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*Scopus және Web of Science дерекқорларында индекстелуі жарияланымдардың халықаралық деңгейде жоғары сұранысқа ие болуын қамтамасыз етеді, олардың дәйексөз алу көрсеткіштерінің артуына ықпал етеді және редакциялық алқаның геология мен техникалық ғылымдар саласындағы өзекті, бірегей және ғылыми тұрғыдан маңызды зерттеулерді жариялауға ұмтылысын айқындайды.*

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*Журнал также включён в международную реферативную и наукометрическую базу данных Emerging Sources Citation Index (ESCI) платформы Web of Science (Clarivate Analytics, 2018).*

*Индексирование в ESCI подтверждает соответствие журнала международным стандартам научного рецензирования и редакционной этики, а также рассматривается компанией Clarivate Analytics в рамках дальнейшего включения издания в Science Citation Index Expanded (SCIE), Social Sciences Citation Index (SSCI) и Arts & Humanities Citation Index (AHCI).*

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## ANALYSIS OF THE INFLUENCE OF UREA NITRATE SALTS ON THE SOILS OF THE BUKHARA REGION

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**Abstract.** *Relevance.* The prolonged and excessive application of phosphate fertilizers in the agricultural soils of the Bukhara region has led to the accumulation of poorly soluble phosphate and metal-ion compounds, reducing soil fertility and nutrient bioavailability — a problem that requires targeted chemical intervention and mechanistic explanation. *Objective.* The aim of this study is to synthesize urea nitrate molecular complexes and evaluate their influence on the solubility of soil phosphate and metal-ion compounds, as well as on the activity of humic substances in the soils of the Zhondor district, Bukhara region. *Methods.* Molecular complexes of the general composition $xCO(NH_2)_2 \cdot yHNO_3$ (x=1, y=1–3), designated mononitrate (MNM), dinitrate (DNM), and trinitrate (TNM), were synthesized and applied to soil samples; the effects on element solubility were analyzed by ICP-AES, while structural changes in humic substances were characterized by EPR spectroscopy at 9.44 GHz using DPPH as an external standard. *Results and conclusions.* ICP-AES analysis showed that at pH < 4.0, DNM and TNM caused retrogradation of phosphorus compounds — mobile $P_2O_5$ decreased by up to 65.8% relative to the control — while MNM most effectively increased the solubility of $Fe_2O_3$ (64-fold) and MgO (73-fold). EPR spectroscopy identified two types of humic acid radicals: active (g=2.0033, ΔH=0.51 mT) and passive (g=2.0021, ΔH=0.48 mT), with TNM treatment raising total free radical concentration to $2.735\times10^{15}$ spin/mm³ and establishing a predominance of active humic forms ($J_1$:$J_2$ = 2:1). To prevent phosphate retrogradation while simultaneously enriching soil nitrogen, urea nitrate compositions with y < 1 (pH > 4.0) are recommended; MNM solutions represent the optimal variant for mobilizing heavy metal-ion compounds in agricultural soils of the Bukhara region.

**Keywords:** urea nitrate, EPR spectroscopy, ICP-AES, soil properties, nutrient availability, retrogradation, humic substances, paramagnetic centers, Bukhara region

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## МОЧЕВИНА НИТРАТ ТҰЗДАРЫНЫҢ БҰХАРА АЙМАҒЫНЫҢ ТОПЫРАҚТАРЫНА ӘСЕРІН ЗЕРТТЕУ

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**Аннотация.** ***Өзектілігі***. Бұхара облысының ауылшаруашылық топырақтарына ұзақ жылдар бойы шамадан тыс мөлшерде фосфатты тыңайтқыштар енгізу нашар еритін фосфор және металл-ион қосылыстарының жинақталуына, топырақ құнарлылығы мен қоректік заттардың өсімдіктерге қолжетімділігінің төмендеуіне әкелді – бұл мәселе мақсатты химиялық ықпал мен механистік түсіндіруді талап етеді. ***Мақсаты***. Осы жұмыстың мақсаты – мочевина нитратының молекулалық кешендерін синтездеу және олардың Бұхара облысы Жондор ауданы топырақтарындағы фосфатты және металл-ион қосылыстарының ерігіштігіне, сондай-ақ гумус заттарының белсенділігіне әсерін бағалау. Әдістері. Жалпы құрамы $xCO(NH_2)_2 \cdot yHNO_3$ (x=1, y=1–3) болатын МНМ, ДНМ және ТНМ молекулалық кешендері синтезделіп топырақ үлгілеріне қолданылды; элементтердің ерігіштігіне әсер ICP-AES арқылы, ал гумус заттарының құрылымдық өзгерістері ДФПГ сыртқы стандарт ретінде пайдаланыла отырып 9.44 ГГц жиіліктегі ЭПР спектроскопиясымен зерттелді. ***Нәтижелер мен қорытындылар***. ICP-AES деректері бойынша pH < 4.0 кезінде ДНМ мен ТНМ фосфор қосылыстарының ретроградациясын тудырды – жылжымалы $P_2O_5$ бақылаумен салыстырғанда 65.8%-ға дейін төмендеді, ал МНМ $Fe_2O_3$ (64 есе) мен MgO (73 есе) ерігіштігін ең тиімді арттырды. ЭПР спектроскопиясы гумин қышқылдарының белсенді (g=2.0033, ΔH=0.51 мТ) және пассивті (g=2.0021, ΔH=0.48 мТ) екі түрлі радикалын анықтады. ТНМ өңдеуі еркін радикалдардың жалпы концентрациясын $2.735 \times 10^{15}$ спин/мм$^3$ дейін арттырып, белсенді гумус формаларының үстемдігін ($J_1$:$J_2$ = 2:1) қалыптастырды. Фосфаттардың ретроградациясын болдырмай топырақты азотпен байыту үшін y < 1 (pH > 4.0) болатын мочевина-нитрат кешендерін қолдану ұсынылады; МНМ ерітінділері Бұхара облысы ауылшаруашылық топырақтарындағы ауыр металл-ион қосылыстарын жылжымалы формаға ауыстыру үшін оңтайлы болып табылады.

