FLORIDA INTERNATIONAL UNIVERSITY
SOUTHEAST ENVIRONMENTAL RESEARCH CENTER

PROVIDING CONTAMINANT DATA FOR COASTAL MANAGEMENT: ASSESSING THE EFFECTS OF LAND BASED SOURCES OF POLLUTION ON COLLIER COUNTY'S ESTUARIES AND THEIR ASSOCIATED WATERSHEDS

Final Report Prepared for Collier County, Florida
Grant # 205001591

November 15, 2009

SERC TECHNICAL REPORT T-410 Revision 3

PROVIDING CONTAMINANT DATA FOR COASTAL MANAGEMENT:

ASSESSING THE EFFECTS OF LAND BASED SOURCES OF POLLUTION ON COLLIER COUNTY'S ESTUARIES AND THEIR ASSOCIATED WATERSHEDS

Prepared for the

Pollution Control and Prevention Department
Collier County, Florida.

By

Piero R. Gardinali, PhD.[1,2]
Principal Investigator
Adolfo, M Fernandez[2], MS.
Ingrid Zamora-Ley[2], MS.

In cooperation with

Genapure Laboratories (formerly USBiosystems)

[1]Southeast Environmental Research Program
and [2]Department of Chemistry and Biochemistry
Florida International University
OE-148, University Park
Miami, Florida 33199

November 2009

TABLE OF CONTENTS

EXECUTIVE SUMMARY

A comprehensive survey of current and past use sediment contaminants was conducted along the four most important watersheds and estuarine systems of Collier County, Florida. As in the previous efforts (1989-1991 and 2001-2002) the study comprised the collection of surface sediments at a total of 89 stations in a county-wide area that included estuarine, inland and special attention sampling sites. Since sediments can act as environmental sinks of many priority pollutants they were chosen as the sampling media for their value as integrative indicators. Based on the recommendations of the 2002 program conducted by FIU, and in consultation with the County and the City of Naples, sites were located along sections of Naples Bay and the Gordon River to assess the recurrent persistence of selected contaminants, in particular polynuclear aromatic hydrocarbons (PAHs) and trace metals. In addition, a comprehensive survey of sediments from inland waterways was also included in the 2007 program to address both findings from the 1989-1991 sediment quality survey conducted by the county and to expand the monitoring effort to sites under the influence of stormwater runoff, agricultural, urban, and industrial activities. Particular attention was placed on the site selection for water bodies that receive water and runoff from major roads, golf courses, agricultural fields, and wastewater treatment facilities. All sites were visited once during the end of the wet season and beginning of the dry season of 2007 (September – December 2007) in order to assess the presence and spatial trends in the sediment contamination and to infer the potential hazards related to such contamination. Contaminants measured in this project (144 parameters) included the most common organic (Polynuclear Aromatic Hydrocarbons (PAHs), Organochlorine Pesticides (OCs), Organophosphate Pesticides (OPs), Phenoxy Acid Herbicides (Phenoxy)) and inorganic

contaminants (trace metals such as lead, zinc, copper, arsenic, and chromium among others). Even though previous studies have recognized that the Gulf coast of Florida is generally less contaminated than the Atlantic coast (MacDonald et al., 1996, Cantillo et al., 1999) all the chemicals that have been identified as a priority for the Atlantic Coast and those identified by the previous surveys in the area were analyzed for this study. In recognition to the shift in usage from chlorinated pesticides to more environmentally responsible products, the target analytes were expanded to include many of the contemporary chemicals in use for crop and ornamental production in southwest Florida. Particular attention was placed on contaminants that are highly toxic, have the potential to bioaccumulate or are heavily used in the County.

All field work and sample collection was conducted by the Environmental Analysis Research Laboratory (EARL) at FIU and all chemical analyses were performed by Genapure Laboratories using National Environmental Laboratory Accreditation Conference (NELAC) accredited methods.

Results from the survey are organized in four main areas: general contaminant assessment, contaminant ranking, assessment of potential effects, and distribution patterns. Findings are also compared to previous studies in an attempt to evaluate temporal trends. In general, stations were first ranked based on the presence of contaminants. For those contaminants where a Sediment Quality Assessment Guideline (SQAGs) has been established, comparison of the occurrence to the guideline is provided. Since both saltwater and freshwater systems were sampled, two sets of SQAGs were used. For compounds like the pesticide Endosulfan, for which environmental criteria is not well described, a simple comparison to published data is provided in the report.

One of the major key findings in the 2007 survey is that, with exception of Endosulfan, all other pesticides monitored in the sediments were below the laboratory method reporting limits and thus unlikely to present any environmental hazard in the areas sampled in the project. If all hits above the method detection limits are used and the term “pesticide” is generalized to incorporate just one of the 58 pesticides/herbicides measured, only 4.5% of the samples tested positive for pesticides and only 1.1% of them had detections above the laboratory reporting level. One single finding of elevated concentrations of Endosulfan (482 ng/g d.w. as total endosulfan) at station CC056 (Oil Well Grade Rd.) just south of a major agricultural field operation was the only detection for the chlorinated pesticide group. Endosulfan is one of the last chlorinated pesticides still in use in Florida. This value is high despite increased uncertainties in the analysis resulting from sample dilution and analytical performance. This detection is close to the maximum reported in the 1989-1991 study for Haldeman Creek (695 ng/g Endosulfan Sulfate) but clearly representative of a fresh input of the insecticide as reflected by the isomer composition (EII>> EI >>>E Sulfate). There is no SQAG promulgated or proposed for Endosulfan and despite the fact that this was an isolated event in an area heavily influenced by agriculture, this sediment concentrations could be toxic for reference organisms such as *C. tentans* (Weston et.al, 2004) and should be further investigated.

Several minor detections of legacy pesticides (dieldrin at 1.69 ng/g; γ-chlordane at 1.22 ng/g; and heptachlor epoxide at 1.42 ng/g) were reported at three other sampling sites. The concentrations are low and between the laboratory method detection limit (MDL) and the method reporting limit (MRL) and thus should be interpreted with caution. These levels of legacy pesticides are well within the ones found in the 1989-1991 and the 2001-2002 surveys that reported no potential concern associated with similar concentrations since none of these values exceeded the available SQAGs. This information, combined to the fact that all these pesticides have been banned decades ago make the risk of their occurrence diminish as time passes on systems where the legacy signature is close to background levels.

For other contaminants anthropogenic signatures in the sediments were more evident and widespread. Both PAHs and metals showed exceedances of SQAGs but the level of concern for PAHs is greater than of copper, the trace element with the most exceedances of the SQAGs. As an example, when considered as Total PAHs three sites in the survey rank not only above the PEC (Probable Effect Concentration) but also showed excursions when compared to the criteria for Petroleum Contamination in sediments described in Florida Administrative Code (FAC) 62-777. Sites CC014 (1.04 mg/kg), CC018 (2.78 mg/kg) and CC036 (1.49mg/kg) exceed the soil cleanup criterion for Benzo(A)anthracene and Benzo(k)fluoranthene (2.64 mg/kg for CC014; 4.94 mg/kg for CC018; and 3.1 mg/kg for CC036 respectively) based on leachability to ground water. Of these three stations, one, CC018 was previously identified during the 1989-1991 survey (GRE896) as exceeding both the ERM (Long & Morgan 1990) and EPA criterion for Total PAHs for freshwater sediments. This finding seems to indicate a long and sustained history of contamination at the site or a continuous release of PAHs in the area.

When all stations are ranked based on the PAH concentrations (Total and individual components) and compared to the lower, more protective end of the SQAGs (Threshold Effect Level (TEL) or Threshold Effect Concentration (TEC)) a maximum of 14.6 % of the sites showed exceedances for one or more PAH making this group of contaminants the one of the greatest environmental concern in the study. Among all sites, the saltwater sediments showed a lower incidence of concentrations above the threshold level of concern (3.4%>TEL) than the freshwater sites that ranked above the TEC at a frequency of 14.6%. It is clear from this distribution that much of the future monitoring efforts should be concentrated in the inland canals and several key areas along north Naples Bay and the Gordon River. No saltwater sediment showed exceedances from the Probable Effect Level (PEL) and the stations with the highest PAH concentrations were CC007 (5.84 mg/kg), CC012 (5.42 mg/kg) and CC016 (1.82 mg/kg). These stations, all located along Naples Bay and the tributaries of the lower reach of the Gordon River, are influenced by boating activities or runoff. In contrast, sediment collected from the freshwater inland canals showed PAHs at generally higher concentrations. Three sites (CC014, CC018 and CC036) ranked above the Probable Effect Concentration (PEC) for at least four different individual PAHs but only one of them (CC018) exceeded the PEC for Total PAHs. The Probable Effect guideline indicates that detrimental effects for biological resources are possible and expresses the highest level of concern regarding sediment quality. In concurrence with this observation, eleven of the twenty parameters assessed for PAHs at these three sites were above the levels reported by NOAA as being significantly toxic for benthic organisms in Tampa Bay. The levels of Total PAHs at station CC036 (20.1 mg/kg) indicate a long-term problem at that site since the concentrations reported in 2007 are very similar than the average value reported for the same site (GRE896, 19.4 mg/kg) during the 1989-1991 program. The three stations discussed above do represent the highest levels of PAHs detected in any sediment monitoring effort in Collier County to date. To bring these numbers to a national perspective, 15.6% of the sites sampled in 2007 ranked above the 85th percentile concentration for Total PAHs (3.2 mg/kg) used in the NOAA Status and Trends Program as their “high” rank for coastal sediments.

The analysis of trace elements did generally concur with previous efforts in the occurrence, spatial distributions and the identity of elements of potential concern. Only two elements exceeded the PEL/PEC guideline in the sediment samples. Copper was elevated in 7.8% of the sites (7/89) with exceedances in both the freshwater environment (CC032, CC021) and the estuarine system (CC001, CC006, CC013, CC066, CC022). Due to the geographical distribution of the sites, is clear that copper inputs have distinctive sources. For example site CC032 is influenced by agriculture while CC021 is located in a heavily urbanized area downstream from a golf course. All of the estuarine sites, with the exception of CC066 are in close proximity of marinas and navigational channels likely influenced by copper formulations in boat bottom paint. When the TEL/TEC criteria is evaluated a total of 31% (28/89) of the sites rank above the guideline concentration. Although threshold levels are only indicative of potential concern copper is the single parameter that shows the highest frequency of excursions for a SQAG. Arsenic is the second element of potential concern with one site showing concentrations above the probable effect benchmark (CC074, 33.6 mg/kg). There is no clear indication of a potential source of arsenic at the station. When the threshold effect levels are evaluated, a total of 18% of the sites (16/89) ranked above the criterion. Half of these sites are located along Naples Bay while the other half are scattered along the urbanized areas of the County. Most of the other trace elements had fewer hits above the TEL/TEC criteria with a large proportion of the sites showing only mild signs of anthropogenic influences. For example, several stations in North Naples Bay show a trace metal distribution that is consistent with the activities in the area (CC012> TEL for Cu, Zn, and Cr) and clearly indicative of local effects. Among sampling sites of particular interest CC014 (located at the southeast corner of Naples Airport on Airport Road) shows the most chemical diversity in terms of contamination with higher than average levels of copper, zinc, lead and elevated concentrations of PAHs.

With few exceptions (elevated PAH concentrations) the results from the present survey are consistent with previous reports for sediment contamination along Collier County's watersheds (Grabe, 1990; Grabe, 1993, Grabe, 1996, Miller and Mcpherson, 1998, Cantillo, et al., 1999; Gottholm and Robertson, 1996; Johnson et al., 1999, Gardinali et al., 2002). As in previous studies, the list of contaminants of potential concern in Collier County watersheds remains consistent. Polynuclear aromatic hydrocarbons (PAHs), copper, arsenic, chromium, zinc and lead are still the parameters showing clear signs of anthropogenic influence with some of them showing indications of potential effects to biological resources. Although the scope of this report is not to address regulatory or compliance issues, the levels of individual compounds such as Benzo(a)anthracene and Benzo(k)fluoranthene in the sediments at stations CC018, CC014 and CC036 combined with the long term trends of contamination at CC018 needs to be further and promptly investigated.

Other important observation from the sediment monitoring program is that stations located in the less urbanized areas of Collier County are less susceptible to anthropogenic effects from contaminants catalogued previously as of potential concern. As an example, of the extensive monitoring or pesticides, only relevant residues of Endosulfan II were detected in 1/89 of the samples in an area clearly dominated by agriculture. None of the contemporary use pesticides and herbicides were detected in the sediment samples above the laboratory detection limits. If SR951 is used as the division between past and future land use changes, it is clear from the results that most of the contaminants are linked to development on the western side of Collier County.

Based on the results of this survey and findings of previous monitoring efforts the following recommendations are provided:

- Contamination by polynuclear aromatic hydrocarbons (PAHs) is the primary concern along Collier County watersheds and should still be the focal point of future monitoring programs.
- Source identification and site specific monitoring is required to evaluate the spatial and temporal extent of the contamination at sites CC018, CC014 and CC036.
- Copper and arsenic are the highest ranking trace elements in the sediment hazard assessment based on the SQAGs. Since sources of copper could be easily identified Best Management Practices (BMPs) will provide the best solution for addressing or controlling the sediment contamination. In the case of arsenic, additional monitoring is required to understand the inputs to Naples Bay.

- A county-wide survey sediment quality assessment should be routinely conducted every 5 years. The monitoring program should include both estuarine and inland stations keeping the focus on potential sources such as marinas, industrial facilities, wastewater release points, storm water runoff, and crop or ornamental production.
- Since the main objectives of these surveys is environmental assessment, the analysis of PAHs should be conducted using more sensitive analytical methodologies capable of sub-part per billion detection levels instead of regulatory methods with sub-part per million detection limits. Such methods are available (NOAA) and will provide the same data quality requirements of a NELAC accredited methodology.
- Keep a comprehensive list of analytes to account for past and present use contaminants :
  - a) Polynuclear aromatic Hydrocarbons,
  - b) Trace Metals,
  - d) Chlorinated hydrocarbons (legacy plus Endosulfan and Chlorpyrifos),
  - e) Re-evaluate the list of constituents for the contemporary biocides to specific needs based on use and ecological relevance.
- Adopt a set of sediment guideline criteria that triggers “warning” and “action required” stages. (i.e. two consecutive detections above the PEL/TEL SQAGs at one site in two monitoring periods). This is particularly important for PAHs, Copper and Endosulfan.

- Adopt “planning guidelines” to trigger action for contaminants that do not have a promulgated SQAG.
- Maintain a concentrated monitoring effort within north Naples Bay and the lower Gordon River in order to assess temporal changes and to track the implementations of BMPs.

INTRODUCTION

Background and Justification

Management of near coastal environments and their associated watersheds requires a careful balance between land usage and sustainability. Urban development is considered a good indicator of economic success while agriculture is likely to be a major economic driver in Southwest Florida where fertile soils allow for yearlong crop production. However, in the last decade, these two activities have become incompatible and almost exclusive of each other because the urban sprawl created by the housing market has placed large portions of agricultural lands in the hands of developers. These two effects create a complex relationship between the land usage, the freshwater components of the associated watersheds, and the coastal receiving waters. Releases of pesticides from urban and commercial horticulture, storm water runoff, and human derived wastewater are among the myriad of process that contribute to the contaminant loading to Collier County’s coastal management zones. Data summarized and generated by our previous assessment of Collier County major watersheds revealed the existence of environmental conditions requiring opposite courses of action for management purposes. The scant but important historical data available for Collier

County watersheds that was summarized for the 2001-2002 sediment monitoring study (Harriss et al., 1971; Carter et al., 1973; Thoemke and Gyorkos, 1988, Grabe 1993; Grabe 1996, Miller and Mcpherson, 1998) indicated some evidence of the presence of legacy agrochemicals such as DDT and its metabolites, components of Chlordane technical mixtures, and Endosulfan in places such as Henderson Creek, Blackwater River, Gordon River, and the freshwater canal systems along the county. Furthermore, data from NOAA's National Status and Trend " Mussel Watch" program that routinely collected oyster tissues at three stations within the county (Naples Bay: NBNB, Rookery Bay-Henderson Creek: RNHC, and Faka Union River: EVFU) have shown signs of increased urban impacts by documenting the presence of low levels of contaminants such as trace metals, pesticides and aromatic hydrocarbons (NOAA, 1999).

Based on these premises, results from the 2001-2002 chemical monitoring survey were organized in three areas for the most important pollutants: ranking, potential effects, and distribution patterns. Stations were ranked based on the presence of contaminants and the spatial patterns and distributions were examined and evaluated. For those contaminants where a Sediment Quality Assessment Guideline (SQAG) has been established (FDEP, 2000 and 2004), comparison of the occurrence to the criterion was provided. One of the key findings was the determination that most of the estuarine-driven county watersheds evaluated were in pristine to semi-pristine condition. In consequence, the effects of accelerated urbanization were difficult to determine over the natural background with the exception of several sites that were heavily influenced by localized urban activity and thus identified as areas of relative concern. Among them, North Naples Bay at the confluence of the Gordon River. Although some families of the compounds monitored were more prevalent than others in the sediments (PAHs and metals over chlorinated pesticides and PCBs) several contaminants in the study, exceeded the “Threshold Effect Levels” (TELs). Metals (arsenic, mercury, chromium, zinc, and copper), and PAHs (mainly high molecular weight ones) were among the selected group of pollutants exceeding the TEL criterion for at least one station in each sampling episode and were thus identified as priority for future assessments. As part of the study conclusions, a set of recommendations were formulated to guide future efforts to prevent further degradation of the County’s coastal environments. These recommendations pointed out to a site specific study for North Naples Bay and an extension of the contaminant monitoring to the main Gordon River watershed. In addition, the team suggested looking for other more contemporary contaminants that could be introduced by future changes of the county’s land usage pattern and/or further development of former agricultural areas. As expected, since the last sediment survey, the county has experienced an incredible rate of sustained urban development that mandated need to formulate elaborate plans to assure that future expansions are commensurate with ecosystem sustainability and to prevent environmental degradation of a relatively pristine area of Florida.

Plans for the urban expansion to areas East of CR 951 are already in motion and numerous alternatives have been proposed. As an example, the County’s Growth Management Plan (GMP) already includes watershed management as one of the key objectives. In this initiative, the environmental value of wetlands and other sensitive estuarine zones have been carefully articulated and identified as a valuable tool for coastal management. Watersheds such as the Main Golden Gate Basin, the Gordon River Basin, the Faka Union Canal Basin and the Barron River Canal Basin among others have been described as potential areas for evaluation due to their general geomorphologic characteristics in combination with past, present and future land usages, their projected changes, and the potential for increased anthropogenic impact. Agriculture practices within Immokalee have also been identified as known sources of pollution loading, past and present, likely to add a complex chemical mixture to the adjacent receiving waters. In addition, progressive implementation of the Picayune Strand restoration efforts will likely modify the water delivery mechanisms through the Faka Union Canal and the adjacent marshes south of US-41. Because of all these compounding factors, we proposed a more comprehensive contaminant survey that will incorporate most of the recommendations from the 2002 report but that will also expand to produce a “baseline” for a large number of contaminants that could be used to assess the present status of watersheds likely to be affected by the future expansion plans. The baseline conditions described here not only provide a much needed starting point for future coastal management decisions but was also a key factor identifying ongoing conditions recognized in past contaminant monitoring efforts that need careful attention.

In deciding what contaminants to be included in the survey it was important to consider past and present practices, usage, mode of transport and environmental stability. It is well known that many of the pollutants (urban, industrial or agriculture-related) introduced along the freshwater distribution systems are likely to associate with sediment particles and will travel and get deposited in areas of low energy or at the heads of the estuarine system. In addition, some of the more contemporary pollutants, designed to have a shorter half-life compared with their 1980’s homologues, have the tendency to get transported preferentially in water. However, since a good portion of them still have considerable partition to particulate phases, and because monitoring water will require a continuous and intensive effort, this study used sediments as a temporal integrator in a similar fashion that for the 2001-2002 study.

As part of the process identifying potential candidates for environmental assessment Collier County Pollution Control and Prevention Department conducted an extensive review of the chemicals that could be potential targets for this “extended” survey (see supporting data in Appendix II). The goal was to target “biocides” (herbicides, pesticides, fungicides, etc.) that by a combination of toxicity, persistence, and usage will likely be released in the county’s watersheds and will be transported to the estuarine system in the water or associated with suspended particles.

Several candidates did stand out because they meet one or more of these conditions. For example, Atrazine is one of the most widely used herbicides in the US. Copper is a common herbicide used in many crops (agricultural and ornamental) but also a potent algaecide used in boat paint. Chlorphyrifos and Endosulfan are highly toxic chlorinated pesticides that may still be in use for household and commercial applications. A number of organophosphates were also in the list (Fenthion, Malathion, Ethyl-Anziphos, Chlorphyrifos, etc.). These compounds degrade quickly in the environment but they are also extremely toxic. Chlorpyrifos, however is both a chlorinated and organophosphate insecticide. Table A1 in Appendix II not only provided a comprehensive list of all the potential pesticides and herbicides that could be present in the watershed but also point to the complex nature of the chemical signature to be analyzed. Such complexity heavily complicates the scope of work since in many cases every one of the compounds identified requires a different analytical protocol in multiple environmental media (water and sediment). Since analysis of water will require a long term continued commitment and because one of the major objectives was to produce a county-wide baseline assessment, the decision for this study was to concentrate on sediments as integrative indicators.

In addition, the East of CR951 development master plan has identified a series of problems and watersheds that will need to be addressed in terms of coastal management. For example, the GMP's Conservation and Coastal Management Element (CCME) Objective 2.1 states that watershed management plans should focus on "appropriate mechanisms to protect the County's estuarine and wetland systems." Policies under this Objective require the plans to focus on the "cumulative impacts of the watersheds on the estuaries as well as the impacts within the watersheds themselves".

Particularly interesting are the policies to achieve with the plans: (a) restoring historic hydroperiods in impacted watersheds where possible: (b) reducing impacts of canal and stormwater discharges to estuaries; and (c) meeting water quality standards in the watersheds and the estuaries into which they flow. This creates the need to assess pollution loading produced by modifications of water delivery from impacted watersheds, to assess the quality of stormwater runoff, and to monitor the water quality of the receiving estuarine end members. Although important, the spatial extent of the potential "assessment" areas required to achieve these goals is quite large.

Another limiting factor is the number of watersheds that have been identified as important, those that have been declared impaired, and those that will likely to become affected by development and changes in land use. Based on criteria put forward by several local and state agencies the Conservancy of Southwest Florida has recommended the following priorities for development of watershed management plans: (a) Wiggins Pass/Cocohatchee River; (b) Naples Bay/Golden Gate Canal System; (c)

Rookery Bay; and (d) Ten Thousand Islands (which includes the Faka Union Canal discharging from Southern Golden Gate Estates). These recommendations include every major water delivery route in the populated areas of Collier County and a rather large geographical setting. Because of all these factors, the sediment monitoring plan was planned and conducted in three main stages aimed to provide a comprehensive chemical monitoring plan to accommodate the major objectives as follow.

a) Establish a baseline for multiple contaminants (past and present use) with emphasis along the main watersheds described as; i) Main Golden Gate Canal Basin + Gordon River Extension Basin, ii) Cocohatchee River Basin, iii) Faka Union Canal Basin and iv) Barron River Canal Basin (Figure 1).

b) Conduct the site specific site survey recommended in the 2002 report to assess changes at the confluence of the Gordon River and North Naples Bay but extending the list of target analytes to cover some additional contemporary use pesticides/herbicides.

c) Assess stations where potential land based sources of pollution are likely to occur (i.e. stormwater runoff, drainage from major agricultural areas, areas influenced by golf course runoff, fresh-saltwater boundaries of estuaries, etc.) and reduce the spatial extent of recurrent sampling to specific problem areas in order to assess sources and potential downstream transport.

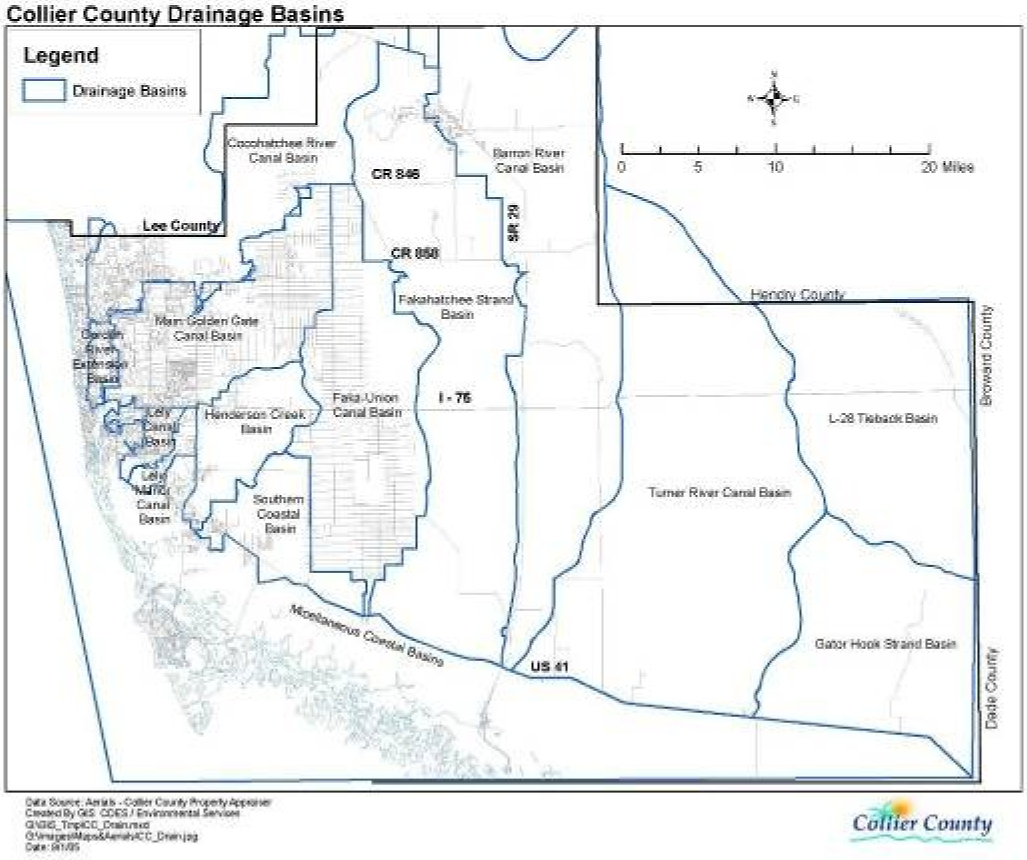


Figure 1 Major watersheds and draining basins in Collier County, Florida.

PURPOSE AND SCOPE

The main objectives for the study were as follows:

- Provide a detailed survey of the presence, concentration levels, spatial and temporal distribution of organic and inorganic anthropogenic contaminants in sediment samples collected within the coastal environments of Collier County.
- Evaluate the potential contributions and effects of the urban and agricultural development along the Cocohatchee River, Upper Gordon River, Henderson Creek, Blackwater River, and Faka Union Canal watersheds as well as the general coastal urban developments to the pollution loading of the estuarine sediments.
- Identify compounds of potential environmental concern and areas showing increased environmental degradation.

- Produce quality data to be used among other parties conducting research in the same study area and to provide regulators with critical information for environmental management purposes.

APPROACH AND METHODS

Analytical Methodology

Given the previous knowledge that levels of some of these contaminants may be low, every effort will be made to collect sediment samples from low energy depositional areas where accumulation of fine particles is high. All the chemical analyses included in this survey were conducted by Genapure Analytical Services (former US Biosystems Inc., FDOH/NELAC E 86240) at their facility in Boca Raton, Florida. All analyses were performed using EPA methods certified to meet NELAC requirements. The methodology employed was as follow: trace metals (EPA 3050/6010B); polynuclear aromatic hydrocarbons (EPA 3550/8270); organochlorine pesticides (EPA 3550/8081); chlorinated herbicides (EPA 3550/8151); organophosphorous pesticides (EPA 8141). All results in the report are presented in dry weight basis. Since all these methods are well described in the literature no further description is provided in the report.

SAMPLING

Sampling Strategy and Site Locations

A total of 92 sites were originally targeted for collection. All sites were located in areas along the selected watersheds where water exchange was important or conducive for contaminant transport or in areas where previous studies have identified anthropogenic signatures. In addition, several stations were located at places where wastewater discharge and storm water runoff could act as local point sources and areas in the watershed where urban or agricultural activities could contribute to a localized contaminant load and transport.

Table 1 shows the list of stations originally selected for the project. The geographical location of the sites is shown in Figure 2. The table also provides cross references to stations from previous or ongoing projects. From this set of samples, a finalized set of stations was produced in consultation with Collier County Pollution Control and Prevention Department and City of Naples personnel.

The final list of sampling stations (88) including the GPS coordinates and collection dates is presented in Table 2. A county-wide map showing the geographical locations of all sampling sites is presented in Figure 3 while an expanded view of the Naples Bay- Gordon River area is shown in Figure 4.

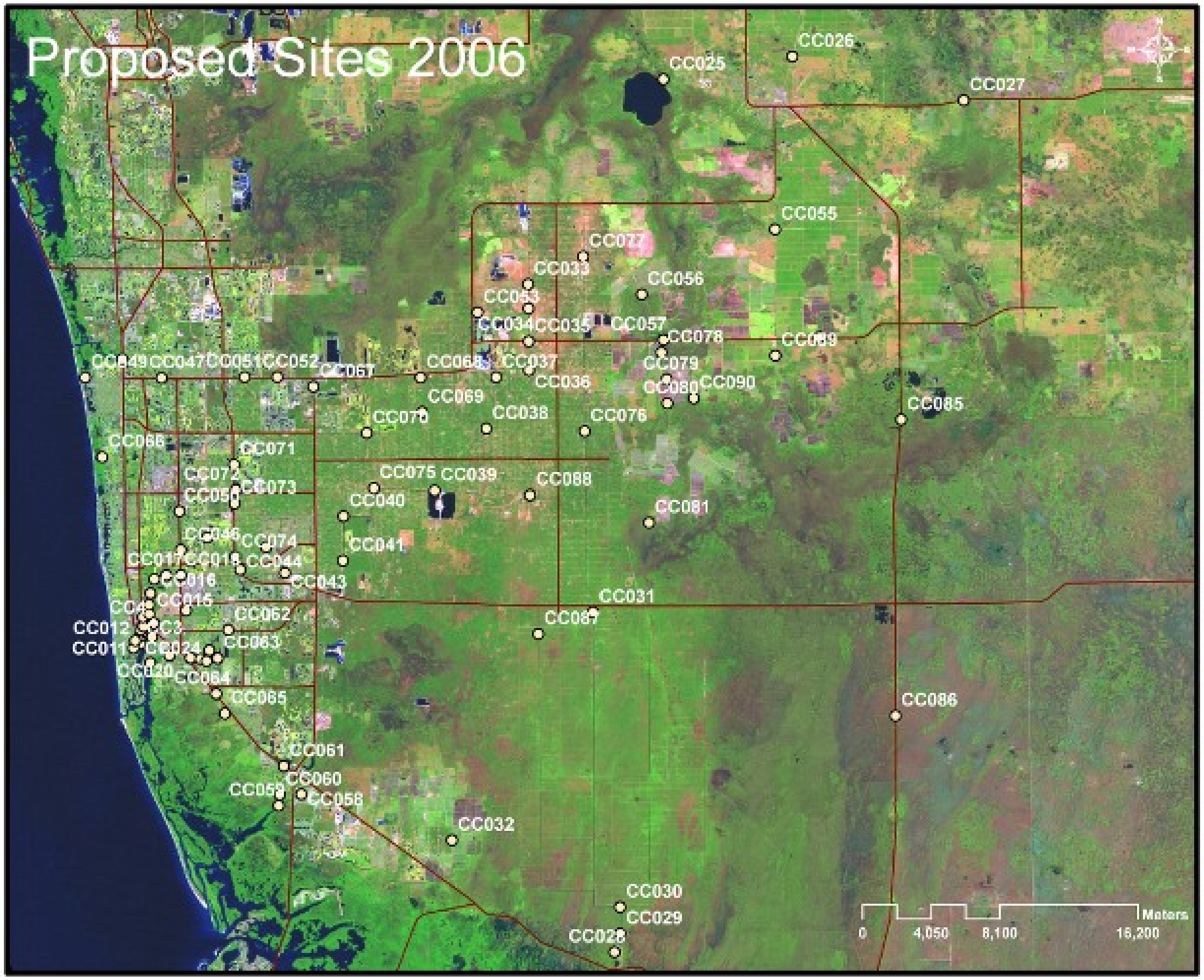


Figure 2 Location of the original sites proposed in 2006.

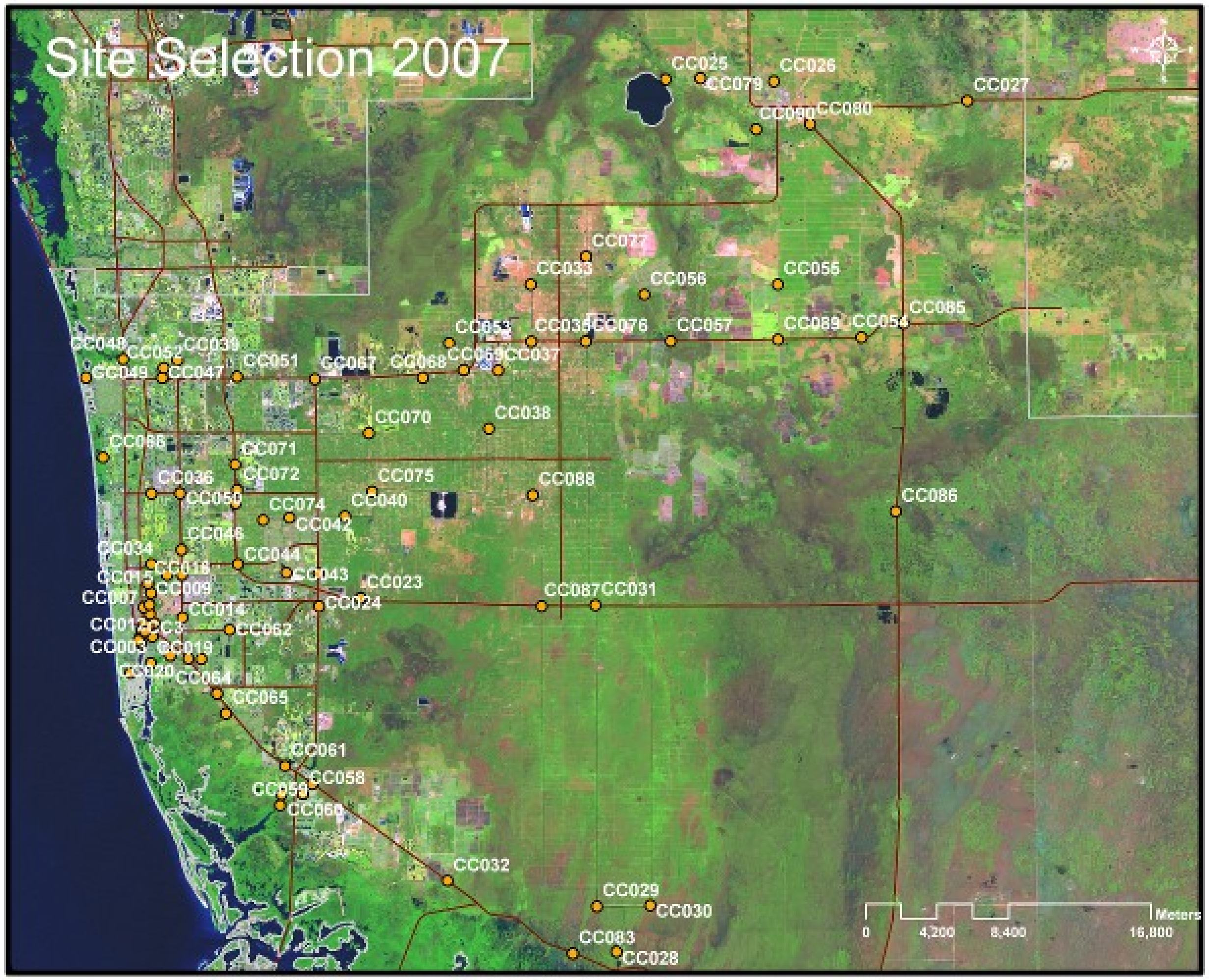


Figure 3 Location of the final sites sampled for the sediment project.

SITE	NAME	LATITUDE	LONGITUDE	DESCRIPTOR	Previously Visited	COLLIER ID	Collection performed at	
1	CC4	26.14220	-81.78850	ACTIVE	2001			
2	CC3	26.13150	-81.79040	ACTIVE	2001			
3	CC001	26.13532	-81.79078	ACTIVE				
4	CC002	26.14220	-81.78850	DELETED				
5	CC003	26.13777	-81.78810	ACTIVE				
6	CC004	26.14071	-81.78641	ACTIVE		GORD60		
7	CC005	26.13859	-81.79009	ACTIVE				
8	CC006	26.14066	-81.78880	ACTIVE				
9	CC007	26.15072	-81.78898	ACTIVE, MOVED		NEW		
10	CC008	26.14729	-81.78534	ACTIVE				
11	CC009	26.15216	-81.78552	ACTIVE		GORD70		
12	CC010	26.13508	-81.78374	ACTIVE				
13	CC011	26.11578	-81.79683	ACTIVE, MOVED		NBAYLLO		
14	CC012	26.13306	-81.79197	ACTIVE, MOVED		NBAYNL		
15	CC013	26.14237	-81.78275	ACTIVE		ROCK62		
16	CC014	26.14549	-81.76620	ACTIVE, MOVED		ROCKE		
17	CC015	26.15824	-81.78468	ACTIVE				
18	CC016	26.16328	-81.78654	ACTIVE, MOVED		BC3		
19	CC017	26.16791	-81.77542	ACTIVE		BC4		
20	CC018	26.16801	-81.76677	ACTIVE		GGCAT31		
21	CC019	26.12123	-81.78453	ACTIVE		HALDNB		
22	CC020	26.12524	-81.77338	ACTIVE				
23	CC021	26.12370	-81.76263	ACTIVE, MOVED		HALDCRK		
24	CC022	26.12354	-81.75488	ACTIVE				
25	CC023	26.15617	-81.66172	ACTIVE, MOVED		LANDFILL		
26	CC024	26.15193	-81.68619	ACTIVE, MOVED		HEND951		
27	CC025	26.43267	-81.48303	ACTIVE				
28	CC026	26.43031	-81.41145	ACTIVE, MOVED		IMKMAD	26.4319	-81.4191
29	CC027	26.42189	-81.30499	ACTIVE		OKALA846		
30	CC028	25.96871	-81.50995	ACTIVE		FAKA		
31	CC029	25.99276	-81.52181	ACTIVE, MOVED		BC8	25.9931	-81.5158
32	CC030	25.99350	-81.49049	ACTIVE, MOVED		BC7		
33	CC031	26.15314	-81.52340	ACTIVE, MOVED		BC10		
34	CC032	26.00599	-81.60958	ACTIVE, MOVED		TOMATO41		
35	CC033	26.32332	-81.56240	ACTIVE				
36	CC034	26.17380	81.78461	ACTIVE, MOVED		GORDONRIV		
37	CC035	26.29298	-81.56184	ACTIVE		GGC@858		
38	CC036	26.21121	-81.78470	ACTIVE, MOVED		GRE896		
39	CC037	26.27745	-81.58108	ACTIVE, MOVED		ORANGETR		
40	CC038	26.24648	-81.58662	ACTIVE				
41	CC039	26.28197	-81.77011	ACTIVE, MOVED		COC@IBIS		
42	CC040	26.19975	-81.67088	ACTIVE				
43	CC041	26.16944	-81.68647	ACTIVE, MOVED		BC23		
44	CC042	26.19881	-81.70361	ACTIVE, MOVED		GGC14		
45	CC043	26.16947	-81.70534	ACTIVE				
46	CC044	26.17397	-81.73378	ACTIVE, MOVED		D2886		
47	CC045	26.18815	-81.75135	ACTIVE				
48	CC046	26.18.138	-81.77896	ACTIVE				

Table 1. Master List of Stations as of June 2007 (Cont). Sample descriptor indicates concordance with other monitoring programs (Collier ID), the location of new or relocated sampling sites (MOVED, NEW), or sites not selected for sampling (DELETED).

