

Freeze/thaw tests for mine waste and suggestions for a protocol for northern climates

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Background

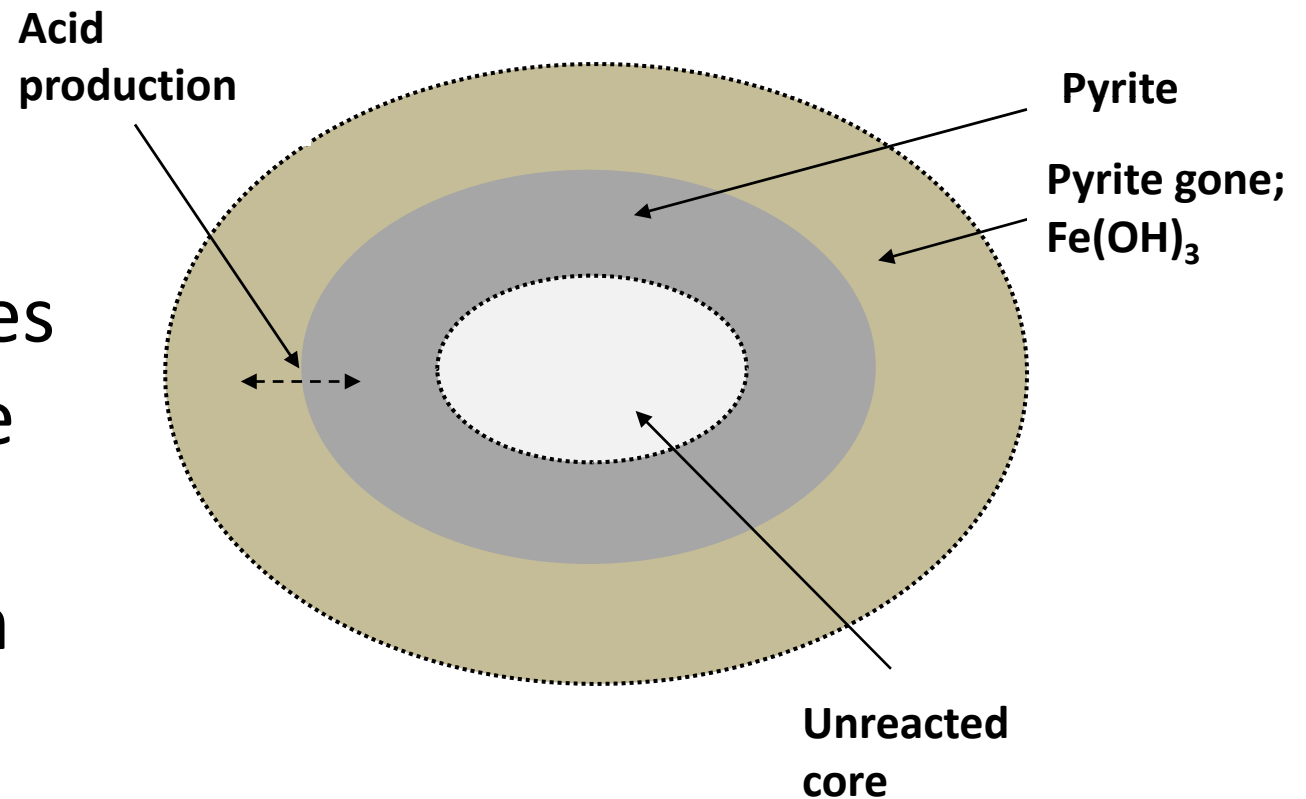
- Sulphide minerals oxidation, mainly the iron sulphide pyrite (FeS_2), generate acid rock drainage (ARD)
- Pyrite oxidation w. O_2 :
 - $\text{FeS}_2(\text{s}) + 3.5 \text{O}_2 + \text{H}_2\text{O} = \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 2 \text{H}^+$
- Oxidation and hydrolysis of Fe(II):
 - $\text{FeS}_2(\text{s}) + 3.75 \text{O}_2 + 3.5 \text{H}_2\text{O} = \text{Fe}(\text{OH})_3(\text{s}) + 2 \text{SO}_4^{2-} + 4 \text{H}^+$
- Pyrite oxidation w. Fe(III):
 - $\text{FeS}_2(\text{s}) + 14 \text{Fe}^{3+} + 8 \text{H}_2\text{O} = 15 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+$
- At high pH:
 - $\text{FeS}_2(\text{s}) + 14 \text{Fe}(\text{OH})_3(\text{s}) + 26 \text{H}^+ = 15 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 34 \text{H}_2\text{O}$

Background, cont.

- Drainage waters with low pH and high trace element concentrations are large problems in Sweden and many other countries
- ARD generation in arctic regions was earlier not considered noteworthy due to slow pyrite oxidation rates at low temperatures
- More recent studies however have shown that ARD is generated in these areas, both from natural weathering of pyritic rocks and of mining waste dumps

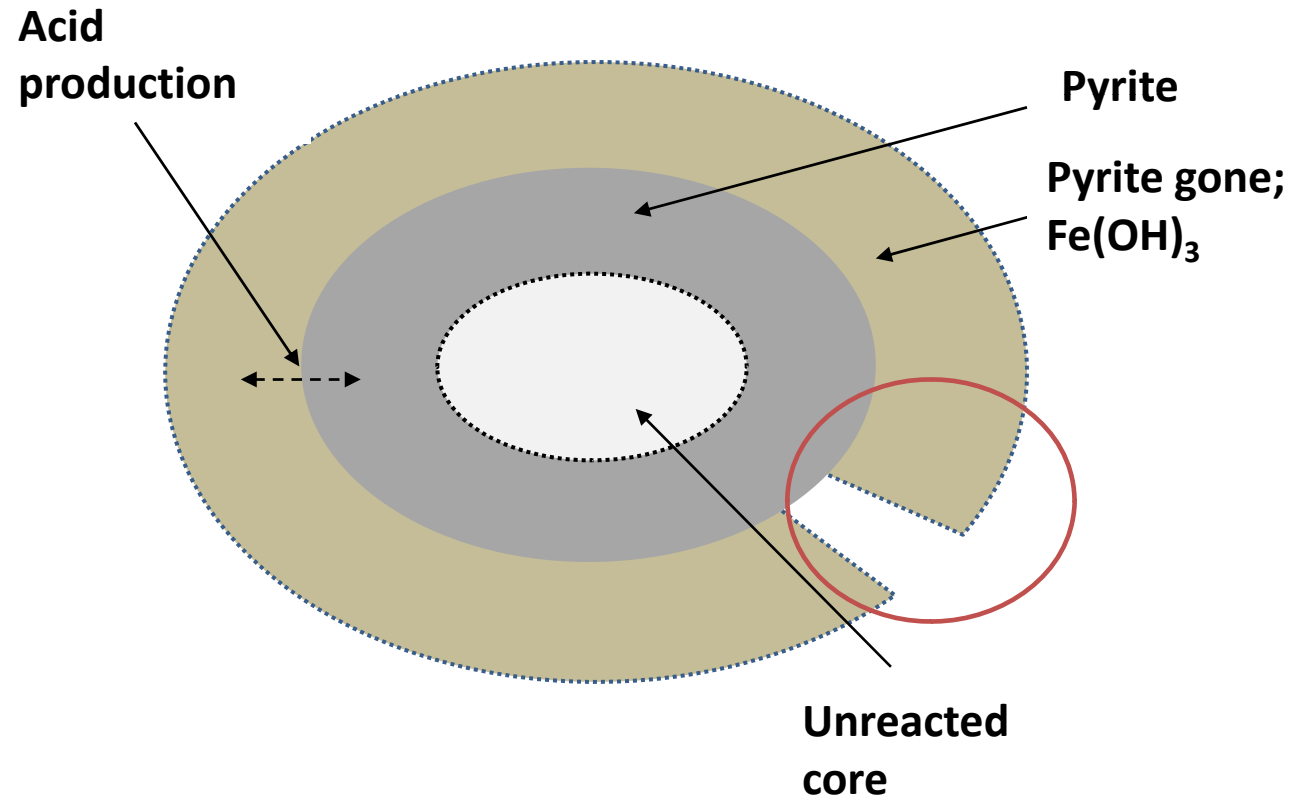
Background, cont.