**Түйін сөздер:** мочевина нитраты, ЭПР спектроскопиясы, ICP-AES, топырақ қасиеттері, қоректік заттардың қолжетімділігі, ретроградация, гумус заттары, парамагниттік орталықтар, Бұхара аймағы

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# АНАЛИЗ ВЛИЯНИЯ МОЧЕВИНО-НИТРАТНЫХ СОЛЕЙ НА ПОЧВЫ БУХАРСКОГО РЕГИОНА

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**Аннотация.** *Актуальность*. Многолетнее избыточное внесение фосфатных удобрений в сельскохозяйственные почвы Бухарского региона привело к накоплению труднорастворимых соединений фосфора и ионов металлов, снижающих плодородие почвы и доступность питательных веществ. Данная проблема требует целенаправленного химического воздействия и механистического объяснения процессов трансформации минеральных и гумусовых компонентов почвы. *Цель*. Синтезировать молекулярные комплексы нитрата мочевины и оценить их влияние на растворимость фосфатных соединений и соединений ионов металлов, а также на активность гумусовых веществ почв Жондорского района Бухарской области. *Методы*. Молекулярные комплексы общего состава $xCO(NH_2)_2{\cdot}yHNO_3$ ($x = 1$, $y = 1–3$), включая мононитрат мочевины (МНМ), динитрат мочевины (ДНМ) и тринитрат мочевины (ТНМ), были синтезированы и нанесены на образцы почвы. Влияние комплексов на растворимость элементов изучали методом ICP-AES, а структурные изменения гумусовых веществ исследовали методом ЭПР-спектроскопии на частоте 9,44 ГГц с использованием ДФПГ в качестве внешнего стандарта. *Результаты и выводы*. По данным ICP-AES, при pH < 4,0 ДНМ и ТНМ вызывали ретроградацию соединений фосфора: подвижность $P_2O_5$ снижалась до 65,8% по сравнению с контролем, тогда как МНМ наиболее эффективно увеличивал растворимость $Fe_2O_3$ - в 64 раза и

MgO - в 73 раза. ЭПР-спектроскопия выявила два типа радикалов гуминовых кислот: активный ($g = 2{,}0033$, $\Delta H = 0{,}51$ мТ) и пассивный ($g = 2{,}0021$, $\Delta H = 0{,}48$ мТ). При этом обработка ТНМ повышала суммарную концентрацию свободных радикалов до $2{,}735 \times 10^{15}$ спин/мм³ с преобладанием активных гумусовых форм ($J_{12} = 2:1$). Для предотвращения ретроградации фосфатов при одновременном обогащении почвы азотом рекомендуется применение нитрат-мочевинных комплексов с $y < 1$ при $pH > 4{,}0$. Растворы МНМ являются оптимальным вариантом для мобилизации тяжелых соединений ионов металлов в сельскохозяйственных почвах Бухарского региона.

**Ключевые слова:** нитрат мочевины, ЭПР-спектроскопия, ICP-AES, свойства почвы, доступность питательных веществ, ретроградация, гумусовые вещества, парамагнитные центры, Бухарский регион

**Introduction.** To date, a number of scientists have studied the composition, structure and properties of nitrogen and phosphorus fertilizers and published scientific results on their analysis of the effects on soil agrochemical indicators, mineralogical state, growth of crop productivity (Gasser, et al, 1967; Irshad M, et al, 2002). Previous studies have demonstrated that urea nitrate and urea phosphate differ in their effects on nitrogen loss and crop growth compared to ammonium nitrate (Gasser et al., 1967; Irshad et al., 2002).

*Literary review.* A group of Chinese scientists studied the effect of nitrogen fertilizers on the absorbency of phosphorus in saline soils, concluding that it is possible to increase the amount of soluble phosphorus by reducing the amount of nitrogen fertilizers applied in saline soils (Liu X, et al, 2021). Periodic feeding of phosphorus fertilizers into the soil will be useful to reduce the risk of phosphorus loss due to the consumption of ineptisols and the reduction of phosphates in the soil. To analyze this feature, the study used the method of $^{31}P$ NMR spectroscopy, to determine the degree of soil saturation to phosphorus, and statistical analysis methods (Wang et al. 2022).

Additionally, the electron paramagnetic resonance (EPR) spectroscopy method has been employed by researchers in the compositional analysis of soil, and a number of scientific findings have been published (Siqueira et al, 2011; Jezierski et al, 2000). EPR spectroscopy has been used to identify soil mineral components including ferrihydrite, hematite, and kaolinite through characteristic $Fe^{3}$ resonance lines (Siqueira et al, 2011).

During the long-term non-rational use of various minerag fertilizers, in the soils of the land used in agriculture, the accumulation of non-absorbable forms of phosphorus fertilizers by plants leads to the fact that the efficiency of their use is very low (Kozak et al, 2021; Xiao et al, 2021).

At the same time, accumulations of heavy metal compounds occur in these soils due to various agrochemical, environmental factors, which are also confirmed by scientific data that lead to a decrease in soil fertility and productivity (Khatun et al, 2022).

In order to avoid the above negative situations or to eliminate the problem that has arisen, it is the problems that await the current scientific and practical solution of the synthesis of substances of special properties and the creation of effective means based on them using existing chemicals in the Republic of Uzbekistan.

*The object of this investigation* is the analysis of urea nitrate salts through spectroscopic methods, with the aim of assessing their impact on soil composition and properties.

In this work, urea was synthesized with nitric acid into mono- (MNM), di- (DNM), and trinitrate (TNM) molecular complexes. Their effects on soil composition were assessed using ICP-AES (metal ion solubility) and EPR spectroscopy (humic substance activity).

**Materials and methods.** Urea ($NH_2CONH_2$, GOST 6691-77, analytical grade) and chemically pure nitric acid (63%, $\rho = 1.385$ g·cm-³, GOST 4461-77, "NAVOI-YAZOT" JSC) were used as starting materials. The soil sample used in this study was collected from agricultural land in the Jondor district of the Bukhara region, Uzbekistan (40°13′N, 64°28′E). This site is representative of the irrigated gray-brown soils (sierozem) typical of the Bukhara region.

