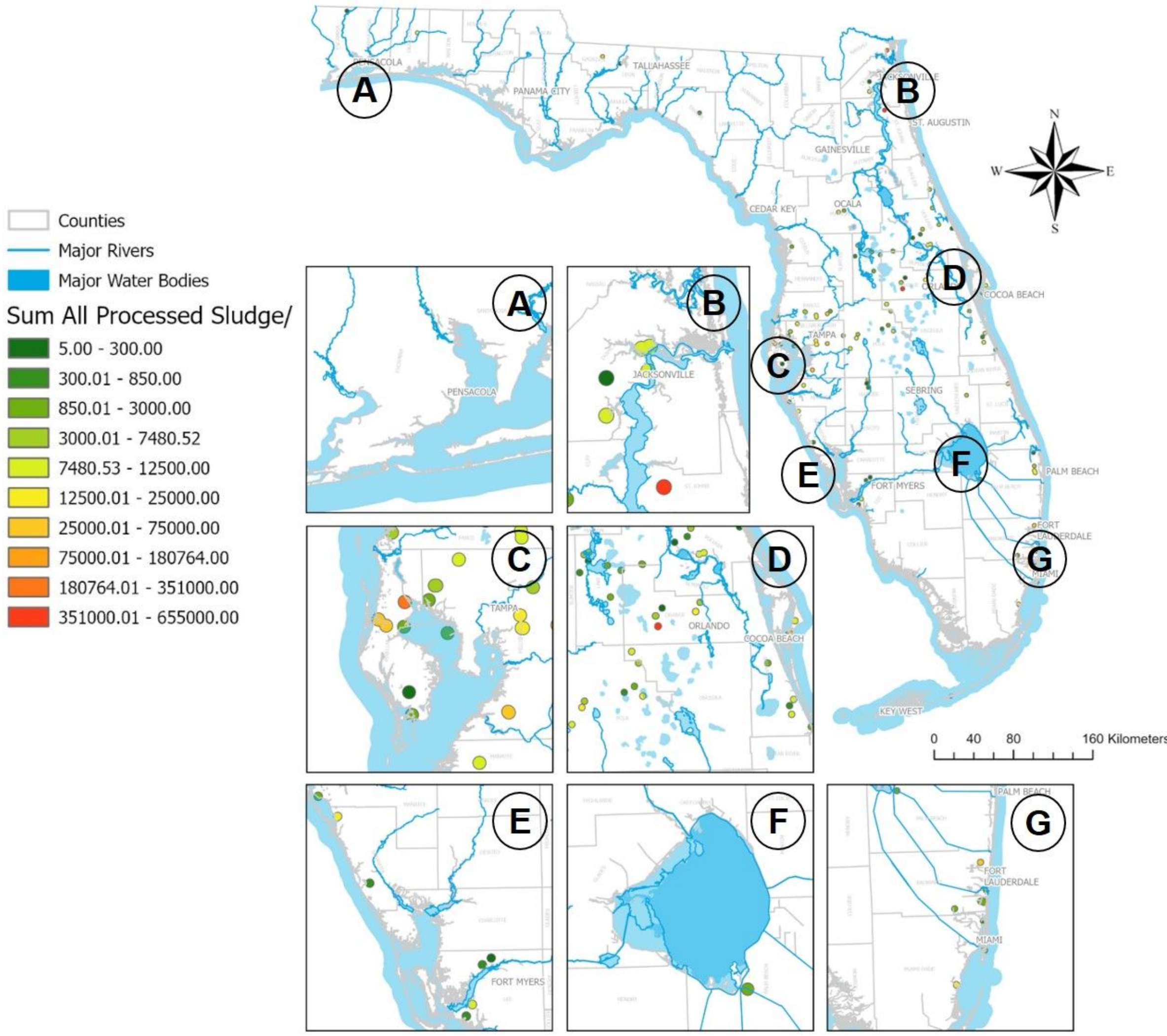
Supporting Information Figure S19. Sum of untreated/partially treated wastewater spills in the state of Florida (to date).



Supporting Information Figure S20. Sum of treated wastewater spills in the state of Florida (to date).



Supporting Information Figure S21. Sum of sludge/solid spills in the state of Florida (to date).



Supporting Information Figure S22. Sum of various liquid spills in the state of Florida (to date).