

## **YEAR 2007 REPORT Introduction:**

The NMRWA strategic plan specifically requires that an appropriate program be created and executed to monitor environmental conditions and impacts of restoration efforts using accepted environmental standards and sampling protocols. Through the water quality monitoring program developed in the past year, we are working towards the following goals:

- Establish post-restoration baseline data on water quality in Nine Mile Run as determined by chemical indicators.
- Evaluate the data to determine sources and dynamics of primary pollutants in the water including nutrients and metals.
- Ascertain the influence of two different sewer systems, Combined Sewer Overflows (CSO's) and Sanitary Sewer Overflows, on the water quality of NMR
- Use baseline database to compare and contrast water quality conditions as future restoration efforts such as permeable paving, rain barrels, and tree planting are implemented.

Sampling parameters used as water quality indicators include the following:

- Metal cations: Sodium, Potassium, Silica, Strontium, Magnesium, and Calcium
- Trace metals: Nickel, Chromium, Manganese, and Cobalt
- Major anions: Nitrate, Nitrate, Chloride, Fluoride, Bromide, and Sulfate
- Stable isotopes of oxygen and nitrogen in nitrate, which are indicative of nutrient source.

Cation and anion analyses have been conducted on samples taken through the spring of 2008, and we expect to complete stable isotope analysis in the fall. Indicators of significant pollution are presented and discussed below.

### **Sampling Locations and Methods:**

In order to meet the goals describe above, we have begun a water quality sampling regime that targets specific regions of the stream (Figure 1). NMR 1 is located at the end of the concrete channel below the Braddock Avenue culvert where NMR first emerges from burial. NMR 2 is located approximately 30 meters downstream of a CSO inflow and 50 meters upstream of the Commercial Avenue crossing of Nine Mile Run. NMR 3 is located in Duck Hollow, where Nine Mile Run flows into the Monongahela River. Sampling at NMR 3 takes place above the first riffle in order to isolate the stream from the Monongahela River backwater. Two sites along the ephemeral Fern Hollow stream, are also sampled during periods of flow. FH 1 is located at the intersection of Nine Mile Run and Fire Lane trail in Frick Park. This is above the Fern Hollow meander/wetland constructed during the stream restoration. FH 2 is located at the mouth of the constructed meander/wetland just before it empties into NMR.

Water for various analyses is collected separately due to different preservation requirements. Water samples for nitrogen isotope analysis are filtered in the field and frozen until analysis. Bulk anion and cation samples are filtered in the lab within 24 hours. Cation samples are acidified and both anion and cation samples are refrigerated until analysis. Major cation analyses are completed on a Spectroflame Modula (FTM 08) axial inductively coupled plasma

atomic emission spectrometer (ICP-AES). Analysis of major anion concentrations (NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub>, SO<sub>4</sub>, Br, F, Cl, and PO<sub>4</sub>) are conducted on a Dionex ICS2000 Ion Chromatograph. For isotopic analysis, samples will be analyzed in a GV Instruments Isoprime Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS) equipped with a Gilson GX271 autosampler and a Trace Gas system.

Low-flow sampling was conducted biweekly for one full year in order to obtain baseline data including temporal and spatial variations in NMR water quality. High-flow, high temporal resolution samples were collected during a summer storm event at NMR 2 and these samples will be analyzed by the end of the year. Comparisons of high and low-flow contaminant fluxes allows characterization of CSO impacts, which are expected to contribute only during high flows, and SSO impacts, which, theoretically, should be absent in all flows. Water from the 13 piped inputs into NMR will also be sampled during subsequent stormflow events, and is expected to allow characterization of spatially variable inputs and determination of relative contributions of various sub-basins.

### **Results:**

In the late spring, summer, and fall of 2007 nitrate concentrations averaged ~6-7 mg/L (The Environmental Protection Agency drinking water standard for nitrate is 45 mg/L nitrate (2007)). During the winter and spring of 2008 average nitrate concentrations have been nearly double those observed in 2007, 11.01 and 13.12 mg/L, respectively (Figure 2). Increased average stream flows and nitrate fluxes are also higher in the 2008 samples analyzed to date (Table 1). Inter-annual variability in nitrate concentrations are evident in preliminary data (Figure 2).

Seasonal changes in chloride concentrations are highly significant in NMR. Winter average chloride concentrations exceed 1,400 mg/L and individual measurements exceeded 6,000 mg/L (Figure 4). (See discussion below for information on chloride toxicity to aquatic life.). Fluoride concentrations increase proportionately with nitrate concentrations, suggesting a similar source for each and that cross-sewer connections represent a significant source of contamination to the stream (Figure 5).

