



Examining the Concentration of Organonitrogen Pesticides in Water at Nile Delta, Egypt

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Abstract: In this study, Organonitrogen pesticides (ONPs) levels were determined in surface and groundwater samples from El-Rahawy area in the southwestern part of Nile Delta, Egypt. Gas Chromatography with Nitrogen Phosphorous Detector (GC-NPD) was proposed to determine the concentration of eleven ONPs, molinate, atrazine, simazine, prometon, propazine, prometryn, simetryn, ametryn, alachlor, terbutryn and metolachlor during winter and summer seasons. The most abundant components were molinate and propazine. The total concentrations of ONPs in the surface samples were from 3.9636 to 75.878 ng L⁻¹ while in groundwater were below the detection limit i.e. 0.02 ng L⁻¹. The results have been discussed and compared with Canadian water quality guidelines for irrigation and fresh water.

Key words: Organonitrogen pesticides • El-Rahawy area • Detection limit • Surface water • Groundwater

INTRODUCTION

The synthetic chemicals are a group of compounds which are absent in nature, instead they are synthesized from simpler compounds or through decomposition of more complex materials. Some of these organic chemicals are toxic and are used against various pests. There is increasing concern that certain chemicals in the environment can cause hazard in exposed humans and wildlife [1, 2].

Organonitrogen pesticides (ONPs), one kind of herbicides with high power for annual control of grass and broad-leaved weeds, have been often widely used as the selected herbicides for crop protection in agricultural domain since 1950s [3, 4]. ONPs and its degradation products occur widely in the global environment as a result of extensive use of organonitrogen compounds as a pre-and post-emergent herbicide, mainly on maize, sorghum and to a lesser degree on other crops and as a non-selective herbicide for general weed control. It is found, at generally unknown levels, in Egyptian aquatic environment. However, they are also in the list of chemical pollutants that need to be more heavily monitored due to their toxicity, persistence and accumulation in environment and their effects on the environment and human health [5].

Organonitrogen herbicides are widely used in agriculture and have been persistent in the aquatic environment for many days after their application. Due to their persistence in the environment, there is a great interest to examine the pollution which originates from these compounds. Their usage today is prohibited in Egypt as well as in other countries, after evidence of their toxicity; persistence and bioaccumulation in the environment became available [6]. The best known members of ONPs are molinate, propazine and simetryn, which are registered and used in huge quantities in agriculture to kill weeds in corn and soybean fields in Egypt [7]. The concentrations of ONPs in waters receiving runoff from agricultural lands are seasonal; the highest concentrations generally being found during the six weeks to two months after application and lower to undetectable concentrations during the rest of the year. In agricultural drains, the concentrations are highest during runoff after storms in the post-application period [8, 9].

ONPs do not adsorb as strongly to soil particles as other commercial herbicides. In most soils, it binds only weakly to soil particles depending on soil temperature, moisture and pH, it can become unbound. Its movement with soil moisture is limited by partial adsorption to soil particles, as well as its low water solubility.

Table 1: Half-life ($T_{1/2}$) for selected pesticides.

Items	Half-life (days)
Molinate	21
Atrazine	100
Simazine	30
Prometon	500
Propazine	200
Prometryn	60
Simetryn	60
Ametryn	250
Alachlor	15
Terbutryn	240
Metolachlor	90

ONPs are persistent, moderately mobile in clay loam soils (have low clay or organic matter content) and it is resistant to breakdown by hydrolysis, photolysis or biodegradation under aerobic soil conditions, degrading with half-lives of 1-15 months after the last application as shown in Table 1. For these reasons, organonitrogen compounds are of the pesticides considered by the EPA to have the smallest potential for leaching into groundwater. Typically, ONPs is found more frequently and usually at lower concentrations in groundwater than in surface water. The peak concentrations in impounded water bodies, such as wells, are usually lower than those in drains and streams; they occur at the same time but may persist for longer because of the longer residence time [10].

The purpose of the present study looked at monitoring the levels and distribution of ONPs in surface and groundwater of the El Rahawy area and estimation of seasonal variations in ONPs concentration. For this purpose a GC-NPD method for the analysis of ONPs in water extracts is proposed and the working conditions given.

