Mitigation of salinization and sodification of chernozems irrigated by brackish water

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Highlights

- *Deep ploughing with a dosage of (cattle) manure of 100 ton/ha, manure alone, industrial Ca-ameliorants, and phosphogypsum were all effective in the amelioration of secondary sodified chernozems in Ukraine.*
- *Deep ploughing (to 75 cm) with manuring caused a higher and longer-lasting increase in the buffering capacity of soil to sodification and salinization compared to the control and calcium ameliorants.*
- *The amelioration measures improved the saline status of the irrigated soil and contributed to an increase in the content of calcium carbonates, water-soluble calcium, and exchangeable calcium.*
- *The introduction of the Ca-ameliorants into the soil contributed to the mobilization of $CaCO_3$ compounds from soil.*
- *Improvement of the physicochemical properties of reclaimed soils obtained by the above-mentioned measures increased crop yield by 10-30%.*

Abstract

This research aimed to assess the impact of deep ploughing, with manuring and manuring alone, as well as the effects of different calcium ameliorants on physicochemical properties, fertility, and crop productivity of calcic chernozems in the Northern Steppe of Ukraine over a period of 7 years. Deep ploughing with manure had long-term positive effects on the mentioned characteristics of chernozems that were irrigated with brackish water over a long period. The bulk density decreased from 1.2 to 0.98 g/cm^3, while the carbonate content increased to 8.7%. The humus layer increased from 50 to 75 cm. The exchangeable sodium and potassium percentage decreased from 7 to 3.9-4.8% and crop yield increased by 21-38%. These positive effects of deep ploughing and manuring persisted throughout the entire 7-year period. The effect of calcium ameliorants lasted shorter (only 3-4 seasons) and was as follows: i) the degree of soil sodicity decreased from medium to weak; ii) the content of exchangeable sodium and potassium decreased from 7 to 4.1-5.5%; iii) the content of carbonates in the root zone increased from 2.7 to 3.3%; iv) the crop yield increased by 10-30%. All measures proved to be effective in mitigating the sodicity and salinity of affected chernozems.

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Introduction

Soil salinization is a global problem: it is encountered on all continents, in all natural zones. Salt-affected soils cover some 6.7-10.0% of the land mass and 10-20% of arable land (Abrol *et al.*, 1988; Daliakopoulos *et al.*, 2016; FAO and ITPS, 2015; Singh, 2022). The Main Report on Status of the World’s Soil Resources (2015) estimates the worldwide extent of salt-affected soils to be some 1 billion ha (FAO and ITPS, 2015). Salt-affected soils are a large group of soils of various genesis and properties, subdivided into two groups: i) saline soils (without a natric/sodic horizon); ii) sodic (also named solonetz or alkali) soils (soils with a well-developed natric sodic horizon). Soils that combine both saline and sodic properties are called saline-sodic soils. Within the aeration zone, saline soils contain water-soluble salts (mainly chlorides, sulfates, bicarbonates, sodium, and potassium carbonates), which individually or in total may exceed the toxicity threshold, decreasing soil fertility and inhibiting the growth and development of most plant species. The fertility of sodic soils is also restricted by their unfavorable chemical and physical properties, including those related to water movement in soil (Baliuk *et al.*, 2015a; FAO and ITPS, 2015; Vargas *et al.*, 2018; Shahid *et al.*, 2018; Chhabra, 2021; FAO, 2022).

Salt-affected soils can be the result of both natural (primary) and human-induced (secondary) processes. Natural salt accumulation processes depend on the interaction of certain climatic (arid and semi-arid regions) and landscape (relief, geomorphology, and hydrogeology of the area) conditions. These processes are very dynamic and in recent years they are increasingly found to be associated with climate change and desertification, leading to significant expansion of the area of salt-affected soils (Corwin, 2021; Singh, 2022). Secondary salinization and alkalinization occur as a result of unsustainable agricultural management practices and mainly depend on the poor quality of irrigation water, inadequate irrigation practices, and lack of or inadequate drainage (Baliuk *et al.*, 2020; Devkota *et al.*, 2022; FAO, 2022; Shahid *et al.*, 2018; Vargas *et al.*, 2018). This secondary (human-induced) salinization has become increasingly severe at the global level in recent years (Ladeiro, 2012; FAO, 2017; FAO, 2022).

In Ukraine, salt-affected soils occupy a relatively small proportion (around 5-7%) of arable land. Primary salt-affected soils in Ukraine are located within the Dnipro-Don and the Black Sea tectonic depressions. Secondary salt-affected soils in Ukraine are located in irrigated croplands of forest-steppe and steppe zones (Baliuk *et al.*, 2015a). The total area of secondary sodic soils within arable land varies between 300 and 400 thousand hectares, whereas the total area of secondary saline soils varies between 50 and 200 thousand hectares in different years. The climate of the larger part of Ukraine is characterized by a significant water deficit during the growing season. Irrigation is therefore used to mitigate the impact of adverse weather conditions on agricultural production (Baliuk *et al.*, 2017). According to the results of our previous research, the use of brackish water for irrigation in the northern steppe leads to secondary salinization and sodification of the soil (Baliuk *et al.*, 2020).

Salt-affected soils require special attention when they are intended for agricultural production, due to the necessity to implement special measures for desalinization. These measures include physical (scrapping**,** subsoiling and/or deep ploughing, leveling, sanding, and mulching), chemical (application of acids, calcium in the form of gypsum, phosphogypsum, nutrients such as NPK, magnesium), physicochemical (incorporation of different organic amendments, manure), hydrological (irrigation, leaching, and drainage) and biological (phytoremediation: salt tolerant crops and biological concentration; microbial remediation) methodologies (Boudabbous *et al.*, 2022; Meng *et al.*, 2016; Roy and Chowdhury, 2020; Sultan *et al.*, 2021; Xong *et al.*, 2011). The effectiveness of the above-mentioned desalinization measures can be increased and prolonged when used in combination. Moreover, the expediency of the technology chosen is determined by soil and climatic conditions, current ecological and agro-reclamation state, specialization of the planned agricultural production, and availability of resources. To avoid and mitigate damage, continuous and comprehensive monitoring of salt-affected soils and waters should be performed (Baliuk *et al*., 2015b; Gorji *et al.*, 2015; FAO, 2022; Hammam and Mohamed, 2020; Singh, 2022; Vargas *et al.*, 2018).

