FERTILIZING POTENTIAL OF WASTES FROM WINE AND ETHYL ALCOHOL PRODUCTION INDUSTRY

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Abstract

In the processing of grapes and the production of alcoholic beverages, a total of about 100,000 cubic meters of wine lees, vinasse, grain mash and molasses are annually formed and accumulated in the Republic of Moldova. These wastes are characterized by a highly acidic chemical reaction and a high content of water-soluble salts. The pH ranges from 3.4 to 3.8 units. The mineral residue constitutes: 1.9 g/dm^3 in vinasse; 12.0 g/dm^3 in wine lees; and 14.9 g/dm^3 in grain mash. In the composition of monovalent cations, sodium and potassium cations predominate, which may form toxic salts if they penetrate into the soil. The cereal mashes are characterized by a higher potential of salinity and sodium enrichment. Also, these wastes contain primary nutritive elements (NPK) absolutely necessary for plant nutrition and soil fertilization. The total content of NPK in kg/m^3 in these wastes constitutes: 1.8 in vinasse; 5.1 in grain mash; 10.6 in wine lees. The dehydrated wine lees and grain mash have a high content of organic matter, 34 % and 51 % respectively. Due to their chemical composition and the highly acidic environment, they have a toxic impact on flora and fauna and a polluting action on surface and ground waters.

The administration of two doses of lees (13 and 26 t/ha), of vinasse (300 and 600 m^3/ha) and of grain mash (50 and 100 m^3/ha) favoured the significant increase of the content of organic matter, mobile phosphorus, and exchangeable potassium in the arable soil layer. The application of wine lees in the dosage of 13 - 26 t/ha ensured a significant increase of grapes by 1.4 – 2.4 t/ha, or by 15 – 25 % more than on the unfertilized control variant, on which 9.5 t/ha were harvested. The vinasse incorporated in a dosage of 300 and 600 m^3/ha had a significant impact on the plant productivity as well. The grape harvest constituted an average of 1.0 – 1.1 t/ha or by 11 – 12 % more than on the unfertilized control variant.

Keywords: *wine yeast, vinasse, grain mash, soil, humus, mobile phosphorus, waste.*

INTRODUCTION

Currently the wineries and divisions of cognac and alcohol production at republican level accumulate about 20-25 thousand tons of wine lees, not less than 50 thousand cubic meters of vinasse and 45-50 thousand of cubic meters of grain mash and molasses as wastes (Statistical Year Book of the Republic of Moldova, 2014). The total volume of wastes in the wine industry is impressive and in continuous growth. The mineral residue of such wastes makes up to 2.0 – 2.7g/dm^{3}which characterizes them as liquids with high mineralization. The SAR indicator is 6.0 higher, while the Stebler coefficient is 9 -16, the norm being 18 and more. The grain mashes have a higher salinity potential, their Stebler coefficient being of 6-7. The greatest danger of saline and alkaline contamination of the soils can be caused by their abusive incorporation and uncontrolled discharge.

The given wastes also contain primary elements necessary for agricultural plant nutrition and soil fertilization, which need insistent recovery. About 210 kg of nitrogen, 100 kg of phosphorus and 750 kg of total potassium are contained in 100 m^3 of wine lees. The grain mashes and the vinasse are less concentrated in nutritive elements, but they are not to be overlooked. These wastes are not used in any way; moreover there are no regulations on their disposal. The mentioned wastes originate from agriculture, so all the elements contained in them are taken from the soil. It would be fair if the soil could recover them through fertilization. The amount of wastes subjected to the study was of about 100,000 tons per year, which contain about 28 thousand of organic matter, 180 tons of total nitrogen, 82 tons of total phosphorus and 257 tons of total potassium.

Being continuously accumulated and discharged without any norms, such wastes cause a polluting impact on the environment, especially on the soil and ground waters [2,3]. There is little research done on their properties and application in agriculture [4, 5, 7, 8, 11] at international level and it is entirely absent in the Republic of Moldova. In this context, it is imperative to solve the issue of the mentioned wastes by applying them in agriculture as fertilizers.

The aim of the present paper is to study the chemical composition of such wastes in order to assess their potential as soil fertilizers and their impact on crop productivity.

