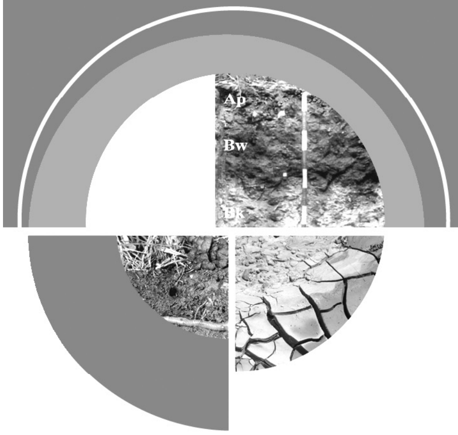

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Aggregate size distribution and geometric mean diameter affected by polymers (PVA&PAM) and humic acid applications under wetting-drying processes

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Abstract

Wetting/drying (WD) processes affect on soil structural and hydraulic properties. The objective of this study was to determine effects of organic polymers (polyvinylalcohol-PVA and polyacrylamide-PAM) and humic acid (HA) on aggregate size distribution (ASD) and geometric mean diameter (GMD) of soils under wetting/drying (W/D) processes. Soil samples were collected from four commonly distributed soil great groups; Typic Ustert, Fluvaquent, Argiustoll and Calciorthid in Erzurum. Soil samples passed through 4.76 mm sieve were treated with 0,05% PVA, 0,01% HA and 0,001% PAM on weight to weight basis and left to WD processes (3, 6 and 9 times) at different moisture levels (field capacity and 90% of saturation). Significant differences were obtained in ASD of treated and non-treated soil samples. In the control sample, the highest proportion (37.3%) of soil aggregate size group had a size of smaller than 0.42 mm, and the lowest proportion (12.9%) had the size of 0.42-0.84 mm. The GMD of soil aggregates in the control changed between 1.46 mm and 1.68 mm. On the average, the proportions of the aggregate size groups of <0.42, 0.42-0,84 and 0,84-2 mm decreased with the rates of 73.0, 32.3 and 2.0%, respectively in the samples treated with PVA, PAM and HA, but , the proportions of the aggregate size group of 2-6,4 mm increased with a rate of 24.3%. Significant amounts of new aggregates greater than 6.4 mm also formed with PVA, PAM and HA applications. Humic acid application was the most effective treatment in increasing of the GMD. The WD cycles decreased the proportions of the aggregate size groups of <0,42, 0,42-0,84, 0,84-2 and 2-6,4 mm, but increased 6,4-12,7 and >12,7 mm aggregate proportions in all the moisture levels. The GMD significantly increased after WD processes. Changes in the proportions of aggregate size groups following WD cycles was the lowest in PVA treated samples as compared to the PAM and HA applied samples. This result suggests that PVA is more effective in stabilizing soil aggregates and on reducing negative effects of WD processes on the stability of small size soil aggregates.

Key words: PVA, PAM, HA, wetting/drying processes, aggregate size distribution, geometric mean diameter

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INTRODUCTION

Wetting-drying (W/D) processes affect on soil structural parameters. Increasing in soil water content by precipitation, irrigation or capillarity and decreasing by solar radiation and wind cause consequences in wetting and drying processes (Rajaram and Erbach 1998; Six et al. 2004; De Oliveira et al. 2005). Many researchers reported that W/D processes altered soil structure leading aggregate formation (Richardson 1976), increasing soil strength (Dexter et al. 1984) and decreasing aggregate stability (Tisdall et al. 1978).

