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Environmental Assessment of Rice Grains (*Oryza sativa* L.) Depending on Cultivars and Quality of Irrigation Water.

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ABSTRACT

The main goal of our study was to determine the environmental feasibility of growing rice varieties under conditions of irrigation using water of different qualities that were obtained by mixing rice systems effluents with pure water from the Dnipro River, and conclude whether or not the effluents are suitable for crop irrigation after previous amelioration, and to determine the level of quality and ecological danger of rice grains for further processing. Field experiments were conducted from 2012 to 2015 at the rice checks of the Institute of Rice at the National Academy of Agrarian Sciences (NAAS) of Ukraine. We studied the effect of mixed water containing 25% of the effluent and drainage water diluted with the pure water of the Dnipro River on the quality indices (content of protein, fat, starch) and the content of heavy metals, residues of pesticides, and nitrates of different rice cultivars, such as Prestyzh, Serpnevyi, Ontario, and Vikont. The results of the study proved the possibility of reuse of the mixed effluent and drainage water for the irrigation of rice. We recommend reuse of the effluent and drainage water for the irrigation of rice in the check systems, which will not affect the yield nor quality of rice grains and related crops, and will provide a high economic effect, ecological balance of the water resources of the Black Sea, and will become a guarantor of quality recreation of people in the recreational zone.

Keywords: rice cultivars, irrigation water quality, effluent and drainage water, quality indices (content of protein, fat, starch), content of heavy metals, residues of pesticides, nitrates.

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INTRODUCTION

The extensive nature of the development of productive forces of society has led to an increase in the intensity and scale of anthropogenic impact on the natural environment, which has led to a dangerous situation - local and regional ecological crises, to the aggravation of the threat of environmental disasters. In addition, anthropogenic pollution of the environment arises as a result of people's activities, including their direct or indirect impact on the intensity of environmental pollution.

In the world of rice production, the value of its quality, relative to performance, is the most valuable. The quality of rice grain is determined by its chemical composition, technological, and culinary characteristics: vitreous, cracking of the endosperm, filamentary and grain form, the general yield of cereals and the whole core, the coefficients of water absorption, and the color, taste, and smell of porridge. Rice cultivation technology uses fertilizers, pesticides, irrigation water of various quality, and therefore it is especially necessary to give an environmental assessment of grain and its compliance with the requirements of the food industry.

Rice Grape and Grade I for baby food products are made from grain grown on checks without the use of pesticides [1].

Investigations of the Institute of Soil Science and Agrochemistry, NASA Rice Institute [2, 3, 4, 5] established that in the soil of Ukraine, every year \$1.75 million dollars' worth of pesticides are introduced. Their excessive, uncontrolled use on agricultural land has led to the discovery of pesticides in groundwater practically in all regions of Ukraine. Given the additional technogenic pollution of water, it can be argued that the entire population of the country consumes water and agricultural products contaminated with pesticides, heavy metals, and nitrates. Laboratory analyzes reveal the presence of herbicides in 70% of agricultural products, and in 14% of such samples, the nitrate content exceeds the permissible standards by 6-8 times.

Along with this, the use of environmentally safe technologies for the cultivation of rice with the use of waste water provides an opportunity to improve the environmental conditions in the Black Sea area [6, 7, 8]. This measure makes it possible to significantly reduce the inefficient use of natural resources while simultaneously improving the efficiency of agricultural production of valuable grain crops.

The main goal of our study was to determine the environmental feasibility of growing rice varieties under conditions of irrigation using water of different qualities that were obtained by mixing rice systems effluents with pure water of the Dnipro River, and conclude whether or not the effluents are suitable for crop irrigation after previous amelioration, and to determine the level of quality and ecological danger of rice grains for further processing.

MATERIALS AND METHODS

We used a number of methods of scientific investigation in our study, namely field and laboratory experiments, and statistical methods and analysis of variance to process data that was obtained in the experiments [9, 10, 11].

