

**BIOMONITORING STUDY OF LYONS CREEK EAST,
WELLAND, ONTARIO.
2002-2003**

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Executive Summary

Previous studies conducted on Lyons Creek East, from as early as 1978, have indicated elevated levels of PCBs in the sediment, and detrimental effects on the biota in the creek. The sediments from the upper portion of the creek have been shown to be highly contaminated with both PCBs and metals.

The study was undertaken jointly with Environment Canada to address and document sediment and water quality in the creek. The study was conducted in two parts: an initial sediment screening survey was conducted in September 2002 to identify areas of elevated sediment contamination (particularly PCBs), and delineate the area of concern. The second, more detailed part of the study included sediment core sampling to identify historical changes in contaminant levels in the sediment, caged mussel surveys to identify PCB uptake from the water column, and fish collections (forage and sport fish) to identify uptake and bioaccumulation of PCBs. The detailed portion of the study was conducted in October 2002 and October 2003.

The initial sediment survey indicated that PCB concentrations were elevated above the Provincial Sediment Quality Guideline Lowest Effect Level criterion on 70ng/g in most of Lyons Creek East, particularly in the upper portion of Lyons Creek. Concentrations were highest in the vicinity of Highway 140 (19000ng/g), and declined considerably downstream. Cluster analysis of the sediment chemistry suggested a change in the overall sediment chemistry which reflected the overall land use: upstream of Highway 140, sediments were high in PCBs and metals indicative of industry, whereas more downstream the sediment chemistry suggested agricultural land use with sediments higher in pesticides and nutrients. Based on these data, the detailed study focused primarily of the upper reaches of the creek.

The detailed study indicated that PCB contamination in the upper portion of Lyons Creek is elevated in all media (i.e. sediment, mussels, forage fish and sport fish), and concentrations in all media exceeded their respective guidelines at more than one location. The data suggest that the extremely high levels of PCBs observed in the upstream sediments are mobile, bioavailable to the biota, and may potentially be toxic to sediment dwelling organisms. Elevated levels were observed in the sediments as far downstream as Doan's Ridge Road. The tissue data from mussels, forage fish and sport fish suggest that the PCBs only tend to be bioaccumulated at levels that are potentially of concern upstream of Highway 140. The extent of PCB contamination in the biota appears to be relatively localized and does not appear to extend to the Niagara River.

The prominent congener pattern in the sediment closely resembles that of aroclor 1248. No obvious source of PCBs in this area was identified. However, the similar homologue patterns in the sediment at the most upstream location, compared to that observed further downstream suggests that, although PCB contamination is primarily downstream of the Welland-pipe property, a previous upstream source exists.

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1 BACKGROUND

In the 1970's, 42 locations in the Great Lakes were identified as "problem areas" by the International Joint Commission (IJC), having aquatic environments that were severely degraded. Of these, 17 were along Canadian lakeshores or in rivers shared by Canada and the U.S. In 1985, the IJC Great Lakes Water Quality Board recommended a Remedial Action Plan (RAP) be developed and implemented for each problem area. The goal of the RAP is to restore the "beneficial uses" of the aquatic ecosystem in each problem area, which were now called "Areas of Concern: (AOCs). One of the areas identified by the IJC as impaired was the Niagara River, and in 1987 Canada and the U.S. signed a joint agreement whereby each country pledged their commitment to restore the environmental integrity of these waters.

Since the early 1900's the Niagara River watershed has shown signs of significant water pollution problems. Increased population, industry and agriculture in the Niagara River watershed have subjected the river to excessive levels of pollutants, such as high levels of bacteria, oil, phosphorus, chlorine, phenols, PCBs and mercury. As part of the Niagara River RAP, tributaries of the river, including Lyons Creek, were identified as part of the river's AOCs. This consideration provides a more consistent ecosystem approach.

In 1999 the Ministry of the Environment (MOE), Environment Canada (EC) and the Niagara Peninsula Conservation Authority (NPCA) entered into an agreement under which the NPCA initiates and co-ordinates activities for the continued development and implementation of the Niagara River RAP.

1.1 Introduction

The headwaters of Lyons Creek originate in the Wainfleet Marsh, and historically drained the southerly section of the Municipality of Welland near Dain City, flowing north-east to the Welland River, discharging to the Niagara River near Chippawa. After the construction of the Welland Ship Canal Bypass in the 1960's, Lyons Creek was bisected in two by the canal. One condition of the canal's construction was that the portion of Lyons Creek downstream of the canal (Lyons Creek East) would have its flow maintained by pumping water from the canal into the creek at a rate that would maintain the original integrity of the creek. Flow from the original headwaters now outlets to the Welland Canal on the west side.

A study of sediments from the west side of Lyons Creek (Environmental Strategies Ltd., 1992), shortly after a spill of PCB oil from the Ontario Hydro Crowland Transformer in May of 1990, indicated elevated levels of PCBs in the sediments. Two types of aroclor were predominant (aroclor 1248 and 1254),

along with trace amounts of aroclor 1260. Aroclors 1248 and 1254 may be the byproduct from the de-chlorination of the more highly chlorinated PCBs, however this process is slow. Due to the possibility that the observed PCB pollution may have occurred prior to the construction of the Welland Ship Canal Bypass, and hence the bisection of Lyons Creek, an extensive study of the east side of Lyons Creek was proposed.

Previous studies, dating from as early as 1978 (Acres, 1978; MOE, 1997; Bedard & Petro, 1998; Boyd et al, unpublished) have shown evidence of elevated levels of PCBs in the sediment and detrimental effects on biota in the creek. The sediments in the upper reaches of Lyons Creek East have been shown to be highly contaminated with metals and PCBs. Elevated nutrient levels have also been observed in the sediments.

In response to a Regional Request initially made by the West Central Regional office of the MOE in 2002, Biomonitoring Section of EMRB, in partnership with the National Water Research Institute (NWRI) of Environment Canada, undertook a site assessment of Lyons Creek East in the late summer/ fall of 2002 and 2003. The study was conducted in two parts. An initial sediment screening survey was conducted on the 29th and 30th September 2002; the objectives were to identify areas of elevated sediment contamination (particularly PCBs), and from this delineate the area of concern, from which locations for more detailed work could be selected. The second part of the study included: sediment core sampling, to identify historical changes in contaminant levels in the sediments; caged mussel surveys, to identify uptake of PCBs from the water column; fish collections (both young-of-year and sport fish) and benthic studies, to identify uptake, bioaccumulation and biomagnification of PCBs. Benthic community structure and sediment toxicity studies were also conducted. The detailed survey was undertaken from the 21st to 24th October 2002 and 6th to 10th October 2003.

2. INITIAL SCREENING SURVEY

2.1 Objectives

The objectives of the initial sediment screening survey were to identify areas of elevated sediment contamination (particularly PCBs), and from this delineate the area of concern and select locations for further, more detailed studies.

2.2 Study Design

Depositional areas with fine silty sediment were targeted for sediment collection. A total of thirty-nine surficial sediment samples were collected from the Lyons

Creek system (Figure 1), focusing mainly on the area between the Lyons Creek pumping station at the Welland Canal to Highway 140 (17 sites). The remaining sites were from downstream of Highway 140, at the C.N. railway tracks to downstream of the QEW. Duplicate samples were collected from two of the stations for QA/QC purposes. The sediment was collected from a flat-bottomed pontoon boat using a Mini-Ponar. Three grab samples were collected from each location, the surface 10cm of each grab retained and homogenized. The sediment samples were sent to the MOE laboratories in Toronto for analysis of PCBs, metals, organochlorines (OCs), PAHs, grain size, and organic content (MOE1993a).

2.3 Data Analysis

Sediment concentrations of the various chemical parameters measured were compared, where applicable, to the Provincial Sediment Quality Guidelines (PSQG) lowest effect level (LEL) and severe effect level (SEL) criteria (MOE, 1993b). The LEL criteria indicate the level of contaminant that can be tolerated by the majority of organisms. The SEL is the level of contamination at which a pronounced disturbance of the sediment-dwelling community can be expected; this is the sediment concentration of a compound that would be detrimental to the majority of benthic species.

Multivariate analyses, such as clustering and ordination were also considered. The primary purpose of clustering was to create groups or 'clusters' in such a way that the sediment chemistry relationships varied most between the groups and least within the groups. The sites were clustered using agglomerative clustering techniques, in which clustering analysis starts with a single sample location/event and agglomerates into larger clusters based on the Bray-Curtis dissimilarity measures.

Multivariate methods of analysis allow all of the sediment chemistry data to be considered simultaneously, and the relationships between the sites based on their sediment chemistry can then be graphically represented in two or more axes. Non-parametric Multi-Dimensional Scaling (NMDS) was used in the analysis (PATN; Belbin, 1993). NMDS calculates a matrix of dissimilarity values from the sediment chemistry data to create the ordination diagram (Jongman et al., 1995). This is done such that the rank order of dissimilarities of the samples are reflected in their distances in ordination space relative to one another. The Bray-Curtis association measure is used in the analysis to express the dissimilarity between the samples.

2.4 Results

All 39 sites sampled in the initial sediment survey were clustered according to their sediment chemistry. This was done to identify any natural groupings between the sites. Seven cluster groups were identified; groups 1, 2, 4, 6 and 7 all contained a single site, whereas groups 3 and 5 were made up of 13 and 21 of the sites respectively. These groupings have been mapped, and are shown in Figure 2.

Ordination using Principle Components Analysis (PCA) allowed the sites to be grouped and plotted according to their similarities in sediment composition (Figure 3). The closer two points are to each other in ordination space, the more similar they are. A downstream trend is observed in ordination space along Axis1, and a distinct separation between groups 3 and 5 along PCA Axis1 is observed (Figure 3a). This separation is influenced by particle size (Figure 3b); group 3 sediments generally tend to have a smaller sediment size than group 5 sediments (Figure 4). Total organic carbon concentrations distribute the data along PCA Axis2 (Figure 3), and help explain some of the separation between the sites, particularly between Group 1 which has high TOC concentration (120 μ g/g TOC) and Group 2 which has low TOC concentrations (21 μ g/g TOC). To address the variable nature of TOC content in the sediment between sites, the sediment can be TOC corrected by dividing the contaminant concentrations in the sediment by its TOC content. Correcting the sediment data for TOC levels does not change the overall groupings or sediment relationships in ordination space (Figure 5a); a downstream gradient along Axis1 is still observed.

2.4.1 Metals

The results from the metals analysis are provided in Table 1. Four metals exceeded the PSQG SEL criteria at one or more sites (Figure 6); manganese exceeded the SEL of 1100 μ g/g at only one of the sites (LC34, 2000 μ g/g), located downstream of Crowland Road. Iron also exceeded the SEL of 40000 μ g/g at this location (44000 μ g/g); the SEL for iron is also exceeded at LC14 and LC16 (54000 μ g/g and 57000 μ g/g respectively), both sites are located upstream of Highway 140. Sediment concentrations of zinc and nickel are both elevated over their SEL criteria (820 μ g/g and 75 μ g/g respectively) at LC02, LC16, LC27 and LC33. Each of these sites is situated in areas where deposition is high. Zinc also exceeds its SEL criteria at 7 other locations: LC08 – LC11, LC14, LC24, and LC34.

The most upstream location (LC01) had the lowest concentrations of most of the parameters measured; calcium and magnesium were highest at this location. In contrast, the next location downstream (LC02) had one of the highest concentrations of many of the parameters measured, and exceeded the SELs for nickel and zinc.

Calcium tended to be highest in the sites upstream of Highway 140. Locations LC14 to LC16, a highly depositional area upstream of Highway 140 and therefore a potential sink for many contaminants originating from upstream of this point, has the highest concentrations for 12 of the 18 metals measured. Four of the remaining 6 metals were highest at LC02, which is situated adjacent to the former Welland Pipe property.

2.4.2 *OC pesticides*

OC pesticides were generally low in all of the samples (Table 2), often in concentrations below the MOE method detection limits. Average values for each of the seven groups identified through cluster analysis (also provided in Table 2) were compared. The only OC pesticide present in any significant concentration was pp-DDE, which exceeded the LEL criteria of 5ng/g at 34 of the 39 sample locations. Group1, 4, 6 and 7, which represents a general area extending from the area adjacent to the Welland Pipe property (LC02) downstream to Highway 140 (LC17) had significantly higher levels of DDE than the most upstream location (Group2, LC01) or downstream of Highway 140. Although agricultural practices appear to be more prevalent in the downstream locations, these data may be more of a reflection of past land uses.

2.4.3 *PAH*

PAHs were generally elevated in the upstream portion of Lyons Creek (LC02 – LC17); the LEL criteria was exceeded at one or more of these locations for 10 of the 12 PAHs for which guidelines are available (Table 3). LC02, located adjacent to the Welland Pipe property, exceeded the PSQG criteria for 10 of the 12 parameters considered. Downstream of Highway 140 PAH levels were lower, exceeding only 4 of the 12 criteria. These values were all lower than those observed upstream of Highway 140 (Table 3).

2.4.4 *PCB*

Sediment concentrations are generally higher in the upper portion of the creek and were elevated above the PSQG LEL criteria of 70ng/g at all sites, except for LC36 (downstream of Crowland) and downstream of the QEW (LC38) (Table 3). PCB concentrations ranged from a high of 19000ng/g at Highway 140 (LC16) to non-detect at the QEW (LC40). An overall downstream decrease in PCB concentration was observed, with dramatic drops in concentration occurring just downstream of the CNR railway (LC20), at Conrail (LC31) and downstream of Crowland Road (LC36) (Figure 1). These trends are reflected in the average concentrations observed in the cluster groupings (Figure 7, Table 3).

2.5 Discussion

PCB concentrations in the sediment are elevated above the Provincial Sediment Quality Guideline (PSQG) Lowest Effect Level (LEL) criteria of 70ng/g in most of the Lyons Creek East locations, particularly in the upper reaches. At the upper reaches concentrations were observed at levels as high as 19000ng/g. Concentrations of PCBs decline considerably after the culvert at Highway 140 (LC16 and LC17), which appears to be acting as a sediment trap for sediments (and contaminants) moving downstream. This is also reflected in the groupings from the cluster analysis, which indicate a change in the overall sediment chemistry downstream of Highway 140. Sediments from the more upstream reaches of the creek tend to be characterized by higher levels of PCBs, whereas more downstream sediments (group 5) have elevated nutrients and pesticides, which reflect the land use. The initial screening survey suggests that the upper portion of the Creek is a source of elevated PCB levels. Based on these data, the more detailed study focused on the upper portion of the Creek (to Highway 140).

Due to the elevated concentrations of PCBs in the creek and the widespread distribution of this compound, the detailed study focused primarily on PCB concentrations and congener distribution of this compound.

3 DETAILED SURVEY

3.1 Objectives

The objectives of the more detailed survey were to further investigate the extent of PCB contamination in Lyons Creek East, whether the PCBs observed were in a bioavailable form, and to identify whether the source is ongoing. Further investigations into the toxicity of PCBs, impairment to the resident benthic fauna and its bioaccumulation into higher organisms were conducted simultaneously to this study by Environment Canada.

Specific areas requiring remediation will also be identified through the joint MOE/EC investigation.

3.2 Study Design

In the past both transects of the creek bed and grab samples have been collected (Acres, 1978; MOE, 1997; Bedard & Petro, 1998; Boyd et al, unpublished); some of these locations were duplicated in this study. Areas for detailed analysis were selected based on the outcome of the screening level

survey, where the fish have been identified in the past as having elevated levels of PCBs in the tissue (Boyd et al, unpublished), as well as from depositional areas identified by Acres (1978) as areas of low elevation (Table 4, Figures 8 & 9).

Sampling for the detailed study was conducted over a 2 year period (2002 and 2003). In 2002, sampling focused primarily on an area between the Lyons Creek pumping station at the Welland Canal to Highway 140, with 2 additional downstream sample locations close to the mouth of the Creek. Sediment was also collected at this time from two reference streams of similar morphology to Lyons Creek (Beaver Creek and Black Creek). In 2003, a total of 13 stations were sampled in Lyons Creek, five of which had been sampled the previous year. An additional two reference streams of similar morphology to Lyons Creek (Tee Creek and Usshers Creek) were also sampled.

3.2.1 *Sediment*

2002 – Sediment cores

Six locations along Lyons Creek (Figure 8) were selected for a more in-depth study of ecosystem health. Cores were collected from the most upstream location of Lyons Creek (LC01), downstream of the Welland Pipe property (LC03), immediately upstream and downstream of Highway 140 (LC16 and LC17 respectively), downstream of McKenny Road (LC29) and Downstream of the QEW (LC38).

Three sediment cores were collected from each location using a KB-corer. The cores were sectioned into 0-10cm, 10-25cm and >25cm sections, and a composite of each section from each of the three cores was homogenized and sent to the MOE laboratory at Resources Road for analysis of PCBs, metals, OCs, PAHs, particle size, and nutrient content (MOE, 1993a).

2002 – Sediment grab samples

Grab samples of surficial sediment were also collected from each of the six sites outlined above (Table 4), as well as from two streams with similar morphological characteristics as Lyons Creek, Black Creek and Beaver Creek, which were used as reference sites (BLC and BEC respectively).

Depositional areas were targeted for the sediment collection, and were sampled using a petit ponar which is designed to 'grab' sediment to a depth of 10cm. A composite of three grabs were homogenized and sent to the MOE laboratory for analysis of congener specific PCBs, metals, particle size, total organic Carbon (TOC), OC pesticides and PAHs (MOE, 1993a).

Table 4: Sampling strategy for detailed study: 2002 -2003

Site	Sediment		Caged Mussels	Forage Fish	Sport Fish
	Grab	Core			
LC01	2002	2002	2002		
LC03	2002	2002	2002/2003	2002/2003	
LC06	2003				
LC08	2003		2003	2003	
LC10	2003				
LC12	2002/2003		2003		
LC14	2003		2003		
LC16	2002/2003	2002	2003	2002/2003	2002/2003
LC17	2002/2003	2002	2002	2003	
LC18	2003		2003	2003	
LC19	2003		2003		
LC22	2003				
LC23	2003		2003		
LC24				2003	
LC29	2002/2003	2002	2002		
LC38	2002/2003	2002	2002	2002	2002
mouth				2002	
Tee Cr	2003		2003		
Usshers Cr	2003		2003	2003	
Beaver Cr	2002		2003	2002	
Black Cr	2002			2002	

2003 – Sediment grab samples

Sediment samples were collected in 2003 from 13 Lyons Creek locations (Table 4, Figure 8), 5 of these duplicate locations collected in 2002 (LC12, LC16, LC17, LC29 and LC38). An additional two reference streams were also sampled; samples were collected from Tee Creek (TC) and Usshers Creek (UC).

As in 2002, depositional areas were targeted for surficial sediment sampling. Three grabs were collected from each location using a petit ponar. The three grab samples were subsequently homogenized and placed into an amber 5P glass organics jar for PCB congener specific analysis, PAHs and OC pesticides, and a 500mL plastic bottle for analysis of TOC, particle size and metals at the MOE laboratory at Resources Road.

3.2.2 *Caged mussels*

Mussels have been shown to be an effective means of biomonitoring PCBs in the aquatic environment (Binelli et al., 2001) as they are able to bioaccumulate organic contaminants from the water (and to some degree from the sediment).

2002

Mussels (*Elliptio complanata*) of a similar size range (65-72cm), collected from Balsam Lake, were kept in aerated Balsam Lake water at room temperature in 22L buckets lined with food-grade plastic inserts until deployment. Ten mussels, randomly selected, were placed into 30cm by 45cm envelope shaped mesh cages, one cage was deployed at each of 5 locations in Lyons Creek (Table 4, Figure 9). LC01 is located at the most upstream location, LC03 is downstream of the Welland Pipe discharge pipe, LC17 downstream of Hwy 140, LC29 is situated downstream of McKenny Road, and LC38 downstream of the QEW.

The mussels were left in place for three weeks. On the 21st October the mussels were retrieved and immediately shucked in the field. Each mussel was placed into an aluminium foil envelope and placed on ice. The mussels were subsequently frozen and a random subset of three individual mussels from each sample were analysed for PCB congeners and lipid content according to the MOE standard laboratory protocol (MOE, 2003). A set of mussels from Balsam Lake was also submitted to the MOE laboratory as a control, and represents background levels of PCB congeners and lipid content observed in unexposed mussels.

2003

In 2003, mussels collected from Balsam Lake were deployed at eight locations (LC03, LC08, LC12, LC14, LC16, LC18, LC19 & LC23: Table 4, Figure 9) along Lyons Creek east, one of which (LC03) was a duplicate location from 2002.

Upon retrieval, three weeks after deployment (October 7th), the mussels were treated in the same manner as in 2002. The mussels were shucked in the field, and the individual mussels wrapped in foil and kept on ice, as in 2002. The mussels were subsequently frozen and a subset of three individuals per site sent to the MOE laboratory for analysis of PCB congeners and lipid content (MOE, 2003). Mussels were also deployed at three of the four reference streams identified in the sediment collections (Beaver Creek (BC), Tee Creek (TC), and Usshers Creek (UC)).

3.2.3 Forage Fish

Forage fish were collected from Lyons Creek in 2002 and 2003, from the Welland River at the mouth of Lyons Creek (mouth), and from three reference creeks: Beaver Creek and Black Creek in 2002, and Usshers Creek in 2003. Bluntnose minnow (*Pimephales notatus*) were targeted for collection in the creeks, this species was not always found so every effort was made to collect an additional species. Three additional species of forage fish: common shiner (*Notropis*

cornutus), golden shiner (*Notemigonus crysoleucas*), and spottail shiners (*Notropis hudsonius*) were also targeted.

The fish were collected using a 3-metre seine net with a 0.6 cm mesh size. Captured fish were immediately placed into aluminium foil pouches and kept on ice until they could be processed. The samples were then transported to the MOE laboratory in Etobicoke. At the laboratory, fish from each site were measured for total length, wrapped in aluminium foil and placed in labelled *Whirl-pak*® plastic bags. The samples were kept at -20°C until they were prepared for analysis. Sample preparation entailed homogenization of composites of five to ten fish and freezing of the samples in glass vials at -20°C. They were then analyzed for PCB congeners and lipid content (MOE 2003).

2002

Forage fish were collected from a total of four locations along Lyons Creek East using a seine net. Fish were collected from the upstream portion of the Creek at Ridge Road (LC03), upstream of Hwy 140 (LC16), below the QEW close to the mouth of Tee Creek (LC38), and at the mouth of Lyons Creek in the Welland River (Table 4, Figure 8). Fish were also collected from two reference streams (Black Creek and Beaver Creek). Although McKenny Road had been identified in the past as having fish with elevated PCB concentrations, no fish could be collected during this study.

Each composite sample was made up of a single fish species. Every effort was made to collect enough fish to allow replicate samples of species to be analysed. Additional samples of a second fish species were collected when possible. An attempt was made to collect the same species from each site to allow for among-site comparisons.

