Nitrogen isotopes as tracers for the nitrogen cycle in Lake Kinneret

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Introduction

This study is focused on the sources and dynamics of dissolved nitrogen species in lake Kinneret, and their relations to the seasonal variations and limnological cycle. To quantitatively reconstruct the nitrogen cycle, the concentrations of nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+) and their vertical distribution and seasonal variations in the water column were determined. In addition, the isotopic composition of nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) of the dissolved inorganic species were measured.

Methodology

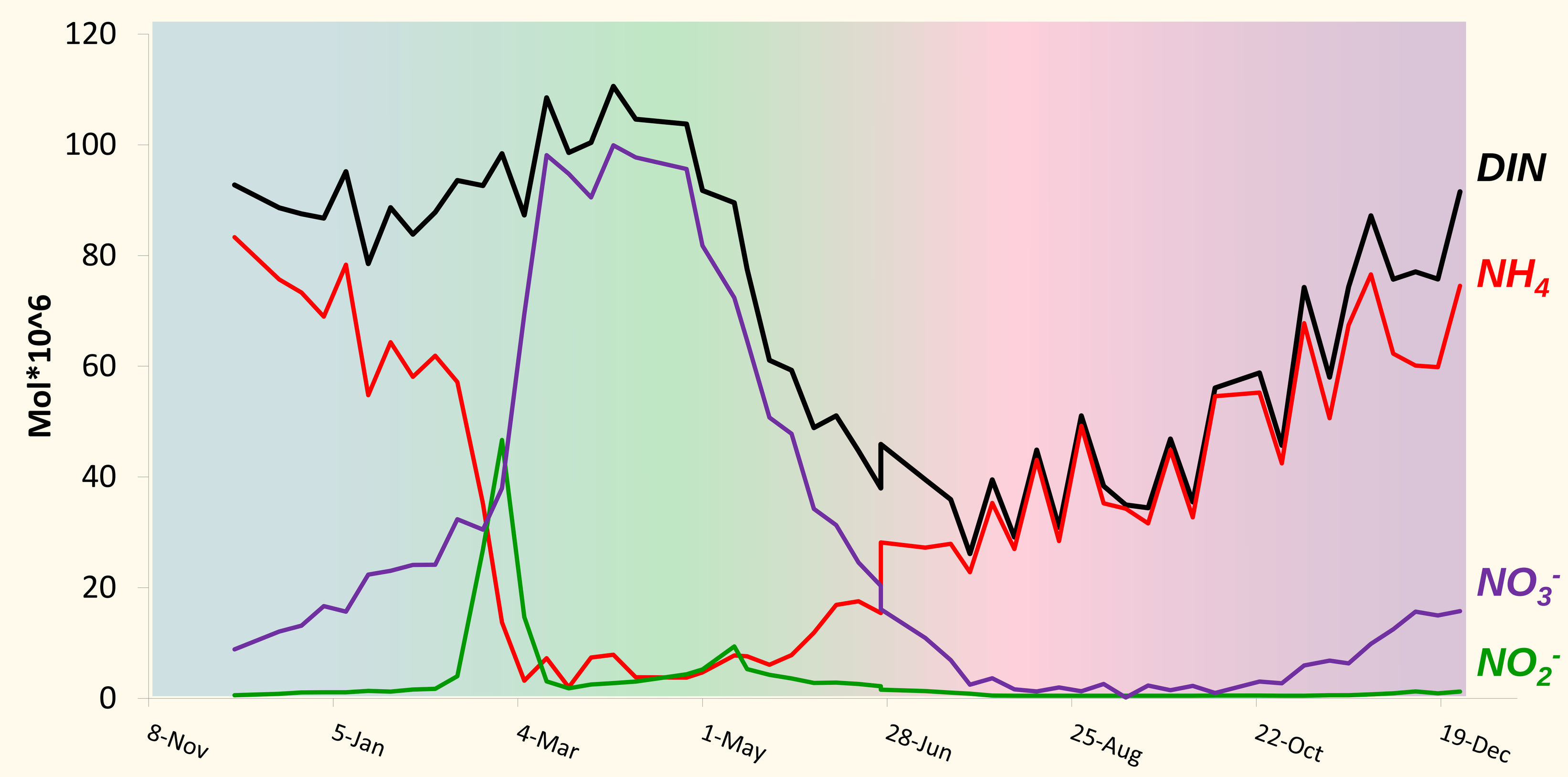
To determine the isotopic compositions of the nitrogen species, each species need to be isolated and transformed to $N_2O_{(g)}$ form, which is then introduced to the IRMS (Isotope Ratio Mass Spectrometer). Conversion of nitrate into $N_2O_{(g)}$ is carried out routinely in the geochemical lab of the Geological Survey of Israel and produce high-quality results. The nitrate is reduced into nitrite using cadmium column, and then and nitrite is reduced to $N_2O_{(g)}$ using azid:

