

# **SOURCES OF ELEVATED CHLORIDE IN LOCAL STREAMS: GROUNDWATER AND SOILS AS POTENTIAL RESERVOIRS**

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*Abstract.* Salinization refers to an increase in the salt concentration of an environmental medium and can often be detected by rising concentrations of chloride (Cl). Researchers have documented increasing Cl concentrations in aquatic systems of rural northeastern United States for decades and multiple studies have correlated increasing Cl levels in surface water with increasing percent road cover and other impervious surfaces. This study examined the potential of groundwater and soils to act as reservoirs of Cl within the watershed of a stream in New York that has shown a doubling of Cl over the past two decades. Groundwater samples were obtained from private drinking wells in the catchment to determine whether concentrations were sufficiently elevated to contribute to the rising Cl levels in the stream. Soil cores from the catchment were irrigated with a NaCl solution for several weeks to examine the potential for Cl retention and release in common local soils. Most well samples had Cl concentrations lower than surface waters although a few elevated locations could act as sources. Soils retained a significant proportion of Cl from irrigation water and so could help explain high Cl during summer months.

## **INTRODUCTION**

Salinization refers to an increase in the salt concentration of an environmental medium, notably water and soil, and can often be detected by rising concentrations of chloride (Cl), an important anion of many salts (Kaushal et al. 2005). Chronic concentrations of Cl can have deleterious effects on the environment and water quality, and are consequently a growing environmental concern. Chloride concentrations as low as 250 mg/L are recognized as harmful to freshwater life (Office of Water, Regulations, and Standards, Criteria and Standards Division 1988), and chronic inputs of Cl are thought to negatively affect plants of wetlands and uplands (Bogemans et al. 1989; Richburg et al. 2001). Further, water becomes salty to the human palate at 250 mg/L and high concentrations of Cl are often associated with high concentrations of sodium, which are harmful to human health (Lewis 1999).

Until recently, rising salinity levels in surface water received little attention, despite documentation of this occurrence over several decades. Researchers have documented increasing Cl concentrations in aquatic systems of rural northeastern United States for decades (Rosenberry et al. 1999; Godwin et al. 2003) and multiple studies have correlated increasing Cl levels with increasing percent road cover and other impervious surfaces (Godwin et al. 2003; Kaushal et al. 2005; Peters & Turk 1981). Kaushal et al. observed winter Cl concentrations in northeastern U.S. streams up to 25% of the concentration of seawater, and also observed Cl concentrations up to 100 times greater than in streams draining forested watersheds.

Road deicing salts (principally NaCl) are likely the largest source of Cl to groundwater and surface water for most of the northern U.S. In 2002, New York State applied approximately 9.36 Mg/lane/km/day, averaging roughly 454 thousand Mg of road-salt annually (Godwin et al. 2003). Several studies have found and confirmed Cl concentrations as high as 14,000 mg/L accumulating in shallow groundwaters of the Metropolitan Toronto area, raising concern for local streams (Pilon and Howard 1987; Taylor et al. 1991).

Road-salt input to streams may occur via two pathways: surface water runoff, resulting in immediate Cl inputs, and delayed, longer-term inputs via soil permeation and eventually groundwater infiltration. The first pathway is detected by a rise of Cl levels in streams during winter months and early spring snow-melt events. The original assumption was that the majority of the applied road-salt would be washed out of catchments each season by

precipitation events and snow-melt. However, a study in the Duffin Creek-Rouge River basin in the Greater Toronto Area found that only 45% of the road-salt applied is removed by overland flow annually, and the remaining 55% enters temporary storage in shallow sub-surface waters (Howard and Haynes 1993).

Salt entering soils and groundwater may be retained for some period, contributing to surface water Cl much later in the season. Both soil retention and accumulation in groundwater may behave as reservoirs of Cl, acting as a sink and eventually a source of Cl in these systems. Research examining rising Cl concentrations in several New York State streams has revealed elevated Cl concentrations in summer baseflows, suggesting a constant input of Cl to the system, rather than via erratic precipitation events (Yozzo et al. 2005). If groundwater Cl concentrations were greater than surface waters, then stream recharge by shallow or regional groundwater might maintain high summer concentrations.

