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Influence of long-term fertilisation on soil manganese availability in Haplic Luvisol under 22-year maize monoculture

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Abstract: This study evaluated the long-term effects of mineral and organic fertilisation on Mn dynamics during 22 years of maize monoculture cultivated on silty loam Haplic Luvisol in the Czech Republic. Nine fertilisation treatments, including unfertilized control, mineral fertilisers, and organic amendments, were evaluated. Soil analyses included pH and contents of readily available Mn (Mn_{H_2O}), potentially available Mn (Mn_{M3}), and pseudo-total Mn (Mn_{AR}). Long-term ammonium-based fertilisation significantly decreased soil pH, with the strongest acidification observed under ammonium sulphate, where pH declined from 6.20 to 4.69. Across most treatments, Mn_{H2O} gradually decreased over time, indicating depletion of labile Mn pools under continuous monoculture. In contrast, ammonium sulphate maintained the highest Mn_{H_2O} contents. Potentially available Mn_{M3} showed higher stability than Mn_{H_2O}, with the highest values recorded under farmyard manure and cattle slurry treatments, suggesting stabilisation of Mn through organic matter inputs. Mn_{AR} exhibited only minor temporal variability. Correlation analysis confirmed a significant negative relationship between soil pH and Mn_{H_2O} ($r = -0.642$), whereas Mn_{M3} and Mn_{AR} showed weak relationships with pH. The results demonstrate that long-term fertilisation primarily affects labile Mn pools through soil acidification, while organic amendments contribute to stabilisation of potentially available Mn pools and greater soil pH stability.

Keywords: corn monoculture; long-term field experiment; soil amendments; soil Mn pools; soil pH

Manganese (Mn) constitutes about 0.085% of the Earth's crust and is widely distributed in soils, sediments, water and biological materials (Panghaal et al. 2019). Total Mn concentrations in surface soils commonly range from 20 to 3 000 mg/kg, with an average of 500–1 000 mg/kg, exceeding most micronutrients except Fe (Rudnick & Gao 2003; Adriano 2001). However, plant-available Mn is often considerably lower, e.g., in Indian soils it ranges from 0.60 to 164 mg/kg, with an overall deficiency of 5.6% (Shukla et al. 2018). In European soils, Mn availability is likewise highly variable and strongly controlled by soil properties. A survey of 148 dryland soils from six European countries showed that less than 1% contained diethylenetriaminepentaacetic acid (DTPA)-extractable Mn below the commonly used deficiency threshold of 1 mg/kg, indicating generally sufficient Mn availability in these soils. Nevertheless, Mn availability decreased with increasing soil pH and increased with total Mn and soil organic C, demonstrating that total Mn concentration alone is not a reliable indicator of its availability to plants (Moreno-Jiménez

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et al. 2022). Studies of Scandinavian agricultural soils further demonstrated substantial variation in Mn availability related to soil redox conditions, highlighting the dynamic nature of plant-available Mn in soils (Mundus et al. 2012). Even in Czech agricultural soils, Mn availability varies considerably depending on soil properties, particularly pH. Across five contrasting long-term experimental sites, initial Mn concentrations ranged from 0.35 to 4.49 mg/kg for readily available Mn (Mn_{H_2O}) and from 2.06 to 55.6 mg/kg for $CaCl_2$-extractable Mn, whereas exchangeable Mn ranged from 8.63 to 69.8 mg/kg (Obeng et al. 2026).

Mn is an essential micronutrient involved in photosynthesis, nitrogen metabolism and enzyme activation (Mousavi et al. 2011; Obeng et al. 2024). It is a critical component of the photosystem II water-oxidising complex, where it drives photolysis and energy generation (Hakala et al. 2006). Mn deficiency reduces photosynthesis and soluble sugar concentrations, leading to lower dry matter accumulation and yield, even without visible leaf symptoms. Depletion is linked to intensive cultivation, monocropping, high-yielding varieties and imbalanced fertilisation without micronutrient inputs (Dwivedi et al. 2012). Although soils often contain substantial total Mn, deficiency typically results from limited bioavailability rather than absolute scarcity (Rengel 2015).

