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

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Environmental Analysis Research Laboratory

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

Engineering and Natural Resources Department
Collier County, Florida.

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EXECUTIVE SUMMARY

A comprehensive survey of current and past use sediment contaminants was conducted along different watersheds and estuarine systems of Collier County, Florida. As in the previous efforts (1989-1991, 2001-2002 and 2007) the study comprised the collection of surface sediments at a total of 57 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 2007 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 polycyclic aromatic hydrocarbons (PAHs) and trace metals. In addition, a comprehensive survey of sediments from inland waterways was also included in the 2014 program to address findings from previous sediment quality surveys. Particular attention was placed on the site selection for water bodies that receive water and runoff from major roads, golf courses, and agricultural fields. All sites were visited once in June 2014 in order to assess the occurrence 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 common organic contaminants such as Polycyclic Aromatic Hydrocarbons (PAHs), Organochlorine Pesticides, Organophosphate Pesticides and Phenoxy Acid Herbicides. Additionally, trace metals such as lead, zinc, copper, arsenic, and chromium among others were also analyzed. 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 Florida International University (FIU) and all chemical analyses were performed by Pace Analytical 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, a comparison of the occurrence to available guidelines is provided. Since both saltwater and freshwater systems were sampled, two sets of SQAGs were used.

All pesticides monitored in the sediments were below the laboratory method reporting limits. 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 8.8% of the samples tested positive for pesticides but none of them had detections above the laboratory reporting level. The detected pesticides were endosulfan (one of the last chlorinated pesticides still in use in Florida, only one detection at 0.260 ng/g), 4,4’-DDE (three detections at 1.3, 1.5 1.9 ng/g) and dieldrin (two detections at 2.60 and 0.120 ng/g), all belonging to the chlorinated pesticide group. The concentrations are low and between the laboratory method detection limit (MDL) and the method reporting limit (MRL) and thus detection should be interpreted with caution. These levels of legacy pesticides are similar to the ones found in previous surveys that reported no potential concern associated with similar concentrations since none of these values exceeded the available SQAGs (although there is no SQAG for endosulfan) with the exception of one site adjacent to a large agricultural area which presented a dieldrin concentration above the Threshold Effects Concentration (TEC) criterion (but still below reporting limits). This information, combined with the fact that all these pesticides have been banned decades ago make the risk of their occurrence to 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. As an example, when considered as Total PAHs one site in the survey ranked not only above the Probable Effect Concentration (PEC), but also showed excursions when compared to the criteria for Petroleum Contamination in sediments described in Florida Administrative Code (FAC) 62-777. Site CC036 presented concentrations for benzo(a)anthracene and benzo(b)fluoranthene that exceeded the soil cleanup criterion based on leachability towards groundwaters. It also presented benzo(a)pyrene-equivalents (a combination of carcinogenic PAHs, see table 5) that exceeded the direct exposure cleanup criterion for commercial sites. That site was previously identified during the 1989-1991 survey (GRE896) as exceeding both the Effects Range-Median (ER-M) criterion (Long and Morgan, 1990) and the EPA criterion for Total PAHs for freshwater sediments. It also was signaled during the 2007 Survey as exceeding available SQAGs. With 36.7 mg/Kg, CC036 was the highest ranking site in total PAH pollution during the present survey. 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 5 % of the sites showed exceedances for one or more PAH, all from freshwater sites (no saltwater sediment showed PAHs above the Method Reporting Limits). Additionally, most stations presented a decreased total PAH concentration during the 2014 survey in comparison with previous efforts. It is clear from these spatial and temporal trends that much of the future monitoring efforts should be concentrated in the inland canals and along selected sites that still showed an increase in PAH pollution and/or exceeded SQAGs. Three sites (CC014, CC064 and CC036) ranked above the Probable Effect Concentration (PEC) for at least one different individual PAH, but only one of them (CC036) 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. To bring these numbers to a national perspective, 5.3% (3/57) of the sites sampled in 2014 ranked above the 85th percentile concentration for Total PAHs (3.2 mg/kg) used in the National Oceanic and Atmospheric Administration (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 (copper and zinc) exceeded the PEL/PEC guideline in the sediment samples. Copper was elevated in 8.8% of the sites (5/57) with exceedances in both the freshwater environment (CC114, CC106 and CC036) and the estuarine system (CC066 and CC112). Due to the geographical distribution of the sites, is clear that copper inputs have distinctive sources. For example site CC066 is a wetland adjacent to resort/golf courses. The freshwater sites are also in the vicinity of golf courses and residential areas. This fact may indicate that the past or current use of copper algaecide for management of water bodies could be an important source of copper in Collier County. In contrast, CC112 is located in Venetian Bay, likely influenced by copper formulations in boat bottom paint due to the presence of multiple marinas and docks. When the TEL/TEC criteria is evaluated, a total of 47% (27/57) of the sites rank above the guideline concentrations for copper. 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 in terms of frequency of exceedances, with 28% (16/57) of sites surpassing the TEL/TEC criteria, although no exceedances of PEL/PEC criteria were observed for that element. The sites exceeding TEL/TEC criteria are scattered along the County and there was no clear indication of arsenic sources. Furthermore, no signs of anthropogenic character was observed for the arsenic measurements.

Most of the other trace elements had fewer hits above the TEL/TEC criteria. For example, zinc presented 3 exceedances (CC036, CC106 and CC112), but one of them (CC036) did surpass the PEC criteria and the levels considered as toxic for sediments, according to available literature. There is also no clear indication of what the zinc sources may be. Lead also presented three exceedances of TEL/TEC criteria (CC036, CC090 and CC043) with levels below those considered toxic for sediments. Sampling sites of particular interest such as CC036 (a “hotspot” with years of documented environmental pollution) and CC014 (located at the southeast corner of Naples Airport on Airport Road) showed 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. Polycyclic 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, benzo(b)fluoranthene and chrysene in the sediments at station CC036 combined with the exceedances of SQAGs for toxic metals and the long term trends of contamination at that site needs to be further and promptly investigated.

In addition to contaminants, several nutrients (total organic carbon (TOC), total Kjeldahl (organic) nitrogen, total phosphorus and total nitrate and nitrite) were included in the 2014 sediment survey. Site CC036 (previously flagged for contamination with trace metals and PAHs) presented the highest amount of TOC, and elemental relationships suggest that the accumulated organic matter has a strong anthropogenic character. Additionally, data suggests that saltwater sites CC112, CC113 and CC117 and freshwater sites CC043, CC031, CC108 and CC103 could be at risk from elevated primary productivity and eutrophication.

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, none of the contemporary use pesticides and herbicides were detected in the sediment samples above the laboratory detection limits (MDLs). However, selected sites presented concentrations of legacy pesticides above MDL (but below reporting 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 polycyclic aromatic hydrocarbons (PAHs) seems to have decreased from 2007 levels but still is the primary concern along Collier County watersheds and should still be the focal point of future monitoring programs.
- Copper and to a lesser extent arsenic, zinc and lead are the highest ranking trace elements in the sediment hazard assessment based on the SQAGs. Since elevated copper is evidently related to algaecide applications, management

methods regarding the application, alternatives to the use of or preventing the need for using copper would be solutions for preventing further contamination.

- In the case of arsenic and zinc, additional monitoring is required to understand their sources and fate.
- 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, commercial areas, golf courses, stormwater 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.
- A comprehensive list of analytes to account for past and present use contaminant should be kept and updated before the follow-up monitoring effort:
    - a) Polycyclic aromatic Hydrocarbons,
    - b) Trace Metals,
    - d) Chlorinated pesticides
    - e) Nutrients
    - 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, Zinc, Arsenic and Lead.

- Adopt “planning guidelines” to trigger action for contaminants that do not have a promulgated SQAGs.
- Maintain a concentrated monitoring effort within north Naples Bay and the lower Gordon River in order to assess temporal changes of contaminant depositions, especially copper and PAHs.

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, 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, stormwater runoff, and human derived wastewater are among the myriad of process that contribute to the contaminant loading to Collier County’s coastal 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 previous 2001-2002 and 2007 chemical monitoring surveys 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 from the 2001-2002 survey 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. The same conclusions were obtained from measurements during the 2007 survey. It was found that sediment quality was overall acceptable except for selected sites that required special attention. However, a widespread detection of polycyclic aromatic hydrocarbons (PAHs) with large frequency exceedances of SQAGs gave this group of chemicals a monitoring priority for follow-up efforts. Specially, some sites were catalogues as of “environmental concern” due to the high levels of PAHs observed and /or a long historical record of pollution.

Although some families of the compounds monitored were more prevalent than others in the sediments collected in both previous surveys (PAHs and metals over chlorinated pesticides and PCBs) several contaminants in those studies, exceeded the “Threshold Effect Levels” (TELs). Metals (mainly arsenic 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 2007 study conclusions, a set of recommendations were formulated to guide future efforts to prevent further degradation of the County’s coastal environments. The team recommended site-specific studies to evaluate sources and spatial/temporal trends of contamination at Haldeman Creek and other selected locations due to the presence of multiple SQAGs exceedances for a variety of chemicals (especially Copper and PAHs). 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.

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 comprehensive contaminant survey that will incorporate most of the recommendations from the 2007 report regarding sites that were identified as of potential concern and sites that would serve as sentinel locations for long term monitoring, along with new locations in order to address the presence of copper in sediments from water bodies with restricted circulation that may be affected by direct runoff or subjected to vegetation management.

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 previous surveys.

As part of the process identifying potential candidates for environmental assessment, in 2007 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 anti-fouling agent used in boat paint and algaecide in aquatic plant control. 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 on 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.

The County recently released its Watershed Management Plan (Collier County, 2011), developed to fulfill GMP commitment to assess and protect the County's water resources. That plan includes recommendations for permanent monitoring of water quality in different locations of the Golden Gate-Naples Bay, Rookery Bay and Ten Thousand Islands (which includes the Faka Union Canal discharging from Southern Golden Gate Estates). These recommendations include major water delivery routes 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 to accommodate the following major objectives.

a) Continue the long-term assessment of multiple urban and agricultural-derived contaminants for the main watersheds of Collier County (Main Golden Gate Canal Basin + Gordon River Extension Basin, Cocohatchee Canal Basin, Faka Union Canal Basin and Barron River Canal Basin)(Figure 1).

b) Continue the site specific-site survey at sites recommended in the 2002 and 2007 report with particular emphasis in PAHs.

c) Develop a copper-specific survey in water bodies that may be directly affected by runoff direct applications.

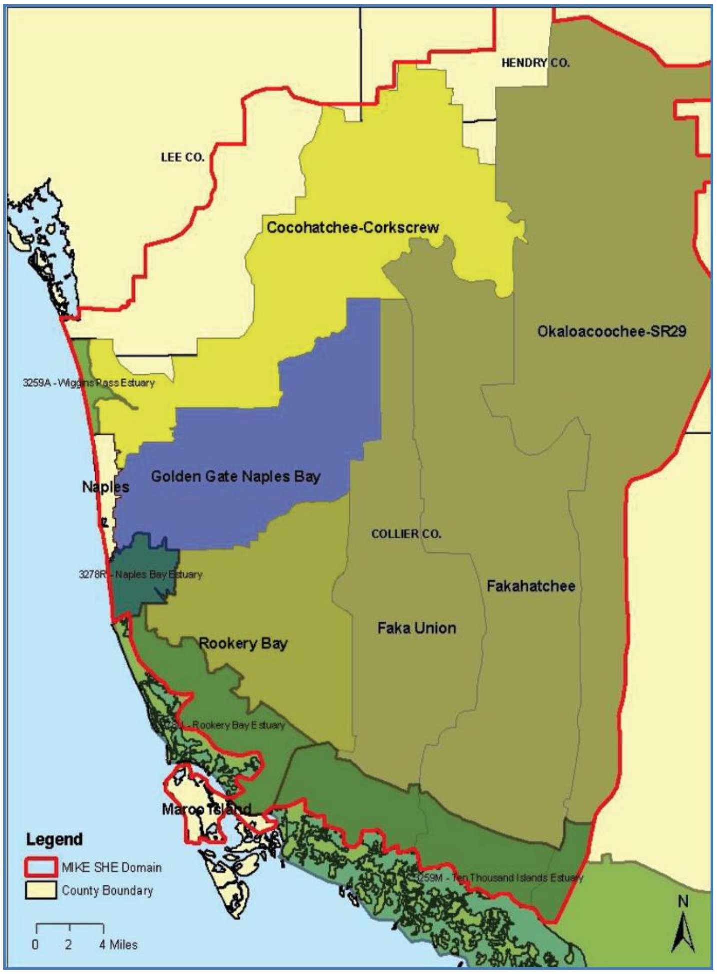

Figure 1 Major watersheds and draining basins in Collier County, Florida. (Adapted from Watershed Management Plan. Collier County, 2011)

PURPOSE AND SCOPE

- Continue the long-term assessment of multiple urban and agricultural-derived contaminants for the main watersheds of Collier County (Main Golden Gate Canal Basin + Gordon River Extension Basin, Cocohatchee River Basin, Faka Union Canal Basin and Barron River Canal Basin)

- Continue the site specific-site survey at sites recommended in the 2002 and 2007 report with particular emphasis in PAHs.

- Develop a Copper-specific survey in water bodies that may be directly affected by runoff or direct applications.

APPROACH AND METHODS

Analytical Methodology

Given the previous knowledge that levels of some of these contaminants may be low, every effort was 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 Pace Analytical Services Inc., (FDOH/NELAC E 83079) at their facility in Ormond Beach, Florida. All analyses were performed using EPA methods certified to meet NELAC requirements. The methodology employed was as follow: trace metals (EPA 3050/6010); polycyclic aromatic hydrocarbons (EPA 3546/8270); organochlorine pesticides (EPA 3546/8081); chlorinated herbicides (EPA 3546/8151); organophosphorous pesticides (EPA 3546/8141); Total Nitrogen Calculation (TKN+NOx Calculation); Total Kjeldahl Nitrogen (EPA 351.2); Nitrogen, NO2/NO3 (EPA 353.2); Total Phosphorus (EPA 365.4); Total Organic Carbon (EPA 9060 Modified). 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 Strategy and Site Locations

During the 2007 study, a total of 88 sites were selected for collection 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 stormwater 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. Of those 88 stations, 40 were targeted for this study based on the results of the previous surveys indicating these as areas of potential concern or as historical sentry locations. Additionally 17 new stations were added for this study to determine the presence of Copper in sediments stormwater ponds that are subjected to vegetation management.

Table 7 shows the list of stations originally selected for the project. 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 Engineering and Natural Resources Department and City of Naples personnel.

The final list of sampling stations (57) including the GPS coordinates and collection dates is presented in Table 1. A County-wide map showing the geographical locations of all sampling sites is presented in Figure 2 while an expanded view of the Naples Bay-Gordon River area is shown in Figure 3.

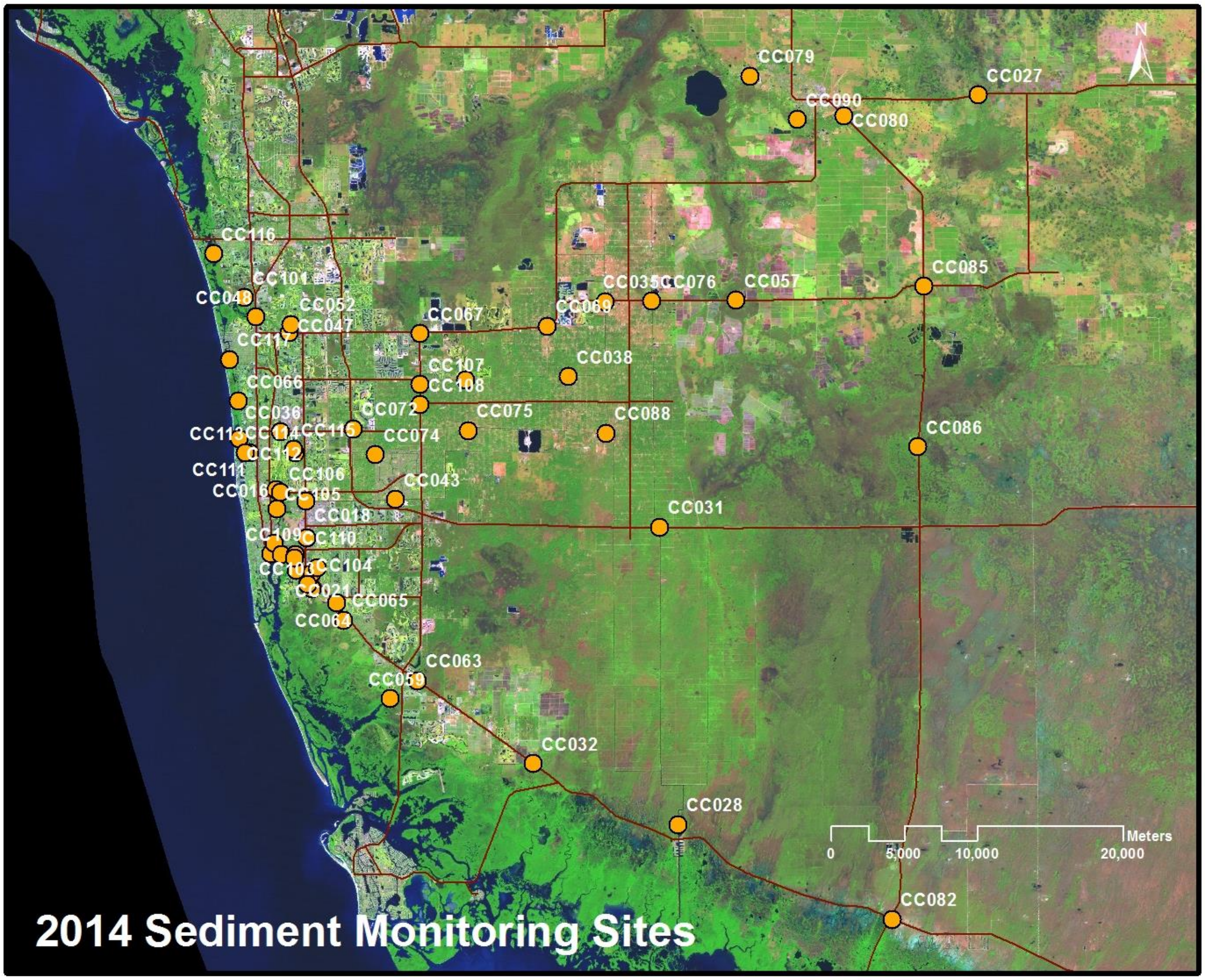

Figure 2 Location of the final sites sampled for the 2014 sediment monitoring.

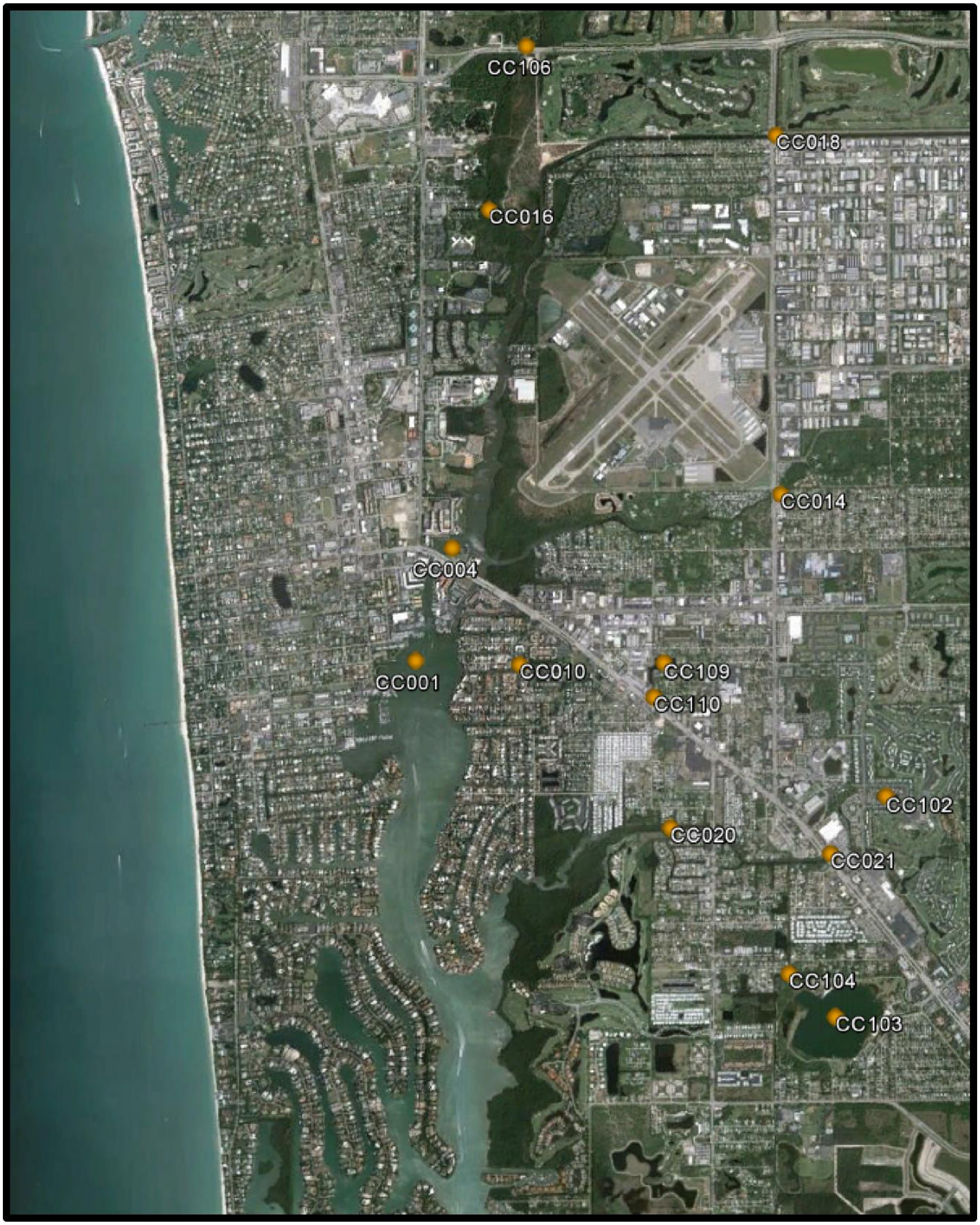

Figure 3 Detailed view of the Naples Bay- Gordon River sampling sites.

Table 1 Final List of Sites Collected During the 2014 Collier County Sediment Survey

SITE	NAME	LATITUDE	LONGITUDE	COLLECTION	REPORTED
1	CC001	25.90911	-80.13855	7/15/2014	7/31/2014
2	CC004	25.76111	-80.53024	7/15/2014	7/31/2014
3	CC010	26.11251	-81.76062	7/15/2014	7/31/2014
4	CC014	26.30348	-81.34251	7/15/2014	7/31/2014
5	CC016	26.42206	-81.30501	7/15/2014	7/31/2014
6	CC018	26.48551	-81.52880	7/2/2014	7/17/2014
7	CC020	26.40633	-81.42953	7/15/2014	7/31/2014
8	CC021	26.12370	-81.76263	7/2/2014	7/17/2014
9	CC027	26.04599	-81.70840	6/25/2014	7/17/2014
10	CC028	26.04599	-81.70838	7/2/2014	7/17/2014
11	CC031	26.12354	-81.76243	7/9/2014	8/19/2014
12	CC032	26.13527	-81.77470	6/18/2014	7/17/2014
13	CC035	26.20090	-81.77570	6/25/2014	7/17/2014
14	CC036	26.19803	-81.80671	7/9/2014	8/19/2014
15	CC038	26.17535	-81.78716	7/8/2014	8/19/2014
16	CC043	25.90907	-80.13832	7/8/2014	8/19/2014
17	CC047	25.90907	-80.13832	7/9/2014	8/19/2014
18	CC048	25.90907	-80.13832	7/9/2014	8/19/2014
19	CC052	26.24108	-81.68839	7/9/2014	8/19/2014
20	CC057	26.29418	-81.47185	6/25/2014	7/17/2014
21	CC059	26.19695	-81.71954	7/2/2014	7/17/2014
22	CC063	26.19695	-81.71954	6/18/2014	7/17/2014
23	CC064	26.28262	-81.80198	6/18/2014	7/17/2014
24	CC065	26.27756	-81.77833	6/18/2014	7/17/2014
25	CC066	26.23014	-81.81371	7/9/2014	8/19/2014
26	CC067	26.10238	-81.78416	7/8/2014	8/19/2014
27	CC069	26.27758	-81.60144	6/25/2014	7/17/2014
28	CC070	26.24394	-81.65736	7/8/2014	8/19/2014
29	CC072	26.21333	-81.73465	7/8/2014	8/19/2014
30	CC074	26.19744	-81.71936	7/8/2014	8/19/2014
31	CC075	26.21266	-81.65528	7/8/2014	8/19/2014
32	CC076	26.29333	-81.52956	6/25/2014	7/17/2014
33	CC078	26.49581	-81.52881	6/25/2014	7/17/2014
34	CC079	26.43337	-81.46260	6/25/2014	7/17/2014
35	CC080	26.40906	-81.39782	6/25/2014	7/17/2014
36	CC082	25.91029	-81.36309	6/18/2014	7/17/2014
37	CC085	26.30328	-81.34243	6/25/2014	7/17/2014
38	CC086	26.20352	-81.34646	6/25/2014	7/17/2014
39	CC088	26.21141	-81.56065	6/25/2014	7/17/2014
40	CC090	26.40633	-81.42953	6/25/2014	7/17/2014
41	CC101	26.29435	-81.81007	7/9/2014	8/19/2014
42	CC102	26.12714	-81.75893	7/2/2014	7/17/2014
43	CC103	26.11403	-81.76221	6/18/2014	7/17/2014
44	CC104	26.11657	-81.76533	6/18/2014	7/17/2014
45	CC105	26.17532	-81.78729	7/2/2014	7/17/2014
46	CC106	26.17372	-81.78422	7/2/2014	7/17/2014
47	CC107	26.24105	-81.68871	7/8/2014	8/19/2014
48	CC108	26.22832	-81.68893	7/8/2014	8/19/2014
49	CC109	26.13520	-81.77399	7/2/2014	7/17/2014
50	CC110	26.13311	-81.77462	7/2/2014	7/17/2014
51	CC111	26.19822	-81.80569	7/2/2014	7/17/2014
52	CC112	26.20675	-81.81320	7/16/2014	7/31/2014
53	CC113	26.19800	-81.80900	7/16/2014	7/31/2014
54	CC114	26.14549	-81.76620	7/2/2014	7/17/2014
55	CC115	26.20037	-81.77571	7/2/2014	7/17/2014
56	CC116	26.32140	-81.83161	7/16/2014	7/31/2014
57	CC117	26.25591	-81.81995	7/16/2014	7/31/2014

Sampling was conducted by FIU field personnel. At each station, 3-250 ml, and 1 – 125 ml glass jars of surface sediments were collected for organic and inorganic analyses. All sediments were collected by hand from the center of the water body using a stainless steel Eckman dredge (9”x9”x9”) equipped with a 10 ft handle or 3/16” polyester line with 45-B10 messenger. 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 Pace Analytical Services 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 4 shows the overall concentrations of all trace metals in the sediments while Figure 5 shows the same set of data but includes the stations ranking above the 75th percentile (outliers) of the County-wide distributions. Figures 6 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). Similarly to the 2007 survey, this study included both estuarine and limnetic sediments and therefore both coastal (TEL/PEL) and inland (TEC/PEC) water SQAGs were used (available SQAGs can be observed in Table 2). 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 it 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 are 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, yellow, orange and red circles for statistically relevant detections. It is important to note that both MDLs and MRLs are sample weight and laboratory dependent and they 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 6, 7, 8, 10 and 11 are presented within the discussion as examples of three elements where SQAGs are exceeded.

Figures 36 to 47 show the similar results for all organic compounds for which a definitive set of SQAGs are available and positive hits (concentrations >MDL) were observed. To compare the distribution of trace elements against their natural abundance, trace metal results are presented in Figures 19 to 24 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). However, these graphs do not provide exposure-based interpretation as 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.

Another set of results is presented as cumulative frequency distribution plots which provide a comparison of the observed toxic trace metal concentrations in the present study with those obtained in years 2001-2002 and 2007 (Figures 25 to 35). Another set of plots to help the interpretation of nutrient data are provided (Figures 48 to 55). Lastly, a set of maps is provided to illustrate the spatial extent of the contaminants along the study area (Figures 56 to 64). 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 2014 survey could be catalogued as Tier 3 sediments (no SQAG exceeded) or Tier 2 (at least one chemical exceeding the TEL/TEC criteria), thus having a low potential for risk of adverse effects to fish and wildlife via bioaccumulation. However, six sites (CC036, CC064, CC066, CC106, CC112 and CC114, 10.5%) can be catalogued as Tier 1 (at least one chemical ranking above the PEL/PEC criteria) and carry considerable risk to aquatic life. Sites CC036 and CC064 exceeded the PEC guideline for at least one of seven different polycyclic aromatic hydrocarbons (PAHs), from which site CC036 also exceeded the PEC guideline for total PAHs. Since CC036 also ranked above PEC for Total PAHs in the previous (2007) survey, these results may indicate that this particular site needs special attention regarding PAH pollution. Regarding trace metals, copper exceeded the PEL/PEC criteria in 4 sites (CC112, CC106, CC114 and CC066, 7%) and zinc exceeded the PEC criteria in one sample (CC036, 2%). 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 6 (11%) of the 57 sites included in the 2014 survey could be catalogued as Tier 1 while a maximum of 26 (45%) stations fall within the Tier 2 category (one or more chemicals exceeding a TEC/TEL criteria). Therefore, 44% of the 2014 survey sites could be catalogued as Tier 3 sediments. The percentage of Tier 1 sites is lower than the 27% national average calculated by Long (Long et al., 1998), indicating that estuarine areas within Collier County are still non-polluted relative to the rest of the United States.

Table 2 Summary of Sediment Quality Available Guidelines (SQAGs). (From MacDonald et al., 2003 and MacDonald, 1994).

SQAG	TEL	TEC	PEL	PEC
Trace metals				
Arsenic	7.24	9.79	41.6	33
Cadmium	0.676	0.99	4.21	4.98
Chromium	52.0	43.4	160	111
Copper	18.7	31.6	108	149
Lead	30.2	35.8	112	128
Nickel	15.9	22.7	42.8	48.6
Zinc	124	121	271	459
Pesticides				
4,4'-DDD	1.22	-	7.81	-
4,4'-DDE	2.07	-	374	-
4,4'-DDT	1.19	-	4.77	-
Chlordane	2.26	3.24	4.79	17.6
Dieldrin	0.715	1.9	4.3	61.8
Endrin	2.67	2.22	62.4	207
g-BHC	0.32	2.37	0.99	4.99
Heptachlor epoxide	-	2.47	-	16.0
PAHs				
2-Methylnaphthalene	20.2	-	201	-
Acenaphthene	6.71	-	88.9	-
Acenaphthylene	5.87	-	128	-
Anthracene	46.9	57.2	245	845
Fluorene	21.2	77.4	144	536
Naphthalene	34.6	176	391	561
Phenanthrene	86.7	204	544	1170
TOTAL LMW PAHs	**312**	**-**	**1442**	**-**
Benzo(a)anthracene	74.8	108	693	1050
Benzo(a)pyrene	88.8	150	763	1450
Chrysene	108	166	846	1290
Dibenzo(a,h)anthracene	6.22	33	135	-
Fluoranthene	113	423	1494	2355
Pyrene	153	195	1398	1520
TOTAL HMW PAHs	**655**	**-**	**6676**	**-**
TOTAL PAH	**1684**	**1610**	**16770**	**22800**

(All units in µg/Kg)

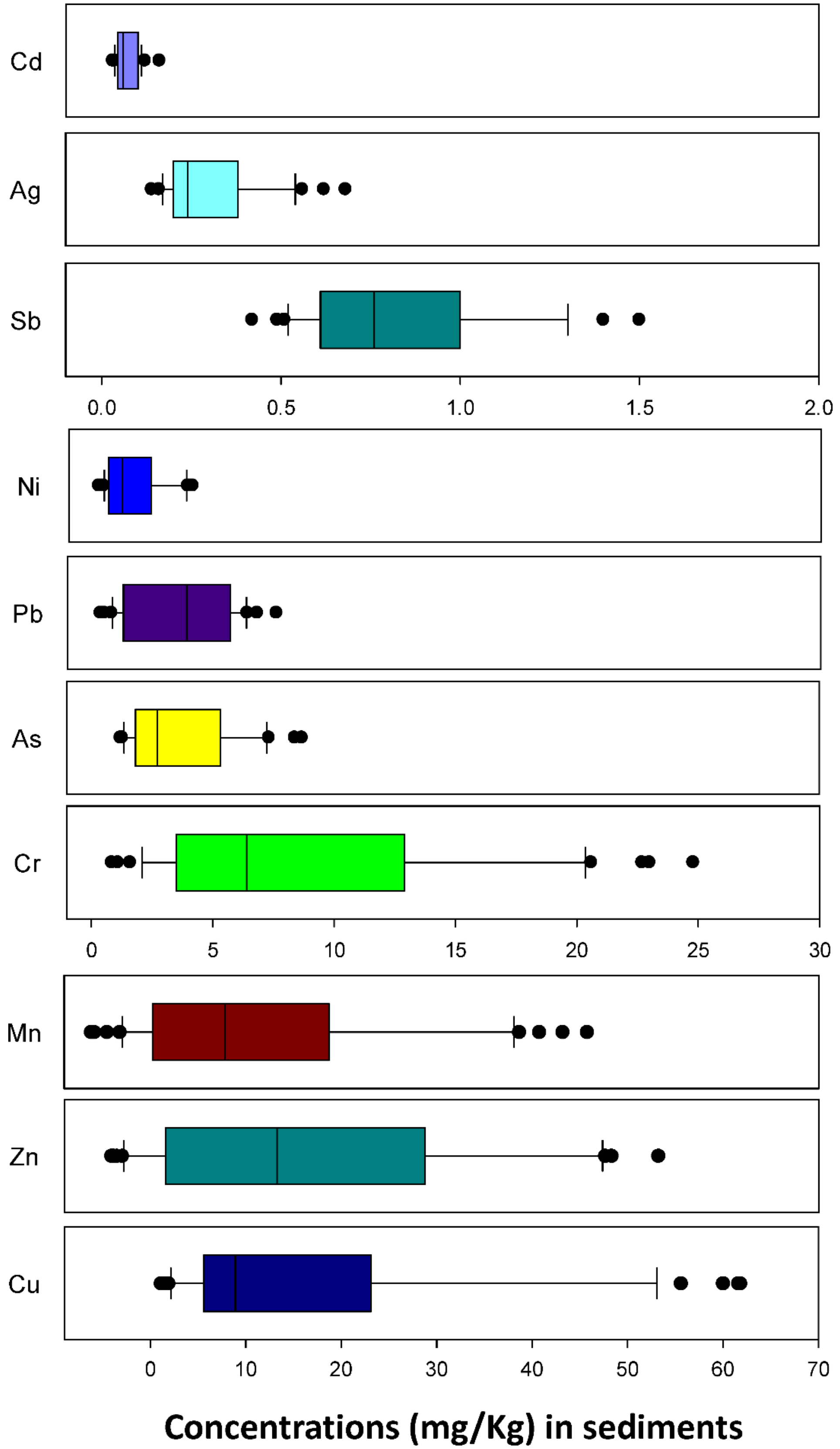

Figure 4 Overall Concentrations of Trace Elements from the 2014 survey.

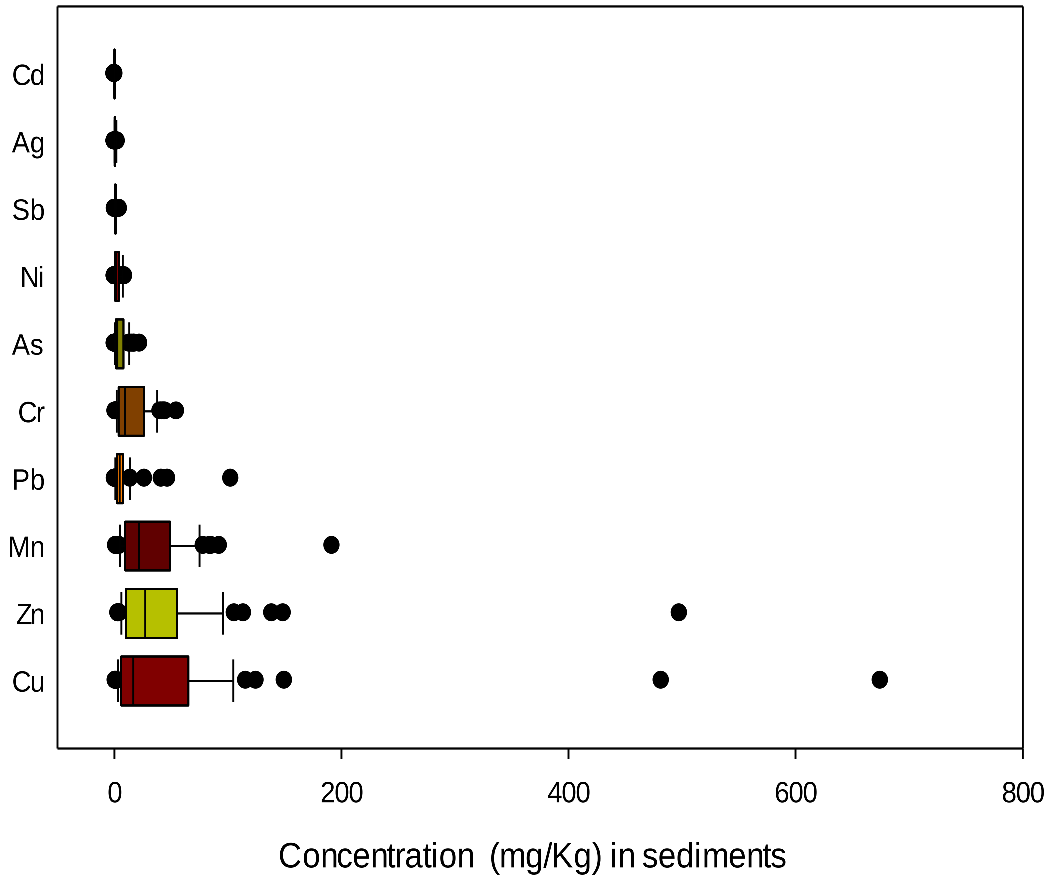

Figure 5 Sediment Trace Elements Distributions Showing Outliers

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 22.4 mg/Kg with an average of 5.03 and a median of 2.60 mg/Kg, respectively. Arsenic was above the MDL for 93% of the samples analyzed. The median arsenic concentrations in sediments reported by NOAA as part of their NS&T program is 6.9 mg/Kg while samples above 12 mg/Kg were considered to be elevated (85th percentile). Only 7 sites (12%) of the 2014 sediment survey ranked above the NOAA "high" classification. Although none of them ranked above the PEL/PEC criteria, the TEL/TEC criteria were exceeded by a total of 13 sites (23%). From this group, a total of 3 sites (CC070, CC074 and CC075) also exceeded the SQAGs in the 2007 survey when CC074 presented an arsenic concentration above PEL/PEC criteria. Sites CC070 and CC075 were also the second and third highest ranking arsenic detection during the 2014 survey. CC070 is adjacent to a golf course and CC075 is 2 miles downstream from a large asphalt mixing facility, although more data is required to allocate specific sources of this metal. Because of the repeated exceedance of SQAGs and the relatively high concentrations observed, these sites may be candidates to be included in follow-up monitoring studies in order to understand the trends of arsenic levels and their associated hazard at these sites.