Many studies have been carried out using various tillage methods (including no-tillage) to rehabilitate salt-affected soil. In the southern dry steppe in Ukraine, where chemical reclamation is often ineffective, the use of ameliorative deep ploughing is commonly recommended. In an earlier study (Baliuk *et al.*, 2015a), we demonstrated that this deep ploughing resulted in a very substantial long-term (40-50 years) improvement of the structure and fertility of treated soils (Vargas *et al.*, 2018). Alcántara *et al.* (2017) noted that although deep ploughing is expensive, the machinery and additional fuel costs were compensated by increased crop yield and amelioration of the soil structure (*e.g.*, uplift of subsoil $CaCO_3$, improved aeration, compaction alleviation). The type of tillage management to be chosen depends on the degree of soil salinity and sodicity, the nature of land use, and the possibility of applying organic fertilizers (Devkota *et al.*, 2022; Li *et al.*, 2020; Xiong *et al.*, 2012; Xong *et al.*, 2011). Manure application combined with deep tillage was found to be more effective than conventional tillage (Meng *et al.*, 2016; Milani *et al.*, 2011) or the application of sulfuric acid or gypsum (Ding *et al.*, 2021).

Calcium-containing by-products of diverse industries can be utilized as ameliorants of sodic and saline-sodic soils. The potential of these amendments as an additional source of micro- and macronutrients (especially calcium) is of great interest. Some studies have established their positive impact on soil quality and crop yield (Alcívar *et al.*, 2018; Bello *et al.*, 2021; Khan *et al.*, 2019; Shaaban *et al.*, 2013; Singh *et al.*, 2022). However, industrial by-products are characterized by individual composition and may contain toxic compounds, which necessitates additional research and constant monitoring (Wang *et al.*, 2021).

The aims of our study were: i) to evaluate the effect of deep ploughing (to 75 cm) with a dosage of (cattle) manure , and manuring alone; ii) to evaluate the effect of different calcium ameliorants (mainly industrial by-products), in a long term (7 years) field experiment on saline-sodic chernozems. To this end, the physicochemical properties and fertility of secondary salinized and sodified ordinary chernozem (northern steppe of Ukraine), its buffering capacity, and crop yields under irrigation were studied.

Materials and Methods

Study area, experimental design, and physicochemical description of the soils

The experiment was carried out at an experimental field of the Institute of Agro-industrial Production, located in the Pokrovsky district of the Donetsk region,12 km from the city of Donetsk, Eastern Ukraine (geographic coordinates 48°03′44″N, 37°40′30″E). This area lies within the northern steppe zone. According to the Köppen-Geiger classification it is characterized by a humid continental climate (Dfa). The average annual rainfall ranges from 490 to 560 mm, with 200 to 374 mm/year during the growing season, with a trend towards lower precipitation over recent years, following a rise in temperature, ranging from 18-19°C in 2000-2003 to 19.8-20.5°C in 2017-2021 (Ukrainian Hydrometeorological Center, https://www.meteo.gov.ua/). The experiment was conducted over a period of 7 years to investigate the impact of deep ploughing with manuring, manuring alone, and application of several calcium ameliorants on secondary salinized and sodified chernozems. In Ukraine a traditional method of soil salinity (primary and secondary) assessment is the analysis of a 1:5 soil-to-water extract, determining: i) total soluble salt; ii) total toxic salt; iii) Ca:Na ratio; iv) pH. The degree of salinity was determined by the content of total and/or of toxic salts, taking into account the type of salinity (sulphate, chloride, or soda). The degree of sodicity was determined by the ratio of exchangeable cations in the soil adsorption complex. Criteria were: i) the sum of exchangeable sodium and potassium, as % of the cation exchange capacity; ii) thermodynamic parameters ($aNa/\sqrt{aCa}$ and/or pNa-

0.5pCa) in the soil solution. The determination of calcium carbonate content, the granulometric composition of the soil, and the characterization of soil salinization type were performed according to Baliuk *et al.* (2017) and Vargas *et al.* (2018).

The initial soil of the experimental plots (before the experiment) was ordinary chernozem (Calcic Chernozem), according to World Reference Base for Soil Resources 2014 (Update 2015), secondarily weakly sodified, light clayey, on loess deposits. Before the experiments, the study area was irrigated, using brackish water, over a period of ten years, which led to clear signs of compaction and sodification. The characteristics of the arable layer of the original soil before the experiments are presented in Table 1. The topsoil (0-25 cm) was characterized by a light clay texture with a physical clay content (<0.01 mm) of 65%. The bulk density of the arable layer was 1.35 g/cm^3.

Experimental design

The experiment on the effectiveness of one-time deep ploughing, with a dosage of manure, manuring alone, and four calcium ameliorants from local resources was laid out in six repeats with a systematic stepwise arrangement of seven treatments: i) untreated control (no deep ploughing, no manure, no ameliorants); ii) manure (single dose of 100 t/ha); iii) deep ploughing at 75 cm + manure (100 t/ha); iv) phosphogypsum ($CaSO_4 \cdot 2H_2O$); v) calcium ameliorant of a soda plant ($CaCO_3$), chemically decomposed with sulfuric acid; vi) calcium ameliorant of a phenol plant ($CaSO_4$) stabilized with carboxymethylcellulose in a water suspension; vii) calcium ameliorant of a steel wire plant ($CaSO_4 \cdot FeSO_4$), untreated, in a water suspension. The size of each experimental plot was 4 m^2.

Deep ploughing

Experimental plots were laid out in a local region with sodic soil. Deep ploughing was carried out to a depth of 75 cm to move the horizon of accumulation of calcium carbonates to the surface. Deep ploughing allows the ameliorative mixing of calcium compounds naturally present within a 35-60 cm layer of soil. This agrotechnology is called *soil self-improvement*. Ploughing was done manually with a spade in autumn, whereafter cattle manure was added to the 0-25 cm soil layer at a rate of 100 t/ha (40 kg/plot) in treatments 2 and 3.

Ameliorants used in the experiment

A half-decomposed cattle manure (100 t/ha, 40 kg/plot) in one dose in autumn was used in treatments 2 and 3, respectively (Table 2). The other ameliorants were applied twice, viz. at the start (the first year) and in the fourth year of the experiment. Their dose was calculated on the basis of the actual sodicity of the soil, using formula 1 (Instructions, 1993):

$$N = \left(\frac{T \cdot b}{100} - \frac{T \cdot b_1}{100}\right) \cdot a \cdot h \cdot p \cdot k \quad (1)$$

where N – ameliorant dose, t/ha; T – adsorption capacity of the reclaimed soil layer, meq (milli-equivalent) /100 g of soil; b – content of exchangeable cations Na + K, % of the sum of exchangeable cations; b_1 – the content of exchangeable Na + K cations at the lower limit of the weak degree of sodicity of the soil, % of the sum of exchangeable cations; a – gram value of 1 meq of ameliorant; h – calculated layer of the soil to be reclaimed, cm; p – soil bulk density, g/cm^3; k - the coefficient that takes into account the content of impurities and moisture in the ameliorant and is calculated according to formula 2:

$$k = \frac{100}{100 - d} \quad (2)$$

where d – the content of impurities and moisture.