The study devoted to rice productivity was carried out during the period from 2012-2015 on the rice irrigation systems of the Institute of Rice at the National Academy of Agrarian Sciences of Ukraine (village Antonivka, Skadovsk district, Kherson region; experimental field coordinates are: 46°08'34"N, 32°57'15"E, 8 m above sea level). We studied the impact of two agricultural factors (irrigation water quality and cultivar) on the rice yields, to wit:

Factor A (Cultivars of rice):

- Prestyzh;
- Serpnevyi;
- Vikont;
- Ontario.

Factor B (Irrigation water quality):

- pure water of the Dnipro River;
- mixed water (75% of the Dnipro River water plus 25% of the effluent and drainage water from the rice irrigation system).

Prestyzh is an early-ripening rice cultivar with a vegetation period of 105 days and potential grain yield of 6.5 t/ha. Serpnevyi is an early-ripening rice cultivar with a vegetation period of 115 days and potential grain yield of 7.0 t/ha. Ontario is a middle-ripening rice cultivar with a vegetation period of 120 days and potential grain yield of 8.5 t/ha. Vikont is a middle-ripening rice cultivar with a vegetation period of 120 days and potential grain yield of 8.5 t/ha. The cultivars are recommended for cultivation in the Steppe zone of Ukraine. All the studied cultivars of rice were originated at the Institute of Rice of the NAAS of Ukraine.

The field experiments were carried out by using the current recommendations for field experiments conduction in agronomy under the irrigated conditions in the South of Ukraine [9, 10, 11].

Rice cultivation technology was standard for the Steppe zone of Ukraine. The previous crop was alfalfa. We conducted double-harrowing using a BDV-7 machine in the second decade of April in the pre-sowing period. Soil leveling was conducted after harrowing by the means of a long-based planner D-719, and bolsters were rolled by a T-150 bulldozer. Additional leveling and planning of the soil surface in the rice check was made by a VP-10 machine. The soil cultivation at a depth of 5-7 cm, combined with application of mineral fertilizers (ammonium sulphate in the dose of 288 kg/ha, simple superphosphate in the dose of 156 kg/ha), followed after leveling. Rice was sown at a depth of 1-2 cm with an inter-row spacing of 15 cm and seed rate of 9 million seeds per hectare.

After sowing, the rice checks were flooded with water for a period of 5-10 days. The soil was then dried until the sprouting of the crop, followed by flooding the check again with a water layer of 10-15 cm. The water layer was decreased for conduction of mechanized work in the rice checks only [12]. Rice crops' chemical protection included spraying with preparation mixtures of Ordram 6E (active substance – molinate) in a dose of 5-6 L/ha and Sirius (active substance - pyrazosulfuron-ethyl) in a dose of 0.2 kg/ha to protect against weeds. We also used fungicides Derozal (active substance - carbendazim) in a dose of 1 L/ha and Impact K (active substance – carbendazim and flutriafol) in a dose of 1 L/ha to protect against rice piricularia disease. At the stage of tilling we gave the crop an additional foliar fertilization with 156 kg/ha of urea.

Yields of rice grain were estimated by using the entire harvesting method. We used a Don-1500 self-propelled combine harvester to perform grain yield determination. Harvesting was conducted at the optimal stage of ripeness for each cultivar.

The yield data was processed by using the analysis of variance and statistical methods within Microsoft Excel and Statistica 5.0 software applications.

Water samples were collected each month within the period of the crop vegetation. The collected water samples were analyzed in the certified laboratory at the Institute of Rice of the NAAS by the generally accepted procedures [13, 14].

RESULTS AND DISCUSSION

Agromeliorative indicators of the quality of irrigation water used in field experiments are presented in Table 1.