The highest concentration of arsenic (22.7 mg/Kg) during the 2014 survey was observed at site CC036, over 4 times higher than the 5.5 mg/Kg reported by Long et al., 1994 to be toxic for Tampa Bay sediments. Twenty other stations (21 total, 37%) also ranked above that value, although they all are well below the probable effect level (PEL, 41.6 mg/kg). As will be discussed in following sections, site CC036 presented SQAGs exceedances of other metals such as copper, lead, zinc and PAHs. This particular site is located in the vicinity of a diversity of commercial/industrial activities such as a car wash, a funeral home with cremation services, a car salvage facility and a variety of car repair shops, and further studies may be required in order to understand if these activities are causing the aforementioned exceedances and/or enable proper remedial action.

Due to the high number of detections and exceedances of SQAGs and the number of sites with recurrent exceedances from the 2007 survey, arsenic may be considered a contaminant of concern in Collier County and further studies to monitor its occurrence and trends may be needed. The geographical distribution of arsenic in the County's sediments measured as part of this study is shown in Figure 56, where an evident spatial trend is not readily observed. Table 3 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 0.690 mg/Kg with an average of 0.136 and a median of 0.073 mg/Kg, respectively. The median cadmium concentrations in sediments reported by NOAA as part of their NS&T program is 0.19 mg/Kg while samples above 0.59 mg/Kg 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. Only 44% of the sampled sites presented cadmium above the analysis MDL values, thus interpretation of observed cadmium concentrations is complex due to the analytical uncertainties. Despite these difficulties these results are higher but in good agreement with the ones reported for the previous surveys and those 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 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 0.85 to 55.0 mg/Kg with an average of 15.3 and a median of 9.2 mg/Kg respectively.

The median chromium concentrations in sediments reported by NOAA as part of their NS&T program is 54 mg/Kg while samples above 120 mg/Kg were considered to be elevated (85th percentile). Only 2 sites (3.5%) exceeded the TEL/TEC SQAG for chromium and no exceedances of the PEL/PEC criteria were observed. Station CC112 in Venetian Bay contained chromium at levels slightly above the TEL and similar to the NS&T national median of 54 mg/Kg. Station CC109 (a closed pond near a commercial area south of Naples Municipal Airport) is the only freshwater site that ranked above the TEC for chromium (44.8 mg/Kg). 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. 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. 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 2014 study were well within these ranges. Concentrations of copper in the sediments ranged from <MDL to 675 mg/Kg with an average of 52.8 and a median of 16.8 mg/Kg respectively. The median copper concentrations in sediments reported by NOAA as part of their NS&T program is 14 mg/Kg while samples above 47 mg/Kg were considered to be elevated (85th percentile). Copper was detected in 100% of the samples, and was the element with more exceedances of the FDEP SQAGs and clearly a contaminant of potential concern, with a total of 4 samples (7%) ranking above the PEL/PEC criteria. From those, the highest concentration of copper (675 mg/Kg) was observed in site CC066, a coastal wetland located near large resorts and golf courses. The concentration of copper measured at this site was more than 6 times higher than the copper PEL of 108 mg/Kg, indicating possible harmful effects on organisms in this particular area and making this site a candidate to be included in following monitoring efforts. Another saltwater station (CC112) exceeded the PEL criteria with a concentration of 125 mg/Kg. CC112 is located on Venetian Bay in the vicinity of small docks/marinas from residential areas, and in front of a culvert that allows water interchange with Clam Bay to the north. The latter water body has been declared impaired on the basis of water concentrations of copper (FDEP, 2014).

The other two sites are CC114 and CC106, all surrounding large residential and golf course areas. However, CC114 (a closed pond inside a residential area) presented a much higher concentration (482 mg/Kg) than the other, corresponding to at least 3 times the corresponding PEC criteria and the second highest copper concentration observed in this study. Since nearby stations (CC105 and CC115) presented copper concentrations below the TEC/TEL guidelines, it is possible that the very high copper concentration observed at CC114 is the result of a localized introduction of copper as algaecide in that closed pond. Station CC106 is located at a Gordon River tributary, and presented a concentration of 150 mg/Kg which is slightly higher than the PEC criteria. This site is connected to a series of locations that presented similar concentrations above TEC/TEL but below PEC/PEL levels, all leading towards Naples Bay (Stations CC106 in the same tributary, CC004 and CC001 which are large marinas in the Gordon River and CC010 which is a small marina). It is important to note that both the Gordon River and Naples bay are also listed as impaired for copper (FDEP, 2014).

Another set of samples which exceeded the TEL/TEC criteria were collected from the Haldeman Creek (CC020 and CC021). CC021 is located where Haldeman Creek intersects US-41 and was identified in both the 2007 and 1989-1991 sediment surveys as exceeding the sediment quality criterion (Grabe, 1994), although copper concentrations at during this survey (60.0 mg/Kg) are much lower than the measurement in 2007 (208 mg/Kg). A nearby closed pond (site CC102) presented twice the copper concentration as CC021 (102 mg/Kg). Haldeman Creek is another water body that is listed as impaired for copper (FDEP, 2014).

The very high concentrations of copper observed in some closed ponds and nearby resort/golf club areas may indicate that the main introduction of Copper in this system is ornamental/algaecide usage, and the similar levels (exceeding TEL) observed throughout the Gordon River and its tributaries may indicate that these waterways may be acting as recipient and transport of copper from urban sources towards the Naples Bay. Therefore, patterns of copper contamination of the sediments suggest that areas under the influence of waters treated with copper for algaecide purposes require special attention with regard to future sampling. These results may indicate that antifouling coatings from marine vessels may represent a secondary source of copper and not the main one as suggested during the 2007 survey. However, since the ban of tin-based anti-fouling formulations, copper-based paints comprise the bulk of the bottom paint market in the US, thus the contributions of boats and marinas should not be ignored and continued to be monitored as this contribution to copper in sediments is unlikely to decline. Given the nature and number of recreational boats permanently docked along Collier County coastline this element is likely to continue to pose a risk in the near future.

As observed in Figure 26 and Table 3, the copper concentrations reported in this study are slightly higher than our in the previous survey from 2001-2002 and 2007, and also higher than those reported by Grabe, 1996 for limnetic sediments (<0.01 to 86 mg/Kg); those reported by Miller and Mcpherson 1998 for the Barron River (2 to 82 mg/Kg), and within the ranges reported for NOAA’s NS&T stations collected at Naples Bay (NBNB, 10-20 mg/Kg); Faka Union River (EVFU, 0-10 mg/Kg) and Henderson Creek (RBHC, 0-10 mg/Kg). Additionally, the normalized enrichment plot for Copper (Figure 20) shows that the heavily contaminated sites (CC066 and CC114) have a strong anthropogenic signature.

Given the current status, the multiplicity of sources and evidences of copper transport into water bodies already considered impaired on the basis of the concentration of copper, this element 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 57 and 58. Ranked concentrations are presented in Figure 7 and enrichment plots are shown in Figure 20. 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 103 mg/Kg with an average of 8.32 and a median of 4.70 mg/Kg respectively. The median lead concentrations in sediments reported by NOAA as part of their NS&T program is 18 mg/Kg while samples above 40 mg/Kg were considered to be elevated (85th percentile). Only three sites (CC043, CC090 and CC036 in order of concentration) exceeded the TEL/TEC SQAG. These three 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.

The highest Lead concentration was observed in station CC043, which is located in the vicinity of the Golden Gate WWTP. This site also exceeded the TEL/TEC criteria for other metals such as copper and arsenic. The normalized enrichment plot (Figure 23) shows a strong anthropogenic character of lead in th is particular site. The second highest lead concentration was observed in Station CC090, located in the vicinity of another wastewater treatment plant (Immokalee WWTP) and also presenting enrichment relative to natural lead abundance. However, the connection between WWTPs and lead in sediment is not evident from the available data. The third sample that exceeded the TEL/TEC criteria was CC036. As discussed before, this particular site is located in the vicinity of a diversity of commercial/industrial activities and presented exceedances of SQAGs for copper and arsenic along with zinc and PAHs as will be discussed later. As can be observed in Figure 29, the Cumulative Frequency Distributions (%CFD) from lead measurements during this survey are similar to the previous 2007 and 2001-2002 efforts. The geographical distribution of lead in the County's sediments measured as part of this study is shown in Figure 59. Ranked concentrations are presented in Figure 10 and enrichment plots are shown in Figure 23.

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. Anthropogenic sources of nickel include mining, electroplating combustion of fossil fuels and other industrial applications. Concentration of Nickel in the sediments sampled in 2014 ranged from 0.240 to 9.30 mg/Kg with an average of 2.76 and a median of 1.30 mg/Kg respectively. The median nickel concentrations in sediments reported by NOAA as part of their NS&T program is 17 mg/Kg while samples above 36 mg/Kg 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 and 2007 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. Ranked concentrations are presented in Figure 9 and enrichment plots are shown in Figure 22.

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-based, corrosion-preventer 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 3.40 to 498 mg/Kg with an average of 46.2 and a median of 27.2 mg/Kg respectively. The median zinc concentrations in sediments reported by NOAA as part of their NS&T program is 67 mg/Kg while samples above 130 mg/Kg were considered to be elevated (85th percentile). Only the CC036 site exceeded the PEC/PEL criteria for zinc during the 2014 survey. Furthermore, the measured concentration in site CC036 also exceeded the concentration reported by Long et al., 1994 as being toxic for Tampa Bay sediments (Table 3). According to the normalized enrichment plot for zinc (Figure 24), the measured concentration in CC036 is considerably enriched from natural abundance, again suggesting that this particular site is under the influence of anthropogenic activity. Therefore, site CC036 is a site of concern for zinc contamination according to the results of the 2014 survey, and since other exceedances of the SQAGs were observed for this site (PAHs, Copper, Lead and Arsenic) it should be considered for further monitoring and/or remedial actions.

Unlike the 2007 survey where seven sample locations (CC001, CC002, CC006, CC013, CC014, CC050, and CC074) rank above SQAGs, during the 2014 survey only three samples (CC036, CC112 and CC106) ranked above SQAGs reducing the number of sites of concern for Zinc contamination in Collier County. With the noted exception of CC036, zinc concentrations in the sediments are in accordance with the results reported in the 2001-2002 and 2007 surveys 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 low impact 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 and organic compounds such as CC036 need to be looked at in much more detail to understand the sources of zinc pollution and enable proper remedial actions. Ranked concentrations are presented in Figure 11 and enrichment plots are shown in Figure 24.

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 13-18.

Metal Contamination Index

The metal contamination index (MCI) (Castro, Fernandez, Gonzalez-Caccia, & Gardinali, 2013) computes the sum of all relative differences between the measured concentrations of elements and their TEL/TEC criteria (the “effect index”, Ei, for each metal), providing a single number to compare sites according to possible hazard to aquatic life. The index is computed as follows:

$$EI = \frac{C_j - SQAG_j}{SQAG_j}$$, j = for each trace metal, 1 to n

and $MCI = \sum_1^n EI$, for EI>0.

Results are observed in Figures 60-63. As expected, the sites with exceedances of the PEL/PEC criteria for metals (CC066, CC114 and CC112 for copper and CC036 zinc) also presented the highest MCI. With the exception of site CC036 and its high concentration of zinc, the MCI map shows a similar distribution to that of the copper concentrations (Figures 57-58).

Trace Metal: Enrichment

A second approach commonly used to evaluate 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 19 to 24 present the aluminum normalized plots for toxic elements. Copper, zinc, and lead showed significant enrichment in selected sites that also exceeded the SQAGs. Other elements like arsenic and chromium did not show anthropogenic enrichment at all despite SQAGs exceedances. Some elements like cadmium were not assessed for enrichment since most of the samples were at or below the MDL. The observed enrichment patterns along with the results presented in the previous sections clearly indicate that copper, zinc, and to a lesser extent lead are being produced by anthropogenic activities and 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). Copper (which exceeded the SQAGs in a larger number of sites) does not seem to correlate with any other element which is consistent with previously discussed observations that point to sources that do not introduce any other metal, such as copper applications as algaecide in selected ponds and waterways near golf courses and copper from antifouling formulations in marine vessels.

The second metal of concern due to its exceedance of PEL/PEC criteria in at least one site (CC036) is zinc. That element correlated well with arsenic, an element that had a large number of exceedances of TEL/TEC criteria including CC036. This indicates that arsenic and zinc may have common sources, most likely industrial activities around that site. The other toxic metal of concern that exceeded TEL/TEL criteria in selected sites was lead, and similarly to copper, this element does not seem to be related to any other element measured. These four elements of concern (As, Cu, Pb and Zn) do not correlate significantly with aluminum either likely due to their enrichment over natural sources.

Table 3 Distribution and comparison of trace element concentrations. All units are mg/kg (dry weight basis) with exception of Mercury (µg/Kg).

	Tampa Bay Sediments Long et al. (1994)		**Collier County**						Grabe (1996)	Miller & Mcpherson (1998)	NOAA's National Status and Trends Program, Sediment Data Cantillo at al. (1999)				
			2001-2002 (Estuaries)		2007 Survey (County wide)		**2014 Survey (County wide)****								
Element	Non-Toxic (mean)	Toxic (mean)	Mean	Max.	Mean	Max.	**Mean**	**Max.**	Limnetic sediments	Barron River Canal	NBNB*	RBHC*	EVFU*	NAT'L MEDIAN	85th Perc. "HIGH"
Arsenic	3.2±2.5	5.5±1.8	2.65±1.26	19.8	4.44	46.8	**5.03**	**22.7**	<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	**0.136**	**0.69**	<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	**15.3**	**55.0**	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	**52.8**	**675**	<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	**8.32**	**103**	<0.01-990	3-40	0-5	0-5	0-5	18	40
Mercury	137.8±150.3	234.3±126.3	52.70±37.30	164.7	157.7	164.7	**NR**	**NR**	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	**2.76**	**9.30**	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	**46.2**	**498**	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. **** This study.**

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. High correlations (coefficient >0.5, *p* value of <0.005) are shown with green rectangles and may indicate that elements may have one or more common sources.

	AL	SB	AS	CD	CR	CU	FE	PB	MN	NI	AG	SR	ZN
AL													
SB	0.21												
AS	0.24	0.58											
CD	0.44	0.39	0.43										
CR	0.78	0.28	0.53	0.35									
CU	-0.02	0.15	0.02	-0.02	0.01								
FE	0.20	0.47	0.79	0.32	0.39	-0.03							
PB	0.18	0.18	0.27	0.16	0.39	-0.01	0.23						
MN	0.35	0.44	0.49	0.39	0.28	-0.03	0.55	0.14					
NI	0.81	0.41	0.49	0.39	0.88	0.04	0.38	0.30	0.22				
AG	0.13	0.62	0.76	0.30	0.31	0.04	0.91	0.22	0.50	0.33			
SR	0.40	0.11	0.32	0.25	0.60	-0.03	0.32	0.08	0.13	0.51	0.25		
ZN	0.19	0.70	0.68	0.17	0.37	0.18	0.44	0.42	0.25	0.44	0.48	0.15	

Polycyclic Aromatic Hydrocarbons (PAHs)

The global occurrence of polycyclic 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 stormwater containing leachates from pavement coatings and 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 studies, 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 only the parent homologues were measured in the 2007 study. During the 2014 survey 2 alkylated PAHs were included in the measurements but failed to produce any concentration above Method Detection Limits, again evidencing the predominance of pyrogenic PAHs in Collier County sediments. Positive detections (>MDLs) have been summarized in Table 5, where it can be observed that in fact heavy PAHs caused the most detections in this survey.

In the present study, PAHs were positively detected in 18 sites (32%), and total PAHs in the sediments ranged from below detection to as high as 36,720 μg/kg. O'Connor, 1998, and Cantillo et al., 1999 reported a median total PAH concentration for the nation's coastal sediments as 380 μg/kg with concentrations above 2300 μg/kg being considered as high (>85th percentile). As can be observed in Table 5, only 4 sites (7%) ranked above the latter benchmark. However, three stations stand out with regard to the PAH concentrations (CC036, CC014 and CC064), ranking highest in Table 5. These three samples not only rank high on total PAHs but also exceeded SQAGs (CC036 exceeded the total PAH PEC criterion while CC114 and CC064 exceeded the Total PAH TEC criterion) and presented concentrations of individual PAHs that also exceeded their corresponding SQAGs. Site CC036 was singled-out before in this work as it presented exceedances of SQAGs for metals such as copper, zinc, lead and arsenic, probably caused by the many surrounding commercial/industrial sites in the area. CC036 was also the second highest ranking site during the 2007 survey with a total PAH concentration of 20,018 μg/kg, thus concentrations of PAHs at this site appear to have increased substantially (36,720 μg/kg in 2014). Furthermore, when compared with samples from Tampa Bay (Long et al., 1994, see Table 6) station CC036 clearly ranks above the levels considered capable of producing significant biological effects for the amphipod bioassay again adding evidence that this particular site may need a detailed, localized study to understand pollution sources influencing the area and their temporal/spatial trends in order to enable proper remediation efforts.

During the 2007 survey, CC018 (located at the northeast corner of the Naples Municipal Airport) ranked highest in total PAHs with 34,639 μg/kg. However the concentration measured at this site decreased to 2,270 μg/kg during the 2014 monitoring effort. This finding is interesting as CC018 was also identified during the 1989-1991 survey (GRE896) as exceeding both the ERM (Long and Morgan, 1990) and EPA criterion for Total PAHs for freshwater sediments. Therefore, the new results indicate that PAH contamination at CC018 may have decreased which would contrast with historical trends, although follow-up monitoring data is required to confirm the decreasing trend at this and other sites.

The southeastern corner of the airport (site CC014) also presents an important reduction in total PAH (17,358 vs 8,217 μg/kg), but the measured concentration still ranks CC014 as the second highest in 2014. The third ranking site (CC064, located nearby to a large construction area next to the Tamiami Trail) also shows lower concentrations during the 2014 survey (7,620 vs 3,928 μg/kg). Except for selected sites (most notably CC036), Table 5 shows that most sites present lower PAH concentrations during the 2014 survey, which may indicate an overall improvement of sediment quality in respect of PAH pollution.

Table 6 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 those previously reported levels. The geographical distribution of PAHs in Collier County for 2014 can be observed in Figures 63 and 64.

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 are presented in Figures 36 to 45. A summary of the results is as follows:

- Station CC036 ranked highest in total PAH concentration, exceeded the PEC and shows an 83% increase from 2007 levels.
- None of the estuarine stations exceeded the PEL criterion for total PAHs.
- Stations CC014, CC064 and CC036 exceeded the TEL/TEC criterion for total PAHs (3/57, 5%).
- CC014 and CC064 presented lower concentrations of total PAHs relative to the 2007 survey. Other sites also show a lower concentration of total PAHs during this study, relative to 2007. Particularly, site CC018 (the highest ranking in 2007) presented a total PAH concentration almost one order of magnitude lower during the present study.
- Site CC036 exceeded the PEC for phenanthrene and almost all HMW PAHs measured (except for dibenzo(a,h)anthracene where it exceeded the TEC but not the PEC). Of particular concern is the high concentration measured for chrysene, as it is over three times higher than the value considered as toxic for Tampa Bay Sediments according to the results by Long et at. (1994).

- Although lower levels of total PAHs were observed at stations CC014 and CC064 relative to the previous survey, these sites still exceeded the corresponding TEC criterion PAHs for all of the high molecular weight homologues measured.
- The MDLs for low molecular weight PAHs is too high to produce detections.

Based on these results, PAHs continue to contribute to sediment quality degradation along heavily urbanized areas of Collier County’s estuarine system, although their concentrations appear to be lower than the previous survey. A follow-up monitoring effort may be necessary to confirm this decreasing trend, preferably using methods with lower detection limits which would allow the inclusion of lower concentrations species such as LMW PAHs and could provide with a more accurate snapshot of PAH contamination.

Again, site CC036 is a site of concern due to the observed increase in total PAHs, the exceedances of SQAGs for total and individual PAHS, and the high concentration of highly toxic PAHs such as chrysene. The co-occurrence of PAHs and high concentrations of toxic metals in this site suggest that an extensive localized study for pollution monitoring and source apportionment may be necessary.

Table 5 Summary of positive detections (>MDL) of PAHs in Collier County during the 2014 Sediment Quality Survey, ranked according to total PAH concentration. (All concentrations in µg/Kg).

RANK	Site	AN	PHEN	Total LMW*	B(a)AN[c]	B(a)PY[c]	B(b)F[c]	B(g,h,i)P	B(k)F[c]	CHRY[c]	D(a,h)AN[c]	FL	I(123-cd)PY[c]	PY	B(a)PY Equiv.[c]	TOTAL HMW**	∑PAH 2014	*∑PAH 2007[a]*
1	**CC036**	250	1370	**1620**	**2200[b]**	**3490**	**5390[b]**	2530	2700	4320		6990	2320	5160	**4512[d]**	**35100**	**36720**	*20089*
2	**CC014**		291	**291**	492	633	1600	610		795	515	1400	831	1050	**1441[d]**	**7926**	**8217**	*17358*
3	**CC064**		93.4	**93.4**	214	344	565	477	222	415	229	506	427	436	**696[e]**	**3835**	**3928**	*7620*
4	**CC109**			**0**			**2480[b]**								**248[e]**	**2480**	**2480**	*NA*
5	**CC018**			**0**			2270								**227[e]**	**2270**	**2270**	*34639*
6	**CC113**			**0**			1780								**178[e]**	**1780**	**1780**	*NA*
7	**CC004**			**0**		75.7	705						746		**221[e]**	**1527**	**1527**	*0*
8	**CC082**			**0**	218	218		587				203		239	**240[e]**	**1465**	**1465**	*120*
9	**CC001**			**0**			659						735		**139[e]**	**1394**	**1394**	*0*
10	**CC016**			**0**		86.9	636						603		**211[e]**	**1326**	**1326**	*5421*
11	**CC111**			**0**		64.1	376		95.4			102	417		**144[e]**	**1055**	**1055**	*NA*
12	**CC079**		35.2	**35.2**	44.8	57.6	93.2	107	39.4	83.9	102	103	123	88.7	**186[e]**	**843**	**878**	*3885*
13	**CC052**			**0**		50.8	346		51.7	91.5		135		95.3	**86**	**770**	**770**	*4974*
14	**CC066**			**0**	61.9	34.6	303					88.6		72.7	**71**	**561**	**561**	*1037*
15	**CC020**			**0**			353								**35**	**353**	**353**	*140.1*
16	**CC043**			**0**		28.8	301								**59**	**330**	**330**	*54.6*
17	**CC101**			**0**		20.2	227								**43**	**247**	**247**	*NA*
18	**CC074**			**0**		31.3						91.9			**31**	**123**	**123**	*4997*

*Light Molecular Weight PAHs: Anthracene (AN); Phenanthrene (PHEN).

**Heavy molecular weight PAHs: Benzo(a)Anthracene (B(a)AN); Benzo(a)pyrene (B(a)PY); Benzo(b)fluoranthene (B(b)F); Benzo(g,h,i)perylene (B(g,h,i)P); Benzo(k)fluoranthene (B(k)F); Chrysene (CHRY); Benzo(a,h)anthracene (B(a,h)AN); Fluoranthene (FL); Indeno(1,2.3-cd)pyrene (I(123-cd)PY); Pyrene (PY).

[a] Observed PAH concentrations during the 2007 sediment survey (for comparison purposes).

[b] Exceeds Florida Administrative Code (FAC) 62-777 Soil Cleanup criteria based on leachability towards groundwaters (800 µg/Kg for B(a)AN; 2400 µg/Kg for B(b)F).

[c] Carcinogenic PAHs according to Florida Administrative Code (FAC) 62-777, added as equivalents of Benzo(a)pyrene according to the following equation:

B(a)PY$_{\mathbf{Equv}}$ = 1*[(B(a)PY)+(D(a,h)AN)] + 0.1*[(B(a)AN)+(B(b)F)+(I(123-cd)PY)] + 0.01* (B(k)F) + 0.001* (CHRY).

-[d]Exceeds Florida Administrative Code (FAC) 62-777 Soil Cleanup criteria based on direct exposure for commercial/industrial sites (700 µg/Kg B(a)PY Equivalents).

-[e]Exceeds Florida Administrative Code (FAC) 62-777 Soil Cleanup criteria based on direct exposure for residential sites (100 µg/Kg B(a)PY Equivalents).

Table 6 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 2001-2002	Collier County Sediments 2007	Collier County Sediments 2014
	Not Toxic (μg/kg)	Significantly toxic (μg/kg)	Range (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	ND
Acenapthylene§	40±1	226±212	NR	3-50	ND-11	ND	ND
Acenaphthene§	60±68	185±230	NR	20-50	ND-14	ND-218	ND
Fluorene§	60±48	273±237	NR	4-29	ND-15	ND-67	ND
Phenanthrene§	295±501	1429±1532	NR	3-130	1-195	ND-1970	ND-1370
Anthracene§	110±154	336±369	NR	5-80	ND-44	ND-320	ND-250
Fluoranthene	1076±1718	3713±3575	<50-4400	20-460	ND-538	ND-5610	ND-6990
Pyrene	1253±1848	3931±3413	<50-5200	30-390	ND-398	ND-5310	ND-5160
Benz(a)anthracene	317±491	1239±1229	<50-13000	3-60	ND-228	ND-2780	ND-2200
Chrysene	589±924	1688±1359	80-3800	10-260	ND-238	NA	ND-4320
Benzo(b,k)fluoranthene	1242±1839	2958±2286	NR	NR	ND-912	ND-6660	ND-8090
Benzo(e)pyrene	469±643	1094±820	NR	NR	ND-294	NA	NA
Benzo(a)pyrene	573±843	1132±968	NR	20-200	ND-282	ND-2980	ND-3490
Perylene	274±350	285±268	NR	NR	ND-105	NA	NA
Indeno(1,2,3,-cd)pyrene	426±566	1139±951	NR	NR	ND-476	ND-2350	ND-2320
Benzo(g,h,i)perylene	450±591	1219±993	NR	NR	ND-318	ND-2370	ND-2530
Dibenzo(a,h)anthracene	182±147	259±217	NR	10-50	ND-104	ND-505	ND-515
Σ LMW PAHs	604±766	2556±2625	NR	NR	2-280	ND-2414	ND-1620
Σ HMW PAHs	6852±9662	18677±15933	NR	NR	1-3423	ND-32225	ND-35100
Total PAHs	7456±10354	21233±18504	Up to 19400	NR	6-4461	ND-34639	ND-36720

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 pesticides are their elevated potential for bioaccumulation (octanol-water partition coefficients (K_{ow}) 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 are 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 on 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 pesticides, they tend to degrade quickly and therefore do not 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 the occurrence of pesticides 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 8.8% of the samples tested positive for pesticides and none of them had detections above the laboratory reporting level.

- One single detection of Endosulfan II (0.26 ng/g dry weight) was observed at site CC115 (adjacent to a golf course).

- Legacy pesticides were also detected: Dieldrin was detected at sites CC057 (2.6 ng/g) and CC090 (0.120 ng/g), which are adjacent to major agricultural areas; and finally 4,4'-DDE was detected also at CC090 (1.50 ng/g) and at CC035 (1.90 ng/g) and CC109 (1.30 ng/g). CC035 is also adjacent to agricultural fields and CC109 is a closed pond near Tamiami Trail.

- The observed concentrations of Endosulfan and legacy pesticides 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 similar to the ones found in the 1989-1991, the 2001-2002, and the 2007 surveys which reported no potential concern associated with similar concentrations since none of those values exceeded the available SQAGs. However, the concentration of Dieldrin at site CC057 does exceed the TEL/TEC criteria SQAG and is higher than the only detection in 2007 (1.69 ng/g) which was at a different site (CC035). Since the pesticide is banned it is safe to assume that the likelihood of detecting increasingly higher concentrations upon future monitoring efforts is low. However, the detection of a very toxic legacy pesticide above SQAGs guidelines may prompt for a detailed analysis of sediments in this area and warrants the continued inclusion of Dieldrin in future sediment quality monitoring efforts.

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 in Collier County is overall 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.

General Distribution of Nutrients

A large portion of the United States coastal waterways have been moderately degraded by excessive introduction of nutrients (carbon, nitrogen and phosphorous) from human activities (Howarth, Sharpley, & Walker, 2002). In general, the unbalancing of nutrient concentrations in the environment by human activities is accompanied by the risk of eutrophication (uncontrolled increases of biomass which is decomposed in aerobic processes, leading to oxygen depletion, toxicity and aquatic life mortality) (Pinckney, Paerl, Tester, & Richardson, 2001) which, according to recent national assessments, is a widespread and increasing problem in coastal resources of the United States (Scavia & Bricker, 2006). In estuarine areas, excessive accumulation of organic matter in sediments (from depositions of particulate organic matter consisting of bacteria, phytoplankton, zooplankton, fecal matter and decaying plant material) can trigger high rates of aerobic microbial activity leading to hypoxic or anoxic conditions at the sediment-water interface. These changes may cause severe stress or death of benthic organisms, increased water column acidity and alteration of natural biogeochemical cycles (Sutula, Green, Cicchetti, Detenbeck, & Fong, 2014; Sutula, 2011). Therefore, nutrient enrichment of coastal areas may have consequences such as fish decline, degradation of seagrass beds and smothering of bivalves and other benthic organisms (Bricker, Ferreira, & Simas, 2003).

In general, nitrogen is considered the limiting nutrient in estuarine systems while phosphorus limits microbial activity in freshwater habitats (Sutula, 2011). The adoption of phosphorus-removal technologies in WWTPs and the ban on phosphate-based detergents in Florida during the 1980’s effectively made nonpoint sources of phosphorus such as fertilizer-containing runoff from agricultural activities, atmospheric depositions and natural occurrence from phosphate rock deposits the most likely sources of this element in Florida waters (Litke, 1999).

The following nutrient parameters were measured during the 2014 survey: total organic carbon (TOC), total Kjeldahl (organic) nitrogen (TKN), total phosphorus and total nitrate and nitrite (NOx). Results are presented as ranked plots (Figures 48-51). Since there are no SQAGs for nutrients in sediments, the ratios of carbon and nitrogen with phosphorus (C:P and N:P ratios, Figures 52-55) were used to help the interpretation of observed nutrient concentrations. Those were compared with predicted stoichiometric relationships in primary producers reported in the literature (Sutula, 2011).

Nitrite and nitrate were not expected to occur at high concentrations in sediments due to their elevated water solubility and lack of affinity for suspended particulate matter. Accordingly, they were detected (>MDL) in only 36% of the sites. However, as seen in Figure 51, two samples (CC109 and CC110) stand out from the rest due to their elevated NOx values which represent 10% and 4% (respectively) of the total nitrogen quantified in both sites. These are two samples from the same pond located inside a large commercial/industrial area called the Gateway Triangle. High amounts of NOx are usually associated with high accumulation of organic matter that is being converted to NOx by bacterial activity or, alternatively, localized introduction of nitrate containing products (such as nitrate-based fertilizers). High concentrations of NOx can be toxic to aquatic wildlife (especially to fish and larvae) (Camargo, Alonso, & Salamanca, 2005) and therefore NOx values in sediments and waters from this location should be monitored in future efforts in order to establish a temporal trend, the extent of the threat and possible mitigation actions.

As can be observed in Figure 48, site CC036 presented the highest amount of TOC. This site was flagged before as exceeding the PEC criterion for total PAH, and as can be observed in Figure 54, the N:P ratio was similar to that of primary producers but the C:P ratio was much higher than expected. Two other sites (CC079 and CC115) presented the same behavior (a high C:P ratio relative to the rest of the dataset but N:P ratios corresponding to those of macro and microalgae) from which CC079 exceeded the TEC criterion for one PAH (dibenzo(a,h)anthracene). Since the N:P ratios are similar to the stoichiometric ratios of primary producers, the high C:P ratios at these sites are probably the product of accumulation of anthropogenic organic matter (i.e., road dust, lubricant runoff, PAHs from internal combustion engines, etc.) rather than a phosphorus depletion. In contrast, Figure 54 also shows that estuarine and saltwater sites are mostly dominated by depositions of organic matter from primary producers.

As said before, nitrogen is considered the limiting nutrient in estuarine systems. Figure 49 shows that sites CC112 and CC113 (both located at Venetian Bay) and CC117 (a residential marina in the Vanderbilt Beach area) presented the highest amounts of total nitrogen in saltwater/estuarine conditions. Since these sites also scored high in the total phosphorus rank (3rd, 7th and 5th, respectively), the high nutrient availability could indicate a higher risk of eutrophication at these estuarine sites than in the rest of the County watersheds.

Regarding freshwater sites (where phosphorus is considered limiting), the highest amounts of total phosphorus were observed at sites CC043, CC031, CC108 and CC103. These sites also presented with low N:P and C:P ratios (compared with stoichiometric signatures of primary producers) which indicates enrichment with inorganic phosphorus. These sites may have a higher risk of eutrophication than the rest of the freshwater sites. Relevant data for nutrients monitored in this study are summarized as follows:

- Total nitrate/nitrite (NOx) values were low in almost all sites except for CC109 and CC110, where the NOx accounted for 10% and 4% of the total nitrogen concentration, respectively. These two samples were sediments from the same waterbody. This location may have an unusual accumulation of organic matter or inputs of nitrate from anthropogenic activities.

- Site CC036 presented the highest amount of total organic carbon and its enrichment vs. nitrogen and phosphorus suggest that the organic matter accumulated at that site has a strong anthropogenic character.

- Estuarine and seawater sites present stoichiometric relationships between C, N and P that suggest the accumulation of organic matter from primary producers.

- According to the concentration of total nitrogen and total phosphorus, saltwater sites CC112, CC113 and CC117 present the highest risk of eutrophication in the saltwater/estuarine systems.

- Data suggests that sites CC043, CC031, CC108 and CC103 are enriched with phosphorus and could be at risk from elevated primary productivity and eutrophication.

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 follows:

- High concentrations of several inorganic and organic pollutants are still observed in Collier County’s watersheds, especially in the urban areas. Continued, long term monitoring is needed to evaluate the impacts of sustained development, road construction and modification of water deliveries;
- Trace metals such as copper, zinc, lead, and arsenic along with PAHs 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;
- Although data suggest that total PAHs levels have overall decreased in the sites that were repeated in the present survey, high molecular weight PAHs are still exceeding SQAGs at three particular stations (CC014, CC064 and CC036);
- Contrary to the general trend observed, one of these stations (CC036) presented a 83% increase from 2007 levels of Total PAHs, with exceedances to all available SQAGs for high molecular weight PAHs. In particular, chrysene levels at CC036 were very high relative to reported measured toxic levels in the literature;
- Although only 3/57 sites exceeded available SQAGs for zinc, levels at CC036 exceeded the PEL/PEC criteria and available toxic sediment reference levels. This site also exceeded SQAGs for copper, arsenic and lead;

- The co-occurrence of elevated concentrations of both PAHs and trace elements at station CC036 and the exceedances of both the available Sediment Quality Assesment Guidelines and Toxic Sediment reference values (from Tampa Bay) indicates that this particular site is under the influence of mixed pollutant inputs that needs to be identified and addressed by a more extensive localized survey;
- The frequency of arsenic detections and exceedances of SQAGs, along with its co-occurrence with other contaminants suggest that this trace metal continues to be a contaminant of concern that has a ubiquitous character in Collier County. A total of 16 sites (28%) exceeded the TEL/TEC criteria, and 21 sites (37%) ranked above toxic sediment levels according to available literature;
- Copper is a contaminant of potential concern in areas around the Gordon River and its tributaries, Naples Bay, Venetian Bay, Haldeman Creek and the Clam Bay watershed. Very high concentrations of Copper were observed in site CC066, in the Clam Bay watershed, with almost 6 times the available probable effect limit (PEL). Another site with very high concentrations of copper was a stormwater pond surrounded by residential areas. The copper distribution pattern may suggest that beautification (i.e., algaecide) activities have become the main source of Copper in sediments of the Collier County, contrasting with the 2007 survey data which suggested that antifouling coatings from marine vessels were the main route for copper introduction;
- Of all pesticides analyzed, three organochlorated pesticides (Endosulfan II, Dieldrin and 44,-DDE) were detected in very small quantities (below reporting limits). The risk associated with watershed-wide contamination pesticides in Collier

County is therefore very low and levels of contamination are well under any of the sediment quality criteria guidelines, with the sole exception of site CC057 in which the measured Dieldrin concentration exceeded the TEL/TEC criteria for this legacy pesticide.

- Although nutrient analysis data from sediments alone are not conclusive to indicate eutrophication risks, selected sites may be at higher risk of eutrophication (specifically, saltwater/estuarine sites CC112, CC113 and CC117 and freshwater sites CC043, CC031, CC108 and CC103).

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 in previous monitoring efforts are still valid after this study. Based on the results of this survey and findings of previous monitoring efforts the following recommendations are provided:

- Data suggests that contamination by polycyclic aromatic hydrocarbons (PAHs) has decreased from 2007 levels, but still is the primary concern along Collier County watersheds and should still be the focal point of future monitoring programs.
- Copper and to a lesser extent arsenic, zinc and lead are the highest ranking trace elements in the sediment hazard assessment based on the SQAGs. Since elevated copper is evidently related to algaecide applications, management

methods regarding the application, alternatives to the use of or preventing the need for using copper would be solutions for preventing further contamination.

- In the case of arsenic and zinc, additional monitoring is required to understand their sources and fate.
- 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, commercial areas, golf courses, stormwater 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.
- A comprehensive list of analytes to account for past and present use contaminant should be kept and updated before the follow-up monitoring effort:
    - a) Polycyclic aromatic Hydrocarbons,
    - b) Trace Metals,
    - d) Chlorinated pesticides
    - e) Nutrients
    - 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, zinc, arsenic and lead.

- Adopt “planning guidelines” to trigger action for contaminants that do not have a promulgated SQAGs.
- Maintain a continued monitoring effort within north Naples Bay and the lower Gordon River in order to assess future temporal changes of contaminant depositions, especially copper and PAHs.

Site Specific Recommendations

- Site CC036 continues to be a “hotspot” in terms of environmental pollution. Source identification and site specific evaluation efforts are required to evaluate the spatial and temporal extent of the contamination at site CC036 with toxic metals and PAHs and how it is affecting Collier County residents.
- 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 and metal contamination is above SQAGs.
- The presence of sustained contamination by multiple metals along stations at Gordon River (CC001, CC004 and CC106) and Haldeman Creek (CC020 and CC021) 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 CC114 and CC066 which presented very high localized high concentrations of copper.

- Perform periodic monitoring of water and sediment nutrient content at sites with high risk of eutrophication (saltwater sites CC112, CC113 and CC117 and freshwater sites CC043, CC031, CC108 and CC103). The evaluation of other eutrophication parameters (water chemistry, vegetation abundance, etc.) at these sites should also be performed and compared with sediment chemistry results.