2003

Forage fish were collected in 2003 from six Lyons Creek locations (LC03, LC08, LC16-18 & LC24: Table 4, Figure 9), and from one reference stream, Usshers Creek (UC). Only two sample locations, LC03 and LC16, duplicated those collected in 2002. As in 2002, each sample was made up of a composite of a single species, and where possible replicate samples and additional species were collected.

In both 2002 and 2003, the sediment and fish samples were all collected at the same time as the mussel retrieval.

3.2.4 Sport fish

2002

Sport fish were collected by electro-fishing from a section of the creek upstream of Hwy 140 (LC 16), and downstream of the QEW (LC38), near the mouth of Tee Creek (Table 4, Figure 8; SF). Bowfin (*Amia calva*), carp (*Cyprinus carpio*), brown bullhead (*Ictalurus nebulosus*), pumpkinseed (*Lepomis gibbosus*), bluegill (*Lepomis macrochirus*), largemouth bass (*Micropterus salmoides*) and black crappie (*Pomoxis nigromaculatus*) were collected from both locations. White suckers (*Catostomus commersoni*) were only collected from LC16, and northern pike (*Esox lucius*), rock bass (*Ambloplites rupestris*), white crappie (*Pomoxis annularis*) and yellow perch (*Perca flavescens*) were only collected from LC38.

Fish tissue samples, consisting of one skinless, boneless dorsal fillet per sample, were sent to the MOE laboratory at Resources Road for analyses of PCBs and lipid content (MOE, 2003). The tissue samples were kept at -20°C until analysis, as outlined for the forage fish.

2003

In 2003, sport fish were only collected from Highway 140. Collections included Bowfin, carp, pumpkinseed, rock bass, largemouth bass, black crappie and white sucker. As in 2002, a skinless, boneless dorsal fillet was collected from each fish collected and this portion of the fish was sent to the MOE laboratory at Resources Road for analysis. Unlike in 2002, the sportfish fillets submitted in 2003 were analysed for congener specific PCBs. The fish were also analysed for lipid content.

3.3 Data analysis

3.3.1 Sediment

Sediment concentrations of the various chemical parameters measured in both the cores and the surficial sediments were compared, where applicable, to the Provincial Sediment Quality Guidelines (PSQG) Lowest Effect Level (LEL) and Severe Effect Level (SEL) criteria (MOE, 1993a).

The proportional contribution (as a percentage) of each PCB congener was calculated and the overall homologue patterns plotted. The homologue patterns were then compared to the homologue patterns for 5 different aroclors (i.e. 1016, 1242, 1248(a&g), 1254(a&g), 1260). These comparisons allow inferences to be

made as to the aroclor mixture of the PCB contamination and thus the possible source.

Multivariate analyses, such as clustering and ordination were also conducted. The primary purpose of clustering is to create groups or 'clusters' in such a way that the sediment chemistry relationship varies most between groups and least within groups. The sites were clustered using agglomerative clustering techniques, in which clustering analysis starts with a single object (site) and agglomerates into larger clusters based on the Bray-Curtis dissimilarity measures.

Multivariate methods of analysis allow all of the sediment chemistry data to be considered simultaneously, and the relationships between the sites based on their sediment chemistry can then be graphically represented in two or more axes. Non-parametric Multi-Dimensional Scaling (NMDS) was used in the analysis (PATN; Belbin, 1993). NMDS calculates a matrix of dissimilarity values from the sediment chemistry data to create the ordination diagram (Jongman et al., 1995). This is done such that the rank order of dissimilarities of the samples are reflected in their distances in ordination space relative to one another. The Bray-Curtis association measure is used in the analysis to express the dissimilarity between the samples. The extent to which NMDS adequately represents the relationships is reflected in the stress value (Kruskal and Wish, 1978). The stress value defines the amount of scatter around the line of best fit through the NMDS distances and the actual distances (Clarke, 1993). As the number of dimensions in the ordination increases, the stress level is reduced. Clarke (1993) suggested the following basic guideline, which was used in this study to select the appropriate stress level:

Stress <0.05	gives an excellent representation with no prospect of misinterpretation
Stress <0.1	corresponds to a good ordination with no real risk of drawing false inferences. A higher dimensional plot is unlikely to add to the overall picture
Stress <0.2	can still lead to a useable picture, although the values at the upper part of the range can potentially be misleading
Stress >0.2	are likely to yield plots which would be dangerous to interpret.

Principal Axis Correlation is used to identify which chemical parameters are contributing to the observed patterns in the analysis. From the vectors generated, the contribution of the original data to the ordination scores can be observed. The significance or magnitude of the relationship between each original variable and the observed pattern is tested using a Monte-Carlo permutation procedure. Repeated simulations using random permutations of the data set (Faith and Norris, 1989) are used to produce a list of randomised correlation coefficients.

Against these, the statistical significance of the different chemical concentrations between sites is assessed in a non-parametric fashion.

Relationships in the individual congener patterns between the sites were also considered using these multivariate techniques, as were the relationships between the individual congener patterns of the sites and those of the different aroclors considered (1016, 1242, 1248a, 1248g, 1254a, 1254g, 1260).

3.3.2 Caged mussels

Total PCB concentrations in the mussels were statistically analysed using a one-way ANOVA. If the ANOVA indicated a significant difference among stations ($p < 0.05$), then the differences between sites were compared using a *post hoc* Tukey test.

Several co-planar (dioxin-like) PCB congeners have been shown to cause a number of toxic responses similar to the most toxic dioxin (2,3,7,8-TCDD) (Van den Berg et al., 1998). Using a toxic equivalency factor (TEF, Table 5) concept, the toxicity of the different co-planar PCB congeners relative to the toxicity of 2,3,7,8-TCDD can be determined. TEF's, in combination with the chemical residue data of each co-planar PCB congener can be used to calculate toxic equivalent (TEQ) concentrations in various media (e.g. fish or mussel tissue). TEQ concentrations for the co-planar PCB congeners in samples are calculated using the following equation:

$$TEQ = \sum_{i=1}^n ([PCB]_i \times TEF_i)_n$$

Within a sample, the individual co-planar PCB congener concentrations are multiplied by their respective mammalian TEFs (Table 5), and all products are summed to give a TEQ value. This takes into consideration the unique concentrations and toxicities of the individual components within the PCB mixture.

The summed TEQ values for each site are compared to the appropriate Canadian tissue residue guideline (TRG) for the protection of wildlife consuming aquatic biota (CCME, 2001). The TRG of 0.79ng TEQ/kg diet wet weight provides a benchmark for PCBs in aquatic life, above which their mammalian predators may be at risk of consuming PCB concentrations known to result in adverse effects.

Congener patterns in the mussel tissue from the different sample sites were compared using ordination and clustering techniques, as described in the sediment analyses. The homologue patterns were also compared to the aroclor congener patterns (as described above).

Table 5: Toxic equivalency factors (TEFs) for selected PCB congeners (Environment Canada, 1998)

IUPAC No.	Structure	TEF (mammalian)*
PCB 77	3,3',4,4'	0.0001
PCB 81	3,4,4',5	0.0001
PCB 126	3,3',4,4',5	0.1
PCB 169	3,3',4,4',5,5'	0.01
PCB 105	2,3,3',4,4'	0.0001
PCB 114	2,3,4,4',5	0.0005
PCB 118	2,3',4,4',5	0.0001
PCB 123	2',3,4,4',5	0.0001
PCB 156	2,3,3',4,4',5	0.0005
PCB 157	2,3,3',4,4',5'	0.0005
PCB 167	2,3',4,4',5,5'	0.00001
PCB 189	2,3,3',4,4',5,5'	0.0001

* 1998 WHO TEF values (Van den Berg et al., 1998)

3.3.3 Forage fish

The concentration of total PCBs in the different forage fish species collected from each location were first compared to the IJC PCB guideline (100ng/g) for the protection of fish-eating wildlife (IJC, 1988). As a variety of forage fish species were collected at each location, which differed between sites, the most common species collected (creek chub) were compared using a one-way analysis of variance (ANOVA). As with the mussel analyses, if the ANOVA indicated a significant difference among the stations ($p < 0.05$), the differences between sites were compared using a *post hoc* Tukey test.

Toxic equivalency values for the selected co-planar PCB congeners (Table 5) were also calculated for the forage fish data. These values were compared to the Canadian TRG (0.79ng TEQ/kg diet wet weight; CCME, 2001).

3.3.4 Sport fish

Total PCB concentrations from sport fish collected in 2002 were compared to historical data (1991-2000). These data were also compared to the consumption restriction guidelines outlined in the *Guide to Eating Ontario Sport Fish, 2005-2006* (MOE, 2005).

In addition to comparing the total PCB concentrations observed in the sport fish collected in 2003 to the consumption guidelines (MOE, 2005), toxic equivalency values, based on co-planar PCB concentrations were calculated for the sport fish collected in 2003. These values were compared to Canadian tissue residue guideline (TRG) for the protection of wildlife consuming aquatic biota (CCME, 2001), as outlined above.

3.4 Results

3.4.1 Sediment

2002 – Sediment cores

Ordination of the data by multivariate analysis showed the sediment cores from the more downstream locations (LC17, LC29 and LC38) all grouping together (Figure 10), suggesting that the chemistry of the sediments, even at depth, are relatively homogeneous and have a similar composition. The more surficial sediments at LC16, located upstream of Highway 140, also have similar sediment chemistry composition to the downstream locations, but at depth move away from the more downstream locations in ordination space (Figure 10). Deeper sediment at this location has a similar sediment composition to LC03 (downstream of Welland Pipe). The upstream location (LC01) has a different composition from all of the other sites (Figure 10a). The observed difference in sediment composition at this location is primarily driven by particle size, and elevated levels of manganese, magnesium and calcium (Figure 10b). Sediment from LC03 and from the deeper sediments of LC16 (>25cm) are characterized by elevated levels of OCs, metals and PCBs. The PCB concentrations at these three sites (LC03<10cm, LC03 10-25cm, and LC16>25cm) all exceed the PSQG SEL, suggesting that these sediments may effect the health of sediment dwelling-organisms (Table 6).

Ordinations of the sediment samples based on their PCB congener composition (Figure 11a) groups together the sediments from LC01, LC17, LC29 (at all depths), and the surficial sediments (<10cm) of LC16, indicating that PCB levels and their congener composition are similar. Five PCB congeners are associated with Axis1 (Figure 11b). These 5 congeners explain the separation of the downstream location (LC38) at all core profiles, the upstream location LC03 (0-25cm) and the deeper sediment at LC16 (>25cm); PCB congener patterns are similar at these locations (Figure 12), but concentrations are generally higher in the surficial sediments at LC03. The most downstream location (LC38) has lower levels of PCBs than the other sites (Figure 12), which is indicated by the separation in ordination space of these samples from the rest of the locations (Figure 11a), and its position away from the direction indicated by the congener vectors (Figure 11b). Generally higher levels of the 'tri' homologues are observed

in the more contaminated samples of Lyons Creek. The tetra and penta homologues also tend to be higher at LC03 and LC16 >25cm (Table 6, Figure 12).

Sediment grab samples (2002 & 2003)

Surficial sediment samples collected from Lyons Creek and the four reference streams in 2002 and 2003 were clustered and ordinated based on their sediment chemistry (Table 7, Figures 13 & 14). Cluster analysis grouped the sediment samples into six groups (Table 7). Group 1 contained seven samples, all of which were from sites below Ridge Road and above Highway 140; five locations were represented (LC06, LC08, LC10, LC12 and LC14), only one of these samples (LC14) were collected from 2002 (Table 7). Group 2 and Group 4 contained one sample each (LC01 and LC03 respectively), both samples were collected in 2002 from above Ridge Road. Group 3 contained 6 samples, two from 2002 and four from 2003; this group represented three Lyons Creek locations from the vicinity of Highway 140 (LC14, LC17 (2002 & 2003) & LC18), and two reference locations (Usshers Creek and Black Creek). Group 5 contained five samples, all from the lower portion of the creek and all collected in 2003; this group represented four sample locations (LC19, LC22, LC23 and LC38). The final group, Group 6, was the largest group and contained 11 samples; six of the 11 samples were collected from the reference streams in 2002 and 2003, the remaining five samples were all collected in 2002 and represent three Lyons Creek location (LC16, LC29 and LC38).

Ordination of the sediment samples, based on sediment chemistry, best explained the cluster groupings with respect to chemical parameters observed in the sediment over three axis (Figures 13 & 14, Stress = 0.052). The ordination plots (Figures 13 & 14) show a strong separation in the site groupings along NMDS Axis1, which correspond to elevated concentrations of PCBs, PAHs and OCs in the upper portion of Lyons Creek (Table 7, Figures 13a,b,c & 14a,b,c). PCBs, PAHs and OCs were generally highest at the site downstream of the Welland Pipe discharge (LC03), often exceeding the PSQG LEL criteria by an order of magnitude (Table 7). Group 1 sites, which represented an area of the creek between Ridge Road and Highway 140 were also elevated in PCBs and many of the PAHs and OCs, although not to the same degree as LC03; only two of the OCs (Dieldrin and DDE), four PAHs (Benzo(a)pyrene, Benzo(g,h,i)perylene, chrysene and Indeno(1,2,3-c,d)pyrene) and PCBs exceeded their respective LEL criteria. Copper, nickel and zinc all exceeded the PSQG SEL criteria at LC03 (Figure 15), zinc exceeded the SEL by almost an order of magnitude and appeared to be associated with NMDS Axis1. The average concentration of zinc from the Group 2 sites also exceeded the PSQG SEL criteria (Table 7). The remaining metals tended to influence the position of the sites in ordination space along NMDS Axes2 and 3. Beryllium, barium, cobalt and vanadium generally were high at the Group 5 sites, and lowest at the most

upstream location (Group 2, LC01) which was reflected in the position of these groups in ordination space along axis 2 with respect to these parameters (Figure 13a & e). Calcium, strontium and to some extent titanium were represented by axis 3, and tended to be higher in the upstream location (Figure 14a & e).

The homologue patterns observed at the different sites along Lyons Creek and from the four reference streams were also considered with respect to the homologue patterns of five different aroclors. In order to make these comparisons, the different proportions of each of the different homologues were calculated and plotted. The homologue patterns are shown in Figure 16. with the exception of the most downstream location (LC38), sediment collected from Lyons Creek in 2002 had homologue patterns which closely resembled aroclor 1248 (Figure 16a). The most downstream location collected at this time (LC38) had a homologue pattern closely resembling aroclor 1016, which is similar to background patterns observed in other studies (e.g. Sinister Creek & Peninsula Harbour, unpublished), and therefore suggests that PCBs in this area are likely indicative of normal background conditions.

Homologue patterns observed in the sediment collected in 2003 also closely resembled aroclor 1248 at most of the locations samples. The sediment collected from downstream of the CN Railway (LC19) and from the most downstream location (LC38) differed from the other samples with the homologue patterns at these two sites resembling a mixture of aroclors 1248 and 1254 (Figure 16b).

Homologue patterns from the sediment collected from the four reference streams in 2002 and 2003 are shown in Figure 16c. The homologue patterns observed at Tee Creek (TC), Usshers Creek (UC) and Beaver Creek (BEC) all resembled aroclor 1254, Black Creek (BLC) had a homologue pattern resembling aroclor 1016.

3.4.2 Caged Mussels

No significant difference in the mussel tissue contaminant concentrations between locations was observed in any of the parameters measured, with the exception of PCBs (Table 8). Despite the lack of a significant difference in lipid content of the mussels between locations (ANOVA, $p=0.074$), the average lipid content of the mussels tended to be slightly higher at the downstream location (LC38), and Balsam Lake reference (1.28% and 1.47% respectively) compared to the other locations. Mussels collected in 2002 from LC03 had marginally lower lipid concentrations (average = 0.63%) compared to the other locations samples that year (0.81-0.87%), suggesting the mussels were not as healthy at this site. The lipid concentrations from the mussels deployed in 2003 were generally lower than that observed in 2002 (0.69% - 1.1%).

Ordination of the mussel data, based on chemical concentrations in the tissue, grouped together the reference creeks (BC, TC & UC), the Balsam Lake reference mussels, the most downstream Lyons Creek location (LC38) and the mussels deployed at most upstream Lyons Creek locations in 2002 (Figure 17). The upstream locations sit on the periphery of this group. These locations do not significantly differ from each other in PCB concentration. PCB concentrations are strongly correlated with Axis1 (Figure 17b) and explain much of the movement in ordination space of the remaining groups along this axis. PCB concentrations at each site within each group did not significantly differ in PCB concentration from each other. With the exception of Group 4, which was found to be similar to both Groups 3 and 6, PCB concentrations between the groups were generally significantly different from each other (ANOVA, $p < 0.001$).

The highest PCB concentrations were observed in the mussels from Group 7, which ranged from 220ng/g to 510ng/g (Table 8, Figure 18). Tissue concentrations in this group as well as Group 5 (mean PCB = 269ng/g) were all above the IJC guideline for the protection of fish-eating wildlife (IJC, 1988) of 100ng/g and were all significantly higher than any other sample (ANOVA, $p < 0.001$). The IJC guideline in these two groups was exceeded by 1.8 to 5 times. All of the samples in Groups 5 and 7 were collected in 2003, and were all located in an area between downstream of Ridge Road (LC08) and of Highway 140 (LC17). Members from Group 6 also exceeded the IJC guideline (mean PCB = 122ng/g, range 75-159ng/g), and members from this group were located from Highway 140 (LC16) to the CN railway (LC19).

Clustering and ordination of the mussel tissue residue samples with the different arochlor compositions, based on the proportion of each congener to the overall pattern, results in the ordination provided in Figure 19. Just as the reference creeks and Balsam Lake samples clustered together based on the raw data, these sites also cluster together based on their PCB congener composition. The remaining Lyons Creek locations that clustered with the reference sites, based on the raw data, cluster into a separate group (02LC1, 02LC3 and 02LC38) which is located in close proximity to the reference sites (Figure 19, Groups 7 and 8). The seven arochlor patterns cluster into 4 distinct groups (Figure 20); aroclors 1016 and 1242 cluster into Group1, arochlor 1248 a & g are the only members of Group 2, Group 4 contains both combinations of arochlor 1254 (a and g), and arochlor 1260 is the only member of Group 5. The three replicate tissue samples from the 2003 samples at LC3 make up Group 6. All other samples from both 2002 and 2003 comprise Group 3. The reference samples and selected Lyons Creek samples which make up Groups 7 and 8 lie within close proximity to aroclors 1060 and 1242, suggesting that the PCBs found in the tissue from these sites resemble a mixture of the two aroclors.

The PCB homologue patterns observed in the mussels from both 2002 and 2003 were all very similar; closely resembling that of either a mixture of aroclors 1016

and 1242 (Group 1: Figure 20a), or aroclor 1248 (Group 2: Figure 20b). The reference streams, mussels from Balsam Lake and the most upstream and downstream locations collected in 2002 (Groups 7 & 8: Figure 20g & h) where all very similar to the pattern observed in Group 1, and this is reflected by the close proximity of these groups in ordination space (Figure 19). The remaining Lyons Creek sites, with the exception of the mussels collected from LC03 in 2003 (Group 6: Figure 20f), resemble aroclor 1248 (Group 3, Figures 19 & 20c). Group 6 resembles the homologue pattern of aroclor 1260 (Figure 20); this pattern is most pronounced along NMDS Axis 3 of the ordination plot (Figure 19b).

Based on the toxic equivalency factors for the co-planar (dioxin-like) PCB congeners (CCME, 2001), an over all Toxic Equivalency Value (TEQ) was calculated for the mussel tissue deployed in both 2002 and 2003. The CCME have a TEQ guideline for mammalian and avian species (CCME, 2001) which aims to protect mammals and birds which consume aquatic organisms; the mammalian TEQ value of 0.79ng TEQ/kg. The TEQs calculated for these sites ranged from zero to 2.54ng TEQ/kg collected in 2002 from LC17 (over three times the tissue residue guideline, Figure 21). Mussels from the reference streams, Balsam Lake and the upstream and downstream locations sampled in both 2002 and 2003 were all below this criterion and were significantly lower than TEQ values observed at the other locations (ANOVA, $p < 0.001$).

3.4.3 *Forage fish*

2002

Forage fish were collected at three locations in Lyons Creek. Bluntnose minnow, a common forage fish, was targeted at each location. Where these fish were not present, alternative species were collected. These were golden shiner for Lyons Creek and Black Creek and common shiner at Beaver Creek.

At LC03 (Ridge Road), near the Welland Canal, 5 replicates of bluntnose minnows were collected. Upstream of Highway 140 (LC16), four replicates of bluntnose minnows were collected. Below the QEW (LC38), only one replicate of bluntnose minnow and five replicates of golden shiners were collected. Samples from the Welland River in the vicinity of the mouth of Lyons Creek included five replicates of bluntnose minnows and five replicates of spottail shiners. Two reference locations were also sampled; Beaver and Black Creek. Four replicates of common shiners were collected from Beaver Creek, and five replicates of golden shiners were collected from Black Creek.

Total PCB concentrations in forage fish samples varied greatly from each location (Figure 22). At LC03, bluntnose minnows had a mean concentration of 3560ng/g wet weight and differed significantly (ANOVA, $p < 0.007$) from the other

locations. Upstream of Highway 140 at LC16, the same species of forage fish had a mean PCB concentration of 7857ng/g wet weight, which was significantly higher (ANOVA, $p < 0.001$) than all other locations, including LC03. At LC38, downstream of the QEW, the only replicate of bluntnose minnow had a total PCB concentration of 48ng/g, golden shiners at this location had an average PCB concentration of 19ng/g. Forage fish at this location did not differ significantly from the reference locations or the Welland River.

Bluntnose minnows from the Welland River had a mean PCB concentration of 35ng/g, and spottail shiners from the same location had a PCB concentration of 7ng/g (Table 9). Common shiners from Beaver Creek had an average PCB concentration of 11ng/g. Golden shiners from Black Creek averaged 26ng/g total PCBs.

Forage fish from Lyons Creek below the QEW, the Welland River, Beaver Creek and Black Creek all had PCB concentrations that are considered relatively low and were all under the IJC guideline (IJC, 1988) for the protection of fish eating wildlife of 100ng/g (Figure 22a). Forage fish collected from the more upstream locations (LC03 and LC16) had total PCB concentrations which exceeded the IJC guideline by up to more than 90 times, and on average 35 times at LC03 and 78 times at LC16 (Figure 22a). These data suggest that there is an upstream source of PCBs that may result in potential harm to biota that may consume the fish from these locations.

The forage fish samples were also analysed for dioxin-like PCBs. Seven dioxin-like PCB congeners were identified in the samples. From these seven congeners, Toxic Equivalency values (TEQs) were calculated (Figure 22b). A similar trend to that observed for the total PCB data was observed in the TEQ data, with the TEQ values for LC03 and LC16 significantly higher than all other sites (ANOVA, $p > 0.001$). Lyons Creek below the QEW, the Welland River, Beaver Creek and Black Creek all had relatively low TEQ values, below the CCME guideline (CCME, 2001) for mammals of 0.79ng/kg TEQ. At LC03 and above Highway 140 (LC16) the fish collected exceeded the TEQ guideline (33.6ng/kg TEQ and 56.8ng/kg TEQ respectively). These concentrations are extremely high and pose a threat to mammals that may consume the fish from these locations.

