SALT IN SOILS: EXTRACTION AND ANALYSIS METHODS

I. Durickovic, G. Derombise, L. Framont-Terrasse, S. Thomann, M. Marchetti
CÉTÉ de l'Est – Laboratoire Régional des Ponts et Chaussées de Nancy, Tomblaine, France
E-mail (corresponding author): ivana.durickovic@developpement-durable.gouv.fr

Abstract – We demonstrate the importance of the sample preparation and extraction procedure for the soil salinity study. A comparison between the most commonly used techniques for the evaluation of salt amount in samples is presented. Several sample preparation and salt extraction procedures were tested. We calculated the efficiency for each procedure thanks to the preparation of soil samples with a precisely known salinity. This enabled us to determine which sample preparation and extraction procedure gives the best efficiency and accuracy. Hence, a series of measurement with the atomic absorption and potentiometry dosing was performed, these being the most commonly used techniques for the evaluation of salt amount in an aqueous sample. The goal of this study is to develop an analysis method for soils contaminated with road salt. The identification of the sample preparation offering the best efficiency will be selected in order to apply it for the development and the implementation of a new optical technique for the soil salinity determination.

Keywords : soil salinity, extraction techniques, atomic absorption, potentiometry dosing.

1. INTRODUCTION

Road salt (mainly sodium chloride) is widely used in winter maintenance as a mean to preserve traffic safety by its de-icing capacities. Under the influence of the traffic [1], as well as the weather conditions, a certain quantity of salt is transported to the road's surrounding environment. The vehicle wheels provoke the salt splashing, it is blown off by the wind, and the rain induces road runoffs. The salt is therefore transferred by multiple means in the road's surrounding environment, and some studies show that it can be found up to 100 meters away from the road [2]. The roadside environment is hence directly exposed to road salt and the environmental drawbacks of this exposure are nowadays well known [3-5], with a special attention being devoted to the roadside vegetation and groundwater. In order to restrict these impacts, it is important to survey the quantities of salt that are present in the soils.

The sodium chloride is decomposed into sodium ions, Na^+, and chloride ions, Cl^-, which penetrate the soil under the influence of streaming water. At the vicinity of the surface, the soil contains mainly sodium ions, as the chloride are transported in the lower soil layers. Therefore, sodium can be found either as a sodium chloride in a solution, or as an exchangeable sodium ion.

In this work, we present a comparison of different sample preparation techniques for the soils contaminated by salt. For this purpose, we tested the most common techniques used for the salt quantification, the atomic absorption spectrometry and the dosing by a potentiometer. These two techniques give complementary information, as the first one provides us the quantity of the sodium ion Na^+, and the second one the quantity of the chloride ions Cl^-. However, these techniques inform us on the concentration of these ions in a liquid and cannot be employed for the measurement on the soil itself. Therefore, the possibility to analyse the solution obtained by lixiviation of the soil as a mean of salt extraction was investigated. So as to find the method with the best extraction efficiency, several parameters of sample preparation were varied, such as the lixiviation time and the extraction solid/liquid ratio. Since the concentration range of the different ions is not the same for the two techniques (atomic absorption measures milligrams of sodium, and potentiometry the concentration of chlorides in grams), solutions with different salt concentration were prepared.

2. SAMPLE PREPARATION

Soil samples were collected in the vicinity of the LRPC laboratory, in the suburban area of Nancy (eastern part of France). For the efficiency and accuracy comparison of the different methods used for the concentration analysis, it is necessary to know the precise concentration of the soil. Thus, in this preliminary study, the soil samples were polluted with a brine of a precisely given concentration. In order to minimize the uncertainties that could be present due to the soil humidity or the size of the soil granular particle, the sample preparation contains several steps.

2.1. Drying and sieving of the soil samples

First of all, for the minimization of the humidity impact on the method precision, the soil samples are preliminary heated on 105°C during 24 hours until the stabilisation of its mass (all of the humidity contained in the sample was evaporated). This process is necessary in order to calculate precisely the quantity of salt in a unitary mass of the soil sample, this one needing to be completely dry.