EXPERIMENTAL PART

The research was conducted in the period 2010 -2014 on samples of wastes originating from grape processing industry and cognac and ethylic alcohol production from cereals. Wine lees, vinasse, cereal mashes and soil served as object of study. The investigations and observations on the assessment of the fertilizing potential of wine lees, vinasse and cereal mashes were carried out at the Experimental Station « Codru » from Chisinau. The experience is located on silt-clay levigated chernozem which contains: humus - 4.31 % ; accessible P_2O_5 – 34.2 ppm; accessible K_2O – 430 ppm ; pH 6.8. The wastes were applied on a grape-bearing vineyard of the sort Sauvignon. The scheme of the experience includes the following variants: 1 – unfertilized

control; 2. –fertilized with wine lees, 13 t/ha (equivalent to N_{100}); 3. - fertilized with wine lees, 26 t/ha (equivalent to N_{200}); 4. –fertilized withvinasse 300 (equivalent to K_{450}); 5 – fertilized with vinasse 600 (equivalent to K_{900}). The research area of the plot was of 55 m^2; the number of repetitions – 3. The testing of the grain mashes was also performed on silt-clay levigated chernozem according to the following scheme: 1 – unfertilized control; 2 – fertilized with grain mashes, 50 m^3/ha (equivalent to N_{120}); 3. – fertilized with grain mashes 100 m^3/ha (equivalent to N_{240}), the research area of the plot is of 120 m^2; the number of repetitions – 4.

The following methods were used in the analysis of the wastes: humidity - STAS 26713-85, organic matter - STAS 27980-88, pH – STAS 27979-88; ashes - STAS 2671 -85, total nitrogen – STAS 26715-75, total phosphorus - STAS 26717- 85, total potassium - STAS 26718 - 85, $N–NO_3$ –after Grandval – Leaju, $N–NH_4$- STAS 26716-85, aqueous extract STAS 26428- 85.

The methods used in soil analysis are the following: - humus – after Tiurin method; $N-NO_3$ –after Grandval – Leaju; mobile phosphorus – by colorimetric dosage determination after Macighin; exchangeable potassium after Macighin through photo-metering flame; pH- potentiometric method; aqueous extract - STAS 26428-85. The statistical processing of the results obtained within the investigation was performed according to B. Dospehov [9].

REZULTS AND DISCUSSION

Wine lees is a waste of the wine industry, which is formed as result of grape juice fermentation with yeast. As a rule, about 10-15% of wine lees is formed from the amount subjected to fermentation, which is in a semi-solid state with a content of solid matter of 12-13%.

Currently, depending on the existing equipment, the wineries extract ethylic alcohol from wine lees through distillation. In addition, they can be dehydrated by press-filters. With or without dehydration the lees is discarded into the environment. The carried out research (Gh., Duca, 2011;O. Chiseli□a, 2010) regarding the possibility to use them as nutritive additions in animal fodder is very interesting. The solid lees is characterized by a content of 48 % humidity, 46.8 % organic matter and 5.3 % of ashes. Potassium, nitrogen and phosphorus predominate among the biophile elements. The content is of 2.6; 1.5 and 07 % respectively in the natural humidity mass (Table 1). One ton of such yeasts contains 48 kg of NPK, with a ratio of 1:0,5:1,7 of these elements, which approximately corresponds to the nutritive needs of the main crops. The proportion of carbon:nitrogen constitutes 16:1, being similar by nitrogen release ability to that of the manure 17:1.

Table 1

Chemical composition of solid wine yeasts from wineries, related to the natural humidity mass

Component and measure unit	x	min	max	S	V %	Sx	Sx%	∆x (±)
pH	3.5	3.20	3.7	0.12	3.5	0.07	2.0	0,2
Humidity , %	48.0	42.0	58.9	9.6	20.0	5.5	11.6	18
Organic matter,%	46.8	38.3	50.3	9.5	20.3	5.5	11.7	17,6
Ash, %	5.3	2.8	8.8	3.1	55.0	1.7	32.0	5.1
Carbon, % C	23.4	19.2	25.5	1.2	5.2	0.6	2.6	2.0
Total nitrogen, % N	1.5	0.77	1.81	0.6	40.0	0.35	23.0	1.1
N-NO_3, ppm	16	7,1	26	0.68	42.5	0.30	0.002	9,9
N-NH_4, ppm	329	269	517	2.41	7.32	1.08	3.28	35,5
Total phosphorus,%P_2O_5	0.70	0.60	0.79	0.12	18.5	0.07	10.6	0.2
Total potassium, %K_2O	2.6	2.3	2.7	0.26	10.2	0.15	5.8	0.5

Note: x – average arithmetic value; min – the minimum encountered value; max –maximum encountered value; S –standard deviation of the average; v – variation coefficient; Sx – precision of average in absolute quantity; Sx% - relative precision of average; ∆x – interval of average likelihood at 95% probability.