Soils within catchments may also function as a reservoir. Chloride is generally considered to behave conservatively in soils, moving through a system with little or no retention. Multiple studies, however, have found that significant amounts of Cl are retained in catchment areas (Lovett et al. 2005; Likens 1995). A recent study in Sweden has shown simultaneous retention and release of Cl, suggesting much less mobility of Cl in the soil profile than previously thought (Bastviken et al. 2006).

This study examined the potential of groundwater and soils to act as reservoirs of Cl within the watershed of a stream that has shown a doubling of Cl over the past two decades. We address both groundwater and soils, focusing on the following questions: (1) Are there elevated concentrations of Cl in local groundwater? (2) Is there retention or release of Cl in important soil types within the watershed? (3) Does soil type have an effect on the amount of Cl retained or released in soils?

## MATERIALS AND METHODS

### *Study Sites*

The study was conducted in the catchment of the East Branch of the Wappinger Creek (EBWC) in Dutchess County, New York (Figure 1). The catchment is characterized by deciduous forest (~55%) with mixed agriculture (29%) and low-density residential housing. The Village of Millbrook, NY operates a small wastewater treatment plant that discharges to the EBWC. The catchment area is 8655 hectares and the EBWC is 3rd order at the point of discharge to the mainstem Wappinger Creek. Mean annual discharge is about 1 m<sup>3</sup>/s ranging from a high of 2.5 in January to summer baseflow of 0.3-0.5 m<sup>3</sup>/s.

#### Surface and groundwater sampling

A longitudinal survey of the mainstem Wappinger Creek was conducted 1 August 2006. Surface water samples were obtained at 10 sites along a 54.5 km stretch of stream beginning near the headwaters of the EBWC and ending near its confluence with the Hudson River.

Surface water samples were obtained from the EBWC twice during the summer of 2006 (i.e., 15 June 2006 and 18 July 2006). Eight sites within the EBWC catchment were sampled, including locations above and below the sewage treatment plant. Water samples were collected using 125 mL polyethylene bottles.

Samples were unfiltered and stored cold until analysis of Cl by an ion specific electrode [ThermoElectron (Orion) 9717BN Chloride Electrode].

Groundwater samples (n = 20) were obtained throughout the EBWC catchment over a two-week period from private drinking water wells. Since most of these were collected by the property owner we do not know the precise well location, but all parcels adjoined the EBWC or one of its tributaries. Samples were collected immediately after the pressure tank where possible or from commonly used faucets as necessary. Owners were

asked to confirm that there was not a water softener before the point of sample collection. The wells were of unknown depths, ages, and recharge rates.

### *Soil retention experiment*

To examine the potential for Cl retention in common local soils we obtained cores from six sites and four different soil series representing two of the most common and two of the most distinct soil classes in the catchment including a common riparian soil (Table 1). Soil cores (n = 20, height = 15 cm) were collected in polyvinyl chloride (PVC) cylinders with an inner cross-sectional area of 20 cm<sup>2</sup>. Samples for characterization of water and organic matter content were collected at each site where soil cores were obtained. The PVC cylinders containing the undisturbed soil cores were stored in a refrigerator for 5 days and thereafter in a temperature controlled (10 °C) chamber. Cores were fitted with a bottom including a small hole for drainage. A small square of screen and approximately 1 cm of gravel that had been previously soaked and rinsed were placed in the bottom PVC end cap. Rubber stoppers were placed loosely on the top of the cylinders to limit evaporation.

The cores were irrigated every 5 days with 2.5 cm (52 mL) of artificial rain (i.e., 8 total irrigations). The amount of artificial rain corresponds to the weekly mean precipitation for spring and early summer. The chemical composition corresponds to local precipitation chemistry (Lovett and Hubbell 1991).