- Thin layers of ferrous and ferric sulphates and (oxy)hydroxides grow on pyrite surfaces and slow oxidation rates



Background, cont.

- In northern climates, repeated freeze/thaw cycles can cause cracks and exposure of new pyrite surfaces



Questions

- Do repeated freezing/thawing cycles affect weathering rates?
- Can we find a standard protocol for prediction of weathering (ARD generation) in northern climates?



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Materials & Methods

- Oxidation experiments were set up in order to study weathering in different climatic conditions
- Waste rock was sampled at the historic mine site Ljusnarsbergsfältet in Kopparberg, Sweden
 - Sulphides (pyrrhotite, pyrite, chalcopyrite and sphalerite) were present in all rocktypes but with different matrix. About 60 % of the rocks had a matrix dominated by amphibole skarn, 35 % had a silicified matrix ("ore-quartzite"), 4 % had a biotite-amphibole-skarn matrix and 1 % a biotite-flourite-amphibole skarn matrix

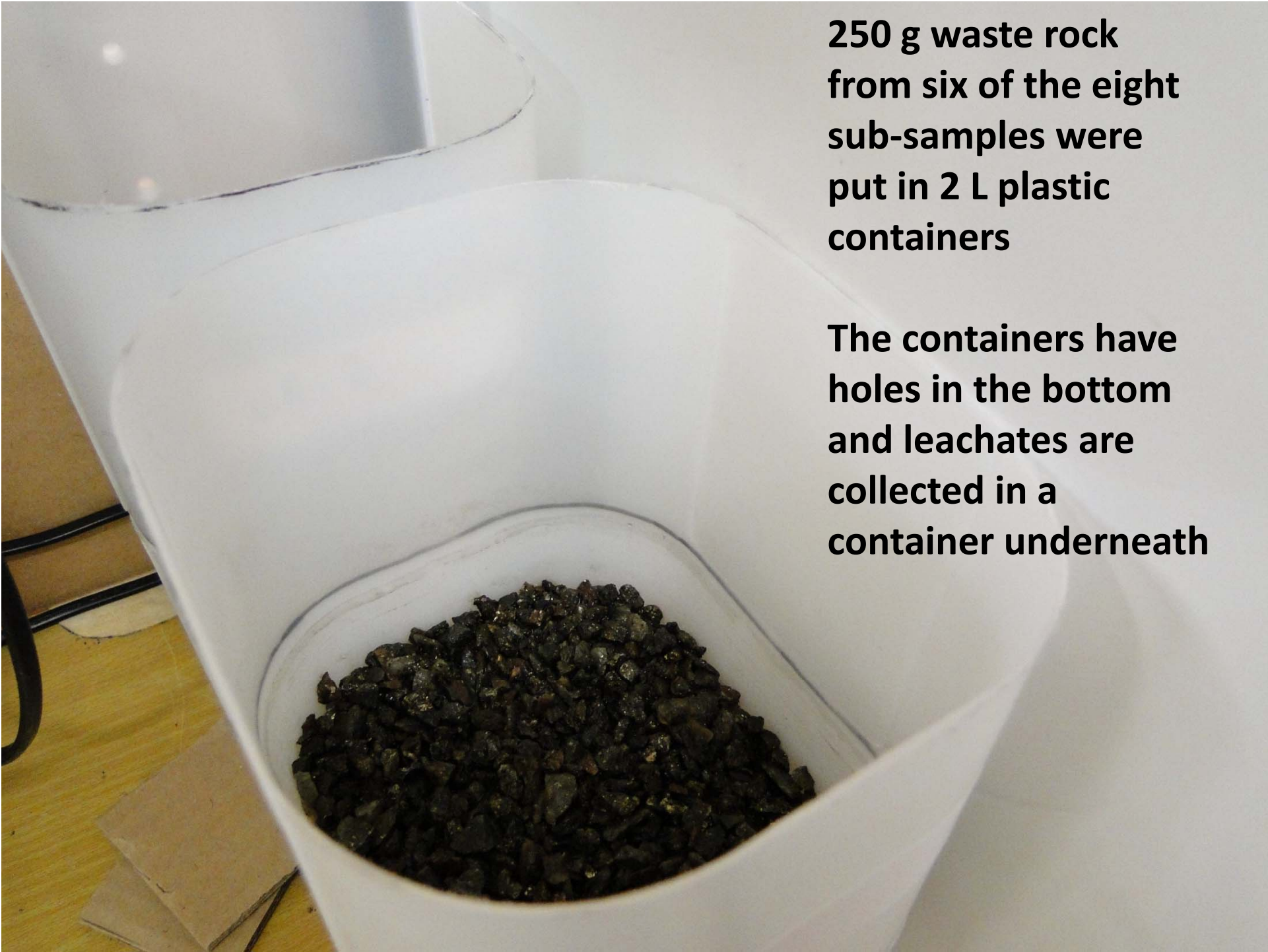




**The waste rock was
crushed and sieved**

**Size fraction 2 to 5 mm
was used for the
experiments**



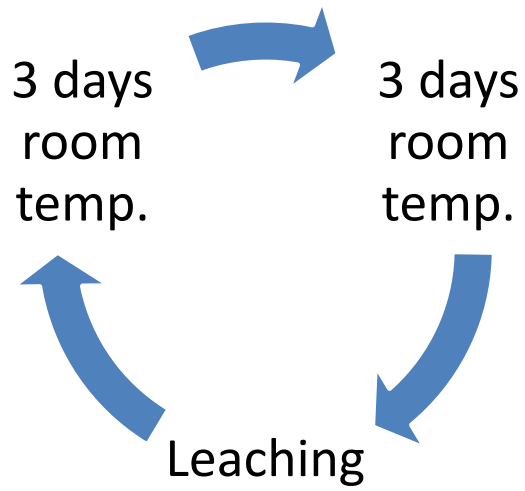


**250 g waste rock
from six of the eight
sub-samples were
put in 2 L plastic
containers**

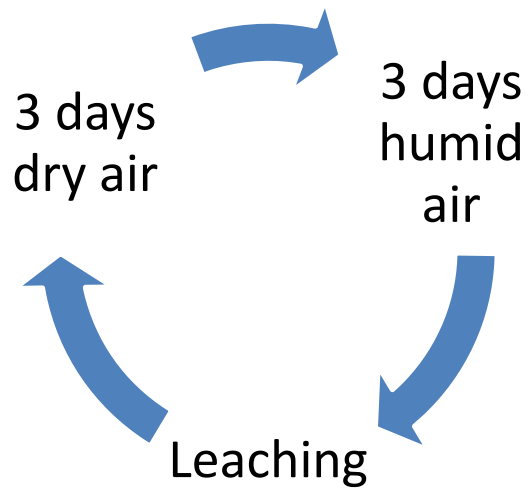
**The containers have
holes in the bottom
and leachates are
collected in a
container underneath**