2003

As in 2002, bluntnose minnow were targeted for collection in Lyons Creek and at the reference stream (Usshers Creek). Golden shiner were also targeted, as no bluntnose minnow were observed at LC08. Since no golden shiner were observed at Usshers Creek, common shiner were collected (Figure 23). Four replicate samples of bluntnose were collected from LC03, LC16, and Usshers;

five replicated were collected from LC17 and LC18; and, two replicates were collected at LC24.

Total PCB concentrations were highest at LC03 (2525ng/g ww). The next highest concentration was observed at LC17 (mean: 1760ng/g ww). PCB concentrations at these two locations did not differ significantly from each other, although LC03 was significantly higher than all other sites (ANOVA, $p > 0.001$). An overall downstream trend in PCB concentrations was observed in the PCB concentrations of bluntnose minnow in Lyons Creek (Figure 23a). Golden shiner increased downstream to LC16 (1700ng/g ww), after which a steady decrease was observed along a downstream gradient (Table 9, Figure 23a).

Unlike the relationships between total PCB concentrations and TEQ values observed in 2002, no such relationship existed in 2003 (Figure 23b). TEQ values did not appear to be linked to the total PCB concentrations, but rather showed a similar pattern to those observed in 2002 in which the highest TEQ values were observed at Highway 140 (LC17, 318ng TEQ/kg) and were significantly higher than all other sites (ANOVA, $p > 0.001$). PCB concentrations were second highest at LC03 (mean: 126ng TEQ/kg). An overall downstream trend is observed in the TEQ values of both bluntnose minnow and golden shiner.

Bluntnose minnow - 2002 vs. 2003

Bluntnose minnows collected in 2002 and 2003 were compared to assess differences between years and within Lyons Creek. The length and lipid concentrations were compared (Figure 24c & d). Although the fish collected in 2002 from LC16 were larger than at the other locations, there were generally no significant differences in the overall size of the fish collected from Lyons Creek or Usshers Creek. Lipid concentrations in Lyons Creek did not significantly differ from each other, either between locations or year. The fish collected from Usshers Creek, however, had significantly more lipid than any of the Lyons Creek sites (ANOVA, $p < 0.001$), suggesting that these fish are healthier than those from Lyons Creek.

PCB concentrations (Figure 24a) in the upper portion of Lyons Creek were considerably higher in 2002 than in 2003; concentrations observed at LC16 in 2002 were significantly higher than any other site sampled (ANOVA, $p < 0.002$), and concentrations at LC03 in 2002 were significantly higher than Usshers Creek (ANOVA, $p < 0.001$). Tissue PCB concentrations at all other sites do not differ significantly from each other, but a general downstream reduction in PCB concentrations was observed (Figure 24). PCB concentrations exceeded the IJC guideline in both years and at all sites from LC03 to LC24, ranging from 340ng/g in 2003 at LC24 to 7857ng/g in 2002 at LC16. PCB concentrations downstream of the QEW, at the mouth of Lyons Creek and in Usshers Creek were all well

below the IJC criteria for the protection of fish-eating wildlife (mean range: 34.8-46ng/g).

Despite the elevated concentrations of PCBs observed in 2002, the overall TEQ concentrations calculated from the 12 co-planar congeners listed in the CCME guidelines (CCME, 2001) were generally higher in 2003. TEQ concentrations in fish collected from all other sites, in both 2002 and 2003 did not differ significantly. TEQ concentrations exceeded the CCME tissue residue criteria at all sites from LC03 to LC24; a similar trend to that observed in total PCB concentrations. Samples collected in 2002 downstream of LC24 were below the CCME criteria. TEQ concentrations from the 2003 collections at Usshers Creek exceeded the CCME criteria. These differences in the 2002 and 2003 TEQ concentrations can be explained by the presence of PCB congener 126, which was present in the 2003 samples, but not in the 2002 samples, and has the highest TEF value (0.1) of all 12 co-planar PCB congeners considered in the TEQ calculations (Table 9).

3.4.4 Sport fish

Sport fish were collected from two locations in 2002; upstream of Highway 140 at LC16, and downstream of the QEW (LC38). Bowfin (*Amia calva*), white sucker (*Catostomus commersoni*), carp (*Cyprinus carpio*), brown bullhead (*Ictalurus nebulosus*), pumpkinseed (*Lepomis gibbosus*), bluegill (*Lepomis macrochirus*), largemouth bass (*Micropterus salmoides*) and black crappie (*Pomoxis nigromaculatus*) were all collected from LC16. Downstream of the QEW all of these fish, with the exception of white sucker, were collected, as well as northern pike (*Esox lucius*), rock bass (*Ambloplites rupestris*), white crappie (*Pomoxis annularis*) and yellow perch (*Perca flavescens*). In 2003, sport fish were only collected from Highway 140 (LC16). At this time, only black crappie, bowfin, carp, largemouth bass, pumpkinseed, rock bass and white sucker were collected. The fish collected in 2003 were analysed for congener specific PCBs as well as total PCBs.

Sport fish have been collected from Lyons Creek at Highway 140 and at the QEW since 1991. The historical total PCB concentrations in the fish collected from 1991 onwards were compared to the 2002 and 2003 data in Figure 25. The mean values have also been compared to the consumption guidelines outlined in the *Guide to Eating Ontario Sport Fish* (MOE, 2005). Fish collected from the QEW (LC38) in 2000 and 2002 were compared (Figure 25), and although PCB concentrations in the carp were the overall highest for both years, only the carp collected in 2000 (mean: 170ng/g) had any consumption restrictions; these fish were restricted to four meals per month. All other fish, for both 2000 and 2002, were below the first level of restrictions (153ng/g: MOE, 2005).

PCB concentrations in the fish collected from Highway 140 (LC16) were considerably higher than those observed at the QEW. Although carp show no statistically significant change in PCB concentrations over the past years (regression, $r^2 > 0.03$), PCB concentrations in the fish from Highway 140 (with the exception of white sucker) appear to have generally declined since 1991. All fish collected have consumption restrictions, with only bluegill from 1991, brown bullhead from 1992 and 2002, and pumpkinseed from 1992 being unrestricted (Table 10, Figure 25).

Two-tailed t-tests were used to compare the 2002 PCB concentrations between the two locations sampled. The mean concentrations of PCBs in the fillets of the fish collected from Highway 140 were significantly higher than those in the same species of fish (bowfin, carp, brown bullhead, pumpkinseed, bluegill, largemouth bass and black crappie) observed downstream of the QEW at LC38 (Tables 10). When the mean concentrations observed in fish from Highway 140 are compared to the *Guide to Eating Ontario Sport Fish* (MOE, 2005) concentrations for restrictions on consumption, there is a complete consumption restriction, with the exception of brown bullhead (140ng/g) for the sensitive population, which includes children under the age of 15 and women of child-bearing age. For the general population, bluegill, bowfin and largemouth bass are restricted to four meals per month (188, 190 and 278ng/g respectively), black crappie, pumpkinseed and white sucker were all restricted to two meals per month (535, 390 and 540ng/g respectively), and carp were restricted to one meal per month (1164ng/g; Figure 25).

In 2003, all of the fish collected at Highway 140 have a complete consumption restriction for the sensitive population, with PCB concentrations in the fish ranging from a mean of 313ng/g in black crappie and rock bass to 1157ng/g in white sucker. For the general population, all of the fish, with the exception of carp and white sucker are restricted to two meals per month (PCB concentrations for this category ranging from 305-610ng/g). Carp and white sucker are restricted to one meal per month (PCB concentrations 610-1220ng/g).

When regressions are run on all the existing data to assess the concentrations which would likely be observed in fish from different size classes, other fish are also restricted for consumption (Table 11). The *Guide to Eating Ontario Sport Fish* advises no more than 8 meals per month should be consumed; hence advisories of '8' in Table 11 suggest that there are no restrictions on the fish of that size category. Upstream of Highway 140 (LC16), all fish listed, with the exception of bluegill, have a complete restriction for the sensitive population (women of childbearing age and children under 15) in the larger size ranges. Carp, brown bullhead, rock bass, black crappie and pumpkinseed are completely restricted at all sizes. Downstream of the QEW, only carp (55cm and greater), largemouth bass (>30cm) and yellow perch (<25cm) have complete restrictions for the most sensitive populations.

For the general population, complete restrictions were observed for carp (<50cm) and white sucker (<35cm). Brown bullhead (30-35cm), largemouth bass (30-40cm) and pumpkinseed (<15cm) were restricted to 1 meal/month, and rock bass (>15cm) and black crappie (20-25cm) were restricted to 2 meals/month. All restrictions were a result of elevated PCBs (Table 11). Bluegill were restricted to 4 meals/month. Downstream of the QEW carp, brown bullhead, largemouth bass and yellow perch were the only fish restricted; carp (<55cm) was restricted to 1 meal/month, and brown bullhead (30-35cm), largemouth bass (35-40cm) and yellow perch (25-30cm) were all restricted to 4 meals/month. There are no restrictions downstream of the QEW that can be attributed to PCBs for any of these fish.

TEQ values were calculated from the concentrations of the 12 co-planar PCBs observed in the fish collected from Highway 140 in 2003. All of the fish species collected exceeded the IJC criteria (0.79ng TEQ/kg) by up to 500 times (white sucker: Table 12, Figure 26). The lowest mean TEQ values were observed in carp (76.2ng TEQ/kg), which had the highest mean PCB concentration (mean: 1116ng/g; Table 10, Figure 26). The co-planar PCB concentrations driving the TEQ values were primarily congener IUPAC number 126 (3,3',4,4',5 pentachlorobiphenyl), followed by congener 118 (2,3',4,4',5 pentachlorobiphenyl) which mirrors the congeners driving the TEQ values in the forage fish from 2003. Carp TEQ values were the only values that differed significantly from those from any of the other species; TEQ values in carp were significantly lower than those observed in largemouth bass (mean: 76.2ng TEQ/kg and 181ng TEQ/kg respectively, $p=0.015$).

4 DISCUSSION

The primary contaminants of concern in Lyons Creek were PCBs. Sediment concentrations were elevated above the PSQG LEL criteria throughout most of Lyons Creek, from the vicinity of the Welland-pipe property, where concentrations at Ridge Road (LC03) were almost at the PSQG SEL, to as far down as McKenny Road (LC29). At the most upstream location (LC01), sediment PCB levels were significantly lower, and were observed below the PSQG LEL criteria. The prominent congener pattern in the sediment of Lyons Creek East closely resembles that of aroclor 1248. No obvious source of PCBs in this area was identified. Similar homologue patterns in the sediment at the most upstream location (LC01) compared to those observed downstream indicate that, although PCB contamination is primarily downstream of Welland-pipe, the contamination may originate from a previous upstream source. A Stelco rolling mill and a Hydro transformer station are located in the West portion of Lyons Creek. A spill from the transformer station did occur prior to the construction of the Welland Canal. Either of the two properties located on the west portion of the creek may

potentially be the source of PCB contamination observed in Lyons Creek East. Some metals (primarily nickel, zinc and copper) were also elevated above the PSQG SEL criteria in the upper portion of the creek (upstream of Highway 140).

Congener patterns observed in the lower portion of the creek (LC38) resembled that of aroclor 1016, which was also observed at one of the reference locations (Black Creek). This aroclor has also been observed at upstream reference locations and reference streams in other studies (Lindsay, Peninsula Harbour: MOE, unpublished) and, together with the relatively low concentrations observed may be indicative of normal background conditions. The low PCB (and metal) concentrations in the downstream areas of Lyons Creek suggests that contamination observed upstream is not entering the Welland River.

The results of multivariate analysis suggest that uptake of PCBs in the portion of the creek from Ridge Road to Highway 140 closely resemble aroclor 1248, whereas those from the most downstream portion and the reference streams resemble aroclor 1016. Mussels from the most upstream and downstream portions of the creek fall within the 90% confidence ellipse plotted around the reference data, suggesting that these locations are similar in PCB concentration and pattern to that observed in the reference creeks. Mussels from between Ridge Road and Highway 140 all fell outside of the 99%-99.9% ellipses, suggesting that these mussels are considerably different in PCB concentration and congener pattern to the reference.

Mussels deployed downstream of Highway 140 (LC17) in 2002 had the highest PCB concentrations; in 2003 the highest concentrations were observed further upstream of LC12. The PCB concentrations at these sites, as well as the other locations between downstream of Ridge Road (LC08) and Highway 140 all exceeded the IJC guideline for the protection of fish-eating wildlife; consumption of these mussels may therefore pose a potential threat to the resident wildlife. The homologue patterns in the clam tissue from the upper portion of the creek closely resembled aroclor 1248. Studies on aroclor 1248 (e.g. Barsotti et al. 1976) have shown that ingestion of 0.1-0.2mg/kg body weight/day of this aroclor over a 2 month period resulted in hair loss, acne and swelling eyelids of Rhesus monkeys. Adverse effects of PCBs on avian wildlife most commonly result in reduced egg productivity and hatchability, as well as reduced chick growth rates. Lillie and co-workers (Lillie et al. 1974) recorded reduced egg productivity and hatchability in white leghorns fed a diet of 1.2mg/kg bw/day of aroclor 1248. The concentrations observed in the mussels from Lyons Creek were in the region of three times less than the doses reported by Lillie et al. (1974).

Toxic equivalent (TEQ) concentrations allow us to assess the toxicity of the coplanar (dioxin-like) PCB congeners. These values can then be compared to the Environment Canada tissue residue guideline (TRG) (CCME 2001); calculated TEQ concentrations above the TRG value put wildlife consuming these organisms at risk of adverse effects. The calculated TEQ values were most

elevated in 2002 at Highway 140. Levels observed in 2003 were similar to those in 2002, with the highest concentrations being recorded at LC12. Mussels located between LC08 and Highway 140 exceeded the CCME TEQ criteria (CCME, 2001). These data suggest bioavailable PCBs exist upstream of Highway 140 at concentrations which may pose an adverse effect to wildlife.

Total PCB concentrations in forage fish collected in 2002 were elevated to concentrations exceeding the IJC criteria for the protection of fish-eating wildlife by as much as 100 times. The highest concentrations in 2003 were observed immediately upstream of Ridge Road, and the next highest levels were observed at Highway 140. While PCB tissue concentrations were considerably lower in 2003, concentrations were still elevated over the IJC criteria at Highway 140 by as much as 25 times. PCB concentrations recorded in the fish tissue above the IJC criteria pose a threat to organisms eating fish from Lyons Creek.

In 2002, only fish collected from upstream of Highway 140 exceeded the CCME TRG (2001: 0.79ng TEQ/kg), in 2003 all the fish collected from Lyons Creek, as well as from Usshers Creek, exceeded the CCME TRG by in excess of 63 to 400 times. The high levels observed in 2003 were primarily driven by congener 126 (3,3',4,4',5 pentachlorobiphenyl) which has an extremely high toxic equivalency factor (TEF = 0.1), followed by congener 118 (2,3',4,4',5 pentachlorobiphenyl). In 2002 congener 126 was not observed and the TEQs were primarily driven by congener 118. In both years fish were collected, the most downstream location (LC38) had the lowest TEQ values. The distinct downstream trend in declining TEQ values further supports the evidence to suggest that the source of PCBs to the system originate from the upper portion of the creek and that these concentrations are at levels which can adversely impact the aquatic organisms in the system and the wildlife feeding on these organisms.

PCB concentrations in the sport fish fillets collected from Highway 140 were significantly higher than those collected from downstream of the QEW; a trend which has been observed in the past. Sport fish have historically been elevated in the vicinity of Highway 140 such that restrictions of as little as 1 meal per month (pumpkinseed, 1994), based on the consumption advice of that time (MOE 1995), have been advised. Carp and white sucker PCB concentrations recorded during this study (2002 and 2003) were observed at levels that would result in consumption restrictions of one to two meals per month. All other species collected from Highway 140 were below 500ng/g, which was the former criterion at which restriction to 4 meals per month were set. The highest concentrations observed during the study were in the carp from 2002, which had as much as 3000ng/g PCBs in the tissue. However, when regressions are run on the data to assess the concentrations likely to be observed in fish of different size classes, all fish have some degree of restriction for their consumption. Minks fed on diets containing perch (0.69mg PCB/kg diet), white sucker (0.63mg PCB/kg diet) and whitefish (0.48mg PCB/kg diet) for seven months exhibited impaired reproduction (Hornshaw et al. 1986). Leghorn chicks fed diets of contaminated

carp with PCB residues as high as 6.6mg PCB/kg diet showed a 40% deformity rate (Summer et al. 1996). The concentrations observed in the fish collected from some of the sites in Lyons Creek have the potential to exceed these doses. Although the carp concentrations collected from Highway 140 were all below the concentrations reported by Summer et al. (1996), white sucker concentration were elevated above those considered by Hornshaw et al. (1986) at which minks exhibited impaired reproduction.

TEQ concentrations in the fillets collected from Highway 140 in 2003 exceeded both the mammalian (0.79ng TEQ/kg) and avian (2.4ng TEQ/kg) TRG (CCME, 2001). As in forage fish, the congener driving these elevated TEQ concentrations was congener 126.

5 CONCLUSIONS

PCB concentrations in the upper portion of Lyons Creek, in the vicinity of Highway 140 are elevated in all media (i.e. sediment, mussels, forage and sport fish). The levels of PCBs observed in this portion of Lyons Creek exceed their respective guidelines at one or more locations:

- The surficial sediment levels observed downstream of the Welland-pipe discharge pipe exceed the PSQG SEL values, and the PCB concentrations are close to, but below the SEL.
- Concentrations of PCBs that have bioaccumulated in the tissue of caged mussels over a three-week period are highest in the vicinity of Highway 140. PCB concentrations in the mussels at this location exceed the IJC guideline for the protection of fish-eating wildlife. PCBs in the mussels further downstream of Highway 140 are also elevated, but do not exceed this guideline. TEQ concentrations, calculated from the dioxin-like PCBs between Ridge Road and Highway 140 exceed the CCME guideline for the protection of wildlife. Since mussels tend to bioaccumulate PCBs primarily from the water, these data suggest that the PCBs observed in the system further upstream are mobile in the water column and are available to the resident biota.
- Forage fish collected from the more upstream locations (LC03 and LC16) had total PCB concentrations which exceeded the IJC guideline by as much as 80 times. These levels suggest that the PCBs observed in the upstream portion of Lyons Creek are bioavailable to the biota at levels that may be harmful to fish-eating wildlife. The TEQ values calculated from the dioxin-like PCBs also exceed the CCME guideline for the protection of fish eating wildlife at these locations.

- Upstream of Highway 140 (LC16), all sport fish have some degree of consumption advisory. It is advised that women of childbearing age and children do not consume any carp, brown bullhead, rock bass, black crappie or pumpkinseed of any size, or largemouth bass greater than 20cm, white sucker greater than 25cm or bowfin greater than 45cm.
- PCB concentrations in the sediments at the downstream portion of Lyons Creek exceed the PSQG LEL, but are at levels that are not considered a threat to the biota and wildlife in the system. PCB levels in the mussel tissue and forage fish were below the IJC guidelines, and generally their respective TEQ values below the CCME guideline. There were also no consumption restrictions due to PCBs for the sport fish collected from this area.

These data suggest that the extremely high levels of PCBs observed in the sediments at LC03 are mobile, bioavailable to the biota, and may potentially be toxic to sediment dwelling organisms. Elevated PCBs in the sediments are observed as far down the system as Doan's Ridge Road. The tissue data from mussels, and forage and sport fish suggest that these PCBs only tend to be bioaccumulated at levels that are of concern in the upper reaches of the Creek (as far down as Highway 140).

The extent of PCB contamination in the biota seems to be relatively localized and does not appear to extend to the Niagara River. No single source has been identified to date, and the PCB congener data tends to suggest that the PCBs observed at LC03 are weathered (Reiner, Pers. Comm.), and the source may therefore be historical.

6 RECOMMENDATIONS

1. The data suggest that the source of PCB contamination is likely historical, and is both mobile and bioavailable. Further work needs to be conducted on the Westerly portion of Lyons Creek to identify the origin of the contamination in Lyons Creek East.
2. PCB contamination in the creek is at levels which may pose both an ecological and human health threat. Exposure pathways need to be identified and a remediation/management strategy needs to be developed to address PCB contamination in Lyons Creek East.

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TABLES

Table 2: Surficial sediment OC pesticide concentrations from the initial screening survey of Lyons Creek East.

