

Investigation of the retention and release of the herbicide MCPA by soils and potential environmental impact to groundwater quality

¹EDGAR HILLER, ¹MILOSLAV KHUN, ¹LENKA ZEMANOVÁ and ²MIKULÁŠ BARTAL

¹Comenius University Bratislava, Faculty of Natural Sciences, Department of Geochemistry, Mlynská dolina, 842 15 Bratislava, Slovak Republic; e-mail: hiller@fns.uniba.sk

²Water Research Institute Bratislava, National Water Reference Laboratory for Slovakia, Nábr. L. Svobodu 5, 812 49 Bratislava, Slovak Republic

Abstract: In this paper, the retention and release of the herbicide MCPA by five different soil types was investigated at two initial concentrations in aqueous solution of 0.5 and 10 mg.l⁻¹. MCPA retention was positively correlated to soil organic matter content ($r = 0.958^{**}$ and 0.970^{**} for $C_0 = 0.5$ and 10 mg.l⁻¹, respectively). No other significant correlations between MCPA sorption and soil properties were found. Conversely, the release of MCPA from soils was negatively correlated to soil organic matter content. Experimental data indicate a primary role of soil organic components to control MCPA retention and release by soils. To estimate leaching potential of MCPA into groundwater, the measured K_{OC} values and average degradation half-life taken from literature were used. The calculated values of groundwater ubiquity score imply that MCPA is the mobile herbicide in all the investigated surface soils and has potential to contaminate groundwater, and hence it represents a threat to human health.

Key words: soils, MCPA, release, retention, groundwater quality

1. Introduction

Herbicides are widely applied for general weed control in agriculture. Increased herbicide use in agriculture has led to a general concern regarding their potential threat as contaminants in the soil and aquatic environment. Mobility of herbicides and their potential to migrate to the other compartments of the environment can be evaluated from sorption-desorption data (Bekbölet et al., 1999). Sorption, which removes a pesticide from the mobile phase of a soil, and hence retards its leaching, is one of the major processes influencing pesticide mobility in soil under laboratory conditions (Celis et al., 2005; Cox et al., 2001; Socías-Viciana et al., 1999), as well as under field conditions (Laabs et al., 2000, 2002). Herbicide sorption processes are undoubtedly one of the major determinants affecting also the persistence in soil and biological activity (Guo et al., 2000; Jensen et al., 2004). Herbicide sorption has to be accounted when predicting their transport in the subsurface and soils (Kodešová et al., 2005; Spurlock et al., 1995). Desorption process of herbicides is also important since it determines the release rate and the potential mobility of herbicides in soil (Boivin et al., 2005; Huang et al., 1998). Several studies showed that significant hysteresis occurred between sorption and desorption (Bekbölet et al., 1999; Boivin et al., 2005; Nemeth-Konda et al., 2002; Thorstensen et al., 2001a). Hysteretic sorption-desorption suggest that sorption of pesticides occurs with a limited degree of reversibility depending upon both the physico-chemical properties of the pesticides and soils (Boivin et al., 2005; Cooke et al., 2004; DeSutter et al., 2003). MCPA (4-chloro-2-methylphenoxyacetic acid) is a herbi-

cide widely used to control annual and perennial weeds, mostly in cereals (Tomlin, 2001). It belongs to the group of acidic herbicides with $pK_a = 3.07$. This herbicide is widely used in Slovakia due to its high selectivity. Although MCPA is only moderately toxic herbicide compared, for example, to triazine herbicides, monitoring its residue in water and soil is crucial because it can affect the nervous system upon adsorption through the skin and its prolonged inhalation can cause dizziness, burning in the chest and coughing (Crespín et al., 2001). Many studies emphasized a significant role of the soil pH to affect retention and release of acidic herbicides - retention is increased when soil pH is decreased (Boivin et al. 2005; Dyson et al. 2002; Spadotto & Hornsby, 2003; Thorstensen et al. 2001a). Total soil organic carbon content and its nature appears to be another important factor influencing sorption-desorption of acidic herbicides (Bekbölet et al. 1999; Haberhauer et al. 2000, 2001; Hiller et al., 2005; Socías-Viciana et al. 1999). In general, the phenoxyacid herbicide MCPA is weakly sorbed by soils (Sørensen et al., 2006) and susceptible to leaching (Jensen et al., 2004; Socías-Viciana et al., 1999). As a consequence of the low MCPA sorption, its relatively high water solubility and leaching potential and of the extensive use, it has been detected in European groundwater resources (GEUS, 2004).

