TRANSFER DYNAMICS OF ROAD DEICING SALTS IN A RETENTION POND FOR ROAD WATER TREATMENT

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ABSTRACT

Sodium chloride used as a deicing salt is known to have adverse effects on the environment. Today, the concentration of chlorides rejected into the environment can only be regulated by controlling the water output flow of road runoff treatment and retention systems. However, road runoff retention ponds are not designed to treat deicing salts. Furthermore, on top of their environmental impacts, several studies showed that road salts increase the mobility of heavy metals.

Only a few studies have been conducted to develop solutions for salt remediation (*e.g.* dolomite filter bed or planted filters in constructed wetland for phytoremediation). Understanding sodium chloride transfer dynamics within these ponds is the first step towards designing a specific treatment for chloride rich waters.

The aim of this study is to evaluate the salt transfers in a retention pond located in Chenevières (France) used for road runoff treatment and flow control. For this purpose, pond water (influent entering and effluent exiting the pond) was collected and NaCl concentrations measured. Meteorological conditions and information about deicing salt application were followed to evaluate the proportion of salt collected by the road drainage system. Na^+ and Cl^- transfer dynamics in the retention pond were assessed.

1. INTRODUCTION

Road maintenance during winter in cold weather areas has led road managers to generalize the use of chemical deicers such as sodium chloride in huge quantities in order to insure users' security [1]. In France, sodium chloride is the major deicing product used for this purpose (currently, it represents more than 99.5% of road deicers in France [2]) and between 800.000 and 2 million tons are applied every winter on French roads. It is spread on roads as brine (aqueous solution of salt) or humidified salt either before the appearance of slippery conditions (preventive salt spreading) or once they are present on the road surface (curative salt spreading). After their application on roads, deicing salts are transported out of the road to stormwater treatment system or directly to the surrounding environment, mainly by wind or road water runoff. Transfer mechanisms are represented in Figure 1.

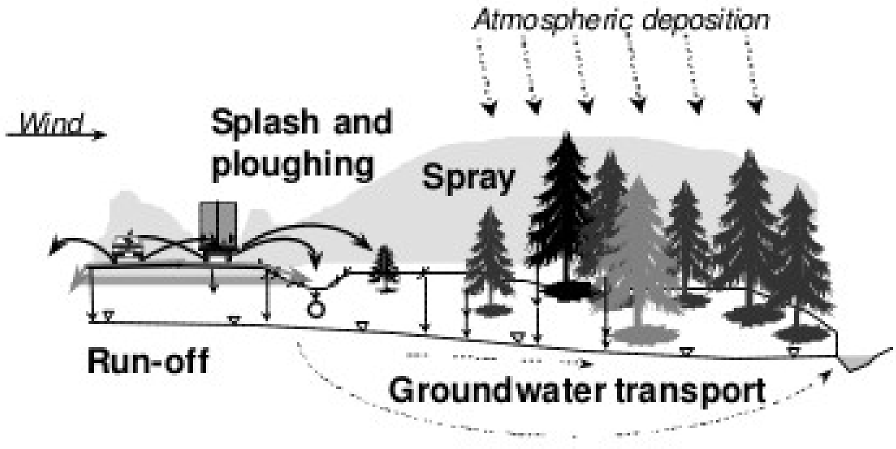

Figure 1 - Road deicing salt dispersion in the roadside environment [3].

Severe impacts have been reported on each environmental compartment because of road salt applications [4]. Indeed, significant increases in chloride and sodium concentrations in surface water, groundwater, roadside soils and organisms, have been reported and were correlated to deicing salt application [5-7]. In some cases, concentrations have even reached toxicity thresholds beginning to threaten biodiversity [8-9].

Yet, there is no available data on the assimilation and exchange processes of sodium chloride into water, sediments and aquatic vegetation in road-water treatment systems.

Moreover, Na^+ and Cl^- ions are known to remobilize heavy metals adsorbed on particles surface (in soils and sludge). Therefore, measuring Na^+ and Cl^- concentrations in road runoff retention ponds is of paramount importance to assess its potential effect on metal remobilisation.

Three main mobilization mechanisms are identified in the literature [5-10]:

- Ion exchange between Na^+ and metallic ions adsorbed on particles surface,
- Dispersion of colloid bearing metals,
- Chloride complex formation.