Cores were subjected sequentially to two different irrigation treatments. For the first four irrigation events (hereafter referred to as the NaCl addition period), enough NaCl was added to the artificial rain to bring the concentration to 643 mg/L Cl. The concentration corresponds to an approximation of the maximum amount of Cl present in highway runoff after a de-icing event in the catchment of the EBWC. For the final four irrigation events no NaCl was added to the artificial rain. After an irrigation the resulting leachate was collected for one hour and the amount of leachate was determined by weight. The pH of the leachate was determined and the samples were stored in a refrigerator until measurement of Cl.

One day after the final irrigation event, wet mass was determined for each core. Water content and loss-on-ignition (LOI) were determined for the reference samples that had been stored in a refrigerator during the incubation period. Dry mass of the incubated soil cores was estimated using the determined water content and the final wet mass of the cores.

### *Analytical procedures*

The concentration of Cl in the soil leachate and all surface and groundwater samples was determined using a ThermoElectron (Orion) 9717BN Chloride Electrode. Before each set of analyses the probe was calibrated with solutions of known Cl concentrations, prepared using NaCl and Nanopure™ water. An aliquot of the leachate or water sample (25 mL) was mixed with a stabilizing solution [5 M NaNO<sub>3</sub> (0.5 mL)] following the manufacturer's recommendation.

The water content was determined by drying a small portion of each reference soil sample to constant weight at 65 °C. Duplicate analyses were conducted for each reference sample. Small subsamples (4-7 g) were then combusted for 4 hours at 450 °C to determine organic content as loss-on-ignition.

The dry mass of the undisturbed soil cores was estimated by weighing the wet soil one day after the final irrigation and using the water content obtained from the reference samples to estimate the dry mass of the undisturbed soil.

Chloride retention in the incubated soil cores for irrigation events was calculated as:

$$Cl \text{ (mg)} = [vol. \text{ (L)} * conc. \text{ Cl (mg/L)}]_{IN} - [vol. \text{ (L)} * conc. \text{ Cl (mg/L)}]_{OUT} \quad (1)$$

This was calculated for each irrigation event and then summed over the NaCl addition and no-salt periods of the experiment. A one way analysis of variance (ANOVA) was used to evaluate whether Cl retention varied by soil type.

## RESULTS

### *Surface water and groundwater*

The longitudinal survey of the mainstem of Wappinger Creek revealed a doubling of Cl concentrations from the headwaters of Wappinger Creek to its confluence with the Hudson River (Figure 2). There was no significant increase in ambient Cl concentrations downstream of the sewage water treatment plant in Millbrook ( $P < 0.35$ ).

Of the 19 groundwater samples taken from wells in the EBWC watershed, only 4 samples had Cl concentrations above the lowest concentration found in the surface water of the EBWC during the two samplings (Figure 3).

### *Soil cores*

The organic matter content (LOI) of the soil samples ranged from 6% to 15%, while the water content ranged from 19% to 44%. The riparian soil had the highest water content.

Each soil core received 416 mL of artificial rain during the entire experimental period, which corresponds to 52 mL per irrigation event. The volumes of leachate leaving each core for the first irrigation event ranged from 14 to 37 mL. The volumes of leachate leaving each core for the final seven irrigations were higher, with a range of 42 to 50 mL. The cumulative amount of leachate leaving the cores during the NaCl addition period ranged from 143 to 172 mL, while the second treatment period had a range of 174 to 196 mL.

The Cl concentration in irrigation water over the first four events was 643 mg/L and the mean across soils for leachates was 520 mg/L (Figure 4). The mean % Cl retention for this period for all groups was 39.9% (Table 2). The amount of Cl added to each soil core as artificial rainwater during the NaCl addition period was 134 mg Cl. The amount of Cl retained after the NaCl addition period ranged from 35 to 80 mg. (Table 2). The percentage of total Cl retention per dry weight of soil after the NaCl addition period varied by soil type ( $P < 0.0003$ ).

