

5. Contaminants

5.1. Background

Contaminants are chemicals that are found at elevated concentrations in any environment. Some are produced solely by human activity, but many are also produced naturally in small quantities. Both anthropogenic (human-made) and naturally occurring compounds may become contaminants when they are introduced into ecosystems at elevated concentrations, often as a result of human activity (examples are polyaromatic hydrocarbons, or PAHs, and metals). Concentrations of naturally-occurring compounds often vary with local geology and environment. Thus, it is much more difficult to detect human input and harmful concentrations for naturally occurring compounds than for those that are produced solely by human activity.

A chemical becomes environmentally significant when it is prevalent, persistent, and toxic. The prevalence of a chemical in any system depends on how much of it goes in and how quickly it goes out, either by flowing out or by degrading. A compound that is persistent breaks down slowly and is removed slowly. The probability of long-term toxic effects increases with persistence. Some types of chemicals are taken up and stored in fat tissues of plants and animals with little or no degradation, i.e., they *bioaccumulate*. Bioaccumulated chemicals are stored in tissues of prey organisms and when prey are eaten, the chemicals can be transferred to predators and travel up the food chain in increasingly higher levels, i.e., they *biomagnify*. Thus, organisms containing the bioaccumulated chemicals act as a reservoir, which is only slowly depleted.

Contaminants can also reside in sediments and in the water. They will partition between biota, sediments and water in ratios that depend on the chemical and the conditions. The sediments of rivers often serve as reservoirs for chemical contaminants. Many of the environmentally important compounds are attracted to the organic matter in sediments and end up there, regardless of how they enter the water body. Plants and animals that live in sediments (benthic organisms) are potentially exposed to contaminated water and sediments, so assessments of their toxic responses to contaminants are particularly important in determining overall river health.



Figure 5.1 Sediment at Talleyrand, LSJR

5.1.1. Assessments of Status and Trends

Chemicals in four environmentally significant categories are evaluated in this report. The categories include 1) polyaromatic hydrocarbons (PAHs), 2) metals, 3) polychlorinated biphenyls (PCBs), and 4) pesticides. These chemicals vary in their chemical structure, their sources, and their specific fates and effects, but they all have a high potential for prevalence, persistence, toxicity and bioaccumulation. Each of the categories is discussed separately.

Sediment contaminants are examined in terms of frequency of occurrence, the concentrations present, and whether any trends up or down exist. The cumulative impact of the chemicals is estimated as well as the relative toxic impact of the different classes in different regions. Methods we used to determine toxic impact are discussed in the next section. It is important to note that most of these data end in 2007.

Water column concentrations of metals are included because more of these compounds will reside in the water column than the other classes of chemicals. The distributions of the metal data are compared to Florida ambient water quality standards. These parameters are regularly monitored and data are current.

The rate at which chemicals are released into the environment clearly affects their potential environmental impact. In addition to examining concentrations of contaminants found in the LSJR sediments and water, we examined the status and trends of reported chemical releases into the atmosphere and waterways of the LSJR using the Toxics Release Inventory database (EPA 2015d; EPA 2015b) and the Risk Screening Environmental Indicators model (EPA 2013e), both provided by the EPA. Releases of all chemicals are discussed in Section 5.4 and releases of the metals and PAHs are discussed in their respective sections.

5.2. Data Sources and Analysis

5.2.1. Water

All data were obtained from the Florida DEP STORET database. STORET is a computerized environmental data system containing water quality, biological, and physical data. Total metal concentrations of the LSJR were used in this analysis. EPA methods 200.7, 200.8, and 206.2 were used to measure arsenic; EPA methods 200.7, 200.8, 213.2, and 6010B were used to measure cadmium; EPA methods 200.7, 200.8, 220.2, and 6010B were used to measure copper; EPA methods 200.7, 200.8, 249.2, and 6010B were used to measure nickel; EPA methods 200.7, 200.8, 272.2, and 6010B were used to measure silver; and EPA methods 200.7, 200.8, and 6010B were used to measure zinc.

The LSJR varies in salinity, with the mainstem predominantly freshwater and some of the tributaries ranging from fresh-to full strength seawater. Salinity may affect the toxicity of some metals to aquatic life, therefore the EPA class III Water Quality Criterion (WQC) values may be different for freshwater and marine water. Likewise, for freshwater, hardness, defined as the total concentration of the divalent cations calcium and magnesium, has also been shown to reduce the toxicity of the metals cadmium, copper, lead, nickel, and zinc; therefore, the freshwater criterion is based on an equation which incorporates the hardness of the water body. For the hardness-dependent metals in this analysis, an average hardness value of 100 mg CaCO₃/L was used for generating the freshwater criteria.

The WQC for marine (haline; surface chloride concentration $\geq 1,500$ mg/L) waters was also used for all of the metals, except for silver, for which no marine water quality criterion has currently been adopted by the U.S. EPA. Therefore, the current proposed WQC value for silver has been used. It must be pointed out that the freshwater and marine WQC are the same for some metals, like arsenic, for example. However, for other metals, like cadmium, the freshwater WQC is substantially different (0.27 $\mu\text{g/L}$ at 100 mg/L hardness) from the marine criterion of 8.8 $\mu\text{g/L}$. Therefore, for river segments or water bodies that have no saltwater influence, the potential for environmental impacts of certain metals may vary.

Data are presented in box and whisker plots, which consist of a five number summary including: a minimum value; value at the first quartile; the median value; the value at the third quartile; and the maximum value. The size of the box is a measure of the spread of the data with the minimum and maximum values indicated by the whiskers. The median value is the value of the data that splits the data in half and is indicated by the horizontal blue line in the center of the boxes. Data are also presented as yearly mean values and compared to the designated reference values. Graphs are presented for the entire LSJR (including tributaries), the freshwater and saltwater portions of LSJR mainstem, as well as for the tributaries in some cases. Data used from the Florida DEP STORET database are of higher quality but are less abundant than data from the EPA STORET. Only total metal concentrations were used in this report, rather than the preferred dissolved metal concentrations, which are used in calculation of water quality criterion values. Total values were used because the dissolved metal concentrations were not reported to a large extent, and in many cases dissolved values only accounted for less than 5% of the total data reported. Additionally, negative values were removed and values designated as present below the quantitation limit (QL) were replaced with the average of the method detection limit (MDL) and practical quantitation limit (PQL). For "non-detect" values, half the MDL was used; and, for values designated as "zero" the MDL was used. Data were rejected and not used if they had the value qualifier code of K, L, O, or Y. Data designated with a matrix of "ground water", "surface water sediment," "stormwater," or "unknown" were removed. Records with no analytical procedure listed were also removed.

5.2.2. Sediment

5.2.2.1. Sediment Data Sources

The data used in this report came from several major studies carried out on the Lower St. Johns River from 1983 to 2007. They were conducted by the SJRWMD (**Delfino et al. 1992; Delfino et al. 1991a; Durell et al. 2004; Higman et al. 2013**) and the Florida Department of Environmental Protection (**Delfino et al. 1991a; Pierce et al. 1988**), Data were used from the National Oceanographic and Atmospheric Administration's National Status and Trends Mussel Watch program (**NOAA 2007b**) and Benthic Surveillance Watch (**NOAA 2007a**) program. Data from STORET databases managed by the EPA (modern) and DEP were included as well. The STORET data were from studies by the National Park Service Water Resources Division, Florida Department of Environmental Protection, and the Marine Research Institute of the Florida Fish & Wildlife Conservation Commission. Savannah Laboratories (**SLES 1988**), **Cooksey and Hyland 2007**, and **Dames and Moore 1983** also generated data that were analyzed in this report. The best and most recent data came from an extensive set of studies conducted by the SJRWMD. This study began in 1996 and provides a long-term sediment quality assessment of the LSJR (**Durell et al. 2004; Durell et al. 1997; Higman et al. 2013**).

A summary of the sources of data is given in Appendix 5.2.A. The database that was generated represents a substantial portion of existing data for LSJR contaminants. It is not exhaustive however, and should be considered a starting point from which omitted past and future studies can be added. In particular, modern pesticides, other important priority pollutants and emerging pollutants, such as endocrine disruptors, should also be included. Future additions of data on concentrations of contaminants in water and organisms will also add to the quality of the assessment.

The contaminants we selected for evaluation had the highest abundance of data available for several years and adequate site information. Sometimes we omitted potentially important contaminants because of analytical differences between studies. The data were first compiled from each source for approximately 200 analytes at nearly 500 sites, over a span of 20 years, and then were culled for location and analytical comparability. We omitted data from some years when the numbers of samples were too few, or when extreme values distorted the analysis. For example, Deer Creek samples in 1991 that consisted of nearly pure creosote (**Delfino et al. 1991b**) were omitted.

Sediment contamination was assessed by calculating average concentrations, percent exceedances of sediment quality guidelines, and average toxicity quotients, or toxicity pressure. These parameters were compared between years and regions of the river. Data below the detection limit were evaluated as zeroes in these calculations. The numbers of samples for each contaminant, year, and area are given in Appendix 5.2.B.

Trends were assessed by plotting median annual concentrations against time and determining the significance of an upward or downward slope of any line (Spearman Rank correlation coefficients $p < 0.05$). Because of the limitations of the data, all trends were confirmed by graphical analysis and Pearson Product coefficient > 0.5 . Trend statistics are given in Appendix 5.2.C.

Advances in analytical technology during the last 20 years have dramatically reduced the concentration at which some chemicals can be detected. This can skew interpretations of temporal trends, which we attempted to avoid by transforming the zero values in the data to minimum detectable levels. Where possible, the reported minimum detection limits were substituted for zero values. In some cases, we estimated a minimum level of detection by finding the lowest nonzero value in a given year and halving it. Using minimum detection limits reduces the possibility of erroneously concluding there is an increasing trend because of differences in analytical detection limits.

There are numerous sources of variability in reported sediment concentrations, including analytical differences, sampling variations, physical and chemical characteristics of the sediment, and even differences in definitions of reporting parameters such as minimum detectable limits. Furthermore, there are large differences in the numbers of samples in different regions, all taken at irregular intervals. These data gaps limit the applicability of many different standard statistical tests. Thus, major harmful contaminants and their spatial and temporal trends can be difficult to positively identify and requires judicious use of statistics and careful review of all data. Box and whisker plots of the data are given in Appendix 5.2.D, which illustrate the distribution of the values for each contaminant in each region for each year.

5.2.2.2. Sediment Quality Guidelines

Environmental toxicology is the study of the effects of contaminants on ecosystem inhabitants, from individual species to whole communities. While toxicity is often viewed in terms of human health risk, human risk is one of the most difficult toxicity "endpoints," or measures, to accurately quantify. The effects on ecosystems and aquatic organisms are the focus of our assessment of contaminants in the LSJR although human health effects from mercury in fish are discussed.

The environmental impact of a toxic compound can be evaluated several ways. One way is by comparing the concentrations in the LSJR to various toxicity measures. When the concentration of a contaminant in sediment is greater than the toxicity measure, it is an *exceedance*. Most sediment quality guidelines for contaminants are based on the impact of contaminants on sediment-dwelling benthic macroinvertebrates, assessing both the individual species' health and the community structure. Since these organisms are at the beginning of the fisheries food chain, their health is a good indicator of general river health. One toxicity measure that is quite protective of the health of aquatic organisms is a *Threshold Effects Level (TEL)*. This is the concentration at which a contaminant begins to affect some sensitive species. When the number of sites that have concentrations greater than the TEL is high, there is a higher possibility that some sensitive organisms are affected. A second, less protective guideline is the *Probable Effects Level (PEL)*. This is the concentration above which many aquatic species are likely to be affected. The TEL and PEL sediment quality guidelines for marine systems are used in this assessment, with emphasis on the latter. These were the guidelines that were most widely available for the compounds of interest, plus much of the heavily impacted areas are in the marine section of the LSJR. Some alternative guidelines are used and identified for some compounds for which there were no marine TEL or PEL guidelines (MacDonald 1994; NOAA 2008). Specific values are listed in Appendix 5.1.A.

In an approach similar to Long et al. 1995 and Hyland et al. 1999, we evaluated overall toxicity of nearly 40 chemicals on the river ecosystem by calculating a PEL quotient, or **toxicity pressure**, for each sample. The quotient is the concentration of a contaminant in the sediment divided by the PEL value. If the quotient, or toxicity pressure, is greater than one, adverse impacts on benthic organisms are probable. As the quotient increases, we can assume that the probability of toxic effects increases. The quotients are used to compare the effects of different chemicals and to understand their relative importance in the impairment of the river health.

While sediment quality guidelines are useful tools, it is important to appreciate the limitations of simple comparisons in the extremely complex LSJR. A major difficulty in assessing toxic impacts is that the accessibility, or bioavailability, of a contaminant to organisms may vary with sediment type. Two sediments with similar contaminant concentrations but different physical and chemical features can produce very different environmental impacts, and we know that LSJR sediments are highly variable. Furthermore, each sediment quality guideline can be specific to certain organisms and endpoints (e.g., death of fish, reproductive effects of sea urchin, sea worm community structure, etc.) and cannot easily be extrapolated to other organisms or endpoints. As a consequence, guidelines from different organizations are sometimes different. Finally, separate guidelines are often established for marine and freshwater environments, though few estuarine guidelines exist that apply to the LSJR. These challenges limit our assessment of the impacts of various contaminants on the LSJR to one that is general and relative in scope.

5.2.2.3. Regions of the LSJR

Within the LSJR basin, there is a large variation in the types of ecosystems, land uses, and hydrology. As a consequence, the distribution and potential impacts of contaminants will vary widely within the basin at any given time. To analyze sediment contaminants in the LSJR, we divided it into four regions (Figure 5.2) with roughly similar hydrologic and land use characteristics. Where possible, trends were tracked within each region, and comparisons were made between the regions.

One region, Area 1, is a composite of the basins of three tributaries on the western side of the LSJR. The western tributaries area is composed of the Trout River (including Moncrief Creek and Ribault River tributaries), Long Branch Creek, the Cedar-Ortega system, Big Fishweir Creek, and Rice Creek. Despite their distance from one another, they were combined because they share the unfortunate characteristic of having such high levels of contamination for some chemicals that they mathematically obscure trends in the rest of the lower basin. The northernmost region, Area 2, the north arm, stretches from the coast at Mayport to Talleyrand, and has an extensive maritime industry. It is strongly tidal with a range of salinity from marine to estuarine. Moving south, the next region is Area 3, or the north mainstem, which includes urban Jacksonville and extends down to Julington Creek.

The southernmost region in the LSJR, Area 4 or the south mainstem, stretches from the Duval County boundary, past Palatka to the Ocklawaha and fresher water. Additional information about the different regions is given in Appendix 5.2.E.

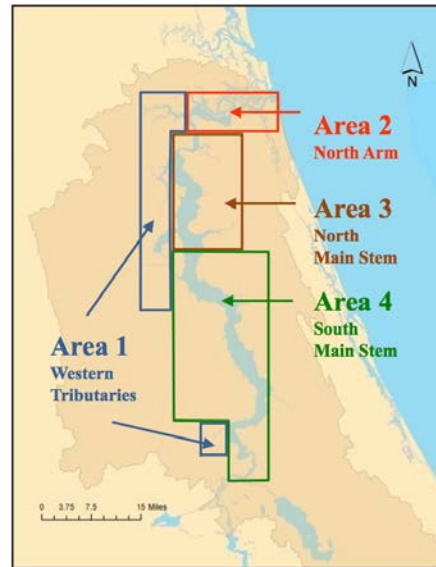


Figure 5.2 Areas of the LSJR studied for sediment contamination: Area 1 – western tributaries (including Trout River, Moncrief Creek, Ribault River, Long Branch Creek, Cedar-Ortega Basin, and Rice Creek); Area 2 – north arm; Area 3 – north mainstem; Area 4 – south mainstem. See Appendix 5.2.E for additional details.

5.3. Toxics Release Inventory: Point sources of contaminants in the LSJR region

The EPA’s Toxics Release Inventory (TRI) program was established as a provision of the Emergency Planning and Community-Right-to-Know Act designed to protect communities from chemical hazards. The legislation was enacted in 1986 after serious industrial accidents in Bhopal India and in West Virginia resulted in numerous fatalities. The program was expanded under the 1990 Pollution Prevention Act so that today the TRI program requires facilities to report the quantities of more than 650 toxic chemicals that they release into the environment. Annually, they must report how much of each of these compounds is released on-site into the air, to surface water, to groundwater, to landfills, and to surface impoundments. They must also quantify how much they treat on-site and how much is transported off-site for treatment or disposal (e.g., to publicly-owned municipal treatment plants or to landfills). Facilities are not required to report their releases if they have fewer than 10 employees or if they discharge less than various threshold limits for different chemicals (EPA 2015d). The reported quantities may be derived from direct measurement, modeling estimates, or by “emission factors.” The emission factors are usually averages of available data on emission rates of facilities in a particular source category (e.g., electric utilities, on-road vehicles) (EPA 2013f).

The TRI provides information that can be used to estimate point source loading of hundreds of chemicals released into the environment by dozens of industries. Local, statewide or national trends can be examined. We determined the annual loading of toxic compounds into the LSJR basin from 2001 to 2013 using data from EPA’s TRI-NET database (EPA 2015b). Emissions into the atmosphere and discharges into LSJR surface waters were analyzed since chemicals released to these media are most likely to affect the LSJR, though significant discharges to land are also reported for many industries (Table 5.1). The environmental impact of atmospheric emissions is more difficult to determine than direct surface water discharges because of uncertainties in the fate of chemicals in the atmosphere and the potential impact from both long-range and local sources. However, higher local emissions will certainly increase the likelihood of local impact. In the following discussion, atmospheric emissions are addressed separately from surface water discharges.

Analyses of air emissions included all reporting facilities in the nine counties in the LSJR watershed: Clay, Duval, Flagler, Putnam, St. Johns, Volusia, Alachua, Baker, and Bradford. Even if facilities are not located directly on the river, nearby emissions are potential sources of pollutants in the river, though exactly how much finds its way into the river is largely unknown. For discharges into the LSJR surface waters, we included facilities that discharged directly into the SJR or its tributaries, as determined by the Form R report submitted by the facilities to the EPA. It is important to note that the magnitude of discharges or emissions does not always directly relate to human health effects or environmental harm. The Risk-Screening Environmental Indicators (RSEI) is a companion EPA program that uses TRI data to screen for overall toxicity (EPA 2013e).

Quantities of chemicals, their individual toxicity, their fate in the environment, and their proximity to people are used to determine discharges of toxicity, rather than pounds. The relative importance of major emissions and discharges to chronic human health is addressed using the results of the RSEI model, although data are only available until 2011. It is important to note that the RSEI analysis does not indicate that there is a human health risk. It only indicates which emissions and discharges in our local environment are the most likely to have chronic human health risks associated with them.

Table 5.1 Reported Releases of Chemicals by Industries in the LSJR Basin (EPA 2015d).

Releases of Chemicals to the Atmosphere¹				
Year	Total Tons	No. Chemicals²	No. Industries	No. Facilities
2001	7,928	69	21	79
2002	8,016	69	21	80
2003	7,697	67	21	78
2004	7,736	68	21	75
2005	7,258	62	21	73
2006	6,898	61	21	71
2007	6,236	6	20	71
2008	5,883	60	21	76
2009	3,774	53	21	70
2010	3,965	55	21	71
2011	3,055	56	21	74
2012	2,179	54	21	71
2013	2,176	59	21	78
Releases of Chemicals to the LSJR and Tributaries³				
Year	Total Tons	No. Chemicals²	No. Industries	No. Facilities
2001	152	28	10	15
2002	168	34	11	16
2003	233	30	10	14
2004	261	22	7	10
2005	302	23	8	11
2006	136	24	6	10
2007	216	28	7	11
2008	188	30	9	12
2009	278	27	8	11
2010	162	29	8	11
2011	205	30	7	11
2012	269	29	7	10
2013	203	26	6	9

¹ Chemical releases from facilities emitting into the atmosphere in nine counties of the LSJR watershed
² Number of unique chemicals or chemical classes released.
³ Chemical releases from facilities discharging to the surface waters of the LSJR and its tributaries.

Typically, industrial facilities emit more chemicals into the atmosphere than into surface water (Table 5.1). The reporting facilities in the nine LSJR counties released 91% of their waste into the atmosphere. These numbers do not include the on-site releases to landfills and surface impoundments.

Between 2001 and 2013, the reported annual release of chemicals to the atmosphere declined by over 70% to 4.4 million pounds (Figures 5.3 and 5.4). Reductions in emissions of hydrochloric and sulfuric acids by St. Johns River Power Park and Northside Generating Station, Seminole Electric and Gainesville Regional Utilities at Deerhaven were responsible for most of the decline. Sulfuric acid declined the most with a 6.2 million pound or 79% reduction over 13 years. Emissions declined for 58 of the 83 reported chemicals between 2001 and 2013. Ammonia, hexane and phenol were major exceptions with increases of 63%, 159% and 595%, respectively.

Despite the substantial reductions in acid gas emissions (sulfuric, hydrochloric and hydrofluoric acids), they still comprised 63% percent of the chemicals reported to be released to the LSJR region atmosphere in 2013, mostly released by electric

utilities. Of the total atmospheric releases in 2013, 30% were composed of methanol, ammonia and styrene that were emitted primarily by electric utilities and the transportation equipment and paper industries. The remaining chemicals released into the atmosphere were organic and inorganic compounds, such as polyaromatic hydrocarbons and metals discussed in more detail in Sections 5.4 and 5.5.

In 2011 (the most recent year for which the RSEI model has data), regular emissions of sulfuric acid had the highest potential for chronic human health risk of all reported atmospheric releases, followed by cobalt, arsenic, and chromium, which were all emitted by the electric utilities. An accidental release of ethylene oxide by BAE Shipyards was also significant in 2011. Releases of formaldehyde by Georgia-Pacific and benzene by BP Products were also among the top ten atmospheric releases that had the highest potential for human health risks (EPA 2013e).

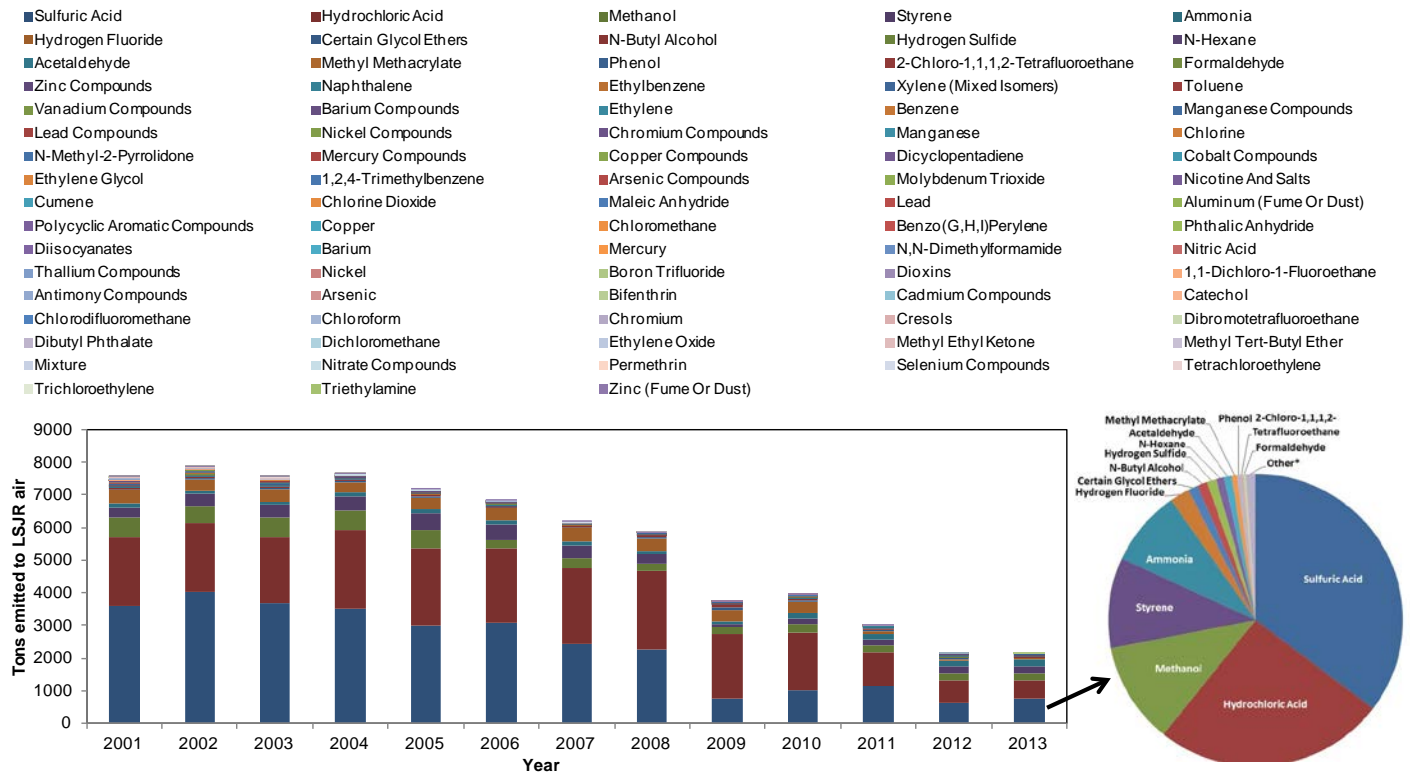


Figure 5.3 Trends and status of 83 chemicals released to the atmosphere by industries in the nine-county LSJR basin as reported in the Toxics Release Inventory (EPA 2015d). Inset shows the distribution of 2,176 tons of chemicals emitted in 2013. The Other category in the inset is composed of 44 chemicals ranging from 3.3 tons of zinc to 40 milligrams of dioxins.

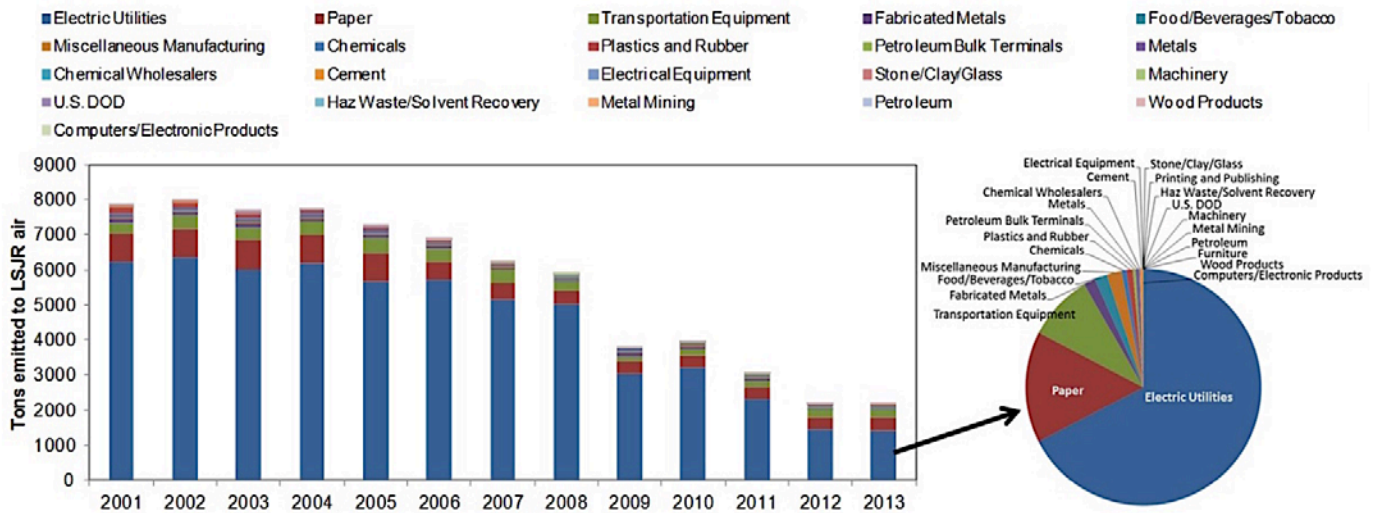


Figure 5.4 Trends and status of 23 industries releasing chemicals to the atmosphere in the nine-county LSJR basin as reported in the Toxics Release Inventory (EPA 2015d). Inset shows the major industries emitting 2,176 tons of chemicals in 2013.

Unlike atmospheric emissions, surface water discharges into the LSJR did not decline between 2001 and 2013, but have increased by 34%. Fluctuations in the extremely large discharges of nitrate and manganese by the paper industry and U.S. DOD affected overall SJR loading during the decade (Figures 5.5 and 5.6). Of the chemicals reported to be released into surface water in 2013, 12 were discharged at greater rates since 2001 and 12 chemicals were discharged at lower rates. The electric utility industry experienced an increase of 186% (nearly 15,000 pounds) in total annual chemicals discharged between 2001 and 2013, much of it in the form of nickel, barium, and cobalt compounds.

In 2013, most of the chemicals reported to be discharged directly into the SJR and its tributaries were nitrates released by the U.S. Department of Defense (over 318,000 lbs.) and manganese by the pulp and paper industry (51,000 lbs.). The paper industry reported no nitrate discharges in 2013, in contrast to 2013 when 105,000 pounds were reported. The nitrate and manganese discharges represented 91% of the total quantity of chemicals released into the LSJR in 2013 (Figures 5.5 and 5.6).