Mn availability is strongly controlled by soil pH and redox potential. In soils, Mn occurs as Mn^{2+}, Mn^{3+} and Mn^{4+}, but only Mn^{2+} is stable in soil solution (Trebien et al. 2011). Acidic or reducing conditions enhance Mn compounds solubility, whereas higher pH promotes oxidation and precipitation as insoluble oxides and hydroxides (Pearson & Greenway 2005; Khoshru et al. 2023). Even minor shifts in pH may cause substantial fluctuations in Mn compounds solubility, ranging from deficiency to toxicity (Wang et al. 2008). Toxicity is less frequent but may occur in waterlogged soils due to Mn^{2+} accumulation (Millaleo et al. 2010).

Soil texture, clay content, organic carbon and cation exchange capacity significantly influence Mn adsorption and mobility (Ghasemi-Fasaei et al. 2012). Organic amendments generally enhance Mn availability by maintaining pH and stimulating microbial processes (Habashy & Abo-Zied 2008; Elbaalawy et al. 2019). In contrast, light-textured soils are prone to Mn leaching losses (Shuman 1979).

Monoculture farming markedly affects Mn dynamics (Belete & Yadete 2023). Continuous cultivation of Mn-demanding crops depletes bioavailable Mn and reduces organic matter inputs necessary for microbial Mn cycling (Mousavi et al. 2011). Long-term monocropping has been associated with declining Mn availability and soil fertility (Zou et al. 2008). Excessive use of acidifying fertilisers may temporarily increase Mn compounds solubility but can also induce toxicity under low pH conditions (Fageria et al. 2002). Conversely, in alkaline soils, Mn becomes immobilised, leading to deficiency (Alejandro et al. 2020). Monoculture further alters microbial communities involved in Mn oxidation-reduction processes, reducing biological regulation of Mn bioavailability (Fu et al. 2017). Soil compaction, erosion and nutrient imbalances – particularly excessive phosphorus or potassium fertilisation – may additionally restrict Mn uptake through chemical interactions or reduced aeration (Millaleo et al. 2010; Khoshru et al. 2023). Overall, Mn dynamics in soils are governed by complex interactions among physicochemical properties, biological processes and management practices, with monoculture systems posing significant risks of both deficiency and toxicity.

Our study is based on following hypothesis: (*i*) long-term application of nitrogen fertilizers (ammonium sulphate, urea ammonium nitrate) will significantly decrease soil pH and consequently increase water-extractable Mn due to enhanced release of Mn^{2+} ions from the solid phase into the soil solution, (*ii*) organic treatments (farmyard manure, slurry, sewage sludge, straw incorporation) will differ from mineral fertilization treatments in their effects on potentially available and pseudo-total Mn pools, (*iii*) water-extractable Mn will show a strong negative correlation with soil pH, whereas Mehlich 3-extractable Mn will show weaker or inconsistent correlation due to extraction of broader soil Mn pools, and (*iv*) pseudo-total Mn will similarly show lower temporal variability and a weaker relationship with soil pH than water-extractable Mn.

The main objective of this study was to evaluate the long-term effects (22 years) of different mineral fertilisers and organic amendments on Mn dynamics in a maize monoculture system at silty loam Haplic Luvisol.

MATERIAL AND METHODS

Site description and experimental design. The study was carried out on the evaluation of a long-term fertilisation experiment at the experimental sta-

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Table 1. Soil and climatic conditions of the experimental site

Location	Parameters
GPS coordinates	50°4'22"N, 14°10T9"E
Elevation (m)	398
Average annual T (°C)	7.7
Average annual rainfall (mm)	493
Soil type	Haplic Luvisol[a]
Soil texture	silty loam[a]
CEC ($mmol_+/kg$)	118
TOC (%)	1.17[b]
pH (0.01 mol/L $CaCl_2$)	6.60[c]
Bulk density (g/cm^3)	1.50
Clay (%) (< 0.002 mm)	5.40
Silt (%) (0.002–0.05)	68.1
Sand (%) (0.05–2 mm)	26.5

CEC – cation exchange capacity; TOC – total organic carbon; soil sampling depth – 0–30 cm; [a]Natural Resource Conservation Service (United States Department of Agriculture); [b]CNS analyser (Elementar Analysensysteme, Germany), after removing carbonates C with HCl; [c]average pH value in the year 1990 at the time of beginning maize monoculture cropping

tions of the Czech University of Life Sciences Prague at Červený Újezd, with basic characteristics given in Table 1. Maize monoculture has been grown here since 1990. The last organic fertilisation before the experiment establishment was carried out in 1988. Fertilising according to the further-mentioned design started in 1993. The size of each experimental plot is 170 m^2. Maize is sown at 8 plants per m^2 with row spacing of 70 cm. The experiment is arranged as a randomised complete block design with four replicates.