*Synthesis of Urea Nitrate and phosphate Salts.* Mononitrate Urea (MNM) Salt Synthesis. To synthesize mononitrate urea salt, 6 g (0.1 mol) of urea was measured and dissolved in 28 ml of 20% $HNO_3$ solution (**ρ** = 1.12125 g/ml) with a molar ratio of urea to nitric acid of 1:1 ($S_{(solid)}:L_{(liquid)}$ = 1:5). The resulting solution was heated to 40°C and stirred for 30 minutes using a magnetic stirrer, leading to the formation of a colorless solid. The reaction equation is as follows:

$$CO(NH_2)_2 + HNO_3 \rightarrow [(NH_2)_2CO \cdot H^+]NO_3^-.$$

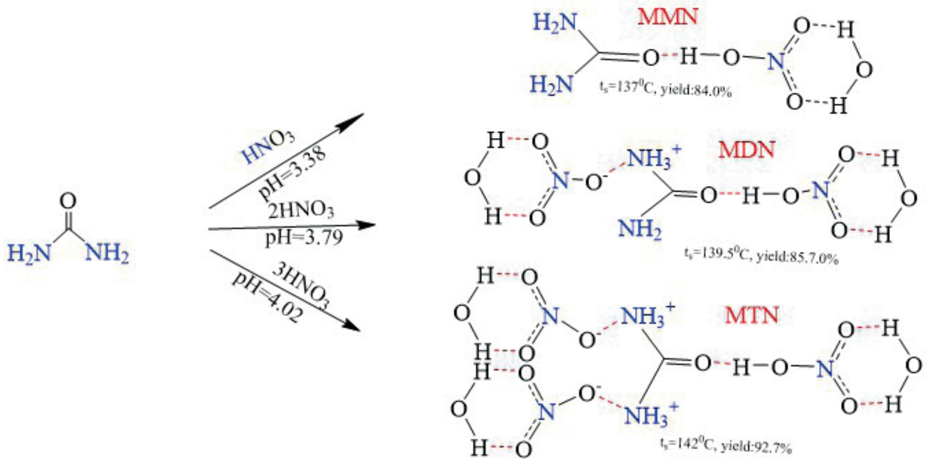
The solid formed was vacuum-filtered after 1 hour, yielding a white, hygroscopic crystalline compound. The mass of the product was 10.332 g, corresponding to a yield of 84%. The melting point ($\tau_{ex}$ ) of the compound was determined to be 137°C. The product is highly soluble in water, and its solution exhibited an electrolytic conductivity of $\chi$ = 160.1 mS/cm (25°C).

Synthesis of Dinitrate and Trinitrate Urea Salts

The synthesis of dinitrate and trinitrate urea salts was performed using the same method, but with adjusted molar ratios of urea to nitric acid ($M:HNO_3$) of 1:2 and 1:3, respectively. The obtained solid products were characterized by the following properties:

Dinitrate urea salt (DNM)**:** Melting point ($\tau_{ex}$□): 139.5°C, Conductivity ($\chi$): 106.2 mS/cm (aqueous solution at 25°C)

Trinitrate urea salt (TNM)**:** Melting point ($\tau_{ex}$□): 142°C, Conductivity ($\chi$): 101.3 mS/cm (aqueous solution at 25°C).




Scheme I. Reaction scheme for the synthesis of urea nitrates.

*Research methods.* The analyses of the substances were carried out using various spectrophotometers. The total and plant-available phosphorus content in the "Bukhara" soil was determined in accordance with the requirements and methodologies outlined in GOST 20851.2-75. The experimental work was conducted using a UV-1900i spectrophotometer (Shimadzu, Japan) and a V-5100 spectrophotometer (Metash Instrument Co., Ltd, China). Plant-available phosphorus was determined using 2% citric acid and 0.2 M Trilon-B solutions in accordance with GOST 20851.2-75.

The content of other elements in the samples was analyzed using a "Quantima-E1440" (ICP-AES) inductively coupled plasma optical emission spectrometer from "GBC Scientific Equipment" company, relative to a standard sample. "Assi Standart" USA standard solution samples were utilized for the analyses.

EPR spectra and the concentration of paramagnetic centers (PMC) were determined for soil samples treated with urea nitrate solutions. EPR spectra were recorded using an "SPINSCAN X", "ADANI RUS" spectrometer (Belarus) operating at a frequency of 9.44 GHz. A stable free radical – diphenylpicrylhydrazyl (DPPH) (g=2.0037±0.0002) – was used as an external standard.

**Results.** To determine the changes in the content of $P_2O_5$, $Ca^{2+}$ and $Mg^{2+}$ ions in soil samples under the influence of MNM, DNM, and TNM. For the experiments, a soil sample from the Jondor district of the Bukhara region was selected. The total content of $P_2O_5$ and its citric acid extractability were determined. The amount of mobile phosphorus in soil is reported with varying values by different authors. Considering the soil type, the mobile phosphorus content is given as 3.0-4.5 mg/100g. For fine-powdered soils, this value is reported as 10-15 mg/100g. In general, information is provided that the solubility of $P_2O_5$ in a 2% citric acid medium is higher than its solubility in a 0.2 M Trilon-B solution.

According to the obtained results, the investigated “Bukhara” soil sample was determined to belong to the high category.

It is known that urea and nitrates, along with molecular complexes based on them, are predominantly used as nitrogen fertilizers for agrochemical purposes. For this reason, the effect of NM salts on soil composition and agrochemical parameters was studied. The primary focus was on investigating changes in the solubility and assimilation of nutrient compounds within the soil.

To achieve this, a “Bukhara” soil sample, currently used in agriculture, was taken and treated with a Q:S=1:3 ratio in an aqueous medium under ambient conditions with mechanical stirring. The resulting soil suspension was filtered to separate the liquid phase (solution) and solid phases. An identical solution and solid residue were obtained from an aqueous suspension of untreated soil (not processed with nitrourea salt solutions) and used as a control sample. The total amount of $P_2O_5$ in the “Bukhara” soil sample, along with its solubility in 2% citric acid and 0.2 M Trilon-B solutions, was determined. Phosphorus assimilability was measured photometrically at λ = 400–440 nm (UV/Vis-1900i spectrometer) following standard extraction procedures. The results are presented in Table 1.

