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Pollutant fate and spatio-temporal variability in the choptank river estuary: Factors influencing water quality

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ABSTRACT

Restoration of the Chesapeake Bay, the largest estuary in the United States, is a national priority. Documentation of progress of this restoration effort is needed. A study was conducted to examine water quality in the Choptank River estuary, a tributary of the Chesapeake Bay that since 1998 has been classified as impaired waters under the Federal Clean Water Act. Multiple water quality parameters (salinity, temperature, dissolved oxygen, chlorophyll *a*) and analyte concentrations (nutrients, herbicide and herbicide degradation products, arsenic, and copper) were measured at seven sampling stations in the Choptank River estuary. Samples were collected under base flow conditions in the basin on thirteen dates between March 2005 and April 2008. As commonly observed, results indicate that agriculture is a primary source of nitrate in the estuary and that both agriculture and wastewater treatment plants are important sources of phosphorus. Concentrations of copper in the lower estuary consistently exceeded both chronic and acute water quality criteria, possibly due to use of copper in antifouling boat paint. Concentrations of copper in the upstream watersheds were low, indicating that agriculture is not a significant source of copper loading to the estuary. Concentrations of herbicides (atrazine, simazine, and metolachlor) peaked during early-summer, indicating a rapid surface-transport delivery pathway from agricultural areas, while their degradation products (CIAT, CEAT, MESA, and MOA) appeared to be delivered via groundwater transport. Some in-river processing of CEAT occurred, whereas MESA was conservative. Observed concentrations of herbicide residues did not approach established levels of concern for aquatic organisms. Results of this study highlight the importance of continued implementation of best management practices to improve water quality in the estuary. This work provides a baseline against which to compare future changes in water quality and may be used to design future monitoring programs needed to assess restoration strategy efficacy.

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1. Introduction

Restoration of the Chesapeake Bay, the largest estuary in the United States, is the focus of a great deal of activity by Chesapeake Bay Program partners, including Federal, State and local agencies, universities, and private organizations within Maryland, Virginia, Pennsylvania, West Virginia, District of Columbia, Delaware, and New York. Federal agencies have recently been tasked with an Executive Order to "use their expertise and resources to contribute significantly to improving the health of the Chesapeake Bay" (Executive Order, 2009). In order to document progress in this restoration effort, detailed water quality data and assessments of potential pollutant effects on ecosystems will be required.

One of the more well-studied tributaries within the Chesapeake Bay watershed is the Choptank River. The University of Maryland Horn Point Laboratory and the National Oceanic and Atmospheric Administration (NOAA) - Oxford Marine Laboratory are both located within its watershed, facilitating a number of long term ecological studies and water quality data collection (Fisher et al., 2006a,b; Sutton et al., 2009; Pait and Nelson, 2009). Additional studies of the Choptank River have been carried out by Maryland Department of Natural Resources, United States Department of Agriculture - Agricultural Research Service (USDA-ARS), and United States Geological Survey

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(USGS) (Ator et al., 2004; Goel et al., 2005; Kuang et al., 2003; Lehotay et al., 1998). The Chesapeake Bay Water Quality Monitoring Network includes three stations in the Choptank River estuary (Fig. 1), and this watershed has also been included in a national study of agricultural best management practices called the Conservation Effects Assessment Project (McCarty et al., 2008).

The Choptank River watershed is similar to many of the agriculturally-dominated areas on the Delmarva Peninsula, and careful studies of this river can provide important information on the effects of land use and watershed management on water quality within the estuary. The mouth of the river is a tidal embayment, and 311 km^2 (15%) of the 2057 km^2 Choptank Basin is open water (Lee et al., 2001). The upstream reaches of the river split into the Tuckahoe Creek to the west and the Upper Choptank to the east (Fig. 1). The current land use in the basin is approximately 60% agriculture, 30% forest, 6% urban/residential and 4% wetlands (Fisher et al., 2006a,b). Primary crops in this area are corn (*Zea mays L.*), soybean (*Glycine max L.*), wheat (*Triticum aestivum L.*), and barley (*Hordeum vulgare L.*). Much of the grain production supports small- and medium-sized animal feeding operations (mostly poultry with some dairy and horse husbandry, USDA, 2007, 2008). Manures from these operations are routinely recycled as a fertilizer for agricultural production. Several wastewater treatment plants are also located on this river (Fig. 1), and a number of marinas with private and commercial boats are located in the lower estuary.

Since 1998, various segments of the Choptank River have been classified as "impaired waters" under the Federal Clean Water Act. The lower estuarine portion of the Choptank River is chronically impaired due to critically low dissolved oxygen at bottom depths, high phytoplankton content, and high nutrient concentrations (MDE, 2004), and the mouth of the Choptank River estuary has undergone an 85% decrease in the amount of area actively supporting submerged aquatic vegetation since 1997 (Orth et al., 2006). The upper reaches of the estuary are well-mixed with higher dissolved oxygen concentrations, but typically exhibit elevated concentrations of nutrients and high concentrations of phytoplankton biomass (USEPA, 2009b). Long-term declines in water quality within the Choptank River have been documented by Fisher et al. (2006a). However, there are no published studies examining spatial trends in multiple contaminant types (nutrients, herbicides, metals) and water quality parameters over time in the Choptank River estuary.

The *US EPA 2008 Report on the Environment* (EROE, USEPA, 2008a) describes levels of environmental concern for many pollutants, noting their status and trends, and explores their potential threats to specific environmental components and to overall ecosystem health. The objective of this work was to evaluate nutrients, herbicides and their primary degradation products, selected metals (As and Cu), dissolved oxygen, total suspended solids, chlorophyll *a*, and temperature simultaneously at multiple stations within the estuary. Results from this project, which was conducted over a three year period from March 2005 to April 2008, provide needed data to assess the potential for negative effects on critical living resources. Data are compared to indicators described in the EROE and to datasets obtained in previous studies of the Chesapeake Bay and its tributaries.

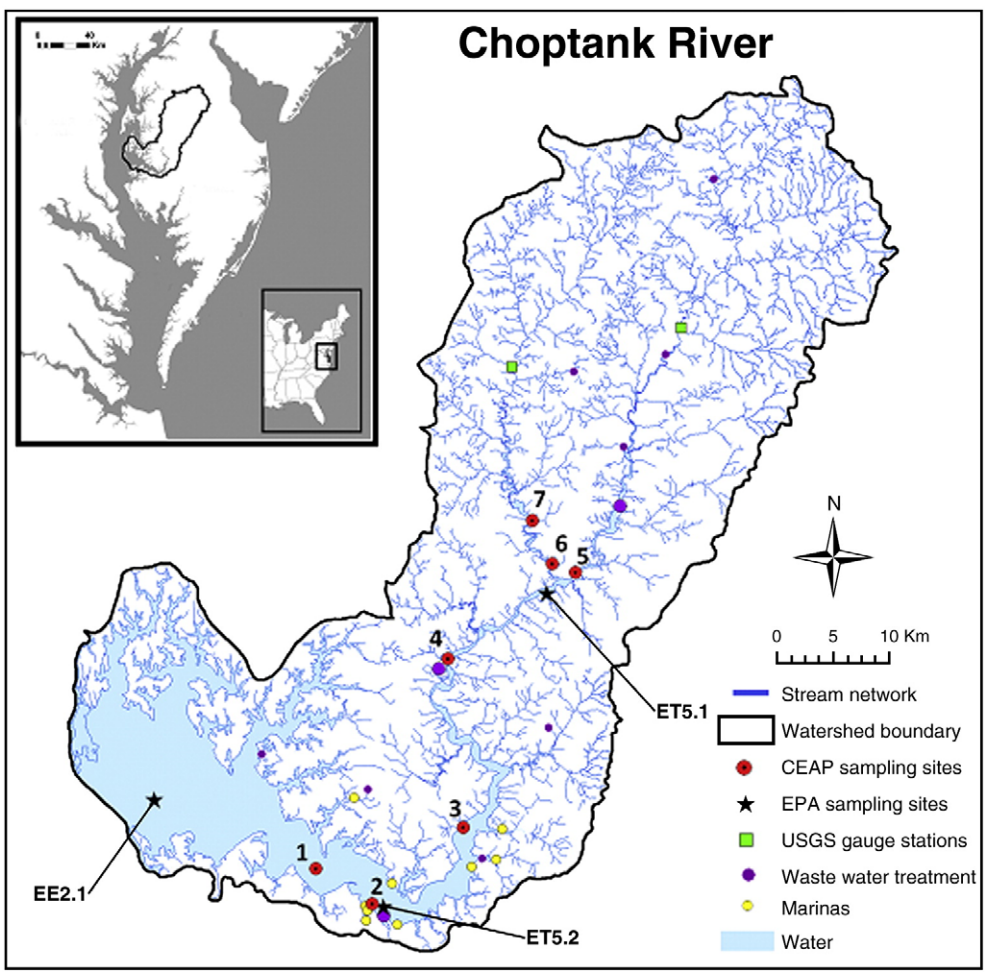

Fig. 1. Map of sampling and monitoring stations and wastewater plants in the Choptank River and basin. Inset: location of the Choptank basin in the Mid-Atlantic region of the USA.