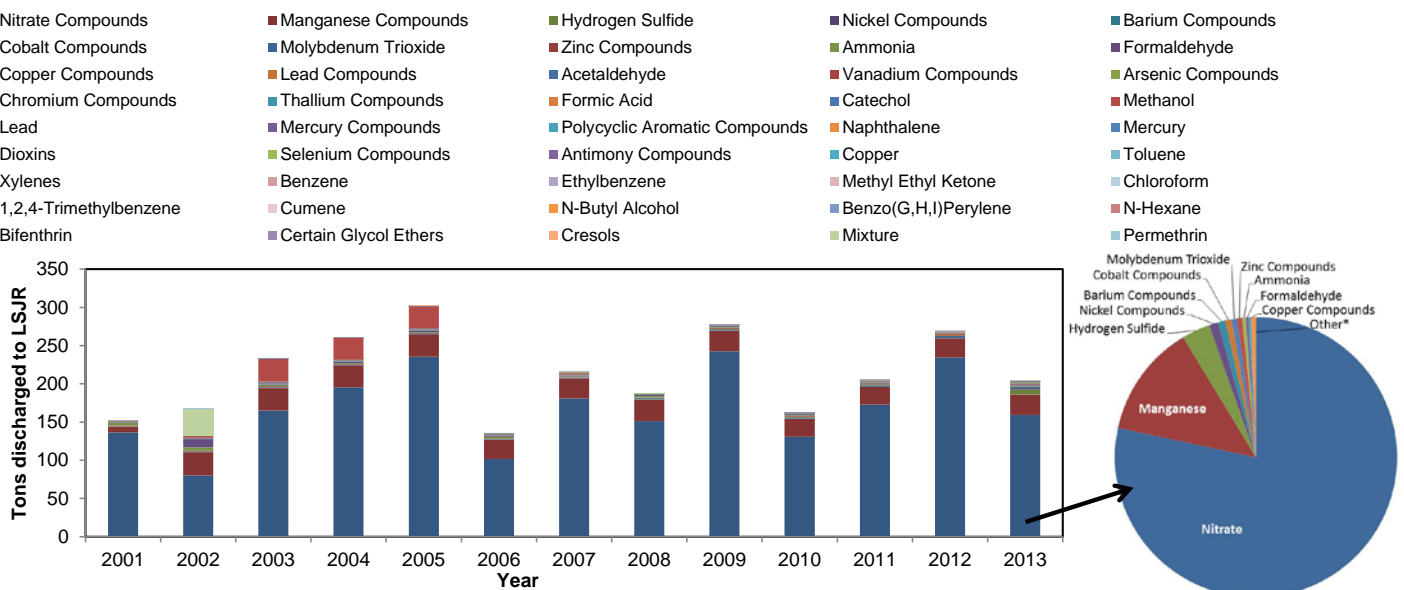


Figure 5.5 Trends and status of 46 chemicals released to the LSJR and its tributaries as reported in the Toxics Release Inventory (EPA 2015d). Inset shows the distribution of over 400,000 pounds of chemicals discharged in 2013. The Other category in the inset is composed of 15 chemicals ranging from 510 pounds of lead compounds to a few milligrams of dioxins.

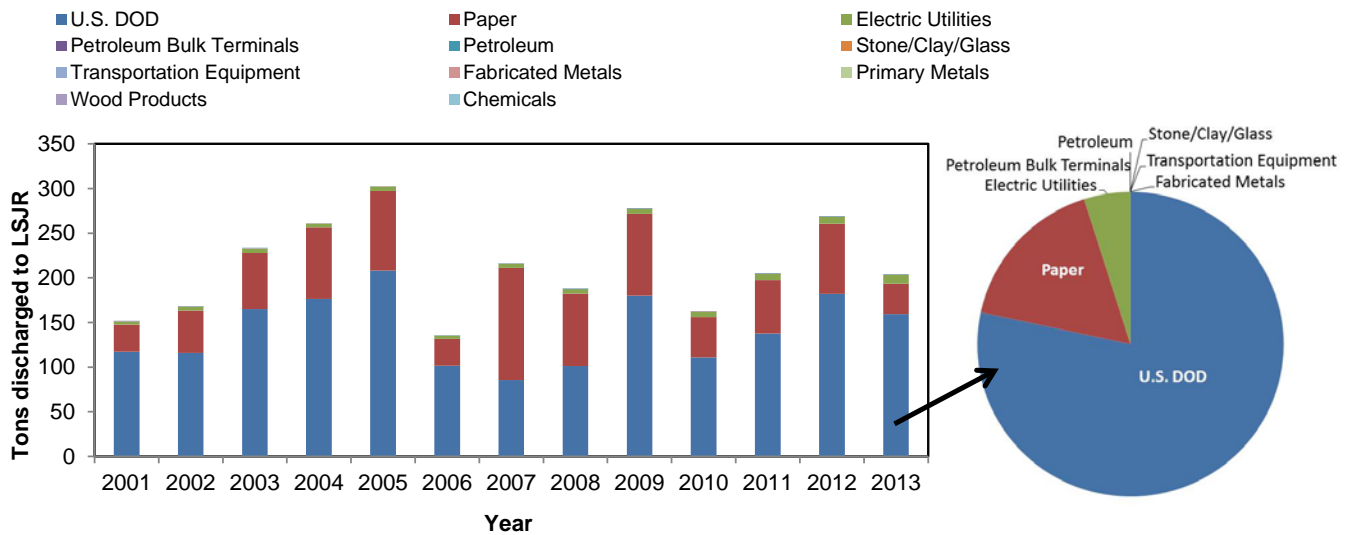


Figure 5.6 Trends and status of 11 industries releasing chemicals into the LSJR and its tributaries as reported in the Toxics Release Inventory (EPA 2015d). Inset shows the major industries discharging over 400,000 pounds of chemicals in 2013.

An analysis of toxicity loading into the LSJR surface waters by industries is greatly hindered by the fact the St. Johns River Power Park/Northside Generating Station, a major discharger, is not included in the EPA RSEI model because there is insufficient or questionable information about the segment of the river where it discharges its effluents. This may result from the reverse flow of the river causing difficulties with the model accuracy or due to inadequate flow information about the region from the National Hydrography Dataset used in the model (EPA 2013c). However, of the remaining discharges in 2013, arsenic, mercury, copper and polyaromatic hydrocarbons released by the other electric utilities contributed most of the total toxicity along with lead, mercury and dioxins discharged by the pulp and paper industries. The major pathway to exposure was found to be fish ingestion.

In summary, industries in the LSJR region reported the release of 4.8 million pounds of chemicals into the air and into the river and its tributaries in 2013, with 91% released into the air. Local emissions to the atmosphere, mostly from electric utilities, are primarily composed of acid gases followed by methanol, styrene, and ammonia. Air emissions have declined by more than two-thirds between 2001 and 2013, which is similar to the rest of the state (EPA 2015c). The LSJR surface waters received over 400,000 pounds of chemicals in 2013, mostly nitrates and manganese released by the U.S. Department of Defense and the paper industry. The rate of discharge of chemicals into the LSJR surface waters in 2013 is 34% greater than in 2001 while the rest of the state discharged 24% less since 2001.

Of all atmospheric emissions in the LSJR region in 2011, sulfuric acid and metals emitted into the atmosphere by electric utilities were most likely to cause chronic human health effects. Of surface water discharges in the LSJR in 2011, metals, polyaromatic hydrocarbons and dioxins discharged by electric utilities and the paper industry had the highest potential for human health risk. It is important to note that this does not mean that there is a human health risk. It means simply that of all the chemicals released into our local environment by industry, these are the most likely to be the most significant in terms of human health.

Overall, TRI data suggest that the mass of contaminants released to the atmosphere from point sources in the LSJR region has significantly declined over a decade though little change in overall surface water discharges has occurred. These reductions in atmospheric emissions may be related to the recently enacted rules for reducing air emissions of mercury and other toxic compounds from coal-fired utilities (EPA 2013d). Emissions are frequently estimated from production-dependent emission factors, thus the decline in reported emissions may reflect the general decline in U.S. industrial productivity during the last several years.

The **STATUS** of point sources of toxics emitted into the atmosphere is *satisfactory* because the rate of emissions is similar to the rest of the state and the **TREND** is *improving*. The **STATUS** of point sources of toxics discharged into the LSJR surface waters is *unsatisfactory* because the rate of discharges exceeds the rest of the state, and the **TREND** is *unchanged*.

5.4. Polyaromatic Hydrocarbons (PAHs)

5.4.1. Background and Sources: PAHs

Polyaromatic hydrocarbons are a class of over 100 different chemicals, some of which are carcinogenic. They are often found in the environment in complex mixtures. Sometimes the patterns of distribution of the different types of PAHs can indicate their sources and fates. They are often subdivided into classes of small, Low Molecular Weight (LMW) compounds, and larger, High Molecular Weight (HMW) compounds. The two subclasses of PAHs tend to have different sources, environmental fates, and toxic effects, although there is considerable overlap in their characteristics.

PAHs arise from two major pathways. Pyrogenic ("fire"-generated) PAHs are formed during the combustion of organic matter, including fossil fuels. The PAHs formed by combustion tend to be the HMW type. Petrogenic ("petroleum"-generated) PAHs are also formed naturally and are precursors and components of complex organic matter including oil, coal, and tar. Petrogenic PAH mixtures tend to have more of the LMW type of PAH.

Although PAHs are naturally occurring, large quantities are introduced into the environment by human activities, particularly through fossil fuel handling and combustion. About 80% of PAH emissions are from stationary sources such as power plants, and 20% come from mobile sources such as automobiles and trucks, but the distribution can change with locale. Urban environments have more vehicular-related PAHs than rural or agricultural areas (ATSDR 1995). They may also be introduced into the aquatic environment from creosote in preserved wood, which may be a significant historic source of PAHs in the north mainstem of the LSJR.

PAHs are mainly introduced into water bodies by the settling of PAH-laden atmospheric particles into the water, and by the discharge of wastewaters containing PAHs. Spills of petroleum products and the leaching of hazardous waste sites into water bodies are other ways that PAHs enter the aquatic environment.

5.4.2. Fate: PAHs

PAHs have a low affinity for the water phase and will tend to bind to phase boundaries, such as surface microlayers and the surface of particles, particularly organic phases (i.e. organisms and the organic fraction of sediments) (Karickhoff 1981). Once they are in the water, the PAHs tend to settle into the sediments fairly quickly, especially the HMW PAHs. The LMW PAHs also associate with particles, but to a lesser extent. As a result, the LMW PAHs can be transported farther by the river's tides and currents.

PAHs can be degraded by microbes and broken down by sunlight. Biodegradation accounts for the majority of removal in slow-moving, turbid waters typical of some of the LSJR. Many aquatic organisms can metabolize and excrete PAHs, particularly the LMW types, so the chemicals are not extensively passed up the food chain. However, HMW PAHs can accumulate in fish, amphipods, shrimp, and clams since they are only slowly degraded and reside in fats in organisms (ATSDR 1995; Baird 1995).

The EPA has focused on 17 different PAHs primarily because they are the most harmful, have the highest risk for human exposure, are found in highest concentrations in nationally listed hazardous waste sites, and because there is information available about them (ATSDR 1995). In our analysis of the LSJR sediment data, 13 of the 17 EPA compounds were examined in detail as well as two that are not on the EPA list. These PAHs were selected for study because of the extensiveness of the data, the uniformity of the study methods, and their presence in the LSJR.

5.4.3. Toxicity: PAHs

Although PAH accumulation does occur in organisms from all trophic levels (Carls et al. 2006; Cailleaud et al. 2009), the PAH concentrations do not biomagnify up the food chain (Broman et al. 1990). High molecular weight (HMW) PAHs are metabolized by most aquatic organisms to some extent; however, vertebrates have a greater metabolizing capacity than invertebrates (Baussant et al. 2001a; Cailleaud et al. 2009). Invertebrates, such as bivalves and polychaetes, are particularly slow to eliminate PAHs (Baussant et al. 2001a; Baussant et al. 2001b). PAH concentrations in several parts of the LSJR continue to be elevated (Section 5.3) as is reflected in the PAH concentrations observed in oysters collected in the LSJR (Section 5.3.4).

Because threshold PAH concentrations in the fish that result in toxicity (critical body residues) of PAHs are relatively constant, acute toxicity in fish is generally thought to be a function of the bioconcentration factor, resulting in narcosis. PAH toxicity occurs in lipids, particularly in the nervous system of fish, resulting in dysfunction (Barron et al. 2002; Barron et al. 2004). Specifically, the narcosis occurs due to PAH accumulation in the lipid bilayer of a biological cell membrane, which at elevated concentrations may disrupt the membrane integrity and function, leading to depression of the central nervous system (Van Wezel and Opperhuizen 1995; Barron et al. 2002; Escher et al. 2002; Escher and Hermens 2002; Barron et al. 2004). Although narcosis is reversible, depending on the PAH concentration, it may result in erratic swimming, reduced predator avoidance, and prey capture ability. PAH acute toxicity values (concentrations causing mortality to 50% of the organism; LC50s) range from 5 to 2,140 mg/L, with the HMW PAHs (e.g. benzo(a)pyrene) being most toxic (Neff and Burns 1996).

The chronic toxicity of PAHs is poorly studied. Donkin et al. 1989 reported a reduced feeding rate and reduced growth in bivalves exposed to PAHs. Flounder fed a phenanthrene-contaminated diet exhibited decreased levels of 17 β -estradiol (Monteiro et al. 2000). While several studies have suggested deformities and long-term growth and survival effects in fish embryos exposed to low levels of PAHs, the mechanism of toxicity is still unclear (Barron et al. 2004; Incardona et al. 2004). Sepúlveda et al. 2002 reported the accumulation of both LMW and HMW PAHs in the livers of Florida largemouth bass collected from different locations in the LSJR. The liver PAH concentrations were highest in the largemouth bass collected from Palatka, followed by Green Cove and Julington Creek, with the lowest concentrations detected in those collected from Welaka. Largemouth bass with elevated PAH and pesticide residues in their livers had decreased sex hormones. Furthermore, females had both lower vitellogenin (egg yolk precursor molecule) concentrations and a lower ratio of fish gonad weight to body weight (gonadosomatic index; GSI), which could affect reproduction in the fish (Sepúlveda et al. 2002).

5.4.4. Current Status: PAHs in Sediments

Polyaromatic hydrocarbons were found mostly at concentrations between the TEL and PEL guidelines. Most (~70%) of the samples in the western tributaries, Area 1, and the north arm, Area 2, had PAH concentrations exceeding the TEL, suggesting a low-level stress on sensitive benthic organisms by these compounds (Figure 5.7). The north arm had the most exceedances of the PELs, indicating that adverse impacts on benthic organisms from PAHs in that region are probable.

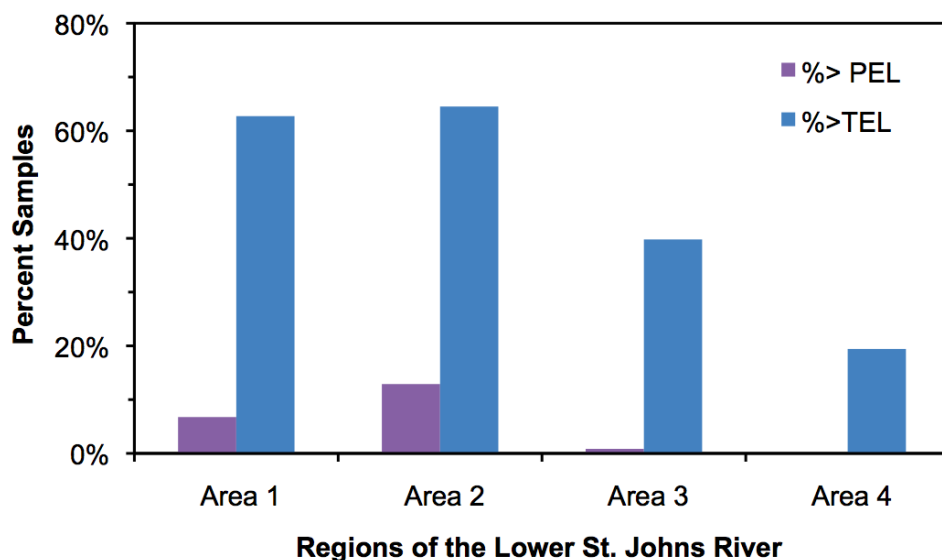


Figure 5.7 Percentage of samples from 2000-2007 with PAH concentrations that exceed Threshold Effects Levels (TEL) and Probable Effects Levels (PEL) for one or more PAHs. Area 1 – western tributaries; Area 2 – north arm; Area 3 – north mainstem; Area 4 – south mainstem. See text in Section 5.2 for data sources.

The toxicity pressure from PAHs was evaluated for each region using all data available since the 2000s. In Figure 5.8, the relative toxicity pressure from each PAH and the cumulative toxic pressure in each region can be compared. The PAHs exert similar overall toxic effects in Areas 1 and 2, but the PAHs responsible for the majority of the effects were different between the two regions, suggesting different sources of PAHs. The north arm, Area 2, is impacted most by acenaphthene (toxicity quotient >1) but fluoranthene, naphthalene, and 2-methyl naphthalene also contribute significantly to the toxicity pressure (toxicity quotient > 0.5).

In Area 1, the western tributaries, anthracene was the largest single contributor to PAH toxicity, while other PAHs exerted similar, low-level effects (Figures 5.8 and 5.9). Within Area 1, the highest levels for anthracene were found in Rice Creek in 2000-2003, with an average concentration nearly ten times the anthracene PEL (89 ppb), as shown in Figure 5.9. Levels near the PEL were also found in the Cedar-Ortega and Trout Rivers. Sediments in the north and south mainstem regions (Areas 3 and 4) had average concentrations between the two guidelines, and were similar in their patterns of PAH contamination. The north arm, Area 2, where the shipping industry is prevalent, sediments had higher proportions of acenaphthene, naphthalene, and 2-methyl naphthalene, LMW PAHs, than the rest of the mainstem.

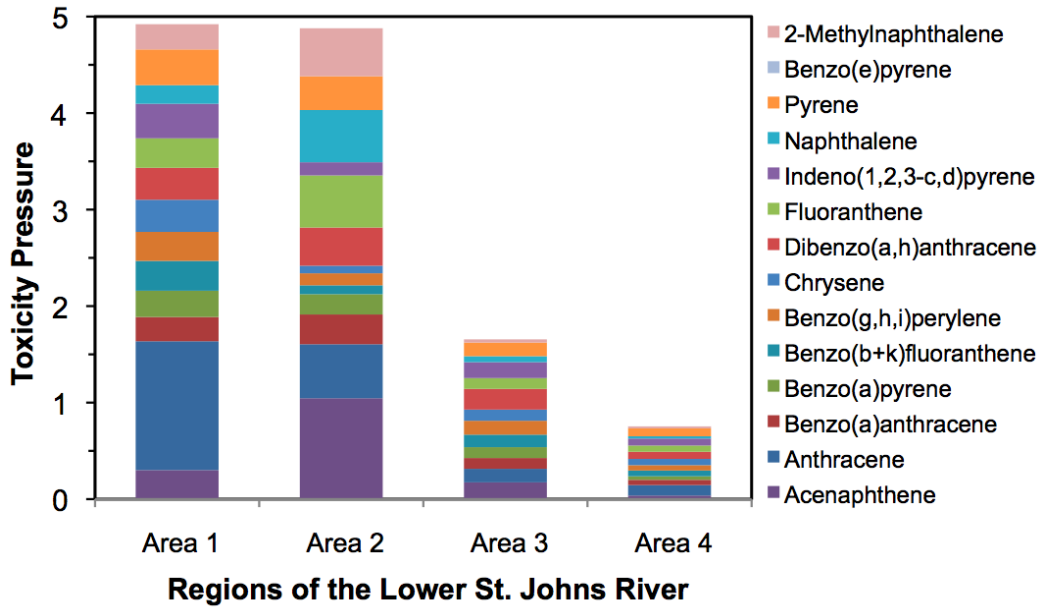


Figure 5.8 Average toxicity pressure of PAHs in sediments from 2000-2007 in the four areas of the LSJR. Area 1 – western tributaries; Area 2 – north arm; Area 3 – north mainstem; Area 4 – south mainstem. See text in Section 5.2 for data sources.

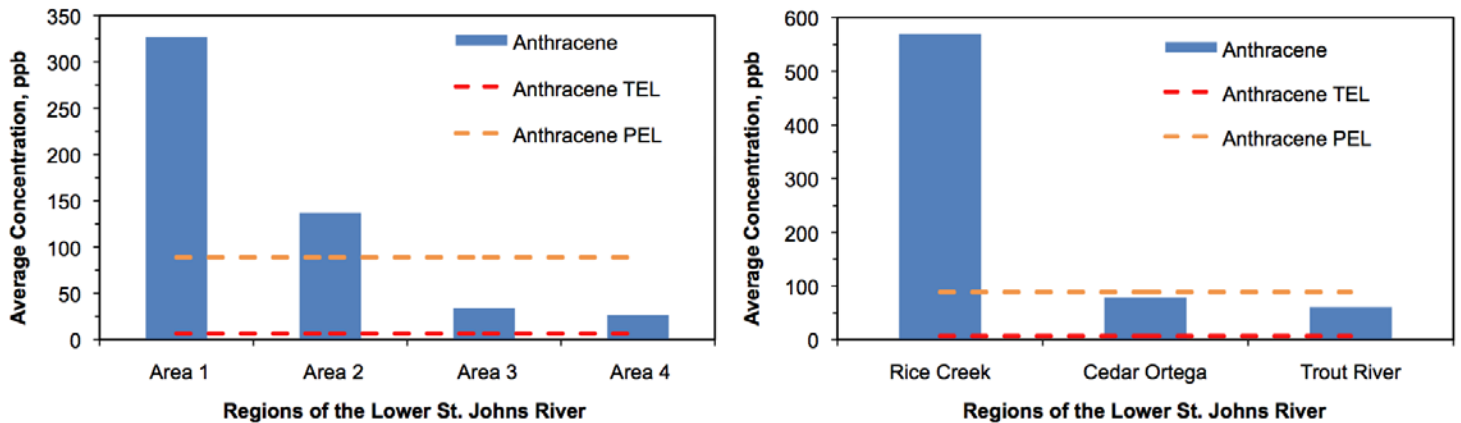


Figure 5.9 Average concentrations of anthracene in sediments from 2000-2007 in the four areas of the LSJR and in three streams in Area 1. Sediment quality guidelines for anthracene are shown as dashed lines. Area 1 – western tributaries; Area 2 – north arm; Area 3 – north mainstem; Area 4 – south mainstem. See text in Section 5.2 for data sources.

5.4.5. Trends: PAHs in Sediments

There was extreme contamination of Deer Creek from the Pepper Industries’ creosote tanks near Talleyrand that was documented in 1991 (Delfino et al. 1991a). Creosote is a product of coal tar that is used for wood preservation. While Deer Creek was the worst contaminated site, there were several other hot spots reported over the years for various PAHs. In the late 1980s, there were several sites all along the LSJR that had extremely elevated levels of PAHs, including acenaphthene in the north mainstem, Area 3, at NAS Jacksonville (278 ppb), fluoranthene in Dunn Creek in the north arm, Area 2, (10,900 ppb), and pyrene in Goodby’s Creek (8470 ppb). Most recently, the highest concentrations of naphthalene and anthracene (LMW PAHs) occurred in Rice Creek in 2002.

There are encouraging signs that some PAH levels have gone down since the late 1980s. Data were not collected continuously over the years, but for many PAHs, high concentrations found in the late 1980s declined dramatically to lower levels in 1996 where they have remained at lower concentrations. This pattern was particularly evident in Areas 3 and 4, the north and south mainstem regions (Figure 5.10) and may reflect recovery from the creosote contamination during that time. Some of the PAH load in the western tributaries has also declined since the 1980s.

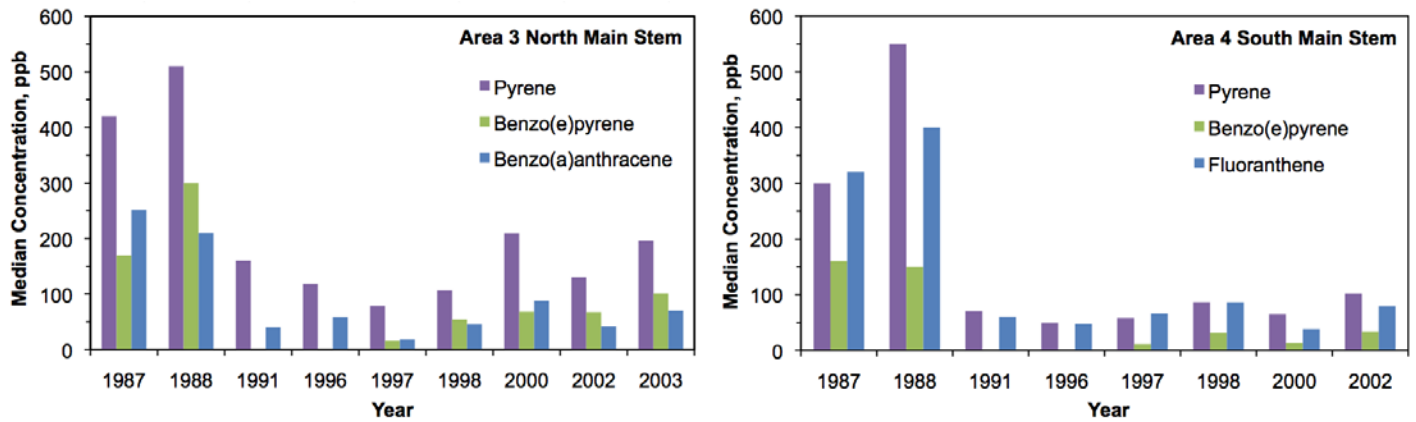


Figure 5.10 Median concentrations of PAHs in sediments from 2000-2007 in Area 3 (north mainstem) and Area 4 (south mainstem). Note that years are not continuous. See text in Section 5.2 for data sources.

However, since the 1990s, several PAH levels may be slowly rising in the mainstem. While there are too few data points for a rigorous trend analysis, there may be a modest increase in most PAHs in Areas 3 and 4, similar to those shown for pyrene in Figure 5.11. Despite the uncertainty due to a lack of data, it is important to continue monitoring locales such as Clay and St. Johns Counties, which are rapidly becoming more urbanized, and can be expected to generate the PAHs typical of those land uses.

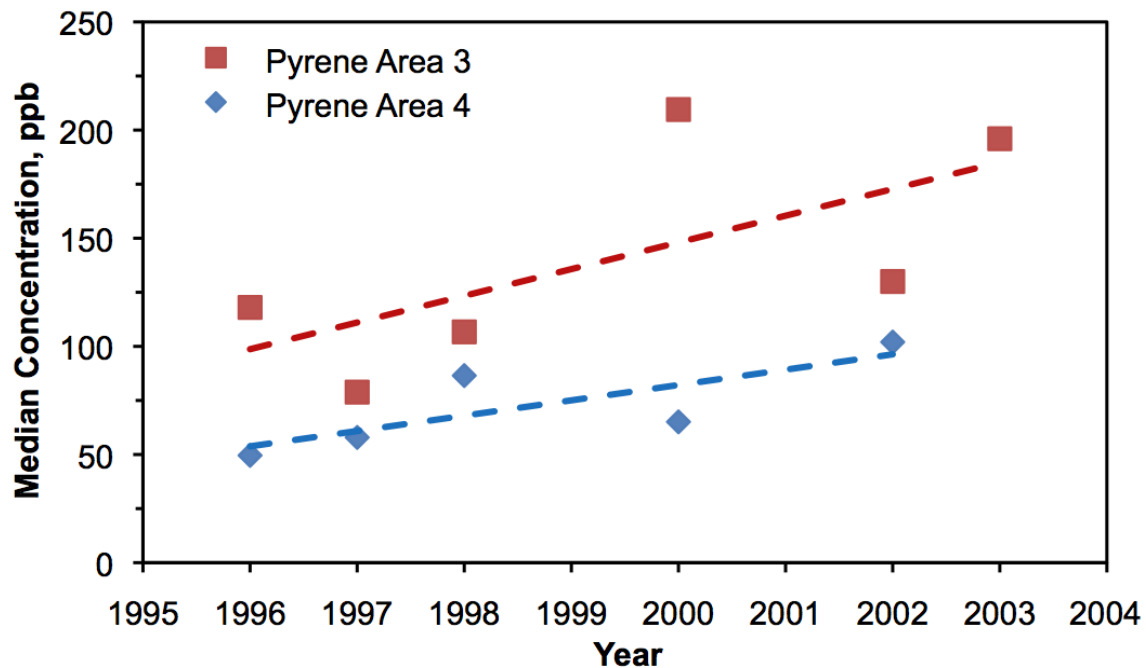


Figure 5.11 Apparent rise of median concentrations of pyrene in LSJR sediments since 1996 in Area 3 (north mainstem) and Area 4 (south mainstem). Dashed lines represent trend lines. See text in Section 5.2 for data sources.

5.4.6. PAHs in Oysters

In the Mussel Watch Project of NOAA's National Status and Trends Program (NOAA 2007b), oysters in Chicopit Bay in the north arm, Area 2, of the LSJR were analyzed for PAHs from 1989-2003 (Figure 5.12). These data show that there is a broad spectrum of PAH contaminants in Chicopit Bay oysters, but the PAHs with the most consistently high levels are pyrene and fluoranthene. There is no apparent decrease in the total PAH values in the oysters, despite decreasing trends of other contaminants such as PCBs, some pesticides, and some metals (O'Connor and Lauenstein 2006).