Mobile $P_2O_5$ in gray-brown soils typically ranges from 25–250 mg/kg (Fang N, et al, 2022; Do Nascimento C. et al, 2018). The “Bukhara” soil was classified as low-mobile, and NM salts were applied to increase phosphorus availability under acidic conditions.

Table 1. Analysis results of the effect of urea nitrate salts on the solubility of phosphorus compounds in the “Bukhara” soil sample.

| T/r | Sample name | Soil suspension pH | $P_2O_5$ * mg/l (%) | $P_2O_5$ ** mg/l (%) | General $P_2O_5$ mg/l (%) | $Ca^{2+}$ mg/l | $Mg^{2+}$ mg/l |
|---|---|---|---|---|---|---|---|
| 1 | Primary Soil | 6.28 ± 0.42 | 41.11 (20.9) | 51.83 (26.36) | 169.7 (8.54) | 260 | 228 |
| 2 | Soil+MNM | 4.6 ± 0.53 | 32.17 (16.36) | 50.04 (25.45) | 125.1 (6.36) | 120 | 72 |
| 3 | Soil+DNM | 4.25 ± 0.38 | 37.53 (19.08) | 47.14 (25.45) | 89.36 (4.54) | 140 | 96 |
| 4 | Soil+TNM | 3.76 ± 0.72 | 33.62 (17.11) | 42.89 (21.81) | 58.08 (2.95) | 140 | 120 |

*Citric acid absorbability; **Trilon-B absorbability.

However, the data presented in Table 1, obtained from the experiments, show an anomalous difference in the solubility of phosphorus compounds in the soil under the influence of NM salts compared to what was expected. It was found that the mobility of accumulated phosphorus compounds (fertilizers) in the soil sharply decreased under the influence of these salts relative to their mobility in water. Based on these results, it was concluded that the problem cannot be positively resolved by the action of the nitrate urea molecular complex solutions [$x CO(NH_2)_2 \cdot y HNO_3$] ($x = 1$, $y = 1 \div 3$) tested in the studies.

The discrepancy between the theoretically expected high solubility from a chemical standpoint and the lack of practical results in soil agrochemistry is explained by the acidic fixation of phosphorus compounds (i.e., retrogradation) occurring in the soil at a pH < 5.5 (Fang N, et al, 2022; Do Nascimento C. et al, 2018). At pH < 4.0, the increased concentration of $Al^{3+}$ and $Fe^{3+}$ ions in the soil solution leads to the formation of sparingly soluble aluminum and iron phosphates according to the reactions:

$$Al^{3+} + H_2PO_4^- \rightarrow AlPO_4\downarrow + 2H^+ \text{ and}$$

$$Fe^{3+} + H_2PO_4^- \rightarrow FePO_4\downarrow + 2H^+.$$

The solubility products of $AlPO_4$ (Ksp = 9.84×10$^{-21}$) and $FePO_4$ (Ksp = 1.3× 10$^{-22}$) are extremely low, which explains the sharp decrease in mobile $P_2O_5$ observed in Table 1. Thus, the acidic conditions created by DNM and TNM, rather than increasing phosphorus availability, promote its irreversible fixation in mineral forms inaccessible to plants. These findings necessitate the development of molecular compositions $[xCO(NH_2)_2 \cdot yHNO_3]$ ($x=1,\ y < 1$) within the solutions of salts formed by $CO(NH_2)_2$ and $HNO_3$, which would yield an optimal pH value of 5.5-6.3 to ensure maximal mobility of phosphorus compounds in the soil.

The results obtained from the effect of synthesized urea nitrate solutions on sparingly soluble salts and on "Vobkent" soil have been described in the authors previous studies (Mardonov et al, 2023). The following conclusion was drawn from these studies. Urea salts of nitric and phosphoric acids with different compositions, highly soluble in water, have been synthesized. Experimental results indicate that aqueous solutions of urea nitrate salts can dissolve various poorly soluble metal ion compounds, including heavy metal ions that accumulate in soil. Preliminary laboratory studies revealed that these synthesized salt solutions influence the bioavailability of $P_2O_5$ for Tr-B and citric acid in soil to varying extents. Among them, urea dinitrate and diorthophosphate demonstrated the highest efficiency, ranging from 8.26% to 11.52% and 8.28% to 9.52%, respectively, compared to the control soil sample, which showed values of 1.07% and 0.787%. The citric acid-soluble phosphorus ($P_2O_5$) in soil represents the amount (in mg or mass %) of sparingly water-soluble but soluble in weakly acidic environments (i.e., under the influence of a 2% citric acid solution) metal ion ($Ca^{+2}$, $Mg^{+2}$, $Al^{+3}$, $Fe^{+2/+3}$) hydrophosphate (dibasic) salts ($HPO_4^{2-}$). This value characterizes the amount of phosphorus from fertilizers and mobile phosphorus compounds in the soil that is assimilable by plants.

*The effect of MNM, DNM, and TNM on the solubility of sparingly soluble salts.* Experiments were conducted to investigate the ability of urea nitrates (MN) salts to enhance the solubility of various metal ion compounds. This enhancement is attributed to the dissociation of $H^+$ ions from $HNO_3$ within the MN salts and the electron-donating properties of the N and O atoms in the amide group of the urea molecule, despite MN salts themselves being less soluble in water compared to isolated urea ($CO(NH_2)_2$, 19g/100g water at 20°C; 35.65g at 30°C) and nitric acid ($HNO_3$). The experiments focused on studying the solubility of sparingly soluble compounds (oxides, phosphates, sulfates, hydroxycarbonates) that may be present or accumulated in industrial equipment, waste products, and agricultural topsoils.

For this purpose, the solubility of $CaHPO_4$, $Fe_2O_3$, $CaSO_4·H_2O$ and $(CuOH)_2CO_3$ under the influence of $[x CO(NH_2)_2·y HNO_3]$ ($x$ = 1, $y$ = 1÷3) (conc.) solutions was investigated.