Table 1
Sampling station names, locations, and water depths.

Station name	Latitude	Longitude	Water depth (m)
1	38.60267	-76.11892	10
2	38.57791	-76.06641	7
3	38.75618	-75.99879	4
4	38.63382	-75.98284	12
5	38.81958	-75.88142	5
6	38.82539	-75.90348	2
7	38.85670	-75.92215	6
USEPA ET5.1	38.80427	-75.90797	10
USEPA ET5.2	38.57579	-76.05595	11
USGS 01491000	38.99719	-75.78581	Weir
USGS 01491500	38.96681	-75.94606	Weir

2. Methods and materials

2.1. Sample collection

The estuary integrates tributary inflows and groundwater inputs from the basin, as well as tidal effects. Estuarine water samples were collected from just below the water surface (0.1 m) at seven locations (Table 1) along the navigable portion of the Choptank River (Fig. 1), using a small research vessel. Sampling dates were selected to represent base flow or near-base flow conditions in the watershed tributaries, at least two days after any significant (greater than 10 mm) rainfall event and flow less than 5 m^3/s at the local USGS monitoring stations (Table 1, Figs. 1, 2). Samples were collected on thirteen dates between March 2005 and April 2008; tide stage varied among sampling dates. Pesticide and nutrient data were available for nearly all dates, whereas metals data were only available for the first five dates: 2005 – 3/30, 6/29, 9/26, and 12/5; and 2006 – 4/6.

Collected samples were stored on ice in glass bottles (nutrient analysis), stainless steel containers (pesticide analysis), or pre-acidified plastic bottles (metals), and were transported to the laboratory and processed within 24 h. Surface water temperature, dissolved oxygen, chlorophyll and salinity were measured *in situ* (0.1 m) using a YSI 6600 multiparameter sonde (YSI, Inc., Yellow Springs, Ohio). A depth profile sampling of these parameters was conducted on six dates: 2006 – 6/8, 7/11, 9/25 and 2006 – 4/11, 5/30, 8/28. Local monitoring data were also available for rainfall from Wye Research and Education Center and from two USGS stream gauge stations (USGS, 2009): Upper Choptank near Greensboro, Maryland (01491000) and Tuckahoe Creek near Ruthsburg, Maryland (01491500). Monitoring data were also obtained for two USEPA Chesapeake Bay Water Quality Monitoring Program monitoring stations on the Choptank River (USEPA, 2009b): ET5.1 and ET5.2 (Fig. 1).

2.2. Sample analysis

Nutrient samples were filtered (4.5 µm) and analyzed for dissolved nitrate (NO_3-N) and dissolved reactive P), using a Lachat QuikChem 8000 flow injection analyzer (Lachat Instruments, Milwaukee, WI; Pote and Daniel, 2000). Arsenic concentrations were determined using the hydride method with inductively coupled plasma optical mission spectrometer (ICP-OES), according to the method outlined by Anderson and Isaacs (1995) and Arikan et al. (2008). Copper concentrations were determined using atomic absorption in which a copper standard solution was prepared by a stepwise dilution from a stock solution of 1000 µg/L in 2% HCl (Certified Atomic Absorption Standard, Fisher Scientific, Fairlawn, NJ).

Water samples stored in stainless steel containers were filtered to 0.7 µm prior to processing for pesticides: atrazine, alachlor, simazine, metolachlor, for the atrazine degradation products, CIAT (6-chloro-*N*-(1-methylethyl)-1,3,5-triazine-2,4-diamine) and CEAT (6-chloro-*N*-ethyl-1,3,5-triazine-2,4-diamine), and for metolachlor degradation products MESA ((metolachlor ethane sulfonic acid, or 2-([2-ethyl-6-methylphenyl][2-methoxy-1-methylethyl]amino)-2-oxoethanesulfonic acid, and MOA (metolachlor oxanilic acid, or 2-([2-ethyl-6-methylphenyl][2-methoxy-1-methylethyl]amino)-2-oxoacetic acid, as described by McConnell et al. (2007).

Method limits of quantification (LOQ) for each analyte are provided in Table 2. Analysis of duplicate samples collected at one

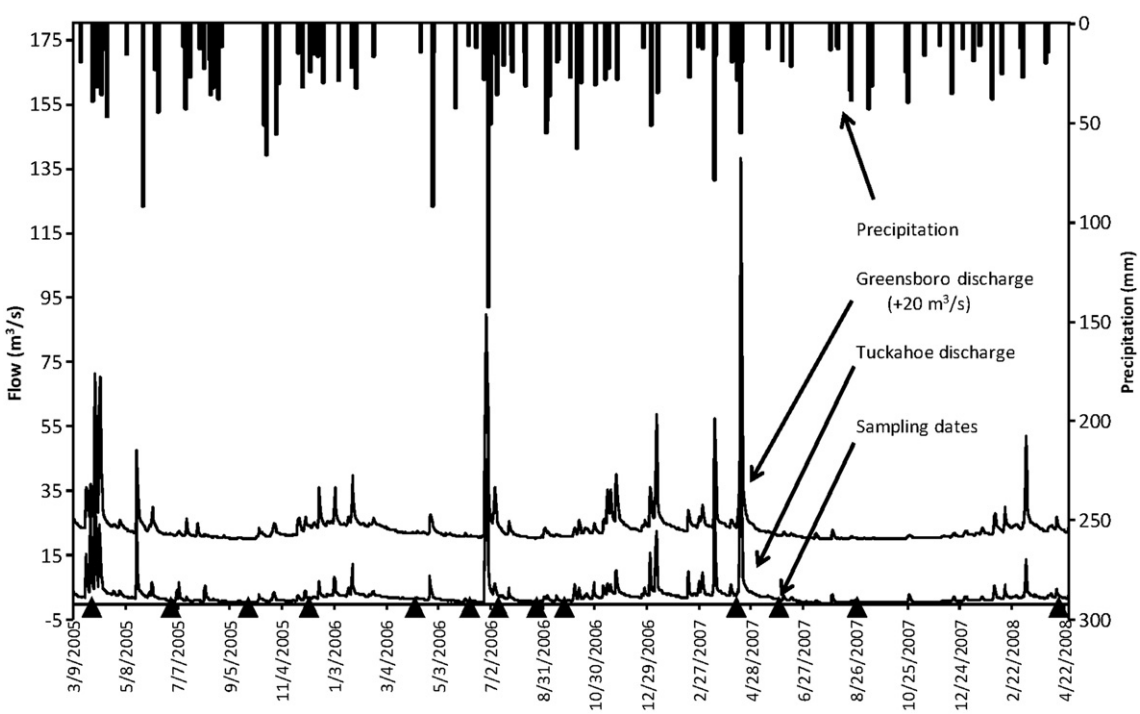

Fig. 2. Sampling dates, precipitation events from Wye Research and Education Center, and discharge from two USGS gauging stations. Flow data from the Greensboro station have been displaced by +20 m^3/s for clarity.

Table 2
Comparison of observed data (all stations, all sampling dates) with existing water quality criteria for ecosystems (see footnotes) and methodological limits of quantification (LOQ).