For the second application of the ameliorants doses were calculated taking into account the sodification effect of water on the soil and displacement of exchangeable sodium and potassium cations from the soil adsorption complex according to formula 3 (Instructions, 1993):

$$N = \left(A - \frac{A_1 \cdot T}{100}\right) \cdot a \cdot h \cdot p \cdot k \quad (3)$$

where N – ameliorant dose, t/ha; A – the total content of exchangeable sodium and potassium cations in the soil adsorption complex,

Table 1. Physicochemical soil properties (arable soil layer) before the experiment.

Soil properties	Units	Mean values
pH (H_2O)		7.7
Water-soluble salts	%	0.10
Toxic salts	%	0.06
Soil organic carbon	%	2.55
Exchangeable calcium	mg/kg of soil	38.8
Exchangeable sodium	mg/kg of soil	2.9
Exchangeable sodium and potassium cations	% out of the total content of all cations	5.3
$CaCO_3$	%	1.5
$N\text{-}NO_3$ +$N\text{-}NH_4$	mg/kg of soil	19.6
P_2O5	mg/kg of soil	260.0
K_2O	mg/kg of soil	206.0
Physical clay (<0.01 mm)	%	65.0
Bulk density	g/cm^3	1.35

meq/100 g of soil; A_1 – permissible content of sodium and potassium in the soil adsorption complex (3%); T – adsorption capacity of the reclaimed soil layer, meq/100 g of soil; a – gram value of 1 meq of ameliorant; h – calculated layer of the soil to be reclaimed, cm; p – soil bulk density, g/cm^3; k is the coefficient taking the content of impurities and moisture in the ameliorant (calculated according to formula 2) into account.

The following active substance (calcium compounds) content was present in the ameliorants used: 80% for phosphogypsum, 60% for calcium ameliorant of a soda plant, 85% for calcium ameliorant of a phenol plant and 72% for calcium ameliorant of a steel wire plant. All ameliorants met national ecological and sanitary requirements. The content of toxic compounds in the ameliorants did not exceed the norms established in Ukraine. Two doses of ameliorants were applied during the course of the experiments to each treatment involved, namely one at the beginning of the experiment (phosphogypsum 7.9 t/ha =3.16 kg/plot; calcium, soda plant 7.5 t/ha = 3.0 kg/plot; calcium, phenol plant 4.6 t/ha = 1.84 kg/plot; calcium, steel wire plant 5.6 t/ha = 2.24 kg/plot) and a second at the fourth year of the experiment (phosphogypsum 5.0 t/ha = 2 kg/plot; calcium, soda and phenol plant each 2.9 t/ha = 1.16 kg/plot calcium, steel wire plant 5.8 t/ha = 2.32 kg/plot). Ameliorants were applied to the soil with irrigation water from a pond (composition of pond water presented in Table 3) in spring before sowing the crops: treated with sulfuric acid to increase the availability of calcium (treatment 5, Table 2, soda plant); stabilized with carboxymethylcellulose, in as water suspension (treatment 6, Table 2, phenol plant), or as water suspension only (treatment 7, Table 2, steel wire plant). The calcium ameliorant of the soda plant was dissolved as follows: with 2.6 l sulfuric acid 75% per 3kg for the first and 1 liter per 1.16 kg of the ameliorant for the second application, until complete dissolution. The dissolved ameliorant was then mixed with 100 l of irrigation water from the pond and applied to the soil. The calcium ameliorant of the phenol plant was dissolved in irrigation water (1.84 kg per 100 l) and stabilized with a suspension (10g/l) of carboxymethylcellulose (Trading company Optkhim) (10 g/l) and subsequently applied to the soil.

The following crops were grown in the experimental plots: fodder beet (*Beta vulgaris*), soybean (*Glycine max*), winter wheat (*Triticum aestivum*), common buckwheat (*Fagopyrum esculentum*), corn for grain (*Zea mays*) and lucerne (*Medicago satíva*). The crop yield was measured in all experimental plots for each repetition by weighing the mass of (wet) grain or green mass.

Irrigation water from the local pond (mentioned under Experimental Design and in Table 3) was used during the whole experimental period. The water mineralization was 2.6-3.1 g/l and sodium adsorption ratio (SAR) was 10.1-11.6 meq/l, resulting in a so-called medium sodium water (Class 2) of good quality, but appreciable hazard. Soil moisture was maintained at 70% of field capacity. Irrigation doses were adapted to the climatic conditions

Table 2. The impact of amelioration measures on the calcium carbonates content and indicators of the salt composition of the soil-to-water extract (pH, the content of water-soluble calcium and sodium) in the 0-50 cm layer (mean of 6 replicates with standard deviation).

Treatment	$CaCO_3$, %	pH	Toxic salts, % meq/100 g of soil	Ion content,		Ca^{2+}/Na^+ ratio	Soil salinity grades
				Ca^{2+}	Na^+		
1st year of experiment							
1. Control	1.5±0.2	7.7±0.1	0.07±0.01	0.41±0.05	1.75±0.12	0.23	Not saline
2. Manure	1.6±0.2	7.7±0.1	0.07±0.01	0.46±0.08	1.70±0.10	0.27	Not saline
3. Deep ploughing and manure	8.7±0.3	7.7±0.2	0.08±0.01	0.56±0.06	1.27±0.09	0.44	Not saline
4. Phosphogypsum	2.1±0.2	7.6±0.1	0.08±0.01	0.87±0.08	1.22±0.10	0.71	Not saline
5. Calcium ameliorant of the soda plant chemically decomposed with sulfuric acid, in water suspension	2.3±0.2	7.6±0.2	0.08±0.01	2.98±0.10	1.53±0.15	1.95	Not saline
6. Calcium ameliorant of the phenol plant in water suspension stabilized with carboxymethylcellulose	2.2±0.2	7.6±0.1	0.07±0.01	0.59 ±0.06	1.12 ±0.09	0.53	Not saline
7. Calcium ameliorant of the steel-wire plant in water suspension only	2.1±0.2	7.7±0.1	0.08±0.01	1.23±0.09	1.33±0.10	0.92	Not saline
LSD_{05}	0.3	0.1	0.015	0.08	0.15		
7th year of experiment							
1. Control	1.6±0.2	8.0±0.1	0.12±0.01	0.36±0.04	1.91±0.10	0.19	Low
2. Manure	1.7±0.2	7.9±0.2	0.08±0.01	0.42±0.03	1.79±0.08	0.23	Not saline
3. Deep ploughing and manure	15.3±0.4	7.7±0.2	0.07±0.01	0.72±0.05	1.19±0.07	0.61	Not saline
4. Phosphogypsum	2.7±0.3	7.7±0.2	0.08±0.01	0.8±0.06	1.1±0.07	0.73	Not saline
5. Calcium ameliorant of the soda plant chemically decomposed with sulfuric acid	2.8±0.3	7.5±0.1	0.07±0.01	1.2±0.06	1.06±0.07	1.13	Not saline
6. Calcium ameliorant of the phenol plant on stable water suspension	2.6±0.2	7.5±0.1	0.08±0.01	0.45±0.03	0.95±0.06	0.47	Not saline
7. Calcium ameliorant of the steel-wire plant	2.7±0.3	7.6±0.1	0.08±0.01	0.74±0.04	0.92±0.09	0.80	Not saline
LSD_{05}	0.3	0.1	0.02	0.08	0.10		

of the corresponding year and based on the demands of the crops: for fodder beet an average of 1200 m^3/ha; soybean, 1100 m^3/ha; winter wheat, 900 m^3/ha; buckwheat, 1000 m^3/ha; corn for grain, 800 m^3/ha; lucerne for the first-cut, 1000 m^3/ha and for the second-cut, 1200 m^3/ha.

