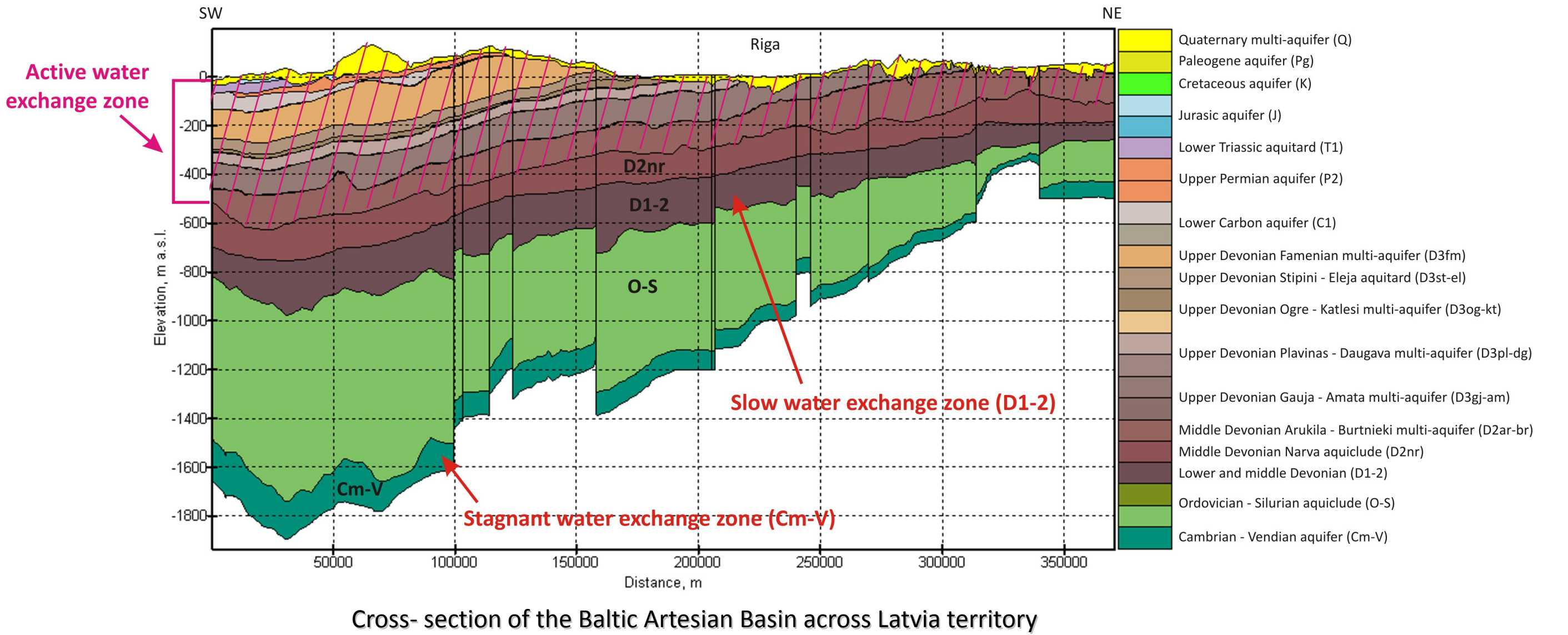
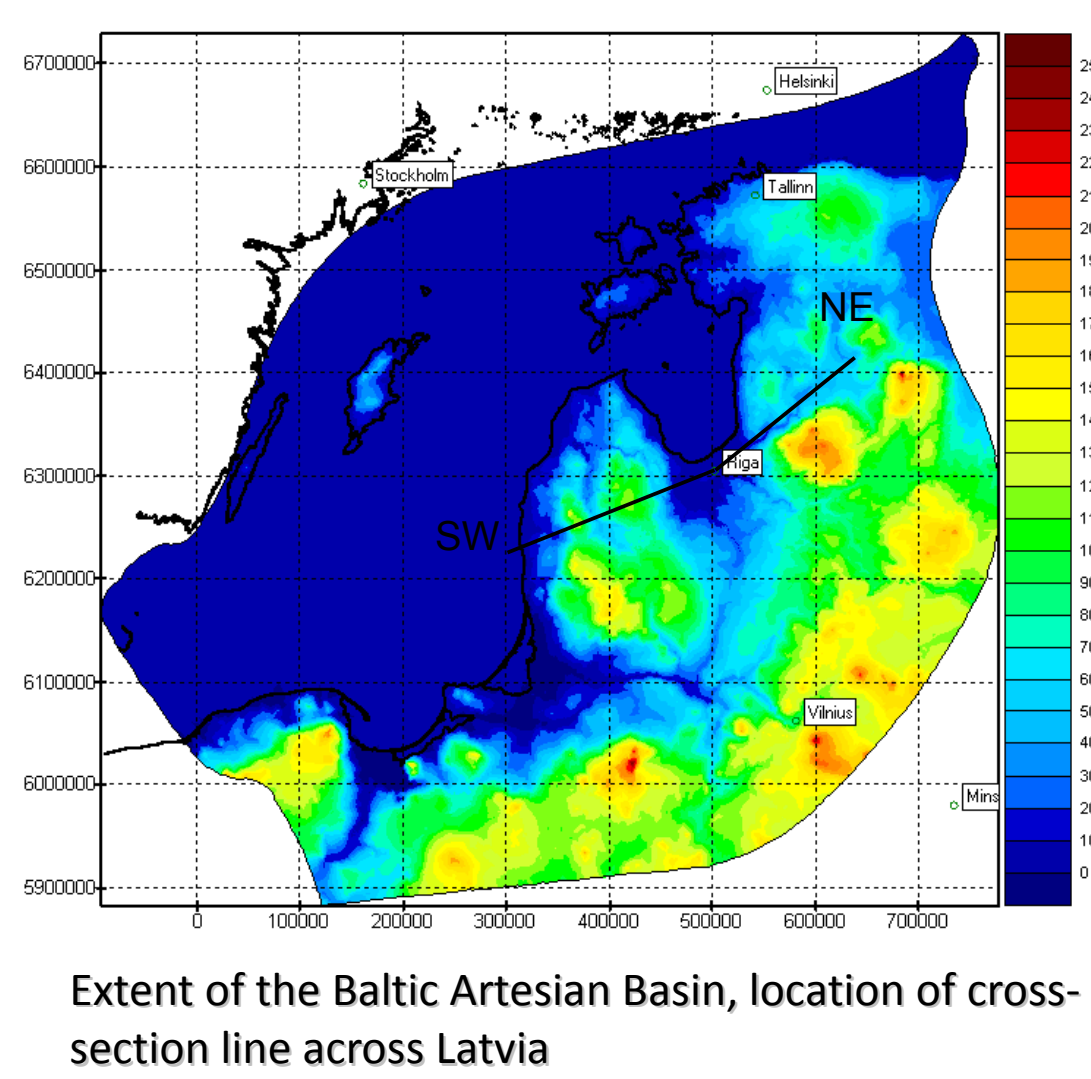