Group		a-BHC (hexachlorocyclohexane) ng/g	Dieldrin ng/g	Endrin ng/g	g-BHC (hexachlorocyclohexane) ng/g	g-Chlordane ng/g	pp-DDD ng/g	pp-DDE ng/g	pp-DDT ng/g								
1	LC02	1	<=W	4	<T	8	<T	1	<=W	2	<=W	5	<=W	750		15	<T
2	LC01	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	5	<T	5	<=W
3	LC03	2	<T	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	400		5	<=W
3	LC04	2	<T	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	120		5	<=W
3	LC05	2	<T	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	160		5	<=W
3	LC06	2	<T	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	100		5	<=W
3	LC07	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	140		5	<=W
3	LC08	2	<T	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	460		5	<=W
3	LC09	2	<T	2	<=W	4	<=W	1	<=W	2	<=W	10	<T	240		5	<=W
3	LC10	2	<T	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	290		5	<=W
3	LC11	2	<T	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	210		5	<=W
3	LC12	2	<T	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	77		5	<=W
3	LC13	2	<T	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	90		5	<=W
3	LC17	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	120		5	<=W
3	LC38	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	1	<=W	5	<=W
3	MEAN	1.8	<=W	2.0	<=W	4.0	<=W	1.0	<=W	2.0	<=W	5.4	<=W	185.2	<=W	5.0	<=W
4	LC15	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	61		5	<=W
5	LC18	2	<T	4	<T	4	<=W	1	<=W	2	<=W	5	<=W	81		5	<=W
5	LC19	2	<T	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	91		5	<=W
5	LC20	3	<T	4	<T	4	<=W	1	<=W	2	<=W	5	<=W	48		5	<=W
5	LC21	2	<T	2	<=W	4	<=W	2	<T	2	<=W	5	<=W	33		5	<=W
5	LC22	2	<T	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	64		5	<=W
5	LC23	3	<T	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	51		5	<=W
5	LC24	1	<=W	8	<T	4	<=W	1	<=W	2	<=W	5	<=W	12		5	<=W
5	LC25	1	<=W	6	<T	4	<=W	1	<=W	2	<=W	5	<=W	46		5	<=W
5	LC26	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	20		5	<=W
5	LC27	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	38		5	<=W
5	LC28	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	18		5	<=W
5	LC29	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	17		5	<=W
5	LC30	1	<=W	16	<T	4	<=W	1	<=W	2	<=W	5	<=W	30		5	<=W
5	LC31	1	<=W	6	<T	4	<=W	1	<=W	2	<=W	5	<=W	11		5	<=W
5	LC32	1	<=W	2	<=W	4	<=W	1	<=W	8	<T	5	<=W	12		5	<=W
5	LC33	1	<=W	4	<T	4	<=W	1	<=W	4	<T	5	<=W	10		5	<=W
5	LC34	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	10		5	<=W
5	LC35	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	4	<T	5	<=W
5	LC39	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	4	<T	5	<=W
5	LC40	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	1	<=W	5	<=W
5	LC36	1	<=W	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	1	<=W	5	<=W
5	MEAN	1.4	<=W	3.6	<=W	4.0	<=W	1.0	<=W	2.4	<=W	5.0	<=W	28.7	<=W	5.0	<=W
6	LC14	4	<T	2	<=W	4	<=W	5	<T	2	<=W	5	<=W	240		5	<=W
7	LC16	2	<T	2	<=W	4	<=W	1	<=W	2	<=W	5	<=W	800		5	<=W
PSQG	LEL	6		2		3		3		8		5					
	SEL*	10000		91000		130000		1000		6000		19000					

SEL* corrected for TOC

<W No measurable response (zero)

<T a measurable trace amount

<W for all sites:

a-Chlordane
Aldrin
b-BHC (hexachlorocyclohexane)
Endosulphan I
Endosulphan II
Endosulphan sulphate

Heptachlor
Heptachlor epoxide
Methoxychlor
Mirex
op-DDT
Oxychlordane

Table 7 cont'd: General chemistry, OC, PAH and PCB concentrations of surficial sediment groupings (as determined through cluster analysis) collected from Lyons Creek in 2002 and 2003 - OC pesticides

	Dieltin	Endosulphan I	Endosulphan II	Endosulphan sulphate	Endrin	g-BHC (hexachlorocyclohexane)	g-Chlordane	Hepachlor	Hepachlor epoxide	Methoxychlor	Mirex	op-DDT	Oxychlordane	pp-DDD	pp-DDE	pp-DDT	DT & Metabolites
Group 1	02LC12	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC06*	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC08A*	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC08B*	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC10*	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC12	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC14*	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	Group 1 average	6.29	4.00	4.00	4.00	4.00	2.00	1.00	1.00	5.00	5.00	5.00	2.00	5.00	78.29	5.00	78.29
Group 2	02LC01	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
Group 3	02LC17	4	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC14	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC17	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC18A*	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	02BLC02	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC01*	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	Group 3 average	2.33	4.00	4.00	4.00	4.00	2.00	1.00	1.00	5.00	5.00	5.00	2.00	5.00	17.00	5.00	17.33
Group 4	02LC03	2	4	16	24	3	2	1	2	5	5	5	2	5	340	5	340
Group 5	03LC19	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC18*	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC23A*	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC23*	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC38*	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	Group 5 average	2.00	4.00	4.00	4.00	4.00	2.00	1.00	1.00	5.00	5.00	5.00	2.00	5.00	13.83	5.00	14.00
Group 6	03TC04	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03TC04*	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	03LC16	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	02LC2901	8	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	02LC2901	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	02LC2902	4	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	02LC2903	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	02LC38	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	02BEC01	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	02BEC02	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	02BLC01	2	4	4	4	4	2	1	1	5	5	5	2	5	140	5	140
	Group 6 average	2.73	4.00	4.00	4.00	4.00	2.00	1.00	1.00	5.00	5.00	5.00	2.00	5.00	9.36	5.00	7.64
PSGG SEL		91000*	130000*	10000*	6000*	5000*	6000*	19000*	6000*	13000*	13000*	6000*	6000*	12000*	71000*	71000*	71000*
PSGG LEL		2	3	3c	7c	5c	7c	5c	7c	5c	7c	5c	7c	5c	7c	5c	7c

<W no measurable amount (zero)
 <T a measurable trace amount
 * SEL to be TOC corrected
 SLC screening Level Concentration
 a = op-pp-DDT
 d-DDT total
 b=90% SLC
 c=10% SLC
 MEI=0.3
 di-chlordane

Table 11: MOE Guide to Eating Ontario Sport Fish restrictions for fish collected from Lyons Creek at Highway 140 and downstream of the QEW. Consumption advisory is provided for different size classes of fish and is expressed in terms of meals/month. 'Sensitive' = women of childbearing age and children under 15. 'General' = the general public.

		Size category												
		15	20	25	30	35	40	45	50	55	60	65	70	75
Lyons Creek at Hwy. 140 Niagara R.M.														
Carp	General		1		1				0			0		
	Sensitive		0		0							0		
Brown Bullhead	General		2		1									
	Sensitive		0											
White Sucker	General		4	2	1		0		0					
	Sensitive		4	0	0			0						
Bowfin	General						4		2		2			
	Sensitive						4		0		0			
Largemouth Bass	General		4	2		1								
	Sensitive		4	0										
Rock Bass	General		2											
	Sensitive		0											
Black Crappie	General			2										
	Sensitive			0										
Pumpkinseed	General		1											
	Sensitive		0											
Bluegill	General		4											
	Sensitive		4											

2003 PCBs
 2002 PCBs
 1994 PCBs
 1991 PCBs

		Size category												
		15	20	25	30	35	40	45	50	55	60	65	70	75
Lyons Creek downstream of QEW Niagara R.M.														
Northern Pike	General							8						
	Sensitive							8						
Carp	General							8	8		1			
	Sensitive							8	8		0			
Brown Bullhead	General		8	8	4									
	Sensitive		8	8	4									
Bowfin	General							8						
	Sensitive							4						
Largemouth Bass	General			8		4								
	Sensitive			8	4	0								
Yellow Perch	General		8	4										
	Sensitive		8	4	0									
Rock Bass	General		8											
	Sensitive		8	4										
Pumpkinseed	General		8											
	Sensitive		8											
Bluegill	General		8											
	Sensitive		8											
Black Crappie	General			8										
	Sensitive			4										
White Crappie	General			8										
	Sensitive			4										

2002 Hg;
 2000 PCBs
 2000 dioxins

FIGURES

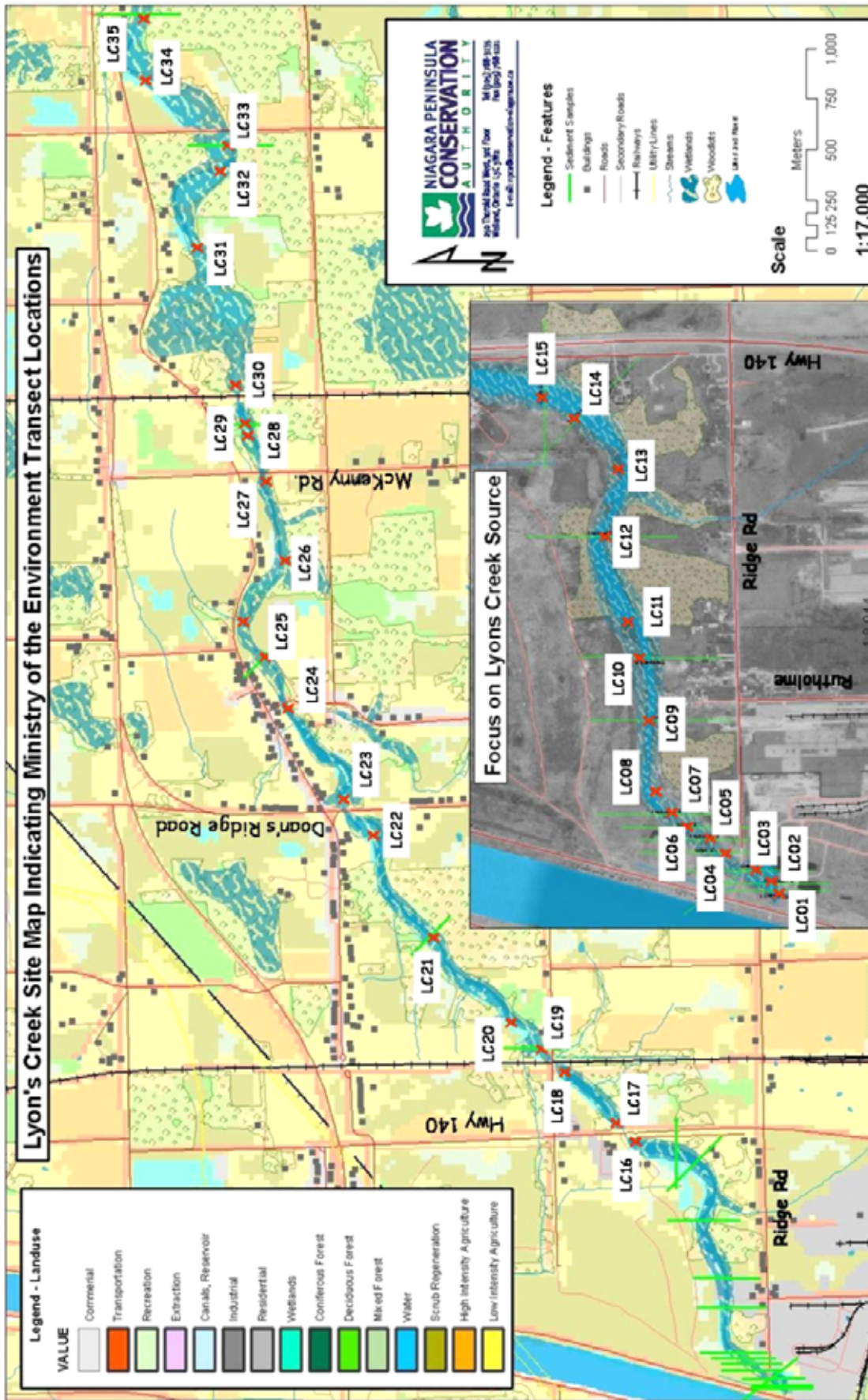


Figure 1: Sediment sample locations for initial screening survey. Samples were also be collected downstream on Montrose (39) and upstream (40) and downstream(38) of QEW



Figure 1b:. Location of reference creeks in relation to Lyons Creek.

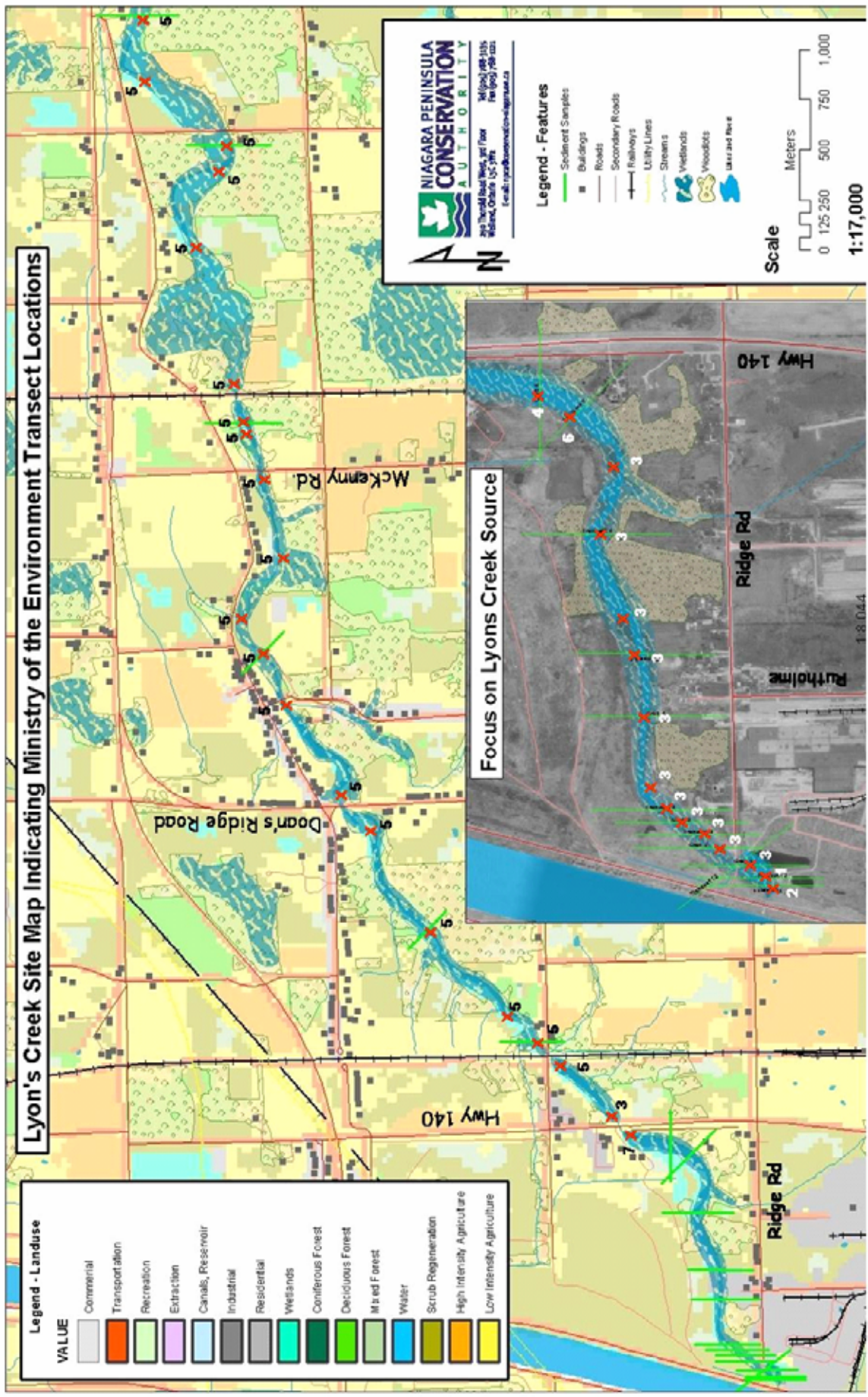


Figure 2: Sediment groupings as a result of cluster analysis on the sediment chemistry data. Group memberships are indicated. Stations located downstream at Montrose (39) and upstream of the QEW (40) were part of Group 5, and downstream of QEW (38) was part of Group 3.

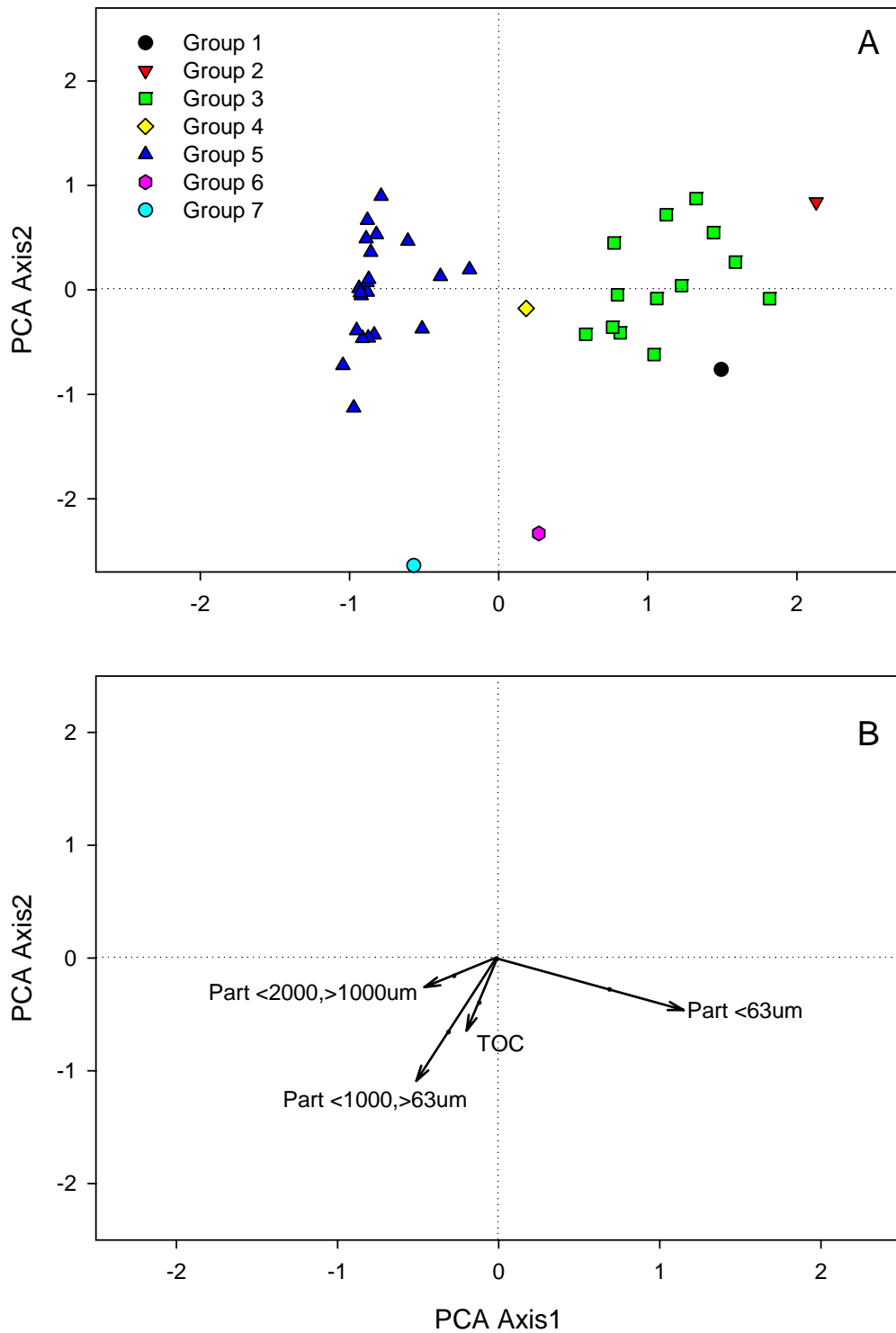


Figure 3: PCA ordination plot of Lyons Creek sediment samples. (A) Depicts the groupings identified through cluster analysis, (B) shows the vectors for Total Organic Carbon (TOC) and the three particle size classes.

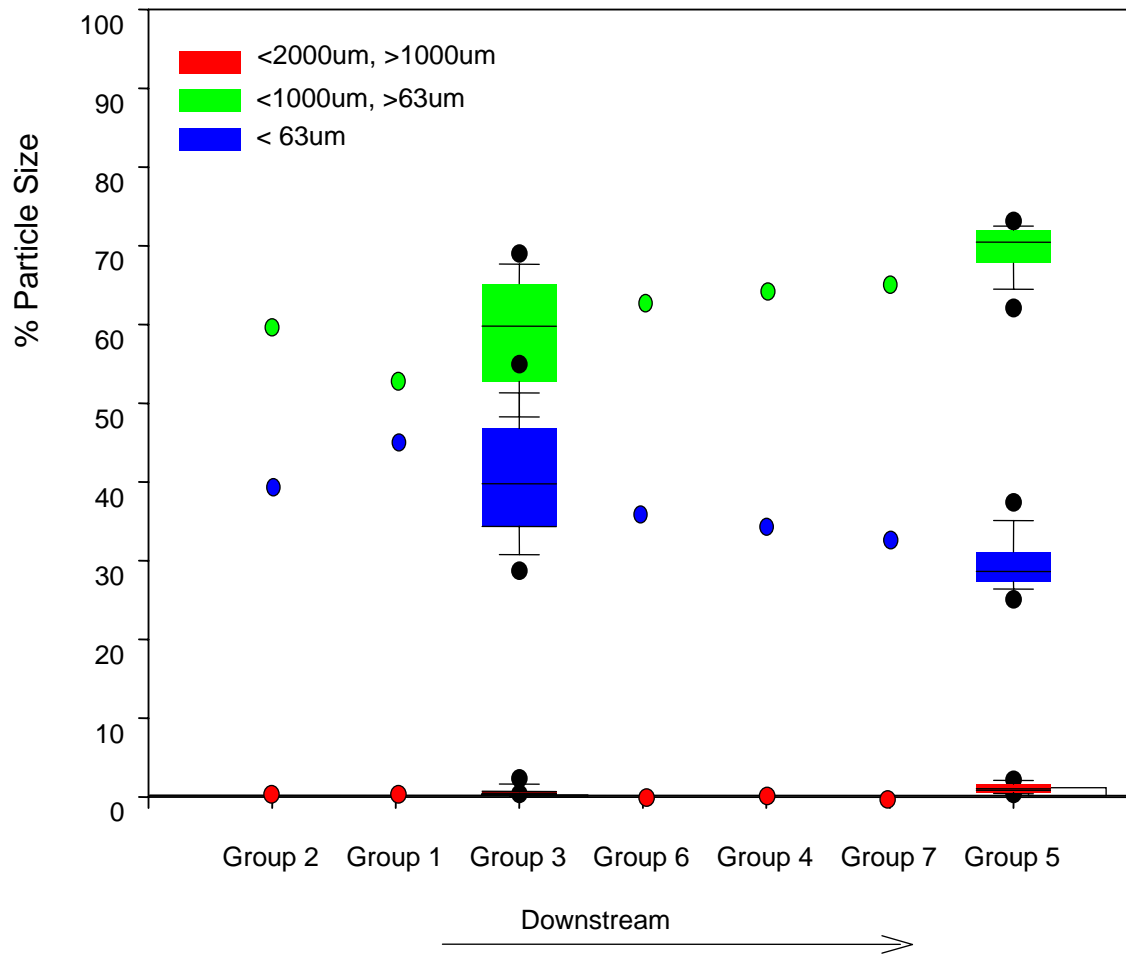


Figure 4: % particle size of the surficial sediment for the 7 identified sediment groupings along Lyons Creek. The range of data are defined by the coloured boxes, the upper and lower portion of the box represents the 90th and 10th percentiles respectively. The median is defined as the black line within each box. Error bars ('whiskers') and outliers (●) are also provided.