A rough sieving was performed in order to eliminate all the soil particles which are greater than 2 μm. This step allowed us to eliminate all the impurities that could be found in the soils, such as small rocks, blades of grass and so on. Moreover, it permited us to uniform the size of the soil particles and hence homogenize its capacity to absorb salt on its surface.

2.2. Soil contamination and salt extraction

The contamination of the soil samples was made with a precise mass of a NaCl brine of known concentration and prepared with distilled water. It is then agitated with a turbula for several hours (3h) to obtain a homogeneous mixture. Another drying cycle of the sample is performed for 24 hours, until full humidity evaporation.

The salt extraction is obtained by lixiviation of the soil with a precise solid/liquid ratio R given in (1):

$$R=\frac{soil\ mass\left(kg\right)}{distilled\ water\ volume\left(L\right)}\ . \tag{1}$$

For homogeneity reasons, the mixture is agitated with a turbula for 20 hours, which is followed by a 24 hour-decanting. Since the dissolution of salt is completed thanks to the contamination with a brine and not with solid salt, the decanting allows the minimization of the soil particles which could disturb the salinity measurements. The supernatant is then collected and filtered in order to eliminate the soil remaining in suspension.

2.3. Salinity analysis methods

The sodium ion, Na^+, concentration is determined by atomic absorption. This technique has a detection range of 0 to 4 mg(Na^+)/L. The non-diluted solutions are filtered with a syringe containing a filtering membrane (0 - 45 µm), not to damage the apparatus' capillary. Since the prepared brines are of concentrations much higher than the apparatus' limit, dilutions were necessary.

For the chloride ion, Cl^-, potentiometric titration with silver nitrate ($AgNO_3$ at 0,01 and 0,1 mol/L) was used. The apparatus used is an automatic titler of Titrando ® shown in Fig. 1.

Fig. 1. Titrando ® automatic titler used for the determination of the chloride ion by potentiometric titration.

This technique is based on the evolution of the potential difference between a silver electrode and one of saturated mercury. The silver nitrate has a titrating role and provokes the precipitation of silver chloride, AgCl. The solution concentration is calculated as a function of the $AgNO_3$ quantity used for the precipitation, with the assumption that all of the chloride ions have precipitated.

3. RESULTS AND DISCUSSION

3.1. Estimation of the standard soil salinity

In order to know how much of the salinity found in a soil is provoked by the road salt, the natural soil salinity needs to be known. Hence, several soil samples were collected over France to estimate the standard levels of salinity in soils. The geographic locations of the sites where the five samples tested were taken is illustrated in Fig. 2 and their corresponding sodium and chloride contents in Fig. 3.

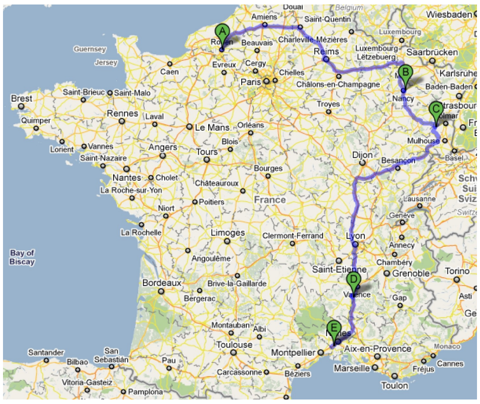

Fig. 2. Collection sites of the soil samples: Rouen (A), Tomblaine (B), Metzeral (C), Plan de Baix (D), Codognan (E).

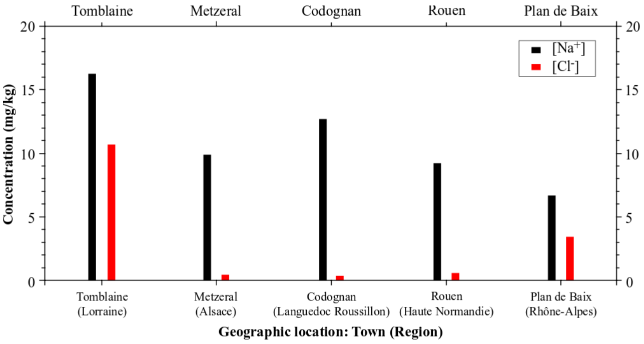

Fig. 3. Chloride and sodium concentration in samples collected at different sites over France.