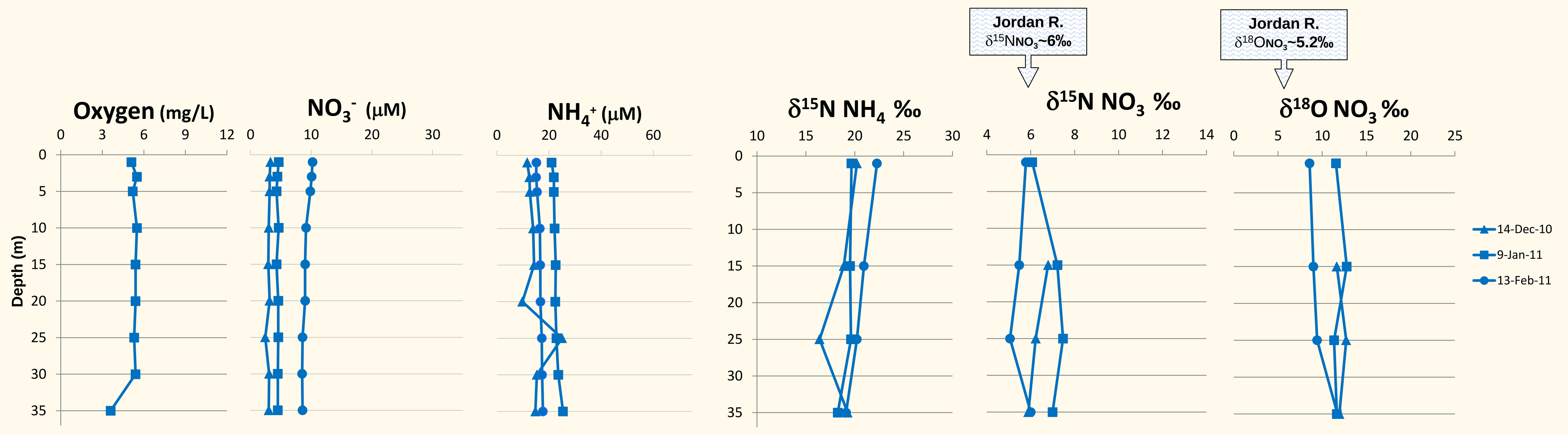
1) $NO_3^-{}_{(aq)} \xrightarrow{Cd} NO_2^-{}_{(aq)} \xrightarrow{N_3^-} N_2O_{(g)}$

Conversion of ammonium to N2O(g) requires the oxidation to nitrite using hypo-bromide after which the nitrite is reduced to $N_2O(g)$ as described above. This method, which was adopted from Zang et al. (2007), was developed in the GSI laboratory in the framework of the present study.

2) $NH_4^+{}_{(aq)} \xrightarrow{BrO^-} NO_2^-{}_{(aq)} \xrightarrow{N_3^-} N_2O_{(g)}$

Seasonal variations of nitrogen inorganic species in lake Kinneret water of the during 2010-2011





Winter

Mixed and oxidized water column.

NO_3^- concentration increase as a result of:

1. ***Nitrification*** (NH_4^+ Oxidation)
2. Exterior NO_3^- supply, runoff

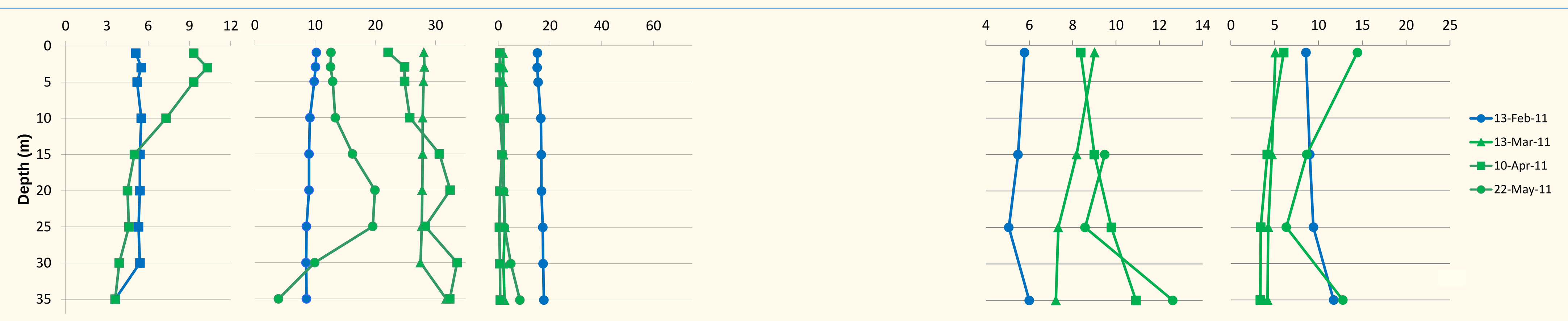
$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$