All fieldwork (deep ploughing, sowing, ameliorant application, harvesting, *etc.*) was carried out using the technology developed for the region of investigation. All operations in the experiment were performed manually.

Soil sampling

Soil samples for chemical analyses were collected at the end of each growing season after the harvest of cultivated crops. They were taken from each repetition from depths of 0-25, 25-50, 50-75, and 75-100 cm according to the national standard DSTU 4287:2004. Soil samples were air-dried, then sieved through a 1 mm sieve, and processed following ISO 11464:2006.

After conducting the experiment over seven years, a soil pit was dug at the plots where deep ploughing was applied, to determine the morphological structure of the soil profile and the bulk density of agro-transformed ordinary chernozem. The description of the soil profile was carried out in accordance with the national classification (DSTU 7535:2014) and Guidelines for Soil Description (FAO, 2006). Soil bulk density was determined according to ISO 11272:2017, for which samples were collected, using the cutting ring method and metal sampler rings. Samples were taken in 4-fold repetition according to the genetic horizons of the soil. In the field, the presence of calcium carbonates was determined by testing with 10% HCl. Drops of acid were applied with a pipette over the entire soil profile. If gas bubbles were seen, then there are carbonates in this horizon (Polupan *et al.*, 1981).

Analytical methods

Soil samples were analyzed for the salt composition of the water extract, soil pH, total content of calcium carbonates ($CaCO_3$), organic carbon (C org), and exchangeable cations adsorption. Soil salt composition was determined by the titrimetric method in a water extract with a soil-to-water ratio of 1:5 (national standards DSTU 7909:2015, DSTU 7908:2015, DSTU 7943:2015, DSTU 7945:2015). The content of water-soluble sodium and potassium was determined using a flame photometer (CL-378, Hungary) (DSTU 7944:2015). Soil pH was determined in a water extract with a ratio of 1:5 by the potentiometric method, using an I-160 MI ionometer with a combined pH electrode ECK-10603 (DSTU 8346:2015). The content of calcium carbonates was determined by the Sokolovich method, with their displacement by sodium fluoride during boiling of the solution and subsequent titration with 0.1N HCl in the presence of phenolphthalein as an indicator (Baliuk, 2005). The content of exchangeable cations in the soil was determined by the Tyurin method according to the national standard (DSTU 7604:2014). Exchangeable cations of calcium and magnesium were extracted with 0.1N NaCl followed by titration with a 0.01N Trilon-B solution. Exchangeable cations of sodium and potassium were extracted from the soil with ammonium acetic acid at pH 4.8, and then their concentration was measured using a flame photometer. Organic carbon was determined by the oxidimetric method with carbon oxidation of humic substances to CO_2 with a solution of potassium dichromate in sulfuric acid (DSTU ISO 10694:2001). Then, the excess of potassium dichromate after its oxidation was measured by titration.

Statistical analysis

Analysis of variance (ANOVA) was used for statistical evaluation of the data obtained. The least significant difference (LSD) as a post-hoc test was used to characterize the significance of the difference between the experimental treatments, used to detect the impact of ameliorative methods on soil properties and crop yield, at $P<0.05$. The significant difference between treatments is indicated by the use of different letters (a-f) in the graphs. The reliability of the difference between indicators was assessed by Fisher's exact test. Correlation analysis was used to establish the relationship between different soil indicators.

Results

Irrigation water quality

During the 7-year experiment water mineralization in the pond ranged from 2.6 to 3.1 g/l, and the pH varied from 7.9 to 8.1 (Table 3). The main salts present were sulfates of magnesium and sodium. The quality of the water was assessed as of limited suitability for irrigation (due to the threat of salinization and alkalization of the soil) and unsuitable for irrigation (due to the threat of sodification of the soil) according to the national standard DSTU 2730:2015.

The influence of deep ploughing with a manure dosage of 100 ton/ha on the profile of ordinary chernozem and its morphological structure

The ameliorative deep ploughing was performed to a depth of 10-15 cm below the effervescence boundary (determined by testing with 10% HCl), which allow the calcium compounds, naturally present within a 35-60 cm layer of soil, to come to the soil surface and to act as an ameliorant of the secondary sodified soil. By deep ploughing the upper humus layer moved to the depth of the transitional horizon. In the first years after ploughing the content of organic carbon in the ploughed layer decreased by approximately

Table 3. Chemical composition of irrigation water from a local pond used for irrigation in the experiment.

Parameter	Mineralization, g/L	pH	Ion content, meq/L						
			HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+
Min	2.6	7.9	6.9	9.0	25.2	7.9	9.5	21.0	0.6
Max	3.1	8.1	7.6	12.0	27.9	15.5	11.2	26.5	0.8
Mean	2.9	8.0	7.1	10.0	26.1	10.9	10.5	22.0	0.7
Standard deviation	±0.23	±0.09	±0.29	±1.11	±0.86	±2.5	±0.57	±2.10	±0.10
Coefficient of variation, %	15	4	14	9	19	22	14	23	7

Number of analyzed samples of water: 14 (n=14).

25%. Organic carbon accumulated in deeper layers. Therefore, in this experimental treatment, we applied 100 t/ha of manure to compensate for this effect. Due to the deep ploughing and consequent movement of the soil horizons a change in the natural structure of the ordinary chernozem profile and its morphological features occurred. As a result of this transformation of the natural soil structure, there was a change in the direction of soil processes and soil properties (Figure 1). The morphological characteristics of the genetic horizons of the ploughed soil are presented in Table 4. As a result of deep ploughing (and manuring) of the soil the thickness of the humus horizon and, concomitantly, the root layer increased on average from 50 cm to 75 cm.

Soil bulk density

The difference in soil bulk density between the treatments with calcium ameliorants and the control was insignificant ($P<0.05$). The results of this indicator in soils of treatments 2 and 3 are given in Table 5. The soil bulk density in the treatments, where deep ploughing with manuring was applied (treatment 3) or manuring without deep ploughing (treatment 2), differed significantly between these two treatments ($P<0.05$). The density varied by 0.98-1.16 g/cm^3 in the treatment of the combined application of deep ploughing and manuring and 1.20-1.31 g/cm^3 for the treatment of single manure application (Table 5).

