

INFLUENCE OF ROAD DE-ICERS ON GROUNDWATER IN THE WALLOON REGION

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1. Summary and Introduction

Mentioned during the Winter Road Congress of LULEA in 1998, the study proposed by the Directorate-General of Roads and Motorways of the Walloon Ministry of Equipment and Transport is based on the main experiences drawn from the detailed study of the influence road de-icers have on aquifers in the Walloon Region which was carried out by the Hydrogeology Department of the Université Libre de Bruxelles (Laurent D. and Laurent E., 2000 and 2001). Our text is split up into three parts.

We first give a general overview of all aquifers in the Walloon Region on the basis of a survey carried out among water producers. Through a comparison with the results of the CEBEDEAU¹ study conducted in 1997, we then comment on the general aquifer evolution as well as on some limited cases of water pollution by salts.

In the second part, we study the results of a series of river and groundwater analyses made within two particularly sensitive sites.

The first site includes the protection area boundary of a site containing very pure mineral water with a particularly low sodium concentration. It is the drainage basin of the Waarfaz lake and Wayai river tributaries.

The second site, situated in a sensitive area because of the aquifer nature, is located near a road of the Great Capacity Network and belongs to the Ardennes as far as climate is concerned. Several drilling operations allowed not only to follow water chemistry evolution on this site but also to carry out tracing and pumping tests. The results drawn from water evolution during the year and from the two tests made are analysed in detail and interpreted in terms of different behaviour of water ions during transport in the drainage ditches and into the aquifer.

The third part includes the original study of the thermodynamic equilibria between water and aquifer minerals. It enables to explain the different behaviours Na⁺ et Cl⁻ ions have during water migration. It develops some recommendations on the mineralogical nature of drainage surfaces and on water treatment.

2. The General Survey

The situation did not change much between 1996 and 1999 and all the aquifers remain in a very favourable condition. As confirmed by the 1992-1998 average contents in the D.G.R.N.E. general survey, chloride contents higher than 50 mg/l remain rare.

3. The Mineral Site

The Warfaaz lake belongs to a strip of the Primary Era, Cambrian system, lower Salmian stage. It is made up of quartzphyllites and phyllites. This strip is surrounded to the north and to the south by Revinian quartzites and back phyllis. The Wayai valley upriver from the lake is situated within a strip of younger alluvia.

¹ N.d.T. : Belgian research and documentation centre for water.

Figure 1 shows the sampling points downstream of the Warfaaz lake. A more detailed map indicates the samples taken around the lake itself and particularly between the lake and a road salt store house located upstream from the lake (Figure 2).