MATERIALS AND METHODS

The study was conducted at Central Laboratory for Environmental Quality Monitoring and the Chemistry Department of Central Water Quality Laboratory, Greater Cairo Water Company from January to June 2010.

Chemicals and Reagents: All chemicals and reagents were of analytical grade and of highest purity possible. LC grade dichloromethane and n-hexane used for the extraction and clean up were obtained from Fisher Scientific. The silica gel used for the cleanup was supplied by BDH laboratories. The acetone and anhydrous sodium

sulphate used in this study were also obtained from BDH laboratories. A mixture of ONPs standards were obtained from Dr. Ehrenstorfer Laboratories, Augsburg, Germany. ONPs stock solutions (approximately 500 mg/l) of individual standards were prepared by dissolving about 0.05 g of pesticide in 100 ml of n-hexane and stored in a freezer at -18°C in glass bottles with PTFE-faced screw caps.

Site Description: El Rahaway drain is located in the southern part of the Nile Delta, Egypt, about 39.5 km north-west of the city of Cairo. It must be noted that, El Rahaway Drain, located between latitudes $30^{\circ} 10' \text{ N}$ to $30^{\circ} 12' \text{ N}$ and longitudes $31^{\circ} 2' \text{ E}$ to $31^{\circ} 3' \text{ E}$ as shown in Figure 1. El-Rahawy drain is about 12.41 km^2 with an average length of 4.5 Km. El-Rahawy drain passes through El-Rahawy village and many villages dotted along it receiving agricultural and domestic wastes in addition to sewage of El-Gieza governorate and discharged these wastes directly without treatment into the Nile River (Rossetta Branch). Figure 1 shows the position of each sampling site. Accordingly the sites under investigation were divided into two types of water samples were collected from El-Rahawy drain area, namely, surface water samples (collected manually) from 2 different sites along El-Rahawy drain and groundwater samples were collected from Hand pump on the observation wells which located beside El-Rahawy drain using clean glass containers (1.5 liter capacity), stored in the refrigerator at $+4^{\circ}\text{C}$ and extracted within 24 hours during rainy and dry seasons, from January to June 2010.

Sample Preparation: Liquid-liquid extraction was used for the extraction of ONPs residues from water samples. One L of each water sample was extracted with 60 ml dichloromethane in a 2 L separatory funnel. The mixture was shaken manually for 5 min, followed by collection of the lower organic layer. The extraction was repeated twice each time with 60 ml dichloromethane. The pooled 180 ml dichloromethane extracts were dried over anhydrous sodium sulfate and filtered. The solvent was evaporated to dryness under vacuum at $\leq 40^{\circ}\text{C}$ and 350 mbar [11].

Calibration and Quantification: Calibration curves were prepared from a stock solution of 10.0 mg/L ONPs dissolved in hexane by serial dilution to reach calibration concentrations of 5, 10, 20, 40 and 50 $\mu\text{g/l}$. Each calibration solution was analysed in threefold by GC-NPD [12]. The peak areas of the corresponding analytes were plotted against the calibration concentrations and the regression