THE GENERAL DESCRIPTION OF MAJOR ION CONCENTRATIONS IN GROUNDWATER OF LATVIA

Andis KALVĀNS, Aija DĒLIŅA
Faculty of Geography and Earth Sciences, University of Latvia, Riga, Latvia.
Contact: andis.kalvans@lu.lv, www.puma.lu.lv

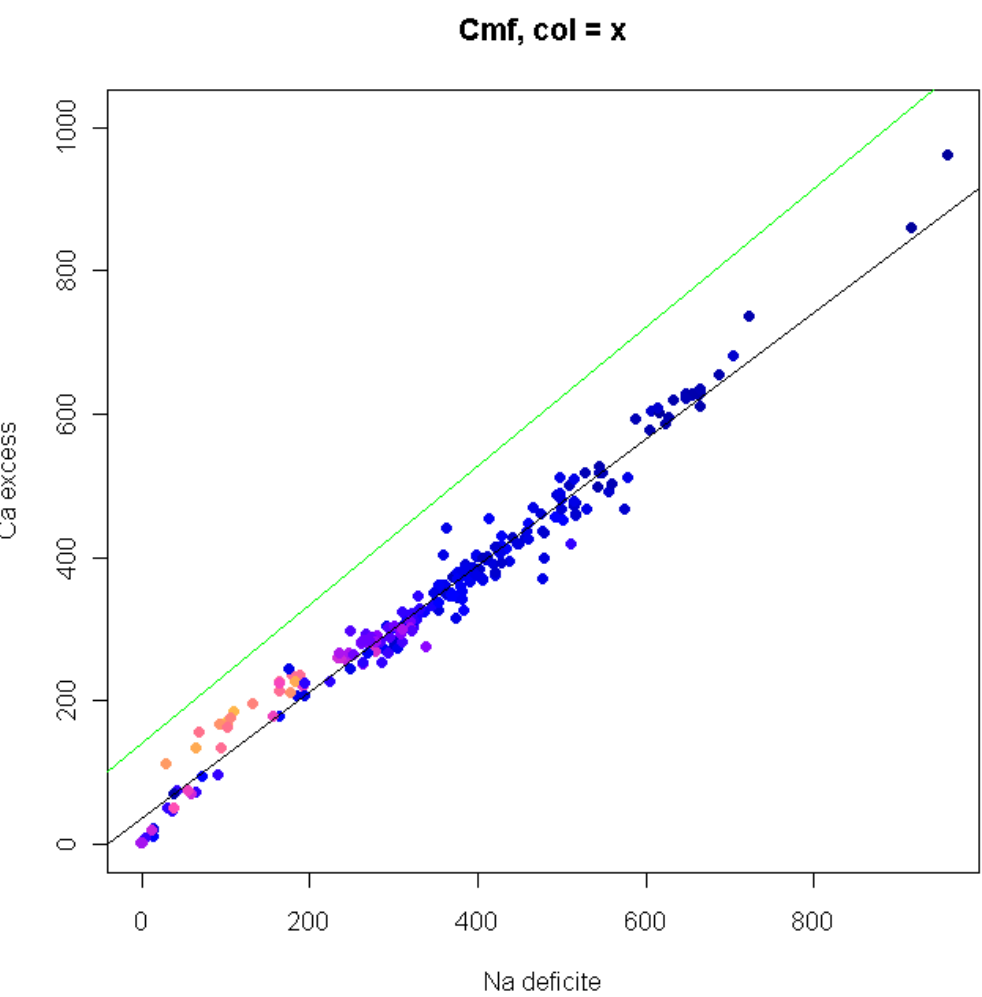
Latvia is situated at the North central part of the Baltic sedimentary basin, where the crystalline basement is found in depth of around 0.6 to 2 km. Three large aquifer complexes with distinct chemical composition of groundwater are identified: the stagnant water exchange zone where Na-Ca-Cl brines are found; the slow water exchange zone where Na-Ca- Cl-SO₄ brackish water is found and active water exchange zone where the freshwater resides. These are separated by distinct regional aquicludes.



