Assessment of Environmental Pollution and Community Health in Northwest Florida

EPA Cooperative Agreement # X-97455002

FINAL REPORT
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List of Tables

LIST OF FIGURES

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Acknowledgements

The impetus for this project arose from community concerns on regional environmental pollution and potential impacts on human health. In order to address the community concerns, the United States Congress provided directed source funding via the U. S. Environmental Protection Agency (EPA) and the Centers for Disease Control and Prevention (CDC) to the University of West Florida to undertake environmental and community health studies pertinent to Northwest Florida. We are grateful to Honorable Bill Nelson, United States Senator from Florida, for his leadership in appropriating funds for our project, and we are also thankful to Honorable Bob Graham, United States Senator from Florida, and Honorable Jeff Miller, Congressman from our District, for their enthusiastic support in this endeavor.

The investigations described in this report were funded by the U. S. Environmental Protection Agency (EPA) through a Cooperative Agreement # X-97455002 awarded to the University of West Florida. The contents of this report are solely the responsibility of the authors and do not necessarily represent the official views of EPA.

During the initial phase of establishing the Cooperative Agreement, Drs. Ken Mitchell and Mr. Raymond Gregory, Air Toxics and Monitoring Branch of EPA Region 4, were extremely helpful in identifying the projects pertinent to our study area. Mr. Gregory served as the Technical Project Officer throughout the course of the Cooperative Agreement, and he provided sustained support, constructive advice, and unfailing encouragement—thereby contributing to the overall success of our project. Mr. Gregory provided invaluable opportunities for our investigators to share our project efforts and to consult with several colleagues at EPA Region 4. I am grateful to Mr. Gregory, Dr. Mitchell, and other EPA staff for their advice and support.

This project was undertaken as a component of our regional consortium, Partnership for Environmental Research and Community Health (PERCH), with the University of West Florida's Center for Environmental Diagnostics and Bioremediation as the lead entity working in collaboration with the public health departments in the Escambia and Santa Rosa counties of Florida. I am especially thankful to Dr. John Lanza, Director of the Escambia County Health Department, for his sustained collaboration and advice during the course of this project, including assistance in identifying external research partners and recruiting several members to serve on an Advisory Committee for PERCH. The latter Committee played a pivotal role in pointing out the community's concerns for regional environmental and public health. Their input was very useful in targeting and prioritizing our research efforts. Our PERCH project received enthusiastic support from diverse agencies—including the governments of the Escambia and Santa Rosa counties, Cities of Pensacola, Pace, Milton, and Gulf Breeze; Emerald Coast Utilities Authority; regional industries; Bay Area Resource Council; Pensacola Chamber of Commerce; Florida Department of Health; Florida Department of Environmental Protection; Florida Fish and Wildlife Commission; Pensacola Naval Air Station; River Keepers; Bream Fishermen's Association; Association of Environmental Professionals; and regional news media, such as the Pensacola News Journal, UWF's Nautilus News and regional TV/Radio stations.

The scope of this project is interdisciplinary, requiring expertise in a variety of fields. We are fortunate to have an extraordinarily talented team of investigators from the University of West

Florida and our partnering institutions—Georgia Institute of Technology, Florida State University, and the University of South Florida. The principal investigators (Task Leaders) from these institutions, their associates, and students have done meticulous research and contributed to the high quality of the project outputs and outcomes. I would like to express my special thanks to the Task Leaders: Drs. Joe Lepo, Johan Liebens, Zhiyong Hu, Carl Mohrherr, Jane Caffrey, Natalie Karouna-Renier, Richard Snyder, and Wade Jeffrey (University of West Florida); Dr. Michel Chang (Georgia Institute of Technology); Dr. William Landing (Florida State University); and Dr. James Studnicki (University of South Florida).

In carrying out a project of this magnitude, involving four institutions and more than 50 personnel, there are enormous challenges in handling administrative responsibilities. I am very thankful to Ms. Tanya Streeter (Office Administrator) and Ms. Juanita Johns (Office Specialist), Center for Environmental Diagnostics and Bioremediation, for their outstanding work in facilitating an orderly coordination of personnel activities, procurements, and all other project needs in an efficient and timely fashion.

I. BACKGROUND

Escambia and Santa Rosa Counties are the two most western counties in the State of Florida. This two-county area is bound on the north and west by Alabama, on the east by Okaloosa County, FL, and on the south by the Gulf of Mexico. Escambia County is separated from Santa Rosa County by the Escambia River and from Alabama by the Perdido River. The area is rich in history and well known for natural resources including beaches, estuaries, coastal dunes, and inland forests. Pensacola Bay and Perdido Bay are the two estuarine systems that dominate the region and all significant activity in the area, past or present, has depended on these resources.

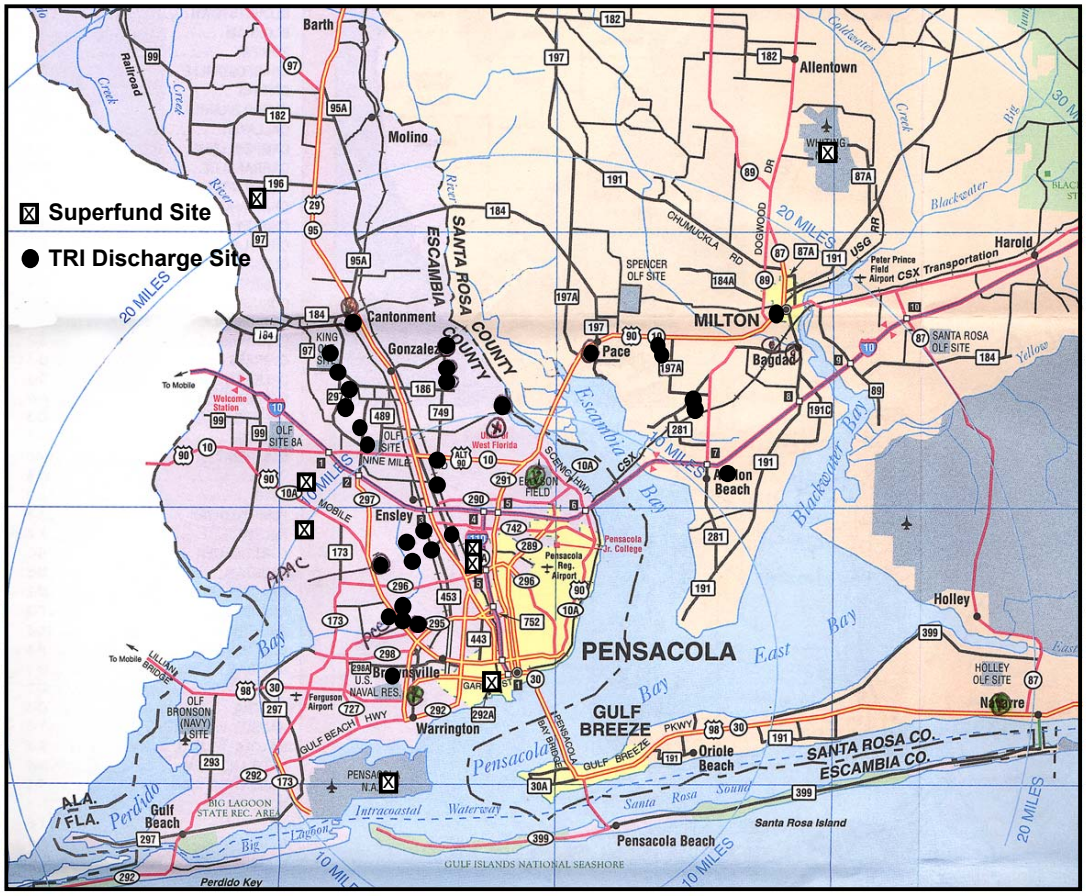

Fig. I-1. Map of current and former superfund sites and TRI (Toxic Release Inventory) facilities.

The 1999 EPA Toxic Release Inventory (http://www.epa.gov/tri/) listed 23 industries for Escambia County and 5 for Santa Rosa County. Toxic chemicals released into the region in 1999 amounted to 52.2 million pounds from Escambia County and 1.25 million pounds from Santa Rosa County, which ranks Escambia County as the 18th highest toxic releasing county in the country. There are several Superfund Sites in the region that are in different stages of site evaluation and remediation. The health concerns of the affected residents, and

the quality of air and water bodies, including the potential impacts of ground water contamination emanating from some of the Superfund sites, are of concern to the community.

In 1998, the Chief Judge of the First Judicial Circuit of the State of Florida impaneled a Special Grand Jury in Escambia County, at the request of the State Attorney, to examine air and water quality in Northwest Florida. This group heard testimony from over 100 hundred witnesses and reviewed hundreds of pertinent documents and reports. The Jury's conclusions were that surface waters are generally degraded, primarily due to industry discharges, sewage treatment, and stormwater runoff. Groundwater supplies have been widely contaminated by poor practices by industry and will continue to be contaminated. Air quality has deteriorated and is unlikely to improve unless changes are made in industry discharges (Grand Jury Report, 1999).

In 2000, Partnership for a Healthy Community sponsored a study entitled *Comprehensive Assessment for Tracking Community Health* (CATCH) for Escambia and Santa Rosa Counties. This study indicated that nearly 40% of the health outcomes indicators for Escambia County were unfavorable while 32% were unfavorable in Santa Rosa County. For example, cardiovascular disease age-adjusted mortality rates are high for both counties and heart disease is high in Escambia County. Rates of all cancers for Escambia County are higher than averages for peer counties and the state. Santa Rosa County has higher rates of strokes than for its peer counties and the state of Florida. The rate of mortality due to birth defects in Santa Rosa County is almost twice the rates for both peer counties and the Florida average.

There is considerable public concern over whether local environmental conditions are leading to deteriorating public health, and on the potential impact of such conditions on the quality of life and economic development in the area, as highlighted in a series of articles published in the Pensacola News Journal in 2001. In response to these public concerns the United States Congress provided directed source funding to the University of West Florida (UWF) to launch studies to determine if a connection exists between elevated levels of illness in Northwest Florida and the levels of the toxic pollutants in the area. The University relegated the responsibility of these studies to the Center for Environmental Diagnostics and Bioremediation (CEDB), with the center's director serving as Project Director.

In view of the community interest in the project and in order to provide a forum for input and exchange of information, the Project Director established an advisory committee composed of 25 members to include representatives of city and county governments (e.g., Pensacola, Milton, Gulf Breeze, Escambia County, Santa Rosa County), Escambia County Utilities Authority, Northwest Florida Water Management District, Florida Department of Environmental Protection, Florida Department of Health, and U.S. Environmental Protection Agency (Gulf Ecology Division, NHEERL), as well as representatives of industries, professional organizations, and environmental advocacy groups. The Project Director convened several meetings of this advisory committee during March-April 2002 to seek input on current knowledge and the prioritized needs pertinent to the assessment of environmental and community health in Northwest Florida. Additional follow-up discussions were held with representatives of many of the above organizations, as well as representatives of Navy and Air Force facilities, to ensure that the objectives and outcomes of the present project would be beneficial for addressing regional environmental and health concerns.

The directed source funding from the U.S. Congress was made available through EPA Region 4 and the Centers for Disease Control and Prevention (CDC). The input derived from the area stakeholders and our planned investigations were discussed with representatives of

the two agencies, and then separate proposals were developed to meet the criteria established by the agencies. Accordingly, we pursued research related to human health, including clinical evaluations and analysis of serum/urine/hair samples, with funding provided by two grants from the CDC. Environmental health assessments—including evaluations of air quality, modeling of air pollution impacts on human health outcomes, measurements of atmospheric deposition of mercury and trace elements to the Pensacola Bay watershed, evaluations of contaminants in surface soils, profiles of pollutants in the sediments of several bayous (Texar, Chico, Grande) and Escambia Bay, and contaminant loads in fish from area waters---have been pursued over a seven-year period (July 1, 2002 to June 30 2009) with support through an EPA Cooperative Agreement.

The University of West Florida's Center for Environmental Diagnostics and Bioremediation (CEDB) served as the lead organization to perform the studies supported by CDC and EPA, and developed a consortium, Partnership for Environmental Research and Community Health (PERCH), involving the public health departments in Escambia and Santa Rosa counties. The EPA-supported project included partnerships with sub-grantees at the University of South Florida, Georgia Institute of Technology, and Florida State University.

Detailed technical reports of individual tasks have been posted on the UWF-CEDB website (http://www.uwf.edu/cedb/perch.cfm). This report summarizes the overall results of the studies conducted with support from the EPA Cooperative Agreement.

II. OUTPUTS

A. Progress Reports

13 quarterly reports and 6 semi-annual reports have been submitted to the EPA during the project period, July 1, 2002 to June 30, 2009.

B. Technical Reports for Individual Tasks

Caffrey, J. M., W. M. Landing, Sikha Bagui, and Subhash Bagui. 2009. Atmospheric Deposition of Mercury and Trace Metals to the Pensacola Bay Watershed
http://uwf.edu/cedb/PERCH_EPA_final_report_Hg_project.pdf

Chang, M. E. 2007. PERCH Air Quality Studies
http://cure.eas.gatech.edu/~chang/perch/

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http://uwf.edu/cedb/PERCH_Accumulation_of_pollutants_in_fish_and_shellfish.pdf

Studnicki, J., and Luther, S. 2004. Identifying Variation in Mortality and Morbidity For Selected Health Outcomes at the Postal Zip Code Level http://uwf.edu/cedb/Perch_USF_EPA_April04.pdf

C. Peer-Reviewed Publications

Hu, Z. 2009. Spatial analysis of MODIS aerosol optical depth, $PM_{2.5}$, and chronic coronary heart disease. *International Journal of Health Geographics*, 8:27.

Hu, Z., J. Liebens, and K. R. Rao. 2008. Linking stroke mortality with air pollution, income, and greenness in northwest Florida: an ecological geographical study. *International J. Health Geographics*, 7:20, pages 1-22.

Hu, Z., J. Liebens, and K. R. Rao, 2007. Exploring relationship between asthma and air pollution: a geospatial methodology using dasymetric mapping, GIS analysis and spatial statistics. *Geoinformatics 2007: Geospatial Information Science. Proceedings of SPIE* Vol. 6753, 67532T. SPIE: The International Society for Optical Engineering.

Hu, Z., J. Liebens, and K. R. Rao. 2008. Assessing health effects of aerosol particles using MODIS AOD remote sensing data. Proceedings of the 31st International Geographical Congress. Tunis, Tunisia.

Hu, Z., J. Liebens and K. R. Rao. (under review). Merging satellite measurement with ground-based air quality monitoring data to assess health effects of fine particulate matter pollution. In J. Maantay & S. McLafferty (Eds.), *Geospatial Analysis of Environmental Health*. Springer Verlag.

Hu, Z. and K. R. Rao. 2009. Particulate air pollution and chronic ischemic heart disease in the eastern United States: a county level ecological study using satellite aerosol data. *Environmental Health*, 8:26.

Liebens, J., C. J. Mohrherr, and K. R. Rao. 2007. Sediment pollution pathways of trace metals and petroleum hydrocarbons in a small industrialized estuary: Bayou Chico, Pensacola, FL. *Marine Pollution Bulletin*, 54: 1529-1539.

Liebens, J., C. J. Mohrherr, K. R. Rao, and C. A. Houser. 2006. Pollution in an urban bayou: magnitude, spatial distribution and origin. *Water, Air, and Soil Pollution*, 174: 235-263.

D. Presentations at Meetings

Caffrey, J. Atmospheric Deposition of Mercury, Trace Metals and Major Ions in the Pensacola Bay Watershed. National Monitoring Conference, Atlantic City, NJ. May 18-23, 2008.

Caffrey, J. Atmospheric deposition of mercury, trace metals and major ions in the Pensacola Bay watershed: implications for Choctawhatchee Bay. Symposium on Choctawhatchee Bay. June 1-2, 2008.

Caffrey, J., and N. Davilla. 2008. Application of the diagenetic model CANDI in Pensacola Bay. Ocean Sciences meeting. Orlando, FL. March 2-7, 2008.

Caffrey, J. M., W. M. Landing, and S.D. Cleveland. 2006. Spatial and temporal variability in precipitation chemistry in the Pensacola Bay watershed. American Chemical society Meeting. March 26, 2006.

Caffrey. J. M., W. M. Landing, and S. D. Cleveland. 2006. Total gaseous mercury concentrations In Pensacola, FL. American Chemical Society Meeting. March 26, 2006.

Cleveland, S.D., W. M. Landing, and J. M. Caffrey. 2006. Mercury deposition to the Pensacola Bay watershed. American Chemical Society meeting. March 26, 2006.

Cleveland, S. D., W. M. Landing, and J. M. Caffrey. 2006. Rainfall mercury deposition and trace element correlations in the Pensacola Bay watershed. 8th International Conference on Mercury as a Global Pollutant. August 2006.

Hu, Z., J. Liebens, and K. R. Rao. 2007. Exploring relationships between asthma and air pollution: a geospatial methodology using dasymetric mapping, GIS analysis and spatial statistics. Geoinformatics 2007: Geospatial Information Science. Proceedings of Spie, volume 6753, 67532T. Spie: The international Society of Optical Engineering.15th International Conference on Geoinformatics, Nanjing, China.

Hu, Z., and K. R. Rao. 2008. Assessing health effect of fine aerosol particles using MODIS aerosol data. The 31st International Geographical Congress, Tunis, Tunisia, August 12-15, 2008.

Hu, Z., and K. R. Rao. 2008. Extraction of particulate matter surface from MODIS Data for linking stroke mortality with air pollution in Northwest Florida." Annual meeting of the Association of American Geographers, Boston, MA, April, 2008.

Karouna-Renier, N. K., S. M. Gibson, R. A. Snyder, and K. R. Rao. 2006. Contamination profiles in Largemouth Bass and Mullet collected in Northwest Florida. SETAC Annual Meeting, Montreal, Canada, November, 2006.

Landing, W. M., S. D. Cleveland, and J. M. Caffrey. 2006. Trace element correlations in rainfall from the Pensacola Bay watershed. American Chemical Society Meeting. March 26, 2006.

Landing, W. M., K. J. Gosnell, and J. M. Caffrey. 2009. Mercury and trace elements in rainfall from the Pensacola airshed: local, regional, and distant sources. 9th International Conference on Mercury as a Global Pollutant. June 2009.

Liebens, J., and K. Flanders. 2007. Associations between spatial patterns of air emissions and morbidity. Annual meeting of the Association of American Geographers. San Francisco, CA.

Liebens, J., C. J. Mohrherr, and K. R. Rao. 2005. Origin and distribution of pollutants in an urban bayou. Annual meeting of the Association of American Geographers, Denver, Co.

Liebens, J., C. J. Mohrherr, and K. R. Rao. 2009. Spatial Distribution and Potential Origin of Pollutants in an Estuary Bordered by Multiple Land Use. Annual Meeting of the Association of American Geographers, Las Vegas, NV.

Liebens, J., and K. R. Rao. 2007. Environmental Quality of Surface Soils in Public Places: Preliminary Results for Escambia and Santa Rosa County. NW Florida Regional Environmental Symposium, Pensacola, FL.

Liebens, J., and K. R. Rao. 2008. Trace Metal Pollution of Soils in Public Places in a Medium Size City. Annual Meeting of the Association of American Geographers, Boston, MA.

Mohrherr, C. J., J. Liebens, and K. R. Rao. 2006. Profiles of pollutants impacting Bayou Chico and Sanders Beach, Pensacola, FL. SETAC 27th Annual North American Meeting, Montreal, Canada.

Mohrherr, C. J., J. Liebens, and K. R. Rao. 2007. Analyses of Industrial Pollution Impacts on Small Urban Estuaries. 17th Annual AEHS meeting and West Coast Conference on Soils, Sediments, and Water, San Diego, CA.

Mohrherr, C. J., J. Liebens, and K. R. Rao. 2007. Sediment PAHs, PCBs, and Dioxins in Bayou Grande. NW Florida Regional Environmental Symposium, Pensacola, FL.

Mohrherr, C. J., J. Liebens, and K. R. Rao. 2008. Organic Pollutants in a Gulf Estuary Bordered by a Naval Air Station and Urban Area. SETAC 29th Annual North America Meeting, Tampa, FL.

Mohrherr, C.J., J. Liebens, J. E. Lepo, and K. R. Rao. 2004. Profiles of pollutants impacting Bayou Texar, Pensacola, FL. Fourth SETAC World Congress, Portland, OR.

Snyder, R. A., N. K. Karouna-Renier, A. Ren, S. Gibson and K. R. Rao. 2008. PCBs in fish and shellfish in the Pensacola Bay system. ASLO- AGU- ERF Ocean Sciences Meeting Orlando, FL, March 2008.

Turaga R.M.R. 2007. Spatial Resolution, Costs, and Equity in Air Toxics Regulation. Twenty-Ninth Annual APPAM Research Conference, Washington, D.C., November 8-10, 2007.

Turaga, R.M.R. 2008. Hot Spots Regulation and Environmental Justice. Thirtieth Annual APPAM Fall Research Conference, Los Angeles, November 6-8, 2008.

Turaga R.M.R., and A. Bostrom. 2004. Assessment Endpoints and Comparative Risk Analysis: The Case of Air Pollution. Twenty-Sixth Annual APPAM Research Conference, Atlanta, GA, October 28-30, 2004.

Turaga R.M.R., and A. Bostrom. 2006. Spatial Resolution in Air Toxics Regulation. Annual Meeting of the Society for Risk Analysis, Baltimore, MD, December 3-6, 2006.

Turaga, R.M.R., A. Bostrom, and D. Noonan. 2007. Spatial Resolution and Equity in Risk-based Regulation. Annual Meeting of the Society for Risk Analysis, San Antonio, TX, December 9-12, 2007.

Turaga, R.M.R., R. A. Gesser, M. E. Chang, A. G. Russell, and A. Bostrom. 2006. The Partnership for Environmental Research and Community Health (PERCH) Phase III, Part 1: Community-scale risk assessment in greater Pensacola, Florida. 14th Joint Conference on the Applications of Air Pollution Meteorology with the Air and Waste Management Assoc., The 86th Annual Meeting of the American Meteorological Society, Atlanta, GA, January 28 to February 3, 2006.

Worley, A., and J. Liebens. 2005. Relationships between health outcomes and air pollution in Northwest Florida. Annual meeting of the Southeastern Division of the Association of American Geographers. Palm Beach, FL.

E. Seminars and Other Presentations

Liebens, J. 2005. Seminar on Bayou Texar "Profiles of Pollution in Bayou Texar" to the FAEP (Florida Association of Environmental Professionals) in Pensacola, FL.

Liebens, J. 2005. Seminar on Bayou Texar "Profiles of Pollution in Bayou Texar" to the Bay Area Resource Council – Technical Advisory Committee in Pensacola, FL.

Liebens, J. 2005. Seminar on "Levels of Radium in the Local Sand and Gravel Aquifer and the Safety of Drinking Water (Radium, AGRICO Chemical Company, and Drinking Water)" to the Local Chapter of the American Society of Safety Engineers in Pensacola, FL.

Liebens, J. 2006. Colloquium talk on "Water and Sediment Quality in an Urban Bayou" to the Department of Geography, Florida State University, Tallahassee, FL.

Mohrherr, C. J. 2007. Seminar on "Health Warnings and Human Health, Swimming Alerts, Fish, and Seafood in Local NWFL Waterbodies" to the Emerald Coast Keepers of Pensacola, FL.

Mohrherr, C. J. and J. Liebens. 2008. Half-hour television interview on the state of the environment in Northwest Florida.

Mohrherr, C. J. 2009. Seminar on "Bayou Chico and Dredging" to the FAEP (Florida Association of Environmental Professionals) in Pensacola, FL.

Mohrherr, C. J. 2009. Seminar on "Bayou Chico and PCBs" to the ACS (American Chemical Society) in Pensacola, FL.

Rao, K. R. 2004. Testimony Before a Grand Jury in Pensacola on the State of Bayous.

Rao, K. R. 2004. Seminar on the Bayous and Other Related Topics Before the Pensacola Chamber of Commerce.

F. Theses/Dissertations

Sara Cleveland. Atmospheric Mercury Input to the Pensacola Bay Watershed. M.S. Thesis, Florida State University Department of Oceanography, Fall Semester 2006.

Turaga, R. M. R. Spatial Resolution, Costs, and Equity in Air Toxics Regulation. Ph. D. Dissertation. Georgia Institute of Technology, August 2007.

III. RESULTS AND OUTCOMES

A. Air Quality Studies

(Task Leader: Michael E. Chang, Georgia Institute of Technology)

1. Introduction

For this component of the PERCH project, a team of researchers at the Georgia Institute of Technology developed a series of studies to investigate if a connection exists between air pollution/air toxics and adverse human health outcomes in the Pensacola area, specifically Escambia and Santa Rosa counties. Over the course of five years (2002-2007), the PERCH Air Quality Study (PAQS) was conducted in three phases.

Based on a preliminary review of ambient monitoring data, available information regarding emissions, other studies, and discussions with various stakeholders, there are three classes of air pollutants that are of particular concern in the Pensacola area: ground- level ozone, fine particulate matter, and air toxics. Unfortunately, there is no scientific or community consensus regarding which of the three classes of pollutants poses the greatest health risk to the Pensacola community, nor is there a standard methodology by which to make inter-comparisons. In Phase I of this study, existing information was used to assess and prioritize local, urban, and regional threats to human health associated with air toxics and criteria pollutants (ozone and particulate matter) in the Pensacola area. In Phase II, a pilot field study was conducted to investigate the relationship between regional-scale measures of air quality provided by the existing regulatory-based air quality monitoring network, and neighborhood-scale measures of air quality that may be more representative of human exposures in the Pensacola area. In Phase III, a multi- pronged modeling and analysis approach was used to identify the primary contributors to PM, ozone, and air toxics pollution and quantify their relative contributions to local ambient concentrations (and hence potential exposures). The intent of this final phase was to provide local decision makers with the relevant technical information needed for developing a comprehensive air quality management strategy.

2. Results and Outcomes

a. Phase I: Assessing the Relative Risks Associated with Criteria and Air Toxic Pollutants in the Pensacola Area

Given limited resources with which to conduct a study of air quality and its potential impact on human health in the Pensacola area, it is rational to attempt to identify the type of pollution that may be presenting the greatest health risk in order to focus resources on that problem. Such a comparative analysis is made difficult, however, by the variety of acute and long-term health outcomes related to the different pollutants. While it is recognized that these various health outcomes are incommensurable, it is important to find ways in which they may be compared in order to prioritize and use efficiently the available research resources, and so that the community may likewise focus its efforts on reducing potential risks.

In this initial phase, a rudimentary study was conducted to assess the per capita costs related to the health impacts from ozone, particulate matter, and air toxics at concentrations observed contemporarily in Pensacola. A second, independent assessment focused on the health benefits that would be obtained if pollutant concentrations in the Pensacola area were decreased such that they were no longer considered a risk for any individual. It is important to note that the methodologies are considerably different for the two studies, and thus the costs cannot be directly compared with the benefits. However, within each assessment, it is reasonable to compare the ***relative*** estimates of costs and ***relative*** estimates of benefits. It is in this sense that both analyses suggested that, of the three pollutants of concern, elevated concentrations of particulate matter may pose the greatest health risk.

Table A-1. Costs of Health Impacts from PM, Ozone, and Air Toxics in Pensacola. (Note: due to different methods used to estimate, these costs should not be directly compared to the benefits below.)

	$/year/person (Medium)
PM	$1838.21
Ozone	$952.69
Air Toxics (Total)	$1.02

Table A-2. Benefits of reduced risks from PM, Ozone, and Air Toxics in Pensacola. (Note: due to different methods used to estimate, these benefits should not be directly compared to the costs above.)

	$/year/person (Medium)
PM	$34.00
Ozone	$0.70
Air Toxics (Total)	$3.50

In other Phase I activities, existing and on-going air quality studies pertinent to the Pensacola region were reviewed. This included the Gulf Coast Ozone Study, the West Florida Ozone Study, and the Fall line Air Quality Study.

Key Findings: For this initial assessment of particulate matter, ozone, and air toxics in Escambia and Santa Rosa Counties, rudimentary analyses suggest that **particulate matter likely presents the greatest risk to human health generally related to air quality in the Pensacola region**. It should be recognized however, that there could be highly localized areas for which other pollutants could pose a greater risk.

Implications: Of the three classes of pollutants, ozone is the most well understood pollutant, though it may not pose the greatest health risk. Less is known about particle pollution and air toxics. In terms of allocating PAQS resources, the investigation's ensuing primary focus (i.e. in Phases II and III) will be on PM, secondary on air toxics, and tertiary on ozone.

b. Phase II: Summer 2003 Pilot PERCH Air Quality Study

Past and current air monitoring and modeling activities in the Pensacola area have been aimed at assessing regulatory compliance and developing strategies for mitigating pollutant loads. These initiatives are well posed and provide leaders at the Florida

Department of Environmental Protection (FL DEP) and in the Pensacola area with the technical information needed to make rational decisions for managing air quality in the region. While there may be some relevance, none of these, however, are specifically targeted for understanding and managing the full array of independent and synergistic human health impacts created by exposure to criteria and hazardous air pollutants. The goal of the PERCH 2003 Pilot Air Quality Field Study is to assess air quality (PM, ozone, and air toxics) at a neighborhood scale and to learn how it relates to regional air quality, which is more well understood. In this phase of the study, the Georgia Tech Mobile Air Quality Laboratory (MAQL) was deployed in a populated region of the Pensacola area from mid-July to mid-August 2003 and where high frequency (on the order of 1 minute to 1 hour averages) atmospheric chemical and physical data at a single site were collected.

After careful consideration of many potential sites, and in consultation with a team from the University of South Florida conducting a study on "Assessing the Impact of Environmental Hazard Exposure on the Health Status of Geographically Defined Populations in Escambia and Santa Rosa Counties," the MAQL was deployed on the grounds of the O.J. Semmes Elementary School (OJS). OJS is located in a residential area centrally located in relation to the main business district to the south, the large industrial facilities to the north, the airport to the east, and the interstate to the west. Monitoring at the OJS site was conducted from July 15 to August 15, 2003. Care was taken to assure the quality of the data, with the methodology and standard operating procedures well documented. The period July 15 to August 15, 2003 was characterized by three distinctly different periods: The first three weeks until August 7 were characterized by relatively frequent showers and thunderstorms in late mornings and early afternoons; this period was followed by four dry sunny days from August 8 to 11 with convectively driven winds, reaching the campaign's lowest relative humidities, highest daytime temperatures, and highest pollutant concentrations. The third distinct period was characterized by strong southerly flow carrying moisture from the Gulf of Mexico that precipitated over the area, resulting in the highest rainfall amounts and overall lowest air pollution concentrations of the entire study period.

Fig. A-1. The MAQL fully deployed and operational at the O.J. Semmes ES site on July 18, 2003

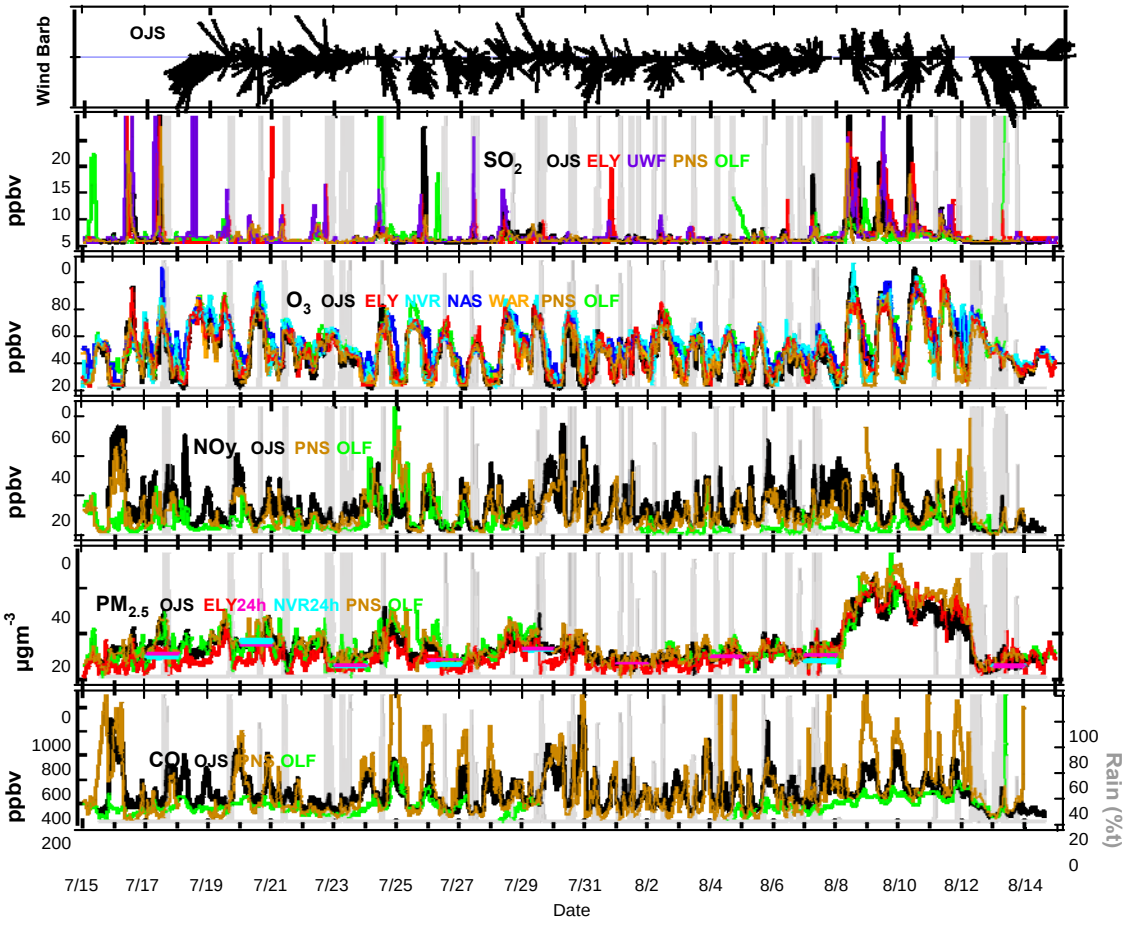


Fig. A-2. Trend of the major air pollutants measured at OJS and other sites between July 15 and August15, 2003

While ozone showed the expected diurnal cycles with daytime maxima at all sites, SO_2 was more sporadic, with the highest concentrations associated with northerly flow at OJS. Both ozone maxima and SO_2 impacts increased during the dry phase, which was also the period of maximum $PM_{2.5}$ and CO background levels. The diurnal variability of CO correlated well with NOy in a bimodal way. The bimodal appearance of CO and NOy seem to be governed by local traffic sources. A linear regression of all CO and NOy data from the entire dataset, however, yields a slope of 12.4 ±0.2, which is significantly more than what would be considered typical of mobile source emissions. Hence, the OJS site seems to be influenced by mixed emissions from multiple sources most of the time. $PM_{2.5}$ mass concentrations were lowest during the most intense rainfall associated with strong southerly flow during the last two days of the campaign.

In assessing the composition of the $PM_{2.5}$, roughly half of the mass is inorganic with sulfate being the largest contributor. The organic fraction is characterized by both primary particulate (particulate that is emitted directly into the atmosphere) and secondary particulate (particulate that is formed in the atmosphere from other constituents). Secondary organic aerosol formation was greatest during the 4-day dry period and corresponding with the highest $PM_{2.5}$ mass concentrations. While experience suggests that the presence of sulfate is often associated with coal combustion, organic aerosols, both primary and secondary, can originate from many sources.

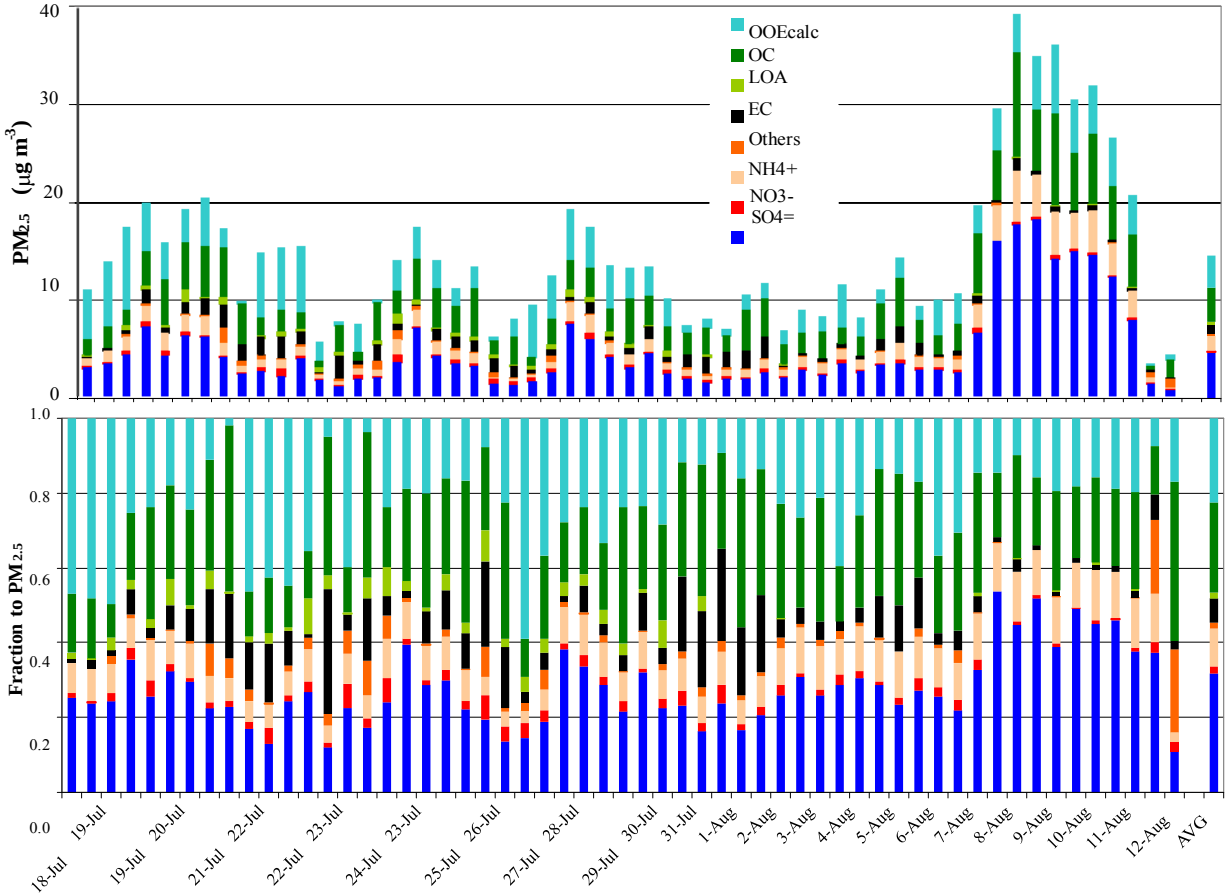


Fig. A-3. Fine particulate matter composition measured at OJS between July 18 and August 12, 2003.

A separate analysis of the gaseous Volatile Organic Compounds (VOCs) sampled at OJS, for which some of the particulate organic carbon may be closely related, suggested that gasoline related sources were the dominant contributors (about 65%) during the study at the O.J. Semmes Elementary School site. Other significant contributions were associated with primers and enamel (18%), refinery fugitives (10%), biogenics (5%), and diesel exhaust (2%).

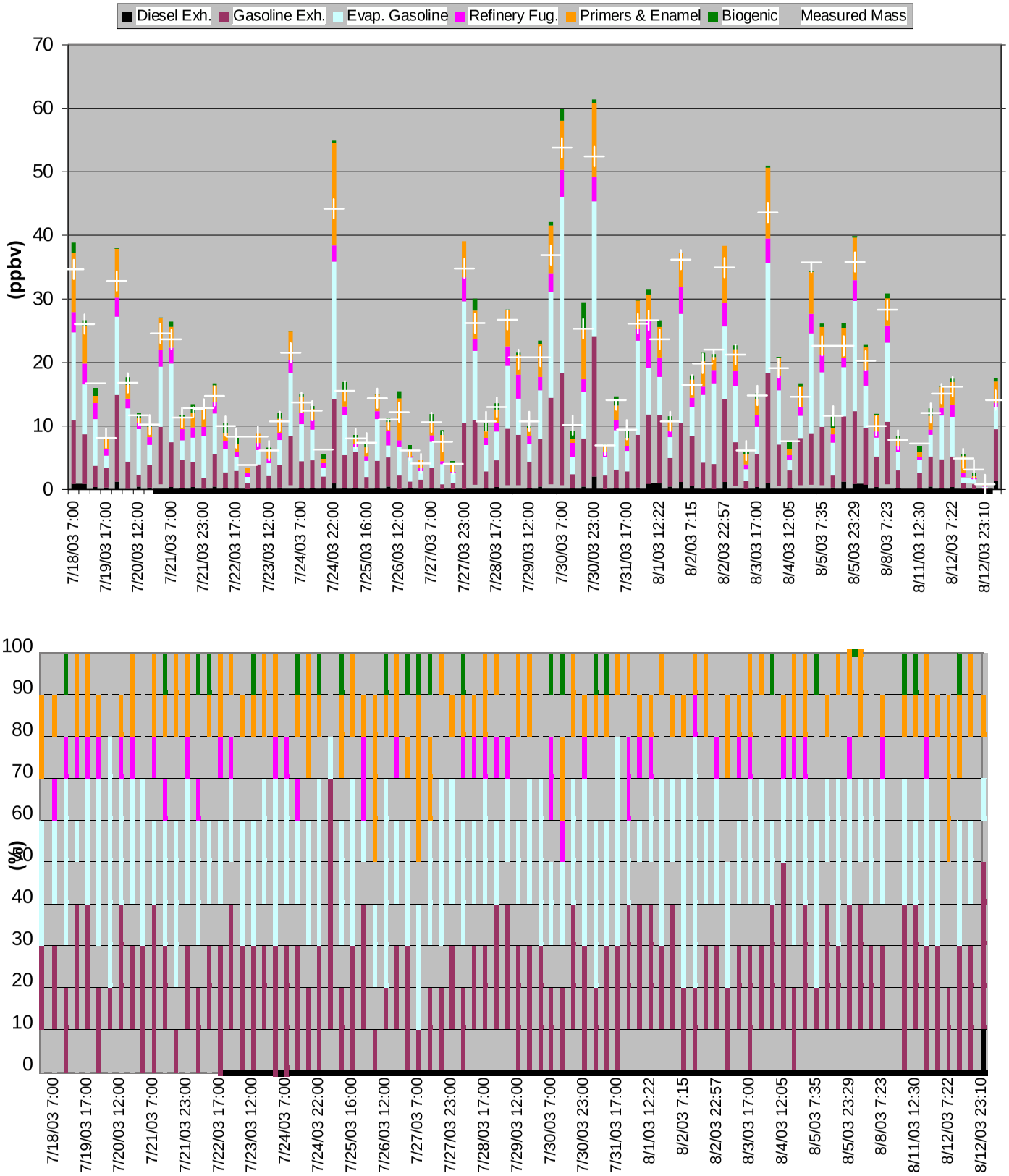


Fig. A-4. Mass (top) and fractional (bottom) VOC contributions from each source at the OJS site 7/18/03 to 8/12/03.

Among the 83 VOC compounds we monitored, seven pollutants were part of the 32 NATA air toxics. They include benzene, chloroform, carbon tetrachloride, methylene chloride, trichloroethylene, perchloroethylene, and 1,3-butadiene. We also monitored toluene, which is a toxic air pollutant by Clean Air Act definition, but it was not considered in the NATA assessment. While there is little reason to expect that the 2003 monitored values should necessarily compare well with the 1996 NATA values given the significant differences in methods, time, and space, and recognizing that little can be gained from such a comparison, it is interesting nonetheless that the concentrations for these seven toxic pollutants agree as well as they do. The implication is that the 1996 NATA estimates are reasonable.

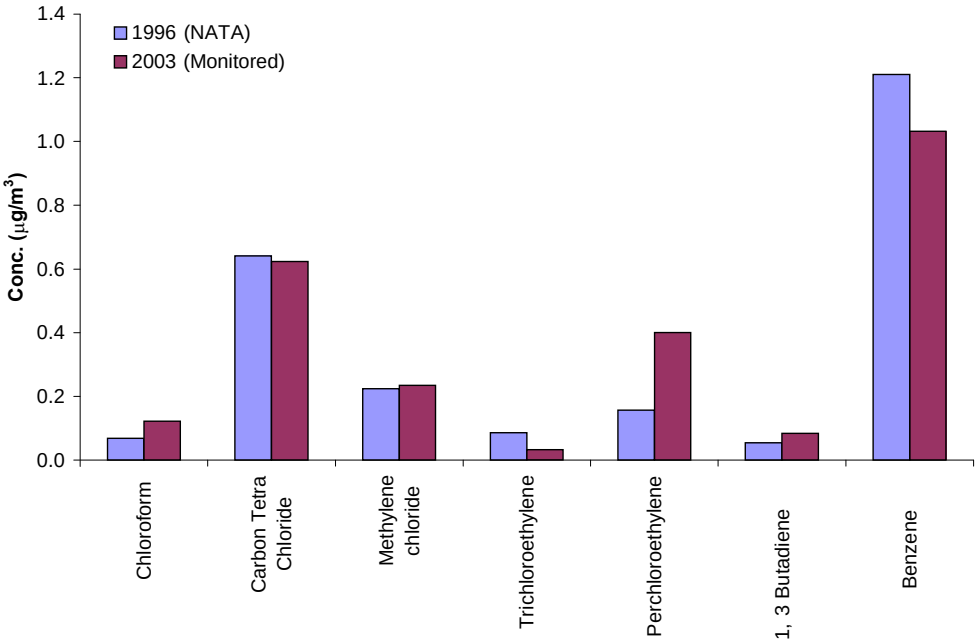


Fig. A-5. Comparison of 1996 modeled NATA and 2003 VOC/toxics monitoring data in Pensacola.

Key findings: analyses showed **sulfate was a large fraction of the observed ambient $PM_{2.5}$ loading**, with high concentrations most often associated with northerly flow. Additionally, **organic carbon was likewise found also to be a large fraction of the ambient $PM_{2.5}$ loading**, with the highest secondary organic aerosol formation concurring with peak $PM_{2.5}$ mass concentrations. Results from a separate study of volatile organic compounds showed that **gasoline related sources are the dominant contributors to ambient gaseous VOC concentrations**, suggesting that these same sources are significantly contributing to the organic aerosol fractions – both primary and secondary. Finally, a limited comparison of air toxic concentrations measured at the O.J. Semmes Elementary School and air toxic concentrations estimated for the Pensacola area by the 1996 NATA showed remarkable (perhaps fortuitous) agreement despite many differences in method, and in temporal and spatial scales.

Implications: coal and gasoline combustion were observed to account for most of the Pensacola atmosphere's particle load during a high pollution event. Additional analyses (see Phase III) are needed to discern between local and regional sources, however.

c. Phase III: Comprehensive Air Quality and Air Toxics Modeling and Analyses

i. Comprehensive PM Analysis

During the Phase II field study, the period August 8 to 12 brought in a polluted dry air mass from northerly directions. Secondary sulfate was shown to cause a large fraction of the $PM_{2.5}$ mass concentration during the 4-day pollution episode at OJS and the greater metropolitan area including the ~170 km distant Gulfport, Mississippi area, constituting more than 40% of the fine PM mass. A systematically higher sulfate loading was observed during the day (50 ± 3 %) exceeding the one at night (43 ± 3 %), while the percent sulfate to total sulfur, i.e. the fraction of sulfur oxidized into the particle phase showed less pronounced differences. Applying a charge balance based on the sulfate- ammonium-nitrate system to each individual sample collected indicated a clearly more acidic aerosol during the polluted period with systematically higher acidity during daytime than during nighttime, corroborating previous indications for photochemically driven heterogeneous radical chemistry and secondary aerosol formation during daytime.

Incorporating data from EPA's Speciation Trends Network (STN), the Interagency Monitoring of Protected Visual Environments (IMPROVE) network, and the South-Eastern Aerosol Research and Characterization Study (SEARCH) network, the coastal and central areas of Mississippi and Alabama, and even extending up to their northern regions, seemed to share the same "air shed" with the greater Pensacola metropolitan area and the NW-FL region, as the sulfate fractions were uniformly maximized on August 10, 2003.

In further analyses, the ratio of organic mass (OM) to organic carbon (OC) averaged 1.7 ± 0.2 for the entire pollution period and 1.8 ± 0.1 for the daytime intervals only, indicating a likely influence from daytime photochemical processing in an oxidizing atmosphere. Since this factor is particularly sensitive to the level of OC oxygenation, only two main sources are thought to influence it substantially, i) atmospheric oxidation, or ii) incomplete low-temperature combustion. Regarding the latter, open biomass burning in the form of prescribed or wild fires provide such combustion regimes, yielding emissions with OM/OC of 1.6 ± 0.4. Further both satellite imagery, modeled back trajectories, and additional analyses suggest that distant fires occurring concurrent to this episode could have influenced the observed airmass in Pensacola.

Key finding: although the effective contributions from satellite-detected ground fires could not be quantified, detailed analyses showed that they played an important role in the polluted event observed at the O. J. Semmes elementary school during the Phase II field study.

Implication: in addition to coal and gasoline combustion, open fires were also a noted source of particles during the observed pollution event.

ii. Source Apportionment of $PM_{2.5}$ in the Pensacola area

The Fall line Air Quality Study (FAQS) $PM_{2.5}$ episode chosen for re-analysis of impacts at Pensacola comprises a 13-day period between July 5 and July 18, 2001, a representative poor air quality episode in the Southeastern U.S. The initial phase of analysis quantified the modeled 24-hour average $PM_{2.5}$ concentration and composition for the episode. The maximum 24-hour average modeled at Pensacola during the episode was 16 $\mu g/m^3$, and the episode average concentration was 10 $\mu g/m^3$. Relative to other cities analyzed in the FAQS domain, $PM_{2.5}$ at Pensacola resembles other areas in terms of predominant constituents, but the modeled $PM_{2.5}$ exhibits two important differences. First, episode average $PM_{2.5}$ is considerably lower at Pensacola (10 $\mu g/m^3$) compared to Atlanta (16 $\mu g/m^3$), Macon (14 $\mu g/m^3$), Columbus (14 $\mu g/m^3$), or Augusta (16 $\mu g/m^3$). Second, although the relative proportion of $PM_{2.5}$ constituents at Pensacola resembles other cities, Pensacola is clearly distinct in that more sulfate, but very little nitrate, comprises $PM_{2.5}$ than at other cities. On an episode average basis, sulfate comprises 67% of the modeled total $PM_{2.5}$ concentration at Pensacola, with ammonium comprising 15%. Primary OC (11%) is the next most prevalent component. In this modeled episode, biogenic secondary organic aerosols are modeled to compose little $PM_{2.5}$ at Pensacola.

On an episode average basis, sulfate concentrations at Pensacola appear to be most sensitive to emissions from states other than Florida or Alabama (43%), followed by Alabama SO_2 emissions (24%) and Florida SO_2 emissions (16%). That Pensacola sulfate concentrations are most sensitive to boundary conditions (BC) is not a surprising result, but the diurnal variability warrants further consideration. Over the course of the 13 simulated days, sulfate concentrations at Pensacola are sensitive to BC as little as 9% and as much as 87%. Sulfate concentrations at Pensacola are sensitive to Alabama SO_2 emissions as little as 0% and as much as 56%. Sulfate concentrations at Pensacola are sensitive to Florida SO_2 emissions as little as 3% and as much as 49%. Even Tennessee, from which emissions must travel a considerable distance, contributes up to 10% on certain days. Meteorology, specifically the variability of prevailing winds throughout the domain during this episode, explains the variability in contributing source regions to sulfate concentrations in Pensacola. High sensitivity of sulfate concentrations in Alabama are expected, but prevailing northerly winds are a necessary condition to contribute to high sulfate concentrations at Pensacola. Under these conditions, there is little to no zonal transport of pollutants along the Gulf of Mexico coastline from source regions such as Mobile, New Orleans, or Houston.

Like sulfate concentrations, day-to-day variability in ammonium concentrations is significant; however, the source regions are different. On an episode average basis, ammonium concentrations at Pensacola appear to be most sensitive to NH_3 emissions from Florida (54%), followed by Alabama NH_3 emissions (20%), and other states' emissions (16%). Unlike sulfate concentrations, which appear to be most sensitive to a regional source (Alabama) of SO_2 emissions, ammonium concentrations are most sensitive to a local source. The diurnal variability in ammonium sensitivity is modest compared to sulfate. Ammonium concentrations at Pensacola are sensitive to Florida NH_3 emissions as little as 33% and as much as 86%. Ammonium concentrations at Pensacola are sensitive to Alabama NH_3 emissions as little as 0.2% and as much as 37%. Ammonium concentrations at Pensacola are sensitive to boundary conditions as little as 2% and as much as 35%. South Georgia

contributes up to 22% on certain days. Like sulfate, sensitivity varies considerably with meteorology.

Key findings: Consistent with observations in Phase II, **sulfate constitutes half or more of the particulate load** in the Pensacola area for a modeled 2001 pollution episode. Rather than local sources, however, **sulfate concentrations were more sensitive to distant sources**. In contrast, ammonium was more sensitive to local sources.

Implications: like ozone, a combination of regional and local controls may be necessary to effectively manage particle pollution in the Pensacola area.

iii. Assessment of Risks from Air Toxics in Escambia and Santa Rosa Counties Using EPA's Regional Air Impact Modeling Initiative (RAIMI) Tools

The Regional Air Impact Modeling Initiative (RAIMI) consists of a set of tools designed "to evaluate the potential for health impacts as a result of exposure to multiple contaminants from multiple sources, at a community level of resolution." RAIMI integrates emission inventory, dispersion model, and risk estimation in a GIS environment and allows estimation and representation of cancer and non-cancer risks from air toxics. Conceptually RAIMI follows the typical steps involved in a multi-source multi-pollutant risk assessment of air toxics. As a first step, an emission inventory of all sources and pollutants released in the community of interest is developed. An air dispersion model such as the Industrial Source Complex (ISC) model predicts ambient air concentrations at a number of receptor locations using emission source characteristics (e.g., exit gas velocity, exit gas temperature, stack height), meteorological parameters (e.g., wind speed and direction, vertical temperature profile, atmospheric stability), land use, and terrain characteristics of the study area. An exposure model takes into account the activity patterns and demographic composition of the area to estimate the actual exposures from ambient concentrations. In the next step, using the toxicity information for different pollutants, individual as well as cumulative cancer and non-cancer risks are estimated. RAIMI is currently capable of estimating cancer and non-cancer risks only from the inhalation pathway.

Application of the RAIMI system with the 1999 National Emission Inventory (NEI) for greater Pensacola indicated four concentrated hotspots of potentially elevated risk in the community.

Risk Zone 1 – Northern Santa Rosa County

Risk Zone 1 is in northern Santa Rosa County in the northeastern part of the model domain in the vicinity of three emission sources: a petroleum/natural gas extraction operation, a natural gas pipeline compressor station, and a landfill. A maximum cumulative risk of 48 in a million is predicted by RAIMI. The peak risk is attributed almost entirely to formaldehyde emissions from the natural gas compressor station, which operates large, natural gas-fired reciprocating internal combustion engines. The surrounding area is nearly entirely forested and rural, suggesting that an assumption of continuous exposure may not be appropriate.

However, individuals who reside within approximately 2 km of the facility could experience chronic cancer risks on the order of 10 in a million or more.

Risk Zone 2 – Northern Santa Rosa County

Risk Zone 2 is in northern Santa Rosa County in the north central part of the model domain in the vicinity of two emission sources: a petroleum/natural gas extraction operation and a landfill. A maximum cumulative risk of 23 in a million is predicted by RAIMI. The peak risk is attributed almost entirely to formaldehyde and toluene emissions from the petroleum/natural gas extraction operation. As in Risk Zone 1, the surrounding area is nearly entirely forested and rural, suggesting that an assumption of continuous exposure may not be appropriate. However, individuals who reside within approximately 0.5 km of the facility could experience chronic cancer risks on the order of 10 in a million or more, and a large radius of approximately 5 km around the operation may be subject to chronic cancer risks on the order of 1 in a million or more.

Risk Zone 3 – Pace Community in Santa Rosa County

Risk Zone 3 is near the Pace community in Santa Rosa County on the other side of Escambia Bay from Downtown Pensacola in the south central part of the model domain in the vicinity of six emission sources: four industrial plants and two landfills. A maximum cumulative risk of 709 in a million is predicted by RAIMI. The peak risk is attributed almost entirely to acrylonitrile emissions from the acrylic fiber manufacturing operation. Unlike Risk Zones 1 and 2, Risk Zone 3 features diverse land uses, including residential areas. Therefore, it is possible that nearby residents are chronically exposed to elevated pollutant concentrations and could experience cancer risks on the order of 10 in a million or more. Residents up to 10 km away from the operation could be subject to chronic cancer risks on the order of 1 in a million or more. The presence of spatially smaller high risk areas in the vicinity of the landfills are also noted in this risk zone. (Note: The magnitude of the estimated risk (709 in a million) in Risk Zone 3 was found to be overstated by approximately a factor of 20 and caused by an error in the NEI. Inspection of other estimated risks surrounding the facility indicate more typically values of 36 to 45 in a million, consistent with the order of magnitude of risk estimates for other industrial operations.)

Risk Zone 4 – Cantonment Community in Escambia County

Risk Zone 4 is near the Cantonment community in Escambia County, about 21 km northwest of Downtown Pensacola, in the southwestern part of the model domain in the vicinity of a large pulp and paper manufacturing operation. A maximum cumulative risk of 5.4 in a million is mostly attributed to methanol, acetaldehyde, benzene and xylene, which are used as chemical solvents in the pulping operation. The surrounding area is largely forested and agricultural, but some residential, commercial, and urban land uses are present, suggesting that residents could be exposed to elevated concentrations and higher cancer risks.

Non-cancer risk due to exposures to air toxics from point sources is not of much concern in Pensacola. Two very small clusters have a Hazard Index of greater than one, however, both these areas are within the industrial land use zones.

Key Findings: Three areas in Santa Rosa County and one area in Escambia County were estimated to have a possible elevated risk of cancer due to emissions from point sources (also called stationary or industrial sources). Only the Pace community in Santa Rosa County had a significant residential presence in close proximity to the industrial source that is primarily accountable for the elevated risk. While of concern, the estimated risks are of a magnitude consistent with risks found near other industrial sources.

Implications: With some exception for residential areas very near or within the industrial zones identified as potential hotspots, analyses using RAIMI appear to suggest that toxic **emissions from point sources are not a widespread source of cancer risk via the inhalation pathway** in the Pensacola area (with the caveat that other pathways were not studied).

iv. Risk Assessment of Mobile Source Air Toxics in Escambia and Santa Rosa Counties

Similar to the point sources analysis described above, mobile source emissions were modeled as a series of point source emissions occurring along the roadways. The following are some general observations based on our analysis of cancer risks. Almost all the regions around modeled roads in both counties are subject to a cancer risk of 1 in a million or greater; large parts of Escambia and a few regions close to main roadways in Santa Rosa are subject to 10 in a million greater cancer risk. Many parts of urban Escambia are subject to estimated cancer risks of more than 100 in a million. In Santa Rosa, 100 in a million or greater cancer risk is mainly concentrated along Interstate 10 (I-10) and US 98 roadways. At a few locations spread over urban Escambia, the estimated cancer risks exceed 1000 in a million with a couple of locations exceeding a cancer risk of 10,000 in a million. In Santa Rosa, comparatively fewer regions are subject to large cancer risks (only four to five locations have an estimated cancer risk of more than 1000 in a million).

In light of the excessively high estimated cancer risk at some locations, further analysis of those high-risk locations was made. The maximum cancer risk of 11,600 in a million occurs on the Blue Angel Parkway near its intersection with US-98 in the southwestern part of Escambia. The point of 11,600 in a million risk is located at a distance of 2m from the centerline of the road, indicating that the point of maximum risk is on the roadway. Further, the estimated cancer risk drops to 14 in a million at a distance of 82m and to 4 in a million within 300m from the centerline of the roadway. Thus, we believe that these excessively high risks are likely an artifact of the uniform receptor grid that is overlaid on the region without regard to the location of the point source emissions. In these cases, the model receptor is located on or very close to a modeled roadway point source which in turn leads to high modeled pollutant concentrations and subsequent high estimates of risk.

The contributions of various pollutants to estimated cancer risk at a few locations were analyzed in order to ascertain a general trend across the entire study area. This analysis was conducted at three locations each for Escambia and Santa Rosa counties. These three locations correspond to the three highest estimated cancer risks in the two counties. In both counties and at all locations, formaldehyde, benzene, and butadiene together contribute to more than 95% of the estimated cancer risk. The relative contribution of these three pollutants is identical at the three locations in Escambia while it varies slightly across the three locations in Santa Rosa. Benzene contributes most, followed by formaldehyde and butadiene.

As in the case of cancer risks, almost all locations are subject to a hazard index (HI) of more than one for non-cancer risks. Higher values of HI (10-100 range) are concentrated in the urbanized areas of Escambia and along I-10 and US 98 in Santa Rosa. A few locations also show a HI of more than 100. The highest value of HI in Escambia is 800 and it occurs on Blue Angel Parkway, the same location where the maximum cancer risk was found. Analysis of the variation of non-cancer risk as a function of distance from road centerline revealed patterns similar to cancer risk analysis. At the locations with the highest HI values, HI decreased to less than 2 at a distance of less than 100m.

Key Findings: **elevated cancer and non-cancer risks due to mobile sources are ubiquitous in the Pensacola area** with higher risks generally along more highly traveled roadways. Arising from the emissions of formaldehyde, benzene, and butadiene from cars and trucks, **risk diminishes by several orders of magnitude a few hundred meters off the roadway**.

Implications: **residential and other populated areas immediately adjacent to busy roadways may incur significantly elevated cancer and non-cancer risks.**

v. Assessment of Acute Health Risks from HCl and HF Emissions from Plant Crist

The 1999 NEI revealed that all HCl (7,559 tons) and HF (153 tons) emissions were reported to come from a single facility, Plant Crist, a coal-fired power plant located approximately 10 miles north of downtown Pensacola. Though these are not carcinogenic, assessments were made to determine if these sizable emissions could be a source of short-term health risks. Acute risks are typically computed analogously to chronic non-cancer risks using a short-term modeled concentration and acute risk-based threshold, such as Acute Guideline Exposure Levels (AEGL), Threshold Limit Values (TLV), and Reference Exposure Levels (REL) compiled by the U.S. EPA, the American Council of Governmental Industrial Hygienists, and the Occupational Safety and Health Administration. For assessing the acute health risks related to the significant emissions of HCl and HF from Plant Crist, we used an alternative approach developed by the Georgia Environmental Protection Division (EPD).

The Georgia EPD approach is convenient for modeling applications since it provides, with an appropriate margin of safety, a conversion of occupational exposure safety thresholds

(typically 8 hours) into more relevant averaging periods (e.g., 24 hours) for assumption of continuous exposures. Using risk-based criteria such as RfC, AEGL, REL, and TLV, an acceptable ambient concentration (AAC) can be calculated for each pollutant to represent acceptable risk levels for acute (15-minute and 24-hour average) time periods as well as chronic exposures (annual average). Short-term acute limits (e.g., 15 minute averages) are derived from 1-hour average model results. Review of the appropriate data for HCl yields an AAC of 20 $\mu g/m^3$ on an annual average basis and 700 $\mu g/m^3$ on a 15-minute average basis. HF has AAC of 5.85 $\mu g/m^3$ on a 24-hour average basis and 230 $\mu g/m^3$ on a 15-minute average basis.

The modeling protocol followed a similar approach as the cancer risk assessment in RAIMI by using the same dispersion model (ISCST3) and meteorological data set. Source parameters were obtained by a review of Florida DEP permit application files. Results of the modeling show that HCl and HF ambient impacts from Plant Crist are 90 to 98% below the risk-based AAC.

> ***Key finding:*** though the emissions of HCl and HF from Plant Crist are sizable, they do not appear to present a significant acute health risk via inhalation.

B. Integration of Health Outcomes, Air Quality, and Socio-Economic Data in Northwest Florida

(Task Leaders: Johan Liebens and Zhiyong Hu, University of West Florida)

1. Background

The local incidence of some illnesses is perceived to be elevated by many citizens in Escambia and Santa Rosa Counties. Many assume that this perceived elevated incidence is due to the multitude of environmental pollution issues in the area, especially air pollution. To address this concern of the citizens, PERCH carried out a health tracking study that compares mortality and morbidity rates in the two-county area with those elsewhere in the state of Florida. To relate the results of this Zip code level health study to air pollution, PERCH evaluated relationships between the health outcomes and the proximity of the Zip codes to air emission sites. This proximity study pointed to possible connections between some specific health outcomes and the location of air emission sites, but was somewhat limited in its potential by the large spatial unit (Zip codes) used in the health tracking study. Therefore, PERCH further assessed the connections between air pollution and health outcomes with two other approaches, air toxics modeling and geostatistical modeling. Results of these four studies (health tracking, proximity analysis, air toxics modeling, and geostatistical modeling) are briefly summarized and related to each other in the remainder of this report.

2. Health Tracking Study

a. Introduction

There is considerable interest in being able to relate geographic patterns of exposure to air pollution to variation in the health status of populations. These spatially defined associations between environmental hazards and population health are referred to as environmental health tracking studies. In its health tracking study, PERCH adopted a strategy to investigate if specific Zip codes in Escambia and Santa Rosa Counties have rates of health indicators that were higher (at a statistically significant level) than matched comparison Zip codes (http://www.uwf.edu/CEDB/Perch_USF_EPA_April04.pdf). Patterns of such differences across multiple indicators and age/race strata could suggest potential Zip codes in the region that should be targeted for study as more detailed environmental data becomes available.

The investigators of the health outcomes study (PERCH project collaborators from the University of South Florida) identified a list of health indicators that were thought to be sensitive to increased exposure to airborne environmental hazards. Both mortality and morbidity indicators were included. The mortality indicators, which might best be characterized as health conditions that would be affected by long-term exposure to environmental hazards, included deaths from: (1) all cancers, (2) lung cancers alone, (3) cardiovascular diseases, (4) any respiratory disease, (5) birth defects, and (6) all causes of death to infants. The morbidity indicators, which might best be characterized as being sensitive to short-term exposure to environmental hazards, included hospitalizations for (1) asthma, (2) cardiovascular disease, and (3) respiratory disease. Two additional morbidity indicators, numbers of live births with very low birth weight and the number of live births with low birth weight were added. While these indicators have not been directly associated with airborne environmental exposures they have been widely used as indicators of poor health in a population.

A cross-sectional observational study design was employed to compare the selected health outcome measures for Zip codes within the two counties with Zip codes having similar demographic and socio-economic characteristics from the remainder of Florida (matches). Escambia and Santa Rosa Zip codes were matched using propensity scores that were calculated through a series of logistic regression equations that included the following independent variables: percent female, percent of the population over 65 years of age, percent of the population that is black, percent of the population that is Hispanic, total population, the percent of households earning $15,000 or less, and per capita income.

A series of generalized linear (Poisson regression) models were developed to test whether standardized 5-year mortality/morbidity ratios for each Escambia and Santa Rosa County Zip code were different than those from the matched comparison Zip codes at a statistically significant level. Specifically, least squares means for each health indicator studied, for five years of data, were compared after adjusting for age, gender, percent of the population that is black, percent of the population over the age of 65 and the percent of households earning $15,000 per year or less. Five years of data were included in the analysis to measure impact over a reasonable time period and to increase the power of the statistical tests.

b. Results

The majority of statistically significant differences for mortality related to birth defect and infant mortality. Only one Zip code (32570) had significantly higher rates across more than one category of disease (Table B-1, Fig. B-1). Table B-1 summarizes the results of the models for mortality by listing the number of health outcomes that had a statistically significantly higher incidence in the given Zip code than in the matching Zip codes. These results are graphically depicted in Fig. B-1.