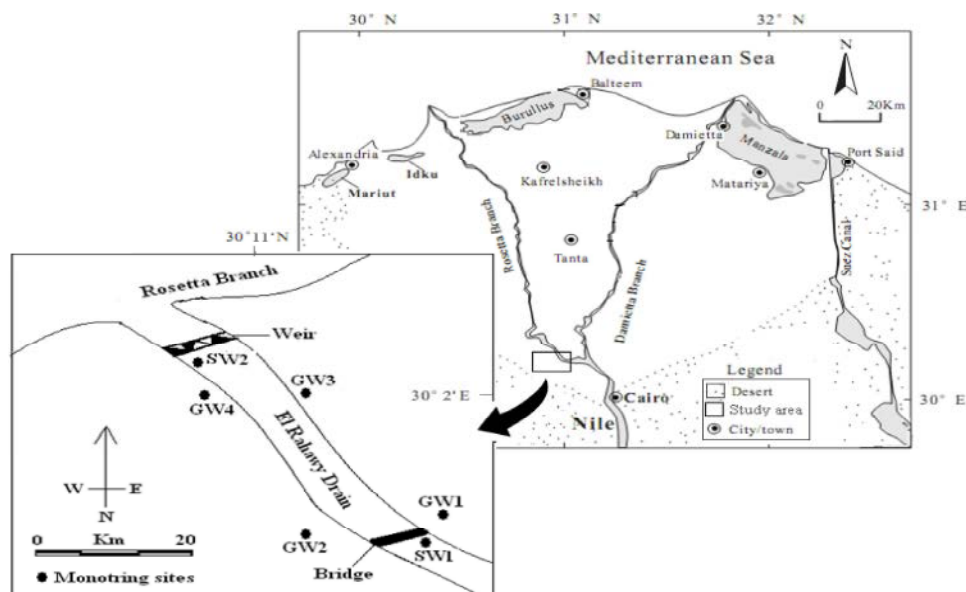


Fig. 1: Map of the study area and sampling sites

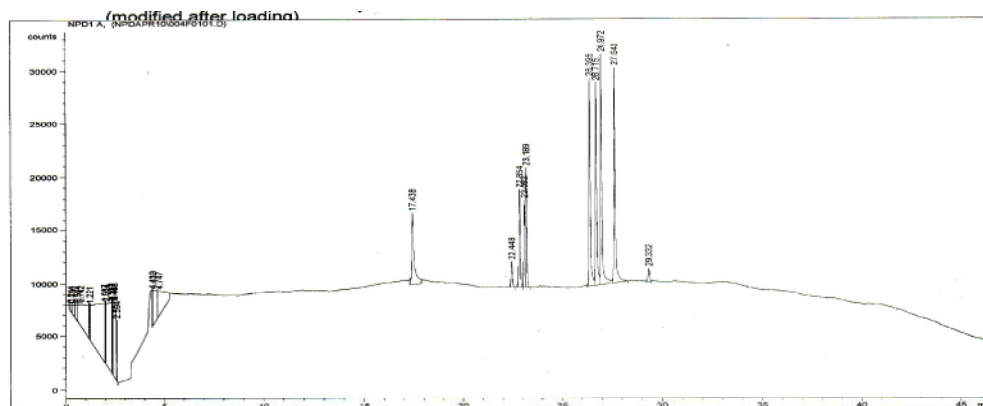


Fig. 2: GC/NPD Chromatogram of standard ONPs ($10 \mu\text{g L}^{-1}$)

coefficient was calculated reaching a mean of $r^2 = 0.9993$ for all analytes. The minimum detection limits of the methods used for extraction of ONPs residue from water is 0.02 ng/L [13]. The retention times obtained for the components of the mixture are based on a signal-to-noise ratio of 3:1, the retention times were as follows: Molinate (17.592 min), atrazine (22.626 min), simazine (22.914 min), prometon (23.302 min), propazine (23.448 min), prometryn (26.534 min), simetryn (26.846 min), ametryn (27.092 min), alachlor (27.667 min), terbutryn (27.760 min) and metolachlor (29.447 min).

Capillary Gas Chromatography-Nitrogen-Phosphorous Detector: ONPs residues in extracts of water samples were measured using a gas chromatograph (GC) and detected using a nitrogen-phosphorous detector (NPD).

The GC (Hewlett Packard, 5890 series II, with its required accessories including Hp chemstation software) was equipped with a fused silica capillary column (length of 6 m, 0.25 mm I.D. and 0.25 μm film thickness). Operating condition for the GC was summarized in one μl of the sample extract was injected with pulsed splitless on column using a HP A1773 autoinjector. The injection temperature was 250°C and Helium was used as carrier gas at a constant flow rate of 3.6 ml/min. The temperature program was 100°C held constant for 5 min, then increased by $3^\circ\text{C}/\text{min}$ to a final temperature of 300°C . The interface temperature was held constant at 280°C . Each sample was analysed twice by GC-NPD after column clean-up. Typical Chromatograms of standard and real samples extracts are presented in Figure 2.

RESULTS AND DISCUSSION

Typical chromatogram obtained for a mixed ONPs standard solution by use of GC-NPD is shown in Figure 2. Four ONPs out of eleven compounds are detected in the water samples including terbutryn, simetryn, propazine and molinate during winter and summer seasons. The last two are detected in less than 50% of samples. Propazine is detected in 2 out of 6 surface and groundwater samples analysed and propazine concentrations vary from 2.713 to 29.464 µg/L. A maximum

value is detected in SW1 during winter and low concentration of 2.713 µg/L is detected in SW1 during summer. The data are shown in tables (2 and 3) and illustrated in figures (3,4,5 and 6), indicating that propazine concentrations represent 63.1% of total concentrations of ONPs in all sampling sites [14, 15]. The variation of ONPs levels from day to day is clear in the study area according to the agricultural cycle system applied in Egypt during summer and winter season. Furthermore, the types of ONPs used are more in winter than in summer as evidenced in the results.