Fig. 3 shows the results obtained for the chloride and sodium concentration for the samples collected in different regions of France. We can notice that the concentration of the sodium ion is rather constant, from 7 to 16 mg/kg(soil). However, the chloride ion is much more affected by the location of the soil collection site. Its concentration is contained in the range between 0 and 3 mg/kg(soil), except for the Tomblaine soil where it is present with a 10 mg/kg(soil) concentration. For the two species, the most elevated concentrations were found in Tomblaine, our first collection site.

3.2. Extraction ratio and lixiviation duration influence

In this part, the influence of the extraction ratio and of the time of lixiviation was studied by the comparison of the efficiencies obtained. Thus, for each soil sample, its natural salt concentration (sodium and chloride) was therefore measured and subtracted from the concentration obtained for the polluted soil samples. The salinity coming the sample pollution thus obtained was compared to the theoretical salinity calculated, knowing the precise volume of the brine used for the pollution of a unitary soil mass.

The extraction ratios R of 1/1, 1/3, 1/5, 1/10, 1/15, 1/20, and two lixiviation times (2 and 20 hours) were applied, and the chloride and sodium concentrations measured for each case. The efficiencies calculated are presented in Fig. 4.

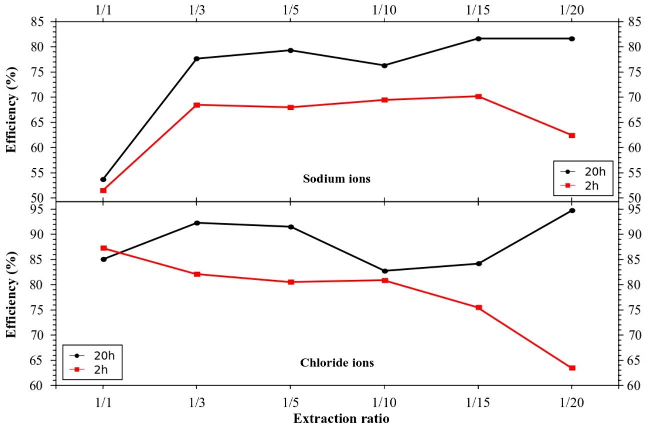

Fig. 4. Efficiency of the concentration determination for the sodium ions (up) and chlorides (down) as a function of the extraction ratio, for two lixiviation times (2 and 20 hours).

Fig. 4 shows the contribution of the time of lixiviation to the extraction efficiency of the sodium and chloride ions. The efficiency was mostly higher by about 10% for the lixiviation of 20 hours compared to the one obtained with a 2 hour-lixiviation. The extraction ratios that offered best efficiencies were those of 1/3 and 1/5. This latter one was chosen, as the quantity of the supernatant was greater, and hence easier to collect for the analysis.

3.3. Validation of the elaborated method

Previous measurements had the objective to determine which sample preparation and salt extraction offered the best efficiency. For these measurements, soil samples were polluted by salt in the laboratory, and their final "theoretical" salinity was therefore known which enabled us to calculate the extraction efficiency. It was necessary to validate the method developed by these measurements before applying it to the analysis of samples with unknown salinities. Therefore, three soil samples were polluted by salt by a third party for the analysis and validation of our method.

The results obtained with three contaminated samples are shown in Table I. The sodium and chloride ions concentration obtained for the test samples are shown, as well as the corresponding mass of NaCl found after the conversion of the mole/L into g/L and taking into account the test sample's volume (200 grams of the contaminated soil with a 1/5 extraction ratio).

TABLE I. Results obtained on three contaminated soil samples: concentrations of ions found in a test sample, the NaCl mass calculated from it, and the efficiency obtained.

	[Na] (g/L)	[Cl] (mole/L)	m_{NaCl} calc. (g)	m_{NaCl} real (g)	Efficiency (%)
Sample 1	0,719	0,0444	5,74	7,50	76
Sample 2	0,458	0,0305	3,85	5,00	77
Sample 3	0,190	0,0096	1,33	1,50	89

We observe a good correlation between the mass of chloride sodium obtained by our method (m_{NaCl} calc.) and the real mass contained in the soil samples (m_{NaCl} real), with the extraction efficiency up to 89 %.

