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INFLUENCES OF GEOCHEMICAL FEATURES OF THE WATERSHED ON METHYLMERCURY EXPORT IN STREAMS:
SPATIAL AND TEMPORAL TRENDS

Kethy Sosso-Kolle

Thesis submitted to the
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ABSTRACT

Methylmercury (MeHg), the organic form of mercury (Hg), is a neurotoxin that bioaccumulates and magnifies through trophic transfer up the aquatic food chain, moving from the primary producers to the top predators and causing health problems in humans. The purpose of this study was to identify biogeochemical features of the watershed that lead to elevated levels of methyl mercury concentrations in the water in 10 stream sub-catchments. The % wetland, proximity of wetland to the stream and the slope of the sub-catchment, dissolved organic carbon, watercolor, conductivity, pH, sulfate and iron were shown to influence methyl mercury concentrations. Duplicate water samples (1L) were taken on a weekly basis between March 2005 and May 2007 and analyzed for MeHg using the GC-AFS for species detection. Many of these variables are covariables, where the slope of the river drainage basin is of critical importance. Shallow slopes are characterized by wetlands and waterlogged soils that result in watersheds with high DOC concentration, low pH and high iron concentration. In these soils, oxygen is low and iron is reduced to the more soluble form and binds to DOC, giving rise to color. MeHg production in these regions is also favored and MeHg binds to DOC and, thus, export from the watershed into the stream, especially during precipitation events.

RÉSUMÉ

Le méthyle mercure (MeHg), la forme organique du mercure (Hg), est une neurotoxine qui se bio-accumule et est concentré par transfert trophique via les producteurs primaires, le long de la chaîne alimentaire aquatique jusqu'aux prédateurs supérieurs, entraînant des problèmes de santé chez l'être humain. L'objectif principal de cette étude était d'identifier les variables biogéochimiques du bassin hydrographique qui mènent aux niveaux élevés des concentrations MeHg dans l'eau de 10 ruisseaux. Le % du marécage dans le bassin, proximité de marécage au ruisseau, la pente du bassin; le taux de carbone organique dissous (COD), la couleur d'eau, la conductivité, le pH, les taux sulfate et le fer ont démontré pouvoir influencer les concentrations MeHg. Des échantillons d'eau (1L) en duplicata ont été prélevés sur une base hebdomadaire entre mars 2005 et mai 2007 et analysés pour détecter les différentes formes de MeHg en utilisant le GC-AFS. Plusieurs des facteurs biogéochimiques varient simultanément, et la pente du bassin de ruisseau est d'importance critique. Les pentes les plus faibles sont caractérisées par des sols inondés et des eaux de ruissellement avec de faible pH et des concentrations de COD et fer élevées. Ces sols inondés ont de faibles concentrations d'oxygène; ce qui favorise la réduction du fer à une forme plus soluble qui se lie au COD et cause la couleur de l'eau. Ces conditions favorisent aussi la production de MeHg, qui ce lie aussi au COD, et donc l'exportation de MeHg aux ruisseaux, particulièrement pendant les périodes pluvieuses.

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LIST OF ABBREVIATIONS

ANCOVA	Analysis of Covariance
ANOVA	Analysis of Variance
DE	Dickie Lake
DOC	Dissolved organic carbon concentration
TFe	Total iron
Fe2+	Iron (II) concentration
Fe3+	Iron (III) concentration
HP	Harp Lake
Load	Methylmercury load
MeHg	Methylmercury concentration
SO_4	Sulfate concentration
THg	Total mercury concentration

1. CHAPTER 1: INTRODUCTION AND OBJECTIVES

1.1. Introduction

Methylmercury, the organic form of mercury, is a neurotoxin that biomagnifies up aquatic food chains and bioaccumulates in fish (Power et al., 2002), which, when consumed, can cause severe health problems to humans and wildlife. This is especially true for exposure of the unborn fetuses (Grigal, 2002; Balogh et al., 2005) where increased consumption of contaminated seafood leads to an increase in placental cord blood (Bjorberg et al., 2003). Fish consumption guidelines and health advisories have been established throughout Europe, Canada and the United States in an attempt to regulate the health risks related to elevated methylmercury levels in fish (Shilts and Coker, 1995; Braune et al., 1999; Grigal, 2002; Balogh et al., 2005).

Mercury, which can be transported from anthropogenic point sources via the atmosphere to even the most remote ecosystems, occurs mainly in three states in the atmosphere: elemental mercury Hg(0), inorganic water-soluble Hg(II) (or Hg^{2+}) and particulate-phase Hg (Hg(p)) (Shroeder and Munthe, 1998; Grigal, 2002; Hall et al., 2005). Although Hg(0) forms more than 95% of mercury in atmosphere, it is the more reactive and soluble Hg(II) that dominates in wet and/or dry deposition to the watershed, followed by Hg(p) (Grigal, 2002). Once in the watershed, depending on its bioavailability and other factors, inorganic reactive mercury is thought to be converted to methylmercury principally by sulfate reducing bacteria (Gilmour et al., 1992).

The transport of Hg as total mercury (THg) and methylmercury (MeHg) from the terrestrial watershed to the basin outlet reflects the collective influence and interaction of various watershed characteristics (Balogh et al., 1998). This review will focus on basin factors, such topography (which includes watershed size, land use/land cover, wetlands, soil quality and nutrient loading), climate and hydrology, and biotic interactions to set the stage for the work to follow. The scope of this review will include research material on focused on watershed characteristics that may be important in controlling MeHg export.

1.2. Watershed Geochemical Characteristics Influencing Methylmercury Export

1.2.1. Topography

1.2.1.1. Watershed Size

Watershed size appears to have more influence on total mercury (THg) export than MeHg export. Based on data obtained from several studies of moderate-sized watersheds in the U.S.A., Canada, central Europe and Scandinavia, Grigal (2002) obtained a weak positive correlation between THg export and watershed size ($r^2 = 0.22$, $n = 49$), with a tendency for increasing basin size to lead to lower (or higher) annual flux, while there was no pattern of MeHg flux with watershed size (Fig. 1, $r^2 = 0.01$, $n = 22$, from Grigal, 2002).

In the case of THg, Griga (2002) explains the decline of THg with increase in watershed to the less effective transport processes in larger watershed and/or in-stream processes such as volatilization and sedimentation, and claims that higher flux would be seen generally in urban watersheds where continuous anthropogenic disturbances and local sources of atmospheric Hg are present (Bigham and Vandal, 1996; Grigal, 2002). The lack of correlation between watershed size and MeHg export in Grigal's review suggests that, in watersheds that are not point sources of atmospheric Hg, other factors such as land use characteristics have a greater impact on the MeHg flux (Balogh et al., 1998; Balogh et al., 2005), which will be discussed later in this review. In conclusion, much of the watershed size's importance might lie in the ratio between the terrestrial and the aquatic portions of the watershed (Grigal, 2002; Gabriel and Williamson, 2004) and the soil's capacity to lock away atmospherically deposited mercury, thus acting as long-term mercury supply to surface water (Johansson et al., 1991; Bishop and Lee, 1997; Gabriel and Williamson, 2004).

1.2.1.2.Soil Properties

Watershed soil properties are important because of the relationship between the soil quality and mercury speciation, which in turn influences bioavailability of mercury for methylation and, hence, MeHg export in lakes and streams. Factors such as pH, ionic strength, redox potential and the concentrations of: dissolved organic carbon (DOC), sulfide, phosphorus and minerals play significant roles in the speciation of mercury (Winfrey and Rudd, 1990; Babiarz et al., 1998; Jackson 1998; Gabriel and Williamson, 2004).

Mercury can form different inorganic and organic complexes, depending on pH, Eh and ionic strength. In the case of Hg2+, chloride and hydroxide ligands, followed by sulfide and DOC ligands are preferentially formed, with sulfide-mercury complexes occurring mainly in anoxic environments such as wetlands or lake sediments (Jackson 1998; Gabriel and Williamson, 2004). Just like Hg2+, MeHg forms complexes with common ligands. There is increased affinity for $R\text{-}S^- > SH^- > OH^- > Cl^-$ functional groups (Gavis and Ferguson, 1972; Dyrssen and Wedborg, 1991). MeHg—humic complexes occur mainly in oxygenated environments but MeHg—sulfide complexes are generally found under anoxic conditions (Hintelmann et al., 1995; Reddy and Aiken, 2001). The main difference in the affinity to other ligands between Hg2+ and MeHg is that the methyl group on MeHg reduces its affinity to other ligands (Amirbahman et al., 2002), making MeHg unable to associate with multiple ligands (Gavis and Ferguson, 1972).

The close relationship between mercury and DOC can be explained in that the formation of mercury—DOC complexes enables transport of mercury from the watershed to the lakes and streams during runoff and flooding events (Driscoll et al. 1995; Johansson and Iverfeldt 1994; Grigal 2002). For both Hg2+ and MeHg, the ability to bind to humic matter decreases at lower pH (Jackson, 1998). This means that more Hg2+ will be available for methylation, thereby affecting MeHg export concentrations. Haitzer and colleagues (2003) carried out experiments on pH dependency of Hg—DOM complex concentrations and compared them with the pH dependency of MeHg—DOM complex concentrations from a recent study by Amirbahman et al (2002), and found that the pattern of decreasing pH leading to decrease mercury—DOM complex formation was the same, differing only in the number mercury of binding site the H+ protons had to compete for with the humic matter (one for MeHg and two for Hg).

Soil pH is an important factor in mercury speciation because of its strong influence on adsorption, where the general trend is that with decrease in pH, the mercury adsorption decreases, which in turn affects mercury's bioavailability in solution (Gabriel and Williamson, 2004). In general, the overall adsorption of mercury to mineral and organic particles is correlated to their surface area, organic content, cation exchange capacity, and grain size (in that order) (Gabriel and Williamson, 2004). In neutral to alkaline soils, mercury shows stronger adsorption to mineral components while showing greater affinity for organic components in acidic soils; with clayey and organic soils having high capabilities for sequestering atmospherically deposited mercury, and decreases in pH and increases in Cl^- leading to decreases in mercury adsorption (Gabriel and Williamson, 2004).

Lastly, nutrient loading from the watershed is also a very important factor in determining MeHg export concentrations. Warner et al. (2005) hypothesized that nutrients would stimulate primary production, which would lead to an increase in organic matter production and deposition, thereby increasing MeHg production. Their results showed that nitrogen and/or phosphorus positively related to sediment MeHg, sediment organic matter offered a significant contribution to sediment MeHg levels ($r^2 = 0.51$, $p < 0.0001$), and a strong positive relationship between total suspended solids (TSS) and total phosphorus ($r^2 = 0.87$). The latter result suggests that particles entering rivers and lakes not only transport mercury but also nutrients stimulate primary production and that land use practices that enhance sediment erosion may also contribute to MeHg production (Warner et al., 2005) (more on TSS and land use later in this review). In addition, nutrients tend to stimulate biomass production which during decomposition can create favorable reducing conditions for methyl mercury formation (Holmes, 2005)

1.2.2. Land Use/Land Cover and Wetlands

1.2.2.1. Land use/Land Cover

Many have reported that land cover/ land use (LULC) of watersheds can influence THg and MeHg export, especially regarding the effect of wetland percent area and type in the watershed. Balogh et al. (2005) compared the LULC characteristics of two watersheds in order to determine if differences in MeHg export could be explained based on those watershed characteristics.

The Minnesota River basin is characterized by an extensive artificial drainage that provides quick and efficient removal of excess water from the land surface and a transport route for soil materials into local waterways, a lack of vegetation cover for long periods of time and hydrologic factors such as precipitation and run-off have a great impact on erosion of large particles and subsequent transport of THg to lakes and streams (Balogh et al., 1998; Balogh et al., 2005). Meanwhile, the Mississippi River basin has abundant wetland percent coverage because of having retained much of its natural drainage system; a third of the basin is covered by forest and there is limited row crop cultivation (Balogh et al., 2005).

As mentioned in the previous section, soil erosion, hence total suspended solids (TSS) is very strongly and positively related to THg concentrations (Balogh et al., 1997; Balogh et al. 1998; Warner 2005), especially aqueous THg (Mastrine et al., 1999). Results in Balogh's study (2005), showed that soil erosion from stream banks and cultivated areas are responsible for the high annual THg yield (in grams of THg /km^2/yr) in the Minnesota River, while the low THg yield suggested that the sandy soil and limited agricultural development and artificial drainage of the Mississippi River basin result in low TSS concentrations (Balogh et al., 2005). These THg yield results are important in relation to MeHg export of the weak yet significant relationship between sediment THg and sediment MeHg, indicating that Hg loading is one important factor governing MeHg production and thus export (Benoit et al., 2003; Warner et al., 2005). Precipitation events and runoff have a great impact on erosion, but will further be discussed in later sections. There was no correlation between MeHg yield and TSS (Balogh et al., 2005; Warner et al., 2005).

Generally, annual MeHg concentrations in the Mississippi River were relatively high, especially during the midsummer or late summer precipitation events when levels exceed 0.9ng/l, while annual MeHg concentrations were lower in Minnesota River and tributaries (Balogh et al., 2005). MeHg from the Mississippi watershed originated from wetlands, where it is produced and later flushed during hydrological events (Balogh et al., 2004), while MeHg concentrations were elevated at certain periods in the Minnesota River, it was due to higher temperatures combined with lower discharge that resulted in MeHg production in the reservoir upstream Blue Earth, one of the Minnesota River's sampling sites (Balogh et al., 2005). There was not as much distinct variation in MeHg yield between the two watersheds compared to the widely varied yields in THg between the two; where MeHg yield is product of MeHg concentration and stream discharge, per area of the catchment. The results of the ratios of MeHg to THg for the Mississippi River and Minnesota and its tributaries show that water draining wetlands had a higher MeHg/THg ratio than other surface waters (St. Louis et al., 1994; St. Louis et al., 1996). In conclusion, the presence of artificial drainage in the Minnesota River basin adversely affected watershed wetland cover, limiting MeHg production and export. Given that wetlands are considered very significant sources of MeHg (Balogh et al., 2004), extensive agricultural development promotes TSS, hence, THg yield, while more wetland area is correlated with high MeHg yields.

Lastly, forest cover is an important watershed characteristic for determining MeHg export, where litterfall acts as a major source of MeHg to forest soils (Munthe et al., 1995; Lee et al., 2000).While the forest canopy can sequester new inputs of elements such as Hg2+ and MeHg into its foliage via stomata (Iverfeldt, 1991; St. Louis et al., 2001), vascular plants can transport mercury from the soil through their roots to their leaves for storage (Godbold and Hutterman, 1988; Bishop, 1998); although the latter phenomenon has only been reported in soil with high mercury concentrations (Lindberg et al., 1979, Cocking et al., 1995). Episodes of elevated MeHg concentrations in streams in the fall season due to direct leaf input to the streams are caused by the the rising water table, increasing the available DOC (and DOC-bound MeHg) to the streams.(Balogh et al., 2003).

1.2.2.2.Wetlands

Wetland Area

Wetlands, especially peat lands, act as sources of MeHg (Hurley et al, 1995; Grigal, 2002), where there is a weak relationship between wetland area and MeHg concentration ($r^2 = 0.14$, n = 23). Snodgrass et al. (2000) found that large surface areas of wetland with frequent flooding and drying cycles have a tendency of releasing particulate-bound Hg species, making Hg bioavailable for methylation. The flooding and drying cycle also causes fluctuations in water oxygen content, influencing microbial activity in wetlands. Kramar et al. (2004) suggested that the distribution of wetlands relative to loon nesting (the proximity of the wetland to the nest) was more important than the total area of wetlands in the control of mercury concentrations in loons.

Type of Wetland

In the Experimental Lake Area in Northern Ontario, Canada, St. Louis and colleagues (1996) carried out an investigation to determine if there was a difference in MeHg and THg exported from catchments with different types of wetland but where all catchments had similar wetland percent cover (14-25%). There were four types of wetlands described in this study: wetlands in upland regions, valley-bottom wetlands, riverine wetlands and basin wetlands.

The annual THg concentrations from the catchments with different wetland types were very similar, with highest concentrations of THg in runoff found in upland catchment, followed by catchments containing valley-bottom wetlands, basin wetlands and riverine wetlands (St. Louis et al. 1996). In terms of wetlands as MeHg sources, the general pattern was as follows, in order of increasing MeHg yield: upland < valley-bottom wetlands < riverine wetlands < basin wetlands, and this was all very closely related to hydrologic events (St. Louis et al. 1996).

For upland catchment, the water discharge was low, probably because this catchment was on a south-facing slope, which resulted in high rates of evaporation (St. Louis et al. 1996). On average, less than 20% of the concentration of MeHg in wet deposition that entered the catchment exited it, meaning that 80—82% of the MeHg that entered catchment was either being stored or demethylated (St. Louis et al. 1996) Demythelation is actually favored in the upland due to its thin, aerobic soil layers, which inhibit anaerobic respiration of bacteria for methylation to occur (St. Louis et al. 1996). Valley-bottom wetlands were much smaller sinks per unit area than the upland wetlands, with high MeHg yield matching high water yield and low MeHg yields matching low water yields (St. Louis et al. 1996); suggesting that wetlands and peatlands store MeHg during dry periods and then transport it out of the wetland during high water flow (Branfireun et al. 1996). The largest source of MeHg was basin wetlands, followed by riverine wetlands.

As a whole, the main variation between catchments with different types of wetlands lies in the strength of the wetland as a source of MeHg. Therefore, it follows that although every wetland is a source of MeHg, every catchment containing a wetland is not a net source of MeHg (St. Louis et al. 1996).

1.2.3. Climate and Hydrology

Given the widely held view that DOC and DOM are vectors for mercury transport from watersheds, it follows that mercury export peaked during high stream flow events when organic matter export was the greatest (Balogh et al. 1997). As discussed in the previous sections, the climate of the watershed has a great impact on MeHg export, either directly via wet and dry deposition of atmospheric Hg and MeHg in snow and rainfall, or indirectly by influencing the mobilization of TSS and THg by runoff events (Balogh et al.1997; Balogh et al. 2003). It is therefore possible to relate MeHg and THg yields to seasons in a particular watershed area. As the proportion of wetland in a watershed increases, there is an attenuation in flood peaks, which translated in an increase in residence time in the watershed for longer periods of bacterial interaction, and hence more MeHg production and export (Fig. 3 from Grigal 2002).

Likewise, there are seasonal patterns in MeHg and THg with snow packs in remote Arctic regions (Loseto et al., 2004). Climatic temperatures of the catchment regulate MeHg output from the snowpack as the snow gradually melts during 2—4 weeks of spring and the MeHg is transported to neighboring streams and lakes with the snowmelt (Lahoutifard et al. 2005). Generally, seasonal variations in MeHg are as follows: MeHg concentrations increase in spring and summer, decrease in the early fall and remain constant through out the winter (Driscoll et al. 1998).

1.2.4. Biotic and Abiotic Factors

Some other watershed characteristics that might affect the MeHg export are sulfate reducing bacteria, the presence of beavers in ponds, temperature, fire and solar radiation among others. It is believed that MeHg production is mainly a biological process involving sulfate reducing bacteria, although the exact types of microorganisms involved and the mechanism of the methylation process are still not-well known (Gilmour et al., 1992). Studies also suggest that MeHg is produced mainly in anoxic environments and that oxygenation of the environment leads to demethylation (Gilmour et al., 1991). An experiment was carried out to determine the effect of sulfate stimulation on methylation in freshwater sediments (Gilmour et al., 1992) and it was found that sulfate addition, at concentrations typical of mildly acid-impacted waters, stimulate production of MeHg from added $HgCl_2$ in reduced sediments slurries up to the optimal sulfate concentration beyond which sulfide would inhibit the methylation process (Gilmour et al. 1992). Thus, MeHg would not only be limited by sulfate but also by the rate at which SRB can produce MeHg and the optimum sulfate concentrations in the environment. Conversely, organisms such as *Escherichia coli* and Saccaromyces are known to reduce Hg2+ to Hg^0, therefore reducing bioavailable mercury for methylation, hence reducing MeHg export (Hansen et al. 1984; Schluter 2000).

The life history of beaver impoundments in relation to MeHg yield from them brings up the question of whether they function as wetlands or recently flooded landscapes (Driscoll et al. 1998). The pattern for these beaver impoundments is for the MeHg production and supply rates to be high, similar to established reservoirs ($\sim 10 \mu g/m^2$-yr) and to decline over time to values reported similar to those of wetlands ($\sim 0.5 \mu g/m^2$-yr) (Driscoll et al. 1998). Finally, factors such as temperature, fire and solar radiation all affect MeHg export in that an increase in temperature makes conditions suitable (warmer) for SRB activity, thus an increase in MeHg export from the wetlands. Conversely, high temperatures also lead to increased Hg^0 volatilization, which decreases bioavailable mercury for methylation (Gabriel and Williamson 2004).

1.3. Thesis Objectives and Hypotheses

The Dorset area, in the Muskoka -Haliburton district of south central Ontario, is undergoing rapid development for tourism in the spring and summer, and features lakes that are being monitored by Ontario Ministry of Environment for water quality. MeHg concentration, load and 6 environmental variables were measured in 10 streams of Dickie and Harp lakes, and the spatial and temporal trends were assessed. Fish are a major source of MeHg to the population, although the sources of MeHg to fish are poorly known. There have been high correlations found between fish MeHg burden and %wetland in lake catchment. This study is relevant to an overall investigation in mercury research and in water quality assessment for the Dorset region, and while most previous work has been on THg, this is a great input to MeHg data. This information will also have application to similar regions around the world such as Sweden, Findland and the east coast of North America.

The main objectives of this study are:

- To determine the spatial and temporal trends in MeHg concentration and export in 10 streams.
- To correlate the spatial and temporal trends of MeHg to the geochemical features of the stream sub-catchment, such as the concentrations of dissolved organic carbon (DOC), total iron (Fe) and sulfate ($S0_4$), color, pH and conductivity.

- To correlate the spatial trends of MeHg to the geophysical features of the stream catchments, such as % wetland and % slope.
- To characterize each sub-catchment in order to predict MeHg concentrations and yield.

The main hypotheses and predictions in this study are:

- DOC is the transportation vector for MeHg and total iron from the watershed basins to the streams. Therefore, streams with higher DOC and color also have higher MeHg concentrations, MeHg yield and total iron concentrations.
- The dissolution of DOC in the drainage basin is influenced by water residence time. Consequently, the degree of steepness of the basin slope is the major driving variable controlling levels of DOC and color in basins and streams.
- Wetlands are waterlogged soils that have low oxygen concentrations and are favorable for growth of bacteria such as SRB, which methylate mercury. Hence, the proportion of wetland in the watershed is correlated to MeHg concentrations and MeHg Yield in streams.

Raw data for this project such as MeHg, stream discharge, pH, Fe, color, conductivity and DOC data, were all shared with Mrs. Tamar Bodek (with whom I shared part of the workload, hence the data). Her thesis project is focused mainly on the impact of the spring freshet on the MeHg export in Harp and Dickie lakes. Data were also shared with Mr. Brad Mills (co-supervised by Dr. Jules Blais and Dr. David R.S. Lean, who initiated the Dorset mercury project) and Mrs. Adrienne Ethier of the University of

Ottawa. All water field and laboratory work was carried out by the Ontario Ministry of Environment (OME), Dorset, with the exception of laboratory work on MeHg data, which was carried out at Dr. Lean's lab by Tamar Bodek and I throughout the project.

2. CHAPTER 2: MATERIALS AND METHODS

2.1. Study sites

Two lakes, Dickie and Harp lakes, and their affluents (4 streams for Dickie and 6 streams for Harp) were investigated in this study. Both lakes are located in the Haliburton-Muskoka district in south central Ontario, Canada (Harp: 45°23', 79°08'; Dickie: 45°09', 79°05'). The bedrock beneath both lakes is predominantly granite, as they are located on the southern edge of the Precambrian Shield. The average slope and mean depth for Dickie Lake are 6% and 5m, respectively, compared to Harp Lake with a 12% inclination and mean depth of 13.3m. This offers a contrast between the two systems where Dickie is shallower than Harp. The main water input for both lakes is via runoff and precipitation, while groundwater inputs are minimal (Mierle and Ingram, 1991). Dickie and Harp lakes have similar catchment areas (406.4ha and 470.7ha, respectively, exclusive of the lake) and lake areas (93.6ha and 71.38ha, respectively).

