4th Imeko TC19 Symposium on Environmental Instrumentation and Measurements
Protecting Environment, Climate Changes and Pollution Control
June 3-4, 2013, Lecce, Italy

SURVEILLANCE OF ROAD DE-ICERS IN THE ENVIRONMENT

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Abstract: In winter maintenance, the application of road de-icing products on transport infrastructures is a common practice for the maintenance of road security. However, these products are transported out of the roads into the surrounding environment by numerous factors (rain, wind, traffic, …). We demonstrate the importance of the surveillance of the road de-icers' dissemination in the environment by the illustration of two applications that are under investigation. In the first application, we survey the salinity of a detention pond used for the road water treatment. In the second one, the salt dissemination around a salt stocking area is investigated.

Keywords: Road de-icer, environmental impacts, sodium, chlorides.

1. INTRODUCTION

The research team ERA 31 of the CÉTÉ de l'Est is developing methods for the pollution detection and pollutant dissemination, mainly linked to transport infrastructures. A specific field of study is the monitoring of the road de-icing materials' evolution before and after application on the road's surface. Indeed, in order to avoid traffic disruption during winter, roads are the subject of a specific maintenance based on the application of de-icing materials [1]. Hence, between 800 000 and 2 millions of tons of road de-icers (mainly sodium chlorides) are applied each year on the roads throughout the France. However, due to several meteorological conditions and to traffic, these chemicals are transported out of the roads. They can hence end up either in the surrounding environment (splashed out by the vehicles or blown away by the wind) or in ponds used for road water runoff remediation and flow control (by flows after precipitations) [2]. Even though it is known that the main source of de-icer losses are due to the salting operations, de-icer's stocking areas can be a source of large losses as well. In order to evaluate the de-icer main inputs in the environment, it is important to survey their dissemination towards the detention ponds or in a stocking area's surrounding environment.

Two examples that are under investigation in our laboratory will be presented. The first study concerns the surveillance of the salinity evolution in a detention pond collecting road water flows. The impact of road salting operations are investigated, as well as the pond's treatment efficiency. The second study concerns the stocking areas, where samples are collected and analyzed in order to investigate the dissemination of the salt.

For the salinity determination, several techniques were used: for the water salinity, a method based on Raman spectroscopy was developed. However, for the monitoring of the Na^+ and Cl^- species separately, conventional techniques such as potentiometry and atomic absorption were used. An adaptation of these techniques for the analysis of soils was elaborated and used [3].

2. SALINITY DETERMINATION

2.1. Water salinity determination

For the means of the road de-icers surveillance on roads and in water, a specific tool was developed based on Raman spectroscopy. This analytical technique permits us to study the vibrational properties of materials [4, 5]. Furthermore, the study of the material's bond vibrations can give us an accurate insight on the material's structure [6, 7]. Indeed, in Raman spectroscopy, each material's bond presents specific signatures, the study of which can permit us to identify the nature of the material, as well as the concentration of the corresponding bond. This technique has been shown as particularly adapted for the characterization of water and aqueous solutions [8].

A method based on the monitoring of the *O-H* stretching mode change induced by the presence of salt in water was previously developed [9]. Indeed, the disrupter of hydrogen bonds provoked by the addition of salt in water was used for a definition of a spectral marker of the brine's concentration. This one is defined as:

$$S_D = \frac{\sum_{i=326}^{650}\left\{\frac{I(i)+I(i-1)}{2}\times[n(i)-n(i-1)]\right\}}{\sum_{i=1}^{325}\left\{\frac{I(i)+I(i-1)}{2}\times[n(i)-n(i-1)]\right\}} \qquad (1)$$

where *I(i)* is the Raman intensity, and *n(i)* the wavenumber corresponding to the CCD pixel number *i*.

A calibration curve was built using the equation 1, and the S_D-concentration correlation established. The calculated concentration was then compared to the brine's real concentration. Figure 1 shows the excellent correlation achieved between the real concentration and the concentration calculated by this method.