Table B-1. Summary of results from mortality models.

Zip code	County	Blacks		Whites	
		All ages	Over 65	All ages	Over 65
32570	SR	3s/1w*	2s/1w	1s/1w	1s/1w
32566/ 32561	SR	2w	2w	-	3s/1w
32534	ES	2s/1w	1s/1w	-	-
32501	ES	1s/2w	1s/1w	1s	-
32577	ES	1s/2w	-	2s	-
32533	ES	1s/1w	-	-	-
32503	ES	1s/2w	-	-	-

* s indicates strong statistical evidence, w indicates weak statistical evidence.

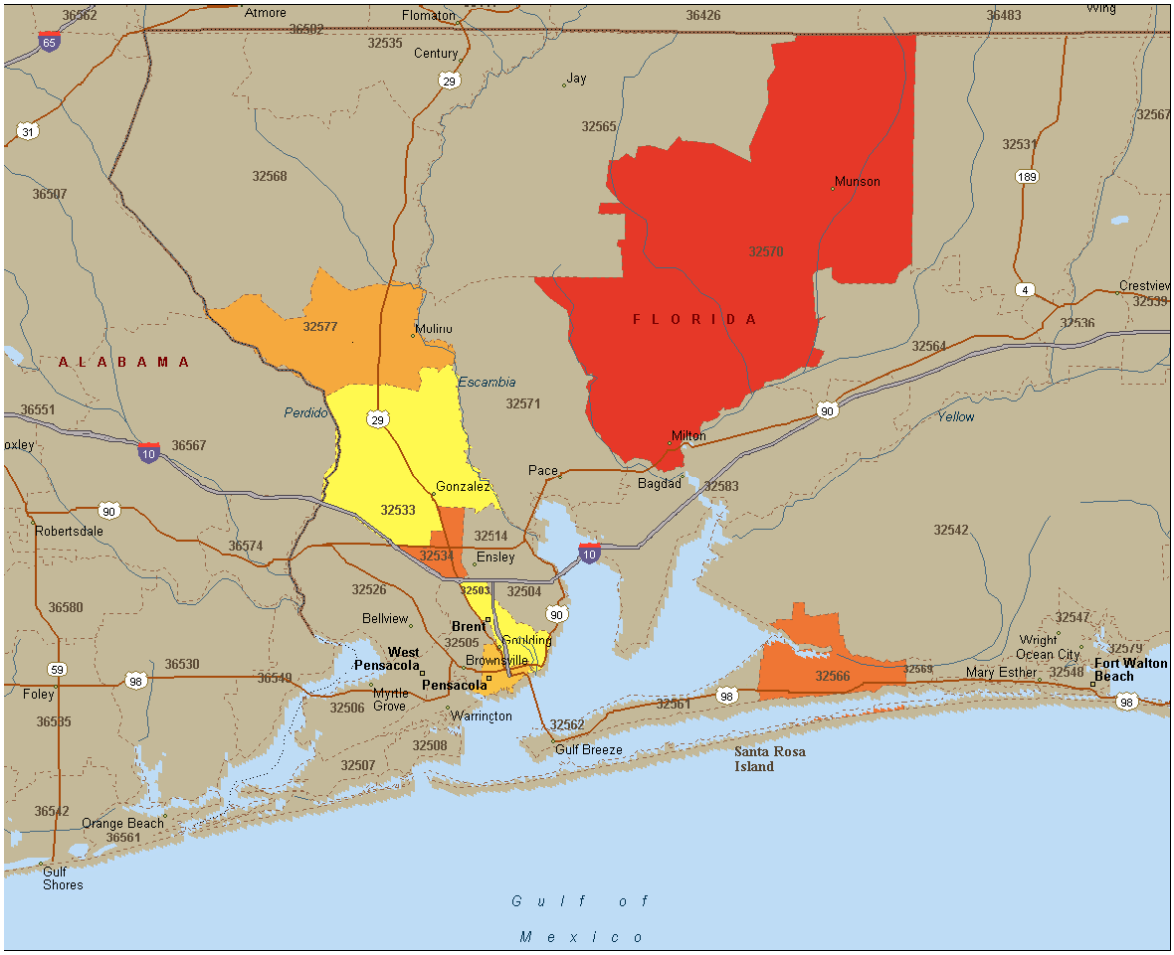


Fig. B-1. Map of summary of mortality models. Darker colors indicate a greater burden of disease.

Fewer statistically significant differences in which Zip codes had higher rates of disease than the matching Zip codes were found in the morbidity models than in the mortality models. The morbidity health indicators, unlike the mortality indicators, fall primarily into one disease group (cardio-respiratory). There were relatively few statistically significant results for models based on the total population or on the total white or black population. More consistent patterns were found in the models for those over the age of 65 (Table B-2). Table B-2 summarizes the results of the models for morbidity by listing the number of health outcomes that had a statistically significantly higher incidence in the given Zip code than in the matching Zip codes. These results are graphically described Fig. B-2.

Table B-2. Summary of results from morbidity models.

Zip code	County	Blacks		Whites	
		All ages	Over 65	All ages	Over 65
32570	SR	1s*	4s	2s	1s
32535/ 32565	ES	2s	3s	3s	1w
32566/ 32561	SR	-	1s	-	3s
32583/ 32530	SR	-	1w	1s	1w
32571	SR	-	1s	-	1w
32533	ES	1s	1w	-	-
32504	ES	-	2s	-	-
32501	ES	-	1w	-	-

* s indicates strong statistical evidence, w indicates weak statistical evidence.

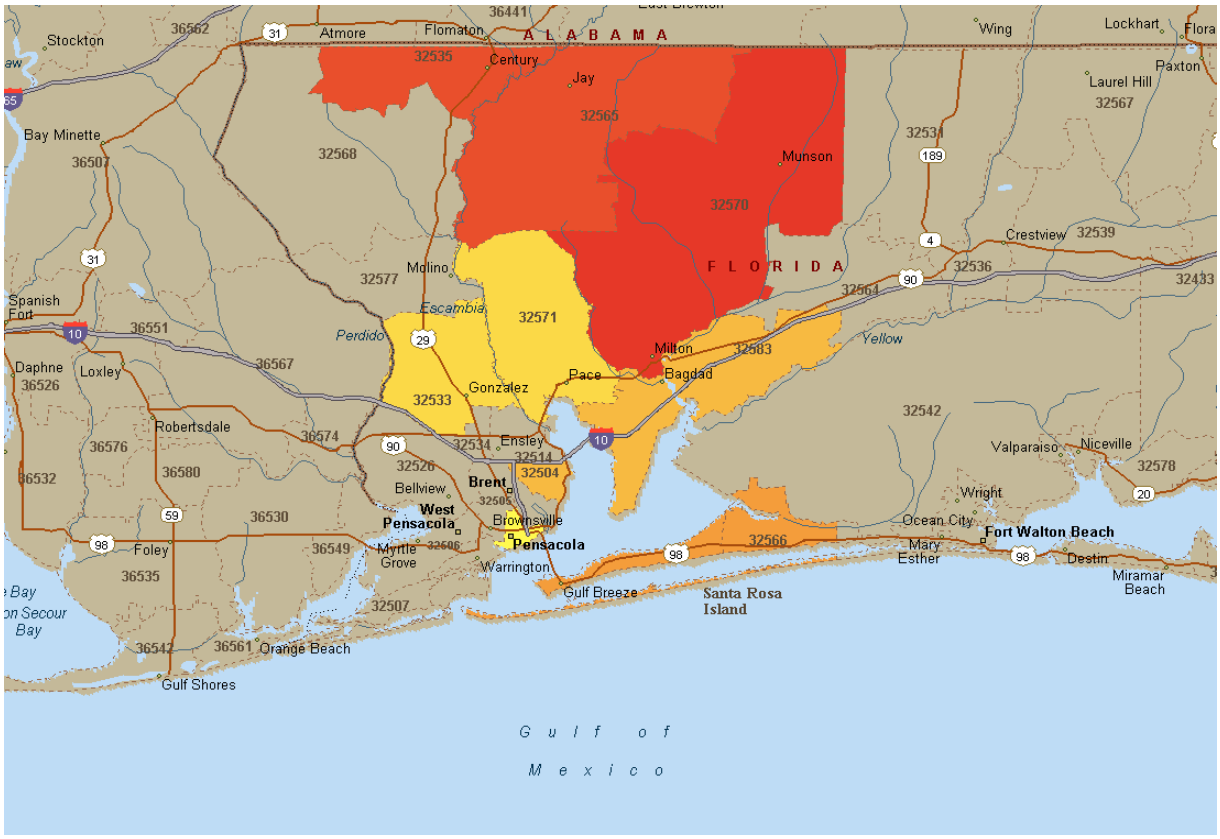


Fig. B-2. Map of summary of morbidity models. Darker colors indicate a greater burden of disease.

c. Health Tracking Conclusions

In general, health outcomes for ZIP codes in Escambia and Santa Rosa Counties differ spatially and some ZIP codes have significantly higher or lower levels of adverse health outcomes than matching ZIP codes elsewhere in Florida (see Fig. B-3 for example). This indicates that for some specific health outcomes and some specific Zip codes the citizen's concerns about high rates may be justified, but this health tracking study did not find evidence that the overall health of the population of Escambia and Santa Rosa Counties is significantly different from that in socio-economically and demographically comparable areas in the remainder of Florida.

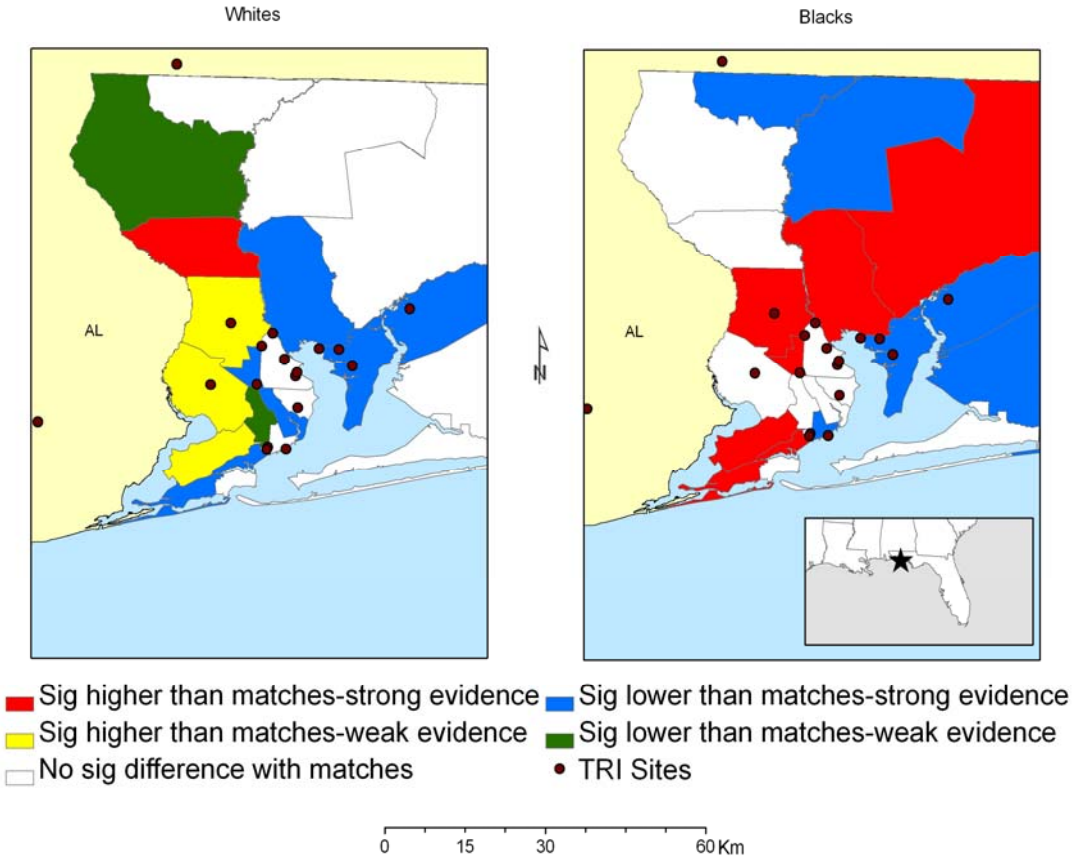


Fig. B-3. Comparison of birth defects in Escambia and Santa Rosa County ZIP codes and associated (matching) ZIP codes.

3. Air Emitter Proximity Study

a. Introduction

To evaluate if the results of the health outcomes study may be influenced by air pollution we compared the results with the geographical distribution of air emitters in the area. For this task we collected various types of spatially referenced data for air emitters. The data included: (1) Year 2000 Toxic Release Inventory (TRI) air pollution data including name, location, and emission data; (2) State of Florida permitted minor source emitters from 2002 with their name, address, and type of permit; and (3) A year 2000 dataset from the local Florida DEP office that had the location of 108 major and minor permitted air emitters in Northwest Florida but did not have emission data.

As a first step in the spatial comparison of health outcomes and air pollution data, a distance index that represents the proximity of a ZIP code to emission sites was developed. Because of the large size of some ZIP codes and the heterogeneity of the population in some ZIP codes the index was initially determined for census block groups. For each block group the distance index was calculated for emission sites within 10 km from the centroid of the block group as follows:

$$\text{Proximity index for block centroid i} = \sum_{j=\#\text{sites}}^{j=1} \left(\log\left(d_{i,j}+1\right)\right)^{-1}$$

where $d_{i,j}$ is the distance from block centroid i to emission site j.

The indexes were summed by block group and the resulting total indexes for the block groups were averaged by ZIP code. Benzene-equivalents for 2002 TRI site air emissions were collected from the Environmental Defense website (http://www.scorecard.org/env-releases/def/tep_cancer.htm). The TRI total emissions and benzene-equivalent emissions were used to weight the proximity index resulting in three indexes, i.e. an unweighted index, a total emission weighted index and a benzene-equivalent weighted index. Benzene-equivalents were not available for the other two emitter data sets (State of Florida and local FL DEP), and only unweighted and/or total emission weighted indexes could be calculated for these data sets.

The average proximity indexes for each ZIP code were statistically compared to cumulative health outcomes and to specific health outcomes. In both cases, ZIP codes within NW FL were compared with each other and with the socio-economically and demographically matching ZIP codes elsewhere in the state. The hypothesis of this study was that if morbidity and/or mortality in the area is linked to air pollution, Zip codes with worse health outcomes than their matching Zip codes should be located closer to air emission sites.

b. *Cumulative* Health Outcomes

In this part of the study the proximity indexes were evaluated for two groups of NW FL ZIP codes: ZIP codes identified by the health tracking study as having *cumulative* evidence for better health outcomes than their respective matching ZIP codes and ZIP codes having *cumulative* evidence for worse health outcomes.

The ZIP codes in NW FL with worse (resp. better) cumulative health outcomes do not systematically have higher (resp. lower) proximity indexes than their associated ZIP codes (e.g. Fig. B-4a and B-4b). Difference of means testing showed a significant difference ($P < 0.05$) between NW FL and associated ZIP codes only for the benzene weighted TRI proximity index and worse outcomes (Fig. B-4b), but not for the other proximity indexes. Consequently, these results for *cumulative* health outcomes do not show a strong relationship between proximity to emission sites and health outcomes in the study area.

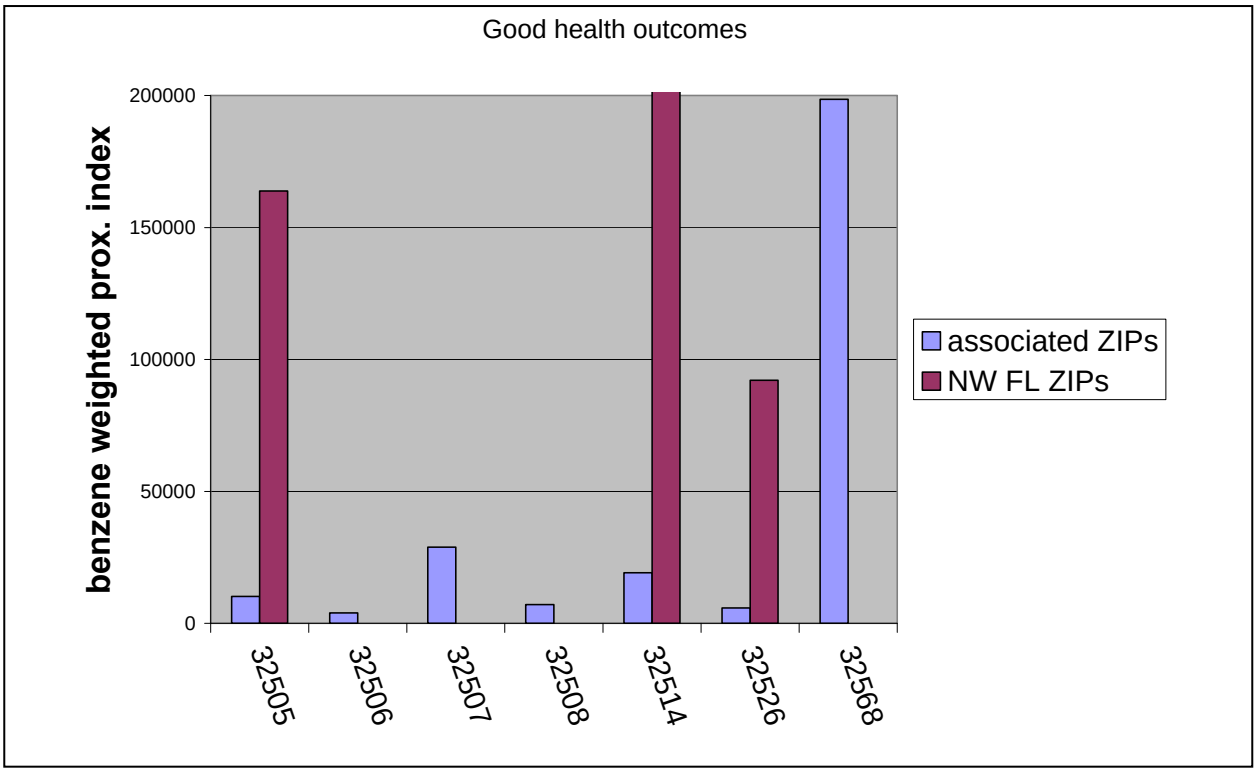


Fig. B-4a. Benzene weighted TRI proximity index for NW FL ZIP codes with better cumulative health outcomes vs. associated ZIP codes.

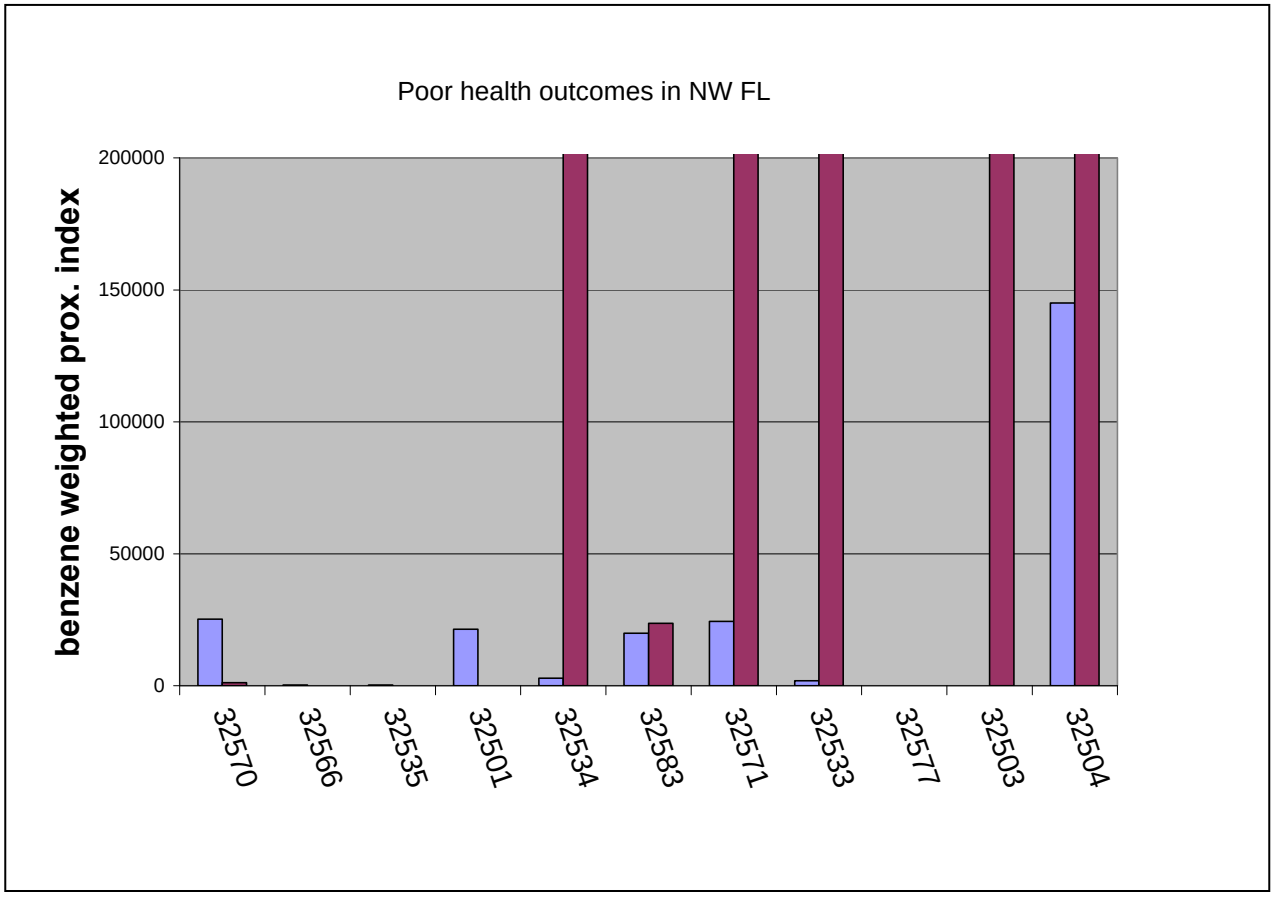


Fig. B-4b. Benzene weighted TRI proximity index for NW FL ZIP codes with worse cumulative health outcomes vs. associated ZIP codes. See Figure 4a for legend.

c. *Specific* Health Outcomes

ZIP codes with a high incidence of some *specific* health outcomes have a higher proximity index than ZIP codes with a low incidence (Fig. B-5a, B-5b), suggesting that there is a link between proximity to emission sites and the incidence of these specific health outcomes. The specific health outcomes for which this relationship holds true varies only slightly between the various proximity indexes and are:

- Mortality: white, >65, cardiac; black, >65, lung cancer; black, birth defects
- Morbidity: black, all ages, asthma; black, >65, cardiac; white, >65, pneumonia

For these 6 specific health outcomes NW FL ZIP codes were also compared to their respective associated ZIP codes. Graphs show that NW FL Zip codes with a higher incidence of these 6 specific health outcomes have a higher proximity index than their matching Zip codes and that NW FL Zip codes with a lower incidence have a lower proximity index than their matching Zip codes (Fig. B-6a, B-6b). This observation corroborates the contention that a link exists between the proximity to emission sites and the incidence of these specific health outcomes. Weaker indications for this link can be observed for mortality in blacks, >65, due to all cancers and morbidity in blacks, >65, due to respiratory illnesses (Fig. B-5a, B-5b; Fig.

B-6a, B-6b). Statistical analysis was not performed because of the low number of cases (ZIP codes) in each category. These observations for *specific* health outcomes, both within NW FL and compared to matching Zip codes, suggest that there is an influence of proximity to emission sites on the incidence of some of the specific health outcomes. These observations are preliminary and have to be confirmed by other analysis using more robust statistics, but they suggest that such further evaluation is warranted.

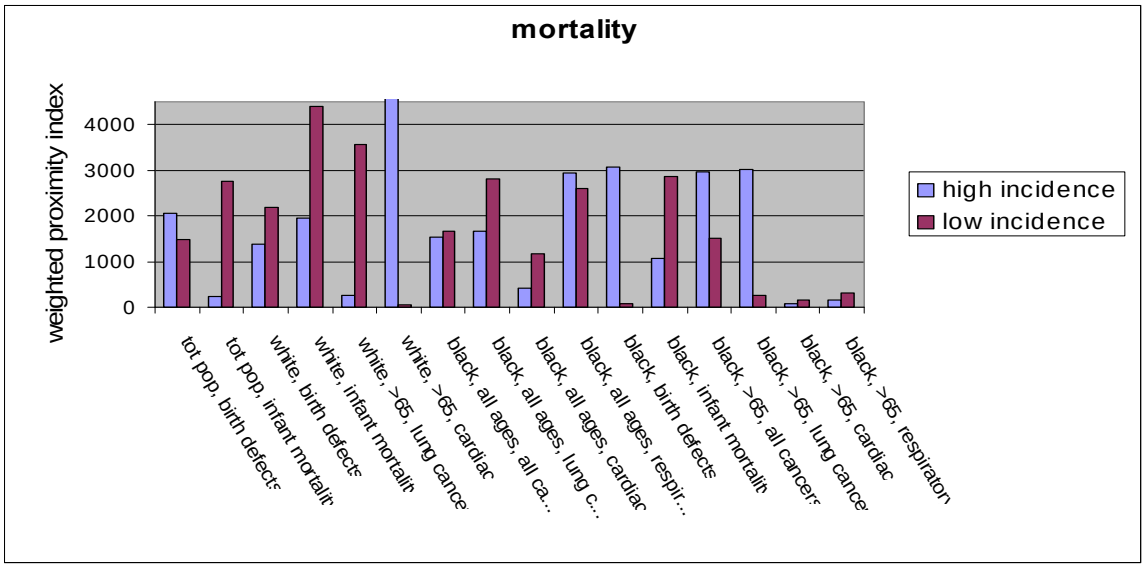


Fig. B-5a. Proximity index for Zip codes with high or low incidence for specific causes of mortality: Comparison within northwest Florida. Based on statewide database.

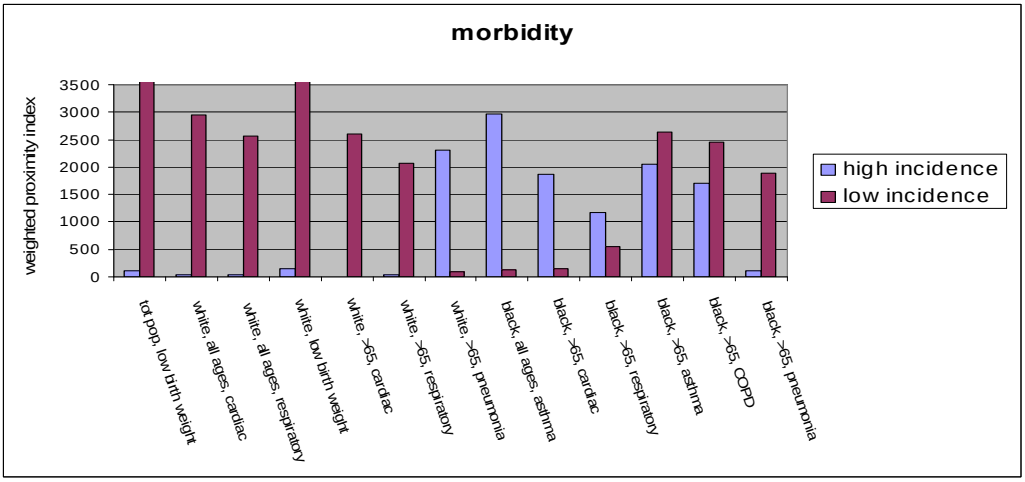


Fig. B-5b. Proximity index for Zip codes with high or low incidence for specific causes of morbidity: Comparison within northwest Florida. Based on statewide database.

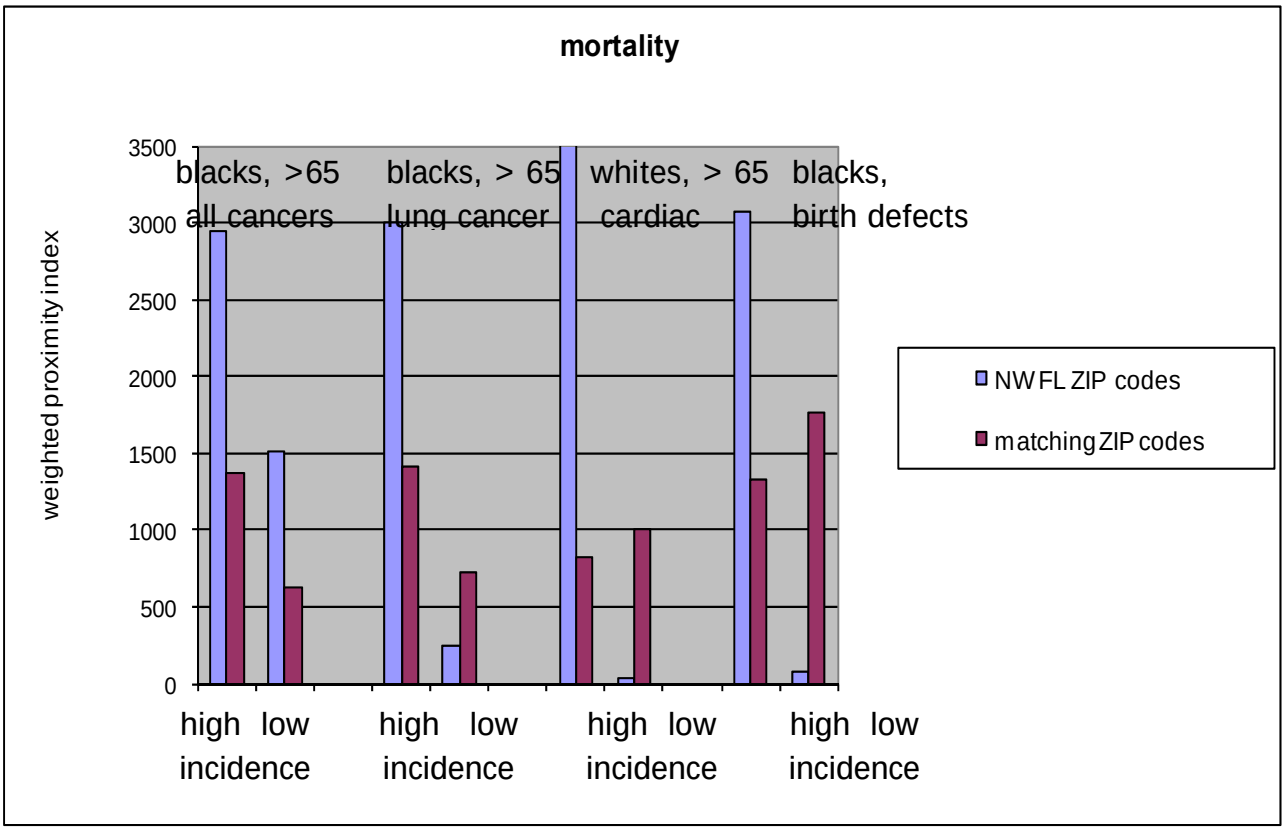


Fig. B-6a. Proximity index for Zip codes with high or low incidence for specific causes of mortality: Comparison with matching Zip codes. Based on statewide database.

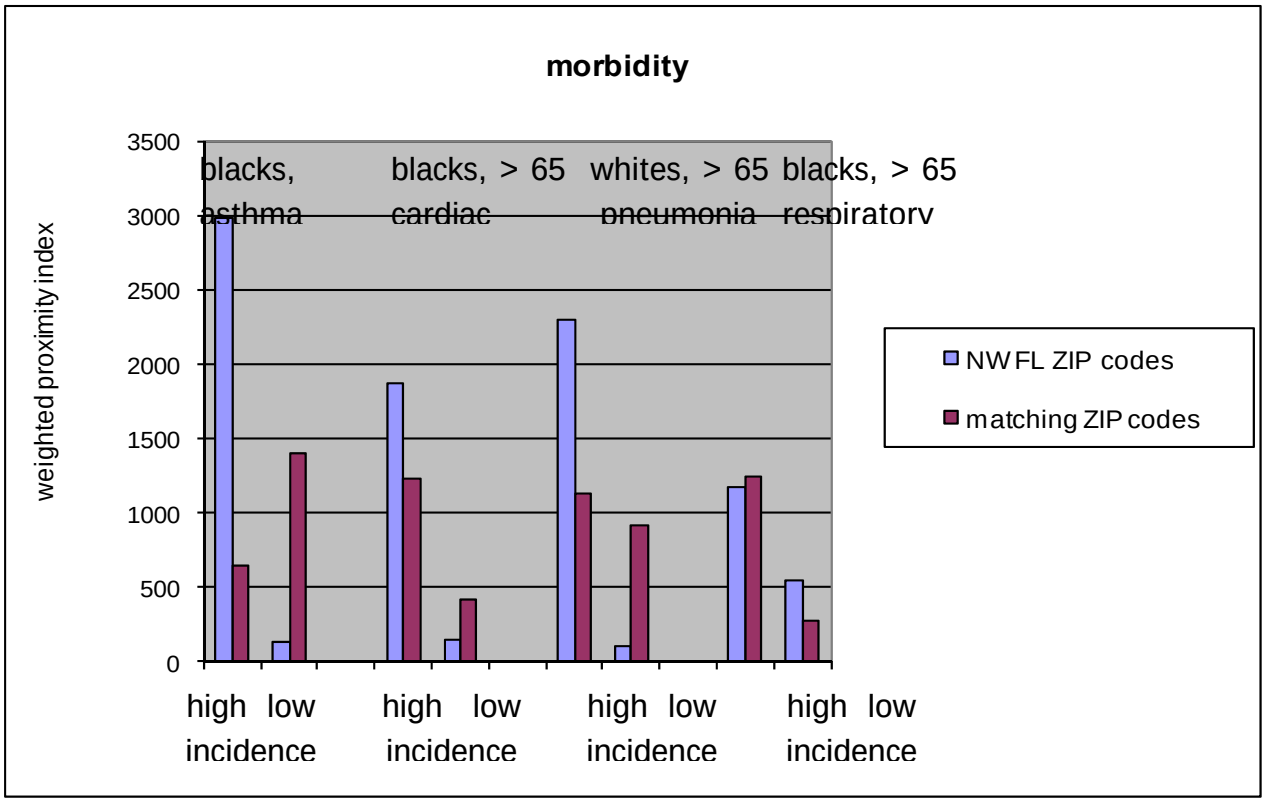


Fig. B-6b. Proximity index for Zip codes with high or low incidence for specific causes of morbidity: Comparison with matching Zip codes. Based on statewide database.

d. Environmental Inequity

To assess environmental equity the TRI-based proximity indexes were averaged at the census tract level and statistically correlated with population density, percent whites, percent non-white, poverty rate, industrial employment, and educational attainment. The unweighted proximity index showed moderately strong and significant correlation with population density and industrial employment. The two emission weighted indexes did not have a strong correlation with the demographic and socio-economic variables. These observations indicate that a spatial relationship exists between the location of TRI sites and two of the variables (i.e. population density and industrial employment) but this does not seem to lead to greater exposure of any racial group to emissions.

To further explore potential connections between proximity to emission sites and the demographic and socio-economic variables multiple-linear-regressions were run. The R^2 value was very low for the two weighted TRI proximity indexes (0.09) but somewhat higher (0.24) for the unweighted proximity index. Non-linear models yielded comparable R^2 values. Population density and industrial employment had a statistically significant effect in the regression for the unweighted proximity index. These results are consistent with the results for the correlation coefficients and also fail to show evidence for environmental inequity in exposure to TRI site emissions.

e. Proximity Study Conclusions

The air emitter proximity study did not find clear evidence for an influence of proximity to emission sites on ZIP code level *cumulative* health outcomes. Some of the *specific* health outcomes are directly related to proximity to emission sites as evidenced by relationships at the Zip code level within NW Florida and comparisons between NW Florida and similar areas elsewhere in the state. Preliminary statistical analysis at the census tract level of the proximity indexes and demographic and socio-economic data does not indicate environmental inequity in exposure to emission sites in NW Florida. PERCH considered this proximity study as only a first step in evaluating relationships between health outcomes and air pollution in Escambia and Santa Rosa Counties because it was hampered by the unavoidable use of spatial units (Zip codes) that are not ideally suited for this type of analysis. Therefore, PERCH further assessed connections between air pollution and health outcomes with two other approaches, air toxics modeling and raster-based geostatistical modeling.

4. Air Toxics Modeling

a. Introduction

As part of its effort to assess all aspects of the environment in Escambia and Santa Rosa Counties, PERCH carried out a comprehensive evaluation of air pollution in the area (Section III. A), conducted by PERCH project collaborators from the Georgia Institute of Technology (http://www.uwf.edu/CEDB/Perch_Air_Quality_Studies.cfm). Based on a review of ambient monitoring data, available information regarding emissions, other studies, and discussions with various stakeholders, three classes of air pollutants were found to be of particular concern in the area: ground level ozone, fine particulate matter $PM_{2.5}$, and air toxics. Health cost estimates associated with these pollutants indicated that $PM_{2.5}$ imposed the highest per person per year costs, followed by ozone and then air toxics. Particulate matter likely presents the greatest air quality risk to human health in the region. Sulfate is a large fraction of the observed ambient $PM_{2.5}$ loading, with high concentrations most often associated with northerly air flow. Additionally, organic carbon was found to be a large fraction of the ambient $PM_{2.5}$ loading. There is community concern regarding air toxics based on TRI discharges from point sources. To further try to relate observations of the health tracking study to air quality measures a multipronged modeling and analysis approach of air toxics was performed. This air toxics modeling study assessed the health risk associated with stationary point sources, traffic sources, and one specific emitter (Gulf Power's Plant Crist power plant). The primary objective of the modeling was to quantify risk levels in the two-county study area to advise policy- and decision- makers about the existence of elevated risks for adverse health outcomes due to toxic air pollution. For its modeling, the study employed the Regional Air Impact Modeling Initiative (RAIMI) system, which consists of a set of tools designed to evaluate the potential for health impacts as a result of exposure to multiple contaminants from multiple sources, at a community level of resolution. RAIMI integrates emission data, meteorological data, a dispersion model, and risk estimation in a GIS environment and allows estimation and representation of cancer and non-cancer risks via inhalation.

b. Results

i. Stationary Point Sources

Application of the RAIMI system with the 1999 National Emission Inventory (NEI) for the study area indicated four concentrated hotspots of potentially elevated cancer risk related to point sources (Fig. B-7).

Risk Zone 1 – Northern Santa Rosa County. Risk Zone 1 is in northern Santa Rosa County in the vicinity of three emission sources: a petroleum/natural gas extraction operation, a natural gas pipeline compressor station, and a landfill. A maximum cumulative risk of 48 in a million was predicted by RAIMI. The peak risk was attributed almost entirely to formaldehyde emissions from the natural gas compressor station. This risk zone overlaps mostly with Zip code 32531, in which the health study did not find significant differences with the matching Zip codes.

Risk Zone 2 – Northern Santa Rosa County. Risk Zone 2 is also in northern Santa Rosa County in the vicinity of two emission sources: a petroleum/natural gas extraction operation and a landfill. A maximum cumulative risk of 23 in a million was predicted by RAIMI. The peak risk was attributed almost entirely to formaldehyde and toluene emissions from the petroleum/natural gas extraction operation.. This risk zone is located in a Zip code (32565) that was merged with another one in Escambia County (32535) by the health study due to low population numbers. This large combined Zip code was among the worst in the morbidity models of the health study, but all of these models were for non-cancer related morbidity. This suggests that the spatial overlap of the risk zone with the Zip code with poor health outcomes is coincidental.

Risk Zone 3 – Pace Community in Santa Rosa County. Risk Zone 3 is near the Pace community in Santa Rosa County in the vicinity of six emission sources: four industrial plants and two landfills. A maximum cumulative risk of 709 in a million was predicted by RAIMI. The peak risk was attributed almost entirely to acrylonitrile emissions from the acrylic fiber manufacturing operation. This risk zone partially overlaps with Zip codes 32571 and 32583, which have worse morbidity than their matching Zip codes for some non-cancer health outcomes but not for cancers, indicating again that a causal relationship between risk and observed health outcomes cannot be demonstrated.

Risk Zone 4 – Cantonment Community in Escambia County. Risk Zone 4 is near Cantonment in Escambia County about 10 km northwest of Downtown Pensacola in the vicinity of a large pulp and paper manufacturing operation. A maximum cumulative risk of 5.4 in a million was mostly attributed to methanol, acetaldehyde, benzene and xylene, which are used as chemical solvents in the pulping operation. This risk zone partly overlaps with Zip codes 32533 and 32534. Zip code 32534 has worse rates than its matching Zip codes for some cancer-related causes of mortality in African Americans. Both Zip codes have worse mortality due to birth defects.

Results for non-cancer risk from stationary point sources showed two very small areas with elevated non-cancer risk on the premises of the emitting facilities (Solutia Inc. and Sterling Fibers). Given their very small size, these risk zones do not provide an explanation for the findings of the health tracking study.

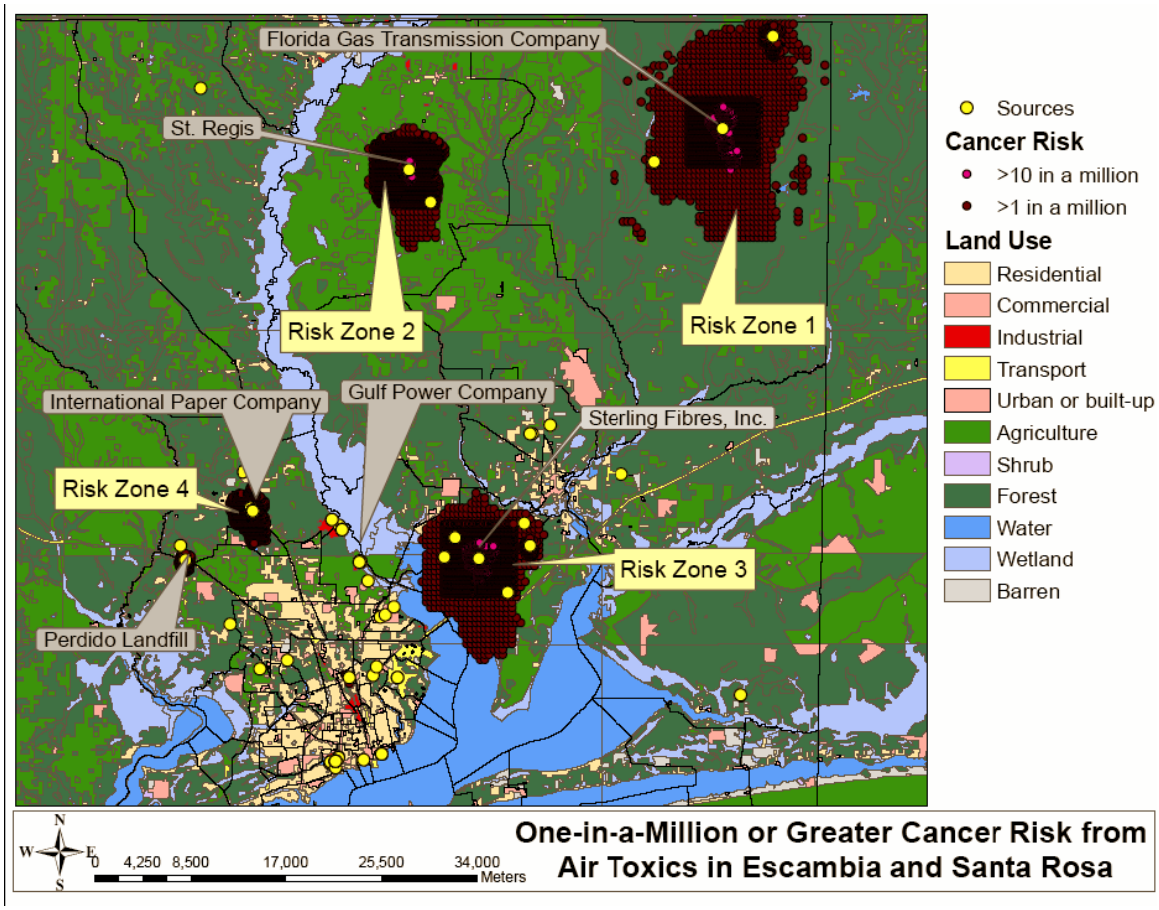


Fig. B-7. Elevated chronic cancer risk zones estimated by the RAIMI system.

ii. Traffic Sources

Almost all the regions around the modeled roads in both counties are subject to a cancer risk of 1 in a million or greater. Large parts of Escambia County and a few regions close to main roadways in Santa Rosa County are subject to 10 in a million greater cancer risk. Many parts of urban Escambia are subject to estimated cancer risks of more than 100 in a million. In Santa Rosa, 100 in a million or greater cancer risk is mainly concentrated along Interstate 10 and US 98 roadways. As in the case of cancer risks, almost all locations are subject to a hazard index (HI) of more than one for non-cancer risks. Higher values of HI (10-100 range) are concentrated in the urbanized areas of Escambia and along I-10 and US 98 in Santa Rosa. The risks diminish by several orders of magnitude a few hundred meters off the roadway. Given the difference in spatial units, these results cannot be compared to those for the health tracking study.

c. Air Toxics Modeling Conclusions

Air toxics modeling identified four zones in the study area with elevated cancer risk due to inhalation of air emissions from stationary point sources. Three of these risk zones overlap with Zip codes that were not found by the health tracking study to have significantly elevated cancer rates, compared to matching Zip codes elsewhere in the state. It is noteworthy that Zip code 32570, which is worse than its matching Zip codes for several cancer related health outcomes is surrounded by but not covered by these three cancer risk zones. The fourth risk zone, just north of Pensacola, partially overlaps with Zip codes where the health tracking study found comparatively high rates of some cancers in some sections of the population. Further detailed study is required to determine if this spatial association of risk and health outcome is causal.

5. Geostatistical Study

a. Introduction

This geostatistical component of PERCH investigated the associations between air pollution and health outcomes in Escambia and Santa Rosa counties using three approaches: mapping spatial patterns of health outcomes and air pollution, exploratory statistical analyses, and statistical modeling. The project was carried out progressively from simple mapping and modeling, to more refined mapping using satellite imagery and advanced spatially extended modeling.

b. Data

Health outcome data were obtained from the University of South Florida CATCH (Comprehensive Assessment for Tracking Community Health) data warehouse, the Florida Department of Health CHARTS (Community Health Assessment Resource Tool Set) database, and the US Centers for Disease Control and Prevention (CDC) WONDER (Wide-ranging Online Data for Epidemiologic Research) records. The downloaded health outcome data at the Zip code level included hospitalizations due to cardiac, respiratory problems, COPD, asthma, low birth weight, and mortality due to all cancers, lung cancer, cardiac, respiratory problems, birth defects, and infant death. Finer resolution health outcome data at the census tract level included mortalities due to COPD, stroke, and lung cancer. Data at the county level included myocardial infarction (MI) and chronic coronary heart disease (CCHD).

Socio-economic/demographic data at the census tract level for total population, male, female, white, black, Asian, Hispanic, 2+ races, 65 and 65+ years old, poverty status, income below poverty, and median household income were extracted from the 2000 Census Summary File.

Point source air pollution data (Fig. B-8) were collected for US EPA Toxic Release Inventory (TRI) sites, Superfund sites, and Florida Department of Environmental Protection monitored solid waste sites, sewer treatment sites, and brown field sites. For mobile source data traffic counts with emission estimates were obtained from the Florida Department of

Transportation. Density surfaces were derived from all point and mobile source air quality data.

A Normalized Difference Vegetation Index (NDVI) raster surface and a greenness surface representing the amount of green space were calculated from a cloud-free Landsat 7 Enhanced Thematic Mapper Plus (ETM+) imagery. Moderate Resolution Imaging Spectrometer (MODIS) daily level 2 (2003-2004) aerosol optical depth (AOD) data in Hierarchical Data Format (HDF) were obtained from the NASA Level 1 and Atmosphere Archive and Distribution System (LAADS Web) at http://ladsweb.nascom.nasa.gov/. MODIS Level 2 data are produced at the spatial resolution of a 10×10 1-km (at nadir)-pixel array.

$PM_{2.5}$ ground data was obtained from the EPA Air Quality System (AQS) online Data Mart at http://www.epa.gov/ttn/airs/aqsdatamart/index.htm. $PM_{2.5}$ values measured within 1 hour of the MODIS imaging time were retrieved for the year 2004. Annual statistical summary $PM_{2.5}$ data for 2003 and 2004 were also obtained for monitoring sites covering the conterminous land. Calculation of annual statistics included exceptional air pollution events.

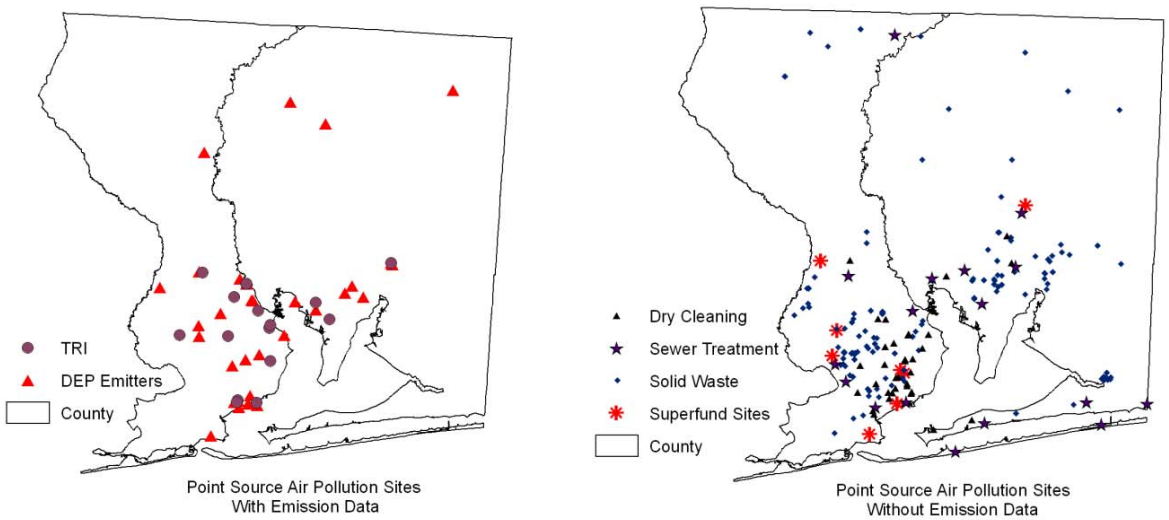


Fig. B-8. Maps of point source polluters.

c. Mapping, Analyses and Modeling Results

i. Mapping

At the census tract level, three characteristic patterns stand out from environmental exposure maps (Fig. B-9): (1) Zip code 32514 (largest circle in Fig. B-9b), where Gulf Power's Plant Crist is located, has the largest emissions (total air or benzene-equivalent) but has low mortality rates (Fig. B-9a, B-9b); (2) all other point source pollutants are concentrated within the urban extent (Fig. B-9c, B-9d); and (3) traffic volume has the highest density in the City of Pensacola, along Interstate 10, and highways 90, 98 and 29 (Fig. B-9e, B-9f).

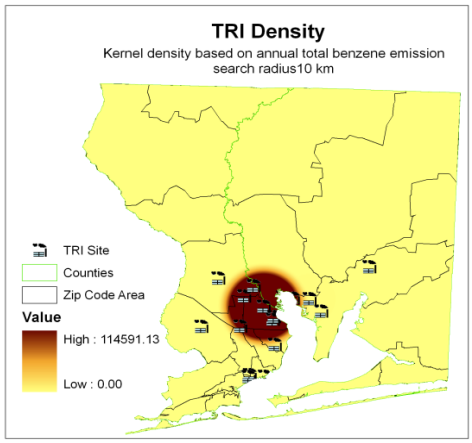
ii. Exploratory Spatial Data Analysis (ESDA)

A parallel coordinate plot was created to show values for Mortality Respiratory Total Population (MRTP) and six environmental exposure variables (TRI total air emission, TRI benzene-equivalent emission, DEP emitters emission, all other point sources, traffic density, and NDVI). Again, Zip code 32514 area stands out as highlighted in the plot and the map due to its high emission values.

A Moran's I plot was generated for total population respiratory hospital admission rates. The Moran's I value is 0.47, indicating strong spatial autocorrelation. Zip codes 32577 and 32568 have much lower respiratory hospital admission rates than their neighbors.

iii. Spatial Lag Model of Asthma and Air Pollution

The model shows relationships between the total population asthma hospitalization rate and air pollution (positive, $0.08 < p < 0.26$) and 'greenness' (negative, $p = 0.23$) (Table B-3).



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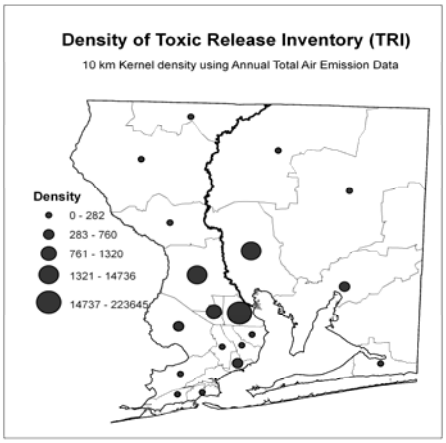

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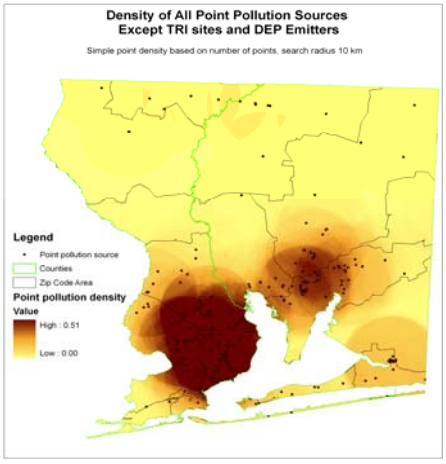

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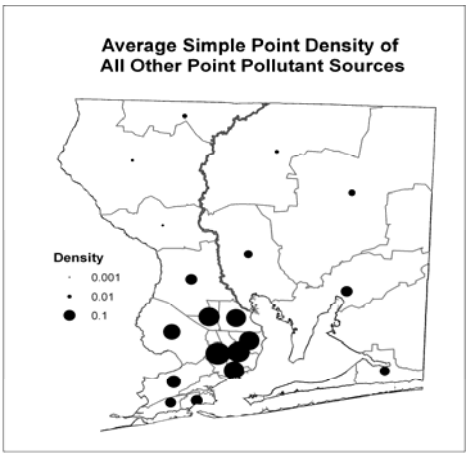

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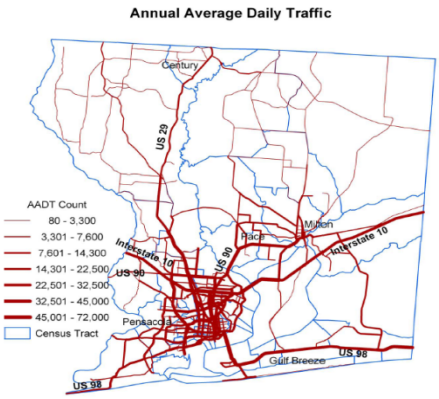

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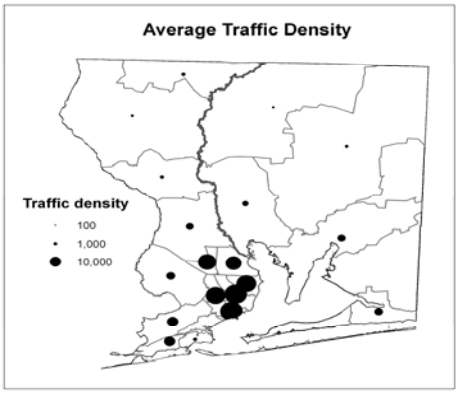

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Fig. B-9. Zip-code level environmental exposure maps.

Table B-3. Spatial lag model of asthma and air pollution.

Variable	Coefficient	Probability
ρ	0.3645	0.087
Constant	0.7242	0.019
Traffic	1.6192e-005	0.110
Greenness	-0.221	0.230
TRI benzene	8.6748e-006	0.256
TRI Total	1.6497e-006	0.147
DEPEMIT	0.0021	0.085
Other point pollution	1.2563	0.115

iv. Mortality Rates of COPD, Stroke, and Lung Cancer Compared With Socio-Economic and Environmental Factors

a. Focused Score Tests

Maps reveal linkages between some of these health outcomes and the environmental and socio-demographic factors. High COPD mortality tends to occur in areas with high poverty rates. Scatter plots show relationships between death rates and suspected factors. Mortality rates of all three diseases show positive relationships with proportion blacks, population age 65 and above, and the poor, as well as mobile and point source air pollution, and negative relationships with median household income, percentage males, and greenness.

Table B-4 shows the results of focused score tests. The table indicates significant focused clustering of the deaths of COPD, stroke, and lung cancer around traffic pollution and point source pollution. The amount of greenness does not show significant relationships with the deaths.

Table B-4. Focused score tests of relationships between mortality rates of COPD, stroke, and lung cancer with socio-economic and environmental factors.

Disease	Foci	T_{sc}^{*}	p value
COPD	Traffic	3.3415	0.00042
	Point source	3.1594	0.00079
	Greenness	0.2946	0.38414
Stroke	Traffic	13.6522	<0.0001
	Point source	9.0468	<0.0001
	Greenness	-7.6334	1.00000
Lung Cancer	Traffic	4.8486	<0.0001
	Point source	3.4729	0.00026
	Greenness	0.2577	0.39834

b. OLS Regression Analyses

Table B-5 shows the OLS univariate regression results. Higher COPD, stroke, and lung cancer mortality rates occurred in census tracts with lower median household income, percentage of male population, and greenness. However, the relationship between stroke and percent male and the relationships between all the three health outcomes and greenness are not significant. All the mortality rates are significantly positively associated with proportion blacks, people age 65 or above, poverty rate, and air pollution from both mobile and point sources. Regression of COPD has the lowest fits with R-square values ranging from 0.01 (greenness) to 0.15 (poverty rate). The models fit best for stroke with R-square values between 0.02 (percent males) and 0.56 (percent blacks). AADT explains 37.84% of the variability in stroke death rate. For lung cancer, the proportion of people age 65 and above has the largest R-square value (0.23).

Tables B6-8 show OLS multivariate regression results for each disease. At the level of 0.10, COPD is significantly positively associated with air pollution from both mobile and point sources, and negatively related to median household income and percent of male population. Stroke shows significant positive relationship with population with age 65 or above and air pollution, and negative relationship with median household income. The same relationships are found for lung cancer death rate. Lung cancer also shows a negative relationship with the percent male population. The stroke model fits best ($R^2 = 0.53$). The lung cancer model has an R^2 value of 0.49. The COPD model has the weakest fit ($R^2 = 0.26$).

Table B-5. Univariate OLS regression of disease rates on suspected factors.

Dependent variable	Independent variable	Slope	*p*-value	*R*-square
COPD	Income	-1.58e-008	0.00450	0.1026
	Black	0.00075	0.00690	0.0932
	Population >65	0.00400	0.00214	0.1187
	Male	-643.033	0.00305	0.1111
	Poor	0.002226	0.00047	0.1513
	Traffic	1.16e-008	0.00323	0.1099
	Greenness	-5.89e-006	0.43225	0.0082
	Point source	0.003351	0.00525	0.0993
Stroke	Income	-1.29E-007	<0.0001	0.2470
	Black	0.00966	0.00000	0.5558
	Population >65	0.03265	<0.0001	0.2830
	Male	-0.0063	0.26835	0.0163
	Poor	0.01607	<0.0001	0.2821
	Traffic	1.136E-007	<0.0001	0.3784
	Greenness	-0.00013	0.00045	0.1522
	Point source	0.01721	0.00680	0.0936
Lung cancer	Income	-3.894e-008	<0.0001	0.1935
	Black	0.00164	0.00085	0.1386
	Population >65	0.00994	<0.0001	0.2272
	Male	-0.00738	<0.0001	0.1910
	Poor	0.00457	<0.0001	0.1975
	Traffic	2.136e-008	0.00247	0.1158
	Greenness	-5.885e-006	0.66302	0.0025
	Point source	0.00650	0.00247	0.1157

Table B-6. Multivariate OLS regression for COPD.

Dependent Variable : **COPD rate**
R-squared : 0.258502 F-statistic : 4.95042
Adjusted R-squared : 0.206284 Prob(F-statistic) : 0.000605213
Sum squared residual:1.75527e-005 Log likelihood : 479.565
Sigma-square :2.47221e-007 Akaike info criterion : -947.13
S.E. of regression : 0.000497214 Schwarz criterion : -933.067
Sigma-square ML :2.27957e-007
S.E of regression ML: 0.000477449

Variable	**Coefficient**	**Probability**
CONSTANT	0.003582364	0.0000160
Income	-1.599449e-08	0.0188372
Population >65	0.00205754	0.1554837
MALE	-0.001912757	0.0997262
Traffic	5.886609e-09	0.0057732
Point source	0.002795998	0.0682218

Table B-7. Multivariate OLS regression for stroke.

Dependent Variable : **Stroke rate**
R-squared : 0.533386 F-statistic : 16.232
Adjusted R-squared : 0.500526 Prob(F-statistic) :1.19759e-010
Sum squared residual: 0.000308776 Log likelihood : 369.17
Sigma-square :4.34896e-006 Akaike info criterion : -726.339
S.E. of regression : 0.00208542 Schwarz criterion : -712.276
Sigma-square ML :4.01008e-006
S.E of regression ML: 0.00200252

Variable	**Coefficient**	**Probability**
CONSTANT	0.002217874	0.0999130
Income	-5.678549e-08	0.0442312
Population >65	0.02213693	0.0001146
Traffic	6.209707e-08	0.0353378
Green	-4.30978e-05	0.1851318
Point source	0.004164622	0.0524035

Table B-8. Multivariate OLS regression for lung cancer.

Dependent Variable : **Lung cancer rate**
R-squared : 0.493561 F-statistic : 13.8389
Adjusted R-squared : 0.457896 Prob(F-statistic) :1.96394e-009
Sum squared residual: 3.872e-005 Log likelihood : 449.106
Sigma-square :5.45352e-007 Akaike info criterion : -886.211
S.E. of regression : 0.00073848 Schwarz criterion : -872.148
Sigma-square ML :5.02857e-007
S.E of regression ML: 0.000709124

Variable	**Coefficient**	**Probability**
CONSTANT	0.006729455	0.0000001
Income	-4.961127e-08	0.0000037
Population >65	0.006191974	0.0048375
MALE	-0.005135011	0.0035637
Traffic	2.799079e-08	0.0041351
Point source	0.006985843	0.0026527

v. Bayesian Hierarchical Modeling of Stroke Mortality and Air Pollution, Income, and Greenness

An ecological geographical approach was adopted using census tract level stroke data and a Bayesian hierarchical model. The mean age-adjusted stroke death rates were 8.39 times the average age-adjusted stroke rate in the US South. Table B-9 provides the estimated posterior mean, median, and associated 95% credible set for each of the fixed effects. Fig.B-10 provides kernel estimates of the corresponding posterior densities. Table B-9 and Fig. B-10 reveal strong negative effects of income and greenness (the posterior densities of β_1 and β_5 primarily covers negative values) and positive effects of both mobile and point source air pollution (the 95% credible sets cover positive values). High risk of stroke mortality was found in areas with low income level, high air pollution level, and low level of exposure to green space.

Table B-9. Markov chain Monte Carlo results for Bayesian hierarchical modelling of stroke mortality vs. income, air pollution, and greenness.*

Fixed Effects	Posterior Mean	Posterior Median	Standard Deviation	MC Error	95% Credible Set
β_0	1.829	1.832	0.083	0.004	(1.661, 1.986)
β_1	-0.193	-0.193	0.047	0.003	(-0.286, -0.097)
β_2	0.089	0.089	0.028	0.001	(0.034, 0.144)
β_3	0.937	0.932	0.276	0.010	(0.419, 1.495)
β_4	0.974	0.980	0.290	0.012	(0.413, 1.522)
β_5	-0.161	-0.161	0.067	0.002	(-0.289,-0.031)

* Posterior means, medians, and 95% credible sets are based on 5,000 postconvergence iterations (from 5,001 to 10,000). Fixed effects are: β_0 - intercept, β_1 - income effect, β_2 - traffic air pollution effect, β_3 - effect of EPA and Florida DEP monitored point source air emission, β_4 - effect of non-monitored point source air pollution, and β_5 - greenness.

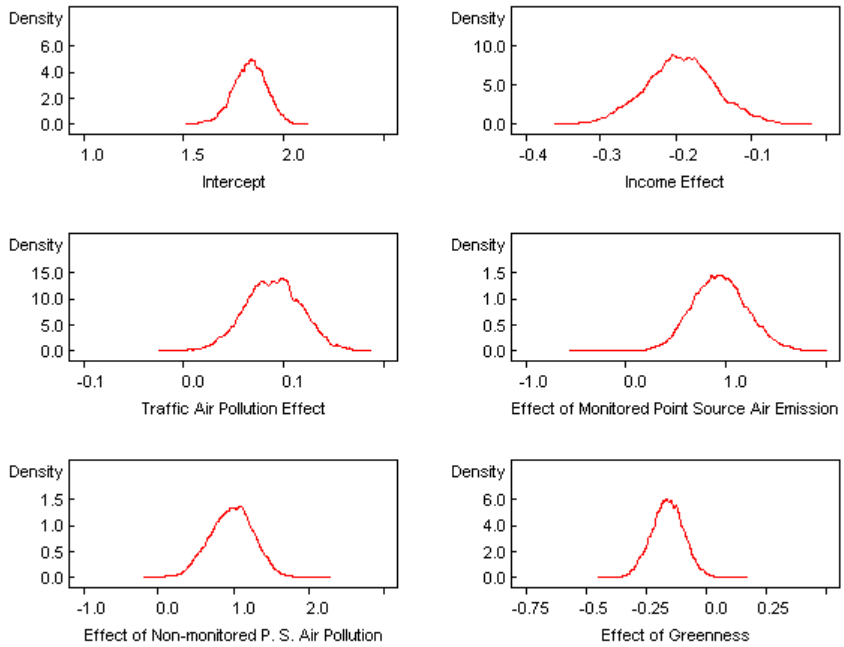


Fig. B-10. Kernel estimates of the posterior density of the fixed effects in the Bayesian hierarchical model.

vi. Correlating MODIS Aerosol Optical Depth Data with Ground-Based $PM_{2.5}$ Observations

Years 2003 and 2004 daily MODIS Level 2 AOD (aerosol optical depth) images were collated with US EPA $PM_{2.5}$ data covering the conterminous USA. Pearson's correlation analysis and geographically weighted regression (GWR) found that the relationship between $PM_{2.5}$ and AOD is not spatially consistent across the conterminous states. The average correlation is 0.67 in the east and 0.22 in the west. GWR predicts well in the east and poorly in the west. The GWR model was used to derive a $PM_{2.5}$ grid surface (Fig. B-11) using the mean AOD raster calculated using the daily AOD data (RMSE = 1.67 $\mu g/m^3$).

There are 4 PM monitors in Escambia and Santa Rosa counties. Table 10 shows EPA monitor source IDs, coordinates, correlations between $PM_{2.5}$ and MODIS AOD, GWR R squares, and GWR constants and AOD coefficients. Fig. B-12 and B-13 show the correlation surface and R squares of geographically weighted regression of $PM_{2.5}$ on MODIS AOD.