A map of the study basins, Harp (HP) and Dickie (DE), shows distribution of their respective streams, sub-catchments and wetland areas, the latter designated by the shaded area (Figure 2.1). Each sub-catchment contains a stream, labeled by station numbers; in this study, the focus was on 6 stations for Harp lake (HP3, HP3A, HP4, HP5, HP6 and HP6A) (Figure 2.3) and 4 stations for Dickie lake (DE5, DE6, DE8 and DE10) (Figure 2.2), giving a total of 10 streams studied. There is an additional stream, DE11, which drains in Dickie Lake (Figure 2.2). According to Ontario Ministry of Environment, monitoring of the stream DE11 ceased due to infringement of private property, and was thus omitted from this study. The streams are often dry during the summer, thus making sampling during the summer sparse and irregular. The physical characteristics of the 10 streams are summarized in Table 2.1.

2.2. Methylmercury Sampling and Analysis

"Clean" sampling and analytic methods were used during this project (Bloom, 1995; Balogh et al, 2005). Water samples were collected in pre-cleaned (using 10% HCl deionised water) 1L Nalgene Teflon bottles as duplicates on a weekly basis at the 12 stations/streams of Dickie and Harp lakes by staff of the Dorset Center, Ontario Ministry of Environment. The water samples were then preserved using 4ml of concentrated HCL per liter of water (i.e. 2% HCl), packed in duplicates in ZIP-LOCK® bags and shipped to the University of Ottawa within a 1 or 2 days of sampling time in coolers. Upon receipt, water sample coolers were stored in dark cold rooms until analysis. Holmes (2005) has shown that no change in MeHg occurs even up to 56 days in storage at 4°C and 23° C. Water samples were collected from March 2005 to May 2007; however, there was no sampling during the following periods: July 2005-October 2005 and December 2005 to March 2006 due to drying up and freezing of the streams, respectively.

The method for MeHg analysis followed the protocol of Cai et al., 1996 and is briefly described here. The pH for the water samples was adjusted to a range of pH 3.00 to 3.05 using 6N KOH, 20% HCL and 20% KOH; pH-adjusted buffer solution (0.2M Acetic acid:0.2M Sodium acetate; 9:1) was also added in order to preserve the mercury speciation. Using water pumps with Teflon tubing, the water samples were run over night through solid-phase microextraction columns containing sulfhydril adsorbent cotton fibers. MeHg was eluded with KBr/$CuSO_4$ solution (2:1) and extracted into 1.5ml amber borosilicate vials with 300μl of dichloromethane. MeHg was quantified by capillary gas chromatography – atomic fluorescence spectrometry with a Hewlett Packard GC with PSA atomic fluorescence detector, with detection limit of 20 pg. The calibration curve was created using duplicates for 5 standards made using deionized water and MeHg from the stock solution in the following concentrations: 0 ppb (blanks), 0.83, 1.67, 2.5 and 3.3 ppb (spikes). Holmes (2005) has also shown that no MeHg is formed on the sulfydryl cotton when properly washed and prepared, and there are no losses of MeHg from neither the sampling Teflon bottles nor the GC-AFS amber borosilicate vials during manipulation and storage for 28 and 7 days, respectively.

2.3. Ancillary Water Quality Measurements

All water sampling was carried out by OME staff at the Dorset Center. Water sampling and analysis for the following parameters was carried out as part of the Ontario Ministry of Environment Dorset Center routine sampling program: total iron (Fe), sulfate (SO_4), dissolved organic carbon (DOC). Conductivity and pH were also measured simultaneously, and thus only MeHg was analyzed at Dr. Lean's lab at the University of Ottawa by Tamar Bodek and I throughout the project period. Other analytical methods and protocols for the determination of iron, sulfate and DOC concentrations, as well as conductivity and pH, are documented in the MOE-LSB Analytical Methods/Quality Assurance Manual (Teresi, 2003) and in the Handbook of Analytical Methods for Environmental Samples (OMOE, 1981; Mierle and Ingram, 1991). Stream discharge was calculated as described by Locke and Scott (1986; Mierle and Ingram, 1991). Using the values obtained for water discharge at each stream, the MeHg Load for a given stream was as follows:

$$\text{Load} = C * V \qquad [1]$$

Where C is the MeHg concentration (ng/L) on given date, V is the stream discharge on given date (L/s) (modified from Sellers et al., 2001). Meanwhile, MeHg Yield was calculated using the following equation:

$$\text{Method I:} \qquad \text{Yield} = (C * V) / A \qquad [2]$$

Where C is the average annual MeHg concentration, F is the mean stream discharge for the given year and A is the area of the stream sub-catchment (modified from Babiarz et al., 1998). Another way of calculating MeHg Yield is as follows:

$$\text{Method II:} \qquad \text{Yield} = \Sigma\, [(C1+C2)/2 * (V / A)] \qquad [3]$$

Where C1 and C2 are MeHg concentrations on two consecutive dates in a given year, V is the stream discharge in the time interval between the two days and A is the area of the stream sub-catchment (modified from Sellers et al., 2001). For this study, yield was measured as $\mu g/m^2/yr$. Both yield calculations were used and their results for each stream were compared.

2.4. Statistical analysis

The statistical analyses applied for the project were both parametric and non-parametric in nature, ranging from one-way Analyses of Variance (ANOVAs) and Kruskal-Wallis tests to Spearman correlations, Analyses of Covariance (ANCOVAs) and regressions, using S-PLUS ® 8.0 for Windows. In order to determine the effects of seasons and stations (stream locations), respectively, on MeHg concentration, one-way

ANOVA was applied. Given the nature of the other parameters measured in this study (Load, pH, DOC, SO_4, Fe, conductivity and color), the non-parametric ANOVA alternative, the Kruskal-Wallis test, was applied to determine the effect of seasons and stations on the respective concentrations. The significance of correlations between pairs of variables was tested with the Spearman correlation test. For the pair-wise correlations with p-values <0.002 (Bonferroni probability correction), further analyses were carried out such as ANCOVAs and linear regressions to quantify the magnitude of the correlations. A non-parametric approach was used for the ANCOVAs (rank-ANCOVAs) and linear regressions (Robust MM regressions), because the data used were not normally distributed and did not satisfy the conditions for parametric analyses.

2.5. Missing Data

The data represented in this study was collected over between March 2005 and May 2007. During the summer of 2005 (June to September 2005), there was no water sampling due to drying up of the Harp and Dickie streams. Likewise, there was no sampling between November 2005 and March 2006 because the streams were frozen and weather conditions were too poor for sampling. In order to be consistent, the data used to show temporal trends in MeHg concentrations and other environmental variable was from March 2005 to May 2007, and the only the data from May 2006 to May 2007 was used for statistical analyses.

Table 2.1: Physical characteristics of the 10 streams draining in Harp (HP) and Dickie (DE) lakes. Streams were monitored and sampled from March 2005 to May 2007.

Stream Station	*Longitude*	*Latitude*	*Basin (m^2)*	*Peat (%)*	*Minor Till Plain (%)*	*Thin Till (%)*	*Slope (%)*
DE5	45°08'41"	79°05'22"	299800	25.4	0	74.6	1
DE6	45°08'46"	79°05'13"	218000	22	0	78	1.6
DE8	45°09'09"	79°05'26"	669600	8.2	13.7	78.1	1
DE10	45°09'18"	79°04'51"	788900	17.1	0	82.9	1
HP3	45°22'28"	79°08'26"	260000	9.3	79.5	11.2	4
HP3A	45°22'29"	79°08'33"	196500	2.9	97.1	0	8
HP4	45°22'49"	79°08'28"	1190900	0	56.1	32.8	5
HP5	45°22'60"	79°07'55"	1905300	13.3	34.5	48.6	3
HP6	45°22'40"	79°07'37"	99700	0	45.2	54.8	8
HP6A	45°22'46"	79°07'42"	152800	8.5	6.6	84.9	10

*where the 3 components (peat, minor till plain and thin till %) do not total 100%, there is the presence of small open water ponds (data from report by Dillon and Molot, 1997).

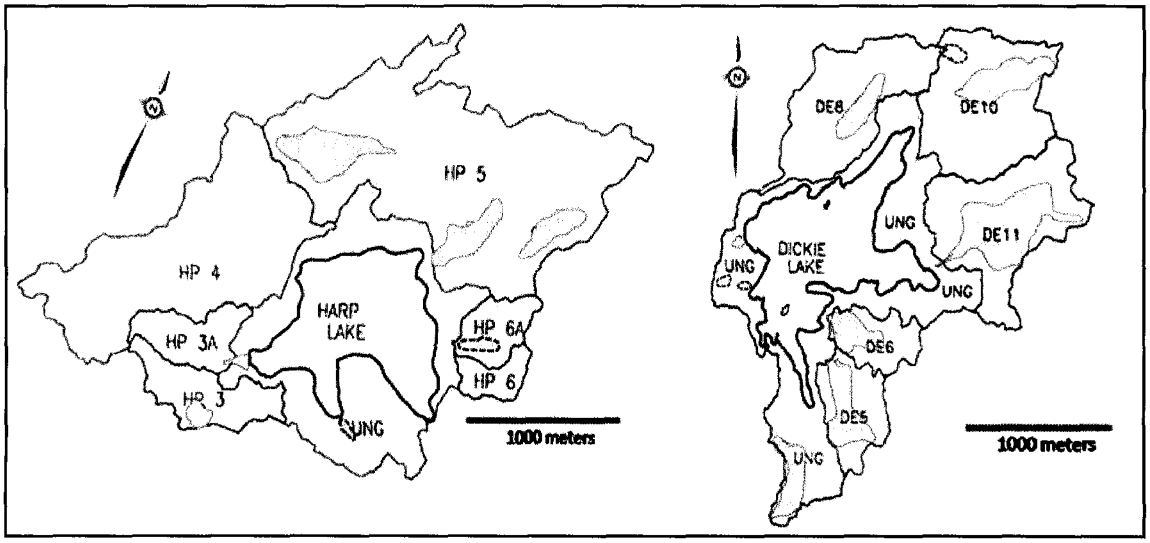

Figure 2.1: Schematics of the two study basins Harp (left; 45°23', 79°08') and Dickie (right; 45°09', 79°05'). Both lakes are located in south-central Ontario. Wetlands are designated with shaded areas.

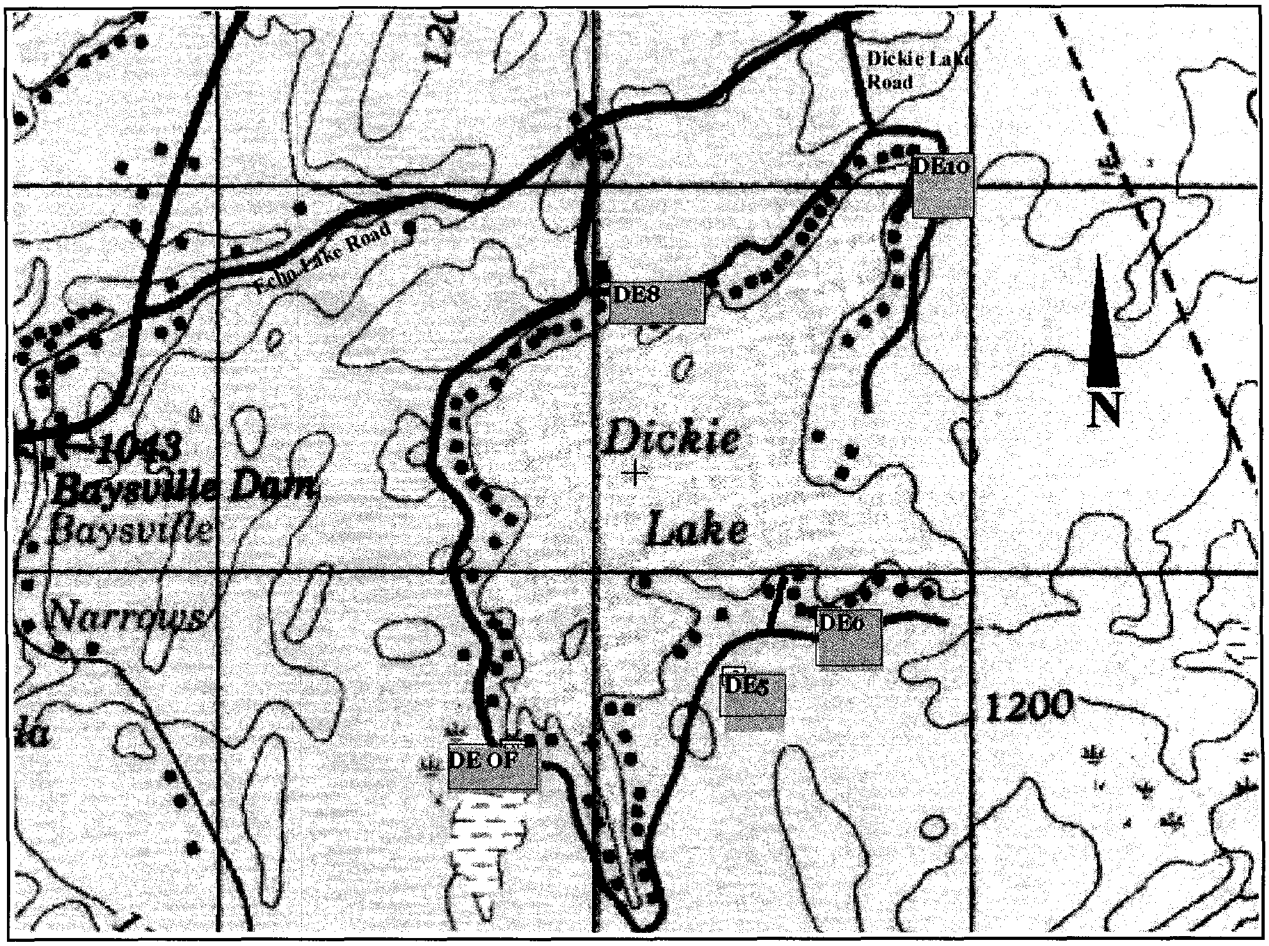

Figure 2.2: Map of Dickie Lake and its surrounding 4 streams (DE10, DE5, DE6 and DE8). Stream DE11 was omitted from the study. Streams were sampled from March 2005 to May 2007. Dickie Lake is located in the Haliburton Muskoka district, south central Ontario (45°09’, 79°05’)

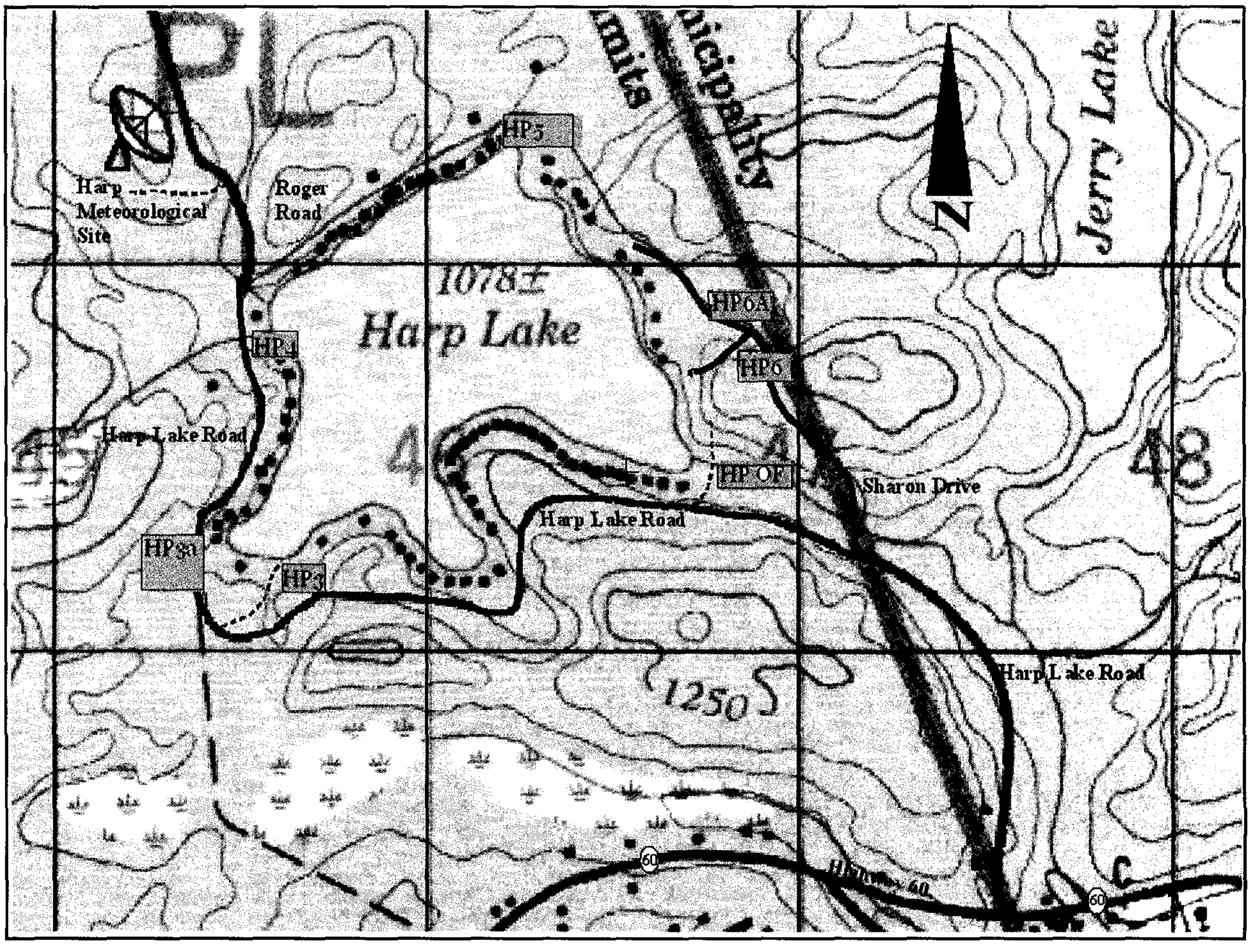

Figure 2.3: Map of Harp Lake and its surrounding 6 streams (HP3, HP3A, HP4, HP5, HP6 and HP6A). Streams were sampled from March 2005 to May 2007. Harp is located in the Haliburton-Muskoka district, south central Ontario (45°23', 79°08')

3. CHAPTER 3: RESULTS

3.1. Spatial Trends

3.1.1. Methylmercury Concentration, Load and Yield

A summary of the annual means, ranges and standard deviations for MeHg concentration, stream discharge and Load are presented in Table 3.1.

Overall, average MeHg concentrations for the year 2006-2007, between May 2006 and May 2007, had values ranging from 0.1 ng/L to 0.9 ng/L; the highest values (0.9 ng/L) occurred at stations DE6 and HP5, while the lowest value at HP6. Harp streams generally had lower means, ranging from 0.2ng/L to 0.3 ng/L, compared to Dickie lake streams (0.5 ng/L to 0.9 ng/L); with the exception of HP5 with its mean MeHg concentration of 0.9 ng/L. The ranking of stations according to average annual MeHg concentrations: DE6=HP5 > DE8 >DE10 > DE5 > HP6A > HP3 > HP4> HP3A >HP6 (Figure 3.1).

Mean stream discharge was highest in HP5 (35.9 L/s) and lowest in HP6 (1.9 L/s). Dickie streams had discharge ranging from 3.2 to 15 L/s, while Harp streams had discharge ranging from 1.9 to 35.9 L/s. Mean Load, the product of MeHg concentration and stream discharge (Equation 1), was highest at HP5 (32.3 ng/s) and was lowest at HP6 (0.3 ng/s). Amongst the Harp streams, HP4 had the second highest discharge (18.9 L/s), giving it a MeHg load of 3.1 ng/s, which is within the range of the MeHg load for Dickie streams.

Figure 3.2 shows the mean MeHg yield results in $mg/m^2/yr$, where the highest yields comes from DE6 (2.7E-04 $\mu g/m^2/yr$) and DE10 (2.6E-04 $\mu g/m^2/yr$), followed by

HP5 with a yield of (2.05E-04 μg/m^2/yr), which is 2 to 3 times higher than the other Harp lake streams. Yield results in Figure 3.2 are obtained using method I (Equation 2), and when compared to the Yield results from method II (Equation 3), there was a difference ranging from 2% to 18% in MeHg Yield results for each stream.

The ANOVA analysis determined that, overall, there is a significant difference across the stations for both MeHg Load (KW chi-square = 293.97, $p <0.005$) and for MeHg concentration ($F=30.9$, $p < 0.005$) (Appendix A).

3.1.2. Geochemical Variables

The mean annual and standard deviation results for DOC, Fe, color, pH, SO_4 and conductivity are summarized in Table 3.2.

Dickie streams are generally characterized with mean values at the higher end of the range for parameters such as DOC (15.7 – 24.2 mg/L), Fe (566 –1226 μg/L) and color (161—265 HU), while HP5 stands out as the only Harp stream with values that fall within the range of Dickie streams (18.3 mg/L for DOC, 1045 μg/L for Fe, and 188 HU for color). Mean annual pH values for Dickie streams ranged from 4.5 to 5.0, while those of Harp streams ranged from 5.0 to 6.3. Likewise, Dickie streams had a tendency for lower SO_4 concentrations (0.9 mg/L to 4.6 mg/L) compared to Harp streams (4.3 mg/L to 6.1 mg/L). Lastly, conductivity values ranged from 16.1 μS/cm (DE5) to 65.3 μS/cm (DE8).

Using the Kruskal-Wallis ANOVA, it was determined that, overall, there is a significant difference across stations for DOC, Fe, color, pH, SO_4 and conductivity, respectively ($p<0.002$ for all ANOVAs, Appendix A)

3.1.3. Correlations

The Spearman correlation matrix for the water quality parameters is shown in Table 3.3. The concentrations of methylmercury in stream waters were positively correlated with Fe (r^2=0.83), color (r^2=0.77) and DOC (r^2=0.71), and negatively correlated with SO_4 (r^2=0.66). Similarly, Fe concentrations were positively correlated with color (r^2=0.74), DOC (r^2=0.75) and negatively correlated to SO_4 (r^2= -0.59). While pH had the strongest correlations with DOC (r^2= -0.56) and color (r^2= -0.52), respectively, the relationship between pH and the other variable was weak but significant (r^2< 0.45). All pair-wise correlations between conductivity and other parameters were weak (r^2<0.40) (all p's < 0.002).

There is a good positive correlation between MeHg concentration and % wetland (r^2 = 0.46, p = 0.03, Figure 3.3), and a negative correlation between MeHg and slope (r^2 = 0.57, p = 0.01, Figure 3.4).

Table 3.1: Mean, range and standard deviation of MeHg concentration (ng/L), Stream discharge (L/s) and MeHg Load (ng/s) of the 10 streams sampled weekly between May 2006 and May 2007 in Harp and Dickie Lakes (n is the sampling frequency).