The liquid wine lees is characterized by a high content of water, about 95,0 %.The content of organic matter and minerals is of 3.4 % and 1.2 % respectively. Total potassium, nitrogen and phosphorus prevail among biophile elements (Table 2). The contents of total potassium constitutes an average of 0.75 %, total nitrogen – 0,21 % and total phosphorus – 0.1 %. Among the cations, monovalent potassium and sodium prevail. Their concentration constitutes 4.2 and 0.47 g/dm3 respectively. Among the bivalent cations, calcium – 240 mg/dm^3 and magnesium 92 mg/dm^3 prevail. Sulphates prevail in the composition of anions. Their concentration makes up on average 0.34 g/dm^3, and 0.13 g/$dm^3$of the chlorine. In the mineral form of nitrogen, N-NH_4 - 121 mg/dm^3prevails and N-NO_3 constitutes 13 mg/dm^3. A cubic meter of lees contains 10.3 kg of NPK. They can be used as a source of nutritive elements.

Table 2

Chemical composition of waste from grape processing and alcohol production

Component and unit of measure	Wine lees	Vinasse	Grain mash
Total phosphorus, % P_2O_5	0.1±0.07	0.02±0.01	0.12±0.07
Total potassium, % K_2O	0.75±0.60	0.12±0.05	0.11±0.02
Humidity, %	95.2±2.3	98.5±1.01	93.4±1.6
pH	3.8±0.7	3.4±0.4	3.7±0.3
Total residue, g/dm^3	46.0±29	15.2±9.2	66.3±4.8
Mineral residue, g/dm^3	42±28	13.5±1.3	14.9±1.4
organic matter, %	34.0±28	1.7±1.2	51.4±5.3
Total nitrogen, % N	0.2±0.2	0.02±0.01	0.28±0.04
N-NO_3, mg/dm^3	13±8	9.5±9.0	5.8±3.6
N-NH_4, mg/dm^3	121±59	67.4±35.6	14.3±6.2
Ca^{+2}, mg/dm^3	240±99	106±33	97±27
Mg^{+2}, mg/dm^3	92±52	84±42	234±86
Na^{+}, mg/dm^3	471±158	172±51	450±194
K^{+}, mg/dm^3	4188±2085	579±418	783±166
Cl, mg/dm^3	131±38	90±28	299±98
SO_4^{-2}, mg/dm^3	340±117	156±88	362±140

Vinasse is formed as waste as a result of wine distillation in order to get wine distillate. However, the processing of secondary products derived from wine distillation in order to obtain alcohol for cognac and rectified alcohol, as well as the wastes resulting from obtaining alcohol from molasses, doesn't currently have solutions for use. The vinasse derived from secondary wine products distillation is primarily used for obtaining tartaric acid compounds. Not being used for other purposes (such as obtaining food for animals), it is basically discharged into the sewer system preventing the development of aerobic biological processes, currently used in wastewater treatment plants, and also significantly damaging the environment [3, 10].

We studied the composition and properties of this waste in terms of its influence on the agrochemical and agro-ameliorative soil properties. We have determined the indicators that directly contribute to the soil quality modification to use vinasse, if possible, as a fertilizing source for the soil and to diminish the negative impact on the quality of natural waters, as result of its direct discharges into surface waters.

From this point of view, vinasse is characterized by an acid environment, pH ranges from 3.0 to 3.8 with an average value of 3.4 units. Dry residue varies from 6.0 to 24.4 g/dm^3, forming an average of 15.2 g/dm^3. The content of organic matter constitutes on average 13.3 g/ dm^3, with a variation between 0.6 to 26 g/dm^3. Mineral compounds content ranges from 0.6 to 3.2 g/dm^3 with an average of 1.9 g/dm^3. The potassium content, with an average value of 0.12 %, prevails in vinasse composition among the biophile elements. The content of total nitrogen and phosphorus makes up an average of 0.02 %. Ammoniacal nitrogen constitutes about 34 % of the total nitrogen content (Table 2). Monovalent cations prevail in vinasse; potassium – 579 and sodium – 172 mg/dm^3. The concentration of the bivalent cations, calcium and magnesium is of 106 and 84 mg/dm^{3}on average, with a corresponding variation from 83-42 to 129-126 mg/dm^3. Sulphates content prevails among anions. Their concentration is of 155 mg/dm^{3}on average. Chlorine content ranges from 62 to 118 mg/dm^3 forming 90 mg/dm^{3}on average.

