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# Formation of soil structure in long-term fertilised sandy soil: Role of the manganese oxides

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**Abstract.** We investigated the role of Mn oxides on the soil structure (contents of dry and water-stable aggregates) of sandy soil under a controlled long-term fertilisation experiment. We examined two experiments: a 94-year-term experiment with: no fertilisers, NPK fertilisers, and CaNPK fertilisers; and a 25-year-term experiment that included: farmyard manure and no mineral fertilisation, farmyard manure + NPK fertilisers, and farmyard manure + CaNPK fertilisers. The results showed that in the 94-year-term trial, Mn oxides were increased in CaNPK treatment. In the 25-year-term experiment, the farmyard manure combined with NPK decreased total Mn and its oxides. In the 94-year-term experiment, the content of dry-sieved macro-aggregates ($DSA_{ma}$) and water-stable macro-aggregates increased due to fertilisation. The result of our study suggests that Mn oxides had positive effects mainly on higher size classes of $DSA_{ma}$ and did not have any effect on water-stable aggregate contents.

**Key words:**
long-term experiments,
manganese oxides,
soil aggregates,
water-stable aggregates

## Introduction

Several theories are currently known about soil structure, but some mechanisms of its formation and stabilisation are still poorly explained. Many external and internal factors significantly influence the formation and stabilisation of soil aggregates, among which there are many to consider. Organic matter, soil texture and cations are considered as the most important (Bronick and Lal 2005; Polláková et al. 2018). There is sufficient information about the impact of $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$, $Al^{3+}$ and $Fe^{3+}$ on soil structure (Bronick and Lal 2005). Studies on the impact of Mn and its oxides are relatively rare, partly because Mn oxides in soils are usually present at much lower contents than Fe oxides (Dixon and White 2002). For this reason, there is an assumption that Mn oxides do not have a more significant effect on soil structure compared to Fe oxides. However, Mn oxides are ubiquitous in soils, where they occur as ped coatings, fine-grained aggregates, nodules and concretions (Dixon and White 2002). Even Mn oxides are capable of retaining other cations and forming weaker bonds with organic particles (Suda and Makino 2016). From the above, it is obvious that Mn oxides must have an impact on soil structure. Therefore, the aim of this study was to determine the extent of Mn oxides on contents of dry and water-stable aggregates in differently fertilised sandy soils.

## Material and methods

The study was conducted at the experimental station of Warsaw University of Life Sciences located near Skierniewice (51°57'54.3"N 20°09'31.8"E). A detailed description of the soil-climatic conditions and the design of the experiments is provided in Šimanský et al. (2019). In the autumn of 2017, the soil samples were taken from: 1) a trial spanning 94 years with treatments consisting of: i. no fertilisers, ii. NPK fertilisers, and iii. CaNPK fertilisers; and 2) a 25-year-long trial with the following treatments: i. farmyard manure (FYM) as control, ii. FYM+NPK, and iii. FYM+CaNPK. The oldest experiment was established in 1923 (the 94-year-term experiment), and the second experiment in 1992 (the 25-year-term experiment). In all long-term trials nitrogen was applied in the form of ammonium sulphate (30 kg $ha^{-1}$ N from 1921 to 1976 and 90 kg $ha^{-1}$ N from 1976 to 2017), phosphorus as superphosphate (30 kg $ha^{-1}$ $P_2O_5$ from 1921 to 1976 and 26 kg $ha^{-1}$ $P_2O_5$ from 1976 to 2017) and potassium as potassium chloride (30 kg $ha^{-1}$ $K_2O$ from 1921 to 1976 and 91 kg $ha^{-1}$ $K_2O$ from 1975 to 2017). Calcium was supplied in the dose 1.6 t $ha^{-1}$ in the form of CaO in 4-year cycles, only in the CaNPK treatments. In the 25-year-term experiment, apart from the mineral fertilisation, FYM was also applied in all treatments (including the control) from 1992 onwards in 4-year intervals in the dose 25 t $ha^{-1}$.