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APPENDIX I Additional Figures

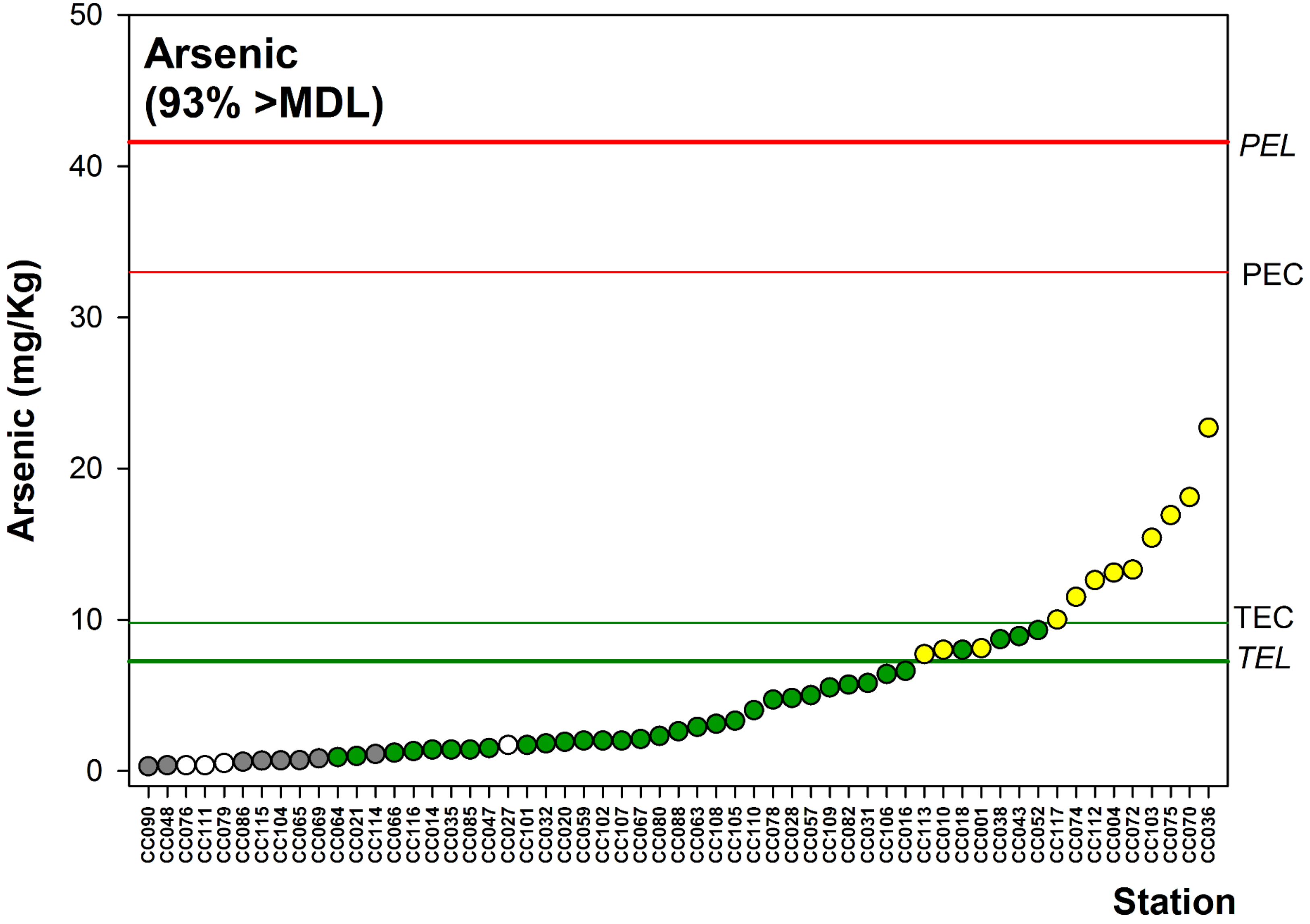

Figure 6 Ranked Distribution of Arsenic in Sediments for the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

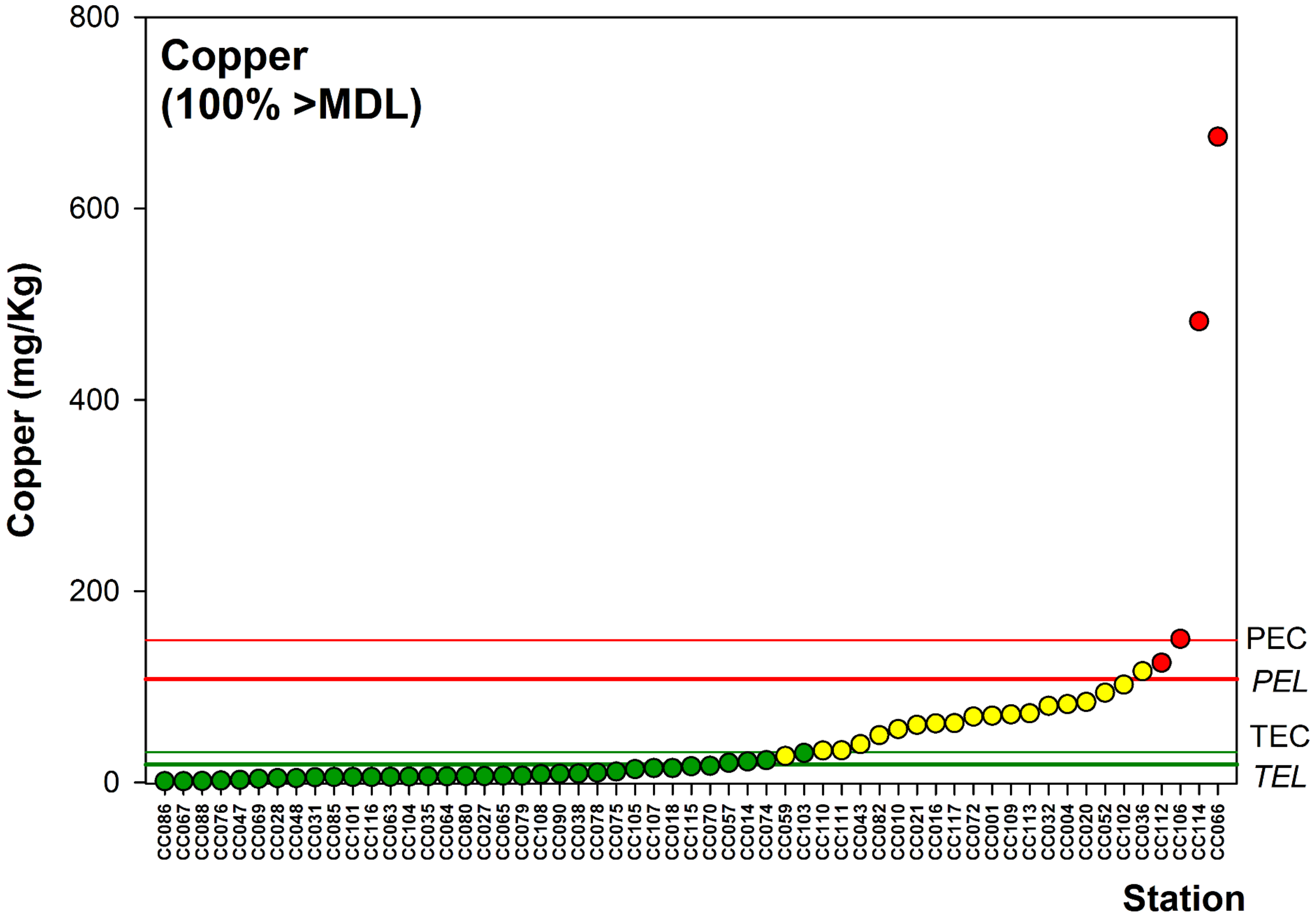

Figure 7 Ranked Distribution of Copper in Sediments for the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

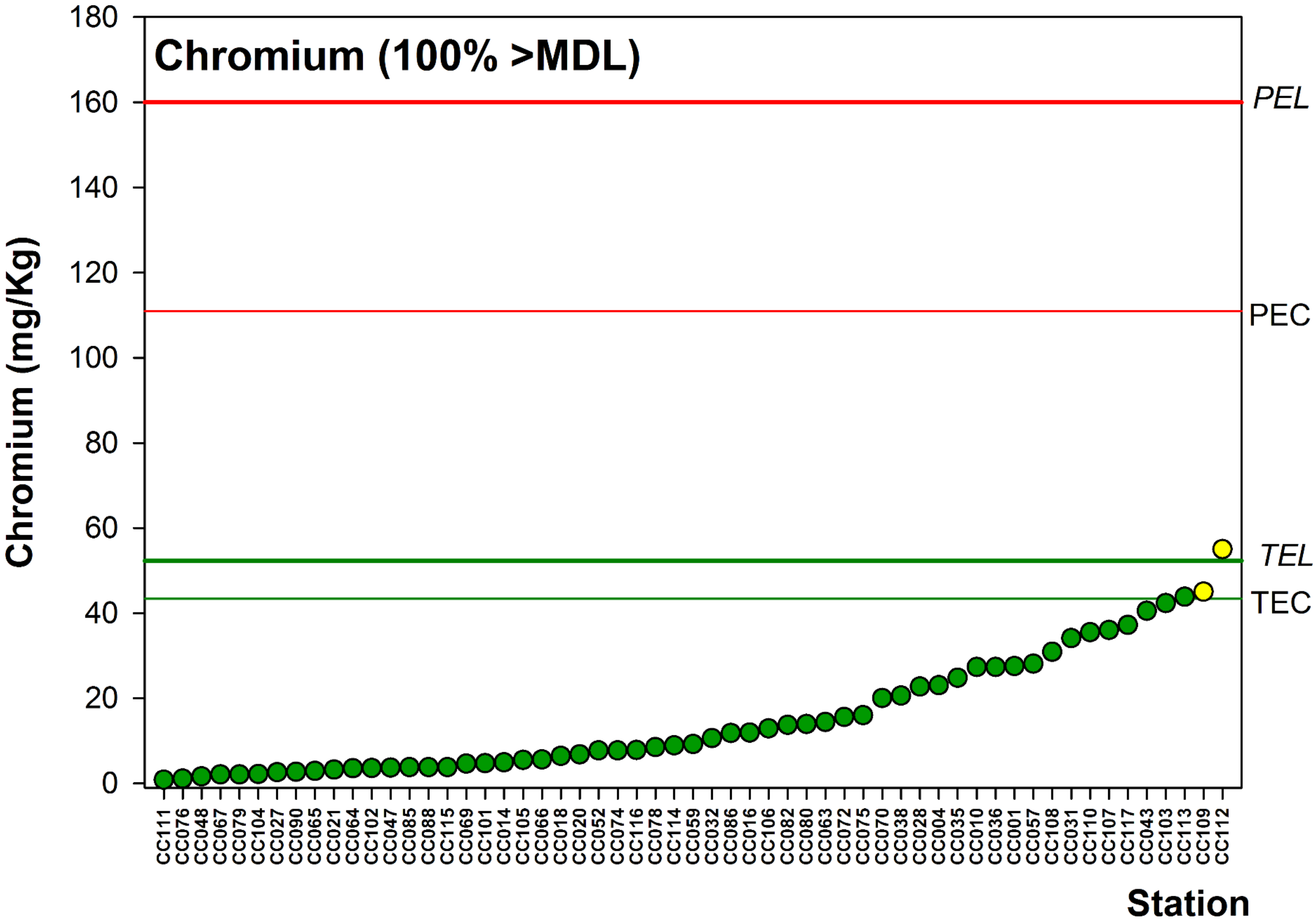

Figure 8 Ranked Distribution of Chromium in Sediments for the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

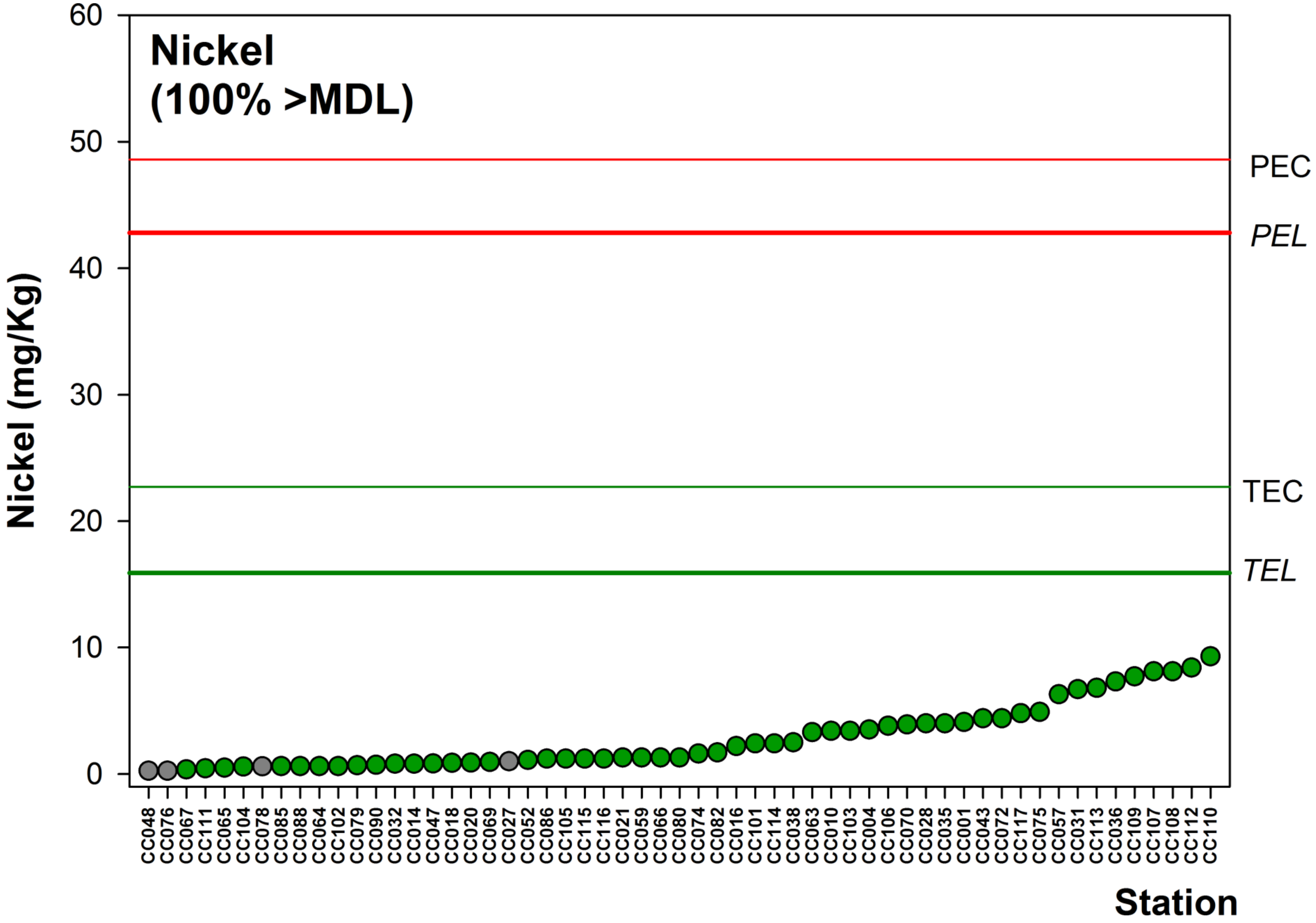

Figure 9 Ranked Distribution of Nickel in Sediments for the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

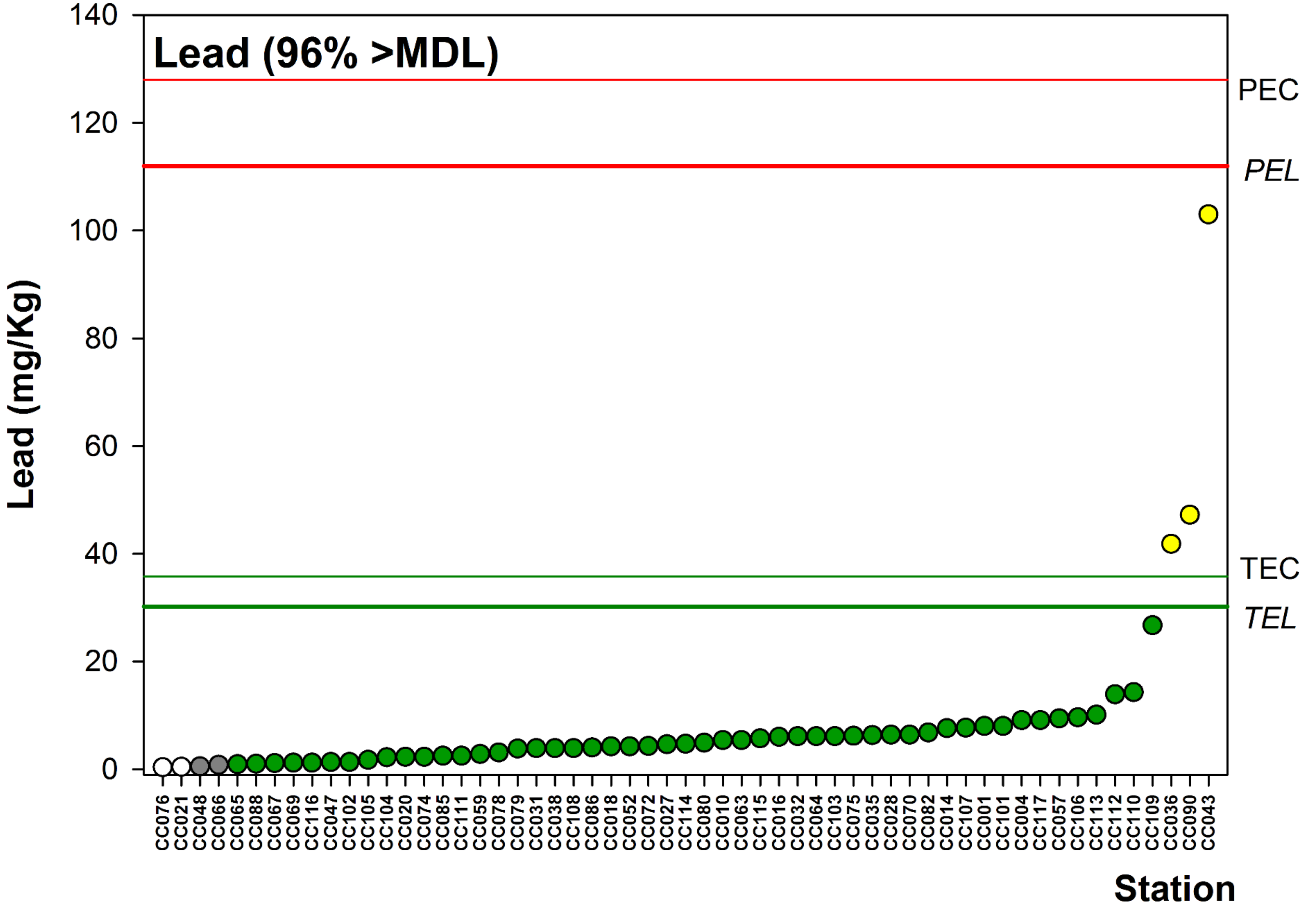

Figure 10 Ranked Distribution of Lead in Sediments for the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

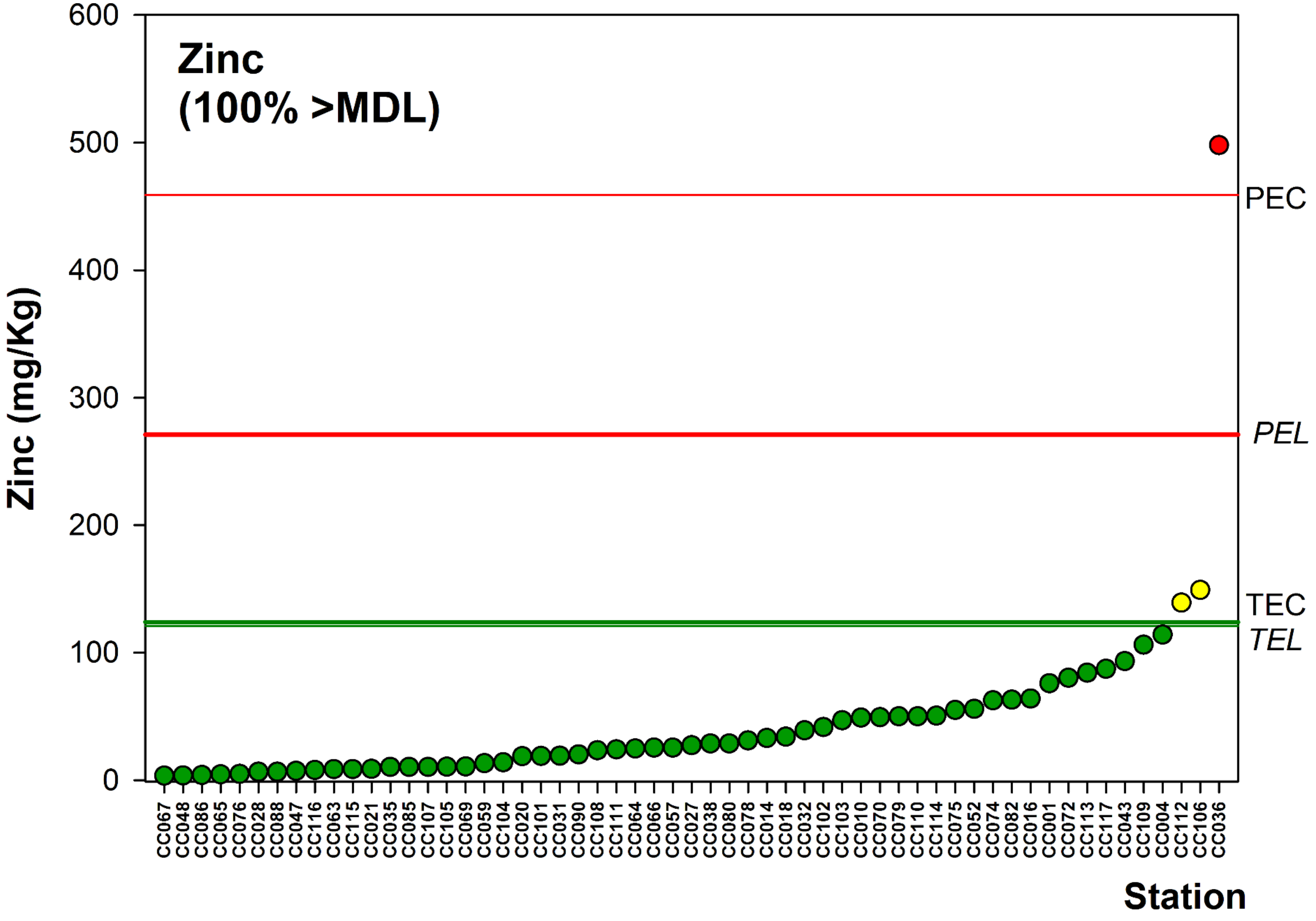

Figure 11 Ranked Distribution of Zinc in Sediments for the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

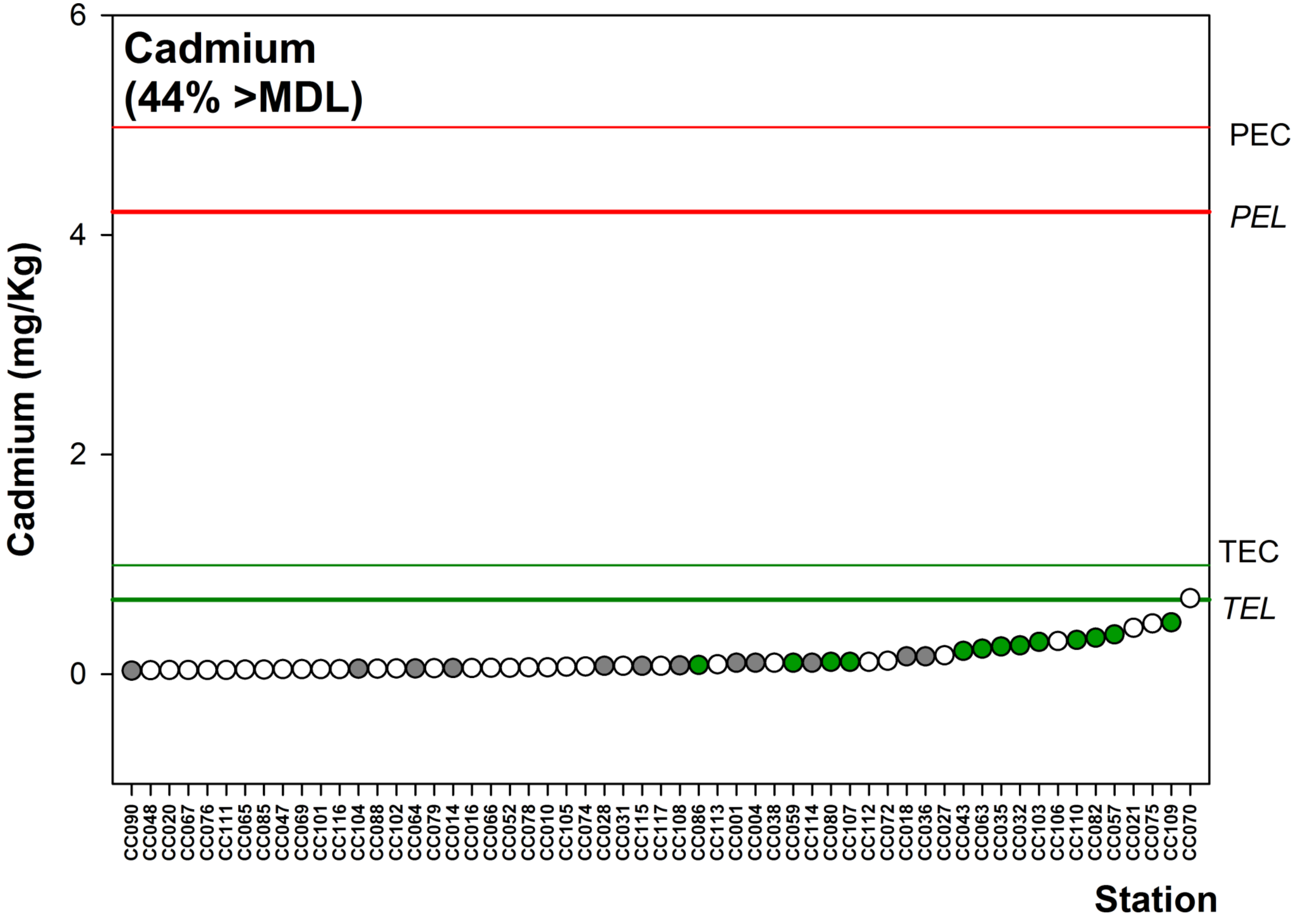

Figure 12 Ranked Distribution of Cadmium in Sediments for the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

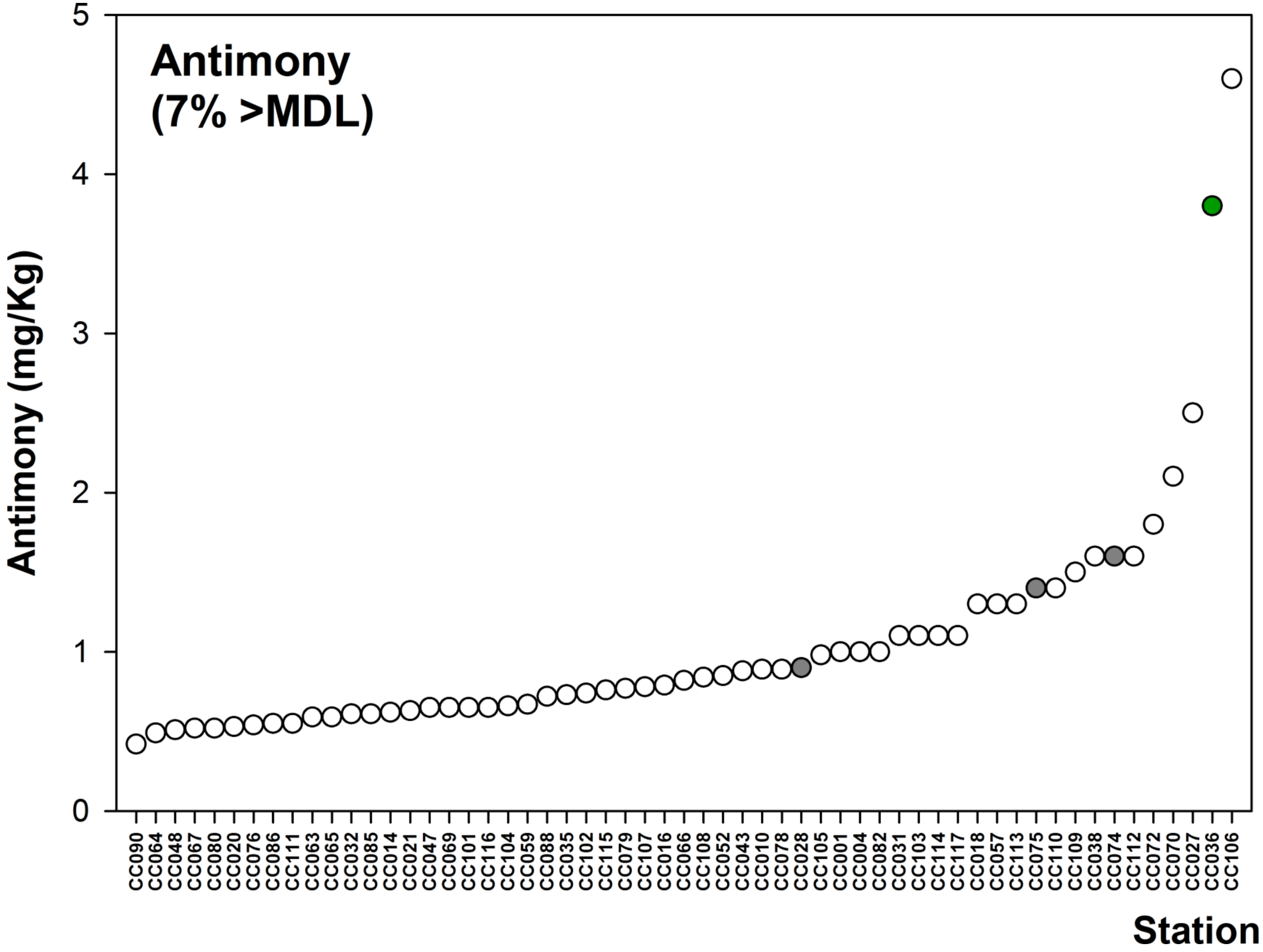

Figure 13 Ranked Distribution of Antimony in Sediments for the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL).

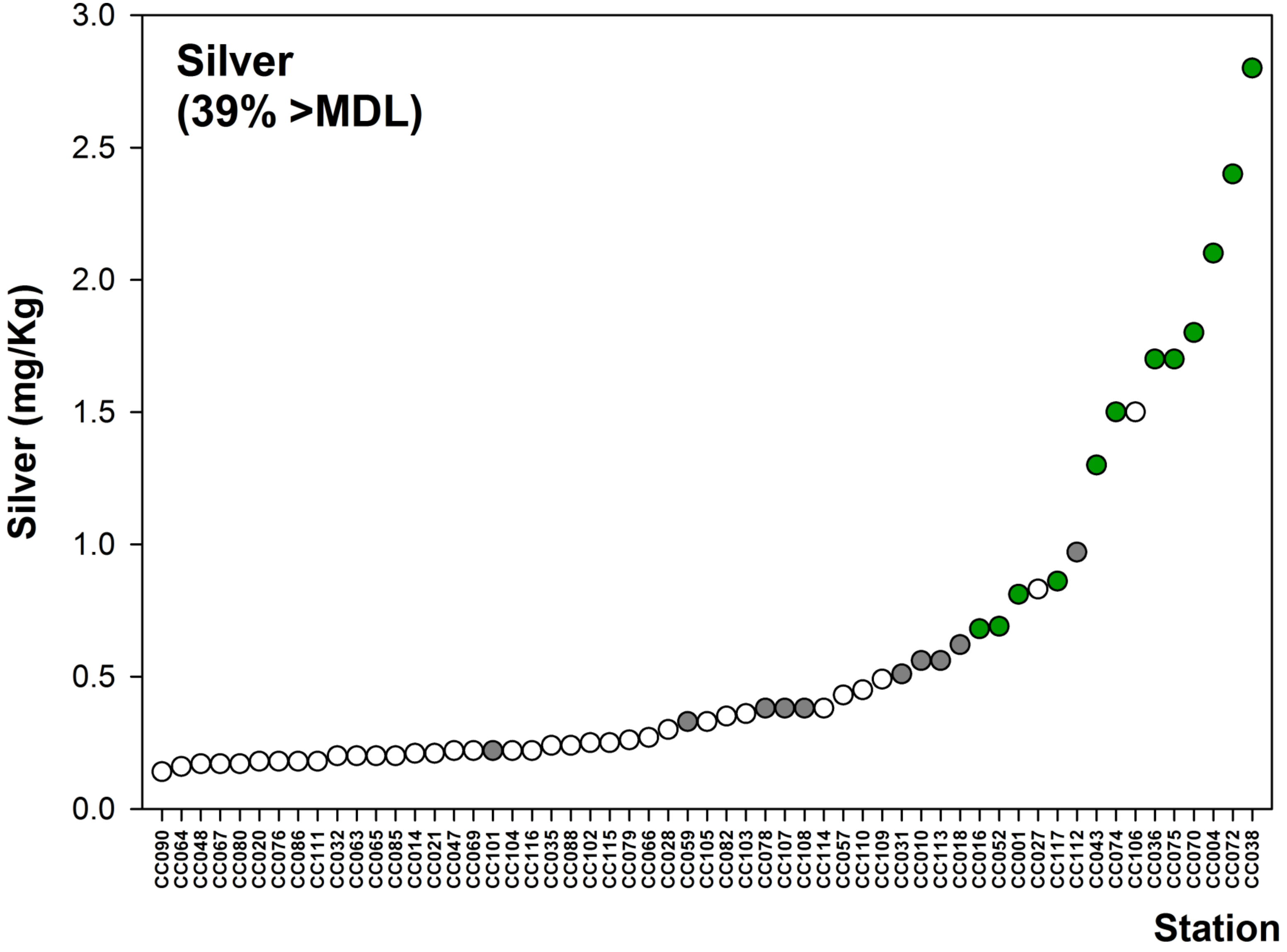

Figure 14 Ranked Distribution of Silver in Sediments for the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL).

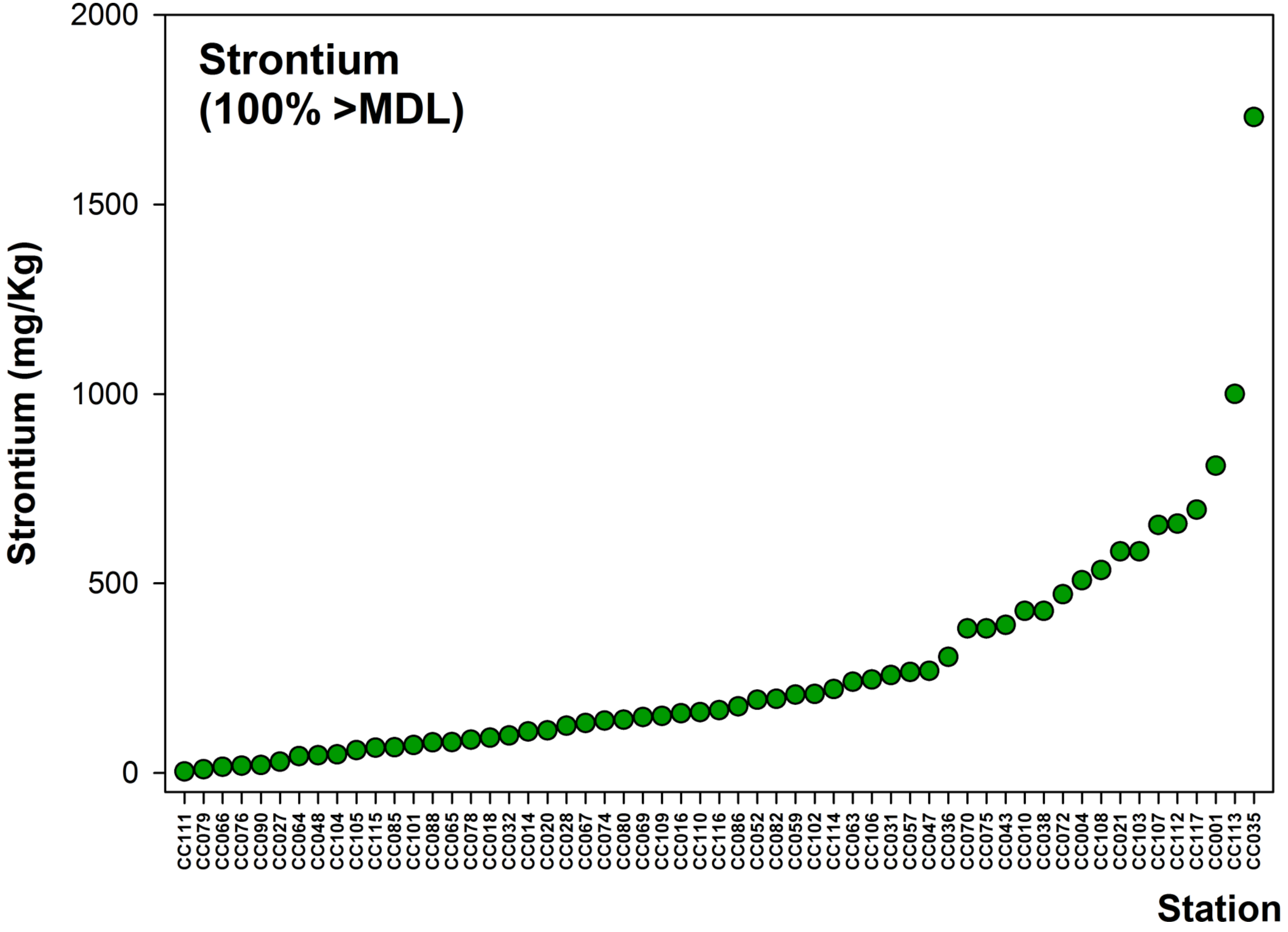

Figure 15 Ranked Distribution of Strontium in Sediments for the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL).