Experimental

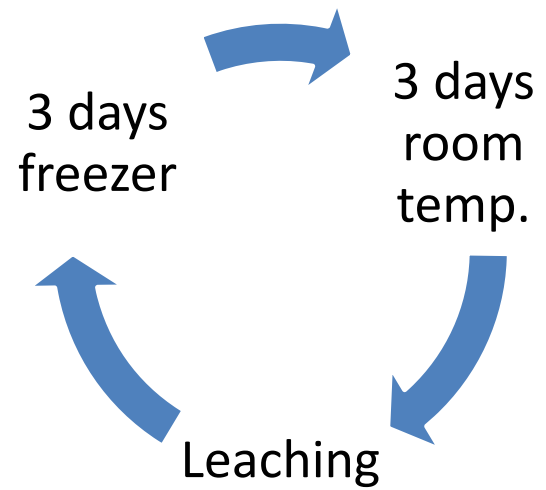
- Methodology based on humidity cell experiments
- Three systems
 - Reference, freeze and humidity
- Weekly cycles of different temperatures and humidity
- Every cycle ended with leaching with 500 mL deionized water
- Samples collected weekly and analysed for pH, Eh, alkalinity, acidity, metals and major anions
- Photographs taken weekly



Reference system



Humidity system

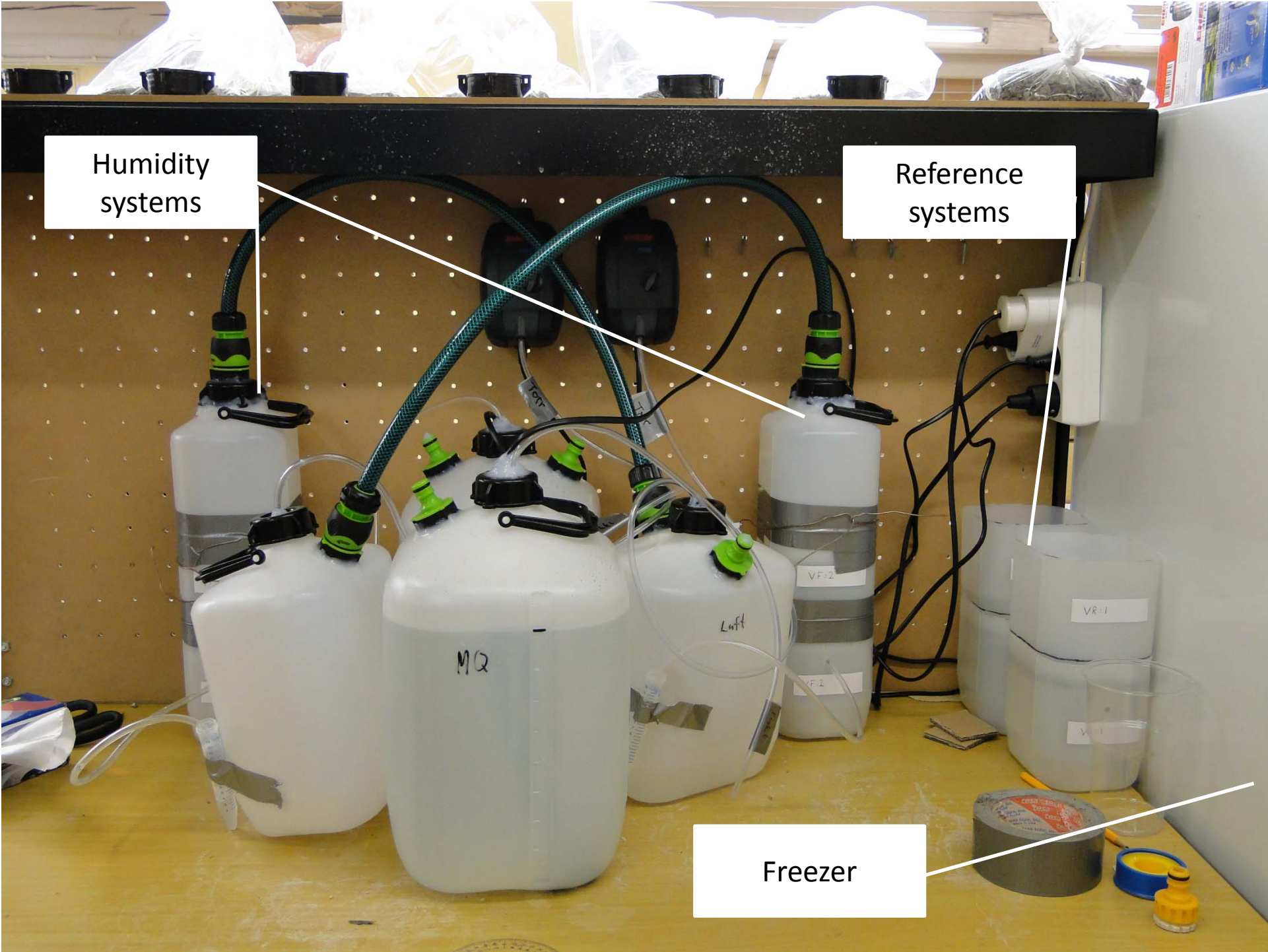


Freeze system

Humidity systems

Reference systems

Freezer

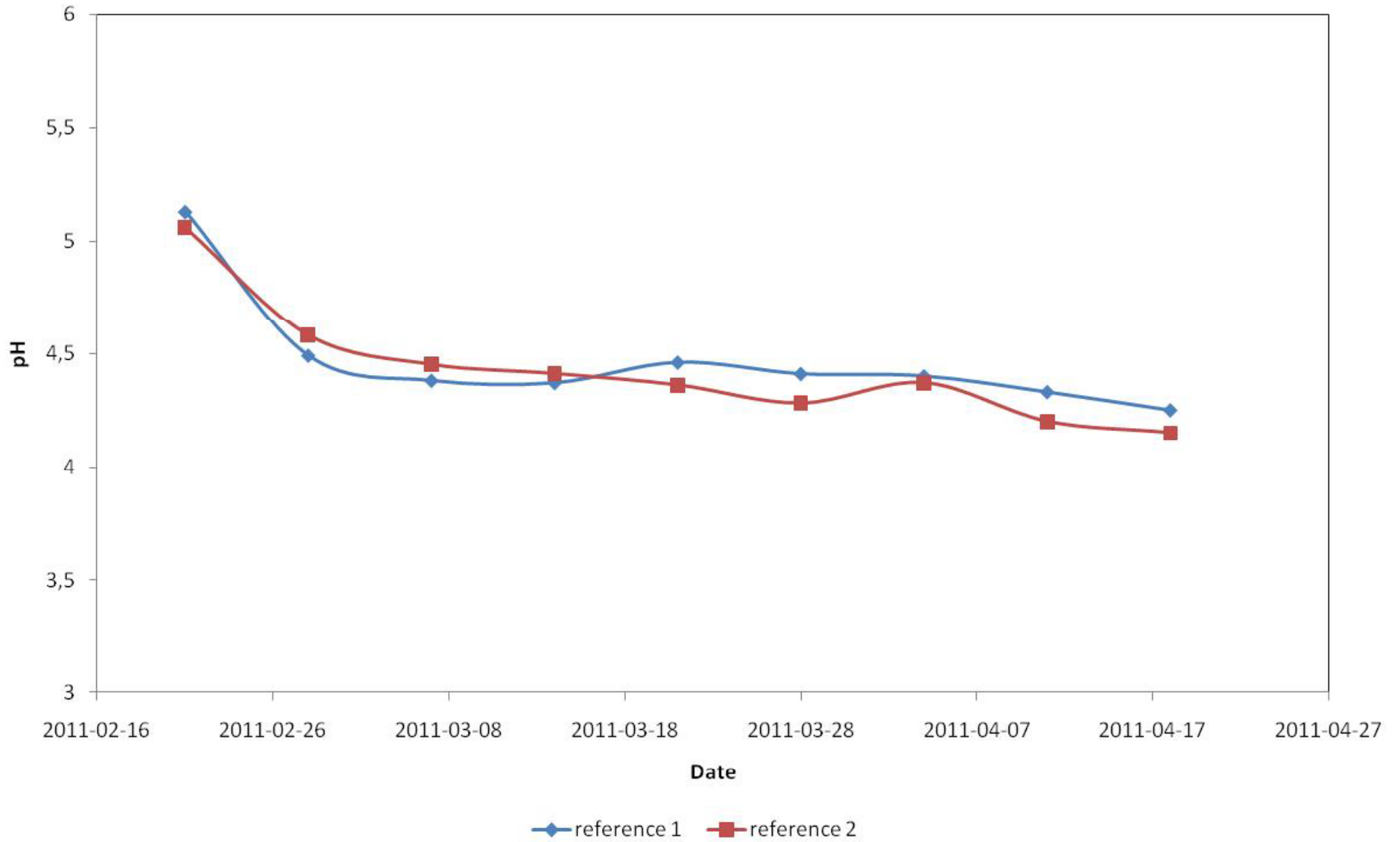


Results & Discussion

- Introductory results show very small changes in pH for the freeze/thaw systems, while pH in reference and humidity cell systems decreased rapidly the first weeks. Accordingly, an increase in both redox potential and electrical conductivity (EC) was noticed in the two latter systems