Table 2: Concentration of ONPs residues in water samples during winter season (µg/L)

Items	SW1	SW2	GW1	GW2	GW3	GW4
Molinate	38.912	51.885	BDL	BDL	BDL	BDL
Atrazine	BDL	BDL	BDL	BDL	BDL	BDL
Simazine	BDL	BDL	BDL	BDL	BDL	BDL
Prometon	BDL	BDL	BDL	BDL	BDL	BDL
Propazine	29.464	22.665	BDL	BDL	BDL	BDL
Prometryn	BDL	BDL	BDL	BDL	BDL	BDL
Simetryn	2.170	1.327	BDL	BDL	BDL	BDL
Ametryn	BDL	BDL	BDL	BDL	BDL	BDL
Alachlor	BDL	BDL	BDL	BDL	BDL	BDL
Terbutryn	BDL	0.001	BDL	BDL	BDL	BDL
Metolachlor	BDL	BDL	BDL	BDL	BDL	BDL
ΣONPs	70.546	75.878	0.000	0.000	0.000	0.000

BDL: below the detection limit

Table 3: Concentration of ONPs residues in water samples during summer season (µg/L)

Items	SW1	SW2	GW1	GW2	GW3	GW4
Molinate	1.2506	2.135	BDL	BDL	BDL	BDL
Atrazine	BDL	BDL	BDL	BDL	BDL	BDL
Simazine	BDL	BDL	BDL	BDL	BDL	BDL
Prometon	BDL	BDL	BDL	BDL	BDL	BDL
Propazine	2.713	3.0698	BDL	BDL	BDL	BDL
Prometryn	BDL	BDL	BDL	BDL	BDL	BDL
Simetryn	BDL	BDL	BDL	BDL	BDL	BDL
Ametryn	BDL	BDL	BDL	BDL	BDL	BDL
Alachlor	BDL	BDL	BDL	BDL	BDL	BDL
Terbutryn	BDL	BDL	BDL	BDL	BDL	BDL
Metolachlor	BDL	BDL	BDL	BDL	BDL	BDL
ΣONPs	3.9636	5.2048	0.000	0.000	0.000	0.000

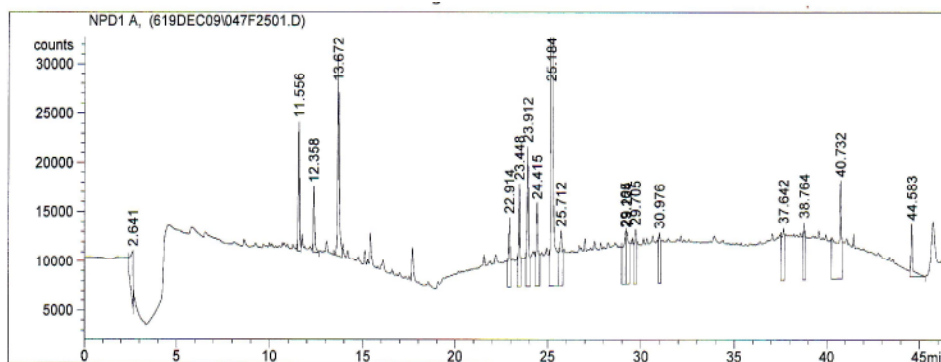


Fig. 3: GC/NPD chromatogram of ONPs residues in water samples in Winter Season at SW1