Taking into account the above and fact that retention and release of weak organic acids has been less studied, the objective of this study was to determine these processes for the herbicide MCPA in six soils and to find the main soil properties governing retention and release of the herbicide by soils. The obtained sorption parameters were used to evaluate MCPA potential to leach and

contaminate groundwater. The sorption-desorption process was studied using batch experiments to obtain the sorbed and desorbed amounts of MCPA by soils.

2. Materials and methods

2.1. Chemicals

Analytical grade MCPA (purchased from Dr Ehrenstorfer GmbH) with 825 mg.l^{-1} water solubility at 25°C and $\text{p}K_a = 3.07$ was used. Primary stock solution of MCPA was prepared by dissolving it in a background solution consisting of deionized and sterilized water (Milli Q+), 10^{-4} M NaN_3 to prevent biological activity and 0.01 M CaCl_2 to keep ionic strength constant. Initial aqueous solutions with 0.5 and 10 mg.l^{-1} of dissolved MCPA were prepared by mixing a background solution and a desired volume of a stock solution.

Tab. 1. Selected characteristics of the soil samples.

Sample code	Soil type	Clay (%)	Silt (%)	Sand (%)	OC (%) ¹	pH _{H2O}	C _{HA} /C _{FA} ²
A1	Rendzina	11.13	51.00	37.87	4.586	6.93	1.09
A2	Pararendzina	9.080	39.17	51.75	2.486	7.86	1.07
A3	Fluvisol	15.32	46.76	37.92	1.922	7.99	1.12
A4	Luvisol	5.750	63.45	30.80	1.212	6.32	1.16
A5	Cambisol	22.08	59.60	18.32	0.893	6.76	0.72
A6	Fluvisol	4.050	21.35	74.60	0.600	8.20	nd ^a

¹OC – organic carbon content; ²C_{HA}/C_{FA} – soil humic and fulvic acid ratio; ^and – not determined. The soils are arranged according to their decreasing organic carbon content.

2.3. Sorption/desorption experiments

Studies of the sorption kinetics (with 1 and 100 mg.l^{-1} of MCPA in 0.01 M CaCl_2 and 10^{-4} M NaN_3 aqueous solution) showed that MCPA sorption in calcareous Fluvisol (the A6 sample) reached an apparent equilibrium within 2 h (data not shown). Therefore, a 48 h equilibration time was considered to be adequate for sorption to attain true thermodynamic equilibrium. The experiments were carried out using the standard batch equilibration method. Prepared initial aqueous solution (5 ml) with 0.5 or 10 mg.l^{-1} of MCPA was added to the soil (2 g). The concentrations are within the range of typical field application rates of $1\text{--}2.5 \text{ kg.ha}^{-1}$ (Tomlin, 2001). The mixture was shaken for 48 h and then centrifuged. Consequently, MCPA equilibrium concentration (C_e) in aqueous solution was determined by HPLC (High Performance Liquid Chromatography).

Desorption experiments followed immediately and were performed using aliquots of samples from the sorption experiments. The supernatant removed was replaced by the same amount of MCPA-free 0.01 M calcium chloride solution. The tubes were shaken for 48 hours. After centrifugation, desorbed amount of MCPA in solution was determined. Tubes containing only MCPA solution without soil were included to determine adsorption onto the surface of the tubes. All sorption and desorption experiments were performed at least in duplicate. No losses of MCPA due to adsorption onto the surface of the tubes or volatilization were observed.

2.2. Selected soils

Five soils were sampled in the surface layers (0–25 cm). They represent the surface A horizon and come from the Laborec river area (Eastern Slovakia). In addition, one soil was sampled from the subsurface (~200 cm) to determine whether there is a difference in MCPA sorption-desorption between surface soils and subsurface soil. This soil represents the subsurface C horizon of calcareous Fluvisol and comes from the Bratislava airport area (Western Slovakia). Physical and chemical characteristics of the soils used were determined according to Fiala et al. (1999) and are shown in Tab. 1. The soil organic carbon measured in this study represents humified materials consisting mainly of the humic acids, fulvic acids and humins (Tan, 1993).