The content of dry-sieved aggregates (DSA) in soil samples were determined using the AS 200 device (Retsch®) and the content of water-stable aggregates (WSA) by the Baksheev method. Total content of manganese ($Mn_t$) was analysed by atomic absorption spectrometry (Perkin Elmer 2100) after digestion of samples in a mixture of 40% HF and 60% $HClO_4$. The content of "free" manganese oxides ($Mn_d$) was analysed by atomic absorption spectrometry (Perkin Elmer 2100) after extraction of samples by Mehra and Jackson procedure (Mehra and Jackson 1960) and the content of amorphous manganese oxides ($Mn_o$) was analysed by atomic absorption spectrometry (Perkin Elmer 2100) after extraction of samples by Schwertmann procedure (van Reeuwijk 1995). The content of crystalline manganese oxides ($Mn_c$) was calculated as follows: $Mn_c = Mn_d - Mn_o$.

All data was analysed using the Statgraphics Centurion XV.I program (Statpoint Technologies, Inc., USA). The data was analysed using one-way ANOVA and the means were compared with LSD test at $P<0.05$. The link between the dry-sieved and water-stable aggregates and Mn oxides was assessed using a correlation matrix.

## Results and discussion

As our results show (Fig. 1), few differences in manganese oxides occurred with dependence on fertilisation and experiment time-span. The content of manganese oxides in soil treated with CaNPK significantly increased in the trial spanning 94 years. Conversely, the greatest decrease in Mn oxides was obtained in FYM+NPK treatment when compared to FYM in the 25-year-term experiment. In the 94-year-term experiment, the increase in Mn oxides in the CaNPK treatment may be associated with CaO application. Through liming, the pH of the soil increases, resulting in a decrease in the availability of Mn in the soil and its accumulation (Suda and Makino 2016). The application of NPK fertilisers can lead to decreasing of soil pH (Ge et al. 2018), which results in the leaching of Mn from the soil, as evidenced by the results of the 25-year trial.

The period of 94 years of continuous mineral fertiliser input statistically increased content of dry-sieved macro-aggregates ($DSA_{ma}$) in size classes 5–1 mm. In case of water-stable aggregates (WSA) determination, the effects of NPK application on water-stable macro-aggregates ($WSA_{ma}$) were observed as an increase in size classes >5, 5–3 and 3–2 mm (Fig. 2A). Compared to the control (no fertilisation), the application of NPK and CaNPK increased ($p=0.0176$) the $DSA_{ma}$ in size class 5–3 mm to almost 1.5 times and to almost double, respectively. In the case of WSA, the $WSA_{ma}$ content increased most remarkably due to NPK fertilisation as follows: $WSA_{ma}$ in size class 3–2 mm < $WSA_{ma}$ in size class 5–3 mm < $WSA_{ma}$ in size class >5 mm. Mineral fertilisers are a significant source of available nutrient through microbial and faunal activity. They can have a simulative effect on the production of higher amounts of above-ground and underground biomass. The biomass increases soil organic carbon