Table 1: Irrigation Water Quality (average for the period from 2012 to 2015± standard deviation)

Quality Factors	Irrigation Water Quality Factor Values		
	pure water of the Dnipro River	mixed water (75% of the Dnipro River water plus 25% of the effluent and drainage water from the rice irrigation system)	Maximum Permissible Concentration (MPC)
Power of Hydrogen pH, units	8.30±0.08	8.10±0.09	6.5-8.5

Total dissoluble solids content, mg/L	379.00±12.20	467.30±17.20	1000
Hydrocarbonates, mg/L	168.40±15.90 (2.81±0.83)	186.00±27.40 (3.10±0.91)	219
Sulphates, mg/L	82.00±14.00 (1.71±0.58)	94.00±14.90 (1.96±0.62)	500
Chlorides, mg/L	40.80±7.30 (1.15±0.41)	45.10±7.70 (1.27±0.44)	350
Calcium, mg/L	44.20±3.20 (2.21±0.32)	47.00±3.40 (2.35±0.35)	180
Magnesium, mg/L	24.30±6.50 (2.03±1.08)	29.00±6.90 (2.42±1.15)	40
Sodium, mg/L	32.90±6.80 (1.43±0.59)	36.00±4.90 (1.57±0.42)	68
Ammonium nitrogen, mg/L	0.15±0.01	0.21±0.01	2.0
Nitrate ions, mg/L	0.99±0.07	1.36±0.07	10.34
Phosphate ions, mg/L	0.12±0.01	0.18±0.02	0.22
Potassium, mg/L	0.12±0.006	0.28±0.01	50
Iron, mg/L	0.004±0.0011	0.003±0.0004	0.3
Zinc, mg/L	0.002±0.0004	0.002±0.0003	1.0
Manganese, mg/L	0.003±0.0009	0.003±0.0006	0.1
Nickel, mg/L	0.0008±0.0003	0.0006±0.0001	0.1
Copper, mg/L	0.0004±0.0001	0.0003±0.0002	1.0
Petrol product, mg/L	0.002±0.0004	0.003±0.0001	0.3
Strontium-90, pKi/l	4.30±0.49	3.23±0.21	20
Cesium-137, pKi/l	1.68±0.23	1.57±0.12	50
SAR, units	1.01±0.46	1.04±0.33	2.0-4.0

The value of Power of Hydrogen pH is within the Maximum Permissible Concentration (MPC) and does not affect the growth and development of rice plants.

Thus, the total dissoluble solids content of the studied types of irrigation water has significant differences: Dnipro Irrigation Water has a total dissoluble solids content of - 379, and zakhshani - 467 mg/l and require a careful approach, taking into account the entire complex of reclamation measures.

Content of Hydrocarbonates, Sulphates, Chlorides, Calcium, Magnesium, Sodium, Ammonium nitrogen, Nitrate ions, Phosphate ions, and Potassium was significantly lower than Maximum Permissible Concentration (MPC), but the dynamics of their concentration increase in mixed water (75% of the Dnipro River water plus 25% of the effluent and drainage water from the rice irrigation system) compared to pure water of the Dnipro River.

The nutrient content found in the studied types of irrigation are ammonium nitrogen, nitrates, phosphates and potassium. The leading element of nutrients among them is nitrate, second is potassium, and the largest in their content are ammonium nitrogen and phosphates. The total content of nutrients in the first place is mixed water (75% of the Dnipro River water plus 25% of the effluent and drainage water from the rice irrigation system), and the smallest in the Dnipro water.

The content of heavy metals (Iron, Zinc, Manganese, Nickel, Copper) in irrigation water is significantly lower than the Maximum Permissible Concentration (MPC).

Also, in mixed water (75% of the Dnipro River plus 25% of the effluent and drainage water from the rice irrigation system), there is a large amount of petroleum products (0.003 mg/l), which is more than 1.5 times than in the Dnipro water.

Irrigation water of the studied systems has a significant amount of radioactive substances. Thus, with the magnitude of the Maximum Permissible Concentration (MPC) of strontium-90 - 20,0 pKi/l, on average in 2012-2015, this figure was 4.30 in the Dnipro water and was 33.1% higher in comparison with mixed waters.

In all studied irrigated waters, the content of cesium-137 was less than the MPC. Thus, in the Dnipro River it contained - 1.68, and mixed - 1.57 pKi/l. Also, in the irrigation waters of the studied irrigation systems, there is a small amount of pesticides, in particular piradosulfuron, prolineazan, and karbendazim, which have no negative impact on the food quality of the cultivated product.

The SAR values are 1.01 and 1.04, and indicate no significant differences between the two irrigation water options.