3. CONCLUSION

The analysis of salt in soils is a rather complex process due to the necessity of the sample preparation and salt extraction. By varying several parameters involved in this process, we succeeded to highlight the most simple preparation and extraction process providing the best efficiency. Atomic absorption and titration by potentiometry were used as a mean to determine the most efficient way to extract the salt from the soil.

The lixiviation time tests pointed out the importance of leaving the lixiviation process for about 20 hours to maximize the salt extraction. Furthermore, we showed that the extraction ratios of solid soil mass to distilled water volume that offered the best results correspond to 1/3 and 1/5, the second ratio being chosen as it is simpler to collect the solution from it.

The importance of taking into account the soil natural salinity was shown, as it can achieve up to 16 mg[Na^+] and 10 mg[Cl^-] per soil unitary mass. Its natural salinity has to be subtracted from the calculated soil salinity, our goal being the detection of the road salt influence on the soil's salinity. This work opened the field to develop, to test and to implement a new optical technique for soil salinity measurement based on a technique developed for the measurement of salinity in aqueous solutions [6].

REFERENCES

[1] G. Blomqvist, M. Gustafsson: "Patterns of Residual Salt on Road Surface"; *6th International Symposium on Snow Removal and Ice Control Technology*, Vol.E-CO63, 2004, pp. 602-608.

[2] M. Gustafsson, G. Blomqvist: "Modeling exposure of roadside environment to air-borne salt"; *6th International Symposium on Snow Removal and Ice Control Technology*, Vol.E-CO63, 2004, pp. 296-306.

[3] A. Lundmark: "Modelling the impacts of deicing salt on soil water in a roadside environment", Technical Report TRITA-LWR.LIC 2024, KTH Land and Water Resources Engineering, 2005.

[4] N. A. Trahan, C. M. Peterson; "Factors impacting the health of roadside vegetation", Technical Report CDOT-DTD-R-2005-12, Colorado Department of Transportation Research Branch, 2007.

[5] G. Blomqvist; "De-icing salt and roadside environment-strategies for impact analyses"; *PIARC 2002, 11th International Winter Road Congress*, 2002.

[6] I. Durickovic, R. Claverie, M. Marchetti, P. Bourson, J. M. Chassot, M. D. Fontana; "Experimental study of NaCl aqueous solutions by Raman spectroscopy: Towards a new optical sensor"; *Applied Spectroscopy,* Vol.64, Number 8, 2010, pp. 853-857.

Author (s): Research associate, I. Durickovic, CÉTÉ de l'Est – Laboratoire Régional des Ponts et Chaussées de Nancy, 71 rue de la Grande Haie, 54510, Tomblaine, France, tél.: +33(0)3 83 18 31 72, fax: +33(0)3 83 18 41 00, ivana.durickovic@developpement-durable.gouv.fr. Research analyst, G. Derombise, CÉTÉ de l'Est –

Laboratoire Régional des Ponts et Chaussées de Nancy, 71 rue de la Grande Haie, 54510, Tomblaine, France, tél.: +33(0)3 83 18 41 37, fax: +33(0)3 83 18 41 00, guillaume.derombise@developpement-durable.gouv.fr. Research analyst, L. Framont-Terrasse, CÉTÉ de l'Est – Laboratoire Régional des Ponts et Chaussées de Nancy, 71 rue de la Grande Haie, 54510, Tomblaine, France, fax: +33(0)3 83 18 41 00, lucie.framont-terrasse@developpement-durable.gouv.fr. Chemist trainee, S. Thomann, CÉTÉ de l'Est – Laboratoire Régional des Ponts et Chaussées de Nancy, 71 rue de la Grande Haie, 54510, Tomblaine, France, fax: +33(0)3 83 18 41 00, sandrine.thomann@developpement-durable.gouv.fr. Research associate, M. Marchetti, CÉTÉ de l'Est – Laboratoire Régional des Ponts et Chaussées de Nancy, 71 rue de la Grande Haie, 54510, Tomblaine, France, tél.: +33(0)3 83 18 31 60, fax: +33(0)3 83 18 41 00, mario.marchetti@developpement-durable.gouv.fr.