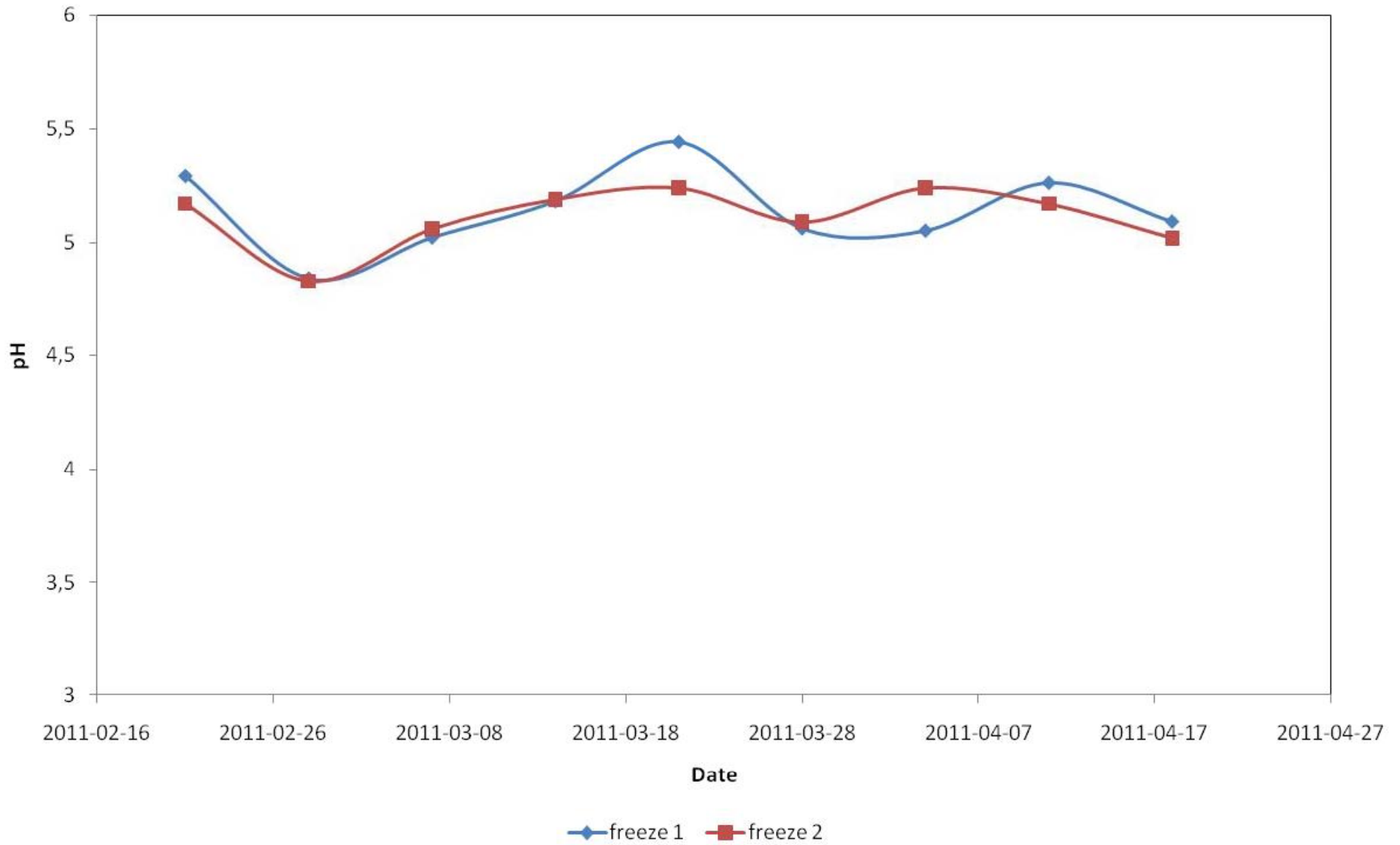
pH

Reference



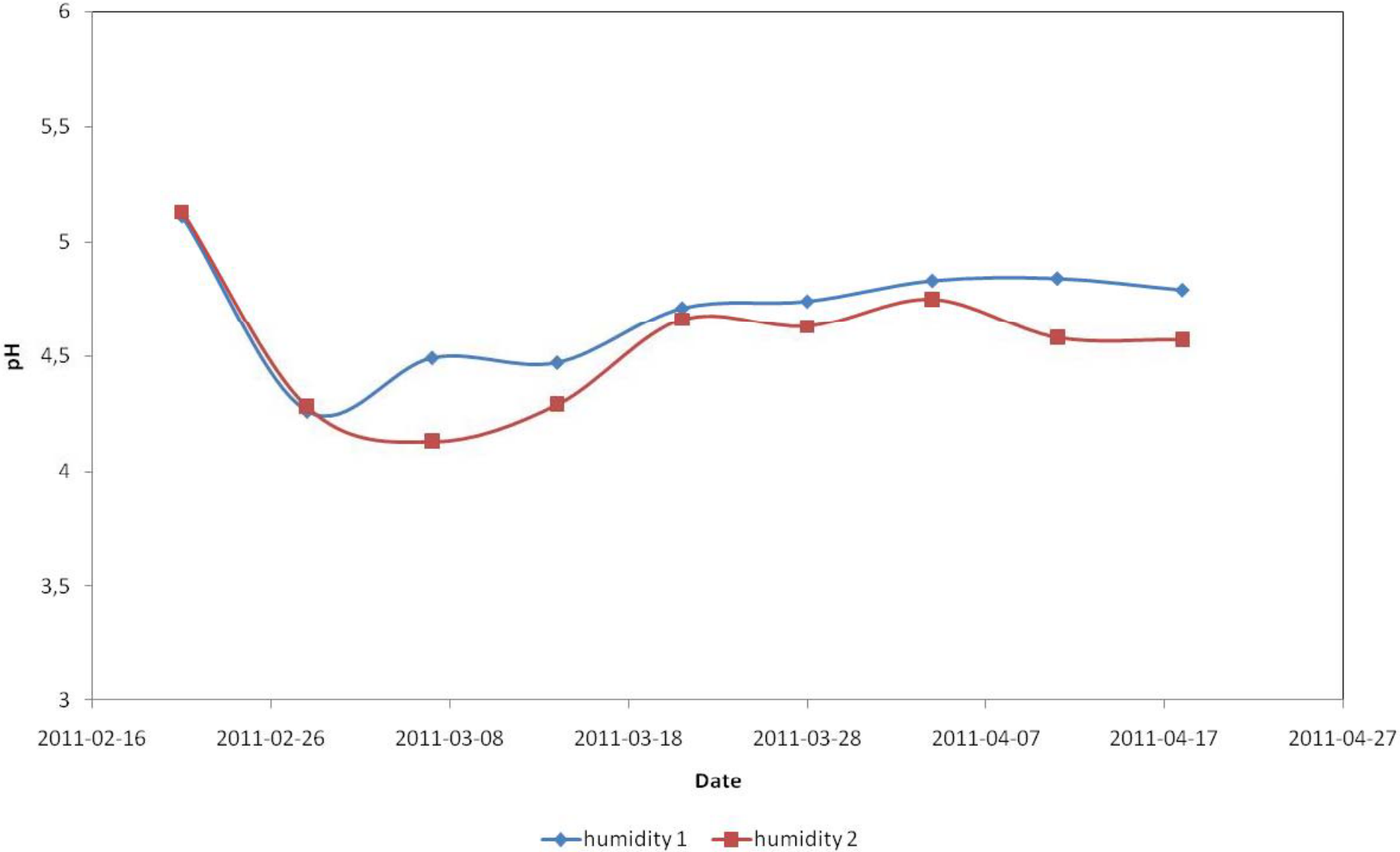
pH

Freeze



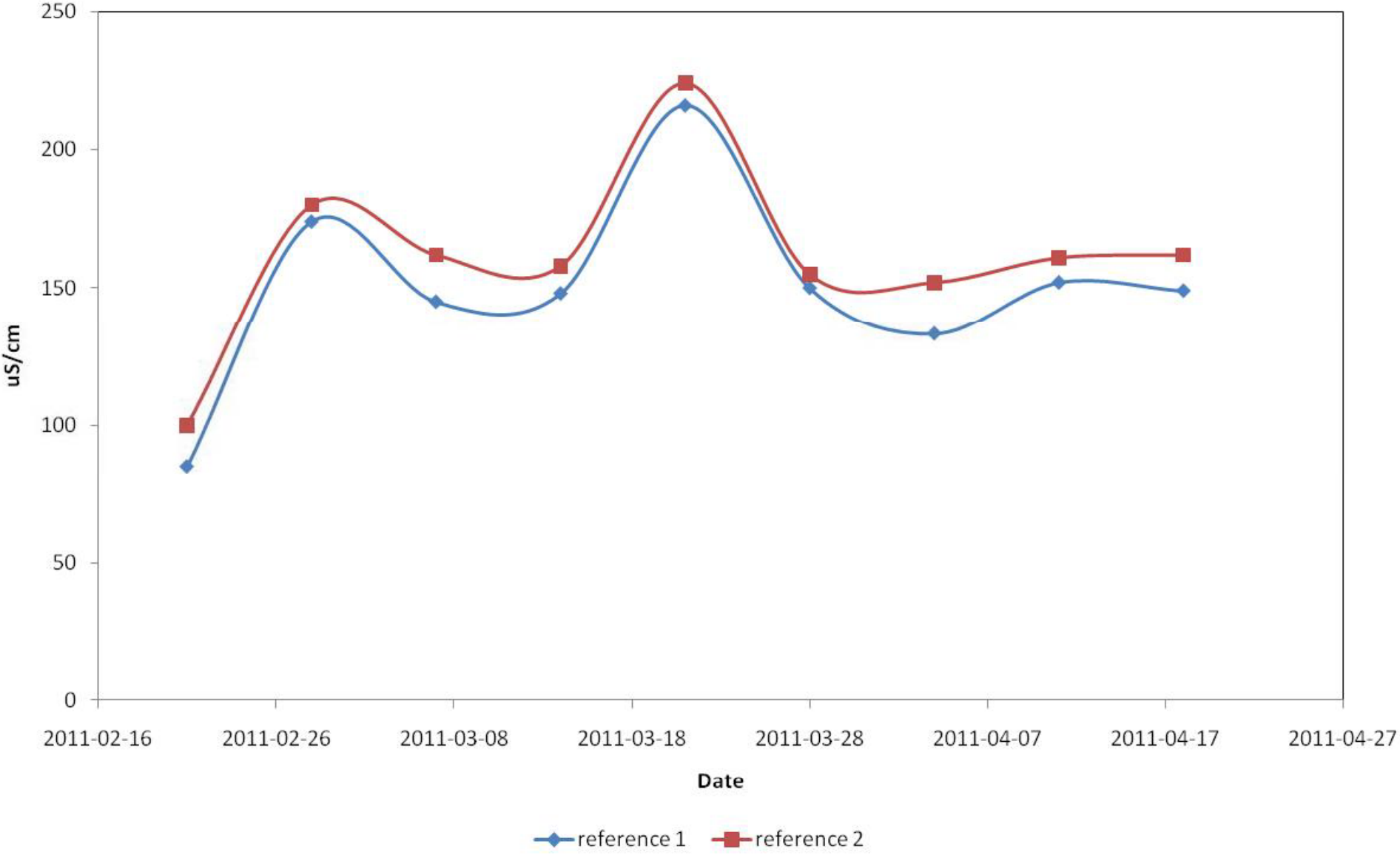
Humidity

pH



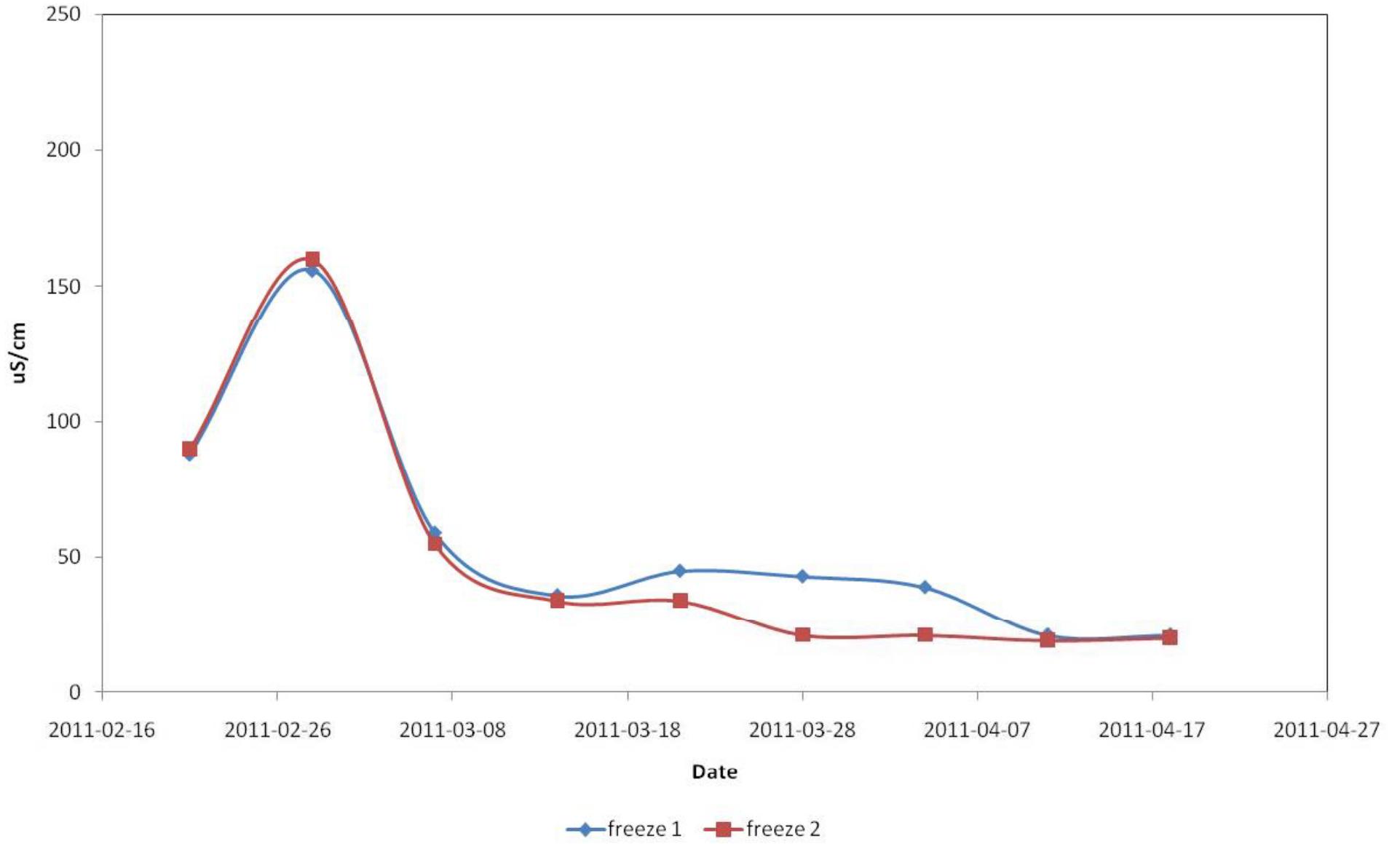