Upon wetting, soil detachability and dispersion occur depending on dispersion of cement material, decrease in cohesion, captured air in soil pores and soil shrinkage. The effects of these factors depend on the initial soil moisture content, wetting procedure and time for wetting (rapid wetting) (Grant and Dexter 1990; Barzegar et al. 1995; Hillel 1998). The effects of W/D processes on soil aggregate stability are complex; some researchers reported that W/D cycles caused increases in aggregate stability (Misra and Teixeira 2001) but some others reported inverse effects (Barzegar et al. 1995; Staricka and Benoit 1995; Denef et al. 2001). Pillai and McGarry (1999) emphasized that W/D processes encourage new aggregate formation and improve soil structure in weakly structured or compacted soils. Grant and Blackmore (1991), Wenke and Grant (1994) and Sarmah et al. (1996) pointed out that W/D processes improve soil structure of Vertisols. Materechera et al. (1992) studied the effects of W/D cycles on aggregate strength and formation in coarse and fine textured soils, and reported that W/D processes increased aggregate strength and the proportion of small-size aggregates. Similarly, Dorioz et al. (1993) found that W/D processes increased microaggregate formation in soils. On the other hand, Haynes and Swift (1990) and Six et al. (2004) reported that W/D processes inversely affect on aggregate stability of agricultural soils, because of their low organic matter contents and rapid wetting. Rajaram and Erbach (1999) left a clay-loam soil at different moisture contents 27, 33 and 40 % for drying and recorded changes in physical properties. They obtained that cone penetration, cohesion and adhesion forces and aggregate size increased, but mechanical stability decreased upon drying. In recent years, a significant number of studies on the effects of different organic-sourced soil stabilizers including synthetic polymers (polyvinyl-alcohol-PVA and polyacriylamide-PAM) and humic acid (HA) on soil structural improvement have been reported. In many of these studies it was reported that application of synthetic organic polymers or humic acid on to soil surface even with very low concentrations have positive effects on aggregate stability (Sojka and Lentz 1994; Nadler et al. 1996; Amezketa 1999; Sivapalan 2002). Many researchers reported that organic polymers applied to soil by sprinkled on soil surface or dissolved in water improved soil aggregation and increased aggregate stability (Bronick and Lal 2005; Chizoba and Chinyere 2006; Kukal et al. 2007). In a study by Piccolo et al. (1997), it was found that W/D processes decreased aggregate stability, but 0.1 g kg^{-1} humic acid application increased the resistance of soil aggregates against inverse effect of W/D processes.

The objective of this study was to determine effects of organic polymers (polyvinylalcohol and polyacrylamide) and humic acid on aggregate size distribution and geometric mean diameter of soils under wetting/drying (W/D) processes.

MATERIALS AND METHODS

Surface samples from the 0-20 cm depth of four soil great groups commonly distributed in Erzurum province; Typic Ustert, Fluvaquent, Argiustoll and Calciorthid were collected, air dried and passed through from the sieves with openings of 2 mm and 4.76 mm. Particle size distribution, aggregate size-distribution, wet aggregate stability (WAS), geometric mean diameter (GMD), soil pH, organic matter content, $CaCO_3$ content, electrical conductivity and cation exchange capacity were determined using the standard methods (Page et al., 1982; Klute, 1986).

The characteristics of the polymers and humic acid used in this study are as follows: PVA; white-granular, molecular weight of 72000 g mol^{-1}, density of 0.4-0.6 g cm^{-3}, 99.5% solubility in water at 70°C , with a chemical formula of $[-CH_2CHOH-]_n$; PAM; high molecular weight (~10000 Mg mol^{-1}), density of 1,19 g cm^{-3}, 100% solubility in water, linear bonded with an chemical formula of $[-CH_2CHCONH_2-]_n$, and HA; leonardit-originated, liquid, contains 26% total humic and fulvic acids and soluble in water.

Soil samples passed through 4.76 mm sieve were treated with PVA (0.05% *w/w*), PAM (0.001% *w/w*) and HA (0.01% *w/w*). The application dose of each treatment was defined by considering the effective dose studies in literature (Piccolo et al., 1997; Kukal et al., 2007; Aksakal and Öztaş, 2010).

The treatments were arranged in a factorial design with 3 replications, and comprised 4 soil types, 4 treatments (control, PVA, PAM and HA), 2 moisture levels for wetting (field capacity, 90% of saturation), and 3 wetting-drying cycles (3, 6 and 9 times).

The PVA, HA and PAM treated samples were separated into different aggregate size fractions (<0.42, 0.42-0.84, 0.84-2, 2-6.4, 6.4-12.7 and >12.7 mm) and the proportion of each size group and its geometric mean diameter was calculated at the end of the W/D cycles. Analysis of variance (ANOVA) was used to determine the treatment effects, and Duncan's multiple comparison test procedure was used for comparing the means (SAS Institute, 1989).