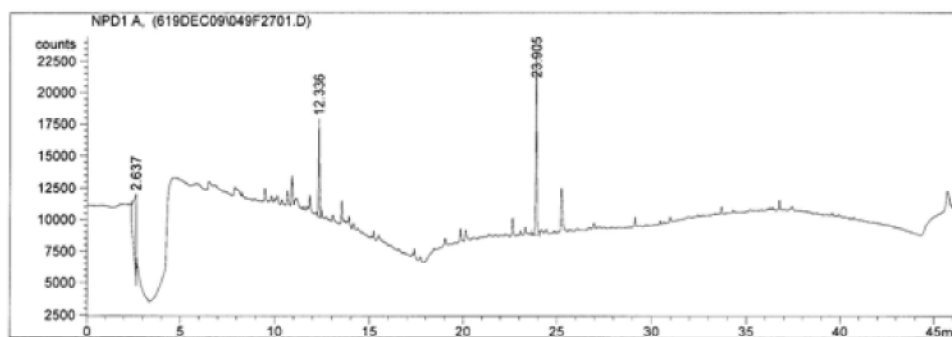


Fig. 4: GC/NPD chromatogram of ONPs residues in water samples in winter Season at SW2

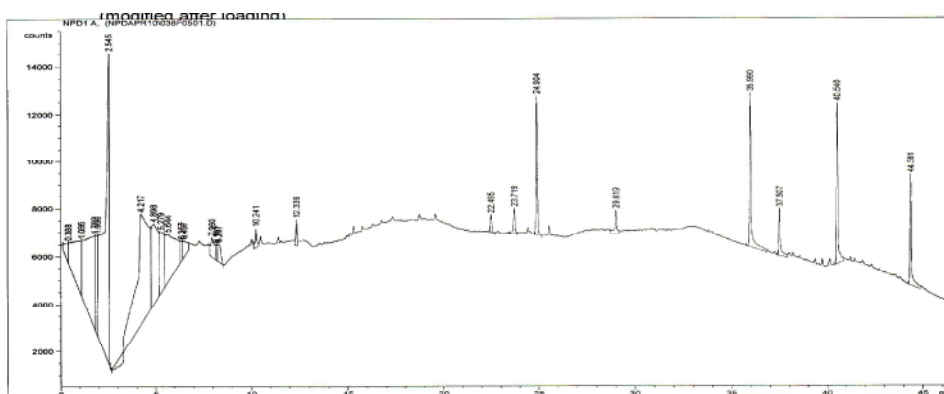


Fig. 5: GC/NPD chromatogram of ONPs residues in water samples in Summer Season at SW1

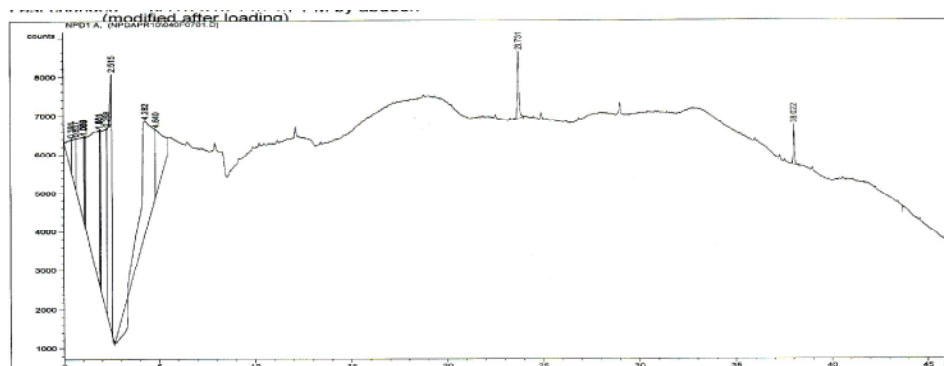


Fig. 6: GC/NPD chromatogram of ONPs residues in water samples in Summer Season at SW2