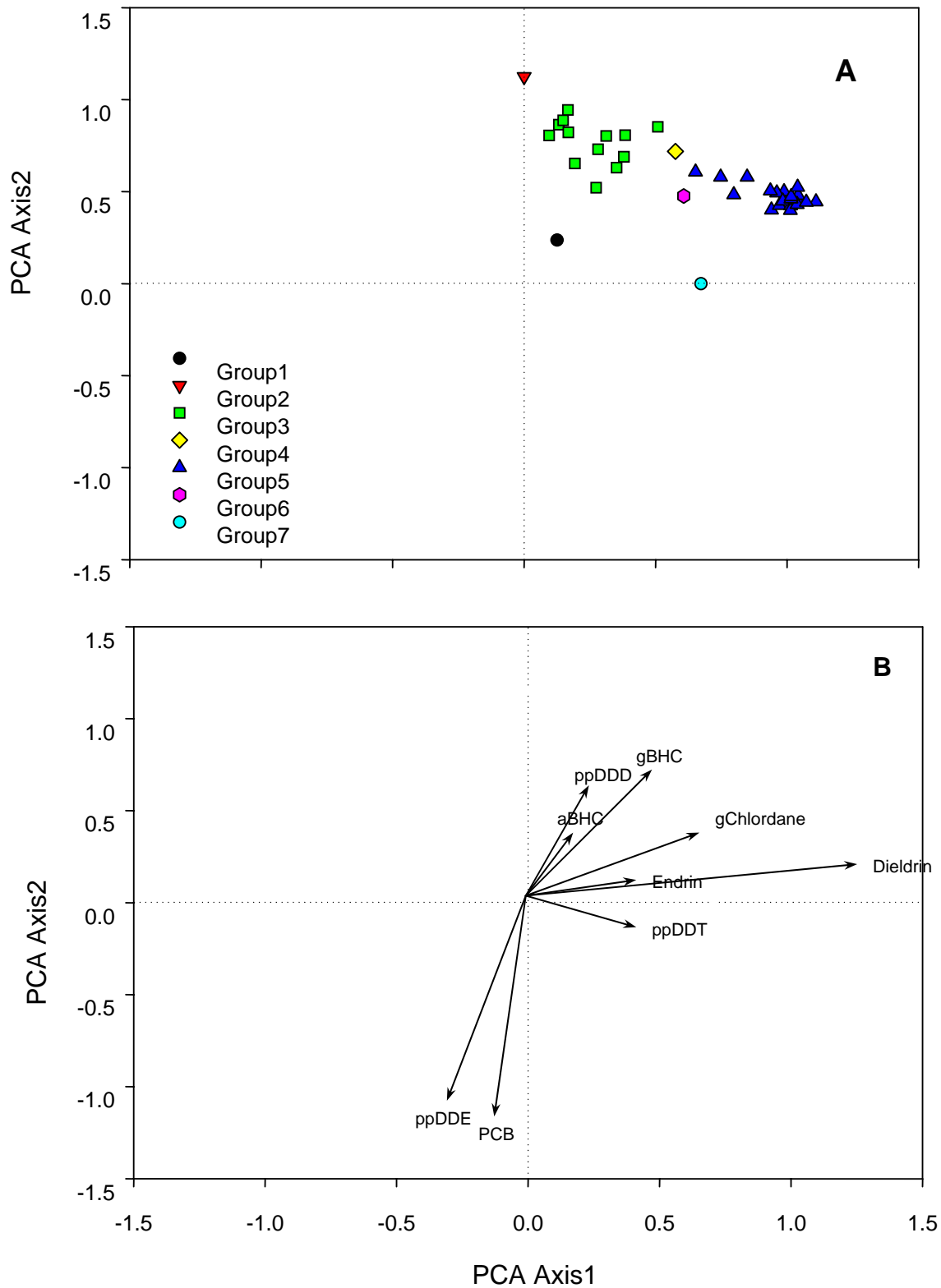


Figure 5: PCA ordination plot of Lyons Creek sediment samples corrected for TOC content. (A) Groupings indicated in the legend were identified through cluster analysis, (B) shows the vectors for PCBs and OC pesticides.

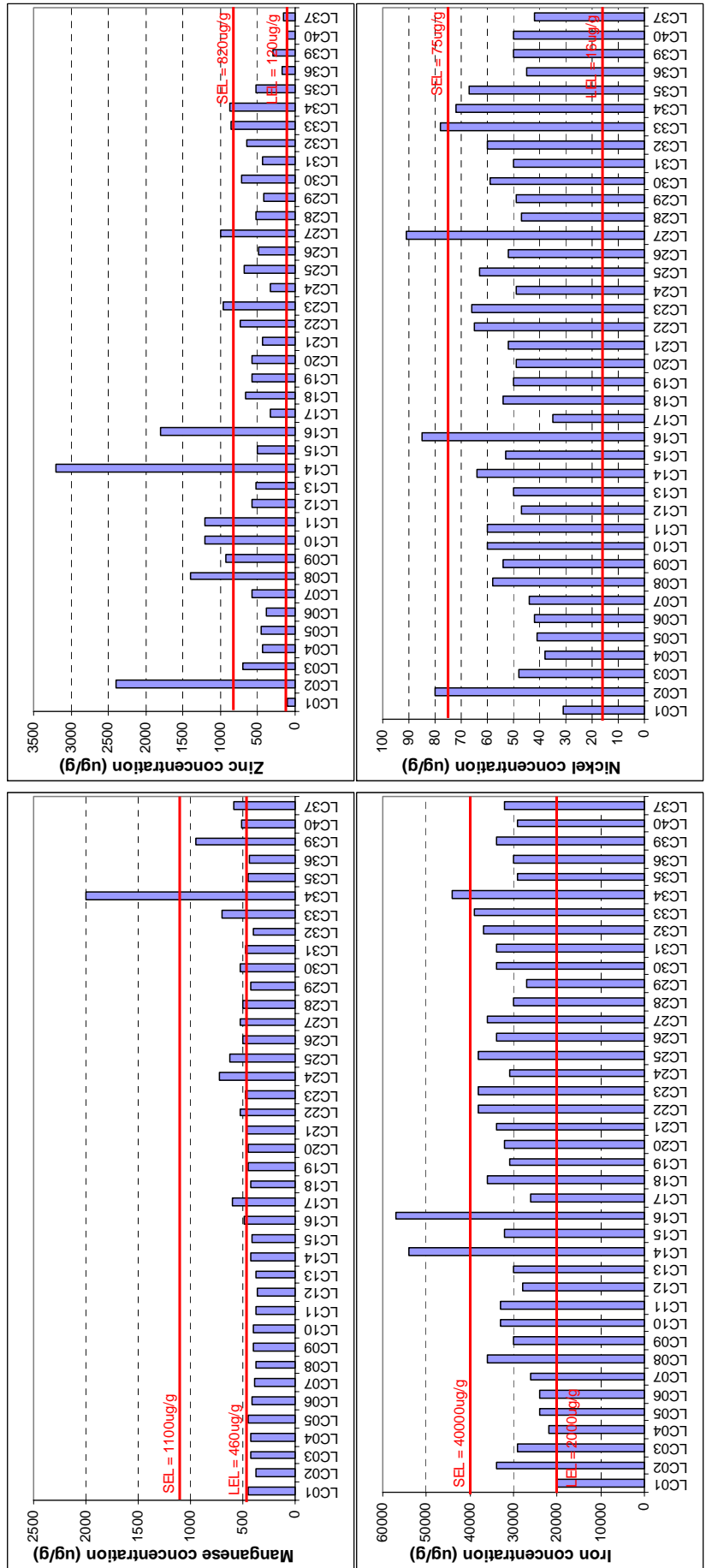


Figure 6: Selected metal concentrations in the surficial sediments collected along Lyons Creek East. The Provincial Sediment Quality Guidelines (PSQG) Lowest Effect Level (LEL) and Severe Effect Level for each metal are also provided.

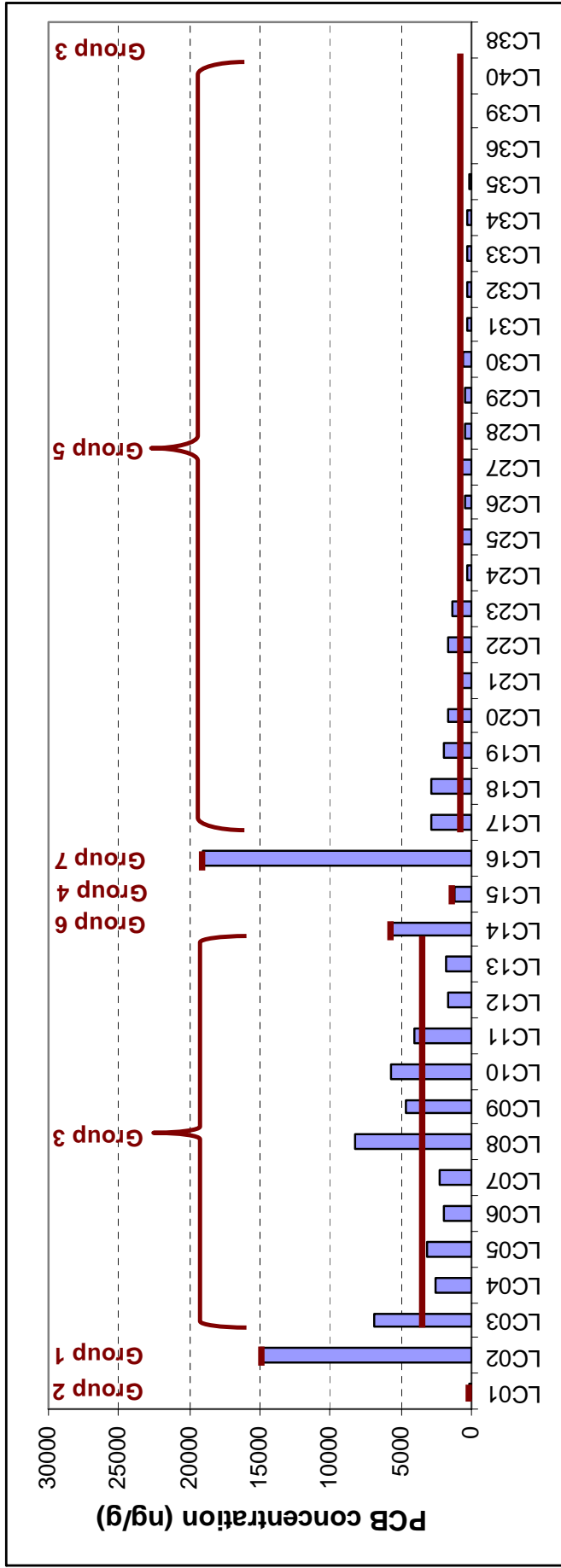


Figure 7: PCB concentrations and sediment grouping relationships for surficial sediments collected from the initial screening survey of Lyons Creek East. Horizontal lines represent mean PCB values for each grouping.

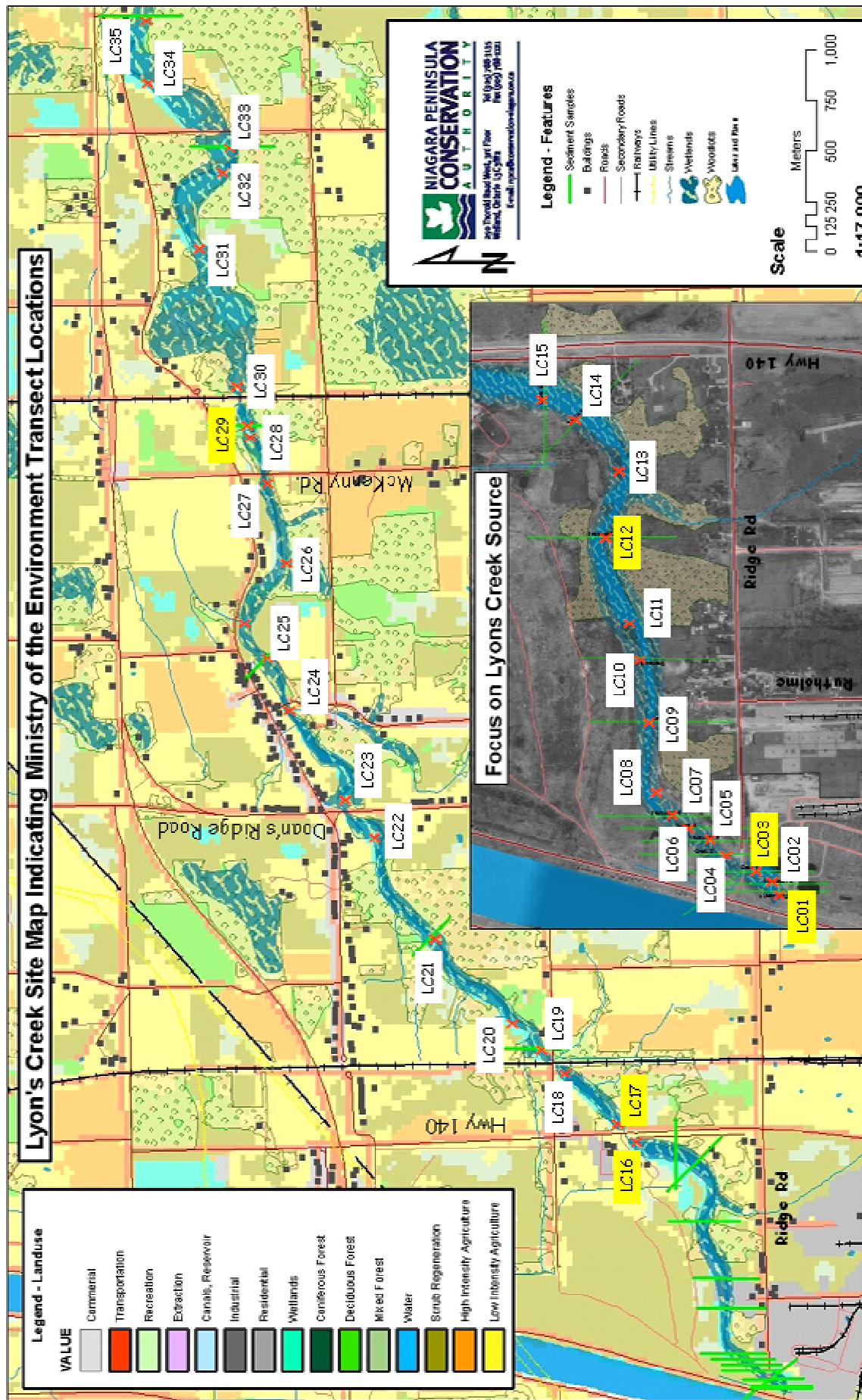


Figure 8: Sample locations for 2002 detailed survey. Locations highlighted represent those samples in 2002 for sediment, and/or mussels, forage fish and sport fish. Samples were also collected downstream of QEW (38) for sediment, mussels, forage fish and sport fish.

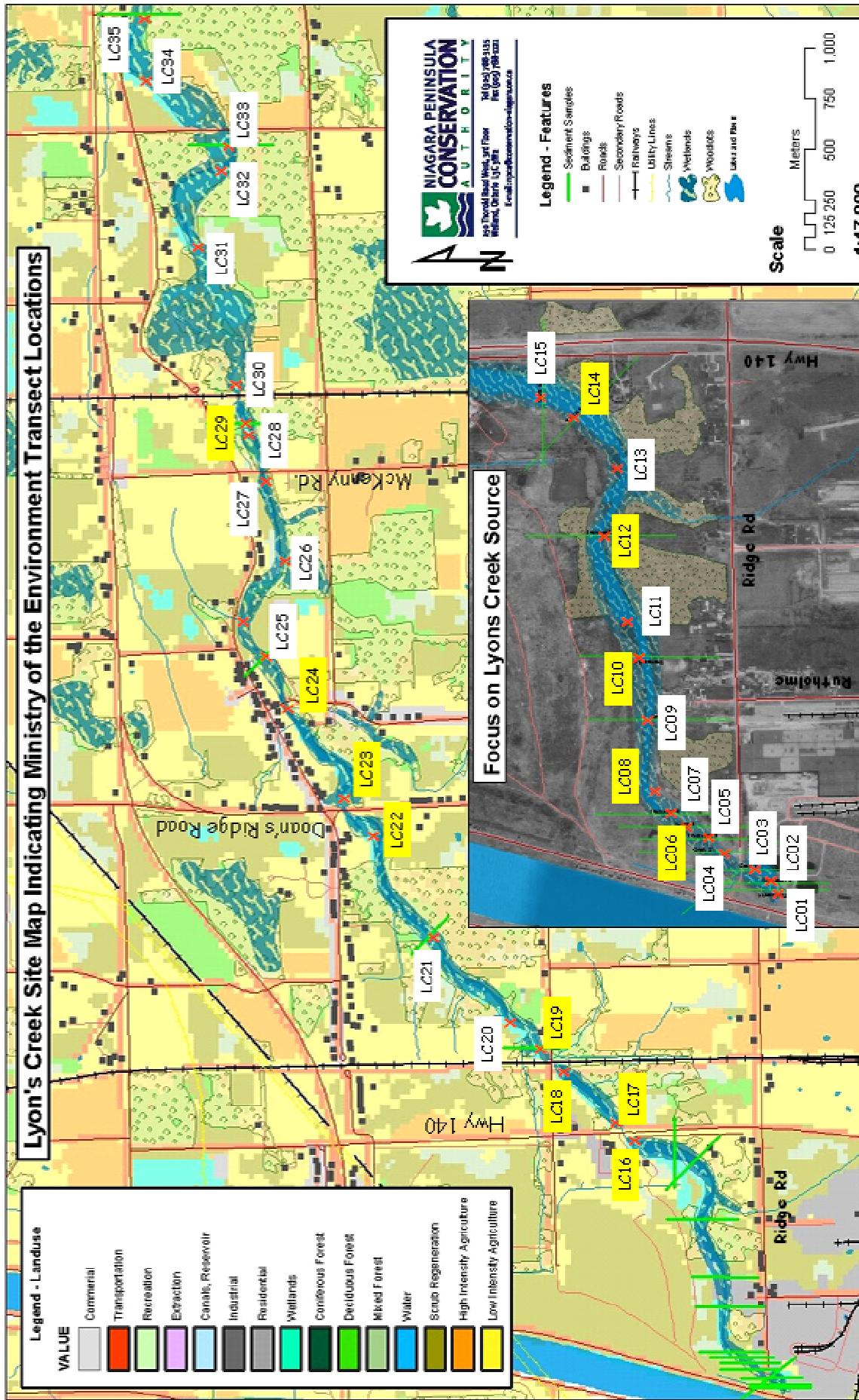


Figure 9: Sample locations for 2003 detailed survey. Locations highlighted represent those samples in 2003 for sediment, and/or mussels, forage fish and sport fish. Samples were also collected downstream of QEW (38) for sediment, mussels, forage fish and sport fish.

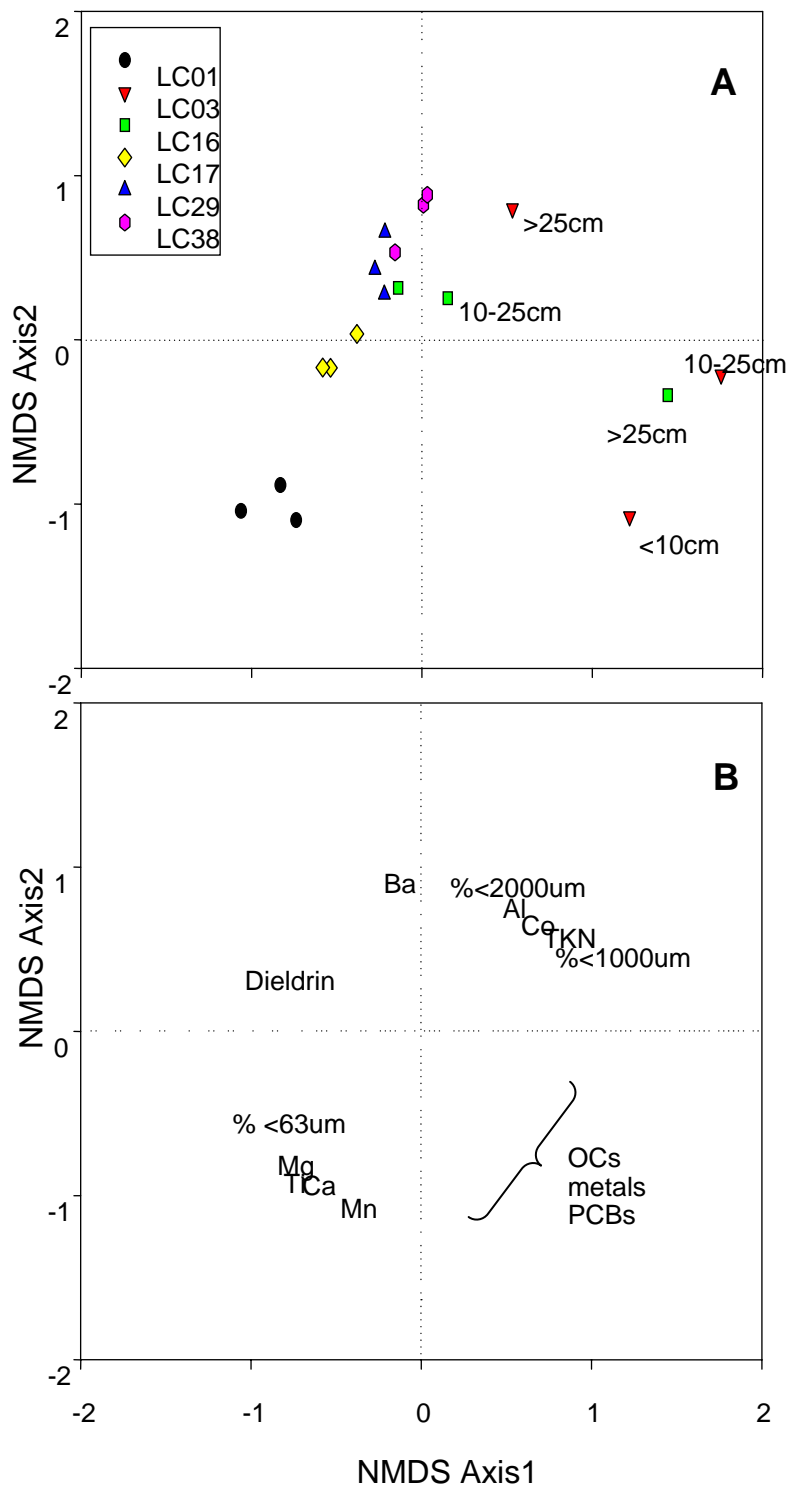


Figure 10: Sediment profile data for Lyons Creek. <10cm represents the surficial 10cm of sediment, 10-25cm represents the sediment collected at a depth of 10-25cm, and >25cm represents the historical sediment collected from a depth of greater than 25cm.