SITE	NAME	LATITUDE	LONGITUDE	DESCRIPTOR	Previously Visited	COLLIER ID	Collection performed at	
49	CC047	26.27256	-81.77896	ACTIVE		BC14		
50	CC048	26.28233	-81.80217	ACTIVE		COCAT41		
51	CC049	26.27254	-81.82380	ACTIVE				
52	CC050	26.21144	-81.76818	ACTIVE, MOVED		ARS@896		
53	CC051	26.27335	-81.73502	ACTIVE, MOVED		QUAILCK		
54	CC052	26.27780	-81.77806	ACTIVE, MOVED		COCPALM		
55	CC053	26.29197	-81.60999	ACTIVE, MOVED				
56	CC054	26.29576	-81.36715	ACTIVE, MOVED				
57	CC055	26.35306	-81.41647	ACTIVE			26.3238	81.4164
58	CC056	26.31824	-81.49525	ACTIVE				
59	CC057	26.29362	-81.47939	ACTIVE, MOVED				
60	CC058	26.05190	-81.69503	ACTIVE				
61	CC059	26.04579	-81.70829	ACTIVE				
62	CC060	26.05165	-81.70764	ACTIVE				
63	CC061	26.06678	-81.70539	ACTIVE				
64	CC062	26.13902	-81.73854	ACTIVE				
65	CC063	26.05711	-81.68955	ACTIVE, MOVED		BC22		
66	CC064	26.10511	-81.74562	ACTIVE				
67	CC065	26.09456	-81.74034	ACTIVE				
68	CC066	26.23021	-81.81342	ACTIVE				
69	CC067	26.27242	-81.68936	ACTIVE, MOVED		BC26		
70	CC068	26.27339	-81.62567	ACTIVE, MOVED		PIPERS		
71	CC069	26.27758	-81.60144	ACTIVE, MOVED		CORK@846		
72	CC070	26.24392	-81.65736	ACTIVE				
73	CC071	26.22681	-81.73572	ACTIVE				
74	CC072	26.21333	-81.73465	ACTIVE				
75	CC073	26.20631	-81.73536	ACTIVE				
76	CC074	26.19744	-81.71936	ACTIVE, MOVED		GREEN@SB		
77	CC075	26.21266	-81.65528	ACTIVE, MOVED		GGC@WHITE		
78	CC076	26.29333	-81.52965	ACTIVE, MOVED		FAKA858		
79	CC077	26.33811	-81.52983	ACTIVE				
80	CC078	26.49581	-81.52881	ACTIVE, MOVED		CORKSCRD		
81	CC079	26.43337	-81.46260	ACTIVE, MOVED		IMKFSHCK		
82	CC080	26.40906	-81.39782	ACTIVE, MOVED		IMKBRN		
83	CC081	26.19712	-81.49058	ACTIVE				
84	CC082	25.90977	-81.36348	ACTIVE, MOVED		BARRIVN		
85	CC083	25.96768	-81.53566	ACTIVE, MOVED				
86	CC084	25.95592	-81.48867	ACTIVE, MOVED				
87	CC085	26.30328	-81.34243	ACTIVE, MOVED		BRN		
88	CC086	26.20352	-81.34646	ACTIVE, MOVED		BC24		
89	CC087	26.15239	-81.55512	ACTIVE, MOVED		BC9		
90	CC088	26.21141	-81.56065	ACTIVE				
91	CC089	26.29459	-81.41619	ACTIVE, MOVED				
92	CC090	26.40632	-81.42966	ACTIVE, MOVED		IMKSLGH		

Table 1. Master List of Stations as of June 2007. Sample descriptor indicates concordance with other monitoring programs (Collier ID), the location of new or relocated sampling sites (MOVED, NEW), or sites not selected for sampling (DELETED).

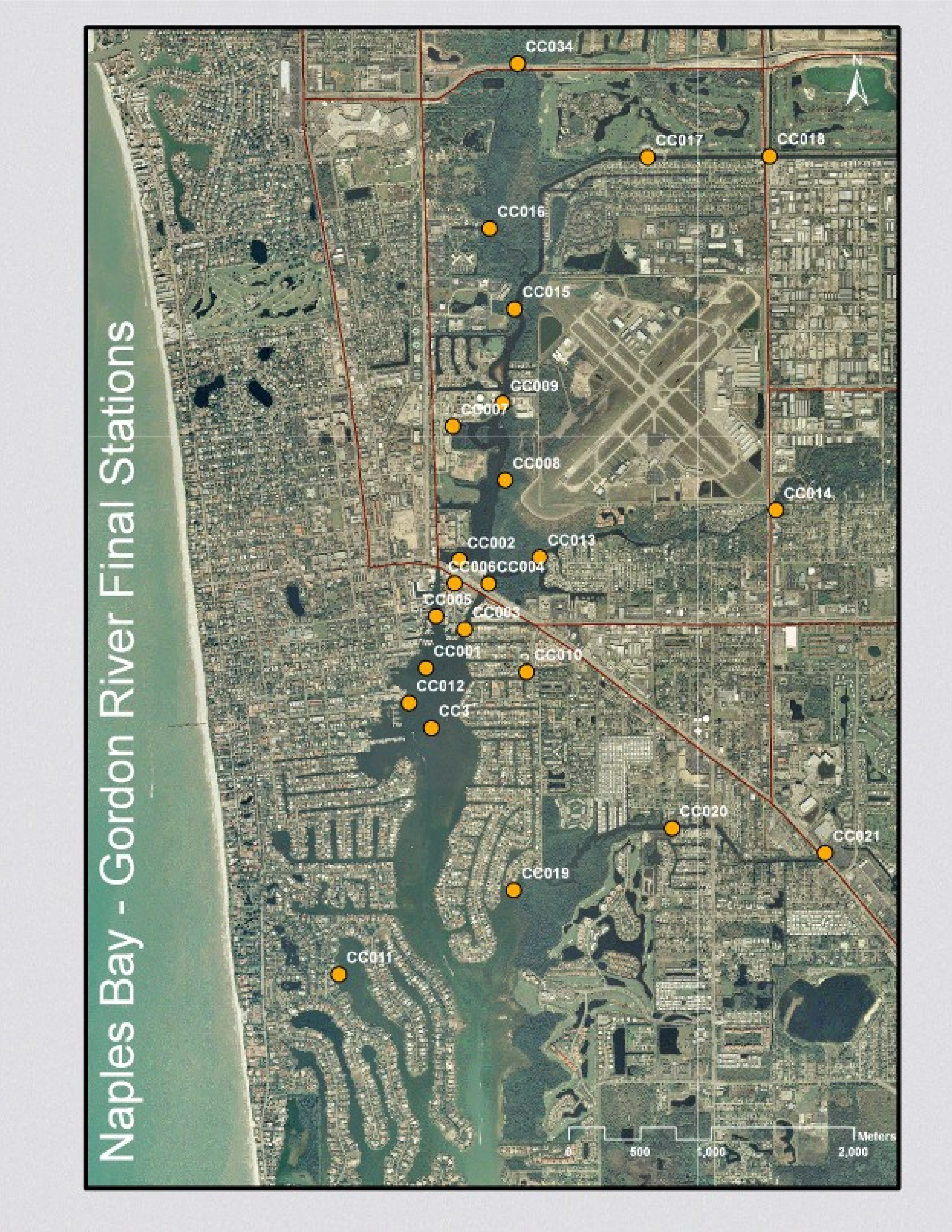


Figure 4 Detailed view of the Naples Bay- Gordon River sampling sites.

SITE	NAME	Collection	Re-collection	Reported
1	CC025	08/13/07	11/02/07	11/20/2007
2	CC027	08/13/07	11/15/07	11/30/2007
3	CC055	08/13/07	11/02/07	11/20/2007
4	CC078	08/13/07	11/15/07	11/30/2007
5	CC079	08/13/07	11/02/07	11/20/2007
6	CC080	08/13/07	11/15/07	11/30/2007
7	CC085	08/13/07	11/15/07	11/30/2007
8	CC086	08/13/07	11/15/07	11/30/2007
9	CC089	08/13/07	11/02/07	11/20/2007
10	CC028	08/30/07	NA	9/18/2007
11	CC032	08/30/07	NA	9/18/2007
12	CC058	08/30/07	NA	9/18/2007
13	CC059	08/30/07	NA	9/18/2007
14	CC060	08/30/07	NA	9/18/2007
15	CC061	08/30/07	NA	9/18/2007
16	CC063	08/30/07	NA	9/18/2007
17	CC064	08/30/07	NA	9/18/2007
18	CC065	08/30/07	NA	9/18/2007
19	CC082	08/30/07	NA	9/18/2007
20	CC083	08/30/07	NA	9/18/2007
21	CC084	08/30/07	NA	9/18/2007
22	CC001	09/14/07	NA	9/26/2007
23	CC002/CC4	09/14/07	NA	9/26/2007
24	CC003	09/14/07	NA	9/26/2007
25	CC004	09/14/07	NA	9/26/2007
26	CC005	09/14/07	NA	9/26/2007
27	CC006	09/14/07	NA	9/26/2007
28	CC007	09/14/07	NA	9/26/2007
29	CC008	09/14/07	NA	9/26/2007
30	CC009	09/14/07	NA	9/26/2007
31	CC011	09/14/07	NA	9/26/2007
32	CC012	09/14/07	NA	9/26/2007
33	CC013	09/14/07	NA	9/26/2007
34	CC015	09/14/07	NA	9/26/2007
35	CC016	09/14/07	NA	9/26/2007
36	CC019	09/14/07	NA	9/26/2007
37	CC020	09/14/07	NA	9/26/2007
38	CC3	09/14/07	NA	9/26/2007
39	CC014	09/20/07	NA	9/30/2007
40	CC017	09/20/07	NA	9/30/2007
41	CC021	09/20/07	NA	9/30/2007
42	CC022	09/20/07	NA	9/30/2007
43	CC029	09/20/07	NA	9/30/2007
44	CC030	09/20/07	NA	9/30/2007
45	CC018	09/27/07	NA	10/10/2007
46	CC036	09/27/07	NA	10/10/2007
47	CC039	09/27/07	NA	10/10/2007
48	CC046	09/27/07	NA	10/10/2007

Table 2 Final List of Sites Collected During the 2007 Collier County Sediment Survey

SITE	NAME	Collection	Re-collection	Reported
49	CC047	09/27/07	NA	10/10/2007
50	CC048	09/27/07	NA	10/10/2007
51	CC049	09/27/07	NA	10/10/2007
52	CC050	09/27/07	NA	10/10/2007
53	CC051	09/27/07	NA	10/10/2007
54	CC052	09/27/07	NA	10/10/2007
55	CC066	09/27/07	NA	10/10/2007
56	CC067	09/27/07	NA	10/10/2007
57	CC010	10/10/07	NA	10/22/2007
58	CC023	10/10/07	NA	10/22/2007
59	CC024	10/10/07	NA	10/22/2007
60	CC031	11/02/07	NA	11/20/2007
61	CC033	11/01/07	NA	11/20/2007
62	CC035	11/01/07	NA	11/20/2007
63	CC037	11/01/07	NA	11/20/2007
64	CC038	11/01/07	NA	11/20/2007
65	CC040	10/10/07	NA	10/22/2007
66	CC041	10/10/07	NA	10/22/2007
67	CC042	10/10/07	NA	10/22/2007
68	CC043	10/10/07	NA	10/22/2007
69	CC044	10/10/07	NA	10/22/2007
70	CC053	11/01/07	NA	11/20/2007
71	CC054	11/02/07	NA	11/20/2007
72	CC056	11/02/07	NA	11/20/2007
73	CC057	11/02/07	NA	11/20/2007
74	CC062	10/10/07	NA	10/22/2007
75	CC068	11/01/07	NA	11/20/2007
76	CC069	11/01/07	NA	11/20/2007
77	CC070	11/01/07	NA	11/20/2007
78	CC071	10/10/07	NA	10/22/2007
79	CC072	10/10/07	NA	10/22/2007
80	CC073	10/10/07	NA	10/22/2007
81	CC074	10/10/07	NA	10/22/2007
82	CC075	10/10/07	NA	10/22/2007
83	CC076	11/02/07	NA	11/20/2007
84	CC077	11/01/07	NA	11/20/2007
85	CC081	11/01/07	NA	11/20/2007
86	CC087	11/01/07	NA	11/20/2007
87	CC088	11/01/07	NA	11/20/2007
88	CC090	11/02/07	NA	11/20/2007
TOTAL SITES SAMPLED		88		88

Table 2 Final List of Sites Collected During the 2007 Collier County Sediment Survey (Cont'd).

Sampling was conducted by FIU field personnel. At every station, two independent samples were collected for organic and inorganic analyses. All sediments were collected by hand from the edge of the water body using a stainless steel Eckman dredge (9”x9”) equipped with an 8ft handle. Only the top 2-3 cm of sediments were sampled from each site. Samples for trace elements (~ 100 mL) were collected from the center of the dredge using disposable, pre-cleaned plastic utensils. Sediments for organic contaminants were then sampled from the dredge and stored in 250 mL certified clean glass containers provided by the analytical laboratory. In sites where access from the road or culverts was not possible, the sampling crew collected sediments by hand from low energy areas showing accumulation of fine grained sediments. All samples were refrigerated at the time of collection (<4ºC) and transported to the FIU labs on ice. Upon arrival to the laboratory, samples were logged in, transferred to the refrigerated sample storage and kept at <4ºC until they were transferred to Genapure custody. All appropriate chain of custody documentation is provided with the analytical results in Appendix III of this report.

RESULTS AND DISCUSSION

General Sediment Quality

The analytical data generated for the sediment samples by the performing laboratory is provided at the end of the report as a separate appendix (Appendix III - Supporting Information). Due to the size and complexity of information produced in the study, sets of figures summarizing the chemistry data will be used to aid the interpretation. The results are divided in two major groups of contaminants (organic and inorganic) and presented in order of relevance. Samples are ranked by their concentration, compared to available environmental guidelines, interpreted in terms of their geographical location and assessed for potential environmental concern. Figure 5 shows the overall concentrations of all trace metals in the sediments while Figure 6 shows the same set of data but includes the stations ranking above the 75th percentile (outliers) of the County-wide distributions. Figures 7 to 13 represent the samples ranked by concentration in reference to the trace element Sediment Quality Assessment Guidelines (SQAGs) promulgated by FDEP (MacDonald, 1994, MacDonald et al., 2003). In contrast to the 2001-2002 report where only estuarine sediments were sampled the 2007 survey included both estuarine and limnetic sediments. Because of this, both coastal (TEL/PEL) and inland (TEC/PEC) water SQAGs were used for this project. An additional piece of information contained in the graphs is the inclusion of both the Method Detection Limits (MDLs) and the Method Reporting Limits (MRLs) in the plots. Since three groups of elements (major, minor, and trace) were analyzed is quite common to have analytes for which the MDL and MRL are low enough to produce 100% detections (Al, Fe, Mn, etc). Some toxic metals however, (As, Cd, Ag, etc) occur in the environment at much lower levels thus often not detected in the analysis. Because of this, the plots show open circles for analytes <MDL; gray shaded circles for detections between the MDL and the MRL and green circles for statistically relevant detections. It is important to note that both MDLs and MRLs are sample weight and laboratory dependent and may affect the interpretations. For the purpose of the discussions to follow, only detections above the MDL (censored data) are considered

for the environmental assessment. Figures 7, 8, and 12 are presented within the discussion as examples of three elements where SQAGs are exceeded.

Figures 22 to 36 show the similar results for all organic compounds for which a definitive set of SQAGs are available. To compare the distribution of trace elements against their natural abundance, trace metal results are presented in Figures 37 to 43 as normalized concentrations against aluminum (concentration of element vs. concentration of aluminum in a log-log scale). This approach has been extensively used by researchers and resource managers in Florida because of the availability of reliable data on the analysis of clean estuarine sediments in the region conducted by Schropp and Windom (1988). Although these graphs do not provide exposure-based interpretation as the previous figures they represent the likelihood that sediments in environmental settings are enriched in the element over its natural abundance as reported by Schropp et al, (1988). Concentrations are judged to be within the natural range when they plot along the prediction line and within the prediction limits. Only samples plotting above the upper prediction line are considered metal-enriched. The third set of results is presented as distribution maps to illustrate the spatial extent of the contaminants along the study area (Figures 44 to 57. To simplify the observations data in the maps are classified as colored symbols showing stations below or above the available SQAGs. In addition, all numbers below the criteria are scaled using the size of the marker to rank stations by concentrations and to reflect the method detection limits

Using the classification of sediments proposed by Long, 2000; the great majority of samples collected from Collier County watersheds during the 2007 survey could be catalogued as Tier2 and Tier3 sediments (relatively unimpacted). However, at least three sites (CC018, CC036, and CC014, 3%) ranked above the Probable Effect Concentration (PEC) criteria for at least three polynuclear aromatic hydrocarbons (PAHs) based on the Inland SQAGs (MacDonald et al., 2003) In addition, two trace metals; Copper and Arsenic exceeded the PEL/PEC criteria in 6 (7%) and 1 (1%) of the sites respectively. Although these SQAGs are not meant to trigger a regulatory response they provide valuable information to resource managers to assess potential environmental hazards, to devise routes of action in future assessments and to guide the implementation of best management practices. Based on this assessment, a maximum of 7% of the sites could be catalogued as Tier 1 (mainly coastal areas due to Copper contamination and inland areas due to PAH contamination) while a maximum of 12 (14%) stations fall within the Tier 2 category (one or more chemicals exceeding a TEC/TEL criteria). As for the 2001-2002 survey the vast majority of the samples analyzed in the survey 79% could be catalogued as Tier 3 sediments. Although no toxicity data was generated during this investigation this sediment distribution (7%Tier 1, 14% Tier 2, 79% Tier 3) is markedly different from the 27%, 42%, 31% national distribution calculated by Long (Long et al., 1998). Once again, these results corroborate the fact that estuarine areas within Collier County are still among the most pristine in the nation.

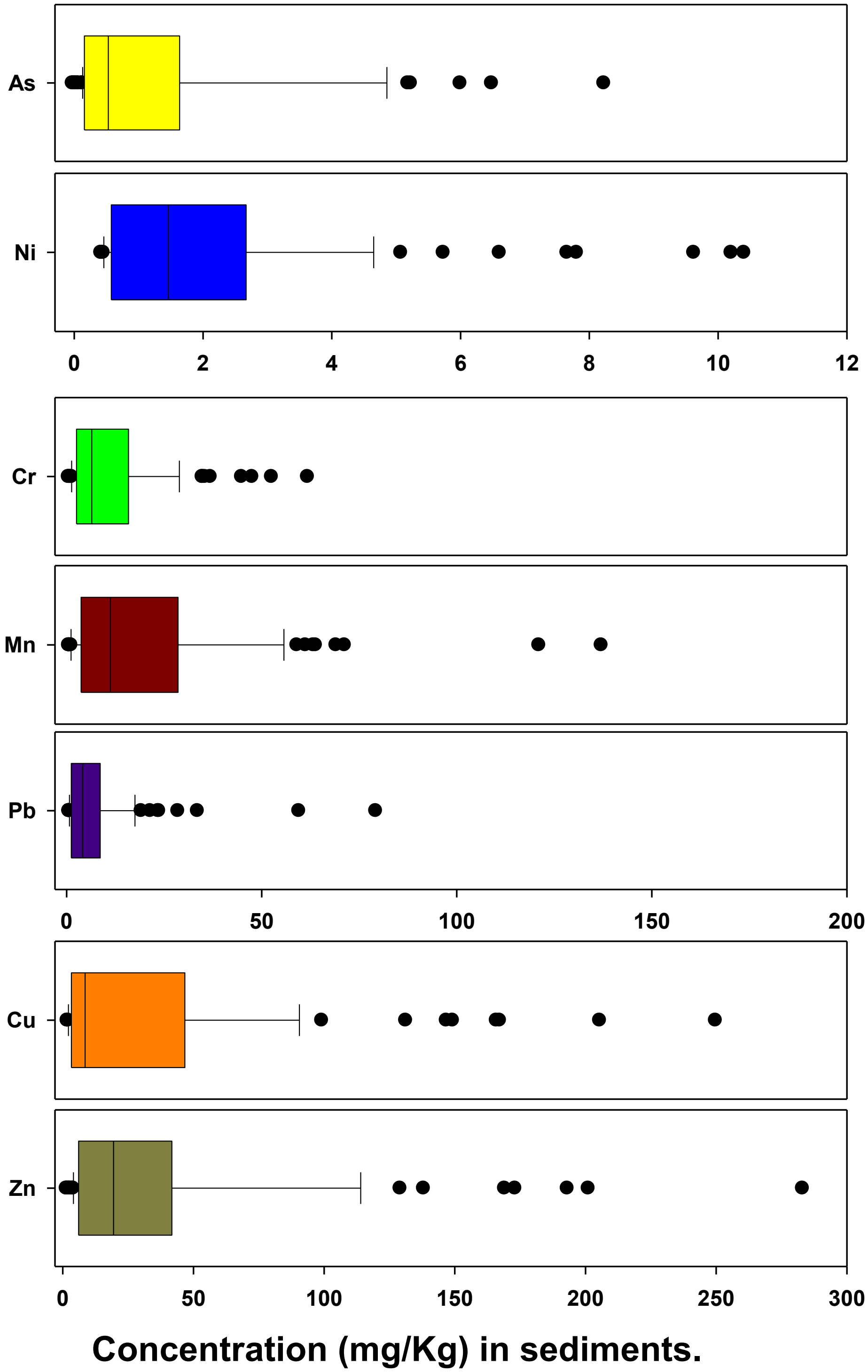


Figure 5. Overall Concentrations of Trace Elements from the 2007 survey.

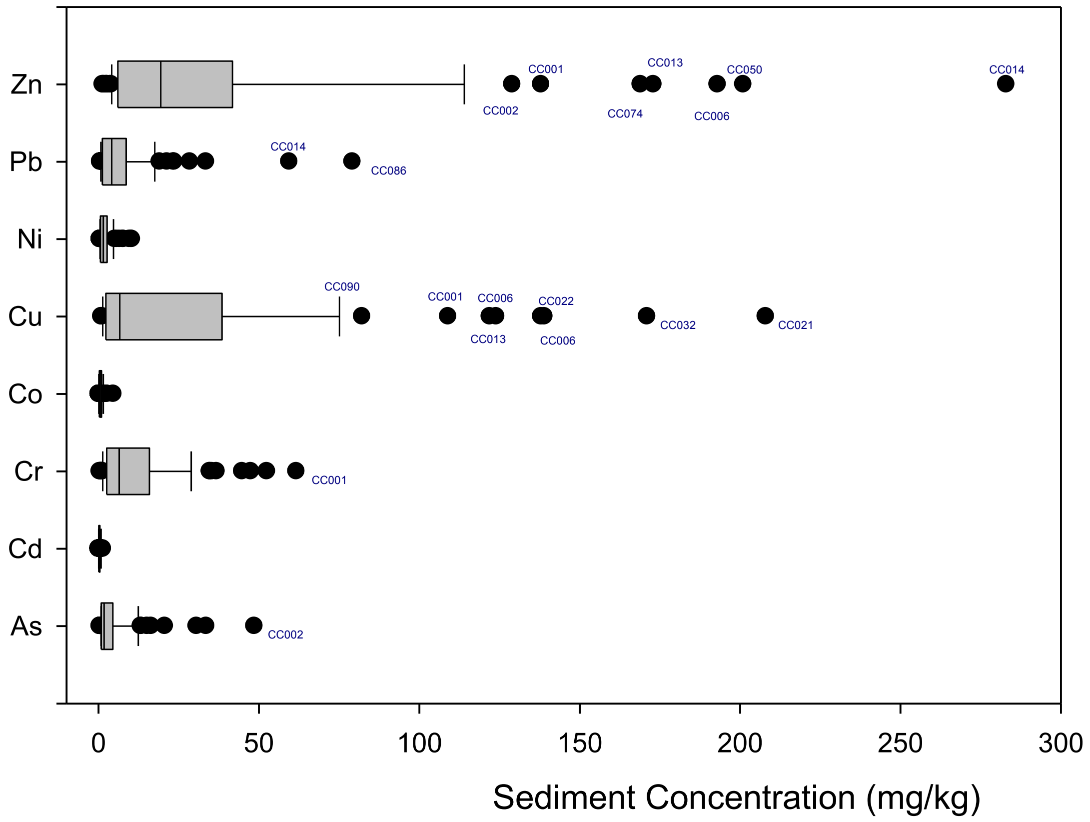


Figure 6. Sediment Trace Elements Distributions Showing Outliers

General Distribution of Contaminants

Trace elements

A total of fifteen elements including major (Fe and Al), minor (Mn, Sr, and Zn) and trace elements (Cr, Co, Ni, Cu, As, Cd, Ag, and Pb) were measured in all sediment samples. To aid the interpretation of the data, four are discussed in this section. Minimum and maximum levels, median and averages, comparison with national levels, and sediment quality criteria will be used to describe the occurrences and spatial distributions when appropriate.

Arsenic

Arsenic is released to the environment by weathering of arsenic rich minerals as well as a result of human activities. Arsenic contamination has been linked both to its use as herbicide (particularly in golf courses) as well as an ingredient in pressure treated wood. However, considerable debate has been generated over the naturally high abundance of arsenic rich minerals (phosphorites) along Florida. Since this survey included limnetic sediments, several stations were located in the proximity of major golf courses. Concentration of arsenic in the sediments ranged from <MDL to 48.6 ppm with an average of 4.54 and a median of 1.74 ppm respectively. Arsenic was above the MDL for 75% of the samples analyzed. The median arsenic concentrations in sediments reported by NOAA as part of their NS&T program is 6.9 ppm while samples above 12 ppm were considered to be elevated (85th percentile). The 85th percentile of the 2007 distributions is 7.98 ppm and only 10%of the samples rank above the NOAA "high" classification. Only one sample in the estuarine system (CC002, US41Bridge at Gordon River) ranked above the PEL criteria. There is no indication of a potential arsenic source in that area but sites located north and south of it did rank above the TEL criteria for coastal sediments. One site on the freshwater watershed (CC074, located along Santa Barbara Boulevard) ranked above the PEC SQAG. This site is adjacent to a large subdivision and in the vicinity of several golf courses although no apparent connection is present among them. Although the average concentrations all samples are relatively low and may not pose a risk for biological endpoints, a total of fourteen stations ranked above the 7.3 ppm reported by Long et al., 1994 to be moderately toxic for Tampa Bay. In particular, several stations in North Naples Bay – Gordon River (CC006 and CC013)

are above the 85th percentile national high reported by NOAA but still well below the probable effect level of 41.6 mg/kg. These results are very similar in geographical distribution and concentrations levels as reported in the 2001-2002 survey. The geographical distribution of arsenic in the county's sediments measured as part of this study is shown in Figures 44 and 45. Table 3 on page 45 provides a comparative summary with other regional and national environmental monitoring projects.

Cadmium

Cadmium is a toxic trace element used in a wide variety of industrial applications especially in electroplating and as a component of pigments and photographic supplies. Nevertheless, cadmium contamination is generally restricted to heavily industrialized areas and is not expected to be an issue within Collier County.

Concentration of cadmium in the sediments ranged from < MDL to 1.3 ppm with an average of 0.32 and a median of 0.18 ppm respectively. The median cadmium concentrations in sediments reported by NOAA as part of their NS&T program is 0.19 ppm while samples above 0.59 ppm were considered to be elevated (85th percentile). FDEP SQAGs proposed a TEL value of 0.68 mg/kg and a PEL of 4.2 mg/kg respectively. None of the samples surveyed had concentrations above the TEL or TEC guidelines (0/88). Higher than expected MDLs used for some of the samples make the interpretation of the cadmium concentrations complex due to the analytical uncertainties. Despite these difficulties these results are higher but in good agreement with the ones reported for the 2001-2002 survey reported by Grabe, 1993, 1996 and Miller and Mcpherson 1998 for other locations within Collier County. Cadmium is not expected to be a concern in the surveyed area but future monitoring programs should consider using more sensitive analytical protocols to effectively assess the hazards related to cadmium levels in the county watersheds. Table 3 provides a comparative summary with other regional and national environmental monitoring projects.

Chromium

Like many other metals, chromium is a common constituent of alloys and is generally used in a wide number of applications. Hexavalent chromium used for chrome plating and trivalent chromium salts are used as dyes. Although this metal is mainly linked to industrial applications, some fertilizers, and pesticides are also a potential environmental source. In addition, chromium can be emitted to the atmosphere by burning of fossil fuels containing high levels of chromium or vanadium. Concentration of chromium in the sediments ranged from 0.39 to 61.7 ppm with an average of 11.4 and a median of 6.4 ppm respectively. The median chromium concentrations in sediments reported by NOAA as part of their NS&T program is 54 ppm while samples above 120 ppm were considered to be elevated (85th percentile). Only 3% of the samples (3/88) exceeded the TEL/TEC SQAG for chromium. Stations CC001 and CC011 in Naples Bay contained chromium at levels slightly above the TEL and similar to the NS&T national median of 54 ppm. Station CC069 (Immokalee Road at Randall Boulevard) is the only freshwater site that ranked above the TEC for chromium (44.8 ppm). These concentrations are well below the levels considered to be significantly toxic for sediments from Tampa Bay (Long et al., 1994) and consistent with the chromium levels observed for Naples Bay (Cantillo et al., 1999). Chromium is not expected to be an element of concern in the area surveyed. The geographical distribution of chromium in the county's sediments measured as part of this study is shown in Figure 46 with a detailed representation of Naples Bay in Figure 47. Table 3 provides a comparative summary with other regional and national environmental monitoring projects.

Copper

Copper is widely distributed in the environment because is a naturally occurring element. However, Copper is also a particularly important element for coastal environments since it is heavily used to control fouling in submerged surfaces. In addition copper is extensively used as an aquatic algaecide and to control unwanted vegetation in the production of valuable crops such as citrus and ornamentals. Other less important but common anthropogenic sources include corrosion of brass and copper pipes used in the distribution of drinking water. Sediments are an important sink and the ultimate reservoir for copper. Overall, researchers have reported concentrations of copper in sediments with ranges from 2-10 mg/kg in uncontaminated places to as high as 5000 mg/kg in clearly impacted sites (EHC200). The sediments of Collier County estuaries and freshwater watersheds analyzed for the 2007 study were well within these ranges Concentration of copper in the sediments ranged from <MDL to 208 ppm with an average of 27.1 and a median of 6.61 ppm respectively. The median copper concentrations in sediments reported by NOAA as part of their NS&T program is 14 ppm while samples above 47 ppm were considered to be elevated (85th percentile). Only 36% of the samples were non-detects for copper. Along with arsenic, copper is the element with more exceedances of the FDEP SQAGs and clearly a contaminant of potential concern. A total of 6 samples (7%) ranked above the PEL/PEC criteria for

copper. Three of them (CC013, CC001 and CC006) are located in Naples Bay in the vicinity of major marinas while the other three have very different characteristics. Station CC021 located where Haldeman Creek intersects US-41 has the highest level detected in this study (208 ppm). This site seems to have a long history of copper contamination since it was already identified in the 1989-1991 sediment survey as exceeding the sediment quality criterion (Grabe, 1994). Another unusual finding was the detection of 171 ppm of copper in sediments at station CC032. This site is in a predominately agricultural area and the copper present could be a result of vegetation control. The patterns of copper contamination of the sediments suggest that areas with large concentrations of boats in permanent moorings/docking berths may require special attention with regard to future sampling. Since the ban of tin formulations copper based antifouling paints comprise the bulk of the bottom paint market in the US, thus contamination of the sediments is unlikely to decline. Given the nature and number of recreational boats permanently docked along Collier County coastline this element is likely to pose a risk in the near future. The copper concentrations reported in this study are in agreement with the ranges reported by our previous survey in 2001-2002, those reported by Grabe, 1996 for limnetic sediments (<0.01 to 86 ppm); those reported by Miller and Mcpherson 1998 for the Barron River (2 to 82 ppm), and within the ranges reported for NOAA's NS&T stations collected at Naples Bay (NBNB, 10-20 ppm); Faka Union River (EVFU, 0-10 ppm) and Henderson Creek (RBHC, 0-10 ppm). Many of the sediment samples analyzed in this study seem to be enriched over the average natural abundance of minerals in Florida. Given the current status and the multiplicity of sources, copper should be considered a priority element in the pollution prevention and management for Collier County. The geographical distribution of copper in the county's sediments measured as part of this study is shown in Figures 48, 49, 50 and 51. Ranked concentrations are presented in Figure 8 and enrichment plots are shown in Figure 40. Table 3 provides a comparative summary with other regional and national environmental monitoring projects.

Lead

Lead is also a component of a variety of crustal minerals. The main application of lead in industry is the manufacturing of lead based batteries. Due to its toxicity, lead usage has been severely limited. As an example production of tetraethyl lead, which was the second most important industrial source of lead, has been in sharp decline in the last decades. Concentration of lead in the sediments ranged from <MDL to 79.2 ppm with an average of 7.54 and a median of 4.11 ppm respectively. The median lead concentrations in sediments reported by NOAA as part of their NS&T program is 18 ppm while samples above 40 ppm were considered to be elevated (85th percentile). Only two sites (CC014 and CC086) exceeded the TEL/TEC SQAG. These two sites are also above the NOAA 85th percentile "high" but below the value reported by Long et al., 1994 as being toxic for Tampa Bay sediments (Table 3) None of the sediments analyzed exceeded the PEL/PEC guidelines for lead. Despite the fact that lead was considered a priority pollutant in the past decades, the elimination of lead additives in gasoline has greatly contributed to the reduction of lead inputs in highly urbanized coastal areas in particular throughout street runoff. Station CC014, located by Airport Road at the southeast corner of Naples Airport presents a particular challenge since it

contaminated with both trace metals (Cu, Pb and Zn) and PAHs. The geographical distribution of lead in the county's sediments measured as part of this study is shown in Figure 53. Ranked concentrations are presented in Figure 11 and enrichment plots are shown in Figure 42.

Nickel

Nickel is among the 20 most abundant elements in the earth crust and occurs in association with other important metallic elements such as iron and copper. Besides being used by the oil industry as a catalyst, nickel is a common constituent of stainless steel and other alloys. Along mining, electroplating and other industrial applications, anthropogenic sources include the combustion of fossil fuels. Concentration of Nickel in the sediments sampled in 2007 ranged from <MDL to 10.4 ppm with an average of 2.17 and a median of 1.46 ppm respectively. The median nickel concentrations in sediments reported by NOAA as part of their NS&T program is 17 ppm while samples above 36 ppm were considered to be elevated (85th percentile). None of the stations surveyed exceeded the proposed guidelines and all concentrations were within previously reported values for samples collected in 2001-2002 within Collier County watersheds. Moreover, the average and median concentrations reported in this study are within the range reported by Long et al, 1994 for non-toxic samples in Tampa Bay. Based on these results, nickel is not expected to be an element of concern for sediment contamination. The geographical distribution of nickel in the county's sediments measured as part of this study is shown in Figure 52. Ranked concentrations are presented in Figure 10 and enrichment plots are shown in Figure 41.

Zinc

Similar to nickel, zinc is an important constituent of rocks and minerals. This element is also an important constituent of alloys and is commonly used to protect metal parts from corrosion. Anthropogenic sources of zinc are quite diverse and include, besides industrial applications, street runoff, municipal wastewater effluents, and waste incineration. Due to the extensive use of zinc anodes and paints, large marinas in restricted waters are a particular issue with regard to zinc contamination. Concentration of zinc in the sediments ranged from 1.30 to 283 ppm with an average of 39.2 and a median of 19.4 ppm respectively. The median zinc concentrations in sediments reported by NOAA as part of their NS&T program is 67 ppm while samples above 130 ppm were considered to be elevated (85th percentile). Unlike for the 2001-2002 survey where only one station (Naples Bay North, CC04) exceeded the TEL guideline, seven sample locations(CC001, CC002, CC006, CC013, CC014, CC050, and CC074) did rank above the TEL/TEC SQAG in the 2007 survey (Figure12). The majority of these sample sites are located along the marinas in Naples Bay with the exception being site CC014 located at the southeast corner of Naples Airport. Due to its multiplicity of sources, zinc shows a cross-correlation with most of the other toxic trace elements (Table 4). With few exceptions, zinc concentrations in the sediments are in accordance with the results reported in the 2001-2002 survey and the studies by Grabe, 1996 and Miller and Mcpherson, 1998. The values are also within the ranges reported by NOAA's NS&T program for sediments in the same area (Table 3). The average and median concentrations for this element are well below the national NS&T median values for unimpacted sites and also on the lower end of the range reported by Long et al., 1994 for non-toxic samples surveyed along Tampa Bay (Table 3). Despite this fact, stations with multiple exceedances of several metals need to be looked at in much more detail to see if zinc is a contaminant of concern. The geographical distribution of zinc in the county's sediments measured as part of this study is shown in Figure 54. Ranked concentrations are presented in Figure 12 and enrichment plots are shown in Figure 43.

Other elements

Besides the basic toxic metals, a number of major and minor elements were also measured in this project. Since the intent was to aid in the normalization and interpretation, they will not be discussed in the report but are provided in Appendix I, Figures 14-21.

Trace Metal: Enrichment

A second approach commonly used to evaluate the potential for trace element contamination is to assess their anthropogenic enrichment by comparison with their expected crustal abundances in "clean" sediments from the same area. This technique, proposed by Schropp et al., 1990 uses the aluminum normalized element concentrations to assess the extent of enrichment. Since trace metals are considered particle-reactive pollutants, they will accumulate in sediments and modify the abundance of naturally occurring elements. It is worth noticing, however, that this comparison has no link to effects to biological endpoints and such is only used to assess the extent of anthropogenic contributions. Figures 37 to 43 present the aluminum normalized plots for all elements for which regression data are available. Of all elements, copper, zinc, and lead showed significant enrichment. Other elements like arsenic showed much more limited enrichment while nickel and chromium did not show anthropogenic enrichment at all. Some elements like cadmium were not assessed for enrichment since most of the samples were at or below the MDL. Although data presented in the Sediment Quality Report for Collier County Estuaries 1989-1991 (Grabe, 1993) are difficult to include in this comparison; elements such as arsenic, cadmium, copper, and zinc were also found in many cases within the classification of “heavily” or “moderately” polluted according to an EPA sediment classification. These observations along with the results presented in the previous sections clearly indicate that copper, zinc, and to a lesser extent arsenic should still be considered a priority when assessing sediment quality for management purposes within Collier County watersheds.

Elemental relationships

In an attempt to identify common sources, a Pearson product correlation matrix was assembled to test co-variability of different elements (Table 4). Not surprisingly, many of the toxic elements seem to be related to each other. Significant deviations include copper and lead that seem to deviate from the other major elements. These two elements do not correlate significantly with aluminum either likely due to their enrichment over natural sources. This finding is one more element to consider when assessing the potential for copper to be a contaminant of concern. While lead sources are being reduced or eliminated, emissions of copper are on the rise.

Table 3 DISTRBUTION AND COMPARISON OF TRACE ELEMENT CONCENTRATIONS. All values are in mg/kg dry weight basis (ppm) with exception of Mercury (ppb).

	Tampa Bay Sediments Long et al. (1994)		Collier County Estuaries 2001-2002 Survey		Collier County Wide 2007 Survey (This Study)		Grabe (1996)	Miller & Mcpherson (1998)	NOAA's National Status and Trends Program Sediment Data Cantillo at al. (1999)				
Element	Non-Toxic (average)	Significantly Toxic (average)	Mean	Maximum	Mean	Maximum	Limnetic sediments	Barron River Canal	NBNB*	RBHC*	EVFU*	NATIONAL MEDIAN	85th Percentile "HIGH"
Arsenic	3.2±2.5	5.5±1.8	2.65±1.26	19.8	4.44±.84	46.8	<0.01-8.8	1-14	5-7.5	5-7.5	2.5-5	6.9	12
Cadmium	0.9±1.0	3.1±2.2	0.003±0.008	0.10	0.115±	0.10	<0.01-1.1	<.01-0.6	0.1-0.2	0.1-0.2	0.1-0.2	0.19	0.56
Chromium	49.5±45.4	93.7±35.8	14.7±9.44	54.4	42.7	54.4	0.05-27	6-77	40-60	40-60	60-80	54	120
Copper	37.9±66.1	102.7±58.9	5.46±7.51	81.1	33.0	81.1	<0.01-86	2-82	10-20	0-10	0-10	14	47
Lead	45.7±65.0	166.7±122.3	3.51±2.45	22.4	11.2	22.4	<0.01-990	3-40	0-5	0-5	0-5	18	40
Mercury (ppb)	137.8±150.3	234.3±126.3	52.70±37.30	164.7	157.7	164.7	NR	20-290	0-50	50-100	0-50	57	220
Nickel	11.4±9.8	21.0±6.9	4.00±2.36	12.2	10.6	12.2	NR	<2-6	0-10	0-10	0-10	17	36
Zinc	106.3±155.0	465.4±371.8	10.76±10.78	124.6	40.7	124.6	0.05-180	5-180	20-40	0-20	0-20	67	130

* NBNB: Naples Bay, RBHC: Rookery Bay, Henderson Creek; EVFU: Everglades, Faka Union Canal. NR: not reported.