After the final four irrigation events in which no additional Cl was added, Cl concentrations in the leachate ranged between 52.7-191.5 mg/L, with a mean of 103.34 mg/L (Figure 4). The soil cores still retained, on average, 0.103 mg Cl / g dry soil (Table 2). The soil cores released an average of 62% (range of 33-93%) of the Cl that had remained in the cores after the NaCl addition period.

Soil type had an effect on Cl behavior in the soil cores (Figure 4). The amounts of Cl retained in the soil cores after the NaCl additions were affected by soil type ( $P < 0.0003$ ). Soil type also affected the total amount of Cl retained after all irrigations events ( $P < 0.0135$ ).

## DISCUSSION

The longitudinal survey of the mainstem Wappinger Creek revealed a significant downstream increase in Cl (Figure 3) suggesting an input of Cl as water moves down the channel. This suggests the presence of a reservoir of Cl in the watershed contributing to the rising ion concentrations during summer.

The source could be either a point or non-point source in the EBWC watershed. Sewage treatment plants are a potential point-source of excess Cl. However, there was no significant increase in Cl concentrations below the sewage treatment plant in Millbrook. The majority of Cl loading to the EBWC is attributed to road deicing salts, but being the middle of the summer, there were no road salt-contaminated surface flows to the stream.

Acknowledging that most of the Cl is derived from road salt, there is likely one or more reservoirs that are retaining Cl during the period of road salt applications and gradually releasing Cl after this period.

As we hypothesized earlier, one potential reservoir for Cl in the watershed is groundwater. Out of the 19 groundwater samples from drinking wells within the watershed, only 4 of them were above or within the range of ambient Cl concentrations in the stream (Figure 3). If groundwater were the source, the concentrations should be above stream concentrations. These results however cannot unequivocally rule out high Cl groundwater in the watershed since we do not know the depth or aquifer contributing to the various wells. If groundwater is indeed behaving as a reservoir for Cl in the system, the likely source is shallower groundwater.

Our other hypothesized reservoir of Cl in the system is the soil. The common assumption, however, is that Cl is highly mobile in soils (i.e., soils do not retain Cl) and therefore, Cl is often used as a tracer in soil water and groundwater. This belief is currently being questioned (Bastviken et al. 2006; Lovett et al. 2005; Oberg & Sanden 2005; Rodstedth et al. 2003). The experiment shows that soils in the EBWC may behave as a temporary reservoir of Cl. This is consistent with several other studies using similar irrigated soil core experiments (Bastviken et al. 2006; Rodstedth et al. 2003). There was net retention of Cl ranging between 26 and 60% after NaCl and artificial rain irrigations to the incubated soil cores. After the initial irrigation events, a minimum of 80% of the irrigation water was recovered after each event, indicating that the majority of the soil water in the cores was replaced during each event. Therefore, Cl retention was not simply incomplete flushing.

During the final four irrigation events (no NaCl) the soil cores behaved as sources and released the Cl. The crucial result is that not all of the Cl was released after this first “rinsing” event (Figure 4). Further, the soil cores required four “rinsing” events (a cumulative water input approximately equivalent to four weeks of rain in the watershed) to flush out more than half of the previously retained Cl. Even after these four events the recovered leachate concentrations were above summertime ambient stream concentrations for Cl.

These results suggest soil retention and gradual release may act as the temporary reservoir and source of Cl linking wintertime salt applications with summertime surface water concentrations. The groundwaters sampled from the various drinking water wells did not consistently contain sufficient Cl to maintain summer stream Cl.