### **Discussion:**

Primary sources of nitrate in the NMR watershed are atmospheric deposition (from the burning of fossil fuels) and sewer (CSO and SSO) cross-connections with groundwater, yet the influence of each source is not well understood. We postulate that the large increase in average nitrate concentrations (~5mg/L higher in 2008) between 2007 and 2008 may arise due to two scenarios.

(1) During the winter and spring 2008 we have seen significantly increased precipitation and subsequent increases in stream base flow. This may increase nitrate concentrations via several mechanisms: a) Greater surface and sub-surface water flow potentially washes more atmospherically deposited nitrate into the stream from impervious surfaces; b) As soil water increases, greater amounts of stored nitrate may be dissolved and flushed into the stream; and c) Shallower water tables increase the potential for flow between sewers and groundwater.

(2) In the fall of 2007, portions of the streambed were re-worked and many smaller pools removed in favor of a few large, deep pools. The smaller number of larger pools potentially

creates fewer “denitrification hotspots” in the upper portion of the stream, and therefore results in higher streamwater nitrate concentration. (Denitrification is a microbially-mediated process that converts nitrate to N<sub>2</sub>).

Although both situations likely combine to contribute to the increase in nitrate, the following evidence suggests increased precipitation has a greater influence. Observed increases in nitrate levels are seen at every sampling location, including Fern Hollow above the confluence with Nine Mile Run (Figure 2). Increased nitrate levels, therefore, occur basin-wide and are not limited to the portion of the stream that was re-worked. Further evidence for increased stream and sewer interactions is increasing fluoride concentrations. Fluoride is added to Pittsburgh drinking water at ~1 mg/L. At this point it is not known to exist in the sedimentary rock found in the NMR watershed, although it may be present in the slag. As concentrations of nitrate increase, fluoride concentrations also increase, suggesting both are sourced from the same input (Figure 5).

Nitrate export from watersheds generally decreases during the growing season as vegetation increases nutrient uptake. Through 15 months of consistent sampling we have observed inter-annual variability in nitrate (Figure 2). However, without further data we cannot yet quantify how much seasonal variability is a result of nutrient uptake or if there may be an overall increase in nitrate due to increase precipitation in 2008. The extent of seasonal nutrient use may be either masked or amplified by the changing groundwater conditions throughout the watershed. Additional sampling through another several years, as well as clarification of nitrate sources via nitrogen and oxygen isotope data, will assist in defining seasonal and inter-annual variability in sources and amounts of nitrate.

Chloride inputs to the watershed include road salt, chloride dissolved in precipitation, and disinfectant used in public drinking water supplies. Chloride concentrations in NMR remain high through the year with extremely high concentrations in the winter (Figure 4). The seasonality evident in changing chloride concentrations through the year is expected due to road salt application in the winter. Chloride, although not a significant pollutant in small amounts, is toxic to fish in higher concentrations. The EPA National Aquatic Life Criteria for Chloride is 860 mg/L for acute (short-term) exposure and 230 mg/L for chronic (long-term) exposure (1988). Chloride concentrations in NMR are above chronic exposure limits (230 mg/L limit) throughout the year and commonly above acute exposure criteria in the winter. These high concentrations likely have substantial impacts on aquatic organisms in NMR and therefore, continued characterization of chloride concentrations is important.

### **Implications:**

There are currently no EPA standards on nitrogen inputs to surface water; however the EPA has established a Maximum Contaminant Level (MCL) of 44.3 mg/L NO<sub>3</sub> in drinking water supplies. On a year-round basis, concentrations in NMR are consistently one quarter to one third of this amount. The affects of accumulated nitrate in riverine and estuary systems include low dissolved oxygen, loss of species diversity, increased mortality of aquatic species, and general eutrophication of the waterbody. Moreover, as a tributary to the Monongahela River, water quality in Nine Mile Run ultimately affects the Mississippi River. In a 2007 report on water quality in the Mississippi River Basin the National Research Council (NRC) states “at the scale of the entire Mississippi River, including its effects that extend into the northern Gulf of Mexico,

nutrients and sediment are the two primary water quality problems... [N]utrients are causing significant water quality problems within the Mississippi River itself and in the northern Gulf of Mexico (2007).“ The export of contaminants from urban headwater streams such as Nine Mile Run therefore contributes to severe, large scale pollution problems. It is imperative to monitor changing nutrient dynamics as the restoration process continues and future restorations are implemented.