The obtained results (m(sample)=3.0 g, Q:S=1:3) revealed that $Fe_2O_3$ dissolved by 9.7% under the influence of MNM, 17.2% with DNM, and 27.8% with TNM. $CaHPO_4$ dissolved by 20.8%, 34.1%, and 50.6% under the influence of UN salts, respectively. $CaSO_4·2H_2O$ dissolved by 2.6%, 2.82%, and 3.05%, while $(CuOH)_2CO_3$ (malachite) dissolved by 2.4%, 3.4%, and 6.34%. In general, an increase in the solubility of these salts was observed with an increasing proportion of $HNO_3$ (y=1<2<3) within the UN composition. Among the studied compounds, an increasing order of solubility (at y=1, 2, 3 values) was determined as $(CuOH)_2CO_3$ < $CaSO_4·2H_2O$ < $Fe_2O_3$ < $CaHPO_4$.

***Discussion.*** Investigation of the effect of urea nitrate salts on the solubility of various metal ion compounds in the "Bukhara" soil. The «Bukhara» soil was treated with $[xCO(NH_2)_2·yHNO_3]$ (x=1, y=1–3) solutions (C = 0.01 mol/l, Q:S = 1:3); untreated soil served as control. ICP-AES analysis of the liquid phases revealed the following element solubility patterns.

Considering individual elements, it was observed that mononitrate urea (MNM) increased the solubility of $Al_2O_3$ in the soil from 61.74 to 181.9 mg/l (a 2.95-fold increase). Conversely, a sharp (paradoxical) decrease in $Al_2O_3$ solubility was observed under the influence of DNM and TNM, i.e., samples with higher $HNO_3$ content.

Among the metal ions of particular importance and constantly monitored in soil composition is the $Ca^{2+}$ ion. Under the influence of mononitrate urea, the amount of $Ca^{2+}$ ions in the soil decreased by 1.8 times, and phosphorus ($P_2O_5$) decreased by 23.41 times (from 4.5 to 0.192 mg/l). Concurrently, an increase in medium acidity was expected to lead to a decrease in the solubility of silicon compounds. However, an increase in $SiO_2$ solubility was observed under the influence of all urea nitrate (1:1 ÷ 1:3) salts.

In conjunction with the above, the solubility of MgO in the soil under the influence of NMs was found to be significantly higher compared to the aqueous suspension (66.17 mg/l): 73.82 times higher with MNM (4884.75 mg/l), 68.84 times higher with DNM (4554.92 mg/l), and 73.15 times higher with TNM (4840.5 mg/l). This indicates that the solubility of NMs, regardless of their composition (y=1, 2, 3), is higher in acidic conditions and is not dependent on y, but is nearly uniform.

Similar changes were observed for soluble $K_2O$ and $Na_2O$ compounds in the soil. The solubility of $K^+$ ion compounds in water was 130.9 mg/l, while under the influence of MNM, it increased to 19820 mg/l, DNM to 213.2 mg/l, and TNM to 194.3 mg/l (Figure 2). This indicates an increase in the order of TNM < DNM < MNM by 1.484, 1.628, and 151.4 times, respectively. Although the solubility of sodium compounds in water (134.3 mg/l) was close to that of $K^+$ ion compounds, and a weak positive dynamic was observed under the influence of NM salts, this characteristic was found to be independent of the molecular ratios of the initial components in the $[xCO(NH_2)_2 \cdot yHNO_3]$ ($x = 1$, $y = 1 \div 3$) complexes; specifically, solubilities of 141.20 mg/l for MNM, 142.40 mg/l for DNM, and 142.25 mg/l for TNM were observed.

The concentration of $Zn^{2+}$ ion compounds in aqueous solution was 0.190 mg/l. Under the influence of MNM, it increased to 5.20 mg/l, or 27.37 times higher. However, under the influence of DNM, a significant 2-fold increase, and under TNM, a 7.9-fold increase was determined. An anomalous change was also observed in the solubility of these ion compounds.

Furthermore, data indicated that $Ba^{2+}$ and $Cu^{2+}$ ion compounds are very sparingly soluble in water, and their values remained almost unchanged under the influence of MNM, measuring 9.05-9.35 and 3.94-4.48 mg/l (respectively) (Table 2). This can be explained by the presence of $Cu^{2+}$ ions primarily as very sparingly water-soluble $Cu_2(OH)_2CO_3$ – hydroxycarbonates (azurite, Ksp = $1.1 \cdot 10^{-46}$ or malachite, Ksp = $1.7 \cdot 10^{-34}$) in the soil. This low solubility (9.40-6.34%) for $Cu_2(OH)_2CO_3$ – malachite was also recorded in our experiments on the solubility under the influence of NM salts. The solubility of $Ba^{2+}$ ion compounds in the analyzed soil sample in aqueous suspension and under the influence of NM solutions was also very low. This can be explained by the potential presence of this ion in the soil as $Ba_5(PO_4)_3(OH)$, a generally sparingly soluble and acid-resistant compound (Ksp = $1 \cdot 10^{-50}$).

Table 2. Solubility of "Bukhara" soil sample under the influence of urea nitrates.

| | Macroelements | | | | | | | Microelements | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample name | P/ $P_2O_5$/ | Si/ $SiO_2$ | Al/ $Al_2O_3$ | Ca/ CaO | Mg/ MgO | K/ $K_2O$ | Na/ $Na_2O$ | Fe/ $Fe_2O_3$ | Cd | Zn | **Ba** | Cu |
| Primary Soil | | | 0,6533/ 3,2665 | 17,50/875 | 0,7925/ 39,625 | 2,606/ 130,3 | 2,689/ 134,45 | 0,1240/ 6,2 | 0,00612/ 0,336 | 0,00377/ 0,1885 | -0,0076 | -0,0624 |
| | 4.496 | -0.8132 | 617,3685 | 1225 | 66,17375 | 156,36 | 181,5075 | 8,866 | | | | |
| Soil + MNM | 0.1919 | -0.4613 | 1,925/ 96,25 | 9,890/ 494,5 | 58,50/ 2925 | 396,4/ 19820 | 2,824/ 141,2 | 1,375/ 568,75 | 0,00696/ 0,348 | 0,1040/ 5,2 | 0,1870/ 9,35 | 0,08957/4,4785 |
| | | | 181,9125 | 692,3 | 4884,75 | 237804 | 190,62 | 813,3125 | | | | |
| Soil + DNM | 0.06117 | -1.436 | 0,04679 /2,3395 | 9,257/ 462,85 | 54,55/ 2727,5 | 4,264/213,2 | 2,848/ 142,400 | -0,0274 | 0,00627/ 0,3135 | 0,00805/ 0,4025 | 0,1610/ 8,05 | -0,0514 |
| | | | 4,421655 | 647,99 | 4554,925 | 255,84 | 192240 | | | | | |
| Soil + TNM | 4.624 | -1.184 | -0,0316 | 8,023/ 401,15 | 57,97/ 2898,5 | 3,886/194,3 | 2,845/ 142250 | 0,4416/ 22,08 | 0,00731/ 0,3655 | 0,02997/ 1,4885 | 0,1739/ 8,695 | 0,07890/3,945 |
| | | | | 561,61 | 4840,495 | 233,16 | 192037,5 | 31,5744 | | | | |