RESULTS AND DISCUSSION

Some physical and chemical properties of the soils studied are given in Table 1. Vertisol and Entisol soils are clay, Mollisol soil is clay-loam and Aridisol soils is loam textured with moderate (Entisol&Aridisol) and low (Vertisol&Mollisol) amounts of organic matter content.

Table 1. Some physical and chemical properties of the soils studied

Property	Vertisol	Entisol	Mollisol	Aridisol
Clay, %	67.5	42.4	31.5	25.4
Silt, %	15.7	29.9	33.7	29.5
Sand, %	16.8	27.7	34.8	45.1
Textural class	C	C	CL	L
Coarse skeleton material, %	2.2	3.2	1.0	16.1
WAS	26.9	45.7	41.1	52.9
GMD	1.68	1.46	1.67	1.65
pH, (1:2,5 water)	7.59	7.96	7.96	7.09
EC, µmhos cm^{-1}	180	295	315	235
Organic matter, %	1.26	2.66	1.87	2.92
$CaCO_3$, %	0.42	15.83	2.53	0.28
CEC, cmol kg^{-1}	47.1	42.8	36.6	40.2

The average wet aggregate stability (WAS) was the highest in Aridisol and the lowest in Vertisol. However, geometric mean diameter (GMD) was almost the same for the soils studied, except for Entisol. The PVA, HA and PAM applications increased aggregate stability of soils There were statistically significant differences in aggregate stability values between the soils and the treatments at $p<0.01$ significant level (Table 2).

Table 2. Multiple comparison test results for the treatments on soil aggregate stability

Soils	Treatments			Mean
	PVA	HA	PAM	
Vertisol	51.3a	31.2b	29.5b	37.3C
Entisol	79.7a	47.3b	49.8b	59.0B
Mollisol	82.4a	44.8b	44.3b	57.2B
Aridisol	85.8a	53.3b	57.3b	65.5A
Mean	74.8A	44.2C	45.2B	

On the average, while the initial aggregate stability values (the overall mean of aggregate size fractions) of the soils were 18.5, 36.5, 36.9 and 42.6 %, they were 37.3, 59.0, 57.2 and 65.5% for Vertisol, Entisol, Mollisol and Aridisol, respectively, after treatment applications. The PVA was the most effective treatment on aggregate stability. The mean aggregate stability of four soils was 33.6% (the control-untreated samples). It was increased up to 74.8 % with an increasing rate of 122.5% for PVA, to 44.2% with an increasing rate of 31.4% for HA and to 45.2% with an increasing rate of 34.5% for PAM.

The proportions of soil aggregates into different aggregate size fractions before and after PVA, HA and PAM applications and the multiple comparison test results are given in Table 3.

Table 3. Proportions of soil aggregates into different aggregate size fractions before and after PVA, HA and PAM applications

Soils	Treatments	Aggregate size groups					
		<0.42	0.42-0.84	0.84-2.0	2.0-6.4	6.4-12.7	>12.7
		Before treatment applications					
Vertisol	Control	35.91a	13.08d	22.47c	28.54b	-	-
Entisol	Control	41.47a	13.03c	22.43b	23.08b	-	-
Mollisol	Control	37.55a	12.38d	21.26c	28.82b	-	-
Aridisol	Control	34.18a	12.97c	26.14b	26.72b	-	-
a: small letters show differences between aggregate size groups							
		After treatment applications					
	PVA	9,58cA	10,59cA	24,03bA	33,02a	21,02bB	1,78d
Vertisol	HA	1,60dB	1,64dB	11,73cB	36,54b	44,58aA	3,92d
	PAM	5,77cAB	5,99cC	18,56bAB	33,40a	32,33aAB	3,97c
Mean		5,65C	6,07C	18,10B	34,32A	32,64A	3,22C
	PVA	14,62c	11,51cd	22,44b	30,61aB	13,07cd	7,76dA
Entisol	HA	8,06d	9,15d	27,48b	34,85aA	18,51c	1,96eB
	PAM	12,35cd	9,98d	24,60b	35,11aA	15,99c	1,99eB
Mean		11,67D	10,21D	24,84B	33,52A	15,86C	3,90E
	PVA	10,26c	9,63c	23,72abA	31,21a	18,22bcB	6,97c
Mollisol	HA	4,50d	4,76cd	18,53bB	31,32a	32,19aA	8,71c
	PAM	11,89c	8,89c	21,32bAB	32,32a	22,51bB	3,08d
Mean		8,88C	7,76C	21,19B	31,62A	24,30B	6,25C
	PVA	20,23cA	13,61dA	26,70b	30,22aB	8,55eB	0,70f
Aridisol	HA	8,01cB	8,47cB	25,89b	35,34aA	20,09bA	2,23c
	PAM	13,82cAB	10,32cAB	26,40b	35,57aA	12,23cB	1,68d
Mean		14,02C	10,80D	26,32B	33,71A	13,62C	1,53E
	PVA	13,67dA	11,34eA	24,22bA	31,27aC	15,22cC	4,30fA
Avg.	HA	5,54eC	6,01dC	20,91cC	34,51aA	28,84bA	4,21fA
	PAM	10,96dB	8,80eB	22,72bB	34,10aB	20,77cB	2,68fB
Overall mean		10,06C	8,71D	22,61B	33,29A	21,60B	3,73E