The results from the sorption experiments were evaluated by the distribution coefficient K_d ($K_d = S_e/C_e$; l.kg^{-1}), where S_e is the amount of MCPA sorbed to the soil. The difference between initial (C_0) and equilibrium MCPA concentration was used to calculate the sorbed amount S_e (mg.kg^{-1}). The K_d values were corrected for soil organic carbon content (OC in %) by calculating K_{OC} ($= (K_d/\text{OC}) \times 100$). Desorption coefficients were calculated using this equation: $K_{des} = S_{des}/C_{des}$, where S_{des} (mg.kg^{-1}) is the amount of MCPA sorbed to the soil after desorption and C_{des} (mg.l^{-1}) is the analytically determined equilibrium amount of MCPA released into a solution.

2.4. Determination of MCPA in the aqueous solution

Concentrations of MCPA in initial aqueous solutions as well as in clear supernatants after sorption-desorption experiments were analysed on a reversed-phase HPLC (Hewlett-Packard model 1100, $5 \mu\text{m}$, $4.6 \times 125 \text{ mm}$ LICHROSPHERE-100 RP column) with fluorescence detector (Hewlett-Packard 1046A). External solution standards were used to establish linear calibration curves for fluorescence detector. The mobile phase used was a mixture of acetonitrile and 0.05 M phosphate acid solution. The flow rate of this mobile phase was kept at the level of $0.4 \text{ ml per minute}$. The average uncertainty for the measured concentrations was about $\pm 10 \%$ and detection limit for the aqueous extracts was 0.02 mg.l^{-1} . Analyses were carried out at National Water Reference Laboratory for Slovakia, Bratislava under standard procedures of this laboratory.

3. Results and discussion

3.1. Effects of soil properties on retention and release of MCPA

Parameters that quantify retention and release of MCPA by soils at two initial concentrations are given in Tab. 2. MCPA was weakly sorbed by all soils used. The highest sorption (~ 30 %) was exhibited by the A1 soil sample with the highest organic carbon content among all the soil samples used, whereas the lowest sorption was observed in the A6 subsurface soil (only ~ 5 %) with the lowest organic carbon content (Tab. 2). The low extent of MCPA sorption could be attributed to the fact that MCPA would be negatively charged above pH 5 and consequently would be repelled by the predominantly negatively charged soil clay minerals or organic matter at pH values of the soils used (Dubus et al., 2001; Nicholls & Evans, 1991). Therefore, the interaction of the MCPA anions with the negatively charged soil mineral and organic matter surfaces at high pH of the soils will likely involve interaction with cationic species such as Ca^{2+} in salt bridge arrangements (Spark & Swift, 2002) or with Fe and Al oxo-hydroxides through specific and nonspecific electrostatic attractions (Vasudevan et al., 2002, 2004).

The obtained distribution coefficients (K_d) for the six soils at both MCPA initial concentrations were within 0.08-1.10 l.kg^{-1} . This corresponded to K_{OC} values be-

tween 15 and 35 l.kg^{-1} . Earlier studies of MCPA sorption on different soils with OC = 0.10-4.90 % gave K_d values in the range of 0.24-1.94 l.kg^{-1} with the corresponding K_{OC} values 27-156 l.kg^{-1} (Haberhauer et al., 2000; Socias-Viciano et al., 1999). Similar results were reported by Sørensen et al. (2006), who studied the sorption of MCPA in two soil profiles and their results showed that MCPA was weakly retained with $K_d = 0.03$ -1.89 l.kg^{-1} . The distribution coefficients for both C_0 increased with increasing soil organic carbon content. This was confirmed by a significant positive correlation between K_d and soil organic carbon content (Fig. 1). No other significant correlations between MCPA sorption and soil properties were found. The results indicate that soil organic matter played a main role in the MCPA sorption. Numerous laboratory studies have demonstrated an effect of soil organic carbon content on the sorption of MCPA and other weakly acidic herbicides (Al Kuisi, 2002; Bekbölet et al., 1999; Boivin et al., 2005; Hiller et al., 2005; Strebe & Talbert, 2001; Sørensen et al., 2006). The relatively constant K_{OC} values (Tab. 2), indicating similar sorption capacity of organic matter present in soils, and little or no difference between the observed K_{OC} and calculated ones (~ 10-35 l.kg^{-1}) from QASR relationship: $\log K_d = 0.93 \log K_{OW} + 1.09 \log f_{OC} + 0.32 C_{fa} + 0.25$ (Binstein & Devillers, 1994) are the another evidences for the primary effect of soil organic carbon content on the MCPA sorption.