Stagnant water exchange zone, Cambrian – Vendian (Cm_f-V) multi-aquifer system

The composition of the Cl- dominated brines at the base of the sedimentary basin is characterised by shift from Na⁺ towards Ca²⁺ as dominant cation, partially associated with depth of the aquifer and the strength of the brine. The concentration of SO₄²⁻ here is inversely linked to the concentration of Ca²⁺ and, according to geochemical modelling, often is close to the solubility limit of the gypsum. The major ion concentrations in the E and W part of the territory are rather different. Therefore two different initial sources for the brine formation were suggested.

Alternatively the observations can be explained by different thermal histories of different parts of the basin, affecting the rate of albitization – exchange of the Na⁺ for Ca²⁺ in the solution due to water-rock interaction.

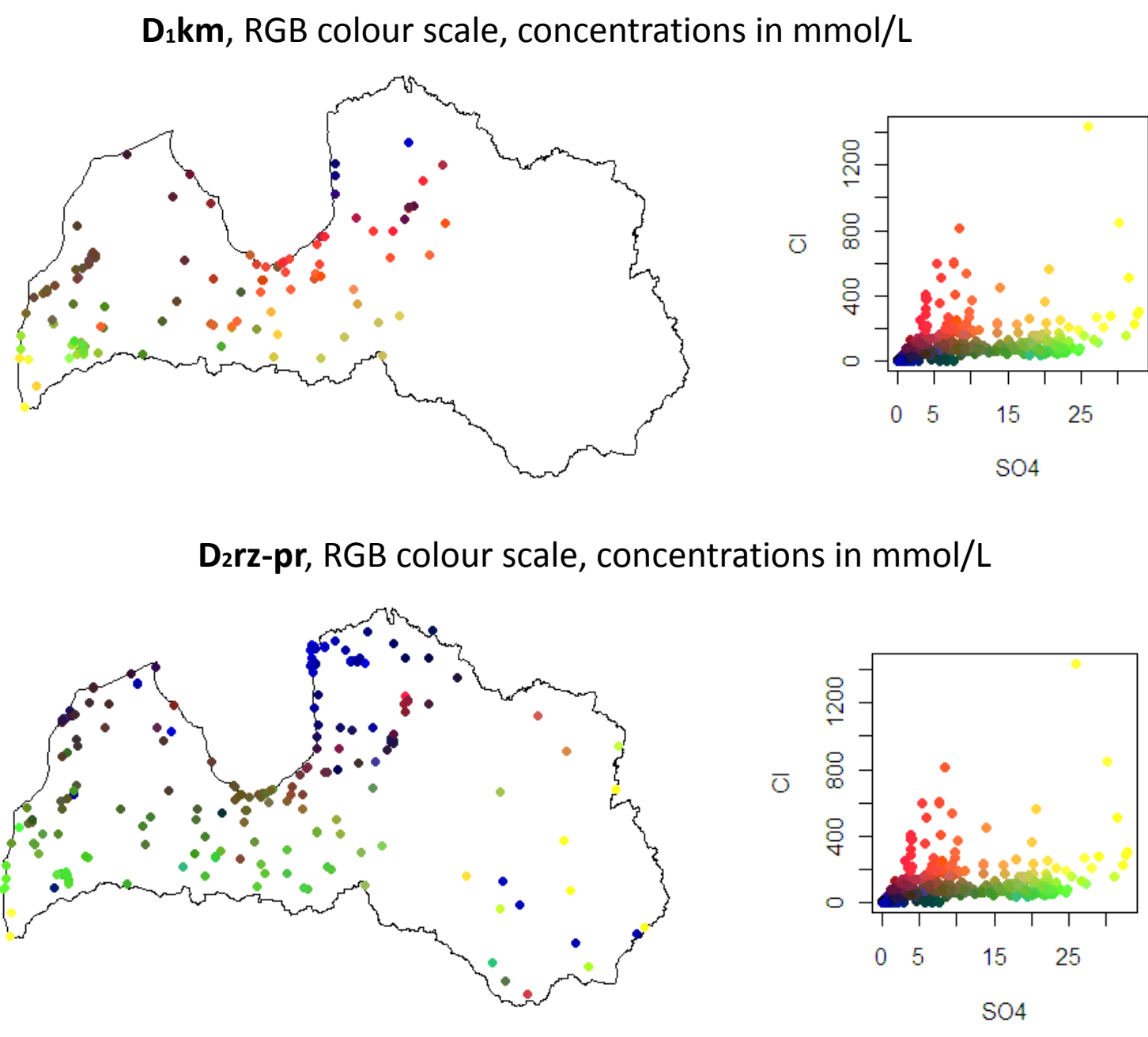


$$Ca_{excess} = \frac{\left[Ca_{meas} - \left(\frac{Ca}{Cl}\right)_{st} \cdot Cl_{meas}\right]^2}{40.08}$$
$$Na_{excess} = \frac{\left[\left(\frac{Na}{Cl}\right)_{st} \cdot Cl_{meas} - Na_{meas}\right]^2}{22.99}$$

Green line: the basin fluid line from Davisson and Criss (1996);
Black line: regression from all data at the Cm aquifer;
Red line: regression from Ca²⁺ excess < 300;
Blue line: regression from Ca²⁺ excess > 300

