

CHAPTER 4

SEDIMENT CONTAMINANTS OF THE GULF OF MEXICO

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4.1 INTRODUCTION

Sediments are an essential constituent of aquatic environments that are vital to the health of organisms and ecosystems. Many organisms live in, ingest or otherwise come into contact with sediments repeatedly during their life cycles. Anthropogenic—human-derived—chemicals introduced into sediments have the potential to harm the health of organisms and ecosystems and are collectively referred to as *contaminants*. Sediment contaminants of the greatest environmental concern are those with concentrations significantly enriched above natural levels due to human influences. In most instances, organisms are adapted to natural levels of chemicals in the environment, and in some cases, these chemicals are essential elements for survival and growth. In contrast, additions of chemicals that are by-products of human activities can degrade sediment quality in the short and long term. Potential adverse effects on biota caused by exposure to contaminants include, but are not limited to, death, disruption of physiology and reproduction, impairment of ecosystem functioning and structure, and ultimately, may impact human health. This chapter summarizes the origins, geographic distributions, and temporal trends in sediment contaminants in the northern Gulf of Mexico from the mid-1980s to early 2010. Contaminant dynamics in coastal sediments are compared to continental shelf/slope and abyssal sediments. *Coastal* refers to all land areas in close proximity to the ocean including estuaries, bays, sounds, wetlands, coral reefs, intertidal zones, sea grass beds, and nearshore oceanic areas. Offshore regions are those areas more distant from the shore including sediments on the continental shelf/slope and abyss. The transition from the nearshore to the offshore is a continuum, and these areas are often oceanographically coupled. However, differences in environmental conditions, the energetics of the settings, and the locations of sources of contaminants make the dynamics of contaminated sediments in these two regions distinct from one another. Most studies of contaminated sediments focus on nearshore, coastal environments in close proximity to human populations. There are limited studies of offshore regions remote from most human activities.

4.1.1 Classes of Contaminants

Chemical structure and reactivity are fundamental determinants of the fate and effects of contaminants in aquatic environments. Contaminants can be single chemical species or mixtures of compounds and are classified as organic (carbon containing) or inorganic (non-carbon containing) substances (USEPA 1989). Organic contaminants are classified based on vapor pressures and water solubility as volatile or semivolatile organic compounds (VOCs and SVOCs, respectively). VOCs are organic chemicals with high vapor pressures at standard

atmospheric pressure and temperature and are typically not acutely toxic but can cause chronic biological effects. VOCs include a diverse assortment of naturally occurring and human-made chemicals that preferentially occur in the atmosphere and are dissolved in water. They rarely occur in or are studied in coastal and marine sediments; therefore, VOCs are not considered further in this summary. SVOCs have low vapor pressures and varying water solubility and are a diverse assortment of naturally occurring and human-made chemicals that occur in the atmosphere, adsorb onto particulate matter in water, and often accumulate in sediments. Due to low water solubility (hydrophobicity), many SVOCs preferentially partition into lipid-rich biological tissues. Environmental exposure to SVOCs can lead to bioaccumulation in organisms and biomagnification via food webs. SVOCs have a wide range of toxicities and can have diverse biological and ecosystem effects. Inorganic contaminant chemicals are defined as non-carbon substances of a mineral origin and include metals and nutrients (USEPA 1989). Metals are metallic elements of high atomic weight that can cause acute and chronic toxicity in organisms. Contaminant nutrients (such as nitrate and phosphate) primarily occur dissolved in water. Nutrient contamination in the Gulf of Mexico is treated elsewhere in reference to water quality (see Chapter 2).

Contaminant SVOCs and metals often persist in the environment, accumulate in sediments over time and increase the potential for, and possibly the levels of, organismal and ecosystem exposure. Beyond the contaminants mentioned above, other human-derived chemicals have the potential to cause environmental degradation, including pharmaceuticals, household chemicals, and personal hygiene products; fire retardants (brominated compounds); and endocrine-disrupting or mimicking compounds. However, most monitoring programs rarely measure these chemicals in sediments, so their importance as contaminants remains largely unknown. Therefore, these contaminants are not included in this chapter.

4.1.2 Scope of the Summary

Reports of sediment contaminants in the periodic literature, monitoring programs, and assessments of national coastal conditions issued by federal, state, and local agencies and programs from the mid-1980s to early 2010 are summarized. Data collections are used to qualitatively describe the regional status and trends in sediment contaminants. Published articles illustrate conclusions drawn from regional monitoring and assessment programs. National assessments are produced by government and academic experts based on data and information from hundreds of documents. Region-wide monitoring and assessments were first initiated in the mid-1980s. The most recent national coastal assessment was completed in 2012. Thousands of sediments from the northern Gulf of Mexico have been analyzed for contaminant concentrations for more than 30 years. Assessment summaries often lag behind the date of data collection by several years due to the process involved. The interpretations from these syntheses are reported in this chapter but the underlying primary data are not reanalyzed.

This summary of sediment contaminant concentrations does not directly address sediment quality, toxicity, and/or biological effects (see Section 4.2.2). National coastal assessments employ additional chemical, toxicological, and biological measurements to assess overall sediment quality and ecological status. Inclusion of these additional variables is beyond the scope of this review, and the reader is referred to the integrated assessment of environmental quality and biological effects contained in the national coastal assessments. The presence or concentration of contaminants in sediments is usually insufficient to infer sediment quality or to predict adverse in situ biological effects because many factors affect the interaction of contaminants, organisms, and ecosystems. However, within national coastal assessments, sediment contaminant concentrations that have been empirically shown to elicit biological effects in the published literature are used to qualitatively describe occurrences and

distributions. While these comparisons are useful to highlight higher versus lower areas of sediment contamination and to suggest the origins of contaminants, sediment quality or prediction of adverse biological effects or toxicity should not be inferred.

4.2 THE ORIGINS AND BEHAVIOR OF CONTAMINANTS IN THE ENVIRONMENT

Chemical contaminants commonly occur in sediments of rivers, lakes, and adjacent oceans (USEPA 1989). Some contaminants were released into the environment years ago and persist, while others continue to be released. Contaminants, in particular the SVOCs and metals that are the focus of this summary, are found in industrial and municipal discharges and emissions, urban and agricultural runoff, accidental spills, and wet and dry atmospheric deposition. Of the 11 environmental concerns identified in United States (U.S.) estuaries, 8 potentially involve contaminants and collectively affect all of the 28 estuaries considered (Figure 4.1).

Releases of contaminants to the environment can be intentional (e.g., permitted discharges) and/or accidental (e.g., spills). Contaminants enter marine environments through the air, dissolved in or absorbed on particles in water, or as solid or liquid discharges. Hydrophobic compounds released into air and water preferentially adsorb onto particulate matter, and often, some portion is eventually deposited in sediments. Contaminants discharged as solids and liquids can result in rapid incorporation into sediments. Concentrations and geographic distributions of sediment contaminants are heterogeneous due to spatial and temporal variations in inputs, sediment deposition and accumulation rates, variable susceptibility to contamination and rates of removal, variations in chemical form and physicochemical properties, and differences in water inflow rates and receiving water residence times. Considerations of contaminant SVOCs in sediments are restricted to those chemicals most commonly studied including hydrocarbons, pesticides, and polychlorinated biphenyls (PCBs) (see Appendix A for details of the origins, toxicity, and environmental fate of SVOCs). Hydrocarbons are generally measured as polycyclic aromatic hydrocarbons (PAHs) that are the portion of petroleum that accounts for most of its toxicity. The contaminant metals considered are those of greatest environmental concern including lead (Pb), mercury (Hg), arsenic (As), cadmium (Cd), silver (Ag), nickel (Ni), tin (Sn), chromium (Cr), zinc (Zn), barium (Ba), vanadium (V), and copper (Cu) (see Appendix B for details of the origins, toxicity, and environmental fate of metals).

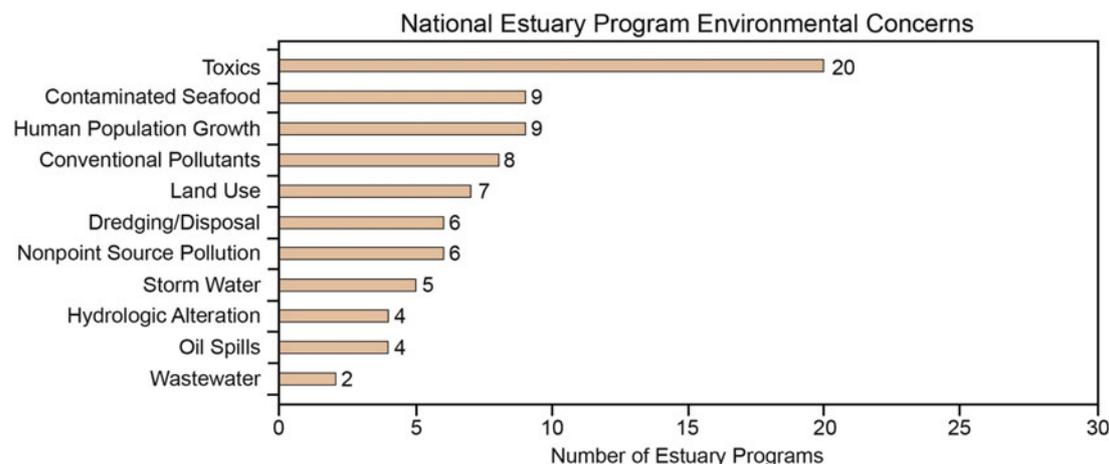


Figure 4.1. Environmental concerns for U.S. National Estuary Programs related to contaminants in sediments: n = number of affected estuaries out of a total of 28 (modified from USEPA 2006).

Some SVOCs (e.g., hydrocarbons) and essentially all metals naturally occur in sediments. Many SVOCs are human-made and do not naturally occur in the environment (i.e., pesticides and PCBs) though there are multiple sources attributable to humans. Natural occurrences (e.g., metals occur in crustal rocks and minerals) and processes (e.g., oil and gas seeps) that release chemicals to the environment must be considered when ascribing the origins and distributions of sediment contaminants. Sediment contaminants of most interest are those elevated above natural abundances.

The mode and composition of contaminant releases often determine their behavior, availability, and fate in the environment. Contaminants originate from point or non-point sources (USEPA 1989). Point sources are single, identifiable release locations that are limited in spatial extent, such as a discharge pipe or smoke stack. Point sources include discharges by municipal sewage treatment plants, overflows from combined sanitary and storm sewers, stormwater discharges from municipal and industrial facilities, and discharges from industrial and military complexes (USEPA 1989). Non-point sources are diffuse including river outflows, land runoff, precipitation, atmospheric deposition, drainage, and/or hydrologic modifications (USEPA 1989). Once released, contaminants interact with the environment based on their physicochemical properties, chemical form, biological reactivity, and the ambient conditions of the receiving media (Figures 4.2 and 4.3).

Contaminants released to the atmosphere can be bound to particles and transported long distances from the site of release. Environmental processes creating derivative or breakdown by-products can alter the chemical structure of contaminants. These alterations can cause

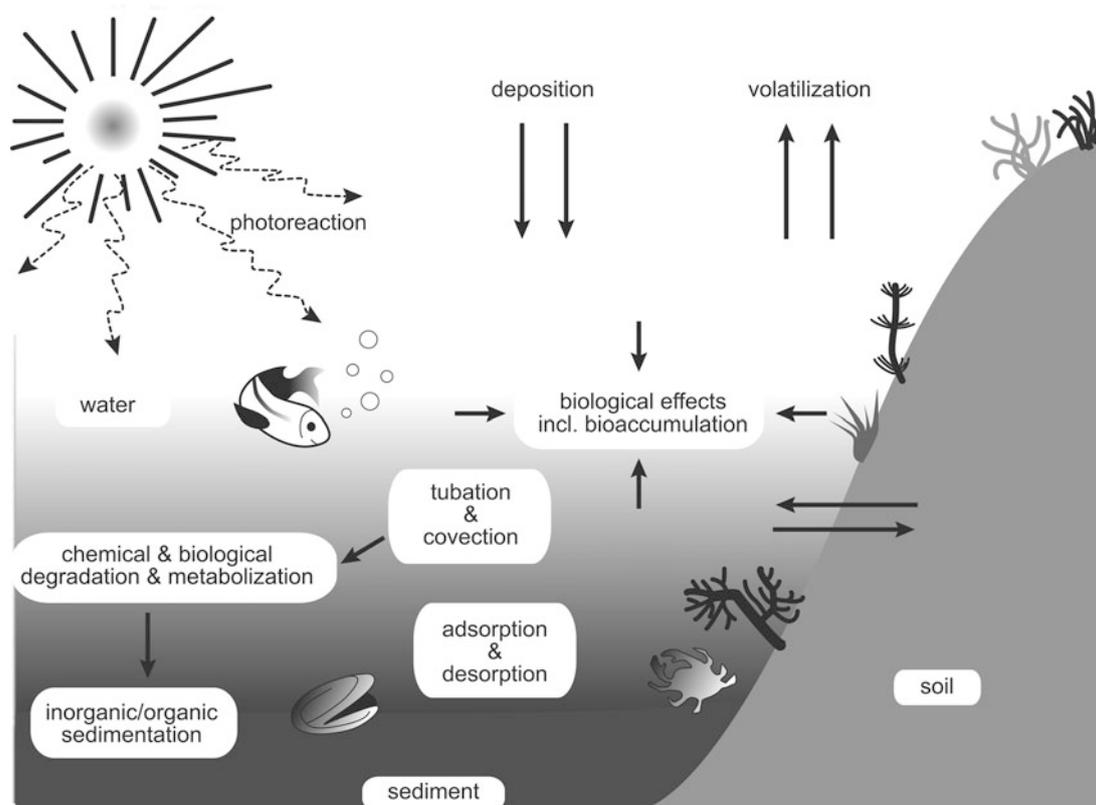


Figure 4.2. Distribution and fate of chemical contaminants in an aquatic environment (from Rydén et al. 2003 citing Römbke and Moltmann 1995). Republished with permission from the Baltic University Programme, Uppsala University and from the Taylor and Francis Group LLC Books whose permission was conveyed through the Copyright Clearance Center, Inc.

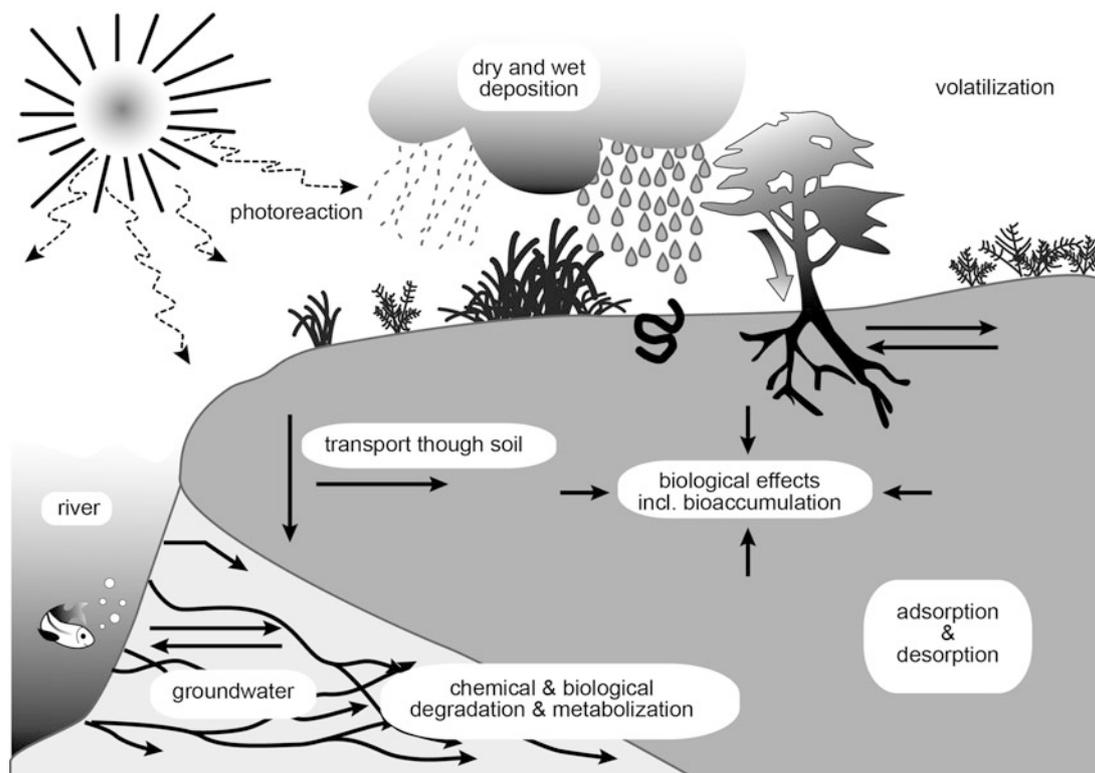


Figure 4.3. Distribution and fate of chemical contaminants in a terrestrial environment (from Rydén et al. 2003 citing Römbke and Moltmann 1995). Republished with permission from the Baltic University Programme, Uppsala University and from the Taylor and Francis Group LLC Books whose permission was conveyed through the Copyright Clearance Center, Inc.

redistribution in water, sediment, and/or biota due to changes in physicochemical properties (e.g., hydroxylation of PAHs increases water solubility). By-products can be more or less toxic than the parent substances. Contaminants that enter water may adsorb onto suspended particles, settle to the bottom, or be taken up by organisms. Resuspension of sediments can reintroduce contaminants to the overlying water column making sediments both a potential source and sink. Contaminants can accumulate in sediments over long periods of time due to periodic or chronic releases. Some processes, including microbiological metabolism, enzymatic detoxification, dissolution, and/or chemical breakdown, remove contaminants from sediments. In situ biological and ecosystem responses are the cumulative outcome of all stressors experienced, and sediments at many locations often contain a complex mixture of contaminants from multiple sources. The interactions of multiple stressors (chemical exposures and others) are poorly understood in most instances.

4.2.1 The Mississippi River

A defining characteristic of the northern Gulf of Mexico is the presence and influence of the Mississippi River, especially in regard to the origins and deposition of sediments. The Mississippi River is a major source of particulates and sediments to the northern Gulf of Mexico. As such, the Mississippi River is a major contributor of sediments in coastal areas near Mississippi River outflows, and river-derived sediments are widely distributed in the offshore continental shelf/slope/abyssal regions of the north-central Gulf of Mexico. In the mid-2000s

the Mississippi River was transporting approximately 136 million metric tons (~150 million tons) of sediment per year to the Gulf of Mexico (Thorne et al. 2008). The quantity and quality of transported sediment has been affected by changes in land use and river management throughout the nineteenth and twentieth centuries. The supply of sediment from tributaries has markedly decreased due to the construction of dams and various diversions of the river and its tributaries over the years. Thorne et al. (2008) concludes that total suspended sediment loads on the lower Mississippi River have declined by approximately 80 percent (%) during the 1851–1982 time period. A comprehensive review of the distribution, sources, and fate of contaminants in the Mississippi River and its massive drainage basin (41 % of the 48 contiguous states of the United States) is beyond the scope of this summary. However general inferences about the importance of the Mississippi River as a source of sediment contaminants are considered.

A summary by the U.S. Geological Survey (USGS) in 1995 assessed contaminant levels in the Mississippi River for the 1987–1992 time period (Meade 1995). Contaminant concentrations in suspended sediments and bed sediments in the Mississippi River rapidly decreased from the northern to the southern regions of the river's drainage basin due to dilution with uncontaminated particulate matter and suspended sediment, evaporative losses, losses due to dissolution in water, chemical and microbial breakdown, and the geographic distribution of chemical discharges. While sediment loads are large, dilution and loss during riverine transport diminish the concentrations of contaminants in suspended sediment discharged into the Gulf of Mexico (Trefry and Presley 1976a, b). Metals naturally occur in sediment so most metal concentrations in offshore sediments are similar to crustal abundances. In contrast, the highest concentrations of contaminant metals are mostly found in coastal areas in close proximity to human activities that release metals. The few exceptions in the offshore region are discussed below.

While difficult to estimate, mass loadings of contaminants from Mississippi River discharges could be quite large compared with other sources (such as those in coastal areas) as the volume of sediment delivered to the Gulf of Mexico is large. However, sediment contaminant SVOC concentrations have been confirmed to be low in river-discharged sediments most likely due to dilution with uncontaminated sediments and pre-discharge losses. Metals naturally occur in sediments, so most river-derived sediment metal concentrations are similar to crustal abundances with little evidence of enhanced concentrations due to contamination, with a few notable exceptions.

4.2.2 Biological Effects Levels: Usage and Limitations

Chemical contaminant concentrations alone are usually insufficient to predict in situ biological responses or detrimental effects. Guidelines based on summaries of literature reports of sediment toxicity data have been developed to qualitatively assess whether sediment contaminant concentrations might be expected to cause biological effects (Long and Morgan 1990; Long et al. 1995). These guidelines are called effects range low (ERL) and effects range median (ERM) (Figure 4.4). The ERL criterion is the concentration of a chemical in sediments that resulted in biological effects approximately 10 % of the time based on the literature. The ERM criterion is the concentration of a chemical in sediments that resulted in biological effects approximately 50 % of the time based on the literature. Long et al. (1995) concluded that these sediment quality guidelines provide reasonably accurate estimates of chemical concentrations that are either nontoxic or toxic in laboratory bioassays. However, the reliability of predicting in situ biological response and sediment toxicity from ERL/ERM guidelines has been questioned (O'Connor et al. 1998). The ERL value is considered to be a concentration “at the low end of a continuum roughly relating bulk chemistry with toxicity” (Field et al. 2002; O'Connor 2004). Concentrations of more than one chemical above the ERL does not increase the probability of toxicity, and categorizing sediments on the basis of chemical concentrations with one or more

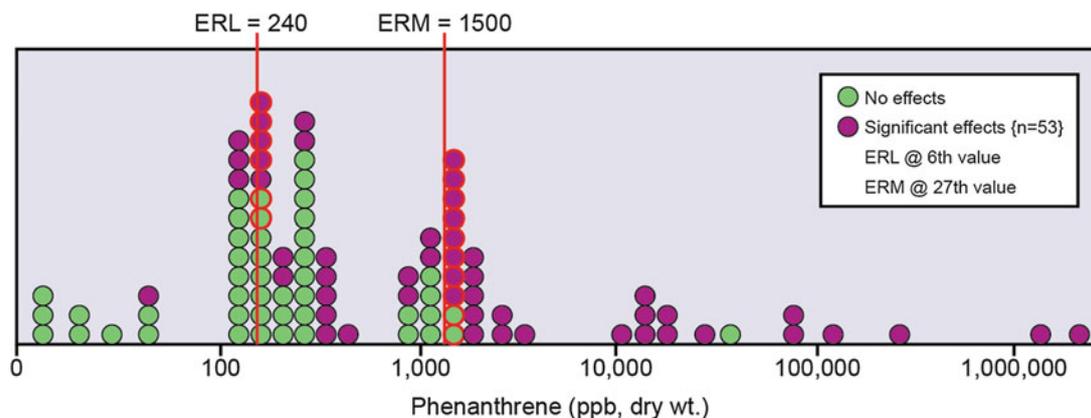


Figure 4.4. Derivation of ERL (effects range low) and ERM (effects range median) values for phenanthrene (a PAH); data showing no adverse effects are *green symbols* and those in which toxicity or some other measure of adverse effects were observed are *purple symbols* (from NOAA 1999).