Variable	Unit	Criteria	Mean	Median	Minimum	Maximum	LOQ
Salinity	n/a	–	4.3	2.3	0.006	14	0.01
Temperature	°C		21.10	22.96	7.95	32.00	0.15
pH	–	–	7.51	7.50	8.38	6.79	–
Dissolved O_2	mg/L	3.0[a]; 5.0[b]	7.4	7	3.8	14.9	0.1
Nitrate + Nitrite	mg/L	None	1.28	0.79	0.01	3.97	0.01
Ammonia	mg/L	N/A[c]	0.21	0.15	0.01	1.1	0.01
Dissolved P	mg/L	None	0.07	0.05	0.01	0.36	0.01
Chlorophyll *a*	µg/L	2.6 -7.6[d]	9.0	8.1	0.9	25	0.1
TSS	mg/L	–	18	15	2	40	0.1
Atrazine	µg/L	10-20[e]	0.28	0.1	0.01	1.86	0.002
Simazine	µg/L	3,700[f]	0.24	0.07	0.01	1.89	0.002
CIAT	µg/L	–	0.14	0.10	0.01	0.64	0.002
CEAT	µg/L	–	0.12	0.05	0.01	0.80	0.002
Metolachlor	µg/L	25,100[g]; 3,900[h]	0.14	0.04	0.001	1.19	0.001
MESA	µg/L	–	1.80	1.70	0.35	5.29	0.01
MOA	µg/L	–	0.39	0.35	0.01	0.89	0.01
Copper	µg/L	4.8[i]; 3.1[j]	12.7	9.9	1.3	40.3	1.0
Arsenic	µg/L	69[i]; 36[j]	0.46	0.40	0.085	1.22	0.15

[a] For no more than 12 hours, interval between excursions at least 48 hours, everywhere (USEPA, 2003).
[b] All times, throughout above-pycnocline waters (USEPA, 2003).
[c] Ammonia toxicity is variable, and varies with pH and temperature(USEPA, 1999).
[d] USEPA (2003).
[e] USEPA (2006b).
[f] 96-h LC_{50} for oysters (WSSA, 1994).
[g] 48-h EC_{50} in *Daphnia magna* (WSSA, 1989).
[h] 48-h EC_{50} aquatic invertebrates (USEPA, 1995).
[i] Acute toxicity (USEPA, 2008b).
[j] Chronic toxicity (USEPA, 2008b).

station per sampling date did not show significant variation. Blank samples did not exhibit any interferences, and blank analyte concentrations were well below the LOQ values.

2.3. Statistical analysis

Single variable regression was used to assess the relationship (r^2) between dependant variables (e.g., observed analyte concentrations) and observed salinity (described above) using SigmaPlot® 10.0 (Systat Software, Inc., Chicago, IL) or Microsoft® Excel 2007 software (http://office.microsoft.com). Box-plot analysis to assess temporal and spatial variability in analyte concentrations, as well as one-way analysis of variance using a Kruskal-Wallis test to test for differences among station medians, were conducted using GraphPad Prism® (GraphPad Software, La Jolla, CA). Unless otherwise noted, statistical significance was determined at an alpha value of 0.05.

3. Results and discussion

Analyte concentrations (nutrients, herbicides, herbicide degradation products, arsenic, and copper) as well as standard water quality parameters (salinity, temperature, dissolved oxygen, chlorophyll *a*) were measured at each of the seven Choptank River sampling stations (Fig. 1), on thirteen synoptic sampling dates between March 2005 and April 2008 (Fig. 2). Observed concentrations (range, mean and median concentrations) for each analyte over all dates and stations are shown in Table 2. Some water quality parameters and contaminant concentrations fell within an acceptable or marginally acceptable range or were below water quality levels of concern while others clearly exceeded accepted or proposed environmental threshold criteria.

3.1. Temperature, salinity, and dissolved oxygen

Observed surface water data for temperature, salinity, and dissolved oxygen (Table 2) were typical for Mid-Atlantic estuaries (Bricker et al., 2007). As expected, water temperature varied significantly ($p<0.05$) by season, but there was no significant difference among stations on each sampling date. All seven stations were determined to be tidally influenced based on a combination of observed salinity values and qualitative field observations. A clear salinity gradient was evident along the river (Fig. 3) with mesohaline concentrations observed near the river mouth (avg. 10.7 ppt at station 1) and oligohaline to freshwater concentrations (avg. 0.17 ppt at station 7) observed in the upstream reaches. At each station, higher salinity values were observed in the summer months versus the late winter early spring when higher runoff occurs; this is consistent with previous studies (Fisher et al., 1988). However, very low salinity values were observed during the sampling event on July 11, 2006 which followed a period of very heavy rains (Fig. 2).

Dissolved oxygen (DO) concentrations above 5 mg/L are rarely injurious to aquatic life, whereas concentrations below 2 mg/L are almost always harmful and are considered a hypoxia threshold (Diaz and Rosenberg, 1995; USEPA, 2008a). Estuarine DO concentrations are expected to decrease with increasing temperature and oxygen demand during the summer months and with increasing salinity (e.g., Boynton and Kemp, 1985). In surface water samples collected in this study, 84% ($n=82$) showed DO concentrations above 5 mg/L, and the remaining 12 samples had DO concentrations in the moderate range of 2 – 5 mg/L. Concentrations (Fig. 4) showed a seasonal cycle with significantly lower ($p<0.05$) concentrations observed during summer months, and a negative linear correlation ($r^2=0.58$) observed between temperature and DO. The seasonal cycles can be seen more clearly in data from the USEPA Chesapeake Bay Water Quality Monitoring Program station ET5.2 which is near station 2 (Fig. 5, USEPA, 2009b). A close correspondence also exists between DO values observed at station 4 and values collected at the USEPA monitoring station ET5.1, where concentrations ranged from 4.6 to 12.5 mg/L and also followed the expected annual cycle with lower values observed in summertime and higher values observed during the cooler months. Moderately low summertime DO concentrations values were also observed in surface waters by Fisher et al. (2006a) in an eight year study, as well as a decreasing trend in Choptank River bottom water DO concentrations.

Estuaries can experience reduced DO concentrations at deeper water depths during periods of eutrophication and vertical stratification, a phenomenon that is often observed in the Choptank at the lower USEPA monitoring station ET5.2 (located near sampling station 2) following large summertime rain events. At the upstream USEPA monitoring station ET5.1, differences between surface and bottom water DO concentrations are generally minimal (less than 0.9 mg/L) indicating that the river is well mixed at this location. Water column DO profiles were measured at each sampling station on six of the sampling dates (data not shown), with results depicting occasional stratification at stations 1 - 3 (>10% DO decrease with depth observed on three of six sampling dates), and little stratification at stations 4 – 7.

3.2. Total suspended solids, chlorophyll a and nutrients

Total suspended solids (TSS) concentrations ranged from 2 to 40 mg/L (Table 2), there were no statistically significant differences between sites or significant seasonal patterns. Chlorophyll *a* concentration provides a measure of phytoplankton biomass. In the Chesapeake Bay, peak chlorophyll *a* levels between 2.6 – 7.6 µg/L (general range less than 3.4 µg/L) are indicative of oligotrophic conditions in tidal and fresh waters; peak values between 8.9 – 29 µg/L (general range from 3.0 to 7.4 µg/L) are indicative of mesotrophic conditions, and peak values above 16.9 µg/L (general range greater than 6.7 µg/L) are indicative of eutrophic

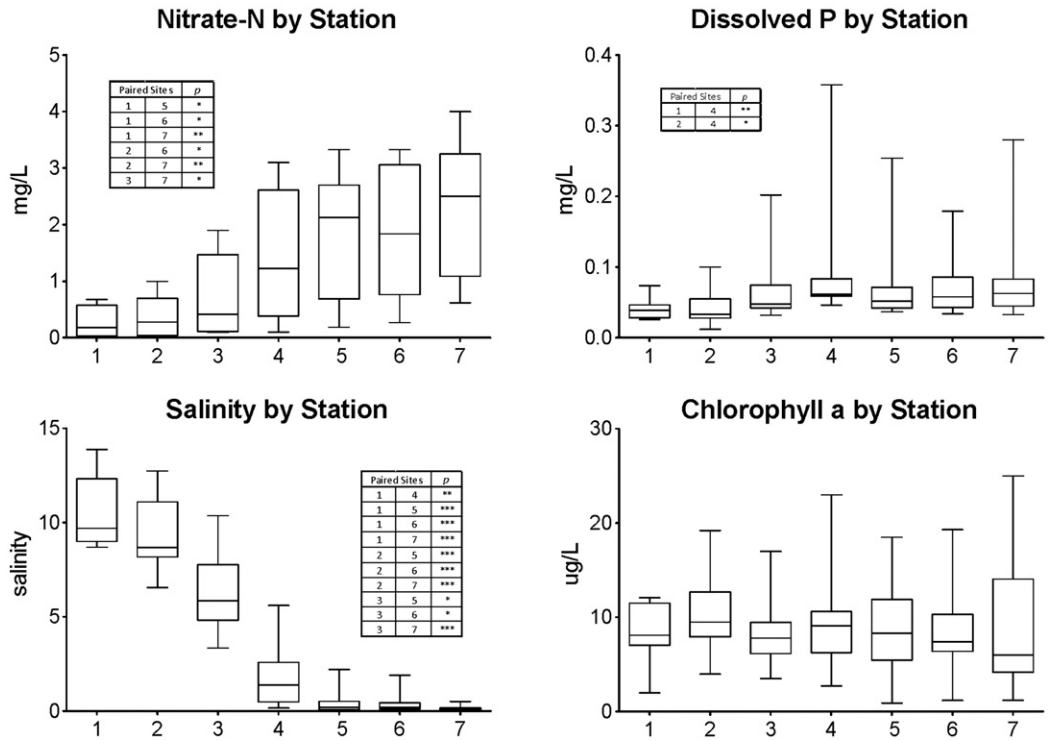

Fig. 3. Box plots of nitrate-N, dissolved phosphorus, salinity, and chlorophyll *a* concentrations by sampling station, noting the minimum and maximum values and the median.