Tab. 2. The sorption distribution coefficients (K_d), desorption coefficients (K_{des}), the amount of MCPA sorbed (P_{sorp}) and desorbed (P_{des}). Mean \pm experimental standard deviation.

Sample code	A1	A2	A3	A4	A5	A6
at MCPA initial concentration $C_0 = 10 \text{ mg.l}^{-1}$						
K_d (l.kg^{-1})	0.96 \pm 0.05 ^b	0.37 \pm 0.003	0.50 \pm 0.04 ^c	0.20 \pm 0.05	0.13 \pm 0.08	0.08 \pm 0.008
K_{OC} (l.kg^{-1})	21 \pm 1.10	15 \pm 0.10	26 \pm 1.90	17 \pm 4.00	15 \pm 8.50	13 \pm 1.60
P_{sorp} (%) ¹	27.7 \pm 1.04	13.0 \pm 0.07	15.7 \pm 0.01	7.40 \pm 1.77	4.94 \pm 2.74	3.01 \pm 0.29
K_{des} (l.kg^{-1})	2.97 \pm 0.11	1.76 \pm 0.05	1.59 \pm 0.14	0.56 \pm 0.12	0.42 \pm 0.37	0.27 \pm 0.12
P_{des} (%) ²	15.2 \pm 0.43	20.2 \pm 1.62	29.9 \pm 3.60	35.7 \pm 0.58	49.9 \pm 21.0	69.3 \pm 10.8
at MCPA initial concentration $C_0 = 0.5 \text{ mg.l}^{-1}$						
K_d (l.kg^{-1})	1.10 \pm 0.39	0.81 \pm 0.24	0.39 \pm 0.07	0.39 \pm 0.05	0.17 \pm 0.04	0.21 \pm 0.18
K_{OC} (l.kg^{-1})	24 \pm 8.50	32 \pm 9.60	21 \pm 3.60	32 \pm 4.40	19 \pm 5.00	35 \pm 30.0
P_{sorp} (%)	30.1 \pm 7.60	24.4 \pm 5.44	13.6 \pm 2.09	13.6 \pm 1.60	6.46 \pm 1.52	7.53 \pm 6.08
K_{des} (l.kg^{-1})	6.21 \pm 0.95	5.37 \pm 1.07	nd ^a	1.04 \pm 0.13	0.73 \pm 0.03	1.70 \pm 2.02
P_{des} (%)	12.8 \pm 3.34	10.9 \pm 0.03	nd ^a	34.5 \pm 17.4	51.5 \pm 4.12	55.5 \pm 33.2

¹ P_{sorp} – the percentage of MCPA sorption; ² P_{des} – the percentage of MCPA released; ^and – not determined; ^bThe average value from 7 samples ($n = 7$); ^cThe average value from 4 samples ($n = 4$); In all other cases, the experiments were performed in duplicate ($n = 2$).

Desorption (release) is of high importance because it affects the degradation rates and leaching behavior of a pesticide at different times and conditions. It is important to evaluate desorption since it determines the amount of herbicide that can be released back to aqueous solution and thus controls the final distribution of the herbicides in soil (Boivin et al., 2005; Haberhauer et al., 2000). In our study, the MCPA desorption from all the soils exhibited hysteresis, i.e. not all the amounts of MCPA sorbed by soils were desorbed within 48 hours (Tab. 2). Hysteresis is a common observed phenomenon, which can be attributed to irreversibility in the sorption process caused

by slow kinetics of desorption, diffusion-limited transport within the particles and/or irreversible binding of MCPA to the soil/sediment particles (Beck et al., 1996; Bekbölet et al., 1999; Cooke et al., 2004; Haberhauer et al., 2000; Jensen et al., 2004; Thorstensen et al., 2001a). When the sorption-desorption hysteresis occurs, there is a difference between the measured sorption and desorption distribution coefficients (K_d and K_{des} , respectively). The high K_{des} values indicate low desorption and vice versa (Bekbölet et al., 1999). The amount of MCPA released after one desorption step, expressed as a percentage of the amount sorbed (P_{des}), is given in Tab. 2 for all the soils used.