Parameters		***Stations***									
		DE10	***DE5***	***DE6***	***DE8***	***HP3***	***HP3A***	***HP4***	***HP5***	***HP6***	***HP6A***
MeHg (ng/L)	***Mean***	0.6	0.5	0.9	0.8	0.3	0.3	0.2	0.9	0.1	0.3
	(n)	(43)	(50)	(49)	(51)	(52)	(45)	(52)	(51)	(45)	(44)
	Min.	0.1	0.2	0.2	0.1	0.1	0.01	0.04	0.09	0.01	0.01
	Max.	1.3	1.8	2.4	3.2	1.0	1.7	0.5	3.3	0.6	2.1
	Std dev	0.3	0.4	0.6	0.8	0.2	0.3	0.1	0.9	0.1	0.4
Discharge (L/s)	***Mean***	15.0	4.5	3.2	12.7	5.3	3.6	18.9	35.9	1.9	2.8
	(n)	(43)	(50)	(49)	(51)	(52)	(45)	(52)	(51)	(45)	(44)
	Min.	1.4	0.2	0.08	0.08	0.1	0.02	0.0	0.7	0.0	0.06
	Max.	82.8	23.9	22.4	82.8	24.0	31.5	96.7	196	19.9	13.4
	Std dev	18.2	4.4	3.8	17	5.6	5.60	19.8	42.7	3.4	2.8
Load (ng/s)	***Mean***	6.5	1.6	1.9	3.9	0.8	0.3	3.0	12.4	0.1	0.4
	(n)	(43)	(50)	(49)	(51)	(52)	(45)	(52)	(51)	(45)	(44)
	Min.	1.1	0.1	0.07	0.2	0.03	0.008	0.2	2.1	0.002	0.001
	Max.	67.3	4.4	6.4	20.9	4.2	4.1	28.1	36.4	0.5	1.8
	Std dev	10.3	0.9	1.6	3.4	0.8	0.6	4.2	8.6	0.1	0.3

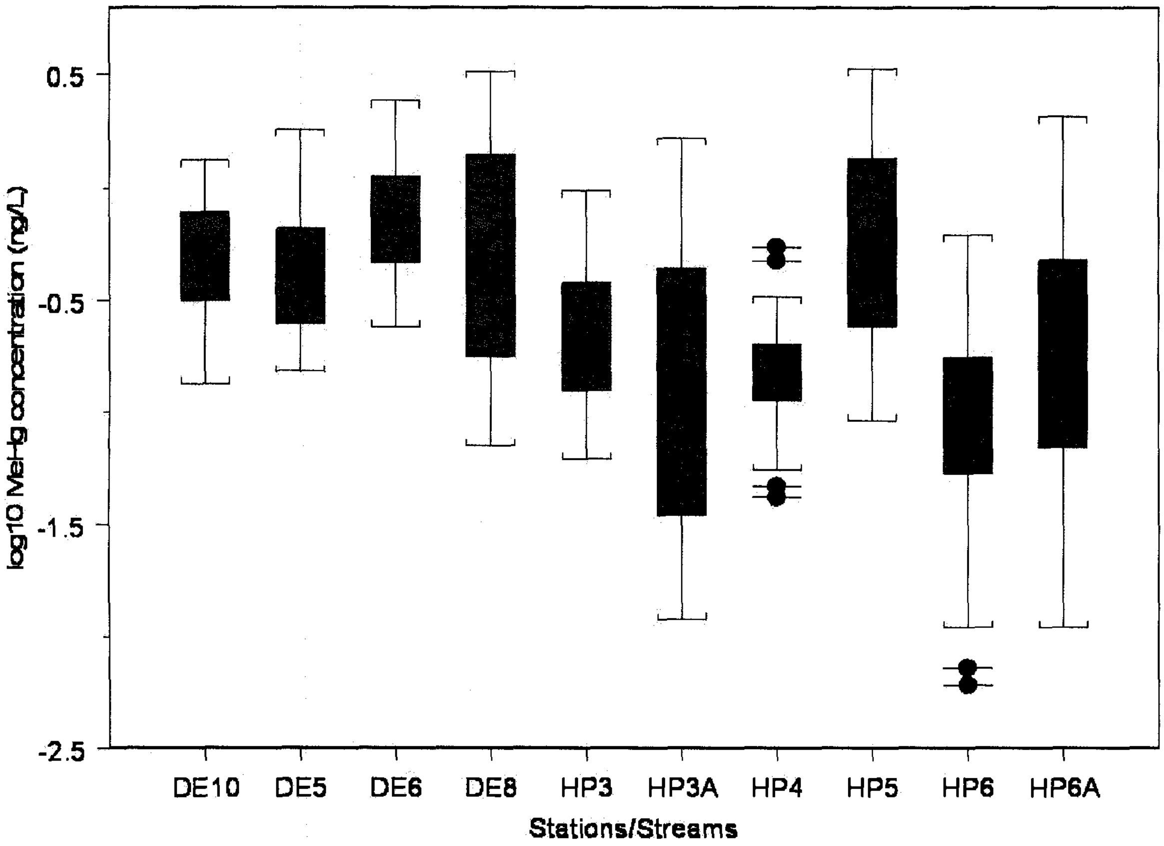

Figure 3.1: Spatial distribution of MeHg (ng/L) of the 10 streams sampled in Dickie and Harp Lakes between May 2006 and May 2007. Data was log10-transformed to normalize the distribution of the data.

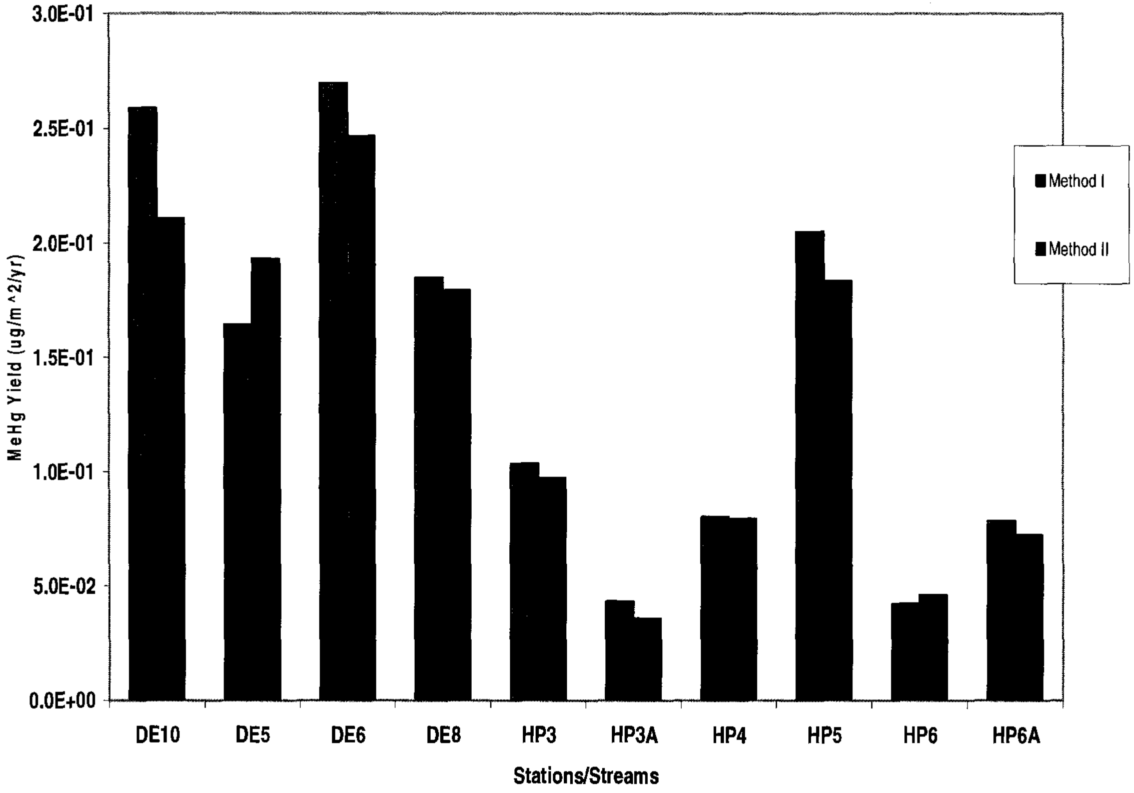

Figure 3.2: MeHg Yield (μg/m^2/yr) for the 10 streams sampled between May 2006 and May 2007, using Method I (Equation 2) and Method II (Equation 3).

Table 3.2: Mean and standard deviation of DOC (mg/L), Fe (µg/L), Color (Hazen Units), pH, Sulfate (mg/L) and Conductivity (µS/cm) of the 10 streams; sampled weekly between May 2006 and May 2007 in Harp and Dickie Lakes (n is the sampling frequency)

Parameters		***Stations***									
		DE10	***DE5***	***DE6***	***DE8***	***HP3***	***HP3A***	***HP4***	***HP5***	***HP6***	***HP6A***
DOC	***Mean***	22.3	15.7	23	24.2	13.8	3.2	6.8	18.2	10.4	14.4
(mg/L)	***(n)***	(43)	(50)	(49)	(51)	(52)	(45)	(52)	(51)	(45)	(44)
	Std dev	12.8	5.6	9.5	12.8	7.8	1.0	2.1	11.5	4.6	9.7
Fe	***Mean***	716	669	1227	566	521	363	232	104	516	342
(µG/L)	***(n)***	(43)	(50)	(49)	(51)	(52)	(45)	(52)	(51)	(45)	(44)
	Std dev	583	392	1030	492	425	505	107	1357	524	404
Color	***Mean***	242	160	265	252	132	23	57	188	68	131
(HU)	***(n)***	(43)	(50)	(49)	(51)	(52)	(45)	(52)	(51)	(45)	(44)
	Std dev	154	73	141	153	77	13	21	147	33	113

Table 3.2: (Continued)

Parameters		***Stations***									
		DE10	***DE5***	***DE6***	***DE8***	***HP3***	***HP3A***	***HP4***	***HP5***	***HP6***	***HP6A***
pH	***Mean***	4.5	4.6	4.5	5.0	5.6	6.0	6.3	5.4	6.0	5.0
	(n)	(43)	(50)	(49)	(51)	(52)	(45)	(52)	(51)	(45)	(44)
	Std dev	0.2	0.2	0.3	0.4	0.3	0.4	0.3	0.3	0.3	0.3
SO_4	***Mean***	3.0	0.9	1.2	4.6	4.8	6.0	5.2	4.3	6.1	4.9
(mg/L)	***(n)***	(43)	(50)	(49)	(51)	(52)	(45)	(52)	(51)	(45)	(44)
	Std dev	1.7	0.9	1.1	2.7	1.8	0.6	1.3	2.0	2.6	3.0
Conductivity	***Mean***	26.7	16.1	32.0	65.3	48.2	29.2	31.2	30.2	57.5	23.3
(µS/cm)	***(n)***	(43)	(50)	(49)	(51)	(52)	(45)	(52)	(51)	(45)	(44)
	Std dev	6.0	3.5	6.3	15.0	16.3	9.0	5.5	6.3	10.8	6.7

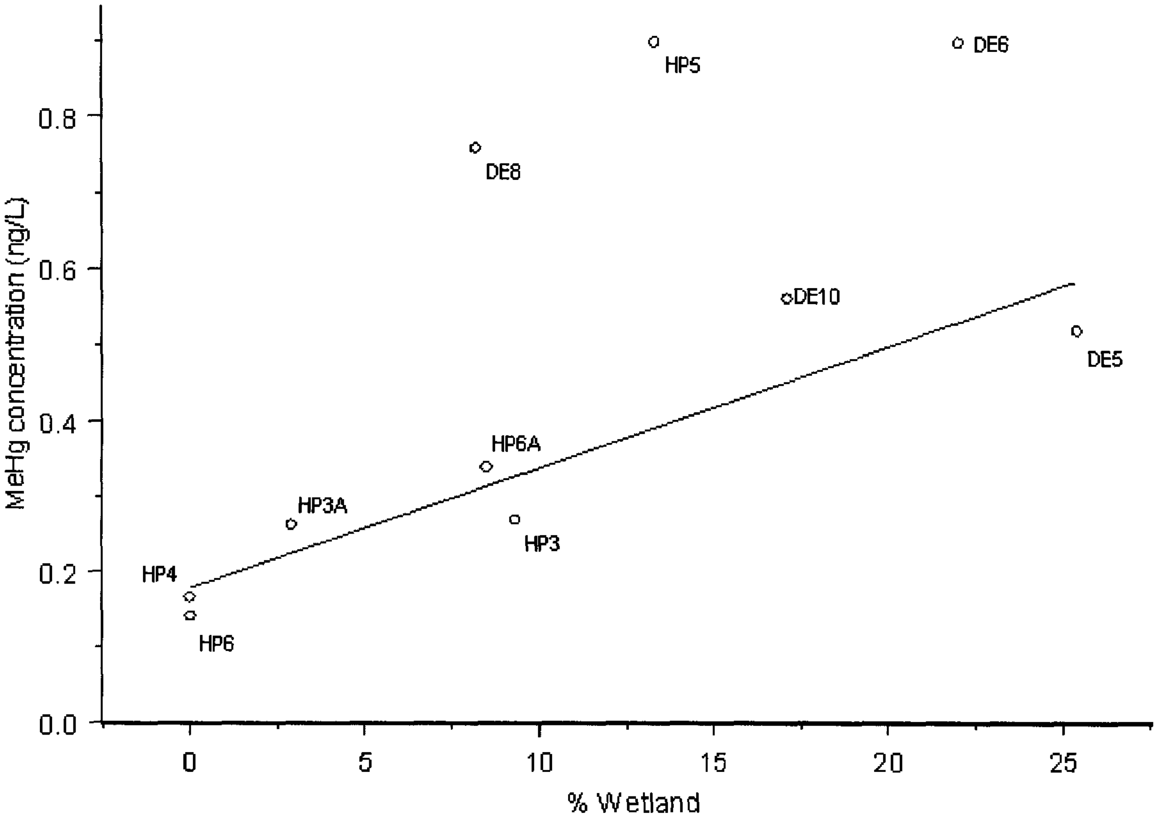

Figure 3.3: Relationship between the proportion of wetland in a sub-catchment and mean MeHg concentration for the period between May 2006 and May 2007; $r^2 = 0.46$, $n = 10$, $p = 0.03$.

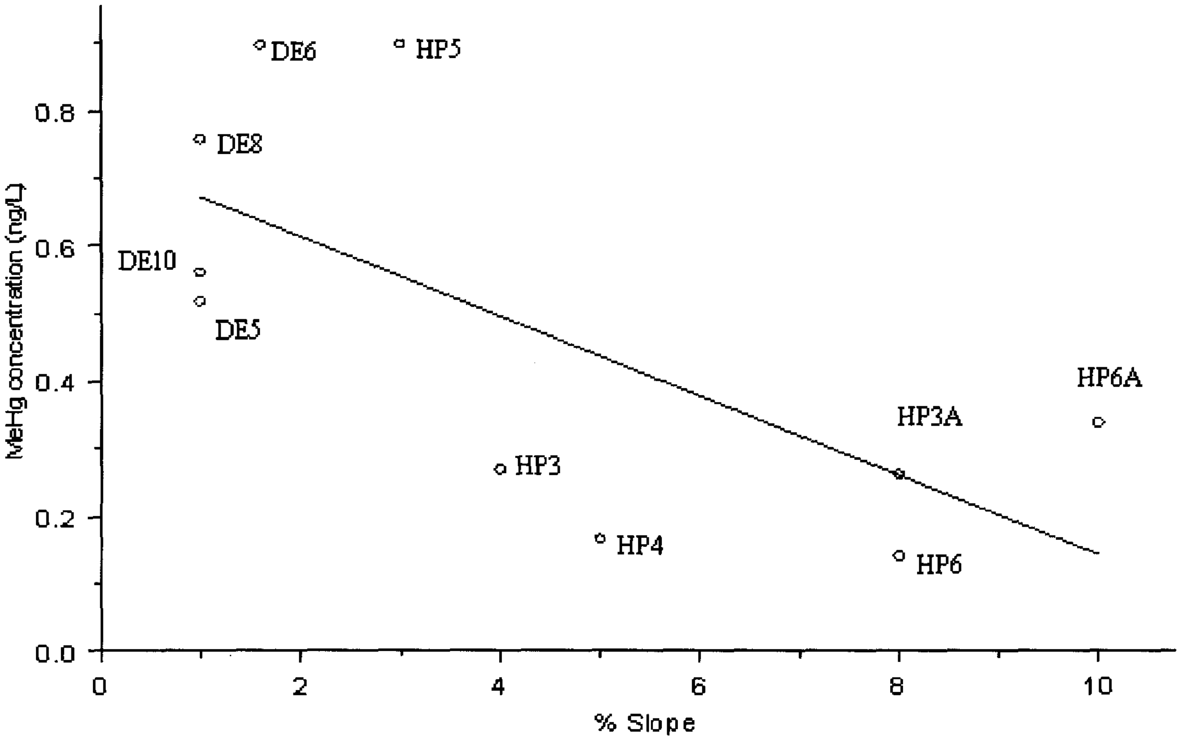

Figure 3.4: Relationship between % slope of a sub-catchment and mean Log_{10} MeHg concentration for the period between May 2006 and May 2007; $r^2 = 0.57$, $n = 10$, $p = 0.01$.

Table 3.3: Matrix of Spearman Correlations (rho values) for MeHg concentration, Load and 6 environmental variables measured from 10 streams draining in Harp and Dickie Lakes. Samples were taken between May 2006 and May 2007. Data presented was $\log_{10}$-transformed, except for pH.

	pH*	***MeHg***	***Load***	***DOC***	***Color***	***Fe***	***Conductivity***	***SO_4***
pH	1.00							
MeHg	-0.40*	1.00						
Load	-0.38*	0.32*	1.00					
DOC	-0.56*	0.71*	0.32*	1.00				
Color	-0.52*	0.77*	0.34*	0.89*	1.00			
Fe	-0.26*	0.83*	0.077	0.75*	0.74*	1.00		
Conductivity	-0.34*	0.0041	-0.13	0.13	0.08	0.18*	1.00	
SO_4	-0.43*	-0.66*	-0.19*	-0.58*	-0.67*	-0.59*	0.33*	1.00

* Significant, $p < 0.002$ (Bonferroni probability correction)

3.2. Temporal Trends

3.2.1. Methylmercury Concentration and Load

There are variations across seasons in MeHg concentrations over the period of May 2006 to May 2007 for Dickie streams (Figure 3.5) and Harp streams (Figure 3.6). For weekly means, maximum MeHg concentrations ranged from 0.5 ng/L (HP4) to 3.3 ng/L (HP5) and minimum MeHg concentrations ranged from 0.006 ng/L (HP6) to 0.2 ng/L (DE6). Results for stream discharge for Harp and Dickie streams are presented in Figures 3.7 and 3.8, respectively; while results for MeHg Load are shown in Figures 3.9 and 3.10, respectively.

Over all 10 stations, average MeHg concentration in the summer was the highest (0.9 ng/L), followed by spring (0.5 ng/L), winter (0.3 ng/L) and fall (0.3 ng/L). Stream discharge was the lowest for all stations during the summer season. MeHg load trends reveal that the fall and spring seasons have the highest MeHg export (4.2 ng/s, or 0.36 mg/day, for both seasons), followed by winter (2.3 ng/s, or 0.195 mg/day) and summer (1.4 ng/s, or 0.124 mg/day). No stream discharge was recorded for DE8 in winter, hence no subsequent MeHg load value. For all 10 stations, the highest MeHg concentrations were reported in the summer; while the highest MeHg load for all 10 seasons were reported during the spring season. More importantly, although the 10 streams have different seasonal MeHg concentrations, all the streams follow the same seasonal pattern, with high peaks in June-July of both 2005 and 2006.

Using the Kruskal-Wallis ANOVA, it was determined that, overall, there is a significant difference across the seasons for MeHg concentration and Load, respectively ($p<0.05$, Appendix A) for the period between May 2006 and May 2007.

3.2.2. Geochemical Variables

3.2.2.1. pH, SO_4 and DOC

As a general trend, Dickie streams had lower mean pH values than Harp streams across seasons. Dickie streams had pH ranging from 4.14 to 4.69 throughout the year, while Harp streams had pH between 5.08 and 5.88 (Figure 3.11). SO_4 concentrations were found to be lower in Dickie streams (Figure 3.16) than in Harp streams (Figure 3.17), and both exhibited the lowest concentrations during the summer.

DOC results showed that Dickie streams (DE10, DE5, DE6 and DE8) had elevated DOC concentrations across the four seasons compared to Harp streams, with the exception HP5 with DOC concentrations similar to Dickie streams. For Dickie streams, DOC was highest in the summer (DE 10, 47.3 mg/L), but were lowest during the spring and winter (Figure 3.12). Clear-water Harp streams exhibited lower DOC concentrations, with DOC concentrations in HP3A reported to be as low as 4.0 mg/L for the fall, 2.9 mg/L for the spring, 2.8 mg/L for the summer and 2.8 mg/L for the winter (Figure 3.13).

3.2.2.2. Iron and Color

On average for all stations, the summer season recorded the highest mean color (265 HU) and Fe (1504 µg/L), when compared to other seasons. Brown-water streams featured elevated color intensity and Fe concentrations, especially during the summer with a maximum of 551 HU and 2093 μg/L, respectively (Figures 3.14 and 3.18). July $12^{th,}$ 2005 (omitted in Figure 3.14) stands out as a potential outlier with a color intensity of 989 HU. However, an equally elevated Fe concentration on the same day (Figure 3.18) suggests the possibility that their simultaneous occurrence is not a coincidence. In Harp streams, color and Fe followed similar seasonal patterns (Figures 3.15 and 3.19), but values were lower than Dickie streams.

Applying the Kruskal-Wallis ANOVA, it was determined that, overall, there is a significant difference across the 4 seasons for DOC, Fe2+, color, pH, SO_4 and conductivity, respectively ($p<0.05$, Appendix A) for the period between May 2006 and May 2007.

3.2.2.3. Conductivity

Among Dickie streams, DE8 consistently featured the highest conductivity values (Figure 3.20), which were always higher than even the Harp stream conductivity range across seasons (Figure 3.21). Mean conductivity values across all the stations were lowest in DE5 for all seasons (15, 16.6, 15.3 and 18 μS/cm for the fall, spring, summer and winter seasons, respectively) and highest in DE8 for all seasons.

3.2.3. Correlations

Seasonal trends were determined by applying the two model variations of the ANCOVA statistical analysis on the significant pair-wise correlations with an assumed causal relationship. The first model tested for the homogeneity of the slopes of each pair-wise regression for each season, indicated by the significance of the interaction term (p <

0.05). The results show that there is no significant difference between the slopes of the following pair-wise regressions across the 4 seasons: $\log_{10}$ Fe versus both $\log_{10}$ conductivity and pH, $\log_{10}$ DOC versus $\log_{10}$ Conductivity, $\log_{10}$ MeHg versus either pH, $\log_{10}$ conductivity, $\log_{10}$ Fe or $\log_{10}$ Load, and $\log_{10}$ Load versus $\log_{10}$ DOC (p > Appendix B).

Where the interaction term was significant, linear Robust MM regressions were applied for each of the 4 seasons. All the regressions were log-transformed to normalize the distribution of the data (Luider et al., 2006). Results are summarized in Table D (Appendix D) and Figures 3.22 to 3.28.

The second ANCOVA model tested the equality of intercepts for pair-wise regressions with slopes of similar magnitude (interaction term of model 1 ANCOVA was not significant). No further analysis was applied to results with significantly different slope intercepts, but a simple regression was reported for results with intercepts that do not vary among seasons. Table C summarizes the results for model 2 ANCOVA, and there is no significance for the regression of MeHg concentration against conductivity ($\log_{10}$-transformed, $r^2 = 0.036$, M-estimate = 0.8)

There was no significance in the correlation between MeHg and % wetland across seasons, hence no seasonal variability within the interaction, but there was seasonal variability in the negative relationship between MeHg and % slope.