Slow water exchange zone, lower and middle Devonian (D₁₋₂) multi-aquifer system

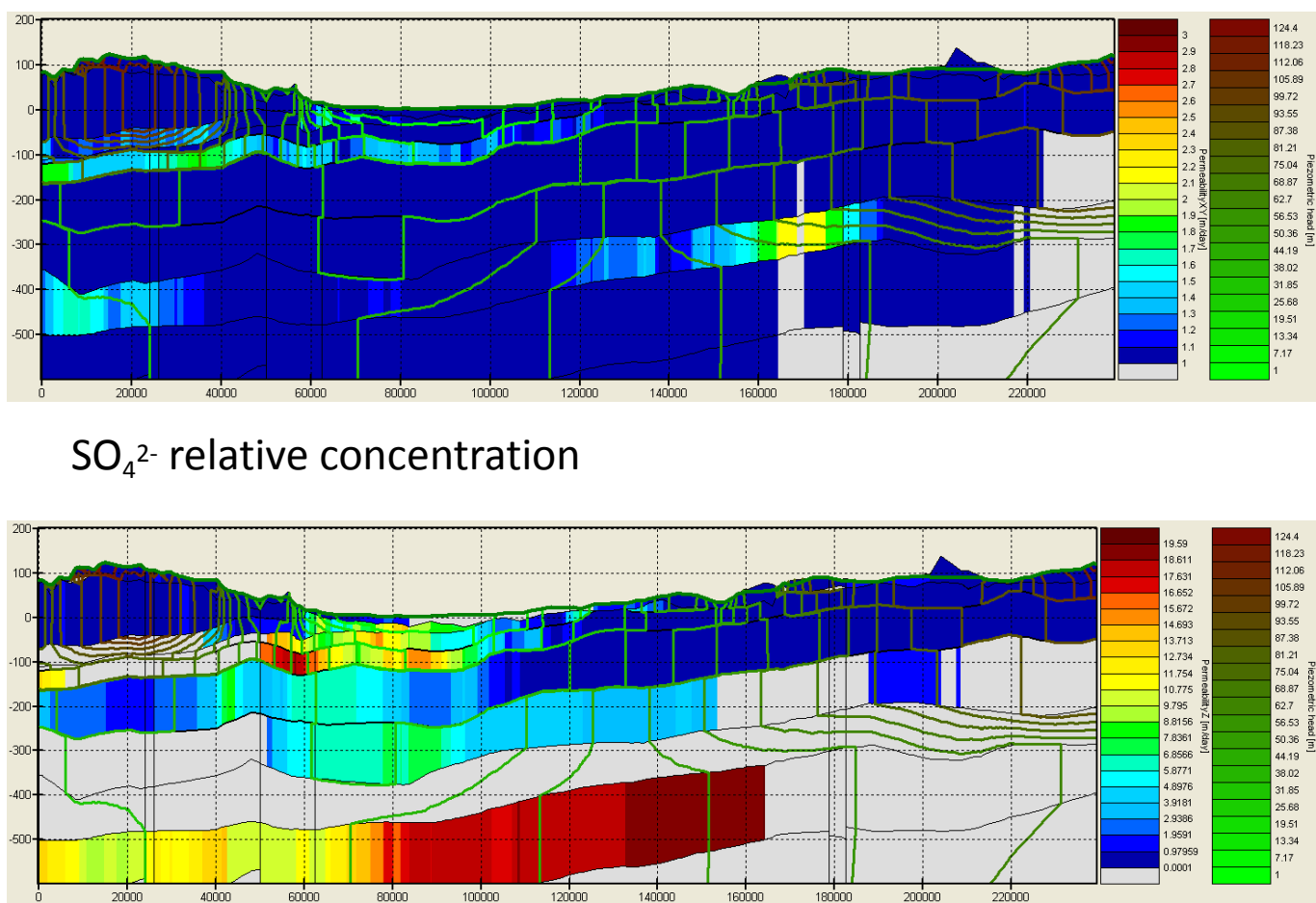
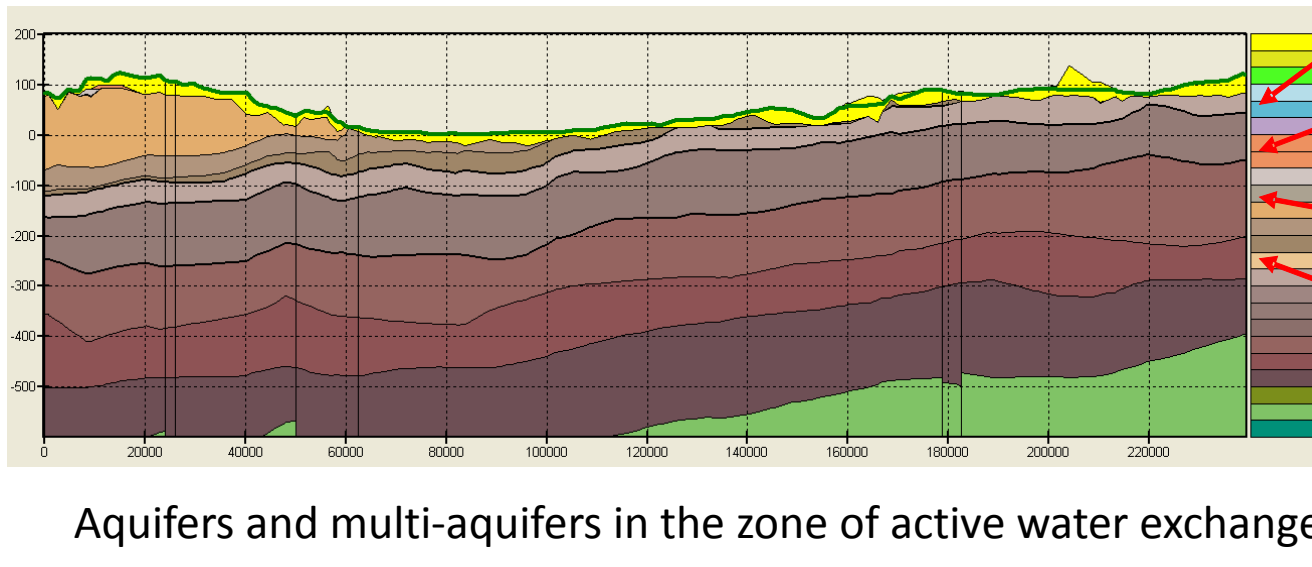
The groundwater composition there can be nicely explained by the mixing of freshwater from above and brine residing deeper in the presence of gypsum during some but no all stages of mixing. In some shallow parts of the zone still bound by the Narva regional aquiclude freshwater is found. The question is posted – could this be a paleogroundwater originating from the extensive continental glaciations that overrided the territory several times during the Pleistocene? Initial isotope studies presented elsewhere seems to give negative answer to this question.