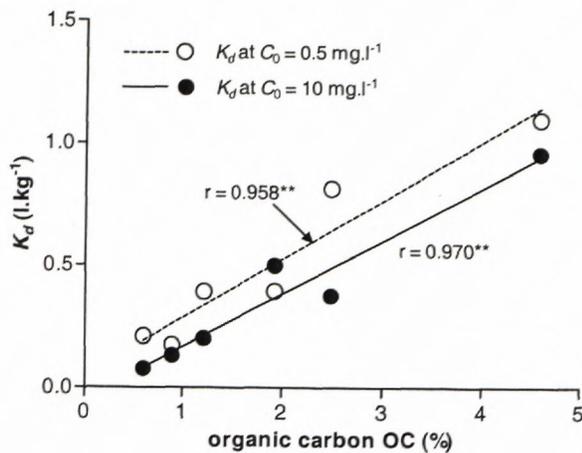


Fig. 1. Relationship between distribution coefficient (K_d) and soil organic carbon content for weak acid herbicide MCPA. ** $P < 0.01$ – significant at the 99 % probability level.

The largest parts of MCPA (the low K_{des} values and high P_{des}) were released from soils with the low organic carbon contents and very low MCPA sorption, as indicated by the K_d values (Tab. 2). Conversely, only about 10-20 % of the originally sorbed amounts of MCPA (the high K_{des} values) were released from soils with the relatively high organic carbon contents and MCPA sorption (Tab. 2). The experimental results show that the release of MCPA from soils is affected by the soil organic carbon content and the percentage of MCPA released is inversely proportional to the organic carbon content (Fig. 2). The relationship between desorption and soil organic carbon content was confirmed by the significant correlations found between OC (%) and K_{des} at both MCPA initial concentrations, 0.5 and 10 mg.l^{-1} (Fig. 2). The decrease in MCPA desorption with the increase in the soil organic carbon content could be due to the restricted diffusion of the herbicide within soil micropores during desorption (Rodríguez-Cruz et al., 2004). Previous studies reported a great importance of soil organic matter for MCPA desorption with the amounts of MCPA released ranging between 15 and 100 % of the sorbed amount in the soils (Sørensen et al., 2006; Thorstensen et al., 2001a). Moreover, it appears that binding strength of MCPA sorption by soils increased when organic carbon content was elevated as the amount of MCPA desorbed was lower in the soil samples with higher organic carbon content (Tab. 2). Thorstensen et al. (2001a) reported that sorption and desorption were inversely correlated for dichlorprop, MCPA and propiconazole in the soils from Norway.

3.2. Estimation of leaching potential

To predict leaching potential of herbicides into groundwater, the groundwater ubiquity score (GUS) (Gustafson, 1989) is often used. It is calculated using the following relationship: $\text{GUS} = \log t_{1/2}(4 - \log K_{OC})$, where GUS represents a dimensionless index, $t_{1/2}$ (d) is the herbicide half-life in soil representing a herbicide persistence and K_{OC} (l.kg^{-1}) is the sorption coefficient

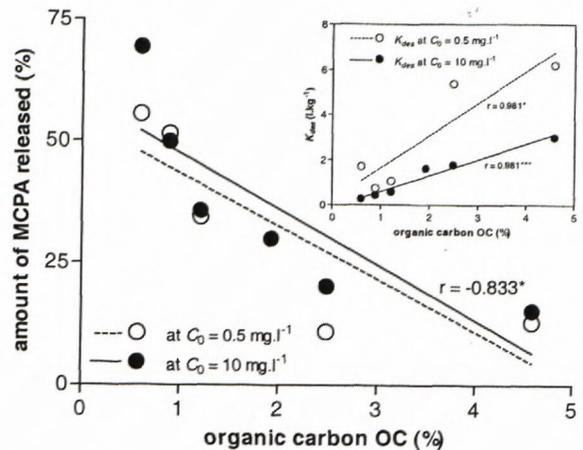


Fig. 2. Relationship between the percentage of MCPA released or desorption coefficient (K_{des}) and soil organic carbon content. *** $P < 0.001$ and * $P < 0.05$ – significant at the 99.9 % and 95 % probability level, respectively.

corrected for soil organic carbon content. Herbicides with $\text{GUS} < 1.8$ are ranked as non-leachers, whereas herbicides with $\text{GUS} > 2.8$ are leachers, and hence will likely contaminate groundwater. Those with GUS between 1.8-2.8 are considered transitional. To calculate GUS for MCPA in all the surface soil samples, the measured organic carbon distribution coefficients (K_{OC} ; Tab. 2) and average half-life (12.67 d) estimated from Crespin et al. (2001), Müller and Buser (1997), Thorstensen et al. (2001b) and Tomlin (2001) were used. The calculated GUS values are presented in Fig. 3.