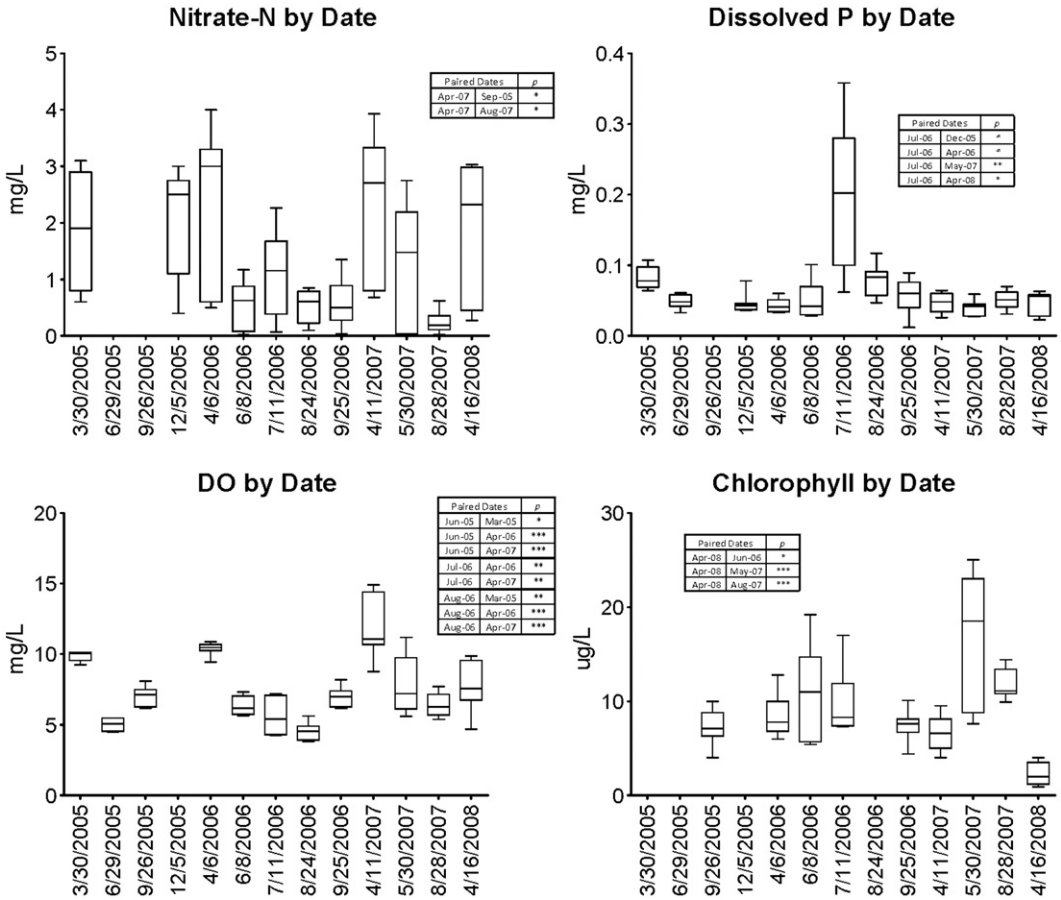

Fig. 4. Box plots of nitrate-N, dissolved phosphorus, dissolved oxygen (DO), and chlorophyll *a* concentrations by sampling date, noting the minimum and maximum values and the median.

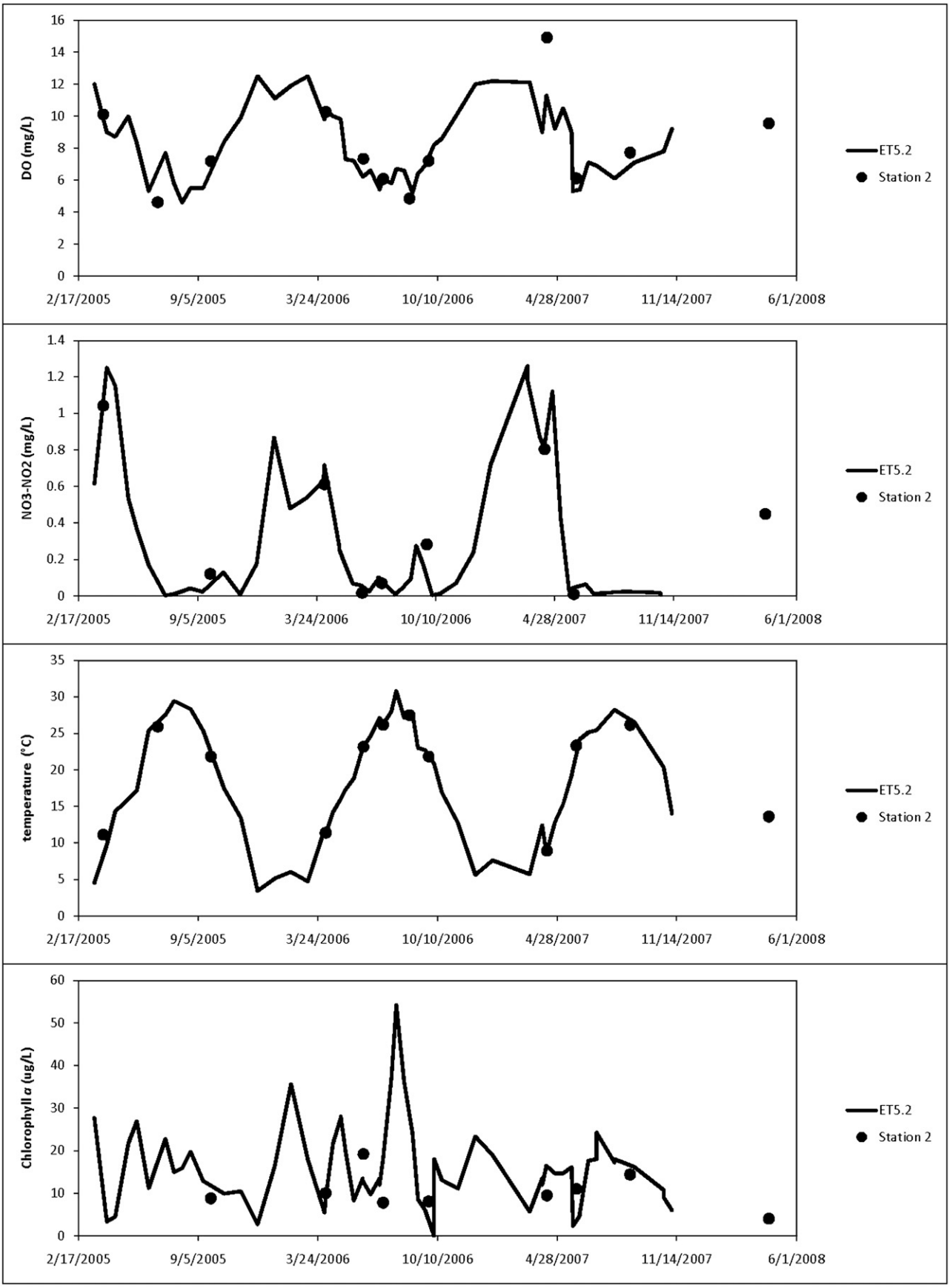

Fig. 5. Dissolved oxygen (DO), temperature, nitrate-N and chlorophyll a concentrations observed at USEPA station ET5.2 (USEPA, 2007) and at station 2 (this study).

conditions (USEPA, 2003). Chlorophyll *a* content of surface waters samples collected in this study ($n=63$) ranged from 0.9 to 25 mg/L, with 10% of samples exceeding 16.9 μg/L. 40% of the samples measured less than 7.6 μg/L, and the median was 8.1 μg/L. A seasonal peak was observed in the early summertime (May-July) and the maximum observed concentration of 25 μg/L was consistent with the maximum value of 26 μg/L observed in the Choptank in 2004 by Fisher et al. (2006a), who noted a doubling in chlorophyll *a* concentrations between 1985 to 2003. In the Choptank River watershed and estuary, the greatest occurrence of zooplankton grazing on phytoplankton is typically in late winter (White and Roman, 1992), while reduced grazing and higher temperatures in summer can lead to maxima in chlorophyll *a*, decreases in nitrate, and decreases in DO in bottom waters, as documented at the USEPA monitoring stations ET5.2 and ET5.1 (Fig. 5; USEPA, 2009b). While the highest chlorophyll *a* concentrations were observed on summertime sampling dates (Fig. 4), no apparent relationship between chlorophyll *a* and nutrient or DO concentrations was observed in the sampling dataset.

