Results of Water Chemistry Monitoring in Selected Steams in Monroe County, Indiana

Prepared for:

Monroe County Drainage Board
Monroe County, Indiana

Prepared by:

Todd V. Royer and Kristin M. Gardner
School of Public & Environmental Affairs
Indiana University – Bloomington

June 2009

Table of Contents

Summary..... 2

Introduction 3

Methods 3

Results and Interpretation 5

Tables 1-9 9-16

Figures 1-10 17-28

Summary

This report presents the results of water quality monitoring undertaken as part of the Monroe County Rainfall and Runoff project, funded in part by the Monroe County Drainage Board. Sampling sites were established on several streams in the Bloomington-Ellettsville area, including Clear Creek, Jack's Defeat Creek, Turtleback Creek, a small stream in Flatwoods Park, and the outflow from the Wal-Mart parking lot. Water samples were collected from October 2006 through February 2009 and analyzed for a variety of water quality parameters, including dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrate-N, and dissolved reactive phosphorus (DRP). Some sites were sampled for only a portion of the study period, and a focused examination of road salt runoff and in-stream chloride concentrations was conducted from September 2007 through March 2009.

DOC occurs naturally in streams due to leaching of soil organic matter and the decomposition of organic matter in the streams (e.g., senescent leaves and algae). DOC concentrations in the streams were within the typical range for temperate zone streams. The concentrations of TDN and nitrate-N at the various sites indicate that anthropogenic nitrogen loading is occurring, particularly during periods of wet weather. At all of the sites, inorganic nitrogen in the form of nitrate appeared to represent the bulk of the TDN. Occasionally DRP concentrations were > 50 $\mu g\ L^{-1}$ which could lead to excessive algal growth if such concentrations were sustained. However DRP concentrations were frequently below the detection limit of 5 $\mu g\ L^{-1}$. For example, more than 50% of the samples of drainage water from the Wal-Mart parking lot were below the detection limit for DRP. Overall, the DRP concentrations we measured do not indicate problematic phosphorus loading to the streams we examined, although continued urbanization could result in elevated TDN and DRP concentrations.

Chloride concentrations were highest during the winter seasons and peaked during winter storm events. Peaks during winter storms were dependent on many factors including antecedent weather conditions, precipitation form, amount, and timing, and air. Outside of winter storms, most of the streams had chloride concentrations < 30 $mg\ L^{-1}$. However, Clear Creek had higher baseline chloride concentrations than the other sites. Clear Creek had the highest winter chloride concentrations, and exceeded the U.S. EPA's 4-day recommended level five times and exceeded the 1-hour recommended level six times during the course of the study. Application of road salt is an important public safety measure, but in highly urbanized areas the use of road salt may be affecting salinity in streams that receive drainage from roadways and other impervious surfaces.

Water quality in the sites we examined tended to decline in response to precipitation, indicating that protecting water quality in these streams is mainly an issue of managing the quantity and quality of stormwater runoff.

Introduction

Throughout the U.S. water resources are increasingly stressed, both in terms of quantity and quality (Jackson et al. 2001). In much of the country, urbanization is creating changes in land cover such as conversion of forest and agricultural lands to residential and commercial areas. These land cover changes often involve an increase in impervious surface which can alter stream hydrology and geomorphology and also increase the runoff of pollutants (Paul and Meyer 2001). Impervious surface in a basin as low as 10% is adequate to cause a loss of ecosystem function and 30-70% impervious surface can cause "severe degradation", including runoff of nutrients and pollutants and reduced diversity of benthic invertebrate and fish communities (Klein 1979; Booth and Jackson 1997). As a result, streams in urbanizing landscapes could be at risk for ecological degradation.

As part of the Monroe County Rainfall and Runoff (MCRR) project, various water quality indicators were measured in Jack's Defeat Creek and Turtleback Creek from October 2006 to March 2009. Sampling sites at Clear Creek, Flatwoods Creek, and the Wal-Mart outflow east of the store were added in January 2008. The purpose of this monitoring was to provide insight into potential water quality issues in the basin and to complement the hydrological data being collected as part of the MCRR project. In addition, pharmaceutical compounds were measured in Jack's Defeat Creek, Turtleback Creek, at the Ellettsville Wastewater Treatment Plant effluent and downstream of the treatment plant on six dates from June 2008 to March 2009. This report provides a summary and interpretation of the water quality data collected during the project. The results of the hydrological portion of the study are presented in Linder (2009).

Methods

Site Descriptions – Three water chemistry monitoring sites were established within Ellettsville in 2006. Two monitoring sites were established on the main stem of Jack's Defeat Creek (JDC) with one site located upstream of Ellettsville (JDCU) and one downstream (JDCL) (Figure 1). The third Ellettsville site was located near the mouth of Turtleback Creek (TBC), a tributary to JDC (Figure 1). In addition to these sites, three sites were added in 2008: Clear Creek (CC) located off Gordon Pike in Bloomington, a small unnamed ephemeral stream (called Flatwoods Creek (FWC)) located within Monroe County's Flatwoods Park, and the outflow pipe draining storm water from Wal-Mart East (WM), located east of the store off Hickory Leaf Drive (Figure 1). These site selections allowed for a range of urbanization with FWC representing a relatively undeveloped area, the Ellettsville sites undergoing urbanization, and the CC site located in a highly urban environment. Finally, pharmaceutical sampling was conducted at JDCL, TBC, the Ellettsville WWTP effluent (WWTP), and in Jack's Defeat Creek approximately 700 meters downstream of the WWTP (JDCW) (Figure 2).

Land cover data were obtained from the 2001 National Land Cover Dataset and watersheds delineated and analyzed using ArcGIS. The sampling sites vary in land use and watershed size (Table 1). Clear Creek is the most urbanized site, with the majority of the land cover composed of developed land. The FWC site is >40% crop cover, with approximately 26% each of forest and pasture. The Ellettsville sites are mainly composed of forest and pasture; the JDC sites have <3% medium and high intensity development while the TBC site lacks medium and high intensity development. The JDCU and TBC sites are near Highway 46; TBC drains a mainly residential area. The JDCL site incorporates the land cover of both the upstream site and TBC, as these watersheds are sub-basins of the JDCL site. The JDCW site drains both JDC sites and the TBC site, in addition to receiving flow from the WWTP effluent. Watershed sizes ranged from 4.8 km^2 to 38 km^2; TBC is the smallest watershed while JDCW is the largest (Table 1).

Field Sampling & Laboratory Analyses

Samples for analysis of water chemistry and pharmaceutical variables were collected by hand from the center of the channel. Occasionally, water chemistry samples were collected with automatic samplers during winter storms. Samples were processed and preserved (if necessary) following standard methods (APHA 2005). Stream discharge (Q) was measured manually at the time of pharmaceutical sample collection. Spot measurements of water temperature, specific conductivity, and dissolved O_2 were made periodically using portable probes and meters. All probes and meters were calibrated on-site according to manufacturers' instructions.

In the laboratory, water samples were analyzed for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) using a Shimadzu TOC analyzer with TN unit. DOC was determined using high temperature combustion and the non-purgeable organic carbon method. Samples for nitrate-nitrogen ($N\text{-}NO_3$), dissolved reactive phosphorus (DRP) and chloride (Cl^-) were analyzed on a Lachat QuikChem 8500 flow injection analyzer. Chloride samples prior to September 2007 were analyzed using a Dionex ion chromatograph. Pharmaceutical samples were analyzed using liquid chromatography tandem mass spectroscopy at the University Hygienic Laboratory, Iowa City, IA.

Quality Assurance

Several procedures were used to maintain high-quality analytical results. Field duplicates were collected periodically to assess consistency in field methods. Precision of the various analytical instruments was assessed according to manufacturers' instructions. Additionally, commercially-certified standards for each water chemistry variable were purchased and routinely analyzed to assess instrument accuracy. Lastly, detection limits were calculated for each variable and values below the detection limit are reported as such. Detection limits were: Dissolved organic carbon (DOC): 0.1 mg L^{-1}; Total dissolved nitrogen (TDN): 0.03 mg L^{-1}; Nitrate-nitrogen (NO_3-N):

0.02 mg L^{-1}; Dissolved reactive phosphorus (DRP): 5 µg L^{-1}; Chloride (Cl^-): 0.6 mg L^{-1}. The detection limit for pharmaceutical and personal care products varied from 1-6 ng L^{-1} as determined and reported by the University Hygienic Laboratory, Iowa City, IA

Results and Interpretation

Tables 2–4 provide a summary of water chemistry measurements at the Ellettsville sites based on water years. A water year runs from autumn baseflow to the next autumn baseflow so that high discharge events during winter and spring are included in the same water year. For example, the 2007 water year runs from October 1st 2006 through September 30th, 2007. Results are presented for the 2007 and 2008 water years and part of the 2009 water year. Tables 5-7 provide a summary of water chemistry measurements at the other sites for the partial water years in which they were sampled.