Table 4 Pearson Product Moment Correlation Matrix for all metal data in the sediment samples. Data are censored by using MDLs for the treatment of non-detects. Significant correlations assumes a coefficient >0.5 at a *p* value or <0.005.

	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.000085	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Cr	▨	0.73	0.47	0.69	0.66	0.63	0.59	0.91	0.60	0.62	0.74
		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Co		▨	0.26	0.75	0.49	0.82	0.56	0.81	0.43	0.49	0.64
			0.0126	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Cu			▨	0.37	0.31	0.36	0.34	0.37	0.53	0.40	0.59
				0.0003	0.0035	0.0005	0.0010	0.0004	<0.0001	<0.0001	<0.0001
Fe				▨	0.33	0.75	0.60	0.70	0.48	0.43	0.66
					0.0016	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Pb					▨	0.30	0.35	0.64	0.37	0.38	0.69
						0.0049	0.0007	<0.0001	0.0003	0.0003	<0.0001
Mn						▨	0.51	0.68	0.37	0.43	0.56
							<0.0001	<0.0001	0.000441	<0.0001	<0.0001
Mo							▨	0.62	0.58	0.59	0.56
								<0.0001	<0.0001	<0.0001	<0.0001
Ni								▨	0.52	0.64	0.76
									<0.0001	<0.0001	<0.0001
Ag									▨	0.53	0.58
										<0.0001	<0.0001
Sr										▨	0.51
											<0.0001

coefficient
p value

The pair(s) of variables with positive correlation coefficients and P values below 0.050 tend to increase together.
For the pairs with negative correlation coefficients and P values below 0.050, one variable tends to decrease while the other increases.
For pairs with P values greater than 0.050, there is no significant relationship between the two variables.

Polynuclear Aromatic Hydrocarbons (PAHs)

The global occurrence of polynuclear aromatic hydrocarbons (PAHs) in aquatic sediments, in particular near highly urbanized environments has been well established (Neff, 1979). PAHs are among the most prevalent contaminants of the marine environment. They are introduced to environmental compartments by a wide variety of processes (biogenic and anthropogenic) and several of them are catalogued as known human carcinogens and mutagens. PAHs are much like trace elements in the sense that they also occur naturally. They are components of fossil fuels such as coal and oil and they are produced when organic matter burns. Nevertheless, the amount of PAHs produced by these natural mechanisms is usually low and sometimes insignificant when compared with the amounts generated by a multitude of human activities such as incineration, combustion engine exhaust, releases from crankcase oil etc. PAHs are universal contaminants (Daskalakis and O'Connor, 1995) and unlike pesticides and other synthetic compounds are difficult to mitigate through usage regulations.

Generally, crude oils contain up to 7% of PAHs (Kennish, 1977), which consists mainly of low molecular weight compounds (2-3 ring structures) with abundant alkyl substitution. Because of these characteristics this group of compounds is considered to be of "Petrogenic" origin. In contrast "Pyrogenic" PAHs are generated by high temperature processes like combustion and contain mainly high molecular weight compounds (4-6 ring structures) with fewer alkylated homologues. Thus interpretation of parameters related to these differences are extremely useful in the identification of potential contamination sources to coastal environments (Sauer and Uhler, 1995).

Other common source of PAHs in particular in coastal environments with heavy boating activities is the presence of creosote treated wood. Creosote was heavily used in the past to protect submerged wooden structures from decay and is a complex mixture of hydrocarbons. PAHs from creosote are typically dominated by 2-ring structures (C_0-C_4 naphthalenes) and 3- and 4-ring (phenanthrene, anthracene, fluoranthene, and pyrene) compounds (Stout et al., 2001). However, creosote is a distillation product from coal and does not contain significant amounts of high molecular weight PAHs (5- and 6- ring) (Stout et al., 2001).

Urban runoff and atmospheric fallout are complex (and highly variable) mixtures of organic rich material including soot, atmospheric dust, engine exhaust particles, and storm water containing residues of lubricants mainly from automobile releases. Despite the fact that urban runoff is spatially and temporally variable, some of its basic characteristics remain constant and makes it different from other PAH sources (Eganhouse et al., 1982). PAHs distribution in urban runoff are typically enriched in high molecular weight PAHs (4 to 6 rings) with their distribution of alkylated homologues exhibiting a typical “pyrogenic” profile ($P_0>C_1>C_2>C_n$) where the parent compound and the lower alkylated homologue clearly dominate the series (Bohem and Farrington, 1984).

As described in our previous study PAHs in Collier County sediments are highly variable in both concentrations and composition. The 2001-2002 study provided a clear indication that PAHs of pyrogenic origin dominate the anthropogenic signature in the estuarine areas. For that reason, and because of the need of a NELAC certified method, only the parent homologues were measured in this study. Total PAHs in the sediments ranged from below detection to as high as 34,639 μg/kg. Of these, the high molecular PAHs constituted the majority with 32,225 μg/kg vs. 2,414 μg/kg for the low molecular weight PAHs. The average total PAHs concentration in Collier County sediments for the 2007 survey was 1645 μg/kg. However, because of the high MDLs obtained using the certified method and the number of non-detects reported, the median concentration does not have any statistical significance. The numbers clearly indicate that the distribution of concentrations is markedly skewed to the low end of the range and only a few samples are expected to be of potential environmental concern. O'Connor, 1998, and Cantillo et al., 1999 reported a median PAH concentration for the nation's coastal sediments as 380 μg/kg with concentrations above 2300 μg/kg being considered as high (>85th percentile). Although 15% of the samples (13/88) do rank above this benchmark evidence of the semi-pristine condition of the county's waterways is the fact that most of the samples were below the method detection limits. However, three stations stand out with regard to the PAH concentrations (CC018, CC036 and CC014). These three samples not only rank high on total PAHs but also contain concentration of the individual isomers that exceed the available SQAGs. Table 5 summarizes the levels of PAHs both as totals and individual homologues reported by other investigators in the same area and in other Southwest Florida estuaries. Despite the fact that comparing environmental data is always method dependent, all of the concentration ranges reported in this study are in good agreement with previously reported levels. Furthermore, when compared with samples from Tampa Bay (Long et al., 1994) the three stations clearly rank above the levels considered capable of producing significant biological effects for the amphipod bioassay.

.

Sediment quality and PAHs

To assess the potential for impact of PAHs in the sediments to the ecological endpoints a comparison with the available Sediment Quality Assessment Guidelines (SQAGs) is also provided. The results, presented in Figures 22 to 36 are quite different from other organic contaminants. A summary of the results is as follows:

- Station CC018 exceeded the PEC for total PAHs
- None of the estuarine stations exceeded the PEL criterion for total PAHs'
- Stations CC007, CC016, CC012, CC014 and CC036 exceeded the TEL/TEC criterion for total PAHs
- Total PAHs (sum of all homologues analyzed) concentrations exceeded the Threshold Effects Level (TEL) in 6% of the samples (3/49).
- The MDLs for low molecular weight PAHs is too high to produce detections.
- Stations CC018, CC036, CC014 and CC059 produce exceedances of the SQAGs for individual PAHs for most of the high molecular weight homologues.
- Overall, up to 5% of the samples exceed a PEL/PEC guideline and up to 14% of the samples exceed a TEL/TEC guideline.
- PAH concentrations in stations CC018, CC036 and CC014 exceed the limits established in FAC 62-777 for petroleum contamination.

Based on these results and compared with all other contaminants surveyed in this study, polynuclear aromatic hydrocarbons are among the compounds most likely to contribute to future sediment quality degradation along heavily urbanized areas of Collier County's estuarine system.

Table 5 Comparative concentrations of PAHs in Southwest Florida estuaries ad their relationship to toxicity.

	Tampa Bay Sediments Long et al., 1994		Collier County Limnetic Sediments Grabe, 1996	Barron River Sediments Miller and Mcpherson , 1998	Collier County Sediments 2003	Collier County Sediments 2007
	Not Toxic (µg/kg)	Significantly toxic (µg/kg)	Range (µg/Kg)	Range (µg/Kg)	Range (µg/Kg)	Range (µg/Kg)
Naphthalene§	39±19	107±120	NR	10-80	1-21	ND
Acenapthylene§	40±1	226±212	NR	3-50	ND-11	ND
Acenaphthene§	60±68	185±230	NR	20-50	ND-14	ND-218
Fluorene§	60±48	273±237	NR	4-29	ND-15	ND-67
Phenanthrene§	295±501	1429±1532	NR	3-130	1-195	ND-1970
Anthracene§	110±154	336±369	NR	5-80	ND-44	ND-320
Fluoranthene	1076±1718	3713±3575	<50-4400	20-460	ND-538	ND-5610
Pyrene	1253±1848	3931±3413	<50-5200	30-390	ND-398	ND-5310
Benz(a)anthracene	317±491	1239±1229	<50-13000	3-60	ND-228	ND-2780
Chrysene	589±924	1688±1359	80-3800	10-260	ND-238	NA
Benzo(b,k)fluoranthene	1242±1839	2958±2286	NR	NR	ND-912	ND-6660
Benzo(e)pyrene	469±643	1094±820	NR	NR	ND-294	NA
Benzo(a)pyrene	573±843	1132±968	NR	20-200	ND-282	ND-2980
Perylene	274±350	285±268	NR	NR	ND-105	NA
Indeno(1,2,3,-cd)pyrene	426±566	1139±951	NR	NR	ND-476	ND-2350
Benzo(g,h,I)perylene	450±591	1219±993	NR	NR	ND-318	ND-2370
Dibenzo(a,h)anthracene	182±147	259±217	NR	10-50	ND-104	ND-505
Σ LMW PAHs	604±766	2556±2625	NR	NR	2-280	ND-2414
Σ HMW PAHs	6852±9662	18677±15933	NR	NR	1-3423	ND-32225
Total PAHs	7456±10354	21233±18504	Up to 19400	NR	6-4461	ND-34639

ND: not detected, NR: not reported, NA: not analyzed. All units in mg/Kg dry weight basis. §: Low molecular weight PAH.

PESTICIDES AND HERBICIDES

Chlorinated pesticides were manufactured to use as biocides to control common plagues affecting a wide variety of crops. In addition, compounds such as DDT were also used to control insects transmitting human deceases such as malaria. Common characteristics of chlorinated hydrocarbons are their elevated potential for bioaccumulation (Octanol-water partition coefficients (Kow's) between 10,000 and 200,000) and their resistance to degradation (compounds are still present in the sediment and biota after decades of restrictions; Lauenstein and Daskalakis, 1998). Because of the combination of land use, agricultural practices application patterns and exposure data, several chlorinated insecticides have been classified as priority contaminants for Florida coastal ecosystems (Pait et al., 1989, Long and Morgan, 1990; Delfino et al., 1991, Cantillo et al., 1997, 1999). Among them DDT and its metabolites (mainly DDE), several components of technical Chlordane, Lindane, cyclodiene based insecticides such as Aldrin, Dieldrin, Mirex, Heptachlor, and Endosulfan and also more contemporary insecticides such as Chlorpyrifos (Dursban). Of all these chlorinated pesticides only Endosulfan is still registered for use in Southwest Florida crops. Despite this recognition, only a few of these compounds have FDEP promulgated SQAGs mainly due to lack of risk data to validate the effects of the observed occurrences to wildlife. Organophosphorous pesticides were introduced decades ago to replace chlorinated pesticides in order to avoid environmental accumulation and to reduce the ecological risk to wildlife. Organophosphates (diazinon, malathion, parathion, chlorphyrifos, etc) are a class of insecticides affecting pest nervous systems by acting on their acetylcholinesterase inhibition. Although more toxic than chlorinated hydrocarbons, they tend to degrade quickly and tend not to accumulate in environmental compartments. Unlike the legacy pesticides many of these 37 or so insecticides are still in use in Florida for commercial and household applications (Wilson and Foos, 2006) and are often detected in areas draining agricultural operations.

Phenoxy herbicides (2,4-D, silvex, 2,4,5-T, etc) have a rather complex mode of action since they resemble plant growth hormones called auxins. Among them, 2,4-D is probably the most widely used herbicide applied to control broadleaf weeds in grasses. These compounds tend to be more volatile and water soluble than their legacy counterparts and thus more difficult to track in the environment as they move from their application point. Phenoxy acid herbicides have been detected in other coastal areas in Florida (Hemming et al, 2005) and are often included as analytes in the long term monitoring programs conducted by the water management districts. Despite the efforts in selecting the right targets and expanding the list of contaminants, very little information was obtained with respect to their environmental occurrence along Collier County's watersheds.

Relevant data for the pesticides and herbicides monitored in this study are summarized as follows:

- If all hits above the method detection limits are used and the term "pesticide" is generalized to incorporate just one of the 58 pesticides/herbicides measured, only 4.5% of the samples tested positive for pesticides and only 1.1% of them had detections above the laboratory reporting level.

- One single finding of elevated concentrations of Endosulfan (482 ng/g d.w as total endosulfan) at station CC056 (Oil Well Grade Rd.) just south of a major agricultural field operation was the only detection for the chlorinated pesticide group. Despite an increased uncertainty in the analytical measurement due to sample dilution and the qualified results for the detection of the metabolite (endosulfan sulfate) below the laboratory reporting limit this levels are still environmentally relevant and need additional assessment.

- Endosulfan is one of the last chlorinated pesticides still in use in Florida. This detection is close to the maximum reported in the 1989-1991 study for Haldeman Creek (695 ng/g Endosulfan Sulfate) but clearly representative of a fresh input of the insecticide as reflected by the isomer composition (EII>> EI >>>E Sulfate).
- There is no SQAG promulgated or proposed for Endosulfan and despite the fact that this was an isolated event in an area heavily influenced by agriculture, this sediment concentrations could be toxic for reference organisms such as *C. tentans* (Weston et al., 2004) and should be further investigated.
- Several minor detections of legacy pesticides (dieldrin at 1.69 ng/g; γ-chlordane at 1.22 ng/g; and heptachlor epoxide at 1.42 ng/g) were reported at three other sampling sites. The concentrations are low and between the laboratory method detection limit (MDL) and the reporting limit (MRL) and thus should be interpreted with caution.
- These levels of legacy pesticides are well within the ones found in the 1989-1991 and the 2001-2002 surveys that reported no potential concern associated with similar concentrations since none of these values exceeded the available SQAGs. This information, combined to the fact that all these pesticides have been banned decades ago make the risk of their occurrence diminish as time passes on systems where the legacy signature is close to background levels.

All these indicators clearly support the results of this study in concluding that the risk associated with watershed-wide contamination by organophosphorous pesticides, phenoxy herbicides and chlorinated pesticides (except endosulfan) in Collier County estuaries is very low and that levels of contamination are still well under any of the sediment quality criteria guidelines proposed by FDEP to assess the potential contamination of coastal environments.

CONCLUSIONS

The overarching conclusion of this study is that the sediment quality along the county watersheds is acceptable with few areas that need special attention with respect to several contaminants of concern. A group of specific key findings however deserve more attention as follow:

- The effects of "Urbanization" are still evident and recurrent in the northern portions of Naples Bay and the Gordon River. Continued, long term monitoring is needed to evaluate the impacts of sustained development, road construction and modification of water deliveries.
- Three groups of chemicals are of particular concern due to their frequency of detection, their environmental concentration, the existence of local point sources or indication of long term contamination records;
- Petroleum product contamination, mainly in the form of PAHs is of environmental concern at three stations (CC018, CC036 and CC014).
- One of these stations, CC036 has a long term record of PAH contamination dating from 1989.

- The co-occurrence of elevated concentrations of both PAHs and trace elements at station CC014 indicates a source of mixed inputs that needs to be addressed by a more extensive localized survey.
- Copper is a contaminant of potential concern in areas around marinas in North Naples Bay but also along Haldeman Creek and the agricultural areas near US-41 in the southern portion of the county.
- Of all pesticides analyzed Endosulfan 2 (one of the isomers present in the commercial formulation) was the only analyte present in the sediment samples at concentrations that could potentially affect biological resources. Despite the added uncertainties in the analysis due to sample dilution and minor deviations from the QA/QC protocols the concentration of Endosulfan 2 at station CC056 is considered elevated and environmentally relevant. Because endosulfan sulfate, the metabolite of endosulfan, was not detected above the laboratory reporting limit at the site the result is likely indicative of a fresh and rather localized input. Since there is yet no promulgated sediment based criterion to assess the hazards posed by this pesticide and because the product is still in use, sustained efforts in the area are still required to prevent future and continued releases.

RECOMMENDATIONS

Since the most relevant question linking sediment contaminants and environmental management is deciding when to intervene the proposed recommendations are geared toward that goal.

County Wide Strategies

Most of the recommendations proposed previous monitoring efforts are still valid after this study; however, increased scrutiny did identify localized areas that require additional attention.

Based on the results of this survey and findings of previous monitoring efforts the following recommendations are provided:

- Contamination by polynuclear aromatic hydrocarbons (PAHs) is the primary concern along Collier County watersheds and should still be the focal point of future monitoring programs.
- Source identification and site specific monitoring is required to evaluate the spatial and temporal extent of the contamination at sites CC018, CC014 and CC036.
- Copper and to a lesser extent arsenic are the highest ranking trace elements in the sediment hazard assessment based on the SQAGs. Since sources of copper could be easily identified BMPs will provide the best solution for addressing or controlling the sediment contamination. In the case of arsenic, additional monitoring is required to understand the inputs to Naples Bay.
- A county-wide, long term sediment quality assessment monitoring program should be routinely conducted every 5 years. The program should include both estuarine and inland stations keeping the focus on potential sources such as marinas, industrial facilities, golf courses, wastewater release points, storm water runoff, and crop or ornamental production.
- Since the main objectives of these surveys is environmental assessment rather than regulation, the analysis of PAHs should be conducted using more sensitive analytical methodologies capable of sub-part per billion detection levels instead of regulatory methods with sub-part per million detection limits. Such methods

are available (NOAA) and will provide the same data quality requirements of a NELAC accredited methodology.

- Keep a comprehensive list of analytes to account for past and present use contaminants :
  - a) Polynuclear aromatic Hydrocarbons,
  - b) Trace Metals,
  - d) Chlorinated hydrocarbons (legacy plus Endosulfan and Chlorpyrifos),
  - e) Re-evaluate the list of constituents for the contemporary biocides to specific needs based on use and ecological relevance.
- Adopt a set of sediment guideline criteria that triggers “warning” and “action required” stages. (i.e. two consecutive detections above the PEL/TEL SQAGs at one site in two monitoring periods). This is particularly important for PAHs, Copper and Endosulfan.
- Adopt “planning guidelines” to trigger action for contaminants that do not have a promulgated SQAG.
- Maintain a concentrated monitoring effort within north Naples Bay and the lower Gordon River in order to assess temporal changes and to track the implementations of BMPs.

Site Specific Recommendations

- Since some of the sediments were catalogued as Tier 1 based on the classification by Long, 2000 all these locations require higher frequency and site specific surveys. In particular, site CC036 where elevated PAH contamination has been present in the last 20 years.

- The presence of sustained contamination by multiple chemicals along Haldeman Creek, CC021 (reported by Grabe 1993 and in this study) and at station CC014 (this study) requires additional effort in identifying potential sources, evaluating historical trends by the use of sediment cores, and the development of management strategies for future abatement. The same statement is valid for sites like CC056 showing fresh inputs of Endosulfan 2 and site CC032 showing localized high concentrations of copper.

REFERENCES

Boehm, P., and Farrington, J. (1984) Aspects of the polycyclic aromatic hydrocarbon geochemistry of recent sediments in the Georges Bank region. *Environmental Sciences and Technology*. **18:** 840-845.

Cai, Y.; Georgiadis, M. and Fourqurean, J. (2000) Determination of arsenic in seagrass using inductively coupled plasma mass spectrometry, *Spectrochimica Acta, Part B*, **55**:1411-1422.

Catillo, A., Lauenstein, G. and O'Connor, T. (1997) Mollusk and sediment contaminant levels and trends in South Florida coastal waters. *Marine Pollution Bulletin*, **34(7):**51-521.

Cantillo, A., Lauenstein, G., O'Connor, T., and Johnson, W. (1999) Status and Trends of Contaminant Levels in Biota and Sediment of South Florida. U.S. Department of Commerce, National Oceanic and Atmospheric Administration (NOAA), Silver Spring, MD.

Daskalakis, K., and O'Connor, T. (1995) Distribution of chemical concentrations in US coastal and estuarine sediment. *Marine Environmental Research*, **40(4):**381-398.

Delfino, J., Coates, J., Davis, W., Garcia, K., Jacobs, M., Marincic, K., and Signorella, L. (1991). Toxic pollutants in discharges, ambient waters, and bottom sediments. Volume I and II. Submitted to Florida Department of Environmental Regulation. Tallahassee, Florida.

Eganhouse, R., Blumfield, D., and Kaplan, I. (1982) Petroleum hydrocarbons in stormwater runoff and municipal wastes: input to coastal waters and fate in marine sediments. Thalassia Jugoslavica, **18:** 411-431.

Gottholm, B., and Robertson, A. (1996) Contaminant levels measured at NOAA's National Estuarine Research Reserves. U.S. Department of Commerce, National Oceanic and Atmospheric Administration (NOAA), Silver Spring, MD.

Grabe, S.(1996) Contamination of limnetic sediments in Collier County, 1991. *The Florida Scientist*, **59(3):** 141-154.

Grabe, S., (1990) Water quality and sediment characterization of Collier County Estuaries: A pilot study. Report PC-SP-90-01. Pollution Control Department, Collier County, Florida.

Grabe, S., (1993) Sediment quality in Collier County estuaries, 1990-1991. Report PC-AR-93-07. Pollution Control Department, Collier County, Florida.

Harriss, R. Mattraw, H., Horvath, G., and Andren, A.(1971) Input, cycling and fate of heavy metals and pesticides pollutants in estuaries of the western Everglades. Report to the National Park Service. Florida State University, Tallahassee, Florida.

Hemming, J., Brown, J., Brim, M., and Jarvis, R. (2005) Sediment quality survey of the Choctawhatchee Bay system in the Florida panhandle. Marine Pollution Bulletin, 50, 889-903.

Johnson, W., O'Connor,T., Cantillo, A., and Lauenstein, G., (1999) Spatial distribution of chlorpyrifos and endosulfan in USA coastal waters and the Great Lakes. National Oceanic and Atmospheric Administration NOAA Technical Memorandum NOS NCCOS CMA 140, Silver Spring, Maryland.

Jones, R., Jacobson, M., Jaffe, R., West-Thomas, J., Arfson, C., and Alli, A. (1995) Method development and sample processing of water, soil, and tissue for the analysis of total and organic mercury by cold vapor atomic fluorescence spectrometry, *Water, Air and Soil Pollution*, **80:**1285-1294.

Kennish, M. (1977) Practical Handbook of Estuarine and Marine Pollution. CRC Press, Boca Raton.

Lauenstein, G, and Cantillo, A. (1998) Sampling and Analytical Methods of the National Status and Trends Program Mussel Watch Project: 1993-1996 Update. NOAA Technical Memorandum NOS ORCA 130. Coastal Monitoring and Bioeffects Assessment Division, Office of Ocean Resources Conservation and Assessment,National Ocean Service,National Oceanic and Atmospheric Administration, Silver Spring, Maryland.
http://ccmaserver.nos.noaa.gov/Pdfpubs.html/techmemo130.pdf

Lauenstein, G., and Daskalakis, K. (1998) U.S. long-term coastal contaminant temporal trends determined from mollusk monitoring programs 195-1993. *Marine Pollution Bulletin*, **37(1-2):**6-13.

Long, E., and Morgan, L. (1990). The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA Tech. Memo. NOS ORCA 52. Seattle, WA.

Long E., Wolfe, D., Carr, S., Scott, J., Thursby, G., Windom, H., Lee, R., Calder, F., Sloane, G. and Seal. T., (1994) Magnitude and Extent of Sediment Toxicity in Tampa Bay, Florida. NOAA Tech. Memo. NOS ORCA 78. Silver Spring, MD.

Long, E., (2000) Degraded sediment quality in U.S. estuaries: A review of magnitude and ecological implications. *Ecological Applications*, **10(2):**338-349.

Long, E., Field, L., Macdonald, D. (1998) Predicting toxicity in marine sediments with numerical sediment quality guidelines. *Environmental Toxicology and Chemistry*, **17(4):**714-727.

MacDonald, D.D. (1994). Approach to the assessment of sediment quality in Florida coastal waters: Volume 1 - Development and evaluation of the sediment quality assessment guidelines. Report prepared for Florida Department of Environmental Protection. Tallahassee, Florida.

Macdonald, D., Carr, S., Calder, F., Long, E., and Ingersoll, C. (1996) Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology*, **5**: 253-278.

Macdonald, D.D., Ingersoll, C.G., Smorong, D.E., Lindskoog, R.A., Sloan, G.,and Biernacki, T (2003) Development and Evaluation of Numerical Sediment Quality Assessment Guidelines for Florida Inland Waters. Technical Report for FLDEP. Available at:http://www.cerc.usgs.gov/pubs/sedtox/sqags_for_florida_inland_waters_01_03.pdf

Miller, R., and Mcpherson, B., (1998) Occurrence and Distribution of contaminants in bottom sediment and water of the Barron River Canal, Big Cypress National Preserve, Florida, October 1998. U.S. Department of the Interior, U.S. Geological Survey, Center for Coastal Geology. http:/sofia.usgs.gov/publications/papers/bottom_sed.

National Oceanic and Atmospheric Administration NOAA (1999) Coastal assessment and data synthesis framework. Online database: http://cads.nos.noaa.gov/, National Coastal Assessment (NCA) Branch, Special Projects Office (SP), National Ocean Service (NOS), Silver Spring, Maryland.

Neff, J., (1979) Polycyclic aromatic hydrocarbons in the aquatic environment. Applied Sciences Publishers, Inc. London.

O'Connor, T. (1998) Mussel watch results from 1986 to 1996. *Marine Pollution Bulletin*, **37(1-2):**14-19.

Pait,A. Farrow, D., Lowe, J., and Pacheco, P. (1989) Agricultural pesticide use in estuarine drainage areas: A preliminary summary for selected pesticides, U.S. Department of Commerce, National Oceanic and Atmospheric Administration (NOAA), Rockville, MD.

Sauer, S. and Uhler, A. (1995) Pollutant source identification and allocation: advances in hydrocarbon fingerprinting. *Remediation*. Winter 1994/95, 25-50.

Schropp S., Lewis, F., Windom, H., Ryan, J., Calder, F., and Burney, L. (1990) Interpretation of Metal Concentrations in estuarine sediments of Florida using aluminum as a reference element. *Estuaries*, **13(3):**227-235.

Schropp, S., and Windom, H. (1988) A guide to the interpretation of metal concentrations in estuarine sediments. Coastal Zone Management Section, Florida Department of Environmental Regulation, Tallahassee, Florida.

Stout, S., Magar, V., Uhler, R., Ickes, J., Abbott, J., and Brenner, R. (2001) Characterization of naturally occurring and anthropogenic PAHs in urban sediments – Wycoff/Eagle Harbor superfund site. *Environmental Forensics* **2**:287-300.

Thoemke, K., and Gyorkos, K. (1988) An analysis of nutrient, chlorophyll, heavy metal and pesticide levels in Rookery Bay National Estuarine Research Preserve. Report to NOAA. Rookery Bay NERP, Naples Florida.

Weston, D., You, J. and Lydy, M. (2004) Distribution and toxicity of sediment-associated particles in agricultural-dominated water bodies of California's Central Valley. Environmental Science and Technology, **38**, 2752-2579.

Wilson, P.C and Foos, J.F. (2006) Survey of carbamate and organophosphorous pesticide export from a South Florida (USA) agricultural watershed: implications of sampling frequency on ecological risk estimation. Environmental Toxicology and Chemistry, **25 (11)**, 2847-2852.

APPENDIX I Additional Figures

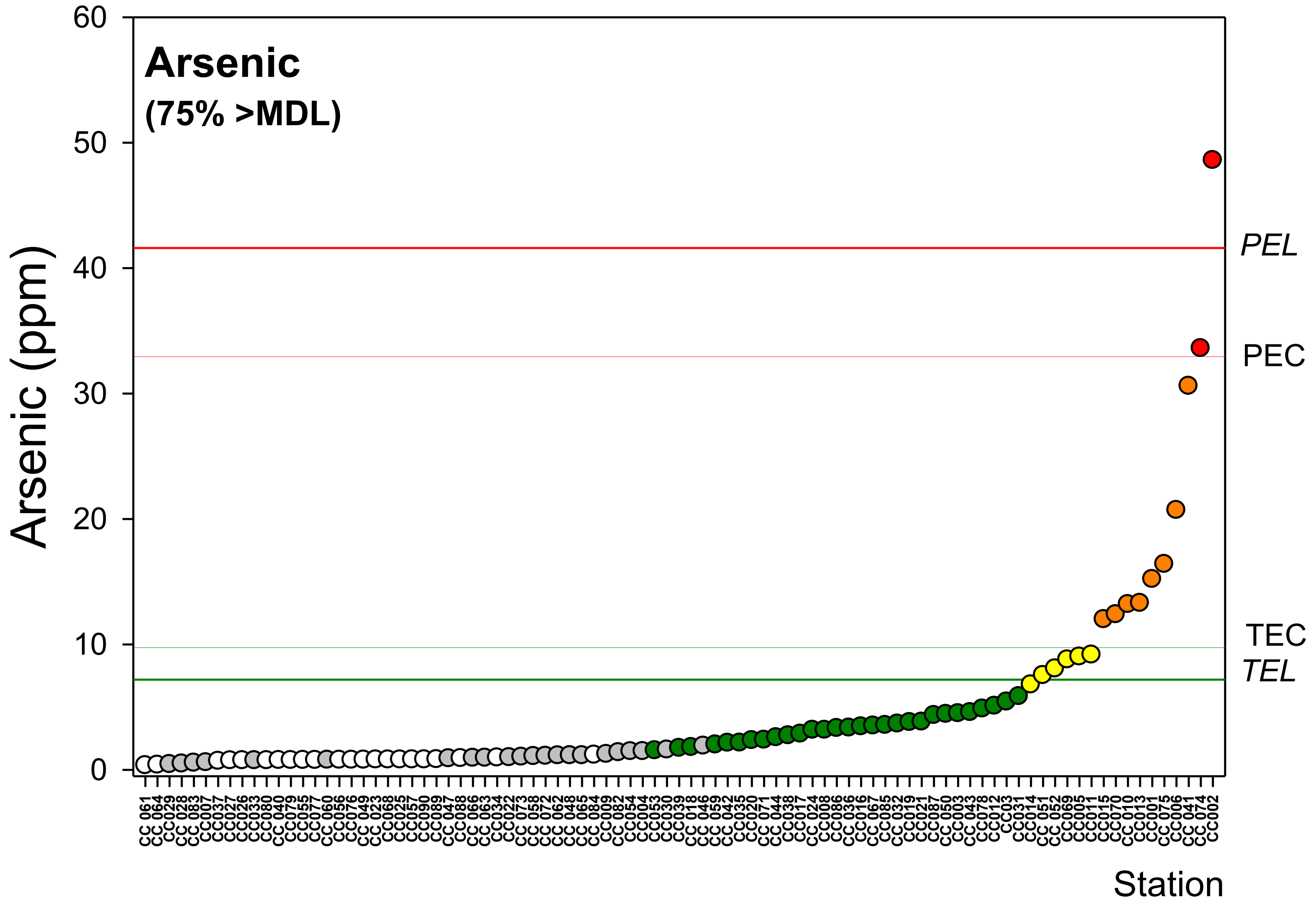


Figure 7 Ranked Distribution of Arsenic in Sediments for the 2007 Survey. (Open circles, MDL, gray circles >MDL but <MRL).

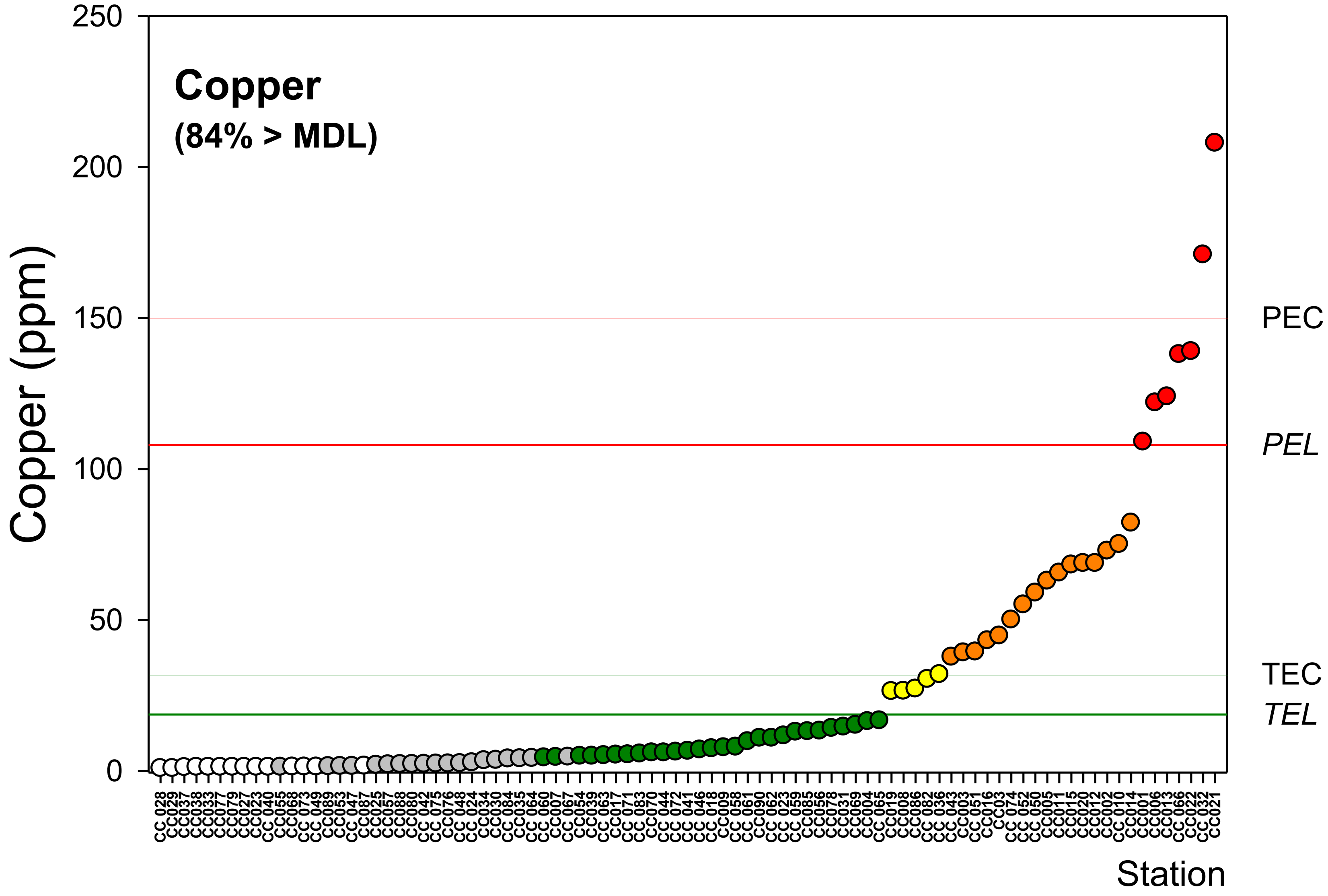


Figure 8 Ranked Distribution of Copper in Sediments for the 2007 Survey.
(Open circles, MDL, gray circles >MDL but <MRL).

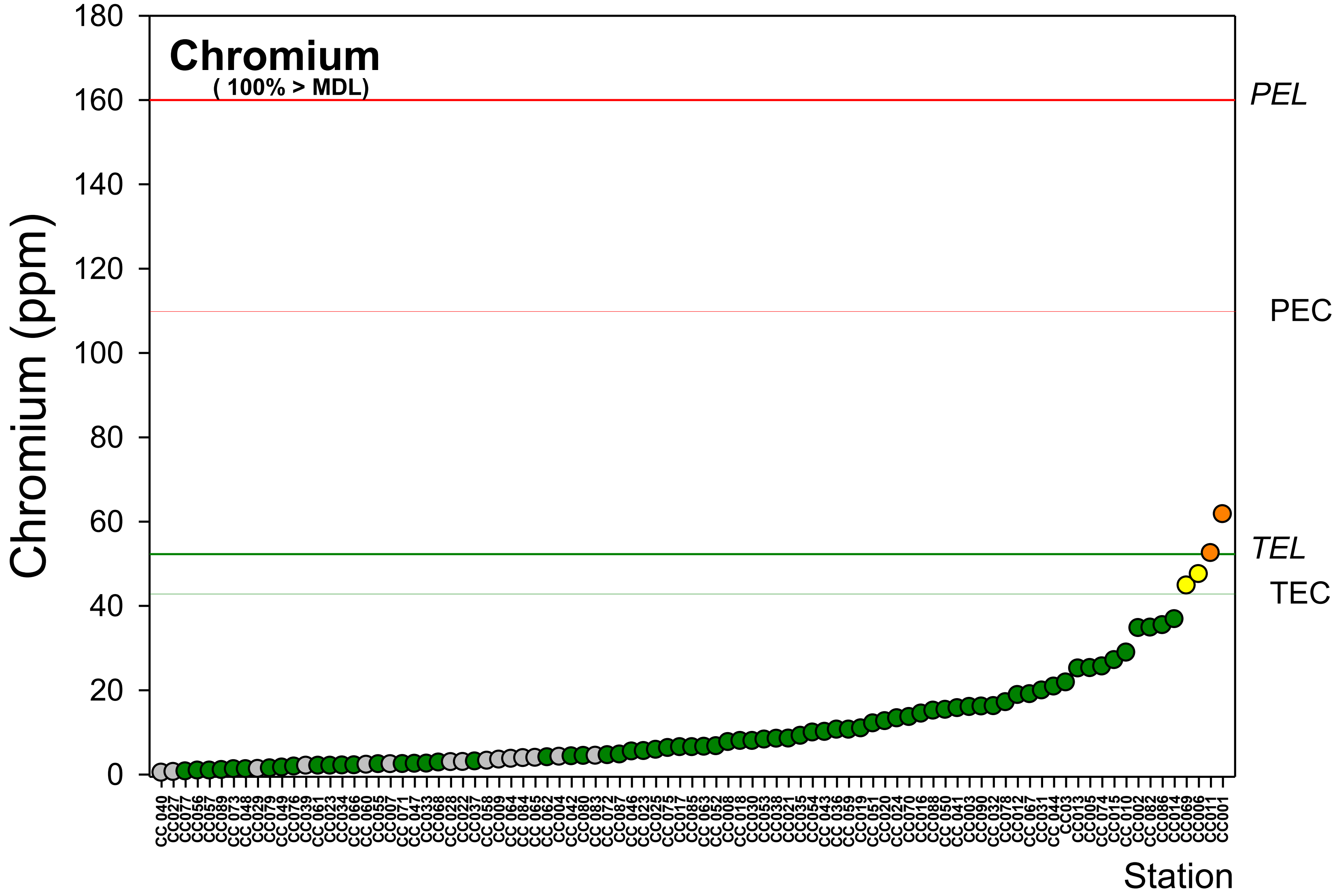


Figure 9 Ranked Distribution of Chromium in Sediments for the 2007 Survey. (Open circles, MDL, gray circles >MDL but <MRL).