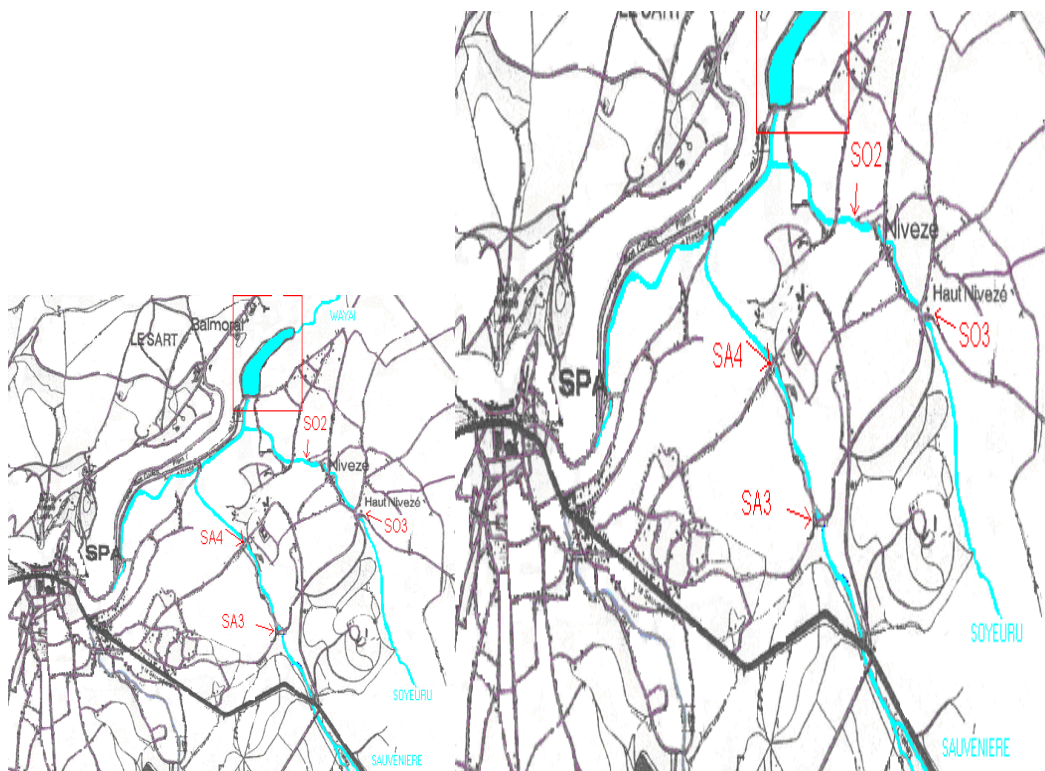


Figure 1: Map of the samples taken downstream of the Warfaaz lake.

Figure 2: Map of the samples taken around the Warfaaz lake.

The chemical analysis campaigns carried out for all sampling points between 1997 and 2001 reveal a very good general condition. Table 1 for instance shows the June 2000 sample analyses.

Well	pH	Cond. μS/cm	HCO ₃ ⁻ mg/l	SO ₄ ²⁻ mg/l	Cl ⁻ mg/l	NO ₃ ⁻ mg/l	Ca ⁺⁺ mg/l	Mg ⁺⁺ mg/l	Na ⁺ mg/l	K ⁺ mg/l	SiO ₂ mg/l	Al μg/l	Fe μg/l
Puits	5,35	240	4	26,8	65,2	<0,2	2,43	10,5	11	0,71	6,92	220	16162
1	6,99	521	11	41,7	127,6	10,7	10,5	3,19	87,8	2,63	5,22	49	58
2	3,97	457	0	41,2	99,3	25	11,7	10,5	45,5	2,9	8,56	1724	391
3	4,22	420	0	55,9	71,2	50,1	14,9	7,75	43,6	4,47	8,77	2082	26
4	5,67	273	0	26,3	68,1	1,34	6,03	6,97	34,3	1,1	7,85	69	122
5	7,03	135	19	20,6	13	6,87	12,6	2,93	8,33	1,96	6,33	149	120
6	7,32	127	23	16,1	11,9	6,03	12	2,39	7,31	2,7	4,88	124	162
7	7	272175	127	2080	80341	<20	607	135	49425	455	<20	<1000	3138
SO3	6,87	69	13	10,5	5,9	1,29	7,58	0,88	4,42	0,63	5,24	167	55
SO2	7,66	121	32	13	6,96	4,77	14,9	1,38	6,29	2,19	5,83	99	59
SA3	7,13	73	13	9,75	7,81	1,14	6,89	1,27	5,27	0,52	5,74	87	53
SA4	6,77	96	21	11,4	8,99	3,52	9,07	1,9	6,23	1,19	6,29	56	178

Table 1 : June 2000 analyses table

The influence of the salt store house can be noticed downstream, more particularly at points 1, 2 and 3 as far as surface water is concerned and at the well for groundwater. The examination of the Na⁺ and Cl⁻ contents' historical background at point 1 on Figure 3 is particularly instructive.