Dissolved Organic Carbon (DOC) and Nutrients

DOC occurs naturally in stream water due to leaching of soil organic matter and the decomposition of organic matter in the streams (e.g., senescent leaves and algae). DOC concentrations are generally controlled by watershed characteristics and DOC itself typically is not considered a pollutant. However, DOC plays an important role in the formation of disinfection byproducts, such trihalomethanes and haloacetic acids. DOC concentrations in the streams were within the typical range for temperate zone streams (e.g., Mulholland 2003), with the temporal variation in concentrations (Figure 3) a response to precipitation.

TDN includes both dissolved organic and inorganic N, although preliminary determinations indicate most of the TDN in these streams is inorganic. Inorganic N is a critical plant nutrient and excess N loading can lead to eutrophication problems in N-limited streams. The concentrations of TDN in JDC and TBC indicate some N-loading to these streams, with concentrations at times exceeding 2.5 mg L^{-1} (Figure 4). The concentrations of TDN did not exceed 1 mg L^{-1} and NO_3-N concentrations did not exceed 0.7 mg L^{-1} at the Wal-Mart East outflow (Table 7). The concentrations of TDN averaged 1.5 and 1.2 mg L^{-1} at CC and FWC, respectively. The maximum TDN concentration at CC was 2.6 mg L^{-1} while FWC had a maximum concentration of 1.8 mg L^{-1}.

Nitrate-nitrogen (NO_3-N) concentrations occasionally exceeded 2.5 mg L^{-1} and routinely exceeded 0.5 mg L^{-1} (Tables 2-4, and Figure 5), which suggests the presence of anthropogenic N sources. Nitrate is a common component of fertilizers applied to lawns and agricultural lands and also can enter water ways from faulty septic tanks; each of these is a potential source of inorganic N in the Jack's Defeat Creek watershed.

Dissolved reactive phosphorus (also called soluble reactive phosphorus) is a critical plant nutrient and anthropogenic loading of DRP to surface waters can lead to nuisance algal blooms. The values for DRP reported in Tables 2-7 do not include numerous samples with DRP concentrations below the detection limit of 5 µg L^{-1}. For example, more than 50% of the Wal-Mart East samples analyzed for DRP were below the detection limit. Figure 5 shows the temporal distribution of all DRP measurements above the detection level at the Ellettsville sites. All sites with the exception of CC and WM had at least one sample > 50 µg L^{-1}; concentrations at CC and WM did not exceed 21 and 37 µg L^{-1}, respectively. As with inorganic N, fertilizers and faulty septic tanks are the likely anthropogenic DRP sources in the basin.

Conductivity and Road Salt Runoff

The complete study on road salt runoff to streams in Monroe County is presented in Gardner (2009). Here we provide a summary of the main findings.

Specific conductivity is a measure of total dissolved ions in the water. It is controlled primarily by the underlying geology of the basin, although it does respond to changes in anthropogenic inputs of ions, such as Cl^- from the runoff of road salt (see below). Mean values of specific conductivity for the sites were in the range of 300–1000 µS cm^{-1} at 25°C, with the lowest values at FWC and the highest at CC and Wal-Mart East.

The application of road salt (generally as sodium chloride) is an important public safety measure. However, it does have an environmental cost. Chloride can have both acute and chronic effects on aquatic organisms. In the northeastern U.S., long-term application of road salt has led to salinization of ground water, which in turn results in elevated chloride concentrations in streams even during summer baseflow (Kaushal et al. 2005). A chloride monitoring program was established in September 2007 for Jack's Defeat Creek that included routine sampling in all seasons and intensive sampling during winter storms and runoff periods. Monitoring at WM, CC, and FWC commenced in January 2008. Chloride concentrations were highest during the winter seasons and peaked during winter storm events (Figures 7 and 8). Peaks during winter storms were dependent on many factors including antecedent weather conditions, precipitation form, amount, and timing, and air temperature (Figures 9 and 10). Before and after winter storm runoff, chloride concentrations were typically < 30 mg L^{-1}. However, the most urban site, CC, had higher baseline chloride concentrations than the other sites. This higher baseline chloride concentration remained during the non-winter months.

Chronic toxicity for aquatic organisms occurs around 250 mg L^{-1}, with acute toxicity levels typically > 1000 mg L^{-1} but exact levels are species and life-stage dependent (Blasius and Merritt 2002). A 1988 EPA chloride criteria report suggests freshwater aquatic organisms and their uses should not be affected unacceptably if the concentration of dissolved Cl^-, when associated with Na^+, does not exceed a 4-d average of 230 mg/L more than once every three years on the average

or a 1-h average of 860 mg/L more than once every three years on the average (EPA 1988). Clear Creek exceed the 4-d recommended level five times and exceeded the 1-h recommended level six times during the course of the study, suggesting highly urbanized aquatic systems are at the greatest risk from road salt runoff.

Pharmaceutical and Personal Care Products

The occurrence of pharmaceutical and personal care products (PPCPs) in streams and rivers has become a topic of environmental concern, particularly in urban areas (e.g., Kolpin et al. 2004). Examples of these compounds include antibiotics, steroids, hormones, and over the counter drugs such as antihistamines and analgesics. As part of a separate project, we began to monitor water samples for these compounds using sites established as part of the MCRR project along with the effluent from the Ellettsville wastewater treatment plant (WWTP) and a site on Jack's Defeat Creek downstream from the effluent outfall. The full analysis of the data on PPCPs is on-going; here we present initial results that may be of interest to resource managers in Monroe County.

We screened for 15 compounds (Table 8) that included both human and animal antibiotics, as well as common human drugs, an insect repellent (DEET), and caffeine. There were 7 compounds that occurred in 50% or more of the 24 samples we analyzed (6 sampling dates X 4 sites). Two compounds were never detected (both animal antibiotics) and 3 other compounds that were detected only once or twice (Table 9). The WWTP effluent and the downstream WWTP site (JDCW) had the highest number of PPCPs detected in samples; however, TBC and JDCL, sites located upstream of any point sources, also had PPCPs in samples (Figure 11) indicating that non-point sources for these compounds exist within the Jack's Defeat Creek watershed.

Conclusion

The water quality in Jack's Defeat Creek, Turtle Back Creek, and Clear Creek was strongly linked to hydrology, particularly precipitation. Nutrient concentrations, winter chloride concentrations, and pharmaceutical and personal care product concentrations all increased in response to precipitation. This type of response indicates non-point sources for these pollutants, which is typical for urbanizing watersheds. Our results indicate that protecting water quality in these streams is mainly an issue of managing the quantity and quality of stormwater runoff. As urbanization continues in the Jack's Defeat Creek watershed, water quality in the stream is likely to decline if impervious surfaces contribute an increasingly greater fraction of the stormwater runoff.

Literature Cited

APHA. 2005. Standard methods for the examination of water and wastewater. 21st Edition. American Public Health Administration, Washington, DC.

Blasius, B.J. and R.W. Merritt. 2002. Field and laboratory investigations on the effects of road salt (NaCl) on stream macroinvertebrate communities. *Environmental Pollution* 120:219–231.

Booth, D.B., and C.R. Jackson. 1997. Urbanization of aquatic systems: Degradation thresholds, stormwater detection, and the limits of mitigation. *Journal of the American Water Resources Association* 33:1077–1090.

Environmental Protection Agency. 1988. Ambient aquatic life water quality criteria for chloride. Office of Research and Development Environmental Research Laboratory. EPA-440/5-88-001.

Gardner, K.M. 2009. The effects of urbanization and deicers on chloride concentrations in south-central Indiana streams and potential impacts on aquatic life. MS Thesis, Indiana University, Bloomington, Indiana. 114 pages.

Jackson, R., S. Carpenter, C. N. Dahm, D. M. McKnight, R. J. Naiman, S. L. Postel, and S. W. Running. 2001. Water in a Changing World. *Ecological Applications* 11: 1027–1045.

Kaushal, S.S. and others. 2005. Increased salinization of fresh water in the northeastern United States. *Proceedings of the National Academy of Sciences* 102:13517–13520.

Klein, R.D. 1979. Urbanization and stream quality impairment. *Water Resources Bulletin* 15:948–963.

Kolpin, D. W., M. Skopec, M. T. Meyer, E. T. Furlong, and S. D. Zaugg. 2004. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. *Science of the Total Environment* 328: 119–130.

Linder, G.A. 2009. Establishment of a hydrologic network and empirical rainfall-runoff modeling in a suburbanizing watershed in south-central Indiana. MS Thesis, Indiana University, Bloomington, Indiana. 115 pages.