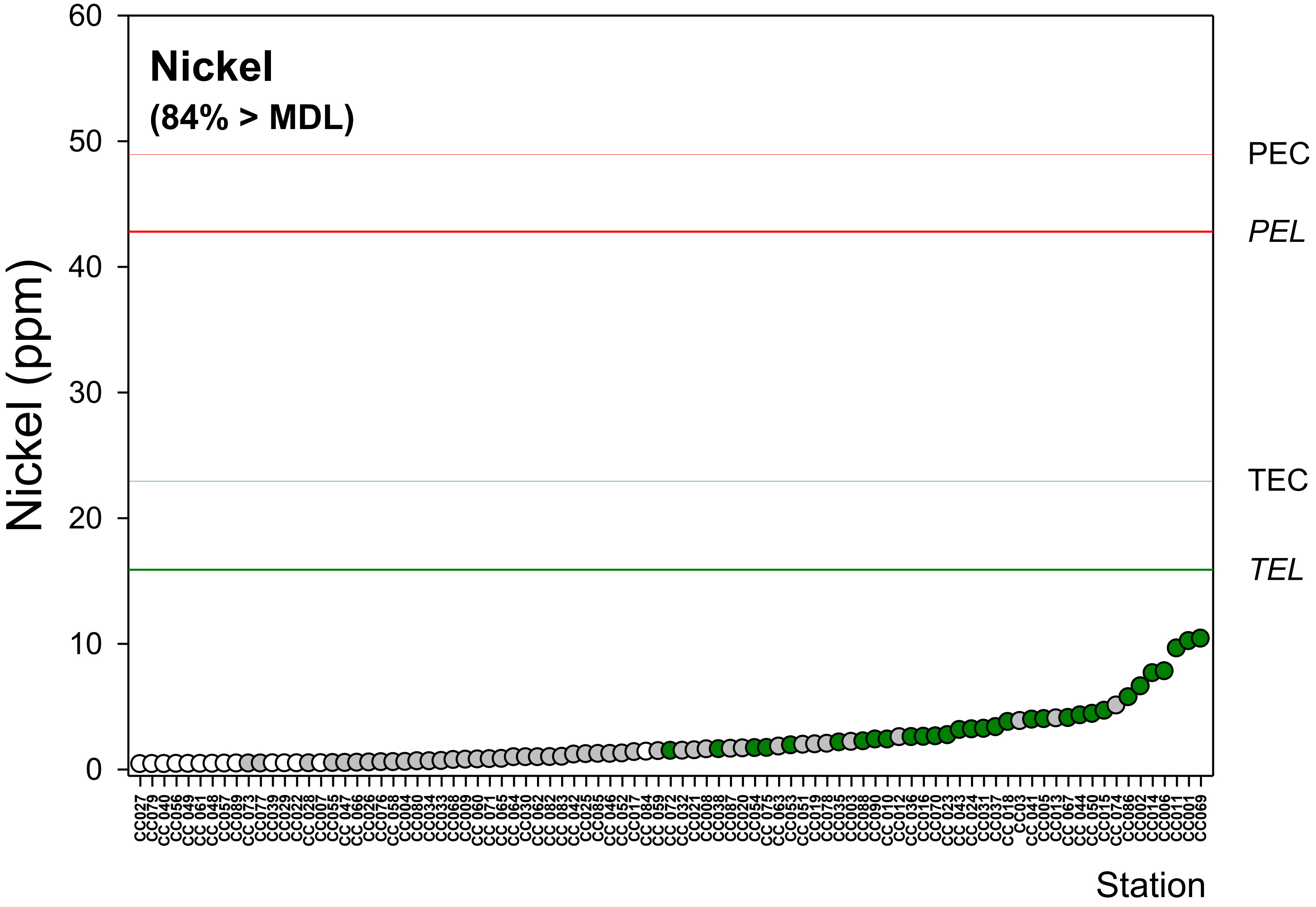


Figure 10 Ranked Distribution of Nickel in Sediments for the 2007 Survey.
(Open circles, MDL, gray circles >MDL but <MRL).

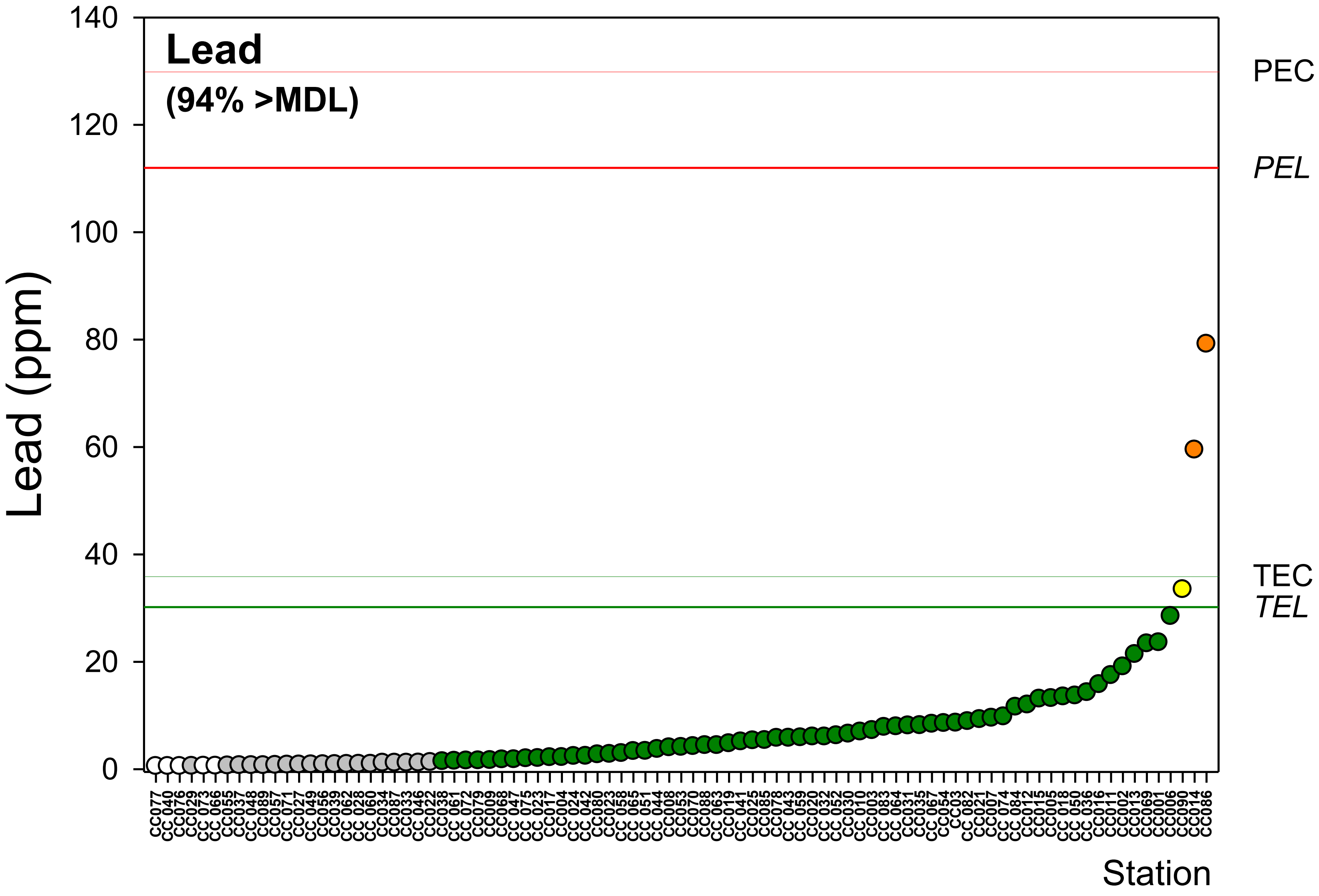


Figure 11 Ranked Distribution of Lead in Sediments for the 2007 Survey.
(Open circles, MDL, gray circles >MDL but <MRL).

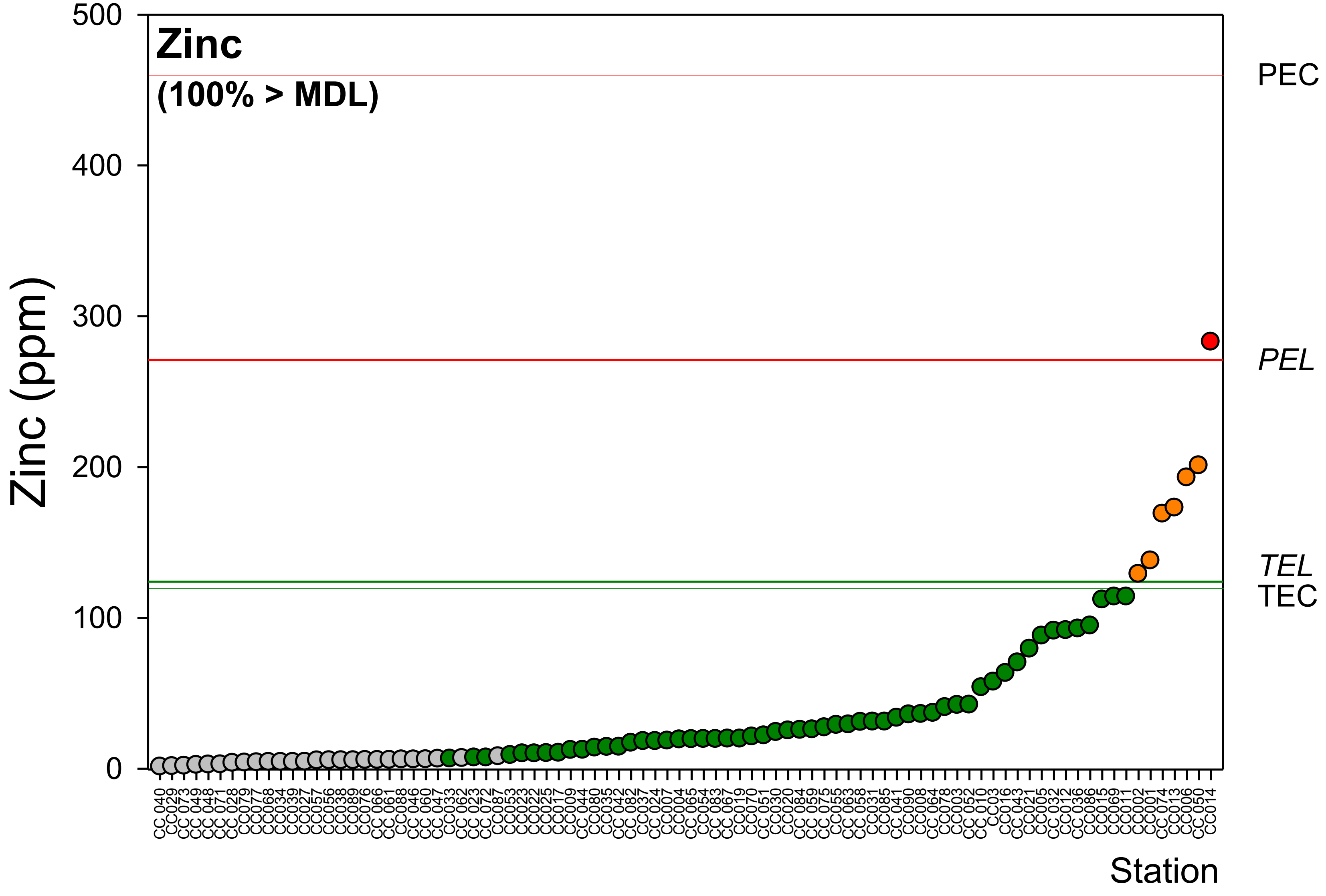


Figure 12 Ranked Distribution of Zinc in Sediments for the 2007 Survey.
(Open circles, MDL, gray circles >MDL but <MRL).

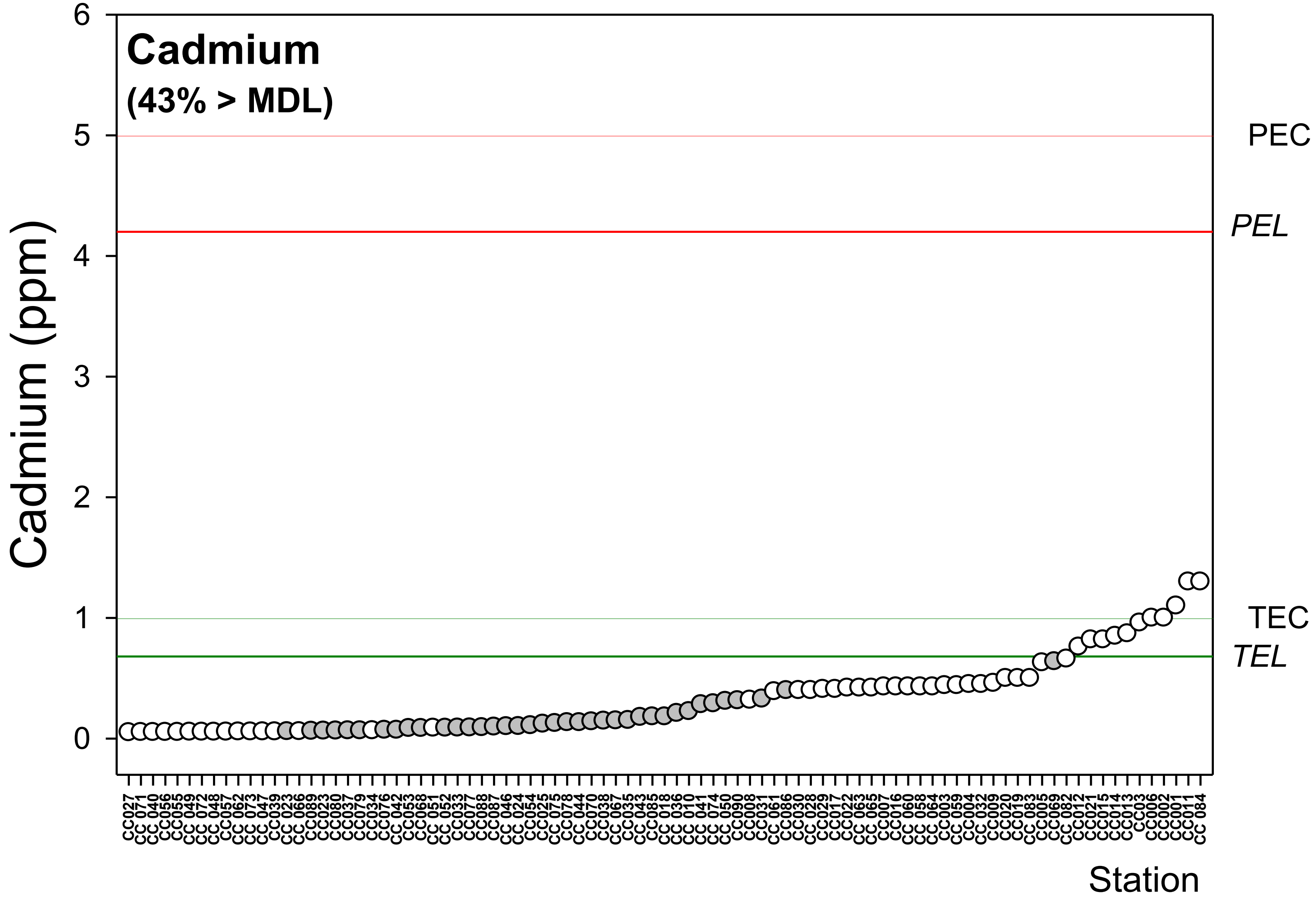


Figure 13 Ranked Distribution of Cadmium in Sediments for the 2007 Survey. (Open circles, MDL, gray circles >MDL but <MRL).

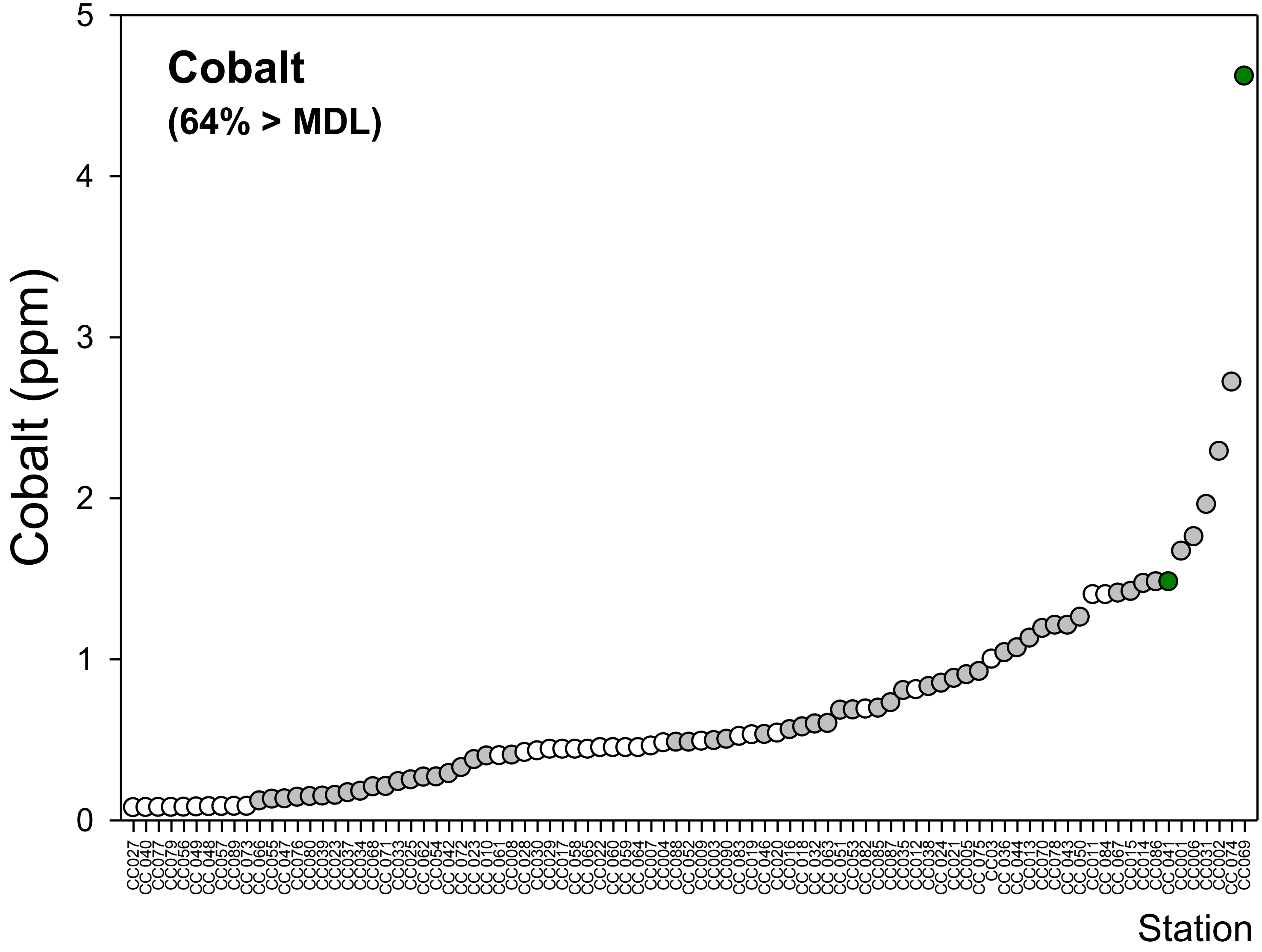


Figure 14 Ranked Distribution of Cobalt in Sediments for the 2007 Survey. (Open circles <MDL; gray circles >MDL but <MRL).

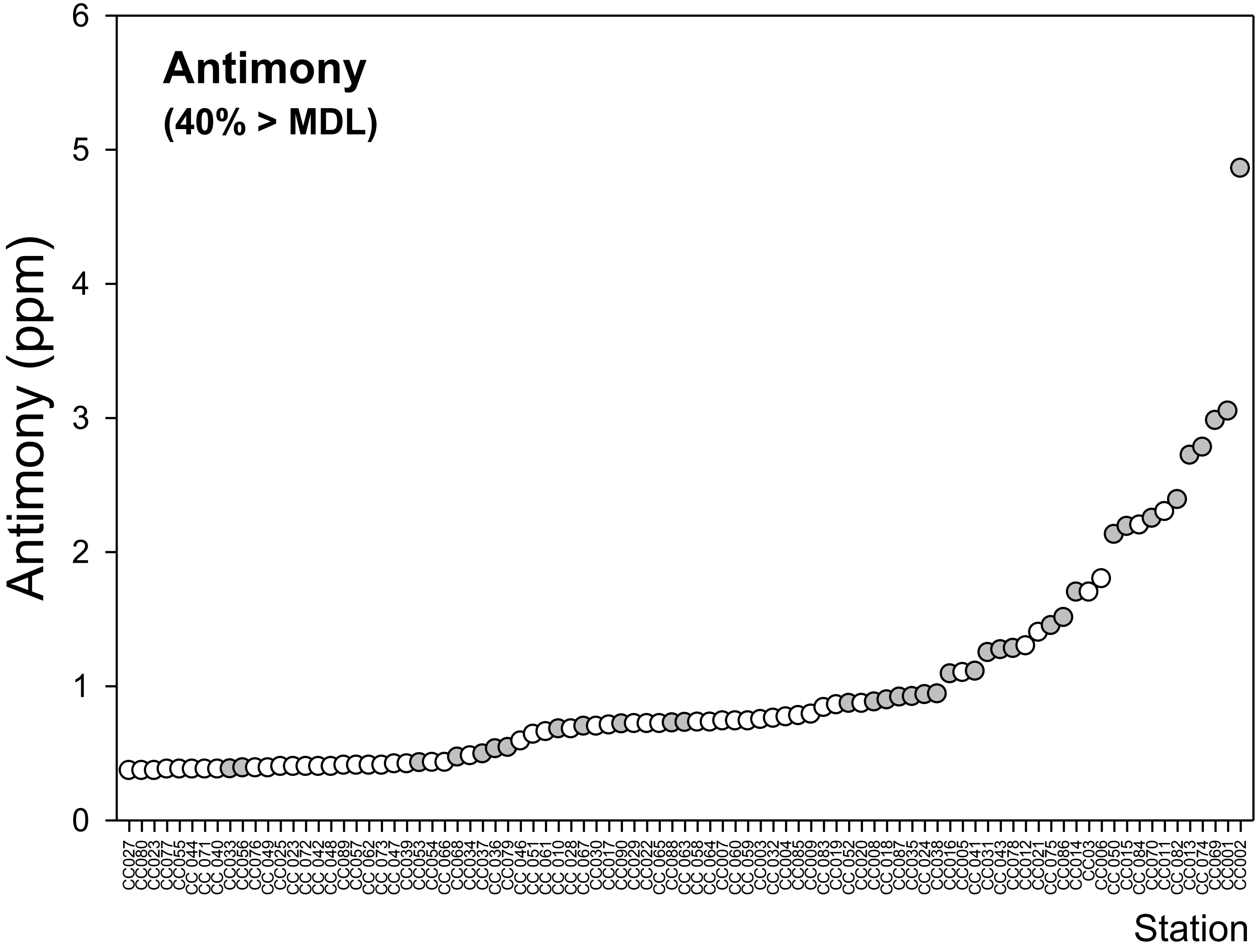


Figure 15 Ranked Distribution of Antimony in Sediments for the 2007 Survey.
(Open circles <MDL; gray circles >MDL but <MRL).

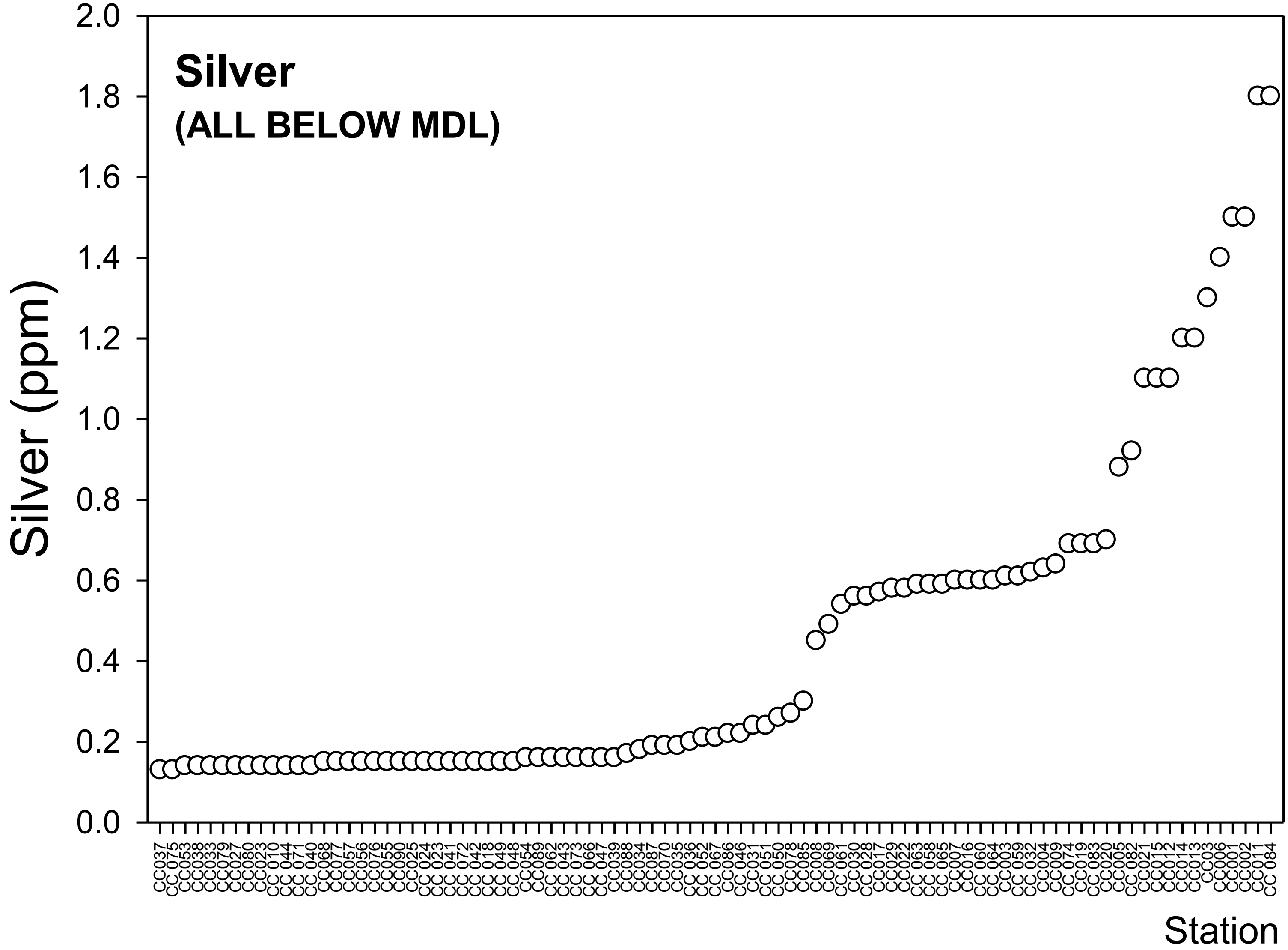


Figure 16 Ranked Distribution of Antimony in Sediments for the 2007 Survey. (All samples <MDL).

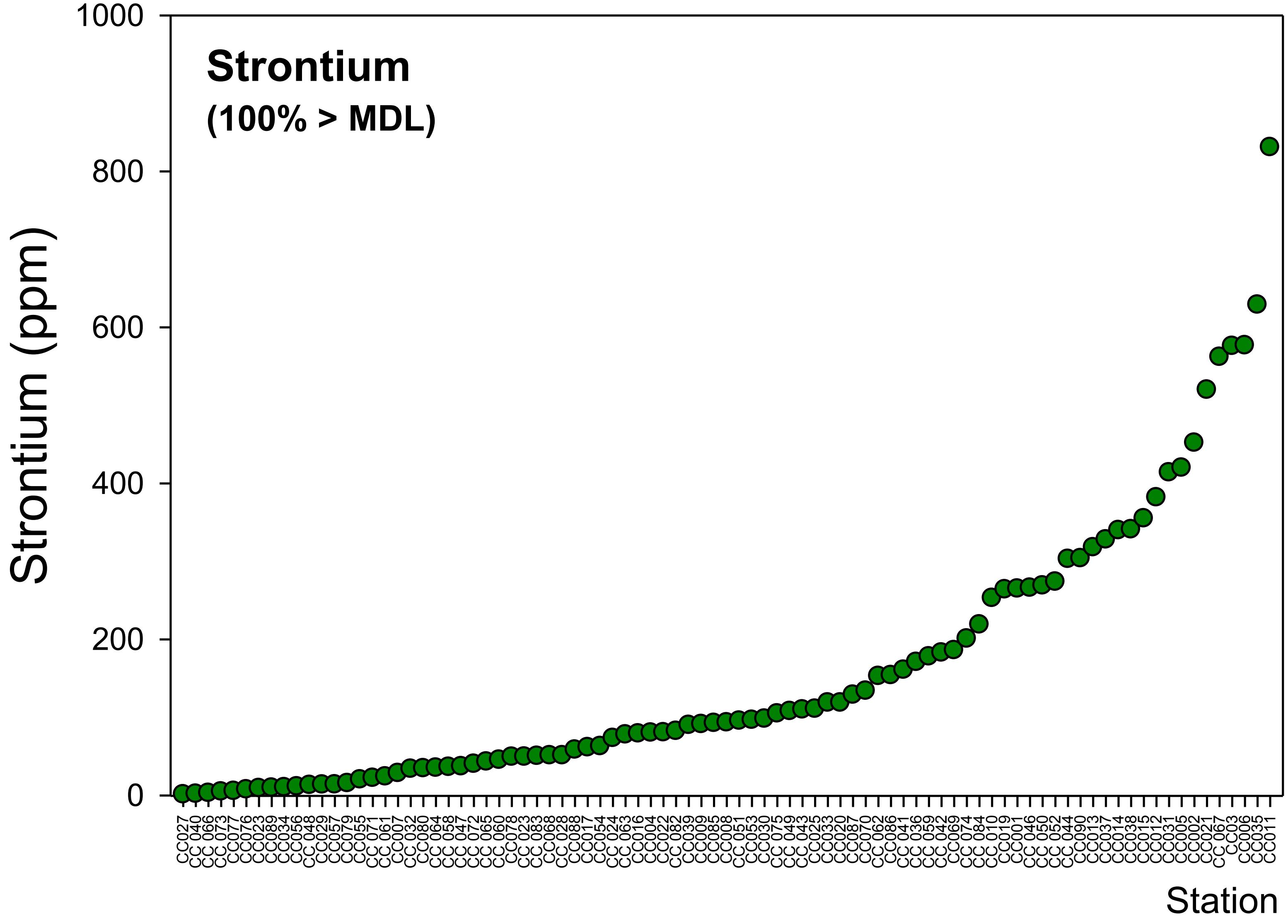


Figure 17 Ranked Distribution of Strontium in Sediments for the 2007 Survey.

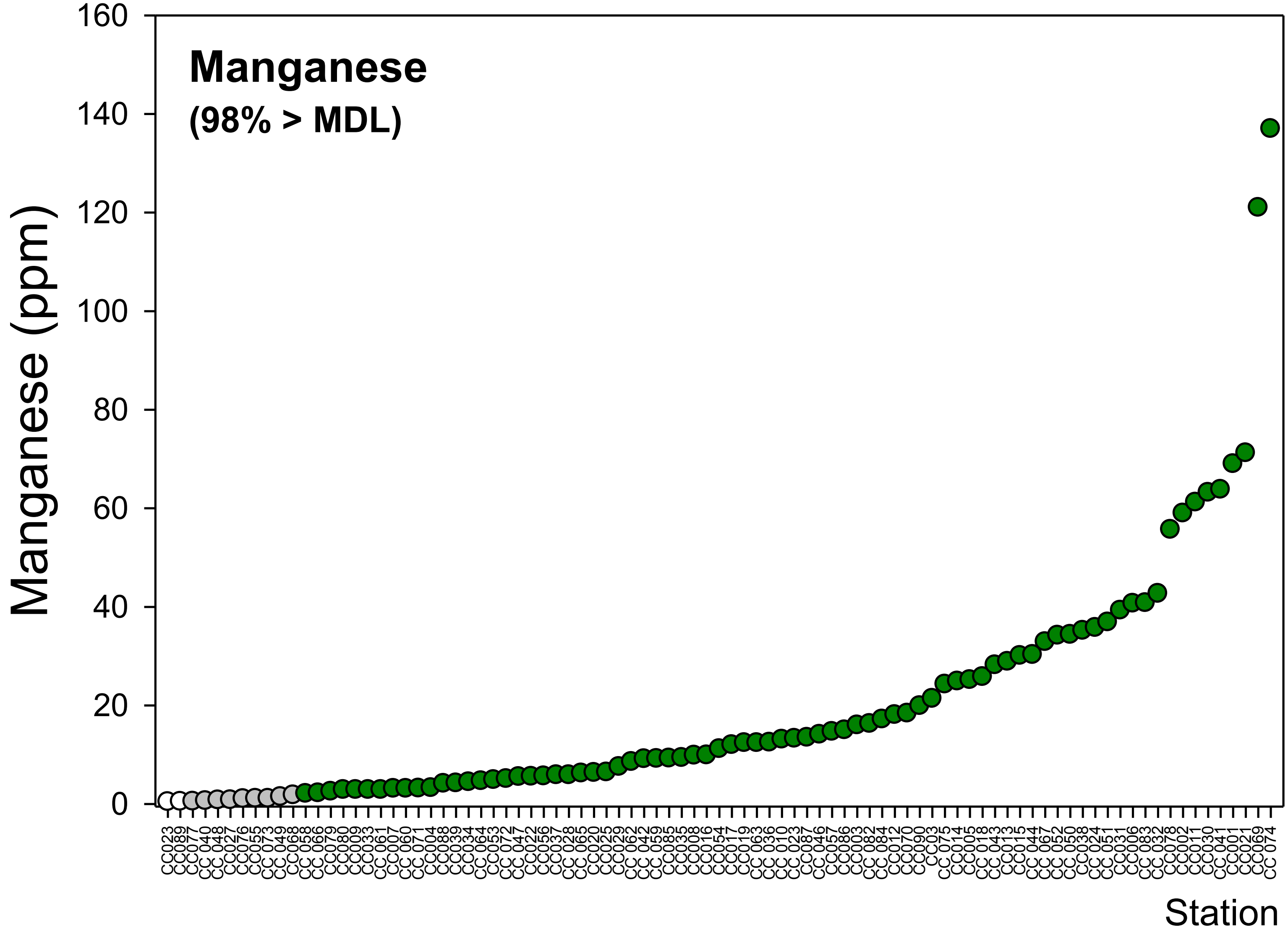


Figure 18 Ranked Distribution of Manganese in Sediments for the 2007 Survey. (Open circles, MDL, gray circles >MDL but <MRL).

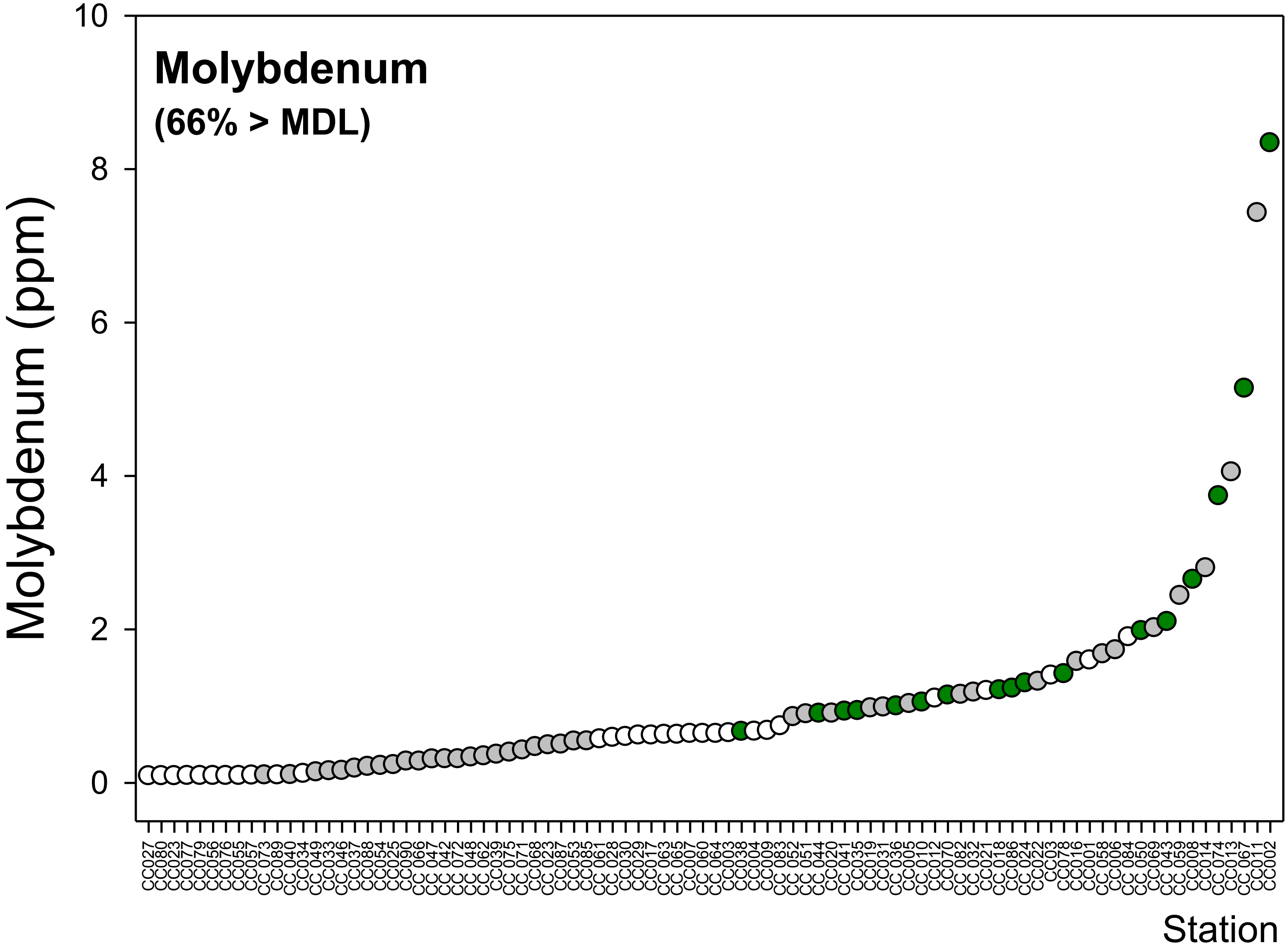


Figure 19 Distribution of Molybdenum in Sediments for the 2007 Survey.
(Open circles, MDL, gray circles >MDL but <MRL).

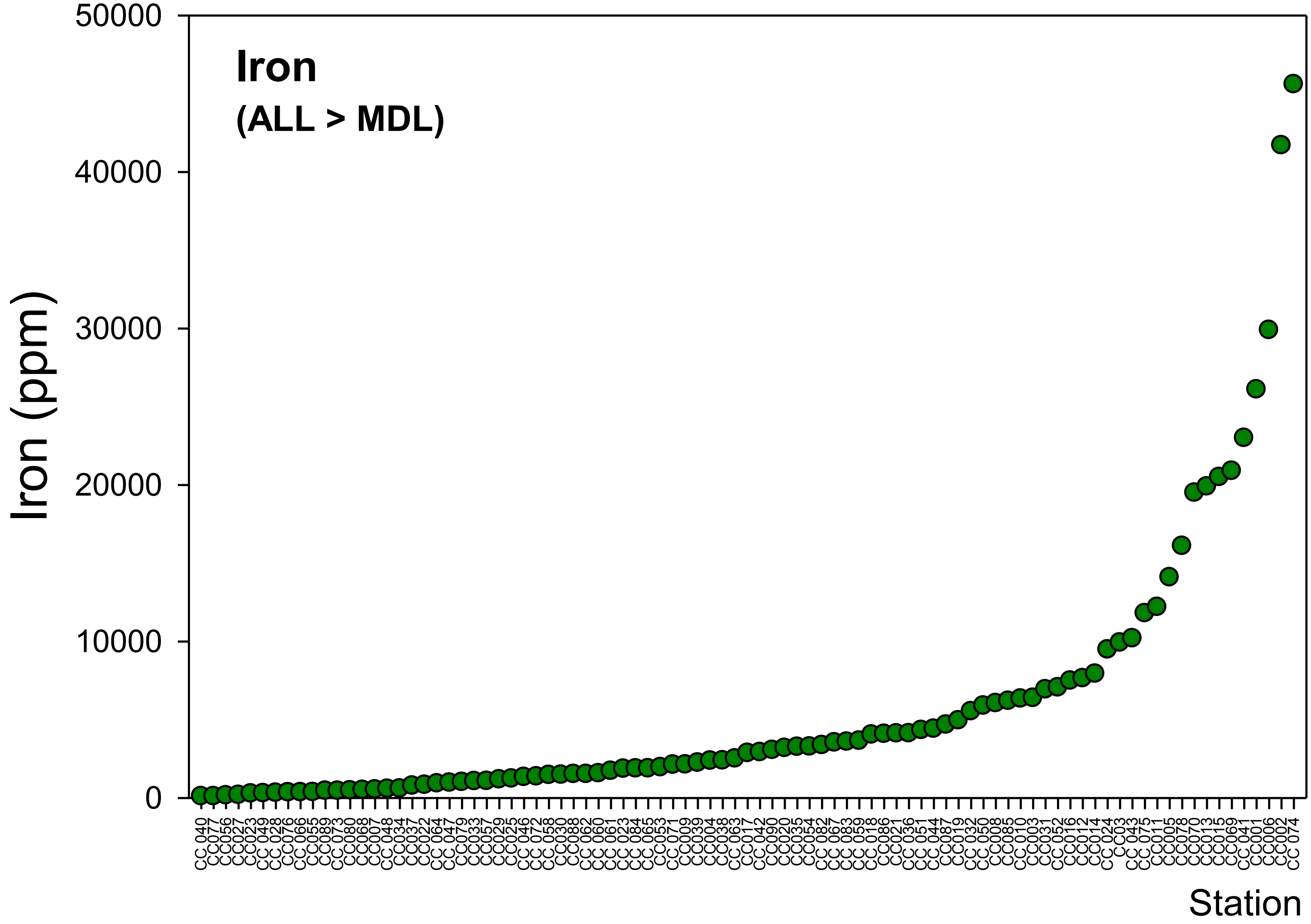


Figure 20 Distribution of Iron in Sediments for the 2007 Survey.