In recent years, the industry for producing ethylic alcohol from cereals (wheat, barley, corn) is actively developing. According to the calculations based on data contained in the Statistical Yearbook of the Republic of Moldova, 2014, in recent years, about 50 thousand cubic meters of grain mash are annually formed in the Republic of Moldova. The specialized literature indicates that almost a third of the dry corn raw material gets into the mash. The content of dry matter in the mash varies between 4 and 8 %, and it is predominantly formed of protein substances, hemicellulose, cellulose, starch, pentose, etc. [6]. We have studied the composition and properties of the grain mash, in terms of its influence on soil ameliorative properties, in order to exploit it as a source of soil fertilization and to decrease its negative impact on the environment.

The grain mash is characterized by containing 93.4 % of water and 6.63 % of dry matter. The content of organic matter varies from 45.9 to 56.9 g/dm^3 with an average value of 51.4 g/dm^3. The mineral residue makes up to 14.9 g/dm^3 with a value of 8.7 %. Among the biophile elements, nitrogen content prevails – 0.28 %, phosphorus - 0.12 % and potassium - 0.11 % (Table 2).

Having analysed the aqueous extract we concluded that the grain mash has an acid reaction with an average value of pH of 3.7 units and varies from 3.4 to 4 units. Among the cations, monovalent potassium and sodium cations prevail – 783 and 450 mg/dm^{3}correspondingly. The concentration of calcium and magnesium cations is of 97 and 234 mg/dm^{3}in average respectively. Sulphates prevails among anions. Their content is on average of 357 mg/dm^3. Chlorine ions concentration varies from 202 to 397 mg/dm^3 with an average value of 299 mg/ldm^3. Grain mash can be used as a fertilizing source considering its biofile elements and the organic matter it contains.

The average data, obtained in a four-year period, demonstrated that the administration of lees in a dosage of 13 and 26 t/ha, leads to a significant increase of the content of organic matter and exchangeable phosphorus in the 0-30 cm soil layer. The increase of the organic matter in the arable layer constituted 0.23% and 0.39 % or 6168 and 10374 kg/ha respectively. The average value of accessible phosphorus, compared to the control variant, grew by 4.7 ppm or 10.6 – 14.5 kg/ha. Incorporation of vinasse in the dosage of 300 (K_{450}) and 600 m^3/ha (K_{900}) also leads to a significant increase of the content of organic matter, mobile phosphorus and exchangeable potassium. The increase of the organic matter compared to the control variant in the 0-30 cm soil layer constituted 0.22 and 0.34 % or 5852 and 9044 kg/ha, of the mobile phosphorus - 2.0 – 3.6 ppm or 4.5 – 8.1 kg/ha (Table 3).

Table 3

Impact of wine waste on the content of nutritive substances in the 0-30 cm layer of levigated chernozem (Technological-experimental Station „Codru")

Variant	organic matter ,%			P_2O_5, ppm			K_2O, ppm		
	average 2011-2014	Increase compared to control variant		average 2011-2014	Increase compared to control variant		average 2011-2014	Increase compared to control variant	
		%	kg/ha		ppm	kg/ha		ppm	kg/ha
Control	4.05	-	-	22,5	-	-	290	-	-
Wine lees, 13 t/ha	4.28	0.23	6118	27.2	4.7	10.6	360	70	160
Wine lees, 26 t/ha	4.44	0.39	10374	28.9	6.4	14.5	380	90	206
Vinasse, 300 m^3/ha	4.27	0.22	5852	24.5	2.0	4.5	400	110	251
Vinasse, 600 m^3/ha	4.39	0.34	9044	26.1	3.6	8.1	440	150	342
DL 05,%	0.17	0.17	4522	1.5	1.5	3.4	67	67	153
P, %	5.1	5.1	5.1	8.9	8.9	8.9	9.1	9.1	9.1

Fertilization with grain mash in the dosage of 50 (N_{120}) and 100 m^3/ha (N_{240}) led to a significant increase of the content of organic matter and mobile phosphorus in the soil. The value of the organic matter increase on average for a period of three years constituted 0.15 % and 0.25 % or 3780 and 6300 kg/ha and of mobile phosphorus – 2.1 and 4.6 ppm or 4.7 and 10.4 kg/ha. As for the accessible potassium content, a sure increase compared to the control variant was statistically recorded at the incorporation of vinasse in the dosage of 300 and 600 m^3/ha and of grain mash in the dosage of 100m^3/ha (Table 4).