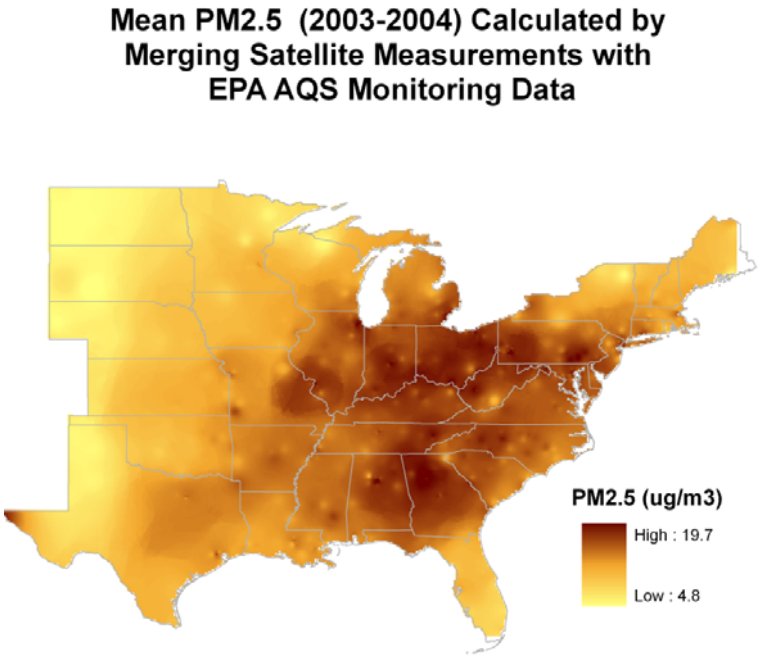


Fig. B-11. $PM_{2.5}$ surface calculated by merging MODIS AOD and EPA $PM_{2.5}$ ground measurements.

Table B-10. Correlation and geographically weighted regression results for the four PM monitoring sites in the study area.

EPA Source ID	Latitude	Longitude	Correlation	GWR R^2	GWR AOD Coefficient	GWR Constant
120330026881011	30.550	-87.376	0.738	0.53	0.023	9.374
120330004881011	30.525	-87.204	0.705	0.509	0.023	9.424
120330025881011	30.437	-87.256	0.647	0.507	0.023	9.386
121130014881011	30.408	-86.890	0.691	0.519	0.023	9.374

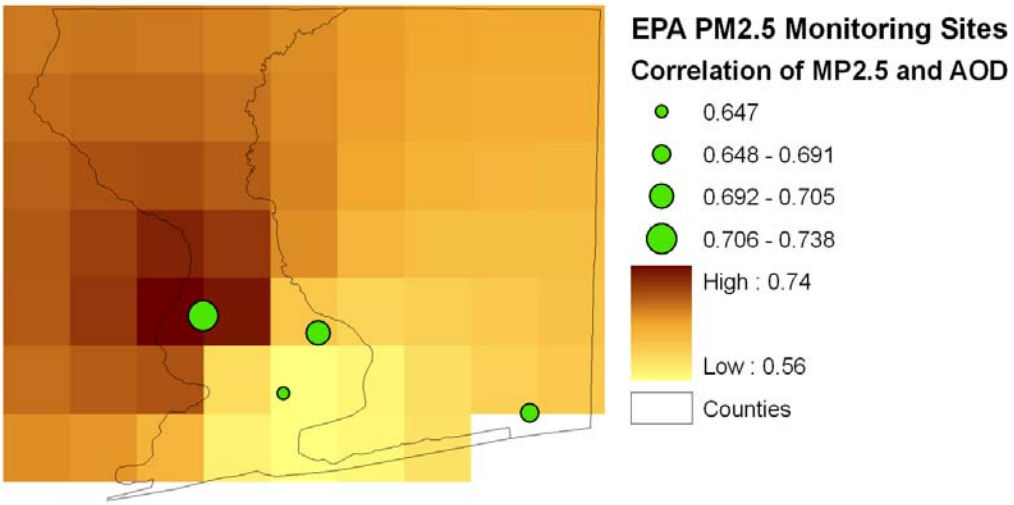


Fig. B-12. Raster surface of correlation between $PM_{2.5}$ and MODIS AOD.

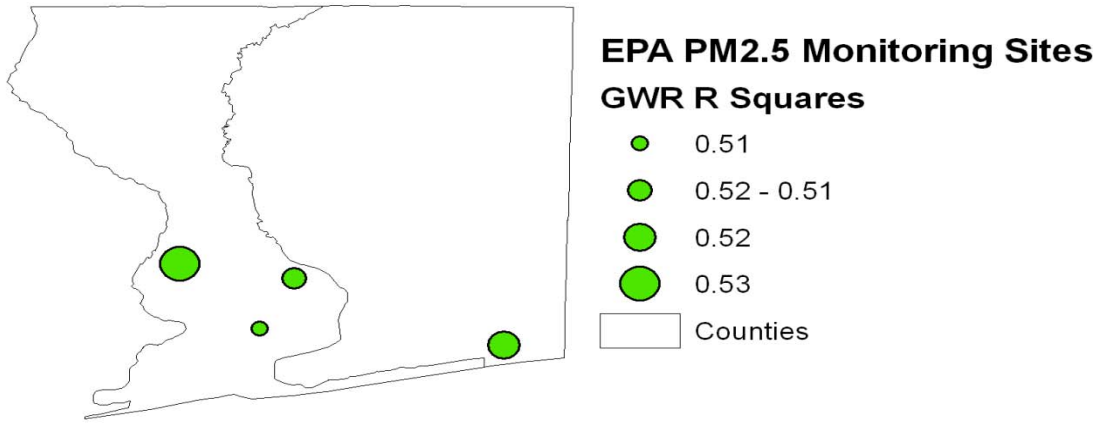


Fig. B-13. R squares of geographically weighted regression of $PM_{2.5}$ on MODIS AOD.

vii. Relationships Between Myocardial Infarction (MI) and AOD

Two models were fitted to examine the effect of AOD on MI. One is a spatial error model and the other is a Bayesian hierarchical model. The spatial error model used SMR as the dependent variable and AOD as the explanatory variable. Model results are shown in Table B-11. The coefficient on the spatially correlated errors (λ) has a positive effect and is highly significant. AOD has a significantly positive coefficient (coefficient = 2.3173, p <0.001). Higher risk of MI is associated with higher aerosol optical depth.

A Bayesian hierarchical model was also fitted with a convolution prior to considering a county specific covariate – AOD. Table B-12 and Fig. B-14 show the model results. The AOD coefficient kernel density curve reveals a positive effect of AOD on MI. The 95%

credible set is (0.3208, 0.4708) for the AOD effect. Similar to the spatial error model above, the Bayesian model showed positive association between MI and AOD.

Table B-11. MI and AOD: spatial error model.

SUMMARY OF OUTPUT: SPATIAL ERROR MODEL - MAXIMUM LIKELIHOOD ESTIMATION

Spatial Weight	: cook_weight.GWT		
Dependent Variable	: SMR	Number of Observations:	589
Mean dependent var	: 0.929524	Number of Variables	: 2
S.D. dependent var	: 0.164615	Degree of Freedom	: 587
Lag coeff. (Lambda)	: 0.561258		
R-squared	: 0.298463	R-squared (BUSE)	: -
Sq. Correlation	: -	Log likelihood	: 324.058852
Sigma-square	: 0.019010	Akaike info criterion	: -644.118
S.E of regression	: 0.137878	Schwarz criterion	: -635.360851

Variable	Coefficient	Std.Error	z-value	Probability
CONSTANT	0.5530958	0.04827483	11.45723	0.0000000
AOD	2.317266	0.2843838	8.148373	0.0000000
LAMBDA	0.5612576	0.06995007	8.02369	0.0000000

REGRESSION DIAGNOSTICS
DIAGNOSTICS FOR HETEROSKEDASTICITY
RANDOM COEFFICIENTS

TEST	DF	VALUE	PROB
Breusch-Pagan test	1	1.926539	0.1651376

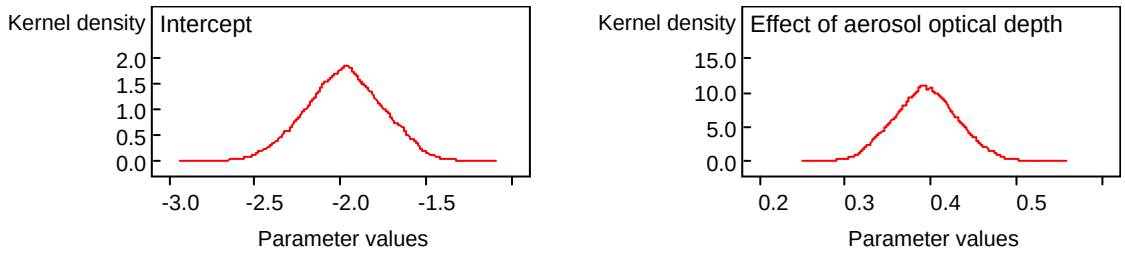
DIAGNOSTICS FOR SPATIAL DEPENDENCE
SPATIAL ERROR DEPENDENCE FOR WEIGHT MATRIX : cook_weight.GWT

TEST	DF	VALUE	PROB
Likelihood Ratio Test	1	51.29031	0.0000000

Table B-12**.** Markov chain Monte Carlo simulation results for Bayesian hierarchical modeling of MI vs. AOD.

Node	Mean	Standard Deviation	MC Error	2.5%	Median	97.5%	Start Iteration No.	Number of Samples
a_0	-1.977	0.2309	0.007435	2.437	-1.976	-1.536	10000	180002
a_1	0.3943	0.03839	0.001234	0.3208	0.394	0.4708	10000	180002

a_0 – Intercept, a_1 - Effect of aerosol optical depth (AOD)



Kernel estimates of the posterior densities of the fixed effects in the Bayesian hierarchical model

Fig. B-14. Coefficient kernel density curves, Bayesian hierarchical model (SMR of MI vs. AOD) for eastern US.

viii. Relationships Between Chronic Coronary Heart Disease (CCHD) and AOD

Race and age standardized mortality rate (SMR) of CCHD was computed for each of the 2306 counties in the eastern USA for the time period 2003-2004. A mean AOD raster grid for the same period was derived from Moderate Resolution Imaging Spectrometer (MODIS) aerosol data and the average AOD was calculated for each county. A bivariate Moran's I scatter plot, a map of local indicator of spatial association (LISA) clusters, and three regression models (ordinary least square, spatial lag, and spatial error) were used to analyze the relationships between AOD and CCHD SMR. The global Moran's I (Fig. B-15) value is 0.2673 (p =0.001), indicating an overall positive spatial correlation of CCHD SMR and AOD. The entire study area is dominated by spatial clusters of AOD against SMR (high AOD and high SMR in the east, and low AOD and low SMR in the west) (permutations = 999, p =0.05) (Fig. B-16). Of the three regression models, the spatial error model achieved the best fit (R^2 =0.28). The effect of AOD is positive and significant (beta = 0.7774, p = 0.01) (Table B-13).

Aerosol particle pollution has an adverse effect on CCHD mortality risk in the eastern US. High risk of CCHD mortality was found in areas with elevated levels of outdoor aerosol pollution, as indicated by satellite derived AOD. Escambia and Santa Rosa counties of Florida have relatively low rates of CCHD (SMR< 1) (Table B-14). The LISA map shows that the two counties have high AOD values but low SMRs (Fig. B-16).

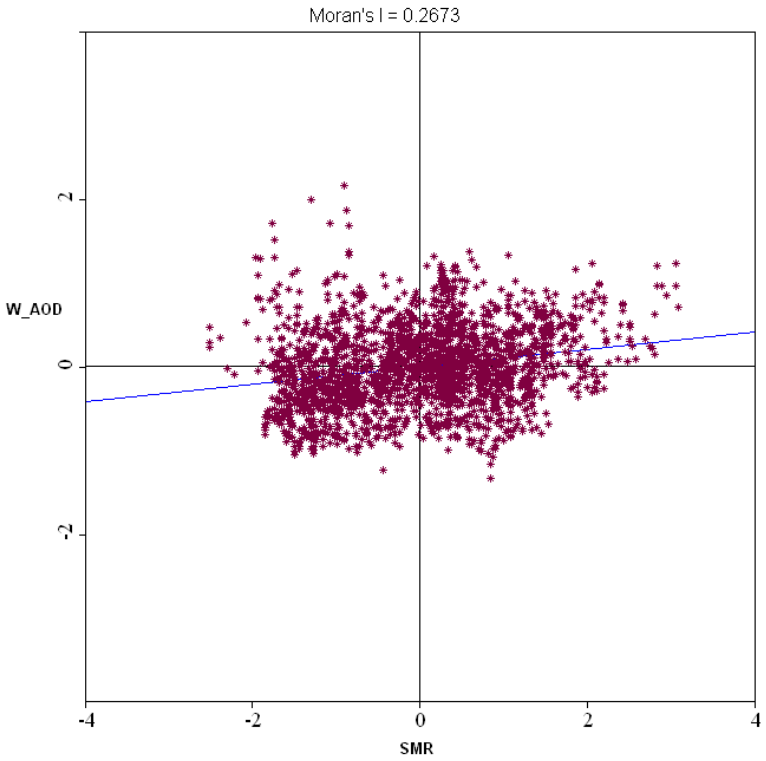


Fig. B-15. CCHD rate and AOD: bivariate Moran's I scatter plot.

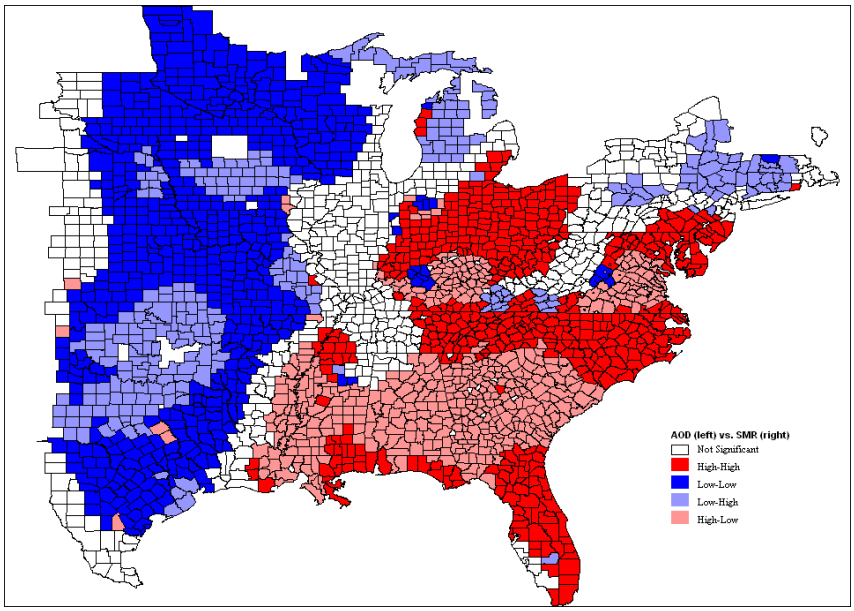


Fig. B-16. CCHD rate and AOD: local indicator of spatial association (LISA).

Table B-13. Spatial error regression model.

Model description					
	Y	No. of variables	No. of observations	Degrees of freedom	
	SMR	2	2306	2304	
Model fit					
		R^2	Log likelihood	AIC	
		0.2800	-201.834	407.669	
Model estimation					
	Variable	Coefficient	Std. Error	t-Statistic	*p*
	CONSTANT	0.7506	0.0509	14.759	0.0000
	AOD	0.7774	0.3022	2.573	0.0101
	λ	0.5678	0.0231	24.600	0.0000
Diagnostic tests					
		Tests	DF	Value	*p*
Heteroskedasticity		Breusch-Pagan	1	0.067	0.7954
Spatial dependence		Likelihood Ratio	1	501.856	0.0000

Table B-14. CCHD, AOD and $PM_{2.5}$ data for Escambia and Santa Rosa Counties.

County	Observed CCHD	Expected CCHD	SMR	AOD	$PM_{2.5}$
Escambia	1584	1675	0.946	0.197	12.334
Santa Rosa	531	542	0.980	0.194	12.507

ix. Association of CCHD with $PM_{2.5}$

A Bayesian hierarchical model was employed to link $PM_{2.5}$ predicted with the GWR model with age-race standardized mortality rates (SMRs) of chronic coronary heart disease (CCHD). The study found that chronic coronary heart disease mortality rate increases with exposure to $PM_{2.5}$. (Fig. B-17 and Table B-15). High risk of CCHD mortality was found in areas with elevated levels of fine particulate air pollution. The association between CCHD mortality and $PM_{2.5}$ justifies the need of further toxicological studies of the influence of fine particulate air pollution on the heart. The evidence of raised CCHD mortality risk in high pollution areas supports targeting policy interventions on such areas to reduce pollution levels. Aerosol remote sensing like that used in the present study could help fill pervasive data gaps that impede efforts to study air pollution and protect public health.

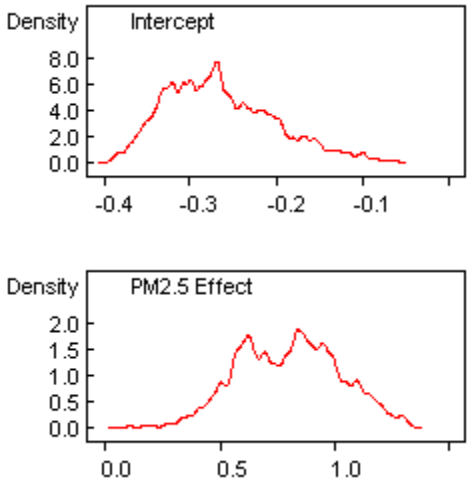


Fig. B-17. Kernel estimates of the posterior densities of the fixed effects in the Bayesian hierarchical model.

Table B-15. Results of Bayesian hierarchical modeling.

Fixed effects	Posterior mean	Posterior median	Standard deviation	MC error	95% Credible set
β_0	-0.264	-0.273	0.064	0.003	(-0.366, -0.117)
β_1	0.802	0.812	0.223	0.010	(0.386, 1.225)

* Posterior means, medians, and 95% credible sets are based on 20,000 post-convergence iterations (from 60,001 to 80,000). Fixed effects are: β_0 - intercept, β_1 – effect of $PM_{2.5}$.

6. Overall Conclusions

The health tracking study carried out by PERCH indicates that some Zip codes in Escambia and Santa Rosa Counties have worse health outcomes than socio-economically and demographically matching Zip codes elsewhere in Florida, but other Zip codes in the area have better health outcomes than their matching Zip codes. These variations in health outcomes do not show clear spatial trends nor are they consistent for any one specific health outcome. An initial study of air pollution suggests that the proximity to stationary air emission sites may influence the incidence of some of the specific health outcomes, but not overall health. Geostatistical modeling corroborates this observation. Other exposures and life style decisions not evaluated in the PERCH studies may also affect the incidence of these specific health outcomes. A PERCH study that examined risk associated with inhalation of air pollution identified four zones with elevated cancer risk. One of these zones, the smallest one, coincides spatially with parts of Zip codes that have an elevated incidence of some health outcomes, but a direct cause and effect between risk and incidence was not established.

7. Outcomes and Perspectives

PERCH project studies provided, for the first time, a detailed analysis of air quality and the potential impacts on human health in Northwest Florida. These analyses included novel methodologies (e.g., proximity index analysis, geostatistical analysis) that could have wider applications nationally and abroad. RAIMI system, first developed and applied by EPA Region 6, has been successfully applied for analysis of air toxics impacts in Northwest Florida—first such application in the geographic area covered by EPA Region 4.

The results this study have been communicated to the scientific community through presentations at professional meetings and publications in peer-reviewed journals and conference proceedings, and thus contributing new knowledge to the areas of investigation. As a result of our findings, additional collaborative work with Florida Department of Health is being done to assist in ongoing environmental public health tracking.

These results have also been widely publicized through local news media (news papers, TV coverage) and by postings at UWF/CEDB web site. As a result, there is an increased awareness of this project's outcomes among the public, and also recognition of issues of concern by the city, county, and state governmental agencies. This should enable them to facilitate measures to improve air quality and protect public health.

C. Atmospheric Deposition of Mercury and Trace Metals to the Pensacola Bay Watershed

(Task Leaders: Jane M. Caffrey, University of West Florida; William E. Landing, Florida State University)

1. Introduction

Contaminants released into air from local, regional, and distant sources are transported and dispersed in the atmosphere and eventually deposited on to land and water surfaces. This deposition occurs at a wide range of scales, from less than a kilometer to hundreds of kilometers from the emission sources. Atmospheric deposition represents a significant source of nutrients and other contaminants in many watersheds, and can have a negative impact on plant and animal communities, ecosystem function, and human health.

Monitoring networks--e.g., National Atmospheric Deposition Program (NADP) and the Mercury Deposition Network (MDN)—examine long-term trends in atmospheric deposition at regional scales, and the derived regional and national trends provide critical information necessary for determining policies to improve air and water quality at the national level. The NADP and MDN programs do not have monitoring stations in our two-county area. In order to improve water quality at the Pensacola Bay watershed level, the contributions of local sources in addition to regional sources need to be determined.

As summarized earlier (Section III.A), the PERCH program partners from the Georgia Institute of Technology have assessed the air quality in the Pensacola area, including the emission sources and the transport of pollutants from local, regional, and distant sources, as well as the potential human health impacts of air toxics from local point sources and mobile sources. This project's contribution to the PERCH program is to identify the atmospheric contaminants deposited by rain in the Pensacola area. Based on current knowledge of local air

pollution releases and stakeholder concerns for environmental quality and human health, rain samples collected at three different sites in the Pensacola Bay area during a period of three years were analyzed for constituents such as mercury, nitrate, sulfate, phosphate, and a suite of trace metals. The temporal and spatial patterns in atmospheric deposition determined at 3 sites in the Pensacola Bay watershed are compared with data from MDN and NADP sites (locations in Table C-1) in the Southeast Region along the Gulf Coast. The historic deposition rates for mercury and phosphorus were also evaluated through analysis of sediment cores and the previously reported unusually high water column mercury levels in a local lake (Woodbine Lake, Pace, Santa Rosa County) were reexamined. The locations of these sampling sites are shown in Fig. C-1.

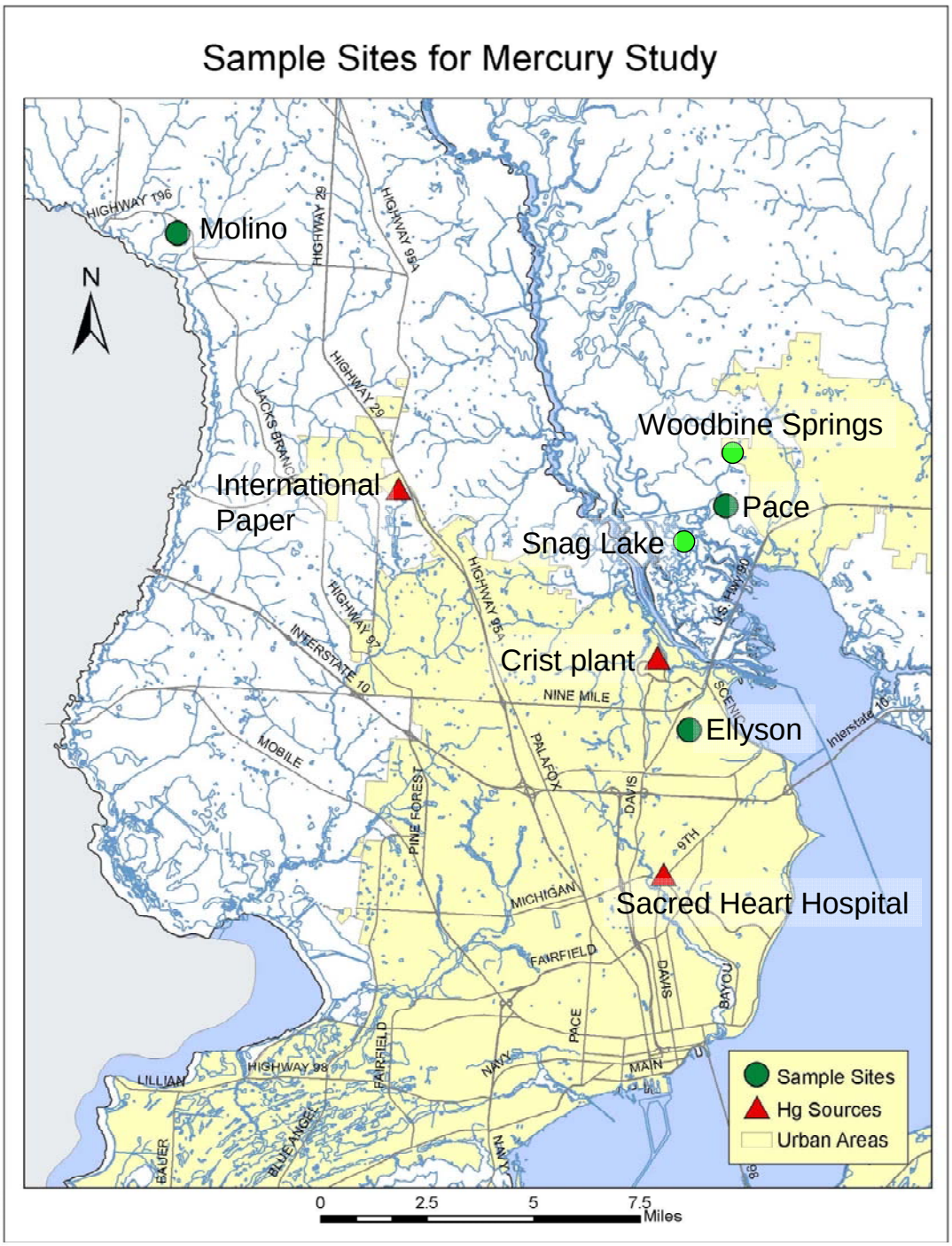


Fig. C-1. Map of Pensacola Bay showing sampling locations: Ellyson Industrial Park, Molino, and Pace for atmospheric deposition collection, Snag Lake for sediment core collection, and Woodbine Springs for water collection. Mercury emission sources: Plant Crist, International Paper, Sacred Heart Hospital medical waste incinerator.

Table C-1 – NADP and MDN sites used to compare with Pensacola Bay data

Site Location	Latitude	Longitude
LA30 (NADP)	30.7819 °N	90.2021 °W
LA 12 (NADP)	29.931 °N	91.7165 °W
LA 28 (MDN)	30.5031°N	90.3769 °W
MS22 (MDN)	30.985 °N	88.9319 °W
AL 24 (NADP, MDN)	30.4746 °N	88.1411 °W
AL02 (NADP, MDN)	30.7905 °N	87.8497 °W
FL14 (NADP)	30.5486 °N	84.6004 °W
FL23 (NADP)	30.1106 °N	84.9902 °W

2. Results and Outcomes

Over the course of this study from November 19, 2004 through January 2, 2008, 565 rain samples were collected from 3 sites. These samples represent about 225 separate rain events in the Pensacola Bay watershed.

a. Mercury Concentrations in Rainfall

Concentrations of mercury and trace metals such as arsenic, selenium, and aluminum were generally higher in low volume samples. With larger storms, trace element and major ion concentrations are diluted leading to a washout effect. This effect was most obvious for mercury and selenium and less apparent for aluminum.

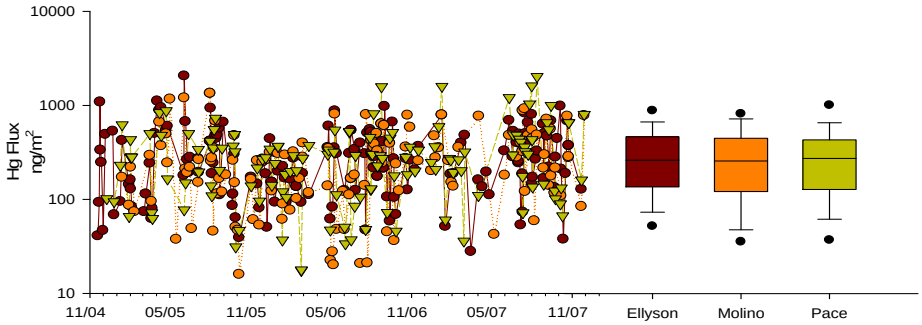


Fig. C-2. Mercury (Hg) deposition (ng/m^2/event) at Ellyson (brown), Molino (orange) and Pace (green) between November 2004 and December 2007 for individual rain events (left side). Box plot (right side) for each site, showing median, 25th and 75th percentiles (box boundary), 10th and 90th percentiles (whiskers), and 5th and 95th percentiles (circles).

Mercury deposition showed no site differences among the three sites in the Pensacola Bay watershed (Fig. C-2). Mercury fluxes from individual events ranged between 13 and 2050 ng/m^2. There were significant seasonal differences. The highest mercury deposition occurred in the summer (403 $\pm$19.9 ng/m^2/event) compared to other seasons (fall 286 $\pm$18 ng/m^2/event, winter 245$\pm$15 ng/m^2/event, spring 333$\pm$24 ng/m^2/event). Inter-annual differences were significant with the highest average deposition in 2007 (400.7 ng/m^2/event) and the lowest in 2006 (286 ng/m^2/event).

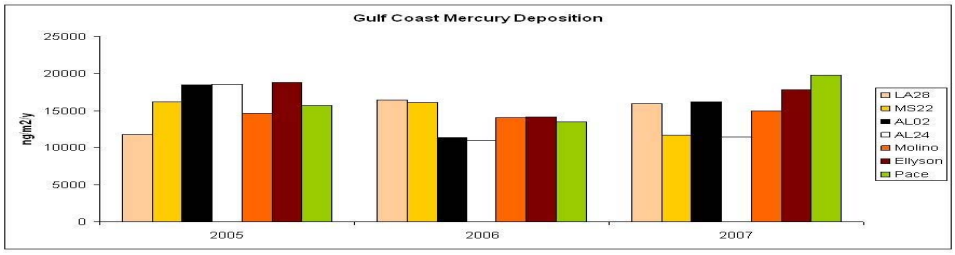


Fig. C-3. Annual mercury deposition at the three Pensacola Bay sites and at regional MDN sites in the Gulf coastal states.

Mercury fluxes and total mercury deposition at the Pensacola Bay sites are similar to those noted at the MDN sites along the central Gulf of Mexico region (Fig. C-3) during our study period (2005-2007). There were no inter-annual differences in mercury fluxes, although seasonal fluxes were significantly different from one another. The total mercury deposition observed at all these sites follows the historic pattern of relatively high mercury deposition rates in the Southeastern U.S. Because of the large number of mercury emission sources in the Southeast region and mixing of air masses from different regions, it is not surprising that we are unable to see a direct effect of local emission sources on the amount of mercury deposited to Pensacola Bay in rain. It is also relevant to note that, based on 2002 data, mercury emissions from nearby Mobile and Escambia counties from Alabama (780 and 880 lbs, respectively) are much higher than those from the principal mercury emission source, Crist coal-fired power plant (180 lbs), in Pensacola. The combined emissions from local and regional sources, largely resulting from coal-fired power plants, seem to influence mercury deposition in our area.

As we observed with the Pensacola Bay data alone, summer fluxes were significantly higher than fluxes during the other months at the MDN sites along the central Gulf of Mexico region. Summer mercury fluxes represented an average of 44% of the total annual mercury flux at these sites and could represent as much as 60% for some sites in some years. Higher summer mercury deposition is not driven by higher rainfall amounts, but by higher concentrations in the rain since the highest rainfall amounts are usually in the spring and fall. Several potential mechanisms that could lead to enhanced mercury concentrations in rain during the summer include greater emissions associated with higher electricity use, scavenging of reactive gaseous mercury from the free troposphere by tall convective thunderstorms, and the concentration of reactive gaseous mercury by the sea breeze effect, where the diurnal alternation of onshore and offshore winds can lead to a buildup of pollutants

in the air mass. As with seasonal differences, inter-annual variability was not strictly driven by rainfall amount since the year with the highest rainfall, 2005, had an intermediate mercury deposition rate.

b. Trace Element Concentrations in Rainfall

Arsenic (As) and tin (Sn) had no consistent differences among the different sites (Table C-2). Average arsenic flux was 4.0 $\mu g/m^2$/event and values ranged between 0.15 and 22.1 $\mu g/m^2$/event. The average tin flux was 2.4 $\mu g/m^2$/event with a range of 0.1 and 247 $\mu g/m^2$/event. In contrast, selenium was different among the sites, with significantly higher deposition at Pace (7.03 $\mu g/m^2$/event) than at either Ellyson (3.96 $\mu g/m^2$/event) or Molino (3.65 $\mu g/m^2$/event) (Table C-3). Most of the trace metals had similar deposition at different sites, except for copper, chromium and zinc (Table C-3). Copper and chromium deposition rates were significantly higher at Ellyson than at Molino. Zinc deposition was significantly higher at Ellyson than at either Molino or Pace. The higher deposition of copper, chromium and zinc at the Ellyson site compared to Molino site may be a result of industrial activity at the Ellyson site and higher emissions of these elements.

Table C-2 – Average deposition of trace metals in rain events at three sites in Pensacola Bay. Average and Standard error (SE). ANOVA test of site differences, p values. NS = non-significant

	Ellyson	SE	Molino	SE	Pace	SE	ANOVA
Aluminum μg/m^2/event	1251	114	992	104	1120	69	NS
Antimony ng/m^2/event	998	76	830	77	918	65	NS
Arsenic μg/m^2/event	4.38	0.46	3.60	0.38	3.86	0.22	NS
Barium μg/m^2/event	21.13	1.40	17.30	1.66	20.52	1.40	NS
Bismuth ng/m^2/event	49.94	5.06	41.86	4.57	46.85	4.07	NS
Cadmium ng/m^2/event	143.2	26.9	120.2	17.5	189.1	16.1	NS
Cobalt μg/m^2/event	0.62	0.05	0.51	0.05	0.58	0.03	NS
Copper μg/m^2/event	7.24	0.52	4.56	0.42	5.93	0.47	p = 0.007
Chromium μg/m^2/event	2.51	0.26	1.53	0.12	1.96	0.11	p 0.003
Cesium ng/m^2/event	120.34	11.07	105.15	12.50	118.90	7.31	NS
Gallium ng/m^2/event	1023	106	885	85	955	51	NS
Iron μg/m^2/event	603	54	485	55	550	36	NS
Lithium ng/m^2/event	1351	149	1073	109	1141	69	NS
Magnesium μg/m^2/event	2473	613	1520	252	1630	100	NS
Manganese μg/m^2/event	26.05	2.23	21.66	2.31	25.19	1.66	NS
Nickel μg/m^2/event	7.60	0.90	6.25	0.59	7.67	0.49	NS
Phosphorus μg/m^2/event	106.4	9.8	137.3	20.5	131.9	10.5	NS
Lead ng/m^2/event	6249	467	5485	595	5745	402	NS
Selenium μg/m^2/event	3.96	0.44	3.65	0.42	7.03	0.80	p = 0.03
Silicon μg/m^2/event	1833	193	1575	211	1728	122	NS
Strontium μg/m^2/event	20.33	3.53	13.77	1.80	15.22	0.85	NS
Tin μg/m^2/event	1.35	0.14	1.48	0.15	1.42	0.10	NS
Vanadium μg/m^2/event	8.18	0.96	6.30	0.76	7.55	0.51	NS
Zinc μg/m^2/event	51.36	7.59	29.23	3.36	31.91	2.58	p = 0.009

c. Precipitation Chemistry

The amount of precipitation was not significantly different among the 3 Pensacola Bay sites, nor were there any significant inter-annual differences. However, seasonal differences were significant with the highest rainfall in the spring and fall and the lowest during winter. H^+ fluxes were similar among the 3 Pensacola Bay sites, with no consistent differences among the stations. Again there were no significant inter-annual differences, but there were significant seasonal differences with the highest H^+ flux in summer and the lowest during winter and fall.

Sulfate fluxes were also similar among the different sites and had no significant seasonal or inter-annual differences. The average sulfate flux was 40.43 mg SO_4/m^2/event and values from individual rain events ranged from 0.5 to 438 mg SO_4/m^2/event.

There were no significant site-to-site differences in nitrate fluxes. The average nitrate flux was 35.6 and values ranged from 0.5 to 285 mg NO_3/m^2/event. Nitrate fluxes in 2007 (19.5 mg NO_3/m^2/event) were significantly lower than in 2005 (45.5 mg NO_3/m^2/event) or 2006 (43.2 mg NO_3/m^2/event). Nitrate fluxes were also significantly lower during the winter (16.5 mg NO_3/m^2/event) and fall (26.0 mg NO_3/m^2/event) compared to spring (56.4 mg NO_3/m^2/event) and summer (45.1 mg NO_3/m^2/event).

Ammonium fluxes were about ten percent of nitrate fluxes and had no site or inter-annual differences. Average ammonium flux was 4.35 and values ranged from 0.04 to 46.3 mg NH_4/m^2/event. The seasonal pattern was the same as nitrate fluxes with higher fluxes in the spring (9.2 mg NH_4/m^2/event) and summer (5.2 mg NH_4/m^2/event) and lower fluxes during the fall (1.9 mg NH_4/m^2/event) and winter (2.5 mg NH_4/m^2/event).

Chloride fluxes had a larger range than the other major element fluxes, with a few fluxes exceeding 1000 mg/m^2/event, particularly at Ellyson. This is likely due to the accumulation of sea salt aerosols in rainwater. The average chloride flux was 58.76 and values ranged from 0.6 to 2,070 mg/m^2/event. There were no significant differences in chloride fluxes among the different sites, years, or seasons.

Sodium fluxes also had a large range and generally tracked the chloride concentrations. As observed with the chloride fluxes, sodium fluxes had no significant differences among the different sites, years or seasons. Average sodium fluxes were 24.5 and values ranged from 0.2 to 938 mg/m^2/event.

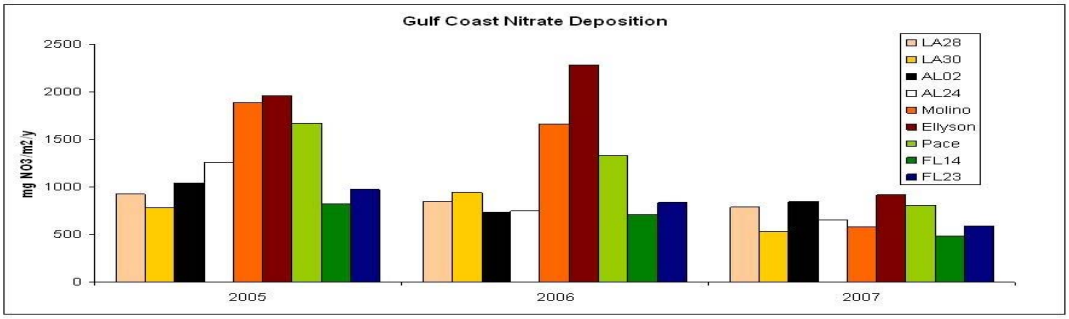


Fig. C-4. Comparison of nitrate fluxes at the three Pensacola Bay sites with data from NADP sites in Gulf coastal states.

Sites in Pensacola Bay area were often higher than NADP sites for H^+, sulfate, nitrate, ammonium, chloride and sodium fluxes (Table C-3). H+ fluxes at Ellyson and Pace were significantly higher than at all other NADP sites, while fluxes at Molino were significantly higher than FL14 and LA30. Sulfate fluxes at Ellyson were significantly higher than all NADP sites, Pace was significantly higher than NADP sites in Florida and Louisiana, while Molino was significantly higher than the NADP sites in Florida. Nitrate fluxes at all Pensacola Bay sites were significantly greater than NADP sites (Fig. C-4). Ammonium flux at Ellyson was greater than FL14 and FL23. Ammonium flux at the NADP site LA30 was also greater than those at FL23. Chloride fluxes at Ellyson were greater than those at Molino and all NADP sites, while Pace was greater than the NADP sites in Florida, Louisiana and at AL02. Sodium fluxes were significantly higher at Ellsyon than at all NADP sites. Pace also had significantly higher sodium fluxes than at all NADP sites except for AL24.

There were significant seasonal differences in sulfate, nitrate, ammonium and chloride fluxes with sulfate, nitrate and ammonium having higher fluxes in the spring and summer than the other seasons. Chloride fluxes were highest in the fall. Inter-annual differences were significant for sulfate and nitrate fluxes with higher fluxes in 2005 and 2006 compared to 2007. H^+ and ammonium flux declined over the three years of observations.

Table C-3 – Analysis of variance in mercury and major ion fluxes for Pensacola Bay sites, National Atmospheric Deposition Program (NADP) sites and Mercury Deposition Network (MDN) sites along the eastern Gulf of Mexico. P values reported, NS is non significant. Seasons are spring (Sp), summer (Su), fall (Fa) and winter (W).

Constituent	Site	Season	Year
Mercury	NS	p<0.001 (Su> Sp, Fa & W)	NS
H^+	p<0.001	p<0.0001 (Su> Sp, Fa & W)	p=0.028 ((2005 > 2006 & 2007)
Sulfate	p<0.001	p<0.0001 (Sp & Su> Fa & W)	p<0.0001 (2005 > 2006>2007)
Nitrate	<0.001	p<0.001 (Sp & Su> Fa & W)	p<0.0001 (2005 & 2006>2007)
Chloride	p<0.001	p=0.03 (Fa> Sp & Su & W)	NS
Sodium	p<0.001	NS	NS
Ammonium	p=0.03	p<0.001 (Sp > Su> Fa & W)	p<0.001 (2005 > 2006>2007)

As noted above, the deposition of major ions (sulfate, chloride, nitrate, sodium, H+, or ammonium) was similar among the Pensacola Bay sites and often significantly higher than NADP sites. The NADP sites in Florida (FL14 and FL23) often had the lowest values of all the sites examined. This may be due to differences in how the sites were located. NADP criteria for site locations is that they should be 10 km away from urban areas or pollution sources or 40 km away from upwind pollution sources or population centers greater than 75,000. The Florida NADP sites are much farther from urban centers and major pollution sources than either the Alabama NADP or our Pensacola Bay sites. Pensacola Bay sites were not chosen by those criteria because we were interested in capturing deposition from local sources. While the Molino site is about 14 km from International Paper and 20 km away from other pollution sources in Pensacola, it still is high for sulfate and nitrate, which are often associated with fossil fuel combustion. Again, mixing of air masses carrying releases from local and regional sources would account for the observed results.

It is of interest to note, however, that the deposition rates in rain for several ions at the monitoring sites show significant correlation to air emissions (Fig. C-5), with correlation coefficients of 0.95 (ammonium), 0.80 (nitrate), and 0.68 (sulfate). These correlations are between the average annual deposition at the monitoring sites (during 2005-2007) and the air emissions reported for the year 2002 in the corresponding counties where the monitors are located. The differences in the correlation coefficients among the ions seem to be attributable to potential differences in the relative influence of local vs transported emissions at the monitoring sites. This is supported by PERCH air quality studies (Section III.A) in which the source apportionment of $PM_{2.5}$ in the Pensacola area indicated that ammonium concentrations were more sensitive to local sources, whereas sulfate concentrations were more sensitive to distant sources.

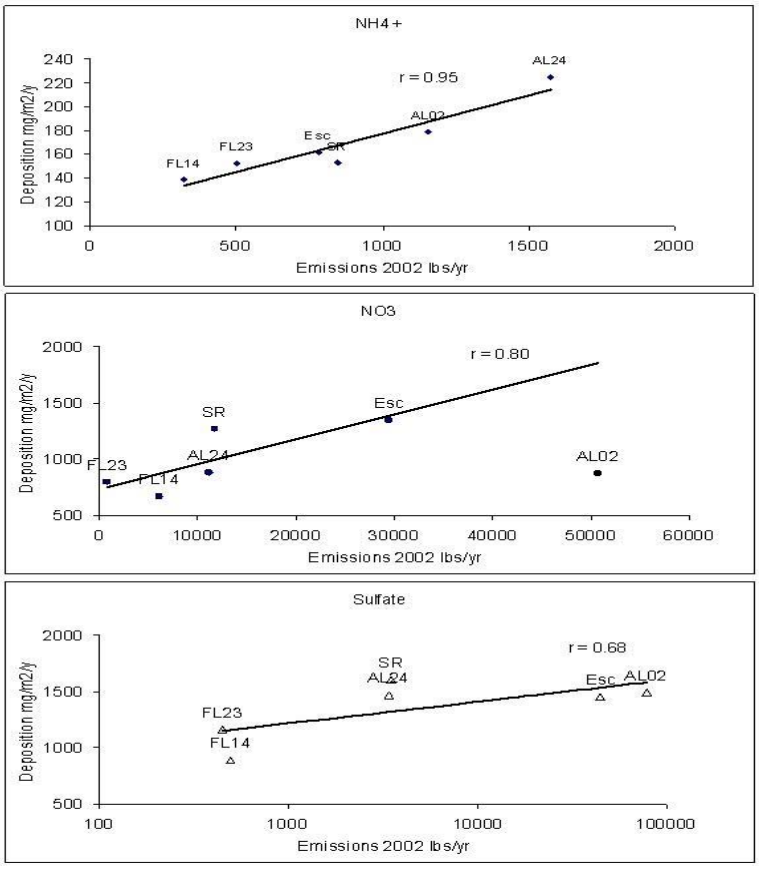


Fig. C-5. Correlation of average annual deposition of ammonium, nitrate, and sulfate (2005-2007 data) with air emissions (2002 data) in the corresponding counties where the monitoring sites are located. Esc: data from Molino and Ellyson sites in Escambia County, FL; SR: data from the Pace site in Santa Rosa County, FL.

d. Correlation Analysis and Source Tracking

Sea salt aerosols have a significant impact on chemistry of rain water in the Pensacola Bay area. Elements associated with sea water were highly correlated, including sodium, chloride, magnesium and strontium. The correlation coefficient among these elements was greater than 0.8 ($p < 0.001$). About 21% of the rainfall events had Cl:Na ratios near the seawater Cl:Na ratio of 1.79. However, chloride fluxes were enriched relative to the seawater ratio in about 63% of the rain events. This suggests that there is another source of chloride in rainwater.

The distance of the sampling site to the Gulf of Mexico determines how significant an effect sea salt aerosols have on rain water composition. Sites that are further from the Gulf have lower average annual sodium fluxes than those near to it. There was a similar pattern for chloride fluxes. Fifty km appears to be the distance where the line becomes asymptotic and the sea salt effect is lost.

Element ratios are a useful tool for examining potential sources in rain water. Our samples were highly enriched in some constituents relative to sodium. The sulfate to sodium ratio was 4 to 100 times greater than seawater ratio. Only 2% of the rain events had sulfate:sodium ratios near the seawater ratio. The highest ratios generally occurred in the summer, particularly in 2005.

In addition to sea salt, dust from the earth's crust is a significant component of the elements found in rain water. Correlation analysis revealed that elements from the earth's crust were highly correlated with one another ($r > 0.8$, $p < 0.001$). These elements were aluminum, barium, cesium, cobalt, chromium, iron, lithium, manganese, and silicon. Although mercury was significantly correlated ($p < 0.01$) with most of these elements, it was not a very strong relationship with most correlation coefficients at 0.40 or less. The ratio of mercury to aluminum in rain was much higher than the ratio found in the earth's crust. Most values generally occurred between the ratios found in coal and industrial emissions such as fossil fuel combustion and other industrial particulate emissions. However, during some rainfall events, the mercury to aluminum ratio was higher even than the industrial emissions ratio. There was a similar pattern in ratios of some other elements to aluminum.

Mercury was more closely correlated with a variety of other elements or major ions that are indicative of pollution sources (Table C-4). The strongest correlations were with selenium, antimony, arsenic and sulfate. Selenium is often associated with coal combustion, while sulfate and nitrate are associated with fossil fuel combustion. Arsenic and selenium were significantly correlated with one another ($r = 0.53$) as were arsenic and antimony ($r = 0.63$) and selenium and antimony ($r = 0.61$). Mercury was also correlated with lead ($r = 0.58$), bismuth ($r = 0.51$) and gallium ($r = 0.51$). Cadmium and zinc were also significantly correlated with each other ($r = 0.70$). These results are similar to those observed in other studies where mercury and trace metals associated with coal combustion and other industrial activities were correlated.

Table C-4. Correlation coefficients of mercury and elements or major ions

Constituent correlated with mercury	Correlation coefficient
Selenium	0.70
Arsenic	0.67
Antimony	0.67
Sulfate	0.64
Nitrate	0.59
Lead	0.58
Gallium	0.51
Bismuth	0.51

From our multi-element data, we estimated the contribution from coal combustion to the rainfall Hg deposition utilizing two methods that included an initial correction of the rainfall chemistry data to subtract out the impacts on trace element chemistry due to mineral dust aerosols. For the first method, we make the assumption that the proportions of mercury and other trace elements vaporized during coal combustion are similar to the stack emission ratios, and that those ratios are carried downwind without alteration until the substances are scavenged and deposited by rainfall. For the second approach, we use the actual rainfall data to find samples with high volatile trace element concentrations. These samples are almost certainly impacted by anthropogenic atmospheric emissions. Based on these analyses, our estimates indicate that 25 to 51% of the mercury in rain samples is attributable to regional coal combustion.

We performed meteorological modeling based on back trajectory and plume dispersion on each rain event during our study period. NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory Model (Hysplit) version 4.7 was used with the archived EDAS 40km grid meteorological dataset for the models. No significant pattern emerged from the resulting model outputs.

Shortly after we completed our three-year sampling for the PERCH project, EPA has conducted mercury and trace metal analyses of the Plant Crist plume. This included quantification of different forms of mercury--reactive gaseous mercury (RGM), which is usually deposited in areas closer to the emissions, and elemental mercury that can be transported to distant sources—as well as diverse trace elements. When EPA releases the results of this study, it may be possible to discriminate between emissions from the Plant Crist and other sources.

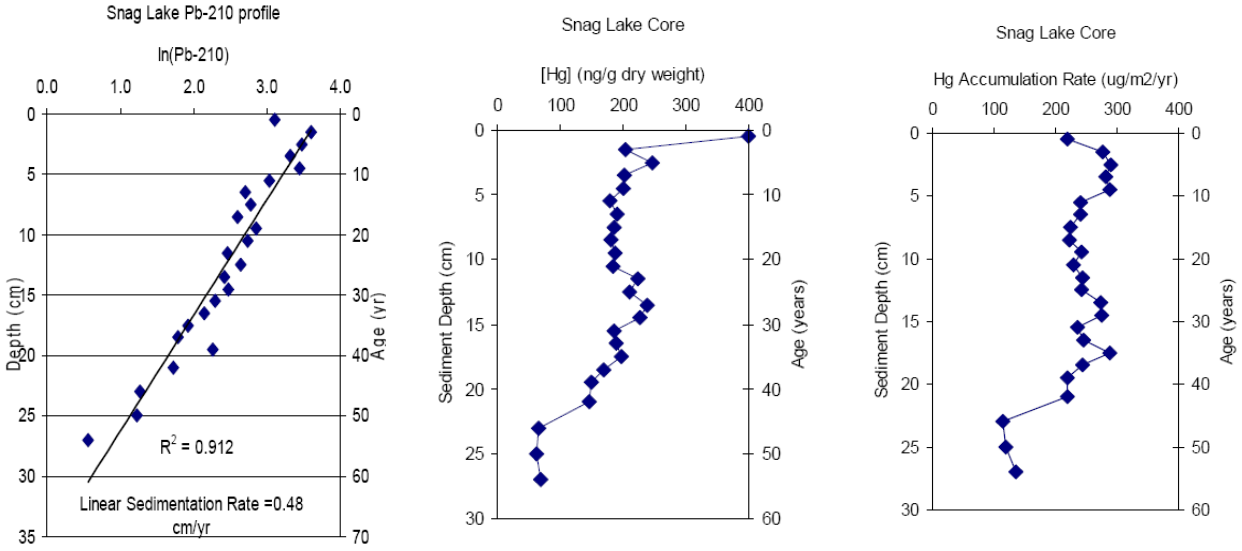


Fig. C-6. Pb-210 profile from Snag Lake, Pensacola. The linear sediment accumulation rate is estimated to be 0.48±0.03 cm/yr (left panel). Mercury concentration in sediment (ng/gdw) in center panel and mercury accumulation in right panel.

e. Historic Mercury Deposition in the Pensacola Bay Watershed

Pb-210 analysis was performed on 10 cores collected from various water bodies in the Pensacola area. The best sediment accumulation history was in Snag Lake (Fig. C-6), with a sedimentation rate of 0.48 cm/year. Mercury concentrations ranged from 60 to 400 ng/gdw with a tripling of concentrations between 1950 and 1970 (Fig. C-6). Based on the sediment core from Snag Lake, mercury deposition in the watershed increased during a period when industrialization was occurring in the region and nation.

Snag Lake sediments were fine grain (silt/clay) with a high water content greater than 60%. The organic content was highest in the 7.5 to 15 cm depth layer which corresponds to the 1980s to 1990s. Phosphorus concentrations were intermittently high during this period, with peaks in sediment phosphorus in the 1970s, early 1990s and again in the late 1990s. This suggests that there were intermittent high phosphorus inputs to the area during this time.

f. Analysis of water samples from Woodbine Springs and Woodbine Lake

Florida Lake Watch Program reported that the water column mercury in Woodbine Lake, Pace, was nearly 15-fold higher than the average levels found in Florida Lakes. Woodbine Lake is fed largely by Woodbine Springs. We analyzed water samples from both the Woodbine Springs and Woodbine Lake (Table C-5). Total mercury was higher in Woodbine Lake (9.2 ng/L) than in the Springs (6.7 ng/L). These values are lower than samples collected in 2004 from Woodbine Lake by the Fish and Wildlife Commission and Lake Watch, but still much higher than the average for Florida Lakes. They also measured mercury concentrations in two ponds at the Pace Water Systems property where our

atmospheric deposition collector is located, and in Downey pond which is just south of the Pace Water Systems property. The mercury values in these ponds were similar to those found in other Florida lakes. pH values were lower in Woodbine Springs (5.0) than in Woodbine Lake (6.6), while conductivity was similar at both sites. Lake values for pH, conductivity, sulfate and chloride were similar between 2004 and 2008, while nitrate concentrations were lower in 2008 than 2004. pH values from the nearby ponds were between 6.6 and 6.7.

Table C-5. Woodbine Springs and Lake water samples. Mercury, pH, conductivity, sulfate, nitrate, and chloride measurements. 2004 data from Florida Lake Watch Program. n.d. no data

Analyte	Woodbine Springs	Woodbine Lake	Woodbine Lake	Florida Lakes average
Year sampled	2008	2008	2004	2004
Total mercury (unfiltered) ng/L	6.69 $\pm$0.45	9.21$\pm$0.90	32.00	2.28
Dissolved mercury (filtered) ng/L	6.17$\pm$0.69	8.13$\pm$0.08	18.00	1.40
Particulate mercury %	7.8	11.2	44	38
pH	5.01	6.56	6.64	n.d.
Conductivity mS	46.1	44.8	44.0	n.d.
Sulfate mg SO_4/L	0.30	0.51	0.73	n.d.
Nitrate mg NO_3/L	6.9	1.2	4.9	n.d.
Chloride mg/L	7.2	7.6	6.9	n.d.

The source of mercury in the Woodbine Springs remains to be investigated. Although the levels of mercury in the Woodbine Lake decreased since 2004, they are still considerably high. Fish collected from this lake have the highest mercury residues among similar fish collected from other lakes and rivers in Northwest Florida (Section III.F). Continued monitoring of Woodbine Lake and Springs is needed, and efforts should be made to identify the sources of mercury discharges into these water bodies so as to determine the feasibility of input reductions.

3. Perspectives

The information about the seasonal and spatial patterns in mercury, trace metals, and major ions in this report should prove useful to the State of Florida as it develops a TMDL for mercury. Because of event driven sampling and analyses of trace metals, this report provides a more detailed evaluation of atmospheric deposition in the region than is possible with the data from MDN and NADP networks. Relatively few studies of this sort exist to inform decision-makers as efforts are made to reduce emissions of mercury and other constituents at state and national levels.

The monitoring we conducted during 2005-2007 for the PERCH project is continuing uninterrupted, with support from the Electric Power Research Institute. The extended monitoring is expected to complement the EPA study done in February 2008, "Mercury Speciation in Coal-fired Utility Boiler Emission Plume", at Plant Crist in Pensacola, and also aid in evaluating the effects of scrubbers being added to Plant Crist on air emissions.

Improvements in air quality and water quality at the watershed level depend on pollution abatements at local and regional emission sources. This is particularly relevant to Pensacola Bay watershed system which contains seven sub-watersheds, most of which cross state lines between Florida and Alabama. About two thirds of the 18,000 square kilometer estuarine drainage area is in Alabama and the remainder is in Florida. In the case of mercury, as noted earlier, emissions from nearby counties in Alabama far exceed the output from Pensacola. Therefore, efforts to reduce mercury emissions from coal-fired power plants at various regional locations are desirable.

D. Pollution of Surface Soils in Escambia and Santa Rosa Counties

(Task Leader: Johan Liebens, University of West Florida)

1. Introduction

In many urban areas surface soils have been shown to be polluted and to have the potential to affect the health of humans, especially that of children. Given the emphasis of PERCH on health implications, this project focuses on pollution of soils in public places such as parks, playgrounds, and sports fields where most interaction takes place between people and soils.

Studies of pollution of urban soils usually assess pollution by trace metals because of the presence of multiple sources for these metals in an urban setting. The most commonly identified sources are vehicular traffic, road infrastructure, power plants, and industrial activities. Several studies at other locations have found trace metal concentrations above national and international regulatory limits. Few studies have employed Geographic Information Systems (GIS), like the present one does, to help identify potential sources of the pollution of soils in county-wide or regional scale.

Even though this project focused on a survey of soils throughout the study area, we used a stratified sampling approach to collect a relatively high proportion of samples from the Palafox Industrial Corridor where soils have locally been evaluated and have been found to be polluted with dioxins/furans, polycyclic aromatic hydrocarbons (PAHs), and trace metals. For instance, at the Escambia Treating Company (ETC) site the US EPA and FL DEP have found elevated levels of creosote, pentachlorophenol, and dioxin/furan in the soil. In 1995, US EPA contractors analyzed soil samples from neighborhoods around ETC and found elevated levels of dioxin, PAHs, As, and Pb. These findings led to the relocation of the residents of these neighborhoods. About 10 years later another neighborhood, the Clarinda Triangle, was found to have As, Pb, dioxin, and PAH levels above FL DEP soil cleanup target level (SCTL) for residential areas. Soils at the nearby Agrico Chemical Company (ACC) site have been found to be contaminated with Pb, F, Cr, As, Mn, V, and PAHs by government agencies. As a result, soils and sediments at the site were capped. In 2003 the Florida DEP sampled soils at the Brown Barge Middle School, located across the street from ACC, and found PAHs and As above their Florida DOH health-based screening values.

The overall goal of this project is to assess if soils in public places in Escambia and Santa Rosa Counties have pollution characteristics that necessitate specific management actions. The project has two components, one that evaluates dioxins/furans and PAHs in the Palafox Industrial Corridor in the context of known local pollution issues and regional background concentrations, and one that assesses trace metal concentrations throughout the study area. As part of this overall goal the project will compare pollutant concentrations with regulatory guidelines, shed light on potential human and natural sources for the pollutants by using multiple methodological approaches, and evaluate the likelihood that the pollutants will affect other parts of the environment based on results of sequential extraction.

Preselection of potential sampling sites took place in a GIS using data provided by local government agencies. Field visits to preselected sites resulted in a total of 126 locations being sampled. Twelve of these locations were located in or near the Palafox Industrial Corridor. At nineteen of the 126 locations 3 to 4 samples were collected to examine the influence of proximity to a road on trace metal levels. At twenty-two of the 126 locations a second sample was collected to study the speciation of the trace metals. Only five of the

locations had CCA treated wood structures. An additional sample was collected near these structures. All samples were analyzed for trace metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn), the 12 from the Palafox industrial corridor along with samples from representative sites from both counties were also analyzed for dioxins/furans and PAHs. To better express the toxicity of the dioxins/furans and PAHs, we transformed their raw concentrations into toxic equivalents with methods promulgated by national and international government agencies. For some aspects of the project the trace metal concentrations were transformed into indexes (index of geoaccumulation, enrichment factor, pollution load index) that are a better measure of the pollution level than the raw concentrations.

2. Results and Outcomes

Results for the Palafox Industrial Corridor (Fig. D-1) show that the dioxin/furan TEQs remain below the US EPA screening level for children (50 ng/kg), which is often used to determine whether further site-specific evaluation is to occur. The TEQ values are comparable to those found by EPA contractors in the same general area but have minor variations that can be explained by small scale spatial variations. Even though the TEQ values are below the screening level they are statistically higher than elsewhere in the study area, which illustrates the influence of the local (former) industry on the soils in the industrial corridor. The zone of elevated TEQs is limited to the Palafox Industrial Corridor and quickly drops off to background levels outside the corridor (Fig. D-2). PAHs show a very similar pattern with elevated benzo(a)pyrene equivalent concentrations being limited to the Palafox Industrial Corridor (Fig. D-3). However, 5 of the 12 samples in the corridor exceed the FL DEP residential SCTL (RSCTL) of 0.1 mg/kg TEQ, and thus may justify further study, especially because the highest value (1.06 mg/kg) was observed in a residential area near a school (Fig. D-4). On the other hand, benzo(a)pyrene equivalent concentrations as high as 1.3 mg/kg have been described as background values in the scientific literature.

Trace metal concentrations are generally below their respective RSCTLs. Arsenic, however, exceeds its RSCTL of 2.1 mg/kg at 33 of the 126 sites and thus is of environmental concern. These 33 samples are from locations throughout the study area in both rural and urban settings and do not show a clear spatial pattern (Fig. D-5). This indicates that there is no specific local point source for the As and suggests that the relatively high values are due to a regionally high background concentration. The average As concentration of 1.38 mg/kg is between the averages obtained in urban settings elsewhere in Florida (Gainesville and Miami) and, consequently, cannot be considered to be exceptionally elevated in the study area.

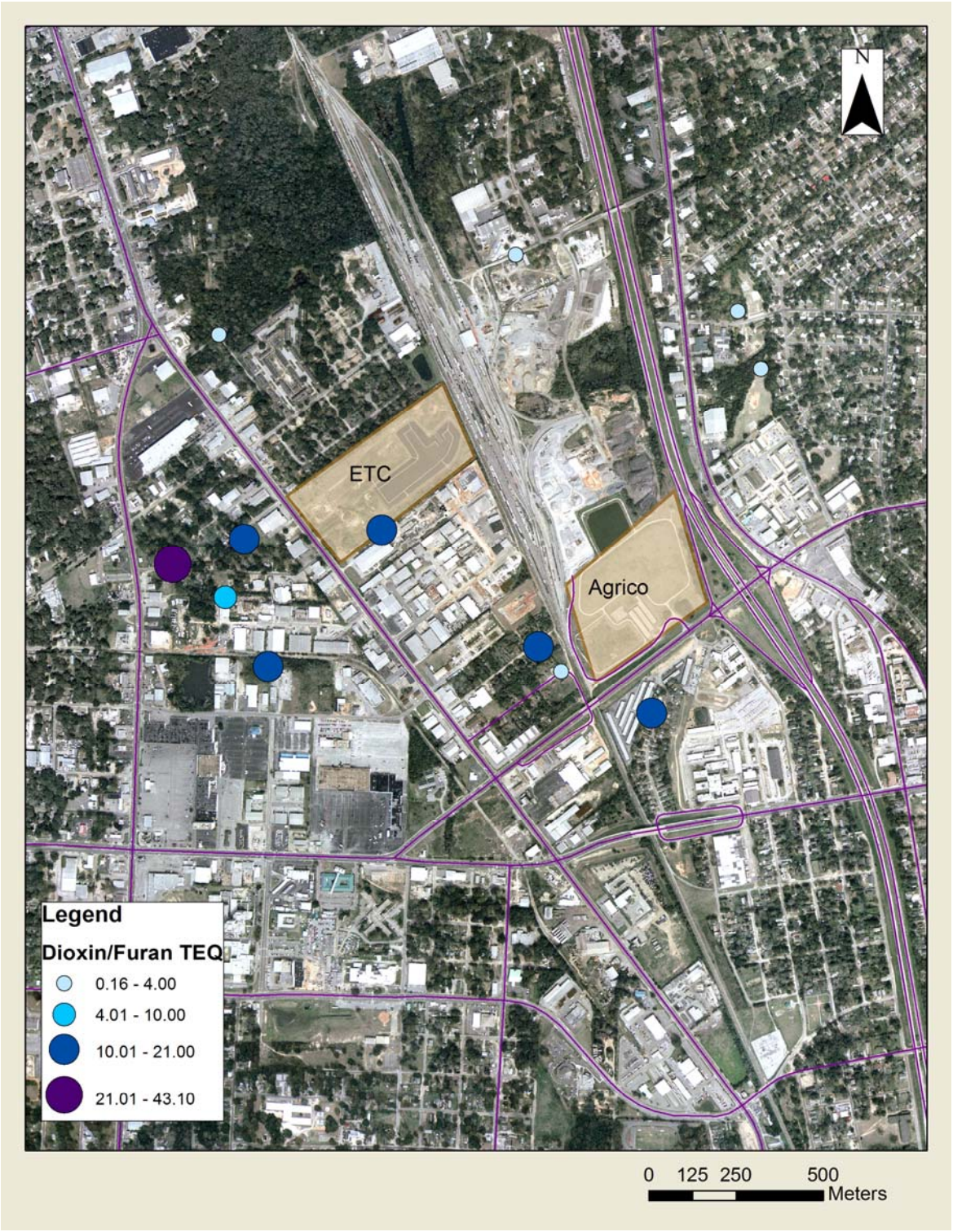


Fig. D-1. Dioxin/furan TEQs [ng/kg] in Palafox industrial corridor.

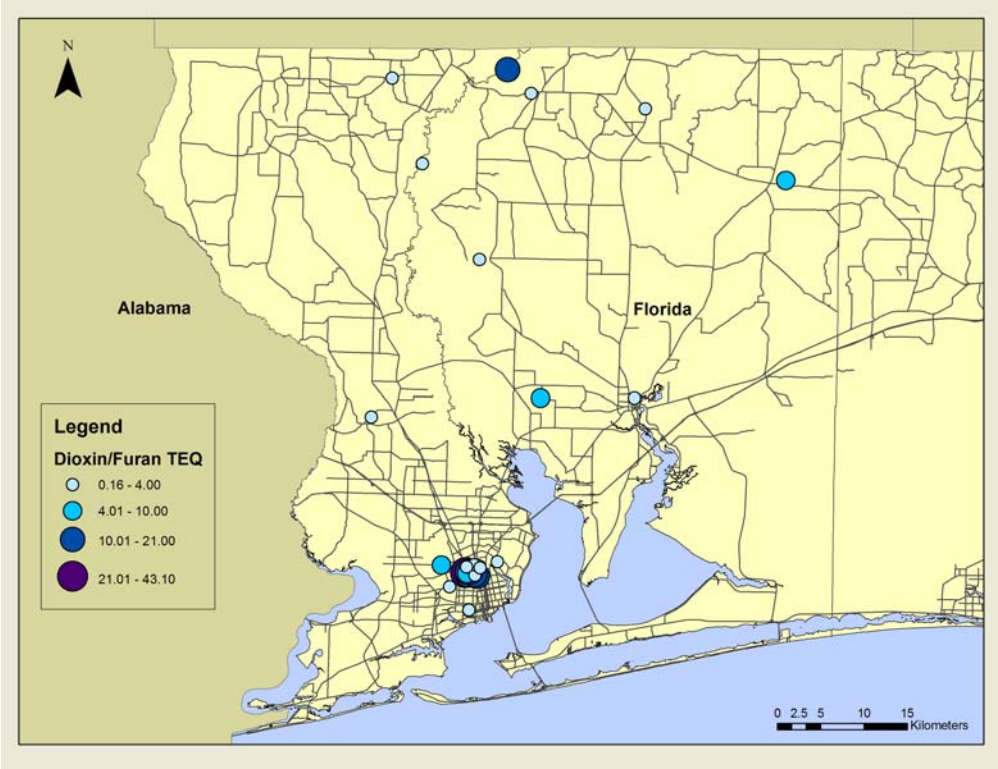


Fig. D-2. Dioxin/furan TEQs [ng/kg] in study area.