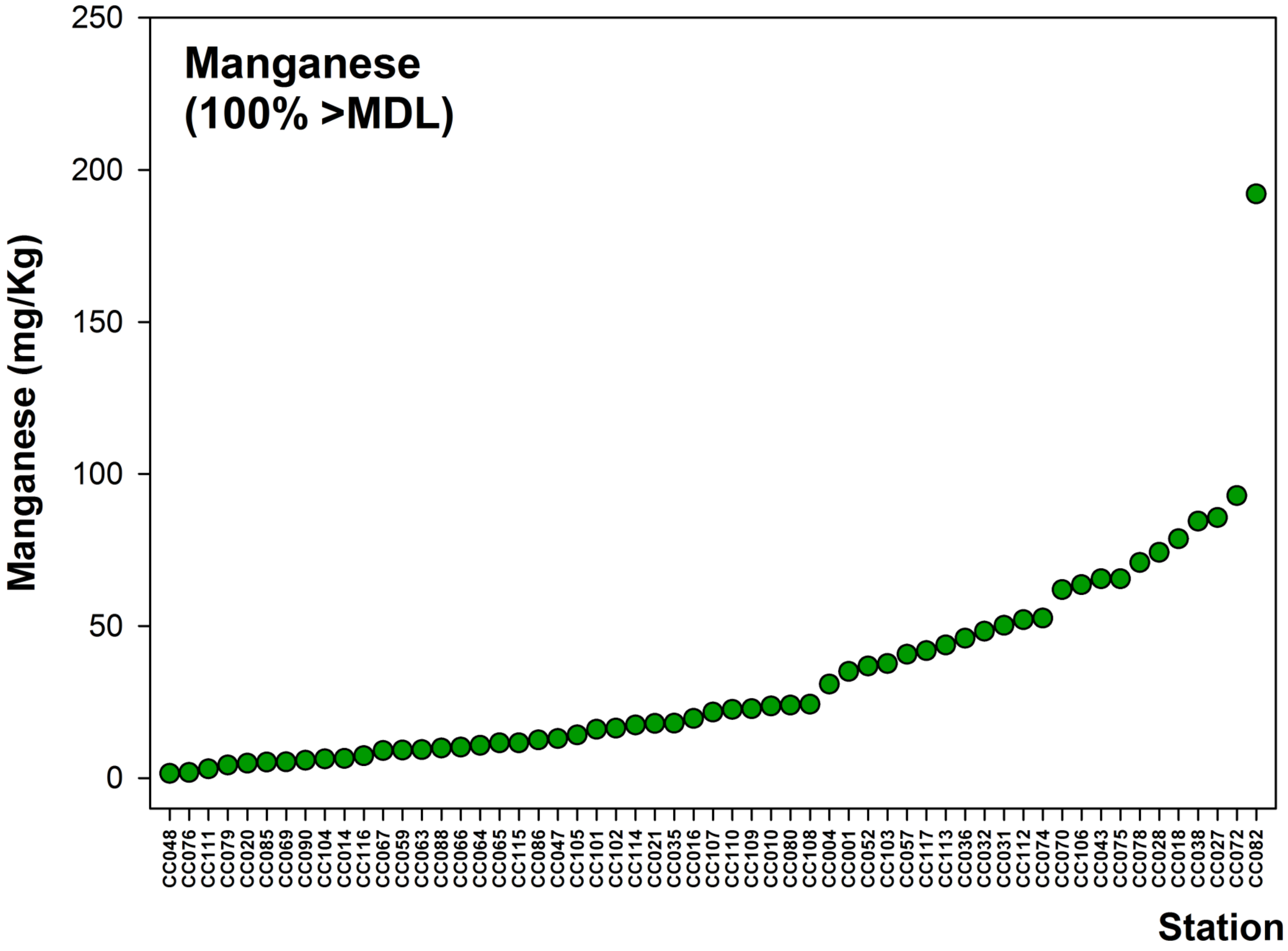

Figure 16 Ranked Distribution of Manganese in Sediments for the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL).

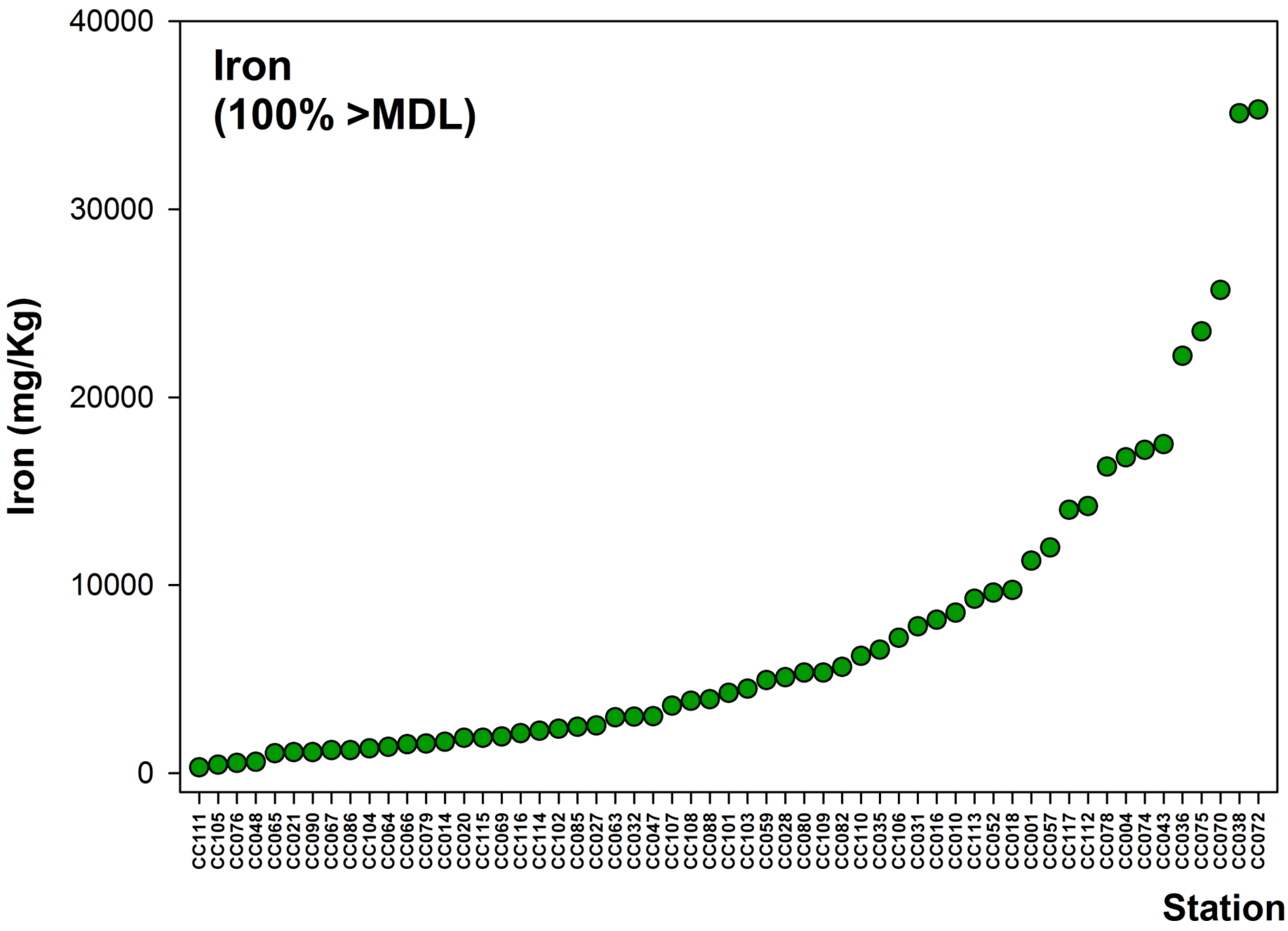

Figure 17 Ranked Distribution of Iron in Sediments for the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL).

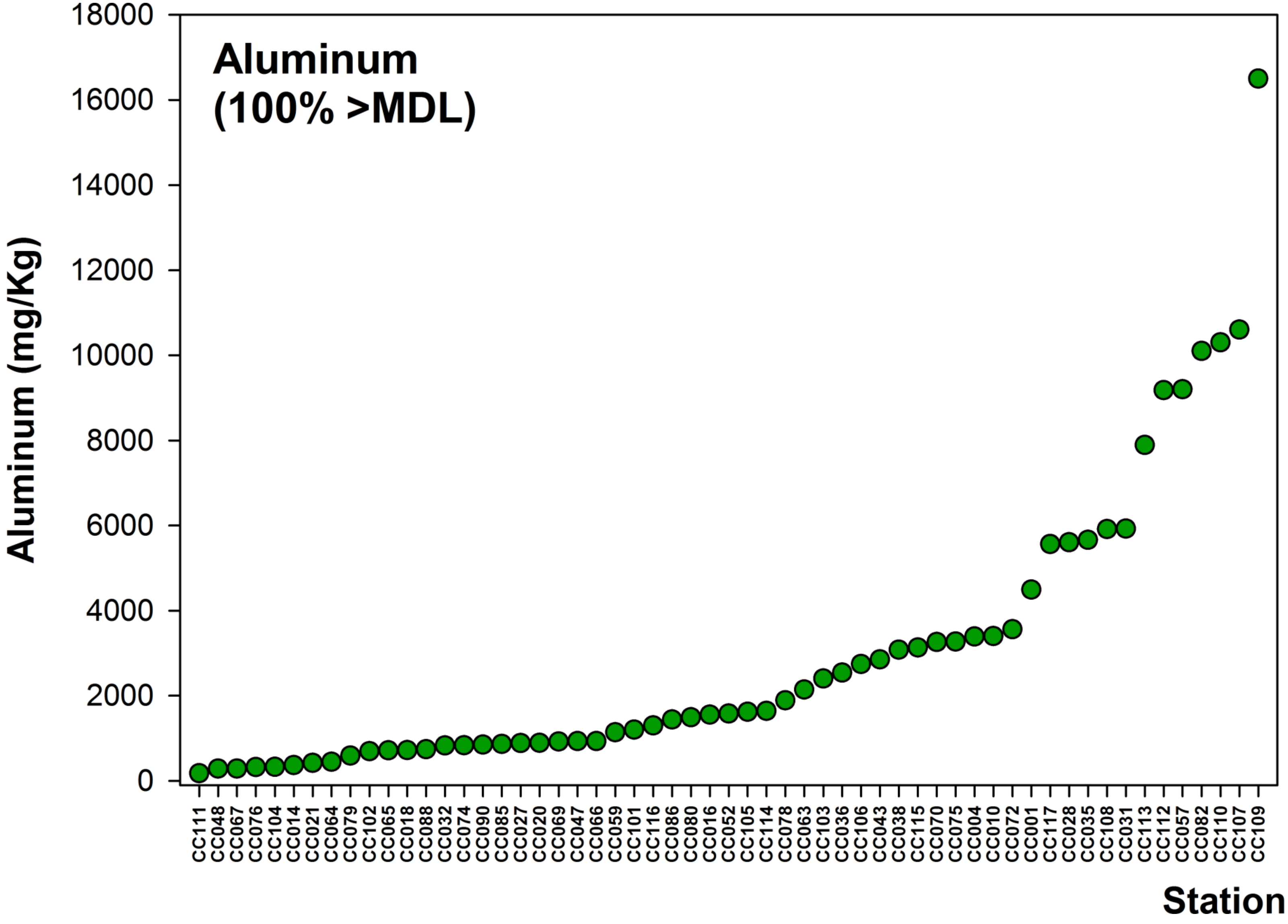

Figure 18 Ranked Distribution of Aluminum in Sediments for the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL).

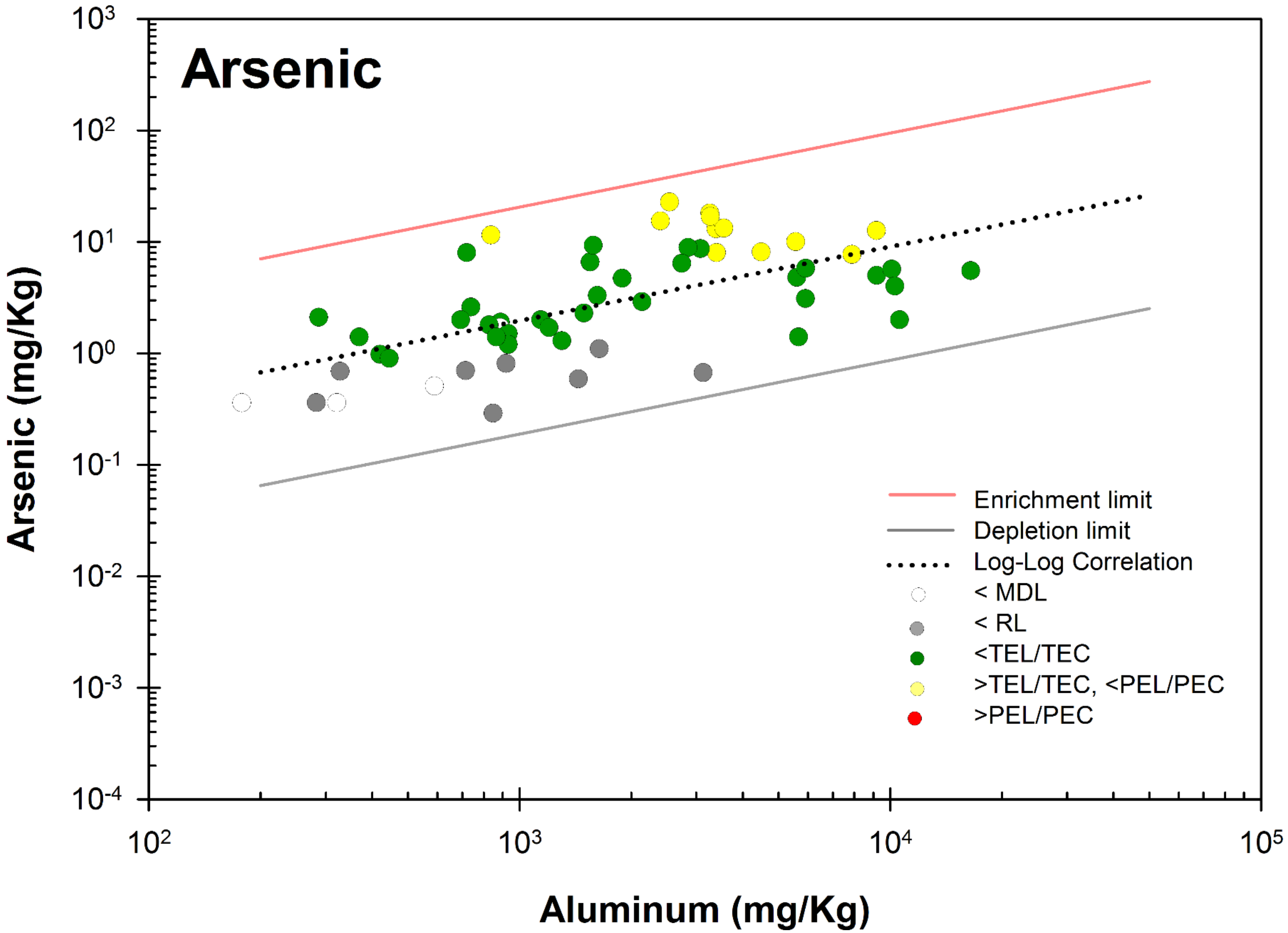

Figure 19 Normalized enrichment plot for Arsenic. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

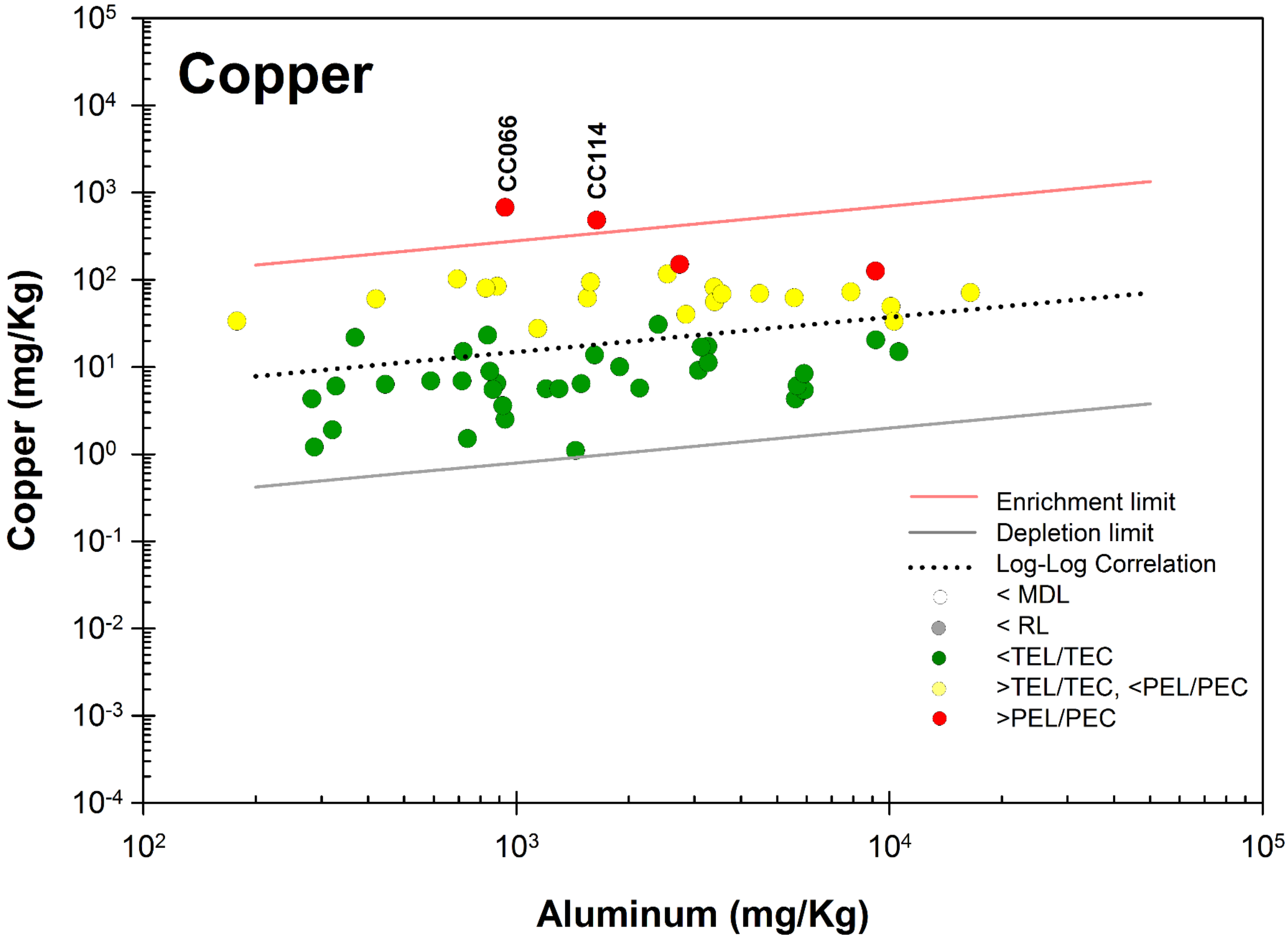

Figure 20 Normalized enrichment plot for Copper. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

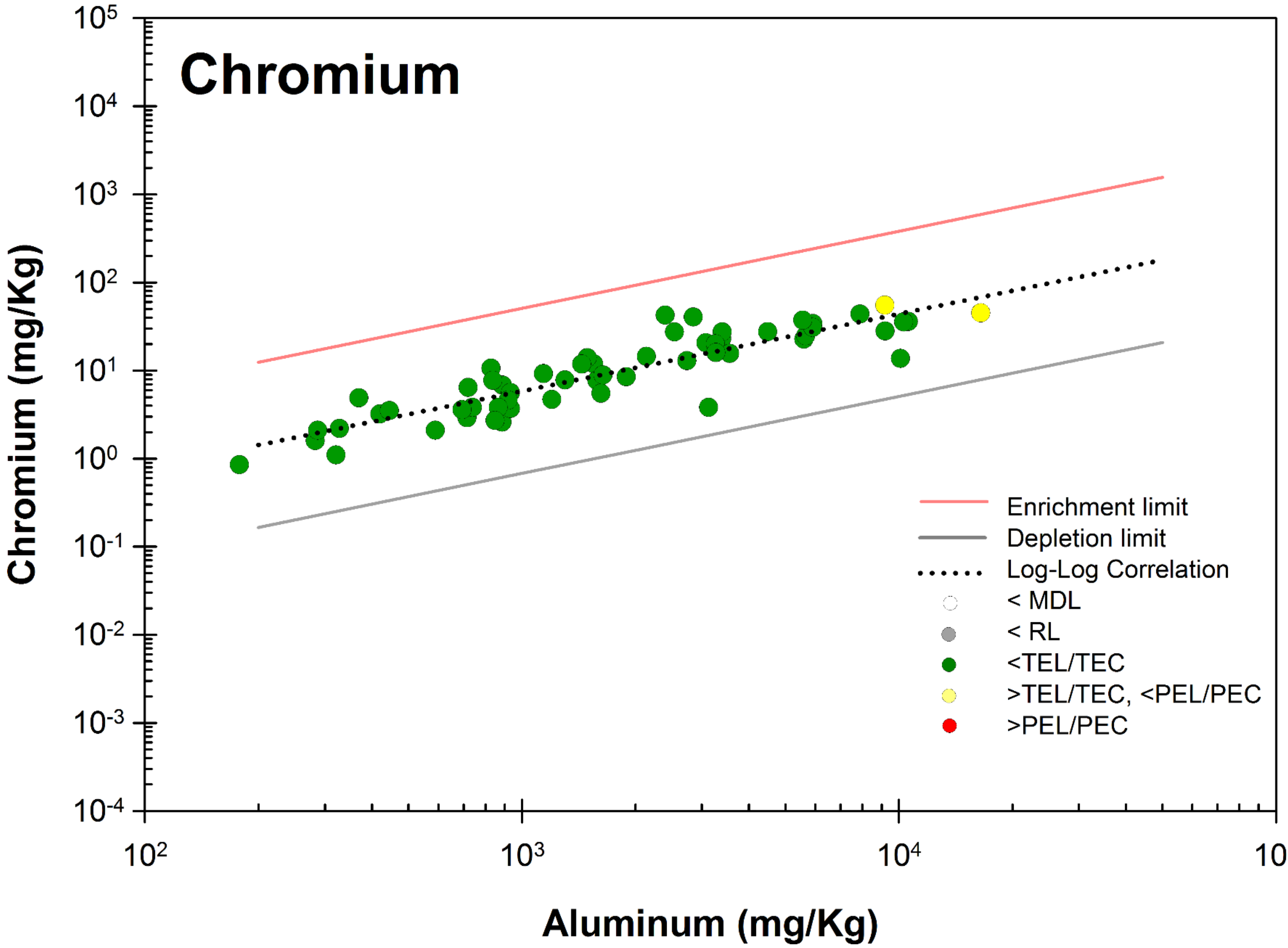

Figure 21 Normalized enrichment plot for Chromium. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

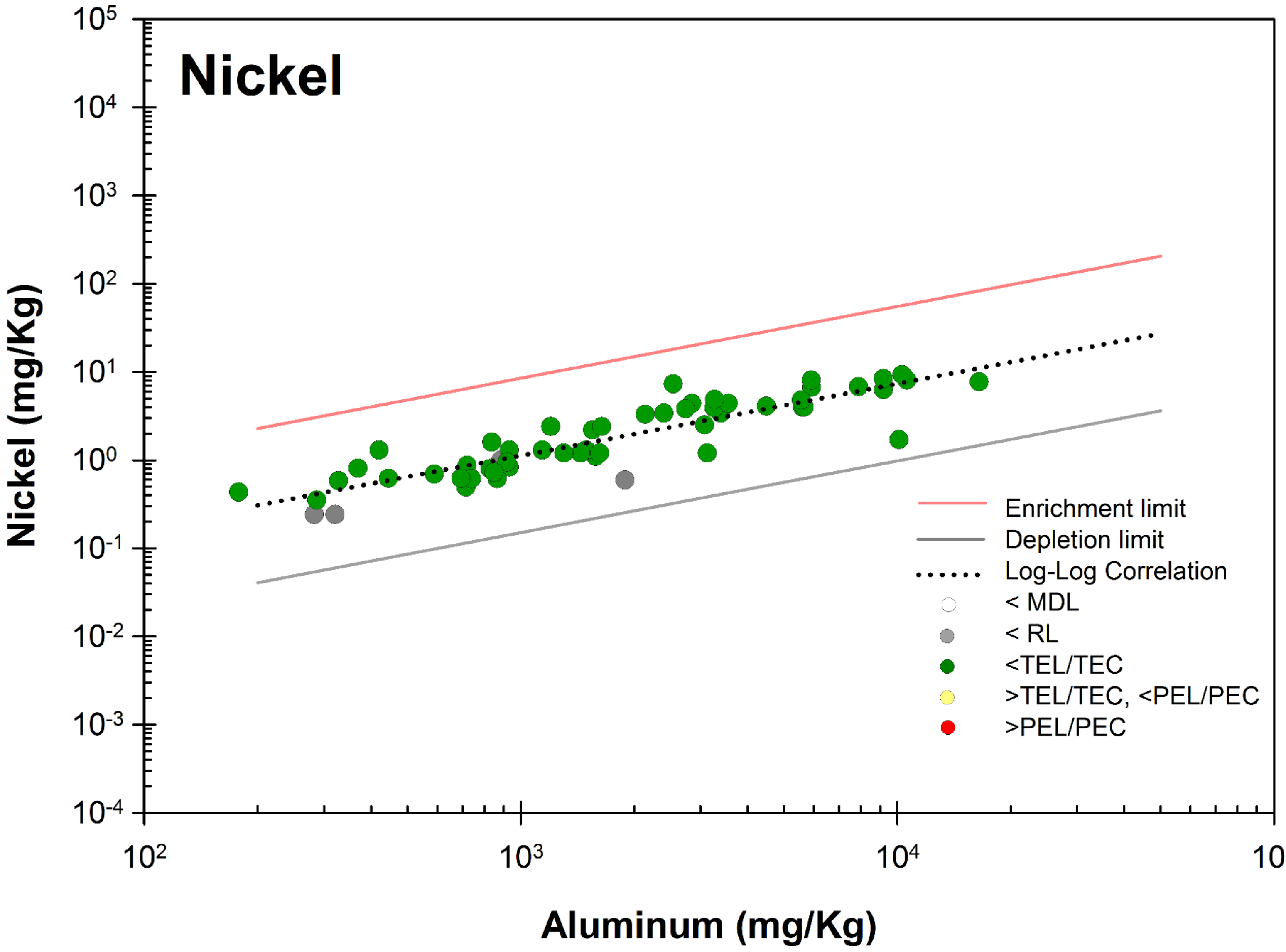

Figure 22 Normalized enrichment plot for Nickel. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

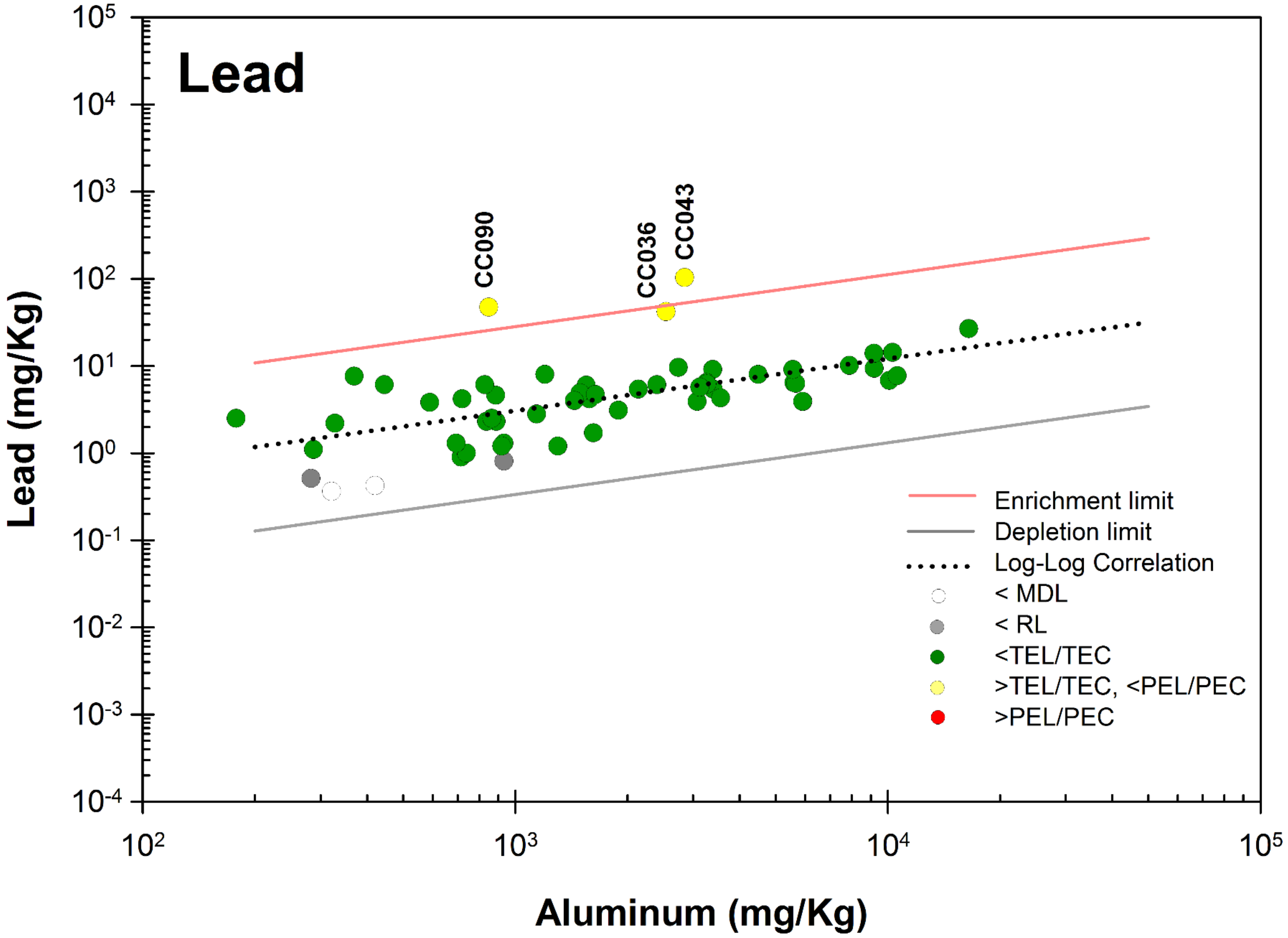

Figure 23 Normalized enrichment plot for Lead. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

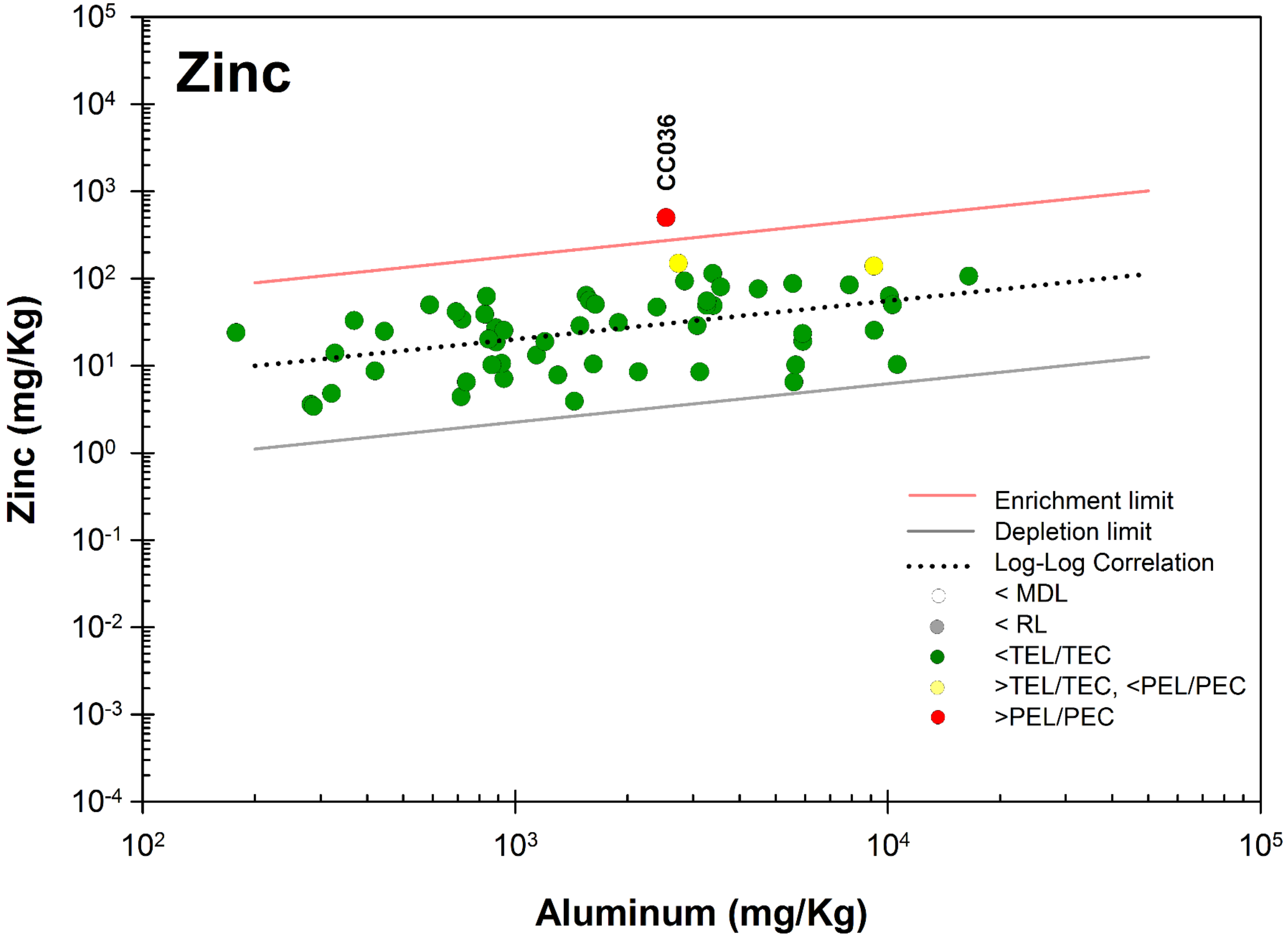

Figure 24 Normalized enrichment plot for Zinc. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

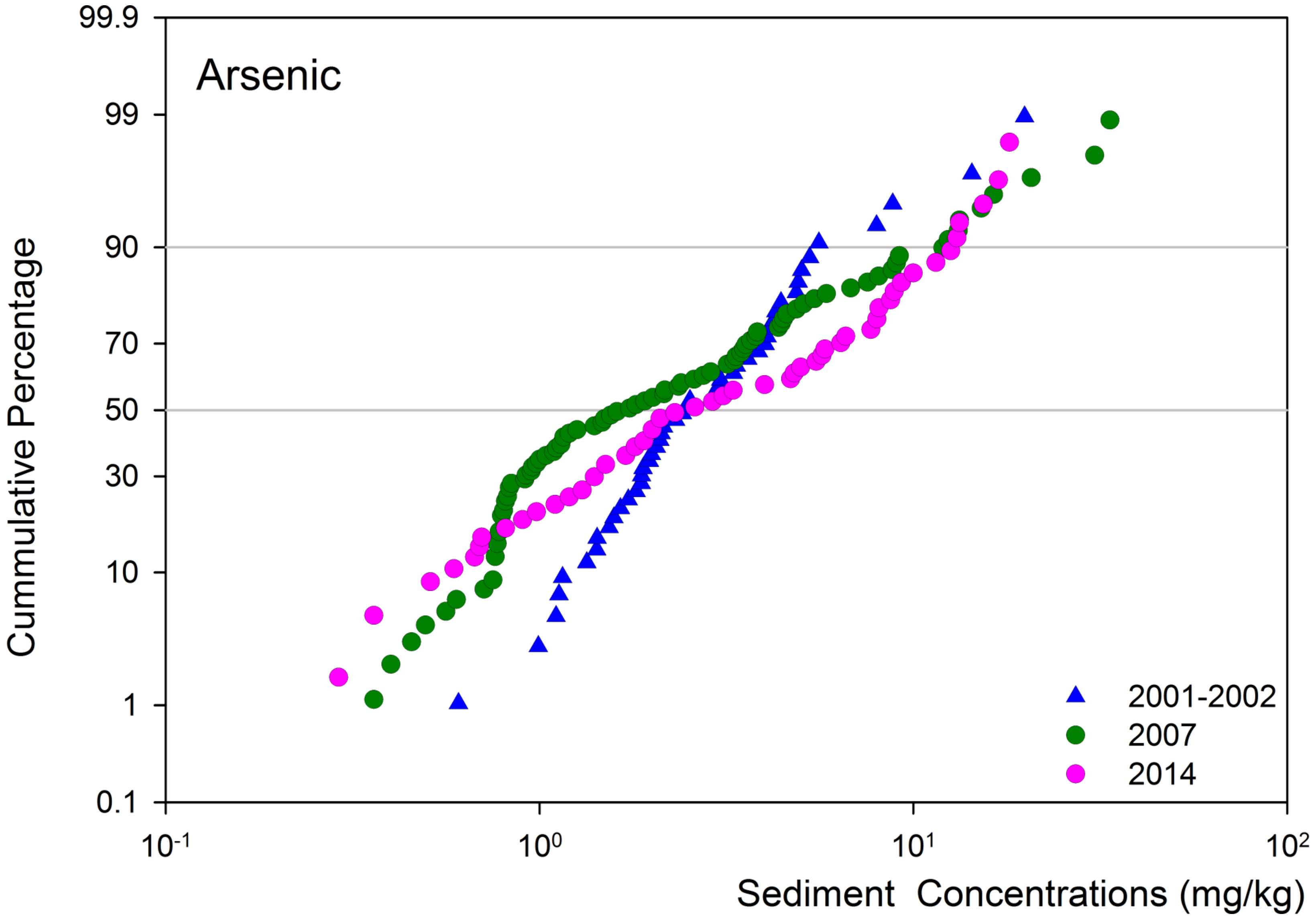

Figure 25 Percent cumulative frequency distributions (%CFD) comparing observed Arsenic concentrations with previous studies.

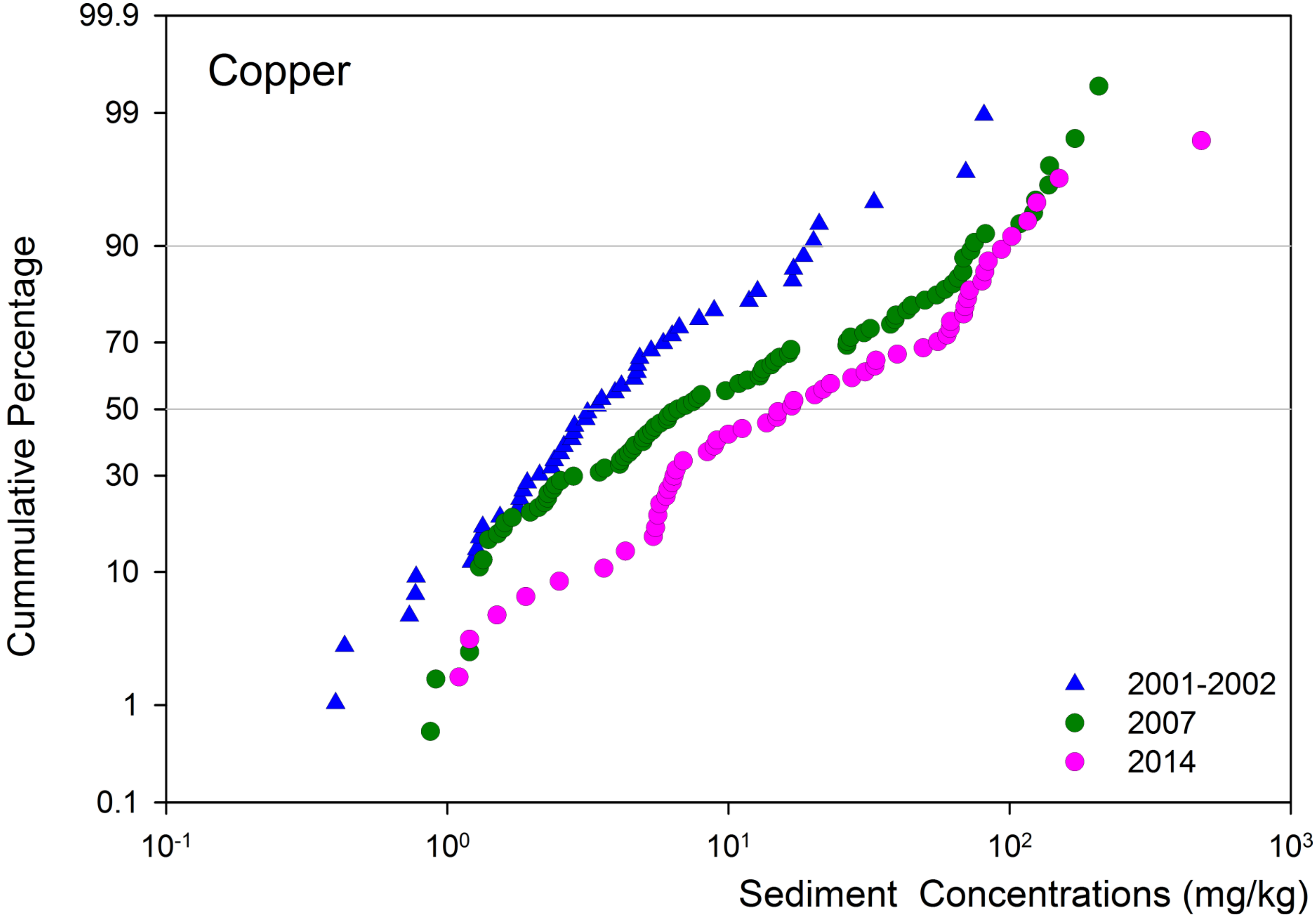

Figure 26 Percent cumulative frequency distributions (%CFD) comparing observed Copper concentrations with previous studies.