#### **Ongoing and Future Efforts:**

These preliminary results demonstrate the need for sustained water quality sampling. We intend to continue sampling indicators of stream water quality on a bi-weekly basis through spring 2009 at the previously identified locations. This will allow us to confirm seasonal trends noted so far and further establish post-restoration baseline data. Additionally, two high-flow events (one storm from summer 2008 and one from winter 2008-09) will be sampled in order to characterize pollutants entering the stream during storm events.

Additionally, the following laboratory analyses will be completed during the next year:

- Analyze archived water samples for trace metals (nickel, chromium, manganese, and cobalt, possibly more) arising from industrial pollutant sources.
- Complete a cross-section down the length of the streambed in order to delineate bed and pool depths for monitoring geomorphic change.
- Analyze the isotopes of nitrogen and oxygen in nitrate samples in order to identify nutrient sources and the scope of each to NMR.

After two years of baseline data is established, we suggest that future long-term monitoring efforts include:

- At least monthly sampling at each sampling location.
- Stormflow sampling once/twice a year (to capture nitrate and Cl patterns)
- One to five year resurveys of streambed elevation in order to monitor changes in bed and pool depths down the length of the stream.

#### References:

(1988). Ambient Aquatic Life Water Quality Criteria for Chloride. PB88-175 047. U. E. P. Agency. Duluth, Minnesota, US EPA Office of Research and Development.

(2007). Mississippi River Water Quality and the Clean Water Act: Progress, Challenges, and Opportunities. Washington, DC, National Research Council

(2007). Technical Factsheet on Nitrate/Nitrite: National Primary Drinking Water Regulations, United States, Environmental Protection Agency (USEPA).

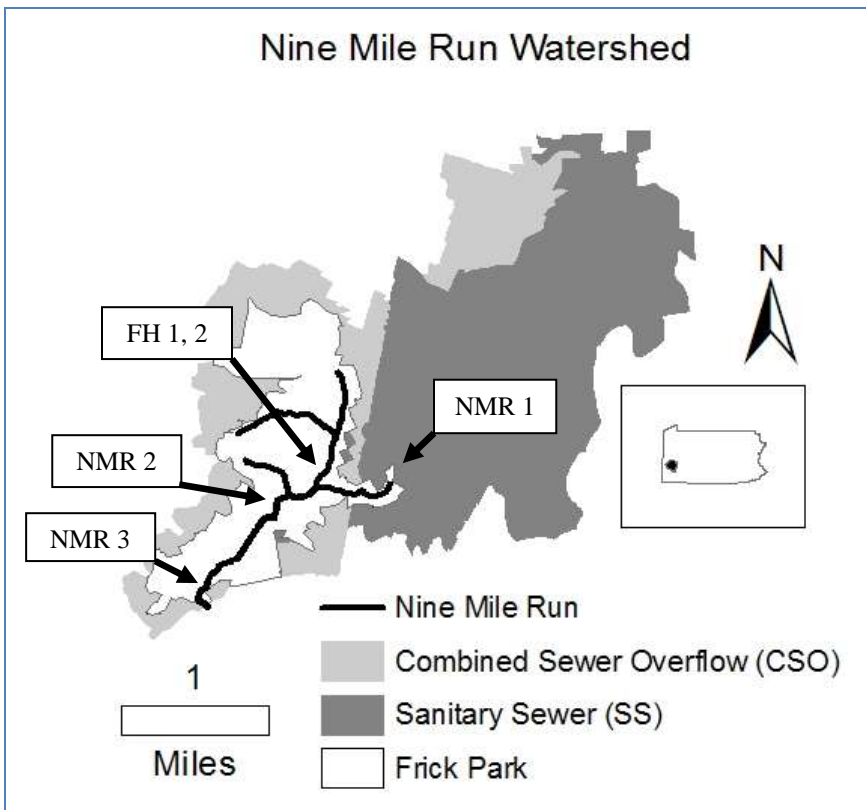


Figure 1: Map of sampling sites.