Mulholland, P.J. 2003. Large-scale patterns in dissolved organic carbon concentration, flux, and sources. Pages 139–160 in: Aquatic Ecosystems: Interactivity of Dissolved Organic Matter (S.E.G. Findaly and R.L. Sinsabaugh, editors), Academic Press, New York.

Paul, M.J., and J.L. Meyer. 2001. Streams in the urban landscape. *Annual Review of Ecology and Systematics* 32:333–365.

Table 1. Monroe County, Indiana study site watershed characteristics and land cover. Wal-Mart East (WM) outflow* and the wastewater treatment plant (WWTP) effluent# were not included in land cover analysis.

Watershed Characteristic	Turtleback Creek (TBC)*#	Jack's Defeat Creek Upstream (JDCU)*	Jack's Defeat Creek Downstream (JDCL)*#	Clear Creek (CC)*	Flatwoods Creek (FWC)*	Downstream of WWTP (JDCW)#
Watershed Size (km^2)	4.8	17.5	27.0	20.8	9.3	38.0
Road Density (km/km^2)	5.0	4.3	4.8	10.9	2.1	4.3

	Land cover within watershed (%)					
Land Cover Type	**TBC**	**JDCU**	**JDCL**	**CC**	**FWC**	**JDCW**
Developed						
Open Space	12.9	9.7	11.7	28.5	4.6	9.5
20-49% Impervious Surfaces	1.7	4.0	3.7	27.9	0.3	2.3
50-100% Impervious Surfaces	0.0	2.4	1.9	22.1	0.2	1.4
Forest	42.4	39.8	40.7	13.8	26.3	47.7
Pasture	30.1	32.8	30.5	6.3	25.9	28.2
Crop	12.4	8.3	8.4	0.1	40.7	7.3

***Water Chemistry Site; #Pharmaceutical Site**

Table 2. Water chemistry summary for the Turtleback Creek site (TBC) during the study.

2007 Water Year	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	83	3.9	2.2	3.1	10.6
TDN (mg L^{-1})	83	1.3	0.4	1.3	2.5
NO_3-N (mg L^{-1})	27	0.6	0.4	0.5	1.4
DRP (µg L^{-1})	36	23	15	18	68
Cl^- (mg L^{-1})	27	20.8	40.5	10.7	218
Specific Conductivity (µS cm^{-1})	55	416	126	375	594

2008 Water Year	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	84	3.3	2.1	2.6	12.2
TDN (mg L^{-1})	84	1.5	0.7	1.6	3.0
NO_3-N (mg L^{-1})	69	1.3	0.8	1.4	3.0
DRP (µg L^{-1})	42	13	14	8	71
Cl^- (mg L^{-1})	167	24	29	14	181
Specific Conductivity (µS cm^{-1})	65	486	122	522	826

Oct 2008 – Mar 2009	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	10	2.7	1.9	1.8	6.4
TDN (mg L^{-1})	12	0.9	0.5	1.0	2.0
NO_3-N (mg L^{-1})	11	1.1	0.5	1.2	1.6
DRP (µg L^{-1})	6	26	26	17	75
Cl^- (mg L^{-1})	108	21	18	14	97
Specific Conductivity (µS cm^{-1})	16	453	138	500	610

Overall	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	177	3.6	2.2	2.8	12.2
TDN (mg L^{-1})	179	1.4	0.6	1.3	3.0
NO_3-N (mg L^{-1})	107	1.1	0.8	1.0	3.0
DRP (µg L^{-1})	84	18	16	13	75
Cl^- (mg L^{-1})	302	22	27	14	218
Specific Conductivity (µS cm^{-1})	136	454	129	489	826

Table 3. Water chemistry summary for the Jack's Defeat Creek upstream site (JDCU) during the study.

2007 Water Year	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	107	4.0	1.8	3.5	9.2
TDN (mg L^{-1})	107	1.3	0.3	1.2	2.2
NO_3-N (mg L^{-1})	35	0.5	0.3	0.5	1.1
DRP (µg L^{-1})	43	16	11	13	68
Cl^- (mg L^{-1})	38	38.2	83.5	18.3	505
Specific Conductivity (µS cm^{-1})	67	442	85	465	556

2008 Water Year	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	86	3.2	1.3	3.0	6.9
TDN (mg L^{-1})	85	1.4	0.7	1.4	3.0
NO_3-N (mg L^{-1})	70	1.2	0.8	1.2	2.9
DRP (µg L^{-1})	35	14	10	9	49
Cl^- (mg L^{-1})	145	81	138	29	856
Specific Conductivity (µS cm^{-1})	58	534	196	518	1,153

Oct 2008 – Mar 2009	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	10	3.0	2.4	2.2	9.2
TDN (mg L^{-1})	11	0.9	0.5	1.1	1.4
NO_3-N (mg L^{-1})	11	1.2	0.5	1.4	1.8
DRP (µg L^{-1})	6	13	7	11	27
Cl^- (mg L^{-1})	31	63	69	30	283
Specific Conductivity (µS cm^{-1})	13	433	108	455	660

Overall	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	203	3.6	1.7	3.2	9.2
TDN (mg L^{-1})	203	1.3	0.5	1.2	3.0
NO_3-N (mg L^{-1})	116	1.0	0.7	0.7	2.9
DRP (µg L^{-1})	84	15	11	12	68
Cl^- (mg L^{-1})	214	71	123	24	856
Specific Conductivity (µS cm^{-1})	137	480	151	472	1,153

Table 4. Water chemistry summary for the Jack's Defeat Creek downstream site (JDCL) during the study.

2007 Water Year	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	79	3.9	2.0	3.1	11.6
TDN (mg L^{-1})	82	1.3	0.4	1.3	2.2
NO_3-N (mg L^{-1})	27	0.6	0.3	0.6	1.1
DRP (µg L^{-1})	38	15	9	14	57
Cl^- (mg L^{-1})	42	48.3	114.8	16.1	715.0
Specific Conductivity (µS cm^{-1})	53	446	112	478	593

2008 Water Year	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	80	3.1	1.3	2.8	6.4
TDN (mg L^{-1})	80	1.5	0.7	1.5	2.9
NO_3-N (mg L^{-1})	64	1.4	0.9	1.3	3.8
DRP (µg L^{-1})	39	13	10	9	46
Cl^- (mg L^{-1})	184	105	140	51	920
Specific Conductivity (µS cm^{-1})	63	570	257	528	1,826

Oct 2008 – Mar 2009	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	9	2.6	1.4	2.4	5.4
TDN (mg L^{-1})	11	0.8	0.4	0.7	1.5
NO_3-N (mg L^{-1})	11	1.1	0.5	1.1	1.8
DRP (µg L^{-1})	5	15	8	14	26
Cl^- (mg L^{-1})	105	80	90	39	526
Specific Conductivity (µS cm^{-1})	15	543	208	486	980

Overall	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	168	3.4	1.7	3.0	11.6
TDN (mg L^{-1})	173	1.3	0.6	1.3	2.9
NO_3-N (mg L^{-1})	102	1.1	0.8	0.9	3.8
DRP (µg L^{-1})	82	14	9	12	57
Cl^- (mg L^{-1})	331	90	124	39	920
Specific Conductivity (µS cm^{-1})	131	516	211	488	1,826

Table 5. Water chemistry summary for the Clear Creek site (CC) during the study.

Jan 2008 – Mar 2009	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	28	3.1	1.2	2.7	7.3
TDN (mg L^{-1})	28	1.5	0.6	1.6	2.6
NO_3-N (mg L^{-1})	25	1.2	0.5	1.2	2.3
DRP (µg L^{-1})	15	13	9	10	37
Cl^- (mg L^{-1})	150	292	264	245	2,100
Specific Conductivity (µS cm^{-1})	52	1,146	753	940	3,564

Table 6. Water chemistry summary for the Flatwoods Creek site (FWC) during the study.

Jan 2008 – Mar 2009	N	Mean	Std Deviation	Median	Maximum
DOC (mg L^{-1})	23	6.7	2.4	6.0	13.1
TDN (mg L^{-1})	23	1.2	0.4	1.2	1.8
NO_3-N (mg L^{-1})	20	1.0	0.4	1.1	1.7
DRP (µg L^{-1})	20	40	44	22	140
Cl^- (mg L^{-1})	50	13	5	14	22
Specific Conductivity (µS cm^{-1})	27	236	98	253	383

Table 7. Water chemistry summary for the Wal-Mart East outflow site (WM) during the study; bd = below detection limit. Missing values indicate no measurement was made.