$\delta^{15}NNO_3^-$ in the winter is controlled by:

1. Negative fractionation during the nitrification process. The product (NO_3^-) is lighter than the source (NH_4^+).
2. $\delta^{15}NNO_3^-$ in the Jordan river ~ 6‰

$\delta^{18}ONO_3^-$ in the spring is dictated by:

1. 2/3 of the oxygen is derived from the water, 1/3 from the dissolved oxygen:
   $\delta^{18}ONO_3^- = 2/3\ \delta^{18}OH_2O + 1/3\ \delta^{18}OO_2$
   $\delta^{18}OH_2O_{(Kinneret)}$ is -0.5 to +1‰; $\delta^{18}OO_{2(diss)}$ is -3 to +3‰
2. $\delta^{18}ONO_3^-$ in the Jordan river ~ 5.2‰



Spring

NO_3^- concentration decrease in the end of the spring as a result of:

1. ***Assimilation***: NO_3^- fixation in the epilimnion
2. ***Denitrification***: organic matter oxidation by NO_3^- in the hypolimnion

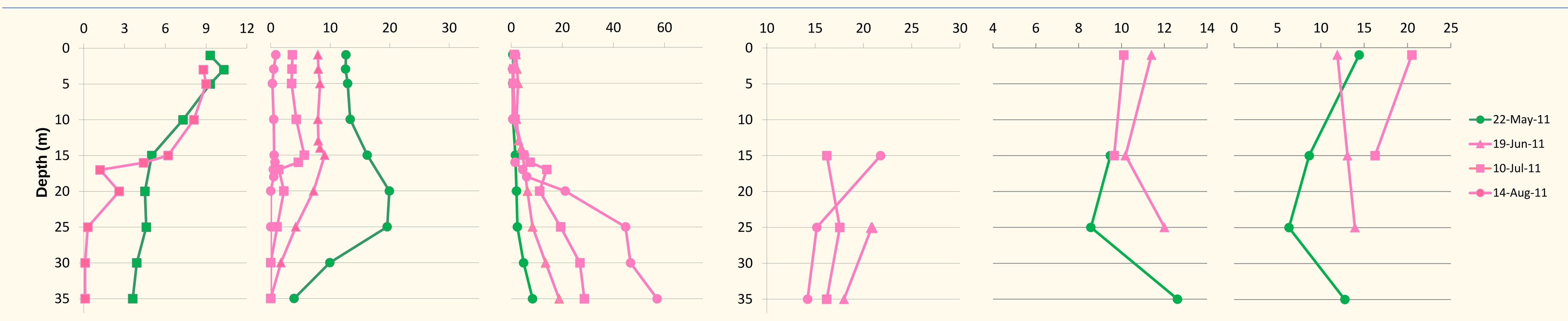
$NO_3^- \rightarrow OM$
$NO_3^- \rightarrow N_2$

$\delta^{15}NNO_3^-$ in the spring is controlled by:

1. Epilimnion: The residual NO_3^- following assimilation is isotopically heavier
2. Hypolimnion: The residual NO_3^- in the denitrification process is isotopically heavier

$\delta^{18}ONO_3^-$ in the spring is dictated by:

1. The residual NO_3^- in the assimilation process in isotopically heavier
2. $\delta^{18}ONO_3^-$ in the Jordan river ~ 5.2‰