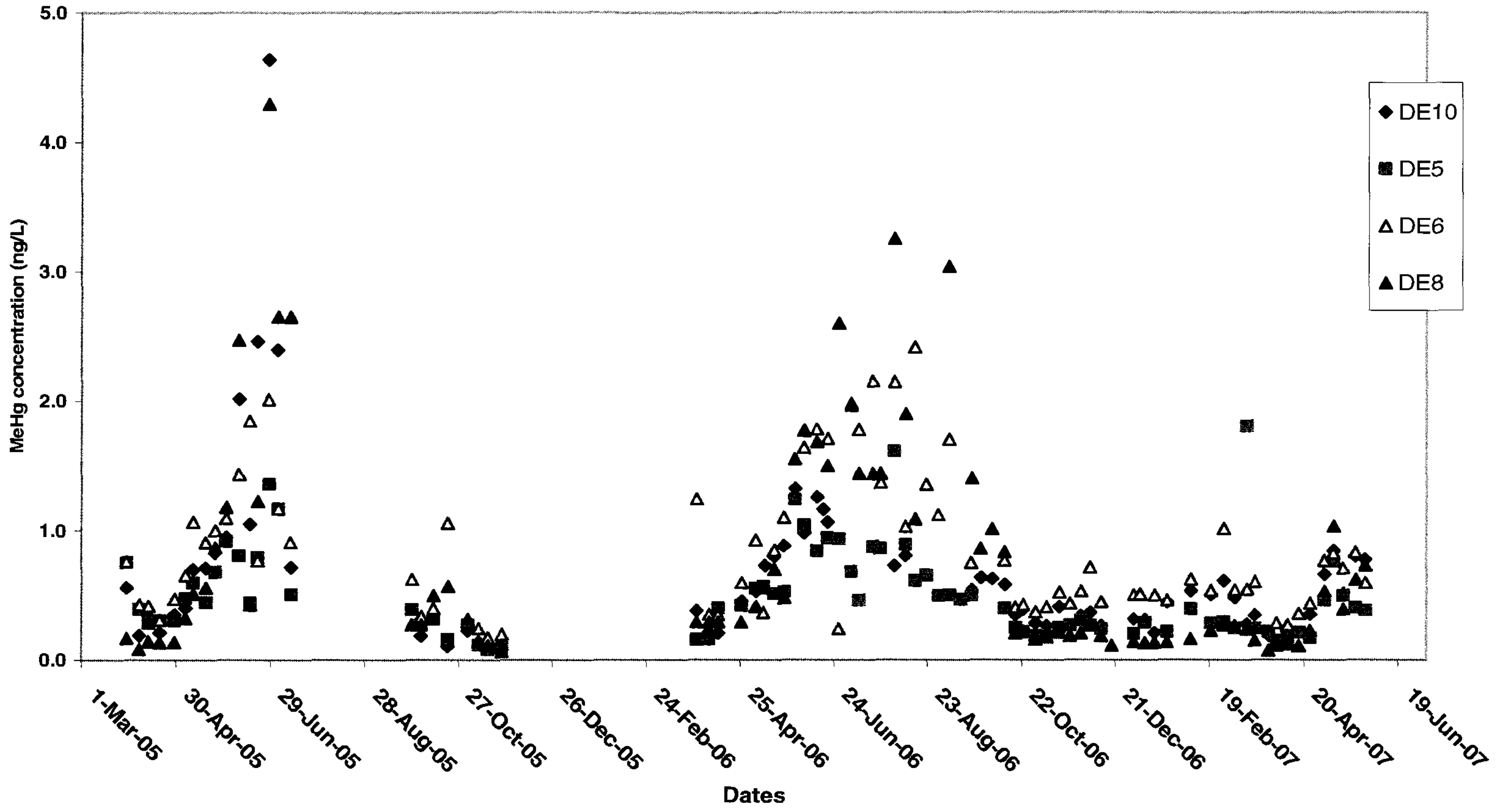

Figure 3.5: MeHg concentration (ng/L) for Dickie streams (DE10, DE5, DE6 and DE8) from March 2005 to May 2007.

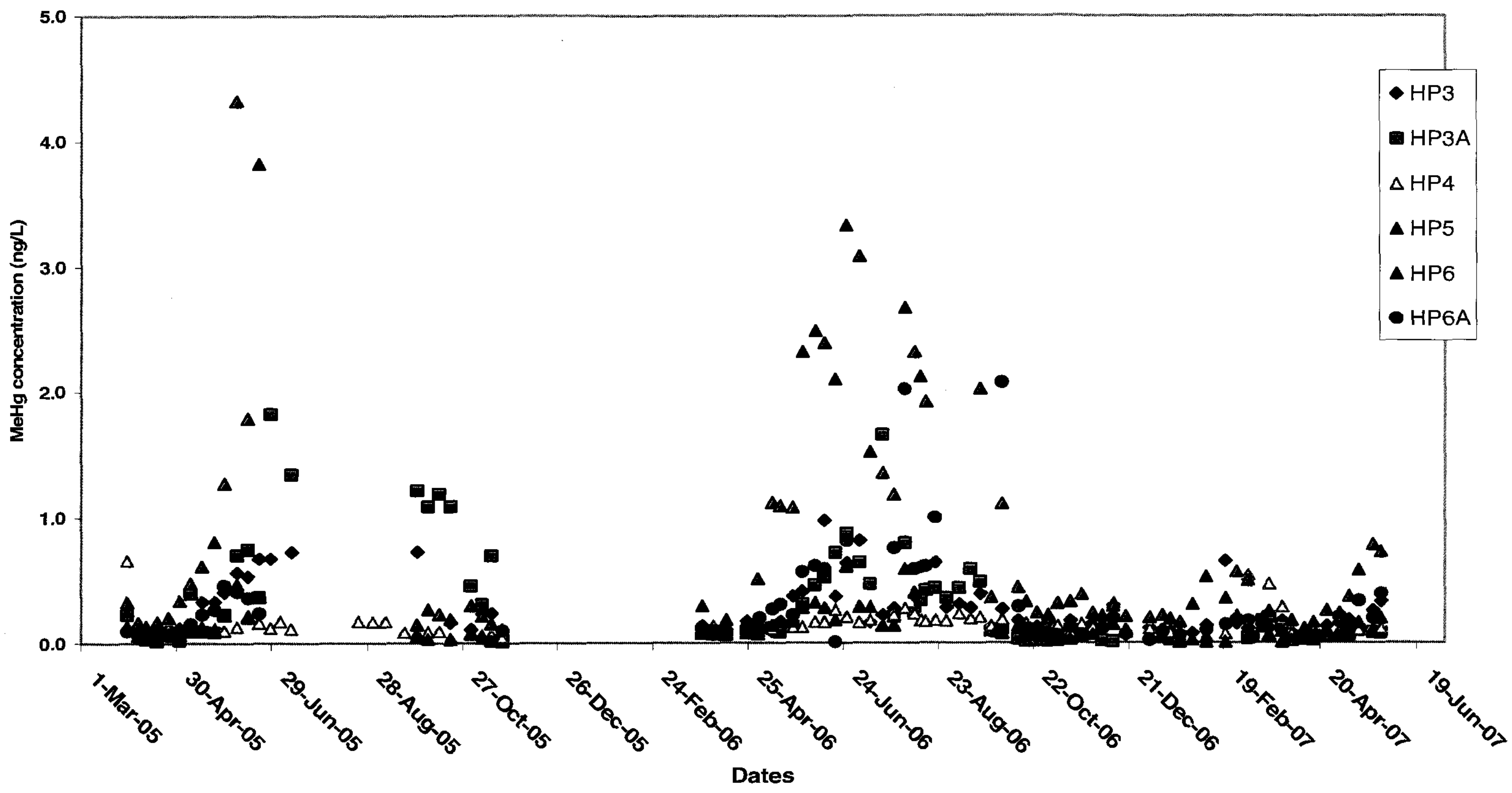

Figure 3.6: MeHg concentration (ng/L) for Harp streams (HP3, HP3A, HP4, HP5, HP6 and HP6A) from March 2005 to May 2007.

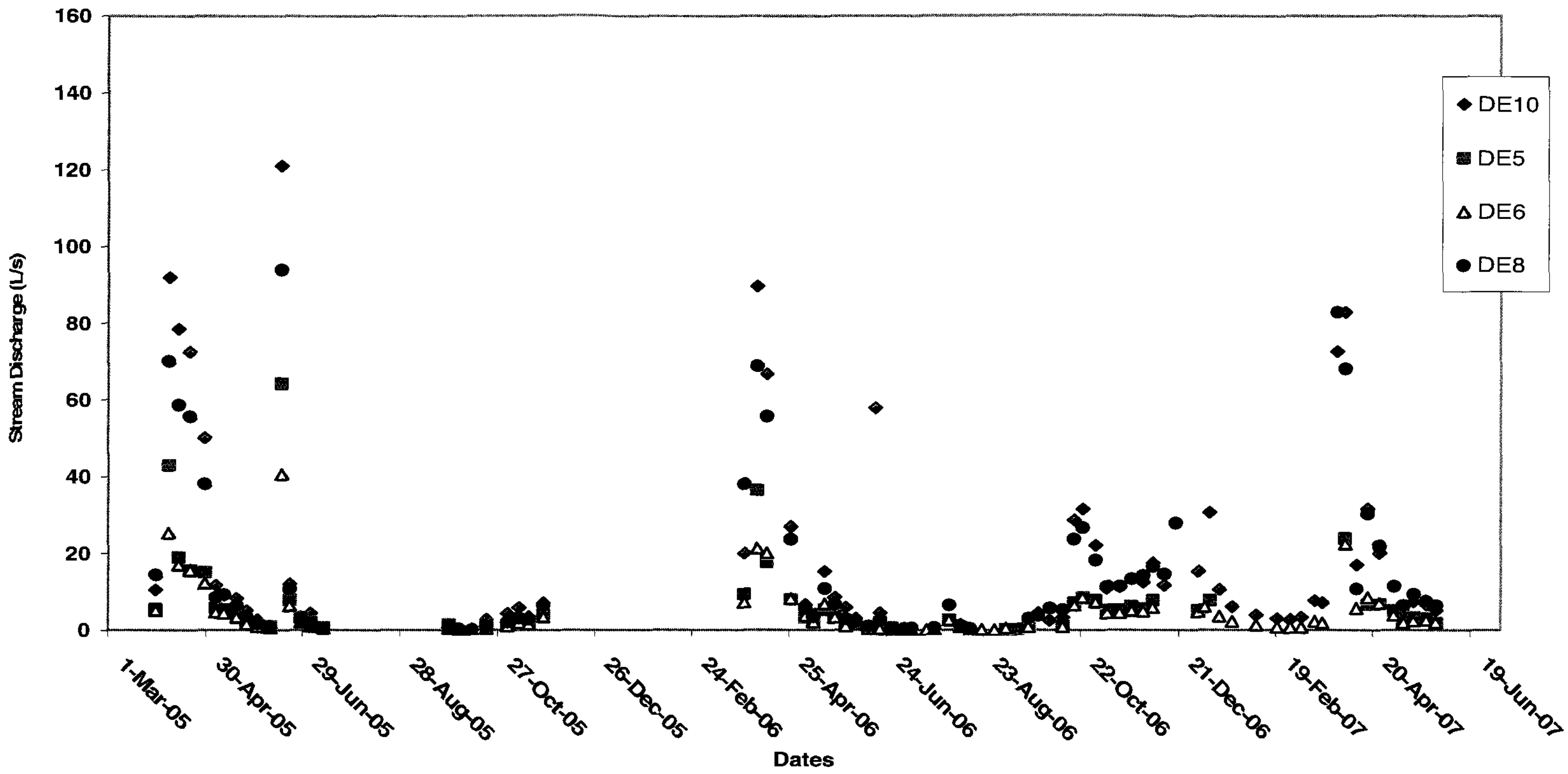

Figure 3.7: Temporal trends in Stream Discharge (L/s) for Dickie streams (DE10, DE5, DE6 and DE8) from March 2005 to May 2007

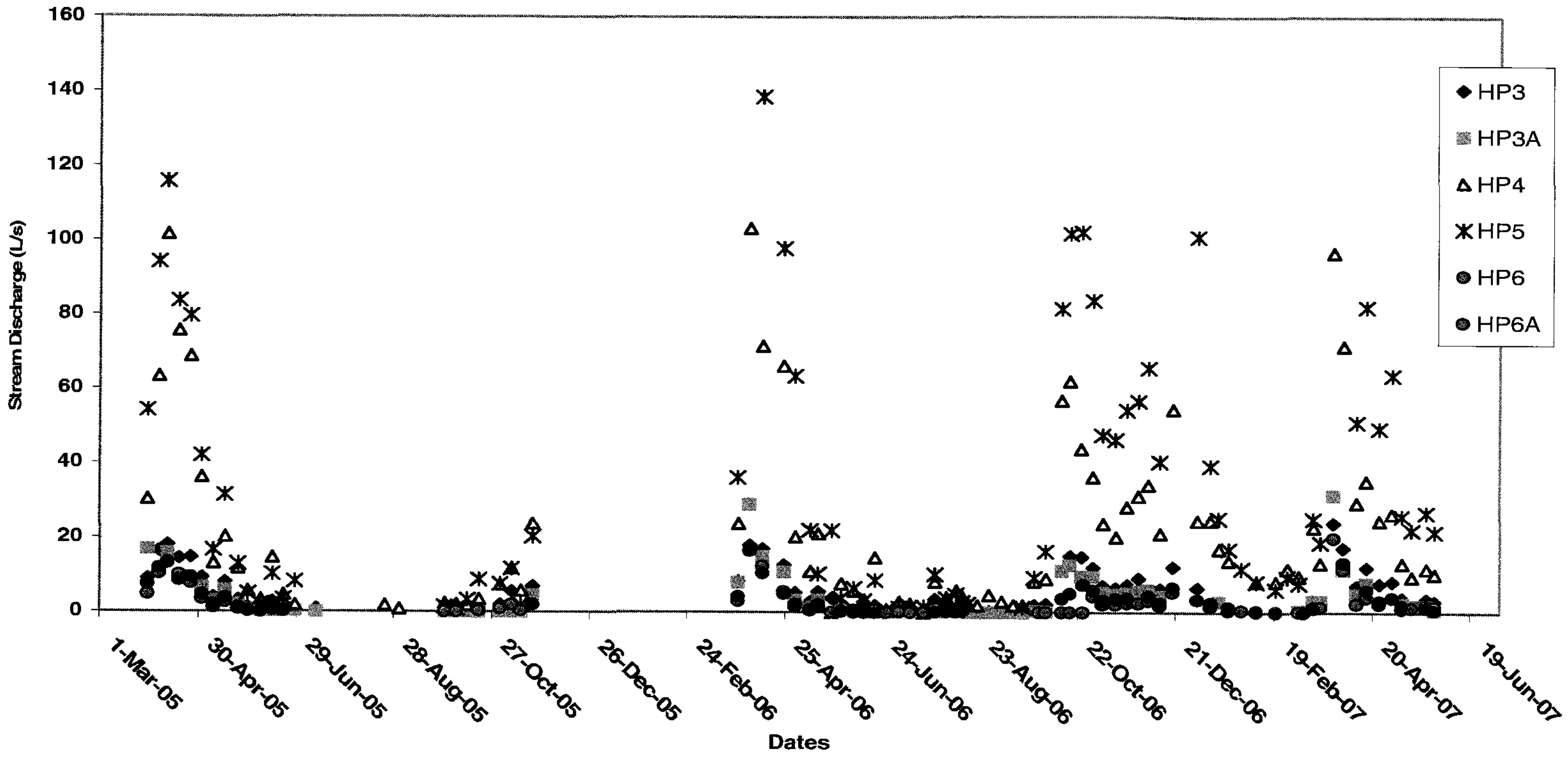

Figure 3.8: Temporal trends in Stream Discharge (L/s) for Harp streams (HP3, HP3A, HP4, HP5, HP6 and HP6A) from March 2005 to May 2007. Two data points stream HP5 were omitted: March 27th, 2007 (196 L/s) and April 2nd, 2007 (174 L/s).

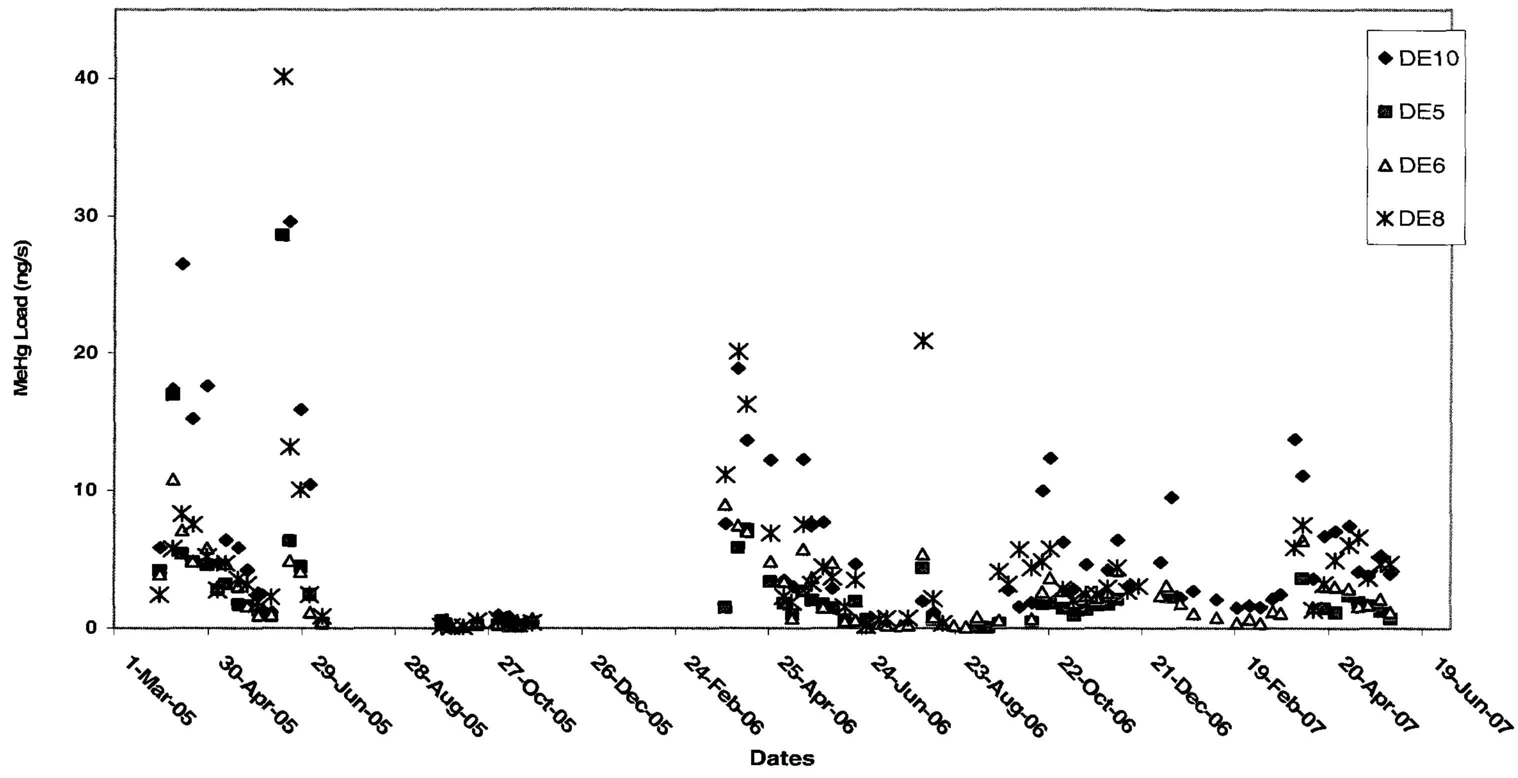

Figure 3.9: Temporal trends in MeHg Load (ng/s) for Dickie streams (DE10, DE5, DE6 and DE8) from March 2005 to May 2007. two data points were omitted: June 16th, 2005 for DE6 (75 ng/s) and June 17th, 2006 for DE10 (67.3 ng/s).

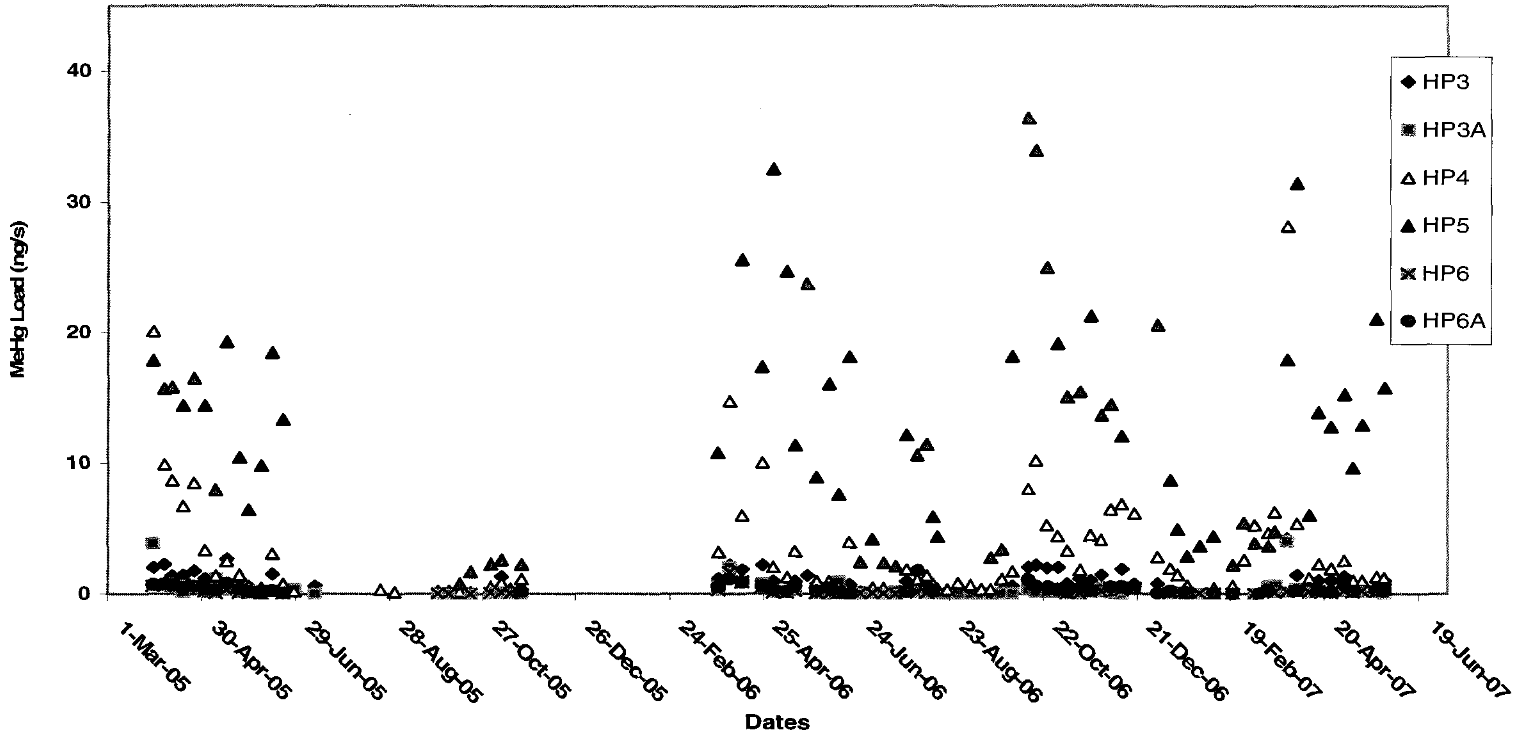

Figure 3.10: Temporal trends in MeHg Load (ng/s) for Harp streams (HP3, HP3A, HP4, HP5, HP6 and HP6A) from March 2005 to May 2007. One data point was omitted for HP5: June 38th, 2005 (61.6 ng/s).