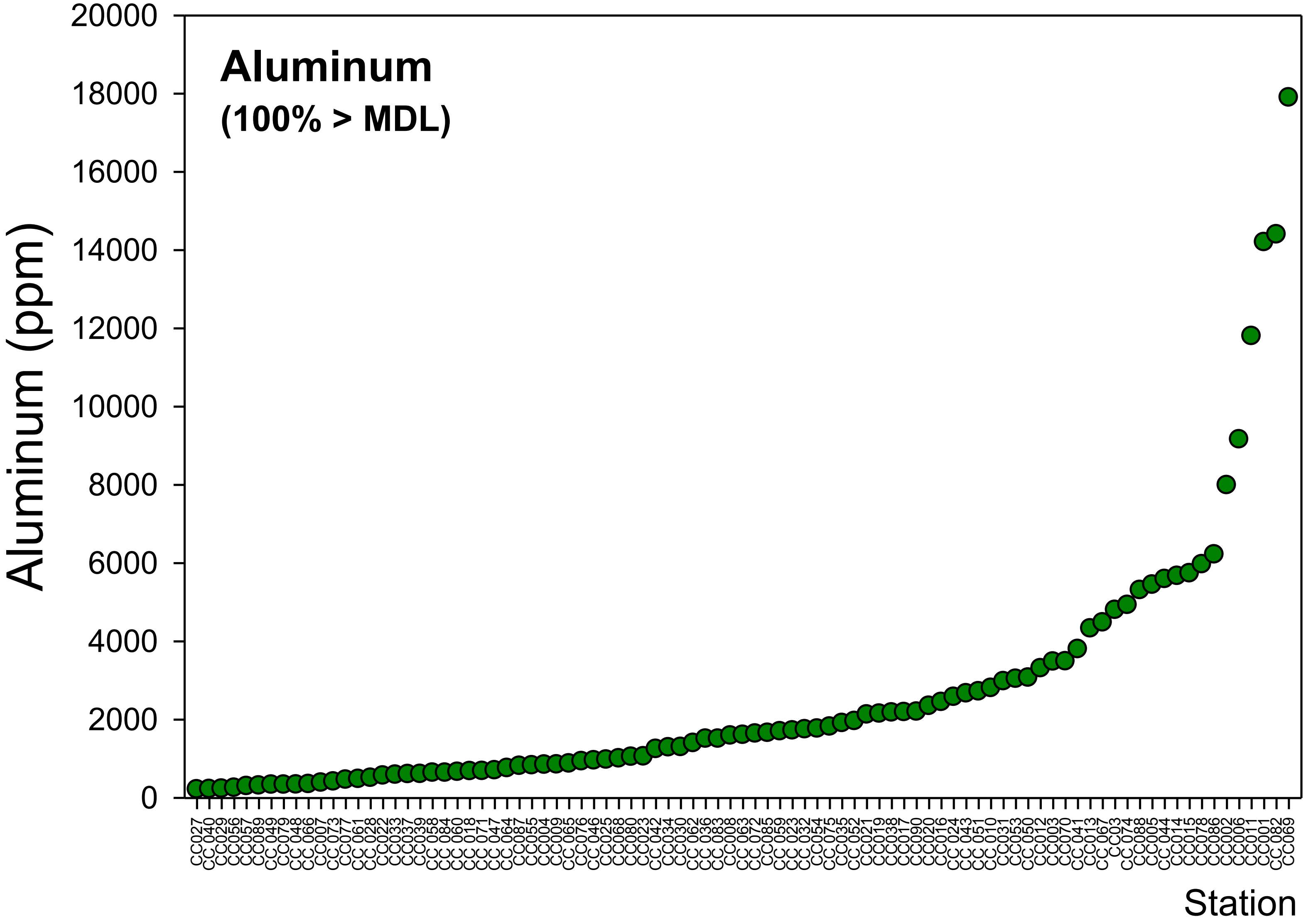


Figure 21 Distribution of Aluminum in Sediments for the 2007 Survey.

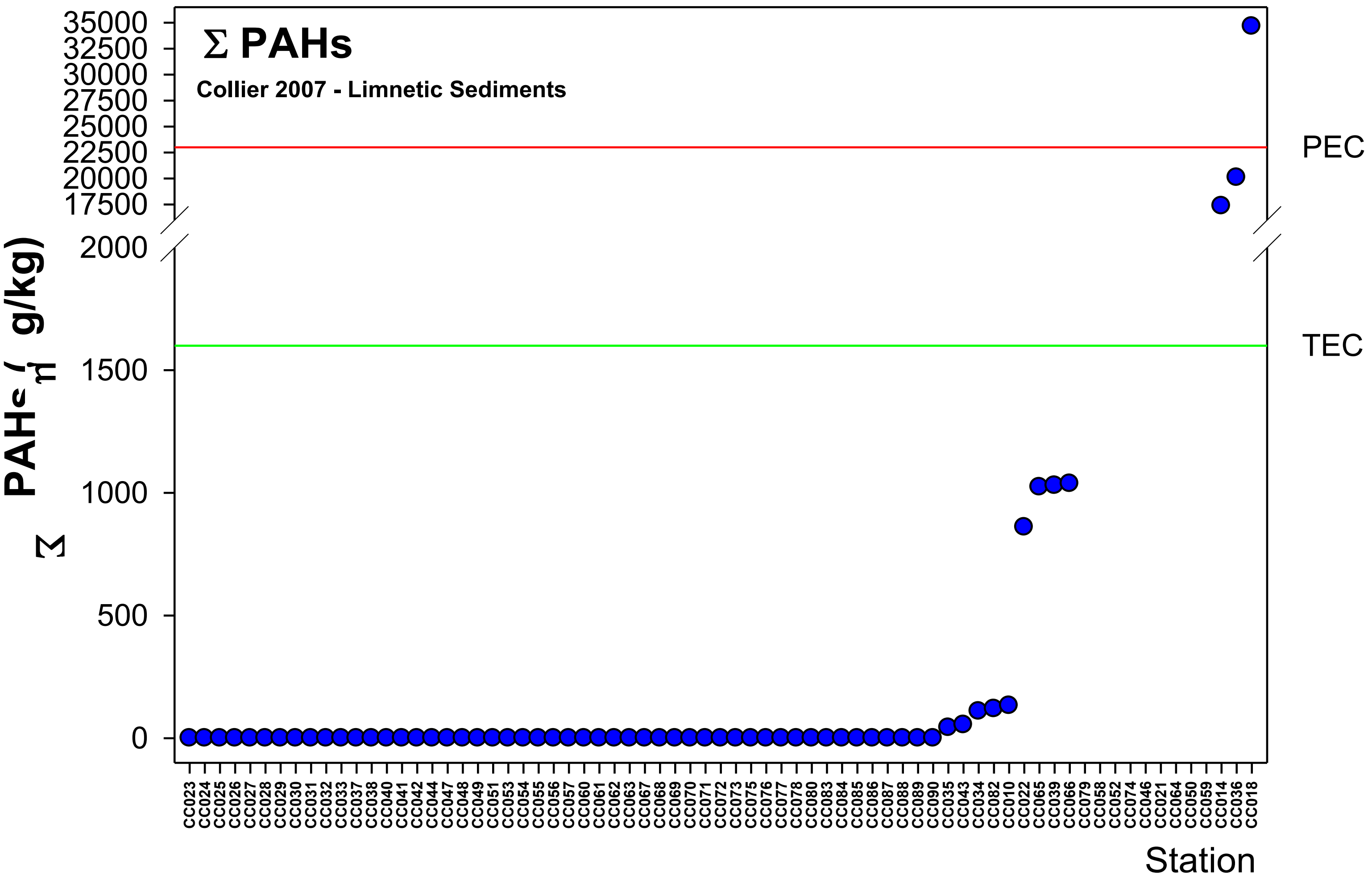


Figure 22 Ranked Concentrations of Total PAHs for Limnetic Sediments in the 2007 Survey.

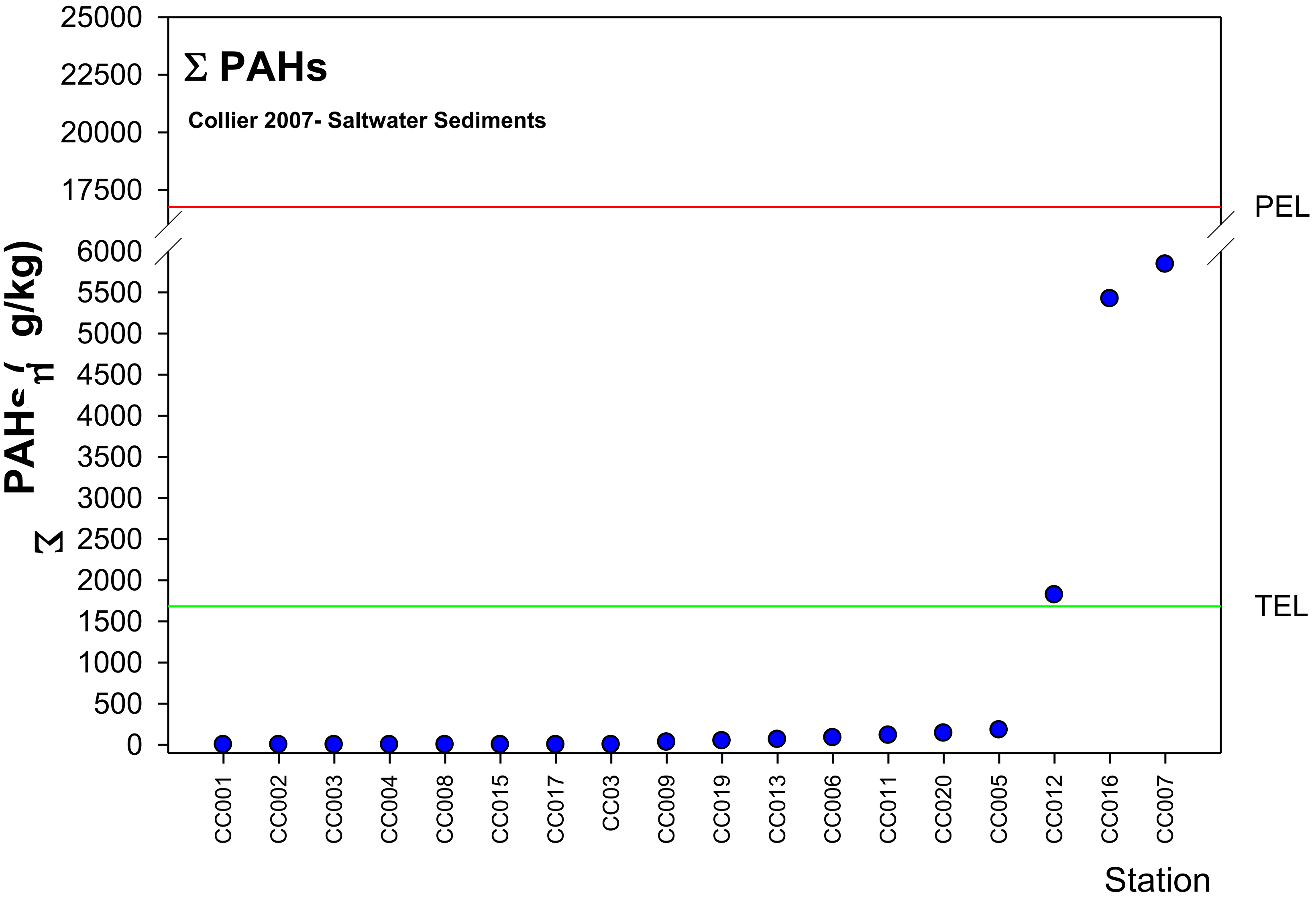


Figure 23 Concentrations of Total PAHs for Coastal Sediments in the 2007 Survey.

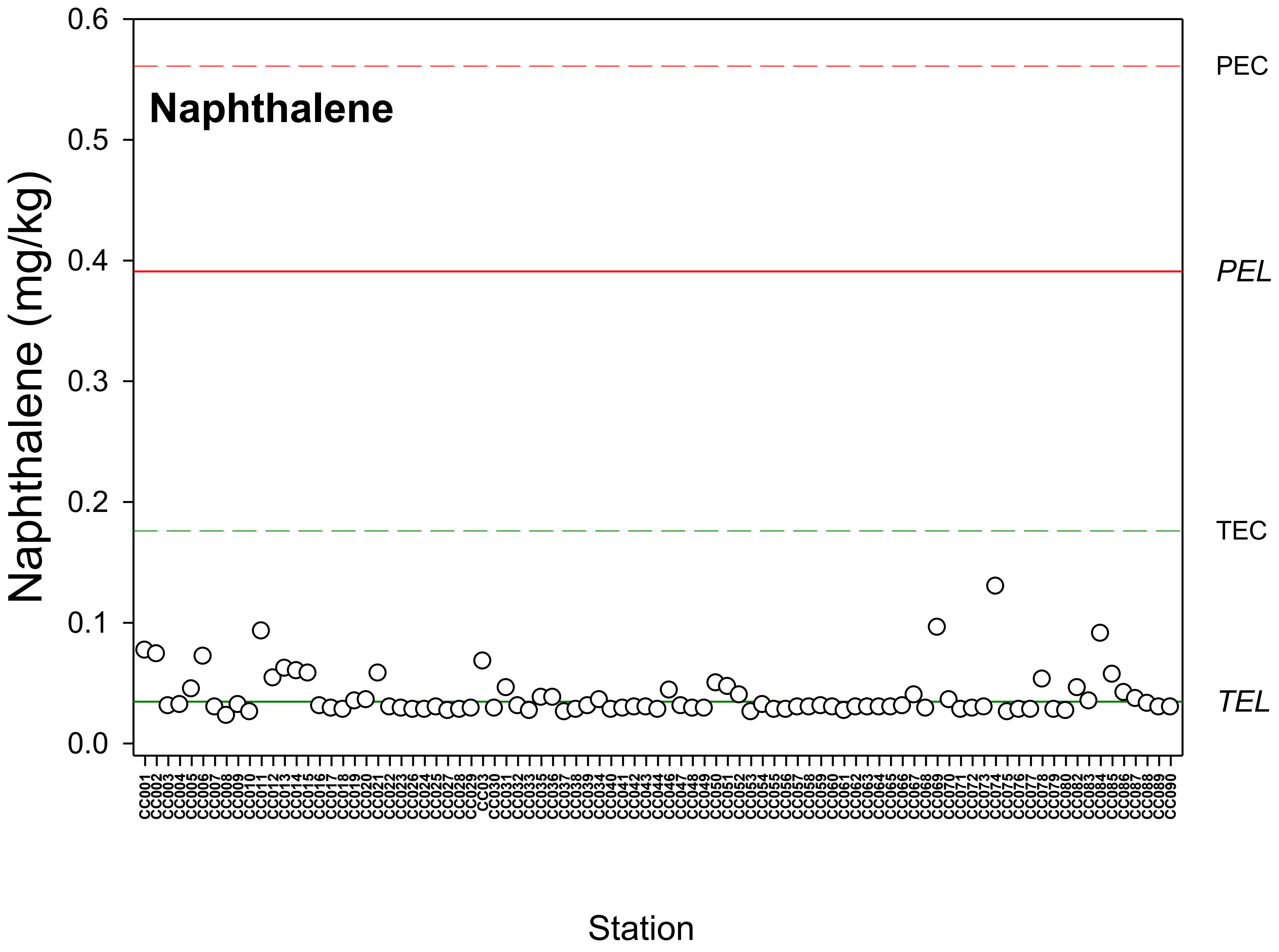


Figure 24 Concentrations of Naphthalene for Sediments in the 2007 Survey. (Open circles, MDL, gray circles >MDL but <MRL).

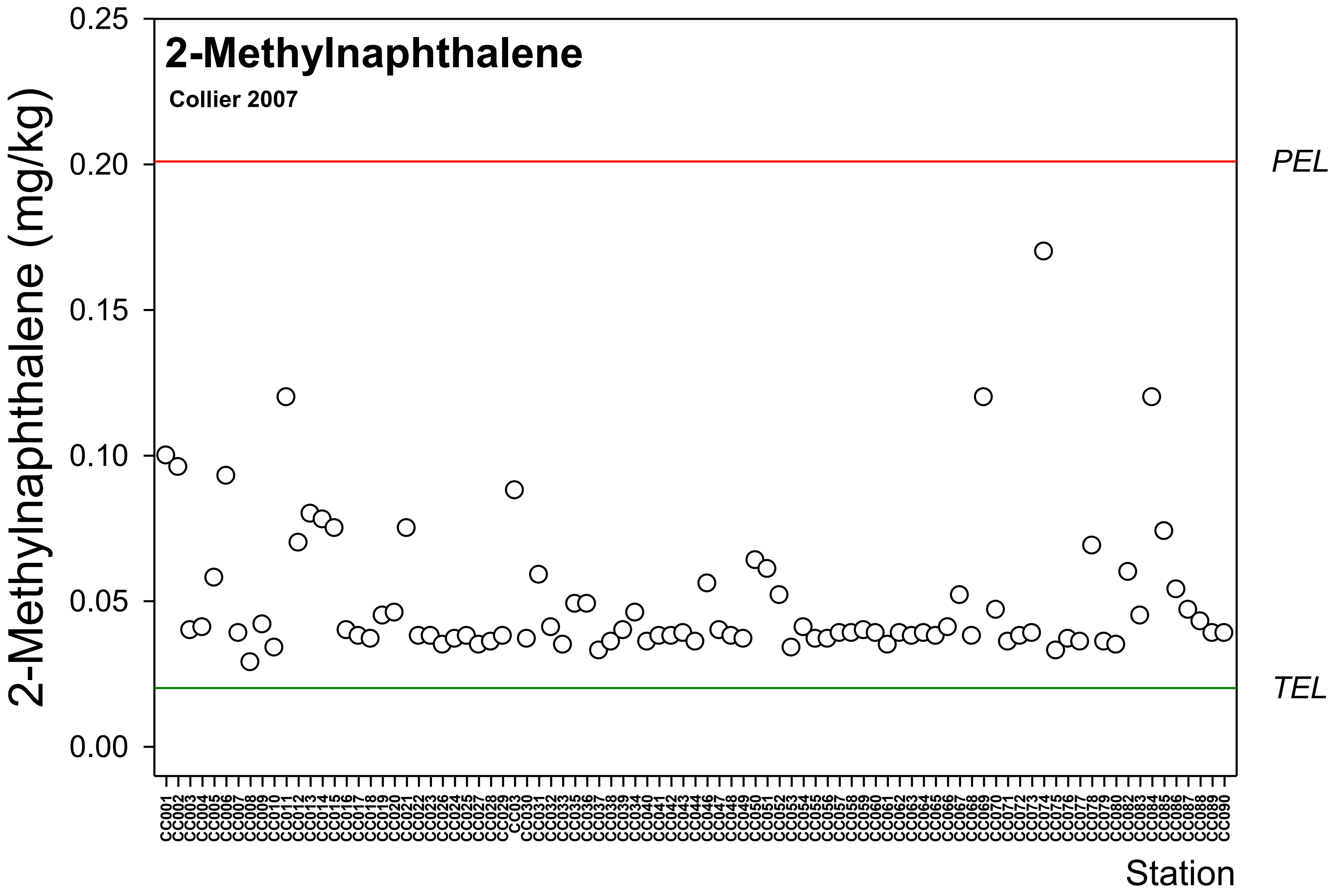


Figure 25 Concentrations of 2-Methylnaphthalene for Sediments in the 2007 Survey. (Open circles, MDL, gray circles >MDL but <MRL).

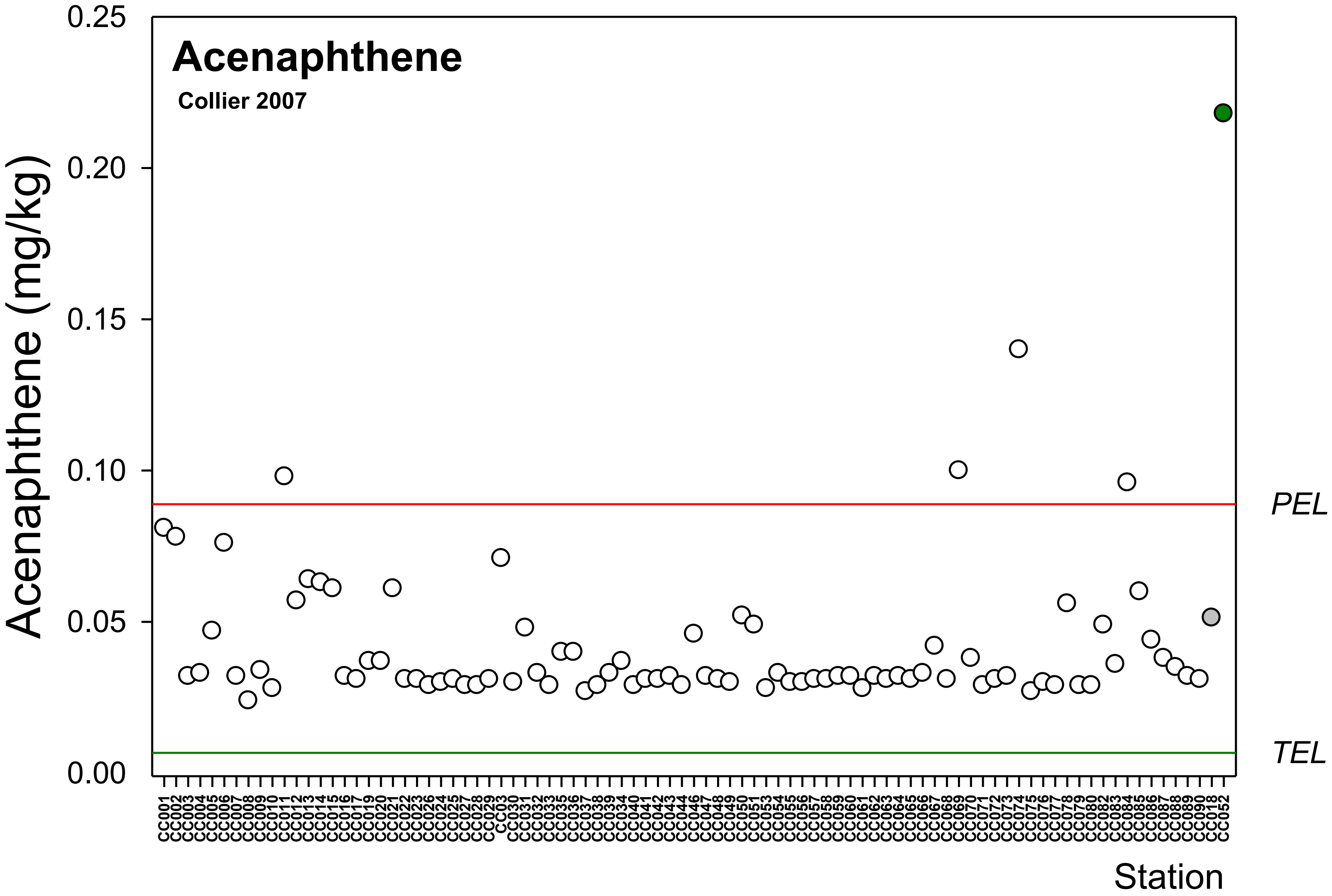


Figure 26 Concentrations of Acenaphthene for Sediments in the 2007 Survey. (Open circles, MDL, gray circles >MDL but <MRL).

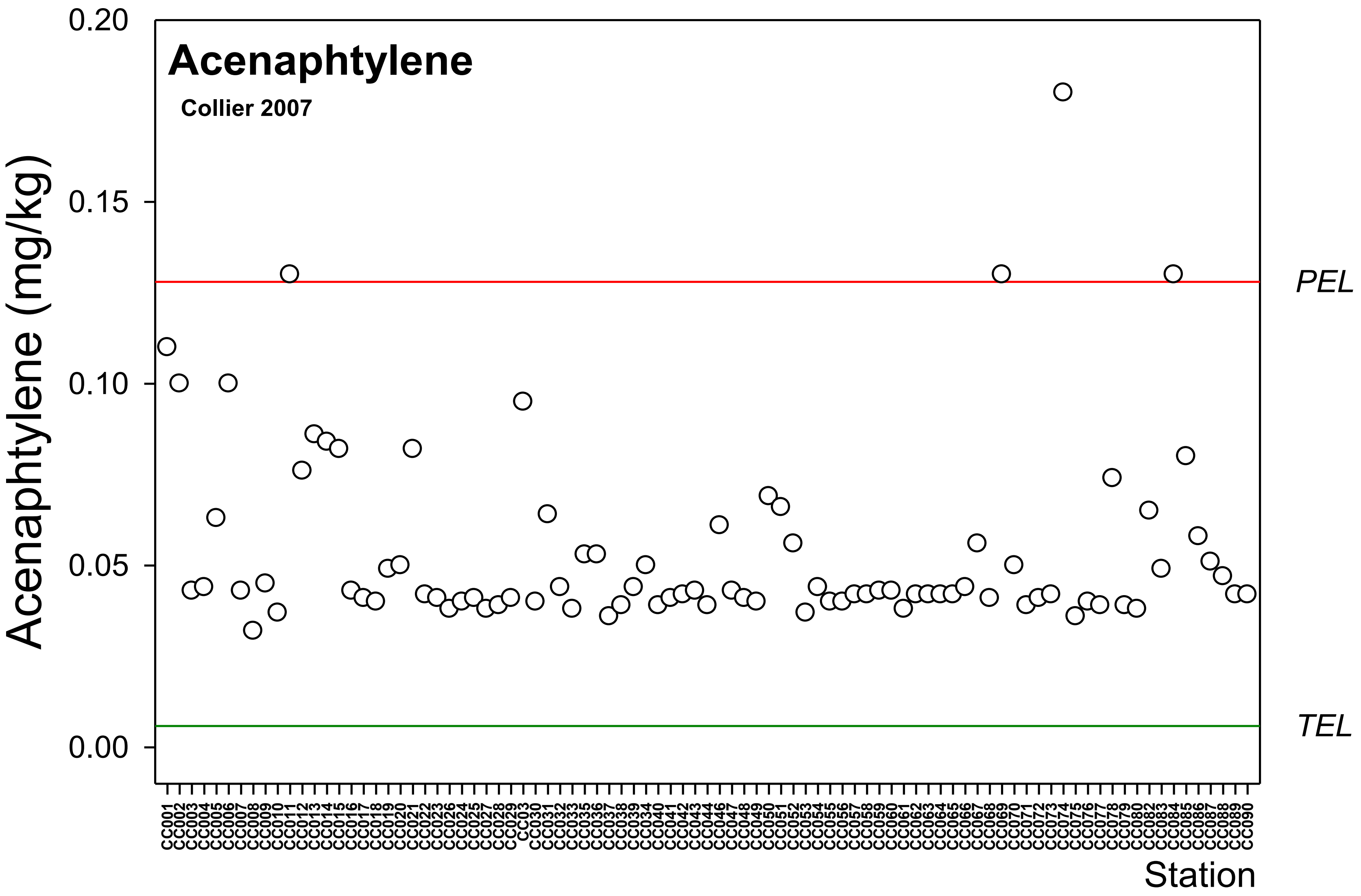


Figure 27 Concentrations of Acenaphtylene for Sediments in the 2007 Survey.
(Open circles, MDL, gray circles >MDL but <MRL).

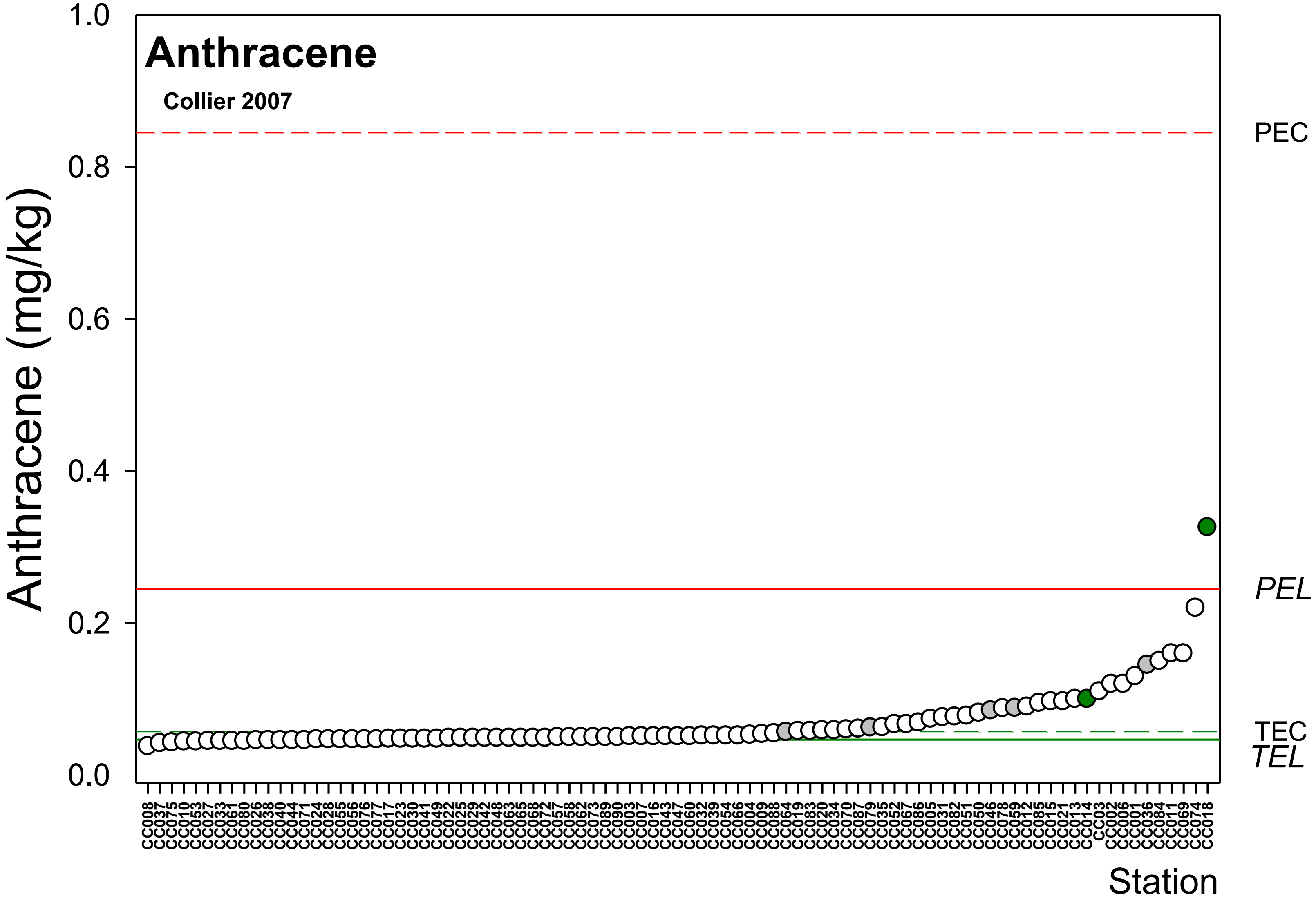


Figure 28 Concentrations of Anthracene for Sediments in the 2007 Survey. (Open circles, MDL, gray circles >MDL but <MRL).

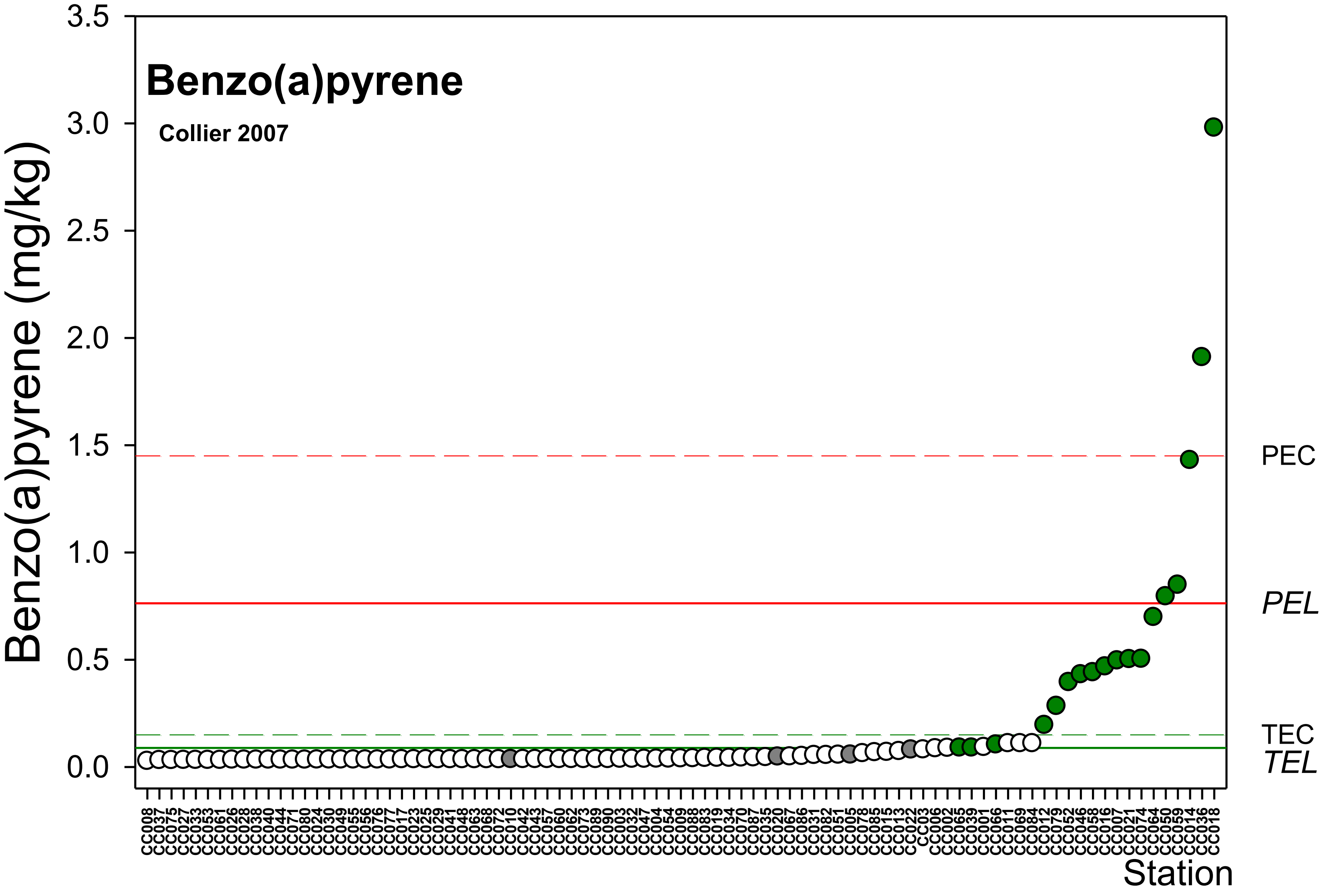


Figure 29 Concentrations of Benzo(a)pyrene for Sediments in the 2007 Survey.
(Open circles, MDL, gray circles >MDL but <MRL).

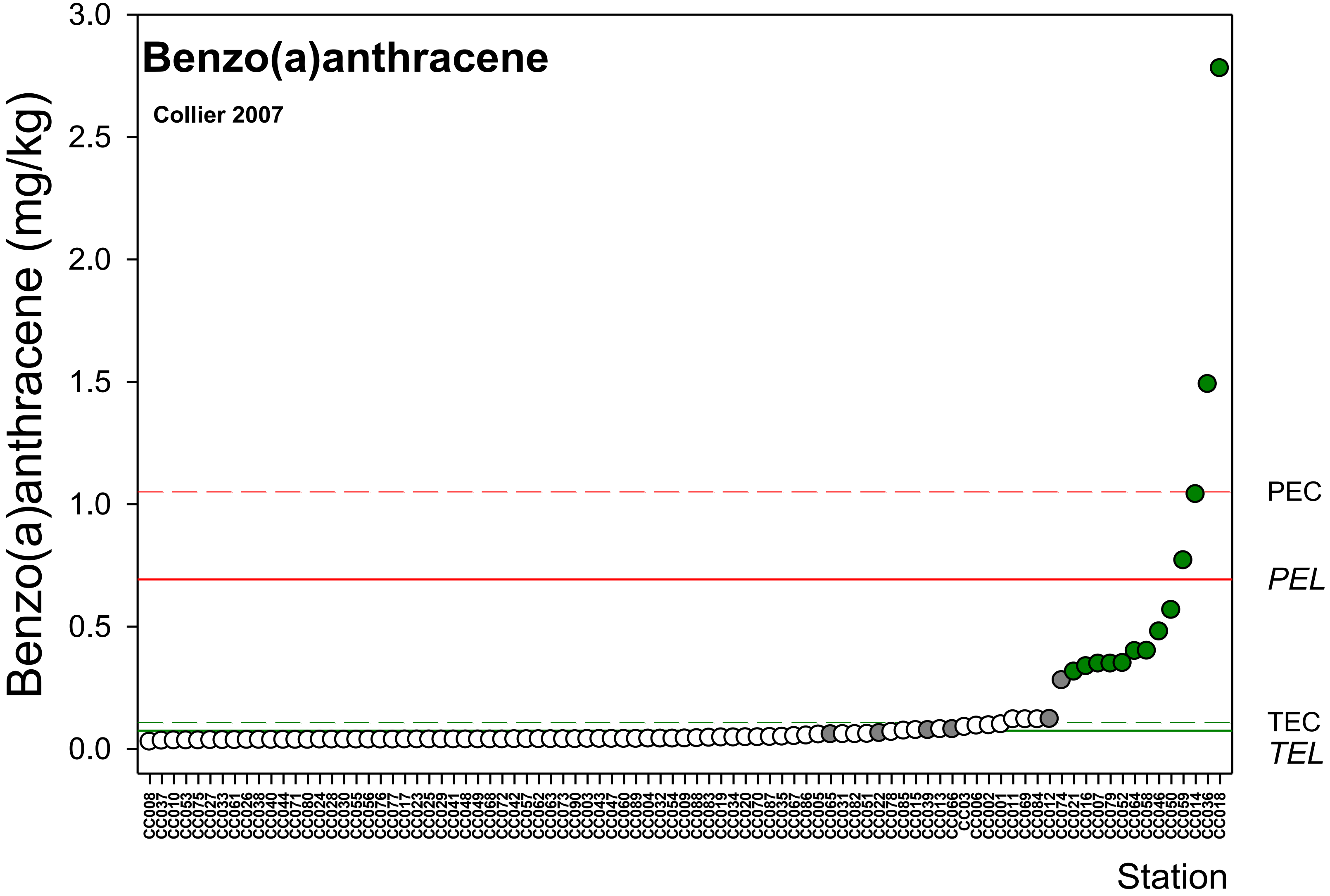


Figure 30 Concentrations of Benzo(a)anthracene for Sediments in the 2007 Survey. (Open circles, MDL, gray circles >MDL but <MRL).