In the 2000s, the sediment PAHs in the Area 2 north arm has a distribution similar to oysters with a predominance of fluoranthene, naphthalene and 2-methylnaphthalene. However, the high levels of acenaphthene found in the sediment in the 2000s were not reflected in oyster tissue.

The PAHs in the oysters have many possible sources, but several are often associated with petroleum contamination, a possible result of Chicopit's proximity to a shipping channel with high boat traffic. This appears especially true in 2003 when the concentrations in oysters approached the levels of the 1980s. The 2003 oysters also had more of the methylated LMW PAHs that suggest petrogenic origins of the compounds. Standards for consumption are sparse for PAHs (EPA 2007), but for the compounds for which there are standards (anthracene, acenaphthene, fluoranthene, fluorene, and pyrene), the levels found in these oysters would not be harmful. However, as noted, there are few direct data about the hazard of consumption of PAHs, including the notoriously carcinogenic benzo(a)pyrene or other PAH carcinogens.

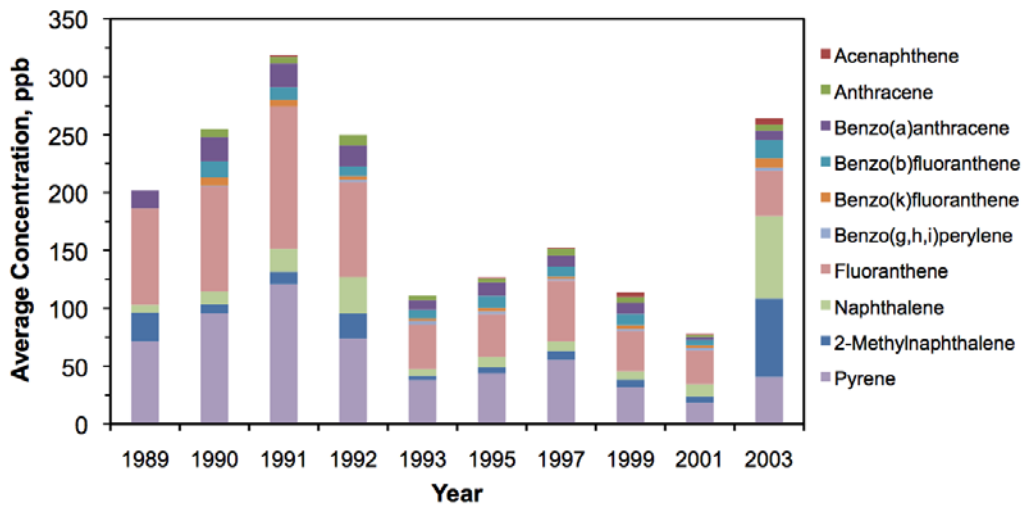


Figure 5.12 Concentration of select PAHs in oysters in Chicopit Bay, LSJR (Area 2 – north arm). Note that years are not continuous. See text in Section 5.2 for data sources.

5.4.7. Point Sources of PAHs and related compounds in the LSJR Region

Reported PAH emissions to the LSJR region atmosphere have dropped by 83% over the last decade, mainly due to reductions in emissions by electric utilities (EPA 2015b). In 2013 the total emitted PAHs was 112 pounds, 100 pounds of which came from the paper industry. Direct surface water discharges of PAHs have declined from nearly 20 pounds in 2001 to a pound in 2013, all of which is now released by electric utilities. Despite the decline in surface water discharges, PAHs represent one of the top ten chemicals that have the highest potential for human health risk of all discharges in the LSJR basin (EPA 2013e).

Overall, there was a significant drop in point source releases of PAHs and related compounds into the air and water in the LSJR region between 2001 and 2013. Several industries have shared in reducing the overall aromatic hydrocarbon loading to the region.

5.4.8. Summary: PAHs

Portions of the LSJR appear to still be recovering from severe creosote contamination from the 1980s, but there are likely to be additional petroleum and combustion sources. The PAHs occur at levels that may be problematic in some areas, and there continues to be widespread contamination. Near the port in the north mainstem, the combined impacts from power plants, shipping, and the maritime industry are likely to cause this region to continue to be the most heavily impacted by PAHs into the future. There is direct evidence that these compounds reside in consumable organisms in the river in that area. There is a possible rise of PAHs in the southern mainstem portion of the river, which may be beginning to suffer the same stress from urban impact that the north mainstem experiences. In summary, PAHs in the LSJR are likely to be a significant source of stress to sediment-dwelling organisms, despite their overall decline since the 1980s. A drop in the release of PAHs into the region by industries since 2001 may affect a gradual improvement in the next few years if the emission rates remain stable or decrease. In the previous report, the STATUS of PAHs in sediments was *unsatisfactory* while the TREND in the north marine/estuarine section was *improving*, and the TREND in the south fresh water section was *worsening*. The STATUS and TREND of PAHs in this year's report were not updated because of lack of data.

5.5. Metals

5.5.1. Background

Metals are naturally occurring components of the mineral part of a sediment particle. Major metals in sediments are aluminum, iron, and manganese and these are often used to differentiate types of sediment (more like terrestrial soil or limestone bedrock). Sediment composition varies naturally with local geography and environment, and so the concentrations of metals in sediments and water bodies also vary naturally. Sediments in the mainstem LSJR have widely different geologic sources. By contrast, the Cedar-Ortega system sediment characteristics suggest common geologic sources (**Durell et al. 2004; Scarlatos 1993**). As a result of this natural variability, it can be difficult to determine if metal levels are elevated because of human activities or simply because of the nature of the sediments. Concentrations of metals of high concern, like lead or chromium, are often compared to aluminum concentrations to try to determine what amount is the result of human input (**Alexander et al. 1993; Schropp and Windom 1988**). However, anthropogenic contributions of excess metals in aquatic environments are generally much greater than natural contributions (**Eisler 1993**).

Metals may enter aquatic systems via industrial effluent, agricultural and stormwater runoff, sewage treatment discharge, fossil fuel combustion, ore smelting and refining, mining processes, and due to leachate from metal-based antifouling paints (**Reichert and Jones 1994; Kennish 1997; Evans et al. 2000; Voulvoulis et al. 2000; Echols et al. 2009**). Coal and oil combustion represent a substantial release of atmospheric metals, often fated for future deposition into water bodies. Metals are only present in these fuels in small quantities; however, massive amounts of fuel are combusted. Metallic contamination also occurs with various metal-working enterprises where metal fabrications are produced and processed. Another avenue for metals to enter into aquatic environments is from leaching from hazardous waste sites (**Baird 1995**). Naturally occurring trace metals such as copper, zinc, and nickel are essential micronutrients required by all organisms; however, in excess, these metals, as well as non-essential metals, such as arsenic, cadmium, lead, silver, and mercury may cause adverse biological effects in aquatic organisms (**Bryan and Hummerstone 1971; Dallinger and Rainbow 1993; Bury et al. 2003; Bielmyer et al. 2005a; Bielmyer et al. 2006a**).

Copper and zinc are two of the most widely used elements in the world and as such are common pollutants found in freshwater and marine ecosystems (**Bielmyer-Fraser et al. 2017**). Copper enters aquatic systems through runoff from rivers adjacent to heavy metal mining areas (**Bryan 1976**); through sewage treatment discharge, industrial effluent, anti-fouling paints, refineries, as well as overflow from stormwater ponds (**Guzman and Jimenez 1992; Jones 1997; Mitchelmore et al. 2003**). Copper is also a constituent of several pesticides commonly used to control algae. Zinc is a major component of brass, bronze, rubber, and paint and is introduced into water systems via commercialized businesses (smelting, electroplating, fertilizers, wood preservatives, mining, etc.) and rainwater run-off (**Eisler 1993**). Although there are freshwater environments with only a few micrograms of zinc per liter, some industrialized areas may have problematic concentrations of over 1000 µg/L Zn (**Alsop and Wood 2000**). Along with copper and zinc, nickel-containing materials make major contributions to many aspects of modern life. The uses of nickel include applications in buildings and infrastructure such as stainless steel production and electroplating; chemical production, such as production of fertilizers, pesticides and fungicides; energy supply, water treatment, and coin production (**Nriagu 1980; Eisler 1988b; Hoang et al. 2004**). The largest use of nickel alloys and a major use of copper and zinc are in corrosion prevention. Although these applications have provided many benefits, they have resulted in increased environmental concentrations, which may have significant impact on aquatic life (**Pane et al. 2003; Hoang et al. 2004**). In the past, lead has also been used to a large extent in corrosion prevention, but legislation in the 1980s has limited the content of lead in paints, reduced the lead in gasoline, and eliminated the use of lead shot nationwide (**Eisler 1988a**). Current concerns about lead contamination in aquatic environments are mainly due to point-source discharges from mining, smelting, and refining processes, mostly for use in the production of batteries (**Eisler 1988a; WHO 1995**). Natural sources of lead such as erosion and atmospheric deposition from volcanoes and forest fires also contribute to the lead found in aquatic environments (**WHO 1995**). Elevated silver concentrations in aquatic animals occur near sewage outfalls, electroplating plants, mine waste sites, or areas where clouds have been seeded with silver iodide. The photographic industry has been the major source of anthropogenic silver discharges in the United States (**Eisler 1996**); however, over the last decade the use of silver, as silver nanoparticles, has substantially increased, particularly for applications in catalysis, optics, electronics, biotechnology and bioengineering, water treatment, and silver-based consumer products. Arsenic and many of its compounds are especially potent poisons, especially to insects, thereby making arsenic well suited for the preservation of wood, which has been its primary historical use.

Chromated copper arsenate, also known as CCA or Tanalith, has been used worldwide in the treatment of wood; however, its use has been discontinued in several areas because studies have shown that arsenic can leach out of the wood into the soil, potentially causing harmful effects in animals and severe poisoning in humans (**Rahman et al. 2004**).

5.5.1.1. Fate

Metals may be suspended in the water column for various time periods, depending on a variety of abiotic and biotic factors. In the water column, metals can reversibly bind to organic and particulate matter, form inorganic complexes, and be passed through the food chain (**Di Toro et al. 2001**). Various chemical reactions favor the transfer of metals through the different phases. Ultimately, metals partition in the sediment over time, as has occurred in the LSJR; however, metals may be remobilized into the interstitial water by both physical and chemical disturbances.

Metal concentrations in saltwater generally range from 0.003-16 µg/L Zn (**Bruland 1980; Bruland 1983**), 0.13-9.5 µg/L Cu (**Kozelka and Bruland 1998**), 0.2 to 130 µg/L Ni (**DETR 1998; WHO 1991**), and from 0.001 to 0.1 µg/L Ag (**Campbell et al. 2000**). The highest metal concentrations reported were measured in estuaries with significant anthropogenic inputs. However, in most cases the concentration of organic ligands, such as humic and fulvic substances, as well as the concentration of inorganic ligands exceed metal concentrations thereby forming complexes and rendering metals less bioavailable to aquatic organisms (**Campbell 1995; Kramer et al. 2000; Stumm and Morgan 1996; Turner et al. 1981; Wang and Guo 2000**). Aquatic animals, particularly zooplankton, have been shown to be highly sensitive to these metals (**Bielmyer et al. 2006a; Jarvis et al. 2013**). Lead concentrations in natural waters generally range from 0.02 to 36 µg/L, with the highest concentrations found in the sediment interstitial waters, due to the high affinity of this metal for sediment (**Eisler 1988a**).

Benthic biota may be affected by metals in the sediment, both by ingestion of metal-contaminated substrate and by exposure through the interstitial water. The presence of metals in the interstitial water is primarily controlled by the presence of iron sulfide in the sediments (**Boothman et al. 2001**). All major pollutants will displace iron and tightly bind to sulfide, thus making them less available to cause toxicity to organisms.

5.5.1.2. Toxicity

Once in aquatic systems, most waterborne metals exert toxicity by binding to and inhibiting enzymes on the gill or gill-like structure of aquatic organisms (**Bury et al. 2003; Bielmyer et al. 2006b**). This leads to a disruption in ion and water balance in the organism and ultimately death, depending on the metal concentration and exposure time. In saltwater, fish drink water to maintain water balance and therefore, the intestine is another site for metal accumulation and ion disruption (**Bielmyer et al. 2005b; Shyn et al. 2012**). Ingestion of metal contaminated diets can also cause intestinal metal accumulation and potentially toxicity to the consumer (**Bielmyer et al. 2005b; Bielmyer and Grosell 2011; Bielmyer et al. 2012b**). Decreased respiration, decreased reproductive capacity, kidney failure, neurological effects, bone fragility, mutagenesis (genetic mutation), and other effects have been observed in aquatic biota after metal exposure. Several water quality parameters can modify the toxicity of metals including: salinity, DO, dissolved organic carbon concentration (humic and fulvic substances), sulfide concentration, pH, water hardness and alkalinity, as well as other variables (**Campbell 1995**). The toxicity of metals may therefore vary in different parts of the LSJR, reflecting the changes in water chemistry (**Ouyang et al. 2006**) as well as the organisms that reside there. Metal toxicological studies using organisms or water from the LSJR are scarce. **Grosell et al. 2007** and **Bielmyer et al. 2013** collected *Fundulus heteroclitus* (killifish) from the LSJR and used them in acute (96 h) toxicological studies in the laboratory to determine the influence of salinity on copper, zinc, nickel, and cadmium toxicity to the larvae. As salinity increased, toxicity generally decreased for the metals tested. In freshwater, significant mortality to larval killifish occurred after exposure to copper (**Grosell et al. 2007**), zinc (**Bielmyer et al. 2012a**), nickel (**Bielmyer et al. 2013**) and cadmium (Bielmyer, unpublished work) at concentrations reported in the LSJR over the past five years (see section 2.7); however significant larval mortality was only observed after exposure to higher nickel concentrations than those found in the LSJR (**Bielmyer et al. 2013**). The presence of killifish is important in the LSJR because they are a common food source for many larger fish. Exposure to these metals for long time periods may cause deleterious effects, such as decreased growth and/or reproduction, in various species at even lower concentrations. Exposure to 50 µg/L for 21 days caused decreased growth in hybrid striped bass in freshwater; whereas, those exposed to the same concentration in saltwater did not suffer growth reduction (**Bielmyer et al. 2006b**). Generally, larval fish are more sensitive to metals than adults, and invertebrates can be even more sensitive than larval fish (**Bielmyer et al. 2007**). In water collected from Green Cove Springs, exposure to silver concentrations as low as 0.34 µg/L for the invertebrate crustacean, *Ceriodaphnia dubia* (common food sources for larval fish), and 6 µg/L for fathead minnows, respectively, caused 50% mortality to the organisms

(Bielmyer et al. 2007). These silver concentrations have been reported to occur in parts of the LSJR. Many zooplankton exposed to metals, particularly through their diets, have been shown to be very sensitive to metals (Bielmyer et al. 2006a) and to accumulate metals (Bielmyer et al. 2012b). Metal exposure to the lower trophic levels may impact higher-level consumers by decreasing food availability and/or by introducing metal exposure via the diet. Sepúlveda et al. 2002 reported the accumulation of both metal and organic contaminants in the livers of Florida largemouth bass collected from four different locations in the LSJR: Welaka, Palatka, Green Cove, and Julington Creek. The highest mean liver metal concentrations were found in bass from Julington Creek (silver, arsenic, chromium, copper, zinc) and Welaka (cadmium, mercury, lead, selenium, tin). The zinc concentrations accumulated in the liver of the fish from Julington Creek were similar to those observed in adult killifish after exposure to 75 µg/L Zn in the laboratory (Shyn et al. 2012). Lead (Pb) can exist as an organometal and has a higher partition coefficient than the other metals discussed here; therefore, Pb would be preferentially distributed in more hydrophobic compartments (Eisler 1988a). Lead has been shown to exert toxic effects on a variety of aquatic organisms with sensitivity of some invertebrates as low as 4 µg/L (Grosell et al. 2006). Chronic lead toxicity in fish includes neurological and hematological dysfunctions (Davies et al. 1976; Hodson et al. 1978; Mager and Grosell 2011).

5.5.2. *Current Status and Trends of Metals in Water and Sediments*

5.5.2.1. Metals in Water

Generally, since 2010, a pattern of stabilized or reduced metal concentrations, particularly the maximum values, has been observed, as compared to previous years, in the LSJR mainstem. This reduction in metal concentration may reflect the recent efforts associated with TMDLs. However, the data set for metals in the water column has been substantially reduced over the years, which may contribute error in the data trend analyses. Each metal is discussed in turn below.

Arsenic With all but one exception (elevated maximum value) in 2000, the arsenic minimum, median, and maximum values in the LSJR mainstem and tributaries have been below the WQC of 50 µg/L since 1997 (Figure 5.13). Past exceedances of the WQC have mainly occurred in Cedar River, Doctors Lake, Durban Creek, and Moncrief Creek (Figure 5.20A). Mean arsenic values have decreased over time in the mainstem with the exception of a spike in 2016 (Figure 5.14). Median and maximum cadmium values in the LSJR have fluctuated since 1997 (Figure 5.15).

Cadmium Mean cadmium concentrations have generally decreased, and have been below WQC (with the assumed hardness value of 100 mg/L) in the entire LSJR since 2009 and in the mainstem since 2001 (Figure 5.16). Maximum values are now at or below WQC as well (Figure 5.15). In the past, cadmium exceedances in the tributaries have occurred specifically in Hogan Creek, as well as Cedar River, McCoy Creek, and Moncrief Creek to some degree (Figure 5.27).

Copper Copper was one of the more commonly found metals in the LSJR, based on this data set. Since 1997, maximum copper concentrations in the predominantly saltwater regions of the LSJR mainstem and tributaries have exceeded the WQC; however, since 2016 all maximum copper concentrations in the LSJR were below the WQC and within acceptable limits (Figure 5.17; 5.27). Overall, maximum copper concentrations have decreased since 2010 in the LSJR and median values have been stable (Figure 5.17). Mean copper values have significantly decreased in the saltwater regions of the LSJR mainstem since 1997 and in the freshwater regions of the mainstem since 2012 (Figure 5.18). Copper has been most problematic in the tributaries, where many exceedances have been documented (Figure 5.17; 5.27).

Lead Since 2008, maximum lead concentrations have decreased in the LSJR (Figure 5.19), with significantly decreased mean values over time in the entire LSJR, particularly the saltwater areas (Figure 5.20). In several tributaries, including Big Fishweir Creek, McCoy Creek, and Moncrief Creek, lead concentrations (median and maximum values) exceeding both freshwater and saltwater criteria have been documented, as have the maximum lead concentrations in several other tributaries; however, since 2016, all lead concentrations were below the WQC values (Figure 5.27).

Nickel Maximum nickel concentrations in the entire LSJR have decreased and remained stable since 2009, with concentrations below the saltwater and freshwater criteria of 8.3 µg/L and 52 µg/L, respectively (Figure 5.21). Additionally, mean nickel concentrations have significantly decreased over time (Figure 5.22). Since 1997, maximum nickel concentrations have been reported above WQC in several tributaries, particularly Doctors Lake, Dunns Creek, and Sixmile Creek; however, as of 2016, all nickel concentrations have been reported below WQC (Fig. 5.27).

Silver Median and maximum silver concentrations in the LSJR mainstem have fluctuated since 1997, with decreased median silver concentrations observed from 2015 until the present time (Figure 5.23). From 2006-2014, mean silver concentrations in the freshwater portion of the LSJR mainstem were elevated above the WQC of 0.07 µg/L; however, the mean silver concentrations were below the WQC since 2015 (Figure 5.24). Maximum silver concentrations within several tributaries were above both freshwater and saltwater WQC since 1997; however, as of 2016, the maximum values are at or below the WQC (Figure 5.23; 5.27).

Zinc Median and mean zinc concentrations in the entire LSJR were below the WQC and within acceptable limits since 1997, and maximum zinc concentrations were below WQC since 2008 (Figure 5.25; Figure 5.26). In the past, elevated maximum zinc concentrations were reported in Doctor's Lake, Dunns Creek, McCoy Creek, and Butcher Pen Creek; however, current reported zinc concentrations are within acceptable limits (Figure 5.27). The metals analyzed in this report are widely used and therefore continue to enter the LSJR through point and nonpoint sources. The majority of the metal concentrations in the water column of the LSJR mainstem were at or below WQC for the last three years. The metal concentrations in the tributaries were generally the highest and therefore most problematic.

For these reasons, the current overall **STATUS** of metals in the water column that were evaluated in this study (including arsenic, copper, cadmium, lead, nickel, silver, and zinc) in the mainstem of the LSRJ is *satisfactory* with a **TREND** of *improving*. The **STATUS** and **TREND** of metal concentrations in the tributaries of the LSJR cannot be determined because of the lack of data, and is therefore *uncertain*.

Data Limitations It should be noted that the data set has decreased tremendously. For example, in 2007, there were 397 data points for nickel concentrations in the tributaries, and, there were only 54 data points for 2017. Additionally, these ratings are for the water column only; sediments act as a reservoir and may still contain high metal concentrations (see below). If sediments are disturbed by dredging or other activities, metals may be remobilized into the water column and may negatively impact aquatic life in the LSJR. Environment Florida's recently released Troubled Waters report shows that US Naval Station Mayport has had more than 12 exceedances of various parameters, including nickel and copper, during a 21-month span between January 2016 and September 2017. The magnitude of potential impact is dependent on many concurring abiotic and biotic factors.

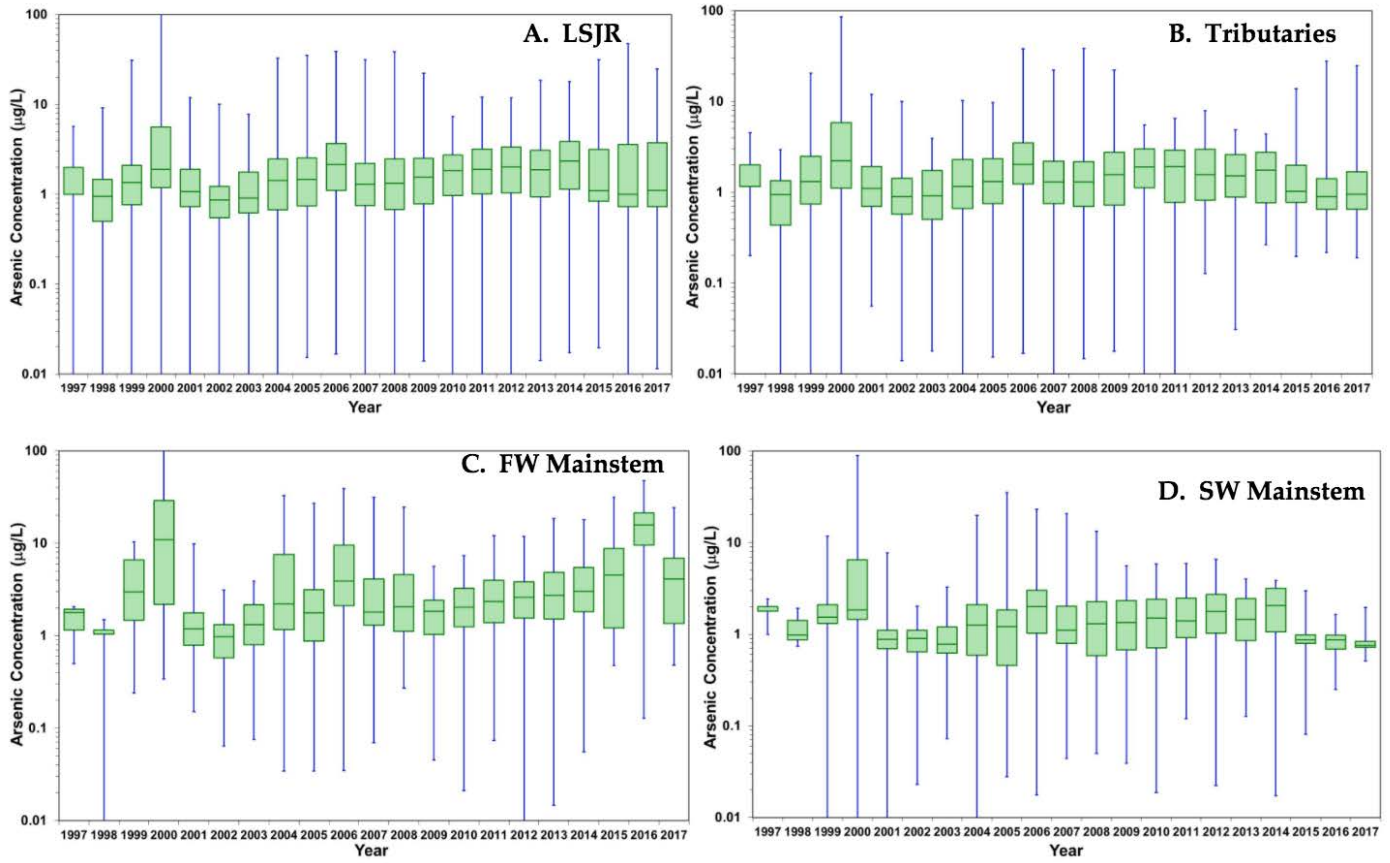


Figure 5.13 Yearly arsenic concentrations ($\mu\text{g/L}$) from 1997 to 2017 in A. the entire LSJR and its tributaries, B. the tributaries of the LSJR, C. the freshwater (FW) portion of the LSJR mainstem, and D. the predominantly saltwater (SW) portion of the LSJR mainstem. Data are presented as a box-and-whiskers plot with the green boxes indicating the median \pm 25% (middle 50% of the data) and horizontal lines indicate the median values. Blue whiskers indicate the minimum and maximum values in the data set.

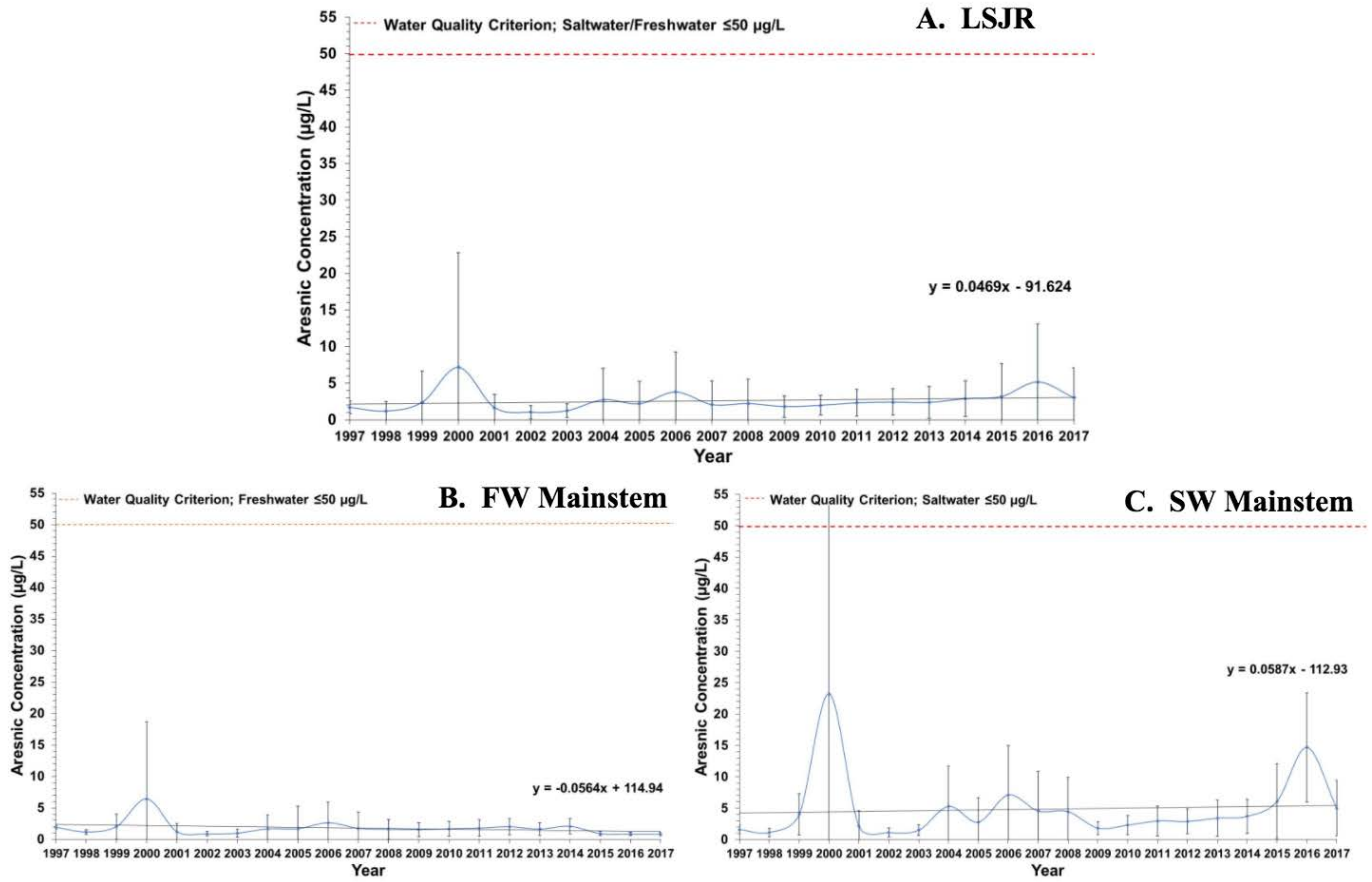


Figure 5.14 Yearly arsenic concentrations from 1997 to 2017 in the A. LSJR mainstem and its tributaries, B. the predominantly freshwater portion of the LSJR mainstem, and C. the predominantly marine/estuarine region of the LSJR mainstem. Data are presented as mean \pm standard deviation. The dotted red horizontal line (not shown due to the scale) indicates the class III water quality criterion for both marine waters and freshwaters.