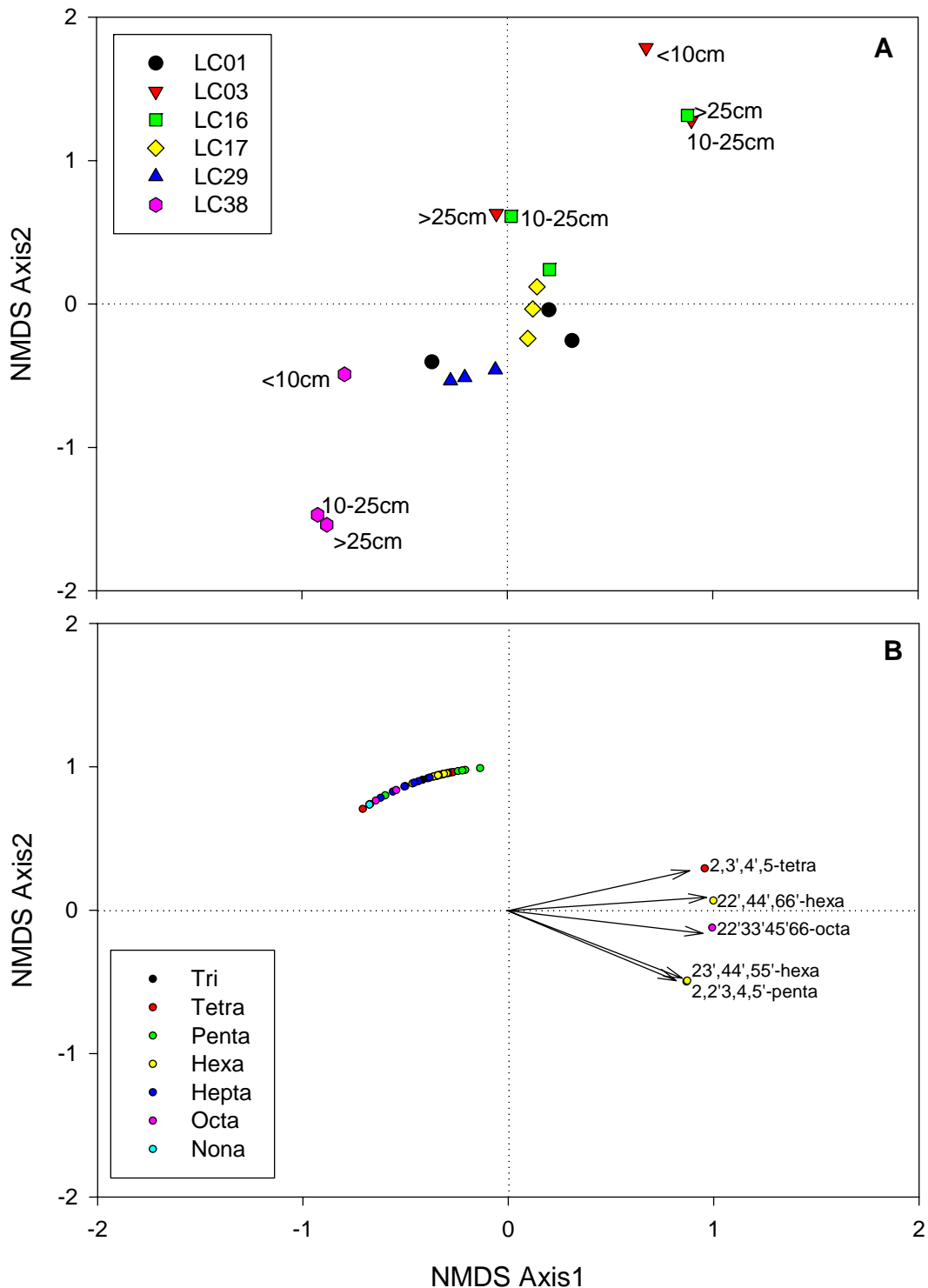


Figure 11: Sediment profiles of PCB congeners for Lyons Creek. (A) sediment cores with sections taken at less than 10cm, 10-25cm and greater than 25cm. (B) vectors of major congener groups

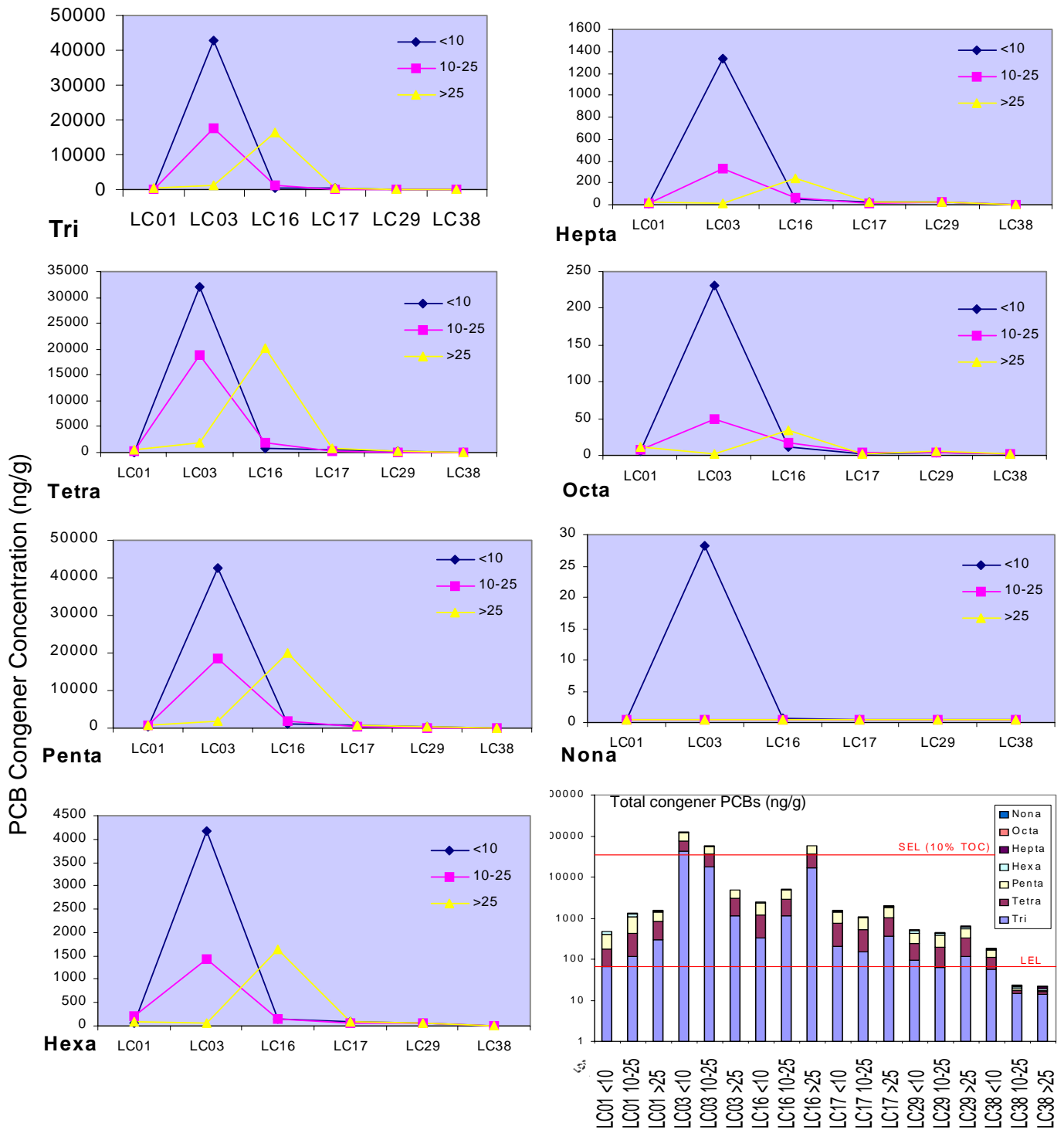


Figure 12: Seven PCB homologues found in the sediment of Lyons Creek. LEL = Provincial Sediment Quality Guidelines Lowest Effect Level criteria (70ng/g), SEL = Severe Effect Level (53,000 ng/g at 10% TOC)

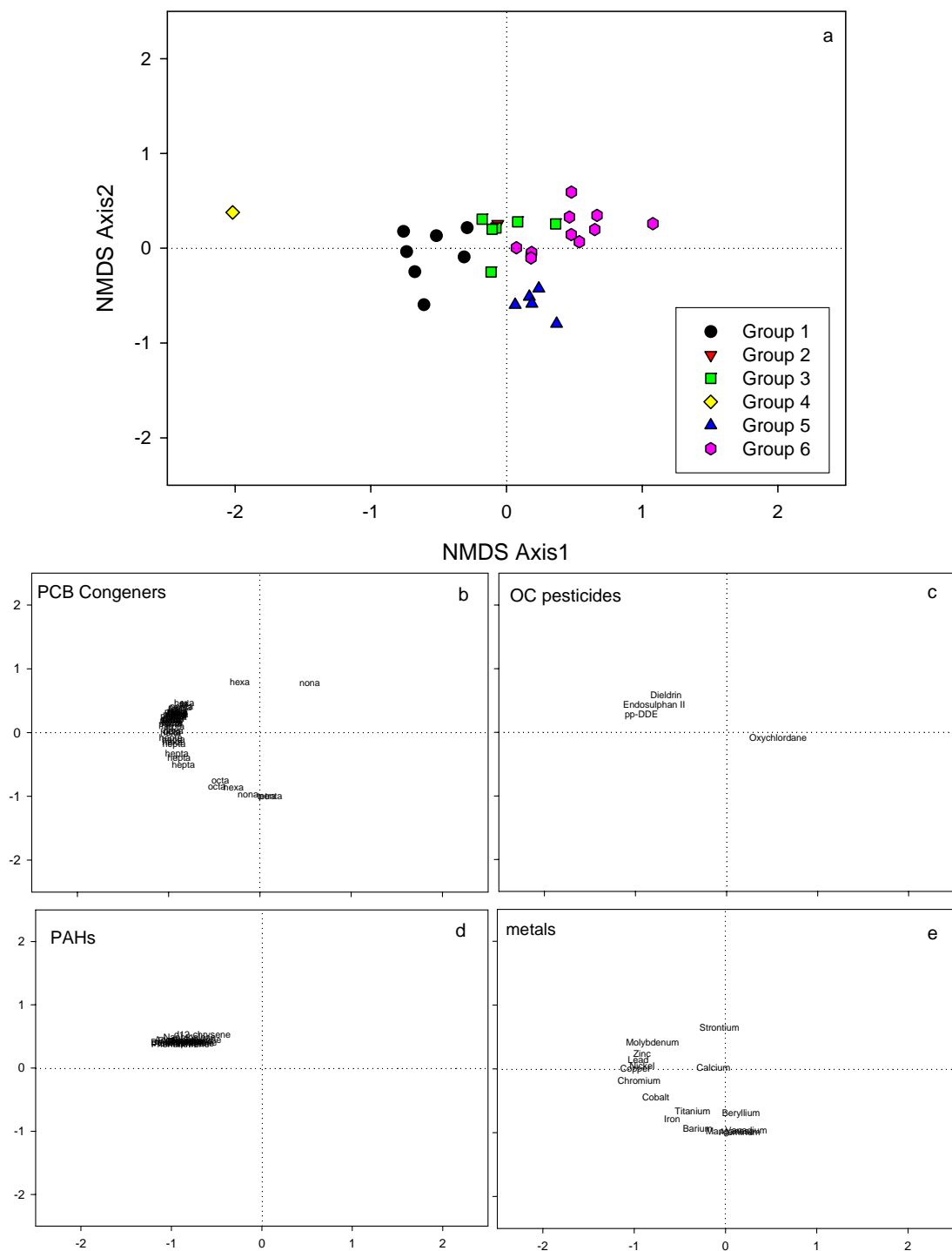


Figure 13: Lyons Creek sediment chemistry, 2002-2003. NMDS Axis1 vs. Axis2. (a) Ordination plot of site groupings. Sediment chemistry vectors are also provided for: PCB congener (b), OC pesticides (c), PAHs (d) and metals (e).

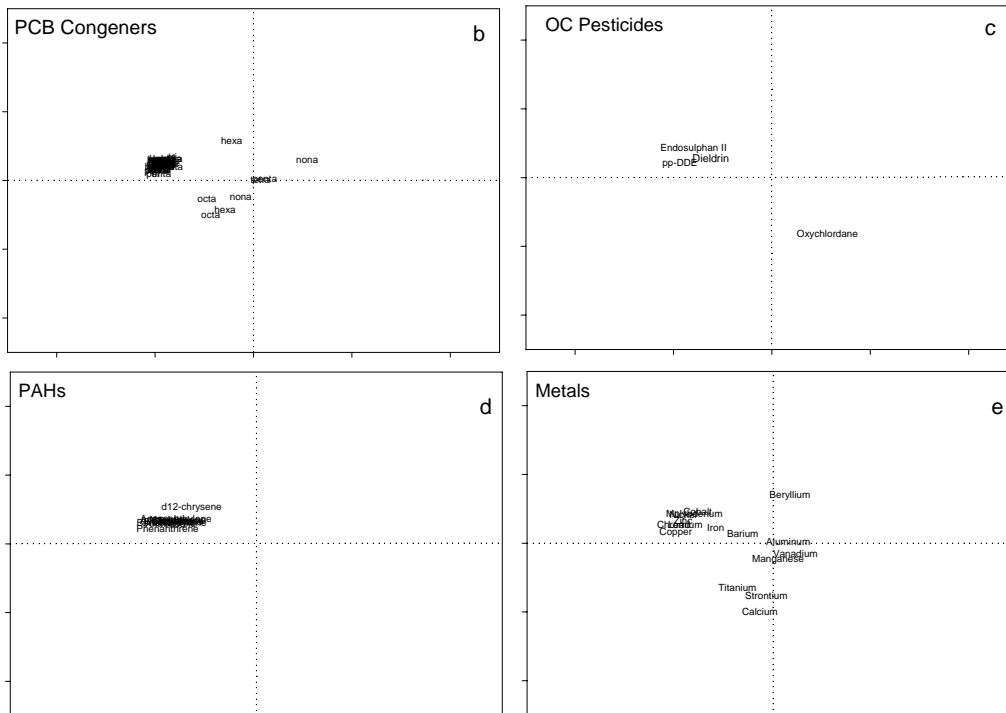
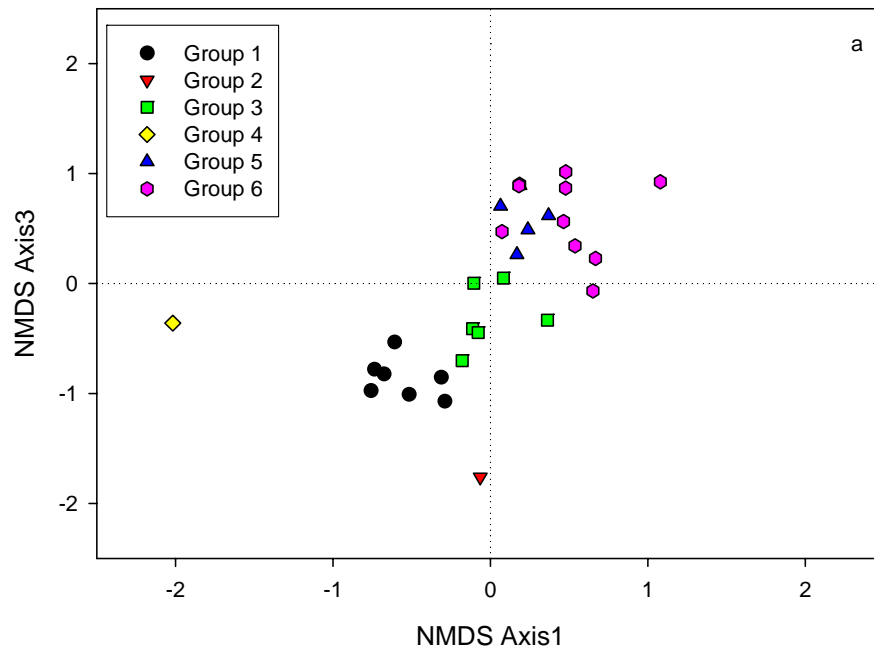


Figure 14: Lyons Creek sediment chemistry, 2002 - 2003. NMDS Axis1 vs. Axis3. (a) Ordination plot of site groupings. Sediment chemistry vectors are provided for: PCB congeners (b), OC pesticides (c), PAHs (d) and metals (e).

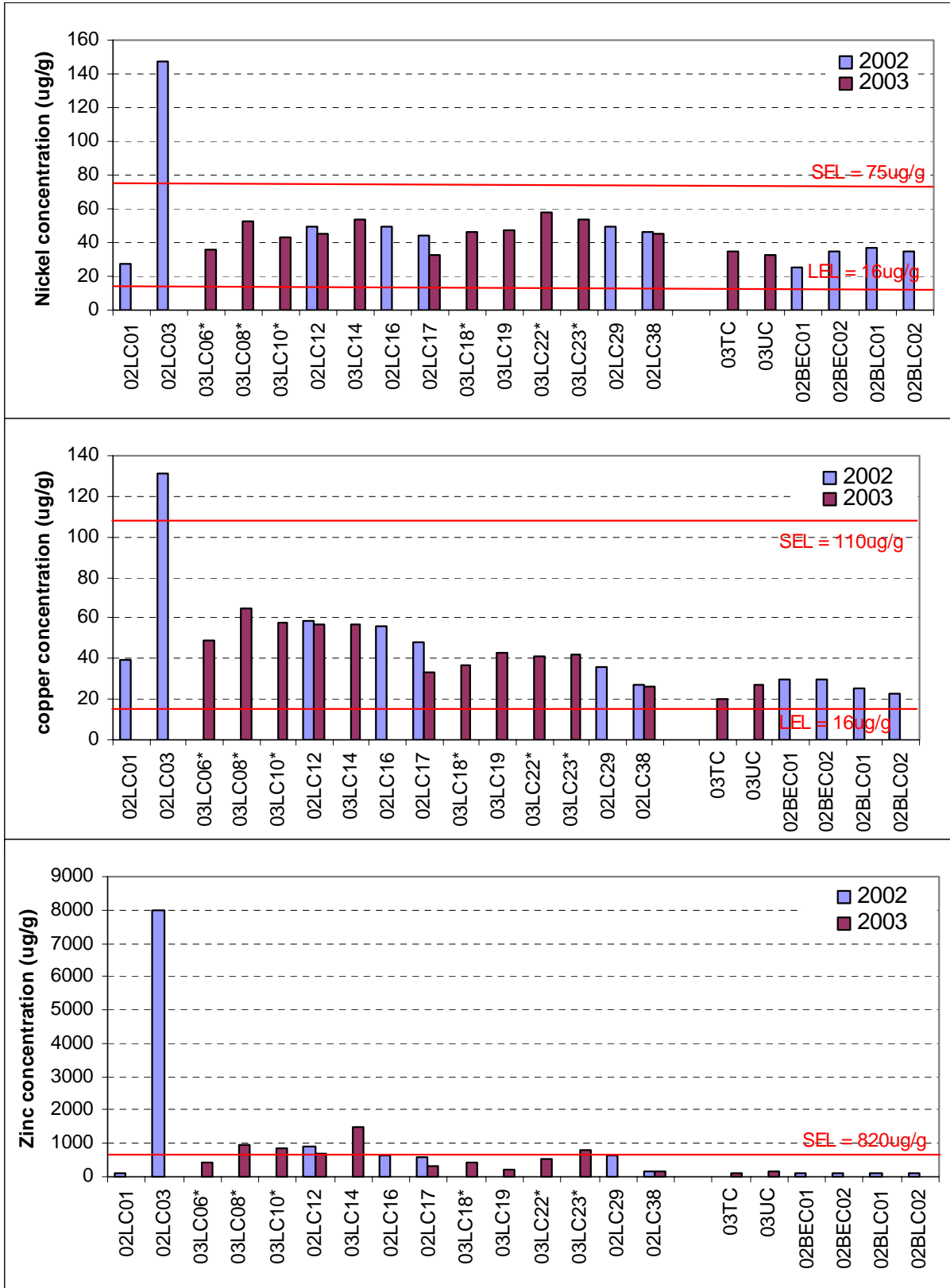
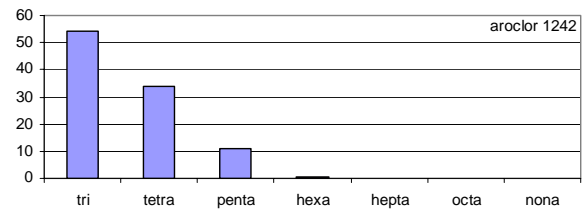
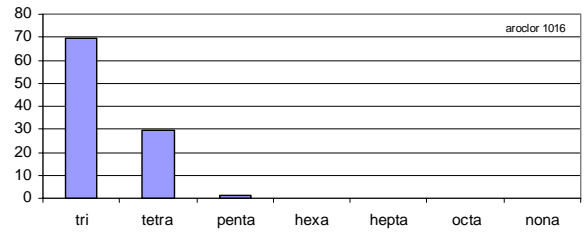
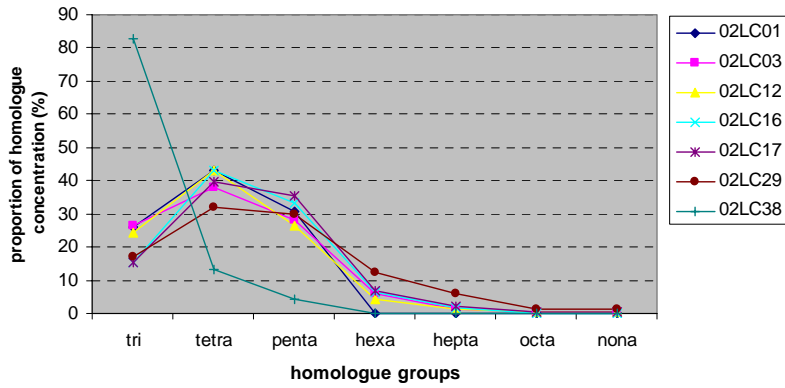
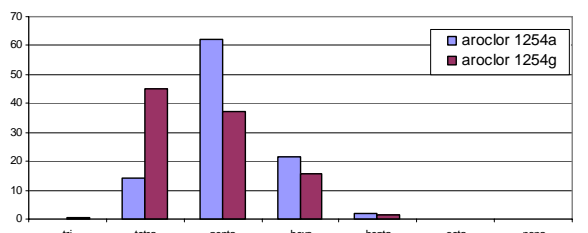
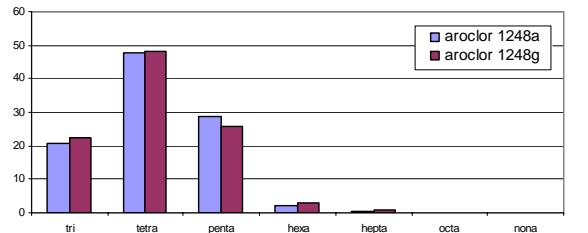
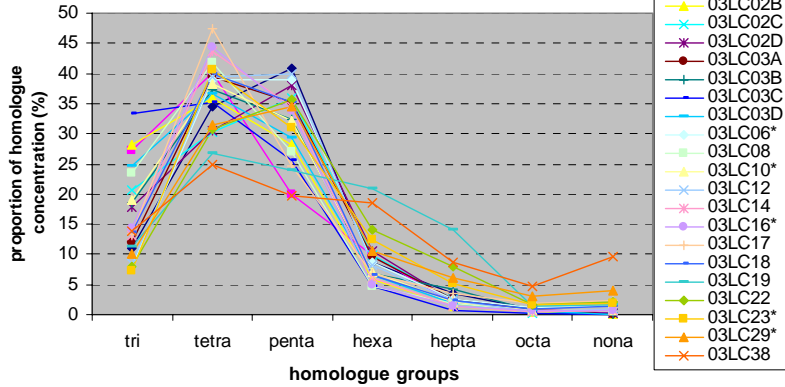


Figure 15: Sediment chemistry concentrations for selected metals from Lyons Creek (2002 & 2003) and the reference creeks (Usshers, Tee, Beaver and Black). PSQG lowest effect levels (LEL) and severe effect levels (SEL) are also provided.