ERL exceedances can lead to misperceptions of the probability that the sediments are in fact toxic. ERL/ERM guidelines are most useful when supporting data such as in situ biological analyses, toxicological assays, and other variables have been measured that confirm suspected cause-and-effect relationships.

Despite the limitations above, by convention, the *National Coastal Condition Reports* (NCCRs) assess coastal sediment quality based on the number of ERL/ERM exceedances (USEPA 2001, 2004, 2008, 2012). In this summary, ERL/ERM values are used only to draw attention to sites where contaminant concentrations exceed levels that may be of biological significance; however, cause-and-effect or toxicity is not inferred. The results of the NCCRs are summarized including exceedances of ERL and ERM values to qualitatively describe the distribution of higher and lower levels of contaminants in sediments and to assist in discerning the sources of the contamination but not for predicting sediment quality or toxicity. In those cases where NCCR conclusions about sediment quality/toxicity are inferred, additional variables have been taken into account, and attribution of degraded benthic conditions solely to elevated chemical concentrations is often not possible.

Furthermore, ERL values used to classify sediment metal concentrations (Cr, Cu, Ni, and As) are close to or less than natural background crustal values for Mississippi River suspended matter and Gulf of Mexico sediments (Table 4.1). In some cases, according to a peer reviewer of this chapter, Long et al. (1995) used concentrations of Cr and Ni that were determined with U.S. Environmental Protection Agency (USEPA) techniques that used an acid leach (without hydrofluoric acid) rather than total dissolution of the sediment to calculate ERL/ERM values. ERL/ERM values also have been revised over the years as additional data have become available, so reports may use differing values to assess exceedances. These limitations should be taken into account when considering the summaries in this chapter. Mapping and categorizing the number of sites that exceed ERL/ERM values are used to assess the location and origins of contaminants but not to infer or predict in situ biological effects or sediment toxicity.

4.3 COASTAL SEDIMENTS

Human population centers and industrial activities are concentrated in and near coastal areas. Coastal areas are often the sites of agricultural activities as well. Much of the water discharged by rivers and runoff from land surfaces enters or flows directly into aquatic

Table 4.1. Summary Data for ERLs and Concentrations of Cr, Cu, Ni, and As in Mississippi River-suspended Matter and Gulf of Mexico Sediments (prepared by an anonymous peer reviewer, 2012)

	Effects Range Low	Mississippi River Particles	Gulf of Mexico Sediment ^a
Cr (µg/g)	81 (none ^b)	72 ^c , 74 ^d	60–90
Cu (µg/g)	34 (70 ^b)	33 ^c , 21 ^d	20–30
Ni (µg/g)	20.9 (30 ^b)	41 ^c , 37 ^d	25–40
As (µg/g)	8.2 (33 ^b)	8 ^d	10–15

Note: µg/g—microgram(s) per gram

^aO'Connor (2004)

^bTrefry and Presley (1976a), Presley et al. (1980), Trefry et al. (1985), Kennicutt et al. (1996); Continental Shelf Associates (2006)

^cTrefry and Presley (1976b)

^dHorowitz et al. (2001)

environments along coasts. In many cases high-energy discharges empty into much lower-energy settings instigating sedimentation and deposition. As such, coastal areas are major locations of contaminant accumulation in marine sediments.

Monitoring programs and national assessments over a 30-year period have concluded that contaminants are widespread in coastal, northern Gulf of Mexico sediments. Coastal condition, benthic condition, and sediment quality across the region have been judged good to poor during this time due to several factors including, but not limited to, the presence of sediment contaminants. The levels of contaminants in fish tissues have been rated as good to poor and contaminants have been widely detected in bivalve tissues, which demonstrates their bioavailability. Uptake alone does not infer adverse biological effects, and organisms can accumulate chemicals from sources other than contaminated sediments (Kimbrough et al. 2008). Benthic condition ratings were based on measures of infauna biodiversity, increased abundances of contaminant-tolerant species, and decreased abundances of contaminant-sensitive species. Benthic condition is a cumulative measure of all stressors, one of which can be the presence of elevated concentrations of contaminants suspected of causing adverse biological effects. Overall sediment quality is often judged based on measures of sediment toxicity, contaminants, and organic carbon content. The role and importance of sediment contaminants in degraded coastal benthic and sediment quality is often difficult to discern due to multiple stressors affecting a location. The following summary describes the origins and geographic distributions of contaminants in coastal northern Gulf of Mexico sediments from the mid-1980s to early 2010. Instances in which contaminants are important factors in degraded coastal, benthic, and sediment qualities are highlighted.

Coordinated efforts to monitor the condition of U.S. coastal regions were initiated in the 1980s (NOAA 1987, 1991; USEPA 2001, 2004, 2008, 2012). The NOAA National Status & Trends (NS&T) Program and the USEPA Environmental Monitoring and Assessment Program (EMAP) are two such efforts (NOAA 1987, 1991; USEPA 1999). The NCCRs “. . . describe and summarize the ecological and environmental conditions in U.S. coastal waters. . . .” (USEPA 2001, 2004, 2008, 2012). The concentrations of contaminants in various matrices were seen as key indicators of condition. The USEPA Office of Wetlands, Oceans and Watersheds’ Coastal Programs initiated these reports to provide a “comprehensive picture of the health of the nation’s coastal waters” (USEPA 2001). The NCCRs are based on data collected from a variety of sources coordinated by USEPA and National Oceanic and Atmospheric Administration (NOAA) with input from the USGS, U.S. Fish and Wildlife Service (USFWS), and coastal states.

One aspect of these national assessments is a region-by-region consideration of sediment quality, sediment contamination, benthic quality, fish tissue contamination, and other measures of environmental quality. The northern Gulf of Mexico is one of the regions assessed. Interpretations of data by these programs are often summarized as national or regional averages, reported on a relative basis within studies, synthesized as ratings (good, fair, and poor) of composite indicators, compared to sediment concentrations suspected of causing biological effects (ERL/ERM values), and mapped based on numbers of exceedances of contaminant concentrations of environmental concern (see Section 4.2.2). To describe the status and trends in sediment contaminants in the northern Gulf of Mexico, these reports are summarized, but the underlying, primary data are not reanalyzed. Descriptions of subsets of data are presented as examples to clarify the underlying causes of trends in environmental quality.

4.3.1 NOAA National Status and Trends Program

The NOAA NS&T Program analyzes surface sediments from coastal and estuarine sites throughout the United States in support of data on contaminant concentrations in biological tissues. Sediments are intentionally collected distant from major points of contamination to quantify the combined influences of many point and non-point sources of chemicals in coastal areas (NOAA 1987, 1988, 1991; Wade et al. 1989; Sericano et al. 1990). Surficial sediments (the top 3 centimeters [cm] or 1.2 in.) are collected as part of the Mussel Watch Program and the Benthic Surveillance Project. The data from sediments collected in the 1980s are first considered; later data are included in NCCRs and other reports.

The NS&T Program data provide one of the earliest comprehensive overviews of contaminant concentrations and distributions in sediments along the coastal northern Gulf of Mexico. Concentrations of PAHs, pesticides, PCBs, and metals were measured in sediments using standard and calibrated methods. NS&T Program reports interpret sediment chemical concentrations on a relative basis and exclude concentrations ten times greater than the next highest concentration as outliers. Chemical concentrations in sediments were observed to have a lognormal distribution. Concentrations greater than the mean plus one standard deviation of all locations in the United States were termed *high* levels. High concentrations identify sediments affected by human activity but do not imply biological significance (NOAA 1991). Based on this definition, high concentrations of sediment contaminants were observed in bays sampled in the northern Gulf of Mexico from 1986 to 1989 (NOAA 1991) as follows:

- Florida Gulf Coast (17 locations sampled):
 - Tampa Bay—PAHs, PCBs, DDT (dichlorodiphenyltrichloroethane), Cd, and Pb
 - Apalachicola Bay—As
 - Panama City—PAHs, PCBs, DDT, and As
 - St. Andrew Bay—PAHs, PCBs, DDT, Hg, and Pb
 - Choctawhatchee Bay—PAHs, PCBs, DDT, Ag, and As
 - Pensacola Bay—As
- Alabama: (only Mobil Bay was sampled)—none
- Mississippi: Biloxi Bay—PAHs
- Louisiana: (13 locations sampled)—none
- Texas: (12 locations sampled)
 - Galveston Bay (Offatts Bayou)—DDT, Sn, and Zn

High concentrations were determined based on 213 sites sampled nationally. It was concluded that adding more sites would not meaningfully change calculated mean or high concentrations. High concentrations were associated with population centers, and sediment contaminant concentrations were generally below those expected to be of biological consequence (NOAA 1991). As indicated, sites were purposely chosen to be representative of the area; highly contaminated sites were purposely avoided.

Based on 301 samples collected in 1986 and 1987 by the NOAA NS&T Program, it was concluded that pesticides and PCBs were pervasive at low concentrations in sediments along the northern Gulf of Mexico coast (Sericano et al. 1990). DDT was detected in more than 88 % of the samples with the highest concentrations found in sediments in bays in Florida, Alabama, and Texas. The highest non-DDT pesticide concentrations in sediments were found in Choctawhatchee, Naples, Tampa, St. Andrew, and Rookery bays, Florida; Biloxi Bay and Breton Sound, Mississippi; Terrebonne and Barataria bays, Louisiana; and Galveston and Matagorda bays, Texas. Pesticide concentrations were similar to those previously reported for coastal sediments from the northern Gulf of Mexico. PCBs were commonly detected in sediments in the northern Gulf of Mexico bays with high concentrations in Texas and Florida bays. PCB concentrations in sediments were spatially heterogeneous within bays. While pesticides and PCBs were ubiquitous in sediments, concentrations were less than ERL values (note that highly contaminated sites were avoided). Tissues from nearby biological organisms exceeded sediment concentrations by several-fold, indicating bioaccumulation.

Other subsets of NS&T Program data have been analyzed to highlight the occurrences and distributions of specific chemicals in coastal environments. For example, Apeti et al. (2009) report that high sediment concentrations of Cd (high was defined as the highest 15 % of concentrations measured at 200 U.S. coastal sites) were located in Tampa Bay (Hillsborough Bay), Florida; the Mississippi River (Tiger Pass and Pass A Loutre), Louisiana; Breton Sound (Sable Island), Louisiana; Galveston Bay (Offats Bayou), Texas; Nueces Bay, Texas, and at a marina near Corpus Christi, Texas. Nevertheless, all sediment Cd concentrations in the northern Gulf of Mexico were below ERL values. Cd concentrations in bivalve tissues were poorly correlated with nearby sediment concentrations (adjusted for grain size) but significantly correlated with proximity to population centers. Diagenetic remobilization of Cd reduced concentrations in surficial sediments and may be one reason for the poor correlation between tissue and sediment concentrations.

4.3.2 USEPA Environmental Monitoring and Assessment Program

The USEPA Environmental Monitoring and Assessment Program (EMAP) measured PAHs, PCBs, pesticides, organotins, and metals in the northern Gulf of Mexico sediments from 1991 to 1995 (USEPA 1999; Maruya et al. 1997; Summers et al. 1994, 1995, 1996). Several bays identified as containing chemical contaminants in sediments corresponded with watersheds identified by the USEPA National Sediment Inventory as “areas of probable concern.” At the time, several USEPA Superfund sites were located near these estuaries including Galveston Bay, Tampa Bay, and the Florida panhandle (Figure 4.5a).

Exceedances of ERL and ERM values were used to assess the potential for sediment contaminant concentrations to have biological effects. According to EMAP, ERL guidelines were exceeded by pesticide and metals concentrations at numerous locations while PAH and PCB concentrations exceeded ERL values at only a few locations (less than 1 % of area) across the northern coastal Gulf of Mexico. There was a fairly even geographical distribution of sites across the northern Gulf of Mexico from the Florida Gulf Coast to Corpus Christi Bay, Texas where contaminants exceeded ERL or ERM values (Figure 4.5b). Based on the percent area of

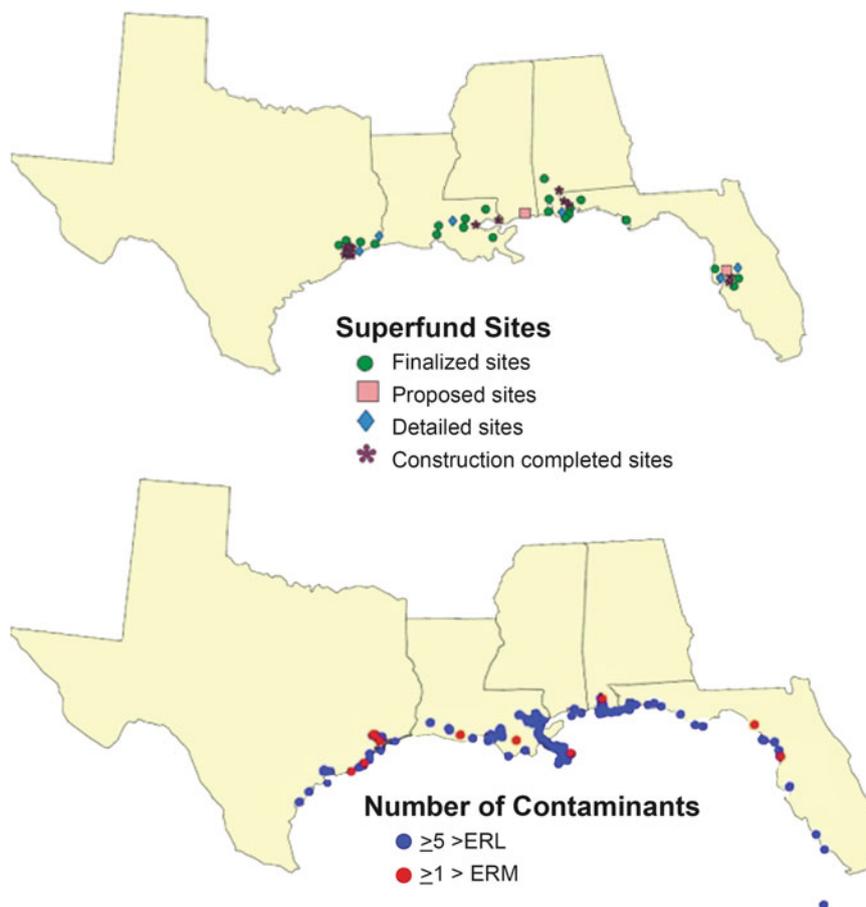


Figure 4.5. (a) Location of coastal Superfund sites in the Gulf of Mexico as of 1999 and (b) sites where SVOCs or metals exceeded ERL or ERM values, 1991–1995 (modified from USEPA 1999).

coastal area judged to be contaminated, the majority of estuarine systems in the Gulf of Mexico were assessed as having fair to good sediment quality. However, several estuaries were identified as having predominantly contaminated sediments, for example Galveston Bay. At the time of the assessment, 50 % of chemical production and 30 % of the petroleum industry in the United States were located in and around Galveston Bay, Texas. Estuarine sediments were judged to be heavily impacted by urban and industrial activities. Galveston Bay has a long history of environmental issues due to expanding human demands and physical alterations of the bay and its watershed over many years. Sediment contaminant distributions indicated that locations in East Bay Bayou, Trinity Bay, marinas, and small lakes had as many as seven chemicals that exceeded ERL values (Figure 4.6). In East Bay Bayou the concentrations of several individual PAHs, including fluorene and phenanthrene, exceeded ERL values. Copper and chlordane concentrations exceeded ERL values at marinas and in Offats Bayou. Offats Bayou sediments also contained elevated concentrations of Pb, Zn, and DDT. As noted above, ERL values used to classify sediment Cu concentrations are close to or less than natural values.

A closer examination of EMAP sediment metal concentrations at 497 sites from 1991 to 1993 in estuaries of the northern Gulf of Mexico was conducted by Summers et al. (1996). Data were normalized to concentrations of Al to identify metals attributable to humans. Cr, Cu, Pb, Ni, and Zn concentrations were highly correlated with Al suggesting a predominantly natural

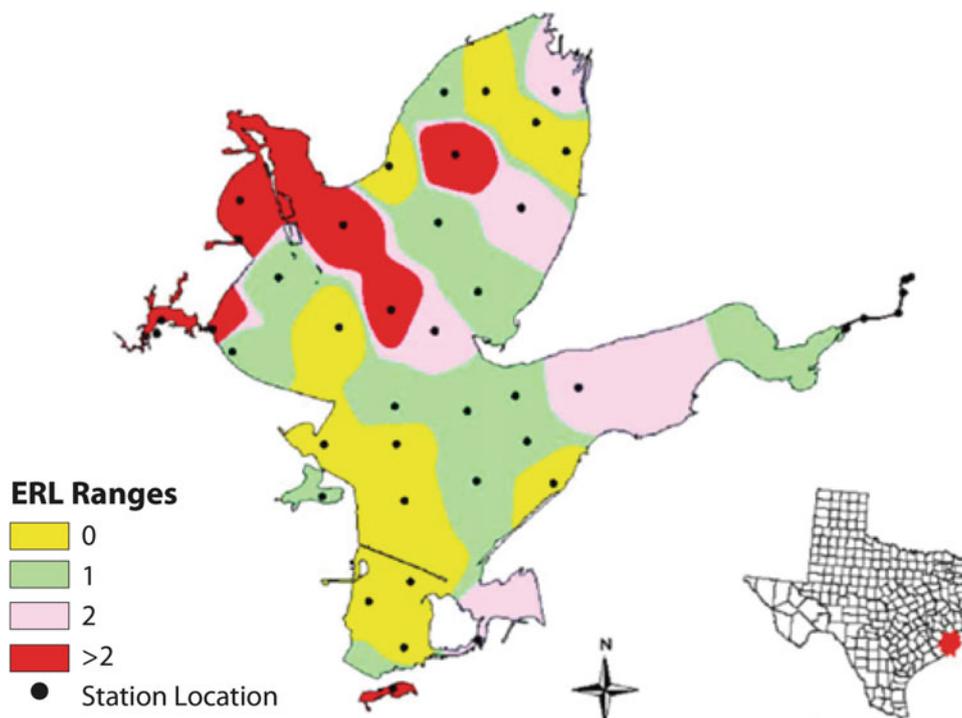


Figure 4.6. Distribution of locations in Galveston Bay, Texas, with chemical concentrations in sediments that exceeded ERL values, 1991–1995 (modified from USEPA 1999).

origin for these metals. This also supports the previous conclusions that ERL values used to classify Cr, Cu, and Ni sediment concentrations are close to or less than natural values and exceedances of these metals should be viewed with caution. As and Ag concentrations were moderately correlated with Al, suggesting a mixed natural and human origin for these metals. Hg and Cd concentrations were weakly correlated with Al suggesting a predominantly human origin for these metals. Of the sites with at least one metal elevated above natural levels, 39 % occurred near population centers, industrial discharge sites, or military bases (Figure 4.7). The remaining sites with at least one metal elevated above natural levels were located in the lower Mississippi River area (7 %) and near agricultural watersheds (54 %) suggesting that non-point sources were important.

4.3.3 USEPA National Coastal Condition Report I

The conditions of coastal sediments in the northern Gulf of Mexico were judged, based on a sediment contamination indicator, to be poor in the USEPA NCCR I report. The assessment is based on data collected from 1990 to 1997 from 500 locations (USEPA 2001). Sediment chemical concentrations exceeded ERL values at many locations; ERM values were exceeded at two locations: one in northern Galveston Bay and one in the Brazos River, Texas (Figure 4.8a). PAH and PCB sediment concentrations exceeded ERL values for less than 1 % of the locations. Pesticides exceeded ERL values for approximately 43 % of the locations. Metals exceeded ERL values for 37 % of the locations. Most of the pesticide ERL exceedances were for dieldrin and endrin (ERL values for these pesticides were near method detection limits). ERL values were exceeded for 12 and 4 % of locations due to DDT and chlordane concentrations, respectively. Enrichments in chemicals above natural levels were attributed to humans. Al concentrations are

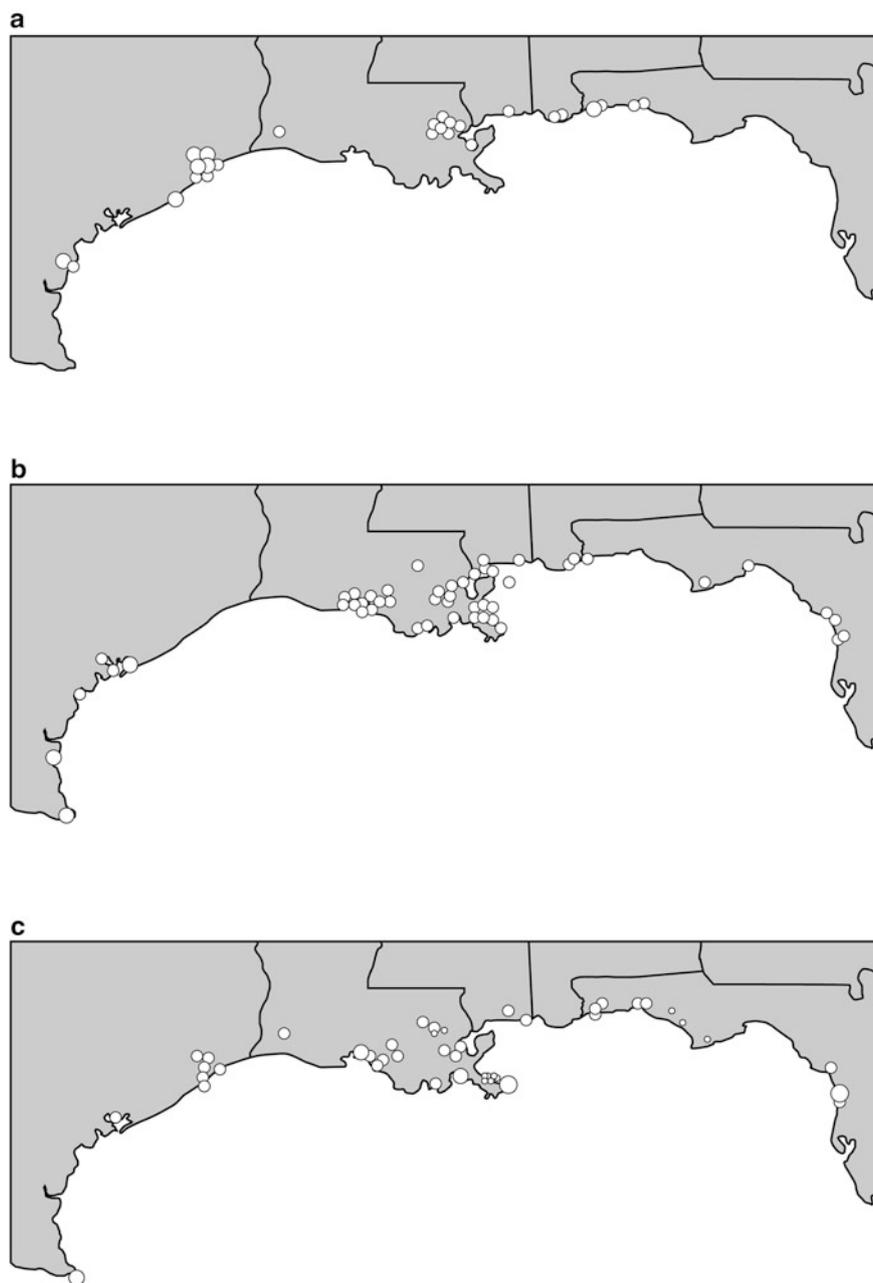


Figure 4.7. Distribution of elevated concentrations of metals in sediments in Gulf of Mexico estuarine sediments for (a) estuaries associated with discharges from human population centers, military installations, or industry and (b) estuaries associated primarily with discharges from agriculture watersheds. Circle sizes in (c) are proportional to the number of metals elevated at a site (the *largest circle* indicates eight elevated metals and *smallest circle* indicates one elevated metal) (modified from Summers et al. 1996).