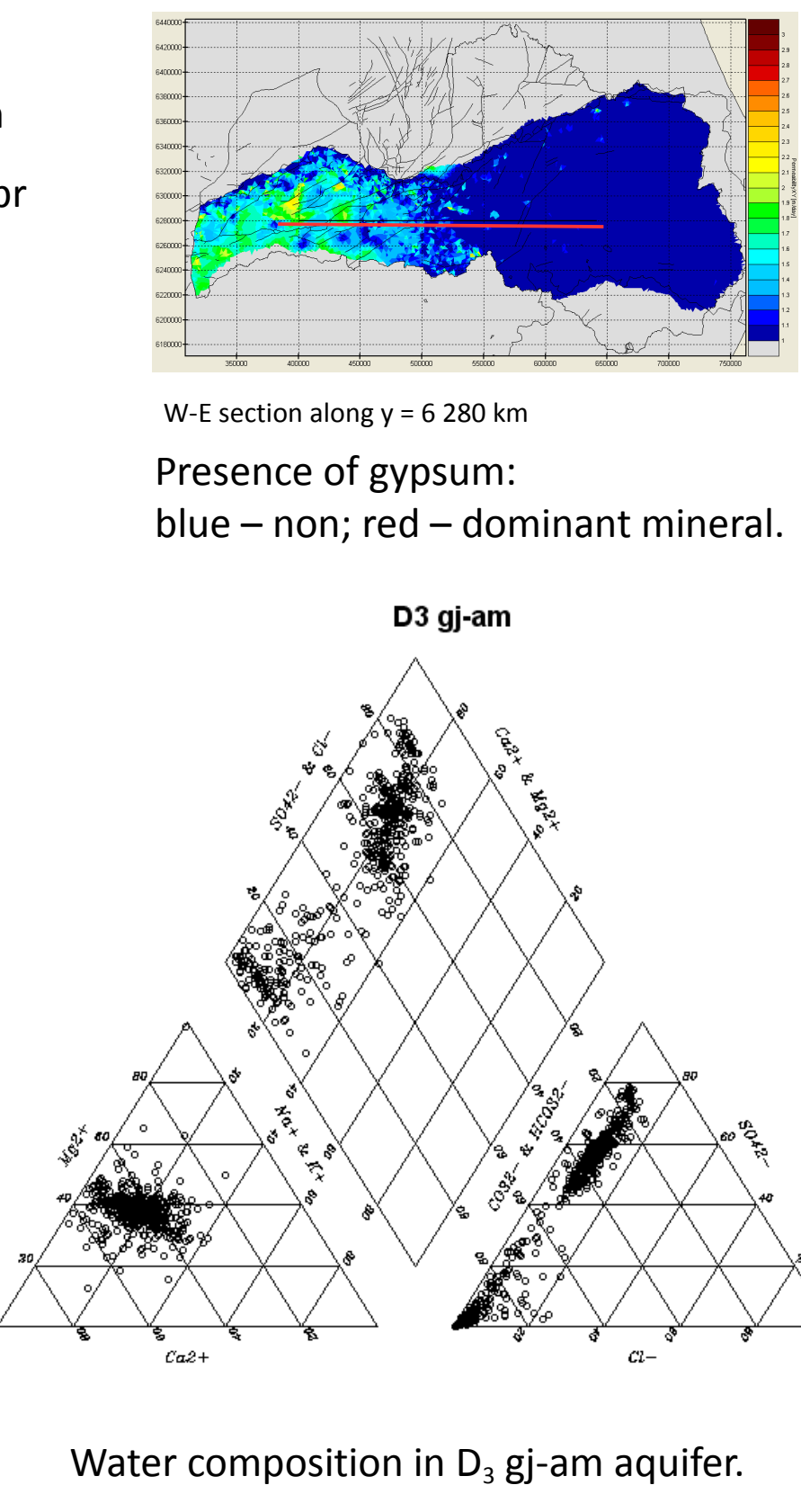
Contrasting water composition in lower and upper parts of slow water exchange zone

Active water exchange zone, middle and upper Devonian (D₂₋₃) multi-aquifer system

The active water exchange zone is characterised by fresh water of Ca-Mg-HCO₃ type with exceptions in cases where gypsum are abundant in sedimentary rocks and sulphate ion prevails.