A chlorophyll *a* maximum usually occurs in the mesohaline areas of estuaries (e.g., Fisher et al., 1988). Phytoplankton may not grow well in the oligohaline portion of the estuary because of high turbidity and little or no stratification, which leads to light limitation of phytoplankton growth. In contrast, in the lower estuary both water transparency and stratification increases, alleviating light limitation (Fisher et al., 1999). In this data set, a chlorophyll *a* maximum occurred at stations 2 – 4 in the lower, mesohaline estuary on five of the nine sampling dates with complete sets of chlorophyll *a* data. On the other four dates, no consistent pattern in chlorophyll *a* concentrations was observed among the stations, indicating little spatial variation or an upstream maximum in phytoplankton along the length of the river. As a result of this diversity of spatial patterns, no consistent spatial pattern in median chlorophyll a concentrations was observed along the length of the river when combined by date (Fig. 3).

Dissolved phosphorus and nitrate-N were detected in all samples and are reported here in accordance with the ranges suggested in the EROE (USEPA, 2008a). Observed concentrations of dissolved P ranged from 0.01 to 0.36 mg/L, with 89% ($n=73$) falling below 0.1 mg/L. The highest synoptic concentrations of dissolved P (0.06 to 0.36 mg/L) were observed on July 11, 2006 (Fig. 4). Although this date represented base flow conditions, it followed a period of heavy storm flow when 25 cm of rain fell over the course of two weeks (Fig. 2); the high values on this date are likely the residual effects of phosphorus mobilization during the storm flow period. Observed concentrations of nitrate-N ($n=72$) ranged from 0.01 to 4.0 mg/L, with 56% of the samples falling below 1 mg/L, 15% between 1 – 2 mg/L, and 29% between 2 – 4 mg/L. A close correspondence was found between nitrate-N concentrations observed in this study (stations 2 and 4) and values collected at the nearby USEPA monitoring stations ET5.2 (Fig. 5) and ET5.1. Both data sources showed a seasonal cycle of nitrate-N concentrations, with the lower values observed in the late summertime likely resulting from smaller loading rates during periods of reduced summertime base flow in the upland watersheds, coupled with a resulting relative increase in upriver saltwater intrusion.

Total ammonia concentrations ($NH_3+NH_4^+$) were also detected in all samples ($n=82$) and ranged from 0.01 to 1.10 mg/L. Only 5 samples were above 0.5 mg/L and 62% were below 0.2 mg/L. No significant spatial or seasonal differences were observed, although higher concentrations were typically observed in the spring and at the mouth of the river (stations 1 – 3). The partitioning between ammonium and ammonia is dependent on pH and temperature. Ammonia is the more toxic species, but in the pH and temperature ranges observed here would represent less than 10% of the total ammonia concentration. These values for ammonia are below the LC_{50} of 0.5 mg/L for most sensitive organisms (USEPA, 1999).

If both nitrogen and phosphorus are abundant, enhanced phytoplankton growth can result in eutrophication and water quality degradation (Nixon, 1995). Symptoms associated with anthropogenically enhanced eutrophication can include increased algal (phytoplankton or macroalgal) growth, changes in algal community composition, increased turbidity and decreased solar penetration, hypoxic or anoxic events, fish kills (Kemp et al., 2005; Richardson et al., 2001), and loss of submerged aquatic vegetation (Orth et al., 2002). The N:P ratio for phytoplankton growth in seawater is approximately 15:1 (Millero, 2006). Primary productivity in many coastal systems is typically nitrogen (N) limited, although phytoplankton productivity may be limited by phosphorus (P) seasonally or in portions of an estuary (Fisher et al., 1999). The Choptank River estuary tends to be nutrient unlimited and well-mixed in its headwaters, shifting to increased vertical stratification and eutrophication in the lower estuary (MDDNR, 2009; USEPA, 2009b). The river occasionally exhibits symptoms of eutrophication including algal blooms and low oxygen events particularly during summertime, and varies between N and P limitation over space and time (Fisher et al., 1999). In nearly half (49%) of the samples from the current study, the N:P ratio was greater than 15:1, and this occurred, without exception, during late fall to early spring, indicating that nitrogen was abundant relative to P. The N:P ratio was typically less than 15:1 during the summer sampling dates, indicating that phosphorus was abundant relative to N. These results are in accordance with previous analyses of Chesapeake Bay Program water quality monitoring data collected in the Choptank River (USEPA, 2009b).

No formal water quality criteria exist for nitrogen and phosphorus in estuarine waters (Hagy and Greene, 2009). Statistical analysis of national water quality data has suggested that appropriate reference levels for nitrogen range from 0.12 to 2.2 mg/L (USEPA, 2008a). Of the observed nitrate-N concentrations in this study, 83% of samples exceeded the lower threshold of 0.12 mg/L. As suggested by the EROE, the reference level of 0.1 mg/L for phosphorus may be too high because nuisance algal growths can occur in water bodies that meet this criterion; a more appropriate criterion may be 0.01 to 0.075 mg/L (USEPA, 2008a). Total dissolved phosphorus in all the samples of this studied exceeded the lower limit of 0.01 mg/L. Use of the more stringent environmental criteria will require more robust efforts to mitigate nutrient concentrations, both N and P, in the Choptank River estuary to restore ecosystem health.

3.3. Nutrient sources and fate

Previous work has shown that streams draining basins dominated by agriculture typically exhibit a clear agricultural signature at the watershed level (Jordan et al., 1997) including high soluble nitrate concentrations under baseflow conditions. In the Choptank River watershed, nutrients are primarily applied on small grains in mid-February to late March and on corn from mid-May to mid-June. The upland subwatersheds contributing to streamflow at stations 5 – 7 are largely dominated by agricultural land use (greater than 60%, McCarty et al., 2008), and this was reflected in higher observed nitrate concentrations at the upstream sampling locations (Fig. 3). Nitrate concentrations showed a consistent decreasing trend along the course of the river, and without exception the highest nitrate concentrations for each sampling event were observed at station 7 and the lowest at station 1, indicating upstream nitrate sources.

Correlations between nutrient concentrations and salinity can be used to examine nutrient input and consumption processes along the length of an estuary. A linear relationship between nutrient concentration and salinity indicates that chemical and/or biological processing of nutrients is low relative to water residence time along the length of the water body, and that mixing with saline waters is the dominant process affecting nutrient concentration in the estuary. During the non-summer months, observed nitrate concentrations exhibited strong negative linear correlations with salinity ($0.92>r^2>0.95$), i.e., nitrate concentration decreased in a linear manner as salinity increased. This suggests

that nitrogen inputs from agricultural head waters dominated any signal from downstream nitrate sources, that dilution by saline waters was dominant, and that biological processing was minimal. In contrast, during the lower flows of summer months, the negative correlations between nitrate concentrations and salinity exhibited curvilinearity, and quadratic polynomial terms were significant ($r^2 > 0.89$),suggesting the influence of processes such as biological uptake and denitrification within the river or progressive dilution by non-agricultural groundwater sources.

Although the observed range of dissolved phosphorus values was greater at upstream sites there was no clear trend in P concentrations among the stations or sampling dates; the negative linear correlation between dissolved P and salinity ranged from poor to strong ($0.01 < r^2 > 0.95$). These observations may indicate that, in addition to dissolved P inputs from agricultural headwaters, significant input sources are present in the downstream reaches of the estuary, waste water treatment plants (WWTPs), urban runoff, or desorption from sediments. The Choptank River watershed contains three major WWTPs (larger points in Fig. 1) with discharges greater than 1000 m^3/s (Fig. 1): Cambridge WWTP (nearest to station 2); Easton WWTP (near station 4), and Denton WWTP (upstream from station 5). In 2005, effluent flows were 12,600, 7,950, and 1,280 m^3/d, respectively (USEPA, 2007). For five sampling dates, dissolved phosphorus was highest at station 4 indicating a potential local source from the nearby WWTP at Easton. The highest observed dissolved P concentration measured in this study (0.36 mg/L) occurred at station 4 on July 11, 2006, following the period of heavy rains (Fig. 2). Elevated phosphorus concentrations were observed throughout the river on this date, but the high value observed at station 4 may be the partial result of effluent discharge from the Easton WWTP. This hypothesis is supported by available data from the WWTP, where phosphate output was three times greater in June than in the previous month (USEPA, 2007). Furthermore, corresponding high nitrate concentrations were not observed on this date presumably because nitrate-N primarily enters the system through groundwater rather than overland flow and the three largest WWTP all perform tertiary treatment for nitrogen.