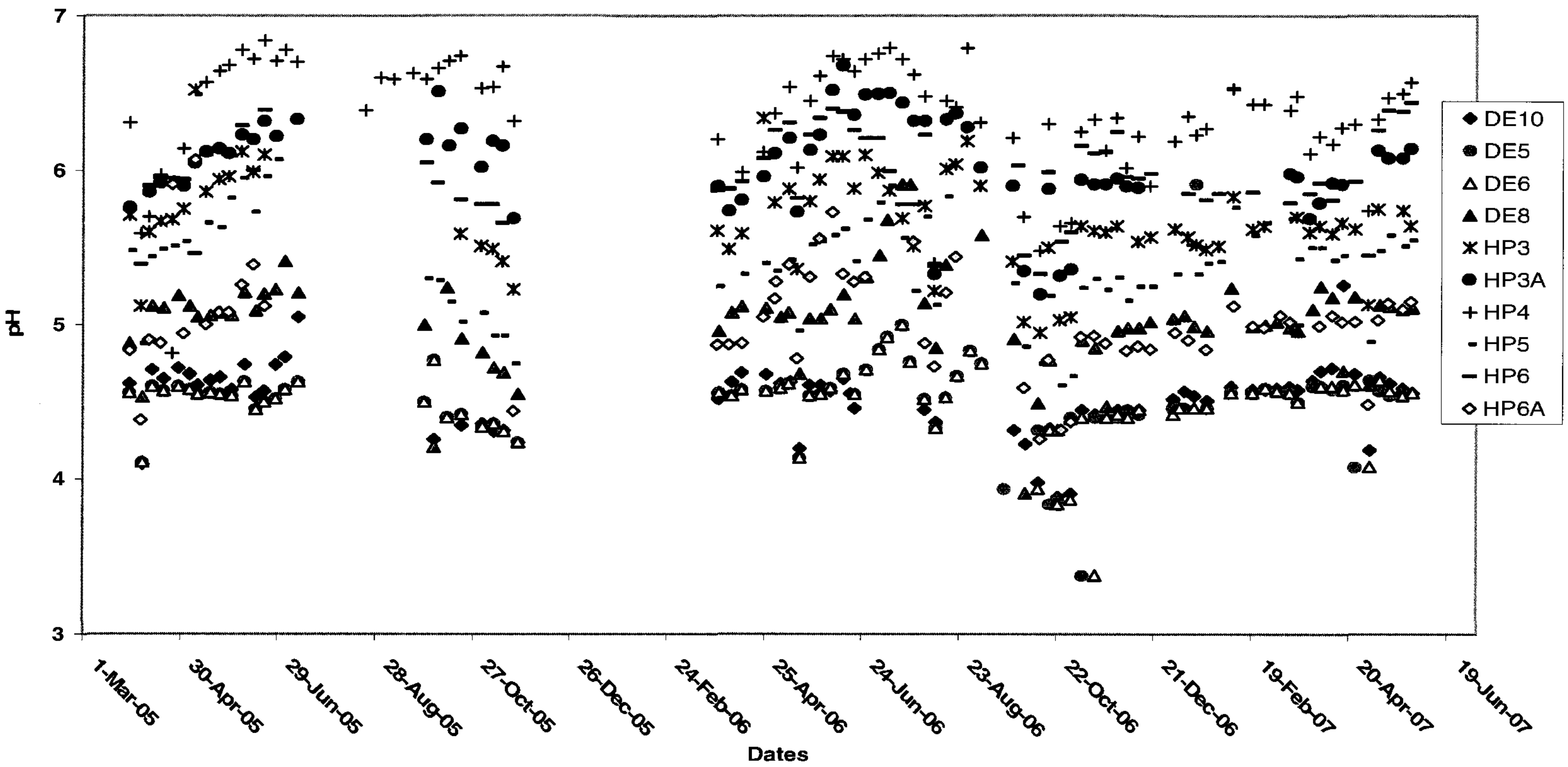

Figure 3.11: Temporal trends in pH for Dickie (DE10, DE5, DE6 and DE8) and Harp (HP3, HP3A, HP4, HP5, HP6 and HP6A) streams from March 2005 to May 2007.

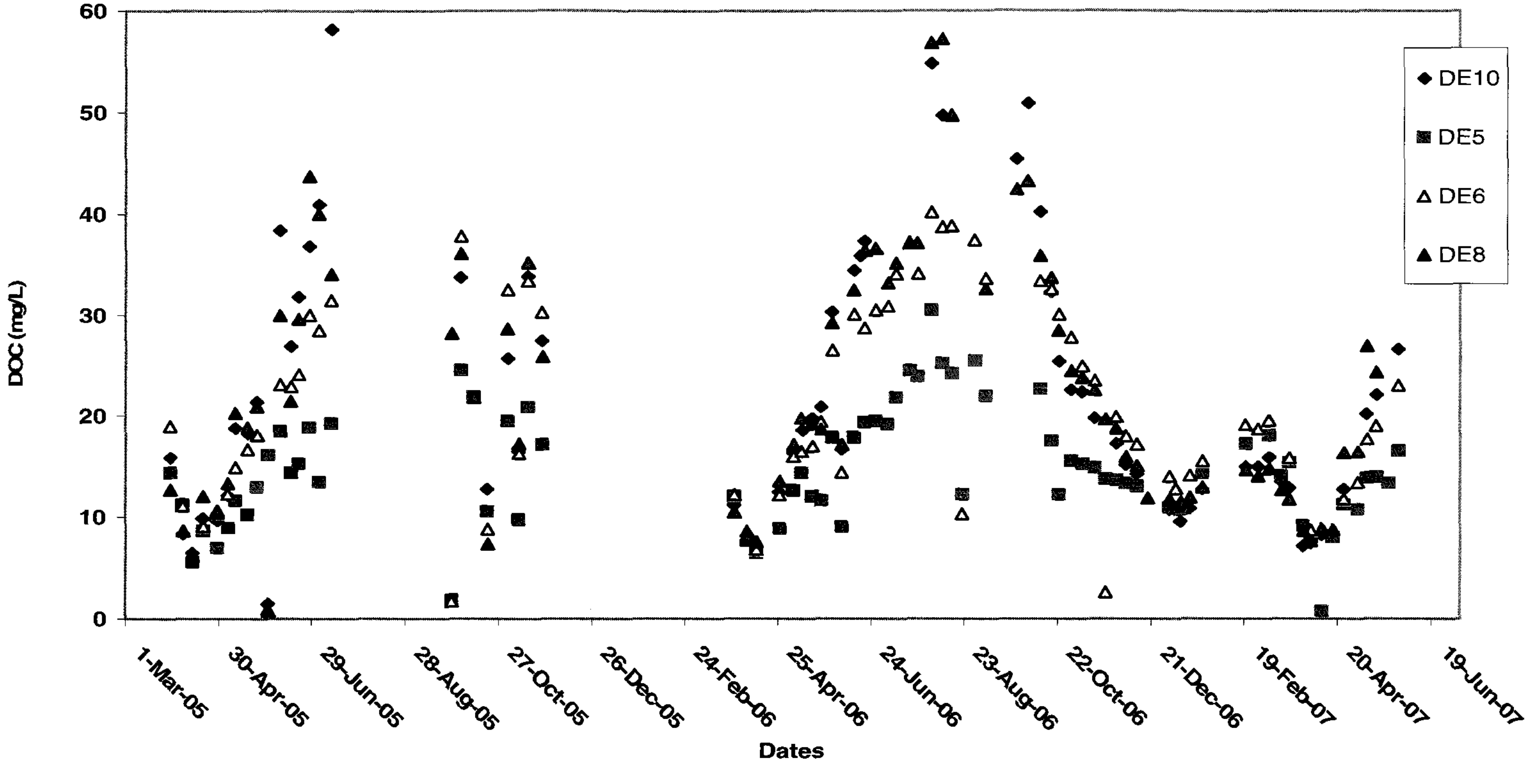

Figure 3.12: Temporal trends in DOC (mg/L) for Dickie streams (DE10, DE5, DE6 and DE8) from March 2005 to May 2007

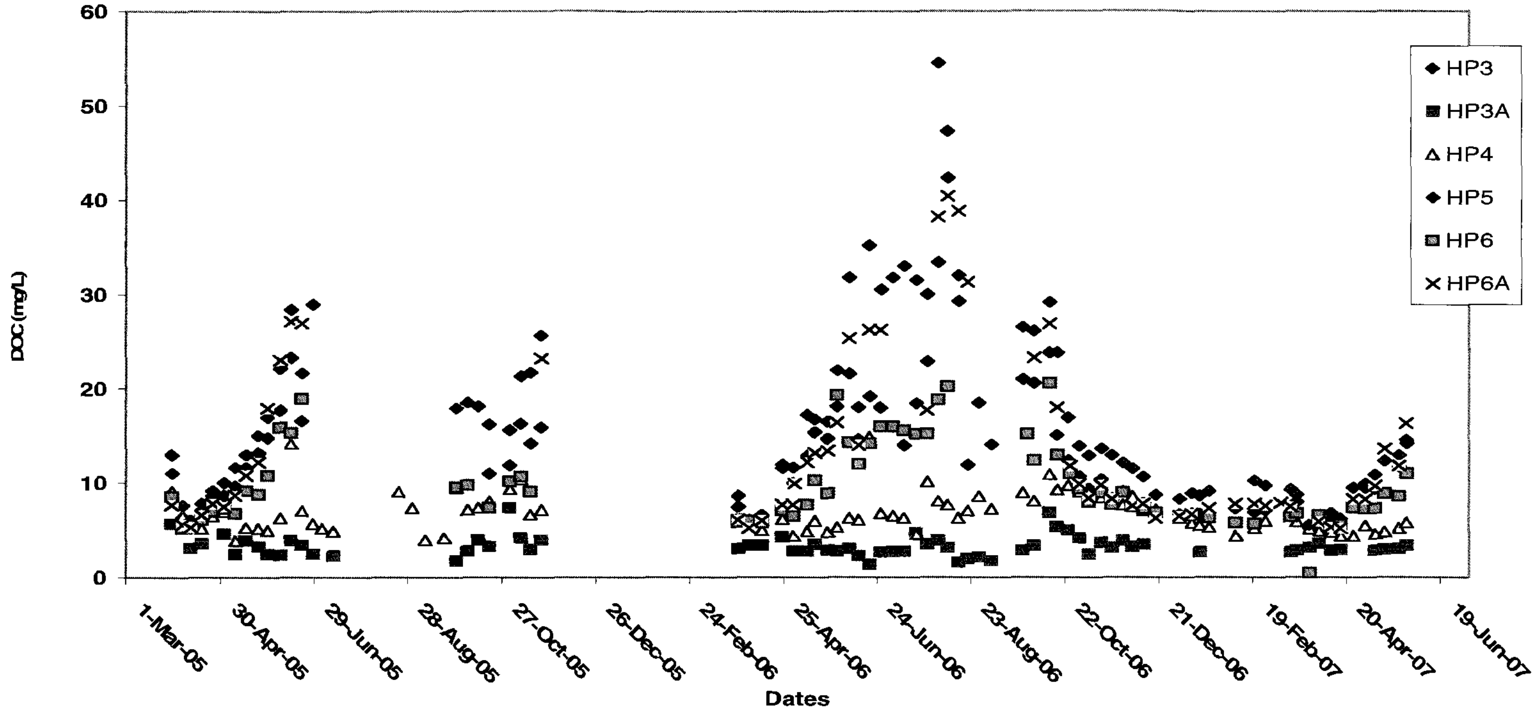

Figure 3.13: Temporal trends in DOC (mg/L) for Harp streams (HP3, HP3A, HP4, HP5, HP6 and HP6A) from March 2005 to May 2007

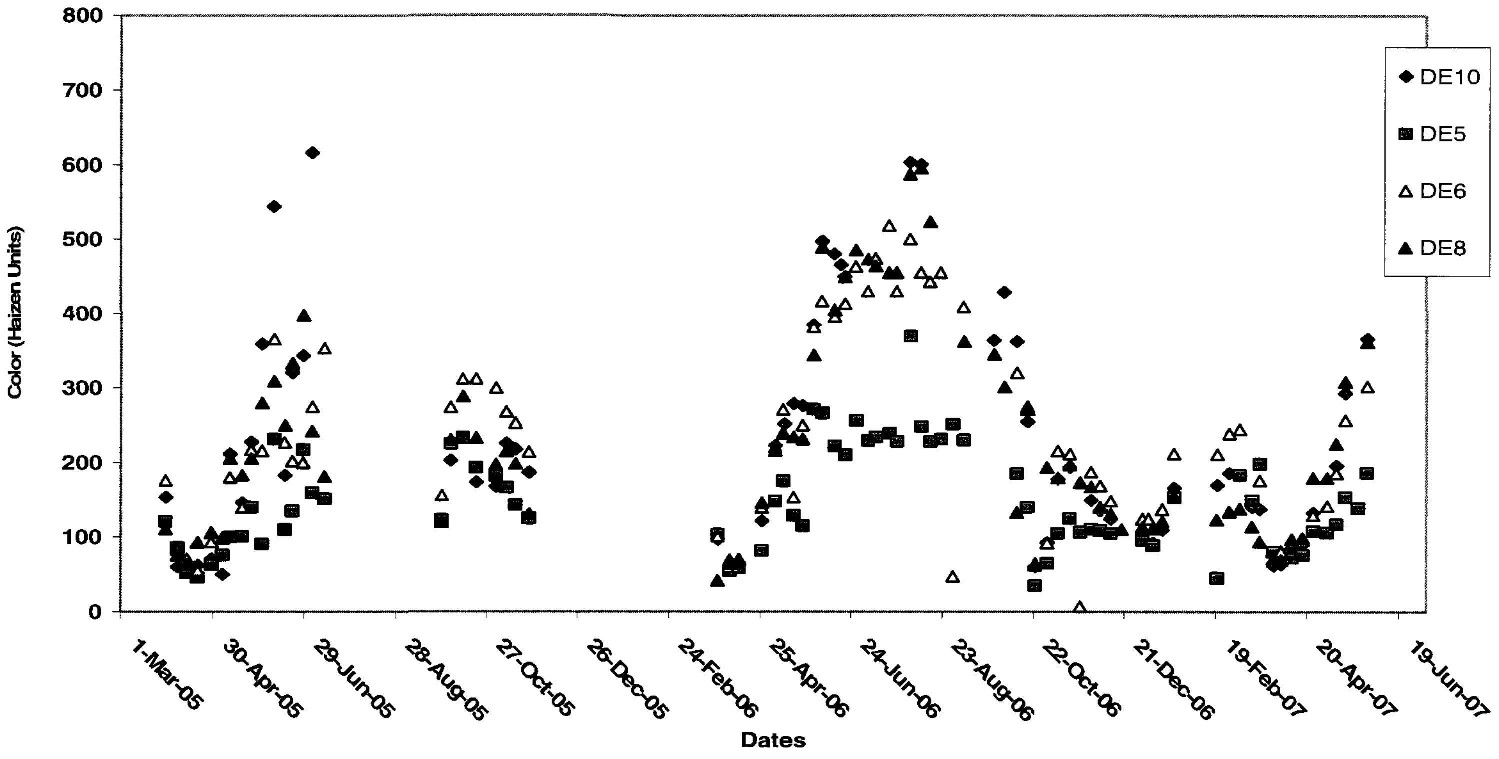

Figure 3.14: Temporal trends in Color (HU) for Dickie streams (DE10, DE5, DE6 and DE8) from March 2005 to May 2007. One data point was omitted for DE10: July 12th, 2005 (989 HU).

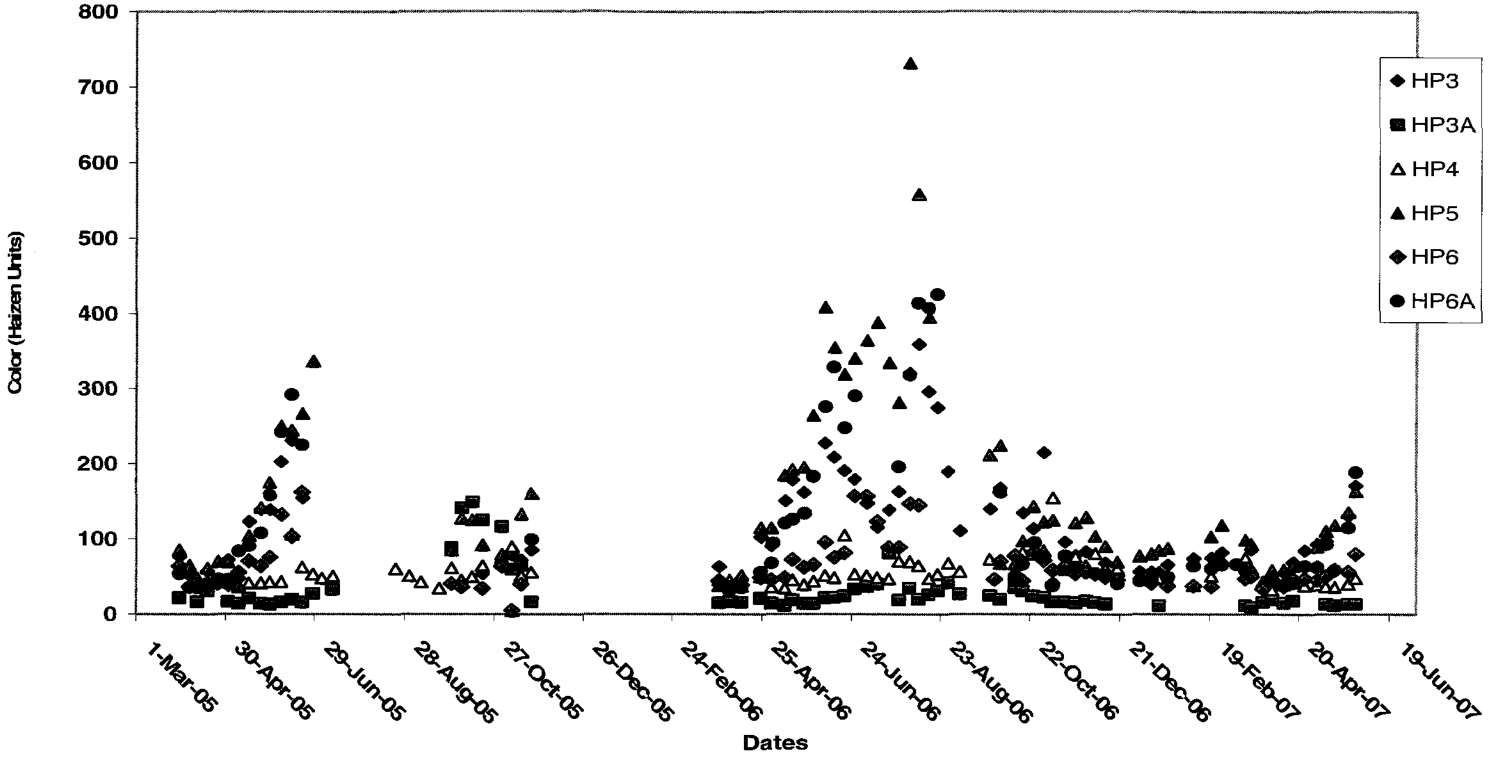

Figure 3.15: Temporal trends in Color (HU) for Harp streams (HP3, HP3A, HP4, HP5, HP6 and HP6A) from March 2005 to May 2007

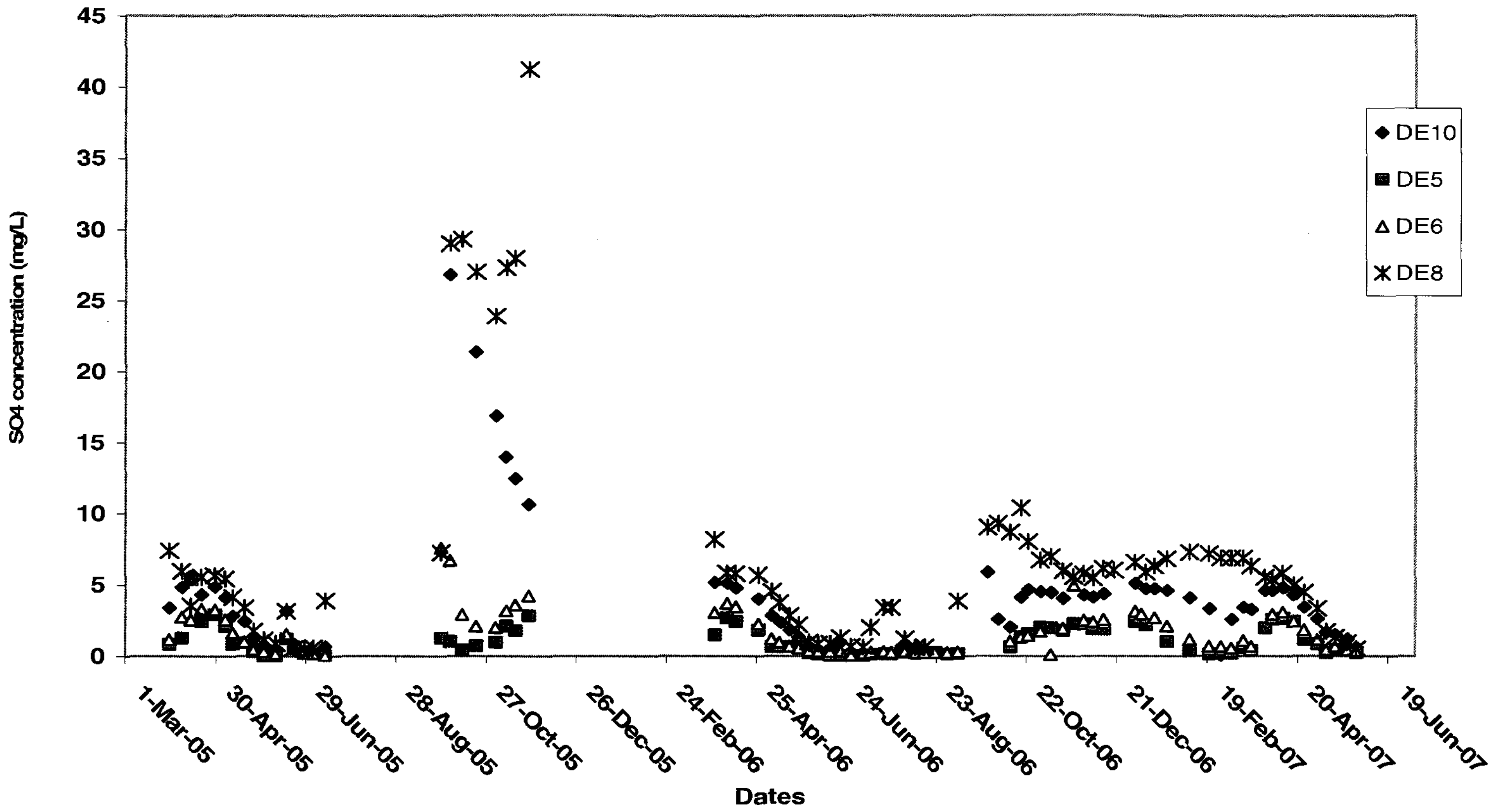

Figure 3.16: Temporal trends in Sulfate (mg/L) for Dickie streams (DE10, DE5, DE6 and DE8) from March 2005 to May 2007

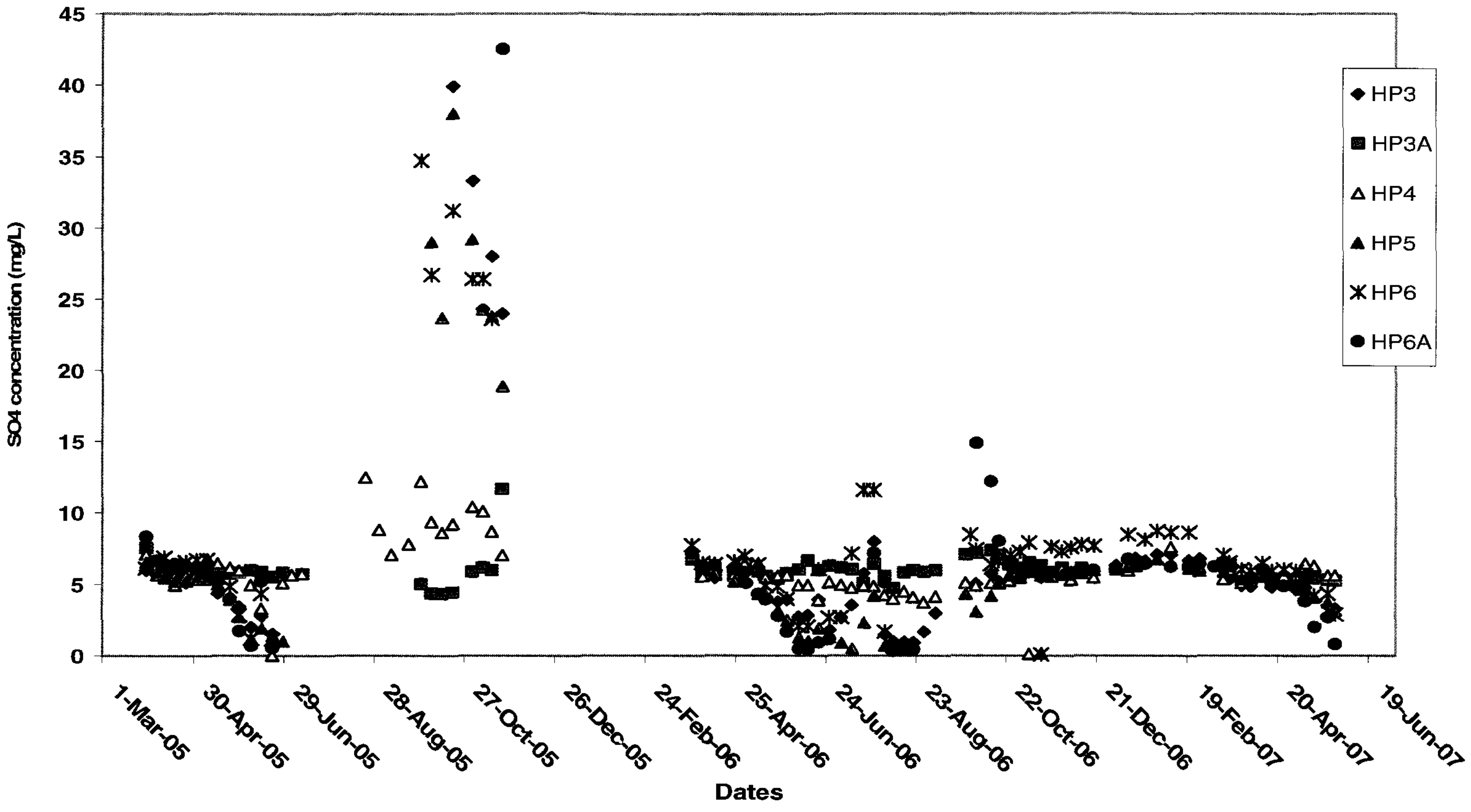

Figure 3.17: Temporal trends in Sulfate (mg/L) for Harp streams (HP3, HP3A, HP4, HP5, HP6 and HP6A) from March 2005 to May 2007. One data point was omitted for HP5: September 28th, 2005 (80 mg/L).