Compared to all the aforementioned metal ion compounds, $Cd^{2+}$ ions possess high toxicity (Khatun et al, 2022). It was determined that the compounds of this ion, whose oxides and salts accumulate in the soil, exhibit very low and almost identical solubility ($6.12\cdot10^{-3} \div 7.31\cdot10^{-3}$ mg/l) in "Bukhara" soil, both in water and under the influence of MNM, DNM, and TNM salts (Figure 1). This indicates that the soil's pH value does not significantly affect the solubility of these cadmium compounds.

The results obtained from ICP-AES analyses of soil samples were arranged in the following order, and graphs illustrating the correlations between the concentrations of various element ions are presented in Figures 1-3, according to Table 2.

The numbers designated on the *x*-axis of the graphs represent:

Aqueous solution of "Bukhara" soil sample,

Solution of "Bukhara" soil sample in MNM,

Solution of "Bukhara" soil sample in DNM,

Solution of "Bukhara" soil sample in TNM. The values designated on the *y*-axis of the graphs represent the solubility values (in mg/l) of the corresponding chemical elements (and their compounds).

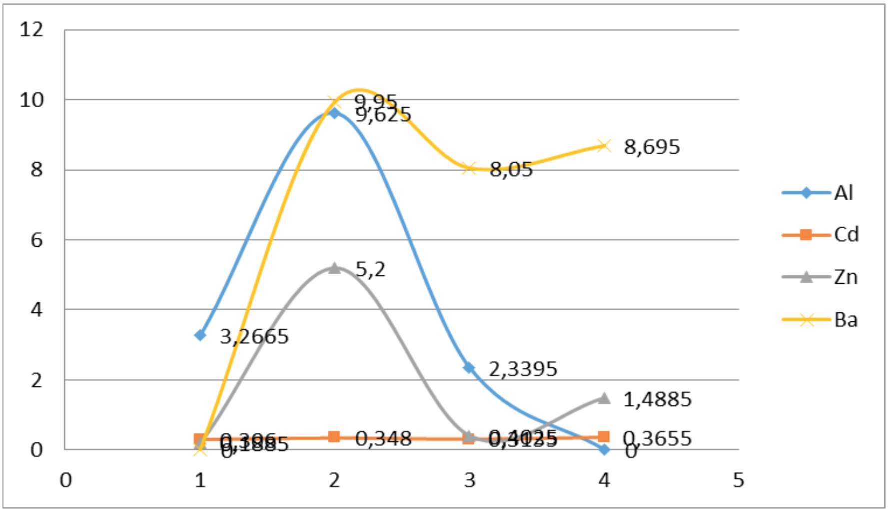



Figure 1. Change in the concentration of $Al^{+3}$, $Cd^{+2}$, $Zn^{+2}$ and $Ba^{+2}$ ions in the solution of a "Bukhara" soil sample under the influence of urea nitrate salt solutions.

Concurrently, the conclusion regarding the increase in the N:P ratio or the total nitrogen content relative to other components leading to an increase in nutrient and microelement concentrations indicated no effect on the current solubility of these ions (Navizaga et al, 2017).

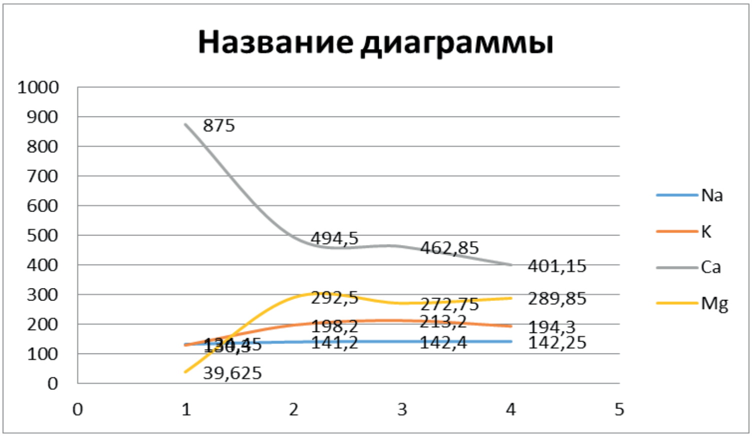



Figure 2. Change in the concentration of $Na^{+}$, $K^{+}$, $Ca^{+2}$ and $Mg^{+2}$ ions in the solution of a "Bukhara" soil sample under the influence of urea nitrate salt solutions.

The solubility of heavy metals in the soil, including $Fe^{+3}/Fe_2O_3$ compounds, was highest under the influence of MNM (568.75 mg/l), which was 64.15 times higher than in water (8.866 mg/l) and 25.73 times higher compared to DNM and TNM (Figure 3).