Date	DOC (mg L^{-1})	TDN (mg L^{-1})	NO_3-N (mg L^{-1})	DRP (µg L^{-1})	Cl^- (mg L^{-1})	Specific Conductivity (µS cm^{-1})
9-Jul-08	3.8	1.0	0.7	11	9	
30-Jul-08	6.2	0.2	0.1	7	8	130
24-Oct-08	8.2	0.9	0.7	21	63	361
15-Nov-08	4.7	2.0	0.4	6	12	171
10-Dec-08	2.9	0.1	0.3	bd	133	
15-Dec-08	3.6	0.2	0.4	bd	137	566
18-Dec-08	4.5	0.5	0.4	11	434	
5-Jan-09	3.6	0.2	0.2	8	256	
6-Jan-09	3.2		0.2		243	
7-Jan-09	4.4	0.1	0.2	bd	504	1,166
8-Jan-09	4.0	0.1	0.2	bd	800	2,657
8-Jan-09	4.2	0.2	0.2	bd	892	2,675
9-Jan-09					868	
11-Jan-09	5.3	0.3	0.3	bd	1,520	
7-Feb-09	6.9	0.5	0.4	bd	1,510	4,360
9-Feb-09	6.3	0.3	0.3	19	1,150	3,659
14-Feb-09			0.2	8	195	811
26-Feb-09	4.9	0.7	0.6	bd	382	1,340
11-Mar-09	6.8	0.4	0.3	bd	352	1,180
8-Apr-09	2.7	0.4	0.4	bd	35	225

Overall	DOC (mg L^{-1})	TDN (mg L^{-1})	NO_3-N (mg L^{-1})	DRP (µg L^{-1})	Cl^- (mg L^{-1})	Specific Conductivity (µS cm^{-1})
N	18	16	19	8	20	13
Mean	4.8	0.5	0.3	11	475	1,230
Std. Dev.	1.5	0.5	0.2	6	487	1,431
Median	4.4	0.3	0.3	9	304	818
Max	8.2	2.0	0.7	21	1,520	5,150

Table 8. Pharmaceutical and personal care products that were screened for in stream water and wastewater effluent samples between June 2008 until March 2009.

Product	Purpose
Acetaminophen	analgesic
Ibuprofen	analgesic
Caffeine	stimulant
1,7-Dimethylxanthine	caffeine metabolite
N,N-diethyl-m-toluamide (DEET)	insect repellant
Cotinine	nicotine metabolite
Carbamazepine	anti-seizure drug
Triclosan	antimicrobial
Trimethoprim	antibiotic (human)
Sulfamethoxazole	antibiotic (human)
Sulfadimethoxine	antibiotic (animal)
Sulfamethazine	antibiotic (animal)
Lincomycin	antibiotic (animal)
Tylosin	antibiotic (animal)

Table 9. The number of times various pharmaceutical and personal care products were detected in stream water and wastewater effluent samples.

Compound	Detections	% of Samples
Cotinine	22	91.7
Sulfamethoxazole	22	91.7
Caffeine	17	70.8
Acetaminophen	16	66.7
N,N-diethyl-m-toluamide (DEET)	13	54.2
Ibuprofen	13	54.2
Carbamazepine	12	50.0
Trimethoprim	11	45.8
Triclosan	8	33.3
Sulfadimethoxine	5	20.8
Lincomycin	2	8.3
1,7-Dimethylxanthine	1	4.2
Tylosin	1	4.2
Sulfamethazine	0	0.0
Sulfathiazole	0	0.0

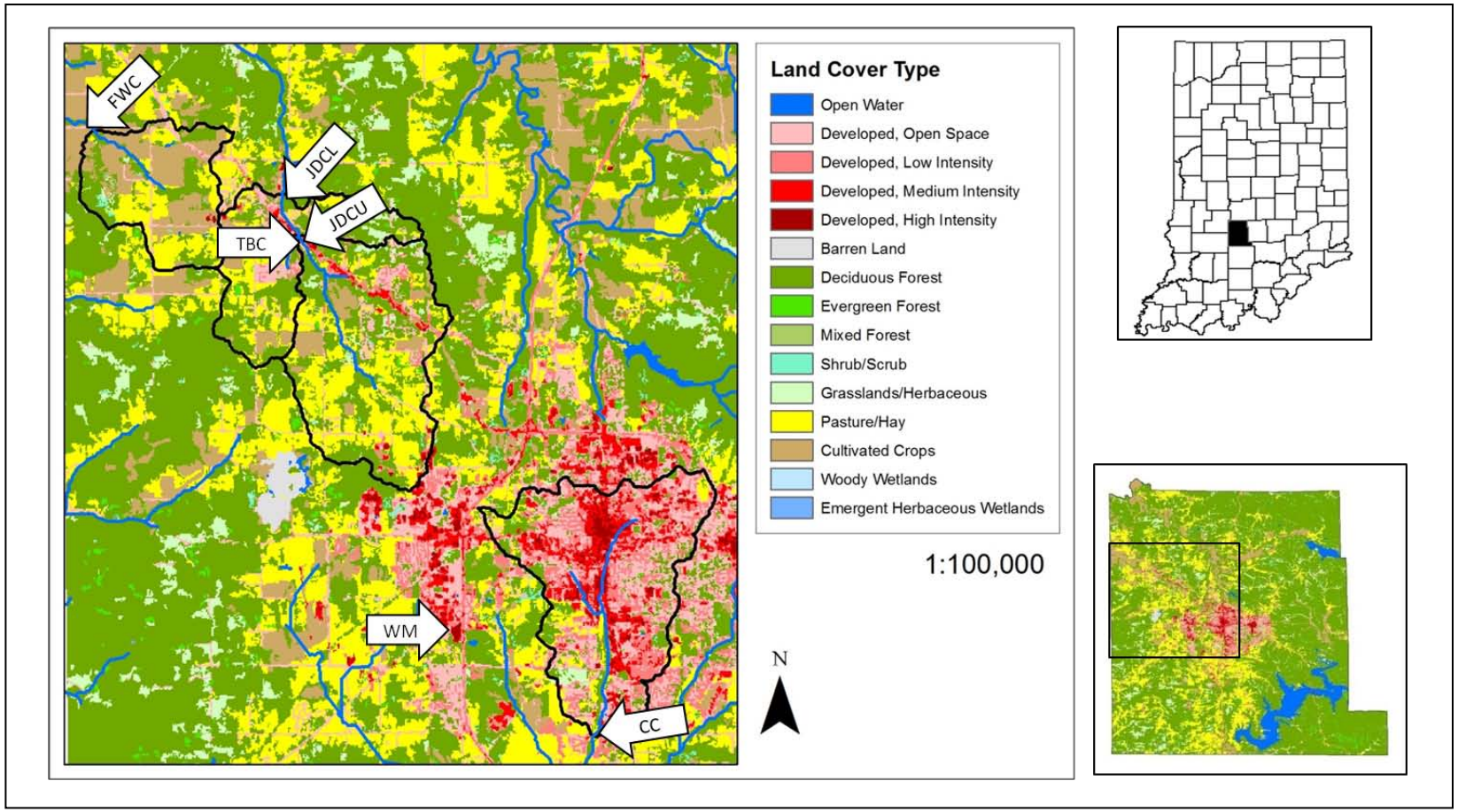

Figure 1. Water chemistry sampling sites (arrows), watershed boundaries (black lines), streams (blue lines), and land use within Monroe County, Indiana.

