Characteristics of chloride loading from urban and agricultural watersheds during storm and non-storm periods

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ABSTRACT

The chloride ion (Cl\(^-\)) can adversely affect an aquatic ecosystem, but it is not clear how Cl\(^-\) moves with runoff and how its transport processes are related to land uses and land cover. This study investigated how the loading characteristics of Cl\(^-\) vary depending on storm events and land cover in a temperate region. We monitored Cl\(^-\) concentrations in three study watersheds that have different compositions of urban and agricultural land uses. In addition, a Mass First Flush ratio (MFFn) was determined to quantify the effect of first flush on Cl\(^-\) loading. Overall, the observed concentrations and loadings in this study were found to be less than those reported in cold northern regions. The monitoring data showed that Cl\(^-\) concentrations and loads observed in an urban watershed were significantly larger than those of a rural watershed. The results suggest water management plans should focus on urbanized areas and their storm water to efficiently reduce chloride loading to downstream waterbodies. However, a further study is recommended to identify the sources and pathways of Cl\(^-\) loaded to waterbodies.

Key words | chloride, land use, nonpoint source pollution, paddy field, urban, water quality monitoring

HIGHLIGHTS

- Cl\(^-\) loading varies depending on storm events and land cover.
- The first flush effect on Cl\(^-\) loading was strong in urban storm runoff.
- The urban watersheds had significantly larger Cl\(^-\) loads than the rural watershed.

INTRODUCTION

Chloride ions are toxic to aquatic life and highly mobile; thus, they are easily transported from source to downstream waterbodies, adversely affecting aquatic ecosystems. Acute and chronic exposure to Cl\(^-\) can have deleterious effects on aquatic flora (Panno et al. 1999) and fauna (Fraser & Thomas 1982; Bollinger et al. 2003). Studies show that Cl\(^-\) concentrations consistently greater than a threshold of 210 mg/L are associated with a decrease in the diversity of benthic communities, an increase in benthic drift (Crowther & Hynes 1977; Molles 1980; Demers 1992) and a decrease in both diversity and populations of aquatic biota (Birge et al. 1985; Evans & Frick 2001; Sanzo & Hecnar 2006; Seilheimer et al. 2007; Karraker et al. 2008; Fay & Shi 2012). Despite of the significant ecological and health implications of Cl\(^-\) loading to waterbodies, it has...
not been a major focus of water quality management and planning. As a non-point source (NPS) pollutant, Cl\(^-\) is difficult to quantify due to its temporal and spatial variations, and its loading characteristics are dependent on land uses (Deletic 1998).

Chloride ions are naturally present in the form of chlorides such as NaCl, KCl, and CaCl\(_2\) (Rook 1974), and they are loaded to water bodies from sewage, plant wastewater, seawater intrusion, rainfall, inflow of manure, and excessive disinfectants. Herlihy et al. (1995) concluded that Cl\(^-\) concentrations could be used as a good surrogate indicator for general human disturbance in a watershed because the Cl\(^-\) concentrations have various sources, even though studies on agricultural watersheds with large fertilizer inputs are few (Lax et al. 2011).

Urbanization represented by increased impervious areas reduces the opportunity for direct runoff to infiltrate into the ground before entering rivers and lakes; thus, Cl\(^-\) concentrations tend to be higher in the streams of urban watersheds. Data collected in Rhode Island, USA, showed that the chloride level sometimes appears as high as 84 mg/L in developed residential and commercial areas while the concentration was around 17 mg/L before development (Hunt et al. 2012). Also, the widespread adoption of chloride as a deicer has rapidly increased chloride concentrations in water bodies, but the ecological implications of these changes have not yet been fully elucidated and does need long-term monitoring (Daley et al. 2009).

One important feature of urban runoff is that pollutant discharge in the initial period of a storm event is substantially higher than in the later period; this is called the First Flush effect (FFe: Gupta & Saul 1996; Deletic 1998; Lee et al. 2002; Sansalone & Cristina 2004; Bach et al. 2010). Quantifying the strength of FFe helps to improve the understanding of urban runoff characteristics and efficiently achieve the goals of NPS pollution controls (Deletic 1998; Lee et al. 2002; Soller et al. 2005). Dimensionless mass/volume curves of stormwater discharges are commonly used to evaluate the pollutant discharge patterns of rainfall events and catchments (Verdaguer et al. 2014). FFe is also defined with the Mass First Flush ratio (MFFn) that describes the percentage of pollutants emitted as a function of the normalized storm duration (Han et al. 2006; Barco et al. 2008).