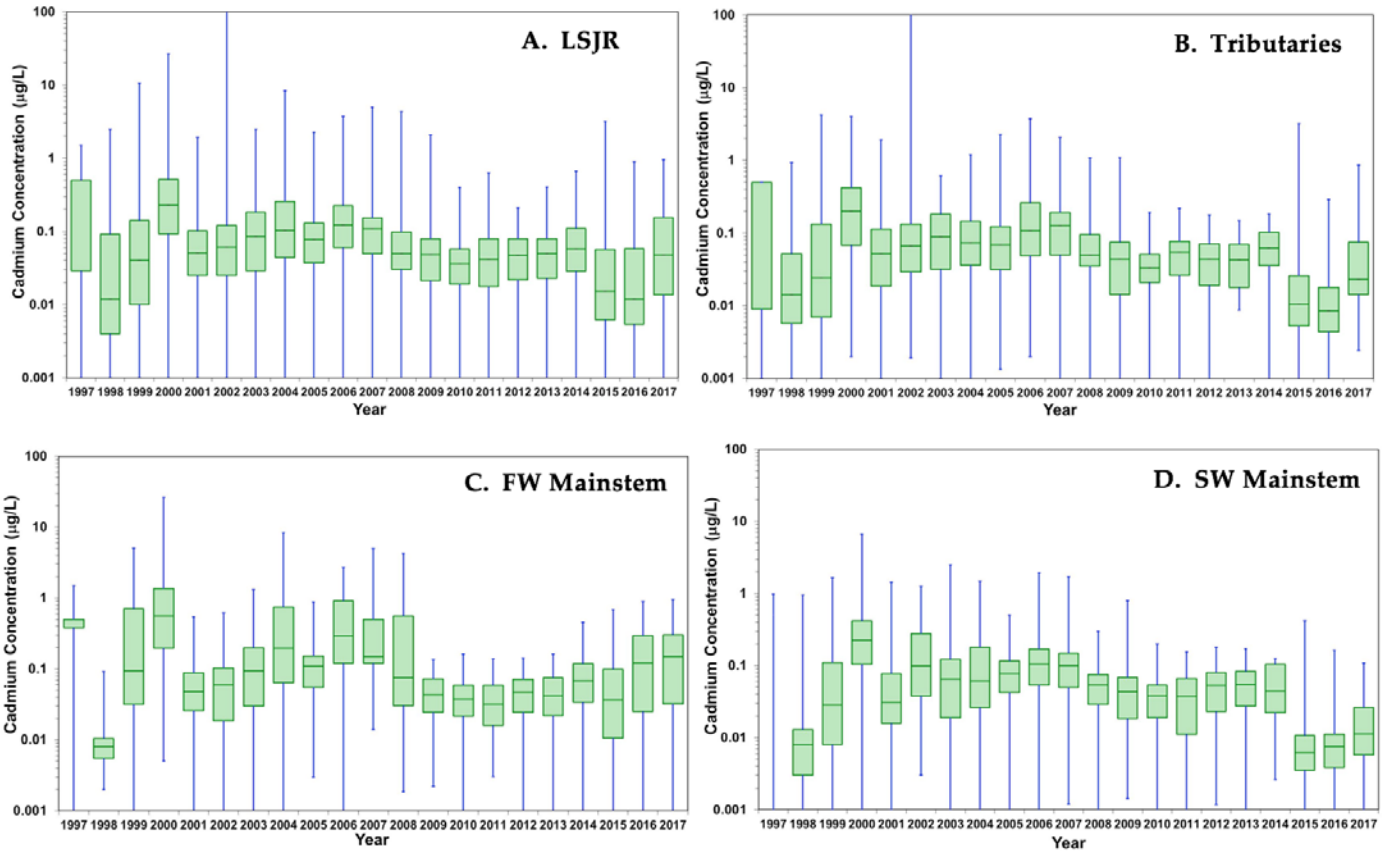


Figure 5.15 Yearly cadmium concentrations ($\mu\text{g/L}$) from 1997 to 2017 in A. the entire LSJR and its tributaries, B. the tributaries of the LSJR, C. the freshwater (FW) portion of the LSJR mainstem, and D. the predominantly saltwater (SW) portion of the LSJR mainstem. Data are presented as a box-and-whiskers plot with the green boxes indicating the median \pm 25% (middle 50% of the data) and horizontal lines indicate the median values. Blue whiskers indicate the minimum and maximum values in the data set.

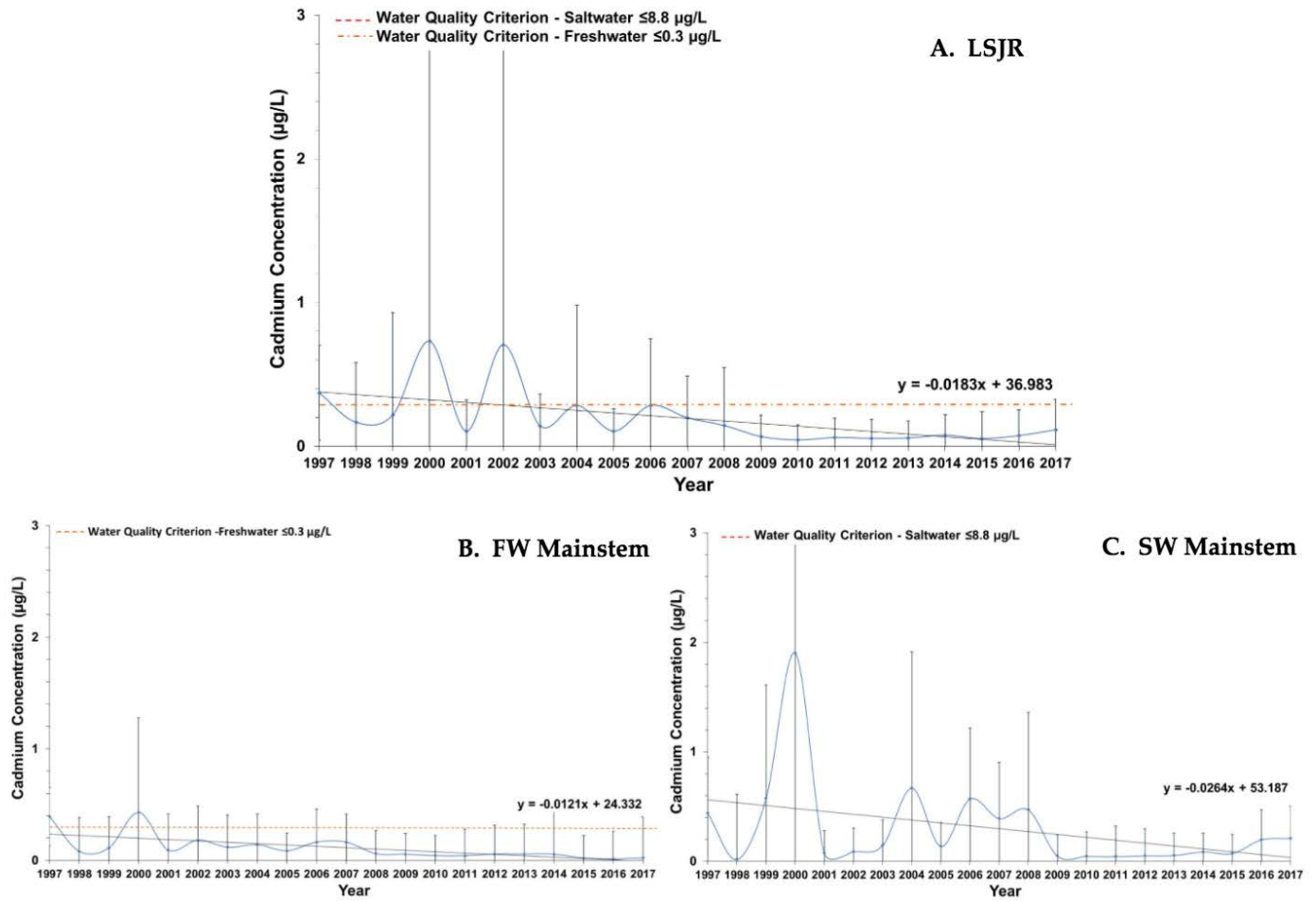


Figure 5.16 Yearly cadmium concentrations from 1997 to 2017 in the A. LSJR mainstem and its tributaries, B. the predominantly freshwater portion of the LSJR mainstem, and C. the predominantly marine/estuarine region of the LSJR mainstem. Data are presented as mean \pm standard deviation. The dotted red horizontal line indicates the class III water quality criterion for marine/estuarine waters and the dotted orange line indicates the class III water quality criterion for freshwaters.

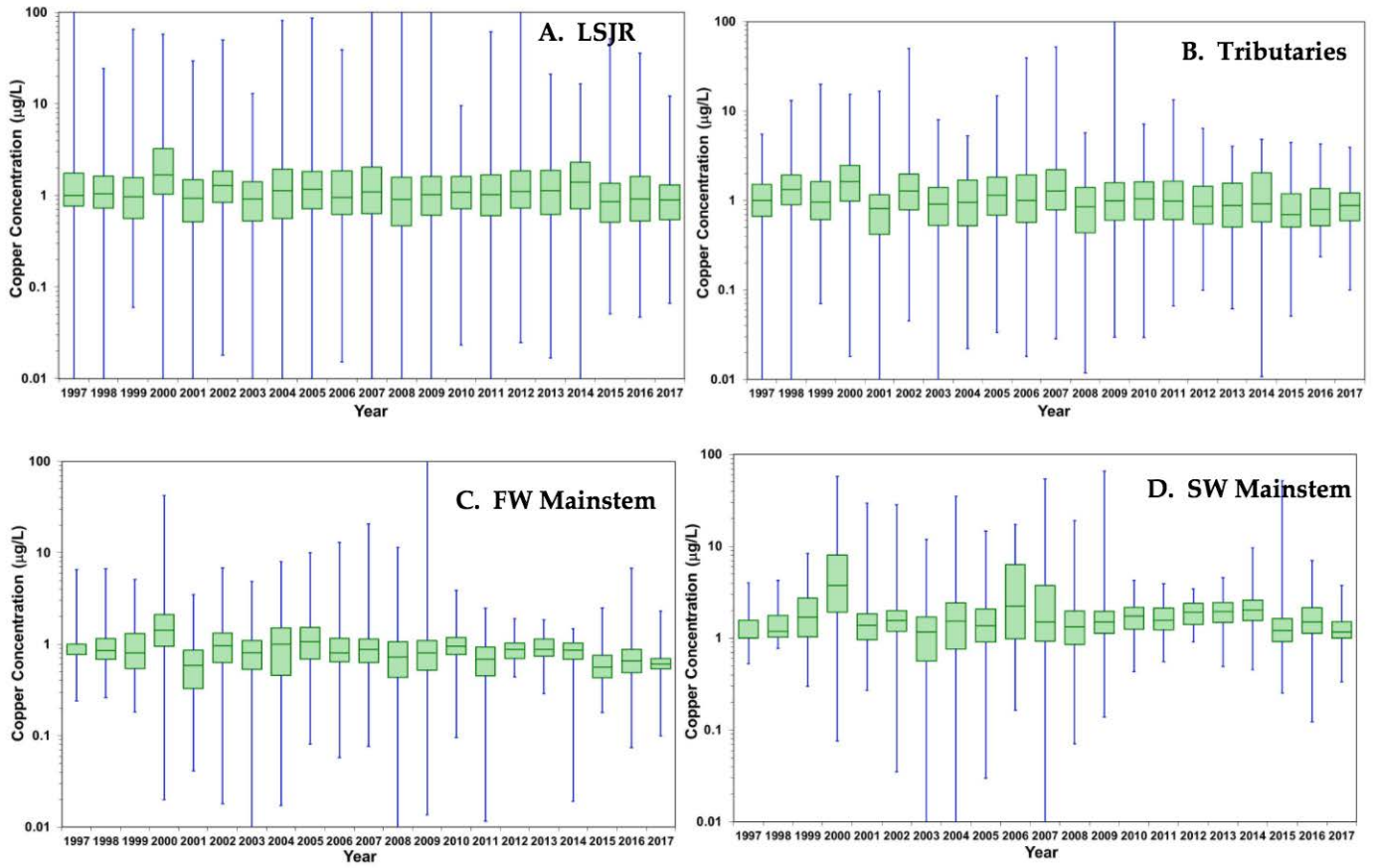


Figure 5.17 Yearly copper concentrations ($\mu\text{g/L}$) from 1997 to 2017 in A. the entire LSJR and its tributaries, B. the tributaries of the LSJR, C. the freshwater (FW) portion of the LSJR mainstem, and D. the predominantly saltwater (SW) portion of the LSJR mainstem. Data are presented as a box-and-whiskers plot with the green boxes indicating the median \pm 25% (middle 50% of the data) and horizontal lines indicate the median values. Blue whiskers indicate the minimum and maximum values in the data set.

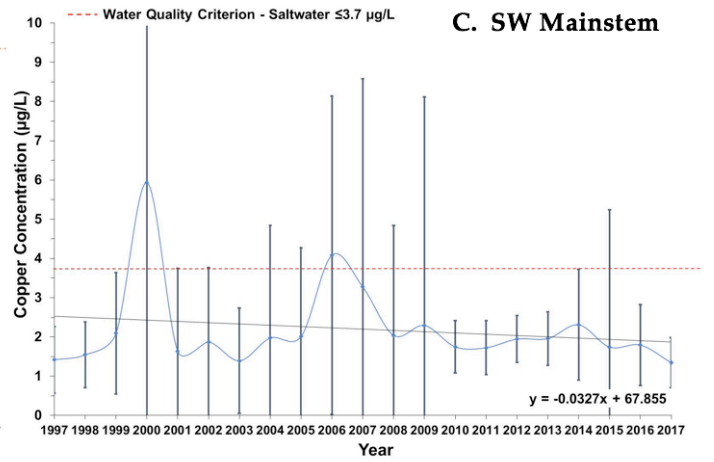
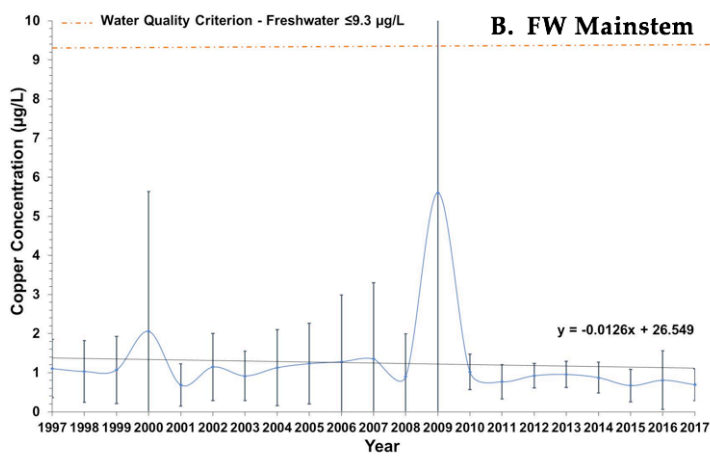
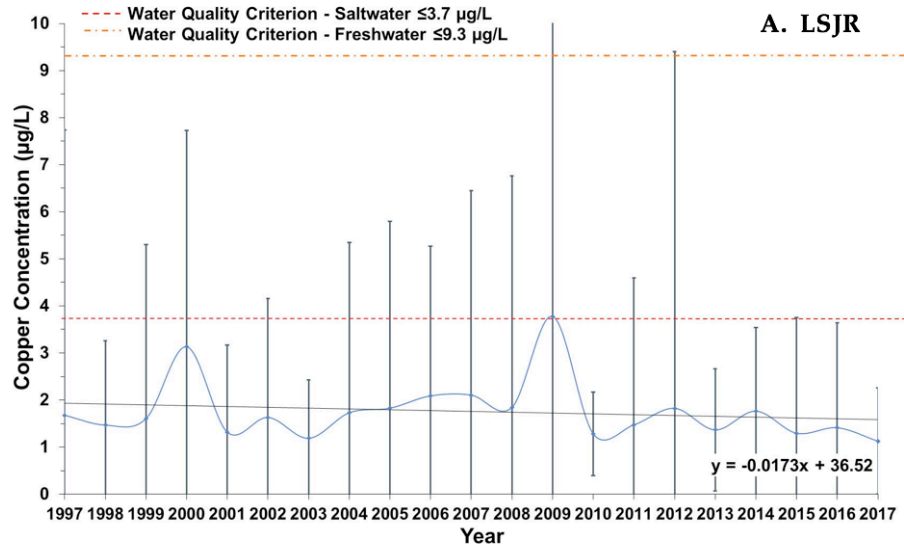


Figure 5.18 Yearly copper concentrations from 1997 to 2017 in the A. LSJR mainstem and its tributaries, B. the predominantly freshwater portion of the LSJR mainstem, and C. the predominantly marine/estuarine region of the LSJR mainstem. Data are presented as mean \pm standard deviation. The dotted red horizontal line indicates the class III water quality criterion for marine/estuarine waters and the dotted orange line indicates the class III water quality criterion for freshwaters.

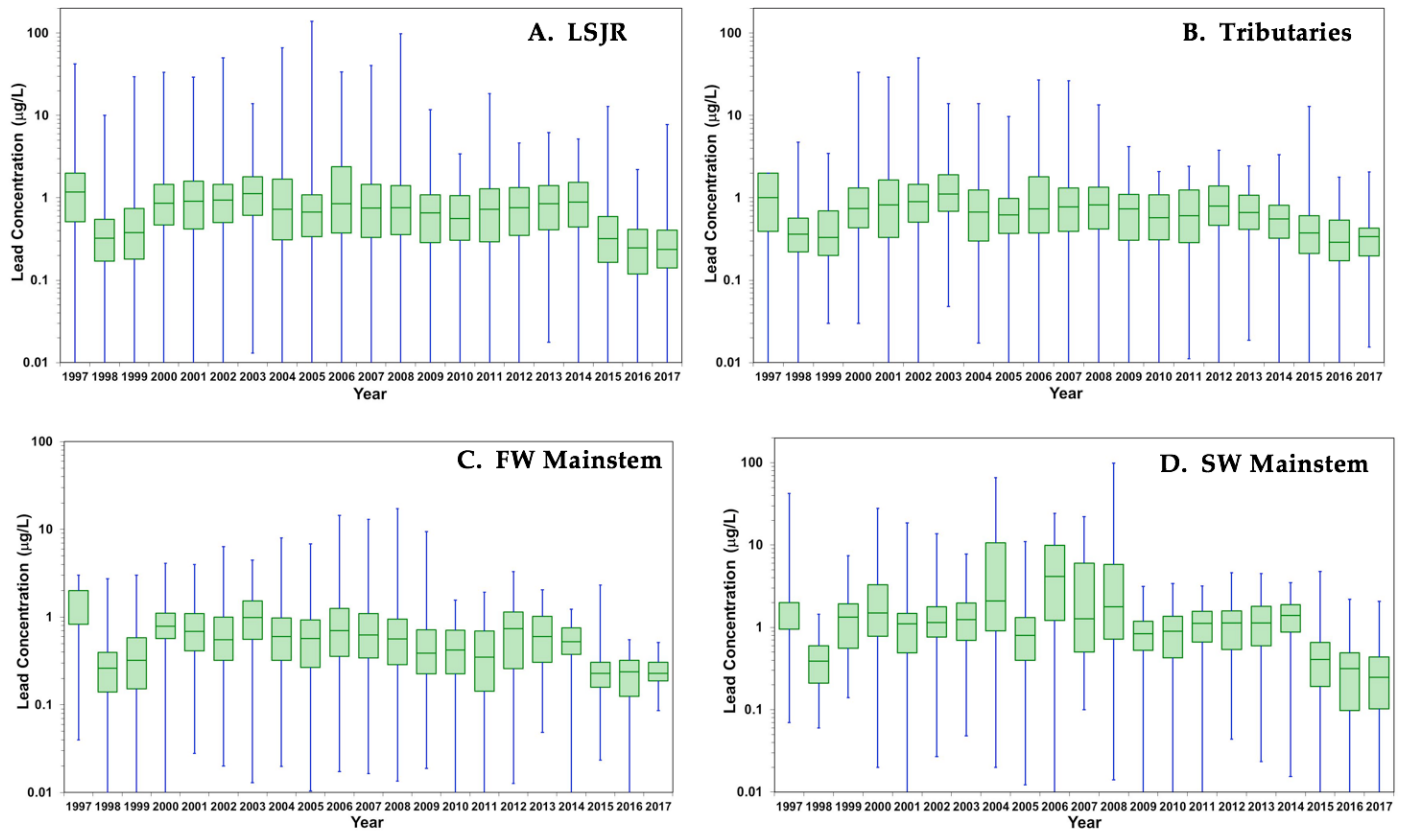


Figure 5.19 Yearly lead concentrations ($\mu\text{g/L}$) from 1997 to 2017 in A. the entire LSJR and its tributaries, B. the tributaries of the LSJR, C. the freshwater (FW) portion of the LSJR mainstem, and D. the predominantly saltwater (SW) portion of the LSJR mainstem. Data are presented as a box-and-whiskers plot with the green boxes indicating the median \pm 25% (middle 50% of the data) and horizontal lines indicate the median values. Blue whiskers indicate the minimum and maximum values in the data set.

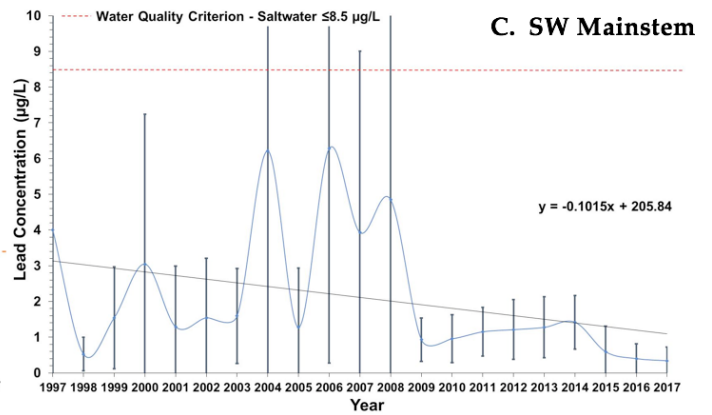
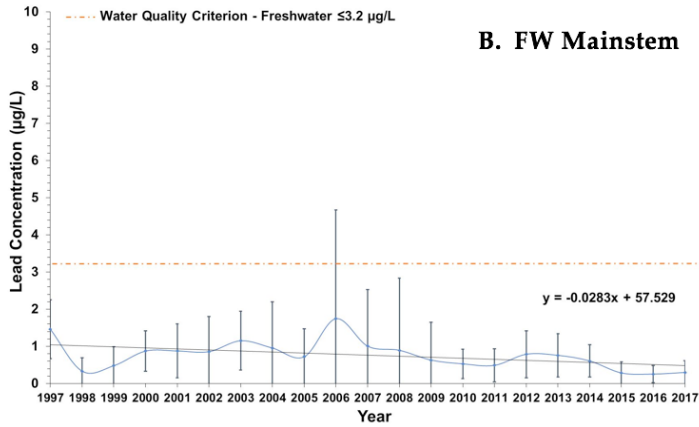
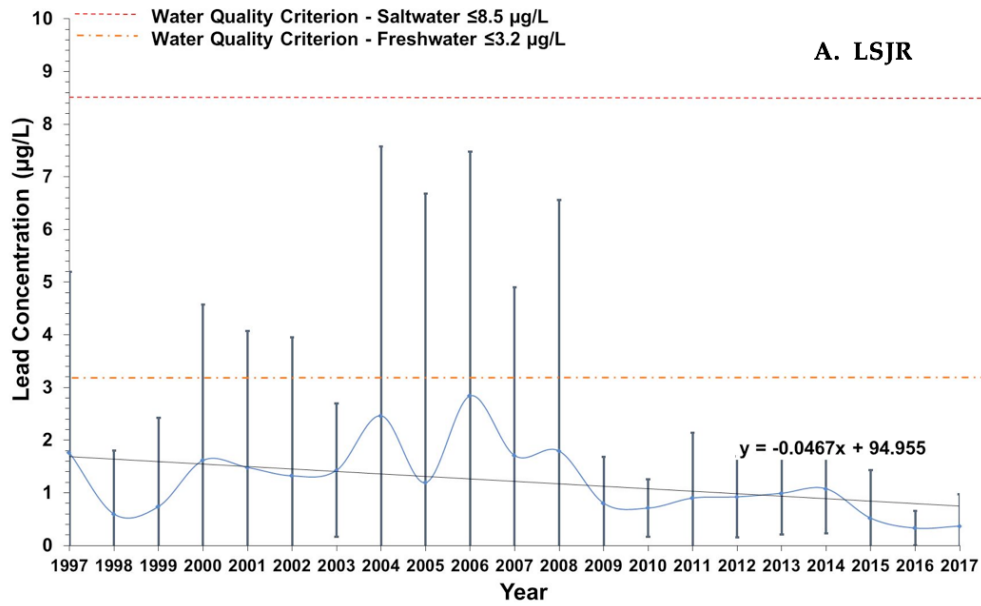


Figure 5.20 Yearly lead concentrations from 1997 to 2017 in the A. LSJR mainstem and its tributaries, B. the predominantly freshwater portion of the LSJR mainstem, and C. the predominantly marine/estuarine region of the LSJR mainstem. Data are presented as mean \pm standard deviation. The dotted red horizontal line indicates the class III water quality criterion for marine/estuarine waters and the dotted orange line indicates the class III water quality criterion for freshwaters.

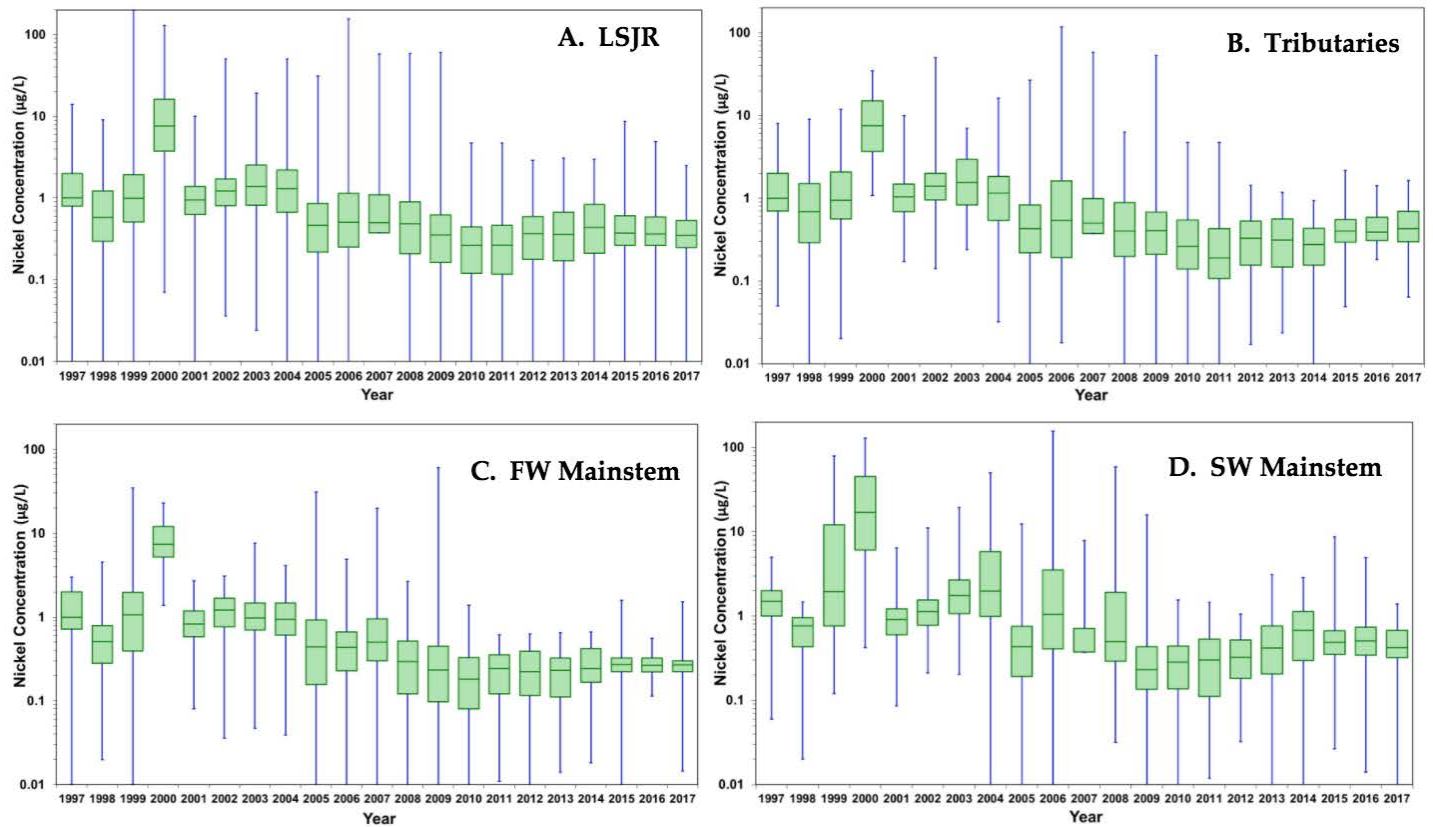


Figure 5.21 Yearly nickel concentrations ($\mu\text{g/L}$) from 1997 to 2017 in A. the entire LSJR and its tributaries, B. the tributaries of the LSJR, C. the freshwater (FW) portion of the LSJR mainstem, and D. the predominantly saltwater (SW) portion of the LSJR mainstem. Data are presented as a box-and-whiskers plot with the green boxes indicating the median \pm 25% (middle 50% of the data) and horizontal lines indicate the median values. Blue whiskers indicate the minimum and maximum values in the data set.