During four years of research, with the help of the workers of the Kherson Regional Sanitary and Epidemiological Station, we monitored the content of heavy metals in rice grains depending on the quality of irrigation water (Table 2).

Table 2: The content of heavy metals in rice grains depending on the varieties studied and the quality of irrigation water, mg/kg (average for the period from 2012 to 2015)

Heavy metals	Cultivars of rice, Factor A	Content of metal in a grain of grains grown under irrigation, Factor B		Maximum Permissible Concentration (MPC), mg/kg	LSD at p<0.05, mg/kg	
		pure water of the Dnipro River	mixed water (75% of the Dnipro River water plus 25% of the effluent and drainage water from the rice irrigation system)		Factor A	Factor B
Mercury	Prestyzh	0.0023	0.0024	0.03	0.0005	0.0006
	Serpnevyi	0.0025	0.0027			
	Vikont	0.0030	0.0031			
	Ontario	0.0026	0.0028			
Arsenic	Prestyzh	0.08	0.08	0.20	0.021	0.009
	Serpnevyi	0.10	0.09			
	Vikont	0.12	0.13			
	Ontario	0.09	0.10			
Copper	Prestyzh	2.04	2.08	10.00	0.28	0.18
	Serpnevyi	2.26	2.32			
	Vikont	2.34	2.70			
	Ontario	2.22	2.30			
Lead	Prestyzh	0.012	0.014	0.5	0.004	0.003
	Serpnevyi	0.014	0.014			
	Vikont	0.015	0.020			
	Ontario	0.013	0.016			
Zinc	Prestyzh	6.18	6.19	50.00	0.50	0.026
	Serpnevyi	6.25	6.30			
	Vikont	6.97	7.04			
	Ontario	6.22	6.25			

Note: The results of analyzes were obtained in the certified laboratory of the Kherson Regional Sanitary and Epidemiological Station.

As you can see, the content of mercury in rice grains on the background of moisture varied: In conditions of irrigation with Dnipro water within 0.0023-0.0030 mg/kg, it was 10-13 times less than the Maximum Permissible Concentration (MPC); and in conditions of irrigation with mixed water, the content of mercury was slightly higher at 0.0024-0.0031 mg/kg.

Among the studied varieties of mercury content on both phonons of humidification, the medium-grade Vikont, 0.003 mg/kg of rice was allocated, which is higher compared to the early-seeded Prestyzh variety by 23.3%. The high content of mercury in the Vikont variety is due to its high vegetative period and higher grain yield.

The difference in contamination between the early-seeded Serpnevyi and the mid-seeded Ontario variety on both backgrounds of moisture was insignificant.

The content of arsenic in varieties in the background of watering with Dnipro water ranged from 0.08-0.12 mg/kg of grain, which is below the Maximum Permissible Concentration (MPC) of 1.7-2.5 times, and on the background of irrigation with mixed waters of 1.5-1.7 times. The difference in the arsenic content index for irrigation backgrounds, as well as the content of mercury, was insignificant. In order to give an explanation of this result, further research is needed.

For the values of the Maximum Permissible Concentration (MPC) of 10 mg/kg, the content of copper in grain under irrigation with Dnipro water in the studied varieties fluctuated between 2.04-2.34, and in the background of irrigation with mixed water fluctuated between 2.08-2.70 mg/kg, with a somewhat higher content of copper in drainage and waste runoffs compared to the Dnipro water.

According to the researched indicator, on both phonons of humidification, a medium-grade variety of Vikont rice was isolated and the content of copper was 3.7-4.3 times was lower than the Maximum Permissible Concentration (MPC). Other varieties had 4.3-4.9 times lower copper concentration values when compared to the MPEC.

The average grade Vikont mathematically significantly allocated to the amount of lead in conditions of humidification of the Dnipro and mixed waters. Significantly higher than all considered indicators of heavy metal content zinc was released, the difference in the background of moisture was not significant.

In chemical analyzes, in irrigation water and irrigated soils, rice checks contain small quantities of pesticides and nitrates [17, 18, 19], the content of which are shown in Table 3 in various grades of rice grains.