a : small letters show differences between aggregate size groups for each soil

A: capital letters show differences between treatments (vertical) and the means of treatments between aggregate size groups (horizontal)

There were statistically significant differences in the proportions of aggregates among the aggregate size groups in all the control and treated soils studied. Although, no aggregate with a size greater than 6.4 mm was obtained in the control, significant amounts of aggregates were obtained in both 6.4-12.7 mm and >12.7 mm aggregate size groups of treated samples.

In the control samples, the mean proportions of aggregates in <0,42, 0,42-0,84, 0,84-2 and 2-6,4 mm size groups were 37.28, 12.86, 23.07 and 26.79%, respectively, they were 10.06, 8.71, 22.61 and 33.29 % for the treated samples. These results indicated that PVA, HA and PAM applications not only caused for producing new aggregates with a size greater than 6.4 mm, they also produced medium size new aggregates.

Table 4. Changes in the proportion of soil aggregates (W_i) in different aggregate size groups treated with PVA, HA and PAM

Soils	Aggregate size groups, mm	Control Wi, %	Mean of PVA, HA & PAM Wi, %	The rate of changes, %
Vertisol	<0,42	35,91	5,65	-84,3
	0,42-0,84	13,08	6,07	-53,6
	0,84-2	22,47	18,10	-19,4
	2-6,4	28,54	34,32	+20,3
	6,4-12,7	0,0	32,64	+∞
	>12,7	0,0	3,22	+∞
Entisol	<0,42	41,47	11,67	-71,9
	0,42-0,84	13,03	10,21	-21,6
	0,84-2	22,43	24,84	+10,7
	2-6,4	23,08	33,52	+45,2
	6,4-12,7	0,0	15,86	+∞
	>12,7	0,0	3,90	+∞
Mollisol	<0,42	37,55	8,88	-76,4
	0,42-0,84	12,38	7,76	-37,3
	0,84-2	21,26	21,19	-0,3
	2-6,4	28,82	31,62	+9,7
	6,4-12,7	0,0	24,30	+∞
	>12,7	0,0	6,25	+∞
Aridisol	<0,42	34,18	14,02	-59,0
	0,42-0,84	12,97	10,80	-16,7
	0,84-2	26,14	26,32	+0,7
	2-6,4	26,72	33,71	+26,2
	6,4-12,7	0,0	13,62	+∞
	>12,7	0,0	1,53	+∞
Mean	<0,42	37,28	10,06	-73,0
	0,42-0,84	12,86	8,71	-32,3
	0,84-2	23,07	22,61	-2,0
	2-6,4	26,79	33,29	+24,3
	6,4-12,7	0,0	21,60	+∞
	>12,7	0,0	3,73	+∞

In treated samples, while the proportion of aggregates in <0,42, 0,42-0,84 and 0,84-2 mm size groups was decreasing, the proportion of aggregates in 2-6.4 mm aggregate size group increased in addition to significant amount of new size aggregate formation in 6.4-12.7 and >12.7 mm aggregate size groups (Table 4).