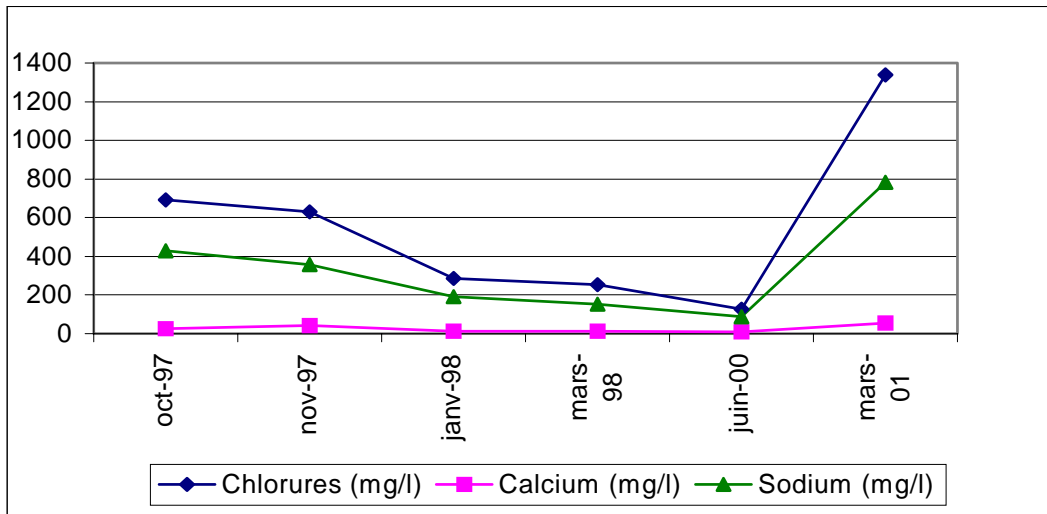


Figure 3. Chlorides, calcium and sodium concentration at point 1

An important content fall is observed in 1998 due to systematic covering after the Parma study (1998).

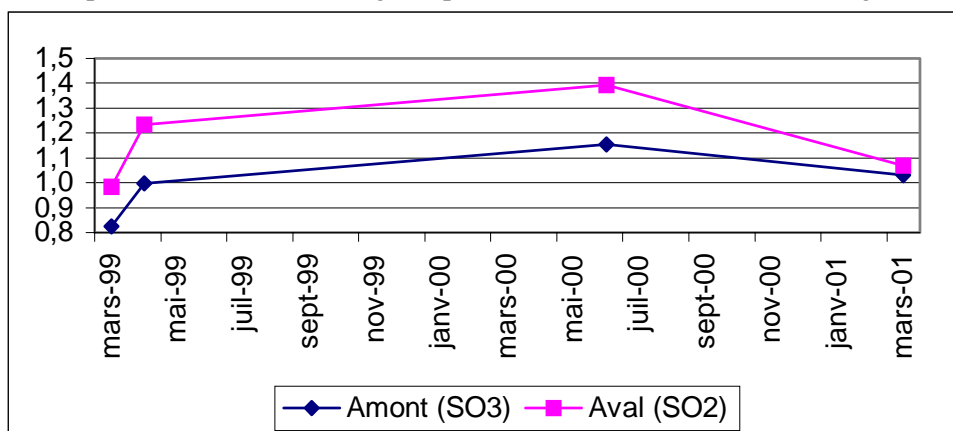
It was pointed out during the sampling campaign in 2001 that the covering had not been systematic after each salting. This is expressed by a dramatic increase in Figure 6 for March 2001.

The future covering building will eliminate this problem for good. In the meantime, systematic covering with tarpaulin is however absolutely necessary after each salting.

The ratio of Na⁺ and Cl⁻ concentrations nearly equals 1 for surface waters (lake tributaries) and is of about 0,3 for the Warfaaz well. For surface waters, the difference between the behaviour of the Na⁺ and Cl⁻ ions is small. On the opposite, ions behave differently for groundwater.

The ratio of Na⁺ and Cl⁻ concentrations going from 1 to 1,4 between the sampling points upstream from and downstream of the Soyeuru indicates the presence of domestic sewage disposals between those two points.

The Na⁺ and Cl⁻ difference between supply water and domestic waste water averages 20 to 50 mg/l for Cl⁻ and 40 to 70 mg/l for Na⁺. The [Na⁺]/[Cl⁻] ratio thus reaches values of about 1,5 to 2,26 according to Bond et Al. (1974). The ratio measured in the river depends on the ratio between the natural flow and the waste water flow. The increase towards values clearly higher than 1 corresponds on our site to the points located near sewage disposals. This increase is shown in Figure 4.



Amont = Upstream - Aval = Downstream

Figure 4 : [Na⁺]/[Cl⁻] ratio for the Soyeuru

4. The Motorway Site

The site is situated along the N5 national road between Frasnes and Couvin (Figure 1) at the very location of the future Couvin bypass road, not far from the Eau Noire. It is located on the southern edge of the Dinant Synclinorium.

The site's geology is characterised by the transgressive phase of Upper Couvinian into Upper Frasnian, a phase during which a calcareous schist sedimentary series appears with, for the full height, coralligenous facies frequently of reef nature. It is a neritic platform sedimentation presenting a calcareous dominant feature and not very deep water. In the south on the opposite, we have, within the same framework and instead of the calcareous sedimentation, a terrigenous sedimentation of pelitic type to which coral constructions are associated to varying degrees.