The whole experiment comprises of 9 fertilising treatments: (1) non-fertilised control (CK), (2) ammonium sulphate (AS), (3) urea ammonium nitrate (UAN), (4) UAN + mineral PK (UAN + PK), (5) UAN + mineral PMg (UAN + PMgS), (6) UAN + winter wheat straw (UAN + St), (7) sewage sludge (SS), (8) farmyard manure (FYM), (9) cattle slurry (CS).

The N, P, K, Mg, S, and Mn doses are shown in Table 2. The whole experiment is based on the same nitrogen level of 120 kg N/ha/year (except control). FYM, SS, CS straw as well as mineral P, K, and Mg fertilisers are applied each year in autumn (October) and immediately incorporated into the soil by ploughing. Mineral nitrogen fertilisers are applied prior to sowing every year in spring. Mn is applied only with organic fertilisers.

Soil sampling, handling, and preparation. Topsoil samples (0–30 cm) were randomly collected from a composite of 7 points/plot with a tube auger (2 cm diameter) and then mixed into plastic bags after maize harvest and before organic fertiliser application. The soil samples were air-dried and sieved through a 2 mm mesh prior to analysis.

Soil analysis. Soil pH was measured using an electronic calibrated pH-meter in 0.01 mol/L $CaCl_2$ (both 1 : 10 weight : volume (w : v) after 60 min of shaking and at least 60 min of standing as slightly modified after ISO 10390 (2021).

Water extractable soil Mn (Mn_{H_2O}) was determined in deionised water (1 : 10 w/v) after 60 min. horizontal shaking at 120 rpm. The suspension was centrifuged (9 000 g). Supernatant was measured for the readily available Mn content.

Table 2. Average yearly doses of selected nutrients (in kg/ha)

Treatment	N	P	K	Mg	S	Mn
Control (CK)	0	0	0	0	0	0
Ammonium sulfate (AS)	120	0	0	0	142	0
Urea ammonium nitrate (UAN)	120	0	0	0	0	0
UAN + mineral P and K (UAN + PK)	120	31.5	150	0	0	0
UAN + mineral P and Mg (UAN + PMgS)	120	31.5	0	60.0	84.0	0
UAN + barley straw (UAN + St)	120	4.34	16.0	5.50	4.34	0.12
Sewage sludge (SS)	120	82.1	45.0	25.5	52.4	1.31
Farmyard manure (FYM)	120	32.6	129	32.0	16.4	2.43
Cattle slurry (CS)	120	23.2	23.2	33.5	16.3	1.21

Mineral P – triple superphosphate (21% P); mineral K – potassium salt (50% K); mineral Mg – kieserite (potassium sulfate, 15% Mg); nutrient doses in organic fertilisers were calculated as average values from the organic fertilisers analysis

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Mn determined using Mehlich 3 (Mn_{M3}) was determined according to the Mehlich (1984) extraction procedure.

The *Aqua regia* extraction. Mn_{AR} was determined with *Aqua regia* extraction solution using the microwave-assisted wet digestion system (MLS, Leutkirch, Germany) under high pressure (Száková et al. 2013).

Measurement of Mn contents in soil extracts. All soil Mn extracts were measured using inductively coupled plasma mass spectrometry (ICP-OES, Varian Vista-Pro, Agilent Technology, Australia).

Mn_{H2O} and Mn_{M3} contents were evaluated in archive samples from the years 1997, 2001, 2004, 2008, 2010, 2013, 2016 and 2019, respectively. Mn_{AR} values were evaluated only in the years 1997, 2008 and 2019, and the pH value at the beginning of the experiment before first fertilising (1993) and in the last evaluated year (2019).