used to determine the natural levels of metals in sediments because Al has few sources attributable to humans. Background Al/metal ratios were determined by analyzing uncontaminated sediments (Windom et al. 1989; Summers et al. 1996). Enrichments above natural levels ranged from 34 % for metals to 99 % for PAHs and PCBs (Figure 4.8b). PAH and PCB

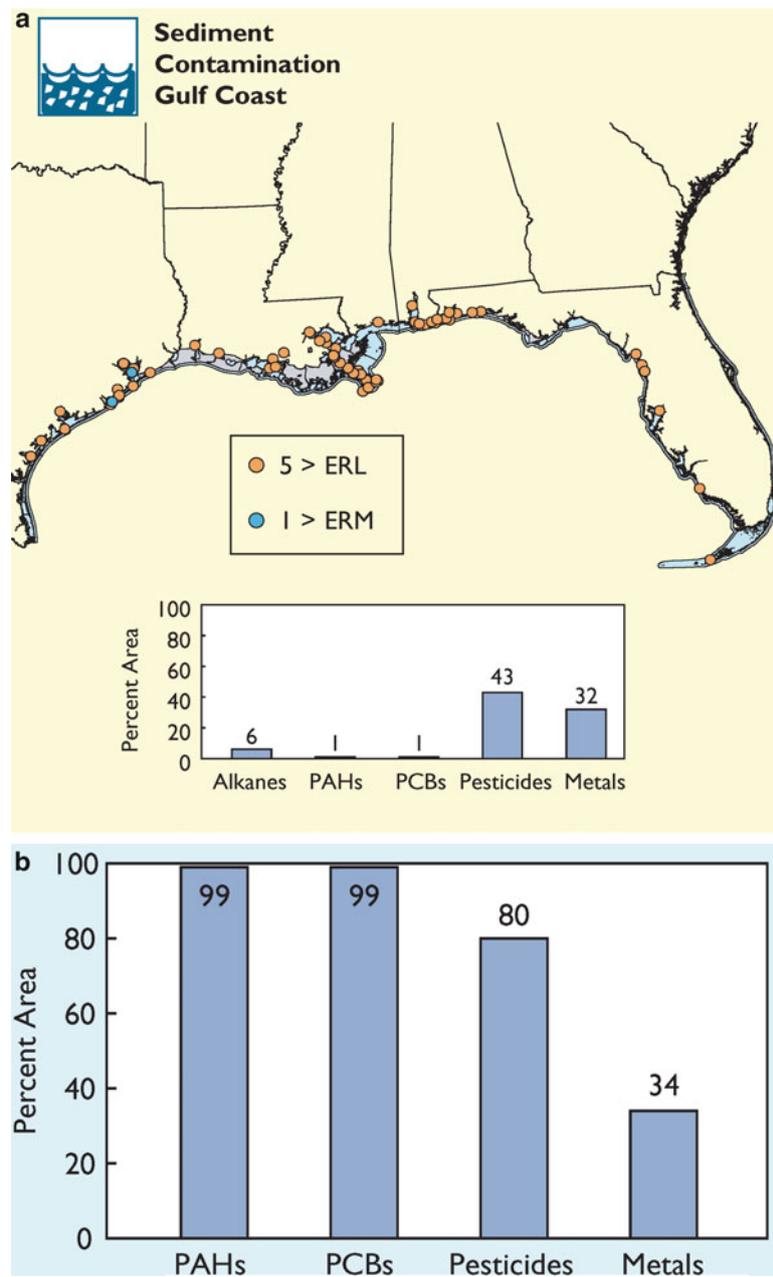


Figure 4.8. (a) Distribution and percentages of locations that exceeded five or more ERL or one ERM value from NCCR I, 1990–1997 and (b) percentage of locations enriched in chemicals above natural levels (modified from USEPA 2001).

enrichments are high as natural levels are zero (for PCBs) or near zero (for PAHs). Few details are provided about which metals exceeded ERL values. As noted above, ERL values used to classify sediment concentrations for Cr, Cu, Ni and As are close to natural values so exceedances based on these criteria should be considered with caution. However, in this instance normalization of metal concentrations to Al does suggest that exceedances were most likely attributable to humans.

4.3.4 USEPA National Coastal Condition Report II

The 2004 NCCR II assessment was based on data collected from 191 locations in the year 2000 (USEPA 2004). The NCCR II sediment quality index included measures of sediment toxicity, sediment contamination, and total organic carbon content (TOC) (Figure 4.9a). Sediment quality was assessed as poor at a location if one of the component indicators was

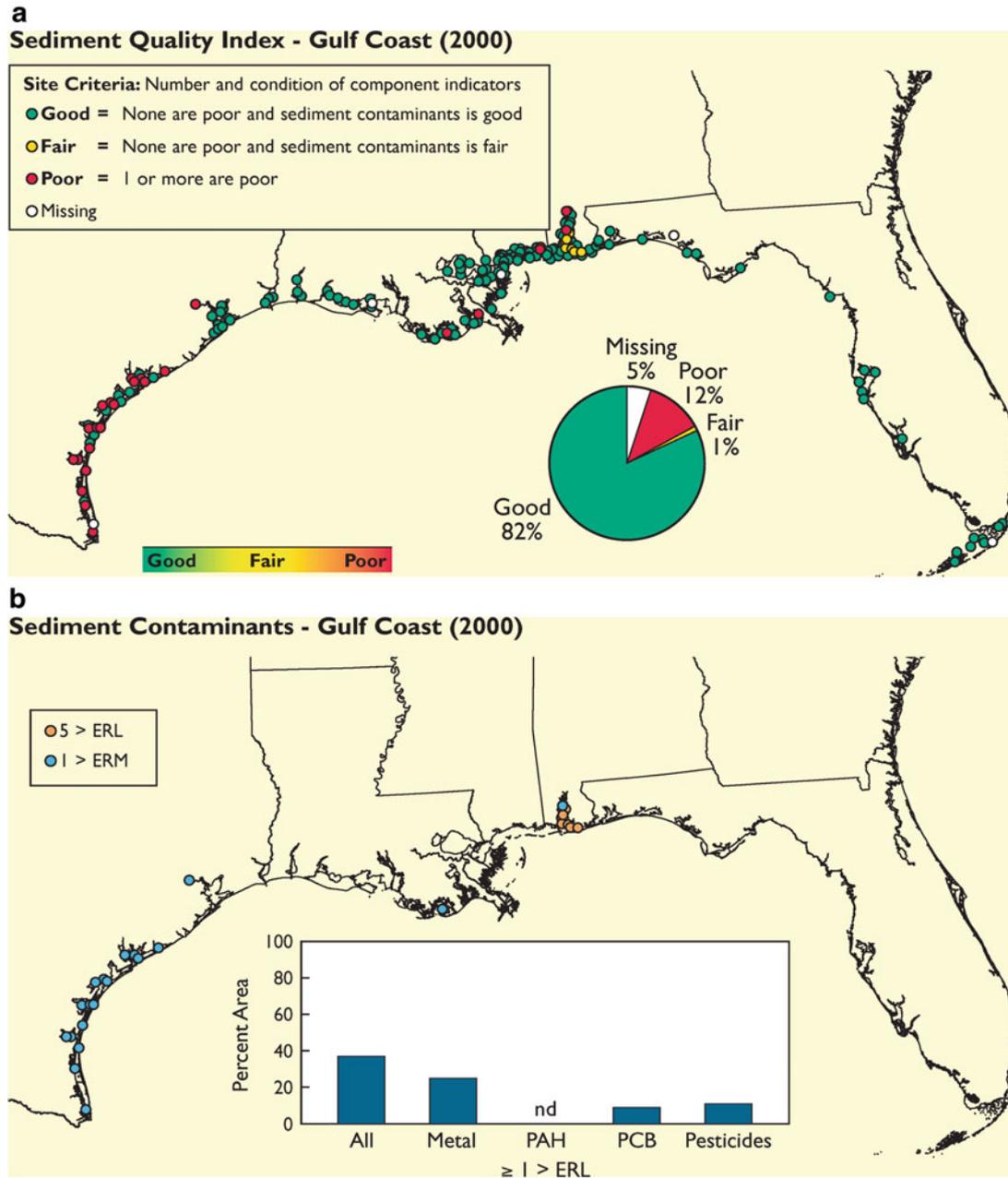


Figure 4.9. (a) Sediment quality index data for northern Gulf of Mexico sediments from NCCR II, 2000 and (b) locations where at least one sediment chemical concentration exceeded the ERM or more than five exceeded the ERL values. The *bar chart* shows the percent of locations where at least one or more sediment chemical concentration exceeded ERL values (modified from USEPA 2004).

categorized as poor, fair if the sediment contaminants indicator was rated fair, and good if all three component indicators were at levels unlikely to cause adverse biological effects. The conditions of coastal sediments in the northern Gulf of Mexico were judged to be fair, with 12 % of the area exceeding thresholds for sediment toxicity, sediment contaminants, and/or sediment TOC (Figure 4.9a). The sediment contaminants index was rated as follows: good (green) if no ERM values were exceeded and fewer than five ERL values were exceeded, fair (yellow) if five or more ERL values were exceeded and no ERM values were exceeded, and poor (red) if one or more ERM values were exceeded. As in the 1991–1997 period, the majority of ERL/ERM exceedances were due to sediment pesticide and metal concentrations. At least one metal exceeded ERL values in 28 % of the locations, 12–14 % of locations exceeded ERL values for at least one pesticide or PCB, and PAHs rarely exceeded ERL values. Exceedances of ERM values were located in Texas bays and one site in Mobile Bay, Alabama (Figure 4.9b). In 2000, ERM exceedances in Texas were much more widespread than in 1991–1997 possibly due to small-scale heterogeneities in sediment chemical distributions. No exceedances were observed along Florida’s Gulf Coast in the year 2000. Small-scale heterogeneity in the distributions of chemicals in sediments may explain differences in exceedances rates between assessments. In Texas and the one site in Mobile Bay there is nearly a one-to-one correspondence between sites rated as poor for the sediment quality index and exceedances of ERM values (Figure 4.9b). This is also true for sites rated as fair for both the sediment quality and the sediment contaminant indices suggesting that in NCCR II, judgments of reduced sediment quality were mostly due to the presence of contaminants. As noted above, ERL values used to classify sediment concentrations for Cr, Cu, Ni and As are close to or less than natural values, so exceedances based on these criteria should be considered with caution.

4.3.5 USEPA National Coastal Condition Report III

The third National Coastal Condition Report—NCCR III—in 2008 was based on data collected from 487 locations in 2001–2002 (USEPA 2008). Sediment quality in the northern Gulf of Mexico was rated overall as poor with 18 % of the coastal area rated poor. The sediment contaminant index was rated as fair and poor for 1 and 2 % of coastal area, respectively (Figure 4.10). This indicates that greater than approximately 97 % of coastal area had fewer than five sediment contaminant concentrations that exceeded ERL values, many fewer than in previous years. Most poor sediment quality ratings in 2000–2002 were due to measured sediment toxicity or elevated TOC concentrations, significantly different from pre-2001 data. Small-scale heterogeneity in the distributions of chemicals in sediments may explain differences in exceedances rates between assessments. Reductions in pesticide usage on adjacent land surfaces may contribute to these differences as well; however, pesticides are persistent in sediments and would be expected to reflect long-term accumulation rather than yearly differences in inputs (Kimbrough et al. 2008). The authors conclude that in coastal northern Gulf of Mexico, sediments had elevated concentrations of metals, pesticides, PCBs, and, occasionally, PAHs, but concentrations were mostly below ERL values. As noted above, ERL values used to classify sediment concentrations for Cr, Cu, Ni, and As are close to or less than natural background values so exceedances based on these criteria should be considered with caution.

4.3.6 USEPA National Coastal Condition Report IV

The fourth National Coastal Condition Report—NCCR IV—was issued in 2012 based on data collected from 879 locations from 2003 to 2006 (USEPA 2012). Alabama, Mississippi, and Louisiana did not collect data in 2005 because of hurricanes Katrina and Rita. Sediment quality

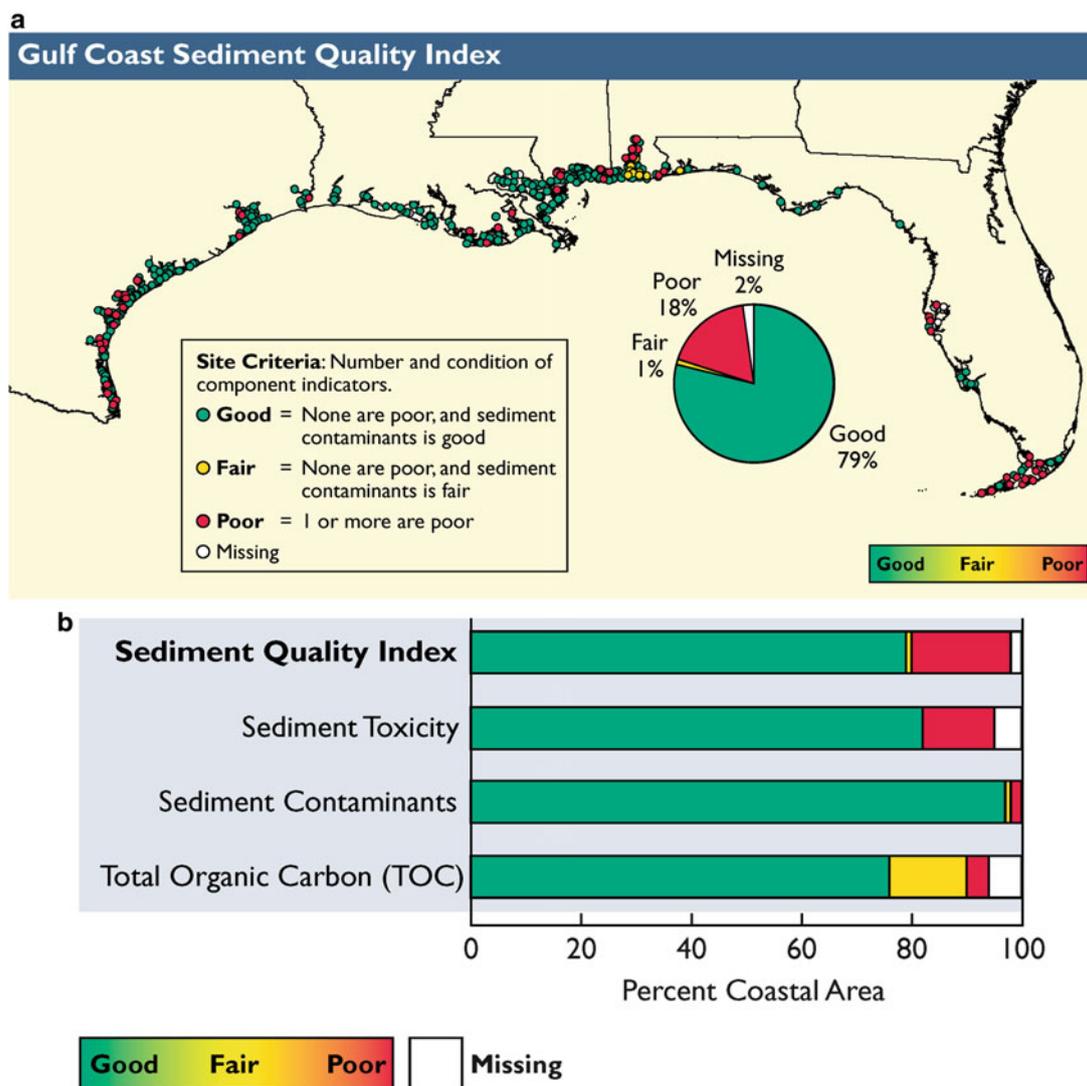


Figure 4.10. (a) Distribution of the sediment quality index ratings from NCCR III, 2001–2002 and (b) the percentage of coastal area achieving each ranking for the sediment quality index and component indicators (modified from USEPA 2008).

in the northern Gulf of Mexico was rated overall as poor with 19 % of the coastal area rated poor for at least one of the component indicators (Figure 4.11). The poor rating for the sediment quality index was mostly due to measured sediment toxicity, consistent with 2001–2002 data. Three locations in Florida Bay had high sediment concentrations of Ag that may have been the cause of the poor ratings for sediment toxicity. In all other instances, toxicity and sediment contamination were not well correlated. The authors suggested that the lack of a correlation of sediment toxicity and contamination may be due to toxicity caused by hydrogen sulfide or high salinity, grain size, contaminants not being bioavailable or not at lethal levels, or the presence of contaminants not measured.

The sediment contaminants indicator overall was rated good with 2 % and approximately 3 % of coastal area rated fair and poor, respectively, indicating approximately 95 % of the

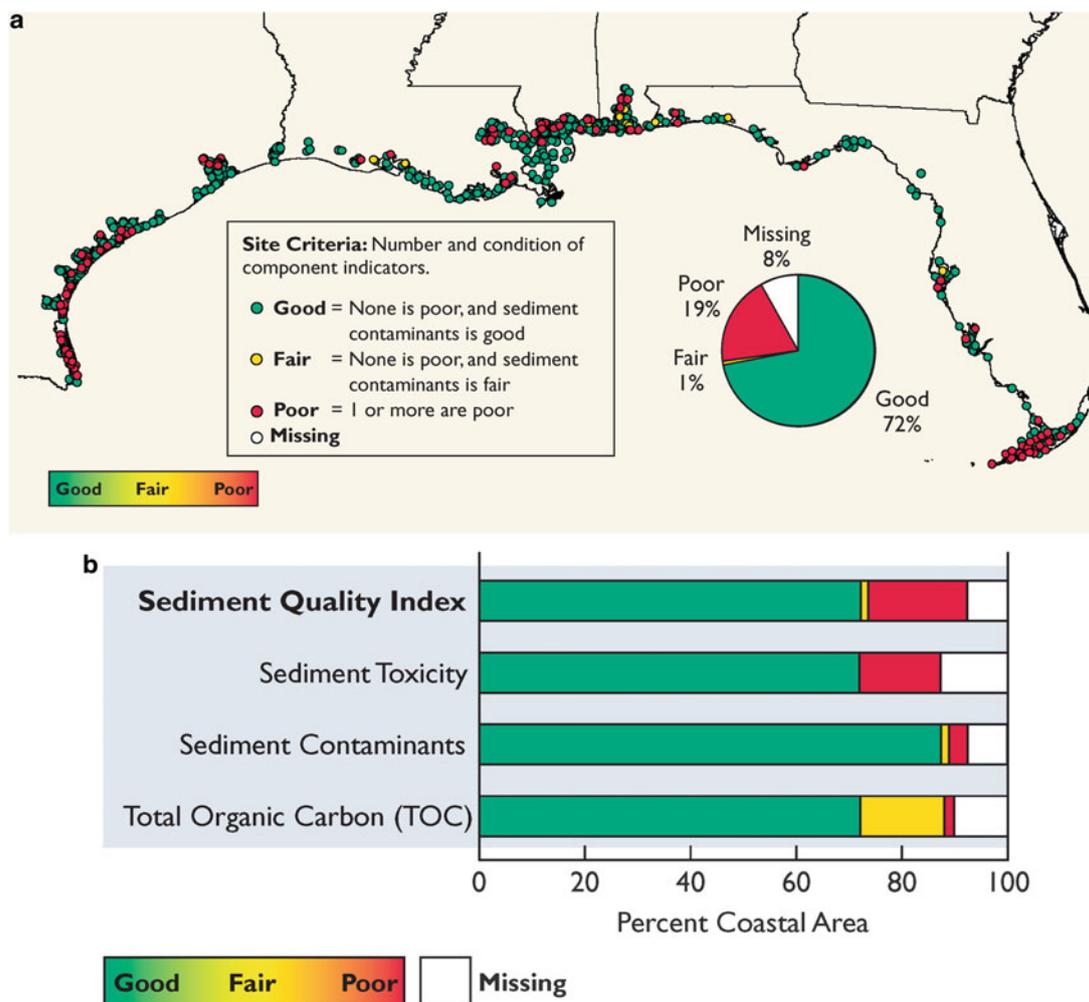


Figure 4.11. (a) Sediment quality index data and (b) the percentage of Gulf coastal area achieving each ranking for the sediment contaminants index and component indicators from NCCR IV, 2003–2006 (modified from USEPA 2012).

coastal area had fewer than five sediment chemical concentrations that exceeded ERL values. While the percentage of areas impacted by contaminants was similar in 2001–2002 and 2003–2006, the location and the cause of the impact were dissimilar except possibly in Mobile Bay. As noted above, sites rated poor were located in Florida Bay where sediment concentrations of Ag exceeded ERM values. Coastal areas rated fair for the sediment contaminants indicator were mostly located in Mobile Bay, Alabama. As in 2001–2002, the authors noted that northern Gulf of Mexico sediments had elevated concentrations of metals, pesticides, PCBs, and occasionally PAHs but concentrations were mostly below ERL values. Small-scale heterogeneity in the distributions of chemicals in sediments may explain differences in exceedance rates between assessments. As noted above, ERL values used to classify sediment concentrations for Cr, Cu, Ni, and As are near or less than natural values so exceedances based on these criteria should be considered with caution.

4.3.7 Gulf of Mexico Bays

Sediment contaminant concentrations in individual bays and estuarine complexes in the northern Gulf of Mexico provide a finer-scale view illustrating the importance of small-scale variations in chemical sources and the impact of local environmental conditions on geographic distributions. The following assessment is based on 2001–2002 data and includes some of the data used in NCCR assessments. The National Estuary Program (NEP) was established under Section 320 of the 1987 Clean Water Act Amendments as a USEPA effort to protect and restore the water quality and ecological integrity of major U.S. estuaries. There are 28 designated estuaries of national significance, and seven are located in the northern Gulf of Mexico (Figure 4.12). In general, the sediment contaminants indicator is rated as more degraded at this finer scale than at the regional scale, illustrating small-scale heterogeneities in chemical sources and sediment contaminant concentration distributions in coastal environments. This difference in ratings also illustrates that the selection of sampling sites can affect the data collected. Sampling locations in close proximity to shorelines and in shallower embayments highlight the steepness of spatial gradients in chemical concentrations as land-based sources are approached (see Regional Environmental Monitoring and Assessment Program [REMAP] data below as well).