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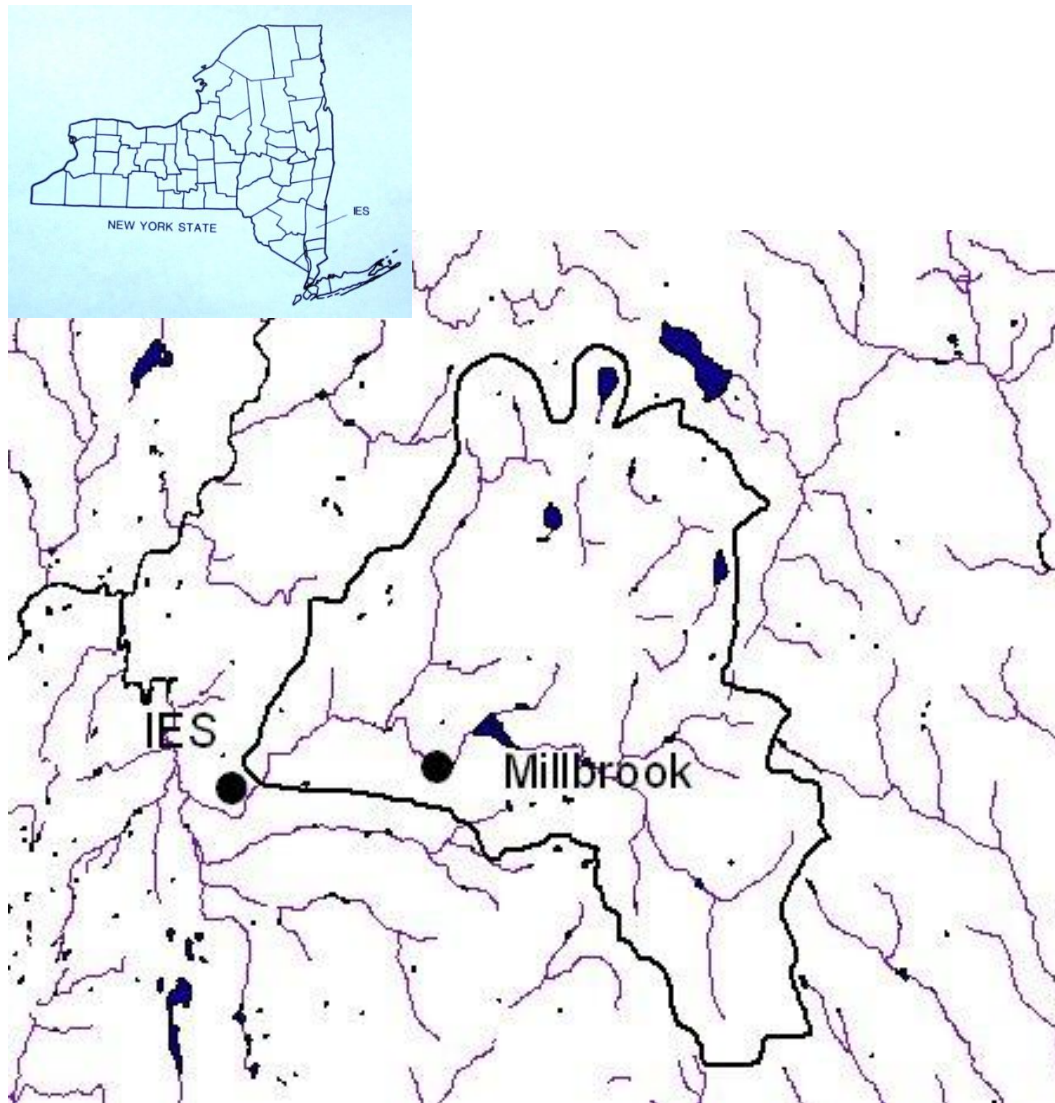
## APPENDIX

**TABLE 1. Soil core sample descriptions** Soil series classifications are according to Dutchess Co. Soil Survey Users Guide (1991). Musym is the map unit symbol used to classify the soils in the soil survey.