Table 3: The content of pesticides and nitrates in grains of rice varieties of different groups of ripeness, depending on the quality of irrigation water (average for the period from 2012 to 2015)

Cultivars of rice, Factor A	The content of pesticides and nitrates in rice grains when irrigated by water		Maximum Permissible Concentration (MPC), mg/kg	LSD at p<0.05, mg/kg grain
	pure water of the Dnipro River	mixed water (75% of the Dnipro River water plus 25% of the effluent and drainage water from the rice irrigation system)		
Pyrazosulfuron-ethyl (Sirius herbicide), mg/kg				
Prestyzh	< 0.001	< 0.001	0.8	0.0004
Serpnevyi	< 0.001	< 0.001		
Vikont	< 0.002	< 0.002		
Ontario	< 0.001	< 0.001		
Propiconazole (Amistor fungicide), mg/kg				
Prestyzh	< 0.005	< 0.005	0.15	0.0008
Serpnevyi	< 0.005	< 0.005		
Vikont	< 0.006	< 0.006		
Ontario	< 0.005	< 0.005		
Carbendazim (Impact fungicide), mg/kg				
Prestyzh	< 0.02	< 0.02	0.60	0.005
Serpnevyi	< 0.02	< 0.02		
Vikont	< 0.03	< 0.03		
Ontario	< 0.02	< 0.02		
Nitrates, mg/kg grains				
Prestyzh	14.6	16.4	300	0.58
Serpnevyi	27.4	29.8		
Vikont	30.4	31.2		
Ontario	23.3	25.5		

The content of Pyrazosulfuron-ethyl (Sirius herbicide, Molecular Formula - $C_{14}H_{18}N_6O_7S$) in early-seasoned varieties Prestyzh and Serpnevyi, and mid-season varieties of Ontario was negligible at <0.001 mg/kg of grain. Only in the middle-aged Vikont variety did the content of this pesticide exceed all studied varieties on both phonons of humidification at 0.001 mg/kg of grain. The concentration of the investigated pesticide, which was obtained from rice grain at the expense of irrigation water and soil at the level of 0.001 - 0.002 mg/kg, is only 13-26% of the value MPEC.

Not obtained when analyzing the difference in pesticide content propiconazole (Amistor fungicide, Molecular Formula - $C_{15}H_{17}Cl_2N_3O_2$) between Prestyzh, Serpnevyi and Ontario. Its essential content was in the grain of the middle-aged variety Vikont (0.006 mg/kg), since the amount of the Maximum Permissible Concentration (MPC) of Amistor is 25-30 times higher than its content in other studied varieties, which is explained by only high grain yield.

A similar dependence is observed in the content of rice grains containing the carbendazim pesticide (Impact fungicide, Molecular Formula - $C_9H_9N_3O_2$). Among the studied varieties, the higher content of this pesticide is again obtained in the grains of the medium-grade Vikont (<0.03 mg/kg), which is less than the Maximum Permissible Concentration (MPC) of 20 times. Thus, the insignificant content of pesticides in irrigation water is due to a decrease in the rules for their application; their impact on the quality of rice grain is not significant, and therefore sanitary and eco-services are allowed to use rice groats in the food industry and as a product for infant food.

Studies have proved the inverse relationship between grain yield of rice and the content of the nitrates in it. Therefore, in the implementation of promising new high-yielding rice varieties, in conditions of use of irrigation water with high mineralization, it is necessary to continuously monitor the increase of salinity of the soil, accumulation of grain of rice of heavy metals, and nitrates to make maximum use of measures for the elimination of possible negative consequences.

Studies [15, 16] have established that the variability of the mass of 1000 grains, film thickness, and grain form for 72-93% of rice varieties depends on the genotype, and the total yield of cereals and the content of the whole nucleus in it depends on the conditions of cultivation (variability 31-37%).

Data on the characteristics of grain rice varieties of varying groups of ripeness, depending on the quality of Dnipro irrigation water and its mixture with drainage and waste waters of the rice irrigation system are shown in Table 4.