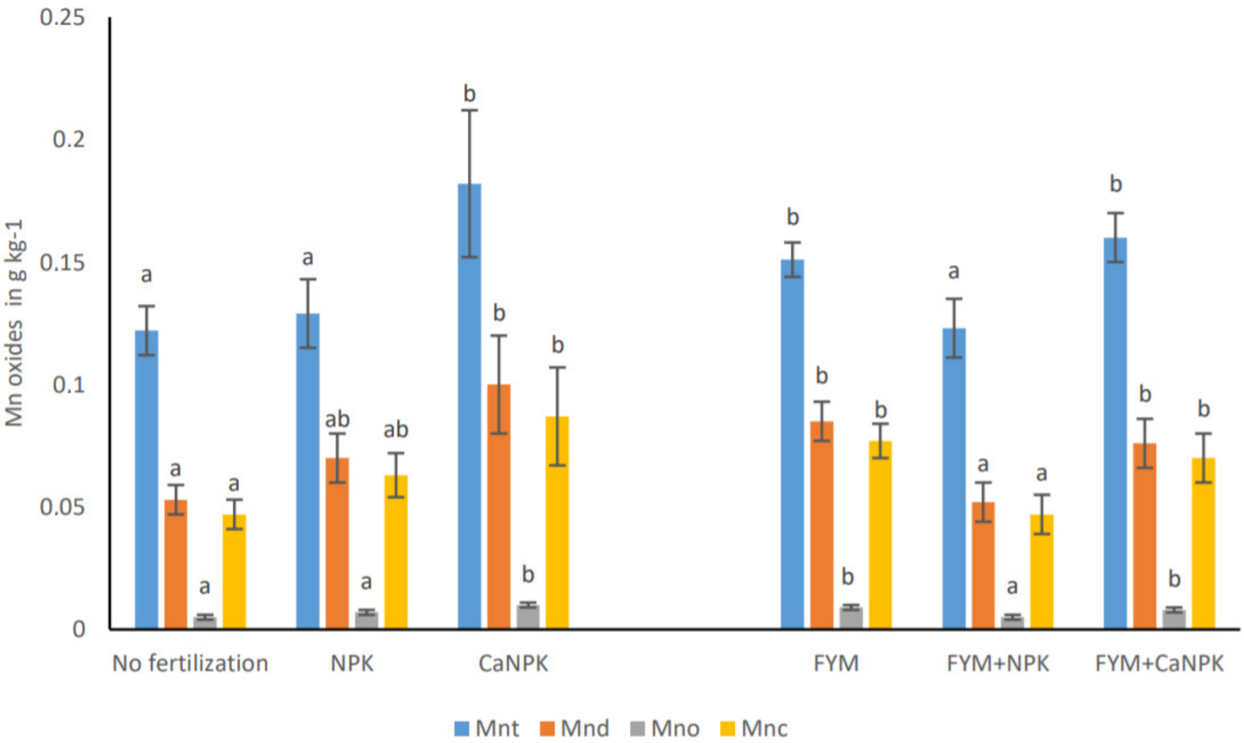


Fig. 1. Contents of Mn oxides with dependence on fertilization

Different letters (a, b) between columns (the same colour) indicate that treatment means are significantly different at P<0.05 according to LSD test.

(SOC) (Rahman et al. 2017) which is ultimately associated with better soil structure state (Nouwakpo et al. 2018). This effect (higher SOC due to mineral fertilisation in this experiment) has already been confirmed (Šimanský et al. 2019). SOC is one of the most important internal factors affecting aggregate formation (Nouwakpo et al. 2018; Polláková et al. 2018), especially in sandy soils (Bronick and Lal 2005). It was interesting to note that Ca had no significant effect on the formation of $WSA_{ma}$ (Fig. 2A), as the influence of Ca on the formation of bridges between SOC and inorganic soil particles contributing to the formation of soil structure is well known (Kobierski et al. 2018). Farmyard manure (FYM) combined with mineral fertilisers did not affect any size classes of DSA as well as WSA (Fig. 2B), which is in contrast with a lot of knowledge published in the existing literature about the effect of FYM and mineral fertilisers on soil structure (Huang et al. 2010). The explanation may be as follows. FYM is an important source of labile organic matter (Liu et al. 2013), which can form temporary bonds between soil particles in the soil (Wang et al. 2016). In addition, when organic matter from FYM decomposes, acids are released into the soil, which can leach Ca out of the soil. The result is reduced aggregation via the mechanism: SOC - Ca - inorganic particle (Bronick and Lal 2005).

When all trials were assessed together, positive significant correlations were observed between Mn oxides and $DSA_{ma}$ >7 mm on the one hand, and negative correlations between Mn oxides and lower size classes of $DSA_{ma}$ and $DSA_{mi}$ on the other. Similar relationships were observed in the 94-year-long experiment, while in the 25-year-long trial between Mn oxides and DSA no significant correlations were detected (Table 1). These results showed that Mn oxides can have positive effects mainly on higher size classes of $DSA_{ma}$ in sandy soils under long-term mineral fertilisation. Mn oxides did not have any effect on content of WSA. Mn with organic matter forms less tight bonds because organic molecules