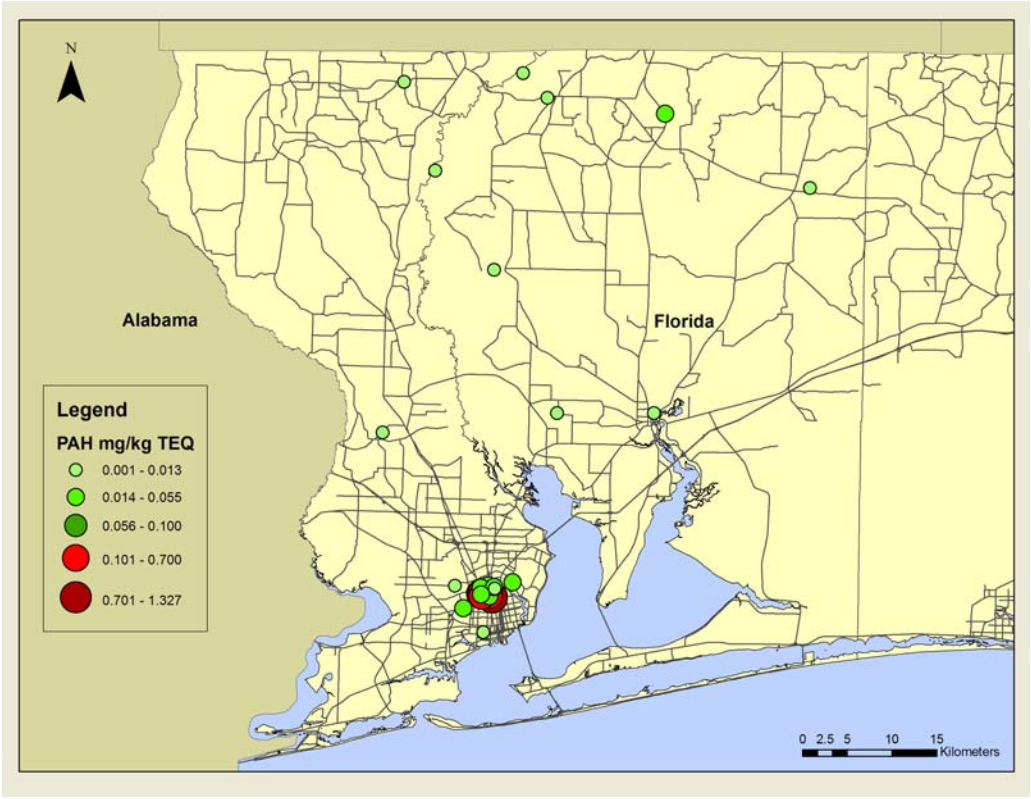


Fig. D-3. Benzo(a)pyrene equivalents [mg/kg] in study area.

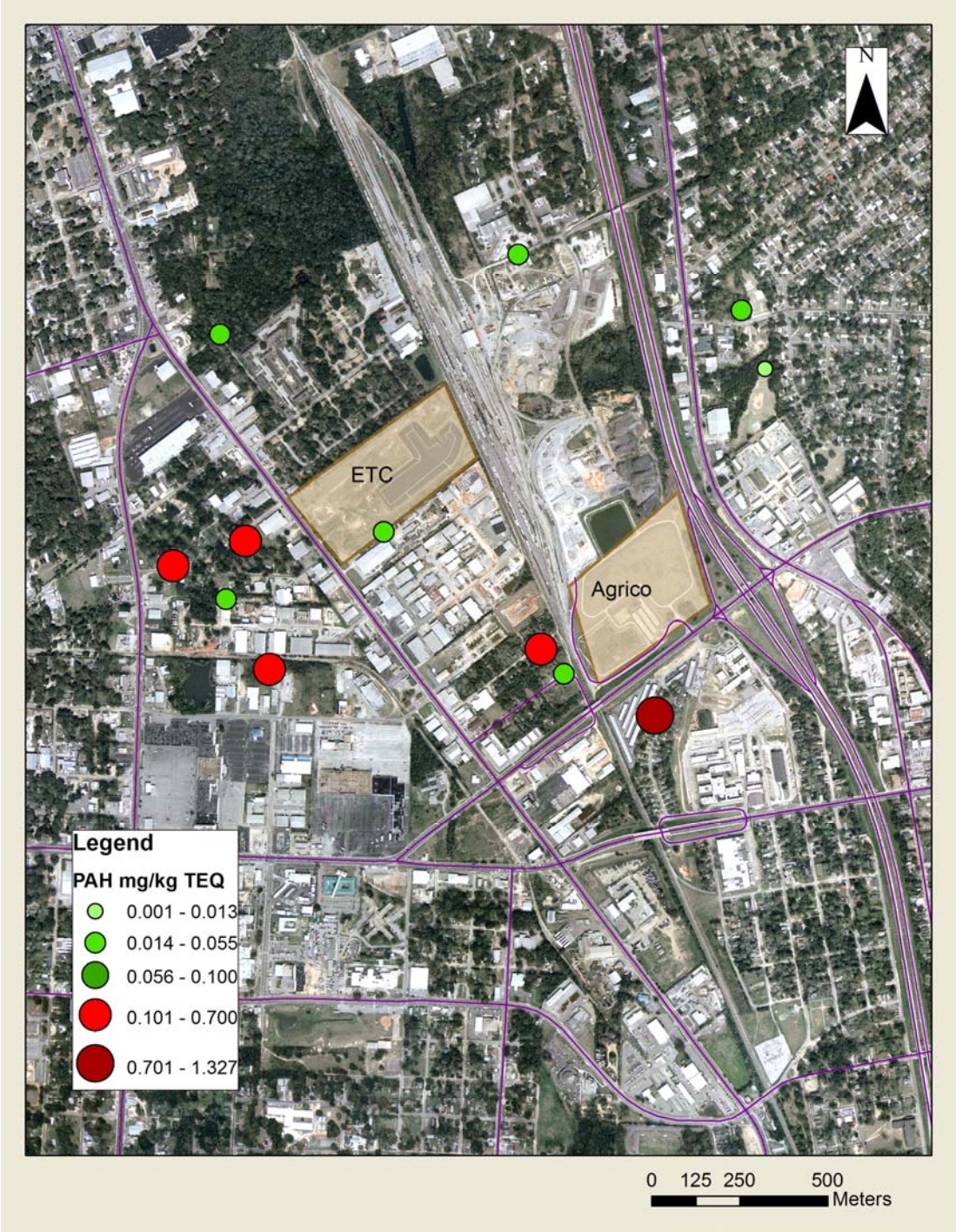


Fig. D-4. Benzo(a)pyrene equivalents [mg/kg] in Palafox industrial corridor. Orange arrow indicates Brown Barge Middle School sample. A motor pool for school buses and other vehicles is adjacent to the school.

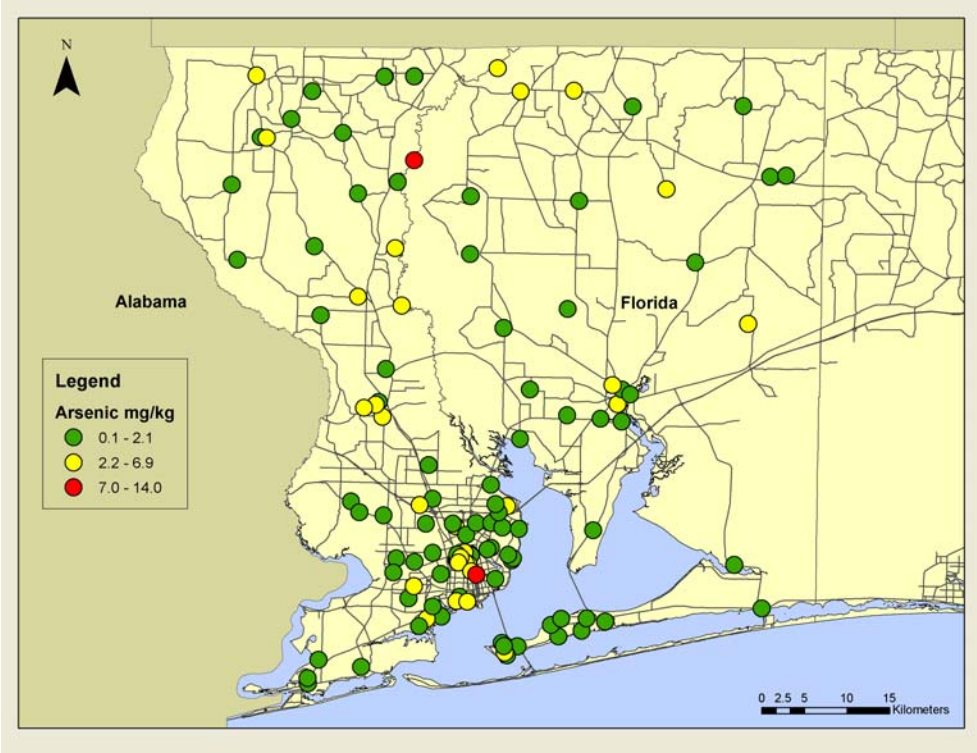


Fig. D-5. Arsenic concentrations [mg/kg] in surface soils. Residential SCTL is 2.1 [mg/kg].

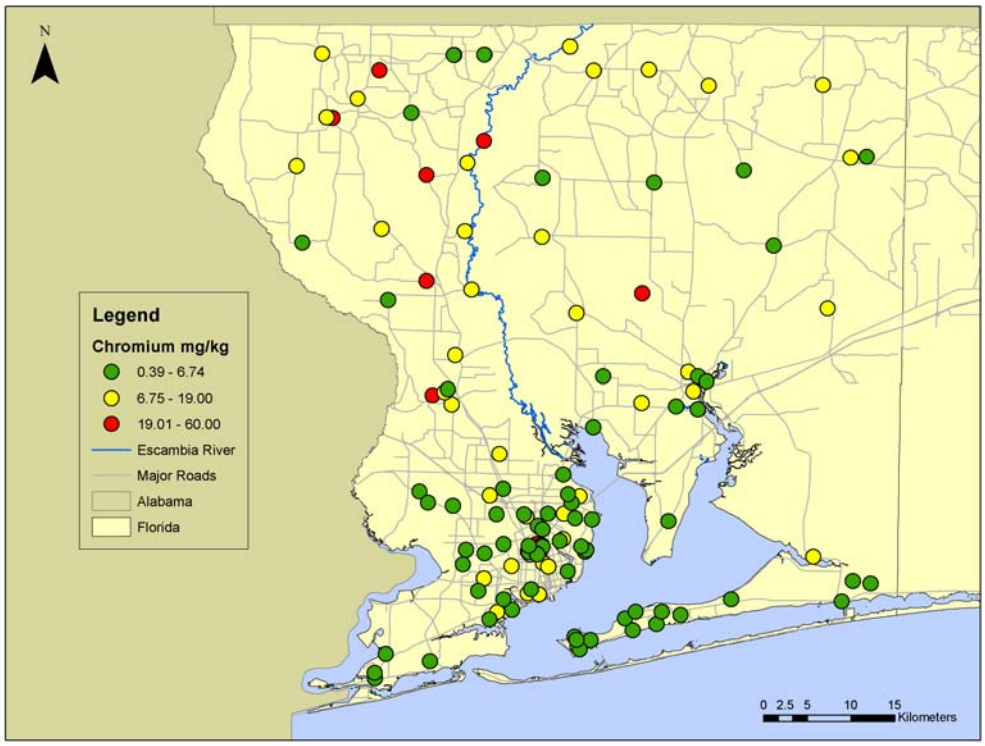


Fig. D-6. Chromium concentrations [mg/kg] in surface soils.

Concentrations for Pb and Zn, two trace metals that often have been linked to transportation sources, are somewhat higher in urban areas than in rural areas. Chromium and Ni, two metals that are also often thought to be derived from anthropogenic sources in urban areas, are statistically significantly higher in rural areas than in urban areas in the present study (Fig. D-6, D-7). Principal component analysis (PCA) shows that these metals are derived mainly from the parent material of the soils, which is more metal-bearing in the rural northern parts of the study area.

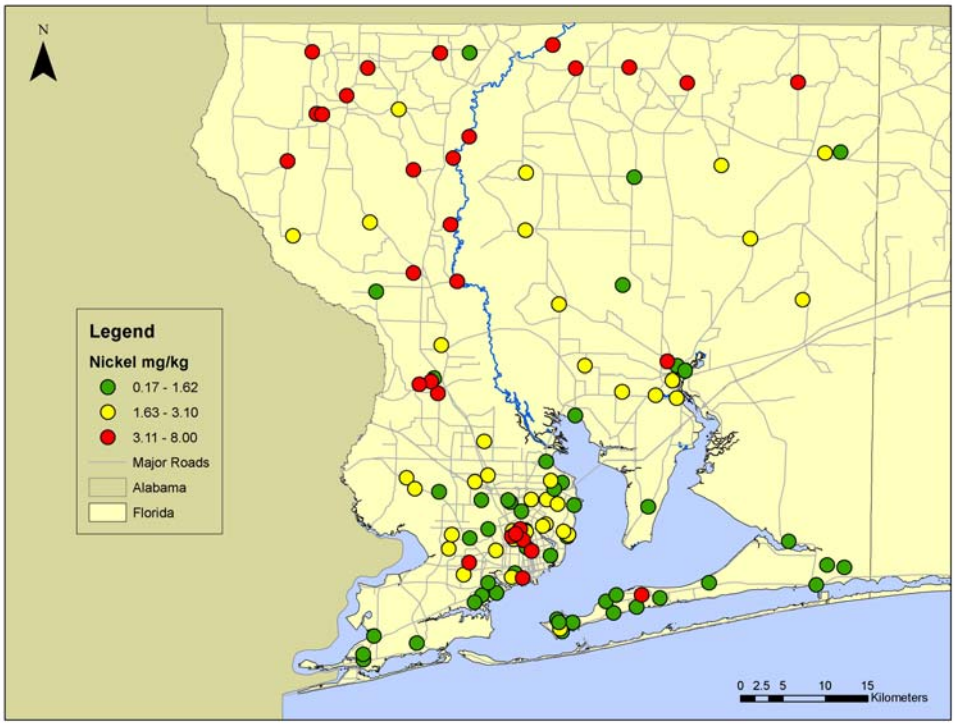


Fig. D-7. Nickel concentrations [mg/kg] in surface soils.

To evaluate if the trace metals originate from anthropogenic activities we applied two indexes that compare observed concentrations to background concentrations. Even though many studies use general crustal values for the backgrounds, we determined local background concentrations that provide a much better basis for comparison. The two indexes yield consistent results and show that Pb and Zn have the largest anthropogenic component (Table D-1). However, levels described by the indexes as "strongly polluted" are reached at 4% to 6% of the sites only for these two trace metals. Most of these sites are in the Palafox Industrial Corridor. Sites characterized as "polluted" by the indexes are along the Escambia River and in the urban parts of the study area. In spite of it exceeding the RSCTL, As reaches "pollution" levels at relatively few sites, indicating that its local background level is high compared to the RSCTL. GIS-based hot spot analysis corroborates some of these observations and clearly shows that trace metal concentrations are elevated in the Palafox Industrial Corridor, as compared to elsewhere in the study area (Fig. D-8).

Table D-1. Proportion [%] of samples at various pollution levels, based on local background concentrations.

Index value	Pollution level	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
		Index of geoaccumulation							
0 - 2	polluted	19.8	7.9	20.6	22.2	18.3	23.0	31.7	25.4
> 2	strongly polluted	1.6	2.4	1.6	1.6	5.6	0.8	0.0	6.3
		Enrichment factor							
2 - 10	polluted	11.1	7.9	8.7	19.8	20.6	19.8	22.2	27.0
> 10	strongly polluted	0.0	1.6	0.8	1.6	4.0	2.4	0.8	4.0

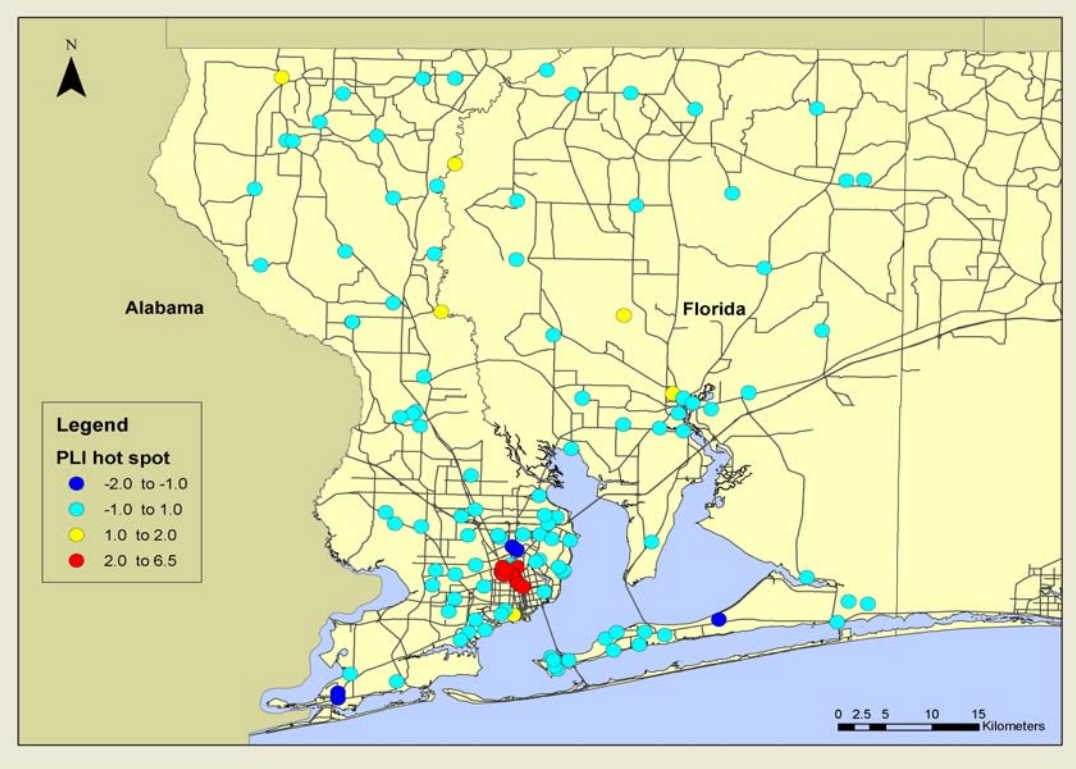


Fig. D-8. Z values from hot spot analysis for PLI index for trace metals. Red color marks cluster of points with PLI values higher in magnitude than can be expected from random chance.

The average concentration of all analyzed trace metals (As, Cd, Cr, Cu, Ni, Pb, Zn), with the exception of Hg, decreases between 2 m and 20 m from the edge of a road. This decrease is statistically significant. The higher concentrations near the road are due to traffic activities, and originate from the wearing of tires and brake pads, tire weights that fall off, oil drips, and emissions. Arsenic has rarely been associated with traffic activities but in the current study follows the trend of the other trace metals. Beyond 20 m the influence of traffic on trace metal concentrations becomes minimal. Only Pb and Zn show signs of further

decrease beyond 20 m. Based on the pollution indexes these two metals have higher pollution levels and at proportionally more sites near a road than in the total dataset. Arsenic is still the only element that exceeds its RSCTL, indicating that trace metal concentrations along roads are not generally a health concern in the study area.

Trace metal concentrations in soil materials at the base of structures made of CCA-treated wood had not been previously studied in the study area. Results of the current project show that the concentrations of Cr, Cu, and As are markedly higher near CCA-treated wood than in the whole dataset (Table D-2). The other trace metals have below average concentrations, most likely because of the very high quartz sand content of the soils near the structures. Arsenic concentrations are substantially higher than the RSCTL but Cr and Cu do not exceed their respective RSCTLs. In principle, the As exceedances may warrant further assessment but this option has to be considered in light of the very limited spatial extent of the pollution and the limited number of CCA-treated structures (five) in the study area. Nevertheless, it seems best to avoid contact with soils in very close proximity to these CCA-treated structures.

Table D-2. Trace metal concentrations [mg/kg] for soil samples collected near CCA treated wood, and descriptive statistics for main dataset.

Sample	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
	Soils near CCA treated wood							
PSS 45	25	BDL	12	16	9.1	0.014	1.8	12
PSS 75	21	BDL	12	24	1.4	BDL	0.27	9.9
PSS 77	15	BDL	15	8.9	0.84	BDL	BDL	0.89
PSS 79	79	BDL	24	32	2.2	BDL	0.48	13
PSS 101	BDL*	BDL	0.35	BDL	0.16	BDL	BDL	1.1
	Main dataset of 126 samples							
minimum	0.13	0.02	0.39	0.19	0.82	0.005	0.17	0.53
maximum	14	1.8	60	54	411	0.38	8	289
geomean	1.38	0.14	6.38	4.25	11.57	0.019	1.95	16.91
RSCTL	2.1	82	210	150	400	3	340	26000

*BDL: Below detection limit.

Trace metal speciation extracts gradually more tightly bound fractions of the metals from the soil materials. This speciation allows for a better evaluation of the potential for transfer of the trace metals to other parts of the environment than do total trace metal concentrations. Arsenic and Zn have the largest proportions in the two most loosely bound fractions of the metals, often considered to be the bioavailable fractions (16.15% and 24.03% respectively). This implies that because of the magnitude of their concentrations and their availability these two trace metals have the greatest potential to negatively affect other parts of the environment. The other metals have relatively low bioavailable fractions. Lead, Cr, and Cu have relatively large organic matter-bound fractions. These fractions are relatively stable but can be released into the rest of the environment by changes in Eh or pH that affect the organic matter. Arsenic and Cr have about 70% in the stable residual fraction, indicating that this portion is unlikely to influence the environment on a human time scale.

Evaluating the radioactivity was a secondary objective of this task and results of our pilot study indicate that the highest gross radioactivity in soils was 56 cpm, and the highest dosage measured was 0.019 mR/hr in our study area. These values are near background levels and do not exceed levels reported in the literature for unpolluted locations, so the radioactivity in surface soils is not of health concern.

3. Perspectives

The present study is the first systematic survey of soil pollution in Escambia and Santa Rosa Counties. Results show that most trace metals in the soils we examined have a clear anthropogenic component but with the exception of As do not exceed the respective RSCTLs. Arsenic deserves most attention in follow-up studies, but as shown by this and other studies it may be elevated because of high regional background concentrations. The PAH benzo(a)pyrene equivalent concentration exceeds the RSCTL in the Palafox Industrial Corridor and may also warrant further consideration.

E. Pollutants in Bayous and Escambia Bay and River

(Task Leaders: Carl J. Mohrherr and Johan Liebens, University of West Florida)

1. Introduction

The urban bayous studied here are small microtidal estuaries that connect to Pensacola Bay. Their surface areas are: 87.4 hectares (Bayou Chico), 157 hectares (Bayou Texar), and 384.5 hectares (Bayou Grande). The sizes of their watersheds are: 4240 hectares (Bayou Chico), 3779 (Bayou Texar), and 4428 hectares (Bayou Grande). The bayous were among the first areas of the region to be developed. Over the last century each of the bayous has been impacted by similar, but also site specific anthropogenic influences directly related to activities in their waters, on their shorelines, and within their watersheds. Escambia Bay is the main estuary of the Pensacola Bay System with an approximate area of 93 km^2 (36 $miles^2$) and a watershed of about 2000 km^2 (772.2 $miles^2$). Its main tributary, the Escambia-Conecuh River of Florida and Alabama, is 230 miles (386.1 km) long. Bayou Texar lies to the east of downtown Pensacola while Bayou Chico lies to the west (Fig. E-1). Bayou Grande is located further to the west and is adjacent to Naval Air Station (NAS) Pensacola and the Warrington urban area.

The bayous and Escambia Bay are invaluable natural resources for the area, as they add to the scenic beauty of the region, facilitate recreational activities (e.g., boating, fishing), serve as navigation routes, and support tourism. Deterioration of these water bodies would be detrimental to the overall economy and quality of life in the region. In the past, fish kills were of concern but these are now rare events. Public health advisories, against swimming and water sports, have been and continue to be issued by the Department of Health because of elevated levels of fecal bacteria in the urban bayous after rain events.

Chemical pollutants from point and non-point sources continue to be of concern as well. Bayou Chico and Bayou Grande have suffered impacts from industrial and military activities. Bayou Texar is down gradient of Superfund site groundwater plumes from ETC (Escambia Treating Company) and AGRICO Chemical Company (ACC). Escambia Bay lies between Escambia County, FL and Santa Rosa County, FL. Escambia Bay and River in the past received releases from multiple sources, including chemical industries, a paper mill, municipal sewage treatment plants, agriculture, and silvaculture.

Small estuaries such as the three main Pensacola bayous are expected to have a limited life due to sedimentation. Sediment fills in and blocks the navigation channels, requiring periodic dredging. Sedimentation observed in Pensacola bayous is a natural process that has been accelerated by anthropogenic activities. Assuming sea levels do not change, these bayous will eventually fill in becoming wetlands, but this may happen sooner rather than later without appropriate stormwater controls and treatment.

An orderly management of the use and health of the bayous and bays should be based on a careful evaluation of the prevailing conditions, including the nature and extent of pollution, and plausible avenues for improvement of environmental and public health. Our project's goal is to determine the profiles of relevant contaminants of concern in the sediments of the three urban bayous and in the Escambia Bay and River, and present the information in a GIS format so that this database can serve as a reference for evaluating changes in the future.

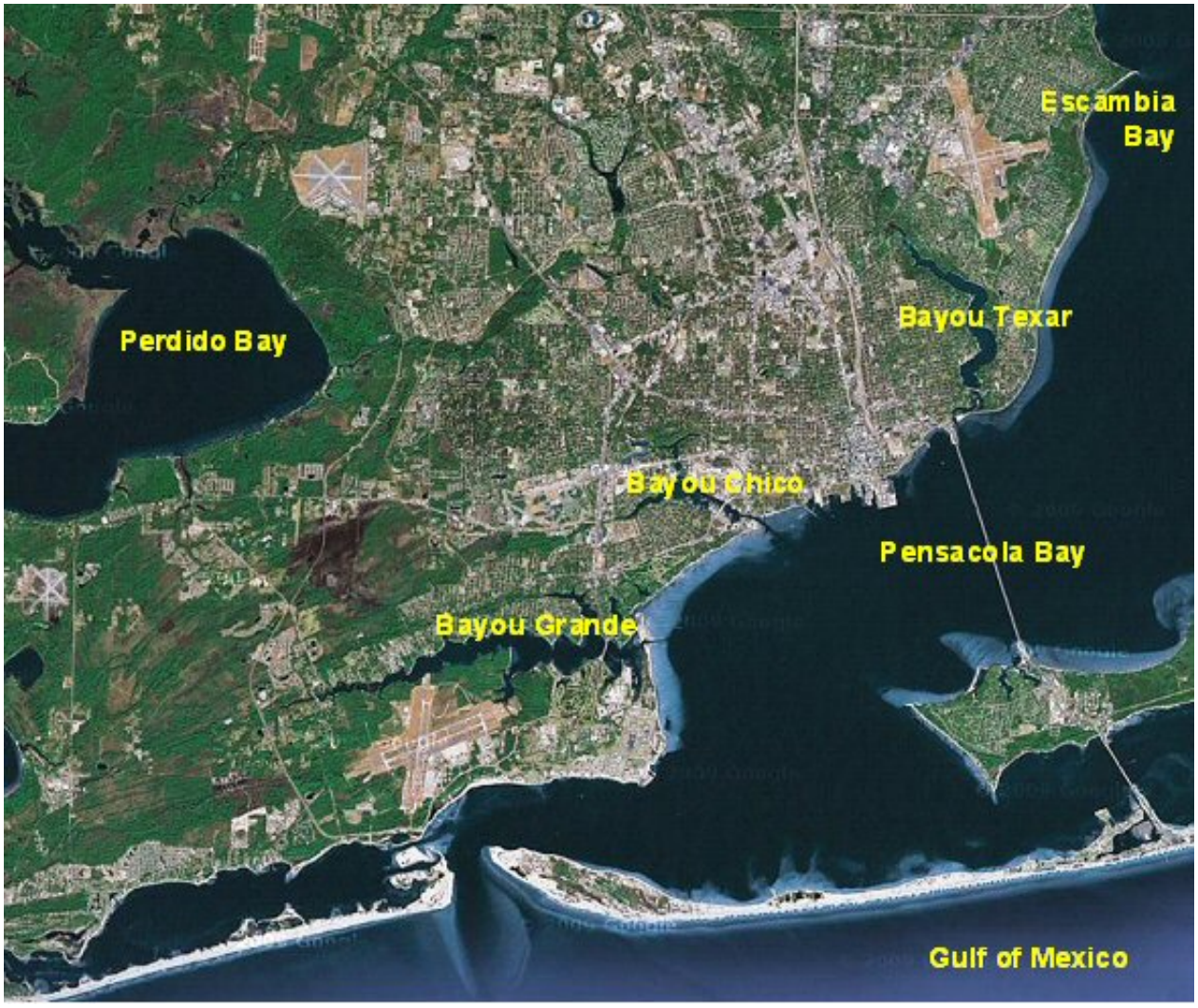


Fig. E-1. Google Earth map of the three Pensacola bayous and adjacent regions of the Pensacola Bay System.

2. Bayou Texar

Bayou Texar is located in the City of Pensacola in the extreme western panhandle of Florida, and is a component of the Pensacola Bay System. Carpenter's Creek drains into the extreme northern end of the bayou. Freshwater inputs come from carpenter's creek in the north and surface flow along the banks of the bayou. Saline waters enter the bayou from Pensacola Bay in the south.

Bayou Texar receives pollutants from a variety of sources, including groundwater plumes from Superfund sites (Fig. E-2). To evaluate the potential negative impacts of pollution, we determined the level and distribution of some of the pollutants in the bayou and identified the most likely sources for them.

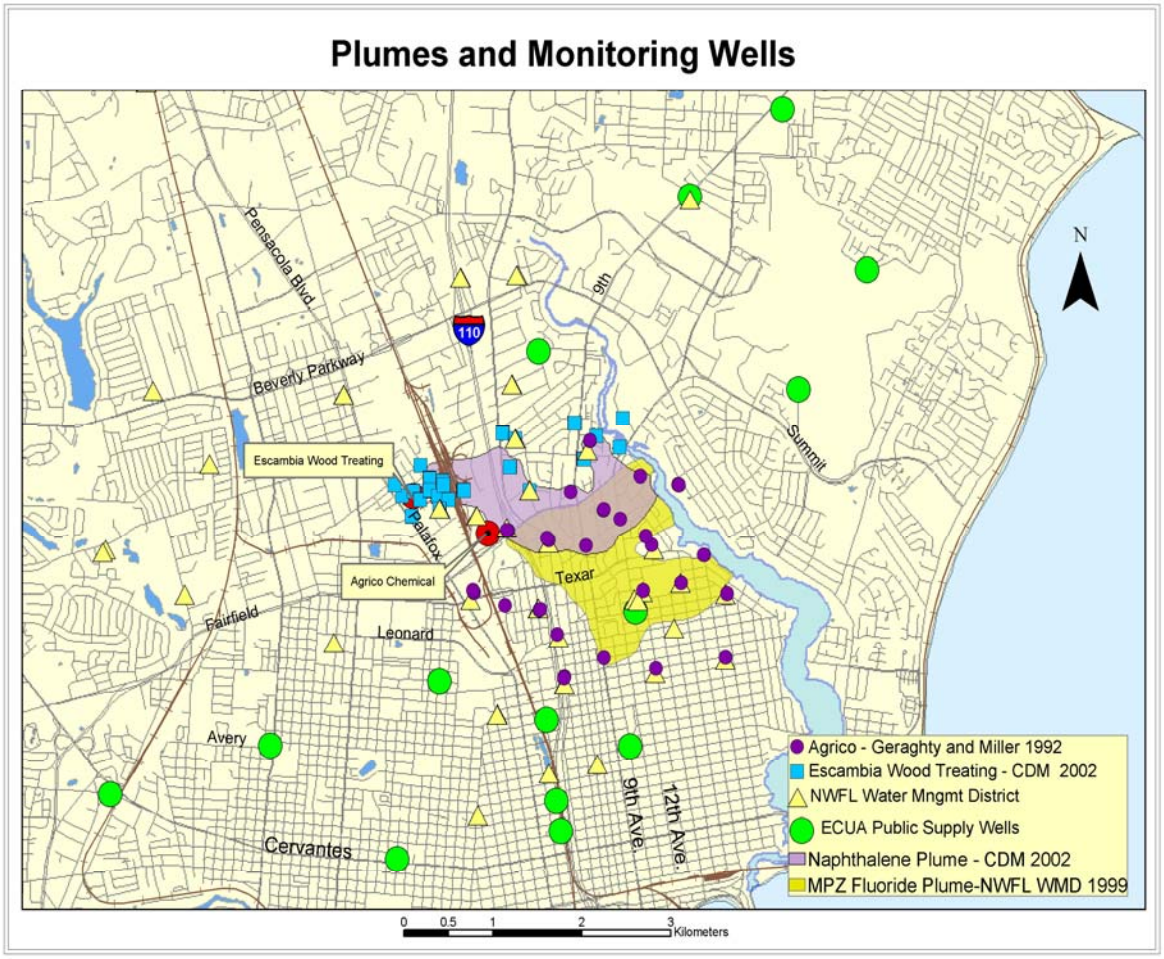


Fig. E-2. Location of Bayou Texar and groundwater plumes emanating from Superfund sites.

a. Pollutants from Groundwater Plumes

Studies by a consulting firm doing Superfund mandated studies indicated that a freshwater groundwater plume from the AGRICO Superfund Site (ACC) carrying fluoride enters the bayou from below in the northern part of the bayou where the polluted Sand and Gravel aquifer intersects the bayou (Fig. E-3). This northern location in the bayou, which we consider to be a "hot zone", corresponds to the northern edge of the ACC plume. For most of the bayou, however, fluoride levels are higher in surface sediments than in deeper

Fig. E-3. Fluoride in Bayou Texar sedimentary pore water.

sediments at the same location (Fig. E-4). This seems to be the result of fluoride entering the water column in the northern section of the bayou, being dispersed by the water and subsequently entering the surface sediments elsewhere in the bayou. Sediment composition

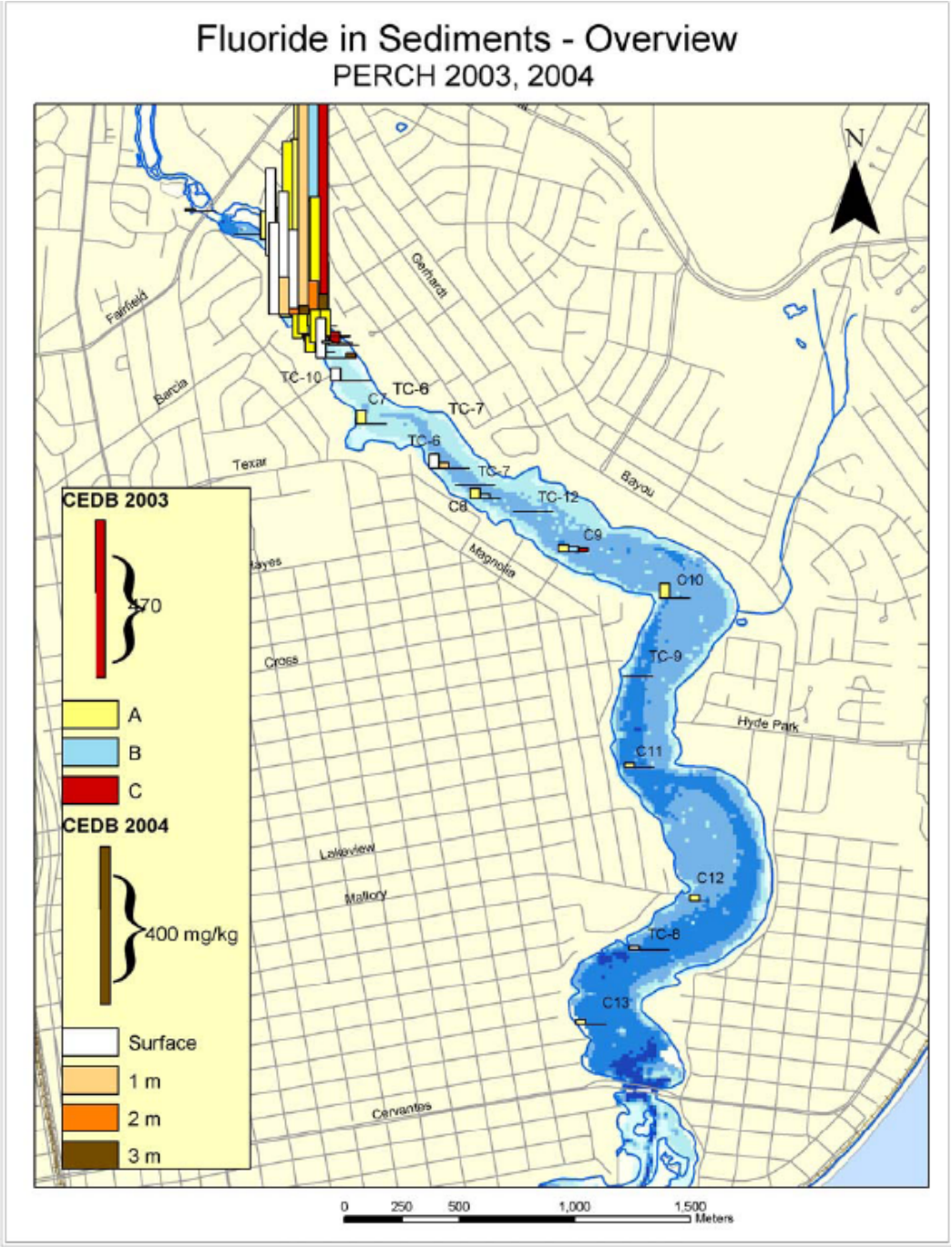


Fig. E-4. Spatial distribution of fluoride in sediments from surface and vibracore samples in Bayou Texar.

has been shown in other studies to account for differences in fluoride concentrations but in Bayou Texar that composition does not seem to affect fluoride systematically.

In Bayou Texar, fluoride concentrations in bottom water do not follow the salinity trend and are highest in the low-salinity waters in the northern section of the bayou. This inverted fluoride/salinity relationship suggests that external fluoride enters the bayou bottom water in the northern section of the bayou that also contains a hot zone where diverse pollutants occur in elevated concentrations. This means that fluoride from the groundwater plume enters the water of Bayou Texar. The fluoride concentrations in the bayou water, however, remain well below the Florida FDEP water cleanup target levels for freshwater surface water and marine surface water.

Radium, another tracer for the ACC groundwater plume, is present in sediments and waters of Bayou Texar, but the levels are expected to have minimal negative impact on the environment. More radium is present in the northern section of the bayou than in the mid and south sections (Fig. E-5). There is some evidence to suggest that the higher levels in the north are due to upwelling of contaminated groundwater from the Sand and Gravel aquifer. The relative proportion of ^{228}Ra to ^{226}Ra in the aquifer indicates that the radium does not directly originate from the ACC Superfund Site but is released from the matrix of the aquifer.

Fig. E-5. Spatial distribution of radium in surface sediments in Bayou Texar.

The groundwater plume from ACC is co-mingled with the groundwater plume from the Escambia Treating Company (ETC) Superfund site. Although the ACC plume components are clearly shown to enter Bayou Texar, we are unable to find evidence that the ETC plume is entering the bayou since we did not find elevated levels of naphthalene in bayou samples.

b. PAHs

Concentrations of PAHs are highest in the northern part of the bayou (Fig. E-6) where they can be expected to have some negative impact on biota. The PAHs were mainly detected in surface sediments and did not contain naphthalene. The forensic ratios of PAHs indicate that creosoted wood pilings present in bayou/creek docks or bridge pilings are not a likely source of the PAHs in the sediments. Ratios of PAHs suggest that the detected PAHs were derived from the combustion of petroleum and non-petroleum products. However, studies of pore water are required to confirm this because analytical detection limits for PAHs are lower for water than for the sediments examined in this study.

Fig. E-6. Spatial distribution of PAHs in surface sediments in Bayou Texar and Carpenter's Creek.

c. PCBs

Bayou Texar does not have any known industrial source of PCBs, but PCBs were detected in the sediments of this bayou. PCBs in a residential bayou can originate from power transformers, building materials, and other diverse sources. The part of this bayou south of the Cervantes Street bridge, including the mouth of the bayou where it meets Pensacola Bay, had

the lowest total PCB concentrations (Fig. E-7). The part of Bayou Texar just south of the 12th Ave. bridge was dredged about 15 years ago and yet sample TG1 located just south of the bridge had the third highest PCB concentration in the bayou indicating that PCBs have entered the bayou since the last dredging. Sample TG13 with a PCB concentration of 243.58 µg/kg was markedly above the other samples (Fig. E-7). Based on the number of detected concentrations above the TEL, i.e. 3 samples out of 13 (23%), the PCB concentrations are lower for this bayou than for the other bayous. The mean PCB concentration of the sediments is 30.7µg/kg but is skewed by the high concentration for TG13. The geomean is 12.40 µg/kg.

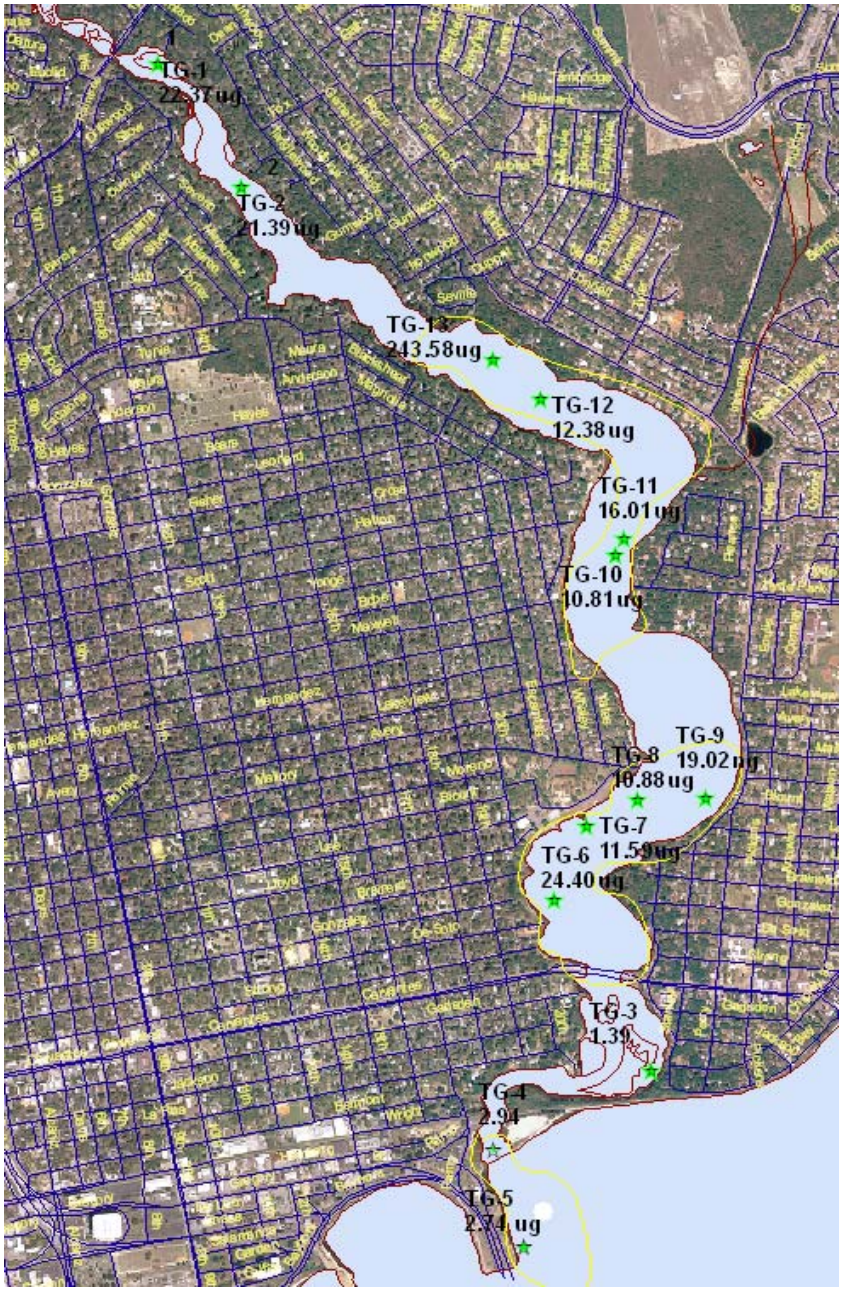


Fig. E-7. Total PCB concentrations in surface sediments of Bayou Texar [µg/kg]. Stars indicate sampling site locations.

d. TEQ for Dioxins/Furans and PCBs

The mean total TEQ of 3.85 ng/kg was dominated by the TEQ of dioxins/furans (84% of the total TEQ on average). The TEQ is lower in Bayou Texar than in the other two bayous (Fig. E-8), reflecting the non-industrialized nature of Bayou Texar's watershed. The TEQ was lowest in Bayou Texar south of the Cervantes Street bridge and highest near the northern end of the bayou (Fig.E-8).

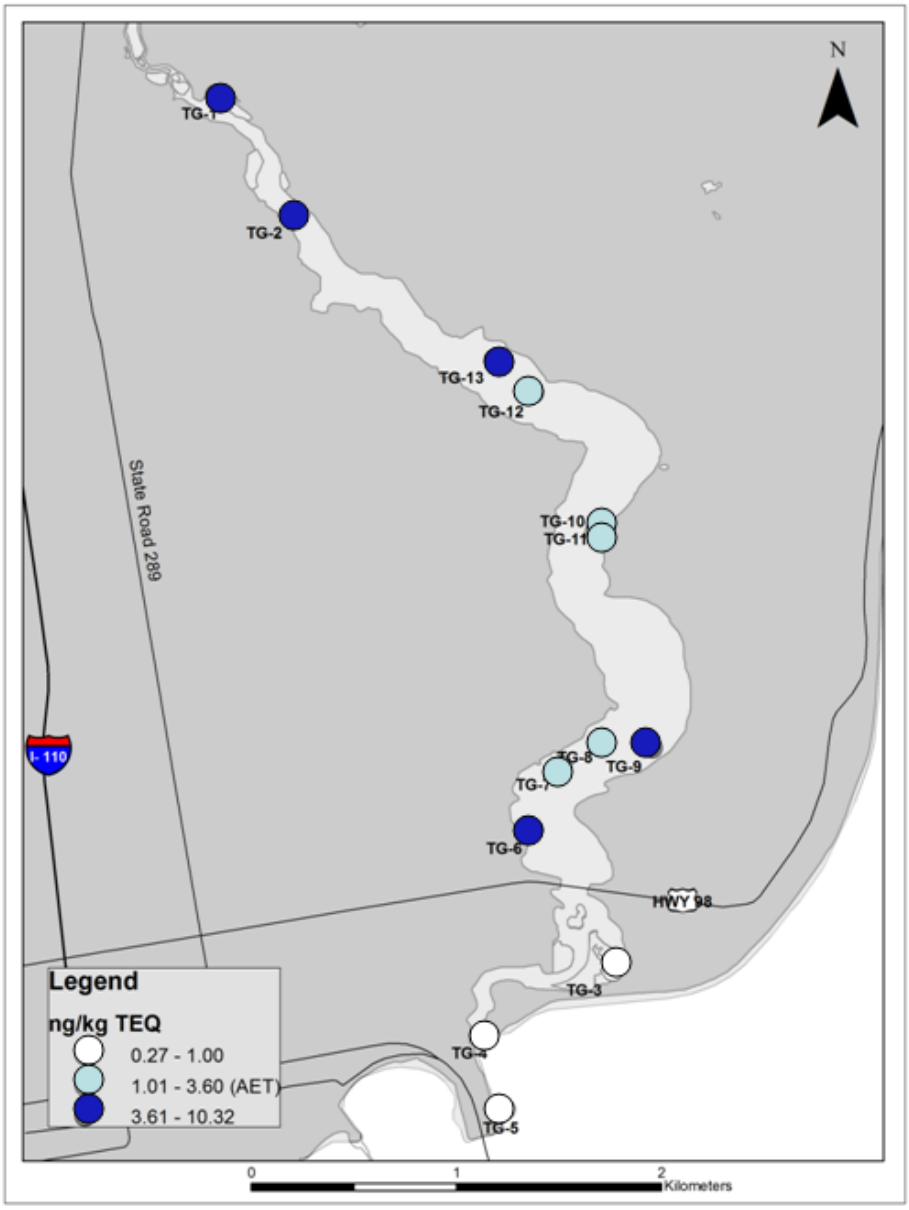


Fig. E-8. Total TEQ for surface sediments in Bayou Texar. NOAA AET is 3.6 ng TEQ/kg.

e. Pesticides

The standard suite of organochlorine pesticides was analyzed for the sediments of the bayou. In Bayou Texar, DDT was detected in 12.5% of the samples, and other pesticides were occasionally detected. Therefore, only minimal deleterious environmental impacts due to organochlorine pesticides can be expected in sediments of Bayou Texar.

f. Metals

Trace metals in Bayou Texar do not seem to come from the groundwater plume, but point and non-point sources are more likely contributors of the metals. This implies that solutions to the heavy metal pollution problem in Bayou Texar should include watershed-wide conservation efforts that concentrate on reduction of sediments and sediment bound pollution. As is the case for all pollutants, metal concentrations are high in the northern section of the bayou and lower elsewhere. Diminished flushing of the northern part of the bayou leads to accumulation of the metals there. In that northern section, the PEL for lead, mercury, copper, and zinc are exceeded, indicating that there is a probable effect on biota that come in contact with the contaminated sediments. Surface lead concentrations, as shown in Fig. E-9, depict the typical distribution of trace metals in Bayou Texar.

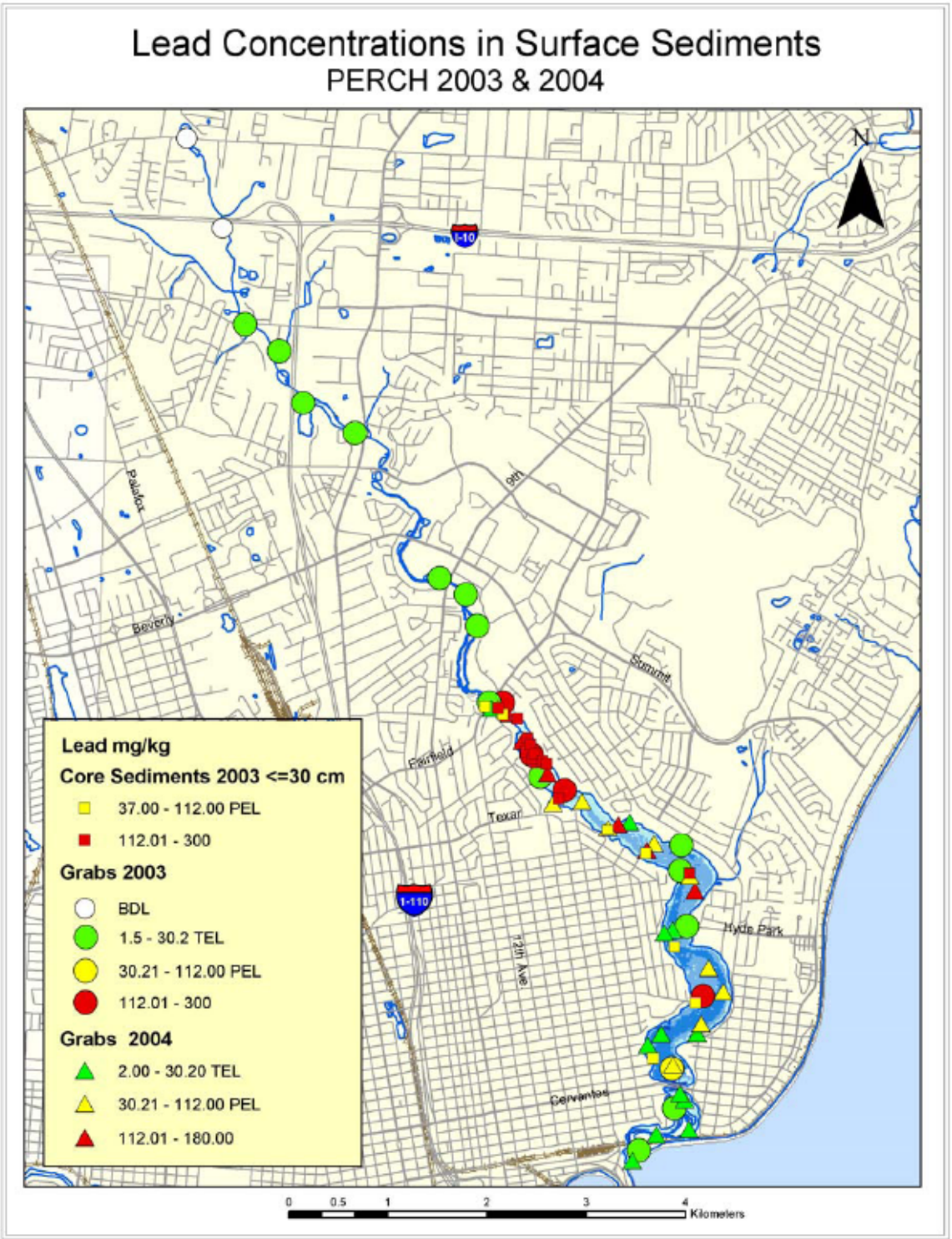


Fig. E-9. Spatial distribution of lead in surface sediments in Bayou Texar and Carpenter's Creek.

g. Perspectives

Dredging has been considered as an option to improve the environmental quality of Bayou Texar. The current study shows that elevated concentrations of most pollutants are present in surficial (top 13 centimeters) sediments only. This implies that not all sediments may have to be disposed of as hazardous waste if the bayou is dredged. The results of our sediment transport study indicate that for any dredging to be successful in the long term, it should create hydrologic conditions favorable for the flushing of the whole bayou by tidal and other currents. Our results show that there is a very strong spatial component to the variation in pollutant concentrations in Bayou Texar. This spatial variation is influenced by the location of the pollution sources and by sediment dynamics, and should be taken into account by future efforts to remediate and restore the bayou. Even variations in pollutant concentration over small distances are sometimes considerable. These observations underscore not only the need for a large number of samples to adequately characterize sediment pollution, but also the importance of spatial analysis for this type of environmental research.

3. Bayou Chico

Bayou Chico has a long history of industrial pollution and is generally considered to be the most polluted of the three urban bayous in the Pensacola area. Point sources and non-point sources have led to high levels of pollutants -- including trace metals, PAHs, PCP, dioxins/furans, and PCBs. The bayou is also adjacent to the American Creosote Works site, a superfund site, and the Omni-Vest landfill that may be affecting Bayou Chico (Fig. E-10). Additionally, the bayou is subject to urban runoff via stormwater discharges into it. Pollutants affecting the water quality of the bayou, and the effect of water quality on bayou flora and fauna, have been the subject of several investigations. Man made changes have affected flushing, resulting in two hot spots. The major hot spot is near a spoil island and a second hotspot is just south of the Navy Blvd bridge.

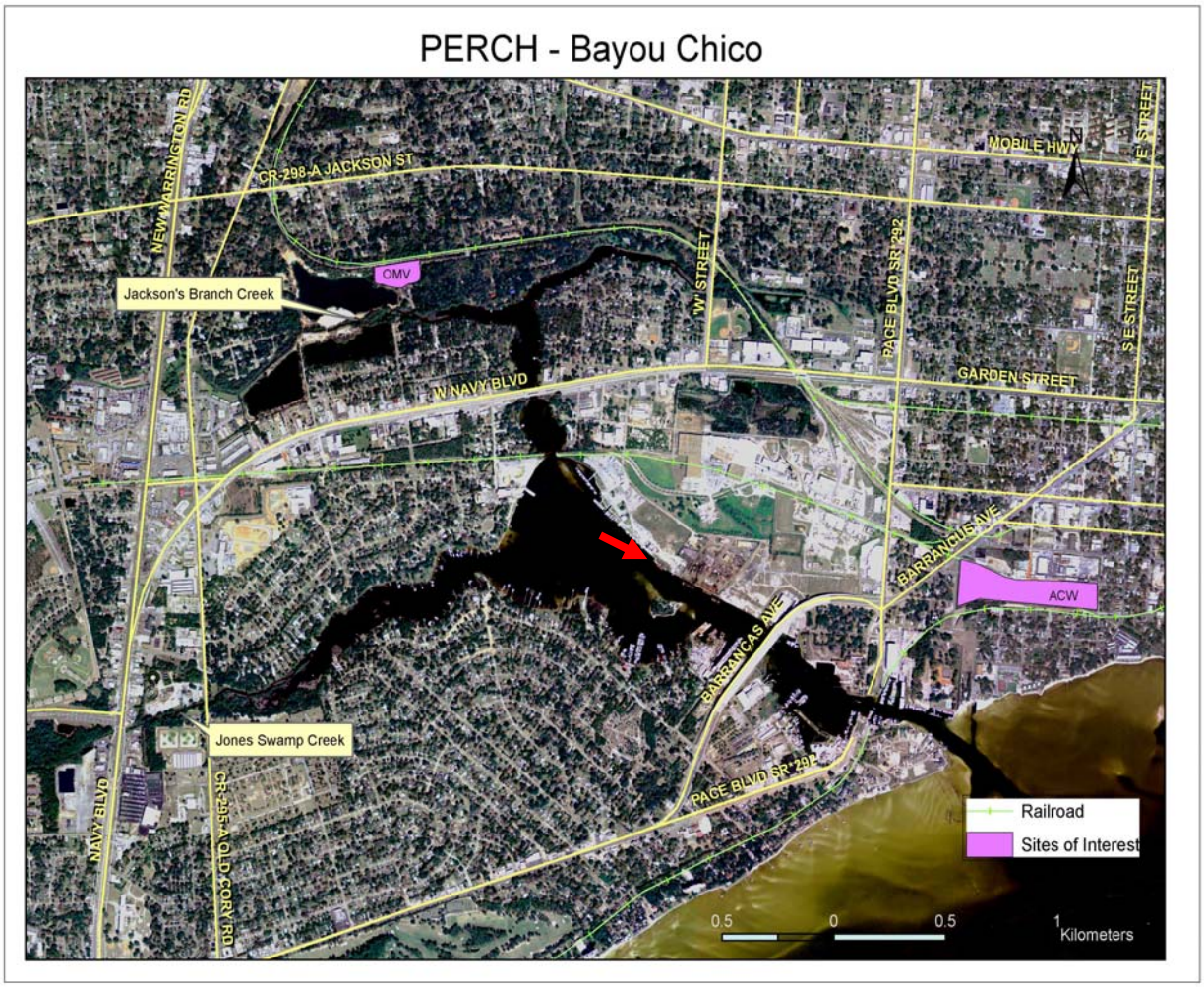


Fig. E-10. Location of Bayou Chico and the OmniVest (OMV) and American Creosote Works sites. Red Arrow indicates major hot spot in bayou about a spoil island.

a. PAHs

In Bayou Chico proper only a limited set of samples were analyzed for PAHs but more samples were collected on and about Sanders Beach just outside the bayou (Table E-1). The highest PAH concentrations for the bayou itself were observed in two areas with restricted flow (spoil island and below the Navy Blvd bridge). These areas also have significant accumulation of other pollutants such as trace metals and PCBs in their sediments. However, the maximum surface PAH concentrations were less than those detected in Bayou Texar and Bayou Grande. Near Bayou Chico there are contaminated aquifers that could impact either the bayou or nearby Sanders Beach, a recreational area for local residents. The most important contaminated aquifer is the one underneath the American Creosote Works (ACW) Superfund Site just to the northeast of the bayou and beach. Vibracores taken in shallow water just offshore Sanders Beach did not show significant PAHs in the lower levels. Vibracores taken on Sanders Beach itself did detect PAHs (Fig. E-11), which seem to be of creosote origin based on forensic ratios. These PAHs may have come from the ACW site but other origins are

possible since the beach showed evidence of having buried demolition debris underneath. There was no evidence of finding creosote elsewhere in our samples in or near Bayou Chico.

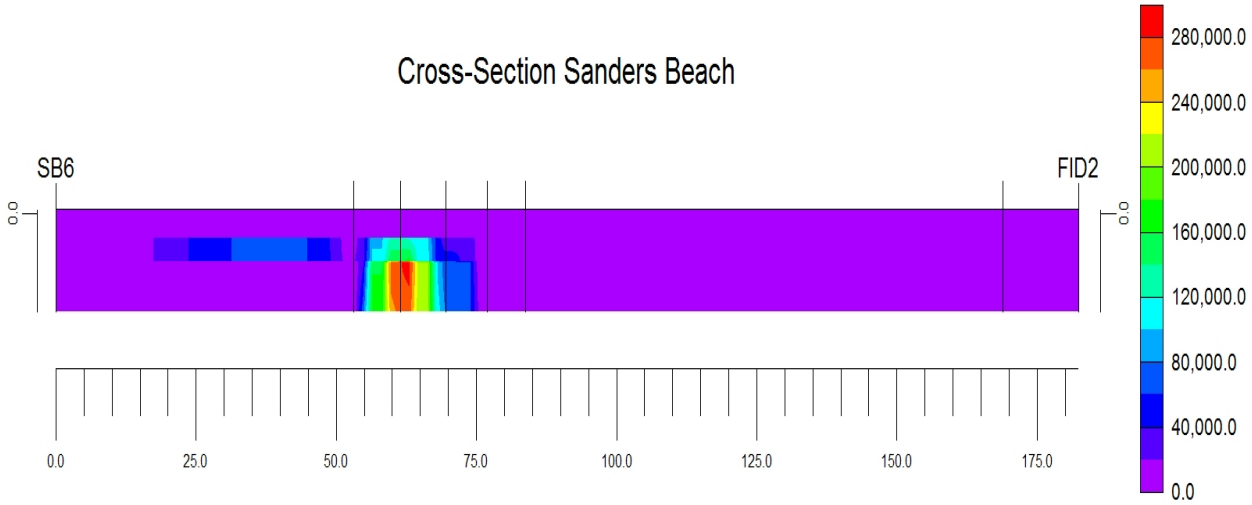


Fig. E-11. Interpreted cross section of total PAH concentrations at Sanders Beach. Axis scales are in meters, concentrations in µg /kg.

Table E-1: PAHs in and about Bayou Chico

Total PAH Data			
	Bayou Chico		
	Sanders Beach	Beach Front	Bayou
N	15	17	4
Mean [1]	24498	1569.9	2981.9
Detected Range	13.5-291940	0.88-8017.2	26.7-5350.4
Exceed TEL [2]	15.4%	5.8%	40%
Exceed PEL	15.4%	0	0

[1] Listed PAH concentrations are for total PAH or the sum of the 18 PAHs detected by EPA method 8270C [µg/kg].
[2] SQAGs are for sum of heavy and light molecular weight PAH. The FDEP TEL is 1,684 µg/kg, and the PEL is 16,770 µg/kg.

In order to determine the source of PAHs the data for the area about Sanders Beach was considered separately from Bayou Chico. The Rostad and Pereira ratios for the most concentrated samples, i.e. those from subsurface locations under Sanders Beach, were less than 100, suggesting PAHs of a creosote origin. Other samples of lower PAH concentrations at Sanders Beach mostly had Rostad and Pereira ratios well above 100, indicating a non-creosote origin. These samples have non-consistent Yunker ratios. Samples collected elsewhere about Sanders Beach mostly had only trace PAH concentrations and exhibited forensic ratios that are less suggestive of creosote PAH origins, as compared to the samples

taken under Sanders Beach. Results of surface samples collected in Bayou Chico suggest multiple origins for the surface PAHs in Bayou Chico and do not demonstrate a significant contribution from the ACW site.

b. Total Petroleum Hydrocarbons

Petroleum hydrocarbons were found in all samples, a result that is not unusual for an urban water body. Total petroleum hydrocarbons were lowest near the mouth of the bayou, in spite of the location of petroleum storage tanks in that area, but increased markedly in the north and main sections of the bayou. Low levels near the mouth are consistent with an exchange in that area between bayou water/sediment and less polluted materials from Pensacola Bay. Sediment quality guidelines do not exist for total petroleum but comparison with other studies shows that levels of total petroleum hydrocarbons in Bayou Chico are comparable to those in marine sediments near industrial and port facilities elsewhere. Qualitative analysis (Fig. E-12a, E-12b) of the composition of total petroleum hydrocarbons suggests that the predominant petroleum hydrocarbons are in the heavy oil range in the arms of the bayou, and of diesel range in the main body.

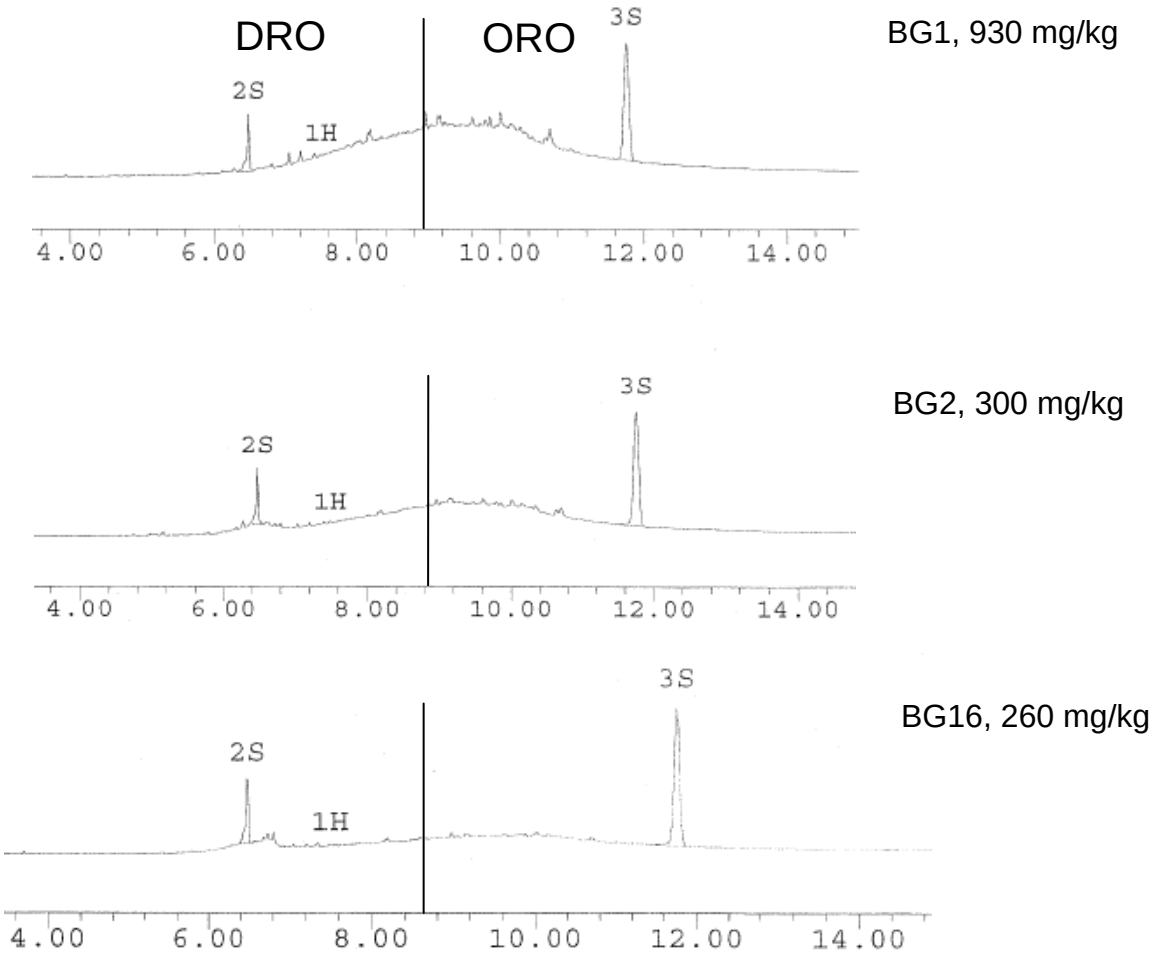


Fig. E-12a. Chromatograms representing FL-PRO results for upper Bayou Chico. ORO peaks to the right represent heavier oils and DRO to the left represent typical areas for diesel/fuel oil origins. The labels 2S, 1H, and 3S are small peaks originating from injected standards.