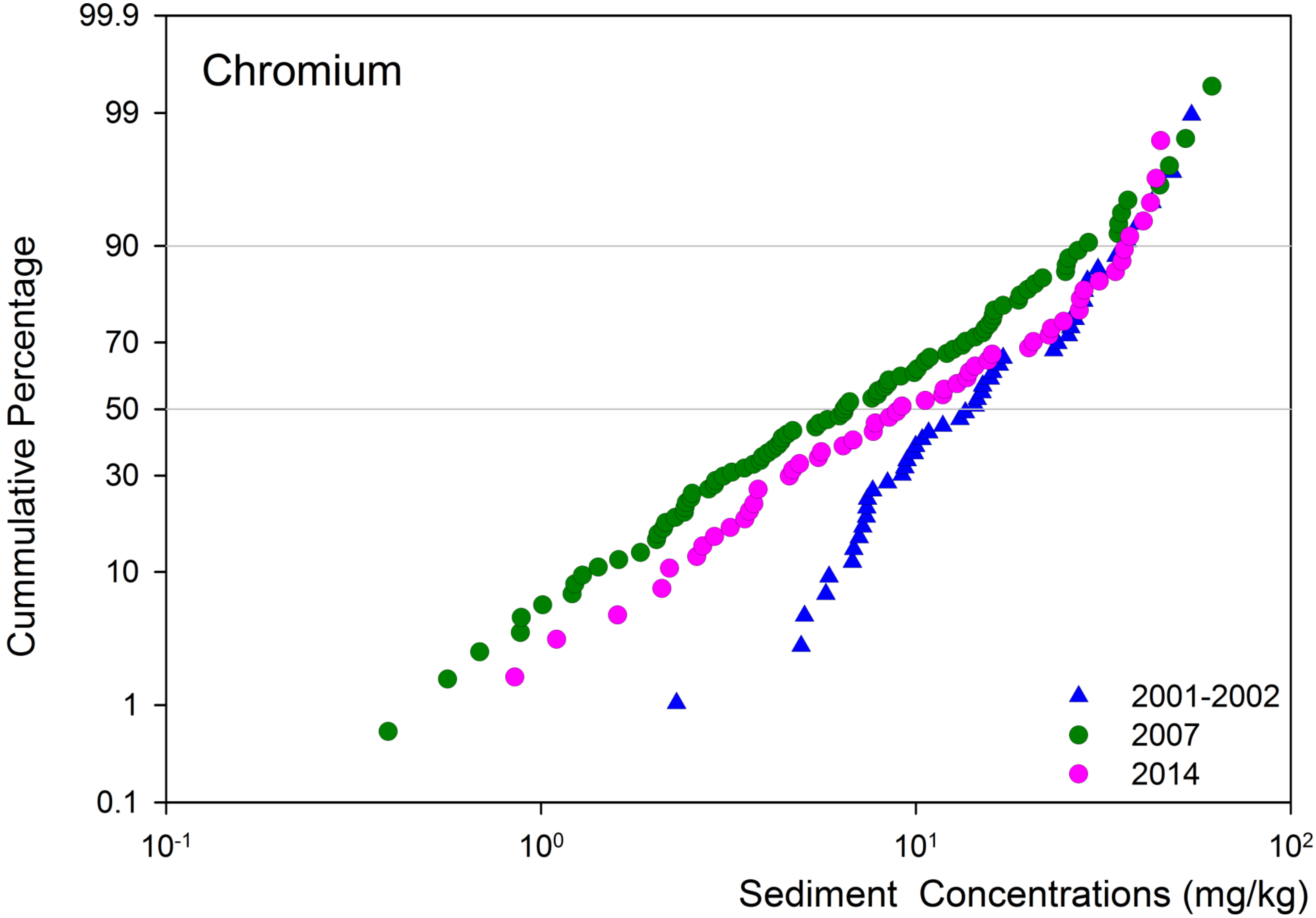

Figure 27 Percent cumulative frequency distributions (%CFD) comparing observed Chromium concentrations with previous studies.

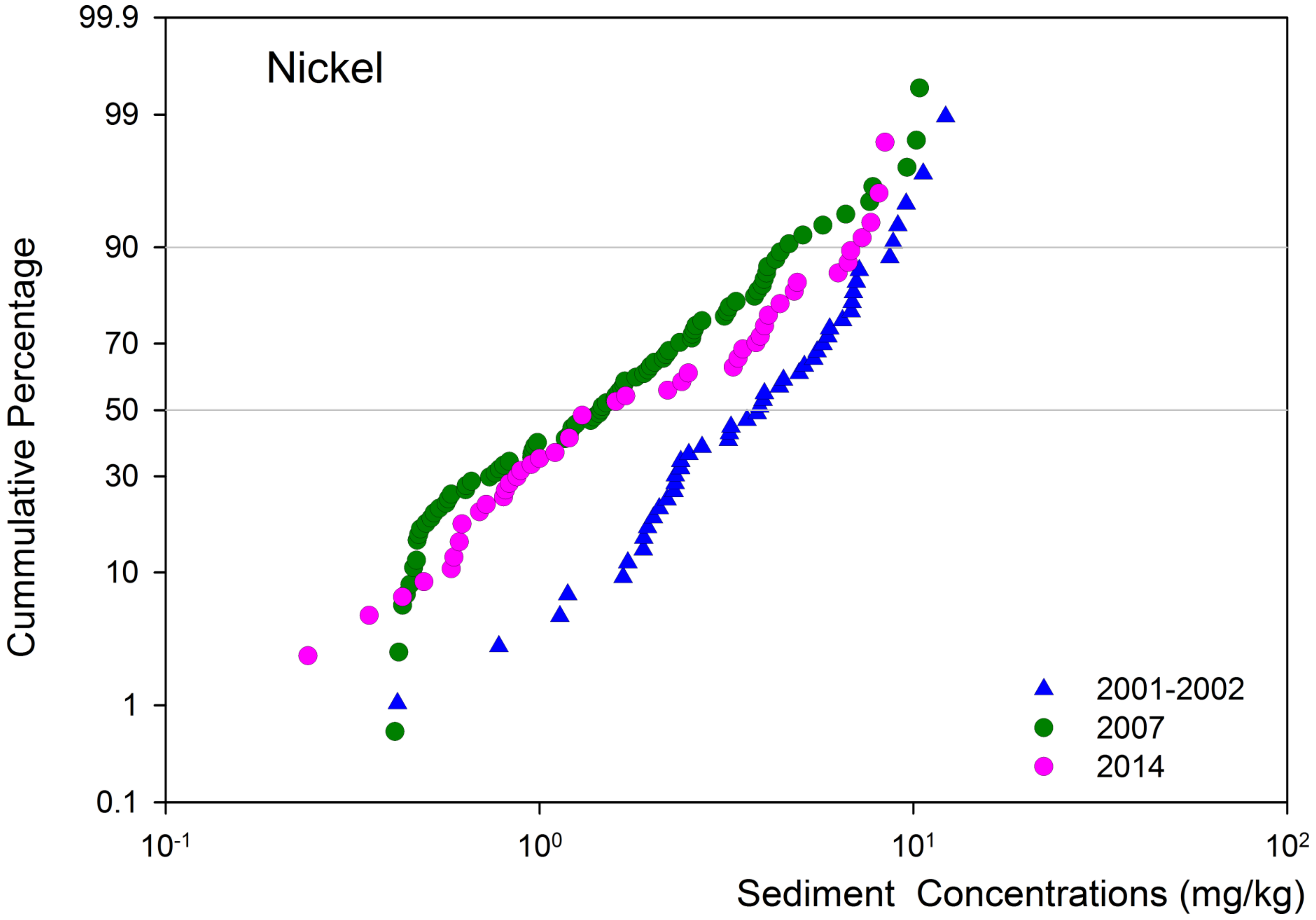

Figure 28 Percent cumulative frequency distributions (%CFD) comparing observed Nickel concentrations with previous studies.

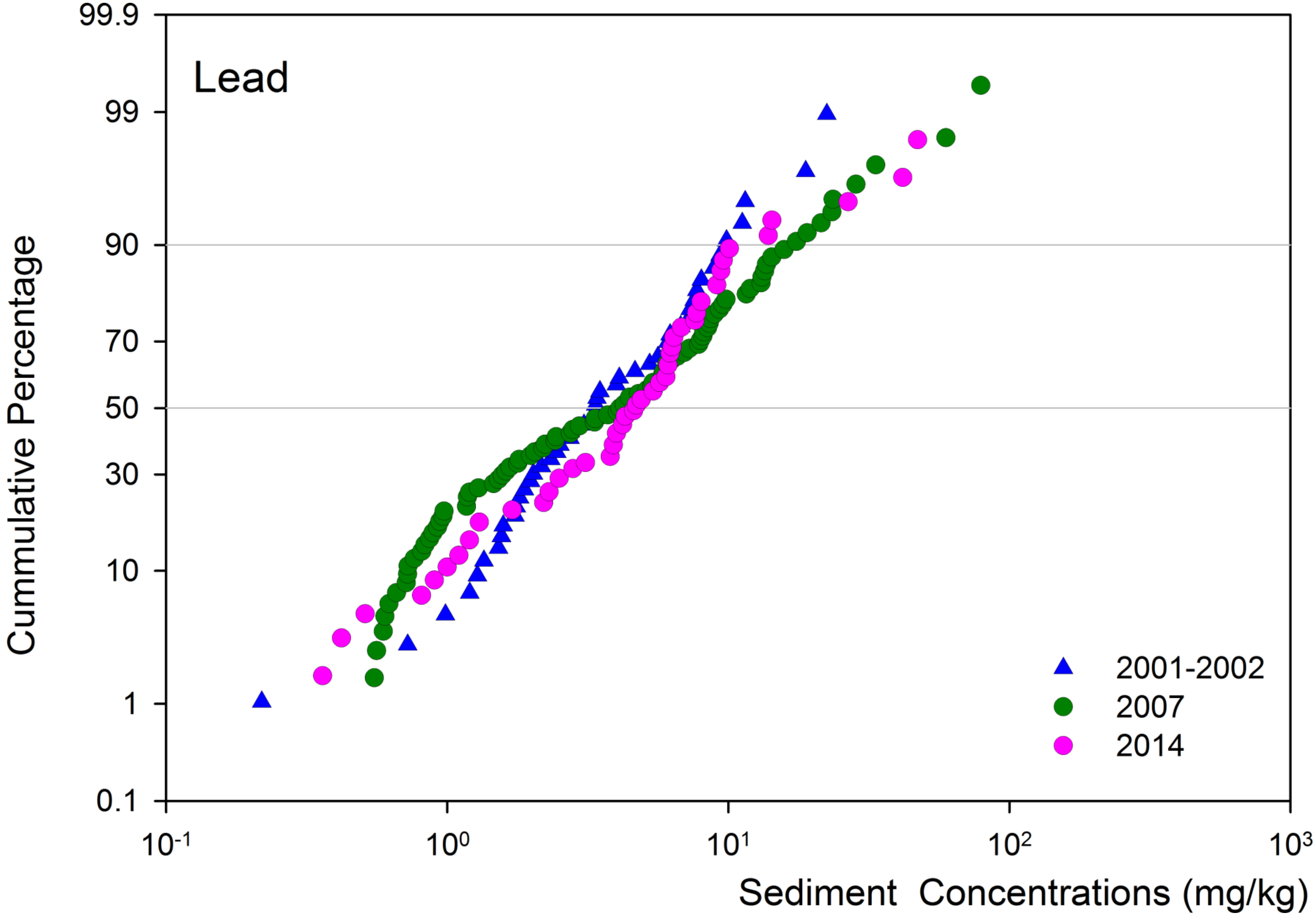

Figure 29 Percent cumulative frequency distributions (%CFD) comparing observed Lead concentrations with previous studies.

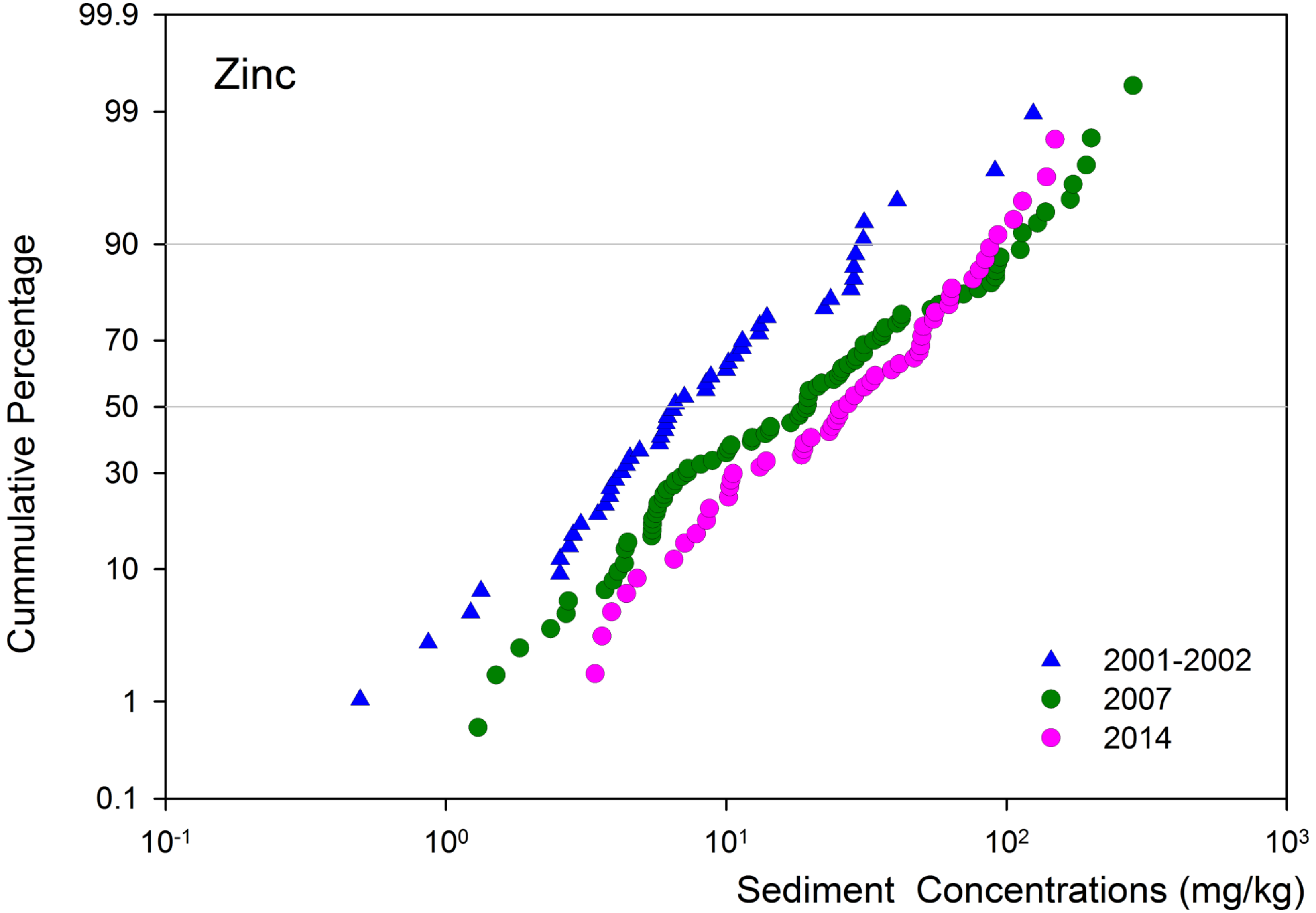

Figure 30 Percent cumulative frequency distributions (%CFD) comparing observed Zinc concentrations with previous studies.

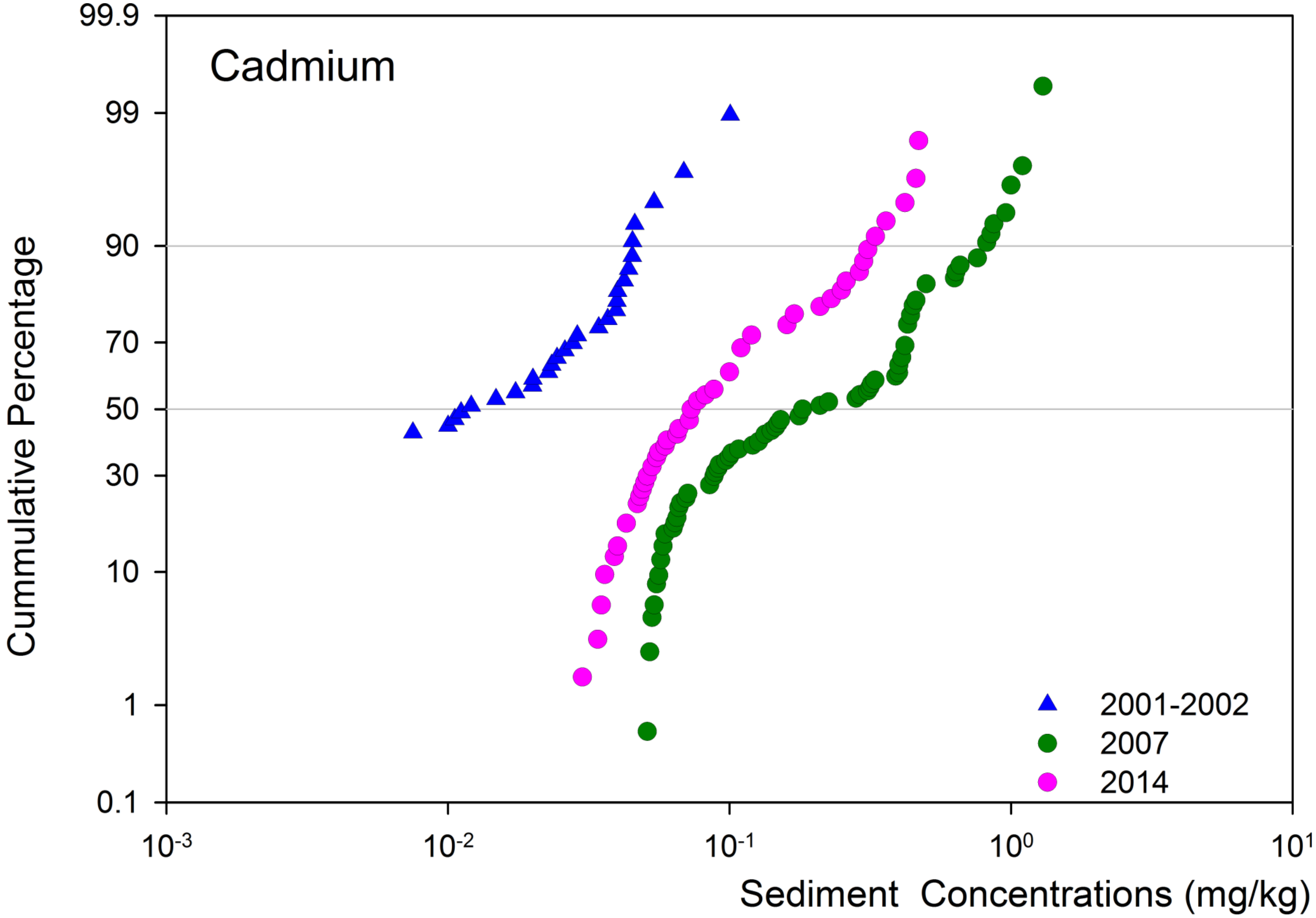

Figure 31 Percent cumulative frequency distributions (%CFD) comparing observed Cadmium concentrations with previous studies.

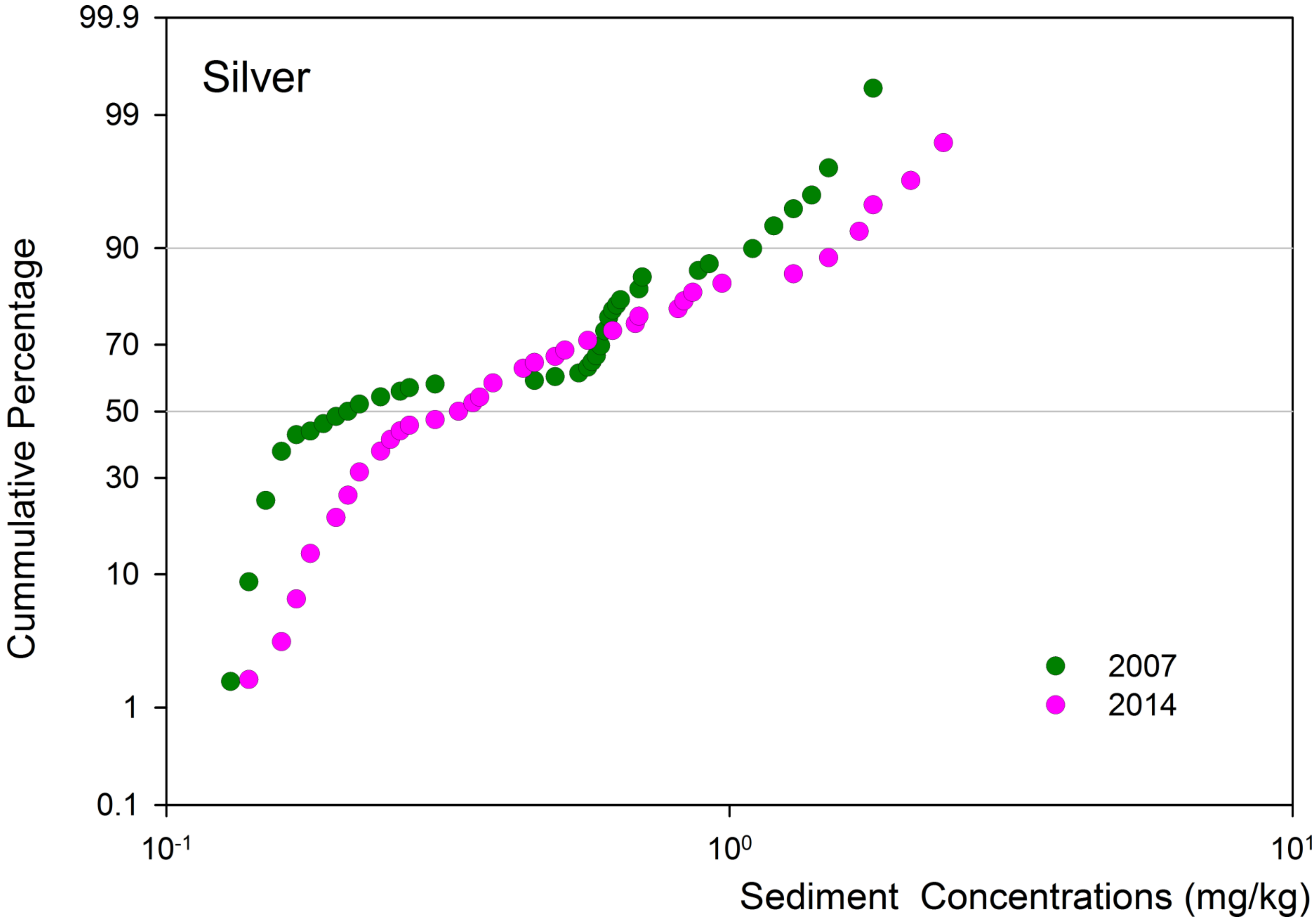

Figure 32 Percent cumulative frequency distributions (%CFD) comparing observed Silver concentrations with the 2007 survey.

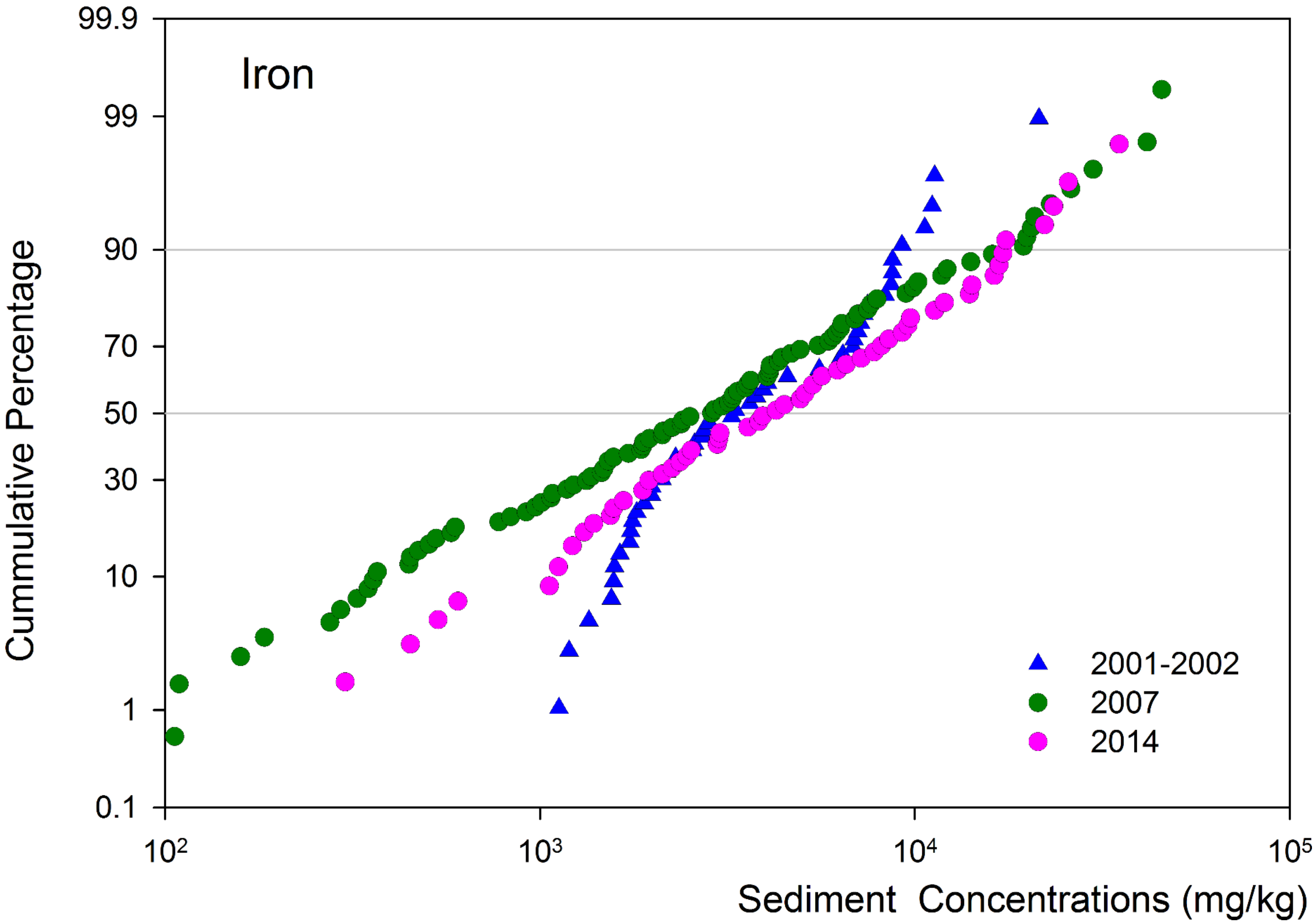

Figure 33 Percent cumulative frequency distributions (%CFD) comparing observed Iron concentrations with previous studies.

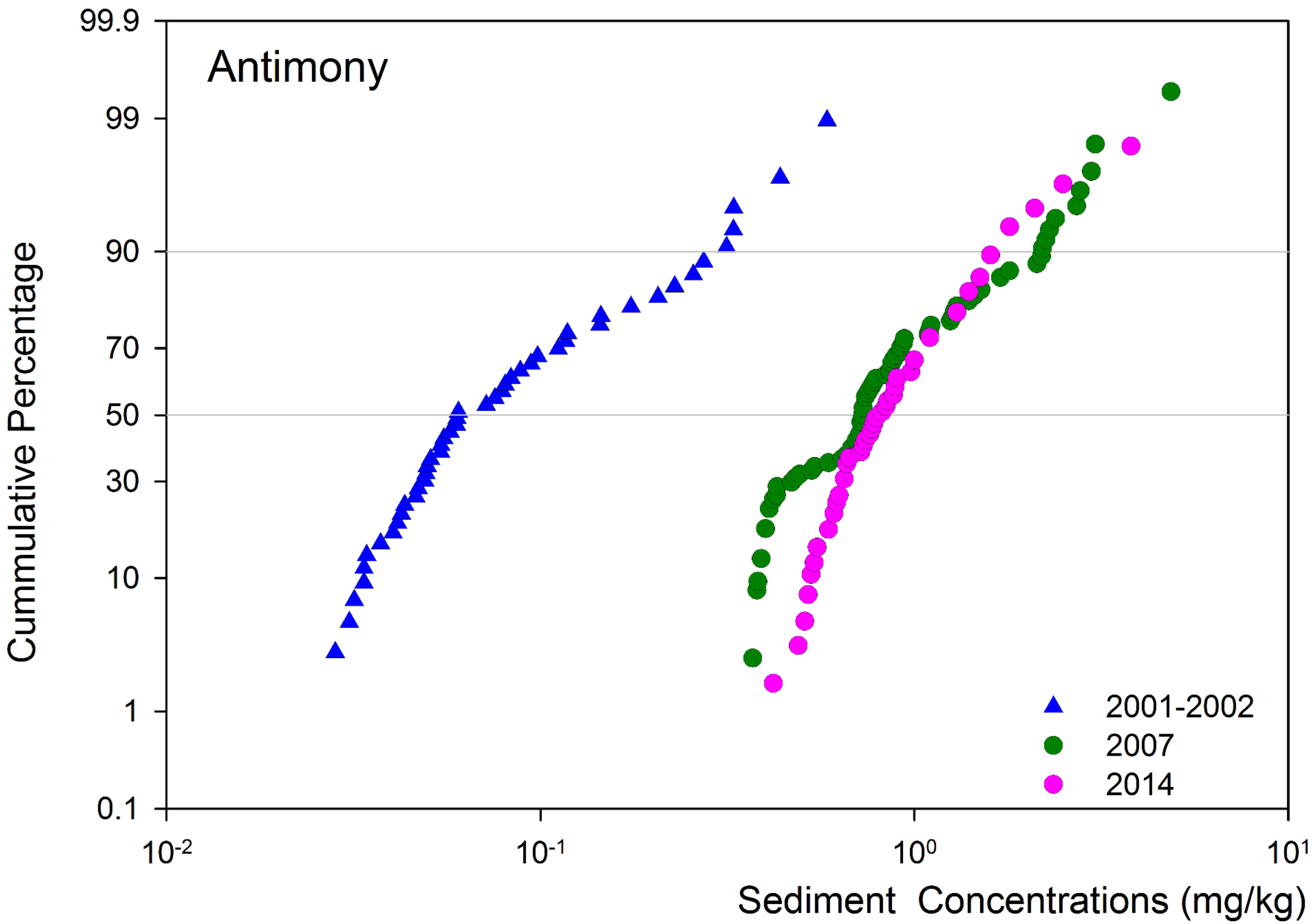

Figure 34 Percent cumulative frequency distributions (%CFD) comparing observed Antimony concentrations with previous studies.

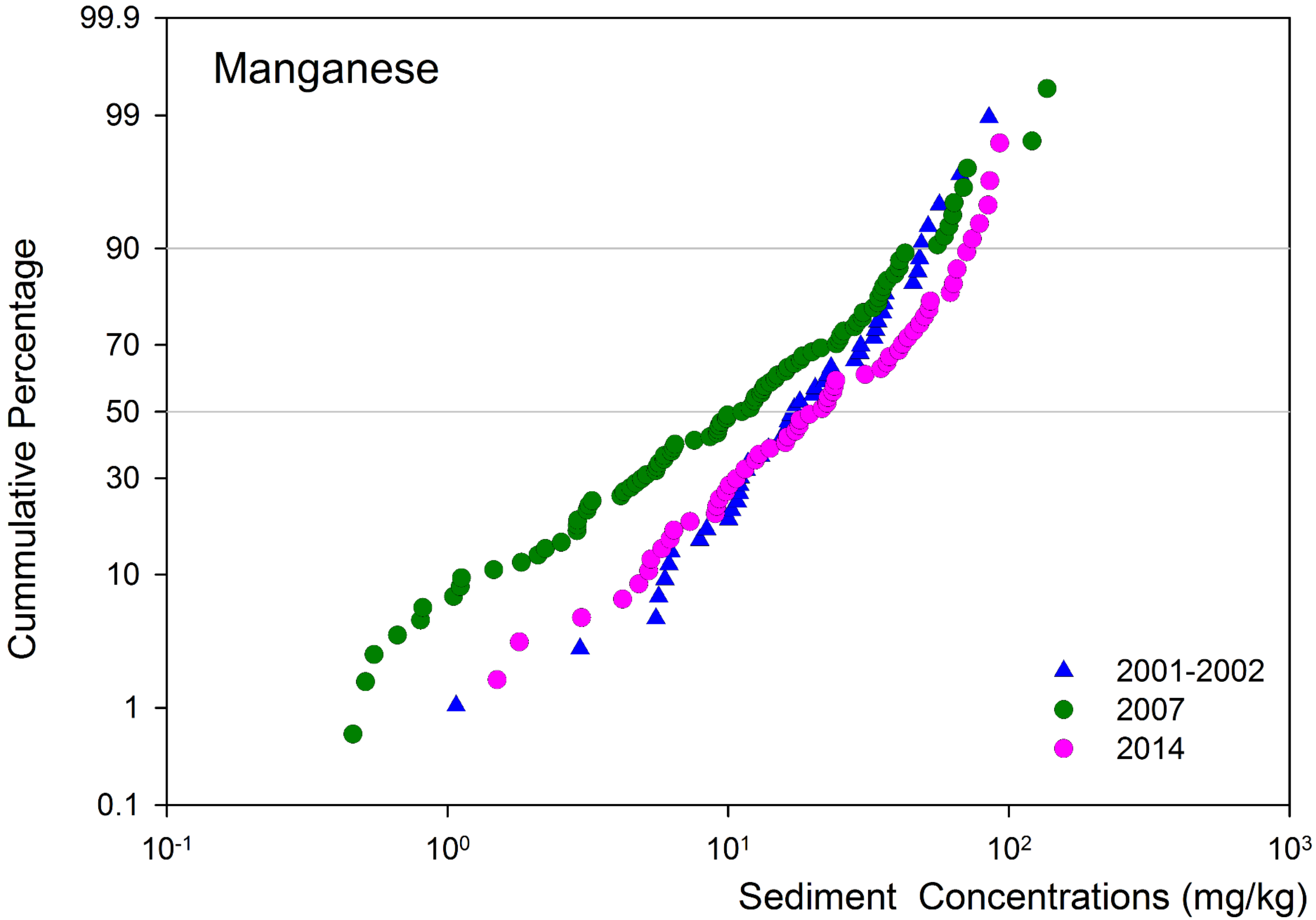

Figure 35 Percent cumulative frequency distributions (%CFD) comparing observed Manganese concentrations with previous studies.