Statistical analysis. Dataset was pre-tested for the normality of distribution. In case of normal distribution, results were evaluated every year using one-way analysis of variance (ANOVA) using STATISTICA software, version 13 (TIBCO, Paolo Alto, California, USA). The treatment effects, significant difference, and mean separations were made using the Tukey's HSD test at $P \leq 0.05$ level of significance. Pearson's correlation test was performer to obtain the relationships among pH and Mn pools at the significancy levels $P \leq 0.05$, $P \leq 0.01$, $P \leq 0.001$, respectively.

RESULTS

Manganese transformations are strongly influenced by soil pH value. Because of this. pH value was determined at the beginning of the experiment as well as in last evaluated year (Table 3). Despite the stabilisation period preceding the differentiated fertilisation treatments, initial soil pH in 1993 varied among experimental plots. This variability may reflect residual effects of previous soil management together with natural spatial soil heterogeneity, which could be relevant given the relatively large plot size (170 m^2). Therefore, changes in pH between 1993 and 2019 should be interpreted as treatment-associated temporal trends rather than exclusively as fertilisation effects.

The strongest acidification effect was observed in the AS treatment, where soil pH decreased from 6.20 to 4.69 (Δ = –1.51). Significant pH declines were also recorded in mineral fertilisation treatments based on UAN, particularly UAN + St and UAN + PMgS. In contrast, organic amendments such as FYM, CS, SS maintained relatively stable soil pH values throughout the experiment. The control treatment showed only a minor decrease in pH over time. These temporal trends indicate substantially stronger soil acidification under long-term ammonium-based mineral fertilisation, whereas considerably smaller pH changes were observed under organic fertilisation.

Table 4 presents the long-term development of readily available Mn (Mn_{H2O}) under different fertilisation treatments in maize monoculture between 1997 and 2019. The results demonstrated a significant effect of fertilisation strategy on Mn availability. In the CK, Mn_{H2O} content gradually decreased from 3.03 to 1.01 mg/kg, indicating depletion of readily available Mn during long-term cultivation without nutrient replenishment. The highest Mn_{H2O} contents were consistently observed in the AS treatment, where values ranged between 4.34 and 8.07 mg/kg. This increase was closely related to strong soil acidification caused by AS (Table 3), which enhanced Mn release into the soil solution. Mineral fertilisation with UAN and combined mineral treatments generally maintained intermediate Mn_{H2O} levels, although a slight decreasing trend over time was also observed. The UAN + St treatment initially showed relatively

Table 3. The pH values in the years 1993 and 2019 and the difference (Δ 2019–1993)

Year	CK	AS	UAN	UAN + PK	UAN + PMgS	UAN + St	SS	FYM	CS
1993	6.58^{abcA}	6.20^{aB}	7.01^{dB}	6.93^{cdB}	6.87^{bcdB}	6.96^{cdB}	6.48^{abA}	7.05^{dA}	6.87^{bcdA}
2019	6.36^{bcdA}	4.69^{aA}	5.91^{bcA}	6.12^{bcdA}	5.91^{bcA}	5.88^{bA}	6.25^{bcdA}	6.81^{dA}	6.70^{cdA}
Δ	–0.22	–1.51	–1.10	–0.81	–0.96	–1.08	–0.23	–0.24	–0.17

CK – nonfertilised control; AS – ammonium sulphate; UAN – urea ammonium nitrate; UAN + PK – UAN with mineral P and K; UAN + PMgS – UAN with mineral P, Mg and S; UAN + St – UAN with barley straw; SS – sewage sludge; FYM – farmyard manure; CS – cattle slurry; different lowercase letters within rows are meaning significant differences among fertilising treatments, different capital letters within columns are meaning significant differences among years (Tukey test, $P \leq 0.05$)

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Table 4. Contents of readily available Mn_{H2O} in mg/kg