Lyons Creek sediment 2002



Lyons Creek sediment 2003



Reference site sediment 2002-03

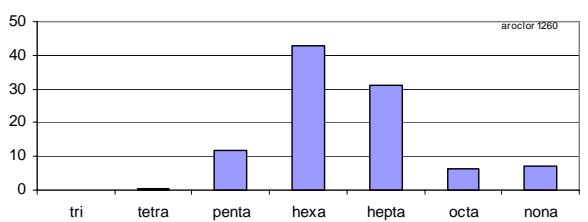
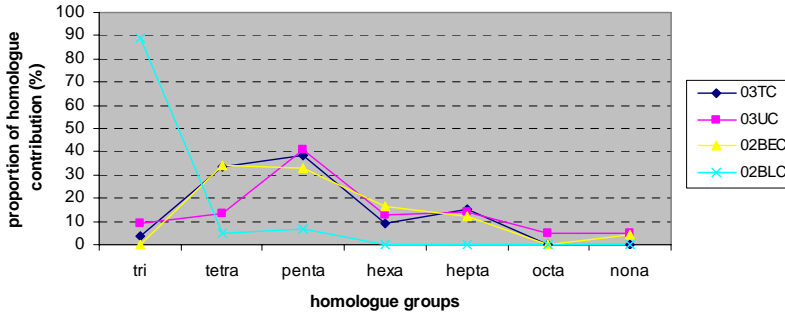


Figure 16: Homologue patterns for PCB sediment concentrations in Lyons Creek and the reference creeks compared to the homologue patterns for aroclors 1016, 1242, 1248 (a&g), 1254 (a&g) and 1260.

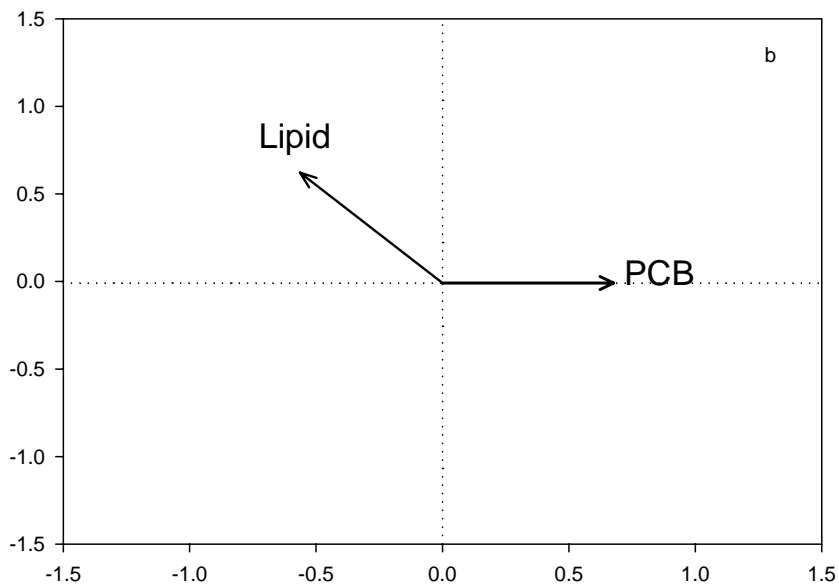
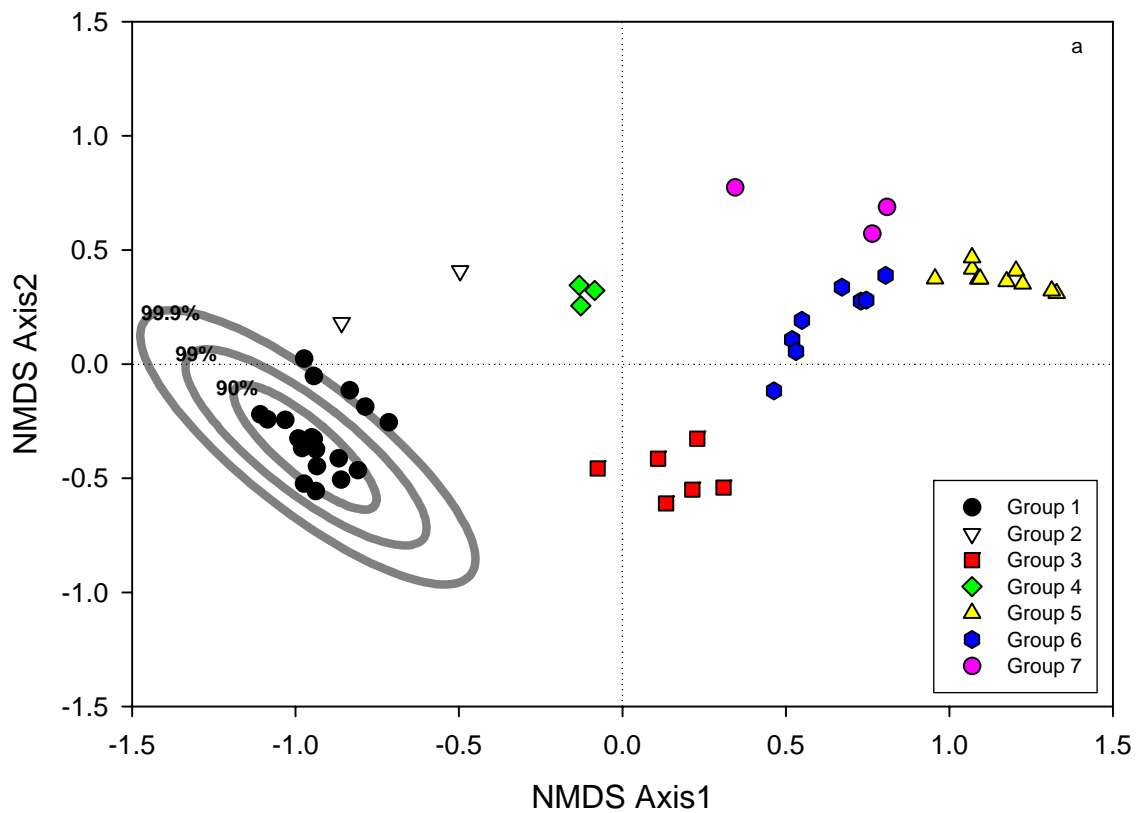


Figure 17: Ordination plot of % lipid and PCB congener concentrations in clams deployed at Lyons Creek and reference streams in 2002 and 2003. 90%, 99% and 99.9% confidence ellipses have been plotted around the reference data.

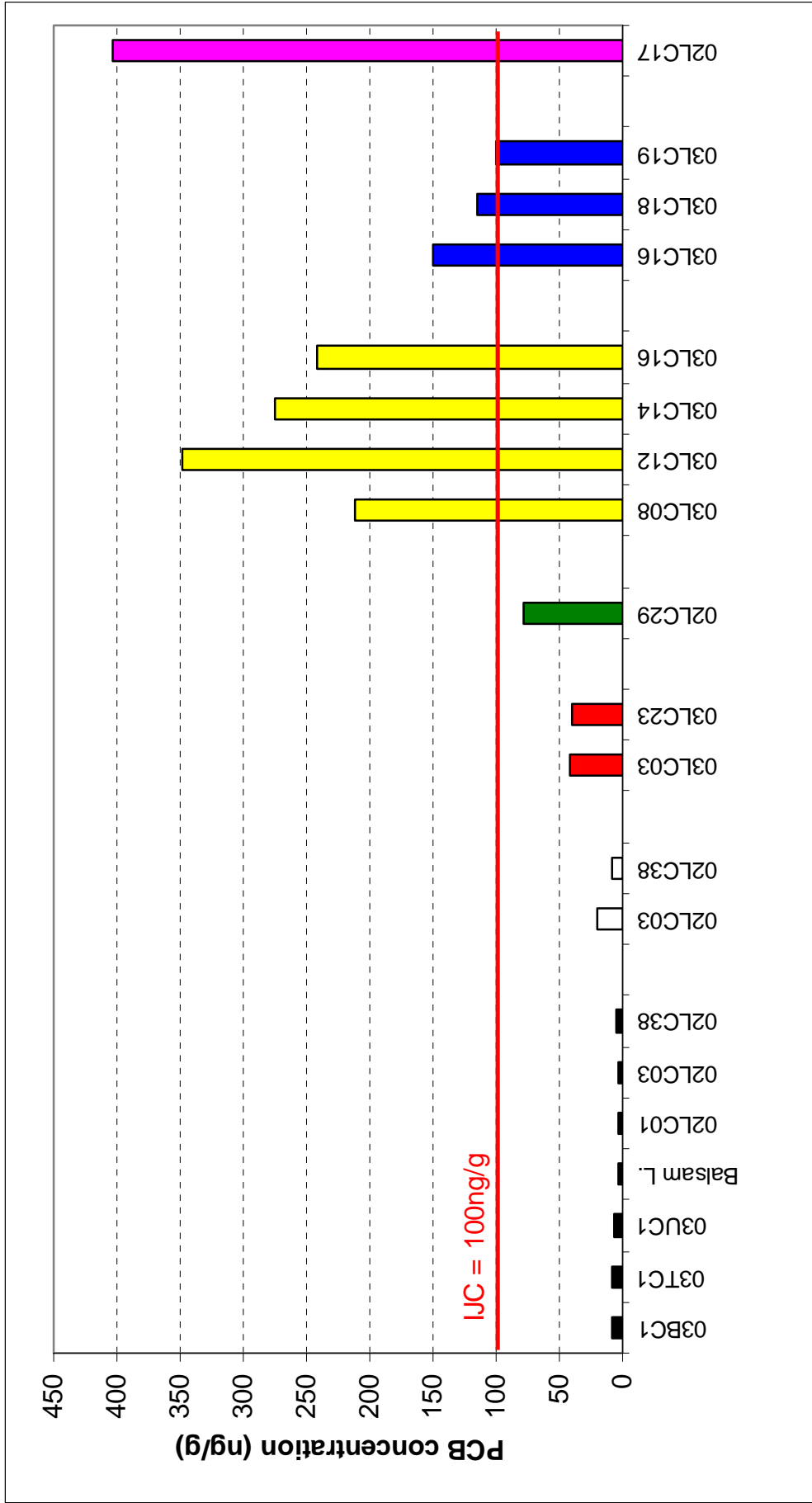


Figure 18: Total PCB concentrations in clam tissue collected from Lyons Creek and reference streams in 2002 and 2003. Groupings identified through cluster analysis are also shown

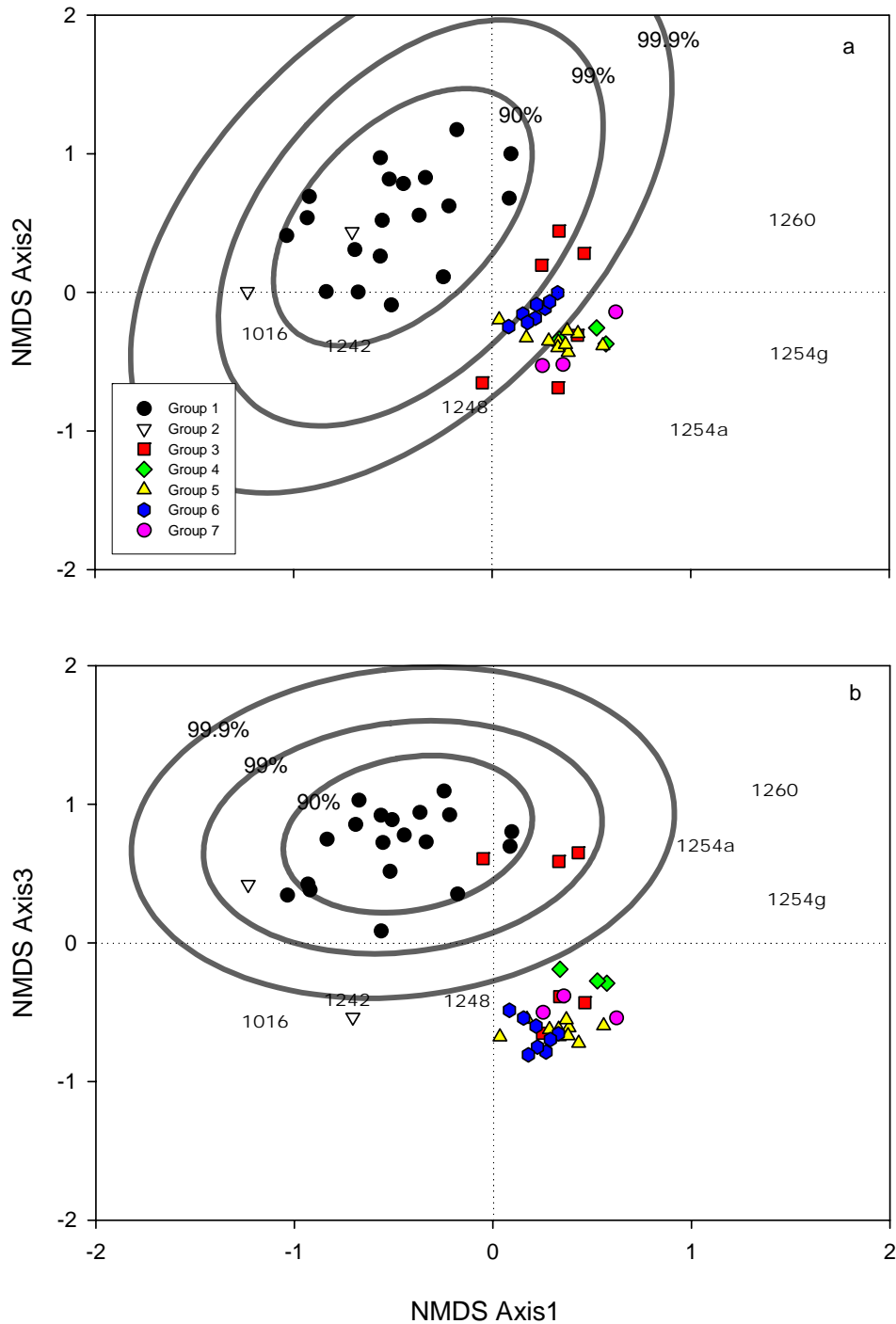


Figure 19: Ordination plots (Axis1 vs. Axis2 and Axis1 vs. Axis3) of clam congener and aroclor data. Sites are grouped according to the groups identified through cluster analysis of the raw data. 90%, 99% and 99.9% confidence ellipses have been plotted around reference data.

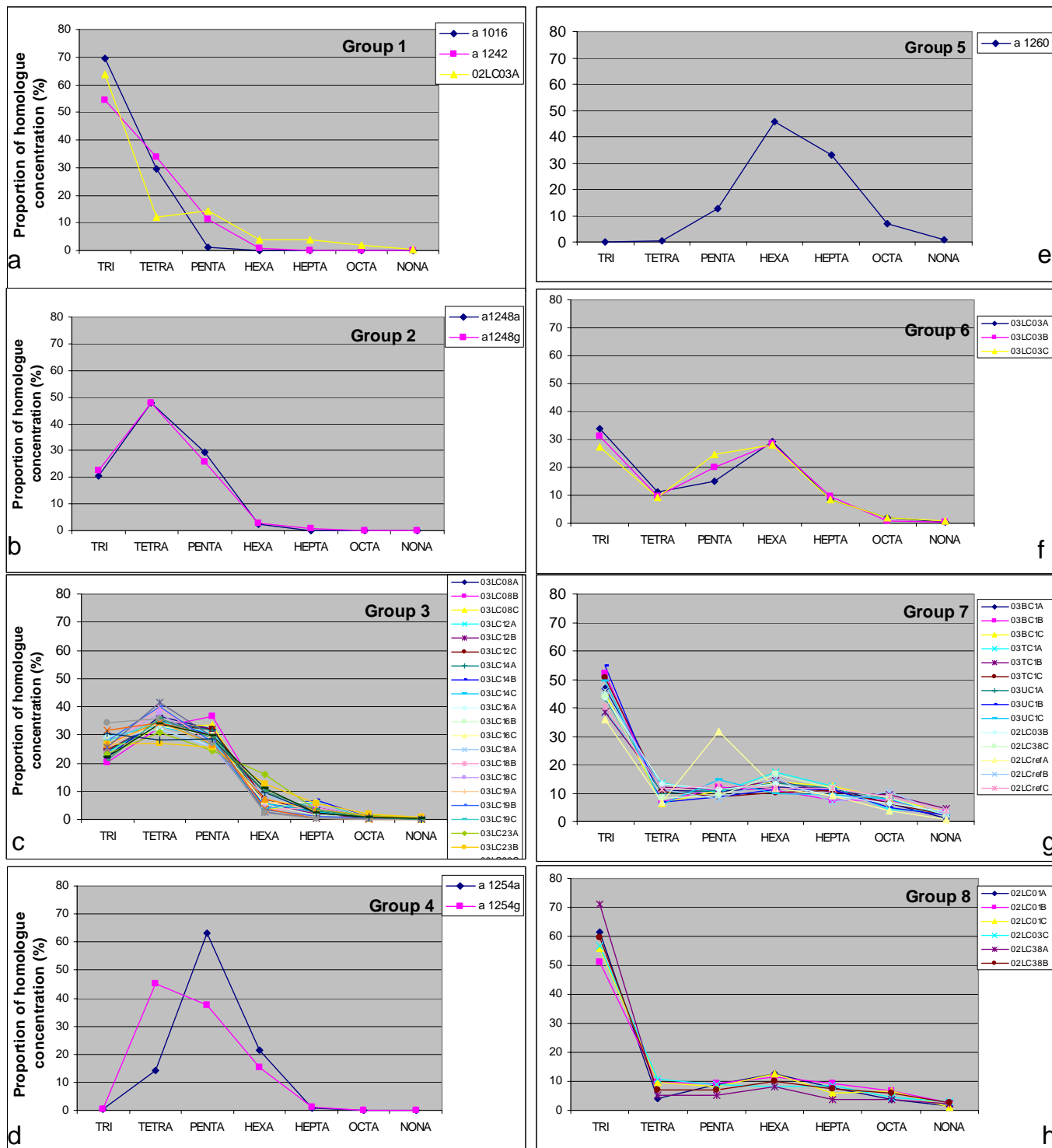


Figure 20: Homologue distribution of PCBs in clams and aroclors. Groupings were identified through cluster analysis

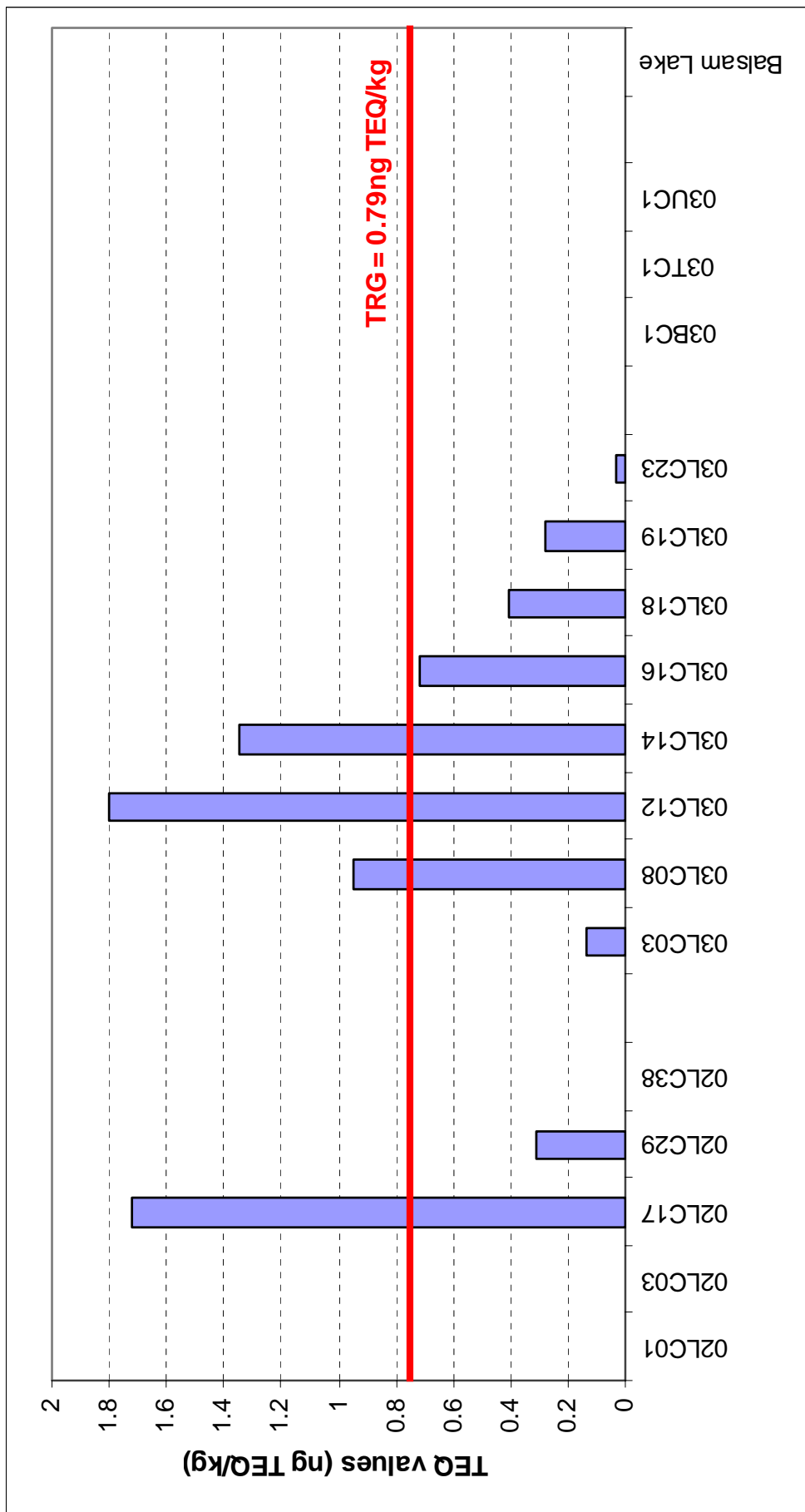


Figure 21: TEQ concentration of co-planar PCBs in clam tissue from Lyons Creek and reference sites deployed in 2002 and 2003. CCME tissue residue guideline (TRG) is also provided