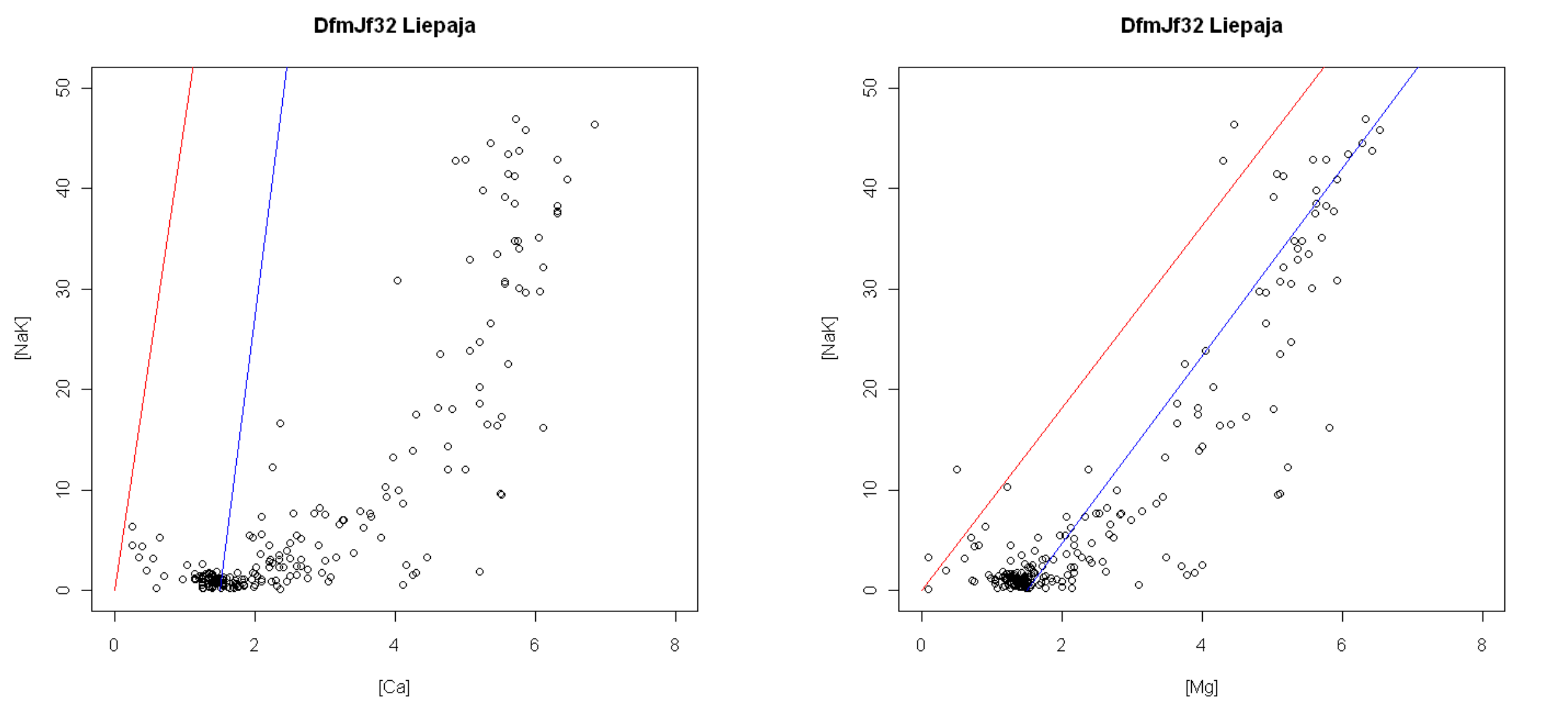
Water composition does not represent the current flow lines: likely position of old/relict groundwater.



Water composition in D₃ gj-am aquifer.