The sediment quality index for the collective NEP estuaries of the Gulf of Mexico region was rated as fair to poor with 18 % of the estuarine areas rated as either fair or poor for the sediment quality indicator (Figures 4.13 and 4.14). As before, the sediment quality index was a composite indicator based on sediment toxicity, contaminants, and TOC content. Sediment contaminant index ratings were also defined the same: good (green) if no ERM values were exceeded and fewer than five ERL values were exceeded, fair (yellow) if five or more ERL values were exceeded, and poor (red) if one or more ERM values were exceeded. Northern Gulf of Mexico NEPs were rated fair for sediment contaminant concentrations with 11 % of the region's estuarine area rated poor (at least one sediment chemical concentration exceeded ERM values) (Figure 4.13). Most sediment quality ratings of poor were due to poor ratings for the sediment contamination indicator, although, on occasion, toxicity and TOC contributed to a poor rating. The largest numbers of locations with fair and poor ratings for the sediment contaminants indicator were located in Texas, including Galveston Bay and Corpus Christi Bay (Figure 4.14).



Figure 4.12. National Estuary Program estuaries (modified from USEPA 2006).

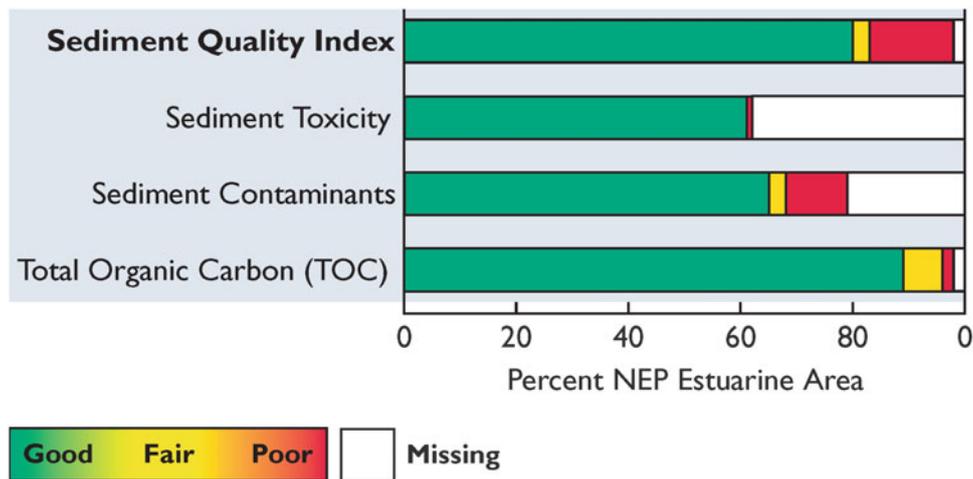


Figure 4.13. Percent of NEP estuarine areas achieving each ranking for the sediment quality index and component indicators, 2000–2002 (modified from USEPA 2006).

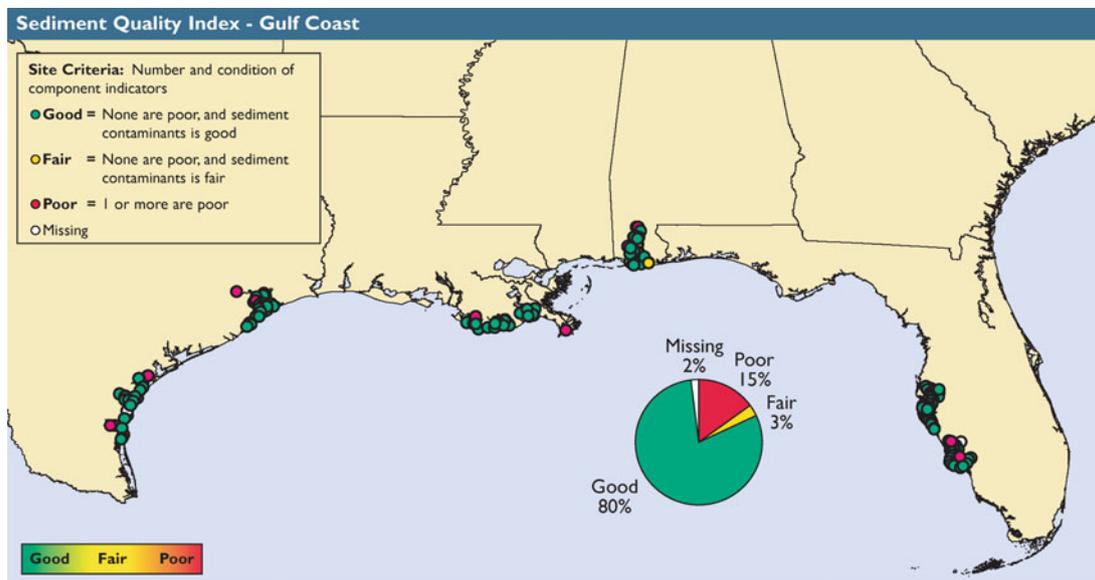


Figure 4.14. Geographic distribution of sediment quality index ratings in NEP estuaries, 2000–2002 (modified from USEPA 2006).

The sediment quality index ratings for individual Gulf of Mexico estuaries ranged from good to poor (Figure 4.15). The sediment quality index for Mobile Bay was rated fair with 9 % of the estuarine area rated poor (due to sediment toxicity). The Barataria-Terrebonne Estuarine Complex (BTEC) was rated good with 8 % of the estuarine area rated poor. Galveston Bay was rated fair to poor with approximately 5 % of the estuarine area rated poor. Coastal Bend Bays were rated poor with 38 % of the estuarine area rated poor. Contaminant data were not collected in Florida (Figure 4.15). The sediment contaminants index was rated good for Mobile Bay and the BTEC, fair for Galveston Bay, and poor for the Coastal Bend Bays (Figure 4.15). The sediment contaminants index was rated poor for 10 % of the Galveston Bay estuarine area.

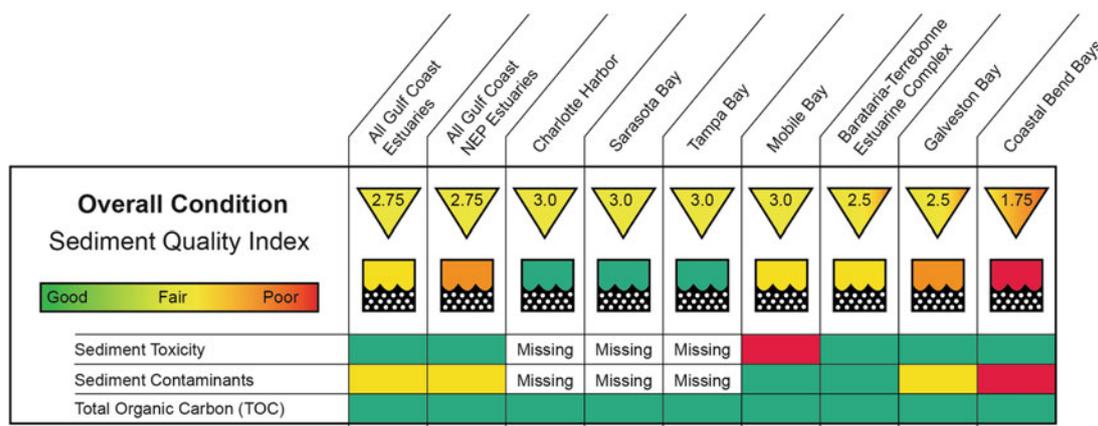


Figure 4.15. Comparison of indices for northern Gulf of Mexico estuaries, 2001–2002 (modified from USEPA 2006).

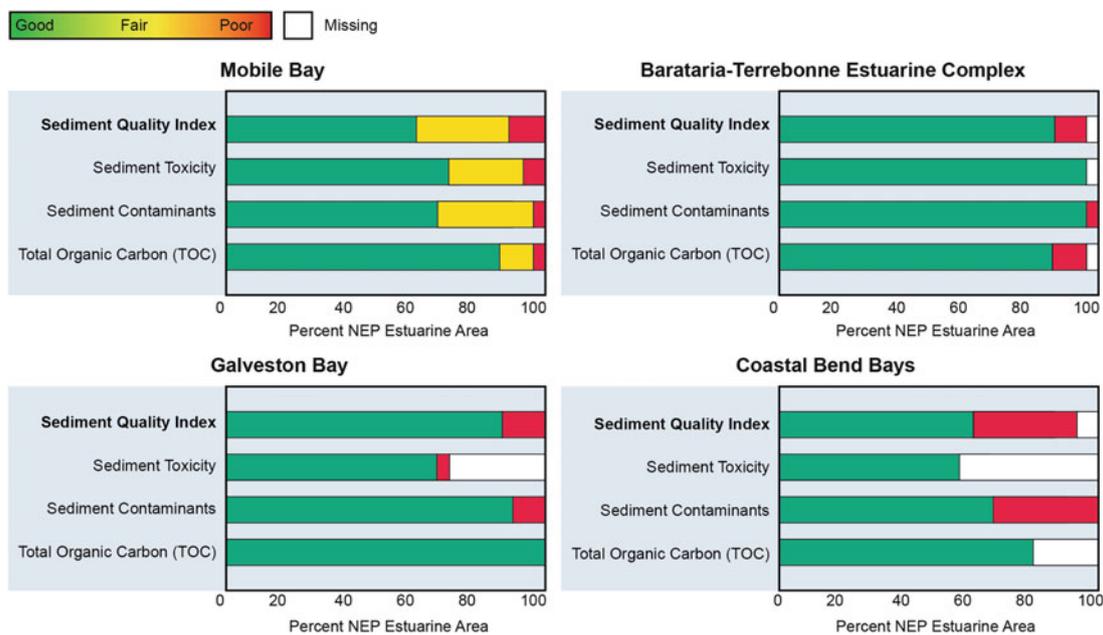


Figure 4.16. Percent of estuarine areas achieving each rating for the sediment quality index and components indicators, 2001–2002 (modified from USEPA 2006).

A closer review of the indicator rankings provides insight into the trends observed in individual estuaries. Correlation of the sediment quality index with the sediment contaminants index can be confounded by the inclusion of sediment toxicity and TOC indices (Figure 4.16). However, for Galveston and the Coastal Bend bays, most of the poor ratings were attributable to sediment chemical concentrations that exceeded ERM values for at least one chemical. The sediment contaminant index for Mobile Bay was rated good with 2 % of the estuarine area rated poor. Sediment quality in Mobile Bay was impacted at locations in the central portion of the bay primarily due to toxicity with occasional contributions from contaminants and/or TOC (Figure 4.17). Contaminants are known to accumulate in Mobile Bay sediments over time. Of the 23 USEPA Total Maximum Daily Load 303(d)-listed streams

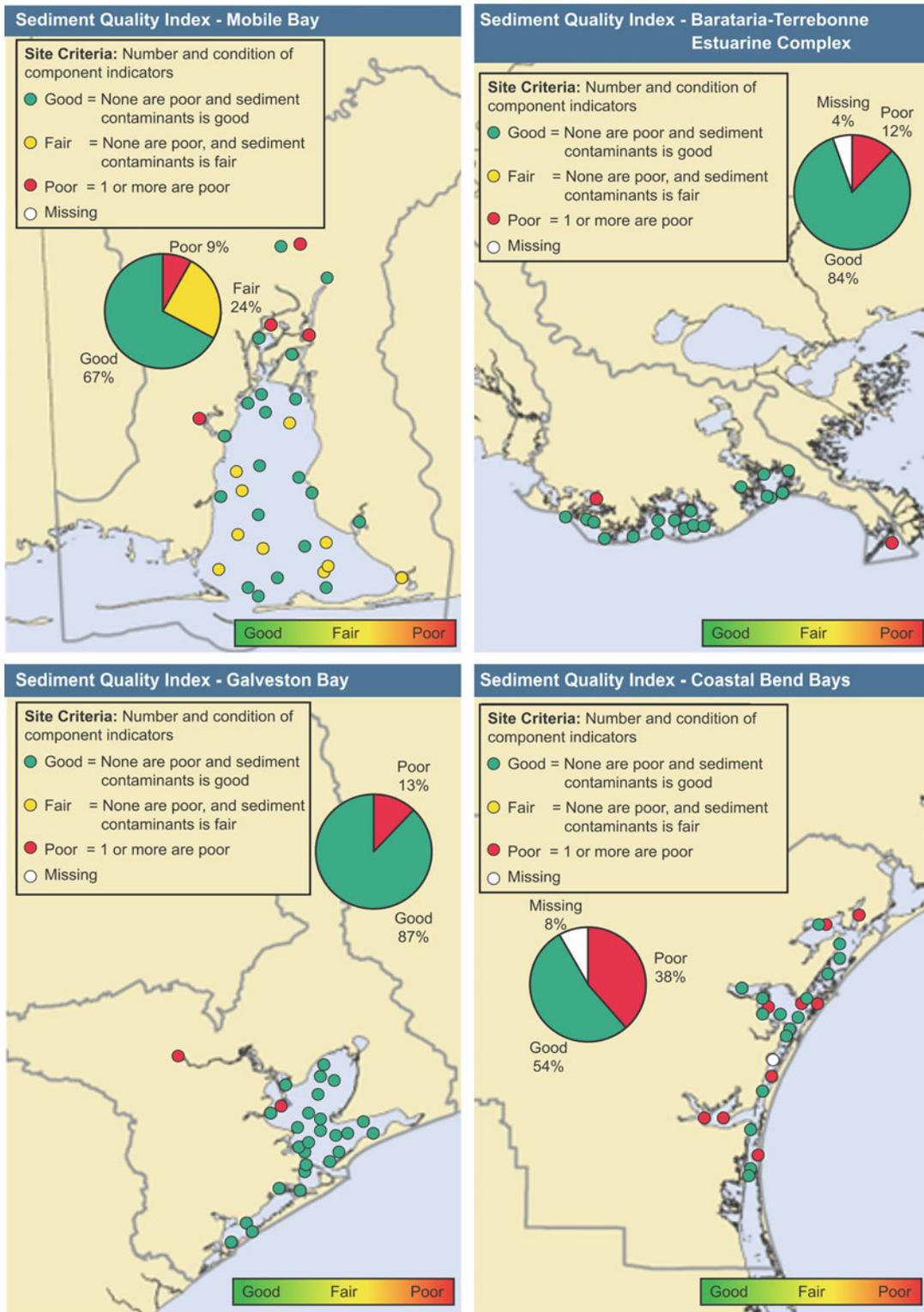


Figure 4.17. Sediment quality index ratings for Mobile Bay, the Barataria-Terrebonne Estuarine Complex, Galveston Bay and Coastal Bend Bays, 2000–2001 (modified from USEPA 2006).

located in the Mobile Bay NEP, 8 were impaired in part due to Hg contamination. Sediment contaminants influenced sediment quality at locations near the shore in the northern portions of Mobile Bay. The BTEC was rated good for the sediment contaminants with 4 % of the area rated poor (Figure 4.17). Two locations were rated poor mostly because of localized, elevated TOC concentrations. Galveston Bay was rated fair for sediment contaminants indicator despite 10 % of the estuarine area being rated poor. SVOCs and metals commonly have elevated concentrations in Galveston Bay runoff, freshwater inflow, and waste discharges and lower, relatively uniform, concentrations in sediments in the central part of the bay. The upper Houston Ship Channel generally had the highest concentration of chemicals. Coastal Bend Bays were rated poor for sediment chemical concentrations with 38 % of the estuarine area rated poor. Concentrations of As, Cd, Hg, and Zn were often elevated in Corpus Christi Bay sediments. The highest levels of pesticides were found in Baffin and Copano bays, Texas. Elevated levels of PAHs, metals, pesticides, and PCBs have been documented in sediments near stormwater outfall sites. A detailed study of Corpus Christi Bay documented elevated concentrations of PAHs, DDT, chlordane, PCBs, As, Pb, Al, Cu, Ni, Zn, Cd, and Cr in sediments near stormwater outfalls (Carr et al. 2000). Park et al. (2002) concluded that the atmosphere was a pathway for persistent, anthropogenic PAHs, PCBs, and pesticides to enter coastal environments. Gas exchange has been shown to be an important transport process for SVOCs between the atmosphere and surface waters. In Corpus Christi Bay urban and industrialized areas, atmospheric inputs of PAHs and PCBs were identified as a continuing source of contaminants (Park et al. 2002).

The Regional Environmental Monitoring and Assessment Program (REMAP) was initiated to test the applicability of the EMAP approach to describe ecological conditions at regional and local scales. In the northern Gulf of Mexico, Galveston Bay was selected as a site for a REMAP project and included the measurement of SVOCs and metals in sediments at 29 random locations (USEPA 1998). The study characterized the condition of Galveston Bay as a whole and four small bays in Galveston Bay and also studied the impact of marinas. Comparisons of EMAP and REMAP results were used to highlight those areas with contaminated sediments. Enrichment was determined using regression equations for each metal against Al concentrations in the sediments (Summers et al. 1996). As noted above, ERL values used to classify sediment concentrations for Cr, Cu, Ni, and As are near or less than natural values so exceedances based on these criteria should be considered with caution. In this instance, normalization to Al provides some assurance that elevated metal levels are due to human activities. In Galveston Bay, As, Cu, Pb, Ni, and Zn concentrations exceeded ERL values but not ERM values at one or more sites. Sites contaminated with the most metals were Offats Bayou, Clear Lake, Moses Lake/Dollar Bay, and two marina sites. The Galveston Bay area had high Cr and Ni sediment concentrations across a large area. The percent of area that exceeded ERL values for As were lower and for Zn were similar to EMAP results for the region. Cu exceedances of the ERL value were found at marina sites and in Offats Bayou but not in the randomly sampled area. Organotin concentrations in sediments exceeded the screening level of 1.0 parts per billion (ppb) in 52 % of the area compared to 31 % for EMAP results. Sites with high dieldrin and endrin concentrations in sediments were located in upper Galveston Bay, Clear Lake, and upper Trinity Bay. Dieldrin and endrin ERL values were exceeded at 17 and 5 % of the area, respectively, in Galveston Bay and 33 and 0 %, respectively for small bay and marina sites, which was lower than EMAP results for the region. Concentrations of other pesticides, including DDT, did not exceed ERL values in either study. Individual PAH concentrations exceeded ERL values in Trinity Bay near several active oil wells. PAH concentrations for sediments at three sites in Galveston were considerably higher than at the other sites. C3-fluorene concentrations exceeded ERL values in 3 % of

Galveston Bay sediments, similar to EMAP results for the region. PCB concentrations in Galveston Bay sediments did not exceed ERL values, compared to an EMAP rate of 1 % exceedances.

4.3.8 Temporal Variations

There is limited data that is useful for distinguishing temporal variations in concentrations of contaminants in coastal, northern Gulf of Mexico sediments. While data have been collected over many years, variations in analytical methods, reporting methods, sampling locations, and small-scale spatial heterogeneity confound detection of trends with time. Based on data collections in the 1980s and the early 1990s it was concluded that distributions and sediment concentrations of SVOCs were similar to previously reported concentrations (Summers et al. 1992, 1994, 1995; Wade et al. 1988). Based on NCCRs, a comparison of yearly sediment contaminant indicator ratings showed no significant temporal trend in the percent coastal area rated poor for 1991–2002 (Figure 4.18b). There was also no significant difference in the percent of area rated poor when the data were averaged for the years 1991–1994 and compared to the averages for the years 2000–2002. The percent of area rated good for sediment contaminant concentrations increased significantly ($R^2 = 0.77$; $p < 0.05$) from 1991 to 2002 (Figure 4.18a). Although the percent area rated as poor remained similar, the sediment contaminants indicator improved, as indicated by a significant decrease ($z = 3.96$; $p < 0.05$) in the combined total percent area rated poor and fair from 16.4 % in 1991–1994 to 5.9 % in 2000–2002. This trend is consistent with reductions in pesticide and ERM concentration exceedances. The incidence of PAH and PCB exceedances is similar during this timeframe or showed no consistent temporal trend. In NCCR IV, these comparisons were again made including additional data for 2003–2006 (USEPA 2012). Data for 2005–2006 were collected using a 2-year survey design, and the data were treated as a single year in trend analyses. The percent of area rated poor for the sediment contaminants indicator decreased from 13 % in 2000 to zero in 2004–2006 (Figure 4.18c). Small-scale heterogeneity in the distributions of contaminants in sediments may explain differences in exceedances rates between assessments.