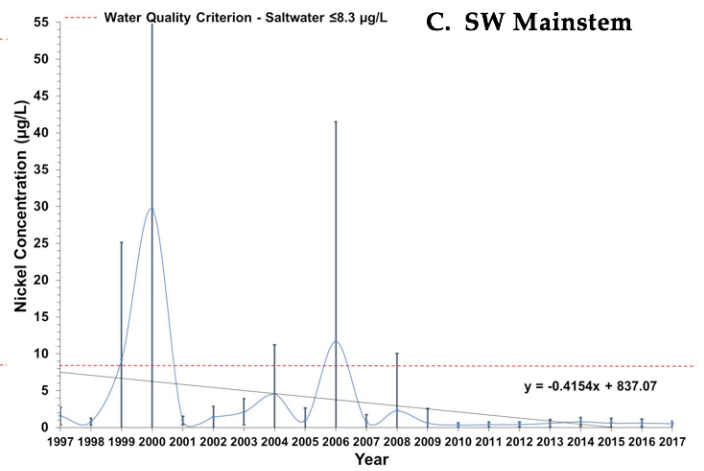
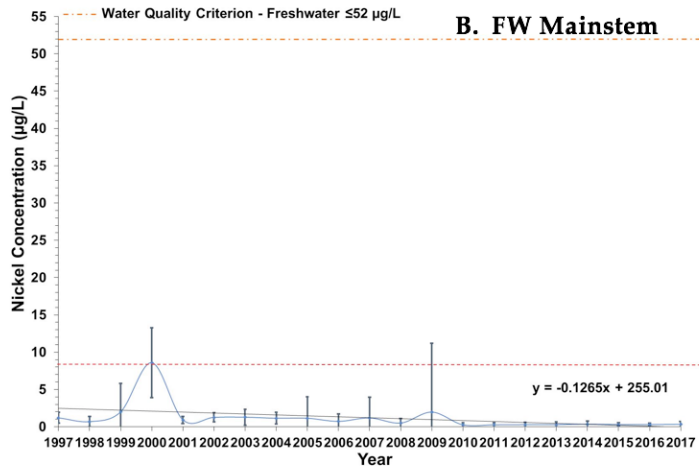
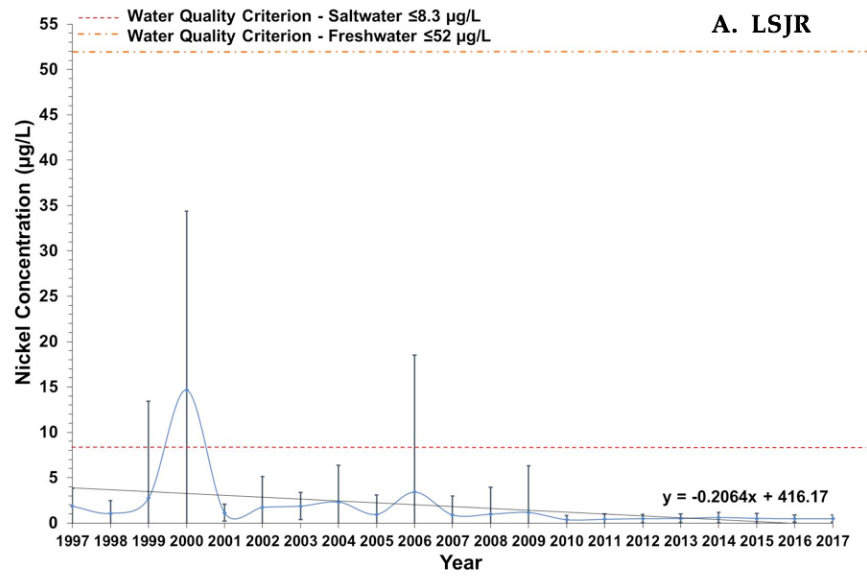


Figure 5.22 Yearly nickel concentrations from 1997 to 2017 in the A. LSJR mainstem and its tributaries, B. the predominantly freshwater portion of the LSJR mainstem, and C. the predominantly marine/estuarine region of the LSJR mainstem. Data are presented as mean \pm standard deviation. The dotted red horizontal line indicates the class III water quality criterion for marine/estuarine waters and the dotted orange line indicates the class III water quality criterion for freshwaters.

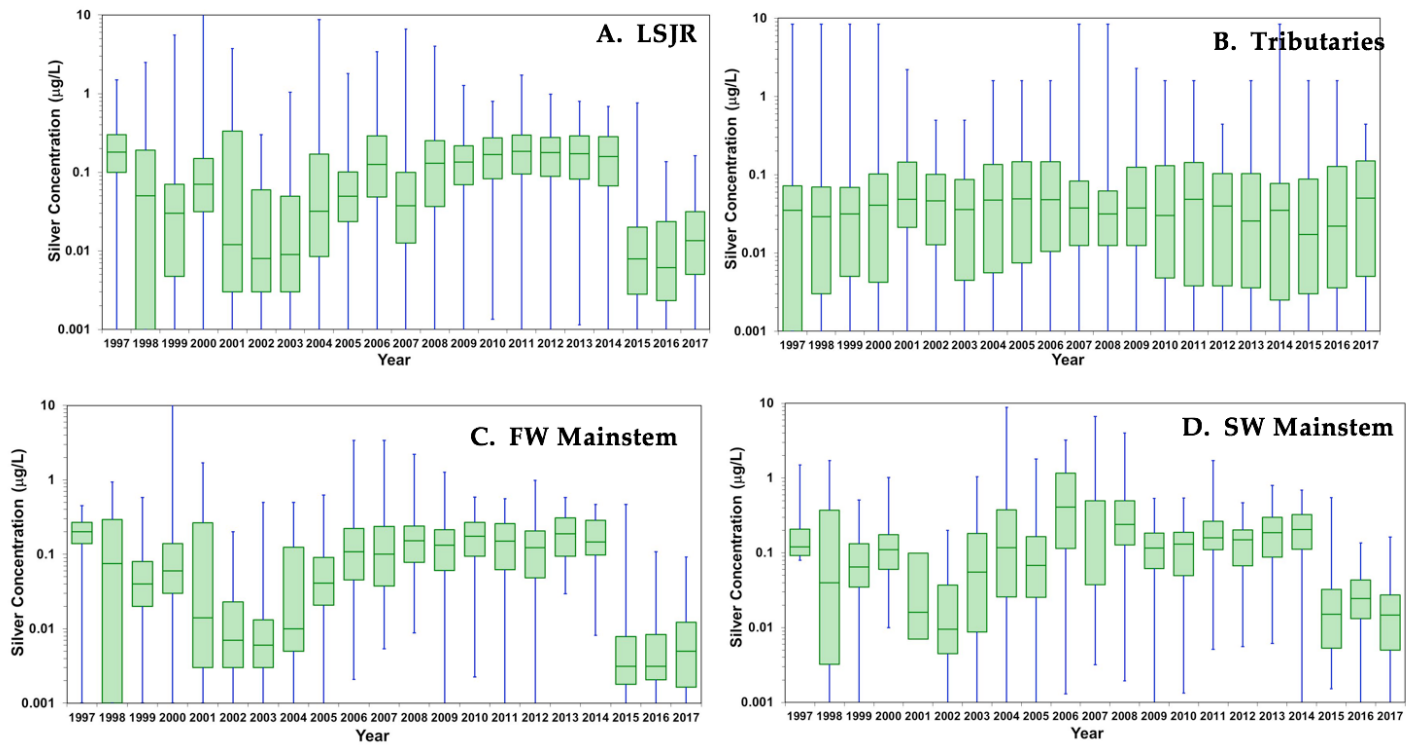


Figure 5.23 Yearly silver concentrations ($\mu\text{g/L}$) from 1997 to 2017 in A. the entire LSJR and its tributaries, B. the tributaries of the LSJR, C. the freshwater (FW) portion of the LSJR mainstem, and D. the predominantly saltwater (SW) portion of the LSJR mainstem. Data are presented as a box-and-whiskers plot with the green boxes indicating the median \pm 25% (middle 50% of the data) and horizontal lines indicate the median values. Blue whiskers indicate the minimum and maximum values in the data set.

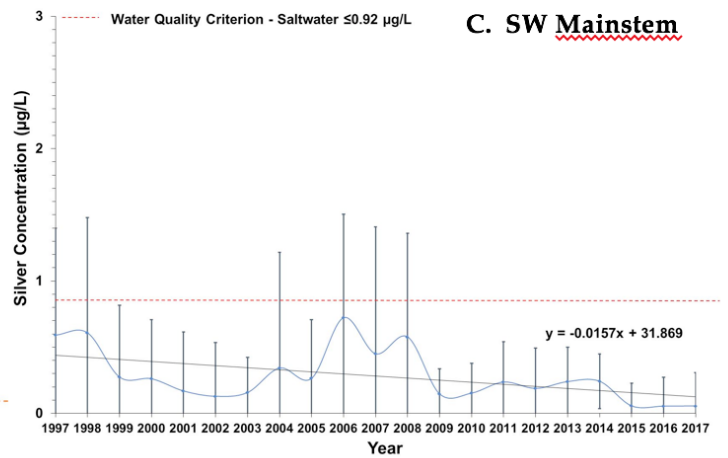
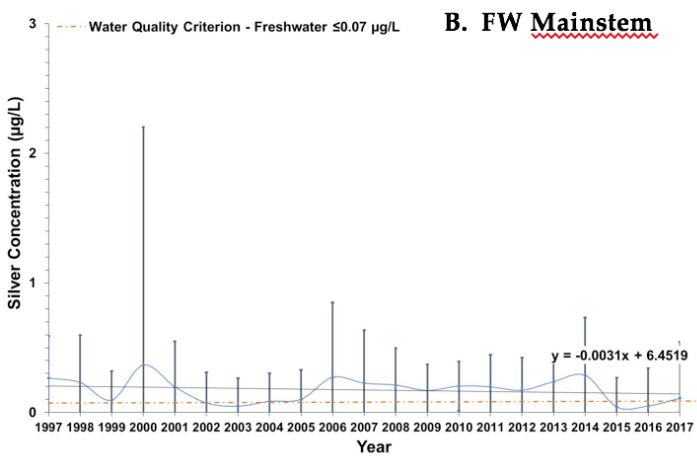
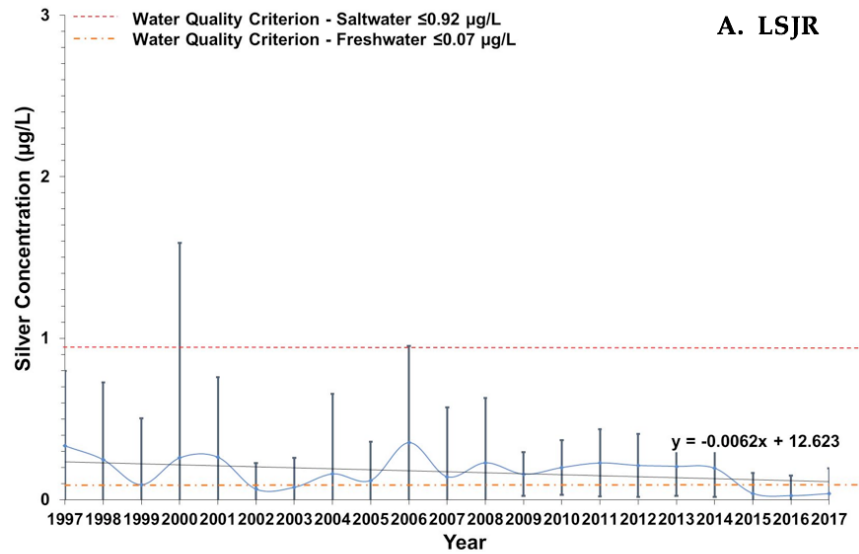


Figure 5.24 Yearly silver concentrations from 1997 to 2017 in the A. LSJR mainstem and its tributaries, B. the predominantly freshwater portion of the LSJR mainstem, and C. the predominantly marine/estuarine region of the LSJR mainstem. Data are presented as mean \pm standard deviation. The dotted red horizontal line indicates the class III water quality criterion for marine/estuarine waters and the dotted orange line indicates the class III water quality criterion for freshwaters.

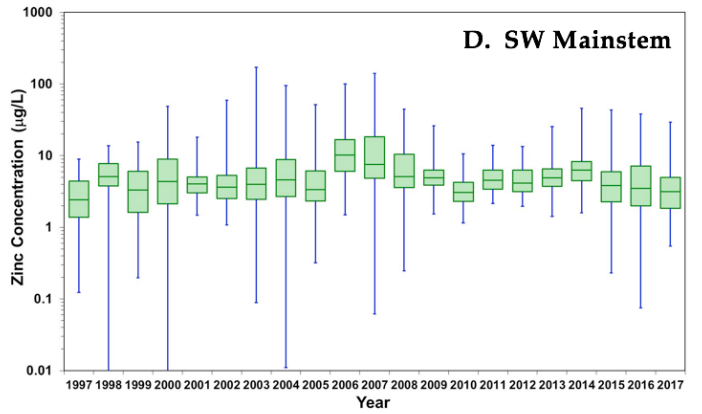
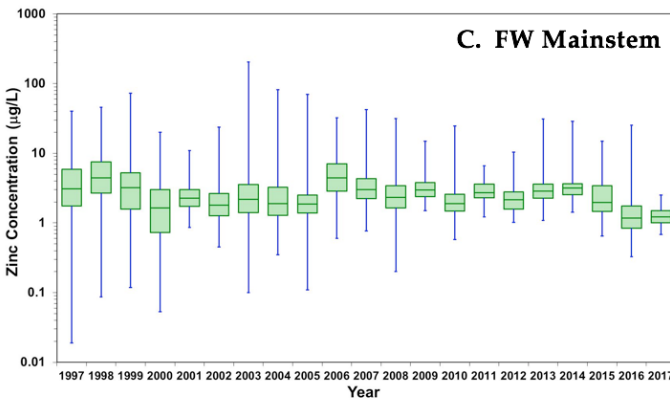
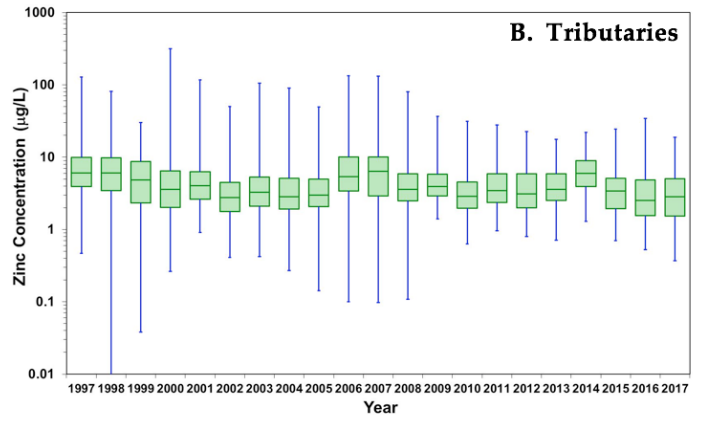
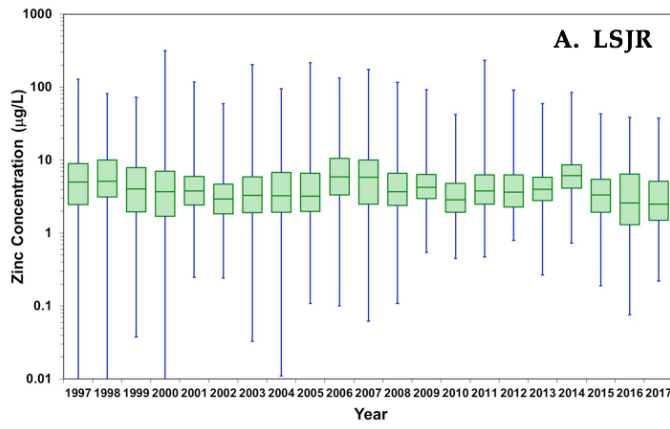


Figure 5.25 Yearly zinc concentrations ($\mu\text{g/L}$) from 1997 to 2017 in A. the entire LSJR and its tributaries, B. the tributaries of the LSJR, C. the freshwater (FW) portion of the LSJR mainstem, and D. the predominantly saltwater (SW) portion of the LSJR mainstem. Data are presented as a box-and-whiskers plot with the green boxes indicating the median \pm 25% (middle 50% of the data) and horizontal lines indicate the median values. Blue whiskers indicate the minimum and maximum values in the data set.

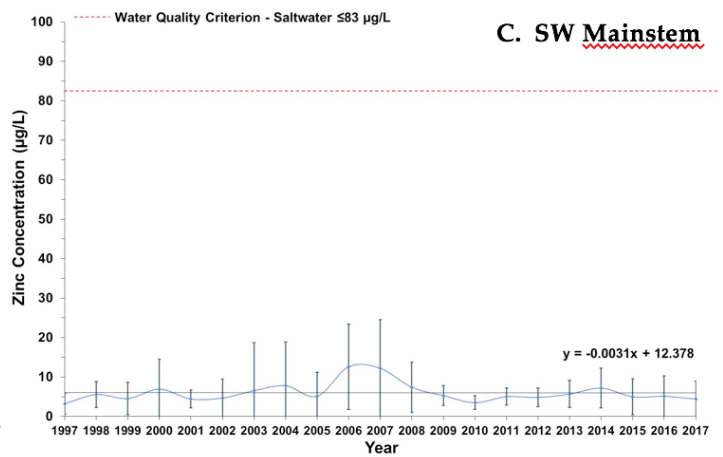
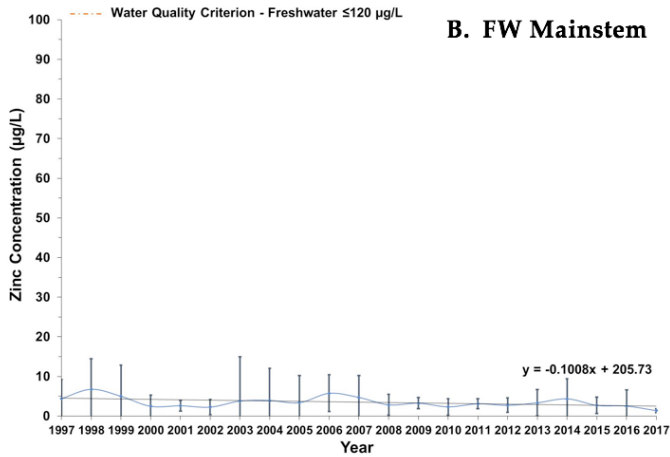
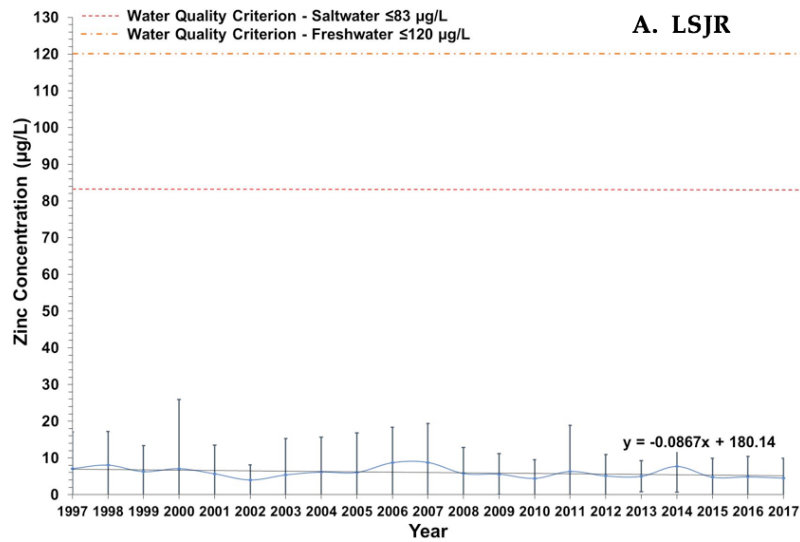
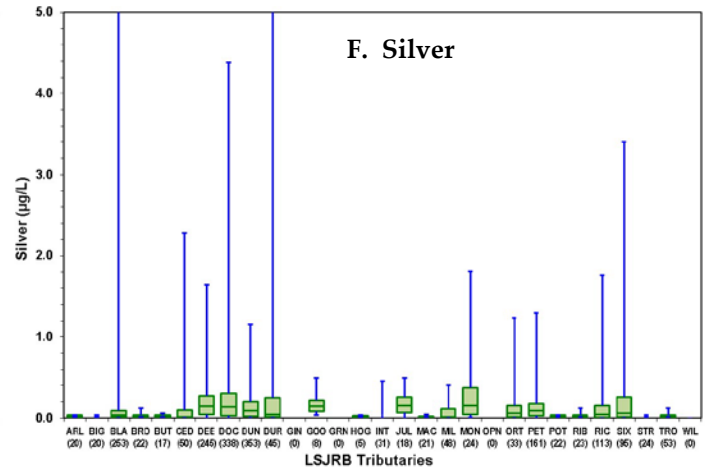
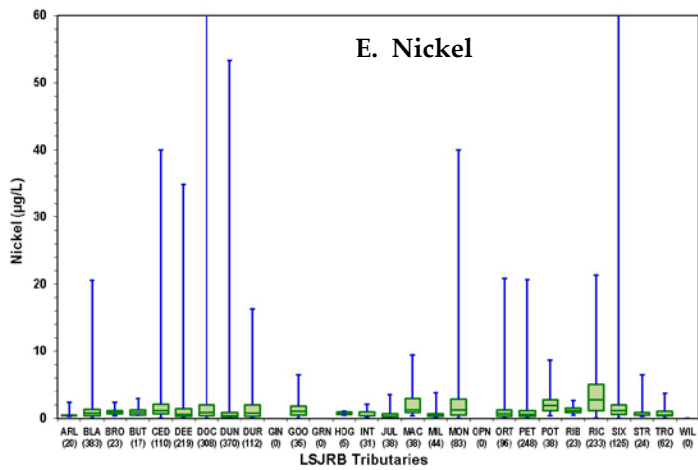
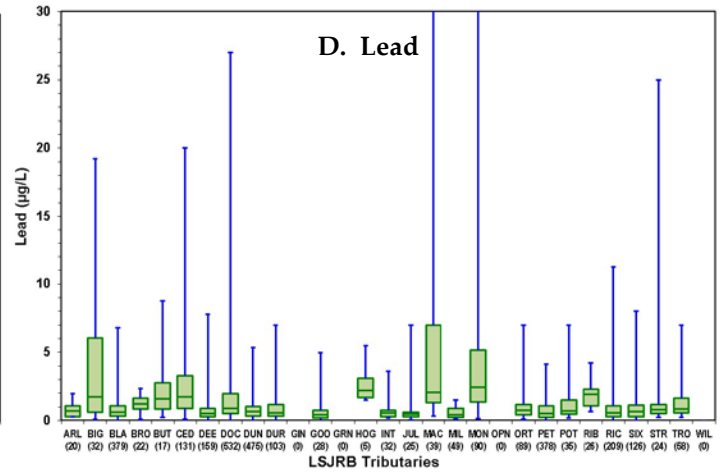
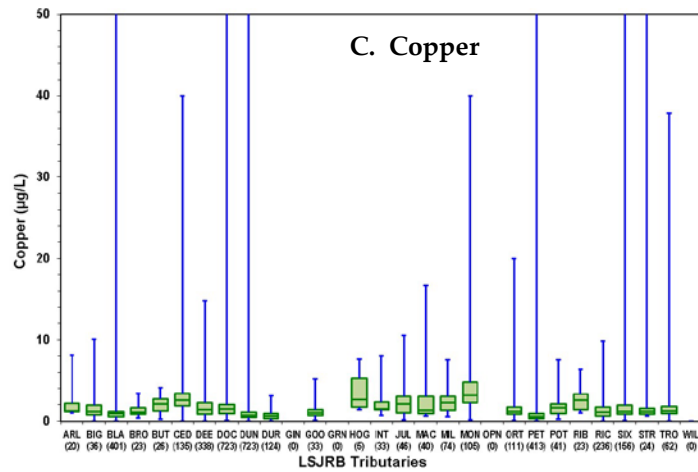
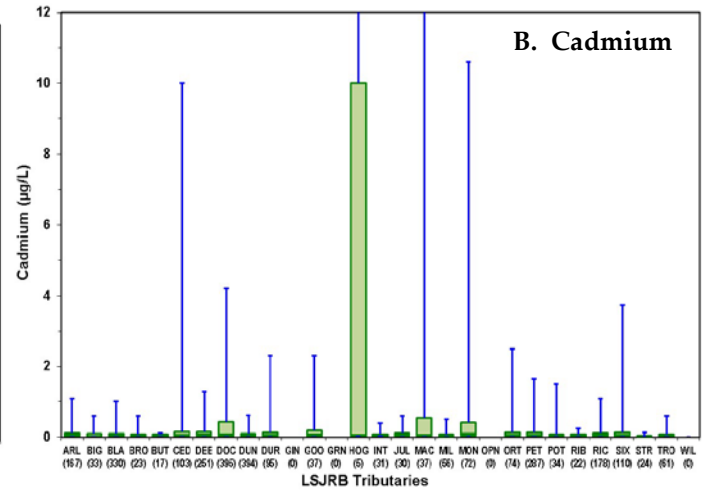
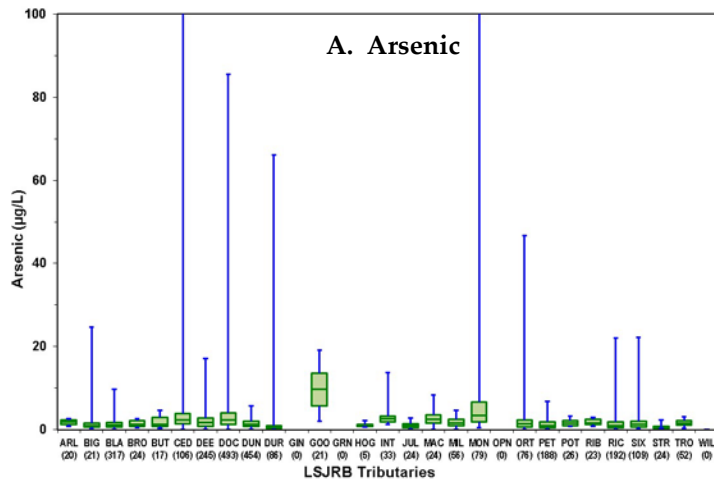


Figure 5.26 Yearly zinc concentrations from 1997 to 2017 in the A. LSJR mainstem and its tributaries, B. the predominantly freshwater portion of the LSJR mainstem, and C. the predominantly marine/estuarine region of the LSJR mainstem. Data are presented as mean \pm standard deviation. The dotted red horizontal line indicates the class III water quality criterion for marine/estuarine waters and the dotted orange line indicates the class III water quality criterion for freshwaters.



Tributary Comparison Key

- ARL – Arlington River
- BIG – Big Fishweir Creek
- BLA – Black Creek
- BRO – Broward River
- BUT – Butcher Pen Creek
- CED – Cedar River
- DEE – Deep Creek
- DOC – Doctors Lake
- DUN – Dunns Creek
- DUR – Durbin Creek
- GIN – Ginhouse Creek
- GOO – Goodbys Creek
- GRN – Greenfield Creek
- HOG – Hogan Creek
- INT – Intracoastal
- JUL – Julington Creek
- MAC – McCoy Creek
- MIL – Mill Creek
- MON – Moncrief Creek
- OPN – Open Creek
- ORT – Ortega River
- PET – Peters Creek
- POT – Pottsburg Creek
- RIB – Ribault River
- RIC – Rice Creek
- SIX – Sixmile Creek
- STR – Strawberry Creek
- TRO – Trout River
- WIL – Wills Branch

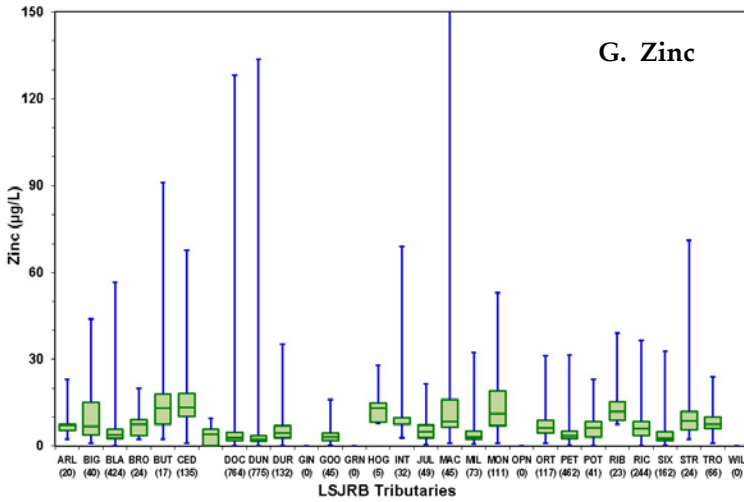


Figure 5.27 Water column variation in A. arsenic, B. cadmium, C. copper, D. lead, E. nickel, F. silver, and G. zinc in over 29 tributaries of the Lower St. Johns River Basin (see key for tributary codes). Data are presented as a box-and-whiskers plot with the green boxes indicating the median $\pm 25\%$ (middle 50% of the data) and horizontal lines indicate the median values. Blue whiskers indicate the minimum and maximum values in the data set. The dotted red horizontal line indicates the class III water quality criterion for predominantly marine waters and the dashed orange line indicates the criterion for mostly freshwaters. Values in brackets below the tributary codes represent the number of data points for each tributary.