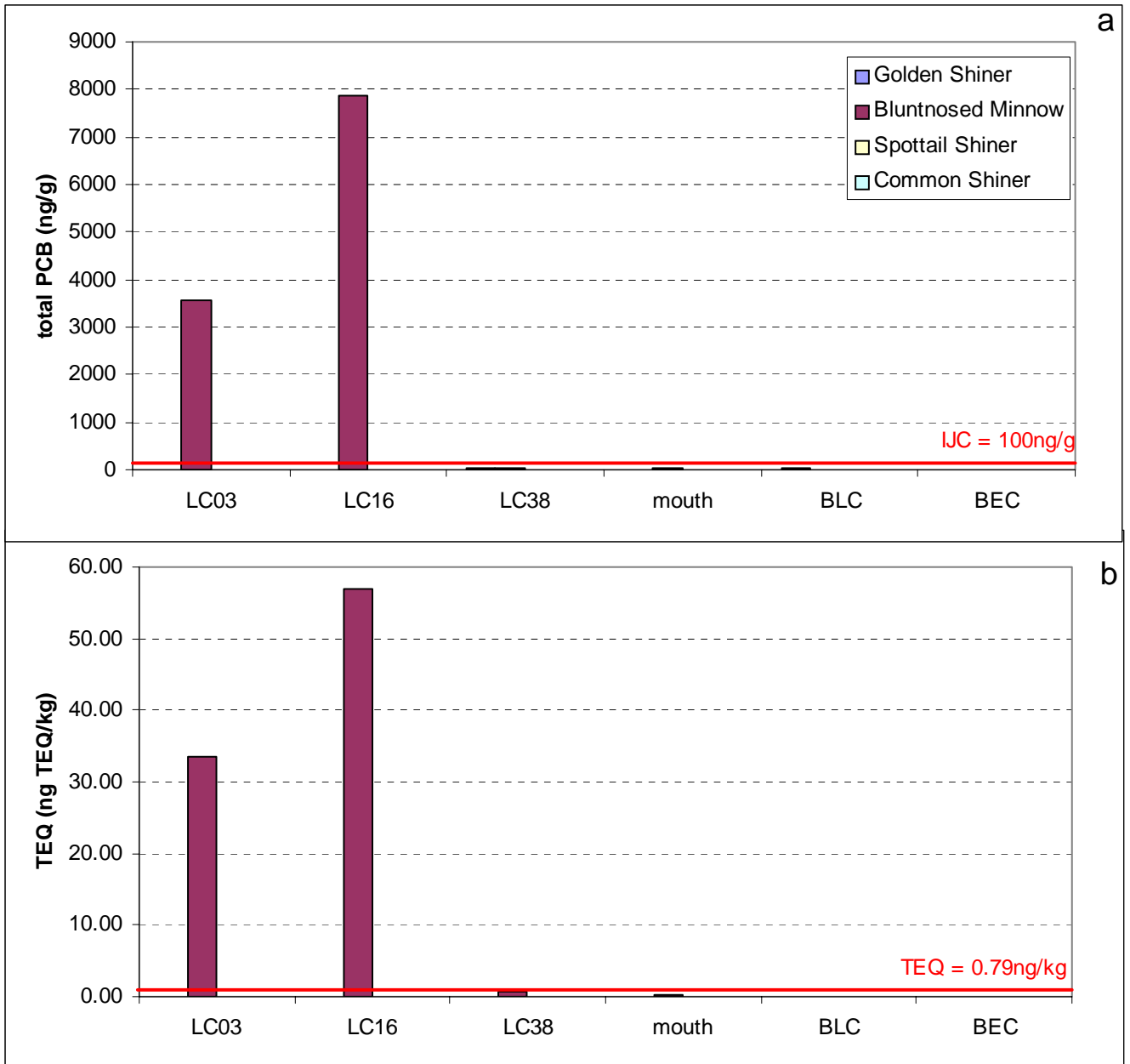


Figure 22: Total PCB and calculated TEQ values for forage fish collected from Lyons Creek and reference streams in 2002

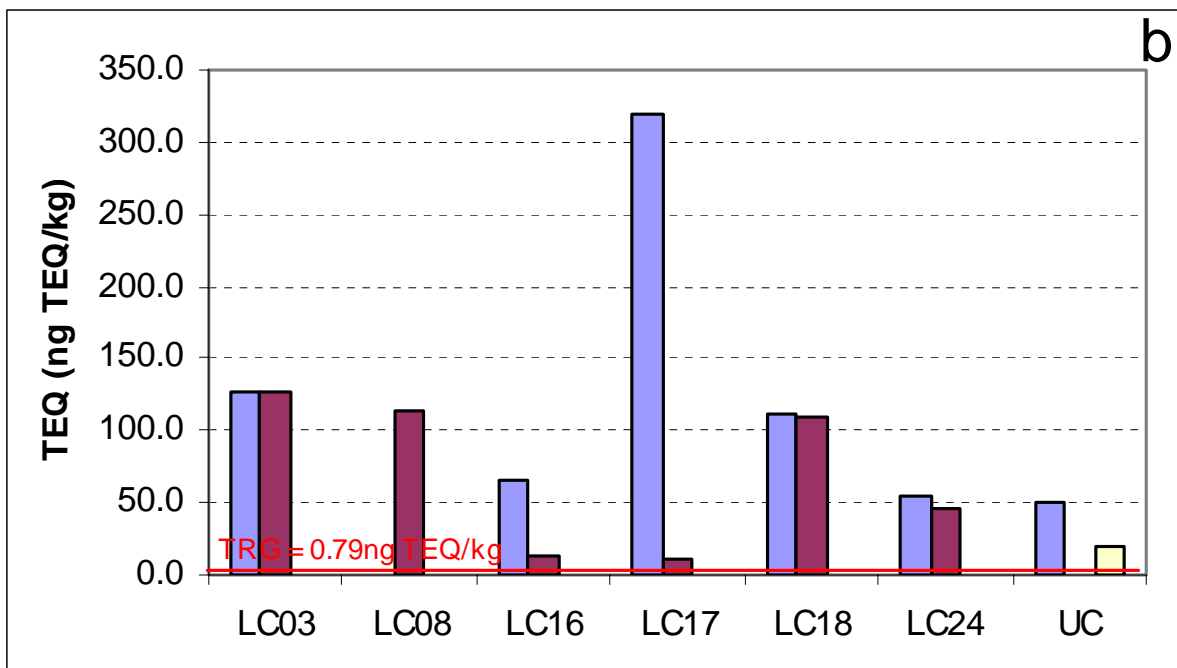
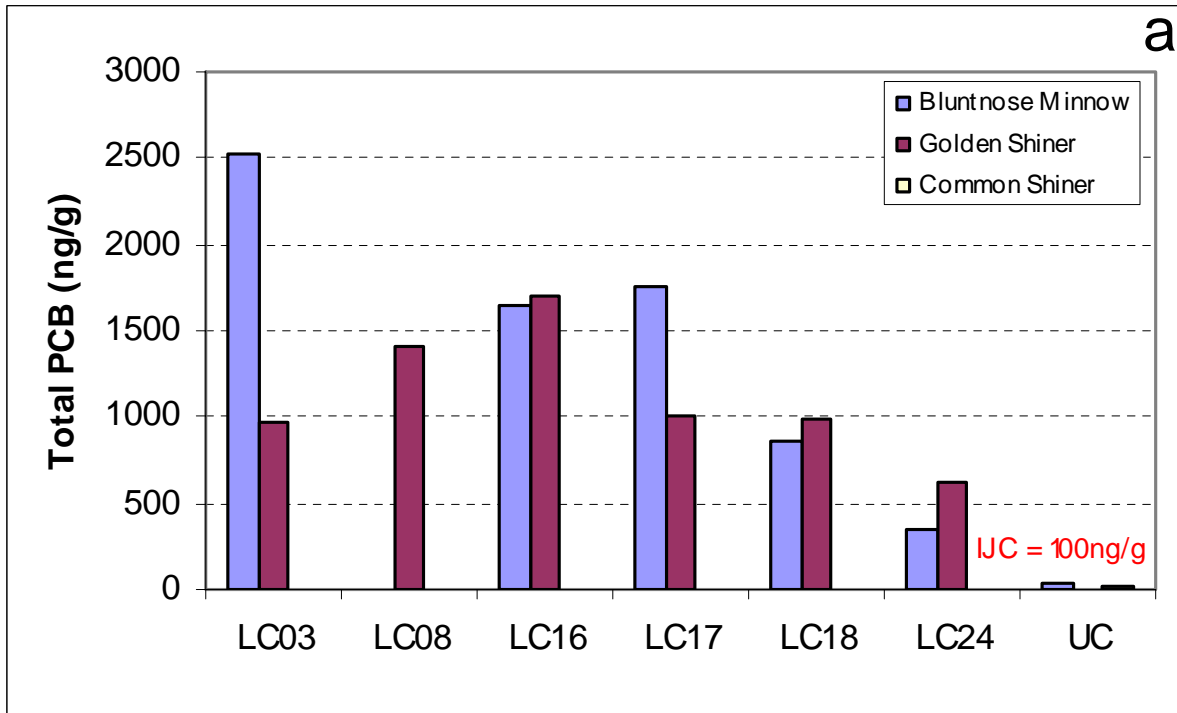


Figure 23: Total PCB and calculated TEQ values for forage fish collected from Lyons Creek and reference streams in 2003

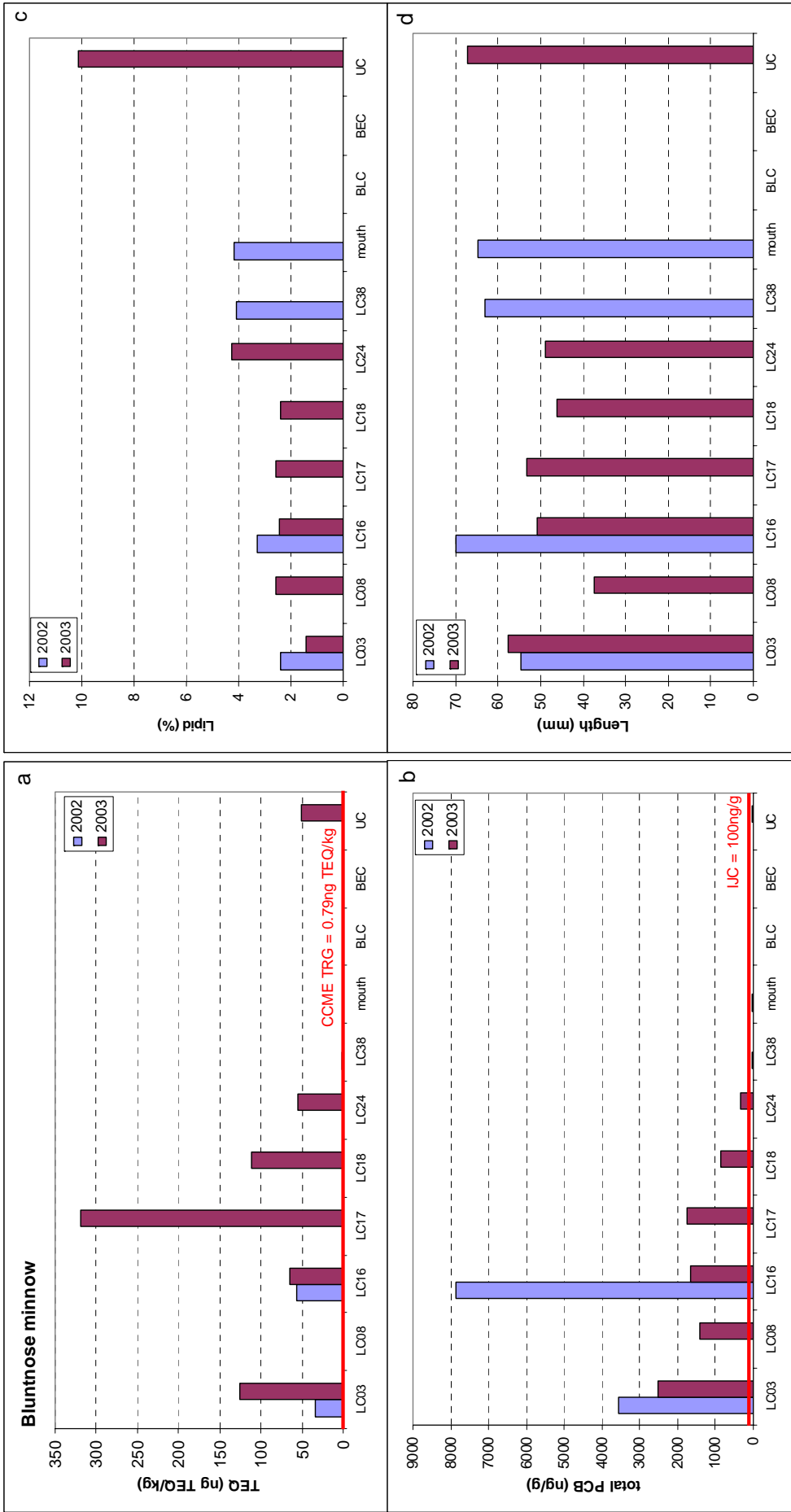


Figure 24: Total PCB concentrations, calculated TEQ values, and lipid and length measurements for bluntnose minnow collected in 2002 and 2003

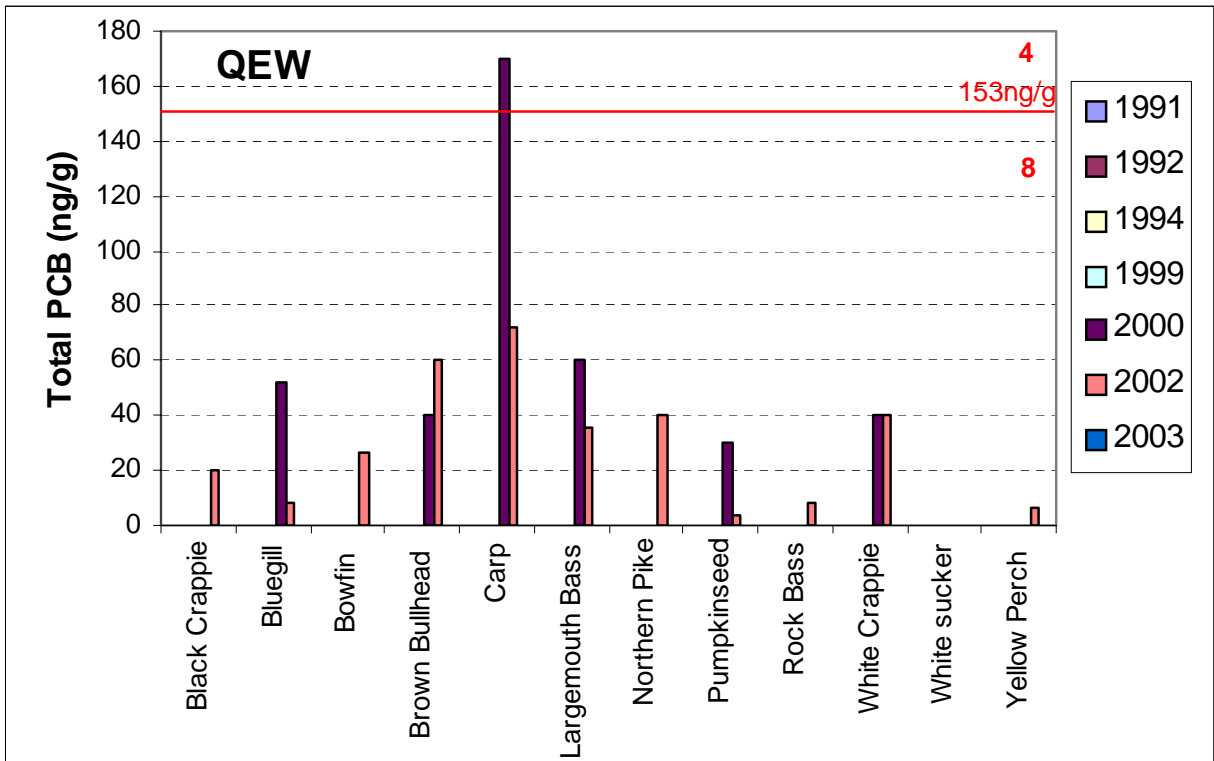
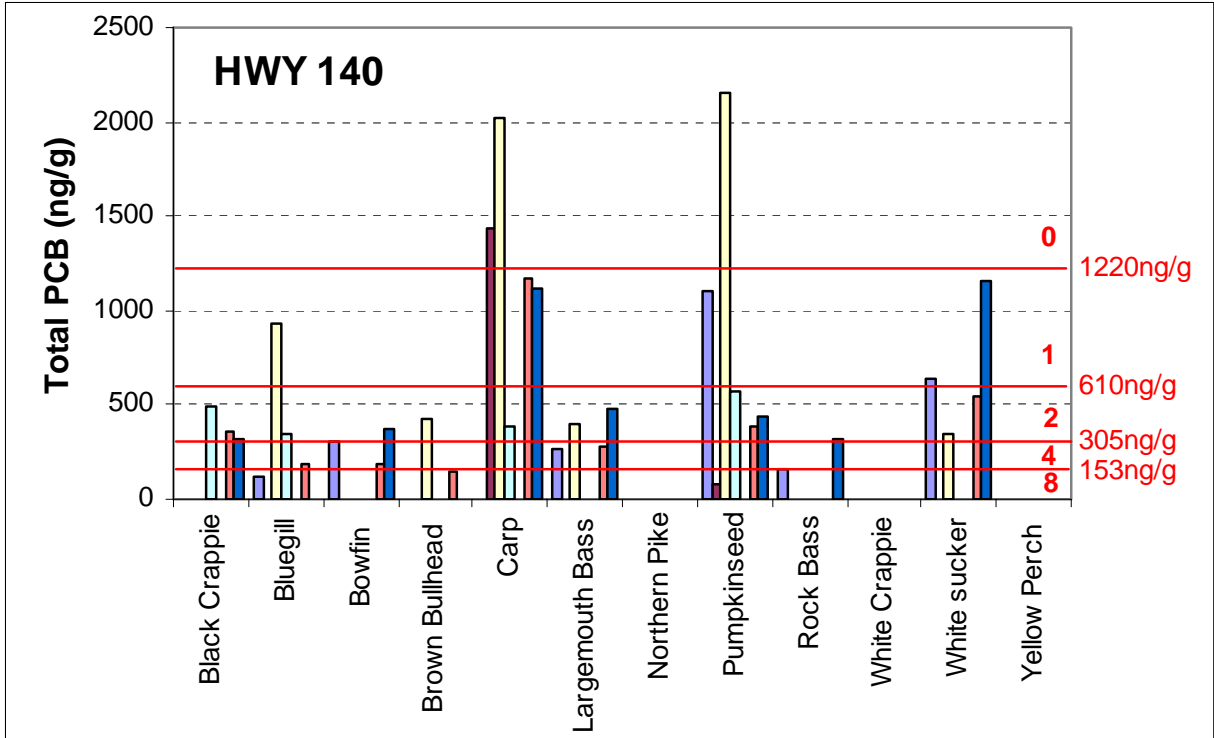


Figure 25: PCB concentrations in sport fish collected from Highway 140 and the QEW from 1991 - 2003. Consumption restrictions are provided; the bolded numbers on the right of the chart indicate the recommended number of meals per month (MOE, 2005)

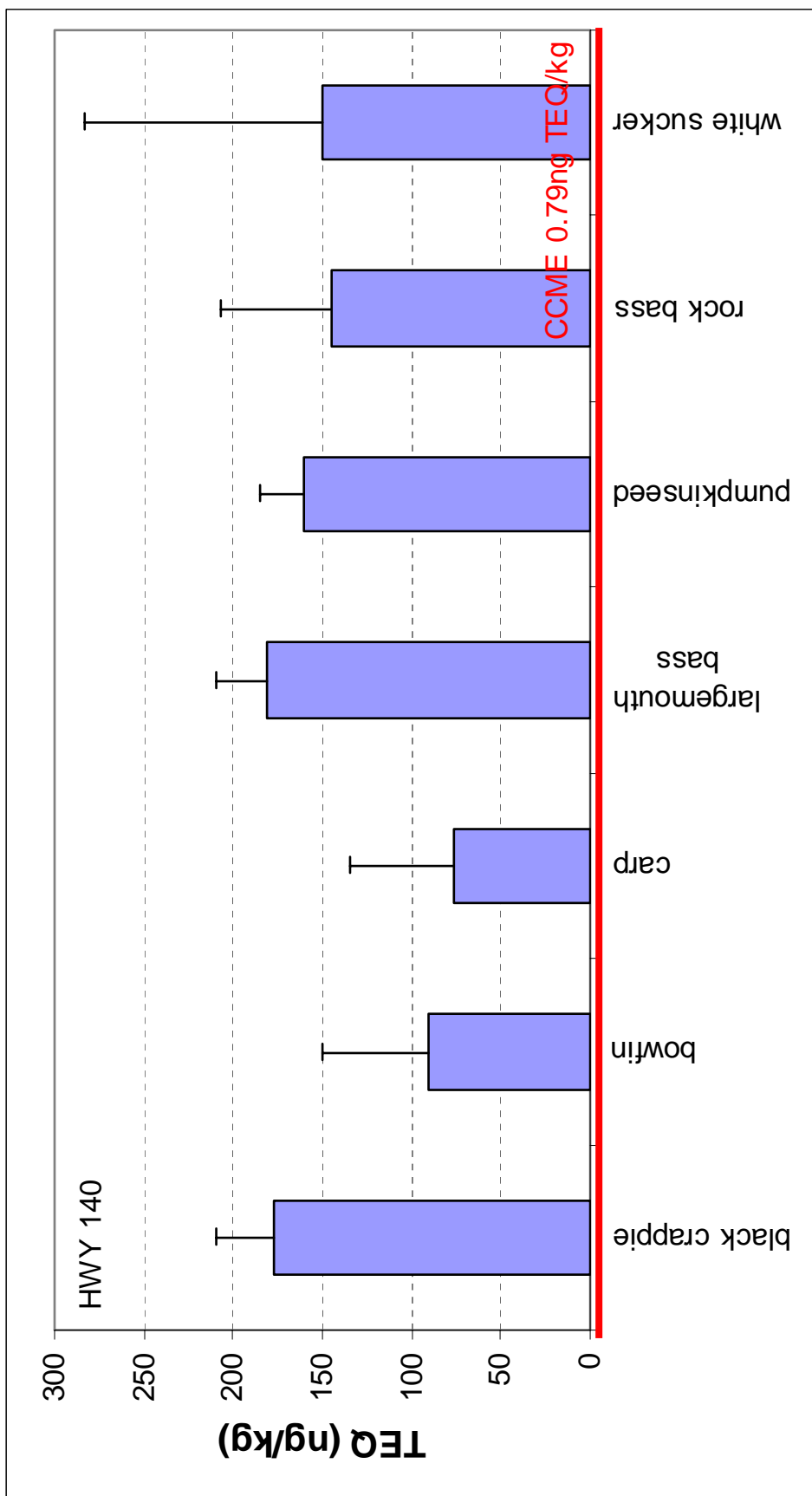


Figure 26: Mean TEQ values calculated for sport fish collected from Highway 140 in 2003. Error bars are shown, and CCME TRG criteria is provided