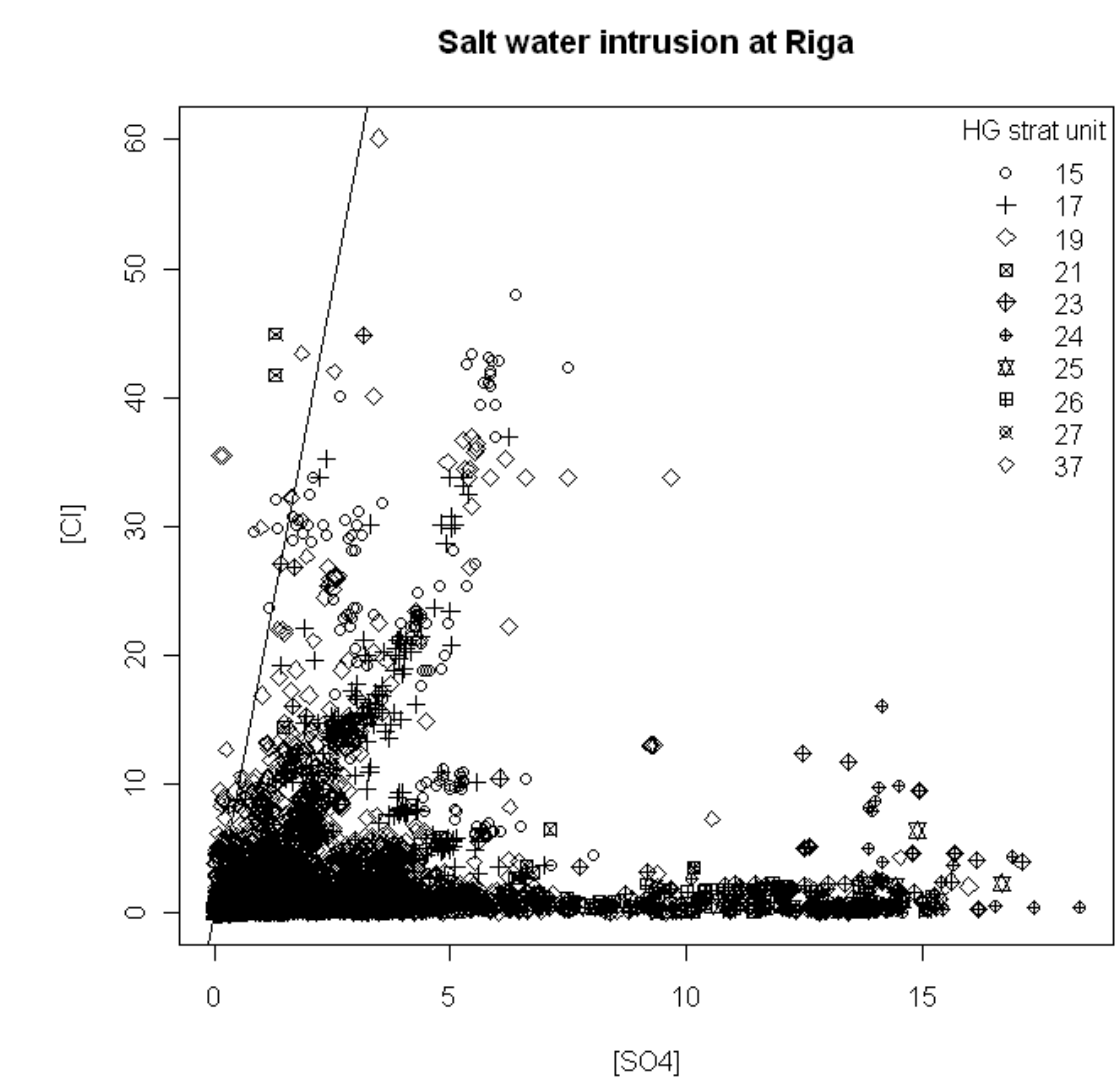
The freshwater composition seems to be mostly controlled by three minerals – calcite, dolomite and gypsum. It is suggested that clay minerals can play a significant role in controlling the relative concentrations of cations, but this is not strictly proven yet.

Well documented modern seawater intrusion induced by water abstraction is found in the territory of the Liepāja City.



Ca²⁺ excess in respect to Na⁺ in area of seawater groundwater mixing in Liepāja City is demonstrated. Calcite dissolution or ion exchange can be blamed for this. The blue line is simple seawater-groundwater mixing line.

The intrusion of salt water from deeper aquifers can be spotted across the territory as well. These zones are usually associated with tectonic faults, enabling the intrusion of salty water through the regional aquicludes. Particularly prominent is the saltwater body in the vicinity of the Riga City. Three major rivers are discharging in the sea there making it a natural confluence zone of groundwater as well. The intensive groundwater abstraction in the city probably enhanced the upwelling of saltwater here, but primary it is a natural phenomenon.