3.4. Herbicides and their degradation products

Large-scale crop production generally includes the use of pesticides (herbicides, fungicides, or insecticides) to protect plants from diseases or pests. Exposure to pesticide residues may negatively affect sensitive species of plants or animals, especially if those species are already under other forms of environmental stress (e.g., habitat destruction or poor water quality conditions. All observed atrazine concentrations were less than 2 μg/L (Figs. 6, 7), which is below the level of concern for population and community risk in aquatic ecosystems (10 to 20 μg/L) for prolonged exposure to atrazine (USEPA, 2006b) and below the US EPA drinking water criteria of 3 μg/L. Observed concentrations exceeded 1 μg/L in nine samples, occurring at upstream stations just after the springtime period (June 2005 and 2006) when pre-emergent herbicides are applied to crops. Fifty percent of all samples ($n = 84$) contained less than 0.1 μg/L and 40% were in the range of 0.1 – 1.0 μg/L. In similar fashion, simazine concentrations were all relatively low with no samples exceeding 2 μg/L ($n = 81$; three samples were below the level of quantification). The simazine level of concern for aquatic organisms is 3.7 mg/L (EXTOXNET, 2009). Six samples exceeded 1 μg/L, which is three orders of magnitude less than the level of concern, and occurred at upstream stations (4, 5, 6, and 7) in June 2005 and 2006. Sixty percent of all simazine samples were less than 0.1 μg/L and 32% were in the range of 0.1 – 1.0 μg/L. While total parent triazine concentrations (atrazine and simazine) were well below 1 μg/L in the great majority of samples (87%), concentrations in four samples exceeded the 3 μg/L drinking water criterion (all collected in June 2006); and another 8% of the samples contained total parent triazine concentrations of 1 – 3 μg/L.

Measurable amounts of the triazinyl herbicide degradation products, CIAT and CEAT, were found in all samples ($n = 84$) except one. In the spring months observed CIAT and CEAT concentrations were 20 to 50% of observed parent compound concentrations during the period; however, in late fall, winter, and very early spring degradation product concentrations were 2 to 3 times higher than parent compounds. Water quality criteria are typically determined for a single compound but organisms are exposed to a multitude of pollutants and stressors simultaneously. Total triazine residues (atrazine, simazine, CIAT, and CEAT) exceeded 3 μg/L in 8 samples, reaching levels greater than 5 μg/L; all were collected in June 2005 and 2006. Even at the highest concentrations, observed triazinyl residues were 50% below the level of concern for chronic exposure for atrazine.

Metolachlor concentrations were lower than triazine concentrations with a maximum concentration observed at less than 1.2 μg/L. Higher concentrations were observed at the upstream stations and during summertime sampling dates. In seven samples, residue levels were below quantification limits, and 77% of the samples had measurable concentrations of less than 0.1 μg/L. The LC_{50} for *Daphnia magna* for chronic exposure to metolachlor is 3.9 mg/L which is three times the highest observed concentration. The primary degradation products of metolachlor, MESA and MOA, were observed in all samples analyzed ($n = 63, 62$, respectively). MOA concentrations ranged from levels similar to the parent compound to an order of magnitude higher than metolachlor, whereas MESA concentrations were consistently one order of magnitude greater than the parent herbicide. In all samples, the total concentration levels of metolachlor and its measured degradation products, MESA and MOA, were several orders of magnitude lower than the levels of concern for metolachlor (Table 2).

MESA and MOA have received increased attention recently. Groundwater residence times of four or more years have been reported (Phillips et al., 1999; Huntscha et al., 2008; Rebich et al., 2004). MESA concentrations were observed at much higher relative to metolachlor in the Lake Greifensee (Switzerland) watershed (Huntscha et al., 2008) where they attribute its increased persistence and low retention to soil properties. Since most of the sulfonic acid metabolites of the acetanilide pesticides exhibit longer residence times in groundwater, cleansing them from exposed watersheds may require long time periods.

3.5. Herbicide fate in the ecosystem

For herbicides such as atrazine and metolachlor, approximately one to six percent of the applied material is expected to leave the farm fields via surface water pathways (Malone et al., 2004). Delivery of the degradation products occurs primarily via groundwater transport, as degradation typically occurs in the unsaturated soil zone (Hancock et al., 2008; Tesoriero et al., 2007). Both the parent compounds and their degradation products have been shown to be transported from farms via groundwater flow (Angier et al., 2002) and are commonly found in Eastern Shore groundwater sampling wells (Ator, 2008). Another transport mechanism for pesticides involves airborne drift during application and/or volatilization (Linders et al., 2000; Prueger et al., 2005) followed by deposition onto vegetation and soils. Subsequent wash off of residues from riparian tree canopies may provide a transport pathway to stream channels during rainfall (Rice et al., 2008).

In the Choptank River, parent herbicide concentrations varied significantly on a temporal scale with the highest concentrations occurring during the spring application period (Fig. 7). A smaller second peak in metolachlor concentration was observed in mid-summer (July 2006) corresponding to the herbicide application time

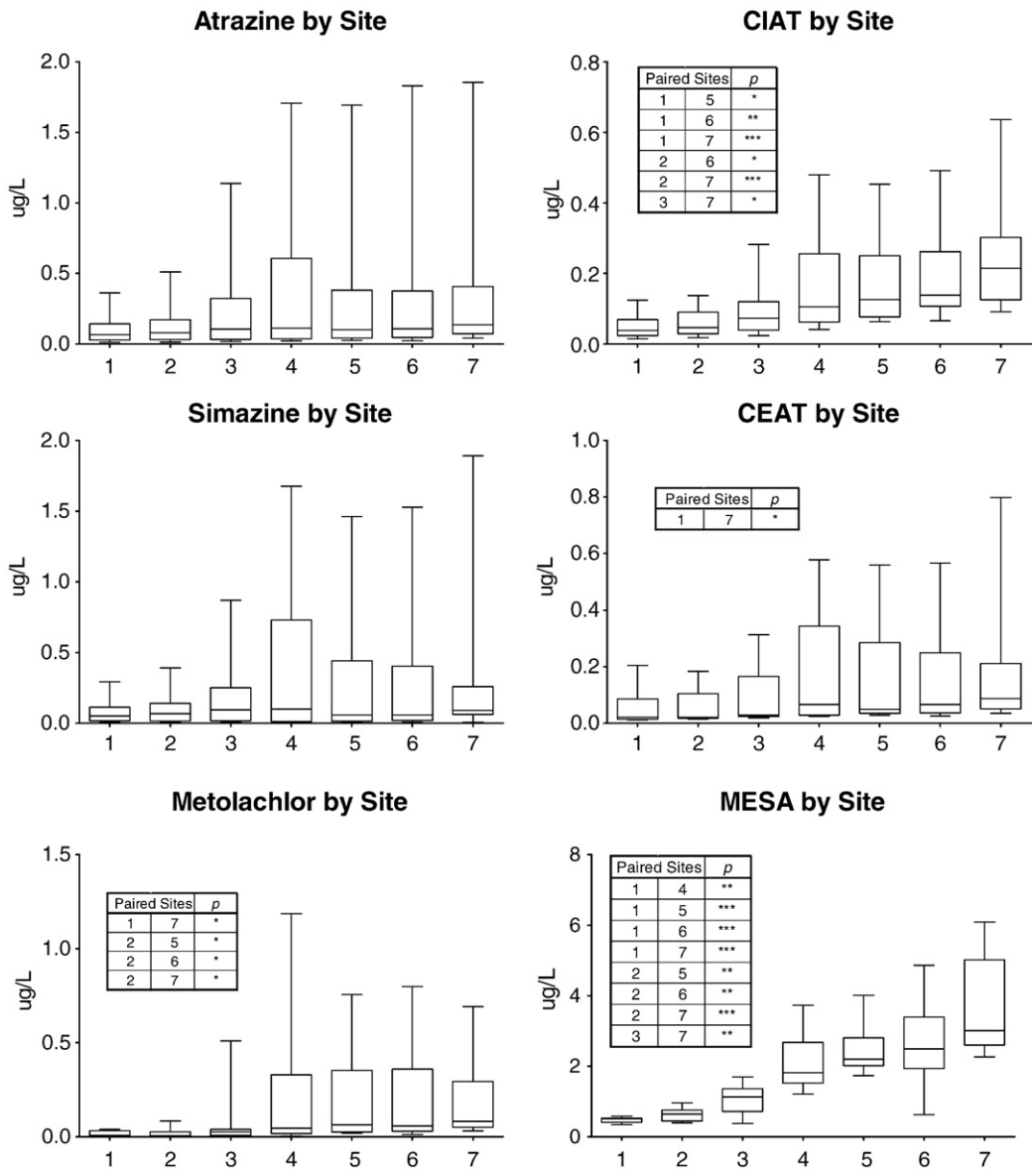

Fig. 6. Box plots atrazine, simazine, metolachlor, CIAT, CEAT, and MESA concentrations by sampling station, noting the minimum and maximum values and the median.