Summer

Thermal stratification, anoxia in the hypolimnion

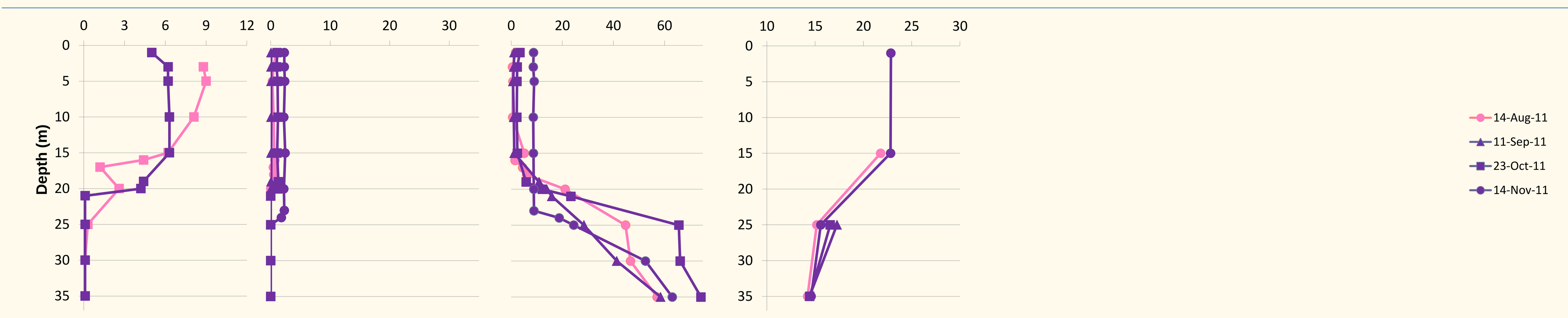
Epilimnion: NO_3^- concentration decrease as a result of ***assimilation***

Hypolimnion: NO_3^- concentration decrease as a result of ***denitrification***
NH_4^+ concentration increase as a result of ***ammonification*** (bacterial decomposition of organic matter)

$NO_3^- \rightarrow OM$
$NO_3^- \rightarrow N_2$
$OM \rightarrow NH_4^+$

$\delta^{15}NNO_3^-$ and $\delta^{18}ONO_3^-$ in the epilimnion become heavier as a result of assimilation

$\delta^{15}NNH_4^+$ values represent the isotopic composition of the decomposed organic matter



Autumn

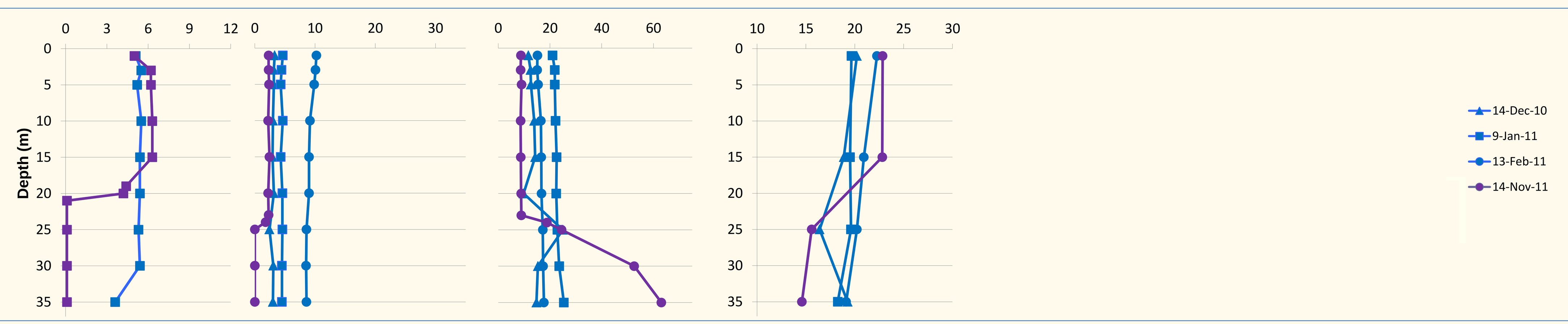
NH_4^+ accumulation as a result of ***ammonification***

$OM \rightarrow NH_4^+$

$\delta^{15}NNH_4^+$ in the hypolimnion remains nearly constant pointing to the isotopic composition of the decomposing organic matter

Minor mixing in the end of the autumn supplies NH_4^+ to the oxidized epilimnion where it undergoes ***nitrification,*** leaving behind residual NH_4^+ which is isotopically heavy

$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$



Winter

Cooling, mixing and oxidizing the water column

Nitrification

$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$

$\delta^{15}NNH_4^+$ is controlled by:

1. Mixing of the isotopic signal of the hypolimnion and the epilimnion
2. The residual NH_4^+ in the nitrification process is isotopically heavier

Conclusions

- Seasonal variations in the DIN are characterized by significant increase in the winter due to external supply of NO_3^- by runoff reaching a maximum in the mid-spring, followed by a decrease in the end of the spring as a result of assimilation and denitrification. Relatively low DIN values characterize the summer, increasing in the autumn as a result of ammonification.
- $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- during the spring indicate that the increasing concentrations are partially due to input of nitrate to the lake water by surface runoff.
- $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- during the summer indicate that the decreasing concentrations are mainly due to nitrate assimilation.
- $\delta^{15}N$ values of NH_4^+ in the hypolimnion during the summer and autumn may point to organic matter with isotopic signal that is heavier than is expected from NO_3^- assimilation.