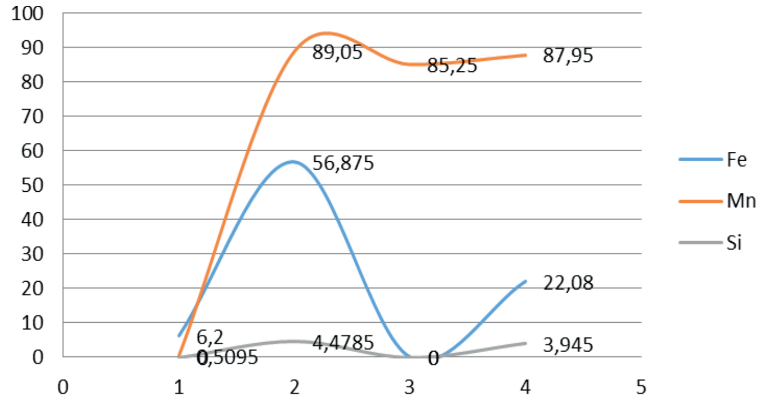



Figure 3. Change in the concentration of $Fe^{+3}$, $Mn^{+2}$ and $Si^{+4}$ ions in the solution of a "Bukhara" soil sample under the influence of urea nitrate salt solutions.

Thus, MNM (y=1) most effectively mobilized metal ions in soil, while higher $HNO_3$ content (y=2, 3) caused phosphate retrogradation at pH < 4.3.

*EPR spectroscopic analysis of the state of humic substances in "Bukhara" soil as a result of the influence of MNM, DNM, and TNM solutions.* This section of the research work presents the results and preliminary analyses of the structural changes in soil samples treated with synthesized urea salts, investigated by Electron Paramagnetic Resonance (EPR) spectroscopy. It is noteworthy that the practice of studying the structural and agrochemical changes in soil and its components under the influence of chemical substances using this method is being applied for the first time in the Republic of Uzbekistan.

The general chemical composition of humic substances corresponds to the following empiric formula: $C_xH_yN_zO_pS_qM_r\ (Al_2O_3)_l\ (SiO_2)_m\ (H_2O)_n$, where M represents metal ions such as $Mn^{+2}$, $Ca^{+2}$, $Mg^{+2}$, $Al^{+3}$, $Fe^{+3}$, $Mn^{+2}$ and x, y, z, p, q, l, m, n are stoichiometric coefficients. The corresponding hypothetical structural formula for a humic acid (HA) fragment, as proposed by Kleinhempel, is presented below (Kleinhempel, 1970).

According to the formulas and schemes presented above, humic substances in soil are primarily complex in composition, consisting of macromolecular fragments containing free radicals, and their quantity determines the agrochemical properties of the soil. Considering this, EPR spectroscopy and NMR spectroscopy methods are employed to determine changes in the properties and quantity of humic substances in the soil (Tkachenko et al, 2020; Flogeac et al, 2005).

According to established EPR-based methodology (Jezierski et al, 2000; Tkachenko et al, 2020), two distinct types of free radicals are identified in soil humic substances: (1) the active form ($HA_{active}$), representing humic acids not bound to the mineral matrix of the soil, characterized by semiquinone-type radicals with g-factor 2.003 and exhibiting higher paramagnetic center (PMC) density; and (2) the passive form ($HA_{passive}$), representing humic acids complexed with metal ions ($Fe^{3+}$, $Mn^{2+}$, $Al^{3+}$) or silicon components of the soil mineral fraction, characterized by g-factor 2.002 and comparatively lower PMC density. The ratio of active to passive forms ($J_1$:$J_2$) serves as a quantitative indicator of soil humic substance quality and agrochemical activity. These radical types and their metal complexes are directly identified and quantified in the EPR spectra of treated soil samples (Figures 4–7) based on characteristic g-factor values and line widths.

Therefore, we utilized EPR spectroscopy to study the quantity and properties of humic acids in "Bukhara" soil, and the following results were obtained. The g-factor, ΔH-line width in mT, and the concentration of paramagnetic centers ($N_{CPC}$-$10^{11}$-$10^{18}$ concentration (conc, spin/mm³ and existing concentration-M)) were used as key indicator parameters. When the "Bukhara" soil sample was treated with urea nitrate (MN): $x CO(NH_2)_2 : y HNO_3$ where $x=1$, $y=1,2,3$ (MNM - mononitrate), (DNM - dinitrate), (TNM - trinitrate) salts respectively, it became evident that metal ions from the soil's mineral components, such as $Mn^{+2}$, $Ca^{+2}$, $Mg^{+2}$, $Al^{+3}$ and $Fe^{+2}/Fe^{+3}$ compounds, transitioned into the aqueous solution, leading to a change in the quantity of organic components—humic substances.

It was determined that chemical interaction with urea nitrate salts did not increase, but rather decreased, the solubility (mobility/assimilability) of mineral substances in the soil. On the other hand, preliminary research results indicated that urea nitrate salts were effective in altering the quantity and increasing the activity of humic substances (paramagnetic centers), which determine the agrochemical effectiveness of the soil.

When "Bukhara" soil interacted with urea nitrate salts, a relative increase in humic compounds in the soil was observed. It was determined that as the proportion of nitric acid in the NM salts increased, quinoid (semiquinone) radicals characteristic of humic acids were formed, as recorded in EPR spectra, and the type and quantitative ratios of humic substances changed.

In the solid-state spectrum of the control "Bukhara" soil sample, EPR lines characteristic of expected humic acid radicals were not observed. Instead, lines characteristic of the $Mn^{+2}$ ion were recorded in a spectrum consisting of 6 equidistant lines, and two lines corresponding to its spin are presented in Figure 4 (g=2.016, ΔH=8.8 0.1 mT).

After treating this soil sample with an MNM solution ($CO(NH_2)_2$ - 49.8% and $HNO_3$ - 51.2%), a complex spectrum was recorded (Figure 5). In the center of the spectrum, doublet lines characteristic of free radical (FR) substances appeared, characterized by parameters $g_1$=2.0033, $\Delta H_1$=0.51 mT, and $g_2$=2.0021, $\Delta H_2$=0.48 mT. This indicates the presence of two types of humic acids (HAs) in the soil: the first being *active* humic acid ($HA_{active}$) and the second *inactive* ($HA_{passive}$) humic substances. It also suggests the presence of low-mobile substances in the soil in compound form with mineral components ($Fe^{+3}$, $Al^{+3}$, $Cu^{+2}$, $Mn^{+2}$ and other $M^{+n}$ ions). Lines characteristic of isomorphically substituted $Mn^{+2}$ ions in the $Ca^{+2}$ ion compounds within the soil were also observed, and a significant decrease in the intensity of the $Mn^{+2}$ ion lines at the center of the spectrum was noted. When calculating the FR content in the mineral base and soil sample from the spectrum, for the 1st line: $N_{CPC}=2.654 \cdot 10^{13}$, Concentration=$3.792 \cdot 10^{12}$ spin/g; Molar = $6.30 \cdot 10^{+6}$ M; and for the 2nd line: $N_{CPC}=6.882 \cdot 10^{13}$, Conc. = $9.745 \cdot 10^{12}$ spin/mm$^3$; Molar=$1.619 \cdot 10^{-5}$ M. This result proves that $HNO_3$ within mononitrate urea interacts with mineralized humic substances in the soil, exhibiting an acidic ($H^+$) decomposing property towards them. Simultaneously, due to the oxidizing property of the $HNO_3$ molecule, the paramagnetic $Mn^{+2}$ ions transformed into diamagnetic $Mn^{+4}$ ions, leading to a decrease in the intensity of the manganese(II) ion lines in the EPR spectrum (Figure 5).