Soil Core	Soil Series	Musym	Mean H <sub>2</sub> O Content (%)	Mean OM (%)	Notes
1-9	Hoosic	HsA	30.8	14.6	Three sets of samples were obtained in a gradient moving away from a major roadway. Each sample set was taken approximately 10 meters apart, beginning 10 meters from the shoulder of the roadway.
			21.7	7.4	
			20.6	7.9	
10-11	Dutchess-Cardigan	DwC	22.21	5.87	This soil series was sampled in two separate locations.
12-13	Dutchess-Cardigan	DwC	27.79	9.53	
14-15	Nassau-Cardigan	NwD	34.69	13.85	This soil series was sampled in two separate locations.
16-17	Nassau-Cardigan	NwD	24.18	7.33	
18-20	Fluvaquents-Udifluvents	Ff	43.23	15.07	This soil series was sampled at approximately 10 meters from the East Brach of Wappingers Creek.

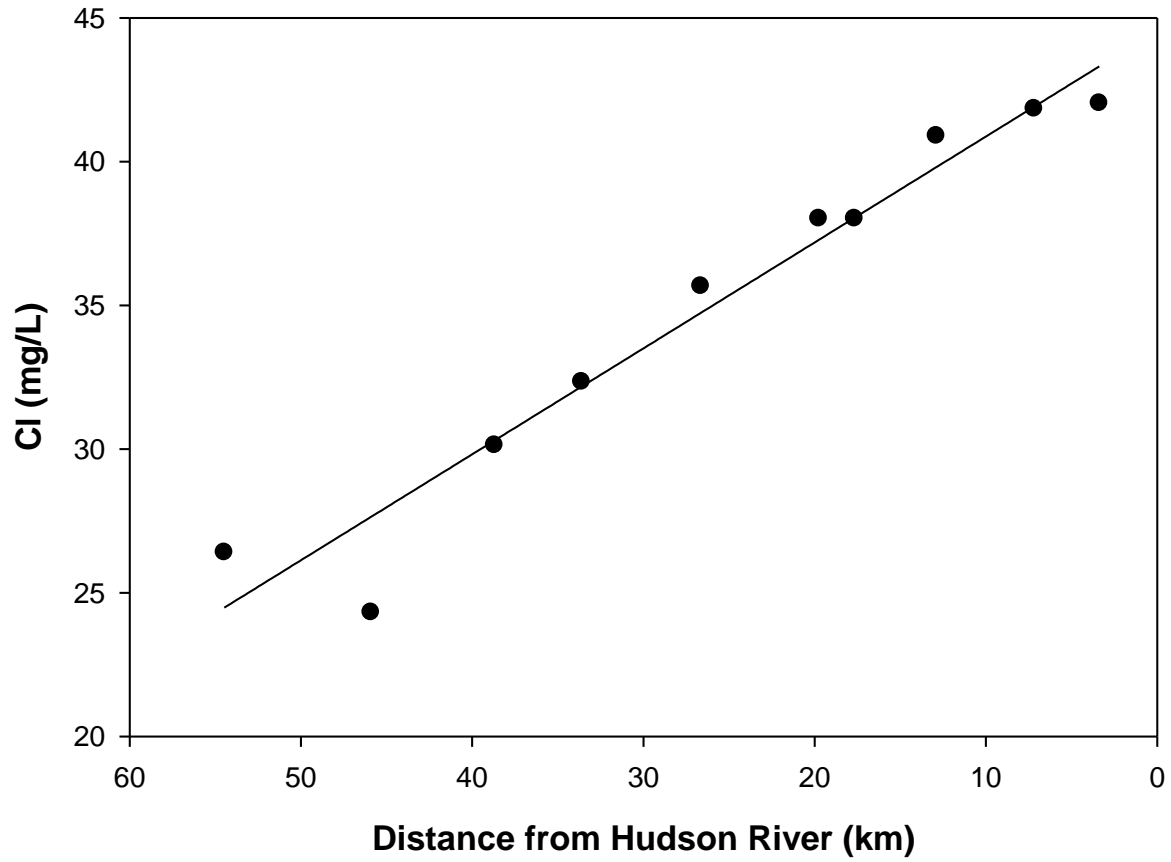
**TABLE 2.** Cl retention in incubated soil cores. Values are averages (SE).