Previous studies have shown that the FFe of pollutants is affected by various watershed characteristics including drainage areas, impervious coverage, rainfall intensity and duration, and antecedent dry days (Wanielista & Yousef 1993; Gupta & Saul 1996; Taebi & Droste 2004). However, the relationship between FFe and Cl\(^-\) concentrations and loads is still unclear due to the lack of observations and monitoring data. In addition, most of the nonpoint pollution studies in Korea have been focused on organic matters represented by BOD, COD, TOC, and nutrients (Choi et al. 2019), but the transport mechanisms of other inorganic pollutants including Cl\(^-\) have not been studied enough to provide clear guidance for watershed management practices. In this study, Cl\(^-\) concentrations monitored in three watersheds within and between storms were investigated with regard to different levels of urbanization in a monsoon climate. The event mean concentrations and annual loads of chloride were compared to examine the urbanization effect on Cl\(^-\) transport. The FFe of Cl\(^-\) was also analyzed by employing the concept of MFFn to provide information and data required for watershed management planning.

**MATERIAL AND METHODS**

Monitoring methods

Cl\(^-\) concentrations were monitored at the outlets of three watersheds: WJ (Woljeong), JS (Jangsu), and PYJ (Pungyeongjeongchen) located in Gwangju city, Korea. WJ and JS are nested in PYJ, which drains an area of 68.9 km\(^2\). The study watersheds have distinctive compositions between urban and agricultural land uses (Figure 1). WJ is mostly covered by agricultural areas (62.2%, mostly rice

![Figure 1](http://iwaponline.com/ws/article-pdf/21/4/1567/903454/ws021041567.pdf)

**Figure 1** | Locations of the study watersheds and NPS monitoring points.
paddy fields) with small urban land uses (6.2%), while JS is relatively highly urbanized with areas covered by a combined sewage system (36.0%) and agricultural areas (28.8%). Overall, PYJ consists of agricultural land uses (46.9%) and urban area (25.7%) (Table 1). The study sites are located around 35° N and the average annual rainfall at the study sites is 1,391 mm, and the average annual maximum and minimum temperatures are 29.3 °C and 1.9 °C, respectively. The annual rainfall is concentrated during summertime since the study sites belong to a monsoon area. A combined system is installed in the urban area.

Korea has cold winters even though it is in a monsoon climate zone. According to the world Koppen-Geiger climate classification updated recently, inland is classified as Dfa (Cold – Dry Winter – Hot Summer), and the coastal areas belong to Dfa (Cold – Without dry season – Hot Summer), Cfa (Temperate – Without dry season – Hot Summer), or Cwa (Temperate – Dry Winter – Hot Summer) depending on their locations (Peel et al. 2007). The use of deicing is common in the cold winter of Korea, but its environmental impacts have not been investigated enough to guide the application of deicing in terms of urban stormwater quality (Lee et al. 2017).

Water quantity and quality monitoring was conducted from January 2015 to December 2016 in accordance with the guideline of the rainfall runoff survey method proposed by the Korean Ministry of Environment (MOE 2012). Rainfall data were compiled from a weather station managed by the Korea Meteorological Administration. In this study, individual rainfall events were separated using the minimum dry period length between two independent events based on the statistical characteristics of historical rainfall events. For instance, the IETD of 17 hours was selected for rainfall records obtained from the weather station (Gwangju) that covers the study watersheds. The period between two consecutive storm events was defined as the non-storm period.

A water pressure gauge (OTT, Germany) was used to measure the depth of flow, and the river cross section was surveyed to calculate flow discharges from measured water depths using a rating curve. The flow discharge data of PYJ were collected from a monitoring station managed by the Korea Ministry of Land, Infrastructure, and Transport. Water was sampled using an automatic sampler (ISCO 1570, USA) every 1 hour in the first 24 hours of a storm event, and then the sampling interval was increased to 6 hours until 48 hours from the beginning of the event according to the monitoring guideline of the MOE (2012).