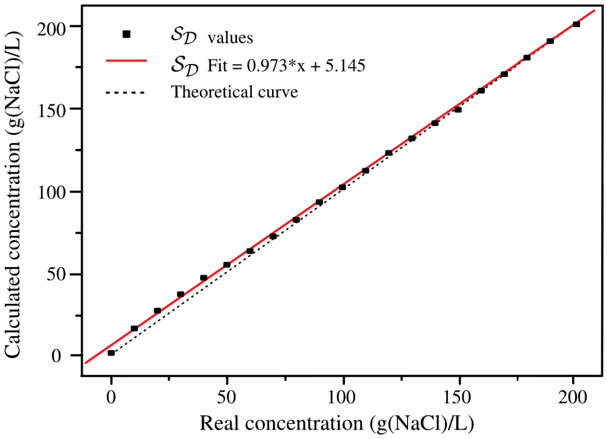

Fig. 1. Correlation between the brine's real concentration and the one obtained by the use of the developed spectroscopic tool.

2.2. Soil salinity determination

Several studies showed that, when present in soils, salt is dissociated, leaving only monoatomic ions Na^+ and Cl^-, which don't necessarily evolve the same way. The sodium ions are usually adsorbed by the soil particles, and stay mainly at the soil's surface. The chlorides, on the other hand, are washed away by water flows and go further in the soil depths, generally achieving subsurface waters [10]. It is therefore not possible to use Raman spectroscopy for the individual surveillance, as these ions do not present specific Raman peaks. The salinity calculation by Raman spectroscopy is therefore slightly erroneous, and differences have been observed between the real salinity and the calculated one (Table 1).

Table 1. Comparison of real and calculated *NaCl* concentration of three soil samples.

Sample	A	B	C
Real concentration (g/L)	5.9	8.0	11.7
Calculated concentration (g/L)	5.7	6.9	13.0

A specific method for the soil analysis by potentiometry and atomic absorption was therefore elaborated and used for the surveillance of the sodium Na^+ and chloride Cl^- ions in soil and water samples of our two experimental sites.

3. APPLICATIONS

3.1. Detention pond for road water treatment

Large quantities of de-icing products spread on roads are transferred to the roadside environment either directly or after passage by diverse treatment or detention systems. In order to diminish the road salt losses, detention ponds are constructed at the road's vicinity with the aim for them to collect the road water flows and diminish the seasonal, chronic and accidental road pollutions. De-icing products used for winter maintenance road treatments are considered to be a seasonal pollution, as numerous studies show that they have adverse effects on groundwater, surface water, soils, and biodiversity [11, 12]. Furthermore, it was shown that these products increase the mobility of heavy metals [12, 13].

However, nowadays it is not known at which extent these detention ponds collect the road water flows containing the de-icing products. Furthermore, these systems do not treat the road de-icing products, and a part of the de-icing products that entered in the detention pond are eventually transported out of it into the environment. It is therefore possible to regulate the chloride rejection in the environment only by controlling the water output flow. A salt remediation is necessary [14, 15].

Before testing potential salt remediation solutions in the detention pond, it is necessary to evaluate the quantities of applied de-icers that are collected by the detention pond, as well as the proportion of the collected de-icers exiting the pond by water output flows. The instrumentation of a specific detention pond located near Nancy in France was set and water and soil samples are regularly collected in the water input and outputs flows.

Fig. 2. Input water flows of the detention pond under investigation at Chenevières (France).

The instrumentation of a specific pond was set in order to determine the road de-icing material's evolution and influence on the pond's environmental media (water, soil and vegetation). The goal is to evaluate in what way and how long, the road de-icer will spread in a detention pond. It will permit us to estimate the pond retention period, as well as its remediation efficiency.

Water samples are collected at the pond's input and output flows weekly and after each salting operation. The first results show that the water input has very variable concentrations of chloride. Indeed, concentrations between 5 and 10 mg/L were observed in November 2012 (before any salt was spread 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 5mg/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). Further investigation has been led in order to determine how much time it takes for the salt to attain the output water flows.

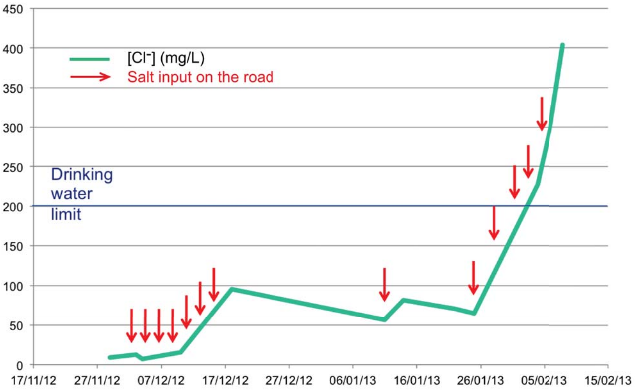

Fig. 3. Correlation between the chloride concentration and the salting operations.