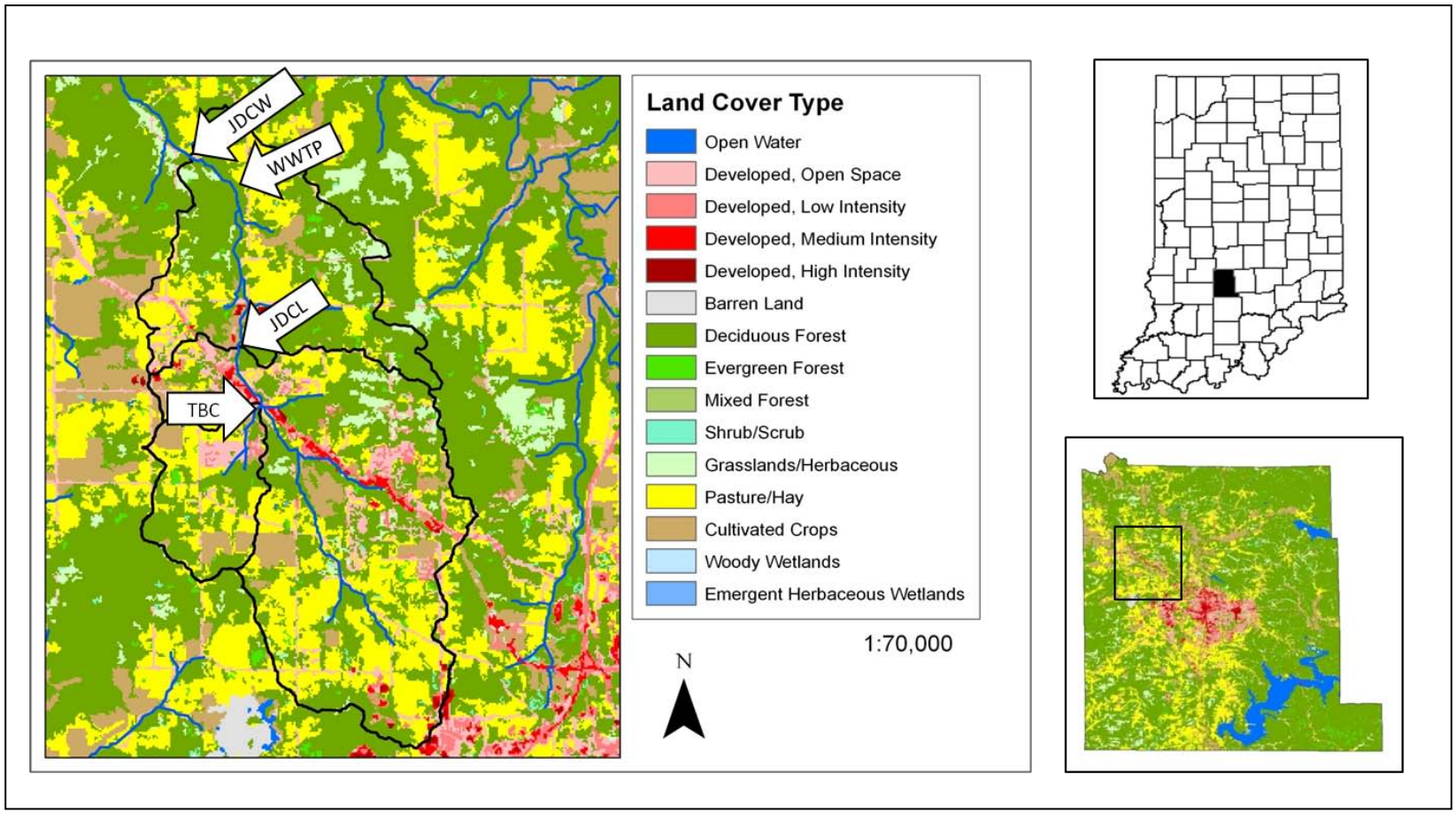

Figure 2. Pharmaceutical sampling sites (arrows), watershed boundaries (black lines), streams (blue lines), and land use within Monroe County, Indiana.

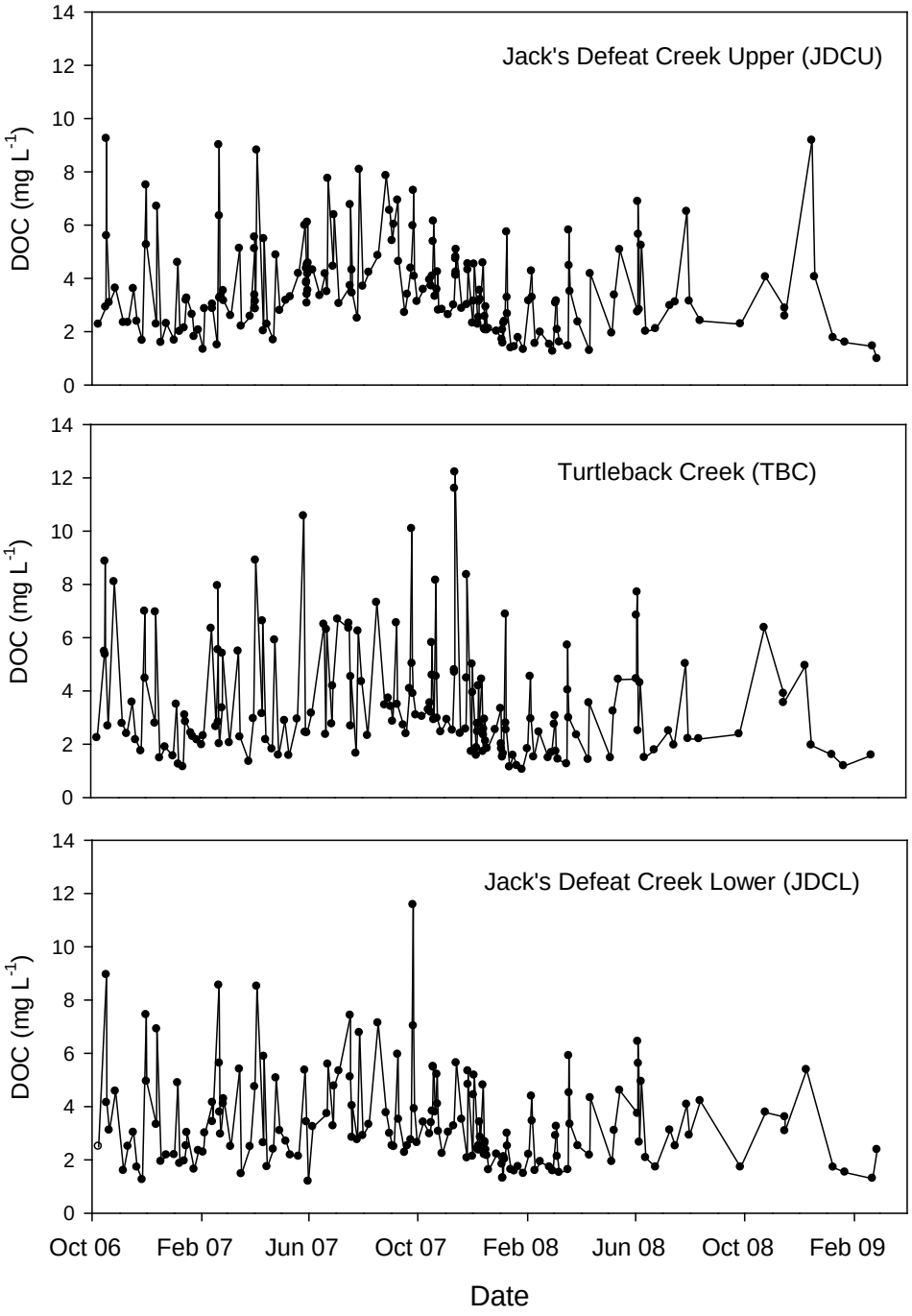

Figure 3. Temporal patterns in dissolved organic carbon (DOC) concentrations at three sites during the study.