The content of calcium carbonates in the soil

In the 0-25 cm layer of the control treatment, the content of calcium carbonates in the first year of the experiment was 1.5%; this fluctuated in the following years between 1.3-1.7%. Therefore, the soil was characterized as having a low buffering capacity against alkalization. There was a significant difference in the content of calcium carbonates in the soil of the control treatment compared to the experimental treatments with amelioration measures (Table 2). After deep ploughing and manuring, calcium carbonates were redistributed, with a significant increase (up to 8.7%) in the

Figure 1. The profile structure of the ordinary chernozem after deep ploughing (and manuring). The description of the soil profile was carried out in accordance with the national classification (DSTU 7535:2014) and Guidelines for soil description (FAO, 2006).

Table 4. Morphological characteristics of the genetic horizons of ordinary chernozem in the treatment with deep ploughing. The description of the soil profile was carried out in accordance with the national classification (DSTU 7535:2014) and Guidelines for soil description (FAO, 2006).

Genetic horizon, cm	Morphology
Upper arable layer of soil after deep ploughing (and manuring), 0-25	Dark pale, heterogeneous in color, loose, fresh, lumpy-powdery in structure, calcareous, violently effervescent from 10% HCl, penetrated by plant roots; there are passages of shrews; gradual transition in color and density
Transitional ploughing, 25-50	Heterogeneous in color, darker than the upper horizon, dark gray spots alternate with dark brown, lumpy-nutty in structure, moist, friable, permeated with plant roots, slightly effervescent from 10% HCl; there are passages of shrews; gradual color transition
Lower transitional horizon, 50-75	Darker than the upper one, loose, moist, lumpy-nutty in structure, densely permeated with plant roots, weakly effervescent from 10% HCl; the transition is sharp in color and density
Loess-like loam, 75-115 and deeper	Pale yellow, moist, dense (compacted), humus streaks, pedogenic carbonates represented by soft masses, violently effervescent from 10% HCl

Table 5. Soil bulk density of the ordinary chernozem in treatments with or without deep ploughing.

Deep ploughing (for 75 cm) + manure, 100 t/ha (treatment 3)		Manure, 100 t/ha (treatment 2)	
Genetic horizons, cm	Soil bulk density, g/cm^3	Genetic horizons, cm	Soil bulk density, g/cm^3
Upper arable layer of soil after deep ploughing, 0-25	0.98±0.02	Upper arable layer 0-20	1.20±0.02
Transitional ploughing, 25-50	1.12±0.03	Transitional 20-45	1.24±0.02
Lower transitional horizon, 50-75	1.16±0.03	Lower transitional, 45-80	1.31±0.03
LSD_{05}		0.08	

upper arable soil layer in the first year of the experiment compared to the control treatment, see Figure 2.

In the experimental treatment with deep ploughing and manuring during the seven-year period, a trend towards an increase in the content of carbonates and their availability due to their dissolution by irrigation water was observed. The $CaCO_3$ concentration varied from 8.7% to 15.3%. It ensured a high buffering capacity of the soil to irrigation alkalinity (Figure 3). In all treatments with the introduction of various calcium ameliorants into the soil, there was a demonstrable statistically significant increase in the content of calcium carbonates (+1.9-2.8%) compared to the control (Figure 3). The buffering capacity of the soil against sodification increased to an average degree. Meanwhile, no significant difference in $CaCO_3$ content was detected between all treatments with (industrial) Ca-containing ameliorants.

pH and salt composition of soil water extract 1:5

In the control treatment with irrigation by brackish pond water for a period of seven years, a slight increase in the pH (H_2O) up to 8.0 was registered compared to the initial 7.7 (Table 2). The concentration of toxic salts also increased, and the soil acquired signs of salinity, although to a low degree. The composition of water-soluble salts of the control treatment was dominated by HCO_3^- and Na^+. The Ca^{2+}/Na^+ ratio changed in the direction of Na^+ increase due to irrigation (from 0.23 to 0.19). It indicates the process of soil salinization. The type of soil salinity was characterized as sulfate-soda calcium-sodium. In the experimental treatments with calcium ameliorants, over the 7-year period, the composition of salts improved compared to the control. There was a statistically significant increase in the content of water-soluble calcium ion and a decrease in water-soluble sodium ion. The ratio of water-soluble Ca^{2+}/Na^+ in the upper 0-50 cm soil layer changed from 0.23 to 0.53-1.83, even already after one year of ameliorant application. The calcium ameliorant of the soda, phenol, and steel wire plant reduced the alkalinity of the soil (pH and HCO_3^-), reducing the irrigation-induced alkalinization by alkaline water with 6.3% after 7 years. Due to the application of calcium ameliorants, the sulfate-soda calcium-sodium salts were replaced by calcium and sodium-calcium sulfates (Table 2). The strongest effect from the use of ameliorants was recorded in the first year after application and the year after that, although this positive effect was observed until the end of the experiment. The content of water-soluble calcium ions was statistically higher and sodium ion content was lower in all experimental treatments with the application of calcium ameliorants compared to the control (Table 2). The soil of the treatments with the application of ameliorants was characterized after 7 years of experimenting as non-saline.

A significant increase in the concentration of water-soluble calcium ion was observed in the treatment with deep ploughing. During the period of the experiment, the Ca^{2+}/Na^+ ratio gradually increased from 0.44 to 0.61 (Table 2). It indicates the improvement of the physicochemical properties of ordinary chernozem using this amelioration method.

The ratio of exchangeable cations in the soil adsorption complex

The original soil of the experimental field was characterized as slightly alkaline. The content of sodium and potassium cations in the soil adsorption complex was 5.3% of the total content of exchangeable cations. In our study, as a result of irrigation by brackish alkaline water, a further transformation of the composition of the soil adsorption complex in the arable layer of the soil of the control treatment was registered. The content of exchangeable sodium and potassium cations significantly increased (Figure 4).

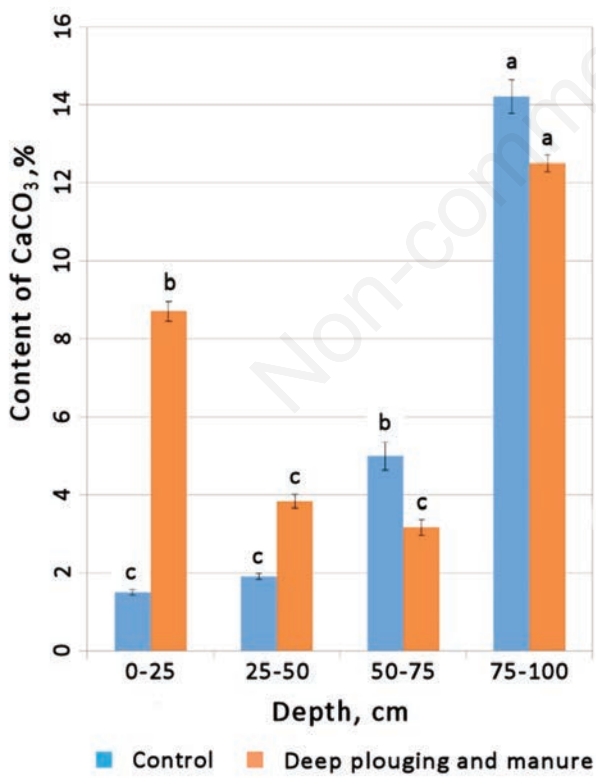

Figure 2. Distribution of calcium carbonates in the profile of ordinary chernozem (the first year of the experiment). All values are estimated by means, using ANOVA. The vertical bars are the standard error. Significant difference is indicated by the use of different letters (a-c) in the graphs ($P<0.05$, LSD_{05}=0.5%).