Reference

EC



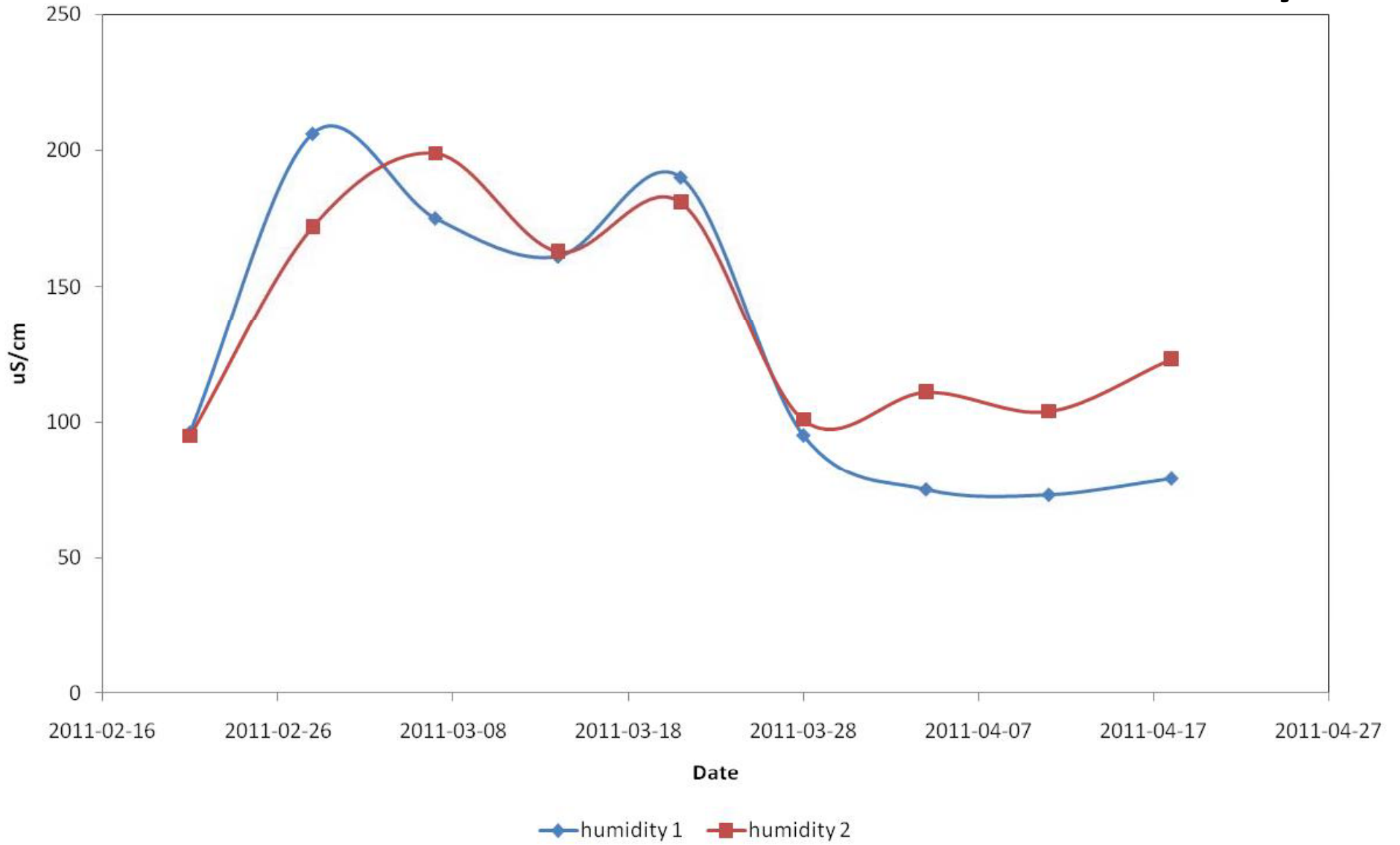
EC

Freeze



EC

Humidity

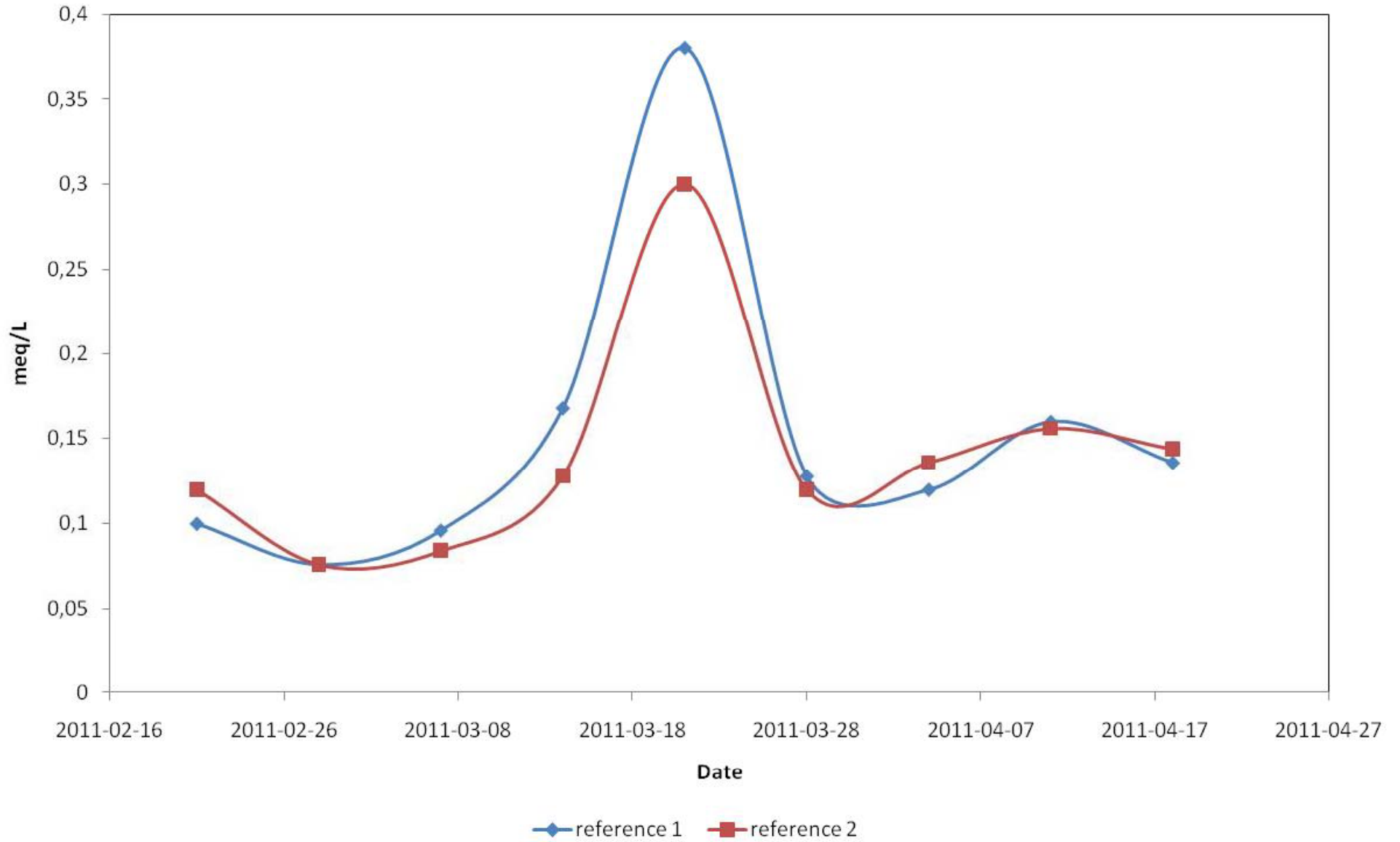


Results & Discussion, cont.

- Acidity and sulphate measurements show the same trends, with higher acidity and sulphate concentrations with lower pH
- Time differences for water to percolate through the material
 - Humidity > Reference > Freeze
 - Probably due to secondary precipitates