period for double-cropped soybeans. This rapid response of receiving waters to agricultural management practices suggests that the primary delivery process for the parent herbicides to the estuary involves surface water transport rather than transport through ground water. Additional evidence for this phenomenon can be observed by contrasting the high concentrations observed in 2006 following a period of abundant rainfall with the smaller peak seen in 2007 when minimal rainfall occurred during the May – September growing season (Fig. 2), thus reducing the opportunity for parent compounds to enter the waterways. Similar seasonal trends were seen for the triazinyl degradation products (Fig. 6), but no seasonal trend was observed for MESA or MOA.

The relationship between salinity and concentrations of herbicides or their degradation products was examined for each sampling date. A moderate negative correlation between salinity and the triazinyl parent herbicide concentrations was observed in spring sampling dates ($0.6 < r^2 > 0.9$); no relationship was found for the other sampling dates. This suggests that atrazine and simazine are primarily delivered to the agricultural head waters in the spring via overland flow and/or volatilization, tree canopy capture, and subsequent wash off. The pattern also suggests that some processing of these parent compounds to form CIAT and CEAT may occur in the estuary. A strong negative linear correlation was seen between salinity and metolachlor concentrations ($r^2 > 0.8$) for nearly all sampling dates, indicating that metolachlor is delivered primarily via the agricultural headwaters, but only a modest amount, if any, is degraded in the river. Both CIAT and MOA had a moderate negative correlation with salinity for nearly all sampling dates ($0.6 < r^2 > 0.9$), whereas no consistent relationship was observed between CEAT and salinity ($0.1 < r^2 > 0.9$). A strong negative correlation was found for MESA and salinity ($r^2 > 0.9$) for all but one of the sampling dates. These results suggest that the herbicide degradation products enter the estuary mostly at the head waters via groundwater processes (e.g., Hancock et al., 2008; Tesoriero et al., 2007). Furthermore, MESA remains stable and some processing of CIAT and MOA occurs in the streams.

3.6. Metal concentrations

Copper and arsenic concentrations were measured during the first five sampling dates and were observed in all samples ($n = 33$). Arsenic is extremely toxic to both marine organisms and humans, and can bioaccumulate in fish, posing a threat to aquatic birds

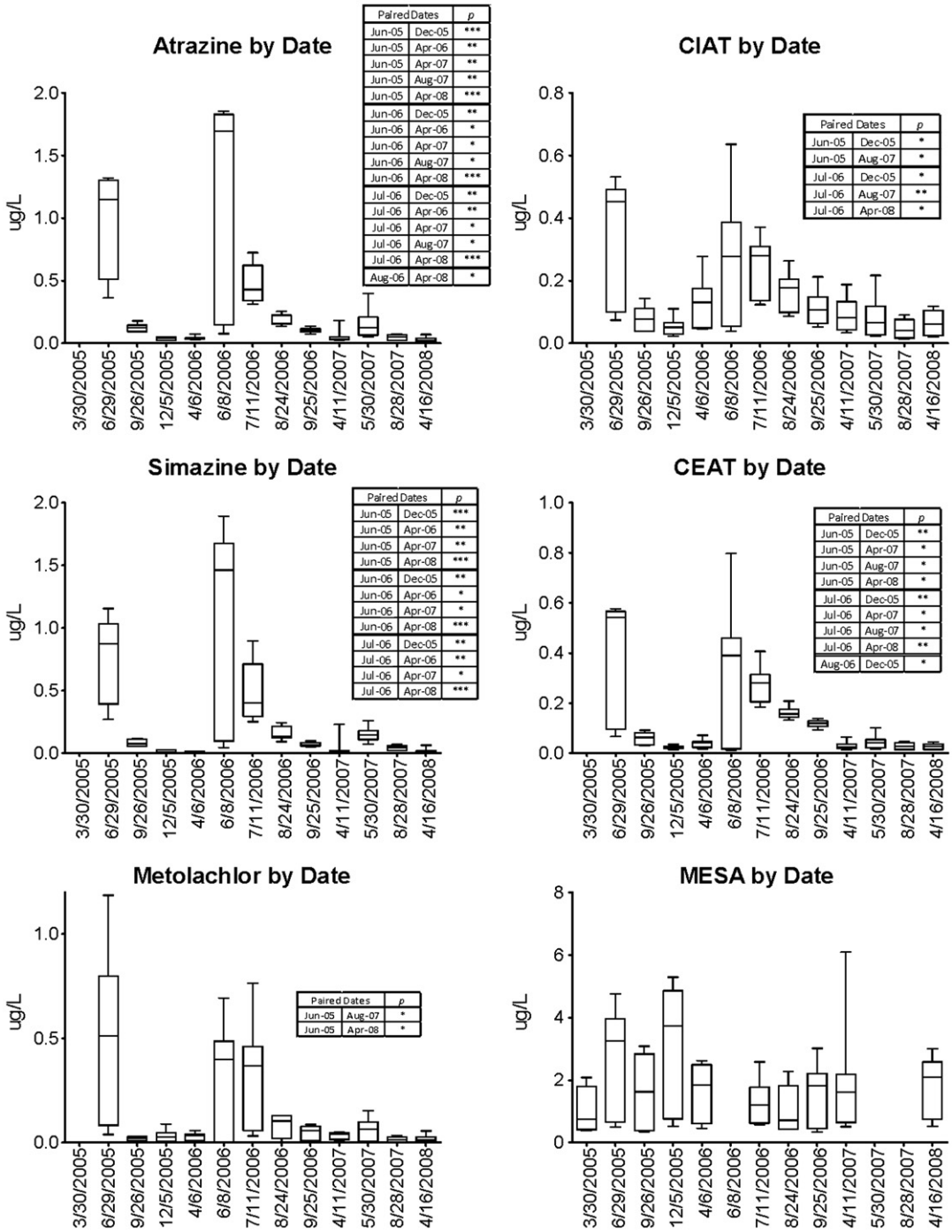

Fig. 7. Box plots atrazine, simazine, metolachlor, CIAT, CEAT, and MESA concentrations by sampling date, noting the minimum and maximum values and the median.

(Fujihara et al., 2004). The organic arsenical compound roxarsone (3-nitro-4-hydroxyphenylarsonic acid) is commonly added to poultry feed to control coccidial intestinal parasites, thereby increasing bird growth rate. Most of the administered roxarsone is excreted into the manure as parent material (Morrison, 1969) which rapidly hydrolyzes in soil into inorganic arsenic (Stolz et al., 2007). Thus, a pulse of arsenic might be expected in late spring following application of manure to agricultural lands; however, this was not observed. No significant differences in median arsenic concentrations were observed among stations or among sampling dates (Fig. 8). All concentrations were less than or equal to 0.6 µg/L with the exception of three samples that were collected in September from stations 1, 2, and 3 in the lower part of the estuary (1.0, 1.2, and 1.1 µg/L As, respectively). All concentrations were well below the US EPA national recommended water quality criteria for both acute and chronic exposure (Table 2) and were below the maximum level of concern of 10 µg/L for drinking water (USEPA, 2006a).