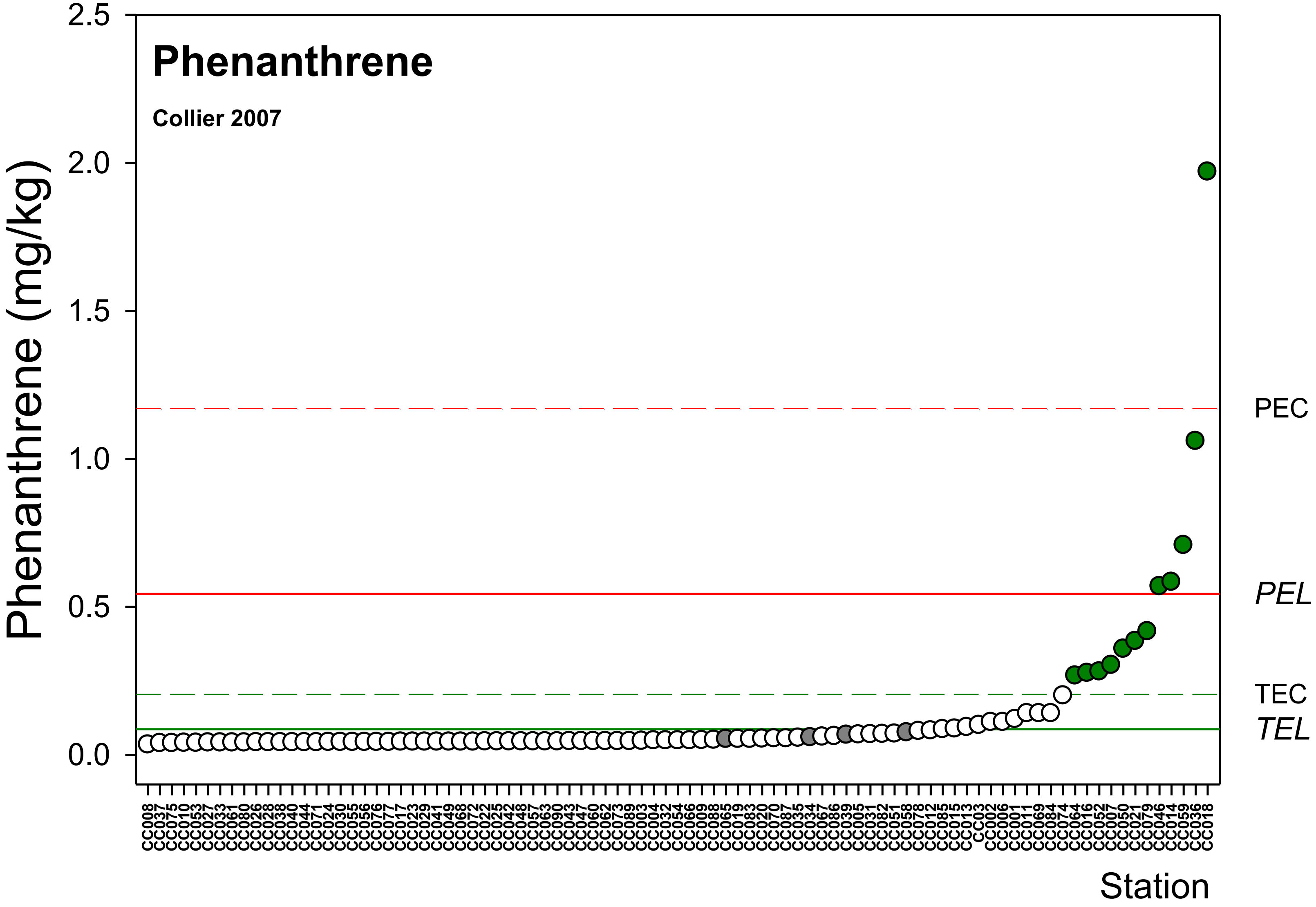


Figure 31 Concentrations of Phenanthrene for Sediments in the 2007 Survey. (Open circles, MDL, gray circles >MDL but <MRL).

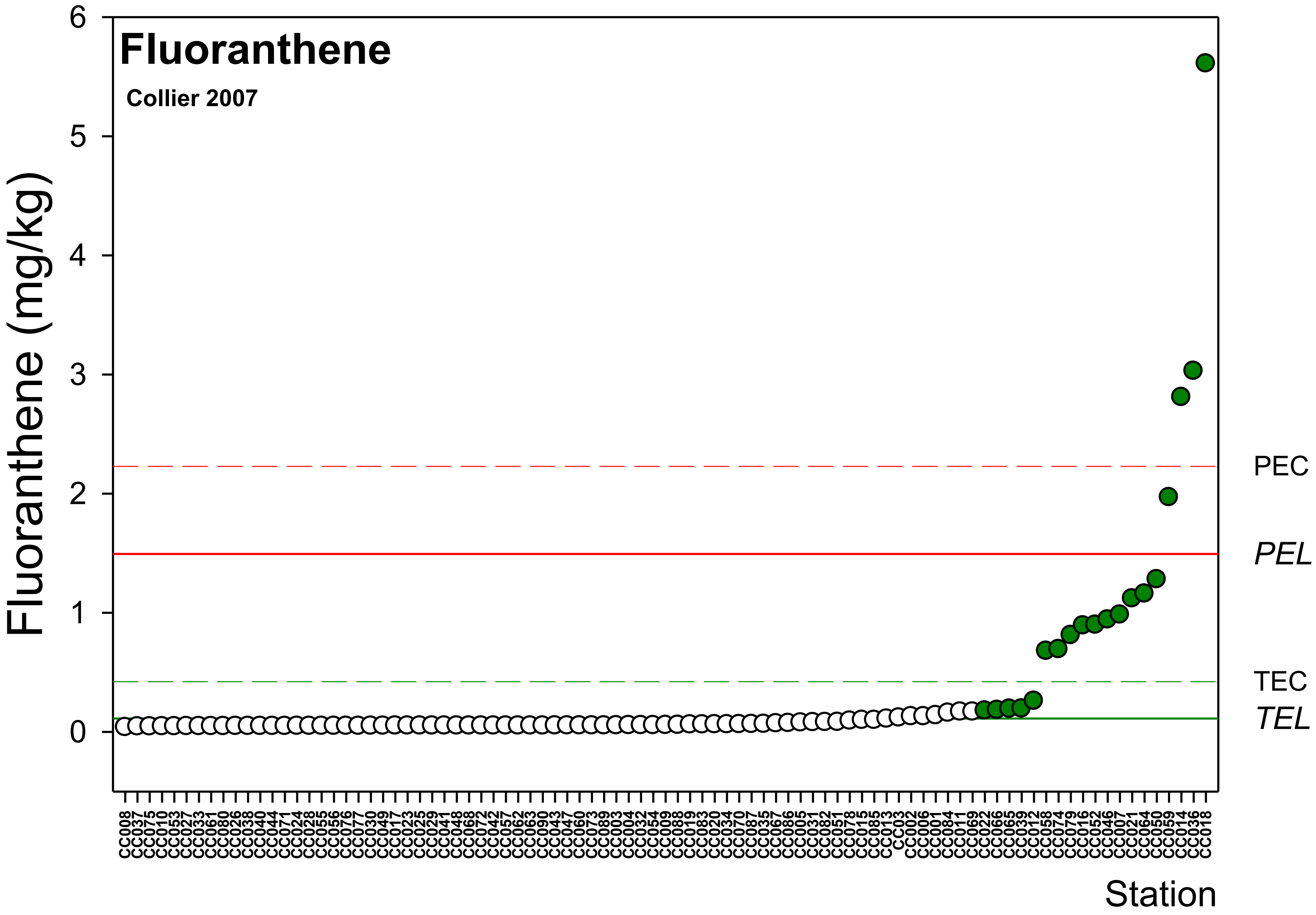


Figure 32 Concentrations of Fluoranthene for Sediments in the 2007 Survey.
(Open circles, MDL, gray circles >MDL but <MRL).

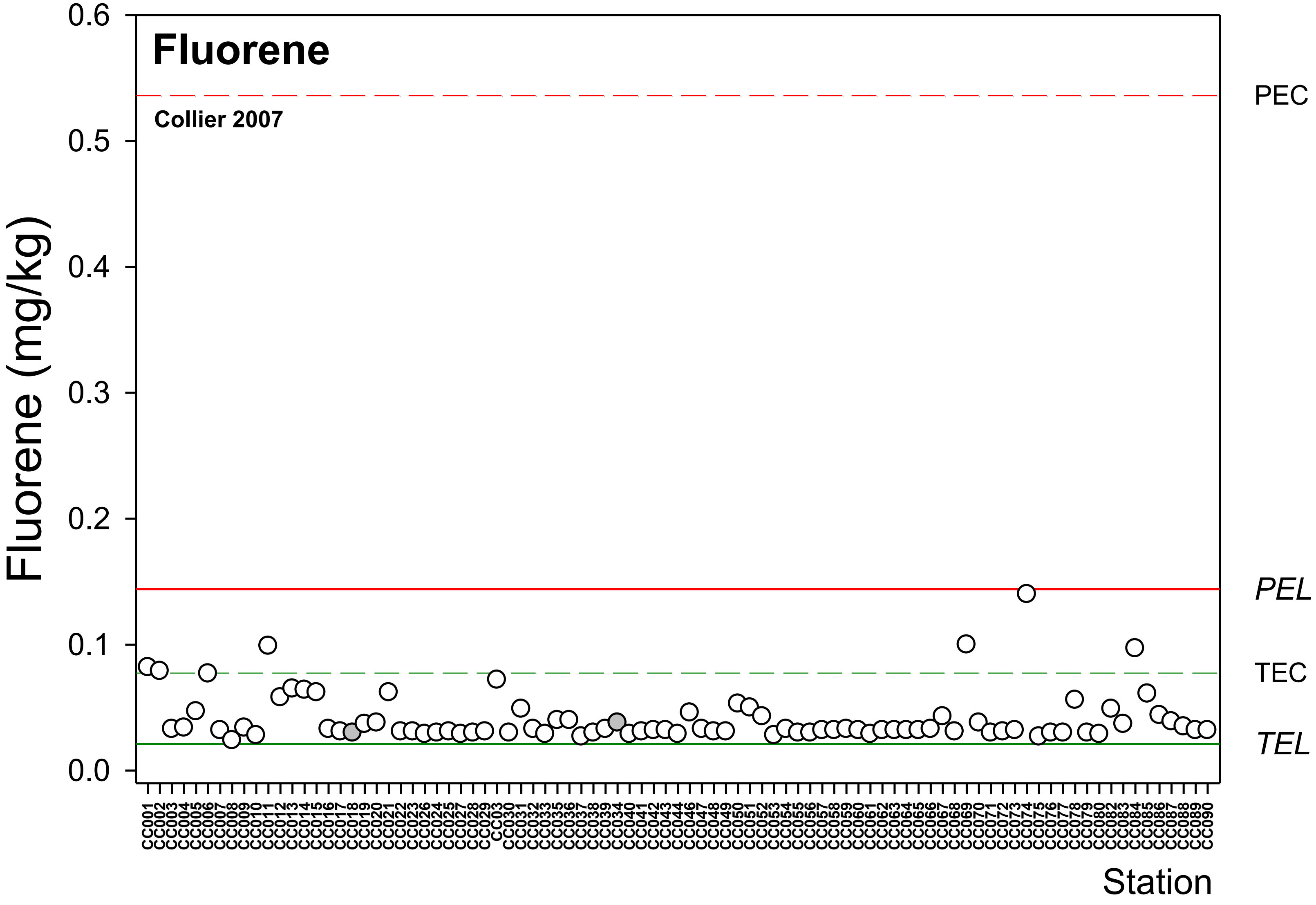


Figure 33 Concentrations of Fluorene for Sediments in the 2007 Survey.
(Open circles, MDL, gray circles >MDL but <MRL).

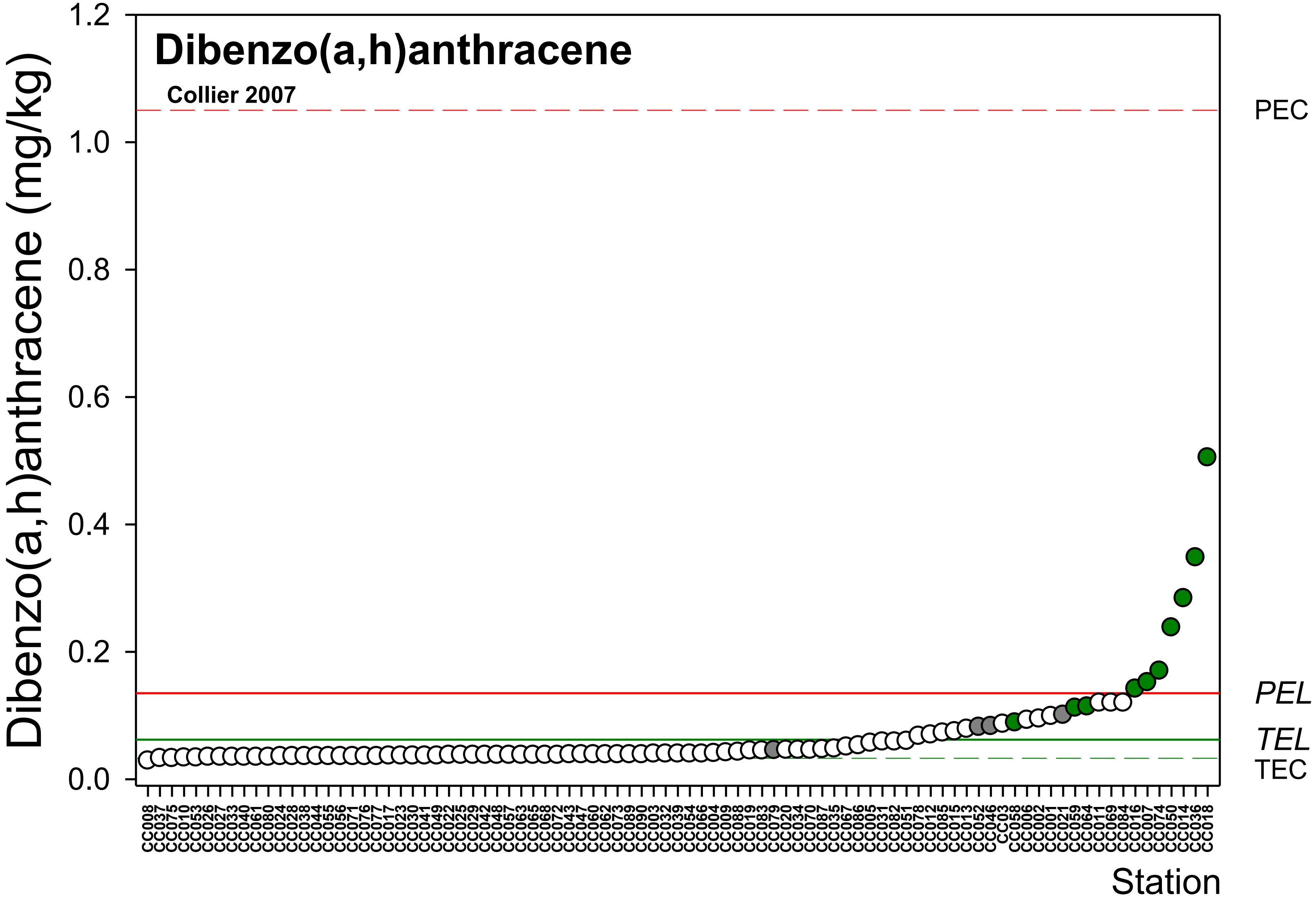


Figure 34 Concentrations of Dibenzo(a,h)anthracene for Sediments in the 2007 Survey. (Open circles, MDL, gray circles >MDL but <MRL).

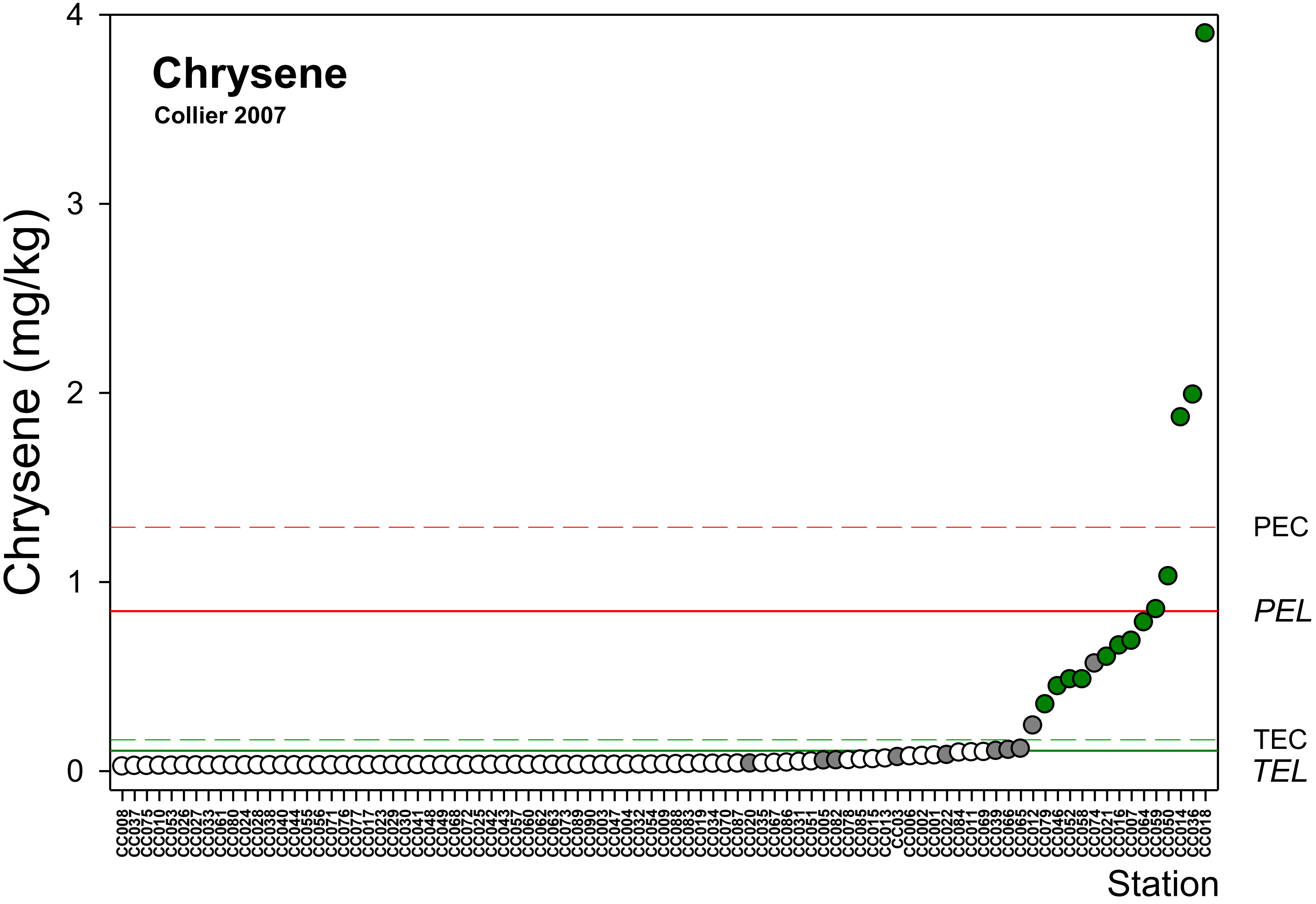


Figure 35 Concentrations of Chrysene for Sediments in the 2007 Survey.
(Open circles, MDL, gray circles >MDL but <MRL).

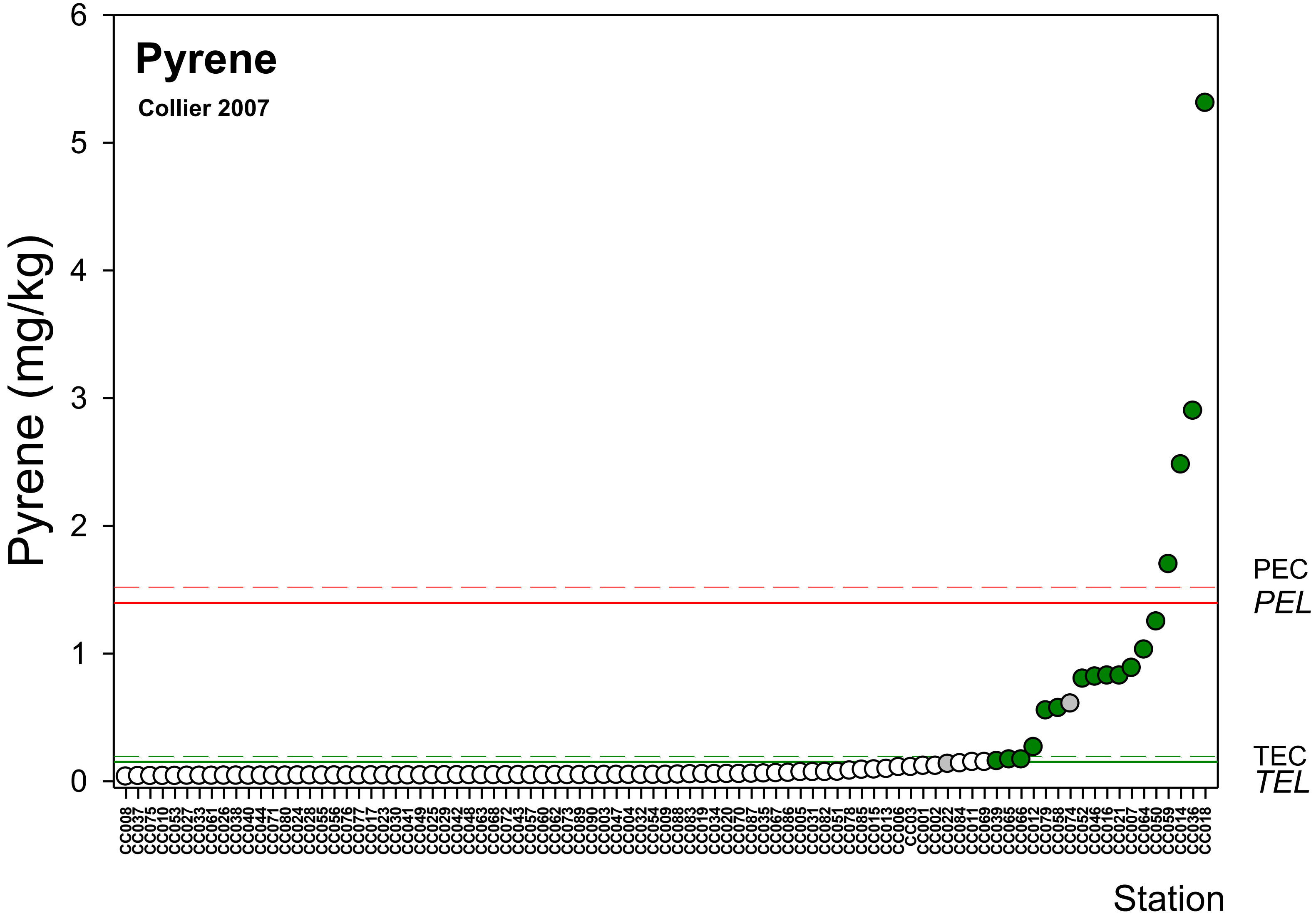


Figure 36 Concentrations of Pyrene for Sediments in the 2007 Survey. (Open circles, MDL, gray circles >MDL but <MRL).

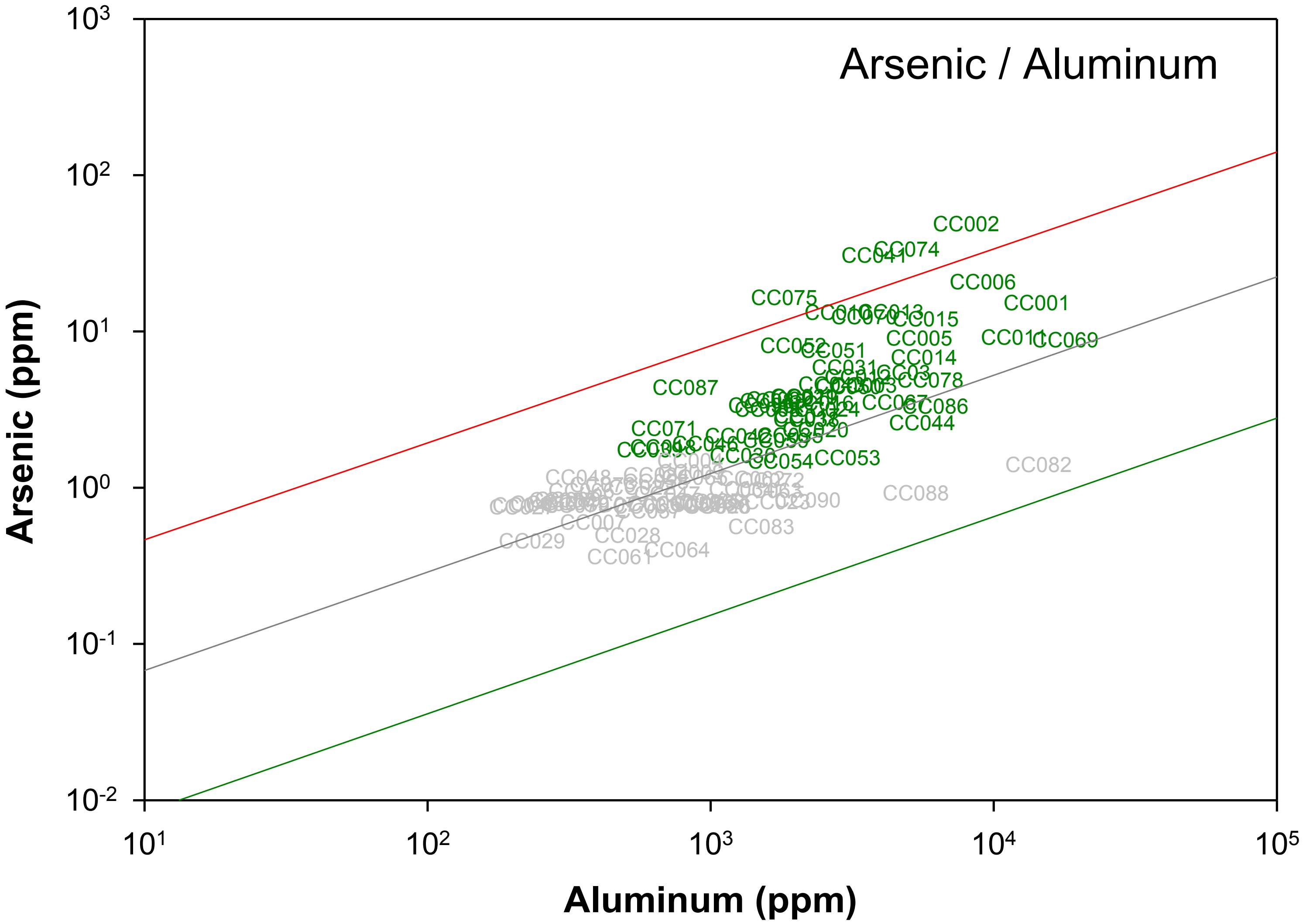


Figure 37 Normalized enrichment plot for Arsenic. Samples in gray are below the MDL.

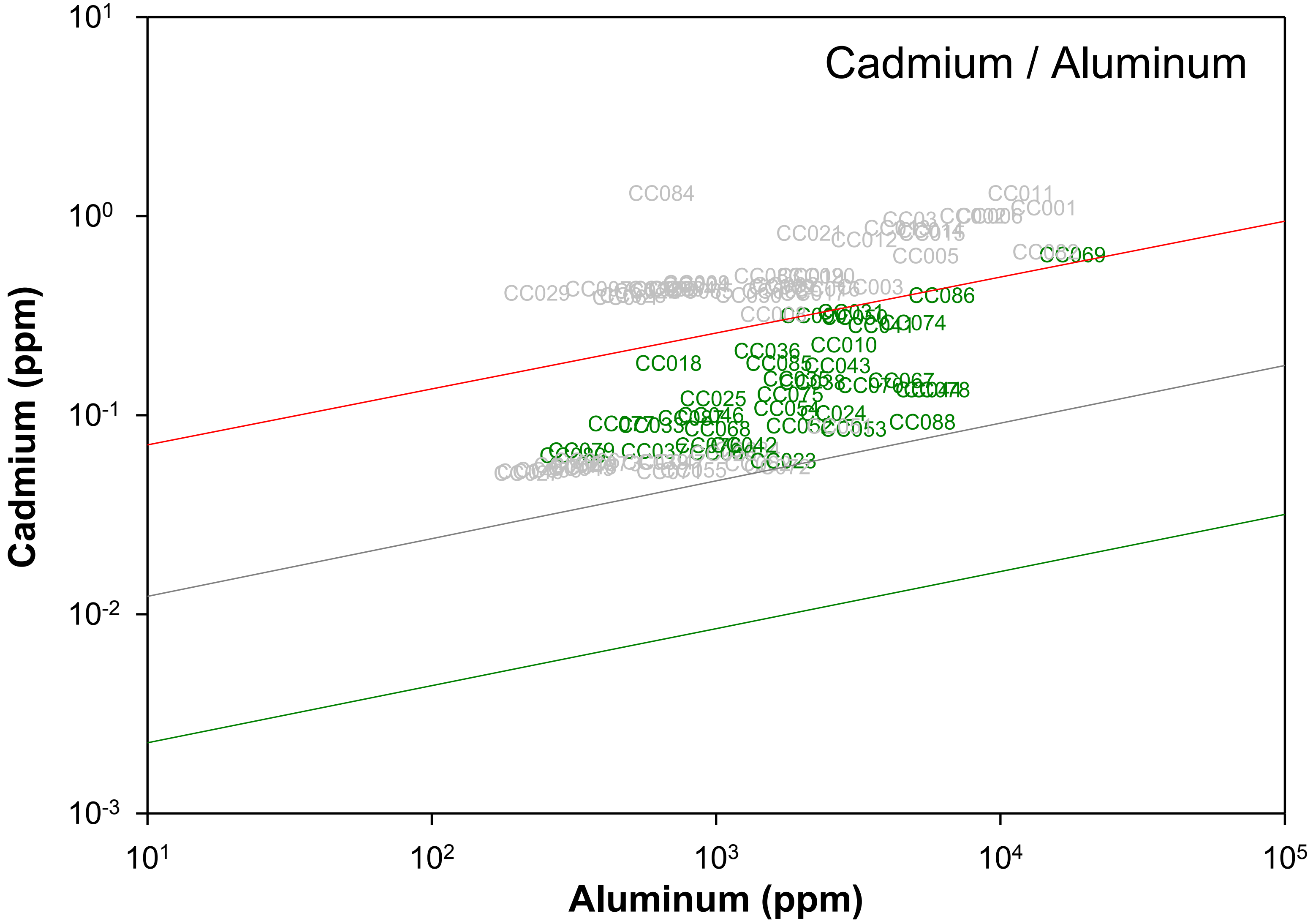


Figure 38 Normalized enrichment plot for Arsenic. Samples in gray are below the MDL.

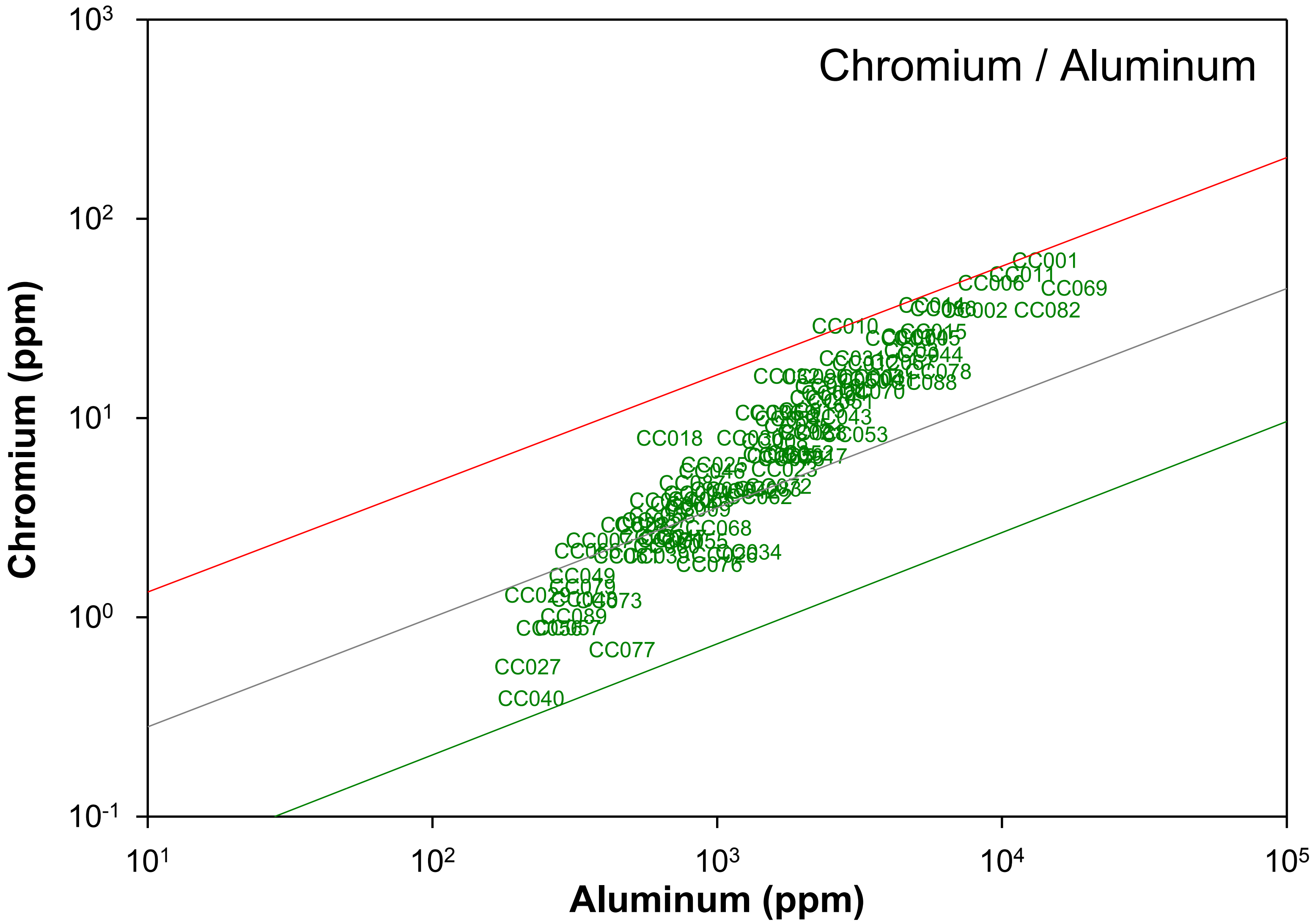


Figure 39 Normalized enrichment plot for Chromium.

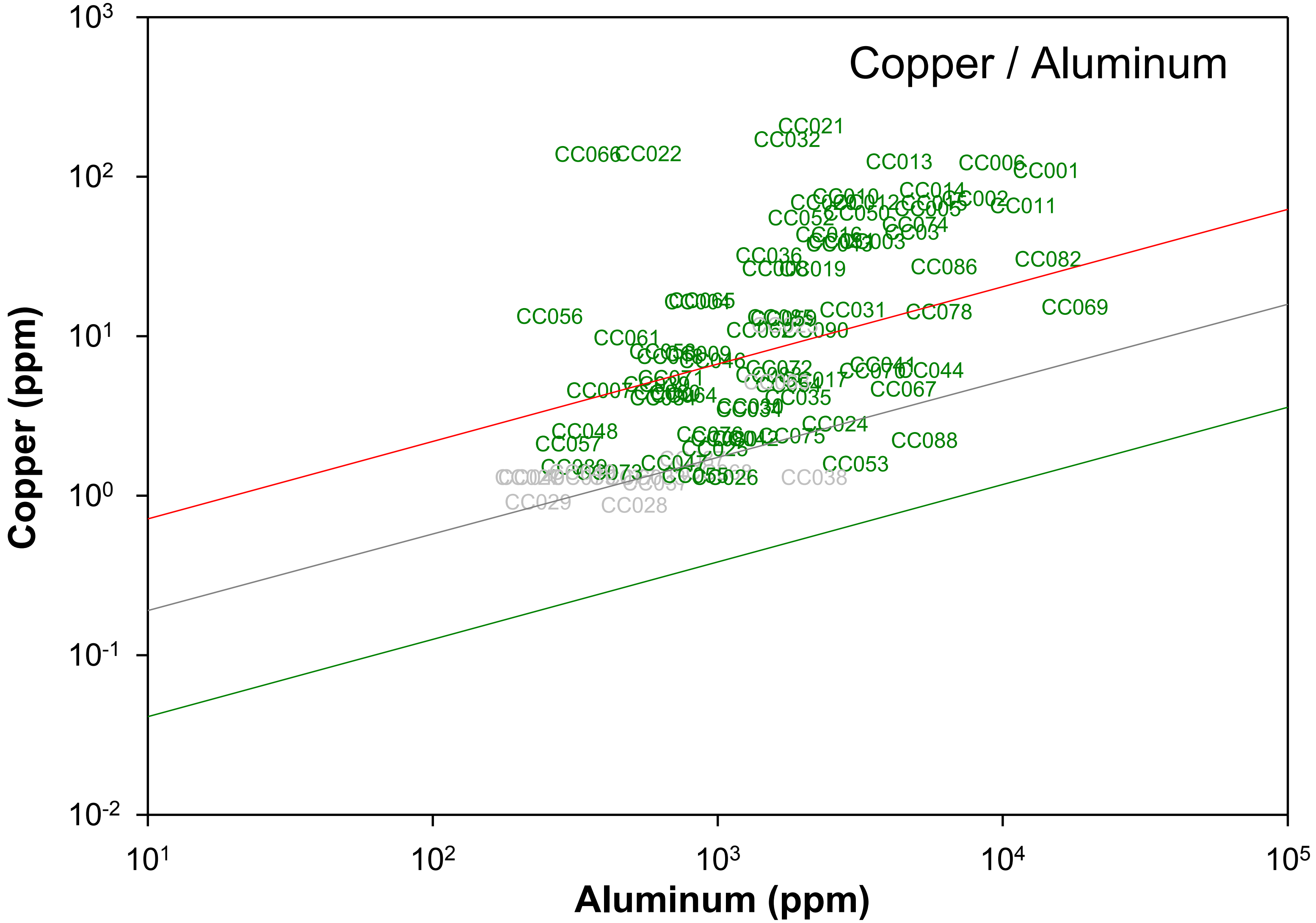


Figure 40 Normalized enrichment plot for Copper. Samples in gray are below the MDL.