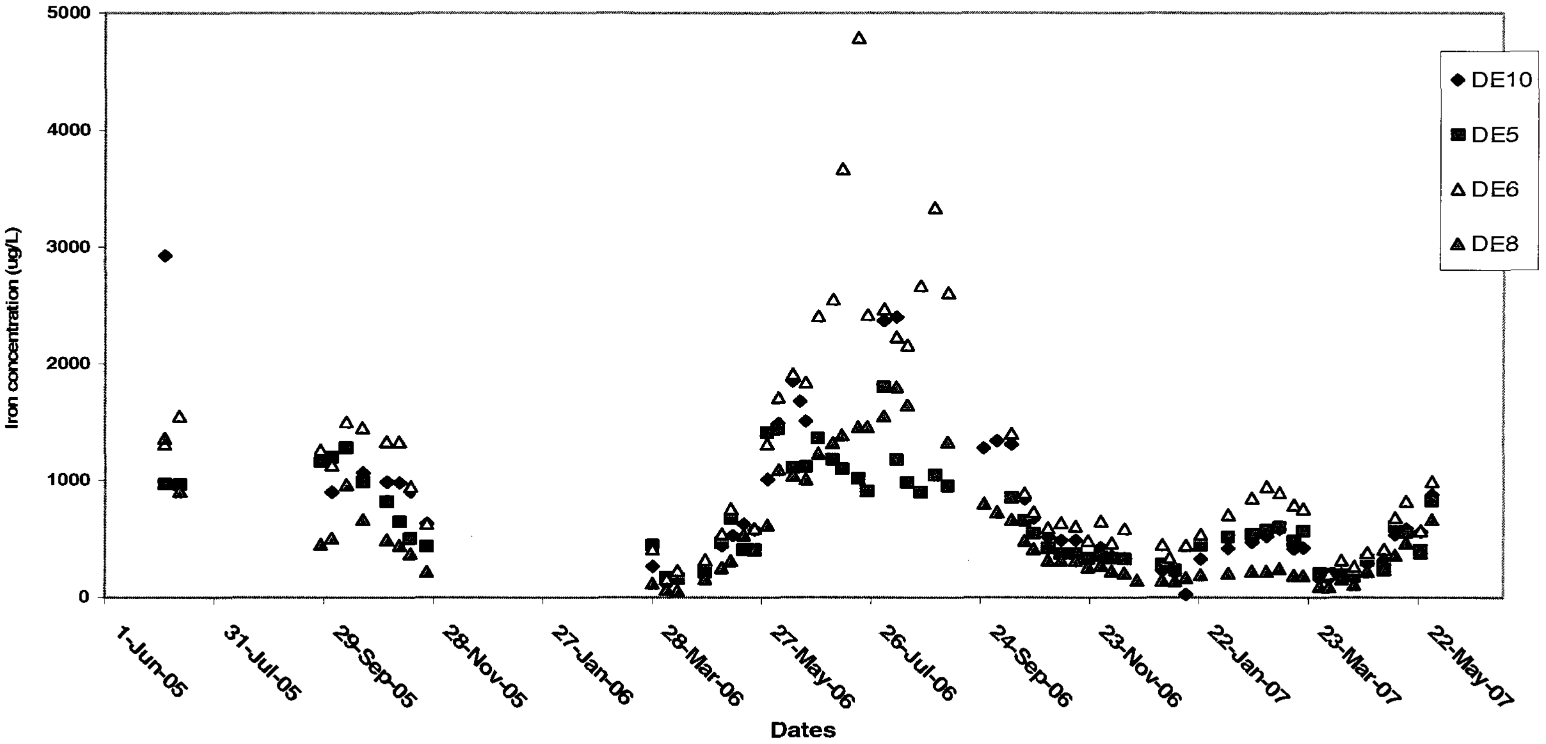

Figure 3.18: Temporal trends in Iron (μg/L) for Dickie streams (DE10, DE5, DE6 and DE8) from June 2005 to May 2007. One data point was omitted for DE10: July 12th, 2005 (5620 μg/L).

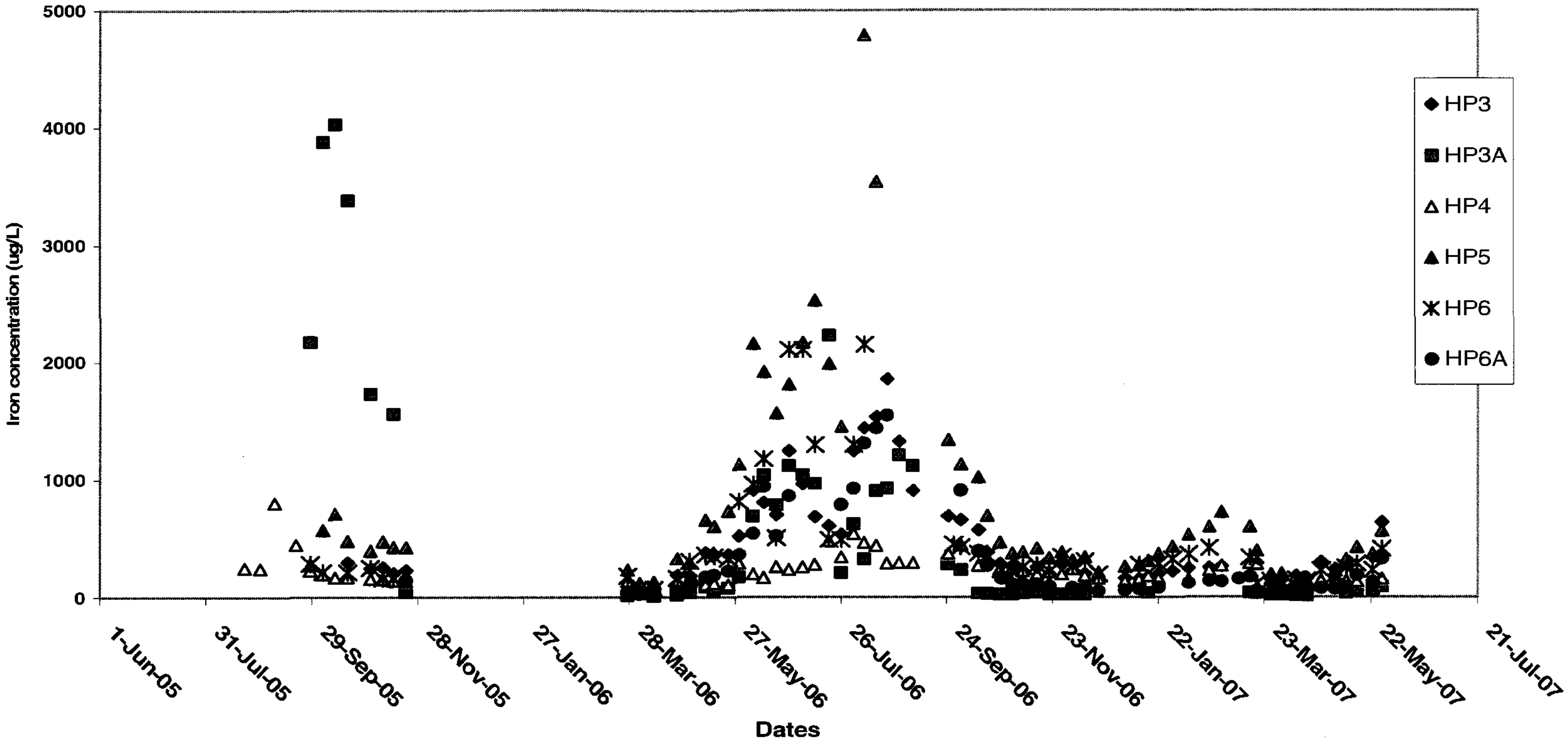

Figure 3.19: Temporal trends in Iron (μg/L) for Harp streams (HP3, HP3A, HP4, HP5, HP6 and HP6A) from June 2005 to May 2007

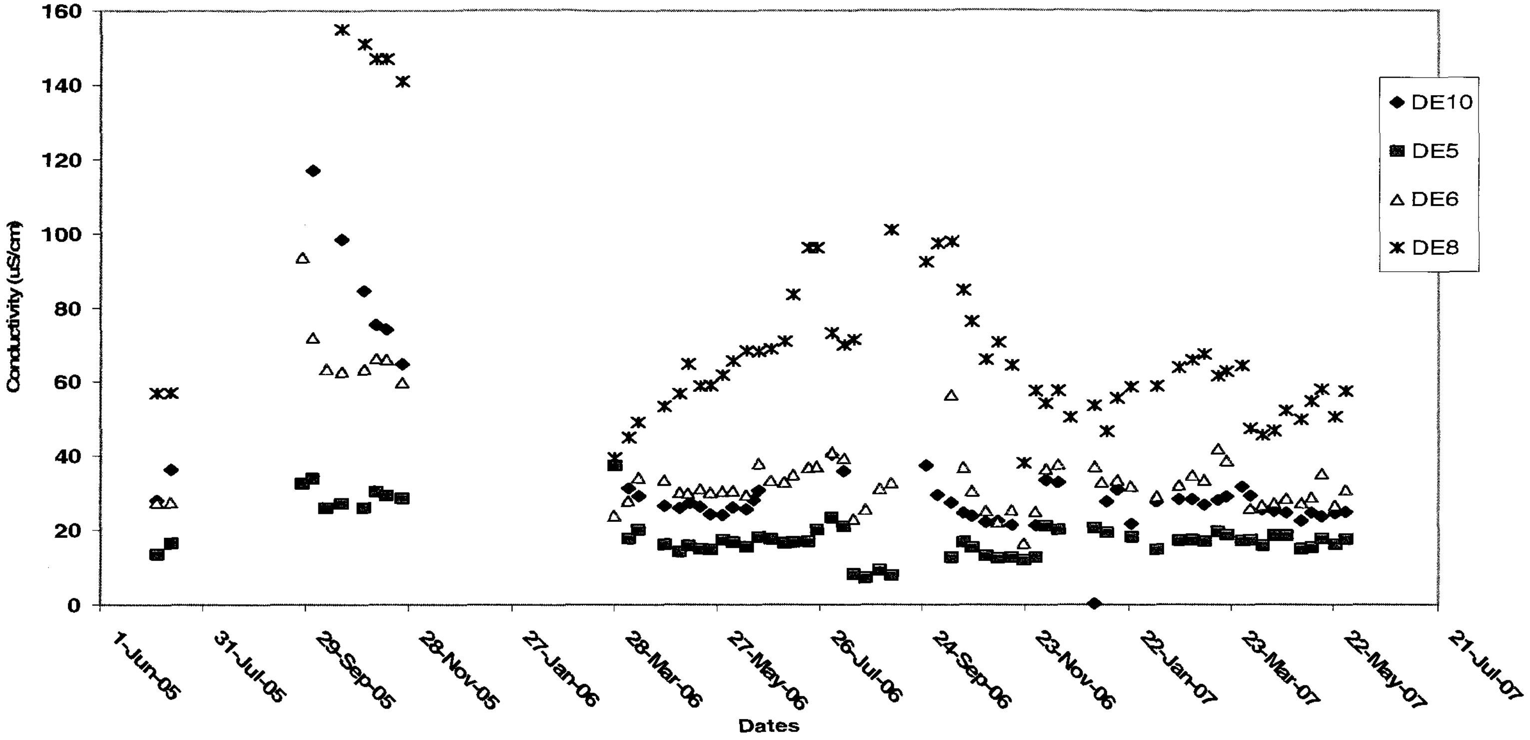

Figure 3.20: Temporal trends in Conductivity (µS/cm) for Dickie streams (DE10, DE5, DE6 and DE8) from June 2005 to May 2007.

One data point was omitted for DE8: October 3rd, 2005 (194 µs/cm)

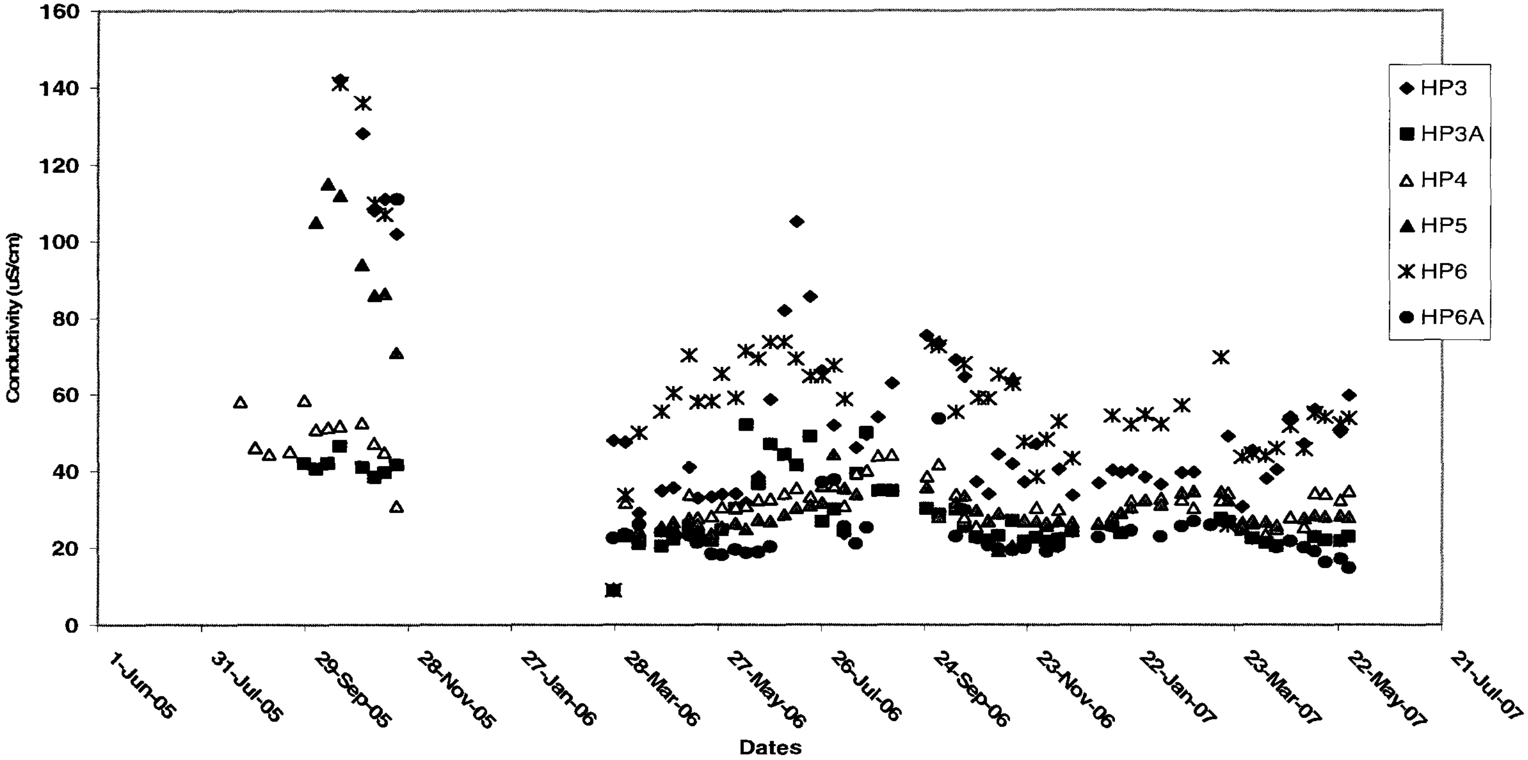

Figure 3.21: Temporal trends in Conductivity (μS/cm) for Harp streams (HP3, HP3A, HP4, HP5, HP6 and HP6A) from June 2005 to May 2007

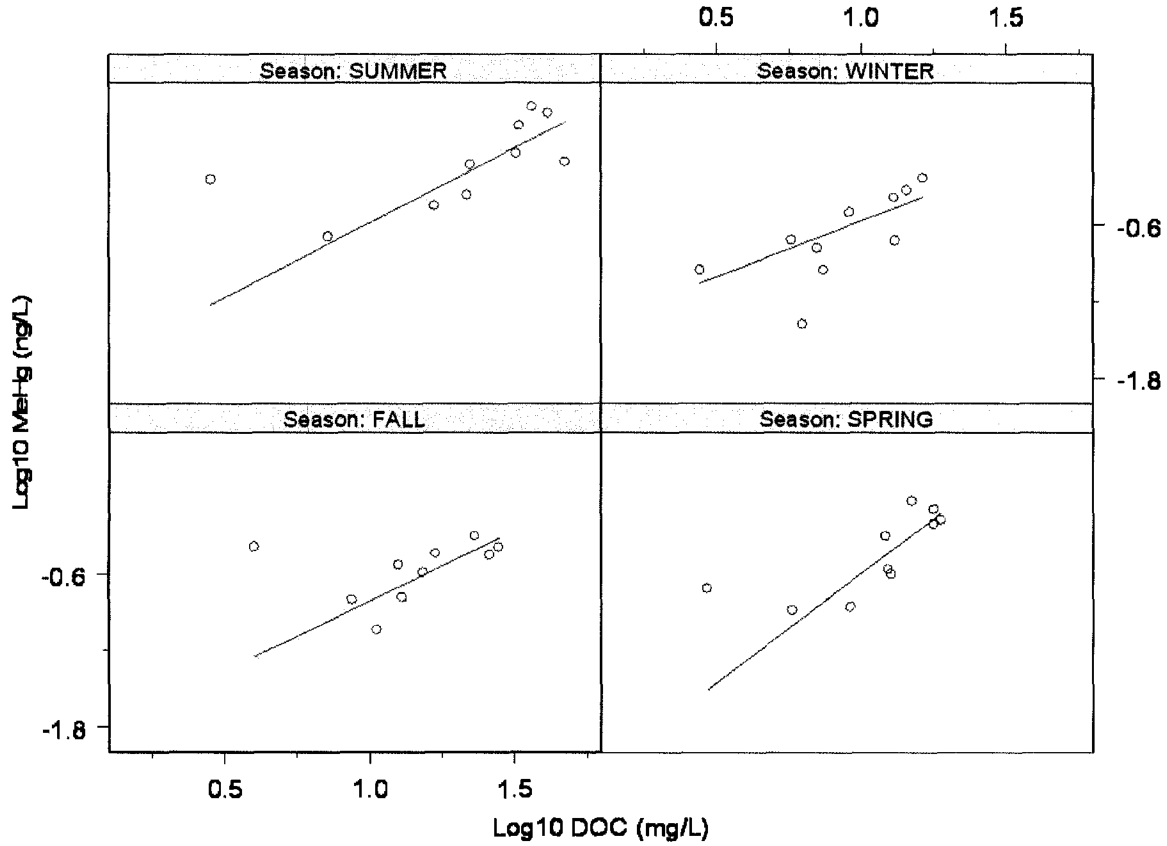

Figure 3.22: Seasonal variations in Log_{10} MeHg concentration (ng/L) as a function of Log_{10} DOC (mg/L) in Dickie and Harp streams sampled between May 2006 and May 2007; Summer (r^2 =0.38 , n=10), Fall (r^2 =0.24 , n=10), Winter (r^2 =0.48 , n=10), and Spring. (r^2 =0.47, n=10). Linear regressions are non-parametric (Robust MM regressions). Each point represents a mean value for each stream in a given season.

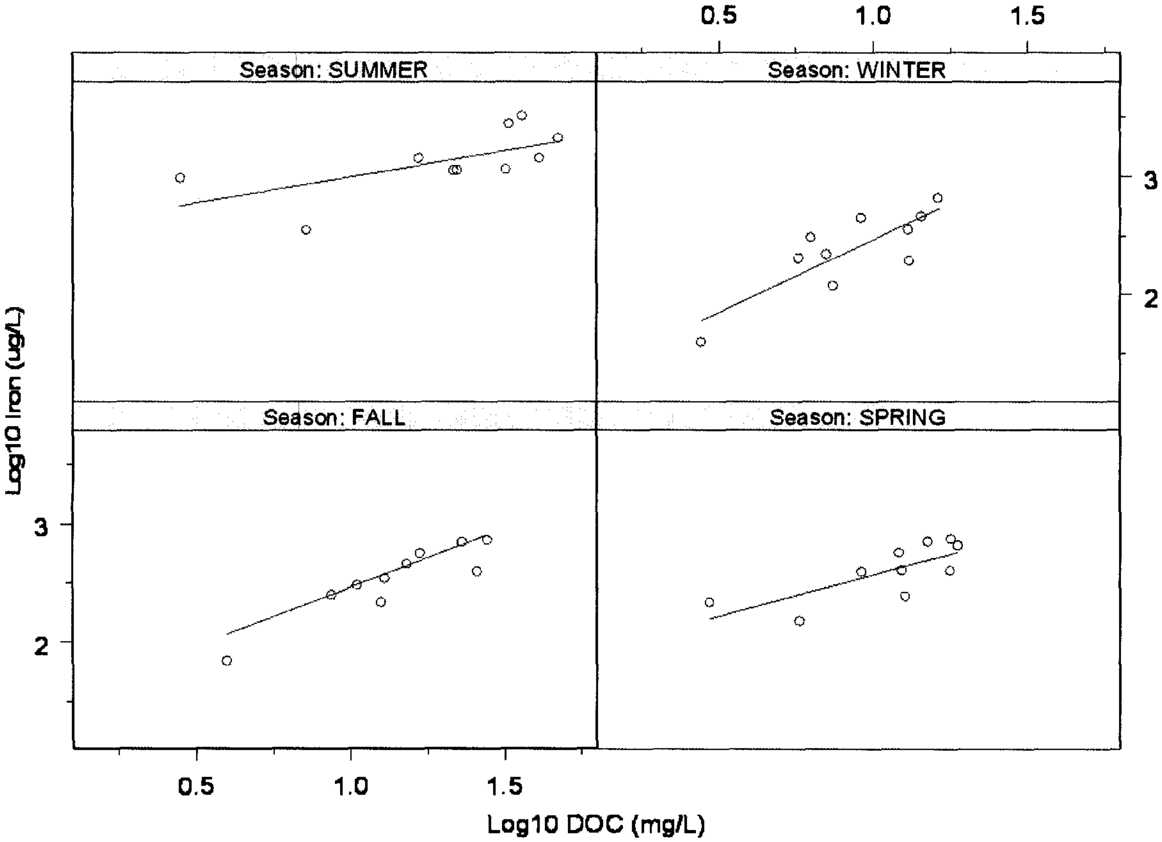

Figure 3.23: Seasonal variations in Log_{10} Iron (μg/L)) as a function of Log_{10} DOC (mg/L) in Dickie and Harp streams sampled between May 2006 and May 2007; Summer (r^2 = 0.19, n=10), Fall (r^2 = 0.91, n=10), Winter (r^2 = 0.48, n=10), and Spring. (r^2 = 0.48, n=10). Linear regressions are non-parametric (Robust MM regressions). Each point represents a mean value for each stream in a given season.