ERL/ERM value exceedances from the NCCRs in the 1990s and 2000s are summarized in Table 4.2. The limitations of ERL values as predictors of sediment quality and/or toxicity should be considered in interpreting the significance of temporal trends. Also note that ERL/ERM exceedances from year to year do not always occur at the same location and the contaminants causing the exceedances can vary. In addition, the percent area impacted was calculated based on a varying number of exceedances (1–5) with fewer than 5 ERL exceedances resulting in a site being rated as good (i.e., 1–4 sediment contaminant concentrations may exceed ERL values at locations but they are not included in the percent of area impacted). A conservative approach was taken in estimating the area impacted using the highest possible percent as a less-than figure for the percent area impacted (i.e., the percent area for exceedances might be significantly lower). Based on these conservative estimates and limitations, pesticide and metal ERL/ERM exceedances decreased from 1990 to 2006 with the largest reductions from 2001 to 2006. PCB and PAH exceedances appear to be similar and low throughout the 1990–2006 time period. The percent of area rated good for the sediment contaminant indicator (fewer than 5 ERL contaminant exceedances) increased from 1991 to 2002, and the percent of area rated poor for the sediment contaminants indicator (no ERM exceedances for all contaminants) decreased from 13 % in 2000 to none in 2004–2006. Overall, these data suggest that the number of sites where pesticide and metal sediment contaminant concentrations exceed levels suspected of causing biological effects (and thus average concentrations) have decreased with time. PCB and PAH sediment concentrations rarely exceeded levels

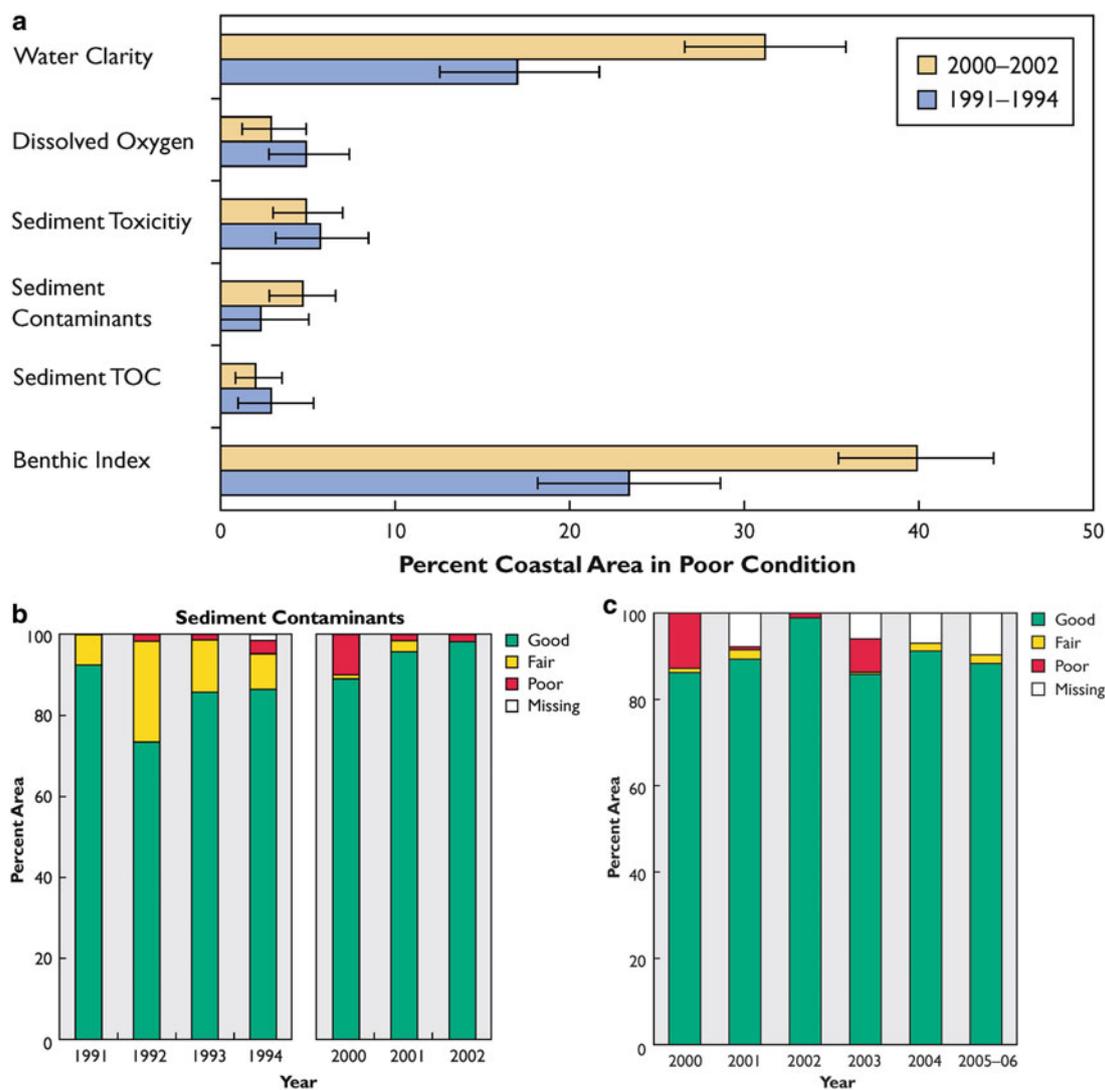


Figure 4.18. (a) Comparison of the average percent area rated poor for ecological indicators, 1991–1994 and 2000–2002; (b) the percent area in good, fair, poor, or missing categories for the sediment contaminants indicator, 1991–2002; and (c) the percent area rated good, fair, poor, or missing categories for the sediment contaminant index, 2000–2006 (modified from USEPA 2008, 2012).

suspected of causing biological effects from 1990 to 2006. Exceptions are areas known to be heavily and chronically contaminated (i.e., parts of Galveston Bay and Houston Ship Channel) and areas subject to major accidental spills or other high-level releases of contaminants.

4.4 CONTINENTAL SHELF/SLOPE AND ABYSSAL SEDIMENTS

In general, the concentrations of human-derived sediment contaminants are expected to decrease with distance off shore. Human activities that have the potential to contaminate sediments mostly occur in coastal areas and/or on adjacent land surfaces. In contrast, naturally

Table 4.2. Summaries of Results from NCCR I, II, III, and IV for Percent of Coastal Area Exceeding ERL/ERM Values (USEPA 2001, 2004, 2008, 2012)

NCCR Report (years of data collection)	Pesticides	Metals	PCBs	PAHs
I (1990–1997)	43 %	37 %	<1 %	<1 %
II (2000)	12–14 % with one pesticide or PCB exceedances <14 %	28 %	12–14 % with one pesticide or PCB exceedances ≪14 %	Rare <1 %
III (2001–2002)	97 % of coastal with <5 ERL exceedances <3 %	97 % of coastal with <5 ERL exceedances <3 %	97 % of coastal with <5 ERL exceedances ≪3 %	97 % of coastal with <5 ERL exceedances <3 %
IV (2003–2006)	95 % of coastal with <5 ERL exceedances	95 % of coastal with <5 ERL exceedances	95 % of coastal with <5 ERL exceedances	95 % of coastal with <5 ERL exceedances
[Note: 1 % of ERM exceedances were for Ag in a Florida Bay]	<5 % <1 % exceed ERM <2 % with <5 ERL exceedances	<5 % <1 % exceed ERM <2 % with <5 ERL exceedances	≪5 % <1 % exceed ERM <2 % with <5 ERL exceedances	≪5 % <1 % exceed ERM <2 % with <5 ERL exceedances

occurring sediment metals occur at higher concentrations in abyssal sediments than in continental shelf and slope sediments due to slow accumulation rates, diagenesis, and the scavenging of metals over long periods of time; however, this offshore increase is a natural phenomenon. PAHs have a major natural offshore source in oil and gas seepage as well, and thus, some of the highest sediment concentrations of PAH are on the continental shelf/slope (NRC 2003).

Coastal environments are often sites of particle and sediment deposition. Being restricted from the open ocean limits offshore transport of coastal contaminants. Contaminants found in coastal areas can be transported to offshore regions by atmospheric circulation and ocean currents, but dilution with uncontaminated sediments would be expected to further reduce sediment contaminant concentrations. Seaward transport is most important in close proximity to river systems that outflow directly into the ocean. For example, the Mississippi River transports material significant distances offshore during periods of high outflow. Hydrocarbons and limited amounts of pesticides and PCBs can be directly released to continental shelf/slope and/or abyssal waters because of use on and discharges from offshore oil and gas platforms and from emissions and discharges from ships and accidental spills (NRC 2003). Surveys of contaminant concentrations in sediments on the continental shelf/slope and in the abyss of the northern Gulf of Mexico are limited. In cases where studies have been conducted, they are mostly directed at specific activities, such as oil and gas platform discharges, or unique environments, such as natural oil and gas seeps. The majority of studies measure only hydrocarbons and metals due to the general absence of pesticides and PCBs in the offshore region.

4.4.1 Natural Oil and Gas Seepage

Seepage of oil and gas is a natural phenomenon that occurs when deeply generated oil and gas migrates to the earth's surface (Wilson et al. 1974; NRC 2003). Deeply buried petroleum reservoirs and source rocks generate oil and gas that can migrate upward into marine sediments if pathways such as faults exist. Sediments overlying prolific oil and gas provinces are well known sites of natural oil and gas seepage worldwide (Wilson et al. 1974; Brooks et al. 1986). Over geologic time (millions of years) much larger amounts of petroleum have been lost to seepage than is trapped in reservoirs (Wilson et al. 1974). Offshore seeps are widespread in the northern Gulf of Mexico, accounting for approximately 95 % of the total oil input to the offshore region (Anderson et al. 1983; Kennicutt et al. 1983; Brooks et al. 1987; Wade et al. 1989; Sassen et al. 2003; NRC 2003). Most petroleum seepage in the Gulf of Mexico is located in the north-western offshore region (Figure 4.19). The full extent of oil and gas seepage in the Gulf of Mexico is difficult to quantify due to challenges in detection (e.g., subsea releases), differences in quantification methods (e.g., satellite observations and direct sampling by corer), dispersion by ocean currents, the paucity of geographic coverage, and variable and uncertain seep volumes and seepage rates (Wilson et al. 1974; De Beukler 2003). Within these limitations, natural seepage of oil has been estimated to exceed 127,000 metric tons (140,000 tons) annually in the northern Gulf of Mexico (NRC 2003).

The immediate effects of oil and gas seepage are mainly in sediments in close proximity to seeps (i.e., within a few hundred meters of the seep's surface expression [Wade et al. 1989]). The low-energy environment of offshore generally limits redistribution of sediments from

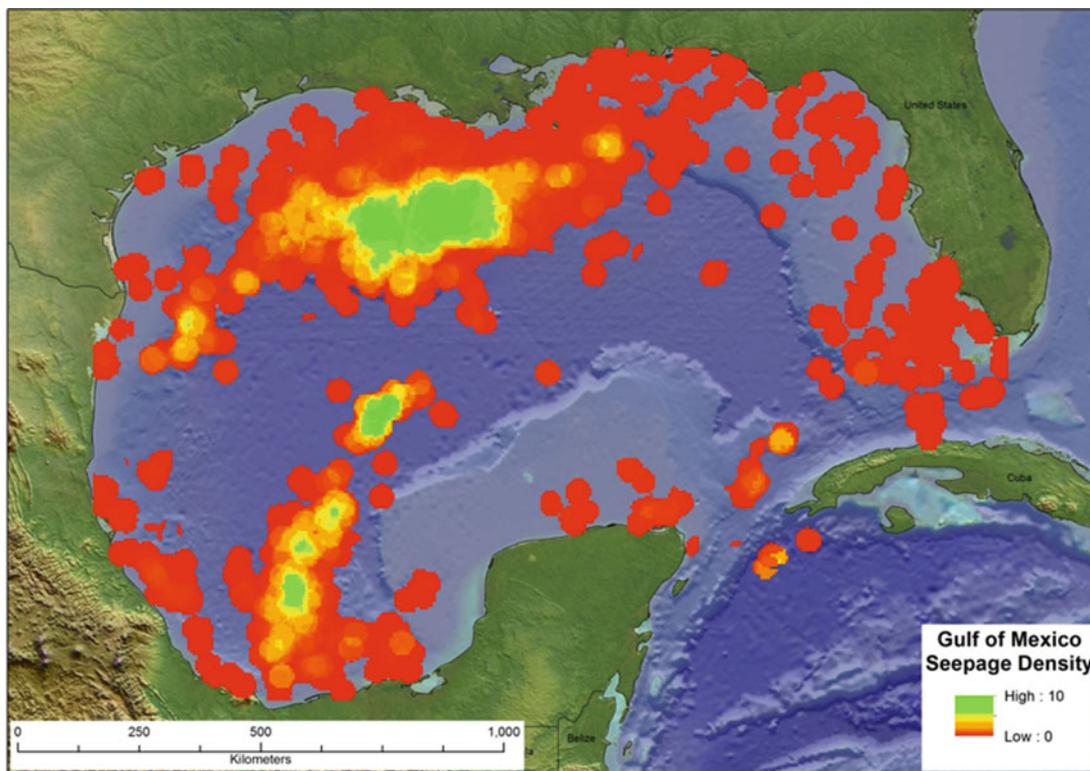


Figure 4.19. Oil and gas seepage in the Gulf of Mexico (determined from analysis of synthetic aperture radar, graphic provided by CGG's NPA Satellite Mapping, used with permission).

seeps; however, mass wasting and turbidity currents have the potential to transport sediments long distances. Most oil constituents have low water solubility and are less dense than water, so seeping oil mostly adsorbs onto the sediment it is seeping through or escapes into the water column rising to the sea surface to form slicks. Some seeps, becoming entrained in sediments on the sea floor, may not reach the water's surface. Those constituents of oil that are soluble in water (i.e., low molecular weight PAHs) can dissolve in the overlying water column (Wade et al. 1989). Adsorption onto sediments leads to heterogeneous and discontinuous distributions of oil in sea-bottom sediments. Oil released into marine environments by sea-bottom seepage undergoes similar physical and chemical processes (except evaporation and photooxidation due to the submerged location) as subaerial releases. Natural processes degrade and metabolize the oil, but oil can be replenished as long as the seep remains active. The persistence of natural oil seeps is estimated to be years and possibly centuries or longer as oil and gas have been generated in the deep subsurface over geologic time (Wilson et al. 1974). Sediments contaminated with petroleum by natural seeps can contain highly variable concentrations of oil due to the point-source characteristics of seepage. Petroleum concentrations in seep sediments can vary from trace amounts at the fringes of a seep to several percent by weight at an active seep or even a separate liquid phase. Oil and gas seep rates vary with time and seeps can be dormant for periods of time (no seepage). Microbial degradation of oil produces authigenic calcium carbonate minerals that can temporarily cap seeps. While seepage is common across the deep water of north-central Gulf of Mexico, the percentage of continental shelf/abyss sea-bottom area containing seep oil is estimated to be limited. A detailed review of oil and gas seepage in the Gulf of Mexico and additional references are provided in Chapter 5 on Oil and Gas Seeps in the Gulf of Mexico.

4.4.2 Other Contaminants Attributable to Humans

Contaminants in northern Gulf of Mexico continental shelf/abyss sediments can have origins in human activities such as discharges from offshore oil and gas platforms, emissions and releases from ships, and accidental spills that occur offshore. Materials can be transported by the atmosphere, oceanic currents, and rivers to offshore regions. The northern Gulf of Mexico is, and has been, one of the most prolific oil and gas provinces in the world for many years (Figures 4.20 and 4.21) (Energy Information 2009). In 2006, there were nearly 4,000 oil and gas platforms in the northern Gulf of Mexico, mostly offshore of Louisiana and Texas (Figure 4.20). In recent years, oil and gas exploration and production in the Gulf of Mexico has expanded outward onto the continental slope.

A survey of background PAH and metal concentrations in continental slope/abyss sediments (greater than 300 meter [m] (984 feet [ft]) water depth) in the northern Gulf of Mexico was conducted by Rowe and Kennicutt (2009). Sediment sampling sites were purposely located many kilometers from petroleum development activities. Sediment PAH concentrations were low (less than 1.0 parts per million [ppm]) at all 50 locations sampled (Figures 4.22 and 4.23). These sites are remote from natural oil and gas seepage and oil and gas exploration activities, and the PAH concentrations detected approached method detection limits. The composition of PAHs was indicative of petroleum and combustion (pyrogenic) sources. Combustion-derived PAH can originate from discharges from ships (e.g., stack emissions and bilge pumping) and oil and gas platforms, atmospheric deposition, and/or riverine transport. Ship traffic and platform operations were judged to be the most likely sources, as atmospheric deposition would produce similar PAH concentrations over large regions and this pattern was not observed. The geographic distribution of PAHs suggested an input of PAHs from the sediment plume of the Mississippi River as low PAH (less than 1.0 ppm) co-occurred with low Ba concentrations (less

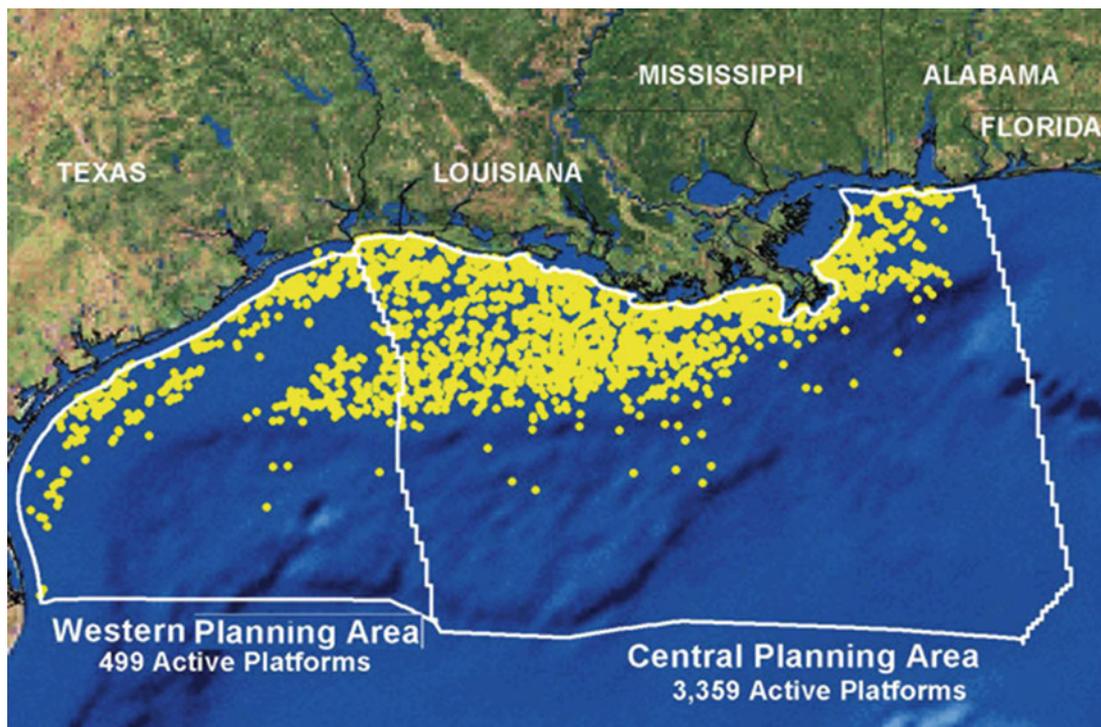


Figure 4.20. Map of the 3,858 oil and gas platforms in the Gulf of Mexico in 2006. The size of the dots used to note platform locations is highly exaggerated and the density of platforms is low. From NOAA (2012).

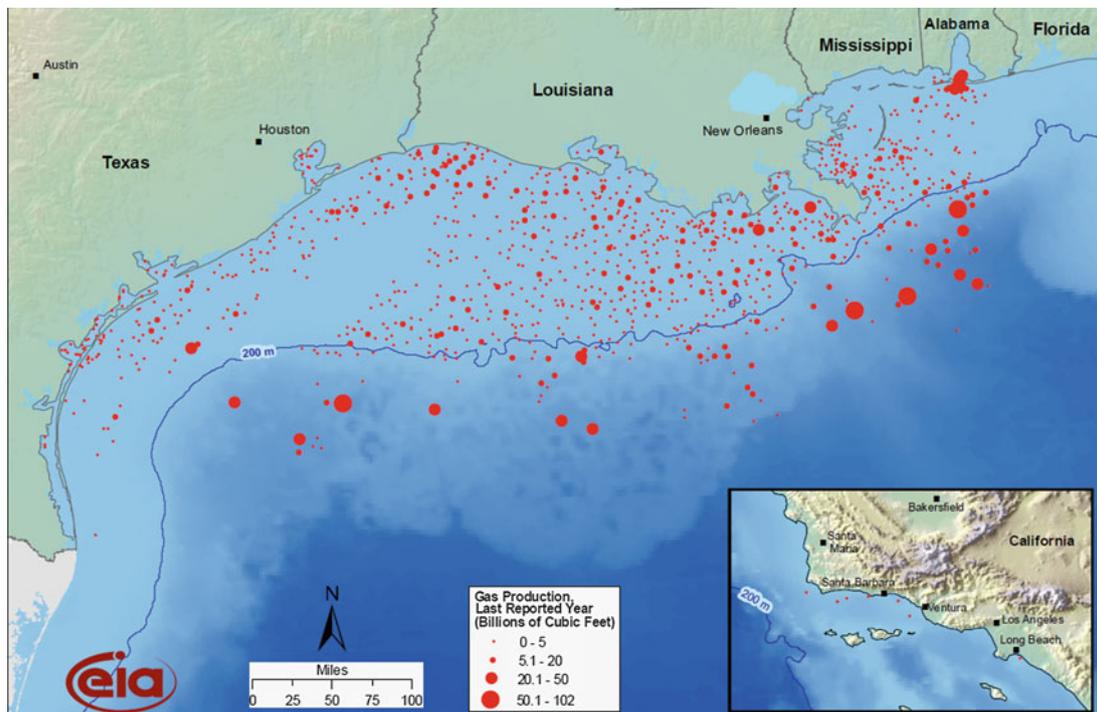


Figure 4.21. Map of offshore gas production in the Gulf of Mexico (from Energy Information 2009).

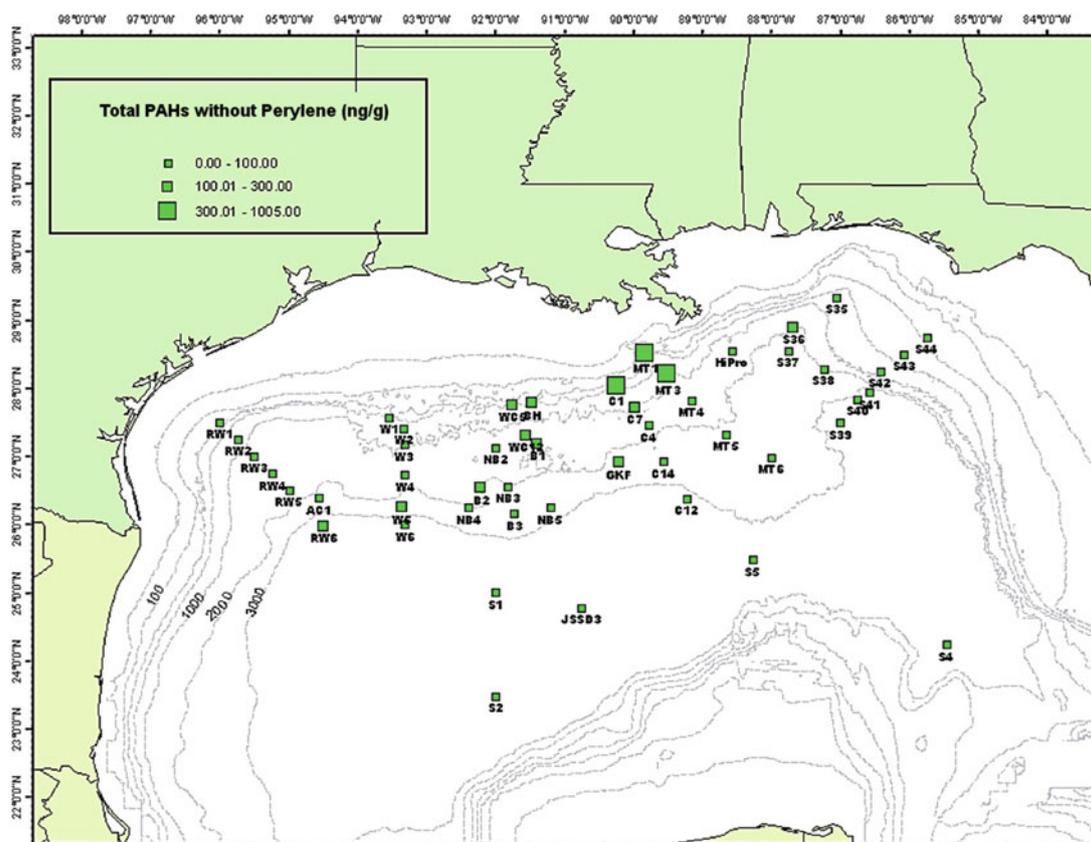


Figure 4.22. Concentration of total polycyclic aromatic hydrocarbons (PAHs: without perylene) in northern Gulf of Mexico continental slope/abyss sediments. Perylene is a naturally occurring PAH and is not suggestive of fossil fuel-derived PAH (ng/g = ppb; 1,000 ng/g = 1 ppm) (modified from Rowe and Kennicutt 2009).

than 0.5 part per thousand [ppt]—a marker for drill mud discharges) (Figure 4.24). A few sites had elevated Ba and PAH concentrations indicating platform discharges as a possible source. Median PAH concentrations were one-quarter that reported for coastal sediments. The highest total PAH sediment concentrations were four or more times lower than ERL values. Elevated PAH concentrations and compositions at three locations near the Mississippi Canyon were believed to be sourced in Mississippi River outflows. Average concentrations of Ag, Cd, Cu, Hg, Pb, and Zn were similar to average crustal abundances and sediments from the northern Gulf of Mexico, which are thought to be uncontaminated. Metal concentrations and ratios were similar to those for Mississippi River Delta sediment as well (Table 4.1). The few elevated metal concentrations were attributed to natural diagenetic remobilization processes. Enrichments of Ba compared to average crustal material and clay-rich sediments were traced to the presence of drilling muds (Figure 4.24).