The PVA, HA and PAM applications increased geometric mean diameter of soils There were statistically significant differences in GMD values between the soils and the treatments at $p<0.01$ significant level (Table 5). On the average, the treatments were the most effective in Vertisol soil and the least effective in Aridisol soil. The GMD increased from 1.68 mm to 5. 28

mm with an increasing rate of 214% in Vertisol, and from 1.65 mm to 3.38 mm with an increasing rate of 105% in Aridisol. The most effective result on increasing GMD was obtained by HA application. Over four soils, while the mean GMD was 5.06 mm with HA, it was 3.54 mm for PVA, 4.16 for PAM.

Table 5. The effects and multiple comparison test results of PVA, HA and PAM on GMD

	Vertisol	Entisol	Mollisol	Aridisol	Mean
Control	1,68aD	1,46bC	1,67aC	1,65aC	1,62D
PVA	4,05aC	3,09abB	4,36aB	2,69bB	3,54C
HA	6,47aA	3,85bA	5,80aA	4,12bA	5,06A
PAM	5,31aB	3,69bA	4,28bB	3,34bAB	4,16B
Mean	5,28A	3,54B	4,81A	3,38B	4,25
Change to control, %	+214,3	+142,5	+188,0	+104,8	+162,3

a: small letter - between soils (comparison in horizontal direction)
A: capital letters – between treatments (comparison in vertical direction)

Changes in the proportion of aggregates (Wi) in different aggregate size groups after W/D processes at different moisture levels (field capacity, 90% of saturation) and W/D cycles are given in Table 6. It is clearly seen that the proportion of soil aggregates in aggregate size groups, except for the largest size group decreased with increases in moisture content and the cycles of W/D processes. But, the decreasing rate was significantly higher in 90% sat. moisture level than field capacity.

Table 6. The proportion of aggregates (Wi) in different aggregate size groups after W/D processes at different moisture levels

Mean of soils	Treatment	Aggregate size groups, mm					
		<0,42	0,42-0,84	0,84-2	2-6,4	6,4-12,7	>12,7
Effect of wetting-drying moisture levels							
Mean	Control	16,86A	9,75A	22,73A	31,67A	16,21A	2,80C
	FC	16,66A	6,93B	15,47B	20,78B	16,85A	23,32B
	90% of sat.	12,38B	5,02C	10,88C	16,47C	14,86B	41,90A
Change, %	FC	-1,2	-28,9	-32,0	-34,4	+3,9	+732,9
	90% of sat.	-26,6	-48,6	-52,1	-48,0	-8,3	+1396,3
Effect of wetting-drying cycles							
Mean	Control	16,86A	9,75A	22,73A	31,67A	16,21A	2,80D
	3 times	13,03B	6,11B	13,76B	18,86B	15,38B	32,86B
	6 times	13,79B	5,83B	12,92C	17,70C	15,97AB	33,81A
	9 times	16,74A	5,99B	12,84C	17,08C	16,22A	31,16C
Change, %	3 times	-22,7	-37,3	-39,5	-40,4	-5,1	+1073,6
	6 times	-18,2	-40,2	-43,2	-44,1	-1,5	+1107,5
	9 times	-0,7	-38,6	-43,5	-46,1	+0,1	+1012,9

The GMD of soils increased significantly following W/D processes, since new soil aggregates greater than a size of 6.4 mm were obtained. While the GMD of the control sample was 3.59 mm, it increased to 5.73 mm at field capacity W/D processes and 7.58 mm at 90% of saturation W/D processes. In other words, the GMD increased with increasing moisture content level at W/D processes, and a significant relationship was found between the moisture content and the GMD (r^2 = 0.997) (Fig.1). Similarly, the GMD of soils also increased by increasing the number of W/D cycles. While the GMD was 3.59 mm at the control sample, it increased to 6.68, 6.80 and 6.48 mm for the 3, 6 and 9 times of W/D cycles.

Changes in the proportion of soil aggregates (Wi) in different aggregate size groups and the GMD before and after PVA, HA and PAM applications are given in Table 7 and 8.