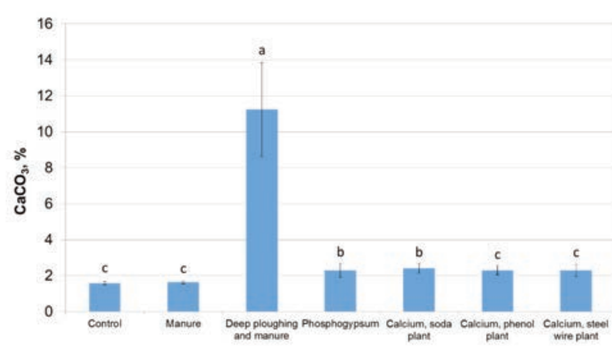

Figure 3. The content of calcium carbonates in the soil of the experimental treatments in the 0-50 cm layer (averaged data for seven years). The results were expressed as the mean content of calcium carbonates (CaCO3)±standard deviation (n=126), using ANOVA. The vertical bars are the standard error. Significant difference between treatments is indicated by the use of different letters (a-c) in the graphs ($P<0.05$, LSD_{05}=0.7%).

As a result, the degree of soil alkalinity of the control treatment increased from slight to moderate levels. The percentage of Na^{+}+K^{+} in the sum of exchangeable cations was 7%. In the experimental treatments with the use of calcium ameliorants, it remained at a low level (3-6% of Na^{+} and K^{+} in the sum of exchangeable cations).

In the soil of all treatments with Ca-containing amendments, exchangeable sodium was significantly replaced by calcium, and the saturation of the soil adsorption complex with calcium increased (Figure 5). This contributed to counteract the irrigation-induced alkalinization. In the first year of the experiment, the application of calcium ameliorants into the soil contributed to a significant increase in the content of exchangeable calcium and a decrease in the total content of sodium (-7%) and potassium (-4.2 to -4.6%) cations (Figure 5). The strongest effect was established in the treatments with calcium ameliorants of the soda, phenol, and steel wire plants. A significant positive effect and after-effect of ameliorants, compared to the control, was observed during the first 3 years after application. When this after-effect faded in the following years, the effectiveness of ameliorants decreased. A distinct anti-alkalinity effect from the application of one-time deep ploughing and manuring against secondary alkalization of ordinary chernozem was registered throughout all seven years of the experiment. The content of exchangeable sodium and potassium cations was significantly lower compared to the control. In the experimental treatments with ploughing the content of these cations decreased to 3.9-4.8% of the sum of exchangeable cations (Figure 5). In the correlation analysis between the concentration of total calcium carbonates in the soil and the content of exchangeable calcium in the soil adsorption complex for the treatments with amelioration measures, a direct positive relationship was established (r=0.88, R^2=0.77, Figure 6). The content of exchangeable calcium increased with an increase in the total content of calcium carbonates in the soil.

Crop yield

Significant increases in crop yield were observed with various treatments, including deep ploughing with manure, manure alone, and the use of calcium ameliorants (Figure 7). The experimental treatments involving deep ploughing and manuring demonstrated the most stable and substantial yield increases, ranging from 21% to 38% (Figure 7). The strong effect of deep ploughing with manuring was associated with an increase in the depth of the root layer (from 50 to 75 cm), an improvement of the nutrient regime, an increase in the anti-alkalinity capacity of the soil, and more optimal water-physical properties of the soil (see Tables 4 and 5 and Figure 1).

The use of manure alone resulted in significant yield increases only for fodder beet (*Beta vulgaris*) and corn (*Zea mays*). The most effective (industrial) calcium ameliorants, increasing yield, were those from the soda and steel wire pant (14-26% yield increase, Figure 7). However, there was no significant increase in the yield of lucerne (*Medicago sativa*) in both above-mentioned treatments (crop cultivated for the first-cut and the second-cut yields). This is mainly related to the biological features of lucerne (*Medicago sativa*) as it is tolerant of soil salinity and alkalinity. Furthermore, the application of phosphogypsum, which improved the physicochemical properties of salinized soil, significantly increased the yield of fodder beet (*Beta vulgaris*), soybean (*Glycine max*), winter wheat (*Triticum aestivum*), and corn (*Zea mays*).

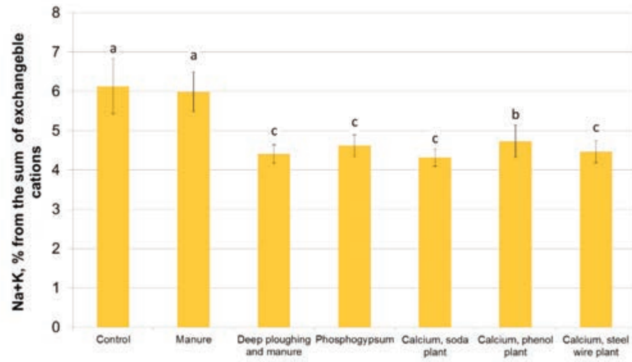

Figure 4. The content of exchangeable sodium and potassium cations in the soil of the experimental treatments (averaged data for seven years). The results were expressed as the mean ratio of the content of exchangeable sodium and potassium cations to their total content in the soil adsorption complex±standard deviation (n=126), using ANOVA. The vertical bars are the standard error. Significant difference between treatments is indicated by the use of different letters (a-c) in the graphs ($P<0.05$, LSD_{05}=0.32%).

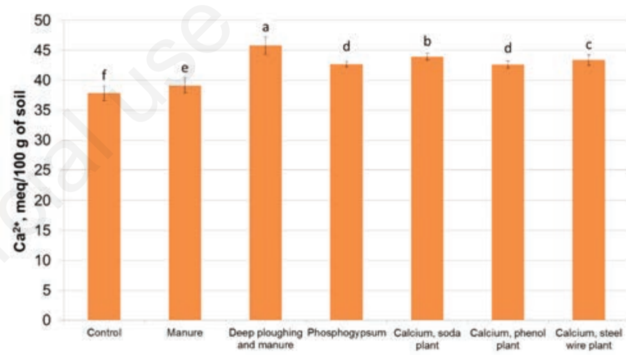

Figure 5. The content of exchangeable calcium cations in the soil of the different treatments in the experiment (averaged data for seven years). The results were expressed as the mean content of exchangeable calcium in the soil±standard deviation (n=126), using ANOVA. The vertical bars are the standard error. Significant difference between treatments is indicated by the use of different letters (a-f) in the graphs ($P<0.05$, LSD_{05}=0,99 meq/100 g).