	1997	2001	2004	2008	2010	2013	2016	2019
CK	3.03^{aB}	2.00^{abAB}	1.85^{aAB}	1.69^{aAB}	1.66^{abAB}	1.74^{aAB}	1.37^{aAB}	1.01^{aA}
AS	5.67^{aA}	4.78^{bA}	5.50^{bA}	4.90^{bA}	4.34^{bA}	7.27^{bA}	8.07^{bA}	5.96^{bA}
UAN	3.38^{aB}	2.11^{abAB}	2.33^{aAB}	2.41^{abAB}	2.56^{abAB}	2.48^{aAB}	2.06^{aAB}	1.39^{aAB}
UAN + PK	2.23^{aB}	1.54^{aAB}	1.45^{aA}	1.58^{aAB}	1.83^{abAB}	1.82^{aAB}	1.45^{aA}	1.12^{aA}
UAN + PMgS	3.38^{aA}	2.31^{abA}	2.45^{aA}	2.99^{abA}	2.45^{abA}	2.45^{aA}	1.84^{aA}	1.25^{aA}
UAN + St	4.19^{aA}	3.33^{abA}	3.00^{abA}	3.35^{abA}	2.00^{abA}	2.72^{aA}	2.14^{aA}	1.39^{aA}
SS	3.16^{aA}	2.24^{abA}	2.00^{aA}	1.92^{abA}	2.17^{abA}	1.67^{aA}	1.31^{aA}	0.97^{aA}
FYM	2.44^{aB}	1.34^{aA}	1.17^{aA}	1.23^{aA}	1.02^{aA}	1.21^{aA}	1.00^{aA}	0.79^{aA}
CS	2.62^{aB}	1.75^{abAB}	1.64^{aAB}	1.44^{aAB}	1.50^{abAB}	1.33^{aAB}	1.03^{aA}	0.73^{aA}

CK – nonfertilised control; AS – ammonium sulphate; UAN – urea ammonium nitrate; UAN + PK – UAN with mineral P and K; UAN + PMgS – UAN with mineral P, Mg and S; UAN + St – UAN with barley straw; SS – sewage sludge; FYM – farmyard manure; CS – cattle slurry; different lowercase letters within columns are meaning significant differences among fertilising treatments; different capital letters within rows are meaning significant differences among years (Tukey test, $P \leq 0.05$)

elevated Mn_{H2O} values, probably due to temporary stimulation of microbial activity and organic matter decomposition after straw incorporation. Organic amendments, particularly FYM and CS, maintained lower but more stable Mn_{H2O} contents throughout the experimental period. SS treatment showed moderate Mn_{H2O} availability during the first years but declined markedly by 2019. Across most treatments, Mn_{H2O} values decreased with time, confirming gradual depletion or stabilisation of labile Mn pools in the soil. Significant differences among treatments were especially evident in the latter sampling years.

Table 5 summarises the development of potentially available Mn (Mn_{M3}). In contrast to water-extractable Mn, the Mn_{M3} pool showed smaller temporal fluctuations and generally higher stability across treatments. The unfertilised control maintained Mn_{M3} values between 154 and 185 mg/kg, suggesting relatively stable reserves of potentially available Mn despite continuous maize monoculture. The AS treatment showed a gradual decline in Mn_{M3} from 177 to 136 mg/kg, indicating progressive depletion of exchangeable and weakly bound Mn forms under strongly acidifying conditions. Similar decreasing trends were observed in the UAN and SS treatments. Conversely, organic fertilisation with FYM and CS maintained the highest Mn_{M3} contents during the entire experiment, with values reaching up to 210 mg kg.

Table 5. Contents of potentially available Mn_{M3} in mg/kg

	1997	2001	2004	2008	2010	2013	2016	2019
CK	169^{abA}	163^{aA}	167^{aA}	154^{abA}	172^{bA}	185^{abA}	164^{abA}	171^{bcA}
AS	177^{aB}	170^{aAB}	168^{aAB}	162^{abAB}	171^{bAB}	184^{abB}	151^{abAB}	136^{abA}
UAN	174^{aB}	164^{aB}	161^{aAB}	144^{abA}	162^{abAB}	174^{abAB}	156^{abAB}	148^{abcA}
UAN + PK	154^{aA}	156^{aA}	158^{aA}	149^{abA}	169^{abA}	178^{abA}	172^{abA}	168^{bcA}
UAN + PMgS	188^{aA}	178^{aA}	169^{aA}	164^{abA}	184^{bA}	187^{abA}	172^{abA}	161^{abcA}
UAN + St	177^{aA}	178^{aA}	166^{aA}	158^{abA}	174^{bA}	184^{abA}	163^{baA}	157^{abcA}
SS	170^{aB}	157^{aAB}	151^{aAB}	138^{aAB}	139^{aAB}	155^{aAB}	132^{aAB}	111^{aA}
FYM	184^{aA}	181^{aA}	184^{aA}	174^{bA}	188^{bA}	207^{bB}	189^{bAB}	188^{cAB}
CS	190^{aAB}	191^{aAB}	178^{aA}	171^{abA}	189^{bAB}	210^{bB}	187^{bAB}	189^{cAB}