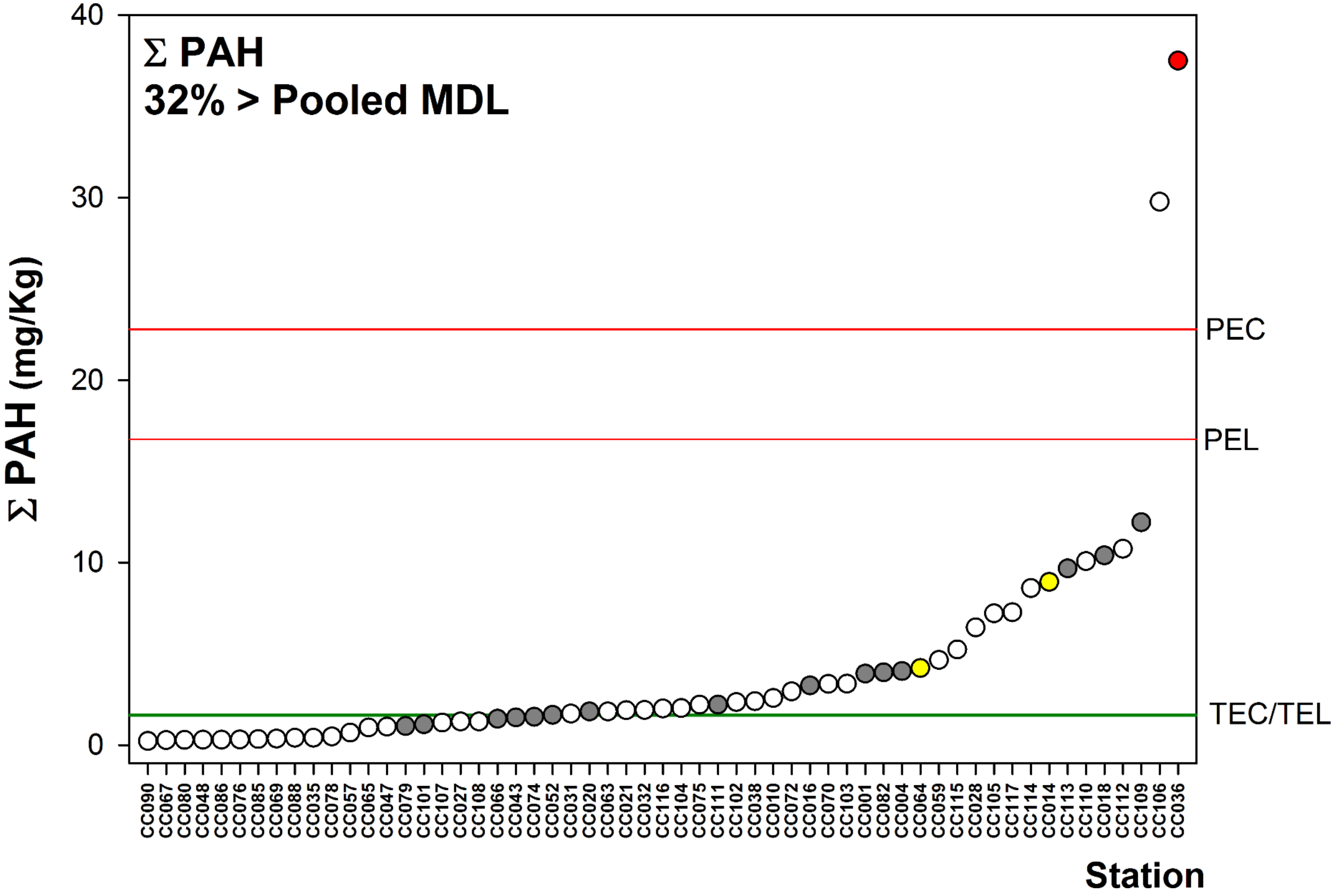

Figure 36 Ranked Concentrations of Total PAHs in the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

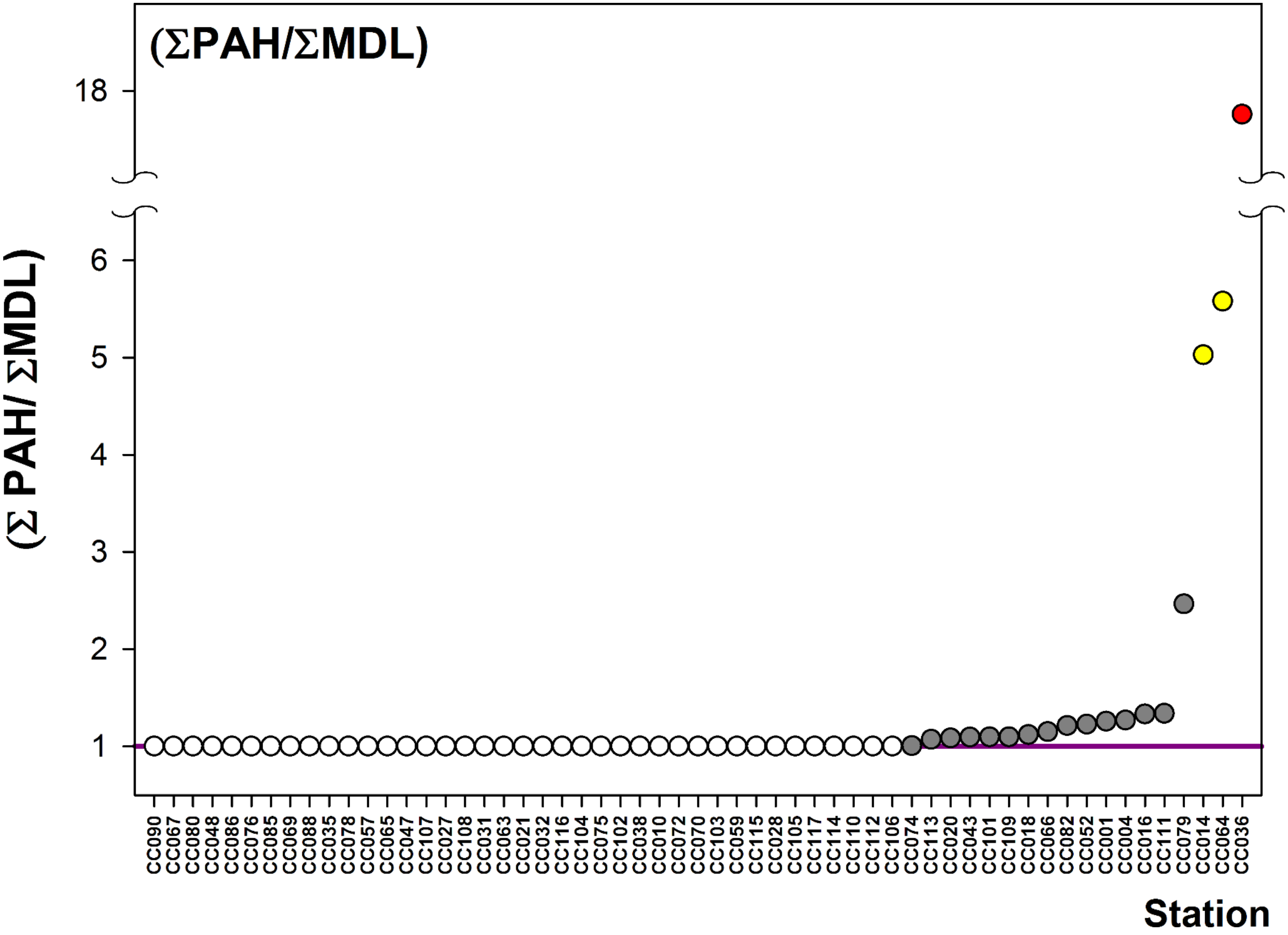

Figure 37 MDL-normalized concentrations of Total PAHs in the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

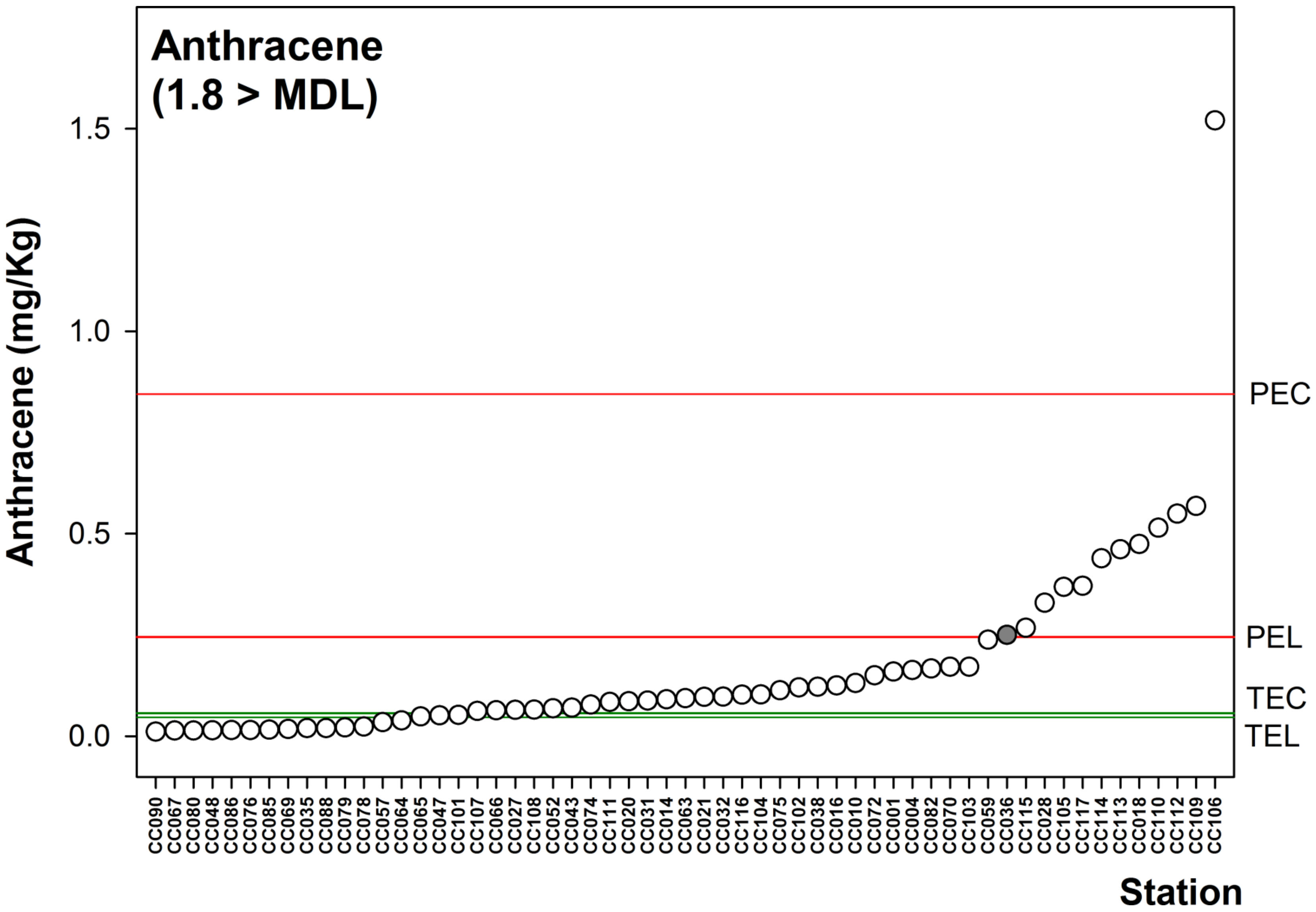

Figure 38 Concentrations of Anthracene for Sediments in the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

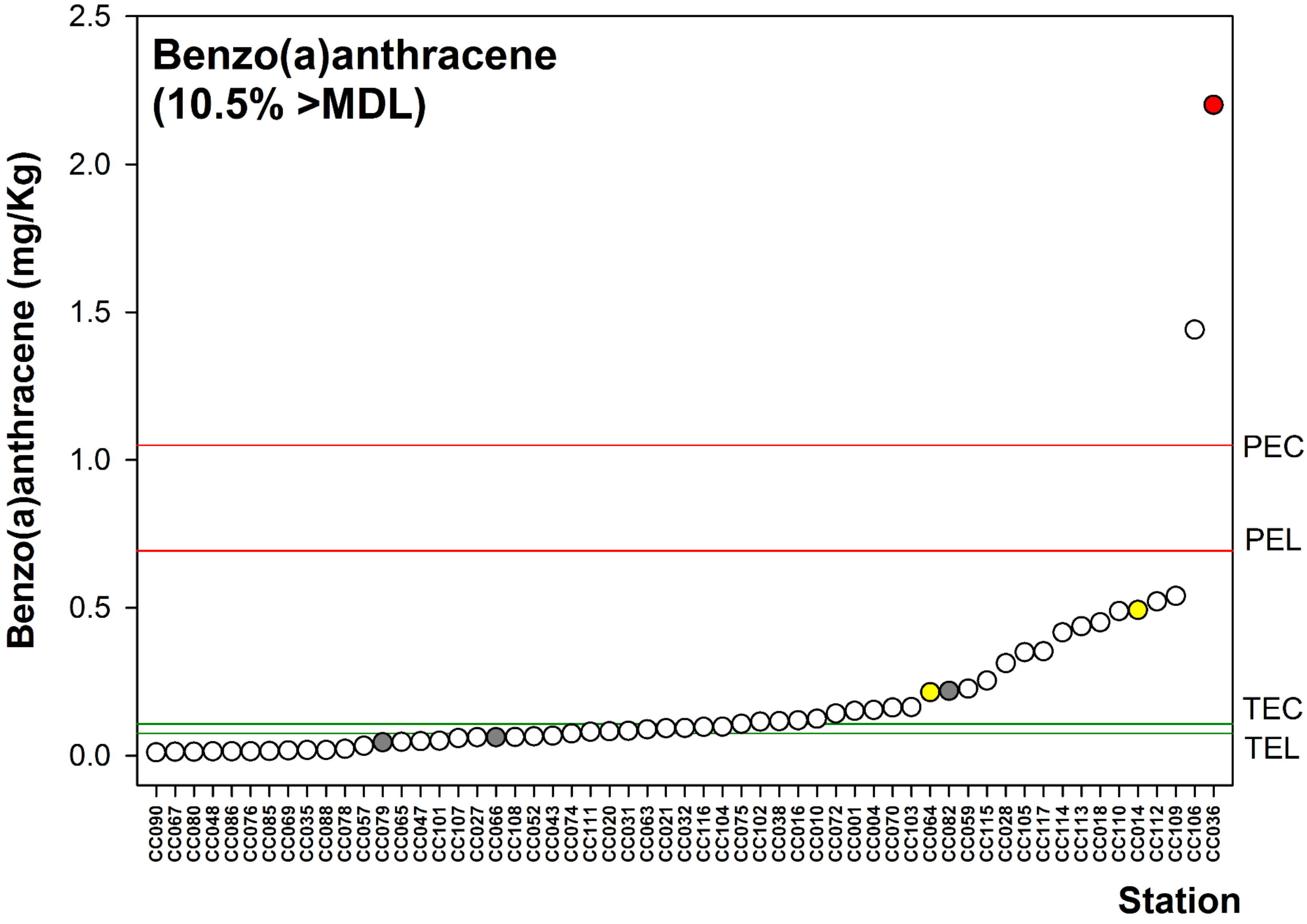

Figure 39 Concentrations of Benzo(a)anthracene for Sediments in the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

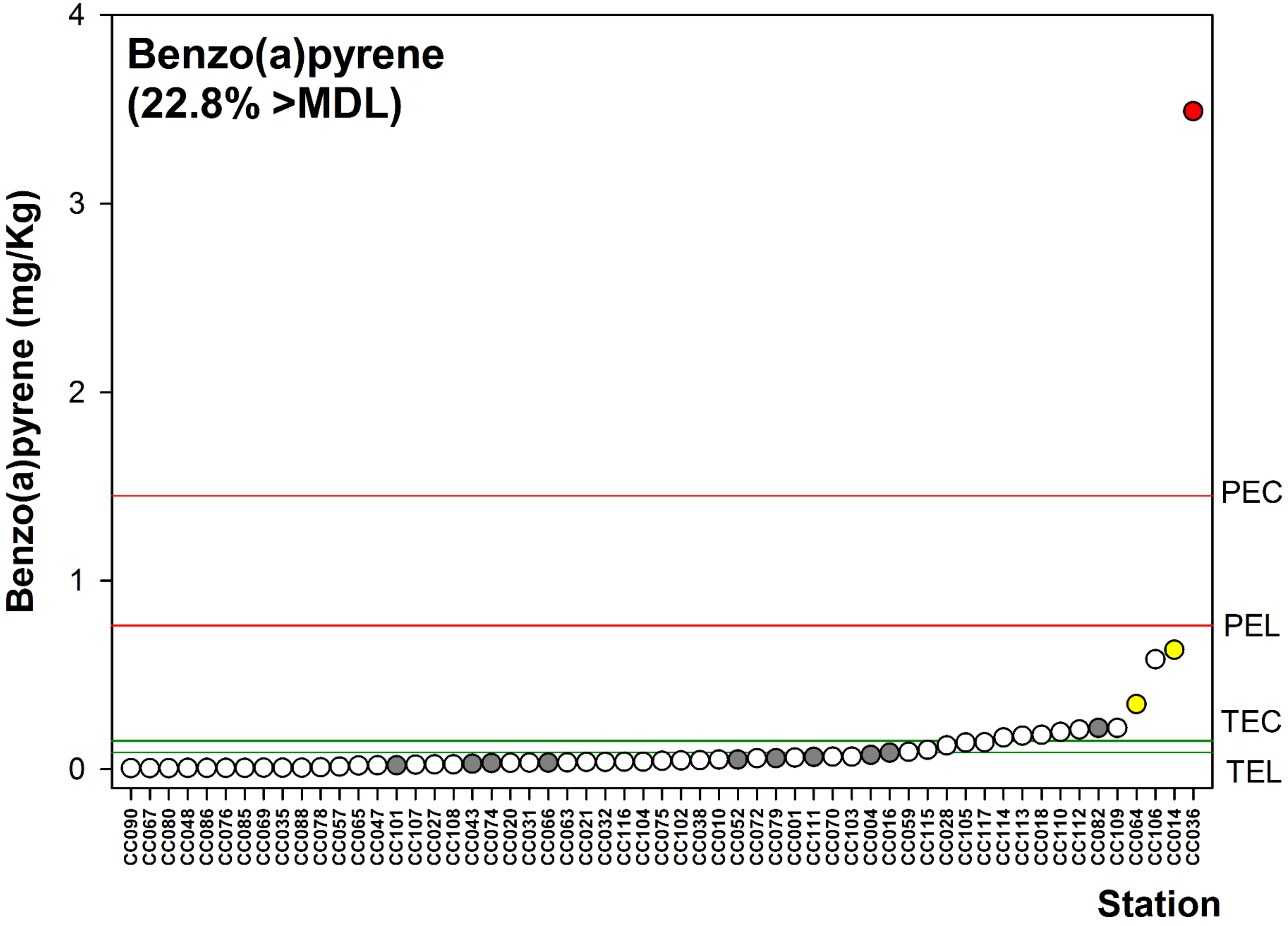

Figure 40 Concentrations of Benzo(a)pyrene for Sediments in the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

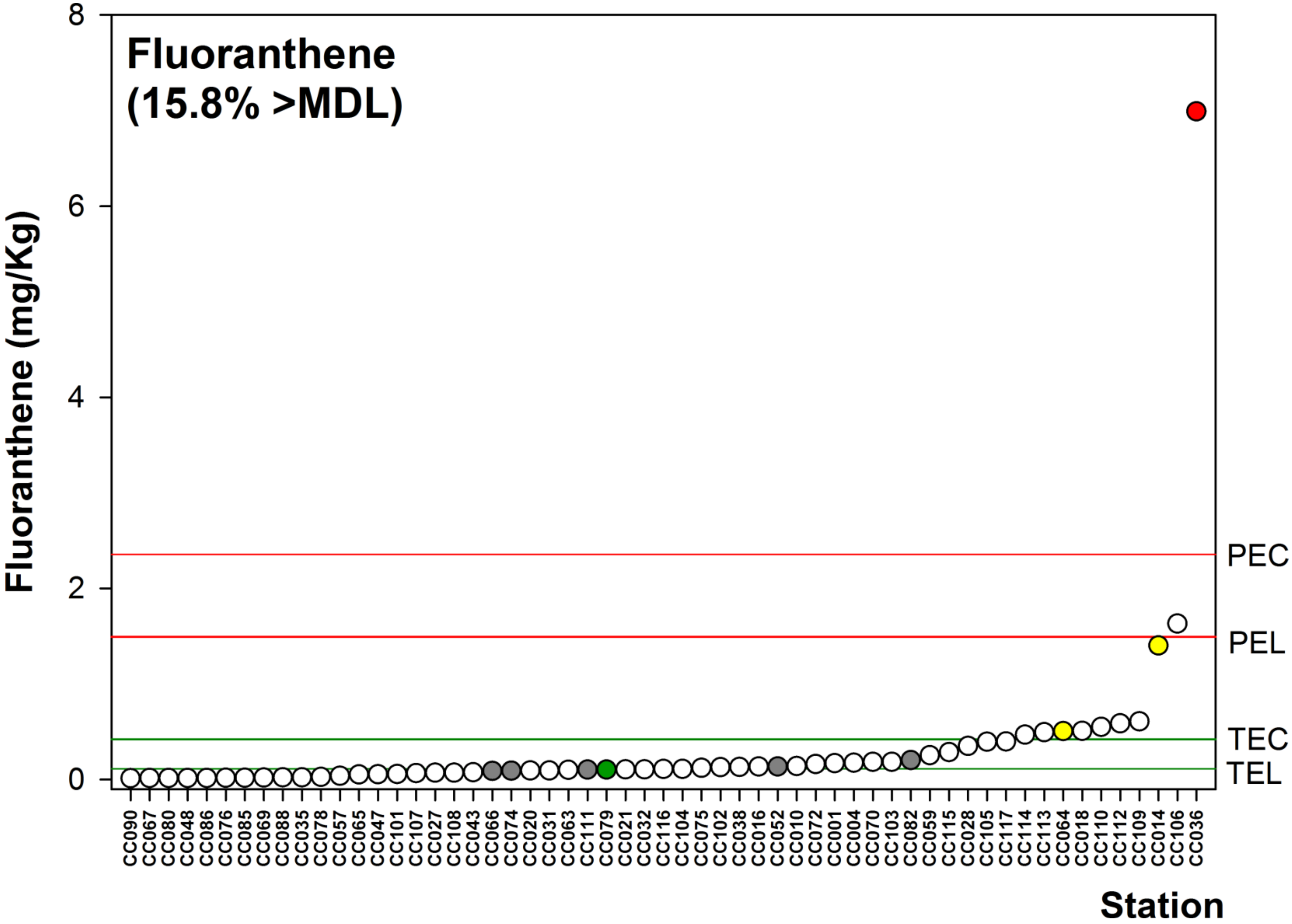

Figure 41 Concentrations of Fluoranthene for Sediments in the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

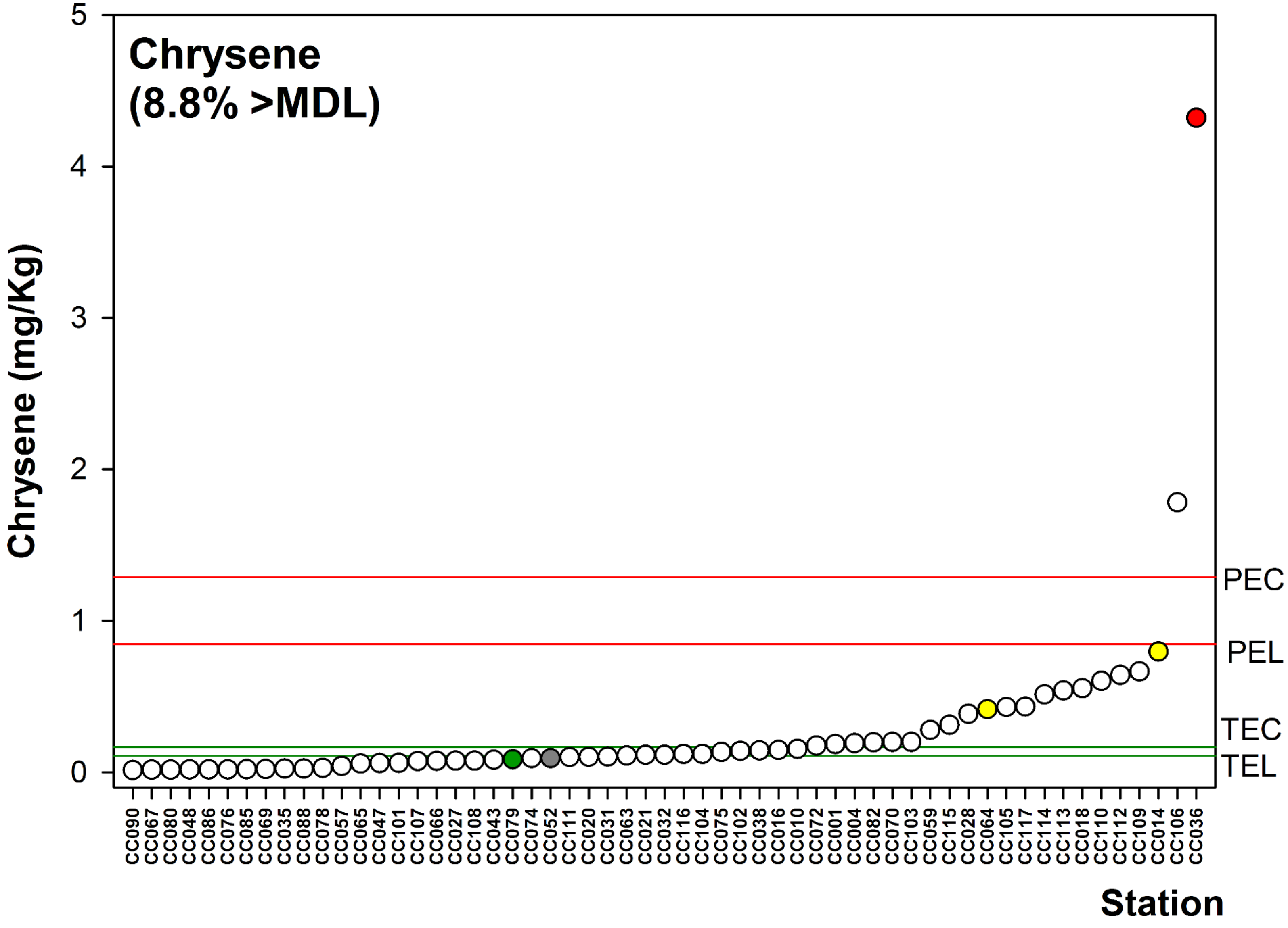

Figure 42 Concentrations of Chrysene for Sediments in the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

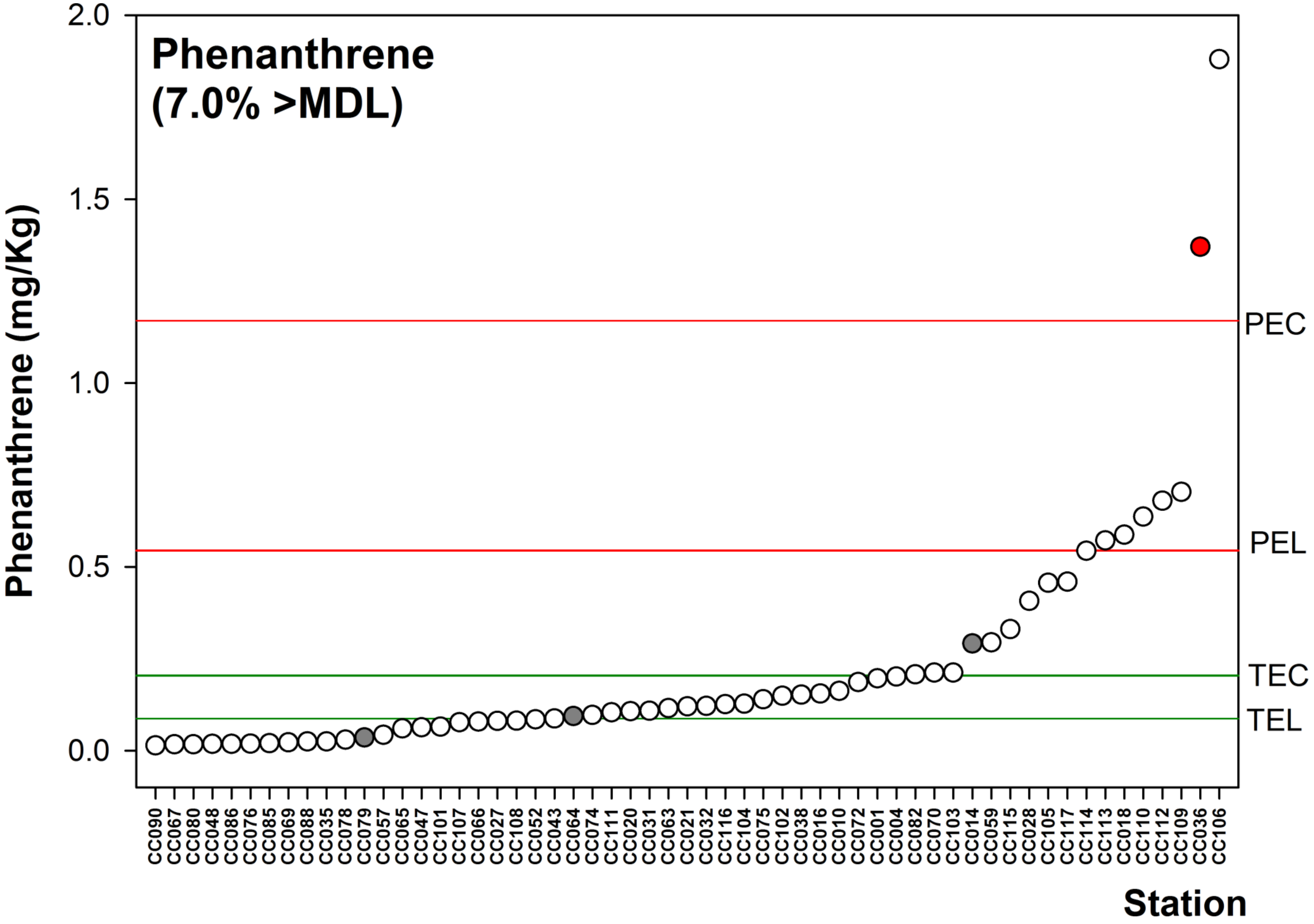

Figure 43 Concentrations of Phenanthrene for Sediments in the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

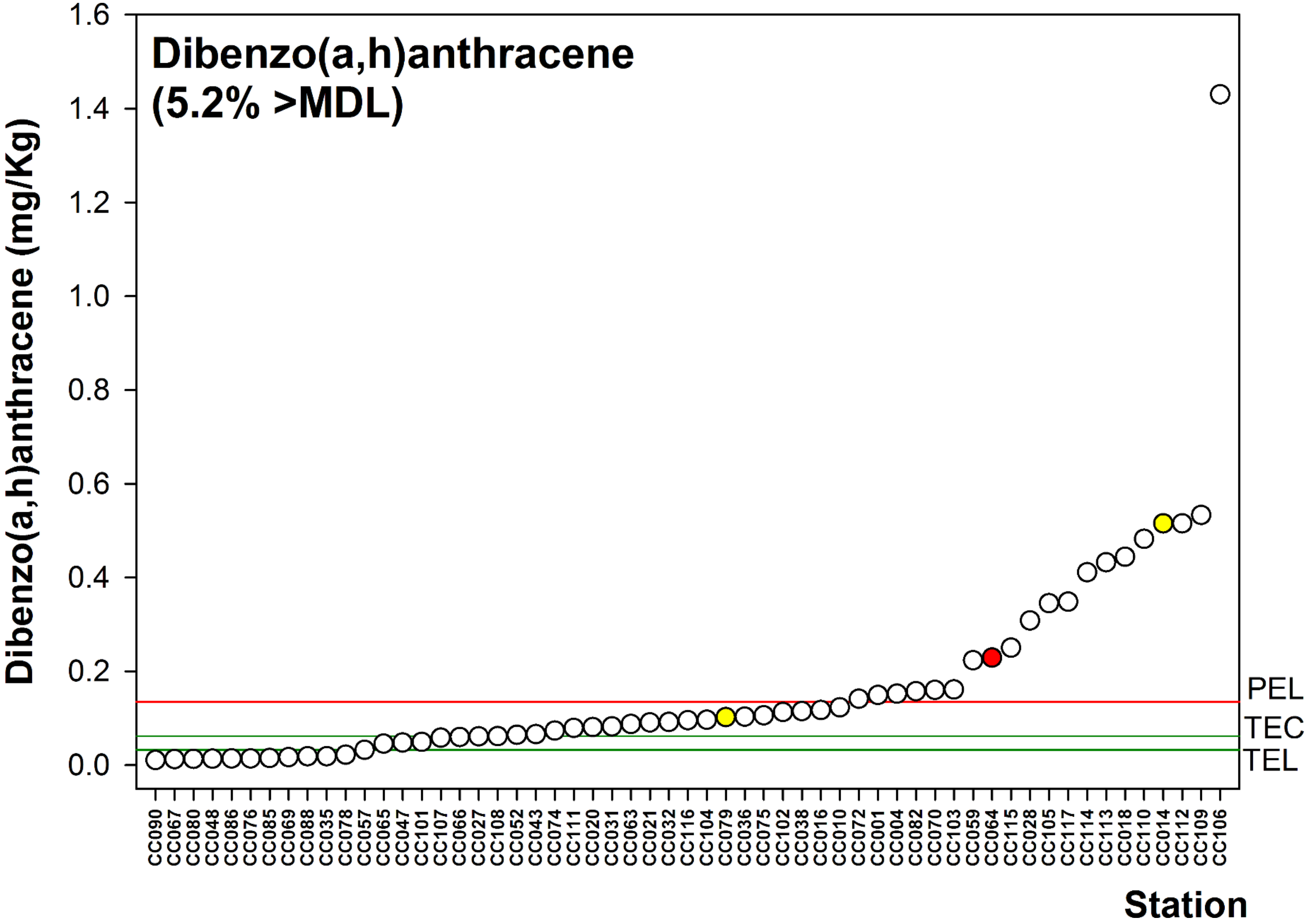

Figure 44 Concentrations of Dibenzo(a,h)anthracene for Sediments in the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

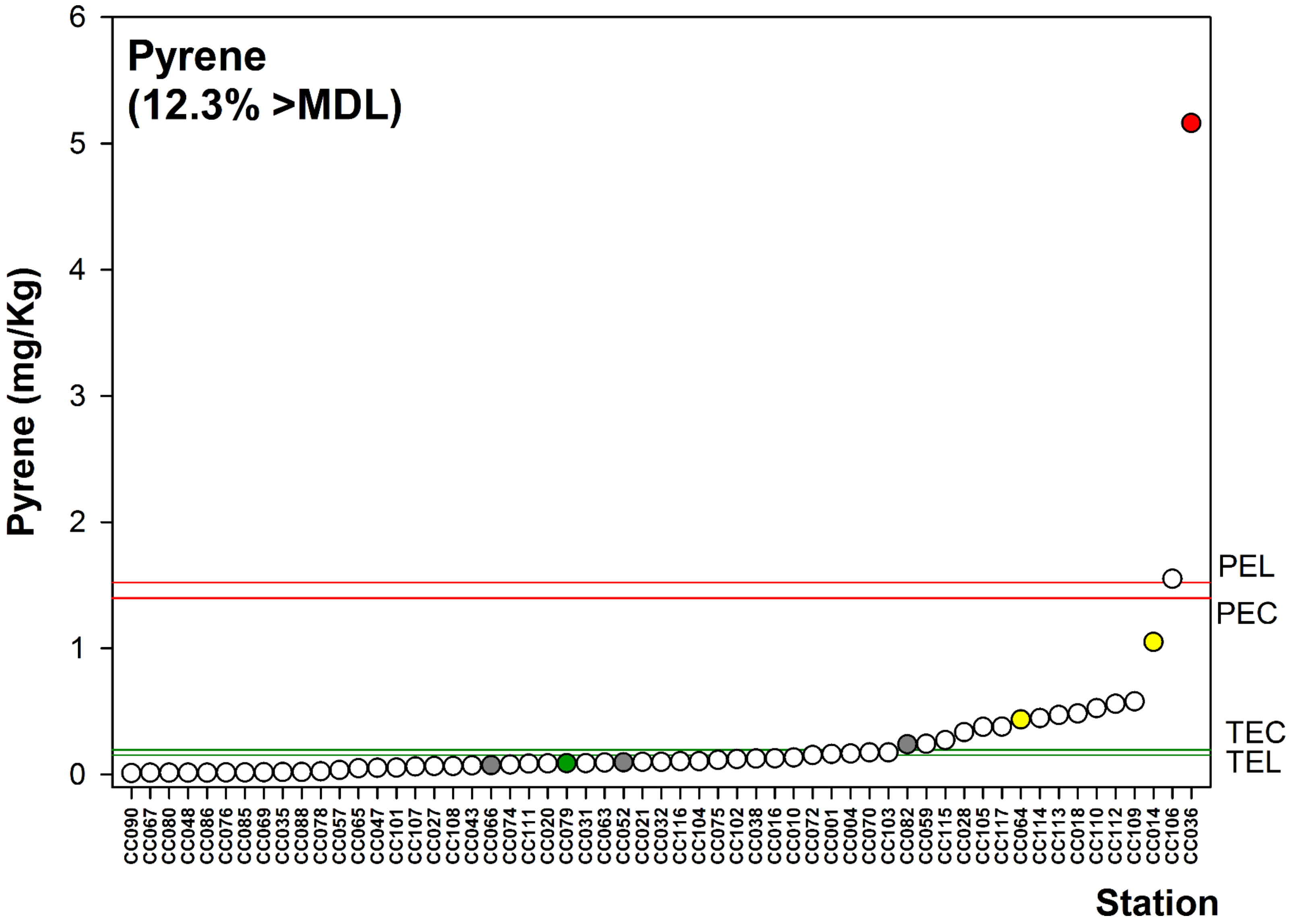

Figure 45 Concentrations of Pyrene for Sediments in the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

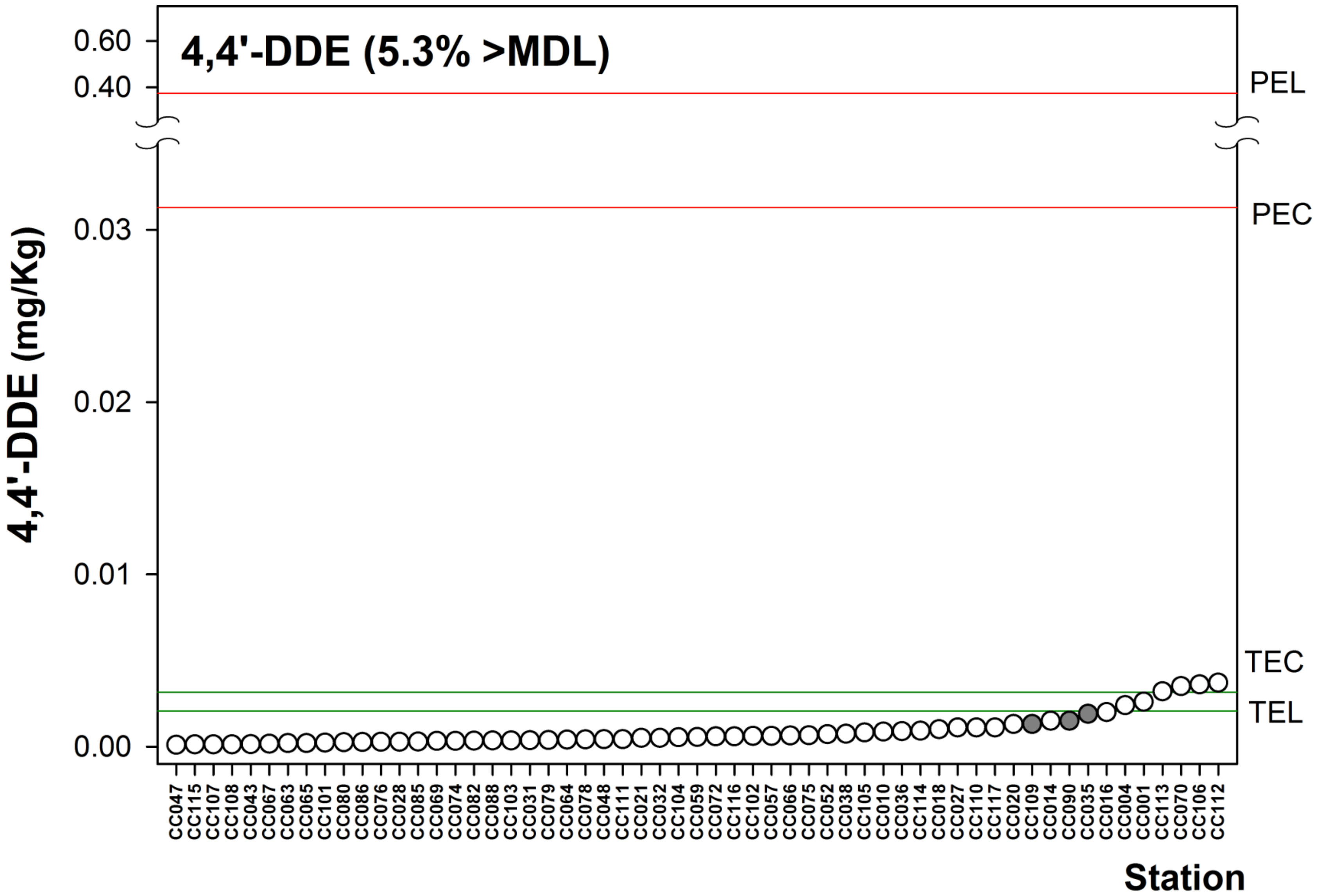

Figure 46 Concentrations of 4,4'-DDE for Sediments in the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

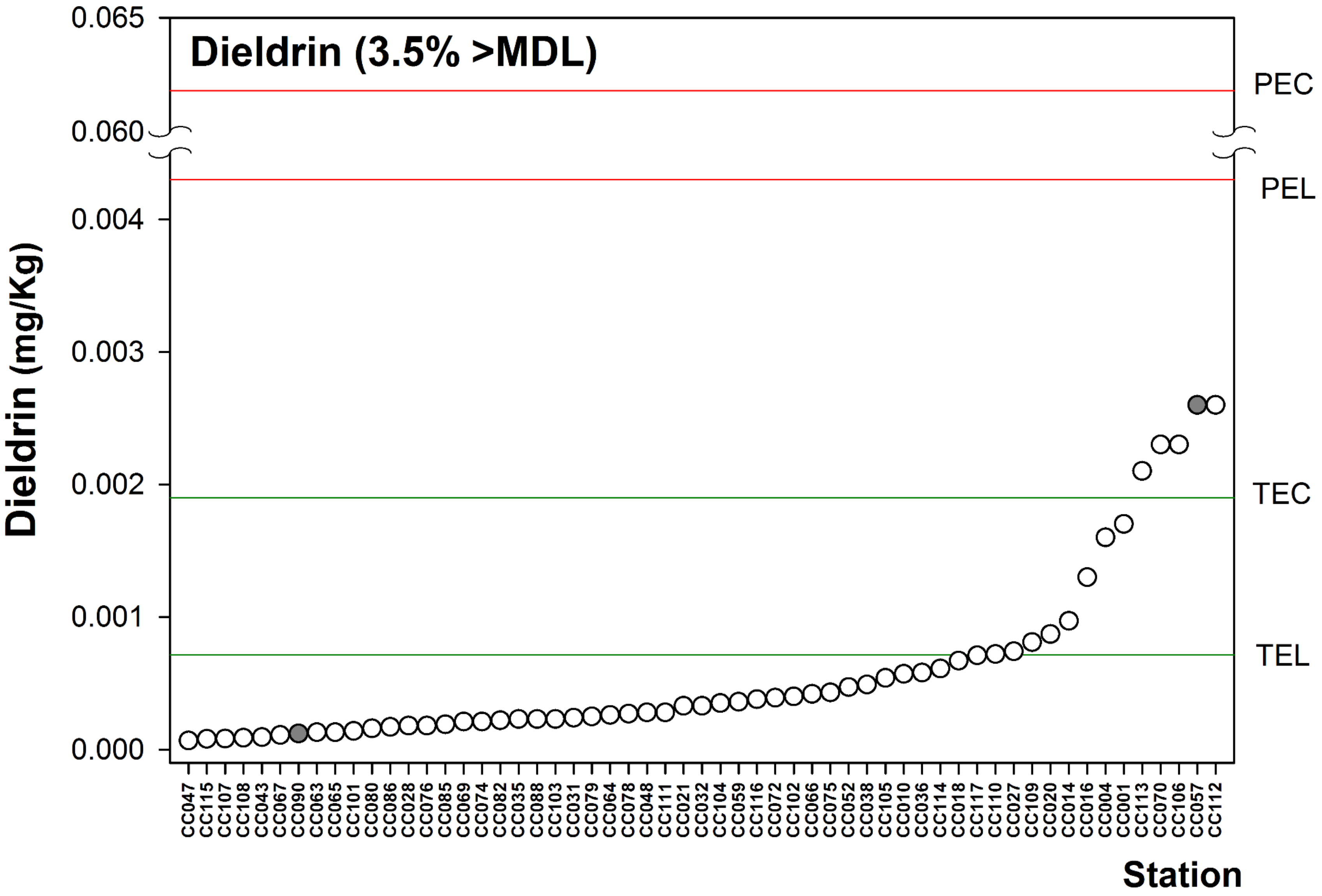

Figure 47 Concentrations of Dieldrin for Sediments in the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL; yellow circles, >TEL/TEC; red circles >PEL/PEC).