5.5.2.2. Metals in Sediments

The metals in sediments that we have evaluated in this study include arsenic, mercury, lead, cadmium, copper, silver, zinc, nickel, and chromium. Metals in general have been elevated over natural background levels in sediments all throughout the LSJR for more than two decades (Table 5.2) and continue to do so today. Many of the sediments that were analyzed since 2000 have had concentrations of chromium, zinc, lead, cadmium, or mercury (discussed in more detail below) that are greater than natural background levels (NOAA 2008), sometimes by very large amounts. Sediments in Rice Creek that were analyzed in 2002 had mercury levels that were about 100 times greater than natural background levels. High metal concentrations were found in sediments elsewhere throughout the river, including the Cedar-Ortega system, Moncrief Creek off the Trout River, Broward Creek, and Doctors Lake.

Table 5.2 Average Metal Concentrations and Percentage of Samples Exceeding Background and Sediment Quality Guidelines in the LSJR Sediments from 2000-2007¹ (see text in Section 5.2 for data sources).

	Average, ppm	Background, ppm ¹	% > Background	TEL ² , ppm	% > TEL	PEL ² , ppm	% > PEL
Copper	29	25	42%	19	50%	108	4%
Chromium	50	13	78%	52	45%	160	1%
Zinc	139	38	72%	124	47%	271	7%
Lead	45	17	65%	30	50%	112	7%
Silver	0.6	0.5	38%	0.7	20%	2	5%
Cadmium	0.6	0.3	66%	0.7	36%	4	0%
Mercury	0.1	0.1	61%	0.1	39%	0.7	1%

¹ BG = Natural background concentrations (NOAA 2008) ² TEL=Threshold Effects Level (sensitive species may be affected); PEL = Probable Effects Level (some species affected)

From the 1980s to 2003, different metals exhibit slightly different trends with time, but none appear to be significantly declining in any area. Two important contributors to overall metal toxicity, zinc in the Cedar River in Area 1, and silver in Area 2, had average concentrations between their respective TELs and PELs, suggesting that the metals found throughout the LSJR individually exert a low-level stress during that time period. Metals in Area 3, the north mainstem, have increased since 1983, but the rate of increase has slowed since the mid-1990s (Figure 5.28). Although a decrease in lead concentrations were not observed from the ban of lead products from gasoline, sediment cores analyzed by other researchers give a more accurate picture of the historical record of contamination. The core studies do show recovery from lead contamination since the 1970s (Durell et al. 2005).

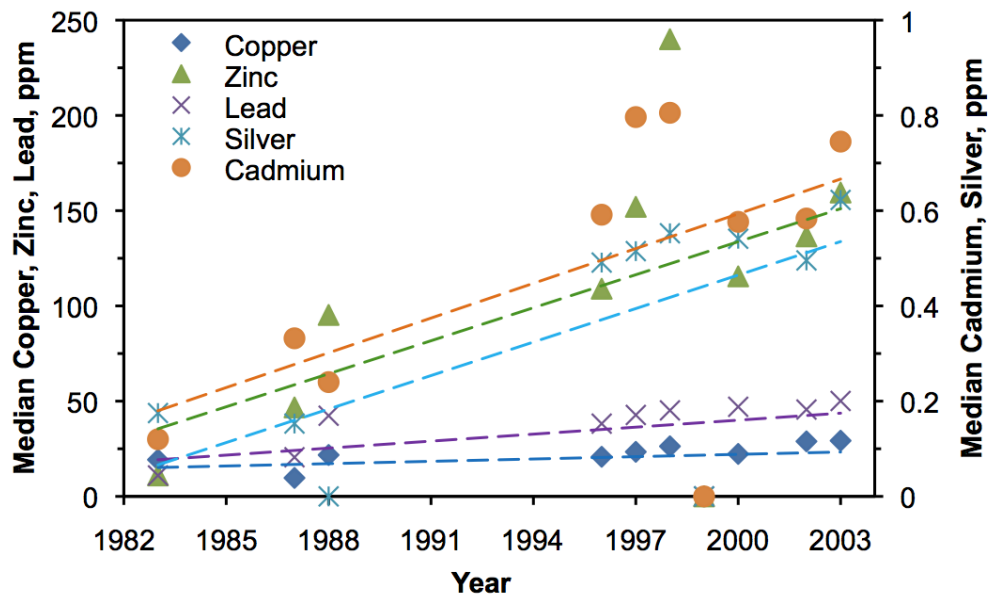


Figure 5.28 Median concentrations of copper, zinc, lead, silver, and cadmium in sediments in Area 3, the north mainstem. Trend lines are shown as dashed lines. See text in Section 5.2 for data sources.

From 2005 to 2016, despite some hot spots, mean metal concentrations in sediments are generally present at concentrations near their TELs; however, for most metals, values above TELs have been reported (Figure 5.29). In particular, lead and mercury continue to be problematic in the LSJR (Figure 5.29). Individually, metals may exert pressure to aquatic life; however, exposure to all metals together may cause synergistic toxic effects, constituting an important class of stressor to the river. It should be noted that the number of sediment samples analyzed for metals has decreased over the past five years by more than 10-fold in some cases. In 2016, there were less than 5 samples for some metals.

For these reasons, the **STATUS** of metals in sediments is *unsatisfactory*, and the **TREND** is *unchanged*.

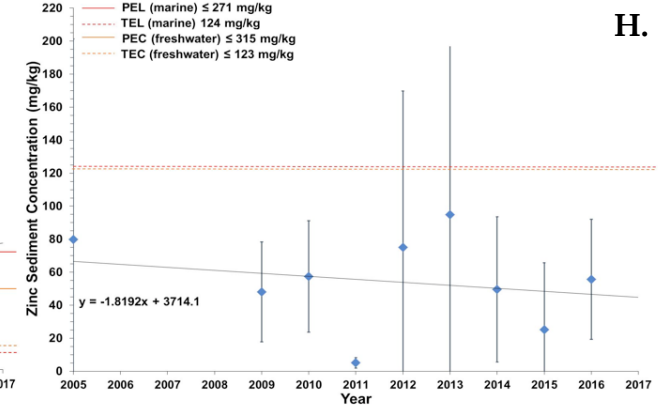
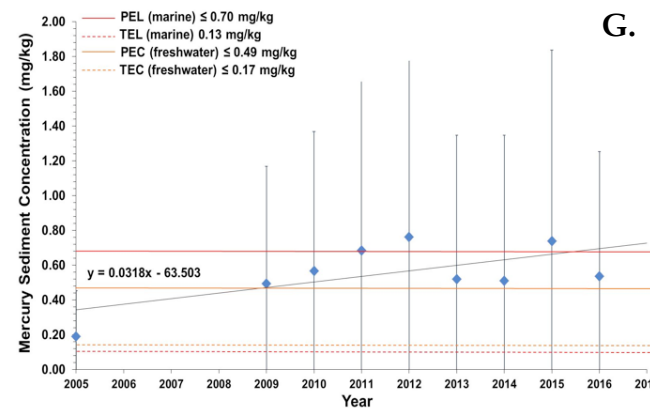
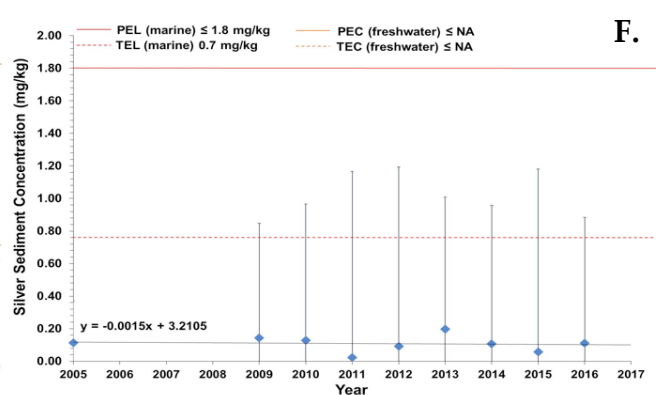
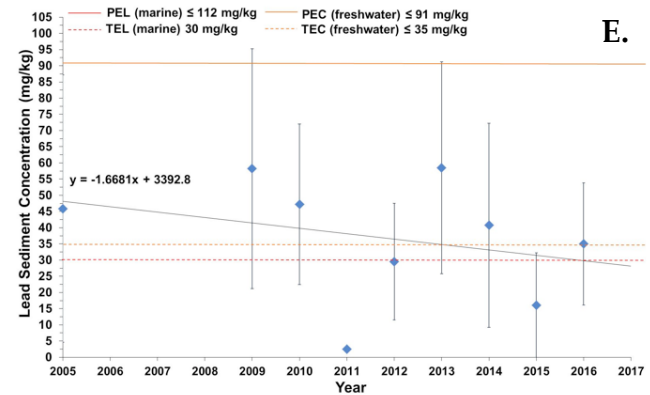
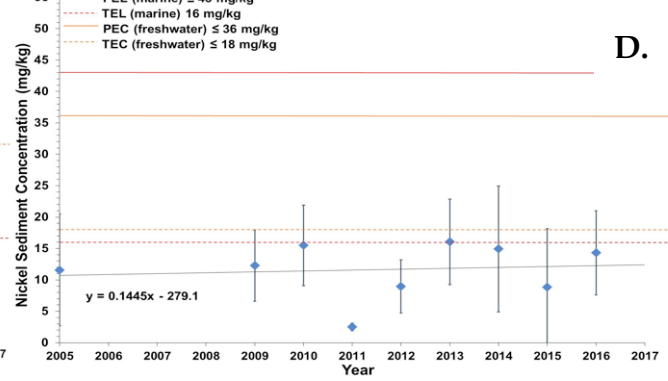
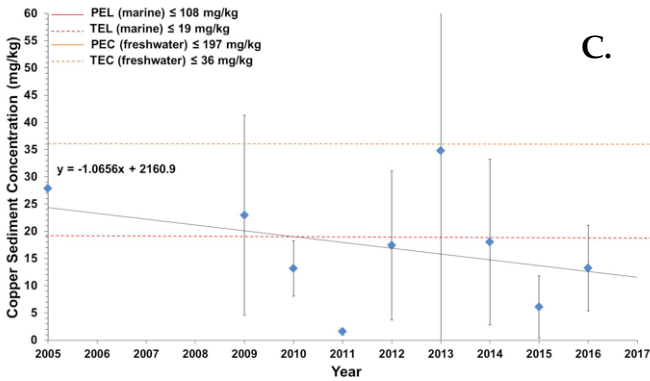
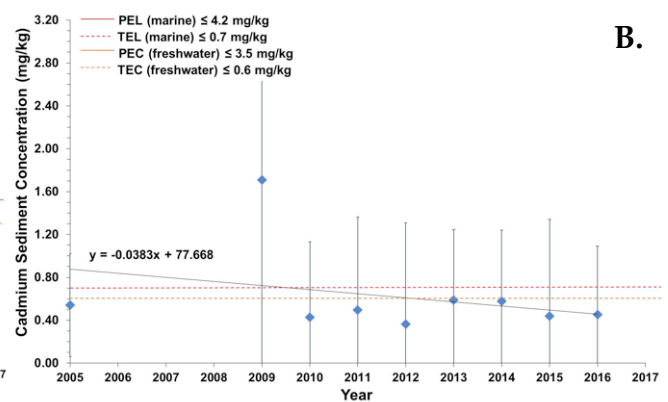
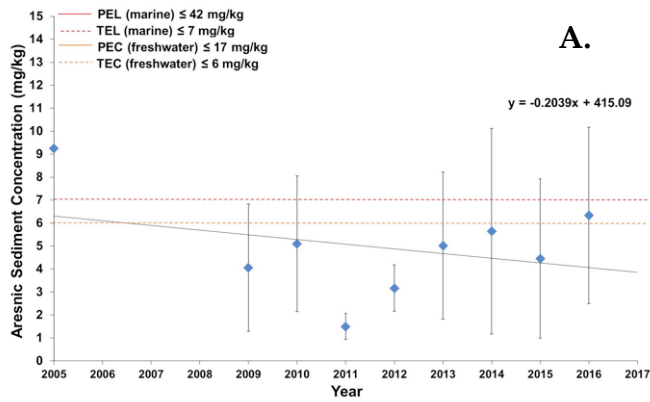


Figure 5.29 Annual Mean Concentrations of A. arsenic, B. cadmium, C. copper, D. nickel, E. lead, F. silver, G. zinc, and H. mercury in the Lower St. Johns River Basin. The dotted red horizontal line indicates the Threshold Effects Level, TEL, for freshwater (sensitive species may be affected); the solid red line indicates the Probable Effects Level, PEL, for freshwater (some species affected); the dotted orange horizontal line indicates the Threshold Effects Level, TEL, for saltwater (sensitive species may be affected); the solid red line indicates the Probable Effects Level, PEL, for saltwater (some species affected).

5.5.3. Point Sources of Metals in the LSJR Region

Most metals emitted to the atmosphere declined significantly between 2001 and 2013, with a 97% reduction in vanadium released by electric utilities accounting for much of the decline (Figures 5.30 and 5.31). In addition, zinc, nickel, copper and cobalt emissions declined significantly from 2002 to 2013 (Figure 5.30). In 2013, releases of 14 different metals to the atmosphere in the LSJR basin were reported. Zinc was the most abundant and comprised about 35% of all metal releases.

In contrast to atmospheric emissions, surface water discharges of metals increased by over 230% to a total of 71,000 pounds between 2001 and 2013. The paper industry released most total metals into the LSJR in 2013 because of the extremely large quantity of manganese that was reported (51,000 pounds). Additional metals discharged by that industry were lead (415 pounds) and mercury (0.26 pounds). Excluding manganese, electric utilities discharged about 50 times more metals than the paper industry and had more diverse effluents with 13 different metals. The metals released by electric utilities totaled 19,712 pounds in 2013 with the top five being barium, cobalt, molybdenum, nickel, and zinc.

Much of the overall increase in metals released to the LSJR is due to the electric utilities, which has had an increase of 250% in its metal discharges since 2001, despite that industry's significant reduction in its air emissions (Figures 5.32 and 5.33). Seven of the 13 metals that were reported in 2013 by the utilities have higher release rates than in 2001. Zinc and nickel increased sharply between 2011 and 2012, while cobalt and barium increased significantly between 2007 and 2008 and have steadily increased since. Reported discharges of mercury and vanadium have decreased since 2001.

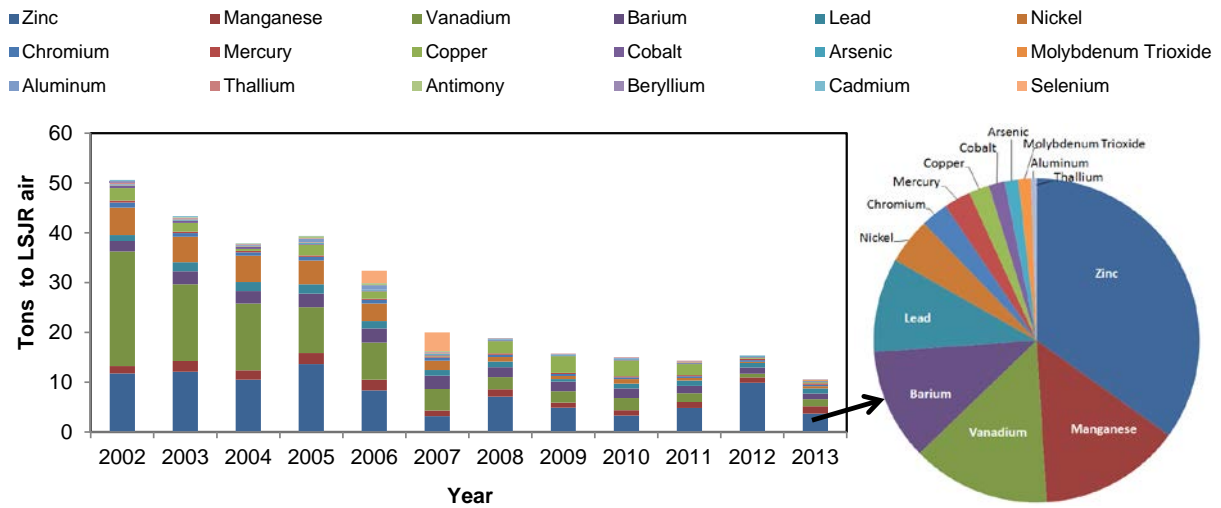


Figure 5.30 Trends and status of 18 metals released into the atmosphere of the nine-county LSJR region as reported in the Toxics Release Inventory EPA 2015d). Inset shows the distribution of 10 tons of metals emitted in 2013.

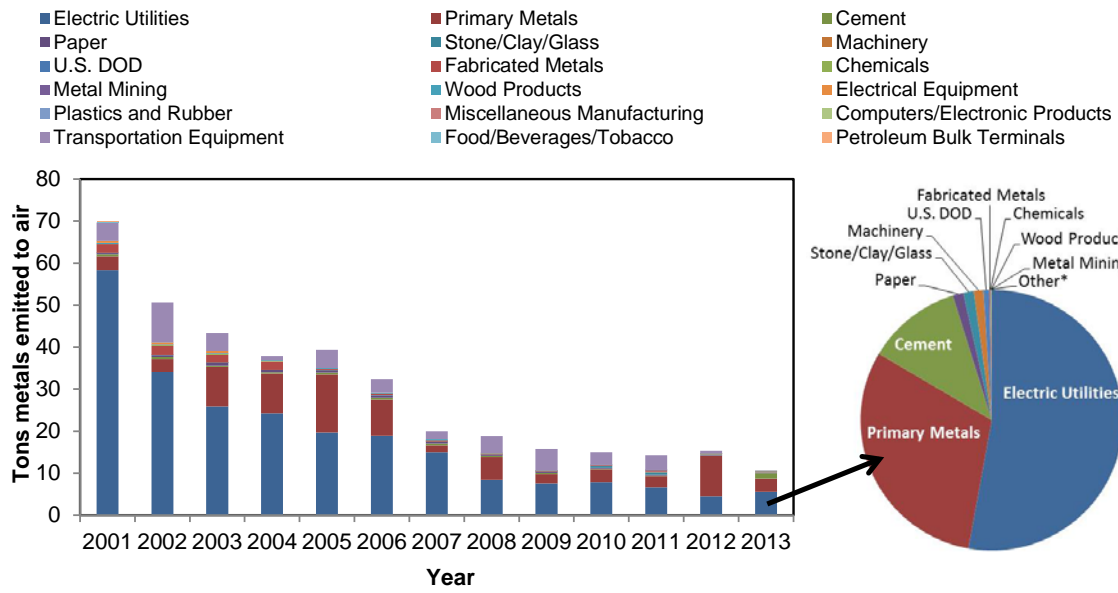


Figure 5.31 Trends and status of 18 industries releasing metals into the atmosphere of the nine-county LSJR region as reported in the Toxics Release Inventory (EPA 2015d). Inset shows the major industries emitting 10 tons of metals in 2013. Other* industries consist of electrical equipment, plastics and rubber, computers/electronic products, and miscellaneous manufacturing which together emitted 4 pounds of metals in 2013.

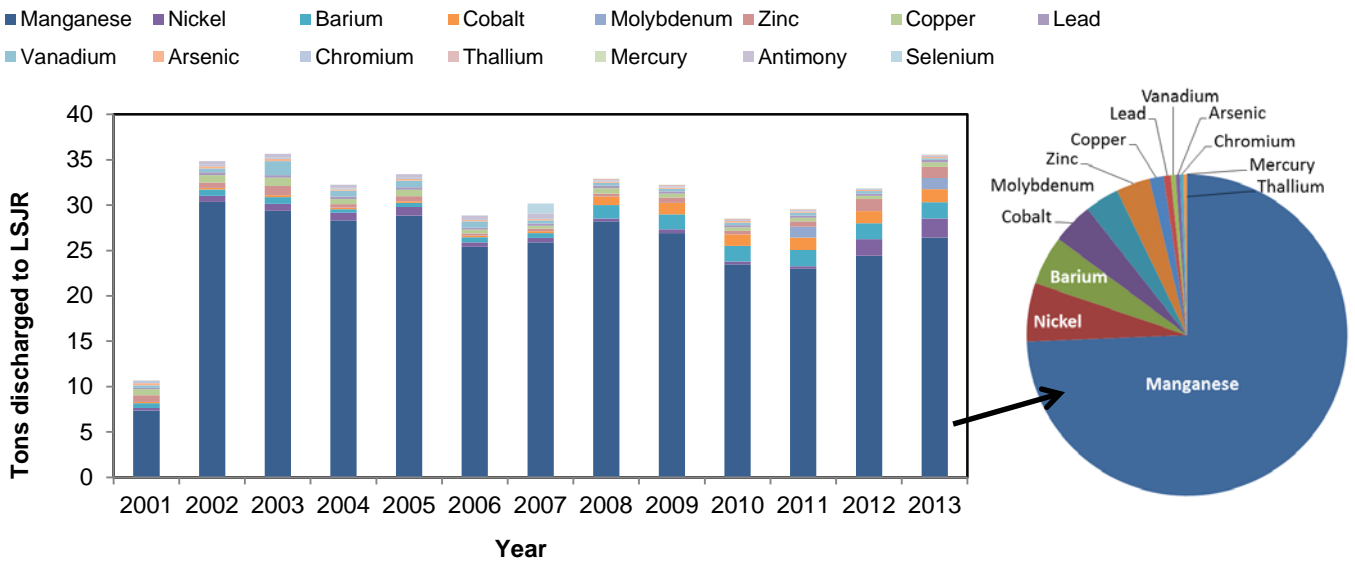


Figure 5.32 Trends and status of 15 metals released to the LSJR and its tributaries as reported in the Toxics Release Inventory (EPA 2015d). Inset shows the distribution of 71,000 pounds of metals discharged in 2013.

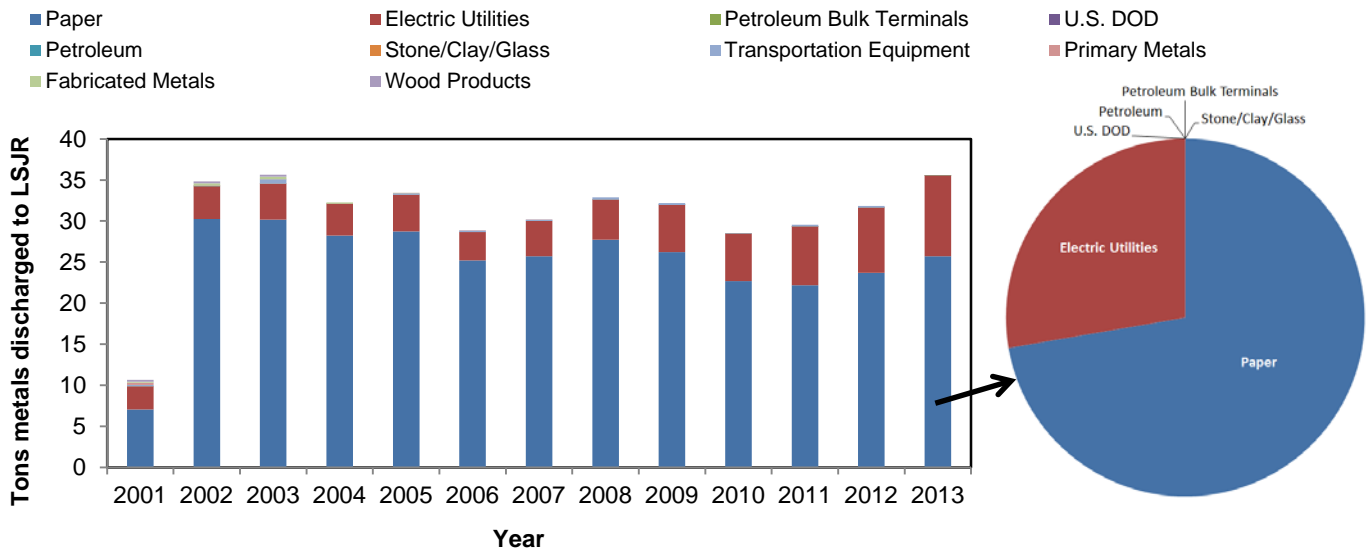


Figure 5.33 Trends and status of 10 industries releasing metals into the LSJR and its tributaries as reported in the Toxics Release Inventory (EPA 2015d). Inset shows the major industries discharging 71,000 pounds of metals in 2013.

5.5.4. Mercury in the LSJR

5.5.4.1. Background: Mercury

Like most metals, mercury has natural and anthropogenic sources. As a constituent of the earth's crust, it is released to the atmosphere by natural geologic processes. However, anthropogenic activities can substantially increase the mobilization of mercury into the atmosphere. In an assessment of national sources of mercury, the EPA determined that approximately 60% of the mercury deposited in the U.S. had anthropogenic sources (EPA 1997b). Though there is evidence there is more mercury in the atmosphere since the Industrial Revolution, there is little certainty about trends since that time (EPA 1997a).

People introduce mercury into the atmosphere by fuel combustion, ore mining, cement manufacture, solid waste incineration, or other industrial activities. Fertilizers, fungicides, and municipal solid waste also contribute to mercury loading but combustion is the primary anthropogenic source (Figure 5.34).

The LSJR emissions reflect national trends in that most waste mercury is emitted from coal power plants (EPA 1997a).

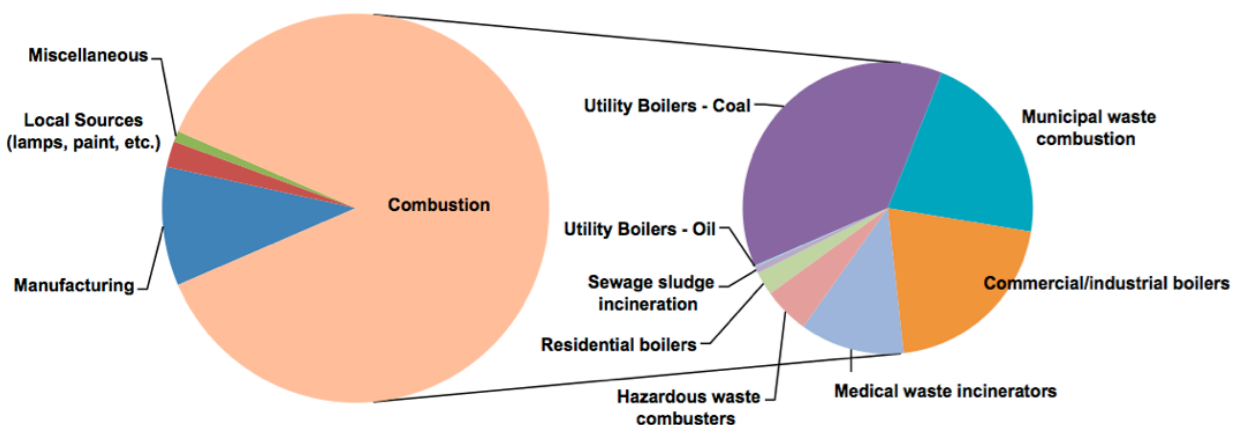


Figure 5.34 National emissions of mercury in the US totaled 158 tons in 1994-1995. Combustion is responsible for the large majority (left graph) with coal combustion the most important type (right graph) (EPA 1997a).

When mercury is released to the atmosphere, the most common type of release (EPA 1997a), its fate is highly dependent on the form of the mercury, meteorological conditions, and the location of the source. Elemental gaseous mercury Hg^0 , is the most abundant in the atmosphere and stays there for long periods of time. Oxidized species, $Hg II$ forms, are more water-soluble and are washed out of the atmosphere and are readily transported to rivers and streams.

Local and regional modeling of the fate of mercury indicates that a substantial portion of emitted mercury travels farther than 50 km from the original source (EPA 1997a). Consequently, it is extremely difficult to isolate specific sources of mercury to a particular watershed. Considerable effort at the federal and state level has been devoted to understanding how mercury travels and cycles throughout the globe.

Once deposited into an aquatic environment, mercury can be transformed by microorganisms to an organic form, methyl mercury. Methyl mercury production is promoted by low nutrients, low oxygen, and high dissolved organic carbon levels which are typical of many Floridian lakes, blackwater streams, and wetlands. Methyl mercury binds to proteins in tissue and therefore readily bioaccumulates. All of the mercury present in prey fish is transferred to predators and the mercury biomagnifies in organisms as it travels up the food chain. High level predators with long life-spans, such as largemouth bass in freshwater and king mackerel in marine systems, accumulate the most mercury in their tissue and therefore they generally have the highest concentrations (Adams and McMichael Jr 2001; Adams et al. 2003). Humans, as top predators, consume mercury in fish also and this is the route by which most people are exposed to mercury (EPA 2001). It is important to realize that when anthropogenic mercury is mobilized to the atmosphere, it will continue to cycle, in some form, through the atmosphere, water bodies, land, or organisms (Figure 5.35).