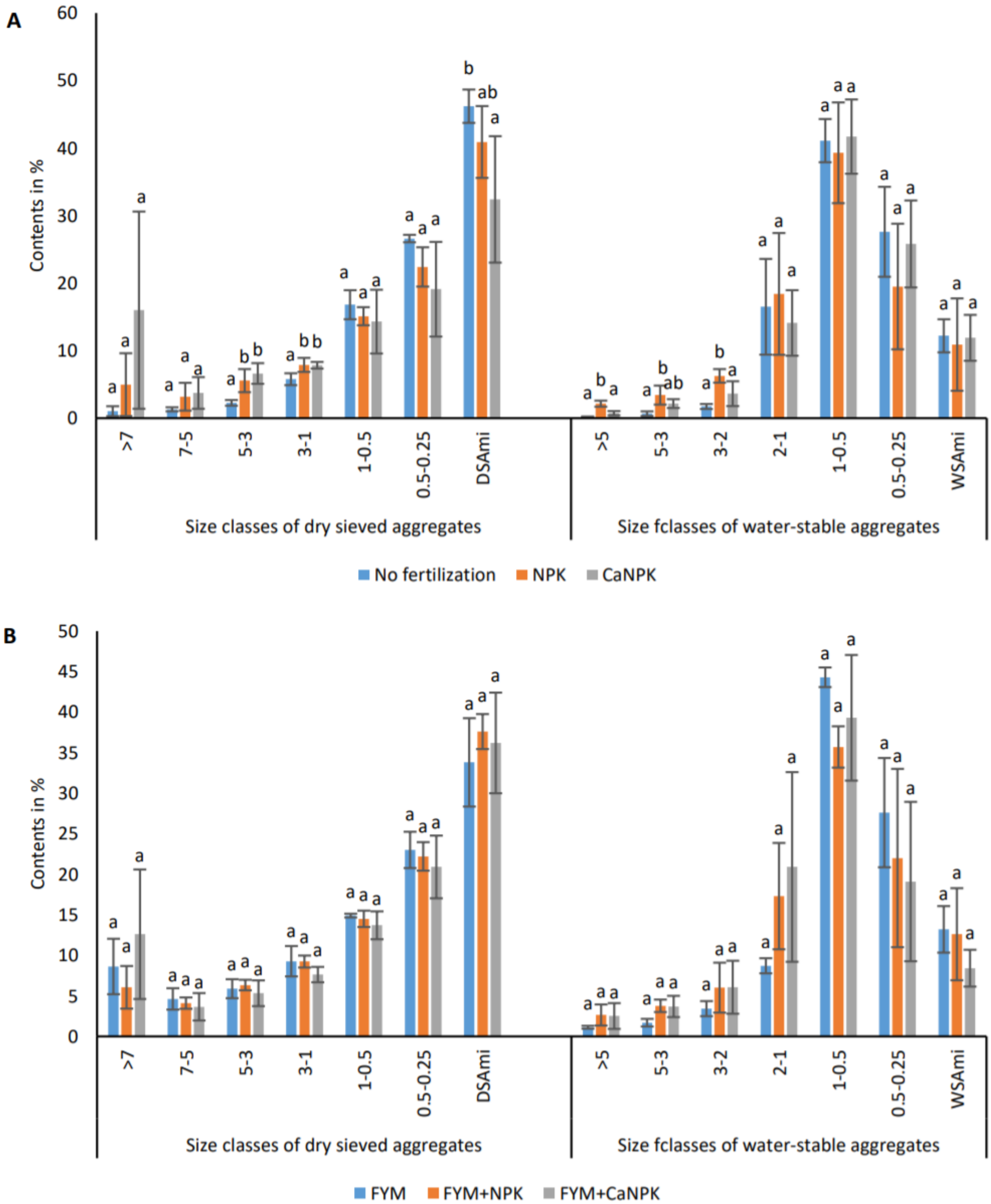


Fig. 2. Contents of dry sieved and water-stable aggregates with dependence on fertilization A) in 94-years-long experiment, and B) in 25-years-long experiment. Different letters (a, b) between columns (the same colour) indicate that treatment means are significantly different at $P<0.05$ according to LSD test.

Table 1. Pearson correlation coefficients between Mn oxides and individual size classes of aggregates in relation with fertilisation