In the EPR spectrum of the soil sample treated with a DNM solution, which has a higher quantitative share of $HNO_3$ (($CO(NH_2)_2$-32.25% and $HNO_3$ - 67.75%), a decrease in the intensity of the active humic acid ($HA_{active}$) line corresponding to $g_1$=2.0033 and an increase in the amount of the passive humic component ($g_2$=2.0021) were observed (the intensity ratio of the lines in the spectrum $J_1$:$J_2$=1:2.25; Figure 6). The total amount of free radicals (FR) in this sample was $N_{CPC1}=1.609 \cdot 10^{14}$, Conc. = $2.30 \cdot 10^{13}$ spin/g; Molar=$3.820 \cdot 10^{-5}$ M. The decrease in the intensity of the active humic acid line is explained by its formation of mineralized complex compounds $[Mn(HA_{active})_n]$ (n=2 or 4) with newly formed $Mn^{+4}$ ions (Jezierski A, et al, 2000). The complete absence of $Mn^{-2}$ ion lines in this spectrum is evidence that it was fully oxidized by the higher amount of $HNO_3$ in DNM (compared to MNM).

Under the influence of the TNM ($CO(NH_2)_2$ - 24.10% and $HNO_3$ - 75.9%) solution, this ratio led to an increase in the amount of active HAs ($J_1$:$J_2$=2:1), and the total FR amount was $N_{CPC1}$=2.735·$10^{15}$, Conc.=3.907·$10^{14}$ spin/g; Molar=6.49·$10^{-4}$ M, as ESR spectra shown in Figure 7.

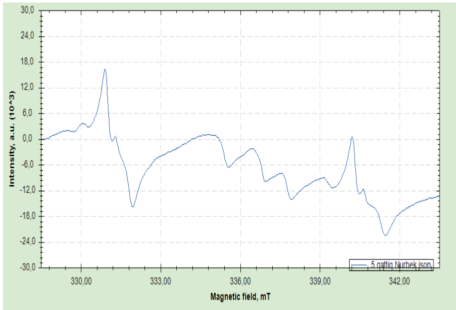



Figure 4. EPR spectrum of “Bukhara” soil.


Figure 5. “Bukhara” soil + MNM EPR spectrum.


Figure 6. “Bukhara” soil + DNM EPR spectrum.


Figure 7. “Bukhara” soil + TNM EPR spectrum.

When the “Bukhara” soil sample is treated with solutions of [$x$CO$(NH_2)_2$:$y$$HNO_3$] molecular complexes of varying compositions ($y$=1,2,3), an increase in the $HNO_3$ proportion within the NM composition affects the quantity of active and passive humic components in the soil. Initially, the components of the MNM solution lead to the decomposition of mineralized humic compounds in the soil. In the subsequent stage, under the influence of the DNM solution, the complete detachment of HA radicals from the mineralized portion, along with the oxidation of paramagnetic $Mn^{+2}$ ions in the soil to a higher oxidation state ($Mn^{+4}$) due to the action of nitrate ($NO_3^-$) ions, led to a decrease in the intensity of Mn-² ion specific lines in Figure 5. This caused the samples to disappear from the spectrum in subsequent stages (Figure 5). The reason why active and passive (g=2.0033, g=2.0021) HA lines decreased to a $J_1$:$J_2$=1:2.25 ratio under the influence of the DNM solution is explained by the selective complex formation between $Mn^{+4}$ ions and $HA_{active}$.

Under the influence of the TNM solution, the intensity of the lines in the spectrum reached a 2:1 ratio, which is explained by the increased proportion of $HNO_3$ in the solution leading to an increase in the amount of *active* HA in the soil sample. This is due to [Mn$(HA_{active})_4$] having transitioned to a mineralized state. A decrease in the intensity of the $HA_{active}$ free radical (FR) specific lines in the EPR spectrum was observed due to a reduction in its FR content. As a result of the interaction of the TNM solution with the "Bukhara" soil sample, the high proportion of $HNO_3$ in this complex facilitated its decomposition, ensuring an increase in $Mn^{2+}$ + $HA_{active}$ (pH < 4) content in the soil, thus providing a basis for this conclusion.

**Conclusions.** Summarizing the results, it can be concluded that urea nitrate salts, while reducing the mobility of phosphorus compounds in the soil (due to retrogradation), simultaneously provide the opportunity to increase the quantity of another key agrochemical component—humic acids (HAs)—and enhance the proportion of active components within them, i.e., to activate HAs bound to mineral components. To determine the amount of humic substances, which are difficult and time-consuming to quantify in soil, and to solve related problems, it is expedient to use the EPR spectroscopy method, based on determining the concentration of free radicals within these substances.

For the first time, structural and chemical compositions of these soil samples were studied using modern physicochemical research methods (ICP-AES and EPR-spectroscopy). This revealed both the transition of metal ions into the aqueous solution in the soil and an increase in the activated state of humic nutrient units in the soil (from a 1:2 ratio to a 2:1 ratio). It was concluded that the synthesized nitrate salts of urea exhibit properties as an agrochemical stimulator, increasing the solubility of accumulated heavy metal ion compounds in the soil, improving soil structure, and enhancing the amount of active forms of humic substances.

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