		Nitrate mg/L	Fluoride mg/L	Chloride mg/L	Discharge (m <sup>3</sup> /sec)
2007	April, May	7.97	0.69	359.45	0.141
	June-August	7.93	0.69	343.64	0.104
	Sept-Nov	6.12	0.51	363.10	0.050
2008	Dec-Feb	11.01	0.65	1466.35	0.203
	Mar-May	13.11	0.76	561.07	0.103

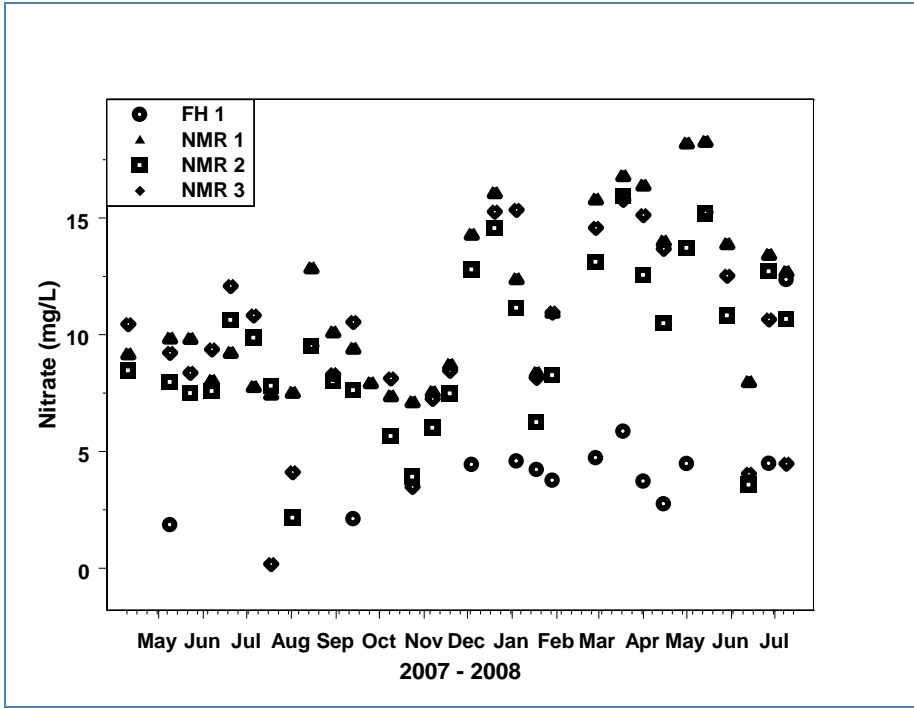


Figure2: Nitrate concentrations over sampling time period. Concentrations show increases at each sampling location beginning in mid-winter 2007 through the spring of 2008.

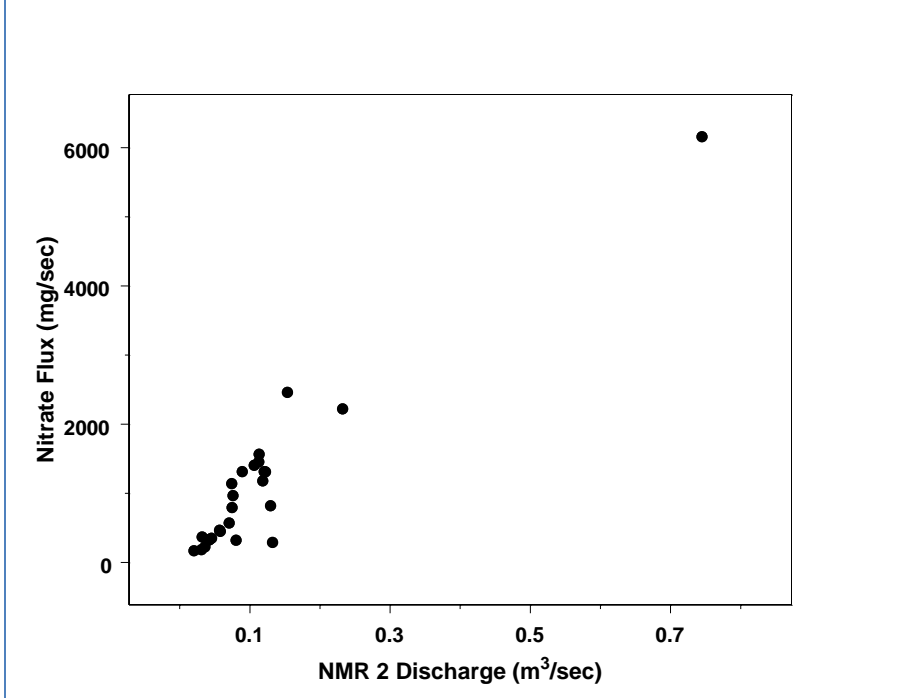


Figure 3: Nitrate flux and discharge. Flux, a representation of amount for each unit time, vary strongly with stream discharge.