These conclusions regarding the distribution and concentrations of naturally occurring metals in offshore northern Gulf of Mexico sediments have been confirmed by many other studies (Table 4.3) (Tieh and Pyle 1972; Tieh et al. 1973; Trefry and Presley 1976a, b; Presley et al. 1980; Trefry et al. 1985; Kennicutt et al. 1996). Presley et al. (1980) reports that sediments from a 1,500 square kilometer (km²) (579 square mile [mi²]) area of the Mississippi River Delta had Pb and Cd concentrations 10–100 % higher than background levels. Vertical

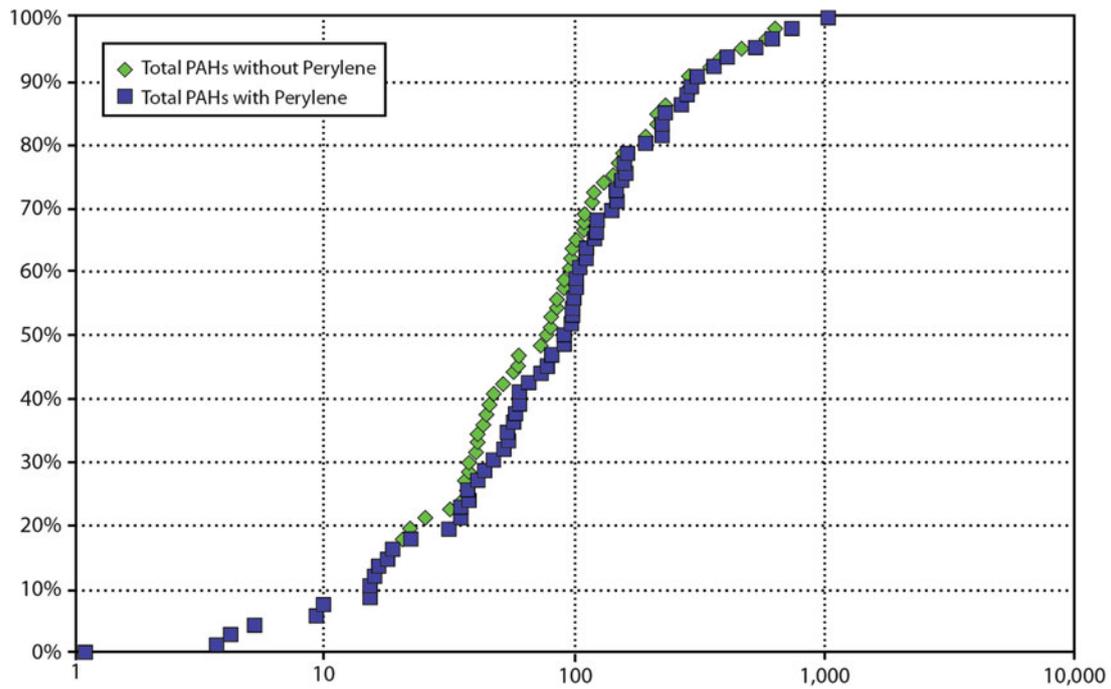


Figure 4.23. Frequency distribution of total PAH and total PAH without perylene concentrations (ppb) versus cumulative percentage in the northern Gulf of Mexico continental slope/abyss sediments. Perylene is a naturally occurring PAH and is not suggestive of fossil fuel-derived PAH (modified from Rowe and Kennicutt 2009).

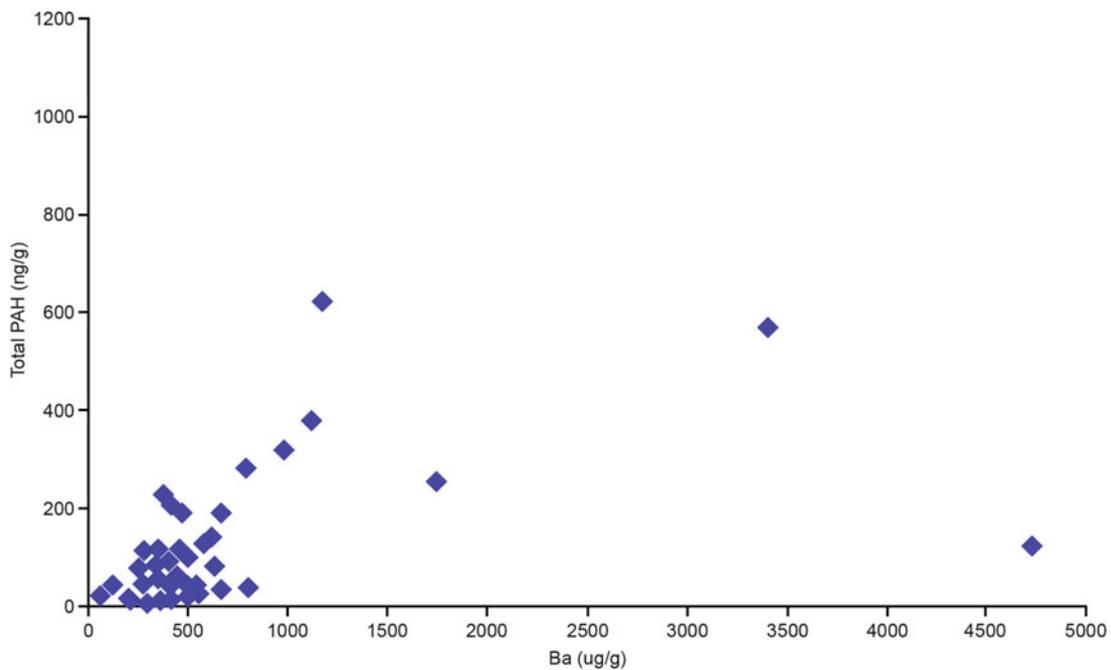


Figure 4.24. PAH concentrations without perylene (ng/g [ppb]) versus barium concentrations ($\mu\text{g/g}$ [ppm]) in the northern Gulf of Mexico continental slope/abyss sediments. Perylene is a naturally occurring PAH and is not suggestive of fossil fuel-derived PAH (modified from Rowe and Kennicutt 2009).

Table 4.3. Examples of Background Contaminant Concentrations in the Gulf of Mexico Sediment, Mississippi River Particulates, and Mississippi Delta Particulates and Cores

	Gulf of Mexico Sediment	Mississippi River Particulates	Mississippi Delta Particulates	Mississippi Delta Sediment Cores
<i>Metal</i>				
Cr (µg/g)	60–90 ^a , 22–100 ^b	72 ^c , 74 ^d , 80 ^e	84 ^e	
Cu (µg/g)	20–30 ^a	33 ^c , 21 ^d , 45 ^e	56 ^e	23–27 ^e , 21–25 ^f
Ni (µg/g)	25–40 ^a , 27–42 ^b	41 ^c , 37 ^d , 55 ^e	56 ^e	32–42 ^e
As (µg/g)	10–15 ^a	8 ^d		
Cd (µg/g)	0.2–0.3 ^b	1.3 ^e	1.5 ^e	0.3–0.8 ^e , 0.2–0.4 ^f
Pb (µg/g)	17–32 ^b	46 ^e	49 ^e	24–41 ^e , 23–37 ^f
Zn (µg/g)	50–70 ^b	193 ^e	244 ^e	110–140 ^e , 125–155 ^f
Ba (µg/g)	805–1,478 ^g			400–1,300 ^f , 50–500 ^h
V (µg/g)				14–50 ^h
<i>SVOC</i>				
PAH (ng/g)	43–748 ^g			200–800 ^f , 180–2,400 ^h
PCB (ng/g)				0–22 ^f
DDT (ng/g)				0–1.6 ^f , <10 ^h

Note: ng/g—nanogram(s) per gram [ppb]; µg/g—microgram(s) per gram [ppm]

^aTrefry and Presley (1976a), Presley et al. (1980), Trefry et al. (1985), Kennicutt et al. (1996), Continental Shelf Associates (2006)

^bUncontaminated far-field sites only CSA (2006)

^cTrefry and Presley (1976b)

^dHorowitz et al. (2001)

^ePresley et al. (1980)

^fSantschi et al. (2001)

^gCSA (2006)

^hTurner et al. (2003)

distributions of contaminant concentrations suggested that these elevated levels were due to human-derived inputs and had occurred over the previous 30–40 years. However, the authors found no indication of metal contamination in other areas of the delta or along the continental shelf of the northwest Gulf of Mexico. The authors conclude that there was little evidence of elevated metal concentrations (except Cd and Pb) attributable to humans along the northwestern Gulf of Mexico continental shelf. In contrast, introductions of metals in such places as Corpus Christi Harbor and the Houston Ship Channel were readily recognized as being elevated above background levels. For additional discussion of the input of contaminants related to the Mississippi River and a historical perspective, see Section 4.4.4.

Other than natural petroleum seepage, discharges associated with the extraction of oil and gas have the greatest potential to contaminate sea-bottom sediments in the offshore region (NRC 2003). The exploration for and extraction of petroleum in the offshore routinely discharges produced waters and drill muds and cuttings. In addition, runoff waters from structures, emissions from platforms, and accidental spills can release contaminants to the

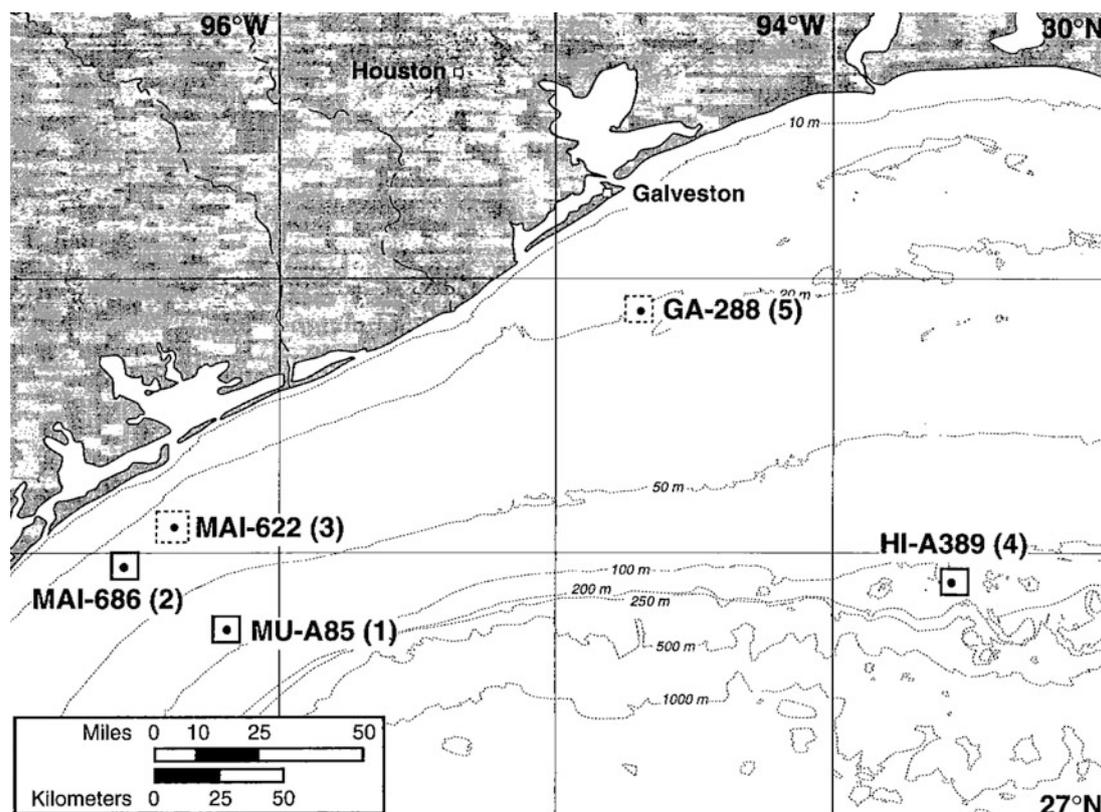


Figure 4.25. Location of the three GOOMEX study sites (sites 1, 2, and 4) (modified from Kennicutt 1995).

offshore environment. The volumes and frequencies of these releases are highly variable and generally low compared with coastal sources. Greater than 90 % of the petroleum released during extraction activities is due to produced water discharges which release low but continuous amounts of dissolved components and dispersed crude oil to the marine environment. Since produced waters mostly contain dissolved contaminants little is deposited in sea-bottom sediments in the deeper water regions of the offshore unless the discharge point is directly onto the sea bottom. In contrast, discharges of drill muds and cuttings during drilling operations are denser than water and often end up deposited on the sea floor close to the platform.

The Minerals Management Service (MMS) program—Gulf of Mexico Offshore Operations Monitoring Experiment (GOOMEX), Phase I: Sublethal Response to Contaminant Exposure measured contaminants in sediments at three offshore platforms (Kennicutt 1995). The GOOMEX study sites were located in the northwestern Gulf of Mexico in water depths from 29 to 125 m (95–410 ft) (Figure 4.25).

During offshore drilling activities, drill muds and cuttings can be discharged in large quantities near the sea surface or shunted to near-bottom waters (Kennicutt 1995). These discharges include a variable mix of drill muds (mainly barium sulfate but also chemical additives including diesel fuel). Cuttings from the drilled sections discharged at the same time can also have variable mineralogy. Drill cuttings are occasionally oil wet with petroleum. The three sites studied in GOOMEX, purposely located outside of the influence of the Mississippi River plume, were active oil and/or gas development and production platforms for more than 10 years. There are limitations in extrapolating the GOOMEX results to other

platforms because each platform has varying drilling and discharge histories, contaminant concentrations in the discharge material, and amounts of material discharged. In addition, platforms are in widely varying water depths, the location of discharges can be different, and oceanographic settings are site dependent (i.e., current patterns can vary greatly). Two of the GOOMEX sites (HI-A389 and MU-A85) shunted platform discharges to the sea bottom. Most platform discharges are released at the sea surface so these two sites can be considered worst-case scenarios for contaminating the seabed. Discharges at the sea surface, especially in deeper water, are likely to be diluted and dispersed prior to sedimentation on the sea floor. The GOOMEX study concluded that the most common contaminants discharged at platforms were PAHs and metals, and those sediments in close proximity to the platform contained elevated concentrations. Pesticides and PCBs were not measured because little or no source was suspected at the site.

PAH concentrations were highest near the platforms and decreased rapidly with distance from the platform (Figures 4.26 and 4.27) (Kennicutt et al. 1996). Spatial patterns of PAHs and metals exhibited strong directional orientations reflective of the local current regime. With a

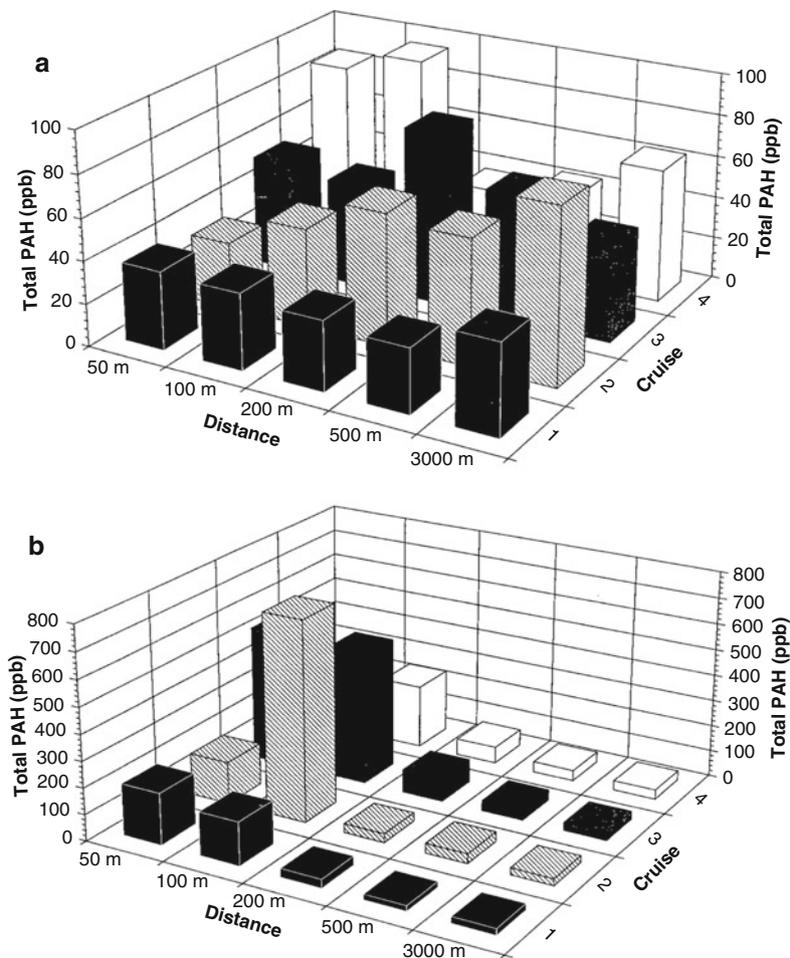


Figure 4.26. Variability in mean PAH concentrations (ppb) in sediments with distance from the platform by cruise at (a) MAI-686, (b) MU-A85, (c) HI-A389, and (d) ERL/ERM exceedances for metals for all cruises (modified from Kennicutt 1995; Kennicutt et al. 1996).

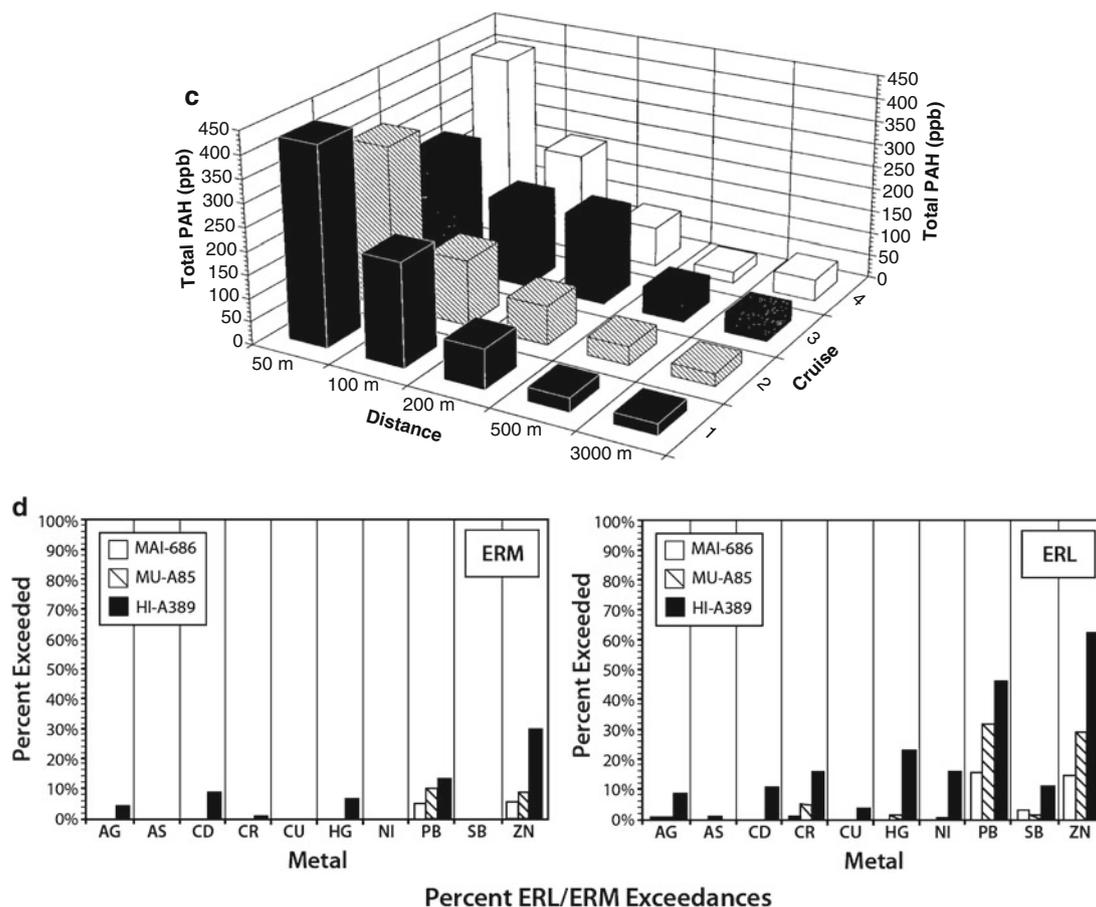


Figure 4.26. (continued)

few exceptions, most PAHs were biodegraded. Between cruises, variations at the sites were small, suggesting that contaminants in sediments were stable over a period of years in these low-energy environments. Compared to coastal sediments, PAH sediment concentrations in the vicinity of these offshore platforms were low and far below ERL values. No significant bioaccumulation of petroleum was observed in megafaunal invertebrates or fish near the platforms. Some sediment metal concentrations exceeded ERL and ERM values (Figure 4.26). The aerial extent of chemicals in sediments was contaminant dependent (i.e., PAHs to 200 m [656 ft]; Ba to greater than 500 m [1,640 ft]) (Figure 4.27).