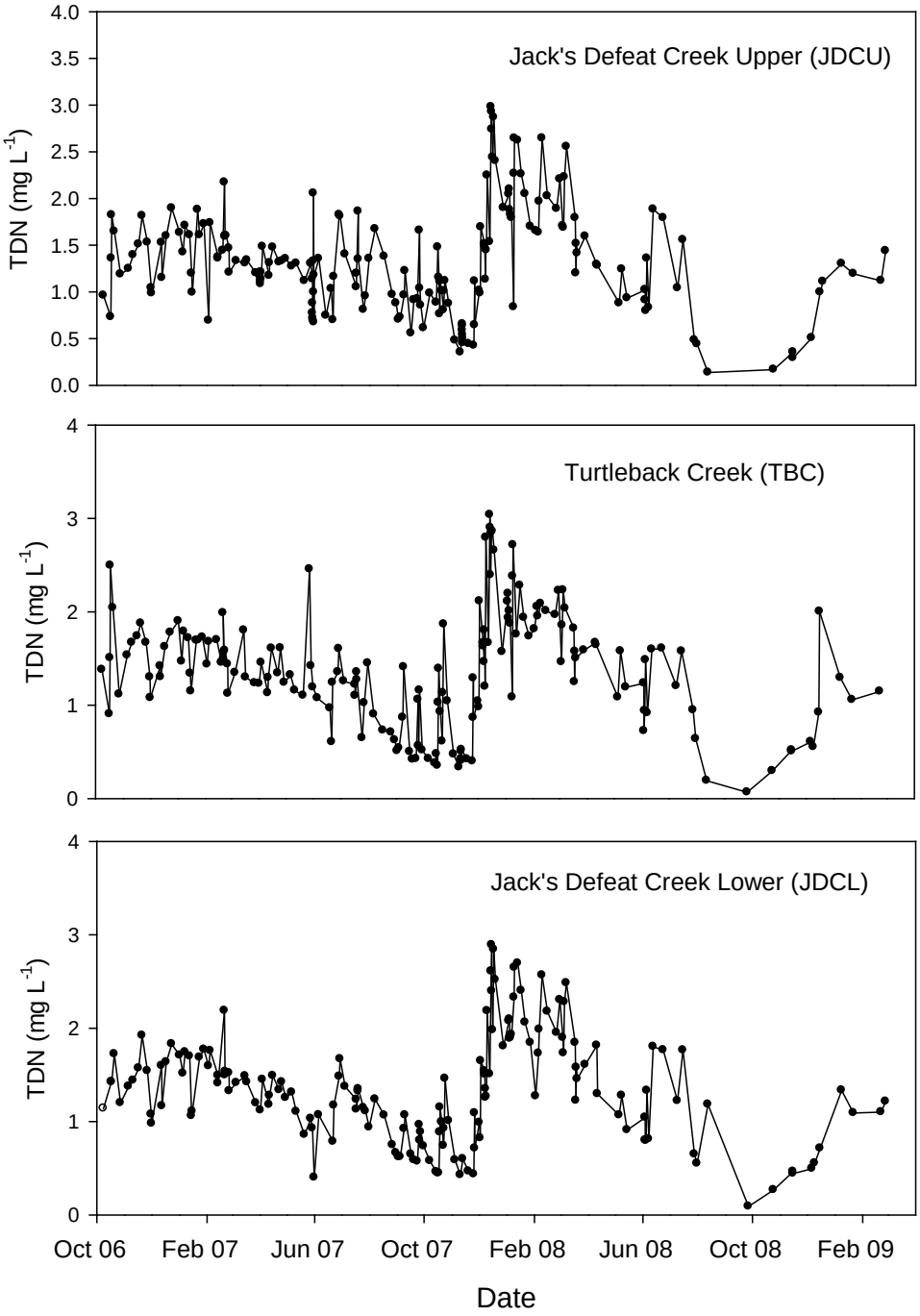

Figure 4. Temporal patterns in total dissolved nitrogen (TDN) concentrations at three sites during the study.

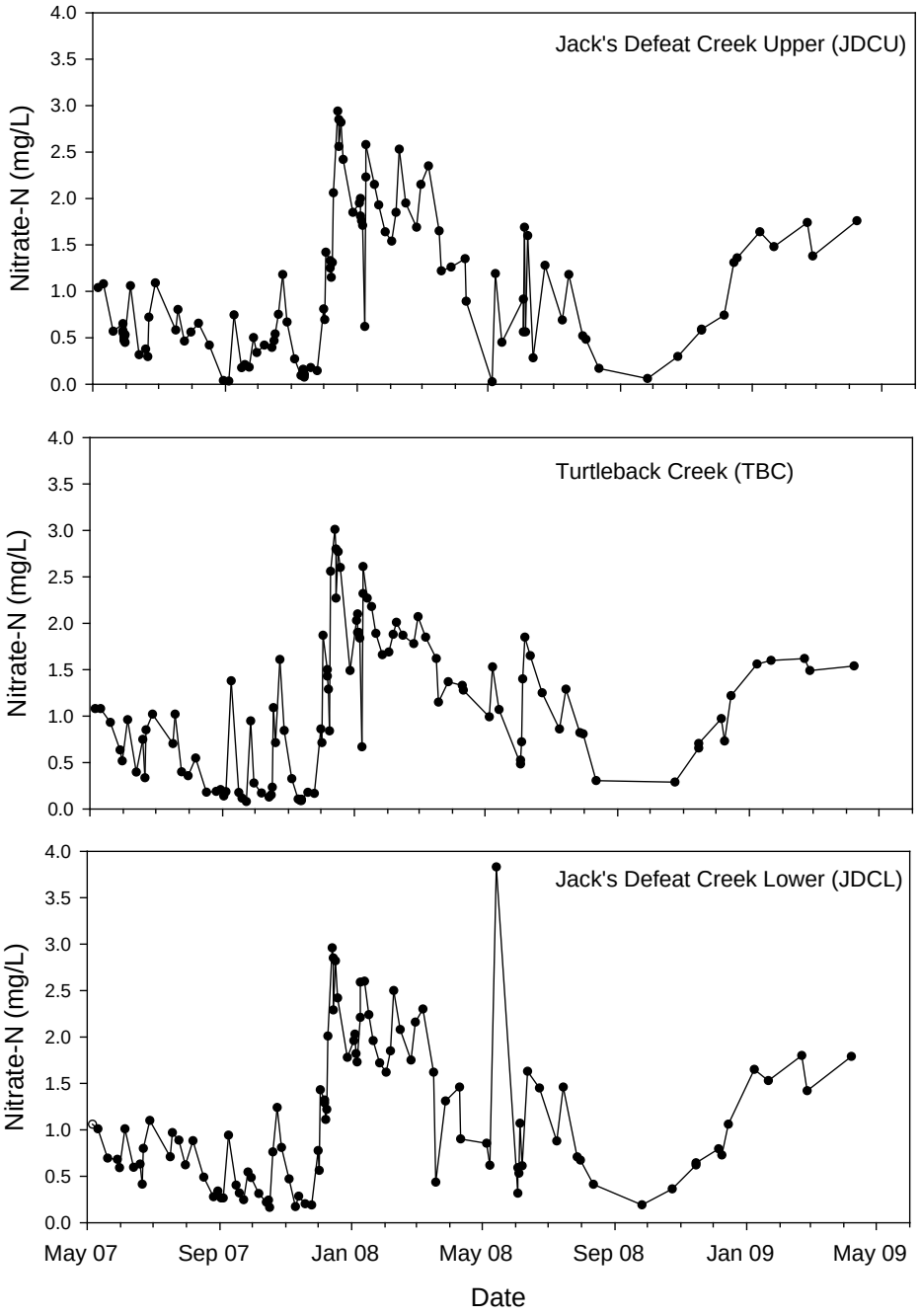

Figure 5. Temporal patterns in nitrate (NO_3-N) concentrations at three sites during the study.

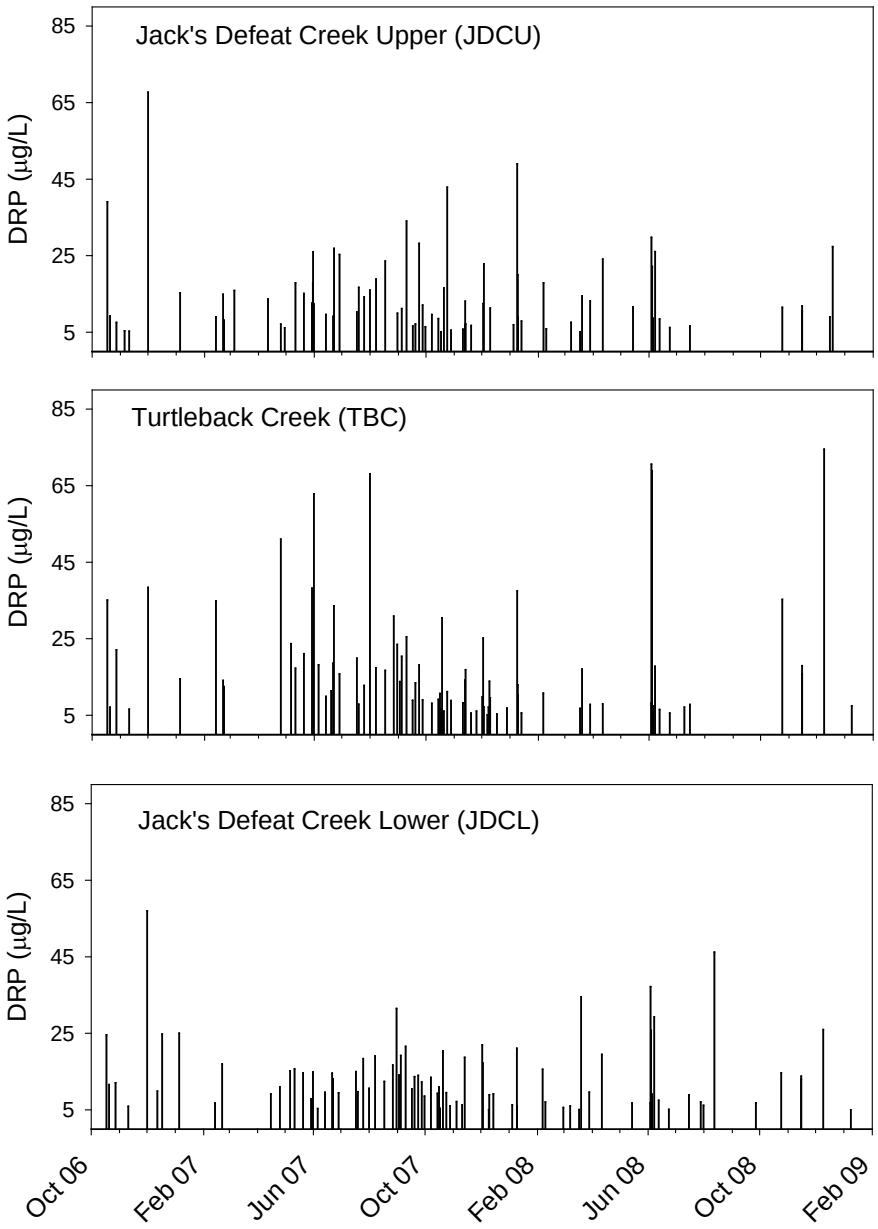

Figure 6. Temporal patterns in dissolved reactive phosphorus (DRP) concentrations at three sites during the study period.