This study was able to capture a total 11 storm events during the monitoring period. Grab sampling (32 times) was conducted weekly or bi-weekly during the non-storm period. The samples were stored in 4 L polyethylene bottles on site and then transported to a laboratory of the Yeongsan River Environment Research Center. The water samples were analyzed according to the standard water pollution test method (APHA 2001). The concentration of chloride in water samples taken from the streams was determined using an ion chromatography (IC) based method (a Dionex™ IC system). The water samples were filtered through a 0.45-μm membrane filter prior to the IC analysis to ensure only dissolved chloride was analyzed and to improve the flow of the analysis system (Brinton et al. 1996).

Data analysis

The Event Mean Concentration (EMC) represents a flow-weighted average concentration, which is computed as the total pollutant mass divided by the total runoff volume for the duration of an event (Ballo et al. 2009). In this study the EMC was used as an index to characterize the water quality of runoff of a storm event (Novotny & Olem 1994). MFPn which quantifies the FFe by calculating the size of first flush intensity and the accumulated load against the cumulative runoff during a rainfall event was calculated by Equation (1). The ‘n’ value represents the percentage amount of runoff volume that carries the pollutant of interest. For instance,

| Watershed | Paddy | Upland | Urban | Forest | Others | Total |
|-----------|--------|--------|-------|--------|--------|-------|
| WJ        | 12.6   | 9.1    | 2.17  | 8.4    | 2.7    | 34.9  |
|           | (36.1) | (26.1) | (6.2) | (24.0) | (7.7)  | (100.0)|
| JS        | 1.0    | 1.3    | 2.9   | 1.6    | 1.2    | 8.0   |
|           | (12.5) | (16.3) | (36.0) | (20.0) | (15.3) | (100.0)|
| PYJ       | 16.9   | 15.4   | 17.7  | 11.0   | 7.9    | 68.9  |
|           | (24.5) | (22.4) | (25.7) | (16.0) | (11.4) | (100.0)|
the MMF10 of Cl\(^-\) means the amount of Cl\(^-\) load transported by the first 10% of runoff in a rainfall event.

\[
\text{MMF}_{10} = \frac{\int_0^t C(t) \times Q(t) \, dt}{M} \times \frac{M}{\int_0^t Q(t) \, dt} 
\]

where \(C(t)\) and \(Q(t)\) are the pollutant concentration and the runoff volume as a function of time, respectively, and \(n\) is the percentage of the runoff volume (ranging from 0% to 100%). \(M\) and \(V\) are the total mass of the emitted pollutant and total runoff volume, respectively.

The annual Cl\(^-\) load by the direct runoff of storm events was estimated by multiplying the average direct runoff load per unit rainfall depth and the 10-year average annual rainfall depth as Equation (2), \(\text{(MOE 1995)}\).

Load = average annual rainfall amount
\[
\times \sum_{i=1}^N \left( \frac{\text{Load by direct runoff}}{\text{Rainfall amount}} \right) / N \quad (2)
\]

where \(N\) is the number of storm events. Annual export of Cl\(^-\) was estimated by adding the load of base flow and direct runoff load. The load of base flow was determined by multiplying flow rate of the base flow and average concentration observed during the non-storm period.

The Eckhardt filter \(\text{(Eckhardt 2005)}\) was applied to separate direct runoff and baseflow from the streamflow of individual storm events by Equation (3).

\[
b_k = \frac{(1 - BFI_{\text{max}}) \times a \times b_{k-1} + (1 - a) \times BFI_{\text{max}} \times y_k}{1 - a \times BFI_{\text{max}}} \quad (3)
\]

where \(b\) is baseflow \((\text{m}^3/\text{s})\), \(k\) is the time step \((\text{min})\), \(y\) is total streamflow \((\text{m}^3/\text{s})\), \(BFI_{\text{max}}\) is the baseflow index, and \(a\) is a recession constant.

The differences between the Cl\(^-\) concentrations of water samples taken in the different study watersheds and periods (storm and non-storm periods) was tested at the significance level of 0.05. When the concentration measurements do not follow the normality assumption, the null hypothesis, there is no difference between the Cl\(^-\) concentrations, as evaluated using the non-parametric Kruskal-Wallis test.