CK – nonfertilised control; AS – ammonium sulphate; UAN – urea ammonium nitrate; UAN + PK – UAN with mineral P and K; UAN + PMgS – UAN with mineral P, Mg and S; UAN + St – UAN with barley straw; SS – sewage sludge; FYM – farmyard manure; CS – cattle slurry; different lowercase letters within columns are meaning significant differences among fertilising treatments, different capital letters within rows are meaning significant differences among years (Tukey test, $P \leq 0.05$)

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Table 6. Pseudo-total Mn contents in mg/kg

Treatment/year	1997	2008	2019
CK	827*	761	803
AS	750	724	753
UAN	839	789	742
UAN + PK	829	766	765
UAN + PMgS	835	764	831
UAN + St	845	782	797
SS	847	779	807
FYM	788	791	789
CS	799	752	747

CK – nonfertilised control; AS – ammonium sulphate; UAN – urea ammonium nitrate; UAN + PK – UAN with mineral P and K; UAN + PMgS – UAN with mineral P, Mg and S; UAN + St – UAN with barley straw; SS – sewage sludge; FYM – farmyard manure; CS – cattle slurry; *no significant differences were found among years as well as fertilising treatments (Tukey test, $P \leq 0.05$)

These results suggest that organic amendments contributed to stabilisation and replenishment of Mn pools through continuous organic matter inputs. Combined mineral fertilisation treatments (UAN + PK and UAN + PMgS) maintained intermediate Mn_{M3} contents with relatively minor long-term changes. The UAN + St treatment also showed relatively stable Mn_{M3} values, indicating a positive effect of straw incorporation on Mn retention in soil. Significant differences among fertilisation treatments became more pronounced in the later years of the experiment. Mn_{M3} showed lower temporal variability than Mn_{H_2O}, indicating greater stability of this broader operationally defined Mn pool.

Table 6 shows the pseudo-total Mn_{AR} contents determined by *Aqua Regia* extraction. In comparison with readily and potentially available Mn pools, Mn_{AR} showed relatively low temporal variability across all fertilisation treatments. The values ranged approximately between 742 and 847 mg/kg, indicating that the majority of Mn remained bound in stable soil mineral pools. No statistically significant differences were observed either among years or fertilisation treatments, confirming the relatively conservative nature of pseudo-total Mn pools. Slight decreases in Mn_{AR} were observed in several treatments, particularly in UAN and FYM, whereas more stable values were maintained under organic amendments such as sewage sludge and cattle slurry. The results indicate that long-term fertilisation practices had only a limited influence on pseudo-total Mn forms.

Table 7 summarises the relative changes in individual Mn pools between 1997 and 2019 and confirms the contrasting behaviour of readily available, potentially available, and pseudo-total Mn pools under long-term fertilisation. The largest changes were observed for Mn_{H_2O}, where most treatments showed substantial decreases ranging from 49.8 to 72.4%, indicating progressive depletion of readily available Mn forms during long-term maize monoculture. The only exception was the AS treatment, where Mn_{H_2O} increased by 5.05%, which directly corresponded with the strongest soil acidification (viz. Table 3). This confirms that lower soil pH enhanced Mn compounds solubility and maintained higher concentrations of water-extractable Mn, as already demonstrated in Table 4.

Changes in Mn_{M3} were considerably smaller than in Mn_{H_2O}, confirming the greater stability of potentially available Mn pools.

Changes in Mn_{M3} were considerably smaller than those in Mn_{H_2O}, indicating greater temporal stability of the potentially available Mn pool. The strongest decrease was observed in the SS treatment (–34.8%), whereas UAN + PK showed the largest relative increase (+9.25%). This increase partly reflected the

Table 7. Differences between the years 1997 and 2019 (in %; 1997 = 100%)