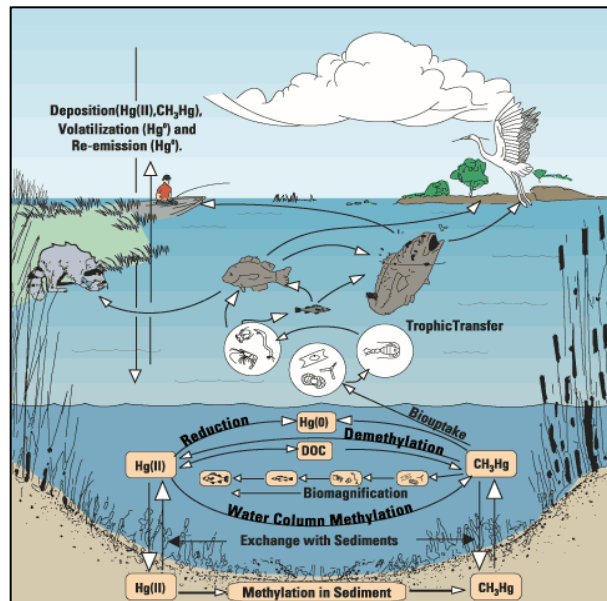


Figure 5.35 The mercury cycle. Mathematical models must accurately describe each step to predict the effect of mercury sources on fish tissue. Source: USGS 2004.

The human health effect of mercury depends on the form, the mode of exposure, and the concentration. Methyl mercury is particularly worrisome because it is the form that is most toxic, it is most easily absorbed through the human gastrointestinal tract and it is released to the bloodstream after consumption. It passes readily into most tissues, including the brain and kidneys, where it can cause permanent damage. Exposure to pregnant women is particularly hazardous since it is passed from mothers to their children through the placenta before birth, and through nursing after birth. Methyl mercury is a neurotoxin and its effect on developing fetus' and children is of high concern. It also appears to affect cardiovascular and immunological health of all human populations. High levels of the metallic form of mercury (Hg⁰) also cause problems but inorganic salts of mercury (Hg II) do not pass as easily into the brain so neural damage is not as certain (ATSDR 2000, EPA 2001).

Both the EPA and FDEP have begun to evaluate the significance of mercury contamination in water bodies based on human health risks from fish consumption, rather than based on simple water column concentrations (EPA 2001, DEP 2009a, FDOH 2016). As discussed in Section 3 of this report and below, when mercury is found in fish or shellfish, health agencies may limit consumption, particularly for women of childbearing age and children. There are 16 fresh water bodies in the LSJR basin for which the FDOH has placed consumption limits for some fish species because of mercury (FDOH 2016). In addition, there were 34 water bodies or segments of water bodies listed as impaired in the 2009 303(d) list for TMDL development based on health effects from consumption of fish contaminated with mercury (DEP 2009a) (see Section 1).

A methyl mercury fish tissue criterion has been developed that is designed to protect the health of general and sensitive populations while allowing people to consume as much fish as possible (EPA 2001, ATSDR 1999). Sensitive populations consist of children and women of childbearing age. To determine if mercury found in fish is harmful to human health, toxicologists use a reference dose (a dose that causes no ill effect) of 0.0001 mg mercury/kg human body weight per day for sensitive populations, and 0.0003 mg mercury/kg human body weight per day for the general population. These are the amounts of mercury that can be safely consumed. When fish tissue exceeds safe levels, FDOH, in concert with FWC and FDEP, issues advisories that recommend limiting consumption to a certain number of meals per week or month, or restricting it entirely. Meals should be limited for the general population when mercury in fish tissue exceeds 0.3 ppm and when it exceeds 0.1 ppm for sensitive populations. When fish tissue exceeds 1.5 ppm, the general population should not eat any of the fish. Sensitive populations should not eat any fish with mercury concentrations greater than 0.85 ppm. (EPA 2001, Goff 2010). As long as monitored fish contain low enough concentrations of mercury so that people will not consume more than the reference dose at standard rates of consumption, then no restrictions will apply.

The FL DEP issued its final report for the statewide mercury TMDL in October 2013 (see Section 1 in this report for additional information on TMDLs). The ultimate goal of the TMDL effort is to reduce the levels of mercury in fish in State waterways to safe levels where fish consumption advisories have been issued. The elements of the multi-year study to establish mercury load limits included measuring the amount of mercury that is present in Florida waterways (in fish, water and sediment), and identifying sources and fates of mercury in the State through atmospheric monitoring and modeling.

Intensive monitoring of atmospheric mercury, along with other metals and air quality parameters, was undertaken at seven sites from 2008-2010. Wet deposition of mercury was monitored at all sites and in Jacksonville, Pensacola, Tampa and Davie dry deposition was also monitored. In addition to atmospheric monitoring, extensive analysis of mercury in fish, primarily largemouth bass, and water quality was undertaken in over 100 freshwater lakes and 100 streams. The selected sites varied in acidity, trophic status and color, all parameters that were thought to affect the fate of mercury in water bodies and its uptake by fish and other organisms. These data are being used to predict levels in unmonitored sites. Mathematical models of the emissions, transport, and rates of deposition of mercury into waterways were developed as well as models to predict the concentrations in fish with different mercury loading rates and in different aquatic environments. Estimating exposure to mercury by different populations and establishing a safe level of consumption was another significant effort in the project (DEP 2007; DEP 2011; DEP 2013c). Results of the studies indicate that the vast majority of the man-made sources of mercury in Florida waters has global sources and that aquatic lakes and streams vary more because of their geochemistry than because of atmospheric loading. The TMDL report indicates significant reductions in mercury emissions have occurred in the last two decades.

No additional reductions will be required of local coal fired power plants due to recent large reductions arising from federal regulation (EPA 2013d) and the global nature of the sources in State waters. NPDES permit-holders will have no additional mercury limits imposed beyond currently enforced water quality criteria because of the limited impact of local atmospheric and point sources, and because of anticipated impending EPA regulations (EPA 2015b).

5.5.4.2. Current and Future: Mercury in LSJR Sediments

The influx of information about mercury sources and levels that will arise from the TMDL process will provide much needed information about the extent of the contamination throughout the state. In the LSJR, there is some mercury information but the amount of data is limited. For example, there is no information for the south mainstem, Area 4, for recent years and other areas in the LSJRB have limited numbers of samples. In addition, changes in standard methods of analysis make it difficult to track trends. The mercury database will be improved with the mercury TMDL process and future river status reports will summarize the results of that regulatory action.

Mean mercury concentrations in sediments collected from various sites along the LSJR Sites are given in Table 5.3. The distribution of mercury, the TEL, PEL, and hot spots in various years is shown in Figure 5.36. Mercury levels that exceed natural background levels and the most protective environmental guidelines are found throughout the mainstem. There are isolated locations in the LSJR, particularly in Rice Creek and the Cedar-Ortega system, where mercury occurs at concentrations high enough to impair the health of organisms. It is possible that mercury will bioaccumulate in those fish, crabs, and shellfish that spend most of their lives at these highly contaminated sites.

It should be noted that the toxicity pressure reflects the overall toxicological stress on the ecosystems of the river. It does not address human toxicity, which arises when we consume toxic metals that have found their way into the environment, via contaminated biota. Human health effects are discussed in the following section.

Because of the high degree of toxicity pressure due to mercury, the high numbers of sites that have mercury in sediments greater than background levels, and the high degree of potential human risk, the **STATUS** of mercury in sediments is *unsatisfactory*, and the **TREND** is *unchanged*.

Table 5.3 Average Mercury Concentrations and Percentage of Samples Exceeding Background and Sediment Quality Guidelines in the LSJR Sediments (see text in Section 5.2 for data sources).

Mercury	1983	1988	1996	1997	1998	1999	2000	2002	2003	2007
Average Conc., ppm	0.5	0.1	0.3	0.2	0.6	0.2	0.2	0.1	0.1	0.1
No. of Samples	13	28	143	52	214	40	45	28	25	16
% > BG ¹	15%	64%	80%	77%	95%	80%	67%	71%	76%	38%
% > TEL ²	15%	32%	63%	75%	75%	53%	36%	39%	48%	38%
% > PEL ²	15%	0%	6%	0%	30%	8%	2%	0%	0%	0%

BG = Natural background concentrations (NOAA 2008) TEL=Threshold Effects Level (sensitive species may be affected); PEL = Probable Effects Level (some species affected)

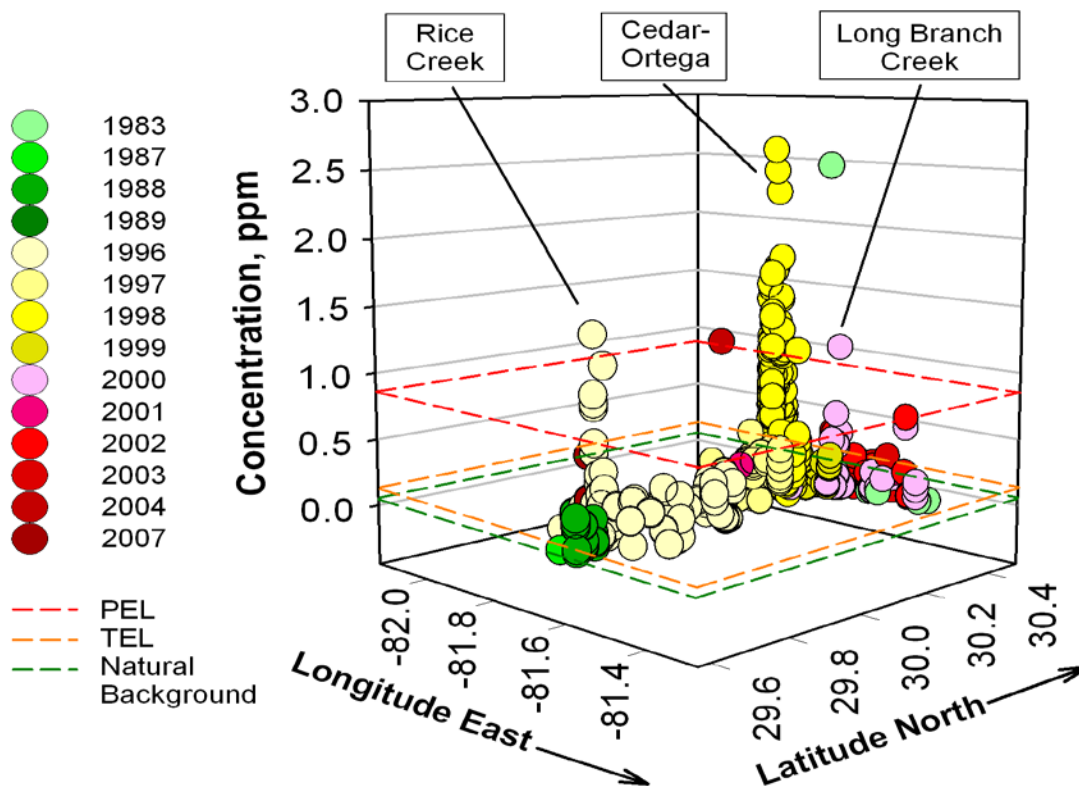


Figure 5.36 Mercury Sediment Quality Guidelines and LSJR sediment hot spots (scale of mercury concentrations does not show Rice Creek 2007 maxima). See text in Section 5.2 for data sources.

5.5.4.3. Mercury in LSJR Fish and Shellfish

The diverse types of fish that live in the LSJR were reviewed in Section 3 in this report. As noted, there is considerable overlap of freshwater, estuarine, and marine species in the dynamic LSJR system. In the following data sets, the marine and estuarine species associated with the LSJR were caught north of Doctors Lake. Of the marine and estuarine species

discussed, King mackerel, Spanish mackerel, gag grouper, and bull shark are generally found offshore, while the others reside largely in coastal and estuarine waters. The freshwater species were caught south of Doctors Lake. The species that are reported are considered important because of their economic significance. Some species are also closely monitored because they are at high risk for elevated concentrations due to their large size and trophic status (Adams et al. 2003).

As shown in Figure 5.37, most species in the northern marine section of the LSJR, had low levels of mercury in their tissue, including blue crabs and oysters. The only data that exceeded FDOH's most restrictive advisory levels for the general population were those reported in the Section 303(d) Impaired Waters listing for mercury. Those data, collected throughout Florida's coastal and offshore waters, resulted in impaired designations for the marine and estuarine mainstem and seven tributaries north of Doctors Lake. The King mackerel and bull shark, top predator species that are large and long-lived, have significantly elevated levels compared to the other species. Levels in marine/estuarine species in the LSJR are comparable to or less than the averages for the individual species for the entire State of Florida (Adams et al. 2003). However, as discussed in Section 3, advisories have been issued for all Florida coastal waters for numerous species including Atlantic croaker, dolphin, gag grouper, King mackerel, sharks, red drum, southern flounder, spotted seatrout, and southern kingfish (FDOH 2016). Additional information about consumption advisories is available in Section 3 of this report.

In the fresh portions of the river south of Doctors Lake, the mainstem, tributaries, and large connected lakes, fish have been extensively sampled in the last 10 years (Figure 5.38). Levels exceeding the 0.3 mg/kg fish tissue criterion have been found primarily for largemouth bass, which caused the southern part of the LSJR mainstem, Lake Broward, and Crescent Lake to be designated as impaired. Not included in this discussion are several smaller, isolated southern lakes that have been listed as impaired due to elevated concentrations of mercury, again primarily in largemouth bass. As with the LSJR marine and estuarine fish, LSJR freshwater fish mercury levels are generally comparable to the rest of the state. Furthermore, the 1998-2005 national average for largemouth bass was 0.46 ppm, which is similar to LSJR values (Scudder et al. 2009).

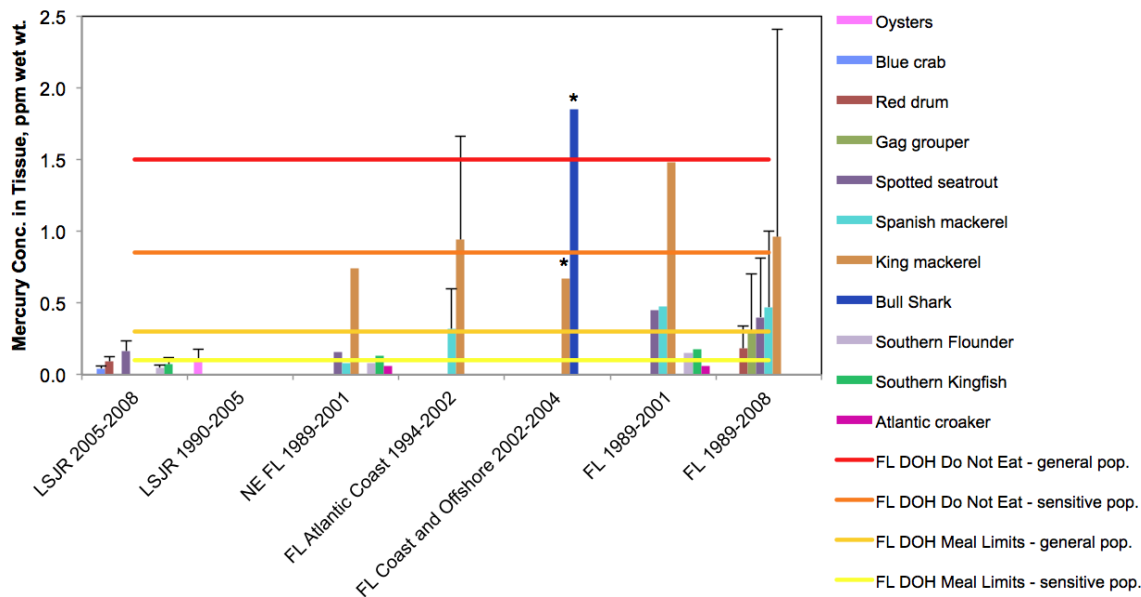


Figure 5.37 Average mercury concentrations in estuarine and marine invertebrates and fish caught in coastal waters, offshore, and in the LSJR north of Doctors Lake. An asterisk means the data set was used for 2009 303(d) impaired water listing for the marine/estuarine mainstem and 7 tributaries north of Doctors Lake. Standard deviation bars are shown. Data sources include Adams et al. 2003; Adams and McMichael Jr 2007; NOAA 2007b; Brodie 2008; Axelrad 2010; Goff 2010.

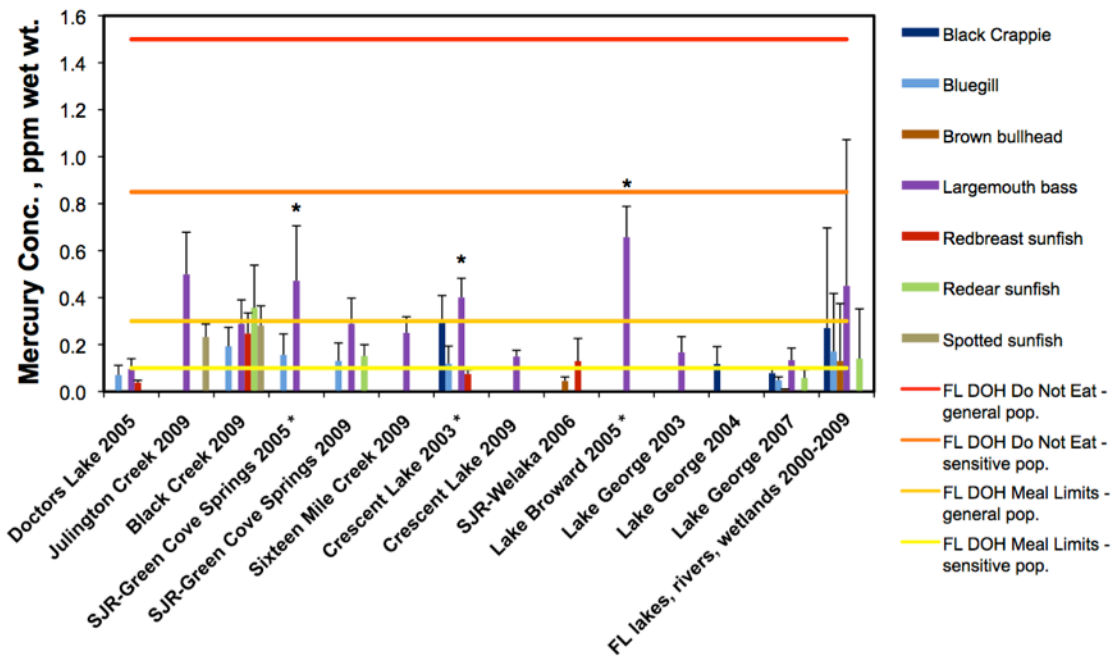


Figure 5.38 Average mercury concentrations in freshwater fish caught in the LSJR mainstem and tributaries south of Doctors Lake, as well as other Florida waterways. An asterisk means the data set was used for 2009 303(d) impaired water listing for the indicated water bodies in the LSJR. Data sources include Axelrad 2010; Goff 2010; Lange 2010.

There are a number of consumption advisories due to mercury contamination in fish in the LSJR region, and most fish contain at least small amounts of mercury. However, high levels of mercury in fish are found mostly in the top predators and in only a few of the fresh water bodies sampled. By consuming mostly lower-level predators and smaller, short-lived fish species (e.g., Atlantic croaker, flounder, sunfish) people can benefit from this healthy food source with minimal risk.

5.5.4.4. Point Sources of Mercury in the LSJR Region

In 2013, 558 pounds of atmospheric mercury emissions in the LSJR region were from four primary industries, including stone/clay/glass (30%), electric utilities (30%), primary metals (25%), and cement (15%). Emissions from gypsum and steel production have grown since 2008, offsetting reductions by the electric utility industry (Figure 5.39). St. Johns River Power Plant and Northside Generating Station reduced their mercury emissions by 71% between 2001 and 2013 (Figure 5.33). While 10 facilities reported mercury emissions, five were responsible for 99% of total atmospheric mercury emissions in 2013 (Figure 5.40).

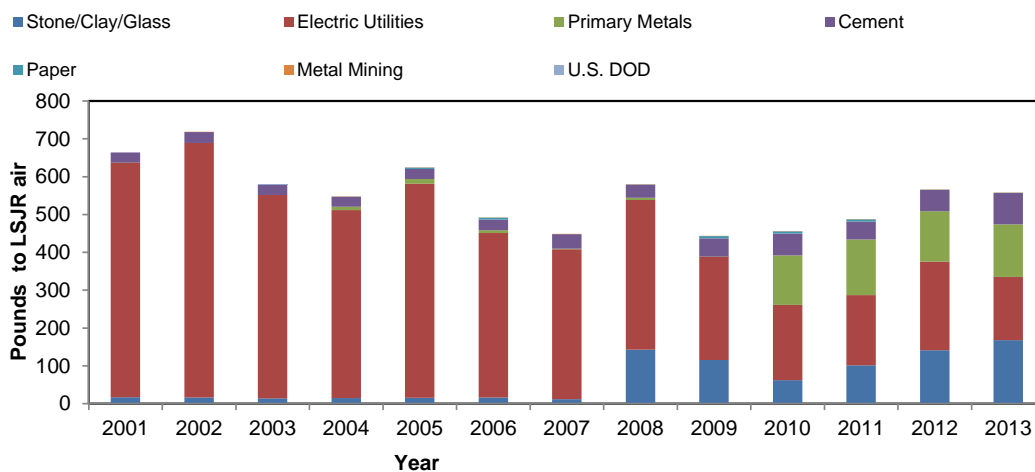


Figure 5.39 Trends and status of emissions of mercury into the atmosphere of the nine-county LSJR basin by industry as reported in the Toxics Release Inventory (EPA 2015d).

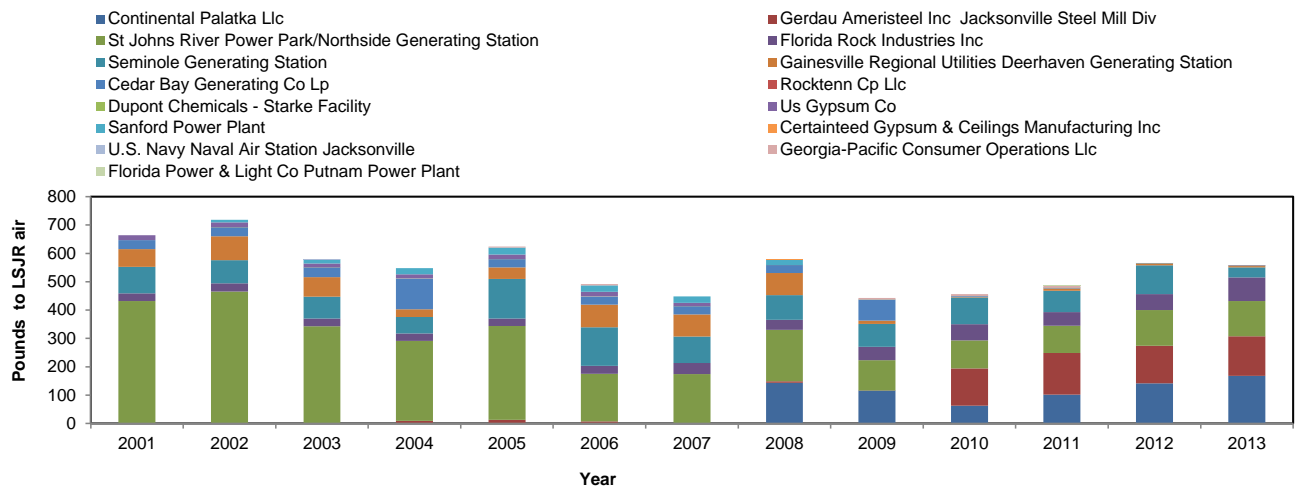


Figure 5.40 Trends and status of emissions of mercury into the atmosphere of the nine-county LSJR basin by the facilities (EPA 2015d).

Mercury releases into the LSJR and tributaries significantly dropped in 2004 with Seminole Generating station dramatically reducing its output of mercury. Coincident with reductions in atmospheric emissions since 2006, St. Johns River Power Park and Northside Generating Station steadily increased their discharges of mercury into surface water until 2011. However, in the subsequent two years there was a dramatic decrease in mercury discharges by that facility. Total discharges of mercury into the LSJR have been reduced by nearly 75% since 2001 (Figure 5.41). The RSEI model of chronic human health toxicity indicates that mercury releases to water by Seminole Electric is among the top potential risks compared to all releases in the region (EPA 2013e). However, we are unable to fully assess the importance of mercury because St. Johns River Power Park/Northside Generating Station, a major discharger, is not included in the RSEI modeling (see Section 5.3).

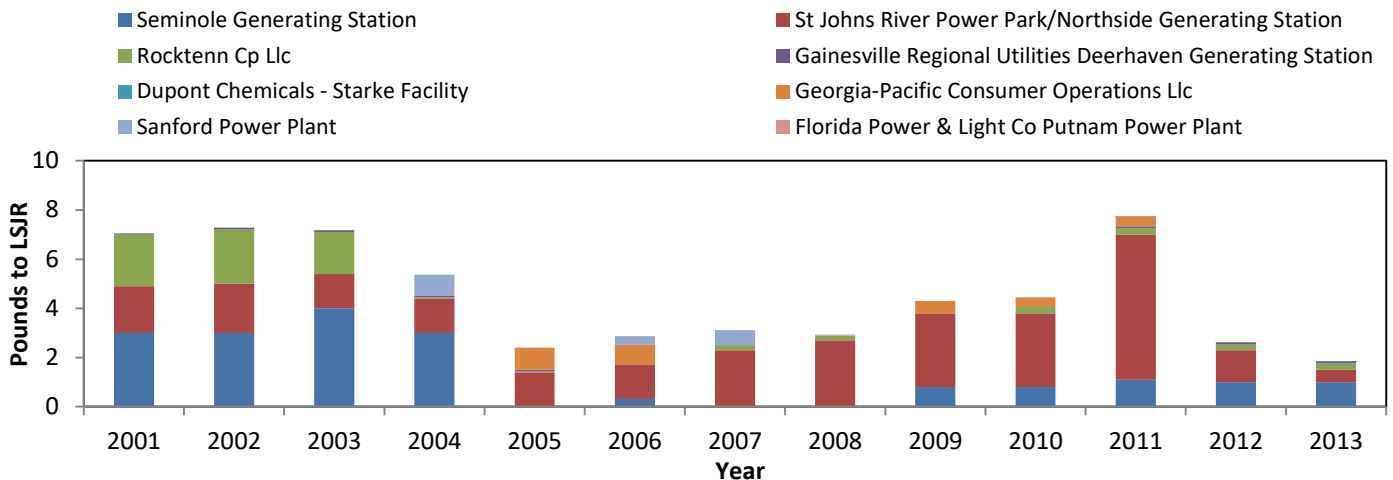


Figure 5.41 Trends and status of discharges of mercury into the LSJR and its tributaries by facility as reported by the Toxics Release Inventory (EPA 2015d).

5.6. Polychlorinated Biphenyls (PCBs)

5.6.1. Background and Sources: PCBs

Polychlorinated biphenyls, PCBs, are synthetic chemical mixtures that were used for their nonflammable and insulating properties until they were restricted in the U.S. in the 1970s. They provided temperature control in transformers and capacitors, and were also used for lubrication and other heat transfer applications. They were sold primarily under the name of Arochlors in the U.S. They are still found in old fluorescent lighting fixtures, appliances containing pre-1977 PCB capacitors, and old hydraulic oil. The characteristics of the fluids were changed by modifying the mixture components, so each of the major Arochlor formulations is composed of different concentrations and combinations of the 209 PCB chemicals. Until the mid 1970s, PCBs were also used in manufacturing processes for a wide range of different substances,

from plastics to paint additives. By 1979, the manufacture of PCBs in the U.S. was prohibited and their import, use, and disposal, were regulated by the EPA (EPA 1979). In the 1980s, Jacksonville was the site of several electrical testing and service businesses which intentionally and unintentionally dispersed PCB-contaminated fluids (i.e., waste oil) into or near the LSJR. Waste oil uses and spills from locomotive wastes has also contributed PCBs near the LSJR. One of the most visible PCB legacies in the U.S. is the Hudson River, where capacitor plants discharged wastewaters into the river resulting in contaminated sediments in rivers and estuaries for decades to come.

PCBs are inert, which makes them industrially valuable but environmentally harmful. They do not react readily by microbes, sunlight, or by other typical degradation pathways. They are not very soluble in water, so the lighter ones tend to evaporate and the heavier ones tend to associate with particles, whether in the air, soil or sediments. Another important consequence of PCBs' chemical properties is that they are compatible with fatty tissue, allowing extensive uptake and bioaccumulation in the fats of plants and animals. They are readily biomagnified because they are not easily metabolized and excreted.