**RESULTS AND DISCUSSION**

**Land use and Cl\(^-\) concentration**

The observed mean concentrations ranged 15.7 mg/L for WJ, 27.3 mg/L for JS, and 23.1 mg/L for PYJ, respectively during the non-storm period. The observed EMCs ranged from 17.5 mg/L for WJ, 21.0 mg/L for JS, and 17.9 mg/L for PYJ, respectively during the storm period (Figure 2). The observed concentrations were lower than those of cold region of the northern hemisphere. The annual average Cl\(^-\) concentrations in New Hampshire streams were 63 and 76 mg/L from watersheds with 3.8–5.7\% urban land use while 201 and 309 mg/L with 28%–31\% urban land use, respectively \(\text{(Trowbridge et al. 2010)}\). In watersheds with a relatively high proportion of urban land cover in Canada, stream Cl\(^-\) concentrations often exceed environmental protection guidelines \(\text{(chronic: 120 mg/L; acute: 640 mg/L)}\) \(\text{(CCME 2011)}\) during winter high flows and the spring freshet \(\text{(Oswald et al. 2019)}\).

The differences between Cl\(^-\) concentrations observed in JS (urban) and PYJ (mixed) during storm and non-storm periods were not statistically significant \(\text{(} p < 0.05 \text{)}\). However, the Cl\(^-\) concentrations of the urbanized watersheds (JS and PYJ) were significantly different than those of the agricultural watershed (WJ) during storm and non-storm periods \(\text{(} p < 0.05 \text{)}\) \(\text{(Table 2)}\).

Yun \textit{et al.} \text{(2015)} reported that the concentrations of chloride were as low as 4.55–4.80 mg/L in the streamflow of a forest-dominant watershed in Korea, which could be considered background concentrations. Kim \textit{et al.} \text{(2009)} monitored 500 rural streams in Korea which were affected by paddy rice cultivation practices and reported that observed mean Cl\(^-\) concentrations were 11.7 mg/L in April, 8.1 mg/L in July, and 10.5 mg/L in October. The observed average concentrations of WJ were 15.7 mg/L and 17.5 mg/L for the non-storm and storm periods, respectively. Poudel \textit{et al.} \text{(2016)} found that the average concentration of Cl\(^-\) was about 22 mg/L from monitoring 66 rainfall events in an agricultural watershed in Louisiana. Lax \textit{et al.} \text{(2017)}
also reported that in two agricultural watersheds in Illinois, the average concentrations of Cl\(^{-}/C\(_0\)\) were 23.7 mg/L and 20.9 mg/L, respectively. Although the cropping patterns and farming practices are different from the case of this study, the previous studies and our observations demonstrate that the Cl\(^{-}/C\(_0\)\) concentrations of agricultural watersheds are not high compared to those of urban areas. Although agricultural areas contribute to total Cl\(^{-}\) in streams (Peterson & Benning 2013), the lower Cl\(^{-}\) concentrations in agricultural water dilute the impact from urban-originated surface water (Lax et al. 2017). This study confirmed these findings. Concentration variations of PYJ, which is the whole watershed outlet, resemble those of WJ where the major land use is paddy field (Figure 2). In Korean paddy fields, irrigated water drains to downstream areas as return flow. Choi et al. (2019) showed that about 40% of water drainage occurred from the paddy fields during non-storm periods. Therefore, Cl\(^{-}\) concentration during non-storm periods might be affected by return flow from the paddy fields.

There are many factors that influence EMCs, such as rainfall depth and intensity, antecedent dry days, and runoff depth (Jung et al. 2013; Jeung et al. 2019). Herlihy et al. (1998) concluded that land use/land cover correlated to stream Cl\(^{-}\) concentrations and suggested that Cl\(^{-}\) concentrations could serve as a proxy for anthropogenic influences. Cunningham et al. (2009) reported a linear relationship between Cl\(^{-}\) concentrations in streams and the percentages of impervious surfaces including parking lots, roadways, and buildings that restrict infiltration. However, Poor et al. (2008) showed that Cl\(^{-}\) might not be an appropriate proxy for human influences within agricultural settings.

Table 2 | Descriptive statistics of Cl\(^{-}\) concentrations during non-storm periods and EMCs of storm periods for the study watersheds

| Event                  | WJ          | JS          | PYJ          |
|------------------------|-------------|-------------|--------------|
| Event                  | Min | Max | Mean | Std. | Min | Max | Mean | Std. | Min | Max | Mean | Std. |
| EMCs of Storm           | 11  | 8.9 | 26.4 | 17.5\(^{a}\) | 5.9  | 3.3  | 63.0 | 21.0\(^{b}\) | 16.7 | 4.4  | 34.0 | 17.9\(^{b}\) | 9.5  |
| Non-storm              | 32  | 4.3 | 31.9 | 15.7\(^{a}\) | 8.0  | 5.2  | 58.2 | 27.3\(^{b}\) | 12.1 | 6.1  | 45.8 | 23.1\(^{b}\) | 10.9 |

\(^{a}\)The mean values followed by the same letter (" or ") are not statistically different from each other at the 0.05 significance level.