The establishment of a relationship between NaCl and heavy metals is a fundamental issue since it was demonstrated that heavy metals remobilization by deicing salts had dramatic effects on pond efficiency. A study conducted on a constructed wetland in the Netherlands showed that when high concentrations of salt were detected in road wastewaters Zn, Cu, Ni and Cd concentrations were higher in the wetland effluent than in the influent [11].

Despite the increasing use and concerns about the environmental impacts of deicers, France has not yet regulated the quantities spread on roads, or developed a specific treatment for wastewaters contaminated by sodium chloride [2]. Meanwhile, countries such as Canada have much more drastic regulation declaring deicing salts as toxic products and limiting their use [12].

Today the concentrations of chlorides rejected into the environment may only be regulated by controlling the water output flow of retention ponds along roadside. Yet no systematic control is performed to measure pollutant concentrations in general (and sodium chloride in particular) in retention ponds [13]. Only few studies have focused on the impact of sodium chloride on these systems and even less have been led to develop solutions for salt remediation (such as dolomite filter bed or planted filters in constructed wetland, [14-

15]).

In order to develop this kind of solutions, transfer dynamics of sodium chloride through retention ponds and road drainage systems has to be assessed, as well as the potential influence of sodium chloride on heavy metals speciation.

2. MATERIALS AND METHODS

2.1. Experimental site: Chenevières retention pond

The study has been carried out on a retention pond located near the national road 59 between Lunéville and Saint-Dié in Lorraine (France). This 4-lane motorway has low traffic (approximately 10,000 cars/day) and is located in an area where deicing salts are used every year in large quantities. A sewer system is draining runoff waters from about 1 km of this road to a water retention pond of approximately 2,800 m^2 in Chenevières (Figure 2).

During the 2011/2012 winter, more than 2.7 t of NaCl and 250 L of 20% concentrated brine were spread on that 1 km portion.

Figure 2 - Photography of Chenevières pond.

2.2. Sampling and sample conservation

Samples were collected one to three times a week from the inlet and the outlet of the pond since November 2012, and since February 2013, samples were also collected directly from the road runoff.

In order to focus on the transfer of deicing salts from the road to the pond, an automated sampler (Sigma 800 automated sampler from American Sigma Inc.) was disposed and used to collect 24 samples of the influent entering the pond (24 samples collected every 1, 2 or 3 h depending on the event).

Sludge samples were collected from 12 points in the pond in November 2012 (before any salting operation) and June 2013 (when chloride concentration in water was back to its minimum) to compare its quality and assess the influence of winter maintenance.

Water samples were kept at 4°C until their analysis, sludge samples were dried at 40 °C in a drying cabinet (according to [16]) and kept at room temperature.

2.3. Meteorological and salting data collecting

Meteorological data (precipitation, air temperature, road temperature and humidity) and quantities of deicing salt spread on the national road 59 were given by the operational maintenance services (DIR-Est) and compared to our results.

2.4. Measurements and analysis

For chlorides, 10-mL subsamples were prepared from each sample and concentration was measured by potentiometric titration with silver nitrate ($AgNO_3$ at 0,01 or 0,1 mol/L) with an automatic titler of Titrando ®.

Sodium concentrations were measured with Atomic Absorption Spectroscopy. This technique has a detection range of 0 to 4 mg/L. Since the samples are of concentrations sometimes much higher than the apparatus limit, dilutions were necessary.

Conductivity and pH were measured at 24 °C for every water sample.

3. RESULTS AND DISCUSSION

3.1. Water quality and ion concentrations

The first results show that the water input has very variable concentrations of chlorides. Indeed, concentrations between 5 and 10 mg/L were observed in November 2012 (before any salting operation occurred on the nearby national road 59 for winter 2012-2013) and concentrations increased up to 2500 mg/L in the input flow after several days of heavy salting operations (more than 1 ton/km in one week).

Concerning the output, concentrations ranged from 5 mg/L to 400 mg/L (knowing that the French limit for drinking water is 200 mg/L) and show correlation with salt spreading and meteorological conditions (Figure 3). Similar concentrations were reported elsewhere [17]