Our site is thus characterised by calcareous shale and silt likely to become sandstone. The development drilling operations conducted for the Couvin bypass road and those done within the framework of our study reveal an alluvium cover overlaying silt or sandstone with very argillaceous layers and a thick calcareous shale layer starting between 8 and 14 m depth. Figure 5 shows the location of the drilling points meant for our tests and for the chemical analyses campaigns.

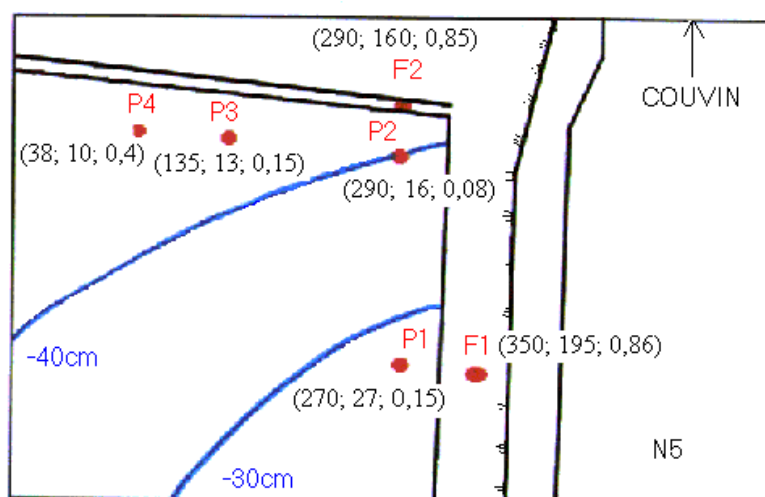


Figure 5. Drilling points location and ion spatial behaviour within the aquifer

This figure indicates the isopiestic line of the calcareous shale and sandstone aquifer.

To sum up the geological description of the drilling operations, it seems that the aquifer rock made up of calcareous shale, calcarenite and silt is topped by more argillaceous layers likely to play the role of a little permeable aquitard.

The mineralogical study carried out by X-ray diffraction analysis and by examination of thin ground sections enables us to identify calcite as being a constituent of the carbonated sample which dominates in the calcareous shale.

The schist sample which is less abundantly found in this rock includes quartz, muscovite, some feldspar but mainly clays : kaolinite, illite, chlorite and montmorillonite. Muscovite sandwiched with chlorite can easily be seen with a microscope.

To define the aquifer flow parameters, a pumping test was done at a flow of 3,13 m³/h on the P3 well, the other wells serving as piezometers. No leakage through an aquitard can be detected showing the very low permeability of the more argillaceous layers above the aquifer.

The typical results of the test are shown in Table 2.

Piezometer	Transmittivity	Storage
P3	1,42 m ² /h	-
P2	1,14 m ² /h	1,28.10 ⁻⁴
P4	3,49 m ² /h	9,43.10 ⁻⁴

Table 2. Typical results of the test

These figures confirm anisotropism and the almost confined characteristic of the aquifer.

Vertical protection against salt water percolation is thus quite good except where the drainage ditches have crossed the argillaceous geological horizons overlaying the aquifer.

To define the spreading parameters within the aquifer, a convergent radial tracing test was made with the help of a NaCl saturated solution.

The solution was continuously injected in the P2 well with a 0,5m³/h flow for a pumping on P3 with a 3,43 m³/h flow.

The results are evaluated from the conductivity curve measured in P3 (Figure 6). The evaluation is based on the common point method and on the characteristic curves of Santy J.P. (1978) and Laurent E. (1979).