Figure 2 | Comparison of Cl\(^{-}\) concentrations measured in the three study watersheds during non-storm (grab) and storm (daily average) periods.
EMCs calculated from observed chloride concentrations and flow discharge rates show variations over storm events (Table 3). As seen in Figure 3, EMCS generally decreased as the rainfall increased, especially in urbanized watersheds such as JS and PYJ (Kim et al. 2005, 2007a, 2007b; Yusop et al. 2005). On the other hand, WJ did not show such a trend presumably because paddy fields have the capacity of storing storm water runoff that carries chloride. In some storm events, for the same reason, higher EMCS for some events were observed in JS (urbanized) than WJ (agricultural or rice paddy fields) (Table 3). In addition, PYJ produced lower chloride EMCs than did JS, as water drained from agricultural areas (WJ) might dilute urban-originated (JS) high Cl⁻ concentrations in PYJ.

Seasonal effects on concentration of Cl⁻

The Cl⁻ concentrations were higher in winter than in other seasons presumably due to deicers distributed in urbanized areas that have dense road networks (Figure 4). Studies identified deicers as the significant nonpoint source of chloride, which accounts for most (greater than 87%) of chloride loads, in both urban and agricultural areas (Kelly et al. 2008; Novotny et al. 2009; Pajak et al. 2015; David et al. 2016). In urban watersheds, wastewater treatment plants were also identified as making a great contribution to Cl⁻ loads (Novotny et al. 2009). Half of applied road salt is thought to enter surface waters at the site of application via roadside drainage networks, and the other half is either removed

Table 3 | Observed EMCS (mg/L) and standard deviation (values in parentheses) of concentrations of Cl⁻ within storm events for the three watersheds

| Event | Date     | Rainfall (mm) | n*  | EMC(standard deviation) mg/L |
|-------|----------|---------------|-----|------------------------------|
|       |          |               |     | WJ                           | JS       | PYJ       |
| 1     | 2015.04.03| 30.5          | 18  | 26.4 (1.6)                   | 24.0 (7.6)| 30.7 (8.9) |
| 2     | 2015.05.11| 27.5          | 22  | 19.0 (2.1)                   | 13.1 (7.6)| 13.6 (8.2) |
| 3     | 2015.07.11| 43.5          | 24  | 15.2 (2.0)                   | 20.7 (16.1)| 17.2 (5.0) |
| 4     | 2015.08.11| 22.0          | 24  | 23.6 (2.7)                   | 63.0 (19.5)| 34.0 (9.8) |
| 5     | 2015.09.23| 14.0          | 12  | 19.2 (1.6)                   | 32.6 (16.3)| 25.7 (8.6) |
| 6     | 2015.10.01| 53.5          | 26  | 8.90 (3.3)                   | 6.60 (6.4) | 8.80 (9.3) |
| 7     | 2016.03.04| 58.0          | 24  | 24.1 (6.8)                   | 25.1 (6.7) | 23.7 (10.4) |
| 8     | 2016.04.27| 51.5          | 22  | 15.4 (4.6)                   | 10.9 (3.9) | 14.1 (6.4) |
| 9     | 2016.08.26| 27.0          | 23  | 10.7 (1.2)                   | 8.30 (4.3) | 9.40 (1.9) |
| 10    | 2016.09.28| 5.5           | 12  | 10.6 (0.7)                   | 23.2 (2.4) | 15.1 (7.3) |
| 11    | 2016.10.16| 52.5          | 24  | 19.4 (6.8)                   | 3.30 (5.4) | 4.40 (6.0) |

*aThe number of water quality samples.

Figure 3 | The relationship between EMC of Cl⁻ and rainfall for the study watersheds.
during snow removal or enters soil and groundwater (Environment Canada 2001).