Table4

Impact of grain mash on the content of nutritive substances in the arable layer of levigated chernozem

Variant	organic matter ,%			P_2O_5, ppm			K_2O, ppm		
	average 2011-2014	Increase compared to control		average 2011-2014	Increase compared to control		average 2011-2014	Increase compared to control	
		%	kg/ha		ppm	kg/ha		ppm	kg/ha
Control	2.93	-	-	23.1	-	-	260	-	-
Grain mash, 50 m^3/ha	3.08	0.15	3780	25.2	2.1	4.7	290	30	68
Grain mash, 100 m^3/ha	3.18	0.25	6300	27.7	4.6	10.4	320	60	136
DL 05,%	0.12	0.12	2048	1.4	1.4	6.9	38	38	63
P, %	8.2	8.2	8.2	7.3	7.3	7.3	10.7	10.7	10.7

The results of the research conducted over a period of four years with the application of wine wastes in the cultivation of grape-vine and field crops demonstrate that they have a beneficial impact on plant productivity (Table 5). Application of wine lees in the dosage of 13-26 t/ha annually, ensured a significant increase of grape harvest on average by 1.4 – 2.4 t/ha, or by 15-25 % more compared to the unfertilized control variant (9.5 t/ha).

Vinasse incorporated in a dosage of 300 and 600 m^3/ha annually had a significant beneficial effect on the productivity of grapevines as well. The increase of harvest on average per year constituted 1.0 – 1.1 t/ha or 11-12 % more compared to the unfertilized control variant.

Table 5

Impact of wine wastes on Sauvignon grape harvest obtained on cambic chernozem, t/ha

Variant	Grape harvest by year of research				Average for four years		
	2011	2012	2013	2014	t/ha	Harvest increase	
						t	%
Control	9.8	7.6	10.6	9.8	9.5	-	-
Wine lees,13 t/ha	10.8	8.7	11.9	12.0	10.9	1.4	15
Wine lees, 26 t/ha	10.9	8.8	14.1	13.9	11.9	2.4	25
Vinasse, 300 m^3/ha	10.8	8.7	12.0	10.5	10.5	1.0	11
Vinasse, 600 m^3/ha	10.6	8.5	12.6	10.6	10.6	1.1	12
DL 05%	0.60	0.64	0.94	0.75	-	0.73	-
P, %	14.3	15.1	17.2	16.1	-	15.7	-

Table 6

Impact on field crop harvest fertilized with grain mash, kg/ha

Variant	Main crop production			Average for three years, cereal units		
	2012, sunflower	2013, Winter wheat	2014, sunflower	kg/ha	Harvest increase	
					kg	%
Control	1230	3818	1170	2449	-	-
Grain mash, 50 m^3/ha	1840	5673	1790	3670	1221	50
Grain mash, 100 m^3/ha	2070	6183	1980	4046	1597	65
DL 05,%	223	520	172	-	305	-
P, %	10.4	12.3	11.6	-	11.4	-

The research has shown that fertilization with grain mash led to a significant increase of field crop productivity. Grain mash applied annually in a dosage of 50 and 100 m^3/ha (equivalent to N_{120} and N_{240}) contributed to obtaining some average increases of production from 1221 to 1597 kg/ha of cereal units or by 50-65 % more compared to the unfertilized control variant.

Conclusions

The incorporation of wastes into the soil as fertilizers contributed to the improvement of levigated chernozem fertility and the growth of crop productivity. Fertilization with wastes from alcoholic beverages production led to a significant increase of the content of organic matter (0.15–0.39 %), of the mobile phosphorus (2.0–6.4 ppm) and of the exchangeable potassium (60 – 150 ppm).

Application of wine lees secured significant increase in the production of grapes (Sauvignon) by 1.4 – 2.4 t/ha on average for a period of four years. The incorporation of vinasse led to an increase of harvest by 1.0 – 1.1 t/ha on average. The applied grain mash contributed to obtaining an average increase of vegetal production by 1200 – 1600 kg/ha cereal units or by 50-65 % compared to the unfertilized control variant. Annual incorporation for a period of four years of wine lees in the dosage of 13 t/ha and of vinasse in a dosage of 300 m^3/ha into grapevines formed a total harvest of 10.9 – 10.5 t/ha ensuring a specific increase in grapes of 8.8 kg/ m^3 from vinasse and 210 kg/t from lees. The quality indicators of the crops have improved under the action of the applied wastes.

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