Sediments at two of the three study sites (HI-A389 and MU-A85) exhibited gradients in Ba, Ag, Cd, Hg, Pb, and Zn concentrations with distance from the platform. Most decreases in metal concentrations correlated with decreasing Ba concentrations, a marker for drill muds, suggesting that Cu and Hg were constituents of the barite ore used in the drill muds. Cd, Pb, and Zn had no known non-drilling discharge sources. At HI-A389, Cd, Pb, and Zn sediment concentrations close to the platform were at levels that exceeded ERL and ERM values. Cr and iron (Fe) concentration distributions suggested there was a platform-related source for these metals other than drill mud and cuttings, possibly from platform drainage. Chemical concentrations were highest at sediment depths of 10–20 cm (4–8 in). At all three sites, Pb

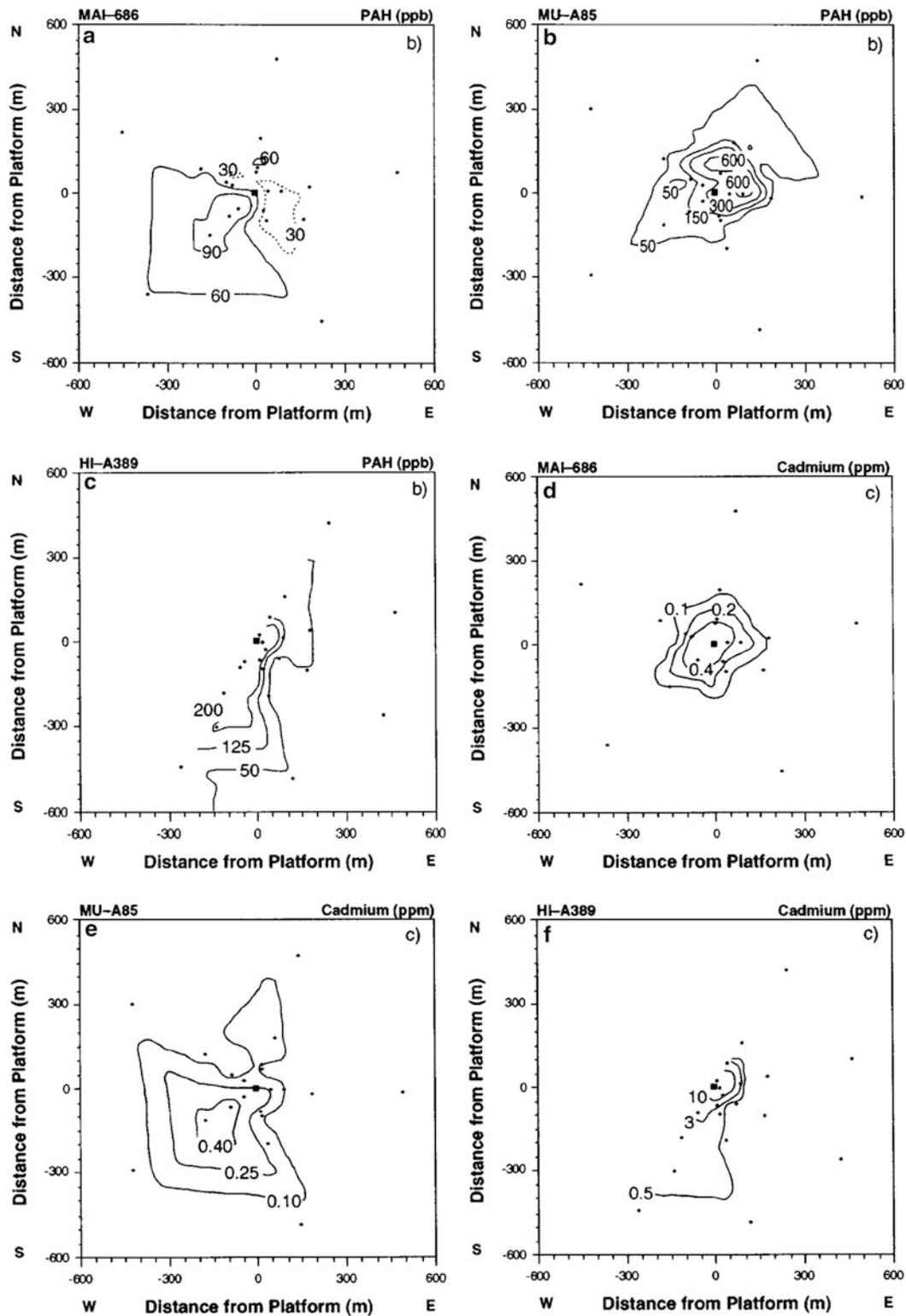


Figure 4.27. (a, b, c) Areal distribution of mean total PAH concentrations (ppb) and (d, e, f) cadmium concentrations (ppm) in sediments as a composite of four cruises at three platforms (MAI-686, MU-A85, HI-A389) in the Gulf of Mexico (modified from Kennicutt 1995; Kennicutt et al. 1996).

concentrations in sediments near the platform increased with time suggesting an ongoing release of Pb from the platform. At platforms in water depths deeper than 80 m (262 ft) contaminant concentrations were similar over a period of years. As noted above, ERL values used for Cr, Cu, Ni, and As are close to natural abundances, so exceedances based on these criteria should be considered with caution.

The GOOMEX study concluded that drill mud and cutting discharges by offshore platforms can lead to elevated contaminant concentrations in sediments within a few hundred meters of a platform. Sediments with elevated contaminant concentrations occur as thin veneers with the thickness of the veneer dependent on discharge volumes and rates and oceanographic conditions and may persist for years in low-energy environments. In higher-energy environments and instances of near-surface release, discharges are dispersed in the water before deposition in sediments and diluted with uncontaminated sediments. Metals and PAHs may be sequestered in mineral matrices (cuttings), limiting their bioavailability. Despite the large number of platforms in the northern offshore Gulf of Mexico, the density is low and the total area affected by the discharge of chemicals is expected to be a small percentage of the offshore area (e.g., within an order of magnitude, a rough estimate is that the total contaminated sediment surface area is 0.0006 % of continental shelf/slope surface area in the northern Gulf of Mexico—assuming approximately 200 m × 200 m (656 ft × 656 ft) surface zone of contaminated sediment is associated with a platform; approximately 4,000 platforms; a Gulf of Mexico surface area of approximately 1.55 million km² (600,000 mi²) with approximately 50 % in the northern region and approximately 33 % of the area underlying the continental shelf/slope area where platforms are located).

Between 2000 and 2002 the benthic impacts of drilling at four sites on the Gulf of Mexico continental slope were studied (Figure 4.28) (CSA 2006). The study was designed to document (1) drilling mud and cuttings accumulations, (2) physical modification/disturbance of the seabed due to anchors and their mooring systems, (3) debris accumulations, (4) physical/chemical modification of sediments, and (5) effects on benthic organisms. All of the sites were in water depths greater than 1,000 m (3,280 ft) and included exploration and post-development sites. Sediments were collected within a 500 m (1,640 ft) radius of the platform and far from the platform to establish background concentrations. With two exceptions, sediment PAH concentrations ranged from 0.04 to 0.748 ppm dry weight. One station had a PAH concentration of 3.5 ppm and another station had a PAH concentration of 23.8 ppm in the top 2 cm (0.75 in.). The source of the PAHs was suggested to be from drilling or production activities. Concentrations of As, Cd, Cr, Cu, Pb, Hg, and Zn were elevated in sediments near the platforms when compared with those far from the platforms. In general, elevated concentrations of metals were associated with high Ba concentrations, but even elevated concentrations were within the expected range of background concentrations for uncontaminated marine sediments.

Transportation and consumption of petroleum is widespread in the Gulf of Mexico but these activities occur mainly in coastal areas. Large petrochemical and refining complexes are located along the Texas coast, making the northern Gulf of Mexico a major destination for seaborne and pipeline transportation of petroleum (Figure 4.28) (NRC 2003). The majority of petroleum consumption occurs on land, and little of the petroleum released by these activities reaches the offshore. A potential source of contamination in the offshore region is use of fuel and emissions by ship and boat traffic including commercial ocean transportation, fisheries vessels, and recreational fishing and tourism. The transportation of petroleum by tankers can result in releases of varying sizes from major spills to small, regular operational releases. These transportation releases occur wherever vessels travel or pipelines are located. Ship traffic is much less densely concentrated in the offshore than in coastal regions, and offshore inputs



Figure 4.28. Sites for the 2000–2002 study of benthic impacts at four oil and gas platforms in the Gulf of Mexico (from Continental Shelf Associates 2006).

from transportation are low. Most petroleum releases from usage and transportation activities are less dense than water, occur at or near the air–sea interface, and are susceptible to removal by natural processes that limit deposition of petroleum in offshore sediments. In the offshore regions of the northern Gulf of Mexico, usage and transportation of petroleum are minor sources of petroleum contamination to sediments, especially compared to natural oil and gas seepage.

The offshore regions of the Gulf of Mexico have experienced oil spills over the years (Figure 4.29). For example, it is estimated that the IXTOC-I blowout in the southern Gulf of Mexico released 431,820 metric tons (476,000 ton) of petroleum over a period of approximately nine months in 1979 (NRC 2003). Oil spills can be sudden, one-time releases or can continue over time. As stated previously, in general, oil is less dense than water and oil spills result in sea surface slicks. However, over time oil weathers (e.g., loss of volatiles, microbial degradation) and incorporates enough denser sediment and particulate matter to sink to the sea bottom. Oil can also be attached to particulates that are ingested by zooplankton and excreted as fecal pellets that rapidly sink to the seafloor. Oceanic currents can keep the oil in suspension and prevent its accumulation on the bottom. In the few instances when the oil is heavier than water, the oil can sink directly to the bottom, especially in low-energy settings. Oil is sometimes released by blowouts during drilling of exploratory wells, pipeline leaks, and shipwrecks. Subsurface releases differ from surface releases in that the oil moves substantial distances beneath the surface before it rises to the surface. An NRC report (2003) concluded that the majority of the oil in most deep water releases rises to the surface having little effect on sea floor sediments. However, each oil spill can have highly differing scenarios and characteristics

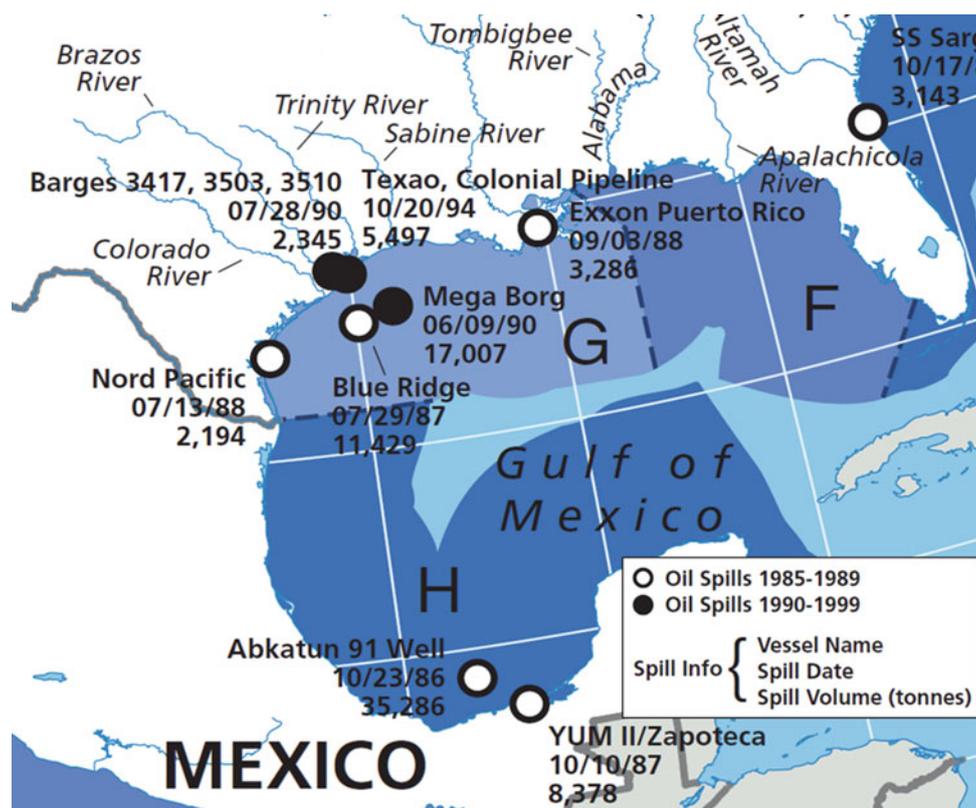


Figure 4.29. Distribution of selected oil spills in the Gulf of Mexico (volumes in tonnes/metric tonnes) of oil spilled; 1 metric ton = 1.102 U.S. short ton) (modified from NRC 2003).

so these generalities should be applied with caution. Benthic tar mats have been observed in the northern Gulf of Mexico (Figure 4.30) (Alcazar et al. 1989). Tars were altered to varying degrees by microbial degradation and dissolution. Most of the benthic tars analyzed were significantly different chemically from oils produced in the northern Gulf of Mexico. These benthic tars appeared to be derived from oils produced in other areas of the world and transported into the Gulf of Mexico by humans or ocean currents.

4.4.3 Mass Loading of Petroleum Hydrocarbons

Average annual loadings of petroleum to the northern Gulf of Mexico have been summarized (NRC 2003). Although these estimates are based on calculations of inputs and not measurements of hydrocarbons in sediment, insight into the complexities of the origins and distributions of hydrocarbons in the northern Gulf of Mexico is provided. Natural oil and gas seeps are by far the predominant sources of loadings of petroleum to the continental shelf/slope region, and there is a near absence of seeps in the coastal regions of the northern Gulf of Mexico (Figure 4.31). Hydrocarbon seeps are concentrated in the north-central region of the Gulf of Mexico at the distal end of the continental shelf and along the continental slope. The high estimated annual petroleum seepage loadings for the offshore northeastern Gulf of Mexico are due to the inclusion of a few oil and gas seeps in the north-central Gulf of Mexico (NRC 2003). Few seeps are known in the northeastern Gulf of Mexico in the coastal or offshore regions, and these regional patterns mirror the distribution of known oil and gas reserves in the

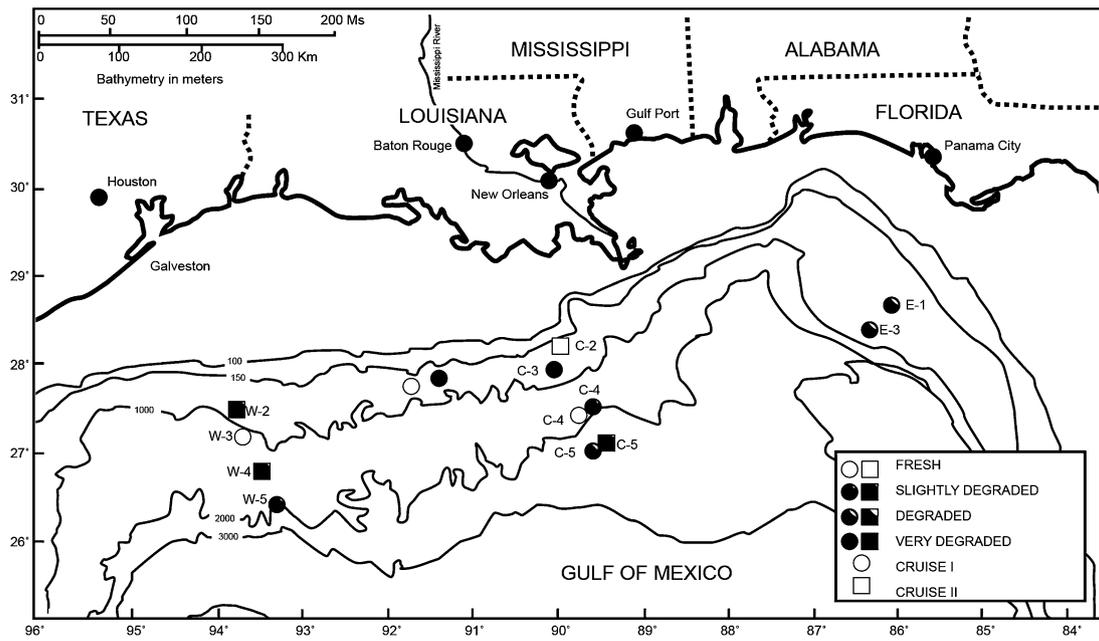


Figure 4.30. Geographic location and degree of degradation of benthic tars collected in trawls in the Gulf of Mexico (modified from Alcazar et al. 1989).

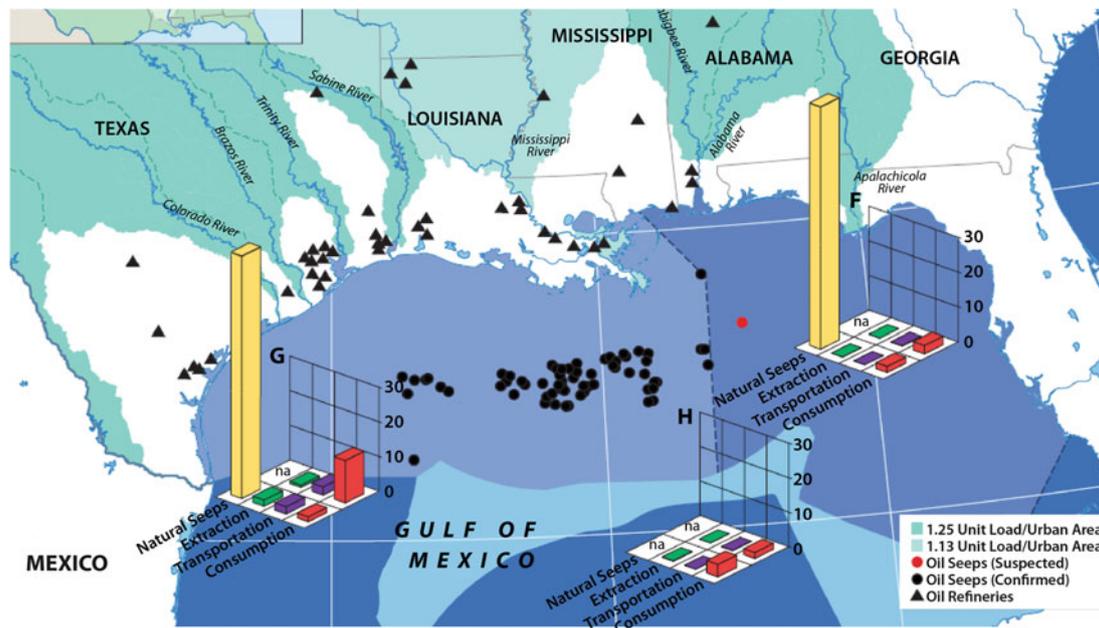


Figure 4.31. Average annual input (1990–1999) of petroleum hydrocarbons (kilotons; 1,000 ton) sources for the offshore (left histogram) and coastal (right histogram) Gulf of Mexico [Key: yellow = natural seeps, green = extraction of petroleum, purple = transportation, and red = usage; unit load/urban areas—hydrocarbons from urban areas in rivers entering Gulf of Mexico] (modified from NRC 2003).

northern Gulf of Mexico. While much less than seeps, the next highest estimated petroleum loadings in the offshore region are from extraction of petroleum and transportation activities. These loadings primarily are due to offshore oil and gas platform discharges and accidental spills included in transportation estimates. In the offshore region, estimated loadings due to petroleum usage are low. Comparing estimated petroleum loadings for extraction of petroleum and transportation in the northwestern and northeastern Gulf of Mexico, higher loadings are estimated for the northwest region where most offshore oil and gas platforms, refineries, and chemical plants are located. The highest estimated loading in the coastal northwestern Gulf of Mexico is for usage of fossil fuels, with transportation sources second highest. In the northeastern Gulf of Mexico, petroleum usage is the largest estimated loading of petroleum in the region both in the coastal and offshore regions (excluding seepage) with higher estimated loadings for usage sources in coastal areas. If all other estimated petroleum loadings across the northern Gulf of Mexico are summed, they are still far lower than estimated offshore seepage loadings. The dominant estimated anthropogenic petroleum loadings to coastal areas are from non-point petroleum usage sources in runoff from adjacent land surfaces. As mentioned, most petroleum refining and chemical operations are located in the northwestern Gulf of Mexico, accounting for the larger estimated loading inputs for petroleum usage in the northwestern as compared to the northeastern coastal regions. In addition there is significantly more onshore and coastal oil and gas production in the northwestern region of the Gulf of Mexico compared to the northeastern region. The Houston area is a major transportation hub for refineries and chemical plants. Therefore, most ship traffic in the Gulf of Mexico is destined for ports in the northwestern region, accounting for the higher transportation-related petroleum loadings in the northwestern as compared to the northeastern region. It is not possible to definitively correlate petroleum loadings and PAH concentrations in sediment, but the relative potential of sources of contamination are highlighted. It is noteworthy that PAH concentrations in coastal areas rarely exceed ERL values, and concentrations of PAH in the offshore region are even lower (with the exception of sites of natural oil and gas seepage). Natural removal processes are efficient and may account for the general lack of accumulation of PAHs in sediments to concentrations above ERL values as compared to persistent contaminants such as pesticides and metals. However, catastrophic spills/releases of large volumes of petroleum can and have resulted in significant environmental impact in coastal and offshore regions.

4.4.4 Temporal Variations

Studies of temporal variations in sediment contaminants on the continental shelf/slope and abyss of the Gulf of Mexico are limited. The analysis of dated cores provides a perspective on the origins of contaminants over time (Presley et al. 1980; Trefry et al. 1985; Santschi et al. 2001; Turner et al. 2003; Overton et al. 1986). Studies of suspended particulates, filtered water, and sediment collected in and near the Mississippi River indicated that more than 90 % of the metal load of the river was associated with particulate matter that was relatively constant in chemical composition (Presley et al. 1980). Mississippi River-suspended material was similar to average crustal rocks for Fe, Al, V, Cr, Cu, cobalt (Co), manganese (Mn), and Ni concentrations. In contrast, Zn, Cd, and Pb were enriched most likely due to the activities of humans. Profiles of contaminant concentrations in sediment cores from the Mississippi River Delta documented concentrations of metals and organic contaminants typical of uncontaminated Gulf of Mexico sediments (Santschi et al. 2001) (Table 4.2). Contaminant inputs, when present, were highest in the 1950s–1970s, decreasing to mostly background levels in more recent times.

In another study, PAHs indicative of pyrogenic sources, hopanes indicative of petrogenic hydrocarbons, and pesticides were studied in a series of sediment cores (Turner et al. 2003;

Overton et al. 1986). The results suggest low but chronic deposition of contaminants from oil and gas exploration activities, natural seeps, and agricultural pesticide usage (Turner et al. 2003). PCBs were not detected. Pesticide and PAH concentrations first increased above background concentrations after World War II. Hopanes, interpreted as indicators of petroleum, were present throughout the cores, and concentrations gradually increased after the 1950s as oil and gas activities intensified. Pesticide concentrations increased with the first use and peak application of pesticides. The authors suggest that decreases in annual usage, the phase-out of certain pesticides in the late 1970s and 1980s, flood events, microbial degradation, gravity-driven sediment transport, and post-depositional mixing from storm surges might account for variations in pesticide concentrations over time (Turner et al. 2003). Pyrogenic and petrogenic PAH contamination in sediments gradually increased from the time of first oil exploration activities in the 1950s. Pyrogenic (combustion sourced) PAH had an inverse relationship with petroleum-derived hydrocarbons. The authors suggest that heavier suspended particles settle out in the shelf area closest to the mouth of the river; therefore, concentrations of contaminants would be expected to be higher near the river's sediment plume and decrease as the sediment plume moves west and offshore (Turner et al. 2003). The highest concentrations of pyrogenic PAH occurred in areas of highest sediment deposition off the mouth of the Mississippi River. Pyrogenic PAH concentrations generally decreased in a westerly direction away from the river mouth. Anomalously high PAH concentrations were possibly associated with marsh-burning practices and estuarine runoff (Turner et al. 2003). The authors suggest that higher hopane concentrations had their origins in natural hydrocarbon seeps and/or oil and gas exploration activities. Sediment Ba distributions coincided with the use of barite as a drill mud in offshore oil and gas exploration. In contrast, sediment concentrations of V, a strengthening component of metal alloys, correlated with national consumption rates for steel. Cu, Cd, and Zn concentrations in sediments fluctuated coincidentally with V but not Ba. The method used in this study leached sediments with acid and peroxide so the sediments were not completely dissolved. V and Al concentrations are only a fraction of the total, and results should be interpreted with caution. The authors conclude that the dominant origin of contaminant metals in offshore sediments was riverine sources and not sources on the continental shelf. The authors further conclude that the Mississippi River was a regional source of pesticides and pyrogenic PAHs to offshore sediments and that atmospheric inputs were minimal. These results are consistent with other historical reconstructions of contaminant loadings (Barber and Writer 1998; Boehm and Farrington 1984; Carr et al. 1996; Overton et al. 1986).