The observed Cl\(^{-}\) concentrations were relatively high in spring compared to fall, which is also attributed to deicer application, due to the delayed dissolution and/or transport of the salts. In summer, the chloride concentrations increased up to 63.0 mg/L for storm events, and their variations were larger than those of the other seasons. Most of the high concentrations greater than 30.0 mg/L were observed in JS, especially in summer (Figure 4). Lax et al. (2017) found that streams within watersheds with both agricultural and urban land uses were susceptible to sustained high Cl\(^{-}\) concentrations in spring and summer. Cl\(^{-}\) trapped within snowbanks and grass patches infiltrates into the subsurface, eventually reaching the water table. The groundwater-fed streams receive a constant supply of Cl\(^{-}\)-rich baseflow throughout the year (Rhodes et al. 2001; Panno et al. 2006; Daley et al. 2009). Groundwater sources can be responsible for the elevated anion concentrations under baseflow conditions. The higher concentration of the urban watershed (JS) during non-storm periods would be affected by sewage and release of accumulated chloride via groundwater.

The elevated Cl\(^{-}\) concentration of JS during summer would be attributed to Combined Sewer Overflow (CSO) and release of accumulated chloride via groundwater. The concentrations of Cl\(^{-}\) in the water samples taken in the non-storm periods tend to be higher than those of the storm periods, especially in the urbanized watershed, JS (Figure 4). A report (Yeongsan River Environment Research Center 2007) shows that the Cl\(^{-}\) concentrations of sewage discharged to the wastewater treatment plant (WWTP) located in Gwangju city ranged from 40 to 100 mg/L. In addition, sewer water leaking from a pipe (joint or broken part), especially in old residential areas, is often suspected as the source of pollutants to the downstream stream (Yeongsan River Environment Research Center 2007). Septic systems, leaky sewer pipes, and lawn fertilizers are known to be major sources of contamination in groundwater beneath urban residential areas (Clawges &

Figure 4 | Seasonal variation of chloride concentrations of storm and non-storm period for different land use watersheds.
Vowinkel 1996; Ellis & Revitt 2002). Hur et al. (2007) observed the highest concentrations of Cl$^-$ of up to 40 mg/L in a stream in South Carolina, USA immediately downstream from two WWTP effluent discharge locations while the concentrations of the head water were about 3 mg/L. The discharge from the WWTP and the leakage might contribute to the increased Cl$^-$ concentrations in the urban watershed (JS) during the non-storm periods.

First flush effect of Cl$^-$

The FFe can be obvious when the slope of normalized cumulative mass emission plotted against normalized cumulative volume is greater than the bisector (Park et al. 2010). The watersheds that have relatively urbanized areas (JS and PYJ) were found to have greater FFe as expected (Figure 5). The Cl$^-$ concentrations rapidly increased and reached their peaks in the beginning of all storm events and then gradually decreased as time went in all the watersheds.

The MFFn of Cl$^-$ loads was calculated by varying the percentages [n values in Equation (1)] from 10% to 100% to further investigate the contributions of first flush to the Cl$^-$ loads (Figure 6). The FFe was stronger in JS and PYJ where relatively large urbanized areas are found, compared to that of WJ. In the case of JS, for instance, 22% of total Cl$^-$ was loaded by the first 10% of runoff volume generated during storm events on average, while the amount of total Cl$^-$ loaded by the first 10% runoff volume was reduced to 13% in WJ (agricultural watershed). The MFF decreased with increases in the n values, as expected (Jeung et al. 2019). The highest FFe occurred with the first 10% of runoff volume in this study. Similarly, Kim (2005) observed the highest FFe of pollutants from a highway with the first 10%, which showed build and wash process on the surface.

Figure 5 | Comparison between cumulative discharges and Cl$^-$ loads in the study watersheds.
Park et al. (2010) also observed the highest FFe combined sewer discharges with the first 10% runoff volume. However, the source and path of Cl\(^-\) in this study is not clear since high FFe occurred in summer and fall. The possible source is leaching of accumulated Cl\(^-\) in soil by deicer or CSO of domestic waste.

**Estimated load of Cl\(^-\)**

This study separated the contribution of direct runoff to the total chloride loads from that of baseflow for each storm event (Figure 7). The results showed that direct runoff contribution of the Cl\(^-\) load per unit area of the relatively urbanized watersheds (JS and PYJ) was greater than that of the agricultural one (WJ) during storm events. Urbanization increases the coverage of impervious surfaces and then the amount of direct runoff, which makes chloride-laden storm runoff be quickly discharged into downstream waterbodies via a combined sewer system. On the other hand, there are a smaller number of chloride sources in the agricultural watershed (WJ) and its pervious areas and rice paddy fields help to reduce the amount of runoff that carries generated Cl\(^-\); thus, Cl\(^-\) loads could be lower in WJ than in JS and PYJ. Such findings and speculations imply that urban areas are much more susceptible to Cl\(^-\) contamination compared to agricultural areas in Korean surroundings during storm periods.