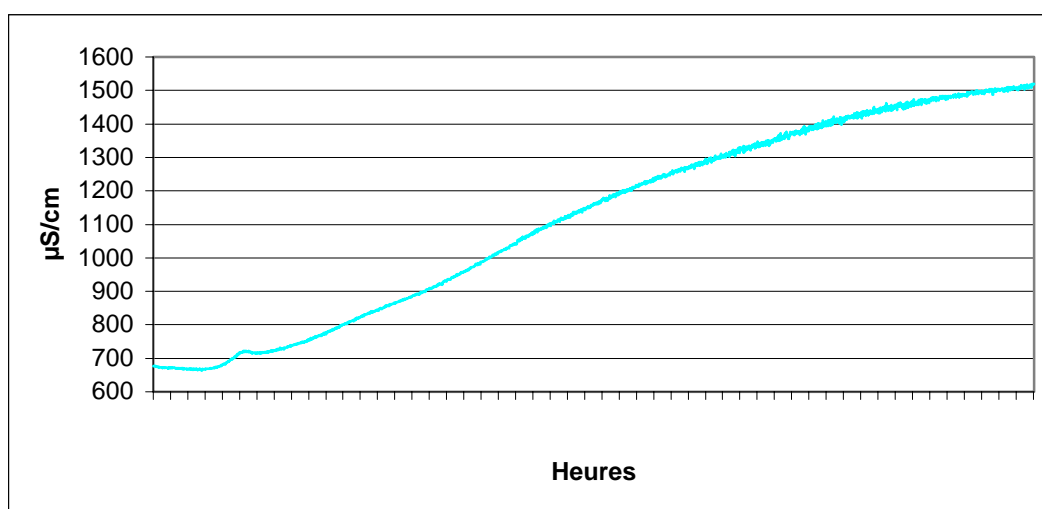


Figure 6. Conductivity curve.

The preliminary control of the injection conditions is based on the generalised radial model (Laurent E., 1992).

The calculation of the dispersion parameters made from the experimental curve produces the following results:

- radial dispersivity $\alpha_r = r/4B = 20 \text{ m}/1,2 = 16,67 \text{ m}$
- average pore speed $V_p = \frac{z}{t} \cdot \frac{r}{B} = 0,2133 \text{ m/h}$
- path-time $t_p = r/V_p = 20/0,2133 = 93,75 \text{ h}$
- dynamic porosity $\omega = (t_p \cdot Q)/(\pi \cdot e \cdot r^2) = 1,71 \cdot 10^{-2}$

Table 3 compares the results of the test made in Couvin with equivalent data concerning the main calcareous and chalk aquifers of the Walloon Region.

Aquifere	Dynamic Porosity	Dispersion coefficient
Carboniferous limestone Karstic area of the Tournaisis	$\omega_d = 5,81 \cdot 10^{-2}$	$\alpha_L = 234$ m
Carboniferous limestone Charleroi zone	$6 \cdot 10^{-3} < \omega_d < 2,5 \cdot 10^{-2}$	$3,75$ m $< \alpha_R < 30$ m
Cretaceous of the Haine Havrée	$\omega_d = 2,87 \cdot 10^{-2}$	$\alpha_R = 6,0$ m
Cretaceous of Brabant	$6,5 \cdot 10^{-2} < \omega_d < 9,85 \cdot 10^{-2}$	$7,0$ m $< \alpha_R < 15,7$ m
Calcareous shale of Couvin	$\omega_d = 1,71 \cdot 10^{-2}$	$\alpha_R = 16,67$ m

Table 3. Dispersion parameters.

The experimental site very well represents the aquifer type where crack porosity develops parameters favourable to the dispersion of dissolved salts.

This table also indicates the numerical values essential to model the dispersion term of an equation concerning the transport of the ions coming from road de-icers.

Four chemical analysis campaigns were conducted on the chosen site concerning water coming from the road drainage ditches and from the four wells. The dates selected cover the periods which precede (one campaign) and follow (one campaign) road de-icers winter spreading as well as those during which salting is carried out (two campaigns).

As an example, Table 4 indicates the results of the campaign carried out on 26 April 2001.

	PH	Cond. mS/cm	HCO ₃ ⁻ mg/l	CO ₂ d. mg/l	SO ₄ ²⁻ mg/l	Cl ⁻ mg/l	NO ₃ ⁻ mg/l	Ca ⁺⁺ mg/l	Mg ⁺⁺ mg/l	Na ⁺ mg/l	K ⁺ mg/l	DCO mgO ₂ /l	Si mg/l	Al mg/l	Fe mg/l
P1	7,7	1,22	265	10	24	275	6	198	20	23	1,7	<15	4,6	<0,05	<0,05
P2	7,0	1,21	270	49	21	285	4	197	21	25	1,6	<15	5,3	<0,05	<0,05
P3	7,0	0,847	270	49	31	130	20	148	13	12	1,1	<15	4,7	<0,05	<0,05
P4	7,2	0,579	320	37	31	26	32	132	4,5	8	1,7	<15	0,5	<0,05	0,1
F1	7,3	0,938	275	25	20	172	<0,1	97	3,1	102	3,2	<15	3,0	<0,05	<0,05
F2	7,0	2,13	180	33	13	620	<0,1	68	2,4	375	4,7	<15	0,6	<0,05	0,4

Table 4. Campaign carried out on 26 April 2001.