Table 7. The proportion of soil aggregates (Wi) in different aggregate size groups before and after PVA, HA and PAM applications

Treatment	W/D Processes	<0,42	0,42-0,84	0,84-2	2-6,4	6,4-12,7	>12,7
Control mean	before	37,28	12,86	23,07	26,79	0,0	0,0
	after	21,39	7,40b	14,09	16,94	10,51	29,69
Change, %		-42,6	-42,5	-38,9	-36,8	+∞	+∞
PVA mean.	before	13,67	11,33	24,22	31,27	15,21	4,30
	after	17,55	9,50b	20,27	26,40	15,08	11,21
Change, %		+28,4	-16,2	-16,3	-15,6	-0,9	+160,7
HA mean	before	5,54b	6,00	20,90	34,51	28,84	4,20
	after	9,35a	4,16	11,45	17,87	19,62	37,55
Change, %		+68,8	-30,7	-45,2	-48,2	-32,0	+794,0
PAM mean	before	10,95	8,79	22,72	34,10	20,76	2,68
	after	11,13	5,00	12,34	18,18	18,41	34,95
Change, %		+1,6	-43,1	-45,7	-46,7	-11,3	+1204,1
Overall mean	before	16,86	9,75	22,73	31,67	16,20	2,79
	after	14,86	6,52	14,54	19,85	15,91	28,35
Change, %		-11,9	-33,1	-36,0	-37,3	-1,8	+916,1

In the PVA, HA and PAM treated samples, the proportion of soil aggregates in <0,42 mm and >12,7 mm aggregate size groups increased but the others decreased at the end of W/D processes. The GMD also increased at the end of the W/D processes in both the control and PVA, HA and PAM treated samples. The highest increase in the GMD occured in Vertisol soil of which clay content was the highest but its aggregate stability was the lowest initially (Table 8).

Table 8. The GMD before and after PVA, HA and PAM applications

Treatment	W/D Processes	Vertisol	Entisol	Mollisol	Aridisol	Mean
Control mean	before	1,68	1,46	1,67	1,65	1,62b
	after	9,22a	4,76c	6,69c	2,35c	5,76a B
Change, %		+448,8	+226,0	+300,6	+42,4	+255,2
PVA	before	4,05	3,09	4,36	2,69	3,55b
	after	6,75b	3,40d	4,55d	2,59c	4,32a C
Change, %		+66,7	+10,0	+4,4	-3,7	+21,8
HA	before	6,47	3,85	5,80	4,12	5,06b
	after	9,29a	7,18a	9,35a	4,58a	7,60a A
Change, %		+43,6	+86,5	+61,2	+11,2	+50,2
PAM	before	5,31	3,69	4,28	3,34	4,16b
	after	9,08a	6,88b	8,64b	4,16b	7,19a A
Change, %		+71,0	+86,4	+101,9	+24,6	+72,8
Overall mean	before	4,38bA	3,02bB	4,03bA	2,95B	3,60b
	after	8,59aA	5,56aC	7,31aB	3,42D	6,22a
Change, %		+96,1	+83,9	+81,3	+15,9	+72,7

CONCLUSION

The results of this study indicated that PVA, HA and PAM applications caused increases not only in aggregate stability but also in new aggregate formation and so the geometric mean diameter.

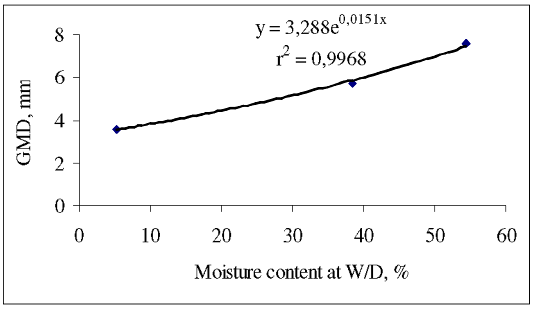

Figure 1. The relationship between GMD and the moisture level at W/D processes

The W/D processes decreased the proportion of soil aggregates in the aggregate size groups with a size of 6.4 mm, but the proportion of soil aggregates in the aggregate size groups with a size greater than 6.4 mm significantly increased. The number of W/D cycles increased the GMD at $p<0.01$ significant level, but no significant differences were obtained among the 3, 6 and 9 times W/D cycles. Similarly, the higher the moisture content of soil at W/D processes, the higher the GMD because of large-sized new aggregate formation. PVA, HA and PAM applications had significant effect of reducing negative effects of W/D processes especially on the dispersion of soil aggregates smaller than 6.4 mm size. Among the treatments the PVA was the most effective substance on protecting aggregate stability without causing clod formation.

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