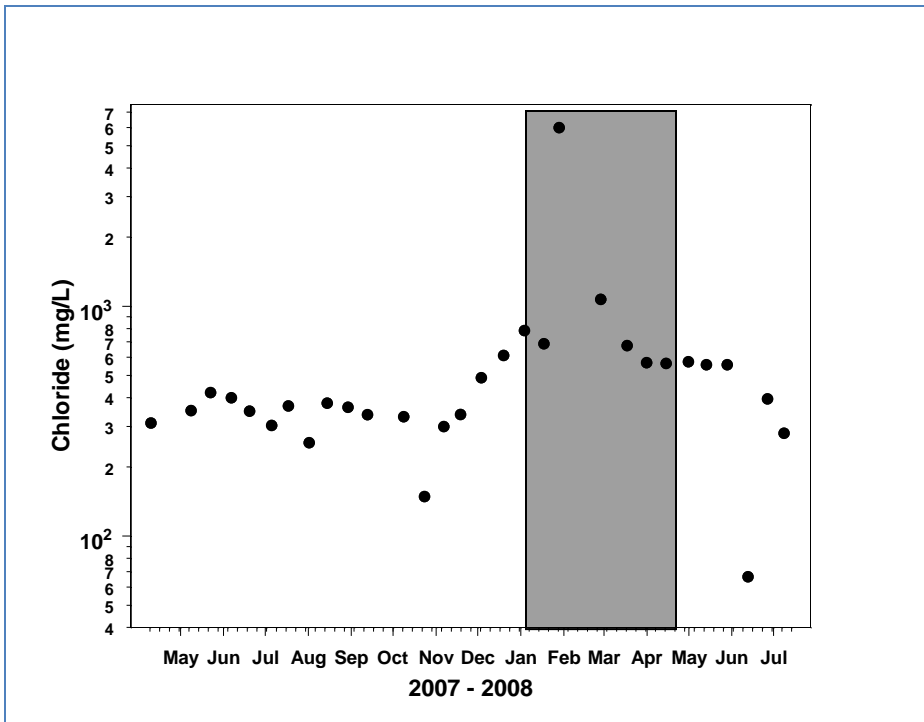


Figure 4: Chloride concentrations over sampling time period. Note that chloride concentrations are shown on a log scale. Shaded region indicates winter months. From December 2007 until June 2008, chloride concentrations are above the EPA acute criteria for chloride (860 mg/L ) and concentrations are commonly above the chronic criteria of 230 mg/L.

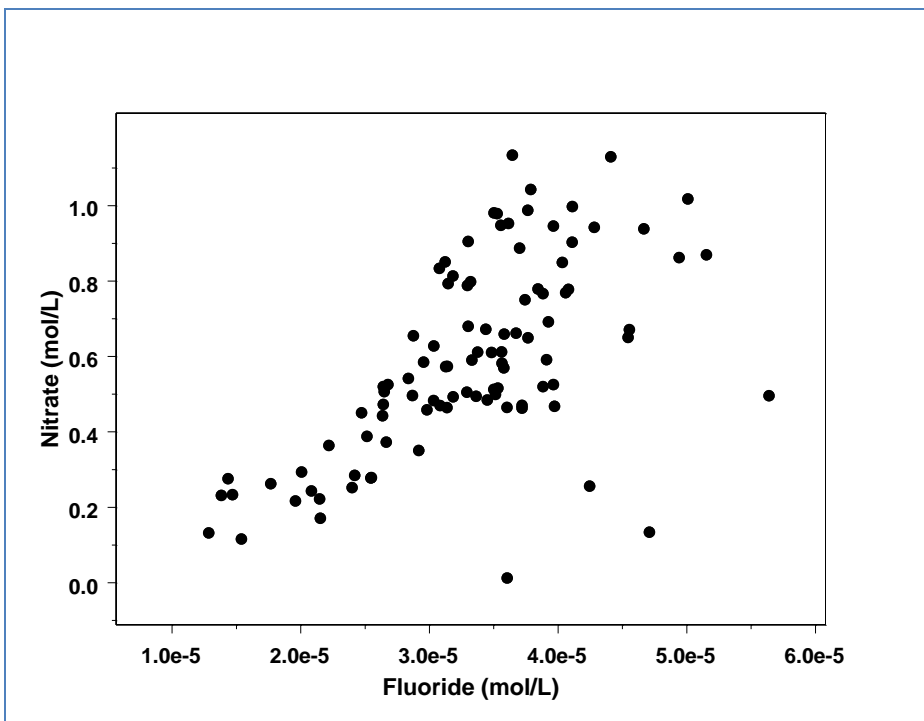


Figure 5: For all sampling locations, nitrate and fluoride molar concentrations vary proportionally.