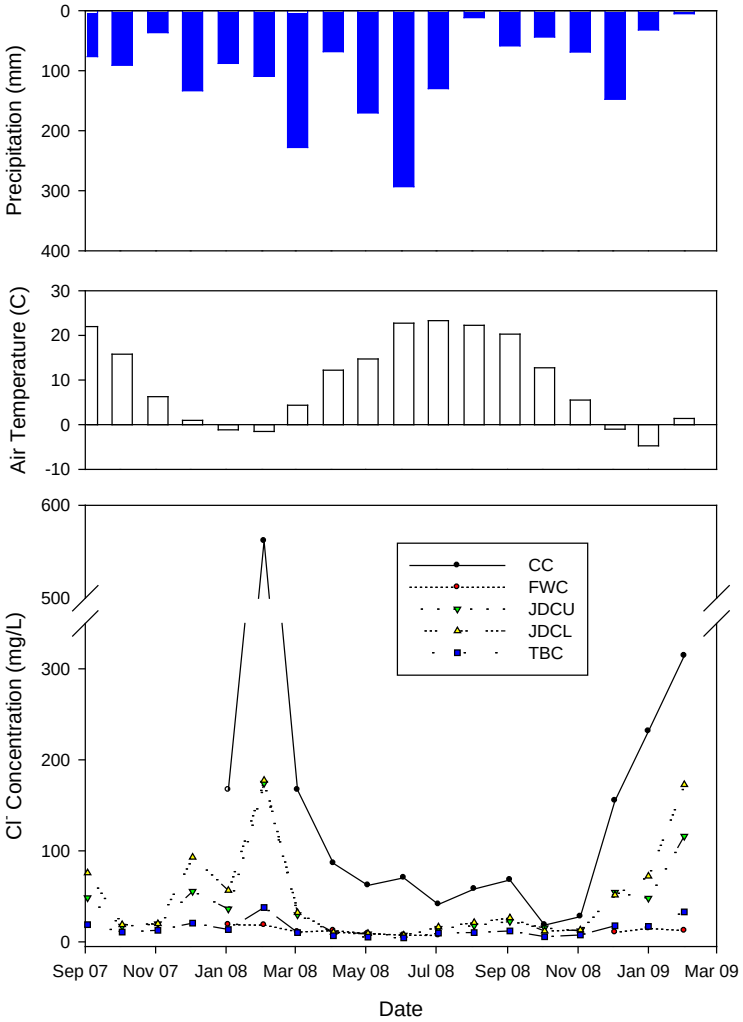

Figure 7. Average monthly precipitation (top), air temperature (middle), and mean monthly chloride concentrations at the study sites (bottom). Sampling at CC and FWC did not commence until January, 2008. FWC was dry during the late summer/early fall months.

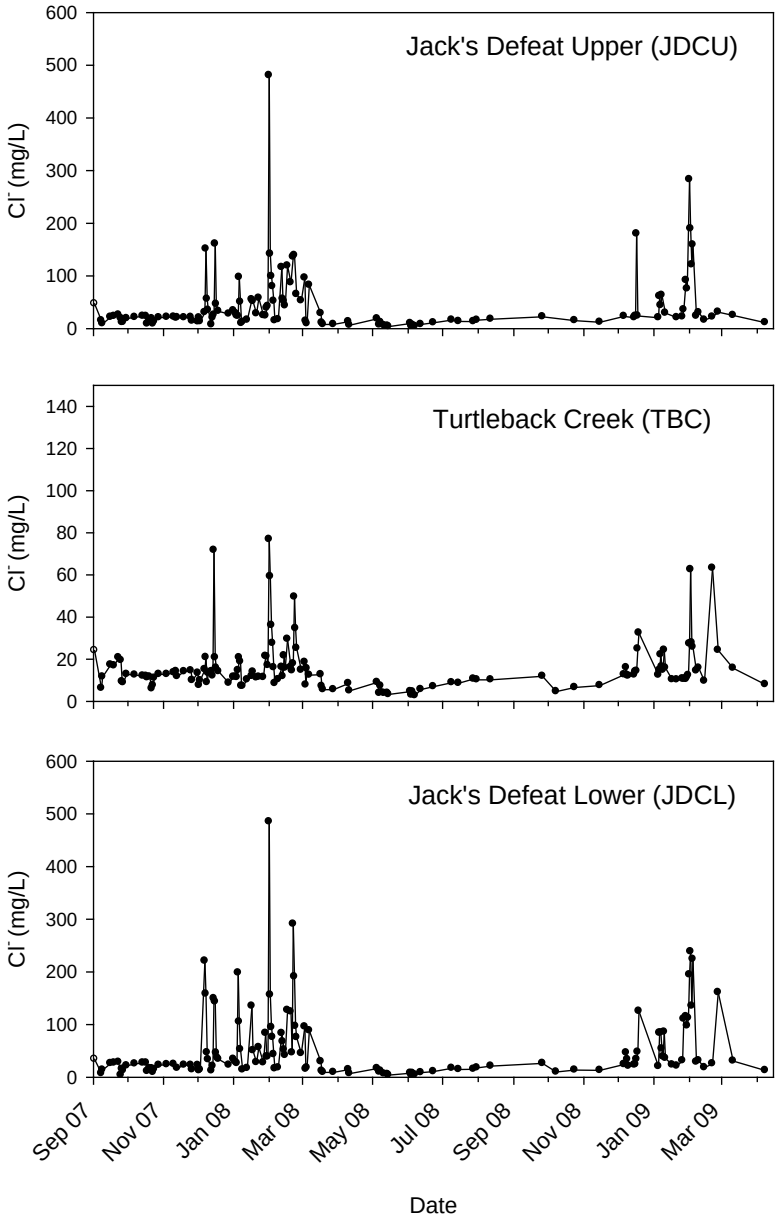

Figure 8. Average daily chloride concentration at the sites from September 2007 until April 2009. Chloride concentration symbols represent a single grab sample or, if more than one sample was taken in a day, the average concentration for that day. Note the difference in y-axis scale.

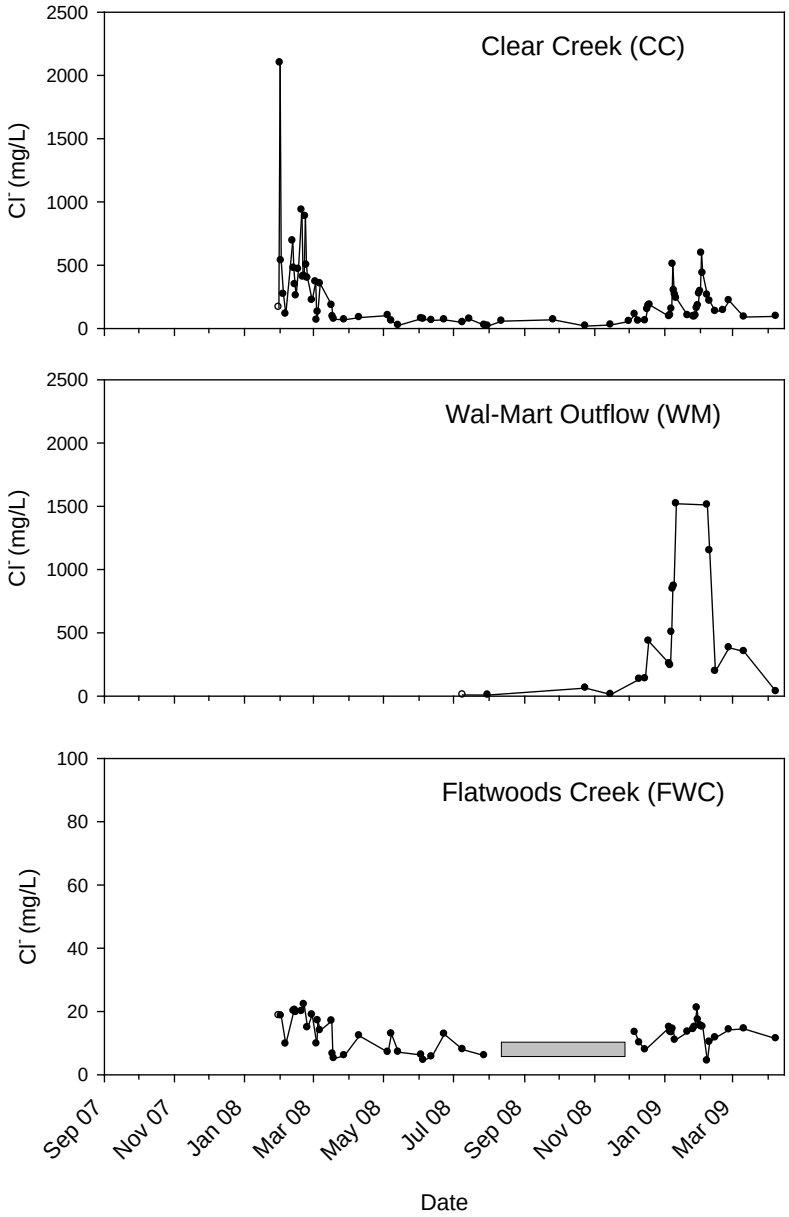

Figure 8 continued. Average daily chloride concentration at the sites from September 2007 until April 2009. Chloride concentration symbols represent a single grab sample or, if more than one sample was taken in a day, the average concentration for that day. The grey bar indicates when the stream was dry at the sampling site. Note the difference in y-axis scale.