Cl\(^-\) loaded by direct runoff per unit rainfall depth and the estimated annual Cl\(^-\) load per unit area of the study watersheds are presented in Figure 8. Direct runoff load of Cl\(^-\) per unit rainfall amount was higher in the urban watershed (JS) than in the rural watershed (WJ). The average annual base flow amount was 290, 350, and 400 mm for WJ, JS, and PYJ, respectively (Yeongsan River Environment Research Center 2017). The average annual load of base flow and direct runoff were estimated and total annual export of Cl\(^-\) was calculated and resulted as 75, 149, and 142 kg/ha/yr for WJ, JS, and PYJ, respectively.
The annual Cl\(^-\) load of the rural watershed dominated by paddy fields is about half those of the relatively urbanized watersheds. The agricultural chloride loads might be originated mainly from fertilizer applied to rice paddy fields and de-icer application (Peterson & Benning 2013). David et al. (2016) monitored two agricultural watersheds in Illinois where chloride was applied as a fertilizer at the rate of up to 49 kg/ha/yr and reported that annual loading of Cl\(^-\) ranges from 61.2 kg/ha/yr to 72.5 kg/ha/yr. Considering the standard fertilizer chloride application rate of 52 kg/ha/yr for paddy fields in Korea (NIAST 2019), the estimated annual loading of Cl\(^-\) from the WJ watershed seems reasonable. Sonzogni et al. (1980) reported that the annual Cl\(^-\) loads of urban land uses varied from 130 kg/ha/yr to 750 kg/ha/yr. Trowbridge et al. (2010) found that annual loading of Cl\(^-\) ranged from 360 kg/ha/yr to 590 kg/ha/yr in watersheds where urban land uses cover 6% to 14% of the drainage areas in New Hampshire, USA. The annual load of Cl\(^-\) estimated in this study is less than that of other studies, especially for the urban watershed, which might be attributed to less road salt application (currently data is not available for the study area) considering that the study area is temperate compared to the sites of other studies, which are located in the northern hemisphere.
CONCLUSIONS

This study investigated how the characteristics of rainfall events and watershed land uses control Cl⁻ loading to runoff. Stream water was sampled at the outlets of three watersheds with different compositions of urban and agricultural land uses during and between storm events. The chloride ion concentrations of the water samples were statistically analyzed to quantify the impacts of the land uses and rainfall events. The monitoring data showed that urban land uses produced a greater amount of Cl⁻ load than did agricultural ones. The FFe was stronger in the urban watersheds than the agricultural one, which might be attributed to the fact that the urban land has more impervious areas and combined sewer systems. In addition, the storage or ponding capacity of rice paddy fields distributed over the agricultural watershed was believed to lessen the FFe and make the streamwater slowly respond to storm events. Such results suggest water management plans and implementation should focus on urbanized areas to effectively reduce Cl⁻ loads to downstream waterbodies.

There must be many different factors that affect Cl⁻ loading to waterbodies, and this study tried to find the statistical association between Cl⁻ loads and the environmental characteristics (rainfall and land use). The observed Cl⁻ concentrations and loadings from the study watersheds located in a temperate climate region were found to be much lower than those reported in cold northern areas. Such a finding implies that salt application as deicer could contribute to Cl⁻ loadings. The hydrological connectivity of the locations to which Cl⁻ is applied to downstream waterways and waterbodies would influence the timing and magnitude of Cl⁻ retention and release. Urbanization may increase the connectivity between the Cl⁻ sources and downstream waterbodies through sewer drainage systems and thus accelerate Cl⁻ loading. For improved watershed-scale Cl⁻ management, it will be necessary to identify the source areas and major transport mechanisms of Cl⁻ and handle Cl⁻ loads at the sources or along the pathways. The use of environment-friendly deicing agents and advanced road washing machines can also help reduce chloride loadings. Furthermore, climate change is projected to increase the frequency and intensity of rainfall events, which will probably impact Cl⁻ loading, as the FFe demonstrated. Long-term monitoring of streamflow and groundwater will help elucidate the urbanization and climate change impacts on Cl⁻ loading and maintain the ecological health of watersheds.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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