Treatment/year	Mn_{H_2O}	Mn_{M3}	Mn_{AR}
CK	-66.8^{b}	1.16^{cd}	2.88^{a}
AS	5.05^{a}	-23.2^{ab}	-0.52^{a}
UAN	-59.0^{b}	-14.8^{abc}	11.50^{a}
UAN + PK	-49.8^{b}	9.25^{d}	7.66^{a}
UAN + PMgS	-63.1^{b}	-14.6^{abc}	0.45^{a}
UAN + St	-66.7^{b}	-11.7^{abcd}	5.69^{a}
SS	-69.3^{b}	-34.8^{a}	4.74^{a}
FYM	-67.7^{b}	1.90^{cd}	7.39^{a}
CS	-72.4^{b}	-0.82^{bcd}	6.49^{a}

CK – nonfertilised control; AS – ammonium sulphate; UAN – urea ammonium nitrate; UAN + PK – UAN with mineral P and K; UAN + PMgS – UAN with mineral P, Mg and S; UAN + St – UAN with barley straw; SS – sewage sludge; FYM – farmyard manure; CS – cattle slurry; Mn_{H_2O} – readily available Mn; Mn_{M3} – potentially available Mn; Mn_{AR} – pseudo-total Mn; different letters within columns are representing significant differences among fertilising treatments (Tukey test, $P \leq 0.05$)

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Table 8. Correlations among studied Mn pools and pH value (Pearson's test, $n = 36$)

	Mn_{H2O}	Mn_{M3}	Mn_{AR}
pH	–0.642***	0.196	–0.191
Mn_{H2O}		–0.254*	–0.028
Mn_{M3}			0.348**
Mn_{AR}			0.236*

Mn_{H2O} – readily available Mn; Mn_{M3} – potentially available Mn; Mn_{AR} – pseudo-total Mn; *,**,***significant correlation at $P \leq 0.05, 0.01, 0.001$

relatively low initial Mn_{M3} concentration under UAN + PK (154 mg/kg in 1997). In 2019, the highest absolute Mn_{M3} concentrations were recorded under FYM and CS (188 and 189 mg/kg, respectively), compared with 168 mg/kg under UAN + PK. Thus, the relative changes and absolute Mn_{M3} concentrations indicate different aspects of the treatment response.

Pseudo-total Mn_{AR} exhibited only minor changes across treatments, ranging from −0.52 to 11.50%, without significant differences among fertilisation variants. These results are consistent with Table 6 and confirm the relatively conservative nature of pseudo-total Mn pools, which were only minimally affected by long-term fertilisation management. Overall, the data indicate that long-term fertilisation primarily influenced the labile Mn pools, whereas pseudo-total Mn remained relatively stable and controlled mainly by inherent soil properties.

Correlation analysis was performed to determine the relationships between the determined Mn fractions and soil pH using the values from 2019 (Table 8). A significant negative correlation was observed between soil pH and Mn_{H_2O} ($r = –0.642$), indicating that lower soil pH was associated with higher concentrations of readily available Mn in 2019. In contrast, Mn_{M3} and Mn_{AR} showed only weak and non-significant relationships with soil pH.

DISCUSSION

Long-term fertilisation significantly affected soil pH and Mn dynamics in the studied maize monoculture. The strongest acidification effect was observed under AS treatment, where soil pH decreased by 1.51 units during the experimental period. Similar but less pronounced decreases were recorded in treatments based on UAN fertilisation. In contrast, organic amendments such as farmyard manure FYM, cattle slurry CS, and sewage sludge SS maintained relatively stable soil pH values. These findings are consistent with previous studies demonstrating that ammonium-based fertilisers promote soil acidification through nitrification processes and subsequent proton release (Zhao et al. 2025), whereas organic amendments exhibit buffering effects due to their organic matter content and cation exchange capacity (Zhang et al. 2023).

Changes in soil pH strongly influenced Mn availability. The significant negative correlation between pH and Mn_{H2O} in 2019 indicated that lower soil pH was associated with higher concentrations of readily available Mn. This relationship was particularly evident in the AS treatment, which had both the lowest soil pH and the highest Mn_{H2O} concentration in 2019. Increased Mn compounds solubility under acidic conditions has been widely documented and results primarily from the reduction of insoluble Mn oxides to Mn^{2+} forms (Rengel 2015; Toro et al. 2021). However, although acidification temporarily increased Mn availability, long-term acidifying fertilisation simultaneously reduced the potentially available Mn pool (Mn_{M3}), suggesting progressive depletion of exchangeable and weakly bound Mn pools through plant uptake and leaching.