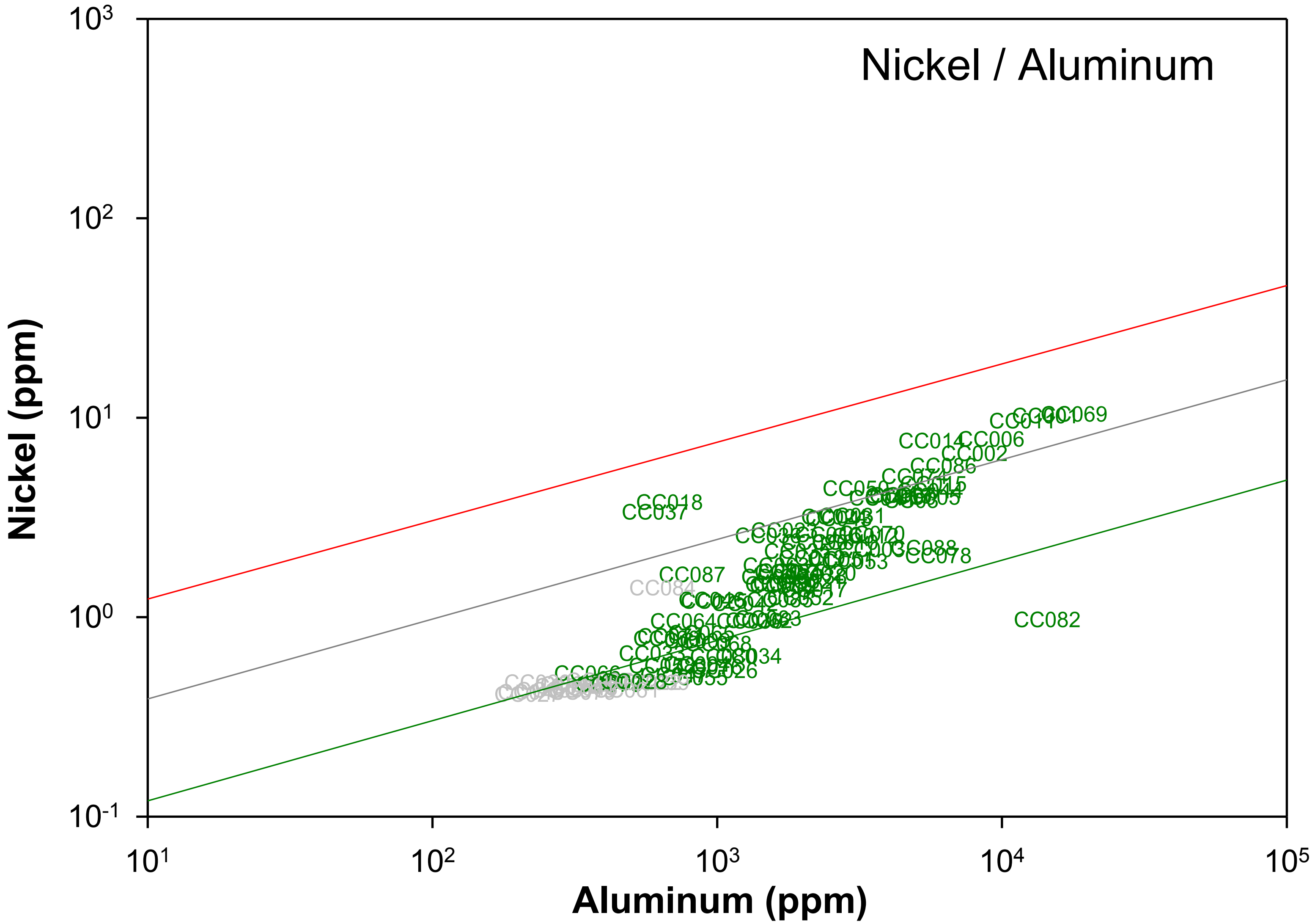


Figure 41 Normalized enrichment plot for Nickel. Samples in gray are below the MDL.

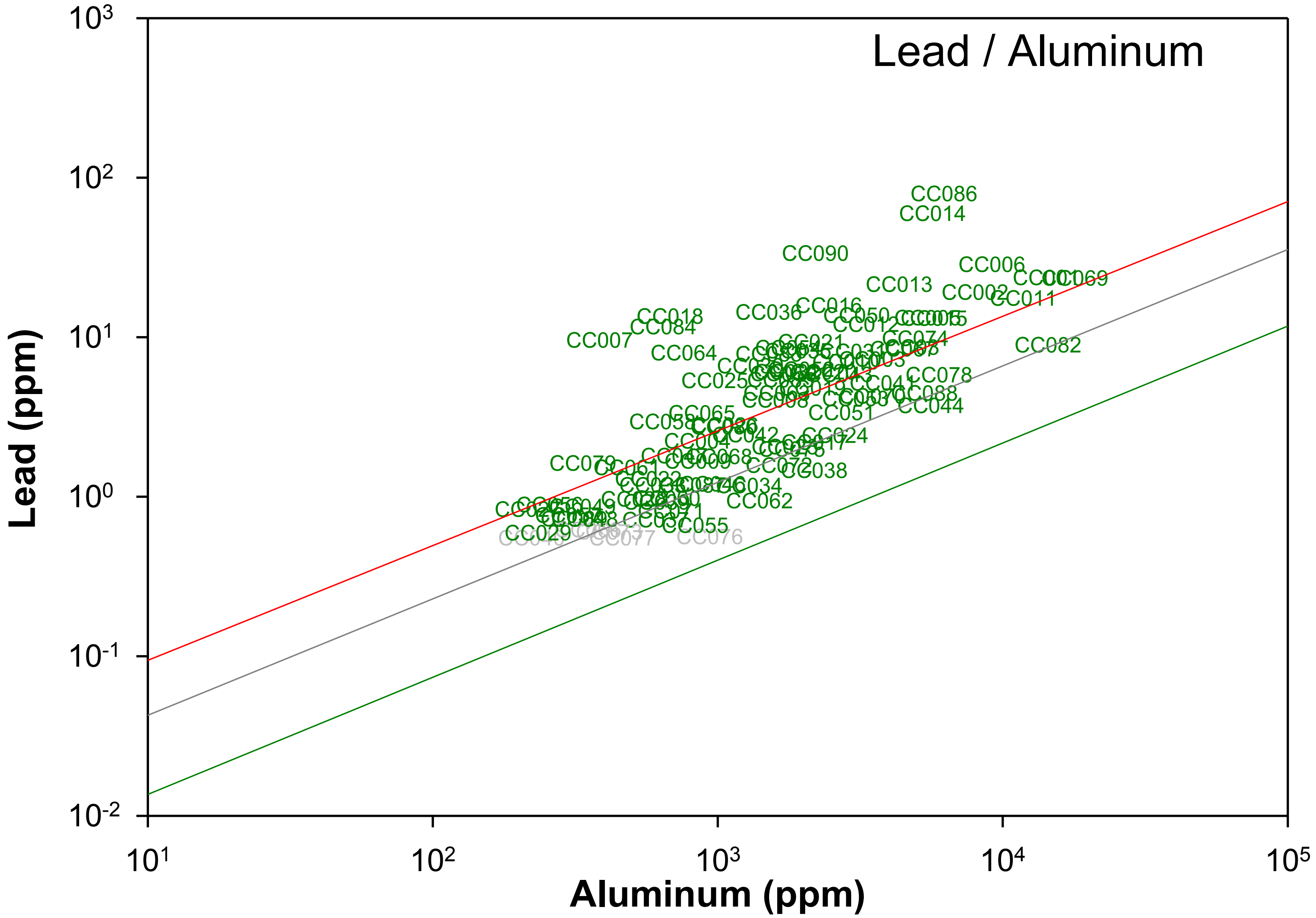


Figure 42 Normalized enrichment plot for Lead. Samples in gray are below the MDL.

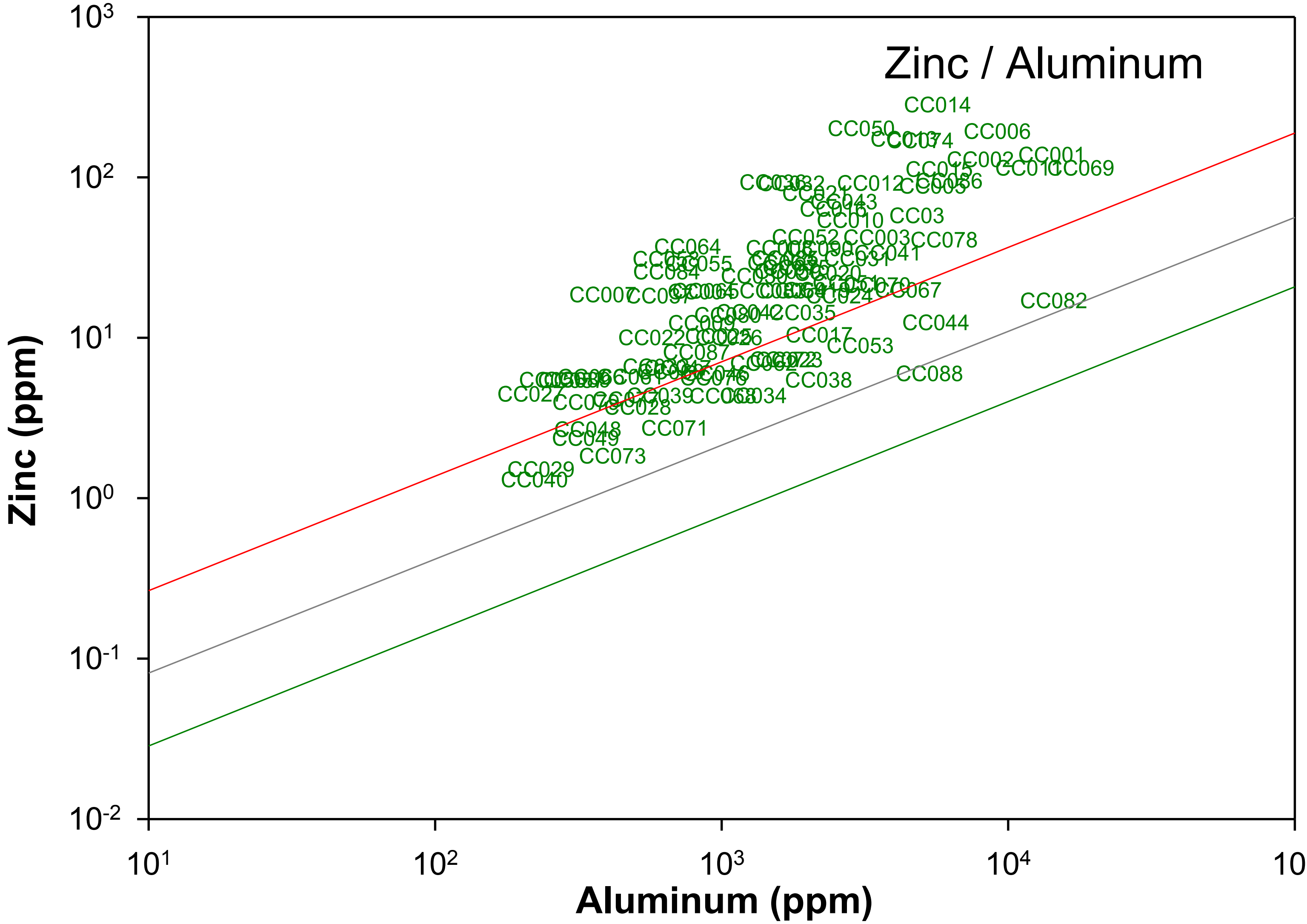


Figure 43 Normalized enrichment plot for Chromium.

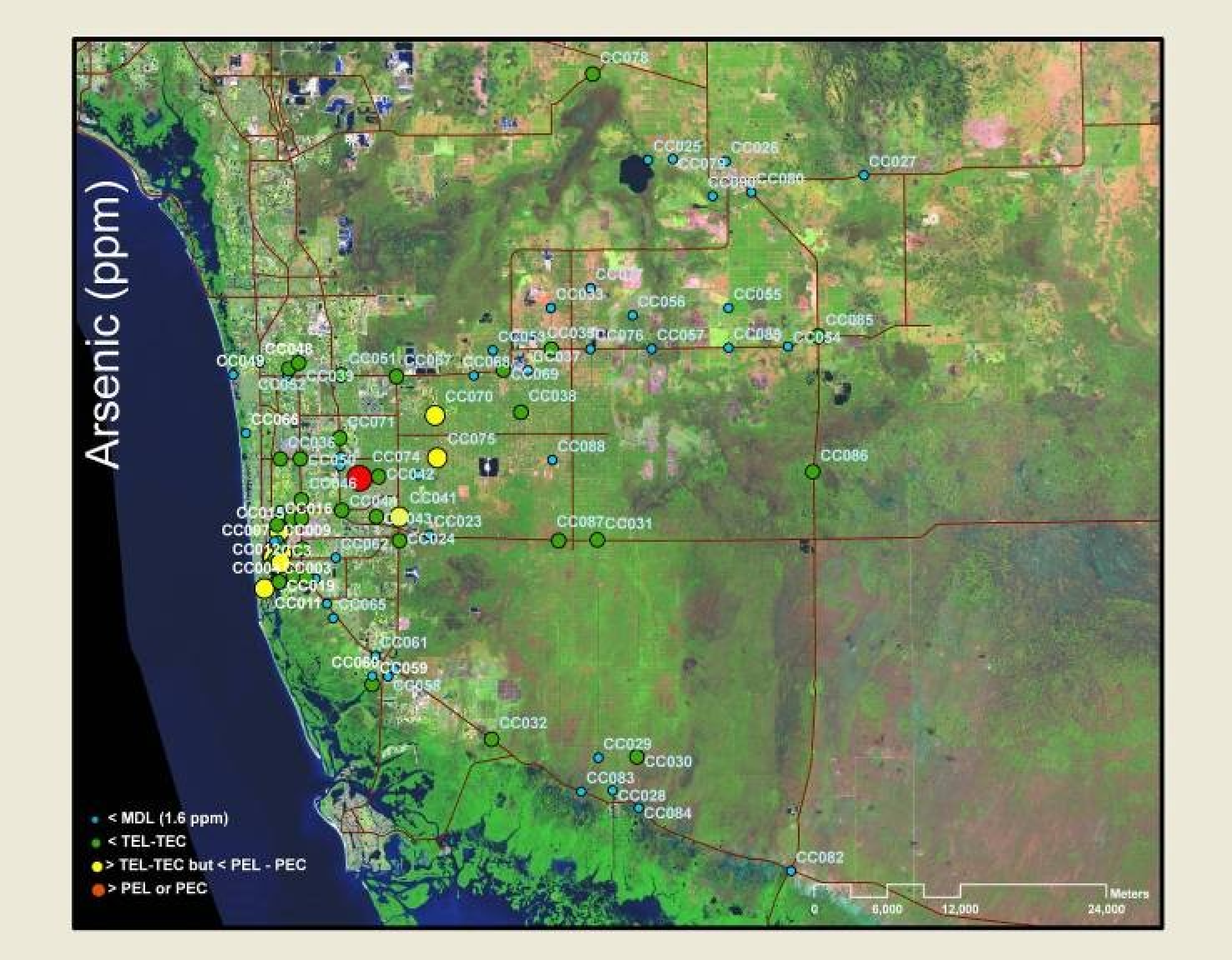


Figure 44 Distribution of Arsenic in Sediments from Collier County 2007.

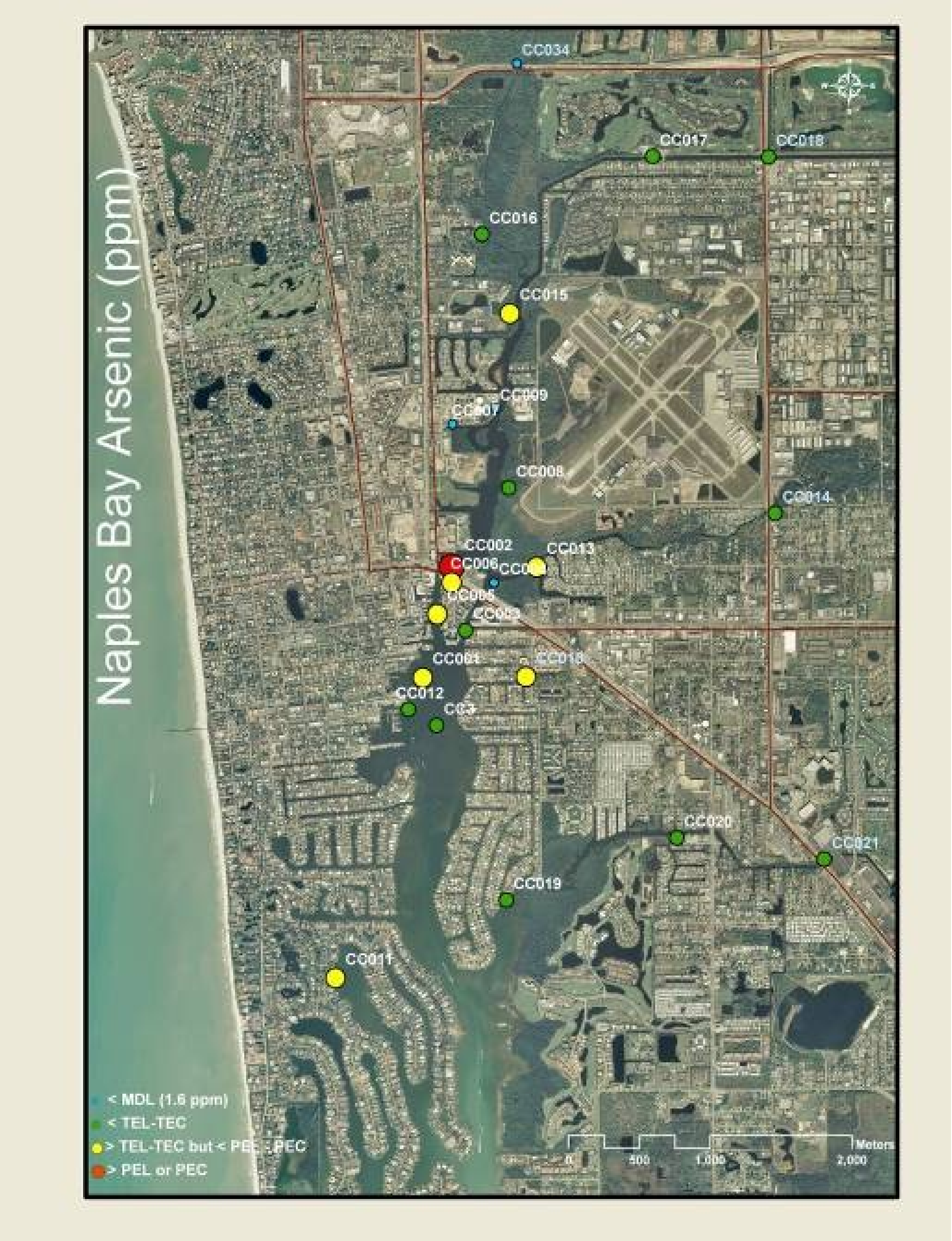


Figure 45 Distribution of Arsenic in Sediments from Collier County 2007. Naples Bay- Gordon River expanded view.

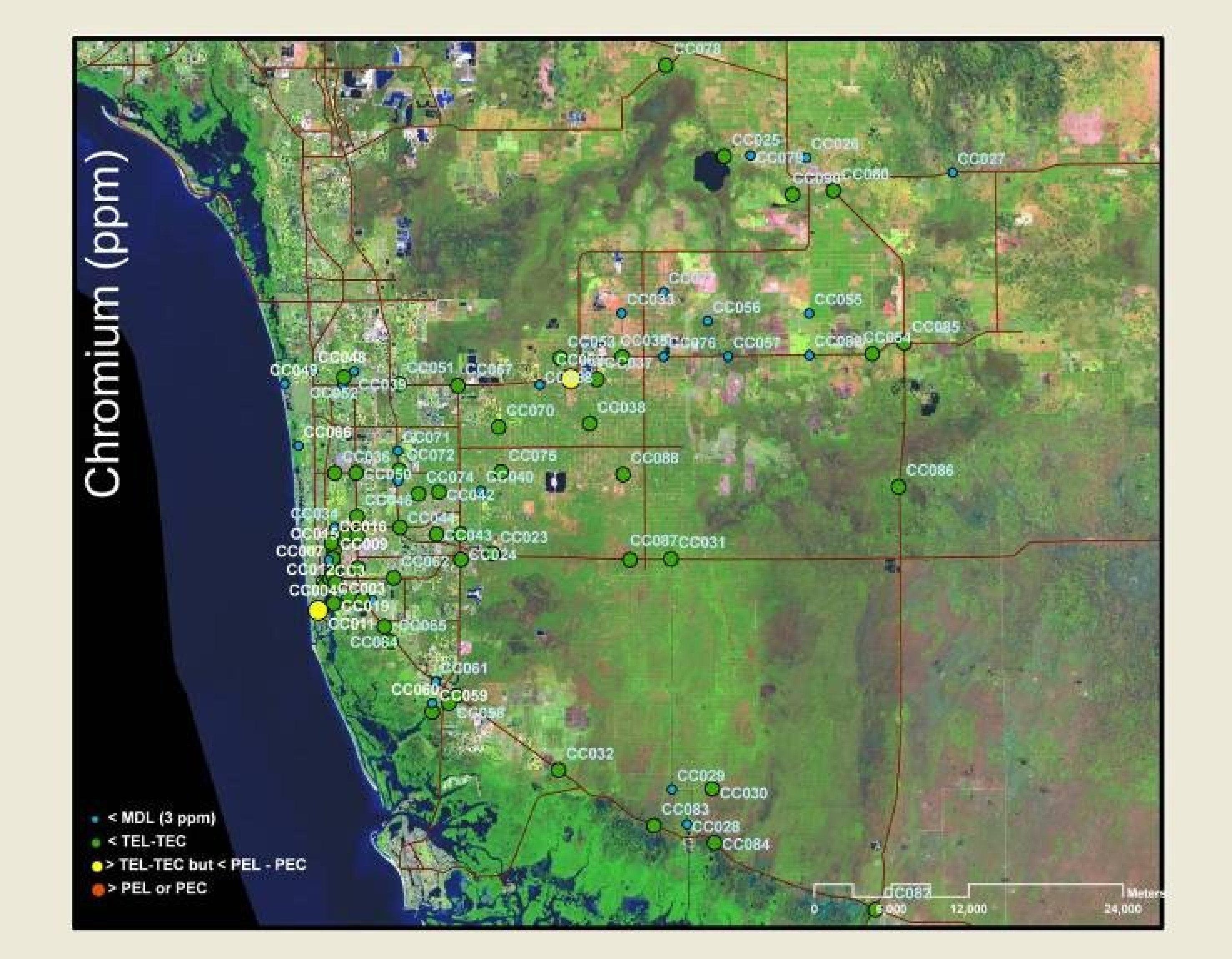


Figure 46 Distribution of Chromium in Sediments from Collier County 2007.

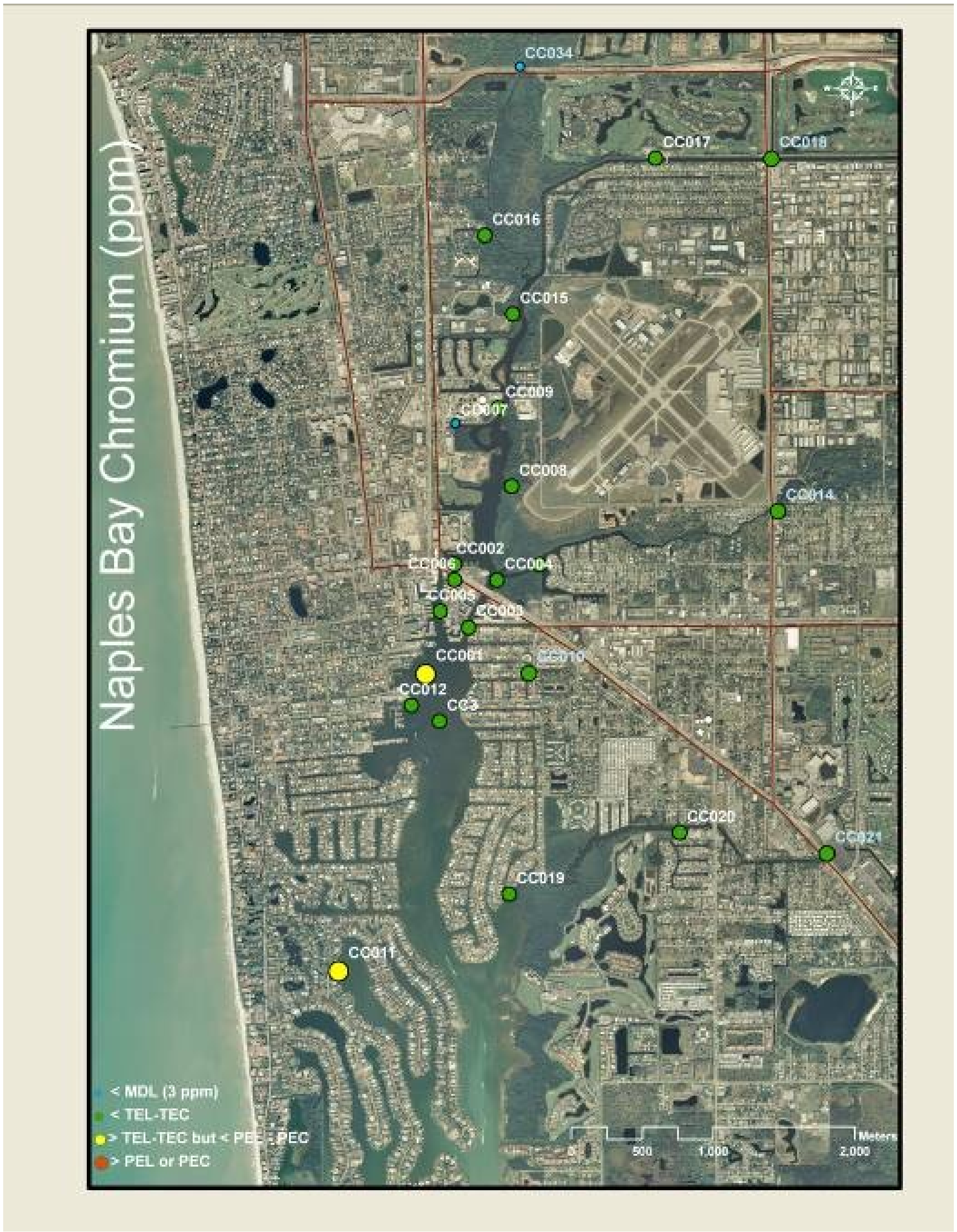
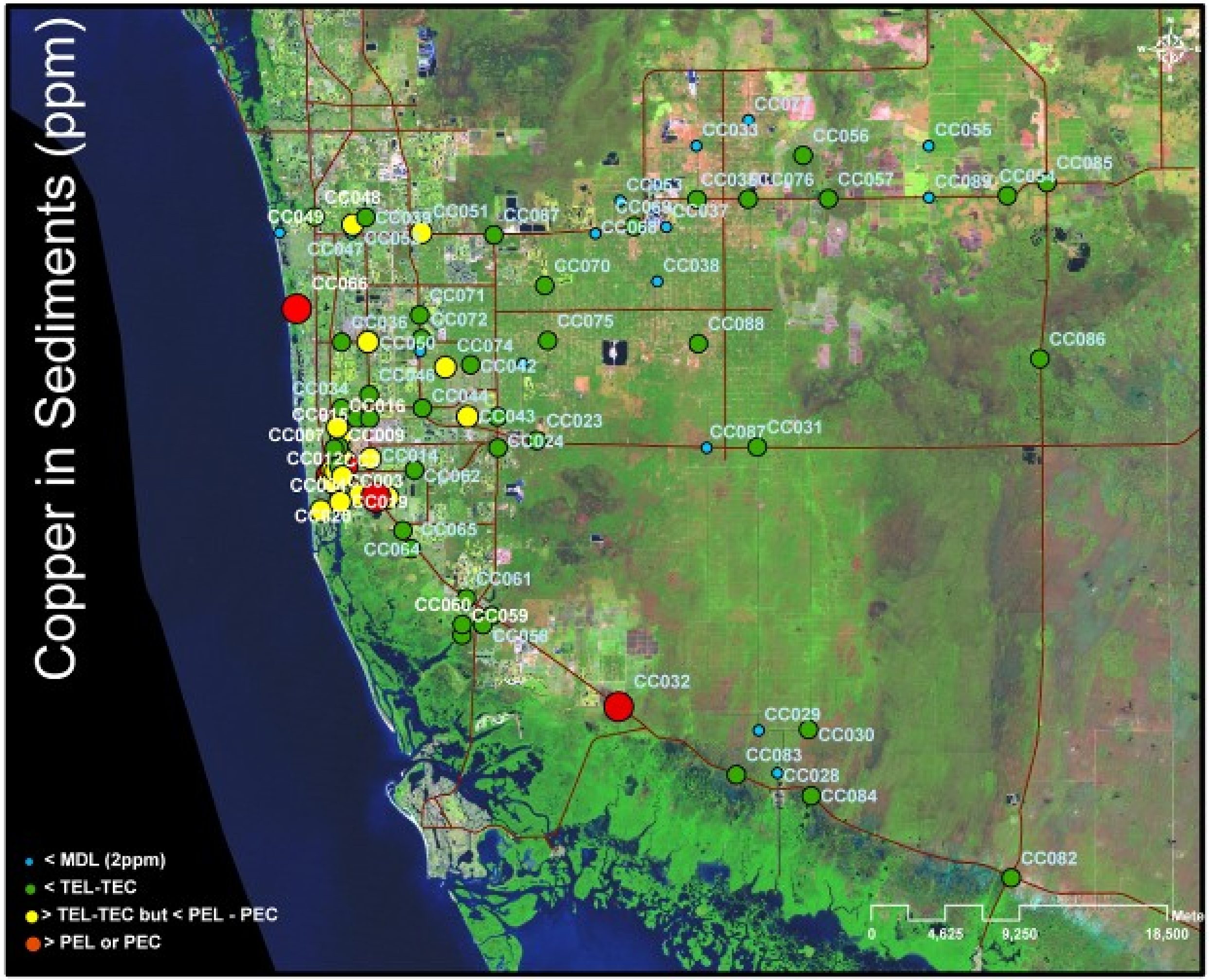


Figure 47 Distribution of Chromium in Sediments from Collier County 2007.



- ● < MDL (2ppm)
- ● < TEL-TEC
- ● > TEL-TEC but < PEL - PEC
- ● > PEL or PEC

Figure 48 Distribution of Copper in Sediments from Collier County 2007.

**Figure 49 Distribution of Copper in Sediments from Collier County 2007.
Naples Bay- Gordon River expanded view.**

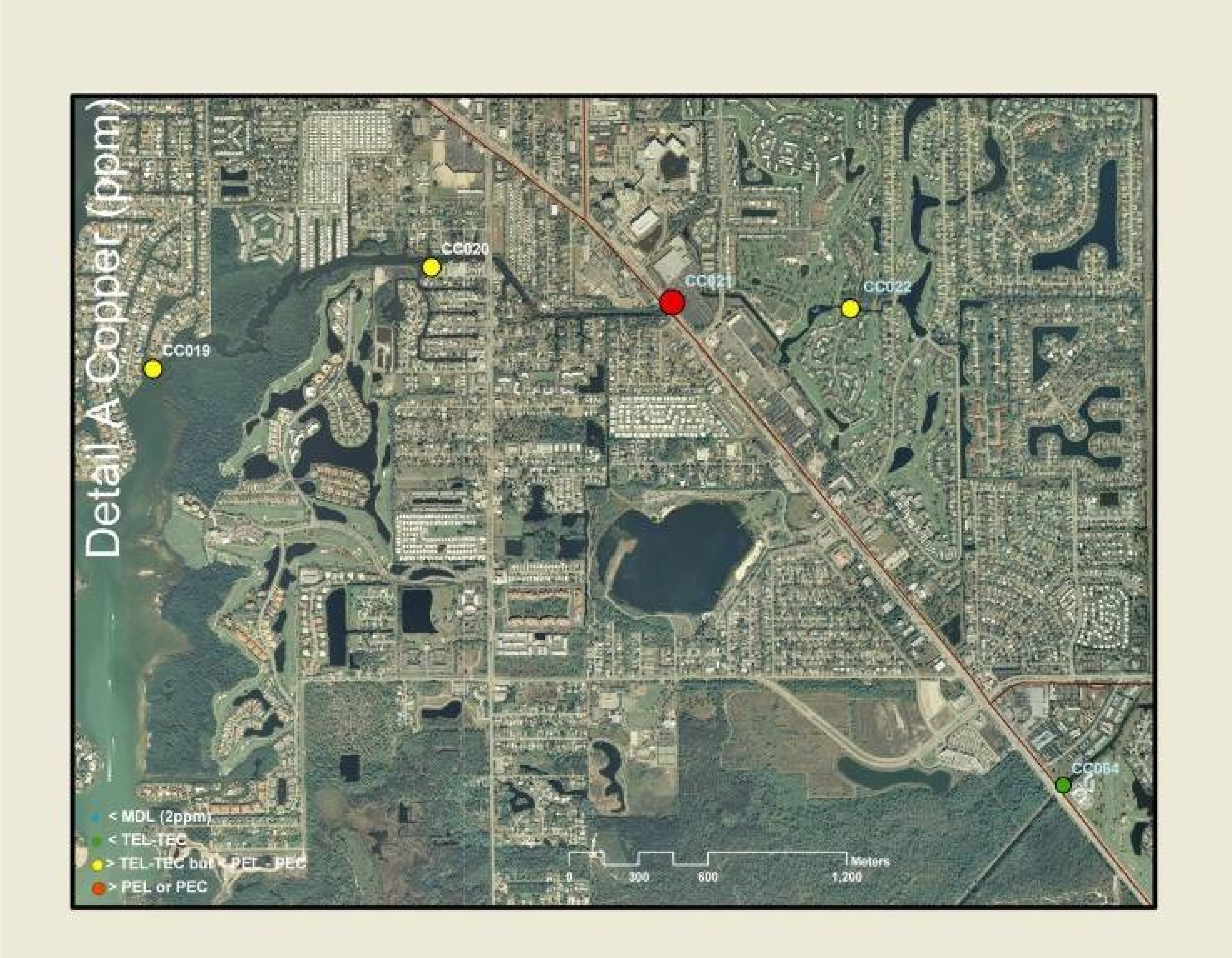


Figure 50 Detail A: Copper Concentrations in Sediments along Haldeman Creek

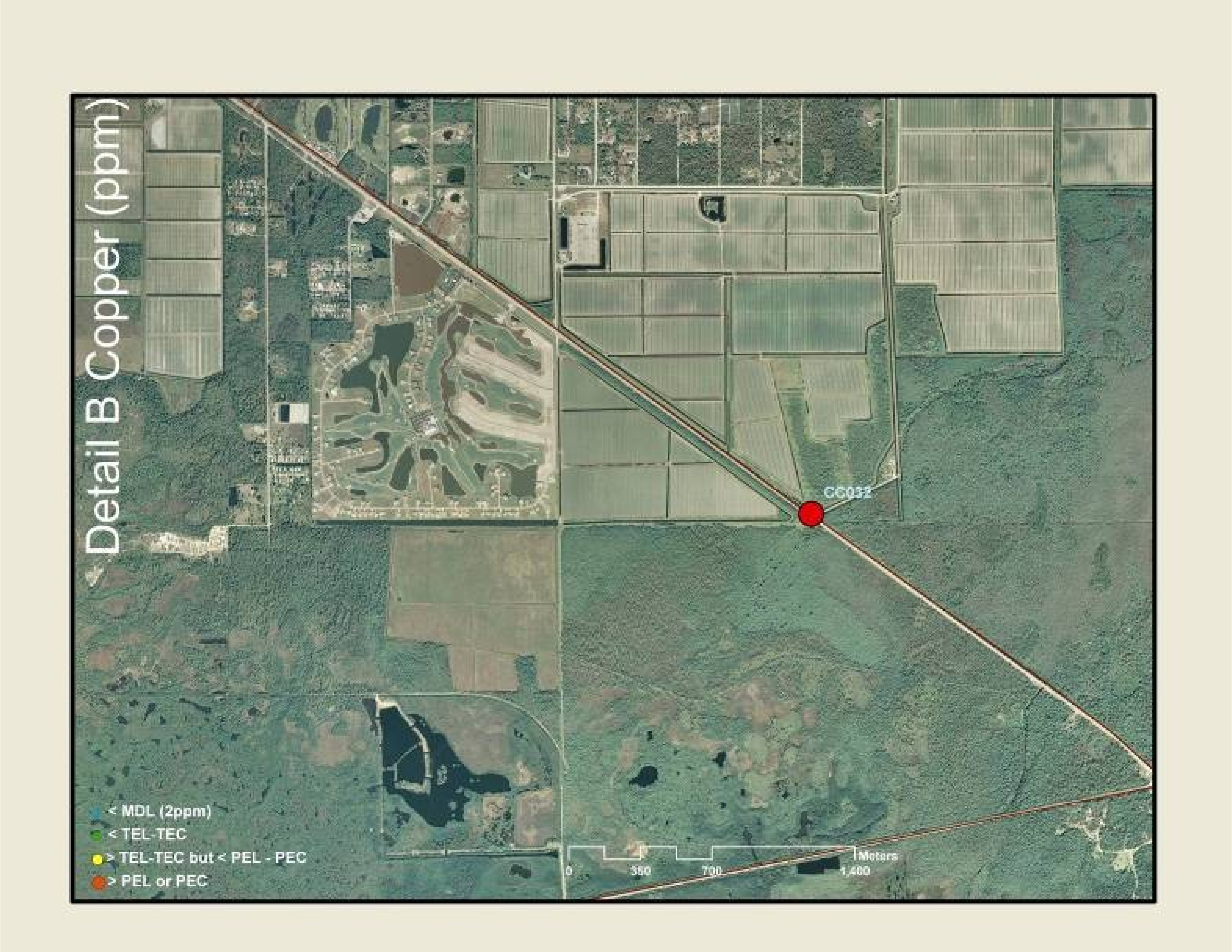


Figure 51 Detail B: Copper Concentration in Sediments from Agricultural Settings (Tomato Rd)

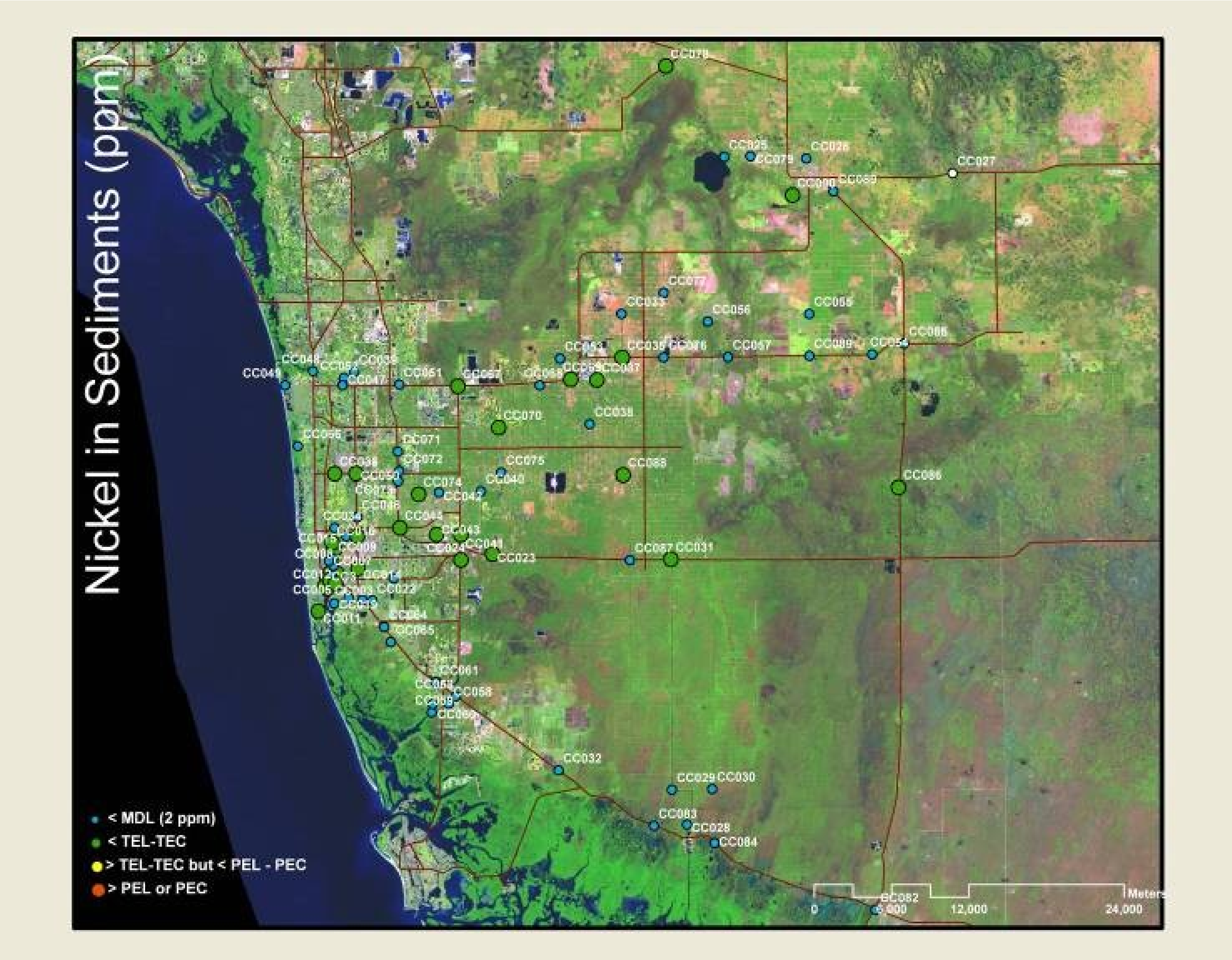


Figure 52 Distribution of Nickel in Sediments from Collier County 2007.

