

# Appendix 7.1

## Test of different ammonium sorption models and parameters

### 1 Background and parameterization

A model for ammonium sorption to clay particles based on the theory by Schouwenburg and Schuffelen (1963) is implemented in Daisy as the  $vS\_S$ -model (see Chapter 7.4).

The earlier version of the  $vS\_S$ -model (now termed  $vS\_S\_Hansen$ ) contained an error in the parameterization of the model (Table 1), resulting in too strong sorption of  $NH_4^+$ . Therefore, a new parameterization of the  $vS\_S$ -model (termed  $vS\_S\_Styczen$ ) is implemented in Daisy 7.0.7 (Table 1).

Based on the  $vS\_S$ -model, parameters for a linear sorption model can be deduced (see Chapter 7.4). The linear sorption model allows definition of a sorption value for clay ( $K_{clay}$ ) and a value for organic material ( $K_{oc}$ ). The earlier default linear sorption model for ammonium, the  $NH_4$ -model (now termed  $NH_4\_Hansen$ ), was parameterized based on the errors in the  $vS\_S\_Hansen$ -model (Table 2). New parameters for the linear model have been deduced based on the  $vS\_S\_Styczen$ -model. These are now implemented as default for ammonium sorption (termed  $NH_4$ ) (Table 2).

Table 1: Parameters for the Hansen and Styczen versions of the  $Vs\_S$ -model. Where  $V_p$  and  $V_e$  [ $kg\ N\ kg^{-1}$  (clay)] are the absorption capacity of the planer sites and edges of the clay, respectively,  $K_p$  and  $K_e$  [ $kg\ N\ m^{-3}$ ] are the half-saturation constants of the planer sites and edges of the clay, respectively.  $V_p$ ,  $K_p$ ,  $V_e$  and  $K_e$  can be viewed as parameters depending on the exchange properties of the clay.

Model/parameter	$V_p$ [ $kg\ N\ kg^{-1}$ (clay)]	$V_e$ [ $kg\ N\ kg^{-1}$ (clay)]	$K_p$ [ $kg\ N\ m^{-3}$ ]	$K_e$ [ $kg\ N\ m^{-3}$ ]
$vS\_S\_Hansen$	$6 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$	0.063	0.014
$vS\_S\_Styczen$	$5.964 \cdot 10^{-3}$	$0.2801 \cdot 10^{-3}$	0.6338	0.01369

Table 2: Parameters for the old ( $NH_4\_Hansen$ ) and new ( $NH_4$ ) linear models for ammonium sorption.

Model/parameter	$K_{oc}$ [ $g\ g^{-1}$ (OC) / $g\ cm^{-3}$ ]	$K_{clay}$ [ $g\ g^{-1}$ (clay) / $g\ cm^{-3}$ ]
Old linear model ( $NH_4$ , now $NH_4\_Hansen$ )	117.116	117.116
New linear model ( $NH_4$ )	213	28

## 2 Test setup

To evaluate the effect of the new, corrected, parameterizations of both the  $vS\_S$ -sorption-model ( $vS\_S\_Styczen$ ) and the linear-sorption-model ( $NH4$ ) two soil setups were simulated for 20 years with weather representing western Denmark. The simulations were run with continuous spring barley cultivation fertilized with  $115 \text{ kg N ha}^{-1}$  each spring. The two soil setups were a sandy soil (JB1), and a loamy soil (JB6).

## 3 Results

Comparing the simulated results with the new parameterizations of the linear model ( $NH4$ ) and the  $vS\_S$ -model ( $vS\_S\_Styczen$ ) with the old parameterizations ( $NH4\_Hansen$  and  $vS\_S\_Hansen$ ) showed minor changes in total N leaching, uptake and harvest for the three soil types over the 20 years (Table 1 and 2). In general, the changes are smallest between the new linear model ( $NH4$ ) and the old linear model ( $NH4\_Hansen$ ) and the largest total difference was between  $vS\_S\_Styczen$  and  $vS\_S\_Hansen$  for JB6. This gave an increased leaching followed by a decrease in uptake over the 20 years (Table 3). However, expressed as percent-difference the changes are minor ( $< 4 \%$ ) (Table 4).