4.5 SUMMARY

Sediments are vital to the health of aquatic environments. However, the presence of elevated concentrations of contaminants can adversely degrade sediment quality, which may affect organisms and ecosystems and possibly human health. The chemicals most widely found in sediments of the northern Gulf of Mexico that have the highest likelihood of causing detrimental biological effects are PAHs, pesticides, PCBs, Pb, Hg, As, Cd, Ag, Ni, Sn, Cr, Zn, and Cu. The potential for harmful effects by these chemicals is due to their toxicological and physicochemical properties, their widespread use and release by humans, bioavailability, accumulation in sediments and lipid-rich biological tissues, and persistence in the environment. Contaminants have been released to the Gulf of Mexico for many years and continue to be released by a wide range of human activities most highly concentrated in coastal areas. Accidental or intentional release of contaminants can be traced to population centers and urban-associated discharges; agricultural practices, industrial, military and transportation activities; and the exploration and production of oil and gas.

PAHs and some metals have natural as well as human-related sources. A portion of these chemicals ultimately end up in coastal, and to a much lesser extent, offshore sediments. Inputs of these chemicals to the environment are spatially and temporally variable in composition and concentrations. Sediments are integrators of input, breakdown, and removal processes. The mixture of contaminants and concentrations found in sediments at a location is often unique and variable over small spatial scales. In the 1980s, the NOAA NS&T Program (NOAA 1991) observed that the highest concentrations of contaminants in sediments were located close to population centers. In the 1990s, EMAP and REMAP (USEPA 1998, 1999) concluded that although measurable concentrations of contaminants were present in almost all estuaries of the northern Gulf of Mexico, less than 25 % of the estuarine area had contaminant concentrations that exceeded concentrations suspected of causing biological effects. NCCR I (USEPA 2001) concludes that the overall coastal condition was fair to poor, with 51 % of the estuaries of the northern Gulf of Mexico in good ecological condition and showing few signs of degradation due to contamination. Sediment quality at the remaining locations was judged poor, and contaminant concentrations exceeded levels suspected of causing biological effects at many locations. Most exceedances were for pesticides and metals while PCB and PAH exceedances occurred at less than 1 % of the locations. Enrichments in sediment contaminant concentrations were attributed to humans. In the 2000s, NCCR II (USEPA 2004) concluded that the overall condition of the northern Gulf of Mexico coast was fair. ERM exceedances occurred mainly in Texas and Mobile Bay, and no exceedances were observed along the Florida Gulf Coast. Pesticides and metals exceeded concentrations suspected of causing biological effects at some locations but few PCB and PAH exceedances were observed. In NCCR III (USEPA 2008), the sediment contaminant index was rated as fair and poor for 1 and 2 % of coastal areas, respectively, indicating that approximately 97 % of the coastal area had fewer than five chemicals that exceeded sediment concentrations suspected of causing biological effects. Elevated concentrations of pesticides and metals and occasionally PCBs and PAHs were observed in sediments but few exceeded concentrations suspected of causing biological effects. In NCCR IV (USEPA 2012), the sediment contaminants indicator was rated good with 2 % and approximately 3 % of coastal areas rated as fair and poor, respectively, indicating that approximately 95 % of the coastal areas had fewer than five chemicals that exceeded concentrations suspected of causing biological effects. Elevated concentrations of metals and pesticides, and occasionally PCBs and PAHs, in sediments were observed but few concentrations exceeded biological effect values. Finer-scale monitoring in bays documented steep gradients in contaminant concentrations close to shore near population centers and industrial complexes. The highest concentrations of contaminants in coastal sediments were generally restricted to hot spots of limited spatial extent associated with unique contaminant sources, but a few bays contained extensive areas of contaminated sediments.

Concentrations of contaminants rapidly decrease with distance offshore. Petroleum found in continental shelf/slope sediments is almost exclusively due to natural oil and gas seepage. Few releases of petroleum in the offshore region attributable to humans reach the underlying sediments. The one exception is the discharge of petroleum and metal-contaminated drill muds and cuttings from platforms. Deposits of contaminated sediments from these discharges are restricted to within a few hundred meters of the discharge point. They usually occur as thin veneers less than a few meters thick and become diluted with uncontaminated sediments with time due to the action of currents. Given the immense area of sea bottom in the offshore region, these localized, contaminated sediment deposits are expected to have limited impact. Contaminant concentrations in the offshore region are low, and PCBs and pesticides are generally absent. Contaminated sediments close to platforms measured over a period of years were similar, with a few exceptions such as increase in Pb concentrations and rates of microbial degradation of petroleum, most likely due to the low-energy setting and slower rates of

removal processes. It is expected that offshore areas will remain relatively uncontaminated by chemicals attributable to humans for the foreseeable future.

In conclusion, sediment contaminants have threatened and will continue to threaten the quality of the environment in the coastal regions of the northern Gulf of Mexico, but much less so in the offshore region. Elevated concentrations of pesticides and metals in coastal areas are of most concern, but the mixture of chemicals and concentrations can be highly variable in time and space. In coastal areas, pesticides and metals account for most exceedances of concentrations suspected of causing biological effects, and these exceedances appear to be decreasing with time. Assessments suggest a decrease in contamination of coastal sediments in the northern Gulf of Mexico, but there is a high degree of spatial and temporal variability from location to location. The usage of some chemicals has been banned and/or decreased over time (e.g., certain pesticides), and sediment concentrations of these chemicals are expected to continue to decline. Continued reductions in emissions and discharges and remediation of contaminated sites can be expected to accelerate improvements in sediment contaminant levels thus reducing the role of sediment contaminants in degrading environmental quality in the northern Gulf of Mexico.

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APPENDIX A: CHARACTERISTICS OF COMMON SVOC CONTAMINANTS

Table A.1. Characteristics of Common SVOC Contaminants (^aERL/ERM values from Long and Morgan 1990 (top) and NOAA 1999 (bottom); origins, toxicity, and fate are modified from Kimbrough et al. 2008)

Sources	Toxicity	Fate	Biological Effect Values (ppb)	
			ERL	ERM
<i>Chlordanes</i> (a group of organic pesticides called cyclodienes. It is a technical mixture whose principal components are alpha-chlordane, gamma-chlordane, heptachlor, and nonachlor)				
Chlordane, an insecticide, is a complex mixture of at least 50 compounds. It was used in the United States during 1948–1983 for agricultural and urban settings to control insect pests. It was also the predominant insecticide for the control of subterranean termites. Agricultural uses were banned in 1983, and all uses were banned by 1988	Exposure to chlordane can occur through eating crops from contaminated soil, fish, and shellfish from contaminated waters, or breathing contaminated air. Chlordane can enter the body by being absorbed through the skin, inhaled, or ingested. At high levels, chlordane can affect the nervous system, digestive system, brain, and liver, and is also carcinogenic. Chlordane is highly toxic to invertebrates and fish	Removal from both soil and water sources is primarily by volatilization and particle-bound runoff. In air, chlordane degrades as a result of photolysis and oxidation. Chlordane exists in the atmosphere primarily in the vapor-phase, but the particle-bound fraction is important for long-range transport. Chlordane binds to dissolved organic matter, further facilitating its transport in natural waters	0.5 [NA]	6 [NA]
<i>Total DDT</i>				
DDT is used against agricultural pests and mosquito control. Its use in the United States was banned in 1972, but it is still used in some countries today	Due to its environmental persistence and hydrophobic nature, DDT bioaccumulates in organisms. Many aquatic and terrestrial organisms are highly sensitive to DDT. As a result of DDT's toxic effects on wildlife, in particular birds, its usage was banned in the United States	DDT transforms to DDD and DDE, the latter being the predominant form found in the environment. Evaporation of DDT from soil followed by long distance transport results in its widespread global distribution. DDT and its transformation products are persistent and accumulate in the	3 [1.58]	350 [46.1]

(continued)

Table A.1. (continued)

Sources	Toxicity	Fate	Biological Effect Values (ppb)	
			ERL	ERM
		environment because they resist biodegradation. DDT that enters surface waters is subject to volatilization, adsorption to suspended particulates and sediment, and bioaccumulation. About half of the atmospheric DDT is adsorbed to particulates		
<i>Dieldrin</i>				
Dieldrin is defined as the sum of two compounds, dieldrin and aldrin. Dieldrin and a related compound (aldrin) were widely used as insecticides in the 1960s for the control of termites around buildings and general crop protection from insects. In 1970, all uses of aldrin and dieldrin were cancelled based on concern that they could cause severe aquatic environmental change and their potential as carcinogens. The cancellation was lifted in 1972 to allow limited use of aldrin and dieldrin, primarily for termite control. All uses of aldrin and dieldrin were again cancelled in 1989	Exposure to aldrin and dieldrin occurs through ingestion of contaminated water and food products, including fish and shellfish, and through inhalation of indoor air in buildings treated with these insecticides. Aldrin is rapidly metabolized to dieldrin in the human body. Acute and long-term human exposures are associated with central nervous system intoxication. Aldrin and dieldrin are carcinogenic to animals and classified as likely human carcinogens	Aldrin is readily converted to dieldrin, while dieldrin is resistant to transformation. Dieldrin bioaccumulates and is magnified through aquatic food chains and has been detected in tissue of freshwater and saltwater fish and marine mammals. Aldrin and dieldrin applied to soil are tightly bound, but may be transported to streams and rivers by soil erosion. Volatilization is the primary loss mechanism from soil. Dieldrin undergoes minor degradation to photodieldrin in marine environments	0.02 [NA]	8 [NA]

(continued)

Table A.1. (continued)

Sources	Toxicity	Fate	Biological Effect Values (ppb)	
			ERL	ERM
<i>Polycyclic aromatic hydrocarbons (PAHs)</i> : NOTE: ERL/ERM values are available for individual PAH compounds)				
PAHs are found in creosote, soot, petroleum, coal, and tar. PAHs can also have natural sources (e.g., forest fires, volcanoes) in addition to anthropogenic sources (auto emissions, home heating, coal-fired power plants). PAHs are formed by the fusing of benzene rings during the incomplete combustion of organic materials. They are also found in oil and coal. The main sources of PAHs to the environment are forest fires, coal-fired power plants, and automobile exhaust and local releases of oil	Made up of a suite of hundreds of compounds, PAHs exhibit a wide range of toxicities. Human exposure to PAHs can come as a result of being exposed to smoke from forest fires, automobile exhaust, home heating using wood, grilling and cigarettes. Toxic responses to PAHs in aquatic organisms include reproduction inhibition, mutations, liver abnormalities and mortality. Exposure to aquatic organisms can come as a result of oil spills, boat exhaust and urban runoff	The fate and transport of PAHs is variable and dependent on the physical properties of each individual compound. Most PAHs strongly associate with particles; larger PAH compounds (high molecular weight) associate to a higher degree with particles relative to smaller PAH compounds (low molecular weight). Smaller compounds predominate in petroleum products whereas larger compounds are associated with combustion	4,000 [4,022]	35,000 [44,792]
<i>Polychlorinated biphenyls (PCBs)</i> (there are 209 possible PCB compounds, called <i>congeners</i> that were marketed as mixtures known as Aroclor)				
PCBs are synthetic organic chemicals composed of biphenyl substituted with varying numbers of chlorine atoms. They were manufactured between 1929 and 1977. PCB use was regulated in 1971; new uses were banned in 1976. PCBs were used in electrical transformers, capacitors,	The main human exposure route for PCBs is through eating contaminated seafood and meats. PCBs are associated with skin ailments, neurological and immunological responses and at high doses can decrease motor skills and cause liver damage and memory loss. Exposure of aquatic	PCBs are persistent in the environment and associate with particles in aquatic systems as a result of their strong hydrophobic nature. They are long lived in the environment; improper disposal and leakage is responsible for environmental introduction	50 [22.7]	400 [180]

(continued)

Table A.1. (continued)

Sources	Toxicity	Fate	Biological Effect Values (ppb)	
			ERL	ERM
lubricants, and hydraulic fluids. Other uses included paints, adhesives, plasticizers, and flame retardants. Manufacturing of PCBs for use as flame retardants and lubricants stopped in 1977. Currently, PCBs are predominately used in electrical applications and can still be found in transformers and electrical equipment	life to PCBs results in birth defects, lowered fecundity, cancer, and death. PCBs are hazardous because they are toxic, degrade slowly, and bioaccumulate			

^aERL—concentration of a chemical in sediments that resulted in biological effects approximately 10 % of the time based on literature

ERM—Concentration that resulted in biological effects approximately 50 % of the time based on literature

APPENDIX B: CHARACTERISTICS OF COMMON METAL CONTAMINANTS

Table B.1. Characteristics of Common Metal Contaminants (^aERL/ERM values from Long and Morgan 1990 (top) and NOAA 1999 (bottom); origins, toxicity, and fate are modified from Kimbrough et al. 2008)

Origins	Toxicity	Fate	Biological Effect Values (ppm)	
			ERL	ERM
<i>Arsenic (As)</i>				
Arsenic has natural and industrial sources. Products that contain arsenic include preserved wood, semiconductors, pesticides, defoliants, pigments, antifouling paints, and veterinary medicines. In the recent past, as	Arsenic is toxic at high concentrations to fish, birds, and plants. In animals and humans prolonged chronic exposure is linked to cancer. Inorganic arsenic, the most toxic form, represents approximately 10 % of total arsenic in bivalves. Less	Human activities have changed the natural biogeochemical cycle of arsenic leading to contamination of land, water, and air. Arsenic in coastal and estuarine water occurs primarily from river runoff and atmospheric deposition. The	33 [8.2]	85 [70]

(continued)

Table B.1. (continued)

Origins	Toxicity	Fate	Biological Effect Values (ppm)	
			ERL	ERM
much as 90 % of arsenic was used for wood preservation. Atmospheric sources of arsenic include smelting, fossil fuel combustion, power generation, and pesticide application	harmful organic forms, such as arsenobetaine, predominate in seafood	major source of elevated levels of arsenic in the nation is natural crustal rock		
<i>Cadmium (Cd)</i>				
Cadmium occurs naturally in the earth's crust as complex oxides and sulfides in ores. Products that contain cadmium include batteries, color pigment, plastics, and phosphate fertilizers. Industrial sources and uses include zinc, lead, and copper production, electroplating and galvanizing, smelting, mining, fossil fuel burning, waste slag, and sewage sludge. Anthropogenic emissions originate from a large number of diffuse sources	Cadmium is toxic to fish, salmonoid species, and juveniles are especially sensitive, and chronic exposure can result in reduction of growth. Respiration and food represent the two major exposure pathways for humans to cadmium	Cadmium has both natural and non-point anthropogenic sources. Natural sources include river runoff from cadmium-rich soils, leaching from bedrock, and upwelling from marine sediment deposits. Cadmium is transported by atmospheric processes as a result of fossil fuel burning, erosion, and biological activities. Land-based runoff and ocean upwelling are the main conveyors of cadmium into coastal environments. Elevated cadmium levels are primarily located in freshwater-dominated estuaries consistent with river transport of cadmium to coastal environments	5 [1.2]	9 [9.6]

(continued)

Table B.1. (continued)

Origins	Toxicity	Fate	Biological Effect Values (ppm)	
			ERL	ERM
<i>Copper (Cu)</i>				
<p>Copper is a naturally occurring ubiquitous element in the environment. Trace amounts of copper are an essential nutrient for plants and animals. Anthropogenic sources include mining, manufacturing, agriculture, sewage sludge, antifouling paint, fungicides, wood preservatives, and vehicle brake pads. The United States ranks third in the world for utilization and second in production. The USEPA phase-out of chromated copper arsenate (CCA) wood preservatives and the 1980s restrictions on tributyltin marine antifouling paints have stimulated a transition to copper-based wood preservatives and marine antifouling paint</p>	<p>Copper can be toxic to aquatic organisms; juvenile fishes and invertebrates are much more sensitive to copper than adults. Although copper is not highly toxic to humans, chronic effects of copper occur as a result of prolonged exposure to large doses and can cause damage to the digestive tract and eye irritation. Atmospheric transport and deposition of particulate copper into surface waters may also be a significant source of copper to coastal waters</p>	<p>The most common form of copper in water is Cu (II); it is mostly found bound to organic matter. Transport of copper to coastal and estuarine water occurs as a result of runoff and river transport</p>	<p>70 [34]</p>	<p>290 [270]</p>
<i>Lead (Pb)</i>				
<p>Lead is a ubiquitous metal that occurs naturally in the earth's crust. Environmental levels of lead increased worldwide over the past century</p>	<p>Lead has no biological use and is toxic to many organisms, including humans. Exposure of fish to elevated concentrations of lead results in</p>	<p>Loadings of lead into coastal waters are primarily linked with wastewater discharge, river runoff, atmospheric deposition, and natural weathering of rock. Lead can</p>	<p>35 [46.7]</p>	<p>210 [218]</p>

(continued)

Table B.1. (continued)

Origins	Toxicity	Fate	Biological Effect Values (ppm)	
			ERL	ERM
because of leaded gasoline use. Significant reductions in source and load resulted from regulation of lead in gasoline and lead-based paints. High levels found in the environment are usually linked to anthropogenic activities such as manufacturing processes, paint and pigment, solder, ammunition, plumbing, incineration, and fossil fuel burning. In the communications industry, lead is still used extensively as protective sheathing for underground and underwater cables, including transoceanic cable systems	neurological deformities and black fins in fish. Lead primarily affects the nervous system, which results in decreased mental performance and mental retardation in humans. Exposure to lead may also cause brain and kidney damage, and cancer	be found in air, soil, and surface water		
<i>Mercury (Hg)</i>				
Mercury is a highly toxic, nonessential trace metal that occurs naturally. Elevated levels occur as a result of human activity. In the United States, coal-fired electric turbines, municipal and medical waste incinerators, mining, landfills, and sewage sludge are the primary emitters of mercury into the air	Mercury is a human neurotoxin that also affects the kidneys and developing fetuses. The most common human exposure route for mercury is the consumption of contaminated food. Children, pregnant women or women likely to become pregnant are advised to avoid consumption of swordfish, shark, king mackerel, and	In the environment, mercury may change forms (between elemental, inorganic, and organic). Natural sinks, such as sediment and soil, represent the largest source of mercury to the environment. Estimates suggest that wet and dry deposition accounts for 50–90 % of the	0.15 [0.15]	1.3 [0.71]

(continued)

Table B.1. (continued)

Origins	Toxicity	Fate	Biological Effect Values (ppm)	
			ERL	ERM
	tilefish and should limit consumption to fish and shellfish recommended by FDA and USEPA	mercury load to many estuaries, making atmospheric transport a significant source of mercury worldwide. Long-range atmospheric transport is responsible for the presence of mercury at or above background levels in surface waters in remote areas		
<i>Nickel (Ni)</i>				
Nickel is a naturally occurring, biologically essential trace element that is widely distributed in the environment. It exists in its alloy form and as a soluble element. Nickel is found in stainless steel, nickel-cadmium batteries, pigments, computers, wire, and coinage; and is used for electroplating	Food is the major source of human exposure to nickel. Exposure to large doses of nickel can cause serious health effects, such as bronchitis, while long-term exposure can result in cancer. There is no evidence that nickel biomagnifies in the food chain	Nickel derived from weathering rocks and soil is transported to streams and rivers by runoff. It accumulates in sediment and becomes inert when it is incorporated into minerals. River and stream input of nickel are the largest sources for oceans and coastal waters. Atmospheric sources are usually not significant	30 [20.9]	50 [51.6]
<i>Tin (Sn)</i>				
Tin sources in coastal water and soil include manufacturing and processing facilities. It also occurs in trace amounts in natural waters. Concentrations in unpolluted waters	Humans are exposed to elevated levels of tin by eating from tin-lined cans and by consuming contaminated seafood. Exposure to elevated levels of tin compounds by humans leads to	Tin enters coastal waters bound to particulates, and from riverine sources derived from soil and sediment erosion. Bioconcentration factors for inorganic tin were reported to be 1900 and 3000	NA	NA

(continued)

Table B.1. (continued)

Origins	Toxicity	Fate	Biological Effect Values (ppm)	
			ERL	ERM
and the atmosphere are often near analytical detection limits. Tin has not been mined in the United States since 1993	liver damage, kidney damage, and cancer	for marine algae and fish. Inorganic tin can be transformed into organometallic forms by microbial methylation and is correlated with increasing organic content in sediment. Tin is regarded as being relatively immobile in the environment and is rarely detected in the atmosphere. It is mainly found in the atmosphere near industrial sources as particulates from combustion of fossil fuels and solid waste		
<i>Zinc (Zn)</i>				
As the fourth most widely used metal, zinc's anthropogenic sources far exceed its natural ones. The major industrial sources include electroplating, smelting, and drainage from mining operations. The greatest use of zinc is as an anticorrosive coating for iron and steel products (sheet and strip steel, tube and pipe, and wire and wire rope). Canada is one of the largest producers and exporters of zinc. The United States is the largest customer for	Zinc is an essential nutrient. Human exposure to high doses of zinc may cause anemia or damage to the pancreas and kidneys. However, zinc does not bioaccumulate in humans; therefore, toxic effects are uncommon and associated with excessively high doses. Fish exposed to low zinc concentrations can sequester it in some cases	Dissolved zinc occurs as the free hydrated ion and as dissolved complexes. Changes in water conditions (pH, redox potential, chemical speciation) can result in dissolution from or sorption to particles. In air, zinc is primarily found in the oxidized form bound to particles. Zinc precipitates as zinc sulfide in anaerobic or reducing environments, such as wetlands, and thus is less mobile, while remaining as the free ion at lower pHs. As a result of natural and	120 [150]	270 [410]

(continued)

Table B.1. (continued)

Origins	Toxicity	Fate	Biological Effect Values (ppm)	
			ERL	ERM
Canadian refined zinc, and the automobile industry is the largest user of galvanized steel		anthropogenic activities, zinc is found in all environmental compartments (air, water, soil, and biota)		
<i>Butyltins</i>				
Tributyltin is used as an antifouling agent in marine paints applied to boat hulls. Slow release from the paint into the aquatic system retards organism attachment and increases ambient environmental levels. The United States partially banned the use of tributyltin in 1988 for use on boats less than 25 m in length, drastically limiting use on many recreational vessels	Tributyltin is an extremely toxic biocide that is regulated as a result of its toxic effects (reproduction and endocrine disruption) on nontarget aquatic species. Organotin compounds are readily bioaccumulated by aquatic organisms from water but there is no evidence for biomagnification up the food chain. Sex changes have been shown to occur in gastropods exposed to elevated levels of tributyltin	Tributyltin is sparingly soluble in water and associates readily with suspended particles in the water column. Butyltins are persistent in the aquatic environment and accumulate in sediment; therefore, they will continue to be a source of butyltin to the aquatic environment. Tributyltin transforms to dibutyltin and then to monobutyltin. Releases of organotins to the atmosphere are not significant due to their low vapor pressure and rapid photodegradation	NA	NA

^aERL—concentration of a chemical in sediments that resulted in biological effects approximately 10 % of the time based on literature

ERM—Concentration that resulted in biological effects approximately 50 % of the time based on literature

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