The analysed parameters enable to track the salts' ions but also include the ions necessary to ionic balance and to calculate the activities required in order to determine the thermodynamic equilibria diagrams. They moreover include heavy metals not indicated in the table.

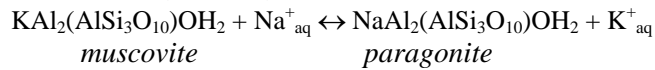
Table 5 shows the results obtained for the ions typical of road de-icers.

F1	Ca ⁺⁺ mg/l	Na ⁺ mg/l	Cl ⁻ mg/l	[Na ⁺] / [Cl ⁻]	F2	Ca ⁺⁺ Mg/l	Na ⁺ mg/l	Cl ⁻ mg/l	[Na ⁺] / [Cl ⁻]	P1	Ca ⁺⁺ mg/l	Na ⁺ mg/l	Cl ⁻ mg/l	[Na ⁺] / [Cl ⁻]
30/05/00	36	22	37	0,92		33	24	37	1		-	-	-	-
24/11/00	64	41	42	1,50		97	24	22	1,68		200	26	275	0,14
23/02/01	70	195	350	0,86		37	160	290	0,85		185	27	270	0,15
26/04/01	97	102	172	0,91		68	375	620	0,93		198	23	275	0,13
P2	Ca ⁺⁺ mg/l	Na ⁺ mg/l	Cl ⁻ mg/l	[Na ⁺] / [Cl ⁻]	P3	Ca ⁺⁺ Mg/l	Na ⁺ mg/l	Cl ⁻ mg/l	[Na ⁺] / [Cl ⁻]	P4	Ca ⁺⁺ mg/l	Na ⁺ mg/l	Cl ⁻ mg/l	[Na ⁺] / [Cl ⁻]
5/10/00	176	23	265	0,13		126	15	120	0,19		124	17	71	0,37
24/11/00	192	15	285	0,08		145	13	139	0,14		127	13	37	0,54
23/02/01	205	16	290	0,08		150	13	135	0,15		128	10	38	0,40
26/04/01	197	25	285	0,13		148	12	130	0,14		132	8	26	0,47

Table 5. Ions typical of road de-icers.

These results point out a large difference of content between the maximal concentrations in the ditches and in the aquifer. The contrast is more marked for sodium than for chlorine.

Let us analyse water reactions to silicates identified in the rock. A first reaction concerns substitution within aquifer muscovites (or illites):



with an equilibrium constant of

$$K_{\text{eq}} = [\text{K}^+]/[\text{Na}^+].$$

Since Gibbs free energy changes for the minerals considered according to their crystalline states, we will consider both the ordered and disordered state of each mineral concerned.

Figure 7 below shows the most favourable reaction.

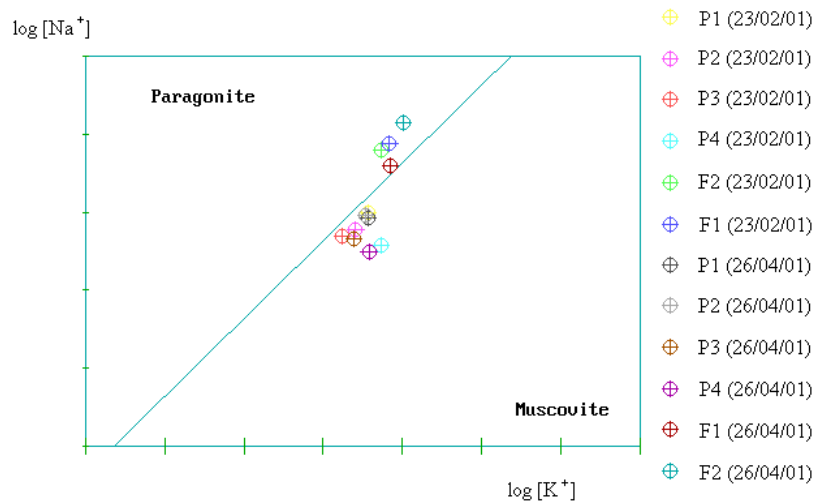


Figure 7: Muscovite – paragonite equilibrium

In practice, disordered muscovite can reduce water's sodium content for Na+ concentrations superior to 25 times the K+ concentration. From the thermodynamic point of view, this process is thus feasible for the most concentrated surface waters (after salting) but can not be active within the aquifer.