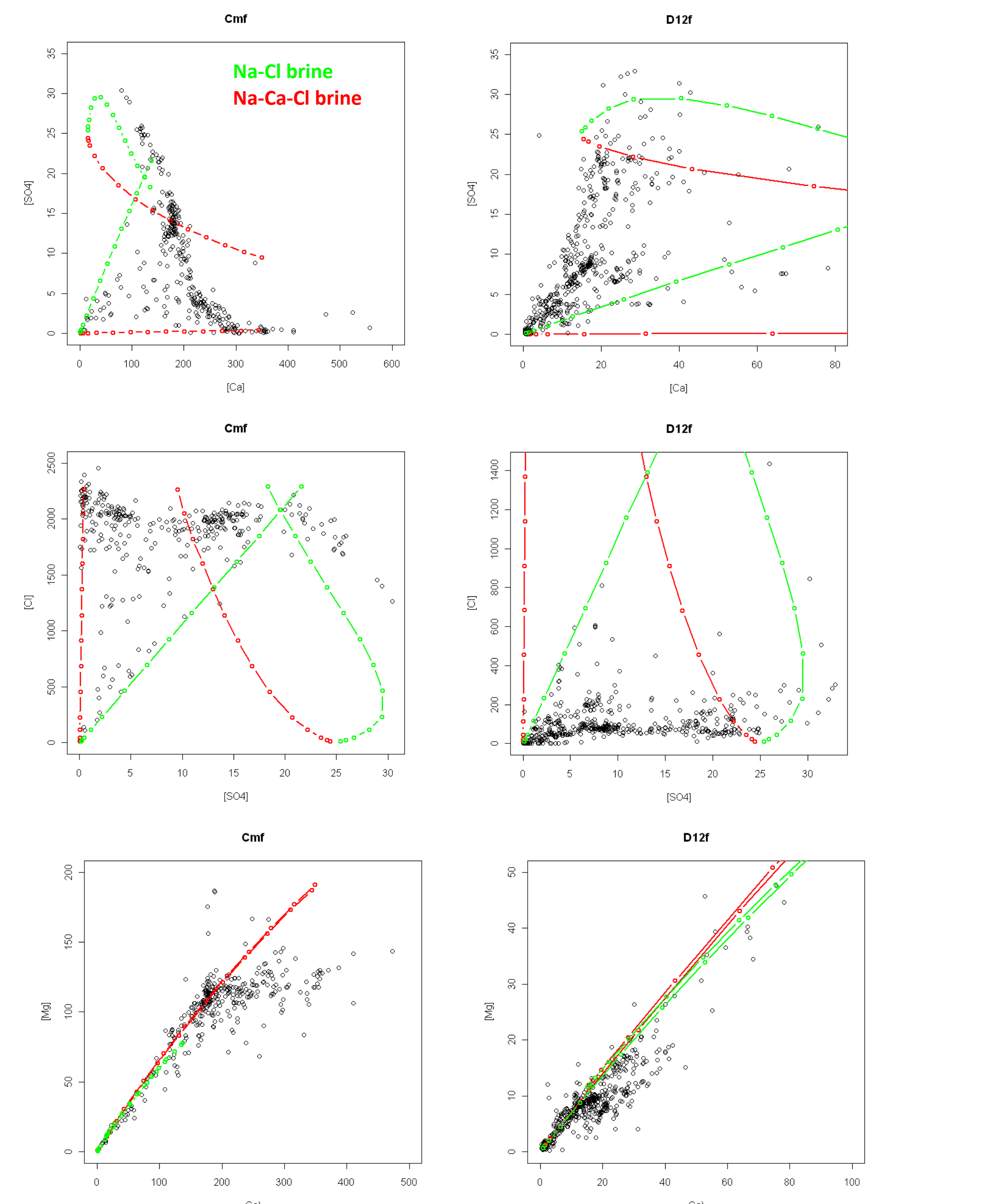
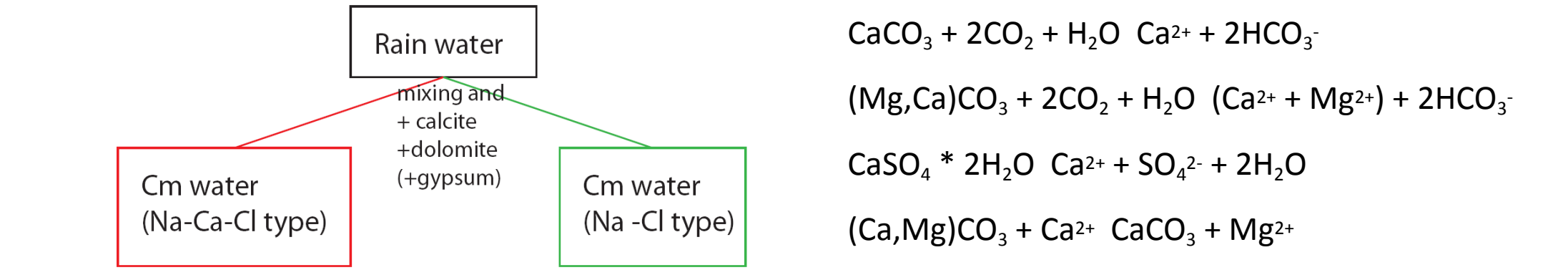


The diversity of groundwater composition in the Riga region: several types of deep saline water, freshwater and, possibly seawater can be identified.

The interesting question is if there is any paleogroundwater trapped in the active or slow water exchange zone of the sedimentary basin that could be distinguished from modern recharge water due to particular isotope signal originating in the Quaternary cold stages or chemical composition – remains of relict sea water or sedimentation water.

Modeling with PHREEQC

	loh	pH	EC (μS/cm)	Density (g/ml)	SO4	NH4	NO3	Cl	Na	K	Ca	Mg	HCO3
Rain water				1,00	0,03	0,00	0,00	0,04	0,04	0,01	0,06	0,02	0,11
Na-Ca-Cl brine	2790	6,0	0,00	1,089	0,38	0,00	0,00	2197,18	1165,78	10,77	410,68	106,33	12,64
Na-Cl brine	3159	6,2	0,00	1,085	20,83	0,00	0,00	2211,27	1833,70	10,00	120,00	87,50	5,76



Model shows much higher [SO₄²⁻] values for the Na-Ca-Cl brine in the presence of the gypsum, than anywhere observed, suggesting that the water have not equilibrated with this mineral. However the observations form a nice continuum from modelled Na-Cl brine equilibrated with gypsum, suggesting that the explanation is more complex.

There is a small offset of the modelled Na-Cl brine composition and the observed trend, pointing to the some systematic error in the model, that could be the temperature, which was not considered in the model.

The model reasonably well explains the relationship between concentrations of SO₄²⁻, Cl- and Ca²⁺ in lower Devonian saline waters: mixing of gypsum contact water and water not equilibrated with gypsum is evident and except few cases it is not possible to identify the original brine type.

The water affected by gypsum dissolution seems not to be fully equilibrated with the dolomite: if the dedolomitization reaction would be completed, then smaller Ca²⁺ concentrations should be observed, both in Cm brine and D₁₋₂ saltwater.