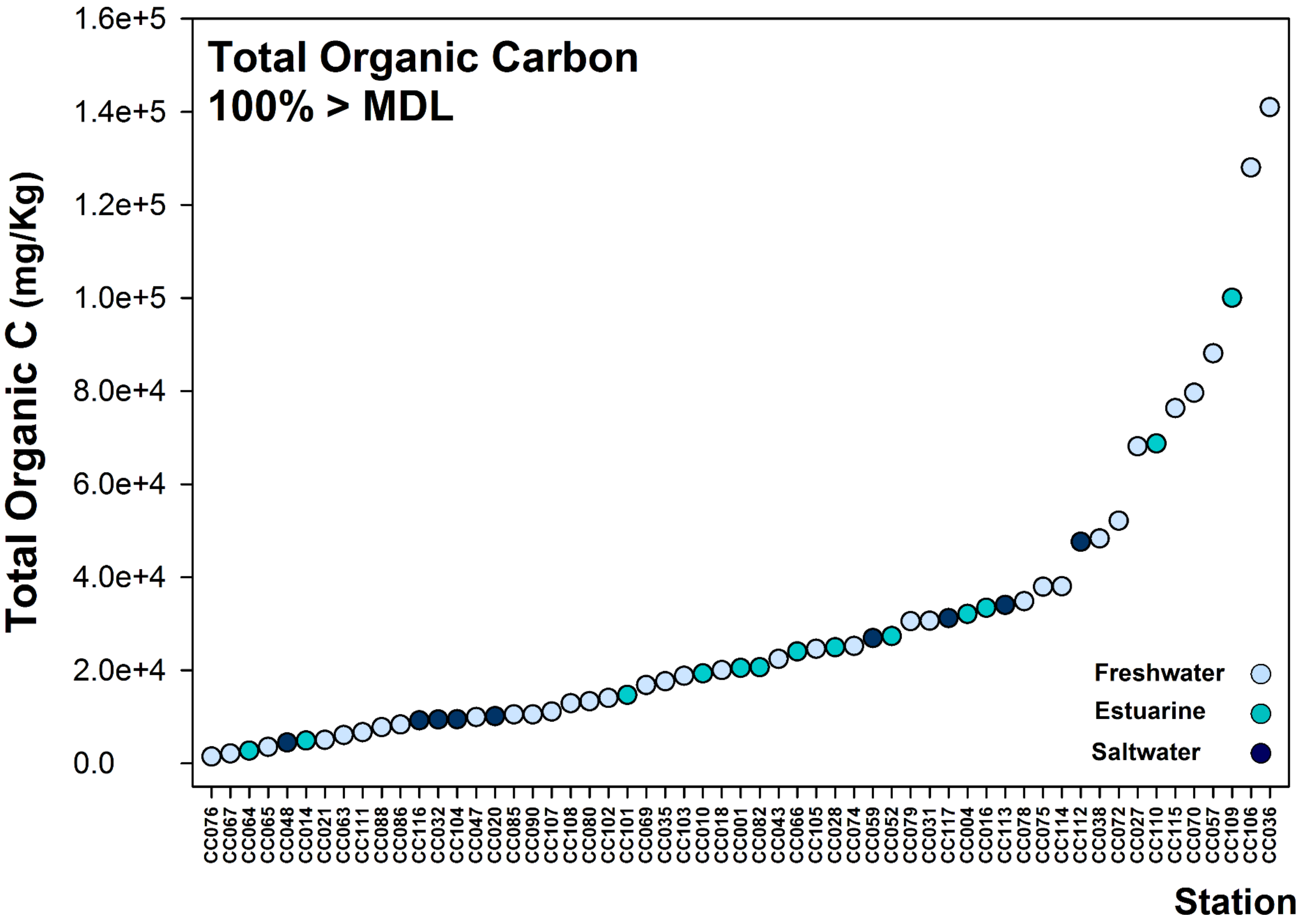

Figure 48 Concentrations of Total Organic Carbon in sediments during the 2014 Survey. Light blue circles, <0.5 PSU (freshwaters); cyan circles >0.5 PSU, <17 PSU (estuarine conditions); dark blue circles, >17 PSU (saltwater).

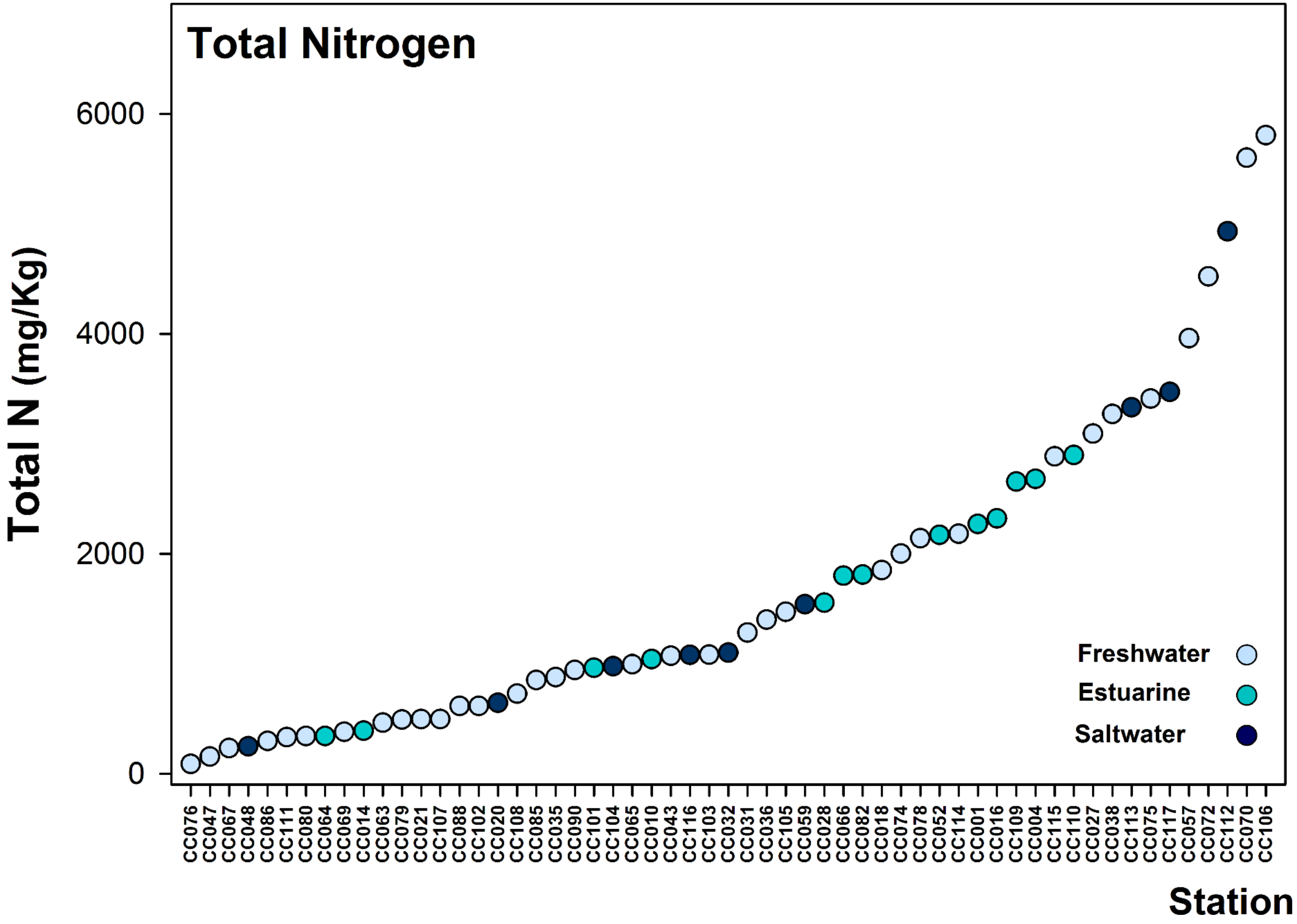

Figure 49 **Concentrations of Total Nitrogen (TKN+NOx) in sediments during the 2014 Survey. Light blue circles, <0.5 PSU (freshwaters); cyan circles >0.5 PSU, <17 PSU (estuarine conditions); dark blue circles, >17 PSU (saltwater).**

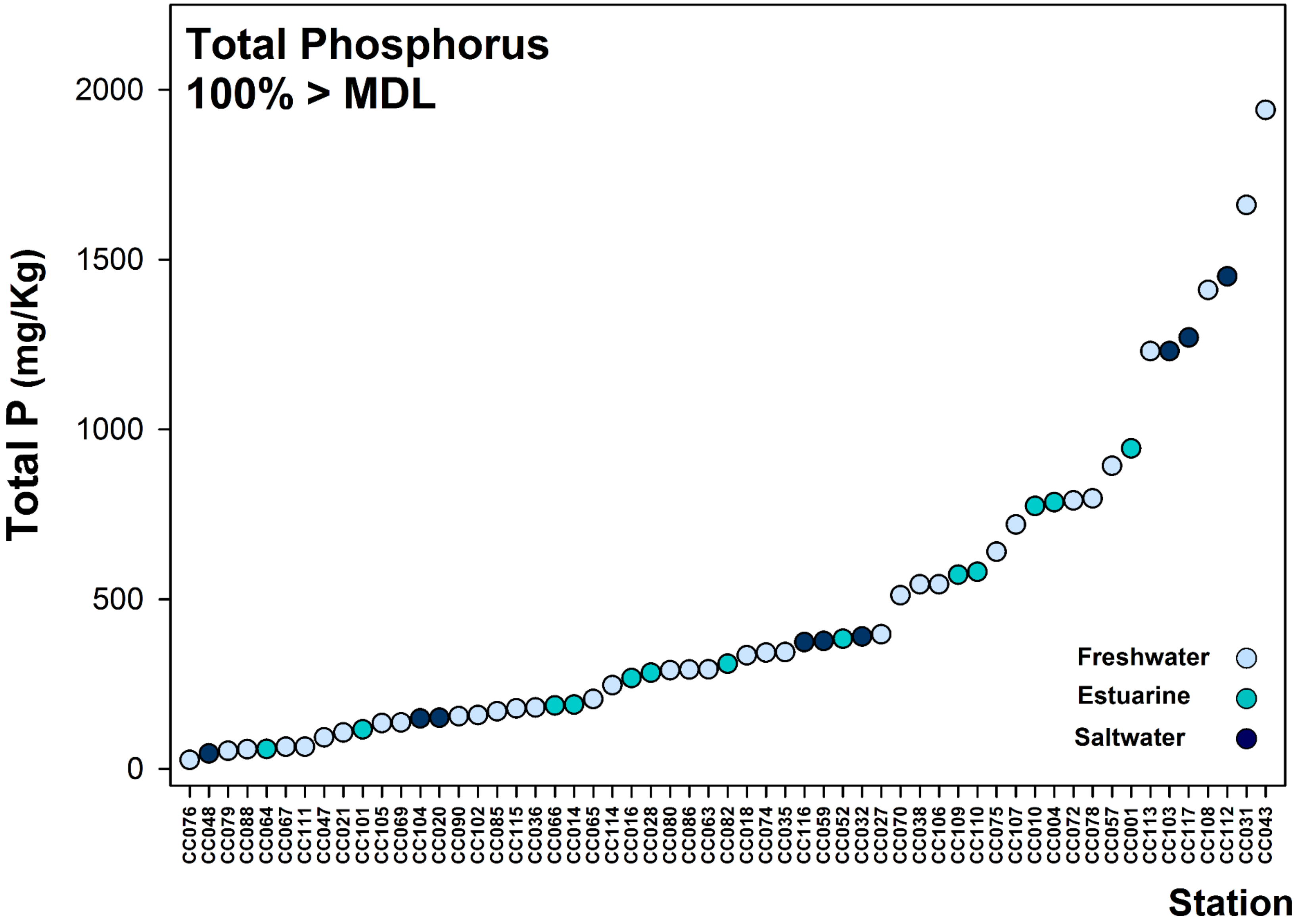

Figure 50 **Concentrations of Total Phosphorus In sediments during the 2014 Survey. Light blue circles, <0.5 PSU (freshwaters); cyan circles >0.5 PSU, <17 PSU (estuarine conditions); dark blue circles, >17 PSU (saltwater).**

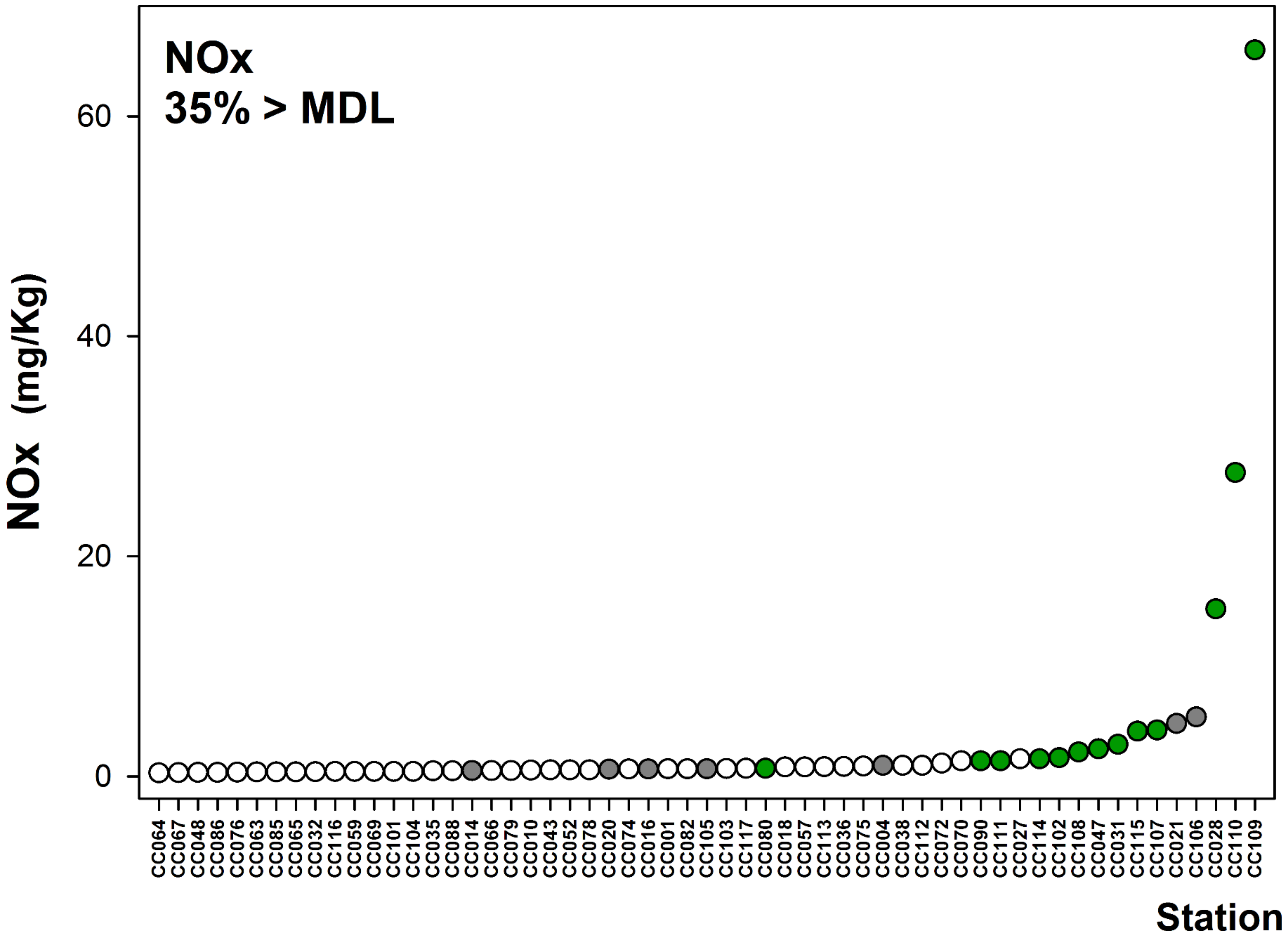

Figure 51 Concentrations of Total nitrate/nitrite (NOx) in sediments during the 2014 Survey. (Open circles, MDL; gray circles >MDL but <MRL).

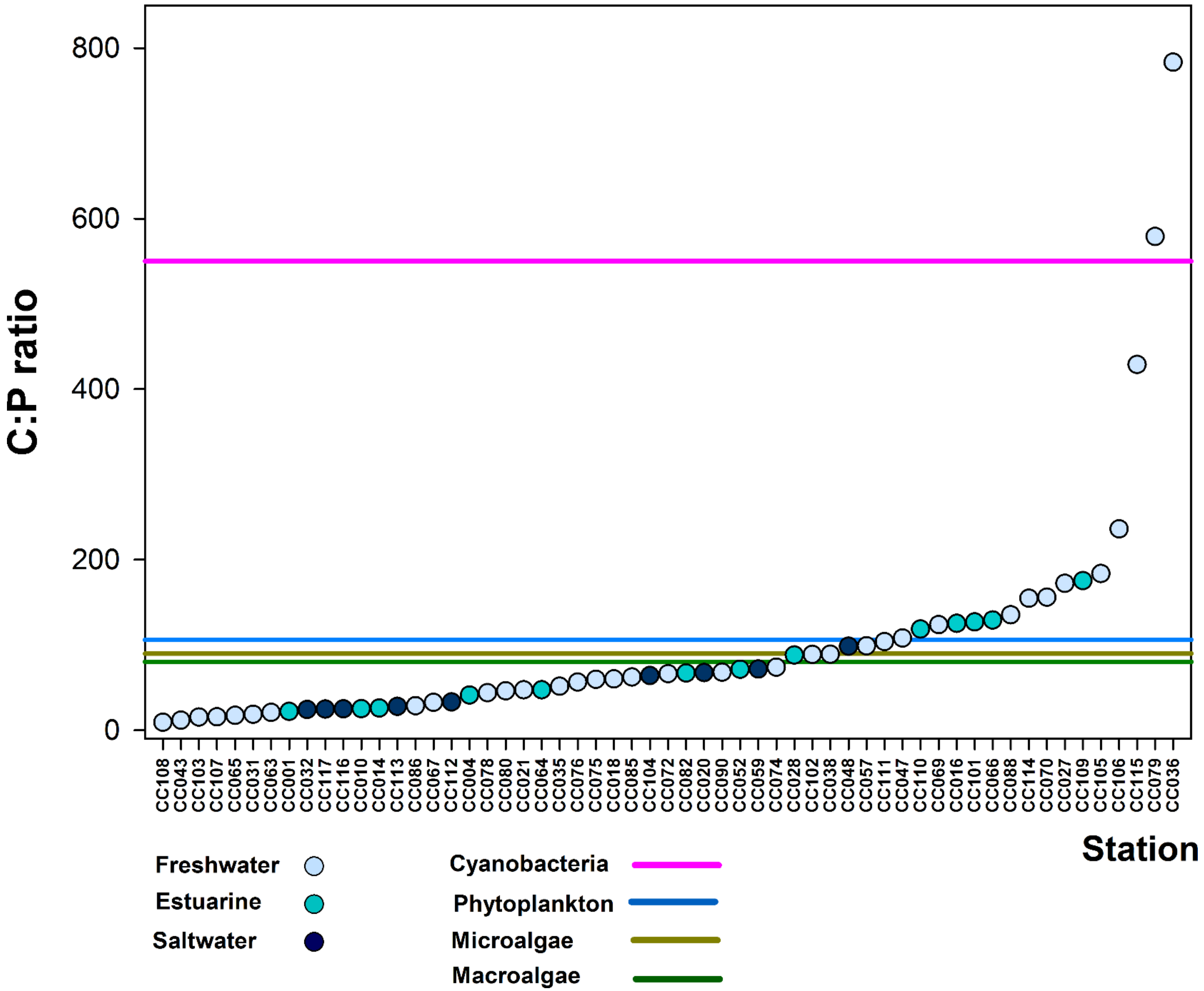

Figure 52 Ranked plot of total organic carbon to total phosphorus ratio (C:P) and comparison with signature stoichiometric ratios typically found in primary producer biomass (Sutula, 2011).

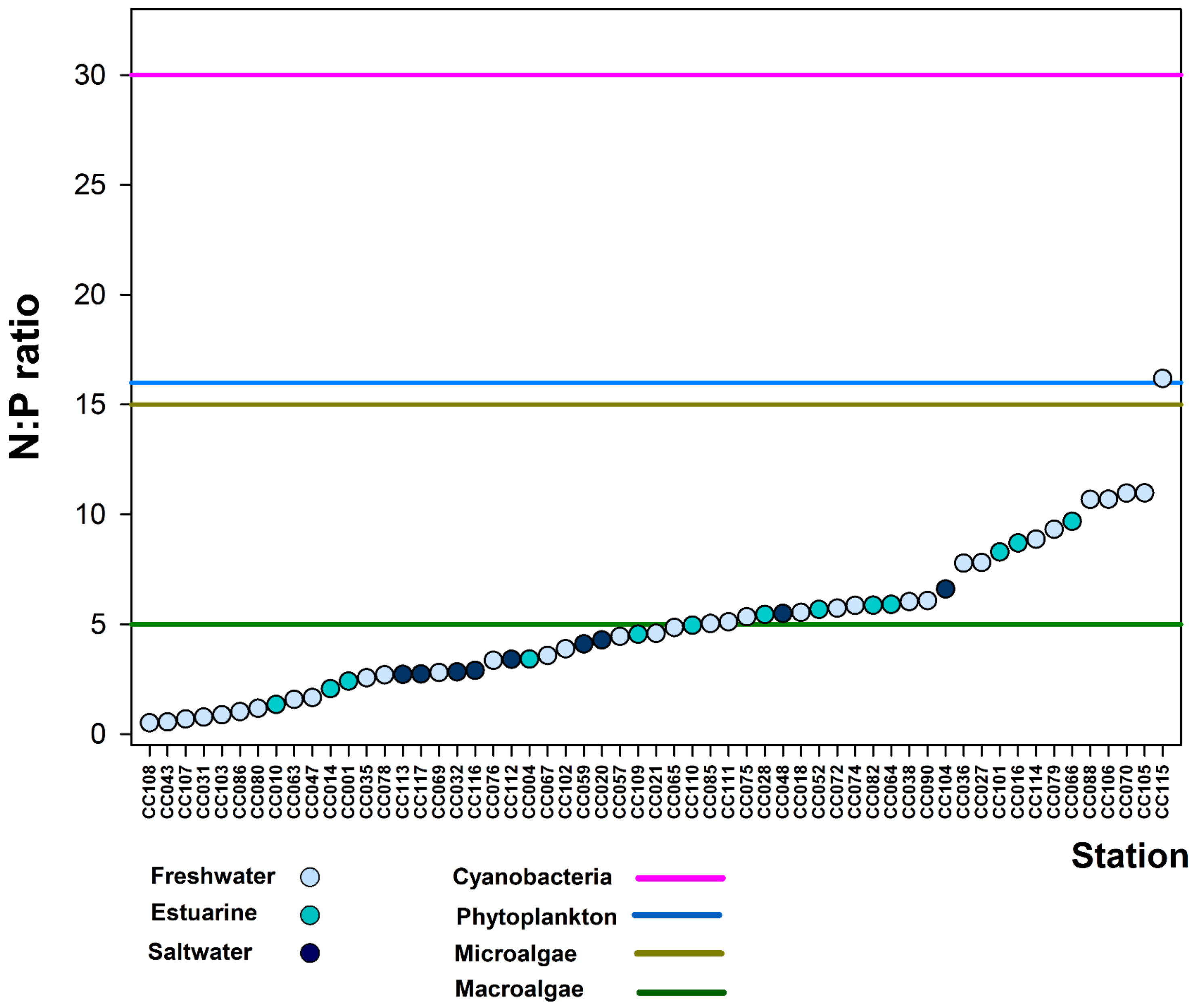

Figure 53 Ranked plot of total nitrogen to total phosphorus ratio (N:P) and comparison with signature stoichiometric ratios typically found in primary producer biomass (Sutula, 2011).

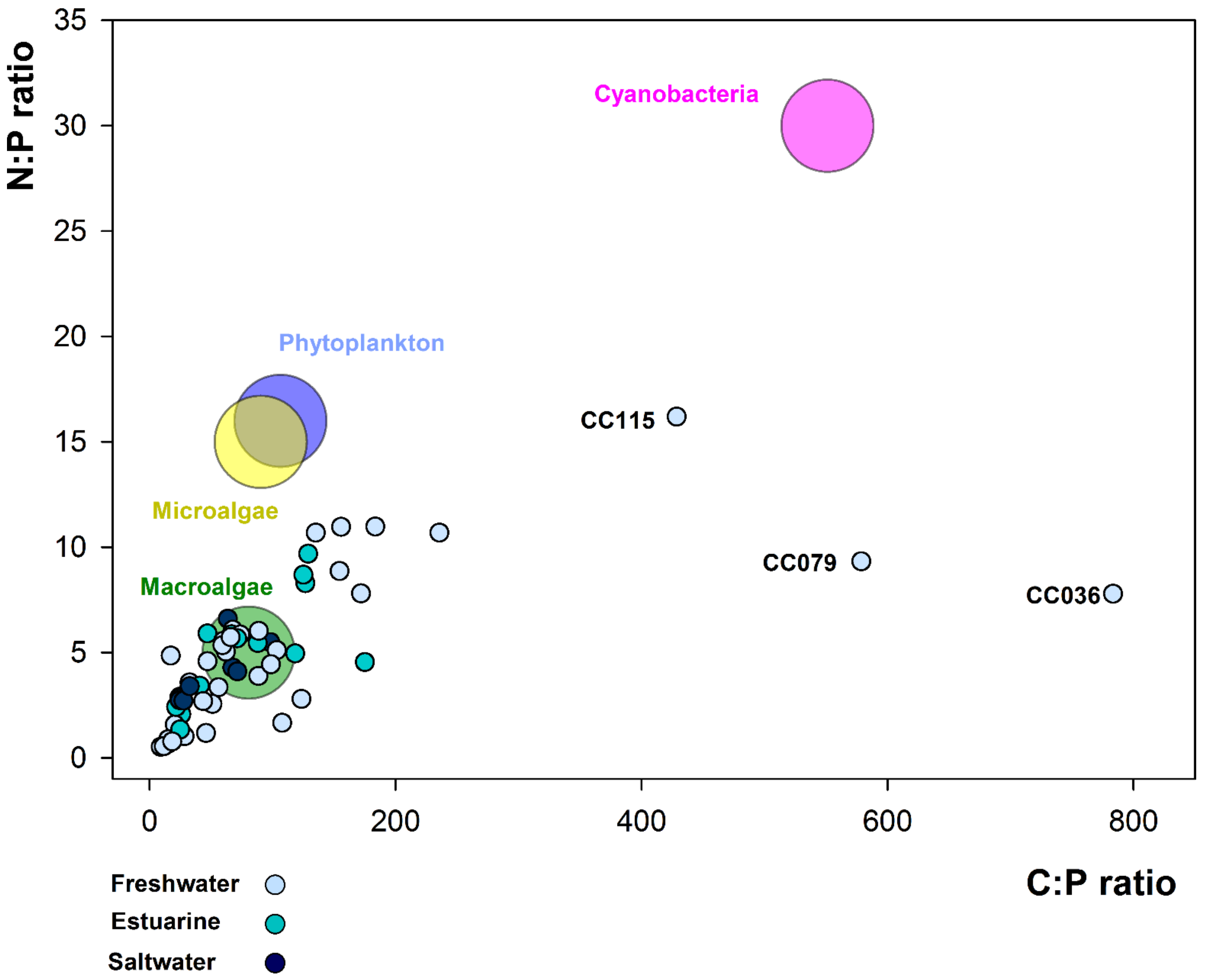

Figure 54 Scatter plot between nitrogen and carbon ratios with phosphorus (N:P vs C:P). Larger colored circles denote signature stoichiometric ratios typically found in primary producer biomass (Sutula, 2011).

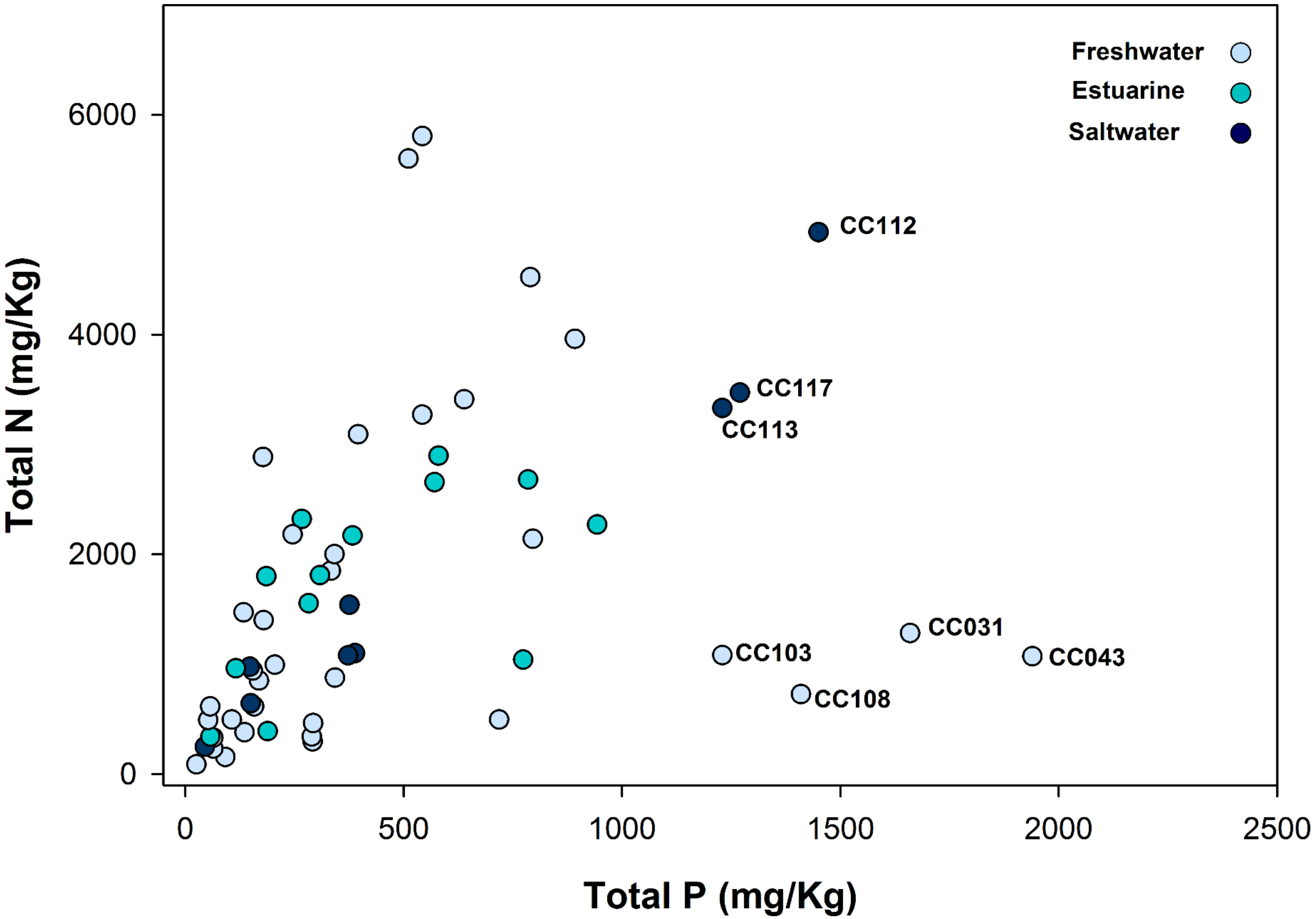

Figure 55 Scatter plot of total phosphorus vs. total nitrogen. Light blue circles, <0.5 PSU (freshwaters); cyan circles >0.5 PSU, <17 PSU (estuarine conditions); dark blue circles, >17 PSU (saltwater).

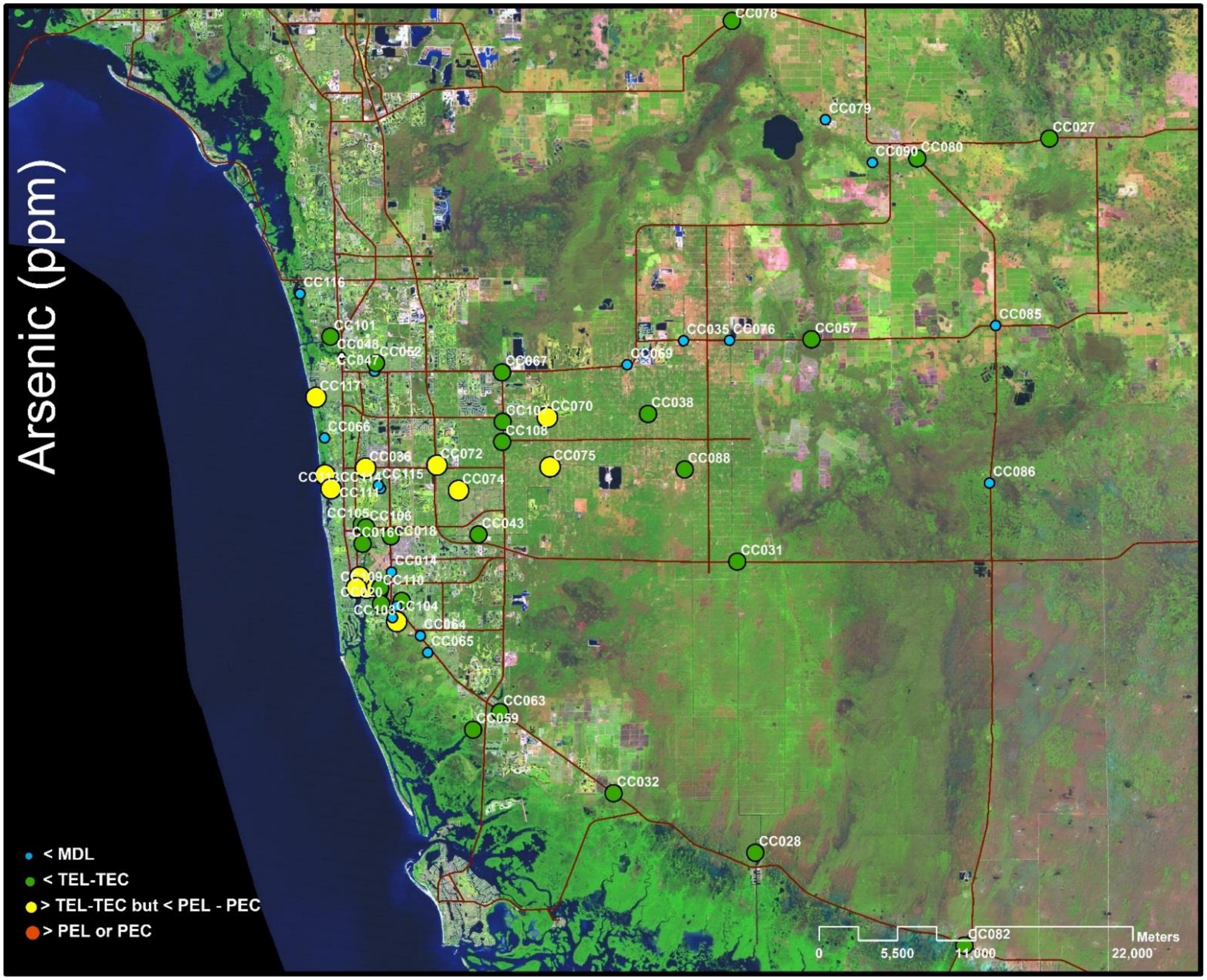

Figure 56 Distribution of Arsenic in Sediments from Collier County 2014. Exceedances of PEL/PEC values (red dots) indicate locations of probable hazardous effects on aquatic wildlife that may require remedial action.