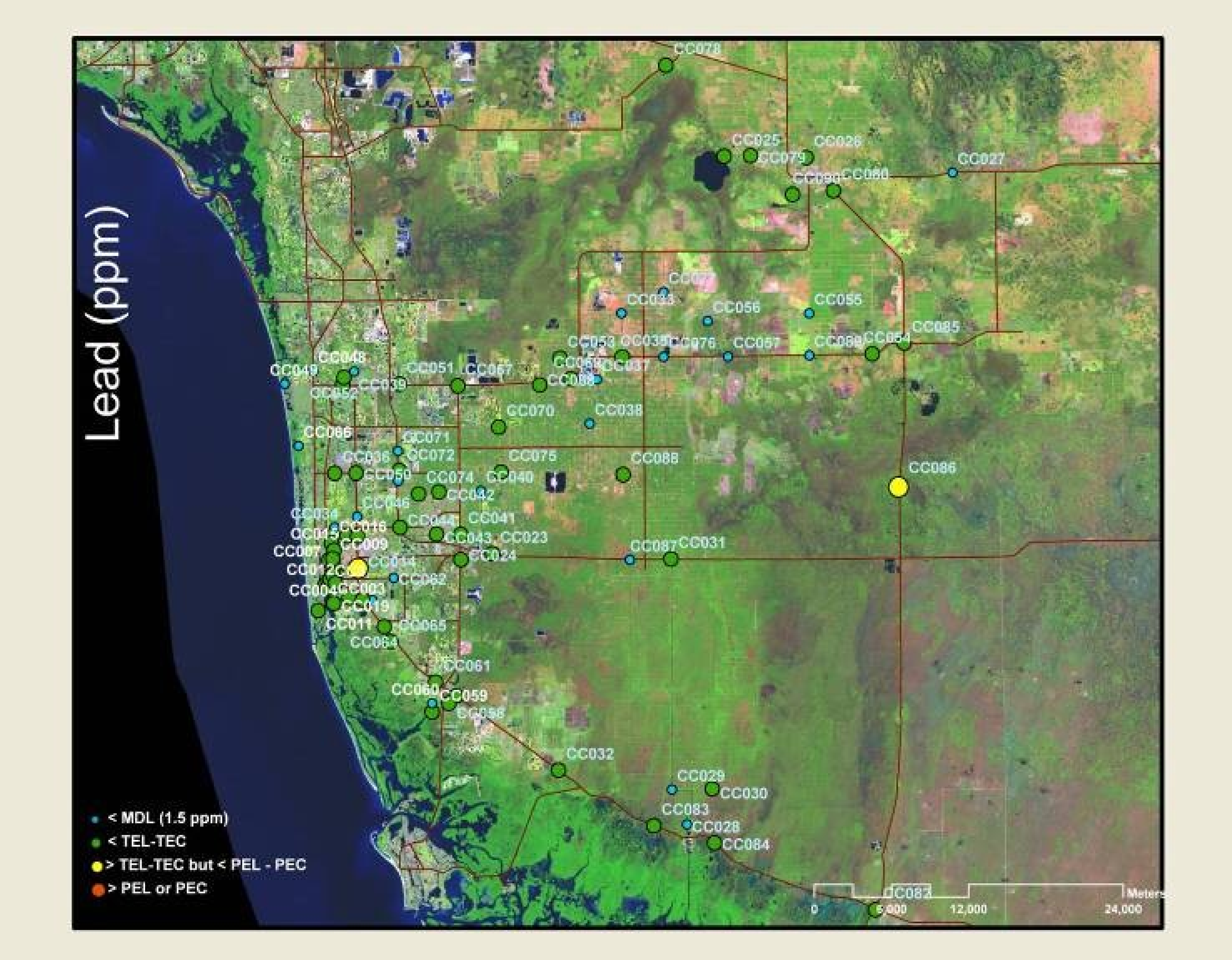


Figure 53 Distribution of Lead in Sediments from Collier County 2007.

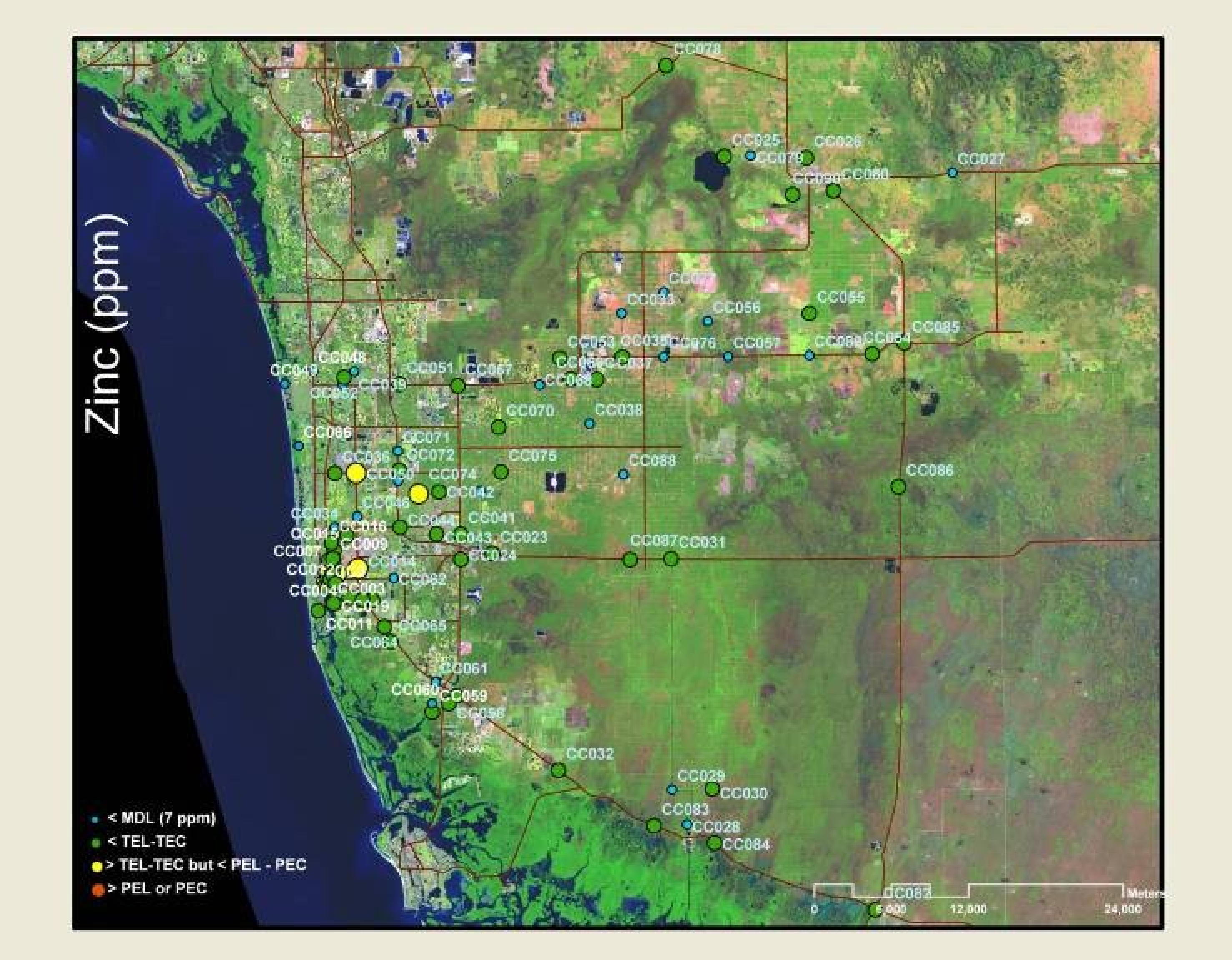


Figure 54 Distribution of Lead in Sediments from Collier County 2007.

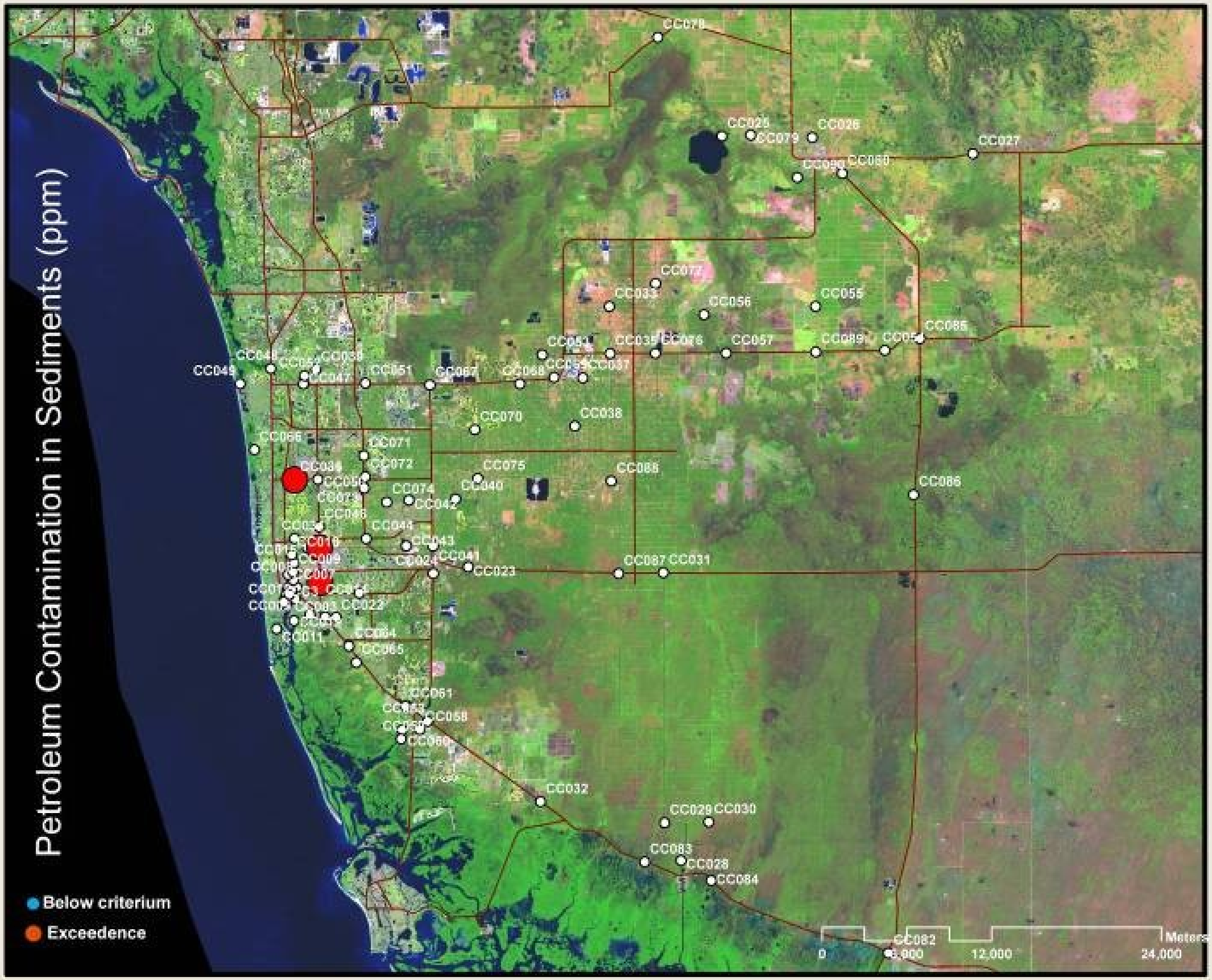


Figure 55 Geographical Distribution of Sites Showing Exceedances of FAC 62-777

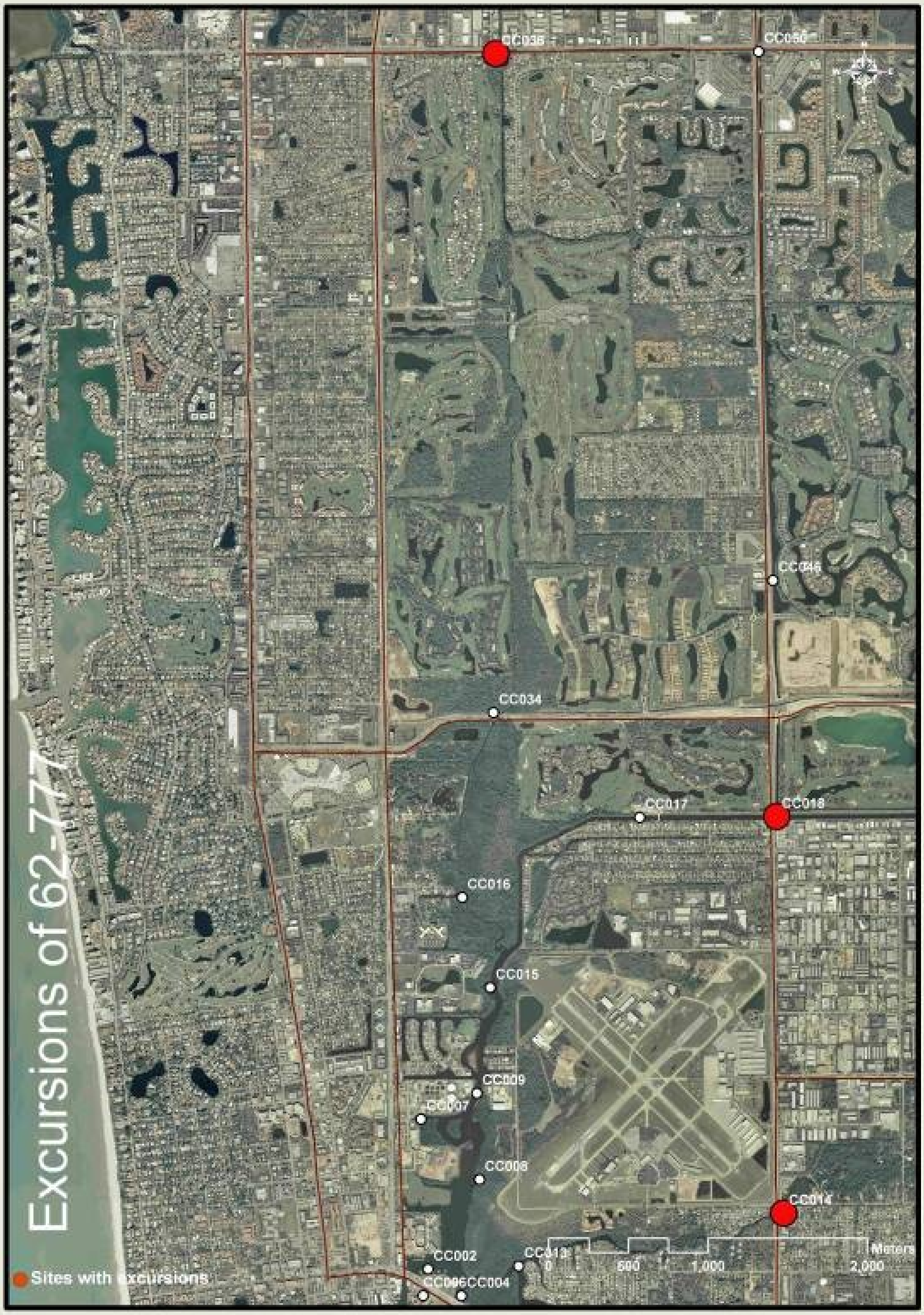


Figure 56 Detailed view of the Geographical Distribution of Sites Showing Exceedances of FAC 62-777.

Figure 57 Concentration of Total Endosulfan in Sediments from Collier County, 2007.

APPENDIX II Survey of pesticide application, chemical properties and analytical methods

chemical	Ag	GC	Mos	Res	RUP		CAS #	Partition	soil mob	soil mob	sed adsor	sed adsor	BCF	BCF	Kow	H20 sol	3	fish tox	inv tox	ins tox	bird tox	Aquatic Effects	bird tox LD50	Ps	Pw	Half life	Env Fate	EFxTa	EFxTi	EFxTb	Norm EFxTa	Norm EFxTi	Norm EFxTb	Other comment	HI Agriculture	HI Mosquito	HI Lawncare	HI Golf Course	HI Total	%	BCF	Soil ads
1,3-	x					O	542-75-6	hi soil mobility; water-	3	hi	3	no	0	5	1.82	4	2800	3	3	7	0	daphnia	mall>10000	6	3	21-28d soil;	17.5	53	123	0	15	36	0		91,569				91,569	0.01	0	1
2,4-D	x	x		x		H	94-75-7/2008	soil-mob	3	hi	3	no	0		2.81	3	infinite;	2	3	3	1	10 mg/L	mall >2000	6	3	10-50d water;	16.5	41	50	17	14	17	6		18,114		346,753	36,009	400,876	0.04	0	1
acephate	x	x		x		I	30560-19-1	soil-mob; air-part or	3	hi	3	no	0	0.1-13	-0.85	4	818,000	7	7	7	2	>1.0	mall 350	3	6	3d soil/6-13d	16	112	112	32	30	30	9	possible	32,990		871,034	732,340	1,636,364	0.17	0	1
aldicarb	x				*	I	116-06-8	air-vapor & part; soil-	3	hi	3	no	0		1.13	3	soluble	3	2	7	7	1.4-5	mall 3.4	6	6	1-15d soil;	18	45	126	126	16	44	44		1,187,476				1,187,476	0.12	0	1
atrazine	x	x		x	*	H	1912-24-9	air-vapor & part; soil-	3	hi	2	mod	0	0.27-132	2.61	2	33 mg/L	2	3	1	1	4.3-100	mall >2000	6	9	30d soil; 96d	17.5	44	18	18	21	8	8				6,159,265	28,791	6,188,056	0.63	0	2
azadirachtin	x					I	11141-17-6	soil-low mob	1	low	1	yes	0		1.9	1	0.05	7	0	1	0	0.48 ppm/96	rat oral 5000	6	6	25-29d water;	12	42	12	0	32	9	0		25,379				25,379	0.00	0	3
azinphos-	x				*	I	86-50-0	air-part; soil-low mob;	1	low	1	yes	0	26	2.75	2	28mg/L	7	7	7	1	620 ppb/48hr	not toxic to	6	6	30-70d	13	91	91	13	61	61	9		55,021				55,021	0.01	0	3
azoxystrobin		x				F	131860-33-8		1	low	1	yes	0	17	2.64	1	6 mg/L	3	7	1	0	1.1ppm fish	mall >5800	6	6	<14d soil;	12	60	12	0	46	9	0		49,663			74,538	124,201	0.01	0	3
basic copper	x					F	7758-98-7	soil-low mob; water-	1	low	1	yes	3	hi		4	soluble	7	7	1	1	larval LC50		6	6		18	126	18	18	64	9	9		1,133,376				1,133,376	0.11	3	3
bendiocarb		x			*	I	22781-23-3		3	hi	3	no	0	12	1.7	3	260	7	7	3	7	o.4-1.8	mall 3.1	3	6	4d water; 42	15	105	45	105	34	14	34					13,173	13,173	0.00	0	1
benefin		x				H	1861-40-1		1	low	2	mod	2		4.69	2	70 ppm	7	3	2	1	0.064-1.1	mall >4640	6	6	4-120d soil;	16	80	32	16	46	18	9					12,098	12,098	0.00	2	2
benomyl	x					F	17804-35-2	soil-low mob; water-	1	low	1	yes	0	159-460	1.36	1	3.6	7	7	1	0	0.05-14	rat oral	9	6	90-180d soil;	15	105	15	0	74	11	0	teratogen;	195,449				195,449	0.02	0	3
bentazon						H	25057-89-0	air-vapor & part; soil hi	3	hi	3	no	0		2.8	1	<1%	2	2	1	2	190 mg/L/96	quail 729	6	3	0.25d air; 6.7-	14.5	29	15	29	13	7	13					180,053	180,053	0.02	0	1
bifenthrin		x		x	*	I	82657-04-3		1	low	1	yes	7	190	6	1	0.1	7	7	7	1	1.6 ug/L/48	mall 1280	6	6	50-550d	19	133	133	19	88	88	13		41,506		11,088,700	38,293	11,168,499	1.13	7	3
bromacil	x					H	314-40-9	soil-mob	3	hi	3	no	0		2.61	3	815	3	1	1	0	40-164	quail >5000	9	6	100d soil;	21	42	21	0	15	8	0	possible	266,395				266,395	0.03	0	1
buprofezin	x						69327-76-0	low mobility in soil;	1	low	1	yes	2		4.31	1	0.382	2	2	1	1	27 mg/L/96	rat oral 2198	6	6	22-59d soil	14	28	14	14	20	10	10		23,563				23,563	0.00	2	3
captan	x					F	133-06-2	soil-low mob; volatile	1	low	1	yes	7	10-1000		1	5.1	7	3	3	0	56-141	mall >5000	3	3	1-10d soil; 1-	14.5	73	44	0	50	30	0	probable	92,681				92,681	0.01	7	3
carbaryl	x	x		x		I	63-25-2	air-vapor & part; soil-	3	hi	3	no	0	9-34	2.36	3	120	7	7	7	2	0.002-4.5	moderte	6	3	0.6d air;	16.5	116	116	33	42	42	12		875,087		489,365	82,045	1,446,497	0.15	0	1
carfentrazon		x				H	128639-02-1		1	low	1	yes	1		3.36	1	12ug/L	3	3	2	1	1.6 mg/L96	quail >2250	3	3	8.6d water;	8.5	26	17	9	20	13	7				18,134	10	18,144	0.00	1	3
chloropicrin	x				*	O	76-06-2	hi soil mobility; water-	3	hi	3	no	0		2.09	3	162	7	7	1	3	0.08 mg/L/48		3	3	4.3hr-5.2d	13.5	95	14	41	29	4	12		44,766,816				44,766,816	4.54	0	1
chlorothalon	x	x		x	*	F	1897-45-6	soil-low mob; air:	1	low	1	yes	0		2.64	1	0.6	7	7	1	0	0.05-0.08	mall >21500	6	3	5-36d soil;	10.5	74	11	0	56	8	0	possible	5,178,706		4,198,922	381,922	9,759,550	0.99	0	3
chlorpyrifos	x	x			*	I	2921-88-2	soil-low mob; water-	1	low	1	yes	3	58-5100	5.27	1	0.4	7	7	7	2	0.11-	mall 167	6	9	2-81d soil/16-	16.5	116	116	33	79	79	23		748,820			76,492	825,312	0.08	3	3
copper	x	x				F	20427-59-2	soil-mob	3	hi	3	no	1	117-694		1	2.9	7	7	1	1	23ppb/96	rat oral 1000	6	6	persistent	17	119	17	17	54	8	8		10,920,385				10,920,385	1.11	1	1
cyfluthrin	x	x		x	*	I	68359-37-5	air-part; soil -immob;	1	low	1	yes	3	400	5.94	1	2mg/L	7	7	7	0	0.0003-0.022	quail 72000	6	3	0.67d surf	13.5	95	95	0	66	66	0				19,348		19,348	0.00	3	3
cyromazine	x					I	66215-27-8		3	hi	3	no	0	<1		1	1.1%	1	1	7	1	>90mg/L/96	rat oral 3387	9	9	150d soil;	20.5	21	144	21	9	66	9		35,281				35,281	0.00	0	1
dazomet		x				I	533-74-4		3	hi	3	no	0	3	0.15	1	insolubl	7	7	1	2	0.16 mg/L/96	rat oral 640	3	3	7d soil; .125d-	11.5	81	12	23	36	5	10					82,826	82,826	0.01	0	1
diazinon	x	x			*	I	333-41-5	soil-low mob; volatil	1	low	1	yes	1		3.81	1	1.1%	7	7	7	7	0.96->100	mall 3.5	6	3	4d air; 14-2d	11.5	81	81	81	47	47	47	chromoso	160,323		4,032,167		4,192,490	0.42	1	3
diclofop-		x			*	H	51338-27-3		1	low	1	yes	1		3-4	1	3 mg/L	7	7	2	1	toxic to fish	quail >2000	6	9	1.7 yr water;	14.5	102	29	15	73	21	10	possible				30,149	30,149	0.00	1	3
dicofol	x					I	115-32-2	air-vapor & part; soil-	1	low	1	yes	2	1600-5700	4.28	1	1.2	7	7	1	1	0.2-0.5	mall 1651	6	9	43d loamy	15.5	109	16	16	73	10	10		513,972				513,972	0.05	2	3
dimethoate	x					I	60-51-5	air-vapor & part; soil-	3	hi	3	no	0		0.78	4	>5000	2	7	1	3	20-60	mall 41.7	6	9	2.5-122d soil;	20.5	92	21	62	32	7	21		53,032				53,032	0.01	0	1
diquat	x	x		x		H	85-00-7	soil-low mob; water-	1	low	1	yes	0		-3.05	3	700g/L	2	2	1	2	21-	mall 564	6	9	10d water;	15.5	31	16	31	18	9	18	plant	155,327			6,552	161,879	0.02	0	3
dithiopyr		x				H	97886-45-8		1	low	1	yes				1	emulsifi	7	3	2	0	0.46 mg/L/96	mall >5620	9	9	water	16.5	83	33	0	59	24	0					28,038	28,038	0.00	1	3
diuron	x					H	330-54-1	air-part; water-adsorb	2	mod	1	yes	0	3-74	2.68	2	36.4	7	7	1	0	0.13-4.9	mall 5000	9	9	28-365d soil;	18.5	130	19	0	73	10	0		3,068,899				3,068,899	0.31	0	3
endosulfan	x					I	115-29-7	air-vapor & part; soil	1	low	1	yes	1		3.83	1	0.58	7	7	3	2	1.4-5.8	mall 205-243	9	3	2d air; 32-	14.5	102	44	29	69	30	20		1,370,060				1,370,060	0.14	1	3
esfenvalerate	x			x	*	I	66230-04-4	air-vapor; soil-immob;	1	low	1	yes	1	400		1	<1mg/L	7	7	7	3	0.24-1.34	rat oral 75	6	6	0.5d air;	13	91	91	39	64	64	28		101,085				101,085	0.01	1	3
ethion	x				*	I	563-12-2	air-vapor & part; soil-	1	low	1	yes	3	1600	5.07	1	2.0	3	7	3	0	1.7-7.6	mall >5000	9	9	>170d soil;	19.5	98	59	0	62	37	0		863,478				863,478	0.09	3	3
etridiazole		x				F	2593-15-9		2	low	1	yes	0	94-328		1	5- mg/L	3	3	3	1	1.21-3.27	rat oral 4000	9	6	103d soil;	16	48	48	16	29	29	10					15,268	15,268	0.00	0	3
fenamiphos		x			*	I	22224-92-6		3	hi	3	no	1	170	3.23	3	700	3	2	1	7	9-11 mg/L/96	acutely toxic	6	3	1.8d water;	17.5	44	18	123	15	6	42	800-414-				109,168	109,168	0.01	1	1
fenbuconazol	x					I	117718-60-2	low mobility in soil;	1	low	1	yes	1	11-400	3.89	1	2.5	7	3	1	1	0.68-1.5	mall 2110	6	9	85d soil;	14.5	73	15	15	52	10	10		23,156				23,156	0.00	1	3
fenbutatin-	x				*	I	13356-08-6	soil-low mob; water-	1	low	1	yes	3		5.1	1	0.005	7	7	1	1	0.27 mg/L/48	rat oral 2631	6	9	8-30d soil;	16.5	116	17	17	79	11	11		48,164				48,164	0.00	3	3
fenpropathri	x				*	I	64257-84-7	low mobility in soil;	1	low	1	yes	7	190	6	1	0.014	3	7	7	1	2.2-3.1	mall 1089	6	6	11-17d soil; 8-	19	95	133	19	63	88	13		73,532				73,532	0.01	7	3
fenthion			x			I	55-36-9	woil-low mob; adsorb	1	low	1	yes	2		4.09	1	2ppm	7	7	7	3	0.8 ug/L/48	mall 5.94	6	6	2.9-21d	14	98	98	42	71	71	30			3,095,484			3,095,484	0.31	2	3
ferbam	x					F	14484-64-1		3	hi	3	no	0		0.8	3	130	2	2	1	1	some hazard	rat oral	6	6	56d soil; 17d	18	36	18	18	13	6	6		30,927			31,503	62,430	0.01	0	1
flutolanil		x				F	66332-96-5		3	hi	3	no	1		3.74	1	9.6	7	7	1	0	toxic to	rat oral >	9	9	300d soil &	21.5	151	22	0	76	11	0					51,927	51,927	0.01	1	1
fosetyl-al	x	x				F	39148-24-8		2	mod	2	low	0		low	3	120g/L	1	1	1	0	428 mg/L/96	avian LD50	3	6	<0.1d soil;	13	13	13	0	6	6	0	ecotox and	63,239			29,304	92,543	0.01	0	2
glufosinate-		x				H	77182-82-2		3	hi	3	no	0		,0.1	4	1370g/L	0	0	1	1	fish &	mall >2000	6	6	3-20d soil; 2-	19	0	19	19	0	6	6				11,053		11,053	0.00	0	1
glyphosate	x	x		x		H	1071-83-6	soil-low mob; water-	1	low	1	yes	0	<1		4	miscible	2	2	1	1	10-135	mall >4500	6	6	<7d water, 2-	15	30	15	15	15	8	8		2,094,770		68,600	346,641	2,510,011	0.25	0	3
halosulfuron-		x				H	100784-20-1		3	hi	3	no	1		slight	4	1630	1	1	1	1	118-131	rat oral 1287	3	3	4-12d soil; 1d	15.5	16	16	16	4	4	4					28,531	28,531	0.00	1	1
imazaquin		x			*	H	81335-37-7		1	low	1	yes	0		2.2	2	60 mg/L	1	1	1	1	280 mg/L/96	mall>2150	9	9	120-180d	17.5	18	18	18	11	11	11					40,127	40,127	0.00	0	3
imidacloprid	x	x		x		I	105827-78-		1	low	1	yes	0		0.57	1	0.51 g/L	1	2	7	1	211-280	mall>2510	9	6	48-190d soil;	15	23	105	15	16	74	11		302,193		46,896	74,134	423,223	0.04	0	3
iprodione	x	x				F	36734-19-7	air-part; soil-mob	3	hi	3	no	1	41	3	2	13.9	3	7	2	2	2.5-7.7	quail 930	6	3	14d soil; 1.1d	16.5	83	33	33	33	13	13		30,985			67,380	98,365	0.01	1	1
lambda-	x	x		x	*	I	91465-08-	soil-low mobility; water-	1	low	1	yes	7	858	7	1	5 ug/L	7	7	3	0	hi fish tox	mall >5000	6	3	28-84d soil;	17.5	123	53	0	83	36	0		21,030		908,765	267	930,062	0.09	7	3
malathion	x		x	x		I	121-75-5	air-vapor; soil hi mob	3	hi	3	no	0	13	2.36	3	145	7	7	7	1	76-8650	mall 1485	3	6	8d soil; 12d	15	105	105	15	34	34	5		30,661		225,725		256,386	0.03	0	1
mancozeb/m	x	x				F	8018-01-7	air-part; soil-low mob;	2	mod	2	no	0	2.1	1.35	1	6.2 ppm	3	7	1	0	4 mg/L/96	mall>6400	3	3	0.3d air; 2d	9.5	48	10	0	30	6	0		4,397,428		6,522,927		10,920,355	1.11	0	2
mecoprop				x		H	93-65-2		3	hi	3	no	1		3.13	3	734mg/	1	1	1	0	100-124	mall>5600	6	9	3-21d soil;	20.5	21	21	0	7	7	0	possible			339,014	43,518	382,532	0.04	1	1
mefenoxam		x				F	70630-17-0	soil-high mob	3	hi	3	no	1	326		4	26g/L	1	7	2	0	>25ug/bee;	quail 5620	6	9	water - does	21.5	86	43	0	28	14	0	related to	93,023				93,023	0.01	1	1
metalaxyl	x					F	57837-19-1		3	hi	3	no	0	7		4	8400	1	2	1	1	>100	non-tox to	6	6	14d water; 14-	19	29	19	19	9	6	6		64,477				64,477	0.01	0	1
methamidop	x				*	I	10265-92-6	soil-mob	3	hi	3	no	0		-0.93	4	>2lg/L	2	7	3	3	51 mg/L/96	quail 57	3	3	5d soil; 4.6h	14.5	65	44	44	16	11	11		101,851			7,729	109,580	0.01	0	1
methomyl	x				*	I	16752-77-5	air-vapor; soil-mob	3	hi	3	no	0		0.6	3	soluble	3	2	7	1	1.1-2.2	quail 3436	6	9	14d soil,	19.5	49	137	20	18	49	7		566,085				566,085	0.06	0	1
methyl	x				*	O	74-83-9	hi soil mobility; water-	3	hi	3	no	0	2	1.19	2	13.4 g/L	3	3	7	3	11ppm/96	quail 73	6	6	12d soil; 20d	17	51	119	51	20	47	20		187,068,315				187,068,315	18.96	0	1
metolachlor	x				*	H	51218-45-2	air-vapor & part; soil-	3	hi	2	mod	1		3.13	3	530	3	2	1	0	2-15 mg/L/96	quail	6	6	.03d air; 67-	18	45	18	0	19	8	0	possible	21,033				21,033	0.00	1	2
metribuzin	x	x				H	21087-64-9	air-vapor & part; soil-	3	hi	2	mod	0		1.7	1	1.05 g/L	2	3	1	2	64-76	mall 460	9	6	1-2d air; 172-	18	45	18	36	24	10	19	probable	190,448			10,752	201,200	0.02	0	1
mevinphos	x				*	I	7786-34-7	air-vapor; soil-mob	2	hi	2	no	0		0.13	4	600 g/L	7	7	7	7	0.06-130	mall 4.63	6	6	3-13d soil;	17	119	119	119	44	44	44		55,441				55,441	0.01	0	2
MSMA		x				H	2163-80-6		1	low	1	yes	7	9800		2	miscible	7	7	7	1	toxic to fish	rat oral 1580	9	9	180d soil;	24.5	172	172	25	100	100	14					705,945	705,945	0.07	7	3
naled			x			I	300-76-5		3	hi	3	low	0		1.38	4	2000	7	7	3	1	0.35 ppb 48	quail 1327	3	6	1d soil; 14d	16	112	48	16	30	13	4			2,783,340			2,783,340	0.28	0	1
napropamid	x					H	15299-99-7	air-vapor & part; soil-	3	hi	2	mod	1	77	3.36	2	73 mg/L	3	2	7	0	9-13 mg/L/96	mall >56,000	9	3	.09d air; .04d	18.5	46	130	0	22	63	0		33,108				33,108	0.00	1	2
norflurazon	x					H	27314-13-2	water-adsorb, non-	1	low	1	yes	0		2.45	2	28 mg/L	3	2	1	1	8.1-16	mall >2510	6	6	30-92d soil;	13	33	13	13	21	8	8		373,774				373,774	0.04	0	3
oryzalin	x	x				H	19044-88-3	air-part; soil low mob;	1	low	1	yes	1	32-328	3.73	1	miscible	3	3	7	2	0.1-2.66	mall 507	6	3	45-120d	11.5	35	81	23	25	59	17	possible	19,183		99,383	57,063	175,629	0.02	1	3
oxadiazon		x				H	19666-30-9		1	low	1	yes	7	24.1	4.8-7.8	1	0.4	7	3	1	1	>0.0 ppm/96	mall 1000	9	6	90-180d soil;	22	110	22	22	70	14	14	for ecotox			42,097,199	176,028	42,273,227	4.28	7	3
oxamyl	x				*	I	23135-22-0	air-vapor; soil-hi mob;	3	hi	3	no	0		-0.47	3	280 g/L	3	3	3	7	toxic to bees;	mall 2.6	6	9	0.67d air; 11-	19.5	59	59	137	21	21	49		163,183				163,183	0.02	0	1
paraquat	x				*	H	4685-14-7	air-part.; water-adsorb	1	low	1	yes	0		-4.22	3	soluble	2	3	1	2	11->100	mall 600	9	9	1000d soil;	18.5	46	19	37	66	28	22	possible	256,363				256,363	0.03	0	3
pebulate	x					H	1114-71-2	air-vapor; soil mob	3	hi	3	no	1		3.83	2	60 mg/L	3	3	3	1	6.3-10ppm/96	mall >2000	6	6	16d soil; 0.6d	18	54	54	18	22	22	7		51,073				51,073	0.01	1	1
pendimethali		x				H	40487-42-1		3	hi	2	mod	3		5.2	1	0.3	7	7	2	1	toxic to fish;	rat oral 1250	9	3	28-172d soil;	19.5	137	39	20	22	22	7				249,804	8,837	258,641	0.03	3	2
pentachloron				x		F	82-68-8		1	low	1	yes	7	14000	4.46	1	0.44mg/	7	7	0	1	0.1ppm fish;	>3700 mg/kg	9	3	5-10 mo soil;	20.5	144	0	21	93	0	13				21,074,140		21,074,140	2.14	7	3
permethrin	x		x	x	*	I	52645-53-1	air-vapor & part; soil	1	low	1	yes	7	480-560	6.5	1	0.006	7	7	7	0	0.002-0.005	quail . 13500	6	6	49d air; 30d	19	133	133	0	85	85	0		464,954				464,954	0.05	7	3
prodiamine		x				H	29091-21-2		1	low	1	yes	3	1300		1	0.013	7	7	1	0	552-829	mall >10,000	6	3	60d soil;	13.5	95	14	0	69	10	0		29,401			358,821	388,222	0.04	3	3
pyridaben	x					I	96489-71-3	soil-slightly mobile	2	mod	2	mod	1			1	1.2 ug/L	7	7	7	1	toxic to	mall >2500	6	3	86d soil;	13.5	95	95	14	56	56	8		69,781				69,781	0.01	1	2
sethoxydim	x					H	74051-80-2	soil-mob	3	hi	3	no	0		1.65	4	4.9	3	2	1	1	1.6-100	mall >2510	6	3	5-25d soil;	17.5	44	18	18	26	11	11		45,958				45,958	0.00	0	1
simazine	x	x			*	I	122-34-9	air-vapor & part; soil-	3	hi	2	mod	0	1-55	2.18	1	6.2	1	3	1	0	>100	mall >5000	6	3	27-102d soil;	13.5	27	14	0	15	7	0		518,896				518,896	0.05	0	2
spinosad	x	x				I		low mobility in soil;	1	low	1	yes	2	<100	4	3	235	3	2	3	1	5-30 mg/L/96	mall >2000	3	9	9-10d soil;	14.5	36	44	15	21	25	8		183,277			1,166	184,443	0.02	2	3
sulfosate	x					H	81591-81-3	low mobility in soil;	1	low	1	yes	0		-3.2	4	4.3 g/L	1	2	1	2	1800	bird 950	6	6	56d soil; 14-	15	23	15	30	12	8	15		94,204				94,204	0.01	0	3
sulfur	x			x		F	7704-34-9	soil-immob	1	low	1	yes	0		low	1	insolubl	1	0	1	0	fish >180	quail >5620	6	6	persistent	12	6	12	0	5	9	0		992,680				992,680	0.10	0	3
thiophanate-	x	x				F	23564-05-8	air-vapor & aprt; soil-hi	3	hi	3	no	0	2.4	1.4	2	26.6	3	3	1	0	2.26-2.6 ppm	mall >5620	6	3	0.2d air; 28d	15.5	47	16	0	18	6	0				1,122,707	63,723	1,186,430	0.12	0	1
trichlorfon		x				I	52-68-6		3	hi	3	low	0	3		4	154g/L	7	7	1	0	550ug/L/96	mall >5000	3	6	6.4d soil; 32d	16	112	16	0	34	5	0					29,730	29,730	0.00	0	1
trifluralin	x	x		x	*	H	1582-09-8	air-vapor & part; soil	1	low	1	yes	7	1689-9586	5.34	1	0.02	7	7	1	0	0.06-0.42	quail >5000	9	0	0.67d air; 116-	19	133	19	0	85	12	0		37,788		104,365	3,111	145,264	0.01	7	3

Table A1 Pesticide Survey conducted by Elizabeth Woods, Collier County Pollution Control and Prevention Department, April 2007.

APPENDIX III Supporting information

Provided as a separate electronic file (Volume II APPENDIX III Supplementary Information.pdf)