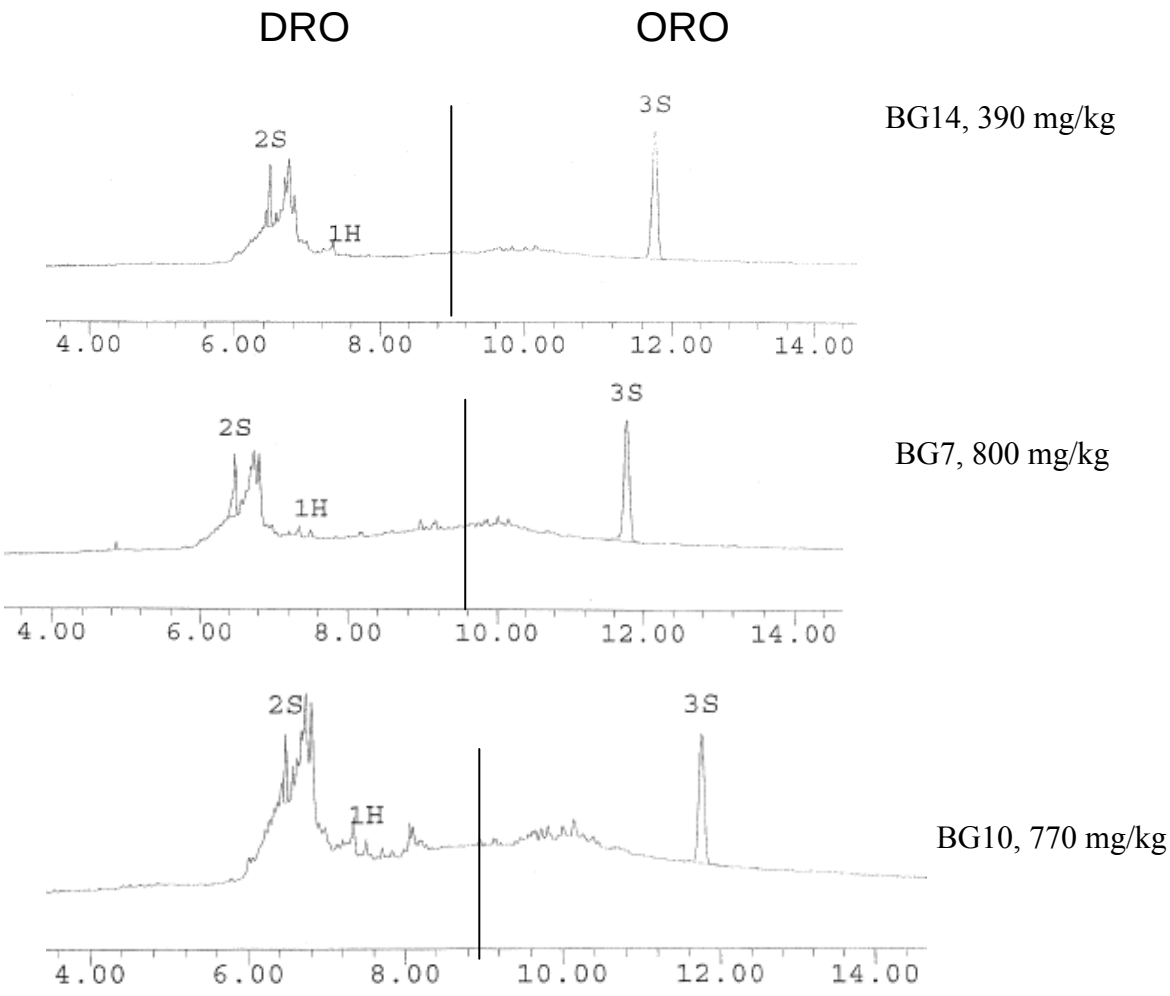


Fig. E-12b. Chromatograms representing FL-PRO results for main body of Bayou Chico. Peaks to the right represent heavier oils and those to the left represent typical peaks for fuel oil origins. The labels 2S, 1H, and 3S are small peaks originating from injected standards.

c. PCBs

For detected PCB mass concentrations, five sites out of seventeen exceed the PEL and an additional eight exceed the TEL (Fig. E-13). This shows that PCBs are a ubiquitous component of Bayou sediments and together with the dioxins/furans they are likely to present a hazard to human health due to their potential for bioaccumulation in seafood. The highest PCB concentrations occurred about the spoil island and below the Navy Blvd bridge.

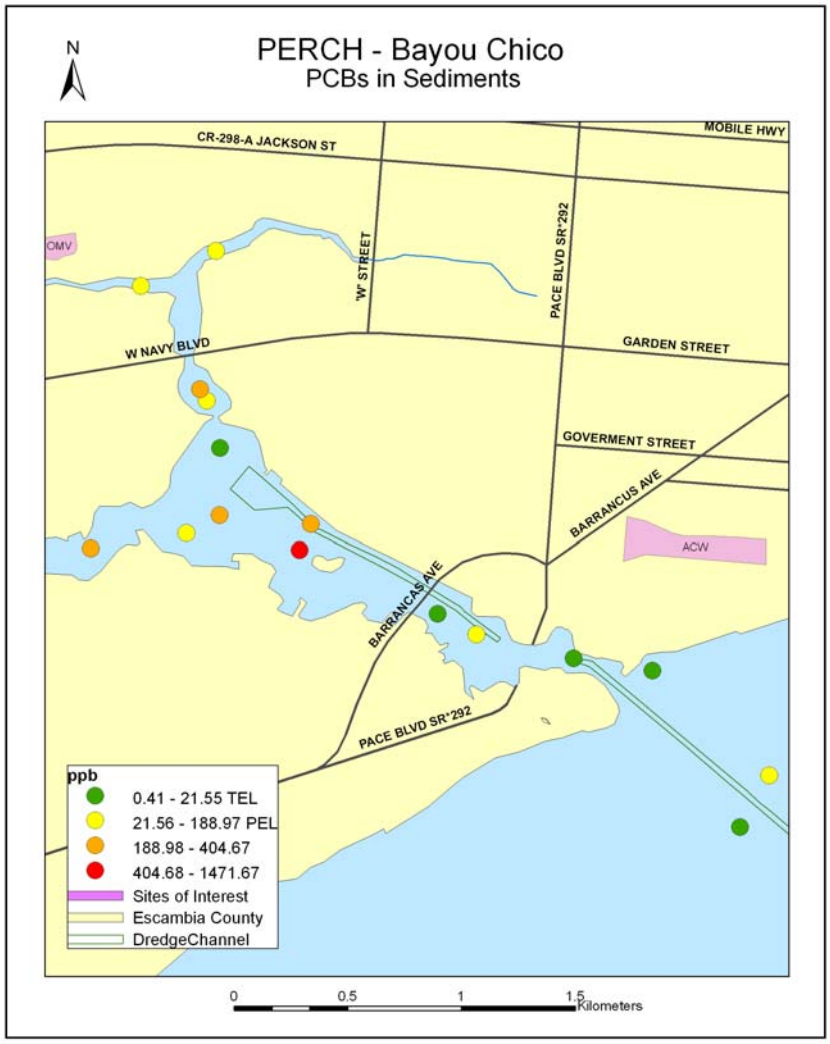


Fig. E-13. Total PCB concentrations in surface sediments of Bayou Chico [µg/kg].

d. Dioxins/Furans

Fig. E-14 shows the combined TEQs for dioxins/furans (79% of the total) and PCBs (21% of the total). Dioxins/furans are also contaminants of concern at ACW, but they are not present at high concentration in the Sanders Beach area or the mouth of the bayou. Dioxin/furan TEQs are high in the rest of the bayou and often exceed their AET (Fig. E-14). Among other places, they were found to be high near the spoil island in the bayou. PCP was also found in areas of the bayou distant from the ACW. The dioxin/furan TEQs and PCP concentrations were not high near the seemingly obvious source at ACW. The origins of dioxins/furans in Bayou Chico are not known.

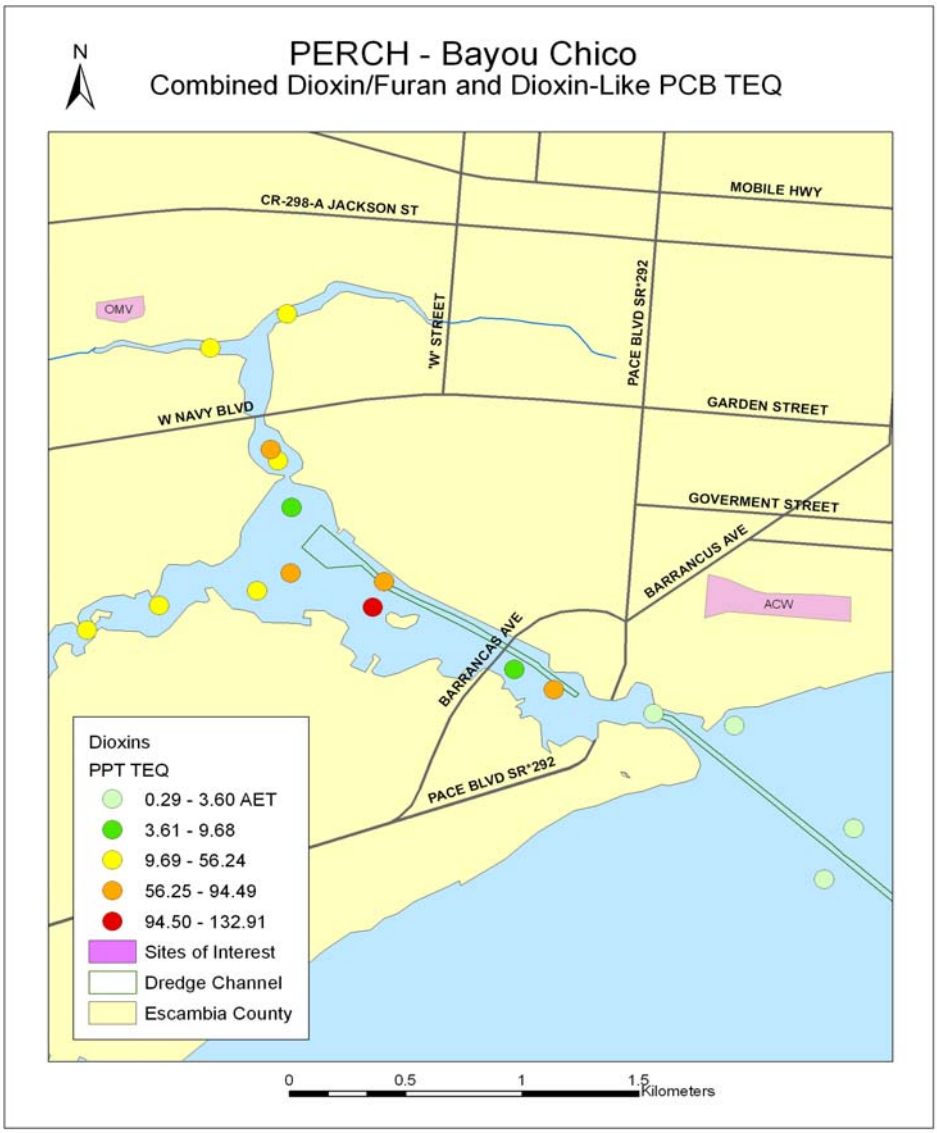


Fig. E-14: Map shows the combined TEQs for dioxins/furans and dioxin-like PCBs.

e. Metals

Analyses of nine trace metals were conducted with surface sediments from 26 sites. Thallium was not detected, total tin was detected in one sample, cadmium in 11, mercury in 23, and arsenic, chromium, copper, lead, and zinc were detected in all 26 samples. The respective TELs are exceeded by arsenic, chromium, and cadmium; the PEL is exceeded by copper, lead, mercury, and zinc. The latter four metals also exceeded their PEL in Bayou Texar, but did not reach the levels found in Bayou Chico. Even compared to other urbanized or industrialized catchments the Bayou Chico levels are high. Since most of the metals exceed their TEL or PEL they can be assumed to have negative impacts on biota in the bayou. The

lowest trace metal concentrations are present at the mouth of the bayou, as is the case for most pollutants, due to the interaction with the less polluted sediment and water from Pensacola Bay. The highest concentrations are generally reached near the spoil island and between the two constrictions in the northern part of the bayou. Fig. E-15 shows the distribution of lead (Pb), a pattern representative of the other metals in this bayou.

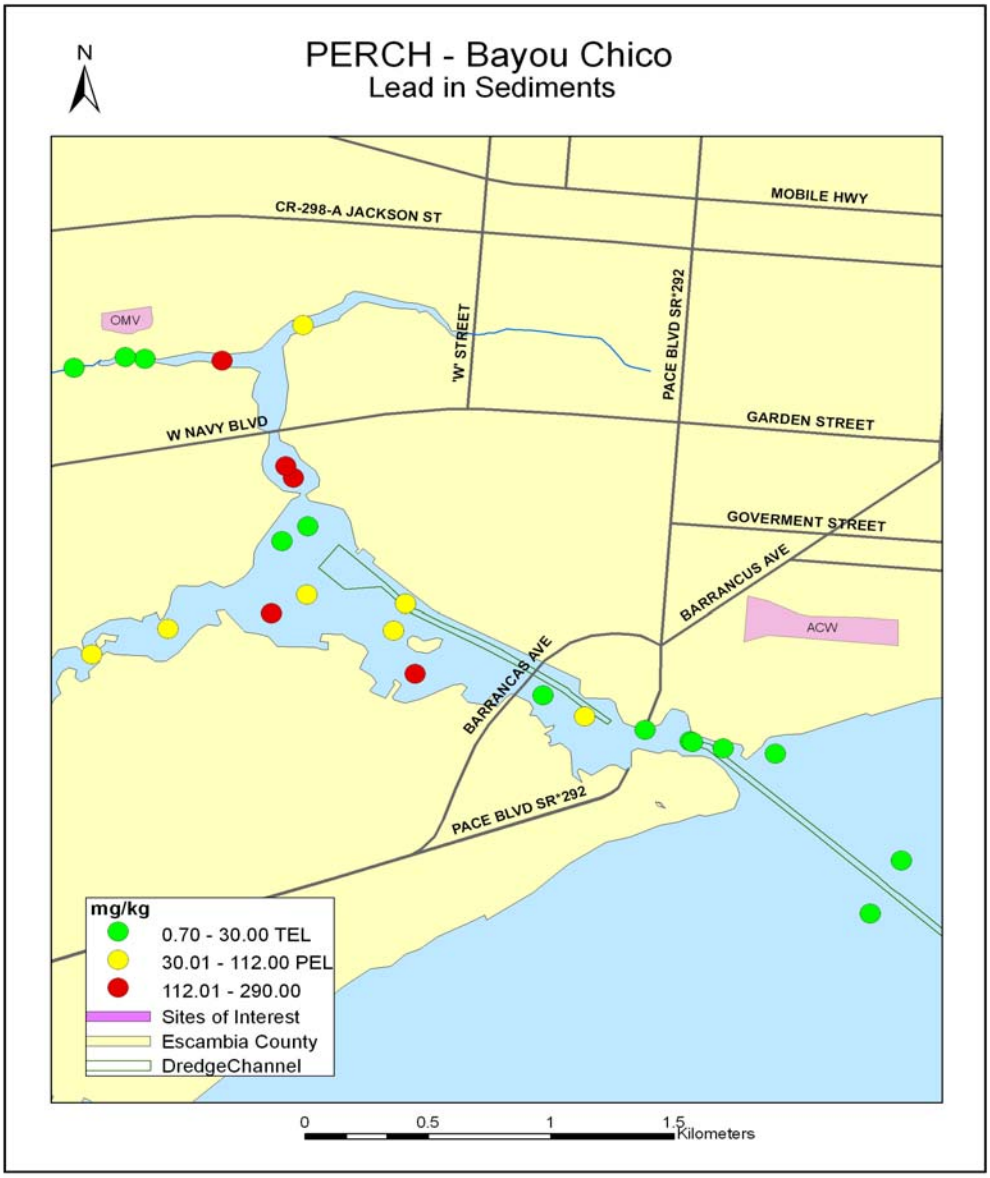


Fig. E-15: Lead concentrations in surface sediments.

f. Perspectives

Many of the pollutants examined in the present study exceed regulatory guidelines, including PAHs, dioxins/furans, PCBs and trace metals. Even though these pollutants may be unlikely to directly affect humans, because of limited direct contact of people with the sediments of Bayou Chico, they can affect human health through accumulation in fish/shellfish consumed by humans. Negative effects on the living environment are also manifested in the reduced populations of some biota. The present study did not find evidence of an effect of the ACW site on the surface environment at Sanders Beach. This is particularly noteworthy because part of the beach area is in front of the Pensacola Yacht Club ditch that at one time has been a major release point of creosote wastes from ACW to the bay. However, some deeper sediments at Sanders Beach are heavily polluted. The Omni-Vest landfill site to the north of Bayou Chico does not currently seem to affect the bayou via Jackson's Branch Creek. Considering the most likely sources for the encountered pollution, solutions for the poor environmental condition of Bayou Chico include reduction of inputs from industry and stormwater. There was recently dredging (2008) in the navigation channel of Bayou Chico and the spoils were disposed in a sand pit connecting to Jackson's Branch Creek, a short distance north of the bayou. Because of the geology of the area the sand pits may hydrologically communicate with groundwater, and additional consideration of the potential implications of the pollution from the dredged sediments is warranted.

4. Bayou Grande

Bayou Grande (Fig. E-16) is the largest of the three urban bayous in the Pensacola metropolitan area. Pollutants affecting the water and sediment quality of the southern half of the bayou have been studied previously in reference to possible releases from the Naval Air Station (NAS) on its southern shore, but not in reference to the entire bayou system. High levels of substances of concern (SOCs) including trace metals, polycyclic aromatic hydrocarbons (PAHs), dioxins/furans, and polychlorinated biphenyls (PCBs) have been found in the sediments.

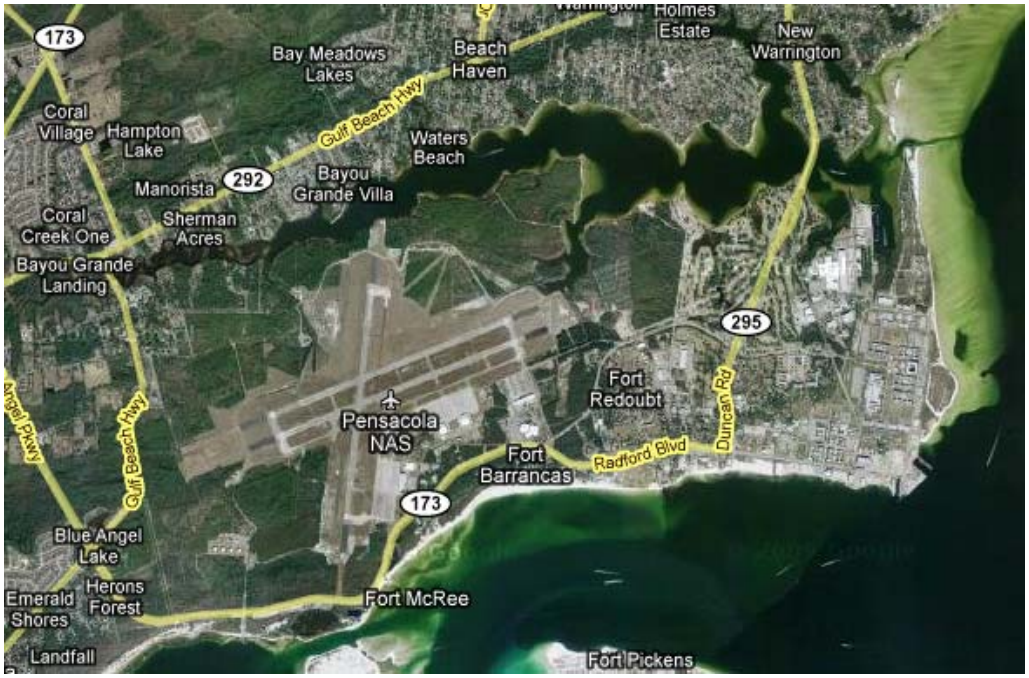


Fig. E-16. Bayou Grande, Warrington is the urban area to the northeast and NAS Pensacola lies to south of Bayou Grande.

a. PAHs

The highest total PAH concentrations (Fig. E-17) were observed in sediments in the Yacht Basin and other embayments of the eastern portion of the main body of the bayou. Florida sediment quality guidelines (TEL - concentrations above which adverse effects on biota are *possible*, and PEL - concentrations above which adverse effects on biota are *probable*) were exceeded in these embayments by several of the PAH species.

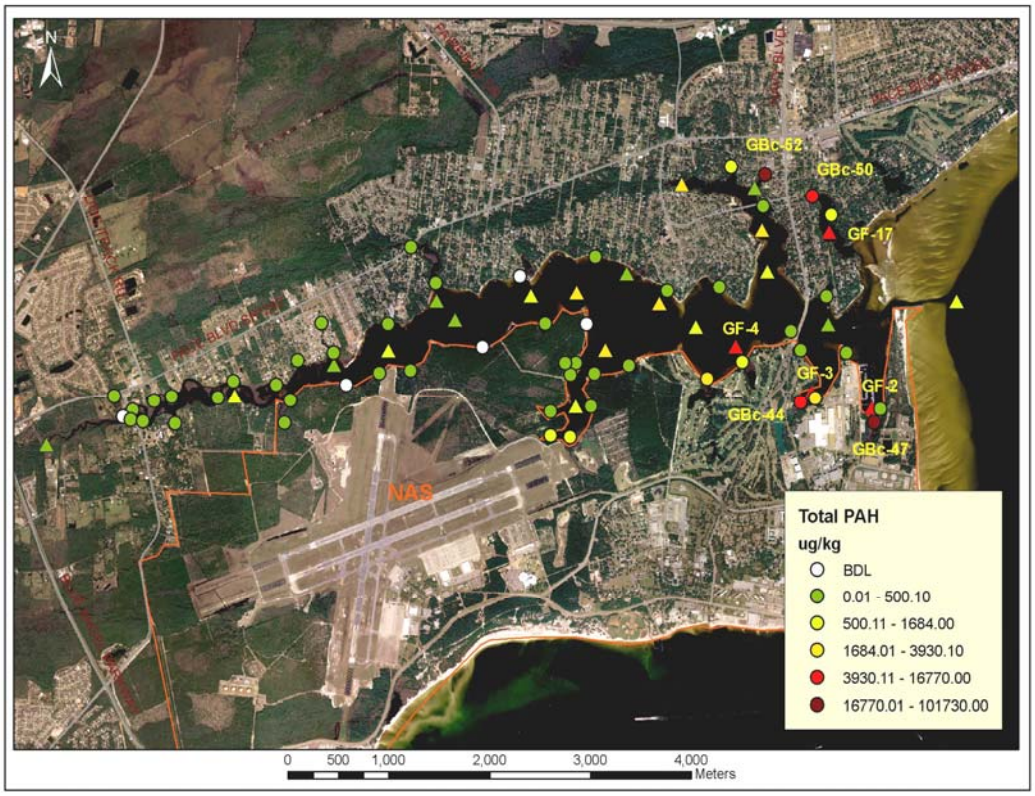


Fig. E-17. Total PAH concentration in sediments. Triangles are GF series, circles are GBc series.

Concentrations of most PAH species decreased abruptly with depth in the vibracores. In water, PAH concentrations were generally low. Naphthalenes are detected at higher concentrations in surface sediment in the main basin of the bayou and also near the shore of NAS than elsewhere in this bayou (Fig. E-17). Naphthalenes were also detected in vibracores at sediment depths ranging to 3 meters. Naphthalenes have been detected in NAS groundwater suggesting that transport by contaminated groundwater from NAS Pensacola to the bayou may be occurring.

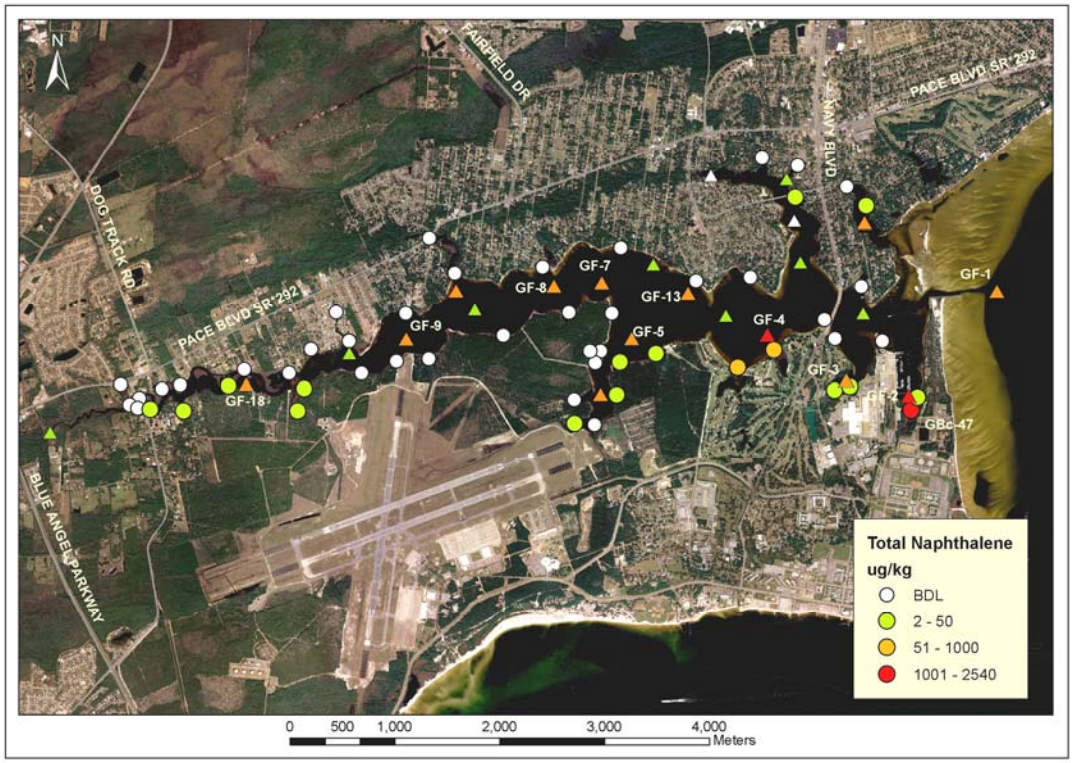


Fig. E-18. Total naphthalenes in surface sediments. Triangles are GF series, circles are GB series. The GB series were taken in shallow areas and the GF series were taken in deeper parts of the bayou.

For the GF series of samples the An/(Pn+An) ratio suggests a coal tar origin for 14 out of 23 of the samples. The Fl/(Fl+Py) and IP/(IP+Bghi) ratios, however, overwhelmingly suggest combustion of grass, wood, and/or coal products as the origin for these PAHs in the channel of the bayou. For the GBc series from the shorelines and the more distal embayment reaches the Rostad and Pereira ratios and An/(Pn+An) ratios show values indicating a mixed origin with combustion and coal tar origins for the sediment PAHs. The IP/IP+Bghi ratios indicate a brush, forest, and/or coal combustion origin for the PAHs with some ratios also indicating combustion of petroleum products. In summary, the PAHs in Bayou Grande sediments exhibit characteristics that suggest multiple origins with varied combustion being prominent, without any evidence of petroleum spills.

b. Total Petroleum Hydrocarbons

For total petroleum hydrocarbons (TPH) there were four detections in 23 sediment samples, and three detections in eight water samples. All detected concentrations were very low and were below the reporting limits for the method. This indicates that although the potential for TPH contamination exists in Bayou Grande, the TPH levels remain low in the bayou. Studies at other bayous (Bayous Chico and Texar) found more detections and higher concentrations of TPH.

c. PCBs

In 15 samples out of 23 the TEL was exceeded and one of the samples exceeded the PEL (GF-15, 193.38 µg/kg) (Fig. E-19). This sample was located at the most northern extension of Navy Point Bayou near a stormwater outfall draining surface waters from the Warrington area. Sample GF-14 from the same area was also high (154.08 µg/kg) but sample GF-19 (7.69 µg/kg) from elsewhere in Navy Point Bayou was not. Sample GF-23 at the mouth of this embayment was also high (76.52 µg/kg). Davenport Bayou, which is separate but adjacent to Bayou Grande, also had high total PCB concentrations (Fig. E-19). Its drainage is also from residential areas in the Warrington community. These findings suggest that some PCBs are originating in the Warrington area, and thus not all PCBs in Bayou Grande originate from NAS Pensacola. This is also suggested by cluster analysis.

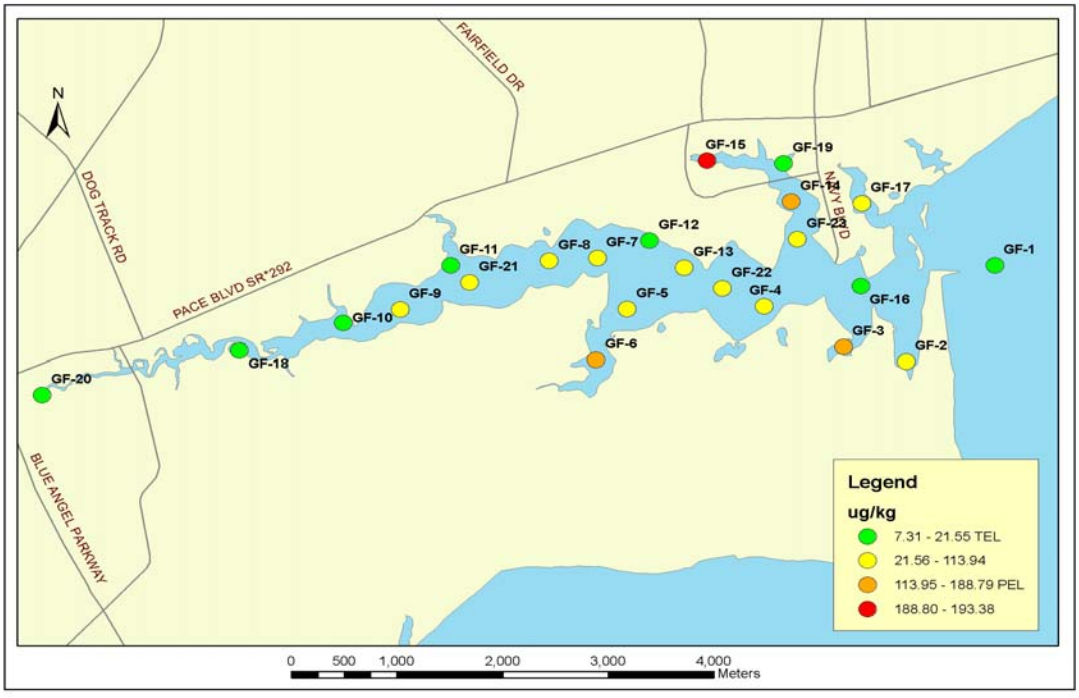


Fig. E-19. Total PCB concentrations in surface sediments.

Cluster analyses (Fig. E-20) indicate that the PCBs in much of Bayou Grande may be derived from NAS Pensacola, but it appears that there is another source along the northern shore, away from NAS and near Warrington and other residential areas.

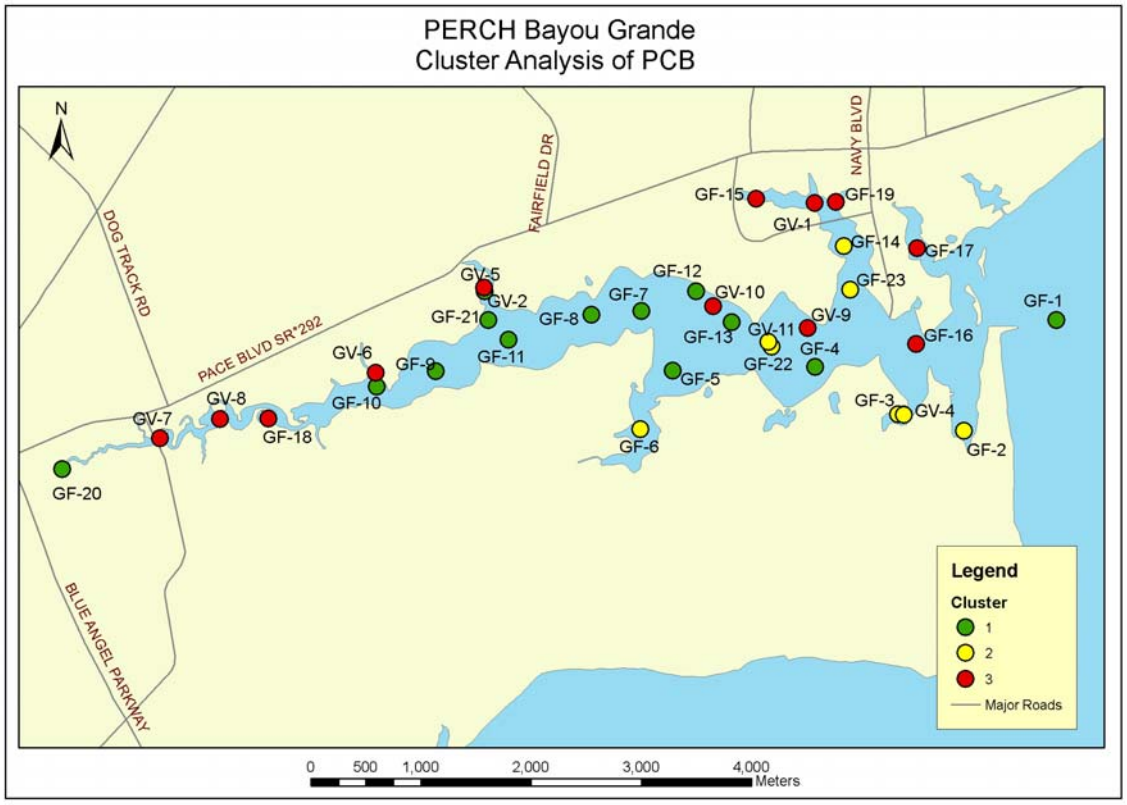


Fig. E-20. Cluster analysis of PCB congener data for surface sediments.

d. TEQs for Dioxins/Furans and PCBs

In Bayou Grande, 17 of the 23 samples had a combined TEQ that exceeded the NOAA sediment quality guideline (AET) (Fig. E-21). Seven of these samples had a TEQ almost three times the NOAA AET. The highest concentrations were found in two embayments along the southern shoreline and in an embayment of the northern shore, but exceedances occurred throughout the bayou. Overall the combined TEQ had the largest relative PCB contribution (44%) when compared to the other water bodies in our study.

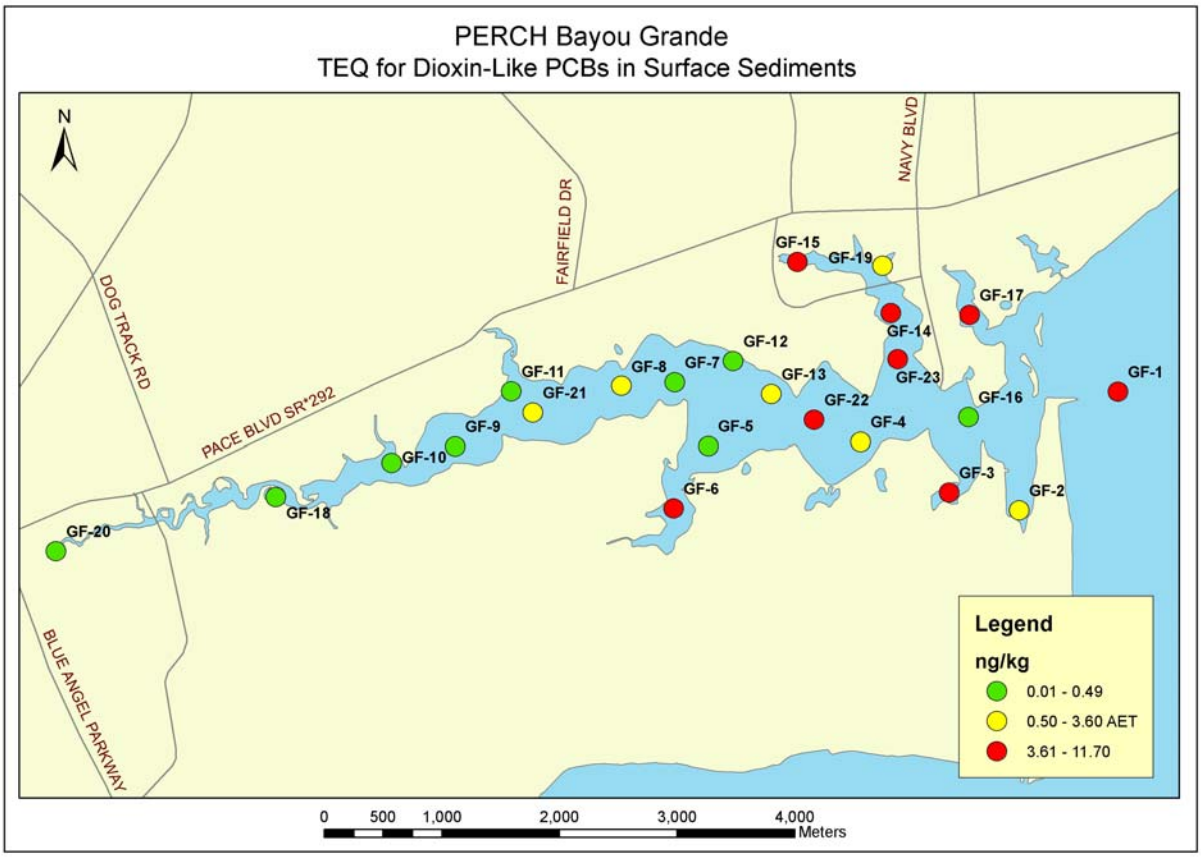


Fig. E-21. Combined TEQ of dioxins/furans and PCBs.

e. Dechlorination of PCBs and Dioxins/Furans

In vibracores systematic differences noted in chlorine profiles associated with sampling depth suggests that stratification of dioxin/furan profiles is present in the sediments. This stratification may be linked to different origins for the dioxins/furans or more advanced dechlorination of the dioxins/furans at greater depth, where sediments and their pollutants are older. Advanced dechlorination at depth is supported by a comparison of the relative proportion of the various dioxin/furan homologues from the depth and surface samples of the GV series (Fig. E-22). For PCB congeners some vibracores had greater percentages of the lesser chlorinated congeners at depth, suggesting that dechlorination also occurs for PCBs.

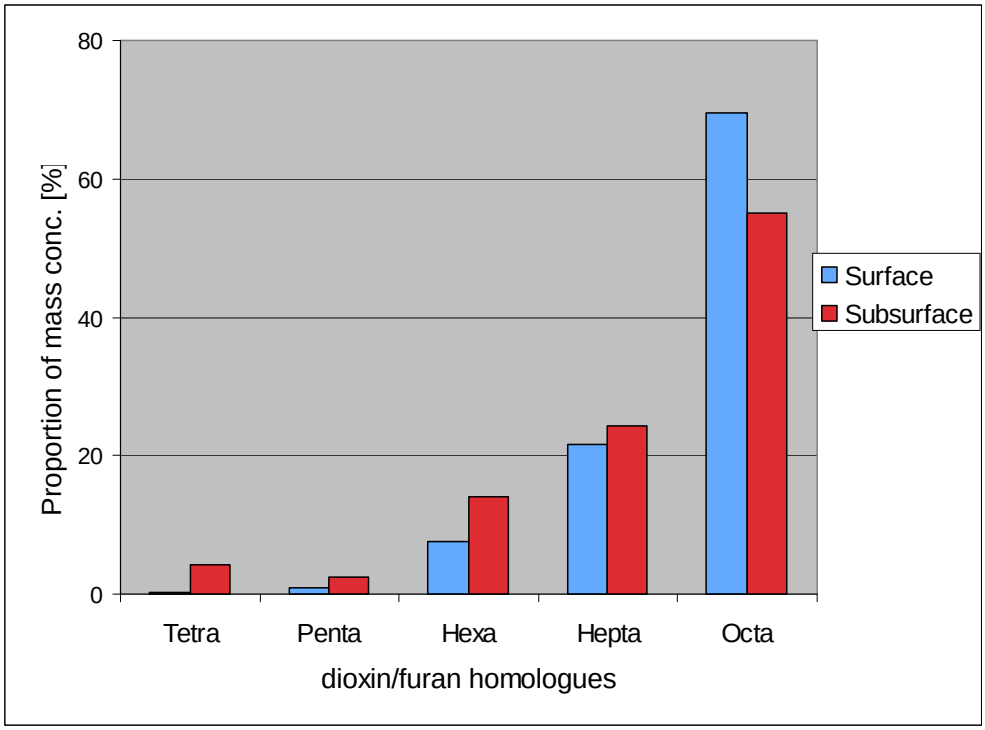


Fig. E-22. Average dioxin/furan homologue profile for GV samples. Homologue proportion is expressed as a proportion of total PCB mass concentration. Values for subsurface samples is the mean for all B (1m), C (2m), and D (3m) depth samples.

f. Pesticides

Only five detections of organochlorinated pesticides occurred in the 23 sediment grab samples from Bayou Grande. These five detections occurred in only two samples in the mid section of the bayou, one of which was for DDT and exceeded the TEL. There were no detections in the water column for any pesticides, which suggests that currently there is no transport of organochlorinated pesticides into Bayou Grande from surface sources.

g. Metals

We tested for 10 trace metals in surface sediments from 78 sites. Selenium was detected in six samples, cadmium in 32 samples, arsenic in 53, mercury in 49, total tin in 54, nickel in 71, and chromium, copper, lead, and zinc were detected in all 78 samples. The respective TELs were exceeded by arsenic, chromium, copper, mercury and nickel; the PEL was exceeded by cadmium, lead, and zinc. Selenium and total tin do not have sediment quality guidelines. Because the metals exceed their TEL or PEL they can be assumed to have negative impacts on biota in the bayou, but their concentrations were generally lower than in Bayous Chico and Texar. Concentrations for mercury, and to some extent nickel, are highest in the channel of the main body of the bayou but most other metals are highest in the upper reaches of the Yacht Basin and Woolsey Bayou near NAS, and in Navy Point Bayou in Warrington. Fig. E-23 shows the surface distribution for lead (Pb), highest concentration in

the eastern section of this bayou; there are hot spots occurring in the two south eastern embayments associated with NAS Pensacola.

Results for the vibracore samples are consistent with those for the surface samples and show higher levels of trace metals in embayments, especially on the south side of the bayou. At depth the concentrations are generally lower for the metals that are of anthropogenic origin, but occasionally the TEL is exceeded even at depth.

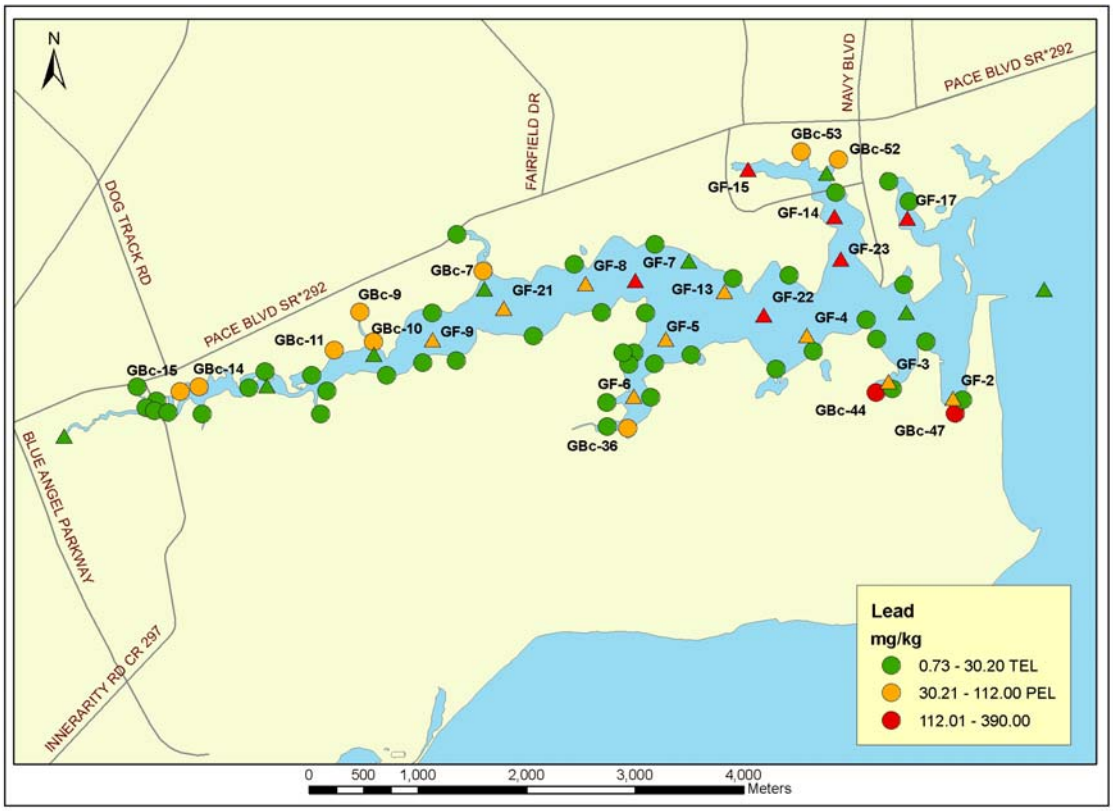


Fig. E-23. Lead in Bayou Grande sediments. (The round symbols indicate samples of the GBc series and triangles indicate samples of the GF series.).

h. Perspectives

Bayou Grande is the largest of the urban bayous in Pensacola. The close proximity of NAS Pensacola to Bayou Grande has resulted in impacts to Bayou sediments. These impacts are most severe in parts of embayments that are located closest to runoff areas from the more developed regions of the NAS. In the Woolsey Bayou embayment, impact (above TEL) was observed to depths of 3 meters for PCBs. What is new in the present assessment of Bayou Grande is that there is evidence showing that the Warrington area is also impacting the bayou. The precise nature of the impacts from both sources is not identical. For example, PAH analyses for samples taken near NAS are characterized by higher concentrations of naphthalenes than those adjacent to Warrington. Relative to the future there is some evidence pointing to the occurrence of natural degradation for dioxins/furans and the more highly chlorinated PCB congeners in the deeper sediments. However, other explanations are also

possible for the observed temporal changes. In any case, as sediment depth increases, total chlorination declines for dioxins/furans and PCBs. The more chlorinated persistent organic pollutants (POPs) at the surface are not as subject to anaerobic degradation and would be expected to be available to biota. Many sediment bound trace metals such as lead will likely remain bound in the sediment since degradation does not occur. It is possible that POPs and metals will be covered by sediments in the future that will hopefully be less contaminated.

5. Escambia Bay

The citizens and governments of Escambia and Santa Rosa Counties as well as the State of Florida and the federal government have been concerned over the environmental state of the Escambia Bay and River System over the years. The concern stems from massive fish kills caused by the severe deterioration of the environmental conditions due to point source releases from industrial and municipal sources that led to eutrophication. Although fish kills are now uncommon, concerns continue on the nature and extent of pollution in this bay, including the lingering impacts of the release of PCBs from a point source (former Monsanto Company) located on the lower Escambia River (Fig. E-24).

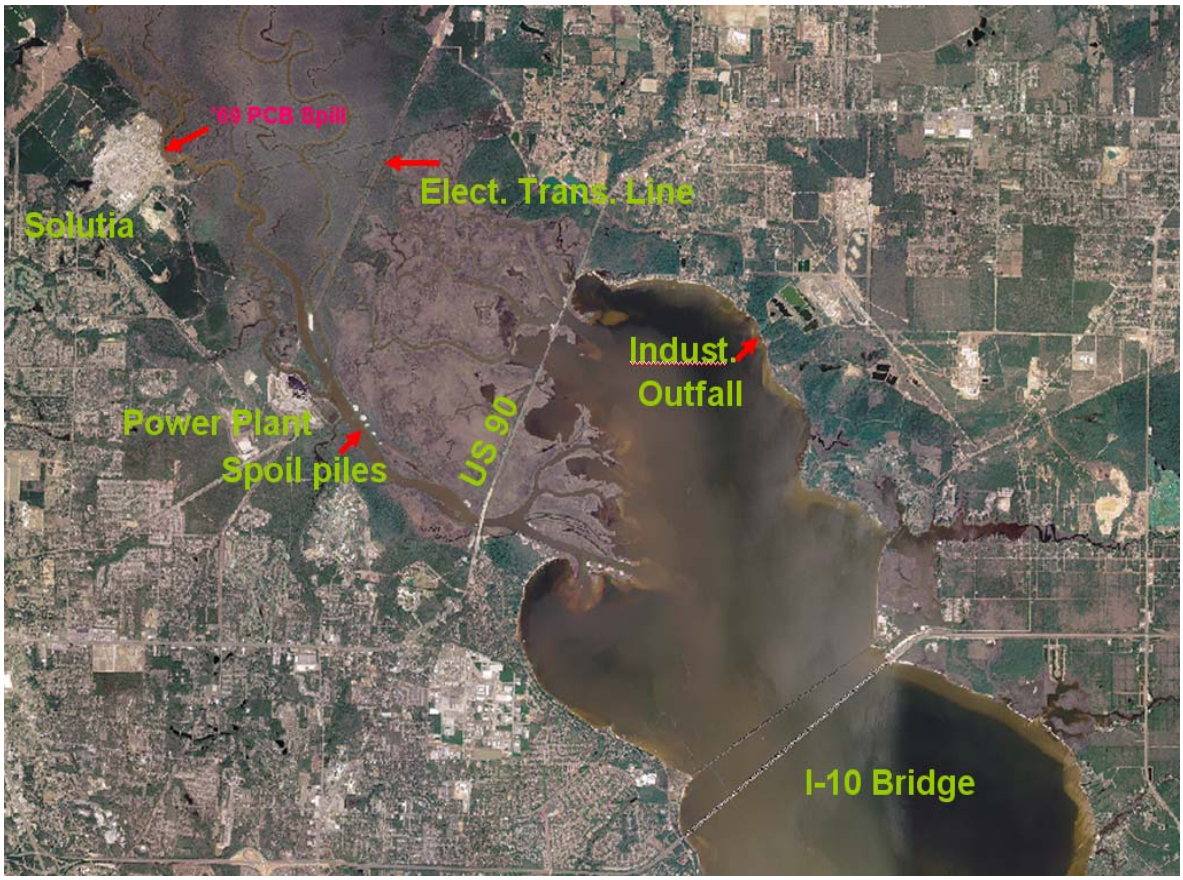


Fig. E-24. Aerial photograph of lower Escambia River and upper Escambia Bay (2004).

This study focuses on determining the profiles of PCBs, dioxins/furans, and other common urban and industrial pollutants in sediments of the Escambia Bay and River System in Florida. The present study is the most complete and systematic study to date of Escambia Bay and River System sediments relative to the number of samples, areas sampled, and the analyses employed. This study was intended to complement related PERCH studies on PCBs, dioxins/furans, and other SOCs in seafood tissues.

The study area was divided into five sections for sampling considerations.

1. Lower bay (south of the I-10 Bridge),
2. Upper bay (between I-10 bridge and US 90 causeway),
3. Lower wetlands (north of US 90 causeway up to the join of the north high tension transmission line and old gas pipe line),
4. Lower river (between river's mouth and Solutia, Inc. to the north), and
5. Upper river (north of the Solutia, Inc. facility)

a. PAHs

For the light molecular weight PAH category there were only 4 samples that exceeded the TEL, and for the heavy molecular weight PAH and the sum of the light and heavy PAH categories only two samples each exceeded the TEL (Fig. E-25a, E-25b). No samples for these three groups exceeded the PEL. The current study's detected ranges for summed light and heavy molecular PAHs were 2.4 to 2859 μg/kg and average of 238.2 μg/kg. The PAH concentrations detected during the current study in Escambia Bay and River are much lower than those in Bayous Texar, Chico, and Grande.

It was not feasible to assess the origins of PAHs using forensic ratios of selected congeners due to numerous nondetects of the required PAH species.

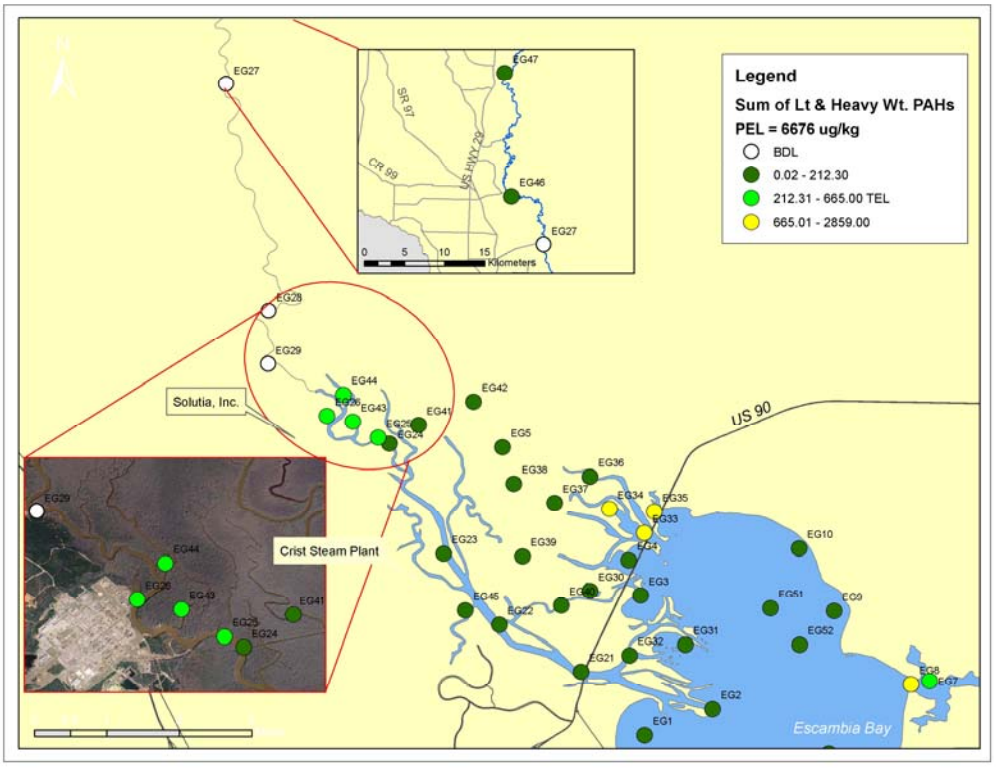


Fig. E-25a. Sum of light and heavy weight PAHs in sediments in Escambia River and upper bay.

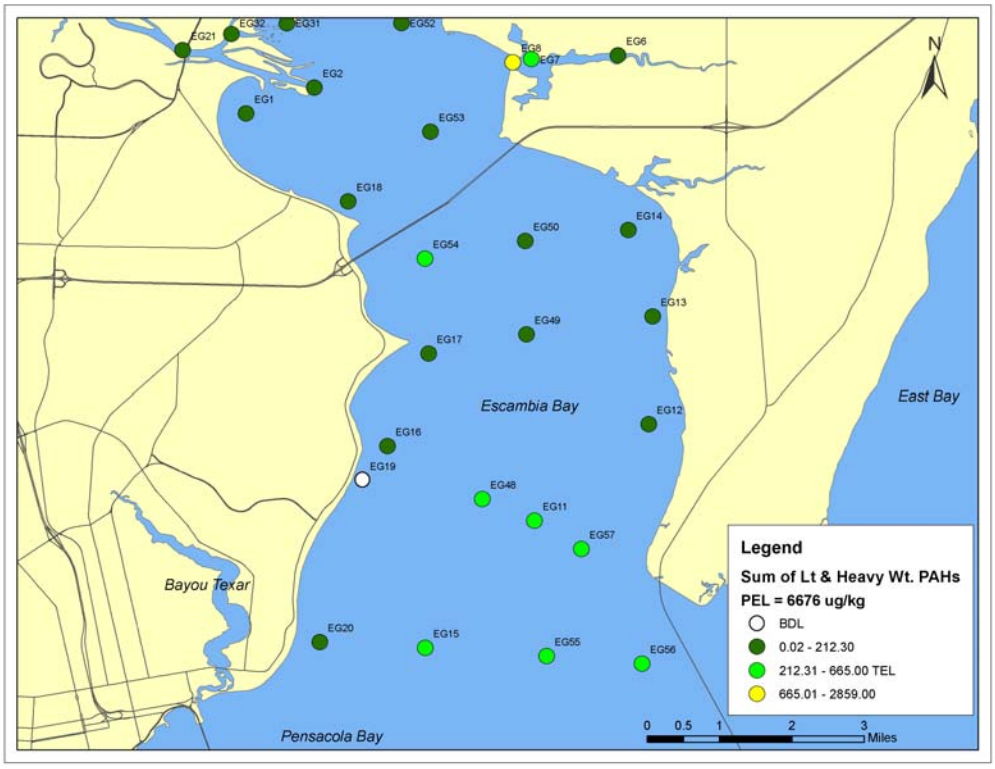


Fig. E-25b. Sum of LMW and HMW PAHs in sediments in Escambia Bay.

b. Total Petroleum Hydrocarbons

Seven out of 57 samples had low but detectable concentrations of total petroleum hydrocarbons (Fig. E26a, E-26b). One of the detections was in the bay, two were in minor channels of the Escambia River, and four detections were in or near to the main channels of Escambia River. The observed concentrations suggest total petroleum in sediments is not of environmental concern in Escambia Bay and River.

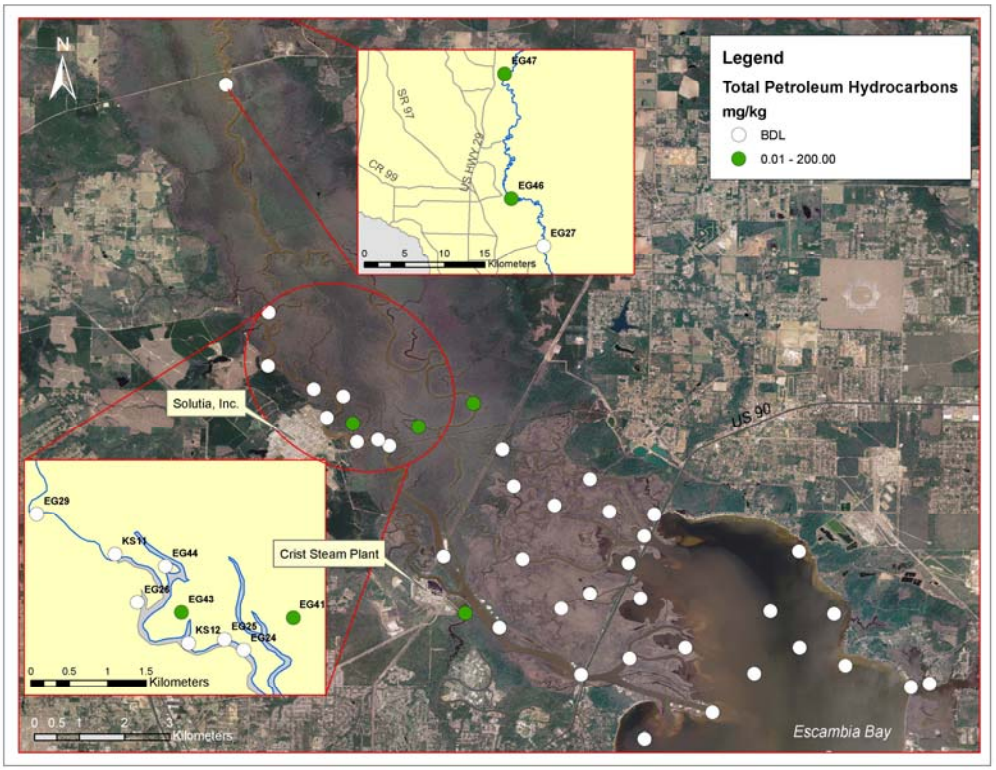


Fig. E-26a. Total petroleum hydrocarbons in sediments in Escambia River and upper bay.

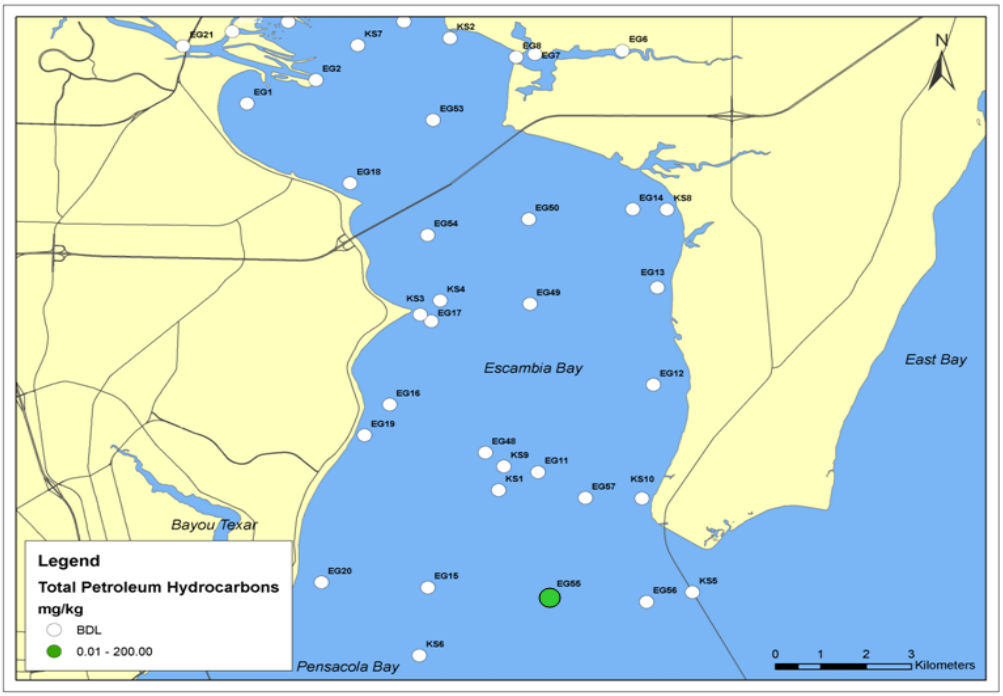


Fig. E-26b. Total petroleum hydrocarbons in sediments in Escambia Bay.

c. PCBs

Total concentrations for the 209 PCB congeners in the sediments ranged from 0.9 µg/kg to 125.9 µg/kg with a mean of 17.9 µg/kg (Fig. E-27a, E-27b). Sixteen samples exceeded the FDEP TEL of 21.6 µg/kg; no sample exceeded the FDEP PEL of 189 µg/kg. The concentrations of the PCBs generally varied according to the region in the Escambia Bay and River System. Overall, the lower Escambia River and upper regions of Escambia Bay had PCB concentrations near the TEL. There were two samples that stood out from the others due to their higher concentrations and also their locations. One was located in Thompson's Bayou, adjacent to where the thermal canal from the Crist Steam Plant bypasses it, and had a PCB concentration of 93.5 µg/kg. The other sample had the highest concentration of all the samples (125.9 µg/kg) and was collected near the Monsanto-Solutia spill site. It appears that there is significant PCB contamination in the sediments in this stretch of the river and, according to FDEP SQAGs, can impair sediment quality. It would be remarkable if this contamination has persisted in an area subjected to dredging and tow boat prop wash since the 1969 release at Monsanto without additional PCB import. In the lower wetlands adjacent to the lower river the mean PCB concentration was 14.1 µg/kg and for the lower Escambia Bay the mean was 11.9 µg/kg. Upriver of the spill site the mean concentration was lower (5.06 µg/kg).

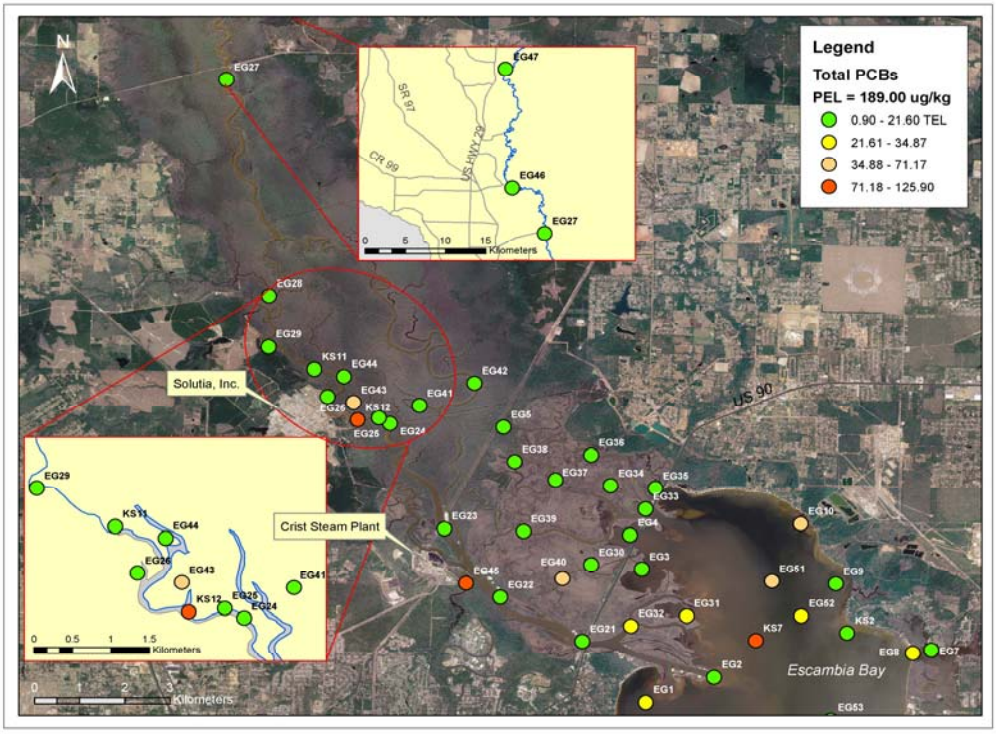


Fig. E-27a. Total sediment PCBs for upper Escambia Bay and River and lower wetlands.