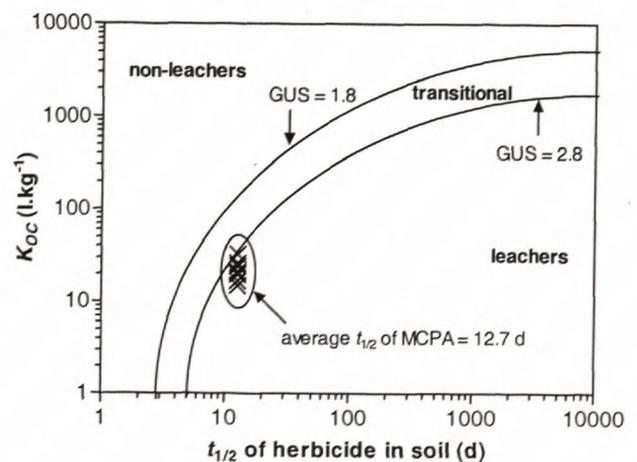


Fig. 3. Prediction of the MCPA leaching potential from the organic carbon distribution coefficients (K_{OC}) determined for the surface soil samples (A1-5) and average half-life ($t_{1/2}$) estimated from literature data. MCPA in all the surface soils used is considered to represent a groundwater contamination risk because all points (crosslets) are within an area labeled as leachers.

On the basis of GUS criteria could be concluded that MCPA represents relatively high leaching potential into groundwater in all five soils as the calculated GUS are higher than 2.8 or approximately equal to 2.8 (Fig. 3). Haberhauer et al. (2002) and Socías-Viciano et al. (1999) demonstrated that MCPA moved easily with the water front in soil columns with more than 70 % and 99 % of

the herbicide collected in the leachate, respectively. Sørensen et al. (2006) investigated sorption-desorption processes and biodegradation of MCPA in two soil profiles and confirmed the high mobility of this herbicide, especially in the deeper parts of the soil profile containing low amounts of soil organic carbon. The high mobility was caused by the low amount of MCPA sorbed to the soils, as well as by the absence of its biological decomposition. Very little or no degradation of MCPA in the deeper parts of soils and aquifers observed by Harrison et al. (1998) and Sørensen et al. (2006) indicate that, if vertical movement of soil solution brings MCPA to the deeper parts of soil profile, the leaching potential and risk of groundwater contamination may be even higher than suggested by the simple analysis presented in our study. The high water solubility of MCPA, its low sorption in the soils with low organic carbon content observed in this study (Tab. 2), as well as in the studies of Sørensen et al. (2006) and Thorstensen et al. (2001a), easy leachability of MCPA in soil columns (Haberhauer et al. 2002; Socias-Viciano et al. 1999) might potentially result in undesirable occurrence of the herbicide in groundwater, and hence it potentially represents an enhanced threat to human health.

4. Conclusions

The retention of MCPA by representative soils seemed to be primarily controlled by the soil organic carbon content. The low distribution coefficient values of MCPA indicate that this herbicide is potentially mobile in all the soils evaluated. The low retention of MCPA by soils was probably a result of the high soil pH. The release of MCPA was influenced by the soil organic carbon content. A significant linear correlation coefficients exist between the percentages of MCPA released or desorption coefficients and the soil OC content. Desorption appeared to be the result of a complex, time dependent interplay of several chemical and physical processes, leading to hysteresis.

To estimate leaching potential of MCPA into groundwater, the measured K_{OC} values as well as average degradation half-life taken from literature were used. The calculated values of groundwater ubiquity score imply that MCPA is the mobile herbicide in all the soils used and has relatively high leaching potential into groundwater. This is very important from an aspect of human health protection.

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