Table 4: Ratio quality indicators of rice varieties of different groups of maturity depending on the quality of irrigation water (average for the period from 2012 to 2015)

Irrigation water quality, Factor B	Cultivars of rice, Factor A	Weight of 1000 grains, r	Vitality, %	Grain husks content, %	Exit groats, %
Pure water of the Dnipro River	Prestyzh	28.7	98.7	18.1	67,5
	Serpnevyi	25.9	94.1	20.5	66,7
	Vikont	31.7	97.4	18.9	67,4
	Ontario	33.4	92.5	17.7	67,6
Mixed water (75% of the Dnipro River water plus 25% of the effluent and drainage water from the rice irrigation system)	Prestyzh	28.2	98.2	17.8	67,3
	Serpnevyi	25.8	94.1	20.2	66,5
	Vikont	31.2	96.9	18.6	67,2
	Ontario	32.9	92.3	17.3	67,4
LSD at $p<0.05$		1.14	3.63	0.38	0.57

As shown in the table, the weight of 1000 grains under the influence of water of different qualities did not change significantly. The average value of the indicator for rice varieties in conditions of irrigation with

Dnipro water was 29.9, and in irrigation with mixed water was 29.5 r (LSD 0.05 = 1.14 r). Significant value was between the studied varieties. The weight of 1000 grains of the average varieties of Vikont and Ontario was significantly higher than that of early varieties Prestyzh and Serpnevyi.

Grain vitality is a basic indicator of its quality, which affects the most important technological and culinary properties. The highest level of early varieties in both irrigation phases was in Prestyzh; the relatives - with an indicator of 96.9-97.4% was observed in the early-seasoned Serpnevyi variety and the mid-grade variety. Ontario had a much lower vitality index at 92.3-92.5%.

A possible explanation for this interaction may have to do with biological characteristics of the rice variety, and weather conditions present during the years of research.

Filamentary, as an indicator of the quality of rice grains, was significantly dependent on the quality of irrigation water. The difference between the ripeness of studied groups and the grades of one group was contrasting, mathematically speaking. For the quality of the quality index - film, the best on both irrigation backgrounds was the early-seeded Serpnevyi, and the worst - the middle-aged variety - Ontario. The prevalence of early-breed Prestyzh and mid-aged Vikont varied in the studied irrigation backgrounds within the range of 17.8-18.9%.

A significant indicator of the quality of rice grains is the yield of groats. The magnitude of the surveyed indicator in the early-frozen Prestyzh variety, the mid-late Vikont, and Ontario varieties was close and fluctuated within the range of 67.2-67.6%, which is less than the value LSD 0.05 – 0.57% (difference of 0.4%). The exceptional value of this indicator was Serpnevyi's early-grape variety (66.5-66.7%), its dependence on the quality of irrigation water was insignificant, the difference is much smaller LSD 0.05 – 0.57%.

Consequently, the mixing of Dnipro water with drainage and wastewater drains improved the quality of mixed irrigation water and does not impair the quality of the cultivated grain.

CONCLUSIONS

Irrigated irrespective of the quality of irrigation water, the content of protein, fat, and the content of starch increases, on the contrary. The best glass-like rice grains were early varieties, particularly Prestyzh. Filamentality, as an indicator of the quality of rice grains, has a significant difference in terms of varieties. He was the highest in Serpnevyi's early-age variety. Regarding the release of cereals, the best were varieties such as Prestyzh, Vikont, and Ontario. Rice grains contain heavy metals, residues of pesticides, and nitrates, but their actual levels are much lower than the values of the MPEC, so this grain is suitable for the manufacture of infant food products.

In order to protect the environment, preserving the ecological balance in the Black Sea bays, it is advisable for specialized farms to grow rice to reduce discharges of drainage and wastewater into the recreation zone, due to their maximum use in rice cultivation technology and related crop rotations. For this, the drainage should be mixed with Dnipro water (Dnipro - 75% + drainage and drainage runoff - 25%), which will not affect the yield or quality of rice grains and related crops, and will provide a high economic effect, ecological balance of the water resources of the Black Sea, and become the guarantor of quality rest of people in the recreational zone.

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