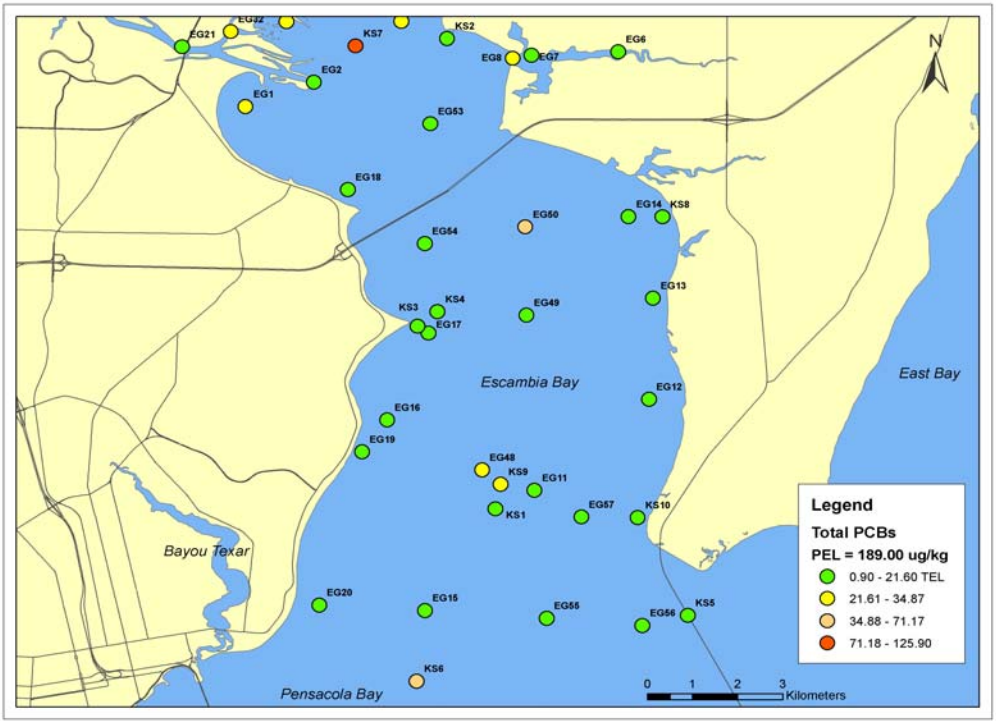


Fig. E-27b. Total sediment PCBs for Escambia Bay.

d. Origins of PCBs

The overall profile for the sediment PCBs shows attributes of degradation via dechlorination that makes forensic determinations of the parent material difficult. The forensic evidence suggests the possibility that besides A1254, which was spilled at the Monsanto-Solutia site, other Aroclors also contributed to the current PCB profile. The possibility of other undocumented PCB releases is to be expected for a bay and river system with multiple industries in its watershed.

e. TEQs for Dioxins/Furans and PCBs

The mean summed TEQ of dioxins/furans and dioxin-like PCBs for the sediments is 2.6 ng/kg (Fig. E-28a, E-28b). Dioxins/furans contribute about 92% and PCBs about 8% of the total TEQ. For summed TEQ about 33% of the samples exceeded the NOAA TEL, but not the NOAA AET. An additional 23% of the samples exceeded both the TEL and AET. This implies that about 56% of samples exhibited summed dioxin/furan and dioxin-like PCB TEQ toxicities that could impact sediment biota adversely. Spatially, the dioxin-like PCB distribution does not coincide with the dioxin/furan TEQ distribution. This is likely due to differences in origin and possibly to different interactions with transporting and degradation processes.

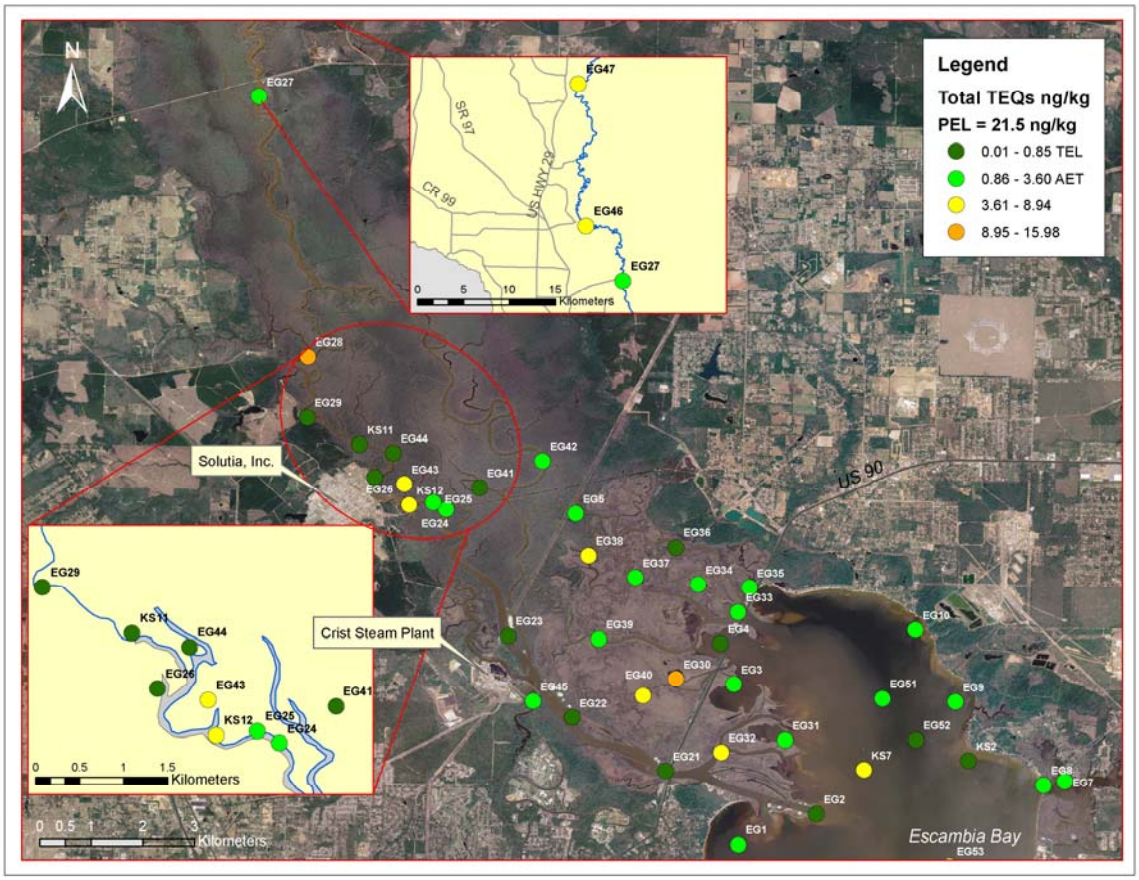


Fig. E-28a. Total combined TEQ in Escambia River and the upper Escambia Bay.

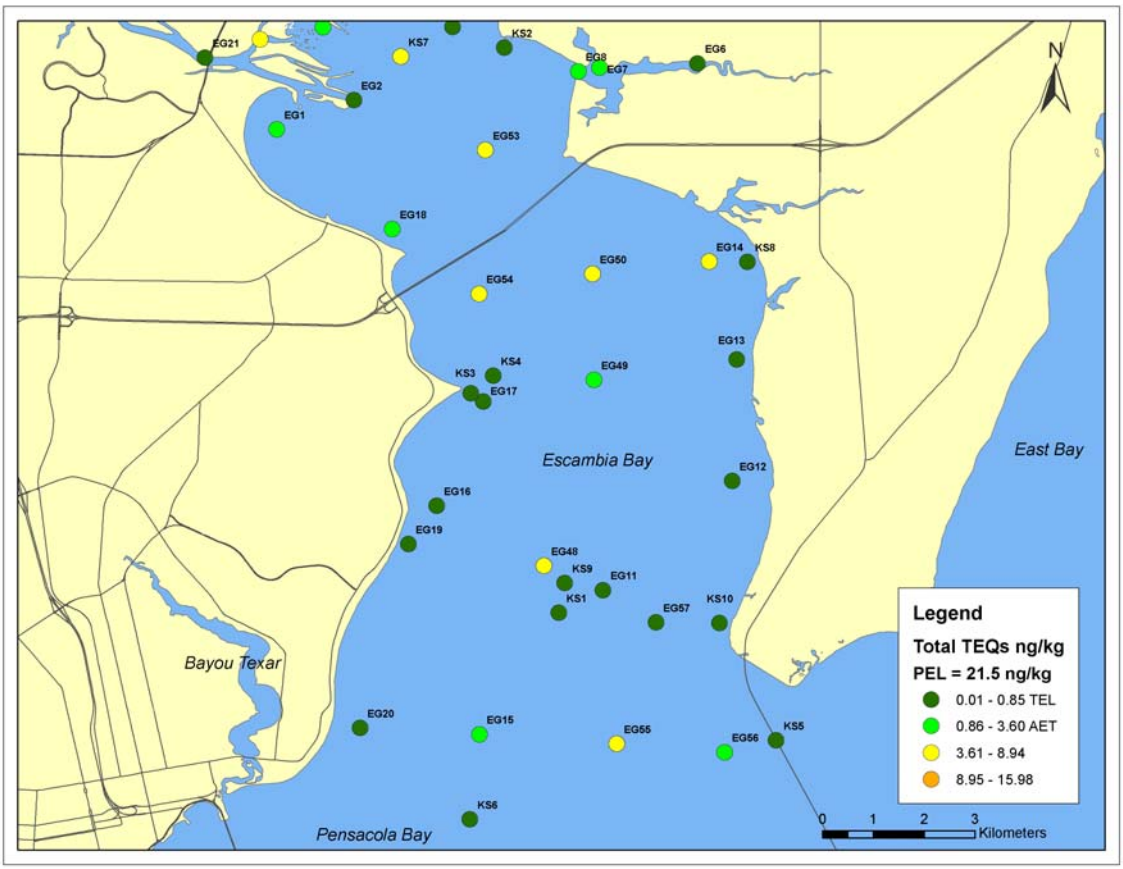


Fig. E-28b. Total combined TEQ in Escambia Bay.

f. Pesticides

For pesticides, only 4,4'-DDT was detected in the sediments with only one exception when two DDT byproducts were detected in the bay (Fig. E-29a, E-29b). DDT was detected in 25% of the sediment samples. All detected 4,4'-DDT concentrations were above the FDEP PEL (4.77 µg/kg) except one sample that only exceeded the TEL (1.19 µg/kg). The DDT was generally associated with the wetlands and river, and this is of concern as some of these areas may serve as nurseries for marine life and DDT could impact fish and shrimp populations.

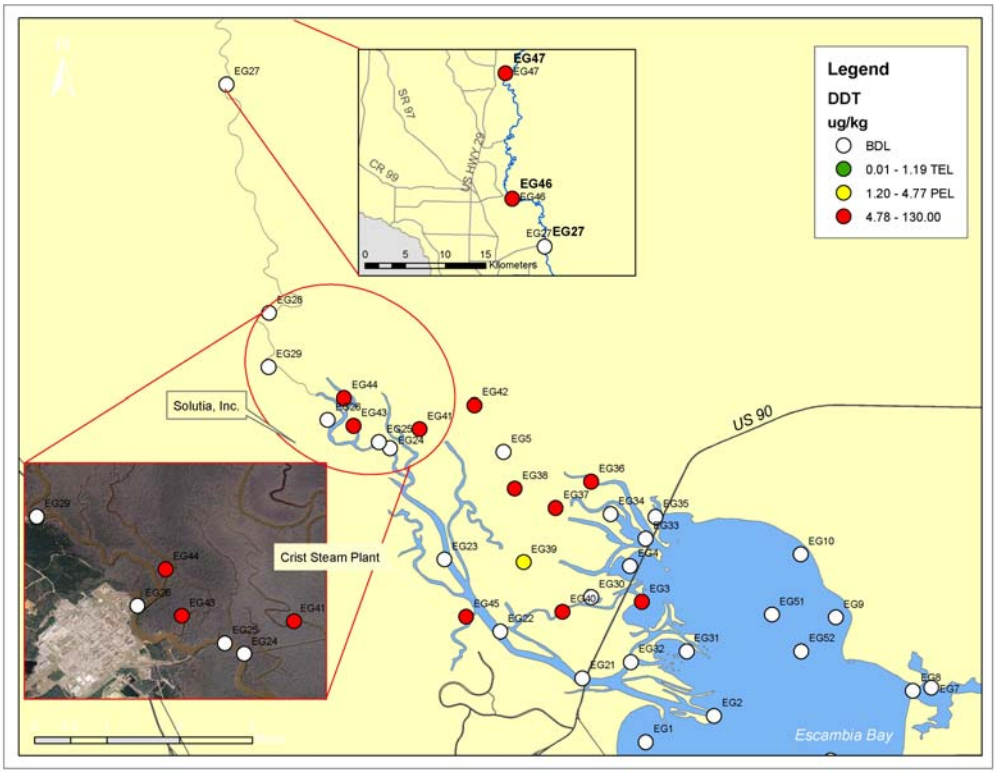


Fig. E-29a. DDT in sediments in Escambia River and upper Escambia Bay.

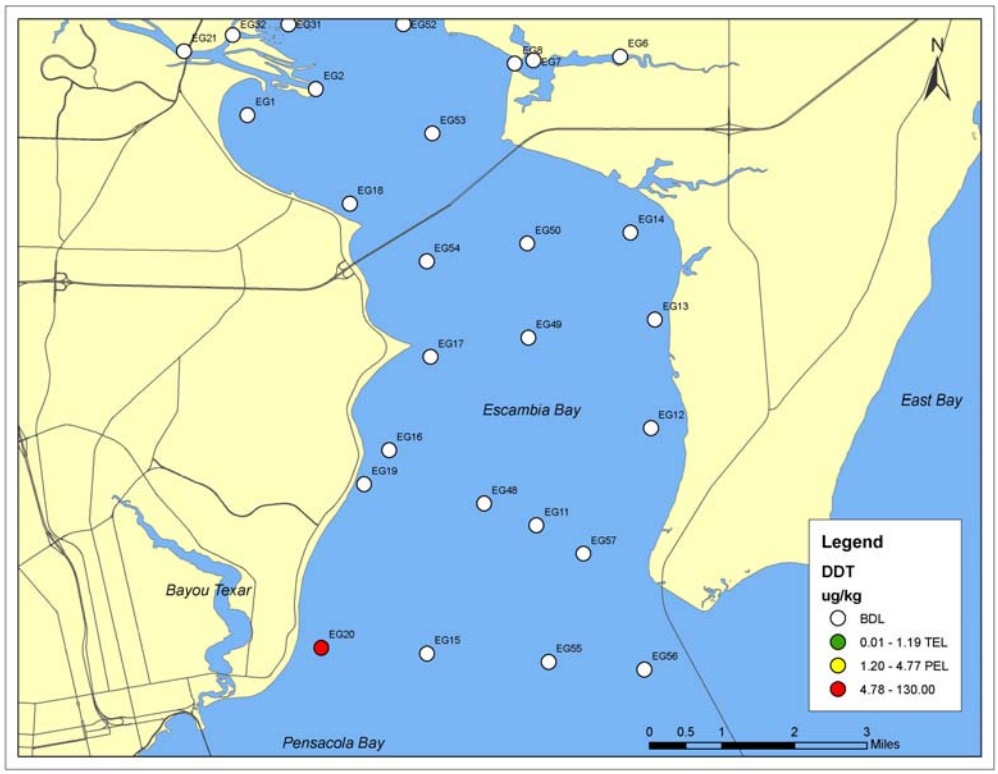


Fig. E-29b. DDT in sediments in Escambia Bay.

g. Metals

A total of 14 common metals were analyzed in sediments and included aluminum, arsenic, cadmium, calcium, chromium, copper, iron, lead, magnesium, mercury, nickel, selenium, tin, and zinc. Ten of these can be considered to be common trace metals: arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, tin, and zinc. Some of these trace metals exceeded their TEL, but not PEL. Overall, there were frequent exceedances of the TEL near an Air Products outfall in the upper region of Escambia Bay. It is not clear if the metals originate from this outfall or were carried to the sediments from other parts of the system. Total arsenic appeared to represent the greatest toxic metal impact to the sediments. It was detected in all 57 sediment samples and 30 samples exceeded the TEL. The basin area (deeper regions of Escambia Bay) appears to be the most contaminated with arsenic. Total cadmium in sediments was detected in 46 sediment samples and 16 samples exceeded the TEL. Total chromium was detected in all 57 sediment samples and 14 samples exceeded the TEL, especially in the lower part of the bay. Total copper was detected in 55 sediment samples but only 4 samples exceeded the TEL. Total lead was detected in all 57 sediment samples and 11 samples exceeded the TEL. Total nickel was detected in all 57 sediment samples and 16 samples exceeded the TEL, especially in the bay's basin. Total zinc was detected in all 57 sediment samples and 6 samples exceeded the TEL. Total selenium was detected in 42 sediment samples and total tin in 35 samples but there are no FDEP SQAGs for these two metals. These observations for trace metals indicate that their concentrations are not extremely elevated but, because they exceed the TEL in some samples, have the potential to negatively impact bottom dwelling organisms.

Fig. E-30a, E-30b show the spatial surface sediment concentrations of arsenic that was the only trace metal to consistently exceed SQAG. The mean of total arsenic sediment concentrations was 10.6 mg/kg, ranging from 0.27 to 35 mg/kg. A total of 30 samples exceeded the TEL of 7.24 mg/kg and none exceeded the PEL of 41.6 mg/kg. Overall arsenic is the biggest contributor to metal sediment toxicity on the basis of FDEP SQAG exceedances. The basin area (deeper regions of Escambia Bay) appears to be the most arsenic contaminated region of the Escambia Bay and River System. The Pearson product-moment correlation coefficient shows a strong positive correlation of 0.83 between clay content and arsenic concentration. This suggests that arsenic is associated with the smallest diameter sediment particles of less than 2 μm, which can be expected to accumulate mostly in the less dynamic deeper parts of Escambia Bay.

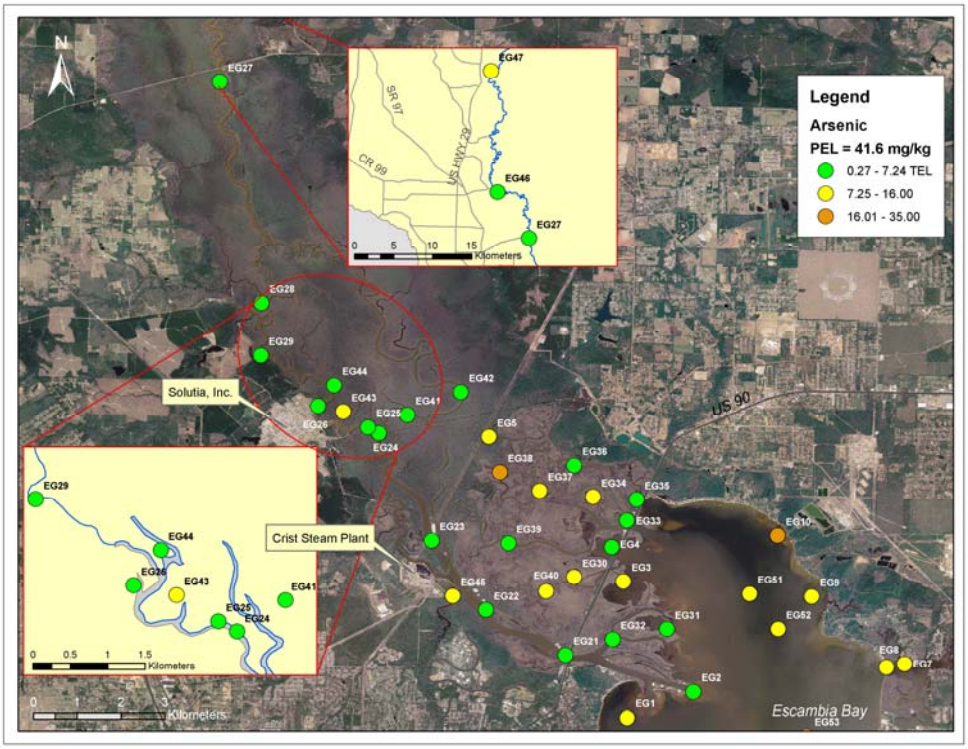


Fig. E-30a. Arsenic in Escambia River and upper bay sediments.

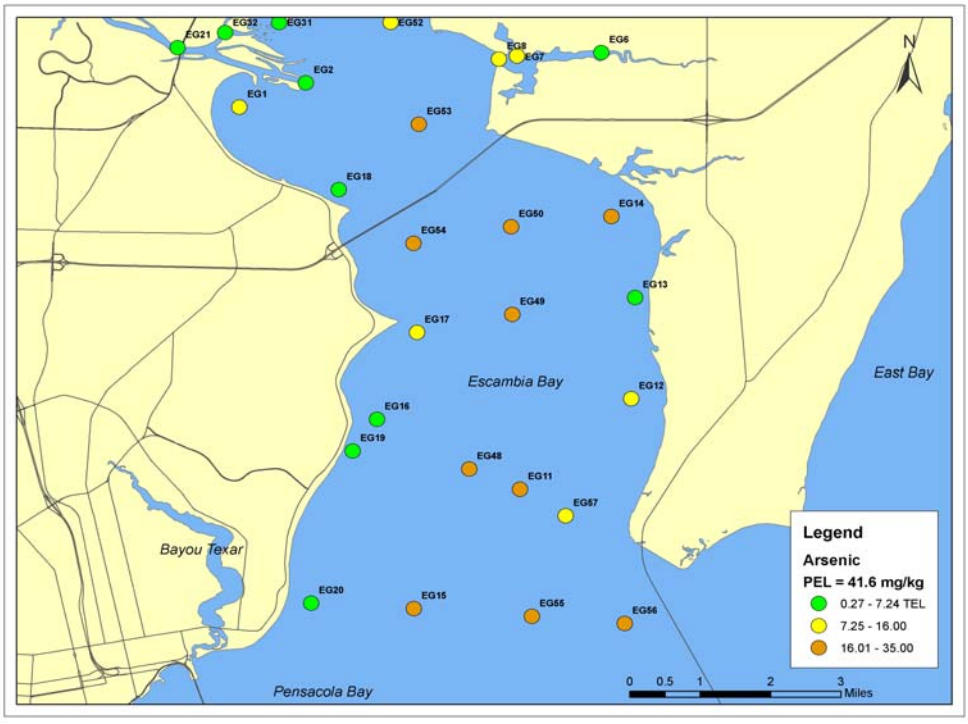


Fig. E-30b. Arsenic in Escambia Bay sediments.

h. Perspectives

The major focus of this study was directed to sediment pollutants that accumulate in the biota. There are several metals (including mercury), dioxins/furans, and PCBs that are of concern. The PCBs and mercury appear to be the most important, with the PCBs being of utmost importance in some bay species. For PCBs the only recognized environmental criteria for Gulf Coast estuarine waters are the FDEP TEL and PEL for metals and total PCBs. Additionally there are the more recent NOAA SQAG: TEL, AET, and PEL for TEQ that were published in 2008. These SQAG only apply to the overall survivability and reproduction of selected benthic organisms that can be maintained under laboratory conditions for toxicity testing. There currently are no applicable state or federal guidelines that are protective relative to accumulation of SOCs for upper trophic level consumers that include many seafood species. Food web studies are required to determine the dynamics of accumulation of target contaminants in upper trophic level organisms such as fish. Part of a recent legal action concerning Escambia sediment PCBs is a demand that there be a 'cleanup' of Escambia Bay presumably to sediment concentrations that will not maintain tissue concentrations of pollutants above federal and state guidelines for seafood consumption. Our study has shown that PCBs are wide spread throughout the Escambia Bay and River system, but only 16 samples out of 69 exceeded the TEL and none exceeded the PEL.

Our overall studies indicate that although the sediment PCBs may only have moderate impacts upon benthic organisms, they are enabling significant accumulation of PCBs in fish/shellfish in Escambia Bay and River System (Section III. F). So, at this point it is difficult to ascertain "safe" sediment PCB concentrations that would allow unmonitored consumption of seafood.

6. Relative Concentrations of Pollutants and Their Temporal Changes in the Pensacola Bay System

This section provides a comparative account of the relative levels of pollutants in the water bodies studied, and to what degree they changed (if any) in recent years.

a. Superfund Sites and Groundwater Plumes

Bayou Texar: In Bayou Texar, the observed levels of fluoride in the pore water and sediments indicates that the release of ACC plume contents into Bayou Texar is continuing at levels comparable to those reported by ENTRIX in 1993. As noted by previous studies, we did not find any evidence that the ETC plume is impacting Bayou Texar. EPA has recently completed the first phase of remediation of the ETC site, involving the burial and capping of contaminated soils, and is planning to remediate the contaminated ground water. These efforts should aid in limiting the spread of contaminants from this Superfund Site.

Bayou Grande: The presence of contaminated groundwater at NAS Pensacola is documented, but its travel and discharge to Bayou Grande has not yet been documented. The detection of naphthalenes at 3-meter depths in Bayou Grande merits further research.

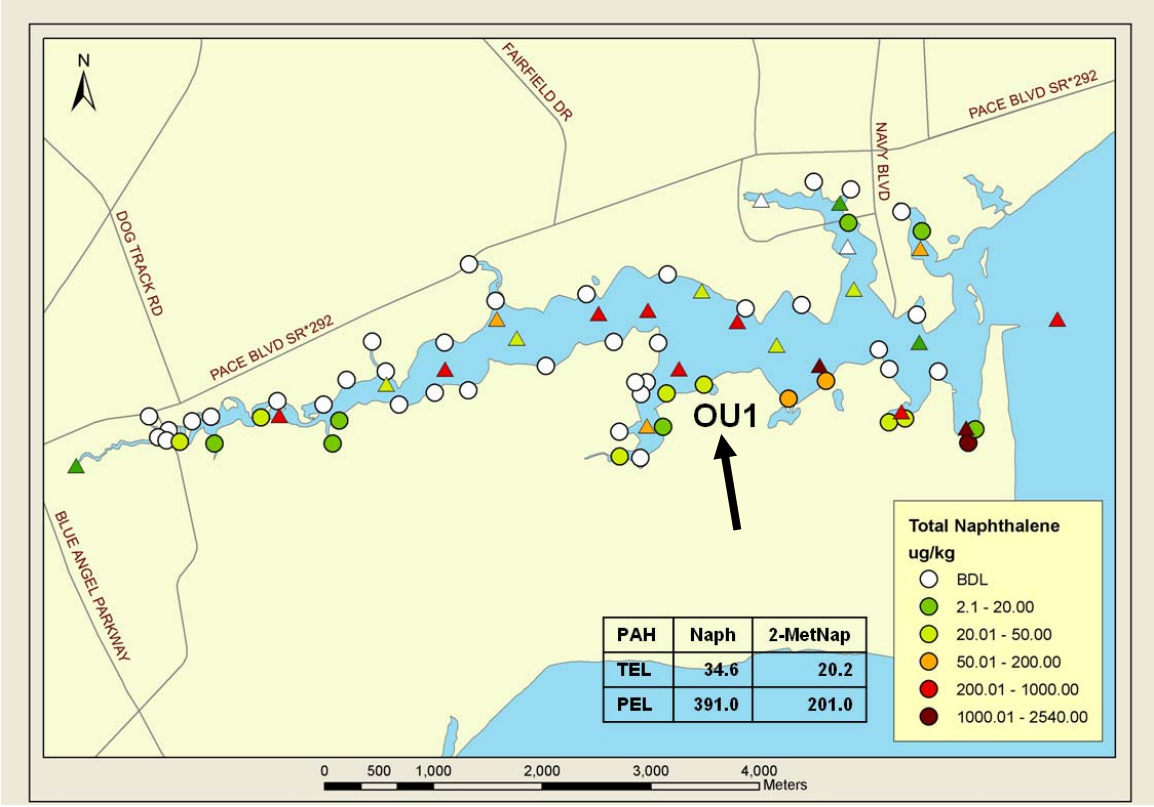


Fig. E-31. Bayou Grande Map showing total naphthalene concentrations and contaminated aquifer that could be a source. OU1 (Operable Unit 1) is indicated by an arrow.

Bayou Chico: We investigated the potential impacts of two plumes, from OmniVest Landfill and American Creosote Works Site. No obvious impacts from the OmniVest site were observed. However, creosote was found under Sanders Beach and does raise concerns. The creosote found under the beach at Sanders Beach is within the influence of a contaminated plume coming from the former American Creosote Works Superfund site, but there is no certainty of how the detected creosote deposit got under the beach.

Escambia Bay: For Escambia Bay a plume of dinitrotoluene is known to be present under the Air Products site, but we did not evaluate its impacts on the Escambia Bay.

b. PCBs

PCB and dioxin/furan TEQs were highest in Bayou Chico and lowest in Escambia Bay and River (Fig. E-32). Bayou Grande had mean PCB concentrations that were higher than in Bayou Texar, but less than what was observed in Bayou Chico.

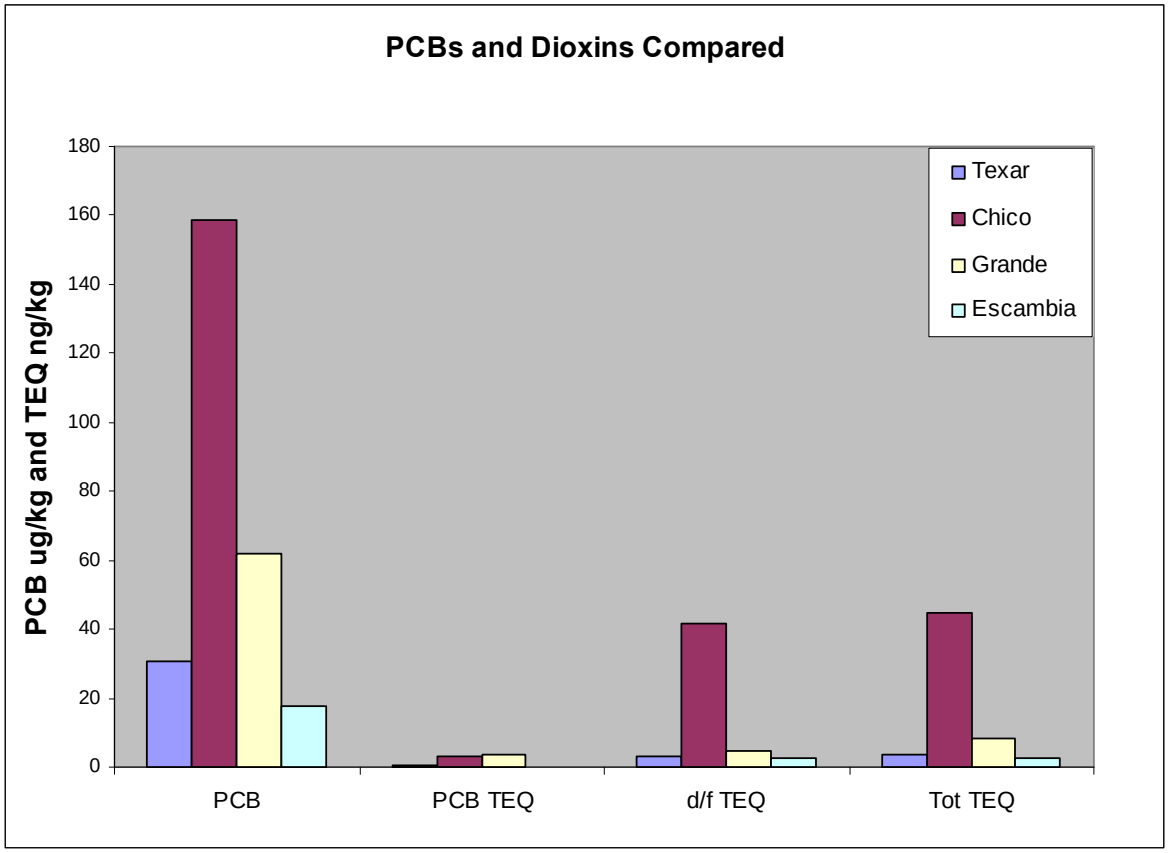


Fig. E-32. Mean concentrations of Total PCB [µg/kg], PCB TEQ [ng/kg], dioxin/furan TEQ [ng/kg], and Total TEQ [ng/kg] in Pensacola estuaries.

In Bayou Texar there has been only minimal change in mean PCB concentration in the recent past (Fig. E-33). In Bayou Grande there appears to have been an overall increase in mean PCB concentration over time, but differences in sample location can explain at least part of this apparent increase since not all of the most contaminated sites in embayments were sampled by previous studies.

Bayou Chico and Escambia Bay were subjected to extensive sampling by past studies making past results more representative and comparable to those of the current study. In Escambia Bay there was an overall decline in PCB concentration between the 1990s and 2008, possibly by as much as 50%. Despite this decrease, the degree of biomagnification of PCBs in the environment is sufficient to cause elevated PCB accumulation in fish/shellfish tissues (Section III. F). In Bayou Chico, PCB concentrations appear to have increased, especially close to a natural sediment trap near a spoil island. The ratio of the means of earlier

studies and the current study suggests that average concentrations may have doubled in Bayou Chico. This observation has to be interpreted with caution given differences in sample location and methods, but points to a need to determine if there is still a site releasing PCBs into Bayou Chico.

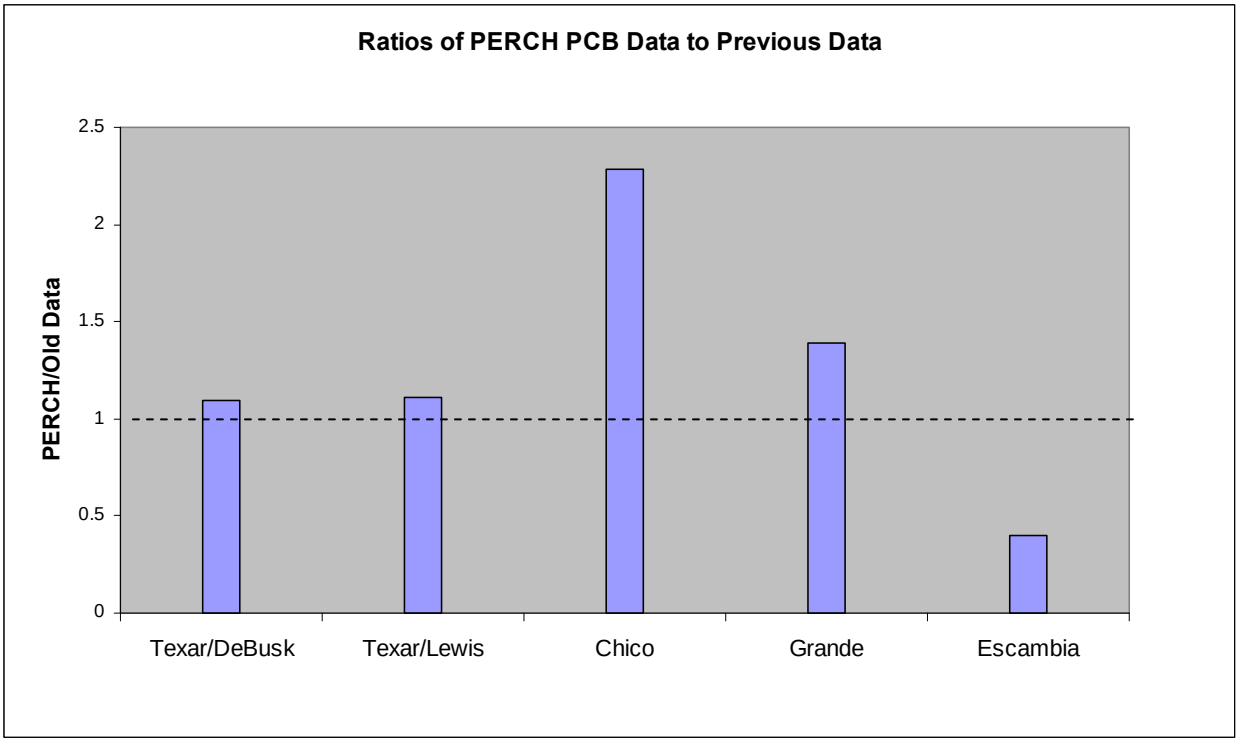


Fig. E-33. Ratio of current PCB concentrations to 1990's PCB concentrations. For Bayou Texar there were two older datasets that were used to calculate two separate ratios. A ratio of 1 is no change, a ratio of 0.5 indicates a 50% decrease and a ratio of 2.0 indicates a doubling of concentration. (DeBusk, W.F., I. Poyer, and L. Herzfeld. 2002. Sediment quality in the Pensacola Bay System. Technical File Report 02-03. Havana, FL: Northwest Florida Water Management District. 76 p; Lewis, M.A., J.C. Moore, L.R. Goodman, J.M. Patrick, R.S. Stanley, and T.H. Roush. 2001. The effects of urbanization on the chemical quality of three tidal bayous in the Gulf of Mexico. *Water, Air, and Soil Pollution*. 127(1-4):65-91.)

c. Dioxins/Furans

Dioxins/furans present in the studied estuaries made up a greater proportion of total TEQ than did dioxin-like PCBs (Table E-2). Dioxins/furans frequently exceeded the NOAA SQAGs, especially the TEL. Overall the dioxin/furan profiles showed octachlorinated dioxin to be the prevalent congener. The highly toxic 2,3,7,8 dioxin and the other less chlorinated dioxins/furans were present in very minor quantities. Natural alteration of the original profiles of the dioxins/furans makes it virtually impossible to use the profile of the sediment dioxins/furans to assess the sources of these toxic chemicals in the estuaries, or to predict anticipated changes because the dioxin/furan contamination is derived from diverse sources and distributed widely.

Table E-2. Means and geomeans for total PCB, along with PCB and dioxin/furan (DF) TEQs.

Estuary		Tot PCB[1] [µg/kg]	TEQ_P [ng/kg]	TEQ_{DF} [ng/kg]	TEQ_{DFP} [ng/kg]
Bayou Texar	Range	1.39-243.58	0.002-4.203	0.22-7.02	0.22-10.05
	Mean	30.73	0.635	3.22	3.85
	Geomean	12.4	0.047	2.11	2.31
Mean TEQ composition			16%	84%	
Bayou Chico	Range	0.57-1470.67	0.0006-21.49	0.023-128.77	0.173-143.69
	Mean	158.49	3.22	41.37	44.59
	Geomean	33.52	0.18	12.53	16.139
Mean TEQ composition			21%	79%	
Bayou Grande	Range	7.31-193.38	0.01-11.69	0.09-10.74	0.3-17.82
	Mean	61.7	3.6	4.6	8.3
	Geomean	36.7	0.7	2.2	4.6
Mean TEQ composition			43.8%	56.1%	
Escambia Bay and River	Range	0.9-125.9	.001-0.045	0.019-15.94	0.02-15.98
	Mean	17.9	0.19	2.43	2.62
	Geomean	8.44	0.04	1.07	1.21
Mean TEQ composition			7%	93%	

1 SQAGs for TEQ are the NOAA TEL (0.85 ng/kg), AET (3.6 ng/kg), and PEL (21.5 ng/kg).

d. Bioaccumulation of Dioxin-Like PCBs and Dioxins/Furans

This aspect is addressed more completely in the next section (III. F), but we present here an example of how the profiles of these contaminants differ in sediments and biota. In Fig. E-27 is depicted the relative composition of dioxin-like PCBs and dioxins/furans in sediments and the hepatopancreas of blue crabs. The relatively greater incorporation of dioxin-like PCBs than dioxins/furans into the hepatopancreas is indicative of selective/differential biomagnification in the hepatopancreas. In the absence of comparable data from earlier years, we are unable to assess whether there have been temporal changes in pollutant loads in fish/shellfish collected from our area waters.

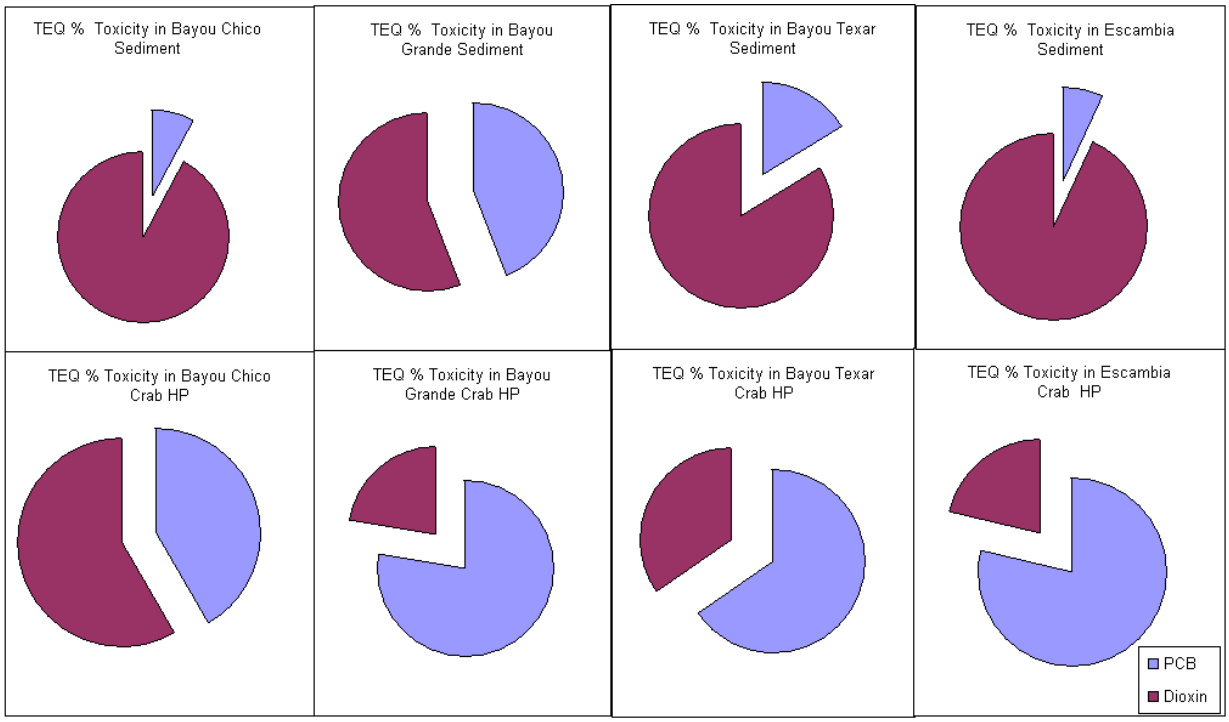


Fig. E-34. Combined TEQ in blue crab and sediments in Escambia Bay and River.

e. PAHs

PAHs are ubiquitous components of sediments, soils, and atmospheric particles. Combustion is a common source, as are petroleum products and coal tar products present in creosotes. The PAHs in the three bayous had different PAH congener compositions, and thus presumably differences in origins. In Bayou Texar forensic ratios of PAHs suggest that the detected PAHs were derived from combustion without a clear distinction being made for the sources of combustion. The PAH ratios in Bayou Grande sediments also exhibit characteristics that suggest multiple origins, but not petroleum spills. The total PAH composition, however, has a significant naphthalene content that appears to be coming from contaminated groundwater. Brush fires on the shores and combustion from internal combustion engines are likely sediment PAH sources.

For Bayou Chico, the area about Sanders Beach was considered separately from Bayou Chico and forensic ratios show a creosote origin for PAHs under the beach that is consistent with an origin from the American Creosote Works Superfund site. Other origins for the beach creosote are also possible. Samples collected elsewhere, near Sanders Beach mostly, had only trace PAH concentrations and exhibited forensic ratios that are less suggestive of creosote PAH origins, as compared to the samples taken under Sanders Beach. Surface samples collected in Bayou Chico had higher total concentrations than sediment surface samples collected elsewhere. The Bayou Chico surface samples appear to have multiple origins and do not demonstrate a significant contribution from the ACW site. For Escambia Bay and River the detected PAH concentrations were insufficient to calculate forensic ratios.

Total PAH surface sediment concentrations were high and often exceeded SQAGs in the bayous, but were much lower in Escambia Bay [329 µg/kg]. The average PAH concentrations we observed for the three bayous are within a range of 2,726 µg/kg (Bayou Texar) to 3,768 µg/kg (Bayou Grande). The higher mean for Bayou Grande is due to two hot spots in the headwaters of two embayments that had extremely high concentrations.

In Bayou Texar, the means from previous studies and the current study are essentially the same. In Bayou Chico there were diverse hot spots and these have greatly influenced the results, but overall little change in PAH concentration seems to have taken place in Bayou Chico in the recent past. Results seem to suggest that in Bayou Grande, PAH concentrations have increased considerably but this may be spurious because previous studies did not sample the most polluted embayments of Bayou Grande, as in the present study. In Escambia Bay and River a modest decrease over time can be noted (Fig. E-35).

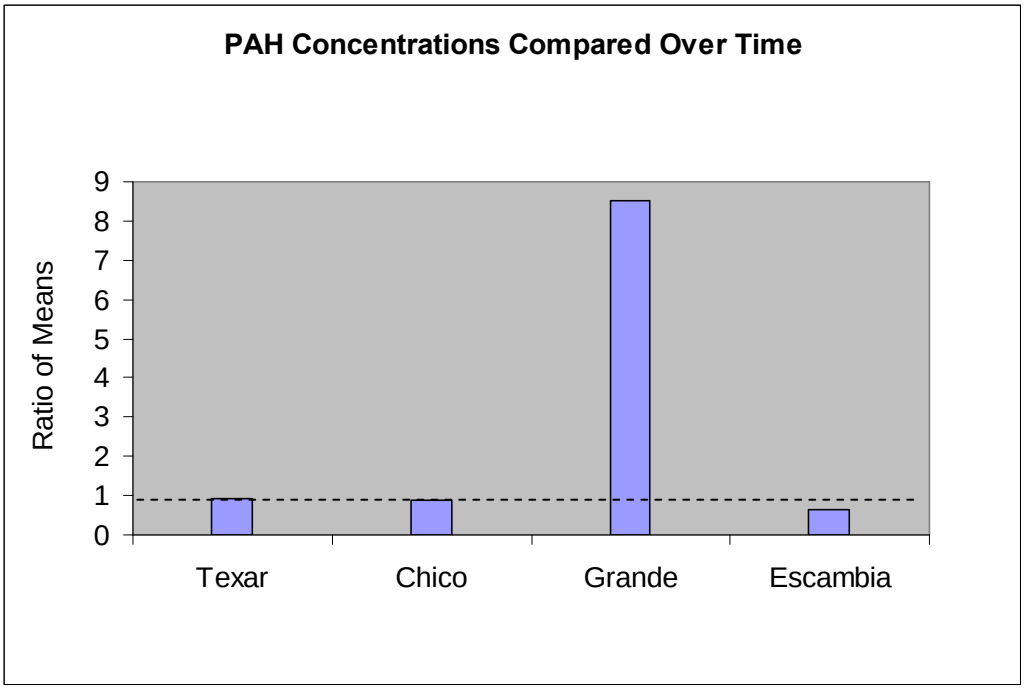


Fig. E-35. Ratios of current PAH concentrations to 1990's PAH concentrations. A ratio of 1 represents no change; a ratio of 0.5 indicates a 50% decrease.

f. Total Petroleum Hydrocarbons

Total petroleum hydrocarbons were detected at higher concentrations, more frequently in Bayous Texar and Chico than in Bayou Grande and the Escambia Bay and River System. Treatment of stormwater and taking measures to prevent accidental fuel releases along with proper disposal of petroleum products will reduce the concentrations of total petroleum in sediments and waters.

g. Pesticides

Organochlorine pesticides were infrequently detected by us in the bayous, but detections were more frequent and more pesticide species were detected in earlier studies (Fig. E-36a, E-36b, E-36c, E-36d). A notable decline in pesticide detections over time was observed when comparing data from the 1990's with our results (Fig. E-36d). In Bayous Texar and Grande our detections indicate that organochlorine pesticides are likely to be of little impact. However, in the Escambia Bay and River system DDT was detected by us in about 25% of the samples (Fig. E-36c). All but one of these samples with DDT detections were in the river and the associated wetlands. The data from 1990 studies shows more frequent detections of pesticides in Escambia Bay than were detected in the current study. The current widespread occurrence of DDT in the Escambia River and wetlands is an environmental concern.

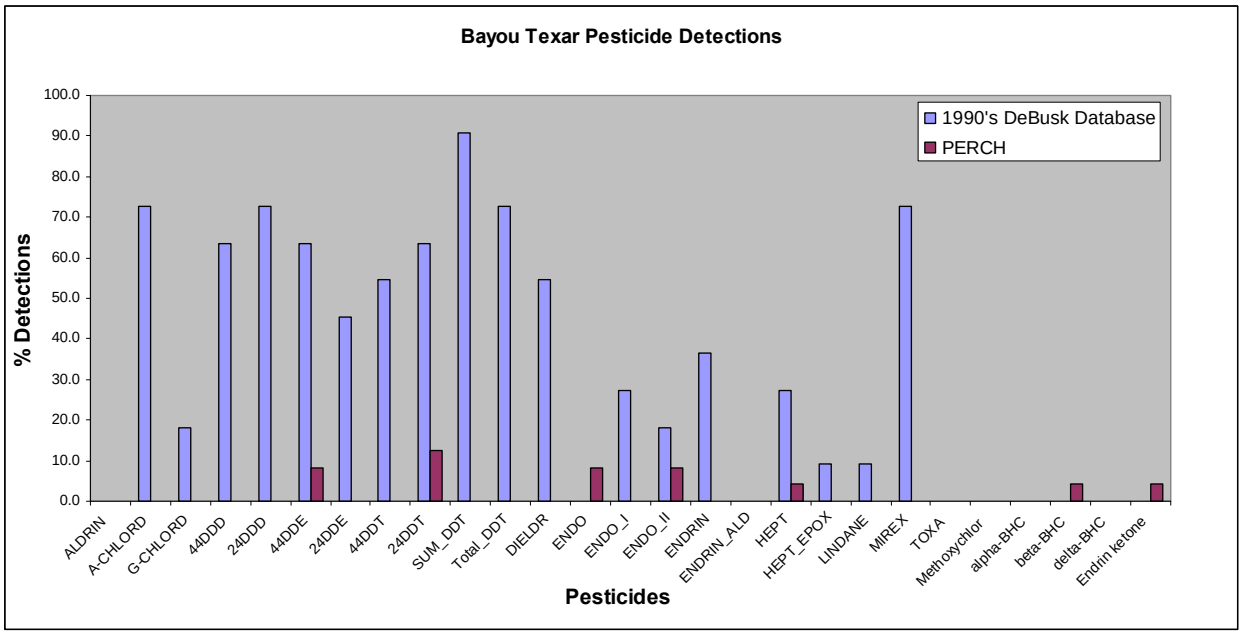


Fig. E-36a. Pesticide detections in Bayou Texar in the 1990's (blue bars) and current study (purple bars).

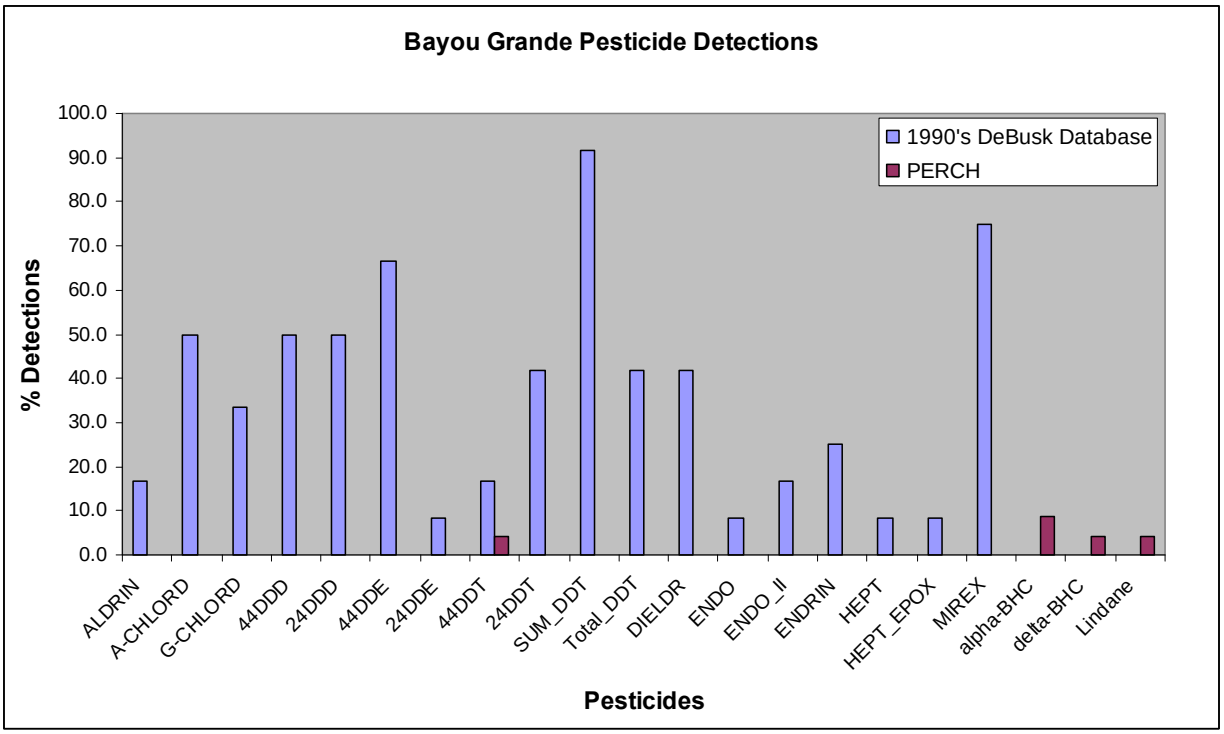


Fig. E-36b. Pesticide detections in Bayou Grande in the 1990's (blue bars) and current study (purple bars).

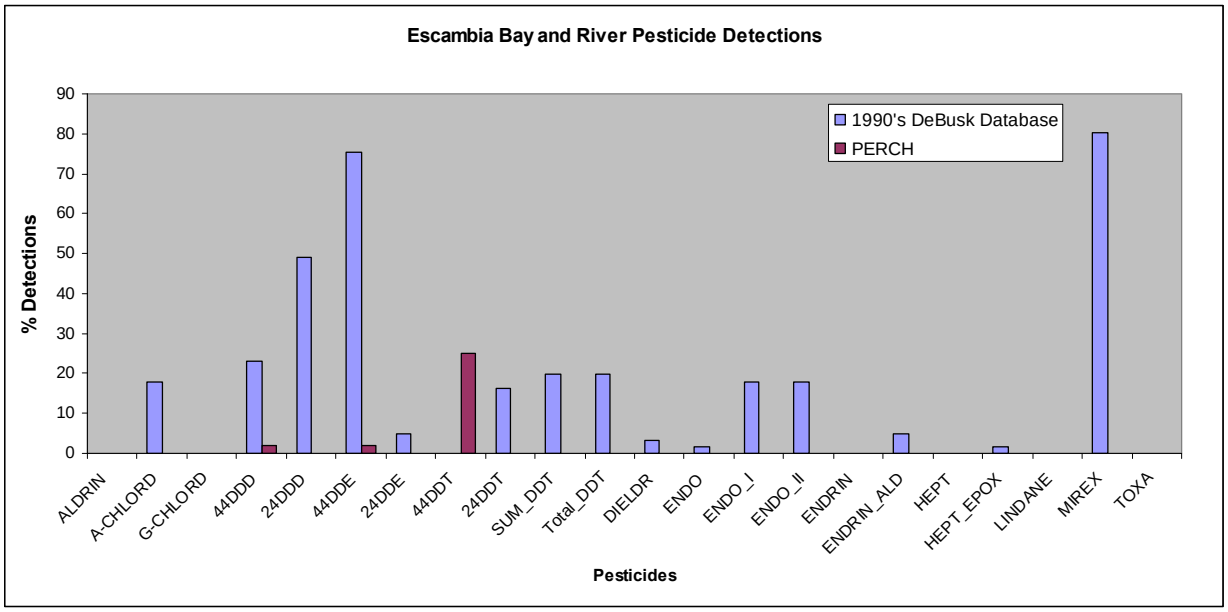


Fig. E-36c. Pesticide detections in Escambia Bay and River in the 1990's (blue bars) and current study (purple bars).

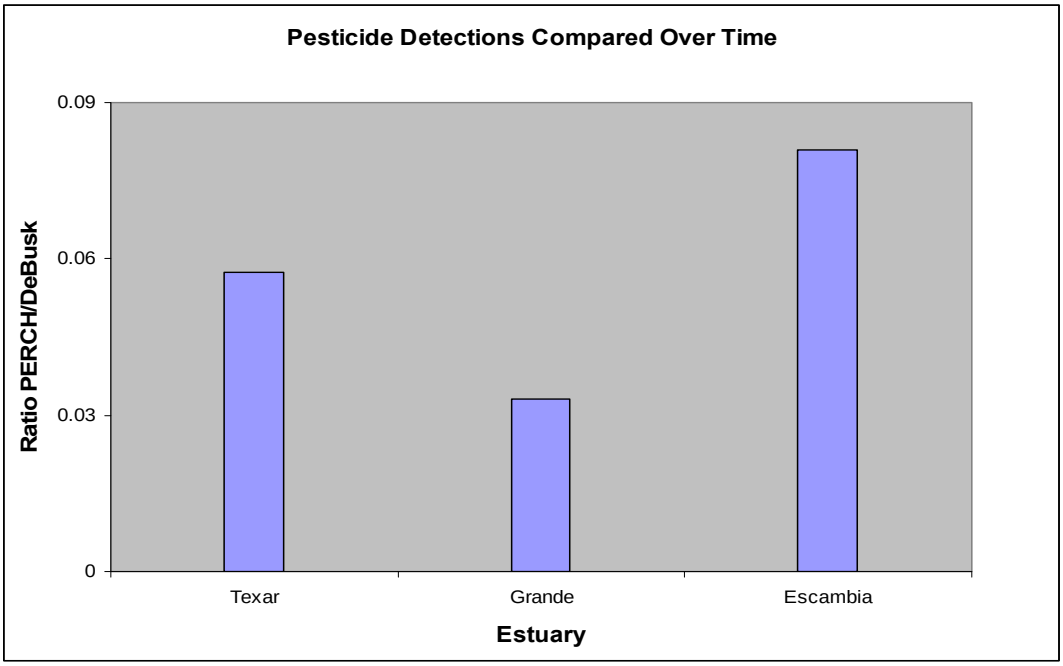


Fig. E-36d. Ratios of current pesticide detections to 1990's pesticide detections. A ratio of 1 represents no change; a ratio of 0.5 indicates a 50% decrease, and 0.1 indicates a 90% decrease.

h. Metals

Trace metal concentrations frequently exceeded SQAGs, but to varying degrees in the various estuaries (Table E-3). Zinc and mercury had the highest concentrations in Bayou Chico and Texar, whereas cadmium and chromium were higher in Bayou Grande. Escambia Bay generally had the lowest trace metal concentrations but was highest in arsenic.

A possible but unverified explanation for the relatively high arsenic concentration in Escambia Bay is that its watershed drains proportionally much more agricultural land than the watersheds of the bayous, and arsenic is used in some agricultural operations.

Table E-3. Metal concentrations (mg/kg) in surface sediments of Pensacola estuaries

Metals	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
Texar	8.51	0.2	24.13	46.91	66.44	0.36	0	242.22
Chico	7.86	0.49	45.76	81.75	65.18	0.22	0	354.81
Grande	7.615	2.065	68.615	20.635	49.675	0.085	6.405	94.1
Escambia	15.7	0.6	46.8	10.4	23.5	0.1	12.6	74.3

Average trace metal concentrations have declined in Bayou Texar since the 1990s (Fig. E-37), possibly due to stormwater management efforts in its watershed. The other estuaries did not show a consistent trend for all metals. Chromium, mercury and nickel concentrations decreased in all estuaries. Arsenic concentrations decreased only in Bayou Texar, and less strongly than the other metals in the same bayou.

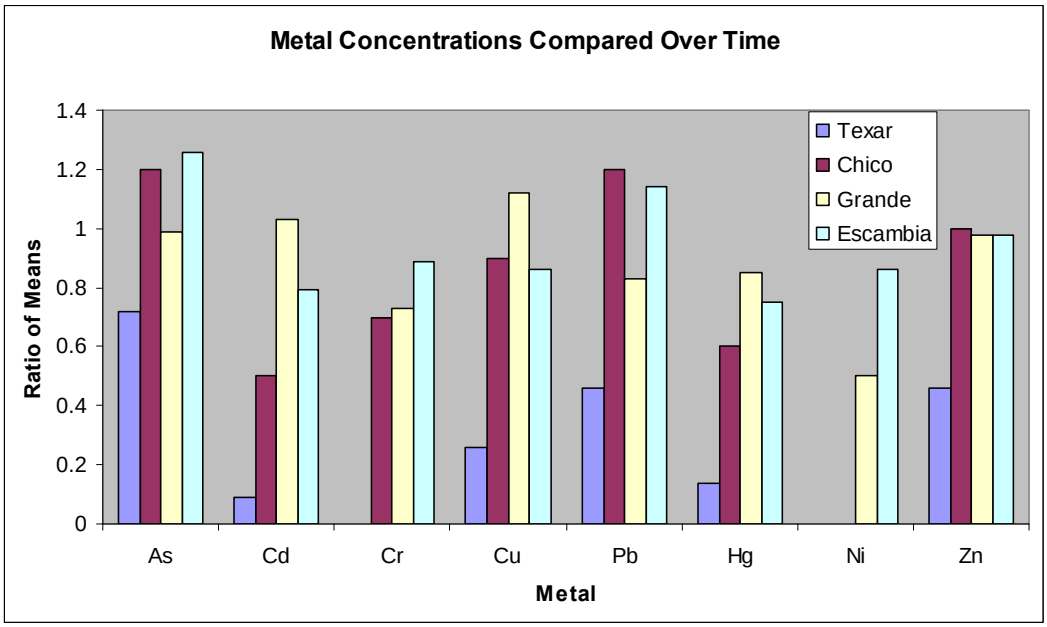


Fig. E-37. Ratios of current trace metal concentrations to 1990's trace metal concentrations.

7. Perspectives

There has been degradation of the Pensacola Bay ecosystem as evidenced by the loss of seagrass and reduced harvests of shrimp and other species in the bay. The loss of seagrass from the Pensacola Bay System has been the most obvious degradation. Seagrass throughout the system is still declining even though the sediment was rated at 92% using a sediment index indicating good or fair condition. One possibility is that pollutants may play a role since a previous study of contaminant concentrations for media associated with 13 Florida seagrass beds found that total organic carbon, mercury, chromium, zinc, total chlordane, total PAHs, total PCBs, DDD and DDE were greater in seagrass-rooted sediments than adjacent non-vegetated sediments. All of the bioaccumulated substances are considered to be generally toxic and it is quite possible that these pollutants are a causal factor in the decline in seagrasses. It is possible that pollutants coming from bayous and outfalls contribute to the deterioration of Pensacola Bay.

The impacts of bayou contaminants are relevant to environmental and human health. PCBs and dioxins were found above SQAGs in the three bayous as were toxic trace metals

and PAHs. Pesticides were not frequently detected in the bayous. However, DDT was detected in many samples in the Escambia System. All organic pollutants are subject to degradation to some degree with the dioxins/furans being the most refractory. Inorganic components of pollution can have very long residence times in sediments, particularly if they are bound to sediment particles or to insoluble precipitates. Trace metals that are released to the environment and ending up in estuarine waters are likely to be scavenged by particles. These particles will eventually reside in the sediments. The chemistry of the specific trace metals varies considerably, but unlike the organic pollutants, metals cannot be destroyed by chemical means since the atomic part always remains intact after any chemical reaction. The compounds that they form may change and the degree of toxicity can change with it. Overall, while the POPs such as PCBs and dioxins/furans can persist for years in the sediments and the biota of a system, the trace metals are even more persistent. A major question for sediment pollution in the Pensacola area is how best to remediate POP and metal contaminated sediments.

Currently it appears that the only practical and effective remediation for metals, PCBs, and dioxins/furans is by the physical removal of the contaminated sediment, which is best accomplished by dredging. Bioremediation of POPs is possible in some cases for hot spots. However, remediation requires the addition of amendments and other materials, and undesirable byproducts may result from the remediation process. For example, negative impact of byproducts has been found to occur from the reductive remediation of PCBs that resulted in the release of low chlorination congeners that were still toxic. It was found that the effectiveness of bioremediation efforts, when assessed on the basis of reduced TEQ, ignored the toxic impacts of the transformed PCBs. These PCBs were still toxic even though they no longer possessed high affinity to the vertebrate aryl receptor.

An issue that is very pertinent to the Pensacola bayous is that not all contaminated materials that become incorporated into the sediments of a bayou are retained in the bayou, especially if there is a change in the outgoing currents. Some of these contaminated materials can be transported out to Pensacola Bay, albeit in lesser final concentrations due to the large area of the bay. However, it is possible that pollutants in reduced concentrations can still cause impacts that have not been directly quantified. The strongest case for pollutants impacting the bay is via POP accumulation in seafood. There are currently no federal or state SQAGs that are intended to be protective relative to biomagnifications of POPs and metals in seafood. A related issue in this regard are proposals to use flushing to “clean up” local bayous. Flushing has been proposed as a solution to sedimentation and pollution issues in Bayous Chico and Texar by local agencies. It can be argued that the pollutants that accompany the sediments are diluted upon entering Pensacola Bay. However, adverse environmental impacts from pollutants transported by flushing to Pensacola Bay are likely to occur. Of the potential impacts in Pensacola Bay PCBs appear to offer the most serious threat in that, significant biomagnification can occur in higher trophic levels of the food chain even from low sediment concentrations. These higher trophic levels include seafood that is consumed by the local human population.

F. Accumulation of Contaminants in Fish and Shellfish from the Northwest Florida Region

(Task Leaders: Richard A. Snyder and Natalie K. Karouna-Renier*, University of West Florida). *currently at USGS, Beltsville, MD.

1. Introduction

Fish tissue is a major source of contaminants such as mercury, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F), and polychlorinated biphenyls (PCBs) for human and wildlife consumers. According to the U.S. Environmental Protection Agency (EPA), 48 states, 1 territory, and 2 tribes have issued mercury advisories and 38 states issued PCB advisories. When we began our studies, there were consumption advisories, based on mercury levels, for bass from the Perdido, Escambia, Blackwater, and Yellow Rivers in our region, as well as for bass from many other locations in the State of Florida. Advisories other than for mercury were very limited in the State of Florida—e.g., consumption advisories due to dioxins in Fenhalloway River and Wagner Creek, and due to pesticides in Lake Apopka. Surveys of fish for contaminants other than mercury have not been done in a systematic fashion at the state level, and this is also true for fish from Northwest Florida. Our goal is to fill this data gap for our region, so as to determine the impacts of pollution in the area rivers, bayous, and bays on the accumulation of contaminants in fish/shellfish consumed by humans and to assess potential health risks.

2. Contaminants in Shellfish

In the first phase of our studies, supported by CDC, we conducted an initial screening level assessment of contaminants in blue crabs (*Callinectes sapidus*) and oysters (*Crassostrea virginica*) collected from various locations in bays and bayous in the Pensacola, FL, area (Karouna-Renier et al., Environmental Pollution, 145: 474-488, 2007). Tissue samples were analyzed for mercury, arsenic, cadmium, chromium, copper, lead, nickel, selenium, tin, zinc, 17 dioxin/furan compounds, and 12 dioxin-like PCB congeners (PCB-77, PCB-81, PCB-105, PCB-114, PCB-118, PCB-123, PCB-126, PCB-156, PCB-157, PCB-167, PCB-169, and PCB-189). Contaminant levels were compared to Screening Values (SV) calculated using the U.S. EPA recommendations for establishing consumption advisories. Four different consumption rates were used in the derivation of the SVs. We identified five chemicals of concern (dioxins/furans/PCBs, arsenic, mercury, cadmium, and zinc) in either crab muscle, crab hepatopancreas, total crab tissue, or oysters based on exceedence of one or more SVs. We also assessed health risks (non-carcinogenic and carcinogenic) that may arise as a result of consumption of these shellfish species. Dioxins/PCBs accounted for 85-99%, 60-90%, 27-94%, and 53-99% of the total excess cancer risks for crab hepatopancreas, total edible crab tissue, crab muscle, and oysters, respectively. The relative contributions of dioxins/furans and dioxin-like PCBs to the TEQs and resultant risks varied with location, as evident from analysis of the crab hepatopancreas samples. Dioxins/furans were a greater contributor in samples from Bayou Chico and Perdido Bay, whereas dioxin-like PCBs were dominant in samples from Bayou Grande and Western Escambia Bay. The locations that exceeded SVs and had the highest carcinogenic or non-carcinogenic health risks were generally located in urbanized water bodies (Bayou Texar, Bayou Grande, and Bayou Chico) or downstream of known contaminated areas (Western Escambia Bay). Oysters collected from commercial

oyster beds in Escambia and East Bays, and crabs collected from East, Blackwater, and Perdido Bays generally had the lowest levels of contaminants. Despite accounting for only 15% of the total tissue, inclusion of hepatopancreas in a crab meal increased contamination to levels above many SVs, and therefore, direct or indirect consumption of hepatopancreas from crabs in the Pensacola Bay system should be discouraged. Many states including Maryland, New York, New Jersey, and Washington, have issued consumption advisories specifically for crab hepatopancreas, and based on the results of our study, a similar advisory may be warranted for blue crabs in the Pensacola Bay System.