Kaolinite transformation into paragonite may, on the other hand, happen under the influence of all water types analysed as shown on Figure 8 below obtained via the ETDE model (Laurent E. 1987) applied to the sodium silicates' equilibrium.

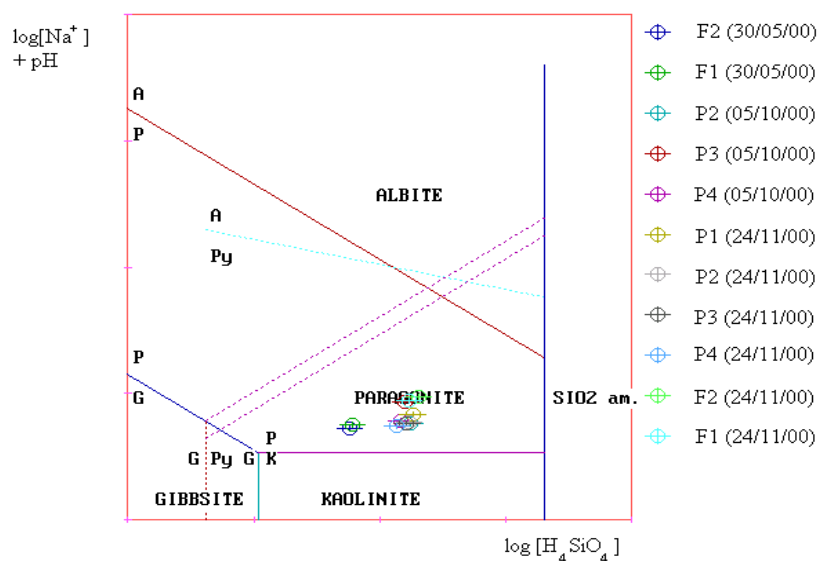


Figure 8: Equilibrium of sodium silicates

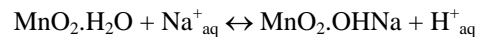
All points representing waters of the Couvin site are located in the stability field of paragonite. Kaolinite and, if need be, feldspar transformation in paragonite can reduce water Na⁺ contents.

Note that as far as the Spa site is concerned, Kramm (1982) had already documented paragonite in the rocks of the Massif of Stavelot.

The reaction to carbon dioxide gas fortified waters had been proven as early as 1987 (Laurent E. 1987), particularly for the site of Chevron (Laurent E. and Wollast R. 1987).

In other words, the presence of kaolinite in the rocks of the two sites contributes to the Na⁺ reduction and thus explains, at least partly, the evolution of the [Na⁺]/[Cl⁻] ratio.

The adsorption power of the metals dissolved in water by disordered iron and manganese hydroxides is known within the framework of manganese nodule genesis and water treatment by filtration. Lan Smiths S. and Jaffe P.R. (1988) introduce the Na⁺ ion in the transport and adsorption model building of the metallic ions in traces in the saturated zone. Adsorption on the disordered minerals of manganese can be written down as follows:



From an equilibrium adsorption, one can represent the reaction by Figure 9.

For the ditch and aquifer waters, one can see that Na⁺ concentrations are insufficient for this phenomenon to have an influence. In practice, contents have to reach 350 mg/l for a pH of about 7,7 so that adsorption occurs. This mechanism can only work for the most concentrated surface waters.