The relatively small changes in total N-uptake are a result of a higher  $\text{NH}_4^+$ -N crop uptake and a lower  $\text{NO}_3^-$ -N crop uptake, due to lower sorption of  $\text{NH}_4^+$ . This results in a total difference in  $\text{NH}_4^+$ -N crop uptake over the 20 years of  $28.3 \text{ kg N ha}^{-1}$  for the JB1 linear new ( $NH4$ ) vs. old ( $NH4\_Hansen$ ) parameterization and  $198.9 \text{ kg N ha}^{-1}$  for the JB6  $vS\_S\_Styczen$  vs.  $vS\_S\_Hansen$ , followed by a similar decrease in  $\text{NO}_3^-$ -N crop uptake. However, it is important to note that the change in  $\text{NH}_4^+$ -N crop uptake only effects a minor part of the total uptake. For all soils there is a decrease in  $\text{NH}_4^+$ -nitrification on 1.-8.8 % which also leads to a decrease in  $\text{N}_2\text{O}$  production from nitrification of 1.1-7.6 %.

Table 3: Total difference [kg N/ha] between new parameterizations of the linear (NH4) and vS\_S-model and the old parameterizations (\_Hansen) for simulated N leaching, uptake and harvest, together with NH4 nitrification, NO3 and NH4 uptake and N2O from nitrification.

	<b>Total Difference</b> [kg N/ha]	<b>N</b> leaching	<b>N</b> uptake	<b>N</b> harvest	<b>NH4 nitri-</b> fication	<b>NO3</b> uptake	<b>NH4</b> uptake	<b>N2O from</b> nitrification
<b>JB1</b>	Linear New (NH4) vs. Old (NH4_Hansen)	4.7	-4.4	-4.0	-29.2	-32.7	28.3	-0.6
	vS_S New (_Styczen) vs. Old (_Hansen)	40.1	-43.6	-35.4	-128.3	-161.9	118.3	-2.6
	Linear New (NH4) vs. Old (NH4_Hansen)	0.3	11.2	7.4	-129.0	-113.6	124.8	-2.6
<b>JB6</b>	vS_S New (_Styczen) vs. Old (_Hansen)	0.5	15.0	9.4	-240.0	168.9	198.9	-4.1

Table 4: Percent difference [%] between new parameterizations of the linear (NH4) and vS\_S-model and the old parameterizations (\_Hansen) for simulated N leaching, uptake and harvest, together with NH4 nitrification, NO3 and NH4 uptake and N2O from nitrification

	<b>Percent Difference</b> [%]	<b>N</b> leaching	<b>N</b> uptake	<b>N</b> harvest	<b>NH4 nitri-</b> fication	<b>NO3</b> uptake	<b>NH4</b> uptake	<b>N2O from</b> nitrification
<b>JB1</b>	Linear New (NH4) vs. Old (NH4_Hansen)	0.4	-0.2	-0.2	-1.1	-1.3	33.6	-1.1
	vS_S New (_Styczen) vs. Old (_Hansen)	3.5	-1.6	-1.8	-4.8	-6.3	114.7	-4.8
	Linear New (NH4) vs. Old (NH4_Hansen)	0.7	0.4	0.3	-4.8	-4.0	84.2	-4.8
<b>JB6</b>	vS_S New (_Styczen) vs. Old (_Hansen)	1.4	0.5	0.4	-8.8	6.8	127.9	-7.6

## 4 References

Schouwenburg, J.C.H. van, Schuffelen, A.C., 1963. Potassium-exchange behaviour of an illite. Neth. J. Agric. Sci. 11, 13–22. <https://doi.org/10.18174/njas.v11i1.17567>