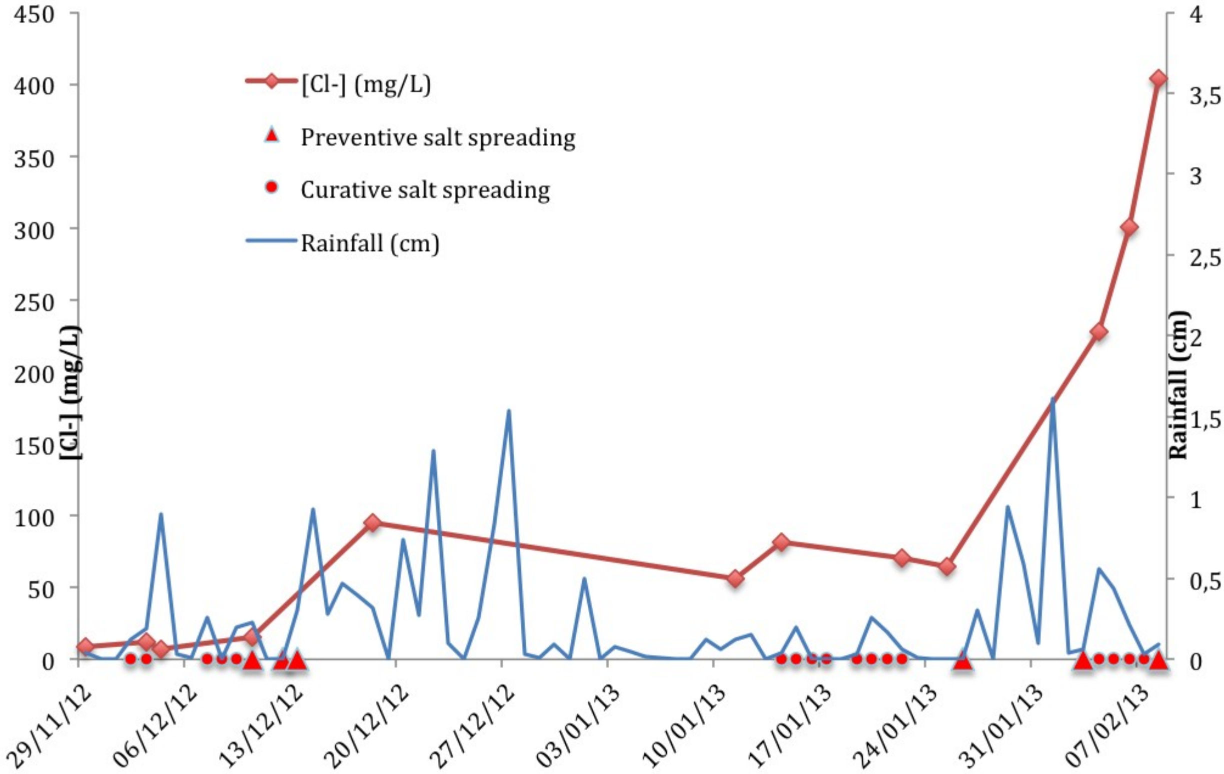

Figure 3. Correlation between the chloride concentration and the salting operations.

3.2. Salt retention period

The automated sampling was used to follow the pond's input conductivity after one salting operation in order to evaluate the pond's salt retention period.

One particular event is presented in Figure 4. Sampling was done in December, between the 18th at 4pm and the 20th at 1pm, and salting operations occurred between the 12th and the 14th.