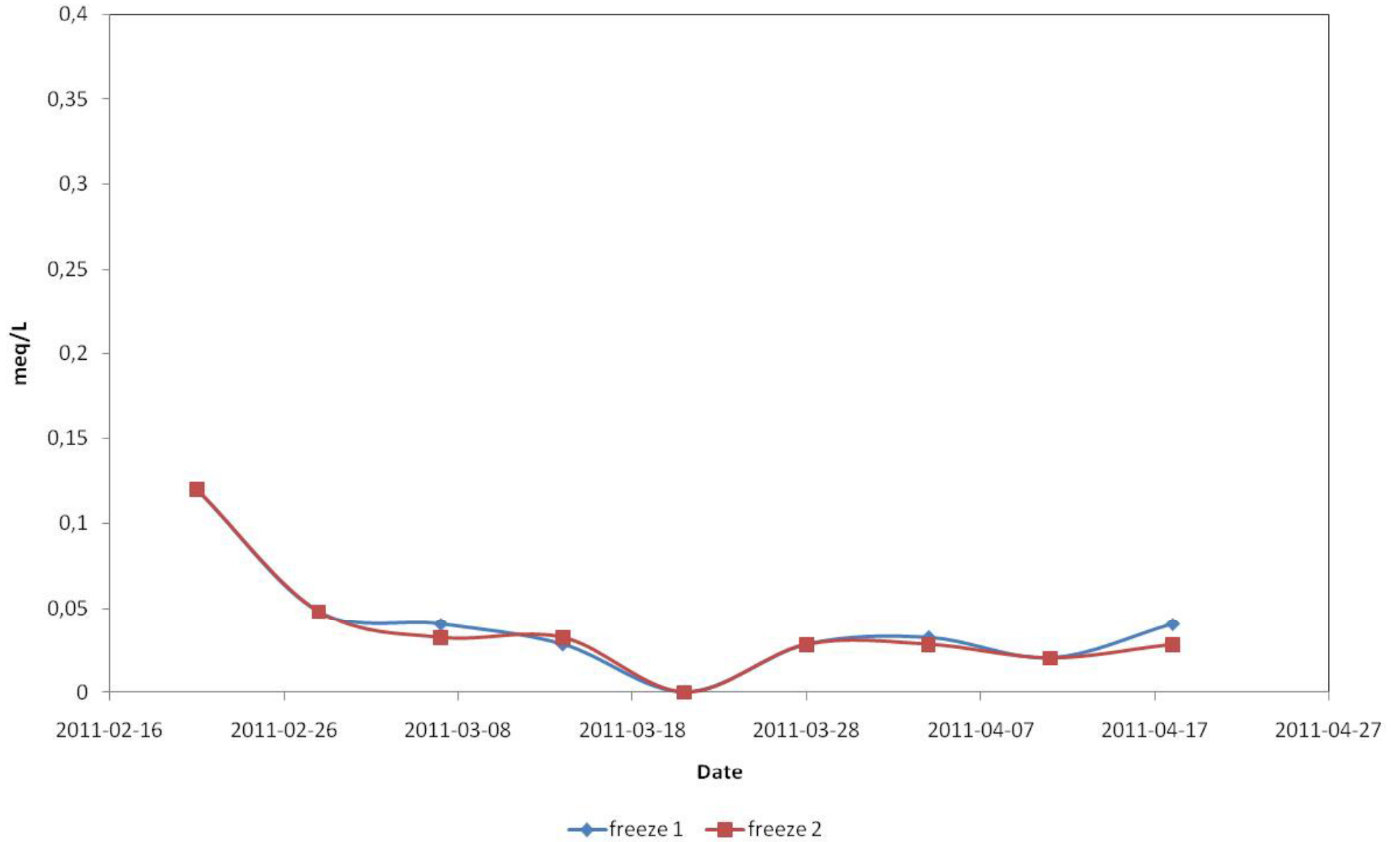
Acidity

Reference



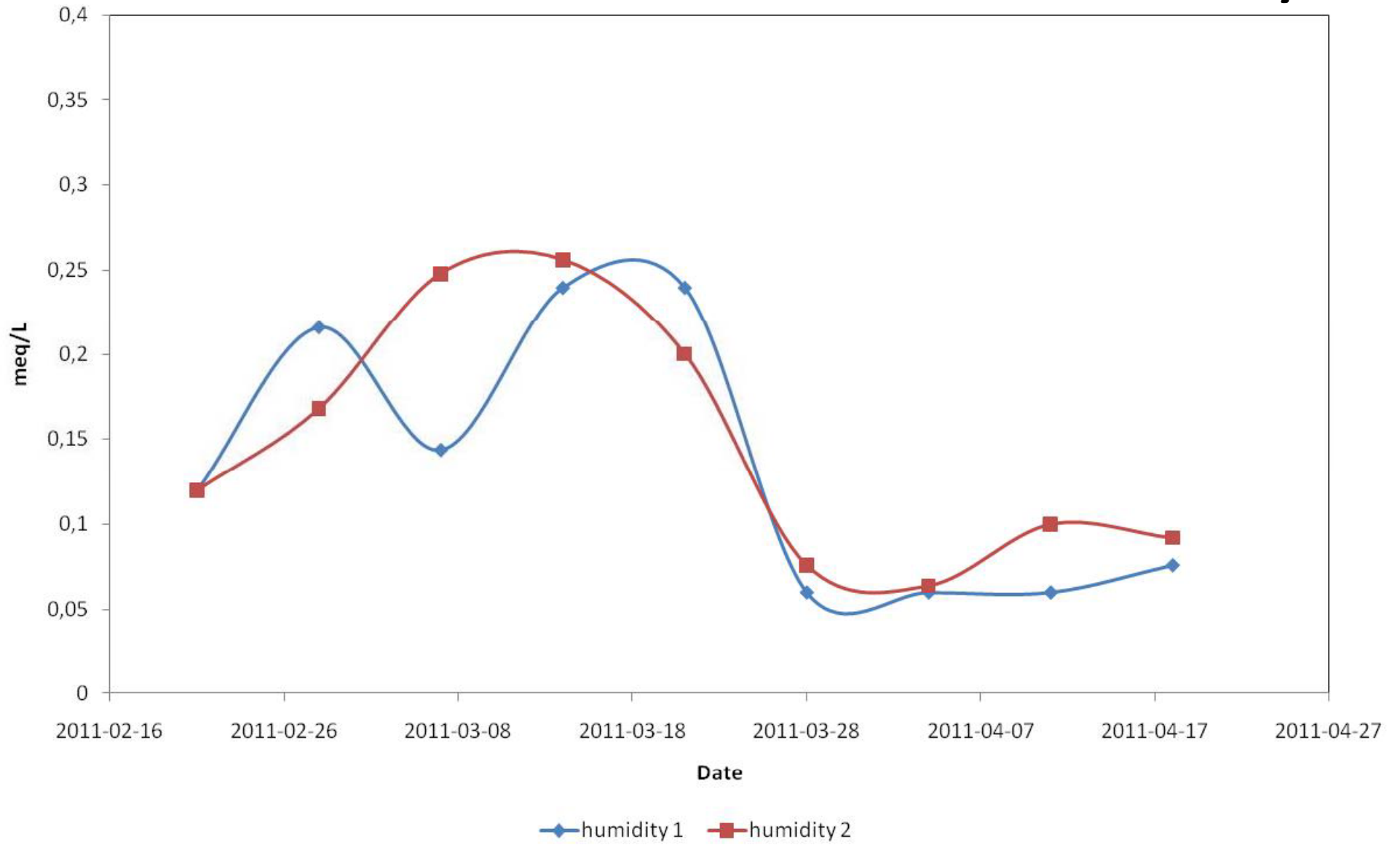
Acidity

Freeze

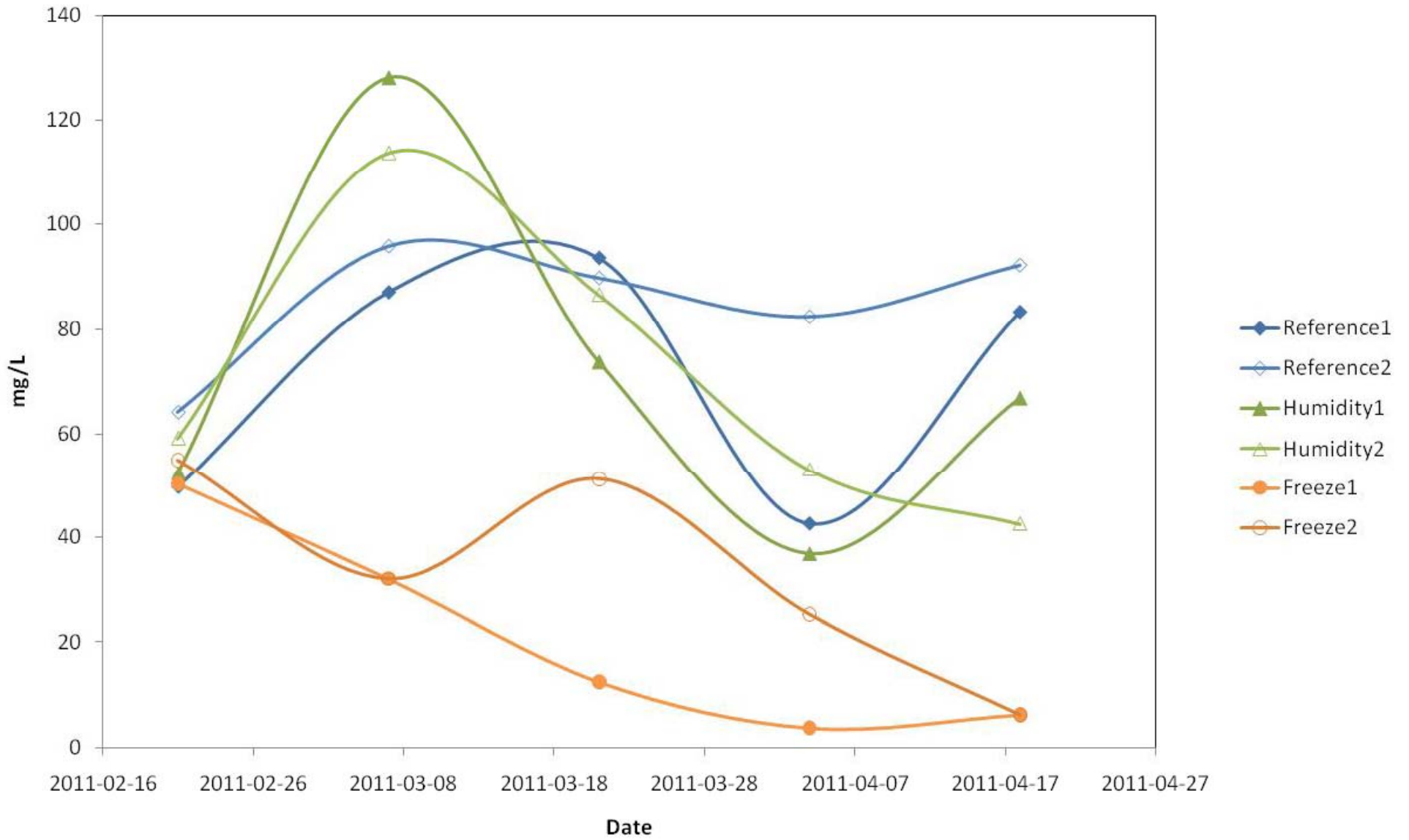


Acidity

Humidity



Sulphate



Reference



Freeze



Humidity



Summary

- Large differences between the three systems
- Freeze system seem to conserve the material rather than increase weathering rates
- At the present, lowest pH (and highest EC, sulphate and acidity) is found in the reference system
- Experiments will continue at least 30 weeks
- Freeze/thaw tests analogous to humidity cell experiments seem to be a good starting point as standard protocol for prediction of ARD in northern climates
- More weathering products are formed in the humidity system and perhaps a scheme freeze – humid air – leaching would enhance effects from freezing/thawing (exposure of new pyrite surfaces due to cracks in weathering products layer)