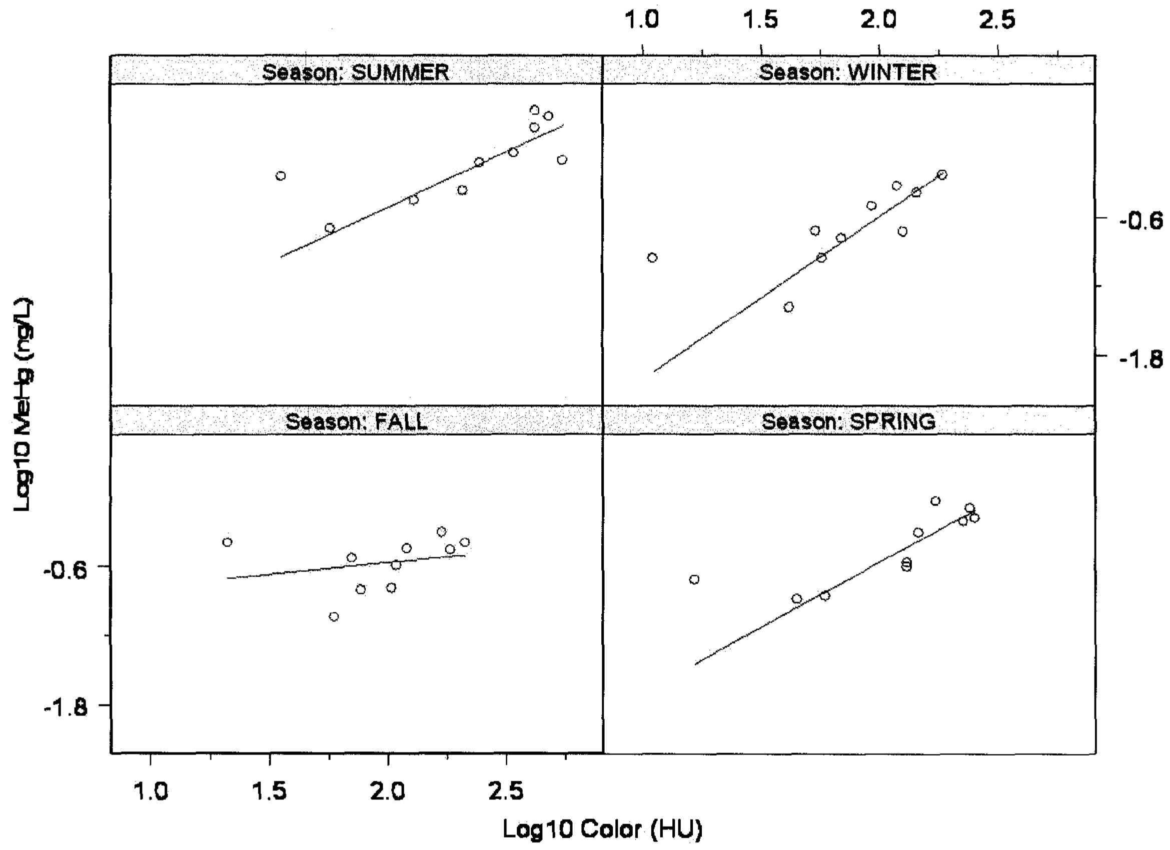

Figure 3.24: Seasonal variations in Log_{10} MeHg concentration (ng/L) as a function of Log_{10} Color (HU) in Dickie and Harp streams sampled between May 2006 and May 2007; Summer ($r^2 = 0.49$, n=10), Fall ($r^2 = 0.2$, n=10), Winter ($r^2 = 0.39$, n=10), and Spring. ($r^2 = 0.6$, n=10). Linear regressions are non-parametric (Robust MM regressions). Each point represents a mean value for each stream in a given season.

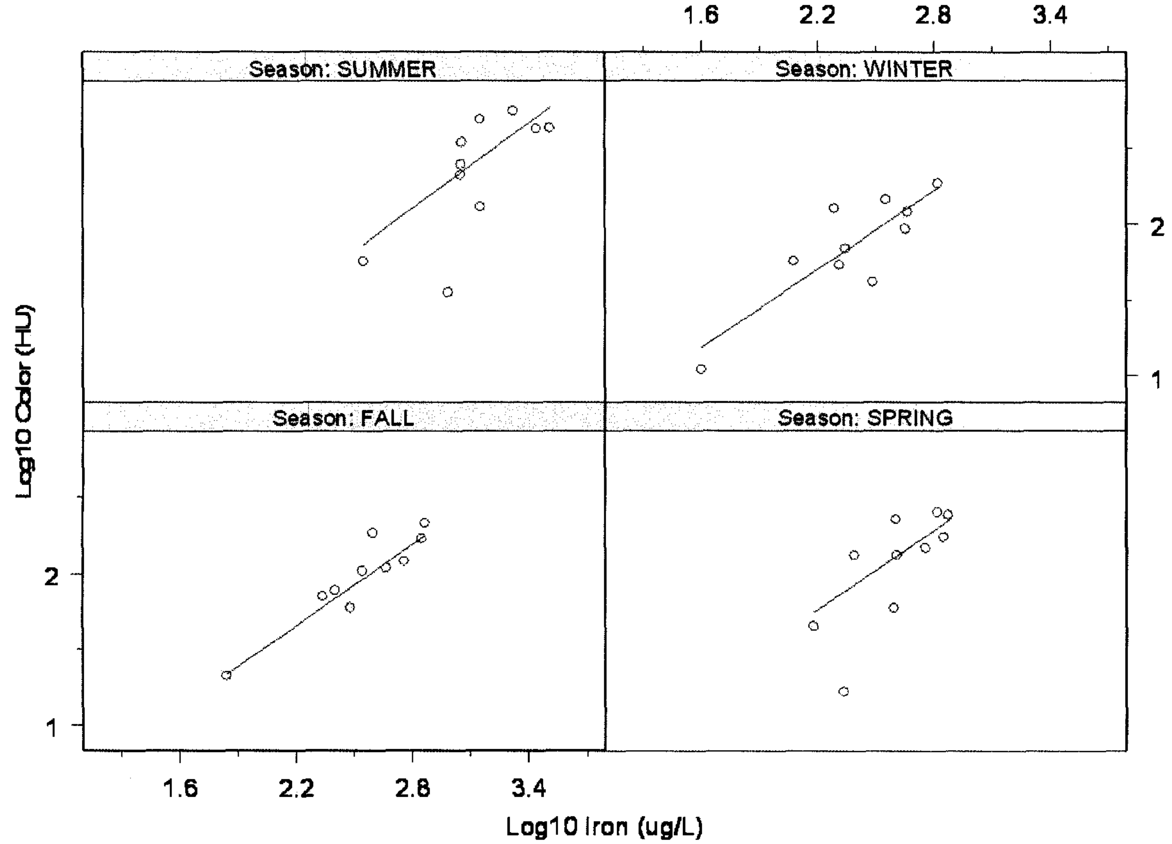

Figure 3.25: Seasonal variations in Log_{10} Color (HU) as a function of Log_{10} Iron (μg/L) in Dickie and Harp streams sampled between May 2006 and May 2007; Summer (r^2 = 0.4, n=10), Fall (r^2 = 0.66, n=10), Winter (r^2 = 0.49, n=10), and Spring. (r^2 = 0.38, n=10). Linear regressions are non-parametric (Robust MM regressions). Each point represents a mean value for each stream in a given season.

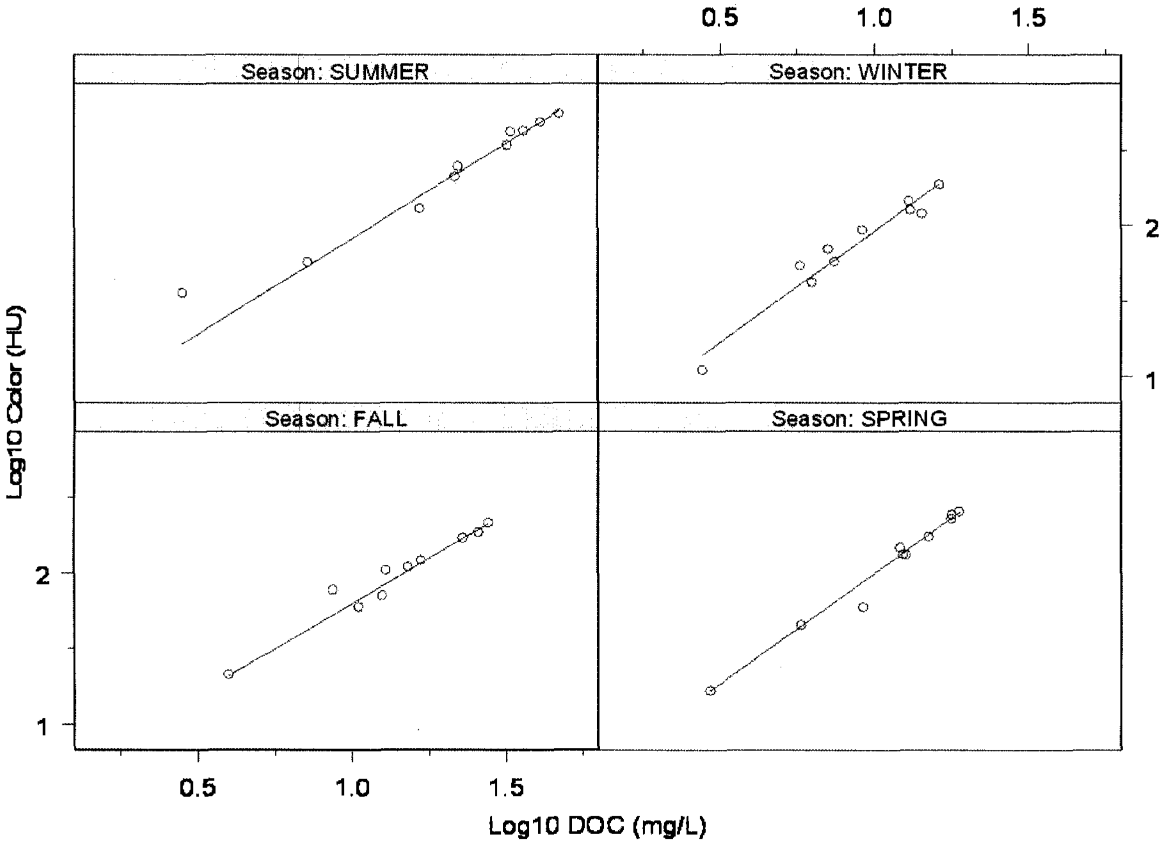

Figure 3.26: Seasonal variations in Log_{10} Color (HU) as a function of Log_{10}DOC (mg/L) in Dickie and Harp streams sampled between May 2006 and May 2007; Summer (r^2 = 0.68, n=10), Fall (r^2 = 0.72, n=10), Winter (r^2 = 0.79, n=10), and Spring. (r^2 = 0.76, n=10). Linear regressions are non-parametric (Robust MM regressions). Each point represents a mean value for each stream in a given season.

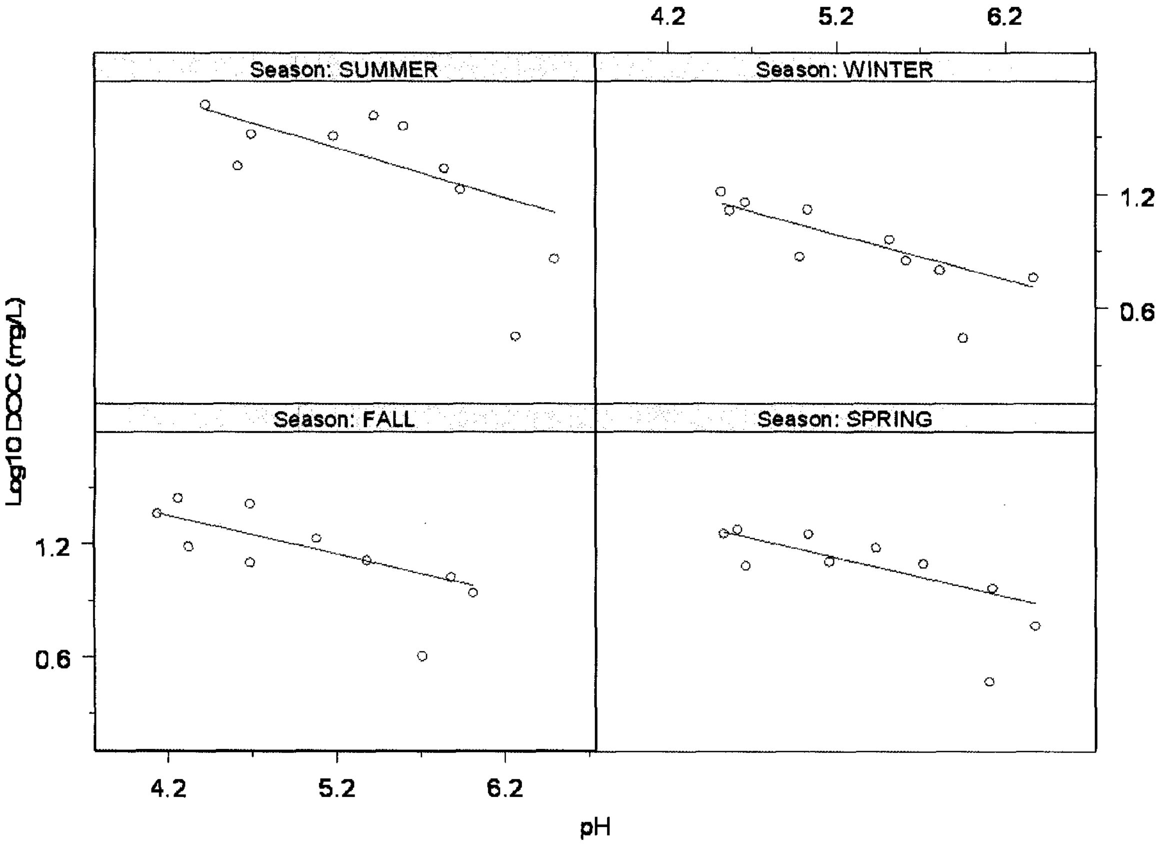

Figure 3.27: Seasonal variations in Log$_{10}$ DOC (mg/L) as a function of pH in Dickie and Harp streams sampled between May 2006 and May 2007; Summer ($r^2 = 0.3$, n=10), Fall ($r^2 = 0.47$, n=10), Winter ($r^2 = 0.6$, n=10), and Spring. ($r^2 = 0.39$, n=10). Linear regressions are non-parametric (Robust MM regressions). Each point represents a mean value for each stream in a given season

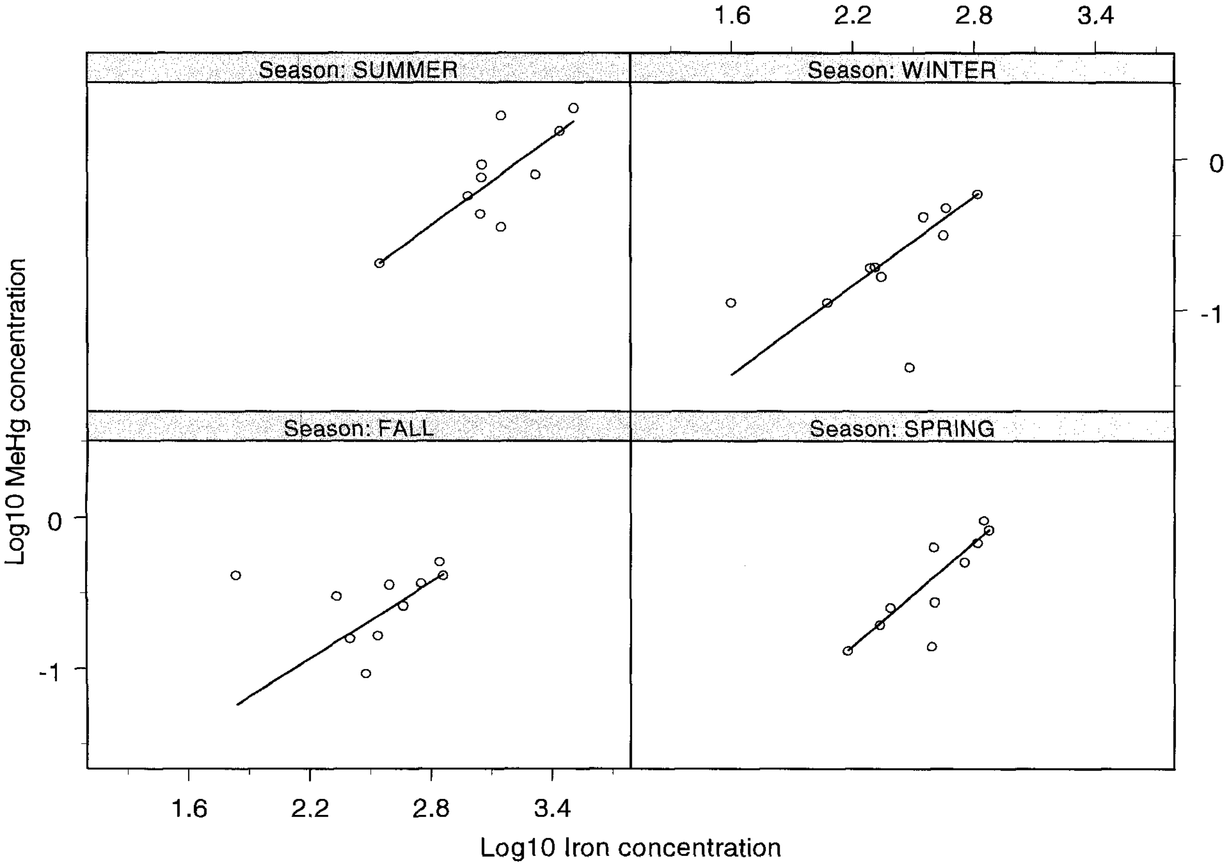

Figure 3.28: Seasonal variations in Log10 MeHg (ng/L) as a function of Log10 TFe (µg/L)in Dickie and Harp streams sampled between May 2006 and May 2007; Summer (r2 = 0.56, n=10), Fall (r2 = -0.01, n=10), Winter (r2 = 0.57, n=10) and Spring (r2 = 0.63, n=10). Linear regressions are non-parametric (Robust MM regressions). Each point represents a mean value for each stream in a given season.

4. CHAPTER 4: DISCUSSION

4.1. MeHg, Seasons and Wetlands

Overall, the general pattern in MeHg for Harp and Dickie streams was as follows: there was a steady increase in MeHg concentrations from mid-March (Spring) to June-July (Summer), where the highest MeHg are recorded for all streams (Fig.3.5 and 3.6). MeHg concentrations then fell steadily throughout the July-September period and there was a flat of constant MeHg concentrations during the late-Fall and Winter seasons. Mean MeHg concentrations in Dickie streams ranged from 0.5 ng/L to 0.8 ng/L in the Spring, while Summer means ranged from 0.8 ng/L to 1.92 ng/L (from May 2006 to May 2007) (Fig. 3.5). Harp streams also had Spring and Summer MeHg concentrations that were two-fold higher than fall and winter values, however the spring and summer values were considerably lower compared to those for Dickie streams (Fig. 3.6). This is with the exception of HP5, a high-colored stream, which had its seasonal MeHg concentrations within the range of Dickie stream concentrations across all four seasons (Fig. 3.6). It therefore follows that high colored streams typically have higher MeHg concentrations than low colored streams (Mierle and Ingram, 1991).

However, MeHg Load is more important than MeHg concentration in relation to annual stream MeHg Yield, where MeHg load (L/s) is the product of MeHg concentration and stream flow. Mean stream discharge was the lowest during the summer (0.2 L/s to 3.15 L/s), followed by Winter (0.8 L/s to 24.6 L/s), Fall (1.8 L/s to 58.9 L/s) and Spring (2.7 L/s to 46.5 L/s) (Fig. 3.7 and 3.8). Likewise, results show MeHg Load was highest in Spring and Fall seasons, while MeHg Load was lower during the summer when most streams were dry or during the winter when the streams were frozen (Fig. 3.9

and 3.10). This depicts the importance of the dilution effect by stream flow to the MeHg export to the watershed in ice-free seasons (Schiff et al., 1998; Waiser, 2006). The spring freshet releases the snow-bound MeHg and DOC during melting, which leads to spring's characteristic elevated MeHg concentrations and load, respectively (Loseto et al., 2004). Results here show there is a 3-fold increase in MeHg concentration and Load with snow melt in spring. For instance, elevated stream flow in HP5 in Spring resulted in a substantial increase in mean MeHg Load from 5.9 ng/s in the Winter to 15.7 ng/s in the Spring (Fig. 3.10). The importance of annual stream discharge in the MeHg export from the watershed is expressed in a modest increase in regression model fit from 25% to 33% when discharge was included in the midst of watershed characteristics climatic factors as parameters (Shanley et al., 2005).

The regression results revealed a strong positive relationship between the log10 MeHg concentration and %Wetland (Figure 3.3). Spring concentrations in Dickie streams were actually twice as values in Winsconsin temperate wetland-forest ecosystems (Hurley et al., 1995) while Summer concentrations were found to be similar to high values reported in similar studies in Minnesota watersheds (Balogh et al, 2003; 2005). For wetland-dominated streams and lakes that dry out during the summer, water loss by evaporation in the wetland increases MeHg concentration as the water is lost (Waiser, 2006). This dry/wet cycle in the wetland enhanced the release of bound mercury, thus more bioavailable Hg2+ for methylation to the streams than permanently flooded wetland would (Snodgrass et al., 2002; Warner et al., 2005).

It is then possible to conclude that MeHg Yield, in mg/m^2/yr, is positively related to the proportion of wetland in the subcatchment, where streams with higher % wetland such as Dickie streams and HP5 had higher MeHg Load values and subsequent high MeHg Yield than low colored Harp streams (Fig. 3.2). Harp and Dickie streams have MeHg Yield ranging from 0.04 to 0.27μg/m^2/yr (Fig. 3.2, Method I). These MeHg Yield results are similar to annual results reported in Kejimkujik catchments with its MeHg yield ranging from 0.09 to 0.3μg/m^2/yr (Clair et al., 2005).

Climate and hydrology also greatly influence the chemical and biological weathering processes, hence the stream water chemical constitution, where high rainfall lead to the dilution of weathered by-products (Luider et al. 2006). The seasonal patterns of MeHg in Harp and Dickie streams in relation to hydrology are further investigated in Tamar Bodek's thesis study (2008, *submitted*). In summary, she concludes that high discharge rates during snowmelt in the Spring accounts for up to 33.9% of MeHg in the runoff to the lakes and that MeHg in snow deposition exits the snowpack with snowmelt, contrary to THg, which may be photoreduced or revolatilized (Lalonde et al., 2002).