| | | $Mn_t$ | $Mn_d$ | $Mn_o$ | $Mn_c$ |
|---|---|---|---|---|---|
| **94-year-term experiment with mineral fertilisation** | | | | | |
| | $DSA_{mi}$ | -0.852** | -0.863** | -0.869** | -0.860** |
| $DSA_{ma}$ | >7 | 0.852** | 0.864** | 0.848** | 0.864** |
| | 7-5 | 0.589 | 0.666* | 0.647 | 0.666* |
| | 5-3 | 0.672* | 0.773* | 0.770* | 0.772* |
| | 3-1 | 0.498 | 0.596 | 0.622 | 0.592 |
| | 1-0.5 | -0.587 | -0.671* | -0.637 | -0.673* |
| | 0.5-0.25 | -0.792* | -0.851** | -0.822** | -0.853** |
| **25-year-term experiment with mineral fertilisation + FYM in 4-year cycle** | | | | | |
| | $DSA_{mi}$ | -0.130 | -0.392 | -0.292 | -0.401 |
| $DSA_{ma}$ | >7 | 0.221 | 0.407 | 0.317 | 0.416 |
| | 7-5 | 0.031 | 0.165 | 0.022 | 0.181 |
| | 5-3 | -0.038 | 0.056 | -0.100 | 0.075 |
| | 3-1 | -0.136 | 0.048 | -0.086 | 0.064 |
| | 1-0.5 | -0.105 | -0.206 | -0.080 | -0.220 |
| | 0.5-0.25 | -0.112 | -0.176 | -0.024 | -0.193 |
| **94-year-term experiment with mineral fertilisation** | | | | | |
| | $WSA_{mi}$ | -0.161 | -0.140 | -0.052 | -0.149 |
| $WSA_{ma}$ | >5 | -0.178 | -0.047 | -0.023 | -0.050 |
| | 5-3 | -0.066 | 0.016 | -0.018 | 0.020 |
| | 3-2 | 0.092 | 0.174 | 0.081 | 0.184 |
| | 2-1 | 0.050 | 0.004 | -0.105 | 0.015 |
| | 1-0.5 | 0.215 | 0.147 | 0.198 | 0.141 |
| | 0.5-0.25 | -0.092 | -0.069 | 0,.010 | -0.078 |
| **25-year-term experiment with mineral fertilisation + FYM in 4-year cycle** | | | | | |
| | $WSA_{mi}$ | -0.577 | -0.410 | -0.237 | -0.428 |
| $WSA_{ma}$ | >5 | -0.311 | -0.083 | -0.014 | -0.090 |
| | 5-3 | -0.234 | -0.158 | -0.188 | -0.154 |
| | 3-2 | -0.002 | 0.017 | -0.141 | 0.036 |
| | 2-1 | 0.240 | 0.140 | -0.052 | 0.162 |
| | 1-0.5 | 0.424 | 0.266 | 0.347 | 0.255 |
| | 0.5-0.25 | -0.219 | -0.133 | 0.016 | -0.150 |

$Mn_t$ – total manganese, $Mn_d$ – free manganese oxides, $Mn_o$ – amorphous manganese, $Mn_c$ – crystalline manganese oxides, $DSA_{ma}$ – dry-sieved macro-aggregates, $DSA_{mi}$ – dry-sieved micro-aggregates, $WSA_{ma}$ – water-stable macro-aggregates, $WSA_{mi}$ – water-stable micro-aggregates; * $P<0.05$; ** $P<0.01$

can dissolve solid Mn oxides through the transfer of electrons (Suda and Makino 2016). In addition, under reducing conditions, Mn oxides hydrate, which may weaken the bonds between SOC and Mn, thereby reducing the stability of the soil aggregates.

## Conclusion

In both long-term experiments, fertilisation had different effects on content of Mn oxides as well as individual size classes of dry and water-stable aggregates. Ninety-four years of continuous CaNPK input significantly increased the content of Mn oxides and distribution of dry-sieved macro-aggregates in size class 5–1 mm, and content of water-stable aggregates in size >2 mm. In the 25-year-long trial, application of NPK together with farmyard manure in 4-year cycles significantly decreased the content of Mn oxides. In this experiment, the application of mineral fertilisers had no effect on the contents of individual size classes of dry and water-stable aggregates. Overall, the relationships between Mn oxides and individual aggregate size classes were different and depended on the length of trial as well as fertilisation. In general, Mn oxides had positive effects only on higher size classes of dry-sieved macro-aggregates on one hand, and did not have any effect on lower classes of dry-sieved macro-aggregates, dry-sieved micro-aggregates and water-stable aggregates on the other hand in sandy soils under long-term mineral fertilisation.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

## Author Contributions

Study design: V.Š., J.J.; data collection V.Š., J.J.; statistical analysis: V.Š., J.J.; result interpretation V.Š., J.J.; manuscript preparation V.Š., J.J.; literature review: V.Š., J.J.

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