Although copper is an essential trace nutrient for plants and animals, at elevated concentrations copper is toxic to many organisms, especially algae and aquatic invertebrates (Kwok et al., 2008). Agricultural uses of copper include application of copper sulfate and copper hydroxide as a fungicide for vegetable crops, and as an herbicide to kill unwanted aquatic vegetation (Extoxnet, 2009). Copper is also used in antifouling paints to protect boat hulls from bioorganisms and has largely replaced the banned tributyltin products (Schiff et al., 2003). The chronic and acute water quality

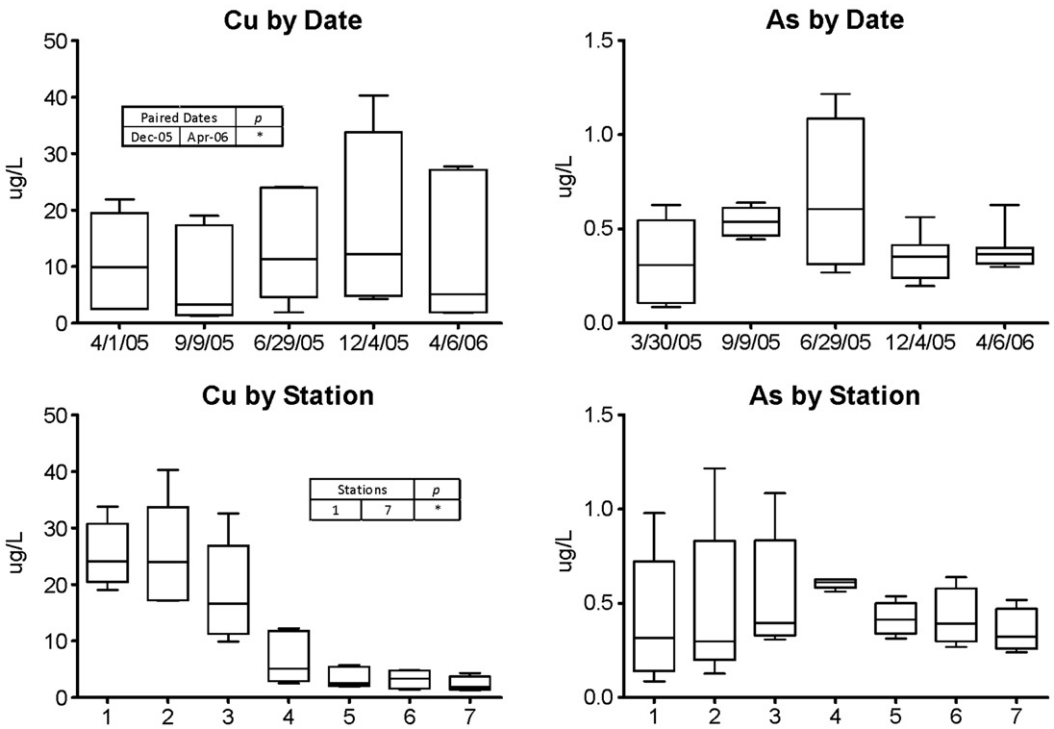

Fig. 8. Box plots arsenic and copper concentrations by sampling station and by sampling date, noting the minimum and maximum values and the median.

criteria for copper are relatively low at 3.1 and 4.8 ug/L, respectively (USEPA, 2008b). Median copper concentrations in this study varied significantly among sampling dates and stations. For all sampling dates, the highest Cu concentrations occurred in the lower part of the estuary (stations 1 - 3), while the lowest concentrations were found at the stations furthest upstream (5 – 7). The average Cu concentration at the upstream stations (4 – 7) was 4.2 µg/L with concentrations ranging from 1.3 to 12.2 µg/L; the average concentration for the downstream stations (1 – 3) was 23 µg/L with concentrations ranging from 9.9 µg/L to 40.3 µg/L. Strong positive linear correlation was observed between copper concentration and salinity on each sampling date ($r^2 = 0.950$ to 0.998) with the four downstream stations exhibiting significantly elevated Cu concentrations in comparison to the upstream locations. These data clearly indicate that agriculture is not the primary source of Cu in the Choptank River, and that there are significant downstream sources of Cu loading to the estuary.

A likely source of the higher Cu concentrations observed may be copper released from the antifouling paints used on boat hulls, which have been shown elsewhere to contaminate waters and sediments (Warken et al., 2004). Recreational boating in the Choptank River area has greatly increased since the mid 1990's, but since 2006 has remained unchanged (Maryland Sea Grant, 2007). The shoreline between stations 2 and 4 is highly populated with leisure boat marinas and repair yards (Fig. 1), whereas few marinas exist above station 4 and boat traffic is reduced in the upstream reaches due to shallow water depths. The average Cu concentration and range observed in the lower stations (1 – 3) of the Choptank (23 µg/L; 10 – 40 µg/L) were greater than Choptank River Cu concentrations documented in a 1986 study of Chesapeake Bay water quality (12 µg/L; 10 – 20 µg/L) (Hall et al., 1988). Hall et al. (1988) also observed that the highest Cu concentrations (70 – 80 µg/L) within several other tributaries of the Chesapeake Bay occurred near marinas and areas of leisure boat activity. Furthermore, recent studies have demonstrated that increased salinity can cause increased copper release from paint chips as Cu_2O is dissolved more readily in the presence of chloride (Singha and Turner, 2009). Overall, the chronic water quality criteria was exceeded in 73% of samples analyzed ($n = 33$) and the acute water quality criteria was exceeded in 64% of samples analyzed. These data indicate that copper exposure especially in the lower Choptank estuary may be problematic for aquatic species which are 1 – 3 orders of magnitude more sensitive to copper concentrations than mammals (Flemming and Trevors, 1989). Contributions of Cu and other pollutants from marina areas are well documented in estuarine systems (e.g., Schiff et al., 2003). Boatyard permitting standards and best management guidelines have been developed to reduce pollution from copper and other boatyard products.

4. Conclusions

In many ways, the Choptank River estuary is similar to the larger Chesapeake Bay ecosystem. For example, both receive significant loads of nutrients from their headwaters and from wastewater treatment plants, both suffer from low dissolved oxygen levels in some regions during the summer months, and both receive inputs of herbicides and their degradation products throughout the year (USEPA, 2003, 2009a; Liu et al., 2002).

Over the course of thirteen synoptic sampling dates (March 2005 to April 2008), water quality in the Choptank River estuary appeared to be affected during the summer months by concentrations of high chlorophyll *a* and moderately low concentrations of dissolved oxygen, as has been reported by others in previous years (Fisher et al., 2006a). In addition, observed nitrate concentrations were highest in winter and often exceeded levels shown to contribute to phytoplankton growth. Consistently and significantly higher nitrate concentrations were observed at the headwater sampling stations, indicating that agriculture is the primary nitrate source for the estuary. Dissolved phosphorus concentrations did not vary over the length of the river, indicating a mix of loading sources, and some evidence points to the importance of wastewater treatment plants to phosphorus loading. The highest dissolved phosphorus concentrations were observed following several weeks of abundant rainfall, indicating residual stormflow effects. Concentrations of copper were consistently elevated in the lower

reaches of the estuary, with less than 90% of samples exceeding ecological levels of concern associated with toxicity to submerged aquatic vegetation. In the upstream reaches, however, observed copper concentrations were well below levels of concern, indicating that agriculture is not a primary source of copper loading to the estuary. It is postulated that copper loss from antifouling boat paints may account for the high observed copper concentrations.

Herbicides and their degradation products were present in detectable levels throughout the study, although observed herbicide concentrations did not approach established levels of concern for aquatic organisms, whether considering the parent compound alone or a combined concentration of parent and degradation products,. The highest concentrations of parent herbicides were observed during a strong early-summer seasonal peak that consistently appeared following springtime herbicide application on adjacent agricultural lands. The data also provide evidence that herbicide degradation products, along with nitrate, are released into the river headwaters via groundwater sources throughout the year, while parent herbicides and phosphorus are more likely delivered to the river by surface flow processes. The metolachlor degradation product MESA was conservative with dilution in the estuary, while the other herbicide degradation products showed varying degrees of transformation.

Contaminants leaving the Choptank River estuary will enter the Chesapeake Bay main stem and may affect water quality in the larger system. Results of this study point to the importance of continued implementation of best management practices to obtain and maintain water quality in the estuary. Effective practices will address reduction of nitrogen and phosphorus loss from farmlands, phosphorus loss from wastewater treatment plants, herbicide losses particularly during the springtime agricultural application period, and copper contamination from boats, marinas, and boatyards.

Results of this work emphasize the important role that simultaneous synoptic measurement of multiple water quality parameters and contaminant concentrations can play in creating a sufficiently clear picture of the primary water quality problems and dynamics within Chesapeake Bay tributaries and other estuaries. These resulting datasets can contribute greatly to the understanding of watershed dynamics, and can contribute to the development of effective strategies for improving water quality and overall ecosystem health. Furthermore, strategic intensive watershed sampling strategies that consider the effects of weather, landscape features, and agronomic practices will afford a more realistic assessment of pollutant sources and risks, and can provide information necessary for effective adaptive management of the Chesapeake Bay and its tributaries.

Disclaimer

Mention of specific products is for identification and does not imply endorsement by NOAA or the U.S. Department of Agriculture to the exclusion of other suitable products or suppliers.

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