4.2. MeHg, DOC, Color and Slope

MeHg forms complexes with dissolved organic matter (DOM) and DOC, which are transportation vectors for MeHg from the watershed to streams and lakes (Johansson and Iverfeldt 1994; Driscoll et al. 1995; Grigal 2002). Color and DOC are related in that color is mainly affected by iron content of fulvic and humic acids, while DOC encompasses all sources of carbon (including fulvic and humic acid); thus DOC and color are not equivalent (Mierle and Ingram, 1991). There is a strong relationship between DOC, MeHg and color, both spatial and temporal, as shown in the Analysis of

Covariance results and the regression plots, and this relationship shows the importance of humic substances in the mobilization of mercury (Vaidya et al, 2000).

Dickie streams and HP5 have MeHg and DOC concentrations in the higher range for all 4 seasons (Figures 3.5 and 3.12, respectively), while Harp streams fall within the lower range for MeHg and DOC concentrations (Figures 3.6 and 3.13, respectively); except for HP6 and HP6A, which have mean temporal DOC concentrations similar to brown-water streams. Conversely, HP6 has no wetland in its catchment, and mean temporal MeHg concentrations are the lowest across the 10 streams. Peckenham et al (2007) suggest that the quality and composition of DOC is more important than the DOC concentration in stream water, where the lower Hg/DOC ratio express lower Hg per unit DOC, thus inefficiency in transporting more Hg per unit DOC. In terms of seasonal variation, the summer and fall seasons, characterized by lower flushing rates, have the highest DOC concentrations (Mierle and Ingram, 1991; Schiff et al., 1998; Waiser, 2006).

Color has seasonal trends that are similar to the seasonal variations in MeHg concentration (Figure 3.14 and 3.15). The similarity between the seasonal patterns of color and MeHg are explained as DOC being transportation vector for MeHg, as well as covarying with color (Mierle and Ingram, 1991). Some of their findings, in terms of seasonality, were that optical density of DOC (HU per unit DOC) is lowest in the fall season due to the presence of non-colored new organic inputs, such as litterfall. It is suggested that the decomposition of this senescent vegetation is controlled by several other factors such as bacterial activity, water dissolved oxygen content, and stream pH.

Typically, watersheds with steep slopes are characterized by less %wetland and thinner organic soil horizons, thus obtaining a large groundwater contribution with its lower organic content (Rasmussen et al., 1989) Shallow slopes have waterlogged soils, thus, water from precipitation will flow along rather than through the organic horizon (Lee et al. 1998). There is a negative relationship between % slope of the sub-catchment and MeHg concentration in streams (Figure 3.4), where a decrease in slope enhances the wetland formation (impeded drainage), which is the one of the main sources of DOC (hence MeHg) to the stream surface water (Rasmussen et al., 1989). Overall, watersheds with low slopes have longer water residence time; where residence time is associated with the photochemical reactions of DOC and MeHg under UV and visible radiation (Rasmussen et al., 1989; Francko, 1990; Sellers et al., 2001).

4.3. MeHg, Iron, pH and SO_4

Iron is a metal present in the aquatic system through the weathering of parent bedrock such as granite and greywacke, both of which are present on the Canadian Shield bedrock (Vaidya et al., 2002). Results show that Fe has similar spatial and temporal pattern as MeHg, with very strong relationships with DOC ($r^2 = 0.75$), color ($r^2 = 0.89$) and MeHg ($r^2 = 0.83$) (all p's < 0.002, Table 3.3), and varies across seasons, with Dickie streams exhibiting higher Fe values across the year than Harp stream, except for HP5 (Figures 3.18 and 3.19, respectively). There is also a good correlation (r2 > 0.50) between TFe and MeHg across the four seasons, except in the Fall (Fig. 3.28). These results are corroborated in a study by Dillon and Molot (1997), where Fe export pooled over 20 stream catchments was weakly correlated to DOC and color export ($r^2 = 0.65$) and %

wetland ($r^2 = 0.53$), suggesting that Fe export is dependent upon the export of organic material from wetlands. Dickie streams and HP5 are thus characterized with elevated DOC and Fe concentrations, while the rest of Harp streams have concentrations at the other end of the spectrum. Vaidya et al (2002) explain the Fe pattern suggesting that the weathering, hydrological and geochemical processes that control iron could also directly control MeHg concentrations, explaining the covariability between the two metals. TFe also directly contributes to color (water transparency), which is influenced by the photo-reduction of Fe3+ to Fe2+ when exposed to UV and visible rays. The iron reduction catalyzes the photo oxidation of colored-DOM in freshwater systems with high DOC, reducing UV and visible absorbance, thus explaining iron's strong relationship with DOC and color (Gao and Zepp, 1998).

Again, similar to MeHg, TFe are affected by pH and alkalinity, where a decrease in pH leads to a decrease in metal-DOM/DOC complexes with either TFe or MeHg, due to proton competition for available bonding sites (Haitzer et al., 2003). Low pH enables the mobilizations of sediment-bound metals and increases their bioavailability to biota (Luider et al., 2006). Brown-water streams (Dickie streams and HP5) exhibit slightly lower pH values and SO_4 concentrations than clear water streams (HP3, HP3A, HP4, HP6 and HP6A) (Figure 3.11). Generally, low pH lakes have high fulvic and humic acid content, which themselves contribute to the free acidity by dissociation of the functional acid group (Meili et al., 1991; Vaidya et al., 2002, Vaidya et al., 2004), which explains the combination of elevated DOC concentration, high MeHg concentration and low pH in streams Dickie streams and HP5. Usually, acidic water systems such as Dickie streams that are situated in shallow soil have a long residence time, which favors the export of recently deposited mercury from the soil (Meili et al., 1991).

Lastly, the granite bedrock weathering particular to the Canadian Shield affects the alkalinity of the water systems, keeping the average alkalinity low in a range -1.87 to 1.45 and a low average pH ranging from 4.3 to 5.9, which are conditions favorable for lower sedimentation rates and hence removal of mercury from the soils and sediments (Vaidya et al., 2002a). pH results for Harp and Dickie streams show that DE10, DE5 and DE6 neatly fall within that range through out the year, while DE8 and HP5 have pH values that vary between 4.5 and 6, and the other Harp streams have pH typically above 5.5 throughout the year (Figure 3.11).

4.4. Conductivity

Since conductivity is largely due to calcium carbonate (relating to alkalinity), it not surprising that in poorly buffered systems to find conductivity and pH negatively correlated ($r^2 = -0.34$, $p < 0.002$, Table 3.3). Luider at al. (2006) used the biogeoclimatic ecosystem classification (BEC) to observe the trends of difference water quality variables through out British Columbia and found that drier regions had high conductivity and elevated DOC concentrations. These finding are reflected in streams such as DE8 with the highest annual DOC concentration (24.2 mg/L, Figure 3.12) and annual conductivity values (65.3 μS/cm, Figure 3.20).

5. CHAPTER 5: CONCLUSIONS

In this study, it was found that the highest MeHg concentrations across all four seasons between May 2006 and May 2007 were recorded in the 4 Dickie streams and HP5, however, all 10 streams studied followed similar temporal trends for MeHg concentrations, with steady increases in Spring, peak values in Summer, steady fall in concentrations in the Fall and constant MeHg concentrations during the Winter. When seasonal means were compared for all 10 streams, Summer concentrations were the highest with values exceeding 0.9 ng/L. In contrast, Summer MeHg Load (L/s) were the lowest while Spring MeHg Load were the highest, depicting the importance of stream discharge in the dilution of stream MeHg concentrations. In general, brown-water streams that have high MeHg Load also have high annual MeHg Yields.

Results also showed that factors such as DOC, TFe and color followed similar temporal and spatial trends as MeHg concentrations and it was concluded that DOC, TFe, color and MeHg were interrelated (covariables). Both TFe and MeHg bind to DOC, which acts as a transport vector from the catchment to the streams. Color is caused by the presence of fulvic and humic acids (DOC components) and its intensity is influenced by the photo-reduction of Fe3+ to Fe2+ when exposed to UV and visible rays.

The proportion of wetland and the slope of the subcatchment also played an important role in the annual MeHg Yield of the 10 streams, where streams with high % wetland and shallow slopes had higher annual MeHg concentrations. Wetlands are waterlogged soils that usually have low oxygen content, low pH and high DOC concentrations, and these conditions favor the methylation and transport of mercury to the streams. The formation of wetland is negatively related to % slope, where shallow slopes have more wetlands (longer water residence time)

Overall, the highest MeHg Yield was found in brown water streams, such as Dickie streams and HP5, that have high DOC and TFe concentrations, low pH and that are located in subcatchments with shallow slopes and high % wetland. Slope, as the only factor independent of the others, was considered the main driving factor for the export of MeHg from the watershed.

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APPENDIX

APPENDIX A

Table A: One-Way Analysis of Variance (ANOVA)

Table A.1: Parametric One-Way ANOVA for Methylmercury (MeHg) concentration

Source of Variation	*Sum of Squares*	*Df*	*Mean Square*	*F*
Seasons	24.1	3	8.0	<0.005
Residuals	92.7	480	0.2	

Where KS = 0.03, p=0.5

Source of Variation	*Sum of Squares*	*Df*	*Mean Square*	*F*
Stations	43.2	9	4.8	<0.005
Residuals	73.7	474	0.2	

Where KS = 0.03, p=0.5

*KS is the Kolmogorov-Smirnov Test of Normality on ANOVA residuals

Table A.2: Kruskal-Wallis One-Way ANOVA

Variables		***Chi-Square****	***Df***	***p***
TFe	Seasons	138.1	3	<0.005
	Stations	127.4	9	<0.005
pH	Seasons	19.3	3	<0.005
	Stations	380.6	9	<0.005
Conductivity	Seasons	18.5	3	<0.005
	Stations	349.1	9	<0.005
DOC	Seasons	54.6	3	<0.005
	Stations	234.3	9	<0.005
Color	Seasons	47.2	3	<0.005
	Stations	249	9	<0.005
Load	Seasons	43.8	3	<0.005
	Stations	294	9	<0.005
SO_4	Seasons	99.7	3	<0.005
	Stations	214.2	9	<0.005

*Kruskal-Wallis Chi-Square

APPENDIX B

Table B: Test of Homogeneity of Slopes (Analysis of Covariance, ANCOVA)

Table B.1: Methylmercury (MeHg) concentration

Source of Variability	*Df*	*F*	*p*
Log_{10} SO_4	1	251	<0.005
Seasons	3	9.4	<0.001
Log_{10} SO_4 * Seasons	3	23.7	<0.005
Residuals	476		

Source of Variability	*Df*	*F*	*p*
pH	1	172	<0.005
Seasons	3	13.3	<0.001
pH * Seasons	3	2.3	0.076
Residuals	476		

Source of Variability	*Df*	*F*	*p*
Log_{10} Load	1	82.5	<0.005
Seasons	3	30	<0.005
Log_{10} Load * Seasons	3	2.2	0.088
Residuals	476		

Source of Variability	*Df*	*F*	*p*
Log_{10} DOC	1	299	0
Seasons	3	24	<0.001
Log_{10} DOC * Seasons	3	17.5	<0.001
Residuals	476		

Source of Variability	*Df*	*F*	*p*
Log_{10} Color	1	329	<0.005
Seasons	3	18.7	<0.001
Log_{10} Color * Seasons	3	14.7	<0.001
Residuals	476		

Source of Variability	*Df*	*F*	*p*
Log_{10} TFe	1	406	<0.005
Seasons	3	4.1	0.006
Log_{10} TFe * Seasons	3	9.2	<0.001
Residuals	476		

Source of Variability	*Df*	*F*	*p*
Log_{10} Conductivity	1	3.5	0.06
Seasons	3	11.8	<0.001
Log_{10} Conductivity * Seasons	3	1	0.4
Residuals	476		

Table B: Test of Homogeneity of Slopes (Analysis of Covariance, ANCOVA) (Continued)

Table B.2: Color

Source of Variability	*Df*	*F*	*p*
Log_{10} SO_4	1	110	<0.005
Seasons	3	6.2	<0.001
Log_{10} SO_4 * Seasons	3	23.3	<0.005
Residuals	476		

Source of Variability	*Df*	*F*	*p*
Log_{10} DOC	1	2565	<0.005
Seasons	3	0.8	0.5
Log_{10} DOC * Seasons	3	12	<0.001
Residuals	476		

Source of Variability	*Df*	*F*	*p*
pH	1	95	<0.005
Seasons	3	10	<0.001
pH * Seasons	3	6.6	<0.001
Residuals	476		

Source of Variability	*Df*	*F*	*p*
Log_{10} TFe	1	486	<0.005
Seasons	3	10	<0.001
Log_{10} TFe * Seasons	3	7.5	<0.001
Residuals	476		

Table B: Test of Homogeneity of Slopes (Analysis of Covariance, ANCOVA) (Continued)

Table B.3: Total Iron (TFe) Concentrations

Source of Variability	*Df*	*F*	*p*
$\text{Log}_{10}\,\text{SO}_4$	1	98.2	<0.005
Seasons	3	6.5	<0.001
$\text{Log}_{10}\,\text{SO}_4$ * Seasons	3	23.6	<0.005
Residuals	476		

Source of Variability	*Df*	*F*	*p*
Log_{10} Load	1	15.7	<0.001
Seasons	3	41.8	<0.005
Log_{10} Load * Seasons	3	5.2	0.002
Residuals	476		

Source of Variability	*Df*	*F*	*p*
pH	1	28.7	<0.001
Seasons	3	16	<0.001
pH * Seasons	3	7.9	<0.001
Residuals	476		

Source of Variability	*Df*	*F*	*p*
Log_{10} DOC	1	571	<0.005
Seasons	3	44.4	<0.005
Log_{10} DOC * Seasons	3	11.7	<0.001
Residuals	476		

Source of Variability	*Df*	*F*	*p*
Log_{10} Conductivity	1	19.6	<0.001
Seasons	3	15.9	<0.005
Log_{10} Conductivity * Seasons	3	0.8	0.5
Residuals	476		

Table B: Test of Homogeneity of Slopes (Analysis of Covariance, ANCOVA) (Continued)

Table B.4: Dissolved organic carbon (DOC) concentration

Source of Variability	*Df*	*F*	*p*
$\text{Log}_{10}\,\text{SO}_4$	1	79.6	<0.005
Seasons	3	1.7	0.16
$\text{Log}_{10}\,\text{SO}_4$ * Seasons	3	15.8	<0.005
Residuals	476		

Source of Variability	*Df*	*F*	*p*
pH	1	101	<0.005
Seasons	3	5.3	0.001
pH * Seasons	3	5	0.002
Residuals	476		

Source of Variability	*Df*	*F*	*p*
Log_{10} Load	1	52	<0.005
Seasons	3	10.3	<0.001
Log_{10} Load * Seasons	3	1.6	0.18
Residuals	476		

Source of Variability	*Df*	*F*	*p*
Log_{10} Conductivity	1	15.6	<0.001
Seasons	3	2.7	0.04
Log_{10} Conductivity * Seasons	3	0.7	0.55
Residuals	476		

Table B: Test of Homogeneity of Slopes (Analysis of Covariance, ANCOVA) (Continued)

Table B.5: pH

Source of Variability	*Df*	*F*	*p*
Log_{10} SO_4	1	321	<0.005
Seasons	3	10.9	<0.001
Log_{10} SO_4 * Seasons	3	4.7	0.002
Residuals	476		

Table 6F: Methylmercury (MeHg) Load

Source of Variability	*Df*	*F*	*p*
Log_{10} DOC	1	51.2	<0.005
Seasons	3	4.5	0.004
Log_{10} DOC * Seasons	3	1.5	0.22
Residuals	476		

APPENDIX C

Table C: Equality of Intercepts (Analysis of Covariance, ANCOVA)

Table C.1: Iron (TFe) Concentration

Source of Variability	*Df*	*F*	*p*
Log_{10} Conductivity	1	17.7	<0.001
Seasons	3	64.5	<0.005
Residuals	479		

Table C.3: DOC

Source of Variability	*Df*	*F*	*p*
Log_{10} Conductivity	1	14.7	<0.001
Seasons	3	13	<0.001
Residuals	479		

Table C.5: MeHg

Source of Variability	*Df*	*F*	*p*
Log_{10} Conductivity	1	2.8	0.1
Seasons	3	43.6	<0.005
Residuals	479		

Table C.6: MeHg

Source of Variability	*Df*	*F*	*p*
Log_{10} Load	1	80.6	<0.005
Seasons	3	64.3	<0.005
Residuals	479		

Table C.2: Iron (TFe) Concentration

Source of Variability	*Df*	*F*	*p*
pH	1	36.2	<0.001
Seasons	3	93.1	<0.005
Residuals	479		

Table C.4: MeHg

Source of Variability	*Df*	*F*	*p*
pH	1	183	<0.005
Seasons	3	88.1	<0.005
Residuals	479		

Table C.5: MeHg

Source of Variability	*Df*	*F*	*p*
Log_{10} TFe	1	545	<0.005
Seasons	3	12.5	<0.001
Residuals	479		

Table C.7: Load

Source of Variability	*Df*	*F*	*P*
Log_{10} DOC	1	49.4	<0.001
Seasons	3	17.2	<0.001
Residuals	479		

APPENDIX D

Table D: Seasonal Linear Regression Results (Robust MM Regressions). All pair-wise regressions are log10-transformed, except the regression of ph against SO_4.

Relationship	*Season*	*Equation*	r^2	*df*	*RSE**	*M-Estimate*
TFe vs. DOC	Winter	$1.23 + 1.23(\log_{10} DOC)$	0.48	8	0.22	0.85
	Spring	$1.87 + 0.7 (\log_{10} DOC)$	0.48	8	0.16	0.96
	Summer	$2.56 + 0.44 (\log_{10} DOC)$	0.19	8	0.20	0.75
	Fall	$1.48 + 0.99 (\log_{10} DOC)$	0.91	8	0.087	1.00
TFe vs. Load	Winter	$2.42 + 0.2 (\log_{10} Load)$	0.11	7	0.34	0.95
	Spring	$2.5 + 0.2 (\log_{10} Load)$	0.29	8	0.22	0.79
	Summer	$3.22 + 0.18 (\log_{10} Load)$	0.23	8	0.21	0.65
	Fall	$2.55 + 0.14 (\log_{10} Load)$	0.088	8	0.27	1.00
TFe vs. SO_4	Winter	$2.76 - 0.46 (\log_{10} SO_4)$	0.25	8	0.25	0.61
	Spring	$2.87 - 0.56 (\log_{10} SO_4)$	0.44	8	0.23	0.90
	Summer	$3.29 - 0.32 (\log_{10} SO_4)$	0.11	8	0.16	0.69
	Fall	$2.92 - 0.47 (\log_{10} SO_4)$	0.16	8	0.24	0.93
Color vs. DOC	Winter	$0.5 + 1.4 (\log_{10} DOC)$	0.79	8	0.095	0.66
	Spring	$0.54 + 1.46 (\log_{10} DO)$	0.76	8	0.027	0.69
	Summer	$0.64 + 1.26 (\log_{10} DOC)$	0.68	8	0.046	0.77
	Fall	$0.6 + 1.19 (\log_{10} DOC)$	0.72	8	0.056	0.77
Color vs. pH	Winter	$3.4 - 0.28 (pH)$	0.49	8	0.14	0.78
	Spring	$4.0 - 0.35 (pH)$	0.52	8	0.18	0.58
	Summer	$4.79 - 0.45 (pH)$	0.56	8	0.32	0.82
	Fall	$3.04 - 0.2 (pH)$	0.35	8	0.17	0.79
Color vs. TFe	Winter	$-0.19 + 0.86 (\log_{10} TFe)$	0.49	8	0.20	0.88
	Spring	$-0.14 + 0.86 (\log_{10} TFe)$	0.38	8	0.23	0.64
	Summer	$-0.51 + 0.93 (\log_{10} TFe)$	0.40	8	0.27	0.64
	Fall	$-0.31 + 0.89 (\log_{10} TFe)$	0.66	8	0.10	0.81
Color vs. SO_4	Winter	$2.22 - 0.43 (\log_{10} SO_4)$	0.23	8	0.25	0.92
	Spring	$2.38 - 0.57 (\log_{10} SO_4)$	0.20	8	0.29	0.79
	Summer	$2.42 - 0.45 (\log_{10} SO_4)$	0.34	8	0.36	0.68
	Fall	$2.24 - 0.28 (\log_{10} SO_4)$	0.054	8	0.26	0.91

* Residual Scale Estimate

Table D: (Continued)

Relationship	***Season***	***Equation***	r^2	***df***	***RSE****	***M-Estimate***
pH vs. SO_4*	Winter	$4.41 + 1.37 (\log_{10} SO_4)$	0.45	8	0.5^a	0.033^b
	Spring	$4.34 + 2.15 (\log_{10} SO_4)$	0.77	8	0.35^a	$<0.0001^b$
	Summer	$5.24 + 1.12 (\log_{10} SO_4)$	0.74	8	0.39^a	$<0.001^b$
	Fall	$3.84 + 1.76 (\log_{10} SO_4)$	0.32	8	0.61^a	0.09^b
DOC vs. Load	Winter	$0.91 + 0.15 (\log_{10} Load)$	0.24	7	0.24	0.78
	Spring	$1.08 + 0.12 (\log_{10} Load)$	0.21	8	0.12	0.76
	Summer	$1.49 + 0.21 (\log_{10} Load)$	0.30	8	0.15	1.00
	Fall	$1.14 + 0.13 (\log_{10} Load)$	0.10	8	0.21	0.55
DOC vs. SO_4	Winter	$1.22 – 0.38 (\log_{10} SO_4)$	0.34	8	0.17	0.95
	Spring	$1.24 – 0.3 (\log_{10} SO_4)$	0.15	8	0.18	0.49
	Summer	$1.42 – 0.20 (\log_{10} SO_4)$	0.10	8	0.27	0.56
	Fall	$1.39 – 0.37 (\log_{10} SO_4)$	0.099	8	0.27	1.00
DOC vs. pH	Winter	$2.22 – 0.23 (pH)$	0.60	8	0.091	0.71
	Spring	$2.19 – 0.20 (pH)$	0.39	8	0.11	0.61
	Summer	$2.82 – 0.26 (pH)$	0.30	8	0.24	0.52
	Fall	$2.22 – 0.21 (pH)$	0.47	8	0.14	0.68
MeHg vs. SO_4	Winter	$-0.16 – 0.82(\log_{10} SO_4)$	0.46	8	0.26	0.56
	Spring	$-0.083 – 0.75 (\log_{10} SO_4)$	0.42	8	0.28	0.60
	Summer	$-0.067 – 0.3 (\log_{10} SO_4)$	0.25	8	0.35	0.48
	Fall	$-0.37 – 0.29 (\log_{10} SO_4)$	0.066	8	0.23	0.48
MeHg vs. DOC	Winter	$-1.44 + 0.87 (\log_{10} DOC)$	0.48	8	0.17	0.89
	Spring	$-2.33 + 1.73 (\log_{10} DOC)$	0.47	8	0.24	0.67
	Summer	$-1.76 + 1.17 (\log_{10} DOC)$	0.38	8	0.24	1.00
	Fall	$-1.92 + 1.11 (\log_{10} DOC)$	0.24	8	0.18	0.45
MeHg vs. TFe	Winter	$-3.0 + 0.98 (\log_{10} TFe)$	0.57	8	0.12	0.22
	Spring	$-3.3 + 1.14 (\log_{10} TFe)$	0.63	8	0.12	0.003
	Summer	$-3.2 + 0.97 (\log_{10} TFe)$	0.56	8	0.20	0.003
	Fall	$-2.8 + 0.84 (\log_{10} TFe)$	-0.01	8	0.21	0.35
MeHg vs. Color	Winter	$-3.41 + 1.41 (\log_{10} Color)$	0.39	8	0.23	0.64
	Spring	$-2.83 + 1.13 (\log_{10} Color)$	0.60	8	0.16	0.65
	Summer	$-2.43 + 0.69 (\log_{10} Color)$	0.49	8	0.21	0.50
	Fall	$-2.61 + 0.98 (\log_{10} Color)$	0.20	8	0.19	0.47

* Residual Scale Estimate

** Parametric regressions applied.

[a] Residual Standard Error

[b] p-value