3. Comparative Analysis of Accumulation of Mercury, Dioxins/Furans, and PCBs in Largemouth Bass and Striped Mullet

The State of Florida issued over 200 separate fish consumption advisories for largemouth bass (*Micropterus salmoides*) as a result of mercury contamination. Consumption advisories based on mercury also exist for marine species such as Spanish and King mackerels, which seasonally enter the Pensacola Bay System. In contrast, the State of Florida consumption advice for striped mullet (*Mugil cephalus*) lists this species as a low-level source of mercury. In 2004, as second phase of our project, we conducted a survey of contaminant levels in largemouth bass from rivers in Northwest Florida, near Pensacola, FL. We also surveyed striped mullet from rivers, bayous, and bays in this area (Fig. F-1).

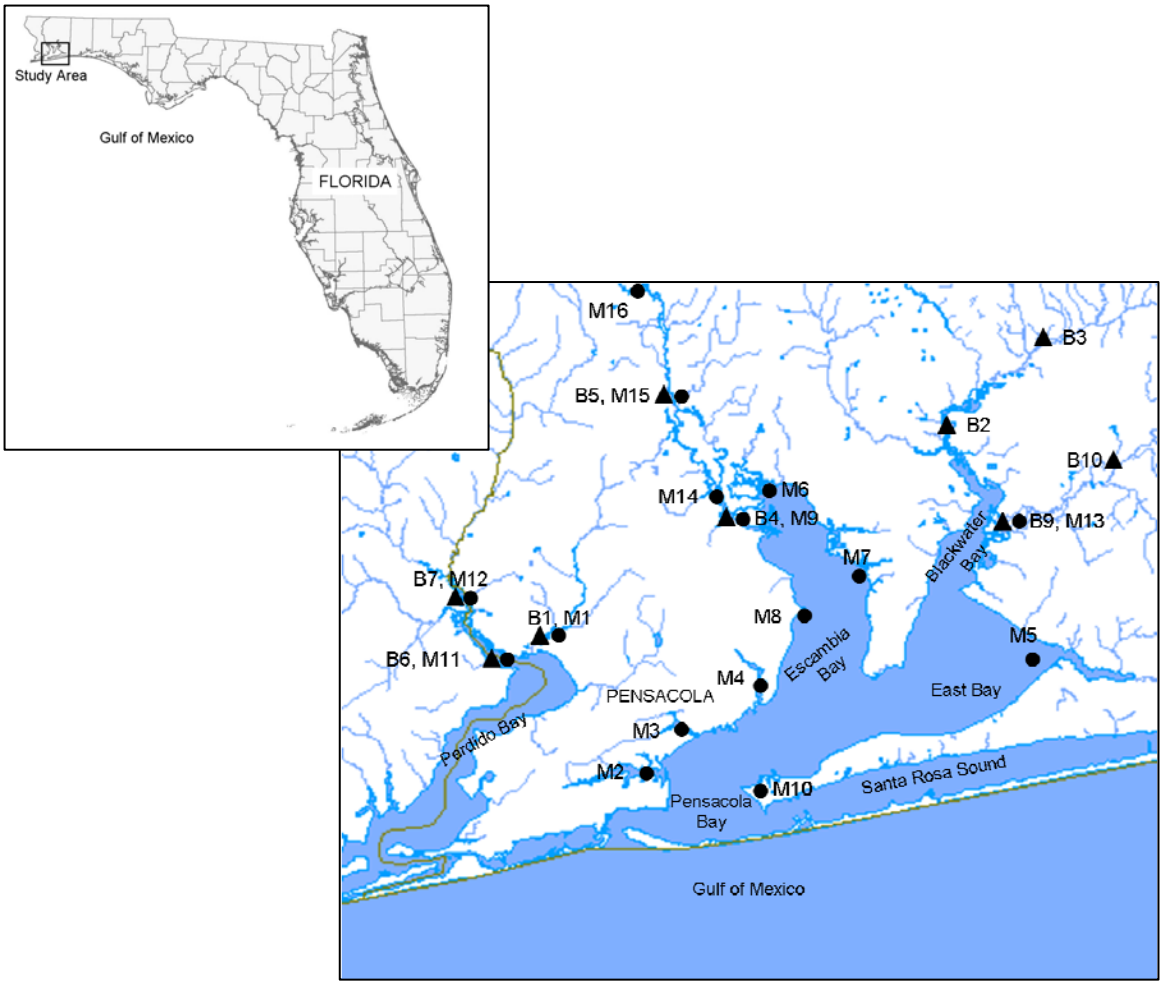


Fig. F-1. Sampling locations for bass and mullet. ▲= bass sampling station, ●= mullet sampling station.

Striped mullet was chosen as a ubiquitous and abundant estuarine fish indicator species, harvested and consumed in large quantities by the local population. Largemouth bass was chosen as a freshwater indicator species as a ubiquitous and sought after recreational sport fish. These two species overlap ranges, with mullet ascending into freshwaters, and bass entering the low salinity parts of the estuaries, providing coverage of the watersheds of the region. These samples were analyzed for mercury, PCDD/F, PCBs, organochlorine pesticides, and arsenic. Prior to this study, surveys of largemouth bass from Northwest Florida had only analyzed for mercury and, to our knowledge, a systematic survey of mullet had not been previously conducted in this region.

We observed elevated levels of mercury in bass collected in waters of the Northwest Florida Panhandle (Table F-1). Largemouth bass collected from all of the study locations exceeded mercury SVs—0.4 mg/Kg, EPA SV based on consumption rate of 17.5 g/day;

0.22 mg/Kg, EPA SV adjusted based on Florida-specific consumption rate of 32 g/day--and the HQs (Hazard Quotient, non-cancer hazard risk) for nearly all samples exceeded 1 (Table F-2). This risk analysis was based on a body weight of 70 kg (~154 lbs) and therefore would potentially underestimate the risk to a lower body weight individual such as a child. We found mercury to be the primary cause of potential adverse health effects in human consumers of the bass. The neurological effects of mercury are most severe in developing infants and children

Table F-1. Contaminant levels in largemouth bass.

Location	TEQ_{DF} ng/Kg	TEQ_{P} ng/Kg	TEQ_{DFP} ng/Kg	ΣPCBs ng/g	ΣPBDE ng/Kg	4,4-DDE ug/Kg	As mg/Kg	In. As mg/Kg	Hg mg/Kg
11-Mile Creek	0.06	0.16	0.22	3.1	1095.4	<DL	0.06	<DL	0.37
Blackwater River Lower	0.02	0.13	0.14	3.2	324.4	<DL	0.18	<DL	0.57
Blackwater River Upper	0.05	0.03	0.08	0.1	1106.5	<DL	0.02	<DL	0.89
Escambia River Lower	0.11	1.53	1.64	39.4	706.1	0.17	0.16	<DL	0.46
Escambia River Quintette B	0.27	0.27	0.54	0.8	616.7	0.81	0.02	<DL	0.56
Perdido River, Lower	0.13	0.14	0.27	2.9	777.6	0.51	0.34	<DL	0.56
Perdido River, Upper	0.09	0.03	0.12	1.3	1319.2	<DL	0.07	<DL	0.66
Shoal River	0.07	0.00	0.08	1.1	199.4	0.24	0.02	<DL	0.63
Yellow River Lower	0.08	0.02	0.10	2.3	1374.4	<DL	0.06	<DL	0.68
Yellow River Upper	0.15	0.02	0.17	0.9	411.3	0.37	0.03	<DL	0.71

<DL = below detection limit

TEQ_{DF}= TEQ for dioxins/furans TEQ_{P}= TEQ for dioxin-like PCBs TEQ_{DFP}= total TEQ

Table F-2. Hazard indices (HI) calculated for largemouth bass samples collected throughout the Pensacola area.

Location	HI Rec	HI FL*
11-Mile Creek	1.0	1.7
Blackwater River Lower	1.5	2.7
Blackwater River Upper	2.2	4.1
Escambia River Lower	1.6	3.0
Escambia River Quintette Bridge	1.4	2.6
Perdido River, Lower	1.4	2.6
Perdido River, Upper	1.7	3.1
Shoal River	1.6	2.9
Yellow River Lower	1.7	3.2
Yellow River Upper	1.8	3.3

*adjusted based on FL-specific consumption rate of 32g/day

and fish consumption advisories therefore commonly target women of child-bearing age and children. The effects of chronic low-level mercury exposure on adults, however, is less clear, but may include increased risk of cardiovascular disease. In a previous study supported by CDC, we found that women in the Pensacola area show increasing levels of hair mercury concentrations with increasing levels of fish consumption (Karouna-Renier et al., Environmental Research, 108: 320-326, 2008), suggesting that consumption practices in the area include fish high in mercury. The Florida Department of Health has recently updated consumption advisories due to mercury suggesting that women of child-bearing age and young children limit their consumption of bass from the Escambia, Perdido, Blackwater, and Yellow Rivers to one meal a month. The advisories for other individuals range from one meal per week to one meal per month, depending on the river system (FDOH, 2008). "No-consumption" advisory has been in effect for bass from a spring-fed lake, Woodbine Lake, Pace, FL, because of much higher levels of mercury found in these fish relative to other locations (Fig. F-2).

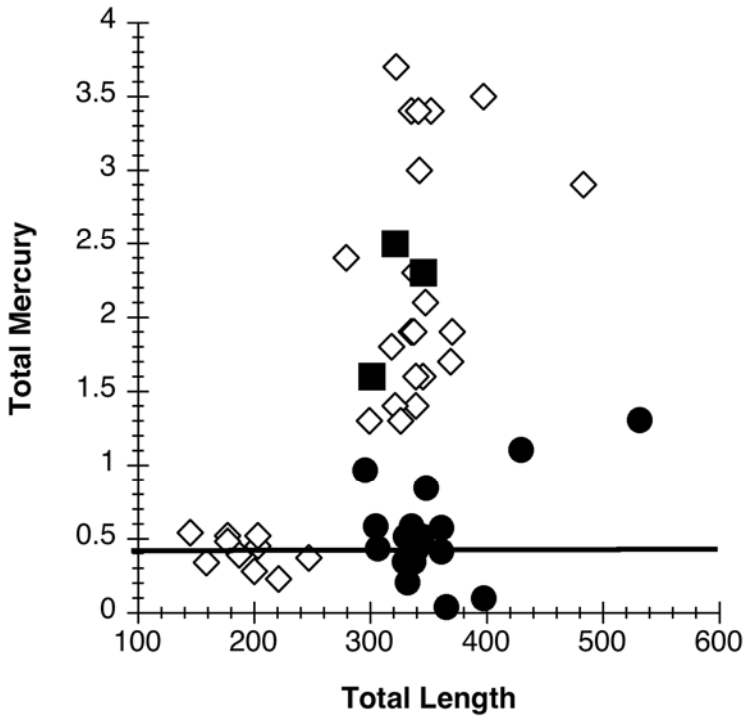


Fig. F-2. Mercury in bass data collected over Escambia, Santa Rosa, and Okaloosa Counties (solid circles and squares), compared to multiyear data from the Florida Fish and Wildlife Commission sampling of bass in Woodbine Lake (diamonds). The results from the UWF work for Woodbine Lake are indicated by the solid squares. Data from all other locations sampled by UWF are indicated by solid circles.

Exposure and uptake of mercury by fish is primarily dietary and is magnified by the transfer of mercury to successively higher trophic levels. Largemouth bass are a top-level predator that readily bioaccumulates mercury. The mercury levels we observed (except for fish from Woodbine Lake) were within ranges reported previously for largemouth bass in Florida and other locations. In contrast, mullet exhibited low levels of mercury (Fig. F-3, Table F-3).

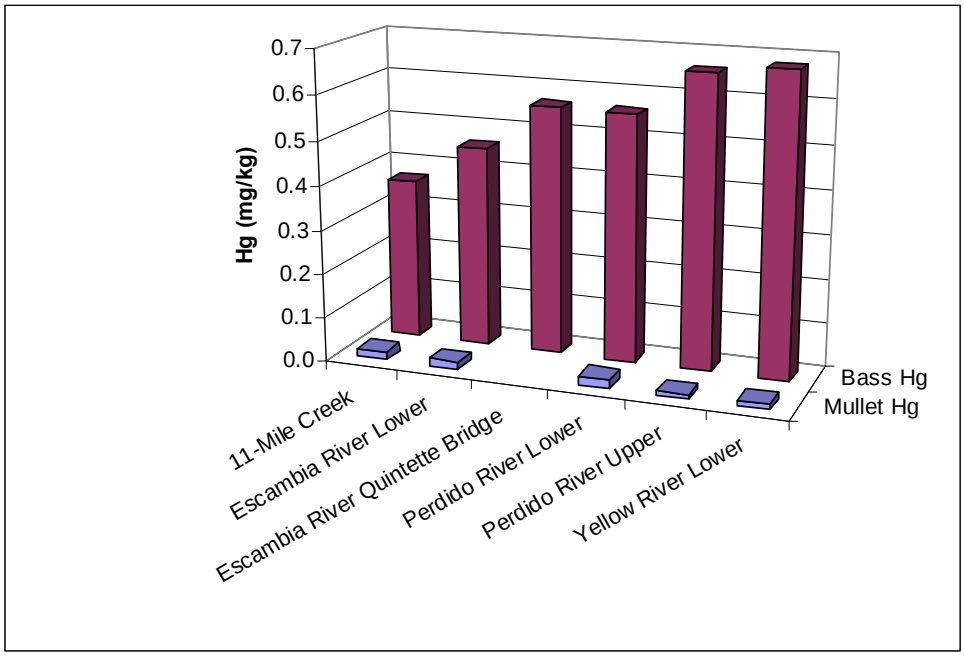


Figure F-3. Comparison of mercury levels in mullet and bass caught in the Pensacola area. Bass mercury levels were from 20 to 70 times those observed in mullet from the identical location, reflecting the higher food chain position of largemouth bass.

Table F-3. Levels of contaminants in mullet collected in the Pensacola area.

Location	TEQ_{DF} ng/Kg	TEQ_{P} ng/Kg	TEQ_{DFP} ng/Kg	ΣPCBs ng/g	As mg/Kg	Inorg. As mg/Kg	Hg mg/Kg	4,4-DDD ng/g	4,4-DDE ng/g	4,4-DDT ng/g	ΣDDT ng/g	Dieldrin ng/g	α-Chlordane ng/g	γ-Chlordane ng/g	Endrin Aldehyde ng/g	Heptachlor ng/g	Heptachlor Epoxide ng/g
11-Mile Creek	0.32	0.25	**0.57**	**14.0**	0.32	<DL	0.018	0.19	0.68	<DL	0.87	0.56	<DL	<DL	0.31	<DL	0.26
Bayou Chico	0.81	0.87	**1.68**	**29.4**	0.45	<DL	0.008	1.05	3.93	1.82	6.80	**8.30**	3.80	0.77	<DL	<DL	0.80
Bayou Grande	0.42	0.47	**0.89**	**18.8**	0.61	<DL	0.008	0.36	1.30	0.37	2.03	0.62	0.32	0.37	<DL	0.26	0.22
Bayou Texar	0.50	0.22	**0.72**	**14.1**	0.46	<DL	0.010	0.28	2.47	0.53	3.27	2.03	0.48	0.42	<DL	<DL	1.07
East Bay	0.13	0.11	**0.24**	8.8	0.43	<DL	0.026	0.32	1.01	0.80	2.14	0.29	<DL	<DL	0.32	<DL	<DL
Escambia Bay NE	0.23	0.61	**0.83**	**32.1**	0.34	<DL	0.018	0.26	1.17	1.07	2.50	0.93	0.33	0.35	<DL	<DL	0.60
Escambia Bay SE	0.30	0.26	**0.56**	8.7	0.40	<DL	0.014	1.00	3.87	1.25	6.12	1.17	0.47	0.66	0.85	0.40	1.35
Escambia Bay SW	0.27	0.29	**0.56**	**22.4**	0.37	<DL	0.024	0.45	1.34	1.20	2.99	0.55	<DL	0.47	<DL	<DL	0.24
Escambia River Crist Plant	0.59	0.79	**1.38**	**59.33**													
Escambia River Lower	0.36	0.52	**0.88**	**48.6**	0.40	<DL	0.017	0.26	1.17	1.00	2.43	1.13	0.32	0.30	0.56	<DL	0.79
Escambia River Quintette Bridge	1.13	0.26	**1.39**	**25.58**													
Escambia River Upper	0.50	0.23	**0.73**	**25.22**													
Hoffmann Bayou	0.64	0.29	**0.94**	**15.2**	0.72	<DL	0.014	0.98	1.68	1.44	4.11	0.79	0.53	0.63	<DL	<DL	0.30
Perdido River Lower	0.20	0.08	**0.28**	3.8	0.45	<DL	0.021	0.15	0.83	0.32	1.30	0.33	<DL	0.39	0.34	<DL	<DL
Perdido River Upper	0.36	0.15	**0.52**	6.4	0.27	<DL	0.010	0.22	1.61	0.26	2.09	0.69	<DL	0.33	0.30	0.41	0.21
Yellow River Lower	0.20	0.08	**0.27**	3.4	0.31	<DL	0.012	0.30	0.89	0.26	1.45	0.43	0.25	<DL	0.34	<DL	<DL

<DL = below detection limit TEQ_{DF}= TEQ for dioxins/furans TEQ_{P}= TEQ for dioxin-like PCBs TEQ_{DFP}= total TEQ

Mullet are heterotrophs that are primarily detritus feeders as adults and appear to prefer very fine particles, which are particularly rich in absorbed organic material. As a result, mullet do not accumulate high levels of mercury in their tissues.

We found elevated levels of PCBs in many of our samples (Table F-3), primarily in mullet. The highest levels of PCBs were observed in samples from Escambia River and Escambia Bay, which contain an historical point source of PCBs. In the late 1960s, an industrial plant on the Escambia River, located approximately 8 km upstream of the river's confluence with Escambia Bay, reported a chronic release (3.8-11.4 L/day) of transformer oil (Pydraul AC) containing Aroclor 1254. Contamination of aquatic biota in Escambia Bay was reported soon afterward, and lingering contamination was recently confirmed by us in blue crabs and oysters (Karouna-Renier et al., 2007). An additional, albeit smaller potential source of PCBs to upper Escambia Bay seems to be an industrial plant located at the northeastern corner of the bay that had discharged PCBs in its wastewaters to Escambia Bay.

Water circulation in Escambia Bay is strongly influenced by water flow from the Escambia River, which produces a southward flow of water along the western shore of the bay. This results in a counter clockwise circulation pattern, with higher salinity water flowing up the eastern shore of the bay. Based on this flow, we could expect that the PCB contamination from the Escambia River would, over time, migrate down the western shore. The data we collected in the present study support these findings. Although the highest PCB concentrations were observed in bass and mullet caught in the lower Escambia River, nearest to the spill location, mullet collected throughout upper Escambia Bay, along the western shore of the bay and even in the upper reaches of the Escambia River were found to contain elevated levels of PCBs (Table F-3). Whether these fish are exposed to the PCBs in the area they were caught or whether they are exposed through periodic migrations into the lower Escambia River is unknown. Samples collected in the southeastern quadrant of Escambia Bay (Escambia Bay SE) had substantially lower PCB levels, reflecting the water circulation pattern in the bay and suggesting that these mullet do not migrate into the upper, more contaminated segments of the bay and river.

We also observed elevated levels of PCBs in mullet from Bayou Chico, Bayou Texar, and Bayou Grande. Our sediment chemistry studies showed that these bayous have elevated PCB levels in the sediments, with the highest concentrations found in Bayou Chico followed by Bayou Grande and Bayou Texar (Section III.E). Mullet samples that we collected at these sites exceeded SVs (EPA SV: 20 ng/g, based on consumption rate of 17.5g/day; 10.9 ng/g, EPA SV adjusted based on FL-specific consumption rate of 32g/day) for total PCBs. Mullet that were caught at the two locations in the lower Escambia River (Escambia River Plant Crist and Escambia River Lower) contained levels of PCBs for which HI exceeded 1 (Table F-4), which indicates that non-cancer health effects may occur. Bass caught at the Escambia River Lower location

Table F-4. Non cancer Hazard Index calculations for mullet samples collected in the Pensacola area.

Location	HI Rec	HI FL *
11-Mile Creek	0.2	0.4
Bayou Chico	0.4	0.7
Bayou Grande	0.3	0.5
Bayou Texar	0.2	0.4
East Bay	0.2	0.3
Escambia Bay NE	0.4	0.8
Escambia Bay SE	0.1	0.3
Escambia Bay SW	0.3	0.6
Escambia River Crist Plant	0.7	1.4
Escambia River Lower	0.7	1.2
Escambia River Quintette Bridge	0.3	0.6
Escambia River Upper	0.3	0.6
Hoffmann Bayou	0.2	0.4
Perdido River Lower	0.1	0.2
Perdido River Upper	0.1	0.2
Yellow River Lower	0.1	0.1

*adjusted based on FL-specific consumption rate of 32g/day

exhibited high levels of both PCBs and mercury, resulting in an HQ above 1 (Table F-2). Potential non-carcinogenic health effects from exposure to PCBs in humans and/or animals include liver, thyroid, dermal and ocular changes, immunological alterations, neurodevelopmental changes, reduced birth weight, and reproductive toxicity (ATSDR, 2000). Excess LCR (Lifetime Cancer Risk) exceeded $1x10^{-4}$ only for two samples (Tables F-5, F-6) – in mullet from Bayou Chico and in bass from Escambia River Lower. In both cases, the primary contributors to the excess LCR were PCDD/F and DL-PCBs (Fig. F-4, F-5).

Table F-5. Excess lifetime cancer risk (LCR) for consumer of mullet in the Pensacola region. LCR were calculated under three exposure scenarios and two consumption rates (EPA CR and FL CR). Sample in bold exceeds the acceptable range.

		70 year LCR		30 year LCR		9 year LCR		*
Map ID	Sampling Location	EPA CR	FL CR	EPA CR	FL CR	EPA CR	FL CR	
M-1	11-Mile Creek	2.2E-05	4.1E-05	9.6E-06	1.7E-05	2.9E-06	5.2E-06	
M-2	Bayou Chico	6.5E-05	**1.2E-04**	2.8E-05	5.1E-05	8.4E-06	1.5E-05	
M-3	Bayou Grande	3.5E-05	6.3E-05	1.5E-05	2.7E-05	4.5E-06	8.2E-06	
M-4	Bayou Texar	2.8E-05	5.1E-05	1.2E-05	2.2E-05	3.6E-06	6.6E-06	
M-5	East Bay	9.5E-06	1.7E-05	4.1E-06	7.4E-06	1.2E-06	2.2E-06	
M-6	Escambia Bay NE	3.2E-05	5.9E-05	1.4E-05	2.5E-05	4.2E-06	7.6E-06	
M-7	Escambia Bay SE	2.2E-05	4.0E-05	9.3E-06	1.7E-05	2.8E-06	5.1E-06	
M-8	Escambia Bay SW	2.2E-05	4.0E-05	9.3E-06	1.7E-05	2.8E-06	5.1E-06	
M-9	Escambia River Lower	3.4E-05	6.3E-05	1.5E-05	2.7E-05	4.4E-06	8.1E-06	
M-10	Hoffmann Bayou	3.7E-05	6.7E-05	1.6E-05	2.9E-05	4.7E-06	8.6E-06	
M-11	Perdido River Lower	1.1E-05	2.0E-05	4.7E-06	8.6E-06	1.4E-06	2.6E-06	
M-12	Perdido River Upper	2.0E-05	3.7E-05	8.6E-06	1.6E-05	2.6E-06	4.7E-06	
M-13	Yellow River Lower	1.1E-05	2.0E-05	4.6E-06	8.4E-06	1.4E-06	2.5E-06	
M-14	Escambia River Crist Plant	5.4E-05	9.8E-05	2.3E-05	4.2E-05	6.9E-06	1.3E-05	
M-15	Escambia River Quintette Bridge	5.4E-05	9.9E-05	2.3E-05	4.2E-05	7.0E-06	1.3E-05	
M-16	Escambia River Upper	2.8E-05	5.2E-05	1.2E-05	2.2E-05	3.7E-06	6.7E-06	

*Florida consumption rate of 32g/day. EPA consumption rate of 17.5g/day.

Table F-6. Excess lifetime cancer risk (LCR) for consumer of bass in the Pensacola region. LCR were calculated under three exposure scenarios and two consumption rates (EPA CR and FL CR). Sample in bold exceeds the acceptable range.

		Cancer Risk 70 year		Cancer Risk 30 year		Cancer Risk 9 year	*
Map ID	**Location**	EPA CR	FL CR	EPA CR	FL CR	EPA CR	FL CR
B-1	11-Mile Creek	8.7E-06	1.6E-05	3.7E-06	6.8E-06	1.1E-06	2.0E-06
B-2	Blackwater River Lower	5.6E-06	1.0E-05	2.4E-06	4.4E-06	7.2E-07	1.3E-06
B-3	Blackwater River Upper	3.1E-06	5.7E-06	1.3E-06	2.4E-06	4.0E-07	7.3E-07
B-4	Escambia River Lower	6.4E-05	**1.2E-04**	2.7E-05	5.0E-05	8.2E-06	1.5E-05
B-5	Escambia River Quintette Bridge	2.1E-05	3.8E-05	9.0E-06	1.6E-05	2.7E-06	4.9E-06
B-6	Perdido River, Lower	1.1E-05	1.9E-05	4.5E-06	8.3E-06	1.4E-06	2.5E-06
B-7	Perdido River, Upper	4.8E-06	8.9E-06	2.1E-06	3.8E-06	6.2E-07	1.1E-06
B-8	Shoal River	2.9E-06	5.4E-06	1.3E-06	2.3E-06	3.8E-07	6.9E-07
B-9	Yellow River Lower	3.9E-06	7.1E-06	1.7E-06	3.0E-06	5.0E-07	9.1E-07
B-10	Yellow River Upper	6.7E-06	1.2E-05	2.9E-06	5.3E-06	8.6E-07	1.6E-06

*Florida consumption rate of 32g/day EPA consumption rate of 17.5g/day.

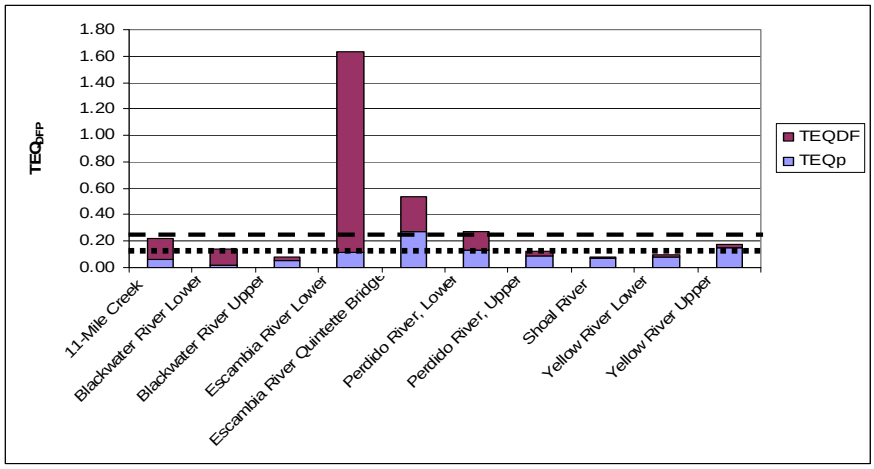


Fig. F-4. TEQ values for largemouth bass collected in the Pensacola region.
– – – = EPA SV ▪▪▪▪▪ =FL SV (EPA SV adjusted based on FL-specific consumption rate of 32g/day).

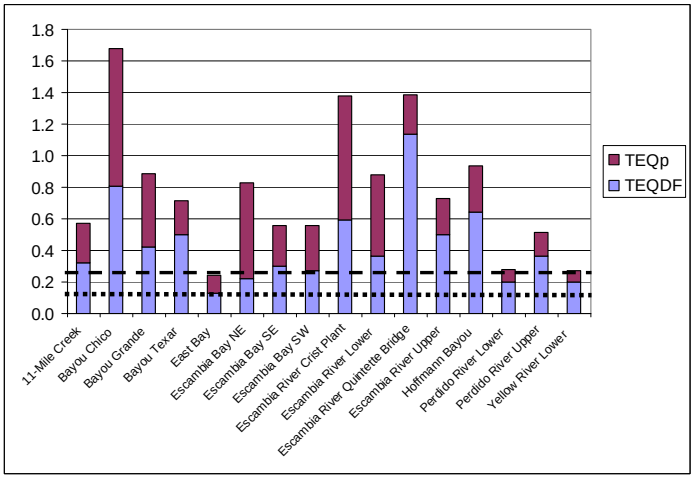


Fig. F-5. Comparison of TEQ values for mullet with human consumption screening values.
– – = EPA SV ▪▪▪▪▪ = FL SV (EPA SV adjusted based on FL-specific consumption rate of 32g/day).

At the six stations common to both species, mullet generally exhibited higher levels of PCBs than largemouth bass (Fig. F-6), potentially reflecting their greater direct contact with sediments due to their foraging behavior. Sediment ingesting organisms possess physiological adaptations such as surfactant rich digestive tracts, which facilitate hydrophobic pollutant

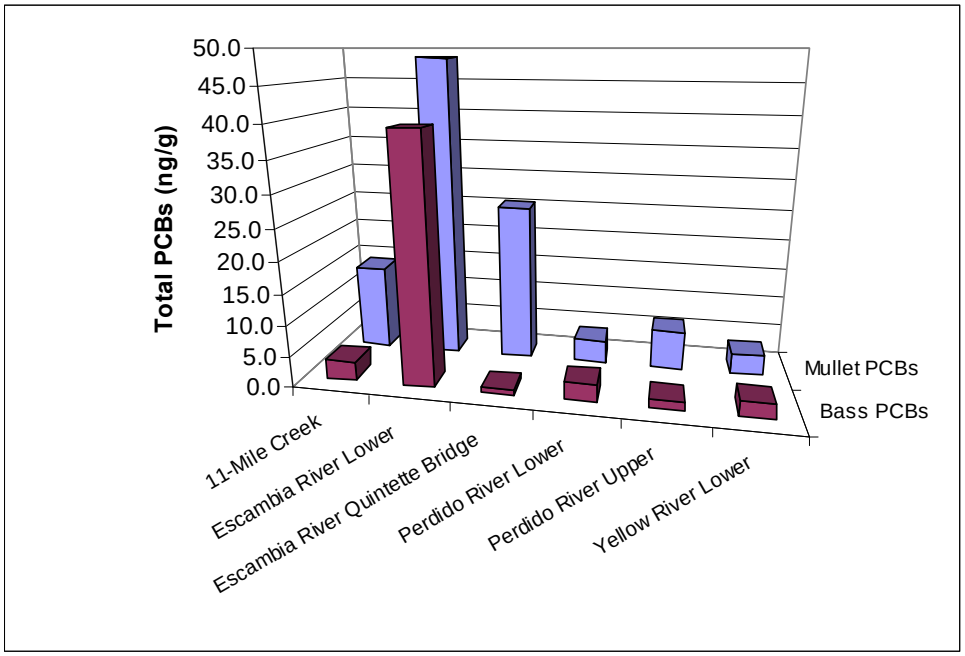


Fig. F-6. Comparison of total PCB levels in bass and mullet from the six common sampling locations.

transfer. In the present study, mullet also accumulated higher levels of dioxins/furans (exceeding SVs in nearly all cases) and organochlorine pesticides than bass. The levels of inorganic arsenic and organochlorine pesticides found in bass and mullet samples did not exceed their respective SVs, and do not seem to pose health risks.

The results of the present study have demonstrated the importance of targeted monitoring of fish for contaminants. Species such as mullet are not commonly included in systematic monitoring programs, even though they represent a widely consumed potential source of contaminants to the human population along the coastal southern United States. Based in part on the data from this study, the Florida Department of Health recently issued a consumption advisory based on PCB contamination (using a threshold total PCB concentration of 50 ng/g). The advisory warns consumers to restrict their consumption of mullet from the Escambia River from south of State Route 184 to the mouth of the river to one meal per week. Our data show that elevated PCB levels are not confined to the fish in the Escambia River but extend to mullet in other parts of Escambia Bay and urbanized bayous within the city of Pensacola. These results demonstrate some of the difficulties human consumers may encounter when selecting fish for consumption with regard to possible health effects – mullet have low levels of mercury but higher levels of organic pollutants whereas bass have high levels of mercury but generally lower levels of organic contaminants.

4. Accumulation of PCBs and Dioxins/Furans in Fishes of Escambia Bay

As described in the previous subsection (III.F.3), our findings of elevated PCB concentrations in bass and mullet in the Escambia River/Bay System were taken into consideration by the Florida DOH in issuing a consumption advisory for fish from the lower section of Escambia River, from south of state Route 184 to the mouth of the river. The advisory was not extended to Escambia Bay, although we found elevated levels of PCBs (exceeding EPA SV of 20 ng/g, but not the Florida DOH's screening threshold of 50 ng/g) in mullet samples from Northeast, Northwest, and Southwest areas of the bay.

In this phase of the project we extended the survey of PCBs and dioxin/furans to additional samples of mullet and to other fish species: *Archosargus probatocephalus* (sheepshead), *Cynoscion arenarius* (white trout), *Cynoscion nebulosus* (spotted seatrout) *Micropogonias undulatus* (croaker) from Escambia Bay. These fish were collected on September 14, 2007, after two years of submarine construction to replace the I-10 bridge across the Escambia Bay. On the date of sample collection, part of the old I-10 bridge across the Escambia Bay was demolished by an underwater explosion. This resulted in mortality of fishes in the vicinity, and these fish were collected by personnel from the Florida Fish and Wildlife Commission and placed on ice for transport to the University of West Florida. Individual specimens were processed for all fish large enough to provide sufficient tissue for analysis. Multiple specimens were sorted into similar-sized composite samples where individuals were too small.

As shown in Table F-7, PCB levels in all of the 21 samples exceeded the EPA SV (20ng/g), and 17 of the samples exceeded the Florida DOH's screening threshold (50 ng/g). The most elevated PCB levels were found in the mullet samples (284 to 1580 ng/g), the highest level being 80-fold higher than the EPA SV and 32-fold higher than the Florida DOH's screening threshold. After reviewing our findings, Florida DOH conducted independent sampling/analysis of mullet from Escambia Bay and some other water bodies in our area and issued a consumption advisory for mullet from the Escambia Bay.

As noted earlier, mullet had relatively higher levels of dioxin/furan TEQs compared to levels in bass. Many of the mullet samples in the previous analysis (Section III.F.3) had dioxin/furan TEQs over the EPA SV of 0.256, even with the dioxin-like PCBs not included. The highest recorded values were from the Escambia River (0.24 to 0.60 ng/kg) and Bayou Chico (0.23 to 0.75 ng/kg). Because of the enormous contribution of the dioxin-like PCBs, the total TEQs for mullet from the I-10 bridge sampling were very high: 12.6 to 69 ng/kg. Lifetime Cancer Risks (LCR) for consumption of these mullet samples are estimated to be as high as 1.6×10^{-3} (Table F-8) and the Hazard Quotients (HQ) as high as high as 36.11 (Table F-9).

Table F-7. Toxic equivalency quotients for dioxins and furans (TEQ_{DF}) co-planar dioxin-like PCBs (TEQ_{P}), combined dioxin furans and PCBs (TEQ_{DFP}), and total PCBs for the samples collected from Escambia Bay near I-10 bridge.

SPECIES	COMPOSITE	% lipid	TEQ_{DF} ng/Kg	TEQ_{P} ng/Kg	TEQ_{DFP} ng/Kg	Total PCBs ng/g
Archosargus probatocephalus	070917M	1	0.18	2.15	2.33	41.1
Archosargus probatocephalus	070917I	0.8	0.19	2.80	2.99	54.1
Archosargus probatocephalus	070917S	1.8	0.32	3.40	3.72	173.0
Archosargus probatocephalus	070917J	0.7	0.21	4.77	4.98	87.7
Archosargus probatocephalus	070917K	0.7	0.17	4.61	4.78	83.7
Archosargus probatocephalus	070917O	0.6	0.10	2.86	2.96	73.6
Archosargus probatocephalus	070917L	2.6	0.86	11.59	12.45	192.0
Archosargus probatocephalus	070917N	1.6	0.28	5.10	5.39	165.0
Cynoscion arenarius	070917F	0.3	0.16	1.61	1.77	336.0
Cynoscion arenarius	070917U	0.6	0.32	3.25	3.57	192.0
Cynoscion arenarius	070917T	0.3	0.05	0.75	0.80	70.9
Cynoscion arenarius	070917E	0.6	0.57	3.20	3.77	105.0
Cynoscion nebulosus	070917H	0.2	0.07	0.68	0.75	27.0
Cynoscion nebulosus	070917G	0.3	0.20	0.68	0.88	26.3
Micropogonias undulatus	070917R	2.4	0.33	2.70	3.03	303.0
Micropogonias undulatus	070917Q	1.5	0.18	2.28	2.47	174.0
Micropogonias undulatus	070917P	3.4	0.50	4.76	5.26	274.0
Mugil cephalus	070917D	4.4	1.07	19.61	20.68	678.0
Mugil cephalus	070917C	2.2	0.52	39.58	40.10	1010.0
Mugil cephalus	070917A	3.9	0.43	12.16	12.59	284.0
Mugil cephalus	070917B	3.3	0.47	68.50	68.97	1580.0

US EPA screening level for TEQ_{DFP} = 0.26 ng/Kg.

State of Florida screening level for TEQ_{DFP} has not been established.

US EPA screening level for total PCB = 20 ng/g.

State of Florida screening level for total PCB = 50 ng/g.

Table F-8. Excess lifetime cancer risk (LCR) from consumption of mullet collected at the Escambia Bay Bridge.

		70 year LCR		30 year LCR		9 year LCR	
Sample #	Sampling Location	EPA CR	FL CR	EPA CR	FL CR	EPA CR	FL CR*
070917A	Escambia Bay I-10 Bridge	4.9E-04	9.0E-04	2.1E-04	3.9E-04	6.3E-05	1.2E-04
070917B	Escambia Bay I-10 Bridge	2.7E-03	4.9E-03	1.2E-03	2.1E-03	3.5E-04	6.3E-04
070917C	Escambia Bay I-10 Bridge	1.6E-03	2.9E-03	6.7E-04	1.2E-03	2.0E-04	3.7E-04
070917D	Escambia Bay I-10 Bridge	8.1E-04	1.5E-03	3.5E-04	6.3E-04	1.0E-04	1.9E-04

*Florida consumption rate = 32g/day. EPA consumption rate = 17.5g/day.

Table F-9. Non-cancer Hazard Quotients calculated for PCB concentrations in mullet collected during the Escambia Bay Bridge construction project.

Sample #	Location	HQ Rec	HQ FL *
070917A	Escambia Bay I-10 Bridge	3.55	6.49
070917B	Escambia Bay I-10 Bridge	19.75	36.11
070917C	Escambia Bay I-10 Bridge	12.54	22.93
070917D	Escambia Bay I-10 Bridge	8.48	15.50

*Based on Florida-specific consumption rate of 32g/day.

The mullet samples collected near the I-10 Bridge in the middle of Escambia Bay had the highest levels of PCBs recorded for any fish species in the current study. Construction activity for replacing the hurricane-damaged I-10 bridge, including boat traffic and driving pilings in to the bay bottom, may have disturbed PCB-laden sediments resulting in a pulse of these compounds into the food webs and biota of the bay.

An analysis of homolog patterns of PCBs in fish samples are presented in Fig. F-7, along with the homolog patterns for the common commercial Aroclor preparations (PCB mixtures; data from: http://www.epa.gov/toxteam/pcbid/aroclor_comp.htm). The major known source of PCB contamination to the Escambia River and Escambia Bay was from a spill of Aroclor 1254. PCB homolog patterns in tissues from mullet and other fish collected near the Escambia I-10 bridge cluster with the homolog fingerprint for this raw product (Aroclor 1254), although homolog proportions appear to be species specific, indicating different partitioning mechanisms (physiological or trophic) for the different species (Fig. F-8). This supports the idea that disturbance to the sediments has exposed biota to unweathered Aroclor 1254.

Mullet tissue samples from the rest of the Escambia Bay and river, however, form a looser cluster with a moderate affinity to Aroclor 1254 (Fig. F-9), suggesting attenuation through biotic transfers and partial degradation of the raw product. PCBs from mullet tissue samples taken from the industrialized bayous (Chico and Grande) cluster with the Aroclor 1260 homolog pattern, suggesting either enrichment of more highly chlorinated homologs with partitioning into the biota, or an alternate source of PCBs. However, other sources of PCB contamination to the regional waterways are undocumented and need to be identified.

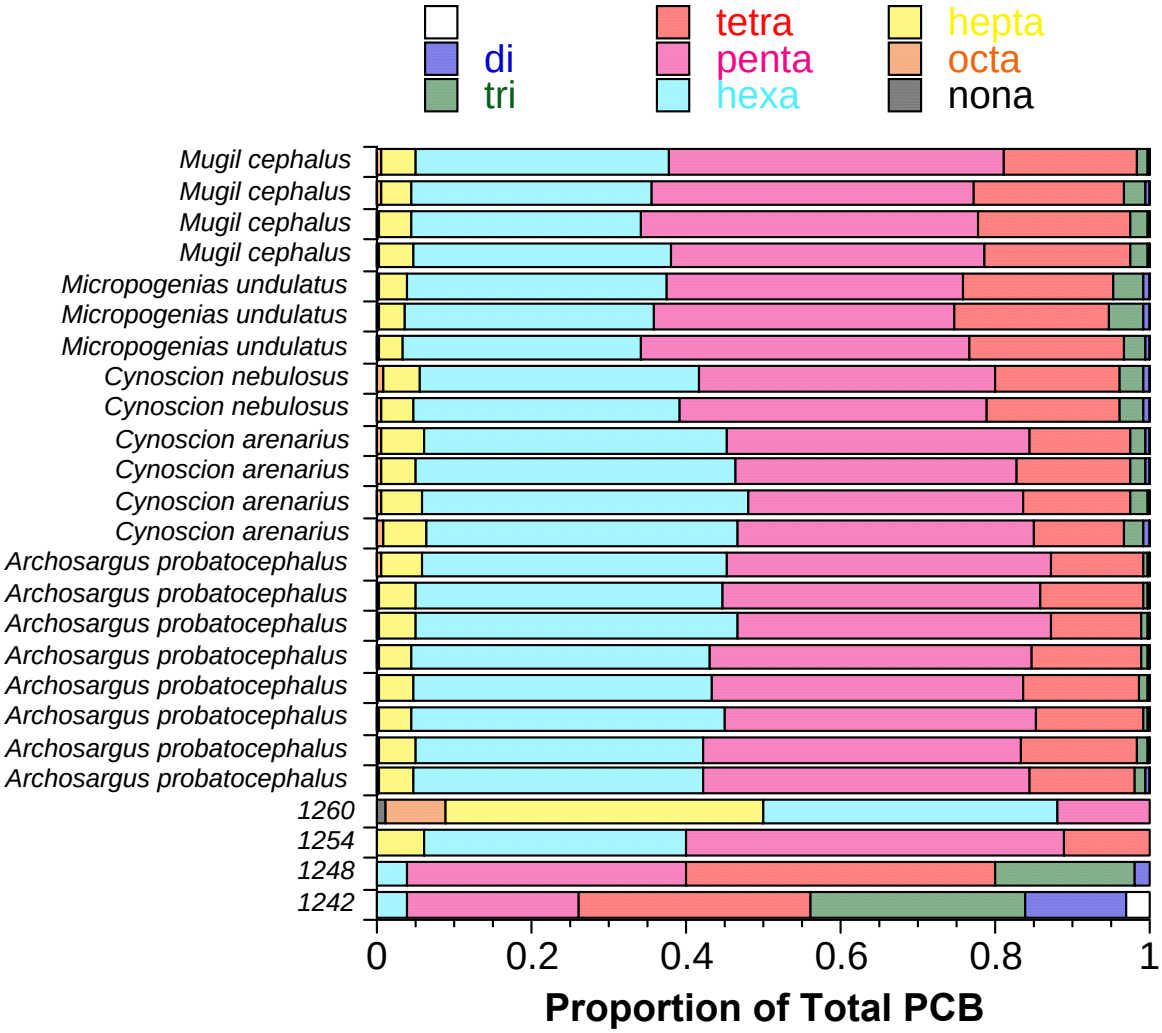


Fig. F-7. Proportions of homologs (percent of total PCB) in the fish samples. The patterns for the fish tissues most closely match the pattern for Aroclor 1254.

Hierarchical Clustering
Method = Ward

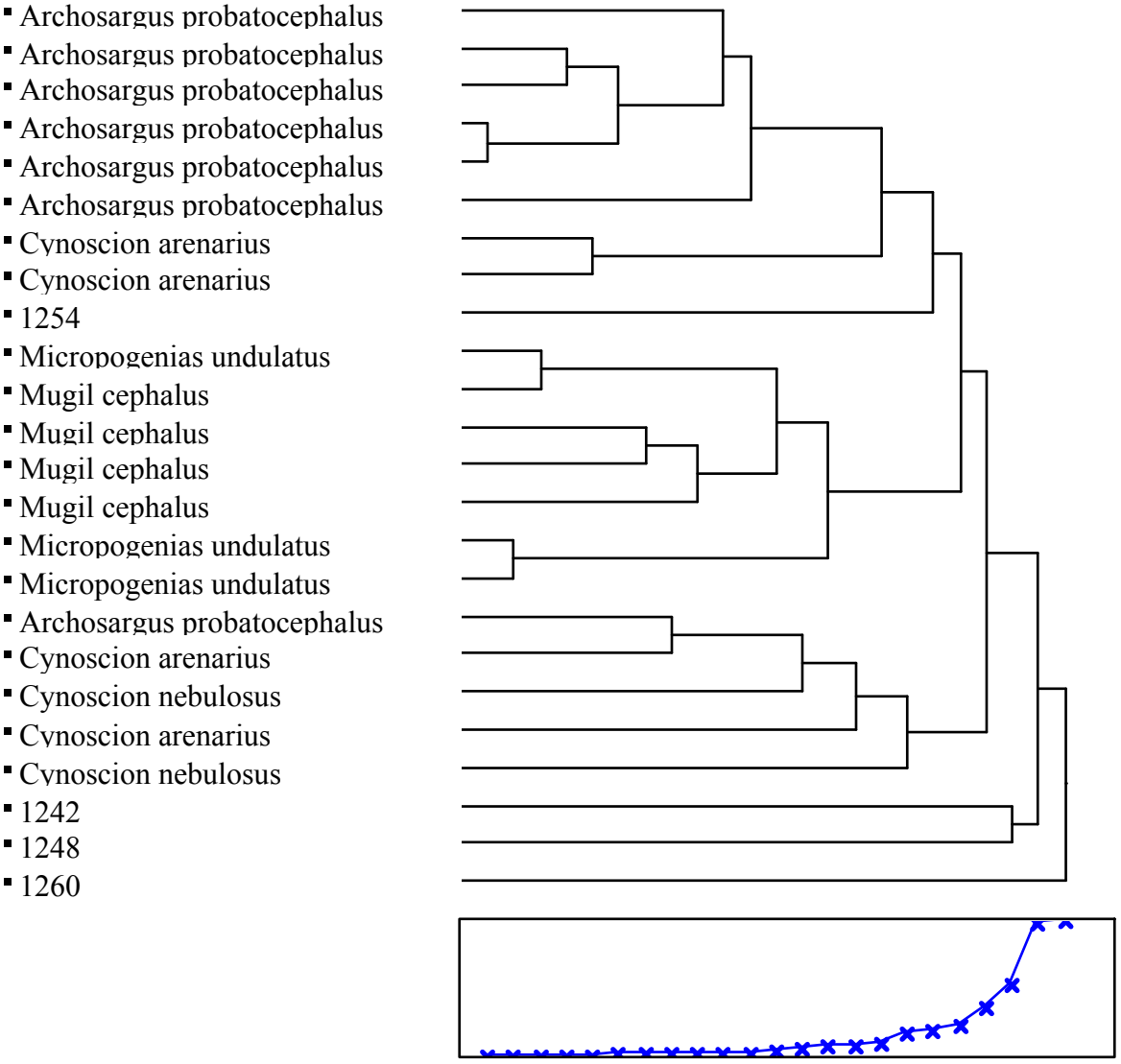


Fig. F-8. Cluster analysis of the data presented in Fig. F-7 to match similarities in patterns. Homolog proportions appear to be species specific, indicating different partitioning mechanisms (physiological or trophic) for the different species. Aroclor 1254 clusters in the center of the fish data, while the other Aroclors sit as outgroups at the bottom.

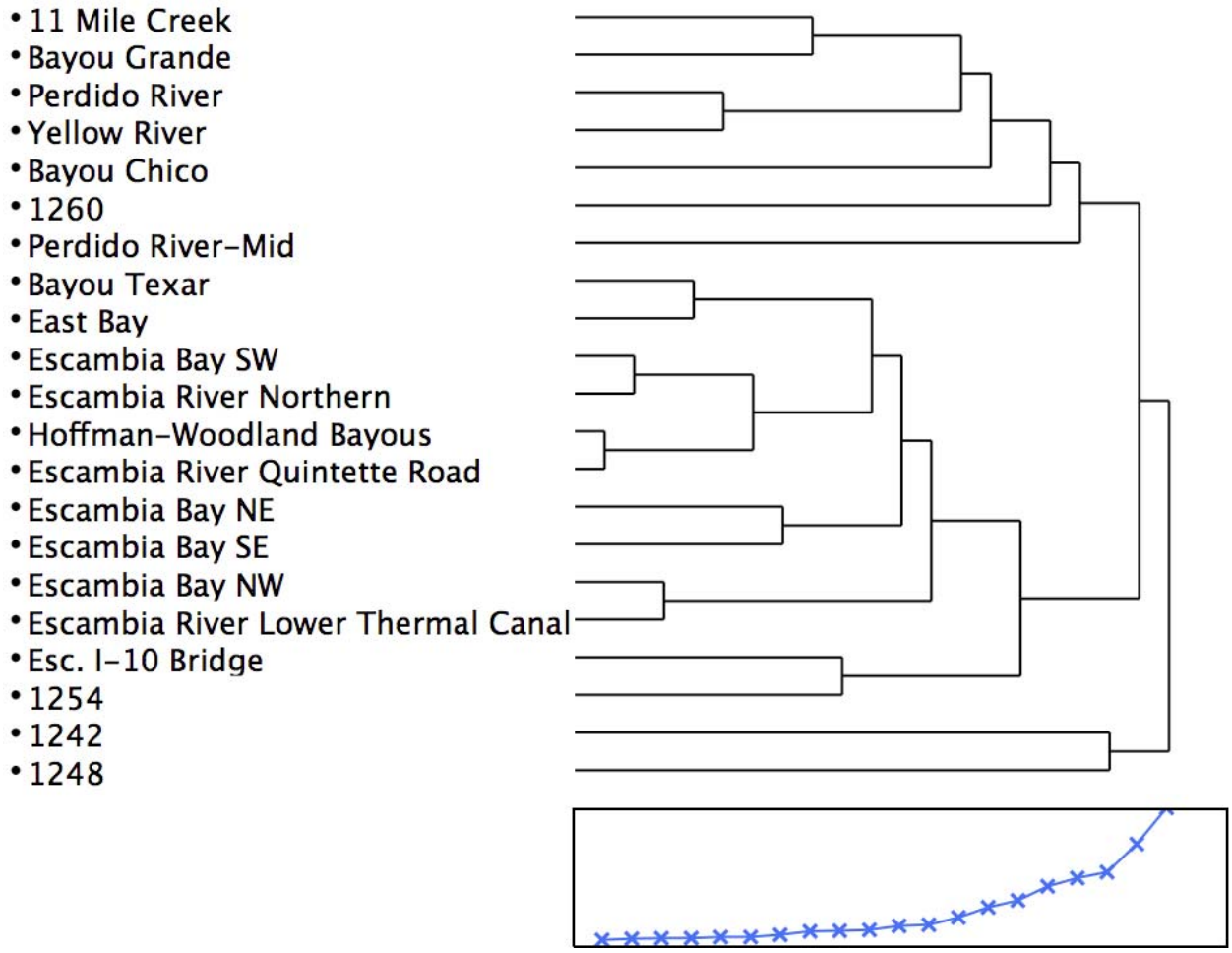


Fig. F-9. PCB homolog "fingerprints" from mullet fillets used in cluster analysis. Numbers refer to commercial Aroclor mixtures as potential sources of the contamination. Note the close relationship of the I-10 bridge samples with Aroclor 1254.

5. Patterns of Mercury and Polychlorinated Biphenyl Concentrations in Estuarine and Marine Fishes of Northwest Florida and the Northern Gulf of Mexico

Seventeen zones within Pensacola Bay and Perdido Bay watersheds (Fig. F-10) have been targeted during this study, in addition to fishes from the offshore environment. Data were recorded on 1199 specimens within 48 species. Individual species information and tabular data will be established as a series of web pages and made available as a hard copy guide for local fishermen and seafood consumers. Highlights of the findings are described below.

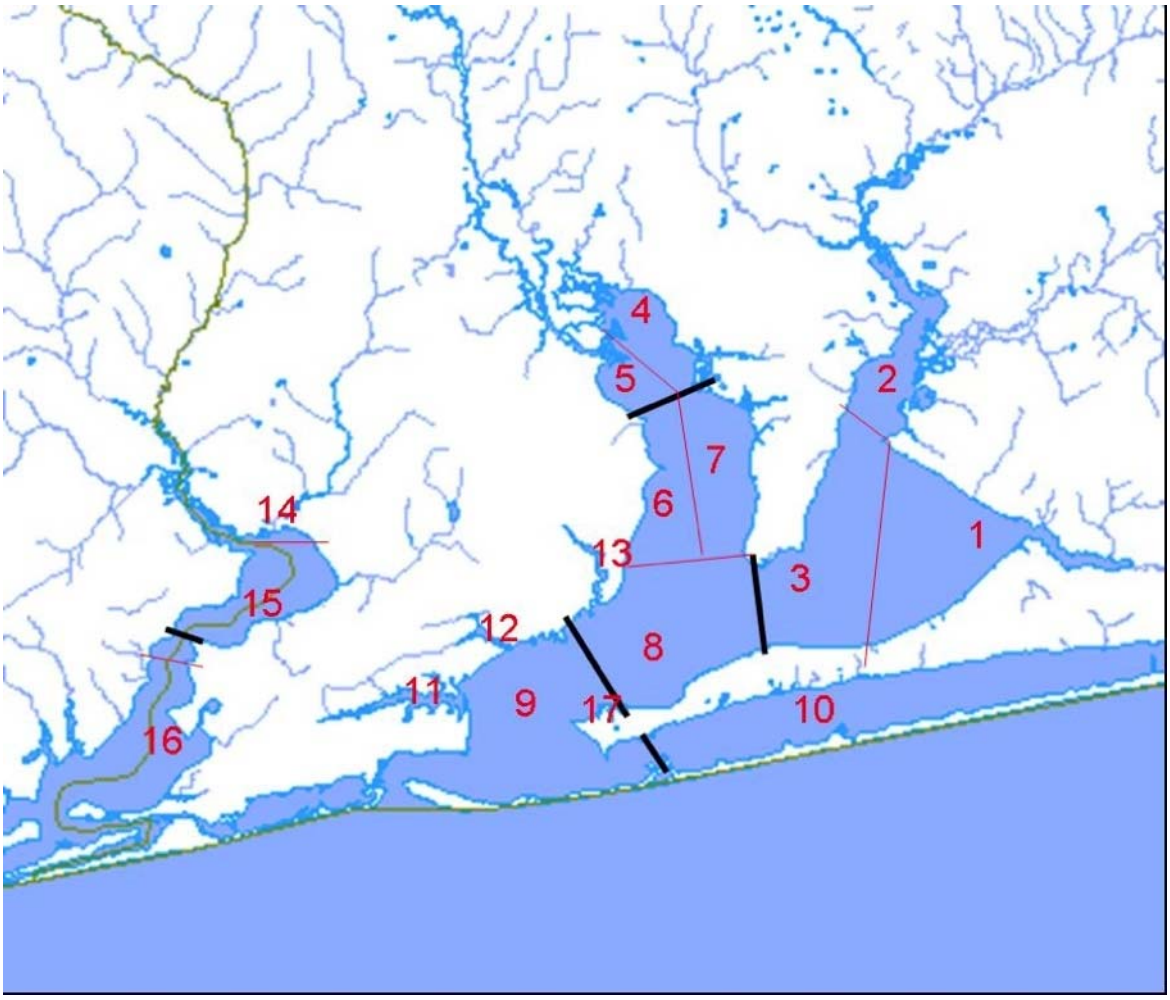


Fig. F-10. Finfish sampling zones in Blackwater, East, Escambia, Pensacola and Perdido Bays.

Based on contaminant analysis of blue crab, American oyster, and mullet samples, Blackwater-East Bays (zones 1-3), lower Pensacola Bay (zone 9), Santa Rosa Sound (zone 10, and Perdido Bay (zones 15-16) may be considered "green areas". Most fish sampled from these areas had contaminants below US EPA screening values for dioxins/furans (DF), PCBs, and Hg. However, with many of the other finfish that are highly mobile and of relatively high trophic status, these patterns tend to be blurred. For example, large red drum caught in East Bay and Santa Rosa Sound, the cleanest zones in the region, had the highest PCB loads recorded for this species (60.3 and 40.3 ng/kg respectively).

While most species bioaccumulate DF, PCBs and Hg with age, there are some notable exceptions. Spotted sea trout and Spanish Mackerel, *Scomberomorous maculatus*, show classic bioaccumulation in individuals for Hg. However, a reverse pattern is seen for PCBs, reflecting exposure to diffuse distribution of Hg in the environment but a relatively restricted distribution of highly contaminated PCB sites. Some of this may be explained by ontogenic shifts in habitat use and prey preferences as the fish becomes less dependent with age on estuarine resources

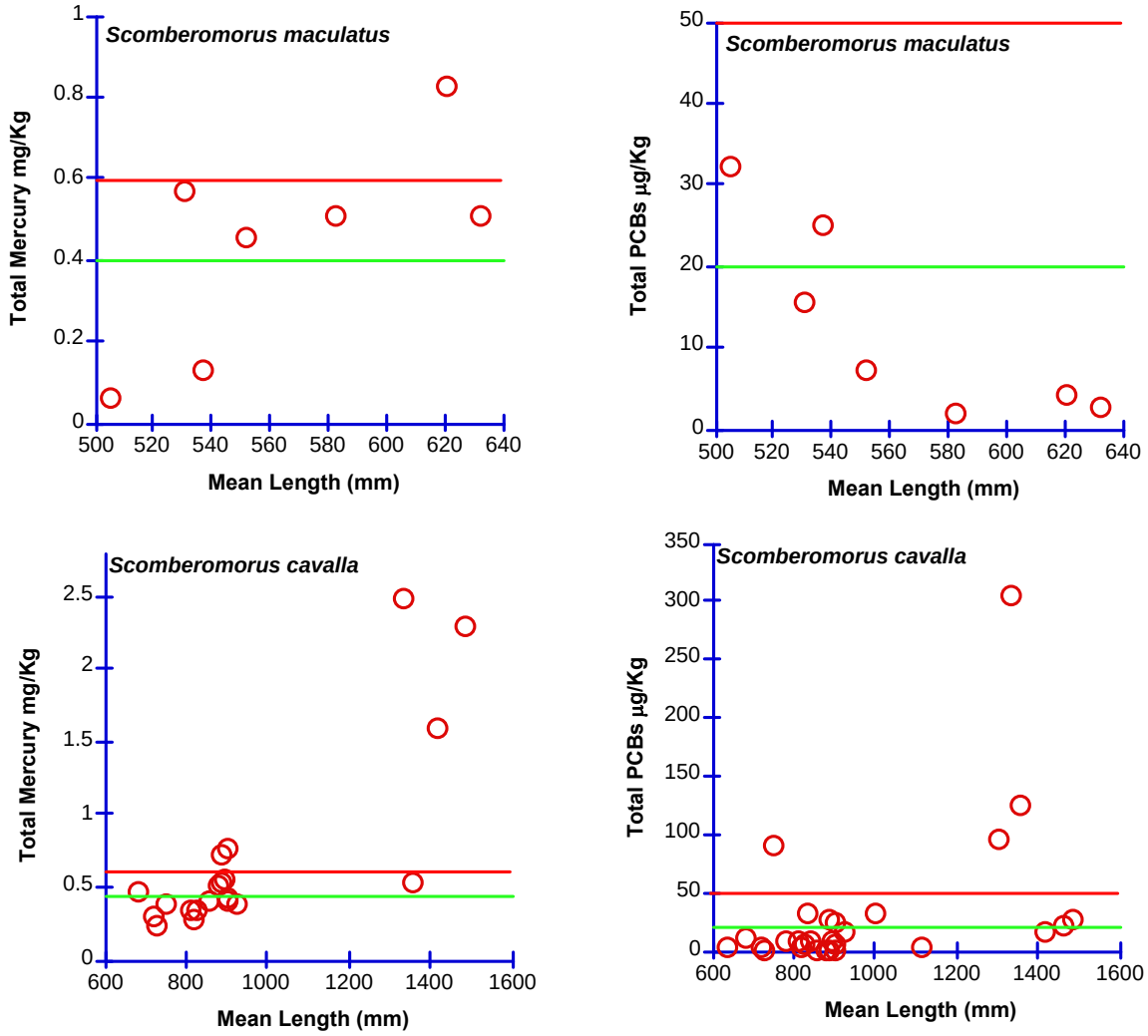


Fig. F-11. Concentrations of total Mercury (left) and total PCBs (right) in Spanish Mackerel, *Scomberomorus maculatus (top*) and King Mackerel, *Scomberomorous cavalla* (bottom). Green lines represent US EPA thresholds for recreational fisher consumption advisories, Red lines represent State of Florida thresholds. Note differences in the contaminant concentration scales between these two species.

where contamination is high. In contrast, the data for king mackerel, *Scomberomorus cavalla*, shows bioaccumulation for both compounds and at much higher levels (Fig. F-11). The higher Hg content in large specimens of these fishes has been well documented. The accumulation of high PCB loads was not. The highly migratory nature of these fishes with varying degrees of estuarine utilization as summer foraging areas likely contributes to the variability seen in the data. Our Hg data for speckled trout tends to agree with the trends of previously reported data, but also adds greater definition of Hg dynamics in this species (Fig. F-12).

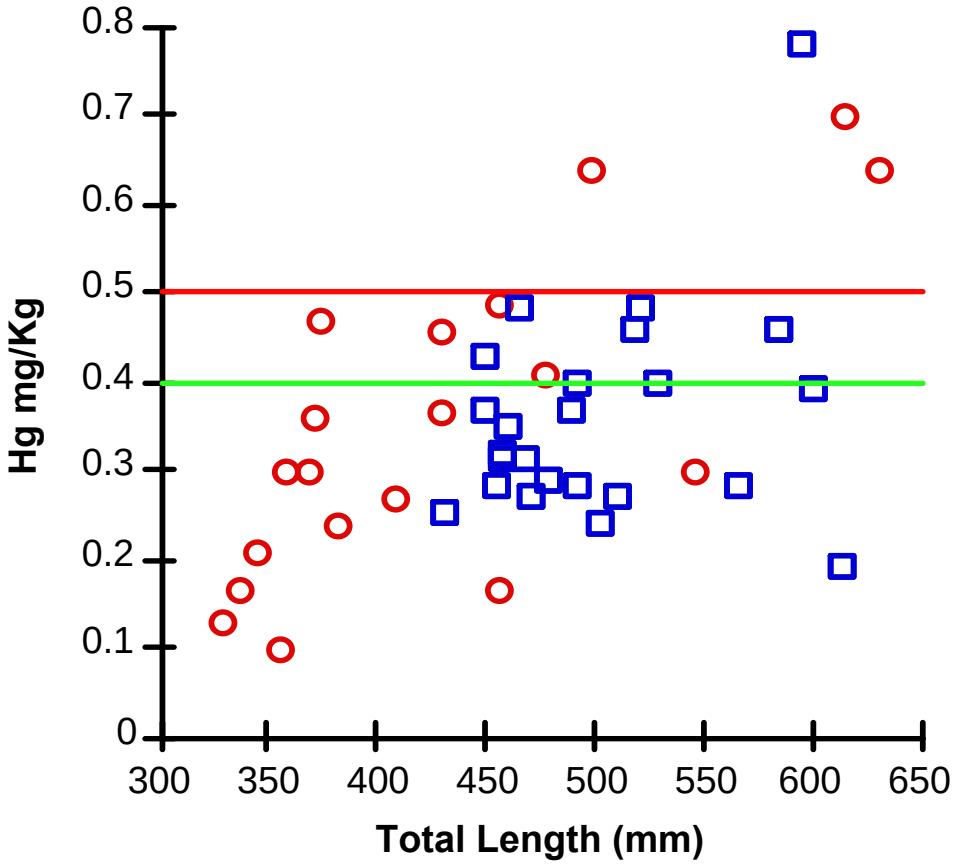


Fig. F-12. Mercury content in Spotted Seatrout, *Cynoscion nebulosus*, in the Pensacola Bay system. Blue squares are data reported by Rider and Adams (Gulf of Mexico Sci., 2: 97-103, 2000). Red circles are data collected in this study. The green line represents the US EPA recreational screening value. The red line represents the State of Florida threshold for limited consumption advisories.

The high concentrations of PCBs in mullet which make an annual spawning run offshore has brought to light a major yet relatively unrecognized flux of these persistent bioaccumulative contaminants from inshore contaminated sites to the offshore shelf environment. Many of the widely harvested predatory fish species, and their prey, make either an annual migration or an ontogenic shift from inshore to offshore, carrying toxic compounds absorbed in the estuaries and closer to the coast to the offshore shelf environment. This inshore to offshore transport is not well documented, yet highly contaminated inland sites around the Gulf Coast may be contributing to offshore contamination via abundant and migratory species like mullet.

While Hg concentrations in offshore fisheries have been examined for some species, the Hg loads for many species are unknown. PCB loads in marine fishes across the Gulf of Mexico are less well known, although high body burdens in estuarine fishes around the Gulf Coast have been documented. This indicates inshore sources have the potential for offshore transport and accumulation in marine species. For several grouper species in our study, the concentrations of mercury and PCBs appeared to correlate with size/age with some samples exceeding the US EPA screening threshold for total PCBs (Fig. F-13).