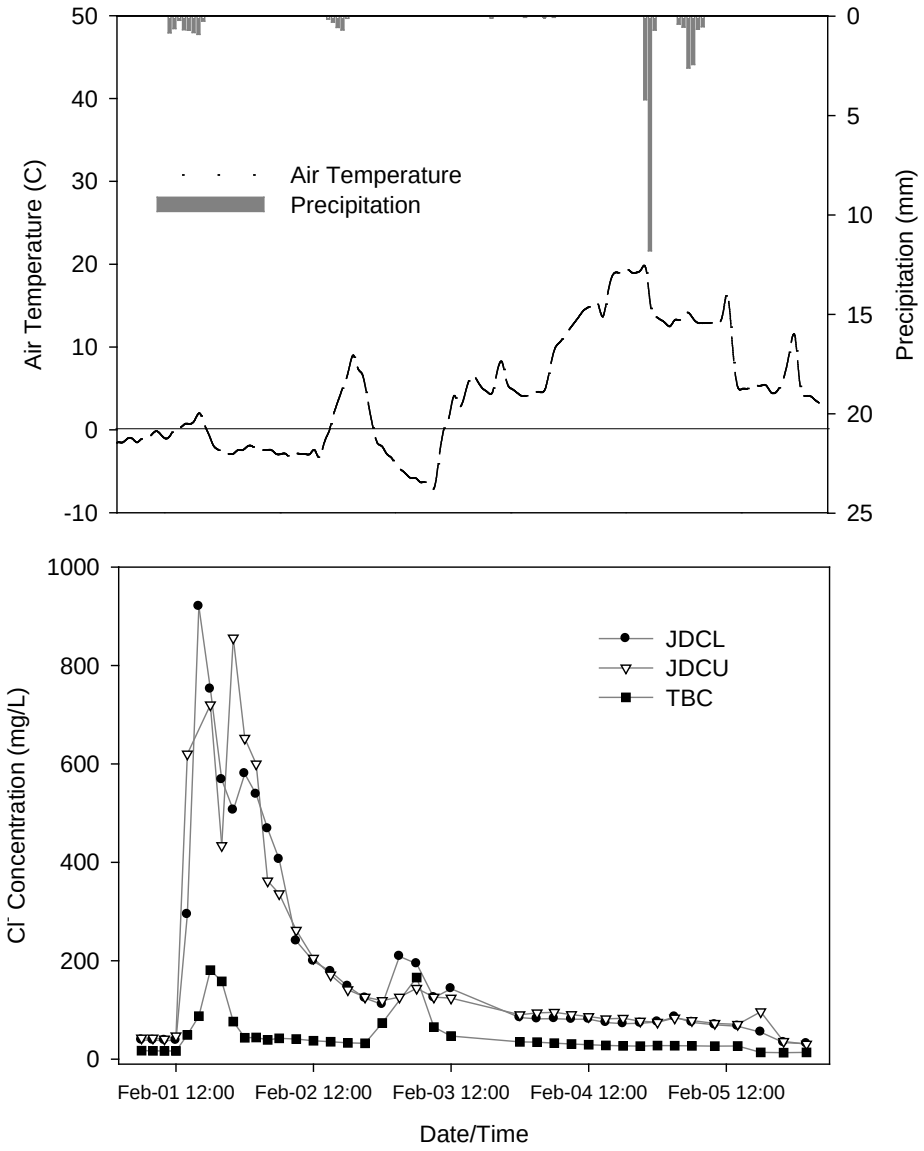

Figure 9. Detailed air temperature and precipitation (top) and chloride concentration (bottom) changes at three sites during a storm event from January 31-Februrary 5, 2008. The solid line indicates the freezing point (0°C).

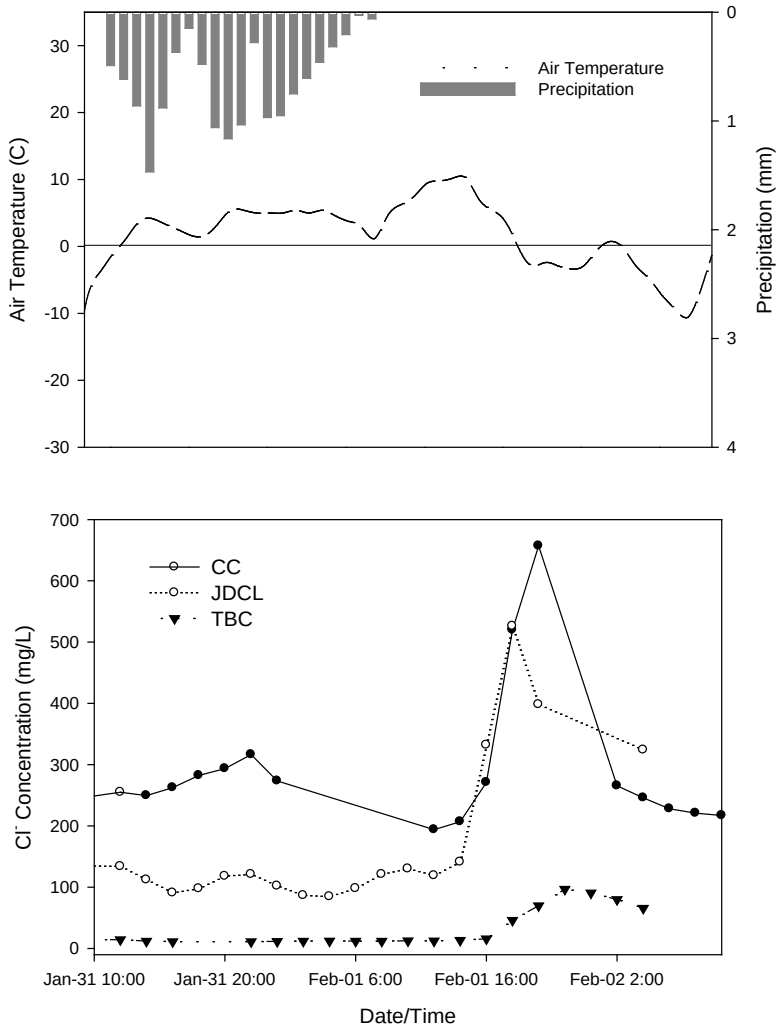

Figure 10. Detailed air temperature and precipitation (top) and chloride concentration (bottom) changes at three sites during a storm event from January 31-February 2, 2009. The solid line indicates the freezing point (0°C).

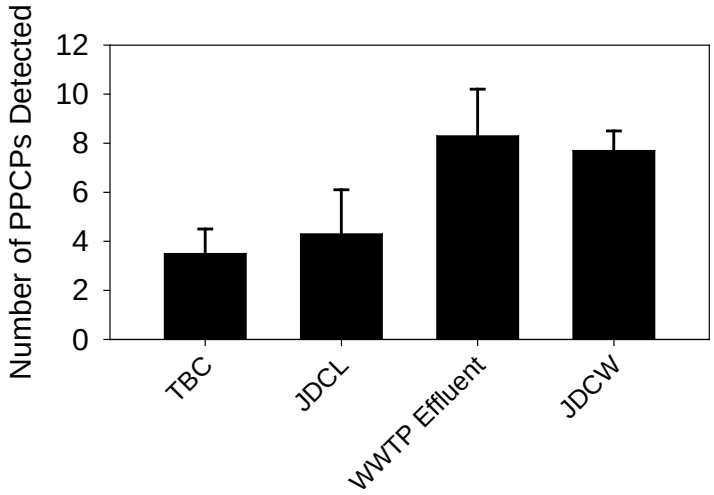

Figure 11. The average (+/- 1SD) number of pharmaceutical and personal care products (PPCPs) detected at the sites on six sample dates between June 2008 and March 2009 that varied in flow and antecedent precipitation.