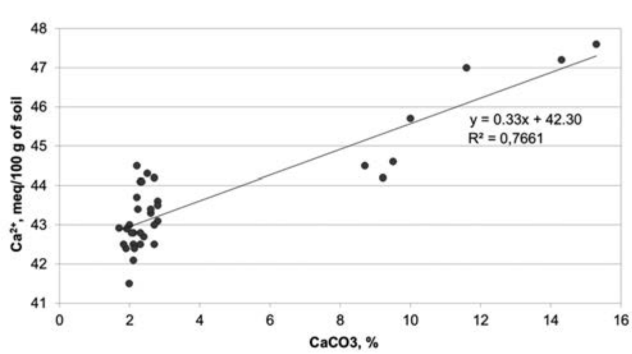

Figure 6. Linear regression between the concentration of total calcium carbonates in the soil and the content of exchangeable calcium in the soil adsorption complex for the treatments with the amelioration measures described in Table 2 over a period of 7 years.

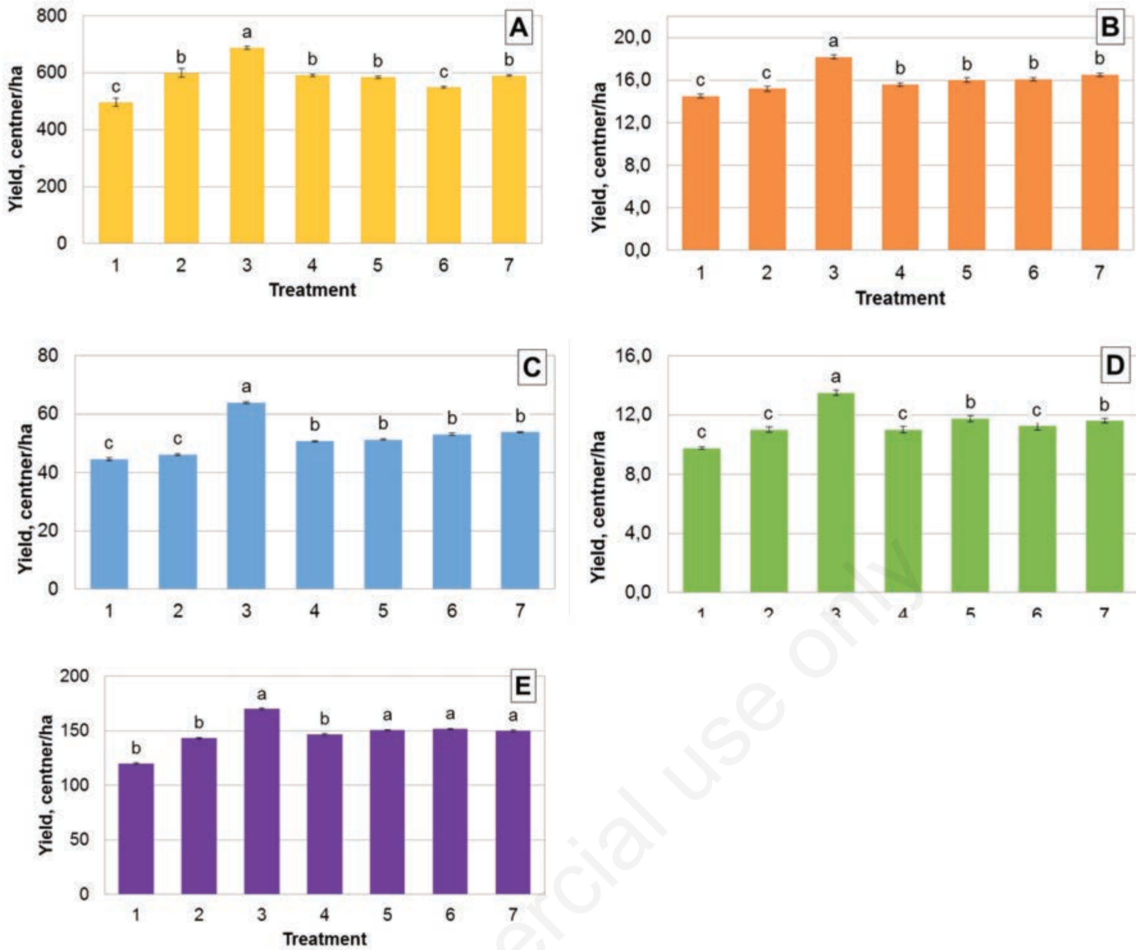

Figure 7. Effect of Ca-containing amendments, manure, and deep ploughing on the yield of agricultural crops: fodder beet (*Beta vulgaris*), root (**A**); soybean (*Glycine max*), grain (**B**); winter wheat (*Triticum aestivum*), grain (**C**); buckwheat (*Fagopyrum esculentum*), grain (**D**); corn (*Zea mays*), grain (**E**). All values are estimated means, using ANOVA. The vertical bars are the standard error. Numbers 1-7 are the treatments of experiment. Significant difference between treatments is indicated by the use of different letters (a-c) in the graphs ($P<0.05$, LSD_{05} fodder beet (roots) - 53.4 centner/ha, soybean (grain) - 1.07 centner/ha, winter wheat (grain) - 4.6 centner/ha, buckwheat (grain) - 1.64 centner/ha, corn (grain) – 27.1 centner/ha).

Discussion

Our study shows that long-term irrigation with poor, brackish water leads to secondary salinization, sodification, and alkalinization, which affects the properties and quality of the ordinary chernozem. Degradation due to irrigation with poor quality water has also been reported worldwide in numerous studies involving different soils and various climatic conditions (*e.g.*, Chhabra, 2021; Devkota *et al.*, 2022; Hopmans *et al.*, 2021; Shahid *et al.*, 2018; Vargas *et al.*, 2018). Monitoring and diagnosing the ecological and agro-ameliorative state of salt-affected soils is the basis for making management decisions and developing a system of synergistic measures for their amelioration. To combat secondary salinization and sodification of soil, the replacement of exchangeable sodium with calcium is most frequently recommended, followed by the advice to apply organic substances to improve soil structure (Bello *et al.*, 2021; Shahid *et al.*, 2018). The positive impact of sodic soil amelioration measures, using calcium ameliorants (apart from irrigation and cultivation measures), on the physico-chemical and chemical properties of the soil, and the growth and yield of the crops as was established in our study, has also been reported by others (Alcívar *et al.*, 2018; Stavi *et al.*, 2021; Singh, 2022).