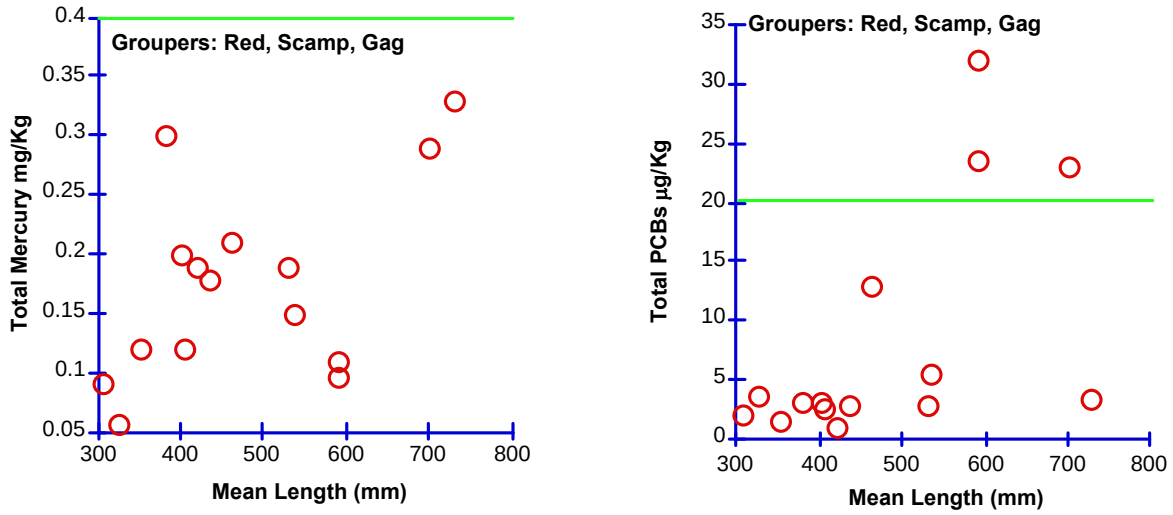


Fig. F-13. Total Mercury (left) and total PCBs (right) loads in Groupers: *Epinephelus morio* (Red), *Mycteroperca microlepis* (Gag), *Mycteroperca phenax* (Scamp). The green lines represent US EPA thresholds for recreational fisher consumption advisories, Red lines represent State of Florida thresholds.

Red Snapper (*Lutjanus campechensus*), a signature offshore reef fish of the Gulf of Mexico that is targeted by both commercial and recreational fisheries, also show bioaccumulation of PCBs and Mercury with increasing size, with a few samples suggesting that a further Gulf-wide investigation of toxin loads in offshore fishes may be warranted. (Fig. F-14).

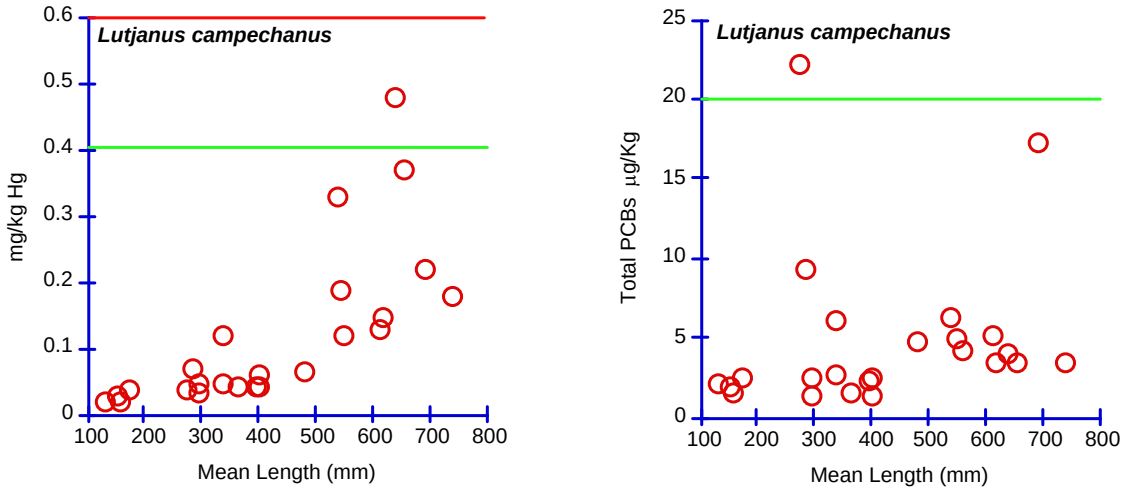


Fig. F-14. Total Mercury (left) and total PCBs (right) loads in Red Snapper, *Lutjanus campechanus*. The red lines represent US EPA thresholds for recreational fisher consumption advisories, the red lines represent State of Florida thresholds.

Mobility of the PCB molecules, their biodegradation, and overall bioavailability are relatively selective processes that effect the appearance of congeners in the tissues of biota relative to the source materials. Partitioning into biota represents a balance of bioavailability via largely aqueous media and the preferential absorption and accumulation in lipids with age and by trophic transfers. Homolog patterns within the biota sampled in this investigation are presented in Fig. F-15 for offshore, estuarine, and fish samples taken at the site of the I-10 bridge blast in Escambia Bay. The homolog patterns for the common commercial Aroclor preparations are plotted with data from http://www.epa.gov/toxteam/pcbid/aroclor_comp.htm for comparison to the tissue profiles.

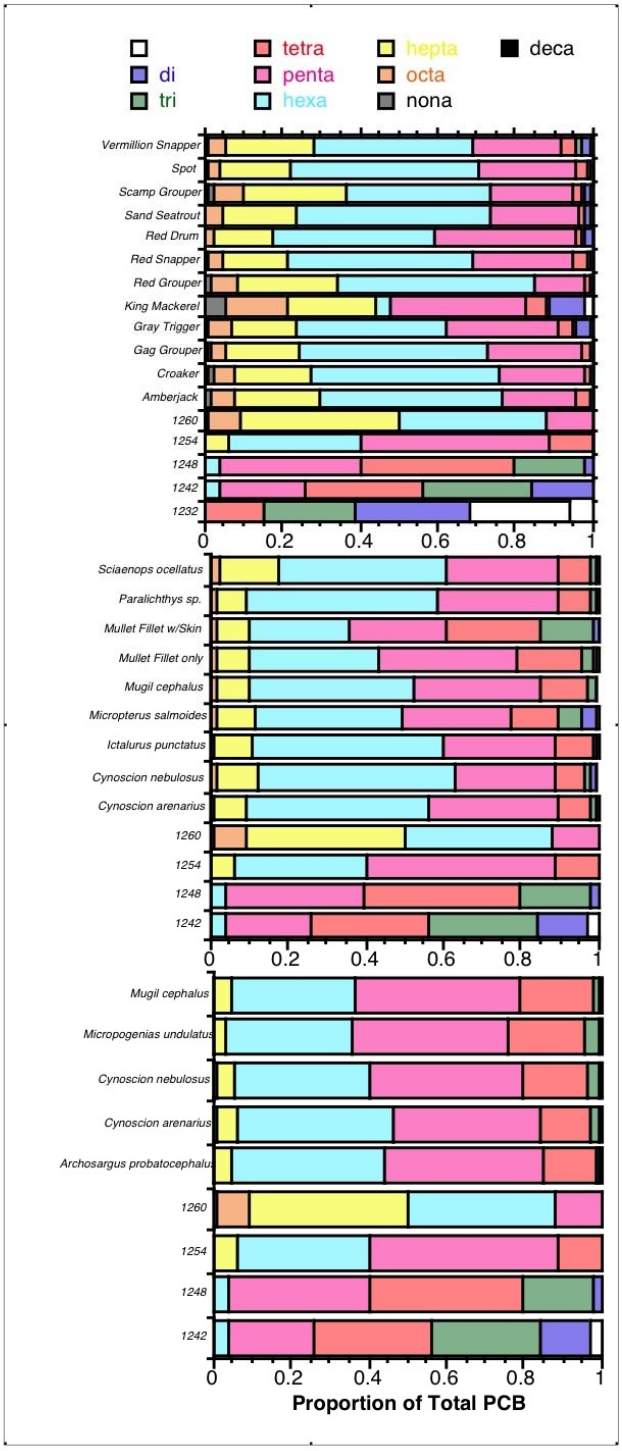


Fig. F-15. Averaged homolog proportions in offshore (top) and estuarine (middle) fish samples and those collected after the demolition blast at the I-10 bridge in Escambia Bay (bottom). Numbers refer to commercial Aroclor preparations.

As with the mullet samples (Fig. F-9), other fish specimens sampled at the Escambia Bay I-10 bridge blast site have a PCB homolog pattern with strong similarity to Aroclor 1254 (Fig. F-15, bottom), the source material for contamination in the Escambia River and Bay. All other PCB data from fish samples in the estuary, which include the previously sampled Escambia Bay and Escambia River fishes, show a moderate affinity to the 1254 pattern, but have enriched hepta- and octa-chlorinated homologs. This may reflect the biological partitioning and the weathering and degradation of the less chlorinated congeners. In the case of Bayou Chico, contamination from other sources of industrial Aroclor use is likely, in addition to biological partitioning and degradation.

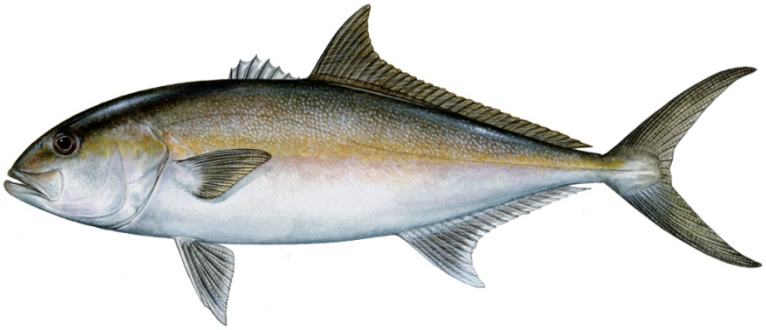
Of interest are the paired skinned and skinless mullet fillets from the Escambia River delta (Fig. F-15 middle). The composite with fillet plus skin had roughly double the total PCB content and was more highly enriched in tri-chlorinated congeners than the skinless fillet composite. An opposite pattern is seen for the TEQ values. The TEQ value for the skin-on sample was one-third the TEQ value of the skinless fillets (ND = 0 TEQ 0.573 versus 1.534 ng/kg). These results indicate a partitioning of not only more highly chlorinated congeners (penta- and hexa-) in the muscle tissue, but the more toxic ones as well.

Moving further away from direct contamination sources, the offshore fish samples show further attenuation of lesser chlorinated congeners and enrichment in the more highly chlorinated ones (Fig. F-15, top). This pattern shift is consistent with differential partitioning in food webs and the biological dispersal of PCBs from the inshore environment to offshore.

6. Overview of Contaminant Loads (Mercury, PCBs, TEQs for Dioxins/Furans/Dioxin-like PCBs) in Individual Fish Species

Our cumulative results from the current EPA-funded project, CDC-funded studies, and the U.S. Navy-funded studies of off-shore fishes prior to the sinking of ex-Oriskany are summarized in the following pages. In order to relate the levels of contaminant loads to potential health risks, the observed levels are compared to US EPA screening values for Hg (0.4 mg/kg), total PCBs (20 ng/g), and TEQ (0.256 ng/kg) for dioxins/furans/dioxin-like PCBs based on recreational fisher consumption rates 17.5 g day^{-1} as target thresholds. State of Florida thresholds for Hg (0.6 mg/kg) and total PCBs (50 ng/g) are also denoted for comparison. The State of Florida does not have a standard screening threshold for TEQ.

The images of fish are used here with permission from the Florida Department of Environmental Protection (Dianne Peebles, artist). The fish pictures are not to scale.



Greater and Lesser Amberjacks

Seriola dumerilli
Seriola rivoliana

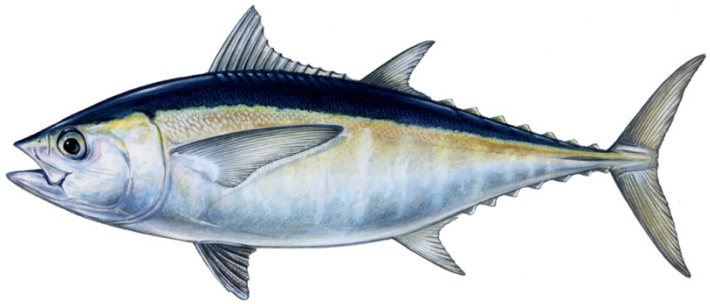
A total of 9 fish (7 Greater, 2 Lesser) were collected over offshore reefs. Mercury concentrations show a tendency to accumulate with size, but only one specimen out of nine exceeded the US EPA screening value. Three fish out of nine were at or exceeded the US EPA screening value for PCBs

Largemouth Bass

Micropterous salmoides

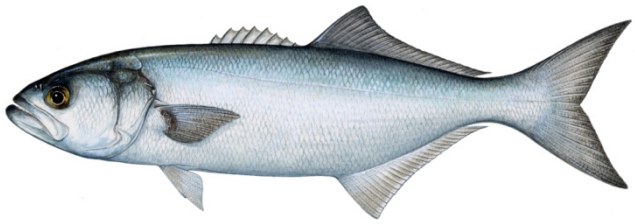
A total of 163 fish from 20 locations were included in 55 samples. Single fish comprised nine samples, and the remaining 46 were composite samples of 3 or more fish. Mercury content was generally high throughout the area, and a State of Florida limited-consumption advisory exists for most of the waterways sampled. A State of Florida no-consumption advisory based on mercury content exists for Woodbine Lake. Samples from this lake had the highest mercury concentrations of any bass sampled.

PCB and Dioxins/Furans content was low in all samples, except for the PCB loads in fish collected from the lower Escambia River, where PCB content in bass triggered a limited consumption advisory based on PCB content from the State of Florida.



Blackfin Tuna
Thunnus atlanticus

Five fish were sampled offshore. This limited sampling suggested bioaccumulation of both mercury and PCBs with size, with two of the larger fish exceeding the US EPA screening value for mercury content, although none of the fish (up to 62 cm) exceeded the PCB or TEQ thresholds.



Bluefish
Pomatomus saltatrix

Samples from 9 fish ranging in size from 34 to 49 cm were collected from Pensacola Bay, Pensacola Pass, and along Santa Rosa Island in the Gulf of Mexico. All fish were at or exceeded the US EPA screening value for mercury, and five out of nine exceeded the State of Florida threshold for limited consumption. Two of the larger fish exceeded the US EPA threshold for total PCB content, and one fish exceeded the State of Florida threshold for PCBs. Six out of nine fish exceeded the US EPA threshold for toxicity (TEQ) of Dioxins/Furans and PCBs.

Bonita
Euthynnus alleteratus

Two specimens were collected offshore, neither exceeded screening values for mercury, PCBs or TEQ.

Croaker
Micropogenias undulatus

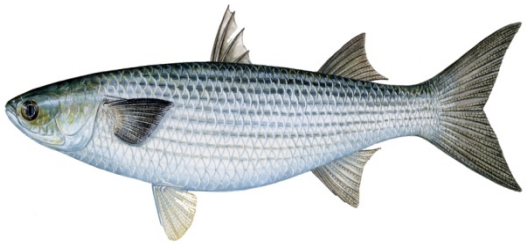
Nine samples containing 50 fish (2 to 13 per composite) had very low concentrations of mercury. PCB content, however, exceed the US EPA threshold in six of nine samples, with three of those collected in the urban bayous (Texar, Chico, Grande) and three during the Escambia Bay I-10 Bridge demolition blast. The PCB content in Escambia Bay samples were three to six times higher than in the samples from the bayous. Samples from East Bay, Hoffman/Woodland Bayou, and offshore had lower concentrations of total PCBs. All samples except from offshore exceeded the US EPA screening value for TEQ (Dioxins/Furans and PCBs).

Dolphin (Mahi)
Coryphaena hippurus

Two fish were sampled from offshore collections, 340 and 1080 cm. Both fish had low mercury content. However the larger fish had 3 times the US EPA total PCB threshold, and also had a 3x elevated TEQ value.

Flounder
Paralichthys spp

Fish were collected at various locations within the bay system. While there appeared a tendency for elevated mercury and PCBs with size, no fish exceeded US EPA thresholds for these compounds. One sample from the lower Escambia river did have an elevated TEQ value.



Striped Mullet
Mugil cephalus

Eighteen locations were targeted over the region providing 56 samples containing 170 fish. All samples were composites of 2 to 4 fish with at least three composites per location in nearly all cases, except four fish from the I-10 demolition blast on the Escambia Bay Bridge that were analyzed individually.

Mercury content was very low in all mullet tested. Mullet contained the highest PCB and Dioxins/Furans concentrations of any fish sampled during this study, especially those fish collected from known PCB contaminated areas. Thirty of 56 samples exceeded the US EPA screening value for total PCBs, and 45 out of 56 samples exceeded the US EPA combined PCB and Dioxins/Furans TEQ screening value. Thirty-two samples exceeded the TEQ value for Dioxins/Furans alone, and 29 samples exceeded the TEQ threshold for PCBs alone.

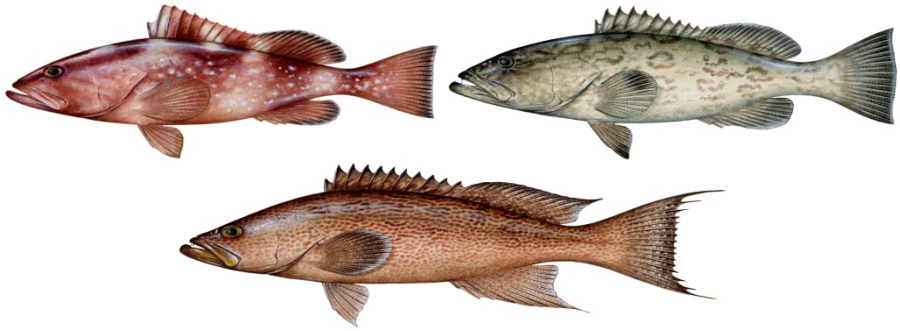
The highest PCB loads and TEQ values were obtained at the Escambia Bay I-10 Bridge site.

Samples of skin-on fillets had twice the PCB load of skinless fillets, but the toxicity (TEQ) was higher for the skinless fillet.

Locations with samples below the US EPA recreational consumption screening value for total PCBs and the combined PCB and Dioxins/Furans TEQ screening value were:

Yellow River, 2 of 3 samples
Bayou Texar, 1 of 3 samples
East Bay, 3 of 3 samples
Escambia Bay NE , 1 of 3 samples; Perdido River, 4 of 7 samples

Red, Gag, & Scamp Groupers
Epinephalus morio, Mycteroperca microlepis, Mycteroperca phenax



Fifteen groupers were sampled from offshore reefs. These fishes show a tendency for bioaccumulation with age for both mercury and PCBs. No samples exceeded the US EPA screening value for mercury, although three samples exceeded the screening value for total PCBs, and four samples exceed the TEQ value for PCBs alone (Dioxin/Furans were not analyzed in these fish).

King Mackerel
Scomberomorus cavalla

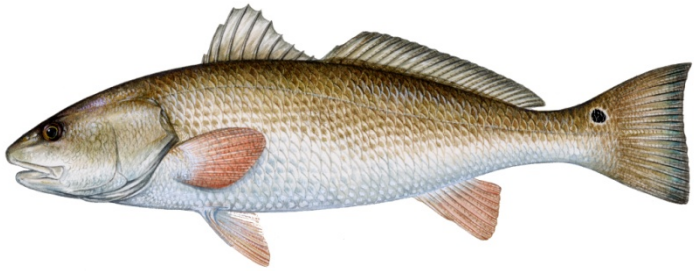
Twenty-eight fish were sampled from offshore Pensacola. Both PCBs and Hg accumulate with age in this species. Mercury content was high in these fish, and a consumption advisory exists based on the mercury content of larger specimens (>32"), which agrees with the recorded sizes of those fishes in this study exceeding the US EPA screening value. Total PCB content also exceeded the US EPA screening value at about the same size. The highest PCB loads of any offshore fish sampled were recorded for this species (92.5 µg/kg). Combined Dioxins/Furans and PCB TEQ values exceeded the US EPA screening value in 11 of 22 fish for which this data was available.

Mingo Snapper
Rhomboplites aurorubens

Samples were obtained over offshore reefs representing 8 samples of 20 fish, with 6 samples as individual specimens. Both PCBs and Mercury content was low in sampled fish.

Pompano
Trachinotus carolinus

Nine fish were collected from Santa Rosa Island Surf and analyzed as individuals. Mercury accumulation with size was apparent, but only one mid-sized fish of nine samples exceeded the US EPA screening value. None of the PCB concentrations were above the US EPA screening value, and higher concentrations were found in smaller fish, consistent with estuarine utilization of juveniles in this species. The fish with the two highest PCB concentrations also had high Dioxins/Furans, and the TEQ values for these fish exceeded the US EPA TEQ screening value.



Red Drum
Sciaenops ocelatus

Fifteen samples including 28 fish from 10 locations were analyzed. With the exception of a single sample, mercury content increased slightly with size but was low in all samples. PCB content increased with size, with 5 samples over the US EPA screening value.

Red Snapper
Lutjanus campechanus

Forty-two fish in 24 samples were collected from offshore reefs, with smaller sized fish making up composites of 2 to 6 fish. Mercury content increased with size, with larger fish approaching the US EPA screening value and one fish exceeding it. PCB content was generally low with one larger fish close to the US EPA screening value and one smaller fish exceeding it. TEQ values followed a similar pattern, with only one smaller fish exceeding the screening value.

Sheepshead
Archosargus probatocephalus

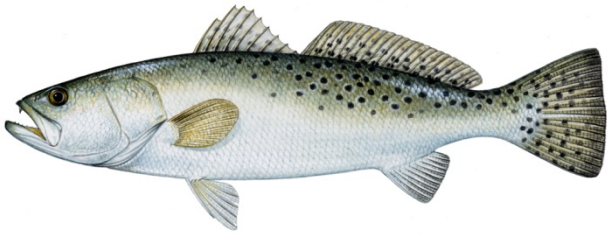
Eighteen fish were sampled at two locations: Pensacola Pass during the annual spawning aggregation, and from the Escambia Bay I-10 Bridge demolition blast. Mercury content was determined for the 8 samples taken from Pensacola Pass, and although accumulation with age was observed, the concentrations were all well below the US EPA screening value. PCB content, however, was high above the US EPA screening value for three of the eight samples from Pensacola Pass where fish had congregated for the annual spawning. All of the samples from the I-10 Escambia Bay Bridge were well above the US EPA Screening value. Only one sample from both locations was below the US EPA screening value for TEQ.

Shrimp
Farfantepenaeus spp.

Shrimp samples (4) from Pensacola Bay were all well below screening values for mercury, PCBs and TEQ.

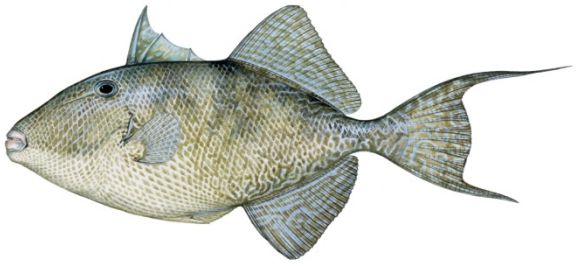
Spanish Mackerel
Scomberomorus maculatus

Seven samples of individual fish were collected from Pensacola Pass and along the Gulf shore line of Santa Rosa Island. Mercury content increased with size of the fish, with five of seven samples exceeding the US EPA screening value. PCBs however, decreased with increasing size, with the two smallest fish exceeding the US EPA Screening value for total PCBs, consistent with younger fish foraging in the estuary and older fish moving offshore. The highest PCB toxicity as TEQ was for two of the larger specimens, indicating that despite lower total PCB, more toxic congeners were more prevalent with age.



Speckled Trout
Cynoscion nebulosus

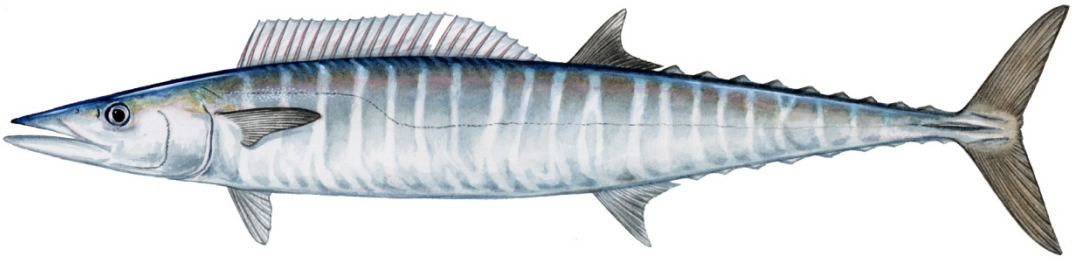
Twelve sample locations included 18 samples and 49 fish. Five samples were individual fish, the others were composites of 3 to 5 fish each. Mercury increased with fish size throughout the area to the point where 8 samples had mercury concentrations higher than the US EPA screening value. With the exception of a single sample, PCB content was lower than for other species sampled in the same locations, including the Escambia I-10 bridge site which had the highest PCB concentrations found during the course of the study. Five of 18 samples were above the US EPA screening value for total PCBs. Eight of 18 samples exceeded the US EPA screening value for TEQ.



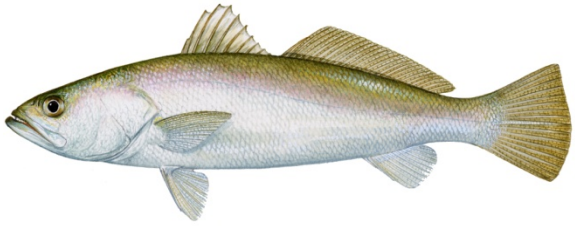
Gray Trigger
Balistes capriscus

Seven samples, 6 as individual fish and one 3-fish composite were collected on offshore reefs. All fish had low mercury, PCBs, and TEQ values well below US EPA screening values.

Wahoo, *Acanthocybium solandri*

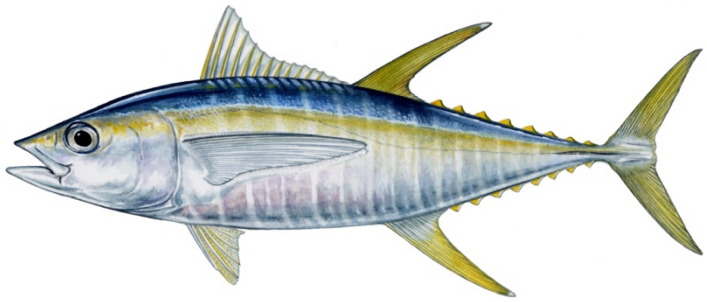


Seven specimens were sampled from offshore of Pensacola in The Gulf of Mexico. Two samples had mercury concentrations above the US EPA screening value, two samples exceeded the US EPA screening value for total PCBs, and had TEQ values based on PCB content that exceeded the screening value for TEQ.



White Trout
Cynoscion arenrius

Eight samples were obtained from offshore, the Pensacola Bay three-mile bridge, and Escambia Bay. All samples were below US EPA screening values for mercury content, and accumulation with size was not apparent. Samples from the Escambia Bay I-10 bridge were the only ones that exceeded the screening value for total PCBs and TEQ.



Yellowfin Tuna

Thunnus albacares

Six samples from individual fish were obtained from Offshore, and all were below screening values for mercury, total PCBs and TEQ.

7. Perspectives

U.S. Geological Survey's recent report on mercury contamination in fish from 291 streams across the nation (http://water.usgs.gov/nawqa/mercury/) shows that every fish had detectable levels of mercury, and about a quarter of the fish contained mercury levels exceeding EPA SV (0.4 mg/kg). Atmospheric mercury is the main source to most of these streams, coal-fired power plants being the largest source of mercury emissions in the United States. Atmospheric deposition of mercury to the Pensacola Bay watershed, as also noted for locations in the Gulf coastal states, is relatively high (Section III.C) and is the likely source of contamination leading to elevated levels of mercury in fish in the area rivers, ponds, lakes, and estuarine environments. There are exceptions, such as the spring-fed Woodbine Lake, in which a geological source seems to contribute excessive amounts of mercury.

All 50 states have mercury monitoring programs, and 48 states issued fish-consumption advisories for mercury in 2006, the most recent year of national-scale reporting to the EPA. As indicated earlier (Section III.C), atmospheric deposition in a given area is influenced not only by local emissions but also by releases from regional and distant sources. Thus, national-level regulatory efforts are needed to achieve reductions in mercury loads affecting human health. In February 2009, EPA announced that it intends to control air emissions of mercury from coal-fired power plants by issuing a rule under the Clean Air Act.

Although fish consumption advisories based on mercury loads have been issued by Florida DOH throughout the state, there has been relatively very little attention to systematically survey and issue fish consumption advisories based on other contaminants. We have shown that, as a result of past point-source discharges and continuing inputs from undocumented avenues/sources (and persistence), there are elevated levels of PCBs in various water bodies of the Pensacola Bay System leading to bioaccumulation in fish/shellfish tissues—in some cases reaching high enough levels posing potential cancer and non-cancer health risks. We are pleased that our findings have in part aided the Florida DOH to issue consumption advisory for mullet from the lower Escambia River, and for extending the advisory recently to mullet from the Escambia Bay. It should be noted that elevated PCB loads are also found in fish/shellfish from other components of the Pensacola Bay System, especially the urban bayous in the area, and this needs to be followed. Florida DOH's screening threshold for PCBs (50 ng/g) is much higher than that issued by EPA (20 ng/g), and considering that the average fish consumption in Florida is higher than the standard (17.5 g/day) used by EPA for calculating this recreational fisher consumption level SV, the higher threshold being used in Florida merits reassessment.

A recent report on ranking cancer risks of organic hazardous air pollutants in the United States (Loh et al., Environmental Health Perspectives, 115: 1160-1168, 2007) indicated that 15% of the risk resulted from exposures through food, mainly due to dioxins. We have shown that TEQs due to dioxins/furans and dioxin-like PCBs are elevated in fish/shellfish, in varying levels, in the different components of the Pensacola Bay System, and also in several of the near-shore and offshore fishes. Florida DOH has not issued a State-wide screening level for TEQs, although EPA set the recreational fisher consumption SV for the national level at 0.256 ng/kg.

In terms of protecting human health, it is necessary to have a systematic analysis of target contaminants in commonly caught and consumed fish and shellfish and to establish justifiable and uniform (national/state) standards so that the consumers have clear information to make informed choices. Given species-specific patterns of contaminant accumulation, it is also necessary to evaluate and communicate about the risks resulting from elevated loads of multiple

contaminants found in a given species, rather than issuing advisories based on only an individual contaminant. This would alleviate some of the difficulties human consumers may encounter when selecting fish for consumption as they weigh the benefits/risks of fish consumption. The nutritional, developmental, and cardiovascular benefits of fish consumption are important. The public depends on regulatory agencies for setting the needed guidelines and fish consumption advisories for safety.

During the course of our CDC-funded studies of mercury levels in hair samples from child-bearing age women in Northwest Florida (Karouna-Renier et al., 2008), only 31% of the 601 women reported knowledge of the consumption advisory based on mercury levels in fish, and pregnant women exhibited lower awareness of the advisory than non-pregnant women. The data suggest that public health education efforts need to be augmented. In this regard, it is noteworthy that the Escambia County Health Department—with support from the Florida DOH—has recently launched a public education campaign (through billboard advertisements, and news releases through diverse media) related to consumption choices pregnant women (and those planning to become pregnant) can have in selecting fish that have relatively low mercury loads.

G. Public Outreach - The PERCH Environmental Bibliography for Northwest Florida

(Task Leader: Carl J. Mohrherr, University of West Florida)

1. Introduction

This Environmental Bibliography was compiled so that all local agencies and concerned citizens may be better informed about the studies pertinent to Northwest Florida. It is intended to facilitate access by environmental researchers and the general public to local environmental literature on a web-accessible database. This was needed since there was no specific local web-accessible database for all local environmental literature. The PERCH Bibliography is a fully searchable database of bibliographical materials pertaining to the environment of Northwest Florida. This database is derived from several preexisting databases and from literature searches intended to include all information relating to the environment of our region. The oldest historical citations go back to the 18th century coinciding with the beginnings of continuous settlement in Pensacola. Environmental topics are extremely diverse, covering multiple scientific and applied disciplines. We have included all environmental information from botanical identification to septic tanks. The PERCH Bibliography for Northwest Florida was constructed by personnel from the UWF Center for Environmental Diagnostics and Bioremediation and the John C. Pace Library at the University of West Florida.

2. Database Components

The Plan was to:

- Design a searchable database
- Input bibliographic data to the searchable database
- Utilize pre-existing collections
  - There were three pre-existing electronic bibliographies for Northwest Florida:
    1-The US EPA Gulf Ecology Division Library
    2-West Florida Regional Planning Council Library
    3-"An Environmental Bibliography for Northwest Florida 1900-1985" by A. J. McErlean

Literature databases from each of the above listed groups as well as all other sources or citations that could be identified were examined and reports concerning environmental issues and research in Northwest Florida were identified and entered into a database that was constructed by Paul Williford, University of West Florida Staff Librarian, currently at the Emerald Coast Campus of the University of West Florida.

Each reference was annotated regarding

1. location of the original,
2. format (paper, CD, web, etc.),
3. type of report (e.g. peer reviewed literature, government "gray" literature, technical report, newspaper report, etc.),
4. and a brief synopsis of the document's purpose and findings.

The completed bibliography has been posted on the internet via the University of West Florida's server. http://fusionmx.lib.uwf.edu/perch/index.cfm

The citations are presently searchable by 9 categories, reference type, author, title content, subject words, abstract content, and annotation content. The majority of items include an abstract or annotation, URL, and holding library. Many items are available at multiple libraries and we routinely list the current accessible holding location available at the time that the data was inputted. In cases where no holdings are known for the cited literature we have noted if PERCH has a hard copy or electronic version of the file. We appreciate constructive feedback and to this end we have provided contact information and an electronic form where interested readers can nominate citations for consideration.

3. Usage Patterns

There are currently 2061 entries available to the public, and the bibliography is being consulted on a daily basis. The +FusionMX Server can generate a variety of statistics relative to its usages by the public. In the period from June 13, 2006 to September 15, 2009 there were a total of 4,054 hits on this server by the public (Table G-1) or an average of 3 per day.

Table G-1. General Statistics for Time range:
6/13/2006 to 9/15/2009

Hits	
Total Hits	4,054
Average Hits per Day	3
Average Hits per Visitor	8.39

The visitors are from 28 different countries, with the visitors from the United States being the dominant group (91% of visitors). Therefore, PERCH Bibliography proved to be and will continue to be a useful resource for the local community and also for researchers throughout the United States and abroad.

IV. SUMMARY AND CONCLUSIONS

Based on the availability of funds, it was necessary to propose specific projects that can be completed within each budget/project period. Accordingly, we conducted a series of interrelated studies, each building upon the results and problems revealed by a preceding study, with a goal of performing as comprehensive analysis as possible to address issues of concern related to environmental and community health in Northwest Florida. These comprehensive studies address the concerns of our community, with the results and conclusions having broader applications/implications for our area and for other regions of the state and the country. Our project results have been disseminated widely through peer-reviewed publications, presentations at professional meetings, presentations to state and federal agencies as well as to stakeholder organizations in the region, and posting our detailed reports at the UWF-CEDB website for public access:

http://www.uwf.edu/cedb/perch.cfm

A. Construction of an environmental bibliography for Northwest Florida

http://fusionmx.lib.uwf.edu/perch/

We found it difficult to locate and retrieve information pertinent to regional environmental health studies, because of the diffuse sources and difficult access to various reports dealing with the environment in the Pensacola area. In order to alleviate this problem, we created an electronic database of environmental studies in Northwest Florida, including more than 2000 citations (with annotated summaries), and posted it on the UWF library's web site accessible to the general public. This bibliography is being used widely, with more than 4,000 hits during the recent three years on the server with visitors from the United States and abroad.

B. Air quality studies

http://cure.eas.gatech.edu/~chang/perch/

These studies were conducted by our collaborators at Georgia Institute of Technology, which included evaluations of historic data, an intensive 30-day field monitoring done utilizing Georgia Tech's mobile laboratory deployed on the grounds of O.J. Semmes Elementary School, and comprehensive air quality and air toxics modeling. Initial evaluations showed that, with regard to public health, particulate matter ($PM_{2.5}$) pollution is of greater concern, than are ozone and air toxics for the Pensacola area. Detailed analysis showed that sulfate was a large fraction of the observed ambient $PM_{2.5}$ loading, with high concentrations most often associated with northerly flow. Coal and gasoline combustion were observed to account for most of the Pensacola atmosphere's particle load during a high pollution event, although open fires were also a possible source of particles during this event. Source apportionment of $PM_{2.5}$ indicated that sulfate constitutes half or more of the particulate load in the Pensacola area for the modeled episode. Rather than local sources, however, sulfate concentrations were more sensitive to distance sources. In contrast, ammonium concentrations were more sensitive to local sources. As

in the case of ozone, a combination of regional and local controls may be necessary to effectively manage particulate air pollution in the Pensacola area.

Risk assessment of air toxics from various sources (e.g., point source emissions; mobile source air toxics), for cancer risks and non-cancer health risks, was done utilizing the RAIMI (Regional Air Impact Modeling Initiative) tools developed by EPA. This analysis enabled the identification of four risk zones for cancer based on point source emissions, and much higher risks emanating from mobile source emissions (additional details in the following section). In view of the community's concern for sizable and sole-source of emissions of HCl and HF from Plant Crist, an assessment was made of the potential health risks. HCl and HF are not known to be carcinogenic, and at the levels released they do not appear to present a significant acute health risk via inhalation.

C. Health outcomes analysis

http://www.uwf.edu/cedb/PERCH_health_outcomes_air_quality.pdf

There is considerable interest in environmental health tracking studies, in which geographic patterns of exposure to pollution are being compared to variation in the health status of populations. We conducted such evaluations in Northwest Florida on the association between air pollution and health outcomes. Initial evaluation dealt with health outcomes comparisons at zip code level geographic units. This analysis showed that the overall health of the population in Escambia and Santa Rosa counties is not significantly different from that of socioeconomically and demographically similar populations in Central and North Florida regions. The health outcomes varied spatially, with some zip codes having significantly higher or lower levels of adverse health outcomes than matching zip codes elsewhere in Florida. Among the health outcome indicators examined, Escambia and Santa Rosa counties showed notably higher incidences of mortality related to birth defects, infant mortality, and mortality in blacks for multiple diseases.

http://www.uwf.edu/cedb/Perch_USF_EPA_April04.pdf

In the next phase, we evaluated whether the observed variations in health outcomes at the zip code level are related to the geographical distribution (proximity and discharges) of air pollution emitters. This study did not find clear evidence for an influence of proximity to emission sites on "cumulative" health outcomes at the zip code level. Some of the "specific" health outcomes, however, seem to be related to the proximity to emission sites as evidenced by relationships at the zip code level within Northwest Florida and similar areas elsewhere in the state. The zip codes with a high incidence of some of the specific outcomes—mortality due to cardiac disease in whites aged >65; mortality due to lung cancer in blacks aged >65; mortality due to birth defects in blacks; morbidity (sickness/hospitalizations) due to asthma in blacks, cardiac diseases in blacks aged >65, and pneumonia in whites aged >65—have a higher proximity index than zip codes with lower incidence, pointing to an influence of the proximity of emission sources on these health outcomes.

Our geospatial statistical analysis of data for the greater Pensacola area showed that high risk of mortality due to COPD (chronic obstructive pulmonary disorder), stroke, and lung cancer was found in areas with low income level and high air pollution levels (from point sources and

mobile sources), and also in blacks and population age 65 and above. We found that aerosol particle pollution (which is correlated to $PM_{2.5}$ particulate pollution) has an adverse effect on mortality due to chronic coronary heart disease (CCHD) in the eastern United States. Escambia and Santa Rosa counties of Florida (at the county level) have relatively lower rates of CCHD (SMR<1), although they have high AOD (Aerosol Optical Density) values. Nevertheless, the periodic episodes of high $PM_{2.5}$ levels observed in our area and their potential impacts on health outcomes merit further investigation.

An additional follow-up assessment included the application of EPA's RAIMI (Regional Air Impacts Modeling Initiative) tools, designed to evaluate the potential for health impacts as a result of exposure to multiple contaminants from multiple sources, at a community level resolution. In this analysis, three areas in Santa Rosa county and one area in Escambia county were estimated to have a possible elevated risk of cancer due to emissions from point sources (stationary or industrial sources). While of concern, the estimated risks are of a magnitude that is consistent with risks found near other industrial sources. Analysis using RAIMI seems to suggest that toxic emissions from point sources are not a widespread source of cancer risk via the inhalation pathway in the Pensacola area (with the caveat that we did not study other exposure pathways).

When similar modeling is done for mobile source emissions using RAIMI, elevated cancer and non-cancer risks are found to be ubiquitous in the Pensacola area with higher risks generally along more highly traveled roadways. Arising from the emissions of formaldehyde, benzene, and butadiene from cars and trucks, the health risks diminish several orders of magnitude a few hundred meters off the roadway. It is important to note that residential and other populated areas immediately adjacent to busy roadways may incur significantly elevated cancer and non-cancer risks.

Continued reductions in industrial emissions, along with improved traffic flows and reduction/modifications in fuel consumption of automobiles, would help improve outdoor air quality. Exposure to outdoor pollution, infiltration of outdoor pollution into buildings, emissions from indoor sources, and uptake of pollutants through food are all known to be important factors to consider in reducing overall personal risk to hazardous air pollutants.

D. Atmospheric deposition of mercury and trace elements to the Pensacola Bay Watershed

http://www.uwf.edu/cedb/PERCH_EPA_final_report_Hg_project.pdf

Mercury contamination associated with increased fossil fuel combustion poses a growing problem in many areas. The southeast, and in particular the Gulf coast, experiences the highest levels of mercury deposition in the United States. Yet, there has not been any monitoring for mercury deposition in Northwest Florida. We have measured the concentrations of mercury, trace metals, and major ions in rainwater samples collected at 3 sites in the Pensacola Bay watershed over a three-year period. Data from our comprehensive analysis will be useful to the State of Florida as it develops a TMDL (Total Maximum Daily Loads) for mercury.

Mercury fluxes and total mercury deposition at the Pensacola Bay sites are similar to those noted at the MDN (Mercury Deposition Network) sites along the central Gulf of Mexico region. The total mercury deposition at all these sites follows the historical pattern of relatively high mercury deposition rates in the Southeastern United States. Mercury concentrations in

rainwater samples show strong correlation with selenium, antimony, arsenic, and sulfate, pointing to their derivation from coal/fossil fuel combustion. We estimate that 25 to 51% of the mercury in our rain samples is attributable to coal combustion. Because of the large number of emission sources in the region and mixing of air masses from the different regions, it is difficult to determine the contribution of local sources for mercury deposited to the Pensacola Bay watershed. Crist Plant in Pensacola is adding scrubbers to reduce emissions of sulfate and mercury. Since emissions from coal-fired plants in the nearby State of Alabama far exceed the emissions from Plant Crist, it is desirable to reduce mercury discharges from coal-fired power plants at various regional locations.

The deposition rates in rain for several ions at our monitoring sites and at several other sites in Florida and Alabama show significant correlation to air emissions, with correlation coefficients of 0.95 (ammonium), 0.80 (nitrate), and 0.68 (sulfate). This is in agreement with air quality studies (reported above) in which the source apportionment of $PM_{2.5}$ in the Pensacola area revealed that ammonium concentrations were more sensitive to local sources, whereas sulfate concentrations were more sensitive to distance sources. This, again, points to the need for emission reductions at local and regional levels for improvement of air quality, ecosystem health, and human health.

The monitoring we conducted during 2005-2007 for this project is continuing uninterrupted with support from the Electrical Power Research Institute. The extended monitoring is expected to complement the EPA study done in February 2008, "Mercury Speciation in Coal-fired Utility Boiler Emission Plume," at Plant Crist in Pensacola, and also aid in evaluating the effects of scrubbers being added to Plant Crist on air emissions.

E. Pollution of surface soils in Escambia and Santa Rosa counties

http://uwf.edu/cedb/Perch_report_surfacesoils.pdf

This project focuses on pollution of soils in public places such as parks, playgrounds, and sports fields where most interaction takes place between people and soils. The results, presented in a GIS format, are based on analysis of samples from 126 locations in the two counties, including 12 from the Palafox industrial corridor, and 5 locations that had CCA-treated wood structures.

Dioxin/furan TEQs (Toxic Equivalency Quotient) in surface soils in the Palafox industrial corridor are below the EPA screening level for children (50 ng/kg), and these levels quickly drop off to background levels outside the corridor. PAHs show a very similar pattern with elevated levels being limited to the Palafox industrial corridor, except that 5 of the 12 samples exceeded Florida DEP's residential SCTL (Soil Cleanup Target Level) of 0.1 mg/kg, which merits further evaluation. Now that the clean up and burial of the contaminated soils on and around the ETC (Escambia Treating Company) Superfund Site has been completed by EPA, exposure to contaminated soils of concern has been abated. The residues we found in the areas outside the cleaned up zone, within the industrial corridor, represent the remnants of past contamination.

Concentrations of Cr, Cu, and As are markedly higher near CCA (Chromated Copper Arsenate)-treated wood structures than in the whole data set, although only As exceeded SCTL. It would be best to avoid contact with soils in very close proximity to the CCA-treated structures.

Trace metal concentrations (Cd, Cr, Cu, Hg, Ni, Pb, Zn) in samples from all other locations are generally below their respective RSCTLs, except for arsenic with levels exceeding its RSCTL of 2.1 mg/kg at 33 of the sites in both rural and urban settings without a clear spatial pattern. This indicates that these levels may reflect regionally high arsenic background concentrations (derived from parent materials of soils and/or atmospheric deposition). Trace metal concentrations are higher near the road, due to traffic-related activities/releases, but the levels decrease between 2 and 20 meters from the edge of the road. We have also measured radioactivity of surface soils, and the observed levels are near background levels and do not pose a health concern.

F. Pollutants in the sediments of urban bayous (Texar, Chico, and Grande) and the Escambia Bay/River

http://www.uwf.edu/cedb/Perch_pollutants_in_Bayou_Texar.cfm
http://www.uwf.edu/cedb/Perch_report_Chico_final_revision_withmaps.pdf
http://www.uwf.edu/cedb/PERCH_Bayou_Grande_Report_Environmental_Assessment.pdf
http://www.uwf.edu/cedb/PERCH_Escambia_Bay_final_report.pdf

The Pensacola Bay System components are invaluable resources for the area, as they add to the scenic beauty of the region, facilitate recreational activities, serve as navigation sources, and support tourism. Chemical pollutants from point and non-point sources affect the environmental health of the Pensacola Bay System. We conducted comprehensive assessment of selected contaminants in the sediments of urban bayous and in the Escambia Bay/River system, and presented the results in a GIS format so that this database can serve as a reference for evaluating changes in the future as well as assist agencies responsible for improving environmental and public health. Our detailed reports are accessible at our website as noted above.

Bayou Texar: This bayou receives pollutants from a variety of sources—storm water runoff, input from carpenter's creek, and groundwater plumes from Superfund sites. We found that the groundwater plume from the AGRICO Superfund site (ACC) continues to discharge fluoride from groundwater into the northern part of the bayou. Although the groundwater plume from the Escambia Treating Company (ETC) site is known to be migrating towards Bayou Texar, we did not find evidence for its discharge into the bayou. Pollutants derived from other (non-point) sources, such as PAHs and trace metals, are elevated with the highest levels being found in surficial sediments in the northern section of the bayou, because of diminished flushing in this part of the bayou. In this area, the PEL (probable effect level) for lead, mercury, copper, and zinc are exceeded, indicating that there is a probable effect on biota. Organochlorine pesticide levels are generally low. PCB concentrations are generally lower than in the other bayous. Reflecting the non-industrial nature of this bayou's watershed, total TEQs (Mean: 3.85 ng/kg) due to dioxins/furans/dioxin-like PCBs are lower in Bayou Texar than in Bayou Chico and Bayou Grande.

Bayou Chico: This bayou has a long history of industrial pollution and is considered the most polluted of the three urban bayous in Pensacola. The bayou is adjacent to the American Creosote Works (ACW) Superfund site and the Omni-Vest landfill, and is also subject to pollution from storm water runoff from an industrial area. Two areas---a spoil island in the central part of the bayou, and an area south of the Navy Blvd bridge---have highly elevated

levels of pollutants such as PAHs, PCBs, and trace metals. Vibracores taken in shallow water just offshore of Sanders beach at the mouth of the bayou did not show significant PAHs in the lower levels, but similar cores taken on Sanders beach itself contained high concentrations of PAHs of creosote origin, likely originating from the ACW site. Trace metal concentrations are generally high in Bayou Chico, exceeding their TEL (As, Cr, Cd) or PEL (Cu, Pb, Hg, Zn). PCBs are ubiquitous, and their levels exceeded the PEL at 5 out of 17 sites and an additional 8 exceeded the TEL. Dioxins/furans are contaminants of concern at ACW, but they are not present in high concentration in the Sanders beach area or the mouth of the bayou. The total TEQs often exceeded their AET in the rest of the bayou, with high levels near the spoil island. There is periodic dredging in the navigation channel of Bayou Chico, and the recent and future placement of the dredged spoils and their potential impacts on pollution of groundwater and on the bayou need to be followed. The spoil island (created from the past dredged spoils), as noted above, is a major hot spot for pollutants in this bayou.

Bayou Grande: Pollutants affecting the water and sediment quality of the southern half of the bayou were studied previously in reference to possible releases from the Pensacola Naval Air Station (NAS). We conducted a more detailed study and presented the contaminant data in a GIS format. In the case of trace metals, several have exceeded TELs (As, Cr, Hg, Ni) and others exceeded PELs (Cd, Pb, Zn). Naphthalenes (reported to occur in NAS groundwater) are detected at higher concentrations in surface sediment in the main basin of the bayou and also near the shore of NAS, pointing to the influence of contaminated groundwater on the bayou. Sediment guideline levels are exceeded by several PAH species. PAHs in this bayou seem to have multiple origins, with combustion of various materials being the major source and do not seem to be caused by petroleum spills. In 15 out of 23 samples, PCBs exceeded the TEL. PCBs in the bayou do not seem to be derived solely from NAS sources, but also from other sources in the watershed. Total TEQs for 17 of the 23 samples exceeded the NOAA sediment quality guidelines, seven of them being 3-fold higher than NOAA AET. Overall the contribution of PCB-like dioxins to the TEQ was 44%, the highest proportion (relative to dioxin/furan contribution) found among other water bodies in the region.

Escambia Bay and River: In addition to addressing the community's concern for lingering residues of PCBs spilled in the 1960s from a point source (former Monsanto Company) into the Escambia River, we conducted a comprehensive analysis of various pollutants in the sediments of Escambia Bay/River System. With a few exceptions, the levels of PAHs and total petroleum hydrocarbons were generally low in the sediments. Among the trace metals, arsenic was the only one that consistently exceeded sediment quality guidelines (30 samples exceeded the TEL, and none exceeded PEL). In some of the samples, several other metals (Cd, Cr, Cu, Pb, Ni, and Zn) exceeded their respective TELs but not PELs. Overall, the sediment concentrations of trace metals in the Escambia Bay/River System are lower than in the urban bayous of Pensacola. Pesticide levels are generally low, as in the bayous, except for the finding of DDT in 25% of the sediment samples. DDT levels in all but one sample exceeded the Florida DEP's PEL (4.77 μg/kg). The detected DDT was generally associated with sediments in wetlands and the river, and is of concern as some of these areas may serve as nurseries for marine life and DDT could impact fish and shrimp populations. The concentrations of PCBs varied with the region, with sediments from lower Escambia River and upper regions of Escambia Bay having PCBs near the TEL (21.6 μg/kg), with the highest value (125.9 μg/kg) near the original spill site. Lower Escambia Bay sediments had mean PCB concentrations of 11.9 μg/kg, and upriver of the spill site they were even lower (5.06 μg/kg). A majority of the samples (56%) in the Escambia

Bay/River System had TEQs exceeding NOAA TEL, and 23% exceeding the NOAA AET. For the combined TEQs, however, PCB-like dioxins accounted for 7% and dioxins/furans accounted for 93%. Spatially, the distribution of dioxin-like PCBs did not coincide with the dioxin/furan TEQ distribution, due to differences in their origin, degradation, and transportation.

Relative pollutant loads and temporal changes: In the case of groundwater plumes from Superfund sites, the ACC plume contents continue to be released at the same level (based on fluoride in sediments and pore water) as reported by ENTRIX in 1993. EPA has recently completed the first phase of remediation of the ETC site, involving the burial and capping of contaminated soils, and is planning to remediate the contaminated groundwater. These efforts should aid in limiting the spread of contaminants from this Superfund site. The migration and discharge of contaminated groundwater plume from NAS into Bayou Grande needs to be followed and documented. Omni-Vest Landfill does not appear to impact Bayou Chico. The creosote found under Sander's beach is in the path of the ACW plume.

Based on the samples we analyzed, the PCB concentrations are highest in Bayou Chico (Mean: 158 μg/kg), with other water bodies having mean concentrations of 61.7 μg/kg (Bayou Grande), 30.7 μg/kg (Bayou Chico), and 17.9 μg/kg (Escambia bay/River). The mean values for the combined TEQs for dioxins/furans/dioxin-like PCBs were: 44.59 ng/kg (Bayou Chico), 8.3 ng/kg (Bayou Grande), 3.85 ng/kg (Bayou Texar), and 2.62 ng/kg (Escambia bay/River). The relative contributions of dioxin-like PCBs to the total TEQ were: 43.8% (Bayou Grande), 21% (Bayou Chico), 16% (Bayou Texar), and 7% (Escambia Bay/River). Although the mean concentrations of total PCBs and TEQs in Escambia Bay/River were the lowest in comparison to the urban bayous, due to the large geographic area covered by the Escambia Bay/River system, there are hot spots of contamination. It is also important to note that whereas PCBs pose non-cancer risks, those contributing to TEQs (dioxin-like PCBs, dioxins/furans) pose cancer risks to humans. We do not have historic comparable data on TEQs in the water bodies studied to assess what temporal changes (if any) occurred. For PCBs, such data is available with the implicit understanding that—because of differences in the number and location of samples, and analytical methods—there are difficulties in drawing reliable conclusions on temporal trends. Nevertheless, it appears, that whereas PCB levels in Bayou Texar are relatively unchanged from the levels noted in the 1990s, the PCB levels in Bayou Grande and Bayou Chico seem to have increased (more so in the latter) which needs to be evaluated. In Escambia Bay the PCB levels seem to have gone down by nearly 50%, but it should be noted that our study included analysis of only surface sediment samples, which would not have identified buried contamination that may be exposed by bioperturbation, storms, dredging, construction, or other activities. In sum, the contamination of sediments with PCBs, dioxins/furans, and dioxin-like PCBs is of concern and should continue to be monitored.

PAH levels in the sediments of Bayou Texar, Bayou Chico, and Escambia Bay/River did not seem to change over two decades, but appear to have increased dramatically (8-fold) in Bayou Grande, although this may be attributable to our sampling at more sites including the most polluted areas compared to previous studies. Compared to the levels detected in the 1990s, the organochlorine pesticide levels in the sediments have decreased substantially although the current levels of DDT in the sediments of Escambia River and wetlands are of concern. Trace metal concentrations frequently exceeded SQAGs but to varying degrees in the bay/bayous. Zinc and Hg had the highest concentrations in Bayou Chico and Texar, whereas Cd and Cr were higher in Bayou Grande. Escambia Bay had the lowest trace metal concentrations, but was highest in arsenic—possibly because of its larger watershed that could contribute to the drainage

of As from surface soils (natural high background levels, or derived from atmospheric deposition) and also from agricultural operations. Since the 1990s Cr, Hg, and Ni concentrations declined in all of the area estuaries. Overall, the concentrations of trace metals declined to a greater extent in Bayou Texar possibly due to stormwater management efforts in its watershed.

G. Accumulation of pollutants in fish and shellfish

http://uwf.edu/cedb/PERCH_Accumulation_of_pollutants_in_fish_and_shellfish.pdf
http://cedb/PERCH_CDC_Final_Report_2007.pdf

The greatest vector for exposure to environmental contaminants in water bodies for wildlife and humans is through consumption of contaminated food. Although fish consumption advisories due to mercury content are issued for many locations in the State of Florida, including advisories for several freshwater and coastal fish in Northwest Florida, there have not been systematic surveys for other pollutants in fish/shellfish consumed by humans. Our study has contributed to filling this data gap for Northwest Florida, and our comprehensive survey of PCBs and dioxins/furans in seafood is unprecedented.

An initial screening level assessment of contaminants in blue crabs (*Callinectes sapidus*) and oysters (*Crassostrea virginica*) revealed several chemicals of concern (dioxins/furans/PCBs, arsenic, mercury, cadmium, and zinc) in crab muscle, crab hepatopancreas, total crab tissue, and oysters based on contaminant levels exceeding Screening Values (SVs). The locations that exceeded SVs and had the highest carcinogenic or non-carcinogenic health risks were generally located in urbanized water bodies (Bayou Texar, Bayou Grande, and Bayou Chico) or downstream of known contaminated areas (Western Escambia Bay). Oysters collected from commercial oyster beds in Escambia and East Bays, and crabs collected from East, Blackwater, and Perdido Bays generally had the lowest levels of contaminants. Despite accounting for only 15% of the total tissue, inclusion of hepatopancreas in a crab meal increased contamination to levels above many SVs, and therefore, direct or indirect consumption of hepatopancreas from crabs in the Pensacola Bay system should be discouraged.

In the next phase, we conducted a survey of contaminant levels in largemouth bass *Micropterus salmoides*) from rivers in Northwest Florida and striped mullet (*Mugil cephalus*) from rivers, bays, and bayous in the region. Largemouth bass collected from all of the study locations exceeded mercury SV (0.4 mg/kg, EPA SV for recreational fisher consumption), and the HQs (Hazard Quotient, non-cancer hazard risk) for nearly all samples exceeded a value of 1, indicating that non-cancer health effects may occur. In contrast, the levels of mercury were very low (0.008 to 0.026 mg/kg) in mullet. This is due to differences in feeding habits: bass are a top level predator, that readily accumulates mercury through the food chain, whereas mullet primarily feed on detritus and sediments.

Largemouth bass had PCB levels exceeding EPA recreational fisher consumption SV (20ng/kg) in the samples from lower part of Escambia River, downstream of a PCB (Aroclor 1254) spill that occurred in the late 1960s, and had relatively low levels of PCBs in samples from upstream of the spill site in Escambia River and in all other locations (Blackwater, Shoal, Yellow, and Perdido rivers). The highest levels of PCBs in the mullet from the Escambia River/Bay System in this phase of the study were in fish caught in the lower Escambia River. PCB loads exceeding the EPA SV were also found in mullet from NE Escambia Bay, SW Escambia Bay, and in the upper reaches of Escambia River, whereas much lower levels were found in mullet from SE Escambia Bay. After reviewing our findings, the State of Florida

Department of Health (DOH) issued a fish consumption advisory based on PCB loads (exceeding 50 ng/kg screening value, set by FL-DOH), warning consumers to restrict their consumption of mullet and bass from the Escambia River from south of State Route 184 to the mouth of the river to one meal per week. In a subsequent evaluation, we determined PCB levels in mullet and several other fish species sampled in Escambia Bay following a demolition blast of a part of the old 1-10 Bridge. Mullet collected from this sampling had the highest levels of PCBs in any of the fish we studied (280 to 1,580 ng/kg). Following our findings, Florida DOH conducted an independent analysis of mullet from several locations in the Pensacola Bay System, found PCB levels exceeding 50ng/kg in mullet caught from Escambia Bay, and issued (on October 1, 2009) a consumption advisory for mullet caught from the Escambia Bay, thereby extending the previous advisory for fish from lower Escambia River.

We found that mullet from East Bay, Perdido River, and Yellow River have relatively low levels of PCBs (3.8 to 8.8 ng/kg), whereas higher levels were noted in mullet from urban bayous, with levels above the EPA SV for recreational fisher consumption in mullet from Bayou Chico. In all of the sampling locations, however, TEQs were above the EPA SV for recreational fisher consumption (0.256 ng/kg). In locations with elevated PCB residues in the environment, the accumulation of dioxin-like PCBs adds to the TEQ load. Thus, the relative contribution of dioxin-like PCBs to the total TEQ varies with the species (differences in uptake/accumulation), and the relative concentrations of bio-available dioxins/furans and dioxin-like PCBs in the environment. Our studies show that the relative contribution of dioxin-like PCBs to TEQ loads in mullet vary by location: 29% (Bayou Texar), 52-53% (Bayou Chico and Bayou Grande), 57% (lower Escambia River), and 98% (Escambia Bay, samples near I-10 bridge). The PCB homolog profile seen in fish sampled near I-10 bridge was nearly identical to the profile of congeners in Aroclor 1254, the formulation that was spilled into Escambia River in the 1960s. This suggests that the bridge construction/demolition activities have disturbed the sediments, causing the PCB-laden deeper sediments to be brought up to the surface and increasing the availability of PCBs to biota in the bay. Mullet samples from the rest of Escambia Bay and River show a moderate affinity for Aroclor 1254 (due to attenuation through biotic transfers and partial degradation of the raw product), whereas PCBs in mullet samples from industrialized bayous (Chico and Grande) cluster with Aroclor 1260 homolog pattern, suggesting either enrichment of more highly chlorinated homologs with partitioning into the biota, or alternate sources of PCBs.

In evaluating the health risks from PCBs, it is necessary to consider not only the non-cancer risks posed by PCBs as a whole, but also the cancer risks posed by dioxin-like PCBs and dioxins/furans. Mullet that were caught in the lower Escambia River had elevated levels of total PCBs for which the hazard quotient (HQ) exceeded 1, which indicates that non-cancer health effects may occur. Bass caught in the lower Escambia River had high levels of both PCBs and mercury, resulting in an HQ above 1. Mullet collected from the Escambia Bay near I-10 bridge yielded much higher HQs (3.55 to 19.75). Excess LCR (Life Time Cancer Risk) exceeded $1x10^{-4}$ (more than one excess cancer per 10,000), for two samples – in mullet from Bayou Chico and in bass from lower Escambia River. In both cases, the primary contributors to the excess LCR were dioxins/furans and dioxin-like PCBs. For mullet from Escambia Bay I-10 bridge sampling, the estimated Life Time Cancer risks from consumption exceeded 1 per 1,000, attributable almost entirely to dioxin-like PCBs . These findings clearly point to the need for conducting systematic surveys of critical toxic pollutants—not only mercury, but also PCBs, dioxin-like PCBs, and dioxins/furans—in commonly caught and consumed fish from various locations.

In the final phase of our study finfish from seventeen zones within Pensacola Bay and Perdido Bay watersheds were surveyed for mercury and PCB loads, including TEQ loads. This study has compiled an unprecedented dataset on the accumulation of dioxins/furans in estuarine and marine biota. These contaminants are widespread, and in many instances TEQ values exceeding acceptable thresholds were found. The overall data for contaminants, coupled with earlier analysis done on offshore fishes in relation to the sinking of ex-Oriskany, includes information on contaminant loads in 1199 specimens within 48 species. Individual species information has been posted in a series of web pages at:

http://uwf.edu/cedb/Atlas_of_contaminants_in_seafood.cfm

Blackwater-East Bays, lower Pensacola Bay, Santa Rosa Sound, and Perdido Bay are relatively clean zones (based on oyster, blue crab, and mullet data), but this pattern does not hold true for fish that are highly mobile and of high trophic status—e.g., large red drum caught in East Bay and Santa Rosa Sound had the highest PCB loads recorded for this species (60 and 40 ng/kg, respectively). While most species bioaccumulate dioxins/furans, PCBs, and mercury with age, there are exceptions: Spotted sea tout and Spanish mackerel show increased loads of mercury with age, but not for PCBs. On the other hand, king mackerel has much higher loads of both mercury and PCBs with increase in age. Red snapper and groupers also show bioaccumulation of PCBs and mercury with increasing age, pointing to the need for Gulf-wide investigation of pollutant loads in offshore fishes.

In terms of protecting public health, it is necessary to conduct a systematic analysis of target contaminants in commonly caught and consumed fish and shellfish to establish justifiable and uniform (national/state) standards to enable consumers to make informed choices. Given species-specific patterns of contaminant accumulation, it is also necessary to evaluate and communicate about the risks resulting from elevated loads of multiple contaminants found, rather than issuing advisories based on only an individual contaminant. This would alleviate some of the difficulties consumers may encounter in selecting fish as they weigh the risks/benefits of fish consumption. Public health education efforts in this regard need to be augmented, as most people are unaware of fish consumption advisories or about choices in fish consumption.

H. Recommendations

Health Outcomes

The noted higher health risks in infants, elderly (age >65), blacks, and the poor need to be followed, and appropriate measures implemented for correcting the apparent disparity in health outcomes for an overall improvement in community health.

Air Quality

A combination of regional and local controls should be implemented to effectively manage particulate ($PM_{2.5}$) pollution in the Pensacola area.

In order to achieve reductions in atmospheric deposition of mercury to the Pensacola Bay watershed, it would be necessary to reduce emissions from coal-fired power plants at various regional locations. Corrective measures are being implemented at Plant Crist in Pensacola, and such measures are needed throughout the southeast.

In view of the elevated cancer and non-cancer risks from emissions along highly traveled roadways, efforts should be directed towards improved traffic flow, improved fuel consumption efficiency of automobiles, usage of hybrid or electricity-powered vehicles, and increased usage of mass transit systems.

Reductions in personal risks from hazardous air pollutants require measures to decrease: exposure to outdoor pollution, infiltration of outdoor pollution into buildings, emissions from indoor sources, and uptake of pollutants through food.

Surface Soils:

CCA(Chromate Copper Arsenate)-treated structures should be removed from public places and playgrounds.

Areas with arsenic above RSCTL should be monitored in relation to residential areas/development.

The elevated PAH levels, exceeding Florida DEP's SCTL, at some locations in the Palafox industrial corridor need to be followed.

Pollutants in the Pensacola Bay System

The presence of contaminated aquifers (mostly groundwater plumes from Superfund Sites) requires continued monitoring of the sediments, pore water, and the waters of local estuaries.

The impacts of point source historical discharges of pollutants (e.g., PCBs discharged to Escambia River/Bay system) need to be monitored, and appropriate corrective/protective actions should be taken.

Whereas periodic dredging is needed to facilitate navigation in rivers/bays/bayous, the placement of the dredged spoils and the potential impacts of pollutants from this source on the corresponding water bodies have to be considered.

Monitoring of sediments for pollutant loads should continue, especially for those areas currently known to contain elevated levels of toxic pollutants in the Pensacola Bay System.

The unexpected detections of DDT above the PEL in the Escambia River and associated wetlands merit further investigation.

Contaminants in fish and shellfish

A systematic survey of target contaminants (not only mercury but also PCBs, dioxins/furans and dioxin-like PCBs) in fish/shellfish needs to be undertaken at the state level, and also extended by appropriate agencies for similar Gulf-wide surveys of contaminants in commonly caught and consumed fishes.

Screening values used to establish consumption advisories differ considerably at state and national levels, even between federal agencies, and efforts should be made to establish uniform standards to protect public health.

Among the pollutants of concern from local water bodies, the screening value adopted by the State of Florida for PCBs (50 ng/kg) is higher than that set by EPA (20 ng/kg) for recreational fisher consumption, and the former threshold should be reevaluated and given the same resolution in its application as done for mercury screening thresholds in relation to sensitive/general population groups and variable consumption rates.

In view of the widespread dioxin/furan loads, along with dioxin-like PCBs, in fish/shellfish, the State of Florida should establish guidelines for issuing consumption advisories based on TEQ loads.

As done in several other states, State of Florida should issue an advisory against consumption of blue crab hepatopancreas, based on toxicant loads.

At the state and national levels, there is a need to augment public awareness of fish consumption advisories and provide information that would enable consumers to understand the benefits/risks from consumption of fish/shellfish.