PCBs are introduced directly into the environment today primarily from hazardous waste sites and improper disposal of old appliances and oils. However, they also may be transported long distances in the atmosphere, either in gas form or attached to particles. The principal route of PCB transport to aquatic environments is from waste stream waters, downstream movement by means of solution and re-adsorption onto particles, and the transport of sediment itself, until eventually reaching estuaries and coastal waters. Like PAHs, sometimes sources of PCB contamination can be elucidated by examining different patterns of contamination of the different PCB constituents, but several processes obscure those patterns. Weathering, currents and tides, multiple sources in a large drainage basin, and repeated cycles of evaporation, sorption and deposition all tend to mix everything up so individual sources are not usually identifiable unless there is a very specific, current source.

Because of methodological developments over the years and variable definitions of "total PCBs", it is not feasible to compare total PCB or mixture concentrations (like Arochlors). Consequently, several individual PCBs were evaluated here and total PCBs were estimated from those values. The specific eight PCBs we decided to evaluate were selected on the basis of their presence in the LSJR and on the availability of comparable data. We estimate that the PCBs we examined in this study represent 20% of the total PCBs that were actually present. More information about the calculations we used to estimate total PCBs is given in Appendix 5.3.A.

5.6.2. *Fate: PCBs*

PCBs have a high affinity for suspended solids (organic matter) and are very insoluble in water. Due to their properties, PCBs are found in much higher concentrations in sediment and biota than in water. Sediment can become a significant source as well, because of desorption, diffusion, and possible re-suspension of PCBs in the water column. Removing contaminated sediments is the predominant mechanism of PCB removal.

5.6.3. *Toxicity: PCBs*

The effects of PCBs on wildlife as a result of waterway contamination have been extensively documented over the years. During the 1960s, mink farmers in the Great Lakes region fed their mink fish from Lake Michigan tributaries that had been contaminated with PCBs. These ranch mink suffered severe outcomes including high mortality rates and reproductive failure. PCB contamination in the Hudson River from 1947-1977 by the General Electric Company led to fishing bans that were not changed until 1995 when fishing became permissible on a catch-and-release basis only. The state of New York recommends that children under age 15 and pregnant women not eat any fish from the 200-mile stretch of the river that has been designated as an EPA Superfund site.

PCBs can bioaccumulate in the fat tissue of organisms since they are highly lipophilic (Fisk et al. 2001; Cailleaud et al. 2009) and can also be directly toxic to aquatic organisms. Cailleaud et al. 2009 reported a preferential accumulation of HMW PCBs and preferential elimination of LMW PCBs in an estuarine copepod. Unlike PAHs, PCBs can biomagnify up the food chain and top-level carnivores are particularly susceptible to toxicity (Guillette Jr. et al. 1999). Since PCBs are chemically inert, they are highly resistant to chemical breakdown and are therefore very persistent in the environment. Sepúlveda et al. 2002 reported the accumulation of PCBs in the livers of Florida largemouth bass collected from different locations in the LSJR. The liver PCB concentrations were highest in the largemouth bass collected from Green Cove and Julington Creek, as compared with those collected from Welaka. PCBs exert toxicity in aquatic organisms primarily via endocrine disruption and neurotoxicity (Fossi and Marsili 2003). Reported effects of PCB exposure include male feminization due to increased

estradiol, reduced male and female fertility, modified immune system, and altered reproductive behavior. Acute toxicity values (96 h LC50s) range from 12 µg/L to 10 mg/L for aquatic invertebrates and range from 8 µg/L to 100 mg/L for fish. **Bergeron et al. 1994** demonstrated an increased percentage of female hatchling turtles after exposure of the eggs to PCBs in the laboratory. Likewise, **Guillette Jr. et al. 1999** reported reproductive abnormalities in the hatchling and juvenile alligators of Lake Apopka, FL, thought to have been caused by embryonic exposure to PCBs and other environmental contaminants. However, **Sepulveda et al. 2004** also recently reported thiamine deficiency in Florida alligators as another potential cause of the population declines.

Due to their endocrine-disrupting properties, PCBs may threaten aquatic ecosystems at both the individual and the population level.

5.6.4. Current Status: PCBs in Sediments

Polychlorinated biphenyls are produced only by human activity so their simple presence denotes human impact. The majority of the sediments contained some PCBs. Specifically; 84-100% of sediment samples collected from 1996 to 2003 in the four river regions contained PCBs. Most had levels that could affect sensitive species, as indicated by concentrations greater than TEL guidelines (Figure 5.42). However, in most of the river, the estimated total PCB concentrations were far below the probable effects level of 189 ppm, producing a low toxicity pressure throughout the basin. The PCBs were often found at levels typical for urban, industrialized environments (**Daskalakis and O'Connor 1995**). Most of the river's sediments had concentrations of PCBs well below the 80 ppb that characterizes a "high" level compared to the rest of the coastal areas in the country (**Durell et al. 2004**).

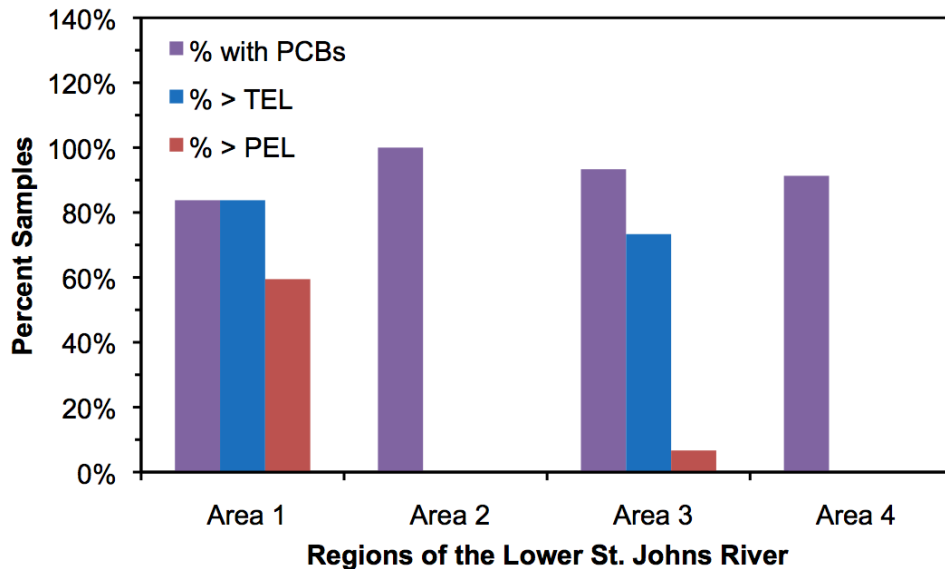


Figure 5.42 Percentage of sediment samples from 2000-2007 that contain PCBs and have PCBs concentrations that exceed Threshold Effects Levels (TEL) and Probable Effects Levels (PEL) for PCBs. See text in Section 5.2 for data sources.

The picture changes somewhat when we partition the river. It becomes apparent that the western tributaries, Area 1, have far more toxicity pressure from PCBs than the mainstem portions of the river. In Cedar River and Rice Creek, the average PCB concentration exceeded, by a factor of ten, the concentrations that are considered high for the nation's coastal areas (**Daskalakis and O'Connor 1995**). Particularly high levels were found in the Cedar-Ortega in the late 1990s. In 2000-2003, Rice Creek was a hot spot for PCBs 105, 118, 128, 180 and 206, the first two of which are among the most toxic (**ATSDR 2000**) (Figure 5.43).

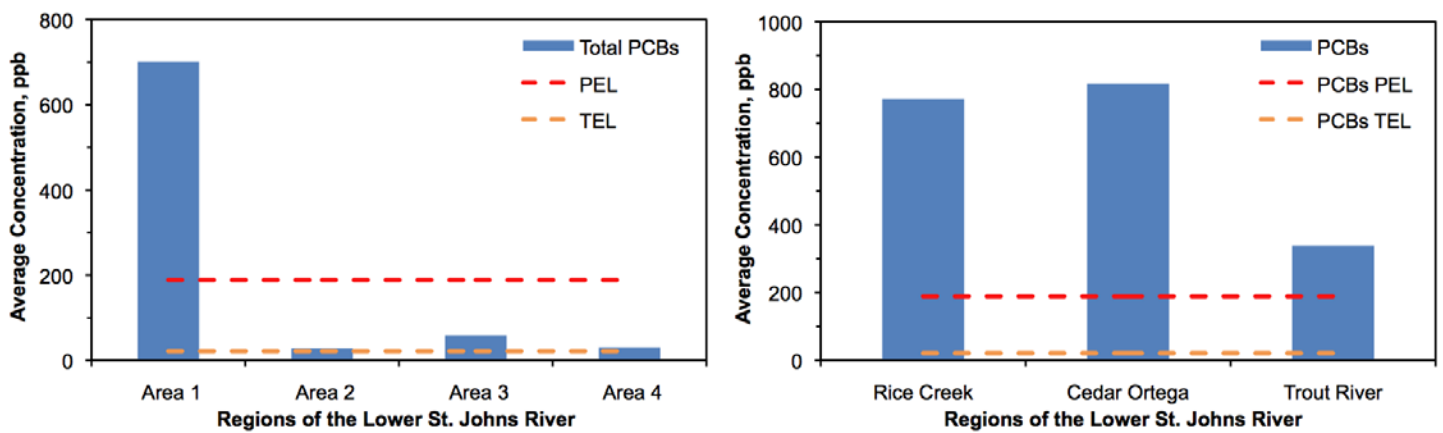


Figure 5.43 Average concentrations of PCBs in sediments from 2000-2007 in the four areas of the LSJR and in three streams in Area 1. Sediment quality guidelines for PCBs are shown as dashed lines. Area 1 – western tributaries; Area 2 – north arm; Area 3 – north mainstem; Area 4 – south mainstem. See text in Section 5.2 for data sources.

5.6.5. Trends: PCBs in Sediments

There are data only for 1996-2003 for PCBs, so trends are difficult to identify. However, the distributions of the PCBs we examined appear to be reasonably constant along the river and across the years, an outcome of the persistence of the long-banned substances.

5.6.6. Summary: PCBs

PCBs persist in the LSJR long after regulatory and environmental controls were put into place. They are weathering but continue to exert their influence, with little discernable changes in concentration over time. Outside of the highly contaminated western tributaries, Area 1, these compounds by themselves are not likely to be major stressors of benthic organisms, but may exert a low-level toxicity pressure throughout the basin. Previously, the **STATUS** of PCBs in sediments was *unsatisfactory*, and the **TREND** was *unchanged*; however, PCBs were not evaluated in this year's report.

5.7. Pesticides

5.7.1. Background and Sources: Pesticides

Pesticides are diverse, primarily including insecticides, herbicides, fungicides and rodenticides. Pesticides enter water bodies from a number of different pathways. They are applied directly to control aquatic nuisances such as water hyacinth. They can be components of runoff from residential, agricultural, and other commercial applications. They also come from the atmosphere, usually attached to particles. As a consequence, pesticides are widespread in residential, urban, and agricultural areas. Pesticides are very different in their chemistry and environmental fate, in large part because pests are also diverse. Target species include mold, bacteria, rats, spiders, barnacles, mosquitoes and more, and each species has a metabolism that is vulnerable to different chemicals.

Pesticide manufacture and use has evolved significantly towards protecting the environment since the times when lead and arsenic compounds were dusted in homes to control insects (Baird 1995). Efforts have been made to create pesticides that can specifically target the pest and that can degrade after their function has been performed. However, pesticides that were used historically continue to be environmentally important because of their persistence.

Organochlorine compounds (OC's; molecules containing carbon and chlorine) were introduced in the 1930s and bear some similarity to PCBs in their characteristics and environmental fate. They were effective for long periods of time against insects in homes, institutions, crops, and livestock, largely because they were nearly non-degradable. Because of their longevity, these compounds remain in the environment today despite being regulated and removed from manufacture up to forty years ago. Several organochlorine compounds and their degradation products are the focus of this review because of their environmental significance and the availability of historic data.

It is important in the future to also evaluate pesticides currently used, which tend to be less persistent but more toxic. The varied land uses in the LSJR basin, along with its extensive recreational and commercial maritime activities, cause a broad spectrum of pesticides to be loaded into the river. The U.S. Army Corps of Engineers directly applies herbicides 2,4-D, diquat, and glyphosate in the southern parts of the river for the control of water hyacinths and water lettuce (**USACE 2012b**). The city of Jacksonville sprays malathion, organophosphates, and pyrethroids for mosquito control (**COJ 2010**). Agriculture in southern LSJR contributes to the pesticide load as well. While estimates of current total pesticide loading rates into the LSJR are elusive, it is reasonable to suppose that some of the most commonly detected pesticides in agricultural, residential, and urban U.S. streams (**Gilliom et al. 2006**) will be present in the LSJRB. These include the herbicides atrazine, metolachlor, simazine, and prometon, as well as the insecticides diazinon, chlorpyrifos, carbaryl, and malathion. Finally, the tributyl tins used by the maritime industry should be reviewed. These common pesticides represent 11 different classes of chemical structures that will have very different fates and impacts on the environment.

In this study, four organochlorine pesticides and their primary degradation products were assessed. These compounds were primarily used as insecticides and removed from market in the 1970s. Aldrin was used against termites and other insects in urban areas. Dieldrin is a degradation product of aldrin, and was also used directly against termites. Endrin targeted insects and rodents, usually in agriculture, and endrin aldehyde is its degradation product. Heptachlor and its degradation product, heptachlor epoxide, are used here as markers for chlordane contamination since the complex chlordane mixtures are difficult to compare across years and analytical methods. Chlordanes were used in agriculture and in households, especially for termite control. Finally, the notorious insecticide dichlorodiphenyltrichloroethane (DDT) and its degradation products, dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) are also reviewed.

5.7.2. *Fate: Pesticides*

OCs, such as DDT, aldrin, dieldrin, endrin, chlordane, and benzene hexachloride, exhibit low volatility, chemical stability, lipid solubility, and a slow rate of biotransformation and degradation. In many cases, the biotransformation products inside the organism could exhibit similar toxicity as the original parent chemical; such is the case for DDT and its biotransformed metabolites, DDE and DDD. This class of insecticides proved to be highly effective and persistent, which was ideal for remediating target pests, but resulted in very long term environmental impacts. These chemicals also have broad spectrum toxicity, meaning they can affect a variety of species, including non-target species. Additionally, like PCBs they can biomagnify up the food chain and resist chemical breakdown in the environment (**Woodwell et al. 1967**). Because of their chemical structure, OCs primarily partition into the fat tissue of biota and primarily the organic fraction of sediment. A biomagnification assessment in the Carman's River Estuary demonstrated significant biomagnification of DDT up the food chain (**Woodwell et al. 1967**). During its peak use, DDT led to a decline in populations of several bird species, such as the bald eagle and the peregrine falcon.

After the ban of OCs, anticholinesterase insecticides such as organophosphates (OPs) and carbamate esters (CEs) were primarily used. This class of insecticides undergoes extensive biotransformation and is therefore considered nonpersistent, relative to the earlier insecticides. These insecticides are water soluble and can remain in the water column and/or can be taken up by organic matter such as plants and animals. **Karen et al. 1998** reported the removal of the OP insecticide, chlorpyrifos, from the water column and accumulation in the plant, *Elodea densa*, after a two-week period.

Pyrethroids are the newest (1980s) major class of insecticide accounting for one third of the world's pesticide application, and are derived from the extract of dried pyrethrum or chrysanthemum flowers. Pyrethroid use has increased with the declining use of OPs (**Baskaran et al. 1999**). Although, pyrethroids are more hydrophobic than OPs, they only minimally accumulate in the environment and do not biomagnify (**Phillips et al. 2010**). Pyrethroids do, however, quickly adsorb to sediment when they enter the aquatic environment (**Miyamoto and Matsuo 1990**). Benthic organisms that inhabit the sediment and porewater may be more at risk for exposure to pyrethroids than pelagic organisms.

5.7.3. *Toxicity: Pesticides*

Due to their prevalence in the LSJR and toxicity, this review will focus on insecticides. Insecticides generally act as neurotoxicants (poison nervous system) to aquatic organisms, although the toxic mechanisms differ between classes (**Karami-Mohajeri and Abdollahi 2011**). OCs, such as DDT, mainly affect sodium channels in the axons of nerve cells, causing them to remain open for longer than normal (**Karami-Mohajeri and Abdollahi 2011**). This results in continual excitability of the nervous tissue. In addition to damage to the nervous system, OCs have also caused reproductive effects

in exposed organisms. Since Lake Apopka, FL became polluted with dieldrin and DDT from various sources, including a pesticide spill in 1980 and agricultural and urban runoff, the wildlife inhabiting the area has suffered severe effects. Due to the biomagnification capabilities of these contaminants, animals at the top of the food chain were most affected. Alligator populations declined due to adverse reproductive outcomes, such as reduced phallus size in males, abnormal ovarian morphology in females, modified sex steroid concentrations in both sexes, and reduced hatching success in alligator eggs (Guillette Jr. et al. 1994; Guillette Jr. et al. 1999). Similar effects have been observed in juvenile alligators from another Florida lake, Lake Okeechobee as well (Crain et al. 1998). Further, Rauschenberger et al. 2004 suggested that yolk OC burdens were predictive of maternal tissue burdens and that some OCs are maternally transferred in the American alligator. After exposure to the OC insecticides, methoxychlor and DDE, accumulation of the contaminants in the ovaries of female bass and an inhibition of sex steroids were reported (Borgert et al. 2004). DDT and other chlorinated pesticides were found in the livers of largemouth bass collected from the LSJR (Sepúlveda et al. 2002). Gelsleichter et al. 2006 reported an elevated liver OC concentration in the livers of stingrays collected from Lake Jesup, in the SJR. Further, they concluded that stingray reproduction was still occurring; however, elevated serum steroid concentrations and white blood cell counts were noted, suggesting that endocrine and immune function may be altered.

The anticholinesterase insecticides have a reduced mammalian toxicity, as compared to OCs. They act by inhibiting acetylcholinesterase, which is the enzyme that destroys acetylcholine, resulting in continual stimulation of electrical activity in the nervous system. OPs are generally more effective than CEs, but they also have been shown to affect more non-target organisms. Karen et al. 2001 reported a significant decrease in brain acetylcholine activity and vertebral yield strength in the estuarine fish, *Fundulus heteroclitus* (commonly found in the LSJR) after exposure to environmentally relevant concentrations (in many areas) of the OP insecticide, chlorpyrifos.

Pyrethroids have an extremely low toxicity to birds and mammals and are less susceptible to biotransformation when ingested; however, they are very toxic to invertebrates and fish. As compared to the other insecticides, they are more specific in the species they target, including a range of household, veterinary, and post-harvest storage insects; and only few chronic effects have been reported as a result of exposure. The primary site of pyrethroid toxicity is the sodium channels in the nerve membrane (Gordon 1997), resulting in repetitive neuronal discharge (similar to DDT). The sodium channels are modified by either preventing inactivation or enhancing activation of the sodium channel when it is at rest (Zlotkin 1999). This action of pyrethroids results in paralysis, collapse, and inhibition of the righting reflex (Moskowitz et al. 1994). Secondary toxicity to aquatic organisms, such as blue-gill and fathead minnow, has been reported, including disruption of ion regulation at the gill and decreased respiration (Bradbury and Coats 1989). The amphipod, *Hyalella azteca* has been shown to be extremely sensitive to pyrethroids (Ding et al. 2010), possibly due to their high lipid content, and thus greater ability to store pyrethroids, relative to other organisms (Katagi 2010).

More toxicological data is needed to discern the effects of the contaminants in the LSJR on the organisms that reside there. The water chemistry in the river could modify the toxicity of many of the contaminants present. However, in many instances more than one type of contaminant has been shown to simultaneously occur. The degree to which exposure to elevated concentrations of multiple contaminants may affect aquatic life in the LSJR is unknown. It is clear that contaminant accumulation has occurred in several species inhabiting the LSJR, therefore the possibility of deleterious effects remains.

5.7.4. Status and Trends: Pesticides in Sediments

Organochlorine pesticides have been found all throughout the LSJR sediments for years (Figure 5.44), an expected outcome given their history of use and persistence. Like PCBs, pesticides were most prevalent in Area 1, the western tributaries, which contained the most sediments with concentrations that exceeded the pesticide PELs. However, the overall detection rate, exceedance rate, and pesticide toxicity pressure is much less than that of the PCBs. Even in the western tributaries, the toxicity quotient was less than one, and in the rest of the river, cumulative toxicity pressure from organochlorine pesticides is fairly minimal with a toxicity quotient close to 0.2. The organochlorine pesticide most responsible for toxicity pressure in the river is DDD, a degradation product of DDT, but in some years and regions, heptachlor and dieldrin were also important (Figure 5.45).

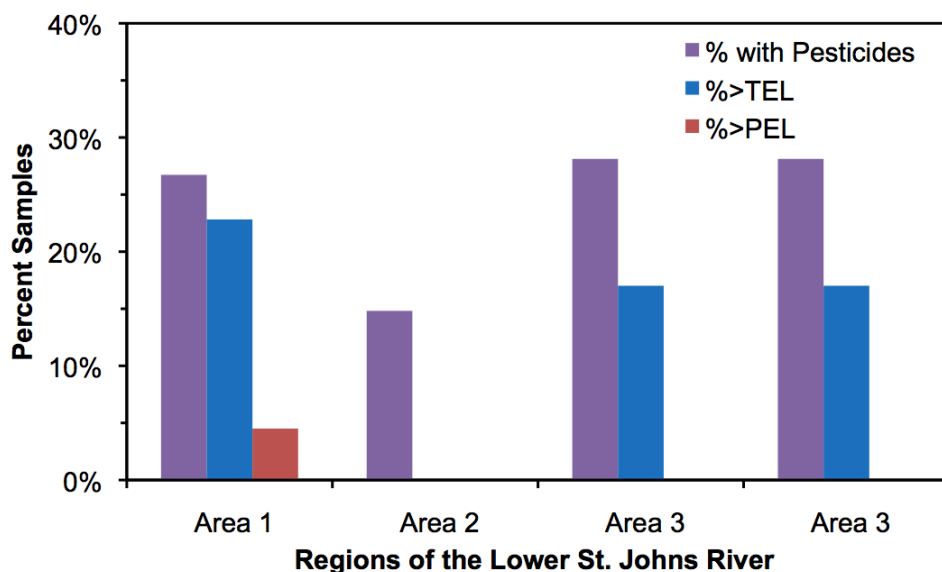


Figure 5.44 Percentage of sediment samples from 2000-2007 that contain organochlorine pesticides and have concentrations that exceed Threshold Effects Levels (TEL) and Probable Effects Levels (PEL) for one or more pesticides. Area 1 – western tributaries; Area 2 – north arm; Area 3 – north mainstem; Area 4 – south mainstem. See text in Section 5.2 for data sources.

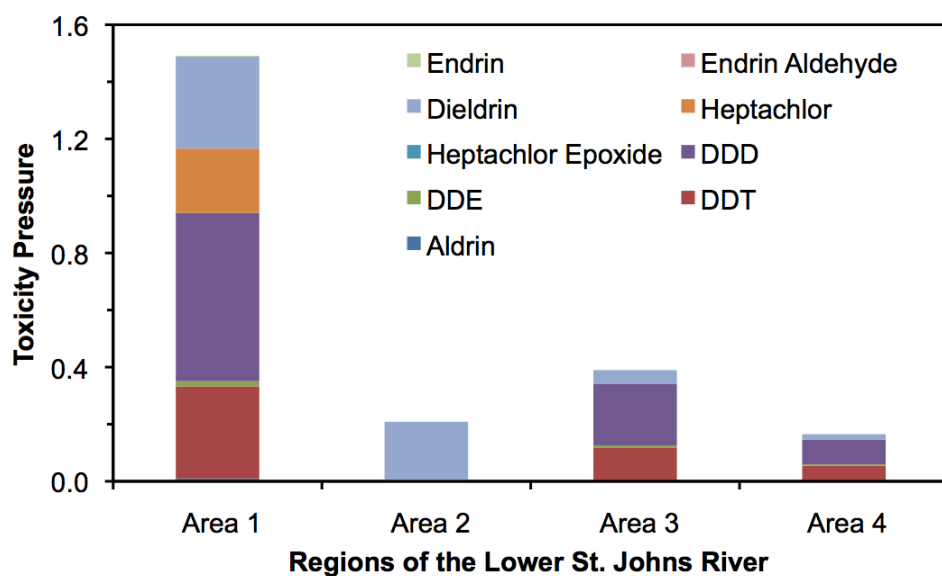


Figure 5.45 Toxicity pressure from different organochlorine pesticides and their degradation products. Area 1 – western tributaries; Area 2 – north arm; Area 3 – north mainstem; Area 4 – south mainstem. See text in Section 5.2 for data sources.

5.7.5. Summary: Pesticides

Organochlorine pesticides are present in the LSJR sediments, mostly at levels that might not cause significant adverse impacts on the benthic ecosystems, but that may add to the overall toxic burden of sensitive organisms. As with many other contaminants, the Cedar-Ortega system is the most contaminated area (Ouyang et al. 2003). The DDT compounds were found most frequently and at the highest levels, compared to the other organochlorine pesticides. They exerted the most toxic pressure, though dieldrin and heptachlor were also significant in recent years. Previously, the STATUS of organochlorine pesticides in sediments was *unsatisfactory* while the TREND was *unchanged*; however, pesticides were not evaluated in this year's report.

5.8. Conclusions

The history of compromised sediment quality in the LSJR from industrial and urban activities continues today in many of the downstream regions of the river (Figure 5.46). Some contaminants, such as organochlorine pesticides and PCBs, are legacies of past misjudgments, but they continue to plague the river by their persistence in the sediments. Other contaminants, such as PAHs, are common byproducts of modern urban life and the shipping industry, though the LSJR may still suffer from PAHs from past mishandling of creosote. Metals are pervasive throughout the basin sediments at levels substantially above what is considered natural background levels and there is no sign that concentrations are diminishing. Overall, the downstream LSJR basin contaminant levels are similar to other large, industrialized, urban rivers. However, upstream in Area 4, the extent of contamination appears less, with no samples that exceeded toxicity standards, but there is also less data about that region so the status is uncertain. Reductions in emissions and discharges of PAHs and metals reported by many industries since 2001 may lead to lower levels of contaminants in the LSJR system in the future.

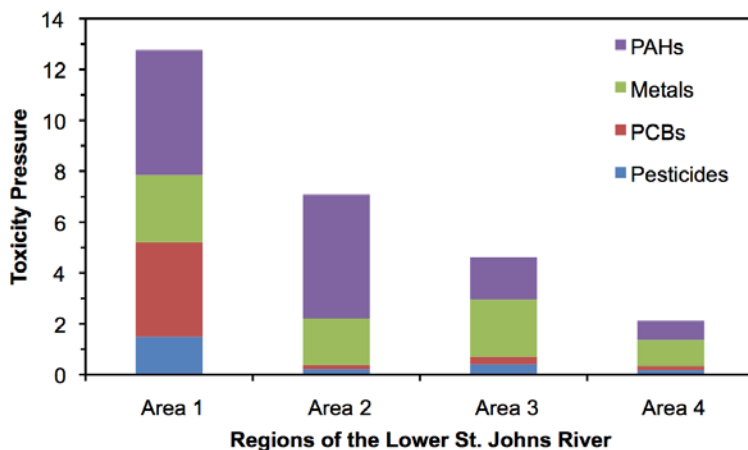


Figure 5.46 Average cumulative toxicity pressures of contaminants in sediments in different areas of the LSJR from 2000 – 2007. Area 1 – western tributaries; Area 2 – north arm; Area 3 – north mainstem; Area 4 – south mainstem. See text in Section 5.2 for data sources.

There are some lower basin sediments with very high levels of contaminants compared to other coastal sediments. In particular, several of the tributaries have shown severe contamination over the years. Of particular concern is the large Cedar-Ortega basin, which has repeatedly exhibited among the highest levels and frequencies of contamination over the years. It has been recognized at least since 1983 that the large, complex network of tributaries is burdened by years of discharges of wastewaters and runoff from small, poorly managed industries, and from identified and unidentified hazardous waste sites. This is particularly true of Cedar River. The Cedar-Ortega basin also suffers from its location in the middle of the LSJR, where the transition between riverine and oceanic inputs promotes sedimentation and reduces flushing. These factors produce a highly stressed system. However, recent construction of a stormwater treatment facility on the Cedar River should improve the situation in that area. Rice Creek is another western tributary of the LSJR that has exhibited long-term pressure from a variety of contaminants and it has often had the highest contaminant concentrations in the region. Relocation of the discharge of a pulp and paper mill effluent from the creek to the mainstem in 2013 will have an unknown impact on the sediment contaminants discussed. The north arm section of the river to Talleyrand is heavily impacted by PAHs, and suffers from proximity to power plants, shipping, petroleum handling, and legacy contamination.

Outside of the areas of highest concern, contaminants act as underlying stressors all throughout the basin. Their individual effects may be minor, but their cumulative effects become important. There are small variations in the specific compounds that are most important from site to site and year to year, but many areas continue to be contaminated by more than one chemical at levels that are likely to be harmful to the river's benthic inhabitants. Even the relatively pristine south mainstem portion of the LSJR has contamination that may affect sensitive organisms.

Overall, the mass of contaminants released to the atmosphere from point sources in the LSJR region has significantly declined over a decade. However, little change in surface water discharges has occurred and there have been significant increases in discharges of some metals. Water concentrations of several metals have generally declined in the last few years in the mainstem and are generally below water quality criteria, though exceptions are copper and silver. Continued efforts are needed to reduce pollutant loadings through stormwater control projects, permitting and best management practices