We found that one-time deep ploughing with a dosage of manure of 100 ton/ha led to an increase in the thickness of the humus horizon and the root zone from 50 to 75 cm. This had a positive effect on the growth and development of agricultural crops, with an increase in their productivity of 21-38%. The effect on crop yield of calcium-containing ameliorants was lower, namely 10-30%. Baliuk *et al.* (2015a) demonstrated for deep ploughing a quite similar yield increase of 20-25% under non-irrigated conditions and up to 40% under irrigation. In their study, they also demonstrated that soils that underwent deep ploughing 50 years ago, still supported higher productivity of agricultural crops than similar soils not subjected to deep ploughing or undergoing chemical amelioration. Deep ploughing over longer periods led in other cases to significantly improved hydro-physical, chemical, physicochemical, and biological soil properties (Vargas *et al.*, 2018). Alcántara *et al.* (2017) found that 36-48 years after deep ploughing (to a depth of 55-90 cm) arable land, soil organic carbon stocks increased by 67%, compared to a reference subsoil. Furthermore, it resulted in substantially lower greenhouse gas emissions compared to conventional and zero-tillage management. In our case deep ploughing with a dosage of manure of 100 ton/ha loosened the soil structure, compared to its state in the control treatment: the compaction density of the soil in the 0-25 cm soil layer decreased by 0.22 g/cm^3, in the 25-45 (50) cm soil layer - by 0.12 g/cm^3. This contributed to the improvement of water-physical properties of ordinary chernozem, as no crust was formed on the surface of the soil after watering and rains. The water-soluble salts were more effectively washed into the lower layers by the downward flow of water and their concentration decreased. As a result, in the winter-spring period, more moisture accumulated in the soil, which contributed to improved emergence and development of seedlings of cultivated crops compared to the control and treatments with chemical ameliorants (present authors, data not shown). Chen *et al.* (2020) observed a decrease in the soil density by 0.1 g/cm^3 to a depth of 40 cm, an increase in organic carbon in the 0-40 cm layer, and a deepening of the root-containing layer after deep ploughing with tillage of plant residues of corn on non-saline soils. The yield of winter wheat increased from 5.9 to 20.2%. As in our study, Meng *et al*. (2016) investigated the effect of applying cattle manure in combination with deep ploughing on the physicochemical properties of the soil and (in their case) the yield of corn on saline soils. They observed over two years a decrease in the soil density of 0.1 g/cm^3, a significant increase in organic matter in the soil, a decrease in exchangeable sodium, and an increase in yield up to 43%. Xong *et al*. (2011) found that deep ploughing up to the subsoil (C horizon), as well as the application of gypsum improved the properties of sodic soil. The pH values in all fields decreased from about 10 to about 9, and the EC values decreased from about 8 $dS{\cdot}m^{-1}$ to about 2 $dS{\cdot}m^{-1}$.

In our field experiment using deep ploughing and one manure dosage, a horizon of calcium carbonate accumulation was brought to the surface that clearly acted as an ameliorant of secondary sodified soil. Calcium carbonates dissolved increasingly from 1.5% to 8.7% in the 0-25 cm layer even during the first year to up to 15% in subsequent years. A significant increase (1.9-2.8%) in calcium carbonates, compared to the control, in the 0-50 cm soil layer occurred in the treatments with chemical calcium ameliorants. Acids can be used to mobilize Ca from ameliorants and soil (Shahid *et al.*, 2018). Our study demonstrated that the effect on $CaCO_3$ content in the soil after one-time deep ploughing with a manure application was more beneficial in terms of soil improvement than the sole introduction of (industrial) Ca ameliorants into the soil. There was also a positive effect on the saline composition of the irrigated soil and on the composition of the soil adsorption complex. As a result, the Ca^{2+}/Na^+ ratio gradually increased compared to the control treatment. Matosic *et al*. (2018) also demonstrated that appropriate tillage/ploughing, and application of organic matter from various sources, are key factors in mitigating the negative effect of soil salinity and sodicity. Tillage improves aeration and alleviates compaction, while organic matter promotes binding soil particles into aggregates. Ding *et al.* (2021) found that although deep tillage reduced soil organic carbon, the application of organic matter (vermicompost) compensated and significantly increased soil organic carbon. They also found that the integration of deep tillage and vermicompost decreased soil salinity and sodicity by 37% and 34%, respectively, compared with zero tillage and unamended soils. In our case, the positive effect of one-time deep ploughing (together with manuring) continued throughout the whole study period. This was also demonstrated in other long-term experiments (Baliuk *et al.*, 2015a over a period of 50 years; Xong *et al.*, 2011; Chen *et al.*, 2020). The latter reported a positive effect of deep ploughing in combination with maize straw return within two years.

Summarizing it can be concluded that the saturation of the soil adsorption complex with calcium using deep ploughing with cattle manure or Ca-ameliorants improved the physical, and physicochemical properties of the soil, its quality and fertility, and also increased the productivity of crops. This was also found for other crops, *e.g.*, for corn (Meng *et al.*, 2016; Chen *et al.*, 2020) and salt-tolerant grass and millet (Xong *et al.*, 2011). It must be said that the effect and after-effect of Ca-ameliorants were short-term and lasted as long as they were dissolving (up to 4 years). Moreover, although the composition of the industrial calcium ameliorants we used was within the boundaries of national regulation, concerning their content of (possible) toxic products, this risk should still be considered when applying these substances, *e.g.*, Mesić *et al.* (2016).

Conclusions

Salinity and sodicity of the soil under irrigation with brackish water had a negative effect on the soil properties and crop productivity in a 7-year field study of secondary sodified chernozem in Ukraine. One-time deep ploughing with one cattle manure dosage, manure alone, and (industrial) calcium ameliorants were shown to improve the physicochemical properties, fertility, and quality of secondary alkalinity soil. The measures provided a reduction in the actual alkalinity of the soil and prevented the alkalinity effect of water on the irrigated soil. These practices are aimed at integrated management of salt-affected soils to ensure sustainable development of agriculture.

Removal of calcium carbonate accumulation in deep soil layers and placing it in the surface layers by deep ploughing provided long-term improvement of the irrigated soil and increased its buffering capacity. In this treatment, an increase in the humus horizon, improvement of water-physical properties, salt composition, an increase in the Ca^{2+}/Na^{+}, and a decrease of the saturation of the soil adsorption complex with exchangeable sodium and potassium were observed. The introduction of (industrial) calcium ameliorants into the soil also helped to reduce the degree of sodicity of the soil, but their effect and after-effect were shorter (up to 4 years). Optimizing the properties of salt-affected soil had a positive effect on crop growth and ensured an increase in yield of 30 to 38% depending on the crop and treatment.

Deep ploughing with additional manuring can be used for the long-term improvement of the quality of salt-affected soil. The effect of Ca-ameliorants is short-term and requires periodically repeated application. The recommended methods and results of this study are of practical importance to optimize the properties of salt-affected soils and manage their use in agriculture.

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