Soil Musym	Total mass Cl retained (mg)	% Cl retention period 1	% Cl retention period 1+2
HsA	68.4 (3.9)	38.5 (1.4)	12.6 (2.1)
DwC	78.5 (2.6)	44.1 (2.2)	14.6 (3.9)
NwD	77.7 (13.6)	42.7 (8.0)	15.4 (3.0)
Ff	75.3 (21.7)	34.7 (7.4)	21.6 (4.2)
All Groups	73.3 (3.7)	39.9 (2.0)	14.9 (1.5)

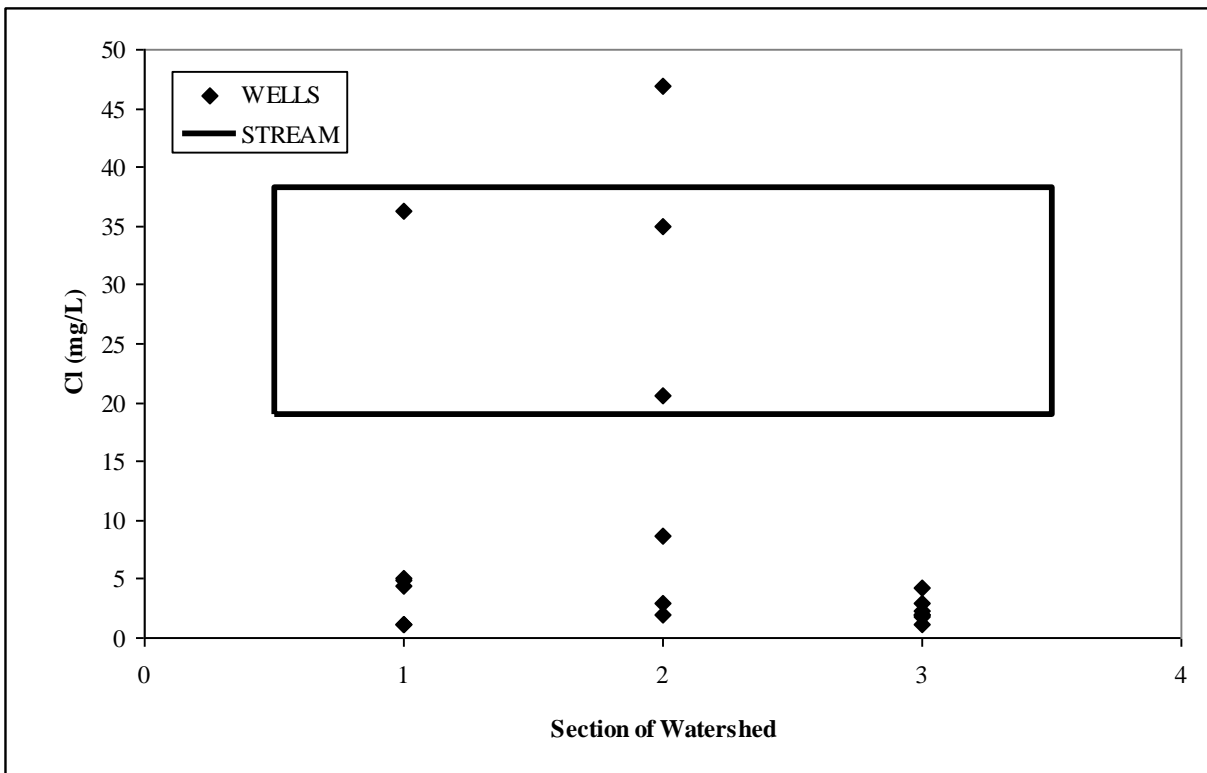


**FIGURE 1.** Watershed of the East Branch of the Wappinger Creek with inset map of New York State.

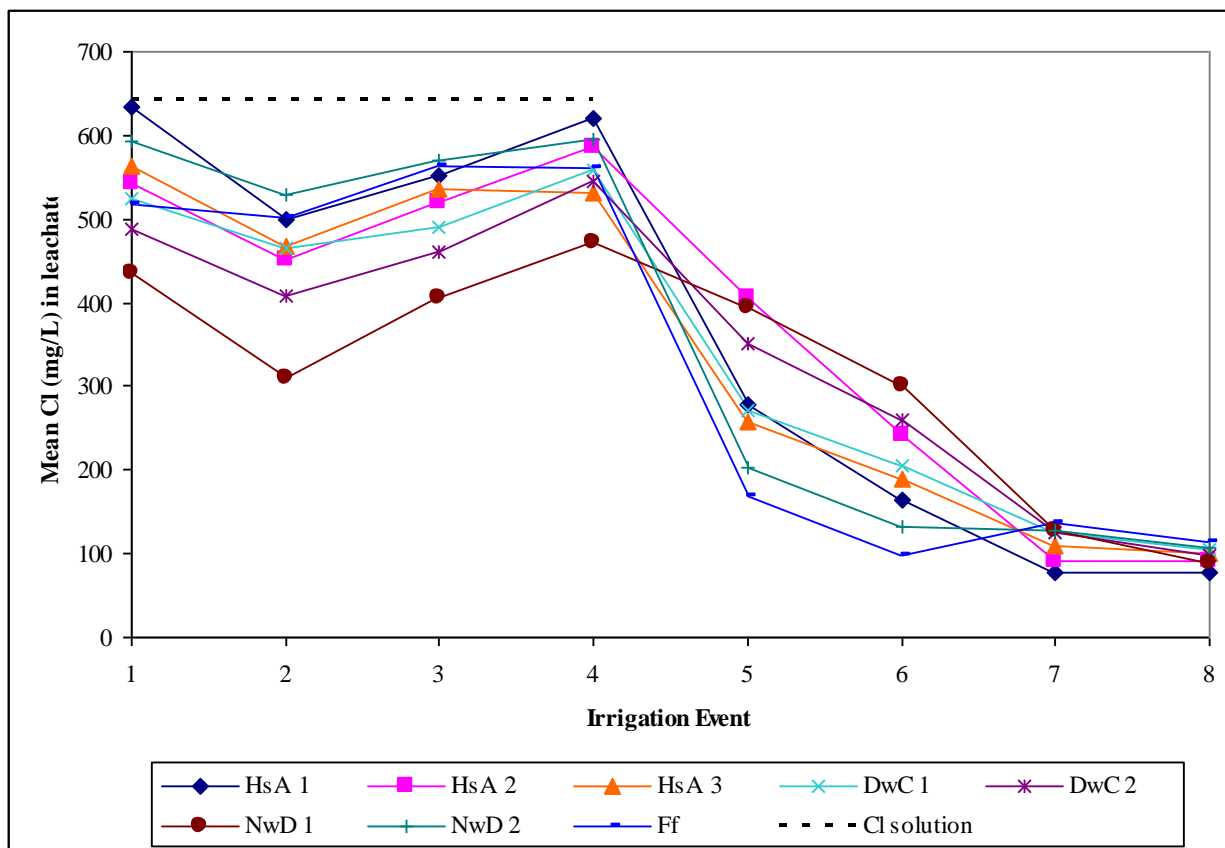




**FIGURE 2.** Chloride concentrations of surface water samples from a longitudinal survey on the mainstem Wappinger Creek. ( $r^2 = 0.9484$ ;  $y = -0.3686x + 44.5582$ ).



**FIGURE 3.** The box delineates the maximum and minimum ambient Cl concentrations in EBWC during June and July 2006. The points denote Cl concentrations of groundwater samples (n = 19) taken from private drinking water wells in three sections of EBWC (1 = lower, 2 = middle, 3 = upper).



**FIGURE 4.** Average concentration of Cl in leachate leaving the incubated soil cores (n = 20) after each irrigation event. During the first four irrigations, 643 mg Cl / L were added to the artificial rainwater (dashed line). Soil types are depicted using their map unit symbols (Table 1).