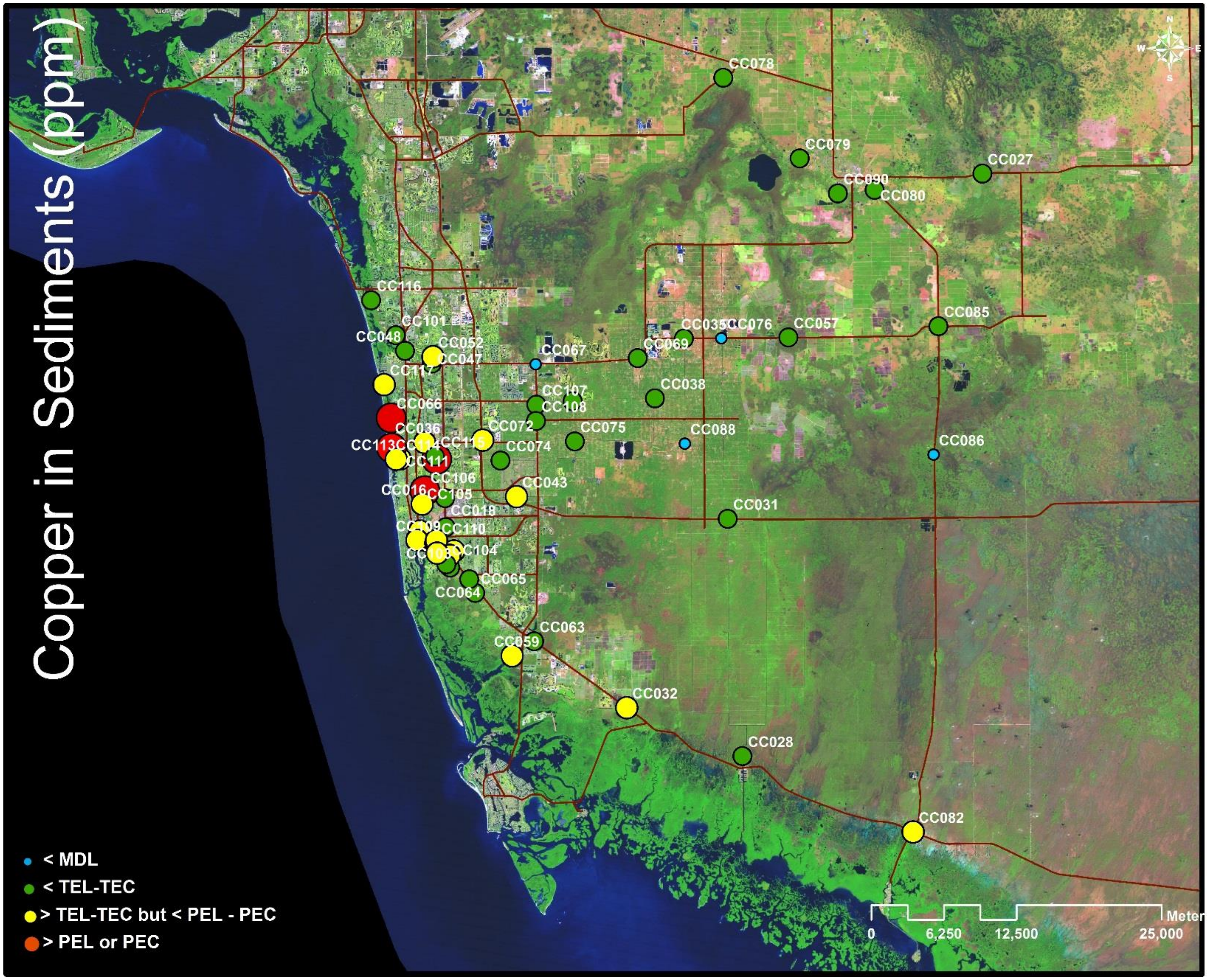

Figure 57 Distribution of Copper in Sediments from Collier County 2014. Exceedances of PEL/PEC values (red dots) indicate locations of probable hazardous effects on aquatic wildlife that may require remedial action.

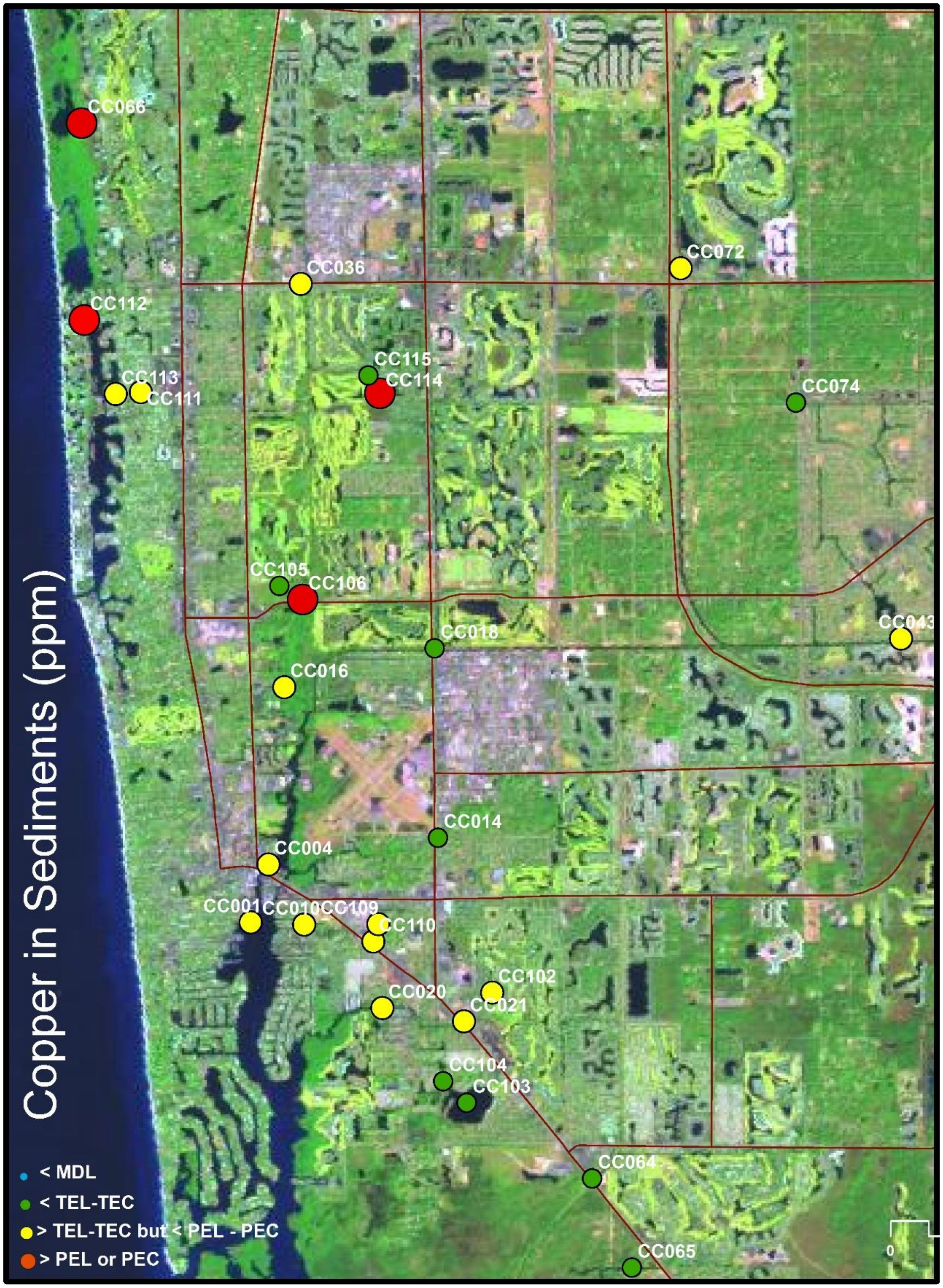

Figure 58 Distribution of Copper in sediments in urban areas of Collier County 2014. Exceedances of PEL/PEC values (red dots) indicate locations of probable hazardous effects on aquatic wildlife that may require remedial action.

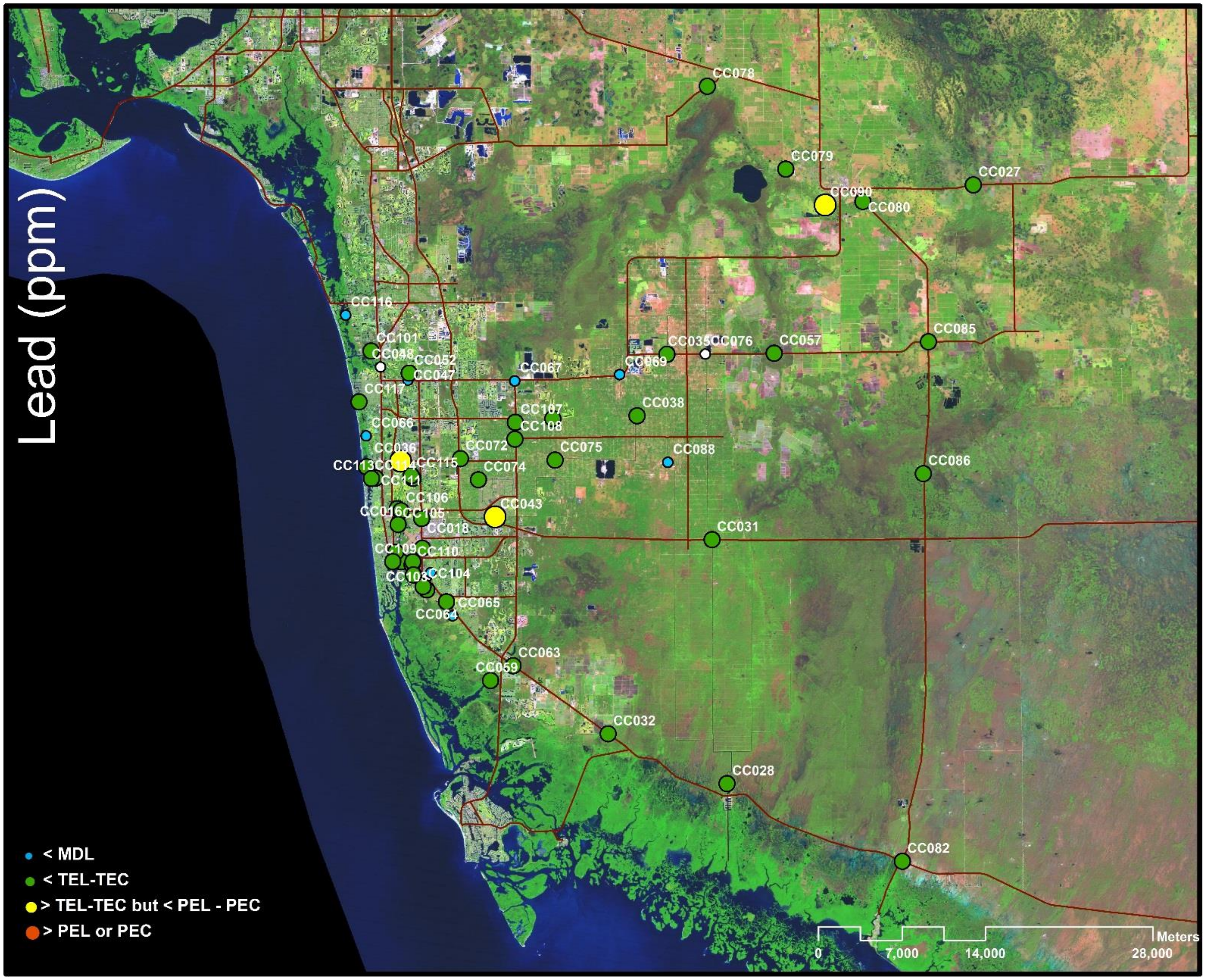

Figure 59 Distribution of Lead in Sediments from Collier County 2014. Exceedances of PEL/PEC values (red dots) indicate locations of probable hazardous effects on aquatic wildlife that may require remedial action.

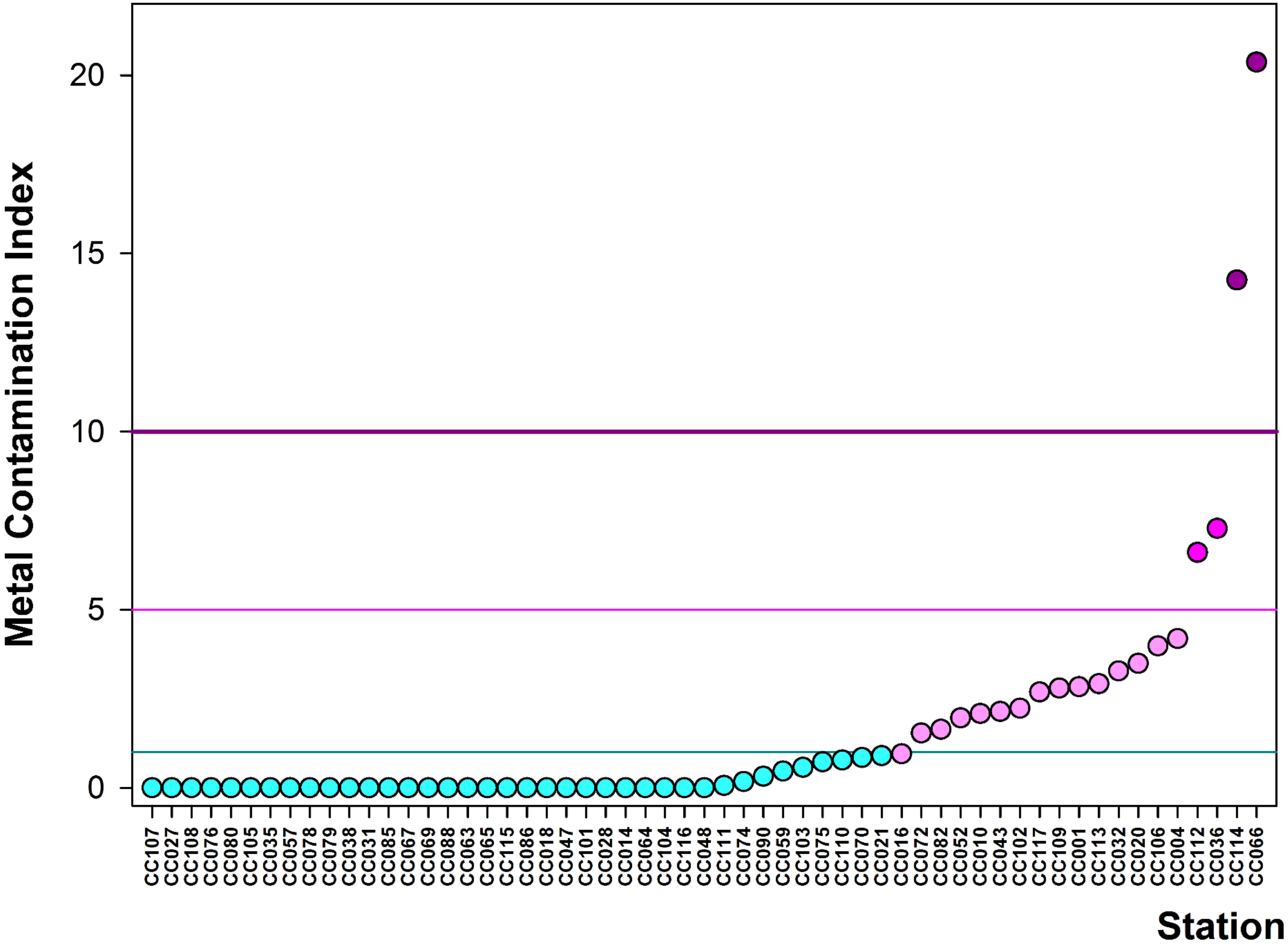

Figure 60 Ranking of sites according to their metal contamination index. Higher values denote higher possibility of hazard to aquatic life due to the combined toxicity of metals. (Cyan circles, MCi <1; Light pink, 1<MCi<5; Dark pink, 5<MCi<10; Purple MCi >10).

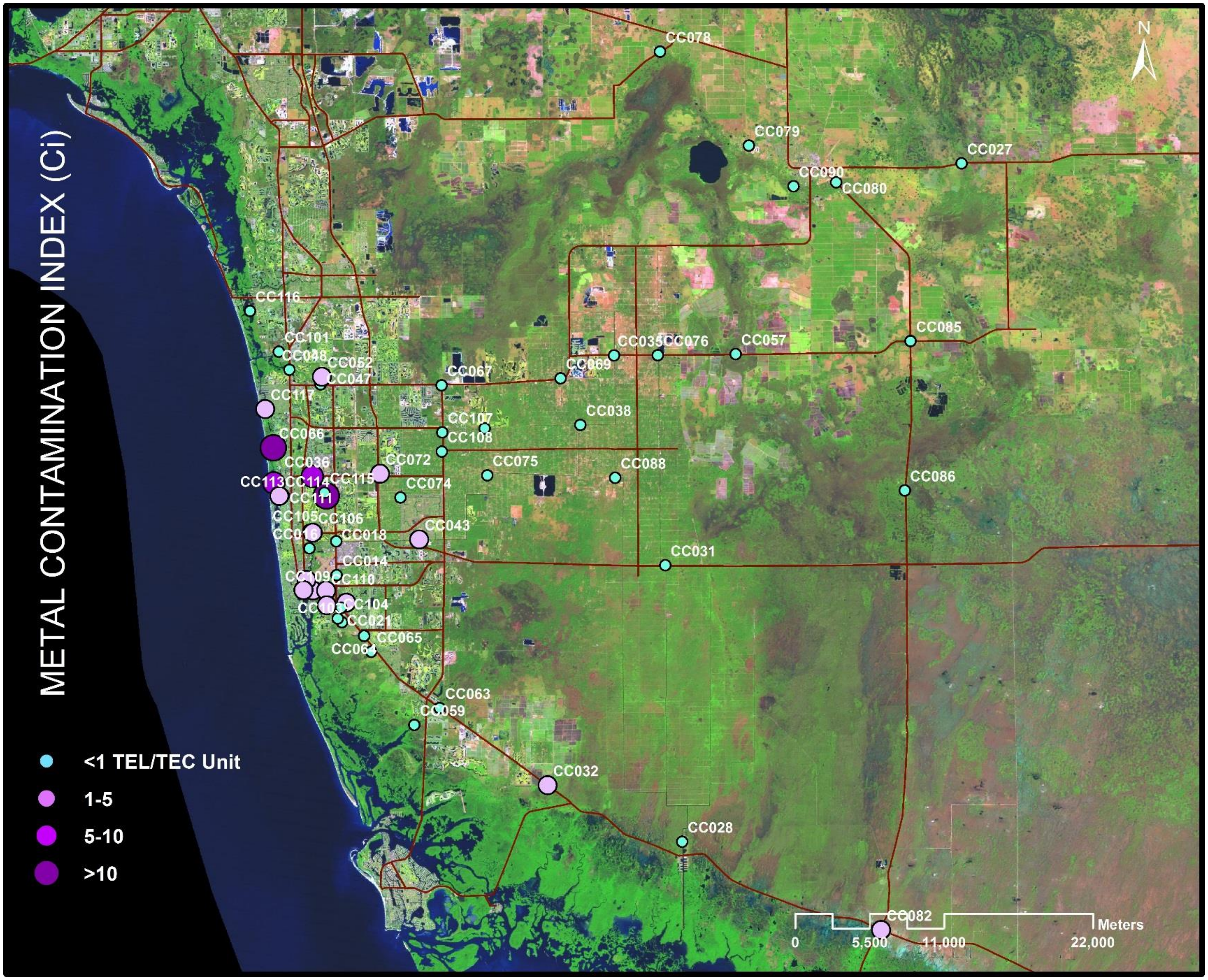

Figure 61 Metal Contamination Index (Ci) relative to TEL/TEC Sediment Quality Available Guidelines. Higher values denote higher possibility of hazard to aquatic life due to the combined toxicity of metals.

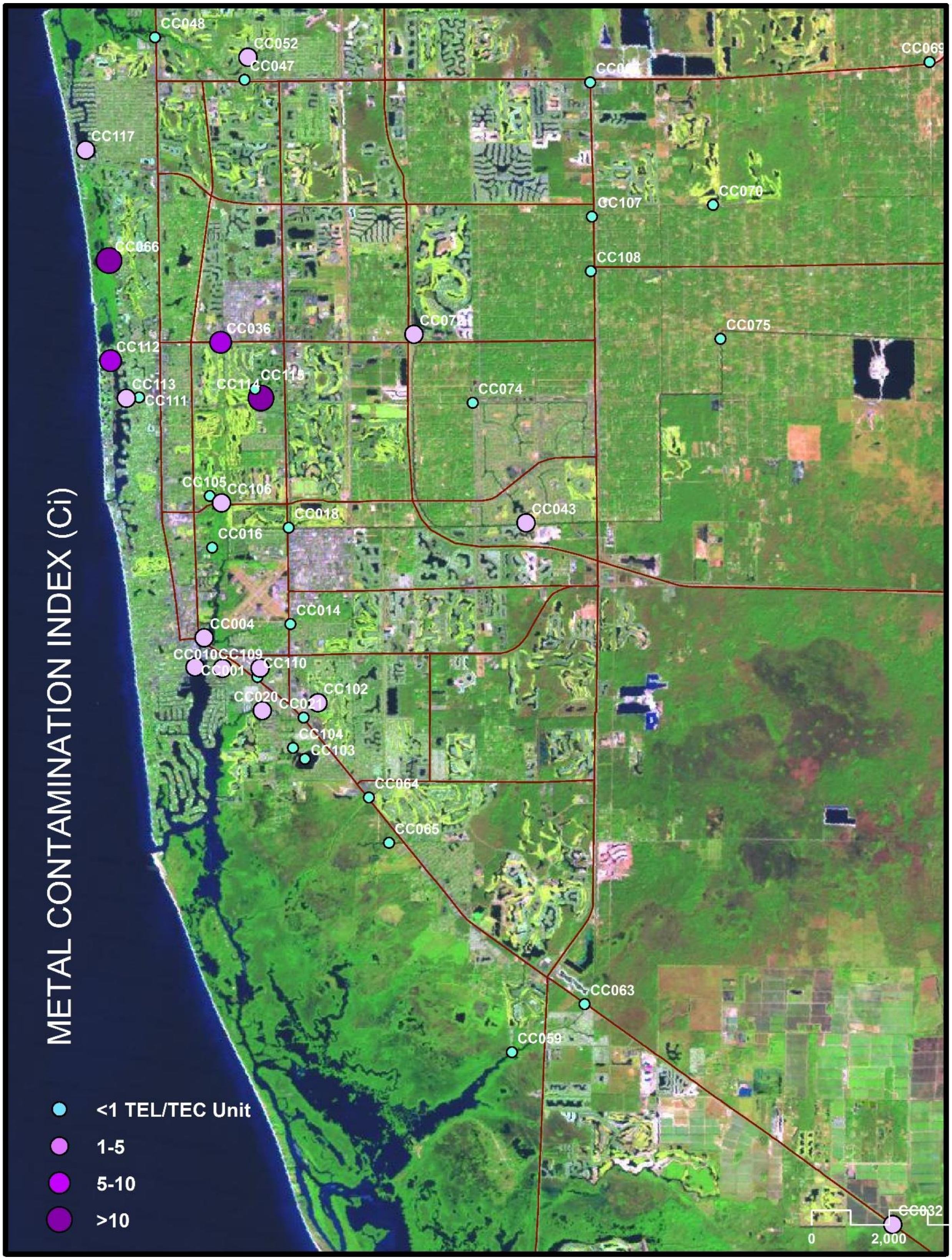

Figure 62 Metal Contamination Index (Ci) relative to TEL/TEC Sediment Quality Available Guidelines in urban areas of Collier County. Higher values denote higher possibility of hazard to aquatic life due to the combined toxicity of metals.

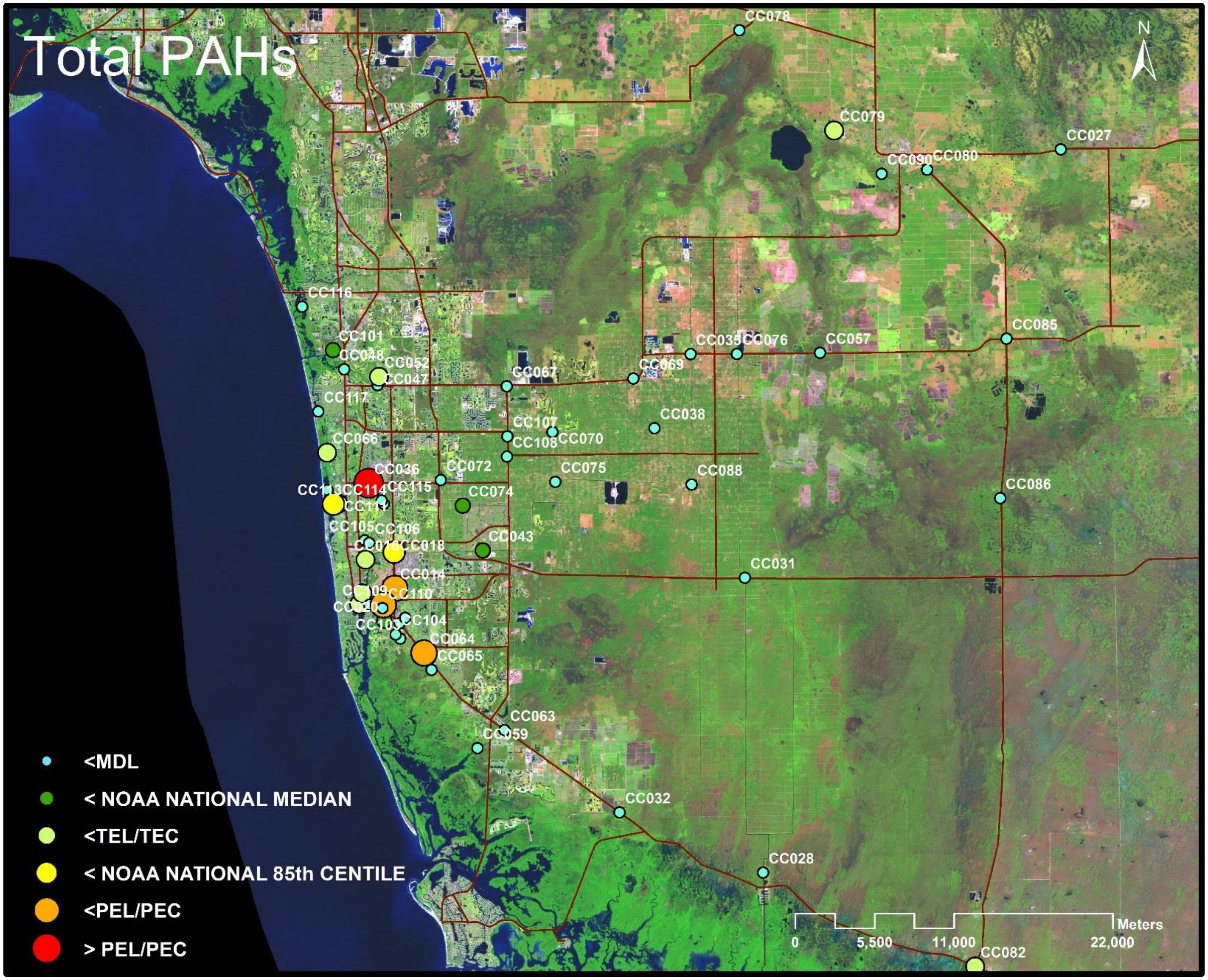

Figure 63 Distribution of concentration of Total Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments from Collier County, 2014 and comparison with NOAA national values and FDEP SQAGs. Exceedances of PEL/PEC values (red dots) indicate locations of probable hazardous effects on aquatic wildlife that may require remedial action.

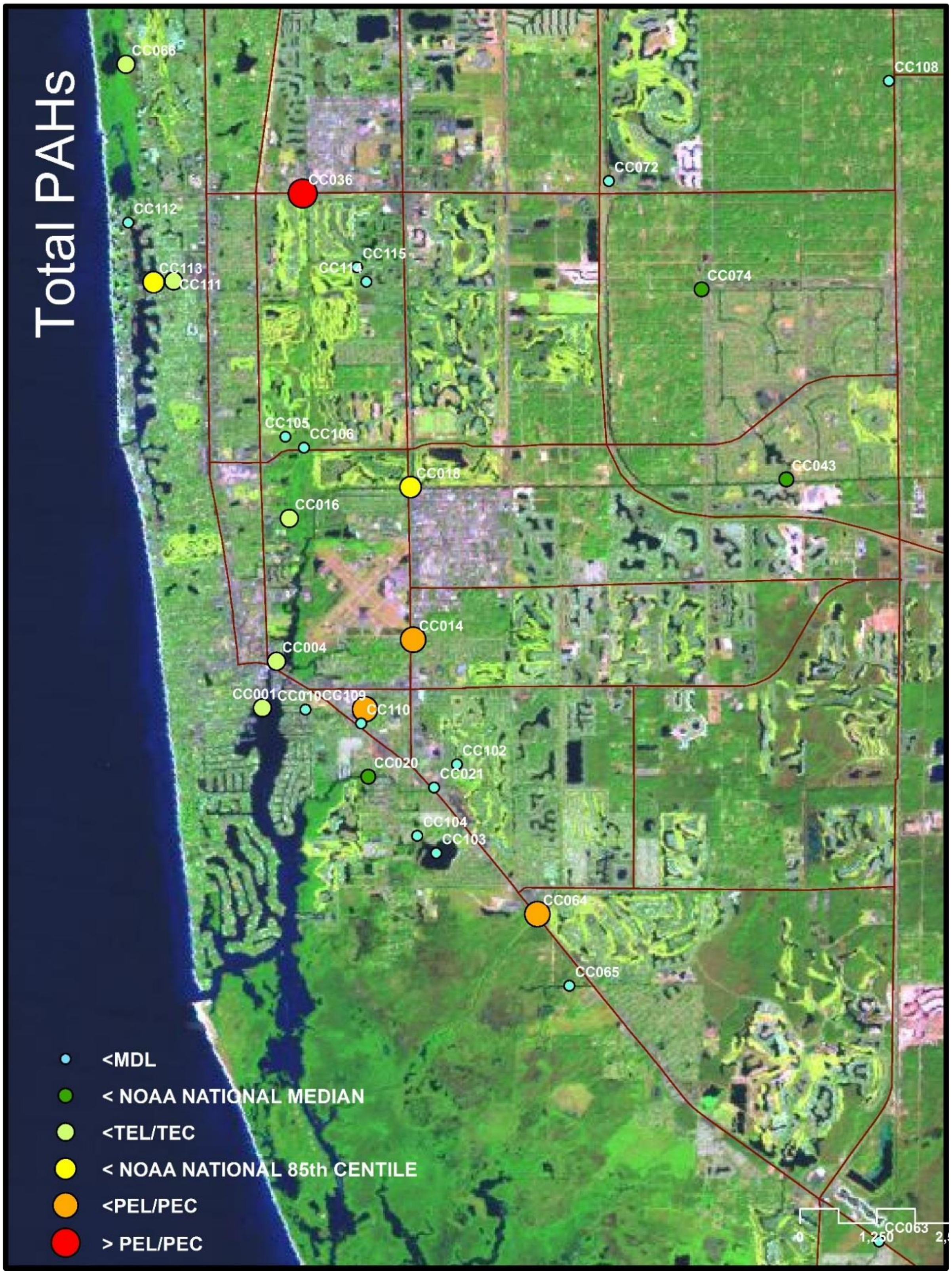

Figure 64 Detailed view of the Geographical Distribution of concentration of Total Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments from Collier County, 2014. Exceedances of PEL/PEC values (red dots) indicate locations of probable hazardous effects on aquatic wildlife that may require remedial action.

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 List of sampling stations during previous surveys

Table 7. Master List of Stations as of June 2014 including previously visited sites and new stations added for this study. 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	COLLIER ID	DESCRIPTOR	PREVIOUSLY VISITED
1	CC4	26.1422	-81.7885		DELETED	2001,
2	CC3	26.1315	-81.7904		DELETED	2001, 2007
3	CC001	26.13532	-81.79078		ACTIVE	2007
4	CC002	26.1422	-81.7885		DELETED	2007
5	CC003	26.13777	-81.7881		DELETED	2007
6	CC004	26.14071	-81.78641	GORD60	ACTIVE	2007
7	CC005	26.13859	-81.79009		DELETED	2007
8	CC006	26.14066	-81.7888		DELETED	2007
9	CC007	26.15072	-81.78898	NEW	DELETED	2007
10	CC008	26.14729	-81.78534		DELETED	2007
11	CC009	26.15216	-81.78552	GORD70	DELETED	2007
12	CC010	26.13508	-81.78374		ACTIVE	2007
13	CC011	26.11578	-81.79683	NBAYLLO	DELETED	2007
14	CC012	26.13306	-81.79197	NBAYNL	DELETED	2007
15	CC013	26.14237	-81.78275	ROCK62	DELETED	2007
16	CC014	26.14549	-81.7662	ROCKE	ACTIVE	2007
17	CC015	26.15824	-81.78468		DELETED	2007
18	CC016	26.16328	-81.78654	BC3	ACTIVE	2007
19	CC017	26.16791	-81.77542	BC4	DELETED	2007
20	CC018	26.16801	-81.76677	GGCAT31	ACTIVE	2007
21	CC019	26.12123	-81.78453	HALDNB	DELETED	2007
22	CC020	26.12524	-81.77338		ACTIVE	2007
23	CC021	26.1237	-81.76263	HALDCRK	ACTIVE	2007
24	CC022	26.12354	-81.75488		DELETED	2007
25	CC023	26.15617	-81.66172	LANDFILL	DELETED	2007
26	CC024	26.15193	-81.68619	HEND951	DELETED	2007
27	CC025	26.43267	-81.48303		DELETED	2007
28	CC026	26.43031	-81.41145	IMKMAD	DELETED	
29	CC027	26.42189	-81.30499	OKALA846	ACTIVE	2007
30	CC028	25.96871	-81.50995	FAKA	ACTIVE	2007
31	CC029	25.99276	-81.52181	BC8	DELETED	2007
32	CC030	25.9935	-81.49049	BC7	DELETED	2007
33	CC031	26.15314	-81.5234	BC10	ACTIVE	2007
34	CC032	26.00599	-81.60958	TOMATO41	ACTIVE	2007
35	CC033	26.32332	-81.5624		DELETED	2007
36	CC034	26.1738	81.78461	GORDONRIV	DELETED	
37	CC035	26.29298	-81.56184	GGC@858	ACTIVE	2007
38	CC036	26.21121	-81.7847	GRE896	ACTIVE	2007
39	CC037	26.27745	-81.58108	ORANGETR	DELETED	2007
40	CC038	26.24648	-81.58662		ACTIVE	2007
41	CC039	26.28197	-81.77011	COC@IBIS	DELETED	2007
42	CC040	26.19975	-81.67088		DELETED	2007
43	CC041	26.16944	-81.68647	BC23	DELETED	2007
44	CC042	26.19881	-81.70361	GGC14	DELETED	2007
45	CC043	26.16947	-81.70534		ACTIVE	2007
46	CC044	26.17397	-81.73378	D2886	DELETED	2007
47	CC045	26.18815	-81.75135		DELETED	
48	CC046	26.18.138	-81.77896		DELETED	2007
49	CC047	26.27256	-81.77896	BC14	ACTIVE	2007
50	CC048	26.28233	-81.80217	COCAT41	ACTIVE	2007
51	CC049	26.27254	-81.8238		DELETED	2007
52	CC050	26.21144	-81.76818	ARS@896	DELETED	2007
53	CC051	26.27335	-81.73502	QUAILCK	DELETED	2007
54	CC052	26.2778	-81.77806	COCPALM	ACTIVE	2007

55	CC053	26.29197	-81.60999		DELETED	2007
56	CC054	26.29576	-81.36715		DELETED	2007
57	CC055	26.35306	-81.41647		DELETED	2007
58	CC056	26.31824	-81.49525		DELETED	2007
59	CC057	26.29362	-81.47939		ACTIVE	2007
60	CC058	26.0519	-81.69503		DELETED	2007
61	CC059	26.04579	-81.70829		ACTIVE	2007
62	CC060	26.05165	-81.70764		DELETED	2007
63	CC061	26.06678	-81.70539		DELETED	2007
64	CC062	26.13902	-81.73854		DELETED	2007
65	CC063	26.05711	-81.68955	BC22	ACTIVE	2007
66	CC064	26.10511	-81.74562		ACTIVE	2007
67	CC065	26.09456	-81.74034		ACTIVE	2007
68	CC066	26.23021	-81.81342		ACTIVE	2007
69	CC067	26.27242	-81.68936	BC26	ACTIVE	2007
70	CC068	26.27339	-81.62567	PIPERS	DELETED	2007
71	CC069	26.27758	-81.60144	CORK@846	ACTIVE	2007
72	CC070	26.24392	-81.65736		ACTIVE	2007
73	CC071	26.22681	-81.73572		DELETED	2007
74	CC072	26.21333	-81.73465		ACTIVE	2007
75	CC073	26.20631	-81.73536		DELETED	2007
76	CC074	26.19744	-81.71936	GREEN@SB	ACTIVE	2007
77	CC075	26.21266	-81.65528	GGC@WHITE	ACTIVE	2007
78	CC076	26.29333	-81.52965	FAKA858	ACTIVE	2007
79	CC077	26.33811	-81.52983		DELETED	2007
80	CC078	26.49581	-81.52881	CORKSCRD	ACTIVE	2007
81	CC079	26.43337	-81.4626	IMKFSHCK	ACTIVE	2007
82	CC080	26.40906	-81.39782	IMKBRN	ACTIVE	2007
83	CC081	26.19712	-81.49058		DELETED	2007
84	CC082	25.90977	-81.36348	BARRIVN	ACTIVE	2007
85	CC083	25.96768	-81.53566		DELETED	2007
86	CC084	25.95592	-81.48867		DELETED	2007
87	CC085	26.30328	-81.34243	BRN	ACTIVE	2007
88	CC086	26.20352	-81.34646	BC24	ACTIVE	2007
89	CC087	26.15239	-81.55512	BC9	DELETED	2007
90	CC088	26.21141	-81.56065		ACTIVE	2007
91	CC089	26.29459	-81.41619		DELETED	2007
92	CC090	26.40632	-81.42966	IMKSLGH	ACTIVE	2007
93	CC101	26.29435	-81.81007	WIGGINSBY	NEW	
94	CC102	26.12714	-81.75893	GLADESCC	NEW	
95	CC103	26.11403	-81.76221	AVALON	NEW	
96	CC104	26.11657	-81.76533	AVALOUT	NEW	
97	CC105	26.17532	-81.78729	FREEDOMPK	NEW	
98	CC106	26.17372	-81.78422	GORDONRIV	NEW	
99	CC107	26.24105	-81.68871	FLOATIS	NEW	
100	CC108	26.22832	-81.68893	CONTROL	NEW	
101	CC109	26.13520	-81.77399	GATEWAY	NEW	
102	CC110	26.13311	-81.77462	GATEOUT	NEW	
103	CC111	26.19822	-81.80569	SWANLAKE	NEW	
104	CC112	26.20675	-81.81320	MOORCLAM	NEW	
105	CC113	26.19800	-81.80900	SWANOUT	NEW	
106	CC115	26.19827	-81.77419	PINEOUT	NEW	
107	CC115	26.20037	-81.77571	PINEWOOD	NEW	
108	CC116	26.32140	-81.83161	LHICKBAY	NEW	
109	CC117	26.25591	-81.81995	VBILTOUT	NEW	

APPENDIX IV **Supporting information**

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