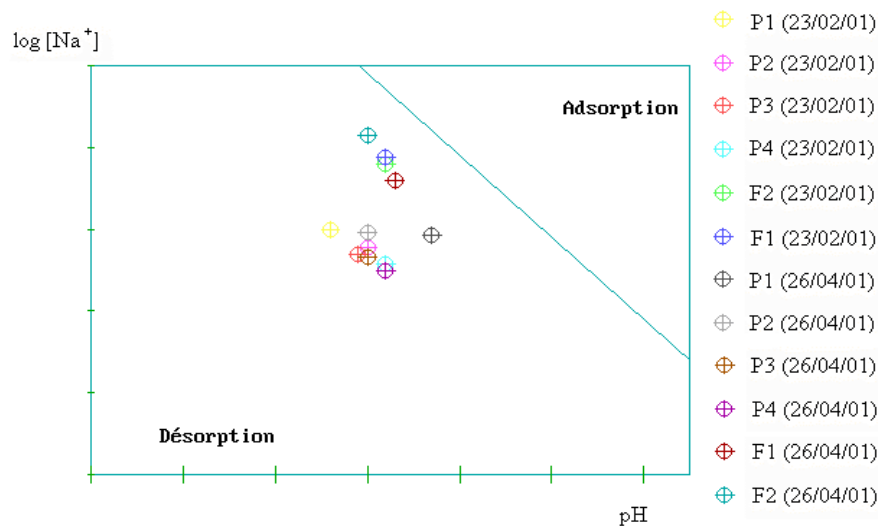


Figure 9 : Adsorption - Desorption

The different behaviour the Na⁺ ion has compared to the Cl⁻ ion can in other words be explained by the replacement reactions between water and aquifer rocks. Within the aquifer, the kaolinite-paragonite reaction seems to be essential. For higher concentrations, particularly within surface waters, the muscovite-paragonite transformation and the adsorption on the disordered iron and manganese hydroxides may reduce the water Na⁺ content.

6. Conclusions

The overall aquifer evolution between 1997 and 2000 is of little importance as far as road de-icers' contribution is concerned. The overall situation remains good. Some points show a slow chloride increase whereas some others registered a reduction of the winter peaks' contents. The sole very high pollution degrees are still due to some rare industrial activity sites.

Within the mineral site, the contents of surface water and groundwater are still excellent. Only points located downstream of the Balmoral salt store house show abnormal contents when there is no covering. The construction of a building covering the store house will eliminate this problem for good. Draining and purification efforts will have to be done to suppress two discharge sites.

The values of the $[Na^+]/[Cl^-]$ concentrations ratio evidenced a different behaviour of the two ions compared to the rocks to be found on the site.

Tests and analyses made on the motorway site enable to carry out a detailed study of the ions' behaviour in the drainage ditches and aquifer waters. The Na^+ ion strongly decreases during percolation whereas the Cl^- ion is mainly curtailed through dispersion in the aquifer.

The Cl^- contents are divided by 4 to 10 between the P2 and P4 wells which are 30 m distant from each other in the direction perpendicular to the road. Hydrogeological and dispersion parameters confirm the sensitivity of this site. The transmittivity, dispersion coefficients and dynamic porosity values of the site have been determined.

Mineralogical analyses enable to better define the aquifer rocks. They reveal the minerals likely to confirm the Na^+ and Cl^- ions' different behaviour. Minerals likely to play a part in the chemical reactions of sodium reduction or to reveal these reactions have particularly been identified.

Among them, we distinguish those that only play a role for high concentrations from those that still occur after a partial content reduction.

The reactions of the HCO_3^- bicarbonate ion with sodium require higher concentrations than those observed on the field. On the other hand, for contents higher than 350 mg/l, adsorption on disordered iron and manganese oxides can decrease the sodium dissolved in ditch water.

The substitution of muscovite for paragonite reduces Na^+ in waters the sodium contents of which are higher than 25 times the potassium contents. The equilibria diagram confirmed the possible reaction for ditches during the salting period. This reaction does however not take place in the aquifer.

Finally, the kaolinite-paragonite reaction can occur in all water types analysed on the site.

The study thus identified the mechanisms explaining Na^+ and Cl^- behaviours. Furthermore, it already enables to make some recommendations on the development of the sites:

- drainage surfaces and ditches will have to include rocks with a high content of minerals reacting with water in order to reduce the water sodium content. The mineralogical study of the rocks found on the site and in the surrounding quarries will orientate this choice according to the studied equilibria.
- ditch bottoms and particularly their seepage zones can be equipped with the same rocks.
- The low permeability layers protecting the aquifer by slow filtering as well as through the studied reactions should not be eliminated when trenching ditches.

Finally, salt water collected before the ditches should be treated taking heed of the studied reactions and a natural treatment pilot plant should be the subject of the future study which will be conducted about the motorway site waters.