3.2. Road de-icing stocking area

Even though the main source of the de-icers dissemination in the environment are the roads, a specific focus was put on stocking areas. Hence, some studied led by the CÉTÉ de l'Est estimated that for a stocking area of a standard size (300 – 400 tons) 5 to 8% of the total de-icer stocked in an open-air area can be lost by its dissolution under a standard pluviometry of 750mm/year. Furthermore, during the transfers from the stock to the de-icer spreader, 50 to 100 kg/spreader are lost.

One stocking area (Figure 4) was chosen as an experimental site for the evaluation of the de-icers losses. The goal was to evaluate at which extent the de-icer can disseminate on the soil surface and in the soil depth.

Fig. 4. Stocking area of de-icing sodium chloride.

The stocking area evaluated in this study is being in use since the 1990's. Its walls are in bad shape, and lead to think that the losses caused by it are important. A first series of samplings were performed at the soil surface at different distances from the stocking areas in order to evaluate the surface dissemination of the de-icer. The results showed that the concentrations of Na^+ and Cl^- were lower than 1g/kg(dried soil) in the vicinity of the stock. However, just aside of it, the concentrations were about 100 times higher, with 30,5g(Na^+)/kg(dried soil) and 68,5g(Cl^-)/kg(dried soil).

Sampling were also performed at different depths in the vicinity of the stocking area in order to evaluate the de-icer vertical dissemination. The results obtained between 0 and 6 meters of depth are presented Figure 5.

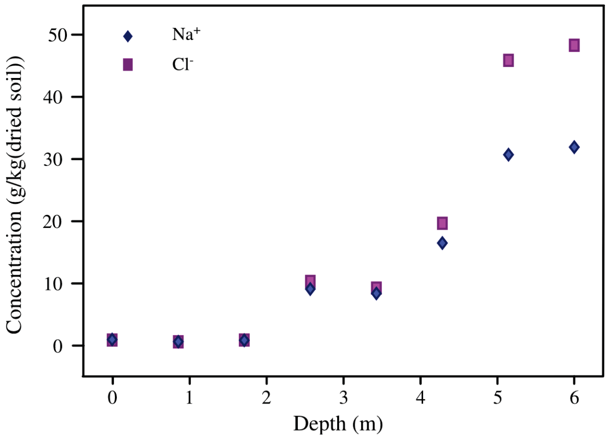

Fig. 5. Sodium and chloride concentrations as a function of the soil depth.

The Na^+ and Cl^- concentrations enhance with the depth at which the sample was collected. According to one Canadian report [16], standard concentrations of sodium and chloride ions are of 100 and 2600 mg/kg for samples collected between 0,1 and 5 meters underneath the stocks. The concentrations we obtained are about 100 higher, reflecting the possible soil saturation that progressively took place.

According to the literature, the sodium ion concentrations in the environment is regulated by different exchange processes between the different environmental compartments (water, soil, biodiversity). A part of them should be adsorbed by the soil's negative charges and maintained in the soil. The chlorides, on the other hand, should follow the water cycle and should not be maintained in the soil, but should accumulate in aquatic zones. The results obtained in the study presented here show a different evolution, as the sodium ions were not present at the soil surface, and their concentration enhances with the soil depth. This could indicate the soil saturation by other cations.

4. CONCLUSION

Sodium chloride used as a road de-icer is nowadays not considered as a priority pollutant. However, an evolution in the practices is necessary as its environmental impacts are becoming well known even though the de-icer quantities that are transported into the environmental compartments are still not well estimated.

Two experimental sites exposed continuously to road de-icers during winters were chosen for a dissemination study. The results obtained from field samples illustrate the importance of the road de-icers dissemination, and thus underline the necessity of their surveillance in the environment.

5. AKNOWLEDGMENT

The authors would like to thank the OptonLaser and the BWTek companies for their technical support, as well as the IFSTTAR and GEMCEA organizations for their financial support.

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