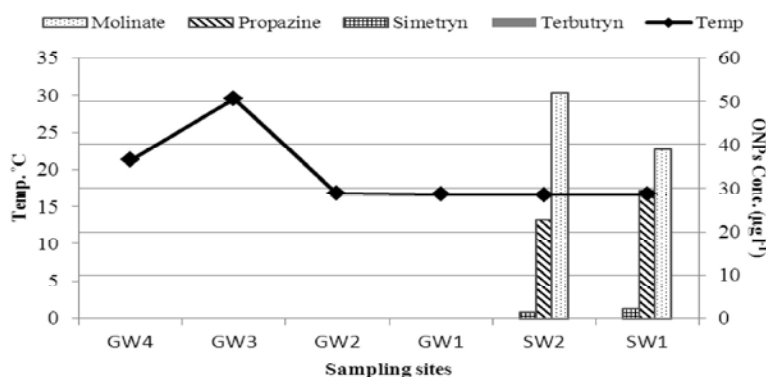


Fig. 7: Concentration of ONPs residues in water samples during Winter Season

Molinate concentrations vary from 1.2506 to 51.885 µg/L and represented 36.9% of ΣONPs. Through, it is detected in 2 out of 6 samples analysed. Minimum concentration of 1.2506 µg/L was detected in SW1 during summer and maximum concentration (51.885 µg/L) in SW2 during winter. As it is previously mentioned, the high concentration of molinate and propazine are observed in surface water samples during winter, shortly after its application on rice and corn crops. Hence, they decrease drastically at the beginning of summer [16, 17].

ONPs with the lower occurrence (one sample) terbutryn is recorded 0.001 µg/L at SW2 whereas simetryn is detected in two samples collected from SW1 (2.17 µg/L) and SW2 (1.327 µg/L). The values of other herbicides decreased quickly throughout the winter, with non-detectable levels in January [18]. In addition to the above, terbutryn did not show such high residue levels, probably due to their relatively low affinity to the water compartment.

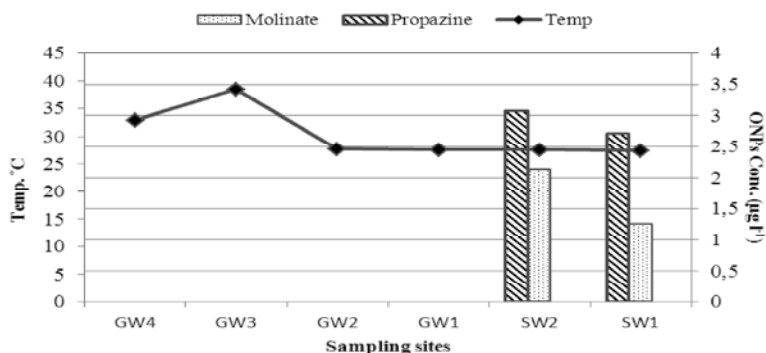


Fig. 8: Concentration of ONPs residues in water samples during Summer Season

Table 4: Concentration of ONPs residue in water according to CWQGs, 2005

ONPs	CWQGs (µg/L)	
	Irrigation water	Fresh water
Molinate	-	-
Atrazine	10	1.8
Simazine	0.5	10
Prometon	-	-
Propazine	-	-
Prometryn	-	-
Simetryn	-	-
Ametryn	-	-
Alachlor	-	-
Terbutryn	-	-
Metolachlor	28	7.8
ΣONPs	-	-

CWQGs: Canadian water quality guidelines for the protection of agricultural water uses

-: No guideline available

In general, the highest concentrations were detected in surface waters receiving runoff from agricultural lands during winter after these applications while lower to undetectable concentrations were observed during the summer because of the increased degradation of herbicides after their application [19, 20]. Finally, the presence of ONPs residues in the surface water samples during both seasons is due to the runoff from the agricultural area, which is reflected at the relatively higher concentrations at the neighboring area as shown in Figures 7 and 8. The values of ONPs concentration were below the detection limits in groundwater samples during both seasons period of 2010, probably because of the length of time needed for water to move from the surface of an agricultural field to groundwater and subsequently to a well [21]. The maximum value of ONPs concentration at SW2 during winter season was 1.840 µg/L whereas the maximum for summer was 1.024 µg/L.

Seasonal variations were observed in ONPs contamination; maximum levels were observed in January 2010 [22, 11]. Consequently, the levels of ONPs in the study area for the surface and groundwater during both seasons are still within safety margins compared to Canadian water quality guidelines for irrigation and fresh water [23] as shown in Table 4.

CONCLUSION

A GC-NPD method has been used for analysis of organonitrogen pesticides and used to monitor ONPs contamination of surface and groundwater from El Rahawy drain. The concentration of ONPs increases in the collected surface water samples from El Rahawy drain. ONPs are found more frequently and usually at higher concentrations in surface water than in groundwater. The data show that ONPs levels in groundwater are generally under the detection limits during winter and summer seasons, as a result of the length of time needed for water to move from the surface of an agricultural field to groundwater and subsequently to a well. These results indicate that reduced ONPs application rates are associated with shortness of half-life time.

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