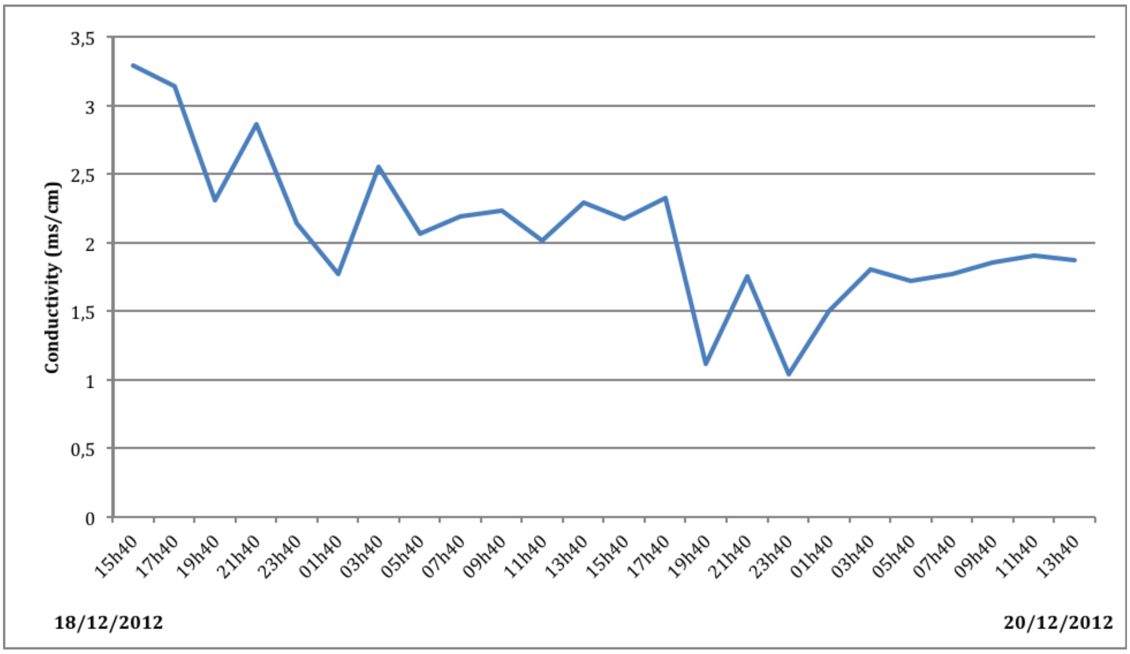

Figure 4. Evolution of conductivity of water input in Chenevieres' pond between 18/12/2012 at 4 pm and 20/12/2012 at 1 pm

Significant and rapid decrease in conductivity was observed associated with 3 mm of rainfall on December the 18th, 0 mm on December the 19th and 7 mm on December the 20th. There is a really fast and clear consequence of rainfall on the road. Indeed, ions concentrations diminish shortly after the beginning of rainfall and a great variation was observed.

3.3. Water toxicity and effects of NaCl on other pollutant

The United States Environmental Protection Agency has released in 2009 an aquatic life criteria table delimiting the recommended concentrations of various pollutants for aquatic life and human health protection [9]. The limits for chlorides are 230 mg/L for the Criteria Continuous Concentration (CCC for chronic toxicity) and 860 mg/L for the Criteria Maximum Concentration (CMC for acute toxicity). Chloride concentrations exceeded the CCC from the beginning of February until the second week of May.

If mechanisms of toxicity remain unclear, chlorides affect homeostasis capacity of living organisms and chloride effects are multiple (direct and indirect). Metal remobilisation and chloride-complex formation with heavy metals can increase toxic effects and synergic toxic effects of chloride and other pollutant request further studies but are probably involved [18-19].

Sodium chloride is known to remobilize cations adsorbed on sediments. Exchanges between Na^+ and K^+ [20], Ca^{2+} and Mg^{2+} [21] occur even at low concentrations (lower than 50 mg/L).

Sodium chloride is also known to remobilize heavy metals (such as Cd, Cr, Cu, Fe, Ni, Pb, etc.) which are known to be road pollutants drained away from road surface by road water runoff [10-22]. Three main mechanisms are described in the literature [5-23]:

- Ion exchange between metals adsorbed on the surface of sediment and dissolved Na^+ which leads to a decrease in [Na^+] in water,
- Colloid-facilitated transport of metals caused by colloid dispersion by sodium and chloride effect,
- Complexation of metals with chloride.

Concentrations encountered in Chenevières pond during winter 2012-2013 ranged between 10 mg/L and 475 mg/L of chloride and sodium. Concentrations encountered in road runoff ranged between 10 mg/L and 4 g/L in chloride, 10 mg/L and 2.7 g/L in sodium.
These concentrations are above the concentrations reported by Norstrroem [23] and similar to those reported bay Bommel-Orsini [24] which were tested and confirmed for heavy metals significant remobilization.

In addition, periods of freezing and melting of the water of the pond (which hapenned several times during the winter 2012/2013) should increase the sodium and chloride concentrations in the pond water. The pellicle of ice formed on the surface of the pond is pure H_20 (solute remain in the water of the pond, forming a brine in which concentrations in chloride increases as freezing occurs), therefore [Cl^-] and [Na^+] certainly increase and so does heavy metals remobilization and water toxicity.

4. PERSPECTIVES AND FURTHER MEASUREMENTS AND ANALYSIS

Considering these results and in order to understand the implications of the large chloride and sodium input in road runoff retention ponds, several analysis still have to be undertaken:

- Measurement of heavy metals concentrations (Cd, Cr, Cu, Ni, Pb and Zn reported as major road pollutants by Clozel [22]) and speciation in water and sludge samples of Chenevières pond,
- Measurements of water volume output and input in order to establish an accurate mass balance of pollutants entering and exiting the pond (particularly NaCl) and calculate the efficiency of the pond,
- Leaching assays (in batch at the beginning) have to be developed in order to analyze heavy metals remobilization in laboratory-controlled conditions.

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