The majority of treatments showed a substantial decline in water-extractable Mn during the 22-year period. In the unfertilized control, Mn_{H2O} decreased by almost 67%, indicating a gradual depletion of labile Mn reserves under continuous maize monoculture without nutrient replenishment. Similar declines were observed in most mineral and organic treatments. These results correspond with previous findings showing that long-term monocropping and intensive cultivation reduce micronutrient availability due to continuous crop removal and reduced organic matter turnover (Mousavi et al. 2011; Zou et al. 2008). The only exception was the AS treatment, where Mn_{H2O} slightly increased over time, further confirming the dominant role of soil acidification in controlling Mn compounds solubility.

Compared with Mn_{H2O}, the Mn_{M3} pool exhibited substantially greater stability. The Mn_{M3} pool showed smaller temporal fluctuations and weaker correlations with soil pH, indicating that this pool represents broader and less reactive Mn forms associated with soil minerals and organic matter. Organic amendments, particularly FYM and CS, maintained the highest Mn_{M3} values throughout the experiment, suggesting that regular organic inputs contributed

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to stabilisation and replenishment of potentially available Mn pools. Organic matter may retain Mn through adsorption, chelation, and improved microbial cycling, thereby reducing Mn losses from the soil system (Omokaro et al. 2024; Sparks 2003). Similar stabilising effects of organic fertilisation on micronutrient dynamics have been reported in long-term fertilisation experiments worldwide. In contrast, mineral nitrogen fertilisation, especially under acidic conditions, tended to decrease Mn_{M3} contents over time. The decline observed in AS and UAN treatments suggests that prolonged acidification may accelerate Mn mobilisation and subsequent depletion of exchangeable Mn pools. This mechanism is consistent with previous reports indicating that intensive nitrogen fertilisation may enhance micronutrient leaching and alter trace element distribution among soil pools (Bhatt et al. 2019; Naeem et al. 2023).

Pseudo-total Mn_{AR} determined by *Aqua Regia* extraction showed only minimal temporal variation and no statistically significant differences among treatments. These results indicate that the majority of soil Mn remained bound within stable mineral structures and was only weakly affected by long-term fertilisation management. Similar findings have been described by other authors, who reported that pseudo-total Mn pools are controlled predominantly by parent material and inherent soil properties rather than short-term agronomic practices (Wei et al. 2006). Although slight increases or decreases in Mn_{AR} were observed in some treatments, these changes were relatively small compared with variations in readily available Mn pools.

The comparison of relative changes between 1997 and 2019 further emphasised the contrasting behaviour of individual Mn pools. Readily available Mn showed the largest declines across most treatments, whereas Mn_{M3} remained comparatively stable, and Mn_{AR} changed only minimally. These results confirm that long-term fertilisation primarily affects the most labile Mn pools, while stable geogenic Mn pools remain largely unaffected. Organic amendments generally improved the stability of potentially available Mn, whereas strongly acidifying mineral fertilisation increased Mn compounds solubility but simultaneously accelerated depletion of exchangeable Mn reserves. These findings were confirmed in a similar study with long-term three-crop rotation performed during the years 1997–2017 (Obeng et al. 2026).

CONCLUSION

Long-term fertilization significantly influenced soil pH and manganese dynamics in maize monoculture cultivated on Haplic Luvisol. Ammonium-based mineral fertilisers, particularly ammonium sulphate, caused substantial soil acidification and increased Mn compounds solubility, resulting in higher concentrations of readily available Mn_{H2O}. However, most treatments showed progressive declines in water-extractable Mn over time, indicating depletion of labile Mn pools during long-term monoculture cultivation. In contrast, organic amendments such as farmyard manure and cattle slurry maintained higher and more stable Mn_{M3} contents, demonstrating their positive role in stabilising potentially available Mn pools and buffering soil pH. Pseudo-total Mn_{AR} remained relatively stable throughout the experiment, confirming that this Mn pool was controlled mainly by inherent soil properties rather than fertilisation management. The study demonstrates that long-term fertilisation was associated with contrasting changes in individual soil Mn fractions. Soil pH was significantly related to readily available Mn_{H2O} in 2019, whereas potentially available Mn_{M3} and residual Mn_{AR} showed no significant relationships with soil pH.

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